Stability of Complex Compounds

Two types of stability

In studying the formation of complex compounds in solution, two kinds of stability have to be distinguished. These are:
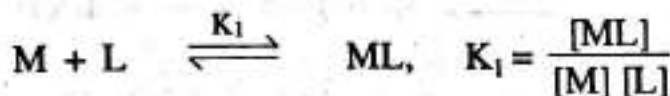
1. Thermodynamic stability. This kind of stability deals with the properties like bond energies, stability constants and redox potentials that affect the equilibrium conditions.
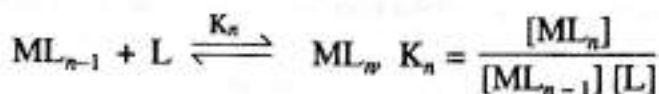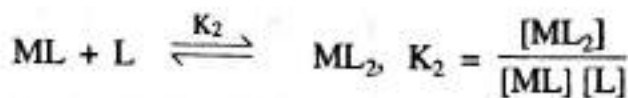
On the basis of thermodynamic stability of complexes in solution, Biltz (1927) has classified the complex compounds into stable and unstable complexes. Stable complexes are those which possess sufficient stability to retain their identity in solution while unstable complexes are those which are reversibly dissociated in solution into their components. Stable and unstable complexes have also been called *penetration* and *normal complexes* respectively.

2. Kinetic stability. This kind of stability deals with the rates of reactions (*i.e.*, reactivity) of complexes in solution, the mechanisms of chemical reactions, formation of intermediate complexes, activation energies for the process etc. On the basis of the rate of reactions (*i.e.* kinetic stability) of the complex in solution, Taube (1950) has classified the complexes into *labile* and *inert* complexes. Labile complexes are those whose one or more ligands in the co-ordination sphere can be rapidly replaced by other ligands and the ability of a complex to replace its one or more ligands by other ligands is called its lability. Inert complexes are those whose one or more ligands can either not be replaced or can be replaced with difficulty by other ligands.

Stepwise formation of complexes : Stepwise formation constants and overall formation constants
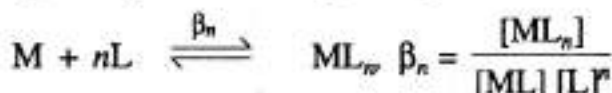
According to J Bjerrum (1941) the formation of a complex in solution proceeds by the stepwise addition of the ligands to the metal ion. Thus the formation of the complex ML_n (M = central metal cation, L = monodentate ligand and n = maximum coordination number of the metal ion M for the ligand L. n varies from one ligand to another for the same metal ion) may be supposed to take place by the following n consecutive steps and equilibrium constants:

$$M + L \; \underset{}{\overset{K_1}{\rightleftharpoons}} \; ML, \quad K_1 = \frac{[ML]}{[M][L]}$$

$$ML + L \; \underset{}{\overset{K_2}{\rightleftharpoons}} \; ML_2, \; K_2 = \frac{[ML_2]}{[ML][L]}$$

$$\vdots \qquad \vdots \qquad \qquad \vdots \qquad \vdots$$

$$ML_{n-1} + L \; \underset{}{\overset{K_n}{\rightleftharpoons}} \; ML_n, \; K_n = \frac{[ML_n]}{[ML_{n-1}][L]}$$

