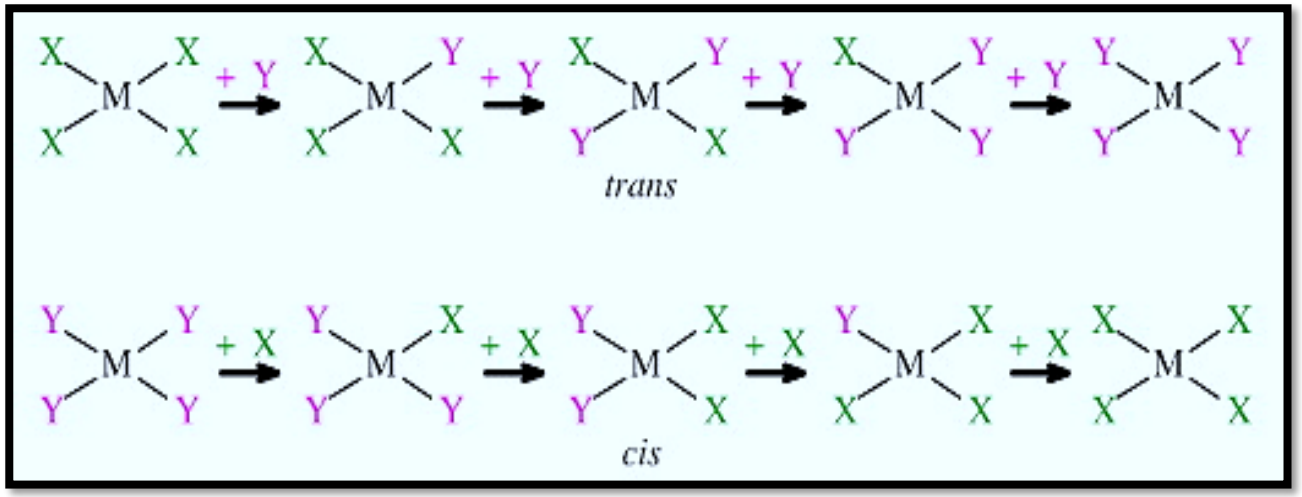
# Thermodynamic and Kinetic Aspects of Metal Complexes

## (Lecture-2)

**B.Sc. 5th Semester (Pass Course)**

**INORGANIC CHEMISTRY**

**(As per MDU, Rohtak Syllabus)**




**Presented by:**

**Dr. Anju Siwach**

**Assistant Professor Chemistry**

**Govt. College, Badli, Jhajjar.**

# CONTENT

- **Irving William Series**
- **Factors affecting stability of metal complexes**
  - ***Nature of metal ion***
  - ***Nature of Ligands***

1. **Statistical factor** : As co-ordinated $H_2O$ molecules are replaced by L
   → so the no. of $H_2O$ molecule decreases in the complex.
   → Hence the probability of replacing water molecules also decreases.
   → As a result K values decrease gradually.

2. **Steric factor** : This arises only when the incoming ligands are bulkier in size than the $H_2O$ molecules.
   → As small sized water molecules are replaced by bulkier ligand so the steric crowding around central metal ion increase, as a result of repulsions, the subsequent steps are retarded. Hence the K values gradually decrease.

3. **Electrostatic factor** : During the complex formation, first step is
   ↳ one L replaces one co-ordinated water molecule to give $[M(H_2O)_{n-1}L]$
   ↳ In 2nd step, another ligand of same charge approaches to the product of 1st stage
   ∴ there arises an electrostatic repulsion between incoming ligand and L already present in the complex.
   → As a result of this repulsion, subsequent steps are retarded Hence, K values decrease

So general trend in K values is $\boxed{K_1 > K_2 > K_3 ---- > K_n}$

**Example :**

| | $\log K_1$ | $\log K_2$ | $\log K_3$ | $\log K_4$ | $\log \beta_4$ |
|---|---|---|---|---|---|
| $[Cu(NH_3)_4]^{2+}$ | 4.3 | 3.6 | 3.0 | 2.3 | 13.2 |
| $[Cd(NH_3)_4]^{2+}$ | 2.6 | 2.1 | 1.4 | 0.9 | 6 |

