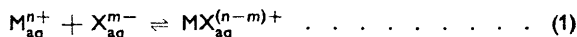


THERMODYNAMICS OF ION ASSOCIATION IN AQUEOUS SOLUTION

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THE acceptance of the Debye-Hückel theory of interionic attraction some thirty years ago permitted satisfactory interpretation of the thermodynamic behaviour of very dilute electrolyte solutions in which long-range interionic effects are important. When the ions are close together, however, the approximations on which the Debye-Hückel theory depends are no longer valid. The energy of their mutual electrical attraction may be considerably greater than the thermal energy which strives to maintain a random distribution. Although there is a continual interchange of ions, the result is the formation of what amounts to a new entity, the ion pair, in the solution, and this persists through a number of collisions with solvent molecules.

Very early work in the field was concerned mainly with a qualitative study of the composition of more stable association products. Thus we have the well known and very stable complexes such as CdI_4^{2-} , HgCl_4^{2-} . In more recent years there has been a change in emphasis in that it is now the physicochemical principles involved in the association process that are of greater interest. This Review will deal only with equilibria of the type



involving ion pairs and their two constituent ions. The question arises as to how close the ions have to be before they can be considered as having lost their thermodynamic independence. This problem was tackled by Bjerrum,¹ who, from purely electrostatic considerations, defined a distance between oppositely charged ions within which they are to be considered as being associated into ion pairs. This distance, q , the ionic separation at which the mutual potential energy is equal to $2kT$, represents the position of minimum probability of finding an ion of opposite charge anywhere on a sphere of radius q surrounding the central ion:

$$q = z_+ z_- e^2 / 2\epsilon kT. \dots \dots \dots (2)$$

in which z_+ and z_- are the valencies of cation and anion, e is the electronic charge, k Boltzmann's constant, and ϵ the dielectric constant.

Analysis of the experimental data shows that the deviations of electrolytes from the simple Debye-Hückel law depend upon short-range interactions between ions of opposite charge. Part of these deviations can be ascribed to ion-pair formation, by assuming that the free ions will obey the

¹ Bjerrum, *Kgl. danske Videnskab. Selskab, Mat.-fys. Medd.*, 1926, 7, No. 9.

law. Bjerrum's equation (2) predicts greater deviations or ion-pair formation the higher the valencies z_+ and z_- and the smaller the dielectric constant of the medium; this is in agreement with experimental results. It should be remembered, however, that the model used in Bjerrum's theory contains a number of simplifying assumptions: the ions are regarded as spherically symmetrical and unpolarisable, and the solvent as a continuum of uniform dielectric constant. These assumptions are open to question and will be discussed below.

We may write, for equation (1), a mass-action constant or thermodynamic association constant (3) in which braces enclose activities,

$$K = \frac{\{MX^{(n-m)+}\}}{\{M^{n+}\}\{X^{m-}\}} = \frac{[MX^{(n-m)+}]}{[M^{n+}][X^{m-}]} \frac{f_{MX^{(n-m)+}}}{f_{M^{n+}}f_{X^{m-}}} \dots \dots (3)$$

square brackets concentrations, and f 's are the corresponding activity coefficients. Various methods can be used to determine these constants, and these will be discussed briefly in the following section.

Experimental Methods.—*Conductivity.* In a symmetrical electrolyte, any ion pairs formed will be effectively uncharged and will not contribute to the conductivity of the solution. The measurement of conductivity, therefore, provides a valuable method of studying such solutions. The free ions being assumed to obey the limiting equation of Onsager, if α is the fraction of free ions at a concentration m , and b is the Onsager slope, the equivalent conductance in dilute solution is given by

$$\Lambda = \alpha[\Lambda_0 - b(\alpha m)^{\frac{1}{2}}]$$

The association constant

$$K = \frac{(1 - \alpha)}{\alpha^2 m f_{\pm}^2} = \frac{[\Lambda_0 - b(\alpha m)^{\frac{1}{2}} - \Lambda][\Lambda_0 - b(\alpha m)^{\frac{1}{2}}]}{\Lambda^2 m f_{\pm}^2} \dots (4)$$

and is obtained by successive approximations for α .

Davies and his collaborators have used this method extensively and have shown that the deviations exhibited by many 2-2 and some 3-3 electrolytes are capable of interpretation in dilute solution. Their data for manganous oxalate provide a good example.² In the concentration range $1-37 \times 10^{-4}M$, α varied between 0.90 and 0.21 but the irregular variations in K were no greater than the experimental uncertainty. Very precise measurements with 3-3-valent lanthanum ferricyanide³ in the concentration range $3-30 \times 10^{-5}M$ yielded K values showing no trend, and the mean at each of three temperatures showed an average deviation of 0.5%.

A notable recent advance has been the work of Fuoss and Onsager⁴ dealing with the time of relaxation and introducing higher Coulomb

² Money and Davies, *Trans. Faraday Soc.*, 1932, **28**, 609.

³ Davies and James, *Proc. Roy. Soc.*, 1948, *A*, **195**, 116.

⁴ Fuoss and Onsager, *Proc. Acad. Nat. Sci.*, 1955, **41**, 274, 1010; *J. Phys. Chem.*, 1957, **61**, 668.

interaction terms in the conductivity equation. Fuoss⁵ has applied the theory to ion-pairing electrolytes, facilitating the calculation of both the association constants and the distances of closest approach of free ions. Calculations have been carried out for several salts in dioxan-water mixtures;⁶ and Nash and Monk,⁷ comparing the new method with that using the older limiting equations, have shown that wherever Davies's method indicates ion association for sodium chloride, potassium chloride, and hydrochloric acid in aqueous dioxan, the Fuoss method does not contradict it. The Fuoss K values, however, are uniformly lower up to $K = 100 \text{ l.mole}^{-1}$.

With unsymmetrical electrolytes the position is more complicated, since the ion pair is now a new, charged entity, contributing to the measured conductivity. Making reasonable assumptions for Λ_0 of such ion pairs, however, Righellato and Davies⁸ have shown for a number of uni-bivalent electrolytes that relatively large errors in the assumed Λ_0 lead only to small errors in the calculated association constants.

The conductivities of mixtures of electrolytes may also be used, since the deviations from additivity may be almost entirely accounted for if the dissociation constants of the possible ion pairs are taken into consideration.⁹ The method has been applied to a considerable number of electrolyte systems and in particular to the association of metal ions with a number of condensed phosphate ions.¹⁰

Solubility. The measurement of solubility of a sparingly soluble salt in the presence of another electrolyte was first used by Davies for the determination of ion-pair formation.¹¹ It was found that, in order that the activity coefficients should be the same in any solution of the same ionic strength, independently of the nature of the added salt, allowance was necessary for incomplete dissociation. Calcium and thallos iodates have conveniently low solubilities and have been widely studied.^{12,13,14} As illustration, the concentrations of ionic species in saturated solutions of thallium iodate in the presence of added electrolyte MX may be obtained from (i) the activity product $[\text{TI}^+][\text{IO}_3^-]f_1^2 = K_{\text{S.P.}}$, (ii) the total concentration of MX = $[\text{X}^-] + [\text{TIX}] = [\text{M}^+] + [\text{MIO}_3]$, (iii) the association constant of MIO_3 , viz., $[\text{MIO}_3]/[\text{M}^+][\text{IO}_3^-]f_1^2$, and (iv) electroneutrality, $[\text{M}^+] + [\text{TI}^+] = [\text{X}^-] + [\text{IO}_3^-]$. Successive approximations for I , the ionic strength, and f_1 permit calculation of the required association constant $[\text{TIX}]/[\text{TI}^+][\text{X}^-]f_1^2$.

⁵ Fuoss, *J. Amer. Chem. Soc.*, 1957, **79**, 3301.

⁶ Fuoss and Kraus, *J. Amer. Chem. Soc.*, 1957, **79**, 3304.

⁷ Nash and Monk, *Trans. Faraday Soc.*, 1958, **54**, 1650.

⁸ Righellato and Davies, *Trans. Faraday Soc.*, 1930, **26**, 592.

⁹ Davies, *J.*, 1938, 448.

¹⁰ Monk *et al.*, *J.*, 1949, 413, 423, 427, 2693.

¹¹ Blayden and Davies, *J.*, 1930, 949.

¹² Davies, *J.*, 1930, 2410.

¹³ Bell and George, *Trans. Faraday Soc.*, 1953, **49**, 619.

¹⁴ Nair and Nancollas, *J.*, 1957, 318.

