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Stability of Metal Complexes

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and Muthukumar Kannan

Abstract

The stability of coordination complex is an important factor that decides the stability and reactivity of a metal complex. The stability of metal complex is governed by two different aspects such as thermodynamic and kinetic stabilities. The correlation between stability and reactivity of coordination compounds has been described in this chapter. This chapter also enlists the factors influencing the stability of metal complexes such as the nature of metal ions, ligands, bonding between metal ions and ligands, etc. In addition, the methods available for the determination of stability constants are given in detail.

Keywords: stability, reactivity, coordination complexes, stability constants

1. Introduction

The stability of metal complex generally means that it exists under favorable conditions without undergoing decomposition and has a considerable shelf life period [1]. The term stability of metal complex cannot be generalized since the complex may be stable to one reagent/condition and may decompose in presence of another reagent/ condition. The stability of metal complexes can be explained with the help of two different aspects, namely, thermodynamic stability and kinetic stability [2]. Nevertheless, a metal complex is said to be stable if it does not react with water, which would lead to a decrease in the free energy of the system, i.e., thermodynamic stability. On the other hand, the complex is said to possess kinetic stability if it reacts with water to form a stable product and there is a known mechanism through which the reaction can proceed. For example, the system may not have sufficient energy available to break a strong bond, although once the existing bond is broken it could be replaced by new bond which is stronger than the older one [1]. Stability of complex compound is assigned to be its existence in aqueous solution with respect to its bond dissociation energy, Gibbs free energy, standard electrode potential, pH of the solution, and rate constant or activation energy for substitution reactions.

1.1 Thermodynamic stability

Thermodynamic stability of a complex refers to its tendency to exist under equilibrium conditions. It determines the extent to which the complex will be formed or be converted into another complex at the point of equilibrium. In other words, thermodynamic stability of complexes is the measure of tendency of a metal ion to selectively form a specific metal complex and is directly related to the metal-ligand bond energies. The thermodynamic stability of complexes is

represented by formation constant. The formation constant is also known as stability constant, which is the equilibrium constant obtained for the formation metal complex [1, 2].

In general, the metal complexes are not prepared from their corresponding starting materials in gaseous phase but are prepared in aqueous solution. In aqueous solution, a metal cation gets hydrated to give aqua complex of the type $[M(H_2O)_x]^{n+}$. When a ligand replaces water molecule from aqua complex ion, a new metal complex is formed and equilibrium is established as shown:

$$[M(H_2O)_x]^{n+} + L \underset{\longleftarrow}{\overset{K_f}{\longrightarrow}} [M(H_2O)_{x-1}L]^{n+} + H_2O \qquad (1)$$
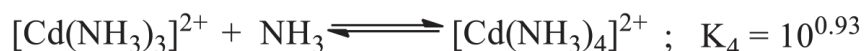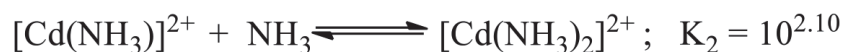
where x is the number of water molecules, n is the oxidation number of the metal cation, and L is the neutral and monodentate ligand. For simplicity, the above reaction can be written in generalized form as given:

$$M + L \underset{\longleftarrow}{\overset{K_f}{\longrightarrow}} ML \qquad (2)$$

The equilibrium constant K_f of the reaction is given by:

$$K_f = \frac{[ML]}{[M][L]} \qquad (3)$$

In the above equation, the concentration of water is not included. Since the solution is dilute, the water molecules which enter the bulk solution do not have much influence on the equilibrium constant. It is observed from Eq. (3) that the higher the value of K_f, the greater will be the stability of the complex formed. A high value of the equilibrium constant ($K_f > 1.0$) also indicates that at equilibrium the activity of complex ML is larger than the product of activities of M and L. Thus, large value of K_f indicates that the ligand L binds to the metal ion more strongly than H_2O and hence L is a stronger ligand than H_2O. If K_f is less than 1.0, then ligand L is weaker than H_2O. Thus stability constant is used as a measure of thermodynamic stability of the complex. With a few exceptions, the value of successive stability constants decreases regularly from K_1 to K_n, that is, $K_1 > K_2 > K_3 > \ldots > K_{n-1} > K_n$. This trend is illustrated by taking formation of $[Cd(NH_3)_4]^{2+}$ as an example [3, 4]:
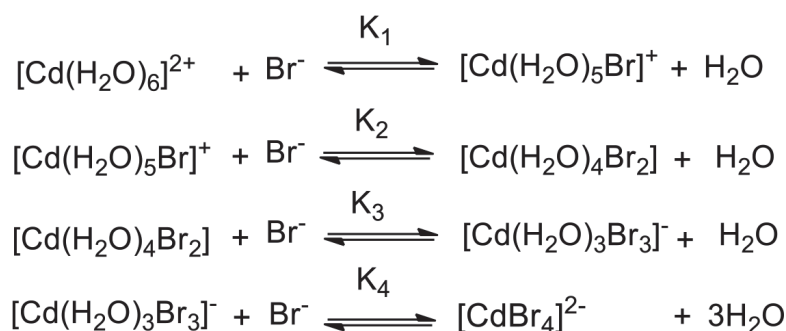
$$Cd^{2+} + NH_3 \underset{\longleftarrow}{\longrightarrow} [Cd(NH_3)]^{2+} \; ; \; K_1 = 10^{2.65}$$

