PG- I Semester

Inorganic Chemistry

Department of Chemistry

L.S COLLEGE MUZAFFARPUR
B. R. A. BIHAR UNIVERSITY

Dr. Priyanka

TOPIC:- METHODS OF DETERMINATION OF STABILITY CONSTANTS.

METHODS OF DETERMINATION OF STABILITY CONSTANTS.

There are many physical and chemical properties which may be used to detect the formation of complex in solution and to measure the stability constants. The detection of the complexes and the determination of the stability constants are very closely related. Most of the methods used for the detection of complexes can also be used to determine their stability constants.

The study of the complexes is supposed to be incomplete without finding the stability or formation constants, because most of the properties and utility of the complexes depend on it.

The value of stability constants may predict the conditions required for complete formation of a given complex. This knowledge of the system is essential for correctly interpreting its optical and kinetic properties of its partition equilibria and its biological behaviour.

Further, it may also help in planning analytical and separation procedures. For example in case where the species is highly coloured or can be precipitated from solution, extracted into an organic solvent or absorbed on an ion exchange or chromatographic column.

Stability constant is related with the thermodynamic parameters, as

$$-RT, \ln k, = \Delta G = \Delta H - T\Delta S$$

Where, ΔG, ΔH and ΔS are changes of free energy of enthalpy and of entropy respectively.

The stepwise or overall stability constant, thermodynamic equilibrium constant gives the value of free energy change, associated with the reaction. The corresponding changes on entropy change of complex formation may be obtained by combining the stability constants with the enthalpy change of complex formation, which is obtained by determining the stability constant at a series of temperatures. The knowledge of entropy is essential for the full understanding of many factors such as size, shape, electronic structure of the central metal and the ligand, the temperature and the composition of the solvent, which influence the stability of the complex.

Let us consider a reaction between a metal M and ligand L to form a complex MmLn.

$$Mm + nL \rightarrow MmLn$$

$$K = \frac{[Mm\ Ln]}{[M]^m[L]^n}$$

where 'K' is stability constant of the complex MmLn. The stability of the complex is quantitatively expressed in terms of dissociation constant 1/k of the complex. The latter is the tendency of the complex to split up into its components.

Some of the most important methods of determining the stability constants are briefly described here.

pH - Metric Method

Bjerrum's Method

It is a potentiometric method for determining the stability constant for complex formation. Although Bjerrum applied the method primarily to the binding of simple molecules or negative ions to positive metal ions. It may be used with equal success with chelating agents. The theoretical relationship outlined by Bjerrum are not restricted to complex formation but may be applied to any equilibrium process regardless of the nature of the interacting substances. Thus, it has been used with success on acid base, and redox equilibria. Although the reactions to be considered involve ions that are more or less completely hydrated, rather than the simple ions, but this fact does not affect the validity of the conclusions, provided the activity of the water is maintained constant.

Formation or dissociation of a complex ion for molecule in the solution always takes place in several steps, which can be easily determined by measuring pH in this method.

Experimental Determination of Stability Constant by Bjerrum's Method

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

Let us consider the equilibrium in which an acid and metal ions are added to a basic ligand in solution. Thus the following equation are obtained:

$$L + H^+ \xrightarrow{Ka} HL^+, \quad Ka = \frac{[HL^+]}{[L][H^+]}$$

Basic Ligand Acid

$$L + M^+ \xrightarrow{KF} ML^+, \quad KF = [ML^+]\ [L][M^+]$$

Basic Ligand metal ion

Here Ka and KF are the acid association constant of the ligand and formation constant respectively.

Now if CH, Cm and CL are the total amounts in moles/litre of acid (H^+) , metal (m^+) and basic ligand (L), we have

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

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

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

Solving the last three equations given above and using the acid association constant of the ligand, Ka. Then we get

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

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

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

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

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

the value of K_1 can be calculated. For the determination of $[ML^+]$, $[M^+]$ and $[L]$, the values of C_H, C_L, C_m, K_a and $[H^+]$, is generally determined potentiometrically using a P_H meter.

