CHAPTER II

THEORY

2.1 Equilibrium Constants, Protonation Constants and Stability Constants

2.1.1 Concentration Constants and Activity Constants

An equilibrium constant is a quotient involving the concentrations or activities of reacting species in solution at equilibrium. Generally it is defined as the ratio of the product of the activities a of the reaction products, raised to appropriate power, to the products of the activities of the reactants, raised to appropriate power, illustrated by equation (2.1) where a, b, c and d are the stoichiometric coefficients of the solution species A, B, C and D respectively.

$$aA + bB \rightleftharpoons cC + dD \qquad K_{eq} = \frac{a_C^c \, a_D^d}{a_A^a \, a_B^b} \qquad (2.1)$$

The determination of the activities of complex ionic species at both infinite solution and in real solution is a complicated and time-consuming task. However concentrations are related to activities by the expression

$$a_X = [X] \, \gamma_X \qquad (2.2)$$

where a_X, $[X]$ and γ_X are activity, concentration and activity coefficient of X respectively. Activity coefficients of reacting species are in general tedious and difficult to measure. They also depend very significantly on the nature and concentrations of other species present in solution so that it is not possible to build universal tables of activity coefficients. Theoretical attempts at calculating activity coefficients, based on the Debye-Hückel approach and its extensions, are at best of only limited accuracy.

Substituting the activities from equation (2.2) in (2.1), then the equilibrium constant can be rewritten as follow.

$$K_{eq} \quad = \quad \frac{a_C^c \; a_D^d}{a_A^a \; a_B^b} \quad = \quad \frac{[C]^c \; [D]^d}{[A]^a \; [B]^t} \quad \cdot \quad \frac{\gamma_C^c \; \gamma_D^d}{\gamma_A^a \; \gamma_B^b} \quad\quad (2.3)$$

where[] indicates molar concentrations. If now it is possible to ensure that the term $\frac{\gamma_C^c \; \gamma_D^d}{\gamma_A^a \; \gamma_B^b}$ remains constant then the term $\frac{\gamma_C^c \; \gamma_D^d}{\gamma_A^a \; \gamma_B^b} \cdot K_{eq}$ is also a constant. Therefore, the equilibrium constant expressed in terms of the reacting species, called equilibrium concentration constant, K_c can be written as indicated by equation (2.4).

$$aA \; + \; bB \; \rightleftharpoons \; cC \; + \; dD \qquad K_c \; = \; \frac{[C]^c \; [D]^d}{[A]^a \; [B]^b} \qquad (2.4)$$

Equilibrium concentration constant, K_c is also known as the stoichiometric equilibrium constant which determined at constant ionic strength where as K_{eq} is indicated by equation (2.1) which is known as an equilibrium activity constant or thermodynamic equilibrium constant.
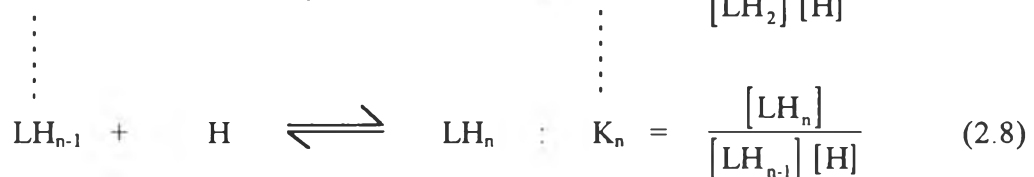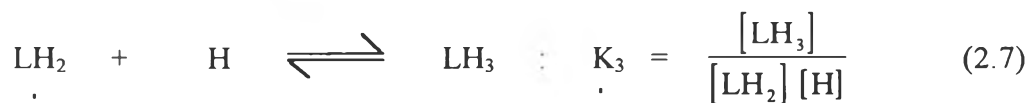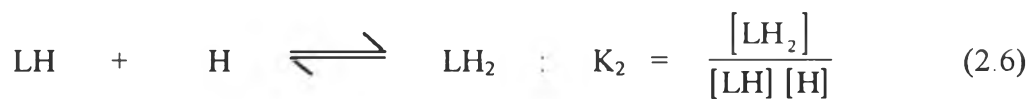
The term $\frac{\gamma_C^c \; \gamma_D^d}{\gamma_A^a \; \gamma_B^b}$ in equation (2.3) may be maintained effectively constant by , having a large excess of an inert background electrolyte present and using only low concentrations of the reacting ionic species so that any change in their concentrations as a result of their reaction together has an insignificant change on the overall ionic strength of the medium. It is generally possible to replace about 5% of the ions in the inert background electrolyte without appreciably altering the activity coefficients of the minor species present. However, in recording a stoichiometric equilibrium constant it is essential to record not only the concentration of the inert background electrolyte, but also its nature, since the activity coefficients depend on the electrolyte. Consequently, of course, in comparing stoichiometric equilibrium constants, only data obtained under
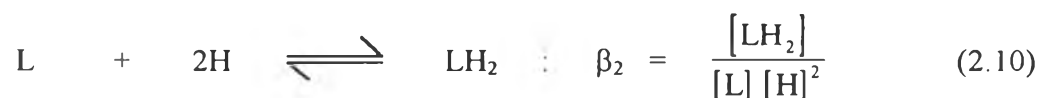
very similar conditions should be used unless the differences between the equilibrium constants are large.
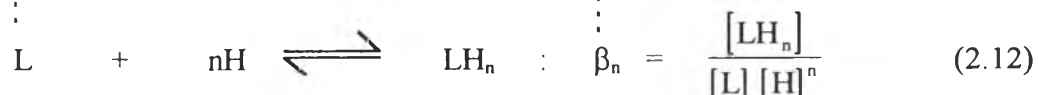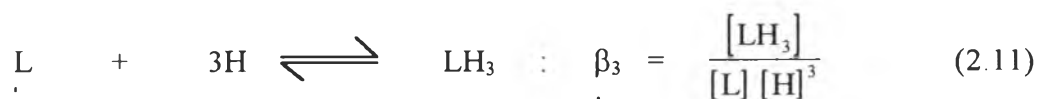
2.1.2   Protonation Constants

