Calculation of Thermodynamic Functions for Ionic Hydration[1]

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Abstract: An electrostatic model is used to calculate the standard state changes in Gibbs free energy, enthalpy, and entropy associated with the transfer of 17 ions from the gas to water at 25°. An off-centered dipole is used to characterize the permanent electrostatic properties of water in the primary hydration shell, and a Born continuum treatment is used to calculate secondary solvation effects. Values of model parameters are obtained by fitting the model to experimental gas-phase single-ion hydration data. From a comparison of calculated and experimental values, the average absolute error, for both free energies and enthalpies of transfer, is less than 5%.

A list of the principal symbols used in this paper is given below.

T	thermodynamic temperature
G	Gibbs free energy
H	enthalpy
S	entropy
Q	total molecular partition function
$Q_{\mathrm{trans}}, Q_{\mathrm{rot}}, Q_{\mathrm{vib}}$	respectively the translational, rotational, and vibrational molecular partition functions
Q'	ratio of products of Q_{trans}, Q_{rot}, and Q_{vib}
D	dielectric constant
ϕ	electrical potential
$U, D', E, E_{\mathrm{i-d}}, E_{\mathrm{i-id}}, E_{\mathrm{l}}, E_{\mathrm{la}}, E_{\mathrm{rep}}, \Delta E_z$	potential energy terms (see text)
$\mathbf{E}_{\mathrm{f}}, E_{\mathrm{f}}$	electric field (vector, scalar)
$\mathbf{D}$	dielectric displacement (vector)
z	valency (ionic charge number irrespective of sign)
e	electronic charge
α_1, α_2	polarizability of water, ion
I_1, I_2	ionization potential of water, ion
μ	permanent dipole moment of water
$r_{\mathrm{g}}, r_{\mathrm{c}}, r_{\mathrm{e}}$	radii of free gaseous ion, compressed ion (solution, solid, in gaseous hydrate), gaseous hydrate, respectively
r	ion-to-water, center-to-center distance ($r_{\mathrm{w}} + r_{\mathrm{c}}$)
$2a$	length of permanent dipole in water
s	distance by which dipole is off-center
n	primary hydration number
M	molecular weight
N	Avogadro number
h	Planck constant
k	Boltzmann constant
c	velocity of light
ω	frequency (cm^{-1})
R	gas constant
$I_{\mathrm{A}}, I_{\mathrm{B}}, I_{\mathrm{C}}$	principal moments of inertia of ionic hydrate
$I_{\mathrm{a}}, I_{\mathrm{b}}, I_{\mathrm{c}}$	principal moments of inertia of water

Introduction

It is tempting to approach the problem of ionic hydration by treating the solvent as a dielectric continuum. This approach is appealing both because it is mathematically elegant and also because it can readily be generalized to apply to a variety of solvents. Born[3] was the first to treat the solvent as a structureless dielectric continuum wherein the dielectric constant remained unchanged and equal to its bulk value up to the surface of the dissolved ions, which were taken to be charged conducting spheres. The Born equation for the electrostatic part of the free-energy change on transfer of an ion of radius a_0 (both in the gas and in solution) from a vacuum to a solvent of dielectric constant D is

$$\Delta G_{\mathrm{e}}{}^{\circ} = \frac{(ze)^2}{2a_0}\left(\frac{1}{D} - 1\right) \tag{1}$$

It was subsequently realized that eq 1 accounts qualitatively but not quantitatively for much of the available data. Specifically, the hydration free energies for positive ions were too large, and so attempts were made to refine the Born treatment. Inasmuch as eq 1 contains two parameters, a_0 and D, the refinements which were proposed generally fell along one of two lines; in one,[4–8] the ionic radius was increased beyond its crystallographic value, and in the other,[9–18] dielectric saturation of the solvent due to the electric field of the ion was introduced, so that the effective dielectric constant of the solvent was reduced. Both of these approaches have the desired effect of reducing (making less negative) the calculated values of $\Delta G_{\mathrm{e}}{}^{\circ}$.

There are, however, some rather severe limitations associated with each of the above refinements. Whereas eq 1, by a suitable alteration of the a_0 values, can be made to fit the hydration free energies derived from experimental data, this procedure is not very satisfying, in that it does not constitute an explanation of ionic hydration. The dielectric saturation approach is certainly more satisfactory in this respect. This approach cannot account, however, for some experimental hydration data now available, such as the hydration data for the fluoride ion. This failure is significant, not because of the numerical discrepancy between the calculated and experimental results, but rather because the dielectric saturation approach predicts that the electrostatic self energy ($\bar{G}_{\mathrm{e}}{}^{\circ}$) of ions in solution

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must always be positive, whereas the experimental estimate of this quantity for the fluoride ion is significantly negative. This discrepancy is illustrated in Appendix A.

