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SIMPLE ELECTROSTATIC CORRELATIONS OF FLUORIDE COMPLEXES IN AQUEOUS SOLUTION

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CONTENTS

A. INTRODUCTION

It was stated in a recent review[1] that "the justification for treating fluorides separately from the other halides would seem to be that very often their chemistry is different". There are, however, some other tangible reasons why metal ion–fluoride complexes warrant special attention, not only relative to the other halides, but indeed in relation to all other species.

Firstly, no other simple species provides as large a number of complexes with measurable stabilities[2]. Secondly, the other halide ions show a much greater tendency than the fluoride ion to form inner and outer sphere complexes[3], complicating discussion of simple trends. However, the greatest impetus to study fluoride complexes is associated with the unique electronic characteristics of the fluoride ion itself.

The fluoride ion is the smallest simple anion which can exist in aqueous solution and, unlike the other halides, has no *d* orbitals of suitable energy to participate in covalent π bonding (either ligands to metal or metal to ligand). These two factors suggest that interactions between metal and fluoride ions, more than for any other ligand, should be governed by electrostatic considerations. Thus, fluoride complexes provide a unique opportunity to test basic electrostatic theories of complexation whilst avoiding the formidable quantum mechanical problems associated with covalent bonding.

Some aspects of fluoride complexation have been discussed briefly in a number of reviews[4-7], but since the most recent of these, a significant body of new data has become available, mainly through the development of a fluoride ion-selective electrode. Sufficient data now exist to allow a realistic appraisal of elementary complexation theories and, for the first time, to make a critical assessment of the reliability of the data themselves. This is the aim of this review.

Accurate measurement of stability constants in solution is fraught with difficulties[8], and it is not unusual to find independent studies differing as to the strength and even the number of complexes present[2]. Fortunately, this situation is improving as investigators standardise their approaches and become more aware of the often subtle factors (e.g. activity coefficient changes[9], calculation procedures[10], etc.) which can cause discrepancies. Improvements are also being wrought by the development of new techniques, such as ion-selective electrodes, and from improved instrumentation in established techniques.

Indeed, the major deficiency nowadays is not the lack of reliable stability constants but the paucity of corresponding enthalpy data. This situation is aggravated because many of the extant enthalpy data have not been obtained by direct calorimetry but, despite widespread criticism[11], from the rather dubious method of measuring the temperature variation of the stability constant. The recent commercial availability of calorimeters should do much to overcome this situation.

Studies of fluoride complexes have in the past been hindered by a number of experimental obstacles. The major difficulty was the lack of a direct method of measuring free fluoride concentrations. This has now been overcome by the invention of the fluoride ion-selective electrode[12] or circumvented by the application of techniques such as polarography[13] which are not dependent on a knowledge of free fluoride concentrations. The second problem in the study of fluoride complexes is the etching of conventional glass equipment by acidic fluoride solutions. This has been solved by the development of HF-resistant plastics such as Teflon and Kel-F. A further complication peculiar to the fluoride ion among the other halides is the low K_a value ($\sim 10^{-3}$ mole.l^{-1}) of HF in aqueous solution[2]. Thus at the low pH values which are often necessary to prevent metal ion hydrolysis in aqueous solution[2] there is competition for the fluoride ion between H^+ (aq.) and the metal ion of interest. This problem is, of course, inherent to the study of all complexes of the anions of weak acids, but it is exacerbated in the case of the fluoride ion by an inability to use the reliable glass electrode because of attack by HF. The problem can be minimised in many cases by careful solution preparation[14]. Furthermore, a number of accurate determinations[2,15-17] of the thermodynamic parameters of complexation between hydrogen and fluoride ions under a variety of conditions have diminished the uncertainties associated with this problem.

TABLE 1

Thermodynamic parameters for the reaction
$M^{n+}\text{ (aq.)} + F^{-}\text{ (aq.)} \rightleftharpoons MF^{(n-1)+}\text{ (aq.)}$

Ion [a]	r_+ [b]	$\log_{10}\beta_1$	ΔH_1 [c]	ΔS_1 [d]	Conditions [e]	Confirmation [f]	Ref. [g]
Be^{2+}	0.34	4.90	−0.35	21		**	15
Mg^{2+}	0.75	1.30	3.2	17		**	19,20
Ca^{2+}	1.05	0.63	3.5	15		**	19,20
Sr^{2+}	1.18	0.15	4	14		**	19,20
Ba^{2+}	1.38	−0.30	~0	~ 0		**	19,20
Sc^{3+}	0.83	6.19	0.4 [h]	30	0.5($NaClO_4$)		7,21,22
Y^{3+}	0.95	3.93	1.2	22	0.5($NaClO_4$)	** [i]	7,23,24
La^{3+}	1.15	2.67	4.0	26		*	24
Ce^{3+}	1.18	2.81	4.8	29		*	24
Pr^{3+}	1.16	3.01	5.7	33			24
Nd^{3+}	1.15	3.09	6.8	37			24
Sm^{3+}	1.13	3.12	9.4	46			24
Eu^{3+}	1.13	3.19	9.2	45		*	24
Gd^{3+}	1.11	3.31	8.9	45		*	24
Tb^{3+}	1.09	3.42	7.5	41			24
Dy^{3+}	1.07	3.46	7.0	39		*	24
Ho^{3+}	1.05	3.52	7.3	40			24
Er^{3+}	1.04	3.54	7.4	41		*	24
Tm^{3+}	1.04	3.56	8.7	45			24
Yb^{3+}	1.00	3.58	9.6	49		*	24
Lu^{3+}	0.99	3.61	9.5	49		*	24
Ac^{3+}	1.18	2.72					25
Zr^{4+}	0.80	~8.8			2.0(Na, $HClO_4$)	*	26
Hf^{4+}	0.86	~8.2			3.0(Na, $HClO_4$)		27
Th^{4+}	1.02	7.80				*	28
Pa^{4+}	0.98	7.87			3.0($HClO_4$)		29
Cr^{3+}	0.65	4.36			0.5($NaClO_4$)		30
U^{4+}	0.97	7.15			2.0($HClO_4$), 20°	*	31
Mn^{2+}	0.91	0.62				*	14
Mn^{3+}	0.62	5.5			2.0($HClO_4$)		32
Np^{4+}	0.95	~8.3 [j]			4.0($HClO_4$), 20°		33
Fe^{2+}	0.83	0.82					14
Fe^{3+}	0.67	5.17	2.4	32	0.5($NaClO_4$)	*	7
Pu^{4+}	0.93	6.77			1.0(HNO_3)		34
Co^{2+}	0.82	0.40					14
Am^{3+}	1.07	3.39			0.5($NaClO_4$)		35
Ni^{2+}	0.78	0.34				*	14
Cm^{3+}	1.06	3.34			0.5($NaClO_4$)		35
Cu^{2+}	0.72	0.70	0.9 [h]	6	0.5($NaClO_4$)	*	21
Ag^{+}	1.13	0.17	2.8 [h]	−10	0.5($NaClO_4$)	*	36
Zn^{2+}	0.83	0.75	2.0	10		*	37
Cd^{2+}	0.99	0.46	1.2	6		*	38

