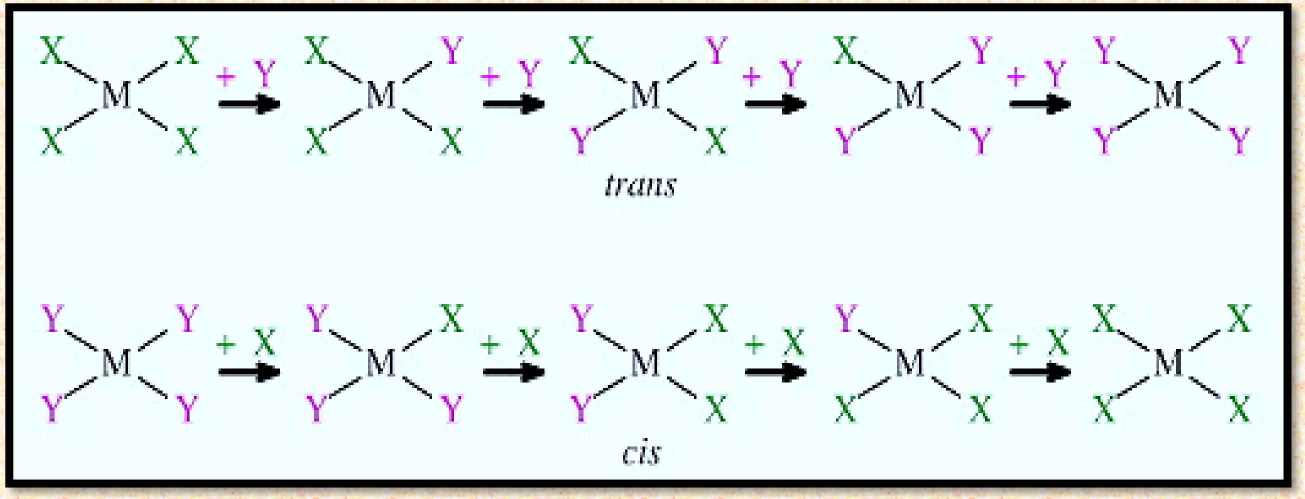
Thermodynamic and Kinetic Aspects of Metal Complexes

(Lecture-1)

B.Sc. 5th Semester (Pass Course)

INORGANIC CHEMISTRY

(As per MDU, Rohtak Syllabus)



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CONTENT

- **Stability of metal complexes**
- **Stability constants**
- **Relationship between K and β**

Stability of Metal Complexes

1. Thermodynamic

2. Kinetic

⇒ STABILITY OF METAL COMPLEXES :

→ The stability of metal complexes is important in understanding the properties of complexes.

→ The stability of metal complexes depend upon nature of metal and ligand as well as on reaction conditions.

→ Stability of co-ordination compounds means " the compound exists for a long time and under suitable conditions, may be stored for a long period of time."

→ Generally, two types of stabilities are recognized for metal complexes ie

Thermodynamic stability

It deals with metal to ligand bond energies, stability constants and the thermodynamic variables etc.

- it is a measure of the extent of formation of a complex at equilibrium.

Kinetic stability

- It deals with the rates and mechanisms of reactions and also with the energies involved in the formation of activated complex

Thermodynamic stability

- As for as complexes in solutions are concerned there are two kinds of stabilities
- **Thermodynamic stability** – Measure of the extent to which the complex will be formed or will be transformed into another species, when the system has reached equilibrium

Kinetic stability

- **Kinetic stability** – refers to the speed with which the transformations leading to equilibrium will occur.
- Under this , the rates of substitutions, racemisations and their mechanisms.
- The factors which are affecting the rates of the reactions are also studied

1. Thermodynamic

Stable | **Unstable**

2. Kinetic

Inert | **Labile**

→ From a thermodynamic point of view, complexes are defined as

Stable | Unstable

→ From the kinetic point of view, complexes are defined to be,

Inert | labile

→ very often these two groups of terms are used incorrectly as a stable complex may be → Inert / labile

and unstable complexes may be → Inert / labile

$[Co(NH_3)_6]^{3+}$ is thermodynamically unstable in acidic solution. But it can be kept in acid solution for several days at room temperature without any noticeable decomposition. This means that $[Co(NH_3)_6]^{3+}$ is kinetically inert.