Potentiometry. Numerous potentiometric methods have been applied to the problem of ion-pair formation, the commonest being the measurement of pH. Cells both with and without liquid junction have been used, the former usually incorporating the glass electrode. Incomplete dissociation in salts of weak acids and bases is readily studied in this way, and workers such as Bjerrum and Schwarzenbach have made noteworthy contributions to the development of the method. Recently, glass electrodes have become available having resistances as low as 0.5 megohm. E.m.f.'s can be measured with conventional Poggendorff potentiometers and no amplifiers are necessary.¹⁵

Very precise e.m.f.'s can be obtained by Harned-type cells



for which

$$-\log m_{\text{H}^+} = (E - E^0)/k + \log m_1 + \log \gamma_{\text{H}^+} \gamma_{\text{Cl}^-}$$

The concentrations of ionic species may be calculated, and hence the association constants of bivalent metal sulphates.^{16,17}

Spectrophotometry. The spectrophotometric method takes advantage of the non-associated nature of dilute solutions of metal perchlorates. The changes in absorption on the addition of other ions are analysed in order to derive extinction coefficients of an assumed new species, the ion pair. The optical density in a cell of unit length for a system such as that depicted in equation (1) would be written

$$D = \epsilon_{\text{M}^{n+}}[\text{M}^{n+}] + \epsilon_{\text{X}^{m-}}[\text{X}^{m-}] + \epsilon_{\text{MX}^{(n-m)+}}[\text{MX}^{(n-m)+}] \quad . \quad . \quad (5)$$

By using wavelengths at which either M^{n+} or X^{m-} ions do not absorb, the right-hand side of eqn. (5) is reduced to two terms. Optical-density measurements in the presence of various values of $[\text{M}^{n+}]$ and $[\text{X}^{m-}]$ enable the determination of K and $\epsilon_{\text{MX}^{(n-m)+}}$. Bell and Panckhurst¹⁸ report for thallos hydroxide a value of K which agrees with that obtained by other methods. The method which is still in course of development has also been extensively used by Monk and his co-workers.¹⁹ Davies and Prue²⁰ have discussed the sources of error in precision spectrophotometry and suggested a technique to minimise their effects.

Reaction kinetics. The measurement of reaction rates provides a useful method for estimating the degree of dissociation of salts in solution. When an ion of a strong electrolyte takes part in a reaction with a neutral molecule, the reaction velocity is usually more closely proportional to the concentration of the ion than to its activity.^{21a} Thus, when the ion is

¹⁵ Covington and Prue, *J.*, 1955, 3696.

¹⁶ Jones and Monk, *Trans. Faraday Soc.*, 1952, **48**, 929.

¹⁷ Nair and Nancollas, *J.*, 1958, 3706; 1959, 3934.

¹⁸ Bell and Panckhurst, *Rec. Trav. chim.*, 1956, **75**, 725.

¹⁹ Bale, Davies, Morgans, and Monk, *Discuss. Faraday Soc.*, 1957, **24**, 94.

²⁰ Davies and Prue, *Trans. Faraday Soc.*, 1955, **51**, 1045.

²¹ (a) Bell and Prue, *J.*, 1949, 362; (b) Bell and Panckhurst, *J.*, 1956, 2836.

present as a salt which is incompletely dissociated the reaction velocity may be used as a measure of its true concentration. The K values are in reasonable agreement with those derived by other methods.

Polarography. In certain cases, the half-wave potential of the metal ion is shifted to more negative values as the concentration of associating anion is increased. Provided the reduction process is reversible, the shift in half-wave potential

$$\Delta E_{\frac{1}{2}} = -(RT/nF) \ln K - (pRT/nF) \ln [X^{m-}] \quad (6)$$

in which n is the number of electrons involved and p the number of X^{m-} ions associated with each cation. The method therefore gives direct information concerning both the composition and stability of the ion pair but suffers from the disadvantage that, in order to ensure that the current is purely diffusion-controlled, the ionic strength must be maintained at a relatively high value with neutral electrolyte. Much of the work has been done at high values of $[X^{m-}]$, leading to $p > 1$,²² since it is then feasible to assume that $[X^{m-}]$ at the surface of the mercury drops is equal to the value in bulk solution. For copper malonate, however, concentrations at the drop surface have been calculated, and experiments at low values of $[X^{m-}]$ have yielded the association constant for the formation of $CuC_3H_2O_4$ in good agreement with that obtained by other methods.²³

Other methods. A number of other properties are affected by ion association in solution and may be used to determine K , such as cryoscopy and vapour pressure,²⁴ the Wien effect,²⁵ nuclear magnetic resonance,²⁶ and sound absorption.²⁷

The Association Constant.—Equation (3) may be written

$$K = K_c \frac{f_{MX^{(n-)+}}}{f_M^{n+} f_{X^{m-}}} \quad (7)$$

in which K_c is the concentration quotient. The determination of K requires the evaluation or elimination of the activity coefficients term. This can be done in two ways: (a) the determination of K_c at various salt concentrations and extrapolation to infinite dilution at which the activity coefficients become unity, or (b) the calculation of activity coefficients from theoretical relationships.

Another way of dealing with the situation has been to use constant ionic media. The equilibria are studied in solutions containing relatively large concentrations of "neutral" or inert electrolyte such as alkali-metal perchlorate or nitrate. It is assumed that these ions do not form complexes

²² Lingane, *Chem. Rev.*, 1941, **29**, 1.

²³ Gelles and Nancollas, *J.*, 1956, 4847.

²⁴ Brown and Prue, *Proc. Roy. Soc.*, 1955, *A*, **232**, 320.

²⁵ Patterson, *J. Phys. Chem.*, 1952, **56**, 999.

²⁶ Richards, *Chem. Soc. Special Publ.*, No. 12, 1958, p. 173.

²⁷ Eigen and Wicke, *J. Phys. Chem.*, 1954, **58**, 702.

with the reacting species, and also that the activity coefficients remain constant. Concentrations are then calculated from the experimental measurements, leading to molarity quotients $Q = [MX^{(n-m)+}]/[M^{n+}][X^{m-}]$ valid only at the ionic strength used. The disadvantages of this method are as follows: (i) The results are not comparable unless determined at the same ionic strength, and, unfortunately, different workers use different ionic strengths. (ii) Too little is known about the variation of activity coefficients at constant ionic strength to permit reliable estimates of uncertainties from this source. (iii) The assumption that perchlorate ions do not form complexes is open to question, especially when their concentration is high. Thus, Sykes²⁸ has shown that the spectrophotometry of ferric perchlorate solutions indicates formation of perchlorate complexes, and the same must surely be true for ions such as Hg_2^{2+} .

Schwarzenbach, one of the first to use 0.1M-neutral salt solutions, has attempted²⁹ to be consistent by using the same activity data to convert pH into concentration. Sillén and his school³⁰ favour the use of very much higher neutral salt concentrations, and a large number of equilibria have been studied. In these cases involving several simultaneous equilibria, the incorporation of activity factors in the measured constants is a necessity for a solution of the problem. Estimation of variable activity coefficients as well as concentrations of several ionic products would lead to insuperable difficulties. Although the constant-ionic-strength procedure is useful in comparing different metals with the same ligand, too many different values of I have been used. It is very desirable to have the thermodynamic constants so that different systems are theoretically comparable and other thermodynamic properties may be obtained.

Measurement of K at various ionic strengths and extrapolation to zero would seem to be a most promising method of determining thermodynamic constants and it has been used in a few instances. There is still some difficulty, however, in the choice of the ionic-strength function to be used for extrapolation.

The estimation of activity coefficients in dilute solutions has been the most widely adopted method. For this, there are a number of expressions from which to choose, each of which contains different assumptions. The simplest equation is the limiting law of Debye

$$\log f_z = -Az^2I^{\frac{1}{2}} \quad (8)$$

where A is the universal constant of the Debye-Hückel theory, and this provides a useful means of extrapolating experimental data to infinite dilution. The limiting law is, however, accurate only at very high dilutions, of the order $I < 10^{-3}$.

²⁸ Sykes, *Chem. Soc. Special Publ.*, No. 1, 1954, p. 64.

²⁹ Schwarzenbach, Kampitsch, and Steiner, *Helv. Chim. Acta*, 1945, 28, 828.

³⁰ Sillén, *Quart. Rev.*, 1959, 13, 146.

The Debye-Hückel equation may be written

$$\log f_z = -Az^2I^{\frac{1}{2}}/(1 + BdI^{\frac{1}{2}}) \quad (9)$$

where B is another fundamental constant and d is the closest distance of approach of the ions. It has been shown³¹ that when we are dealing with systems containing mixed electrolytes, as is often the case, it is thermodynamically inconsistent to use this formula for estimating activity coefficients. Moreover, it cannot be readily extended to include such cases. In so far as the ion-size parameter d is unknown, the activity coefficient cannot be calculated unambiguously. There is the further effect of dielectric saturation in the vicinity of an ion since, as Gurney has pointed out,³² the intensity of the field at a distance of 2 Å from the centre of a singly charged ion in a vacuum amounts to 3.6×10^8 v/cm. In such a field, the free energy lost by the polar water molecules will be considerable, and there is a large uncertainty in the value ϵ to be used for calculating A and B . The universal adoption of the macroscopic ϵ implies that we are considering the effect of a weak field on a large number of solvent molecules, instead of a strong field, such as is found in the ion's vicinity, on the small number of surrounding molecules. Gurney has shown, however, that the two methods of treatment result in approximately the same energy contribution, so the predicted effect is at least of the right order of magnitude.

To eliminate as many arbitrary parameters as possible, equations of the type

$$\log f_z = -Az^2I^{\frac{1}{2}} + \beta I \quad (10)$$

have been used by Harned and his co-workers,³³ in which β is an empirical constant whose value is determined by the best straight line to fit the experimental points. Other workers have used the full Debye-Hückel expression with the addition of a linear term,

$$\log f_z = -\frac{Az^2I^{\frac{1}{2}}}{1 + BdI^{\frac{1}{2}}} + \beta I \quad (11)$$

but this suffers from the disadvantage of having two arbitrary parameters. Guntelberg³⁴ suggested the use of the formula

$$\log f_z = -\frac{Az^2I^{\frac{1}{2}}}{1 + I^{\frac{1}{2}}} \quad (12)$$

containing no adjustable parameter. Obviously such a formula cannot compete in accuracy with those containing parameters, but it has the

³¹ Guggenheim, "Thermodynamics," North Holland Publ., Amsterdam, 1949.