TABLE 1 (continued)

Ion [a]	r_+ [b]	$\log_{10}\beta_1$	ΔH_1 [c]	ΔS_1 [d]	Conditions [e]	Confirmation [f]	Ref. [g]
Hg^{2+}	1.12	1.03	0.8 [h]	8	0.5($NaClO_4$)		21
Al^{3+}	0.55	6.31	0.7	31		**	39
Ga^{3+}	0.62	4.38	2.5	29		** [k]	39,40/7
In^{3+}	0.92	3.69	2.2	24		** [k]	41
Tl^{+}	1.29	? [l]				*	42
Sn^{2+}	1.02	4.00				*	43,44,10
Pb^{2+}	1.32	1.47				*	45,46
Sb^{3+}	0.92	~6			2.0(Na, $HClO_4$)		47
Bi^{3+}	1.20	4.7			1.89($HClO_4$)	*	48

[a] Ions arranged in same order as ref. 2.

[b] Empirical cation radii in Angstrom, from A.R. von Hippel (Ed.), *Molecular Science and Molecular Engineering*, Technology Press of M.I.T./Wiley, 1959, pp. 148–9.

[c] Enthalpy in kcal.mole^{-1}, rounded off to the second significant figure.

[d] Entropy in cal.deg^{-1}.mole^{-1}, rounded off to the second significant figure.

[e] Unless otherwise stated, measurements were made at $I = 1.0M$ ($NaClO_4$) and $T = 25°C$.

[f] One asterisk denotes $\log\beta_1$ value has been independently confirmed (to two or more significant figures). Two asterisks indicate enthalpy (and entropy) values have been similarly confirmed.

[g] Only major reference is given except where confirmatory references cannot be obtained from the standard compilation[2].

[h] Indicates ΔH_1 was determined from temperature variation of the stability constant. All other values were calorimetrically determined.

[i] ΔH_1 and ΔS_1 in good agreement with one independent determination[7] which gives $\Delta H_1 = 2.2$ kcal.mole^{-1}, $\Delta S_1 = 25$ cal.deg^{-1}.mole^{-1}, but in serious disagreement with another determination[24] which gives $\Delta H_1 = 8.0$ kcal.mole^{-1} and $\Delta S_1 = 44$ cal.deg^{-1}.mole^{-1}.

[j] Obtained by assuming $\log\beta_1$ (HF) = 3.5 at 4.0 ($HClO_4$), 20°C.

[k] Only fair agreement of ΔH_1 and ΔS_1 with other reports.

[l] $\beta_1 \approx 0$, $\log_{10}\beta_1 = ?$

B. PRESENTATION OF DATA

(i) Selection of data

Table 1 lists thermodynamic parameters for the formation of the first fluoride complex of most metal ions. The data have been taken from standard compilations[2,18] which cover the literature up to 1968–9 and from a survey of the general literature up to the end of 1972. The data in Table 1 have been limited to simple metal ions. Although this means many well known and well studied ions such as VO^{2+}, UO_2^{2+}, etc., are excluded, it is necessary if comparisons of data with metal ion properties are to be meaningful. Similarly, only the formation of the first complex is considered. The data in Table 1 are, in the author's opinion, the most reliable from the published literature but of course they cannot be considered definitive. Further explanation is contained in the footnotes of the table.

(ii) Choice of standard conditions

Choice of standard conditions is somewhat arbitrary. Temperature presents no problem because almost all measurements are reported[2] at 25°C, but the media which have been employed are much more varied. Formerly, quotation of stability constants at zero ionic strength was favoured by many authors[6,21] on the grounds that specific medium effects were eliminated. These so-called "thermodynamic stability constants" were usually obtained by determining the variation of the stability constants with ionic strength and extrapolating to zero. This procedure may be criticised on the following grounds.

(1) All extrapolation procedures are based on electrolyte theories, such as that of Debye and Huckel[49], which are derived from non-thermodynamic considerations. Constants obtained in this manner can hardly be called "thermodynamic".

(2) The variation of many stability constants sometimes cannot be expressed as a simple function of ionic strength, making any extrapolation rather awkward.

(3) In order to prevent activity coefficient changes[9] or hydrolysis of the metal ion[50], most stability constant measurements are made at ionic concentrations for which common electrolyte theories do not apply.

Conversion of stability constants measured at one (usually high) ionic strength to a zero ionic strength value by the use of empirical or semi-empirical equations employed by some authors[6,21] would not appear to be very reliable.

An ionic strength of 1.0 is frequently used by many workers[2] and has been chosen as the standard medium for this review as a suitable compromise. Where data are not available at this ionic strength the most reliable value at the closest ionic strength has been chosen. Variation in the choice of salt for the medium, especially if it is a perchlorate salt (e.g., the use of $LiClO_4$ rather than the usual $NaClO_4$) would not be expected to cause a significant alteration to the quoted value. Thus, although some of the stability constants reported in Table 1 may include some specific interaction effects, the data as a whole have the advantage of reflecting relative values of real solutions rather than some hypothetical and unobtainable ideal state.