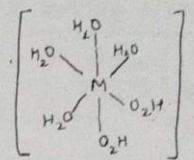
In $[Cu(NH_3)_4]^{2+}$ ⇒ $\log \beta_4 > 8$ ∴ It is a stable complex
while $[Cd(NH_3)_4]^{2+}$ ⇒ $\log \beta_4 < 8$ ∴ It is not a stable complex

## EXCEPTIONS TO THE GENERAL TREND IN K VALUES :

| System | $\log K_1$ | $\log K_2$ | $\log K_3$ | $\log K_4$ | $\log \beta_4$ |
|---|---|---|---|---|---|
| $Cd^{2+}/I^-$ | 2.08 | 0.77 | 2.15 | 1.48 | 6.48 |
| $Cd^{2+}/Br^-$ | 1.56 | 0.54 | 0.06 | 0.37 | 2.53 |

→ This anomaly in the trend in K values suggests a major structural change.

→ Generally, the aqua complexes are 6-co-ordinated while, halo complexes are tetrahedral.




→ The reaction of 4th $Br^-$ group in $Cd^{2+}/Br^-$ with the complexes with 3 $Br^-$ group is -

$$[Cd(H_2O)_3Br_3]^- + Br^- \longrightarrow [Cd(Br)_4]^{2-} + 3H_2O$$

octahedral (1+1 = 2 particles) → Tetrahedral (1+3 = 4 particles)

→ This reaction is accompanied by increase in no of particles and hence entropically favoured

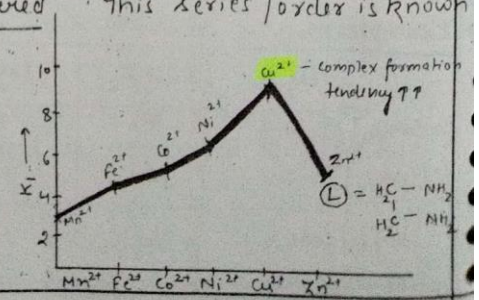
→ Hence $K_4$ value increase in $Cd^{2+}/Br^-$ system

## IRVING-WILLIAMS SERIES :-

In case of border line class of metal ions, stability of complexes with a given ligand is in order - (d9 → shows J.T distortion)

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

ie trends in $K_1$ values is altered. This series/order is known as Irving-Williams series.



## FACTORS AFFECTING THE STABILITY OF CO-ORDINATION COMPOUND :-

Stability of co-ordination compounds / metal complexes depends upon nature of metal as well on ligand.

Various factors affecting the stability are -

1. Charge of central metal ion
2. Size of central metal ion
3. Nature of the ligand
4. Basicity of the ligands
5. Chelating ability of the ligand
6. Chelate ring size
7. No. of chelate rings.
8. Steric effect
9. Stereochemical requirement of ligands

### Charge of central metal ion :

→ Metal complexes having higher positive oxidation states are always more stable than those of the lower oxidation states.

→ Greater is the positive oxidation state of central metal ion, greater will be its attraction for the ligands hence greater will be stability of the complex.

① $[Fe(CN)_6]^{3-}$ is more stable than $[Fe(CN)_6]^{4-}$

- $Fe^{3+}$ : (+3) oxidation state; $\log \beta = 31.5$
- $Fe^{2+}$ : (+2) oxidation state; $\log \beta = 8.3$

② $\log \beta$ values of EDTA complexes with the metals in +2, +3 oxid. sta

| ie | | | |
|---|---|---|---|
| $Fe^{2+}$ = 14.3 | $Co^{2+}$ = 16.2 | $V^{2+}$ = 12.7 |
| $Fe^{3+}$ = 25.1 | $Co^{3+}$ = 36.0 | $V^{3+}$ = 25.9 |

### 2. Size of central metal ion :

→ Stability of complexes increase with decrease in size of central metal ion

→ As keeping the charge constant, size decrease (of central metal ion) the charge per unit surface area increases ∴ metal's attraction for the ligand increases and hence the stability also increases

