# CHAPTER II

THEORY

2.1   Equilibrium Constant

2.1.1 Equilibrium Concentration Constant

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

$$aA + bB \rightleftharpoons cC + dD \qquad K_{eq} = \frac{a_C^c a_D^d}{a_A^a a_B^b} \qquad (2.1)$$
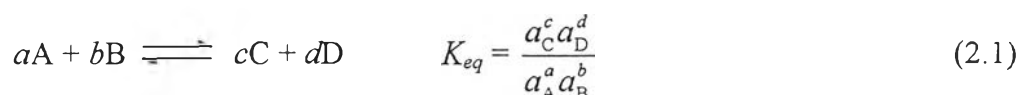
The determination of the activities of complex ionic species at both infinite dilution and in real solutions is a complicated and time-consuming task   Because concentration parallel activities of ionic solutes as illustrated by equation (2.2) where a_x, γ_x and [x] are activity, activity coefficient and concentration of x, respectively, when the ionic strength is controlled by a non-reacting electrolyte present at a concentration far in excess.

$$a = \gamma_x[x] \qquad (2.2)$$

Then the activity in the equation (2.2) can be substituted in equation (2.1). Therefore, the equilibrium constant (K_{eq}) can be rewritten as follow.

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

It is obviously indicated that the term $\dfrac{\gamma_C^c \gamma_D^d}{\gamma_A^a \gamma_B^b}$ is constant, then the term $K_{eq} \dfrac{\gamma_A^a \gamma_B^b}{\gamma_C^c \gamma_D^d}$ is also a constant. Therefore, the equilibrium constant can be expressed in terms of the reacting species, called equilibrium constant, K_c can be written as illutrated by equation (2.4).

$$aA + bB \rightleftharpoons cC + dD \qquad K_C = \frac{[C]^c [D]^d}{[A]^a [B]^b} \tag{2.4}$$
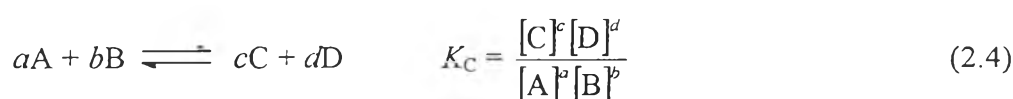
Equilibrium constant, K_c is known as the stochiometric equilibrium constant where as K_{eq} is indicated by equation (2.1) which is known as an equilibrium activity constant or thermodynamic equilibrium constant.

The term $\dfrac{\gamma_C^c \gamma_D^d}{\gamma_A^a \gamma_B^b}$ in equation (2.3) may be maintained effectively constant by,

a) having a large excess of an inert background electrolyte present which does not react with metal, ligand or metal-ligand species which are in the studied-system.

b) using only low concentrations of metal and ligand 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.

The ionic strength, μ is normally defined by the equation $\mu = \dfrac{1}{2}\sum c_i z_i^2$, where c_i and z_i are the concentration and the charge of species i, respectively. However, it has also been shown that ionic strength should be defined by the equation $\mu = \dfrac{1}{2}\sum c_i |z_i|$. The two definitions are identical for univalent ions but when significant concentrations of multivalent ions are present the latter should be used.
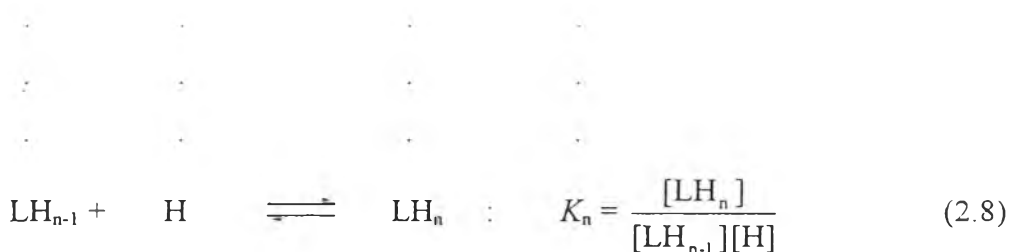
In general, it is possible to replace about 5% of the ions in the background electrolyte without appreciably altering the activity coefficients of the minor species
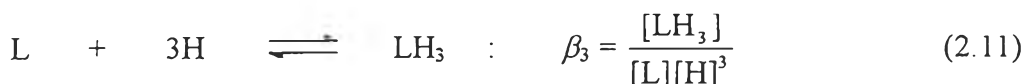
present. Because one of the principal applications of stability constant data is compare one ligand with another or one metal ion with another, the stochiometric stability constants are usually as good as thermodynamic stability constants. However, in recording a stochiometric stability constant, it is essential to record not only the concentration of the background electrolyte but also its nature, since the activity coefficients depend on the electrolyte. Consequently, of course, in comparing stability constants, only data obtained under very similar conditions should be used unless the differences between the stability constants are large.

