SOME THERMODYNAMIC MEASUREMENTS RELATING TO SOLUTION PROCESSES

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Abstract

The interest in this thesis is the thermodynamic approach to the elucidation of the structures of dilute ionic solutions. Solvation enthalpies of group Ia, IIa and VIIb ions in water, formamide and the two N-methyl derivatives of formamide are derived from recently published heat of solution data and from heat of solution measurements made by the author, and are compared with theoretical values calculated using an extended form of Buckingham's theory. The interpretation of aolvation entropies suggests that certain structural effects occur in the process of ion solvation. By including these in the theoretical calculations, good agreement between experiment and theory is obtained.

The experimental results presented include:

(a) the standard enthalpies of formation and solution in water of magnesium bromide, magnesium iodide, and all of the group IIa fluorides;

(b) the standard enthalpies of solution in water of the group IIa bromates, and of a number of tetra-alkylammonium salts;

(c) the standard enthalpies of solution in formamide, N-methylformamide and N,N-dimethylformamide of a number of group IIa halides and halates.

The following thermodynamic parameters are calculated for the group Ia and IIa halides and halates using the most modern data available: standard enthalpies of formation, lattice enthalpies, solvation enthalpies, entropies in the gas solution and solid state, solvation entropies, lattice entropies, lattice free energies, solvation free energies.

Some consideration is given to the estimation of solvation parameters for complex ions.

Using a new empirical approach, the corresponding functions for the individual ions are derived.

An account is given of the construction and method of use of the calorimeter, and of an apparatus for the isopiestic comparison of vapour pressures.

SECTION 1

Introduction - Part 1

A remark made by Dr. R.J. Gillespie (1) at a discussion of the Faraday Society ten years ago, "Our understanding of ion-solvent interactions can undoubtedly be improved by obtaining information about solutions in solvents other than water", seems to have been taken to heart in the last few years(refs 2-19). Apart from the Russians, whose work has mostly been concerned with solutions in various alcohols, much of this interest has been in high dielectric constant solvents such as heavy water, formamide and its N-methylated derivatives. The reason for studying this type of solvent is that in them one expects complete dissociation of electrolytes, and consequently, the interpretation of experimental data is freed from the complications of ion-ion interactions. There is a variety of evidence to show that this is the case in the high dielectric constant solvents mentioned (20-24).

1.1.1

This thesis is concerned with solutions in water, formamide (F), N-methyl formamide (NMF) and N,N-dimethyl formamide (DMF). The experimental measurements consist mostly of the standard enthalpies of solution of a number of main group 11 halides and halates, which, together with corresponding data for the main group 1 halides taken from the literature, are combined with newly derived values for the lattice enthalpies to obtain solvation enthalpies using the following thermodynamic cycle:

$$\begin{tikzcd}
 & M^+(g) + X^-(g) \arrow[dr, "\Delta H^o_{solv}"] & \\
MX(c) \arrow[ur, "\Delta H^o_L"] \arrow[rr, "\Delta H^o_s"] & & M^+(sol^n) + X^-(sol^n)
\end{tikzcd}$$

Cycle 1

The lattice enthalpies used are not the same as the more usual function, the lattice energy: they refer to the change in enthalpy accompanying the separation of the ions in the crystal to form an infinitely dilute ideal gas, all at 298.15°K, and are obtained by substituting the appropriate enthalpy data in the Born-Haber cycle as follows:

$$\begin{tikzcd}
 & M^+(g) & + & X^-(g) \\
MX(c) \arrow[ur, "\Delta H^o_L", "(2)"'] & & & \\
M(s.s.) \arrow[u, "(1)\ \Delta H^o_f"] \arrow[r, "\Delta H_{sub}", "(5)"'] & M(g) \arrow[uu, "I\ (3)"'] & & \\
+ & & & \\
\frac{1}{2}X_2(s.s.) \arrow[rrr, "\frac{1}{2}D", "(6)"'] & & & X(g) \arrow[uuuu, "-E\ (4)"']
\end{tikzcd}$$

Cycle 2

The terms together with the data sources are: (3) the ionisation potential of the metals taken from NBS circular 467 (25); (4) the electron affinity of the halogen atoms from Berry and Reimann's recent data (26); (5) the enthalpy of sublimation of the metal - Lewis and Randall (27); (6) the dissociation enthalpies of the halogens, including the appropriate evaporation and fusion enthalpies for bromine and iodine - Lewis and Randall (27); (7) the standard enthalpies of formation of the crystals - these were recalculated from the latest available data, as discussed below.

The two cycles are written out for a uni-univalent salt - the extension to include salts with ions of higher valency is self-evident. Of course, both cycles could be applied to any other thermodynamic function.

The main source of standard enthalpies of formation is the National Bureau of Standards circular 500 (28). Unfortunately, certain sections of the data in this collection were obtained during the last century (some of the group 11a halides, for example). Inspired by the recent publication of the relevant data, it seemed expedient to re-calculate the required standard enthalpies of formation. The newly published data were (a) the conventional (ie. relative to the aqueous proton) standard enthalpies of formation of the aqueous group 1a cations, (29). (b) the standard enthalpies of formation of the aqueous halide anions (30-33). (c) the standard enthalpies of solution of the group 1a halides (34), and the halides of calcium strontium and barium (35). (d) the standard enthalpies of solution of Ca, Sr, and Ba metals in dilute hydrochloric acid (35). (e) values obtained by this author for the standard enthalpies of solution and formation of magnesium bromide and iodide, and for the standard enthalpies of solution of all the group 11a fluorides. Standard enthalpies of formation of aqueous ion pairs were combined with standard enthalpies of solution of the corresponding crystal to give the required standard enthalpies of formation of the crystals. The data used and the results obtained are recorded in section 2.1.

1.1.2

It is not always possible to use the Born-Haber cycle to determine lattice enthalpies. In the case of the halates, for example, there are no electron affinity data. In such a situation it becomes necessary to estimate values for the lattice enthalpy. The most reliable method for doing this appears to be to make use of the linear relationship observed between ion pair hydration enthalpies and (a) reciprocal anion crystal radius, or (b) anion lyotropic number (36-37). For example, Finch and Gardner (38) plotted graphs of the hydration enthalpies of the calcium halides (among others) versus the halide lyotropic numbers. Interpolation of the chlorate lyotropic number gave the hydration enthalpy of calcium chlorate. The value thus obtained was combined with the enthalpy of solution of calcium chlorate in cycle 1 to give the lattice enthalpy. A modified form of this technique is used in section 2.6 to estimate the lattice enthalpies of the group lla halates. Also, a new correlation, between cation hydration enthalpy and the effective cation radius is used to estimate lattice enthalpies of some tetraalkyl ammonium halides.

1.1.3.

The entropies of crystalline salts are listed in NBS 500. The list is by no means complete, and has been supplemented by a number of estimated values by Latimer (39). Values are also given for the conventional entropies of the aqueous ions. The chief source of data for crystal entropies is specific heat measurements as a function of temperature, extending from room temperature to near absolute zero. The crystal entropy is obtained by evaluating the integral

$$S_{298.15} = \int_{0}^{298.15} \frac{C_p dT}{T} + \Delta S\,(\text{phase changes}) \qquad (1.1.3,1)$$

Extrapolation of the specific heat data to absolute zero is usually done with the aid of the Debye theory of specific heats, which shows that at very low temperatures C_v is proportional to the cube of the temperature. Also C_p approaches C_v as the temperature approaches zero. The data used in section 2.7 are all from NBS 500 except in certain cases where more modern data are available, or where it has been necessary to use estimated values.

There are three methods for obtaining entropies for ions in solution, (a) partial molal free energies combined with partial molal enthalpies, the free energy data coming from measurements of the standard potentials of suitably chosen electrochemical cells. Entropy data in NMF has been obtained in this way (7). (b) Measurement of the temperature derivative of the standard potentials of suitably chosen electrochemical cells. (c) Combination of free energies of solution, obtained from solubility studies, with standard enthalpies of solution to give entropies of solution; followed by combination of the latter with crystal entropies.

Having derived a set of entropies for the aqueous ions, it is then possible to use method (c) in reverse to obtain unknown crystal entropies. This technique has been used by Ionin (40) to obtain entropies of some group 11a halide hydrates, and is extended in section 2.2 to include some alkali metal halides. The free energy of solution is related to the activity of the solute in the solid (c) and solution (S) phases by the equation:

$$\Delta G_s^o = RT\ln a_s / a_c \qquad (1.1.3,2)$$

The activity of a crystal is by convention set equal to unity. Hence, introducing the solute activity co-efficient, equation 1.1.3,2 becomes:

$$\Delta G_s^o = RT \ln \gamma m_s \qquad (1.1.3,3)$$

For ionic crystals, it is necessary to use the mean ion activity co-efficient, and to replace m_s by the product of the saturation concentrations of the ions raised to the appropriate stoichiometric powers. Ionin selected his data from Robinson and Stoke's compilation of activity co-efficients (41); the data in section 2.2 comes from the same source, but includes some more modern values. Some of the entropy data obtained by this method do not compare at all well with Latimer's estimated values or with the usual periodic trends observed for entropies. The discrepancy is probably due to uncertainties in the activity co-efficients, which often have large values at high concentrations and often change rapidly with concentration. Workwas started on a project to obtain activity co-efficients for the group IIa halates in saturated solutions, in order to calculate values for their free energies and entropies of solution. The isopiestic comparison method (42-43) was used, but due to various difficulties only a few preliminary results were obtained. However, a full description of the apparatus is given in section 4.3 and the results are presented in section 4.3.3.

1.1.4.

Entropy data for non-aqueous solutions are very scarce: the publication of Luksha and Criss (7) mentioned above, the theses of Luksha and Held (44-45), and a report published by Criss (46), contain all the published entropy data in formamide, NMF and DMF. Fortunately it is possible to extend the available data by using a correspondence principle. These principles are applicable to a wide variety of data, and their use had been reviewed by Cobble (47). The one of interest in this work is Criss's (46) observation of a linear relationship between the entropies of ion pairs in formamide and NMF and the entropies of the corresponding ion pairs in water, in the form:

$$\overline{S}^{o}_{solv.} = a + b\ \overline{S}^{o}_{water} \qquad (1.1.4,1)$$

where a, and b are constants specific for each solvent. This equation is used in section 2.4 to estimate unknown partial molal entropies in formamide and NMF, and to estimate individual ion partial molal entropies. The data thus obtained is probably only accurate to within a few entropy units, but is adequate for the arguments used in this thesis.

1.1.5

The entropies of the gaseous ions are calculable using the methods of statistical mechanics. In terms of the appropriate partition function Q, the entropy is given by the formula:

$$S = R\left[\ln Q + T\left(\frac{d\ \ln Q}{dT}\right)_V\right] \qquad (1.1.5,1)$$

For a monatomic gas the entropy is due to translational motion only, and the partition function is:

$$Q_T = \frac{(2\pi mkT)^{3/2}Ve}{h^3\ \ N} \qquad (1.1.5,2)$$

where V is the molar volume, m is the mass of one molecule. Substituting into equation 1.1.5,1, and introducing the molecular weight M:

$$S_T = R(\ln V + \frac{3}{2}\ln T + \frac{3}{2}\ln M + \frac{3}{2}\ln\frac{2\pi k}{h^2} - \frac{5}{2}\ln N + \frac{5}{2}) \qquad (1.1.5,3)$$

This equation is known as the Sackur - Tetrode equation, and it is used in section 2.3 to calculate the entropies of the main group 1 and 11 cations and the group V11b anions in the ideal gaseous state.

For polyatomic molecules vibrational and rotational contributions to the entropy have to be included. Assuming that the three types of motion make separate contribution to the total partition function, it is convenient to deal with each contribution separately. The translational contribution to the entropy is calculated using the Sackur - Tetrode equation as for monatomic gases. The rotational contribution is obtained using a simple rigid rotor model; the partition function is:

$$Q_r = \frac{(\pi I_1 I_2 I_3)^{1/2} \; (8\pi^2 \, kT)^{3/2}}{sh^3} \qquad (1.1.5,4)$$

the I's are the principle moments of inertia of the molecule, and s is the symmetry number - the number of rotational orientations that differ only in the exchange of identical particles. Substitution of equation 1.1.5,4 into equation 1.1.5,1 gives the rotational contribution to the entropy:

$$S_r = R\left[\ln \frac{(\pi I_1 I_2 I_3)^{1/2} \; (8\pi^2 \, kT)^{3/2}}{sh^3} + \frac{3}{2} \right] \qquad (1.1.5,5)$$

The vibrational contribution is obtained via the normal modes of vibration. If the frequencies of the normal vibrations are $w_1, w_2, \ldots\ldots w_n$, then, writing z_i for hw_i/kT, the partition function is:

$$Q_v = \prod_{z=1}^{w} (1 - e^{-z_i})^{-1} \qquad (1.1.5,6)$$

where the product extends over all the normal modes of vibration.

The vibrational entropy is thus:

$$S_v = R \sum_i z_i \cdot \frac{e^{-z_i}}{1 - e^{-z_i}} - \ln(1 - e^{-z_i}) \qquad (1.1.5,7)$$

The total entropy is then the sum of the translational, the vibrational and the rotational contributions. In section 2.3 the entropies of the gaseous chlorate, bromate and iodate ions are calculated, and the data obtained is used to derive solvation entropies and lattice entropies. The idea of lattice entropies (corresponding to lattice enthalpies in this work) was first introduced by Altshuller (48). Because of the publication of more modern data, and because Altshuller does not appear to include the necessary mixing and expansion entropies, a new set of lattice entropies have been calculated in section 2.7. The entropy and enthalpy data are combined to give solvation free energies (section 2.10), and lattice free energies (section 2.8); The latter function does not appear to have received any attention before.

The main interest in this thesis is in the solvation enthalpies and free energies. Part two of the introduction is concerned with the methods that have been used to interpret solvation energies.

Introduction - Part 11

1.2 The Interpretation of Ion Solvation Energies

The term energy is used in the title of this section with deliberate vagueness, as it has been pointed out by Halliwell and Nyburg, and Bockris, (49-50), in recent papers on this subject, that many authors, when dealing with solvation thermodynamics, have not specifed with which thermodynamic function they are concerned. In many cases one finds experimental free energies, say, being compared with enthalpies or changes in potential energy, or even sums of different thermodynamic functions, the term "energy" being used to cover lack of precision. Following Halliwell and Nyburg (49), care has been taken by this author to relate all energy terms discussed to the appropriate thermodynamic function whenever possible.

By the word "interpretation" is meant (a) the *a priori* calculation of ion solvation energies based on a reasonable physical model, (b) the comparison of the calculated values with experimentally determined values, and (c) employment of the agreement or disagreement between (a) and (b) to obtain information about the nature of ionic solutions. To this end it is necessary to consider first of all the structures of the pure solvents, and then, the possible effects that the introduction of ions may have on those structures,

1.2.1

Recent work on the structure of liquid water has been reviewed by Conway and by Stoughton (51-52). An earlier review by Robinson and Stokes (41) describes the more general ideas of the structure which are of interest here. It appears that liquid water must be considered to have a rather loosely 4-co-ordinated structure, intermolecular bonding being provided by hydrogen bonds. An alternative approach is to say that liquid water retains a good deal of the tetrahedral structure of ice. If this idea for the structure of water is assumed it is possible to explain (1) the high boiling point, melting point and entropy of vapourisation of water compared to similar hydrides such as ammonia, hydrogen fluoride, and hydrogen sulphide, where the degree of intermolecular association is lower; (2) the maximum in the density - temperature relationship occuring at four degrees centigrade; (3) the high molar volume of ca. 30 A^3 compared with the close-packed molar volume of 3.48 A^3.

There is also some Raman and infra-red spectroscopic evidence (53-54) which confirms these views. In contrast to this evidence, two papers by Van Eck and his co-workers on the X-ray analysis of liquid water (55-56) suggest that the co-ordination may be octahedral rather than tetrahedral.

The structures of liquid formamide and its N-methyl derivatives have not been studied with the same interest that has been applied to water. The only evidence available is the tentative interpretation of some dielectric dispersion studies by Bass (57) which suggest that NMF consists of linear chains of solvent molecules held together by hydrogen bonds between the carbonyl group and the hydrogen on the nitrogen atom. The crystal structure of solid formamide has been determined by X-ray analysis (58); it has been shown to consist of sheets of formamide molecules joined by nitrogen-carbonyl hydrogen bonds. The sheets are mutually parallel, and held together by Van der Waals forces, the distance between the sheets being 3.1A compared with the radius of the formamide molecule of about 2.6A. It seems reasonable to propose that, since the forces holding the layers of formamide molecules together are probably of the same order of magnitude as kT at room temperature, liquid formamide consists of sections of the sheets, with a good deal of two dimensional structure prevailing - this viewpoint is adopted in a later section in order to account for the magnitudes of ion solvation enthalpies. The high boiling points, dielectric constants and latent heats of evaporation of formamide and NMF (see table 1) are consistent with the molecular association required by the above models of the liquid structure.

There is no evidence available for the structure of liquid or solid DMF. Its boiling point, melting point and dielectric constant are lower than those of its two homologues, suggesting that there is less molecular association in the liquid state; in this connection the presence of the two methyl groups on the nitrogen atom precludes the possibility of carbonyl-nitrogen hydrogen bond formation. The relevant parameters used in this discussion are collected and compared in table 1.

	Water	Formamide	NMF	DMF
m.p.(°C)	0	2.55(60)	-2.74(3)	-61 (61)
b.p.(°C)	100	210.5 (61)	65 @4mm(3)	153 (61)
D	78.358(59)	109.5 (62)	171 (57)	37.2(57)
ΔH_V	10.52 (28)	14.7 (60)	-	10.97(63)

Table 1

Some physical properties of the solvents.

1.2.2

Most of the work on *structural effects of ion solvation* has been concerned with aqueous solutions. The interpretation of entropies of solvation by Frank and Evans (64) shows that even for the solution of a non-polar solute in water there is some modification to the structure of the solvent. It is to be expected, then, that a charged particle such as an ion would have a considerable effect on the structure of the solvent particularly in the immediate vicinity of the particle; and, indeed, the calculations of Frank and Evans show exactly this. As their ideas have given such a clear insight into the nature of ionic solutions, the next few paragraphs contain an outline of the methods used by Frank and Evans and of the conclusions they reached.

Comparison of the loss of entropy in the process of dissolving non-polar gases in (a) non-polar solvents, and (b) water, shows that the entropy loss is 15-35eu. greater in the case of the water solution. This means that the non-polar gases cause an increase in the structure of water in which they dissolve. Some of the data on which these conclusions are based is listed in table 2.

	ΔS_1	ΔS_2		ΔS_3	ΔS_4
He	9.6	26.5	Li^+	39.6	-1.1
Ne	9.3	28.8	Na^+	33.9	4.0
Ar	11.3	30.2	K^+	25.3	12.0
K	-	32.3	Rb^+	23.1	14.1
Xe	-	33.6	Cs^+	21.3	15.7
Rn	-	34.3			

Table 2

Entropy data on the hydration of the inert gases and the alkali metal cations. (See text for definitions)

The data are taken directly from Frank and Evan's paper, and the standard states they used are not the same as those used in the rest of this thesis: the data refer to the hypothetical unit fugacity gas phase, and the hypothetical unit mole fraction solution phase.

ΔS_1 is the loss of entropy on solution of the inert gases in benzene, ΔS_2 is the loss of entropy on solution of the inert gases in water, ΔS_3 is the loss of entropy on solution of the gaseous alkali metal cations in water. The significance of ΔS_4 will be pointed out below.

The interesting thing about these figures comes out in a comparison of ΔS_2 and ΔS_3. The entropy loss on solution of most of the alkali metal cations is significantly less than the corresponding entropy change for the inert gas with the same electronic structure. This means that the inert gases have a greater structure making effect than the cations, in spite of the structure making that occurs in primary hydration sphere (see below). Frank and Evans went further in their analysis by estimating the entropy loss ΔS_3, by what they describe as a series of guesses: these were (a) the entropy of formation of the primary hydration sphere, (b) the entropy due to the reduction of free volume of the ion, (c) the entropy due to the polarisation of the water beyond the primary hydration sphere. When the sum of these three entropy losses is subtracted from ΔS_3, the result is ΔS_4, which was attributed to the structural effect of the ion on the solvent. Except for Li^+ this term is positive, meaning that there is an increase in the disorder in the bulk of the solvent. To resolve this entropy data with the idea of a highly ordered primary solvation sphere, Frank and Evans suggested that there are three regions around an ion in aqueous solution: the highly ordered primary solvation sphere, in which the water structure is completely broken down; the bulk of the solvent; and in between these, an intermediate region in which the water structure is partially broken down. The net structural effect of an ion depends on whether the ordering effect in the primary hydration sphere is greater or less than the dis-ordering effect in the intermediate region. These ideas will be returned to in section 3.3.1, where they will be applied to help interpret the effect of ions on formamide and NMF.

A discussion of primary solvation spheres leads naturally to a consideration of hydration (solvation) numbers. Bockris (65) has suggested that the term primary solvation number should refer to "The number of solvent molecules near to an ion which have lost their translational degrees of freedom and move as one entity with the ion during its Brownian motion". Bockris has reviewed the available data (50), and his conclusions are summarised in table 3.

Ion	Li	Na	K	Rb	F	Cl
Primary Solvation Number	5 ± 1	5 ± 1	4 ± 2	3 ± 1	4 ± 1	1 ± 1

Table 3

Ion	Br	I	Mg	Ca	Ba
Primary Solvation Number	1 ± 1	1 ± 1	12 ± 1	9 ± 2	7 ± 2

Table 3 ; continued

primary hydration numbers of some ions.

It is rather hard to reconcile the very low values for the halogens with the idea of a primary hydration sphere as used by Frank and Evans (above) or with the high stabilisation energy that results from the electrical interaction of the ion with four or six solvent molecules (see section 3.3.2 and 3.3.4). However, the point will be argued out in detail in section 3.3.1, when it becomes necessary to choose values for solvation numbers.

1.2.3

The calculation of ion solvation energies

This section consists of a brief account of the more important and relevant methods that have been used to calculate ion solvation energies. The interest in discussing these methods is not so much what answers were obtained (since, until recent years, the experimental individual ion solvation energies used for comparison with calculated values seemed to be very much a matter of personal opinion - see section 1.2.4), but, in the models that were used and the assumptions that were made. Hence one can attempt to distill the better parts of all these treatments to evolve a model for ion solvation which one hopes is at least a better approximation to the truth than has been obtained previously.

One of the earliest attempts at account for ion solvation free energies was published by Born (66). Since it will be necessary to consider later how the Born equation can be modified, it is as well to give its derivation from first principles. The energy density associated with an electric field in a vacuum at a point with cartesian co-ordinates x, y, z, is given by:

$$U_{x,y,z,} = \frac{X^2_{x,y,z,}}{8\pi} \quad \text{using c.g.s. units} \qquad (1.2.3,1)$$

where $X_{x,y,z,}$ is the electric field at x,y,z,

Thus the energy in a volume element dV, the position of which is defined by a radius vector $\underline{r}$ is:

$$dU_r = \frac{X_r^2}{8\pi} dV \qquad (1.2.3,2)$$

If the field is that due to a charged sphere, then the system has spherical symmetry. The origin of co-ordinates is taken as the centre of the sphere. Thus, the volume of the sphere just containing the volume element is give by:

$$V = \frac{4}{3}\pi r^3$$

Hence: $dV = 4\pi r^2 dr$

If q is the charge on the sphere then,

$$X_r = \frac{q}{r^2}$$

Substituting into equation 1.2.3,2

$$dU = \frac{q^2}{2r^2}\,dr \qquad (1.2.3,3)$$

The total energy of the field due to the charged sphere is obtained by integrating equation 1.2.3,3 from the surface of the sphere to infinity

$$U = \frac{q^2}{2}\int_a^{\infty} \frac{1}{r^2}\,dr = \frac{q^2}{2a} \qquad (1.2.3,4)$$

If the sphere is immersed in a medium of dielectric constant D, then the energy becomes

$$U = \frac{q^2}{2aD} \qquad (1.2.3,5)$$

Born considered the process of ion hydration to consist of the removal of the ion (considered as a charged sphere) from the gas phase to the aqueous phase - the energy change being due to the change of dielectric constant. Since the energy change in the process described (considered to occur isothermally) corresponds to the maximum work obtainable from the system, the energy change must be a free energy change. Born's equation is obtained as the difference between equations 1.2.3,5 and 1.2.3,4 for a mole of ions:

$$G = -\frac{Nz^2e^2}{2r}\left(1 - \frac{1}{D}\right) \qquad (1.2.3,6)$$

Here, z is the valency of the ion.

Since the equation takes no account of the structural features of ion solutions, it can not be expected to give values in very good agreement with experimental values. There are two other objections to the use of this equation: (a) the dielectric constant of the solvent may be modified by the high electric field in the vicinity of the ion (several million volts per cm 10 A away from an ion of radius 1A); (b) it is difficult to assign a value to the radius of an ion in solution, and whatever value is chosen may well be different from the radius in the gas phase. The original use of the Born equation involved the crystal radii and the normal or macroscopic dielectric constant of water - the values thus obtained were numerically higher than the experimental values, by 30 to 100% for monovalent cations, with even greater discrepancies for higher valency ions.

Although the Born equation gives such a poor fit to the experimental data, it is of immense interest because the values obtained are of the right order of magnitude: this shows the essentially electrostatic nature of the ion solvent interactions. It also predicts a linear relationship between free energies of solvation and the reciprocal crystal radius, which is found experimentally for anions, and which is found to be of use in dividing ion-pair solvation energies into the individual ionic contributions (see section 2.11)

Differentiation of 1.2.3,6 with respect to temperature gives the electrostatic contribution to the entropy of solvation. The result has been recombined with the original equation to give the Born-Bjerrum equation (67) for the enthalpy of solvation:

$$\Delta H_{solv} = -\frac{Nz^2e^2}{2r}\left[1 - \frac{1}{D} - \frac{T}{D^2}\left(\frac{\partial D}{\partial T}\right)_p\right] \qquad (1.2.3,7)$$

Many of the calculations of solvation energies that have appeared in the literature have been based on modification of the Born equation. The empirical alteration of the radii of the ions to obtain a better fit from the Born equation by Latimer, Pitzer and Slansky (68) will be discussed in detail in section 1.2.4. A recent paper by Stokes is of interest in the connection (69). Stokes suggests that the radii of the ions in the gas phase should be the Van der Waals radii rather than the crystal radii; and he calculates the Van der Waals radii from the interatomic distances in the corresponding inert gas crystals using the quantum mechanical scaling principle. The values obtained for the Van der Waals radii are 20 - 40% greater than the crystal radii. In the solution phase, the ion is considered to be surrounded by a layer in which the dielectric constant changes from the value 5 at the surface of the ion to the macroscopic value at the boundary of the layer. Outside the layer the solvent is assumed to have its

Normal dielectric properties. The appropriate expression for the energy due to the field of the ion in the aqueous phase (the electrostatic partial molal free energy) is obtained by integrating equation 1.2.3,3 over the two regions:

$$\mu^{elec} = \frac{q^2}{2}\left[\int_a^{a+b}\frac{1}{r^2}\frac{dr}{D^1} + \int_{a+b}^{\infty}\frac{1}{r^2}\frac{dr}{D}\right]$$

$$= \frac{q^2}{2}\left\{\left[-\frac{1}{r}\right]_a^{a+b}\frac{1}{D^1} + \left[\frac{-1}{r}\right]_{a+b}^{\infty}\frac{1}{D}\right\} \qquad (1.2.3,8)$$

D^1 is the dielectric constant in the primary sphere; a is the radius of the ion; (a+b) is the radius of the primary sphere; D is the macroscopic dielectric constant. On rearrangement,

$$\mu^{elec} = \frac{q^2}{2}\left[\frac{b}{a(a+b)D^1} + \frac{1}{(a+b)D}\right] \qquad (1.2.3,9)$$

a is taken as the Pauling crystal radius, r_p; D^1 has the mean value of 9; b is taken as zero for monovalent anions, the diameter of the water molecule, d_w, for monovalent anions, or twice the diameter of the water molecule for divalent and trivalent cations. Hence, for one mole of ions:

$$\mu^{elec} = \frac{N z^2 e^2}{2}\left[\frac{nd_w}{r_p\left(r_p+nd_w\right)9} + \frac{1}{\left(r_p+nd_w\right)D}\right] \qquad (1.2.3,10)$$

From this must be subtracted the electrostatic free energy of the gaseous ions calculated using equation 1.2.3,4. The values Stokes obtained were shown to compare very well with experimental values: the average deviation was 1.5% for the cations, but 2 - 13% for the anions. The choice of experimental data for comparison was particularly fortunate, since it is shown in section 3.1, where Stoke's method is applied to non-aqueous solvents, that nothing like so good a fit is obtained with the data derived in this work.

The possibility of variation of the solvent dielectric constant in the intense field near an ion was considered by Laidler and Pegis (70). Their treatment was based on the Born equation, using crystal radii multiplied by the factor 1.25, and taking account of possible dielectric saturation effects calculated from a theoretical equation developed by Booth (71). Agreement between experiment and theory was rather better than that given by the simple Born equation, both for free energies and entropies. The division of ion-pair solvation free energies into the individual ionic contributions was made on an arbitrary choice of a single ion value to give the best fit for the theoretical data: it is shown in section 1.2.4 that this arbitrary choice is about 30 kcals different from the values chosen by most other workers in this field.

It has been noted by Conway in a recent review on the subject (51) that "At the present time (1966), continuum theories of ionic hydration based on the Born equation have reached an asymptotic limit of usefulness or applicability." Considering the rather poor results that are obtained in an attempt to apply a modified form of the Born equation to non-aqueous solvents in section 3.1, this author would agree entirely. It is more fruitful to consider the more important and fundamental theories of ion solvation that deal with the details of ion solvent interactions. Two important early papers by Bernal and Fowler and Eley and Evans (72-73) serve as the basis for the interpretation used in this thesis. As the work of the former two authors has been shown by Bockris (50) to contain a number of errors, attention will be turned to the work of Eley and Evans. These authors assumed a tetrahedral ice - like structure for water, and a co-ordination number of four for the monovalent ions. They used a cyclic process to calculate the solvation energies, consisting of the following five steps:

(a) A tetrahedral group of five water molecules is eveporated from the liquid to the gas phase, leaving a cavity in the liquid.

(b) This tetrahedral group in the gas phase is dissociated into five separate water molecules.

(c) Four of these five water molecules are co-ordinated around the gaseous ion under consideration.

(d) The ion solvent complex thus formed is returned to the cavity left in the bulk of the solvent.

(e) The single remaining gaseous water molecule is recondensed to the liquid phase.

The largest contribution to the solvation energy comes from process (c): Eley and Evans considered this to be the electrostatic interaction energy between the ion and four solvent molecules, taking the water molecule to be a sphere with its centre at the centre of the oxygen atom. The interaction energy is:

$$\sum_{i}^{4} \frac{Ze\,\alpha_i e}{r_i}$$

where $\alpha_i e$ is the fractional charge on each atom of the molecule. ($\alpha = 0.49$ for the hydrogen, and 0.98 for the oxygen). Account was taken of the possibility of different orientations of water molecules near anions and cations. Ion solvent repulsion and dispersion forces were neglected as was the solvent - solvent interaction energy in the primary hydration sphere. The energy change in process (b) was calculated electrostatically using the same method as in (c). The difference between energy changes (a) and (b) was calculated as the energy needed to reorientate the water molecules in the immediate vicinity of the ion (no details were given) together with the polarisation energy of the solvent outside the primary hydration sphere, calculated using the Born equation. Process (e) was taken as the heat (enthalpy) of condensation of water. The sum of these five processes was taken as the solvation energy. It is interesting to note that process (d) involves a free energy change, (the Born polarisation term), processes (a) and (e) are enthalpy changes, and the remaining processes are changes in electrostatic potential energy. The total change was considered to be the enthalpy of solvation. There may be some justification for this, but the authors did not show it. The results obtained were rather inconsistent: for example, it is possible to use their results to calculate the solvation enthalpy of the proton by combining each calculated individual ion value with the corresponding conventional value: if the calculated values are self-consistent, then the values for the solvation enthalpy of the proton should all be equal - Eley and Evans' data give values over a range of 25 kcals per mole.

Eley and Evans' cyclic argument has been used in a modernised form in a recent publication by Muirhead-Gold and Laidler (74). The steps in the cycle were essentially the same, but there were some important differences in the methods of calculation. A co-ordination number of six was assumed; thus, process (a) was six times the heat of evaporation of water. The electrostatic interaction energy (c) was calculated using a computerised technique that took account of all possible interactions: dispersion and repulsion forces were included. The model used for the water molecule was a system consisting of three point charges and a polarisable dipole. Process (d) was taken as equal to the enthalpy of formation of 0.448 x 12 out of the twelve possible hydrogen bonds between the molecules in the primary hydration sphere and the rest of the solvent, plus the Born polarisation energy. Processes (e) and (b) were not included. Some more details are given in section 3.3.3.

The calculation of the electrostatic contribution to ion solvent interactions has been placed on a rigorous footing by Buckingham. (75). Buckingham's treatment depends on a rather lengthy mathematical analysis, so only his conclusions are given here. However, since many of the calculations in this thesis are based on Buckingham's work, the theory is developed from first principles in Appendix I.