³² Gurney, "Ionic Processes in Solution," McGraw-Hill, New York, 1953.

³³ Harned and Owen, "Physical Chemistry of Electrolytic Solutions," 2nd edn. Rheinhold, New York, 1950.

³⁴ Guntelberg, *Z. phys. Chem.*, 1926, **123**, 243.

advantage that it can be extended to solutions of several electrolytes. Davies has proposed the formula

$$-\log f_z = Az^2 \left(\frac{I^{\frac{1}{2}}}{1 + I^{\frac{1}{2}}} - 0.2I \right) \quad (13)$$

which has the form of the modification of the Debye-Hückel equation suggested by Guggenheim.³⁵ It corresponds to an \bar{a} value in eqn. (9) of 4.2–4.4 Å for 2–2 electrolytes up to $I = 0.1$.²⁴ Davies³⁶ has shown that the equation is in good agreement with the actual values of the mean ionic activity coefficients of dilute solutions of 1–1, 1–2, and 2–1 electrolytes, the average deviation being about 2% in 0.1M-solution and proportionately less at lower concentrations. The equation has been applied to the activity data of many electrolytes in which incomplete dissociation was assumed, and the derived K values agreed with those obtained from conductivity measurements.

Recently, Guggenheim has criticised the use of the constant 0.2 in the Davies equation for other than 1–1 electrolytes.³⁷ He proposed a value of 2.0 for 2–2 electrolytes, corresponding to a more realistic distance of approach to define association of about 9Å. In the case of lanthanum ferrocyanide, in which, on the assumption that the forces involved are purely electrostatic, the corresponding distance would be 40Å, Panckhurst and Woolmington³⁸ have shown in a spectrophotometric study that the effect on K of using the required constant 6.0 in eqn. (13), is negligible. The activity-coefficient corrections were rather small in this work since $I < 6 \times 10^{-3}$ M. For the stable copper oxalate ion pair,³⁹ the use of the suggested 2.0 in place of 0.2 in eqn. (13) leads to a reduction in K of about 15–20%. The bivalent metal sulphates, which are considerably less stable, have been studied by a freezing-point method,²⁴ and it has been shown that the results can be fitted equally well by various choices of \bar{a} . This does not seem to be the case in the same systems studied by an e.m.f. method involving mixed electrolytes.¹⁷

Prue⁴⁰ has pointed out that the arbitrariness arises because properties that are really complicated functions of the separation of pairs of ions are treated as if they changed sharply at a certain separation. Even though the precision of the experimental results is improved, this arbitrariness will persist and can only be removed by refinement of the model. Some information about the interatomic distances in complexes in solution can be obtained from X-ray studies⁴¹ and, in certain cases, the structure of the crystalline solid may be used to justify a particular choice of distance

³⁵ Guggenheim, *Phil. Mag.*, 1935, **19**, 58.

³⁶ Davies, *J.*, 1938, 2093.

³⁷ Guggenheim, *Discuss. Faraday Soc.*, 1957, **24**, 53.

³⁸ Panckhurst and Woolmington, *Proc. Roy. Soc.*, 1958, *A*, **244**, 124.

³⁹ McAuley and Nancollas, *Trans. Faraday Soc.*, 1960, **56**, 1165.

⁴⁰ Prue, *Ann. Reports*, 1958, **55**, 14.

⁴¹ Nilsson, *Arkiv Kemi*, 1958, **12**, 513.

parameter. Beevers and Lipson's X-ray data for copper sulphate⁴² were used to show that, at least for this salt, a distance of approach of the free ions of about 4 Å was reasonable. In view of the difficulties involved in the calculation of activity coefficients, some workers regard the derived K values more in the nature of adjustable parameters. If the concept of ion association were successful only in accounting for thermodynamic properties, this view might be justified. Davies has shown, however, that the same K will also account for the conductivity data and in some cases yet other properties.⁴³ Additional evidence that different experimental methods of determining K refer to the same species has been put forward by other workers.⁴⁴ Although it has been suggested that, *e.g.*, in the case of magnesium sulphate, the activity-coefficient data can be interpreted in terms of the Debye-Hückel theory by using an essentially smaller a parameter without invoking ion association, the idea of ion-pair formation has been confirmed independently by sound-absorption measurements.²⁷

The terms "ion pair" and "complex" have been used by different workers to distinguish between different types of association, and sometimes with different meanings. A distinction proposed by Smithson and Williams⁴⁵ is that the former involves solvent interposed between the ions, $M^{n+}(H_2O)X^{m-}$, as distinct from $MX^{(n-m)+}$. For transition metals they suggest that ion-pair formation, unlike complex formation, will be expected to have very little effect on the low-intensity absorption bands in the visible spectrum. These are due to forbidden $d-d$ transitions, the wavelength depending upon the separation of the d -states which in turn is a function of the polarisation of the cation by the associating anion. Ion-pair formation will be expected to have very little effect on the $d-d$ splitting because of the large separation of M^{n+} and X^{m-} . On this basis, spectrophotometric measurements on cobaltous sulphate and thiosulphate indicate ion pairs in the former and complexes in the latter, even though their thermodynamic association constants are about equal: $K(\text{CoSO}_4) = 2.3 \times 10^2$ and $K(\text{CoS}_2\text{O}_3) = 1.2 \times 10^2$.

The free-energy change accompanying ion association may be written

$$\Delta G^\circ = G^\circ[\text{MX}^{(n-m)+}]_{\text{aq}} - G^\circ[\text{M}^{n+}]_{\text{aq}} - G^\circ[\text{X}^{m-}]_{\text{aq}} \quad . \quad . \quad . \quad (14)$$

where G° 's are standard molar free energies of the species. Using the above definition of terms, Duncan and Kepert⁴⁶ recognise two types of behaviour: metal-ion complexes in which $-\Delta G^\circ$ values fall with increasing $G^\circ[\text{M}^{n+}]_{\text{aq}}$, and ion pairs in which $-\Delta G^\circ$ is almost independent of $G^\circ[\text{M}^{n+}]_{\text{aq}}$. When two ions interact without disturbing their hydration sheaths, the energy will depend on the ionic charges and the distance

⁴² Beevers and Lipson, *Proc. Roy. Soc.*, 1934, *A*, **146**, 570.

⁴³ Davies, "The Structure of Electrolytic Solutions," ed. Hamer, Wiley, 1959, Chapter 3.

⁴⁴ Austin, Matheson, and Parton, *op. cit.*, ref. 43, Chap. 24.

⁴⁵ Smithson and Williams, *J.*, 1958, 457.

⁴⁶ Duncan and Kepert, *op. cit.*, ref. 43, Chap. 25.

between them, and this distance, being a function of the hydration radius, does not vary appreciably.

Difficulties arise if we wish to distinguish between ion pairs, resulting from electrostatic forces between the ions, and complexes in which covalent forces are also involved. Bjerrum's treatment may be applied to see whether it is adequate to explain the experimental results in terms of crystallographic radii. The experimental K value for lanthanum ferricyanide being used in the Bjerrum formula¹

$$K = 4\pi f_a^2 \exp(z_+ z_- e^2 / \epsilon k T r) r^2 \cdot dr$$

the calculated closest distance of approach is 7.2 Å, a value which suggests that the cation probably retains its primary solvation sheath in the associated form. In contrast to this, impossibly small distances are calculated for PbCl^+ and CdCl^+ (which are simply first stages in the formation of higher halide complexes) and for thallosium-ion pairs, and this has been used as evidence for covalent-bond formation. At the other extreme, the Bjerrum theory fails for a large number of 2-1-valent salts in which ion pairs cannot be detected, and Davies has suggested that definite classification into ion pairs and complexes on this basis should not be made.⁴³

W , the work done in the formation of an ion pair from the separate ions in solution, may be written

$$W = \Delta G^\circ / N - kT \ln 55.5 \quad \dots \quad (15)$$

where N is Avogadro's number. Gurney³² has emphasised the importance of the term $-kT \ln 55.5$ which makes the K values dimensionless and is characteristic of a reaction in aqueous solution in which the number of solute particles is decreased by unity; 55.5 being the number of moles contained in 1000 g. of water. W may conveniently be regarded as consisting of two parts,³² W_{env} representing long-range electrostatic forces dependent upon environment and increasing with temperature, and W_{non} representing short-range or quantum-mechanical forces, insensitive to environment and independent of temperature.

$$W = W_{\text{env}} + W_{\text{non}} = -kT(\ln K + \ln 55.5) = -kT \ln K_x \quad (16)$$

Davies⁴⁷ has suggested that the more associated nature of the hydroxides of most metals than of their other compounds may be due to the absence of the hydration shell which protects the cation. Whereas for most anions the configuration $\text{M}^{n+}(\text{H}_2\text{O})\text{X}^{m-}$ may represent their distance of closest approach to the cation, $\text{M}^{n+}(\text{H}_2\text{O})\text{OH}^-$ would tend to pass over into $\text{M}^{n+}\text{OH}-(\text{H}_2\text{O})$, thus displacing a water molecule of hydration. The hydroxides are thus a particularly useful series for comparison. Between OH^- and Ca^{2+} , Sr^{2+} , Ba^{2+} , Mg^{2+} , and La^{3+} ions, the only short-range forces will be forces of repulsion, since the electronic shells of the cations

⁴⁷ Davies, *J*, 1951, 1256.

contain the same number of electrons as neutral rare-gas atoms. The association constants for these ion pairs will therefore be only moderately large (Table 1), governed mainly by W_{env} , and it is not surprising that $\log K$ varies linearly with z^2/r_+ , where r_+ is the radius of the cation, a relationship shown by Davies.⁴⁷ On the other hand, Fe^{3+} , V^{3+} , and V^{4+} do not have rare-gas structures, and quantum-mechanical forces of attraction together with the electrostatic attraction will lead to the large K values in Table 1. As would be expected, this second group of ion pairs does not fit in with Davies's pK relationship.

