THE FREE ENERGIES OF HYDRATION

OF IONS AND DIPOLES

by

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PREFACE

This work is divided into four parts. The first is a general introduction. The second and third parts are discussions of the free energy of hydration of ions and of dipolar molecules, on the basis of a continuum dielectric model. The fourth part is a treatment of the hydration of ions in which water is regarded as a structured solvent.

The calculation of free energies of hydration of ions, on the basis of a continuum dielectric model, may well be regarded as passé. Several such calculations have been published very recently; the results of such calculations are needed in the discontinuous model of hydration developed in the fourth part of this work. A simple but good model, in which water is considered as a structureless dielectric, was needed for the second part of the work. The first treatment of the hydration of ions is one that filled both these needs; its results are of some interest both in their own right and as support for those on the hydration of dipolar molecules. For these reasons it is believed that inclusion of the continuum model of hydration of ions, in this work, is fully justified.

I wish to thank Professor K. J. Laidler for his great patience, continued encouragement and support and for his interest in the work. I am most grateful to Professors

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My thanks are due to the staff of the computing centres at the Universities of Ottawa and Toronto. I especially thank Mrs. D. Toop and Mr. T. Rowe, of the University of Ottawa Computing Centre and Mr. I. Farkas of the Institute of Computing Science at the University of Toronto. Without their co-operation this work would have never been completed.

I dedicate this work to my mother and to my step-father, D. H. Clarke, not only for their encouragement, but also for their confidence throughout the long years.

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CHAPTER I

GENERAL INTRODUCTION

1. Introduction.

It has long been recognised that the thermal effects accompanying solution must be explained in terms of interactions between the solvent and solute, and between solute molecules and other solute molecules. The interactions between solute and solute are difficult to interpret, since they depend on concentration and on the properties of the pure solute. Thus, a purely theoretical treatment of the solution process for ethanol is not possible unless an adequate theory of the properties of the liquid alcohol exists. However, a considerable simplification is made if the process of solvation, as opposed to solution, is considered. Solvation occurs when solute is transferred from the vapour phase into the solution. The two processes are related by the Born-Haber cycle shown in Figure 1. Here, MX is any substance, salt or otherwise, and G is any molal thermodynamic function. Algebraically,

$$\Delta G_{solution} = \Delta G_{solvation} + \Delta G_{evaporation}$$

The process of solvation depends on the properties of the solution formed, and hence on the concentration, but not on the properties of the pure solute.

A second simplification is made in considering the process to take place at such low concentrations that the

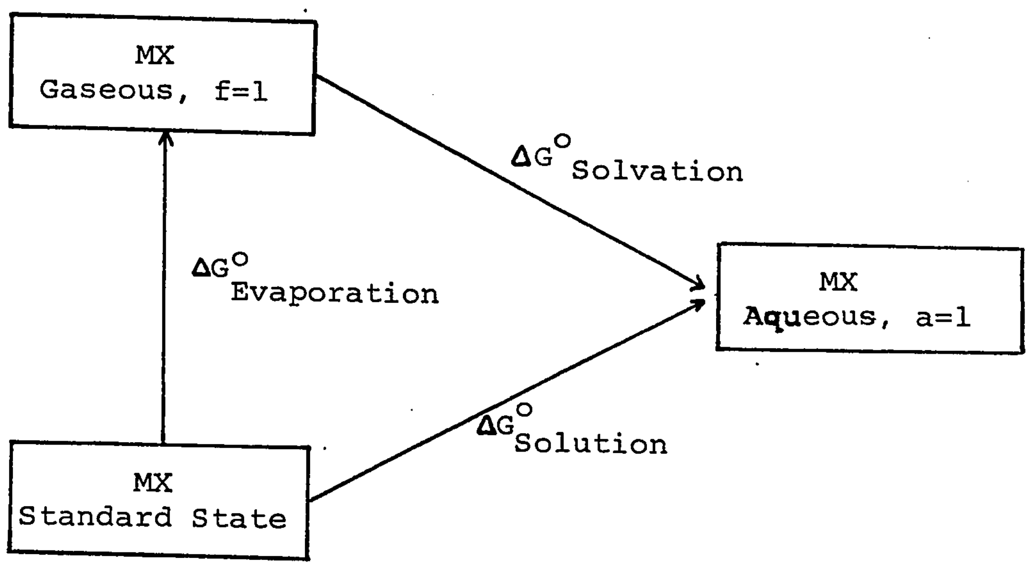


Figure 1.

Relationship between Solution and Solvation.

solute molecules do not interact with each other. This may be accomplished experimentally by extrapolating data obtained at finite concentrations to the intercept at zero concentration of solute, obtaining data at "infinite dilution". The state of infinite dilution has formed the basis of all treatments of solutions. For instance, the Debye-Hückel theory of solutions of finite concentration considers first the infinitely dilute solution and then estimates the effect of increasing the solute concentration to some finite value.

2. Theoretical Treatments of Solvation

The process of solvation is one in which the solute is taken from the vapour phase and transferred into a solution. It is to be emphasized that, in both initial and final states, the solute is considered to behave ideally from the thermodynamic viewpoint. For the vapour,

$$PV = RT$$

where P is the pressure, V the molal volume, R the gas constant and T is the temperature. Likewise, for the solution,

$$P_2 = kN_2$$

where P_2 is the vapour pressure of the solute and N_2 is its mole fraction. k is a constant, which will depend on the particular solute.

It was for such a process that Born (1) developed his theory of solvation of ions. He considered that the solvent was a continuous dielectric medium and that the ion was a sphere bearing the ionic charge. The energy (w) stored in a dielectric medium owing to the introduction of a given charge distribution is given by

$$w = \frac{1}{8.\pi} \cdot \int \vec{D}.\vec{E}.d\tau \qquad (1)$$

where $\vec{D}$ and $\vec{E}$ are the vector dielectric displacement and the field strength respectively. τ is an element of volume, and the integration is to be taken over all uncharged regions of the dielectric.

In a homogeneous, isotropic medium,

$$\vec{D} = \epsilon_i \vec{E} \qquad (2)$$

where ϵ_i is the dielectric constant. Thus,

$$\vec{D}.\vec{E} = \epsilon_i E^2 = D^2 / \epsilon_i \qquad (3)$$

In the case of a charged sphere, of radius r_o, the dielectric displacement is given by

$$\vec{D} = ze/r^2 \qquad r_o < r \qquad (4)$$

$$= \infty \qquad r_o \geq r$$

Substituting (3) and (4) into (1) gives

$$w = \frac{1}{8.\pi} \cdot \int_{r_o}^{\infty} \frac{z^2 e^2}{\epsilon_i r^4} \cdot d\tau$$

In spherical polar coordinates

$$d\tau = r^2 . \sin \phi . d\phi . d\theta . dr$$

so that

$$w = \frac{z^2e^2}{2}\int_{r_o}^{\infty} \frac{1}{\epsilon_i r^2} \quad dr \qquad (5)$$

Born assumed that the dielectric constant was indeed constant with respect to field. The integration in (5) can then be performed analytically, giving

$$w_{vacuum} = z^2e^2/2r_o$$

$$w_{water} = z^2e^2/2.\epsilon_i.r_o$$

The work of hydration is the difference between these quantities. Hence

$$w_{hydration} = \frac{z^2e^2}{2r_o}\left(\frac{1}{\epsilon_i} - 1\right)$$

It is possible to assign radii to the monatomic ions. Tables of such radii have been prepared by Pauling (2), by Goldschmidt (3) and by Ahrens (4). These authors use different assumptions in their calculations. Although the tables do not agree perfectly, in most cases there is very little discrepancy. Using such values for r_o, Born calculated energies of hydration that agreed with experiment, so far as the general trend was concerned. Quantitatively, the agreement was not good.

Another approach to calculating works of hydration is one where water is regarded as an array of molecules. It is assumed that several water molecules become closely bound to the ion, forming a complex. The free energy of formation of the complex may be calculated from the polarisability and dipole moment of water.

3. The Present Work

This work is divided into three main parts. The first, dealt with in Chapter II, is concerned with the hydration of ions on the basis of the assumption of a continuous dielectric. The principal modification to the Born treatment is that the dielectric coefficient of water is assumed to depend on the field strength. The second part (Chapter III) is concerned with the hydration of dipolar molecules, using essentially the same approach. The third part (Chapter IV) treats the hydration of ions in terms of a discontinuous model. In this model, water molecules are evaporated and form a complex with the ion and this complex is then returned to the solution; the free energy of hydration of the ion is the sum of several terms, which are evaluated.

CHAPTER II

THE FREE ENERGIES OF HYDRATION OF IONS USING A CONTINUUM DIELECTRIC MODEL

1. The Dielectric Coefficient

In the equation

$$D = \epsilon_i . E$$

ϵ_i is the dielectric coefficient. It has long been realised that this must depend on the magnitude of the field strength. On the molecular level, an electric field will polarise the molecules that form the dielectric. This polarisation includes atomic and electronic polarisation and also the orientation of the molecular dipoles, if any exist. It is characteristic of dielectrics that there are strong forces resisting these effects. As the field is increased the resistance to polarisation becomes very large. On a macroscopic scale, at low field strengths the dielectric displacement is proportional to the field strength. As the field is increased, the resistance to further polarisation on the molecular level increases rapidly, and the proportionality between field strength and dielectric displacement is lost.

In 1950, Grahame (5) introduced a theory of the dependence of dielectric constant on field strength, in a paper on the diffuse double layer in electrochemistry. His treatment is semi-empirical. He considered that at low field strengths the dielectric coefficient must be very close to the zero-field value, while it must approach a low constant value as the field is increased indefinitely. He proposed that

$$\epsilon_d = \frac{\epsilon_o - C}{(1 + \frac{b}{m} \times E^2)^m} + C \tag{6}$$

In (6), ϵ_d is the differential dielectric coefficient defined by

$$\epsilon_d \doteq \frac{d\vec{D}}{d\vec{E}} , \tag{7}$$

ϵ_o is the bulk or zero-field dielectric coefficient and b and m are constants to be determined. The constant C represents the limiting value as the field becomes infinite. Malsch (6) had measured the effect of high fields on the dielectric coefficient of water. Grahame was able to fit his equation to Malsch's data, using $b = 1.2 \times 10^{-13}$ cm^2 $volts^{-2}$. (1 volt = $\frac{1}{3} \times 10^{-2}$ e.s.u. of potential, so that $b = 1.08 \times 10^{-8}$ e.s.u.). In 1951, Booth (7) presented a purely theoretical treatment of the same problem. He found that

$$\epsilon_i = n^2 + \frac{4\pi N}{E.V} \cdot \frac{\sum_{n=0}^{\infty}(3E/2kT)^{2n+1}.[(2n+1)!]^{-1}.(2n+3)^{-1}.(\vec{\mu}.A[\vec{M}^{2n+1}])}{\sum_{n=0}^{\infty}(3E/2kT)^{2n}.\ [(2n+1)!]^{-1}.A[M^{2n+1}]} \tag{8}$$

where ϵ_i is the integral dielectric coefficient, which is defined by (2). n is the optical refractive index and N is the number of molecules contained in the volume V. E is the (scalar) field strength; k and T have their usual significance.

M is defined by

$$\vec{M} = \sum_{i=1}^{N} \vec{\mu}_i$$

where M and μ_i are both vectors, μ_i being the dipole moment of the i'th molecule, and where

$$A\ (f) = \frac{\int_{(N-1)}^{}\cdots\int f.\exp(-U_N/kT)\ dX}{\int_{(N-1)}^{}\cdots\int \exp(-U_N/kT)\ dX}, \tag{9}$$

$$dX = dX_1.dK_2.dX_3\ \ldots\ldots\ldots\ldots dX_{N-1} \tag{10}$$

and U_N is the potential of all the intermolecular forces among the N dipoles that together form the system.

The calculation of A presents great difficulties. Making various approximations, Booth derived

$$\epsilon_i = n^2 + \frac{28.N_O.\pi.(n^2 + 2).\mu_v}{3.\sqrt{73}.E} . L\ \left(\frac{\sqrt{73}E.\mu_v(n^2 + 2)}{6kT}\right) \tag{11}$$

where L(x) is the Langevin function,

$$L(x) = \text{Coth}\ (x) - 1/x$$

Slightly later, Booth (8) published a more exact treatment of certain aspects of his derivation. The treatment required extensive numerical integration, and he presented the results in the form of a curve. Grahame compared this curve with the integral dielectric coefficient obtained from his equation (6) using m = 1, 2, and 3, and C = n^2. He also showed the curve of equation (11) on the same graph. There was excellent agreement between Booth's curve and that obtained with m = 1, up to field strengths of 10^7 volts per cm. At higher fields, Grahame's curve lay slightly above Booth's. At all field strengths, the curve with m = 1 lay closer to Booth's than that given by (11). The use of Grahame's expression for the dielectric coefficient of water is thus to be preferred to the use of Booth's approximate equation. Laidler and Pegis (9) integrated (6) with m = 1, obtaining

$$\epsilon_i = n^2 + \frac{\epsilon_o - n^2}{b^{\frac{1}{2}}.E} \cdot \mathrm{Tan}^{-1} (b^{\frac{1}{2}}.E) \qquad (12)$$

Throughout this work, this equation is used for the dielectric coefficient of water.

2. The Model

In a homogeneous, isotropic dielectric

$$D = \epsilon_i E \qquad (2)$$

where ϵ_i is independent of field strength. An elementary theorem of electrostatics proves that under these conditions a function ϕ exists such that

$$E = -\nabla \phi. \qquad (13)$$

ϕ is the well-known electrostatic potential. It is arbitrarily set to zero at infinity. If

$$\rho = \rho. (i_1, i_2, i_3) \qquad (14)$$

where ρ is the volume charge density and i_1, i_2, i_3 are independent coordinates in 3-space, then it can also be shown that

$$\nabla^2 \phi = -\frac{4\pi}{\epsilon_i} \cdot \rho \tag{15}$$

In nearly all problems it is possible to find a surface that encloses all the charged regions of space. Then, inside the surface, $\nabla^2 \emptyset$ is given by (15), and outside it is identically zero. The surface may conveniently be located at the interface of two different dielectric media. Subject to the additional boundary condition that, at the surface

$$\emptyset \text{ inside} = \emptyset \text{ outside} \quad ,$$

equations (13) and (15) are sufficient to determine the field strength as a function of the coordinates.

At this point it should be emphasized that a continuous charge distribution $\rho(i_1, i_2, i_3)$ is experimentally indistinguishable from a collection of point charges. The charge distribution will determine the magnitude and location of the charges (and vice versa). Operationally, the two are identical.

An ion or dipolar molecule sets up a very intense, inhomogeneous, anisotropic field. ϵ_i in (2) is no longer constant but behaves as described by (12). Under these conditions (15) is no longer valid and the treatment just described may not be used. Kirkwood (10) considered a problem similar to that presented by a dipolar molecule. He used an unsaturatable dielectric, and assigned a value of 2 to the dielectric constant of the molecule.

According to (12) the dielectric coefficient at very high fields is the square of the optical refractive index. For water at 25° C, this has a value of 1.78, which is close to that used by Kirkwood. In this work the molecule is regarded as a number of point charges. These are contained by a surface $r = r_o$ for ions and $\xi = \xi_0$ for dipoles, (ξ is the coordinate analogous to the radius in the ellipsoidal coordinate system). The molecule is assumed to consist of the same material as the dielectric medium. This avoids the difficulties discussed above. All except perhaps the largest univalent ions will behave as if they were made of a material of dielectric constant 1.78.

3. The Mathematical Treatment

Calculation of the free energy of hydration of ions requires evaluation of the integral in

$$w_{hydration} = \frac{z^2e^2}{2} \int_{r_0}^{\infty} \frac{1}{r^2} \left(\frac{1}{\epsilon_i}\right) dr - \frac{z^2e^2}{2r_o} \qquad (16)$$

According to (3) and (4), the integral in (16) may be recast in the form

$$\frac{z^2e^2}{2} \int_{r_0}^{\infty} \frac{1}{r^2} \cdot \left(\frac{1}{\epsilon_i}\right) dr = \frac{ze}{2} \int_{r_0}^{\infty} E dr \qquad (17)$$

(4) represents a transcendental equation in E. However, the solution in r is simple. (16) may be integrated by parts giving

$$\frac{z^2e^2}{2}\int \frac{1}{r^2}\cdot\left(\frac{1}{\epsilon_i}\right) dr = \frac{ze}{2}\left(E.r - \int rdE\right)_{r_o}^{\infty}$$

$$= \frac{ze}{2}\left((Er)_\infty - E_o r_o - \int_{E_o}^{E_\infty} rdE\right) \qquad (18)$$

where $(E.r)_\infty$ is the limit of (E.r) as r approaches infinity, E taking the value of E_∞. E_o is the field strength corresponding to the radius r_o. As $r \to \infty$, $\epsilon_i \to \epsilon_o$; from (4) the value of $(E.r)_\infty$ must be zero. Therefore,

$$w_{hydration} = \frac{ze}{2}\left(-E_o r_o - \int_{E_o}^{E_\infty} rdE\right) - \frac{z^2e^2}{2r_o} \qquad (19)$$

The integral was evaluated using a seven point Newton-Cotes formula. Further details are given in Appendix II. The work of hydration was calculated for ions of various radii, using an IBM 1620 computer. The programme was written in Fortan II D language.

4. Thermodynamic Standard States

In the continuum dielectric model an isolated ion was considered. An infinite volume of dielectric was introduced and the free energy change was calculated. Experimental free energy changes refer to one mole of ions, initially in vacuum, with unit fugacity, which are transferred to water to form an ideal solution of unit activity. It was necessary to make a correction to the calculated free energies in order that calculated and experimental values should be directly comparable.

Let the ion be contained in a very large volume, V litres, which is initially empty and later filled with water. Then the thermodynamic pressure, P, in the initial state, and the molality, m, in the final state are

$$P = R.T/N_o.V \tag{20}$$

$$m = 1000/N_o.\rho.(V \times 1000) \tag{21}$$

where N_o is Avogardo's number and ρ is the density of water in gm. per ml. at 25°C. For an ideal gas, the pressure and fugacity, f, are equal. The hypothetical standard states for the gas and solution are

$f = 1$ atmosphere

$m = 1$ moles per 1000 grams of solvent

Then

$$F_g = F_g^{\circ} + RT.\ln(RT/N_oV) \tag{22}$$

$$F_s = F_s^{\circ} + RT.\ln(1/N_opV) \tag{23}$$

where F is the free energy, the superscript $^{\circ}$ indicates the standard state and the subscripts $_g$ and $_s$, the gaseous state and solution.

The calculated free energies are: $\Delta F_{calc.} = F_s - F_g$

and the standard free energies are: $\Delta F^{\circ} = F_s^{\circ} - F_g^{\circ}$

Therefore

$$\Delta F_{calc.} = \Delta F^{\circ} + RT.\ln(1/pRT)$$

$$\Delta F^{\circ} = \Delta F_{calc.} + 1.89 \text{ kcal per mole.} \tag{24}$$

5. Orientation Effects and the Thermodynamics of Hydration of the Proton

Buckingham (11) pointed out that an anion and a cation of the same radius must have different hydration free energies. The water molecules around anions and cations must have different orientations; this will be reflected in an orientation free energy. If the water dipole is reversed when an anion replaces a cation, as in Buckingham's model and in the model discussed later in this work, the two free energies of orientation will be of equal magnitude and of opposite sign, to a first approximation.

The hydration of a single ionic species is not directly observable; all experimental work must be done with salts. The free energies of hydration of individual ions may be estimated on the basis of assumptions. The "Relative Free Energies of Hydration" are those determined by arbitrarily assigning zero to the free energy of hydration of the proton. This scale of free energies is used in Rossini's (12) monumental compilation of thermodynamic properties. Another scale of free energies is obtained on the assumption that anions and cations of large equal radii should have the same free energies of hydration. Such a scale is obtained by setting

$$\Delta F^{o}_{hydr.} (Cs^{+}) = \Delta F^{o}_{hydr.} (I^{-}) \qquad (25)$$

so that

$$\Delta F^{o}_{hydr.} (Cs^{+} \text{ or } I^{-}) = \tfrac{1}{2} \Delta F^{o}_{hydr.} (CsI).$$

Although the orientation effect discussed above does not allow (25) to be better than an approximation, this scale of free energies is of more interest than the relative scale; it provides an estimate of the actual quantities involved. Numerous attempts were made to find the absolute values of the thermodynamic functions of hydration of the proton, for such a value would yield an absolute scale. One of the most reliable estimates was published by Halliwell and Nyburg (13)

If ΔH_h is a relative enthalpy of hydration, $(\Delta H_h \ (H^+) = 0)$, and ΔH^o the absolute enthalpy

$$\Delta H_h (M^{Z+}) = \Delta H_h^o (M^{Z+}) - Z_+ \Delta H_h^o (H+) \qquad (26)$$

$$\Delta H_h (X^{Z-}) = \Delta H_h^o (X^{Z-}) + Z_- \Delta H_h^o (H+) \qquad (27)$$

$$\Delta H_h (M^{Z+}) - \Delta H_h (X^{Z-}) = \Delta H_h^o (M^{Z+}) - \Delta H_h^o (X^{Z-}) - (Z_+ + Z_-) \Delta H_h^o (H^+)$$

Abbreviating $\Delta(\Delta H (M^{Z+}) - \Delta H (X^{Z-}))$ as $\Delta(\Delta H)$ and considering a uni-univalent electrolyte

$$\Delta(\Delta H_h) = \Delta(\Delta H_h^o) - 2\Delta H_h^o (H^+) \qquad (28)$$

The term $\Delta(\Delta H_h^o)$ may be approximated for hypothetical ions of equal radii by use of any of the theories of hydration of ions. Halliwell and Nyburg used Buckingham's theory. $\Delta(\Delta H_h)$ may be found, again for ions of the same radii, by drawing curves of $\Delta H_h (M^{Z+})$ and $\Delta H_h (X^{Z-})$ against a suitable function of radius. Buckingham's treatment, and indeed that given in this work, suggests that $\Delta(\Delta H_h^o)$ should vary largely as $(R + a)^{-3}$, where R is the ionic radius, and a is the distance from the ion's surface to the ideal dipole, equivalent to the water molecule. Buckingham assumed this was at the centre of a sphere of radius 1.38Å, so approximately

$$\Delta(\Delta H_h^o) \propto (R + 1.38)^{-3}$$

Halliwell and Nyburg accordingly plotted $\Delta H_h (M^+)$ and $\Delta H_h (X^-)$ against $(R + 1.38)^{-3}$ and were able to find a smooth curve for

$\Delta(\Delta H_h)$ for the uni-univalent ions. Now in any theory

$$\underset{R \to \infty}{\mathrm{Lt}} \; \Delta(\Delta H_h^o) = 0$$

Referring to (28),

$$\underset{R \to \infty}{\mathrm{Lt}} \; \Delta(\Delta H_h) = -\, 2\Delta H_h^o(H^+)$$

$\Delta(\Delta H_h)$ was plotted against $(R + 1.38)^{-3}$ giving a line with a slight curvature. The authors reasoned that the curvature should become small at high radii, and used a straight line extrapolation; they concluded that the enthalpy of hydration if the proton is -261 kcal per mole. This procedure has been criticized by Conway (14) who argued that there was insufficient evidence to justify the straight line extrapolation and that the true enthalpy might reasonably differ by $\pm$ 7 kcals per mole from the extrapolated value.

Slightly later, Noyes (15) presented a much more detailed treatment for separating the partial molal thermodynamic functions of individual univalent ions. His argument parallels that of Halliwell and Nyburg to a large extent. He estimated that the free energy of hydration of the proton was -259.2 $\pm$ kcal per mole. In a later paper,(16), he corrected this to -260.7 $\pm$ 1 kcal per mole. This estimate was used in this work.

Halliwell and Nyburg's work also provided a facile method of estimating the orientation term discussed above.

Let ΔF_c be the calculated free energy of hydration, and let C(R) be a function defined by

$$\Delta F_c(M^{Z+}) = \Delta F_h^o(M^{Z+}) - Z_+.C(R) \tag{29}$$

$$\Delta F_c(X^{Z-}) = \Delta F_h^o(X^{Z-}) + Z_-.C(R) \tag{30}$$

Then

$$\Delta(\Delta F_c) = \Delta(\Delta F_h^o) - (Z_+ + Z_-).C(R)$$

In the continuum dielectric model

$$\Delta(\Delta F_c) = 0,$$

so

$$\Delta(\Delta F_h^o) = (Z_+ + Z_-).C(R) \tag{31}$$

On the other hand,

$$\Delta F_h(M^{Z+}) = \Delta F_h^o(M^{Z+}) - Z_+.\Delta F_h^o(H^+) \tag{26}$$

$$\Delta F_h(X^{Z-}) = \Delta F_h^o(X^{Z-}) + Z_-.\Delta F_h^o(H^+) \tag{27}$$

So that

$$\Delta(\Delta F_h) = \Delta(\Delta F_h^o) - (Z_+ + Z_-).\Delta F_h^o(H^+)$$

It follows from (31) that

$$\Delta(\Delta F_h) = (Z_+ + Z_-).(C(R) - \Delta F_h^o(H^+))$$

and so

$$C(R) = \frac{\Delta(\Delta F_h)}{Z_+ + Z_-} + \Delta F_h^o(H^+) \tag{32}$$

Substitution of (32) into (29) and (30) gives

$$\Delta F^o(M^{Z+}) = \Delta F_c(M^{Z+}) + Z_+ \; x(\frac{\Delta(\Delta F_h)}{Z_+ + Z_-} + \Delta F_h^o(H^+)) \tag{33}$$

$$\Delta F^o(X^{Z+}) = \Delta F_c(X^{Z-}) + Z_- \; x(\frac{\Delta(\Delta F_h)}{Z_+ + Z_-} - \Delta F_h^o(H^+)) \tag{34}$$

6. The Ionic Radii

All workers agree that some form of correction should be made when crystallogrophic radii are applied to continuum models of hydration. This correction was usually of an arbitrary nature and was originally applied to force correspondence between the predicted and experimental trends. Two types of correction were used: in one, a constant was added to the radii, and in the other, the radii were multiplied by an arbitrary factor. Attempts were made to justify the corrections and these led to two widely differing schools of thought.