① Keeping the charge constant, as we go from $Fe^{2+}$ to $Ni^{2+}$ size of metal ion decreases hence $\log \beta$ values increases so is the stability ie

$[Fe(H_2O)_6]^{2+} + 3en \longrightarrow [Fe(en)_3]^{2+}$ $\log \beta = 14.3$

$Fe^{2+}$ size = 0.76 A°

value ↑

$[Ni(H_2O)_6]^{2+} + 3en \longrightarrow [Ni(en)_3]^{2+}$ $\log \beta = 18.5$

$Ni^{2+}$ size = 0.72 A°

② The gradual increase in stability / $\log \beta$ values of tripositive (lanthanide ion - EDTA) complexes as we move from La to Lu because due to lanthanide contraction, there is a steady decrease in size of central metal ion, hence the stability increase

| anthanides | $La^{3+}$ | $Ce^{3+}$ | $Pr^{3+}$ | $Nd^{3+}$ | $Pm^{3+}$ | $Sm^{3+}$ | $Eu^{3+}$ | $Gd^{3+}$ | $Tb^{3+}$ | $Dy^{3+}$ | $Ho^{3+}$ | $Er^{3+}$ | $Tm^{3+}$ | $Yb^{3+}$ | $Lu^{3+}$ |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Size (A°) | 1.15 | 1.11 | 1.09 | 1.08 | 1.06 | 1.04 | 1.03 | 1.02 | 1.00 | 0.99 | 0.97 | 0.96 | 0.95 | 0.94 | 0.93 |
| Log β or pK value | 15.50 | 15.98 | | | | | | 17.37 | 17.93 | | 18.74 | | 19.32 | 19.51 | 19.83 |

As size of $Ln^{3+}$ decrease, regular rise in $\log \beta$ value for $[Ln(EDTA)]^-$

③ In alkali group metals, as size increases down the group, the stability with a particular ligand-complex decrease in order

$Li^+ > Na^+ > K^+ > Rb^+ > Cs^+$

## 3) Nature of ligand atom :-

→ The ligand atoms which directly bound to metal ions in complexes are generally electronegative elements ie halogens, oxygen, sulphur, phosphorus, nitrogen etc.

→ Eg → Complexes formed by halide ions :-

(i) for most of the metals, order of stability is $F^- > Cl^- > Br^- > I^-$

(ii) But in case of metals like $Pt^{2+}$, $Cu^+$, $Ag^+$, $Hg^{2+}$, $Tl^+$, order get reversed. for eg. in silver halide complexes, order of stability is $AgI > AgBr > AgCl > AgF$.

→ The reason for such order is the back donation from metal to ligand occurs in addition to the transfer of $e^-$ from $L \rightarrow M$.

→ For this back donation, Ligands should have vacant orbitals so Iodine being last electronegative among all halogens, it can easily accept the back donated electrons by the metal.

∴ Hence, the order of stability is reversed as that of observed in most of the other metal ions.

## 4) Basicity of the Ligands :- ↑Basic① ↑Stable Complex

→ Basicity means the tendency of electron pair donation.

→ Greater is the basicity of the ligand, greater will be the tendency to donate electron pairs. It means, the more basic ligand will form more / stable complex.

→ J. Bjerrum studied the stability of amine complexes of $Ag^+$ and $Hg^{2+}$ wrt basicity of ligands and he observed that the increase in basicity of ligands increases the stability of complexes

eg →

| ligand | log K ($Ag^+$) |
|---|---|
| $CH_3-NH_2$ | 3.34 |
| $CH_3-CH_2-NH_2$ | 3.65 |
| $CH_3-CH_2-CH_2-NH_2$ | 3.85 |

↓ as we move down, basicity of ligand increases, hence log K values ($Ag^+$) also increases

## 5) Chelating ability of the ligand :-

→ When a bidentate or polydentate ligand is co-ordinated through 2 or more donor atoms to the same metal ions forming a ring structure. Such ring-structured complexes are called chelates

→ The process is called chelation and the ligand is called chelating ligand.

