CHAPTER II

DETERMINATION OF STABILITY CONSTANTS
The study of metal complexes involves a particularly important class of chemical equilibria - that between metal ions, which form acceptors and the ligands, which are the donors. The metal complex formation takes place due to the co-ordination of the ligand to the metal ion with profound changes in the properties of the metal ion. In order to understand these reactions, a measure of the extent of metal complex formation under the experimental conditions is essential. This can be provided by a knowledge of the equilibrium constants for the reactions.

When a metal complex is formed from a metal ion and one or more ligand molecules, the equilibrium constant is generally called the "stability constant" (sometimes also called the "formation constant") for the reaction. It is generally assumed that the co-ordination of the ligand molecule takes place in a stepwise fashion as follows (charges being omitted for the sake of clarity)

\[
\begin{align*}
M + L & \rightleftharpoons ML \\
ML + L & \rightleftharpoons ML_2 \\
ML_{i-1} + L & \rightleftharpoons ML_i \\
ML_{N-1} + L & \rightleftharpoons ML_N
\end{align*}
\] (2.1)
where \( M \) and \( L \) stand for the metal and ligand respectively.

The stepwise stability constants \( K_1, K_2, \ldots, K_i \ldots \) are defined by

\[
K_1 = \frac{a_{ML}}{a_M a_L}
\]

\[
K_2 = \frac{a_{ML_2}}{a_{ML} a_L}
\]

\[
K_i = \frac{a_{ML_i}}{a_{ML_{i-1}} a_L}
\]

where the \( a \)'s refer to the activities of the species concerned. The \( K_i \)'s then are referred to as "thermodynamic stability constants". However, in practice the activities are, as a first approximation, replaced by concentration terms to give the so-called "stoichiometric stability constants", defined as:

\[
K_i = \frac{[ML_i]}{[ML_{i-1}] [L]}
\]

The 'overall stability constants', usually denoted by \( \beta_2 \), refer to the formation of a particular complex species from its component molecules or ions e.g.
\[ \beta_1 = k_1 = \frac{\sum \text{ML}_1}{\sum \text{M} \cdot \sum \text{L}_1} \]

\[ \beta_2 = k_1 k_2 = \frac{\sum \text{ML}_2}{\sum \text{M} \cdot \sum \text{L}_2^2} \]

\[ \beta_i = k_1 k_2 \cdots k_i = \frac{\sum \text{ML}_i}{\sum \text{M} \cdot \sum \text{L}_i} \quad (2.4) \]

Otherwise expressed, \[ \beta_1 = \prod_{i=1}^{n} k_i \quad (2.5) \]

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

\[ \text{L} + \text{H} \rightleftharpoons \text{LH} \quad k_1^H = \frac{\sum \text{LH}_1}{\sum \text{L} \cdot \sum \text{H}_1} \]

\[ \text{LH} + \text{H} \rightleftharpoons \text{LH}_2 \quad k_2^H = \frac{\sum \text{LH}_2}{\sum \text{LH}_1 \cdot \sum \text{H}_1} \]

\[ \text{LH}_{j-1} + \text{H} \rightleftharpoons \text{LH}_j \quad k_j^H = \frac{\sum \text{LH}_j}{\sum \text{LH}_{j-1} \cdot \sum \text{H}_1} \quad (2.6) \]

The proton-ligand stability constant \( k_i^H \) is the reciprocal of the dissociation constant of the acid whose dissociation may be depicted as follows:
In a manner similar to the metal-ligand equilibria, one can also define an overall proton-ligand stability constant as follows:

$$\beta_i^H = \frac{\prod_{i}^{\infty} \prod_{j}^{\infty} \prod_{k}^{\infty} L_i^H}{\prod_{i}^{\infty} \prod_{j}^{\infty} \prod_{k}^{\infty} H_i^L} = k_1^H k_2^H \cdots k_i^H = \prod_{i=1}^{\infty} k_i^H \quad (2.7)$$

In the treatment of the complex equilibria, it is generally assumed that the ionic or molecular species involving H, L and M, other than those occurring in the above equilibria do not exist in solution.

Methods of determination of stability constants

There are many solution properties which change measurably as a result of complex formation. Though, in principle, the measurement of all these properties give information about 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 determination of the stability constants experimentally. Some of these methods are briefly described below. The method
based on pH measurements will, however, be described in greater detail subsequently.