In order to get better results, the ligand must be a medium weak acid or base and the formation constant, K_1, should be within a factor of 10^5 of the value of the acid association constant of the ligand, K_a.

Irving Rossotti Method

Calvin-Bjerrum pH titration technique as adopted by Irving & Rossotti is generally used for determining the proton-ligand and metal-ligand formation constants. The procedure consists of:

(A) Determination of the formation curve of the system. This is expressed as a plot of $\bar{n}$ (formation function) against pL for metal ligand system and a plot of $\bar{n}_A$ against pH for a proton-ligand system (Definitions of the terms $\bar{n}$, $\bar{n}A$ and pL are given below).

(B) The calculation of the values of formation constants by solution of the formation function of the system or otherwise.

(C) The conversion or the stoichiometric constants into thermodynamic constants.

$\bar{n}$ term, was introduced by Bjerrum who called it the 'formation functions' or 'ligand number ' and is defined as the average number of ligand bound per metal atom or ion present in whatever form.

$$\bar{n} = \frac{\textit{Total number of ligand } (L) \textit{bound to metal } (M\ )}{\textit{Total number of M present in system}}$$

or $$\bar{n} = \frac{\sum_{i=o}^{n} .i[MLi]}{\sum_{i=o}^{n} .[MLi]} \quad \text{.....................................(8.5)}$$

which can be written using equation (8.1) as,

$$\bar{n} = \frac{\sum_{i=o}^{n} .i.\beta[L]^{i}}{\sum_{i=o}^{n} .\beta_1 [L]^{i}} \quad [\beta = 1]\text{...............................(8.6)}$$

A similar function for the proton-ligand sustems is $\bar{n}A$, which defined as the average number of protons bound per not complex bound ligand molecule, and can be given by.

$$\bar{n}A = \sum_{i}^{i} .i.\beta^{H}[H]^{i} \qquad \frac{}{i=o} [\beta^{H}$$

$=$ 1]........................(8.7)

i o

$\sum .\beta_{H}[L]$ i

i

$i=o$

whereas, pL gives the free ligand exponent and may be defined as.

$$pL = \log . \frac{1}{[L]}$$

(A) Construction of the Formation Curves:

In Irving Rossotti method, this involves pH-titration of the following three sets of mixtures (keeping total volume constant) against a carbonate free standard alkali:

(a) Mineral acid

(b) Mineral acid + Ligand solution

(c) Mineral acid + Ligand solution + Metal ion solution.

The ionic strength in each set is kept constant by adding appropriate quantities of a neutral electrolyte solution. The temperature of the solution in each case is kept constant. On plotting the observed pH against the volume of alkali, one obtains (a) and acid titration curve, (b) a ligand titration curve and (c) a metal-complex titration curve, corresponding to the above titrations. [Fig. 8.2(a)]

The calculation of $\bar{n}$ are made from the volume of alkali required to produce the same pH value in the metal and ligand titrations. Similarly $\bar{n}$A values are calculated from the volume of alkali required to produce the same pH value in the ligand and mineral acid titrations. According to Irving and Ressotti, $\bar{n}$A and $\bar{n}$ can be expressed as-

$$\bar{n}A = \frac{Y\,TLo - \frac{(V^n - V^1)(N + E^o)}{(V^o + V^1)}}{TL_o} \qquad \text{....................(8.8)}$$

$$\underline{n} = \frac{(V^{iii1} - V^n)(N + E^o) + TL_o}{(V_o + V^1)\ \bar{n}\ .TCM_o} \qquad \text{....................(8.9)}$$

Where V^o is the initial volume of the solution, E^o, TL_o are the initial concentrations of the mineral acid and the reagent respectively and

$V^{'}$, $V^{''}$ and $V^{'''}$ are the volume of alkali of a given normality, N, required during the acid, the ligand and the metal titration respectively at a given pH (B). While the term Y gives the number of titrable hydrogen ions arising from the chelating agent and TM_0 gives the initial concentrations of the metal.

