

Metal-ligand Equilibrium in solⁿ

~~Stability of Complexes in Aqueous Solution~~

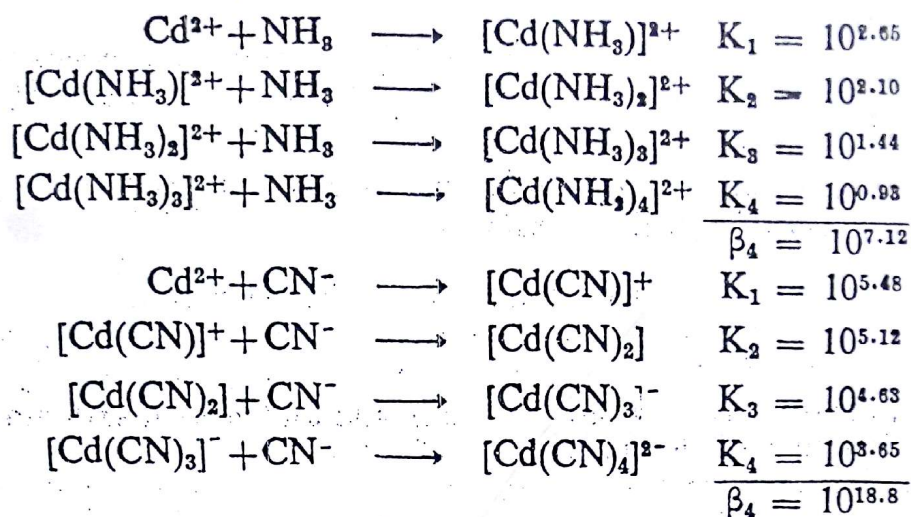
Definition of Stability

The term "stability" can be used in a number of different ways. The statement that a complex is 'stable' is rather loose, since several interpretations can be placed upon it. When the term "stability" is used without qualification, it means that the complex exists and under suitable conditions it may be stored for a long time. This term cannot be generalised for complexes, since a complex may be quite stable to one reagent and may decompose readily in presence of another reagent. This term may also refer to the action of heat or light on a compound.

In studying the formation of complexes in solution, two kinds of stability of complexes come in question. These are :

✓ (i) **Thermodynamic Stability.** - This is a measure of the extent to which the complex will form or will be transformed into another species (under certain conditions), *when the system has reached equilibrium.* When we are concerned with this type of stability, we deal with metal-ligand bond energies, stability constants, etc.

✓ (ii) **Kinetic Stability.** This refers to the speed with which transformations leading to the attainment of equilibrium will occur. When we are interested in kinetic stability, and this is primarily for complex ions in solutions, we deal with rates and mechanisms of chemical reactions such as substitution, isomerisation, racemisation and electron or group transfer reactions, as well as with the thermodynamic variables involved in the formation of intermediate species or activated complexes. In the kinetic sense it is more proper to call the complexes inert or labile complexes rather than stable or unstable complexes. The complexes in which the ligands are rapidly



The steady decrease in the values of K_1, K_2, \dots, K_n with increasing number of ligands is due to the fact that as more and more ligands move into the coordination zone, less and less aqua-molecules are available to fresh ligands for replacement. With progressive intake of ligands the metal ion becomes less electron greedy. In case of the complexes of the charged ligands the more important factors responsible for the steady decrease are statistical, steric hindrance and coulombic factors.

The higher the value of stability constant for a complex ion, the greater will be its stability. Alternatively $1/K$ values sometimes called **instability constant**, give a measure of the extent to which the equilibrium representing the formation of a complex lies to the right. A high value of $1/\beta_n$ (or $1/\beta$) means a complex ion.

Stepwise and cumulative stability constants are also expressed as $\log_{10} K_1 \dots \log_{10} K_n$ and $\log_{10} \beta_n$ respectively.

In all the above equilibria we have not specified the charge of metal ion and degree of solvation. The former omission is of no importance, since the equilibria may be expressed as above whatever the charges. Omission of water molecules is a matter of convention, since it is usually convenient and harmless. This omission should not be allowed whenever necessary. Square brackets indicate the concentrations of the enclosed species.

Relationship between β_n and K_1, K_2, \dots, K_n .

K 's and β 's are related to one another. Consider, for example, the expression for β_3 viz.

$$\beta_3 = \frac{[\text{ML}_3]}{[\text{M}][\text{L}]^3}$$

On multiplying both numerator and denominator by $[\text{ML}][\text{ML}_2]$ and on rearranging, we get

$$\begin{aligned}
 \beta_3 &= \frac{[\text{ML}_3]}{[\text{M}][\text{L}]^3} \cdot \frac{[\text{ML}][\text{ML}_2]}{[\text{ML}][\text{ML}_2]} \\
 &= \frac{[\text{ML}]}{[\text{M}][\text{L}]} \cdot \frac{[\text{ML}_2]}{[\text{ML}][\text{L}]} \cdot \frac{[\text{ML}_3]}{[\text{ML}_2][\text{L}]} \\
 &= K_1 \cdot K_2 \cdot K_3
 \end{aligned}$$

Thus :

$$\beta_n = \frac{[ML]}{[M][L]} \cdot \frac{[ML_2]}{[ML][L]} \cdot \dots \cdot \frac{[ML_n]}{[ML_{n-1}][L]}$$

$$= K_1 \cdot K_2 \cdot \dots \cdot K_n \quad \dots(i)$$

or :

$$\beta_n = \sum_{n=1}^{n=n} K_n$$

From relation (i) it is evident that the overall stability constant, β_n (or simply β), is equal to the product of the successive (*i.e.* stepwise) stability constants $K_1, K_2, \dots, K_{n-1}, K_n$. This in other words means that the value of stability constant for a given complex is actually made up of a number of step-wise stability constants as is evident from Table 14.1 in which the value of overall stability constant as β_n and $\log_{10}\beta_n$ for $[\text{Ni}^{II}(\text{NH}_3)_6]^{2+}$ ion and those of stepwise stability constants as $K_1, K_2, \dots, K_5, K_6$ and $\log_{10} K_1, \log_{10} K_2, \dots, \log_{10} K_6$ corresponding to the six equilibria given in the first column through which $[\text{Ni}^{II}(\text{NH}_3)_6]^{2+}$ ion can be regarded as being formed, are given. This table shows that

$$\beta_n = K_1 \times K_2 \times \dots \times K_5 \times K_6$$

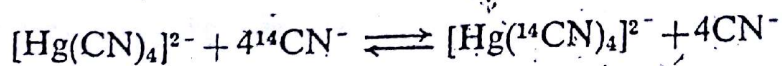
and

$$\log_{10} \beta_n = \log_{10} K_1 + \log_{10} K_2 + \dots + \log_{10} K_6$$

In Table 14.1 we also see that $\log K_6$ is negative ($= -0.10$). This negative value shows that the pentamine complex, $[\text{Ni}(\text{H}_2\text{O})(\text{NH}_3)_5]^{2+}$ is thermodynamically favoured with respect to the hexamine complex, $[\text{Ni}(\text{NH}_3)_6]^{2+}$ [see equilibrium No. (vi)].

Kinetic Vs. thermodynamic stability

Since the terms : labile and inert show the speed or rates at which the substitution of one ligand by other occurs, these terms represent the kinetic stability of complexes. These terms should, therefore, not be confused with or used for thermodynamic stability terms *viz. unstable and stable* respectively. Although thermodynamically stable complexes may be labile or inert, and unstable complexes which are usually labile may also be inert, there is no correlation between thermodynamic and kinetic stability terms, *e.g.* $[\text{Hg}(\text{CN})_4]^{2-}$ which is thermodynamically very stable (formation constant $= 10^{42}$) is labile, since in solution it exchanges CN^- ligands with labelled cyanide ions, $^{14}\text{CN}^-$ at a very fast rate.



Thus the stability of this complex does not ensure its inertness.

Thus :

$$\begin{aligned}\beta_n &= \frac{[ML]}{[M][L]} \cdot \frac{[ML_2]}{[ML][L]} \cdot \dots \cdot \frac{[ML_n]}{[ML_{n-1}][L]} \\ &= K_1 \cdot K_2 \cdot \dots \cdot K_n \quad \dots(i)\end{aligned}$$

or

$$\beta_n = \sum_{n=1}^{n=n} K_n$$

From relation (i) it is evident that the overall stability constant, β_n (or simply β), is equal to the product of the successive (*i.e.* stepwise) stability constants $K_1, K_2, \dots, K_{n-1}, K_n$. This in other words means that the value of stability constant for a given complex is actually made up of a number of step-wise stability constants as is evident from Table 14.1 in which the value of overall stability constant as β_n and $\log_{10}\beta_n$ for $[\text{Ni}^{II}(\text{NH}_3)_6]^{2+}$ ion and those of stepwise stability constants as $K_1, K_2, \dots, K_5, K_6$ and $\log_{10} K_1, \log_{10} K_2, \dots, \log_{10} K_6$ corresponding to the six equilibria given in the first column through which $[\text{Ni}^{II}(\text{NH}_3)_6]^{2+}$ ion can be regarded as being formed, are given. This table shows that

$$\beta_n = K_1 \times K_2 \times \dots \times K_5 \times K_6$$

and

$$\log_{10} \beta_n = \log_{10} K_1 + \log_{10} K_2 + \dots + \log_{10} K_6$$

In Table 14.1 we also see that $\log K_6$ is negative ($= -0.10$). This negative value shows that the pentamine complex, $[\text{Ni}(\text{H}_2\text{O})(\text{NH}_3)_5]^{2+}$ is thermodynamically favoured with respect to the hexamine complex, $[\text{Ni}(\text{NH}_3)_6]^{2+}$ [see equilibrium No. (vi)].