2.1.2 Acidity and Basicity Constants

Just as complex equilibria can be characterized by stability and instability constants, the acid-base equilibria of the ligand can be treated by protonation and deprotonation constant. Protonation or basicity constant is the equilibrium constant for the addition of the nth proton to a charged or uncharged ligand. The reciprocal of protonation constant or acidity constant which is defined as the equilibrium constant for the splitting of nth proton from a charge or uncharged ligand. The equations for these equilibrium constants are shown as follow :

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

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

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

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

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

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

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

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

$$L \quad + \quad nH \quad \rightleftharpoons \quad LH_n \quad : \quad \beta_n = \frac{[LH_n]}{[L][H]^n} \tag{2.12}$$

The K_i 's and β_i 's are called the stepwise and cumulative protonation constants, respectively (where i represents 1, 2 ,3,...n).
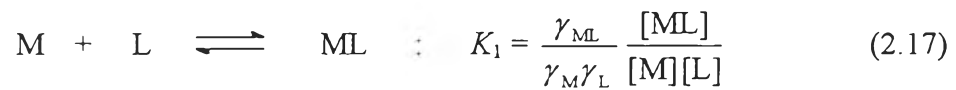
2.1.3 Stability Constants

Because of equilibrium constants depend on interaction of metal and ligand are referred to as stability constants. There are two types of stability, namely thermodynamic and kinetic. Equilibrium constants characterize the stability of the complexes which are usually called stability constants and sometimes are represented in the reciprocal of stability constant, namely instability constant.

If the studied solution have ligand, L and metal ion, M and corresponding equilibrium constants are expressed as follow.
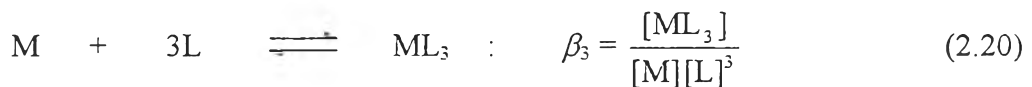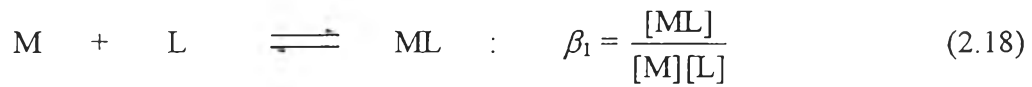
$$M \quad + \quad L \quad \rightleftharpoons \quad ML \quad : \quad K_1 = \frac{[ML]}{[M][L]} \tag{2.13}$$

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

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

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

All equilibrium constants which are stepwise constants from equations (2.13) to (2.16) are specifying in stochiometric stability constants which are shown in concentration term; since the term activity are constants. If the equilibrium constants are indicated by the product of activity coefficient term and concentration term as illustrated by equation 2.17, where γ_M, γ_{ML}, γ_L are activity coefficients, corresponding to their species.

$$M + L \rightleftharpoons ML \quad : \quad K_1 = \frac{\gamma_{ML}}{\gamma_M \gamma_L} \frac{[ML]}{[M][L]} \tag{2.17}$$

The overall or cumulative stability constants for n equilibria are expressed as follow

$$M + L \rightleftharpoons ML \quad : \quad \beta_1 = \frac{[ML]}{[M][L]} \tag{2.18}$$

$$M + 2L \rightleftharpoons ML_2 \quad : \quad \beta_2 = \frac{[ML_2]}{[M][L]^2} \tag{2.19}$$

$$M + 3L \rightleftharpoons ML_3 \quad : \quad \beta_3 = \frac{[ML_3]}{[M][L]^3} \tag{2.20}$$

$$M + nL \rightleftharpoons ML_n \quad : \quad \beta_n = \frac{[ML_n]}{[M][L]^n} \tag{2.21}$$

The result of β_n can be obtained the products of K_1 to K_n.

