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Course Title:	Advanced Coordination Chemistry
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Unit:	I
Sub Title:	Stability of coordination compounds
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INTRODUCTION

Generally complexes are designated as stable or unstable. The general meaning of stability is supposed to be related with the concept, whether a particular complex can be converted into other easily or not. As a matter of fact, this is kinetic aspect of stability; which deals with the rate of the reaction and its mechanism. The other aspect of stability is thermodynamic aspect. In which stability of a complex is related with the amount of energy released during its formation or the amount of energy required to break it.

In this unit we describe complex forming equilibria in solution and the various factors affecting it. We will also discuss the various factors affecting stability constants for the formation of complexes in solution. In the end of the unit we shall describe the method used for determining stability constants of the complexes formed in solution. Which involves quantitative characterisation of the complex-forming reaction in solution.

You may recall what you have already studied about the basic concept of chemical equilibria in solution.

OBJECTIVES

The main aim of this unit is to study the complex formation equilibria in solution. After going through this unit you should be able to:

- describe stepwise and overall formation constants;
- explain thermodynamic importance of stability constants;
- discuss factors affecting stability of complexes; and
- describe methods of determining stability constants for binary complexes in solution.

STEP-WISE AND OVERALL FORMATION CONSTANTS

The term stability is a loose term, 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. The term can not be generalised for complexes. A complex may be quite stable to one reagent and may decompose readily in presence of another reagent.

In studying the formation of complexes in solution, two types of stability of complexes is found:

1. Thermodynamic Stability

This is a measure of the extent of which the complex will form or will be transformed into another species under certain conditions, when the system has reached in equilibrium. When we are concerned with this type of stability, we deal with metal-ligand bond energies, stability constant etc.

2. Kinetic Stability

This refers to the speed with which transformation leading to the attainment of equilibrium will occur. When we are interested in kinetic stability for complex ions in solutions, we deal with rates and mechanism of chemical reactions. These reactions may be substitution, isomerisation, recombination and electron or group transfer reactions. In the kinetic sense, it is more proper to call the complexes inert or labile complex rather than stable or unstable complex. The complexes in which the ligands are rapidly replaced by others are called labile, while those in which substitution occurs slowly are called inert complexes.

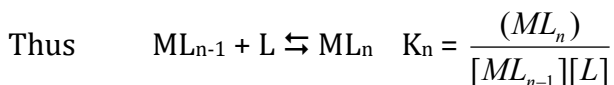
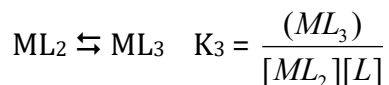
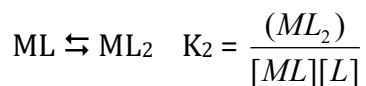
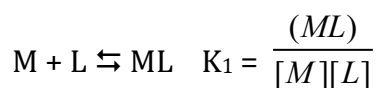
Stepwise and Overall Formation Constants

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

where M = central metal cation

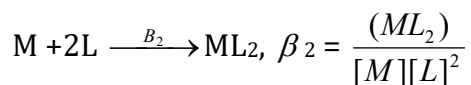
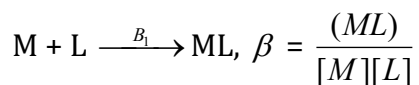
L = monodentate ligand

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



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

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



$$\text{Thus } M + nL \xrightarrow{B_n} ML_n, \beta_n = \frac{(ML_n)}{[M][L]^n} \dots\dots\dots(8.1)$$

The equilibrium constants, $\beta_1, \beta_2, \beta_3, \dots\dots\dots \beta_n$ are called overall formation or **overall stability constants**. β_n is called as n^{th} overall (or cumulative) formation constant or overall stability constants.

The higher the value of stability constant for a complex ion, the greater will be its stability. Alternatively $1/k$ values sometimes are called instability constant.

Stepwise and cumulative stability constants are also expressed as $\log_{10}K_1, \log_{10}K_2, \dots\dots\dots \log_{10}K_n$ and $\log_{10}\beta_n$ respectively.