$$[Cd(NH_3)]^{2+} + NH_3 \underset{\longleftarrow}{\longrightarrow} [Cd(NH_3)_2]^{2+} \; ; \; K_2 = 10^{2.10}$$

$$[Cd(NH_3)_2]^{2+} + NH_3 \underset{\longleftarrow}{\longrightarrow} [Cd(NH_3)_3]^{2+} ; \; K_3 = 10^{1.44}$$

$$[Cd(NH_3)_3]^{2+} + NH_3 \underset{\longleftarrow}{\longrightarrow} [Cd(NH_3)_4]^{2+} \; ; \; K_4 = 10^{0.93}$$

The steady decrease in the value of stepwise formation constants from K_1 to K_n is due to:

i. Increase in the number of ligands in coordination sphere that causes to decrease the number of H_2O molecules to be replaced and thus the probability of replacement of water molecules decreased

ii. Electrostatic factor

iii. Steric hindrance with increase in number of ligands

iv. Statistical factors (number of replaceable positions)

However, in some cases, it is found that $K_{n+1} > K_n$ because of unusual structural changes and changes in electronic configuration of the metal ion. The change in electronic structure of the metal ion causes the variation in the crystal field stabilization energy (CFSE). The complex with higher CFSE value will be stable, and the equilibrium constant for that complex formation will be high. One such example is the formation of $[CdBr_4]^{2-}$ complex in aqueous solution. The reaction of aqua complex $[Cd(H_2O)_6]^{2+}$ with Br^- ligand exhibits four stepwise equilibrium or stepwise formation constants K_1, K_2, K_3, and K_4. The order of stepwise formation constants is observed as follows, $K_1 > K_2 > K_3 < K_4$, which is not in agreement with the common trend of $K_1 > K_2 > K_3 > K_4$. Aqua complex of most of the M^{2+} ions including Cd^{2+} are octahedral, whereas the halo complexes of Cd^{2+} ion are tetrahedral. The reaction sequence for the formation of $[CdBr_4]^{2-}$ is given as follows:

$$[Cd(H_2O)_6]^{2+} \ + \ Br^- \ \underset{}{\overset{K_1}{\rightleftharpoons}} \ [Cd(H_2O)_5Br]^+ \ + \ H_2O$$

$$[Cd(H_2O)_5Br]^+ \ + \ Br^- \ \underset{}{\overset{K_2}{\rightleftharpoons}} \ [Cd(H_2O)_4Br_2] \ + \ H_2O$$

$$[Cd(H_2O)_4Br_2] \ + \ Br^- \ \underset{}{\overset{K_3}{\rightleftharpoons}} \ [Cd(H_2O)_3Br_3]^- + \ H_2O$$

$$[Cd(H_2O)_3Br_3]^- \ + \ Br^- \ \underset{}{\overset{K_4}{\rightleftharpoons}} \ [CdBr_4]^{2-} \ \ \ \ \ \ + \ 3H_2O$$

In the final step, there is an unusual structural change from six coordinated octahedral $[Cd(H_2O)_3Br_3]^-$ complex to four coordinated tetrahedral $[CdBr_4]^{2-}$ complex in addition to change in the electronic configuration which lead to $K_4 > K_3$.

The formation constant (K_f) is related to the standard Gibbs free energy change ($\Delta G°$) and standard electrode potential ($E°$) according to following equations:

$$\Delta G° = -RTlnK_f \tag{4}$$

$$\Delta G° = -nFE° \tag{5}$$

$$\text{hence } RTlnK_f = nFE° \tag{6}$$

Since $\Delta G°$ is a thermodynamic property, the formation constant is the measure of thermodynamic stability. From Eqs. (4) to (6), it can be interpreted that the thermodynamic stability of a complex can be measured in terms of formation constant, Gibbs free energy change, and standard electrode potential. A high negative value of $\Delta G°$ indicates that the position of equilibrium favors the product (complex); hence the complex formed will be more stable.

1.2 Stepwise formation of complex and stepwise formation constants

The formation constant describes the formation of a complex from metal cation and ligands. Bjerrum (1941) defined that the formation of a metal complex in aqueous solution takes place by replacing the water molecule by another ligand (L)

[5, 6]. It is assumed that this reaction does not occur in a single step but occurs in several steps, and each step is characterized by its individual equilibrium constant called as stepwise formation constant (K). For example, consider the formation of a complex [ML_n] formed by the following reactions:

$$M + L \xrightleftharpoons{K_1} ML$$

By assuming the value of activity coefficients as unity, the equilibrium constant K_1 for the complex (ML) having one ligand (L) will be given as