TABLE 1. *Ion association reactions*

Reaction	K^{298} (l.mole ⁻¹)	ΔG° (kcal. mole ⁻¹)	ΔH° (kcal. mole ⁻¹)	ΔS° (cal.deg. ⁻¹ mole ⁻¹)	Ref.
$\text{Pb}^{2+} + \text{NO}_3^-$	15.1	-1.62	-0.57	3.5	<i>a</i>
$\text{Pb}^{2+} + \text{Cl}^-$	41	-2.20	1.25	11.6	44
$\text{Pb}^{2+} + \text{Br}^-$	72	-2.53	0.3	9.4	44
$\text{Pb}^{2+} + \text{I}^-$	83	-2.62	-0.3	7.8	44
$\text{Cd}^{2+} + \text{Cl}^-$	91	-2.67	0.98	12.2	44
$\text{Cd}^{2+} + \text{Br}^-$	141	-2.93	-0.32	8.8	44
$\text{Cd}^{2+} + \text{I}^-$	282	-3.34	-2.05	4.3	44
$\text{Tl}^+ + \text{OH}^-$	6.67	-1.12	0.37	5.1	13
$\text{Tl}^+ + \text{Cl}^-$	4.76	-0.93	-1.43	-1.7	13
$\text{Tl}^+ + \text{Br}^-$	7.67	-1.2	-2.45	-4.2	14
$\text{Tl}^+ + \text{NO}_3^-$	2.15	-0.45	-0.65	-1.0	14
$\text{Tl}^+ + \text{CNS}^-$	6.25	-1.09	-2.96	-6.4	13
$\text{Tl}^+ + \text{N}_3^-$	2.44	-0.53	-1.33	-2.7	14
$\text{Ag}^+ + \text{Cl}^-$	2.0×10^3	-4.5	-2.7	6	<i>b</i>
$\text{Ag}^+ + \text{IO}_3^-$	6.8	-1.13	5.14	20.3	<i>c</i>
$\text{Ca}^{2+} + \text{OH}^-$	25	-1.91	1.19	10.4	13
$\text{Ca}^{2+} + \text{OH}^-$	23	-1.86	1.25	11.3	<i>d</i>
$\text{Sr}^{2+} + \text{OH}^-$	6.7	-1.12	1.15	7.6	<i>d</i>
$\text{Ba}^{2+} + \text{OH}^-$	4.4	-0.87	1.75	8.8	<i>d</i>
$\text{Mg}^{2+} + \text{OH}^-$	380	-3.5	—	—	<i>e</i>
$\text{La}^{3+} + \text{OH}^-$	2×10^3	-4.1	—	—	47
$\text{Fe}^{3+} + \text{OH}^-$	6.4×10^{11}	-16.1	-3.0	44	<i>f</i>
$\text{V}^{3+} + \text{OH}^-$	5×10^{12}	-17.2	-3.7	45.5	<i>g</i>
$\text{U}^{4+} + \text{OH}^-$	2.5×10^{13}	-18.2	-2.5	52	<i>h</i>
$\text{Ca}^{2+} + \text{SO}_4^{2-}$	200	-3.15	1.65	16.1	13
$\text{Mg}^{2+} + \text{SO}_4^{2-}$	234	-3.22	4.55	26.1	17
$\text{Mn}^{2+} + \text{SO}_4^{2-}$	181	-3.07	3.37	22.6	17
$\text{Co}^{2+} + \text{SO}_4^{2-}$	230	-3.21	1.74	16.6	17
$\text{Ni}^{2+} + \text{SO}_4^{2-}$	211	-3.16	3.31	21.7	17
$\text{Zn}^{2+} + \text{SO}_4^{2-}$	240	-3.25	4.01	24.4	17
$\text{Mg}^{2+} + \text{CH}_3\text{CO}_2^-$	17.6	-1.69	-1.52	0.6	<i>a</i>

Reaction	K^{298} (l.mole ⁻¹)	ΔG° (kcal. mole ⁻¹)	ΔH° (kcal. mole ⁻¹)	ΔS° (cal.deg. ⁻¹ mole ⁻¹)	Ref.
Ca ²⁺ + CH ₃ ·CO ₂ ⁻	17.5	-1.69	0.91	8.7	<i>a</i>
La ³⁺ + CH ₂ (CO ₂) ₂ ²⁻	1.0 × 10 ⁵	-6.79	4.8	39	<i>i</i>
Gd ³⁺ + CH ₂ (CO ₂) ₂ ²⁻	2.5 × 10 ⁵	-7.32	5.1	42	<i>i</i>
Lu ³⁺ + CH ₂ (CO ₂) ₂ ²⁻	5.3 × 10 ⁵	-7.77	5.2	44	<i>i</i>
La ³⁺ + Fe(CN) ₆ ³⁻	5.5 × 10 ³	-5.09	2.0	23.9	3
La ³⁺ + Co(CN) ₆ ³⁻	5.8 × 10 ³	-5.13	1.33	21.7	<i>j</i>
Mg ²⁺ + edta ^{4-b}	3.5 × 10 ⁸	-11.65	3.14	50.5	<i>k</i>
Ca ²⁺ + edta ^{4-b}	3.3 × 10 ¹⁰	-14.34	-6.45	26.9	<i>k</i>
Co ²⁺ + edta ^{4-b}	1.15 × 10 ¹⁶	-21.9	-4.4	59.7	<i>k</i>
Ni ²⁺ + edta ^{4-b}	2.0 × 10 ¹⁸	-24.96	-8.35	56.7	<i>k</i>
Zn ²⁺ + edta ^{4-b}	1.7 × 10 ¹⁶	-22.12	-5.61	56.3	<i>k</i>
Al ³⁺ + edta ^{4-b}	6.9 × 10 ¹⁵	-21.60	12.58	116.6	<i>k</i>
Y ³⁺ + edta ^{4-b}	6.2 × 10 ¹⁷	-24.26	0.32	83.8	<i>k</i>

a Ionic strength = 1.0. *b* Ionic strength = 0.1.

References: *a*, Nancollas, *J.*, 1955, 1458; 1956, 744; *b*, Jonte and Martin, *J. Amer. Chem. Soc.*, 1952, 74, 2053. *c*, Renier and Martin, *ibid.*, 1956, 78, 1833. *d*, Gimblett and Monk, *Trans. Faraday Soc.*, 1954, 50, 965. *e*, Stock and Davies, *ibid.*, 1948, 44, 856. *f*, Milburn, *J. Amer. Chem. Soc.*, 1957, 79, 537. *g*, Furman and Garner, *ibid.*, 1950, 72, 1785. *h*, Betts, *Canad. J. Chem.*, 1955, 33, 1775. *i*, Gelles and Nancollas, *Trans. Faraday Soc.*, 1956, 52, 680. *j*, James and Monk, *ibid.*, 1950, 46, 1041. *k*, Staveley and Randall, *Discuss. Faraday Soc.*, 1958, 26, 157.

Returning to the case of thallos ion pairs, Davies⁴⁷ found that the hydroxide behaved similarly to the second group above, and gave this as additional evidence that covalent bonding is involved in this ion pair. Although this is supported by the impossibly low Bjerrum distance, Bell and George¹³ have pointed out that such calculations involve the macroscopic ϵ of water which it has been shown is inappropriate in the vicinity of an ion. The relative positions of the maxima in the spectra of thallos hydroxide, chloride, and bromide are very similar to those of the free ions OH⁻, Cl⁻, Br⁻, and this again points to the absence of specific covalent effects.⁴⁸ The appearance of new lines in the Raman spectrum is strong evidence for covalent-bond formation, but no such effect could be found for a nearly saturated (1.5M) solution of thallos hydroxide.⁴⁰

The new technique of nuclear magnetic resonance may also provide information about solution structure, shifts in the nuclear magnetic resonance frequency of various nuclei being ascribed to the changes in their immediate environment. Richards²⁶ has found that the thallium resonance line shifts with increasing concentration of thallos hydroxide owing to the varying concentrations of the species in equilibrium, Tl⁺, OH⁻, and TlOH. A detailed study gave $K(\text{TlOH}) = 5$, in agreement with solubility (6.7),¹³ spectrophotometric (5),⁴⁸ and kinetic (7)^{21b} estimates.

⁴⁸ Bell and Panckhurst, *Rec. Trav. chim.*, 1956, 75, 725.

The type of bonding must still remain an open question, although there is strong evidence that the association properties of the thallos ion are determined by other than purely electrostatic forces.