C. SIMPLE ELECTROSTATIC CORRELATIONS WITH log β_1

Various specialised theories have been propounded to explain the (often subtle) differences in stability constants of particular groups of ions, e.g. crystal field effects for the first transition row metal ions[11], etc. Although such theories are often highly successful in accounting for minor variations within particular groups of ions (and are interesting in themselves) for the present purpose they only represent embellishments on more basic concepts and thus will not be considered further. This obviously precludes any simple theory from *exactly* accounting for the fluoride stability constants of all cations. However, it is important to consider what general patterns, if any, do in fact emerge from simple correlations in order to determine inadequacies in both theory and data.

Two simple approaches may be used to treat electrostatic interactions quantitatively.

(a) Ion–ion. The Coulombic attraction between a cation and anion of charge Z_+ and Z_-

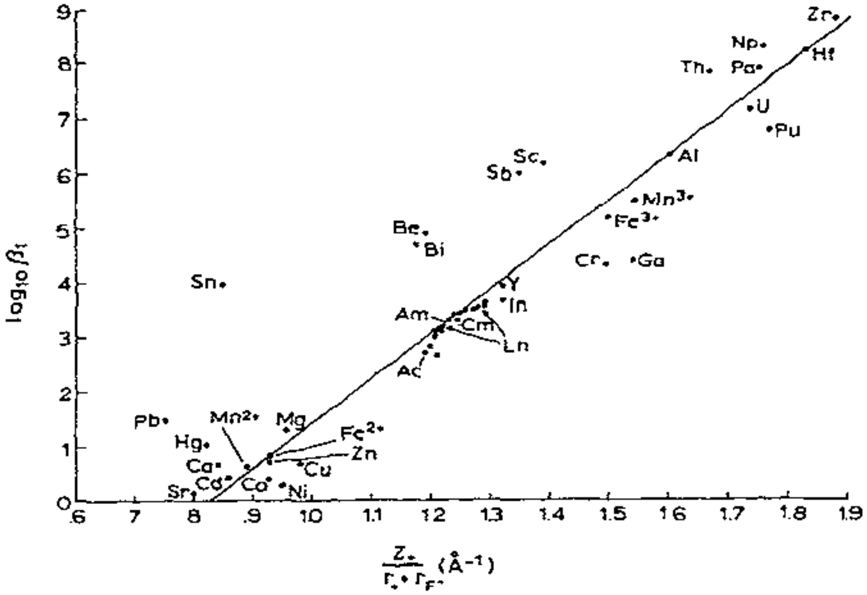

Fig. 1. Plot of $\log_{10}\beta_1$ vs. $Z_+/(r_+ + r_-)$. Data from Table 1 assuming $r_{F^-} = 1.33$ Å. (——) Computer fitted (least squares) line of best fit.

respectively in a medium of dielectric constant ϵ may be written as

$$-\left[\frac{Z_+Z_-e^2}{\epsilon r}\right]$$

where e is the electronic charge and r the distance of separation. Thus $\log\beta_1$ might be expected to correlate with $(Z_+/(r_+ + r_-))$, where r_+ and r_- are the radii of the cation and anion respectively ($r = r_+ + r_-$). A plot of this function against $\log\beta_1$ is shown in Fig. 1*.

(b) Ion–dipole. Ionic hydration energies can be accounted for reasonably well by a consideration of ion–dipole interactions only (the Born equation). This equation may be expressed[51]

$$-\Delta G_{\mathrm{hyd}} = \left[\frac{162Z_+^2}{r_+}\right]$$

The formation of 1 : 1 fluoride complexes in aqueous solution may be represented

$$M(H_2O)_x^{n+} + F(H_2O)_y^- \rightleftharpoons MF(H_2O)_z^{(n-1)+} + (x+y-z)H_2O \qquad (1)$$

Thus, in so far as the hydration energy of M^{n+} is directly related to Z_+^2/r_+, $\log\beta_1$ values would also be expected to correlate with this quantity[52]. This plot is shown in Fig. 2.

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* Straight lines in Figs. 1, 2 and 4 have been fitted to all points except Pb, Sn, Hg, Be, Bi and Sb. These are excluded for reasons which will become obvious later in the text. Charges on these ions are as in Table 1.

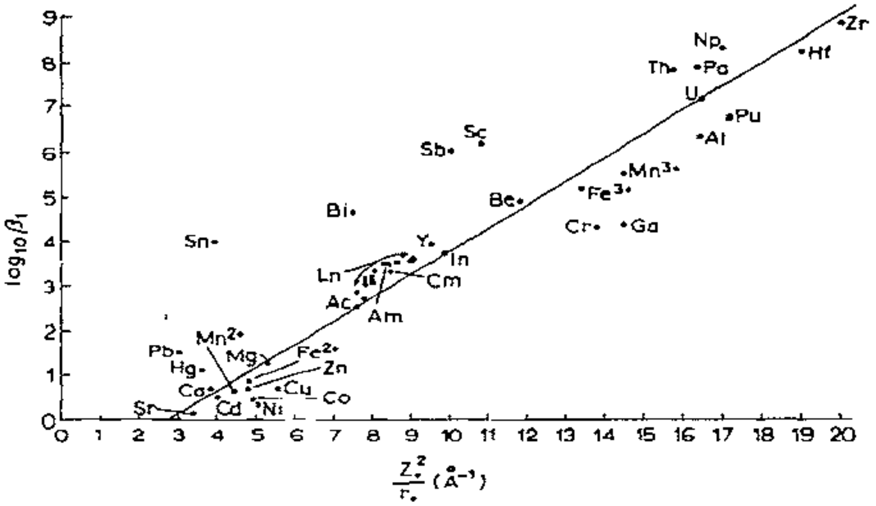

Fig. 2. Plot of $\log_{10}\beta_1$ vs. Z_+^2/r_+. Data from Table 1. (——) Computer fitted (least squares) line of best fit.

Comparison of Figs. 1 and 2 indicates that both electrostatic models show a reasonable correlation with $\log \beta_1$ values for most ions. This is not necessarily unexpected as the two approaches are really complementary rather than alternative. However, when the uncertainties in ionic radii and the stability constants are considered, the extent of agreement is gratifying.

