

THERMODYNAMICS AND KINETIC ASPECTS OF METAL COMPLEXES

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□ The stability of the metal complexes formed depend on the

- i. Nature of metal atom
- ii. Nature of ligands
- iii. Reaction conditions

□ The stability of metal complexes is discussed under two main types:

- a) Thermodynamic stability**
- b) Kinetic stability**

THERMODYNAMIC STABILITY

- Refers to the ability of a compound to exist and be stored for a long period of time .

KINETIC STABILITY

- Refers to the faster rate of formation of a particular species.

THERMODYNAMIC STABILITY OF COMPLEXES

- It is the measure of the amount of complex formed at equilibrium.
- Stronger the interaction between the metal ion and the ligand, more will be the thermodynamic stability of the complex.
- In other words, greater the value of equilibrium constant, greater will be the stability of the complex.

Comparison of Equilibrium constant values (K_s)

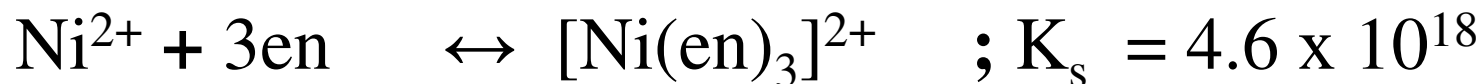
Consider the formation of copper complex with **unidentate ligands** NH_3 and CN^-



The above values show that Copper complex with **cyanide ligand is more stable.**

Also shows that CN^- is a **stronger ligand than** NH_3

Comparison of Ni complexes with **unidentate (NH₃)**
and bidentate ligand (en)



The equilibrium constant value for bidentate ligand (en) **is more** than that for unidentate ligand (NH₃) .

So, Ni forms **more stable complex** with bidentate ligand (**en : ethylene diamine**).

The thermodynamic stability of complexes is also sometimes given/shown in terms of **Dissociation constant**.

Dissociation constant is the **reciprocal** of stability constant.

$$K_{\text{diss}} = 1 / K_{\text{s}}$$

Smaller the value of dissociation constant, **more** will be the stability of the complex.

Larger the value of dissociation constant, **lesser** will be the stability of the complex.

STABILITY CONSTANTS OF COMPLEXES

The stability of complexes can be given in terms of **two types** of stability constants.

TYPES:

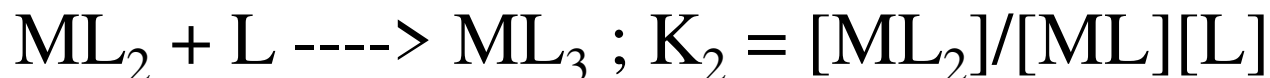
1. Stepwise stability constant
2. Overall stability constant
OR
Commulative stability constant

STEPWISE STABILITY CONSTANT

Consider the formation of the complex ML_n



1. Stepwise formation



.....and so on till



There are **n such equilibria** where n represents maximum coordination number of the metal ion for the ligand L.

$K_1, K_2, K_3 \dots \dots \dots K_n$ are known as stepwise stability constants.

The value of these constants decrease in the order

$$\mathbf{K_1 > K_2 > K_3 > \dots \dots \dots > K_n}$$

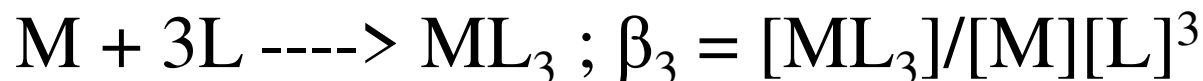
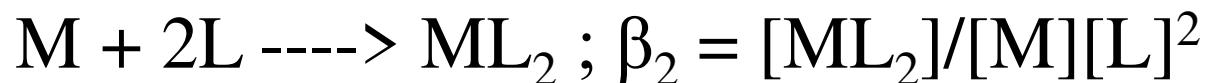
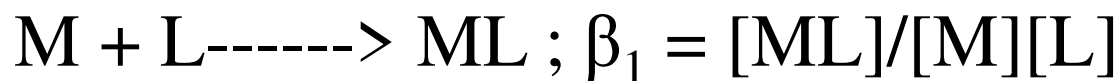
Because the ligand already bonded to metal ion repels the incoming ligand.