$$K_1 = \frac{[ML]}{[M][L]}$$

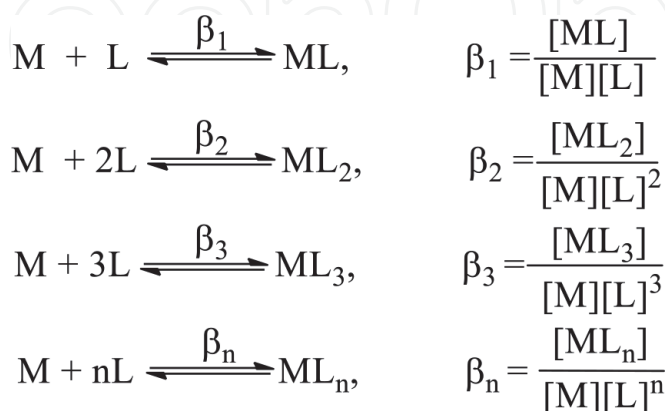When the metal complex ML reacts with one more ligand L,

$$ML + L \xrightleftharpoons{K_2} ML_2$$

and the equilibrium constant K_2 will be

$$K_2 = \frac{[ML_2]}{[ML][L]}$$

Similarly, for the formation of the complex ML_n from ML_{n-1} and L, the equilibrium constant is represented as follows,

$$K_n = \frac{[ML_n]}{[ML_{n-1}][L]}$$

The equilibrium constants K_1, K_2, ... , K_n are known as stepwise formation constants. On the other hand, the equilibrium constant for the overall reaction may be considered as

$$M + L \xrightleftharpoons{\beta_1} ML, \qquad \beta_1 = \frac{[ML]}{[M][L]}$$

$$M + 2L \xrightleftharpoons{\beta_2} ML_2, \qquad \beta_2 = \frac{[ML_2]}{[M][L]^2}$$

$$M + 3L \xrightleftharpoons{\beta_3} ML_3, \qquad \beta_3 = \frac{[ML_3]}{[M][L]^3}$$

$$M + nL \xrightleftharpoons{\beta_n} ML_n, \qquad \beta_n = \frac{[ML_n]}{[M][L]^n}$$

where β_1, β_2, β_3, ... , β_n are the equilibrium constants called as overall formation constants and K_1, K_2, K_3, ... , K_n are stepwise stability or formation constants. The products of stepwise constants are Ks and βs are related one another. For example, consider the product of stepwise formation constants K_1, K_2, K_3, ... , K_n.

$$K_1 \times K_2 \times K_3 \times \ldots K_n \quad = \frac{[ML]}{[M][L]} \times \frac{[ML_2]}{[ML][L]} \times \frac{[ML_3]}{[ML_2][L]} \times \cdots \frac{[MLn]}{[ML_{n-1}][L]}$$

$$= \frac{[ML_n]}{[M][L]^n} = \beta$$

Above equation indicates that the overall formation constant (β) is equal to the product of the stepwise formation constant K_1, K_2, K_3, ..., K_n.

1.3 Kinetic stability

Kinetic stability is related to the reactivity of the metal complexes in solution and deals with the rate of the reaction, its activation energy, etc. Kinetic stability is also related to how fast a compound reacts rather than how stable it is. It aids in determining the rate at which the reaction occurs to establish the equilibrium [7].

The term kinetic stability of complexes is classified into labile and inert by Taube on the basis of rate of the reactions. When the rate of substitution of ligands is high, the complex is said to be labile. For example, the copper complex of the formula $[Cu(NH_3)_4(H_2O)_2]^{2+}$ is labile. In aqueous solution the complex is blue in color, and when concentrated hydrochloric acid is added to this solution, the solution turns green giving rise to complex $[CuCl_4]^{2+}$. On the other hand, in inert complexes the rate of ligand exchange is very slow, and the ligands are very exchanged with difficulty. For example, the cobalt complex $[Co(NH_3)_6]^{3+}$ reacts slowly, and no reaction takes place at room temperature when conc. HCl was added to the aqueous solution. However, only one NH_3 ligand was found to be substituted by Cl ligand, when the aqueous solution of the complex was heated with 6M hydrochloric acid.
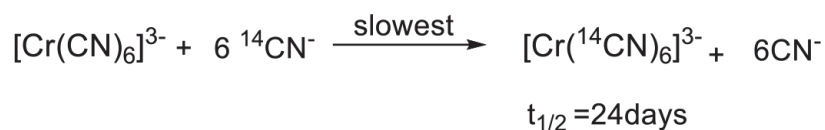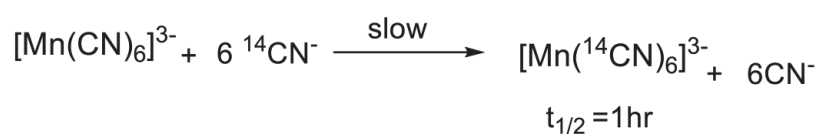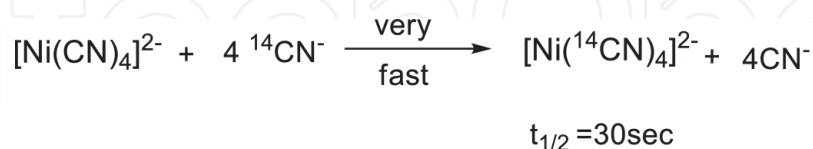
2. Relation between thermodynamic and kinetic stabilities

For metal complexes, the stability and reactivity are described in thermodynamic and kinetic terms, respectively. In particular, the terms stable and unstable are related to thermodynamic aspects, whereas labile and inert terms are related to kinetic aspects. As a rule of thumb, a metal complex is said to be labile if it reacts within 1 min at 25°C, and if it takes longer time, it is considered to be inert.