It has been claimed[53] that straight line correlations like the above are fortuitous because all the functions used are approximately linear functions of $1/r_+$ for the values of ionic radii found in nature. That this is not so for the correlations in Figs. 1 and 2 can be readily seen from the data in Table 1. Any relationship between $\log \beta_1$ and $1/r_+$ is obviously charge-dependent (e.g. Sr^{2+} and La^{3+}) but even for ions of the same charge, any correlation is poor. This is amply demonstrated by the data shown in Fig. 3; it may be concluded that the correlations in Figs. 1 and 2 represent real effects.

As with most models it is the exceptions which provide a more fruitful field for further consideration. Figures 1 and 2 are particularly useful in that they show which ions are "anomalous" in terms of "normal" electrostatic behaviour. Many of these ions, e.g. Sc^{3+}, Cr^{3+}, Pu^{4+}, have been poorly investigated and warrant further study before any conclusions can be drawn about them. There is, however, a group of ions from the lower right hand side of the Periodic Table, including Hg^{2+}, Pb^{2+}, Sn^{2+}, Sb^{3+}, and Bi^{3+} whose $\log \beta_1$ values are decidedly "anomalous". These ions, which seem to form a distinct class, will be further discussed later.

D. REFINEMENTS TO SIMPLE THEORIES

It is well known that simple electrostatic theories contain compensating features which can give better correlations between ionic parameters and experimental data than seem logically possible (an interesting example of this is given on p. 169 of ref. 52). To test such a possibility a few logical refinements will be attempted.

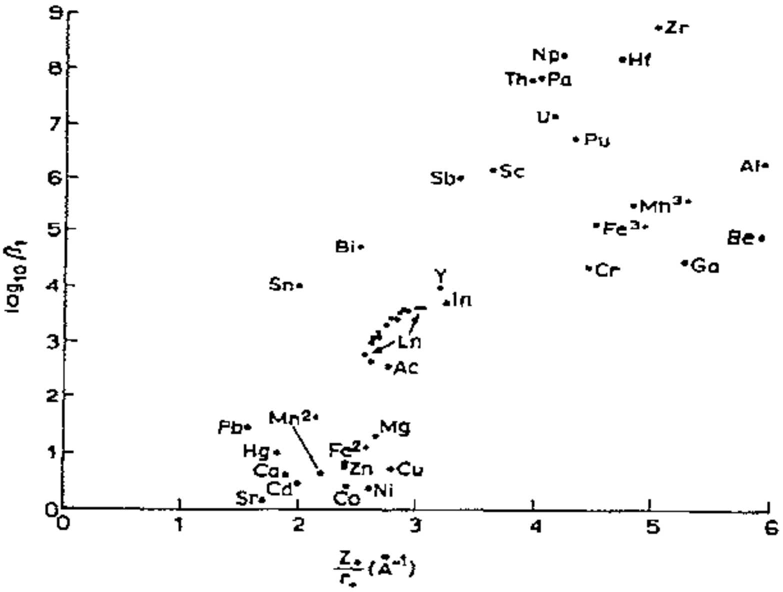

Fig. 3. Plot of $\log_{10}\beta_1$ vs. Z_+/r_+. Data from Table 1.

(i) *Effective radius*

The choice of individual ionic radii is somewhat arbitrary as quite different sets of values have been proposed by various authors[54]. Furthermore, recent direct X-ray determinations of electron-density distributions have indicated that commonly accepted single ion values based on a number of arbitrary assumptions are gravely in error[55]. This factor and the use of crystal radii (see Table 1) for ions which are known to be hydrated in aqueous solution needs to be clarified.

The function $Z_+/(r_+ + r_-)$ (Fig. 1) is a measure of the electrostatic attraction of the ions *in the complex.* Assuming all the complexes are inner sphere (i.e. the constituent ions are not separated by water molecules), then the distance of separation of ions in the complex is probably quite similar to the separation observed in crystals. Also, the function uses a sum of anionic and cationic radii and therefore does not suffer the arbitrariness of single ion radii. Thus the radii chosen should be satisfactory for the function $Z_+/(r_+ + r_-)$. However, in the Z_+^2/r_+ function (Fig. 2), r_+ refers to the radius of the uncomplexed hydrated ion. Use of any set of crystal radii does not, except as a crude approximation, seem justified, and a more realistic alternative must be found.

Various methods have been proposed for determining ion size in aqueous solution but most (e.g. that of Stokes and Robinson[56]) require a knowledge of the hydration number of the ion. Unfortunately, the literature on hydration numbers is in a state of almost complete confusion[57,58]. No values are generally accepted and the disagreement between values obtained by different methods is disconcerting, so it seems that this attractive avenue of approach cannot be pursued at this stage.

A useful semi-empirical result first introduced by Latimer et al.[59] is to add 0.85 (the radius of an oxygen atom in a water molecule) to the crystal radius to give an effective

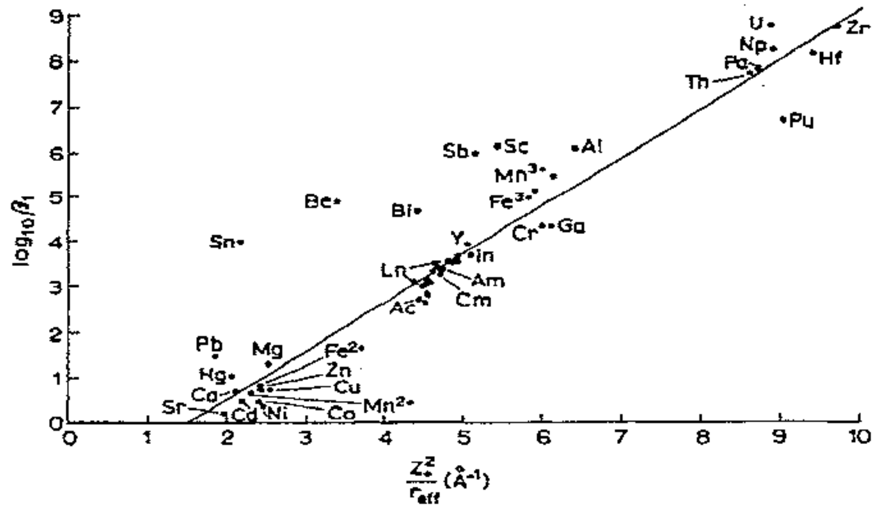

Fig. 4. Plot of $\log_{10}\beta_1$ vs. Z_+^2/r_{eff}. Data from Table 1. $r_{eff} = r_+ + 0.85$. (——) Computer fitted (least squares) line of best fit.

solution radius. Figure 4 gives a plot of log β_1 vs. Z_+^2/r_{eff}. The fit to the straight line in Fig. 4 is somewhat better than Fig. 2 and is now in better agreement with Fig. 1. It is obvious, however, that the uncertainties in the absolute values of single ion radii and the indirect relation of log β_1 to Born-type functions must inevitably mean correlation of these two properties is less straightforward than with the simple Coulombic function.