Buckingham suggested that a polar molecule such as water may be thought of as an array of point charges. Such an array can be shown to have a dipole moment, a quadrupole moment, an octupole moment, and so on. It is possible to calculate the energy of interaction of an ion (considered as a polarisable sphere) with the multipole moments of a number of water molecules. The difficulty with the practical application of this idea is that there ~~is~~ are not ~~much~~ many numerical data available for multipole moments. Dipole moments are well known for most common molecules, but it is usually necessary to estimate quadrupole and higher moments (see below). Fortunately, moments higher than quadrupole moments make only very small contributions to ion-solvent interactions (because they involve high-power reciprocal radius terms), and consequently, they may be neglected.

Buckingham assumed that the water molecule has a charge distribution which is symmetrical about the dipole moment axis - thus the water molecule could be reresented by a single dipole moment and a single principal quadrupole moment. He further assumed that the solvent dipole moment vector is normal to the ion surface, and that the co-ordination is tetrahedral. The elecrostatic interaction energy for a single ion is thus:

$$U_e = - \frac{|Z| e \mu}{R^2} + \frac{Z e \theta}{R^3} \; .... \qquad (1.2.3,11)$$

where θ is the principal quadrupole moment, and R is the distance between the centre of the ion and the centre of the water molecule. In the symmetrical model used the net multipole moments induced in the ion itself are zero, but the field of the ion will induce a series of multipole moments in the solvent molecules.

Due to lack of data it is only possible to take the induced dipole moment into account (the leading term in a relatively small amount of energy) and this gives rise to an energy:

$$U_i = - \frac{(Ze)^2 \alpha}{2R^4} \qquad (1.2.3,12)$$

where α is the polarisability of the solvent.

The dispersion energy was calculated from the equation:

$$U_d = - \frac{3I_1\ I_2}{2(I_1+I_2)} \frac{\alpha_1 \alpha_2}{R^6} \qquad (1.2.3,13)$$

where the I's are the ionisation potentials of the ion and the solvent.

Repulsion energies were ignored. The mutual interaction energy between the four co-ordinated solvent molecules was calculated from the expression:

$$U_m = \frac{15}{8}\sqrt{\frac{3}{2}}\ \frac{\mu^2}{R^3} - \frac{135}{32}\sqrt{\frac{2}{3}}\ \frac{Z\mu\theta}{|Z|R^4} - \frac{675}{256}\ \frac{\alpha\mu^2}{R^6} - \frac{243}{1024}\ \frac{\alpha^2 I}{R^6} \qquad (1.2.3,14)$$

In order the terms are : dipole - dipole; dipole - quadrupole: interactions between dipoles induced by the field due to the permanent solvent dipoles; dispersion energy. Buckingham neglected to include quadrupole - quadrupole interaction term $(1/r^5)$, and he took no account of the screening effect the ion might have on the mutual interaction energy terms.

To the sum of all these potential energy terms Buckingham added a Born polarisation enthalpy, included the latent heat of evaporation of water (the emergy required to make a hole in the solvent to put the ion in) and compared the result with experimental ion hydration enthalpies. Since no account was taken of possible reorientation effects in the solvent, it is not surprising that Buckingham's answers were about 10-20% too high and show even more internal inconsistency than those of Eley and Evans. It is shown in section 3.3.3 - 3.3.6 that when the appropriate re-orientations are accounted for the agreement between experiment and theory is much improved.

One of the interesting points about Buckingham's theory is the way it can account for the surprisingly large differences in solvation enthalpy between anions and cations of the same size: nearly 50 kcals per mole for K^+ and F^- as an example. The theoretical reasons for this are the ion-quadrupole interaction term and the dipole-quadrupole interaction term. All the other terms in Buckingham's theory change sign when the sign of the charge on the ion changes sign. Thus, these two terms increase the magnitude of the hydration enthalpy of cations, but decrease the magnitude of the anion hydration enthalpy. The difference between the hydration enthalpies of an anion and a cation of the same size is given by Buckingham's theory as:

$$\Delta H^- - \Delta H^+ = -\frac{8|Z|e\theta}{R^3} + \frac{135}{16}\sqrt{\frac{2}{3}}\,\frac{\mu\theta}{R^4} \qquad (1.2.3,15)$$

It is thus possible to use the difference in solvation enthalpy between cations and anions of the same size to estimate a value for the solvent quadrupole moment.

Somsen (4) has applied these ideas to the calculation of solvation enthalpies in non-aqueous solvents. His work, too, suffers from a mixing of thermodynamic parameters, and he made no attempt to take account of solvent re-orientation effects. In spite of this, he obtained a very good fit to his experimental data.

1.2.4.

The division of solvation energies into the individual ionic contributions

One of the difficulties of dealing with ion solvation phenomena is that theoretical calculations give individual ion solvation energies while experiments give ion pair values. Thus, one is faced with the problem of dividing the ion pair values into the individual ionic contributions so that a proper comparison with theory can be made. Although much of the work that has been done on this problem has been of an empirical or semi-empirical nature, it will be shown in the summary at the end of this section that there is a surprising agreement between the main contributors in this field.

Latimer, Pitzer and Slansky's method of division (68) depends on an empirical relationship between the relative ion solvation energies of the group la cations (relative to Cs^+) and the halides (relative to I^-) to their respective effective radii. The effective radii were obtained by adding constants to the Pauling crystal radii - 0.1A for the anions, 0.85A for the cations. The numbers being chosen to give the best straight lines. The authors give some justification for their choice of constants by saying that (a) the effective radius of an ion in aqueous solution is the distance between the centre of the ion and the centre of the dipoles of the water molecules in the primary hydration sphere, (b) for anions the hydrogens of the co-ordinating waters are directed towards the ion, but for the cations the oxygen is directed towards the ion. Hence, the effective radius is larger for cations than for anions. Using these effective radii, the solvation free energy of CsI is divided between the ions so that the values obtained are equal to those predicted by the Born equation. Solvation entropies are divided in a similar manner, and the free energies and entropies thus obtained are combined to give solvation enthalpies. It has been argued (76) that such modifications to the cryatal radii are probably not justifiable.

Verwey (77) made use of the relationship between solvation free energies and the reciprocal crystal radius predicted by the Born equation. He plotted a graph of cation hydration free energy (relative to Li^+) and a graph of anion hydration free energy (relative to F^-) both as a function of the reciprocal crystal radius. ie:

$$\Delta G^-_{hyd} - \Delta G_{hyd}(F^-) = \frac{A}{r^-}$$

$$\Delta G^+_{hyd} - \Delta G_{hyd}(Li^+) = \frac{B}{r^+} \qquad (1.2.4,1)$$

Extrapolation to infinite radius gave the absolute values of the solvation free energies of the lithium and fluoride ions.

A similar technique has been applied by Somsen (4) to data in non-aqueous solvents. He plotted the solvation enthalpies of a series of halides of the same cation against the reciprocal of the anion crystal radius Extrapolation of the resulting straight line to infinite radius gave the cation solvation enthalpy. Somsen showed in a later publication that his extrapolation gave values within about six kcals per mole of his "absolute" values (5).

The most striking thing about these extrapolation methods is their internal self-consistency, which is nearly always as good as the accuracy of the extrapolation. Accurate extrapolation is usually difficult however, because of the length of the extrapolation and the deviations of the graphs from linearity. In section 2.11 a method is introduced which shows the same good internal consistence, yet give a very definite extrapolation.

The latest way of determining individual ion solvation enthalpies is based on Buckingham's theory (75) and was published by Halliwell and Nyburg (49). The definitions of conventional ion solvation enthalpies are:

$$\Delta H_c\,(X^{z-}) = \Delta H(X^{z-}) + z\Delta H(H^+) \qquad (1.2.4,2)$$

and

$$\Delta H_c\,(M^{z+}) = \Delta H(M^{z+}) - z\Delta H(H^+) \qquad (1.2.4,3)$$

where the unmarked enthalpies refer to absolute values. Subtracting equations (1.2.4,2) and (1.2.4,3):

$$\Delta H_c\,(M^{z+}) - \Delta H_c(X^{z-}) = \Delta H(M^{z+}) - \Delta H(X^{z-}) - 2Z\,\Delta H(H^+) \qquad (1.2.4,4)$$

According to Buckingham (75) the difference between the absolute solvation enthalpies of anions and cations of the same size is given by an equation of the form:

$$\Delta\cdot\Delta H = \frac{A}{R^3} + \frac{B}{R^4} \qquad (1.2.4,5)$$

Thus, from equation 1.2.4,4, for ions of the same size:

$$\frac{\Delta\cdot\Delta H_c}{Z} = A/R^3 + B/R^4 - 2\Delta H(H^+) \qquad (1.2.4,6)$$

Halliwell and Nyburg neglected the small term in R^4 and plotted a graph of the left hand side of this equation against $1/R^3$. The resulting curve was extrapolated to infinite radius, where the intercept gave twice the absolute hydration enthalpy of the proton. The data for the differences between the hydration enthalpies of ions of opposite charge and the same size was obtained from plots of anion and cation solvation enthalpies (conventional) versus $1/r^3$ drawn on the same graph. Values of $\Delta \cdot \Delta H_c$ were interpolated at various hypothetical ionic radii.

This method has been critisized by Conway and Salomon (78). Their main critisism was about Buckingham's assumption that the solvent molecule dipole moment vector is always normal to the ion surface - they suggested that the orientation of the vector would be different for anions than for cations, as in Eley and Evan's treatment (73). It is argued later, section 3.3.1, that Buckingham's assumption is justifiable.

A practical difficulty with Halliwell and Nyburg's technique is the length the extrapolation needs to be made, (see the graphs in section 3.2). The authors overcame this to a certain extent by using estimated data for some large ions such as tetramethylammonium Unfortunately such data is not available for non-aqueous solvents.

Somsen has applied this method in a slightly modified form (5) to obtain absolute solvation enthalpies in non-aqueous solvents. Although the method is not used directly in this thesis, it will be shown (section

3.2 that the data obtained is entirely consistent with it.

Halliwell and Nyburg took great care to show that the theory they used was applicable to enthalpies and not potential energies as was the case with Buckingham's original work.

In order to make a rapid comparison between the various determinations of individual ion solvation enthalpies that have been made, values for the hydration enthalpy of the proton were derived and are summarised in chronological order in table 4. In principle, at least, the a priori calculations of solvation energies discussed in section 1.2.3 could also be considered to give values for individual ion solvation energies. However, the internal inconsistencies of such data are usually so large as to render them practically worthless.

Author(s)	Date	Value	Reference
Fajans	1919	262	179
Latimer, Pitzer & Slansky	1939	259	68
Verwey	1940	258	77
Mischenko	1952	264	80
Oshida & Horiguchi	1955	267	81
Halliwell & Nyburg	1963	261	49
Noyes	1964	267	82
Somsen	1966	258	5
This work		257	

Table 4 : Proton Hydration Enthalpies

The mean of the values in table 4 is 261 ± 6 kcals per mole. Laidler and Pegis' arbitrary choice, (70, see section 1.2.3.) of 292 for the proton hydration enthalpy seems rather high considering the figures listed in table 4.

The determination of individual ion partial molal entropies, and thence, individual ion solvation entropies has been reviewed by Bockris (50). There appears to be a distinct possibility of obtaining a definite experimental value for the absolute partial molal entropy of the hydrogen ion using a thermocell. Values obtained so far are in the range minus 4.7 to minus 6.3. The latest determination (83) has given a value of minus 5.5, in agreement with Gurney's semi-empirical value obtained from viscocity measurements (84). Partial molal entropy data in aqueous solutions used in this thesis have been based on this latest value for the partial molal entropy of the aqueous hydrogen ion.

SECTION II

Results

The fundamental physical constants used in the calculation of the data presented in this section are those adopted by the U.S. National Bureau of Standards in October 1963. The derived constants are taken from a publication by Cohen, Crowe and Dumond (85). The atomic weights used were on the chemical scale based on the carbon twelve isotope.

All numerical enthalpy and free energy data are given in kcals per mole unless otherwise stated, and all entropy data are given in calories per degree per mole.

Errors are quoted as the standard deviation of a single observation from the mean, except for the data on the group 11a halates and fluorides, where twice the standard deviation is quoted.

The standard states adopted are : (a) solution phase. Enthalpies - infinitely dilute solution; entropies and free energies - hypothetical unit activity. (b) Gas phase - ideal gas at unit molality. All at 298.15^{o}K. The gas entropy data is also given for the more usual unit fugacity standard state - the distinction is carefully made in the text.

2.1.

Standard enthalpies of formation

The conventional partial molal enthalpies of the aqueous alkali metal and halide ions are listed in table 5

Li^+	-66.56	F^-	-80.20	(30)
Na^+	-57.47	Cl^-	-39.95	(31)
K^+	-60.30	Br^-	-29.11	(32)
Rb^+	-60.01	I^-	-13.79	(33)
Cs^+	-61.69			

Table 5 : Conventional partial molal enthalpies of the alkali metal and halide ions.

The cation data are taken from a recent paper by Gunn (29) The anion data are from the sources indicated in the table, with dilution data from the revised version of NBS 500 (31). Sums of these data for ion-pairs were combined with the relavent standard enthalpies of solution taken from Parker's compilation (34) of selected values, to give the required standard enthalpies of formation. Table 6 gives the results obtained; the standard enthalpies of solution are shown in parentheses.

LiF (1.130) -147.9	NaF (0.218 -137.9
LiCl (-8.850) -97.66	NaCl (0.928) -98.35
LiBr (-11.670) -83.99	NaBr (-0.144) -86.43
LiI (-15.130) -65.22	NaI (-1.800) -69.46
KF (-4.238) -136.3	RbF (-6.240) -134.0
KCl (4.115) -104.37	RbCl (4.130) -104.09
KBr (4.750) -94.16	RbBr (5.230) -94.35
KI (4.860) -78.96	RbI (6.000) -79.81

Table 6

(continued overleaf)

CsF	(-8.810) -133.1
CsCl	(4.250) -105.89
CsBr	(6.210) -97.01
CsI	(7.970) -83.46

Table 6 : Standard enthalpies of formation of alkali metal halides. Standard enthalpies of solution in parentheses.

The largest uncertainties in these data are in the partial molal enthalpies : a few parts in the second decimal place or smaller.

The next two tables (7,8) give the data for a similar treatment to obtain the standard enthalpies of formation of the group 11a halides. The partial molal enthalpies of the aqueous cation were derived from the heats of solution of the metals in hydrochloric acid published by Ehrlich, Peik and Koch (35)

$$M(c) + 2HCl(aq) = MCl_2(aq) + H_2(g)$$

Hence,

$$\Delta H_f^o\ MCl_2(aq) = \Delta H_{obs} + 2\ \Delta H_f^o\ HCl(aq)$$

and

$$\Delta H_f^o\ M^+\ (aq.\ conventional) = \Delta H_{obs}.$$

The necessary dilution data, the enthalpy of solution of magnesium chloride and the enthalpy of solution of magnesium in hydrochloric acid were taken from NBS 500. Most of the remaining enthalpies of solution were included in Ehrlich, Peik and Koch's paper, and these were used with the exception of the value for barium chloride which came from a more recent paper by Vorov'ew (86).

Mg^{2+}	-110.7
Ca^{2+}	-130.5
Sr^{2+}	-130.3
Ba^{2+}	-128.7

Table 7 : Conventional aqueous partial molal enthalpies of the alkaline earth cations.

MgF_2	(-2.0)	-269.1±0.3	CaF_2	(1.69)	-292.6±0.3
$MgCl_2$	(-37.1)	-153.6±0.1	$CaCl_2$	(-19.3)	-191.1
$MgBr_2$	(-43.3)	-125.8±0.3	$CaBr_2$	(-24.6)	-164.1
MgI_2	(-49.9)	-88.5±0.2	CaI_2	(-29.2)	-128.9
SrF_2	(0.4)	-291.1±0.3	BaF_2	(0.7)	-289.8±0.3
$SrCl_2$	(-12.1)	-198.1	$BaCl_2$	(-3.1)	-205.5±0.2
$SrBr_2$	(-16.8)	-171.7	$BaBr_2$	(-5.6)	-181.3
SrI_2	(-23.2)	-134.7	BaI_2	(-10.8)	-145.5

Table 8: Standard enthalpies of formation (and enthalpies of solution) of the alkaline earth halides.

Unless indicated otherwise, the uncertainties in the standard enthalpy of formation data are ± 0.4. The standard enthalpies of solution of all the main group 11 fluorides, and of magnesium bromide and iodide in water were determined by this author; those of the first named salts by measuring the enthalpy of precipitation from aqueous solution - details are given below. He also made an independent check on the aqueous partial molal enthalpies of magnesium, bromide and iodide, using the reaction:

$$MgO(c) + 2HX(aq) = MgX_2(aq) + H_2O(l)$$

The ancillary data used were: ΔH_f^o $H_2O(l)$. -68.32 (31); ΔH_f^o MgO(c), -143.7 ± 0.3 (87); ΔH_f^o HX(aq) as in table 5 above: dilution enthalpies from NBS 500 (or the revised version when available). The results obtained were:

$$\Delta H_f^o \; MgBr_2(aq) = -168.7 \pm 0.3$$
$$\Delta H_f^o \; MgI_2\;(aq) = -138.1 \pm 0.3$$

These compare very well with the sums of the conventional partial molal enthalpies: 169.1 ± 0.1 and 138.4 ± 0.1 respectively.

For some of the group 11a iodides there is no heat of dilution data available - in the above derivations the values for the corresponding bromides were substituted.

The standard enthalpy of solution of <u>Calcium fluoride</u> was determined by studying the enthalpy change in the reaction between crystalline calcium chloride and excess aqueous sodium fluoride saturated with calcium fluoride. The following notation is used:

$$\Delta H_f\;(MX,\; m_1,\; m_2,\; m_3,\; m_4,\; \ldots\ldots\ldots m_n)$$

means the enthalpy of formation of MX solution of molality m_1 in the presence of (n - 1) other salts of molalities m_2, m_3, m_4, ... m_n. Heats of dilution are expressed in the form ΔH_d (MX, $m_1 \longrightarrow 0$); this means the enthalpy of dilution of MX from molality m_1 to infinite dilution. The suffixes used are: 1, the initial sodium fluoride concentration; 2, the initial calcium fluoride; 3, the excess NaF; 4, the sodium chloride concentration.

$$\Delta H_{obs} = 2\Delta H_f(\mathrm{NaCl}\ m_4;\ M_2,\ m_3) + \Delta H_f^o\ \mathrm{CaF_2(c)} - \Delta H_f\ (\mathrm{NaF},\ m_1;\ m_2) - \Delta H_f^o\ (\mathrm{CaCl_2(c)}) \qquad (2.1,1)$$

Assuming that (a) the solubility of the calcium fluoride stays the same throughout the reaction (ie. is independent of the ionic environment and the temperature over the range of the experiment - ca. 0.5°C) (b) the calcium fluoride precipitates in its standard state; and, using the following approximations:

$$\Delta H_f\ (\mathrm{NaCl},\ m_4;\ m_2,\ m_3) = \Delta H_f\ (\mathrm{NaCl},\ m_4;\ 0,\ 0) = \Delta H_f^o\ (\mathrm{NaCl},\ 0;\ 0,\ 0) - \Delta H_d\ (\mathrm{NaCl},\ m_4 \longrightarrow 0)$$

$$\Delta H_f\ (\mathrm{NaF},\ m_1;\ m_2) = \Delta H_f\ (\mathrm{NaF},\ m_1;\ 0) = \Delta H_f^o\ (\mathrm{NaF},\ 0;\ 0) - \Delta H_d\ (\mathrm{NaF},\ m_1 \longrightarrow 0)$$

and the identity:

$$\Delta H_f^o\ \mathrm{CaCl_2(c)} = \Delta H_f^o\ (\mathrm{CaCl_2},\ 0) - \Delta H_s^o\ (\mathrm{CaCl_2})$$

in equation (2.1,1)

$$\Delta H_{obs} = -\Delta H_s^o\ (\mathrm{CaF_2}) + \Delta H_s^o\ (\mathrm{CaCl_2}) - 2\Delta H_d\ (\mathrm{NaCl},\ m_4 \rightarrow 0) + 2\Delta H_d(\mathrm{NaF},\ m_1 \longrightarrow 0)$$

The dilution enthalpies were taken from Parker's compilation (34), and the standard enthalpies of formation have all been given in tables 6 and 8. The experimental measurements are listed in Appendix II, and the mean value for the standard enthalpy of solution of calcium fluoride is included in table 8.

The remaining group lla fluorides are all more soluble than calcium fluoride (MgF_2 0.130; CaF_2 0.016; SrF_2 0.119; BaF_2 1.614 g/litre at 25°C, 89) and attempts to treat them in the same manner as CaF_2 gave rise to marked pre-reaction precipitation. The reaction studied was the solution of crystalline sodium fluoride in aqueous alkaline earth halide solution (molality m_5) making the appropriate correction for the small amount of fluoride that was not precipitated (m_8). Writing the excess molality of MCl_2 as m_6, and the molality of the NaCl as m_7, then

$$\Delta H_{obs} = 2\Delta H_f \text{ (NaCl, } m_7\text{; } m_6\text{, } m_8) + (1 - x)H_f(MF_2, m_8; m_6, m_7) + x\Delta H_f^o \text{ }(MF_2, c) - 2\Delta H_f^o \text{ (NaF, c)} - \Delta H_f \text{ }(MCl_2, m_5) \qquad (2.1,2)$$

The following approximations were used:

$$\Delta H_f \text{ (NaCl, } m_7\text{; } m_6\text{, } m_8) = \Delta H_f \text{ (NaCl, } m_7\text{; 0, 0)}$$
$$= \Delta H_f^o \text{ (NaCl, 0; 0, 0)} - \Delta H_d \text{ (NaCl, } m_7 \longrightarrow 0)$$

where x is the fraction of the fluoride precipitated.

$$\Delta H_f \text{ }(MF_2, m_8; m_6, m_7) = \Delta H_f \text{ }(MF_2, m_8; 0, 0)$$
$$= \Delta H_f^o \text{ }(MF_2, 0; 0, 0) - \Delta H_d \text{ }(MF_2, m_8 \longrightarrow 0);$$

together with the identities:

$$\Delta H_f\ (MCl_2,\ m_5) = \Delta H_f^o\ (MCl_2,\ 0) - \Delta H_d\ (MCl_2,\ m_5 \longrightarrow 0)$$

and

$$\Delta H_f^o\ (NaF,\ c) = \Delta H_f^o\ (NaF,\ 0) - \Delta H_s^o\ (NaF)$$

equation 2.1,2 becomes:

$$\Delta H_{obs} = -x\,\Delta H_s^o\ (MF_2) + 2\,\Delta H_s^o\ (NaF) - 2\,\Delta H_d\ (NaCl,\ m_7 \longrightarrow 0) + \Delta H_d\ (MCl_2,\ m_5 \longrightarrow 0) + (1 - x)\,\Delta H_d\ (MF_2,\ m_8 \longrightarrow 0)$$

The solubilities of the group 11a fluorides in the calorimetric fluid were assumed to be the same as their aqueous solubilities (the common ion concentration was very small since the precipitant, MCl_2 was present in a very small excess). The same assumptions with regard to standard states and the temperature effect on solubility were made as for CaF_2. The heats of dilution of NaF and NaCl came from Parker (34), and that of MCl_2 from NBS 500 (28). The small term $\Delta H_d\ (MF_2,\ m_8 \longrightarrow 0)$ was neglected. The standard enthalpy of solution of sodium fluoride was given in table 6.

The mean values for the enthalpies of solution are given in table 8, and the detailed experimental results in Appendix II.

The standard enthalpy of formation of <u>magnesium fluoride</u> has recently been determined directly (88) by measuring the enthalpy of combustion of magnesium metal in fluorine; the result, -268.7 ± 0.3, is in good agreement with the value derived in table 8.

2.2

Most of the crystal entropies used in the later calculations are taken from NBS 500. There are, however, some more recent values. These are: NaBr - 20.71, NaI - 23.58, (90); $BaCl_2$ - 29.56 (91); Ca, Sr, Ba iodates, respectively 34.80, 50.80, 57.10 (92). It was necessary to estimate all the other entropy data required. The data for use in equation 1.1.3,3, together with the free energies of solution obtained, and the data sources are listed in table 9.

Salt	Saturation Molality	$\gamma_{\pm}$	ΔG_s^o	Ref.
$LiBr_2.2H_2O$	19.60	485.0	-10.88	41
$LiCl.H_2O$	19.97	62.4	- 8.45	41
RbCl	7.78	0.583	- 1.83	95
CsCl	11.40	0.516	- 1.57	94
RbI	7.63	0.500	- 1.59	93

Table 9 : Parameters for the calculation of free energies of solution.

The free energies of solution were combined with the partial molal free energies of the ions, from NBS 500, to give the free energies of the crystals. Combination of these with the standard enthalpies of formation of the crystals gave the entropies of formation (from the elements) of the crystals which, together with the entropies of the appropriate elements yielded the absolute entropies of the crystals - this is summarised in table 10. Also included are some entropies derived from Ionin's paper (40) see introduction, section 1.1.3.) assuming that each molecule of water makes a contribution of 9.5 ± 1.2 to the total entropy of a hydrated crystal (see Latimer, 39, who chose a slightly different value). The final column contains values from Latimer's book (39).

The values obtained agree quite well with the established values in some cases, but the discrepancy is very large in others. Reasons for this have been suggested in section 1.1.3. Because they fit better into the already established trends in the lattice entropy data (48) Latimer's estimates are used in later sections when no experimental C_p data are available.

2.3

The entropies of the gaseous monatomic ions calculated from the Sackur - Tetrode equation are listed in table 11. Using the usual standard state of an ideal gas at unit fugacity and 298.15°K, equation 1.1.5,3 takes the simple form:

$$S_t = R\left(\frac{3}{2}\ln M + 14.2439\right) - 2.3143 \qquad (2.3,1)$$

When considering solvation effects it is more appropriate to use a standard state corresponding to that used for the solution phase, ie. one mole of ideal gas per litre. The difference between the two standard states is the entropy change in the compression of one mole

	ΔG_f^o (c)	ΔH_f^o (c)	ΔS_f (c)	ΣS (el.)	S^o(c)	S^o(c)(Latimer)
$LiCl. H_2O$	-149.81	-170.31	- 68.75	89.06	20.31	24.8
$LiBr. 2H_2O$	-197.29	-229.94	-109.5	136.33	26.82	(35.5)
RbCl	- 96.98	-102.91	- 19.91	43.24	23.34	(22.6)
CsCl	- 86.66	-103.5	- 56.48	46.44	10.04	(23.3)
RbI	- 78.21	- 78.5	- 0.96	30.55	29.59	28.21
$MgCl_2$	-	-	-	-	20.86	21.4
$MgBr_2$	-	-	-	-	25.17	(29.4)
$CaCl_2$ (ex.$6H_2O$)	-	-	-	-	11.10	27.2
$CaCl_2$ (ex.$4H_2O$)	-	-	-	-	12.81	27.2
$CaBr_2$	-	-	-	-	15.83	31.0
$SrCl_2$	-	-	-	-	26.73	28.0

Table 10 : Derivation of crystal entropies

(estimates in parentheses)

Ion	Unit fugacity s.s.	Unit volume s.s.
Li^+	31.7656	25.4127
Na^+	35.3360	28.9831
K^+	36.9194	30.5665
Rb^+	39.2504	32.8975
Cs^+	40.5667	34.2138
Be^{2+}	32.5444	26.1915
Mg^{2+}	35.5019	29.1490
Ca^{2+}	36.9935	30.6406
Sr^{2+}	39.3243	32.9714
Ba^{2+}	40.6635	34.3106
F^-	34.7684	28.4155
Cl^-	36.6296	30.2740
Br^-	39.0497	32.6968
I^-	40.4286	34.0757

Table 11 : Entropies of gaseous monatomic ions.

of the gas from 24.45 litres to one litre, which is R ln 24.45 = 6.3529. Entropies in both standard states are given in table 11.

In order to apply equations 1.1.5,5 and 1.1.5,7 to calculating the entropies of the gaseous halate ions, it is necessary to know the shapes and sizes of the molecules, and the fundamental vibrational frequencies. All the molecules are pyramidal, with the halogen at the apex of the pyramid: the relevant structural parameters are summarised in table 12.

	X - O	O - O	O - X - O angle	Ref
ClO_3^-	1.459 ±0.01	2.362±0.01	108.1±1.0°	(96)
BrO_3^-	1.64 ±0.02	2.61±0.02	(ht of pyramid 0.66A)	(97)
IO_3^-	1.82 ±0.02	2.74±0.02	97°8'±20'	(98)

Table 12: Structural parameters for the halate ions.

There are six fundamental vibrational frequencies, of which two are doubly degenerate.

Ion	Frequencies				Ref.
ClO_3^-	930	610	980(dd)	480(dd)	99
BrO_3^-	795	435	825(dd)	355(dd)	99
IO_3^-	754	373	774(dd)	334(dd)	100

Table 13 : Fundamental frequencies of the halate ions

The frequencies are given in table 13, and were assigned an arbitrary uncertainty of ± 5% to account for any change in frequency in transferring data from the solid to the gaseous state.

Using these data in equation 1.1.5,5 and 1.1.5,7, the entropies of the halate ions in the ideal gas state, and 298.15°K were calculated. The data was computer processed, and the errors due to uncertainties in the structural parameters were determined. The values for the absolute entropies obtained are in table 14.

	Unit fugacity S.S.	Unit volume S.S.
ClO_3^-	64.43 ± 0.26	58.07 ± 0.26
BrO_3^-	66.85 ± 0.30	60.50 ± 0.30
IO_3^-	68.94 ± 0.33	62.59 ± 0.33

Table 14 : Absolute entropies of the halate anions.

2.4

The correspondence principle mentioned in section 1.1.4 was used to obtain partial molal entropies of the group 1a, 11a, and V11b ions in formamide and NMF. Criss found that partial molal entropies of ion pairs in formamide, NMF and DMF were related to the corresponding partial molal entropies in water by the equations:

$$\bar{S}^o_{\text{Formamide}} = -2.9 + 0.68\ \bar{S}^o_{\text{water}}$$

$$\bar{S}^o_{\text{NMF}} = -7.21 + 0.62\ \bar{S}^o_{\text{water}}$$

$$\bar{S}^o_{\text{DMF}} = -34.7 + 0.82\ \bar{S}^o_{\text{water}} \qquad (2.4,1)$$

The entropy data for the first two solvents were obtained from studies of electrochemical cells, while for DMF, they were obtained by determining saturation solubilities. According to Breck and Lin (83, see also section 1.2.4) $\bar{S}^o$ K^++ (H_2O) = 19.0. Interpolating this value in equation 2.4,1, the values of the partial molal entropy of the potassium ion in formamide and NMF were found to be respectively 10.0 and 4.6. Taking these values as a basis for dividing ion pair partial molal entropies, a set of values for the individual ion partial molal entropies in formamide and NMF were derived and are listed in table 16. The ion pair data used in the calculation are listed in table 15.

	Formamide	NMF
LiCl	11.4	-8.7
NaCl	12.5	10.3
KCl	21.3	15.1
RbCl	24.9	-
CsCl	27.1	21.3
NaF	3.5	-
KBr	24.6	-
KI	28.5	-
CsI	41.0	-
NaBr	-	13.8

Table 15 : Partial molal entropies, taken from Ref. 46.

	Formamide	NMF
Li^+	0.1	-19.2
Na^+	1.2	- 0.2
K^+	10.0	4.6
Rb^+	13.6	-
Cs^+	15.8	10.8
F^-	2.3	-
Cl^-	11.3	10.5
Br^-	14.6	14.0
I^-	18.5	-

Table 16 : Ion partial molal entropies derived from the data in table 15.

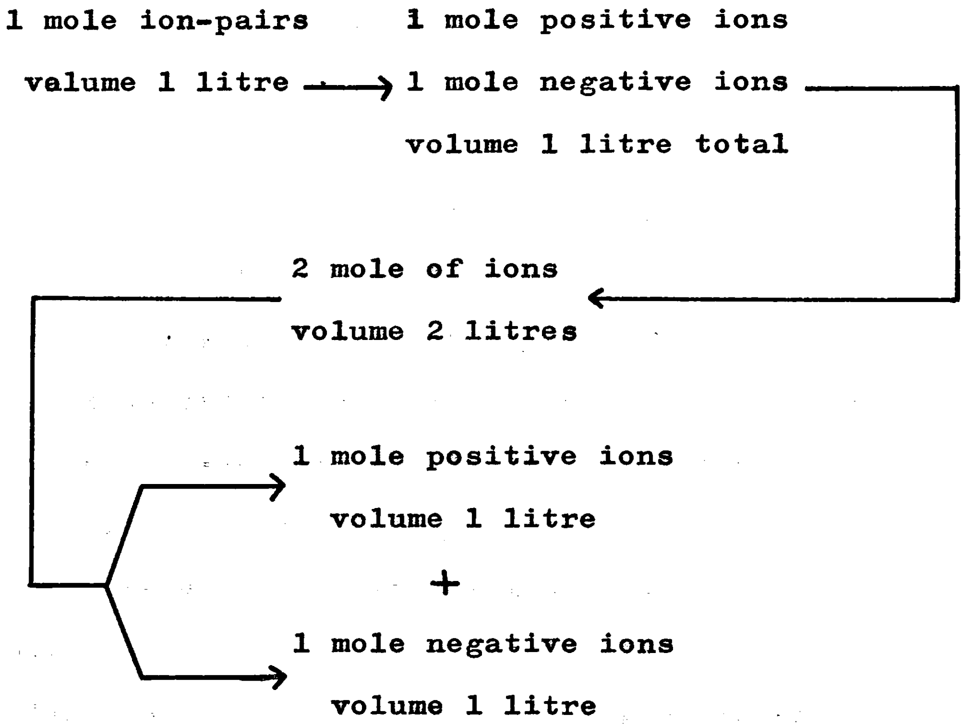
For the remaining ions, the values of the ion partial molal entropies (aqueous) divided by the valency squared, were interpolated in equation 2.4,1, to give estimates of the ion partial molal entropies in formamide and NMF - the results are given in table 17.