From the observed values of [L] for each n value, values of pL^- are calculated utilising the equation given by Irving and Rossotti:

$$pL^- = \log_{10} \frac{\sum_{n=o}^{n=j} \beta_n^H \left(\frac{1}{\text{anti}\log\beta}\right)^n}{TCL_0 - \bar{n}\,.TCM_0} \cdot \frac{V^0 + V^{iii}}{V^o} \quad \text{....................(8.10)}$$

Values of proton-ligand formation constants, K_1^H, K_2^H etc. obtained from the proton-ligand formation curves plotted between values of $\bar{n}_A$ and pH [Fig. 8.2(b)].

The pH value at $\bar{n}_A = 0.5$ gives the value of $\log K_1^H$ while the pH value at $\bar{n}_A = 1.5$ gives the value of K_2^H and so on.

Similarly, the values of stepwise stability constants of metal-complexes are obtained from the formation curve plotted between the values of n and pL^- [Fig. 8.2(c)].

The value of formation constants are generally refined using least square method.

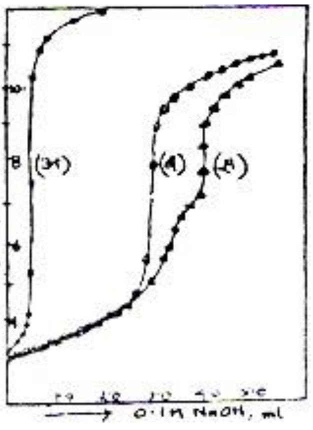
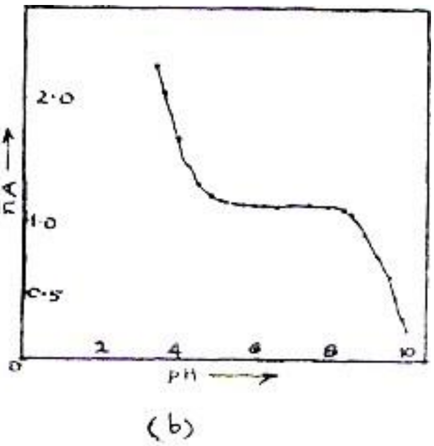
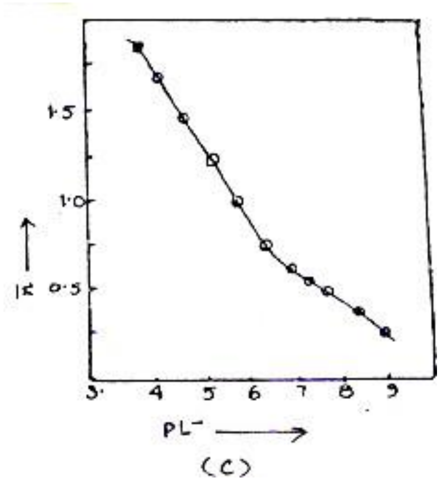


Fig. 8.2: (a) pH - Titration Curves



(b) Proton-Ligand formation curve



(c) Metal-Ligand formation curve

Spectrophotometric Method

1. Job's Method

From the knowledge of stoichiometry of the complex, the value of K (the stability constant) can be determined form the expression given below, if the value of m and n are known:

$$K = \frac{m^{n-1} \times n^{m-1} \times (P-1)^{m+n-1} [n-(m+n)]}{C^{m+n-1} \times P^{n-1} [P(m+n)^{x-1}]^{m+n}}$$

where, K = Stability Constant

1/K = Dissociation Constant of the complex.

P = Ratio of the concentration of the ligand to the concentration of metal.

C_1 = Molar concentration of metal solution.