→ Due to chelation, extra stability is attained by the complex This extra stability is termed as chelate effect.

eg →

| complexes | log β-values |
|---|---|
| $[Ni(NH_3)_6]^{2+}$ | 8.6 |
| $[Ni(en)_3]^{2+}$ | 18.6 |

↓ stability increased due to chelation in $[Ni(en)_3]^{2+}$ complex hence log β values also increases

→ The chelate effect is explained thermodynamically as →

eg When an aquated $Ni^{2+}$ ion is treated with ethylenediamine the coordinated $H_2O$ molecules are replaced by (en) molecules to form a chelate →

ie $[Ni(H_2O)_6]^{2+} + 3en \longrightarrow [Ni(en)_3]^{2+} + 6H_2O$

$1 + 3 = 4$ particles $\qquad 1+6 = 7$ particles

→ this process of chelation leads to increase in no. of particles (4→7) which results in an increase of randomness in the system. This in turn leads to a (+ve) entropy change ($\Delta S^\circ$) which leads to more (-ve) $\Delta G_f^\circ$ values as $\Delta G_f^\circ = \Delta H^\circ - T\Delta S^\circ$ (-ve) (-ve) (+ve)

→ $\Delta G_f$ is related to log K or log β as

$$\Delta G_f^\circ = -RT \ln K$$

Hence more is the (-) $\Delta G_f^\circ$ value, more will be ln K value so more will be the stability of complex.

## 6) Chelate ring size :-

→ when there is no (=) bond in chelate ring, generally 5 membered ring will be most stable.

→ when there is (=) bonds, a 6-membered ring is the more stable

eg → (i) No (=) bond → complexes of calcium ⇒

$(HOOC-CH_2)_2N-(CH_2)_n-N(CH_2COOH)_2$ → $Ca^{2+}$

| | | | | |
|---|---|---|---|---|
| When | n = 2 | Ring size = 5 | log K = 10.7 | stability ↓ |
| but | n = 3 | Ring size = 6 | log K = 7.1 | |

It means 5-membered ring is more stable when there is no (=) in chelate ring.

(ii) there is (=) bond → then 6-membered ring is more stable as:

eg (acetylacetonato) ⇒

$CH_3-\overset{O}{\overset{\|}{C}}-CH_2-\overset{O}{\overset{\|}{C}}-CH_3 \rightleftharpoons CH_3-\overset{O}{\overset{\|}{C}}-CH=\overset{OH}{\overset{|}{C}}-CH_3$

Keto form ⇌ enol form

→ when (acac) form complex with metal (M) the complex is resonance stabilized which leads to extra stability of 6-memb. ring.

ie

enol form

$CH_3-\overset{O}{\overset{\|}{C}}-CH=\overset{OH}{\overset{|}{C}}-CH_3 \longrightarrow CH_3-\overset{O}{\overset{\|}{C}}-CH=\overset{O^\ominus}{\overset{|}{C}}-CH_3 \xrightarrow{+M}$

Resonance stabilized ⟷ Metal complex (6-membered)

## 7) No. of chelate rings :-

→ Greater is the no. of chelate rings, greater will be the stability of the complex. This is due to the increase in no. of particles, hence greater increase in positive entropy change.

→ eg →

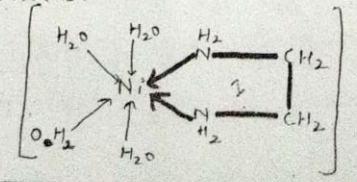
① $[Ni(H_2O)_6]^{2+} + en \longrightarrow [Ni(en)(H_2O)_4]^{2+} + 2H_2O$

$1+1 = 2$ particles $\qquad 1+2 = 3$ particles

no. of particles increase

ie in $[Ni(en)(H_2O)_4]^{2+}$ there is one chelate ring

ie

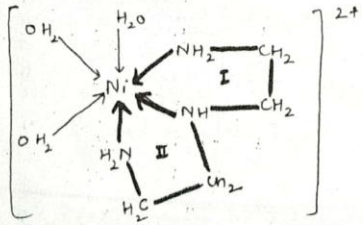


(ii) When $H_2O$ molecules replaced by (dien) molecule, there is an increase of particles from 2 to 4, there are 2 chelate rings ie

$$[Ni(H_2O)_6]^{2+} + \text{dien} \longrightarrow [Ni(\text{dien})(H_2O)_3]^{2+} + 3H_2O$$

