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UNIFIED THEORY OF METAL ION COMPLEX FORMATION CONSTANTS

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ABSTRACT

A new concept in solution chemistry, electronicity, has been derived and developed. Electronicity describes quantitatively the ability of a ligand to complex a metal ion which, in turn, allows the prediction of the formation constants of metal ion complexes. The principle of electronicity quantifies onto one scale the earlier concepts of hard and soft acids and bases.

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EDITORIAL NOTE

From 27 April 1987, the Australian Atomic Energy Commission (AAEC) is replaced by Australian Nuclear Science and Technology Organisation (ANSTO). Serial numbers for reports with an issue date after April 1987 have the prefix ANSTO with no change of the symbol (E, M, S or C) or numbering sequence.

PREFACE

This paper has been published in the Journal of Chemical Research [1987, (S): 4-5; (M): 0110-0181]. The Journal provides reprints of the synopsis but not of the microfiched main paper. However, in lieu of reprints, the publishers have kindly consented for the paper to be issued in the approved format in the AAEC/E Report series. It is not to be considered as a separate, or duplicate, publication from the one appearing in the above mentioned journal.

CONTENTS

Introduction

Interest in the formation (stability) constants of metal ion complexes, though always sustained, has increased greatly in recent years, largely because of the fundamental need of such data in any investigation of environmental pollution. It has long been recognised, however, that the determination of these thermodynamic quantities is difficult because great demands are made on both experimental design and techniques, and methods of data analysis and interpretation. In particular, the unavoidable need to determine the free (unreacted) concentration of at least one component in the equilibrium system has led to considerable problems in this field. There are numerous compilations of formation constants,[1-5] both exhaustive and critical, but few attempts have been made to unify these data on a common, theoretical basis.

Our recent work[6-14] has involved the determination and prediction of the formation constants of hydroxo-metal complexes, both mononuclear and polynuclear. We now extend this work to provide a theoretical basis for the prediction of metal ion complexes of any ligand, for mononuclear, polynuclear and mixed-ligand complexes. It is hoped that this attempt at a completely general and unified treatment will provide an insight into the nature and dynamics of the formation of metal ion complexes. The predictive powers of such a treatment, if adequate, would prove to be of great value, especially where the formation constants cannot be determined experimentally with any degree of accuracy. We will now describe this treatment in three parts; first, a statistical approach, second, an empirical approach, and lastly, a synthesis and extension of these two approaches.

Results and Discussion

Part One

The Statistical Approach: The Sylva-Davidson Equation

Consider the reaction of a unidentate ligand, L, with a metal ion, M (charges omitted throughout):

$$M + L \rightleftharpoons ML \quad . \tag{1}$$

By the Law of Mass Action, the formation constant for this single step reaction, the step-wise formation constant, K_1 (see symbol table in Appendix), is given by equation (2):

$$K_1 = \frac{[ML]}{[M][L]} \quad , \tag{2}$$

where the square brackets represent activity or concentration units. Reaction (1) can, more generally, be regarded as one of a succession of step-wise reactions, as in equation (3),

$$ML_{q-1} + L \rightleftharpoons ML_q \quad , \tag{3}$$

and the appropriate step-wise formation constant is given by equation (4)

$$K_q = \frac{[ML_q]}{[ML_{q-1}][L]} \quad . \tag{4}$$

The formation constant of ML_q can also be considered in terms of the overall reaction (5) for which the <u>overall</u> formation constant is given by equation (6):

$$M + qL \rightleftharpoons ML_q \tag{5}$$

$$\beta_{1q} = \frac{[ML_q]}{[M][L]^q} \quad . \tag{6}$$

It follows from the above that $K_1 = \beta_{11}$, and that in general

$$\beta_{1q} = K_1K_2K_3 \ldots K_{q-1}K_q \quad . \tag{7}$$

The preceding discussion assumes the formation of mononuclear species only. For polynuclear species, overall formation constants are usually considered for reaction (8), namely equation (9):

$$pM + qL \leftrightharpoons M_pL_q \tag{8}$$

$$\beta_{pq} = \frac{[M_pL_q]}{[M]^p[L]^q} \quad . \tag{9}$$

In general, any complex M_pL_q is referred to by its formula or as a (p,q) species.

Formation constants depend only on the energy status (enthalpy and entropy, or useful and non-useful work potential) of the initial and final states of the reaction. Thus, the species (p,q) can, for example, be considered as being formed in the two steps (10) and (11):

$$M + mL \rightleftharpoons ML_m \qquad (10)$$

$$ML_m + nML \rightleftharpoons M_pL_q \qquad (11)$$

from which follow equations (12) and (13) for the stoicheiometric coefficients:

$$m=q+1-p \quad , \qquad (12)$$

$$n=p-1 \quad . \qquad (13)$$

Equations (10) and (11), and hence (12) and (13), are completely arbitrary and chosen merely for convenience in the following discussion.

The step-wise nature of complex formation means that the ratios of the consecutive formation constants can be statistically predicted, as pointed out by Bjerrum,[15] on the basis of the following simplifying assumptions:

(i) all possible coordination sites of the metal ion are (energetically) equivalent;

(ii) the tendency of the complex ML_q to dissociate a ligand entity is proportional to the value of q; and

(iii) the tendency of a complex ML_q to gain an additional ligand molecule is proportional to (N-q), where N is the maximum possible value of q.

It follows that, for reaction (3), the step-wise formation constant can be written as relationship (14):

$$K_q \propto \frac{(N-q+1)}{q} \qquad (14)$$

and hence

$$K_{q+1} \propto \frac{N-q}{q+1} \qquad (15)$$

and the consecutive formation constants, $K_1, K_2, \ldots, K_q$, will be successively proportional to the terms in (16).

$$N,\ (N-1)/2,\ \ldots\ ,\ (N-q+1)/q,\ (N-q)/(q+1),\ \ldots\ ,\ 2/(N-1),\ 1/N\ . \qquad (16)$$

Thus, the ratio of any two consecutive constants is given by equation (17):

$$\frac{K_{q+1}}{K_q} = \frac{k(N-q)/(q+1)}{(N-q+1)/q} = \frac{kq(N-q)}{(N-q+1)(q+1)} \qquad (17)$$

where k is a proportionality constant. Hypothetically, since the chemical pathway is completely arbitrary, there need be no upper limit to the value of N, so that summing N to infinity gives

$$\frac{(N-q)}{(N-q+1)} = 1, \qquad (18)$$

and

$$\frac{K_{q+1}}{K_q} = k\left(\frac{q}{(q+1)}\right) . \qquad (19)$$

Thus, if equation (7) is written as (20), then (21) follows:

$$\beta_{1m} = K_m K_{m-1} K_{m-2} \ldots K_2 K_1 \qquad (20)$$

$$\frac{K_m}{K_{m-1}} = k\left(\frac{(m-1)}{m}\right) . \qquad (21)$$

Substitution of equation (21) into (20) provides the following result:

$$\begin{aligned}\beta_{1m} &= \left(\frac{k(m-1)}{m} K_{m-1}\right) K_{m-1} K_{m-2} \ldots K_2 K_1 \\ &= \left(\frac{k(m-1)}{m}\right)\left(\frac{k(m-2)}{(m-1)} K_{m-2}\right)^2 K_{m-2} \ldots K_2 K_1 \qquad (22) \\ &= \left(\frac{k(m-1)}{m}\right)\left(\frac{k(m-2)}{(m-1)}\right)^2\left(\frac{k(m-3)}{(m-2)} K_{m-3}\right)^3 K_{m-3} \ldots K_2 K_1\end{aligned}$$

$$= \frac{K_1{}^m k^{[1+2+3+\ldots+(m-1)]}}{m!} \quad .$$

Since $K_1 = \beta_{11}$ and $1+2+3+\ldots+(m-1) = m(m-1)/2$, equation (22) can be simplified to (23):

$$\beta_{1m} = \frac{\beta_{11}{}^m k^{m(m-1)/2}}{m!} \quad . \tag{23}$$

In the second step of the process, reaction (11), where M_pL_q is formed from ML_m and nML and $n=(p-1)$, the application of the Law of Mass Action gives

$$\beta_n = \frac{[M_pL_q]}{[ML_m][ML]^n} \tag{24}$$

and hence, from equation (9),

$$\begin{aligned} \beta_{pq} &= \frac{\beta_n[ML_m][ML]^n}{[M]^p[L]^q} \\ &= \frac{\beta_n\beta_{1m}[ML]^n}{[M]^n[L]^n} \\ &= \beta_n\beta_{1m}\beta_{11}{}^n \quad . \end{aligned} \tag{25}$$

In these reactions, where M_pL_q is considered to be produced by the addition of ML to ML_m entities, there need not be a limit to the number of additions. Since such additions neither alter the number of sites available for further addition nor the number of ML entities available for dissociation (noting the simplifying assumptions of Bjerrum[15]), we can also assume that the ratio of any adjacent pair of step-wise constants is equal, and equal to unity, since the various steps will be all energetically similar. Thus, by this approximation, it follows that

$$\beta_n = K_1^{\,n} \ . \tag{26}$$

Thus, for example, in the formation of the (2,2) dimer from the (1,1) monomer, it follows from a consideration of (7) that

$$K_1 = \frac{\beta_{22}}{\beta_{11}^{\,2}} \ . \tag{27}$$

The combination of equations (25), (26), and (27), and replacement of m and n with (q+1-p) and (p-1), respectively, as in equations (12) and (13), leads to the following result:

$$\begin{aligned} \beta_{pq} &= \beta_n \beta_{1m} \beta_{11}^{\,n} \\ &= K_1^{\,n} \beta_{11}^{\,n} k^{m(m-1)/2} \beta_{11}^{\,m}/m! \qquad (28) \\ &= \left(\frac{\beta_{22}}{\beta_{11}^{\,2}}\right)^{(p-1)} \beta_{11}^{\,(p-1)} \ \frac{k^{(q-p)(q+1-p)/2}\beta_{11}^{\,(q+1-p)}}{(q+1-p)!} \ . \end{aligned}$$

Taking logarithms, and collecting and rearranging terms in (28), yields the simpler expression

$$\log \beta_{pq} = (q+2-2p)\log \beta_{11} + (p-1)\log \beta_{22} - \log U_{pq} \ , \tag{29}$$

where

$$\log U_{pq} = \log\left[(q+1-p)!\right] - \tfrac{1}{2}(q-p)(q+1-p)\log k \ . \tag{30}$$

Equation (29) is interesting, since, with the exception of the log U_{pq} term, it corresponds to the simplified Sylva-Davidson equation, which gives good results[6-8,14] for metal ion hydrolysis reactions. The significance of the log U_{pq} term is discussed below.

As written, equation (29) is inapplicable if a (2,2) dimer is not formed,[8] a situation which is more common[13,14] than previously thought. It is therefore necessary to make (29) more general, along the lines previously used.[13] Thus, for any species (r,s) the formation will be as in equation (31):

$$\log \beta_{rs} = (s+2-2r)\log \beta_{11} + (r-1)\log \beta_{22} - \log U_{rs} \tag{31}$$

which, by rearrangement, gives equation (32):

$$\log \beta_{22} = \left[\log \beta_{rs} + \log U_{rs} - (s+2-2r)\log \beta_{11}\right]/(r-1). \tag{32}$$

Substitution of equation (32) into (29), after rearrangement, gives equation (33):

$$\log \beta_{pq} + \log U_{pq} = q\log \beta_{11} - \frac{(p-1)}{(r-1)}\left[\log \beta_{rs} + \log U_{rs} - s\log \beta_{11}\right] . \tag{33}$$

Further, consideration of the formation of another polymeric species, (t,u), using the above results, yields equation (34), which is the generalised Sylva-Davidson equation (ignoring the log U terms):

$$\log \beta_{pq} + \log U_{pq} = \left[A(\log \beta_{tu} + \log U_{tu}) + B(\log \beta_{rs} + \log U_{rs})\right]/C \ , \tag{34}$$

where,

$$A = q(r-1) - s(p-1) \tag{34.1}$$

$$B = u(p-1) - q(t-1) \tag{34.2}$$

$$C = u(r-1) - s(t-1) \ . \tag{34.3}$$

The form of (34) is different from that previously given,[8,13] having simpler expressions for the coefficients A, B, and C; the two forms can, however, be readily shown to be identical by simplifying the former.

At this stage, it is worthwhile exploring some of the results obtained from equation (34). Thus, consider the formation of a (1,2) species in relation to the known values of β_{11} and any other polymeric species M_rL_s. In this example, p=t=u=1, q=2, and r and s are of any value. Substitution of these values into equation (34) yields the following: A=2(r−1), B=0, and C=(r−1) and, $\log \beta_{12} + \log U_{12} = 2(r-1)(\log \beta_{11} + \log U_{11})/(r-1) = 2(\log \beta_{11} + \log U_{11})$. As would be expected, data for a polymeric species (r,s) are irrelevant when considering the β value of any monomer. The value of U_{11} is obtained from equation (3), namely: $\log U_{11} = \log \left[(1+1-1)!\right] - (1-1)(1+1-1)\log k = 0$, as expected for the (1,1) species. Thus,

$$\log \beta_{12} \quad = \quad 2 \log \beta_{11} - \log U_{12} \quad . \tag{35}$$

It follows from equation (35) that for any monomeric species, (1,q),

$$\log \beta_{1q} \quad = \quad q \log \beta_{11} - \log U_{1q} \quad , \tag{36}$$

where

$$\log U_{1q} \quad = \quad \log (q!) - \tfrac{1}{2}q(q-1)\log k \quad . \tag{37}$$

Similarly, if the formation of (1,q) is considered in terms of the step-wise constants, $\log K_q$, and the first complexation step, $\log K_1$ (= $\log \beta_{11}$) then, $\log \beta_{1q} = q\log \beta_{11} - \log U_{1q}$, $\log \beta_{1,q-1} = (q-1) \log \beta_{11} - \log U_{1,q-1}$, and $\log K_q = \log \beta_{1q} - \log \beta_{1,q-1} = (q-q+1) \log \beta_{11} - (\log U_{1q} - \log U_{1,q-1})$. Substituting for the log U terms gives equation (38):

$$\log K_q \quad = \quad \log K_1 - \log q + (q-1)\log k \quad . \tag{38}$$

The Sylva-Davidson approximation, as originally given,[6-8] sets $\log \beta_{12} = 2 \log \beta_{11}$. This was known to be only an approximation since electrostatic arguments alone[13] indicate that $\log \beta_{12} < 2 \log \beta_{11}$.

The results obtained above, namely equation (35) or generally, equation (38), quantify the extent of this approximation in terms of the log U_{1q} contributions. We are here still circumscribed by the limitations of the statistical (Bjerrum) approach, nevertheless, the result is significant.

The log U terms can be considered as a measure of the intrinsic tendency of a metal ion (electron acceptor) to form a chemical (coordinate) bond with a ligand (electron donor) to produce a metal 'complex'. It is a property common to both the metal ion and the ligand and is manifested by the decreasing tendency of ML to form ML_2 relative to the tendency of M to react with L to give ML. That log $U_{11} = 0$ follows automatically since we are dealing with the formation of (1,1) from (1,0) and (0,1) species (free metal ion and free ligand, respectively), that is, from reference states.

The significance of the log U_{pq} term in the formation of polynuclear species is not as obvious but it accounts for the increasingly poorer estimates provided by the earlier Sylva-Davidson equation[7,8] as the molecularity increases.

In 1953 van Panthaleon van Eck,[16] by utilising the Bjerrum approach, proposed an empirical equation to describe formation constants, and arrived at a result which is closely related to our present results; thus (using the present nomenclature) he proposed the empirical relationship (39) (his equation (10)):

$$\log \beta_{1q} = q\log \beta_{11} - \lambda q(q-1) \quad , \tag{39}$$

where λ is an empirical constant which he did not explore further. Using our approach, an explicit expression for λ can be obtained from equations (36), (37), and (39), leading to equation (40) in which λ is no longer merely an empirical parameter:

$$\lambda = \left[\log (q!)/q(q-1)\right] - \tfrac{1}{2}\log k \quad , \tag{40}$$

and which is now in terms only of the stoicheiometry of the monomeric species ML_q, and the proportionality constant, k, relating two consecutive formation constants. It remains to examine more fully the nature and significance of this latter parameter.

Part Two

The Empirical Approach: The Brown-Sylva Electronicity Principle

Electronicity: A New Concept in Solution Chemistry

This task required an examination of the available experimental data[1-5] and the concomitant values of k in order to seek out a consistent and recurring relationship for all metal ion-ligand systems. We have found such a relationship which is described by equation (41) (for mononuclear complexes):

$$\log k = -e^{-(\varepsilon_M - \varepsilon_L)^2} \quad . \tag{41}$$

In equation (41) we have introduced a new unifying concept, represented by ε_M and ε_L, as a fundamental property of both metal ions and ligands. We have chosen to refer to this concept as <u>electronicity</u> ('freeness' of the valence electrons). This property describes quantitatively the ability of a ligand to complex a metal ion. A description of electronicity in terms of more fundamental parameters is being attempted. It will be seen that the use of this concept will quantify a number of other concepts such as A- and B-character, 'hard' and 'soft' metal ions and ligands, and charge- and frontier-controlled reactions,[17-20] in the context of complex formation. It will also eliminate some results of these older concepts which lead to apparent paradoxes[20] and will unify both metal ions and ligands onto the one scale of values. The right-hand side of equation (41) will in what follows be referred to as ψ and relate the affinity of the two entities for each other; the larger the value of ψ the greater is the bond strength between the ions.