	Formamide	NMF
Rb^+	-	7.17
F^-	-	-5.23
I^-	-	12.38
Mg^{2+}	-38.24	-53.16
Ca^{2+}	-28.04	-43.84
Sr^{2+}	-25.48	-41.48
Ba^{2+}	-17.04	-33.80

Table 17 : Ion partial molal entropies interpolated from equation 2.4,1.

The uncertainties in the estimated data are probably fairly high - perhaps as much as four entropy units. They are adequate, however, since the structural interpretation in section 3.3.1 requires only orders of magnitude, and the entropy term is only a few percent of the solvation free energy (section 2.11).

The entropy data listed in the above table (16, 17) are not standard partial molal entropies since they do not refer to the usual conventional standard state. To understand the discrepancy, consider the division of a 1 : 1 ion-pair partial molal entropy to occur in the following stages:



In this scheme the ions end up in their standard states; so that if the entropy changes in the processes indicated are added to the ion partial molal entropies derived above, the standard ion partial molal entropies are obtained. The first stage involves as entropy of demixing $\sum_i RX_i \ln(X_i)$ per mole where X_i is the mole fraction of the i'th component. Stage 2 is an entropy of de-compression, $-R \ln(V_1/V_2)$. The net effect per mole of ions is minus 0.69 for the uni-univalent salt, and minus 0.537 for a di-univalent salt. Taking the last few remarks into account, the results of this section, the standard partial molal entropies of the ions in water, formamide and NMF are summarised in table 18. Criss did not give sufficient data on DMF to enable a similar set of partial molal entropies in DMF to be derived.

2.5

The data used in the calculation of the lattice enthalpies of the main group 1 and 11 halides, and the results obtained are given in table 19 and 20. The standard enthalpies of formation are those obtained in section 2.1; the sources of the rest of the data have been listed in section 1.1.1.

The errors in the data used in these two tables are generally indicated by the number of significant figures quoted (except ΔH^o_f, for which see section 2.1). The uncertainties in the lattice enthalpies are quoted as the most significant uncertainty in

	Water	Formamide	NMF
Li^+	- 2.8	- 0.6	-19.9
Na^+	8.2	0.5	- 0.9
K^+	18.3	9.3	3.9
Rb^+	22.5	12.9	6.5
Cs^+	25.6	15.1	10.1
Mg^{2+}	-39.7	-38.7	-53.7
Ca^{2+}	-24.7	-28.5	-44.3
Sr^{2+}	-20.9	-26.0	-42.0
Ba^{2+}	- 8.5	-17.5	-34.3
F^-	2.5	1.6	- 5.9
Cl^-	18.0	10.6	9.8
Br^-	24.1	13.9	13.3
I^-	30.9	17.8	11.7
ClO_3^-	43.8	-	-
BrO_3^-	43.7	-	-
IO_3^-	32.5	-	-

Table 18 : Standard ion partial molal entropies

Salt	ΔH_f^o	ΔH_{sub}	$\frac{1}{2}D$	I	-E	ΔH_L
LiF	-147.9	38.44	18.4	124.30	-79.51	249.5±1
LiCl	- 97.66	38.44	28.54	124.30	-83.32	205.62±0.01
LiBr	- 83.99	38.44	26.90	124.30	-77.55	196.08
LiI	- 65.22	38.44	25.61	124.30	-70.64	184.22
NaF	-137.9	25.9	18.4	118.49	-79.51	221.2±1
NaCl	- 98.35	25.9	28.54	118.49	-83.32	188.0±0.1
NaBr	- 86.43	25.9	26.90	118.49	-77.55	180.1
NaI	- 69.46	25.9	25.61	118.49	-70.64	168.9
KF	-136.3	21.45	18.4	100.06	-79.51	196.8±1
KCl	-104.37	21.45	28.54	100.06	-83.32	171.10±0.01
KBr	- 94.16	21.45	26.90	100.06	-77.55	165.02
KI	- 78.96	21.45	25.61	100.06	-70.64	155.44
RbF	-134.0	19.5±1	18.4	96.30	-79.51	188.7±1.4
RbCl	-104.09	19.5	28.54	96.30	-83.32	165.1±1
RbBr	- 94.35	19.5	26.90	96.30	-77.55	159.5±1
RbI	- 79.81	19.5	25.61	96.30	-70.64	150.6±1
CsF	-133.1	18.67	18.4	89.78	-79.51	180.5±0.1
CsCl	-105.89	18.67	28.54	89.78	-83.32	159.56±0.01
CsBr	- 97.01	18.67	26.90	89.78	-77.55	154.81
CsI	- 83.46	18.67	25.61	89.78	-70.64	146.88

Table 19 : Lattice enthalpies of the group 1a halides

Salt	ΔH_f^o	ΔH_{sub}	D	ΣI	-2E	ΔH_L
MgF_2	-269.1	35.6	36.8(±)	522.88	-159.02	705.4±2.0
$MgCl_2$	-153.57	35.6	57.08	522.88	-166.64	602.49±.1
$MgBr_2$	-125.18	35.6	53.80	522.88	-155.10	583.0±0.5
MgI_2	- 88.5	35.6	51.22	522.88	-141.28	556.9±0.3
CaF_2	-292.6	42.2	36.8	414.66	-159.02	627.3±2.0
$CaCl_2$	-191.1	42.2	57.08	414.66	-166.64	538.5±0.2
$CaBr_2$	-164.1	42.2	53.80	414.66	-155.10	519.7
CaI_2	-128.9	42.2	51.22	414.66	-141.28	492.7
SrF_2	-291.1	39.2	36.8	385.56	-159.02	593.7±2.0
$SrCl_2$	-198.1	39.2	57.08	385.56	-166.64	513.4±0.2
$SrBr_2$	-171.7	39.2	53.80	385.56	-155.10	495.2
SrI_2	-134.7	39.2	51.22	385.56	-141.28	469.4
BaF_2	-289.8	42.5±.5	36.8	350.78	-159.02	560.9±2.1
$BaCl_2$	-205.5	42.5	57.08	350.78	-166.64	489.3
$BaBr_2$	-181.3	42.5	53.80	350.78	-155.10	473.3±0.2
BaI_2	-145.53	42.5	51.22	350.78	-141.28	448.7

Table 20 : Lattice enthalpies of the group 11a halides

the data used in the calculation; where there is more than one significant uncertainty, the root mean square of the significant uncertainties is given. The values obtained are several kcals per mole higher than those obtained by previous, similar calculations (69, 101): this is mainly due to the choice of electron affinity data.

2.6

In section 2.11 a set of values for individual ion hydration enthalpies was derived. The anion hydration enthalpies were found to be linearly related to the anion lyotropic numbers. The data were fitted to a straight line usin g a computerised least squares technique, giving the equation:

$$\Delta H^{-}_{hydr.} = 6.48 \pm 0.03\ N_1 - 159.29 \pm 0.27 \qquad (2.6,1)$$

Interpolation of the lyotropic numbers of the halate anions gave the hydration enthalpies of the halates. The lyotropic numbers used were taken from those used by Finch and Gardner (38) - the data and results are in tables 21 and 22.

	ClO_3^-	BrO_3^-	IO_3^-
N_1	10.7±0.2	9.5±0.2	6.3±0.3
$\Delta H_{hydr.}$	90.5±1.6	-97.7±1.6	-118.5±1.6

Table 21: Lyotropic numbers and hydration enthalpies of the halate anions.

Cation solvation enthalpies were also taken from section 2.11 and were combined with the above anion

	ClO_3^-	BrO_3^-	IO_3^-	
Li^+		-218.2	-239.0	ΔH_{hydr}
		- 0.3	1.6	ΔH_s^o
		218.6	237.4	ΔH_L
		(212.3)	(234.6)	
Na^+	-183.1	-190.8	-211.6	ΔH_{hydr}
	- 5.2	- 6.4	- 4.9	ΔH_s^o
	188.2	197.3	216.5	ΔH_L
	(183.8)	(192.8)		
K^+	-163.0	-170.7	-191.5	ΔH_{hydr}
	- 9.9	- 9.8	- 6.6	ΔH_s^o
	172.8	180.6	198.1	ΔH_L
	(170.4)	(178.2)	(195.6)	
Rb^+	-157.0	-164.7	-185.5	ΔH_{hydr}
	- 11.4	- 11.7	- 8.2	ΔH_s^o
	168.4	176.4	193.6	ΔH_L
	(164.9)	(173.2)	~~(1~~	
Cs^+		-159.0	-179.8	ΔH_{hydr}
		- 12.1	- 9.0	ΔH_s^o
		171.1	188.8	ΔH_L
		(166.0)		

Table 22: Continued on page 63

	ClO_3^-	BrO_3^-	IO_3^-	
Ca^{2+}	-549.7	-565.3	-606.7	ΔH_{hydr}
	5.6	- 0.6	- 13.2	ΔH_s^o
	544.1 (542)	565.9	619.9	ΔH_L
Sr^{2+}	-517.4	-533.0	-574.4	ΔH_{hydr}
	- 0.6	- 4.9	- 14.8	ΔH_s^o
	518.0 (513)	537.9	589.2	ΔH_L
Ba^{2+}	-484.3	-499.9	-541.3	ΔH_{hydr}
	- 5.6	- 10.5	- 16.3	ΔH_s^o
	489.9 (485)	510.4	557.6	ΔH_L

Table 22 : Hydration enthalpies, solution enthalpies, and lattice enthalpies of the group 1a and 11a halates.
(Literature estimates in parentheses)

data to give solvation enthalpies of the alkali and alkaline earth halates. Lattice enthalpies were derived via cycle 1 in section 1.1.1, using heats of solution taken from the following sources: group 1a halates from Parker's collection (34) with the exception of Rb, Cs, Na iodates which came from a recent paper by Bousquet (102); the group 11a chlorates from Finch and Gardner's paper (38); the 11a bromates were determined by this author (see section 2.9); the 11a iodates by Bousquet (92).

The reliability of the lattice enthalpies thus obtained depends on the validity of the interpolations made: as there are no electron affinity data available for the halate anions it is impossible to calculate their lattice enthalpies using the Born - Haber cycle, and thus check independently on the values obtained. The data in parentheses in table 22 are lattice enthalpy estimates made using the same sort of technique by Morris (37) and Finch and Gardner (38). The values obtained in the work are substantially larger than previous estimates. This is mainly due to the new lattice enthalpy scale based on Berry and Reimann's electron affinity data.

The hydration enthalpies of the group 1a cations were found to be linear with the reciprocals of their effective radii as derived by Conway (76). A least squares analysis showed the appropriate equation to be:

$$\Delta H^{+}_{hyd.} = \frac{-105.57 \pm 0.27}{r_{eff.}} - 9.31 \pm 0.17 \qquad 2.6,2$$

The value for Li^{+} was not included in the data used to derive the above equation, since (a) it caused considerable divergence from linearity, and (b) the equation was to be used for extrapolation to large radii. The significance of the effective radii used is discussed in section 2.12. It is sufficient to note at this juncture that they are derived to correspond to the unhydrated molar volumes of the ions in solution. In a further publication, Conway derived corresponding values for the radii of the tetraalkylammonium salts by interpreting some experimental data on their partial molal volumes (103). These radii were interpolated in equation 2.6,2 to give the hydration enthalpies of the tetraalkylammonium ions. Following a similar procedure as that used for the halates (above) solvation enthalpies and lattice enthalpies were calculated for some tetraalkylammonium halides : the data and results are in tables 23 and 24. The solution enthalpy data came from the following sources: This author n-Pr_4NI, n-Bu_4NI, see Appendix II; Y. Chi Wu (18) Me_4NI, Et_4NI, Me_4NBr, Et_4NCl, Et_4NBr; the remainder from Parker's compilation (34).

Also in table 23 are some of Halliwell and Nyburg's estimates (104). The estimates listed above are con-

	Cl^-	Br^-	I^-	
Me_4N^+	-140.4	-133.7	-124.0	ΔH_{hyd}
	- 1.0	- 5.9	- 10.1	ΔH^o_s
	141.4	139.6	134.1	ΔH_L
	(120.0)	(116.9)	(112.4)	
Et_4N^+	-133.6	-126.9	-117.2	ΔH_{hyd}
	3.1	- 1.5	- 6.7	ΔH^o_s
	130.5	128.4	123.9	ΔH_L
$n\text{-}Pr_4N^+$			-113.4	ΔH_{hyd}
			- 2.7	ΔH^o_s
			116.1	ΔH_L
$n\text{-}Bu_4N^+$			-111.1	ΔH_{hyd}
			- 3.6	ΔH^o_s
			114.7	ΔH_L

Table 23 : Hydration, solution and lattice enthalpies of some tetraalkylammonium salts

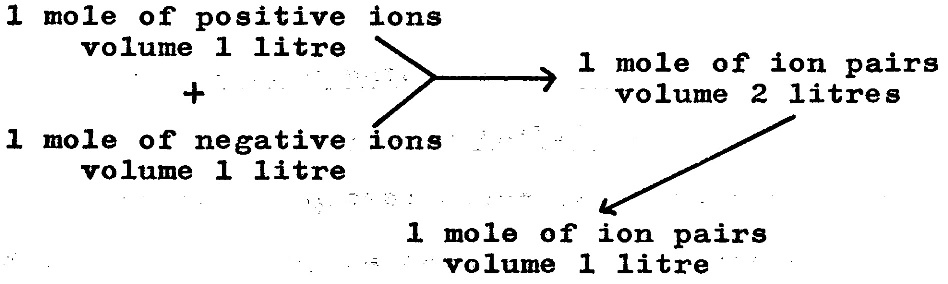
	Me_4N^+	Et_4N^+	$n\text{-}Pr_4N^+$	$n\text{-}Bu_4N^+$
$r_{eff.}$	2.85	3.48	3.98	4.37
$\Delta H_{hydr.}$	-46.4±0.2	39.6±0.3	35.8±0.3	33.5±0.2

Table 24: Effective radii and hydration enthalpies of the tetraalkylammonium cations.

sidered to be more reliable than any previously made because they make use of experimental radii rather than radii calculated by adding up bond lengths, etc.

2.7

Lattice entropies were obtained as the differences between ion-pair sums of gas entropies as derived in section 2.3, and crystal entropies from the sources indicated in section 2.2. When calculating ion-pair gas entropies from single ion values some care had to be taken to ensure that the values obtained referred to the correct standard state. The standard state required is that of one moleof pairs of ions randomly mixed to give one litre of ideal gas at temperature of 298.15°K. Consider the combination of single ion entropies to occur in the following stages:



The first step is an entropy of mixing, $-R \sum_i X_i \ln X_i$, the second step is an entropy of compression, $-R \ln V_1/V_2$. The process above is written out for a uni-univalent salt - the extension to salts with higher valency ions follows the same principles. The net entropy change in the above cycle is 1.38 eu. for a uni-univalent salt, and 1.61 eu for a di-univalent salt. Including the above, the gas entropies, crystal entropies and lattice entropies of the 1a and 11a halides were calculated and are collected in table 25; and those of some of the halates in table 26.

The reliability of the data in the above two tables is limited by the reliability of the crystal entropy data: when this has been determined experimentally, the uncertainty is probably a few tenths of an entropy unit; the uncertainty in the estimated crystal entropies is probably ten times as large.

2.8

From the lattice enthalpies and entropies in tables 19, 20, 21, 25 and 26, values for lattice free energies were calculated, and are listed in tables 27 and 28.

2.9

The standard enthalpies of solution used in the calculation of solvation enthalpies were obtained from the following sources: group 1a halides in formamide, Somsen (2); group 1a halides in NMF, Somsen (3), and Held and Criss (8); group 1a halides in DMF, Held (45) group 11a halides and halates in all three solvents and water, this author. The data is summarised in the next seven tables. The uncertainties in the literature data are indicated by the number of significant figures quoted. The results in tables 29, 30,

	Fluoride	Chloride	Bromide	Iodide	
Li	55.21	57.06	59.49	60.87	$S^o(g)$
	8.57	(13.20)	(16.50)	(18.10)	$S^o(c)$
	46.64	43.86	42.99	42.77	S^o_L
Na	58.78	60.63	63.06	64.44	$S^o(g)$
	14.00	17.30	20.71	23.58	$S^o(c)$
	44.78	43.33	42.35	40.86	S^o_L
K	60.37	62.22	64.65	66.03	$S^o(g)$
	15.91	19.76	23.05	24.94	$S^o(c)$
	44.46	42.46	41.60	41.09	S^o_L
Rb	62.70	64.55	66.98	68.36	$S^o(g)$
	(17.40)	(22.60)	25.88	28.21	$S^o(c)$
	45.30	41.95	41.10	40.15	S^o_L
Cs	64.01	65.86	68.29	69.67	$S^o(g)$
	(19.10)	(23.30)	29.00	31.00	$S^o(c)$
	44.91	42.56	39.29	38.67	S^oL
Mg	87.60	91.30	96.16	98.92	$S^o(g)$
	13.68	21.40	(29.40)	(34.80)	$S^o(c)$
	73.92	69.90	66.76	64.12	S^o_L

Table 25 : Continued on page 70

	Fluoride	Chloride	Bromide	Iodide	
Ca	89.09	92.79	97.65	100.41	$S^o(g)$
	16.46	27.20	31.00	34.00	$S^o(c)$
	72.63	65.59	66.65	66.41	S^o_L
Sr	91.42	95.12	99.98	102.74	$S^o(g)$
	(21.40)	28.00	(33.80)	(39.20)	$S^o(c)$
	70.02	67.12	66.18	63.54	S^o_L
Ba	92.76	96.46	101.35	104.08	$S^o(g)$
	23.10	29.56	(35.50)	(40.90)	$S^o(c)$
	69.66	66.90	65.85	63.18	S^o_L

Table 25 : Gas entropies, crystal entropies, lattice entropies of the group 1a and 11a halides. Estimated values in parentheses.

	Chlorate	Bromate	Iodate	
K	90.02	92.45	94.54	$S^o(g)$
	34.17	35.65	36.20	$S^o(c)$
	55.85	56.80	58.34	S^o_L
Rb	92.35	-	-	$S^o(g)$
	36.30	-	-	$S^o(c)$
	56.05	-	-	S^o_L
Ca	-	-	157.43	$S^o(g)$
	-	-	34.80	$S^o(c)$
	-	-	122.63	S^o_L
Sr	-	-	159.76	$S^o(g)$
	-	-	50.80	$S^o(c)$
	-	-	108.96	S^o_L
Ba	152.06	-	161.10	$S^o(g)$
	(53.70)	-	57.10	$S^o(c)$
	98.36	-	104.00	S^o_L

Table 26 : Gas entropies, crystal entropies, lattice entropies of the group 1a and 11a halates. Estimated values in parentheses.

	Fluoride	Chloride	Bromide	Iodide
Li^+	235.6	192.55	183.27	171.47
Na^+	221.2	175.1	180.1	156.7
K^+	183.6	158.45	152.62	143.19
Rb^+	175.2	152.6	147.3	138.6
Cs^+	167.1	146.88	143.10	135.36
Mg^{2+}	683.1	581.7	563.1	537.8
Ca^{2+}	605.0	519.0	499.9	475.9
Sr^{2+}	573.0	493.4	475.5	450.5
Ba^{2+}	540.2	469.4	453.7	429.9

Table 27 : Lattice free energies of the group 1a and 11a halides.

	Chlorate	Bromate	Iodate
K^+	156.2	163.7	180.8
Rb^+	151.7	-	-
Ca^{2+}	-	-	583.4
Sr^{2+}	-	-	556.7
Ba^{2+}	460.6	-	526.6

Table 28 : Lattice free energies of some group 1a and 11a halates.

	Fluoride	Chloride	Bromide	Iodide
Li^+	-	-9.42	-13.39	-18.26
Na^+	-	-2.10	- 4.41	- 7.43
K^+	-3.18	0.82	0.23	- 1.02
Rb^+	-5.27	0.71	0.75	0.23
Cs^+	-7.60	0.95	1.81	2.22

Table 29 : Standard enthalpies of solution of the alkali metal halides in formamide (2).

	Fluoride	Chloride	Bromide	Iodide
Li^+	-	-	-	-21.11
Na^+	-	(-1.24)	(-4.39)	- 8.26 (-8.26)
K^+	-2.60	0.37(0.31)	-0.82	- 3.22
Rb^+	-	-	-	- 1.64
Cs^+	(0.89)	-	-	0.71

Table 30 : Standard enthalpies of solution of some alkali metal halides in NMF from ref. 3. Held's data in parentheses (8)

	Fluoride	Chloride	Bromide	Iodide
Li^+	-	-14.5	-21.3	-
Na^+	-	-	- 7.39	-13.95
K^+	-	-	- 3.89	-
Cs^+	-	-	-	- 4.25

Table 31 : Standard enthalpies of solution of some alkali metal halides in DMF. (45)

	Chloride	Bromide
Ca^{2+}	-21.90±0.24	-29.60±0.29
Sr^{2+}	-17.56±0.16	-25.35±0.12
Ba^{2+}	-10.41±0.17	-15.35±0.14

Table 32 : Enthalpies of solution of some alkaline earth halides in formamide (this work).

	Chloride	Bromide
Ca^{2+}	-24.31±0.17	-34.05±0.13
Sr^{2+}	-17.11±0.15	-28.02±0.05
Ba^{2+}	very slow dissolution	-18.00±0.09

Table 33 : Standard enthalpies of solution of some alkaline earth halides in NMF (this work).

	Chloride	Bromide
Ca	-23.81±0.80	-39.57±0.2
Sr	-15.82±0.09	-34.13±0.08
Ba	low solubility	low solubility very slow dissolution.

Table 34 : Standard enthalpies of solution of some alkaline earth halides in DMF (this work)

	Water	Formamide	NMF	DMF
$Ca(ClO_3)_2$	-	-11.3±0.3	-13.8±0.1	-18.4±0.2
$Sr(ClO_3)_2$	-	-8.28±0.07	-1.96±0.12*	-14.96±0.44*
$Ba(ClO_3)_2$	-	-4.95±0.06	-7.68±0.12*	-12.80±0.16*
$Ca(BrO_3)_2$	0.59±0.12	-4.64±0.10	-4.42±0.10	-4.35±0.05
$Sr(BrO_3)_2$	4.89±0.07	-3.21±0.10	-	-
$Ba(BrO_3)_2$	10.50±0.13	0.27±0.10	-	-

Table 35 : Heats of solution of some alkaline earth halates. *indicates a datum obtained by extrapolation to zero conectration.

	Chloride	Bromide
Ca^{2+}	25.3±5.4	22.6±1.0
Sr^{2+}	14.4±0.7	28.7±0.9

Table 36 : Heats of dilution of the alkaline earth halides in DMF - values of the constant A in equation 2.9,1.

	Chloride	Bromide
Ca^{2+}	19.6±1.4	27.9±1.4
Sr^{2+}	-1.7±1.3	22.4±0.4
Ba^{2+}	-	3.7±0.6

Table 37 : Heats of dilution of the alkaline earth halides in NMF - values of the constant A in equation 2.9,1.

	Chlorate	Bromate
Ca^{2+}	-	-
Sr^{2+}	5.30±0.32	-
Ba^{2+}	3.48±0.32	-

Table 38 : Heats of dilution of some alkaline earth halates in NMF - values of the constant A in equation 2.9,1

$SR(ClO_3)_2$ - 10.3±2.4

$Ba(ClO_3)_2$ - 9.9±0.8

Table 39 : Heats of dilution of some alkaline earth halates in DMF - values of the constant A in equation 2.9,1.

31, 33, 34, and 35 were obtained by extrapolating heat of solution data obtained over a range of concentrations to infinite dilution. The data from which the extrapolations were made is detailed in Appendix II.

To aid the extrapolation, the data were fitted to the straight line predicted by the Debye-Hückel limiting law,

$$\Delta H_s\ (m) \quad = \quad \Delta H_s^o + Am^{\frac{1}{2}} \qquad 2.9,1.$$

where A is a constant specific for each solvent, using a computerised least squares analysis : experimental values of A are listed in table 36 - 39. For water, formamide and a few other cases, the heats of solution were found to be independent of the concentration within the experimental uncertainty: the values in tables 32 and 35 are the mean values, and it is assumed that these are identical with the standard heats of solution in the subsequent use of them.

The literature data was extended by the use of the following device: the heats of solution were combined with the standard enthalpies of formation of the crystals to give a set of partial molal enthalpies in the three solvents - these are listed in tables 40, 41 and 42. Taking an arbitrary value for the partial molal enthalpies in eachsolvent: $\Delta H_f^o Cs^+$ (Formamide) = 0, $\Delta H_f^o K^+$(NMF) = 0, and $\Delta H_f^o Li^+$(DMF) = 0, were the arbitrary values chosen, and the relative partial molal enthalpiesthus obtained are listed in tables 43 - 45.

CsF	-140.7	CsCl	-104.94
CsBr	- 95.20	CsI	- 81.24
LiCl	-107.08	NaCl	-100.45

Table 40 : Standard partial molal enthalpies of some alkali metal halides in formamide.

	F^-	Cl^-	Br^-	I^-
Li^+	-	-	-	-86.33
Na^+	-	-99.59	-90.82	-77.72
K^+	-138.9	-104.00	-94.98	-82.18
Rb^+	-	-	-	-81.45
Cs^+	-	-105.00	-	-82.75

Table 41 : Standard partial molal enthalpies of the alkali metal halides in NMF.

LiCl -112.2, LiBr -105.3, NaBr -93.82,
KBr -98.05, CsI -87.71, NaI -83.41.

Table 42 : Standard Partial molal enthalpies in DMF.

F^- -140.7, Cl^- -104.94, Br^- -95.20,
I^- -81.24, Li^+ -2.14, Na^+ -4.49.

Table 43 : Relative partial molal enthalpies in formamide $(\overline{H}^{o}Cs^{+} = 0)$

Li^+	Na^+	K^+	Rb^+	Cs^+	F^-
-4.15	4.36	0.00	0.73	-0.79	-138.9

Cl^-	Br^-	I^-
-104.00	-94.98	-82.18

Table 44 : Relative ($K^+ = 0$) ion partial molal enthalpies in NMF

Li^+	Na^+	K^+	Cs^+	Cl^-	Br^-	I^-
0.00	11.5	7.2	7.2	-112.2	-105.3	-94.9

Table 45 : Relative ($Li^+ = 0$) ion partial molal enthalpies in DMF.

In cases, such as sodium and caesium in NMF, where data derived from different salts give different values for the relative partial molal enthalpy, the mean value was taken. These relative values were then added together in pairs to give new partial molal enthalpies for salts, and these were combined with standard enthalpies of formation to yield new standard enthalpies of solution: the data obtained in this manner is given in tables 46 to 48.

Held (45) gives some data for the enthalpy of solution of magnesium chloride in NMF and DMF, but due to the very high rate of change of enthalpy of solution with concentration, he was unable to extrapolate his

LiF	NaF	
-142.8	-136.2	$\overline{H}^o$(form)
-147.9	-137.9	ΔH_f^o(c)
5.1	1.7	ΔH_s^o

Table 46 : derived standard heats of solution in formamide.

	Fluoride	Chloride	Bromide	
Li^+	-143.1	-108.15	-99.13	$\overline{H}^o$(NMF)
	-147.9	- 97.66	-83.99	ΔH_f^o (c)
	4.8	- 10.49	-15.14	ΔH_s^o
Na^+	-143.3	-	-	$\overline{H}^o$(NMF)
	-137.9	-	-	ΔH_f^o (c)
	- 5.4	-	-	ΔH_s^o
Rb^+	-138.2	-103.27	-94.25	$\overline{H}^o$(NMF)
	-134.0	-104.09	-94.35	ΔH_f^o
	- 4.2	- 0.82	0.10	ΔH_s^o
Cs^+	-139.7	-	-95.77	$\overline{H}^o$(NMF)
	-133.1	-	-97.01	ΔH_f^o
	- 6.6	-	1.24	ΔH_s^o

Table 47 : Derived standard heats of solution in NMF

	Chloride	Bromide	Iodide	
Li	-	-	-94.9	$\bar{H}^o$(DMF)
	-	-	-65.2	ΔH_f^o (c)
	-	-	-29.7	ΔH_s^o
Na	-100.7	-	-	$\bar{H}o$ (DMF)
	- 98.4	-	-	ΔH_f^o (c)
	- 2.3	-	-	ΔH_s^o
K	-105.0	-	-87.7	$\bar{H}^o$ (DMF)
	-104.4	-	-79.0	ΔH_f^o (c)
	- 0.6	-	- 8.7	ΔH_s^o
Cs	-105.0	-98.1	-	$\bar{H}^o$ (DMF)
	-105.9	-97.0	-	ΔH_f^o (c)
	0.9	- 1.1	-	ΔH_s^o

Table 48 : Derived standard heats of solution in DMF.

data to infinite dilution. He obtained a similar effect with lithium chloride and bromide, particularly in the low concentration region (ca. 10^{-4}m.), where the ΔH vs $m^{\frac{1}{2}}$ graph was found to have a slope nearly 300 times that predicted by the Debye-Hückel theory.

The values for the Li^+ salts in NMF quoted are based on Somsen's datum for LiI, which was obtained at slightly higher concentrations than Held's data, but showed no anomalous dilution effects.

The Debye-Hückel limiting law (103) gives the value of the coefficient A in equation 2.9,1 as:

$$RT^2 \left[\frac{\pi N e^6}{1000}\right]^{\frac{1}{2}} \left[\frac{\sum_i V_i Z_i^2}{kDT}\right]^{\frac{3}{2}} \left[\frac{1}{D}\left(\frac{\partial D}{\partial T}\right)_p + \frac{1}{T} + \frac{1}{3V}\left(\frac{\partial V}{\partial T}\right)_p\right] d^{\frac{1}{2}}$$

where, the V_i's are the numbers of ions with valency Z_i; D is the dielectric constant of the solvent, d is the density, and $\frac{1}{V} \cdot \left(\frac{\partial V}{\partial T}\right)_p$ is the coefficient of cubical expansion.

The physical constants for use in this equation were taken from references 105, 62, 106, 57, 107, 108 and 109, giving values for A: formamide 0.7; NMF 4.1; DMF 10.4 kcal, mole.$^{3/2}$ kg$^{\frac{1}{2}}$ for di-univalent salts. Boyd et al. have shown that the corresponding value of A for water is 3.7 (110). Agreement between experiment and theory is quite good in some cases, but poor in others: the small slope predicted for formamide is probably too small to be detected with the apparatus used - hence no heats of dilution in formamide were detected; for the other solvents agreement is quite good for the halates and for the barium halides, but for the other halides the experimental slopes are as much as seven times the theoretical slopes. Considering the results of Held (45 and above, section 2.9) on magnesium chloride, LiCl and LiBr, which extended into much more dilute solutions, it seems likely that the slopes would be different at lower concentrations, It is difficult to estimate what errors may have been introduced by the use of the linear extrapolation of high concentration data to infinite dilution, but if Held's data on magnesium chloride is anything to go by, the errors may be as high as 20 - 30 kcals per mole, since the anomalous behaviour was found to occur at concentrations lower than those available in this study. The quantity of interest is, however, the solvation enthalpy, which is about 500 - 600 kcals per mole for the group 11a halides, so that an error of 30 kcals per mole in the heat of solution causes an error of 5% at most in the solvation enthalpy.

By applying cycle 1 (section 1.1.1) to the heats of solution listed in the last section and the lattice enthalpies derived in section 2.5, a set of values for the solvation enthalpies in water and the three solvents was derived and is listed in tables 49 to 51.

	Water	Formamide	NMF	DMF
LiF	248.4	244.4	244.7	-
LiCl	214.47	215.04	216.11	220.1
LiBr	207.75	209.47	211.22	217.4
LiI	199.35	202.48	205.33	213.9
NaF	221.0	219.5	226.6	-
NaCl	187.1	190.1	189.3	190.3
NaBr	180.2	184.5	184.5	187.5
NaI	170.7	176.3	177.2	182.8
KF	201.0	200.0	199.4	-
KCl	166.98	170.28	170.73	171.7
KBr	160.27	164.79	165.84	186.9
KI	150.58	156.46	158.66	164.1
RbF	194.9	194.0	192.9	-
RbCl	161.0	164.4	164.3	-
RbBr	154.3	158.7	159.4	-
RbI	144.6	150.4	152.2	-

Table 49 : Continued on page 85.