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Since the terms : labile and inert show the speed or rates at which the substitution of one ligand by other occurs, these terms represent the kinetic stability of complexes. These terms should, therefore, not be confused with or used for thermodynamic stability terms *viz. unstable and stable* respectively. Although thermodynamically stable complexes may be labile or inert, and unstable complexes, which are usually labile may also be inert, there is no correlation between thermodynamic and kinetic stability terms, *e.g.* $[\text{Hg}(\text{CN})_4]^{2-}$ which is thermodynamically very stable (formation constant $= 10^{42}$) is labile, since in solution it exchanges CN^- ligands with labelled cyanide ions, $^{14}\text{CN}^-$ at a very fast rate.



Thus the stability of this complex does not ensure its inertness.

| Six equilibria | Values of K_1, K_2, \dots, K_6 and β_n | Values of $\log_{10} K_1, \log_{10} K_2, \dots, \log_{10} K_6$ and $\log_{10} \beta_n$ |
|---|---|---|
| (i) $[\text{Ni}(\text{H}_2\text{O})_6]^{2+} + \text{NH}_3 \xrightleftharpoons{K_1} [\text{Ni}(\text{H}_2\text{O})_5(\text{NH}_3)]^{2+} + \text{H}_2\text{O}$ | $K_1 = 5 \times 10^2$ | $\log_{10} K_1 = 2.70$ |
| (ii) $[\text{Ni}(\text{H}_2\text{O})_5(\text{NH}_3)]^{2+} + \text{NH}_3 \xrightleftharpoons{K_2} [\text{Ni}(\text{H}_2\text{O})_4(\text{NH}_3)_2]^{2+} + \text{H}_2\text{O}$ | $K_2 = 1.3 \times 10^2$ | $\log_{10} K_2 = 2.11$ |
| (iii) $[\text{Ni}(\text{H}_2\text{O})_4(\text{NH}_3)_2]^{2+} + \text{NH}_3 \xrightleftharpoons{K_3} [\text{Ni}(\text{H}_2\text{O})_3(\text{NH}_3)_3]^{2+} + \text{H}_2\text{O}$ | $K_3 = 40$ | $\log_{10} K_3 = 1.60$ |
| (iv) $[\text{Ni}(\text{H}_2\text{O})_3(\text{NH}_3)_3]^{2+} + \text{NH}_3 \xrightleftharpoons{K_4} [\text{Ni}(\text{H}_2\text{O})_2(\text{NH}_3)_4]^{2+} + \text{H}_2\text{O}$ | $K_4 = 12$ | $\log_{10} K_4 = 1.08$ |
| (v) $[\text{Ni}(\text{H}_2\text{O})_2(\text{NH}_3)_4]^{2+} + \text{NH}_3 \xrightleftharpoons{K_5} [\text{Ni}(\text{H}_2\text{O})(\text{NH}_3)_5]^{2+} + \text{H}_2\text{O}$ | $K_5 = 4$ | $\log_{10} K_5 = 0.60$ |
| (vi) $[\text{Ni}(\text{H}_2\text{O})(\text{NH}_3)_5]^{2+} + \text{NH}_3 \xrightleftharpoons{K_6} [\text{Ni}(\text{NH}_3)_6]^{2+} + \text{H}_2\text{O}$ | $K_6 = 0.8$ | $\log_{10} K_6 = -0.10$ |
| On adding (i) to (vi) $[\text{Ni}(\text{H}_2\text{O})_6]^{2+} + 6\text{NH}_3 \xrightleftharpoons{\beta_n} [\text{Ni}(\text{NH}_3)_6]^{2+} + 6\text{H}_2\text{O}$ | $\beta_n = K_1 \cdot K_2 \dots K_5 \cdot K_6$ $= 9.98 \times 10^7$ | $\log_{10} \beta_n = \log_{10} K_1 + \log_{10} K_2 + \dots + \log_{10} K_6$ $= 7.99$ |

On the other hand the complex, $[\text{Co}(\text{NH}_3)_6]^{2+}$ which is thermodynamically unstable can remain unchanged in acid solution for weeks. Thus this complex is unstable but inert in acid solution.

It may be concluded from this description that the *inert complexes are not necessarily thermodynamically stable and that labile complexes are not necessarily thermodynamically unstable.*

The stability of a complex depends on the reaction energy while the lability of a compound depends on the activation energy. Larger the activation energy, lower will be the lability of the compound, i.e. the compound with larger activation energy will react slowly.

Labile and Inert Octahedral Complexes according to VBT

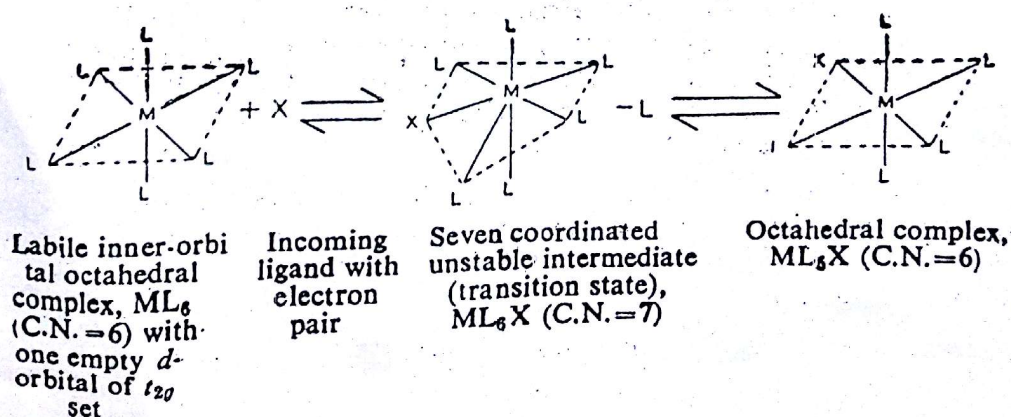
We have seen that according to VBT octahedral complexes are of two types (i) *outer orbital complexes* which involve sp^3d^2 hybridisation, and (ii) *inner-orbital complexes* which result from d^2sp^3 hybridisation. Note that the two d -orbitals involved in sp^3d^2 and d^2sp^3 hybridisation are $d_{x^2-y^2}$ and d_{z^2} orbitals (e_g set).

With the help of VBT it is possible to predict which octahedral complex is labile and which is inert as shown below :

(i) **Outer-orbital octahedral complexes.** Outer-orbital octahedral complexes (sp^3d^2 hybridisation) are generally *labile*, e.g. the octahedral complexes of Mn^{2+} ($3d^5$), Fe^{2+} ($3d^6$), Fe^{3+} ($3d^5$), Co^{2+} ($3d^7$), Ni^{2+} ($3d^8$), Cu^{2+} ($3d^9$) and Cr^{2+} ($3d^4$) exchange ligands rapidly and hence are labile. In terms of valence-bond theory this observation can be correlated with the weakness of the bonds of sp^3d^2 type as compared with d^2sp^3 bonds.

(ii) **Inner-orbital octahedral complexes.** Since the six d^2sp^3 hybrid orbitals are filled with the six electron pairs donated by the six ligands, d^n electrons of the central metal will occupy d_{xy} , d_{yz} and d_{zx} orbitals. This distribution for labile and inert inner-orbital octahedral complexes is shown in Table 14.2 from which the following points are obvious.

(a) In the labile inner orbital octahedral complexes there is at least one d -orbital of t_{2g} set empty so that this empty d -orbital may be used to accept the electron pair from the incoming ligand in forming the transition state (unstable intermediate) with coordination number of seven. The formation of transition state can be shown as :



Due to the extremely fast reactions of these complexes it has not been possible to determine whether the intermediate exists in these reactions.

(b) In the inert inner-orbital octahedral complexes every d -orbital of t_{2g} set (i.e. d_{xy} , d_{yz} and d_{zx}) contains at least one electron.

Labile and Inert Octahedral Complexes According to CFT

Whether an octahedral complex reacts by an S_N1 dissociation or S_N2 association mechanism the symmetry is lowered and a decrease in CFSE usually occurs in going from octahedral to 5-coordinated square pyramidal activated intermediate or from octahedral to 7-coordinated pentagonal bipyramidal transition state. The change in CFSE in going from octahedral to square pyramidal (S_N1 mechanism) and in going from octahedral to pentagonal bipyramidal (S_N2 mechanism) structure is called *activation energy* and is denoted by E_a . The values of E_a have been calculated by Basolo and Pearson and are given in Tables 14.3 and 14.4. The values of CFSE mentioned are in the units of Dq and have been given for both the fields *viz* strong field (spin paired or low spin complex) and weak field (spin free or high spin complex) and for both the mechanisms. In these tables negative values of E_a denote a loss of CFSE when octahedral complex is changed into an activated complex which may be square pyramidal or pentagonal bipyramidal. In cases where the CFSE of the activated complex is greater than that of octahedral complex, E_a has been given zero value. Thus in case of these complexes it has been assumed that there is no loss in CFSE when they are changed into activated complexes.

The octahedral complexes formed by the ions for which there is *large loss in CFSE* are *least labile*, i.e. such complexes are *inert*. On the other hand octahedral complexes given by ions for which there is *little or no loss in CFSE* are *labile*, i.e. such complexes react rapidly. Following examples make these facts evident :

- (i) Both high spin and low spin octahedral complexes of d^0 , d^1 and d^2 ions will react rapidly, i.e. these are *labile complexes*, since there is no loss in CFSE for these ions by either mechanism.
- (ii) We have seen that according to VBT inner-orbital octahedral complexes of d^3 , d^4 , d^5 and d^6 ions are inert (see Table 14.2). These inner-orbital complexes are called low-spin or spin-paired complexes by CFT. CFT also predicts that low-spin complexes of these ions are also inert whether the mechanism is assumed to be S_N1 or S_N2 , since there is a loss in CFSE values (as indicated by the negative values).

