Course Name: **Stability constants of metal complexes and their applications**

Paper Number: **101**

Section: **A**

Course Instructors: **Dr. Sandeep Kaur (Associate Professor)**
Dr. Heena Dahiya (Guest Faculty)
Dr. Sanjay Kumar Saroj (Guest Faculty)

M. Sc. PART I
SEMESTER – I
Paper 101- Inorganic Chemistry-I (Core course 1) (100 Marks/ 4 Credits)
Course A: Stability constants of metal complexes and their applications

Stoichiometric and thermodynamic equilibrium constants, stepwise formation of complexes, formation functions, φ, n and αC and relationship between different functions. Calculation of stability constants. Graphical Methods: using sets of data {φ, [A]}; {αC, [A]} and { n , [A]}.

Curve fitting method, Elimination method, Numerical method, Potentiometric method, Method of corresponding solutions, Ion exchange method, Solvent extraction, Polarographic method and Spectrophotometric methods, which include Job's method of continuous variation, Logarithmic method, Bent and French mole ratio method. Turner and Anderson methods and Yatsimirskiis method.

Analytical applications of complex formation; gravimetric analysis, complexometric titrations (Conditional constants, titration curves, titration error, detection of end point using metal indicators and instrumental methods. Indicator errors, Indicator correction, etc. Simultaneous titrations, stepwise titrations, back titrations). Use of masking and demasking agents in complexometric titrations.

Recommended Texts:

1. Inczedy, J. Analytical applications of complex equilibria Halsted Press: New York, NY (1976).
2. Martell, A. E. & Calvin, M. Chemistry of the Metal Chelate Compounds. Prentice-Hall: N. Y. (1952).
3. Ringbom, A. Complexation in Analytical Chemistry Wiley: New York (1963).
4. Hartley, F. R., Burgess, C. & Alcock, R. M. Solution Equilibria. Prentice-Hall: Europe (1980).
5. Beck, M. T. Chemistry of Complex Equilibria van Nostrand Reinhold: New York (1970)
6. Rossotti, F. J. C. & Rossotti, H. The Determination of Stability Constants McGraw Hill: London (1961).
7. Mendham, J.; Denney, R.C.; Barnes, J. D.; Thomas, M., Vogel’s Textbook of Quantitative Chemical Analysis. Pearson Education Ltd. (2000)

1. Stability constants of metal complexes and their Applications :

Complexes :

Complexation reaction : can be regarded as the exchange of solvent molecules for ligands.

$\mathbf{M(H_2O)_n + L \rightleftharpoons M(H_2O)_{n-1}L + H_2O,}$ where M is the central metal ion and L is the ligand.

In metal complexes, the central ion is a metal ion or possibly a proton. The ligand is an organic or inorganic anion or neutral molecule.

Simple ions occur very rarely as such - only in gaseous phase – because if they are present in solutions, they are always solvated. The number and orientation of the solvent molecules around an ion are determined by the volume and charge density of the ion, and the spatial requirement of the solvent molecules.

Thus during complexation, the solvent molecules surrounding the central ion may be successively exchanged for other ligand ions or molecules.

$\mathbf{M(H_2O)_n + n\,L \rightleftharpoons ML_n + n\,H_2O,}$

n = number of ligands in the complex which is equal to the coordination number if the ligand is bound to the central ion at one site.

The charge of the complex formed may differ from that of the original solvated ion. The sign and magnitude of the charge of the complex formed are given by the algebraic sum of the charges of the ions constituting the complex.

For eg : $[Cu(NH_3)_4]^{2+} \equiv +2 + (4x0) = +2$

$[Fe(CN)_6]^{3-} \equiv +3 + (6 \text{ x } -1) = -3$

$[ZnCl_2(H_2O)_2]^0 \equiv +2 + (2 \text{ x } -1) + 2 \text{ x } 0 = 0$

2. Complex formation Equilibria :

The formation of the metal complexes can be represented by the following general reaction :

$mM + nL \rightleftharpoons M_mL_n$

The thermodynamic equilibrium constant of the reaction is :

$$\beta_t = \frac{\mathbf{a}_{M_mL_n}}{\mathbf{a}_M^m \ \mathbf{a}_L^n} \quad \text{(P, T = constant)}$$

where a = activities of the species.--------------- **Eqn. 1**

And these can be expressed as the product of concentrations and activity coefficients, therefore,

$$\beta_t = \frac{[M_mL_n]}{[M]^m \ [L]^n} \bullet \frac{\mathbf{f}_{M_mL_n}}{\mathbf{f}_M^m \ \mathbf{f}_L^n}$$

where square brackets denote the concentration in mole/L and '**f**' is the activity coefficient. When ionic strength, I = 0, the activity coefficient is equal to unity. Therefore,

$$\beta_{M_mL_n} = \frac{[M_mL_n]}{[M]^m \ [L]^n} \quad \text{(P, T, I = constant)}$$

<u>This is known as thermodynamic equilibrium constant or stoichiometric equilibrium constant.</u>

According to Debye - Huckel theory, the activity coefficients in dilute solutions depend only on the ionic strength and Ionic strength of a solution is a measure of the concentration of ions in that solution.

