

CHAPTER II

THEORY

2.1 Classification of Metals and Ligands

2.1.1 Principle of Hard and Soft Acids and Bases

For a number of years, chemists have examined a considerable body of stability constant data to see what generalization could be made. The object of this was twofold : firstly by analyzing the trends in the known stability constants it was hoped that it might be possible to predict the values of unknown stability constants, and secondly, it was hoped to obtain an insight into why a particular metal ion shows a preference for one ligand rather than another. Pearson⁽²²⁾ has suggested that the interaction of metals and ligands can be understood in terms of their 'hardness' or 'softness'. This is formalized in the Principle of Hard and Soft Acids and Bases, (HSAB), in which an acid is any electron acceptor (Lewis acid), a base is any electron donor (Lewis base), and acids and bases are considered to bond by sharing at least one pair of electrons. We might expect the equilibrium constant of reaction (2.1)



to be given by

$$\log K = S_A S_B \quad (2.2)$$

where S_A and S_B are strength factors for the acid and base respectively. However, when series of bases are tested against a number of acids it is found that the order of

base strength obtained is a function of the reference acid. Accordingly the two-parameter Equation (2.2) was extended to a four-parameter equation :

$$\log K = S_A S_B + \sigma_A \sigma_B$$

(2.3)

where σ is a parameter that measures some characteristics other than strength - this is known as 'softness'. Values of the parameters are set by (a) measuring K , (b) setting the value of σ for the proton arbitrarily at zero, which turns out to be reasonable since σ values appear to be related to the polarizability of the species, and (c) setting the intrinsic strength of the proton arbitrarly at 1. In this way σ values for a series of acids and bases can be evaluated. These values suggest that non-polarisable, which we may call 'hard', species give low σ values, and polarisable, 'soft', species give higher σ values (Table 2.1). The division of acids and bases on the basis of experimentally determined stability constants into hard, soft and borderline is shown in Table 2.2.

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Table 2.1 Properties of Hard and Soft Acids and Bases.

Acid (electron acceptor)		
Property	Hard	Soft
Polarisability	low	high
Electropositivity	high	low
Positive charge or oxidation state	high	low
Size	small	large
Type of bond usually associated with the acid	ionic, electrostatic	π
Outer electron on acid	few and not easily excited	several, easily excited

Base (electron donor)		
Property	Hard	Soft
Polarisability	low	high
Electronegativity	high	low
Negative charge	high	low
Size	small	large
Type of bond usually associated with the base	electrostatic	π
Available empty Orbitals on the base	high energy, inaccessible	low lying, accessible

Table 2.2 Hard and Soft Acids and Bases.

Acids

Hard	Soft
H^+ , Li^+ , Na^+ , K^+ Be^{2+} , Mg^{2+} , Ca^{2+} , Sr^{2+} , Mn^{2+} Al^{3+} , Sc^{3+} , Ga^{3+} , In^{3+} , La^{3+} N^{3+} , Cl^{3+} , Gd^{3+} , Lu^{3+} Cr^{3+} , Co^{3+} , Fe^{3+} , As^{3+} , CH_3Sn^{3+} Si^{4+} , Ti^{4+} , Zr^{4+} , Th^{4+} , U^{4+} Pu^{4+} , Ce^{3+} , Hf^{4+} , WO^{4+} , Sn^{4+} UO_2^{2+} , $(CH_3)_2Sn^{2+}$, VO^{2+} , MoO^{3+} $BeMe_2$, BF_3 , $B(OR)_3$ $Al(CH_3)_3$, $AlCl_3$, AlH_3 RPO_2^+ , $ROPO_2^+$ RSO_2^+ , $ROSO_2^+$, SO_3 I^{7+} , I^{5+} , Cl^{7+} , Cr^{6+} RCO^+ , CO_2 , NC^+ HX (hydrogen bonding molecules)	Cu^+ , Ag^+ , Au^+ , Tl^+ , Hg^+ Pd^{2+} , Cd^{2+} , Pt^{2+} , Hg^{2+} , CH_3Hg^+ , $Co(CN)_5^{2-}$, Pt^{4+} , Te^{4+} Tl^{3+} , $Tl(CH_3)_3$, BH_3 , $Ga(CH_3)_3$ $GaCl_3$, GaI_3 , $InCl_3$ RS^+ , RSe^+ , RTe^+ I^+ , Br^+ , HO^+ , RO^+ I_2 , Br_2 , ICN , etc. trinitrobenzene etc. chloranil, quinones, etc. tetracyanoethylene, etc. O , Cl , Br , I , N , $RO\cdot$, $RO_2\cdot$ M^0 (metal atoms) bulk metals CH_2 , carbenes
Borderline	
Fe^{2+} , Co^{2+} , Ni^{2+} , Cu^{2+} , Zn^{2+} , Pb^{2+} , Sn^{2+} , Sb^{3+} , Bi^{3+} , Rh^{3+} , Ir^{3+} , $B(CH_3)_3$, SO_2 , NO^+ , Ru^{2+} , Os^{2+} , R_3C^+ , $C_6H_5^+$, GaH_3	