OVERALL / COMMULATIVE STABILITY CONSTANT

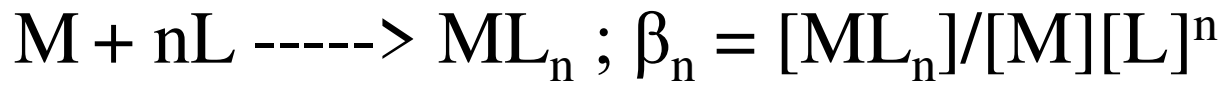
For the equilibrium reaction



Overall formation:



..... and so on till



where $\beta_1, \beta_2, \beta_3, \dots, \beta_n$ are known as overall or commulative stability constants.

The two stability constants (stepwise and overall) are related to one another.

Consider the expression for β_3

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

Multiply the numerator and the denominator by
 $[ML][ML_2]$

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

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

Thus from above, we can say

$$\beta_1 = K_1$$

$$\beta_2 = K_1 \cdot K_2$$

$$\beta_n = K_1 \cdot K_2 \cdot K_3 \dots\dots\dots K_n$$

and

$$\beta_n = \prod_{i=1}^n K_i$$

Taking log, we get,

$$\log \beta_n = \log K_1 + \log K_2 + \log K_3 + \dots \dots \log K_n.$$

log β is also used to measure the stability of the complex.

Larger value of stability constant indicates that the equilibrium lies towards the **right hand side** i.e. towards the formation of the complex ion.

A complex is said to be stable if **log $\beta > 8$** .

KINETIC STABILITY OF COMPLEXES

It refers to the **speed (rate of reaction)** with which the transformations leading to equilibrium will occur.

Kinetic stability is given in terms of **lability or inertness**.

The complexes which **rapidly exchange** one or more of their ligands in the coordination sphere by some other ligands are called **labile complexes**.

This phenomenon is known as **lability**.

If the ligand exchange reaction is slow or does not occur, then the complexes are called **inert complexes**.

The kinetic stability of a compound is different from its thermodynamic stability.

In other words, the inertness or lability of a complex has nothing to do with its thermodynamic stability.

The complex $[\text{Co}(\text{NH}_3)_6]^{3+}$ ion, is found to be **kinetically stable** (inert) in **acidic medium** for a long period.



The **large value of K** indicates that the reaction proceeds in the forward direction.

It means the is complex of cobalt on the reactant side is **inert in acidic medium kinetically** but **thermodynamically it is unstable** in acidic medium.

GENERALISATIONS

Inert complexes have substitution reaction **half life period larger** than a minute.

Labile complexes have substitution reaction **half life period lesser** than a minute

FACTORS AFFECTING LABILITY

Charge of the central metal ion:

Higher the charge on the central metal ion, lesser will be reactivity / greater will be the inertness.

Radii of the ion:

Reactivity decreases with decreasing atomic radii.

Charge/ radius ratio:

Greater the value of z / r , greater is the inertness.

Geometry of the complex:

Complexes having coordination number 4 are more labile.

FACTORS AFFECTING THE STABILITY OF COMPLEXES

The stability complexes primarily depends on **two main factors** :

A. Nature of central metal atom / ion

- i) Charge on central metal ion
- ii) Size of central metal ion
- iii) Electronegativity of the metal ion

B. Nature of ligand

- i) Size and charge of ligand
- ii) Basic character
- iii) Chelation
- iv) Steric effect

A. *NATURE OF CENTRAL METAL ATOM / ION*

i) CHARGE ON CENTRAL METAL ION

Higher the charge or charge density (z/r), **greater** will be the stability of the complex.

Smaller and highly charged central metal ion allows ligands **closer approach** leading to strong interaction with the ligand.

This can be observed from the table

Complex ion	Charge on the ion	Ionic radii (Å ^o)	Value of log β	stability
[Fe ^{III} (CN) ₆] ³⁻	+3	↑ Almost same ↓	31.0	↑ Stability increases
[Fe ^{III} (CN) ₆] ⁴⁻	+2		8.3	
Co ^{III} complex	+3	↑ Almost same ↓	high	↑ Stability increases
Co ^I complex	+2		low	

ii) SIZE OF CENTRAL METAL ION

Smaller the size of the central metal ion, greater will be the stability of the complex.

The stability of complexes increase with decrease in ionic radii of the metal ion as can be seen from the table.

Ion	Mn²⁺	Fe²⁺	Co²⁺	Ni²⁺	Cu²⁺	Zn²⁺
Ionic radii (pm)	91	83	82	78	69	74

Order of Stability : Mn²⁺ < Fe²⁺ < Co²⁺ < Ni²⁺ < Cu²⁺ > Zn²⁺

IRVING WILLIAM SERIES

It is the order of stability of the divalent ions.