	Water	Formamide	NMF	DMF
CsF	189.3	188.1	187.1	-
CsCl	155.31	158.61	158.46	158.7
CsBr	148.60	153.00	153.57	155.9
CsI	138.91	144.66	146.39	151.1

Table 49 : Solvation enthalpies (sign reversed) of the alkali metal halides.

	Water	Formamide	NMF	DMF
MgF_2	707.4	-	-	-
$MgCl_2$	639.6	-	-	-
$MgBr_2$	626.3	-	-	-
MgI_2	606.8	-	-	-
CaF_2	625.6	-	-	-
$CaCl_2$	557.8	560.4	562.8	562.8
$CaBr_2$	544.3	549.3	553.8	559.3
CaI_2	524.9	-	-	-
SrF_2	593.3	-	-	-
$SrCl_2$	525.5	531.0	530.5	529.2
$SrBr_2$	512.0	518.6	523.2	529.3
SrI_2	492.6	-	-	-
BaF_2	560.2	-	-	-
$BaCl_2$	492.4	499.7	-	-
$BaBr_2$	478.9	488.7	491.3	-
BaI_2	459.5	-	-	-

Table 50 : Solvation enthalpies of some group 11a halides (sign reversed).

	Water	Formamide	NMF	DMF
$Mg(ClO_3)_2$	631.6	-	-	-
$Mg(BrO_3)_2$	647.0	-	-	-
$Mg(IO_3)_2$	688.6	-	-	-
$Ca(ClO_3)_2$	549.7	555.4	557.9	562.5
$Ca(BrO_3)_2$	565.3	570.5	570.3	570.2
$Ca(IO_3)_2$	606.7	-	-	-
$Sr(ClO_3)_2$	517.4	526.3	528.0	533.0
$Sr(BrO_3)_2$	533.0	541.1	-	-
$Sr(IO_3)_2$	574.4	-	-	-
$Ba(ClO_3)_2$	484.3	494.9	497.6	502.7
$Ba(BrO_3)_2$	499.9	510.1	-	-
$Ba(IO_3)_2$	541.3	-	-	-

Table 51 : Solvation enthalpies of some alkaline earth halates (sign reversed)

The accuracy of the solvation enthalpy values is limited by the accuracy of the lattice enthalpy data, although, for reasons mentioned above some of the solution enthalpy data may be in error by larger amounts than indicated.

2.10

Using the partial molal entropies of the ions as discussed in section 2.4, and the entropies of the gaseous ions as calculated in section 2.3, values of ion solvation entropies were derived. Similarly, a set of values for the hydration entropies of the group la and lla halides and halates was obtained. Of course, in the latter calculation the same care had to be taken with standard states as in the lattice entropy calculations : accordingly, the gas entropy used were those listed in table 25, and the aqueous entropies were taken from NBS 500. Tables 52 to 54 contain the results of this section.

The uncertainties in the solvation entropy data are largely due to uncertainties in the partial molal entropies : for the experimental data probably a few tenths of an entropy unit, but for the estimated data, a range of as much as four entropy units.

Hydration entropies from table 53 and hydration enthalpies from tables 49 and 50 are combined in table 55 to give hydration free energies.

	Water	Formamide	NMF
Li^+	28.21	26.01	45.31
Na^+	20.78	28.48	29.88
K^+	12.27	21.27	26.67
Rb^+	10.40	20.00	26.40
Cs^+	8.61	19.11	24.11
Mg^{2+}	68.85	67.85	82.85
Ca^{2+}	55.34	59.14	74.94
Sr^{2+}	53.87	58.97	74.97
Ba^{2+}	42.81	51.81.	68.61
F^-	25.92	26.82	34.32
Cl^-	12.27	19.67	20.47
Br^-	8.60	18.80	19.40
I^-	3.18	16.28	22.38
ClO_3^-	14.3	-	-
BrO_3^-	16.8	-	-
IO_3^-	30.1	-	-

Table 52 : Ion solvation entropies (sign reversed).

	Fluoride	Chloride	Bromide	Iodide
Li^+	54.11	40.46	36.79	31.37
Na^+	46.68	33.03	29.36	23.94
K^+	35.87	24.52	20.85	15.43
Rb^+	35.30	21.65	17.98	12.56
Cs^+	34.51	20.86	17.19	11.77
Mg^{2+}	120.40	93.20	85.76	74.81
Ca^{2+}	106.89	79.69	72.25	61.31
Sr^{2+}	105.42	78.22	70.78	59.84
Ba^{2+}	94.36	67.46	59.35	49.08

Table 53 : Hydration entropies of the group 1a and 11a halides (sign reversed).

	Chlorate	Bromate	Iodate
Li^+	42.46	44.99	58.28
Na^+	35.03	37.56	50.85
K^+	26.52	29.05	42.34
Rb^+	23.65	26.18	39.47
Cs^+	22.86	25.39	38.68
Mg^{2+}	97.10	102.16	128.74
Ca^{2+}	83.59	88.65	115.23
Sr^{2+}	82.12	87.18	113.76
Ba^{2+}	71.06	76.12	102.70

Table 54 : Hydration entropies of the group 1a and 11a halates (sign reversed)

	Fluoride	Chloride	Bromide	Iodide
Li^+	232.27	202.41	196.79	190.00
Na^+	207.09	177.26	170.36	163.57
K^+	190.31	159.67	154.06	145.98
Rb^+	184.38	154.55	148.94	140.86
Cs^+	179.02	149.10	143.48	135.41
Mg^{2+}	671.2	611.9	600.8	584.5
Ca^{2+}	593.1	534.1	522.8	506.7
Sr^{2+}	562.0	502.2	490.9	474.8
Ba^{2+}	532.1	472.3	461.2	444.9

Table 55 : Hydration free energies of the group 1a and 11a halides (sign reversed)

2.11

The division of solvation enthalpies into the individual ionic contributions was made using an entirely new empirical method. Stokes (69) has shown that it is possible to calculate the electrostatic contribution to the free energy of gaseous ions (section 1.2.3), using the formula $\frac{Nz^2 e^2}{2r}$, where r is the Van der Waals radius of the gaseous ions. Since this formula contains no temperature dependent terms it also gives the electrostatic enthalpy of the ions. By adding to the solvation enthalpy of ion-pairs the sum of the electrostatic enthalpies of the constituent gaseous ions, a set of values for the partial molal enthalpies relative to the electrostatic enthalpies of the gaseous ions was obtained : these are termed ΔH^{elec}_{solv}(rel.) and are listed in table 56.

The quantity $\Delta H^{elec.}_{solv.}$(rel.) is small compared to the solvation enthalpy. It should, therefore, be possible to divide it into its individual ion contributionsmore accurately than the solvation enthalpy. $\Delta H^{elec.}_{solv.}$(rel.) was found to be a linear function of the cube of the reciprocal effective anionic radius. (see section 2.12) ie.

$$\Delta H^{elec.}_{solv.}(\text{rel.}) = A + B/(r^-)^3 \qquad 2.11,1$$

The intercept, A, is the cation contribution to $\Delta H^{elec.}_{solv.}$(rel.), and this, combined with Stokes (69)

	ΔH^{elec}_{gas}	Water	Formamide	NMF	DMF
NaF	209.8	-11.2	-9.7	-16.8	-
NaCl	196.5	9.4	6.4	7.2	6.2
NaBr	195.0	14.8	10.5	10.5	7.5
NaI	187.9	17.2	11.6	10.7	5.1
KF	186.3	-14.7	-13.7	-13.1	-
KCl	173.0	6.0	2.7	2.3	1.3
KBr	171.5	11.2	6.7	5.7	2.6
KI	164.4	13.8	7.9	5.7	0.3
RbF	179.2	-15.7	-14.8	-13.7	-
RbCl	165.9	4.9	1.5	1.6	-
RbBr	164.4	10.1	5.7	5.0	-
RbI	157.3	12.7	6.9	5.1	-
CsF	170.1	-19.2	-18.0	-17.0	-
CsCl	156.8	1.5	-1.8	-1.7	-1.9
CsBr	155.3	6.7	2.3	1.7	-0.6
CsI	148.2	9.3	3.5	1.8	-2.9
MgF_2	736.7	29.6	-	-	-
$MgCl_2$	710.1	70.5	-	-	-
$MgBr_2$	707.1	80.1	-	-	-
MgI_2	692.9	86.1	-	-	-

Table 56 : Continued on page 94

	ΔH^{elec}_{gas}	Water	Formamide	NMF	DMF
CaF_2	622.6	-2.3	-	-	-
$CaCl_2$	596.0	38.2	-	-	-
$CaBr_2$	593.0	48.7	-	-	-
CaI_2	578.8	53.9	-	-	-
SrF_2	582.9	-10.5	-	-	-
$SrCl_2$	556.3	30.8	-	-	-
$SrBr_2$	553.3	41.3	-	-	-
SrI_2	539.1	46.5	-	-	-
BaF_2	542.5	-17.7	-	-	-
$BaCl_2$	515.9	23.5	-	-	-
$BaBr_2$	512.9	34.0	-	-	-
BaI_2	498.7	39.2	-	-	-

Table 56 : Column 2 ΔH^{elec}_{gas} - sums of electrostatic ion enthalpies in the gas phase from Stokes (69). Remaining columns $\Delta H^{elec.}_{solv.}$ (rel). using $\Delta H_{solv.}$ data from tables 49 and 50.

value for $\Delta H_{gas}^{elec.}$ for the corresponding cation gives the cation contribution to the solvation enthalpy. The data were fitted to equation 2.11,1 using a computerised least squares technique, and the values of the constants A and B obtained are listed in table 57. In the case of DMF there is no data available for fluorides, and the data for the other halides did not fit at all well to the straight line. It was not possible, therefore, to use this method for obtaining ion solvation enthalpies in DMF.

The electrostatic enthalpies of the gaseous ions and the derived values for the cation solvation enthalpies are shown in table 58. To indicate the internal consistency of the data, each cation solvation enthalpy has been used to derive an independent value for the solvation enthalpy of the chloride ion; these are also included in Table 58.

With one exception (Na/NMF) the values derived for the solvation enthalpies show the most remarkable consistency, the largest deviation from the mean being two tenths of a kcal. The average values obtained for the solvation enthalpies of the chloride ion in table 58 (group la cations only) - water 94.0; formamide 91.1; NMF 88.9 - were used to derive an internally consistent set of ion solvation enthalpies from the ion pair solvation enthalpies in tables 49, 50 and 51. The result in table 59, is used for comparison with

	Water		Formamide		NMF	
	A	B	A	B	A	B
NaX	29.7±0.4	-198±2	23.7±0.4	-230±4	28.5±0.9	-324±11
KX	26.3±0.3	-198±2	20.1±0.3	-233±4	17.5±0.5	-210±6
RbX	25.1±0.3	-197±2	19.1±0.4	234±4	16.8±0.5	-219±6
CsX	21.8±0.3	-198±2	15.6±0.4	-232±4	13.5±0.5	-219±6
MgX_2	110.7±0.6	-392±5	-	-	-	-
CaX_2	78.3±0.7	-390±5	-	-	-	-
SrX_2	71.4±0.6	396±5	-	-	-	-
BaX_2	64.0±0.6	-395±5	-	-	-	-

Table 57 : Parameters for equation 2.11,1

	ΔH^{elec}_{gas}	Water		Formamide		NMF	
		ΔH_{hyd}	$\Delta H_{hyd}(Cl^-)$	ΔH_{solv}	$\Delta H_{solv}(Cl^-)$	ΔH_{solv}	$\Delta H_{solv}(Cl^-)$
Na^+	122.8	93.1	94.0	99.1	91.0	94.3	95.0
K^+	99.3	73.0	94.0	79.2	91.1	81.8	88.9
Rb^+	92.2	67.1	93.9	73.1	91.3	75.4	88.9
Cs^+	83.1	61.3	94.0	67.5	91.1	69.6	88.9
Mg^{2+}	562.7	452.0	93.8	-	-	-	-
Ca^{2+}	448.6	370.3	93.8	-	-	-	-
Sr^{2+}	408.9	337.5	94.0	-	-	-	-
Ba^{2+}	368.5	304.5	94.0	-	-	-	-

Table 58 : Ion gas enthalpies, solvation enthalpies, and derived solvation enthalpies for the chloride ion in water, formamide and NMF. Sign for the solvation enthalpies reversed.

	Water	Formamide	NMF
Li^+	120.5	123.9	127.2
Na^+	93.1	99.0	100.4
K^+	73.0	79.2	81.8
Rb^+	67.0	73.3	75.4
Cs^+	61.3	67.5	69.6
Mg^{2+}	451.6	-	-
Ca^{2+}	369.8	378.2	385.0
Sr^{2+}	337.5	348.8	352.7
Ba^{2+}	304.4	317.5	323.3
F^-	128.0	120.5	117.6
Cl^-	94.0	91.1	88.9
Br^-	87.3	85.6	84.0
I^-	77.6	77.3	76.9

Table 59 : Ion solvation enthalpies. (sign reversed)

theoretical values in section 3.

The ion hydration enthalpies have already been shown to be in good agreement with previosly determined values (table 4). The only data for comparison in the other two solvents are those of Somsen (5), which were derived using Halliwell and Nyberg's technique (49). Agreement is quite good: eg. Somsen obtained Na^+/formamide -99.6; Na^+/NMF -102.1; Cl^-/formamide -88.1; Cl^-/NMF -84.8. The differences in the anion data are largely due to Somsen's choice of H_L values, based on different electron affinity data.

The ion solvation enthalpies in table 59 were combined with the ion solvation entropies in table 52, to give values of ion solvation free energies. These are listed in table 60.

2.12

The effective ionic radii used in sections 2.11 and 2.6 were calculated using a semi-empirical equation derived by Conway (76). Conway suggested that ions in aqueous solution retain their crystal radii, and that any observed increases in the radii of ions in solution were due to dead space around the ion. For ions with radii very much larger than the radius of the solvent molecule, the volume of the ion is related to the crystal radius by the equation:

$$v = (4/3)\ \pi r^3\ N \qquad 2.12,1$$

	Water	Formamide	NMF
Li	112.09	116.2	113.7
Na	86.9	90.5	91.5
K	69.4	72.9	73.9
Rb	63.9	67.3	67.5
Cs	58.7	61.8	62.4
Mg	431.1	-	-
Ca	353.3	360.6	362.7
Sr	321.4	331.2	330.4
Ba	291.6	302.1	302.9
F	120.3	112.5	107.4
Cl	90.4	85.2	82.8
Br	//84.7	80.0	78.2
I	76.7	72.5	70.2

Table 60 : Ion solvation free energies. Unit molality ideal gas hypothetical unit molality solution. (sign reversed).

when the ion and solvent molecules have the same radii, close-packing is assumed in the vicinity of the ions and,

$$v = (2r)^3N \qquad 2.12,2$$

There is a smooth transition between these limiting types of behaviour, and the volume is given by:

$$v = \frac{4\pi N}{3}\left[1 + \left(\frac{3 \times 8}{4\pi} - 1\right)\frac{r_s}{r}\right] r^3 \text{ ml.} \qquad 2.12,3$$

where r_s is the solvent molecule radius. The effective radius of the ion is given by:

$$r_{eff.} = (3v/4\pi N)^{1/3} \text{ cm.} \qquad 2.12,4$$

This equation was derived for ions in aqueous solutions, and Conway showed that it gave results in good agreement with experiment. The use of this equation for ions in non-aqueous solvents is, of course, questionable, although the values obtained (table 61) seem reasonable, and the results obtained using them in this section are in good accord with published data.

	Water	Formamide	NMF
F^-	1.69	1.90	1.93
Cl^-	2.16	2.39	2.43
Br^-	2.33	2.54	2.58
I^-	2.52	2.70	2.74

Table 61 : Effective radii calculated from equations 2.12,3 and 2.12,4 using Pauling crystal radii.

Solvent radii taken as: water 1.38A; Formamide 2.6A; NMF 2.8A

To see what effect the choice of radii might have on the parameters in equation 2.11,1, all the least squares were repeated using the following additional sets of radii: aqueous - Pauling radii, Gourary and Adrian's electron diffraction radii (132), Pauling radii changed by 0.1A, Conway's radii changed by 0.1A; non-aqueous - Conway radii changed by 0.1A, Pauling radii. Rather than tabulate all the data obtained, the values obtained for the intercept A for one ion are given. For the potassium halides in water, in the same order as the radii are listed above, A = 23.2±0.5, 19.7±0.6, 22.0±0.5, 27.4±0.3. For potassium halides in formamide, again in the same order as above: A = 21.1±0.3, 15.7±0.4. Comparison with the values given in table 57, shows that in spite of variations in radius values of nearly 50%, the variation in the intercept, and hence in the values of the solvation enthalpies, is 7 kcals at most. The choice of Conway's radii was made (a) on physical grounds: the solvation enthalpy is expected to depend on a semi-empirical effective radius rather than the crystal radius, (b) the standard deviations on the intercepts are significantly smaller using Conway's radii, (c) the results obtained for the individual ion solvation enthalpies agree well with those obtained previously, and with those obtained theoretically in the next section.

SECTION III

Interpretation

3.1

The first attempt at interpreting the ion solvation energies derived in section 2.11 was by fitting the ion solvation free energies to the same sort of modification of the Born equation as used by Stokes (69 see section 1.2.3). The values of the dielectric constants in the primary solvation sphere were chosen to give the best fit for the alkali metal cations - the values were: water 3.00; formamide 4.00; NMF 4.20. For the sake of consistency with the model used in section 3.3, all the ions have been considered to be surrounded by a primary solvation sphere of radius $r_p + 2r_s$ where r_p is the Pauling radius of the ion and r_s is the radius of the solvent molecule. The values for the latter are given in table 61, and were taken from the work of Somsen (5, 6). From equation 1.2.3,10, using the following values for the macroscopic dielectric constants; water 78.358 (59); formamide 109.5 (62); NMF 171 (57) - values for the quantity μ^{elec}_{solv} were calculated, and are listed in table 62. Also listed are the electrostatic free energies of the gaseous ions μ^{elec}_{gas}. Table 63 contains the theoretical values for the electrostatic solvation free energy, $\Delta\mu_s$, obtained as the difference of μ^{elec}_{solv} and μ^{elec}_{gas} together with a small term to represent the non-electrostatic part of the solvation free energy $\Delta\mu_n$; and the experimental values from table 59. The non-electrostatic contribution was calculated by comparison with the corresponding quantity for the inert gases. Noyes (111) has shown that the solvation free energies of the inert gases can be represented by the equation:

$$\Delta G^o_n = 0.16 + 6.76/r \text{ kcal/mole}$$

By interpolating the Pauling radii of the ions in this equation the solvation free energies of inert species (ie. not charged) of the same size as the ions were obtained - these were taken as the non-electrostatic contributions to the solvation free energies, and are listed in table 64. It was assumed that the same values could be used for the non-aqueous solvents. The different standard state used by Noyes makes a difference of 0.06 kcals per mole to the free energy data, assuming ideal gas behaviour - this difference has been ignored in the calculations.

The agreement between experiment and theory is poor, particularly for the halides where the theoretical values are only just over 50% of the experimental values. It would, of course, be possible to improve the fit if the data by choosing a primary solvation sphere dielectric constant for each ion. However, not only would such a procedure be physically unjustifiable, but in the case of the halides a negative value for the

	μ^{el}_{solv}(water)	μ^{el}_{solv}(F)	μ^{el}_{solv}(NMF)	$-\mu^{el}_{g}$
Na^+	42.8	36.8	35.5	122.8
K^+	27.6	24.7	23.9	99.3
Rb^+	23.9	21.6	21.0	92.2
Cs^+	19.9	18.3	17.9	83.1
Ca^{2+}	162.5	140.1	135.3	448.6
Sr^{2+}	137.0	119.9	116.0	408.9
Ba^{2+}	108.2	96.9	93.9	368.5
F^-	26.8	24.0	23.4	87.0
Cl^-	18.0	16.8	16.4	73.7
Br^-	16.2	13.8	14.9	72.2
I^-	14.0	13.4	13.1	65.1

Table 62 : μ^{el}_{solv} and μ^{el}_{g} values. (The latter from Stokes (69)).

	Water	Formamide	NMF
Na^+	73.1 (86.9)	78.8 (90.5)	80.1 (91.5)
K^+	65.5 (69.4)	69.4 (72.9)	70.2 (73.9)
Rb^+	63.6 (63.9)	65.9 (67.3)	66.5 (67.5)
Cs^+	59.1 (58.7)	60.7 (61.8)	61.1 (62.4)
Ca^{2+}	279.2 (353.3)	301.6 (360.6)	306.4 (362.7)
Sr^{2+}	265.8 (321.4)	282.7 (331.2)	286.8 (330.4)
Ba^{2+}	255.2 (291.6)	266.5 (302.1)	269.5 (302.9)
F^-	55.1 (120.3)	57.9 (112.5)	58.5 (107.4)
Cl^-	51.8 (90.4)	53.0 (85.2)	53.4 (82.8)
Br^-	52.5 (84.7)	54.9 (80.0)	53.8 (78.2)

Table 63 : Continued on page 106

	Water	Formamide	NMF
I^-	47.7 (76.7)	48.3 (72.5)	48.6 (70.2)

Table 63 : Calculated solvation free energies - experimental values in parentheses. (signs reversed).

Li^+	11.3,	Cs^+	4.1,	F^-	5.1
Na^+	7.2,	Ca^{2+}	6.9,	Cl^-	3.9
K^+	5.2,	Sr^{2+}	6.1,	Br^-	3.5
Rb^+	4.7,	Ba^{2+}	5.1,	I^-	3.4

Table 64 : Non-electrostatic contributions to the ion solvation free energies.

dielectric constant would be required! Stokes obtained such good agreement in his paper because the individual ion solvation free energies with which he compared his calculated values were rather different to those derived in section 2.11. To illustrate: his halide data is numerically about 20 kcals per mole smaller, and his alkali metal cation data correspondingly 20 kcals per mole larger. It should also be noted that Stokes had some experimental justification for his choice of dielectric constant. There is no such justification for the values chosen above - they were merely reasonable values chosen to give as good a fit as possible with the experimental data. Even if the agreement between experiment and theory had been very much better, it would not have given much information on the problem in hand - the nature and structure of dilute ionic solutions. In view of this, and in view of the semi-empirical nature of the approach there seems little point in pursuing this method of calculation any further.

3.2

Calculations based on Buckingham's theory of ion - solvent interactions seem to offer the most useful interpretation of solvation energies, but before doing any detailed electrostatic calculation, the theory was used to provide evidence for the correctness of the division of solvation enthalpies into the individual ionic contributions made in section 2.11. The method followed was very similar to that used by Halliwell and Nyberg (49 and section 1.2.4) to obtain the value of the solvation enthalpy of the proton. According to equation 1.2.3,15:

$$\Delta H^{-} - \Delta H^{+} = \frac{2|z|e\theta}{R^{3}} + \frac{135}{64}\sqrt{\frac{2}{3}}\,\frac{\mu\theta}{R^{4}} \qquad 1.2.3,15$$

where the left hand side represents the difference in solvation enthalpies between two ions of opposite charge but of the same size, and R is the sum of the solvent radius and the ionic radius. Equation 1.2.3,15 is written out for tetrahedral co-ordination of the solvent molecules around the ion, but this does not affect the argument. Equation 1.2.3,15 predicts that a graph of ($\Delta H^- - \Delta H^+$) as a function of some power of the reciprocal radius passes through the origin, provided the values of the ion solvation enthalpies are the absolute values - if the ion solvation enthalpies differ from the absolute values by a constant amount, say q, then the graph has an intercept on the ΔH axis equal to 2q.

To obtain values for ($\Delta H^- - \Delta H^+$) the solvation enthalpies were fitted to straight lines of the form:

$$\Delta H^{\pm} = A/r_p + B \qquad 3.2,1$$

using a computerised least squares technique. For the reasons given in section 2.6 the data for lithium were not included. The values obtained for A and B are listed in table 65.

	ΔH^-		ΔH^+	
	A	B	A	B
Water	-184.5±0.29	7.7±0.2	-69.9±0.3	-19.9±0.2
Formamide	-158.3±0.3	-4.1±0.2	-68.6±0.2	-27.1±0.2
NMF	-150.3±0.7	-6.8±0.4	-66.9±0.4	-30.4±0.4

Table 65 : Parameters in equation 3.2,1.

For each solvent values for R were interpolated in the equations for ΔH^- and ΔH^+ (the same value for R in each) to give the solvation enthalpies for a series of (hypothetical) anions and cations of the same radius. These are given in tables 66 to 68 which also give $\frac{1}{2}(\Delta H^{-} - \Delta H^{+})$ (symbol $\frac{1}{2}\Delta.\Delta H$) and the corresponding values of R. The radii of the solvent molecules were the same as those used in section 3.1.

The graph of $\frac{1}{2}\Delta.\Delta H$ vs. $1/R^3$ was found to be linear for water, and a least squares analysis of data showed the intercept to be 0.38 ± 0.02 with the deviation of the points from the line less that 0.5%. This intercept is of the same order of magnitude as the uncertainty in the intercept in the ΔH^{elec}_{solv}(rel) vs. $1/R^3$ plots used to determine the ion solvation enthalpies (see table 57).

The corresponding graphs for the non-aqueous solvents were not linear, and consequently, the data was treated graphically (graph on page 112). The extrapolation is too long for it to be made with any certainty; probably the best that can be done is to say that it is not a strain on the data to make the extrapolation through zero. The uncertainty in the solvent radii (taken as 0.1A) makes the extrapolation even more difficult. The results of this section give some support for the choice of ion solvation enthalpies made in section 2.11. Of course it would have been possible to make the primary division of solvation enthalpies into the ionic contributions using the Halliwell and Nyberg type approach as described above - this has been done for non-aqueous solvents by Somsen (5).

r	1.3	1.4	1.5	1.6	1.7	1.8	1.9	2.0
$-\Delta H^{+}$	73.65	69.81	66.48	63.57	61.00	58.72	56.67	54.84
$-\Delta H^{-}$	134.25	124.11	115.32	107.63	100.85	94.82	89.42	84.56
$-\frac{1}{2}\Delta.\Delta H$	30.30	27.15	24.42	22.03	19.92	18.05	16.37	14.86
R	2.68	2.78	2.88	2.98	3.08	3.18	3.28	3.38

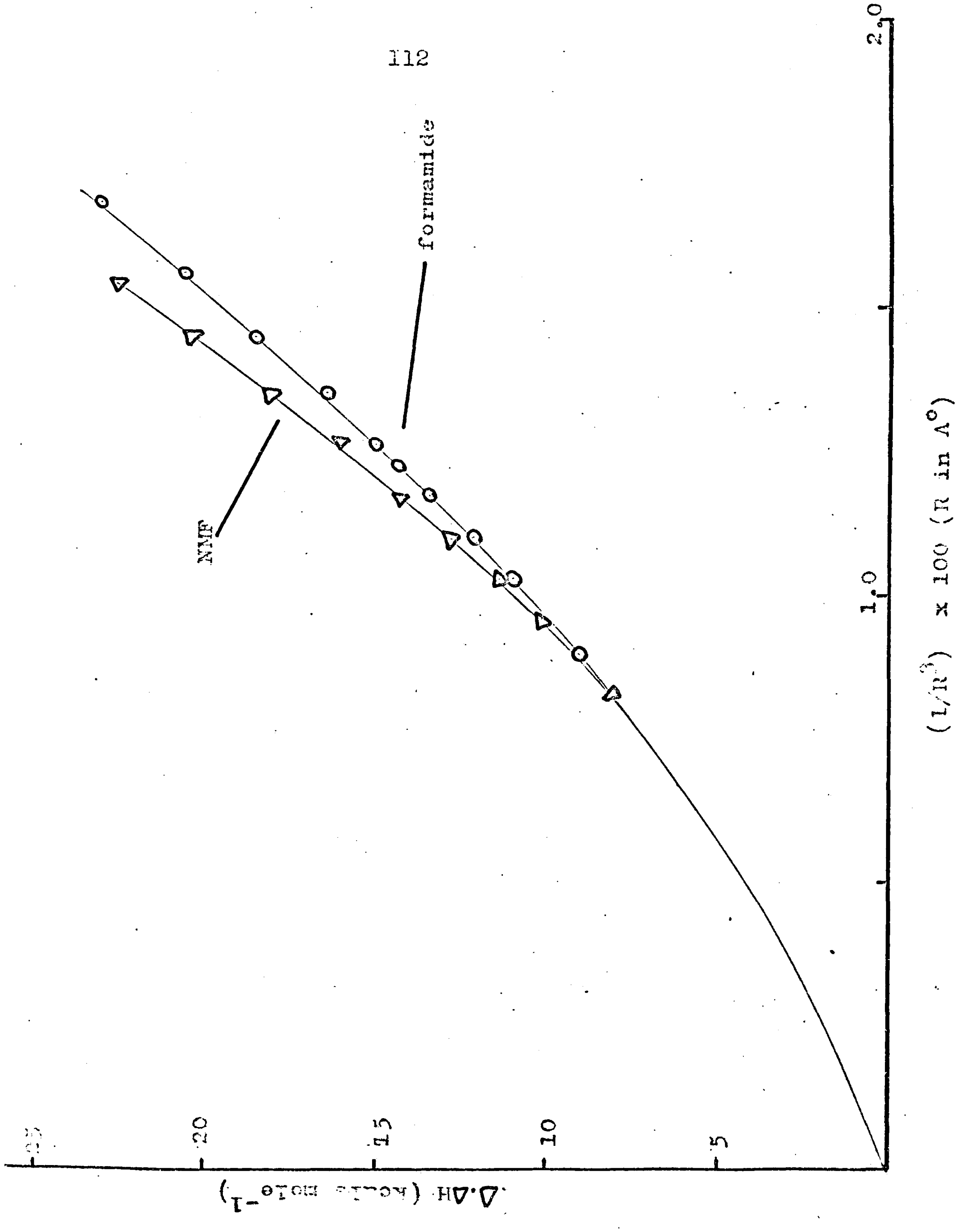
Table 66 : Derivation of $\Delta.\Delta H$ values in water.

r	1.3	1.4	1.5	1.6	1.7	1.8	1.9	2.0
$-\Delta H^{-}$	125.84	117.14	109.60	103.01	97.19	92.02	87.39	83.22
$-\Delta H^{+}$	79.87	76.10	72.83	69.97	67.45	65.20	63.20	61.39
$-\frac{1}{2}\Delta.\Delta H$	22.98	20.52	18.38	16.52	14.87	13.41	12.09	10.91
R	3.9	4.0	4.1	4.2	4.3	4.4	4.5	4.6

Table 67 : Derivation of $\Delta.\Delta H$ values for formamide

r	1.3	1.4	1.5	1.6	1.7	1.8	1.9	2.0
$-\Delta H^-$	122.45	114.19	107.03	100.76	95.24	90.32	85.93	81.97
$-\Delta H^+$	81.92	78.24	75.05	72.26	69.80	67.62	65.66	63.90
$-\frac{1}{2}\Delta . \Delta H$	20.27	17.97	15.99	14.25	12.72	11.35	10.13	9.03
R	4.1	4.2	4.3	4.4	4.5	4.6	4.7	4.8

Table 68 : Derivation of $\Delta . \Delta H$ values in NMF.



$\frac{1}{2}\Delta.\Delta H$ vs. $1/R^3$ for formamide and NMF

But, as it was intended to use Buckingham's theory to make a priori calculations of solvation enthalpies it is rather begging the question to use the same theory to obtain the "experimental" results for comparison.

3.3

This section contains the application of Buckingham's theory to the calculation of ion solvation enthalpies. The first few paragraphs contain a careful statement of the models used and of any assumptions made.

3.3.1

Ions were considered to be polarisable spheres with radii equal to their radii on Pauling's scale (112); they were assumed to retain these radii in solution and in the gas phase.

The structures of the bulk solvents have been discussed previously (section 1.2.1). For the sake of simplifying the calculations, the water molecule is considered to be spherical with a radius equal to half the inter-molecular distance in ice, ie. 1.38A; the molecules of formamide and NMF were considered to be cylindrical with an axis of symmetry parallel to the dipole moment; their radii have been estimated by Somsen (5,6) as 2.6A and 2.8A respectively.

Ions in solution were assumed to exist as solvated complexes, ie. surrounded by a number of permanantly attached solvent molecules - this seems in good accord with Frank and Evan's interpretation of ionic solutions, (see section 1.2.2) and with the idea of primary hydration numbers discussed in the same section. It is rather difficult to decide how many solvent molecules there are in the primary solvation sphere. Previous work of this type has been done assuming values of four or six. e.e Eley and Evan's (73) and Buckingham (75) assumed four; while Moelwyn-Hughes (113) and Verwey (114) assumed six. What little evidence there is available applies to aqueous solutions only: the primary solvation numbers justify four or six (see section 1.2.2) for the alkali metal cations and the higher molecular weight alkaline earth cations; VanEck (55,56) has published a limited amount of X-ray data justifying the value six. For the calculations in this section the value six has been assumed for all the ions this value was chosen because it gave the best fit to the experimental data. This point is taken up again later (section 3.3.4) where some further calculations based on tetrahedral co-ordination are presented, and in sections 3.3.5 and 3.3.6 where theory and experiment are compared. Frank and Evan's idea of a primary solvation sphere in which there is a complete breakdown of the solvent structure suggests that in this region the predominating interactions are those between the ion and the co-ordinating solvent molecules.