2.2   Secondary concentration variables

In order to evaluate the stability constant, K, for a simple system such as

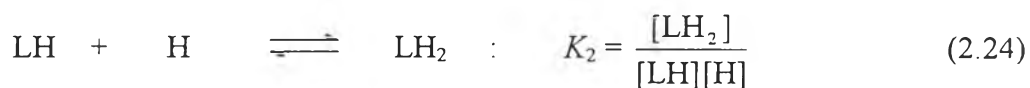$$M + L \rightleftharpoons ML \quad : \quad K_1 = \frac{[ML]}{[M][L]} \tag{2.22}$$

it is, in theory, 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, $[ML]$.

The advantages of the large amount of data obtained are confirming the system as illustrated by equation (2.21) and evaluating stability constant, K. To take full of advantage of the large amount of data obtained, a number of ingenious and subtle algebraic dodges have been developed. They are collectively known as secondary concentration variables.

2.2.1 The protonation formation, $\bar{p}$

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

$$L + H \rightleftharpoons LH \quad : \quad K_1 = \frac{[LH]}{[L][H]} \tag{2.23}$$

$$LH + H \rightleftharpoons LH_2 \quad : \quad K_2 = \frac{[LH_2]}{[LH][H]} \tag{2.24}$$

$$LH_{n-1} + H \rightleftharpoons LH_n \quad : \quad K_n = \frac{[LH_n]}{[LH_{n-1}][H]} \tag{2.25}$$

where n is a number of the proton bind to the ligand, L. The mass balance equation for the total concentration of the ligand and proton can be illustrated by

$$[L]_T \quad = \quad [L] + [LH] + [LH_2] + ... + [LH_n] \tag{2.26}$$

$$[H]_T \quad = \quad [H] + [LH] + 2[LH_2] + ... + n[LH_n] \tag{2.27}$$

A function, $\bar{p}$, defined as the average number of proton, H, bind to the ligand, L, can be expressed in equation (2.28)

$$\bar{p} = \frac{\text{total bound proton}}{\text{total ligand}} = \frac{[H^+]_T - [H^+] + [OH^-]}{[L]_T} \tag{2.28}$$

where $[H^+]$ is concentration of the free proton obtained from the measurement. $[OH^-]$ is the concentration due to the titrant base, which can be converted to $[H^+]$, *via* the relation of the autoprotolysis constant of methanol. The relationship between the $\bar{p}$ and the in creasing of proton, as log $[H^+]$ should be illustrated the curve as shown in Figure 2.1.
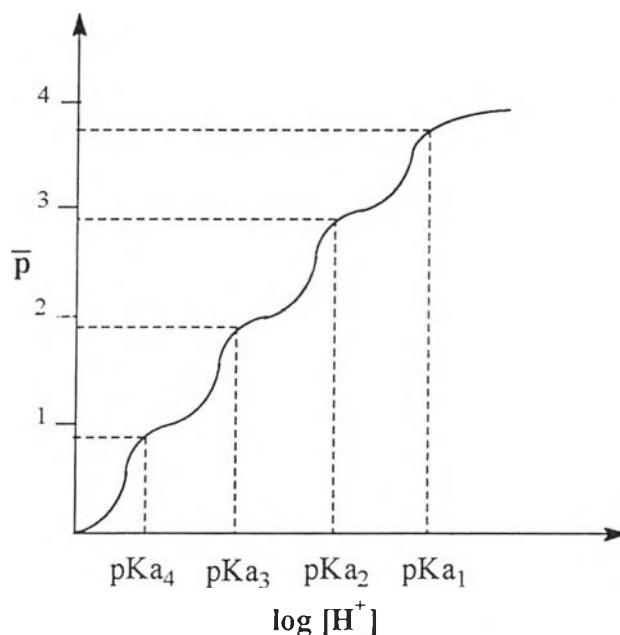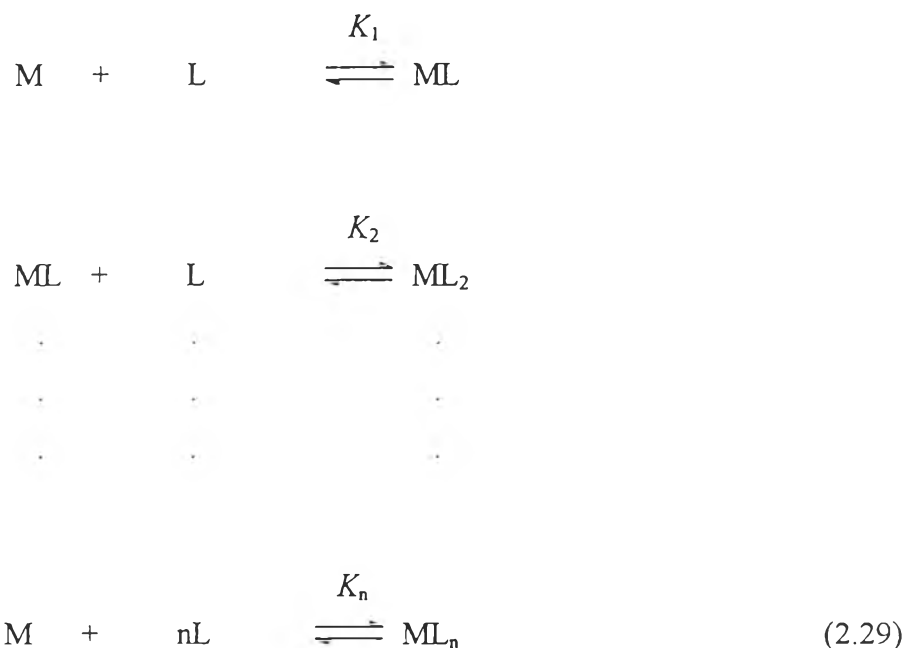