Order of Stability : $\text{Mn}^{2+} < \text{Fe}^{2+} < \text{Co}^{2+} < \text{Ni}^{2+} < \text{Cu}^{2+} > \text{Zn}^{2+}$

If divalent ions of alkaline earth metals are included, then the order of stability is

$\text{Ba}^{2+} < \text{Sr}^{2+} < \text{Ca}^{2+} < \text{Mg}^{2+} < \text{Mn}^{2+} < \text{Fe}^{2+} < \text{Co}^{2+} < \text{Ni}^{2+} < \text{Cu}^{2+} > \text{Zn}^{2+}$

This order arises due to:

- Decrease in size of ion across the series
- From **Mn^{2+}** onwards due to ligand stabilization effect

From **Ba²⁺** to **Mg²⁺**, there is a continuous decrease in size (or increase in charge density).

This results in strong metal ligand interaction from **Ba²⁺** to **Mg²⁺** and the stability of metal ligand bond increases from **Ba²⁺** to **Mg²⁺**

From **Mn²⁺** to **Cu²⁺**, there is increase in stability due to additional crystal field stabilization energies.

There is discrepancy with **Cu²⁺** due to Jahn – Teller effect / distortion.

iii) ELECTRONEGATIVITY

Stability of a complex also depends on the electronegativity / electronic charge distribution of the metal ion.

Ahrland, Chatt and Davis classified the metal ions into three classes based on their electronegativities.

These classes are:

- Class 'a' metals
- Class 'b' metals
- Borderline metals

Class 'a' metals

Electropositive in nature

Include

- Hydrogen, Alkali and alkaline earth metals
- Lanthanides and actinides
- Transition metals having lesser number of electrons (Sc to Cr)
- Non transition metals
- They have **few number of d electrons** beyond an inert gas core.
- They form stable complexes with ligands in which **coordinating atoms** are **N, O, F**

Class 'b' metals

Less electropositive metals

Include

- Heavy metals like Rh, Pd, Ag, Ir, Pt, Au, Hg, Pb etc.
- They have **relatively large number of d electron** beyond an inert gas core.
- Class 'b' metals form stable complexes with ligands **having P, S, As, Br and I**, which **can accept electrons** from the metal to form π bond. (**M \rightarrow L π back bonding**)

Borderline metals

Fall **in between** class 'a' and class 'b' metals

Include

- Mn to Cu, Tl to Po, Mo, Te, Ru, W, Re, Os and Cd
- They form complexes of **varying stabilities**.
- Borderline metals **do not show** any noticeable trend.

- ❖ Certain metal ions exert a **greater electronegative / polarizing effect** on the ligands leading to increase in bond stability.

OR

- ❖ The ligands may **exert an external electric field** on the metal ion .
- ❖ This results in **polarization or deformation** of valence orbitals or a **specific effect** on certain valence energy levels.
- ❖ Both cases lead to **increase** in bond strength.

- ❖ In such cases, covalent bonding gains importance.
- ❖ For example: Silver forms insoluble halide salts of the type AgX and stable halide complex ions AgX_2 in the order of stability $\text{I}^- > \text{Br}^- > \text{Cl}^- > \text{F}^-$.
- ❖ This can be seen from $\log \beta$ values

Complex	AgF	AgCl	AgBr	AgI
Log β	0.3	3.2	4.5	8.0

B. NATURE OF LIGAND

i) SIZE AND CHARGE OF THE LIGAND

- Smaller the size of the ligand, more will be the stability of the complexes it forms.
- F^- forms more stable complexes as compared to other halide ions as can be seen from the stability constant values.

Complex	Log β
FeF^{2+}	6
$FeCl^{2+}$	1.3

ii) BASIC CHARACTER OF THE LIGAND

- Basic character refers to the tendency to donate electrons.
- Greater the ease of donation of electron pairs by the ligand, greater will be the stability of the complexes formed by it.
- Greater the basic strength of the ligand, more will be its tendency to form complexes.
- A strong base is a good electron donor like NH_3 , CN^- , F^- etc.

- The basic strength of a molecule determines the stability of the complex that the molecule/ligand forms with H^+ ion.
- In other words , the ligand which bonds with H^+ ion strongly should form stable complexes with metal ions.
- For example, F^- ion should form more stable complexes than other halide ions.
- NH_3 should be a better ligand than H_2O .