$I = \frac{1}{2}\sum_{i=1}^{n} CiZi^2$, where c = concentration of the individual ions in solution in mole/L and z = charge

When I = 0, a = 1. The average activity coefficients do not change much in the range of ionic strength from 0.1 to 0.5 and can be considered as practically constant, as

$$-\log f_{z\pm} = Az^2\left[\frac{\sqrt{I}}{1+\sqrt{I}}\right] - 0.2\ I,$$ **Davies equation**

<u>Equilibria of mononuclear complexes :</u>

The complexes are usually formed in a stepwise manner,

$M + L \rightleftharpoons ML$ ……………….**A**

$ML + L \rightleftharpoons ML_2$ ……………… **B**

ML_{n-1} + L $\rightleftharpoons$ ML_n ……………… **C**

The successive stability constants characterizing the formation of the different species are as follows :

$K_1 = \frac{[ML]}{[M][L]}$ $K_2 = \frac{[ML2]}{[ML][L]}$ ……………………..

$K_n = \frac{[MLn]}{[MLn-1][L]^n}$

Therefore, $[ML] = K_1[M][L]$

$[ML_2] = K_2[ML][L] = K_1K_2[M][L]$ …………… and $[ML_{n-1}] = K_1K_2 \ldots K_n [M][L]^n$

Now, $\beta_1 = K_1$, $\beta_2 = K_1K_2$, ……………. $\beta_n = K_1K_2 \ldots K_n$

or $\beta_n = \prod_{i=1}^{n} K_i$

In general, the value of the first stability constant is largest and the values of successive stability constants decrease.

In solutions in which various species are present simultaneously in amounts which depend upon the K values, in these cases, the amounts of the particular species can be calculated if all the stability constants and the total metal ion, ligand and hydrogen ion concentrations are known, or conversely, the stability constants can be calculated if the composition of the system can be determined.

That is why, the relationships between the constants (K or β) and quantities measurable by analytical methods ([L], n, etc) are very important.

Average ligand number (suggested by Niels Bjerrrum**)** = This gives the degree of complex formation. It is the mean number of ligands bound to one metal ion, i.e.

$\overline{n} = \frac{C_L - [L]}{C_M} = \frac{Total\ bound\ ligand}{Total\ metal}$, for unidentate ligands, $\overline{n}$ (characteristic of the extent of complexation) gives the average coordination number

C_L = Total ligand concentration

C_M = Total metal concentration

For the complexation reactions shown in page 2, K_1, K_2…..K_n are known as shown in page 3.

Total concentration of ligand or metal, whether it is complexed or not is given as below :

$$C_L = [L] + [ML] + 2[ML_2] + \ldots\ldots + n[ML_n]$$

$$= [L] + \beta_1[M][L] + 2\beta_2[M][L]^2 + \ldots\ldots + n\beta_n[M][L]^n$$

$$= [L] + [M]\sum_{i=1}^{N} i\beta_i[L]^i$$

$$C_M = [M] + [ML] + [ML_2] + \ldots\ldots + [ML_n]$$

$$= [M] + K_1[M][L] + K_1K_2[M][L]^2 + \ldots\ldots + K_1 K_2 \ldots\ldots K_n[M][L]^n$$

$$= [M] + \beta_1[M][L] + \beta_2[M][L]^2 + \ldots\ldots + \beta_n[M][L]^n$$

$$= [M]\{1 + \sum_{i=1}^{N} \beta_i[L]^i\}$$

Hence, $$\overline{n} = \frac{[L]+[M]\sum_{i=1}^{N} i\beta_i[L]^i-[L]}{[M]\{1+\sum_{i=1}^{N}\beta_i[L]^i\}}$$

$$= \frac{[M]\sum_{i=1}^{N} i\beta_i[L]^i}{[M]\{1+\sum_{i=1}^{N}\beta_i[L]^i\}}$$

$$= \frac{\sum_{i=1}^{N} i\beta_i[L]^i}{\{1+\sum_{i=1}^{N}\beta_i[L]^i\}} \qquad \text{If } \beta_0 = 1 = \frac{[M]}{[M][L]^0} \qquad \text{, then } \overline{n} = \frac{\sum_{i=1}^{N} i\beta_i[L]^i}{\sum_{i=0}^{N}\beta_i[L]^i\}}$$

The last equation is the **complex formation function**. The equation shows that average ligand number depends only on the concentration of the free ligand and is independent of that of the metal ion.

If the concentrations of the ligand and the overall stability constants are known, average ligand number can be calculated using the complex formation function.

When the total concentration of the ligand is much higher than that of the metal ion, i.e., $C_L >> C_M$ and the ligand is not involved in reactions other than the complex formation, then $[L] \approx C_L$, i.e. , the total ligand concentration can be used instead of the free ligand concentration.