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

The formation of the complex ML_n may also be expressed by the following steps and equilibrium constants:
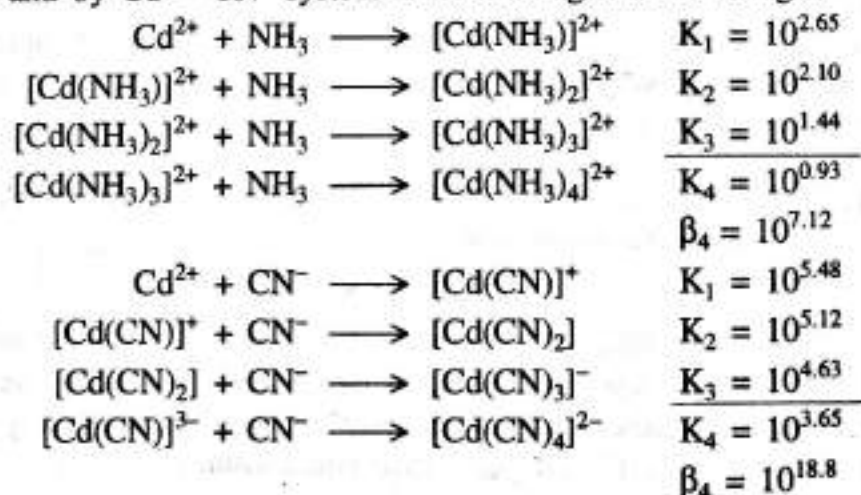
$$M + L \; \underset{}{\overset{\beta_1}{\rightleftharpoons}} \; ML, \; \beta_1 = \frac{[ML]}{[M][L]}$$

$$ML + 2L \; \underset{}{\overset{\beta_2}{\rightleftharpoons}} \; ML_2, \; \beta_2 = \frac{[ML_2]}{[M][L]^2}$$

$$\vdots \qquad \vdots \qquad \qquad \vdots \qquad \vdots$$

$$M + nL \; \underset{}{\overset{\beta_n}{\rightleftharpoons}} \; ML_n, \; \beta_n = \frac{[ML_n]}{[ML][L]^n}$$
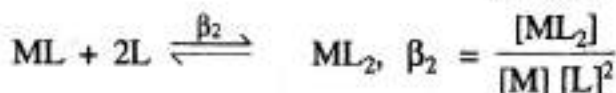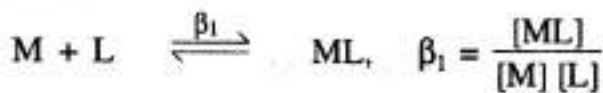
The equilibrium constants β_1, β_2 ......β_n are called *overall (or cumulative) formation constants or overall (or cumulative) stability constants.* β_n is termed as nth overall (or cumulative) formation constant or overall (or cumulative) stability constant.

With a few exceptions the values of successive stability constants decrease regularly from K_1 to K_n. *i.e.*,

$$K_1 > K_2 > K_3 ..... > K_{n-1} > K_n.$$

The above order is illustrated by the data for the Cd^{II} —NH_3 system where the ligands are neutral molecules and by Cd^{II}—CN^- system where the ligands are charged.

$$Cd^{2+} + NH_3 \longrightarrow [Cd(NH_3)]^{2+} \qquad K_1 = 10^{2.65}$$
$$[Cd(NH_3)]^{2+} + NH_3 \longrightarrow [Cd(NH_3)_2]^{2+} \qquad K_2 = 10^{2.10}$$
$$[Cd(NH_3)_2]^{2+} + NH_3 \longrightarrow [Cd(NH_3)_3]^{2+} \qquad \underline{K_3 = 10^{1.44}}$$
$$[Cd(NH_3)_3]^{2+} + NH_3 \longrightarrow [Cd(NH_3)_4]^{2+} \qquad \overline{K_4 = 10^{0.93}}$$
$$\beta_4 = 10^{7.12}$$

$$Cd^{2+} + CN^- \longrightarrow [Cd(CN)]^+ \qquad K_1 = 10^{5.48}$$
$$[Cd(CN)]^+ + CN^- \longrightarrow [Cd(CN)_2] \qquad K_2 = 10^{5.12}$$
$$[Cd(CN)_2] + CN^- \longrightarrow [Cd(CN)_3]^- \qquad \underline{K_3 = 10^{4.63}}$$
$$[Cd(CN)]^{3-} + CN^- \longrightarrow [Cd(CN)_4]^{2-} \qquad \overline{K_4 = 10^{3.65}}$$
$$\beta_4 = 10^{18.8}$$

The steady decrease in the values of K_1, K_2, ... 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.

Stepwise and cummulative stability constants are also expressed as $\log_{10} K_1 \ldots \log_{10} K_n$ 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 concentration of the enclosed species.