1. **Potentiometric method**

This method is mainly employed for the systems in which the ligand possesses neither acidity nor basicity by means of which its concentrations can be followed conveniently. Here, the activity of the metal ion is measured as a function of varying ligand concentration, by measuring the potential $E$, of the metal-metal ion electrode,

$$E = E^0 + \frac{RT}{2F} \ln \left( \frac{a_{M^{2+}}}{a_{L}} \right)$$

The problem here is to relate the measured values of $E$, and hence of $a_{M^{2+}}$ at various concentrations of ligand to the equilibrium constants for the system.

The total concentration of the metal ion, $T_M$, free and in all of the possible complexes is given by

$$T_M = \sum M + \sum ML + \sum ML_2 + \sum ML_3 + ...$$

Using the overall stability constants, $\beta_1$s

$$T_M = \sum M + \beta_1 \sum ML + \beta_2 \sum ML^2 + \beta_3 \sum ML^3 + ...$$

$$= \sum M \left\{ 1 + \beta_1 \sum L + \beta_2 \sum L^2 + \beta_3 \sum L^3 + ... \right\} \quad (2.8)$$
If the total metal concentration is only a small fraction of the total ligand concentration, then the free ligand concentration, $[L^-]$ may be taken to a good approximation, as the same as the total ligand concentration. If, for example, $i = 4$, the e.m.f. measurements of four solutions containing different amounts of ligand provide sufficient data to define four simultaneous equations in $\gamma_k$s which can be solved for the $\gamma_k$s. In practice, an entire curve of $E$ versus $[L^-]$ is obtained from which these constants can be evaluated accurately.

2. Solvent extraction method

If one of the series of complexes formed in aqueous solution is electrically neutral and can be extracted into an immiscible organic solvent, this method can be advantageously used. The simple methods like radioactive tracer technique or spectrophotometer are usually used to estimate the extracted species.

If the method employed can measure the amount of the metal in both the phases in whatever form it exists, then the following relation holds good:

$$D = \frac{M_o}{M} = \frac{\text{Concentration in organic phase}}{\text{Concentration in aqueous phase}}$$
Supposing that the ligand is monoprotic and bidentate and the highest complex formed is 1:2, then,

\[ D_C = \frac{\sum ML_2^2}{\sum M\overline{L} + \sum ML\overline{L} + \sum ML_2} \]  \hspace{1cm} (2.9)

If the activity coefficients in each phase are assumed to be constant throughout the range of concentrations used, then,

the partition coefficient, \( k_{DC} = \frac{\sum ML_2^2}{\sum ML_2} \) \hspace{1cm} (2.10)

and the overall stability constant \( \beta_2 = \frac{\sum ML_2}{\sum M\overline{L}\overline{L} + \sum ML_2} \) \hspace{1cm} (2.11)

Hence, from the equations (2.10) and (2.11), we get

\[ \sum ML_2 \beta_2 = k_{DC} \beta_2 \sum M\overline{L}^2 \] \hspace{1cm} (2.12)

The equation (2.9) can then be written as:

\[ D_C = k_{DC} \beta_2 \sum L\overline{L}^2 / 1 + \beta_1 \sum L\overline{L} + \beta_2 \sum L\overline{L}^2 \] \hspace{1cm} (2.13)

Taking the logarithms, one gets:

\[ \log D_C = k_{DC} \beta_2 \sum L\overline{L}^2 + 2 \log \sum L\overline{L} - \log \left( 1 + \beta_1 \sum L\overline{L} + \beta_2 \sum L\overline{L}^2 \right) \] \hspace{1cm} .... (2.14)
Hence, taking the limits, one gets

\[
\text{Lt. } \log D_c = \log k_{\text{DC}}^2 + 2 \log L_7 \quad (2.15)
\]

The asymptote to this curve at \( L_7 \to 0 \) will give the \( \log k_{\text{DC}} \), while the asymptote as \( L_7 \to \infty \) gives \( \log k_{\text{DC}}^2 \), since,

\[
\Rightarrow \log D_c = \log k_{\text{DC}} \quad (2.16)
\]

\( \beta_2 \) can thus be obtained.

3. Polarographic method\textsuperscript{60,61}

The quantitative relationship between the shift of the half-wave potential and the stability constant of the complex formed has been shown by Lingane\textsuperscript{62} to be

\[
\Delta E_\frac{1}{2} = (E_{1s}) - (E_{1c}) = \frac{2.303 RT}{2F} \log \beta_i
\]

\[
+ \frac{2.303 RT}{2F} n \log L_7 \quad (2.17)
\]

where \((E_{1s})\) and \((E_{1c})\) are the half wave potentials of the simple and complex species respectively, and \( n \) is the number
of electrons involved in the electrode reaction. A plot of \( \Delta E_h \) versus \( \log \sum L^i \) is expected to give a straight line from the slope of which \( \alpha \) can be calculated.