The ion with maximum loss of CFSE will form the most inert (i.e. least labile) complex. Thus the order of inertness of low-spin complexes formed by d^3 , d^4 , d^5 and d^6 ions is :

| | |
|-------------------------------------|----------------------------------|
| Order of inertness : | $d^6 > d^3 > d^4 > d^5$ |
| Loss in CFSE for S_N1 mechanism : | -4.00 -2.00 -1.43 -0.86 |
| Loss in CFSE for S_N2 mechanism : | -8.52 -4.26 -2.98 -1.70 |

Table 14.2. Distribution of d^n -electrons in various t_{2g} orbitals for labile and inert inner-orbital octahedral complexes according to VBT.

| Type of the complex | d^n configuration | Distribution of d^n electrons (shown by arrows) in t_{2g} orbitals. Electrons shown by crosses in e_g orbitals have been donated by six ligands to enter d^2sp^3 hybrids and are in opposite spins | | | | | | Examples of central metal ions | | | | |
|---|---------------------|--|-----------------------|-----------------------|-----------------|-----------------|-----------------|--------------------------------|-----------------|-----------------|-----------------|---|
| | | d | | | s | p | | | | | | |
| | | t_{2g} | | | | e_g | p_x | p_y | | | | p_z |
| | | xy | yz | zx | x^2-y^2 | | | | | | | |
| Inner-orbital labile octahedral complexes | d^0 | | | | $\times \times$ | $\times \times$ | $\times \times$ | $\times \times$ | | | | $\times \times$ |
| | d^1 | \uparrow | | | $\times \times$ | $\times \times$ | $\times \times$ | $\times \times$ | $\times \times$ | $\times \times$ | $\times \times$ | Ti(+3), V(+4), Mo(+5), W(+5), Re(+6) |
| | d^2 | \uparrow | \uparrow | | $\times \times$ | $\times \times$ | $\times \times$ | $\times \times$ | $\times \times$ | $\times \times$ | $\times \times$ | Ti(+2), V(+3), Nb(+3); Ta(+3), W(+4), Re(+5), Ru(+6) |
| | d^3 | \uparrow | \uparrow | \uparrow | $\times \times$ | $\times \times$ | $\times \times$ | $\times \times$ | $\times \times$ | $\times \times$ | $\times \times$ | V(+2), Cr(+3), Mo(+3), W(+3), Mn(+4), Re(+4) |
| Inner-orbital inert octahedral complexes. | d^4 | $\uparrow \downarrow$ | \uparrow | \uparrow | $\times \times$ | $\times \times$ | $\times \times$ | $\times \times$ | $\times \times$ | $\times \times$ | $\times \times$ | $[\text{Cr}(\text{CN})_6]^{4-}$, Mn(CN) $_6^{3-}$, Re(+3), Ru(+4), Os(+4) |
| | d^5 | $\uparrow \downarrow$ | $\uparrow \downarrow$ | \uparrow | $\times \times$ | $\times \times$ | $\times \times$ | $\times \times$ | $\times \times$ | $\times \times$ | $\times \times$ | $[\text{Mn}(\text{CN})_6]^{4-}$, Re(+2), $[\text{Fe}(\text{CN})_6]^{3-}$, Ru(+3), Os(+3), Ir(+4) |
| | d^6 | $\uparrow \downarrow$ | $\uparrow \downarrow$ | $\uparrow \downarrow$ | $\times \times$ | $\times \times$ | $\times \times$ | $\times \times$ | $\times \times$ | $\times \times$ | $\times \times$ | $[\text{Fe}(\text{CN})_6]^{4-}$, Ru(+2), Os(+2), Co(+3) (except CoFe_6^{3-}), Rh(+3), Ir(+3) |
| | d^6 | $\uparrow \downarrow$ | $\uparrow \downarrow$ | $\uparrow \downarrow$ | $\times \times$ | $\times \times$ | $\times \times$ | $\times \times$ | $\times \times$ | $\times \times$ | $\times \times$ | |

Consequently the order of lability or the reactivity (*i.e.*, rate of reaction) will be reverse of that shown above, *i.e.*

Order of lability : $d^6 < d^3 < d^4 < d^5$

Experiments have also supported the above order.

- (iii) High-spin octahedral complexes of d^3 ion will react slowly, *i.e.* these are *inert complexes*, because for this ion there is substantial loss in CFSE whether the substitution mechanism is assumed S_N1 or S_N2 .
- (iv) High-spin octahedral complexes of d^5 ion react rapidly, *i.e.*, these are *labile complexes*, since there is no loss in CFSE.
- (v) Both high-spin and low-spin octahedral complexes of d^8 ion (*e.g.*, Ni^{2+}) are *inert*, since for any mechanism there is significant loss of CFSE. Note that, according to VBT, d^8 ion ($3d_{xy}^2, 3d_{yz}^2, 3d_{zx}^2, 3d_{x^2-y^2}^1, 3d_{z^2}^1$) will form outer-orbital complexes which will be *labile*. Thus we see that in case of d^8 ion VBT and CFT give different predictions.
- (vi) Both high-spin and low-spin octahedral complexes of d^{10} ion are *labile*. The reasons are the same as for other labile complexes.

Table 14.3. Loss in CFSE, E_a (in the units of Dq) in the formation of a square pyramidal intermediate in octahedral substitution reactions on the basis of S_N1 dissociation mechanism.

| d^n ion | S_N1 dissociation mechanism | | | | | |
|--------------|---|----------------------|-------|--|----------------------|-------|
| | Octahedral (oct.) (C.N.=6) | | | Square pyramidal (squ. py.) (C.N.=5) | | |
| | Strong ligand fields (spin-paired or low-spin complexes) | | | Weak ligand fields (spin-free or high-spin complexes) | | |
| | Oct. (C.N.=6) | squ. py. (C.N.=5) | E_a | Oct. (C.N.=6) | Squ. py. (C.N.=5) | E_a |
| d^0 | 0 Dq | 0 Dq | 0 Dq | 0 Dq | 0 Dq | 0 Dq |
| d^1 | 4 | 4.57 | 0 | 4 | 4.57 | 0 |
| d^2 | 8 | 9.14 | 0 | 8 | 9.14 | 0 |
| d^3 | 12 | 10.00 | -2.00 | 12 | 10.00 | -2 |
| d^4 | 16 | 14.57 | -1.43 | 6 | 9.14 | 0 |
| d^5 | 20 | 19.14 | -0.86 | 0 | 0.00 | 0 |
| d^6 | 24 | 20.00 | -4.00 | 4 | 4.57 | 0 |
| d^7 | 18 | 19.14 | 0 | 8 | 0.14 | 0 |
| d^8 | 12 | 10.00 | -2.00 | 12 | 10.00 | -2 |
| d^9 | 6 | 9.14 | 0 | 6 | 9.14 | 0 |
| d^{10} | 0 | 0.00 | 0 | 0 | 0.00 | 0 |

Table 14.4. Loss in CFSE, E_a (in the units of Dq) in the formation of a pentagonal bipyramidal intermediate in octahedral substitution reactions on the basis of S_N2 association mechanism.

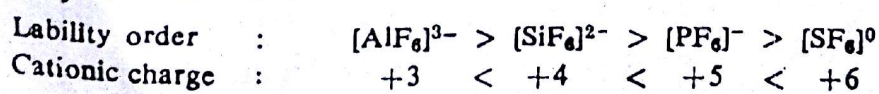
| S_N2 association mechanism | | | | | | |
|-------------------------------|---|-------------------------|-------|--|-------------------------|-------|
| Octahedral (oct.) (C.N.=6) | | | → | Pentagonal bipyramidal (pent. bipy.) (C.N.=7) | | |
| d^n ion | Strong ligand fields (spin-paired or low-spin complexes) | | | Weak ligand fields (spin-free or high-spin complexes) | | |
| | Oct. (C.N.=6) | pent. bipy. (C.N.=7) | E_a | Oct. (C.N.=6) | pent. bipy. (C.N.=7) | E_a |
| d^0 | 0 Dq | 0 Dq | 0 Dq | 0 Dq | 0 Dq | 0 Dq |
| d^1 | 4 | 5.28 | 0 | 4 | 5.28 | 0 |
| d^2 | 8 | 10.56 | 0 | 8 | 10.56 | 0 |
| d^3 | 12 | 17.74 | -4.26 | 12 | 7.74 | -4.26 |
| d^4 | 16 | 13.02 | -2.98 | 6 | 4.93 | -2.07 |
| d^5 | 20 | 18.30 | -1.70 | 0 | 0.00 | 0 |
| d^6 | 24 | 15.48 | -8.52 | 4 | 5.28 | 0 |
| d^7 | 18 | 12.66 | -5.34 | 8 | 10.56 | 0 |
| d^8 | 12 | 7.74 | -4.26 | 12 | 7.74 | -4.26 |
| d^9 | 6 | 4.93 | -1.07 | 6 | 4.93 | -1.07 |
| d^{10} | 0 | 0.00 | 0 | 0 | 0.00 | 0 |

Other Factors Affecting the Lability of a Complex

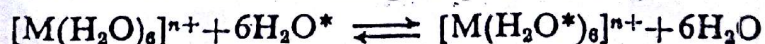
In the preceding pages we have seen that how the electronic configuration of the central metal ion forming the complex affects the lability of the complex. In addition to this the following factors also influence the lability.

