

→ Stability of Metal Complexes:

In the formation of metal complexes in solution, two types of stability of complexes are taken into consideration. These are:

1. Thermodynamic stability
2. Kinetic stability.

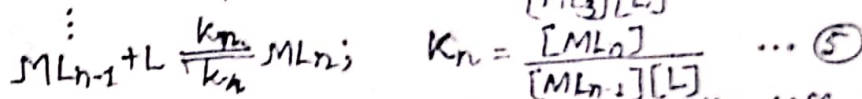
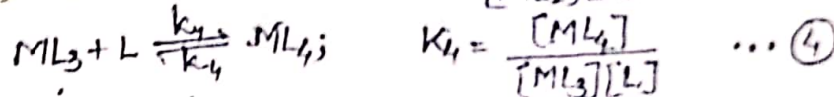
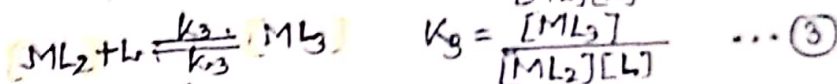
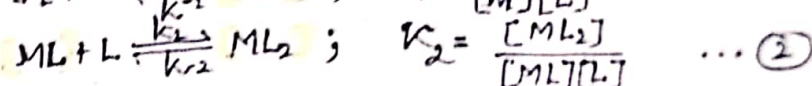
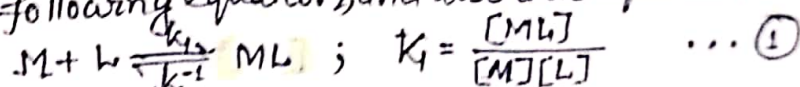
1. Thermodynamic stability: Thermodynamic stability of a complex measures the extent to which this complex will persist in the solution under certain conditions. This deals with the properties like M-L bond energy, stability constant, redox potentials etc. Stronger is the M-L bond, it will be less dissociated in aqueous solution, and hence greater is the stability. Complexes may be stable or Penetration or unstable or normal depending on M-L bond energy. Stable complexes retain their identity in solution while unstable complexes dissociate reversibly in solution.

In studying the thermodynamic stability of complexes, following two types of equilibrium constants are considered:

- (a) Stepwise stability constant
- (b) Overall stability constant.

* (a) Stepwise stability constant / Stepwise formation of complexes:

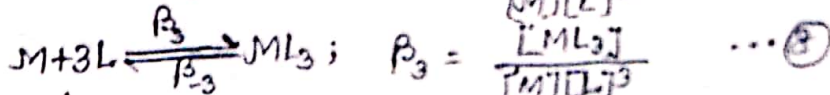
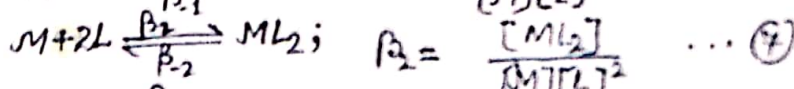
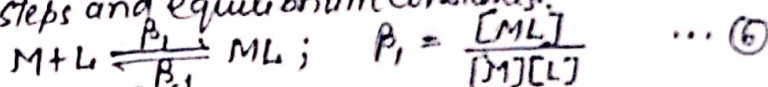
According to Bjerrum, the formation of a complex in solution can take place by the stepwise addition of the ligands (L) to the metal atom/ion (M), only soluble mononuclear complexes are formed. The system at equilibrium may be represented by following equation, and also their equilibrium constants:



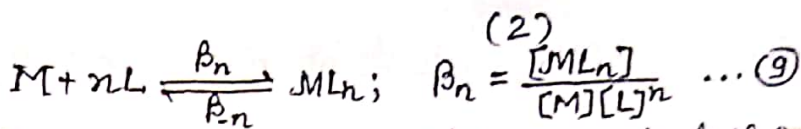
Here $k_1, k_2, k_3, k_4, \dots, k_n$ are rate constants of the different steps of complex formation. $K_1, K_2, K_3, \dots, K_n$ are equilibrium constants, known as stepwise stability/formation constants, n is number of such equilibria following the complex formation which may be maximum coordination no. of metal atom/ion or n .