The argument for adding a constant to the ionic radii is based on the discontinuous nature of the solvent. If in a hypothetical experiment a small neutral particle were to be examined under very great magnification, it would be found that the particle was surrounded by four water molecules, tetrahedrally disposed. Quantum-mechanically, these molecules have no surface: the electron-probability approaches zero exponentially. It is, however, very useful to regard them as having surfaces, and if this were done, it would be seen that a certain volume of free space exists round the particle. If the particle were to be replaced by an ion, the configuration might change owing to the existence of non-spherical electron orbitals. If the size of the ion were to be increased, the water molecules might take up a cubic, an octahedral or a more complicated geometry, but regions of free space would still exist close to the ion. Various workers have proposed treatments in which this free space is smeared out into an annular shell. The thickness of this shell may be calculated, subject to reasonable assumptions, but it was usually determined semi-empirically. In these models, the ion was considered to have a dielectric constant of unity, so the shell thickness, (α), could be added to the ionic radius, R:

$$R' = R + \alpha$$

where R' is the "effective ionic radius". Latimer, Pitzer and Slansky (17) used an argument, related to the above, but based on the distance from the ion to the water dipole. They used the bulk dielectric constant of water and found corrections

$$\alpha = \begin{cases} 0.1 \text{ Å for anions} \\ 0.85 \text{ Å for cations.} \end{cases}$$

Their calculated free energies were in quite good agreement with the experimental values available. In a more recent series of papers, Gluekauf (18) calculated free energies of hydration using Booth's dielectric constant, (vide page 10.) His treatment made use of a correction similar to that of Latimer, Pitzer and Slansky, and he justified the correction by an argument very similar to that described above. In this case

$$0.55 \leqslant \alpha \leqslant 0.65 \text{ Å}$$

The value of α was dependent on the value taken by a parameter equivalent to b in (12). A single value of α was obtained by an empirical method.

Gluekauf's value should be preferred to the values obtained by Latimer, Pitzer and Slansky: it seems unlikely that the water dipole for a cation should be 0.75Å further from the ion than that for an anion. The enthalpies of hydration of cations found by Gluekauf agreed quite well with the experimental data. However, the agreement was not very good for anions. His calculated entropies agreed well with the experimental results for uni-valent cations, but rather poorly for divalent cations. Although this kind of treatment gives very reasonable results, it is open to a serious objection. All such treatments depend on the Born equation and this considers ions in solution and in vacuum. In the latter case, the corrections made by these treatments are clearly invalid, especially as the vacuum term must be the major part of the calculated free energy or enthalpy. Such corrections may be legitimately made in the calculation of entropies, since it is universally assumed that the ionic radii are temperature independent.

The alternative approach to justifying a correction to the ionic radii, was, and remains, frankly empirical. Couture and Laidler (19) examined the apparent molal volumes of single ionic species. They decided that the best correlation between the apparent molal volume and the ionic radius was found when the radii were multiplied by an arbitrary factor of 1.25. Laidler and Pegis (9) used this correction in estimating the thermodynamic functions of hydration of ions, speculating that the apparent increase in the radii might be due to expansion of the ions when they were removed from the very intense fields existing in the crystal.

The effective radii, in the continuum model, were taken to be the crystal radii multiplied by a factor of 1.25. The crystal radii used were those given by Goldschmidt (3).

7. Empirical Free Energies of Hydration

Compilations of data on the thermodynamics of hydration of ions have been published by Noyes (16) and by Yatsimirski and his co-workers (20). The free energies given by Noyes were based on

$$\Delta F_h^o(H^+) = -260.7 \text{ kcal per mole.}$$

Yatsimirski and co-workers used

$$\Delta H_h^o(H^+) = -265 \text{ kcal per mole}$$

$$\Delta S_h^o(H^+) = 0 \text{ e.u.}$$

in their calculations. They estimated that the true value of the entropy was -3.4 e.u. Noyes concluded that the value lay between -5 and zero entropy units. The value of -3.4 e.u. was used in this work. Yatsimirski's free energies for the proton was recalculated on this basis.

This gave

$$\Delta F_h^o(H^+) = -264 \text{ kcal per mole.}$$

The free energy of hydration used in this work is -260.7 kcals per mole. The data of Noyes and Yatsimirski, et al. were recalculated:

$$\Delta F_h^o = \Delta F_R + Z((-260.7) - \Delta F_R(H^+))$$

where the superscript ^{o} refers to the new value, and the subscript $_R$ to the old one.

It was found that there was quite good agreement between the two sets of data on cationic hydration. However, the agreement was bad when anion free energies were compared. In particular, Noyes's value for the fluoride ion was -86.7 kcal per mole.; Yatsimirski's was -104.5 kcal per mole. Stokes (21) noted that recent work by Randle (22) showed that the true value was about -102.1 kcal per mole., (on the scale $\Delta F_h^o(H^+)$ = -260.7). It seemed probable that Noyes's compilation of free energies was more accurate than Yatsimirski's. In this work, Noyes's values were used for the experimental free energies, except that Randle's value was used for the fluoride ion.

Table 1

Free Energies of Hydration of the Inert Gases

	ΔF_{nes}, Kcal per mole
He	4.7
Ne	4.3
Ar	3.9
Kr	3.6
Xe	3.2

Noyes pointed out that even the rare gases have a free energy of hydration. Models based on electrostatic theory can not account for this. The free energy of hydration of an ion may be written

$$\Delta F_h^o = \Delta F_{es} + \Delta F_{nes} \tag{35}$$

where the subscripts stand for electrostatic and non-electrostatic. Noyes used an empirical method of calculating the non-electrostatic term, which was based on the free energies of hydration and the radii of the inert gases. In the present work, this term was approximated as the free energy of hydration of the rare gas that was isoelectronic to the ion under consideration. These free energies were taken from Noyes's paper and are given in Table 1.

8. Results and Discussion

Noyes (15) and Stokes (21) have discussed the problem of the potential, (V), at the vacuum-water interface. This potential is of unknown magnitude, although it can not be large. The movement of charge through a potential requires work; this work is ZeV ergs for a charge Ze. Noyes considered the problem in great detail, proposing that the process of hydration should be defined such that only neutral species cross the interface, as in

$$M^{Z+}(g) + Z.e^{-} \xrightarrow{H_2O} M^{Z+}(aq.) + Z.e^{-}(aq.)$$

This process avoids the difficulties caused by the interfacial potential, but introduces the hydration of electrons. Stokes pointed out that both

$$F_R(M^{Z+}) = F^o(M^{Z+}) - Z_+ F^o(H^+) \quad (36)$$

and the corresponding equation for anions contain terms that have the same charge dependence as the interfacial potential work term. Since the calculation of $\Delta F^o_h(H^+)$ depends on these equations, no further consideration on the interfacial potential is needed.

Calculated free energies of hydration were defined as

$$\Delta F_{calc} = \Delta F_{es} + 1.89 + \Delta F_{nes} \text{ kcal per mole.} \quad (37)$$

The term 1.89 is the correction to the standard state, which was discussed on page 16.

ΔF^* was defined as

$$\Delta F^* = \Delta F^o_h - 1.89 - \Delta F_{nes}$$

Graphs were drawn of ΔF^* for anions and cations as functions of $1/(R+1.38)^3$, where R was the effective radius of the ion. These are shown in Figure 2. $\Delta(\Delta F^*)$ was determined at several values of $1/(R+1.38)^3$. It was found that a graph of $\frac{1}{2}\Delta(\Delta F^*)$ against $1/(R+1.38)^3$, (Figure 3) was a line with slight curveature.

The results of the calculations are given in Table 2. The "Effective Radius" was 1.25 times the Goldschmidt radius of the ion, except in the case of Be^{2+}. This ion is so small that it fits loosely in the cage formed by four tetrahedrally arranged water molecules. An ion of radius 0.57Å would just touch the molecules forming the cage. Therefore the effective radius of Be^{2+} was taken to be 1.25x0.57 or 0.71Å.

In Table 2, ΔF_{ct} is the free energy calculated by equation 16. ΔF_{or} is the correction for the different orientation of water near anions and cations. This term should be estimated by equations (33) and (34), using data from anions and cations of the same charge. The sulphide ion is the only suitable polyvalent ion for which data is available. Therefore ΔF_{or} was estimated to be $\frac{1}{2}Z\pm.\Delta(\Delta F_h^*)_{Z=1}$. This was an approximation, and the true value may differ significantly from that used.

Columns 6, 7 and 8 of Table 2 are the total electrostatic free energy of hydration, ΔF_{es}, the calculated value, ΔF_{calc} and the standard free energy, ΔF_h^o.

$$\Delta F_{es} = \Delta F_h^o + \Delta F_{or}$$

$$\Delta F_{calc} = \Delta F_{es} + 1.89 + \Delta F_{nes}$$

The error,

$$\text{Error} = \frac{\Delta F_{calc} - \Delta F_h^o}{\Delta F_h^o} \times 100$$

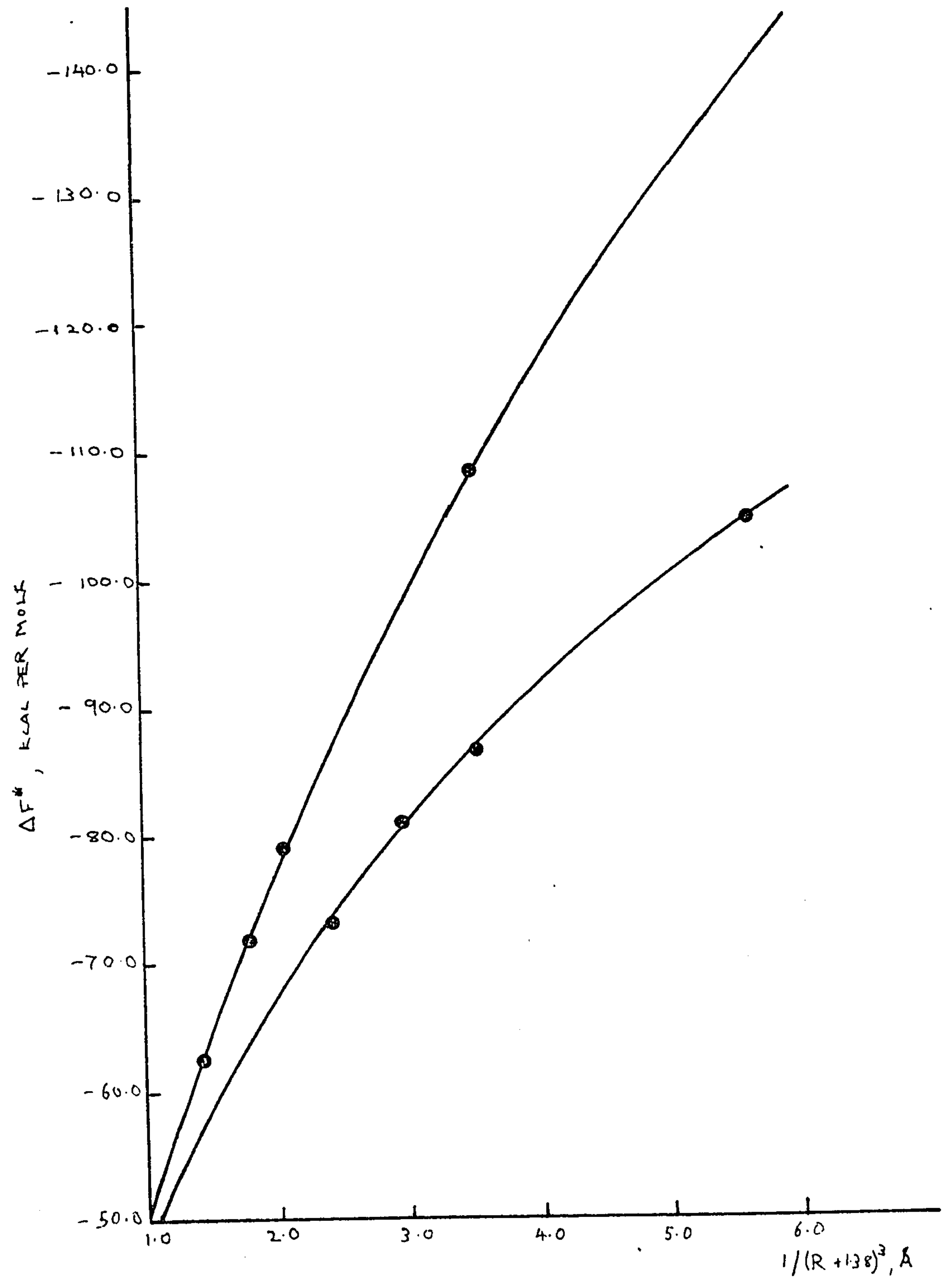
is listed in the last column.

The calculated free energy is quite close to the standard value for most of the ions. The model used for the hydration is not sophisticated, since it was primarily needed for the second part of this work. It is to be expected that the calculations should be least accurate for ions of small radius and high charge. Thus the large errors for Li^+, Be^{2+} and Al^{3+} are not surprising. It is also to be noted that ΔF_{or} for these ions had to be estimated by a rather long extrapolation of the curve in Figure 3.

Figure 2.

Electrostatic Free Energies, ΔF^*, of Hydration

Plotted against $1/(R + 1.38)^3$

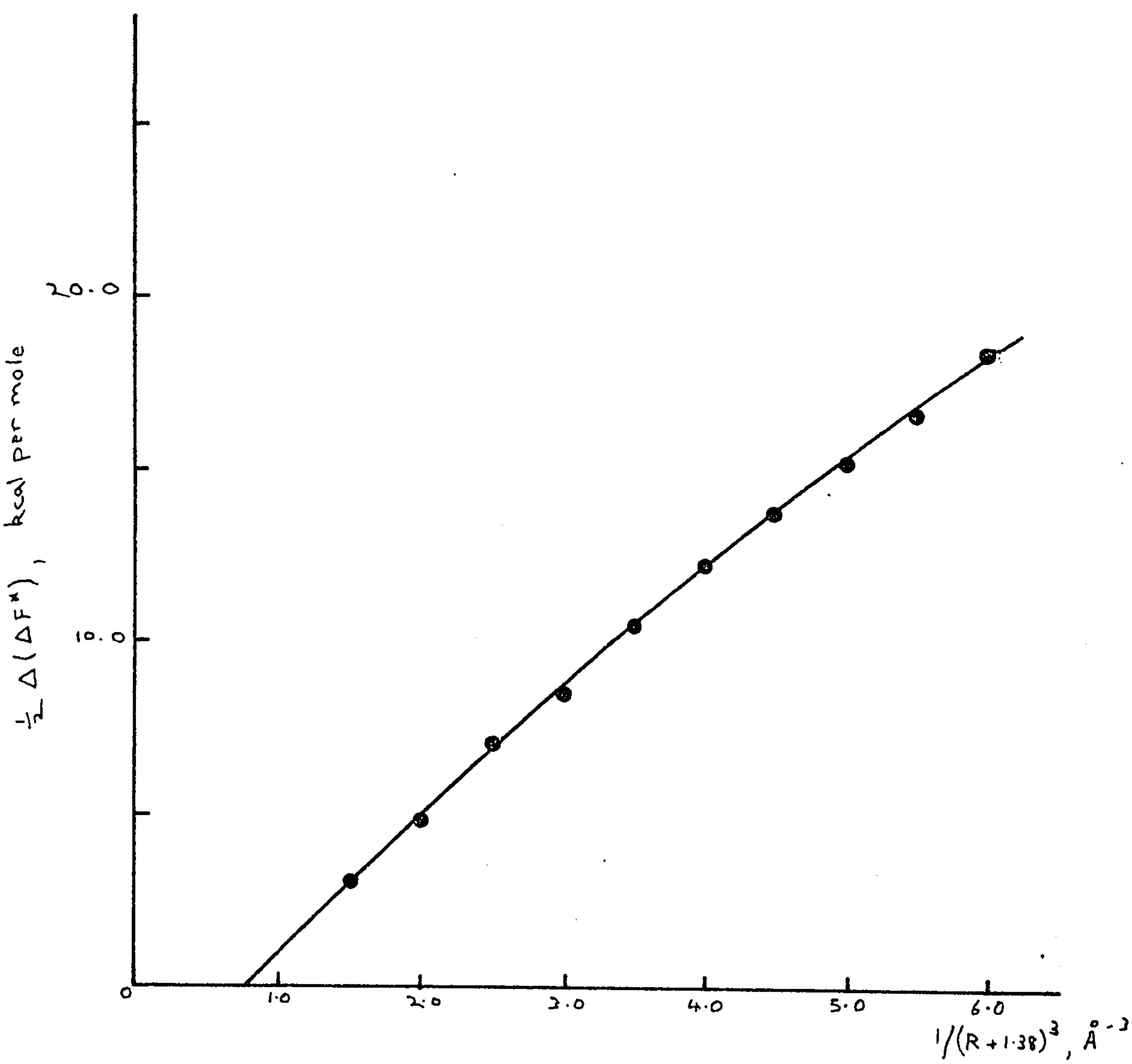


-140.0
-130.0
-120.0
-110.0
-100.0
-90.0
-80.0
-70.0
-60.0
-50.0
ΔF*, KCAL PER MOLE
1.0
2.0
3.0
4.0
5.0
6.0
1/(R+1.38)³, Å

Figure 3.

Electrostatic Free Energies, $\frac{1}{2}\Delta(\Delta F^*)$, of Hydration

Plotted against $1/(R+1.38)^3$



½ Δ(ΔF*), kcal per mole
20.0
10.0
0
1.0
2.0
3.0
4.0
5.0
6.0
1/(R + 1.38)³, Å⁻³

Table 2.

Free Energies of Hydration, kcals. per mole.

Ion	Radius[a], Å	Effective[b] Radius, Å.	$-\Delta F_{ct}$	ΔF_{or}	$-\Delta F_{es}$	$-\Delta F_{calc}$	$-\Delta F_h^o$	Error, %.
Li^+	0.78	0.98	142.4	23.7	118.7	112.1	122.6	8.3
Na^+	0.98	1.23	121.5	17.4	104.1	97.9	98.5	0.6
K^+	1.33	1.66	96.1	10.4	85.7	79.9	80.8	1.1
Rb^+	1.49	1.86	87.3	8.6	78.7	73.3	75.7	3.3
Cs^+	1.65	2.06	79.1	6.7	72.4	67.3	68.0	1.0
F^-	1.33	1.66	96.1	-10.4	106.5	100.3	102.1	1.9
Cl^-	1.81	2.26	72.3	-5.3	77.6	71.8	73.3	2.2
Br^-	1.96	2.40	67.0	-4.2	71.2	65.8	66.4	0.9
I^-	2.20	2.75	59.6	-2.7	62.3	57.2	57.5	0.5
Be^{2+}	0.34	0.71	627.9	59.8	568.1	561.5	584.0	3.9
Mg^{2+}	0.78	0.98	506.3	47.4	458.9	452.7	455.9	0.7
Ca^{2+}	1.06	1.33	412.5	31.2	281.3	357.5	381.2	1.5
Sr^{2+}	1.27	1.59	365.0	23.4	341.6	336.2	341.4	1.5
Ba^{2+}	1.43	1.79	334.9	18.8	316.1	311.0	315.7	1.5
$S^=$	1.74	2.18	289.1	-11.8	200.9	295.1	303.7	2.6
Al^{3+}	0.57	0.71	1324.7	89.7	1235.0	1228.4	1103.7	10.4
Sc^{3+}	0.83	1.04	1010.4	67.2	943.2	937.0	941.7	0.5
Y^{3+}	1.06	1.33	867.7	46.8	820.9	815.1	862.2	5.5
La^{3+}	1.22	1.53	790.2	37.8	754.2	747.0	782.0	4.5

a). Goldschmidt, (3), radii
b). 1.25 x (Goldschmidt radii), except for Be^{2+}, (see text).

9. Comments on the Model

The model used in this section is one in which water is considered to be a continuum dielectric. It was chosen as the simplest model that has any correspondence with physical reality, since such a model was needed in calculations of the free energy of hydration of dipolar molecules. It was to be expected that the results would be best for large ions of low charge and that they would correspond to the average free energy of hydration of an anion and a cation of the same radius. The results are as good as may be expected using such a model.

CHAPTER III

THE HYDRATION OF DIPOLAR MOLECULES

1. The Model

For the purposes of this work, a dipolar molecule was considered as two equal and opposite point charges. These charges were enclosed by the surface formed by rotation about its major axis of an ellipse whose foci were located at the charges. As in the case of the hydration of ions, the free energy of hydration was considered to be the difference between the work of placing this charge distribution in a dielectric medium described by (12) and that of placing it in a vacuum. In each case the work was calculated by integration of (1) from the surface of the ellipsoid.

2. The Coordinate System

Integration from a surface is most easily performed if a coordinate system can be found in which

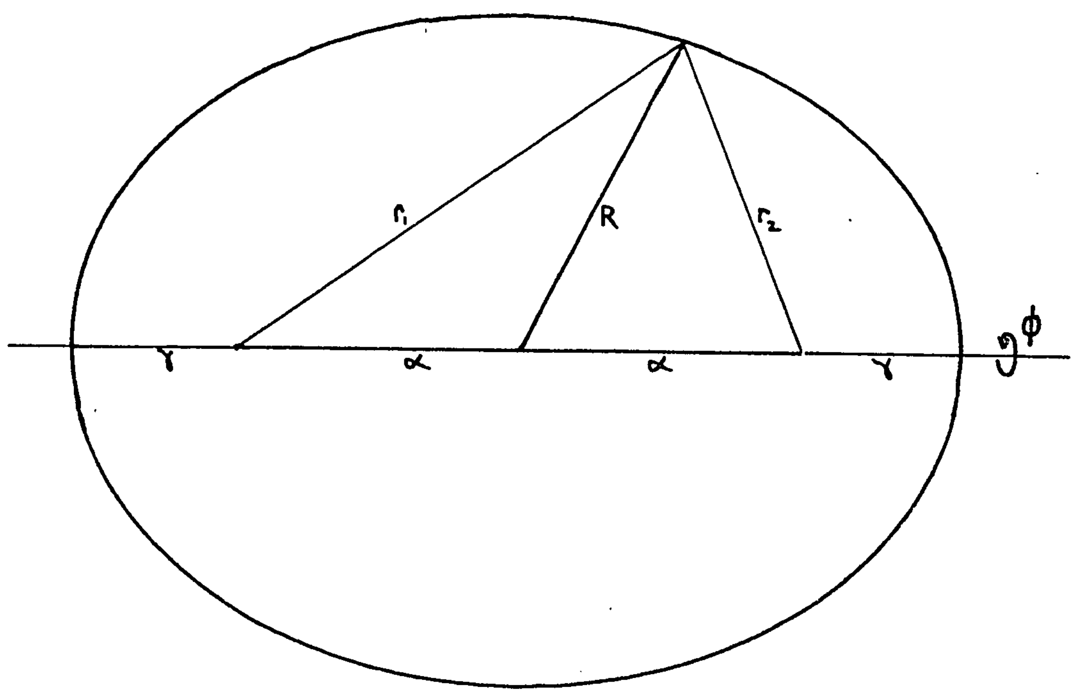
$$p = p_o$$

where p is a given coordinate and p_o is a constant. The prolate spheroid system shown in Figure 4, was chosen in which

$$\begin{aligned} \xi &= (r_1 + r_2)/2\alpha \\ \eta &= (r_1 - r_2)/2\alpha \\ \phi &= \phi \end{aligned} \tag{38}$$

Figure 4.

The Coordinate System



$$\xi = (r_1 + r_2)/2\alpha$$

$$\eta = (r_1 - r_2)/2\alpha$$

$$\phi = \phi$$

where r_1 and r_2 are the distances between a point and the foci, 2α is the separation between the foci and ϕ is the angle of rotation of the plane of the ellipse from a given plane. In this system,

$$\xi = \xi_0$$

describes a surface. For points in real space,

$$\begin{aligned} 1 \leqslant \xi \leqslant \infty \\ -1 \leqslant \eta \leqslant 1 \\ 0 \leqslant \phi \leqslant \pi \end{aligned} \tag{39}$$

The volume element dV is

$$dV = \alpha^3(\xi^2 - \eta^2)d\xi . d\eta . d\phi \tag{40}$$

3. <u>The Dielectric Displacement</u>

If ξ and η are constant, the dielectric displacement is given by

$$D^2 = \frac{4\lambda^2 e^2}{\alpha^4} \cdot \frac{1}{(\xi^2 - \eta^2)^4} \cdot (\eta^2(3.\xi^2 + \eta^2) + \xi^2 - \eta^2) \tag{41}$$

The derivation of this is given in Appendix III. In (41), λ is the dipolar charge.

4. The Work of Hydration

Equation (1) gives the work of placing the charge distribution in a dielectric as

$$w = \frac{1}{8\pi}\int D.E.dV$$

The dielectric constant of free space is unity, and the dielectric coefficent of the medium is ϵ_i. The work of hydration is therefore

$$w = \frac{1}{8\pi}\int D^2\left(\frac{1}{\epsilon_i} - 1\right).dV$$

In this coordinate system this becomes

$$w = \frac{\lambda^2 e^2}{2\alpha}\int_{-1}^{+1}\int_{\xi_0}^{\infty}\left(\frac{1}{\epsilon_i} - 1\right)\cdot\left(\xi^2 - \eta^2\right)^{-3}\cdot\left(3\xi^2\eta^2 + \eta^4 + \xi^2 - \eta^2\right)d\xi\cdot d\eta \qquad (42)$$

where λe is the magnitude of the dipolar charges and $\xi = \xi_0$ is the equation of the ellipsoid's surface. Different values of ξ_0, λ and α were chosen. The integrations were performed at the University of Toronto, using an IBM 7094 computer. A Monte-Carlo technique was used; full details are given in Appendix III.

5. Correction to Standard States

There are two main sources of experimental free energies of hydration of dipolar molecules. These are the works of Rossini, (12), and of Butler, (23). The calculated free energies must be increased by 1.89 kcal. per mole if they are to be compared to the data compiled by Rossini. This was discussed on page 16.