There have been several attempts to correlate experimental association constants with properties of the ions concerned. Williams⁴⁹ has emphasised, however, that, even with a closely related series of cations, the association constants may refer to the formation of ion pairs having different degrees of hydration. The alkaline-earth ions constitute an interesting series, and if we assume that the ion pairs are formed as a result of purely electrostatic interactions, the K 's should be in the inverse order of the cationic radii, *i.e.*, $Mg > Ca > Sr > Ba$. We have already noted that Davies observed this to be the case with the hydroxides, and the organic salts also follow this general order. The K for magnesium oxalate is 20 times that for the barium oxalate or magnesium sulphate and such a large difference may denote actual contact between the magnesium and oxalate ions.⁴³ With acetate and formate ions, the entropies of formation of magnesium ion pairs are anomalous (Table 1) and there is some evidence that the anion can displace a water molecule from the hydrated Ca^{2+} , Sr^{2+} , and Ba^{2+} ions but not from the smaller Mg^{2+} . In the nitrates, iodates, sulphates, and thiosulphates, the order of K is completely reversed and the measured values are undoubtedly related to the radii of the hydrated and not the bare cations. The K values are of a magnitude to be expected from Bjerrum's theory, the anion competing rather unsuccessfully with the water molecule for positions adjacent to the cations.⁴³

Comparisons of association constants with such properties as ionisation potentials of the metal atoms and lattice energies of the salts have also been made with varying success in closely related systems. The extension of these correlations to bond type should be made with care. There is no doubt that covalent character is an important factor contributing to stability, but it is not safe to assume perfect correlation. A number of authors have found⁵⁰ that $\log K_{MX}$ is linearly related to $\log K_{HX}$ for a large number of systems, and such a relation is of use for predicting hitherto unknown K values.

Heat and Entropy Changes.—Unfortunately, one cannot use the free-energy changes as diagnostic of the type of association without considering the heat, ΔH° , and entropy, ΔS° , contributions in detail. ΔG° may be written

$$\Delta G^\circ = -RT \ln K = \Delta H^\circ - T \Delta S^\circ \quad (17)$$

and in order to gain an insight into the factors which affect the equilibrium, it is more useful to regard the free-energy change as being a consequence of the changes in heat and entropy. There are, for instance, endothermic

⁴⁹ Williams, *J.*, 1952, 3770.

⁵⁰ *E.g.*, Irving and Rossotti, *Acta Chem. Scand.*, 1956, 10, 72.

reactions which are made possible by favourable entropy changes, also there are exothermic reactions which do not take place because of unfavourable entropy changes. Any comparison which is made of K values at a single temperature involves the assumption that ΔG° is dominated by the heat term and that changes in ΔS° may be neglected. It is clearly desirable, therefore, to obtain ΔH° and this can be done in two ways: (i) studies of the association constant over a range of temperature leading to the calculation of ΔH° from the van't Hoff isochore, $d \log K/dt = \Delta H^\circ/RT^2$, and (ii) direct calorimetric methods.

The second method is more reliable since there is rather a large uncertainty in heat changes derived from temperature coefficients of equilibrium constants. However, there are comparatively few equilibria for which heat and entropy data are available and most of these have been obtained by method (i). Therefore, although we must not put too much weight on their exact numerical values, they are useful for making comparisons. Measurements over too small a temperature range may lead to large errors in ΔH° . Thus conductivity data⁵¹ at 25° and 35° give $\Delta S = 22 \text{ cal. deg.}^{-1} \text{ mole}^{-1}$ for PbCl^+ , which is considerably higher than the more precise calorimetric value in Table 1. The use of a larger temperature range leads to a more reliable ΔH° . Thus an e.m.f. method⁵² over a 45° range yields $\Delta H^\circ = -5.6 \text{ kcal./mole}$ for the formation of the HSO_4^- ion, in good agreement with Pitzer's calorimetric value,⁵³ -5.2 kcal./mole . It should be emphasised, however, that the use of a large temperature range does not completely eliminate the errors in ΔH° , and there is a need for more calorimetric measurements.

The proton acids form a very large group of compounds for which accurate data are available over a wide range of temperature. Some selected data are given in Table 2. Assuming, in eqn. (16), that W_{env} is almost entirely electrostatic in origin, we may replace it by W_{el} and assume that as a function of temperature, it is inversely proportional to ϵ .³² It will not be strictly proportional to ϵ^{-1} owing to dielectric saturation in the neighbourhood of the ion. Thus we expect W to be composed of W_{el} , increasing with temperature, and W_{non} , independent of temperature. For the systems in Table 2, we find that the K values may decrease or increase or may pass through a maximum. However, in no case does $-kT \ln K_x (=W)$ pass through a maximum or minimum but it rises steadily, providing good evidence for this picture of ionic forces. It is possible to interpret qualitatively the temperatures at which the K values pass through a maximum or minimum. Extending the arguments to ion-association reactions of type (1), we may express ϵ by means of the empirical formula

$$\epsilon = \epsilon_0 e^{-T/V} \text{ or } 1/\epsilon = e^{T/V}/\epsilon_0 \quad (18)$$

⁵¹ Nancollas, *J.*, 1955, 1458; 1956, 744.

⁵² Nair and Nancollas, *J.*, 1958, 4144.

⁵³ Pitzer, *J. Amer. Chem. Soc.*, 1937, 59, 2365.

TABLE 2. Proton transfer reactions

Reaction	K (l.mole ⁻¹)	ΔH° (kcal. mole ⁻¹)	ΔS° (cal.deg. ⁻¹ mole ⁻¹)	Ref.
$H^+ + CH_3 \cdot CO_2^-$	5.7×10^4	0.10	22.1	<i>a</i>
$H^+ + C_2H_5 \cdot CO_2^-$	7.4×10^4	0.17	22.9	<i>a</i>
$H^+ + C_3H_7 \cdot CO_2^-$	6.6×10^4	0.70	24.4	<i>a</i>
$H^+ + H_2N \cdot CH_2 \cdot CO_2^-$	6.0×10^9	-10.60	9.2	<i>a</i>
$H^+ + SO_4^{2-}$	83	5.2	26.3	53
$H^+ + SO_4^{2-}$	110	5.6	26.7	52
$H^+ + H_2PO_4^-$	130	1.88	16.0	53
$H^+ + HPO_4^{2-}$	1.6×10^7	-0.80	30.3	53
$H^+ + PO_4^{3-}$	8.9×10^{11}	-3.50	43	53
$H^+ + H_2Cit^-$	1.34×10^8	-1.01	11.0	<i>b</i>
$H^+ + H Cit^{2-}$	5.77×10^4	-0.58	19.8	<i>b</i>
$H^+ + Cit^{3-}$	2.49×10^6	0.80	32	<i>b</i>

H_3Cit = Citric acid. References: *a*, Everett and Wynne Jones, *Trans. Faraday Soc.*, 1939, 35, 1384. *b*, Bates and Pinching, *J. Amer. Chem. Soc.*, 1949, 71, 1274.

where ν is a temperature characteristic of the solvent and ϵ_0 is a constant.³² If W_{e1} were proportional to ϵ^{-1} , eqn. (16) could then be written

$$\ln K_X = -C(a + e^{T/\nu})/T \quad (19)$$

where $Ca = W_{non}/k$ and $Ce^{T/\nu} = W_{e1}/k$. Differentiation of (19) with respect to T and equation to zero gives the temperature (T^*) at which the association constant passes through a minimum,

$$\left. \begin{aligned} T^* &= \nu(1 + a/e^{T^*/\nu}) \\ \text{or} \quad T^* &= \nu(1 + W_{non}/W_{e1}^*) \end{aligned} \right\} (20)$$

where W_{e1}^* is the value of W_{e1} at $T = T^*$. The value of K will rise over the whole range of temperature if T^* lies below freezing point of the solvent, and it is noteworthy that the position of the minimum depends, not on the value of $(W_{non} + W_{e1})$, but on their ratio. When W_{non}/W_{e1} is small, as would be expected in the alkaline-earth hydroxide ion pairs, the predominant effect with rise of temperature will be to decrease the mutual potential energy and K will increase. For other ion pairs involving the OH^- ion, W_{non} becomes important, W_{non}/W_{e1} may be large, and the predominant effect will be the tendency for thermal agitation to cause dissociation of the ion pairs. This predicts the right kind of behaviour, as is shown in Table 1; ΔH° is positive for the alkaline-earth hydroxides and negative for the others.

If the reaction (1) involves the displacement of a water molecule by the associating ion, the heat changes may be made up in the following

energetically equivalent manner:⁴⁶ (1) Removal of the hydrated ions M^{n+} and X^{m-} from solution, and placing them in the gas phase with loss of their co-ordinated water molecules. (2) Movement of the two ions into adjacent positions. (3) Return of the ion pair into solution with reorientation of water molecules, each ion being assumed to occupy a single co-ordination position in the octahedral arrangement of the other ion.

By using this thermodynamic cycle, calculations from which can be regarded as being accurate only to about ± 5 kcal. mole⁻¹, it is possible to explain a number of observed facts. For instance, calculations show that in sodium chloride the formation of ion pairs in which the Na^+ ion is adjacent to the Cl^- ion is energetically most unlikely.⁴⁶ The interposition of a water molecule between them, however, makes the ion association exothermic and the degree of association, α , in a 0.1M-solution would be about 0.33% for $\epsilon = 1$ (this value of ϵ being assumed in the vicinity of the ions: for $\epsilon = 79$, $\alpha = 0.0041\%$). Eigen and Wicke²⁷ have obtained 0.2% from activity data, so it would appear that the small amount of ion pair formed in sodium chloride solution consists of $Na^+(H_2O)Cl^-$. When this approach is applied to nickel sulphate there is a wide discrepancy between the calculated and the experimental degree of association. Since the calculations were made on a model having adjacent nickel and sulphate ions, it is concluded that no such ion pairs exist in these solutions.⁴⁶ The absence of any spectral shift on adding sodium sulphate to nickel sulphate solutions also indicates that any association must take place through water molecules.