- This type of behaviour is observed in case of **class 'a' metals**.
- **Class 'a' metals** attract electrons and form stable complexes with ligands having N, O and F atoms.
- This is not true for **class 'b' metals**.
- **Class 'b' metals** form stable complexes with ligands having atoms which are capable of accepting π - electrons from metal atom/ ion, like P, S, Br, I etc.

ii) PRESENCE OF RING STRUCTURE

a. CHELATION

- Stability of a complex is greatly **increased** if the bonding between metal ion and ligand leads to **formation of a ring structure**.
- Such structures are called **chelates** and the phenomenon is called **chelation**.
- Chelates are **cyclic/ ring compounds** formed when a ligand binds the central metal atom/ ion through two or more donor atoms of a binding ligand.

- Increased stability of complexes is called **chelate effect**.
- Chelated complexes formed by multi – dentate ligands like ethylene diamine (en), EDTA, acetylacetonato ion (acac^-) are **found to be more stable** than those formed by unidentate ligands like NH_3 , CN^- , F^- etc.

Complex	Log β	Stabilities
$[\text{Ni}(\text{NH}_3)_6]^{2+}$	9	Less stable
$[\text{Ni}(\text{en})_3]^{2+}$	19	More stable

- This increased stability can be explained in terms of **favourable entropy change** during chelation.
- During complex formation with **NH₃ ligand**, six H₂O molecules are replaced by six NH₃ ligand



- There is **no change** in the number of molecules on both sides of above equation.

- During complex formation with **en ligand**, six H₂O molecules are replaced by three en ligand



- There is an **increase** in the number of molecules on R.H.S. of the above equation.
- The increase in the number of molecules leads to **greater disorder/ randomness, greater entropy**.
- **Increase** in entropy of a system, leads to **greater stability**.

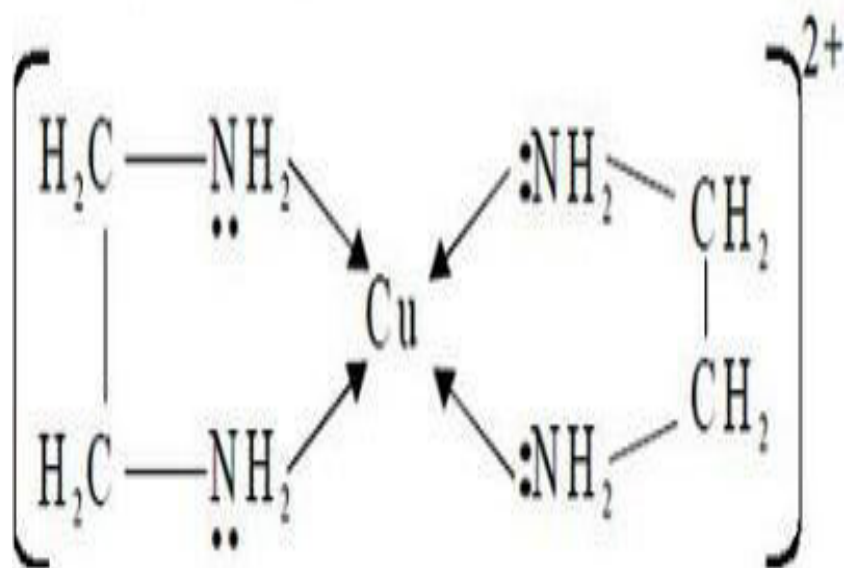
b. NUMBER OF CHELATE RINGS

- **More** the number of chelate rings in a complex, **more** will be the stability of the complex.