If this is the case then the dipoles of the solvent molecules will always be normal to the ion surface since this orientation produces the maximum stabilisation energy; the configuration used in all the calculations in this section is solvent molecules normal to the ion surface for anions and cations.

To gain some insight into what might happen in the secondary solvation sphere, use was made of the entropy data derived in section 2.4. Table 69 contains the solvation entropy data from table 52 together with the entropies of solution of the iso-electronic inert gases taken from Noyes' paper (111) and corrected to apply to the same standard states.

As observed by Frank and Evans (see section 1.2.1) for most of the ions the loss of entropy on hydration is smaller than the loss of entropy on dissolution of the corresponding inert gas in water. Thus most of the ions have a structure breaking effect on water as compared with the inert gases. There is no entropy of solution data for the inert gases in the non-aqueous solvents. but it is unlikely that the values are very different from the values in water. The loss of entropy on solvation of most of the ions (in formamide and NMF) is much greater than the loss of entropy on dissolution of the corresponding inert gas (assumed the same as for water). This suggests that the ions

	Water	Formamide	NMF	Water	
Li^+	28.21	26.01	45.31	12.20	He
Na^+	20.78	28.48	29.88	16.09	Ne
K^+	12.27	21.27	26.67	15.75	Ar
Rb^+	10.40	20.00	26.40	17.13	Kr
Cs^+	8.61	19.11	24.11	19.21	Xe
F^-	25.92	26.82	34.32	16.09	Ne
Cl^-	12.27	19.67	20.47	15.75	Ar
Br^-	8.60	18.80	19.40	17.13	Kr
I^-	3.18	16.28	22.38	19.21	Xe

Table 69 : Minus ion solvation entropies and the entropies of solution of the inert gases in water. Ideal gas unit molality solution, unit activity.

have a greater structure - making effect on the solvents than do the inert gases. The hydration of ions generally (except for Li^+, Na^+ and F^-) involves a net breaking of the water structure, but it would appear from the entropy values that the solvation of ions in formamide and NMF involves the net formation of a considerable amount of structure in the solvent. The reason for this net structure making could be in the fact that the non-aqueous solvents have no three dimensional structure. Thus when an ion enters formamide or NMF it does not have to break up the structure of the solvent to pull solvent molecules into its primary solvation sphere, - this is in contrast to the situation in water - it merely interacts with the solvent molecules at the edges or ends of the sheets or chains of hydrogen-bonded solvent molecules to form a quasi-crystalline structure in the immediate vicinity of the ion. The edge or end molecules that interact with the ion form the primary solvation sphere - the remainder of the interacting molecules (those in the main body of the sheets or chains) form the secondary solvation sphere.

3.3.2

The electrostatic interaction energy between an ion and six solvent molecules was calculated using the theory given by Buckingham (57 and section 1.2.3). In addition to the interactions included by Buckingham, repulsion forces between the ion and the solvent; and quadrupole - quadrupole interactions between the co-ordinated solvent molecules were accounted for.

(a) Repulsion forces.

The results of section 1.2.3 show that the ion-solvent interaction energy may be expressed as a power series in 1/R:

$$U = A/R^2 + B/R^3 + C/R^4 \;.....;.... + N/R^n \qquad 3.3.2,1$$

Here the repulsion energy has been written in the form N/R^n where n and N are constants; this is an approximation since quantum-mechanical considerations show that an exponential function is more appropriate. However, the repulsion energy is a relatively small term, and it is unlikely that the error in using the inverse R function is very significant.

At equilibrium, $dU/dR = 0$; hence:

$$-2A/R^3 - 3B/R^4 - 4C/R^5 - \ldots\ldots\ldots\ldots - nN/R^{n+1} = 0$$

and thus:

$$N/R^n = -2A/nR^2 - 3B/nR^3 - 4C/nR^4$$

Substituting in equation 3.3.2,1

$$U = \frac{A}{R^2}(1 - 2/n) + \frac{B}{R^3}(1 - 3/n) + \frac{C}{R^4}(1 - 4/n) + \ldots\ldots \qquad 3.3.2,2$$

Thus the repulsion energy term can be included by multiplying each factor in $1/R^p$ in the total energy expression by $(1 - p/n)$.

Values for n have been given by Pauling (112) for the repulsion energies in crystals, but since it is difficult to relate the structure of the solvent in the vicinity of the ion to the structure of a crystal in a definite way, the calculations presented below were based on the commonly used value $n = 9$.

In the following equations the repulsion energy factors are all included, and the equations are written for octahedral co-ordination unless otherwise stated.

(b) <u>Ion - dipole interaction energy</u>

The basic equation (cp. equation 1.2.3,11) is

$$U_{i-d} = \frac{-14}{3} \frac{zeN\mu}{R^2} \qquad 3.3.2,3$$

The dipole moments are water 1.84D; formamide 3.71D (115); NMF 3.84D (116). Using these, and substituting the other constants and the relevant conversion factors:

$$U_{i-d} \text{ (water)} = -594.046\ z/R^2$$
$$U_{i-d} \text{ (formamide)} = -1197.777\ z/R^2 \qquad 3.2.2,4$$
$$U_{i-d} \text{ (NMF)} = -1239.748\ z/R^2$$

These equation are written to give U in kcals/mole when R is in angstroms.

(c) <u>Ion-quadrupole interaction energy</u>

$$U_{i-Q} = 4\ z\ e\ \theta\ N/R^3 \qquad 3.2.2,5$$

The quadrupole moments were calculated from equation 1.2.3,15, (details in section 3.3.7) and the values obtained were : water 2.59±0.08 X 10^{-26} esu.; formamide 6.1±0.6 x 10^{-26}esu.; NMF 5.9±1.0 x 10^{-26}esu.

Hence:

$$U_{i-Q} \text{ (water)} = 716.728\ z/R^3$$
$$U_{i-Q} \text{ (formamide)} = 1513.708\ z/R^3$$
$$U_{i-Q} \text{ (NMF)} = 1461.129\ z/R^3 \qquad 3.2.2,6$$

all in kcals/mole.

(d) <u>Ion-induced dipole interactions</u>

$$U_{ind} = \frac{-5\ z^2\ e^2\ \alpha\ N}{3R^4} \qquad 3.2.2,7$$

The polarisabilities used were : water 1.44 x 10^{-24} cm^3 (117); formamide 4.2 x 10^{-24} cm^3 (5); NMF 6.3 x 10^{-24} cm^3 (6)

U_{ind} (water) = $-798.026\ z^2/R^4$

U_{ind} (formamide) = $-2327.577\ z^2/R^4$

U_{ind} (NMF) = $-3491.366\ z^2/R^4$ 3.2.2,8

in kcals / mole.

(e) Dispersion energy

$$U_d = \frac{-3\ I_1\ I_2\ \alpha_1\ \alpha_2\ N}{(I_1 + I_2)\ R^6} \qquad 3.2.2,9$$

The ionisation potentials of the ions were listed in tables 19 and 20. The ionisation potentials of the solvents were : water 12.56 eV (118); formamide 10.2 eV (119); in the absence of an experimental value, the ionisation potential of NMF was taken to equal to that of formamide. The polarisabilities of the ions were taken from a paper by Tessman et al. (120) - the values are listed in table 70.

Li	0.03	Ca	1.1	F	0.64
Na	0.41	Sr	1.6	Cl	2.96
K	1.33	Ba	2.5	Br	4.16
Rb	1.98			I	6.43
Cs	3.34				

Table 70 : Polarisabilities of the ions.

Using this data:

$$U_d\ (\text{water}) = \frac{-1251.262\ I_1}{(I_1 + 12.56)}\ \frac{\alpha_1}{R^6}$$

$$U_d \text{ (formamide)} = \frac{-2963.778\ I_1\ \alpha_1}{(I_1 + 10.2)\ R^6}$$

$$U_d \text{ (NMF)} = \frac{-4445.664\ I_1\ \alpha_1}{(I_1 + 10.2)\ R^6} \qquad 3.2.2,10$$

With the ionisation potentials in eV, and the polarisabilities in A^3, the energies are in kcals/mole.

(f) Interaction energy between the co-ordinated solvent molecules

The equation given here contains an additional term to those in equation 1.2.3,14 - the quadrupole-quadrupole interaction. For details see Appendix I.

$$U_m = \left[\frac{3(12 + \sqrt{2})\mu^2}{4\sqrt{2}\ R^3} - \frac{9(6\sqrt{2} + 1)\ z\mu\theta}{8\ |z|\ R^4} + \frac{(171\sqrt{2} + 18)\theta^2}{32\ R^5} - \frac{(219 + 36\sqrt{2})\alpha\mu^2}{16\ R^6} - \frac{297\alpha^2 I}{256\ R^6} \right] N \qquad 3.2.2,11$$

The data and their sources have been given already.

$$U_m \text{ (formamide)} = 939.613/R^3 - 1731.686z/|z|R^4 + 1554.213/R^5 - 4679.050/R^6 - 1604.532/R^6$$

$$U_m \text{ (water)} = 231.120/R^3 - 406.655z/|z|R^4 + 348.445/R^5 - 394.601/R^6 - 232.266/R^6$$

$$U_m \text{ (NMF)} = 1006.616/R^3 - 1730.108z/|z|R^4 + 1448.114/R^5 - 7519.059/R^6 - 3610.184/R^6 \qquad 3.2.2,12$$

The individual energies and the total energies obtained by substitution of the radius values in

Ion	Dipole -dipole	dipole -quadrupole	Quadrupole -quadrupole	induced dipole - induced dipole	Dispersion	Total
Li^+	29.77	-26.46	11.45	-6.55	-3.85	4.36
Na^+	18.27	-13.80	5.07	-2.45	-1.45	5.64
K^+	11.61	- 7.54	2.38	-1.00	-0.59	4.86
Rb^+	9.88	- 6.08	1.82	-0.72	-0.42	4.48
Cs^+	7.99	- 4.58	1.28	-0.47	-0.28	3.94
Ca^{2+}	17.36	-12.89	4.66	-2.23	-1.31	5.59
Sr^{2+}	14.62	-10.25	3.50	-1.58	-0.93	5.36
Ba^{2+}	11.36	- 7.32	2.30	-0.95	-0.56	4.83
F^-	11.26	+ 7.21	2.26	-0.93	-0.55	19.25
Cl^-	7.12	+ 3.93	1.05	-0.37	-0.22	11.51
Br^-	6.26	+ 3.31	0.85	-0.29	-0.17	9.96
I^-	5.21	+ 2.59	0.63	-0.20	-0.12	8.11

Table 71 : Calculation of the mutual interaction energy between six octahedrally co-ordinated water molecules.

Ion	Dipole -dipole	Dipole -quadrupole	Quadrupole -quadrupole	Induced dipole - induced dipole	Dispersion	Total
Li^+	28.67	-18.48	5.79	-4.36	-1.49	10.13
Na^+	21.00	-12.20	3.45	-2.34	-0.80	9.11
K^+	15.48	- 8.12	2.09	-1.27	-0.44	7.74
Rb^+	13.83	- 6.99	1.71	-1.01	-0.35	7.19
Cs^+	11.90	- 5.72	1.34	-0.75	-0.26	6.51
Ca^{2+}	20.31	-11.67	3.26	-2.19	-0.75	8.96
Sr^{2+}	18.11	-10.01	2.69	-1.74	-0.60	8.45
Ba^{2+}	15.25	- 7.96	2.03	-1.23	-0.42	7.67
F^-	15.13	+ 7.88	2.00	-1.21	-0.42	23.38
Cl^-	10.96	+ 5.12	1.16	-0.64	-0.22	16.38
Br^-	9.98	+ 4.52	1.00	-0.53	-0.18	14.79
I^-	8.71	+ 3.77	0.80	-0.40	-0.14	12.74

Table 72 : Calculation of the mutual interaction energy between six octahedrally co-ordinated formamide molecules.

Ion	Dipole -dipole	Dipole -quadrupole	Quadrupole -quadrupole	Induced dipole - induced dipole	Dispersion	Total
Li^+	25.61	-14.48	3.99	-4.87	-2.34	7.91
Na^+	19.09	- 9.79	2.44	-2.70	-1.30	7.74
K^+	14.29	- 6.65	1.51	-1.52	-0.73	6.90
Rb^+	12.84	- 5.77	1.26	-1.22	-0.59	6.52
Cs^+	11.12	- 4.76	0.99	-0.92	-0.44	5.99
Ca^{2+}	18.49	- 9.38	2.31	-2.54	-1.22	7.66
Sr^{2+}	16.58	- 8.12	1.93	-2.04	-0.98	7.37
Ba^{2+}	14.08	- 6.53	1.48	-1.47	-0.71	6.85
F^-	13.98	+ 6.46	1.45	-1.45	-0.70	19.74
Cl^-	10.27	+ 4.28	0.88	-0.78	-0.38	14.27
Br^-	9.39	+ 3.80	0.75	-0.65	-0.31	12.98
I^-	8.25	+ 3.20	0.60	-0.50	-0.24	11.31

Table 73 : Calculation of the mutual interaction energy between six octahedrally co-ordinated NMF molecules.

equation 3.2.2,12 are listed in tables 71 - 73.

(g) The Born polarisation enthalpy

Although the Born polarisation enthalpy is not a part of the electrostatic interaction energy between an ion and six solvent molecules, it is an important contribution to the theoretical value of the ion solvation enthalpy, so it seemed convenient to include it here. It was calculated from equation 1.2.3,7 as the enthalpy due to the charge on a sphere of radius ($r_p + 2r_s$) in a medium with the solvent macroscopic dielectric constant.

The dielectric constants used were: water 78.358 (59); formamide 109.5 (62); NMF 171 (57). The temperature derivatives of the dielectric constants were; water -0.3595 (59); formamide -0.4 (62); NMF -1.6 (57). Thus:

ΔH_B (water) $= -148.462\ z^2/R$

ΔH_B (formamide) $= -147.885\ z^2/R$

ΔH_B (NMF) $= -149.304\ z^2/R$

The values obtained for the six energy terms (a) - (f) and the Born polarisation enthalpy are listed in table 74 to 76, together with the total for each ion.

3.3.3

Calculation of ion hydration enthalpies

Ion hydration enthalpies were calculated using a modified form of the cyclic process used by Muirhead-gold and Laidler:

Ion	Ion - dipole	Ion - quadrupole	Induced	Dispersion	Mutual	Born	Total
Li^+	-151.53	92.33	- 51.92	-0.53	4.36	-44.19	-151.48
Na^+	-109.4228	56.66	- 27.08	-2.53	5.64	-40.02	-116.75
K^+	- 80.8874	36.01	- 14.80	-3.01	4.86	-36.30	- 94.13
Rb^+	- 72.6252	30.64	- 11.93	-3.11	4.48	-35.01	- 87.56
Cs^+	- 63.0294	24.77	- 8.98	-3.33	3.94	-33.36	- 79.99
Ca^{2+}	-211.5209	107.68	-101.18	-6.24	5.59	-158.36	-364.03
Sr^{2+}	-188.5830	90.65	- 80.42	-6.27	5.36	-152.66	-331.92
Ba^{2+}	-159.41	70.45	- 57.47	-5.84	4.83	-144.49	-291.93
F^-	- 79.13	-34.84	14.16	-0.41	19.25	-36.03	-145.32
Cl^-	- 58.38	-22.10	7.71	-0.79	11.51	-32.49	-109.96
Br^-	- 53.57	-19.41	6.50	-0.81	9.96	-31.52	-101.85
I^-	-47.4038	-16.16	5.08	-0.80	8.11	-30.18	- 91.51

Table 74 : Calculation of electrostatic interaction energies between the ion and six water molecule

Ion	Ion - dipole	Ion - quadrupole	Induced	Dispersion	Mutual	Born	Total
Li^+	-116.97	51.69	-22.20	-0.07	10.13	-25.50	-102.92
Na^+	- 95.04	37.86	-14.66	-0.50	9.11	-24.05	- 87.28
K^+	- 77.55	27.91	- 9.76	-0.81	7.74	-22.65	- 75.12
Rb^+	- 71.95	24.93	- 8.40	-0.93	7.19	-22.14	- 71.30
Cs^+	- 65.08	21.45	- 6.87	-1.13	6.51	-21.46	- 66.58
Ca^{2+}	-185.88	73.22	-56.05	-1.27	8.96	-95.56	-256.58
Sr^{2+}	-172.18	65.28	-48.10	-1.44	8.45	-93.45	-241.44
Ba^{2+}	-153.54	54.97	-38.25	-1.57	7.67	-90.31	-221.03
F^-	- 76.38	-27.28	- 9.47	-0.12	23.38	-22.54	-112.41
Cl^-	- 61.59	-19.75	- 6.15	-0.31	16.38	-21.10	- 92.52
Br^-	- 57.86	-17.98	- 5.43	-0.34	14.79	-20.68	- 87.50
I^-	- 52.86	-15.71	- 4.53	-0.38	12.74	-20.09	- 80.83

Table 75 : Calculation of electrostatic interaction energies between the ion and six formamide molecules.

Ion	Ion - dipole	Ion - quadrupole	Induced	Dispersion	Mutual	Born	Total
Li^+	-107.24	41.60	-26.13	-0.08	7.91	-24.08	-108.02
Na^+	- 88.16	31.01	-17.66	-0.54	7.74	-22.79	- 90.40
K^+	- 72.68	23.21	-12.00	-1.15	6.90	-21.54	- 77.26
Rb^+	- 67.68	20.86	-10.40	-1.04	6.52	-21.09	- 72.83
Cs^+	- 61.50	18.06	- 8.59	-1.29	5.99	-20.48	- 67.81
Ca^{2+}	-172.62	60.07	-67.69	-1.3759	7.66	-90.62	-264.58
Sr^{2+}	-160.54	53.87	-58.54	-1.58	7.37	-88.74	-248.17
Ba^{2+}	-143.97	45.76	-47.08	-1.76	6.85	-85.93	-226.13
F^-	- 71.64	-22.72	-11.66	-0.14	19.74	-21.45	-107.87
Cl^-	- 58.34	-16.68	-7.73	-0.36	14.27	-20.15	- 88.99
Br^-	- 54.95	-15.25	- 6.86	-0.40	12.98	-19.78	- 84.26
I^-	- 50.39	-13.39	- 5.77	-0.44	11.31	-19.24	- 77.92

Table 76 : Calculation of electrostatic interaction energies between the ion and six NMF molecules.

$$\begin{tikzcd}
M(g)^{z+} + 6H_2O(g) \arrow[r, "(2)\ \Delta H^{elec}"] & M(H_2O)_6^{z+}(g) \arrow[d, "\begin{array}{l}(3)\ \Delta H_f^o\ \text{some H-bonds} \\ (4)\ \Delta H_B \\ (5)\ \text{translational contr. to} \\ \Delta H(\text{evap. complex})\end{array}"] \\
M(g)^{z+} + 6H_2O(liq). \arrow[u, "(1)\ 6 \times \Delta H(\text{evap. } H_2O)"] \arrow[r, "\Delta H\ \text{ion hydration}"] & M(H_2O)_6^{z+}(aq)
\end{tikzcd}$$

The ion hydration enthalpy is the sum of the enthalpies (1) to (5).

(1) six times 10.52 kcals per mole (28).

(2) For an ideal gas reaction $\Delta H = \Delta U + \Delta(PV)$.
$\Delta(PV) = RT\Delta n$. In this case $\Delta n = -6$, hence
$\Delta H = \Delta U - 6RT = \Delta U, -3.55$, where ΔU is the interaction energy between the ion and six solvent molecules as obtained in the previous paragraph.

(3)The hydrogen bond energy in liquid water was taken from Pimental and McClellan's book (121) as 3.4 kcals.

In view of the rather open structure of water discussed in section 1.2.1, it seems unlikely that the water molecules in the complex will form all the hydrogen bonds possible with the bulk of the solvent (two per molecule). Muirhead-Gold and Laidler (74) in their similar treatment assumed that the complex formed 12 x 0.448 hydrogen bonds, where 0.448 is the fraction of the possible number of hydrogen bonds that are formed in the bulk of the solvent. (122) However, since the structure of the water in the secondary hydration sphere is expected to be rather modified (see section 1.2.2) it is difficult to relate the number of hydrogen bonds formed by the complex to the average number of hydrogen bonds formed by a water molecule in the bulk of the solvent.

In this treatment it was assumed that the hydrogen bond capacity of the solvent molecules in the complex was nearly saturated, and that ten out of the possible twelve hydrogen bonds were formed.

(4) included in the previous paragraph.

(5) Estimated by comparison with inert gas data, Noyes (111) has shown that the enthalpies of solution of the inert gases in water can be represented by the equation:

$$\Delta H = -10.83 + 14.13/r \qquad 3.3.3,1$$

Values for enthalpy change (5) were obtained by interpolating values for the radii of the complexes ($r_p + 2r_s$) in equation 3.3.3,1. The values obtained are listed in table 77.

Li	-6.63	Na	-7.03	K	-7.38
Rb	-7.50	Cs	-7.66	Ca	-7.07
Sr	-7.20	Ba	-7.40	F	-7.41
Cl	-7.74	Br	-7.83	I	-7.96

Table 77 : Data for the translational contribution to the latent heat of condensation of hydrated complexes from equation 3.3.3,1.

Table 78 gives the sums of enthalpy changes (1), (3) and (5) denoted by ΔH_c, the total theoretical values for the hydration enthalpies, and the experimental values from the table 59 for comparison.

	ΔH_c	$-\Delta H$ ion hydration	
		Calc	exp.
Li^+	22.5	132.6	(120.5)
Na^+	22.1	98.3	(93.1)
K^+	21.7	76.0	(73.0)
Rb^+	21.6	69.6	(67.0)
Cs^+	21.4	62.1	(61.3)
Ca^{2+}	22.0	345.6	(369.8)
Sr^{2+}	21.9	313.6	(337.5)
Ba^{2+}	21.7	273.8	(304.4)
F^-	21.7	127.2	(128.0)
Cl^-	21.4	92.1	(94.0)
Br^-	21.3	84.2	(87.3)
I^-	21.1	76.0	(77.6)

Table 78 : Theoretical hydration enthalpies obtained as the sum of the enthalpy changes in column 2 and the total energies in table 74 increased in magnitude by 6RT. Experimental values in parentheses.

3.3.4

Tetrahedral co-ordination

In order to consider the possibility of tetrahedral co-ordination of the water molecules in the hydrated complex, use was made of Somsen's calculations of the ion-solvent interaction energy (5). Somsen's calculations were made in exactly the same manner as those presented in the last section except that slightly different radii and quadrupole moments were used. Somsen made calculations for both tetrahedral and octahedral co-ordination in the hydration sphere, and since his values for the electrostatic interaction energy for the octahedral case are in good agreement with those obtained in table 74, it is probably fair to adopt his tetrahedral data directly. Using the same cycle written for tetrahedral co-ordination, and assuming that the hydrated complex forms all of the possible eight hydrogen bonds with the bulk of the solvent, the results are listed and compared with the experimental values in table 79.

3.3.5

Discussion of ion - hydration enthalpies

The di-valent ions excepted, the agreement between experiment and theory is most encouraging. Particularly for the halides, the best agreement was obtained using co-ordination number six. For the alkali metals, the mean of the tetrahedral and octahedral

	$-(U^{elec} + \Delta H_B)$	ΔH_c	$-\Delta H$ ion hydration calc.	 exp.
Li^+	103.5	8.3	97.6	(120.5)
Na^+	87.3	7.9	81.8	(93.1)
K^+	74.2	7.5	69.1	(73.0)
Rb^+	69.7	7.4	64.7	(67.0)
Cs^+	64.9	7.2	60.1	(61.3)
F^-	121.4	7.5	116.3	(128.0)
Cl^-	90.6	7.2	85.8	(94.0)
Br^-	83.8	7.1	79.1	(87.3)
I^-	74.4	6.9	69.9	(77.6)

Table 79 : Calculation of hydration enthalpies for tetrahedral co-ordination. The first column of figures is the electrostatic interaction energy plus the Born Polarisation enthalpy taken directly from Somsen's paper (5). The experimental values are from table 59.

values agrees rather better with the experimental data, suggesting that a more appropriate co-ordination number for these ions is five - this would be quite a reasonable value considering the primary hydration numbers given in table 3. For the di-valent ions the experimental values are slightly underestimated by the theory. This suggests that a higher co-ordination number should be used for these ions. Some preliminary calculations using a co-ordination number of eight for barium indicated that a value of about -310 kcals would be obtained (experimental value: -304.4)

3.3.6

Calculation of ion solvation enthalpies

The solvation of ions in formamide and NMF has been shown to involve no breaking of the solvent structure; the interaction occuring between the ion and the edge or end molecules of the sheets or chains that these solvent form in the liquid state. It thus becomes rather hard to apply the same cyclic process that was used to calculate the hydration enthalpies, because there is no data available to calculate the enthalpy required to remove say, a sheet of formamide molecules from the liquid to the gas, Hence,a rather different approach was adopted: the solvation enthalpy of an ion was considered to consist of two parts. (a) A non-electrostatic contribution; ΔH_n taken as equal to the hydration enthalpy of the inert gas nearest in size to the ion (111). (b) The electrostatic part, which was taken as the electrostatic interaction energy between the ion and six solvent molecules as calculated in tables 75 and 76. The change in the product PV for a reaction of this type occuring in the solution phase is small (in kcals, at least) and the energy change in the reaction may be identified with the enthalpy change. The values for the enthalpy changes

(a) and (b) together with their sum, the theoretical ion solvation enthalpy, and the experimental values for comparison, are given for each ion in tables 80 and 81.

	$-U^{elec}$	ΔH_n	$-\Delta H$ ion solvation Calc.	 Exp.
Li^+	102.9	-2.4	105.3	(123.9)
Na^+	87.3	-2.4	89.7	(99.0)
K^+	75.1	-2.4	77.5	(79.2)
Rb^+	71.3	-2.4	73.7	(73.3)
Cs^+	66.6	-2.4	69.0	(67.5)
Ca^{2+}	256.6	-2.4	259.0	(378.2)
Sr^{2+}	241.4	-2.4	243.8	(348.8)
Ba^{2+}	221.0	-2.4	223.4	(317.5)
F^-	112.4	-2.4	114.8	(120.5)
Cl^-	92.5	-2.7	95.2	(91.1)
Br^-	87.5	-2.7	90.2	(85.6)
I^-	80.8	-5.0	85.8	(77.3)

Table 80 : Calculation of solvation enthalpies in formamide.

The Born polarisation enthalpy has been included in U^{elec}.

	$-U^{elec}$	$-\Delta H$ ion solvation Calc.	Exp.
Li^+	108.0	110.4	(127.2)
Na^+	90.4	92.8	(100.4)
K^+	77.3	79.7	(81.8)
Rb^+	72.8	75.2	(75.4)
Cs^+	67.8	70.2	(69.6)
Ca^{2+}	264.6	267.0	(385.0)
Sr^{2+}	248.2	250.6	(352.7)
Ba^{2+}	226.1	228.5	(323.3)
F^-	107.9	110.3	(117.6)
Cl^-	89.0	91.7	(88.9)
Br^-	84.3	87.0	(84.0)
I^-	77.9	82.9	(76.9)

Table 81 : Calculation of ion solvation enthalpies in NMF.

As with the hydration enthalpies, the fit is goes for the mono-valent ions, but rather poor for the di-valent ones. The reason is probably the same as in the aqueous case, and a change of co-ordination number to eight would bring the values up by about 70 - 80 kcals. The values for Li^+, Na^+ and F^- are somewhat under-estimated by the theory. Table 69 shows that all of these ions have large negative entropies of solvation, indicating a considerable amount of structure making in the solution. It is possible that these ions, which have the largest negative solvation entropies, cause some additional hydrogen bond formation in the solvent. If this were the case then it would be necessary to include in the theoretical solvation enthalpies the enthalpy of formation of a number of hydrogen bonds. Such a procedure would give slightly larger (numerically) theoretical solvation enthalpies for the ions mentioned and better agreement with the experimental values.

3.3.7

Estimation of the solvent quadrupole moments

One of the minor failings of the type of electrostatic calculation just presented is the fact that there are no experimental values for the solvent multipole moments. Fortunately, contributions from octupole and higher moments are relatively small as pointed out in section 1.2.3. The quadrupole moments were calculated from equation 1.2.3,15 using the data in table 66 - 68.

(a) water. Using the physical constants and appropriate conversion factors (solvent parameters as in section 3.3.2), and rearranging:

$$\Theta = \frac{\Delta . \Delta H \times 4.1840 \times 10^{-27}}{(-231.5675/R^3 + 131.3867/R^4)}$$

With R in Angstroms, and $\Delta . \Delta H$ in kcals per mole, Θ is given in esu. The values of Θ obtained at different radii are shown in table 82.

R	2.68	2.88	3.18	3.38
$\theta \times 10^{-26}$	2.67	2.63	2.55	2.49

Table 82 : Quadrupole moment of water.

The mean value is $\underline{\theta = 2.59 \pm 0.08 \times 10^{-26} \text{ esu}}$.

(b) Formamide.

$$\theta = \frac{\Delta .\ \Delta H \times 4.1840 \times 10^{-27}}{(-231.5675/R^3 + 264.9155/R^4)} \text{ e.su.}$$

R	3.9	4.1	4.3	4.5
$\theta \times 10^{-26}$	7.0	6.4	5.8	5.3

Table 83 : Quadrupole moment of formamide.

The mean value is $\underline{\theta = 6.1 \pm 0.6 \times 10^{-26} \text{ esu}}$.

(c) NMF.

$$\theta = \frac{\Delta .\ \Delta H \times 4.1840 \times 10^{-27}}{\left(-\frac{213.5675}{R^3} + \frac{274.1990}{R^4}\right)}$$

R	4.1	4.3	4.6	4.8
$\theta \times 10^{-26}$	7.1	6.3	5.4	4.8

Table 84 : Quadrupole moment of NMF.

The mean value is $\underline{\theta = 5.9 \pm 1.0 \times 10^{-26} \text{ esu}}$.

Section IV

Experimental

4.1

Preparation of materials

(a) Formamide

Formamide, supplied by BDH Ltd., was purified using the method of Verhoek (123). This involved distillation under reduced pressure, while being maintained just alkaline to bromothymolblue by the addition of caustic soda pellets. The distillation was done twice at about 0.5mm of mercury, and the product obtained had specific conductance of 1 x 10^{-4} ohm^{-1} cm^{-1} (literature value 5 x 10^{-5} (123)). The water content, determined by a Karl Fisher titration, was always less than 0.04%. Somsen has found that a small percentage of water has a negligible effect on the heats of solution (2).

(b) N-methylformamide

NMF (Hopkins and Williams) was mixed with about 10% by weight of ethanol. The ethanol, together with impurities such as water, dimethylamine etc., was distilled off as an azeotropic mixture at about 0.5mm. The residue was then distilled at the same pressure, and maintained just alkaline to bromothymolblue throughout. The product after one such treatment had a specific conductance of less than 1 x 10^{-6} $ohm^{-1}cm^{-1}$, and a water content of less than 0.02%. The maximum specific conductance of the NMF used by Held and Criss for heat of solution measurements was 8 x 10^{-6}. (8).

(c) N,N-dimethylformamide

DMF was purified in essentially the same way as NMF. The differences were (a) the DMF - ethanol mixture was maintained alkaline to bromothymol blue during the entire distillation, (b) the impurity azeotrope was distilled off at atmospheric pressure using a 60cm. insulated column packed with single turn helices, (c) the main distillation was done at water-pump pressure. After one distillation the specific conductance was 0.3 x 10^{-6} $ohm^{-1}cm^{-1}$ (literature values 0.03 - 1.83 x 10^{-6} (45)), and the water content less than 0.02%.

After purification, all solvents were stored in the dark and in a refrigerator to prevent auto-decomposition. Precautions were taken to minimise the exposure of the solvents to the air during transfer to the calorimeter. A check on the water content of several samples after calorimetry showed the water content had increased by only 0.01%.

(d) Group 11a chlorates.

The samples used for calorimetry were prepared by dehydrating the commercial hydrates at 100°c at water-pump pressure over silica gell. (the barium salt was recrystallised from water first). Analysis for chlorate showed the following purities: $Ca(ClO_3)_2$ 99.2%; $Sr(ClO_3)_2$ 99.0%; $Ba(ClO_3)_2$ 99.5%. The magnesium salt decomposed on dehydration.

In an attempt to prepare these salts with higher purities for the isopiestic measurements, the calcium chlorate was recrystallised by slow evaporation of a concentrated aqueous solution (filtered) over sulphuric acid. The resulting hydrate was dehydrated as above and analysis for chlorate showed 100.7% of the theoretical amount. Strontium chlorate was prepared by reaction of chloric acid (aqueous) and strontium carbonate, both of the purest quality available. The resulting solution was evaporated slowly over sulphuric acid to give crystals which were recrystallised in the same way as calcium chlorate, above. The final product was dried over calcium chloride in a vacuum desiccator for several days, and was found to be 99.5% pure.