Relationship or Interaction Between β_n and $K_1, K_2, K_3, \dots\dots\dots K_n$

K 's and β 's are related to one another consider for example, the expression for β_3 is:-

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

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

$$\begin{aligned} \beta_3 &= \frac{[ML_3]}{[M][L]^3} \times \frac{[ML][ML_2]}{[ML][ML_2]} \\ &= \frac{[ML]}{[M][L]} \times \frac{[ML_2]}{[ML][L]} \times \frac{[ML_3]}{[ML_2][L]} \\ &= K_1 \times K_2 \times K_3 \end{aligned}$$

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

$$= K_1 \times K_2 \times \dots \times K_n$$

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

From above relation, it is clear that the overall stability constant β_n is equal to the product of the successive (i.e. stepwise) stability constants, $K_1, K_2, K_3, \dots, K_n$. This in other words means that the value of stability constants for a given complex is actually made up of a number of stepwise stability constants.

8.2.1 Thermodynamic Importance of Stability Constants

In order to reach accurate conclusions regarding the nature of the forces acting within complex species during their formation in solution, the energy changes accompanying the reaction in question i.e. a complete thermodynamic characterisation of the reactions is necessary at the very least, determination of enthalpy (ΔH), entropy (ΔS) and free energy (ΔG) changes accompanying complexation.

In the language of thermodynamics, the equilibrium constant of the reaction is a measure of the change in free energy, heat content and entropy. A more useful manner of stating equilibrium constant is in terms of the standard free energy change ΔG , i.e. the difference of free energy between the products and the reactants in a standard state, which is related to equilibrium constants by the thermodynamic expression:

$$- RT \log K = \Delta G = \Delta H - T \Delta S \dots\dots\dots(8.2)$$

The reactions tends to go in the direction written, when ΔG is negative.

Enthalpy change (ΔH) gives the amount of heat either consumed or liberated per mole of products and is related to the strength of the ligand to metal bonds, compared to that of the metal to solvent bonds.

Entropy change (ΔS) is related to the change in randomness (the disorder) of a system. As is quite evident from the relation given above (8.2), complex formation is most favoured by the negative enthalpy and positive entropy changes (either of the two or both) as may be expressed by the equation:

$$\log K = \frac{\Delta S - \Delta H / T}{2.303 R} \dots\dots\dots(8.3)$$

In many reactions both the heat and entropy changes favour complex formation but their relative importance changes markedly with minor variations from ML to M'L or ML'.

FACTORS AFFECTING STABILITY

Factors related with Metal

The nature of the metal ions and the effect of the different physical properties of the metal ions on the stability of the complex are:

1. Stability (or stability constant) increases with decreasing size of metal ion. K generally varies as $1/r$.
2. Stability constants for a complex increase with the charge of the central ion. The K for the Fe(II) complexes will be less than the K for the corresponding Fe(III) complexes.
3. The ions with high polarizability give complexes with higher stability constants. Thus Cu(I) complexes have higher K values than the similar sized Na⁺ complexes, similarly of Ca²⁺ and Cd(II) or Al (III) and Ga(III) the former have low K values for the complex formation.
4. Electronegativity increases the polarizing power and the ions with higher electronegativity give stable complexes.
5. **Ionization Energies:** The electronegativity, covalent nature and ionic radii can be related to the ionization energies of the atoms. It is found that the stability constants for the metal complexes with a ligand increase with the ionization energies of the metallic species.

Observations of Bjerrum-Nielsen and others show that although most of the metals of the periodic table form complexes, this tendency is the most with transition metals. The reason being that the chelate effect is almost an entropy effect for the metal ions of the nontransitional group, while for the transition metals it is

partly an enthalpy effect which increases the crystal field strength. The increase in crystal field strength increases the points of attachment of the ligand to the metal ion imparting greater chelating tendency to the latter (cf. CFS). Fig.