If the heat changes upon ion-pair formation depended only upon the hydration steps in the above picture, then we should expect to find a simple relation between heats of hydration of gaseous ions and z/r where r is the ionic radius. Williams⁵⁴ has shown that no such simple relation exists either in this case or when the heats are correlated with ionisation potentials. Staveley and his co-workers^{55,56} have measured, by direct calorimetry, the heats of formation of some bivalent metal ethylenediaminetetra-acetates and have shown that there are no obvious regularities in the values. ΔH° values must be associated with electrostatic and covalent interactions between the ions, together with additional stabilisation due to the different available bonding orbitals of the cations. For the transition series of metals, Orgel⁵⁷ has proposed that this additional stabilisation is due to the splitting of the d -level in the electrostatic field of the ligand groups, and has shown that this accounts for the main features of the heats of solvation throughout the series. George⁵⁸ has suggested that this phenomenon is of primary importance in the case of complex ions.

Examination of the data in Tables 1 and 2 shows that, in most cases, for

⁵⁴ Williams, *J. Phys. Chem.*, 1954, **58**, 121.

⁵⁵ Care and Staveley, *J.*, 1956, 4571.

⁵⁶ Staveley and Randall, *Discuss. Faraday Soc.* 1958, **26**, 157.

⁵⁷ Orgel, *J.*, 1952, 4756.

⁵⁸ George, *Rec. Trav. chim.*, 1956, **75**, 671.

reactions of type (1) between cations and anions with a resultant reduction in the number of ions in solution and a concomitant neutralisation of charge, there is an entropy change favouring ion-pair formation. Frank and Evans⁵⁹ have suggested that the ions in solution order water molecules around them to form an "iceberg," the process being similar to the localised freezing of a liquid. Ion-pair formation tends to break down this "iceberg" structure and the decreased orientation of solvent molecules leads to a positive entropy change. At first sight this is not always the case, since one must take into account with polyatomic ions the loss in configurational and rotational entropy which accompanies the association. Also it is important to compare only those reactions which involve the same change in number of solute species, and this has been emphasised by a number of workers.^{60,61b} In eqn. (17), the entropy value depends upon the concentration units used in the calculation of K , ΔS° referring to the molality scale. Gurney³² was the first to recognise this problem of standard states and, using the arguments already outlined, he defined a quantity called the unitary entropy $S^{\circ'}$ as the difference between the partial molar entropy S° and the absolute value of the partial molal configurational entropy:

$$S^{\circ'} = S^\circ - R \ln 55.5 = S^\circ - 8 \Delta n \quad (21)$$

Δn being the change in number of solute species when the reaction takes place.

Williams⁵⁴ compared ΔS of a large number of reactions in which complexes of the type MX_p are formed, where $p = 1-4$ without correction for Δn . He found four systems in which ΔS was negative instead of positive. Bent⁶⁰ applied the above corrections to Williams's data and showed that in all cases, excepting silver thiosulphate, the anomalies were removed. In $Ag(S_2O_3)_2^{3-}$ it is possible to explain the negative entropy as a loss of configurational and librational entropy of the $S_2O_3^{2-}$ ion upon ion-pair formation.

There is more regularity in the entropy changes on ion-pair formation than in the heat changes, and reactions which have been rather thoroughly studied are those between the anions of weak acids and the hydrogen ion. Some data are included in Table 2 and it can be seen that a ΔS of about 22 cal. deg.⁻¹ mole⁻¹ is fairly common for this type.^{61a} The value of ΔS° for the association of hydrogen and glycine anions is not as positive as +22 cal. deg.⁻¹ mole⁻¹. In this case, the resulting molecule, whilst neutral, has a zwitterion structure which will exert strong orientating effects on surrounding water molecules, just as did the separated ions. If we can assume that the interaction of the carboxylate group with water molecules is not appreciably altered by the association with the hydrogen ion at the

⁵⁹ Frank and Evans, *J. Chem. Phys.*, 1945, 13, 507.

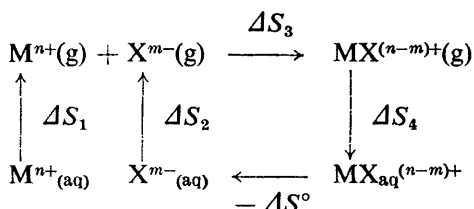
⁶⁰ Bent, *J. Phys. Chem.*, 1956, 60, 123.

⁶¹ King, (a) *J. Chem. Educ.*, 1953, 30, 71; (b) *J. Phys. Chem.*, 1959, 63, 1070.

other end of the molecule, then ΔS° for the association of the glycine and hydrogen ions might be expected to be similar to ΔS° for reactions such as $\text{H}^+ + \text{Me}\cdot\text{NH}_2 \rightleftharpoons \text{Me}\cdot\text{NH}_3^+$, and King has shown this to be the case.^{61a} The other acids in Table 2 for which $\Delta S^\circ \ll +22 \text{ cal. deg.}^{-1} \text{ mole}^{-1}$ for the reaction between univalent ions are those in which the functional acidic group is not the only one possessing polarity.

The entropy of association becomes appreciably more positive as the negative charge on the anion increases (Table 1), and this is due to $d > 1$ in the dependence of S°_i of polyatomic ions upon z^d . In the case of the strong acids which are completely dissociated in solution, while association between the hydrogen ion and the acid anion will be accompanied by a favourable entropy change, the heat change must be unfavourable.^{61a} After making corrections for the difference of the symmetry numbers of the acid and conjugated base, King has shown^{61b} that the ΔS° values for the closely related phosphoric and citric acid dissociation reactions are linearly related to Δz^2 , Δz^2 being the difference between the sum of the squares of the charges on the products and on the reactants.

We may write the entropy change in reactions of type (1) in terms of an entropy cycle⁶²



where $-\Delta S_1$ is the entropy change accompanying the hydration of the gas-phase cation, $-\Delta S_2$ and ΔS_4 are the corresponding values for the anion and ion pair respectively, and ΔS_3 is the association entropy change in the gas phase.

The observed entropy change in solution may thus be written

$$\Delta S^\circ = \Delta S_1 + \Delta S_2 + \Delta S_3 + \Delta S_4 \quad \dots \quad (22)$$

If ΔS_3 does not change appreciably for a series of related reactions, ΔS° should be dependent upon the differences in hydration effects, $\Delta S_1 + \Delta S_2 + \Delta S_4$. For a given cation and a series of simple anions in which ΔS_4 remains approximately the same, we should expect a linear relation between ΔS° and the hydration entropy of the anion. This has been found to hold approximately in a number of cases.^{44, 62, 63} Staveley and Randall⁵⁶ have observed, for a number of bivalent metal ethylenediaminetetra-acetates, direct linear relation between ΔS (association) and $1/r_+$. These fall into two groups as is shown in Fig. 1, (curve iv) those metal

⁶² Evans and Nancollas, *Trans. Faraday Soc.*, 1953, **49**, 363.

⁶³ Evans and Uri, S.E.B. Symposium No. 5, Cambridge, 1951.

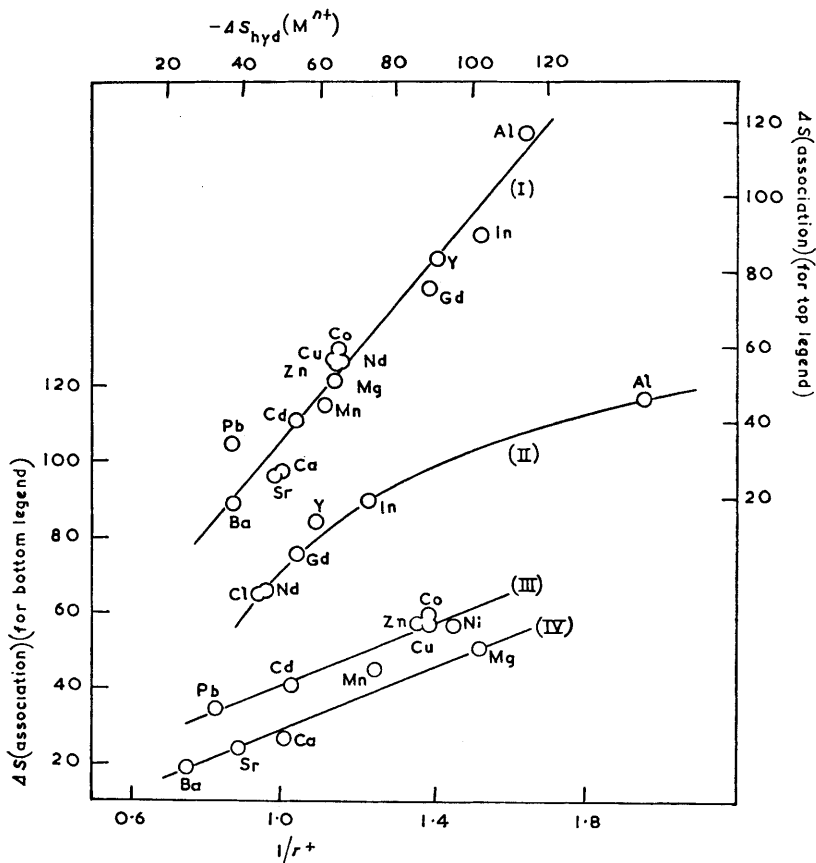


FIG. 1. *Metal-ethylenediaminetetra-acetate complexes.* (ii), (iii), and (iv), plots of ΔS (association) against $1/r_+$ (reproduced, by permission, from *Discuss. Faraday Soc.*, 1958, 26, 159); (i) plot of ΔS (association) against $-\Delta S_{\text{hyd}}(M^{n+})$.

ions with inert-gas structures, and (iii) the transition-metal ions. The relationship is no longer linear for the trivalent cations (curve ii). In Fig. 1, ΔS is also plotted against $-\Delta S_{\text{hyd}}(M^{n+})$ and it is noteworthy that a single, quite reasonable linear relation (line i) is sufficient to include all charge types.