Mole fraction of the ith complex species in solution is given by :

$$\Phi_i = \frac{[ML_i]}{C_M} = \frac{\beta_i[M][L]^i}{[M]+\beta_1[M][L]+\beta_2[M][L]^2+ \ldots\ldots\ldots + \beta_n[M][L]^n} = \frac{\beta_i[L]^i}{1+\beta_1[L]+\beta_2[L]^2+ \ldots\ldots\ldots + \beta_n[L]^n}$$

$$= \frac{\beta_i[L]^i}{1+\sum_{i=1}^{N}\beta_i[L]^i} = \frac{\beta_i[L]^i}{\sum_{i=0}^{N}\beta_i[L]^i} \qquad \text{, as } \beta_0 = 1$$

Similarly, mole fraction of the free metal ion or degree of complex formation is given by :

$$\Phi_0 = \frac{[M]}{C_M} = \frac{Free\ metal\ ion\ concn}{Total\ metal\ ion\ concn} = \frac{[M]}{[M]+\beta_1[M][L]+\beta_2[M][L]^2+ \text{……….} + \beta_n[M][L]^n}$$

$$= \frac{1}{1+\beta_1[L]+\beta_2[L]^2+ \text{……….}+ \beta_n[L]^n} = \frac{1}{1+\sum_{i=1}^{N}\beta_i[L]^i} = \frac{1}{\sum_{i=0}^{N}\beta_i[L]^i}\ \text{, as } \beta_0 = 1$$

Hence, Φ_i and Φ_0 depend on concentration of ligand i.e., [L].

$$\Phi_i = \Phi_0\beta_i[L]^i \quad , \quad \frac{\emptyset_i}{\emptyset_0} = \beta_i[L]^i$$

$$\bar{n} = \frac{\sum_{i=1}^{N} i\beta_i[L]^i}{\{1+\sum_{i=1}^{N}\beta_i[L]^i\}} = \frac{\sum_{i=1}^{N} i\beta_i[L]^i}{\sum_{i=0}^{N}\beta_i[L]^i} = \Phi_0\sum_{i=1}^{N} i\beta_i[L]^i = \Phi_0\sum_{i=1}^{N} i\,\frac{\emptyset_i}{\emptyset_0}$$

$$= \sum_{i=1}^{N} i\,\emptyset_i$$

Also from definition of mole fractions, $\Phi_0 + \Phi_1 + \Phi_2 + \Phi_3 + \ldots.. + \Phi_N = \sum_{i=0}^{N}\emptyset_i = 1$

Therefore, $\bar{n} = \sum_{i=0}^{N} i\,\emptyset_i$

The mole fraction multiplied by 100 gives the amount of the species as a percentage of the total metal ion concentration.

If L and Y are two ligands, and β and γ are the corresponding overall stability constants, then :

$$\Phi_i = \frac{\beta_i[L]^i}{1+\beta_1[L]+\beta_2[L]^2+ \text{………}\gamma_1[Y]+\gamma_2[Y]^2}$$

3. CONDITIONAL EQUILIBRIUM CONSTANTS :

- The dependence of the stability constants of the complexes on the ionic strength is already known.
- It is very rare that the metal ions and the ligands which are involved in the complexation reaction are the only species present in the system.
- The constituents of the complex may also take part in equilibrium reactions with other species present in the system. This may also include the ions which are produced by the solvent.

- The ligand may be protonated and it may also be competed for by other metal ions present in the solution, if any. Therefore, the real concentration of the free ligand may differ in solutions of the same total ligand concn.
- Similarly, the real concn of the free metal ion may differ in solutions of the same total metal concn. This is because the metal ion may interact with other complexing ligands present, including hydroxide ions.
- Therefore, comes into picture, the name <u>**Conditional constant**</u>. It expresses the notion of the term which can be assumed as constant only under given conditions of concentration and pH. The general form of <u>**the overall conditional stability constant**</u> for a mononuclear complex is :

  $\beta'_n = \frac{[ML_n]}{[M'][L']^n}$, where [M′] is the apparent free metal ion concn, which means the concn of metal ion that has not reacted with complexant L and similarly, [L′] s the apparent ligand concn i.e., the concn of the ligand not bound to the central ion M. This may include the ocncn of the ligand whether L is in protonated or non-protonated form, or in the form of complexes with other metal ions.

<u>**Relationship between the apparent and free metal ion concn :**</u>

Let Y be the interfering complexant which reduces the free metal ion concn. Therefore,

$$\frac{[M']}{[M]} = \frac{[M] + [MY] + [MY_2] + \ldots\ldots\ldots}{[M]}$$

By the use of the overall stability constant, γ_n of the complexes formed in the side reaction, the above equation can be written as :

$$M + Y \rightleftharpoons MY, \qquad \gamma_1 = \frac{[MY]}{[M][Y]} \qquad \text{Hence,} \quad [MY] = \gamma_1[M][Y]$$

$$\frac{[M']}{[M]} = \frac{[M] + \gamma_1[M][Y] + \gamma_2[M][Y]^2 + \ldots\ldots\ldots}{[M]} = \frac{1 + \gamma_1[Y] + \gamma_2[Y]^2 + \ldots\ldots\ldots}{1} = \alpha_{M(Y)}$$

The quantity $\alpha_{M(Y)}$ is called the <u>**side reaction coefficient or α– coefficient**</u> for M reacting with Y. From the above relation $\alpha_{M(Y)}$ can be calculated.