1 + 1 = 2 particle  1 + 3 = 4 particles

In $[Ni(\text{dien})(H_2O)_3]^{2+}$ → there are 2 chelate rings

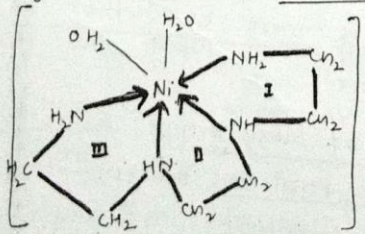


(iii) When $H_2O$ molecules replaced by (trien) molecules, there is an increase of particles from 2 to 5. ie

$$[Ni(H_2O)_6]^{2+} + \text{trien} \longrightarrow [Ni(\text{trien})(H_2O)_2]^{2+} + 4H_2O$$

1 + 1 = 2 particles  1 + 4 = 5 particles

In $[Ni(\text{trien})(H_2O)_2]^{2+}$ → there are 3 chelate rings



So

| ligand | No. of rings | complex | log K values |
|---|---|---|---|
| en | 1 | $[Ni(en)(H_2O)_4]^{2+}$ | 7.9 |
| dien | 2 | $[Ni(dien)(H_2O)_3]^{2+}$ | 10.7 |
| trien | 3 | $[Ni(trien)(H_2O)_2]^{2+}$ | 14.9 |

↓ as no. of rings ↑, log K values ↑

8) **Steric effect** :-

→ When a bulky group either attached to donor atom or near donor atom, cause mutual repulsion between the ligands which results in the weakening of the metal to ligand bonds

→ Example Complexes formed by $Ni^{2+}$ with (en) and with N,N'- dimethyl ethylene diamine.

| log K | $Ni^{2+}$ – en complex | $Ni^{2+}$ – N,N'- dime-en complex |
|---|---|---|
| log $K_1$ | 7.6 | 7.7 |
| log $K_2$ | 6.5 | 4.7 |
| log $K_3$ | 5.0 | 1.5 |

As the no. of ligands (bulky) increase, log K values decreased the K values of the $Ni^{2+}$ – N,N'-dimet-en complexes are less than $Ni^{2+}$-en complexes. This is due to the steric repulsions caused due to methyl substitution.

But $K_1$ value of $Ni^{2+}$- substituted en complex is more than $Ni^{2+}$- en complex. This is due to the fact that (N-N'- dime -thyl ethylene diamine) is more basic than (en) hence stability ($K_1$ value) is more.

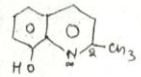
But as the no. of bulky groups increased around central metal ion, steric repulsions arises, thus by decreasing stability of the complexes

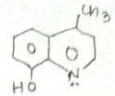
Example → $Ni^{2+}$ complexes formed with 8-hydroxyquinoline and 2,4- methyl substituted -8-hydroxyquinoline

↳

ie $Ni^{2+}$ complex with

(i) 8-hydroxyquinoline (ii) 2-methyl-8hydroxyquinoline (iii) 4-methyl derivative





$\log \beta_2 = 21.4$

$\log \beta_2 = 17.8$

least stable complex

∵ steric hindrance caused by methyl group at 2-c which is near to donor atom so mutual repulsions caused between ligands.

$\log \beta_3 = 22.3$

Most stable complex

∵ bulky group ($-CH_3$) is too far away from donor N-atom.

9) **Stereochemical Requirement of ligands** :-

→ The stereochemical requirements of the ligands affect the stabilities of the complexes.

→ for example :

(i) **Trien** : $(H_2N-CH_2-CH_2-NH-CH_2-CH_2-NH-CH_2-CH_2-NH_2)$ is more suited to planar arrangement

: The preferred stereochemistry of $Cu^{2+}$ is square planar so $Cu^{2+}$ will prefer trien for complex formation.

(ii) **Tren** : $N(CH_2CH_2NH_2)_3$ is more suited to tetrahedral arrangement.

: $Zn^{2+}$ prefers tren over trien because preferred stereochemistry is tetrahedral.

*Thank you*