(ii) Effective charge

The agreement which exists between the two electrostatic approaches (Figs. 1 and 4) shows positively that many of the metal ions of the lower right hand side of the Periodic Table have "anomalously" large fluoride stability constants, i.e. their log β_1 values are much higher than would be expected on electrostatic grounds.

The lower ability of *d* and *f* orbitals compared with *s* and *p* orbitals to shield the nuclear charge of an atom (or ion) is well known. Hence, effective charges on ions to the right of the transition series in the Periodic Table would be expected to be greater than ions of the same formal charge to the left of the transition series. On this basis ions such as Hg^{2+}, Sb^{3+} etc. would be expected to have much higher log β_1 values than formally similar ions Sr^{2+}, Y^{3+} etc. Very little use seems to have been made of this important concept, probably because of the difficulty in making a quantitative correction.

Probably the simplest method is to calculate the effective nuclear charge using Slater's rules[60]. Unfortunately, charges obtained in this way become unreliable[61] as soon as orbitals with total quantum number greater than 4 are reached. More precise orbitals, such as Hartree–Fock type[61], could be used alternatively but the length of the calculations places them outside the scope of this review.

Despite the lack of rigour, a few semi-quantitative calculations derived from Slater-type effective nuclear charges seem worthwhile. Values for a number of elements have been listed by Allred and Rochow[62] and will be used for convenience. The values listed for strontium and tin are respectively 2.50 and 5.30. If strontium is considered to represent "normal" electrostatic behaviour, i.e. lies close to the lines of best fit in Figs. 1 and 4, then a rough correction for effective charge can be made by multiplying the formal charge by the ratio 5.30/2.50. This correction shifts tin(II) from the far left to the far right of the lines in Figs. 1 and 4, i.e. the "corrected" $\log \beta_1$ value is now less than the "normal" electrostatic value. Analogous corrections to the other ions of this group have a similar effect. Despite the crudity of this procedure it nevertheless suggests that the position in Figs. 1 and 4 of ions in this "group" is the result of more than an effective charge factor.

(iii) Other possible factors

One distinguishing feature of the metal ions of the lower right hand side of the Periodic Table is their high polarisability (e.g. compare the values[63] of Sr^{2+} ($\alpha = 1.7$ Å^3) and Pb^{2+} ($\alpha = 4.8$ Å^3)).

Although the concept of polarizability is poorly understood, it has been related by some workers[63] to covalency. In the Introduction it was pointed out that the fluoride ion in aqueous solution has a relatively low tendency to form covalent bonds. Thus it is conceivable that the interaction of this "group" of ions with the fluoride ion would be less favourable than expected on electrostatic grounds (after allowing for effective charge differences). In the "hard-soft" terminology of Pearson[64] this would be expressed as the interaction of like ions being preferred over unlike ions.

Doubtless, given the complexity of chemical interactions, other factors are also at work in determining the positions of ions in Figs. 1 and 4. The position of the unstudied Tl^{3+}/F^- system is of interest. On an electrostatic basis one would expect $\log \beta_1$ (TlF^{2+}) ≈ 3.4. However, on the basis of the β_1 values of the Bi^{3+} — and Pb^{2+} — fluoride systems, $\log \beta_1$ (TlF^{2+}) may in fact be much larger: an interesting situation awaiting experimental resolution.

E. CORRELATIONS WITH ENTHALPY AND ENTROPY

In order to gain greater insight into equilibrium solution processes than can be obtained from $\log \beta_1$ values alone (in effect ΔG) it is usual to consider the enthalpy and entropy components of ΔG separately[11], these quantities being related by the familiar thermodynamic equation

$$\Delta G = \Delta H - T\,\Delta S$$

(i) Correlations with ΔH_1

Inspection of the data in Table 1 indicates that the formation enthalpy ΔH_1 of the first metal ion—fluoride complex shows no systematic dependence on metal ion properties, all values being very close to zero. Note that this does not mean that the enthalpy change associated with the metal ion–fluoride bond formation itself is small, but simply that the enthalpy change of the overall process of complex formation in solution is small.

The observed enthalpy change of reaction (1) may be written, omitting charges for simplicity

$$\Delta H_1 = \Delta H_{\text{M-F}} - \Delta H_{\text{M-H}_2\text{O}} - \Delta H_{\text{F-H}_2\text{O}} \tag{2}$$

where $\Delta H_{\text{M-F}}$ represents the enthalpy change associated with the formation of the metal ion–fluoride bond, and $\Delta H_{\text{M-H}_2\text{O}}$ and $\Delta H_{\text{F-H}_2\text{O}}$ represent the enthalpy changes associated with the breaking of ion–water bonds which must occur if an inner sphere complex is formed.

The implication of eqn. (2) is that ΔH_1 is basically the result of two very large terms, one bond making and favouring the reaction ($\Delta H_{\text{M-F}}$) and the other bond breaking and opposing it ($\Delta H_{\text{M-H}_2\text{O}} + \Delta H_{\text{F-H}_2\text{O}}$). For a series of metal ions both bond making and bond breaking terms would be expected to depend on, and to show variation with, the properties of the metal ions to a very similar extent and thus no correlations with such properties will be observed.