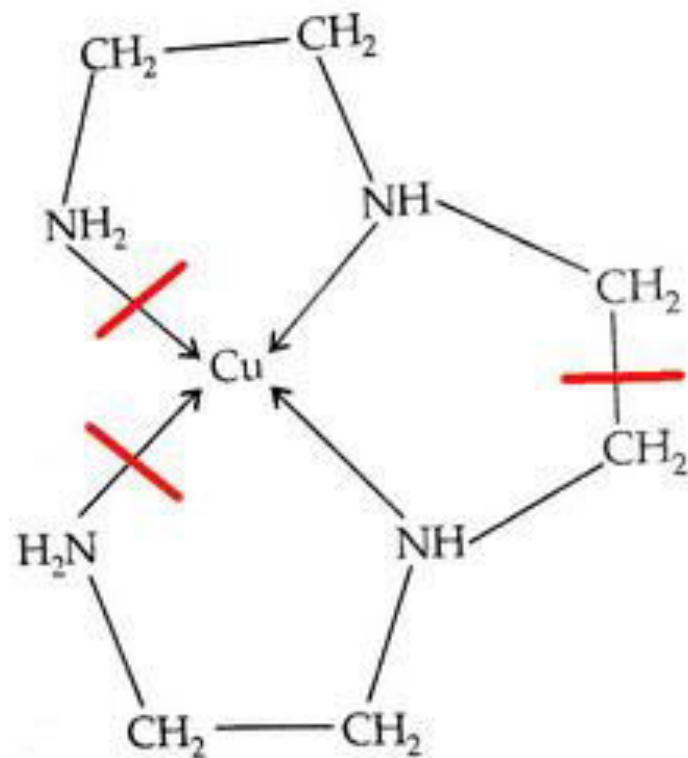
Complex	No. of chelate rings	Log β
$[\text{Cu}(\text{NH}_3)_6]^{2+}$	0	12.6
$[\text{Cu}(\text{en})_2]^{2+}$	2	20.0
$[\text{Cu}(\text{trien})]^{2+}$	3	20.5



No. of rings : 2



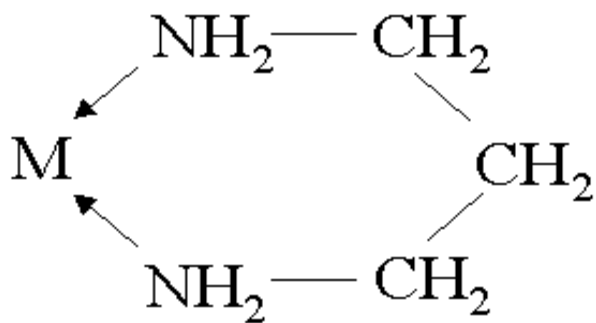
No. of rings : 3



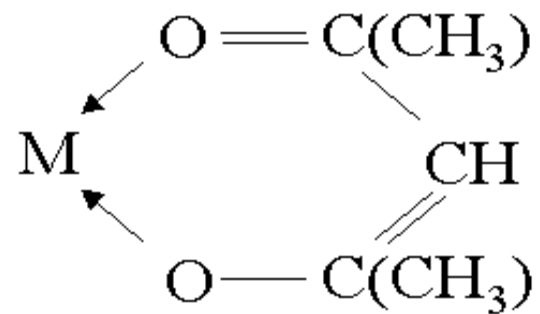
c. SIZE OF THE CHELATE RING

- The stability of the chelate depends on the **size of the ring**.
- Metal chelates having **five membered rings** are found to be **most stable**.
- Chelating ligands like **ethylene diamine, oxalate ion, glycine, dimethylglyoxime** form quite stable 5 membered chelates.
- Chelates having **six membered ring** are **less stable**.

- Only those 5membered chelates are **more stable** than 6 membered where atoms on the rings are joined by **single bonds**.
- 6 membered chelates having **unsaturation / double bond** in the ring are **more stable** than 5 membered chelates.



trimethylenediamine



acetylacetonato (acac)

- In the above structure, **6 membered chelate having double bond is more stable** because:
 - i. Rings are **symmetrical** with $M - O$ bonds being equal in length.
 - ii. **Due to resonance** the $C - O$ and two $C = C$ bonds are equal in length.
- Rings of size more than 6 are known but they are **not very stable**.

- The **instability of higher membered rings** is due to:
 - a. The **extra energy** required to bring the coordinating atoms of the ligand close to the metal ion for bonding against electrostatic forces.
 - b. Reduced effective concentration** of the other end of the ligand for molecules which form 7 or higher membered rings.
 - c. Relative difficulty** of finding a sterically non crowded ring configuration.

d. STERIC EFFECTS

- Ligands having bulkier/ larger groups **form less stable complexes** as compared to ligands having small groups.
- Bulkier groups present near the donor atom cause **mutual repulsion**.
- Metal ligand bond **weakens** & stability of the complex **decreases**.
- This is called **Steric Hindrance**

- Ethylene diamine ($\text{H}_2\text{NCH}_2\text{CH}_2\text{NH}_2$) forms more stable complexes than its substituted tetramethyl derivative i.e. $(\text{CH}_3)_2\text{NCH}_2\text{CH}_2\text{N}(\text{CH}_3)_2$.
- Ni (II) forms less stable complexes with 2 – methyl – 8 – hydroxy quinoline as compared to 8 – hydroxy quinoline, due to geometry of the ligand coupled with the stereochemistry of the compound.