The acid-base equilibria of the ligands can be treated by protonation and disprotonation constant. Protonation constant is the equilibrium constant for the addition the nth proton to a charged or uncharged ligand. Protonation constant is known as basicity constant. The reciprocal of protonation constant is called disprotonation constant and defined as the equilibrium constant for the splitting off n^{th} proton from a charged or uncharged ligand. Disprotonation constant is also known as acidity constant. The following equations define these constants and show their interrelation.

$$L \quad + \quad H \quad \rightleftharpoons \quad LH \quad : \quad K_1 = \frac{[LH]}{[L][H]} \tag{2.5}$$

$$LH \quad + \quad H \quad \rightleftharpoons \quad LH_2 \quad : \quad K_2 = \frac{[LH_2]}{[LH][H]} \tag{2.6}$$

$$LH_2 \quad + \quad H \quad \rightleftharpoons \quad LH_3 \quad : \quad K_3 = \frac{[LH_3]}{[LH_2][H]} \tag{2.7}$$

$$\vdots$$

$$LH_{n-1} \quad + \quad H \quad \rightleftharpoons \quad LH_n \quad : \quad K_n = \frac{[LH_n]}{[LH_{n-1}][H]} \tag{2.8}$$

Another way of expressing the equilibria relations can be shown as follow:

$$L \quad + \quad H \quad \rightleftharpoons \quad LH \quad : \quad \beta_1 = \frac{[LH]}{[L][H]} \tag{2.9}$$

$$L \quad + \quad 2H \quad \rightleftharpoons \quad LH_2 \quad : \quad \beta_2 = \frac{[LH_2]}{[L][H]^2} \tag{2.10}$$

$$L \quad + \quad 3H \quad \rightleftharpoons \quad LH_3 \quad : \quad \beta_3 \quad = \quad \frac{[LH_3]}{[L][H]^3} \qquad (2.11)$$

$$L \quad + \quad nH \quad \rightleftharpoons \quad LH_n \quad : \quad \beta_n \quad = \quad \frac{[LH_n]}{[L][H]^n} \qquad (2.12)$$
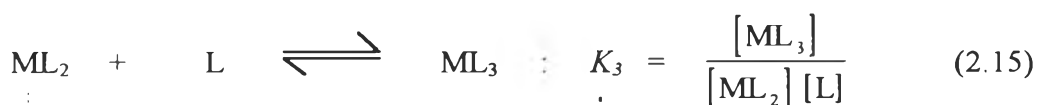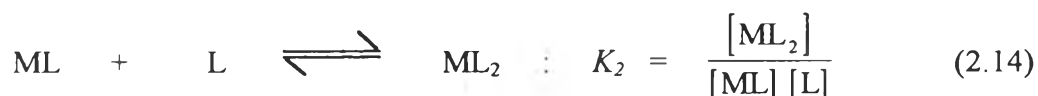
The K_i's are called the stepwise protonation constants and the β_i's are called the overall or cumulative protonation constants.
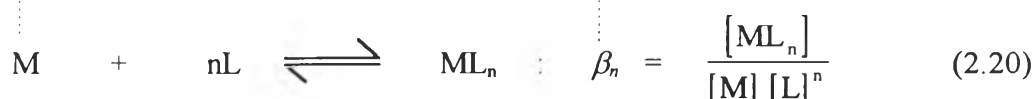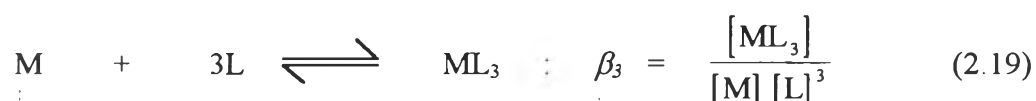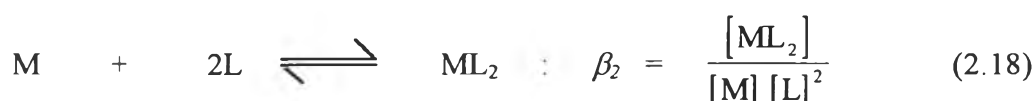
2.1.3 Stability Constants

The thermodynamic stability of complex equilibria can be characterized by stability constant and instability constant. Stability constant is a *n* equilibrium constant for the interaction of metal with ligand. Sometime stability constant is called as formation constant. In older literature, the inverse of stability constant is used and this is known as instability constant.

If the solution containing metal ions, M and ligand, L the system at equilibrium may be described by the following equations and equilibrium constants.

$$M \quad + \quad L \quad \rightleftharpoons \quad ML \quad : \quad K_1 \quad = \quad \frac{[ML]}{[M][L]} \qquad (2.13)$$

$$ML \quad + \quad L \quad \rightleftharpoons \quad ML_2 \quad : \quad K_2 \quad = \quad \frac{[ML_2]}{[ML][L]} \qquad (2.14)$$

$$ML_2 \quad + \quad L \quad \rightleftharpoons \quad ML_3 \quad : \quad K_3 \quad = \quad \frac{[ML_3]}{[ML_2][L]} \qquad (2.15)$$

$$ML_{n-1} \quad + \quad L \quad \rightleftharpoons \quad Ml_n \quad : \quad K_n \quad = \quad \frac{[ML_n]}{[ML_{n-1}][L]} \qquad (2.16)$$