X = Concentration of ligand for which the concentration of complex is maximum.

m = The number of moles of a metal required to combine with "n" moles of ligand.

for (1:1) Metal ligand ratio in the complex

m = n = 1

$$K = \frac{(P-1)(1-2x)}{C_1 \times [(P+1)(x-1)]^2}$$

Vosburgh and Cooper as well as Katzin and Gebert have extended Job's treatment to systems in which two or more complexes are formed. The ratio of the concentration of metal should not be equal to 1 i.e. non-equimolecular solutions of ligand and metal should be used.

2. Turner Anderson Method

Turner and Anderson have modified Job's method and have successfully used for determination of stability constant. By plotting a continuous variation curve for a given range of compositions and then repeating the procedure for more dilute solutions. If the initial concentrations of the metallic ions and ligands are 'a' and 'b' respectively, then

$$K = \frac{X}{(a-x)(b-x)}$$

where, K = Stability Constant

X = Concentration of the complex

It is assumed that Beer's Law is obeyed, i.e. the optical density of the solution is proportional to the concentration of the complex in the given range. If, therefore, any two solutions on the two curves have the same optical density, as shown in the graph a_1, a_2 and b_1, b_2 represent the concentrations of the metal and the ligand respectively on the two curves, then:

$$K = \frac{X}{(a_1 - x)(b_1 - x)} = \frac{X}{(a_2 - x)(b_2 - x)}$$

Where, the subscripts 1 and 2 refer to the reagent concentrations. Thus K be calculated by solving the equation.

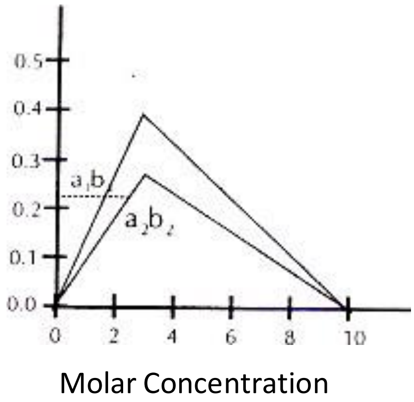


Fig. 8.3 :

Deskin has extended the method to the study of complexes formed in the ration of 1:2, then:

$$M + 2L = ML_2$$

$$K = \frac{X}{(a - x)(b - 2x)^2}$$

Taking the concentration a_1, a_2 and b_1, b_2 for the same absorbance i.e., the same value of x, we have

$$K = \frac{X}{(a_1 - x)(b_1 - 2x)^2} = \frac{X}{(a_2 - x)(b_2 - x)^2}$$

The value of x is determined from the relation

$$4x^2(a_1-a_2+b_1-b_2)-x(4a_1b_1-4a_2b_2+b_1^2-b_2^2)+(a_1b_1^2-a_2b_2^2)=0$$

i.e. $AX^2 + BX + C = 0$

Where, $A = 4(a_1 - a_2 + b_1 - b_2)$

$-B = 4(a_1b_1 - 4a_2b_2 + b_1^2 - b_2^2)$

or $b_1(4a_1 + b_1) - b_2(4a_2 + b_2)$

$C = (a_1b_1^2 - a_2b_2^2)$

By solving the quadratic equation:

$$K = \frac{(-B) + \sqrt{(B^2 - 4AC)}}{2A}$$

$$K = \frac{(-B) + \sqrt{(B^2 - 4AC)}}{2A}$$

By knowing the value of X, the value of K can be calculated. Similarly, if metal and ligand react in the ratio 2:1 then.