In the same way, the ratio $\frac{[L']}{[L]}$ can be calculated for the side reaction of ligand, L with B :

$$\frac{[L']}{[L]} = \frac{[L] + [LB] + [LB_2] + \ldots\ldots\ldots}{[L]}$$

$$\frac{[L']}{[L]} = \frac{[L] + \gamma_1[L][B] + \gamma_2[L][B]^2 + \ldots\ldots\ldots}{[L]} = \frac{1 + \gamma_1[B] + \gamma_2[B]^2 + \ldots\ldots\ldots}{1} = \alpha_{L(B)}$$

The side reaction of the ligand is mostly protonation. Therefore, in such cases, $\alpha_{L(H)}$ is given by means of the protonation constants : $\alpha_{L(H)} = 1 + K_1[H^+] + K_1K_2[H^+]^2 + \ldots\ldots$

Now, putting the values of [M′] and [L′] in the equation given below :

$$\frac{[M']}{[M]} = \alpha_{M(Y)} \quad \text{and} \quad \frac{[L']}{[L]} = \alpha_{L(B)}$$

$$\beta'_n = \frac{[ML_n]}{[M'][L']^n} = \frac{[ML_n]}{[M][L]^n \alpha_{M(Y)} \alpha^n{}_{L(B)}} = \frac{\beta^n}{\alpha_{M(Y)} \alpha^n{}_{L(B)}}$$

Taking log on both sides,

$$\log \beta'_n = \log \beta_n - \log \alpha_{M(Y)} - n \log \alpha_{L(B)}$$

If M and L are involved in more than one side reaction, the α values are summed to give an overall value :

$\alpha_M = \alpha_{M(Y)} + \alpha_{M(X)} + \ldots\ldots - (i-1)$ and

$\alpha_L = \alpha_{L(B)} + \alpha_{L(H)} + \ldots\ldots - (i-1)$ where **i** is the number of side reactions

The correction − (i−1) is necessary since all α functions involve 1, representing free M or free L. In practice one or two α terms predominate, therefore, − (i−1) can often be neglected including the other α terms.

The complex itself may undergo side-reactions, for eg,

(i) Formation of protonated complexes

(ii) Formation of mixed ligand complexes

Therefore, in these cases an appropriate α-coefficient is calculated and inserted in the numerator of the equation calculated for β'_n.

The α-functions are the reciprocal values of the partial mole fractions of the free metal ion and free ligand, as this refers to the amount which does not take part in the main reaction.

$$\alpha_M = \frac{1}{\emptyset'_M} \quad \text{and} \quad \alpha_L = \frac{1}{\emptyset'_L}$$

If no side reactions are involved, the value of the α-function is 1. In such cases, $\frac{[M']}{[M]} = 1$, therefore, $[M'] = [M]$ and similarly, $\frac{[L']}{[L]} = 1$, hence, $[L'] = [L]$.

The importance of conditional constants is that they can be applied in calculations like true constants, to yield answers that refer to particular conditions.

Role of hydrogen ion concn in complex formation :

The hydrogen ion concn plays an important part in complex formation. This is because ligands are usually strong **Bronsted Bases** and hence are easily protonated, and hence the free ligand concn depends on pH.

In the presence of metal ion which forms mononuclear complexes, the total ligand concn is given by the following equation :

$$C_L = [L] + \beta_1[M][L] + 2\,\beta_2[M][L]^2 + \ldots\ldots\ldots + K'_1\,[H][L] + K'_1K'_2\,[H]^2[L] + \ldots\ldots$$

$$= [M]\sum_{i=1}^{N} i\beta_i[L]^i + [L]\alpha_{L(H)} \text{ ------------------------------} \textbf{Eqn 1}$$

In the absence of complexing metal ions,

$C_L = [L]\alpha_{L(H)}$ or $[L] = \frac{C_L}{\alpha_{L(H)}}$

Also if $C_L >> C_M$, the first term on the right hand side may be neglected in the **Equation 1**, above, hence, $C_L = [L]\alpha_{L(H)}$

Taking log on both sides : **$\log [L] = \log C_L - \log \alpha_{L(H)}$**

The amount of ligand bound in the complex is given by the first term on the right hand side of **Eqn 1** and if we divide this by the total metal ion concn, it gives the average number of ligands bound by one metal ion :

$$C_L = [M] \sum_{i=1}^{N} i\beta_i [L]^i + [L]\alpha_{L(H)}$$

or, $C_L - [L]\alpha_{L(H)} = [M] \sum_{i=1}^{N} i\beta_i [L]^i$

or $\overline{n} = \dfrac{C_L - [L]\alpha_{L(H)}}{C_M} = \dfrac{[M] \sum_{i=1}^{N} i\beta_i [L]^i}{C_M}$ because $\overline{n} = \dfrac{C_L - [L]}{C_M}$

$$= \frac{[M] \sum_{i=1}^{N} i\beta_i [L]^i}{[M]\{1 + \sum_{i=1}^{N} \beta_i [L]^i\}} = \frac{\sum_{i=1}^{N} i\beta_i [L]^i}{\{1 + \sum_{i=1}^{N} \beta_i [L]^i\}}$$

Thus the normal equation for $\overline{n}$, is modified in this way if protonation of the ligand is to be taken into account.