* (b) Overall / Cumulative formation / stability constant:

The formation of a mononuclear complex, ML_n may also be expressed by following steps and equilibrium constants.

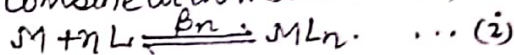


⋮



Here $\beta_1, \beta_2, \beta_3 \dots \beta_n$ are equilibrium constants of cumulative steps of complex formation, known as overall or cumulative formation/stability constants, β_n is known as n^{th} Overall formation or stability constant.

* Relation between stepwise & Overall stability constants: A complex, ML_n is formed when n ligands (L) combine with metal atom (M) in single step.



The stability or formation constant (β_n) for above equilibrium is given as

$$\beta_n = \frac{[ML_n]}{[M][L]^n} \dots \textcircled{2i}$$

If n ligands (L) are added or combined to the metal (M) one by one, i.e. n steps, then formation of a complex (ML_n) can be supposed to take place through n equilibria as shown above (1 to 5).

Multiplying equations (1) to (5) we get.

$$K_1 \times K_2 \times K_3 \times K_4 \dots K_{n-1} \times K_n = \frac{[ML]}{[M][L]} \times \frac{[ML_2]}{[ML][L]} \times \frac{[ML_3]}{[ML_2][L]} \times \frac{[ML_4]}{[ML_3][L]} \dots \frac{[ML_n]}{[ML_{n-1}][L]}$$

$$= \frac{[ML_n]}{[M][L]^n} \dots \textcircled{2ii}$$

From equation (ii) & (2ii), $\beta_n = K_1 \times K_2 \times K_3 \times K_4 \dots \times K_n$ or, $\beta_n = \sum_{n=1}^n K_n \dots \textcircled{iv}$

or, $\log \beta_n = \log K_1 + \log K_2 + \log K_3 \dots + \log K_n$ [Here β_n = Overall stability/formation constant & $K_1, K_2, K_3 \dots K_n$ are stepwise stability/formation constants]

Thus, the value of a stability constant for a given complex is actually consist of a number of stepwise stability constants ($K_1, K_2, K_3 \dots K_n$) equal to coordination number. For example, in formation of $[Cu(NH_3)_4]^{2+}$, $\beta_4 = K_1 \times K_2 \times K_3 \times K_4$ ($n=4$)

* Instability constant?

In aqueous solution, a complex species dissociates to a very small extent. When a complex species dissociates, there lies an equilibrium between the undissociated & dissociated species in the solution. Thus, stability of complex species in solution can be expressed in the form of equilibrium constant of the dissociation reaction/equation, called dissociation or instability constant (K_i).

For example, the dissociation of $[Cu(NH_3)_4]^{2+}$ ion in solution can be given as:



Dissociation/Instability Constant, $K_i = \frac{[Cu^{2+}][NH_3]^4}{[Cu(NH_3)_4]^{2+}} \dots \textcircled{i}$

The formation of above complex ion from its constituents will be expressed as



The formation constant for this reaction (equilibrium) is given as stability constant, β_n or $\beta_4 = \frac{[Cu(NH_3)_4]^{2+}}{[Cu^{2+}][NH_3]^4} \dots \textcircled{ii}$ Equation (ii) is reciprocal of equation (i).

Thus, the instability constant can be defined as the reciprocal of the stability constant of a complex species; i.e. $K_i = \frac{1}{\beta_n}$. Hence, higher value of β_n /lower value of K_i , the greater will be stability of complex species in solution.

⇒ Factors affecting the stability of metal complexes: There are a number of factors which affect the stability of metal complexes. Some of these factors depend on the nature of the central metal atom/ion, while others depend on the nature of the ligands bonded to metal.