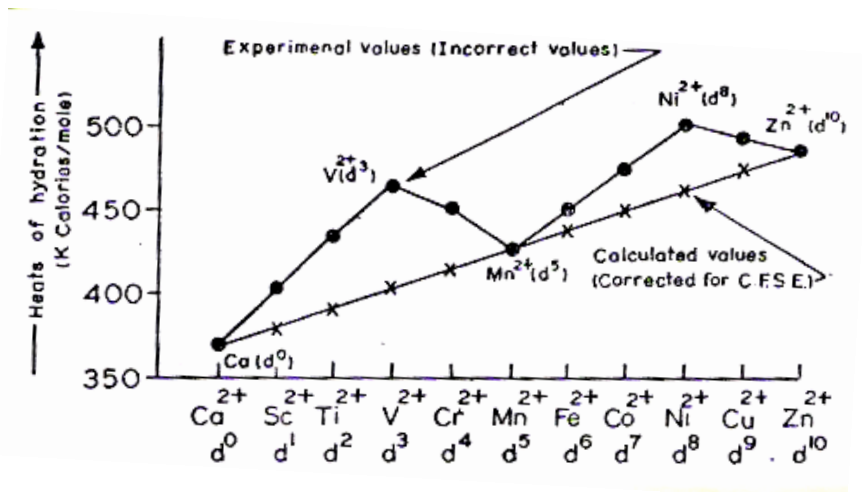


Fig.: CFSE affecting stability of aquo-complexes

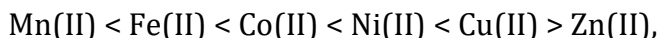
Chatt Ahrland classified the metals into a and b classes while a class metals form stable complexes with ligands having the coordinating atoms, N, O, F (second period elements), b class metals form stable complexes with ligands in which donor atom is P, S, Cl (third or latter period elements).

The a class metals include H, alkali and alkaline earth metals; the elements from Sc to Cr, Al to Cl, Zn to Br and lanthanides and actinides. While amongst b class Rh, Pd, Ag, Ir, Pt, Au and Hg are included.

Elements from Mn to Cu, Tl to Po, Mo, Te, Ru, W, Re, Os, Cd are border line metals.

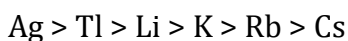
It can be said with some approximation that increase in the ionic charge of the metal ion and donor, will bring an increase in the chelating tendency while the increase in ionic radius will decreases it. Thus small cation size, comparatively large ionic charge and appropriate electronic arrangements are responsible for the maximum ability of complex formation by transition elements.

Mellor and Maley have shown that the stabilities of the complexes of bivalent metal ions follow the order: Pd > Cu > Ni > Pb > Co > Zn > Cd > Fe > Mn > Mg irrespective of the nature of the ligand. Irving and Williams from the analysis of the data on stability constants of transition metal ions, found that the order

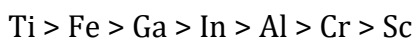


holds good. This order according to them follows logically from a consideration of the reciprocal of ionic radius and second ionization potential of the metal, and is known as 'Natural Order of Stability'.

Univalent ions have not been extensively studied but data on the complexes of the univalent ions with dibenzol methanate ion shows the order of the stability as:



For tetravalent metals much less information is available, the greater ease of hydrolysis of these ions making potentiometric titrations more difficult. Irving and Williams suggest from a considerable limited number of investigations that a rough order of stabilities be:



Factors Related With Ligands

The properties of the ligands which affect the stability of the metal complexes are as under:

1. **Basicity of the ligands:** The greater is the Lewis base strength, higher is expected to be the stability constant of the complex. Thus K values for the complexes are expected to change in a manner similar to the changes in the proton association constant (BH) for the ligands.

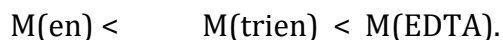
2. **Dipole moment and polarizability of the ligands:** Due to the greater electrostatic interactions between the metal ion and the ligands, polarity and polarizability of ligand results in higher K for the complexes.
3. **(M→L) π -bonding** always increases the stability of the complex.
4. **Steric factor:** It play an important rule in determining the stability constants for the complexes. Thus the 2 methyl derivative of 3 hydroxyquinoline gives much less stable complexes then the parent compound because of the steric hindrance caused by the methyl group adjacent to the site of co-ordination.