(i) **Charge of the central ion.** Highly charged ions form complexes that react slowly, i.e. with the increase of the charge of the central metal ion for the isoelectronic complexes there is a decrease in lability, e.g.

(a) The lability of the complexes, $[AlF_6]^{3-}$, $[SiF_6]^{2-}$, $[PF_6]^-$ and $[SF_6]^0$ is in the order :



(b) The rate of water exchange represented by



decreases with the increase of cationic charge in the series : $[\text{Na}(\text{H}_2\text{O})_n]^+$, $[\text{Mg}(\text{H}_2\text{O})_n]^{2+}$, $[\text{Al}(\text{H}_2\text{O})_6]^{3+}$ in the order :

Rate of water exchange , $[\text{Na}(\text{H}_2\text{O})_n]^+ > [\text{Mg}(\text{H}_2\text{O})_n]^{2+} > [\text{Al}(\text{H}_2\text{O})_6]^{3+}$
 Cationic charge : +1 < +2 < +3

(ii) **Radii of the central ion.** Complexes having central atoms with small ionic radii react more slowly than those having larger central ions, *i.e.*, the lability increases with the increase of ionic radius, *e.g.*,

Order of lability : $[\text{Mg}(\text{H}_2\text{O})_6]^{2+} < [\text{Ca}(\text{H}_2\text{O})_6]^{2+} < [\text{Sr}(\text{H}_2\text{O})_6]^{2+}$
 Cationic Size (Å°) : 0.65 < 0.99 < 1.13

(iii) **Charge-to-radius ratio values.** For a series of octahedral complexes containing the same ligands, the complexes having the central metal ions with the largest charge-to-radius ratio will react slowest. The validity of this rule is evident from Fig. 14.1 which contains half-lives for the exchange of water by some hydrated metal ions.



From this figure the following points may be noted :

(a) Of the first-row transition elements, $[\text{Ni}(\text{H}_2\text{O})_6]^{2+}$ (a d^8 system) has the largest value of half life, *i.e.* it reacts slowest. The same conclusion has been drawn from CFT. The hydrated M^{2+} ions, $[\text{M}(\text{H}_2\text{O})_x]^{2+}$ of the first-row transition elements are all high-spin complexes.

(b) $[\text{Cu}(\text{H}_2\text{O})_6]^{2+}$ reacts most rapidly. This may be due to the fact that the two water molecules above and below the square

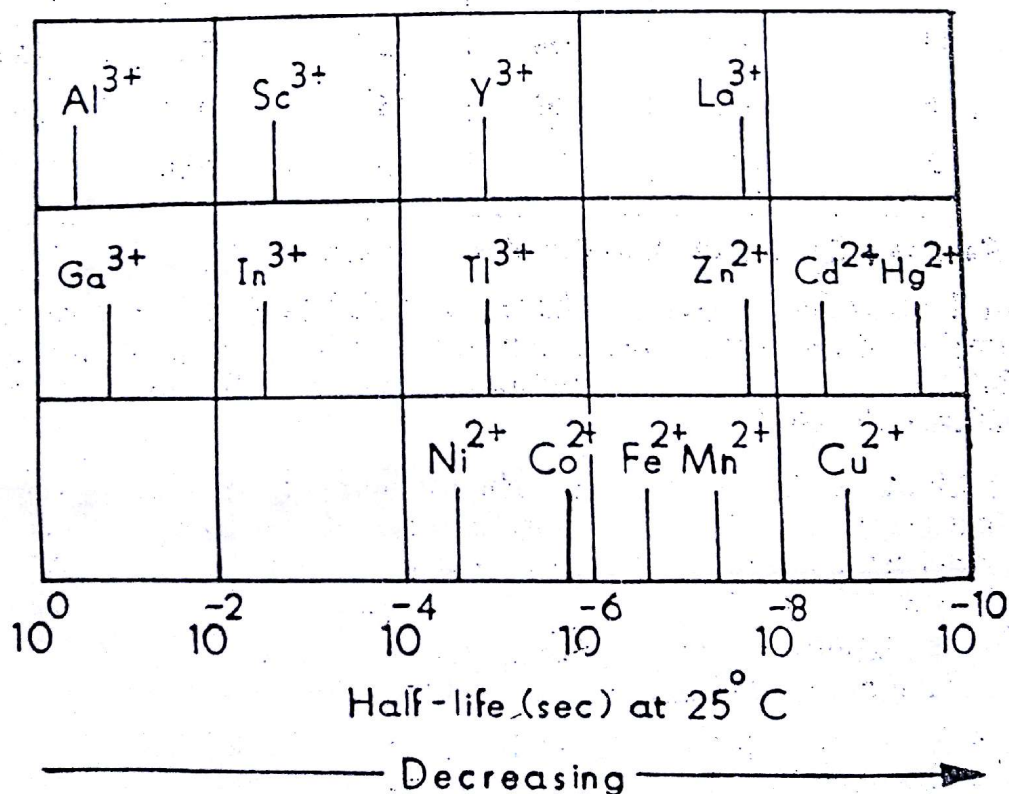
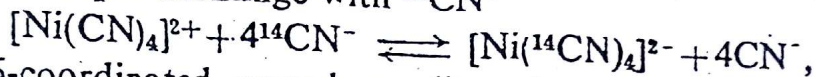


Fig. 14.1. Half-lives (in sec) at 25°C for the exchange of water by some hydrated metal ions.

plane of the tetragonally distorted octahedral shape of $[\text{Cu}(\text{H}_2\text{O})_6]^{2+}$ are exchanged. The remaining four water molecules lying in the square plane react slowly.

For square planar complexes charge-to-radius ratio does not work.

(iv) **Geometry of the complex.** In general 4-coordinated complexes (both tetrahedral and square planar) react more rapidly than analogous 6-coordinated complexes, e.g. the very stable $[\text{Ni}(\text{CN})_4]^{2-}$ undergoes rapid exchange with $^{14}\text{CN}^-$



while 6-coordinated complexes like $[\text{Mn}(\text{CN})_6]^{4-}$ and $[\text{Co}(\text{CN})_6]^{3-}$ which have almost about the same stability as $[\text{Ni}(\text{CN})_4]^{2-}$ undergo slow exchange. The greater rapidity of reactions of 4-coordinated complexes may be due to the fact that there is enough room round the central ion for the entry of a fifth group into the coordination sphere to form an activated complex. The presence of this additional group helps in the release of one of the original four ligands already present in the 4-coordinated complexes.

Factors Affecting the Stability of Complexes

A number of factors affect the stability of complexes. Some of these factors depend on the nature of the central ion, while others depend on the nature of the ligand.

(a) ^{Nature} Properties of the Central Metal Ion

With reference to the properties of the central metal ion the following factors may be mentioned :

(i) **Charge and size.** In general the metal ion with larger charge and smaller size form more stable complexes. A smaller but more highly charged cation permits a more closer approach of the ligands and larger electrostatic attraction resulting from large charge on the cation gives a more stable complex. These points are illustrated in the following examples :

(a) The stability of the hydroxide complexes of the alkaline earth metals in which the central metal cation contains the same

Table 14.5. Effect of the central metal ions with equal charges but with different ionic size on the stability of complexes.

| Complex ion | Charges on the central metal ion | Size of the central metal ion, (Å°) | Value of β | Stability |
|--|----------------------------------|---|------------------|---|
| $[\text{Be}^{\text{II}}(\text{OH})]^+$ | +2 | 0.31 | 10^7 | Stability of complex ions increasing \uparrow |
| $[\text{Mg}^{\text{II}}(\text{OH})]^+$ | +2 | 0.65 | 120 | |
| $[\text{Ca}^{\text{II}}(\text{OH})]^+$ | +2 | 0.99 | 30 | |
| $[\text{Ba}^{\text{II}}(\text{OH})]^+$ | +2 | 1.35 | 4 | |

charge increases with the decrease of the size of the central metal ion as shown by their stability constant values (see Table 14.5).

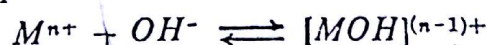
(b) The stability of the complexes having the central metal cations with almost equal size but with different charges increases with the increase of the charge on the central metal ion. This is shown in Table 14.6.

Table 14.6. Stability for Fe^{3+} , Fe^{2+} , Co^{3+} and Co^{2+} complexes.

| Complex ion | Changes on the central metal ion | Size of the central metal ion (\AA°) | Value of $\log_{10}\beta$ (stability constant) | Stability of the complex ion |
|-------------------------|----------------------------------|--|--|------------------------------|
| $[Fe^{III}(CN)_6]^{3-}$ | +3 | ↑ almost same ↓ | 31.0 | ↑ increases |
| $[Fe^{II}(CN)_6]^{4-}$ | +2 | | 8.3 | |
| Co^{3+} -complex | +3 | ↑ almost same ↓ | higher | ↑ increases |
| Co^{2+} -complex | +2 | | low | |

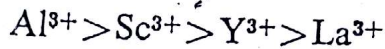
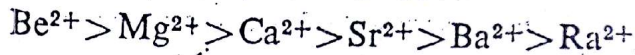
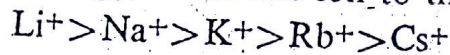
Combination of the factors *viz.* charge and size of the central metal cation shows that it is charge/radius ratio for the central ion (called *ionic potential* or *polarising power* of the cation) which is important. A large value of charge/radius ratio for a central ion means that the central ion will be forming more stable complexes. The correlation between charge-to-radius ratio and stability of OH^- complexes of some metal ions is shown in Table 14.7. It may be noted from this table that charge on the metal ion is somewhat more important than its ionic radius.