There will be n such equilibria, where n represents the maximum coordination number of the metal ion M for the ligand L. Another way of expressing the equilibria relations can be shown as follow:

$$M \; + \; L \; \rightleftharpoons \; ML \; : \; \beta_1 \; = \; \frac{[ML]}{[M][L]} \tag{2.17}$$

$$M \; + \; 2L \; \rightleftharpoons \; ML_2 \; : \; \beta_2 \; = \; \frac{[ML_2]}{[M][L]^2} \tag{2.18}$$

$$M \; + \; 3L \; \rightleftharpoons \; ML_3 \; : \; \beta_3 \; = \; \frac{[ML_3]}{[M][L]^3} \tag{2.19}$$

$$M \; + \; nL \; \rightleftharpoons \; ML_n \; : \; \beta_n \; = \; \frac{[ML_n]}{[M][L]^n} \tag{2.20}$$

Since there can be only n independent equilibria in such a system, it is clear that the K_i's and β_i's must be related. The relationship is indeed rather obvious. Consider, for example, the expression for β_3 let us multiply both numerator and denominator by [ML] [ML$_2$] and then rearrange slightly :

$$\beta_3 \quad = \quad \frac{[ML_3]}{[M][L]^3} \cdot \frac{[ML][ML_2]}{[ML][ML_2]} \tag{2.21}$$

$$= \quad \frac{[ML]}{[M][L]} \cdot \frac{[ML_2]}{[ML][L]} \cdot \frac{[ML_3]}{[ML_2][L]} \tag{2.22}$$

$$= \quad K_1 . K_2 . K_3 \tag{2.23}$$

It is not difficult to see that this kind of relationship is perfectly general, namely.

$$\beta_k \quad = \quad K_1 . K_2 . K_3 ... K_k \quad = \quad \prod_{i=1}^{i=k} K_i \tag{2.24}$$

The K_i's are called the stepwise formation constants and the β_i's are called the overall or cumulative formation constants (or stepwise stability constant and overall stability constants).

2.2   Analysis of Data

2.2.1   Definitions of the Basic Components and Basic Equations

The first step in the description of equilibrium systems is the definition of the components. In the chemistry of complex equilibria, it is obvious to choose the free ligand(s) and species such as proton and metal ion(s) that they are not capable of further dissociation as the basic components. The components of some m-component equilibrium system are denoted by k_1, k_2, ... k_m and their total concentrations by T_1, T_2, ... T_m. The number of species namely metal ions(s), ligand(s), proton, proton complexes, mono-nuclear and polynuclear complexes, is n, and they are symbolized by A_1, A_2, ... A_n. In a species A_j, the number of component i is given by the *stoichiometric coefficients* α_{ji}. The series A_1, A_2, ... A_n is chosen so that its first m members are the same as the components k_1, k_2, ... k_m i.e. $A_i = k_i$ if $i \leq m$. The stoichiometric coefficients for the components are therefore 1 if $j = i$, and 0 if $j \neq i$. To illustrate the notations, let us consider a system containing a metal ion **M**, a ligand **L, H^+** and **OH** ions, ligand protonated species **LH** and **LH$_2$**, parent complexes **ML** and **ML$_2$**, a protonated complex **MLH**, and a mixed hydroxo complex **ML(OH)**. The compositions of the species A_1, A_2, ..., A_{10} in this three components system are given by the α_{ji} value tabulated in Table 2.1.

Table 2.1 α_{ji} values for an equilibrium system containing components (M, L and H) and species.

	Species	Components		
		stoichiometric coefficient, α_{ji}		
		k_1	k_2	k_3
		M	L	H
k_1	A_1 = M	1	0	0
k_2	A_2 = L	0	1	0
k_3	A_3 = H	0	0	1
	A_4 = LH	0	1	1
	A_5 = LH_2	0	1	2
	A_6 = ML	1	1	0
	A_7 = M_2L	2	1	0
	A_8 = MLH	1	1	1
	A_9 = MLH_{-1} or ML(OH)	1	1	-1
	A_{10} = H_{-1} or OH^-	0	0	-1

The arrangement of the α_{ji} data in Table 2.1 is termed the *composition matrix* of the equilibrium system. The first *m* rows of the composition matrix contain the *m*-order unit matrix relating to the components, while the other rows refer to the other species in the system, in an arbitrary arrangement. With the exception of the first *m* rows and the final row relating to OH^-, each row of the composition matrix corresponds to a

chemical reaction. The stoichiometric numbers give the numbers of the various components in the composition of the given species. Thus, the equilibrium reaction describing the formation of the species may be written in the form

$$\alpha_{j1} k_1 + \alpha_{j2} k_2 + \dots + \alpha_{jm} k_m \; \rightleftharpoons \; A_j \tag{2.25}$$

On application of the law mass action to the individual formation processes, the formation constant of some species A_j is defined by

$$\beta_j = \frac{[A_j]}{[k_1]^{\alpha_{j1}}[k_2]^{\alpha_{j2}}\dots[k_m]^{\alpha_{jm}}} \tag{2.26}$$

The notations used so far provide a simple possibility for expressing the total concentrations of the components $k_1, \dots, k_m$. Since the number of component i in some optional species A_j is α_{ji}, A_j contributes to the total concentration of component i with α_{ji} times of its own concentration, i.e.

$$T_i = \sum_{j=1}^{n} \alpha_{ji} [A_j] \tag{2.27}$$

Expressing the concentration of A_j from eq. (2.26) substituting into eq. (2.27) and considering every component, we obtain the following system of equations

$$T_1 = \sum_{j=1}^{n} \alpha_{j1} \beta_j [k_1]^{\alpha_{j1}} [k_2]^{\alpha_{j2}} \dots [k_m]^{\alpha_{jm}} \tag{2.28}$$

$$T_2 = \sum_{j=1}^{n} \alpha_{j2} \beta_j [k_1]^{\alpha_{j1}} [k_2]^{\alpha_{j2}} \dots [k_m]^{\alpha_{jm}} \tag{2.29}$$

$$T_m = \sum_{j=1}^{n} \alpha_{jm} \beta_j [k_1]^{\alpha_{j1}} [k_2]^{\alpha_{j2}} \dots [k_m]^{\alpha_{jm}} \tag{2.30}$$