In the case of successive complex formation, this plot consists of several segments, when the stabilities are widely different. The corresponding stability constants are then determined analogously from these segments. In the case of overlapping equilibria, the following equation deduced by DeFord and Hume can be applied:

\[
\text{antilog} \left( \frac{0.4343ZF}{RT} \Delta E_h + \log \frac{I_s}{I_c} \right) = \sum_{i=1}^{N} \beta_i \sum L^i
\]

Here, \( I_s \) and \( I_c \) are the diffusion constants of the non-complexed and the complexed species respectively. Equation (2.18) can be solved by using computers or by the Leden method, the principle of which is given below.

If all the measurements are done at the same ionic strength, the right hand side of (2.18) may be denoted by \( F_0 \sum L^i \), a function of free ligand concentration and written as:

\[
F_0 \sum L^i = \beta_0 + \beta_1 \sum L^1 + \beta_2 \sum L^2 + \ldots + \beta_N \sum L^N
\]

\ldots \quad (2.19)
A new function $F_1 \sum L^7$ may then be defined as:

$$F_1 \sum L^7 = \left\{ \frac{F_0 \sum L^7 - \gamma_0}{\sum L^7} \right\} = \beta_1 + \beta_2 \sum L^7 + \beta_3 \sum L^7^2 + \ldots \ldots \quad (2.20)$$

A plot of $F_1 \sum L^7$ versus $\sum L^7$ gives a curve having a limiting slope of $\beta_2$ at $\sum L^7 = 0$ and an intercept equal to $\beta_1$. Similarly, other functions may be derived, giving finally, the expression:

$$F_N \sum L^7 = \left\{ \frac{F_{N-1} \sum L^7 - \gamma_{N-1}}{\sum L^7} \right\} = \gamma_N \quad (2.21)$$

In general case such plots mentioned above are made for each function till all the species are accounted for.

4. **Optical methods**

The change of spectral properties on complex formation is the basis of a number of methods of determining the stability constants. Spectrophotometric methods involving absorbance measurements in the ultraviolet, visible and infrared regions have been made use of for this purpose.

One of the commonly used methods is based on the principle of continuous variation, which is generally attributed to Job who applied it to complex systems. The principle of the method may be explained as follows.
Suppose that the metal ion and the ligand form a complex as follows:

\[ m\, M + n\, L \rightleftharpoons M_L^n \]  \hspace{1cm} (2.22)

A series of solutions in which the sum of the total concentration of M and L is a constant C, but where the relative proportions of M and L vary are prepared.

\[ T_M + T_L = C \]  \hspace{1cm} (2.23)

If one defines a quantity \( x \) as

\[ x = \frac{T_L}{T_M + T_L} \]  \hspace{1cm} (2.24)

the equilibrium concentrations of the species M, L and \( M^n_{mL} \) are given by:

\[ \sum_{M_L^n} = C(1-x) - m\sum_{M_L^n} \]  \hspace{1cm} (2.25)

\[ \sum_{L_L^n} = cx - n\sum_{M_L^n} \]  \hspace{1cm} (2.26)

\[ \sum_{L^m_{mL}} = \sum_{M_L^n} \sum_{L^m_{mL}} \]  \hspace{1cm} (2.27)

The concentration of the complex reaches a maximum at a value of \( x \), which may be called \( x_{\text{max}} \). It can be shown then that

\[ \frac{n}{m} = \frac{x_{\text{max}}}{1-x_{\text{max}}} \]  \hspace{1cm} (2.28)
The ratio of stoichiometric coefficients can thus be obtained.

In the case of a stable complex, the curve of absorbance versus \( x \) consists of strictly linear intersecting portions whereas in moderately stable complexes, there is no such linearity. The stability constant can, however, be calculated from the deviation between the curve and that obtained by extrapolation from the slopes near the extreme values of \( x \).

Among the other methods which make use of absorbance measurements are the mole-ratio methods, which are particularly useful in the case of successive complex formations. Here, the total concentration of the metal ion is kept constant, while the total concentration of the ligand is increased. If the absorbance is plotted as a function of the total ligand concentration, the graphs give linear sections, whose intersections provide the ligand to metal ratios in the complexes.