Butler determined free energies of hydration from equilibrium vapour pressure measurements. His standard states were defined such that

$$F_g = F_g^o + RT.\ln(f)$$
$$F_s = F_s^o + RT.\ln(N_2) \qquad (43)$$

where the subscripts $_g$ and $_s$ indicate gas and solution; f is the fugacity of the vapour in millimetres of mercury and N_2 is the mole fraction of the solute. At equilibrium,

$$F_s = F_g$$

and therefore

$$F_s^o - F_g^o = \Delta F_h^o = RT.\ln(f/N_2)$$

where ΔF_h^o is the standard free energy of hydration. The calculations in this work are such that the molecule is initially in vacuum and finally in solution. As before, (cp. page 16) the virtual pressure, P, now in millimetres of mercury, is given by

$$P = 760RT/N_oV$$

with R in litre atmospheres per ^oK. The virtual mole fraction, N_2, is calculated as

$$N_2 = \frac{1}{N_o} \cdot \left(\frac{1000.\rho V}{M} + \frac{1}{N_o} \right)^{-1}$$
$$\doteq M/1000.\rho VN_o$$

where ρ is the density of water in grams per millilitre, M is its molecular weight and V is in litres. Substituting these values in equation (43),

$$F_s - F_g = \Delta F^o_h - RT.\ln(760.\rho.R.T./M)$$

This is the calculated free energy change. Inserting numerical values

$$\Delta F^o_h = \Delta F_{calc} + 8.20 \text{ kcal per mole.}$$

In addition to this, a correction was made for the non-electrostatic free energy. As before

$$\Delta F_{calc} = \Delta F_{es} + \Delta F_{nes}$$

Estimation of ΔF_{nes} proved rather difficult, since the species corresponding to the inert gases cannot be precisely defined. In some cases, the definition was quite simple: for alcohols, the "neutral" species was the parent hydrocarbon.

6. Bond Lengths and Angles and Dipole Moments

The bond lengths and angles used in the calculations were taken from the Chemical Society's Special Publication, Number 11 (24). The dipole moments were taken from McClellan's compilation (25) of experimental dipole moments. Whenever possible, dipole moments determined in the gas phase were used in the calculations. For some organic compounds, different determinations varied by as much as 20%. Their dipole moments were selected on the basis that in a homologous series, the compound with fewer carbon atoms had the greater dipole moment. This seemed a reasonable assumption and led to consistent free energies of hydration.

7. Results.

The results of the Monte-Carlo calculations are presented in Tables 3 to 5, as "normalised" free energies of hydration. These were defined as being the calculated values of the free energies, divided by $-(10\lambda)^2$. It is predicted that the free energies should vary roughly as the square of the dipolar charge. This normalisation reduces the results to a directly comparable scale, and simplifies the problem of interpolating between values of the relevant parameters.

The free energy of hydration of a dipole is a function of the three parameters: the charges, the charge separation and the extent of the surface of the dipole. It would be impractical to present diagrams of the cross-sections through a four dimensional surface and so no graphs of the results are given. The free energy of hydration corresponding to a given set of parameters may easily be determined by interpolation between the tabulated values.

Table 3.

Normalised Free Energies of Hydration,

10^{-2}. kcal. mole^{-1}electron^{-2}, for 0.50Å. Charge Separation.

	Charge, Electrons.			
ζ_0	0.10	0.30	0.55	0.75
1.050	52.080	50.919	50.916	50.628
1.261	9.237	8.428	8.174	8.083
1.471	4.013	3.402	3.211	3.135
1.682	2.275	1.832	1.687	1.636
1.893	1.448	1.140	1.025	0.981
2.104	0.975	0.761	0.676	0.643
2.314	0.685	0.537	0.471	0.445
2.525	0.494	0.397	0.355	0.324
2.737	0.360	0.300	0.259	0.242
2.956	0.264	0.230	0.199	0.184
3.157	0.201	0.181	0.158	0.147
3.368	0.155	0.143	0.127	0.118
3.578	0.121	0.116	0.103	0.096
3.789	0.094	0.092	0.084	0.079
4.000	0.075	0.074	0.069	0.065

Table 4.

Normalised Free Energies of Hydration,

10^{-2}.kcal. mole^{-1}electron^{-2}, for 1.25Å Charge Separation.

ξ_o	Charge, Electrons. 0.10	0.30	0.55	0.75
1.050	23.07	21.64	20.95	-
1.261	5.11	4.15	3.76_6	3.624
1.471	3.22	1.87	1.61_2	1.553
1.682	1.26	1.07	0.93_5	0.874
1.893	0.74_3	0.67_1	0.59_6	0.556
2.104	0.46_1	0.44_2	0.40_1	0.374
2.314	0.30_2	0.29_8	0.28_0	0.264
2.525	0.20_8	0.20_8	0.20_1	0.193
2.737	0.14_7	0.14_7	0.14_6	0.14_2
2.956	0.10_7	0.10_7	0.10_5	0.10_6
3.157	0.08_1	0.08_8	0.08_0	0.08_0
3.368	0.06_2	0.06_2	0.06_2	0.06_2
3.578	0.04_8	0.04_8	0.04_8	0.04_8
3.789	0.03_7	0.03_8	0.03_8	0.03_8
4.000	0.03_0	0.03_0	0.03_0	0.03_0

Table 5.

Normalised Free Energies of Hydration,

10^{-2}.kcal. mole^{-1}electron^{-2}, for 2.50Å. Charge Separation.

ξ_0	Charge, Electrons; 0.10	0.55	0.75
1.050	13.95	11.23	10.94
1.261	3.173	2.401	2.271
1.471	1.295	1.104	1.039
1.682	0.652	0.613	0.585
1.893	0.371	0.368	0.359
2.104	0.231	0.231	0.229
2.314	0.151	0.151	0.151
2.525	0.104	0.104	0.104
2.737	0.073	0.073	0.073
2.956	0.053	0.053	0.053
3.157	0.040	0.040	0.040
3.368	0.031	0.031	0.031
3.578	0.024	0.024	0.024
3.789	0.019	0.019	0.019
4.000	0.015	0.015	0.015

8. Comparison with Experiment

Rossini and his collaborators,(12), listed data on free energies of hydration for only a few nonionic substances that have dipole moments. These are hydrogen sulphide, selenide and fluoride, formic acid and methanol, cyanogen hydride and cyanogen iodide. In addition to these, they gave the free energy of condensation of water. Butler,(23), gave data on numerous alcohols, some paraffins, amimes, esters ethers and other compounds. In some cases, the model could not be used to calculate the free energies of hydration. This was due to difficulties in assigning the charge separations and to uncertainties in the dipole moments and the other parameters. Each group of compounds is discussed in detail below.

a) The Group VI Hydrides

These compounds have the general formula RH_2. The three atoms form an isosceles triangle. The Chemical Society,s Special Publication No. 11,(24), McClellan, (25), and Rossini, (12), give the data in Table 6. These molecules are among the simplest for which the necessary data are available. Nonetheless, calculation of the free energies of hydration involves a serious difficulty. The model on which the calculations are based is one where the free energy of hydration of a pure macroscopic dipole is determined. These molecules are triatomic and it must be supposed that each nucleus is a centre of charge. The model can not properly be used.

It is quite simple to calculate the effective charges on the nucleii, given the bond lengths and angles and dipole moments. Further calculations can only be made if one of two gross approximations is used. It may be assumed that the molecule behaves as a linear dipole whose length is the height of the isosceles triangle, or that it behaves as two independent dipoles of length equal to the internuclear distance. Both of these views are unrealistic in terms of the proposed model. If the molecule is considered to be a single linear dipole, the ellipsoidal surface should logically be chosen to surround both hydrogen atoms. This would lead to very large values of ζ_0, and hence to very small hydration free energies. If the second approach to calculating the free energies is used, the values obtained for a single dipole should be multiplied by some factor, because more than one dipole makes up the molecule. This factor should be less than two. The obvious choice for the factor is Secant ($\theta/2$) where θ is the angle between the bonds. This would lead to inconsistencies if θ was close to zero or 180°.

Table 6.

	H_2O	H_2S	H_2Se	
Bond Length:	0.958	1.323	1.47	Å
Bond Angle:	104.45	92.1	91	degrees
Dipole Moment:	1.84	0.9	0.4	Debyes
Free Energy, ΔF_h^o:	2.05	1.35	1.4	kcals per mole

Neither of these approaches to calculating the free energies of hydration of molecules that have significant quadrupole moments, in addition to a dipole moment, is very realistic. Unfortunately, one of them must be used. It was found that the second approach gave the better results: this was considered sufficient justification for using it.

The charge per bond in hydrogen selenide was calculated to be 0.04 electrons, using the data in Table 6. The charge separation was 1.47Å and γ, half the Se-Se distance in Se_2 was 1.02Å. This choice gave

$$\xi_o = 2.46$$

Inspection of Table 4, is enough to show that

$$\Delta F_{es}.(H_2Se) \approx 0$$

Making the correction to the standard state,

$$\Delta F^o_h = 1.89 + \Delta F_{nes}$$

No data were available to allow an estimate to be made of ΔF_{nes} so it was assumed to be zero, for this molecule and for water and hydrogen sulphide. This compared quite well with the experimental value of 1.4 kcal per mole.

The calculations for hydrogen sulphide were similar. For this molecule, the effective charge per bond was 0.1 electrons. The charge separation was 1.323Å and γ, half the S-S distance in compounds such as H_2S_2 , was 1.08Å. The corresponding value of ξ_o was 2.542. Using these values, it can be seen from

Tables 4 and 5 that ΔF_{es} is very close to 0.2 kcal per mole. Multiplying by Secant (92.1/2) and correcting the value to the standard state, gives a free energy of +1.6 kcal per mole for the hydration of hydrogen sulphide. This value is only 0.25 kcal per mole from the experimental value.

For water, the effective charge per bond was 0.326 electrons. γ was half the O-O distance in peroxides, 0.74Å, and ξ_o was 2.545. The normalised free energies of hydration, $-\Delta F_{es}(10\lambda)^{-2}$, are shown in Table 7 for various charges and ξ_o's, for a charge separation of 0.958Å. The last row of the Table shows the values obtained by graphical interpolation for $\xi_o = 2.545$. Interpolation between these last values gave a normalised free energy of 0.252 kcal mole^{-1} electron^{-2} and a free energy of -2.68 kcal per mole for the parameters used. Multiplying by Secant (104.45/2) and correcting to the standard state gave a free energy of condensation for water of -2.49 kcal per mole. The experimental value is -2.05 kcal per mole, and the agreement is quite good.

For this group of molecules, the correlation between differences of free energies was much better than the correlation between the absolute values. Thus, if it were assumed that ΔF_{nes} was the same for all of these molecules and if it were further

Table 7.

Normalised Free Energies for Water

ξ_o	Charge, electrons 0.1	0.3	0.55	0.75
2.104	0.610	0.550	0.493	0.459
2.314	0.421	0.380	0.350	0.324
2.525	0.272	0.263	0.247	0.237
2.737	0.197	0.191	0.184	0.175
2.545	0.264	0.256	0.239	0.227

assumed that ΔF_{nes} was given by

$$\Delta F_{nes} = (\Delta F^{o}_{h} - \Delta F_{es})_{H_2Se}$$

$$= -0.49 \text{ kcal per mole,}$$

then

$$\Delta F^{o}_{h}(H_2S) = +1.60 - 0.49$$

$$= +1.11 \text{ kcal per mole}$$

and

$$\Delta F^{o}(H_2O) = 2.49 - 0.49$$

$$= 2.00 \text{ kcal per mole}$$

Then the errors for H_2Se, H_2S and H_2O are zero, 0.24 and 0.05 kcal per mole. In view of the approximations used in the calculations, it can only be said that the agreement is surprisingly good.

b) The Alcohols

It was assumed that for all the alcohols the $C\hat{O}H$ angle was 108.9^{o} and that the O-H bond was 0.958Å long. The C-O separation was taken to be 1.427Å and it was assumed that the elliptical surface bisected this bond. On this basis, ξ_o was 2.167. The normalised free energies in Table 8 were obtained by interpolation from Tables 3 and 4 for a separation of 0.958Å. The last row of the table shows the interpolated values at $\xi_o = 2.167$.

Table 8

Normalised Free Energies

	Charge, Electrons			
ζ_o	0.10	0.30	0.55	0.75
1.893	0.94	0.81	0.72	0.68
2.104	0.61	0.55	0.49	0.46
2.314	0.42	0.38	0.35	0.32
2.525	0.27	0.26	0.25	0.22
2.167	0.55	0.49	0.44	0.42

The data on the dipole moments of the alcohols are not very consistent: McClellan (25) lists six values, ranging from 1.61 to 1.71 debyes, for the dipole moment of methanol, measured in the gas phase. The data for other alcohols are similar. However, he indicates that 1.71 debyes is the preferred value for methanol. It was assumed that the higher alcohols should have lower dipole moments and the values 1.71, 1.70, and 1.67 debyes were selected for methanol, ethanol and 1-butanol. These values correspond to the charges of 0.371_6, 0.369_5 and 0.362_9 electrons. The electrostatic free energies calculated by interpolation for these charges are -6.55, -6.42 and -6.11 kcal per mole. Butler found that the free energy of hydration of methane was 10.23 kcal. per mole. This includes 8.20 kcal. per mole for the correction to standard state.

If it is assumed that the non-electrostatic term is the same for all the alcohols and for methane, then this term ammounts to 2.03 kcal. per mole. Using this value, it was found that the predicted and experimental free energies were very close to each other. The values, and the differences are given in Table 9.

Table 9

	Predicted	Experimental	Difference
Methanol	3.68	3.09	0.59
Ethanol	3.81	3.19	0.62
1-Butanol	4.12	3.49	0.63

The differences are very nearly constant. They are all less than 20% of the experimental values. If the electrostatic and experimental free energies are used to calculate the non-electrostatic free energy, for any one of these alcohols, the recalculated free energies would all agree with the experimental values to within $\pm$ 50 calories per mole.

c) The Ethers

Reference (24) only gives bond data on dimethyl and diethyl ethers. In these two compounds, the C-O bonds have almost the same length, and the C-O-C angles differed by only 3°. It was assumed that the C-O distance was 1.43Å and that the C-O-C angle was 108^{o} for all the others.

Butler gave free energy data for the hydration of diethyl-, ethylpropyl- and dipropyl- ethers. The dipole moments of these compounds are 1.17, 1.16 and 1.03 debyes respectively.

The free energies of hydration were calculated in the same way as those for the Group VI hydrides, (see a), above). The charges per bond were 0.145, 0.142 and 0.128 electrons. It was assumed that the dipolar surfaces, ζ_o , extended half the C-O bond distance beyond the dipole; ζ_o was 2.000 .

Values of the free energy of hydration were found by interpolating from Tables 3 to 5 for a charge separation of 1.43Å, and for a $_o$ of 2.000. The normalised free energies of hydration were 0.50 kcal mole^{-1} for each of these compounds. The free energies were -1.05, -1.01 and -0.81 kcal. per dipole. It is unlikely that the nonelectrostatic term would be the same for the ethers and the alcohols. There is some evidence that the larger the molecule,the smaller is this term, (cp. Table 1). It was assumed that the term was zero for these compounds. The free energies found by multiplying the free energies per dipole by Secant(54) and correcting to the standard state were 6.41, 6.48 and 6.82 kcal.mole^{-1}. The experimental values,from Butler, were 6.24, 6.48 and 6.82 kcal. per mole. The calculated values were all within 0.25 kcal.per mole of the experimental values, although the differences were not almost constant, as had been found for the two series of compounds discussed above.

d) Acetone

For acetone, the dipole moment, (25), is 2.68 debyes, the C-O and C-C distances are 1.24 and 1.55Å and the angle between the two C-C bonds is 117°, (24). The charge on the dipole was calculated to be 0.450 electrons, and it was assumed that the surface of the dipole just touched the methyl carbon atoms. This gave a value for ζ_0 of 2.250 .

The normalised free energy of hydration was found, by interpolation, to be 0.33 kcal per mole. The free energy of hydration was thus 1.52 kcal per mole, when corrected to the standard state used by Butler. This assumed that the non-electrostatic term was zero. The experimental value was 4.29 kcal per mole. The agreement was poor, but it may be that the non-electrostatic term is significant. Unfortunately, Butler did not give data on any other ketones.

e) Other Compounds

Butler also reported free energies of hydration for a number of nitriles, amines and acetates, and for glycerol and glycol. All of these substances have complicated molecular geometries and could not be treated with this model.

Rossini reported data on hydrogen fluoride. This substance ionises appreciably in water. A correction for this ionisation might be made, but the uncertainty in the correction would be as great as or greater than the final result.

9. Comments on the Model.

Using reasonable assumptions, the model described in the previous sections may be used to predict free energies of hydration of dipolar species. The predicted values are quite reasonable, in themselves, but in some cases the agreement with experiment is poor. This disagreement may be attributed to one or more of many reasons. The most obvious source of error is in the assignment of dipole moments. McClellan selected 1.71 debyes as the best estimate for the dipole moment of methanol. However, in his compilation he included values ranging from 1.60 to 3.10 debye. The latter value was determined in the liquid phase, where hydrogen bonding might be expected to have an influence. Nonetheless, the discrepancy is large. For chloroform, in the vapour phase, the range is from 0.96 to 1.86 debye. The free energy of hydration is predicted to vary, very roughly, with the square of the effective charge. Thus, changing the dipole moment by 10% alters the free energy by more than 20%. Most of the calculated free energies are small: when they are corrected to the standard state, this error may be greatly enhanced. The second major source of error is the choice of ξ_0, the surface of the ellipsoid around the dipole. This choice is arbitrary, to a very large extent. The best one can do is to make reasonable assumptions. The comparison of predicted and experimental results is another source of error: in the model, the dipole was assumed to lie along a single bond. Practically all the experimental values are for molecules such as the Group VI hydrides, amines, alcohols, esters, and organic acids. In all of these, more than one bond is involved, and in some cases there is reasonable doubt that any bond should be considered more polarised than any other. On Mulliken's (26) scale, oxygen has an electronegativity of 3.5, hydrogen of 2.1 and carbon of 2.5. In view of this, the assumption that only the O-H bond in alcohols is polarised must be considered as a gross approximation. The situation is similar when an attempt is made to calculate the free energy of molecules such as water, hydrogen sulphide and selenide and chloroform: the water molecule might be treated as two dipoles, at an angle to each other or as a single dipole lying on the HÔH bisector. The first treatment was used in this work. The choice was one of expediency and has no theoretical justification. The model for the hydration of dipoles has been used to calculate free energies of hydration. In spite of all the defects in the model, the calculated free energies were quite close to the experimental values. In the calculations, parameters were selected on a fairly arbitrary basis. However, all the choices were made in the light of experimental data such as bond lengths and angles.

10. Summary

A model for calculating the free energy of hydration has been proposed. The dipole was considered to be two charges separated by a finite distance. There are no molecules which really conform to this model. However, the free energies of hydration of some fairly simple molecules have been calculated and were found to be in good agreement with the experimental values.

CHAPTER IV

FREE ENERGIES AND THE DISCONTINUOUS SOLVATION OF IONS

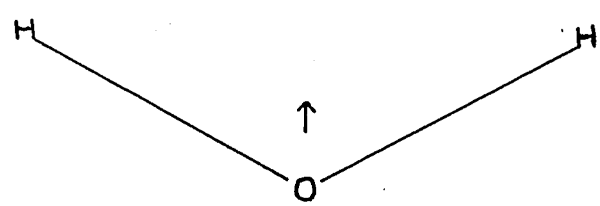
1. The Model

The hydration of ions and of dipolar molecules has been discussed in terms of a continuous dielectric medium. The model used was satisfactory, insofar as it went, but it was physically unrealistic, since all solvents are arrays of molecules. Near an ion, the discontinuous nature of the solvent predominates and such concepts as dielectric constant loose all significance.

In 1959, Buckingham, (11), proposed a treatment for the hydration of ions. He considered a solvent water molecule to be an uncharged array of ideal multipoles; he took explicit account of the intrinsic and induced dipole and quadrupole moments of water. The model used in this work is macroscopic. A water molecule is assumed to consist, electrically, of three point charges which are located on the nucleii of the two hydrogen atoms and the oxygen atom, and of an induced point dipole located on the mid-point of the $H\hat{O}H$ bisector, as shown in Figure 5. The magnitudes of the charges were calculated from the known bond lengths and angles and the dipole moment. Two cases were considered. In one, the oxygen atoms of the water molecules formed a regular tetrahedron round the ion; in the other case, they formed a regular octahedron. The electrostatic potentials between all the charges, including the ion's, between the charges and the induced dipoles and between the

Figure 5.

The Structure Assumed for the Water Molecule.



H-Ô-H 104.45°

O-H 0.958 Å.

$$\mu = \alpha z e / (r_{\text{ion-dipole}})^2$$

dipoles and the other dipoles were summed. This sum was minimized with respect to rotation of the solvent molecules about the ion- (heavy atom) radius. In the case of cation solvation, the heavy atom, the induced dipole and the ion lay on the same line, with the heavy atom closer to the ion than the induced dipole. In anionic solvation, the induced dipole was between the ion and the heavy atom, but otherwise the model was unchanged. The free energy of solvation was calculated according to the Born-Haber cycle shown in Figure 6 , where M is an anion or a cation. Algebraically,

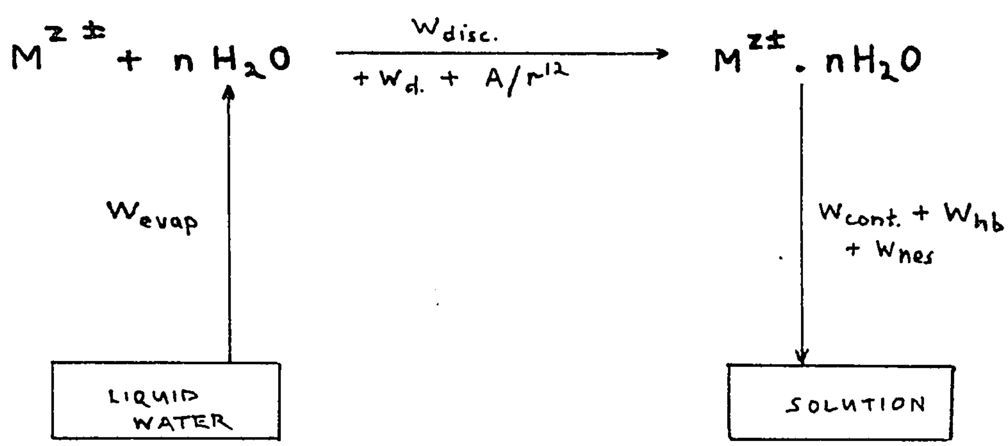
$$w_{hydr.} = w_{calc.} + w_{disp.} + w_{rep.} + w_{evap.} + w_{cont.} + w_{h.b.} + w_{nes.} \quad (43)$$

Here, $w_{hydr.}$ is the total work of hydration and $w_{calc.}$ is that obtained by minimizing the electrostatic interactions. $w_{disp.}$ is the work against dispersion forces and $w_{rep.}$ is obtained against a $1/(\text{radius})^{12}$ repulsion; $w_{cont.}$ and $w_{h.b.}$ are the work of placing the complex $M.nH_2O$ in a continuous dielectric and the work of forming new hydrogen bonds between the solvating molecules and the bulk solvent. w_{nes} is the non-electrostatic term discussed on page 16.

a) The work term arising from the electrostatic charges was estimated for various ion to heavy atom radii, by a programme called HYDR8S, which used a number of subroutines. In short, this programme calculated the coordinates of the (4n+1) objects

Figure 6.

The Born-Haber Cycle Used in the Discontinuous Model for the Solvation of Ions.



$$\Delta F = W_{evap} + W_{disc} + W_{d} + A/r^{12} + W_{cont} + W_{hb} + W_{nes}$$

that comprised the system of n solvent molecules and the ion. It then calculated the sum of the electrostatic energy terms that were unaffected by rotation of the solvent molecules. The sum of the remaining electrostatic terms was minimized by a subroutine MINIM.

b) $w_{evap.}$ was the work of evaporating n water molecules from the liquid state or from infinitely dilute solution at 25°C. $w_{h.b.}$ was the work of forming new hydrogen bonds when the complex was returned to solution. It was assumed that each hydrogen atom could form a hydrogen bond in the case of solvation of cations, and that the oxygen atom could form one bond in the hydration of anions. Nemethy and Scheraga's (27) data on the hydrogen bond were used; at 25°C. the hydrogen bond strength was taken as 3.57 kcals per mole and it was assumed that each bond existed for only 44.8% of the time. On this basis

$$w_{h.b.} = -2n \times 1.60 \text{ kcals per mole for cations}$$
$$= -n \times 1.60 \text{ kcals per mole for anions} \qquad (44)$$
$$w_{evap.} = +10.52 \text{ kcals per mole}$$

The data for the evaporation were taken from Rossini. These data are enthalpies, but since they are of different sign, the error introduced should be small. It was necessary to include the term $w_{h.b.}$ in this model since the evaporation of water in w_{evap} includes the breaking of such bonds. In the continuum model, no such bonds are broken.

c) w_{cont} represents the work of placing the complex in the continuous dielectric medium. Despite the efforts of Frank and his co-workers, (28), the structure of water is not known well enough to permit calculation of the work of returning the complex to a discontinuous medium. Even if the data were available, the calculations would probably take years using the fastest computers available. The surface of the complex is far enough from the ion that the approximations in using the continuum model should be quite good.

d) w_{disp} represents the work of bringing the (n+1) species together against the dispersion forces. This term was calculated according to the approximate London equation:

$$w_{disp} = -\frac{3}{2}\frac{\alpha_1 \cdot \alpha_2}{r_{12}^6}\frac{I_1 \cdot I_2}{I_1 + I_2} \quad \text{e.v.} \qquad (45)$$

where r_{12} is the separation between the two centres, the I's are the ionisation potentials and the α's the polarisabilities of the two species, (ion and water, or water and water). Such interactions were assumed to be significant between the ion and the solvating molecules, and between nearest neighbour solvent molecules. It was considered that the second nearest neighbour solvent molecules were so far separated that the dispersion forces between them were negligible. This term involves the polarisabilities and ionisation potentials of the ions. In contrast to most of the other terms, it is not a smooth function of the ionic radii.

e) w_{nes} was the non-electrostatic term. It was discussed in Chapter II. This term is also not a smooth function of the radii.

f) The term w_{rep} represented the inpenetrability of the ion and the solvent molecules. It was represented as

$$w_{rep} = A(r)/r^{12} \tag{46}$$

where A(r) was an undetermined function of r, the radius. A(r) must be of such nature that the free energy is a minimum at each ionic radius. The total free energy is given by equation (43). In this w_{disp} and w_{nes} are not smooth functions of the radii. However, these terms are small. w_{hb} and w_{evap} are constants. The remaining terms are w_{calc} , w_{cont} and A/r^{12}. The sum of these was minimised by solving numerically for A(r) in the equation

$$\frac{d}{dr}(w_{calc} + A/r^{12} + w_{cont}) = 0 \tag{47}$$

2. Choice of the Ionic Constants

The radii used in this section for calculating the free energies of hydration were the unadjusted Goldschmidt, (3), radii. The ionic polarisabilities were those used by

Muirhead-Gould and Laidler (29). The ionisation potentials for the cations were for the process

$$M^{Z+} \rightarrow M^{Z+ +1} + e \tag{48}$$

The values were taken from the Handbook of Chemistry and Physics (30). By analogy with (48), the ionisation potentials for the univalent anions should be the electron affinity of the parent halide.

$$X^{-} \rightarrow X + e$$

These values were taken from Sidgwick (31). The radii, polarisabilities and ionisation potentials used are shown in Table 10. If an ion has a radius of 0.57Å it can fit in the cage formed by four tetrahedrally arranged water molecules without forcing them apart. Consequently, ions of radius less than this should be considered to have an effective radius of 0.57Å. The only ion affected as the Berillium ion. In Table 11 and in the following pages this ion is taken to have a radius of 0.57Å.