Figure 2.1 Plot of the protonation formation function, $\bar{p}$ against the logarithm of the free proton concentration, log $[H^+]$ for tetra acid.

2.2.2 The complex formation function, $\bar{n}$

Consider a metal ion, M, and a ligand, L, interacting in a solution of constant ionic strength. The equilibria present are :

$$M \quad + \quad L \quad \overset{K_1}{\rightleftharpoons} \quad ML$$

$$ML \quad + \quad L \quad \overset{K_2}{\rightleftharpoons} \quad ML_2$$

$$M \quad + \quad nL \quad \overset{K_n}{\rightleftharpoons} \quad ML_n \tag{2.29}$$

The maximum value of n, written N, will be a function of both the maximum coordination number of the metal ion and the multidentism of the ligand. Now, we can write mass balance equations for both the total metal ion, and total ligand concentrations :

$$[M]_T \quad = \quad [M] + [ML] + [ML_2] + \ldots + [ML_n] \tag{2.30}$$

$$[L]_T \quad = \quad [L] + [ML] + 2[ML_2] + \ldots + n[ML_n] \tag{2.31}$$

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

$$\bar{n} = \frac{\text{total bound ligand}}{\text{total metal}} = \frac{[L]_T - [L]}{[M]_T} \tag{2.32}$$

Substituting equations (2.30) and (2.31) in (2.33) yields

$$\bar{n} = \frac{[ML] + 2[ML_2] + ... + n[ML_n]}{[M] + [ML] + [ML_2] + ... + [ML_n]} \tag{2.33}$$

In summation terms equation (2.33) becomes

$$\bar{n} = \frac{\sum_{n=1}^{n=N} n[ML_n]}{[M] + \sum_{n=1}^{n=N} [ML_n]} \tag{2.34}$$

where N is the maximum coordination number for the metal if L is a monodentate ligand. Inspection of equation (2.34) shows that it will not help a great deal in evaluating $\bar{n}$, as $[ML_n]$ and [M] are not in general readily obtainable as experimental observables. K_n is defined by

$$K_n = \frac{[ML_n]}{[ML_{n-1}][L]} \tag{2.35}$$

and β_n as

$$\beta_n = \frac{[ML_n]}{[M][L]^n} \tag{2.36}$$

In addition, $\beta_n = K_1.K_2.K_3...K_n$ (2.37)

and, on substituting Equation (2.35) into (2.33) gives

$$\bar{n} = \frac{K_1[M][L] + 2K_1K_2[M][L]^2 + ... + nK_1K_2...K_n[M][L]^n}{[M] + K_1[M][L] + K_1K_2[M][L]^2 + ... + K_1K_2...K_n[M][L]^n} \tag{2.38}$$

and after dividing through by [M] and remembering equation (2.37)