Thermodynamic stability refers to the energy change that occurs while starting materials are converted to products, that is, ΔG, for the reaction. The change in free energy is given by the equation ΔG = ΔH−TΔS = −RTlnK, where ΔS is the entropy, ΔH is the enthalpy, and K is the equilibrium constant for the reaction. Kinetic stability refers to reactivity or the ability of the metal complex to undergo ligand substitution reactions. Complexes which undergo extremely rapid ligand substitution reaction are referred to as labile complexes, and complexes that undergo extremely slow ligand substitution reaction are referred to as inert complexes. Sometimes the thermodynamic and kinetic stabilities of complexes are parallel to one another, but often they do not. One of the suitable examples for thermodynamically stable and kinetically inert complex is $[Ni(CN)_4]^{2-}$ as it undergoes ligand substitution reaction very rapidly. On the other hand, the cobalt complex $[Co(NH_3)_6]^{3+}$ is thermodynamically unstable but kinetically inert. The complex $[Co(NH_3)_6]^{3+}$ is thermodynamically unstable since the complex was observed to decompose very rapidly with rate in the order of 10^{25} in acidic solution. However, no ligand substitution reaction is found when the complex is kept in acidic solution for several days; hence the complex is kinetically inert. From the above two examples, it can be interpreted that the stability of a complex mainly depends upon the

conditions, and it is always recommended to specify the conditions such as pH, temperature, etc. while mentioning the stability of the complex. In brief, it is not necessary for a stable complex to be inert and an unstable complex to be labile.

Consider the three complexes $[Ni(CN)_4]^{2-}$, $[Mn(CN)_6]^{3-}$, and $[Cr(CN)_6]^{3-}$. All the complexes are thermodynamically stable, but kinetically they behave in a different manner. The rate of exchange can be measured when carbon-14-labelled cyanide ions are reacted with metal complexes in solution. It indicates that $[Ni(CN)_4]^{2-}$ is labile, $[Mn(CN)_6]^{3-}$ is less labile, and $[Cr(CN)_6]^{3-}$ is inert and proves that not all stable complexes are inert and vice versa.

$$[Ni(CN)_4]^{2-} + 4\ {}^{14}CN^- \xrightarrow{\text{very fast}} [Ni({}^{14}CN)_4]^{2-} + 4CN^-$$

$$t_{1/2} = 30\text{sec}$$

$$[Mn(CN)_6]^{3-} + 6\ {}^{14}CN^- \xrightarrow{\text{slow}} [Mn({}^{14}CN)_6]^{3-} + 6CN^-$$

$$t_{1/2} = 1\text{hr}$$

$$[Cr(CN)_6]^{3-} + 6\ {}^{14}CN^- \xrightarrow{\text{slowest}} [Cr({}^{14}CN)_6]^{3-} + 6CN^-$$

$$t_{1/2} = 24\text{days}$$

3. Factors affecting the stability of metal complexes

There are several factors that can affect the stability of the metal complexes [2, 5, 8, 9], which include:

1. Nature of the central metal ion

2. Nature of the ligand

3. Chelating effect

4. Macrocyclic effect

5. Resonance effect

6. Steric effect or steric hindrance

3.1 Nature of central metal ion

3.1.1 Charge on metal cation

In metal cations, higher oxidation state forms more stable complex than lower oxidation states with ligands such as NH_3, H_2O, etc. Even few exceptions are there like CO, PMe_3, o-phenanthroline, bipyridyl, CN^-, which form more stable complex with lower oxidation state metals.

3.1.2 Size of central metal cation

The stability of metal complex increases with decrease in size of the metal cations. For M^{2+} ions, the general trend in stability for complexes is

$$Ba^{2+} < Sr^{2+} < Ca^{2+} < Mg^{2+} < Mn^{2+} < Fe^{2+} < Co^{2+} < Ni^{2+} < Cu^{2+} > Zn^{2+}$$
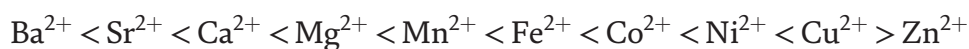
This trend in stability is known as Irving-Williams series.

This order of stability is also in good agreement with the charge to radius ratio concept because the radii decrease from Ba^{2+} to Cu^{2+} and then increased to Zn^{2+}. The order of size of dipositive ions is

$$Ba^{2+} > Sr^{2+} > Ca^{2+} > Mg^{2+} > Mn^{2+} > Fe^{2+} > Co^{2+} > Ni^{2+} > Cu^{2+} < Zn^{2+}$$
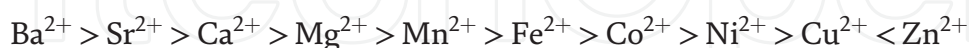
3.2 Nature of ligands

Basic character of ligands: The greater is the basic character of ligand, the more easily it can donate its lone pair of electrons to the central metal ion and hence greater is the complex stability. In 3D-series metal ion, order of stability of complex with NH_3, H_2O, and F^- is:

$$NH_3 > H_2O > F^-$$
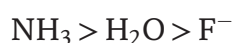
The nature of metal-ligand bond also affects the stability of metal complexes. The higher the covalent character, the greater will be the complex stability. For example, the stabilities of silver complexes have different halide ligands which are in the following order:

$$AgI_2^- > AgBr_2^- > AgCl_2^- > AgF_2^-$$
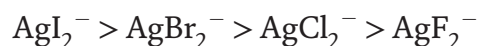
Ligands having vacant p- or d-orbital tend to form π bond and hence form stable complexes with metals. Ligands that are capable of forming such π bond are CO, CN^-, alkene, phenanthroline, etc.