The term 'hard' is applied to both metal ions and ligands and indicates low polarisability and hence high polarising power of the valence or bonding electrons. These 'hard' entities would be of low electronicity since the free electron-like properties are diminished because of the dominance of the positive nuclear charge (or, equivalently, the poor screening of the inner electrons). 'Soft' atoms or ions, on the other hand, can be readily polarised and hence have low polarising power and also high electronicity because the valence electrons are more electron-like, being less influenced by the positive nuclear charge.

Using equation (41) in (38) leads to equation (42):

$$\log K_q = \log K_1 - \log q - (q-1)\psi \ . \tag{42}$$

The corresponding equation for the overall constant is given by equation (43):

$$\log \beta_{1q} = q \log \beta_{11} - \log (q!) - \tfrac{1}{2}q(q-1)\psi \ . \tag{43}$$

For polynuclear complexes, consideration must be given to the multiplicity of the bonds required to form the structure of the species, rather than to a simple M-L entity. This is achieved by the introduction of the term $(2-\theta_M)$ where θ_M is the number of metal ions bonded to each ligand.[13] The use of equations (29), (30), and (41), then leads to a more fundamental variant of the Sylva-Davidson equation, equation (44):

$$\log \beta_{pq} = (q+2-2p) \log \beta_{11} + (p-1) \log \beta_{22} - \log \left[(q+1-p)!\right] - \tfrac{1}{2}(q-p)(q+1-p)(2-\theta_M)\psi . \tag{44}$$

Finally by using equations (30), (34), and (41), the most general form of the Sylva-Davidson equation (45) can be obtained:

$$\begin{aligned}\log \beta_{pq} = {} & ([q(r-1)-s(p-1)][\log \beta_{tu} + \log ((u+1-t)!) + \\ & \tfrac{1}{2}(u-t)(u+1-t)(2-\theta_M)\psi] + \\ & [u(p-1)-q(t-1)][\log \beta_{rs} + \log ((s+1-r)!) + \\ & \tfrac{1}{2}(s-r)(s+1-r)(2-\theta_M)\psi])/[u(r-1)-s(t-1)] \\ & - [\log ((q+1-p)!) + \tfrac{1}{2}(q-p)(q+1-p)(2-\theta_M)\psi] \ .\end{aligned} \quad (45)$$

The significance of θ_M in the above equations requires more description. In the mononuclear case, that is, in the formation of ML_q (or $M(L_1)_{q-r}(L_2)_r$), it is irrelevant since only one metal ion needs to be considered. In the polynuclear case, where M_pL_q is formed, it becomes operative since the influence of more than one metal ion needs to be considered simultaneously. This can be further illustrated if complexes, both polynuclear and containing different ligands, that is $M_p(L_1)_{q-r}(L_2)_r$, are considered. When applying the principle of electronicity, it is important to understand that the process of complex formation must be independent of pathway, but it is necessary to conceptualise a given pathway which will give a result the same as that of any other pathway. These arguments for mixed-ligand, polynuclear species lead to a slightly but significantly different expression for log k which, of course, reduces to the simpler form in the appropriate circumstances (noting that the total number of ligands is q-r+r=q):

$$\log k = -(2-\theta_M)e^{-1/q\sum_{1}^{q}(\varepsilon_M - \varepsilon_L)^2} \ . \quad (46)$$

The Empirical Equation: The Hydroxide Case

The generalised Sylva-Davidson equation (equation (45)), derived above, allows the estimation of any constant, log β_{pq}, from the known values of any other two constants (of the same metal ion), β_{rs} and β_{tu}. Therefore, when estimating a formation constant of a particular system, some prior knowledge of the system is needed but, because of a lack of the appropriate data, this is not always possible. To overcome this problem an equation is required which estimates the formation constant of a system independently of other associated formation constants; it would do this by relating properties of the reacting ions or molecules to the formation constants.[13] To accomplish this derivation, the available literature[1-5] was examined to find if there were any relationships between the formation constants of metal ion complexes and the properties of the reacting ions (e.g. ionic charge and radius, electronic structure, etc). We have used this empirical approach successfully previously[13] and many of the equations which follow in this work have been derived in the same manner.

In the earlier work[13] we showed that β_{11} values for hydroxo-metal complexes can be well predicted in almost all instances by the linear equation

$$\log \beta_{11} = \mathrm{Int}_1 + \mathrm{Slp}_1[g_1(z_M/r_M^2 + g_2)] \quad , \qquad (47)$$

where Int_1 and Slp_1, the intercept and slope values of the linear equation are, respectively, -14.52(0.10) and 0.139(0.007). The standard deviations follow in parentheses - a convention which will be used throughout this paper. g_1 and g_2 are given by equations (48) and (49):

$$g_1 = (1+2S+D)(z_M+2); \qquad (48)$$

$$g_2 = g(n)(z_M-1) + 0.1d(n-3)^2(1-S) \quad . \qquad (49)$$

In these expressions, z_M is the formal cationic charge of the metal ion, r_M is the ionic radius (those of Shannon and Prewitt[21] were almost always satisfactory), S depends on the absence (S=0) or presence (S=1) of s-electrons in the outermost shell of the ion (those ions exhibiting the inert pair effect), D=1 if d-orbitals are available for bonding (otherwise D=0), and g(n) is a Slater function[22] (g(n)=1 when n, the principal quantum number, is greater than unity, otherwise g(n)=0). As written, equation (47) appears to be a function of z_M/r_M^2 but the presence of z_M in both g_1 and g_2 makes it an implicit function of z_M^2/r_M^2.

Using equations (47), (48) and (49), it was demonstrated[13] that the metal cations fall into four distinct groups, a x $f[z_M^2/r_M^2]$, where a is a proportionality constant, and a=1, 2 (two groups), and 4, as follows:

(i) Metal ions for which D=0 and (hence) S=0, e.g. Groups 1A and 2A of the Periodic Table and aluminium(III); here, a=1.

(ii) This group is the largest and comprises Group 3A, the lanthanides, the first-row transition metal ions, zinc(II), gallium(III), and possibly the actinides (depending on the relative energies of the d- and f-electrons); here, a=2.

(iii) Here, S=0, n>3 and D=1; this group includes the second- and third-row transition metal ions and Groups 2B, 3B, 4B, and 5B in their group valency states; a=2 also.

(iv) This group consists of those ions which exhibit the 'inert (valence) pair' effect since S=1; examples are Tl(I), Sn(II), Pb(II), and Bi(III). Here, a=4.

In our earlier work[13] we pointed out that the polynuclear hydroxo-complexes of metal ions involve fewer stoicheiometries than might have previously been believed, these being (2,1), (2,2), (3,3), (3,4), (3,5), (4,4), (4,6), (4,7), (4,8), (4,12), (6,8), (6,12), and (6,15) (and possibly some nonamers for bismuth(III)). It was suggested that for q/p>2, these stoicheiometries are only formalisms since some oxo-bridging would be expected. There appears to be four classes of hydroxo-complexes as determined by their 'structure types':

(i) Type I. The species (3,3), (3,4), (3,5), (4,4), (6,8), examples are magnesium(II), nickel(II), lead(II), aluminium(III), beryllium(II), and cadmium(II), with three hydroxo-bridges per metal cation (i.e. $\theta_M=3$).

(ii) Type II. The species (2,2), (3,4) and (3,5) - both common to Types I and II - and possibly (4,6) and (4,7), examples are dioxouranium(VI), scandium(III), copper(II), iron(III), and chromium(III), with two hydroxo-bridges per metal cation.

(iii) Type III. The species (4,8), (4,12), and (6,15), examples are zirconium(IV), thorium(IV), bismuth(III), and uranium(IV), with two or more hydroxo-bridges per metal cation.

(iv) Type IV. The (2,1) species which in most cases is not reliably documented but is said to include beryllium(II), lead(II), cadmium(II), and zinc(II) with one hydroxo-bridge per metal cation.

We can assume[13] that the condensation process involved in the formation of each of the four types of polynuclear (hydroxo-) species is energetically different for each type, but approximately the same within each type, irrespective of the stoicheiometry of the species. We can then write a simplified form of the Sylva-Davidson equation:

$$\log \beta_{pq} = q \log \beta_{11} + \left[(p-1)/(r-1)\right](\log \beta_{rs} + \log U_{rs} - s\log \beta_{11}) - \log U_{pq} \quad , \qquad (50)$$

where p and q refer to the stoicheiometry of the unknown species, and r and s represent the stoicheiometry of any other known polynuclear species. The condensation step, given by $\log \beta_c$, for the (r,s) species, can then be expressed as

$$\log \beta_c = \left[1/(r-1)\right](\log \beta_{rs} + \log U_{rs} - s\log \beta_{11}) \quad . \qquad (51)$$

By analogy with equation (47), equation (52) follows:

$$\log \beta_c = [\text{int,type(i)}] + [\text{slp,type(i)}][g_1(z_M/r_M^2 + g_2)] \quad , \qquad (52)$$

where type (i) represents types I to IV as appropriate. Thus, a single value of the slope and intercept can be determined for any metal ion undergoing condensation processes of one or more of the four types, which allows the calculation of log β_c for each metal ion of that type. Hence, the value of log β_{pq} can be calculated from equation (53):

$$\log \beta_{pq} = q\log \beta_{11} + (p-1)\log \beta_c - \log U_{pq} \quad . \qquad (53)$$

Finally, equation (54) follows from the expression for log β_{11} in equation (47), and log β_c in equations (51) and (52):

$$\log \beta_{pq} = [q(\text{Int}_1)+(p-1)(\text{Int}_2)] + [q(\text{Slp}_1)+(p-1)(\text{Slp}_2)] \qquad (54)$$

$$[g_1(z_M/r_M^2 + g_2)] - \log U_{pq} \quad .$$

Here, Int_1 and Slp_1, and Int_2 and Slp_2 are, respectively, the least squares slope and intercept values of linear equations for the (1,1) species and the polymeric (p,q) species.

In practice, although the treatment is completely general, the argument has been developed using the hydroxide ion. It should also be noted that, in principle, the above applies equally to polyoxometallate systems. However, in this context, there is no longer a distinction between metal ion and ligand. Furthermore, the concept applies equivalently to multidentate ligands; the equation development for such ligands is outlined below.

The Empirical Equation: The General Case

On extending equation (47) to involve unidentate ligands generally, it was found that the expressions for g_1 and g_2 given above for hydroxide (equations (48) and (49)) are only one form of more general expressions, namely equations (55) and (56), which are now written to include the electronicity of the ligand:

$$g_1 = (1+D+\varepsilon_L{}^2S)(z_M+2) \quad ; \qquad (55)$$

$$g_2 = g(n)(z_M-1) - 0.05d\left[(\gamma-1)(\varepsilon_L{}^4-3)-1\right]\left[n-(3+2\gamma)\right]^2 \left[1-\gamma z_M\right](1-S) \quad . \qquad (56)$$

Of particular interest is the need for a new parameter, γ, in equation (56). This we may term the ligand parameter, which has a value of either zero or unity depending on the nature of the ligand. If we consider the corresponding acids of the ligands, it is noteworthy that these acids have been assigned to one of two classes, an 'oxo-acid' (e.g. perchloric acid) or a 'binary acid' (e.g. hydrochloric acid).[23,24] These classes are characterised, respectively, by the presence of X-O-H and X-H groups. The latter classification does not correspond completely with the grouping of the ligands defined here by the value of γ, and it seems likely that the classification given for the acids[23,24] is not completely suitable.

The present work classifies ligands into the following groups:

(i) Class 1. These ligands have only one donor atom which can accommodate a proton. The acids can be either weak or strong and consist of a diverse group of monoprotic acids such as hydrochloric and thiocyanic acids, and water and ammonia. Exceptions, are the derived ligands O^{2-}, S^{2-} and N^{3-}, which are polyprotic acids. Also included here (see Class 2) are hydrogen peroxide, hydrazine, hydroxylamine, hyponitrous and hypochlorous acids, and similar molecules. Here, $\gamma=0$.

(ii) Class 2. This class consists of oxo-acids which, again, may be weak or strong; examples of these acids are perchloric, sulphuric, acetic, and carbonic acids, and the hydrogen carbonate and hydrogen phosphate ions (that is, charge is not relevant to the classification). Here, $\gamma=1$.

Multidentate ligands must be classified according to the nature of the donor atoms present and thus can be either class 1, class 2, or both simultaneously (see below).

The most significant difference between the two classes is that in the class 2 ligands there is an ambiguity of the protonation site which is absent in the class 1 ligands. Therein lies the discrepancy between our classification of the corresponding acids of the ligands and that of acids previously referred to[23,24] since, for example, whereas hypochlorous acid has been classified as an oxo-acid, it falls into our class 1 of ligands.

The status of the fluoride ion is anomalous since a fluoro-metal ion complex may be produced from either the monomeric F^- ion or from some polymeric form; this ligand can thus be considered as belonging to both classes. As is discussed later, the fluoride ion is anomalous in a variety of ways.

Electronicity and Previous Concepts

Metal ions occur in aqueous solution as hydrated ions, $[M(H_2O)_n]^{z+}$, and the value of n is referred to as the hydration number. This is, however, an idealised concept[13,25] since there are primary, secondary, and further increasingly weaker interactions reaching into the bulk solvent whose properties are accordingly altered. All of these are constantly changing owing to the very rapid exchange reactions which occur between water molecules of slightly differing energy status. Nevertheless, the concept serves a useful purpose, and a primary hydration sphere can be considered as consisting of the maximum number of water molecules equidistant (or nearly so) from the metal ion, averaged over time. This number is conveniently thought of as the coordination number of the metal ion (under the given conditions, since it may change if the conditions change).

Metal ions in solution are not interactively independent of the solvent, nor of the accompanying anion or added ligands (molecules or anions). There are competitive reactions between the water molecules of the primary or other spheres and the accompanying anion or ligand. We will define a 'metal ion complex' as that entity produced when one or more primary sphere water molecules is displaced by a different entity. On the other hand, if a secondary or other outer sphere water molecule is displaced, the species produced may be regarded as an 'ion pair' and will not be of interest here except that, although distinctly different, in practice, the distinction between the two concepts is blurred.

The 'hardness' and 'softness' of metal ions and ligands have been quantified by Klopman[18] in terms of an 'intrinsic quantity' or 'softness', $E^{\neq}$. More recently, Parr and Pearson[20] discussed similar concepts in terms of the 'absolute hardness' of metal ions and ligands, η_a and η_b, respectively. However, the use of two different scales by both approaches, one for each of metal ions and ligands, has lead to confusion and even apparently paradoxical results[20] and there is a real difficulty in properly explaining, even qualitatively, the nature of, and differences between, hard-hard, soft-soft, and hard-soft interactions, in terms of covalent or ionic bonding. Thus, according to the principle of hard and soft acid and bases (HSAB), soft-soft interactions are 'strong', being covalent in nature. There is said to be a paradox, however, for hard-hard interactions, since, according to HSAB, these ought also to be strong but ionic; thus, taking the two extremes (ionic and covalent bonding), the bonding does not vary between these two extremes. Parr and Pearson[20] are unconvincing in their explanation, in terms of either ionic or covalent bonding, of the paradox of hard-hard interactions. They also propose that hard-soft interactions are 'generally weak' but neither suggest nor imply ionic or covalent bonding.[20]

There is, thus, some confusion regarding the nature and strength of ionic as opposed to covalent bonding in solution. The Brown-Sylva electronicity principle (BSEP), however, is clear in this context: *hard-hard and soft-soft interactions lead to strong complex formation and hence covalent bonding in solution, whereas hard-soft interactions lead to ionic bonding and hence weak or negligible complex formation in solution*.