$2M + L = M_2L$

Taking the concentration a_1, a_2 and b_1, b_2 for the same absorbance i.e., for the same value of X, we have

$$K = \frac{X}{(a_1 - 2x)^2 (b_1 - x)} = \frac{X}{(a_2 - 2x)^2 (b_2 - 2)}$$

or $4^2(a_1 - a_2 + b_1 - b_2) - (4a_1b_1 - 4a_2b_2 + a_1^2 - a_2^2 + (a_1^2 b - a_2^2 b_2) = 0$

i.e. $AX^2 + BX + C = 0$

Where, $A = 4(a_1 - a_2 + b_1 - b_2)$

$-B = (4(a_1b_1 - 4a_2b_2 + a_1^2 - a_2^2)$

or $b_1(4a_1 + b_1) - b_2(4a_2 + b_2)$

$C = (a_1 b_1 - a_1^2 b_2)$

By solving the quadratic equation, the value of X is determined

$$K = \underline{(-B) + \sqrt{(B^2 - 4AC)}\ 2A}$$

or $X = \underline{(-B) - \sqrt{(B^2 - 4AC)}\ 2A}$

Mushran has modified this method so as to suit for 1:3 complexes.

3. Mole Ratio Method

The you and jones method can also be utilised for determination of the stability constants.

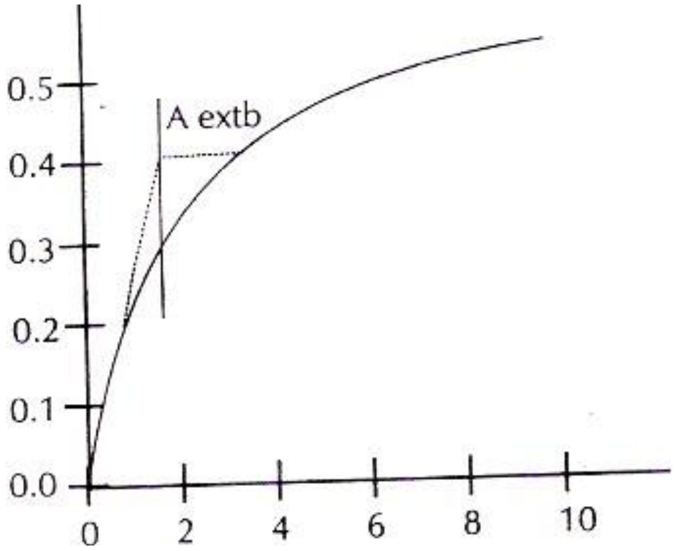


Fig. 8.4

The extrapolated value (A extp.) (fig. 8.4) near the "equivalence point" on the plots correspond to the total absorbance of the complex. If the complex formed is complete. Actually the complex is slightly dissociated in this region, and the absorbance read is somewhat low. The ratio of the true absorbance to the extrapolated absorbance is the mole fraction of the complex actually formed.

$$\frac{A}{Aextp} = \frac{[mx]}{\underline{C}}$$

where $\underline{C}$ is the total analytical concentration (expressed in moles/litre) of the metal or ligand, whichever has the limiting concentration at the point in question. Therefore

$[MX] = A/A\ extp.\ \underline{C}$

$M = Cm - (mx) = Cm\ (A/A\ extp.\ )\ \underline{C}$

$X = Cm - (mx) = Cx - (A/A\ extp.)\ \underline{C}$

Stability constant $K = \frac{[MX]}{[M][X]}$

$$\therefore K = \frac{[(A / A\ \text{extp.})\ \underline{C}]}{[(C_m - A / A\ \text{extp.})\ C\ ][(C_x - A / A\ \text{extp.}) C^{-}\ ]}$$

Where A = Absorbance at the metal ligand ratio.

A extp. = The extrapolated value of Absorbance.

Cm = Concentration of the metal at equivalence point.

Cx = Concentration of the ligand at equivalence point.

$\underline{C}$ = Total analytical concentration of the ligand.

When metal ligand ratio and the ratio shown by extrapolation do not be on the same ordinate, then the value Cx and $\underline{C}$ will not be the same. $\underline{C}$ is calculated at the point of intersection of the extrapolated curve.

4. Raghav Rao's Method

Subbarama Rao and Raghav Rao used job's method of continuous variation and molar ratio method for determination of stability constants. They used equimolar solutions of metal and ligand with optical density as he index property. This method is also known as graphical method.