Commercial barium chlorate was recrystallised twice from water, and the crystals obtained were dried for 48 hours on a water-pump over calcium chloride ($4H_2O$). analysis showed $Ba(ClO_3)_2.H_2O$ 100.6%.

(e) Group lla bromates.

Commercial samples were recrystallised from water-ehtanol mixtures and were dried at 125°C on a water-pump vacuum. Analysis for bromate gave: $Ca(BrO_3)_2$

100.0%; $Sr(BrO_3)_2$ 99.9%; $Ba(BrO_3)_2$ 100.1%. The magnesium salt decomposed on drying. The exact details of the recrystallisations were: Sr and Ba salts, main solvent water using ethanol to reduce the solubility at the boiling point; Ca bromate, a saturated solution in water, excess ethanol added, and on standing in the cold for about twelve hours, crystals separated.

(f) Magnesium bromide

Equimolar proportions of magnesium hydrate hexahydrate and ammonium bromide were moistened with a little aqueous hydrogen bromide. The mixture was dried on a water-pump vacuum at 200°C overnight, after which the ammonium bromide was sublimed off at about 400°C. The residue consisting of crude anhydrous magnesium bromide, was transferred to a silica tube which was then evacuated and sealed. The end of the tube containing the residue was maintained at about 800°C, and over a period of several days crystals of magnesium bromide distilled into the cooler parts of the tube. Bromine analysis showed 99.9% of the theoretical amount.

(g) Magnesium iodide.

The preparation was by reaction between the elements using a method similar to that used by Biltz and Hüttig (124). A mixture of iodine and magnesium was placed at the bottom of a sealed and evacuated hard glass tube. The whole tube was placed in a furnace and heated to about 600°C for several days. Most of the elements reacted during this period, and the product was purified by shaking the crude material into one end of the tube, and subliming it by heating at about 600°C. After a few days, crystals of magnesium iodide (analysis for iodine showed 100.1%) appeared on the cooler parts of the tube. The crystals were a pure white colour, and showed no traces of free iodine.

(h) Ca, Sr, and Ba chlorides.

These were all prepared by dehydration of the analaR hydrates in a slow stream of anhydrous hydrogen chloride. The process was carried out over a period of a week, the temperature being gradually increased from room temperature to 500°C. Finally the products were freed of excess hydrogen chloride using a rapid stream of hot, dried, oxygen-free nitrogen. Chloride analysis showed: $CaCl_2$ 99.8%; $SrCl_2$ 99.6%; $BaCl_2$ 100.2%.

(i) Calcium bromide

Calcium bromide hexahydrate was dehydrated in a slow stream of anhydrous hydrogen bromide following a similar procedure as that used for calcium chloride. The product was found to contain 99.8% of the theoretical amount of bromine. The hydrogen bromide was obtained from a cylinder, but was purified before use by passage through a trap maintained at -65°C using a chloroform/liquid nitrogen slush mixture. It was necessary to make a special piece of apparatus entirely of glass for transferring the hydrogen bromide since hydrogen bromide attacked rubber, P.V.C. and similar materials forming volatile derivatives which were absorbed by the calcium bromide.

(j) Sr and Ba bromides

These were obtained by dehydration of the hydrates under a water-pump vacuum at elevated temperatures, The temperature and times used were: Sr salt, overnight at 180°C, followed by a few hours at 300°C; Ba salt, overnight at 80°C, 24 hours at 120°C, a few hours at 300°C. In both cases the drying agent used was silica gell. Analysis: $SrBr_2$ 100.6%, $BaBr_2$ 100.0%, based on the halogen content.

(k) Magnesion oxide.

Heating the analaR salt for a few hours at about 1000°C gave a material which analysed as 100.1% MgO (acidimetric).

(l) Sodium fluoride

A saturated aqueous solution of analaR sodium fluoride was treated with a few per cent of potassium chloride to remove silica as potassium fluosilicate (125). After filtration, the sodium fluoride was precipitated by the addition of iso-propanol. After drying for aeveral days at 200°C, fluoride analysis showed 100.4% of the theoretical amount.

(m) Tetra n-propylammonium iodide

A double recrystallisation from analaR acetone followed by drying at 60°C over silica gell under a water-pump vacuum for a few days, gave a product with 101% of the required iodine content.

(n) Tetran-butylammonium iodide

The treatment was similar to that used for the propylammonium salt, except that the solvent used for the recrystallisation was a mixture of ether and methylethyl ketone. Analysis showed 100.4% of the theoretical iodine content.

Storage and handling

After preparation, all salts were handled in a glove bag filled with dry nitrogen. The dry nitrogen was generated by boiling liquid nitrogen (126).

All the water sensitive materials were stored in sealed vessels in a desiccator over phosphorus pentoxide. The desiccator was kept in the dark.

4.2

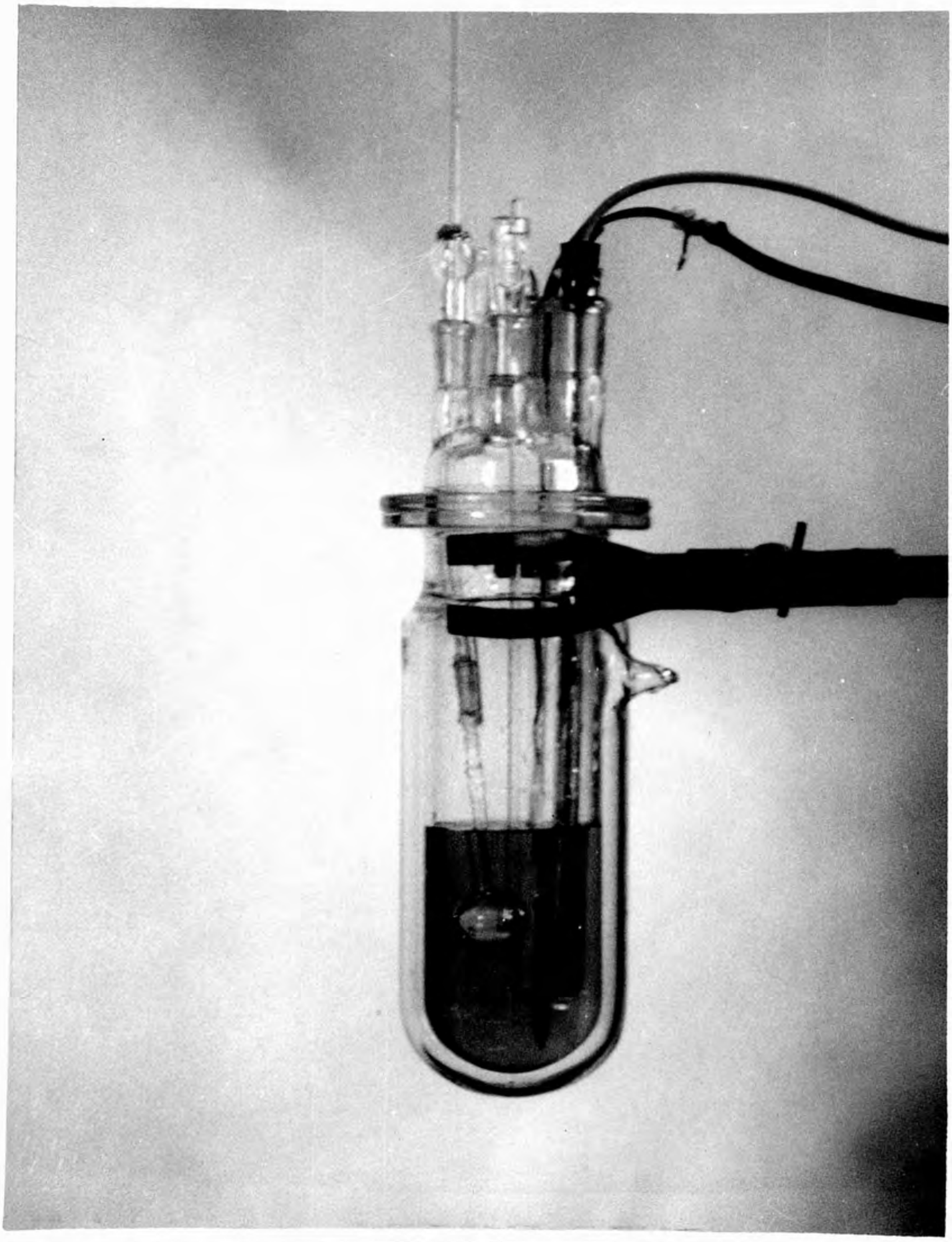
The calorimeter

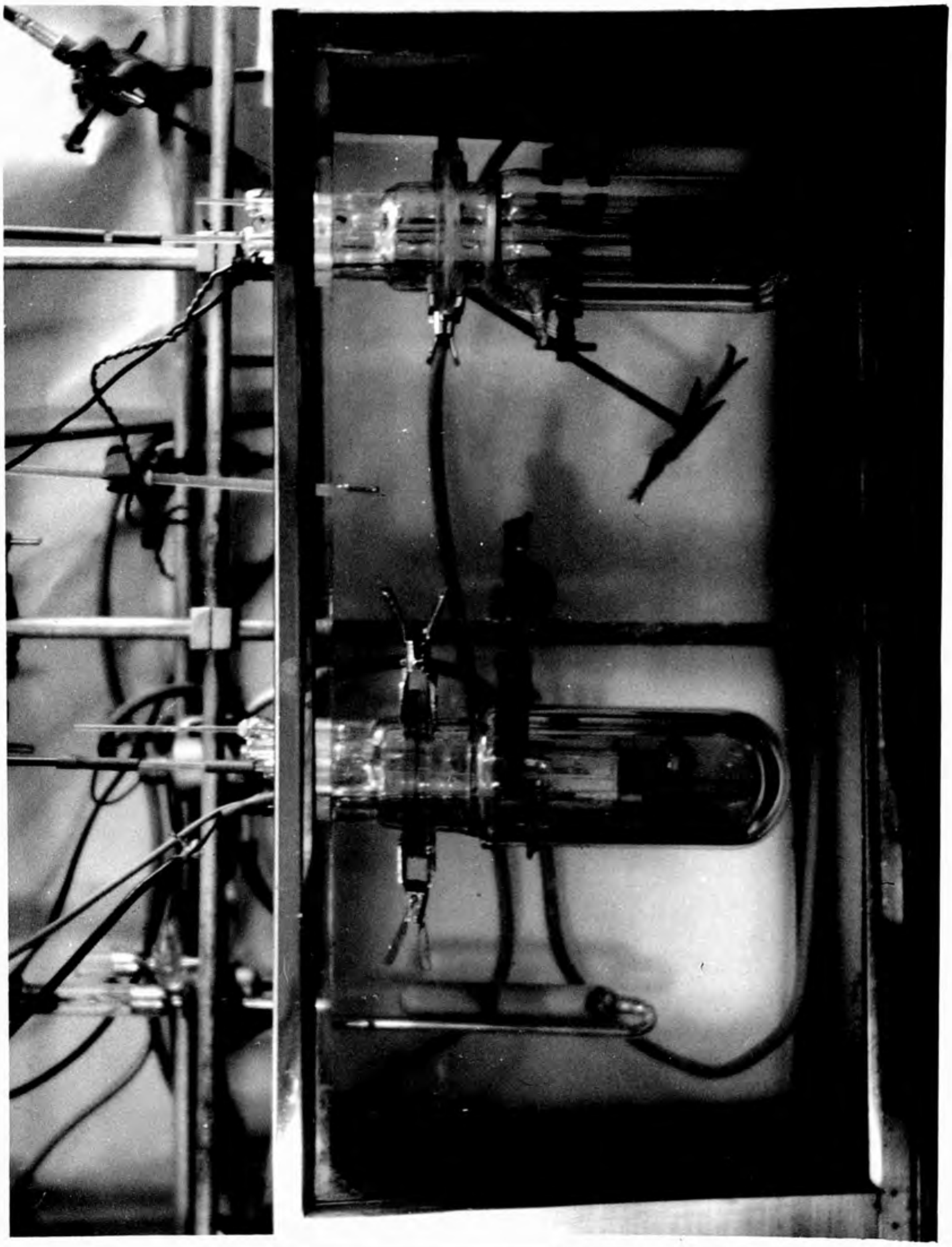
The calorimeter was constructed out of a cylindrical flanged glass Dewar Vessel with a capacity of nearly half a litre. The lid was fitted with several quickfit female joints of various sizes to take the necessary inserts. The photographs show a pair of calorimeters as used in a thermostat, and a close-up of a single calorimeter showing the detailed construction and the inserts.

The samples were held in fragile glass ampoules made from B5 sockets. These were supported on a B5 cone/precision glass rod and sleeve arrangement designed so that the ampoules could be held just under the surface of the calorimeter liquid during equilibration, and could be pushed down into the rotating stirrer blades for breakage. It was sometimes found convenient to construct the ampoules out of larger sockets (B7, say), particularly when working with samples of low density.

The stirrer was made out of a piece of precision glass rod using the corresponding precision glass tube mounted in a B14 cone as the support. The stirrer was driven by a constant-speed 1/30 horse-power electric moter supplied by Parvalux Ltd. The motor had a drive shaft at each end, and, by using flexible drive to the calorimeters, the stirrers for a pair of calorimeters were driven off the same motor. The calorimeters were entirely immersed in a thermostat kept at 25.00 ± 0.01°C.

Temperature measurement was by a thermister arranged as one arm of a conventional d.c. Wheatstone's Bridge. The other arms of the bridge consisted of two fixed resistors and a Muirhead decade box (smallest divisions 0.1 ohm). A scalamp galvanometer





(7902/s, W.G. Pye &Co. Ltd.) was used as the detector, and with an F53 thermistor supplied by the Standard Telephone and Cable Co. Ltd., temperature sensitivity was about 0.001°C.

The resistance-temperature relation for a thermistor has been shown to be of the form:

$$R = A \exp (B/T)$$

or, more accurately:

$$R = AT^{-C} \exp(D/T)$$

where A, B, C and D are constants for each thermistor (127). To use these relations it is necessary to determine the values of the constants by calibration against another thermometer. However, if it can be arranged that the temperature changes in the reaction and calibration are nearly equal, and that the temperature of the calorimeter at the start of the calibration is close to the temperature at the start of the reaction, then the expression of the ratio of the temperature changes takes the convenient and simple form:

$$\frac{\Delta T_1}{\Delta T_2} \doteq \frac{\log R_1/R_2}{\log R_3/R_4}$$

where R_1 and R_2 are the initial and final resistances of the reaction period, and R_3 and R_4 the corresponding resistances of the calibration period. It was found convenient to use this simpler expression for all the calorimetric work presented.

It is, of course, necessary to correct for any heat losses from the calorimeter. This was done from a series of time/resistance readings, using a graphical procedure. Resistance readings were taken at half minute intervals from five minutes before the reaction was started until at least five minutes after the reaction had finished, and were used to construct a resistance vs. time curve. In the case of an instantaneous reaction, the after period line was back-extrapolated to the time at which the reaction occured, and the resistance change was read off from the graph. For a reaction taking longer than the interval between resistance readings, Dickinson's equal area method was used (128). Temperature correction methods in calorimetry have been reviewed recently by Macleod (129) who concluded that "Dickinson's method can be recommended for calorimetric work where a precision of about 0.2% is acceptable."

In many reaction it was very helpful to follow the course of the reaction as it occured. Hence the temperature changes were monitored using a miniature platinum resistance thermometer (100ohm, Degussa) coupled to a six inch pontentiometric recorder (sensitivity 0.01°C).

The system was calibrated by electrical heating. Two different designs were tried for the heater. Both were constructed from an extended B14 male joint, with the end dipping into the calorimetric fluid being closed with about a ten centimetre length of thin-walled glass tubing. In the first design, which was used for most of the work, the heating element was a coil of Constatin wire (ca. 25 ohms per foot) wound on a former made from thin glass tubing. The coil was supported on thick insulated copper leads which also carried the current, and good thermal contact was ensured by filling the botton ten centimetres of the heater tube with oil. In the later design the former was made from brass rod about fifteen centimetres long, and of a diameter to fit the glass heater tube snugly; The rod also served as one of the current conductors. Insulation was provided by covering the rod with a layer of polyurethane lacquer. The heater wire was wound into grooves specially cut in the end of the rod, and were sealed into place and insulated by another coating of polyurethane lacquer. The lower end of the heater tube was filled with mercury to provide really good thermal contact. The main advantage of this design was its mechanical stability: it was possible to remove the heater element from the tube as often as needed with no chance of damaging the windings. In the first design the wires were supported mainly by their own tension and could easily be displaced and perhaps shorted by a small movement of the supporting wires. Also, the new design had a much faster thermal response; as soon as the heater switch was turned off the heating stopped, instead of there being a lag of perhaps several minutes as with the old design.

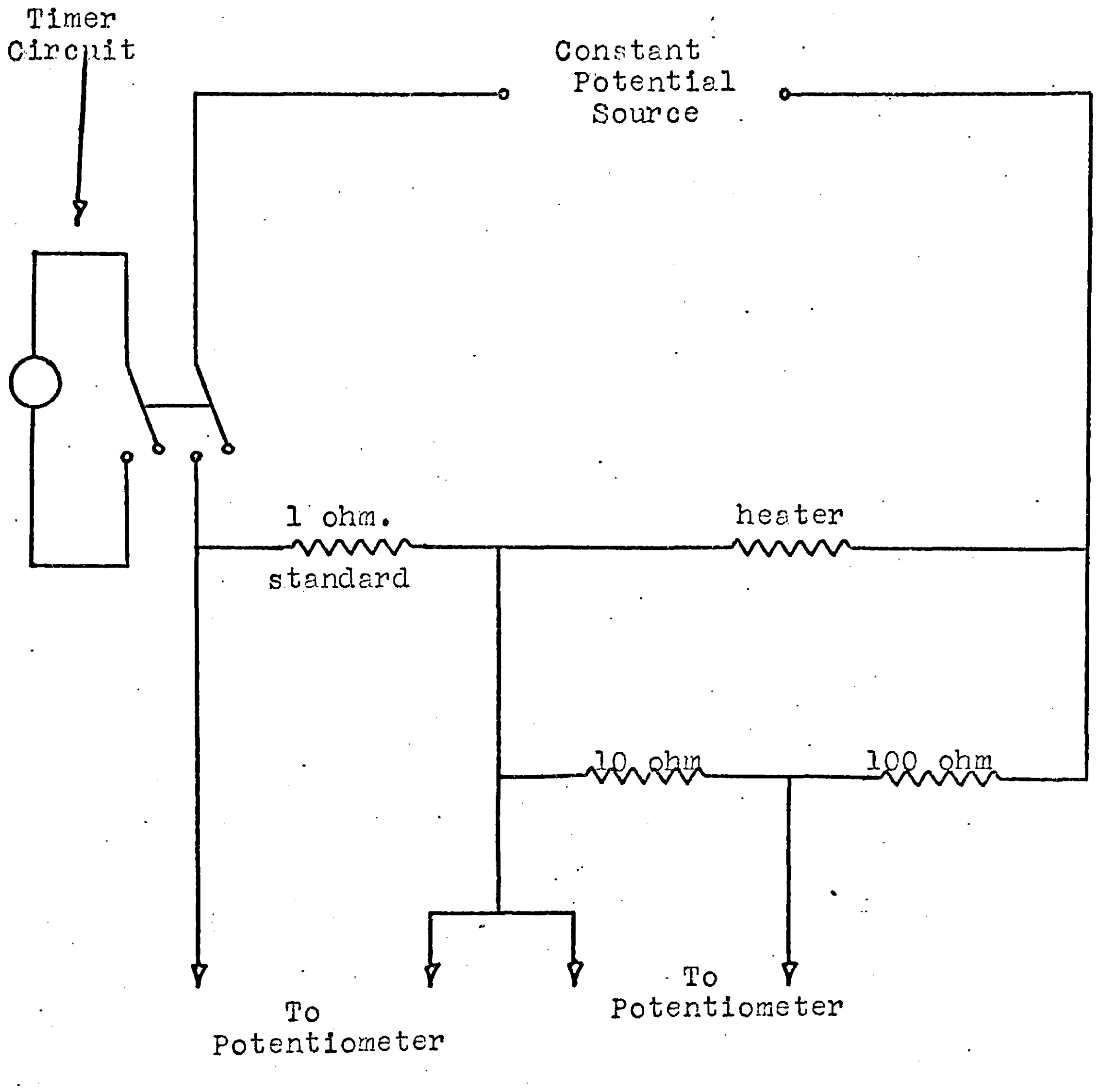
The power through the heater was measured by comparing the potential developed across the heater with potential across a standard resistance in series, using a potentiometer. The circuit used is shown in the figure on page 153. The resistors for the potential dividor were supplied by Arcol Precision Resistors (2W. tolerance 0.025%). The potentiometer was a Tinsley type 3387B used in conjuction with a Pye Scalamp galvanometer, giving a sensitivity of 0.00005V. The current to drive the heater was obtained from a constant potential source supplied by J. Langham Thompson Ltd. The standard resistance was a one ohm standard (0.99996ohm) supplied by W.G. Pye Ltd.

If the suffix 1 refers to the small resistance of the potential divider, 2 to the larger and s to the standard resistance, then the power output is given by:

$$P = \frac{V_1 (R_1 + R_2)}{R_1} \left[\frac{V_s}{R_s} - \frac{V_1}{R_1} \right] \quad \text{joules}$$

or, substituting the values used,

$$P = 11V_1 (V_s - V_1/10)$$



Circuit used for measuring power input to the heater

The heating period was timed using a synchronous electric timer accurate to 0.02 secs, connected to the heater circuit via a two way switch, so that the timer was switched on automatically with the heater.

The expression used for the calculation of an enthalpy change has the form:

$$\Delta H = \frac{\log(R_1/R_2) \text{ x } P \text{ x time x } f \text{ x M.W.}}{\log\,(R_3/R_4)\ (\text{wt. of sample}) \text{ x } 4.1840 \text{ x } 1000}$$

Where f is factor (ca. 0.98) correcting for the heat generated in the heater lead, and H is in kcals per mole. The use of this expression is illustrated below when the data obtained in an actual **run** are given.

Procedure: When being used with non-aqueous solvents the calorimeter bodies were dried in an oven at 200°C and allowed to cool in a desiccator before use; precautions were taken to minimise the exposure to the atmosphere of the inside of the calorimeter during loading. Ampoules were similarly dried before use, and were loaded in a glove bag filled with dried nitrogen.

After loading, the calorimeter was placed in the thermostat, and the temperature of the contents of the calorimeter was brought up to 25°C by electrical heating. Withthe stirrer running, the system was left for an hour at least (usually several hours) so that it could come to themal equilibrium. It was usually possible to start a reaction or calibration with no variation of temperature with time over the five minute pre-reaction period. After an exothermic reaction it was necessary to cool the contents of the calorimeter back to 25°C for the calibration. A further insert was included in the calorimeter for this purpose, consisting of a glass tube with its sealed end dipping into the calorimetric fluid, down which liquid nitrogen was poured as required. After cooling, the calorimeter was again left for aperiod of hours to re-equilibrate. In the case of an endothermic reaction, it was necessary to start the reaction at a temperature above 25°C, such that the final temperature was 25°C. After the reaction had occured the thermostat temperature was readjusted as that the calibration started at 25°C.

The accuracy and precision of the calorimeter were checked using two standard reactions, one exothermic, the other endothermic. For the enthalpy of solution of potassium chloride in water at 25°C and a mean solvent/solute mole ratio (N) of 200, the mean of eight observations was 4.22±0.01 kcals/mole (literature value 4.200±0.009, (133)). For the enthalpy of solution of tris-(hydroxymethyl)aminomethane in 0.1M aqueous HCl at N = 600, the mean of twelve observation was -7.15±0.05 kcal/mole (literature value at N = 1350, 7.107±0.004 (134)).

The enthalpy of dilution of THAM has been shown to be negligible (134). The details of the individual determinations are shown in tables 85 and 86.

T	N	ΔH_s
25.0	333	4.22
25.0	325	4.20
25.1	148	4.19
25.0	216	4.22
24.0	230	4.21
24.9	458	4.24
25.0	556	4.22
24.9	506	4.21

Table 85 : Data for the heat of solution of KCl in water.

T	N	ΔH_s
25.0	978	-7.20
25.0	780	-7.11
25.0	1031	-7.15
24.9	886	-7.10
25.0	793	-7.20
25.0	732	-7.04
25.0	670	-7.17
24.9	754	-7.19
25.0	718	-7.20
25.0	780	-7.14
25.0	728	-7.17

Table 86

Table 86 : Data for the heat of neutralisation of
THAM in dilute hydrochloric acid.

A calculation of the maximum accuracy to be expected from the calorimeter (135) has shown that for temperature changes between a third of a degree and one degree, the uncertainty (assuming ideal conditions and pure reagents etc.) in an enthalpy of solution is 0.5% to 0.25%. In the above standard reactions, both the spread of results, and the agreement with the literature values are within these limits.

To clarify the method of using the calorimeter, and to illustrate the method of calculation, the observations made in a typical determination are given in the form of a log.

Heat of solution of $CaCl_2$ in NMF.

Reaction

Time	Resistance	Remarks
0	3235.8	Start of pre-reaction period
½	3235.8	
1½	3235.9	
2	3235.9	
2½	3235.9	
3	3235.9	
3½	3235.9	
4	3235.9	
4½	3235.9	

Time	Resistance	Remarks
5	3235.9	
5½	3196.9	Ampoule broken at 5m. 12s.
6	3186.4	
6½	3185.8	Reaction complete. Contents of calorimeter cooling gradually.
7	3186.4	
7½	3187.2	
8	3187.6	
8½	3188.3	
9	3188.8	
9½	3189.4	
10	3190.0	
10½	3190.4	
11	3190.9	
11½	3191.4	
12	3191.7	End of post reaction period

R_1 = 3235.9; R_2 (by back extrapolation) = 3185.4

Calibration

Time	Resistance	Remarks
0	3236.7	
½	3236.4	
1	3236.2	
1½	3235.9	
2	3235.5	
2½	3235.4	
3	3235.2	

Time	Resistance	Remarks
3½	3235.0	
4	3234.5	
4½	3234.3	
5	3224.5	Heater and timer on at 4.55
5½	3186.5	$V_1 = 0.4601$, $V_s = 0.6167$
6	3183.9	Heater and timer off at 5.35 Time of heating 40.34 s.
6½	3184.7	
7	3185.5	
7½	3186.1	
8	3186.6	
8½	3187.2	
9	3187.6	
9½	3188.2	Calorimeter slowly cooling during post-reaction period
10	3188.7	
10½	3189.0	
11	3189.4	

By graphical extrapolation: $R_3 = 3234.0$, $R_4 = 3183.6$

Hence,

$$\frac{\text{Log } (R_1/R_2)}{\log (R_3/R_4)} = 1.0014$$

P = 2.8883 joules

And, since f for this heater was 0.986, and the weight of the sample was 0.1382 gms.,

$$\Delta H = \frac{-2.8883 \times 0.986 \times 40.34 \times 1.0014 \times 111.00}{4.1840 \times 0.1382}$$

$$= \underline{-\ 22.08 \text{ kcals/mole}}$$

4.3

The isopiestic comparison of vapour pressures

The original intention when starting the work in this section, was to obtain a series of measurements of the activities of aqueous solutions of the group 11a halates over the whole of the concentration ranges available, in order to obtain free energies of solution (see section 1.1.3). Due to various technical difficulties, it was not possible to make very much progress towards that end. However, the apparatus was constructed, and some results were obtained, so it seems worthwhile describing what was done, indicating the failings of the apparatus, and suggesting any modifications which may improve it.

Since this section does not form an integral part of the argument presented in this thesis, it will be treated as an independent section, and the results, the discussion and the experimental will be kept together.

4.3.1

Principles of the method

A detailed discussion of the theory is given by Robinson and Stokes (41). If two solutions of non-valatile solutes are left for a sufficient length of time in a closed vessel at constant temperature, then solvent will distill from one to the other until both solutions have the same vapour pressure. For aqueous solutions the vapour pressure may be identified with the fugacity of the solvent. The activity of the solvent is defined as the ratio of its fugacity in a given state to its fugacity in a standard state. For two aqueous solutions in isopiestic equilibrium, the standard state is, of course, the same for both solutions, (the pure solvent is the usual convention), hence, since their vapour pressures are equal, their solvent activities are also equal. Thus if the activity of the water in a solution of one substance is known, then its activity in a solution of another, unknown substance can be determined by the isopiestic method. The activity of the solute may readily be obtained from a series of values of the solvent activity over a range of concentration, using the Gibbs - Duhem equation. Writing the equation in terms of activity co-efficients γ, and using suffix 1 to refer to the solvent and suffix 2 to refer to the solute,

$$\ln \gamma_2 = - \int_0^{x_1'} \frac{x_1}{x_2} d \ln \gamma_1 \qquad 4.3.1,1$$

Isopiestic measurements do not normally extend to concentrations lower than about 0.1M. However, if equation 4.3.1,1 is integrated graphically, then it is usually possible to extrapolate the data to zero concentration with sufficient accuracy for 1:1 electrolytes. For more complex electrolytes, techniques are available for dealing with the low concentration region (see, for example, Guggenheim and Stokes 136).

The method is a comparative one, and it is necessary therefore to have a reference electrolyte solution, for which the activities are accurately known. The most common reference electrolytes are sodium and potassium chlorides for water activities down to about 0.8, calcium chloride for water activities down to about 0.2, and sulphuric acid which gives solutions with water activities as low as 0.0004.

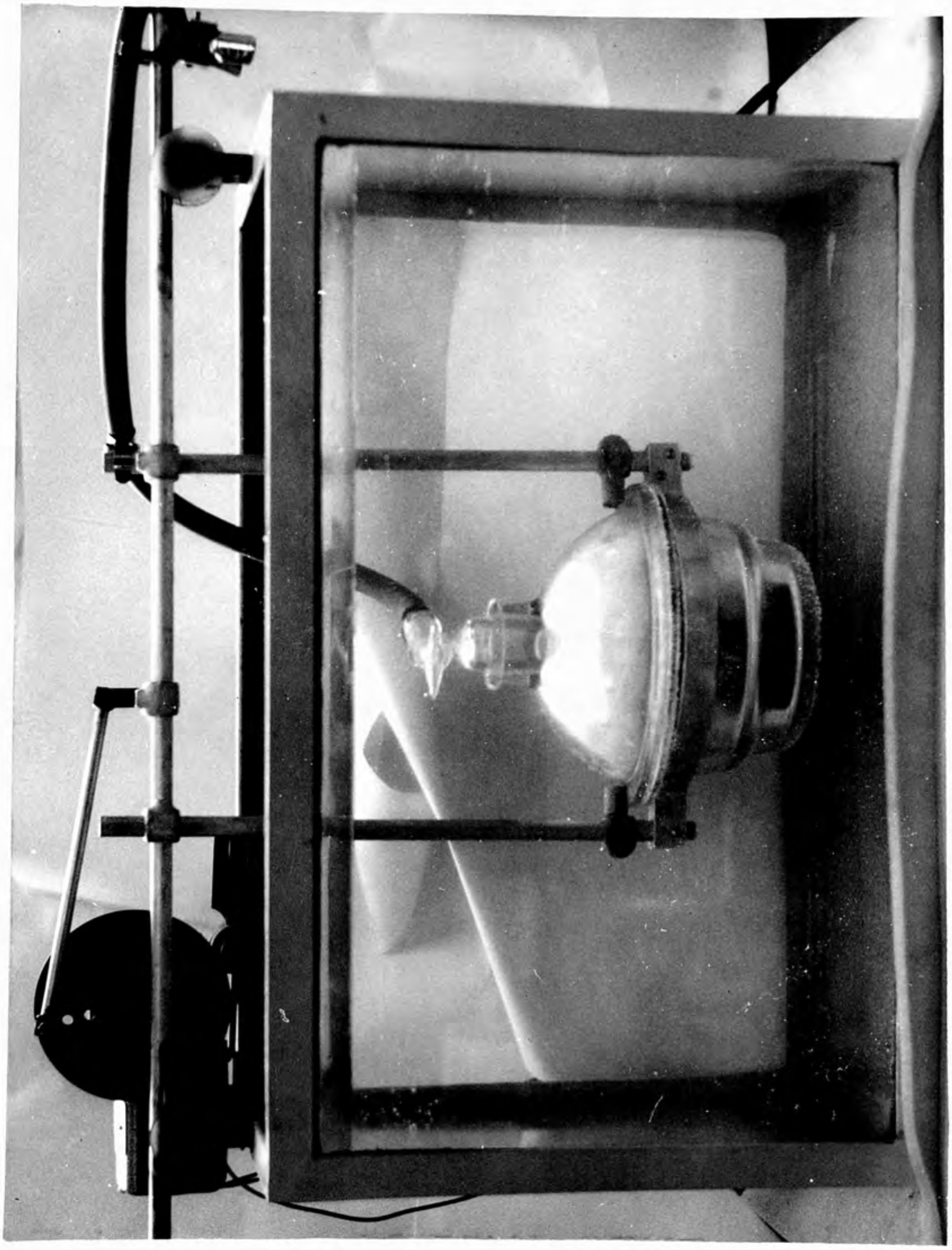
4.3.2

The apparatus was made out of a six inch internal diameter glass vacuum desiccator. Inside the desiccator was a steel block shaped to fit the bottom of the desiccator. A set of four nickel crucibles to hold the solutions under test was clamped onto the top of the steel block, which was specially flattened to ensure good thermal contact. The clamp consisted of a cross-shaped piece mounted on a threaded central rod; a wing nut could be srewed down the centre rod to push the cross piece onto the tops of the crucibles, and thus clamp them hard onto the steel block. The desiccator and its contents were mounted in a thermostat tank, and the solutions were agitated by rocking the desiccator to and fro. A photograph is shown of the apparatus in the thermostat tank, illustrating the mechanism for rocking the desiccator.