Table 2.2 (continued) Hard and Soft Acids and Bases**Bases**

Hard	Soft
H ₂ O, OH ⁻ , F ⁻ CH ₃ CO ²⁻ , PO ₄ ³⁻ , SO ₄ ²⁺ Cl ⁻ , CO ₃ ²⁻ , ClO ₄ ⁻ , NO ₃ ⁻ ROH, RO ⁻ , R ₂ O NH ₃ , RN ₂ , N ₂ H ₄	R ₂ S, RSH, RS ⁻ I ⁻ , SCN ⁻ , S ₂ O ₃ ²⁻ R ₃ P, R ₃ AS, (RO ₃)P CN ⁻ , RNC, CO C ₂ H ₄ , C ₆ H ₆ H ⁻ , R ⁻
Borderline	
C ₆ H ₅ NH ₂ , C ₅ H ₅ N, N ₃ ⁻ , Br ⁻ , NO ₂ ⁻ , SO ₃ ²⁻ , N ₂	

The Principle of Hard and Soft Acids and Bases as originally put forward states that "Hard acids prefer to bind to hard bases and soft acids prefer to bind to soft bases". Hard-soft interactions tend to be weak. This principle gives a qualitative prediction of what will happen when an acid and a base meet. Unfortunately from a quantitative point of view Equation (2.3) is not exact or even nearly exact, because it is too simple to represent the complexity of charges that occur when electron donating groups combine with electron-acceptors.

2.1.2 Ionic Size, Coordination Number, Oxidation State and Stereochemistry

The concept of ionic is valuable for the rationalization and interpretation of the vast quantity of experimental data relating to metal complexes in which the

is primarily electrostatic. For an isolated ion, its radius is determined simply by the resultant force of attraction, after allowance has been made for the screening effect of intervening shells of electrons, between the nuclear charge and the outermost electrons. This quantity can be readily calculated. In condensed phases, we are always concerned with an ion in association with neutral molecules or ions of opposite charge and so there are additional attractive or repulsive forces operative that will affect its size. The size of an ion is not invariant but depends on its coordination number, the nature of the molecules or ions with which it is linked, and the extent to which the bonding departs from the purely electrostatic because of polarization effects. In the case of transition-metal ions, certain numbers of d-electrons can give rise to either high-spin or low-spin configurations according to the magnitude of the surrounding ligand field. This is an additional factor which affects the size of these ions.

By simple geometry, the larger the metal ion, the greater the number of ligand atoms which can surround it so that each may still be regarded as in contact with the central ion. Low coordination numbers are therefore to be expected for ion like Li^+ , Be^{2+} , and ions of low oxidation state in the first transition series. Correspondingly, high coordination numbers are found for the heavier alkali and alkaline-earth metal ions, the lanthanides and the actinides. For monatomic anionic ligands, the limiting size of the metal ion for a specified coordination number can be estimated by calculation of the radius ratio (radius of metal ion/radius of ligand). This purely geometrical approach cannot be directly applied to metal chelates unless, which is not generally the case, the 'size' of the donor atoms is accurately known.