The Determination of Electronicity Values

The most direct access to the values of the electronicity of ligands is through the values of log β_{11} of complexes of metal ions possessing the inert pair effect. Equations (47), (55), and (56) apply and, noting that D=S=g(n)=1, lead to equation (57):

$$\varepsilon_L = [[(\log \beta_{11} - \mathrm{Int}_1)/\mathrm{Slp}_1(z_M+2)(z_M/r_M{}^2 + z_M - 1)] - 2]^{\frac{1}{2}} \quad . \qquad (57)$$

Thus, for a lead(II) complex which, in practice, is the most useful since more data are available, z_M=2 and r_M=0.99 Å (0.099 nm), it follows that

$$\varepsilon_L = [[(\log \beta_{11} - \mathrm{Int}_1)/12.16\mathrm{Slp}_1] - 2]^{\frac{1}{2}} \quad . \qquad (58)$$

Further access to the electronicity values can be obtained for ligands with γ=0 (hydroxide, chloride, thiocyanate etc.) by considering the log β_{11} values of complexes of metal ions from the second and third long periods, where D=1 and S=0 (i.e. indium(III), silver(I), cadmium(II), rhodium(III) etc.), and equations (47), (55), and (56). Such considerations produce equation (59)

$$\varepsilon_L = [2+[((\log \beta_{11} - \mathrm{Int}_1)/\mathrm{Slp}_1) - (2(z_M+2)$$

$$(z_M/r_M{}^2 + z_M - 1))]/0.1d(z_M+2)(n-3)^2]^{1/4} \quad . \tag{59}$$

An equation similar to (59) can also be developed for the fluoride ion by taking into account the complexes of metal ions of the first and second long periods with D=1 and S=0. In many cases it was not possible to compare adequately the electronicity of the ligand obtained from more than one metal ion because of the paucity of data, but when this was possible, satisfactory agreement could be obtained.

The fundamental difference between the present approach and those of Klopman,[18] and Parr and Pearson,[20] is our use of a *single* scale for the measure of the appropriate parameter (electronicity, softness ($E^{\neq}$),[18] absolute hardness (η)[20]). Thus, our approach resolves the dichotomy and the attendant inconsistency between metal ions and ligands that is present in the earlier work. However, if metal ions and ligands are treated *separately*, we are still able to relate our concept of electronicity with the earlier work, as in equations (60), (61), and (62), even though this earlier work lacks rigour in its interpretation:

$$\varepsilon_L = 7.0 - \eta_B \quad \text{(Parr and Pearson)}^{20} \quad ; \tag{60}$$

$$\varepsilon_L = 11.0 + 0.9E^{\neq} \quad \text{(Klopman)}^{18} \quad ; \tag{61}$$

$$\varepsilon_M = 1.8 - 0.3E^{\neq} \quad \text{(Klopman)}^{18} \quad . \tag{62}$$

It should be noted that the treatment of metal ions by Parr and Pearson[20] cannot be rationalised in this way, hence the absence of a fourth equation; their results for these ions would appear to be questionable.

Whereas the electronicity value of a ligand can be calculated directly from the first formation constant of a metal ion complex of that ligand, as shown by equations (57) and (59), the values for metal ions require values of ligand electronicities; thus, manipulation and rearrangement of equation (42) leads to the explicit expression (63);

$$\varepsilon_M = \varepsilon_L \pm \left[-\ln \left[\log K_1 - \log K_q - \log q)/(q-1)\right]\right]^{\frac{1}{2}} \quad . \qquad (63)$$

Note that equation (63) is written in terms of step-wise formation constants and that the difference, $\log K_1 - \log K_q$, incorporates the proportionality constant relating consecutive formation constants.

Table 1 provides the values of electronicity of metal ions and ligands in ascending order calculated by the methods outlined in the present work together with comparative values obtained from the work of Klopman,[18] and Parr and Pearson,[20] using equations (60), (61), and (62). It can be seen that the agreement is excellent and, therefore, this unified approach satisfactorily encompasses all the earlier work.

The Correlation Between Stability and Dissociation Constants

For any given ligand, the intercept (Int_1) and slope (Slp_1) values of the linear equation (47) can be determined by plotting the experimental $\log \beta_{11}$ values[1-5] of metal ion complexes of the ligand against the function $g_1(z_M/r_M^2 + g_2)$ (where g_1 and g_2 for each complex, are calculated using equations (55) and (56)). Figure 1 illustrates the plots for the sulphate, ammine, and chloride ions, and Table 2 lists the values of Int_1 and Slp_1, calculated from similar plots, for a number of ligands. The experimental data[1-5] used for this purpose necessarily refers to thermodynamic constants[13] (that is, at zero ionic strength) so, where necessary, they have been converted either by the method of Baes and Mesmer[26] or Phillips.[27] Although not always entirely satisfactory, doubtless because of their widely

TABLE 1

ELECTRONICITY VALUES OF METAL IONS AND LIGANDS

Ion	Electronicity			Ion	Electronicity		
	Present work	From Klopman	From Parr and Pearson		Present work	From Klopman	From Parr and Pearson
(a) Ligands							
F^-	-0.064	0.038	-0.010	OH^-	1.401	1.595	1.415
HPO_4^{2-}	0.184			NH_3	1.569		
$H_2PO_4^-$	0.282			NO_3^-	1.639		
SO_4^{2-}	0.699			SCN^-	1.674		
HCO_3^-	1.027			$S_2O_3^{2-}$	1.865		
NO_2^-	1.098		2.545	IO_3^-	1.927		
CH_3COO^-	1.123			BrO_3^-	2.184		
CO_3^{2-}	1.260			Cl^-	2.344	2.054	2.305
ClO_4^-	1.319			Br^-	2.942	2.702	2.760
ClO_3^-	1.353			I^-	3.361	3.521	3.305

Ion	Electronicity		Ion	Electronicity		Ion	Electronicity	
	Present work	From Klopman		Present work	From Klopman		Present work	From Klopman
(b) Metal Ions								
Al^{3+}	0.015	0.000	Np^{3+}	0.795		Ga^{3+}	1.156	1.368
Zr^{4+}	0.021		Eu^{3+}	0.803		Cr^{3+}	1.161	1.302
Sc^{3+}	0.085	0.081	Ac^{3+}	0.845	0.816	Sn^{2+}	1.387	1.149
Hf^{4+}	0.130		Ce^{3+}	0.855	0.702	In^{3+}	1.472	1.680
Th^{4+}	0.187		U^{3+}	0.856		Bi^{3+}	1.539	1.854
Y^{3+}	0.321	0.381	Pr^{3+}	0.918	0.933	Fe^{2+}	1.547	1.677
La^{3+}	0.488	0.579	Lu^{3+}	1.042		Co^{2+}	1.583	1.788
Am^{3+}	0.687		Mg^{2+}	1.049	1.260	Mn^{2+}	1.692	1.656
Be^{2+}	0.726	0.675	Cm^{3+}	1.099		Pb^{2+}	1.831	1.806
Yb^{3+}	0.733	1.278	Fe^{3+}	1.112	1.212	Ni^{2+}	2.069	1.902
Pu^{3+}	0.782		Ba^{2+}	1.146	1.266	Zn^{2+}	2.095	2.097
Tl^+	2.191	2.412	Hg^{2+}	2.319	2.217	Tl^{3+}	2.459	2.520
Ag^+	2.239	2.229	Cu^{2+}	2.332	2.136	Cd^{2+}	2.731	2.412

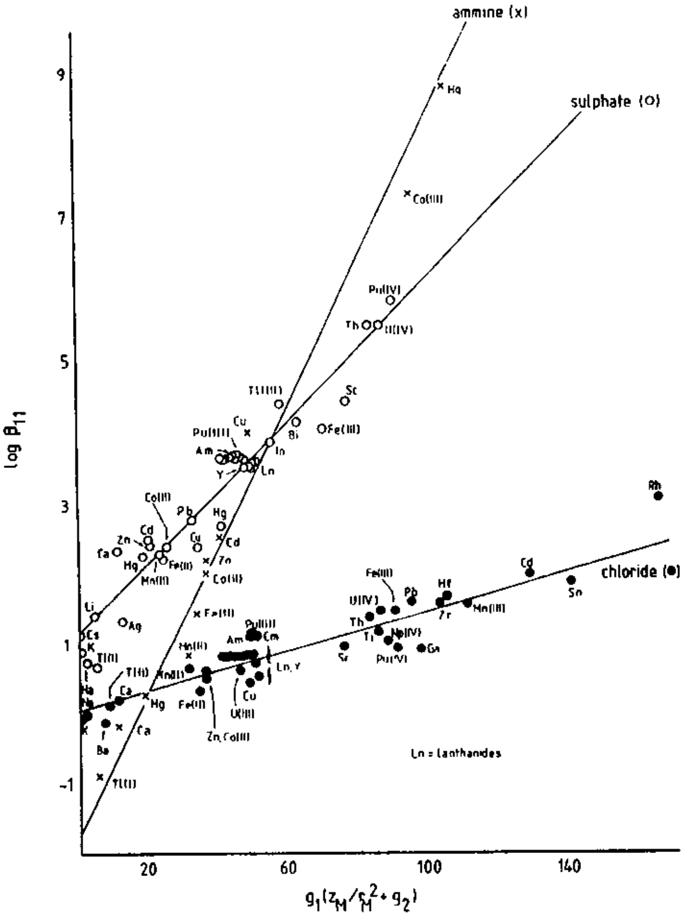

Figure 1 Experimental log β_{11} values plotted against the function $g_1(z_M/r_M^2 + g_2)$ for the sulphate, ammine, and chloride ions

different origins, these values are nevertheless sufficiently consistent for definite relationships to be established. However, the process of data selection emphasised the need for a vast amount of experimental work to be done in this area, and for greater care and rigour to be used in carrying it out.

The 'hardness/softness' concepts of Klopman[18] and Parr and Pearson[20] envelope and partially quantify, at least in terms of metal ion-ligand complexation, the earlier acid-base concept of Lewis.[28,29] We might expect that there is a qualitative correlation between the tendency for an anion (the base) to react with a hydrogen ion and for the same anion to react with a metal ion (the acid). Indeed, many correlations have been made between the proton dissociation constants of a series of related ligands and the stability constants of

TABLE 2

LEAST SQUARES INTERCEPT AND SLOPE VALUES FOR SOME UNIDENTATE LIGANDS

Ligand	Intercept(Int_1)[a]	Slope(Slp_1)[a]	Correlation coefficient	Number of complexes
OH^-	-0.52(0.10)[b]	0.139(0.007)	0.9971	53
F^-	-0.40(0.10)	0.098(0.002)	0.9936	44
Cl^-	0.03(0.06)	0.0141(0.0005)	0.9726	49
Br^-	0.07(0.10)	0.0082(0.0003)	0.9801	22
I^-	0.29(0.12)	0.0047(0.0002)	0.9890	16
$CO_3{}^{2-}$	2.13(0.17)	0.104(0.003)	0.9850	32
$SO_4{}^{2-}$	1.10(0.13)	0.050(0.003)	0.9399	42
$NO_2{}^-$	-0.21(0.23)	0.065(0.011)	0.9163	9
$NO_3{}^-$	-0.01(0.10)	0.017(0.002)	0.8155	39
$ClO_4{}^-$	0.29(0.27)	0.015(0.008)	0.6482	7
$ClO_3{}^-$	0.06(0.15)	0.010(0.004)	0.6778	12
$BrO_3{}^-$	-0.37(0.16)	0.025(0.003)	0.9259	12
$S_2O_3{}^{2-}$	1.25(0.15)	0.040(0.005)	0.9072	14
$H_2PO_4{}^-$	0.17(0.23)	0.049(0.006)	0.9413	12
$HPO_4{}^{2-}$	0.80(0.29)	0.106(0.010)	0.9635	11
$HCO_3{}^-$	-0.01(0.25)	0.073(0.011)	0.9354	8
$IO_3{}^-$	0.03(0.19)	0.042(0.005)	0.9387	15
CH_3COO^-	-0.13(0.08)	0.066(0.002)	0.9897	21
NH_3	-1.72(0.22)	0.101(0.005)	0.9906	11
SCN^-	-0.25(0.24)	0.026(0.004)	0.8339	25

a Estimated standard deviations given in parentheses.

b The value of Int_1 given in the text (-14.52) is equal to $-0.52-pK_w$ and derives from the differing conventions used for hydrolysis as compared to other complexation reactions.

the corresponding metal ion complexes.[30-35] However, a more generalised treatment, based on simple correlations has not been derived as quite clearly additional factors other than the pK_a of the ligand, are involved. If two ligands with similar proton dissociation constants but differing charges react with the same metal ion, it can be shown that the ligand with the larger negative charge will form a complex of greater stability; for example, the complexes of the $H_2PO_4{}^-$ ion (pK_a=2.16), with Mg^{2+} and Am^{3+} have log β_{11} values of 1.17 and 2.51, respectively, whereas the log β_{11} values of the complexes of the same metal ions with the SO_4^{2-} ion (pK_a=1.99) are 2.23 and 3.6. Another example of the complexity is revealed by the stability reversals in groups of ligands such as the halides; most metal ions follow the stability sequence, $F^- > Cl^- > Br^- > I^-$ when reacting with the halide ions, but metal ions such as Tl^{3+}, Hg^{2+}, and Pb^{2+} follow the opposite sequence, i.e. $I^- > Br^- > Cl^- > F^-$.[17]

The BSEP allows an indirect correlation to be made between the proton dissociation constants of all ligands and the stability of their corresponding metal ion complexes simply because all of the above factors are considered. Indeed, linear relationships can be obtained by plotting first, the slope value (Slp_1) of each ligand given in Table 2 against the correpsonding pK_a value and second, the intercept value in the same table against the function $Slp_1[1+(3-z_L)(z_L+1)]$, where z_L is the charge of the ligand; these plots are given in Figures 2 and 3. The line of best fit obtained in each figure (solid line) can be expressed by equations (64) and (65):

$$Slp_1 = 0.031\ (0.002) + 0.0078\ (0.0004)\ pK_a \quad ; \tag{64}$$

$$Int_1 = 0.11\ (0.06) - 4.10\ (0.34)\ [1+(3-z_L)(z_L+1)]Slp_1 \quad . \tag{65}$$

The correlation coefficients are, respectively, 0.9840 and 0.9436.

The form of equations (64) and (65) is quite interesting as the pK_a values, which are solely ligand dependent, are related to other parameters which are also ligand dependent (Slp_1 and Int_1). Previous treatments,[30-35] however, have attempted to correlate the pK_a values with a parameter that is both metal ion and ligand dependent - the formation constant of the metal ion-ligand complex. Consequently, these treatments cannot quantify the coordinating affinities of a metal ion and ligand; e.g. the Sc^{3+} ion has a greater affinity for the F^- ion than it has for the I^- ion (compare the electronicity values given for these ions in Table 1). It is not surprising, therefore, that these treatments[30-35] have had limited success only with related

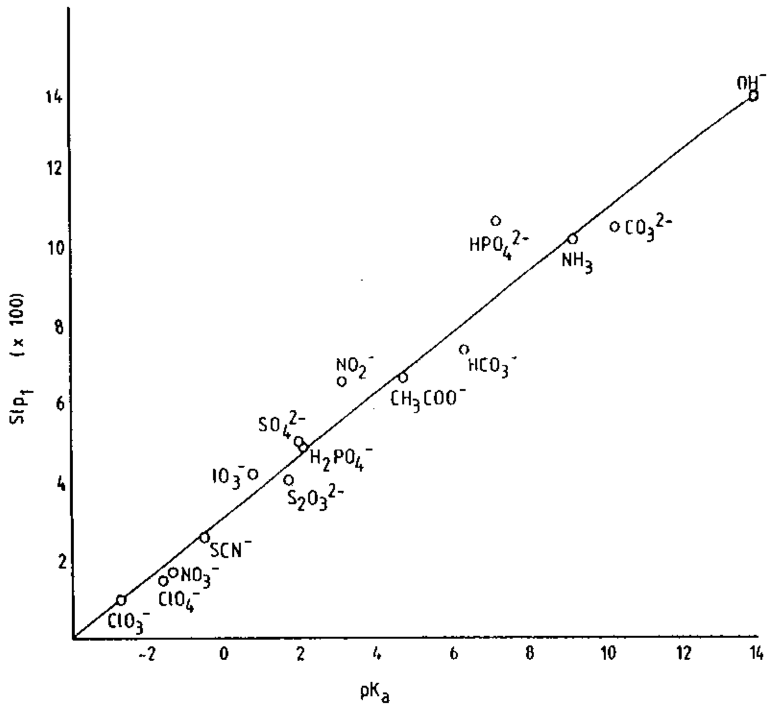

Figure 2 Slope values (Slp_1) plotted against pK_a values for a number of ligands

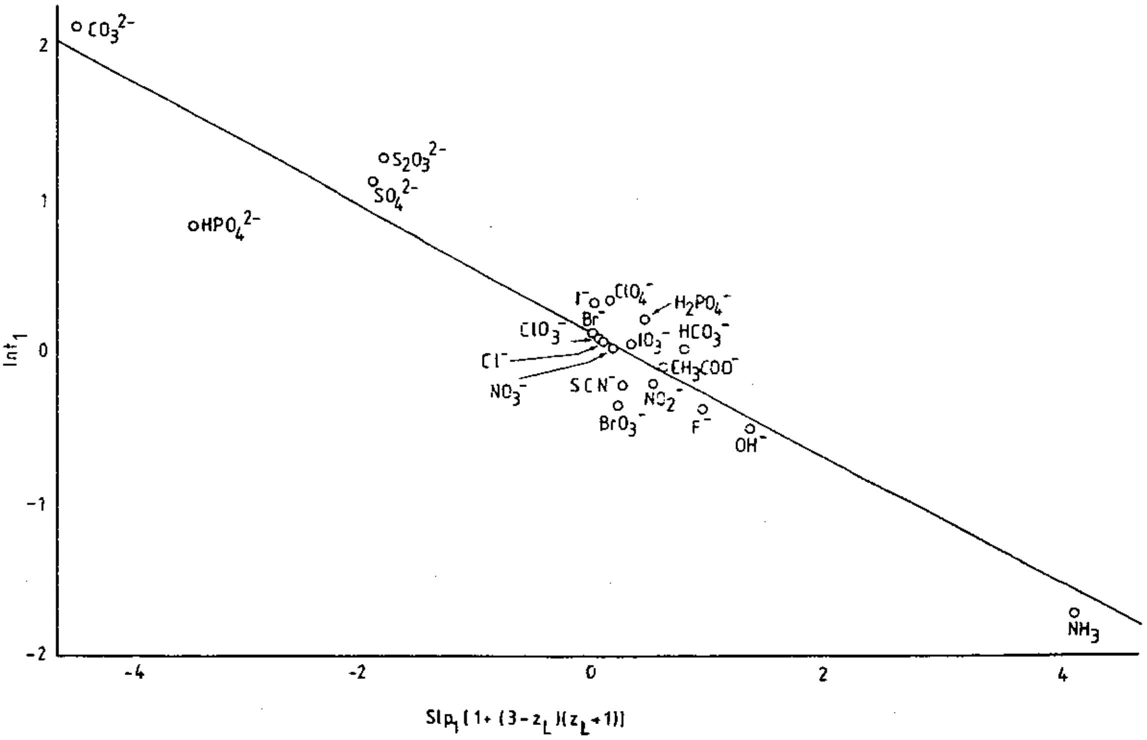

Figure 3 Intercept values (Int_1) plotted against the function $Slp_1\left[1 + (3-z_L)(z_L+1)\right]$ for a number of ligands

ligands where the pK_a and electronicity values of the ligands are similar. Implicit in the present treatment, however, is the quantification of the affinity of a metal ion for a ligand through the functions g_1 and g_2 and, conversely, the quantification of the affinity of a ligand for a metal ion through equations (64) and (65). When used together, the ability to predict the stability of any metal ion complex is possible.