Since it was planned to work with solutions of low water activities, it was necessary to plate one of the crucibles with a metal resistant to aqueous sulphuric acid. A layer of rhodium 0.0004 inches thick was tried, and proved to be successful for long enough to obtain a single set of readings. After that it showed signs of being attacked by the sulphuric acid - this was probably due to poor quality or incomplete plating. The results on the chlorate solutions were obtained using sodium chloride as the comparison standard, and it was, therefore, not possible to extend measurements into very concentrated solutions.

4.3.3

The procedure for using the apparatus was to place the three unknown solutions in the crucibles together with the comparison standard in the plated crucible. The crucibles were clamped onto the steel block inside the desiccator; the desiccator was evacuated and put in the thermostat. The system was then rocked, and the crucibles were weighed every few days until there was no change inweight between consecutive weighings. The solutions were then analysed to give the equilibrium concentrations, or, more conveniently, the con-



centrations were determined from the change in weight that had occured since the crucibles were placed in the apparatus (the initital concentrations and weights of the solutions having been recorded). Only dry air was let into the desiccator, and the crucibles were covered with lids as soon as they had been removed from the apparatus; all weighings were made as quickly as possible to avoid any avaporation losses. It was necessary to leave the system for at least a week to attain equilibrium. This is rather long compared with the times that other workers have required, and the reason may be that other workers have used metals with high thermal conductivities such as copper or silver rather than steel on which to rest the crucibles. It is also common practice to plate the block with a noble metal to prevent corrosion. In this first set-up the block was covered with a thin layer of grease; this was not entirely successful.

The apparatus was tested by allowing three solutions of sodium chloride and one solution of sulphuric acid to come to isopiestic equilibrium. The water activities found after a period of a week were:

NaCl			H_2SO_4
(a)	(b)	(c)	
0.9678	0.9669	0.9675	0.9688

The water activities were calculated from the measured concentrations and the water activity data given by Robinson and Stokes (41). It would thus appear that the apparatus gives accurate results, since the above are the same to within 0.2%.

A little new data was obtained for the group lla chlorates. The following solutions were found to be in isopiestic equilibrium:

$Ca(ClO_3)_2$	$Sr(ClO_3)_2$	NaCl	$BaClO_3)_2$	Water Activity
0.3895	0.3134	1.1272	0.4970	0.9626
0.2358	0.1821	0.6838	0.2821	0.9797
0.1670	0.1207	0.5556	0.2097	0.9821

Where each horizontal line represents an equilibrium set of molalities. The corresponding water activities of the sodium chloride solution taken from Robinson and Stokes data are shown in the final column.

Appendix 1

Buckingham's theory of ion - solvent interactions

Buckingham's original theory was first published at a discussion of the Faraday Society in 1957 (75). His ideas on quadrupole moments were amplified in a later quarterly review (131). The treatment given here is based on material from both sources: the general ideas from the former publication; the mathematical argument from the latter. The main part of the theory requires the calculation of the potential produced by a cluster of point charges - this is given in full. The mutual interaction energy between say, six octahedrally co-ordinated solvent molecules, is a much more complex calculation, and only the essential steps in the argument are given.

A polar solvent molecule may be regarded as a cluster of point charges. Thus , if the electrostatic potential, ϕ , produced by such a cluster can be calculated, then the electrostatic interaction energy between the solvent molecule and an ion considered as a polarisable sphere is given by $Ze\phi$, where Ze is the charge on the ion.

(1). The electrostatic potential produced by a charge cluster.

Consider a cluster of charges, e_i, at points $(x_{i_1}, x_{i_2}, x_{i_3})$, given by position vectors $\underline{r}_i$, relative to an origin O. It is required to find the potential, ϕ , produced by this system at a point P, the co-ordinates of which are X_1, X_2, X_3. (figure A1)

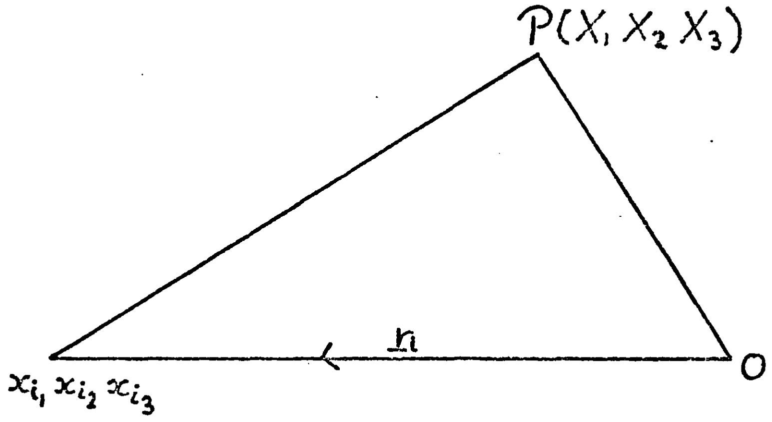


Figure A1.

From elementary electrostatics,

$$\phi = \sum_i (e_i/D_i) \qquad \text{A1.}$$

where the D_i are the distances of the point charges from P.

Equation A1 can be expanded in terms of the partial derivatives of $1/D_i$ with respect to x_1, x_2, and x_3 at the origin by means of Taylor's theorem. The working becomes much more concise if a tensor notation is adopted, in terms of which the expansion of equation A1 becomes,

$$\phi = \sum_i e_i \left[\frac{1}{D_i} + \left(\frac{d(1/D_i)}{dx_{i_a}} \right)_0 x_{i_a} + \frac{1}{2} \left(\frac{d^2(1/D_i)}{dx_{i_a} dx_{i_b}} \right)_0 x_{i_a} . x_{i_b} \right.$$

$$+ \ \frac{1}{6}\left(\frac{d^3(1/D_i)}{dx_{i_a}\,dx_{i_b}\,dx_{i_c}}\right)_0 x_{i_a}.x_{i_b}.x_{i_c} \ + \ \ldots\ldots\ldots \qquad \text{A2.}$$

Here, the a,b,c suffixes represent tensor components. For typing convenience the partial derivatives in equation A2 and in the rest of this appendix have been written as ordinary differentials.

Equation A2 can be written in a particularly elegant form if it is assumed that the distances of the charges from 0 are small compared to the distance of P from 0. In that case, each D_i can be replaced with R, the distance of the cluster from P.

The first derivative is calculated as follows:

$$\frac{d(1/R)}{dx_a} = \frac{dR}{dx_a} . \frac{d(1/R)}{dR} = -\frac{1}{R^2} . \frac{dR}{dx_a} \ .$$

Since

$$R^2 = (X_a - x_a)(X_a - x_a),$$

$$\frac{dR}{dx_a} = \frac{1}{2}.(-2). \frac{(X_a - x_a)}{\left[(X_a - x_a)(X_a - x_a)\right]^{\frac{1}{2}}} ,$$

hence,

$$\left(\frac{dR}{dx_a}\right)_0 = \frac{-X_a}{R} \qquad \text{A3.}$$

And,

$$\left(\frac{d(1/R)}{dx_a}\right)_0 = \frac{X_a}{(R)^3} \qquad \text{A4.}$$

The second derivative is obtained by differentiation of the first derivative with respect to x_b:

$$\frac{d(1/R)}{dx_a dx_b} = \frac{d}{dx_b} \cdot \frac{X_a - x_a}{R^3}$$

$$= (X_a - x_a)\frac{d(1/R^3)}{dx_b} + \frac{1}{R^3}\frac{d(X_a - x_a)}{dx_b}$$

$$= -\frac{3}{R^4} X_a \frac{dR}{dx_b} + \frac{1}{R^3}\frac{d(X_a - x_a)}{dx_b} .$$

From equation A3,

$$\left(\frac{dR}{dx_b}\right)_o = -\frac{X_b}{R}$$

hence,

$$\left[\frac{d^2(1/R)}{dx_a dx_b}\right]_o = \frac{3X_a X_b}{R^5} + \frac{1}{R^3} \cdot \frac{d(X_a - x_a)}{dx_b} \qquad \text{A5.}$$

The latter derivative in equation A5 has the value zero when $a \neq b$, and -1 when $a = b$. This is conveniently expressed using the Kronecker delta:-

$$\left[\frac{d^2(1/R)}{dx_a dx_b}\right]_o = \frac{3X_a X_b - R^2\delta_{ab}}{R^5} \qquad \text{A6.}$$

Differentiation with respect to x_c gives the third derivative:

$$\frac{d^3(1/R)}{dx_a dx_b dx_c} = \frac{d}{dx_c}\left[\frac{3(X_a - x_a)(X_b - x_b) - R^2\delta_{ab}}{R^5}\right]$$

$$= \frac{3}{R^5}\left[(X_a - x_a)\frac{d(X_b - x_b)}{dx_c} + (X_b - x_b)\frac{d(X_a - x_a)}{dx_c}\right.$$

$$\left. + \tfrac{2}{3}(X_c - x_c)\delta_{ab}\right]$$

$$-\frac{5}{R^6}\left[3(X_a - x_a)(X_b - x_b) - R^2\delta_{ab}\right] \cdot \left[\frac{-(X_c - x_c)}{R}\right]$$

Hence,

$$\left[\frac{d^3(1/R)}{dx_a dx_b dx_c}\right]_0 = \frac{3}{R^5}\left[\tfrac{2}{3}X_c\delta_{ab} - X_a\delta_{bc} - X_b\delta_{ac}\right] + 5\left[\frac{3X_aX_bX_c}{R^7} - \frac{X_c\delta_{ab}}{R^5}\right]$$

$$= \frac{3\left[5X_aX_bX_c - R^2(X_a\delta_{bc} + X_b\delta_{ac} + X_c\delta_{ab})\right]}{R^7} \qquad \text{A7.}$$

The fourth and higher derivatives may be obtained in a similar manner.

Introducing the following parameters:

$$q = \sum_i e_i$$

$$\mu_a = \sum_i e_i x_{i_a}$$

$$Q_{ab} = \sum_i e_i x_{i_a} x_{i_b}$$

$$O_{abc} = \sum_i e_i x_{i_a} x_{i_b} x_{i_c}$$

and the derivatives from equations A4,5 and 6 into equation A2,

$$\phi = \frac{q}{R} + \frac{X_a\mu_a}{R^3} + \frac{Q_{ab}(3X_aX_b - R^2\delta_{ab})}{2R^5} + \frac{O_{abc}}{2R^7}\left[5X_aX_bX_c - R^2(X_a\delta_{bc} + X_b\delta_{ac} + X_c\delta_{ab})\right] \qquad \text{A8.}$$

Q_{ab} and O_{abc} may be regarded as the components of the quadrupole and octupole moments of the system respectively.

By suitable choice of axes, the quadrupole and octupole moment tensors can be reduced to three principal quadrupole or octupole moments. For example, Q_{ab} can be written in matrix form as:

$$Q_{ab} = \begin{bmatrix} Q_{x_1x_1} & Q_{x_1x_2} & Q_{x_1x_3} \\ Q_{x_2x_1} & Q_{x_2x_2} & Q_{x_2x_3} \\ Q_{x_3x_1} & Q_{x_3x_2} & Q_{x_3x_3} \end{bmatrix}$$

By rotation and translation of the axes, this matrix may be diagonalised to give:

$$\begin{bmatrix} Q_{x_1x_1} & 0 & 0 \\ 0 & Q_{x_2x_2} & 0 \\ 0 & 0 & Q_{x_3x_3} \end{bmatrix}$$

Hence, equation A8 can be written,

$$\phi = \frac{q}{R} + \frac{X_a\mu_a}{R^3} + \frac{Q_{aa}(3X_aX_a - R^2)}{2R^5} + \frac{O_{aaa}(5X_aX_aX_a - 3R^2X_a)}{2R^7} + \ldots\ldots \qquad \text{A9.}$$

For a system with an axis of charge symmetry, the tensors Q_{aa} and O_{aaa} can be replaced by scalars, giving equation A9 the form:

$$\phi = \frac{q}{R} + \frac{\mu_a\cos\theta}{R^2} + \frac{Q(3\cos^2\theta - 1)}{R^3} + \frac{O(5\cos^3\theta - 3\cos\theta)}{2R^5} + \ldots\ldots \qquad \text{A10.}$$

Equation A10 gives the potential at a point R,θ, relative to an origin on the axis of the distribution, and it is the basic equation for calculating the ion-solvent interaction energies.

If ze is the charge on an ion, then the energy of interaction between the ion and one solvent molecule is given by:

$$U = -ze\phi$$

Thus, equation A10 gives

$$U = -\frac{|z|e\mu}{R^2} - \frac{Qze}{R^3} - \frac{|z|Oe}{R^5} - \ldots \qquad \text{A11.}$$

where θ has been set equal to zero for positive ions and π for negative ions. It should be noted that the valency, z appears in the terms involving even powers of $\cos\theta$, while the modulus of the valency appears in the terms involving odd powers of $\cos\theta$, to take account of the different values of θ for anions and cations.

(2). The mutual interaction energy between the solvent molecules in the primary solvation sphere.

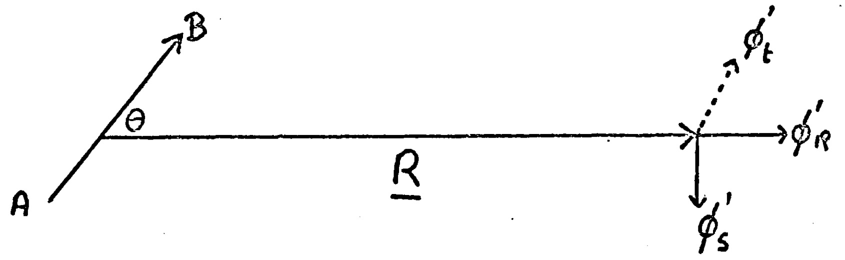
Buckingham showed that the interaction energy between two charge systems could be expressed in terms of the multipole moments of one system, and the potential and its derivatives with respect to position of the second system at the centre of mass of the first system.

For example,

$$U_{12} = q_2\phi_2 - \mu_2\phi_2' - \tfrac{1}{2}Q_2\phi_2'' - \tfrac{1}{6}O_2\phi_2''' \ldots \qquad \text{A12.}$$

The derivatives in equation A12 can be obtained by differentiation of equation A10.

The figure below shows the dipole moment, AB, of a charge cluster, and the three mutually perpendicular components of the field due to the cluster at a point defined by the vector $\underline{R}$. θ is the angle between the dipole moment and $\underline{R}$, and ζ is the angle between the plane containing ϕ'_r and ϕ'_s , and the plane containing $\underline{R}$ and the dipole moment vector.



Buckingham showed that the first derivatives of the potential are:

$$\phi'_r = -\frac{\partial\phi}{\partial R} = \frac{q}{R^2} + \frac{2\mu\cos\theta}{R^3} + \frac{3Q(3\cos^2\theta - 1)}{2R^4} + \frac{2O(5\cos^3\theta - 3\cos\theta)}{R^5} \ldots\ldots\ldots$$

$$\phi'_s = \frac{-1}{R}\cdot\frac{\partial\phi}{\partial\theta} = \sin\theta\left[\frac{\mu}{R^3} + \frac{3Q\cos\theta}{R^4} + \frac{3O(5\cos^2\theta - 1)}{2R^5} \ldots\right]$$

$$\phi'_t = \frac{-1}{R\sin\theta}\cdot\frac{\partial\phi}{\partial\zeta} = 0$$

A13.

he also calculated the second derivatives as:

$$\phi''_{rr} = \frac{-2q}{R^3} - \frac{6\mu\cos\theta}{R^4} - \frac{6Q(3\cos^2\theta - 1)}{R^5} + \ldots\ldots$$

$$\phi''_{ss} = \frac{q}{R^3} + \frac{3\mu\cos\theta}{R^4} + \frac{3Q(7\cos^2\theta - 3)}{2R^5} + \ldots\ldots$$

$$\phi''_{tt} = \frac{q}{R^3} + \frac{3\mu\cos\theta}{R^4} + \frac{3Q(5\cos^2\theta - 1)}{2R^5} + \ldots\ldots$$

$$\phi''_{rs} = \frac{-3\mu\sin\theta}{R^4} - \frac{12Q\sin\theta\cos\theta}{R^5} - \ldots\ldots$$

$$\phi''_{st} = \phi''_{tr} = 0 \qquad \text{A14.}$$

For convenience, ζ was set equal to zero by suitable choice of axes.

In order to calculate the interaction energy between two polar solvent molecules, let the distance between the centres of mass of the two molecules be R, let the dipole moment vectors be inclined to the vector, $\underline{R}$, joining the two centres at angles θ_1 and θ_2, and let the planes containing (R, θ_1) and (R, θ_2) be inclined at an angle ζ. The system is electrically neutral, hence all the terms involving q are zero. By substitution of the derivatives A13 and 14 into equation A12, the energy, U, is given as:

$$U = \frac{\mu_1\mu_2}{R^3}\left[2\cos\theta_1\cos\theta_2 + \sin\theta_1\sin\theta_2\cos\zeta\right] +$$

$$
\begin{aligned}
&+ \frac{3}{2R^4}\Big\{\mu_1 Q_2\Big[\cos\theta_1\,(3\cos^2\theta_2 - 1) + 2\sin\theta_1\sin\theta_2\cos\theta_2\cos\zeta\Big] \\
&+ \mu_2 Q_1\Big[\cos\theta_2\,(3\cos^2\theta_1 - 1) + 2\sin\theta_1\sin\theta_2\cos\theta_1\cos\zeta\Big]\Big\} \\
&+ \frac{3Q_1Q_2}{4R^5}\Big[1 - 5\cos^2\theta_1 + 17\cos^2\theta_1\cos^2\theta_2 - 5\cos^2\theta_2 \\
&+ 2\sin^2\theta_1\sin^2\theta_2\cos^2\zeta + 16\sin\theta_1\sin\theta_2\cos\theta_1\cos\theta_2\cos\zeta\Big] + \ldots \qquad \text{A15.}
\end{aligned}
$$

As an example of the application of equation A15, the following is an outline of the derivation of the interaction energy between six solvent molecules arranged at the corners of a regular octahedron. Assuming that the dipole moment vectors of all the solvent molecules point directly towards the centre of the octahedron (the position occupied by the ion in a solvated complex), and that the distance between the centre of mass of the solvent molecules and the centre of the octahedron can be taken as equal to the sum of the ion and solvent radii (denoted by R^*), then there are twelve interactions for which

$$\theta_1 = 45^\circ = \theta_2$$

and

$$R = \sqrt{2}R^*,$$

and three interactions for which

$$\theta_1 = \theta_2 = 0$$

and

$$R = 2R^*.$$

In all cases $\zeta = 0$. Interpolating these values into equation A15, the first three terms of equation 3.2.2,11 (pg. 121)are obtained.The last two terms in this equation are included to account for (a) the energy of interaction between the dipoles induced by the field due to the permanent solvent molecule dipoles ,(b) the dispersion energy.

Appendix II

Details of heat of solution experiments

The following tables list the details of the heat of solution experiments from which the mean values used in this thesis were calculated. All the experiments were performed so that the data refers to 25.0 ±0.1°C. The times, t, listed, are the mean times of the reaction periods. The m's refer to molalities.

Solution of MgO in 0.5m aqueous HBr; t = 2min.

wt. MgO (in g.)	m. MgO	$-\Delta H_{obs}$(kcal. mole^{-1}MgO)
0.1429	0.0284	35.1_5
0.1568	0.0311	35.3
0.1478	0.0293	35.1_5
0.1668	0.0276	35.1
0.1509	0.0250	35.4
0.1406	0.0232	35.1
0.1469	0.0243	35.4

Solution of MgO in 0.5m aqueous HI; t = 2min.

wt. MgO (in g.)	m. MgO	$-\Delta H_{obs}$(kcal. mole^{-1}MgO)
0.1424	0.0235	35.0
-.1546	0.0256	34.9
0.1510	0.0250	35.3
0.1587	0.0262	35.2

Solution of $MgBr_2(c)$ in 0.5 molal HBr : t (instant)

wt. $MgBr_2$ (in g.)	m. $MgBr_2$	$-\Delta H_{obs}$(kcal.mole^{-1}$MgBr_2$)
0.1022	0.00444	43.4
0.1670	0.00726	43.4
0.1612	0.00700	42.9
0.1359	0.00590	42.8_5

Solution of $MgI_2(c)$ in 0.5 molal HI : t (instant)

wt. MgI_2 (in g.)	m. MgI_2	$-\Delta H_{obs}$(kcal.mole^{-1}MgI_2)
0.0949	0.00341	49.5
0.2153	0.00774	50.1
0.1227	0.00441	49.6
0.2490	0.00895	49.9

Precipitation of CaF_2 from aqueous NaF and $CaCl_2(c)$

t = 1 min.

wt. $CaCl_2$	m_1	m_4	$-\Delta H_{obs}$ (kcal.mole^{-1}$CaCl_2$)	$\Delta H^o_s(CaF_2)$
0.1887	0.6805	0.0272	21.1_5	1.71
0.2679	0.6323	0.0378	21.0	1.55
0.2763	0.6138	0.0398	21.2	1.72
0.3350	0.8736	0.0484	21.1	1.69
0.3420	0.8521	0.0494	21.0_5	1.66
0.3879	0.4038	0.0560	21.2	1.71
0.4195	0.5062	0.0606	21.2	1.78

Precipitation of MgF_2 from aqueous $MgCl_2$ and NaF(c) :

t = 2 min.

wt. NaF (in g.)	m_5	m_7	ΔH_{obs} (kcal.mole^{-1}NaF)	x $\Delta H_s^o(MgF_2)$
1.1608	0.114	0.221	2.11	-2.03
1.1505	0.111	0.219	2.11	-2.03
1.3195	0.128	0.252	2.10	-2.05
1.1070	0.113	0.211	2.13	-2.05

Precipitation of SrF_2 from aqueous $SrCl_2$ and NaF(c)

t = 12 min.

wt. NaF (in g.)	m_5	m_7	ΔH_{obs} (kcal.mole^{-1}NaF)	x $\Delta H_s^o(SrF_2)$
1.9073	0.197	0.363	-0.2_5	0.3
1.4820	0.145	0.283	-0.4	0.5
2.0674	0.215	0.395	-0.2	0.3

Precipitation of BaF_2 from aqueous $BaCl_2$ and NaF(c)

t = 9 min.

wt. NaF (in.g.)	m_5	m_7	ΔH_{obs} (kcal,mole^{-1}NaF)	x $\Delta H_s^o(BaF_2)$
2.0787	0.207	0.396	-0.8	0.8
1.5416	0.163	0.294	-0.6	0.7
1.3849	0.150	0.264	-0.6	0.7
1.5931	0.162	0.304	-0.5	0.6

Heat of solution of n-Bu_4NI in water

wt. of salt (in g.)	molality	ΔH_{obs}
1.0211	0.0222	3.61
1.4579	0.0316	3.60
1.9306	0.0418	3.54
1.7804	0.0386	3.49

Heat of solution of n-Pr_4NI in water

wt. of salt (in g.)	molality	ΔH_{obs}
1.1180	0.0286	2.74
1.3380	0.0342	2.67
1.5723	0.0402	2.69
1.7006	0.0434	2.75

Salt/Solvent	Molality (m)	ΔH_{obs} (kcal.mole^{-1})
$Ca(ClO_3)_2$ in F (t = 1-2 min.)	0.0132	-11.3
	0.0160	-11.0
	0.0270	-11.4
	0.0284	-11.5
	0.0295	-11.2
	0.0210	-11.4
	0.0312	-11.3
	0.0361	-11.6
	0.0379	-11.1
	0.0454	-11.4
	0.0490	-11.2
$Sr(ClO_3)_2$ in F (t = 3 min)	0.0237	- 8.38
	0.0331	- 8.29
	0.0395	- 8.27
	0.0400	- 8.26
	0.0418	- 8.19
	0.0433	- 8.33
	0.0485	- 8.18
	0.0533	- 8.33

Ba(ClO$_3$)$_2$ in F (t = 3-4 min)	0.0347	-4.94
	0.0444	-4.84
	0.0458	-4.96
	0.0498	-4.97
	0.0507	-4.97
	0.0562	-5.00
Ca(ClO$_3$)$_2$ in NMF (t = 1 min)	0.0105	-13.8
	0.0110	-13.8
	0.0193	-13.6
	0.0268	-13.8
Sr(ClO$_3$)$_2$ in NMF (t = 10 min)	0.0165	-9.34
	0.0177	-9.16
	0.0273	-9.06
	0.0311	-9.04
	0.0452	-8.81
Ba(ClO$_3$)$_2$ in NMF (t = 1 min)	0.0202	-7.22
	0.0261	-7.04
	0.0502	-6.85
	0.0527	-6.91
Ca(ClO$_3$)$_2$ in DMF	0.0100	-18.6
	0.0110	-18.5
	0.0127	-18.6
	0.0133	-18.1

	0.0152	-18.8
(t = 1 min)	0.0169	-18.4
	0.0173	-18.2
	0.0173	-18.5_5
	0.0174	-18.2_5
	0.0216	-18.2
	0.0132	-13.9
	0.0156	-13.6
	0.0271	-13.1_5
	0.0286	-13.1
$Sr(ClO_3)_2$ in DMF	0.0389	-12.7
(t = 5 min)	0.0452	-12.4
	0.0503	-12.9_5
	0.0507	-12.8
	0.0090	0.69
	0.0092	0.44
$Ca(BrO_3)_2$ in H_2O	0.0101	0.64
(t = 2 min)	0.0101	0.59
	0.0446	4.93
	0.0448	4.87
$Sr(BrO_3)_2$ in H_2O	0.0463	4.99
(t = 3 min)	0.0478	4.79
	0.0498	4.89

	0.0119	10.6
$Ba(BrO_3)_2$ in H_2O	0.0122	10.3
(t = 3 min)	0.0140	10.6
	0.0145	10.5
	0.0200	-4.80
	0.0296	-4.65
	0.0398	-4.57
$Ca(BrO_3)_2$ in F	0.0467	-4.63
(t = 2 min)	0.0491	-4.54
$Sr(BrO_3)_2$ in F	0.0252	-3.1
(t = 30 min)	0.0290	-3.3
$Ba(BrO_3)_2$ in F	0.0095	0.2
(t = 12 min)	0.0102	0.4
	0.0500	-4.40
	0.0556	-4.52
$Ca(BrO_3)_2$ in NMF	0.0607	-4.57
(t = 3-4 min)	0.0614	-4.36
	0.0784	-4.27
$Ca(BrO_3)_2$ in DMF	0.0238	-4.3
(t = 12 min)	0.0268	-4.4

$CaCl_2$ in F (t = 2-3 min.)	0.0328	-21.79
	0.0246	-22.01
	0.0251	-21.84
	0.0258	-21.82
$SrCl_2$ in F (t = 1 min)	0.0173	-17.33
	0.0226	-17.67
	0.0130	-17.65
	0.0079	-17.57
$BaCl_2$ in F (t = 5 min)	0.0232	-10.53
	0.0116	-10.12
	0.0577	-10.50
	0.0386	-10.49
$CaBr_2$ in F (t = 1 min)	0.0123	-29.27
	0.0191	-29.63
	0.0073	-29.58
	0.0080	-29.89
$SrBr_2$ in F (t = 1 min)	0.00723	-25.41
	0.0105	-25.30
	0.0103	-25.47
	0.0120	-25.20

	0.0161	-15.52
$BaBr_2$ in F	0.0258	-15.25
(t = 3 min)	0.0180	-15.32
	0.0125	-22.08
$CaCl_2$ in NMF	0.0076	-22.61
(t = 1-2 min)	0.0197	-21.26
	0.0187	-21.99
	0.0171	-17.45
$SrCl_2$ in NMF	0.0098	-17.12
(t= 2 min)	0.0152	-17.06
	0.0150	-17.57
	0.0089	-31.00
$CaBr_2$ in NMF	0.0062	-31.79
(t = 2 min)	0.0053	-32.27
	0.0155	-30.72
	0.0088	-31.51
	0.0116	-25.67
$SrBr_2$ in NMF	0.0062	-26.23
(t = 1 min)	0.0157	-25.17
	0.0270	-17.34
$BaBr_2$ in NMF	0.0162	-17.53
(t = 3 min)	0.0081	-17.47
	0.0263	-17.37
	0.0123	-17.86

	0.0493	-16.53
	0.0356	-19.77
$CaCl_2$ in DMF (t = 15 min)	0.0164	-21.30
	0.0149	-23.55
	0.0066	-20.48
	0.0059	-20.52
	0.0116	-14.58
	0.0106	-14.06
$SrCl_2$ in DMF (t = 4 min)	0.0253	-13.66
	0.0217	-13.59
	0.0242	-13.48
	0.0164	-14.01
	0.0215	-36.27
$CaBr_2$ in DMF (t = 1 min)	0.0063	-37.63
	0.0096	-37.46
	0.0102	-37.21
	0.0153	-36.57
	0.0106	-31.23
$SrBr_2$ in DMF (t instant)	0.0035	-32.37
	0.0082	-31.68
	0.0122	-30.81

References

1. R.J. Gillespie. Disc. Farad. Soc. 24, (1957)

2. G. Somsen & J. Coops, Rec. Trav. Chim. 84, 985 (1965)

3. L. Weeda & G. Somsen, ibid, 85, 159 (1966)

4. G. Somsen, ibid, 85, 517 (1966)

5. idem, ibid, 85, 526, (1966)

6. L. Weeda & G. Somsen, ibid, 86, 263, (1967)

7. E. Luksha & C.M. Criss, J. Phys. Chem. 70, 1496 (1966)

8. R.P. Held & C.M. Criss, ibid, 69, 2611, (1965)

9. K.P. Mishchenko & V.P. Tungusov, Teoreticheskaya i Ekaperimental'naya Khimiya 1, 55, ~~19~~ (1965)

10. L.P. Zhilina & K.P. Mishchenko, ibid 1, 361, (1965)

11. K.P. Mishchenko & M.L. Klyaeva, ibid, 1, 201 (1965)

12. L.N. Erbanova, S.I. Drakin & M.Kh. Karapet'yants. Zhur. Fiz. Khim, 38, 1450, (1964)

13. Idem, ibid, 39, 1467, (1965)

14. S.I. Drakin & Chang Yu-min, ibid, 38, 1526 (1964)

15. R. Gopal & M. Hussain, J. Ind. Chem. Soc. 40, 272 (1963)

16. G.A. Strack, S.K. Swanda, L.W. Bahe, J. Chem, Eng. Data. 9, 416 (1964)

17. D. Davies & G. Benson, Canad. J. Chem. 43, 3100 (1965)

18. Yung-Chi Wu & H.L. Friedman. J. Phys. Chem. 70, 166, (1966)

19. D. Feakins, B. Smith & L Thakur. J. Chem. Soc (A) 1966, 714 (and references therein to three earlier, similar papers).

20. E.N. Varenko. Zhur. Fiz. Khim. 21, 371 (1947) 23, 959, (1949)

21. L.R. Dawson & E.J. Griffith. J. Phys. Chem. 56, 281, (1952)

22. C.M. French & K.H. Glover, Trans. Farad. Soc. 51, 1418, (1955)

23. L.R. Dawson & W.W. Wharton. J. Electrochem. Soc. 107, 710 (1960)

24. J.E. Prue & P.J. Sherrington, Trans. Farad. Soc. 57, 1795, (1961)

25. "Atomic Energy Levels". Circular of the National Bureau of Standards No. 467, U.S. Govenment Printing Office, Washington, D.C., 1948-1958

26. R.S. Berry & C.W. Reimann. J. Chem. Phys, 38, 1540 (1963)

27. "Thermodynamics", G.N. Lewis and M. Randall, second revised edition by K.S. Pitzer and L. Brewer, McGraw Hill, 1961.

28. "Selected values of chemical thermodynamic properties", Circular of the National Bureau of Standards No. 500, U.S. Government Printing Office, Washington, D.C., 1952.