These equations are the most important in describing complex equilibrium systems. They are essentially the mass balance expressed in terms of the concentrations of the

components, the formation constants of the species, and the stoichiometric numbers. For the descriptions of special equilibrium systems, use is frequently made of the charge balance too, which reflects the principle of electroneutrality. However, the charge balance is always applied instead of the mass balance for some component. The left-hand side of eq. (2.30) features the total concentrations; these are usually termed the analytical concentrations. However, the total and analytical concentrations relating to the proton are not identical concepts, though they are often confused. In the subsequent discussion, the analytical concentration of the proton refers to the proton concentration added to the system, and the total concentration is the quantity defined by. Therefore, the total proton concentration may be negative as a result of the negative stoichiometric numbers.
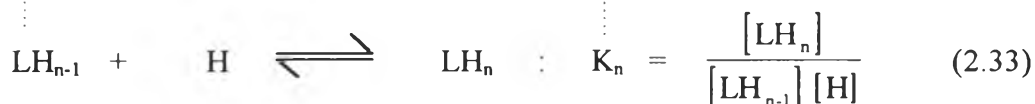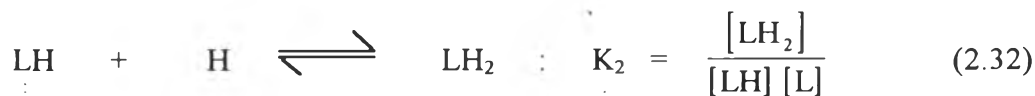
2.2.2   Secondary Concentration Variables

In order to evaluate the stability constant (K) for a simple system, in theory, it is only necessary to prepare a single solution containing a known total amount of metal ion $[M]_T$ and ligand $[L]_T$ and measure one of the three remaining unknown concentrations. These are the free metal ion concentration $[M]$, the free ligand concentration $[L]$ and the metal -ligand complex concentration $[ML]$.

In order to evaluate these stability constants, it is necessary to find a relationship between them and the experimentally determined variables ($[M]$, $[L]$, $[H]$ etc.). This relationship is often established via the definition of secondary concentration variables. It is from these variables that the stability constants are calculated.

2.2.2.1 The protonation formation function ($\bar{p}$)

Protonation equilibria of a ligand **L** interacting in a solution of constant ionic strength can be written as follow :

$$L \quad + \quad H \quad \rightleftharpoons \quad LH \quad : \quad K_1 \;=\; \frac{[LH]}{[L]\,[H]} \qquad (2.31)$$

$$LH \quad + \quad H \quad \rightleftharpoons \quad LH_2 \quad : \quad K_2 \;=\; \frac{[LH_2]}{[LH]\,[L]} \qquad (2.32)$$

$$LH_{n-1} \quad + \quad H \quad \rightleftharpoons \quad LH_n \quad : \quad K_n \;=\; \frac{[LH_n]}{[LH_{n-1}]\,[H]} \qquad (2.33)$$

When n is a number of the proton bind to the ligand L. The mass balance equations for the total concentration of the ligand and proton can be written below.

$$[L]_T \;=\; [L] + [LH] + [LH_2] + \ldots + [LH_n] \qquad (2.34)$$

$$[H]_T \;=\; [H] + [LH] + 2\,[LH_2] + \ldots + n\,[LH_n] \qquad (2.35)$$

A function $\bar{p}$ defined as the average number of proton H bind to the ligand L :

$$\bar{p} \;=\; \frac{\text{total bound proton}}{\text{total ligand}} \;=\; \frac{[H^+]_T - [H^+] + [OH^-]}{[L]_T} \qquad (2.36)$$

when $[H^+]$ is concentration of the free proton obtained from the measurement. $[OH^-]$ is the concentration due to the titrant which can be converted to $[H^+]$ via the relation of the autoprotolysis constant of methanol. The relationship between the $\bar{p}$ and the increasing of proton, as log $[H^+]$, should illustrate the curve as shown in Figure 2.1
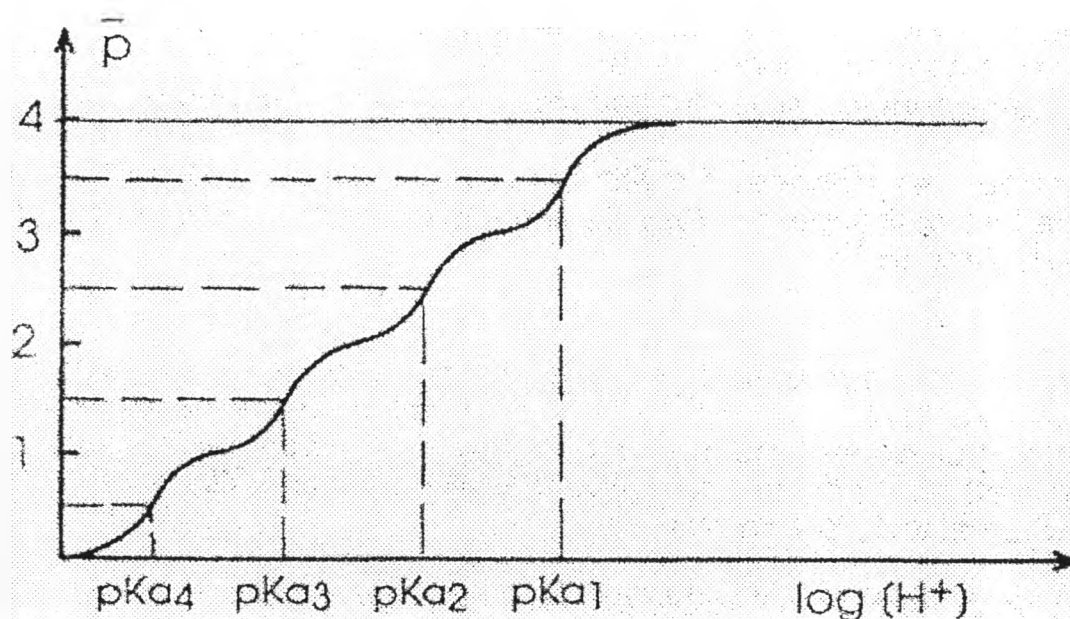
Figure 2.1 Plot of the protonation formation function ($\bar{p}$) ,against the logarithm of the free proton concentration (log [H$^+$]) for tetraacid.