The determination of the pK_a for such ligands as chloride, bromide and iodide is experimentally very difficult because of their inaccessible values. However, these values can be predicted from their respective slope values given in Table 2 and equation (64). The values calculated are, respectively, -2.19, -2.96, and -3.42. The first two values are in the ranges previously calculated by Hogfeldt,[36] namely -1.05 to -2.60 and -2.15 to -4.65, using the Hammett acidity function; a value for HI was not given.

To make chemical sense the linear equation (64) must always have a positive slope; thus, as $g_1(z_M/r_M^2 + g_2)$ increases, so must $\log \beta_{11}$. The minimum conceivable value of Slp_1 is thus zero and, as such, equation (64) suggests that no acid can have a pK_a value less than approximately -4.0 which suggests the existence of an 'absolute' pK_a scale, differing from the conventional scale by four units.

As already stated, polynucleation is conceptually general but, very few ligands actually form polynuclear species in solution. Indeed, the hydroxide ion is the only ligand for which these species have been substantially verified and, as such, we are able to divide the polymer formation of this ion into four distinct types[13] (see above) as determined by their structural form. Furthermore, we have shown[13] that the formation constants of these polynuclear species can be determined by using equation (54). In the equation, Int_2 and Slp_2 are the linear least squares slope and intercept values for each of the structure types. By analogy with equations (64) and (65), we would expect these parameters to be dependent upon a property of the ligand; to define this dependence we propose the empirical equations (66) and (67):

$$Slp_2 = 0.187\theta_L^2 - 0.814\theta_L + 0.78 \quad , \tag{66}$$

$$Int_2 = 3.58 - 62.67Slp_2 \quad , \tag{67}$$

where θ_L is the number of ligand molecules bonded to each metal ion. Two interesting points arise from these equations: first, the prediction of a formation constant of a polynuclear species requires a value of θ_M (from equation (44)) and θ_L, since these values mirror the effect of the multiplicity of the metal ion-ligand bonding on the electronicities of the separate entities; second, there is a similarity between equations (65) for Int_1 and equation (67) for Int_2 (both involve the corresponding Slp value).

An additional feature that requires comment is the behaviour of the fluoride ion since, of all the unidentate ligands considered, it alone does not comply. The anomalous behaviour is emphasised by the fact that the ion does not belong to one class of ligand unequivocally (γ=0 or 1) but to both simultaneously. Thus, in the expression for g_2, equation (56), γ=0 for the first and third appearance of the parameter and γ=1 for the second. Also, the accepted pK_a value for hydrofluoric acid does not predict the expected value of Slp_1, nor that of Int_1, as determined by least squares analysis for the (1,1) fluoro-complexes. Indeed, the acid dissociation constant of the acid is about six orders of magnitude larger than would be expected from the present approach. There is some ambiguity in the protium/fluoride speciation scheme because of the formation of polynuclear species such as (2,3) and (3,4)[37,38] a property absent from other protium/ligand systems. The protium/ligand systems. The pK_a of the fluoride ion, as determined from the Slp_1 in Table 2, is 8.59; speciation calculations show that the most probable stoicheiometry of this species is H_2F_2. Furthermore, this latter species and its formation constant are not inconsistent with the self-ionisation equilibria found in liquid HF.[23]

Oxometal Ions

The treatment of oxometal ions such as dioxouranium(VI), dioxouranium(V), oxovanadium(IV) must be different from that of the simple M^{z+} type metal ions. It has been shown[39] that, in the solid state, the ionic radius of these ions depends upon both the nature and number of ligands bonded to the central metal ion. The observation of a similar effect occurring in aqueous solution would not be unexpected. For example, if equation (47) is used to determine the value of the function $g_1(z_M/r_M{}^2 + g_2)$, and hence, indirectly, the value of the ionic radius, (by substituting the relevant values of log β_{11}, Int_1, and Slp_1 into equation (47) and solving for the value of the function) a different value of this function is obtained which depends on the nature of the ligand of the complex used in the calculation. It is therefore necessary to find a relationship to describe the varying nature of the ionic radius of the oxometal ions. We have found a linear expression for the relationship between the pK_a of a ligand and the value of $g_1(z_M/r_M{}^2 + g_2)$ as determined from the first formation constant of that ligand with the oxometal ion. This linear relationship is illustrated in Figure 4 for the dioxouranium(VI) ion and similar relationships have been found for all other oxometal ions.

Information can be gained from the slope and intercept values determined from plots similar to those illustrated in Figure 4. We have found that the slope determined for all bivalent metal ions is ca. 2.25, and for all monovalent ions it is approximately half of this value. Thus, we are able to express the slope as a function of the ionic charge of the oxometal ion. The intercept can be used to determine, indirectly, the maximum distance the ligand can be separated from the oxometal ion to still be considered bound in the primary hydration sphere. (This value is defined as the maximum ionic radius.) Therefore, by expanding equation (47) we are able to describe the behaviour of the complexation of oxometal ions, using equation (68):

$$\log \beta_{11} = Int_1 + Slp_1\left[g_1(z_M/r_M{}^2 + g_2) + 1.125z_M(pK_a+4)\right] , \qquad (68)$$

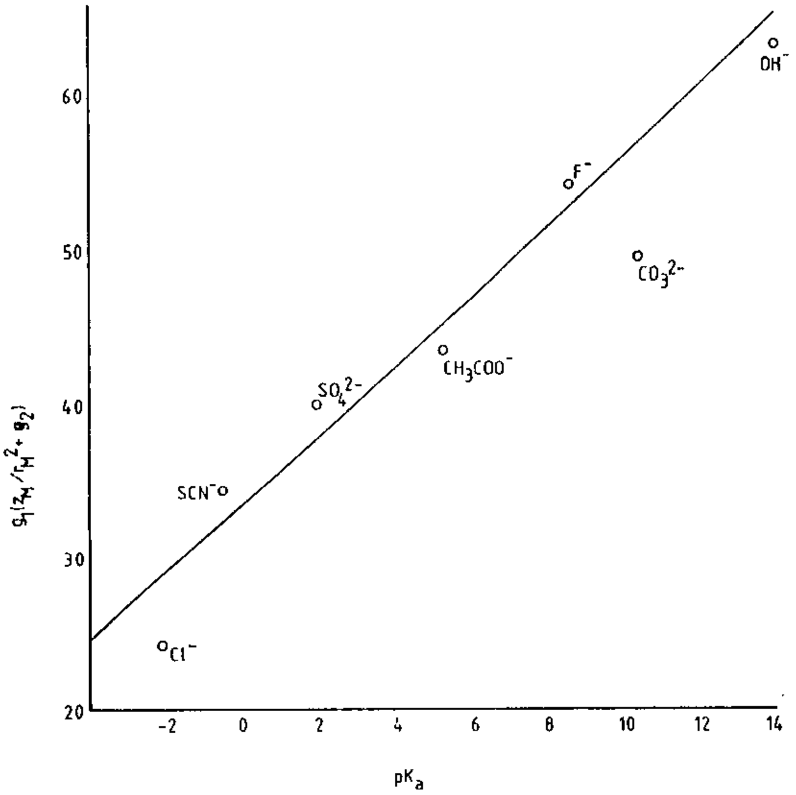

Figure 4 The value of the function $g_1(z_M/r_M^2 + g_2)$ plotted against the pK_a of a ligand for dioxouranium(VI)

where r_M is the maximum allowable ionic radius determined from the type of plots shown in Figure 4. Also, the 'absolute' rather than the conventional pK_a of the ligand is used. Since the intercept value calculated from these plots reflects the smallest possible value of $g_1(z_M/r_M^2 + g_2)$, and hence the largest value of the ionic radius, the use of the 'absolute' pK_a of a ligand is essential. The value of the function $g_1(z_M/r_M^2 + g_2)$ can only be greater than the value of the intercept and this can only be achieved by using the 'absolute' pK_a of the ligand. Table 3 gives a comparison of experimental and predicted formation constants for selected complexes of both oxometal and simple metal ions.

Multidentate Ligands

To extend the treatment developed so far for unidentate ligands only, to multidentate ligands, it is necessary to clarify the nature of the 'chelate effect' which is said to occur when a multidentate ligand coordinates to a metal ion. The importance of this phenomenon has been the subject of much controversy in recent years,[40-44] however, there appears to be no substantial difference between the two schools of thought except that one of them focuses on the entropy change whereas the other considers only the net effect on the free energy change and hence the change in the formation constant for given reactions. Irrespective of the net effect on the free energy change of a reaction, we regard the chelate effect as being the inevitably favourable entropy change which accompanies such reactions.

The maximum chelate effect is realised when there is no substantial adverse enthalpy effect. This adverse effect can be caused, for example, by changes brought about in the metal ion-donor atom bond energies due to steric effects. When chelate ring sizes are compared in terms of the chelate effect (entropy change minus the sum of adverse enthalpy effects) it is generally found that 4-R < 5-R > 6-R > 7-R (n-R is an n-membered chelate ring) since

(i) 4-membered rings usually cause undue steric effects on the ligand in conforming to the steric requirements of the metal ion;

(ii) 7-membered rings and greater involve a progressively decreasing favourable entropy effect because the second or subsequent donor atom becomes further removed from the metal ion and ultimately tends towards unidentate character; and

(iii) 5- and 6-membered rings are favoured (least adverse enthalpy effect) and, generally, 5-membered rings appear to conform completely to the steric and bonding requirements of the metal ion and steric strain on the ligand - indeed, in this case, the coordination of subsequent donor atoms can often be considered to occur simultaneously.

The physical explanation of the favourable entropy change is not difficult to visualise qualitatively.[23] When ligand molecules enter the coordination sphere of a metal ion, the water molecules of hydration are displaced and the entropy of the system will increase if the number of free molecules increases. Thus, in a unidentate ligand system, there is no increase in the number of molecules since each ligand displaces one water molecule. In a multidentate ligand system, each ligand displaces more than one water molecule, producing an increase in the number of free molecules.

A quantitative explanation, however, is not straightforward. To explain the net effect on the free energy change of a reaction, and hence the formation constant of a metal-chelate complex, it is probably prudent to examine, initially, the most simple case; that is, to compare uncharged unidentate ligands with analogous bidentate ligands. Although similar concepts would apply to charged ligands, these ligands have the added complication of electrostatic interactions.[41] In this context, therefore, it is common to consider the complex formation of the ligands, methylamine and ethylenediamine, where the latter may be regarded as two methylamine molecules joined together by the elimination of two hydrogen atoms.[41] Complexation reactions involving ethylenediamine can be thought of as the simultaneous reaction of two methylamine molecules with a metal ion, and each metal ion-donor atom bonding strength will be determined in accordance with the value of $g_1(z_M/r_M{}^2 + g_2)$. The net effect on the ligand is to double the value of the $g_1(z_M/r_M{}^2 + g_2)$ function, so in the more general case, we may extend equation (47) to equation (69):

$$\log \beta_{11} = \mathrm{Int}_1 + \mathrm{Slp}_1[g_1(z_M/r_M{}^2 + g_2)]c_n \quad , \qquad (69)$$

where c_n is the complexation number (the number of available protonation sites) of the ligand (e.g. c_n=2 for ethylenediamine), and Int_1, Slp_1, g_1 and g_2 are calculated in the same manner as before. It should be noted that for unidentate ligands, c_n is unity, so for these ligands, equation (69) simplifies to equation (47), as is required. This relationship will be valid when the donor atoms are identical and, in the case of charged ligands, electrostatic complications have been considered.

The step-wise formation constants, K_q, for these multidentate ligands can be determined from equation (70):

$$\log K_q = \log K_1 - (1+\gamma)\log\left[((q-1)c_n+1)((q-1)c_n+2) \ldots ((q-1)c_n+c_n)\right] - (q-1)(2-\theta_M)\phi \quad . \tag{70}$$

This equation is similar to equation (42) for unidentate ligands, but now includes the expanded term (the second term of the equality), and is analogous to the log q term originally contained in the expression. In equation (42), the log q term is, in part, a measure of the intrinsic tendency of a metal ion to form a chemical bond with a subsequent ligand. For unidentate ligands, it represents the decrease in the q-th step-wise formation constant (relative to the value of K_1) arising when the q-th ligand fills the q-th coordination site of the metal ion, based on purely structural considerations. However, when a multidentate ligand coordinates a metal ion, the addition of the q-th ligand does not fill the q-th coordination site of the metal ion and, furthermore, more than one coordination site will be filled simultaneously. This behaviour is described within the expanded logarithmic term in equation (70).

A feature of equation (70) is the expression $(1+\gamma)$ before the expanded logarithmic term. This expression is necessary to be able to predict the step-wise formation constants of the class 2 ligands. Because equation (70) must reduce to the appropriate equation for unidentate ligands, equation (42) becomes

$$\log K_q = \log K_1 - (1+\gamma)\log q - (q-1)(2-\theta_M)\phi \quad . \tag{71}$$

The physical reasons for the need to use this expression are, at this stage, not apparent.

It is more than often the case that the donor atoms of a multidentate ligand are not identical and, furthermore, have different affinities for the metal ions they complex. The relative affinity of a donor atom for a metal ion is dependent upon the electronicities of all the entities involved in the complexation reaction and this affinity, $(\psi_r)_i$, of the i-th donor atom can be calculated using equation (72):

$$(\psi_r)_i = \psi_i / \sum_{i=1}^{c_n} \psi_i \quad , \qquad (72)$$

where ψ_i is the actual affinity of the i-th donor atom (when considered independently of the other donor atoms) for the metal ion. It should be noted that the sum of the relative affinities of the c_n donor atoms is equal to unity. Thus, the stability of these complexes can be calculated from

$$\log \beta_{11} = \sum_{i=1}^{c_n} (\psi_r)_i \, (\mathrm{Int}_1)_i + \sum_{i=1}^{c_n} (\psi_r)_i (\mathrm{Slp}_1)_i (\sum_{i=1}^{c_n} (\psi_r)_i \left[g_1 (z_M / r_M{}^2 + g_2) \right]_i) c_n \qquad (73)$$

When all the function groups are identical, equation (73) reduces to equation (69). Similarly, equation (70) is expanded to

$$\log K_q = \log K_1 - \sum_{i=1}^{c_n} (\psi_r)_i (1+\gamma_i) \log \left[(1+c_n(q-1)) (2+c_n(q-1)) \ldots (c_n + c_n(q-1)) \right] - (q-1)(2-\theta_M) \sum_{i=1}^{c_n} (\psi_r)_i \psi_i \quad . \qquad (74)$$

Thus, for the reaction of a bidentate ligand such as glycine ($\varepsilon_{COO} = 0.74$ and $\varepsilon_{NH} = 1.41$) with cadmium(II) for example, the relative affinities of the metal ion, from equation (72), are 0.103 for the carboxylate group and 0.897 for the amine group. The values of the formation constants can then be determined from equations (73) and (74). Also listed in Table 3 is a comparison of predicted and experimental formation constants for some multidentate ligands. The agreement obtained for all of the complexes listed in the table is most satisfactory.