1. Factors depending on nature of central metal: The factors which depend on the nature of central metal atom/ion are:

(i) Size of central metal atom/ion: Stability of metal complexes is inversely related to the size of metal ion/atom when ligands are same and metal ions have same charge on them. Thus, the stability of complexes of the cations/atoms belonging to same group decreases from top to bottom in the group/series of elements. For example,

(a) The stability of hydroxide complexes of Gr. 2, in the order: $\text{Be}^{2+} > \text{Mg}^{2+} > \text{Ca}^{2+} > \text{Sr}^{2+} > \text{Ba}^{2+} > \text{Ra}^{2+}$

Ionic radius (\AA): (0.31) (0.65) (0.99) (1.13) (1.35) (1.40)

(b) The stability of the complexes of Mn^{2+} , Fe^{2+} , Co^{2+} , Ni^{2+} , Cu^{2+} , Zn^{2+} (1st transition series) order:

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

$r(\text{\AA})$ (0.91) (0.83) (0.82) (0.78) (0.69) (0.74)

This sequence/order of stability is commonly known as Irving-Williams order of stability of complexes of M^{2+} ions.

* Size of Mg^{2+} ion is smaller than the size of Ca^{2+} ion, and hence, should form more stable complexes than Ca^{2+} but EDTA complex of Mg^{2+} is less stable than that of Ca^{2+} . Since M-L bond (less overlap) is weaker in former case.

* A metal ion with high ionic potential/polarising power/charge density (charge/size) will form more stable complexes, when sizes & charge of metal ions differ.

(ii) Charge on metal ion: The stability of the complexes of metal ions, having almost identical size & same ligand, decreases with the decrease of the charge on them. For example, the stability of complexes of TK^{4+} , Y^{3+} , Ca^{2+} & Na^{+} ions with same ligand is in the order:

$\text{TK}^{4+} (0.95 \text{\AA}) > \text{Y}^{3+} (0.93 \text{\AA}) > \text{Ca}^{2+} (0.99 \text{\AA}) > \text{Na}^{+} (0.95 \text{\AA})$. This can be explained as

as greater the charge on metal ion, the more closely approach of the ligand towards metal ion and hence larger electrostatic attraction will be in between metal ion & ligand.

(iii) Nature of metal atoms/ions: Chatterjee & Hirland have classified metals into three classes on the basis of their electron acceptor character: Class-A, Class-B & borderline metals.

(a) Class-A metals are s, Gr. 1, Gr. 2 elements, Sc_{21} to Cr_{24} , Al_{13} to Cl_{17} , Zn_{30} to Br_{35} , In , Sn , Sb , lanthanides and actinides. They have inert gas conf. ($ns^2 np^6$). They form more stable complexes with ligands having donor atoms N, O, F than those of P, S, Cl.

(b) Class-B metals are Rh, Pd, Ag, Ir, Pt, Au, Hg, having pseudo inert gas conf. ($s^2 p^6 d^{1-10}$). They form the π -bond with ligating atoms. They form stable complexes with ligands like PMe_3 , S^{2-} & I^- having vacant d-orbitals of low energy. They form the complexes of reversed stability.

The order of stability for complexes of Class-A & B metals with ligands heavier atoms:

Class-A metals: $\text{F}^- > \text{Cl}^- > \text{Br}^- > \text{I}^-$; $\text{O} > \text{S} > \text{Se} > \text{Te}$; $\text{N} > \text{P} > \text{As} > \text{Sb} > \text{Bi}$

Class-B metals: $\text{F}^- < \text{Cl}^- < \text{Br}^- < \text{I}^-$; $\text{O} < \text{S} < \text{Se} < \text{Te}$; $\text{N} < \text{P} < \text{As} < \text{Sb} < \text{Bi}$

(c) Borderline metals are Mn_{25} to Cu_{29} , Cd , Tl to Po , Mo , Te , Ru , W , Re , Os . No definite order of stability of these metal complexes.