Relationship between β_n and $K_1, K_2 \ldots K_n$

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

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

On multiplying both numerator and denominator by $[ML][ML_2]$ and on rearranging, we get

$$\beta_3 = \frac{[ML_3]}{[M][L]^3} \cdot \frac{[ML][ML_2]}{[ML][ML_2]}$$

$$= \frac{[ML]}{[M][L]} \cdot \frac{[ML_2]}{[ML][L]} \cdot \frac{[ML_3]}{[ML_2][L]}$$

$$= K_1 \cdot K_2 \cdot K_3$$

Thus,

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

$$= K_1 \cdot K_2 \ldots \ldots K_n \qquad \ldots(i)$$

or,

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

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 $K_1, K_2, \ldots K_{n-1}, K_n$. This is 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 1.3 in which the value of overall stability constant as β_n and $\log_{10}\beta_n$ for $[Ni(NH_3)_6]^{2+}$ ion and those of stepwise stability constants as $K_1, K_2 \ldots, K_5, K_6$ and $\log_{10} K_1, \log_{10} K_2 \ldots, \log_{10} K_6$ corresponding to the six equilibria given in the first column through which $[Ni(NH_3)_6]^{2+}$ ion can be regarded as being formed, are given. This table shows that

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

and

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

In Table 1.3 we also see that $\log K_6$ is negative ($= -0.10$). This negative value shows that the pentammine complex, $[Ni(H_2O)(NH_3)_5]^{2+}$ is thermodynamically favoured with respect to the hexammine complex, $[Ni(NH_3)_6]^{2+}$ [See equilibrium No. (vi)].

Kinetic vs. thermodynamic stability

Since the terms viz. 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. $[Hg(CN)_4]^{2-}$ which is thermodynamically very stable (formation constant $= 10^{42}$) is labile, since in solution it exchanges CN^- ligands with labelled cyanide ions, $^{14}CN^-$ at a very fast rate.

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

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

On the other hand the complex, $[Co(NH_3)_6]^{3+}$ 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.

Factors affecting the stability of metal complexes

The stability (or stability constants) of metal complexes depends on the following factors:

A. Properties of central metal ion

The following properties of central metal ion affect the stability of the metal complexes:

1. Size of central metal ion. For a given ligand the stability (or stability constant) of the complexes of the metallic ions having the same charge on them decreases with the increase of the size of the central metal ion. Thus the stability of complexes given by the cations belonging to the same group and having the same charge decreases as we proceed from top to bottom in the group, since the size of the metallic cations increases in the same order. For example:

(*i*) The stability of hydroxide complexes given by alkali metal ions (Li^+, Na^+ etc.), alkaline earth metal ions (Be^{2+}, Mg^{2+} etc.) and III B group ions (Sc^{3+}, Y^{3+} and La^{3+}) is in the order:

(*a*) Li^+ ($r = 0.60$ Å) > Na^+ ($r = 0.95$ Å) > K^+ ($r = 1.33$ Å) > Rb^+ ($r = 1.48$ Å) > Cs^+ ($r = 1.69$Å).

(*b*) Be^{2+} ($r = 0.31$ Å) > Mg^{2+} ($r = 0.65$ Å) > Ca^{2+} ($r = 0.99$ Å) > Sr^{2+} ($r = 1.13$ Å) > Ba^{2+} ($r = 1.35$ Å) > Ra^{2+} ($r = 1.40$ Å).

(*c*) Sc^{3+} ($r = 0.81$ Å) > Y^{3+} ($r = 0.93$ Å) > La^{3+} ($r = 1.15$ Å).

It may be noted that EDTA complex of Mg^{2+} ($r = 0.65$ Å) is less stable than that of Ca^{2+} ($r = 0.99$Å).

(*ii*) The inverse relation between the size of the central metal ion and the stability of the complexes formed is also confirmed when we see that the stability of the complexes of Mn^{2+}, Fe^{2+}, Co^{2+}, Ni^{2+}, Cu^{2+} and Zn^{2+} ions with a given ligand increases from Mn^{2+} to Cu^{2+} and then decreases at Zn^{2+} (These ions are *divalent* ions of the elements of 1st transition series).