3. Results.

Since the free energy term due to the dispersion forces is not a smooth function of the ionic radii, an effective free energy of hydration was defined by

Table 10.

Ion	Radius, Å	Polarisability, $Å^3$	Ionisation Potential, eV.
Li^+	0.78	0.03	75.26
Na^+	0.98	0.24	47.06
K^+	1.33	0.89	31.66
Rb^+	1.49	1.81	27.36
Cs^+	1.65	2.79	23.40
F^-	1.33	0.81	4.3
Cl^-	1.81	2.98	4.0
Br^-	1.96	4.24	3.8
I^-	2.20	6.25	3.4
Be^{2+}	0.34	0.04	153.1
Mg^{2+}	0.78	0.12	79.72
Ca^{2+}	1.06	0.53	50.96
Sr^{2+}	1.27	0.86	42.8
Ba^{2+}	1.43	1.69	35.5
S^{2-}	1.74	----	----
Al^{3+}	0.57	0.07	119.4
Sc^{3+}	0.83	0.3	73.9
Y^{3+}	1.06	1.02	40
La^{3+}	1.22	1.58	20
H_2O	1.38	1.444	12.56

$$\Delta F_{ef} = \Delta F_h^o - 1.89 - \Delta F_{nes} - \Delta F_{disp} \qquad (49)$$

The effective free energy should be a smooth function of the radii. The remaining terms on the right hand side of (43) gave the predicted free energy:

$$\Delta F_p = \Delta F_{evap} + \Delta F_{disc} + A/r^{12} + \Delta F_{con} + \Delta F_{hb} \qquad (50)$$

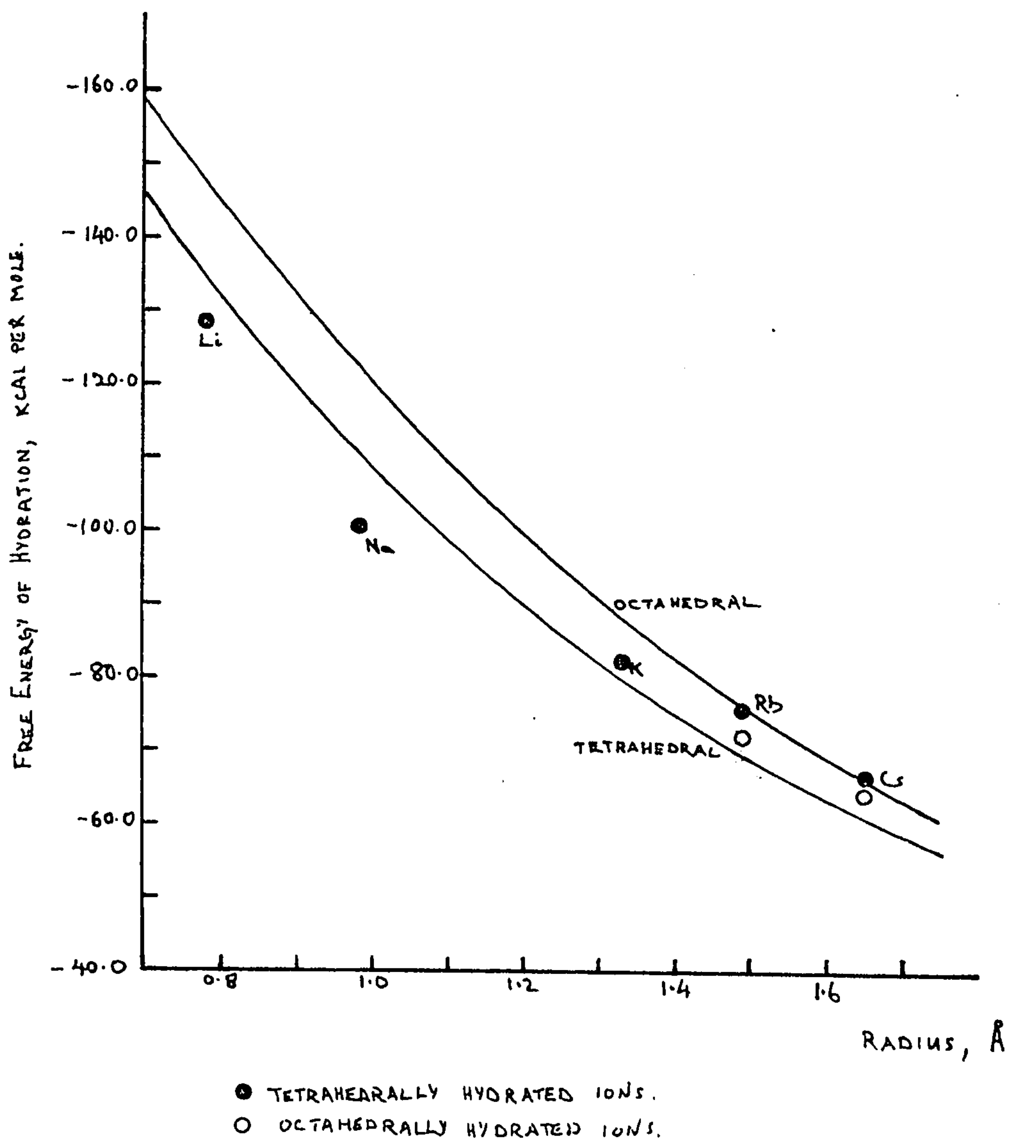
ΔF_{ef} and ΔF_p are compared in Figures 7 to 10. The data are also given in Table 11.

4. Discussion.

There is good evidence that the very small cations are tetrahedrally hydrated, and it seems reasonable that the larger ions should be octahedrally hydrated. It is to be expected that the experimental free energies of hydration of medium sized ions should lie between the predicted curves for tetrahedral and octahedral hydration. This effect was found with many of the experimental values for the cations. The experimental values for the hydration of a few of the cations fell outside the two theoretical curves. This may possibly be explained by one or more of the causes of error discussed below. When there was doubt if an ion should be treated as tetrahedrally or octahedrally hydrated, a point for both types of hydration was entered in the graph, (Figures 7 to 10). The change in ΔF_{ef} was due to a change in the potential due to the dispersion forces.

Figure 7.

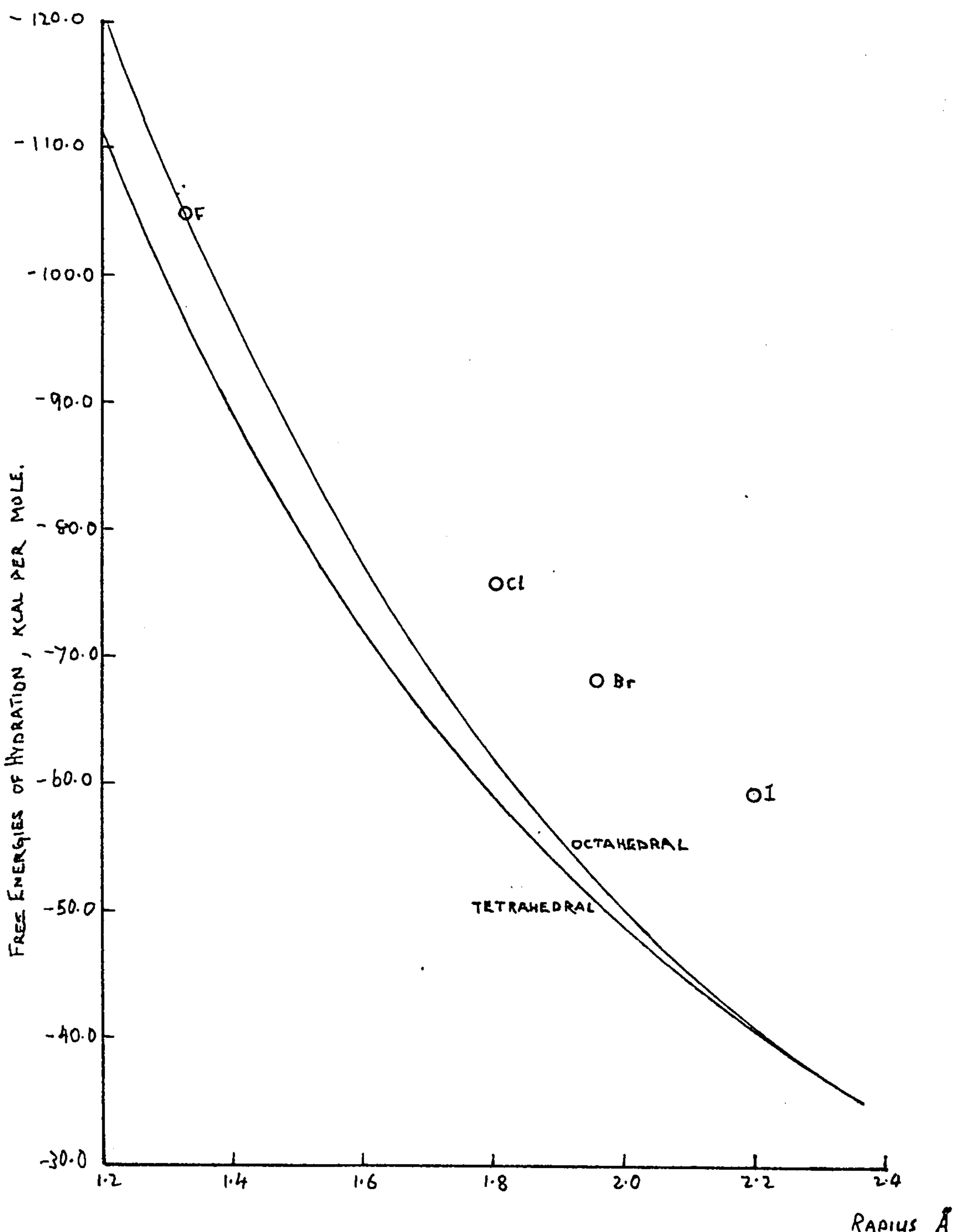
Comparison Between Observed, (points), ΔF_{ef}, and Predicted, (curves), ΔF_p, Free Energies of Hydration for the Univalent Cations.



-160.0
-140.0
-120.0
-100.0
-80.0
-60.0
-40.0
FREE ENERGY OF HYDRATION, KCAL PER MOLE.
0.8
1.0
1.2
1.4
1.6
RADIUS, Å.
Li
Na
K
Rb
Cs
OCTAHEDRAL
TETRAHEDRAL
● TETRAHEDRALLY HYDRATED IONS.
○ OCTAHEDRALLY HYDRATED IONS.

Figure 8.

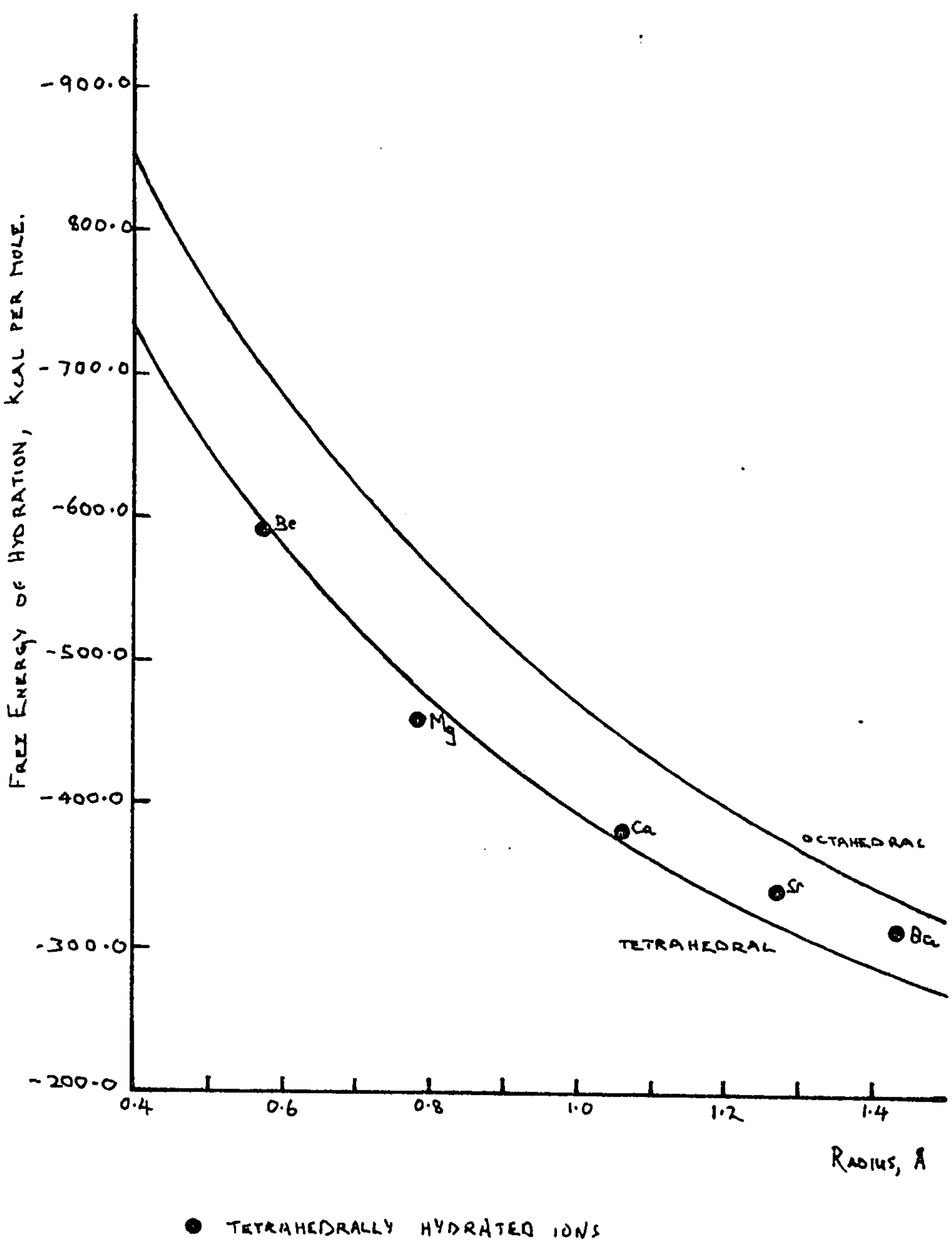
Comparison Between Observed, (points), ΔF_{ef} and Predicted, (curves), ΔF_p, Free Energies of Hydration for the Univalent Anions.



O Octahedrally Hydrated Ions.

Figure 9.

Comparison Between Observed, (points), ΔF_{ef} and Predicted, (curves), ΔF_p, Free Energies of Hydration for the Divalent Cations.



-900.0
800.0
-700.0
-600.0
-500.0
-400.0
-300.0
-200.0
Free Energy of Hydration, Kcal per mole.
0.4
0.6
0.8
1.0
1.2
1.4
Radius, Å
Be
Mg
Ca
Sr
Ba
OCTAHEDRAL
TETRAHEDRAL
TETRAHEDRALLY HYDRATED IONS

Figure 10.

Comparison Between Observed, (points), ΔF_{ef} and Predicted, (curves), ΔFp, Free Energies of Hydration for the Trivalent Cations.

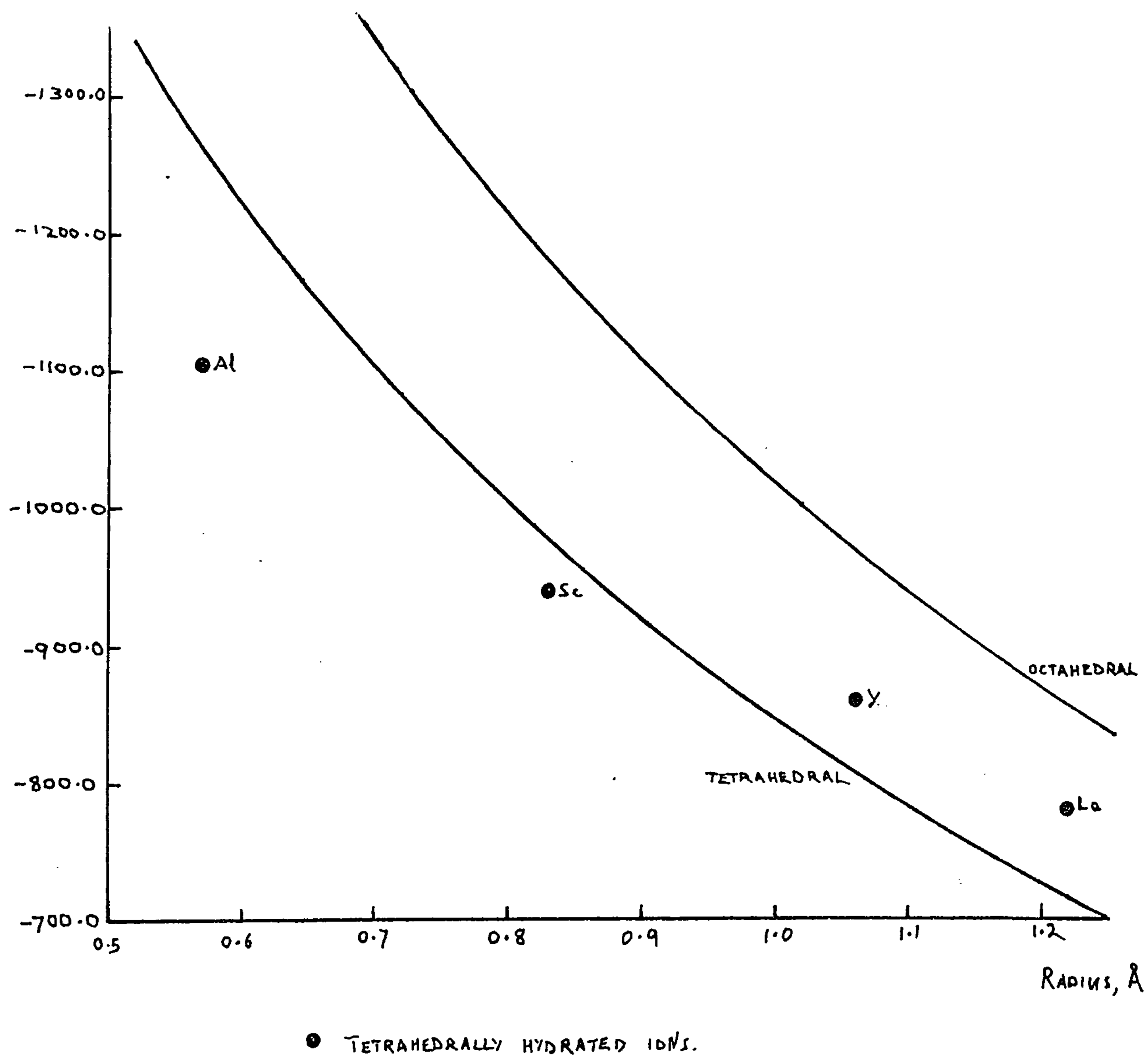

-1300.0
-1200.0
-1100.0
-1000.0
-900.0
-800.0
-700.0
0.5
0.6
0.7
0.8
0.9
1.0
1.1
1.2
Radius, Å
Al
Sc
Y
La
OCTAHEDRAL
TETRAHEDRAL
TETRAHEDRALLY HYDRATED IONS.

Table 11.

Free Energies of Hydration, kcal per mole.

Ion	Radius, A.	Orientation	$-\Delta F_h^o$	$-\Delta F_{disp}$	$-\Delta F_{ef}$	$-\Delta F_p$
Li^+	0.78	T	122.6	2.1	128.1	134.8
Na^+	0.98	T	98.5	3.3	101.4	110.8
K^+	1.33	T	80.8	4.3	80.4	80.7
Rb^+	1.49	T	75.7	5.8	75.4	70.7
		O	75.7	9.5	71.7	77.0
Cs^+	1.65	T	68.0	5.8	67.3	61.9
		O	68.0	8.4	64.7	66.7
F^-	1.33	O	102.1	3.4	104.9	105.4
Cl^-	1.81	O	73.3	3.2	75.9	61.7
Br^-	1.96	O	66.4	3.2	68.7	52.1
I^-	2.20	O	57.5	3.0	59.4	39.4
Be^{2+}	0.57	T	548.0	4.3	587.3	601.1
Mg^{2+}	0.78	T	455.9	4.0	458.1	484.0
Ca^{2+}	1.06	T	381.2	5.8	381.2	320.3
Sr^{2+}	1.27	T	341.4	5.0	341.9	320.3
Ba^{2+}	1.43	T	315.7	5.0	315.8	285.9
$S^{=}$	1.74	O	303.1	(0)	308.9	327.4
Al^{3+}	0.57	T	1103.7	5.5	1104.8	1266.8
Sc^{3+}	0.83	T	941.7	7.1	940.8	977.4
Y^{3+}	1.06	T	862.2	10.0	857.0	806.1
La^{3+}	1.22	T	782.0	8.5	779.0	714.6

Table 12.

Some Quantities Used in Calculating The Free-Energies of Hydration.

Ionic radius	R	A.
Ion-oxygen distance	R + 1.38	A.
Radius of hydrate	R + 2.76	A.
Oxygen-dipole distance, in water	0.30	A.
Oxygen-hydrogen distance in water	0.96	A.
H-O-H angle in water	104.5	°
Dipole moment of water	1.84	D.
Polarisability of water	1.44	A^3.

5. Sources of Error

The experimental and theoretical free energies of hydration of the larger cations were quite close to each other. The very small cations had free energies that were less negative than predicted, while the predicted values for the univalent anions were seriously in error. These discrepancies may be explained quite readilly, and actually follow from the nature of the model. The several sources of error are described below.

a) Inadequacies of the model.

The model used in this work for the hydration of anions is one where the hydrogen atoms of solvating water molecule are both closer to the surface of the anion than is the oxygen atom of the same water molecule. Several authors, (32), have proposed a model in which only one of the hydrogen atoms is near the anion. The second atom is placed near the outside of the primary hydration sphere. In view of the very strong forces that must exist between the hydrogen atoms in the model used in this work, the alternative model may be more realistic. Calculation of the free energy of hydration would be difficult. It would be necessary to assume that the hydrogen atoms closest to the ion had fixed positions, possibly at the vertices of a tetrahedron or an octahedron. The potential energy of the system could then be minimised with respect to the positions of

A better model would be one in which four or six water molecules were allowed to rotate freely, with their surfaces touching the ion, subject to the restriction that their geometries should not change. The potential energy of the complex would be minimised with respect to rotation of the molecules in three dimensions. It would be possible to allow for the compressibility of the water by calculating the force between the molecule and the ion, and moving the charges toward the ion by a distance proportional to the force. This procedure would involve minimisation of the potential energy with respect to at least twelve paramaters; the potential energy function would be much more complicated than the one used in this work. The model would be, in some respects, similar to Vaslow's, (35). Vaslow showed that the energy of a single water molecule and an ion is not minimised unless the water dipole is at a significant angle to the ion's radius. For the Lithium ion the angle of minimum energy was between 50^{o} and 62^{o}, (the value depending on the choice of components of the quadrupole tensor). The corresponding energies were -19.85 and -18.78 kilocalories per mole, compared to an energy of -16.16 kilocalories per mole when the radius and the dipole met in a straight line. However, Vaslow's calculations were for association between only a single water molecule and an ion. The results would probably be greatly changed if several water molecules were considered.

A second fault inherent in the molecule is that the polarisability of the water molecules was assumed to be constant. The fields near an ion must be very intense, especially when the ion is di- or tri-valent. The polarisability of the molecules must be a function of field strength, just as is the dielectric coefficent of the bulk solvent. This effect would lead to estimation of free energies that are too negative, especially for small, polyvalent ions.

The model used for the hydration of anions is not really adequate for the calculation of free energies. It seems probable that the model could be improved, for both anions and cations, by using a field dependant polarisability for the hydrating water molecules, and by allowing the molecules to rotate freely, as described above.

b) Errors Due to the Minimisation.

The work of formation of the complex was minimised with respect to rotation of the water molecules about their axes. The experimental free energy must be a time average, and so will necessarily be greater than the predicted value. As the ionic radius is decreased, the potential energy well will become deeper and narrower. It is therefore to be expected that the experimental free energy will be greater than the predicted free energy, and that the difference will decrease with increasing ionic size.

c) The London Equation.

Use of the approximate London equation (45) to calculate the energy due to the dispersion forces is a major simplification. It is unlikely that the equation is even roughly valid for such dissimilar species as an ion and a water molecule. In addition to this, there is significant uncertainty in the ionic polarisabilities used in calculating this term.