$$\bar{n} = \frac{\beta_1[L] + 2\beta_2[L]^2 + \ldots + \beta_n[L]^n}{1 + \beta_1[L] + \beta_2[L]^2 + \ldots + \beta_n[L]^n} \tag{2.39}$$

which may be more conveniently written in summation terms

$$\bar{n} = \frac{\sum_{n=1}^{n=N} n\beta_n[L]^n}{1 + \sum_{n=1}^{n=N} \beta_n[L]^n} \equiv \frac{\sum_{n=1}^{n=N} n\beta_n[L]^n}{\sum_{n=1}^{n=N} \beta_n[L]^n} \tag{2.40}$$
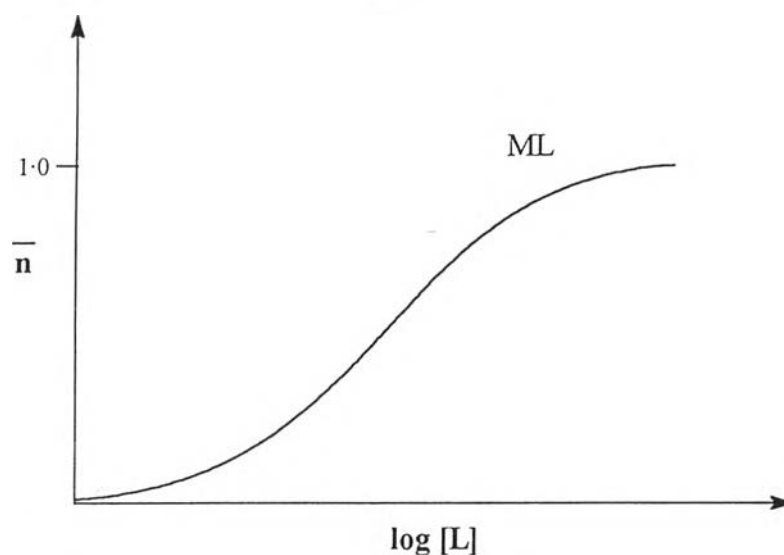

Figure 2.2 Plot of the formation function $\bar{n}$, against the logarithm of the free ligand concentration, log[L] for mononuclear complex.

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

$$\alpha_c = \frac{[ML_c]}{[M]_T} \quad \text{for } c = 0, 1, 2, \ldots N \tag{2.41}$$

This variable α_c is the 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

$$\alpha_T = \sum_{c=1}^{c=N} \alpha_c \tag{2.42}$$

Hence, α_T is the fraction of total metal metal bound to ligand in the form of a complex. By an analogous procedure to that used to derive equation (2.40) we can show that :

$$\alpha_c = \frac{\sum_{c=1}^{c=N} \beta_c [L]^c}{1 + \sum_{c=1}^{c=N} \beta_c [L]^c} \equiv \frac{\sum_{c=1}^{c=N} \beta_c [L]^c}{\sum_{c=1}^{c=N} \beta_c [L]^c} \tag{2.43}$$

One interesting solution to equation (2.41) is when c = 0 and hence

$$\alpha_o = \frac{[M]}{[M]_T} \tag{2.44}$$

This function, α_o, gives the species distribution for the free metal ion in the solution.

2.2.4 The degree of complex formation, ϕ

The degree of complex formation, ϕ, is defined as :

$$\phi = \frac{[M]_T}{[M]} = 1 + \sum_{n=1}^{n=N} \beta_n [L]^n \tag{2.45}$$

At this stage it is valuable to summarize the definitions of the three secondary concentration variables that we have met so far. This, together with experimental data that must be available to use of them, is given Table 2.1.

Table 2.1 Summary of the secondary concentration variables, $\bar{n}$, α_c, and ϕ.

Variable	Title	Definition	Experimental observables required
$\bar{n}$	Complex formation function	$\dfrac{[L]_T - [L]}{[M]_T}$	$[M]_T$, $[L]_T$, $[L]$
α_c	degree of formation	$\dfrac{[ML_c]}{[M]_T}$	$[M]_T$, $[L]_T$, $[L]$
ϕ	Degree of complex formation	$\dfrac{[M]_T}{[M]}$	$[M]_T$, $[M]$

2.3 Calculation of equilibrium constants

The acidity and basicity constants were calculated by fitting the pH data to the SUPERQUAD [65] which has been widely used to calculate the equilibrium constants of many ligands in solution. The SUPERQUAD program also permits refinement of an reactant concentration or standard electrode potential. The refinement of any reactant concentration or stand electrode potential. The refinement is incorporated into new procedure which can be used for model selection. The assumption for evaluation of formation constants by SUPERQUAD could be described as follows.