Another example :

Another pH dependent phenomenon to be considered when dealing with aqueous solutions is the formation of hydroxo-complexes, which is another side reaction of the metal ion, and has to be taken into account when calculating conditional equilibrium constants. Hydroxo complexes are formed by dissociation of protons from the corresponding aquo-complexes.

$$[Fe(H_2O)_6]^{3+} \overset{\mathbf{k_1}}{\rightleftharpoons} [Fe(H_2O)_5OH]^{2+} + H^+$$

$$[Fe(H_2O)_5OH]^{2+} \overset{\mathbf{k_2}}{\rightleftharpoons} [Fe(H_2O)_4OH]^{+} + H^+$$

In cases where only the formation of mononuclear complexes is to be considered, the hydroxo-complex formation can be taken into account simply by using the **α − function** in equilibrium calculations.

The pH below which practically no hydroxo-complexes are formed depends on the stability constant of the hydroxo-complex first formed, since the first stability constant is usually the greatest.

For the function, $\alpha_{M(OH)} = 1 + \beta_1[OH] + \ldots..$ to be smaller than 1.01, the second term must be smaller than 10^{-2}. Therefore,

$\log \beta_1 + \log [OH^-] \leq -2$

$\log \beta_1 + \log [H^+] + \log [OH^-] \leq -2 + \log [H^+]$

$\log \beta_1 - 14 \leq -2 - pH$

$\mathbf{pH \leq 14 - 2 - \log \beta_1}$

Determination of the stability constants of Mononuclear Complexes :

In the case of mononuclear complexes, correlations exist between the concentrations C_L, C_M, [L], [M], $[ML_n]$, etc, the average ligand number $\bar{n}$, and the mole fractions $\emptyset_i$, and it is possible to establish the relationship between two variables experimentally for the determination of stability constants.

The methods available for determining stability constants are mainly based on the preparation of a series of solutions containing known amounts of complex-forming components in which the concentration of one component is gradually varied and the concn of one of the reactant or products is followed directly or indirectly by a suitable analytical method.

Usually the concentration of the metal ion is kept constant and that of the ligand varies within wide limits.

The most suitable analytical methods are those which do not disturb the equilibria existing in solution and by which low concentrations can be selectively determined with high accuracy.

Instrumental methods of analysis are based on the measurement of an intensive physico-chemical property which is proportional to the concn of a substance.

In the investigation of complex formation which is stepwise, where several species are present in the solution, it is very important to have a selective analytical method by which the concn of a single species can be determined in presence of others, independently of the composition of the solution. **Such as by Potentiometry or ion-exchange method, etc.**

POTENTIOMETRIC METHODS :

From these methods, the activity of the free metal and of the free ligand can be directly determined.

Direct methods : (A) Measurement of free metal ion concn :

A series of solutions is prepared in which the total concn of the metal ion is constant and the ligand concn gradually increases.

Usually in order to make the stability constants calculated from analytical concentrations unambiguous, the ionic strength should be the same in each solution. Hence, in general the concn of the complex forming substances should be low and a large concn of inert electrolyte should be present to ensure constant ionic strength.

Therefore, in potentiometric method also, the constant ionic strength is ensured by adding an inert electrolyte to each of the solutions.

If the potential of a reversible M^{z+}/M electrode is measured in a solution of concn, C_M in the absence and presence of complexing agent :

Cell is :

Reference electrode	**C_L, C_M constant ionic strength**	**Metal electrode M^{z+} / M**

In the complexed state, when more complex species are formed, the free metal ion concn is calculated from the following expression :

$$\frac{C_M}{[M]} = \{[M] + \beta_1[M][L] + \beta_2[M][L]^2 + \ldots\ldots + \beta_N[M][L]^N\} / [M]$$

$$= 1 + \sum_{i=1}^{N} \beta_i [L]^i = A_{M(L)}$$

The function $A_{M(L)}$ obtained is the reciprocal of the function, ∅ (mole fraction) for the free metal ion. Therefore, $[M] = \frac{C_M}{A_{M(L)}}$

Now for the two conditions, the **Emf equation** can be written as :

1. When no complexing agent is present : $[M] = C_M$

$$E_1 = E^0_M + \frac{0.059}{n} \log a_M$$

$$E_1 = E^0_M + \frac{0.059}{n} \log [M] f_M$$

$$E_1 = E^0_M + \frac{0.059}{n} \log C_M f_M$$, where f_M is activity coefficient