Reddy and Seshoish used the same graphical method using conductance and optical density as the index property.

Import Question For Revision

(i) Irving-Rossotti method is a modification of.....................method.

(ii) $\bar{n}$ is called......................................and is defined as ....
....

(iii) pL^- = ...

(iv) Formation-curve is a plot between........................and.....................

(v) Turner Anderson method is a modification of .... method used for determination of ....by plotting .... curve for a given range of ....

(vi) The extra plotted value in the mole ratio plot near the equivalence point corresponds to .... the complex.

Revision Metal-Ligand Equilibria in solution

- Stability of complexes in aqueous solutions is related with the thermodynamic aspect, which deals with metal-ligand bond energy and stability constants.
- The formation of ML_n complex in solution is supposed to take place in n steps. In each step one mole of ligand is bound with the metal ion replacing a mole of the coordinated water.
- The equilibrium constants K_1, K_2, K_3, ...K_n for the reaction in each step of the complex formation are known as 'stepwise formation constants' and are related with the 'overall stability or formation constant' βn , i.e. the equilibrium constant for the overall reaction: $M + nL \leftrightarrows ML_n$,

as : $\beta n = K_1, K_2, K_3, \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots K_n$

or $\beta n = \sum_{n=1}^{n=n} K_n$

- The equilibrium constant is related to the thermodynamic expression as follows:

  $- RT \log K = \Delta G = \Delta H - T\Delta S$.

- The factors affecting stability of complexes are mainly related with the metal ion and the ligands.
- The factors due to metal are primarily related with the size of the ion, its charge, possibility of π-bonding and CFSE gained.
- Stability is proportional with the charge and ionic potential (e/r-ratio) but is inversely proportional with the size of the metal ion.
- M→L, π-bonding increases it, while L→M, π-bonding decreases it.
- Similarly higher is the CFSE higher will be the stability.
- a-groups metal form stable complexes with ligands N, O, F doner atoms; while b groups metals give more stable complexes with the ligands, having P, S and Cl donor atoms.
- The Irving Williams order of stability is:

  Mn (II) < Fe (II) < Co(II) < Ni(II) < Cu(II) > Zn(II).

- Factors related with the ligands are mainly basicity, dipole moment and polarizability of ligands, possibility of π-bonding and steric factor.
- Stability is proportional with the basicity, dipole and polarizability of ligands.
- M→L, π -bonding (complexes with the unsaturated ligands) increases the stability.

- Shape of the ligand molecule also affects stability e.g. while triethylene teramine gives complex with metal ions having dsp^2 hybridisation(sq. planar geometry); β , β^{I}, β^{II} triamminotriethylamine gives stable complex with metal ions having sp^3 hybridisation (Tetrahedral geometry).
- Chelates are more stable compared to non chelates.
- Stability increases with the number of rings formed per mole of the ligand e.g.

M(en)	<	M(trien)	<	M(EDTA)
(1 ring)		(2 ring)		(5 ring)

- Higher stability of chelates is mainly related with the entropy factor.
- The stability constants of metal complexes in solution are determined generally using two methods: one the potentiometer (pH) titration method due to Bjerrum and its modification by Irving and Rossotti; and the other one spectrophotometer methods due to job and its modification by Turner-Anderson.
- In Irving Rossotti method stability constants are computed by plotting formation curves, between $\bar{n}$ (the formation function) and pL^-.
- $\bar{n}$ is the average number of ligand bound per metal atom or ion; while pL is the free ligand exponent; $\log \frac{1}{[L]^-}$
- According to half integral method:

  The value of pL^- at 0.5 $\bar{n}$ = Log K_1

  The value of pL^- at 1.5 $\bar{n}$ = Log K_2 and so on.
- The values of stability constants are generally refined by least square method.

- Turner and Anderson method involves plotting a continuous variation curve for a given composition and repeating the procedure for more dilute solutions.