It is interesting to note that even for the strongest complexes ΔH_1 is positive, i.e. is unfavourable to complex formation. Only Be^{2+} and Ag^+ appear to have negative ΔH_1 values. Complexation reactions of Ag^+ are normally considered to be governed by covalent interactions[4,65,66], which suggests that a certain amount of covalency might be associated with Be^{2+}/F^- interactions. This is also expected[67] on the basis of the exceptionally high electronegativity of Be^{2+} ($\chi = 1.5$) compared with similar ions (e.g. Mg^{2+}, $\chi = 1.2$). The possibility of covalent bond formation, which in the present context may be considered as a "specific interaction", probably accounts for the anomalous position of Be^{2+} in Figs. 1 and 4.

(ii) Correlations with ΔS_1

Although the enthalpy data in Table 1 show no systematic correlation with metal ion properties, the corresponding entropy data are insufficient to allow definite conclusions to be reached. However, some comments are worthwhile.

Figure 5 shows a plot of the most reliable ΔS_1 data against $(Z_+/(r_+ + r_-))$. The lanthanide values have not been included because they appear to be suspiciously high*. Despite the limited availability of data a rough linear correlation is apparent. This may be explained as follows.

The observed entropy change for reaction (1) may be written, omitting charges for simplicity,

$$\Delta S_1 = S^0_{\text{M-F(aq.)}} + (x + y - z)\, S^0_{\text{H}_2\text{O}} - S^0_{\text{F(aq.)}} - S^0_{\text{M(aq.)}} \tag{3}$$

For a series of metal ions $S^0_{\text{F(aq.)}}$ and $(x + y - z)$ will be approximately constant. The remaining terms in eqn. (3), which would be expected to correlate with metal ion proper-

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* Unfortunately, no independent enthalpy data are available for the lanthanide fluoride complexes. $\Delta H_1(YF^{2+})$ reported in the same paper as the lanthanides[24] is in serious disagreement with two other determinations (see Table 1). It is pointed out, however, that if the lanthanide data are correct, then the "correlation" in Fig. 5 would not be observed.

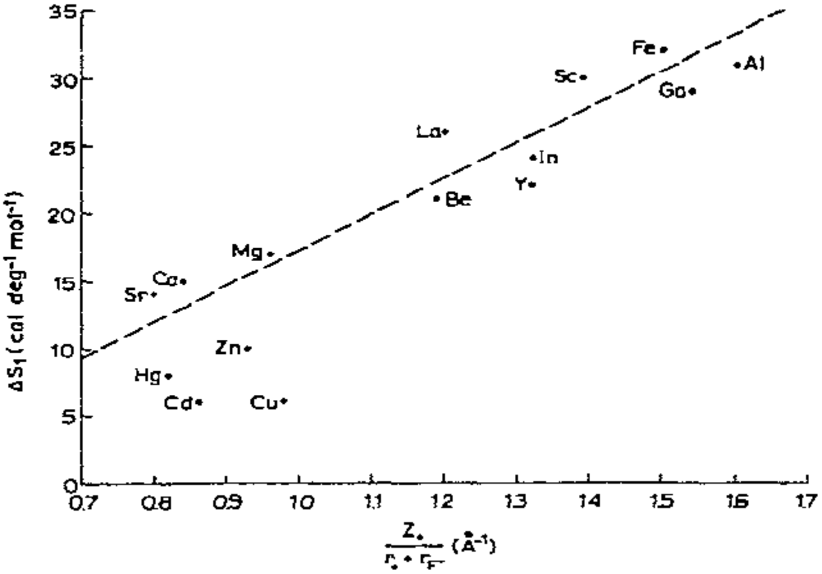

Fig. 5. Plot of ΔS_1 vs. $Z_+/(r_+ + r_-)$. Selected data from Table 1 (see text). (- - -) Line of best fit.

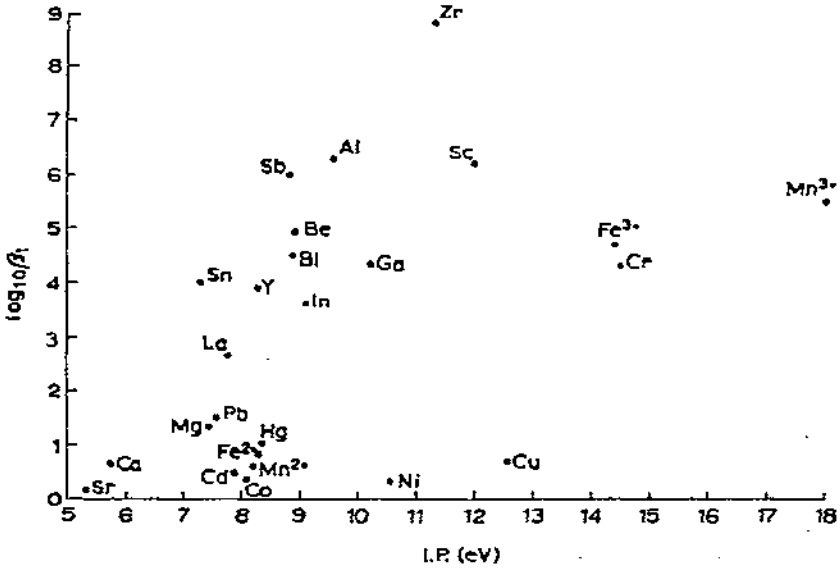

Fig. 6. Plot of $\log_{10}\beta_1$ vs. ionisation potential ($M^{n+} \rightarrow M^{(n+1)+} + e$). Data from Table 1 and ref. 71.

ties, then account for the trend in Figure 5.

The importance of metal ion—water interactions in determining relative complexation entropies is indicated by the following measurements. Eigen and co-workers[68] have determined rates of water exchange for reaction of the type

$$M(H_2O)_x^{n+} + H_2O^* \rightleftharpoons M(H_2O)_{x-1}(H_2O^*) + H_2O \qquad (4)$$

Their results are summarised for a number of ions in Fig. 6. If the rate of water substitution in reaction (4) is *assumed* to be determined by $M^{n+} - H_2O$ bond rupture, the rate constants in Fig. 6 reflect the strength of interaction between the ions and solvent water. As the values in Fig. 4 also show a good correlation with polarisability[63,69] (considering the uncertainties) then, providing this assumption is correct, increasing polarisability of metal ions may be equated with decreasing solvent ordering (as postulated by Ahrland[65]). Thus, as observed in Fig. 5, polarisable ions such as Hg^{2+}, Cd^{2+}, etc. will have much smaller ΔS_1 values than non-polarisable ions such as Al^{3+}, Fe^{3+}, etc. However, it must be remembered that the inadequacies of the data may obviate some of these conclusions.