2.2.2.2 The complex formation function ($\bar{n}$)

Let us consider a metal ion **M** and a ligand **L** interacting in a solution of constant ionic strength. The equilibria present are:

$$M \quad + \quad L \quad \rightleftharpoons \quad ML \qquad K_1 = \frac{[ML]}{[M][L]} \qquad (2.37)$$

$$ML \quad + \quad L \quad \rightleftharpoons \quad ML_2 \qquad K_2 = \frac{[ML_2]}{[ML][L]} \qquad (2.38)$$

$$ML_{n-1} \quad + \quad L \quad \rightleftharpoons \quad ML_n \qquad K_n = \frac{[ML_n]}{[ML_{n-1}][L]} \qquad (2.39)$$

The maximum value of n, written N, will be a function of both the maximum coordination number of the metal ion and the multidentate nature of the ligand . We

can now write mass balance equations for both the total metal ion and total ligand concentrations

$$[M]_T \quad = \quad [M] + [ML] + [ML_2] + \dots + [ML_n] \qquad (2.40)$$

$$[L]_T \quad = \quad [L] + [ML] + 2[ML_2] + \dots + n[ML_n] \qquad (2.41)$$

A function $\bar{n}$ defined as the average number of ligands L attached to the metal M may be written

$$\bar{n} = \frac{\text{total bound ligand}}{\text{total metal}} = \frac{[L]_T - [L]}{[M]_T} \qquad (2.42)$$

Substituting equations (2.40) and (2.41) in (2.42) yields

$$\bar{n} = \frac{[ML] + 2[ML_2] + \dots + n[ML_n]}{[M] + [ML] + [ML_2] + \dots + [ML_n]} \qquad (2.43)$$

In summation terms equation (2.43) becomes

$$\bar{n} = \frac{\sum_{n=1}^{n=N} n[ML_n]}{[M] + \sum_{n=1}^{n=N}[ML_n]} \qquad (2.44)$$

where N is the maximum coordination number for the metal if L is a monodentate ligand. However K_n and β_n are defined by

$$K_n = \frac{[ML_n]}{[ML_{n-1}][L]} \qquad (2.45)$$

$$\beta_n = \frac{[ML_n]}{[M][L]^n} \qquad (2.46)$$

In addition , $\beta_n = K_1 K_2 K_3 .... K_n$ (2.47)

and on substituting equation (2.45) into (2.43) gives

$$\bar{n} = \frac{K_1[M][L] + 2K_1 K_2[M][L]^2 + ... + nK_1 K_2 ... K_n [M][L]^n}{[M] + K_1[M][L] + K_1 K_2[M][L]^2 + ... + K_1 K_2 ... K_n [M][L]^n}$$ (2.48)

and after dividing through by [M] and remembering equation (2.47)

$$\bar{n} = \frac{\beta_1 [L] + 2\beta_2 [L]^2 + ... + n\beta_n [L]^n}{1 + \beta_1 [L] + \beta_2 [L]^2 + ... + \beta_n [L]^n}$$ (2.49)

which may be more conveniently written in summation terms

$$\bar{n} = \frac{\sum_{n=1}^{n=N} n \beta_n [L]^n}{1 + \sum_{n=1}^{n=N} \beta_n [L]^n} \equiv \frac{\sum_{n=1}^{n=N} n \beta_n [L]^n}{\sum_{n=0}^{n=N} \beta_n [L]^n}$$ (2.50)
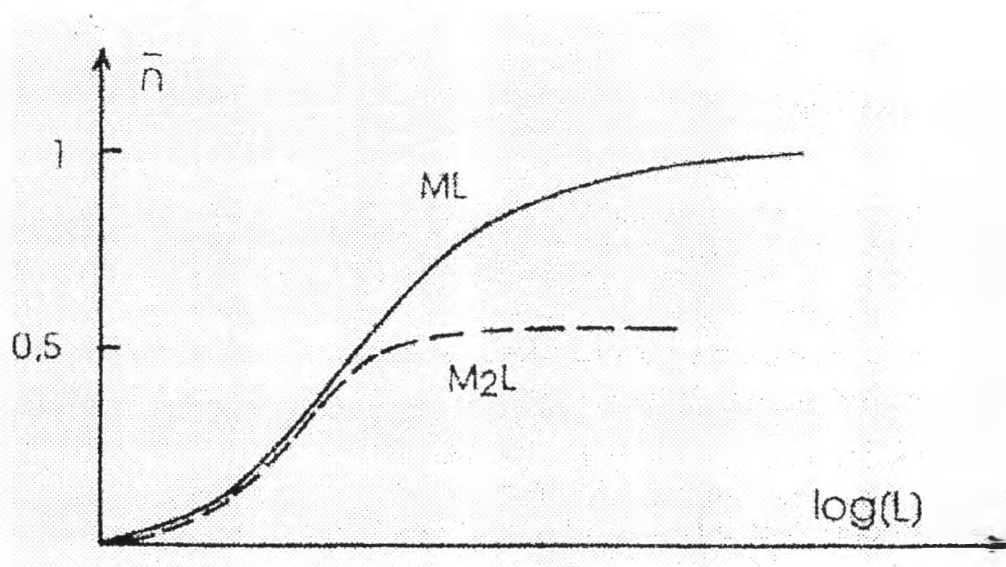

Figure 2.2 Plot of the formation function $\bar{n}$, against the logarithm of the free ligand concentration (log [L]) for mononuclear complex and binuclear complex.