Kinetic Vs Thermodynamic stability

- The terms labile and inert refer to the reactivity of a complex only.
- Not to be confused with its stability.
- An inert complex may be stable or unstable.
- Similarly a labile complex may be stable or unstable

→ **For Example :-**

$$[Ni(H_2O)_6]^{2+} + 4CN^- \longrightarrow [Ni(CN)_4]^{2-} + 6H_2O$$

CN^- ion forms a very stable complex with Ni^{2+}. Ni^{2+} prefers CN^- rather than H_2O as a ligand.

∴ $[Ni(CN)_4]^{2-}$ is thermodynamically more stable than $[Ni(H_2O)_6]^{2+}$

But when ^{14}C-labelled ($^{14}CN^-$) is added to the solution, it soon or instantaneously incorporated into the complex ie

$$[Ni(CN)_4]^{2-} + 4\,^{14}CN^- \longrightarrow [Ni(^{14}CN)_4]^{2-} + 4CN^-$$

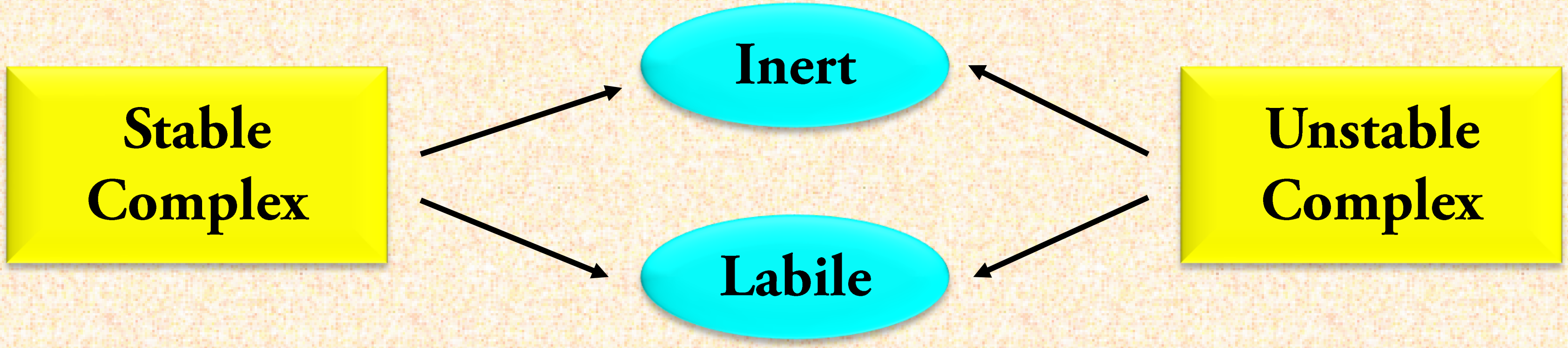
This means, $[Ni(CN)_4]^{2-}$ is Kinetically labile