A further limitation of the dielectric continuum model is that it predicts, contrary to experience,[19] that positive and negative ions of the same size and valency will be stabilized to the same extent by hydration. It has been suggested[19] that negative ions are more strongly hydrated than positive ions of the same size and valency, and Buckingham[20] has proposed that this may be a result of the quadrupole moment of water which stabilizes negative ions and destabilizes positive ions. In order to account for the difference in the heats of hydration of the potassium and the fluoride ions, Buckingham required that the value of the quadrupole function $(\textcircled{H}_a + \textcircled{H}_b)$ for water be $+3.9 \times 10^{-26}$ esu (Appendix B). Subsequently Glaeser and Coulson,[21] by using a variety of different wave functions for the isolated water molecule, obtained theoretical estimates of the principal quadrupole moments of water. Using these theoretical estimates, we have obtained the value $+0.719 \times 10^{-26}$ esu for the function $(\textcircled{H}_a + \textcircled{H}_b)$ (Appendix B). It thus appears that the quadrupole function for water is too small to account for the probable differences in the heats of hydration of positive and negative ions, and so an explanation for these differences must be sought elsewhere. Furthermore, Glaeser and Coulson pointed out that multiple point-charge models give unrealistic values for the higher multiple moments of water. This, together with the mathematically cumbersome nature of multiple point-charge models, tends to negate their usefulness, and so in the present work such models were not adopted.

Models

Ions. The ions are taken to be charged conducting spheres, both in the gas phase and in solution. We have adopted the important suggestion of Stokes[16] that the radii of the free ions in the gas phase are considerably larger than their radii in solution, and we have used Stokes' values for the radii of the free gaseous ions. There is mounting evidence which indicates that X-ray crystallographic estimates of ionic radii in solid lattices represent also to a good approximation the respective radii of the bare ions in solution.[22] There are at present four sets[23-26] of values of crystallographic radii of the alkali metal and halide ions; three of these agree closely but differ from the fourth set (that of Gourary and Adrian). The Goldschmidt scale has been chosen here to represent the radii of the bare ions in solution, although use of either the Pauling or the Waddington scale would not significantly alter the final results.

Water. In order to overcome the difficulties which arise from a dielectric continuum model of the solvent, we consider two regions in the solvent around the dissolved ion, and these regions will be treated differently in calculating their respective contributions to the solvation energy of the ion. The first region contributes to what will be termed primary solvation, and this region, which is in the immediate vicinity of the ion, is taken to consist of discrete water molecules. For the purpose of calculating primary solvation energies, the water molecules are taken to be isotropic polarizable spheres, each containing a permanent off-centered dipole. The dipole is considered to be off-centered to allow for the possibility that positive and negative ions of the same size and valency are unequally hydrated. The dipole, in its interaction with the central ion, is taken to be finite in length, but in its lateral interactions with other primary water molecules it is taken to be point shaped. The reason and justification for this latter approximation are given below (E_{1a} calculation).

In the second region, the water is taken to be a dielectric continuum in which the dielectric constant is equal to that of pure bulk water. Dielectric saturation is assumed not to occur in this secondary region for reasons which are discussed below (see step 4 of Calculations).

This approach, wherein the solvent is considered to consist of discrete molecules in the primary hydration region but is a dielectric continuum in the region of secondary hydration, has been used previously[20,27] in conjunction with models of the water and the ions which are different from those chosen in this study. Moreover, unlike these previous studies which interpreted either $\Delta G°$ or $\Delta H°$, the present approach yields reliable estimates of both $\Delta G°$ and $\Delta H°$.

Selection of Data

Stokes' values for the radii of the free gaseous ions and the Goldschmidt radii for the bare ions in solution are entered in columns 2 and 3, respectively, of Table I.