The charge on the metal ion also influences the coordination number. If this charge is low, say +1 or +2, then the acceptance of only a few lone pairs of electrons from a small number of ligands could lead to the accumulation of enough negative

charge on the metal to prevent the coordination of additional ligands. When the charge is high, for example +3 or +4, then a high coordination number can be reached without too much negative charge building up on the metal. Metals in very high oxidation states (+6 and +7) generally show low coordination number because the small ionic size makes it sterically impossible for a large number of ligand atoms to be coordinated. In the case of complexes where the bonding between metal is determined by the number of σ -bonding orbitals available on the metal for combination with ligand orbitals of the same symmetries and similar energies. The most complete description of the bonding within such complexes is given by molecular orbital theory. All possible interactions between metal and ligand orbitals are considered and calculations permit quantitative estimates of the electronic energies within the molecular orbitals formed.

Wherever we concerned with a metal atom or ion which has a spherically symmetrical core of non-bonding electrons, as $1s^2$, ns^2np^6 and $(n-1)d^{10}$ outermost electrons ions, the arrangement of ligands is that of maximum symmetry, irrespective of whether the bonding is electrostatic or covalent. For example, a 4-coordinate complex is tetrahedral, a 5-coordinate complex is trigonal bipyramidal, a 6-coordinate complex is octahedral, and so on. Where the non-bonding core is non-spherical, for example in transition-metal ions, distortions from maximum symmetry occur for asymmetric distributions of electrons (Jahn-Teller effect). Thus tetragonal distortion within complexes of a d^9 high spin ion like Cu^{2+} , and of d^8 low spin ion like Ni^{2+} , effectively results in square-planar stereochemistry around the metal. In special cases, the shape of the complex is determined primarily by the stereochemistry and electronic characteristics of the prismatic stereochemistry on a 6-coordinated metal ion instead of the more symmetrical octahedral arrangement.

2.2 Equilibrium Constants, Protonation Constants and Stability Constants

2.2.1 Equilibrium Constants

There are two major areas of solution chemistry. The first of these is concerned with the chemical nature and concentration of each of the species present at equilibrium. The second concerns the rate and mechanism by which the species added to the solution come to equilibrium. These two aspects of solution chemistry



are closely related. Consider a system

where k_f and k_r are the forward and reverse rate constants. The rate at which the reaction proceeds in a forward direction, which equals the rate of loss of A ($-dA/dt$), is given by

$$-dA/dt = k_f\{A\}\{B\} \quad (2.5)$$

where $\{X\}$ is the activity of species X. In addition, the rate of the reverse reaction, which equals the rate of formation of A (dA/dt), is given by

$$dA/dt = k_r\{C\}\{D\} \quad (2.6)$$

At equilibrium the rates of the forward and reverse reactions are equal, and so

$$k_f\{A\}\{B\} = k_r\{C\}\{D\} \quad (2.7)$$

which may be rearranged to give

$$\frac{k_f}{k_r} = K^\theta = \frac{\{C\}\{D\}}{\{A\}\{B\}} \quad (2.8)$$

where k_f/k_r , being a constant, is written as a single constant K^θ , and is known as an equilibrium constant. Equation (2.8) is known as Guldberg and Waage's relationship and can be used as a basis for measuring equilibrium constants provided that the reaction takes place by a one-step mechanism. Equilibrium constants that refer to the interaction of metal ions and ligands are commonly referred to as stability constants.

2.2.2 Equilibrium Constants Involving Concentrations and Activities

The law of mass action is strictly valid only when activities are used instead of concentrations. Because the activity of a species is equal to the product of its concentration and its activity coefficient, then is a simple relationship between the stoichiometric equilibrium constants (involving concentrations) and the thermodynamic equilibrium constant (involving activities), K^θ

$$K = \frac{\{ML\}}{\{M\}\{L\}} = \frac{[ML]}{[M][L]} \times \frac{\gamma_{ML}}{\gamma_M \cdot \gamma_L} \quad (2.9)$$

where the activities are written in { } brackets, and γ denotes an activity coefficient.