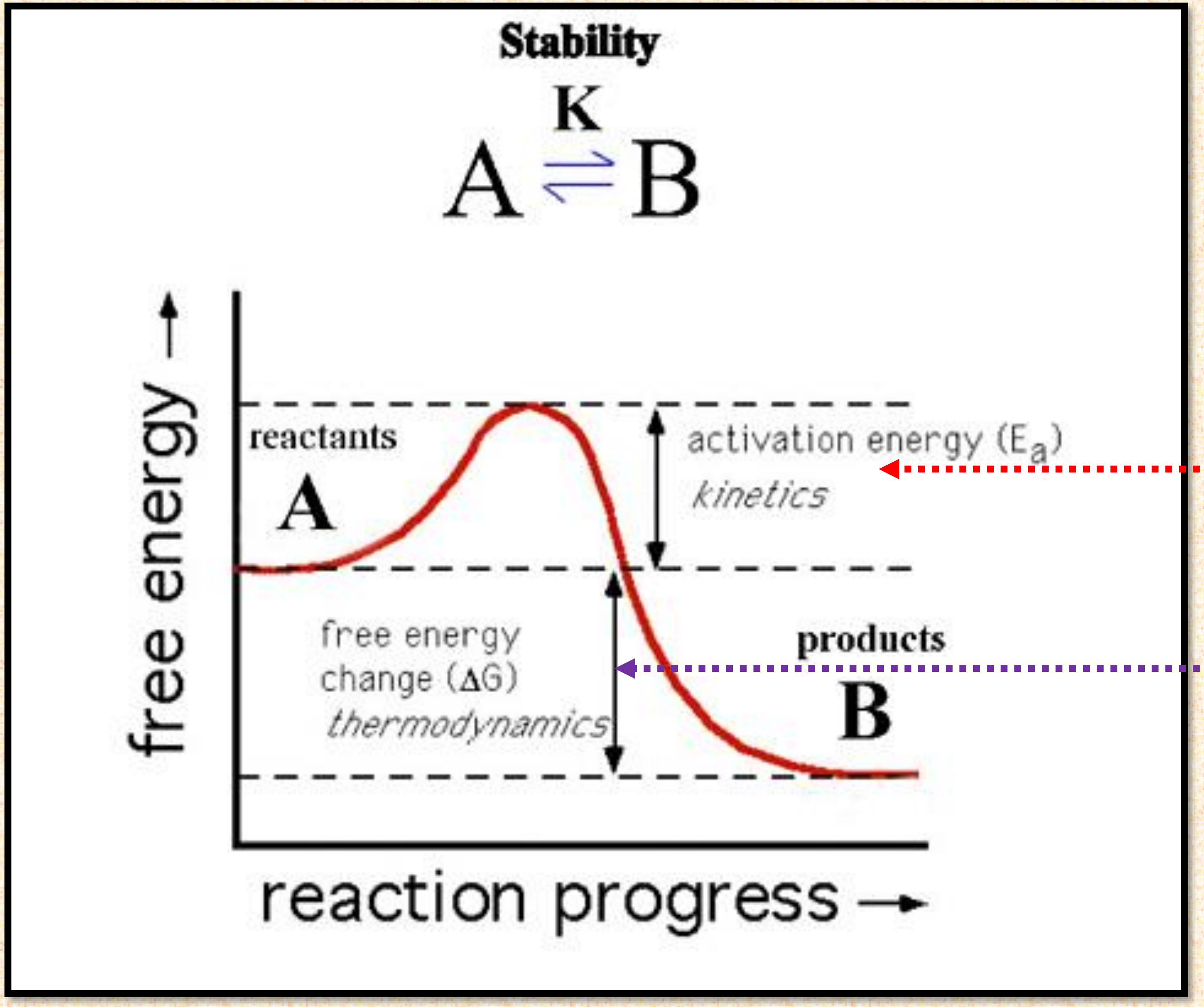
$[Fe(H_2O)_6]^{3+}$ and $[Cr(H_2O)_6]^{3+}$ have almost same bond energy. So Both are equally stable from thermodynamic point of view.

But → $[Fe(H_2O)_6]^{3+}$ is labile and exchanges its ligands rapidly

→ $[Cr(H_2O)_6]^{3+}$ is inert and exchanges its ligands very slowly

Hence, thermodynamic and kinetic stabilities are not at all related





Greater is E_a
Complex is kinetically inert

Kinetic Stability

depends upon

Thermodynamic Stability

Greater is ΔG
Complex is thermodynamic stable

Stability Constants

1. Stepwise Stability Constant (K)

2. Overall Stability Constant (β)

STABILITY CONSTANTS :

Co-ordination compounds are supposed to be formed from their constituents in aqueous solution by a stepwise replacement of co-ordinated water molecules by ligands.

So, different steps involved in the formation of complex are as follo[ws]

$$[M(H_2O)_n] + L \overset{K_1}{\rightleftharpoons} [M(H_2O)_{n-1}L] + H_2O$$

$$[M(H_2O)_{n-1}L] + L \overset{K_2}{\rightleftharpoons} [M(H_2O)_{n-2}L_2] + H_2O$$

$$[M(H_2O)_{n-2}L] + L \overset{K_3}{\rightleftharpoons} [M(H_2O)_{n-3}L_3] + H_2O$$

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$$[M(H_2O)L_{n-1}] + L \overset{K_n}{\rightleftharpoons} [ML_n] + H_2O$$

For each step, there is a equilibrium constant, $K_1, K_2, K_3 \cdots K_n$.

These equilibrium constants $K_1, K_2 \cdots K_n$ are called Stepwise stability constants or formation constant or Successive stability constants

They are called stability constant : larger is the value of $K_1, K_2 \cdots$ greater will be the stability of system.

If reaction takes place in single step, then

$$[M(H_2O)_n] + nL \overset{\beta_n}{\rightleftharpoons} [ML_n] + nH_2O$$

for such reaction, there is equilibrium constant β_n which is called Overall stability constant or overall formatn constant or Cummulative stability constant

Stepwise and Overall Formation Constants

According to J. Bjerrum (1941) the formation of a complex in solution proceeds by the stepwise addition of the ligands to the metal ion. Thus the formation of the complex ML_n may be supposed to take place by the following n consecutive steps.

