CHAPTER II

DETERMINATION OF STABILITY CONSTANTS
CHAPTER - II

A. DETERMINATION OF STABILITY CONSTANTS:

A.1. GENERAL CONSIDERATIONS:

The Study of metal complexes involves a particularly important class of chemical equilibria that between metal ions (acceptors) and the ligands (donors). In order to understand the profound changes that take place in the properties of the metal ion due to the co-ordination of ligand to the metal ion, a measure of the extent of metal complex formation under the experimental condition is essential. The knowledge of the equilibrium constants for these reactions provides the necessary information.

When a metal complex is formed from a metal ion and one or more ligand molecules, the equilibrium constant is generally called "Stability Constant" and sometimes as "Formation Constant". If \( N \) is the maximum number of ligand molecules which can coordinate to a metal ion, then a series of equilibria involved during the formation of a chelate and corresponding complex (chelate) formation constants would be represented as follows.

\[
ML + L \rightarrow ML ; \quad K = \frac{ML}{ML} \\
(2.1)
\]

\[
ML + L \rightarrow ML ; \quad K = \frac{ML}{ML} \\
(2.2)
\]

\[
ML + L \rightarrow ML ; \quad K = \frac{ML}{ML} \\
(2.3)
\]
Where M and L represent the metal and ligand respectively (charges are omitted for the sake of generality). Here "a" terms denote the activities of the constituents in the solution while $K_T$ are referred to as "Thermodynamic Stability (formation) Constants".

However, in practice, the activities are, as a first approximation replaced by concentration terms denoted by $[\ ]$ when we get the so-called "Stoichiometric stability constants" defined as

$$K = \frac{[ML]}{[M][L]} \quad \text{...(2.4)}$$

The products of the stepwise stability constants also give the characteristic constants, called "overall stability constants" usually denoted by $B$, thus

$$B = K = \frac{[ML]}{[M][L]} \quad \text{...(2.5)}$$

$$B = K K = \frac{[ML]}{[M][L]} \quad \text{...(2.6)}$$

$$B = K K \ldots K = \frac{[ML]}{[M][L]} \quad \text{...(2.7)}$$

otherwise expressed as,

$$B = \prod_{i=1}^{n} K$$

The definitions given here are restricted to simple mononuclear species; i.e., two species that contain only one central metal group per complex and only one type of ligand. For a mixed mononuclear complex, $MLB$, containing two types of ligands (L and $n B$), $B$ and $B$, the overall stoichiometric stability constant may be defined as
B = \frac{[MLB]^n}{[M][L]^m[B]^n}^{mn} \quad \ldots \quad (2.9)

Just as the complex equilibria can be characterised by stability constants as described above, the acid-base equilibria of the ligands can be treated in terms of protonation or stoichiometric proton-ligand stability constants, as follows:

\[ \text{H}^{+}L + \text{H}^{+} \rightleftharpoons \text{LH}^{+} \quad K = \frac{[\text{LH}^{+}]}{[\text{H}^{+}][L]} \quad \ldots \quad (2.10) \]

\[ \text{LH}^{+} + \text{H}^{+} \rightleftharpoons \text{LH}^{2+} \quad K = \frac{[\text{LH}^{2+}]}{[\text{H}^{+}][\text{LH}^{+}]} \quad \ldots \quad (2.11) \]

\[ \text{LH}^{i-1} + \text{H}^{+} \rightleftharpoons \text{LH}^{i} \quad K = \frac{[\text{LH}^{i}]}{[\text{H}^{+}][\text{LH}^{i-1}]} \quad \ldots \quad (2.12) \]

\[ \text{LH}^{j-1} + \text{H}^{+} \rightleftharpoons \text{LH}^{j} \quad K = \frac{[\text{LH}^{j}]}{[\text{H}^{+}][\text{LH}^{j-1}]} \quad \ldots \quad (2.13) \]

It can be easily seen that the proton-ligand stability constant \( K \) is the reciprocal of the dissociation constant of the acid \( i \) whose dissociation may be depicted as shown below:

\[ \text{LH}^{i} \rightleftharpoons \text{LH}^{i-1} + \text{H}^{+}; \frac{1}{K} = \frac{[\text{LH}^{i-1}][\text{H}^{+}]}{[\text{LH}^{i}]} \quad \ldots \quad (2.14) \]