Ions:	Mn^{2+}	Fe^{2+}	Co^{2+}	Ni^{2+}	Cu^{2+}	Zn^{2+}
Ionic radii (Å):	0.91	0.83	0.82	0.78	0.69	0.74
Order of stability of complexes :	Mn^{2+} <	Fe^{2+} <	Co^{2+} <	Ni^{2+} <	Cu^{2+} >	Zn^{2+}

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

2. Charge on the central metal ion. For a given ligand, the stability of the complexes of the metallic ions having almost the same size but different charges on the them decreases with the decrease of the charge on them. Thus the stability of complexes given by: (*a*) La^{3+}, Sr^{2+} and K^+ ions. (*b*) Co^{3+} and Co^{2+} ions. (*c*) Fe^{3+} and Fe^{2+} ions, and (*d*) Th^{4+}, Y^{3+}, Ca^{2+} and Na^+ ions with the same ligand is in the order:

(*a*) La^{3+} ($r = 1.15$ Å) > Sr^{2+} (= 1.13 Å) > K^+ (= 1.33 Å)

(*b*) Co^{3+} ($r = 0.63$ Å) > Co^{2+} (= 0.74 Å)

(*c*) Fe^{3+} ($r = 0.64$ Å) > Fe^{2+} ($r = 0.76$ Å)

(*d*) Th^{4+} ($r = 0.95$ Å) > Y^{3+} (= 0.93 Å) > Ca^{2+} (= 0.99 Å) > Na^+ (= 0.95 Å).

If the factors 1 and 2 mentioned above are combined, then we can say that with the increase of ionic potential of the central metal ion (Ionic potential of the metal ion = charge on the metal ion/size of the ion), the stability of the complexes with the same ligand also increases. For example, the stability of hydroxide complexes of Li^+, Ca^{2+}, Ni^{2+}, ... Be^{2+} ions whose ionic potential increase from Li^+ to Be^{2+} ions also increases in the same direction as shown below.

Central metal ion (charge on the ion is shown in parentheses)	Ionic radius (Å)	Ionic potential	Order of stability of complexes
Li^+ (+1)	0.60	1/0.60 = 1.6	
Ca^{2+} (+2)	0.99	2/0.99 = 2.0	
Ni^{2+} (+2)	0.72	2/0.72 = 2.97	Increasing / Increasing
Y^{3+} (+3)	0.93	3/0.93 = 3.22	
Th^{4+} (+4)	0.95	4/0.95 = 4.20	
Al^{3+} (+3)	0.50	3/0.50 = 6.0	
Be^{2+} (+2)	0.31	2/0.31 = 6.45	

3. Electronic configuration of the central metal ion. In case of metallic ions which have the same radius and same charge (e.g., Na^+ and Cu^+; Ca^{2+} and Cd^{2+} or Sn^{2+}; Sc^{3+} and Ga^{3+} or Sb^{3+} ions), the outer electronic configuration of the ions plays an important role in determining the stability of the complexes. The complexes given by metal ions possessing inert gas (8-electron ions), pseudo inert gas (18-electron ions) and pseudo inert gas plus two (18 + 2 electron ions) electronic configuration are less stable than those given by transition metal ions which have $(n - 1)d$ orbitals available for accepting the electron pairs donated by the ligands. The stability of transition metal complexes depends on, besides ionic potential, other factors like crystal field stabilisation energy, electron pairing energy, stereochemistry, availability of empty d_{z^2} and $d_{x^2-y^2}$ orbitals for π bonding or back donation. The use of inner d-orbitals gives stronger metal–ligand bonding than the use of s- and p-orbitals or outer d-orbitals. The various factors influencing the stability of complexes given by transiton metal ions ultimately depends on the number of electrons present in $(n - 1)d$ orbitals. The stability constants of the complexes given by the transition metal d^n ions for the equilibrium:

$$[M(H_2O)_n] + nL \longrightarrow MLn + nH_2O$$

follow the order :

$$d^0 < d^1 < d^2 < d^3 \gtrless d^4 > d^5 < d^6 < d^7 < d^8 \gtrless d^9 > d^{10}.$$

The sequence $d^3 > d^4$ and $d^8 > d^9$, is expected when the John-Teller effect is low and the coordination number is 6. The sequence $d^3 < d^4$ and $d^8 < d^9$, however, is expected when the John-Teller effect is large and the coordination number is 4.