2.2.3 Protonation Constants

The acid-base equilibria of the ligands can be treated by protonation or basicity constants and deprotonation or acidity constants respectively. The protonation constant ($K_{H,n}$) is the equilibrium constant for the addition of the n^{th} proton to a charged or uncharged ligand, to be defined. The reciprocal values of these constants are called the deprotonation constant ($K_{a,n}$) which is the equilibrium constant for the splitting off the n^{th} proton to a charged or uncharged ligand, to be defined. The following equations define these constants and show their interrelation.

$$K_{a,1} = \frac{[H_{z-1}L][H]}{[H_zL]} = \frac{1}{K_{H,z}} \quad (2.10)$$

$$K_{a,2} = \frac{[H_{z-2}L][H]}{[H_{z-1}L]} = \frac{1}{K_{H,z-1}} \quad (2.11)$$

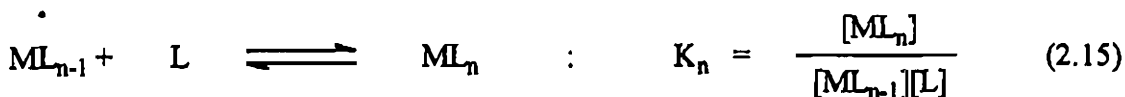
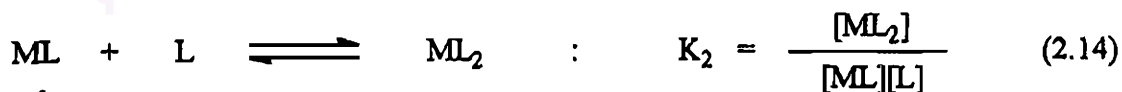
$$K_{a,z+1-n} = \frac{[H_{n-1}L][H]}{[H_nL]} = \frac{1}{K_{H,n}} \quad (2.12)$$

The value of z , the number of dissociable protons, is not free from some ambiguity.

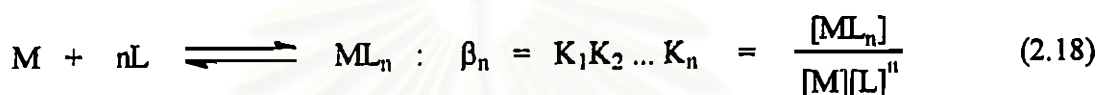
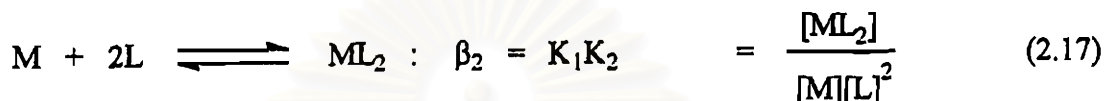
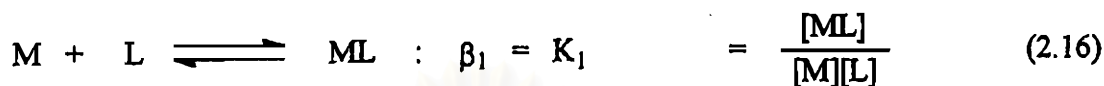
2.2.4 Stability Constants

The thermodynamic stability of complex equilibria can be characterized by stability constant and instability constant. The stability constant (K_n) is equilibrium constant characterize the stability of the complexes. Sometimes, it is called as formation constant. Its inverse (that is $1/K$) is known as an instability constant and was at one time widely favored by Russian inorganic chemists.

When M is the metal ion, L is the ligand, charges are omitted, and $[X]$ is the concentration of X , the stepwise formation of parent complexes can be described by the following set of equilibrium constants



If the products of the individual stability constants also give characteristic constants, these can be called overall or cumulative formation constants or stability products usually denoted by



$$\text{In general } \beta_n = \prod_{i=1}^n K_i$$

2.2.5 Stoichiometric Stability Constants

In practice many analytical techniques yield concentrations rather than activities. The most expedient solution to what is a very major problem is to rewrite the thermodynamic stability constant (K^\ominus) in term of both concentration and activity coefficients which has been shown in Equation (2.9)

If now it were possible to ensure that the term $\gamma_{ML}/\gamma_M\gamma_L$ remained constant (albeit at the expense of not knowing its absolute value) then K defined by Equation (2.7) would also be a constant.

$$K = \frac{[ML]}{[M][L]} \quad (2.19)$$

K is known as a stoichiometric stability constant. The term $\gamma_{ML}/\gamma_M\gamma_L$ in Equation (2.9) may be maintained effectively constant by,

(a) having a large excess of an inert background electrolyte present, that is an electrolyte which does not react with any of the metal, ligand, or metal-ligand species, and

(b) using only low concentrations of metal and ligand so that any change in their concentrations as a result of their reaction together has a insignificant change on the overall ionic strength of the medium