George⁶⁴ has shown, more generally, that the equation

$$\Delta S = \Delta S_2 + \text{Constant} \quad \dots \quad (23)$$

satisfactorily interprets the results of a number of cation-anion association reactions. The value of the constant to be used for different systems

⁶⁴ George, *J. Amer. Chem. Soc.* 1959, 81, 55.

varies from +10 for Fe³⁺ with OH⁻, F⁻, Cl⁻, Br⁻, to -40 for CH₃CO₂⁻ with Ca²⁺, Sr²⁺, Ba²⁺. The relation is illustrated in Fig. 2 which differs from that of George in that the more precise calorimetric data have been used for lead and cadmium halides.⁴⁴ It is seen that there is good evidence for the validity of this approximate equation, and the implication is that the change of hydration of the ions on ion-pair formation is the important factor in these cases.

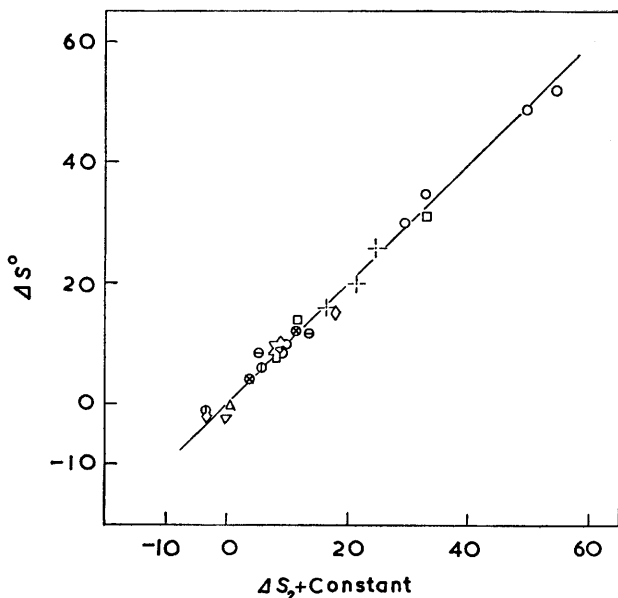


FIG. 2. Plot of ΔS° against $(\Delta S_2 + \text{Constant})$. For the hydroxide ion pairs, 8 cal. deg.⁻¹ mole⁻¹ is added to ΔS° to allow for loss of rotational entropy on association (reproduced, by permission, from *J. Amer. Chem. Soc.*, 1959, **81**, 5530, with substitution of calorimetric PbX⁺ and CdX⁺ data⁴⁴).

Reaction	Constant	Reaction	Constant
⊙ Fe ³⁺ with OH ⁻ , F ⁻ , Cl ⁻ , Br ⁻	+10	◇ Tl ⁺ with OH ⁻ , Cl ⁻ , Br ⁻	-26
⋄ Co(NH ₃) ₆ with Cl ⁻ , Br ⁻ , I ⁻	+2	△ H-CO ₂ ⁻ with Ca ²⁺ , Sr ²⁺ , Ba ²⁺	-39
⊗ Cd ²⁺ with Cl ⁻ , Br ⁻ , I ⁻	-10	▽ CH ₃ CO ₂ ⁻ with Ca ²⁺ , Sr ²⁺ , Ba ²⁺	-40
⊖ Pb ²⁺ with Cl ⁻ , Br ⁻ , I ⁻	-9	⊕ Cl ⁻ with Tl ⁺ , Ag ⁺	-16
⊠ Sn ²⁺ with OH ⁻ , Cl ⁻ , Br ⁻	-11		

The calculation of the terms on the right-hand side of eqn. (22) makes possible the derivation of ΔS° . The entropy change in the gas phase contains both translational and rotational terms:

$$\Delta S_3 = S_{\text{trans}}(\text{MX}^{(n-m)+}) - S_{\text{trans}}(\text{M}^{n+}) - S_{\text{trans}}(\text{X}^{m-}) - S_{\text{rot}}(\text{X}^{m-}) + S_{\text{rot}}(\text{MX}^{(n-m)+}) \quad (24)$$

which may be obtained statistically. If the ion pair can be considered as a linear molecule⁶⁵

$$S_{\text{trans}}(\text{MX}^{(n-m)+}) + S_{\text{rot}}(\text{MX}^{(n-m)+}) \\ = 2.287 (7 \log T + 3 \log M + 2 \log I_B - 2 \log \sigma) - 6.661 \quad . \quad . \quad (25)$$

where I_B is the moment of inertia about its axis, and σ the symmetry number. For rigid molecules which are not linear,

$$S_{\text{trans}}(\text{MX}^{(n-m)+}) + S_{\text{rot}}(\text{MX}^{(n-m)+}) \\ = 2.287 (8 \log T + 3 \log M + \log I_A I_B I_C - 2 \log \sigma) - 7.697 \quad . \quad (26)$$

The product $I_A I_B I_C$ of the principal moments of inertia may be evaluated as was done for a number of systems^{14,17} by means of the relation⁶⁶

$$I_A I_B I_C = \begin{vmatrix} +I_{xx} & -I_{xy} & -I_{xz} \\ -I_{xy} & +I_{yy} & -I_{yz} \\ -I_{xz} & -I_{yz} & +I_{zz} \end{vmatrix}$$

where I_{xx} , I_{xy} . . . are the moments and products of inertia with respect to a co-ordinate system having the centre of mass as origin:

$$I_{xx} = \sum m_i (y_i^2 + z_i^2) \dots$$

$$I_{xy} = \sum m_i x_i y_i \dots$$

$$\text{where } M = \sum m_i$$

In some cases the entropy change due to the loss of free internal rotation accompanying association must be taken into account:⁶⁵

$$S(\text{f.i.r.}) = 2.287 (\log T + \log I_r - 2 \log n) + 89.93 \quad . \quad . \quad (27)$$

where n is the number of indistinguishable positions of the groups with respect to each other and I_r , the reduced moment of inertia, is given by

$$I_r = I_r^\circ [1 - I_r^\circ (\lambda_{rA}^2/I_A + \lambda_{rB}^2/I_B)]$$

In this formula, I_r° is the moment of inertia of the "rotating top" and λ_{rA} and λ_{rB} are direction cosines. Such corrections have been applied in the case of iodate and nitrate ion pairs.⁶⁷

The entropies of the free ions, required for the calculation of ΔS_1 and ΔS_2 , are in many cases known with some certainty⁶⁸ and there are a number of empirical relationships by means of which estimates may be made when individual data are not available. Since the binding of a water molecule to an ion will occur with a decrease in entropy, the partial molar entropies of the various ions will be related to their respective degrees of

⁶⁵ Herzberg, "Infra-red and Raman Spectra," Van Nostrand, New York, 1945

⁶⁶ Wilson, *Chem. Rev.*, 1940, 27, 17.

⁶⁷ Nancollas, *Discuss. Faraday Soc.*, 1957, 24, 108.

⁶⁸ Latimer, "Oxidation Potentials," Prentice-Hall, New York, 1952.

hydration. A number of workers have noted correlations with functions of the charges and radii of the ions. Powell and Latimer⁶⁹ have shown that for all the simple monatomic ions the equation

$$\bar{S}^{\circ} = \frac{3}{2} R \ln M + 37 - 270z/r_e^2. \quad \dots \quad (28)$$

holds very well. r_e , the effective radius, includes an approximate correction for hydration and is taken as $r^+ + 2.00 \text{ \AA}$ for cations and $r^- + 1.00 \text{ \AA}$ for anions. In terms of an electrostatic model, Born has proposed a value, $z^2/2\epsilon r$, for the potential energy of a conducting sphere in a continuum of dielectric constant ϵ and this leads to an entropy contribution

$$S_{el}^{\circ} = \frac{z^2 e^2}{2r\epsilon} \cdot \frac{d \ln \epsilon}{dT} \quad \dots \quad (29)$$

related to z^2/r and not to z/r^2 . This has been emphasised by Laidler,⁷⁰ who pointed out that relations such as eqn. (28) using a corrected radius and referring to $S_{H^+}^{\circ} = 0$ have no fundamental validity. Although ionic entropies are usually based on this standard, there is good evidence³² that $S_{H^+}^{\circ}$ (absolute) = $-5.5 \text{ cal.deg.}^{-1} \text{ mole}^{-1}$, and, when the entropies were referred to this, Laidler found for all monatomic cations the relation following z^2/r_+ ,

$$\bar{S}^{\circ}_{(abs)} = \frac{3}{2} R \ln M + 10.2 - 11.6z^2/r_+$$

r_+ being the unadjusted ionic radius. This represents a true dependence according to the Born model.