3.3 The chelate effect

The chelate effect is that the complexes resulting from coordination of metal ions with the chelating ligand are thermodynamically much more stable than the complexes with non-chelating ligands [10, 11]. Chelating ligands are molecules which can bind to single metal ion through several bonds and are also called as multidentate ligands. Simple (and common) examples include ethylenediamine and oxalate. Non-chelating ligands are ligands that bond to just one site, such as chloride, cyanide, and water.

The chelate effect can be understood by comparing the reaction of a metal ion, respectively, with a chelating ligand and with a monodentate ligand having similar/comparable donating groups. During the comparison study, the number of coordination should be maintained equal in both the cases, for example, the value obtained while adding a bidentate ligand is compared with the value obtained for two monodentate ligands. For example, coordination of metal ion with chelating ligand 2,2′-bipyridine can be compared with that of monodentate pyridine ligand. Another such comparison can be made between coordination behavior of chelating 1,2-diaminoethane (ethylenediamine = en) and monodentate ammonia. Such

comparison studies revealed that the metal complex formed from chelating ligands are thermodynamically more stable than the complex formed from monodentate ligand. For example, formation of complexes from hydrated cadmium ion, $[Cd(H_2O)_4]^{2+}$ with methylamine (CH_3NH_2), ethylenediamine (en) and triethyle-netetramine (trien), and their stability is in the following order:

$$[Cd(CH_3NH_2)_4]^{2+} < [Cd(en)]^{2+} < [Cd(trien)]^{2+}$$

3.4 Macrocyclic effect

A macrocyclic ligand is a cyclic molecule that contains nine or more atoms in the cyclic structure and has three or more potential donor atoms which can coordinate to the metal ion. It has been observed that the stability of metal complexes in the presence of macrocyclic ligand of appropriate size is higher than the stability of complexes coordinated to open-ended multidentate chelating ligands. Some notable examples of macrocyclic ligands include cyclic crown polyether, heme, etc. [12].

3.5 Resonance effect

Resonance increases the stability of the complexes. For example, acetylacetonate anion ligand shows resonance, and as a result it forms stable complexes upon reacting with metal ion (**Figure 1**). The ligand-metal π bonding increases the delocalization of electrons compared to free enolate as shown below and leads to increased stability (**Figure 2**).
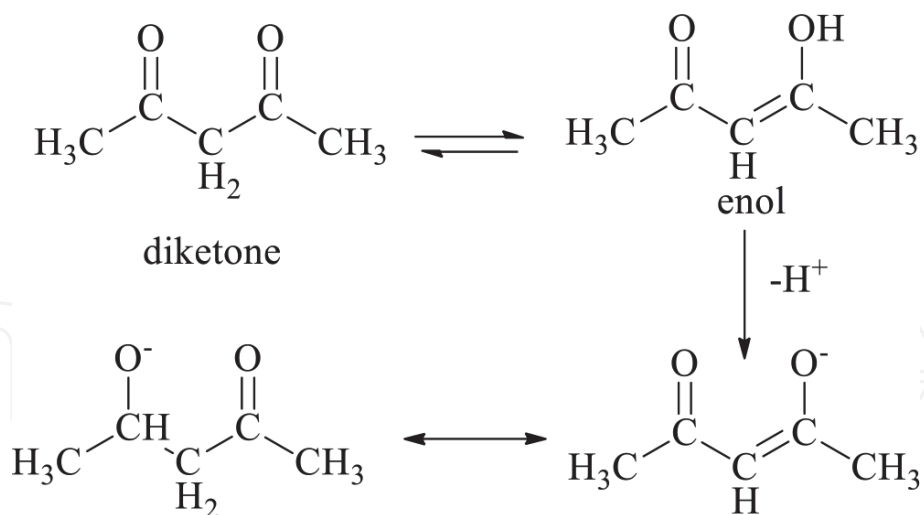

Figure 1.
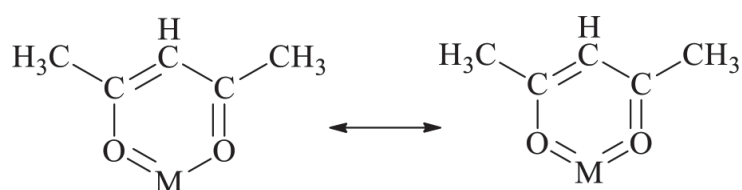*Resonance structure of acetonylacetonate ligand.*

Figure 2.
Acetonylacetonate-metal complex.

3.6 Steric effect

The presence of bulky substituents in the ligands can affect the stability of the metal complex, and this type of destabilization of metal complex due to bulkiness of the substituent is called as steric effect [13]. For example, consider the ligand 8-hydroxy quinoline and its methyl substituted derivative 2-methyl-8-hydroxy quinolone. Both are bidentate ligands and form chelated complexes with Ni^{2+} ion as shown in **Figure 3**.