An interesting result arising from the use of equation (74) to predict the stability of metal ion-amino acid complexes is an apparent increasing discrepancy between the predicted and experimental values of log K_q ($q>1$) as q increases. The experimental constants are increasingly more stable than is predicted by the equation. However, it is probable that the enhanced stability is due to hydrogen bonding between subsequent amino acid molecules and, therefore, we may account for this enhanced stability by adding to equation (74) the quantity, $(q-1)e^{-(\varepsilon_{COO} - \varepsilon_{NH})^2}$; i.e. the affinity of the carboxylate group of one amino acid molecule for the amino group of another.

Part Three

Syntheses and Extensions of the Two Approaches

We now combine the two approaches given above and, assuming that they are valid, attempt to demonstrate that this synthesis leads to a completely unified description of metal ion complex formation constants wherein all significant variables are taken into consideration. The discussion is restricted to unidentate ligands (for both mononuclear or polynuclear species) but the same principles apply to both multidentate and mixed-ligand complexes. This requires the extension of equation (54) to incorporate precipation reactions (that is, a phase change), gaseous reactions (largely of theoretical interest only since there is little or no available data), ionic strength/ionic medium effects (which can be quite different since mixed-ligand complexes are involved in the latter), the influence of changes in the dielectric constant (and hence

TABLE 3

EXPERIMENTAL AND PREDICTED VALUES OF THE FORMATION CONSTANTS OF SELECTED METAL ION - LIGAND COMPLEXES AT 25°C AND ZERO IONIC STRENGTH

Complex	$\log \beta_{1q}$		Complex	$\log \beta_{1q}$	
	Pred.	Exp.$^{1-5}$		Pred.	Exp.$^{1-5}$
$[\mathrm{Li(OH)}]$	-13.70	-13.64	$[\mathrm{Al(F)_4}]^-$	17.98	18.47
$[\mathrm{Na(SO_4)}]^-$	1.01	0.09	$[\mathrm{Al(F)_5}]^{2-}$	19.62	20.73
$[\mathrm{Ag(OH)}]$	-11.81	-12.00	$[\mathrm{Al(F)_6}]^{3-}$	20.19	20.46
$[\mathrm{Ag(OH)_2}]^-$	-24.42	-24.45	$[\mathrm{Mn(NH_3)}]^{2+}$	1.69	0.90
$[\mathrm{Tl(N_3)}]$	0.26	0.39	$[\mathrm{Mn(NH_3)_2}]^{2+}$	2.10	1.57
$[\mathrm{Tl(IO_3)}]$	0.24	0.40	$[\mathrm{Mn(NH_3)_3}]^{2+}$	1.35	1.17
$[\mathrm{Be(F)}]^+$	6.11	5.92	$[\mathrm{Zr(Cl)}]^{3+}$	1.50	1.57
$[\mathrm{Ba(CO_3)}]$	2.87	2.78	$[\mathrm{Zr(Cl)_2}]^{2+}$	2.70	2.63
$[\mathrm{Mn(OH)}]^+$	-10.01	-9.97	$[\mathrm{Zr(Cl)_3}]^+$	3.71	3.75
$[\mathrm{Mn(OH)_2}]$	-21.23	-22.20	$[\mathrm{UO_2(SO_4)}]$	2.65	2.76
$[\mathrm{Mn(OH)_3}]^-$	-33.55	-34.80	$[\mathrm{UO_2(SO_4)_2}]^{2-}$	4.05	4.0
$[\mathrm{Mn(OH)_4}]^{2-}$	-46.92	-48.30	$[\mathrm{UO_2(SO_4)_3}]^{4-}$	4.46	4.70
$[\mathrm{Co(S_2O_3)}]$	1.99	2.05	$[\mathrm{NpO_2(HPO_4)}]^-$	3.08	3.3
$[\mathrm{Co(S_2O_3}]^{2-}$	2.46	2.40	$[\mathrm{TcO(OH)}]^+$	-1.67	-1.0
$[\mathrm{Cd(I)}]^+$	2.37	2.28	$[\mathrm{TcO(OH)_2}]$	-4.08	-3.2
$[\mathrm{Cd(I)_2}]$	3.77	3.92	$[\mathrm{Co(C_2O_4)}]$	4.51	4.7
$[\mathrm{Pb(HPO_4)}]$	3.69	4.07	$[\mathrm{Co(C_2O_4)_2}]^{2-}$	6.62	6.86
$[\mathrm{Pb(HPO_4)_2}]^{2-}$	6.72	6.44	$[\mathrm{Cd(en)}]^{2+}$	5.46	5.47
$[\mathrm{Am(SO_4)}]^+$	3.20	3.6	$[\mathrm{Cd(en)_2}]^{2+}$	9.80	9.85
$[\mathrm{Am(SO_4)_2}]^-$	4.80	5.0	$[\mathrm{Cd(en)_3}]^{2+}$	13.72	12.29
$[\mathrm{Am(SO_4)_3}]^{3-}$	5.04	5.29	$[\mathrm{Fe(gly)}]^+$	4.41	4.31
$[\mathrm{Bi(NO_3)}]^{2+}$	2.38	2.32	$[\mathrm{Fe(gly)_2}]$	7.49	8.07
$[\mathrm{Bi(NO_3)_2}]^+$	3.16	2.99	$[\mathrm{Pu(NTA)}]$	12.98	13.13
$[\mathrm{Al(F)}]^{2+}$	6.34	6.68	$[\mathrm{Ni(IDA)}]$	8.52	9.24
$[\mathrm{Al(F)_2}]^+$	11.38	12.02	$[\mathrm{Ni(IDA)_2}]^{2-}$	14.20	15.71
$[\mathrm{Al(F)_3}]$	15.24	15.72	$[\mathrm{In(EDTA)}]^-$	28.61	28.18

alterations in the solvent), the temperature dependence of formation constants (and thus, consideration of the free energy of reactions) and lastly, a description of redox reactions.

Precipitation Reactions

The availability of data for this type of reaction is unavoidably inadequate largely because of the paucity of chemical information. Thus, whereas both solution equilibrium and solubility product data are readily available for hydroxo-metal ion complexes, the equivalent data are not available for the sulphur analogues; data available from other insoluble salts (for example, chloride, sulphate, acetate, bicarbonate, nitrate) is virtually non-existent; and, other salts (for example, carbonate and phosphate) usually precipitate as mixed hydroxo-metal ion complexes of variable composition. The general theory, though able to make some predictions, cannot be validated because of these data limitations. The following discussion is therefore restricted to hydroxo-metal ion complexes. Even in this instance there are problems (in addition to the ubiquitous experimental deficiencies) associated with variable composition (degrees of dehydration) and anion retention.

Whereas solution equilibria very often preserve the coordination number of the metal ion, the formation of a solid phase commonly causes the coordination number to change; when this occurs it will invariably be a reduction. This is often due to the formation of mixed oxo-hydroxides or oxides rather than simple hydroxides, although the formation of the latter may still cause a reduction in coordination number. It should also be remembered that in the solid state, as opposed to the aqueous state, the complex is present in 'infinite concentration'. Each of these features must be accommodated.

Baes and Mesmer[26,45] studied the solution equilibria and the formation of solid phases in metal ion-hydroxide systems. They demonstrated that for the 'stable' hydroxide, oxo-hydroxide, or oxide of a metal ion, M^{z+}, there is an approximate correlation between the first hydrolysis constant, K_{11}, and the solubility product, K_{s10} (using the nomenclature of Baes and Mesmer), thus

$$M(OH)_z \text{ (solid)} + (z-1)M^{z+} \rightleftharpoons zM(OH)^{(z-1)+} , \tag{75}$$

and

$$K = \frac{\left[M(OH)^{(z-1)+}\right]^z}{\left[M^{z+}\right]^{(z-1)}} = (K_{11})^z K_{s10} ; \tag{76}$$

corresponding expressions apply for the oxo-hydroxo- or oxo-complexes. From equations (75) and (76), equation (77) was found to be approximately followed:

$$(K_{11})^z K_{s10} = 10^{-5.6} \tag{77}$$

The value of the index in equation (77), namely -5.6, approximates the logarithm of the concentrations of M^{z+} and $M(OH)^{(z-1)+}$ when these two species are present in equal amounts at equilibrium with the solid phase;[26] however, inadequacies in the treatment mean that this purely empirical value is very limited in its predictive ability. Indeed, we believe that the product $(K_{11})^z K_{s10}$ is not a constant, but is dependent upon (a) the electronic properties of the precipitating metal ion, therefore, a dependency on $g_1(z_M/r_M{}^2 + g_2)$ will be found, and (b) the number of water molecules lost in the precipitation reaction (that is in the formation of oxo-hydroxides and oxides; e.g. $Fe(OH)_3 \rightleftharpoons FeOOH + H_2O$).

Using our nomenclature, equation (76) can be rewritten as

$$\beta_p = (\beta_{11})^{z_M} \beta_s , \tag{78}$$

where β_s is the solubility product and β_p is the precipitation constant of the metal ion-hydroxide precipitate. Rearranging this equation and taking its logarithm, lead to equation (79):

$$\log \beta_s = \log \beta_p - z_M \log \beta_{11} . \tag{79}$$

we have found that $\log \beta_p$ in this equation can be determined from equation (80):

$$\log \beta_p = (-5.30-3.6N) + 0.018\ (4N-1)\left[g_1(z_M/r_M^2 + g_2)\right] , \tag{80}$$

where N is the number of water molecules lost in the formation of the solid product. Thus, using the expressions for $\log \beta_{11}$ and $\log \beta_p$ equation (79) becomes

$$\log \beta_s = (14.46z_M-3.6N-5.5) - \left[0.14z_M+0.018(1-4N)\right] \left[g_1(z_M/r_M^2 + g_2)\right] , \tag{81}$$

and allows the prediction of the solubility products of hydroxo-metal ion species in a similar fashion to all other formation constants. Figure 5 illustrates the excellent agreement obtained between the predicted and literature values of 28 metal ions by plotting the solubility product, $\log \beta_s$, against the right-hand side of equation (81). The slope of this plot is unity and the intercept -5.5 (noting the form of equation (81)); the correlation coefficient is 0.9952.

It is to be expected that the solubility products of other complexes can be determined using an equation similar to equation (81) but, unfortunately, not enough data is available for these complexes to reach any definite conclusions. It is clear that more work is required in order to be able to predict these constants with any degree of certainty.

Gaseous Reactions

The extensive interactive preference of particular metal ions in aqueous solution for one ligand rather than another, as quantified by the electronicities of the two ions, is a property restricted to polar solvents. Indeed, in

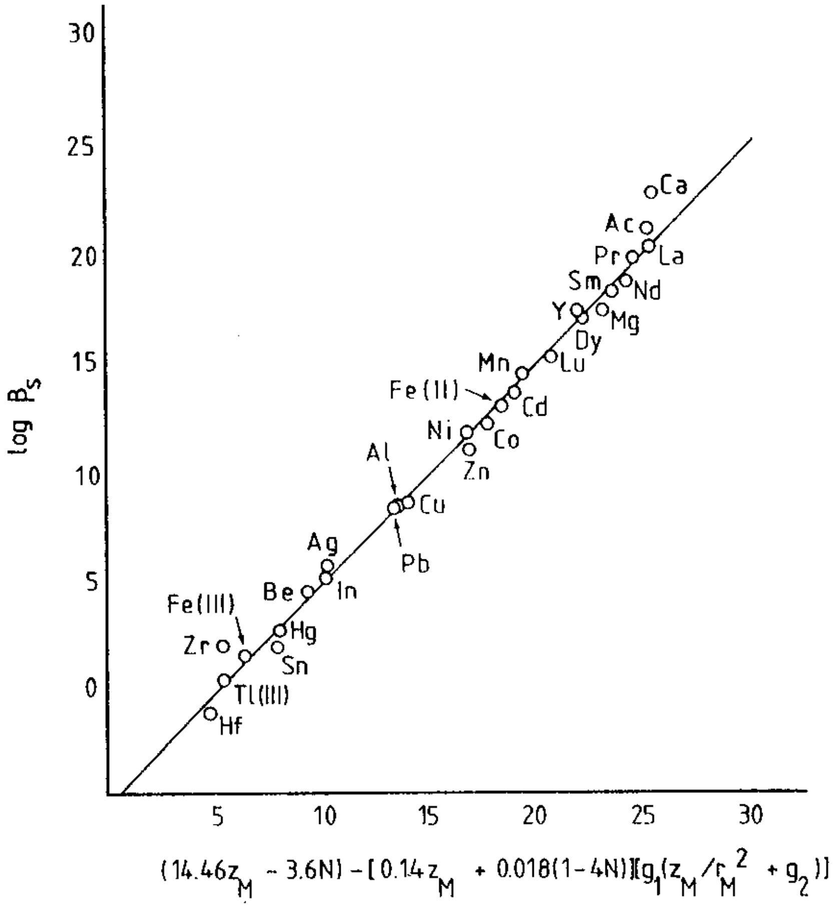

Figure 5 Comparison of literature and predicted solubility products values for hydroxo-metal ion complexes

less polar solvents, all ions tend toward zero electronicity (that is, they are less polarisable) and, furthermore, in the gas phase all ions exhibit zero electronicity (little or no polarisability). In the gas phase, therefore, all reactions are ionic in nature because all of the ions have high polarising powers and are similar to those reactions, in solution, involving two ions of low electronicity. The explanation for this behaviour stems from the fact that reactions between ions of high electronicity are enthalpy dominated whereas those between ions of low electronicity are entropy dominated.

Ionic Strength/Ionic Medium Effects

The activity of an ion depends significantly on the concentrations and nature of all other species in solution. Therefore, the experimental measurement of formation constants at zero ionic strength (thermodynamic formation constants) is not possible owing to unavoidable changes in the ionic strength, and hence in the activities of the ions in solution, throughout the course of an experiment. The vast majority of formation constants, therefore, have been measured[1-5] in the presence of a supporting electrolyte (stoicheiometric formation constants) of sufficient concentration, relative to that of the complexing ions, to ensure that the activities of the ions in solution remain constant. However, the use of a different background electrolyte, whether differing in ionic strength or medium, will lead to a different stoicheiometric formation constant for the same species, thus making the comparison of such constants tenuous and, the estimation of the thermodynamic formation constant difficult.

Extensions and variations of the approach developed by Debye and Huckel[46] have been used,[5,26,27,47] with some success, to overcome these difficulties. Indeed, the relationship between thermodynamic and stoicheiometric formation constants has often been expressed by an equation of the form

$$\log \beta_{pq} = \log \beta_{pq}{}^{\circ} + a\Delta z^2 I^{\frac{1}{2}}/(1+I^{\frac{1}{2}}) + bI \qquad (82)$$

where β_{pq} is the stoicheiometric formation constant, $\beta_{pq}{}^{\circ}$ is the thermodynamic formation constant, I is the ionic strength, a is the Debye-Huckel constant, Δz^2 is the square of the charge of each species summed over the formation reaction of the complex, and b is a constant dependent on the nature and concentration of the background electrolyte. The value of this equation is that it provides reasonably correct estimations of the activity coefficients of the ions in solution.[26,48] The interactive strength between ions of opposite charge is estimated within the b parameter, thus applying the means to quantify the existing four-way competition of the metal ion and ligand of the complex with those of the metal ion and ligand of the supporting electrolyte.

As was described earlier, the ability of an ion to complex is measured by the electronicity value of the ion. Thus, it is appropriate to express the interaction between ions, estimated within the b parameter, in terms of the electronicity values of the ions. Also, the work of Baes and Mesmer[26] shows that there is an apparent dependence of the value of b, at least for hydrolysis species, on the ionic strength.

Considering this dependence, we propose the following expression for the estimation of the parameter:

$$b = \frac{0.4}{I^{\frac{1}{2}}} \; \frac{e^{-[((\varepsilon_M)_m-(\varepsilon_L)_c)^2 + ((\varepsilon_M)_c-(\varepsilon_L)_m)^2]}}{e^{-[((\varepsilon_M)_m-(\varepsilon_L)_m)^2 + ((\varepsilon_M)_c-(\varepsilon_L)_c)^2]}} , \qquad (83)$$

which upon rearrangement and the collecion of like terms, becomes

$$b = \frac{0.4e^{2[(\varepsilon_M)_m-(\varepsilon_M)_c][(\varepsilon_L)_c-(\varepsilon_L)_m]}}{I^{\frac{1}{2}}} . \qquad (84)$$

In equation (84), $(\varepsilon_M)_m$ and $(\varepsilon_L)_m$ are the electronicity values of the ions of the medium, and $(\varepsilon_M)_c$ and $(\varepsilon_L)_c$ are the electronicity values of the complex.