4. Electronegativity and polorising power of the cental metal ion. The bonding between a central metal 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 electron-attracting tendency) would give more stable complexes. Similarly, the central metal ion with high polarising power gives more stable complexes. For example, complexes given by Cu^+ and Cd^{2+} ions are more stable than those given by Na^+ and Ca^{2+} ions respectively.

5. Ionisation energy of the central metal ion. Generally the stability of complexes given by M^{2+} ions increases with the increase of first plus second ionisation potential for M^{2+} ions.
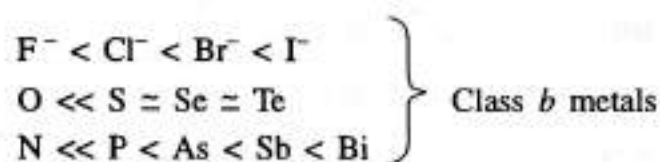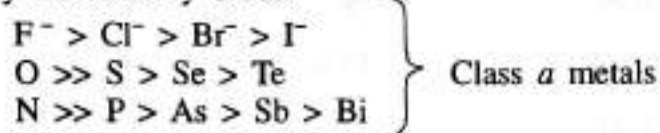
6. Class _a_ and class _b_ metals. Chatt and Ahrland have classified the metals into three categories: _a_, _b_ and borderline, on the basis of their electron-acceptor properties. This classification is shown below (normal valence states are assumed).

(a) _Class a metals:_ H, the alkali and alkaline earth metals, the elements Sc → Cr, Al → Cl, Zn → Br, In, Sn, Sb and I, the lanthanides and actinides

(b) _Class b metals:_ Rh, Pd, Ag, Ir. Pt, Au, Hg

(c) _Borderline metals:_ The elements Mn → Cu, Ti →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:

$$\left.\begin{array}{l} F^- > Cl^- > Br^- > I^- \\ O \gg S > Se > Te \\ N \gg P > As > Sb > Bi \end{array}\right\} \text{Class } a \text{ metals}$$

$$\left.\begin{array}{l} F^- < Cl^- < Br^- < I^- \\ O \ll S \simeq Se \simeq Te \\ N \ll P < As < Sb < Bi \end{array}\right\} \text{Class } b \text{ metals}$$

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.

B. Properties of the ligand

The following properties of the ligand affect the stability of the metal complexes.

1. Size and charge of ligand. If a ligand is smaller, it can approach the metal ion more closely forming a stable bond. Similarly, a highly charged ligand would also form a strong bond with the metal. Thus the high charge and small size of a ligand leads to the formation of stable complexes. For example the stability of the complexes of a given metal ion with halide ions used as ligands is in the order: $F^- > Cl^- > Br^- > I^-$. This order is applicable for class _a_ metals. When class _b_ metals (_e.g._ Pd, Ag, Pt, Hg etc.) are used, the above order of stability is reversed, _i.e._, for class _b_ metals the order is : $F^- < Cl^- < Br^- < I^-$.

2. Dipole moment of ligands. For neutral ligands, the larger the magnitude of permanent dipole moment, the greater is the stability of the complexes. For example, the order of stability of complexes formed by some neutral ligands is as : ammonia > ethylamine > diethylamine > triethylamine.

3. Basic character of ligands. The more basic is the ligand, more easily it can denote 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 more 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. ($NH_3 > H_2O > HF$). This behaviour is observed for alkali, alkaline earth and other electropositive metals like first row transition elements, lanthanides and actinides.

4. π-bonding capacity of ligands. The ligands like CN^-, CO, PR_3, AsR_3, SR_2, alkenes, alkynes which are capable of forming π-bonds with transition metal ions give more stable complexes.