Figure 3.
Chelating complexes of Ni(II) ion showing steric effect.

The complex (II) is less stable than complex (I) because of bulky group attached to an atom adjacent to donor atom which cause a steric hindrance and lower the stability of the complex.

3.7 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. Some of the notable examples of complexes that have high CFSE are low spin $5d^6$ complexes of Pt^{4+} and Ir^{3+} and square planar $5d^8$ complexes of Pt^{2+}. All these complexes are thermodynamically stable and kinetically inert, which undergo ligand substitution reactions extremely slowly [3, 4].

4. Determination of stability constants

The determination of metal complexes involves several methods including spectroscopic and potentiometric methods. The determination of stability constant is very significant to understand the role and behavior of ligand(s) in stabilizing the metal complexes and found applications in the fields of biology, environmental study, metallurgy, food chemistry, and many other industrial processes. Some of the methods that are used for the determination of stability constants are given as follows.

4.1 Spectroscopic methods

UV-Vis spectroscopic technique has been used to determine the stability constant and composition of a complex [14]. The formation of metal complex is indicated by the change in absorbance in the UV-Vis spectroscopy. The relationship between absorbance (A) and concentration is given by Beer's law as shown.

$$A = \varepsilon.c.l.$$

where ε = molar extinction coefficient, l = path length of the absorption cell, c = concentration of the complex.

From the above equation, the concentration (c) of the metal complex can be calculated by measuring absorbance (A) using spectrophotometer and knowing the molar extinction coefficient (ε) at that wavelength (λ) and path length (l). For example, consider the formation constant (K_f) for the following reaction:

$$M^{n+} + L \xrightleftharpoons{K_f} ML^{n+}, \quad K_f = \frac{[ML^{n+}]}{[M^{n+}][L]} \tag{7}$$
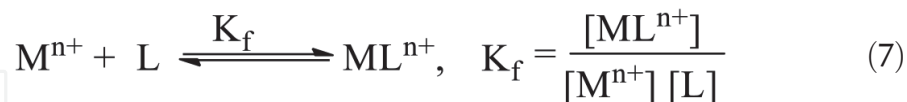
By knowing the values of $[ML^{n+}]$, $[M]$, and $[L]$, Kf can be calculated. $[ML^{n+}]$, $[M]$, and $[L]$ can be calculated as follows:

$$C_M = [M^{n+}] + [ML^{n+}] \tag{8}$$

$$C_L = [L] + [ML^{n+}] \tag{9}$$

where C_L and C_M are the total concentrations of the ligand and metal ion, respectively.

From Beer's law

$$A = \sum_{ML^{n+}} \times l \times [ML^{n+}] \tag{10}$$

On rearranging

$$[ML^{n+}] = A / \sum_{ML^{n+}} \times l \tag{11}$$

On substituting Eq. (11) in (8), we get

$$C_M = [M^{n+}] + A / \sum_{ML^{n+}} \times l$$

$$\text{or } [M^{n+}] = C_M - A / \sum_{ML^{n+}} \times l \tag{12}$$

Similarly, from Eqs. (9) and (11), we get

$$[L] = C_L - A / \sum_{ML^{n+}} \times l \tag{13}$$

By introducing the values of $[ML^{n+}]$, $[M^{n+}]$, and $[L]$ from Eqs. (11) to (13) in the formation constant Eq. (7), we can determine the value of K_f.

4.2 Job's method or method of continuous variations (MCV)

Job's method of continuous variations (MCV) is used to determine the complex formation as well as stability constants [14, 15]. Job's method is basically used to determine the composition of metal complexes, and this is the modified version of spectroscopic method. This method is applicable in the case of solutions, where the formation of one metal complex takes place.

This method includes the following steps:

i. Make a volume of 10 mL solutions of metal complex containing different proportions of metal ion as well as ligand. The number of solutions should be 10.

Sr. no. of solution:	1	2	3	4	5	6	7	8	9	10
Volume of metal ion (mL)	0	1	2	3	4	5	6	7	8	9
Volume of ligand (mL)	9	8	7	6	5	4	3	2	1	0

Here the total concentration of the solution is constant, i.e., sum of concentration of the metal, C_M, and the ligand, C_L, is fixed. Therefore:

$$C_M + C_L = C \text{ (constant)} \tag{14}$$

ii. In the next step, optical densities of the solutions prepared in the previous step are to be determined spectrophotometrically at the wavelength of light which is strongly absorbed by metal complex but does not get absorbed by metal ion and ligand.

iii. A plot between mole fraction (*mf*) of the ligand and absorbance or optical density is to be drawn. The plot obtained is shown in **Figure 4**.

On the extrapolation of the curve, the legs of the curve intersect each other at a point which is the point of maximum absorbance.