2. When complexing agent is present: $[M] = \frac{C_M}{A_{M(L)}}$

$$E_2 = E^0_M + \frac{0.059}{n} \log \frac{C_M f_M}{A_{M(L)}}$$

The difference between 1 and 2 is :

$$E_1 - E_2 = \Delta E = E^0_M - E^0_M + \frac{0.059}{n} \log C_M f_M - \frac{0.059}{n} \log \frac{C_M f_M}{A_{M(L)}}$$

$$\Delta E = \frac{0.059}{n} \log A_{M(L)}$$

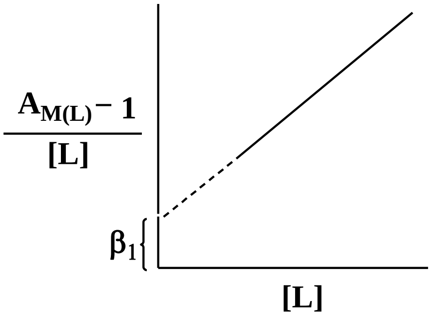
<u>Calculation of complex products from related ligand concn and $A_{M(L)}$ data.</u> This can be done by using the above equation in graphical method of calculation : (as shown by **Leden**). Also known as **elimination method**.

The principle is as follows :

$$\frac{A_{M(L)}-1}{[L]} = \frac{\frac{C_M}{[M]}-1}{[L]} = \frac{1 + \sum_{i=1}^{N} \beta_i [\mathrm{L}]^i - 1}{[L]} = \{\beta_1[L] + \beta_2[L]^2 + \ldots\ldots + \beta_N[L]^N\} / [L]$$

$$\frac{A_{M(L)}-1}{[L]} = \beta_1 + \beta_2[L] + \ldots\ldots + \beta_N[L]^{N-1}$$

Plotting, $\frac{A_{M(L)}-1}{[L]}$ vs [L], we get β_1 from intercept (after extrapolation)

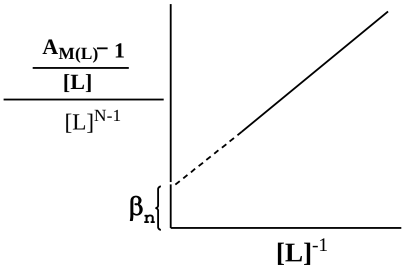


Again, $\frac{\frac{A_{M(L)}-1}{[L]} - \beta_1}{[L]} = \beta_2 + \beta_3[L] + \ldots\ldots + \beta_N[L]^{N-2}$

Plotting, $\frac{\frac{A_{M(L)}-1}{[L]} - \beta_1}{[L]}$ vs [L], we get β_2 from intercept (after extrapolation). Similarly for β_N.

$$\frac{\frac{A_{M(L)}-1}{[L]}}{L^{N-1}} = \beta_1[L]^{1-N} + \beta_2[L]^{2-N} + \ldots\ldots + \beta_N$$

$$= \beta_N + \beta_{N-1}[L]^{-1} + \ldots\ldots + \beta_1[L]^{1-N}$$



If only one complex species is formed, i.e., ML_n,

$M + nL \rightleftarrows [MLn]$ β_n is the stability constant for this reaction

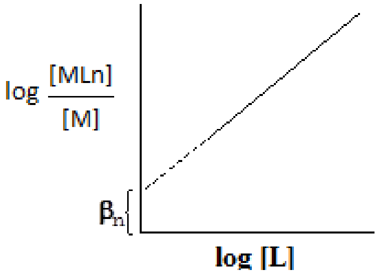
Hence, the overall complex formation constant can be calculated using the equation :

$\beta_n = \frac{[ML_n]}{[M][L]^n}$ as $[ML_n] = C_M - [M]$ and $[L] = C_L - n[ML_n]$

Taking log on both sides, $\log \beta_n = \log \frac{[ML_n]}{[M]} - n \log [L]$

$\log \frac{[ML_n]}{[M]} = n \log [L] + \log \beta_n$

Plotting $\log \frac{[ML_n]}{[M]}$ versus log [L] will give a slope = n and intercept = log β_n, from which one can obtain β_n.



(B). <u>Determination of free ligand concn :</u>

A series of solutions is prepared in which the total concn of the central metal ion is the same but the concn of the ligand is varied within wide limits.

The concn of the free ligand is determined potentiometrically in each solution by using ion-specific electrode.

The average ligand number is calculated for each solution using the following equation :

$$\bar{n} = \frac{C_L - [L]}{C_M}$$

From the calculated $\bar{n}$, and related [L] data, the overall stability constants are determined by using the following equation :

$$\bar{n} = = \frac{\sum_{i=1}^{N} i\beta_i [L]^i}{\{1 + \sum_{i=1}^{N} \beta_i [L]^i\}}$$

Ion-specific electrodes used are silver-silver halide electrodes, Calomel is the reference electrode.

SPECTROPHOTOMETRIC METHODS :

The optical properties of solutions containing complexes differ from those of the constituted ions or molecules. The change in the optical behaviour is closely related to the formation of coordinated bonds. Thus analytical methods based on the measurement of light absorption can be used to study complex equilibria. And the determination is done at an appropriate choice of the wavelength. The basis of this is the **Beer-Lambert law**.