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

1. For each chemical species $A_a B_b \ldots$ in the solution equilibria there is a chemical constant, the formation constant, which is expressed as a concentration quotient in equation (2.61).

$$B_{ab\ldots} = \left[\frac{A_a B_b \ldots}{[A]^a [B]^b}\right] \tag{2.46}$$

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 the 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 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 (2.62), where [A] is the concentration of the electro-active ion, E is the measured potential, and $E°$ is the standard electrode potential.

$$E = E° + S_L \log[A] \tag{2.47}$$

The ideal value of the slope, S_L is of course $\dfrac{RT}{nF}$, but we assume only that it is a constant for a given electrode. The values of $E°$ and S_L are usually obtained in a separate calibration experiment. Further there is a modified Nernst equation (2.48).

$$E = E° + S_L \log[H^+] + r[H^+] + s[H^+]^{-1} \tag{2.48}$$

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

3. Systematic errors must be minimized by careful experimental work. Sources of systematic error include electrode calibration, sample weightings and dilutions, standardization of reagents (use of carbonate-free alkali in particular), temperature,

variation and water quality. Water may be contaminated by titratable species which can pass trough distillation column 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 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 exists 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 Potentiometry

Potentiometry has been and still the most popular method for the determination of stability constants because of its high accuracy and precision.

The major limitation in the use of potentiometry is the essential requirement that a suitable reversible electrode exists. Electrodes develop potential that are dependent on the activities of the species present. These potential originate from two main types of phenomena, namely oxidation-reduction equilibria and the formation of ionic concentration gradients across membranes. In the case of an oxidation-reduction equilibrium of the type,

$$M^{m+} + ne^- \rightleftharpoons M^{(m-n)+} \qquad (2.49)$$

the observed potential, E is given by the Nernst equation,

$$E = E^\circ + \frac{RT}{nF} \ln \frac{a_M^{(m-n)+}}{a_M^{n+}} \qquad (2.50)$$

where $E°$ is the standard potential at 25 °C when all the species are at unit activity, F is one faraday of charge (9643 coulomb.mol^{-1}), n is number of electrons involved, and a_x is the activity of species x. In the case of ionic potential gradients, the observed e.m.f. is given by,

$$E = E°_{M^{n+}} + \frac{RT}{nF} \ln a_{M^{n+}} \tag{2.51}$$

where $E°_{M^{n+}}$ is the standard potential of the M^{n+} electrode at 25 °C. Because of activity is related to concentration and if the activity coefficients are maintained constant by using a sufficiently high concentration of an inert background electrolyte, then the equation (2.66) in terms of concentrations, and replacing $E°'$ in $E°$, can be rewritten by

$$E = E°' + \frac{RT}{nF} \ln[M^{n+} \tag{2.52}$$

where $E°' = E° + \frac{RT}{nF} \ln[M^{n+}] \tag{2.53}$

2.5 Inert background electrolyte

To study acid-base characteristics of ligand their complexation properties toward metal, inoic strength are controlled by inert background electrolyte present at a concentration far in excess that of the reacting ionic species under investigation. Another name of inert background electrolyte is inert background solution or supporting electrolyte 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 is to keep the overall ionic strength and activity coefficient constant. Properties of the chosen inert background electrolyte must meet the following requirement

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 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 are classified into aqueous solvent, non-aqueous solvent and their mixtures

In aqueous system, sodium perchlorate ($NaClO_4$), sodium nitrate ($NaNO_3$), sodium chloride ($NaCl$), potassium nitrate (KNO_3) and potassium chloride (KCl) potassium perchlorate ($KClO_4$) are usually used as the background electrolytes. In case of non-aqueous system, tetraethylammonium perchlorate (Et_4NClO_4), tetramethylammonium chloride (Me_4NClO_4) and tetrabutylammonium trifluoro-methanesulfonate ($Bu_4NCF_3SO_3$), tetraethylammonium nitrate (Me_4NNO_3). Tetrametylammonium perchlorate (Me_4NClO_4) and tetrabutylammonium perchlorate (Bu_4NClO_4) are widely used as the background electrolytes.