The use of the electron affinities of the parent halogens for the ionisation potentials of the halides was probably a source of serious error.

The sign and magnitude of these errors can not be predicted.

d) The Ionic Radii.

The Goldschmidt radii were used in these calculations. The uncertainty in the radii was discussed earlier, (page 22).

e) Errors Independent of the Ion.

The calculation of the free energy of hydration includes three constants, the free energies of hydration of the proton, of evaporation of water and of the formation of hydrogen bonds. The first two of these are known quite accurately, but the last is only known approximately. An error of only one kilocalorie per mole in the free energy of formation of the hydrogen bond would alter the predicted values for the hydration of tetrahedrally coordinated anions and cations by 4 and 8 kilocalories per mole. The changes for octahedrally coordinated ions would be 6 and 12 kilocalories per mole. It is quite reasonable to consider that the true free energy of formation of the hydrogen bond might differ as much as four kilocalories per mole from the value used.

APPENDIX I

NOTES ON THE FORTRAN LANGUAGE

1. Introduction

FORTRAN is an abbreviation for FORmula TRANslation. It is a language especially well adapted for use in scientific computing. One of the features of Fortran is that the language may be modified to make it more versatile or to adapt it to differing computer facilities, without changing its basic character in any way. At the present, Fortran II and Fortran IV are in use. The programmes designed for execution on the IBM 1620 II computer at the University of Ottawa were written in Fortran IID, a modification of Fortran II. Those designed for execution on the IBM 7094 computer at the University of Toronto were written in Fortran IV.

A Fortran programme is written as a series of statements. These are punched on cards or on paper tape, using a standardized code. Each statement is an instruction or a series of instructions to the computer. It specifies the operations to be performed, controls the input and output of data, provides information about the quantities to be used and gives instructions about their storage, or may exercise internal control over the execution of the programme. Each statement may be associated with a number, the "statement number".

The quantities to be manipulated in the programme are either CONSTANTS or VARIABLES. Variables are given names of up to six letters or figures, the names always starting with a letter. The name is often mnemonic of the quantity it represents. Examples are: R, SUM, SUMR1, SUMR2, ISKIP, I and KJ. Fortran considers two kinds of numbers, floating and fixed point numbers. The latter are restricted to integral values, and are mainly used as indices. The former may take any value in the real number system. Fixed point constants are written with no decimal point, and the names of the variables must start with a letter from I to N inclusive. Examples are 3, 345, L, IMDA, KOUNT and JILL. Floating point constants are always written with a decimal, and may have an exponent. An exponent is written as E±NN. Thus 1.2345E-17 stands for 1.2345×10^{-17}. Floating point variables have names starting with any letter other than those used for fixed point constants. The arithmetics for fixed and floating point numbers are not identical, and the two types of numbers may not be used together in an arithmetical expression. Variables may be subscripted when desired. The computer treats such variables as arrays. One, two and three dimensional arrays are allowed. Subscripts are indicated by parentheses: A(1), B(1, 12) and C(2,4,1) stand for A_1, $B_{1,12}$ and $C_{2,4,1}$.

Fortran IV is a more versatile language than Fortran II. It can handle complex numbers and numbers with twice the number of digits normally used, (see "Precision", below). It also allows the programmer to override the rules of naming variables. The statements

```
REAL IGUANA
INTEGER START
DOUBLE PRECISION X
COMPLEX Y
```

define IGUANA, START, X and Y to be floating point, fixed point, double precision and complex variables respectively.

2. Precision

Although computers are often used to manipulate data and generate results that are only correct to two or three significant figures, the calculations usually employ many more digits to avoid errors due to truncation of numbers. In Fortran II the number of digits used may be controlled by the programmer. Fixed point numbers may have from 4 to 10 digits, and a floating point number from 2 to 28 digits with an exponent. Once a precision has been specified it is used for all numbers of the same type that occur in a programme and its associated subprogrammes. In Fortran IV, fixed point numbers have eleven digits and floating point numbers have nine digits and an exponent. Double precision numbers have 17 digits and an exponent. In all cases, numbers with less than the specified number of digits are completed automatically by insertion of zeros in the appropriate positions.

3. Arithmetic Statements

These statements take the form of equations. They do not however imply equality between the right- and left-hand sides. Examples are

```
OVER3=1./3.
A=B+C*D-E/F
Q=T-(C*D)/(E*F)+S**3
A=A+B
```

Here, + and - have their usual significance. * and / stand for multiplication and division, and ** stands for exponentiation. The arithmetic operations are performed from left to right, and parentheses are used to avoid ambiguity. A*B**3 stands for $A \times B^3$, while (A*B)**3 stands for the cube of AB. Similarly, A/B*C stands for $\frac{A \times C}{B}$, but A/(B*C) means $\frac{A}{B \times C}$. The statement A=A+B should be understood as "Take the numbers stored in the locations called A and B. Add them together, and store the sum in the location called A."

4. Input-Output Statements

These statements allow the computer to read data from an external source, and to print or otherwise output the results of calculations. They provide communication between the programmer and the computer, and between the computer and auxiliary devices. In Fortran IID the important statements are

```
READ N1, LIST
PRINT N1, LIST
RECORD(M) LIST
```

and

```
FETCH(M) LIST.
```

In Fortran IV they are

```
READ (5,N1) LIST
```

and

```
WRITE (6,N1) LIST.
```

In all of these statements, LIST is a list of variables. N1 is the statement number of a "Format" statement. The latter specifies the manner in which the data are to be transmitted. M in RECORD(M) and FETCH(M) is any previously defined fixed point variable. These two statements refer to storage of information on an auxiliary storage device, the "Disk Drive".

5. Control Statements

These control the internal logic of the programme. "GO TO N1" is an instruction to transfer execution of the programme to the statement numbered N1. "GO TO (N1, N2, N3,...), J" transfers control to statement N1 if J=1, to N2 if J=2 and so on. The "IF" statement allows internal modification of the course of the programme, depending on the value of a specified quantity. The statement

IF (X) N1, N2, N3

transfers control to statement N1, N2 or N3 when X is negative, zero or positive respectively. X may be a simple variable or an arithmetic expression.

Fortran IV uses a second type of "IF" statement. This makes decisions on the basis of the truth or falsehood of a statement. This instruction has the form

IF (X) Statement. (46)

Here X is a logical expression. These are only permitted in Fortran IV. They are declarations about the relationship between quantities. Examples are "A.GT.B", which is an assertion that A>B, and "(A*B-C/3.).EQ.Z" which asserts that

$$A \times B - \frac{1}{3} . C = Z.$$

If the expression X is true, then the statement in (46) is executed, and execution of the next statement follows. If X is false, the next statement is executed immediately.

The instruction

DO N1 I = J,K,L

means "Starting with I=J, execute all the following statements up to and including that numbered N1. Then increase I by L and repeat the process. Continue doing this until I>K, and then execute the statement after N1". If L=1, the statement may be written "DO N1 I=J, K".

6. Other Statements

There are three statements which specify the size of arrays, give instructions about the arrangement of data and create identities between variables. These are the DIMENSION, COMMON and EQUIVALENCE statements. "DIMENSION A(2,5,2), B(6)" specifies that A is a 2x5x2 array and that B is a one-dimensional array of six numbers. "COMMON A,B,C,..." is an instruction to store A in the highest order address, B in the next highest, C in the next and so forth. Such statements are very often used to provide communication between a main programme and its associated subprogrammes. The statement "EQUIVALENCE (A,B,C), (T,F)" is used to create an identity between the variables A, B and C and between T and F. The "equivalenced" variables have the same storage position.

The statements "FUNCTION FUNC(X)", "SUBROUTINE SUBR(X)" and "SUBROUTINE SUBR" inform the computer that the programme that follows is: a function with an argument X, a subroutine with an argument X and a subroutine without an argument. Functions are subprogrammes used to calculate a single specific quantity. The functions ATAN(X) and ACOS(X) might be used to calculate $\mathrm{Tan}^{-1}X$ and $\mathrm{Cos}^{-1}X$. If the statements

Y=ATAN(X)

and Z=ACOS(W)

occurred in the main programme, control would be passed to the appropriate subprogramme, which would supply the required value. Subroutines do not necessarily return any value to the main programme. They may be used to invert matrices, find minima, perform integrations or differentiations, print out data, and, in general, perform any operations required. Control is transferred to a subroutine SUBR by the instruction "CALL SUBR" or "CALL SUBR(X)" if the subroutine requires an argument.

Further details on Fortran may be found in the many books on the subject.

7. A Note on Typography

In writing programmes, there is a possibility of confusing 0 (zero) and O (a letter). It is therefore customary to write the letter as Ø and the zero as 0. This practice is used on the following pages. The printers used in conjunction with computers write zero as an oval character and Ø as a rectangle with rounded corners.

APPENDIX II

THE CALCULATION OF THE FREE ENERGIES OF HYDRATION OF IONS

1. Newton-Cotes Formulae

Given a function f(x) that is subject to certain conditions of continuity, it is always possible to write

$$f(x) = a_o + a_1 x + a_2 x^2 + \ldots\ldots + a_i x + a_{i+1} \cdot x^{i+1} \ldots\ldots \qquad (47)$$

and by taking enough terms, the sum, S, of the series may be made to approximate f(x) as closely as desired within a specified range of x.

$$\left| S - f(x) \right| \leqslant \epsilon$$

where ϵ is a small number, as small as required.

Equation (47) may be recast in the form

$$f(x) = a_o + a_1 (x-x_1) + a_2 (x-x_1)(x-x_2) + \ldots\ldots + a_n \prod_{i=1}^{n} (x-x_i) + \ldots\ldots \qquad (48)$$

Here the a_i are of course different from those in (47), and the x_i are constants.

If the function f(x) is known at certain discrete values of x,

$$Y_i = f(x_i)$$

then it is possible to determine the coefficients a_i uniquely.

Thus

$$Y_1 = a_o$$

$$Y_2 = a_o + a_1 (x_2 - x_1)$$

$$Y_3 = a_o + a_1 (x_3 - x_1) + a_2 (x_3 - x_1)(x_3 - x_2) \qquad (49)$$

$$Y_n = a_o + \sum_{j=1}^{n-1} a_j \cdot \prod_{i=1}^{j-1} (x_n - x_i)$$

If the points (x_i, y_i) are evenly spaced with respect to x, such that $x_i - x_{i-1} = H$ then the calculation of the a_i is even simpler. Equation (49) becomes

$$Y_1 = a_o$$
$$Y_2 = a_o + a_1 H$$
$$\vdots$$
$$Y_n = a_o + a_1 (n-1)H + \ldots\ldots + a_{n-i} \prod_{i=1}^{n-1} (iH)$$

Equation (48) may be integrated over the range a to b:

$$I = \int_a^b (f(x)\,dx) = \left[a_o x + a_1 \cdot \left(\frac{x^2}{2} - x_1 x\right) \ldots\ldots \right]\Bigg|_a^b$$

Although this equation is complicated, it becomes much simpler when specific forms are derived. Thus, if only two points are known, a_o and a_1 can be calculated. The resulting truncation is equivalent to the assumption that f(x) is linear in x, within the range $a \leqslant x \leqslant b$. Then

$$I = \left[a_o x + a_1 \ (x^2 - 2x_1 x)/2\right]\Big|_a^b$$

If $a = x_1$, $b = x_2$, $H = x_2 - x_1$,

$$I = a_o H + a_1 H^2/2$$

Substitution of the values of a_o and a_1 from (49) shows that this is equivalent to the simple trapezoid rule for integration:

$$I = (x_2 - x_1) \cdot (Y_1 + Y_2)/2$$

If three equally spaced points $(x_1, Y_1), (x_2, Y_2), (x_3, Y_3)$ are chosen such that

$$x_2 - x_1 = x_3 - x_2 = H$$

then

$$I = \frac{1}{3}. (Y_1 + 4Y_2 + Y_3).H$$

which is Simpson's "One third" rule for integration. Similar equations may be developed for integration over a range for any required number of points. Such equations may be added together. For instance, the integral over the points (x_1, Y_1) to (x_5, Y_5) may be calculated by

$$I_{13} = \frac{1}{3}. (Y_1 + 4Y_2 + Y_3).H$$

$$I_{35} = \frac{1}{3}. (Y_3 + 4Y_4 + Y_5).H$$

where I_{ij} represents the integral between x_i and x_j. Addition gives

$$I_{15} = \frac{1}{3}. (Y_1 + 4Y_2 + 2Y_3 + 4Y_4 + Y_5).H$$

and in general

$$I_{1n} = \frac{1}{3}.H(Y_1 + Y_n) + \frac{2}{3}H(2Y_2 + Y_3 + 2Y_4 + \ldots\ldots + Y_{n-2} + 2Y_{n-1})$$

$$= \frac{1}{3}.H(Y_1 - Y_n) + \frac{2}{3}H. \sum_{i=1}^{(n-1)/2} (2Y_{2i} + Y_{2i+1})$$

The advantage in using the Newton-Cotes formulae lies in the particular simplicity and symmetry of the coefficients of Y. Kopal, (36), lists these coefficents for a large number of different formulae.

In the integration of (19) the equation

$$I_{17} = \frac{1}{140} \cdot H. (41Y_1 + 216Y_2 + 27Y_3 + 272Y_4 + 27Y_5 + 216Y_6 + 41Y_7) \quad (50)$$

was used repetitively.

2. Richardson's Extrapolation

Consider the integral $\int_a^b f(x)dx$ which has been discussed above. By suitable change of variable,

$$\int_a^b f(x)dx = \int_0^1 u(r)dr$$

Let there exist n+1 points $(r_i, u(r_i))$, $0 \leq i \leq n$, and let these be evenly spaced such that $r_i - r_{i-1} = h$, and nh=1. Then,

$$\int_0^1 u(r)dr = \int_0^{nh} u(r)dr = \sum_{i=1}^{n} a_i u_i + R_n$$

where u_i is an abbreviation of $u(r_i)$ and where R_n is the error caused by truncation after n+1 terms. The function may be approximated by a MacLaurin's series:

$$u(r) = u_o + ru_o^{(1)} + r^2 u_o^{(2)}/2! \ldots\ldots$$

and the integral by

$$\int_0^{nh} u(r) \; dr = \sum_{i=0}^{\infty} (nh)^{i+1} u_o^{(i)}/(i+1)!$$

The same series may be used to calculate the u_i:

$$u_o = u_o$$

$$u_1 = u(r_o + h) = u_o + hu_o^{(1)} + h^2 u_o^{(2)}/2! \ldots\ldots$$

so that

$$u_i = u(r_o + ih) = u_o + (ih)u_o^{(1)} + (ih)^2 u_o^{(2)}/2! \; .....$$

and

$$R_n = \sum_{i=0}^{\infty} n^{i+1} h^{i+1} u^{(i)}/(i+1)! - \sum_{i=0}^{n} a_i \cdot \sum_{j=0}^{\infty} (ih)^j u_o^{(j)}/j! \qquad (50a)$$

Let

$$R_n = \sum_{i=n+1}^{\infty} b_i u_o^{(i)}$$

Then by inspection of (50a)

$$b_o = nh - \sum_{i=0}^{n} a_i$$

$$b_1 = n^2 h^2/2! - \frac{h}{2}\sum_{i=0}^{n} i a_i$$

$$b_j = (nh)^{j+1}/(j+1)! - \frac{h^j}{j!} \sum_{i=0}^{n} a_i i^j$$

There is only one polynomial of order n that passes through n+1 points. It follows that if the function is a polynomial in r of greater than nth order

$$b_o = b_1 = b_2 = \; ..... \; = b_n = 0$$

and

$$R_n = \sum_{i=n+1}^{\infty} b_i u_o^{(i)}$$

The predominant term will be the first

$$R_n \approx b_{n+1} \cdot u_o^{(n+1)} = \frac{h^{n+1}}{(n+1)!} \left(\frac{hn^{n+1}}{n+2} - \sum_{i=0}^{n} i^{n+1} \cdot a_i \right) \cdot u_o^{(n+1)}$$

This gives

$$\int_0^1 u(r)\,dr = h.\sum_{i=0}^{n} a_i u_i + \frac{h^{n+1}}{(n+1)!}\left(\frac{kn^{n+1}}{n+2} - \sum_{i=0}^{n} i^{n+1} a_i\right).u_o^{(n+1)}$$

Then

$$\int_0^m u(r)\,dr \approx h.\sum_{i=0}^{nm} a_i u_i + \frac{h^{n+1}}{(n+1)!}\cdot\frac{hn^{n+1}}{n+2}\cdot\sum_{i=0}^{m-1} u_{ni}^{(n+1)}$$

Suppose that the integral is approximated twice, the first time using all the points and the second time using only the alternate points. Let the estimates be I_1 and I_2 and let the true integral be I_o. Then

$$I_o = I_1 + \frac{h^{n+1}}{(n+1)!}\cdot\frac{hn^{n+1}}{n+2}\sum_{i=0}^{m-1} u_{ni}^{(n+1)}$$

$$I_o \doteq I_2 + \frac{(2h)^{n+1}}{(n+1)!}\cdot\frac{2hn^{n+1}}{n+2}\sum_{i=0}^{\frac{m}{2}-1} u_{2ni}^{(n+1)}$$

Now it is always possible to find ρ such that

$$\sum_{i=0}^{k} u_{ni}^{n+1} = k.u^{(n+1)}(\rho)$$

so that

$$I_o = I_1 + \frac{h^{n+1}}{(n+1)!}\;\frac{n^n}{n+2}\;.(m).u^{(n+1)}(\rho_1)$$

$$= I_2 + \frac{(2h)^{n+1}}{(n+1)!}\cdot\frac{2n^n}{n+2}\cdot\left(\frac{m}{2}\right).u^{(n+1)}(\rho_2)$$

Usually

$$p_1 \approx p_2 = p$$

$$\therefore \quad I_o = I_1 + h^{n+1}C$$

$$= I_2 + (2h)^{n+1}C$$

where

$$C = \frac{1}{(n+1)!} \frac{n^n}{n+2}.\text{m.u.}(n+1)$$

$$\therefore \quad I_2 - I_1 + Ch^{n+1}\left(2^{n+1} - 1\right) = 0$$

Hence

$$C = \frac{I_1 - I_2}{2^{n+1}-1} \cdot \frac{1}{h^{n+1}}$$

and

$$I_o = I_1 + \frac{I_1 - I_2}{2^{n+1}-1} = \frac{2^{n+1}.I_1 - I_2}{2^{n+1}-1} \qquad (50a)$$

Equation (50a) is essentially an extrapolation to zero step-size. The value calculated is not in fact the true integral, since several approximations were made in the course of the derivation. I_o is however a better estimate of the integral than I_1 or I_2. This procedure is due to Richardson and has become known as Richardson's Extrapolation.

3. The Programme

The programme used in calculating the free energies of hydration of ions is given on pages 143 et sequentia.

The programme starts by defining two arithmetic statement functions, D(E) and EPSX(E). These give the dielectric displacement and coefficient corresponding to a specified field strength, E. The variables R and E are defined as one dimensional arrays, each of thirteen numbers. Some constants are defined, including A1, A2, A3, and A4. The Newton-Cotes formula for integration over seven points is

$$\int_0^{6H} Y.dx = H*\left(\frac{41.}{140.}(Y_1+Y_7) + \frac{216.}{140.}(Y_2+Y_6) + \frac{27.}{140.}(Y_3+Y_5) + \frac{272.}{140.}Y_4\right) \qquad (51)$$

and the definitions were

A1 = 82./140.
A2 = 216./140.
A3 = 27./140.
A4 = 272./140.

A1 is twice the first Newton-Cotes coefficient.

The programme called a subroutine LCNT, which read a title. This was printed at the top of each page of results. A card was then read giving the limits EMIN and EMAX of the integration. The limits were chosen to correspond to a very large radius and to one of about 0.3 Å. The step-size H was defined as

H = (EMAX-EMIN)/6001.

The initial conditions were defined as follows

SUMR1 = 0.

SUMR2 = 0.

E(1) = EMIN

EX = EMIN

A further definition

$$AREA = ZE/\epsilon_i*RX + EX*RX$$

was made where ZE is the product of the ionic valency and the electronic charge, ϵ_i is the integral dielectric coefficient and RX is the radius corresponding to EX. E(2) to E(13) were calculated as

$$E(I) = E(I-1) + H$$

and the calculations of the corresponding radii, R(1) to R(13) were made. Then the calculations

```
SUMR1 = SUMR1+A1*R(13)+A2*(R(3)+R(11))+A3*(R(5)+R(9))+A4*R(7)
SUMR2 = SUMR2+A1*(R(7)+R(13))+A2*(R(2)+R(6)+R(8)+R(12))
               +A3(R(3)+R(5)+R(9)+R(11))+A4*(R(4)+R(10))
```

were performed. Then E(1) and R(1) were equated to E(13) and R(13). Thirteen new radii and the new values of SUMR1 and SUMR2 were calculated as before. This process was repeated until E(13)>EMAX. Every three repetitions, the work of hydration was calculated, as will be described below.

Earlier, equation (19) was derived,

$$w = \tfrac{1}{2}Ze\left(-E_oR_o - \int_{E_o}^{E_\infty} r\,dE\right) - Z^2e^2/2R_o$$

where W is the work of hydration for an ion of radius R_o.

This may be written in the form

$$W = \frac{Z^2E^2}{2}\cdot\left(\frac{1}{\epsilon_o \cdot RX} - \frac{1}{R_o}\right) + \frac{ZE}{2}\left(EX.RX - E_oR_o + \int_{EX}^{E_o} RdE\right)$$

where ϵ_o is the bulk dielectric constant, and E_o is the field strength at R_o. If the Newton-Cotes formula is applied over the range E(1) to E(13) using (51),

$$\int_{E(1)}^{E(13)} RdE = H*\left(0.5*A1*(R(1)+2.*R(7)+R(13))+A2*(R(2)+R(6)+R(8)+R(12)) +A3*(R(3)+R(5)+R(9)+R(11))+A4*(R(4)+R(10))\right)$$

If the alternate points are used,

$$\int_{E(1)}^{E(13)} RdE = 2.*H*\left(0.5*A1*(R(1)+R(13))+A2*(R(3)+R(11))+A3*(R(5)+R(9)) +A4*R(7)\right)$$

When these equations are applied many times

$$\int_{EX}^{E(13)} RdE \approx I_1 = H*(SUMR2+.5*A1*(RX-R(13)))$$

$$\approx I_2 = 2.*H*(SUMR1+.5*A1*(RX-R(13)))$$

where E(13) and R(13) are understood to be the values appropriate to the highest field strength considered.

Applying Richardson's extrapolation

$$\int_{EX}^{E(13)} RdE = (128.*I_1-I_2)/127.$$

$$= H*(64.*SUMR2-SUMR1+31.5*A1*(RX-R(13))/63.5$$

This quantity was called "TERM". At any point in the calculation where

$$E_o = E(13)$$

$$R_o = R(13)$$

equation (19) may thus be written

W = .5*CONV*ZE(TERM-ZE/R(13)-E(13)*R(13))

where CONV is a factor to convert ergs per molecule to kcal per mole. Whenever the work of hydration was calculated, the radius, work and field strength were printed out.

APPENDIX III

THE HYDRATION OF DIPOLES

1. Derivation of Equation (41).

An exact determination of the free-energy of hydration of dipolar molecules would require calculation of the energy of the dipole in water and in vacuo. The latter part of the problem is relatively simple, but the former is extremely difficult. To solve the problem, it would be necessary to determine the potential or the field at all points in space. Once one of these is known the energy can be calculated either as the sum of the products of the charges and their potentials, or as the integral of $\vec{D}.\vec{E}$ over all space. In this problem it is impossible to find $\vec{D}.\vec{E}$ directly, so the potential must be found in either method. Since the dielectric is non-linear, it is unlikely that the potential can be written as the product of terms dependant on only one of the coordinates. One possible form of the potential, (V), is:

$$V(\xi,\eta,\emptyset) = \sum\sum\left\{a_{nm}P_n^m(\xi^{-1}) + b_{nm}P_n^m(\eta) + c_{nm}P_n^m(\xi^{-1})P_n^m(\eta) + f_{nm}Q_n^m(\xi) + g_{nm}Q_n^m(\eta) + h_{nm}Q_n^m(\xi^{-1})Q_n^m(\eta)\right\}$$

The Legendre functions are used here because they give relative simplicity to the solution in the case of the dipole in vacuo. The coefficents may be determined, in principle, from the equation

$$\nabla\cdot(\epsilon_i\nabla V) = 0 \qquad (52a)$$

and from the boundary conditions:

$$V(\xi,\eta,\phi) < \infty \tag{52b}$$

$$V(\infty,\eta,\phi) = 0 \tag{52c}$$

$$V(\xi,\eta,\phi) = -V(\xi,-\eta,\phi) \tag{52d}$$

$$V_1 = V_2 \tag{52e}$$

$$\epsilon_{i1} \frac{\partial V_1}{\partial n} = \epsilon_{i2} \frac{\partial V_2}{\partial n} \tag{52f}$$

In (52e) and (52f), the subscripts 1 and 2 refer to conditions just inside and outside any small area $d\eta . d\phi$ of any surface, ξ, and n is the normal to that surface.

The most obvious method of solving the system of equations (52) is to find a first approximation to the potential, using a linear dielectric constant. This would be used to find a map of the field, and hence a map of the (non-linear) dielectric coefficent. This would be used to find a second approximation to the potential, to the field and to the dielectric coefficent. This process would be continued until the field at any point changed by no more than some predetermined amount.