In a manner similar to the metal-ligand equilibria, one can also define an overall proton-ligand stability constant as follows:

\[ \text{H}^{i} \text{L} = \frac{[\text{LH}^{i}]}{[\text{H}^{+}][\text{L}]} = K K \quad \ldots \quad K = \frac{K}{a_{\text{H}^{i}}} \quad \ldots \quad (2.15) \]

is generally assumed that the ionic or molecular species involving \( \text{H,L} \) and \( M \), other than those occurring in the above equilibria do not exist in solution. This is equivalent to assuming the absence of polynuclear complexes, proton bearing complexes,
unionised metal salt, hydroxyl bearing complexes and metal ions. It is required to emphasise here that, in subsequent treatment, concentrations are used for activities.

A.2. METHODS OF DETERMINATION OF STABILITY CONSTANTS:

When a complex is formed many of the properties of the solution undergo a measurable change. Though, in principle, the measurement of all these properties give information regarding the stability of the different species, one has to carefully select that property which can be (a) conveniently measured, and (b) clearly related to the concentration of one of the species of the metal ion, the free ligand, or one of the complexes formed for the experimental determination of the stability constants.

Spectrophotometric, potentiometric, pH metric, solvent extraction, polarographic methods, etc., are the methods commonly employed for this purpose.

A.2.1 THE METHOD BASED ON pH MEASUREMENTS:

This method involves the measurement of $H^+$ concentration by using a pH meter. As the measurement by pH meter does not describe the equilibrium, this is a popular and widely used method. This method is highly suited for those chelates which are either soluble in water or mixed organic solvents such as water-ethanol, water-dioxan; etc., and an appropriate correction for pH should be made in the case of mixed solvents.
A.2.2 THE THEORITICAL BASIS:

For the purpose of determining the stability constants, Bjerrum introduced the concept of degree of formation or ligand number \( \bar{n} \) which he defined as the average number of ligands bound per metal ion in any of its several forms depicted in equation (2.1) to (2.3) i.e.,

\[
\bar{n} = \frac{\text{total concentration of the bound ligand}}{\text{total concentration of the metal ion present in any of its form}}
\]

\[
\bar{n} = \frac{[ML]+2[ML]+3[ML]+...+N[ML]}{[M]+[ML]+[ML]+...+[ML]}
\]

Substituting for \([ML]\) from equation (2.4) and dividing through-out by \([M]\), we get

\[
\bar{n} = \frac{K[L]+2K[L]+...+NK[L]}{1+K[L]+K[L]+...+K[L]}
\]

(2.16)

If overall stability constant is used instead of the stepwise constants, one gets

\[
\]

(2.17)
Another similar function $\tilde{n}$ may be defined for the proton-ligand equilibria depicted in equation (2.15) as follows:

$$
\tilde{n} = \frac{\sum_{i=0}^{j} B_i [H]^i}{\sum_{i=0}^{j} B_i [H]^i [L]^i} \quad \ldots (2.19)
$$

Where $B_i = 1$ if $i \geq 1$

If we represent the total concentration of the metal ion $M$, and the total concentration of the ligand $L$, which are both known, by $T_M$ and $T_L$ respectively, then

$$
T_M = \sum_{i=0}^{N} [ML]^i = [M] E \sum_{i=0}^{N} B_i [L]^i \quad \ldots (2.20)
$$

and

$$
T_L = \sum_{i=0}^{j} [LH]^i + E \sum_{i=0}^{N} i [ML]^i
$$
Both \( T \) and \( T' \) are taken as molar concentrations of the metal and the reagent respectively.

The condition of electroneutrality in solution is given by:

\[
[H] - [OH] + S^+ \sum_{i=0}^{j} (i-m)[LH]^+ + \sum_{i=0}^{N} (i-p)[ML] = 0 \quad \ldots (2.22)
\]

Where \( S \) is the sum of the products of the concentrations of the ions and their respective charges, and \(-m\) and \(+p\) are the valencies of \( L \) and \( M \) respectively. A constant ionic strength is to be maintained by the addition of neutral electrolytes.