2.2.2.3 The degree of formation (α_c)

For any individual component of the system, a variable α_c can be defined such that

$$\alpha_c = \frac{[ML_c]}{[M]_T} \qquad \text{for c = 0, 1, 2, ...N} \tag{2.51}$$

This variable α_c is partial mole fraction of the component ML_c. The degree of formation of the system as a whole may be considered, and another variable α_T can be defined

$$\alpha_T = \sum_{c=1}^{c=N} \alpha_c \tag{2.52}$$

where α_T is the fraction of total metal bound to ligand in the form of a complex. By an analogous procedure to that used to derive equation (2.50), we can write α_c in summation terms

$$\alpha_c = \frac{\displaystyle\sum_{c=1}^{c=N} \beta_c [L]^c}{1 + \displaystyle\sum_{c=1}^{c=N} \beta_c [L]^c} \equiv \frac{\displaystyle\sum_{c=1}^{c=N} \beta_c [L]^c}{\displaystyle\sum_{c=0}^{c=N} \beta_c [L]^c} \tag{2.53}$$

One interesting solution to equation (2.51) is when c =0 and hence

$$\alpha_0 = \frac{[M]}{[M]_T} \tag{2.54}$$

This function, α_0 gives the species distribution for the free metal ion in the solution. When no complex formation takes place then α_0 is unity because $[M]_T = [M]$. Hence it is possible to plot a series of the component distribution curves of α_c versus $[M]_T$ or $[L]_T$. The α_c function is used to show at a glance the relative proportions of each of the species present in solution.

2.2.2.4 The degree of complex formation (ϕ)

A third secondary concentration variable ϕ is defined as :

$$\phi = \frac{[M]_T}{[M]} = 1 + \sum_{n=1}^{n=N} \beta_n [L]^n \qquad (2.55)$$

At this stage it is valuable to summarize the definitions of three secondary concentration variables that we have met so far. This, together with experimental data that must be available to use each of them, is given in Table 2.2 .

Table 2.2   Summary of the secondary concentration variables

Variable	Title	Definition	Experimental observable required
$\bar{n}$	complex formation function	$([L]_T - [L]) \, / \, [M]_T$	$[M]_T, [L]_T, \, [L]$
α_c	degree of formation	$[ML_c] \, / [M]_T$	$[M]_T, [L]_T, \, [L]$
ϕ	degree of the complex formation	$[M]_T \, / [M]$	$[M]_T, [M]$

2.2.3   Linear Method, Errors and Statistics

Stability constants are not directly measurable but must be calculated from an observed response function of a fixed, but experimentally adjustable, variable. Since the response data are subject to random error and indeed may be subject to systematic errors if we have not controlled the experiment well, the stability constants will be calculated with limited precision. However, it is important to have an estimate of the precision of any calculated constants, as it will indicate the reliability of the value obtained and in turn

the efficiency of the experiment. In addition we need to have an idea about mathematical model is in describing the data.

2.2.3.1 Model Building

Experiments attempts to find some functional form for the way quantities in nature are related. We try to build up a mathematical model. It may be an assumed one, in which case we need to measure of how good the model is in describing our data, or it may be derived from first principles and then tested experimentally. The model may be approximate, which may still be acceptable, especially initially, and may then be refined or modified in the further experimental observations. The typical experiment consists of fixing one group of variables called independent variables, at known values and then making observations of another dependent variables. In stability constant work the independent variables might be temperature, ionic strength, or the concentration of one or more components and dependent variables the e.m.f. or pH or absorbency of the solution. We then calculate or estimate the parameters of interest from the assumed functional from relating the dependent to the independent variables.

The parameters for our model are calculated by fitting them to the experimental data. This may be done either graphically or by a mathematical procedure, such as least-squares. The latter calculates the values of the parameters which the sum of the squares of the residuals is defined as the difference between the observed and calculated data points at each fixed value of the independent variable is a minimum. In addition the method of least-squares allows us to obtain estimates of the errors in the parameters of interest and to estimate the 'goodness of fit' of the assumed model, that is, it allows us to test alternative hypothesis.

2.2.3.2 Random Errors

Random or observational errors are assumed to follow a Gaussian or normal distribution , expressed mathematically as

$$f(r_x) = \frac{1}{\sqrt{2}\sigma_x} e^{-r_x^2/2\sigma_x^2} \qquad (2.56)$$

where r_x is the residual of x or observed value - true value, σ_x^2 is the variance of x and σ_x is the standard deviation.

The probability of observing the i th residual, P_i in the region r_{xi} to $r_{xi} + dr_{xi}$ is:

$$dP_i = \frac{1}{\sqrt{2}\sigma_x} e^{-r_{xi}^2/2\sigma_x^2} dr_{xi} \qquad (2.57)$$

Now the probability of obtaining a given set of n observations, P is the product of the probabilities of each of i th measurements.

$$dP = \prod_{i=1}^{i=n} dP_i = \prod_{i=1}^{i=n} \left(\frac{d\ r_{xi}}{\sqrt{2}\ \sigma_x}\right) e^{-\left(\frac{1}{2\sigma_x^2}\right)\sum r_{xi}^2} \qquad (2.58)$$

Based on the statistical principle of maximum likelihood this probability becomes a maximum when the sum of the squares residuals is a minimum.

$$\sum_{i=1}^{n} r_{xi}^2 = \text{minimum} \qquad (2.59)$$

Hence the origin of the term 'least squares' is apparent.