The entropies of a large number of complex ions have been treated by Cobble,⁷¹ who proposed for inorganic complexes the equation

$$\bar{S}^{\circ} = 49 - 99z[f(r_+ + r_-)] + n\bar{S}_{H_2O} \quad \dots \quad (30)$$

f is a structural factor and n is the number of water molecules displaced from the hydration shell of the cation on ion association. The need for the structural factor is thought to be due to the "open" structure of the complexes. Owing to the non-uniform charge distribution their centre of gravity does not approach the central ion as closely as with a monatomic ion, so that the sum of the crystal radii is smaller than the effective radius of the ion. Cobble found that an f value of 0.65 made possible the interpretation of the entropies of a large number of complex ions. The agreement was not very good in all cases but, on the other hand, the accuracy of the entropy data is not high. The equation is an empirical one, but it is also related to a model in which the anions replace n molecules of water from the hydration shells of the fully co-ordinated aquated cations.

⁶⁹ Powell and Latimer, *J. Chem. Phys.*, 1951, **19**, 1139.

⁷⁰ Laidler, *Canad. J. Chem.*, 1956, **34**, 1107.

⁷¹ Cobble, *J. Chem. Phys.*, 1953, **21**, 1443, 1446, 1451.

In comparing the entropy changes upon ion association it is important to allow for the various translational and rotational contributions. It is therefore useful to use eqn. (22) to calculate $\Delta S_{\text{hyd}}(\text{MX}^{(n-m)+})$ from the estimated ΔS_{1-4} . Data are given in Table 3; and in Fig 3 $\Delta S_{\text{hyd}}(\text{MX}^{(n-m)+})$ has been plotted against $z/(r_+ + r_-)$. It is seen that for the hydroxide ion pairs, the values fall fairly well on a straight line—although there is little

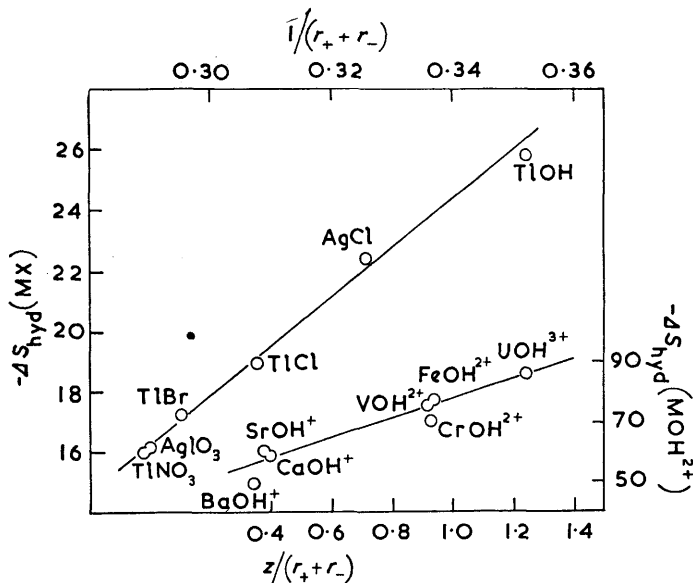


FIG. 3. Plots of $\Delta S_{\text{hyd}}(\text{MX})$ against $1/(r_+ + r_-)$ and of $-\Delta S_{\text{hyd}}(\text{MOH}^{2+})$ against $z/(r_+ + r_-)$.

to choose between a $z/(r_+ + r_-)$ and a $z^2/(r_+ + r_-)$ relationship. The system UOH^{3+} refers to experiments at $I = 1$ and is therefore not strictly comparable with the others; the value of $\Delta S_{\text{hyd}}(\text{UOH}^{3+})$ will probably be in error by a few entropy units. The experimental and interpretative uncertainties for the alkaline-earth hydroxides are likely to be greatest owing to their lower association constants. For ion pairs carrying no residual charge, Fig. 3 shows the good linear relation between $\Delta S_{\text{hyd}}(\text{MX})$ and $(r_+ + r_-)^{-1}$. The values of $\Delta S_{\text{hyd}}(\text{TlN}_3)$ and $\Delta S_{\text{hyd}}(\text{TlCNS})$ in Table 2 are considerably lower than would be expected from this relation. There is some doubt about the S° values for the azide and thiocyanate ions but it is unlikely that they will be in error by more than 2–3 cal. deg.⁻¹ mole⁻¹. Also, entropy contributions due to bending vibrations will account for some of the discrepancy. The latter will undoubtedly be present in the nitrate and iodate ion pairs, but it is possible that in these cases the entropy is already over-corrected in the term for free internal rotation.

It is interesting to consider the way in which the entropy of hydration of the ion pair is influenced by the values of W_{env} and W_{non} . If we compare BaOH^+ and PbCl^+ , the values of $(r_+ + r_-)$ are not very different, but, whereas in BaOH^+ the only short-range forces will be those of repulsion, in PbCl^+ , W_{non} will contribute, leading to a greater neutralisation of charge. This is reflected by the considerably smaller value of $-\Delta S_{\text{hyd}}$ (PbCl^+) in Table 3.

TABLE 3. *Thermodynamic properties.**

Ion pair	S_g ($\text{MX}^{(n-m)+}$)	ΔS°	S° ($\text{MX}^{(n-m)+}$)	$-\Delta S_{\text{hyd}}$ ($\text{MX}^{(n-m)+}$)	$(r_+ + r_-)^{-1}$
CaOH^+	53.8	10.8	- 4.8	58.6	0.397
SrOH^+	56.0	7.6	- 4.3	60.3	0.376
BaOH^+	58.4	8.8	9.3	49.1	0.347
VOH^{2+}	53.7	45.5	-22	75.7	0.457
FeOH^{2+}	53.9	44	-23.2	77.1	0.469
CrOH^{2+}	53.8	—	-16.4	70.2	0.462
UOH^{3+}	58.5	52	-28.5	86.0	0.413
TIOH	58.8	5.1	33.0	25.8	0.352
TICl	60.9	- 1.7	41.9	19.0	0.308
TIBr	62.8	- 4.2	45.5	17.3	0.295
TINO_3	80.4	- 1.0	64.4	16.0	0.289
TICNS	69.8	- 6.4	60	9.8	ca. 0.30
TIN_3	66.7	- 2.7	59.7	7.0	ca. 0.32
AgCl	58.9	6	36.5	22.4	0.326
AgIO_3	82.2	20.3	66.0	16.2	ca. 0.29
MgSO_4	68.2	26.1	2.0	66.2	0.26
CaSO_4	69.5	16.1	7.0	62.5	0.24
MnSO_4	70.1	22.6	6.7	63.4	0.25 ₂
CoSO_4	70.2	16.6	- 1	71	0.25 ₅
NiSO_4	70.2	21.7	3	67	0.25 ₆
ZnSO_4	70.3	24.4	3.0	67.3	0.25 ₇
$\text{CH}_3 \cdot \text{CO}_2 \text{Mg}^+$	65.0	0.6	- 1.0	66.1	ca. 0.35
$\text{CH}_3 \cdot \text{CO}_2 \text{Ca}^+$	66.5	8.7	22.2	44.3	ca. 0.31

* All S values are in terms of cal. deg.⁻¹ mole⁻¹.

The entropy of association can yield qualitative information about the degree of hydration of the ions in the ion pair. If the ion-pair formation takes place without the elimination of water molecules of hydration, then the entropy change will be expected to be less positive. Considering only the charges on the ions, it would be expected that ΔS° for the formation of $\text{LaFe}(\text{CN})_6$ and $\text{LaCo}(\text{CN})_6$ would be considerably more positive than the values in Table 1. We have already seen that there is good evidence that these ion pairs involve the hydrated lanthanum ion, and the smaller

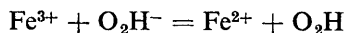
positive value of ΔS° substantiates this view. The water molecules in the first sphere of co-ordination would not gain freedom when the ion pair is formed.

The measurement of the entropy changes accompanying ion-association reactions has important implications in reaction kinetics of ionic processes in aqueous solution. We can write the velocity constant of ionic reactions of the type.

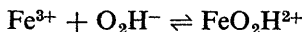


as $k = \nu \exp(\Delta S^*/R) \exp(\Delta H^*/RT)$

and enquire how ΔS^* , the difference in entropy between the activated complex and the reactants, varies with the ionic charges m and n . Since the transition state is an association complex, this entropy change (ΔS^*) will vary in the same way as ΔS (association) for the same ions. Confirmation of this is obtained by comparing ΔS^* for the reaction



with ΔS (association) for the equilibrium



These values are 52 and 49 cal. deg.⁻¹ mole⁻¹ respectively.⁶²

Similar observations have been made by Powell⁷² for reactions such as



An empirical relation gives the translational entropy change for the formation of a single molecule by the combination of two non-electrolyte molecules as -14 cal.deg.⁻¹ mole⁻¹. Thus if we imagine the activated complex as being formed from NH_3 (26 cal.deg.⁻¹ mole⁻¹) and $HOCl$ (31 cal.deg.⁻¹ mole⁻¹), its estimated entropy is $26 + 31 - 14 = 43$. This compares very well with the experimental entropy value, 44 cal.deg.⁻¹ mole⁻¹.

An attempt has been made throughout this Review to present the physicochemical principles involved in studies of ion-pair formation. Clearly, the determination of reliable thermodynamic data is very desirable, and, so far as the heats of formation are concerned, a calorimetric approach seems to be promising. Entropy values are important in that they give information about the structures of ion-solvent and ion pair-solvent complexes. However accurate the experimental data, these entropies will always involve the assumptions implicit in the calculation of ΔG° .

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⁷² Powell, *J. Phys. Chem.*, 1954, **58**, 528.