Consider the formation of neutral fluoro complexes

$$M^{n+}(H_2O)_x + n\,F^-(H_2O)_y \rightleftharpoons MF_n(H_2O)_z + (x + ny - z)H_2O$$

for which the observed entropy charge may be written

$$\Delta S_n = S^0_{MF_n(aq.)} + (x + ny - z)S^0_{H_2O} - nS^0_{F(aq.)} - S^0_{M(aq.)}$$

Again, for a series of metal ions the S^0_F and $S^0_{H_2O}$ terms will be approximately constant. This time, however, the complexed species (MF_n) are neutral and thus will be expected to have small and approximately equal ordering effects on the solvent. This leaves $S^0_{M(aq.)}$ as the only significant term. Thus, a better correlation may be observed between metal ion properties and ΔS_n rather than ΔS_1. Unfortunately, almost no reliable entropy data exist for these complexes so this idea must remain only as an interesting possiblity for the present.

Metal ion fluoride complexation is often said to be "entropy-controlled", i.e. the stability of the complex is mainly due to a large positive value of ΔS. (Some authors[70] have quibbled over the use of the term "entropy-controlled" but it seems a useful concept to this writer.) This large positive ΔS value is often said to arise from the release of $(x + y - z)$ molecules of bound water from the primary hydration shells of the complexing ions, see eqns. (1) and (3). The fluoride ion, having a very high charge density has a stronger primary hydration shell than, for example, the other halides, and hence gives larger ΔS values on complexation.

A more realistic explanation is that the charge neutralisation which occurs on complexation increases the disorder of *all* water molecules affected by the presence of the complexing ions in the solvent. That is, the release of a specific number of water molecules from the primary hydration shells is only a part of the overall entropy change. The greater magnitude of entropy-changes for fluoride complexes compared with, for example, the other halides is because of its greater *overall* ordering of solvent molecules. Thus use of symbols x, y and z in previous discussion, does not imply that specific numbers of water molecules are taking part in reactions, but is merely for representational convenience.

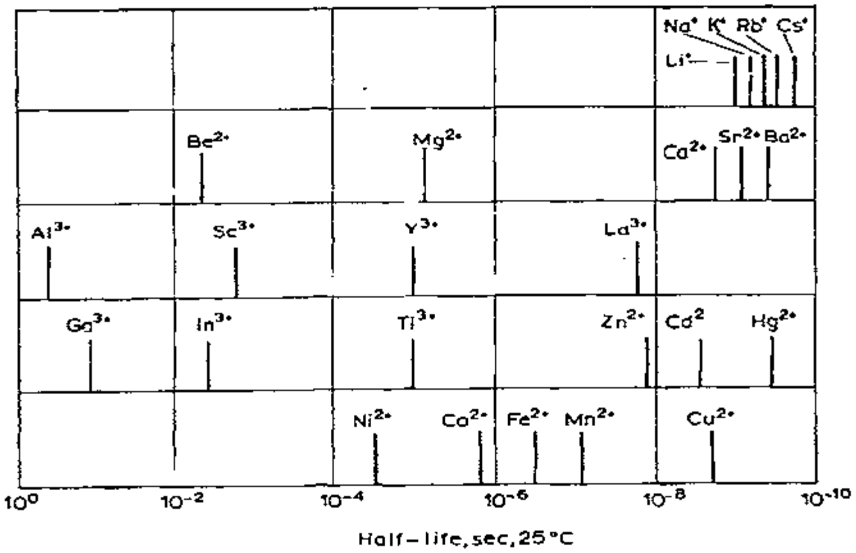

Fig. 7. Half lives for water substitution in the inner coordination sphere of metal ions. Data from ref. 68.

It is interesting to note in passing that the same factors which are responsible for the very small ΔH_1 values, namely the similarity of the $M^{n+}-H_2O$ and $F^- - H_2O$ interactions, are also responsible for large positive ΔS_1 values.

F. OTHER CORRELATIONS

(i) Correlations with other metal ion properties.

Many correlations of complexation parameters with metal ion properties have been summarised by Rossotti[11]. Apart from the functions discussed above, those used most frequently employ ionisation potentials (or electron affinities) of the metal ion.

Figure 7 shows a representative plot of some log β_1 values against the appropriate metal ionisation potentials[71]. Little correlation between the two variables is observed. A similar spread is obtained if the total ionisation potential is used. Other commonly employed functions such as $z\chi$ (χ = electronegativity) have been shown by Rossotti[11] to be equivalent to ionisation potentials.

(ii) Correlations with the other halide ions.

Although until recently it has been experimentally easier to study the complexation reactions of chloride, bromide and iodide ions, the data which exist for such complexes are surprisingly few. Table 2 lists a critical selection of the data from the "Stability Con-

TABLE 2

Comparison of $\log_{10}\beta_1$ values of halide complexes in aqueous solution [a]

Metal ion	F^-	Cl^-	Br^-	I^-
Sc^{3+}	6.19	1.07	1.21	
Y^{3+}	3.93	0.36	0.45	
Zr^{4+}	8.8	0.30		
Hf^{4+}	8.2	0.38	−0.10	− 0.46
Th^{4+}	7.80	0.18		
Cr^{3+}	4.34	−0.65	−2.65	− 4.16
U^{4+}	7.15	0.78	0.30	0.18
Mn^{3+}	5.5	0.95		
Fe^{2+}	0.82	0.36		
Fe^{3+}	5.17	0.66	−0.30	
Co^{2+}	0.40	−0.14	−0.12	
Ni^{2+}	0.34	−0.24	−0.12	
Cu^{2+}	0.70	0.74	0.55	− 1.52
Ag^+	−0.17	3.31	4.30	8.13
Zn^{2+}	0.75	−0.2 (37)	−0.6 (37)	− 1.5 (37)
Cd^{2+}	0.46	1.35(72)	1.76(38)	1.88(72)
Hg^{2+}	1.03	6.62	8.94	12.87
Ga^{3+}	4.45		−0.10	− 0.24
In^{3+}	3.69	2.15(41)	1.98(41)	1.00(41)
Tl^+	< 0	0.64	1.05	
Tl^{3+}		7.10	9.62	11.41
Sn^{2+}	4.0	1.15	0.73	0.70
Pb^{2+}	1.47	0.94(73)	1.09(73)	1.27(73)
Sb^{3+}	6	2.3		
Bi^{3+}	4.71	2.34	2.36	2.90

[a] Fluoride values are taken from Table 1. All other values taken from ref. 2 unless indicated by a reference in parentheses.

stant Handbook"[2]. Although there is much less uniformity of experimental conditions, data at 25°C and ionic strength 1.0*M* are quoted wherever possible. As only general trends are of interest in the following discussion the differences should be unimportant. Values listed in the fluoride column are taken from Table 1. Metal ions are included only if data exist[2] for more than one of the halide complexes.