Table 14.7. Effect of the charge-to-radius ratio on the stability of some OH^- complexes.



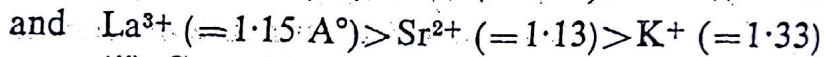
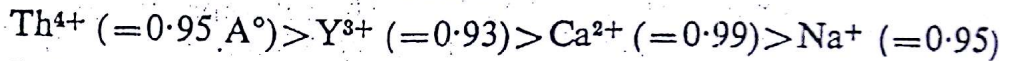
| Central metal cation (M^{n+}) | Ionic Radius (\AA°) | Charge-to-radius ratio | Stability constant of the complex |
|-----------------------------------|---------------------------------------|------------------------|-----------------------------------|
| Li^+ | 0.60 | 1.7 | 2 |
| Ca^{2+} | 0.99 | 2.0 | 3×10^1 |
| Ni^{2+} | 0.69 | 2.9 | 3×10^3 |
| Y^{3+} | 0.93 | 3.2 | 1×10^7 |
| Th^{4+} | 1.02 | 4.0 | 1×10^{10} |
| Al^{3+} | 0.50 | 6.0 | 1×10^9 |
| Be^{2+} | 0.31 | 6.5 | 1×10^7 |

The stability of the complexes of non-transition metals of the same group has been found in the following order provided that the ligand is not changed from one ion to the next.

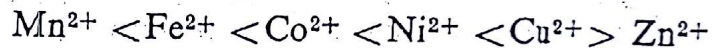


There are also some exceptions to the above order, e.g. EDTA complex of Mg^{2+} is less stable than that of Ca^{2+} .

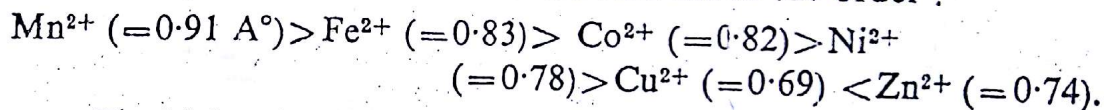
For the metal ions of approximately constant ionic radius, the stability constants are in the order :



(ii) **Crystal Field Effects and natural order (or Irving-William order) of stability.** Stabilities of high spin complexes of the ions between Mn^{2+} and Zn^{2+} with a given ligand frequently vary in the order :



This order which is called **natural order** (sometimes called the **Irving-William order**) of stability is consistent with charge-to-radius ratio concept, since the radii of these ions are in the order :



The high spin complexes of these ions are primarily octahedral with the exception of those of Cu^{2+} which forms tetragonally distorted octahedral complexes.

The relative stability of high spin octahedral $[\text{M}^{\text{II}}\text{L}_6]^{2+}$ complexes of the first-row transition elements as predicted by crystal field theory is shown in Fig. 14.2.

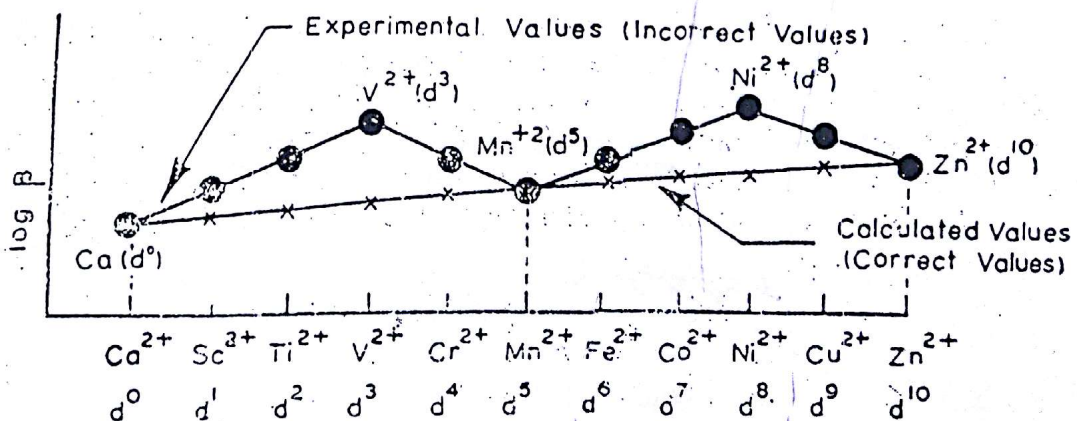
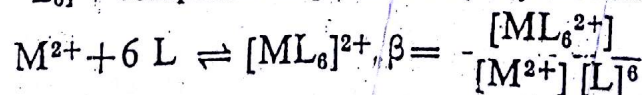


Fig. 14.2. The logarithms of stability constants for a series of $[\text{M}^{\text{II}}\text{L}_6]^{2+}$ complexes as predicted by crystal field theory.



It is obvious from this figure that the octahedral complexes of V^{2+} (d^3 ion) and Ni^{2+} (d^8 ion) ions are the most stable with respect to their neighbours. This is because of the fact that the high spin (weak ligand) octahedral complexes of these ions have the greatest crystal field stabilisation energy values (CFSE's values) as given below :

$$d^1 = 0.4 \Delta_0, d^2 = 0.8 \Delta_0, d^3 (V^{2+}) = 1.2 \Delta_0, d^4 = 0.6 \Delta_0, d^5 = 0.0$$

$$d^6 = 0.4 \Delta_0, d^7 = 0.8 \Delta_0, d^8 (Ni^{2+}) = 1.2 \Delta_0, d^9 = 0.6 \Delta_0, d^{10} = 0.0$$

The order of stability as predicted by crystal field theory and shown in Fig. 14.2 is the same as natural order of stability for complexes of these metals except for Cu^{2+} . The discrepancy for Cu^{2+} is not completely understood but is certainly related to the fact that Cu^{2+} complex assumes a distorted octahedral structure in order to assume maximum CFSE.

If the experimental values shown by dots are corrected for CFSE for each ion (the correction is done by subtracting the calculated CFSE values given as above from the experimental values), we get a smooth curve which has *corrected values* (shown by crosses), since it indicates the expected regular increase in values. The ions *viz.* Ca^{2+} (d^0), Mn^{2+} (d^5) and Zn^{2+} (d^{10}) which do not have CFSE have experimental values on the smooth curve.

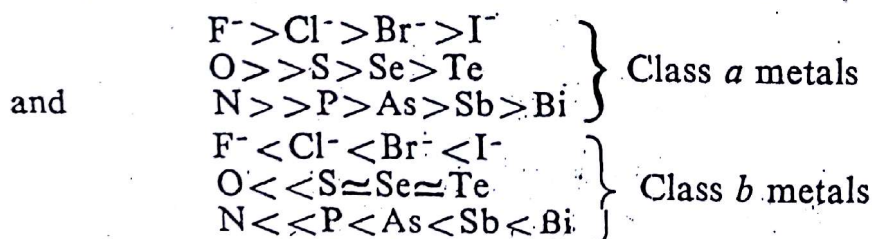
(iii) **Class a and Class b metals.** Chatt and Ahrland have classified the metals into three categories : *a*, *b* and *borderline*, on the basis of their electron acceptor properties. This classification is shown below (normal valence states are assumed).

Class a metals : H, the alkali and alkaline earth metals, the elements Sc \rightarrow Cr, Al \rightarrow Cl, Zn \rightarrow Br, In, Sn, Sb and I, the lanthanides and actinides.

Class b metals : Rh, Pd, Ag, Ir, Pt, Au, Hg.

Border line metals : The elements Mn \rightarrow Cu, Tl \rightarrow Po, Mo, Te, Ru, W, Re, Os, Cd.

Class a metals form *more stable* complexes with ligands having the coordinating atoms from the second period elements (*e.g.* N, O, F) than those of an analogous ligand in which the donor atom is from third or later period (*e.g.* P, S, Cl). Class b metals have the relative stabilities reversed. If the ligand contains the heavier donor atoms, class a and b metals are characterised by the stability order :



Class b metals are characterised by the presence of a number of *d*-electrons beyond an inert-gas core. These *d*-electrons are used to form π -bond with ligand atoms. It is believed that the stability

of the complexes of class *b* metals results from covalent contribution to metal-ligand bonds and from the transfer of electron density from the metal to the ligand via π -bonding. The most stable complexes of class *b* metals are formed with ligands like PMe_3 , S^{2-} and I^- which have vacant *d*-orbitals or like CO CN^- which have vacant molecular orbitals of low energy.

For *borderline metals* the stability constants do not display either class *a* or class *b* behaviour uniquely.

(iv) **Electronegativity of the central ion.** The bonding between a central ion and a ligand is, to some extent, due to the donation of electrons by the ligand to the central ion. Thus, it might be concluded that a central ion with higher electronegativity (*i.e.* a central ion with a strong electro-attracting tendency) would give the most stable complexes.

(b) ^{Nature} ~~Properties~~ of the Ligand.

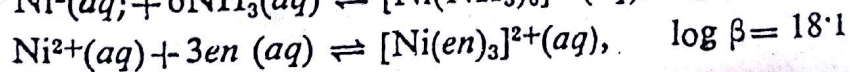
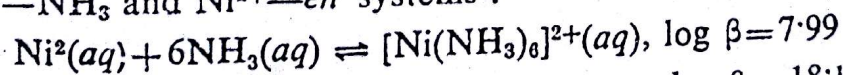
With reference to the role of the ligands in determining the stability of the metal complexes, the following factors are important :

(i) **Size and charge of ligand.** For charged ligands, the higher the charge carried by them and the smaller their size, the more stable are the complexes formed ; *e.g.*, the F^- ions, which are smaller, form stable complexes than the Cl^- ions which are larger ions. This fact is evident from the stability constant values of $[\text{Fe}^{\text{III}} \text{F}]^{2+}$ and $[\text{Fe}^{\text{III}} \text{Cl}]^{2+}$ ions which are 10^6 and 20 respectively. Thus for class *a* metals the order of stability of the halide complexes is $\text{F}^- > \text{Cl}^- > \text{Br}^- > \text{I}^-$, but this order is reversed for class *b* metals (Pt^{II} , Cu^{I} , Ag^{I} , Hg^{II} etc).