The equation again emphasises the importance of the concept of electronicity, and also provides a further means (although complicated) by which the values may be estimated. A comparison of predicted and experimental values of the formation constants of some complexes measured in the presence of a supporting electrolyte is given in Table 4. The agreement obtained is excellent but, as might be expected, the difference between the experimental and predicted formation constants is larger for polynuclear complexes where the inherent errors of such calculations are magnified.

TABLE 4

COMPARISON OF PREDICTED AND EXPERIMENTAL VALUES OF THE FORMATION CONSTANTS OF SOME COMPLEXES MEASURED IN THE PRESENCE OF A SUPPORTING ELECTROLYTE AND AT 25°C

Complex	Ionic medium	Ionic strength (mol dm^{-3})	b	log β_{pq}		Ref.
				Pred.	Exp.	
$Al(OH)^{2+}$	--	0	--	-4.98	-4.97	26
	$NaClO_4$	0.01	5.40	-5.11	-5.15	26
	$NaClO_4$	0.02	3.82	-5.16	-5.19	26
	$NaClO_4$	0.03	3.12	-5.19	-5.21	26
	$NaClO_4$	0.045	2.54	-5.22	-5.24	26
	$NaClO_4$	0.06	2.20	-5.25	-5.26	26
	$NaClO_4$	0.1	1.71	-5.30	-5.30	26
	$NaNO_3$	0.1	0.53	-5.42	-5.33	14
	$NaClO_4$	1.0	0.54	-5.46	-5.48	26
InF^{2+}	--	0	--	5.17	4.66	2
	$NaClO_4$	0.5	0.57	4.18	3.75	2
	$NaClO_4$	1.0	0.40	4.04	3.69	2
	$NaClO_4$	2.0	0.28	3.94	3.74	2
$Fe(SO_4)_2^-$	--	0	--	6.91		
	$NaClO_4$	1.0	0.16	2.98	3.18	1
	$NaClO_4$	3.0	0.09	2.00	2.11	2
$Sc_3(OH)_5^{4+}$	--	0	--	-15.82	-16.34	26
	$NaClO_4$	0.01	5.30	-16.05	-16.02	26
	$NaClO_4$	0.1	1.67	-16.39	-17.02	26
	KNO_3	0.1	0.55	-16.50	-17.567	11
	$NaClO_4$	1.0	0.53	-16.82	-17.33	26

Temperature Dependence

The formation constants of all complexes have a significant dependence on the temperature of reaction. Temperature has a pronounced effect on the mobility of ions, the ability of a ligand to dissociate from its concomitant proton and, hence, the stability of a complex. The ability to predict the formation constants of complexes thus requires an understanding of the temperature dependence of dissociation constants because of the presence of the pK_a of a ligand in equation (64).

Ackermann[49] studied the temperature dependence of the dissociation constant of the water molecule from 0 to 130°C and found that the data could be fitted by equation (85):

$$pK_a = -948.876 + 24746.26T^{-1} + 405.8639 \log T - 0.48796T + 0.0002317T^2 \quad , \tag{85}$$

where T is the temperature in Kelvin. For the present purposes, however, we have chosen to use a simpler form of such equations, wherein only those terms in T and T^{-1} are considered, as is shown in expressions (86) and (87), for the temperature dependence of the dissociation constant of the hydrogen sulphate and dihydrogen phosphate ion,[1] respectively:

$$pK_a = -6.94721 + 775.3835T^{-1} + 0.0212472T \quad ; \tag{86}$$

$$pK_a = -3.9762 + 1775.812T^{-1} + 0.0175089T \quad . \tag{87}$$

Similarly, we have found that the data of Ackermann[49] can be expressed by the much simpler equation (88), namely

$$pK_a = -6.732577 + 4574.544T^{-1} + 0.01806279T \quad . \tag{88}$$

We have surveyed the literature[1-5] in an attempt to express the temperature dependence of the dissociation constants of other ligands in a similar fashion, that is, we have sought equations of the form

$$pK_a = A + BT^{-1} + CT \quad , \qquad (89)$$

where A, B, and C are constants for each ligand. The values determined for these constants are summarised in Table 5 for a number of ligands.

A rise in temperature will cause a significant decrease in the dielectric constant of any solution. The variation with temperature (over the range 0-100°C) of the dielectric constant of water, for example, can be described by equation (90):[50]

$$\phi = 78.54\left[1-4.579\times10^{-3}(t-25)+1.19\times10^{-5}(t-25)^{2} - 2.8 \times 10^{-8}(t-25^{3}\right] \quad , \qquad (90)$$

where ϕ is the dielectric constant and t is the temperature in centigrade. Over the given temperature range, equation (90) can be equivalently expressed in the form

$$\log \phi = \sigma + \alpha T \quad , \qquad (91)$$

where σ and α are constants; for water σ=2.486(0.001) and α=-0.001981(0.000003). The correlation coefficient is 0.9994. Substitution of equation (91) into equation (89) leads to equation (92).

$$pK_a = \left[A + BT^{-1}\right] + (C/\alpha)\left[\sigma - \log \phi\right] \qquad (92)$$

This dual relationship is not surprising since the temperature dependence of the proton dissociation constant of a ligand originates from two distinct sources.[51-53] The first, an energy dependence, arises from short-range quantum mechanical exchange forces that are not broken by thermal agitation and, the second, an electronic dependence, from electrostatic interactions that vary in essentially the same way as the macroscopic (bulk) dielectric constant of the medium.[51]

A close examination of the values of A, B, and C given for the ligands in Table 5 reveals some interesting correlations. Indeed, there is a linear correlation between the pK_a of a ligand at 25°C and the value of B for that ligand, as is illustrated in Figure 6. Thus, B can be expressed by equation (93):

TABLE 5

THE TEMPERATURE DEPENDENCE OF THE DISSOCIATION CONSTANT OF SOME LIGANDS

Ligand	A	B	C
SO_4^{2-}	-6.94721	775.3835	0.0212472
HPO_4^{2-}	-3.9762	1775.812	0.0175089
OH^-	-6.73258	4574.544	0.0180628
F^-	-1.8341	396.0088	0.0123944
CO_3^{2-}	-5.43127	2744.705	0.0219929
HCO_3^-	-18.98354	4020.251	0.0397288
NH_3	-0.79347	2860.013	0.0014914
NO_3^-	14.12283	-2673.96	-0.0219024
$H_2PO_4^-$	-3.68204	668.3749	0.0120424
ClO_4^-	4.80857	-1153.945	-0.0083434
IO_3^-	29.87028	-4526.184	-0.0465848
CH_3COO^-	-2.56064	1079.596	0.0123983
NO_2^-	-9.0864	2100.508	0.0174461
$S_2O_3^{2-}$	-4.91635	287.742	0.0190414

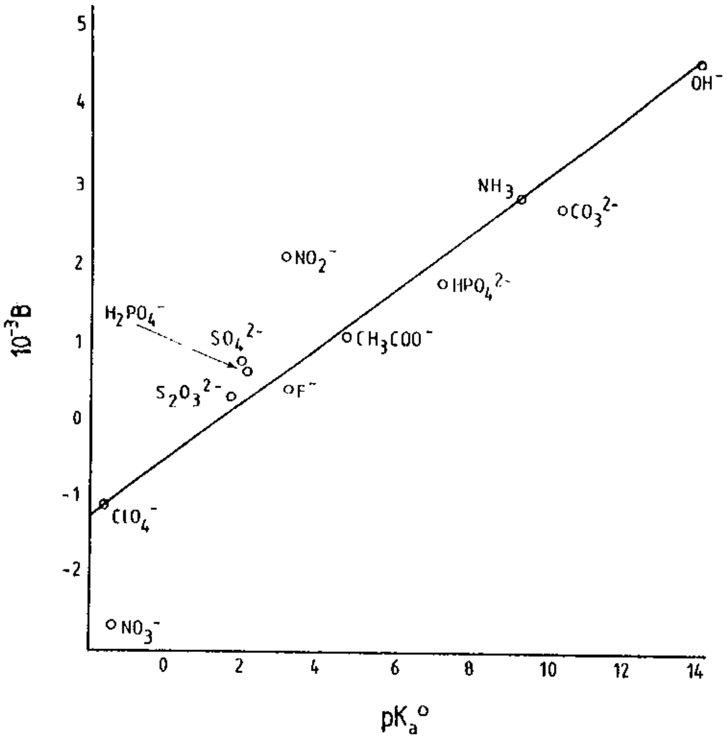

Figure 6 The value of B in equation (93) plotted against the pK_a of a ligand at 25°C

$$B = 371.3(48.7)pK_a^\circ - 575.7(313.7) \quad ; \tag{93}$$

where pK_a° is the pK_a of the ligand at 25°C and zero ionic strength. The correlation coefficient is 0.9238. Furthermore, a linear correlation between the pK_a of a ligand (at 25°C) and a function dependent on the ligands ionic charge and type, as is shown in Figure 7. We can therefore express C by equation (94):

$$C = 0.0187\gamma + 0.0368z_L + 0.01704z_L^2 - (0.00477z_L + 0.00204z_L^2)pK_a^\circ \quad ; \tag{94}$$

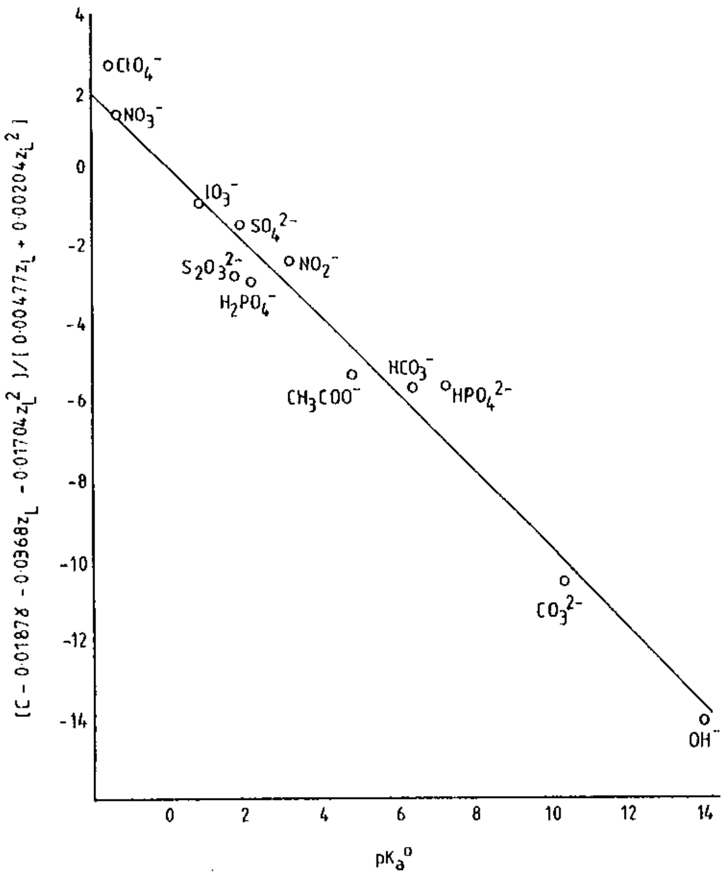

Figure 7 A linear correlation involving the C parameter (equation (94))

the correlation coefficient for the equation is 0.9821. The value of A can be determined by substituting equations (93) and (94) into equation (92), and solving the equation with the pK_a value of the left-hand side equal to $pK_a°$. This solution produces

$$A = 1.9309 - 0.2453pK_a° - \left[(0.0187\gamma+0.0368z_L+0.01704z_L^2 - (0.00477z_L + 0.00204z_L^2)pK_a°)/\alpha\right]\left[\sigma - \log \phi°\right] \quad , \tag{95}$$

where $\phi°$ is the dielectric constant of the solvant at 25°C. Thus, it is possible to determine the pK_a of a ligand at any temperature if the pK_a of the ligand at 25°C, the dielectric constant of the solvent at that temperature, and the value of σ and α in the appropriate temperature range are known. A comparison of predicted and literature values for the pK_a of water and acetic acid as a function of temperature is given in Table 6.

TABLE 6

THE TEMPERATURE DEPENDENCE OF THE pK_a OF WATER AND ACETIC ACID AT ZERO IONIC STRENGTH: A COMPARISON OF PREDICTED AND LITERATURE VALUES

Temperature (°C)	pK_a		pK_a	
	Pred.	Exp.[a]	Pred.	Exp.[a]
	Water		Acetic Acid	
0	14.952	14.955	4.8201	4.7807
10	14.541	14.534	4.7872	4.7622
20	14.172	14.161	4.7647	4.7562
25	13.999	13.999	4.7560	4.7560
30	13.837	13.833	4.7506	4.7570
40	13.534	13.533	4.7438	4.7688
50	13.261	13.263	4.7448	4.7870
60	13.014	13.015	4.7452	4.8119
70	12.792	12.800		
80	12.593	12.598		
90	12.416	12.422		
100	12.260	12.259		

[a] Data from Ref. 1.

We are now able to use equations (92)-(95) in describing the temperature dependence of the Int_1 and Slp_1 functions which will, in turn, allow the estimation of formation constants at any temperature. In this regard, the temperature dependence of the Int_1 and Slp_1 functions can be expressed by equations (96) and (97), respectively,

$$Int_1 = 0.01632T - 4.7558 - 4.1\left[1+(3-z_L)(z_L+1)\right]Slp_1 \quad , \tag{96}$$

$$Slp_1 = 0.031 + 0.0078pK_a \quad , \tag{97}$$

where the pK_a is determined using equations (92)-(95). The formation constant of a complex at a given temperature can be calculated using equations (47), (96), and (97). The predicted values of the formation constants of some complexes at various temperatures (and at zero ionic strength) are compared with the literature values in Table 7.

TABLE 7

COMPARISON OF PREDICTED AND LITERATURE[1-5] VALUES OF THE FORMATION CONSTANTS OF SOME COMPLEXES AT VARIOUS TEMPERATURES AND ZERO IONIC STRENGTH

Complex	Temperature (°C)	log β_{11}	
		Predicted	Experimental
$FeOH^+$	100	-7.00	-6.86
$CdNH_3{}^{2+}$	40	2.81	2.63
$MgSO_4$	150	4.34	3.9
$CaCO_3$	60	3.81	3.5
KNO_3	40	0.30	-0.5
$CoSCN^+$	45	1.26	1.66
$CaH_2PO_4{}^+$	40	0.74	0.6
$FeOH^{2+}$	150	1.03	-0.12
$ZnSO_4$	100	3.05	3.2
$FeCl^{2+}$	100	3.18	2.94
$EuSO_4{}^+$	65.1	3.65	4.22
$ZnCH_3COO^+$	35	1.42	1.46
$BiBr^{2+}$	55	3.37	3.28
$CuCl^+$	150	3.27	2.57
MnC_2O_4	45	4.44	4.06
$AgIO_3$	50	0.87	0.96
ThF^{3+}	5	8.01	8.46

It should be noted that in equations (96) and (97), Slp_1 is independent, and Int_1 dependent, on the reaction temperature but, such a result is not surprising. The definition of the 'absolute' pK_a scale developed earlier necessarily requires an independence of all variables; any variation resulting from such parameters is considered in the determination of the pK_a value and, once determined, falls on the linear scale. Thus, two ligands may both have the same value of Slp_1 and pK_a but be measured under vastly different experimental conditions. Contrary to the parameter independence of the value of Slp_1, it is necessary for the value of Int_1 to be dependent upon all variables. The value of Int_1 is the smallest possible value, under the designated experimental conditions, of a metal ion complex with a particular ligand; it may be considered as the formation constant of the theoretical complex of the ligand with a metal ion of infinite size.[13] This value, like the value of any other formation constant, must be dependent on such variables as temperature, pressure, and solvent.

Pressure Dependence

An increase in temperature causes a decrease in the dielectric constant of water (or any other solvent) since the increased thermal motion of the molecules destroys some of the 'structure' of the bulk solvent. In a similar way, the application of increased pressure (at constant temperature) causes an increase in the dielectric constant because the structure is enhanced. If it is assumed, as a first approximation (as is done with temperature above), that this change is dominant, then pK_a values and formation constants will also vary with pressure largely as a result of this change, though, as might be expected, this effect will be considerably smaller than the temperature effect.

Owen et al., using resonant frequency techniques,[54] determined simultaneously the temperature and pressure dependence of the dielectric constant of water. They demonstrated that

$$-10^6 \ln \phi(t,p) = -10^6 \ln \phi(0,0) + 2a_1p + 2a_2pt + 2a_3pt^2 + 2a_4p^2 + 2a_5p^2t + 2a_6p^2t^2 + 2a_7t + 2a_8t^2 \quad , \qquad (98)$$

where (standard deviations were not given) a_1=-22.5713, a_2=-0.032066, a_3=-0.00028568, a_4=0.0011832, $a_5=2.7895\times10^{-5}$, $a_6=-0.1476\times10^{-6}$, a_7=2300.64, a_8=-0.13476, ln $\phi(0,0)$=4.47615, t is in degrees centigrade, and p=(P(bars)-1), the measurements being carried out in the ranges 0-70°C and 1-1000 bars (10^5-10^8 Pa.).