The discussion so far has assumed that the measurements of x have all come from the same population distribution, that is, the variance of the residuals are equal. If this is not so, equation (2.57) should be rewritten as :

$$dP_i = \frac{1}{\sqrt{2}\sigma_{xi}} e^{-r_{xi}^2/2\sigma_{xi}^2} dr \qquad (2.60)$$

and the equation (2.58) becomes

$$dP = \prod_{i=1}^{i=n} dp_i = \prod_{i=1}^{i=n} \left(\frac{d\, r_{xi}}{\sqrt{2}\, \sigma_{xi}} \right) e^{-\frac{1}{2}\Sigma\left(r_{xi}^2 / \sigma_{xi}^2 \right)} \tag{2.61}$$

and the least-squares principle gives:

$$\sum_{i=1}^{i=n} \left(\frac{r_{xi}^2}{\sigma_{xi}^2} \right) = \text{minimum} \tag{2.62}$$

A quantity inversely proportional to the variance is termed the weight of an observation. Hence:

$$w_{xi} = \frac{\sigma_0^2}{\sigma_{xi}^2} \tag{2.63}$$

where σ_0^2 is known as the variance of an observation of unit weight. In practice σ_0^2 will often have the value of unity. The quantity now to be minimized is the sum of the weighted squares of the residuals.

$$\sum_{i=1}^{i=n} w_{xi}\, r_{xi}^2 = \text{minimum} \tag{2.64}$$

In practice we cannot know the true value of x , but the principle of least-squares attempts to adjust the estimate of x according to equation (2.64). Generally the experimental data are function of the parameter x so that r_{xi} in equation (2.64) is defined as:

$$r_{xi} = \left[f(x_i) - f(\bar{x}) \right] \tag{2.65}$$

and $\bar{x}$ is the least-squares estimator of the true value of the parameter.

2.2.3.3 Systematic Errors

Systematic errors are caused by the limitations of the apparatus, or experimenter, and introduce bias into the data resulting in inaccurate parameters. Thus it is possible to obtain high precision with poor accuracy, as indicated diagrammatically in Figure 2.3.
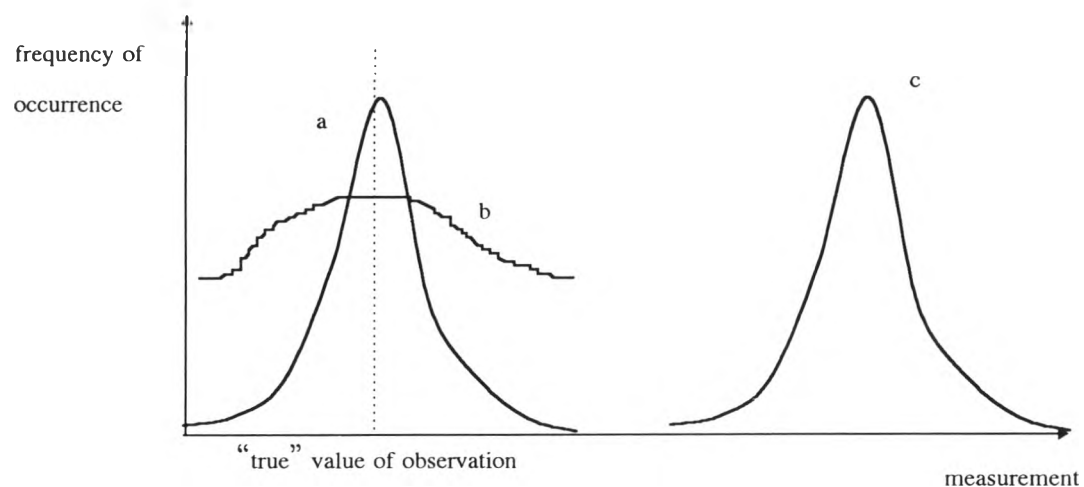

Figure 2.3 Diagrammatic representation of types of experimental error : (a) high precision, high accuracy ; (b) low precision, high accuracy (due to large random errors); (c) high precision, poor accuracy (due to systematic errors).

2.2.4 Non-Linear Parameter Estimation

2.2.4.1 Least -squares-extension case

To extend least-squares theory to the non-linear case, that is the situation where the dependent variables are non-linear functions of the independent variables, we take equation and express the dependent variables (observables) as a function of the unknowns by a Taylor series expansion. Thus if the initial estimates of the

parameter values are $\left(x_1^0 \; x_2^0 \; ... x_m^0 \right)$ then the observables are expressed about this point in parameter space by:

$$o_i = f_i \left(x_1^o ... x_m^0 \right) + \left(\frac{\partial f_i}{\partial x_i} \right)_0 \left(x_1 - x_1^o \right) + ... + \left(\frac{\partial f_i}{\partial x_m} \right)_0 \left(x_m - x_m^o \right) \qquad (2.66)$$

that is

$$o_i = f_i \left(x_1^o ... x_m^0 \right) + \sum_{j=1}^{j=m} \left(\frac{\partial f_i}{\partial x_j} \right)_0 \Delta x_j \qquad (2.67)$$

where terms higher than first order have been neglected. Therefore the change in the observables Δo_i on making the corrections Δx_j are given by

$$\Delta o_i = o_i - f_i \left(x_1^o ... x_m^0 \right) = \sum_{j=1}^{j=m} \left(\frac{\partial f_i}{\partial x_j} \right)_0 \Delta x_j \qquad (2.68)$$

2.2.4.2 Hypothesis testing

Another quantity which has been used in non-linear estimation situations is the Halmilton R-factor. In this procedure the R-factor defined by :

$$R = \left[\frac{\sum\limits_{i=1}^{i=n} w_i \left(o_i^{calc} - o_i^{obs} \right)^2}{\sum\limits_{i=1}^{i=n} w_i \left(o_i^{obs} \right)^2} \right]^{\frac{1}{2}} \qquad (2.69)$$

is compared with R $_{lim}$ calculated from :

$$R_{\text{lim}} = \left[\frac{\sum\limits_{i=1}^{i=n} w_i\, e_i^2}{\sum\limits_{i=1}^{i=n} w_i \left(o_i^{\text{obs}}\right)^2} \right]^{\frac{1}{2}}$$
(2.70)

where e_i is the residual in the i th equation calculated form estimates of the errors in all the experimental quantities using error propagation rules, o_i^{calc} and o_i^{obs} are the calculated and the observed values of the response variable respectively, w_i are the appropriate weighting factors. A satisfactory fit is assumed if $R < R_{\text{lim}}$.