For monodentate neutral ligands, the higher the dipole moment and smaller the size, the more stable are the complexes formed.

(ii) **Basic character of ligands.** The more basic is the ligand, more easily it can donate electron pairs to the central ion and hence more easily it can form complexes of greater stability. The ligands that bind H^+ firmly form stable complexes with metal ions. Thus F^- should form stable complexes than Cl^- , Br^- or I^- , and NH_3 should be better ligand than H_2O which in turn should be better than HF . This behaviour is observed for alkali, alkaline earth and other electropositive metals like first-row transition elements, lanthanides and actinides.

✓ (iii) **Chelate effect.** Complexes containing chelate rings are usually more stable than similar complexes containing no rings. *i.e.* multidentate ligands (chelating ligands) in general form more stable complexes than the monodentate ligands. This is termed as **chelate effect**. This effect is obvious from the values of stability constants of $\text{Ni}^{2+}-\text{NH}_3$ and $\text{Ni}^{2+}-en$ systems :



Note that NH_3 is a monodentate ligand while ethylene diamine, $\text{NH}_2\text{—CH}_2\text{—CH}_2\text{—NH}_2$ (*en*) is a bidentate ligand. Obviously the complex $[\text{Ni}(\text{en})_3]^{2+}$ is much more stable than $[\text{Ni}(\text{NH}_3)_6]^{2+}$, since the former complex contains chelate rings while the latter one has no chelate ring. The chelate effect is also evident from the fact that the stability of NH_3 , ethylene diamine, $\text{NH}_2\text{—CH}_2\text{—CH}_2\text{—NH}_2$ (*en*) and triethylenetetra amine, $\text{NH}_2\text{—}(\text{CH}_2)_2\text{—NH—}(\text{CH}_2)_2\text{—NH—}(\text{CH}_2)_2\text{—NH}_2$ (*trien*) complexes of Cu^{2+} ion is in the order :

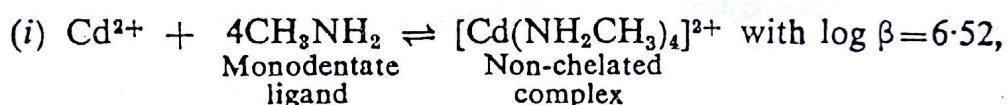
$$\log \beta = \begin{array}{ccc} [\text{Cu}(\text{NH}_3)_4]^{2+} < [\text{Cu}(\text{en})_2]^{2+} < [\text{Cu}(\text{trien})]^{2+} \\ 12.7 & < & 19.7, < & 20.5, \end{array}$$

In order to understand this effect we should note the following well-known thermodynamic relationship :

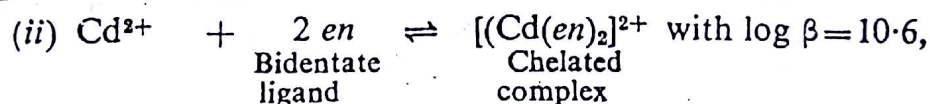
$$-RT \ln \beta = \Delta G^\circ = \Delta H^\circ - T\Delta S^\circ \quad (\Delta H^\circ \text{ is negative})$$

Here ΔG° = Standard free energy change, R = Gas constant, T = Absolute temperature, ΔH° = Enthalpy (or heat) change and ΔS° = Entropy change.

Enthalpy change between chelated and non-chelated complex is small due to similar metal-donor atom linkages as is evident from the thermodynamic data given for the following two reactions leading to the formation of non-chelated and chelated complex respectively.



$$\Delta H^\circ = -57.3, \Delta S^\circ = -67.3, -T\Delta S^\circ = 20.1 \text{ and } \Delta G^\circ = -37.2$$



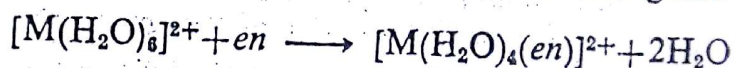
$$\Delta H^\circ = -56.3, \Delta S^\circ = +14.1, -T\Delta S^\circ = -4.2 \text{ and } \Delta G^\circ = -60.7.$$

All the thermodynamic data are given in KJ/mole.

It follows from the above relation that β increases as ΔG° becomes more negative. The value of ΔG° becomes more negative when that of ΔS° becomes more positive (see above), *i.e.* more positive value of ΔS° will lead to a more negative value of ΔG° and hence a more stable complex is formed. In the language of thermodynamics the equilibrium constant of a reaction is the measure of the heat released in the reaction and the entropy change during the reaction. The greater the amount of heat released in a reaction, the more stable are the reaction products. The entropy of a system is a measure of the amount of disorder. The greater the amount of disorder produced in the products during the reaction relative to the reactants, the greater the increase in entropy during the reaction and hence the greater the stability of the products.

The fact that the stability of the complex increases with the increase of entropy can be illustrated by the following example : when ethylene diamine molecule, $\text{NH}_2\text{—CH}_2\text{—CH}_2\text{—NH}_2$ (*en*) is

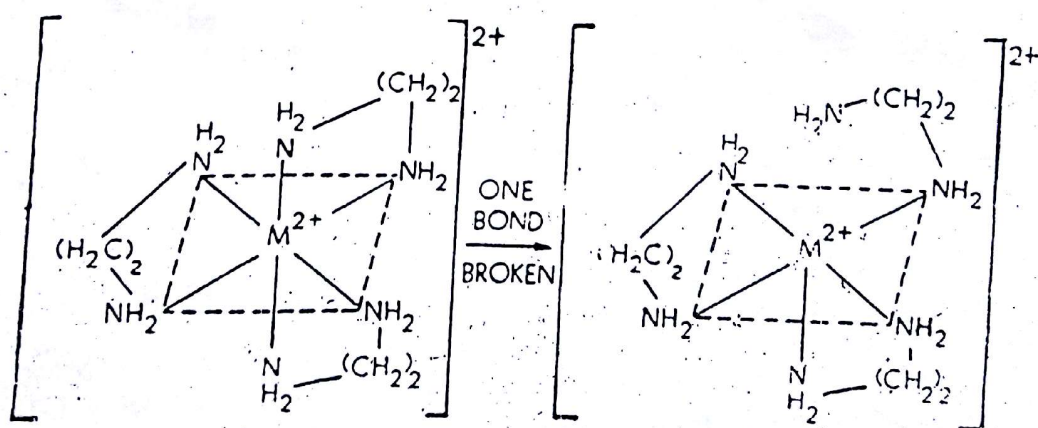
allowed to react with hydrated complex ion, $[M(H_2O)_6]^{2+}$, it replaces two H_2O molecules from it, since it is a bidentate ligand.



This process increases the number of particles in the system and hence its disorder and entropy. Thus the complex, $[M(H_2O)_4(en)]^{2+}$ is more stable than $[M(H_2O)_6]^{2+}$.

Following Sidwick the explanation of the chelate effect may be presented more pictorially. If one of the two metal-ligand bonds of a bidentate chelate system is broken, the remaining bond still remains attached with the metal ion so that the broken bond can be re-established. On the other hand if the metal-ligand bond of a monodentate complex (non-chelated complex) is broken, the ligand will leave away from the vicinity of the metal ion. Thus a chelated complex dissociates less than a non-chelated complex and hence will register a higher stability constant. This explanation is illustrated by the following example :

The removal of an NH_3 molecule from the non-chelated complex, $[M(NH_3)_6]^{2+}$ in aqueous solution results in breaking of the bond and the displaced ligand molecule *viz.* NH_3 molecule moves away from the vicinity of the metal ion, M^{2+} . But when one bond of the chelated complex, $[M(NH_2-CH_2-CH_2-NH_2)_3]^{2+}$ is broken, the metal ion, M^{2+} still remains attached to the ligand, $NH_2-CH_2-CH_2-NH_2$ by the second bond and hence displaced $-NH_2$ is not allowed to move away from the metal ion.



Thus there is greater possibility of the reformation of the broken bond in the chelated complex than in the non-chelated complex. This explains the greater inherent stability of a chelated complex as compared to a non-chelated complex.

(iv) Chelate ring size. The larger the number of the chelate rings in a complex, the greater is its stability. This is illustrated in Table 14.8.

Table 14.8. Overall stability constant values (i.e. $\log_{10} \beta$ values) for some ammonia and polyamine complexes illustrating the effect of chelate ring size on the stability of the complexes.