In a modified method due to Bent and French one assumes that if the complex is weak, \( \Sigma L_7 = T_L \) and \( \Sigma M_7 = T_M \) and from the logarithm of the equilibrium constant in the reaction (2.22),

\[
\log \Sigma_{MnL_7} = m \log \Sigma M_7 + n \log \Sigma L_7 + \log \eta \tag{2.29}
\]
A plot of log of absorbance as a function of $T_L$ at constant $T_M$ will then give a straight line with slope $n$. Similarly, a plot of log $A$ vs. $T_M$ at constant $T_L$ will give a straight line with slope $m$. The stability constant is then obtained by analysing log $A$ by the method of least squares.

These methods, however, have to be interpreted with great caution as they are associated with a measure of unreliability.66

5. The method based on pH measurements

Since this is the method that has been employed in this work in determining the stability constants of the metal complexes, a more detailed description of this method will be given below.

5.1 The theoretical basis

For the use of this method the concept of the degree of formation introduced by Bjerrum1 is of fundamental importance. The degree of formation $\bar{n}$ is defined as the average number of ligands bound per metal ion in any of its several forms depicted in equation (2.1), i.e.,

$$\bar{n} = \frac{\text{total concentration of the bound ligand}}{\text{total concentration of the metal ion in any of its form}}$$
\[ \bar{n} = \frac{\sum M_1 \bar{L}^1 + 2 \sum M_2 \bar{L}^2 + 3 \sum M_3 \bar{L}^3 + \ldots + N \sum M_N \bar{L}^N \times \sum M \bar{L} + \sum M \bar{L} + \sum M \bar{L} + \ldots + \sum M \bar{L} \times \sum M \bar{L}}{\sum M \bar{L} + \sum M \bar{L} + \sum M \bar{L} + \ldots + \sum M \bar{L}} \]  

... (2.30)

Substituting for \( \sum ML_1 \) from equations (2.4) and dividing throughout by \( \sum M \bar{L} \), we get:

\[ \bar{n} = \frac{K_1 \sum L \bar{L}^1 + 2K_1K_2 \sum L \bar{L}^2 + \ldots + NK_1 \ldots K_N \sum \bar{L}^N}{1 + K_1 \sum L \bar{L} + K_1K_2 \sum L \bar{L}^2 + K_1K_2 \ldots K_N \sum \bar{L}^N} \]  

... (2.31)

using the overall stability constants in (2.4) instead of the stepwise constants, one gets,

\[ \bar{n} = \frac{\beta_1 \sum L \bar{L}^1 + 2 \beta_2 \sum L \bar{L}^2 + 3 \beta_3 \sum L \bar{L}^3 + \ldots + N \beta_N \sum \bar{L}^N}{\beta_1 \sum \bar{L}^1 + \beta_2 \sum \bar{L}^2 + \beta_3 \sum \bar{L}^3 + \ldots + \beta_N \sum \bar{L}^N} \]

\[ = \sum_{i=0}^{N} \frac{\beta_i \sum \bar{L}^i}{\sum_{i=0}^{N} \bar{L}^i} \]  

(2.32)

where \( \beta_0 = 1 \).

Another function \( \tilde{n} \) may be defined in a similar manner for the proton-ligand equilibria, such as the ones depicted in equations (2.6).
\[
\bar{\eta}_A = \frac{\sum_{i=0}^{N} \beta_i^H \sum H_j^i}{1 + \sum_{i=0}^{N} \beta_i^H \sum H_j^i}
\]

where \( \bar{\eta}_A \) may be described as:

\[
\bar{\eta}_A = \frac{\text{total concentration of proton bound to ligand}}{\text{total concentration of ligand not bound to metal}}
\]

\[
\bar{\eta}_A = \frac{\sum_{i=0}^{N} \beta_i^H \sum H_j^i}{\sum_{i=0}^{N} \beta_i^H \sum H_j^i}
\]

(2.34)

where \( \beta_0^H = 1 \).

We may 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.

\[
T_M = \sum_{i=0}^{N} \sum H_j^i = \sum M_j \sum_{i=0}^{N} \beta_i^H \sum L_j^i
\]

(2.35)

and

\[
T_L = \sum_{i=0}^{N} \sum H_j^i + \sum_{i=0}^{N} 1 \sum ML_j^i
\]

(2.36)

Both \( T_M \) and \( T_L \) are taken as molar concentrations of the metal and the reagent respectively.
The condition of electroneutrality in solution is given by:

$$\sum_{i=0}^{J} (1-m) \sum_{j=0}^{N} (p-m) = 0$$

where \( S \) is the sum of the products of the concentrations of the ions and their respective charges, and \(-m\) and \(+p\) are the valences of \( L \) and \( M \) respectively. In the study of these equilibria, a constant ionic strength is maintained by the addition of electrolytes.