2.3 Computation of Equilibrium Constants by SUPERQUAD Programme

The computer programme, SUPERQUAD[26] has been widely used to calculate stability constants of species in solution equilibria from data obtained by potentiometric method. The formation constants are determined by minimization of an error-square sum based on measure electrode potentials. The programme also permits refinement of any reactant concentration or standard electrode potential. The refinement is incorporated in to new procedure which can be used for model selection. The assumptions for computation of formation constants by SUPERQUAD could be described as follows.

Assumptions : There are number of assumptions underlying the whole treatment, and each needs to be considered explicitly.

1. For each chemical species A_aB_b... in the solution equilibria, there is a chemical constant, the formation constant, which is expressed as a concentration quotient in equation (2.71).

$$\beta_{ab\cdots} = \frac{[A_aB_b\ldots]}{[A]^a[B]^b\ldots}$$
(2.71)

A, B... are the reactants (SUPERQUAD allows up to four of them) and [A], [B] are the concentrations of free reactant; electrical charges may be attached to any species,

but they are omitted for sake of simplicity in this discussion. Since the thermodynamic definition of a formation constant is as an activity quotient, it is to be assumed that the quotient of the activity coefficients is constant, an assumption usually justified by performing the experiments with a medium of high ionic strength .

2. Each electrode present exhibits a pseudo-Nernstian behavior, equation (2.72), where [A] is the concentration of the electro-active ion,

$$E = E^{\circ} + S_L \log [A] \tag{2.72}$$

E is the measured potential, and E° is the standard electrode potential. The ideal value of the slope S_L is of course RT/nF, but we assume only that it is a constant for a given electrode. The value of E° and S_L are usually obtained in a separate calibration experiment. Further there is a modified Nernst equation.

$$E = E^{\circ} + S_L \log [H^+] + r [H^+] + s [H^+]^{-1} \tag{2.73}$$

This equation was first suggested as means of taking into account junction potentials in strongly acidic and strongly basic condition.

3. Systematic errors must be minimized by careful experimental work. Sources of systematic error include electrode calibration, sample weighings and dilutions, standardization of reagents (use of carbonate-free alkali in particular), temperature variation and water quality. The last-named factor is more significant today than it was in the past, as water may be contaminated by titrable species which can pass through distillation columns by surface action. All statistical tests are based on the assumption that systematic errors are absent from the data.

4. The independent variable is not subject to error. Errors in the dependent variable are assumed to have a normal distribution. If these assumptions are true use of the principle of least squares will yield a maximum likelihood result, and computed residuals should not show systematic trends.

5. There exits a model of the equilibrium system, which adequately accounts for the experimental observations. The model is specified by a set of coefficients a, b , ..., one for each species formed. All least-squares refinements are performed in terms of an assumed model. Examination of a sequence of models should yield a best model which is not significantly different from the true model. Choice of the best model is known as species selection.

2.4 Inert Background Electrolyte

The study acid-base characteristics of ligand and their complexation properties toward metal, ionic strength will be controlled by inert background electrolyte present at a concentration far in excess that of the reacting ionic species under investigation. Inert background electrolyte is sometime called inert background solution or supporting electrolyte which is defined as eletrolyte which does not react with any of reacting species such as metal ion, ligand or metal-ligand species in the equilibrium being studied. The main function of the inert background electrolyte to keep the overall ionic strength and activity coefficient constant. Properties of the chosen inert background electrolyte must meet the following requirements

(1) a strong and non reacting (inert) electrolyte,

(2) no part of electrolyte involved in equilibrium under investigation,

(3) its cation must not associate with the ligand and with the complex species,

(4) its anion must not associate with the central metal ion and with the complex species,

(5) redox reaction must not occur between the constituents of the inert electrolyte and the central ion or ligand,

(6) its solubility has to be large enough,

(7) its contribution to the measured physical or chemical property must be negligible.

Inert background electrolytes that are commonly used in aqueous solvent are sodium salts such as the perchlorate or nitrate e.g. sodium perchlorate ($NaClO_4$), sodium nitrate ($NaNO_3$), perchlorate is usually more suitable than any other ions.

Sodium chloride (NaCl) has been used as a inert background electrolyte, but its use is less common that perchlorate or nitrate because chloride ions often form complexes with metal ions under study. Potassium salts such as potassium nitrate (KNO_3) and potassium chloride (KCl) have also been used occasionally, but potassium perchlorate ($KClO_4$) is unsuitable due to its low solubility in water.

Common background electrolytes used in the methanolic solution are tetraethylammonium perchlorate (Et_4NClO_4), and tetramethylammonium chloride (Me_4NCl). The Me_4NCl is not suitable for investigating the complex formation in the methanolic solution because chloride ions can form complexes with many transition metal ions. The background electrolytes for basicity study of the ligands and their complexation in the ethanolic solution is the tetramethylammonium nitrate (Me_4NNO_3). For the study chemical equilibria of the ligands and their complexation, the suitable background electrolytes in acetonitrile are tetramethylammonium perchlorate (Me_4NClO_4) and tetrabutylammonium perchlorate (Bu_4NClO_4).

The tetrabutylammonium trifluoromethanesulfonate ($Bu_4NCF_3SO_3$) was recently introduced to be used as the inert background electrolyte in methanol[27]. The $Bu_4NCF_3SO_3$ was examined for being used as the inert background in methanolic solution in order to avoid the use of explosive substance such as perchlorate salts.