**B. EXPERIMENTAL AND COMPUTATIONAL METHODS:**

The equations given above state all the relations between the concentrations of the ionic and the molecular species present in the solution. Several experimental techniques and methods of calculation have been used to obtain the values of the formation constants from the above equations.

A survey of the experimental methods and the procedures adopted for calculation of the formation constants have been made by Martell and Calvin, Irving and Rossotti; Rossotti and Rossotti and Hearon and Gilbert and others. In the majority of cases these methods consist of three steps:

1. The formulation of the formation curve of the system from experimental data.
(b) The calculation of stoichiometric stability constants by solution of the formation function of the system or otherwise.
(c) The conversion of the stoichiometric constants into thermodynamic constants.

Calvin-Bjerrum pH titration method is the most commonly used method; this allows the accumulation of a large amount of data in a relatively short time. Irving and Rossotti have modified this in such a way that there is no necessity to convert pH values into stoichiometric \([H^+]\) ion concentration. Besides, this method has an added advantage of determining the acid dissociation constants under the same experimental conditions as the formation constants. It may also be used in water-organic solvent mixtures without the specific knowledge of the pH values in these media and their relation to the stoichiometric hydrogen ion concentration.

A set of three titrations are usually carried out as given below:

(i) a titration of a mineral acid solution containing a solution of neutral electrolyte added to maintain a constant ionic strength against a standard alkali.

(ii) a titration of the same amount of mineral acid, neutral electrolyte and the ligand solution of known concentration against the same standard alkali, and
(iii) a titration of the same quantity of the mineral acid and neutral salt solution, the ligand and a known concentration of metal salt solution against the same standard alkali.

In all these titrations, the solvent composition 50% (v/v) and final volume is kept constant 50 ml.

The plot of the measured pH values against the volume of alkali added in each case gives a set of three curves, where the ligand titration curve (ii) appears to be displaced towards the right and shows lower values of pH than the (i). If the ligand is acidic, and when the metal complex is formed, in (iii), still lower pH values are indicated for the same volume of alkali and the curve appears displaced further to the right than (ii).

B.1.1. CALCULATION OF $\bar{A}$ and $\bar{A}$ VALUES:

The stoichiometric hydrogen ion concentration $[H]^+$ at any point in the acid titration curve (i) is given by:

$$[H]^+ = [E]^+ + [OH]^+ - [Na]^+$$

where $[Na]^+$ is the concentration due to the addition of alkali as sodium hydroxide and $[E]^+$ is the concentration of mineral acid in solution.

The corresponding equation for the reagent (ligand) titration curve (ii) is given by:

$$[H]^" = [E]^" + [OH]^" - [Na]^" + \bar{A}^T - \bar{A}^" L L$$

.....(2.24)
The term $yT_L$ represents the number of titratable hydrogen ions in gram ions per litre arising from the chelating agent when it is an acid $H_yL$. $y$ is zero for a base. The last term $\tilde{n}_A^T$ gives the number of $H$ ions removed as a result of the formation of proton-ligand complexes and results from the definition of $\tilde{n}_A$ given by the above equation (2.18).

If the pH metric readings are identical in titration curves of both solutions (i) and (ii), and their ionic strengths are same, then

$$[H]^' = [H]^" \quad \ldots (2.25)$$

Since $[H]$ and $[OH]$ are related by the ionic product of water which is constant at constant ionic strength and temperature,

$$[OH]^' = [OH]^" \quad \ldots (2.26)$$

So from (2.23) and (2.24) the following relation is obtained:

$$\tilde{n}_A^T = \frac{\{(E^" - E^') - ([Na]^" - [Na]^') + yT_L\}}{L} \quad \ldots (2.27)$$

Under the conditions in which $V^o$ the initial volume of solution, and $E^o$ the initial concentration of the mineral acid, are the same in the two titrations (i) and (ii), $T_L$ is the initial total ligand concentration in titration (ii) and the
alkali used is of the same normality \( N \), the equation given below would be obtained when the volume \( V' \) and \( V'' \) of the alkali are required to be added for reaching same pH values,

\[
E'' = \frac{\circ E}{\circ (V' + V'')} \quad \ldots(2.28)
\]

\[
[Na]'' = \frac{\circ N}{\circ (V' + V'')} \quad \ldots(2.29)
\]

and

\[
TL'' = \frac{\circ T}{\circ (V' + V'')} \quad \ldots(2.30)
\]