The abbreviations used in this Table have the following meaning :

en = ethylene diamine, $\text{NH}_2\text{CH}_2\text{CH}_2\text{NH}_2$

trien = triethylene tetramine, $\text{NH}_2(\text{CH}_2)_2\text{NH}(\text{CH}_2)_2\text{NH}(\text{CH}_2)_2\text{NH}_2$

tren = triamino triethylamine, $(\text{NH}_2\text{CH}_2\text{CH}_2)_3\text{N}$

dien = diethylene triamine, $\text{NH}_2\text{CH}_2\text{CH}_2\text{NHCH}_2\text{CH}_2\text{NH}_2$

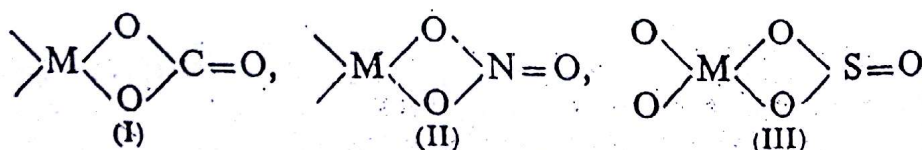
penten = tetrakis (aminoethyl) ethylene diamine,
 $(\text{NH}_2\text{CH}_2\text{CH}_2)_2\text{NCH}_2\text{CH}_2\text{N}(\text{CH}_2\text{CH}_2\text{NH}_2)_2$

M – Metal.

| Metal complexes | No. of chelate rings | Values of stability constants ($\log_{10} \beta$ values) | | | | | | |
|----------------------------------|----------------------|---|------------------|------------------|------------------|------------------|------------------|------------------|
| | | Mn^{2+} | Fe^{2+} | Co^{2+} | Ni^{2+} | Cu^{2+} | Zn^{2+} | Cd^{2+} |
| M (NH_3) ₄ | 0 | — | 23.7 | 5.31 | 7.79 | 12.59 | 9.06 | 6.92 |
| M (en) ₂ | 2 | 4.9 | 7.7 | 10.9 | 14.5 | 20.2 | 11.2 | 10.3 |
| M(trien) | 3 | 4.9 | 7.8 | 11.0 | 14.1 | 20.5 | 12.1 | 10.0 |
| M (tren) | 3 | 5.8 | 8.8 | 12.8 | 14.0 | 18.8 | 14.6 | 12.3 |
| M (dien) ₂ | 4 | 7.0 | 10.4 | 14.1 | 18.9 | 21.3 | 14.4 | 13.8 |
| M (penten) | 5 | 9.4 | 11.2 | 15.8 | 19.3 | 22.4 | 16.2 | 16.2 |

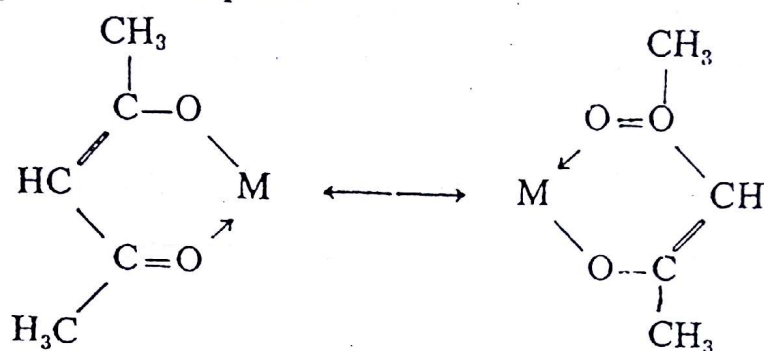
Table 14.8 clearly shows that the greater the number of chelate rings in the complex, the greater is the stability of the complex.

The stability of the complexes also depends on the number of the atoms present in the ring. The chelates containing 3-membered ring including the metal are very unstable and hence are unknown. 4-membered chelate rings are rare and occur in carbonate (I), nitrate (II) and sulphate (III) chelates.



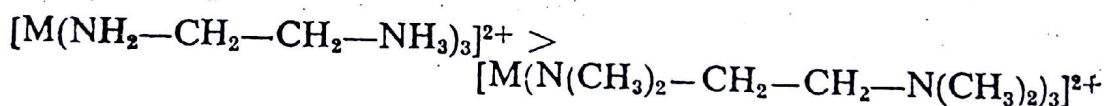
The most common and the most stable chelates are 5- and 6-membered chelates. 5-membered chelates are frequently more stable than the 6-membered chelates when the atoms in the ring are joined by single bonds only. On the other hand 6 membered chelates are more stable than 5-membered chelates of heterocyclic ligands or of

ligands involving conjugation in the chelate ring. For example, acetylacetonate complexes of the metal ions which contain 6-membered conjugate chelate rings are more stable than the corresponding ethylene diamine complexes which contain only 5-membered chelate rings. In acetylacetonate complexes the π -electron density gets spread up over the whole ring which increases the stability of this 6-membered ring system. The possibility of the resonance in its chelate ion is an additional factor contributing to the stability of acetylacetonate complexes.

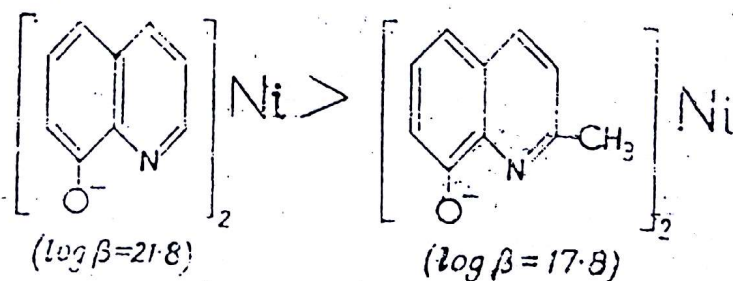


(v) **Steric effects.** When a bulky group is either attached to or present near the donor atom of a ligand, mutual repulsion among the ligands occurs and consequently the metal-ligand bond is weakened. Thus large bulky ligands form less stable complexes than do the analogous smaller ligands. This effect is commonly referred to as **steric hindrance** (steric effect or steric strain). This effect can be illustrated by the following examples :

(a) ethylene diamine, $\text{NH}_2-(\text{CH}_2)_2-\text{NH}_2$ complexes are more stable than those of tetramethyl ethylene diamine, $(\text{CH}_3)_2\text{N}-(\text{CH}_2)_2-\text{N}(\text{CH}_3)_2$ which is the tetramethyl substituted derivative of $\text{NH}_2-(\text{CH}_2)_2-\text{NH}_2$. Thus :



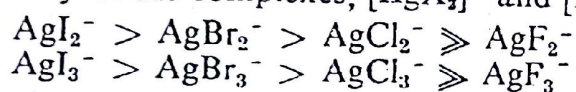
(b) Complex of Ni^{2+} with 8-hydroxy quinoline is more stable than that of 2-methyl-8-hydroxy quinoline. Thus :



The strain effect is sometimes due to the geometry of ligand coupled with the stereo-chemistry of the metal complex. For example triethylene tetraamine, $\text{NH}_2-(\text{CH}_2)_2-\text{NH}(\text{CH}_2)_2-\text{NH}-(\text{CH}_2)_2-\text{NH}_2$ (*trien*) can coordinate its all the four nitrogens at the corners of a square but triethyltriamine, $(\text{NH}_2-\text{CH}_2-\text{CH}_2)_3\text{N}$ (*tren*) can not do so. Thus straight-chain in *trien* forms more stable complexes with Cu^{2+} ion than does the branched-chain in *tren* because *tren* is unable to assume the preferred square planar geometry.

Other Factors

The amount of metal-ligand covalent character also influences the stability of the complexes of relatively electronegative metals like those in copper and zinc families and Sn and Pb. For example the order of stability of the complexes, $[\text{AgX}_2]^-$ and $[\text{AgX}_3]^-$ is as :



This order is attributed to the increase in covalent character in Ag—X bond from Ag—F to Ag—I.

EXPERIMENTAL DETERMINATION OF STABILITY CONSTANT AND COMPOSITION OF A COMPLEX by

1. Spectrophotometric Method

Most of the complexes absorb light differently than the metal ions from which they are formed. The relationship between the absorbance or optical density (A) at a particular wavelength and concentration is expressed by Beer's law which is given as :

$$A = \epsilon \cdot l \cdot c$$

where ϵ = mole extinction coefficient

l = length of the absorption cell

c = concentration of the complex (in moles/litre)

If we measure the absorbance (A) with a spectrophotometer, know the extinction coefficient (ϵ) at that wave length and the cell length (l), the concentration (c) can be calculated from the Beer's law equation given above.

How the spectrum of a metal ion, M^{2+} , changes on coordination with ligand, L, has been shown in Fig. 14.3 which contains representative spectra of a metal ion, M^{2+} (shown by broken lines) and its complex ion, ML^{2+} (shown by unbroken lines). It will be seen that the absorption by the complex takes place over the entire region

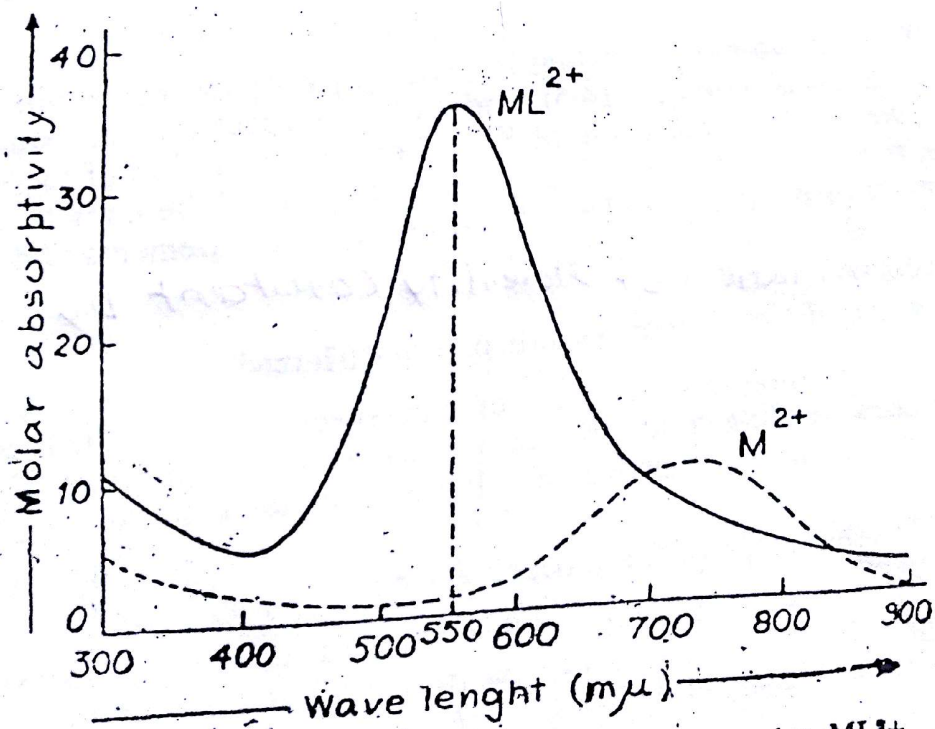
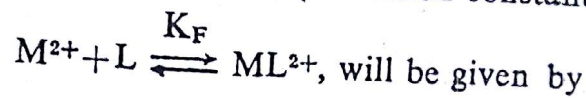


Fig. 14.3. Spectrum of a metal ion, M^{2+} and its complex, ML^{2+}

Stability of Complexes in Aqueous Solution

of the metal ion absorption, while at 550 $m\mu$ only the complex absorbs.