The above equations give all the relations between the concentrations of the ionic and molecular species in solution.

5.2 Experimental methods

A survey of the experimental methods and the procedures adopted for the calculation of the formation constants have been made by Martell and Calvin,\textsuperscript{67} Irving and Rossotti,\textsuperscript{68} and Rossotti and Rossotti,\textsuperscript{69} Hearon and Gilbert\textsuperscript{70} and others.

The most commonly employed method is the use of the Calvin-Bjerrum pH titration method, which allows the accumulation of a large amount of data in a relatively short
time. Irving and Rossotti have used this method in such a way that the necessity of converting the pH values to stoichiometric $\left[H^+\right]$ ion concentration is avoided. This method has the further advantage that the acid dissociation constants of the ligand can be determined 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 required:

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

ii) a titration of the same quantity of mineral acid, the added electrolyte and the ligand solution of known concentration against the standard alkali; and

iii) a titration of the same concentrations of the mineral acid, the ligand, the added electrolyte and a known concentration of the metal salt solution against the standard alkali.

The measured pH values against the volume of the alkali added give 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, 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 still further to the right than (ii).

5.3 Calculation of $\bar{n}_A$ and $\bar{n}$

In the acid titration curve (i), the hydrogen ion concentration at any point is given by:

$$\sum_{H^+} = E' + \sum_{OH^-} - \sum_{Na^+}$$  \hspace{1cm} (2.38)

where $\sum_{Na^+}$ is the sodium ion concentration due to the addition of alkali as sodium hydroxide, and $E'$ is the concentration of the mineral acid in solution.

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

$$\sum_{H^+}'' = E'' + \sum_{OH^-}'' - \sum_{Na^+}'' + y T_L'' - \bar{n}_A T_L''$$  \hspace{1cm} (2.39)

where the total initial concentration of dissociable protons arising from the reagent is given by $y T_L''$, if the reagent is an acid $H_y L$. The last term, $\bar{n}_A T_L''$ gives the number of hydrogen ions removed as a result of the formation of the proton-ligand complexes.
If the pH meter readings are identical for both solutions in (1) and (11), and their ionic strength the same, then, \( \sum_{\text{H}^-} = \sum_{\text{H}^+} \) and \( \sum_{\text{OH}^-} = \sum_{\text{OH}^+} \) ... (2.40)

It then follows that:

\[
\tilde{n}_A = \frac{(E'' - E') - \left( \sum_{\text{Na}^-}'' - \sum_{\text{Na}^+}'' \right)}{T_L''} \]

... (2.41)

If one supposes that the initial volume of the solution \( V_0 \), the initial concentration of the mineral acid \( E^0 \) and the total initial ligand concentration, \( T_L^0 \) are the same in each of the titrations, (i) and (ii) and that the volumes \( v', v'' \) of alkali of concentration \( N \), were added to reach the same pH values, then

\[
E'' = \frac{V_0 E^0}{(V_0 + v'')}
\]

(2.42)

\[
\sum_{\text{Na}^-}'' = \frac{v'' N}{(V_0 + v'')^{-}}
\]

(2.43)

and

\[
T_L'' = \frac{V_0 T_L^0}{(V_0 + v'')^{-}}
\]

(2.44)

Similar equations can be obtained for \( E', \text{Na}' \). With the help of these equations, equation (2.41) becomes:
\[ \bar{n}_A = \left( \frac{y T_L^0 + \frac{(V' - V_1)}{(V^0 + V') (N^0 + E^0)}}{T_L^0} \right) / (V^0 + V') \] (2.45)

The \( \bar{n}_A \) values can thus be obtained from titrations (1) and (ii).

In the calculation of the values of \( n \) for metal-complex formation, these \( \bar{n}_A \) values may be directly used.

If now we consider the titration curve for a mixture of mineral acid, ligand and metal ions-titration (iii), for any point on the curve, we have,

\[ \sum H^{m} = E'' + yT_L^m + \sum OH^{m} - \sum Na^{m} - \bar{n}_A (T_L^m - \bar{n}_A T_M^m) \]

\[ \sum \sum H = \sum \sum H'' \] and \[ \sum OH'' = \sum OH'' \] (2.47)
Also,

\[ \tilde{n}_A'' = \tilde{n}_A'' \]  

(2.48)

under these circumstances,

\[ \tilde{n}'' = \frac{(E''-E''') + (T''_L-T''_M)(y-\tilde{n}_A'') - \sum N亚 - \sum Na亚}{\tilde{n}_A'' T_M} \]