Similar equations can be derived for \( E' \) and \([Na]'\). Then the equation (2.27) becomes;

\[
\bar{\eta}'' = \frac{\{(yT - (V' - V'')(N + E') / (V' + V')\}}{\circ T \circ L} \quad \ldots(2.31)
\]

\[
\bar{\eta}'' = y - \{ \frac{(V'' - V')}{\circ (V' + V')} \times \frac{(N + E')}{\circ (V' + V')} \} \quad \ldots(2.32)
\]

Thus \( \bar{\eta}A \) values can be obtained from the titration (i) and (ii) using this equation (2.32).

For any point on the metal titration curve (iii), we have the relation,
The last term in (2.33) has the same significance as the last term in (2.24) with the difference that the former takes into account the decrease in the concentration of the uncomplexed ligand after the formation of definite amount of metal complex. The term \(\bar{n}' \cdot T \cdot\)' arises from the definition of \(\bar{n}\) in equation (2.16).

If the ionic strength in the titrations (ii) and (iii) are the same, then for the same pH meter reading in titration (iii) equations (2.25) and (2.26) corresponding to titration (ii), under the conditions of same ionic strength and temperature we have,

\[
[H]'' = [H]'', \quad [OH]'' = [OH]''.
\]

...(2.34)

Also,

\[
\bar{n}'' = \bar{n}''.
\]

....(2.35)

Consequently, the expression (2.36) follows:

\[
\bar{n}''' = \frac{(E''-E''')+(T''-T''')(y-\bar{n}'')(y-\bar{n}''')}{[Na]' - [Na]''} \quad \text{...(2.36)}
\]

From the above expressions and equations similar to, (2.28) to (2.30), the expression,
would result under considerations given below:

(a) \( V, E, T \) and \( N \) are the same as for the reagent titration,

(b) \( V'\) is the volume of alkali required to reach the same pH value in metal titration, and (c) \( T \) is the initial concentration of metal.

B.1.1.2 CALCULATION OF \( pL \):

Equation (2.21) is written as follows in the modified form using equations (2.17) and (2.20)

\[
T'' = [L]'' \sum_{i=0}^{j} B_i [H]'' + \bar{\alpha} T'' \tag{2.38}
\]

where \( B_0 = 1 \).

Rearranging this equation, one gets:

\[
[L]'' = \frac{1}{T'' - \bar{\alpha} T''} \sum_{i=0}^{j} B_i [H]'' \tag{2.39}
\]

In the above equation, inserting the value of \( T'' \) and \( T'' \) in the form similar to that in (2.30) one gets:
$$
\sum_{i=0}^{i} \frac{\sum_{j=0}^{j} H_{i} (\text{antilog}[H]) \ (V + V')} {10^T - \tilde{n}''T}
$$

$$
\begin{align*}
\text{pL} &= \log \left\{ \frac{\sum_{i=0}^{i} \left(1/\text{antilog}[H] \right) \ (V + V')} {10^T - \tilde{n}''T} \right\} \quad \ldots(2.40)
\end{align*}
$$

For a bimolecular acid, for example, using the usual notation of proton ligand formation constant using equation (2.15) the above equation reduces to:

$$
\begin{align*}
\sum_{i=0}^{i} \frac{H_{i} [H] + K H_{1} [H] + K H_{2} [H]} {10^T - \tilde{n}''T}
\end{align*}
$$

$$
\begin{align*}
\text{pL} &= \log \left\{ \frac{\sum_{i=0}^{i} \left(H_{i} [H] + K H_{1} [H] + K H_{2} [H]\right)} {10^T - \tilde{n}''T} \right\} \quad \ldots(2.41)
\end{align*}
$$

The \text{pL} values may thus be obtained corresponding to the same measured \text{pH} values at which \tilde{n} are calculated. The formation curve is then drawn for the system by plotting the \tilde{n} values as a function of \text{pL}.

**B.2. METHODS OF DETERMINING THE STOICHIOMETRIC STABILITY CONSTANTS:**

As stated above this is essentially a solution of the formation function (2.16) or its alternative form (2.17) viz.,
This has received considerable attention due to the following reasons.