(4)
 (iv) Electronegativity of metal: The higher the electronegativity of central metal atom, more stable complexes will be formed. e.g., $Mn^{2+} < Fe^{2+} < Co^{2+} < Ni^{2+} < Cu^{2+} < Zn^{2+}$ increasing order of stability of their complexes as electronegativity increase from Mn to Zn.

(v) Electrode potential ($E_{M^{n+}/M}^0$) of metal ions: Metal ions (e.g. Li^+ , Ba^{2+} , Mg^{2+} , Al^{3+}) having large negative electrode potential ($E_{M^{n+}/M}^0$) have more tendency to form complexes with ligands having highly electronegative donor atoms (e.g. N, O, F etc.) as metal ions lesser tendency to attract electrons. On the other hand, metal ions (Ag^+ , Pt^{2+} etc.) having large positive $E_{M^{n+}/M}^0$ have greater tendency to accept electrons and thus form more stable complexes with ligands containing highly polarizable donor atoms (e.g. P, S, Cl etc.).

2. Factors depending on nature of the ligands: The factors which depends on the nature of ligands are:

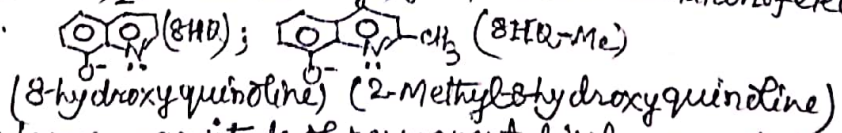
(i) Size & Charge: If a ligand is smaller, it can approach the metal ion more closely forming a stable M-L bond. Similarly, a highly charged ligand would also form a strong M-L bond. Thus, the high charge and small size of a ligand leads to the formation of stable complexes. For example, the order of stability of Hg^{2+} complexes with halides (X) is: $I^- < Br^- < Cl^-$.

(ii) Basic character: The more basic is the ligand (i.e. donor atom is less electronegative), more easily it can donate electron pair (l.p) to the central metal atom/ion, and hence it forms greater stable complexes more easily. For example, order of stability of complexes of Co^{3+} with NH_3 , H_2O & F^- is $NH_3 > H_2O > F^-$. which form ring with M.

(iii) Chelate effect: Stability of complexes containing bi or polydentate ligands is higher than those containing monodentate ligands. This increased stability of a complex containing ring is called chelate effect, and the ligand is called chelating ligand. Thus, the chelating ligands form more stable complexes than monodentate ligands.

For example, $[Ni(NH_3)_6]^{2+} < [Ni(en)_3]^{2+} < [Ni(trien)_2]^{2+}$ increasing order of stability as denticity increases; NH_3 (monodentate) $<$ en (ethylenediamine, bidentate) $<$ $trien$ (tridentate)

(iv) Steric effects: Presence of bulky/larger group near the donor atom of a ligand, mutual repulsion among the ligand makes complex less stable. Thus, complexes containing heavy/bulky ligands are generally less stable than that containing smaller simpler ligands, called steric strain/hindrance effect. For example, $[Ni(SHQ)_2]$ is more stable than that of $[Ni(SHQ-Me)_2]$, since Me (methyl) group hindered donation of electrons from N atom to $Ni(II)$ ion.



(v) Dipole moment: The larger magnitude of permanent dipole moment for neutral ligands, the greater is the stability of the complexes, as more tendency to bind with central metal ion. For example, Order of stability of complexes formed by neutral ligands: $NH_3 > CH_3NH_2 > M(CH_3)_2 > N(CH_3)_3$.

(vi) π -bonding capacity: The ligands like CN^- , CO , R_3P , R_2S , alkenes ($C=C$), alkynes ($C\equiv C$), which are capable of forming M-L bonds (M = transition metal) give more stable complexes. This is because transition metal atoms/ions have d-orbitals for back bonding (π).