Where M = central metal cation

L = monodentate ligand

n = maximum co-ordination number for the metal ion M for the ligand

$$M + L \leftrightarrows ML \quad K_1 = \frac{(ML)}{[M][L]}$$

$$ML \leftrightarrows ML_2 \quad K_2 = \frac{(ML_2)}{[ML][L]}$$

$$ML_2 \leftrightarrows ML_3 \quad K_3 = \frac{(ML_3)}{[ML_2][L]}$$

Thus

$$ML_{n-1} + L \leftrightarrows ML_n \quad K_n = \frac{(ML_n)}{[ML_{n-1}][L]}$$

The equilibrium constants, K_1, K_2, K_3, ...K_n are called **stepwise stability constants.**

The formation of the complex MLn may also be expressed by the following steps and equilibrium constants.

$$M + L \xrightarrow{\beta_1} ML,\ \beta = \frac{(ML)}{[M][L]}$$

$$M + 2L \xrightarrow{\beta_2} ML_2,\ \beta_2 = \frac{(ML_2)}{[M][L]^2}$$

Thus $$M + nL \xrightarrow{\beta_n} MLn,\ \beta_n = \frac{(MLn)}{[M][L]^n} \qquad \text{.................(8.1)}$$

The equilibrium constants, β_1, β_2, β_3, ... β_n are called overall formation or **overall stability constants.** βn is called as n[th] overall (or cumulative) formation constant or overall stability constants.

Relationship between K and β:

Step 1

Let us consider the formation of complex ML_n - in simple mann
(ignoring aquated cation)

$\boxed{\text{In terms of } K}$ (consider three steps in the formation)

(i) $M + L \rightleftharpoons ML \Rightarrow K_1 = \frac{[ML]}{[M][L]}$

(ii) $ML + L \rightleftharpoons ML_2 \Rightarrow K_2 = \frac{[ML_2]}{[ML][L]}$

(iii) $ML_2 + L \rightleftharpoons ML_3 \Rightarrow K_3 = \frac{[ML_3]}{[ML_2][L]}$

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n^{th} $ML_{n-1} + L \rightleftharpoons ML_n \Rightarrow K_n = \frac{[ML_n]}{[ML_{n-1}][L]}$

$K_1, K_2, K_3 \cdots K_n$ are the stepwise stability constants.

Step 2

$\boxed{\text{In terms of } \beta}$ (consider first three steps of formation of complex ML_n

(i) $M + L \rightleftharpoons ML$ $\beta_1 = \frac{[ML]}{[M][L]}$

(ii) $M + 2L \rightleftharpoons ML_2$ $\beta_2 = \frac{[ML_2]}{[M][L]^2}$

(iii) $M + 3L \rightleftharpoons ML_3$ $\beta_3 = \frac{[ML_3]}{[M][L]^3}$

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n^{th} $M + nL \rightleftharpoons ML_n$ $\beta_n = \frac{[ML_n]}{[M][L]^n}$

$\beta_n \rightarrow$ is known as n^{th} overall stability constant.

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

Divide and multiply β_3 by $[ML][ML_2]$

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

Step 3

Step 4

or $\beta_3 = \frac{[ML]}{[M][L]} \times \frac{[ML_2]}{[ML][L]} \times \frac{[ML_3]}{[ML_2][L]}$

$$\boxed{\beta_3 = K_1 \times K_2 \times K_3}$$

For a system having <u>n steps</u> :-

$$\boxed{\beta_n = K_1 \times K_2 \times K_3 \times \text{-----} K_n}$$

Hence, <u>overall stability constant β_n</u> is the product of stepwise stabi constants of the system.

The value of the constants are represented on logarithmic scale

$$\boxed{\log_{10}\beta_n = \log_{10}K_1 + \log_{10}K_2 + \log_{10}K_3 + \text{-----} + \log_{10}K_n}$$

Step 5

The overall stability constant is generally used as a guide to the stability of the complex i.e

- For extremely stable complexes :- $\beta_n \approx 10^{30}$ order (maybe)
- For extremely unstable complexes :- β_n may be even < 1
- Also, if value of $\boxed{\log \beta_n > 8}$, the complex is regarded as "stable" complex.

Lastly.....

TRENDS IN K VALUES :

The K values generally decrease with increase in substitution of H_2O by L ie value $\Rightarrow$ $\boxed{K_1 > K_2 > K_3 > \cdots > K_n}$

This gradual decrease in K values is attributed to 3 factors

1. statistical factor,
2. Steric factor,
3. Electrostatic factor.

Thank you