There are two major objections to this procedure. Firstly, the labour and cost would be prohibitive. Secondly, there is no guarantee that the process would converge to a true solution. If an estimate of the free-energy is to be found, an approximation must be used. The approximation used in this work is based largely on the geometry of the model. The surface $\eta = 0$ must be a zero-potential surface. The potential should vary comparatively slowly in this region, so that the field at any surface ξ should be low in this region. Thus, the dielectric coefficent should be nearly linear. On the other hand, the absolute value of the field must be a maximum at $\eta = \pm 1$. Here, the field is practically normal to the surface. It is not difficult to show that the angle between the radii from the charges and the tangent to the surface, (Ω), is

$$\Omega = \mathrm{Atan}((\xi^2 - 1)/(1 - \eta^2))^{\frac{1}{2}}.$$

This has maximum and minimum values at $\eta = 0$. If $\xi = 2$, an average value used in this work, then this minimum angle has a value of 60°. Moreover, the average angle is

$$\Omega_{Av} = \int_0^1 \Omega \, d\eta$$
$$= \tfrac{1}{2}(\pi - 1 - (\xi^2 - 1)\ln((\xi^2 - 1)/\xi^2))$$

Again, if the value of ξ is two, the average angle is 86°. Thus, the field is small, and the dielectric is nearly linear, at the points where the angle between the major component of the field and the surface is furthest from 90°. It is largest, and the dielectric is non-linear, when the angle is closest to a right angle. As an approximation, it is not unreasonable to calculate the dielectric displacement and field as the sum of components given by

$$\vec{D} = \epsilon_L \vec{E} = (\lambda e/r^3)\cdot\vec{r} \quad .$$

Addition of the components of D, followed by a change to ellipsoidal coordinates gives equation (41):

$$D^2 = \frac{4\lambda^2 e^2}{\alpha^4}\cdot(\xi^2-\eta^2)^{-4}\cdot(\eta^2(3\xi^2-\eta^2)+\xi^2-\eta^2)$$

2. The Newton-Raphson Approximation

It was desired to perform the numerical integration

$$\int D^2.(\frac{1}{\epsilon_i} - 1).dV$$

Now ϵ_i is a transcendental function of E:

$$\epsilon_i = n^2 + \frac{\epsilon_0 - n^2}{b^{\frac{1}{2}}.E}.\text{Atan}(b^{\frac{1}{2}}E) \quad .$$

It follows that

$$D = \epsilon_i E = \frac{2\lambda e}{\alpha^2(\zeta^2 - \eta^2)^2}.(3\zeta^2\eta^2 + \eta^4 + \zeta^2 - \eta^2)^{\frac{1}{2}}$$

is a transcendental equation in E. It is not possible to solve such equations analytically; numerical methods must be used. In this case the equation was solved using the Newton-Raphson approximation.

Let a function f(x) exist such that

$$f(\alpha) = 0.$$

If x_o is an approximation to α, then x_1 is a better approximation, where

$$x_1 = x_o - \frac{f(x_o)}{f'(x_o)}$$

provided $f'(x_o) = \left(\frac{df(x)}{dx}\right)_{x_o} \neq 0$. The approximation may be applied many times

$$x_{i+1} = x_i - \frac{f(x_i)}{f'(x_i)} \qquad (53)$$

and if the derivative never passes through or very close to zero, the approximation converges on to the true root of the equation. The initial approximation must be reasonably close to the solution if the successive iterations are to converge rapidly, or, in extreme cases, at all.

The theory of the process is quite simple. Figure 11 shows a graph of f(x), an arbitrary function, against x. The curve was drawn so that only one root exists in the region considered. The points x_o and x_0' were chosen to lie on either side of the root α. The figure also shows the tangents through $f(x_o)$ and $f(x_o')$. These intersect the X-axis at x_1 and x_1'. The two cases are very similar, and only one need be considered. By simple geometry,

$$f'(x_o) = \left(\frac{df(x)}{dx}\right)_{x_o} = \frac{f(x_o)}{x_o - x_1}$$

$$\therefore \quad x_1 = x_0 - \frac{f(x_o)}{f'(x_o)}$$

The situation is more complicated if α is a multiple root, or if two roots lie very close together. Under these conditions $f'(\alpha) \approx 0$, and (53) does not converge. It is possible to make allowance for this, but such a situation can not occur in the solution of (41).

Figure 11.

Solution of the Equation

$$f(x) = 0$$

by the Newton-Raphson Approximation.

3. Interpolation

In the numerical solution of (41) by the Newton-Raphson approximation a fairly good initial estimate of E was needed. In order to provide this, values of ϵ_i were calculated for given values of the dielectric displacement. The initial estimates of the field strength and dielectric coefficient were found by interpolation between these values, using (48) with truncation after five terms in the series.

4. The Integration

Even using high-speed computers, numerical integration in more than one dimension is a time-consuming process. As an example, in integrating f(x,y), $x_o \leq x < \infty$, $y_o \leq y \leq \infty$, a grid of at least 1000 positions in each dimension should be used. This would take a prohibitively long time, especially if the solution of a transcendental equation was needed in each calculation. The "Monte-Carlo" technique of integration goes some way towards solving the problem. This is a statistical approach to integration. It is best described in the case of a one-dimensional integration; the extension to many dimensions is obvious.

If it is desired to estimate

$$I = \int_a^b f(x)\,dx$$

it is usually possible to find suitable constants Q and C such that

$$f(x) = Q.g(y) + C \qquad (54)$$

where y=0 when x=a, y=1 when x=b and where

$$0 \leqslant g(y) . \frac{dx}{dy} \leqslant 1$$

The problem of calculating the integral is transformed to that of calculating

$$I = \int_a^b (Q.g(y) + C)\,dx$$
$$= \int_0^1 (Q.g(y) + C)\frac{dx}{dy} . dy$$

If f(x) does not change its sign when x takes up any of its possible values, C may be chosen at zero. Then

$$I = Q.\int_0^1 g(y)\frac{dx}{dy} . dy$$

Let

$$g(y)\frac{dx}{dy} = h(y). \qquad (54a)$$

h(y) will lie between zero and one, and so will y. h may be considered to be a curve drawn in a unit plane. If the area under this curve is A,

$$I = Q.A$$

Let two numbers R and y_o be chosen at random in the range zero to one. If $h(y_o) \geqslant R$, these two numbers specify a point lying under the curve. If $h(y_o) < R$, the point lies above the curve. Suppose that this were to be done many, (N), times and that M points were found to lie under this curve:

$$\mathop{Lt}_{N\to\infty} \frac{M}{N} = A$$

Thus the integral may be estimated by approximating the ratio of the number of points under the curve to the number of points in the plane. The extension to integration in n-space is simple: (n+1) random numbers are chosen.

5. The Programme

a) Two main programmes and two subprogrammes were used in the course of the Monte Carlo integration. The first of these, called "BOUND", was a programme to calculate the maximum field strengths at the surfaces ξ_0 of the dipoles under consideration. These were required in the calculation of the normalizing factors, Q in equation (54). The second main programme "DIPOLE" performed the integration. It used the two subprogrammes "ESOLVE" and "YNTPRL". It also used "RANDR" which is a library subroutine available at the University of Toronto computing centre. It is a "random number" generator, and it will be described briefly below. When values of ξ and η

were chosen in the main programme by RANDR, control was transferred to ESOLVE which calculated the dielectric displacement, (D), according to (41). The subprogramme then checked to determine if D was one of the 30 tabulated values read in earlier by DIPOLE. If it was not, control was passed to YNTPRL, which interpolated between these values to provide an initial estimate of the dielectric coefficent and thence of the field strength E. Once these had been obtained, ESOLVE performed a series of Newton-Raphson approximations until a sufficently accurate root of the equation had been obtained. This was used to calculate a function of E, equivalent to h(y) in (54a), which was compared to a randomly generated value. 175,000 such calculations were made for each different dipole.

b) The programme BOUND was used to obtain the boundary values of the field strength. The programme made use of ESOLVE. Values of the charge and of the charge separation were read from cards. Fifteen values of ZETA were next read. These were followed by thirty values of EPSI, the dielectric coefficent and of CX; in this programme the latter values were the dielectric displacement. ETA was fixed at a value of +1, since preliminary calculations had shown that it was at this value that the field strength was a maximum for a given ξ. The values of E and of FUNC(E), (defined in (58) below) was then determined for each of the ξ_0, for each of the 35 different combinations of OLMBDA and ALPHA2. The results were printed and were punched on cards.

c) The library function RANDR is a random number generator available to users of the IBM 7094 computer at the University of Toronto. It uses an argument R and is designed to alter R in a pseudo-random manner. The new value of R is used as the argument the next time RANDR is called. Its authors (33) claim that the values obtained, which lie between ± 1, have an excellent random character, except that the last digit tends to be alternately odd or even.

d) The function YNTPRL was named as a mnemonic for "INTERPOLATING". (When used as an initial, I denotes a fixed point variable, and cannot be used to start a floating point name). The subprogramme is given on pages 151 et sequentia. YNTPRL used as data the 30 values of CX and EPSX that had earlier been read by the main programme and stored in the common area. These variables were values of dielectric dispersion and the associated values of dielectric displacement.

The subprogramme used as arguments C, the actual dielectric displacement, and I, the subscript of the smallest member of CX for which $(C-CX_i) > 0$. The substitutions

$$Y(K) = EPSX(L)$$

$$X(K) = CX(L)$$

were made, with L = K - 2 + I, and K running from 1 to 5. This placed C near the middle value of the X(K)'s, in the position where the most accurate interpolation is possible. The coefficients a_i in

$$EPSI = \sum_{i=0}^{5} a_i \prod_i (C-CX(I)) \qquad (55)$$

were calculated, (where EPSI=ϵ_i);a standardized procedure was used. YNTPRL, the value of the dielectric coefficient corresponding to the dielectric displacement C, was determined from the same equation, (55).

e) ESOLVE was a function that solved the equation

$$D = \epsilon_i E$$

for a given value of D. The subprogramme has two arguments, ZETA2 and ETA2. These are the squares of ζ and η, the coordinates. It used the Newton-Raphson solution to the equation. If $f(E) = \epsilon_i E - D$ then $f'(E) = \epsilon_d$ where ϵ_d is the differential dielectric coefficient defined in (7). Functions EPS(E) and DEPS(E) were defined, to give ϵ_i and ϵ_d for a given value of E. DZETA, a double precision variable, was calculated as the difference between ZETA2 and ETA2. D, another double precision variable, was calculated according to (41). C was set equal to D and CM12 to $Cx10^{-12}$. A check was made to see if C was equal to one of the CX. If it was, a value

ESOLVE = CX(I)/EPSX(I)

was returned to the main programme. If it was not, the smallest value of CX such that (C-CX(I))>0 was found, and control was passed to YNTPRL. The variable EPSI was equated to the value returned and the calculations

```
E=C/EPSI
DEPSI=EPS(E)
TOP=E*DEPSI-D
COR1=0.
```

were made. These were followed by

```
COR2=TOP/DEPS(E)
E=E-COR2
DEPSI=EPS(E)
TOP=E*DEPSI-D                    (56)
```

and ER=ABS(TOP)

In these calculations, TOP was f(E) and DEPS(E) was f'(E). ER was the absolute value of (TOP). This was used to control the course of the calculations. When ER became less than CM12, ESOLVE and EPSI were equated to the current values of E and DEPSI, and control was returned to the main programme. The process described by equation (56) was repeated until this condition was met.

f) It follows from equation (1) that the free energy of hydration requires calculation of

$$\frac{1}{8\pi}\int D^2.\left(\frac{1}{\epsilon_i}-1\right).dV$$

Let this be denoted by VINT. Then using equation (40),

$$\text{VINT} = \tfrac{1}{4}\alpha^3\int_{-1}^{1}\int_{\xi_0}^{\infty} D^2.\left(\frac{1}{\epsilon_i}-1\right).(\xi^2-\eta^2).d\xi.d\eta \qquad (57)$$

If a new variable X is introduced such that

$$X=\xi_0/\xi \qquad \text{and } d\xi = -(\xi^2/\xi_0).dX$$

$$\text{VINT}=\frac{\alpha^3}{4\xi_0}\int_{-1}^{+1}\int_{0}^{1} D^2.\left(\frac{1}{\epsilon_i}-1\right).\xi^2.(\xi^2-\eta^2)\,dXd\eta$$

All the terms in η are of even order, so

$$\text{VINT}=\frac{\alpha^3}{2\xi_0}\int_{0}^{1}\int_{0}^{1} D^2.\left(\frac{1}{\epsilon_i}-1\right).\xi^2.(\xi^2-\eta^2)\,dXd\eta.$$

$$=\frac{\alpha^3}{2\xi_0}\int_{0}^{1}\int_{0}^{1}(E^2\epsilon_i-D^2).\xi^2.(\xi^2-\eta^2)\,dXd\eta$$

Let

$$-(\epsilon_i E^2-D^2).\xi^2(\xi^2-\eta^2) = \text{FUNC}(E) \qquad (58)$$

and let the maximum value of this function for a given surface ZETAO be FMØST. Then

$$\text{VINT} = \frac{-\alpha^3}{2\xi_0}.\text{FMØST}\int_{0}^{1}\int_{0}^{1}\frac{\text{FUNC}(E)}{\text{FMØST}}.dXd\eta$$

Furthermore, if several surfaces ZETAO(I) are considered, whose maximum values of FUNC(E) are FMØST(I), and if X is now defined by

ZETA=ZETALØ/X

where ZETALØ is the smallest of the ZETAO(I),

$$\text{VINT(I)} = -\frac{\alpha^3}{2\cdot\text{ZETAL}\text{Ø}}\cdot \text{FM}\text{Ø}\text{ST(I)}\int_0^1\int_0^1 \frac{F}{\text{FM}\text{Ø}\text{ST(I)}}\, dX d\eta$$

provided that

F=O, if ZETA < ZETAO(I)

= FUNC(E), if ZETA > ZETAO(I)

= .5*FUNC(E), if ZETA = ZETAO(I)

This is essentially a procedure of expanding the scale to the most suitable value for each surface.

It was desired to find the free energy of hydration for 15 surfaces on each of the 35 dipoles described by combination of 5 charge separations and 7 charges. The integration was to be performed at the University of Toronto, and it was therefore desirable that the data should be changed as little as possible from one run to another. This was accomplished by reading the value of a variable START. This was defined in the programme to be a fixed point variable, and it was given values from 1 to 35 inclusive. For each run, the data appropriate to all the dipoles were read in.

Those appropriate to a given dipole were selected according to the value of START.

The programme defined the size of arrays and made allocation of variables to the COMMON storage area. It defined two functions, DEV(DY,EN) and FUNC(E). The former provided some estimate of the maximum error of integration; the latter was the same as described in (58). The identities

LØALP≡NQ≡NALP

LØLAMB≡NR≡MLAMDA

were defined next. Initial values were given to some variables, including

HITS(I)=0. $1 \leqslant I \leqslant 15$

The card giving START was read and

LØALP=(START-1)/7+1

LØLAMB=START-7*(LØALP-1)

were calculated. It should be noted that all these were fixed point numbers, so that if START=7, LØALP=1. Several more variables were initialized and the 15 values of ZETAO(I) were read. This was followed by the reading of the 5x7x15 matrix FMAX whose elements were the maximum values of FUNC(E) calculated by BOUND. Five values of ALPHA2, 7 of CHARGE and thirty pairs of CX and EPSX were read by the computer. These were the charge separations, the charges and the tabulated values of dielectric displacement and coefficient. Specific values of ALPHA2, CHARGE and FMAX were selected:

ALP=.5*ALPHA2(NALP)

PLM=CHARGE(MLAMDA)

FMØST(I)=FMAX(NALP,MLAMDA,I) $1 \leqslant I \leqslant 15$,

and ZETALØ was taken as the lowest of the ZETAO. CØN1 was defined as

CØN1=CØNV*ALP3

where ALP3 was the cube of ALP, and CØNV, (=1.4394E13), was the conversion from ergs per molecule to kcal per mole. DIPØLE was defined as

DIPØLE=ALPHA2(NALP)*PLM*EL*1.E18

Here DIPØLE was the dipole moment, expressed in Debyes and EL, (=4.803E-10), was the electronic charge. The process of integration was then started.

Three positive random numbers X, ETA and TESTER were generated, using RANDR and the absolute value function, ABS. ZETA was calculated as

ZETA=ZETALØ/X.

ZETA2 and ETA2 were the squares of ZETA and ETA. These were used as the arguments of ESØLVE, which

a) Calculated the dielectric displacement,

b) Solved (2) for E.

c) Calculated EPSI, whose value was returned to the main programme via the COMMON area, and

d) Equated ESØLVE to E and returned control of the main programme.

The latter set

```
FX=FUNC(E)
```

It then performed the process described by (59), below, with J=1 to 15:

```
CHECK=FMØST(J)*TESTER
F=FX         if ZETA>ZETAO(J)
 = .5*FX     if ZETA=ZETAO(J)          (59)
 = 0         if ZETA<ZETAO(J)
HITS(J)=HITS(J) + 1    ,if CHECK<F
```

This process was repeated 175,000 times, after which the free energies were estimated:

```
VINTS=HITS(I)/175000
CALP=CONI*FMOST(I)
DELH=-.5*VINT*CALP/ZETALØ
```

where DELH was the free energy of hydration in kcals per mole.

APPENDIX IV

THE DISCONTINUOUS SOLVATION OF IONS

1. Introductory

The free-energy term, $w_{calc.}$ in (43) was calculated using the IBM 7094 computer at the University of Toronto. The main programme, HYDR8S, controlled the course of the calculations, using a number of subprogrammes to calculate intermediate results. ACOS(X) was a function sub-programme, used to calculate the value of $Cos^{-1}X$. SEPCOS was used to calculate the separation between specified points, the angle at the dipole between the radius and a specified point and the potential energies between the electrostatic species. MINIM was a pattern search programme. It was used to find a minimum in the potential energy, with respect to rotation of the solvating molecules about the ion-molecule radii. COORDS was a subroutine that calculated the coordinates of the hydrogen atoms, given the angles of rotation of the molecules about the radii. POTF used these coordinates as data. It systematically selected pairs of points and referred them to SEPCOS for calculation of the potential energies. It then summed the energies of all the pair combinations considered. OUTPTM was a subroutine used to print out the results.

2. The Electrostatic Interactions

In this model, the complex is formed in vacuum, and the dielectric constant to be used for all the electrostatic interactions is unity. The potential energy between two point charges DELT1 and DELT2 is DELT1*DELT2/S1, where S1 is the charge separation in centimetres. The potential between an ideal dipole and a point charge may be derived by considering first unideal dipole, as shown in Figure 12 (a). Let the dipole be comprised of two equal and opposite charges $\pm\lambda$, separated by 2α. The potential energy, P, of the ideal dipole is found by letting $\alpha \to 0$ and $\lambda \to \infty$ in such a manner that the dipole moment μ, $(=2\alpha\lambda)$, is constant. If δ is the point charge,

$$P = \delta.\lambda.(1/r_1 - 1/r_2)$$

$$r_1^2 = (a+2\alpha)^2+b^2$$

$$= S^2 + 2S.\alpha.\cos\psi + \alpha^2$$

Similarly

$$r_2^2 = S^2 - 2S.\alpha.\cos\psi + \alpha^2$$

$$\therefore \quad P = \frac{\delta\lambda}{r_1 r_2} . (r_2 - r_1)$$

Expanding the roots,

$$P = \frac{\delta\lambda}{r_1 r_2} . (S^2+\alpha^2)^{\frac{1}{2}} . \left(1 - \tfrac{1}{2} . \frac{2S\alpha\cos\psi}{S^2+\alpha^2} - \tfrac{1}{2} . \tfrac{1}{4}\left(\frac{2S\alpha\cos\psi}{S^2+\alpha^2}\right)^2 \ldots\right) - \left(1 + \tfrac{1}{2} . \frac{2S\alpha\cos\psi}{S^2+\alpha^2} + \ldots\right.$$

$$= \frac{-\mu\delta}{r_1 r_2} \cdot (S^2 + \alpha^2)^{\frac{1}{2}} . \frac{S.\cos\psi}{S^2 + \alpha^2} + \text{(Higher terms in } \alpha\text{)}$$

$$\operatorname*{Lt}_{\alpha \to 0} P = -\mu\delta\cos\psi/S^2 \qquad (60)$$

The dipole-dipole interaction is found similarly. In the case considered, the two dipoles are at equal distances, R, from the ion. Figure 12(b) shows the configuration.

$$P = \lambda^2(1/r_1 + 1/r_2 - 2/r_3)$$

$$r_1 = 2(R-\alpha)\,\mathrm{Cos}\,\psi$$

$$r_2 = 2(R+\alpha)\,\mathrm{Cos}\,\psi$$

$$r_3^{\,2} = (R+\alpha)^2 + (R-\alpha)^2 + 2(R+\alpha)(R-\alpha)\,\mathrm{Cos}\,2\psi$$

$$r_3 = 2R.\mathrm{Cos}\,\psi.(1+\alpha^2\mathrm{Tan}^2\psi/R^2)^{\frac{1}{2}}$$

$$\therefore P = \frac{\lambda^2}{r_1 r_2 r_3}\cdot(r_3(r_1 + r_2) - 2r_1 r_2)$$

$$= \frac{8\lambda^2\mathrm{Cos}^2\psi}{r_1 r_2 r_3}(R^2(1 + \alpha^2\mathrm{Tan}^2\psi/R^2)^{\frac{1}{2}} + \alpha^2 - R^2)$$

Expanding the surd,

$$P = \frac{8\lambda^2\alpha^2\mathrm{Cos}^2\psi}{r_1 r_2 r_3}\cdot(\tfrac{1}{2}\mathrm{Tan}^2\psi + 1 + f(\alpha^2))$$

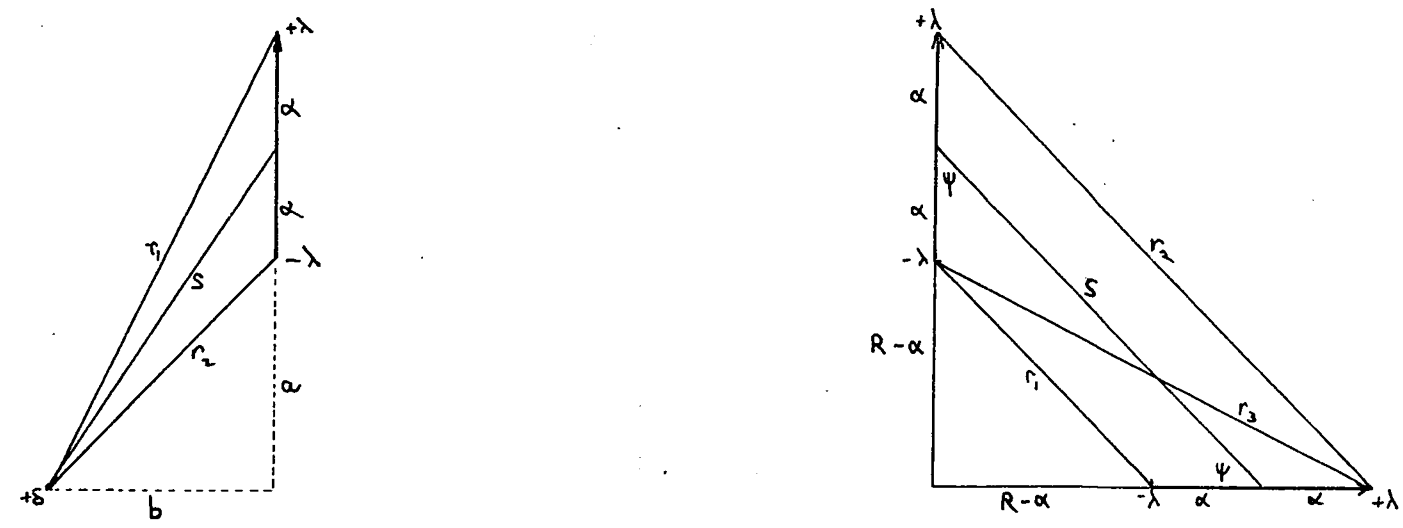
where $f(\alpha^2)$ represents terms in α^2 and higher powers.

$$\therefore \mathop{\mathrm{Lt}}_{\alpha \to 0} P = \frac{\mu^2}{S^3}(1 + \mathrm{Cos}^2\psi) \qquad (61)$$

Figure 12.

(a). The potential between a point charge and a dipole.

(b). The potential between two dipoles.



(a)

(b)

3. The Magnitude of the Dipoles

The dipoles considered above are field induced. It was intended that they should approximate the flow or charge that occurs when a solvent molecule is brought close to an ion. It was supposed that the magnitude of the dipole would be proportional to the field strength, the proportionality constant being the conventional polarisability, α. It was recognized that the polarisability should probably depend on field strength, in a manner analogous to the dielectric coefficient. The difficulties in making allowance for this are very large, since no theory of the effect exists. It seems likely, however, that the error introduced by ignoring the effect should not be large; the induced dipoles were much further from the ion than was the dielectric in the continuum model. It was considered that the dipoles were induced by the ion's field only. The fields due to the charges on the neighbouring solvent molecules were small in comparison and this approximation should introduce little additional error. Subject to these provisos

$$\mu = \alpha . z . e / r^2$$

where μ is the dipole moment, ze the ionic charge and r the ion-dipole separation.

4. The Programmes

a) ACOS(X) was a function subprogramme that generated the value of $\mathrm{Cos}^{-1}X$. It used one of the Hastings (34) approximations. These approximations are widely used in numerical calculations. They are only valid over a specified range of argument. Within that range, the Hastings approximations are the polynomials of given order that provide the best approximations to the desired function. In essence, they are power series for the functions, that have been optimised by use of the Tchebysheff polynomials. In common with many such optimised polynomials, the approximation may be very poor when the argument lies outside the specified range. For instance, the approximation for Sin(X), $0 \leqslant X \leqslant 1$, would be good, while that for $\mathrm{Sin}(2\pi+X)$ might be poor. The approximation used in ACOS(X) was valid in the range $0 \leqslant X \leqslant 1$ and was

$$\mathrm{Cos}^{-1}X = (1.-X)^{\frac{1}{2}}.\ \phi(X)$$

$$\phi^*(X) = A_o + A_1.X + A_2.X^2 + A_3.X^3 + A_4.X^4$$

In this, $\phi(X)$ is the true polynomial, and $\phi^*(X)$ the approximation. The constants A_i were

A_o = 1.57078786

A_1 = -.2141245

A_2 = .08466649

A_3 = -.03575663

A_4 = .00864884

b) SEPCØS was a sub-programme that calculated the separation between two points, the value of Cosψ in (60) and (61) and the potential between two points. It used the standard equation for the separation, S, between two points specified by polar coordinates $(p, \theta, \emptyset)$:

$$S^2 = p_1^2 + p_2^2 - 2p_1p_2.\mathrm{Cos}(w)$$

where

$$w = \mathrm{Arccos}(\mathrm{Cos}\emptyset_1.\mathrm{Cos}\emptyset_2 + \mathrm{Sin}\emptyset_1.\mathrm{Sin}\emptyset_2.(\mathrm{Cos}(\theta_1 - \theta_2)))$$

When necessary, SEPCØS also calculated Cosψ as

$$\mathrm{Cos}\,\psi = (p_1^2 - p_2^2 + S^2)/(2p_1.S)$$

c) MINIM was a "pattern search" programme, written as a subroutine. The basic programme was provided by D.M.Bishop. Although the programme is "sophisticated" and therefore very difficult to follow, the basic idea is quite simple. Consider a function $F = F(X_1, X_2, .., X_n)$, where the X_i are variable paramaters. For simplicity , let n = 1. In the first step, the value of F is calculated using some initial value of X_1 , say x_1. Let this be F_1. F_2 and F_3 are calculated with

$$X_1 = x_1 + \alpha\Delta x_1$$

where Δx_1 is a predetermined increment, and α takes the values ±1. If F_1 is the smallest of the values found, Δx_1 is reduced and new values of the F's are calculated. Once F_2 or F_3 is found that is smaller than F_1 the value of α that gave this is retained and a new F is calculated with

$$X_1 = x_1 + 2\alpha \Delta x_1$$

The process is repeated until there is no further reduction of F; then Δx_1 is reduced, the value of α that gives the lowest value of F is selected and the whole procedure is repeated, until Δx_1 has been reduced below some predetermined value.