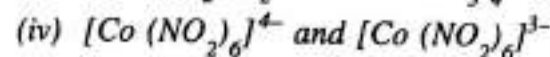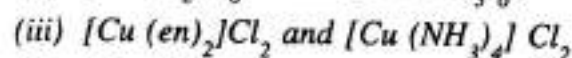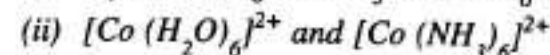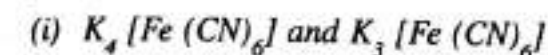**5. Steric hindrance.** When a bulky group is either attached to or is present near a donor atom of a ligand, repulsion between the donor atom of the ligand and the bulky group is produced and this mutual repulsion weakens the metal-ligand bonding and hence makes the complex less stable. For example the complex of Ni^{2+} ion with 2-methyl-8-hydroxy quinoline ($\log_{10}$ β= 17.8) is less stable than that with 8-hydroxy quinoline ($\log_{10}$ β=17.8). The effect of the presence of bulky group on the stability of a complex is commonly called steric hindrance.

C. Stability of chelates

See "*Factors affecting the stability of chelates*" discussed on page 32.

SOME TYPICAL PROBLEMS WITH SOLUTIONS

Problem 1. *Out of the following pairs of complexes which one is more stable? Also given reason for your answer.*

(i) $K_4[Fe(CN)_6]$ and $K_3[Fe(CN)_6]$

(ii) $[Co(H_2O)_6]^{2+}$ and $[Co(NH_3)_6]^{2+}$

(iii) $[Cu(en)_2]Cl_2$ and $[Cu(NH_3)_4]Cl_2$

(iv) $[Co(NO_2)_6]^{4-}$ and $[Co(NO_2)_6]^{3-}$

(*Delhi 2000*)

Solution. (*i*) We know that for a given ligand, the stability of complexes of the metallic ions having different charges decreases with the decrease of the charge on them. Thus, since Fe has +2 charges in $K_4[Fe(CN)_6]$ and +3 charges in $K_3[Fe(CN)_6]$, $K_4[Fe(CN)_6]$ is less stable than $K_3[Fe(CN)_6]$.

(*ii*) Both the complex ions have Co in the same oxidation state (= +2). Here since NH_3 ligand is more basic than H_2O ligand, NH_3 will donate electron pair to the central Co^{2+} ion more easily than H_2O and hence will form more stable complex. Thus $[Co(NH_3)_6]^{2+}$ ion is more stable than $[Co(H_2O)_6]^{2+}$ ion.

(*iii*) We know that since *bis* (ethylene diamine) copper (II) chloride, $[Cu(en)_2]Cl_2$ has two 5-membered rings in its structure, it is a chelated (cyclic) complex. On the other hand, tetrammine copper (II) chloride, $[Cu(NH_3)_4]Cl_2$ is a non-chelated complex. Thus, being chelated complex, $[Cu(en)_2]Cl_2$ is more stable than $[Cu(NH_3)_4]Cl_2$ (Also see the figure geven below)

Structure of [Cu(en)₂]Cl₂   Structure of [Cu(NH₃)₄]Cl₂
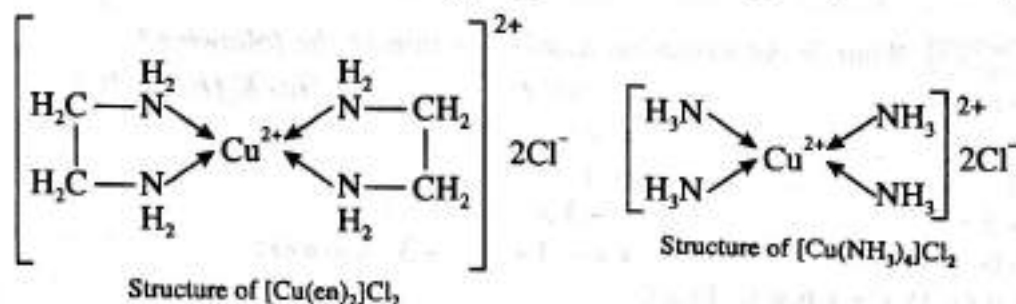
(*iv*) Since Co^{3+} ion present in $[Co(NO_2)_6]^{3-}$ ion is smaller in size than Co^{2+} ion present in $[Co(NO_2)_6]^{4-}$ ion, this ion (*i.e.*, Co^{3+} ion) will draw the lone pair of electrons present on NO_2^- ion (ligands) towards itself more strongly than Co^{2+} ion and hence $[Co^{3+}(NO_2)_6]^{3-}$ ion is more stable than $[Co^{2+}(NO_2)_6]^{4-}$.