(i) Although the number of pairs of values of $\tilde{n}$ and $[L]$ which are required for solving the equation is only $N$, since there are $N$ unknowns, usually a much larger number of values are available, the question of utilising all the experimental data, so as to obtain the most representative values, thus arises.

(ii) Equation (2.17) can be written as

$$\sum_{i=0}^{N} (\tilde{n} - i) B_i[L] = 0 \quad \ldots \ldots (2.42)$$

It is clear that values of $\tilde{n}$ near an integer must be used very cautiously, since $(\tilde{n} - i)$ becomes susceptible to small errors in $\tilde{n}$. This raises the question of choice of suitable values of $\tilde{n}$ and $L$.

(iii) The data obtained experimentally may not, sometimes, be fully representative of the complete formation curve.

The different workers have adopted different methods suitable to their experimental conditions. These have been reviewed by Irving and Rossotti, Hearon and Gilbert and Rossotti and Rossotti. Some workers determined the stability constants even by methods which do not make use of the concept of the degree of formation explicitly. Of all these methods, those suggested by Bjerrum have been widely used especially for the system where $N = 2$. Irving and Rossotti have shown that for systems the least
square treatment of n, pL data yields the most representative values of K. In the present work, the suitable modifications of these methods have been used because N happens to be of the order of 2 in most of the cases studied. They are described below:

B.2.1. THE METHOD OF BJERRUM:

Bjerrum introduced a term called "spreading factor" to relate two successive stability constants $K_i$ and $K_{i+1}$. These two are not equal even in the ideal cases when the chemical and electrical interactions between M and L are independent of the number of ligands already attached, owing to a statistical effect suggested by Wegscheider and Adams. This arises because the tendency to split off a group is proportional to $i)$ the number of groups already attached. The tendency to add an additional group is proportional to $(N-i)$ the number of unfilled positions. In the ideal case, the ratio between the two stability constants is written as,

$$\frac{K_i}{K_{i-1}} = \frac{(i+1)(N-i+1)}{i(N-i)} \ldots (2.43)$$

Bjerrum wrote this ratio as:

$$\frac{K_i}{K_{i+1}} = \frac{(i+1)}{i} \cdot \frac{(N-i+1)}{(N-i)} \ldots (2.44)$$
to represent a general case, where $X$ is the spreading factor which will be equal to unity in the ideal case. For $N > 2$ (usually 3, 4 or 6), the value of $X$ is assumed to be constant for the whole system with any value between 0 to $\infty$. This assumption is exactly valid for $n=3$, when the formation curve is symmetrical.

When $N = 2$,

$K_2 = 4X$ and since $B_1 = K_2$ by equation (2.8), then

$$K = 2X_2$$

Equation (2.16) now becomes for $N = 2$

$$\frac{1}{2} \left( 2X_1 B \right)_{[2]}^2 + 2B_2 [L]$$

$$\bar{n} = \frac{1}{2} \left( 1 + 2X_1 B \right)_{[2]}^2 + B_2 [L]$$

Equations (2.45) and (2.46) can be used for the formation of $\bar{n}$ against $pL$ for various values of $X$ and $B$. The curve has a wave-like character, the two steps being separated completely.

Plots of $\bar{n}$ against $pL$ for a given value of $B$, say 10 at

$$2$$

Plot of $\bar{n}$ against $pL$ for various values of $X$ show that for high values of $X > 100$, the curve has a wave-like character, the two steps being separated completely.

The solution of the formation function depends on $X$ and it is obtained for the mid point slope ($\Delta$) of the formation curve in case of $N = 2$ as follows:
\[ \Delta = \left( \frac{d\bar{n}}{dp_L} \right)_{\bar{n}=1} = -\frac{2.303}{(1+x)} \quad \ldots \ldots (2.47) \]

For \( N = 2 \) following relation is obtained from (2.16).

\[ \log K = p_L + \log \left[ \frac{2}{1 + (1 + 12 \frac{K}{K})} \right]^{1/2} \quad \ldots \ldots (2.48) \]

\[ \log K = p_L - \log \left[ \frac{2}{(1 + (1 + 12 \frac{K}{K})} \right]^{1/2} \quad \ldots \ldots (2.49) \]

where the suffixes of \( L \) denote the value of \( \bar{n} \). When \( X \) is high, \( \frac{K}{K} \) is very small (2.48) and (2.49), thus reduce to

\[ \log K = p_L \quad \ldots \ldots (2.50) \]

\[ \log K = p_L \quad \ldots \ldots (2.51) \]

respectively.