Table I. Selection of Data for Ions

Ion	r_g, Å	r_c, Å	$\alpha_2 \times 10^{24}$, cc/ion	I_2, eV
Li^+	1.121	0.78	0.03	75.3
Na^+	1.352	0.98	0.24	47.1
K^+	1.671	1.33	0.89	31.7
Rb^+	1.801	1.49	1.81	27.4
Cs^+	1.997	1.65	2.79	23.4
Mg^{2+}	1.180	0.78	0.12	79.7
Ca^{2+}	1.480	1.06	0.53	60.0
Sr^{2+}	1.625	1.27	0.86	42.8
Ba^{2+}	1.802	1.43	1.69	35.5
Al^{3+}	1.046	0.57	0.07	119.4
Sc^{3+}	1.328	0.78	0.30	73.9
Y^{3+}	1.481	0.93	1.02	40.0
La^{3+}	1.642	1.22	1.58	20.0
F^-	1.909	1.33	0.81	4.3
Cl^-	2.252	1.81	2.98	4.0
Br^-	2.298	1.96	4.24	3.8
I^-	2.548	2.20	6.25	3.4

We have employed Muirhead-Gould and Laidler's selection of data[27] for the polarizabilities and ionization potentials of the ions, and these are entered in columns 4 and 5, respectively, of Table I. The known parameters of water were taken from published values, namely polarizability (α_1) 1.50×10^{-24} cc, permanent dipole

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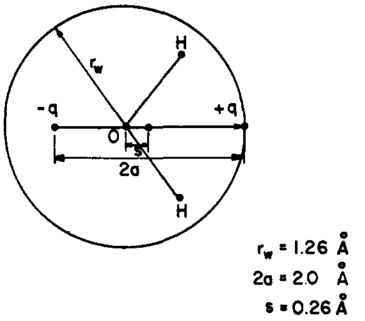

Figure 1. Permanent electrostatic distribution in water from gas-phase calibration data. (Since $\mu = 1.85 \times 10^{-18}$ esu cm, $q = \mu/2a = 0.1926e$.)

moment (μ) 1.85×10^{-18} esu cm, square of refractive index 1.795, and bulk dielectric constant at 25° (D) 78.30.

The experimental values of $\Delta G_t°$ and $\Delta H_t°$ (Table IV, columns 13 and 15) were calculated from Rosseinsky's tabulation,[28] together with the following proton transfer values: $\Delta G_t°(H^+) = -260.5$ kcal mol^{-1}, $\Delta H_t°(H^+) = -269.8$ kcal mol^{-1}. The experimental basis for these values of $\Delta G_t°(H^+)$ and $\Delta H_t°(H^+)$ is thoroughly reviewed by Desnoyers and Jolicoeur,[29] and therefore only the final result is given here.

Calculations

The calculations described below were performed with the aid of an IBM System/360 Model 65 computer at the University of Florida Computing Center.

Calibration of the Model. To calculate the contribution to the hydration energy due to primary hydration, it is necessary first to have estimates of the three parameters describing the model for water, namely the length of the off-centered dipole ($2a$), the amount by which the dipole is off-centered (s), and the effective radius of the water molecule (r_w) (see Figure 1). Estimates of the values of these quantities were obtained by fitting our model of water to recently published experimental data[30,31] for the stepwise reactions of a variety of gaseous ions with water vapor. This procedure removes the arbitrariness that would otherwise result from the introduction of three unknown parameters.

In connection with the fitting procedure, it is necessary to choose a value for the radius of the central ion in the gaseous ionic hydrate. According to Stokes' view,[16] adopted here, the free gaseous ions are characterized by van der Waals radii which are considerably larger than their respective crystallographic radii, the latter assumed to be appropriate in solution. Since much of the hydration energy of an ion comes from primary hydration, it is not unreasonable to assume that a small and highly hydrated gaseous ion will also be compressed in the gaseous hydrate to its crystallographic radius. To fit the model, therefore we have chosen published enthalpy data[30,31] at 25° for small ions (Li^+, Na^+, K^+, F^-), each at the highest degree of hydration for which data were available (sixfold in each case). The fluoride ion data[31] were extrapolated from fivefold hydration. It was assumed that under these conditions use of the crystallographic radius for the central ion in the gaseous hydrate is appropriate. The experimental values used for the standard enthalpy of formation of the sixfold gaseous hydrate were the sums (at 25°) of the first six stepwise standard enthalpies of hydration given by Kebarle, *et al.*

The gas-phase hydration reaction, where all reactants and products are at 1 atm, may be represented by the two-step process

Process I

$$6H_2O(g) + \text{ion } r_g(g) \xrightarrow{A} 6H_2O(g) + \text{ion } r_c(g) \xrightarrow{B} (\text{ion } r_c \cdot 6H_2O)(g)$$

The net standard state enthalpy change for this gas-phase reaction is

$$\Delta H°(g) = \Delta H_A° + \Delta H_B° \qquad (2)$$

$\Delta H_A°$ may be identified with the Born free energy that is required to compress the gaseous ion from a radius of r_g to r_c, since $\Delta S°$ for this process is zero. Hence

$$\Delta H_A° = \Delta G_A° = \frac{N(ze)^2}{2}\left(\frac{1}{r_c} - \frac{1}{r_g}\right)$$

$$\Delta H_A° \text{ (kcal)} = 166z^2\left(\frac{1}{r_c} - \frac{1}{r_g}\right) \qquad (3)$$

where r_c and r_g are in ångströms.