The ionic strength (μ) is normally defined by the equation

$$\mu = \frac{1}{2} \sum c_i z_i^2 \quad (2.20)$$

where c_i is the concentration and z_i is the charge of species i ; accordingly ionic strength has the units of concentration (that is, mol.L⁻¹). However, it has recently been shown that ionic strength should be defined by the equation

$$\mu = \frac{1}{2} \sum c_i |z_i| \quad (2.21)$$

The two definitions are, of course, identical for univalent ions, but when significant concentrations of multivalent ions are present the latter should be used. It is generally possible to replace about 5% of the ions in the background electrolyte without appreciably altering the activity coefficients of the minor species present.

2.3 Potentiometric pH Measurements

Potentiometry is one of the most convenient and successful techniques employed for metal complex equilibrium measurements. It is usually sufficient to use the highly accurate glass electrode for measuring the hydrogen ion concentration in a procedure termed potentiometric titration, whereby, for example, standard base is added in increments to a well-characterized acid solution of the ligand in the absence of and in the presence of known total metal ion concentration. In most typical cases, the

p[H] is varied between >2 and <12 during which time some 50-100 equilibrium readings are obtained constituting the potentiometric equilibrium curve.

A problem that is frequently encountered with very stable complexes of multidentate ligands is the inability to neutralize, in the absence of metal ions, one or more of the donor groups of the ligand without raising the pH above 12, which is the practical upper limit for accurate pH measurements. While this does not affect the accuracy of the equilibrium determinations in the working pH range, 2 - 12, it renders impossible the expression of the stabilities in terms of the fully dissociated ligand, L^n , and comparisons of such constants with the corresponding values of other metal complex systems cannot be made.

2.4 Computation of Equilibrium Constants by SUPERQUAD Program

The computer program, SUPERQUAD,⁽²³⁾ has been widely used to calculate stability constants of species in solution equilibria from data obtained by potentiometric method. The stability constants are determined by minimization of an error-square sum based on measure electrode potentials. The program also permits refinement of any reactant concentration or standard electrode potential. The refinement is incorporated into a new procedure which can be used for model selection. The assumption for computation of stability constants by SUPERQUAD could be described as follows.

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

1. For each chemical species $A_a B_b \dots$ in the solution equilibria there is a chemical constant, the stability constant, which is expressed as a concentration quotient (Equation (2.22)).

$$\beta_{ab\dots} = \frac{[A_a B_b \dots]}{[A]^a [B]^b \dots} \quad (2.22)$$

$A, B \dots$ are the reactants (SUPERQUAD allows up to four of them) and $[A], [B]$ are the concentration 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 stability constant is an activity quotient, it is 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 (2.23), where $[A]$ is the concentration of the electro-active ion.

$$E = E^\ominus + S_L \log[A] \quad (2.23)$$

E and E^\ominus are the measured potential and the standard electrode potential, respectively. The ideal value of the slope, S_L , is RT/nF , but it is assumed as a constant for a given electrode. The values of E^\ominus and S_L are usually obtained in a separated calibration experiment. If a glass electrode is calibrated in terms of hydrogen-ion concentration. An equivalent potential is created according to Equation (2.24).

$$E = 10 + RT/nF \times \text{pH} \quad (2.24)$$

The alternative calibration method uses measurements in volts and determination of E^\ominus from a Gran plot derived from a titration of a strong acid with a strong base.

3. Systematic errors must be minimized by careful experimental work. Sources of systematic error include electrode calibration, sample weighting and dilutions, standardization of reagents (use of carbonate-free alkali in particular), temperature variation and water quality. The last factor is more significant today than it was in the past, as water may be contaminated by titratable species which can pass through distillation columns by surface action. All statistical tests are based on the assumption that systematic errors 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 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, \dots , one for each species formed. All least-squares refinements are performed in term 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'.