Suppose ML_n is the formula of the complex, then

$$n = C_L/C_M \tag{15}$$

Eq. (14) can be rewritten as:

$$C_M/C + C_L/C = C/C = 1 \tag{16}$$

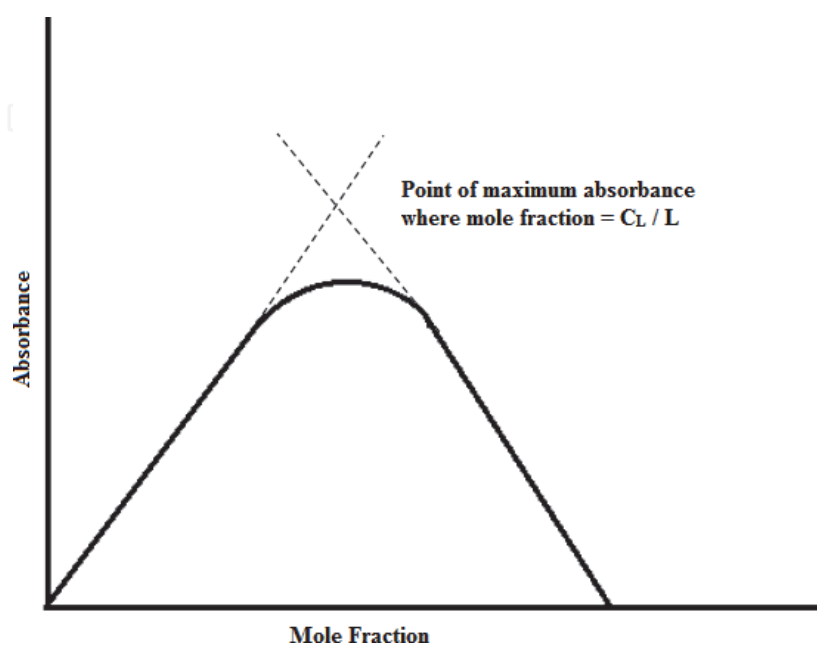From this equation, namely,

$$C_L/C = mf \tag{17}$$

Figure 4.
Determination of the composition of metal complex Job's method of continuous variation.

On reducing Eq. (16), we get.

$$mf + C_M/C = 1$$

or
$$C_M/C = 1 - mf \qquad (18)$$

By dividing (17) by (18), we get.

$$C_L/C \text{ X } C/C_M = mf/1 - mf$$

or
$$C_L/C_M = mf/1 - mf$$

or
$$n = mf/1 - mf \qquad (19)$$

The composition of the complex, ML_n, can be determined by the value of n as obtained from Eq. (19). There are some drawbacks of this method. One of the drawbacks is that this method is applicable where, under experimental conditions, only one complex is formed. Also, the total volume of the solutions which contain metal ion and ligand should not be changed. The method of continuous variations has also found tremendous application in the field of organometallic chemistry [16].

4.3 Bjerrum's method

The type and extent of interaction existing between the metal ion and ligand can be investigated by various experimental methods [17–21], and each method requires different experimental conditions and resulted in differences in the interpretation of reaction mechanism and stability constants. Bjerrum's method to determine the stability constant is also known as potentiometric method. This method is based on the competition between hydrogen ion and metal ion for ligand which is a weak base. Consider a metal ion and an acid such as nitric acid are added to a ligand in aqueous solution; the following equations are obtained:

When acid reacts with ligand

$$L + H^+ \xrightleftharpoons{K_a} HL^+; \; K_a = \frac{[HL^+]}{[L][H^+]}$$

where K_a is acid association constant of the ligand

When metal ion reacts with ligand

$$L + M^+ \xrightleftharpoons{K_f} ML^+; \; \text{where } K_f = \frac{[ML^+]}{[L][M^+]} \qquad (20)$$

where K_f is the formation constant.

Let us consider C_H, C_M, and C_L are the total concentrations of acid, metal ion, and ligand, respectively. Then

$$C_H = [H^+] + [HL^+]$$

$$C_L = [L] + [ML^+] + [HL^+]$$

$$C_M = [M^+] + [ML^+]$$

By solving above three equations and using the acid association constant K_a, we get

$$[ML^+] = C_L - C_H + [H^+] - \frac{C_H - [H^+]}{K_a[H^+]}$$

$$[M^+] = C_M - [ML^+]$$

$$[L] = \frac{C_H - [H^+]}{K_a[H^+]}$$

The concentration terms of $[ML^+]$, $[M^+]$, and $[L]$ can be calculated potentiometrically by using a pH meter and by substituting the values of $[ML^+]$, $[M^+]$, and $[L]$ in the formation constant (K_f); Eq. (20) can determine the value of K_f.

In the potentiometric or pH-metric determination of stability constant, a ligand and an acid such as nitric acid are titrated against standard NaOH during which period the pH of the solution has to be measured after each addition. Throughout the experimental studies, several conditions must be maintained such as

For electrical neutrality

$$[H^+] + [Na^+] = [OH^-] + [L^-] \qquad (21)$$

The total concentration of the ligand is given as follows:

$$L_{Total} = [HL] + [L^-] \qquad (22)$$

The protonation of the ligand can be represented as

$$HL \quad \rightleftharpoons \quad H^+ \ + \ L^-$$

The equilibrium constant K_a is given as

$$K_a \quad = \quad \frac{[H^+][L^-]}{[HL]} \qquad (23)$$

By combining Eqs. (21)–(23), we get

$$pK_a \quad = \quad - \log [H^+] \quad + \quad \log \left(\frac{L_{Total} - \{[Na^+] + [H^+] - [OH^-]\}}{[Na^+] + [H^+] - [OH^-]} \right)$$

$[OH^-]$ and $[H^+]$ are negligible as compared to $[Na^+]$ at near neutral solution. Hence Eq. (24) becomes

$$pK_a \quad = \quad - \log [H^+] \quad + \quad \log \left(\frac{L_{Total} - [Na^+]}{[Na^+]} \right)$$

The above equation is used to calculate the value of pK_a of ligand.