The quantity $\Delta H_B°$ is calculated by the equations

$$\Delta H_B° = \Delta E_z + RT^2(\partial \ln Q'/\partial T)_P \qquad (4)$$

$$\Delta E_z = E + \frac{1}{2}hc\sum_i \omega_i \qquad (5)$$

ΔE_z represents the change in zero-point energy of step B, Q' the ratio of $(Q_{trans}Q_{rot}Q_{vib})$ for the products of reaction B divided by the same terms for the reactants, and E the change in potential energy at 0°K for step B. The second term in eq 5 corrects for the change in the zero-point vibrational energy of step B. Hence

$$\Delta H°(g) = 166z^2\left(\frac{1}{r_c} - \frac{1}{r_g}\right) + E + \frac{1}{2}hc\sum_i \omega_i + RT^2\left(\frac{\partial \ln Q'}{\partial T}\right)_P \qquad (6)$$

Equation 6 was used to fit the model to the experimental gas-phase data. This was done by recalculating $\Delta H°$(g) with this equation for a variety of values of the parameters sought.

The factor n which appears in many of the forthcoming equations refers to the number of water molecules which contribute to the primary hydration of the ion. In the transfer function calculations several values of n were used, but for purposes of fitting eq 6 to the experimental gas-phase data its value was always 6.

Evaluation of E. The quantity E is here taken to consist of a sum of potential energy terms

$$E = E_{i-d} + E_{i-id} + E_l + E_{la} + E_{rep} \qquad (7)$$

where each energy term in eq 7 refers to 0°K. The calculation of these energy terms is considered in the following sections.

(a) E_{i-d} (ion-dipole) represents the energy of interaction of the charge on the central ion with the n perma-

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nent, off-centered dipoles of the surrounding primary water molecules. Since the interaction refers to 0°K, and since higher multiple moments of water are ignored, the C_2 (dipole) axis of a primary water molecule points directly to or away from the center of the ion. Therefore, if we denote the electrical potential at the center of the ion being hydrated due to one of these off-centered dipoles by $\phi_\pm$ depending on whether the ion is positive or negative, then[32a]

$$\phi_\pm = \left(\frac{e}{r \pm s}\right)\sum_{l=0}^{\infty}\left(\frac{a}{r \pm s}\right)^{l}[P_l(\mp 1) - P_l(\pm 1)] \quad (8)$$

whence

$$(E_{i-d})_\pm = \mp\frac{nze\mu}{(r \pm s)^2}\sum_{l=0}^{\infty}\left(\frac{a}{r \pm s}\right)^{2l} \quad (9)$$

In eq 8 and 9 $P_l(x)$ represents the Legendre function of x, $2a$ is the length of the dipole ($a > 0$), s is the distance, along the C_2 axis of water in the direction of the positive pole of the dipole, by which the center of the dipole is displaced from the geometric center, and r is the ion-to-water center-to-center distance ($r_c + r_w$). Since we impose the condition $(r \pm s) > a$ (that is, that the dipole must lie within the water molecule), the series represented by eq 9 converges absolutely. It was therefore possible to evaluate $(E_{i-d})_\pm$ to any desired accuracy by taking a finite number of terms in eq 9. In practice, the first eight terms in the sum were taken.

(b) E_{i-id} (ion-induced dipole) corresponds to the energy of interaction of the charge on the central ion with the n dipoles in the primary water molecules induced by this charge. The dipole induced by the primary water molecules in the central ion is zero, since the calculations (both for the calibration step and for the transfer functions) are performed only for electrically symmetric arrangements of the primary water molecules. Furthermore, because the water molecule is taken to be isotropic with respect to its polarizability, E_{i-id} is not dependent upon the sign of the charge on the ion. Hence[32b]

$$(E_{i-id}) = -n\left(\frac{1}{2}\frac{(ze)^2\alpha_1}{r^4}\right)\left(\sum_{l=0}^{\infty}\frac{l(D_\infty + 2)}{lD_\infty + l + 1}\left(\frac{r_w}{r}\right)^{2l-2}\right) \quad (10)$$

in which α_1 is the polarizability and the square of the refractive index is used to approximate the high-field dielectric constant (D_∞) of the primary water molecules.[33] It was found in trial calculations that the sum represented in eq 10 converged rapidly; the first eight terms in the sum were used.