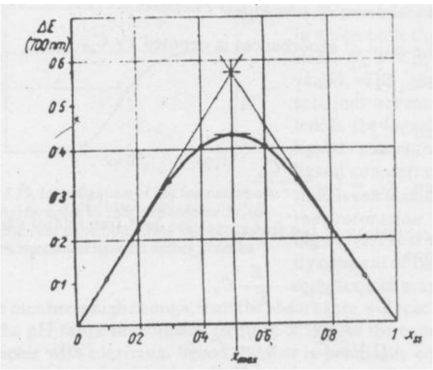
(A). <u>Method of Continuous Variation :</u> This is also known as Job's method.

The principle is : Mole ratio of metal ion and ligand is varied between 0 and 1 at constant total concn which is $C = C_L + C_M$ and the absorbance of the solutions of different composition is measured.

The absorbances are then plotted against the mole fraction, x_L of the ligand. If only one species, i.e, ML_n is formed, then : $n = \frac{x_{max}}{1 - x_{max}}$

Where the absorbance is measured at a wavelength where neither the metal ion nor the ligand but only the complex absorbs. Here, **n** can be calculated from the abscissa of the maximum of the curve i.e., x_{max}

The stability constant can also be calculated from the curve by drawing tangents to the initial and final points of the curve. The points on the tangents drawn to the first part of the curve are proportional to the concn of complex equivalent to the total ligand concn as the complex formation is limited by ligand concn.



The points on the tangent drawn to the last part of the curve give the absorbances which would be measured if the metal were completely present in the form of the complex.

The ratio of the observed absorbance to that indicated by the tangent, for the same value of x, is equal to the mole-fraction of the metal ion in the complex, when $x > x_{\max}$.

Therefore,

$\frac{A}{A_{ex}} = \frac{[ML_n]}{C_M} = \emptyset_n \; or \; \emptyset_i$ -------------------- **1** and **[ex----stands for extrapolated]**

the mole fraction of the ligand in the complex when $x < x_{\max}$

$\frac{A}{A_{ex}} = \frac{n[ML_n]}{C_L}$ …………………….. **2**

The concn of the complex species can be expressed as follows from the above two equations :

From equation **1**, $[ML_n] = \frac{A}{A_{ex}} \times C_M$

From equation **2**, $[ML_n] = \frac{A}{A_{ex}} \times \frac{C_L}{n}$

Hence, $C_M = \frac{C_L}{n} = C_x$

If multiplier of the ratio of absorbances is denoted by C_x :

If $x > x_{\max}$ then $C_x = C_M$

If $x < x_{\max}$ then $C_x = \frac{C_L}{n}$

If $x = x_{\max}$ then $C_x = C_M = \frac{C_L}{n}$

From these equations the concn of the free metal ion and free ligand can be expressed as follows:

$$[M] = C_M - \frac{A}{A_{ex}} C_x$$

$$[L] = C_L - n\frac{A}{A_{ex}} C_x$$

The overall stability constant is given by :

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

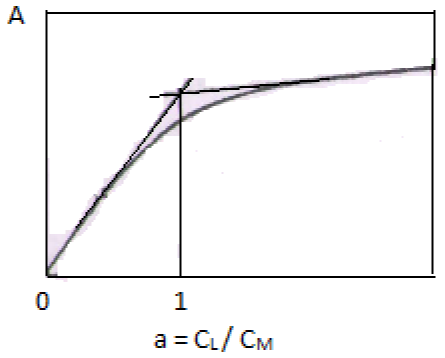
$$= \frac{\frac{A}{A_{ex}} C_x}{\left[C_M - \frac{A}{A_{ex}} C_x\right][C_L - n\frac{A}{A_{ex}} C_x]^n}$$

The absorption spectrum of the complex is used to choose the optimum wavelength, where the absorption of the complex is high and also where a small shift in the wavelength does not cause an appreciable change in the absorbance.

(B). Mole - Ratio Method :

The principle of the method is that a series of solutions is prepared in which the concn of one complex (usually C_M) is kept constant and that of the other varied. The absorbances of solutions is measured at a suitable wavelength and plotted versus the ratio of the variable and constant concns, i.e., the ratio of the concn of $\frac{C_L}{C_M} = a$.

If only one stable complex is formed, which has selective light absorption, then the absorbance increases approximately linearly with the mole-ratio and then becomes constant. The abscissa of the point of intersection of the two tangents gives the number of ligands in the complex, if it was the ligand concn that was varied.



The stability constant can be calculated from the coordinates of the points of the straight lines and the curve in a similar way as in the case of the method of continuous variation. For the formation of ML complex, $\emptyset_{ML} = \frac{[ML]}{C_M} = \frac{[ML]}{C_x} = \frac{A}{A_{ex}}$

$$K_{ML} = \frac{\frac{A}{A_{ex}} C_x}{\left[C_M - \frac{A}{A_{ex}} C_x\right]\left[C_L - \frac{A}{A_{ex}} C_x\right]}$$

Before, the intersection, $C_x = C_L$ and after that $C_x = C_M$. **Conditions : similar to those in the case of method of continuous variation.**

If the stability of the complex is greater, peak is sharper, hence, tangents can be drawn easily and if the stability of the complex is less, drawing of the tangents becomes uncertain.