The actual programme is much more sophisticated than the above outline indicates. It has provision for changing more than one variable at a time, it can minimise a function of many variables and it has provision for distinguishing saddle-points from true minima.

d) Whenever MINIM altered one of the parameters , (the angles of rotation of the solvent molecules about the ion-molecule radii), the subroutine CØØRDS was used to calculate the new coordinates of the hydrogen atoms and the new potential energy of the system. This potential energy was a function of the orientation of the solvent molecules, but the dipole-dipole interactions, those between the oxygen atoms, and all the interactions involving the ion were not dependent on the orientations. The other potentials varied with orientation. The sum of the potentials in the first group was calculated in the main programme. As a result, these potentials did not enter into the minimization problem. The sum of the potentials in the second group was obtained by calculating the potentials associated with the hydrogen atoms on the various axes. If the axes were labelled 1, 2, 3, 4,....., n the potentials associated with the axes were P_1, P_2, P_3, P_4,.....,P_n. P_1 was defined to include the interactions of the hydrogen atoms on the first axis with the oxygen atoms on axes 2, 3, 4,...., n and with the hydrogen atoms and the dipoles on the same axes. P_2 included interactions of the second axis hydrogen atoms with the oxygen atoms and the dipoles on axes 1, 3, 4,.....,n and with the hydrogen atoms on the 3rd, 4th,.....nth axes. The other potentials were calculated in like manner, so that if there were only four axes, P_4 did not include any hydrogen-hydrogen interactions. The subroutine CØØRDS first determined which axes had been rotated. In the case of solvating water molecules, rotation through θ° and through $(\theta + 180)^\circ$ are equivalent. If any of the rotated axes had been changed so that its rotation from the arbitrary origin was more than 180°, or had taken a negative value, a constant of value π was added or subtracted as appropriate. A note was made of the highest ranking axis that had been altered. This was labelled the JO'th axis. The new coordinates of those hydrogen atoms that had been moved were determined, and the potential energies appropriate to the first to the JO'th axis inclusive were calculated, using the subroutine POTF. A summation of the potential energies associated with all the axes was made and XO, the energy being minimized, was equated to the sum.

f) POTF was the function used to generate the potentials described above. Its argument, LONG, was the number of the axis whose potential was to be calculated. The potential associated with the "LONG" axis was calculated by systematically pairing the hydrogen atoms on that axis with the species on the higher order axes, using SEPCOS to calculate the potential energy between each pair.

g) The main programme, HYDR8S, is given on pages 153 et sequentia. The programme defined the size of arrays, assigned variables to COMMON storage and equivalenced certain variables. It read a title, a table heading and values of variables, such as the number of axes to be considered, the number to be varied in the minimization, the initial radius, angles of rotation and so on. The title and table heading were printed and the initial conditions were defined. A matrix AX, was read. The numbers in this matrix, (-1,0 and +1) were instructions to the programme for calculating the coordinates of the charges and dipoles. These coordinates were then calculated and determination of the rotation-independent part of the electrostatic potential followed. Control of the calculations was transferred to MINIM. When MINIM had completed the minimization and the result had been printed, control was returned to the main programme, the radius was incremented, and the process was repeated as many times as was required.

APPENDIX V

RESULTS OF THE MINIMISATION OF THE FREE ENERGY OF HYDRATION OF IONS.

In the following pages the first column is the ion-oxygen radius, in centimeters, and the second column is the free energy of forming the complex, in kcal per mole.

RESULTS FOR TETRAHEDRAL HYDRATION, UNIVALENT CATIONS.

```
+1.0000000E-08-0.4428100E+03
+1.1000000E-08-0.4228900E+03
+1.2000000E-08-0.3849100E+03
+1.3000000E-08-0.3432700E+03
+1.4000000E-08-0.3036700E+03
+1.5000000E-08-0.2681100E+03
+1.6000000E-08-0.2370100E+03
+1.7000000E-08-0.2101200E+03
+1.8000000E-08-0.1869800E+03
+1.9000000E-08-0.1670900E+03
+2.0000000E-08-0.1499500E+03
+2.1000000E-08-0.1351400E+03
+2.2000000E-08-0.1223000E+03
+2.3000000E-08-0.1111200E+03
+2.4000000E-08-0.1013400E+03
+2.5000000E-08-0.9275900E+02
+2.6000000E-08-0.8519100E+02
+2.7000000E-08-0.7849000E+02
+2.8000000E-08-0.7253400E+02
+2.9000000E-08-0.6722000E+02
+3.0000000E-08-0.6246100E+02
+3.1000000E-08-0.5818500E+02
+3.2000000E-08-0.5432900E+02
+3.3000000E-08-0.5084100E+02
+3.4000000E-08-0.4767700E+02
```

RESULTS FOR OCTAHEDRAL HYDRATION, UNIVALENT CATIONS.

```
+1.0000000E-08+0.3278100E+03
+1.1000000E-08+0.1873400E+02
+1.2000000E-08-0.1312500E+03
+1.3000000E-08-0.2002700E+03
+1.4000000E-08-0.2273500E+03
+1.5000000E-08-0.2327400E+03
+1.6000000E-08-0.2279800E+03
+1.7000000E-08-0.2166100E+03
+1.8000000E-08-0.2029800E+03
+1.9000000E-08-0.1887700E+03
+2.0000000E-08-0.1748700E+03
+2.1000000E-08-0.1617000E+03
+2.2000000E-08-0.1494800E+03
+2.3000000E-08-0.1382600E+03
+2.4000000E-08-0.1280100E+03
+2.5000000E-08-0.1187000E+03
+2.6000000E-08-0.1102400E+03
+2.7000000E-08-0.1025700E+03
+2.8000000E-08-0.9561200E+02
+2.9000000E-08-0.8928700E+02
+3.0000000E-08-0.8353300E+02
+3.1000000E-08-0.7829100E+02
+3.2000000E-08-0.7350700E+02
+3.3000000E-08-0.6913200E+02
+3.4000000E-08-0.6512400E+02
```

RESULTS FOR TETRAHEDRAL HYDRATION, UNIVALENT ANIONS.

```
+2.0000000E-08-0.2451600E+03
+2.1000000E-08-0.2140600E+03
+2.2000000E-08-0.1877900E+03
+2.3000000E-08-0.1656400E+03
+2.4000000E-08-0.1469300E+03
+2.5000000E-08-0.1310600E+03
+2.6000000E-08-0.1175400E+03
+2.7000000E-08-0.1059600E+03
+2.8000000E-08-0.9597500E+02
+2.9000000E-08-0.8732800E+02
+3.0000000E-08-0.7979600E+02
+3.1000000E-08-0.7319900E+02
+3.2000000E-08-0.6739400E+02
+3.3000000E-08-0.6226000E+02
+3.4000000E-08-0.5770000E+02
+3.5000000E-08-0.5363000E+02
+3.6000000E-08-0.4998500E+02
+3.7000000E-08-0.4670700E+02
+3.8000000E-08-0.4374800E+02
+3.9000000E-08-0.4106900E+02
+4.0000000E-08-0.3863400E+02
+4.1000000E-08-0.3641500E+02
+4.2000000E-08-0.3438700E+02
+4.3000000E-08-0.3252800E+02
+4.4000000E-08-0.3082000E+02
```

RESULTS FOR OCTAHEDRAL HYDRATION, UNIVALENT ANIONS.

```
+1.5000000E-08+0.3533900E+03
+1.6000000E-08+0.1197000E+02
+1.7000000E-08-0.1450800E+03
+1.8000000E-08-0.2072500E+03
+1.9000000E-08-0.2267900E+03
+2.0000000E-08-0.2258900E+03
+2.1000000E-08-0.2155800E+03
+2.2000000E-08-0.2013900E+03
+2.3000000E-08-0.1861100E+03
+2.4000000E-08-0.1711100E+03
+2.5000000E-08-0.1570100E+03
+2.6000000E-08-0.1440800E+03
+2.7000000E-08-0.1323600E+03
+2.8000000E-08-0.1229200E+03
+2.9000000E-08-0.1132700E+03
+3.0000000E-08-0.1046200E+03
+3.1000000E-08-0.9687400E+02
+3.2000000E-08-0.8991900E+02
+3.3000000E-08-0.8366500E+02
+3.4000000E-08-0.7802700E+02
+3.5000000E-08-0.7293200E+02
+3.6000000E-08-0.6831800E+02
+3.7000000E-08-0.6412700E+02
+3.8000000E-08-0.6031100E+02
+3.9000000E-08-0.5682700E+02
```

RESULTS FOR TETRAHEDRAL HYDRATION, DIVALENT CATIONS.

```
+1.0000000E-08-0.1803500E+04
+1.1000000E-08-0.1608400E+04
+1.2000000E-08-0.1394600E+04
+1.3000000E-08-0.1196600E+04
+1.4000000E-08-0.1024500E+04
+1.5000000E-08-0.8790000E+03
+1.6000000E-08-0.7572600E+03
+1.7000000E-08-0.6557500E+03
+1.8000000E-08-0.5710500E+03
+1.9000000E-08-0.5001500E+03
+2.0000000E-08-0.4405300E+03
+2.1000000E-08-0.3901500E+03
+2.2000000E-08-0.3473500E+03
+2.3000000E-08-0.3107900E+03
+2.4000000E-08-0.2793900E+03
+2.5000000E-08-0.2522800E+03
+2.6000000E-08-0.2287500E+03
+2.7000000E-08-0.2082300E+03
+2.8000000E-08-0.1902500E+03
+2.9000000E-08-0.1744200E+03
+3.0000000E-08-0.1604400E+03
+3.1000000E-08-0.1480200E+03
+3.2000000E-08-0.1369600E+03
+3.3000000E-08-0.1270700E+03
+3.4000000E-08-0.1181900E+03
```

RESULTS FOR OCTAHEDRAL HYDRATION, DIVALENT CATIONS.

```
+1.0000000E-08-0.1070100E+01
+1.1000000E-08-0.7024800E+03
+1.2000000E-08-0.9686400E+03
+1.3000000E-08-0.1032500E+04
+1.4000000E-08-0.1004200E+04
+1.5000000E-08-0.9367200E+03
+1.6000000E-08-0.8559300E+03
+1.7000000E-08-0.7741200E+03
+1.8000000E-08-0.6969000E+03
+1.9000000E-08-0.6265000E+03
+2.0000000E-08-0.5634900E+03
+2.1000000E-08-0.5076600E+03
+2.2000000E-08-0.4584200E+03
+2.3000000E-08-0.4150800E+03
+2.4000000E-08-0.3769300E+03
+2.5000000E-08-0.3433100E+03
+2.6000000E-08-0.3136400E+03
+2.7000000E-08-0.2873700E+03
+2.8000000E-08-0.2640700E+03
+2.9000000E-08-0.2433300E+03
+3.0000000E-08-0.2248300E+03
+3.1000000E-08-0.2082600E+03
+3.2000000E-08-0.1933900E+03
+3.3000000E-08-0.1800100E+03
+3.4000000E-08-0.1679200E+03
```

RESULTS FOR TETRAHEDRAL HYDRATION, DIVALENT ANIONS.

```
+2.0000000E-08-0.8752400E+03
+2.1000000E-08-0.7451700E+03
+2.2000000E-08-0.6381500E+03
+2.3000000E-08-0.5500400E+03
+2.4000000E-08-0.4772500E+03
+2.5000000E-08-0.4168200E+03
+2.6000000E-08-0.3663600E+03
+2.7000000E-08-0.3239700E+03
+2.8000000E-08-0.2881200E+03
+2.9000000E-08-0.2576300E+03
+3.0000000E-08-0.2315400E+03
+3.1000000E-08-0.2090800E+03
+3.2000000E-08-0.1896500E+03
+3.3000000E-08-0.1727300E+03
+3.4000000E-08-0.1579400E+03
+3.5000000E-08-0.1449300E+03
+3.6000000E-08-0.1334600E+03
+3.7000000E-08-0.1232800E+03
+3.8000000E-08-0.1142200E+03
+3.9000000E-08-0.1061200E+03
+4.0000000E-08-0.9885300E+02
+4.1000000E-08-0.9231300E+02
+4.2000000E-08-0.8640500E+02
+4.3000000E-08-0.8105100E+02
+4.4000000E-08-0.7618600E+02
```

RESULTS FOR OCTAHEDRAL HYDRATION, DIVALENT ANIONS.

```
+1.5000000E-08+0.6067100E+03
+1.6000000E-08-0.4669600E+03
+1.7000000E-08-0.8789100E+03
+1.8000000E-08-0.9967500E+03
+1.9000000E-08-0.9852400E+03
+2.0000000E-08-0.9202300E+03
+2.1000000E-08-0.8370000E+03
+2.2000000E-08-0.7517400E+03
+2.3000000E-08-0.6714900E+03
+2.4000000E-08-0.5989300E+03
+2.5000000E-08-0.5346500E+03
+2.6000000E-08-0.4783000E+03
+2.7000000E-08-0.4303800E+03
+2.8000000E-08-0.3873500E+03
+2.9000000E-08-0.3498500E+03
+3.0000000E-08-0.3171100E+03
+3.1000000E-08-0.2884500E+03
+3.2000000E-08-0.2633000E+03
+3.3000000E-08-0.2411400E+03
+3.4000000E-08-0.2215600E+03
+3.5000000E-08-0.2041900E+03
+3.6000000E-08-0.1887400E+03
+3.7000000E-08-0.1749400E+03
+3.8000000E-08-0.1625700E+03
+3.9000000E-08-0.1514600E+03
```

RESULTS FOR TETRAHEDRAL HYDRATION, TRIVALENT CATIONS.

```
+1.0000000E-08-0.4009400E+04
+1.1000000E-08-0.3499500E+04
+1.2000000E-08-0.2983300E+04
+1.3000000E-08-0.2522900E+04
+1.4000000E-08-0.2132100E+04
+1.5000000E-08-0.1807300E+04
+1.6000000E-08-0.1539400E+04
+1.7000000E-08-0.1318800E+04
+1.8000000E-08-0.1136800E+04
+1.9000000E-08-0.9858800E+03
+2.0000000E-08-0.8602100E+03
+2.1000000E-08-0.7549700E+03
+2.2000000E-08-0.6663200E+03
+2.3000000E-08-0.5912200E+03
+2.4000000E-08-0.5272200E+03
+2.5000000E-08-0.4723900E+03
+2.6000000E-08-0.4251500E+03
+2.7000000E-08-0.3842600E+03
+2.8000000E-08-0.3486700E+03
+2.9000000E-08-0.3175700E+03
+3.0000000E-08-0.2902500E+03
+3.1000000E-08-0.2661700E+03
+3.2000000E-08-0.2448400E+03
+3.3000000E-08-0.2258800E+03
+3.4000000E-08-0.2089700E+03
```

RESULTS FOR OCTAHEDRAL HYDRATION, TRIVALENT CATIONS.

```
+1.0000000E-08-0.7588700E+03
+1.1000000E-08-0.1962300E+04
+1.2000000E-08-0.2366300E+04
+1.3000000E-08-0.2377700E+04
+1.4000000E-08-0.2232300E+04
+1.5000000E-08-0.2030500E+04
+1.6000000E-08-0.1818600E+04
+1.7000000E-08-0.1617200E+04
+1.8000000E-08-0.1434400E+04
+1.9000000E-08-0.1272400E+04
+2.0000000E-08-0.1130500E+04
+2.1000000E-08-0.1007000E+04
+2.2000000E-08-0.8997500E+03
+2.3000000E-08-0.8065900E+03
+2.4000000E-08-0.7255800E+03
+2.5000000E-08-0.6549900E+03
+2.6000000E-08-0.5933100E+03
+2.7000000E-08-0.5392500E+03
+2.8000000E-08-0.4917200E+03
+2.9000000E-08-0.4497900E+03
+3.0000000E-08-0.4126700E+03
+3.1000000E-08-0.3797200E+03
+3.2000000E-08-0.3503600E+03
+3.3000000E-08-0.3241200E+03
+3.4000000E-08-0.3005900E+03
```

PROGRAMME IONS3.

```
      EPSX(E)=SQN+EPSM*ATAN(B*E)/(B*E)
      D(E)=E*EPSX(E)
      DIMENSION E(13),R(13)
      SQN=1.78
      EPSM=NOSKP3(SQN)
      EPSM=76.76
      B2=1.08E-8
      B=SQRT(B2)
      CONV=1.43920E13
      A1=82./140.
      A2=216./140.
      A3=27./140.
      A4=272./140.
   10 CALL LCNT(999)
      READ 50,Z,EMIN,EMAX,NUMB
   50 FORMAT(I1,2(1X,E16.9),I2)
      ZE=Z*4.80294E-10
      EX=EMIN
      E(1)=EX
      RX=SQRT(ZE/D(EX))
      R(1)=RX
      AREA=ZE/(EPSX(EX)*RX)+EX*RX
      SUMR1=0.
      SUMR2=0.
      H=(EMAX-EMIN)/6001.
 8888 DO 300 J=1,500
      DO 200 I=2,13
      E(I)=E(I-1)+H
  200 R(I)=SQRT(ZE/D(E(I)))
      SUMR1=SUMR1+A1*R(13)+A2*(R(3)+R(11))+A3*(R(5)+R(9))+A4*R(7)
      SUMR2=A1*(R(7)+R(13))+A2*(R(2)+R(6)+R(8)+R(12))+A3*(R(3)+R(5)+R(9)
     1+R(11))+A4*(R(4)+R(10))+SUMR2
```

.......CONTINUED.

PROGRAMME IONS3, CONTINUED.

```
210 TERM=AREA+H*(64.*SUMR2-SUMR1+31.5*A1*(RX-R(13)))/63.5
    DELE=.5*CONV*ZE*(TERM-ZE/R(13)-E(13)*R(13))
    PRINT 250,Z,R(13),DELE,E(13)
    CALL LCNT(1)
250 FORMAT(1H ,2HZ=I3,10H,  RADIUS=E14.7,17H CM.,  ENTHALPY= E14.7,24H
   1 KCAL/MOLE,  FIELD STR.=E14.7,7H E.S.U.)
260 R(1)=R(13)
300 E(1)=E(13)
    NUMB=NUMB-1
    IF (NUMB) 400,400,10
400 CALL EXIT
    END
```

PROGRAMME DIPOLE.

```
      DIMENSION ZETA0(15),GAMMA(15),ALPHA2(5),CHARGE(7),FMAX(5,7,15),HIT
     1S(15),CX(30),EPSX(30),FMOST(15)
      COMMON SQN,EPSM,ALP2,PLM,EL,B,B2,JUNK,CX,EPSX,C2,EPSI
      DEV(EY,EN)=.6745*SQRT((1.-EY)/(EY*EN))
      FUNC(E)=-ZETA2*(ZETA2-ETA2)*(E*E*EPSI-C2)
      INTEGER START
      EQUIVALENCE  (LOALP,NQ,NALP),(LOLAMB,MLAMDA,NR)
      R=.81667074
      B2=1.08E-8
      B=SQRT(B2)
      DO 1000 K=1,15
 1000 HITS(K)=0.
      READ (5,7778) START
      LOALP=(START-1)/7+1
      LOLAMB=START-7*(LOALP-1)
      KAPPA=2
      EL=4.803E-10
      EL2=EL*EL
      CONV=1.4394E13
      PRECN=5.E-5
      SQN=1.78
      EPSM=76.76
      READ (5,1) (ZETA0(I),I=1,15)
    1 FORMAT(10F6.3/5F6.3)
      ZETALU=ZETA0(1)
      READ (5,2) (((FMAX(I,J,K),I=1,5),J=1,7),K=1,15)
    2 FORMAT(5E14.8)
      READ (5,3) (ALPHA2(I),I=1,5)
    3 FORMAT(1X,5E9.2)
      READ (5,4) (CHARGE(I),I=1,7)
    4 FORMAT(1X,7F5.2)
      READ (5,7777) (CX(I),EPSX(I),I=1,30)
```

......CONTINUED.

PROGRAMME DIPOLE, CONTINUED.

```
 7777 FORMAT(2E16.10)
 7778 FORMAT(I4)
      WRITE (6,6)
    6 FORMAT( 1H1,19HJ.S.MUIRHEAD-GOULD., 3X,36HMONTE-CARLO INTEGRATION
     1FOR DIPOLES., 3X,30HPROJECT --ENERGY-- NO. U00002./1H0)
   10 ALP=.5*ALPHA2(NALP)
      ALP2=ALP*ALP
      ALP3=ALP2*ALP
   20 CON1=CONV*ALP3
      PLM=CHARGE(MLAMDA)
      DIPOLE=ALPHA2(NALP)*PLM*EL*1.E18
      PLM2=PLM*PLM
      INDEX=0
      DO 40 I=1,15
      FMOST(I)=FMAX(NALP,MLAMDA,I)
   40 GAMMA(I)=ALP*(ZETA0(I)-1.)
      DO 130 IT1=1,1000
      DO 130 IT2=1,175
   50 X=ABS(RANDR(R))
      IF (X) 53,51,53
   51 FX=0.
      GO TO 703
   53 ZETA=ZETAL0/X
      ZETA2=ZETA*ZETA
   55 ETA=ABS(RANDR(R))
      TESTER=ABS(RANDR(R))
      ETA2=ETA*ETA
      INDEX=INDEX+1
   57 IF (MOD(INDEX,20000).EQ.0) KAPPA=1
      GO TO (58,70),KAPPA
   58 PRINT 61,INDEX
   61 FORMAT(1H ,I6)
```

......CONTINUED.

PROGRAMME DIPOLE, CONTINUED.

```
 70 E=ESOLVE(ZETA2,ETA2)
    IF (E-.999999999E38) 702,701,701
701 INDEX=INDEX-1
    GO TO 50
702 FX=FUNC(E)
703 DO 90 J=1,15
    CHECK=FMOST(J)*TESTER
    IF (ZETA0(J)-ZETA) 73,72,71
 71 F=0.
    GO TO 75
 72 F=.5*FX
    GO TO 75
 73 F=FX
 75 IF (CHECK-F) 80,80,90
 80 HITS(J)=HITS(J)+1.
 90 CONTINUE
    GO TO (100,130),KAPPA
100 SHOTS=INDEX
    KAPPA=2
    HIT=AMIN1(HITS(1),HITS(2),HITS(3),HITS(4),HITS(5),HITS(6),HITS(7),
   1HITS(8),HITS(9),HITS(10),HITS(11),HITS(12),HITS(13),HITS(14),HITS(
   215))
    VINT=HIT/SHOTS
    IF(VINT.EQ.0.0) GO TO 130
    ERR=DEV(VINT,SHOTS)
120 IF (PRECN.GE.ERR) GO TO 140
130 CONTINUE
140 WRITE (6,142) ALPHA2(NALP),PLM,DIPOLE
142 FORMAT(1H0/1H ,8X,18HCHARGE SEPARATION= 8PF9.2,15H AO.     CHARGE=0
   1PF5.2,28H EL.CHARGE,    DIPOLE MOMENT=F8.4,7H DEBYE./1H0,29X,6HGAMM
   2A.,11X,8HENTHALPY,11X,10HCONFIDENCE/1H ,31X,3HAO.,11X,10HKCAL/MOLE
   3.,11X,8HPER CENT/1H )
```

......CONTINUED.

PROGRAMME DIPOLE, CONTINUED.

```
145 SHOTS=INDEX
    DO 149 I=1,15
    VINT=HITS(I)/SHOTS
    IF (VINT) 146,146,147
146 CONF=0.
    GO TO 148
147 CONF=100.*(1.-DEV(VINT,SHOTS))
148 CALP=CON1*FMOST(I)
    DELH=-.5*VINT*CALP/ZETA0(I)
    WRITE (6,151) GAMMA(I),DELH,CONF
149 CONTINUE
    WRITE (6,152) SHOTS
    WRITE (6,155) (HITS(I),I=1,15)
    START=START+1
    WRITE (6,156) START
151 FORMAT(1H ,27X,8PF7.4,10X,0PE12.5,9X,F8.3)
152 FORMAT(1H ,5X,F7.0,13H TRIALS MADE.)
155 FORMAT(1H0/1H ,10F8.0/1H ,5F8.0)
156 FORMAT(1H0,10X,13HINTEGRATION  I2,18H  TO BE DONE NEXT.)
160 STOP
    END
```

FUNCTION ESOLVE.

```
      FUNCTION ESOLVE(ZETA2,ETA2)
      DIMENSION CX(30),EPSX(30)
      COMMON SQN,EPSM,ALP2,BLM,EL,B,B2,JUNK,CX,EPSX,C2,EPSI
      DOUBLE PRECISION EPS,DEPS,D,E,DEPSI,COR1,COR2,TOP,CM12,DZETA
      EPS(E)=SQN+EPSM*DATAN(B*E)/(B*E)
      DEPS(E)=SQN+EPSM/(1.+B2*E*E)
      DZETA=ZETA2-ETA2
      D=2.*BLM*EL*DSQRT(ETA2*(3.*ZETA2+ETA2)+DZETA)/(ALP2*DZETA*DZETA)
      C=D
      C2=C*C
      CM12=1.D-12*C
      IF (C-CX(28)) 1,3,2
    1 EPSI=78.54
      GO TO 6
    2 DO 4 J=3,28
      I=31-J
      IF (C-CX(I)) 4,3,5
    3 ESOLVE=C/EPSX(I)
      RETURN
    4 CONTINUE
    5 EPSI=YNTPRL(C,I)
    6 I=0
      E=C/EPSI
      DEPSI=EPS(E)
      TOP=E*DEPSI-D
      COR1=0.D0
   40 I=I+1
      IF (I-15) 42,42,41
   41 ESOLVE=.999999999E38
      RETURN
   42 COR2=TOP/DEPS(E)
      E=E-COR2
```

......CONTINUED.