29. S,R. Gunn. J. Phys. Chem. 71, 1386, (1967)

30. J.D. Cox, Private communication.

31. Selected Values of Chemical Thermodynamic Properties, National Bureau of Standards, Technical Notes 270-1 and 270-2, 1965

32. S. Sunner & S. Thoren, Act. Chem. Scand. 18, 1528 (1964)

33. P.B. Howard & H.A. Skinner, J. Chem. Soc. 1536 (1966)

34. V.B. Parker, Thermal Properties of Aqueous Uni-univalent electrolyes, National Bureau of Standards NSRDS - NBS 2, (1965)

35. P. Ehrlich, K Peik & E. Koch, Z. Anorg. Allgem. Chem. 324, 113, (1963)

36. E.H. Buchner, Kolloid Zschr. 75, 1 (1936)

37. D.F.C. Morris. J. Inorg. Nucl. Chem. 6, 295, (1957)

38. A. Finch & P.J. Gardner, J. Phys. Chem. 69, 384, (1965)

39. W.M. Latimer, "The Oxidation States of the Elements and their Potentials in Aqueous Solutions", 2nd Ed. Prentice-Hall, Inc., New York, 1952

40. M.V. Ionin, Zhur. Fiz. Khim., 38, 1457 (1964)

41. R.A. Robinson & R.H. Stokes, "Electrolyte Solutions". Academic Press, Inc., New York (1959)

42. D.A. Sinclair & R.A. Robinson, J.A.C.S. 56 1830. (1934)

43. G. Scatchard, W.J. Hamer & S.E. Wood, J.A.C.S, 60, 3061, (1938)

44. E. Luksha, Ph.D. Thesis, Univ. of Vermont (1965)

45. R.P. Held, Ph.D. Thesis, Univ. of Vermont (1965) (Also published by U.S. At. Energy Commission TID 22374 (1965))

46. C.M. Criss, U.S. At. Energy Commission Rept. T I D. 22366 (1965)

47. Cobble, Ann. Rev. Phys. Chem. 17, (1966)

48. A.P. Altshuller, J. Chem. Phys. 26, 404, (1958)

49. H.F. Halliwell & S.C. Nyburg, Trans. Farad. Soc. 59, 1126, (1963)

50. B.E. Conway & J. O'M. Bockris, "Modern Aspects of Electrochemistry", Vol I, chapter 2, Butterworths. (1954)

51. B.E. Conway. Ann. Rev. Phys. Chem, 17, (1966)

52. R.W. Stoughton. Ann. Rev. Phys. Chem. 16, (1965)

53. M. Magat, Trans. Farad. Soc. 33, 114, (1937)

54. C.H. Cartwright & J. Errera, Proc. Roy. Soc. 154A, 138, (1936)

55. C.L. Van Panthaleon van Eck, H. Mendel & W. Boog., Disc. Farad. Soc. 24, 200, (1957)

56. C.L. van Panthaleon van Eck, H. Mendel & J.Fahrenfort, Proc. Roy. Soc. (London) A247, 472, (1958)

57. S.J. Bass, W.I. Nathan, R.M. Meighan & R.H. Cole, J. Phys. Chem., 68, 509, (1964)

58. J. Ladell & B. Post, Acta, Cryst. 7 559, (1954)

59. B.B. Owen, R.C. Miller, C.E. Milner & H.L. Cogan, J. Phys. Chem. 65, 2065 (1961)

60. G.F. Smith. J. Chem. Soc. 1931, 3257.

61. A. Weissberger, "Techniques of Organic Chemistry" Vol. VII, Organic Solvents. 2nd. Ed. Interscience Publ. Inc., New York. (1957)

62. G.R. Leader, J.A.C.S. 73, 856, (1951)

63. B.E. Geller, Zhur. Fiz. Khim. 35, 1105, (1961)

64. H.S. Frank & M. Evans. J. Chem. Phys. 13, 507 (1945)

65. J. O'M. Bockris, Quart. Rev., 3, 173, (1949)

66. M. Born, Z. Physik, 1, 45 (1920)

67. N. Bjerrum & E. Larsson, Z. Physik. Chem. 127, 358, (1927)

68. W.M. Latimer, K.S. Pitzer & C.M. Slansky, J. Chem. Phys. 7, 108, (1939)

69. R.H. Stokes, J.A.C.S., 86, 979, (1964)

70. K.J. Laidler & C. Pegis, Proc. Roy, Soc. (London) A241, 80, (1957)

71. F. Booth, J. Chem. Phys. 19, 391, 1327, 1615 (1951)

72. J.D. Bernal & R.H. Fowler, J. Chem. Phys. 1, 515, (1933)

73. D.D. Eley & M.G. Evans, Trans. Farad. Soc. 34, 1093, (1938)

74. J.S. Muirhead-Gold & K.J. Laidler "Chemical Physics of Ionic Solutions". Eds. B.E. Conway & R.G. Barradas, John Wiley & Sons (1966), Pg. 75.

75. A.D. Buckingham. Disc. Farad. Soc. 24, 151 (1957)

76. B.E. Conway, R.E. Verrall & J.E. Desnoyers, Z. Physik. Chem. 230, 157 (1965) (Leipzig)

77. E.J.W. Verwey, Chem. Weeckblad, 37, 530, (1940)

78. B.E. Conway & M. Salomon, "Chemical Physics of Ionic Solutions". see ref. 74.

79. Fajans. Verh. dtsh. physik. Ges. 21, 709 (1919)

80. K.P. Mishchenko, Zhur. Fiz. Khim. 26, 1736 (1952)

81. Oshida & Horiguchi. Bull. Kobayasi Inst. of Phys. Res. 5, 61 (1955)

82. R.M. Noyes, J.A.C.S. 86, 971, (1964)

83. W.G. Breck & J. Lin, Canad. J. Chem. (1965),2223,

84. R.W. Gurney, Ionic Processes in Solution. McGraw-Hill, New York, (1953)

85. E.R. Cohen, K.M. Crowe & J.W. DuMond, "The fundamental constants of physics". Interscience Publishers, New York, (1957)

86. Vorov'ev, Zhur. Neorg. Khim. 11, 738 (1966)

87. JANAF Thermochemical Tables, first addendum, National Bureau of Standards, (P.B. 168, 370-1), (1966)

88. E. Rudzitis, H.M. Fider & W.N. Hubbard, J. Phys. Chem, 68, 2978, (1964)

89. H. Stephen & T. Stephen, "Solubilities of Inorganic and Organic Compounds". Vol. I, Pergamon, (1963)

90. T.E. Gardner & A.R. Taylor, U.S. Bureau of Mines Rept. Invest. No. 6435, (1964)

91. Goodman & Westrum, J. Chem. Eng. Data. 11 294-5, (1966)

92. J. Bousquet & P. Vermande, Bull. Soc. Chim. France, 1552, (1966)

93. Makarof. Z. Fiz. Khim. 35, 605, (1961)

94. Ibid, Idem. 32, 1618 (1958)

95. Gazith. A.E.C. Accession No. 11048 Rept. No. IA 1004

96. Bower, Sparks & Trueblood, U.S. Govt. Research Repts., 32, 119, (1959) P.B. Rept. 139994

97. Santoro. Acta. Cryst. 13, 1017, (1960)

98. Ibers, Acta. Cryst. 9, 225, (1956)

99. Rocchiccioli, Ann. Chim. (Paris), 5, 999 (1960)

100. Durig, J. Phys. Chem. 69, 3886, (1965)

101. A. Finch & P.J. Gardner, J. Inorg. Nucl. Chem. 27, 535, (1965)

102. J. Bousquet, Bull. Soc. Chim. France. (1967) 240.

103. B.E. Conway, R.E. Verrall & J.E. Desnoyers. Trans. Farad. Soc., 62, 2738, (1966)

104. H.F. Halliwell & S.C. Nyburg. see ref 49.

105. L.R. Dawson, T.M. Newell & W.J. McCreary. J.A.C.S. 76, 6024, (1954)

106. Yu. I. Sinyakov, A.I. Gorbanev, Y.M. Povarov & Yu.M. Kesslev, Izv. Akad. Nauk. S.S.S.R. otd. Khim. Nauk., 1514 (1961)

107. J.R. Ruhoff & E.E. Reid, J.A.C.S., 59, 401 (1937)

108. B.V. Ioffe, Zhur. Obshchei. Khim. 25, 902, (1955)

109. G.R. Leader, J.F. Gormley, J.A.C.S. 73, 5731 (1951)

110. G.E. Boyd, J.W. Chase & F. Vaslow. J. Phys. Chem. 71, 573, (1967)

111. R.M. Noyes, J.A.C.S. 84, 513, (1962)

112. L. Pauling "The Nature of the Chemical Bond and the Structure of Molecules and Crystals". 3rd. Ed., Cornell University Press, Ithaca, New York, 1960.

113. E.A. Moelwyn-Hughes, Proc. Cambridge Phil. Soc. 45, 477, (1949)

114. E.J.W. Verwey, Rec. Trav. Chim. 61, 127 (1942)

115. R.J. Kurland & E.B. Wilson. J. Chem. Phys. 27, 585, (1957)

116. R.M. Meighan & R.H. Cole. J. Phys. Chem. 68, 503 (1964)

117. C.J.F. Bötcher, Rec. Trav. Chim, 65, 1991 (1946)

118. H. Hartmann in : Landolt-Börnstein, "Zahlenwerte und Functionen aus Physik, Chemie, usw." part 3II, p. 360 (1951)

119. H.D. Hunt & W.T. Simpson. J.A.C.S. 75, 4540 (1953)

120. J.R. Tessman, A.H. Kahn & W. Shockley. Phys. Rev. 92, 890

121. Pimentel and McClellan. "The Hydrogen Bond", Freeman (1960)

122. G. Nethemy & H.A. Sheraga. J. Chem. Phys., 36, 3382, (1962)

123. F.H. Verhoek, J.A.C.S. 58, 2577, (1936)

124. W. Biltz & G.F. Hüttig, Z. Anorg. Allgem. Chem. 119, 116, (1921)

125. I.V. Tananaev. J. Appl. Chem. U.S.S.R., 5, 332. (1932)

126. J.H. Robertson, J.Sci. Instr., 1963, 40, 506.

127. Becker, Green & Pearson, Bell System Technical Journal, 26, 170, (1947).

128. H.C. Dickinson. Nat.Bur.Stand. Bull., 11, 189, (1915)

129. A.C. Macleod, Trans Farad. Soc., 63, 289, (1967)

130. H.S. Harned & B.B. Owen, "The Physical Chemistry of Electrolytic Solutions", Reinhold 1958, 3rd. edition.

131. A.D. Buckingham, Quart. Rev. 13, 183, (1959)

132. B.S. Gourary & F.J. Adrian, Solid State Physics, 10, 127 (1960). See also M.J. Blandamer & M.C.R. Symons, J. Phys. Chem. 67, 1304, (1963)

133. S.R. Gunn. Rev. Sci. Instr. 29, 377 (1958), see also Idem, J. Phys. Chem. 69, 2902, (1965)

134. R.J. Irving & I. Wadsö. Acta. Chem. Scand., 18 195, (1964).

135. P.J. Gardner, Ph.D. Thesis. University of London. (1963)

136. E.A. Guggenheim & R.H. Stokes. Trans. Farad. Soc. 54, 1646, (1958).

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Solvation Studies. I. Some Alkaline Earth Chlorates and Bromates in High Dielectric Solvents

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The standard enthalpies of solution of the chlorates and bromates of calcium, strontium, and barium in formamide (F), N-methylformamide (NMF), and N,N-dimethylformamide (DMF) are reported. Similar data for the bromates in water are also reported. Enthalpies of dilution are compared with those predicted by the Debye–Hückel limiting law. Solvation energies are evaluated and compared with those calculated from a Born model.

Ion solvation in nonaqueous media has become a subject of intensive study only during the past 5 years.[1–8] By evaluating the difference in energy of solvation and hydration (energetics of transfer) it is hoped to gain some insight into solvent structure under the influence of ion fields. In the present work, solvents of high dielectric constant (NMF, 171; F, 109; H_2O, 78; and DMF, 37; data at 25°), in which contributions to thermodynamic properties from ionic aggregates might be avoided, are considered. Conductance measurements[8b] have indicated that the solvent of lowest dielectric constant (DMF) is a strong dissociating medium.

In the past, free energies of solvation (usually from emf measurements) have been studied more extensively than the corresponding enthalpies. In this paper, the approach is calorimetric, and enthalpies of solution of some main group II bromates and chlorates are determined in the above solvents over the concentration range 0.01 to 0.05 *m*. Such data for di-univalent electrolytes are scarce.

Experimental Section

Solvents. (i) Formamide (B.D.H.) was purified by distillation according to Verhoek.[9] The product had a specific conductance of 1×10^{-4} ohm^{-1} cm^{-1} (lit.[9] 5×10^{-5}) and a water content of 0.04% (Karl Fischer).

(ii) N-Methylformamide (Hopkins and Williams) was mixed with 10% by weight of ethanol which was removed by distillation in conjunction with impurities (water, dimethylamine, etc.) as azeotropes. It was then distilled under reduced pressure, and throughout the distillation, the distilland was maintained alkaline to bromothymol blue. The specific conductance was 1×10^{-6} ohm^{-1} cm^{-1} and the water content was 0.01%. Held and Criss[6] consider this solvent to be satisfactory for calorimetry when its specific conductance is less than 8×10^{-6} ohm^{-1} cm^{-1}.

(iii) N,N-Dimethylformamide (B.D.H.) was treated with ethanol as above and distilled under reduced pressure from alkali. The specific conductance was 0.3×10^{-6} rising to 0.9×10^{-6} ohm^{-1} cm^{-1} over 3 months; the water content was 0.02%.

Solutes. (i) Chlorates were the same samples as used in previous work.[10]

(ii) The bromates (Hopkins and Williams) were obtained as hydrates, recrystallized from ethanol–water mixtures, and desolvated at 14 mm and 125° for 24 hr. Iodometric analysis for bromate gave:

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(1) L. Weeda and G. Somsen, *Rec. Trav. Chim.*, **85**, 159 (1966).

(2) G. Somsen and J. Coops, *ibid.*, **84**, 985 (1965).

(3) G. Somsen, *ibid.*, **85**, 517 (1966).

(4) G. Somsen, *ibid.*, **85**, 526 (1966).

(5) D. Feakins and P. Watson, *J. Chem. Soc.*, 4734, 4686 (1963).

(6) R. P. Held and C. M. Criss, *J. Phys. Chem.*, **69**, 2611 (1965).

(7) Y.-C. Wu and H. L. Friedman, *ibid.*, **70**, 501, 2020 (1966).

(8) (a) K. Shug and A. Dadgar, *ibid.*, **68**, 106, 112 (1964); (b) J. E. Prue and P. J. Sherrington, *Trans. Faraday Soc.*, **57**, 1795 (1961).

(9) F. H. Verhoek, *J. Am. Chem. Soc.*, **58**, 2577 (1936).

(10) A. Finch and P. J. Gardner, *J. Phys. Chem.*, **69**, 384 (1965).

Table I

Salt–solvent	T, °C	Molality, m	$\Delta H_{obsd}(T)$, kcal mole^{-1}
	τ = 1–2 min		
$Ca(ClO_3)_2$–F	24.9	0.0132	−11.3
	24.9	0.0160	−11.0
	25.0	0.0270	−11.4
	24.9	0.0284	−11.5
	24.8	0.0295	−11.2
	24.8	0.0210	−11.4
	25.2	0.0312	−11.3
	24.9	0.0361	−11.6
	24.9	0.0379	−11.1
	25.0	0.0454	−11.4
	25.0	0.0490	−11.2
	τ = 3 min		
$Sr(ClO_3)_2$–F	24.9	0.0237	−8.38
	25.0	0.0331	−8.29
	24.9	0.0395	−8.27
	25.0	0.0400	−8.26
	25.0	0.0418	−8.19
	24.9	0.0433	−8.33
	24.9	0.0485	−8.18
	24.9	0.0533	−8.33
	τ = 3–4 min		
$Ba(ClO_3)_2$–F	24.9	0.0347	−4.94
	25.0	0.0444	−4.84
	24.9	0.0458	−4.96
	25.0	0.0498	−4.97
	25.0	0.0507	−4.97
	24.9	0.0562	−5.00
	τ = 1 min		
$Ca(ClO_3)_2$–NMF	25.0	0.0105	−13.8
	25.0	0.0110	−13.8
	25.0	0.0193	−13.6
	25.0	0.0268	−13.8
	τ = 10 min		
$Sr(ClO_3)_2$–NMF	24.9	0.0165	−9.34
	24.9	0.0177	−9.16
	24.9	0.0273	−9.06
	24.9	0.0311	−9.04
	24.9	0.0452	−8.81
	τ = 1 min		
$Ba(ClO_3)_2$–NMF	25.0	0.0202	−7.22
	25.0	0.0261	−7.04
	25.0	0.0502	−6.85
	25.0	0.0527	−6.91
$Ca(ClO_3)_2$–DMF	25.0	0.0100	−18.6
	25.0	0.0110	−18.5
	25.0	0.0127	−18.6
	25.0	0.0133	−18.1
	25.0	0.0152	−18.8
	25.0	0.0169	−18.4
	25.0	0.0173	−18.2
	24.9	0.0173	−18.55
	24.9	0.0174	−18.25
	25.1	0.0216	−18.2
	τ = 5 min		
$Sr(ClO_3)_2$–DMF	25.0	0.0132	−13.9
	25.2	0.0156	−13.6
	24.9	0.0271	−13.15
	25.0	0.0286	−13.1
	25.0	0.0389	−12.7
	24.9	0.0452	−12.4
	24.9	0.0503	−12.95
	25.1	0.0507	−12.8
	τ = 1 min		
$Ba(ClO_3)_2$–DMF	24.9	0.0141	−11.55
	24.9	0.0154	−11.56
	24.8	0.0329	−11.05
	24.9	0.0437	−10.72
	24.9	0.0445	−10.64
	24.9	0.0543	−10.63
	τ = 2 min		
$Ca(BrO_3)_2$–H_2O	24.9	0.0090	0.69
	25.0	0.0092	0.44
	25.0	0.0101	0.64
	25.0	0.0101	0.59
	τ = 3 min		
$Sr(BrO_3)_2$–H_2O	25.0	0.0446	4.93
	25.0	0.0448	4.87
	25.0	0.0463	4.99
	25.0	0.0478	4.79
	25.0	0.0498	4.89
	τ = 3 min		
$Ba(BrO_3)_2$–H_2O	25.0	0.0119	10.6
	24.9	0.0122	10.3
	25.0	0.0140	10.6
	24.9	0.0145	10.5
	τ = 2 min		
$Ca(BrO_3)_2$–F	25.0	0.0200	−4.80
	25.0	0.0296	−4.65
	24.9	0.0398	−4.57
	25.0	0.0467	−4.63
	25.0	0.0491	−4.54
	τ = 30 min		
$Sr(BrO_3)_2$–F	25.0	0.0252	−3.1
	25.1	0.0290	−3.3
	τ = 12 min		
$Ba(BrO_3)_2$–F	25.0	0.0095	0.2
	25.0	0.0102	0.4
	τ = 3–4 min		
$Ca(BrO_3)_2$–NMF	25.0	0.0500	−4.40
	25.0	0.0556	−4.52
	25.0	0.0607	−4.57
	25.0	0.0614	−4.36
	24.9	0.0784	−4.27
	τ = 12 min		
$Ca(BrO_3)_2$–DMF	24.9	0.0238	−4.3
	25.0	0.0268	−4.4

Table II

Salt	Solvent	$\Delta H_s(m)$	m	ΔH_s°, kcal mole^{-1}	a, kcal mole$^{-3/2}$ kg$^{1/2}$
$Ca(ClO_3)_2$	F	-11.3 ± 0.3	0.01–0.05	...	...
$Sr(ClO_3)_2$	F	-8.28 ± 0.07	0.02–0.05	...	...
$Ba(ClO_3)_2$	F	-4.95 ± 0.06	0.03–0.06	...	...
$Ca(ClO_3)_2$	NMF	-13.8 ± 0.1	0.01–0.03	...	...
$Sr(ClO_3)_2$	NMF	...	...	-9.96 ± 0.12	5.30 ± 0.32
$Ba(ClO_3)_2$	NMF	...	...	-7.68 ± 0.12	3.48 ± 0.32
$Ca(ClO_3)_2$	DMF	-18.4 ± 0.2	0.01–0.02	...	...
$Sr(ClO_3)_2$	DMF	...	...	-14.96 ± 0.44	10.3 ± 2.4
$Ba(ClO_3)_2$	DMF	...	...	-12.80 ± 0.16	9.9 ± 0.8
$Ca(ClO_3)_2$	H_2O	-5.60 ± 0.02	0.005–0.01	...	...
$Sr(ClO_3)_2$	H_2O	0.61 ± 0.05	0.01	...	...
$Ba(ClO_3)_2$	H_2O	5.64 ± 0.05	0.01	...	...
$Ca(BrO_3)_2$	F	-4.64 ± 0.10	0.02–0.05	...	...
$Sr(BrO_3)_2$	F	-3.21 ± 0.10	0.03	...	...
$Ba(BrO_3)_2$	F	0.27 ± 0.10	0.01	...	...
$Ca(BrO_3)_2$	NMF	-4.42 ± 0.10	0.05–0.08	...	...
$Ca(BrO_3)_2$	DMF	-4.35 ± 0.05	0.02–0.03	...	...
$Ca(BrO_3)_2$	H_2O	0.59 ± 0.12	0.01	...	...
$Sr(BrO_3)_2$	H_2O	4.89 ± 0.07	0.05	...	...
$Ba(BrO_3)_2$	H_2O	10.50 ± 0.13	0.01	...	...

$Ca(BrO_3)_2$, 100.0%; $Sr(BrO_3)_2$, 99.9%; and $Ba(BrO_3)_2$, 100.1% (analyses were accurate to ±0.1%).

Calorimeter. This was of the constant temperature environment type fully immersed in a thermostat controlled to 25 ± 0.01°. Samples (weighed to ±0.05 mg) were contained in fragile glass ampoules which were broken under 125 ml of solvent. A full description may be found elsewhere.[11] The precision and accuracy of the system were checked by two standard reactions: (i) the enthalpy of solution of potassium chloride in water, $\Delta H_s(25^\circ, N = 200) = 4.216 \pm 0.012$ kcal mole^{-1} (lit.[12] 4.206 kcal mole^{-1} at 25° and N = 200, enthalpy of dilution corrections were taken from ref 13) and (ii) the enthalpy of neutralization of tris(hydroxymethyl)aminomethane (THAM) in excess 0.1 M hydrochloric acid, $\Delta H(25^\circ, N = 670\text{–}1030) = -7.15 \pm 0.05$ kcal mole^{-1} (lit.[14] 7.104 kcal mole^{-1} at N = 1330 and 25°); N is the mole ratio of water to solute. The enthalpy of dilution of THAM is negligible.[14] The errors are quoted as twice the standard deviation of a single observation.

Results

The data are presented in terms of the equation

$$\Delta H_{\text{obsd}}(T) = \Delta H_f^\circ[\text{M}^{\text{II}}(\text{XO}_3)_2, \text{ solution of molality } m] - \Delta H_f^\circ[\text{M}^{\text{II}}(\text{XO}_3)_2, \text{ cryst}] \quad (1)$$

where M^{II} is Ca, Sr, or Ba and X is Cl or Br. In general, the bromates were both slower to dissolve and less soluble in all solvents than the corresponding chlorates. This factor precluded accurate measurement of enthalpies of dilution for most of the bromates. The approximate time taken for complete dissolution (τ) is included in Table I in which ΔH_{obsd} is tabulated at the temperatures T (°C).

Strontium and calcium bromates were too insoluble in both NMF and DMF for enthalpies of solution to be measured. In selected cases, the above data were extrapolated to infinite dilution according to

$$\Delta H_s = \Delta H_s^\circ + am^{1/2} \quad (2)$$

In cases where there existed an obvious linear correlation between ΔH_s and $m^{1/2}$, the value of ΔH_s° was determined from a least-squares analysis. In other cases, a mean value of ΔH is quoted with an error equal to the range if there are less than five values or equal to twice the standard deviation of a single observation if there are five or more values. These data and literature data[10] for $\Delta H_s[\text{M}^{\text{II}}(\text{ClO}_3)_2]$ in H_2O are collected in Table II.

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[11] A. Finch and P. J. Gardner, *J. Chem. Soc.*, 2985 (1964).

[12] S. R. Gunn, *Rev. Sci. Instr.*, **29**, 377 (1958); F. D. Rossini, *et al.*, *J. Phys. Chem.*, **69**, 2902 (1965).

[13] F. D. Rossini, *et al.*, "Selected Values of Chemical Thermodynamic Properties," National Bureau of Standards Circular 500, U. S. Government Printing Office, Washington, D. C., 1952.

[14] R. J. Irving and I. Wadsö, *Acta Chem. Scand.*, **18**, 195 (1964).

Table III

Salt	$-\Delta H_L$, kcal mole^{-1}	$-\Phi$(in H_2O), kcal mole^{-1}	$-\Phi$(in F), kcal mole^{-1}	$-\Phi$(in NMF), kcal mole^{-1}	$-\Phi$(in DMF), kcal mole^{-1}
$Ca(ClO_3)_2$	542	548	553 (5)	556 (8)	560 (12)
$Sr(ClO_3)_2$	513	512	521 (9)	523 (11)	528 (14)
$Ba(ClO_3)_2$	485	479	490 (11)	493 (14)	498 (19)
$Ca(BrO_3)_2$	563	562	568 (4)	567 (5)	567 (5)
$Sr(BrO_3)_2$	531	526	534 (8)	...	...
$Ba(BrO_3)_2$	503	493	503 (10)	...	...

An alternative procedure for evaluating $\Delta H_s°$, suggested by a referee, gave essentially the same results. The procedure was to define $\Delta H_s° = \Delta H_s - am^{1/2}/(1 + m^{1/2})$, where a is the theoretical limiting slope, evaluate $\Delta H_s°$ for each $\Delta H_s(m)$, and plot against molality.

Discussion

Debye–Hückel limiting law slopes ($\mathfrak{S}_H$, Harned and Owen's notation)[15] for di-univalent electrolytes in F,[16,17] NMF,[18,19] and DMF[20–22] were evaluated at 25° using physical data from the references indicated. The equation for the enthalpy of solution of diunivalent electrolytes is

$$\Delta H_s(m) = \Delta H_s°(m \longrightarrow 0) + {}^2/_3\sqrt{6}\mathfrak{S}_H d_0^{1/2} m^{1/2} \quad (3)$$

where d_0 is the density of the solvent at 25°. The coefficients of the $m^{1/2}$ term for F, NMF, and DMF are 0.7, 4.1, and 10.4 kcal mole$^{-3/2}$ kg$^{1/2}$, respectively. These are in good agreement with the experimental a values (see Table II). The limiting slope for solutions in F is sufficiently small to be within the experimental error with which a values could be determined. Hence it is not surprising that no clear correlation was noted for ΔH_s and $m^{1/2}$ in the case of F solutions. Although the data are not sufficiently accurate to be definitive, they suggest that both strontium and barium chlorates are completely ionized and dissociated in dilute NMF and DMF solutions and probably in F also.

Values of combined ion solvation enthalpy (Φ) may be evaluated from a knowledge of the crystal lattice energy (ΔH_L, 298°K) and the relation[23a]

$$\Delta H_L = \Phi - \Delta H_s° \quad (4)$$

In the case of the di-univalent salts examined here

$$\Phi = \phi(M^{2+}) + 2\phi(XO_3^-) \quad (5)$$

where

$$\phi(A^{z\pm}) = \Delta H_f° A^{z\pm}(\text{solvated}) - \Delta H_f° A^{z\pm}(g) \quad (6)$$

These ϕ values are "conventional" in the sense that they are based on $\phi(H^+) = 0$. For the bromates, values of Φ were obtained[10] by an empirical interpolation method[23b] (interpolating on a Φ *vs.* lyotropic number graph for $M^{II}X_2$ salts using $N_1(BrO_3^-) = 9.5$) and the lattice energies obtained from eq 4 and aqueous enthalpies of solution (for this purpose ΔH_s is assumed to be equal to $\Delta H_s°$). From the lattice energies of the bromates and those already available[10] for the chlorates, combined ion solvation energies were evaluated for the salts in F, NMF, and DMF. These data are tabulated in Table III with enthalpies of transfer given by $\Phi(\text{transfer}) = \Phi(M^{II}(XO_3)_2 \text{ in } H_2O) - \Phi(M^{II}(XO_3)_2 \text{ in solvent})$ in parentheses.

Although the values of Φ are only as accurate as the lattice energy estimates (±5%), the enthalpies of transfer are as accurate as the enthalpy of solution measurements (generally within 1%).

The simplest model of solvation is that of Born in which the difference in electrostatic free energy of a charged rigid sphere under vacuum and a continuous dielectric is computed and identified with the solvation free energy. On this model an enthalpy of transfer from solvent 1 to solvent 2 is given by

$$\Phi_1 - \Phi_2 = \frac{e^2}{2}\left[\frac{z_+^2}{r_+} + \frac{z_-^2}{r_-}\right] \times \left[\frac{1}{\epsilon_1} - \frac{1}{\epsilon_2} + \frac{1}{\epsilon_1}\left(\frac{\partial \ln \epsilon_1}{\partial \ln T}\right)_P - \frac{1}{\epsilon_2}\left(\frac{\partial \ln \epsilon_2}{\partial \ln T}\right)_P\right] \quad (7)$$

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(15) H. S. Harned and B. B. Owen, "The Physical Chemistry of Electrolytic Solutions," 2nd ed, Reinhold Publishing Corp., New York, N. Y., 1950, pp 37, 226.

(16) L. R. Dawson, T. M. Newell, and W. J. McCreary, *J. Am. Chem. Soc.*, **76**, 6024 (1954).

(17) G. R. Leader, *ibid.*, **73**, 856 (1951).

(18) Yu. I. Sinyakov, A. I. Gorbanev, Yu. M. Povarov, and Yu. M. Kesslev, *Izv. Akad. Nauk SSSR, Otd. Khim. Nauk*, 1514 (1961).

(19) S. J. Bass, W. I. Nathan, R. M. Meighan, and R. H. Cole, *J. Phys. Chem.*, **68**, 509 (1964).

(20) J. R. Ruhoff and E. E. Reid, *J. Am. Chem. Soc.*, **59**, 401 (1937).

(21) B. V. Ioffe, *Zh. Obshch. Khim.*, **25**, 902 (1955).

(22) G. R. Leader and J. F. Gormley, *J. Am. Chem. Soc.*, **73**, 5731 (1951).

(23) (a) T. C. Waddington, *Advan. Inorg. Chem., Radiochem.*, **1**, 157 (1959). (b) In this reference ΔH_L is defined as positive, contrary to the treatment here.

If solvent 1 is H_2O and 2 is taken as F, NMF, and DMF, then the terms in the second bracket (at 25°) are -3.98×10^{-3}, 5.29×10^{-3}, and 5.29×10^{-3}, respectively. Assuming for any one salt the first term is constant, these data are clearly not in accord with those in Table III.

The deficiencies of the Born model are conventionally "resolved" by (a) the adjustment of the crystal radii (r_+, r_-) by a factor reflecting the effective radius in solution, a value lying between the gas and crystal radii;[24] (b) allowing for electrostriction at the vicinity of the ion surface by including terms expressing the variation in dielectric constant with field strength;[25] or (c) retaining the Born model as describing the electrostatic contribution only and adding additional terms for the energy to form a cavity in the solvent, the energy required to solvate a neutral species, etc.[26-28] From our results two trends are clear: (i) that solvation energies decrease with increasing cation size but increase with increasing anion size—only the first of these is compatible with a Born model; (ii) there is no obvious correlation between Φ and the dielectric constant. The only generalization that can be made is qualitative; *i.e.*, the solvation energy is a maximum in the least "structured" solvents. It is accepted that water has appreciable three-dimensional lattice structure at 25° and it is known[29] that formamide crystal is a layer lattice, hydrogen bonded within the layer and van der Waals interactions existing between the layers. It is probable that some of this two-dimensional structure persists in the liquid phase. Evidence from dielectric relaxation studies[19] indicates that NMF exists in hydrogen-bonded chains of aligned dipoles. Intermolecular bonding in DMF will be very much weaker than with the other solvents and hence may be considered the least "structured." Also, for some alkali chlorides,[30] the free energy of solvation shows the same trend. If hydrogen bonding in the solvent is preferential to the formation of ion–solvent interactions, then the least "structured" solvents will possess the greatest ion-solvating influence. Also, a model including a term for the energy of a cavity formation gains credence, for presumably it will be energetically more favorable to form a cavity in a structureless solvent than the converse.

Estimates of the energy required to form a cavity usually identify this term with the latent heat of vaporization. Use of this term when comparing the magnitude of solvation of a particular ion in one solvent relative to another is questionable. Account must be taken of the relative sizes of the cavity and the ion that is to fill it, and the compressional or distortion energy that follows the placing of an ion in an over- or under-sized cavity.

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[24] W. M. Latimer, K. S. Pitzer, and C. M. Slansky, *J. Chem. Phys.* **7**, 108 (1939).

[25] T. J. Webb, *J. Am. Chem. Soc.*, **48**, 2589 (1926). See also D. C. Grahame, *J. Chem. Phys.*, **21**, 1054 (1953), and references therein.

[26] C. L. de Ligny and M. Alfenaar, *Rec. Trav. Chim.*, **84**, 81 (1965).

[27] R. M. Noyes, *J. Am. Chem. Soc.*, **84**, 513 (1962).

[28] C. L. van Panthaleon van Eck, see ref 2.

[29] J. Ladell and B. Post, *Acta Cryst.*, **7**, 559 (1954).

[30] Yu. M. Povarov, Yu. M. Kesslov, A. I. Gorbanev, and V. E. Kazaranov, *Izv. Akad. Nauk SSR, Ser Khim.*, 1895 (1964).