At constant temperature, therefore, equation (98) reduces to

$$\ln \text{ (or log) } \phi = A + Bp + Cp^2 \quad , \qquad (99)$$

but, again, we have chosen to use the simpler form, namely equation (91):

$$\log \phi = \sigma + \alpha P \quad , \qquad (100)$$

where σ and α are constants (differing from those determined earlier) and P is the pressure. The dielectric constant may therefore be expressed as a function of both temperature and pressure by a combination of equations (91) and (100):

$$\log \phi = a_1 + a_2T + a_3P + a_4PT \quad , \qquad (101)$$

where a_1, a_2, a_3, and a_4 are constants which depend on the nature of the solvent. For water, a_1=2.4867, a_2=-0.00198704, $a_3=6.406\times10^{-6}$, and $a_4=4.104\times10^{-8}$; in the ranges 1-2000 bar (0.1-200 MPa) and 0-100°C; the difference between the calculated values from equation (101) and those from equation (98) is ca. 0.5% or less.

The value of the pK_a of the ligand can then be determined from an equation of the form

$$pK_a = \left[A + BT^{-1}\right] + \left[C/(a_2 + a_4P)\right]\left[\log \phi - a_1 - a_3P\right] \quad . \qquad (102)$$

In this equation, the values of A, B, and C are pressure dependent because of the dependency of $pK_a°$ on pressure. Furthermore, the formation constant of a complex can be determined from equations (47) and (97), and an equation similar to (96) but with an added term which is pressure dependent. Unfortunately, the lack of data limits us from a more definitive description.

The Effect of Solvent

The formation constant of a metal ion complex in solution is dependent not only on the competition of the metal ion and ligand of the complex, with the metal ion and ligand of the background electrolyte, but also on the competition of all the ions present in solution for each other with the solvent. The nature of the solvent may have a marked influence on the value of the formation constant of a metal ion complex; for example, differences are observed[55] between aprotic and protic solvents when the ions of the complex have high hydration energies and thus are strongly solvated.

The concepts discussed in the previous two sections may also be used to describe the effect of the solvent on formation constants. Equation (102) can be used to determine the pK_a of a ligand in a particular solvent, however, the values of A, B, and C now will not only be pressure dependent but also dependent upon the nature of the solvent. For example, the predicted value of the pK_a of the hydrogen sulphate ion at 100°C in D_2O ($pK_a°=2.34$, $\log \phi°=1.8935$, $\sigma=2.485$, and $\alpha=0.001984$) is 3.38, which compares favourably with the literature value[2] of 3.28. Furthermore, the formation constants of a complex in a particular solvent can be determined by using equation (47) and (97), again with an equation similar to equation (96) but with an added term which is dependent upon the nature of the solvent. In D_2O at 100°C, for example, the formation constant of $ZnSO_4$ is predicted to be 3.48; this seems a reasonable value when compared with the literature value[2] of 3.2 for $ZnSO_4$ in H_2O at 100°C; the pK_a of deuterium oxide is larger than that of hydrogen oxide.

We have used D_2O for comparative purposes here because of its similarity to H_2O. Comparisons with other solvents are, again, circumvented owing to a paucity of available data on formation constants, pK_a values, dielectric constants and especially, the lack of a means to determine the electronicity value of an ion in a particular solvent. At this point, it is only possible to make generalisations until such data become available. The need for these data is essential for a better understanding of the mechanics of complex formation.

Thermodynamic Aspects

We wish to discuss briefly the Gibbs free energy (ΔG), the enthalpy (ΔH), and entropy (ΔS) of reactions in terms of temperature and, for the sake of simplification, at constant pressure and in aqueous (H_2O) solution. The appropriate relationships derived earlier mav be incorporated into the fundamental thermodynamic equation (103)

$$-2.303RT\log K = \Delta G = \Delta H - T\Delta S \quad , \qquad (103)$$

and the values of the thermodynamic parameters determined. In the equation R is the universal gas constant.

The stability constant of any reaction (whether it be proton dissociation or complex formation) can be described by an equation of the form of equation (89), taking into account the temperature dependence of the constant. This dependence leads to distinct maxima (or minima) when the constant is plotted against 1/T, as is illustrated in Figure 8, and is caused by the dual depend-

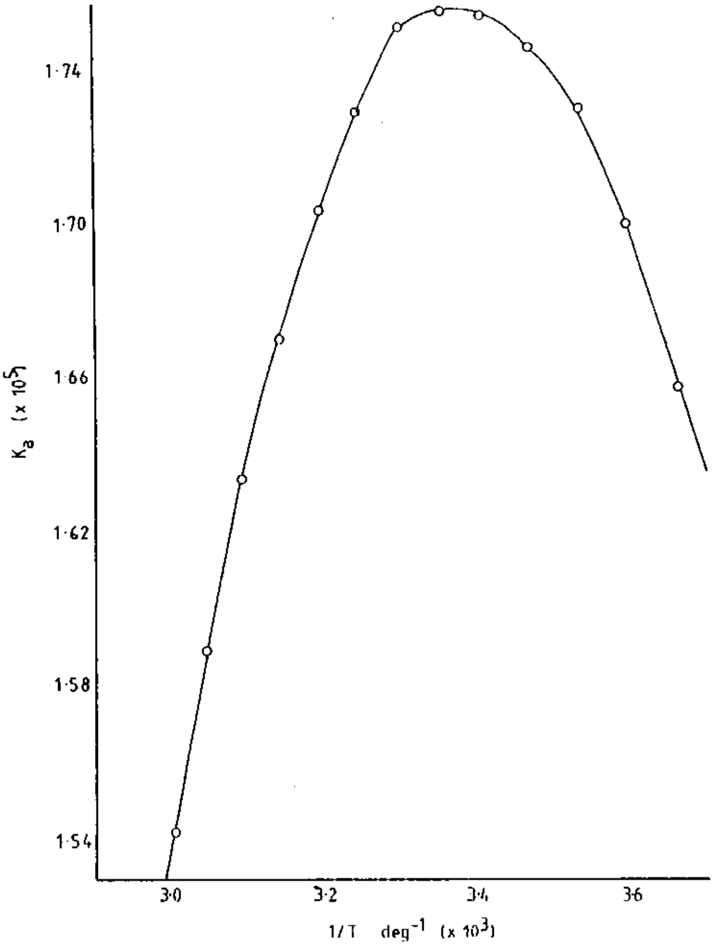

Figure 8 Temperature dependence of the pK_a of a ligand

ence described earlier. Burgess et al. observed that the dual dependence led to three conditions:[51]

(a) When the quantum mechanical forces are very much greater than the electrostatic forces, the minimum in the formation constant will lie well below ambient temperature, thus the reaction will be endothermic.

(b) When the quantum mechanical forces are of the same magnitude as the electrostatic forces, the minimum in the stability constant will be in the vicinity of ambient temperature, and the reaction will be zerothermic.

(c) When the quantum mechanical forces are much less than the electrostatic forces, the minimum in the formation constant will be well above ambient temperature, and the reaction will be exothermic.

This observation although being most helpful in understanding heats of reactions, gives no information on the entropy of the reaction, and hence no information about the strength of the reaction. A better understanding can be acquired of the latter entities by considering the electronicities of the two ions of the formed complex, and the type of complex formed, as is shown in Table 8. This table, however, is also a major simplification of the real-life situation, as it lists only the canonical extremes. In reality, the four cases listed in the table, as well as every conceivable case in between, is realised. Despite these limitations the table is a useful guide to the types of reaction and the thermodynamics governing them.

TABLE 8

A SUMMARY OF REACTION TYPES AND THEIR RELEVANT THERMODYNAMIC PARAMETERS

Reaction type (and example)	Electronicities[a]	K	log K	ΔG	ΔH and $T\Delta S$	Heat of reaction
Hard-hard (AlF^{2+})	$\varepsilon_M \simeq \varepsilon_L \simeq 0$ $(\Delta\varepsilon)^2 \simeq 0$	Large Positive	Large Positive	Large Negative	ΔH small $T\Delta S$ large positive	Exothermic, Zerothermic, Endothermic
Soft-soft (HgI^+)	$\varepsilon_M \simeq \varepsilon_L \simeq 3$ $(\Delta\varepsilon)^2 \simeq 0$	Large Positive	Large Positive	Large Negative	ΔH large negative $T\Delta S$ small	Exothermic
Hard-soft ($ScBr^{2+}$)	$\varepsilon_M \simeq 0$ $\varepsilon_L \simeq 3$ $(\Delta\varepsilon)^2 \simeq 9$	Very small Positive	Small Positive to Large Negative	Small Negative to Large Positive	ΔH and $T\Delta S$	Exothermic, Endothermic, Zerothermic
Intermediate-Intermediate ($In(OH)^{2+}$)	$\varepsilon_M \simeq \varepsilon_L \simeq 2$ $(\Delta\varepsilon)^2 \simeq 0$	Large Positive	Large Positive	Large Negative	ΔH large negative $T\Delta S$ large positive	Exothermic

[a] $(\Delta\varepsilon)^2 = (\varepsilon_M - \varepsilon_L)^2$

Before considering the thermodynamic parameters relevant to complex formation, we will discuss those relating to the dissociation constants of ligands because of their simpler and inherently important (within complex formation) behaviour. Thus, combination and rearrangement of equations (90) and (103) leads to

$$\log K_a = \frac{\Delta S}{2.303R} - \frac{\Delta H}{2.303RT} = -\left[A+B/T+CT\right] \quad , \tag{104}$$

This equation, upon differentiation with respect to 1/T, gives equation (105).

$$\frac{\delta(\log K_a)}{\delta(1/T)} = \frac{-\Delta H}{2.303R} = -B+CT^2 \quad , \tag{105}$$

thus

$$\Delta H = 2.303R(B - CT^2) \quad . \tag{106}$$

From this equation and equation (104), the value of ΔS can be determined by substitution, and is expressed in equation (107):

$$\Delta S = -2.303R(A + 2CT) \quad . \tag{107}$$

The thermal capacity at constant pressure can be determined from equation (108):

$$\Delta C_p = \frac{\delta(\Delta H)}{\delta T} = -4.606RCT \quad ; \tag{108}$$

The predicted values of $\log K_a$, ΔH, ΔS, and ΔC_p of the dissociation of water are compared with literature values[56] at zero ionic strength, in the temperature range 0-100°C, in Table 9. The agreement obtained is quite remarkable, except for the values of ΔC_p, which no doubt is the result of the use of the truncated equation for the pK_a of a ligand in this work.

Determination of the thermodynamic parameters for complex formation constants requires the use of equations (36), (47), (89), (96), and (97). The combination of these equations gives rise to equation (110) which expresses

TABLE 9

THERMODYNAMIC PARAMETERS OF THE DISSOCIATION OF WATER AT 0-100°C AND IN ZERO IONIC STRENGTH[a]

Temp.	$\log K_a$		ΔH kJ mol^{-1}		ΔS J mol^{-1} deg^{-1}		ΔC_p J mol^{-1} deg^{-1}	
	Pred.	Exp.[55]	Pred.	Exp.[55]	Pred.	Exp.[55]	Pred.	Exp.[55]
0	-14.952	-14.941	62.13	62.57	-58.87	-56.99	-193.1	-316.7
25	-13.999	-13.993	57.09	55.81	-76.54	-80.67	-210.7	-231.4
50	-13.261	-13.272	51.60	50.67	-94.21	-97.28	-228.4	-185.8
75	-12.694	-12.709	45.67	46.29	-111.88	-110.33	-246.1	-169.0
100	-12.260	-12.264	39.29	42.03	-129.55	-122.17	-263.8	-174.5

[a] A = -6.7788 C = 0.01769

B = 4622.13 R = 8.314 J mol^{-1} deg^{-1}

$\log \beta_{1q}$ (at zero ionic strength) as a function of temperature:

$$\log \beta_{1q} = q\Big[0.01632T - 4.7558 - 4.1\big[1+(3-z_L)(z_L+1)\big] \big[0.031+0.0078(A+BT^{-1}+CT)\big]\big[g_1(z_M/r_M{}^2 + g_2)\big]\Big] - \log U_{1q} \quad (109)$$

Differentiation of this equation with respect to 1/T gives rise to the following expression for ΔH:

$$\Delta H = 2.303Rq\Big[0.01632T^2 - 0.0078(B-CT^2)\big[g_1(z_M/r_M{}^2 + g_2) -4.1(1+(3-z_L)(z_L+1))\big]\Big] , \quad (110)$$

and differentiating this equation with respect to T is ΔC_p:

$$\Delta C_p = 2.303Rq[0.03264T + 0.0156CT[g_1(z_M/r_M^2 + g_2) - 4.1(1+(3-z_L)(z_L+1))]] \quad . \tag{111}$$

Substitution of equations (110) and (111) into equation (103), with rearrangement, leads to the following expression for ΔS:

$$\Delta S = 2.303R[q[0.03264T - 4.7558 + [0.031 + 0.0078(A+2CT)] [g_1(z_M/r_M^2 + g_2) - 4.1(1+(3-z_L)(z_L+1))]] - \log U_{1q}] \quad . \tag{112}$$

For the hydroxide ion, the adopted convention is to express the hydrolysis reactions as follows:

$$M^{z_M+} + qH_2O \rightleftharpoons M(OH)_q^{(z_M-q)+} + qH^+ \quad , \tag{113}$$

and, as a result, the expressions for the thermodynamic parameters differ from those given in equations (111)-(114), namely:

$$\Delta H = 2.303Rq[B - CT^2 + 0.01632T^2 - 0.0078(B-CT^2) [g_1(z_M/r_M^2 + g_2) - 4.1(1+(3-z_L)(z_L+1))]] \quad ; \tag{114}$$

$$\Delta S = 2.303R[q[0.03264T - A - 2CT - 4.7558 + [0.031 + 0.0078(A+2CT)[g_1(z_M/r_M^2 + g_2) - 4.1(1+z_L) (z_L+1))]] - \log U_{1q}] \quad ; \tag{115}$$

$$\Delta C_p = 2.303Rq[0.03264T - 2CT + 0.0156CT [g_1(z_M/r_M^2 + g_2) - 4.1(1+z_L)(z_L+1))]] \quad . \tag{116}$$

The predicted values of the thermodynamic parameters of metal ion complexes are compared with literature values in Table 10 for a number of complexes. The agreement within the table, although not exceptional is in reasonable agreement with the literature values.

TABLE 10

THERMODYNAMIC PARAMETERS OF SOME METAL ION COMPLEXES AT 25°C AND ZERO IONIC STRENGTH

Complex	$\log \beta_{11}$		ΔH kJ mol^{-1}		ΔS J mol^{-1} deg^{-1}	
	Pred.	Exp.	Pred.	Exp.	Pred.	Exp.
$FeOH^{2+}$	-1.71	-2.17	46.17	43.51	122.19	104.60
$HgCl^{+}$	6.91	7.43	-37.82	-20.08	5.42	71.12
$MnSO_4$	1.98	2.26	35.34	14.10	156.45	94.56
$AgIO_3$	0.45	0.63	28.31	21.51	103.62	84.94
$PbCl^{+}$	1.32	1.58	16.09	18.33	79.26	92.05
$ZnSO_4$	1.86	2.36	34.85	17.11	152.52	102.51
$CaHPO_4$	2.58	2.55	27.64	13.79	142.15	96.23
$CaH_2PO_4{}^{+}$	0.49	0.60	28.01	14.23	103.32	66.94
$ScSO_4{}^{+}$	4.28	4.04	44.65	26.40	231.82	165.69
$CdCl^{+}$	1.97	1.97	9.83	3.35	70.69	48.96
$FeBr^{2+}$	0.80	0.60	17.39	25.52	73.61	100.52
$AlOH^{2+}$	-4.98	-4.97	56.55	49.79	94.43	71.84
ZnS_2O_3	1.78	2.29	35.23	12.97	152.27	87.86
CdI^{+}	2.37	2.28	-30.13	-9.62	-55.65	12.55
$CoOH^{+}$	-9.25	-9.65	70.12	61.09	58.14	20.08

Redox Equilibria

The extension of the Brown-Sylva Electronicity Principle to redox (oxidation-reduction) reactions is straightforward since the tendency for such reactions to occur is governed by same principles outlined above. In practice, however, the paucity of appropriate data limits the extent of the foundation required to accomplish this.

In these reactions electrons are transferred between two forms of an element (e.g. the ClO_4^- and Cl^- ions of chlorine). For example, the simple redox reaction involving the two ions of one metal can be written

$$M^{z_M+} + ne^- \rightleftharpoons M^{(z_M-n)+} , \tag{117}$$

where n is the number of electrons transferred.