A generalisation of these relationships can be expressed as,

\[ \log K = p_L \quad \text{since} \quad K >> K. \quad \ldots \ldots (2.52) \]

The \( \log K \) values obtained in this manner are known "Half integral" values. From the equation (2.48) and (2.49) \( X \) can be calculated with certain degree of accuracy in \( K \) and \( K \) for equations (2.50) and (2.51) to be valid, by assigning value to the second term in equation (2.48) and (2.49) such that it is equal to the permissible error and then by calculating the values of \( K/K \). The results obtained in this way are given below in the table II.1.
<table>
<thead>
<tr>
<th>Permissible error in log K values</th>
<th>Maximum values of</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>log K /K</td>
</tr>
<tr>
<td></td>
<td>1</td>
</tr>
<tr>
<td>-0.001</td>
<td>3.18</td>
</tr>
<tr>
<td>-0.005</td>
<td>2.42</td>
</tr>
<tr>
<td>-0.01</td>
<td>2.10</td>
</tr>
<tr>
<td>-0.02</td>
<td>1.78</td>
</tr>
<tr>
<td>-0.10</td>
<td>0.96</td>
</tr>
</tbody>
</table>

For log K to be accurate within ±0.02, which is the usual accuracy with which the pH meter can be read, log K /K need only to be 1.78 or X be 3.90. Hence, the half integral values can be used in such cases.

Depending upon the accuracy desired for values of X, the two portions of the formation curves 0 < n < 1 and 1 < n < 2 can be treated for 1:1 complexes, the most representative values of K is then the average of all K values obtained from equation

\[ \bar{n} + (\bar{n} + 1) K [L] = 0 \]  

... (2.53)

which is obtained from (2.16) or by plotting -log \( \bar{n} / (1 - \bar{n}) \) versus -log[L] = (pL) and reading the intercept. Similarly K value is obtained by treating the second portion of the curve by plotting -log \( (2 - \bar{n}) / (\bar{n} - 1) \) versus pL.

There is no need to resort to the lengthy calculations by successive approximation method recommended by Bjerrum for all
cases where X is not very large, since the accuracy in the calculation of the value of K is restricted on account of limitations imposed on accuracy of pH measurement.

B.2.2. LEAST SQUARE METHOD OF IRVING AND ROSSOTTI:

For the case N = 2, equation (2.16) may be transformed into the following linear form:

\[
\frac{\bar{n}}{1} = \frac{(2-\bar{n}) [L]}{K_{12} K_{1} - K_{12}} \text{ ...(2.54)}
\]

Since this represents an equation for a straight line, a plot of \( \frac{\bar{n}}{(\bar{n}-1)[L]} \) versus \( \frac{(2-\bar{n})[L]}{(\bar{n}-1)} \) is expected to give a straight line with an intercept equal to \( K_{1} \) and slope equal to \( K_{12} K_{1} \). As \( [L] \) may vary by several powers of ten, determination of \( K_{1} \) and \( K_{2} \) from such a plot is not very convenient. On the other hand, a number of values of \( \bar{n}/(\bar{n}-1)[L] \) and \( (2-\bar{n})[L]/(\bar{n}-1) \) may be obtained and tabulated for several points on the curve and equation (2.54) solved to get \( K_{1} \) and \( K_{2} \) values. It has been shown by Irving and Rossotti that the values of \( \bar{n} \) obtained from the experimental pH values together with the log \( K_{1} \) and log \( K_{2} \) value calculated by the least square method agree with the experimental values of \( \bar{n} \) better than those obtained from \( K_{1} \) and \( K_{2} \) values calculated by half integral and average method.

While using this method, the points lying within the range \( 0.9 < \bar{n} < 1.10 \) are best rejected in view of the susceptibility of \( (\bar{n}-1) \) to even small errors in \( \bar{n} \), when \( \bar{n} \) is close to an integer.
This method has the advantage of using all the experimental points and can be applied even when the formation curve is incomplete.