For all the ions considered here, and particularly for the smaller ions (Li^+, Mg^{2+}, Al^{3+}, Sc^{3+}, Y^{3+}), eq 10 represents an appreciable improvement over the frequently used charge-induced point-dipole formula

$$(E_{i-id}) \approx -n\left(\frac{1}{2}\frac{(ze)^2\alpha_1}{r^4}\right) \quad (11)$$

which can be obtained from eq 10 by considering only the first two terms in the summation.

(c) E_l (London dispersion) represents the dispersion interaction energy of the central ion with the surrounding primary water molecules. It was calculated by the equation

$$E_l = -n\left(\frac{3}{2}\frac{\alpha_1\alpha_2}{r^6}\frac{I_1I_2}{I_1 + I_2}\right) \quad (12)$$

Although eq 12 yields only approximate values for the dispersion energy, it is sufficiently accurate for our purpose, since E_l is small relative to the other terms in eq 7.

(d) E_{la} (lateral) represents the energy of interaction between the primary water molecules around the central ion. A detailed calculation of this quantity, which includes the interaction of all possible moments (due to the ion, the permanent moments in the water, the induced moments in the water, etc.), is cumbersome and is not justified here because of the approximations that are inherent in the first-order calculations $(E_{i-d})_\pm$ and E_{i-id}. We have therefore approximated E_{la} by considering only the permanent interactions between the surrounding water molecules, taken for this calculation to be point dipoles. The error in the final transfer energy calculations resulting from these approximations is small, both because E_{la} is not a principal contributor to E and because of the cancellation of errors that results from using these approximations both in the calibration and in the final transfer function step. Moreover, the mathematical simplification that is achieved by making these approximations is considerable. Thus, E_{la} was calculated by

$$(E_{la})_\pm = \frac{\mu^2\delta_1}{(r \pm s)^3} + \frac{\alpha_1{}^2I_1\delta_2}{r^6} \quad (13)$$

where δ_1 and δ_2 are constants whose values depend on n. For the calibration step, n was 6 (Table II). The first term in eq 13 represents the permanent dipole–permanent dipole repulsion energy, and the second, the London stabilization energy. It is assumed in the derivation of eq 13 that the dielectric constant operative in these lateral interactions is unity.

Table II. Formulas Used to Calculate Characteristic Constants of the Gaseous Ionic Hydrates

n	Assumed structure	δ_1	δ_2	δ_3	$(I_AI_BI_C)$,[a] $(mr^2)^3$
3	Regular trigonal	$\frac{7}{4\sqrt{3}}$	$-\frac{1}{12}$	$\frac{7}{6\sqrt{3}}$	$\frac{27}{4}$
4	Regular tetrahedral	$\frac{15}{8}\sqrt{\frac{3}{2}}$	$-\frac{243}{1024}$	$\frac{15}{16}\sqrt{\frac{3}{2}}$	$\frac{512}{27}$
6	Regular octahedral	$\frac{3(12 + \sqrt{2})}{4\sqrt{2}}$	$-\frac{297}{256}$	$\frac{12 + \sqrt{2}}{4\sqrt{2}}$	64

[a] m is the weight in grams of one water molecule. r is the ion-to-water, center-to-center distance in centimeters.

(e) E_{rep} (repulsion). One general electron-cloud repulsion term was used for the gaseous ionic hydrate

$$(E_{rep}) = B/r^{12} \quad (14)$$

The value of the repulsion constant B was determined by solving the equation

$$(\partial E/\partial r)_{r\,=\,(r_c\,+\,r_w)} = 0 \quad (15)$$

wherein E is given by eq 7. In this way, the value of B was redetermined for each ion and for each set of values of the parameters a, s, and r_w.

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(32) C. J. F. Böttcher, "Theory of Electric Polarization," Elsevier, Houston, Texas, 1952: (a) p 17; (b) p 151; (c) p 110.

(33) H. Fröhlich, "Theory of Dielectrics," 2nd ed, Oxford University Press, London, 1958, p 140.

Evaluation of $(\partial \ln Q'/\partial T)_P$ and $\Sigma_i\omega_i$. A precise evaluation of the changes in the rotational and vibrational partition functions which occur in step B of process I is obviously a difficult task. These changes, however, may be evaluated approximately with the help of two assumptions, one relating to internal rotation and the other to vibration in the gaseous hydrate. The quantity Q' is taken as a product of translational, rotational, and vibrational contributions, and hence

$$\left(\frac{\partial \ln Q'}{\partial T}\right)_P = \left(\frac{\partial \ln Q_{\text{trans}}}{\partial T}\right)_P + \left(\frac{\partial \ln Q_{\text{rot}}}{\partial T}\right) + \left(\frac{\partial \ln Q_{\text{vib}}}{\partial T}\right) \quad (16)$$

where Q_{trans}, Q_{rot}, and Q_{vib} represent ratios for the respective partition functions of step B in process I.