In complex formation hydrogen behaves just like a metal ion. Therefore, a ligand with a larger affinity for proton will show the same behaviour towards the metal ions. According to Riley any factor which can increases the localization of negative charge in the co-ordinating ligands makes the electron more readily available and thus increasing the co-ordinating ability of a base. The correlation between the basic strength of the ligand and the stability constant of the complexes was pointed our first by Calvin and Wilson.

Ring Formation and Size of the Ring

Ring complexes or chelates are very stable due to reduced strain. The number of ring formed, the size of the rings and stabilizing or interfering resonance interactions are determined by the structure of the chelating agent. The work of Ley on the chelates of amino-acids showed that five and six membered rings are the most stable. Much evidence has accumulated since then to prove that all chelates have either five or six membered rings. Pfeiffer observed that in general the five membered rings is the more stable when the ring is entirely saturated but when one or more double bonds are present, the six membered rings is favoured. Schwarzenbach and Co-workers have observed that there is a decrease in chelate stability with the increase in ring size. The stability of a five membered ring is not chiefly due to entropy but rather to the enthalpy of formation; the example being 1,

2, 3 triamine- propane tetra chloroplatinum. Further the stability increases with the increase in the number of rings in the molecule:



(one ring) (two rings) (five rings)

Steric Effect:

Steric hindrance can influence stability in many ways, e.g.

- (i) Metal-ligand bonds are weakened due to the presence of bulky group near the coordinating site.
- (ii) The substituting group prevents the ligand from assuming the planar configuration and hence introduce strain in the metal-donor bond.
- (iii) Steric hindrance is also due to strained structure of the chelated ring, since it breaks the usual linear configuration of the complexes.

From the study of the copper complexes of substituted malonic acids Riley concluded that ethyl and propyl groups had a larger effect than methyl in reducing the stability.

Resonance Effects

The stability of a chelated ring will depend on the possibilities of resonance in the ring and on how these will fit in with resonance in the organic ligand itself. That resonance may affect the formation of a chelate was first shown by Calvin and Wilson. The double bond resonance has been attributed as a reason to be unusual stability of histamine cobalt chelate.

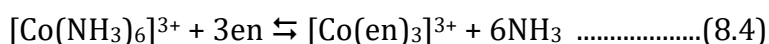
Orbital hybridisation

There are certain factors which serves to make a specific bonding arrangement stable. As an example, the shape of β , β' , β'' triaminotriethylamine is such that the bonding atoms must be grouped tetrahedral round a metal atom. The

ligand will therefore tend to form a stable complex with a metal such as zinc, which favours sp^3 hybridisation in its 4-co-ordinate compounds, rather than with one such as copper which is limited to dsp^2 (planar) hybridisation. Similarly, triethylene tetra amine gives stable complex with metal ions having dsp^2 hybridisation, rather than sp^3 hybridisation.

Chelate Effect and Its Thermodynamic Origin

The chief factor responsible for the stability of the chelate ring is the entropy change which can be viewed statistically or as probability factor. Considering the electronic effect of the donor atom to be the same in the monodentate and the bidentate ligands, it can be seen that the dissociation of a monodentate from a complex will be higher than that in the chelating bidentate. The dissociation of the M-L bond in monodentate will release the ligand completely from the coordination sphere of the metal, so that it can be easily swept off by the solvent. But the dissociation of one M-L bond for the bidentate ligand does not release the ligand completely (for which simultaneous dissociation at both ends is required). Hence the stability constant for metal chelate must be higher. Consider the equilibrium reactions (Fig. 8.4):



Assuming that (i) Co-N bond strength in the two complexes is same (the f value of ammonia and ethylenediamine are within 3%), and (ii) the entropy changes due to structure making and structure breaking are negligible due to the similar size of the complexes, it can be seen that the ΔS° will increase for the reaction as the number of moles of the products are more than those for the reactants. This will help the reaction to go to the right.