In all the methods based on the formation function for \( \tilde{h} \), \( p_L \) data are required to satisfy equation (2.16). The formation curve then consequently is symmetrical. A visual test of symmetry is that of consequence deciding the proper method of solution.

B.3. CONVERSION OF STOICHIOMETRIC STABILITY CONSTANTS INTO THERMODYNAMIC CONSTANTS:

The stoichiometric stability constants \( K_i \) are related to the corresponding thermodynamic constants \( K_i^T \) by the expression,

\[
K_i^T = K_i^{\text{fML}} / K_i^{\text{fML}} \cdot f_{i-1} \quad \text{(2.55)}
\]

where \( f_{\text{ML}} \), \( f_{\text{ML}} \), and \( f_L \) are the activity coefficients of the respective species, though only the thermodynamic stability constants can be related to other thermodynamic quantities associated with the complex formation. The thermodynamic stability constants are rarely used due to the paucity of accurate data and activity coefficients of the various species. The failure to get these data may be ascribed to the following reasons:

(i) The incomplete validity of several assumptions made in the calculations.

(ii) Inaccurate information regarding the factors like liquid junction potentials involved in the experimental techniques, and
(iii) lack of knowledge of single ion activity coefficients.

In addition to these, the fact that many of the measurements are made in mixed solvent media make the determination of activity coefficients of doubtfull validity for a generalised treatment.

Hence, the stoichiometric stability constants themselves are used directly to obtain the thermodynamic quantities, since the effect of the activity coefficient term is made constant by maintaining the ionic strength of the medium uniform throughout the titration, by adding neutral electrolytes NaClO at much higher concentration (0.1M) than those of the reacting species (0.004M).

B.4. THERMODYNAMIC QUANTITIES FOR STABILITY CONSTANTS:

The free energy change ($\Delta G$) accompanying the formation of a complex in a homogenous liquid system is given by

$$\Delta G = \Delta G^\circ + RT \ln K \quad \ldots \ldots (2.56)$$

at equilibrium this equation (2.56) becomes,

$$\Delta G^\circ = - RT \ln K \quad \ldots \ldots (2.57)$$

and since

$$\Delta G^\circ = \Delta H^\circ - T \Delta S^\circ \quad \ldots \ldots (2.58)$$

one may write
\( \ln K = -\frac{\Delta H^\circ}{RT} + \frac{\Delta S^\circ}{R} \) \quad \ldots(2.59)

\( R \ln K = \Delta S^\circ - \Delta H^\circ \left(\frac{1}{T}\right) \) \quad \ldots(2.60)

or \( 2.303 R \log_{10} K = \Delta S^\circ - \Delta H^\circ \left(\frac{1}{T}\right) \) \quad \ldots(2.61)

Assuming that \( \Delta H^\circ \) and \( \Delta S^\circ \) for a reaction are independent of temperature in the temperature range involved according to the equation (2.59), \( \ln K \) will be a linear function of \( 1/T \). Therefore, a graph of \( 2.303 R \log K \) versus \( 1/T \) is expected to give a straight line with the slope \( -\Delta H^\circ \). The intercept on the log \( K \) axis will then be \( \Delta S^\circ \). The plots of \( -2.303 R \log K \) values against \( 1/T \) are shown in the figs. 4C.1 to 4C.6.

If \( K \) and \( K \) are stability constants at two different temperatures \( T \) and \( T \), then,

\[
\log \frac{K}{K} = -\frac{\Delta H^\circ}{2.303R} \left(\frac{1}{T} - \frac{1}{T}\right) \quad \ldots(2.62)
\]

In the above equations (2.58) to (2.62) \( \Delta H^\circ \) is the enthalphy change under the standard conditions. If the stability constants of complex formation are determined at two different temperatures, \( \Delta H^\circ \), \( \Delta S^\circ \), \( \Delta G^\circ \), can be calculated easily, using above equations. Strictly speaking, thermodynamic stability
constants are to be used to evaluate these quantities. But, in practice, the stoichiometric stability constants are used, because of the paucity of the accurate data on activity coefficients of the various species.
REFERENCES
(CHAPTEII)