(a) **Translation.** From the equation for the translational partition function of a molecule in a perfect gas at 1 atm, it is apparent that, for step B of process I

$$(\partial \ln Q_{\text{trans}}/\partial T)_P = -5n/2T \quad (17)$$

where n is 6 in the calibration step.

(b) Rotation. The rotational partition function of the gaseous hydrate will contain contributions from the rotation of the hydrate as a whole and from internal rotation of the bound water molecules. Molecular models of the gaseous hydrate indicate that, for $n \leqslant 6$, axial rotation of the water molecules about their respective dipole axes is only slightly hindered, and therefore we assume that each of the bound water molecules rotates freely about its dipole axis. With this assumption, the rotational partition function of the gaseous hydrate is[34]

$$(Q_{\text{rot}})_{\text{hydrate}} = \frac{1}{\pi\sigma}\left(\frac{8\pi^3(I_AI_BI_C[I_b]^n)^{1/(3+n)}kt}{h^2}\right)^{(3+n)/2} \quad (18)$$

where σ is the symmetry factor (2^n); I_A, I_B, and I_C are the principal moments of inertia of the gaseous hydrate about its three principal axes; and I_b is the moment of inertia of water about its dipole axis (1.921×10^{-40} g cm^2). A combination of eq 18 with the usual expression for the rotational partition function of free water vapor, followed by differentiation, results in the relation

$$(\partial \ln Q_{\text{rot}}/\partial T) = (3 - 2n)/2T \quad (19)$$

(c) Vibration. There are a total of $3(3n + 1) - 6$ internal modes of motion in the gaseous hydrate. Of these, $3n$ are due to internal vibrations in the bound water molecules (assumed unchanged in the hydrate), and n are due to the free internal rotation described above. The remaining $(5n - 3)$ vibrational modes are due to the motions of the bound water molecules with respect to the central ion. Two of these modes may be attributed to oscillations of the bound water molecules about their smallest and largest principal axes of inertia. These two vibrational frequencies may be estimated by assuming a harmonic oscillation of the water dipole about each of these two principal axes. Thus each bound water molecule is assumed to oscillate about a principal axis of inertia in a Coulombic field due both to the central ion and to the neighboring water molecules. The potential energy of a bound water molecule relative to its minimum energy is written as

$$U_\pm = D_\pm'(1 - \cos\theta) \quad (20)$$

where

$$D_\pm' = \frac{|z|e\mu}{(r \pm s)^2}\sum_{l=0}^{\infty}\left(\frac{a}{r \pm s}\right)^{2l} - \frac{\delta_3\mu^2}{(r \pm s)^3} \quad (21)$$

In eq 21, δ_3 is a numerical constant whose value is dependent on n (Table II, column 5), and θ is the acute angle through which the dipole axis is displaced from the ion-dipole line of centers. It may be shown that, for small harmonic oscillations[35]

$$\omega_a^0 = \frac{1}{2\pi c}\left(\frac{D_\pm'}{I_a}\right)^{1/2} \quad (22)$$

and

$$\omega_c^0 = \frac{1}{2\pi c}\left(\frac{D_\pm'}{I_c}\right)^{1/2} \quad (23)$$

where for water[36] $I_a = 1.02 \times 10^{-40}$ g cm^2 and $I_c = 2.947 \times 10^{-40}$ g cm^2. Since the polarizability of water is assumed to be isotropic, the two fundamental frequencies ω_a^0 and ω_c^0 do not contain contributions from induced moments.

The effect of the remaining $(5n - 5)$ fundamental vibrational frequencies in the gaseous hydrate was estimated by assuming that each of these frequencies was the same as the frequency of the fundamental breathing mode. This "equal frequency" approximation may at first sight appear to be crude. Inspection of spectroscopic data for polyatomic molecules, however, suggests that it may serve as a reasonable first approximation. This may be illustrated with the example of $SiBr_4$, where the fundamental breathing frequency is 249 cm^{-1},[37] of the same order as the breathing frequencies of the gaseous hydrates (Table III).