A number of features are immediately apparent from the data in Table 2. Firstly, simple correlations of the type observed for fluoride complexes do not exist for the other halide complexes. Secondly, differences in stability of successive halide complexes of the same metal ion are greatest between the fluoride and chloride complexes. Thus, with very few exceptions the stability constants of metal ions always fall into two well defined sequences: $F \gg Cl > Br > I$ (class "a"[4] or "hard"[64] ions), or $F \ll Cl < Br < I$ (class "b"[4] or "soft"[64] ions). These sequences are illustrated clearly in Fig. 8 by U^{4+} and Ag^+ respectively (data from Table 2).

The first sequence basically reflects decreasing electrostatic interaction due to increasing halide size. Stability constant differences are most pronounced between fluoride and chloride because of commensurately greater change in size ($r_- = 1.33$, 1.81, 1.96,

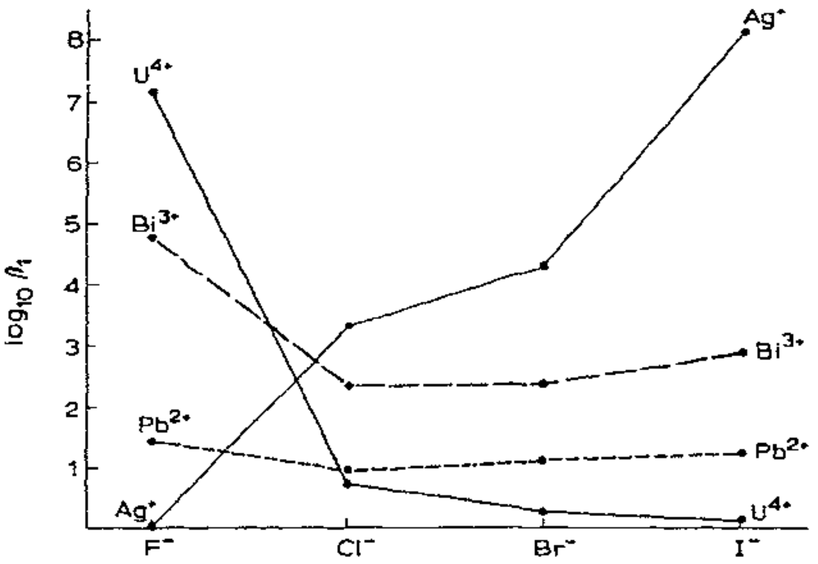

Fig. 8. Comparison of $\log_{10}\beta_1$ data for the halide complexes of various types of metal ions (see text).

and 2.20 Å for F$^-$, Cl$^-$, Br$^-$ and I$^-$ respectively). The second sequence largely reflects the increasing strength of covalent interaction of the halide ions down the group. That this difference is also greatest between the fluoride and chloride complexes is a reflection of the well known electronic differences which exist between first and second row elements of the Periodic Table[74], probably due to the absence in the former of *d* orbitals at energy levels suitable for bond formation. The interplay of these two factors accounts for the absence of correlations between metal ion properties and the stability constants of the non-fluoride halides.

Figure 8 also includes plots of two ions from the lower right hand side of the Periodic Table. Ions in this group, including Tl$^+$, Sn^{2+}, Pb^{2+}, Bi^{3+} and probably others (see Table 2) show abnormally little variation in the strength of their halide complexes compared with most other ions (see Fig. 8). Such behaviour may be superficially attributed to the interplay of electrostatic and covalent factors, but it also stresses the singular behaviour of this "group" compared with the other metal ions. Furthermore, it lends weight to a previous contention (made in relation to the fluoride complexes) that the strength of complexation of these ions is governed by a number of subtle factors which are relatively unimportant for other metal ions. Consequently, their behaviour cannot be even semi-quantitatively explained by simple theories.

Thus classifications[4,7,64-66] which attempt to unite all ions into one system must ignore obvious differences in behaviour, just as this short review has not made any allowance for crystal field[11] or symmetry[6] differences among metal ions. Such simplifications must be borne in mind if confusion and subsequent misuse are to be avoided.

G. CONCLUSIONS

The fluoride complexes of metal ions in aqueous solution form a unique series both in extent and character. The stability constants of these complexes correlate very well with simple electrostatic parameters such as ion size and charge. Large deviations can mostly be accounted for by making allowances for effective size or specific interactions, although a small number of ions remain "anomalous". The behaviour of these metal ions, which are all found in the lower right hand side of the Periodic Table, is probably related to their unusual electronic properties such as higher effective charge and polarisability. Enthalpy values for the complexation reactions were found not to correlate with ionic properties although there is some indication that entropy values might.

Stability constant correlations are good enough to suggest that some reported data may be incorrect.

H. THE FUTURE

The most important work which needs to be done on fluoride complexes in aqueous solution at present is:

(1) Determination of β_n values for the unstudied but experimentally difficult ions such as Ti^{2+}, V^{2+}, V^{3+}, Cr^{2+}, Ti^{3+}, Co^{3+} and for simple omissions such as Tl^{3+} and Rh^{3+}.

(2) Careful reinvestigation of all unconfirmed stability constants (see Table 1) using standardised conditions and techniques, where possible.

(3) Careful investigation or reinvestigation of *all* enthalpy values by calorimetry under standard conditions, where possible.

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