... (2.49)

As before, under the conditions, similar to those stated for arriving at equation (2.45), we get,

\[ \tilde{n}''' = \frac{(v'''-v''') \left\{ \frac{N+E^O}{N} + \frac{T^O_L (y-\tilde{n}_A''')}{T_M} \right\}}{(v''+v'') \tilde{n}_A'''} \]

(2.50)

5.4 Measurement of pH in water-organic solvent media

In calculating the \( \tilde{n}_A \) and \( \tilde{n} \) in aqueous solutions, it is common practice to take the reading of the pH meter, B, which we assume gives:

\[ B = -\log_{10} \left\{ \frac{1}{H} \right\} = \log \frac{1}{H} \]

This is because, these readings have already been correlated with the known \( \left\{ \frac{1}{H} \right\} \) values of buffer solutions used for standardising the instrument. The validity of the use of these pH-meter readings in the case of water-organic solvent
media is based on the findings of Van Uitert and Haas\textsuperscript{72} who showed that a general relationship:

\[ -\log_{10}\sqrt{H} = B + \log f + \log U^0 \]  \hspace{1cm} (2.51)

applies not only for water but for water-dioxan mixtures and even to pure ethanol\textsuperscript{15} In the above equation, \( f \) is the activity coefficient of hydrogen ions in the solvent mixture under the consideration at the same temperature and ionic strength, and \( U^0 \) corresponds to the correction at zero ionic strength. For water, \( U^0 = 1 \) and at unit activity coefficient, \( \sqrt{H} = \frac{1}{\text{antilog } B} \). The \( f \) values may be obtained from the tables of Harned and Owen\textsuperscript{73} and the \( U^0 \) values from Van Uitert and Haas\textsuperscript{72}.

Equation (2.51) may then be written as:

\[ \frac{1}{\text{antilog } B} = \sqrt{H} f U^0 \]  \hspace{1cm} (2.52)

and in this form substituted in equation (2.34) for the easily determinable values of \( \sqrt{H} \).

The proton-ligand stability constants that are thus obtained are termed "practical constants", denoted by \( K^H_j \). They are related to the stoichiometric constants by the expression:
\[ k_j^H = \xi u_H^O \cdot k_j^H \]  
(2.53) 

and 
\[ \beta_j^H = (\xi u_H^O)^j \cdot k_j^H \]  
(2.54) 

\[ \log f u_H^O \] may be obtained as the intercept of the linear plot of \( nH \) against \( B \), using solutions of known hydrogen ion concentrations and used to convert "practical" constants into stoichiometric constants. However, these refinements are not in fact, necessary for calculating the stability constants of metal-ligand complexes.  

5.5 Calculation of \( p_L \) 

From equations (2.32), (2.35) and (2.36), one can obtain the relation:

\[ T_L'' = \bar{n}_T M'' = \sum_{j} \beta_j^{H} \sum_{i=0}^{j} (\beta_j^{H})^{i} \]  
(2.55) 

Rearranging this, one gets:

\[ \frac{1}{L_j^{m''}} = \frac{\sum_{i=0}^{j} \beta_j^{H} (\beta_j^{H})^{i}}{T_L'' - \bar{n}_T M''} \]  
(2.56) 

By a simple transformation one can obtained the expression:

\[ \log \frac{1}{L_j^{m''}} = p_L = \log_{10} \left\{ \frac{\sum_{i=0}^{j} \beta_j^{H} (\beta_j^{H})^{i}}{(\xi u_H^O)^j (T_L'' - \bar{n}_T M'')} \right\} \]  
(2.57)
Substituting equation (2.52) in the above and putting the values of $T_L''$ and $T_M''$ in a form similar to that in (2.44), one gets,

$$p_L = \log_{10} \left\{ \frac{\sum_{i=0}^{j} \beta_i^H \left( \frac{1}{\text{antilog B}} \right)^j}{T_L^0 - \bar{n} \ T_M^0} \frac{\gamma^O + \gamma^m}{v^O} \right\}... \quad (2.58)$$

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

5.6 Methods of determining the stoichiometric stability constants

Since the experimental data consists of values of $\bar{n}$ corresponding to various values of $\gamma L / \gamma$, the use of $N$ such pairs of values is sufficient to solve for the $N$ values of $\beta$, for any set of equilibrium reactions such as those given in equation (2.1). There are usually a much larger number of values available, although such data may not, at times, be fully representative of the complete formation curve. Further, a suitable choice of $\bar{n}$ and $\gamma L / \gamma$ values becomes necessary as shown below:

Equation (2.32) may be written in the following alternative form:
From the equation one can see that \((\bar{n}-1)\) becomes susceptible to even small errors in \(\bar{n}\), when the value of \(\bar{n}\) is close to an integer. This necessitates great care in the choice of the \(\bar{n}\) and \(\sum L_j\) values.