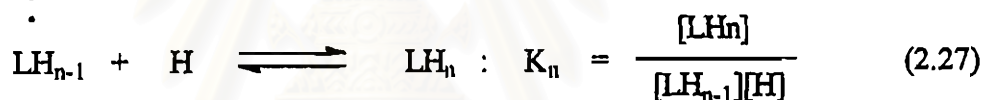
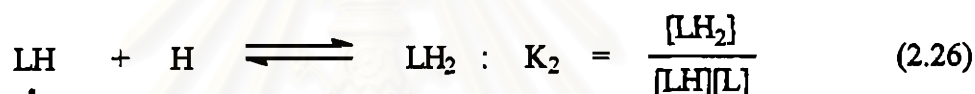
2.5 Treatment of Data : Secondary Concentration Variables

In order to evaluate the stability constant, K , for a simple system. It is necessary to prepare a single solution condition 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, $[ML]$. Moreover, it is necessary to find a relationship between them and the experimentally determined

variables ([M], [L], etc.). This relationship is often established via the definition of secondary concentration variables. It is from these variables that the stability constants are calculated. In this subject four of these functions are derived.

2.5.1 The Protonation Function, \bar{p}

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



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.

$$[L]_T = [L] + [LH] + [LH_2] + \dots + [LH_n] \quad (2.28)$$

$$[H]_T = [H] + [LH] + 2[LH_2] + \dots + [LH_n] \quad (2.29)$$

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

$$\bar{p} = \frac{\text{total bound proton}}{\text{total ligand}} = \frac{[H^+]_T - [H^+] + [OH^-]}{[L]_T} \quad (2.30)$$

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.

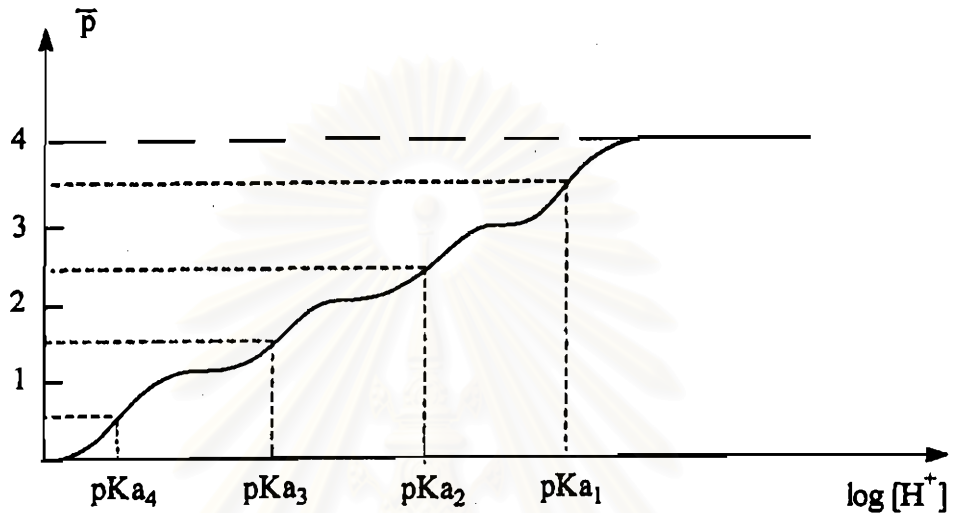
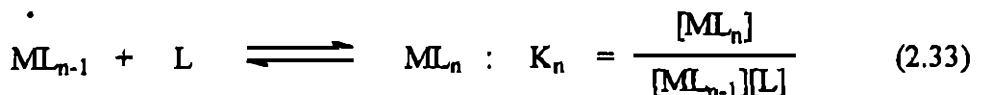
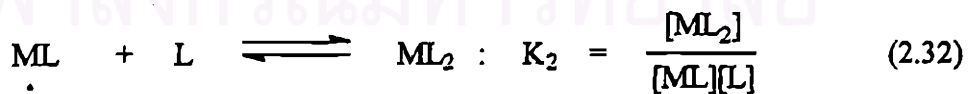


Figure 2.1 Plot of the protonation formation function (\bar{p}), against the logarithm of the free proton concentration ($\log[H^+]$) for tetraacid.