When a ligand is titrated with a solution containing M^{n+} ion and an equivalent amount of H^+, the resulting solution will have an equilibrium mixture of H^+, OH^-, HL, L^-, M^{n+}, $M^{(n-1)+}L$, $M^{(n-2)+}L_2$, etc. By measuring the pH values with the help of pH meter and knowing the concentrations of M^{n+}, H^+, HL, etc., one can calculate the stepwise stability constants K_1, K_2, K_3, etc. During the evaluation of equilibrium

constants, the concentrations of M^{n+} and L^- are varied, and such variations in the concentration will lead to changes in the ionic strength of the solutions. In order to maintain the constant ionic strength, a large excess of an ionic salt is added to the reaction mixture. The presence of large excess of ionic salt will compensate any changes in the ionic strength of the solution. The ionic salts that are added for such purpose should not react with M^{2+} or L^-, and commonly used salts include KNO_3 and $NaClO_4$, due the low affinity of NO_3^- and ClO_4^- ions for most of the M^{2+} ions. For example, KNO_3 was added in excess during the binding study of the ligand p-aminobenzoic acid with Ni, Mg, and Co metal ions. The p-aminobenzoic acid has two coordination sites such as amino and carboxylate groups and has a pK_a value of 5.9153. The stability constant values obtained for Ni, Mg, and Co complexes are depicted in **Table 1**.

The stability constant values for Ni shows the trend 2:3 < 1:5 < 1:1 < 1:2, while the trend for Co is 1:2 < 2:3 < 1:1 < 1:5 and for Mg it is 1:5 < 1:2 < 1:1 < 2:3. The values obtained from the above study indicates that 1:2 complex of Ni complex is more stable, whereas Co complex is stable in 1:5 ratio and that of Mg is more stable in the ratio of 2:3.

4.4 Irving and Rossotti method

The Irving and Rossotti method for the determination of stability constant is also based on the principle of potentiometric method [21]. Using this method, the formation curve of metal complex can directly be calculated with the help of pH meter. Another major advantage of this method over the Bjerrum's method is that the calculation is simple and does not require hydrogen ion concentration. Moreover, this method can be used for types of ligands that are conjugate to weak acids. The calculation of stability constant using this method involves the following steps.

Step 1: The following solutions were titrated separately against base solution

a. Titration with free acid (A)

b. Titration with free acid + ligand (A + L)

c. Titration with free acid + ligand + metal (A + L + M)

Step 2: Calculation of formation functions n, nA, and PL using the values used/obtained from above three titrations

The term formation function "n," also called as ligand number, is defined as the average number of ligands attached per metal center and is calculated using the following equation

$$n = \frac{\text{Total number of ligands coordinated to metal}}{\text{Total number of metal}}$$

Metal	M:L ratio			
	1:1	1:2	1:5	2:3
Ni	8.492	14.8593	8.3598	3.4649
Mg	8.4664	8.3392	7.0794	11.1943
Co	8.590	5.3186	8.6337	6.2330

Table 1.
Stability constant values obtained for Ni, Mg and Co complexes having different metal to ligand ratio.

The term nA is similar to n and is defined as the average number of protons bound to the ligand which are not coordinated to the metal center. PL gives the free ligand exponent. All the three terms n, nA, and PL can be calculated with the help of following equations

$$nA = \gamma - \frac{(V_2 - V_1)(N + \mathcal{E}^0)}{(V_0 + V_1)T^0L} \tag{25}$$

$$n = \frac{(V_3 - V_2)(N + \mathcal{E}^0)}{(V_0 + V_2)nAT^0M} \tag{26}$$

$$PL = \log\left\{1 + \frac{\frac{[H^+]}{K_2} + \frac{[H^+]^2}{K_1K_2}}{(T^0L - T^0M)\overline{n}}X\frac{(V_0 + V_3)}{V_0}\right\} \tag{27}$$

where N is the normality of base used; V_0 is the initial volume of the solution; V_1, V_2, and V_3 are the volume of base consumed during the (A), (A + L), and (A + L + M) titrations, respectively, at same pH value; T^0L is the initial concentration of ligand; $\mathcal{E}^0$ is the initial concentration of acid; γ is the number of titrable or replaceable protons.

Step 3: Determination of formation curves: by plotting formation function (n) against PL and nA against pH for a HL (protonated ligand) system.

The value formation constants corresponding to formation of protonated ligand are obtained by plotting nA against pH. Similarly, the stepwise stability constants for the formation of metal complexes are obtained from the formation curve resulted by plotting n against PL.

5. Conclusions

The thermodynamic and kinetic stability of coordination compounds along with the various factors affecting the stability of metal complexes have been discussed in this chapter. Stability constant and its determination have also been listed.

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Conflict of interest

There is no conflict of interest.

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