There are several methods adopted by different workers for the determination of stability constants using these values which have been reviewed by Irving and Rossotti\(^6\) and Hearon and Gilbert.\(^7\) Of these methods, the method suggested by Bjerrum\(^1\) and the least square method of Irving and Rossotti\(^6\) are the ones that are most commonly employed, particularly for systems where \(N = 2\). A description of these methods will now be given:

5.6a. The method of Bjerrum

This method makes use of a term defined by Bjerrum as the "spreading factor \(x\)" in order to relate two successive stability constants \(K_N\) and \(K_{N-1}\). According to Bjerrum,

\[
\frac{K_N}{K_{N-1}} = \left(\frac{1+\frac{1}{2}}{1}\right) \left(\frac{N-1 + \frac{1}{N-1}}{N-1}ight) x^2
\] (2.60)

where \(x\) is equal to unity in the ideal case but when \(N > 2\), it was assumed to be constant for the whole system with any
When \( N = 2 \), it turns out that

\[
\frac{K_1}{K_2} = 4 x^2 \quad \text{and since} \quad \beta_2 = K_1 K_2, \quad \text{we get}
\]

\[
K_1 = 2 x \beta_2^{\frac{3}{2}}
\]  \hspace{1cm} (2.61)

If one introduces this value in equation (2.31), for the condition \( N = 2 \), one gets

\[
\bar{n} = \frac{2x \beta_2^{\frac{3}{2}} \sum L_7 + 2 \beta_2 \sum L_7^2}{1 + 2x \beta_2^{\frac{3}{2}} \sum L_7 + \beta_2 \sum L_7^2}
\]  \hspace{1cm} (2.62)

The shape of the plot of \( \bar{n} \) vs \( pL \) depends on the value of \( x \). If \( x \gg 100 \), the curve has a wave-like character, indicating that the two steps are distinct; at \( x \ll 2 \), it is difficult to distinguish the two successive steps, while \( x = 0 \), the consumption of the ligand occurs in a single step.

The value of \( x \) itself is usually obtained from the mid-point slope \( \Delta \) of the curve obtained by plotting \( \bar{n} \) as a function of \( dpL \) from the relation:

\[
\Delta = -2.303 \left( \frac{1}{1+x} \right)
\]  \hspace{1cm} (2.63)

One can show that, for the case \( N = 2 \),
\[
\log K_1 = \frac{\rho L_1}{2}, \quad \log \left\{ \frac{2}{1+(1+12 \frac{K_2}{K_1})^{1/2}} \right\} \quad (2.64)
\]

and
\[
\log K_2 = \frac{\rho L_3}{2} - \log \left\{ \frac{2}{1+(1+12 \frac{K_2}{K_1})^{1/2}} \right\} \quad (2.65)
\]

where the subscripts of \( \rho L \) correspond to the \( \bar{n} \) values.

Under the condition that \( x \) has high or moderately high values, \( K_2/K_1 \) becomes very small and hence the above equations reduce to:

\[
\log K_1 = \frac{\rho L_1}{2} \quad (2.66)
\]

and
\[
\log K_2 = \frac{\rho L_3}{2} \quad (2.67)
\]

A generalisation of these relationships can be expressed as:

\[
\log K_\bar{n} = \frac{\rho L_{\bar{n}}}{2} \quad (2.68)
\]

since \( K_{\bar{n}-1} \gg K_{\bar{n}} \).

The log K values obtained in this manner are known as "half integral" values.

The equation (2.66) and (2.67) imply that at \( \bar{n} = \frac{1}{2} \), only M and ML are present in solution in significant quantities and ML_2 makes negligible contribution. From equations
(2.64) and (2.65), it is possible to calculate the values of 
x for a certain degree of accuracy in $K_1$ and $K_2$, for the 
equations (2.66) and (2.67) to be valid. It can be done by 
assigning a value to the second term in equation (2.64), and 
(2.65) such that it is equal to the permissible error and 
then calculating the values of $K_2/K_1$. The results obtained 
in this way are tabulated in Table II-1.