Problem 2. *Explain why* $Fe(NH_4)_2(SO_4)_2$ *is a salt but* $K_4[Fe(CN)_6]$ *is a complex compound.*

(*M.D. Rohtak 97*)

**Solution.** $Fe(NH_4)_2(SO_4)_2$ is a salt, since its solution gives the reactions of all its constituent ions namely Fe^{2+}, NH_4^+ and SO_4^{2-} ions. On the other hand, $K_4[Fe(CN)_6]$ is not a salt, since its solution does not give the reactions of K^+, Fe^{2+} and CN^- ions. This compound gives the reactions of K^+ (simple ion) and $[Fe(CN)_6]^{2-}$ (complex ion) ions only.

Problem 3. *What are the differences between double salts and complex compounds?*

Solution. When a double salt is dissolved in water, it gets dissociated completely to give all its constituent ions. For example aqueous solution of Mohr's salt, $FeSO_4.(NH_4)_2SO_4.6H_2O$ which is a double salt gives all its constituent ions as shown below:

$$FeSO_4.(NH_4)_2SO_4.6H_2O \longrightarrow Fe^{2+} + 2SO_4^{2-} + 2NH_4^+ + 6H_2O$$
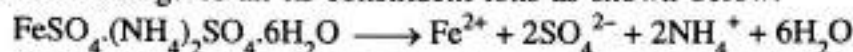
On the other hand, when a complex compound is dissolved in water, it does not give all its constituent ions. For example aqueous solution of $K_4[Fe(CN)_6]$ which is a complex compound does not give K^+, Fe^{2+} and CN^- ions. Rather it gives K^+ and $[Fe(CN)_6]^{4-}$ (complex ion) ions

$$K_4[Fe(CN)_6] \longrightarrow 4K^+ + [Fe(CN)_6]^{4-}$$
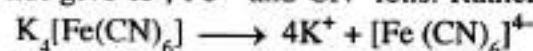
Problem 4. *$FeSO_4$ solution mixed with $(NH_4)_2SO_4$ solution (in the molar ratio of 1 : 1) gives the test of Fe^{2+} ion but $CuSO_4$ solution mixed with liquid NH_3 (in the molar ratio of 1 : 4) does not give the test of Cu^{2+}. Explain why?*

Solution. When $FeSO_4$ solution is mixed with that of $(NH_4)_2SO_4$, we get a double salt, $FeSO_4.(NH_4)_2SO_4.6H_2O$ (called Mohr's salt). This salt dissociates completely in aqueous solution to give all its constituent ions.

$$FeSO_4.(NH_4)_2SO_4.6H_2O \longrightarrow Fe^{2+} + 2NH_4^+ + SO_4^{2-} + 6H_2O$$
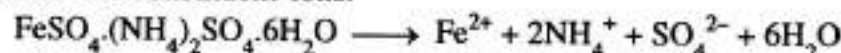
Thus the aqueous solution of $FeSO_4 . [NH_4]_2SO_4.6H_2O$ gives the test of Fe^{2+} ion.

When $CuSO_4$ solution is mixed with liquid NH_3, we get a complex compound, $[Cu(NH_3)_4]SO_4$ which dissociates to give $[Cu(NH_3)_4]^{2+}$ and SO_4^{2-} ions

$$[Cu(NH_3)_4]SO_4 \longrightarrow [Cu(NH_3)_4]^{2+} + SO_4^{2-}$$
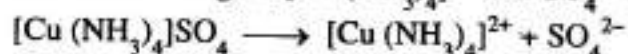
Thus since Cu^{2+} ions are not obtained in the free state, the aqueous solution of $[Cu(NH_3)_4]SO_4$ does not give the test of Cu^{2+} ions.