Table III. Energy and Entropy Contributions in the Calculations of $\Delta G_3°$ and $\Delta H_3°$ of Cycle I for Four Sample Ions

	Ion and degree of hydration			
	Na^+ ($n = 4$)	I^- ($n = 3$)	Ba^{2+} ($n = 4$)	Al^{3+} ($n = 6$)
$E_{\text{i-d}}$ [a]	−97.45	−41.53	−132.85	−683.56
$E_{\text{i-id}}$ [a]	−61.09	−6.14	−101.07	−2479.54
E_1 [a]	−3.91	−1.52	−8.59	−6.59
E_{1a} [a]	+6.02	+1.49	+4.00	+18.26
E_{rep} [a]	+43.96	+10.88	+65.38	+1367.77
$RT^2(\partial \ln Q'/\partial T)_P$ [a]	−4.85	−0.92	−4.25	−11.50
$^1/_2hc\Sigma_i\omega_i$ [a]	+11.73	+3.33	+10.28	+80.80
ω_a^0 [b]	+629.77	+495.29	+769.99	+1390.6
ω_c^0 [b]	+371.23	+291.96	+453.89	+819.69
ω_f^0 [b]	+480.16	+153.81	+397.55	+2174.3
$(\Delta S°_{\text{trans}})_3$ [c]	−134.21	−102.77	−137.18	−202.86
$(\Delta S°_{\text{rot}})_3$ [c]	−0.29	+8.33	+0.80	−14.41
$(\Delta S°_{\text{vib}})_3$ [c]	+12.12	+28.38	+15.59	+0.23
$\Delta G_3°$ [a]	−69.1	−14.7	−131.1	−1649.6
$\Delta H_3°$ [a]	−105.6	−34.4	−167.1	−1714.4
$\Delta S_3°$ [c]	−122.4	−66.1	−120.8	−217.0

[a] In kcal mol^{-1}. [b] In cm^{-1}. [c] In cal mol^{-1} °K^{-1}.

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(34) J. O. Halford, *J. Chem. Phys.*, 2, 694 (1934).

(35) E. A. Moelwyn-Hughes, "Physical Chemistry," 2nd ed, Pergamon Press, London, 1961, p 86.

(36) T. L. Hill, "An Introduction to Statistical Thermodynamics," Addison-Wesley, Reading, Mass., 1960, p 176.

(37) G. Herzberg, "Molecular Spectra and Molecular Structure. II. Infrared and Raman Spectra of Polyatomic Molecules," Van Nostrand, Princeton, N. J., 1945, p 167.

If one assumes that all of the nine fundamental vibrations of $SiBr_4$ are equal to 249 cm^{-1}, then the total vibrational entropy at 25° of $SiBr_4$ is 15.66 cal mol^{-1} $°K^{-1}$. Use of the actual vibrational frequencies of $SiBr_4$[37] results in a total vibrational entropy at 25° of 19.66 cal mol^{-1} $°K^{-1}$. Since discrepancies of this magnitude are acceptable in the present work, the equal frequency approximation was adopted.

The fundamental breathing frequency of the gaseous hydrate was estimated with the equations

$$\omega_f^0 = \frac{1}{2\pi c}\left(\frac{k'}{R'}\right)^{1/2} \tag{24}$$

and

$$R' = \left(\frac{M_{H_2O}M_{ion}}{(M_{H_2O} + M_{ion})}\right) \tag{25}$$

and the force constant k' was determined from

$$k' = (1/n)(\partial^2 E/\partial r^2) \tag{26}$$

with E given by eq 7.

From a combination of the equal frequency approximation with the conventional equation for the vibrational partition function

$$\left(\frac{\partial \ln Q_{vib}}{\partial T}\right) = \frac{1}{T}\left(\frac{(5n - 5)X_f e^{-X_f}}{1 - e^{-X_f}} + \frac{X_a e^{-X_a}}{1 - e^{-X_a}} + \frac{X_c e^{-X_c}}{1 - e^{-X_c}}\right) \tag{27}$$

where

$$X_j \equiv (hc\omega_j^0)/kT = 1.43868\omega_j^0/T$$

The energy due to the zero-point motion in the gaseous hydrate can now be estimated with the relation

$$\frac{1}{2}hc\sum_i \omega_i^0 = \frac{1}{2}hc[(5n - 5)\omega_f^0 + \omega_a^0 + \omega_c^0] \tag{28}$$

All the terms needed to calculate $\Delta H°(g)$ by eq 6 are now obtainable. Thus, $\Delta H°(g)$ at 25° was calculated by separately varying the parameters r_w, a, and s for each of Li^+, Na^+, K^+, and F^-, with $n = 6$. In each case the constraint $r_w \geq (a \pm s)$ was applied; that is, both charges must lie within the surface of the model adopted for the water molecule. In this way it was found that the calculated values of $\Delta H°(g)$ agreed best with the data of Kebarle, *et al.*,[30,31] (mean absolute error of 4%) when r_w = 1.26 Å, s = +0.26 Å, and a = 1.0 Å. These were the values of the water-model parameters which were used for all the ions in the hydration calculations described below. The permanent charge distribution in water indicated by the above values of the parameters is illustrated in Figure 1.