2.5.2 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 :



The maximum value of \bar{n} , written N, will be a function of both the maximum coordination number of the metal ion and the multidentate properties of the ligand. Having defined this system mass balance equations for both the total metal ion and total ligand concentrations can be written now :

$$[M]_T = [M] + [ML] + [ML_2] + \dots + [ML_n] \quad (2.34)$$

$$[L]_T = [L] + [ML] + 2[ML_2] + \dots + n[ML_n] \quad (2.35)$$

A function, π , defined as the average number of ligand, L, attached to the metal, M, may be written

$$\bar{n} = \frac{\text{total bound ligand}}{\text{total metal}} = \frac{[L^+]_T - [L]}{[L]_T} \quad (2.36)$$

Substituting Equation (2.34) and (2.35) in (2.37) yields

$$\bar{n} = \frac{[ML] + 2[ML_2] + \dots + n[ML_n]}{[M] + [ML] + [ML_2] + \dots + [ML_n]} \quad (2.37)$$

In summation terms Equation (2.37) becomes

$$\bar{n} = \frac{\sum_{n=1}^{n=N} n[ML_n]}{[M] + \sum_{n=1}^{n=N} [ML_n]} \quad (2.38)$$

where N is the maximum coordination number for the metal if L is a monodentate ligand. Inspection of Equation (2.38) 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

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

and β_n as

$$\beta_n = \frac{[ML_n]}{[M][L]^n} \quad (2.40)$$

$$\text{In addition, } \beta_n = K_1 K_2 K_3 \dots K_n \quad (2.41)$$

And, on substituting Equation (2.39) into (2.37) gives

$$\bar{n} = \frac{K_1[M][L] + 2K_1K_2[M][L]^2 + \dots + nK_1K_2 \dots K_n[M][L]^n}{[M] + K_1[M][L] + K_1K_2[M][L]^2 + \dots + K_1K_2 \dots K_n[M][L]^n} \quad (2.42)$$

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

$$\bar{n} = \frac{\beta_1[L] + 2\beta_2[L]^2 + \dots + n\beta_n[L]^n}{1 + \beta_1[L] + \beta_2[L]^2 + \dots + \beta_n[L]^n} \quad (2.43)$$

which may be more conveniently written in summation terms

$$\bar{n} = \frac{\sum_{n=1}^{n=N} n \beta_n [L]^n}{1 + \sum_{n=1}^{n=N} \beta_n [L]^n} \equiv \frac{\sum_{n=1}^{n=N} n \beta_n [L]^n}{\sum_{n=0}^{n=N} \beta_n [L]^n} \quad (2.44)$$

It is immediately apparent from Equation (2.40) that \bar{n} is solely dependent on the free ligand concentration, $[L]$, and is independent of $[M]_T$, $[L]_T$, and the free metal ion concentration $[M]$. The complex formation function, \bar{n} , first introduced by Niels Bjerrum⁽²⁴⁾ and later developed by Jannik Bjerrum⁽²⁵⁾, is the starting point for many of the methods used in the calculation of stability constants.

2.5.3 The Degree of Formation, α_c

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

$$\alpha_c = \frac{[ML_c]}{[M]_T} \quad \text{for } c = 0, 1, 2, \dots, N \quad (2.45)$$

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

$$\alpha_T = \sum_{c=1}^{c=N} \alpha_c \quad (2.46)$$

Hence, 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) α_c shows that :

$$\alpha_c = \frac{\sum_{c=1}^{c=N} \beta_c [L]^c}{1 + \sum_{c=1}^{c=N} \beta_c [L]^c} \equiv \frac{\sum_{c=1}^{c=N} \beta_c [L]^c}{\sum_{c=0}^{c=N} \beta_c [L]^c} \quad (2.47)$$

One interesting solution to Equation (2.45) is when $c = 0$ and hence

$$\alpha_0 = \frac{[M]}{[M]_T} \quad (2.48)$$

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 component distribution curves ($N + 1$ of them) of α_c versus $[M]_T$ or $[L]_T$. The α_c function is used in a recent atlas of metal-ligand equilibria in solution to show at a glance the relative proportions of each of the species present in solution.

2.5.4 The Degree of Complex Formation, ϕ

A fourth secondary concentration variable, ϕ , is defined as :

$$\phi = \frac{[M]_T}{[M]} = 1 + \sum_{n=1}^{n=N} \beta_n [L]^n \quad (2.49)$$

This function finds an application in the methods of Leden and Froneaus which calculate the stability constants based on the degree of complex formation, ϕ .

Table 2.3 Summary of the secondary concentration variables, \bar{n} , α_c and ϕ .

Variable	Title	Definition	Experimental observables 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 complex formation	$[M]_T/[M]$	$[M]_T/[M]$