It is quite often the case that more than one valency state of a particular metal can occur in solution simultaneously whereas some cannot occur in solution at all. The U^{3+} ion, for example, is oxidised to U^{4+} in aqueous solution, liberating hydrogen. Thus, the elemental speciation must be determined before any geochemical modelling or experimental design can be performed. The speciation is, in the main, dependent upon the standard electrode potential, E°, of the reaction; this value no doubt depends on oxidant and reductant properties. It would not be surprising, therefore, to expect that there is a correlation between the standard electrode potential and the electronicities of the initial and final states of the element.

If we consider, in the first instance, only those reactions, represented by equation (117), with a transfer of only one electron (n=1), we find that the standard electrode potential, E°, can be estimated by equation (118), as illustrated in Figure 9:

$$E^\circ = \text{intercept} + \text{slope}\ (\varepsilon_{OX} - \varepsilon_{RED})^2 \tag{118}$$

In the equation, ε_{OX} and ε_{RED} are the electronicities of the oxidant and

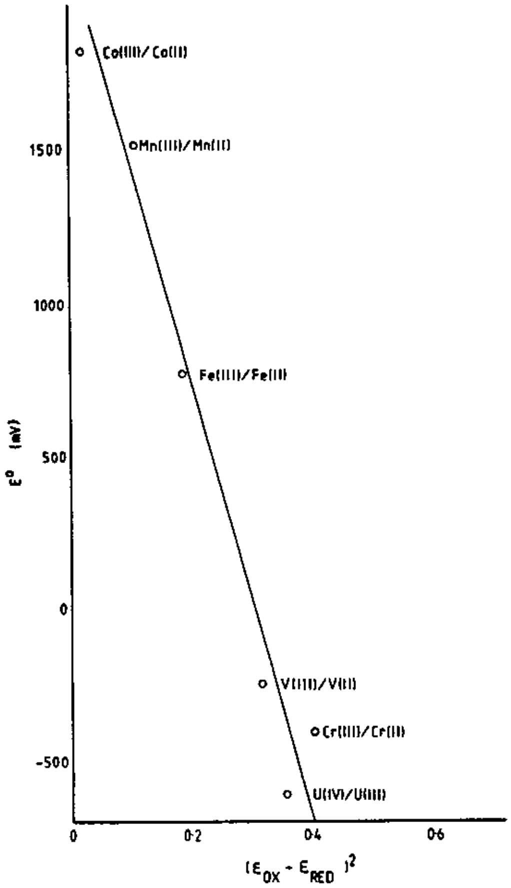

Figure 9 Dependence of the standard electrode potential (E°) on the function, $(\varepsilon_{OX} - \varepsilon_{RED})^2$

reductant, respectively, and the intercept=2169.9(90.3) and the slope= -7150.4(701.3); the correlation coefficient is 0.9813. Similar calculations for reactions involving two and three-electron transfers yield values of intercept=1245.6(196.1) and slope=-1349.2(129.5) (correlation coefficient =0.9909), and intercept=836.6(214.4) and slope=-424.0(75.6) (correlation coefficient=0.9419), respectively.

However, not all redox reactions can be represented by equation (117); for example, in acid solution, the reactions are expressed by equation (119):

$$MO_x^{z_M+} + 2(x-y)H^+ + ne^- \rightleftharpoons MO_y^{(z_M+2x-2y-n)+} + (x-y)H_2O \quad . \qquad (119)$$

It is possible, nonetheless, to express the standard electrode potentials of these reactions by equation (118). Thus, for those reactions involving a two-electron transfer, intercept=1414.3(11.0) and slope=-21202.7(325.7) five-electron transfer, intercept=1606.4(55.1) and slope=-433.7(94.3) (correlation coefficient=0.9771); and for six-electron transfer reactions, intercept =1636.2(99.6) and slope=-261.1(73.7) (correlation coefficient=0.9621).

From these relationships it is possible to determine the value of the electronicity of either the oxidant or the reductant if the electronicity of the other is known. This may be achieved by using equation (120):

$$\varepsilon_{UNK} = \varepsilon_{KNOWN} \pm \left(\frac{E° - \text{intercept}}{\text{slope}}\right)^{\frac{1}{2}} \quad ; \qquad (120)$$

electronicities calculated using this equation are listed in Table 11. Thus, we may use the standard electrode potential to determine the value of the electronicities of ions which cannot be determined from their formation constants because of the unavailability of these latter entities.

Reactions in basic solutions have not been considered here simply because most electronicity values can be determined from the equations used above. It is probable that similar relationships would be applicable in these instances.

Conclusion

Simple electrostatic arguments[57,58] used for the estimation of formation constants are totally inadequate and it is not apparent what form, if any, of the f(z,r) parameter should be used.[24,26,57,58] This matter was discussed and resolved by Brown, Sylva, and Ellis[13] who demonstrated a method of predicting the formation constants of hydrolysis products of metal ions, both mononuclear and polynuclear. The method shows that the correct form of f(z,r) is z^2/r^2 , although this is not immediately apparent. This extension revealed the existence of a hitherto unknown fundamental property of metal ions

TABLE 11

ELECTRONICITY VALUES CALCULATED FROM STANDARD ELECTRODE POTENTIALS

Entity	ε	Entity	ε	Entity	ε
Metals		Metals		Metals	
Ag	2.677	Ni	3.115	Hg	2.860
Cu	2.961	Pb	2.839	Sn	2.399
Cs	2.696	V	2.648	Sr	2.963
K	2.692	Zn	3.315	Ti	2.644
Li	2.567	Ba	2.899	Ac	3.692
Na	2.662	Ce	3.590	Pr	3.707
Rb	2.695	Ga	2.971	Eu	3.569
Tl	2.783	La	3.238	Gd	3.732
Ca	2.857	Nd	3.381	Am	3.416
In	3.261	Np	3.336	Tm	3.685
Be	2.204	Sc	2.708	Yb	3.439
Mg	2.687	U	3.350	Lu	3.742
Cd	3.836	Y	3.071	Pu	3.382
Co	2.646	Al	2.443	Rh	1.857
Cr	2.953	Th	4.025	Pd	2.490
Fe	2.654	Hf	3.814		
Mn	2.990	Zr	3.568		
Metal ions		Metal ions		Metal ions	
Ce^{4+}	0.536	Sn^{4+}	0.486	Pu^{4+}	0.372
Eu^{2+}	1.406	Ti^{2+}	1.184	Np^{4+}	0.263
In^{2+}	2.082	Tl^{2+}	1.863	Hg_2^{2+}	2.420
In^{+}	2.629	Yb^{2+}	1.421		
Oxometal ions		Oxometal ions		Oxometal ions	
UO_2^{+}	0.575	PuO_2^{+}	0.626	MnO_4^{-}	2.208
UO_2^{2+}	0.034	PuO_2^{2+}	0.372	MnO_4^{2-}	2.682
NpO_2^{+}	0.525	VO^{2+}	0.387		
NpO_2^{2+}	0.114	VO_2^{+}	0.639		

and ligands, namely electronicity, which enables the prediction of the formation constants of metal ion complexes under any experimental conditions, and unifies all aspects of solution chemistry.

The fundamental equation, equation (41), defines electronicity in terms of differences in the values of the step-wise formation constants and was arrived at by a search for a common factor concealed in the values of these constants. The exploitation of the fundamental nature of the electronicity of metal ions and ligands requires the invocation of a remarkably small number of parameters (all of which are constrained in the treatment - that is, they are not determined by empirical means) considering the universal nature of its application.

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APPENDIX

GLOSSARY OF SYMBOLS

M	metal ion
L	ligand
p	number of metal ion atoms in complex (sometimes represented by r and t)
q	number of ligand molecules in complex (sometimes represented by s and u)
K_q	step-wise formation constant
β_{pq}	overall formation constant
U_{pq}	structural term
ε_M	electronicity of metal ion
ε_L	electronicity of ligand
k	proportionality constant
ψ	$-e^{-(\varepsilon_M-\varepsilon_L)^2}$
θ_M	number of metal ions bonded to each ligand
θ_L	number of ligand molecules bonded to each metal ion
z_M	ionic charge of metal ion
z_L	ionic charge of ligand
r_M	ionic radius of metal ion
Int_1 Slp_1	intercept and slope values of linear equations for (1,1) species
Int_2 Slp_2	intercept and slope values of linear equations for (p,q) species
g_1 g_2	defined in equations (55) and (56)
s	presence/absence of s-electrons in outermost shell of ion
D	presence/absence of d-orbitals in outermost shell of ion
g(n)	Slater function[22]
d	number of d-electrons in outermost shell of ion
n	principle quantum number
β_c	condensation constant
γ	ligand type
$E^{\neq}$	'softness' (Klopman[18])
η_A η_B	'absolute hardness' (Parr and Pearson[20])
K_a	acid dissociation constant
ψ_i	affinity of i-th donor atom of multidentate ligand for the metal ion
$(\psi_r)_i$	relative affinity of the i-th donor atom
K_{s10}	solubility product (Baes and Mesmer[26,45])
β_s	solubility product
β_p	precipitation constant
N	number of water molecules lost in forming hydroxo-metal ion precipitate
β_{pq}°	thermodynamic (overall) formation constant
a	Debye-Huckel constant
Δz^2	the square of the charge of each species summed over the formation reaction of the complex
I	ionic strength

b	defined by equation (84)
$(\varepsilon_M)_m$ $(\varepsilon_L)_m$	electronicities of ions of the medium (m)
$(\varepsilon_M)_c$ $(\varepsilon_L)_c$	electronicities of ions of the complex (c)
T	temperature in Kelvin
ϕ	dielectric constant
t	temperature in centrigrade
α σ	constants for dielectric constant
A	defined by equation (95)
B	defined by equation (93)
C	defined by equation (94)
$pK_a°$	pK_a at 25°C and zero ionic strength
$\phi°$	dielectric constant at 25°C
P	pressure in bars
ΔG	Gibbs free energy of reaction
ΔH	enthalpy of reaction
ΔS	entropy of reaction
ΔC_p	thermal capacity of reaction at constant pressure
R	gas constant (8.314 J mol^{-1} deg^{-1})
E°	standard electrode potential
ε_{OX} ε_{RED}	electronicity of oxidant and reductant

REFERENCES

1. L.G. Sillén and A.E. Martell, 'Stability Constants of Metal-Ion Complexes', Special Publ., The Chemical Society, London, 1964, no. 17; 1974, No. 25.

2. E. Högfeldt, 'Stability Constants of Metal-Ion Complexes. Part A: Inorganic Ligands', I.U.P.A.C. Chemical Data Series, Pergamon Press, Oxford, 1982, No. 21.

3. D.D. Perrin, 'Stability Constants of Metal-Ion Complexes. Part B: Organic Ligands', I.U.P.A.C. Chemical Data Series, Pergamon Press, Oxford, 1979, No. 22.

4. R.M. Smith and A.E. Martell, 'Critical Stability Constants. Volume 4: Inorganic Complexes', Plenum Press, New York, 1976.

5. D.R. Turner, M. Whitfield, and A.G. Dickson, Geochim. Cosmochim. Acta, 1981, 45, 855.

6. R.N. Sylva and M.R. Davidson, J. Chem. Soc., Dalton Trans., 1979, 232.

7. R.N. Sylva and M.R. Davidson, J. Chem. Soc., Dalton Trans., 1979, 465.

8. R.N. Sylva and P.L. Brown, J. Chem. Soc., Dalton Trans., 1980, 1577.

9. P.L. Brown, J. Ellis, and R.N. Sylva, J. Chem. Soc., Dalton Trans., 1982, 1911.

10. P.L. Brown, J. Ellis, and R.N. Sylva, J. Chem. Soc., Dalton Trans., 1983, 31.

11. P.L. Brown, J. Ellis, and R.N. Sylva, J. Chem. Soc., Dalton Trans., 1983, 35.

12. P.L. Brown, J. Ellis, and R.N. Sylva, J. Chem. Soc., Dalton Trans., 1983, 2001.

13. P.L. Brown, R.N. Sylva, and J. Ellis, J. Chem. Soc., Dalton Trans., 1985, 723.

14. P.L. Brown, R.N. Sylva, G.E. Batley and J. Ellis, J. Chem. Soc., Dalton Trans., 1985, 1967.

15. J. Bjerrum, 'Metal Ammine Formation in Aqueous Solution', P. Haase and Son, Copenhagen, 1957.

16. C.L. van Panthaleon van Eck, Rec. Trav. Khim., 1953, 72, 529.

17. S. Ahrland, J. Chatt, and N.R. Davies, Quart. Rev., 1958, 12, 265.

18. G. Klopman, J. Amer. Chem. Soc., 1968, 90, 223.

19. R.G. Pearson, J. Amer. Chem. Soc., 1963, 85, 3533.

20. R.G. Parr and R.G. Pearson, J. Amer., Chem. Soc., 1983, 105, 7512.

21. R.D. Shannon and C.T. Prewitt, Acta Crystallogr., 1969, B25, 925.

22. J.C. Slater, Phys. Rev., 1930, 36, 57.

23. F.A. Cotton and G. Wilkinson, 'Advanced Inorganic Chemistry', John Wiley and Sons, New York, 1966.

24. J.E. Huheey, 'Inorganic Chemistry', Harper and Row, New York, 1978.

25. T.J. Swift and R.E. Connick, J. Chem. Phys., 1962, 37, 307.

26. C.F. Baes, Jr., and R.E. Mesmer, 'The Hydrolysis of Cations', John Wiley and Sons, New York, 1976.

27. S.L. Phillips, 'Hydrolysis and Formation Constants at 25°C', University of California, Berkeley, 1982.

28. G.N. Lewis, 'Valence and the Structure of Molecules', Chemical Catalogue Co., New York, 1923.

29. J.J. Katz and G.T. Seaborg, 'The Chemistry of the Actinide Elements', Methuen, London, 1957.

30. E. Nieboer and W.A.E. McBryde, Can. J. Chem., 1970, 48, 2549.

31. H. Irving and H. Rossotti, Acta Chem. Scand., 1956, 10, 72.

32. F.J.C. Rossitti, 'Modern Coordination Chemistry', J. Lewis and R.G. Wilkins, eds., Interscience, New York, 1960.

33. J.G. Jones, J.B. Poole, J.C. Tomkinson, and R.J.P. Williams, J. Chem., Soc., 1958, 2001.

34. A.E. Martell and M. Calvin, 'Chemistry of Metal Chelate Compounds', Prentice-Hall, New York, 1952.

35. Y.T. Chen, Zeit. Phys. Chem., 1962, 220, 231.

36. E. Högfeldt, J. Inorg., Nucl. Chem., 1961, 17, 302.

37. L.H. Jones and R.A. Penneman, J. Chem. Phys., 1954, 22, 781.

38. R.P. Bell, K.N. Bascombe, and J.C. McCoubrey, J. Chem. Soc., 1956, 1286.

39. W.H. Zachariasen, Acta Crystallogr., 1954, 7, 795.

40. R.D. Hancock and F. Marsicano, J. Chem. Soc., Dalton Trans., 1976, 1096.

41. D. Munro, Chem. Brit., 1977, 13, 100.

42. G. Schwarzenbach, Helv. Chim. Acta, 1952, 35, 2344.

43. A.W. Adamson, J. Am. Chem. Soc., 1954, 76, 1578.

44. G. Beech, Q. Rev., Chem. Soc., 1969, 23, 410.

45. C.F. Baes and R.E. Mesmer, Am. J. Sci., 1981, 231, 935.

46. P. Debye and E. Hückel, Z. Physik., 1923, 24, 1985.

47. C.W. Davies, 'Ion Association', Buttersworth Inc., Washington 1962.

48. K.S. Pitzer and L. Brewer, 'Thermodynamics', revised ed. by G.N. Lewis and M. Randall, McGraw-Hill, New York, 1961.

49. T. Ackermann, Z. Elektrochem., 1958, 62, 411.

50. 'Handbook of Chemistry and Physics', C.R.C. Press, Cleveland, 56th ed., 1975.

51. F.R. Hartley, C. Burgess, and R. Alcock, 'Solution Equilibria', Ellis Horwood Ltd., Chichester, 1980.

52. R.W. Gurney, 'Ionic Processes in Solution', McGraw-Hill, New York, 1953.

53. G. Anderegg, Helv. Chim. Acta, 1968, 51, 1856.

54. B.B. Owen, R.C. Miller, C.E. Milner, and H.L. Cogan, J. Phys. Chem., 1961, 65, 2065.

55. S. Ahrland and N. Björk, Coord. Chem. Rev., 1975, 16, 165.

56. R.H. Busey and R.E. Mesmer, J. Chem. Eng. Data, 1978, 23, 175.

57. C.W. Davies, J. Chem. Soc., 1951, 1256.

58. H. Irving and R.J.P. Williams, J. Chem. Soc., 1953, 3192.