Problem 5. *Explain why Be^{2+} ion has much stronger tendency to form complexes than Mg^{2+} ion.*

(Meerut 1980 S)

Solution. Smaller ion has greater tendency to attract the lone pair of electrons on the ligands and hence forms the complex compound more readily than the larger ion. Now since Be^{2+} ion is smaller in size than Mg^{2+} ion, the former accepts the lone pair of electrons donated by F^- ion (ligand) and forms the complex ion, $[BeF_4]^{2-}$. On the other hand, since Mg^{2+} ion is larger in size than Be^{2+} ion, this ion does not form $[MgF_4]^{2-}$ ion.

Problem 6. *What is the oxidation number of iron in the following?*

(i) $Fe(CO)_5$ (ii) $[Fe(C_2O_4)_3]^{3-}$ (iii) $K_3[Fe(CN)_6]$

(iv) $Fe_4[Fe(CN)_6]_3$ (v) $[Fe(C_5H_5)_2]$

Solution. Suppose oxidation number of Fe atom is x. Then:

(i) $x + 5 \times 0 = 0$ (ii) $x + 3 \times (-2) = -3$

$\therefore x = 0$ (**Answer**) $\therefore x = -3 + 6 = +3$ (**Answer**)

(iii) $3 \times (+1) + x + 6 \times (-1) = 0$

$\therefore x = -3 + 6 = +3$ (**Answer**)

(iv) We know that the common oxidation number of Fe is $+2$ or $+3$. Thus $Fe_4[Fe(CN)_6]_3$ can be represented as shown at (a), (b), (c) or (d).

(a) $Fe_4^{2+}[Fe^{3+}(CN)_6]_3$. Here : $4 \times (+2) + 3 \times [+3 + 6 \times (-1)] = +8 - 9 = -1$

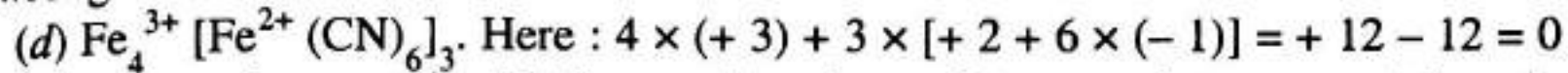Since the sum of oxidation numbers is not equal to zero, the representation shown at (a) is wrong

(b) $Fe_4^{2+}[Fe^{2+}(CN)_6]_3$. Here : $4 \times (+2)1 + 3 \times [+2 + 6 \times (-1)] = +8 - 12 = -4$

Since the sum of oxidation numbers is not equal to zero, the representation shown at (b) is also wrong.

(c) $Fe_4^{3+} [Fe^{3+} (CN)_6]_3$. Here : $4 \times (+3) + 3 \times [+3 + 6 \times (-1)] = +12 - 9 = +3$
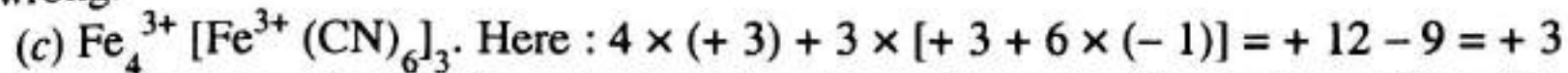
Since the sum of oxidation numbers is not equal to zero, the representation shown at (c) is also wrong.

(d) $Fe_4^{3+} [Fe^{2+} (CN)_6]_3$. Here : $4 \times (+3) + 3 \times [+2 + 6 \times (-1)] = +12 - 12 = 0$

Here since the sum of oxidation numbers is equal to zero, the representation shown at (d) is correct. Thus :

Fe atom written outside the coordination sphere has oxidation number $= +3$ and Fe atom given inside the coordination sphere has oxidation number $= +2$. (**Answer**)

(v) In $[Fe (C_6H_5)_2]$, the ligand is cyclopentadienyl ion, $C_5H_5^-$ whose O.N. $= -1$.

Thus : $x + 2 \times (-1) = 0$ $\therefore x = +2$ (**Answer**)