FUNCTION ESOLVE, CONTINUED.

```
      DEPSI=EPS(E)
      TOP=E*DEPSI-D
      ER=DABS(TOP)
   43 IF (COR1+COR2) 44,45,44
   44 COR1=COR2
      IF (ER-CM12) 50,50,40
   45 E=E+.5*COR2
   50 ESOLVE=E
      EPSI=DEPSI
      RETURN
      END
```

FUNCTION YNTPRL.

```
      FUNCTION YNTPRL(C,I)
      DIMENSION CX(30),EPSX(30),A(5),Y(5),T(5),X(5)
      COMMON SQN,EPSM,ALP2,BLM,EL,B,B2,JUNK,CX,EPSX
      J=I-3
      DO 10 K=1,5
       L=J+K
       Y(K)=EPSX(L)
   10 X(K)=CX(L)
      MAX=5
      MAX1=4
      A(1)=Y(1)
      DO 1 I=1,MAX
    1 T(I)=Y(I)
      DO 7 K=1,MAX1
      L=K+1
      A(L)=0.
      DO 3 J=1,K
      DIV=X(J)-X(L)
    2 T(J)=T(J)/DIV
    3 A(L)=A(L)+T(J)
      DIV=X(L)-X(K)
    4 T(L)=T(L)/DIV
      A(L)=A(L)+T(L)
      M=L+1
      IF (MAX-M) 7,5,5
    5 DO 6 N=M,MAX
      DIV=X(N)-X(K)
    6 T(N)=T(N)/DIV
    7 CONTINUE
      YNTPRL=0.
      DO 8 J=1,5
       L=6-J
```

......CONTINUED.

FUNCTION YNTPRL, CONTINUED.

```
8 YNTPRL=YNTPRL*(C-X(L))+A(L)
  RETURN
  END
```

PROGRAMME HYDR6S.

```
      DIMENSION BLM(12,3),JI(12),JKL(61),RHO(61),RHO2(61),THETA(61),PHI(
      DIMENSION D(12),FP(12),CP(12),AX(61,6),ELMDA(12),ROT(12)
      COMMON NOXL,NLMDA,NDPF,NDPL,NHF,NDPL1,NPTS,ICASE,IHATS,JK,JKL,KI,K
     1J,I,J,JI,BLM,RHO,RHO2,PIOV3,OVER3,RADDEG,DEGRAD,GAMMA,R12,R1,RFXUV
     22,RFXSQ,DELT1,DELT2,DELT,DELTH,DELTO,DMU,CONST,S1,S2,COSXI,POT,CON
     3V,E2,PI,THETA,PHI,HSINB,I70,D,TAU,BESTE,TWOPI,MAX,X0,DECLIN,FP,CP,
     4R,AX,ELMDA,ROT,BEGIN,TRIALS
      DIMENSION TITLE(20),HEAD(30)
      DIMENSION A(6)
      EQUIVALENCE (DECLIN,RHFX)
      EQUIVALENCE (A1,A(1)),(A2,A(2)),(A3,A(3)),(A4,A(4)),(A5,A(5)),(A6,
     1A(6))
    1 READ (5,8) TITLE,HEAD
      WRITE (6,9) TITLE,HEAD
    8 FORMAT(18A4/2A4/18A4/12A4)
    9 FORMAT(1H1,20A4/1H0/1H ,30A4)
      READ (5,702) LIMIT,RCHNG
  702 FORMAT(I2,E9.2)
      READ (5,11) DELT,DELTO,DELTH
   11 FORMAT(3E12.6)
      READ (5,12) R,H,CONV,ALPHA,NLMDA,ICASE,MAX,ISKIP
   12 FORMAT(4(E12.6,1X),I3,1X,I1,I3,I3)
      TAU=.03/CONV
      GO TO (1201,14,14),ISKIP
C     THESE ANGLES MUST BE IN RADIANS.
 1201 READ (5,13) BETA,BEGIN,(ELMDA(I),ROT(I),I=1,NLMDA)
   13 FORMAT(F10.7,2X,F10.7)
      READ (5,701) (FP(IP),CP(IP),D(IP),IP=1,MAX)
  701 FORMAT(3E9.2)
   14 HSINB=H*SIN(BETA)
      HCOSB=H*COS(BETA)
      FX=HCOSB
```

......CONTINUED.

PROGRAMME HYDR8S, CONTINUED.

```
      NOXL=NLMDA+1
      NDPF=NOXL+1
      NDPL1=2*NLMDA
      NDPL=NDPL1+1
      NHF=2*NOXL
      IHATS=ICASE/3+2
      GO TO (20,20,30),ICASE
   20 NPTS=4*NLMDA+1
      GO TO (50,40),ICASE
   30 NPTS=5*NLMDA+1
      GO TO 50
   40 FX=-FX
   50 PI=3.14159265
      OVER3=1./3.
      PIOV3=PI*OVER3
      RADDEG=180./PI
      DEGRAD=PI/180.
      E2=2.30682326E-19
      CONV=CONV*E2
      DO 210 INCRS=1,LIMIT
      BESTE=.999999999E38
      X0=.999999999E38
      R12=R*R+2.*FX*R+H*H
      R1=SQRT(R12)
      GAMMA=ATAN(HSINB/R1)
      RFXOV2=R+.5*FX
      RFXSQ=RFXOV2*RFXOV2
      RHFX=R+FX
      GO TO (60,83,60),ISKIP
C
C     CALCULATION OF COORDINATES.
C
```

......CONTINUED.

PROGRAMME HYDR8S, CONTINUED.

```
   60 DO 80 I=1,NLMDA
      READ (5,51) BLM(I,1)
   51 FORMAT(F8.3)
   80 BLM(I,1)=BLM(I,1)*DEGRAD
      I70=125*MAX
      GO TO (801,84,84),ISKIP
  801 DO 82 K=2,NPTS
C     A    1          2          3          4          5
C     1  OX/N         H         DIP        TOP        BOT
C     0   H/D       O/D/N      O/N/H       TILT       TOP
C    -1   -          -          -          BOT        -
C     A6=0,3 FOR WATER, =0,2,4 FOR AMMONIA
C     JKL IS THE AXIS
C     NOTH=1 ,IF NOT HYDROGEN
C          =2 ,IF HYDROGEN.
   81 FORMAT(6F4.1,2I3)
   82 READ (5,81) (AX(K,I),I=1,6),JKL(K),NOTHX(K)
      GO TO 84
   83 I70=50*MAX
   84 DO 130 K=1,NPTS
      IF (K-1) 110,110,85
   85 DO 86 I=1,6
   86 A(I)=AX(K,I)
      NOTH=NOTHX(K)
      JK=JKL(K)
      RHO(K)=A1*R+A2*R1+A3*RFXOV2
      RHO2(K)=RHO(K)*RHO(K)
  120 GO TO (121,122),NOTH
  110 PHI(K)=0.
      THETA(K)=0.
      GO TO 130
  121 THETA(K)=BEGIN+ROT(JK)
```

......CONTINUED.

PROGRAMME HYDR8S, CONTINUED.

```
      PHI(K)=PI-ELMDA(JK)
      GO TO 130
  122 IF (A4) 123,124,123
  123 PHI(K)=A4*GAMMA+A5*PI
      THETA(K)=BLM(JK,1)
      GO TO 130
  124 ANG=BLM(JK,1)+A6*PIOV3
      HSCOS=HSINB*COS(ANG)
      SINL=SIN(ELMDA(JK))
      COSL=COS(ELMDA(JK))
      PHI(K)=ACOS((-RHFX*COSL+HSCOS*SINL)/R1)
      THETA(K)=BEGIN+ROT(JK)+ATAN(HSINB*SIN(ANG)/(RHFX*SINL+HSCOS*COSL))
  130 CONTINUE
      PARAM=IHATS
      TWOPI=(PI+PI)/PARAM
  160 FLOAT=NLMDA
      DMU=ALPHA*DELT/RFXSQ
      CONST=FLOAT*DELT*(DELTO/R-DMU/RFXSQ+PARAM*DELTH/R1)
      KI=1
      KJ=1
      DO 180 I=2,NLMDA
      MARK1=I+1
      DO 170 J=MARK1,NOXL
      CALL SEPCOS(1)
  170 CONST=CONST+DELTO*DELTO/S1
      MARK1=NOXL+I
      DELT1=DELTO
      DO 180 J=MARK1,NDPL
      CALL SEPCOS(2)
  180 CONST=CONST+POT
      DO 200 J=NDPF,NDPL1
      MARK1=J+1
```

......CONTINUED.

PROGRAMME HYDR6S, CONTINUED.

```
      DO 190 I=MARK1,NDPL
      CALL SEPCOS(2)
  190 CONST=CONST+DMU*DMU*(1.+COSXI**2)/(S1*S2)
      LBJ=J-NLMDA+1
      DO 200 I=LBJ,NOXL
      CALL SEPCOS(2)
  200 CONST=CONST+POT
      CALL MINIM
  201 ISKIP=2
  210 R=R+RCHNG
      GO TO 1
      END
```

FUNCTION ACOS.

```
      FUNCTION ACOS(X)
      DIMENSION BLM(12,3),JI(12),JKL(61),RHO(61),RHO2(61),THETA(61),PHI(
     161),NOTHX(61)
      DIMENSION D(12),FP(12),CP(12),AX(61,6),ELMDA(12),ROT(12)
      COMMON NOXL,NLMDA,NDPF,NDPL,NHF,NDPL1,NPTS,ICASE,IHATS,JK,JKL,KI,K
     1J,I,J,JI,BLM,RHO,RHO2,PIOV3,OVER3,RADDEG,DEGRAD,GAMMA,R12,R1,RFXOV
     22,RFXSQ,DELT1,DELT2,DELT,DELTH,DELTO,DMU,CONST,S1,S2,COSXI,POT,CON
     3V,E2,PI,THETA,PHI,HSINB,I70,D,TAU,BESTE,TWOPI,MAX,X0,DECLIN,FP,CP,
     4R,AX,ELMDA,ROT,BEGIN,TRIALS
      ACOS=SQRT(1.-X)*((((.00864884*X-.03575663)*X+.08466649)*X-.2141245
     13)*X+1.57078786)
      RETURN
      END
```

FUNCTION SEPCOS.

```
      SUBROUTINE SEPCOS(IX)
      DIMENSION BLM(12,3),JI(12),JKL(61),RHO(61),RHO2(61),THETA(61),PHI(
     161)
      DIMENSION D(12),FP(12),CP(12),AX(61,6),ELMDA(12),ROT(12)
      COMMON NOXL,NLMDA,NDPF,NDPL,NHF,NDPL1,NPTS,ICASE,IHATS,JK,JKL,KI,K
     1J,I,J,JI,BLM,RHO,RHO2,PIJV3,OVER3,RADDEG,DEGRAD,GAMMA,R12,R1,RFXOV
     22,RFXSQ,DELT1,DELT2,DELT,DELTH,DELTO,DMU,CONST,S1,S2,COSXI,POT,CON
     3V,E2,PI,THETA,PHI,HSINB,I70,D,TAU,BESTE,TWOPI,MAX,XO,DECLIN,FP,CP,
     4R,AX,ELMDA,ROT,BEGIN,TRIALS
      GO TO (600,600,600,615),IX
  600 CSOMGA=COS(PHI(I))*COS(PHI(J))+SIN(PHI(I))*SIN(PHI(J))*COS(THETA(I
     1)-THETA(J))
      S2=RHO2(I)+RHO2(J)-2.*RHO(I)*RHO(J)*CSOMGA
      S1=SQRT(S2)
      GO TO (615,620,610),IX
  610 POT=DELT1*DELT2/S1
  615 RETURN
  620 COSXI=(RHO2(J)-RHO2(I)+S2)/(2.0*RHO(J)*S1)
      POT=-DELT1*DMU*COSXI/S2
      RETURN
      END
```

SUBROUTINE COORDS.

```
      SUBROUTINE COORDS(IX)
      DIMENSION BLM(12,3),JI(12),JKL(61),RHO(61),RHO2(61),THETA(61),PHI(
     161)
      DIMENSION D(12),FP(12),CP(12),AX(61,6),ELMDA(12),ROT(12),POTEN(12)
      COMMON NOXL,NLMDA,NDPE,NDPL,NHE,NDPL1,NPTS,ICASE,IHATS,JK,JKL,KI,K
     1J,I,J,JI,BLM,RHO,RHO2,PIOV3,OVER3,RADDEG,DEGRAD,GAMMA,R12,R1,RFXOV
     22,RFXSQ,DELT1,DELT2,DELT,DELTH,DELTO,DMU,CONST,S1,S2,COSXI,POT,CON
     3V,E2,PI,THETA,PHI,HSINB,I70,D,TAU,BESTE,TWOPI,MAX,XO,DECLIN,FP,CP,
     4R,AX,ELMDA,ROT,BEGIN,TRIALS
      EQUIVALENCE (DECLIN,RHFX)
      EQUIVALENCE (XO,POTX)
      TRIALS=TRIALS+1.
      POTX=0.
      I70=I70-1
      DO 41 JA=1,NLMDA
      MRAC=NHF+IHATS*(JA-1)-1
      GO TO (5,4),IX
    4 IF(BLM(JA,1)-BLM(JA,2)) 5,41,5
    5 IF (BLM(JA,1)-TWOPI) 7,6,6
    6 BLM(JA,1)=BLM(JA,1)-TWOPI
      GO TO 9
    7 IF (BLM(JA,1)) 8,9,9
    8 BLM(JA,1)=BLM(JA,1)+TWOPI
    9 BLM(JA,2)=BLM(JA,1)
      JO=JA
      DO 40 IA=1,IHATS
      MRAC=MRAC+1
      IF (AX(MRAC,4)) 10,11,10
   10 PHI(MRAC)=AX(MRAC,4)*GAMMA+AX(MRAC,5)*PI
      THETA(MRAC)=BLM(JA,1)
      GO TO 40
   11 ANG=BLM(JA,1)+AX(MRAC,6)*PI
```

......CONTINUED.

SUBROUTINE COORDS, CONTINUED.

```
      HSCOS=HSINB*COS(ANG)
      SINL=SIN(ELMDA(JA))
      COSL=COS(ELMDA(JA))
      PHI(MRAC)=ACOS((-RHFX*COSL+HSCOS*SINL)/R1)
      THETA(MRAC)=BEGIN+ROT(JA)+ATAN(HSINB*SIN(ANG)/(RHFX*SINL+HSCOS*COS
     1L))
   40 CONTINUE
   41 CONTINUE
      DO 70 JA=1,JO
   70 POTEN(JA)=POTF(JA)
      DO 80 JA=1,NLMDA
   80 POTX=POTX+POTEN(JA)
  110 RETURN
      END
```

FUNCTION POTF.

```
      FUNCTION POTF(LONG)
      DIMENSION BLM(12,3),JI(12),JKL(61),RHO(61),RHO2(61),THETA(61),PHI(
     161)
      DIMENSION D(12),FP(12),CP(12),AX(61,6),ELMDA(12),ROT(12)
      COMMON NOXL,NLMDA,NDPF,NDPL,NHF,NDPL1,NPTS,ICASE,IHATS,JK,JKL,KI,K
     1J,I,J,JI,BLM,RHO,RHO2,PIOV3,OVER3,RADDEG,DEGRAD,GAMMA,R12,R1,RFXOV
     22,RFXSQ,DELT1,DELT2,DELT,DELTH,DELTO,DMU,CONST,S1,S2,COSXI,POT,CON
     3V,E2,PI,THETA,PHI,HSINB,I70,D,TAU,BESTE,TWOPI,MAX,X0,DECLIN,FP,CP,
     4R,AX,ELMDA,ROT,BEGIN,TRIALS
      POTF=0.0
  300 NDUM=2*(NLMDA+LONG)
      GO TO (301,301,302),ICASE
  301 NHYD1=NDUM+2
      GO TO 303
  302 NHYD1=NDUM+3
  303 K=0
  304 I=NDUM
      ICORD1=JKL(NDUM)
      DO 306 J=2,NOXL
      IF (ICORD1-JKL(J)) 305,306,305
  305 DELT2=DELTO
      CALL SEPCOS(3)
      POTF=POTF+POT
  306 CONTINUE
      DO 308 J=NDPF,NDPL
      IF (ICORD1-JKL(J)) 307,308,307
  307 CALL SEPCOS(2)
      POTF=POTF+POT
  308 CONTINUE
      IF (NDUM+1-NPTS) 1308,1309,1309
 1308 DO 309 J=NHYD1,NPTS
      DELT2=DELTH
```

......CONTINUED.

FUNCTION POTE, CONTINUED.

```
      CALL SEPCOS(3)
      POTF=POTF+POT
  309 CONTINUE
 1309 K=K+1
      IF (2-K) 312,311,310
  310 NDUM=NDUM+1
      GO TO 304
  311 IF (ICASE-2) 312,312,310
  312 RETURN
      END
```

SUBROUTINE OUTPTM.

```
      SUBROUTINE OUTPTM
      DIMENSION BLM(12,3),JI(12),JKL(61),RHO(61),RHO2(61),THETA(61),PHI(
     161)
      DIMENSION D(12),FP(12),CP(12),AX(61,6),ELMDA(12),ROT(12)
      COMMON NOXL,NLMDA,NDPF,NDPL,NHF,NDPL1,NPTS,ICASE,IHATS,JK,JKL,KI,K
     1J,I,J,JI,BLM,RHO,RHO2,PIOV3,OVER3,RADDEG,DEGRAD,GAMMA,R12,R1,RFXOV
     22,RFXSQ,DELT1,DELT2,DELT,DELTH,DELTO,DMU,CONST,S1,S2,COSXI,PUT,CON
     3V,E2,PI,THETA,PHI,HSINB,I70,D,TAU,BESTE,TWOPI,MAX,X0,DECLIN,FP,CP,
     4R,AX,ELMDA,ROT,BEGIN,TRIALS
    7 DELT2=(BESTE+CONST)*CONV
      DO 71 NI=1,NLMDA
   71 BLM(NI,3)=BLM(NI,1)*RADDEG
      WRITE (6,8) R,DELT2,(BLM(NI,3),NI=1,NLMDA),TRIALS
    8 FORMAT(1H ,8PF6.3,2X,0PE12.5,2X,13(1X,F7.2))
      RETURN
      END
```

SUBROUTINE MINIM.

```
      SUBROUTINE MINIM
C     PATTERN SEARCH PROGRAMME, PROVIDED BY D.M.BISHOP.
      DIMENSION BLM(12,3),JI(12),JKL(61),RHO(61),RHO2(61),THETA(61),PHI(
     161)
      DIMENSION D(12),FP(12),CP(12),AX(61,6),ELMDA(12),ROT(12)
      DIMENSION T(12),P(12),I(12),F(12),C(12)
      COMMON NOXL,NLMDA,NDPF,NDPL,NHF,NDPL1,NPTS,ICASE,IHATS,JK,JKL,KI,K
     1J,N,J,JI,BLM,RHO,RHO2,PIOV3,OVER3,RADDEG,DEGRAD,GAMMA,R12,R1,RFXUV
     22,RFXSQ,DELT1,DELT2,DELT,DELTH,DELTO,DMU,CONST,S1,S2,COSXI,POT,CON
     3V,E2,PI,THETA,PHI,HSINB,I70,D,TAU,BESTE,TWOPI,MAX,XO,DECLIN,FP,CP,
     40,AX,ELMDA,ROT,BEGIN,TRIALS
      EQUIVALENCE (P,BLM)
      TRIALS=0.
      DELT1=DELTH
      DO 100 IP=1,NLMDA
      F(IP)=FP(IP)*DEGRAD
  100 C(IP)=CP(IP)*DEGRAD
C     GET INITIAL ENERGY
      DO 1 IP=1,MAX
    1 I(IP)=0
      I51=2
      I44=0
      I41=0
      I45=0
      CALL COORDS(1)
    9 TEMPE=XO
   14 BESTE=TEMPE
C     BEGIN INITIAL SEARCH
      DO 11 IP=1,MAX
      T(IP)= P(IP)
      IF (C(IP)) 31,32,31
   32 I(IP)=0
```

......CONTINUED.

```
      GO TO 11
   31 P(IP)=P(IP)+C(IP)
      CALL COORDS(2)
      IF (I70) 82,8,8
    8 IF (XO-BESTE) 12,33,33
   33 P(IP)=P(IP)-2.0*C(IP)
      CALL COORDS(2)
      IF(I70)82,7,7
    7 IF (XO-BESTE) 34,35,35
   34 C(IP)= -C(IP)
      GO TO 12
   35 P(IP)= P(IP) +C(IP)
      IF (I(IP)-2) 36,37,36
   36 I(IP)= 0
   37 GO TO 11
   12 IF(I(IP)-2) 38,39,38
   38 I(IP)=0
   39 IF (ABS(BESTE-XO)-TAU) 41,40,40
   40 I45=1
      I(IP)=1
   41 BESTE= XO
   11 CONTINUE
C     END INITIAL SEARCH
   70 DO 13 IP=1,MAX
      IF(I(IP)-1) 13,2,13
   13 CONTINUE
      IF (I45) 42,3,42
   42 DO 6 IP=1,MAX
      IF (I(IP)-2) 45,46,45
   46 C(IP)= C(IP)*D(IP)
      I(IP)=0
   45 IF (ABS(C(IP))-F(IP)) 47,6,6
```

......CONTINUED.

SUBROUTINE MINIM, CONTINUED.

```
   47 C(IP)= 0.0
    6 CONTINUE
      I45=0
      GO TO 22
    3 DO 15 IP=1,MAX
      IF (ABS(C(IP))-F(IP)) 15,16,16
   15 CONTINUE
      GOTO81
   16 IF (I41) 19,48,19
   48 I50=0
C     BEGIN PAIRING ROUTINE
   19 DO 20 I49=I51,MAX
      I60=I49-1
      DO 20 I46=1,I60
   18 I41=1
      DO 20 I47=1,3,2
      DO 20 I48=1,3,2
      IF (C(I46)) 49,20,49
   49 IF (C(I49)) 50,20,50
   50 R= I47-2
      S=I48-2
      P(I49)=P(I49)+C(I49)*R
      P(I46)=P(I46)+C(I46)*S
      CALL COORDS(2)
      IF(I70)82,93,93
   93 I45=0
      IF(XO-BESTE)51,52,52
   51 I50=0
      I51=I49
      GOTO9
   52 P(I49)=P(I49)-R*C(I49)
      P(I46)=P(I46)-S*C(I46)
```

......CONTINUED.

SUBROUTINE MINIM, CONTINUED.

```
   20 CONTINUE
      I50=1
      I51=2
C     END PAIRING
      DO30IP=1,MAX
   30 C(IP)=C(IP)*D(IP)
      I45=0
      GOTO22
    2 TEMPE=BESTE
      DO23IP=1,MAX
      R=P(IP)
      IF(I(IP)-1)53,54,53
   54 P(IP)=2.0*P(IP)-T(IP)
   53 T(IP)=R
      IF(I44-1)57,23,57
   57 I(IP)=0
      IF(C(IP))55,23,55
   55 I(IP)=1
   23 CONTINUE
      CALL COORDS(2)
    4 IF(XO-BESTE)58,59,59
   58 BESTE=XO
   59 DO24IP=1,MAX
      IF(I(IP)-1)24,60,24
   60 P(IP)=P(IP)+C(IP)
      CALL COORDS(2)
      IF(I70)82,5,5
    5 IF(XO-BESTE)26,61,61
   61 P(IP)=P(IP)-2.0*C(IP)
      CALL COORDS(2)
      IF(I70)82,94,94
   94 IF(XO-BESTE)63,62,62
```

......CONTINUED.

SUBROUTINE MINIM, CONTINUED.

```
   63 C(IP)=-C(IP)
      GOTO26
   62 P(IP)=P(IP)+C(IP)
      I(IP)=2
      GOTO24
   26 I45=1
      I44=1
      BESTE=XO
   24 CONTINUE
      IF(BESTE-TEMPE)2,64,64
   64 DO25IP=1,MAX
      IF(I(IP)-1)25,65,25
   65 I(IP)=2
   25 P(IP)=T(IP)
      I44=0
      GOTO14
   22 IF(XO-TEMPE)9,66,66
   66 DO29IP=1,MAX
   29 P(IP)=T(IP)
      GOTO14
 0081 CONTINUE
 0082 I70=-1
      CALL OUTPTH
      RETURN
      END
```

CLAIMS TO ORIGINALITY.

Two models have been proposed for the hydration of ions. Both of these were shown to be of some use in the calculation of free energies of hydration. The first of these was a very simple model. It was primarily designed to serve as a basis for a model for calculating the free energies of hydration of dipolar molecules. It proved to be satisfactory, within its limits. The second model, one in which the primary solvating water molecules were treated as discreet particles, was also moderately satisfactory. In practice, the calculated free energies of hydration of some ions differed greatly from the experimental values. These deviations could be explained very reasonably on the basis of the model.

The model proposed for the hydration of dipolar molecules was quite successful. It developed that there was no experimental data on the free energies of hydration of molecules that could be discussed in terms of the model, unless a number of major simplifications were made. Despite this, it proved possible to obtain excellent agreement between the experimental and predicted free energies for several classes of compounds.

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