If the free metal ion or ligand also absorbs at the same wavelength chosen, then the absorbance due to the metal or ligand has to be subtracted from the absorbance measured, and the difference in absorbances is plotted as the ordinate.

Conditions for the applicability of this method :

1. It is the most widely used method, but if the stability constant is small or very large, or n is greater than 3, the evaluation is uncertain.
2. The method cannot be used when more than one complex is formed simultaneously.
3. Metal and ligand should not react with the other constituents present in the solution.
4. As the majority of the ligands are weak bases, the commonest side reaction is protonation of the ligand. Therefore, if the protonated form of the ligand is to be taken into account in the case of aqueous solutions the pH must be kept constant by using buffer solutions during the experiments and therefore, the free ligand concn and the stability constant will be conditional

which is $\beta_n = \beta'_n \alpha^n_{L(H)}$, if $\alpha_{L(H)}$ has been calculated from the pH used in all the experiments and from the protonation constants.

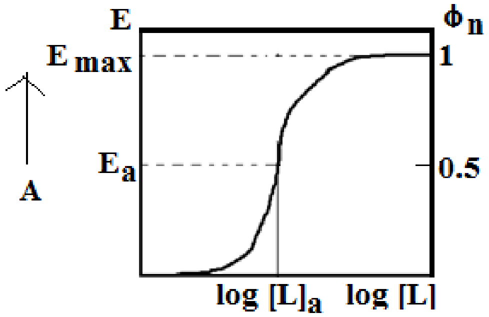
5. Similarly, possible side-reactions of the metal (formation of hydroxides or complexes with buffer components) have to be taken into account if the position of the equilibrium is not to shift during the experiments.
6. Validity of the Beer-Lambert's law is a basic condition for the applicability of the method, it is advisable to use low concn of complex forming constituents.
7. To ensure constant ionic strength, an inert electrolyte is added in a concn greater than that of the complexing constituents.

Bjerrum′s Method : Graphical method

(Inczedy : Page 141- Page 143)

This method can be used in the case of successive complex formation, if the ligands tend to protonate (and the protonation constants are known) and the complex with maximum number of ligands has selective light absorption at the wavelength chosen. When determining stability constants, it is necessary to know the composition of the complex species formed.

A series of solutions is prepared in which both C_M and C_L are constant, $C_L >> C_M$ but the pH is varied. The absorbances of the solutions are measured and plotted vs the logarithm of the free ligand concn.



The free ligand concn is calculated from the pH and the protonation constants by using the following equation : $[L] = \frac{C_L}{\alpha_{L(H)}}$ or $\log [L] = \log C_L - \log \alpha_{L(H)}$

If the overall stability constant of the light absorbing complex with maximum coordination number is high enough, then the absorbance will reach a limiting value in the pH range investigated (see figure above).

As the concn of the complex with maximum ligand number is practically equal to C_M when the limiting value is reached, the mole-fraction $\emptyset_N$ can be calculated at any point of the curve by dividing the actual absorbance by the maximum absorbance, i.e.,

$$\emptyset_N = \frac{[ML_N]}{C_M} = \frac{E_a}{E_{max}}$$

From the values [L] and $\emptyset_N$, stability constants can be calculated by using the **Sillén's** curve – fitting method or by using the following equation : $\emptyset_i = \frac{\beta_i [L]^i}{1 + \sum_1^N \beta_i [L]^i}$ --------- 1

If N = 1 (complex ML), then **eqn 1** above can be written as, $\emptyset_1 = \frac{\beta_1 [L]}{1 + \beta_1 [L]}$

$$\emptyset_1 + \emptyset_1 \beta_1 [L] = \beta_1 [L] \qquad \emptyset_1 = \beta_1 [L] - \emptyset_1 \beta_1 [L]$$

$$\frac{\emptyset_1}{1 - \emptyset_1} = \beta_1 [L] \qquad \log\left(\frac{\emptyset_1}{1 - \emptyset_1}\right) = \log \beta_1 + \log[L]$$

Plotting the left hand side of the above equation against log [L] gives a straight line, the intercept of which is log β_1.

A great advantage of studies made by changing the pH is that the free ligand concn can be changed sensitively over a wide range without changing the ionic strength appreciably.The drawback of this method is that above pH 7, the results may be falsified by competing formation of metal-hydroxo complexes.

The conditions for the applicability of the method are :

The maximum ligand number should not be greater than 2 (or 3) and only the complex species with maximum coordination number should have appreciable absorption at the wavelength chosen.

If N = 1, another light – absorbing constituent is permissible.

The value of β_N has to be high enough for E_{max} to be reached in the pH range investigated but not so high that the metal ion is present in the form of ML_N even in acid solution (pH < 3).

The first protonation constant should be large and the metal ion should not be involved in any side reaction in the pH range studied.

The practical directions given for determination of protonation constants and application of the method of continuous variation apply.

The complete series of measurements can be made on one solution of known composition by adding to it small protions of standard alkali solution from a burette, and measuring the pH and absorbance of the solution simultaneously. It is important that the dilution of the solution during the measurements is negligible or can be corrected for (without causing further other errors).