Clearly, the value of K_F (formation constant) for the reaction :



$$K_F = \frac{[ML^{2+}]}{[M^{2+}][L]} \quad \dots(14.1)$$

In order to obtain the value of formation constant, K_F , solutions containing known amounts of total M^{2+} and total L are equilibrated. The absorption of these solutions at 550 $m\mu$ is measured and the value of K_F is evaluated as follows :

We know that :

$$C_M = [M^{2+}] + [ML^{2+}] \quad \dots(14.2)$$

$$C_L = [L] + [ML^{2+}] \quad \dots(14.3)$$

and

$$A = \epsilon_{(ML^{2+})} \cdot l \cdot [ML^{2+}] \text{ (From Beer's Law)}$$

or

$$[ML^{2+}] = \frac{A}{\epsilon_{(ML^{2+})} \cdot l} \quad \dots(14.4)$$

where

C_M = total concentration of the metal ion

C_L = total concentration of the ligand.

Put the value of $[ML^{2+}]$ obtained from equation (14.4) in equation (14.2) and (14.3) to get the values of $[M^{2+}]$ and $[L]$. Thus :

$$[M^{2+}] = C_M - \frac{A}{\epsilon_{(ML^{2+})} \cdot l} \quad \dots(14.5)$$

$$[L] = C_L - \frac{A}{\epsilon_{(ML^{2+})} \cdot l} \quad \dots(14.6)$$

Thus, if we put the values of $[ML^{2+}]$, $[M^{2+}]$ and $[L]$ as obtained from equations (14.4), (14.5) and (14.6) respectively in equation (14.1), we shall get the value of K_F . For the evaluation of the value of K_F , the values of A , $\epsilon_{(ML^{2+})}$, l , C_M and C_L must be known. The constancy of K_F is checked by repeating the measurements at different C_M and C_L values.

Determination of stability constant by

2. Method of Continuous Variation (Job's Method)

This method is a variation of the spectrophotometric method and is used to determine the composition of a complex. This is mainly used for solutions where only one complex is formed.

Different steps of the procedure are :

(i) Make 10 solutions of the complex containing metal ion and ligand in such proportions that the total volume of each solution is 10 ml. as shown below :

| | | | | | | | | | | | |
|--------------------------------|---|----|---|---|---|---|---|---|---|---|----|
| Solutions No. (10 solutions) | : | 1 | 2 | 3 | 4 | 5 | 6 | 7 | 8 | 9 | 10 |
| Volume of the metal ion (ml) : | | 0 | 1 | 2 | 3 | 4 | 5 | 6 | 7 | 8 | 9 |
| Volume of the ligand (ml) : | | 10 | 9 | 8 | 7 | 6 | 5 | 4 | 3 | 2 | 1 |

Thus we see that the sum of the concentration of the ligand, C_L and that of the metal ion, C_M is constant. Only their ratios, $C_L : C_M$ are changed. Thus :

$$C_L + C_M = C \quad \dots(i)$$

where C is a constant.

(ii) Determine the optical densities of the solutions as prepared in step (i) with the help of a spectrophotometer at such a wave length of light that the complex absorbs strongly and the metal ion and the ligand donot.

(iii) Draw a graph between the mole fraction of the ligand, $m. f. \left(m. f. = \frac{C_L}{C} \right)$ and optical density (or absorbance). The graph obtained is of the type as shown in Fig. 14.4.

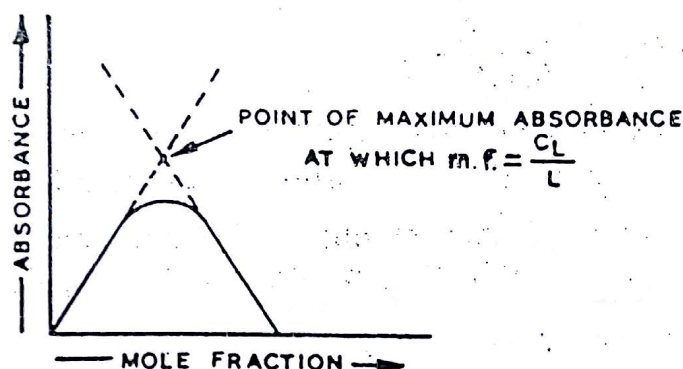


Fig. 14.4. Job's method of continuous variation for the determination of the composition of a complex.

When the legs of the curve are extrapolated, they cross each other at a point at which the absorbance is maximum.

If the formula of the complex is ML_n , then

$$n = \frac{C_L}{C_M} \quad \dots(ii)$$

Equation (i) can also be written as :

$$\frac{C_L}{C} + \frac{C_M}{C} = \frac{C}{C} = 1 \quad \dots(iii)$$

With the help of equation viz.,

$$m. f. = \frac{C_L}{C} \quad \dots(iv)$$

equation (iii) reduces to :

$$m. f. + \frac{C_M}{C} = 1$$

or
$$\frac{C_M}{C} = 1 - m. f. \quad \dots(v)$$

Dividing equation (iv) by equation (v), we get

$$\frac{C_L}{C} \times \frac{C}{C_M} = \frac{m.f.}{1-m.f.}$$

or

$$\frac{C_L}{C_M} = \frac{m.f.}{1-m.f.}$$

or

$$n = \frac{m.f.}{1-m.f.} \quad [\text{See equ. (ii)}] \quad \dots(vi)$$

From the value of n as given by equation (vi) we can determine the composition of the complex, ML_n .

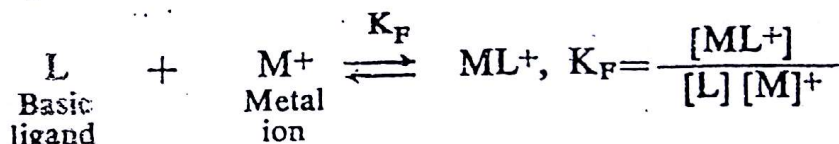
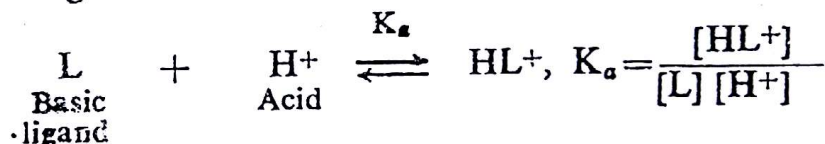
Limitations. (i) This method can be used when only one complex is formed under the experimental conditions.

(ii) This method is used when there is no change in the total volume of the solutions containing metal ions and ligand.

3. Potentiometric Method (Bjerrum Method) *pH metric method.*

When the ligand is a weak base or acid, competition between hydrogen ions and metal ions for the ligand can be used for the determination of the formation constant.

Let us consider the equilibria in which an acid and metal ions are added to a basic ligand in solution. Thus the following equations hold good :



Here K_a and K_F are the acid association constant of the ligand and formation constant respectively.

Now if C_H , C_M and C_L are the total amounts in moles/lit of acid (H^+), metal (M^+) and basic ligand (L), we have

$$C_H = [\text{H}^+] + [\text{HL}^+]$$

$$C_L = [\text{L}] + [\text{ML}^+] + [\text{HL}^+]$$

$$C_M = [\text{M}^+] + [\text{ML}^+]$$

Solving the last three equations given above and using the acid association constant of the ligand, K_a , we get :

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

$$[\text{M}^+] = C_M - [\text{ML}^+]$$

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

Thus, on putting the values of $[ML^+]$, $[M^+]$ and $[L]$ from the above equations in

$$K_F = \frac{[ML^+]}{[M^+][L]},$$

the value of K_F can be evaluated. For the determination of $[ML^+]$, $[M^+]$ and $[L]$, the values of C_H , C_L , C_M , K_a and $[H^+]$ must be known. The last quantity, $[H^+]$, is generally determined potentiometrically using a pH meter.

In order to get precise results, the ligand must be a medium weak acid or base and the formation constant, K_F , should be within a factor of 10^5 of the value of the acid association constant of the ligand, K_a .

References :

1. F. J. C. Rossotti and H. Rossotti. *The Determination of Stability Constants*, McGraw-Hill, New York, 1961.
2. J. Bjerrum, G. Schwarzenbach and L. G. Sillen (eds.) *Stability Constants of Metal-Ion Complexes*, Part I, *Organic Ligands*, Part II, *Inorganic Ligands*, Chemical Society of London, 1957, 1958.