Table II-1: Spreading factors and permissible errors in 
$\log K_1$

<table>
<thead>
<tr>
<th>Permissible error in $\log K_1$ values</th>
<th>Maximum values of</th>
<th>$\log K_1/K_2$</th>
<th>$K_1/K_2$</th>
<th>$x$</th>
</tr>
</thead>
<tbody>
<tr>
<td>- 0.001</td>
<td>3.18</td>
<td>1500.00</td>
<td>19.36</td>
<td></td>
</tr>
<tr>
<td>- 0.005</td>
<td>2.42</td>
<td>260.80</td>
<td>8.08</td>
<td></td>
</tr>
<tr>
<td>- 0.01</td>
<td>2.10</td>
<td>126.30</td>
<td>6.37</td>
<td></td>
</tr>
<tr>
<td>- 0.02</td>
<td>1.78</td>
<td>60.91</td>
<td>3.90</td>
<td></td>
</tr>
<tr>
<td>- 0.10</td>
<td>0.96</td>
<td>9.20</td>
<td>1.52</td>
<td></td>
</tr>
</tbody>
</table>

For $\log K_1$ to be accurate with in $\pm$ 0.02, which is 
the usual accuracy with which the pH-meter can be read, the 
$\log K_1/K_2$ need only to be 1.78 or $x$ be 3.90. Hence, the 
half-integral values can be used in such cases.
The least square method of Irving and Rossotti

The equation (2.31) may be transformed into the following form for the case $N = 2$:

\[
\frac{n}{(n-1)\sqrt{L'}} = \frac{(2-n)\sqrt{L'}}{(n-1)} \frac{K_1K_2 - K_1}{n} \quad (2.69)
\]

This represents an equation for a straight line. A plot of $\frac{n}{(n-1)\sqrt{L'}}$ versus $\frac{(2-n)\sqrt{L'}}{(n-1)}$ is expected to give a straight line with an intercept of $K_1$ and a slope of $K_1K_2$. However, since $\sqrt{L'}$ may vary by several powers of ten, it is not very convenient to determine the value of $K_1$ and $K_2$ from such plots. On the other hand, a number of values of $\frac{n}{(n-1)\sqrt{L'}}$ and $\frac{(2-n)\sqrt{L'}}{(n-1)}$

may be tabulated for several points on the curve and the equation (2.31) solved to get the values of $K_1$ and $K_2$. Irving and Rossotti have shown that the values of $\bar{n}$ obtained from the experimental values of $pL$, together with the $K_1$ and $K_2$ values calculated by a least square method, agree with the experimental $\bar{n}$ values better than those obtained from the $K_1$ and $K_2$ values calculated by any other method.
In the use of this method, the points lying within the range $0.9 < \bar{n} < 1.1$ are most 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.

5.7 Thermodynamic quantities from stability constants

Strictly speaking, only the thermodynamic stability constants can be related to other thermodynamic quantities associated with complex formation. The stepwise thermodynamic stability constants $T_{K_i}$ are related to the stoichiometric constants $K_i$ by the expression:

$$ T_{K_i} = K_i \frac{f_{ML_i}}{f_{ML_{i-1}} f_L} \quad (2.70) $$

where $f_{ML_i}$, $f_{ML_{i-1}}$ and $f_L$ are the activity coefficients of the respective species. In practice, thermodynamic stability constants are seldom used due to the paucity of accurate data on activity coefficients of the various species. The failure of many of the attempts to obtain these data may be ascribed to the following reasons:

1) the non-availability of accurate information regarding factors such as liquid junction potentials involved in the experimental techniques;
ii) the lack of knowledge of single ion activity coefficients; and

iii) the incomplete validity of the several assumptions made in the calculations.

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

Under these circumstances, the stoichiometric stability constants are themselves employed directly to obtain thermodynamic quantities through the following relationships:

The free energy change accompanying the formation of the complex is given by:

\[ \Delta G = -2.303 \, RT \log K \]  \hspace{1cm} (2.71)

The enthalpy and entropy changes are related to the free energy change by the expression:

\[ \Delta G = \Delta H - T \Delta S \]  \hspace{1cm} (2.72)

Assuming that \( \Delta H \) is independent of temperature, the variation of the stability constant with temperature is given by
The complex formation involving a favourable entropy change is accompanied by small, negative $\Delta H$ (a weak bond formation) and is indicated by the stability constant changing little with temperature. On the other hand the formation of a strong bond is indicated by a marked dependence of the stability constant on temperature. These are usually compared by large unfavourable entropy changes.

\[
\frac{d \log K}{dT} = \frac{\Delta H}{2.303 RT^2} \tag{2.73}
\]