The value found for the effective radius of water in the ionic hydrate, 1.26 Å, is smaller than the ice radius of 1.38 Å.[38] It should be borne in mind, however, that the effective van der Waals radius of a molecule depends on the strength of the intermolecular forces, and, as such, water bound in an ionic hydrate may be expected to be more compressed than water in ice. Halliwell and Nyburg,[39] from a study of the X-ray structures of crystalline hydrates, determined the range of values 1.24–1.59 Å for the radius of the water molecule, with a mean value of about 1.38 Å. These authors also point out, however, that some of their estimated radii may be too large due to the effect of crystal-structural constraints. It is noteworthy that the value 1.26 Å determined here coincides exactly with the hard-core collision radius of water vapor determined by Monchick and Mason.[40] This suggests that the hard-core collision radius for other solvents, where available, may be used to calculate solvation energies in those systems.

It is evident from Figure 1 that the direction of "off-centeredness" (s = +0.26 Å) of the dipole is such that negative ions will be more stabilized than positive ions of the same size and valency.

It was found that when a fit of the model to the gas-phase data was attempted by using $\Delta G_g°$ (calculated as described below) rather than $\Delta H_g°$, the fit was not satisfactory. This may be due in part to the approximations used here to determine the internal rotational and vibrational partition functions. The uncertainty that results from these approximations is more strongly reflected in $\Delta G_g°$ than in $\Delta H_g°$. The discrepancy may also result in part from experimental uncertainty introduced in the rather large temperature extrapolations[30,31] which were required for much of the data.

Calculation of the Thermodynamic Transfer Functions

The changes in the Gibbs free energy, enthalpy, and entropy which accompany the transfer (t) of 1 mol of single ions from the standard state in the gas (ideal ion gas at 1 atm) to the standard state in solution (hypothetical 1 m solution of ions) were calculated at 25°

Cycle I

$$\begin{tikzcd}
\substack{\text{ion } r_c(g)\\ 1 \text{ atm}} & + & \substack{nH_2O(g)\\ 1 \text{ atm}} \arrow[r, "3"] & \substack{(\text{ion } r_c \cdot nH_2O)(g)\\ 1 \text{ atm}} \arrow[d, "4"] \\
\substack{\text{ion } r_g(g)\\ 1 \text{ atm}} \arrow[u, "1"] & + & nH_2O(l) \arrow[u, "2"] \arrow[r, "t"] & \substack{(\text{ion } r_c \cdot nH_2O)(\text{soln})\\ \text{hyp } 1\ m}
\end{tikzcd}$$

by means of Cycle I. Since G and H are state functions

$$\Delta G_t° = \sum_{i=1}^{4} \Delta G_i° \tag{29}$$

and

$$\Delta H_t° = \sum_{i=1}^{4} \Delta H_i° \tag{30}$$

The entropy of transfer is calculated by

$$\Delta S_t° = (\Delta H_t° - \Delta G_t°)/T \tag{31}$$

Step 1, Cycle I. The changes $\Delta G_1°$ and $\Delta H_1°$ were calculated by eq 3.

Step 2, Cycle I. This step represents the evaporation of n mol of pure liquid water to the ideal vapor. Since water vapor is very nearly ideal at 25° and 1 atm pressure, $\Delta G_2°$ (kcal) = $2.05n$ and $\Delta H_2°$ (kcal) = $10.52n$.

Step 3, Cycle I. The calculations for this step were repeated for n = 3, 4, and 6 wherein the primary water molecules were assumed to be distributed in a symmetrical trigonal plane, as a regular tetrahedron and

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(38) See ref 23, p 465.

(39) H. F. Halliwell and S. C. Nyburg, *Trans. Faraday Soc.*, **59**, 1126 (1963).

(40) L. Monchick and E. A. Mason, *J. Chem. Phys.*, **35**, 1676 (1961).

Table IV. Thermodynamic Functions for the Hydration of Ions at 25°[a]

Ion	n	r_e, Å	Cycle I								$\Delta G_t°$		$\Delta H_t°$		$T\Delta S_t°$	
			$\Delta G_1°$	$\Delta H_1°$	$\Delta G_2°$	$\Delta H_2°$	$-\Delta G_3°$	$-\Delta H_3°$	$-\Delta G_4°$	$-\Delta H_4°$	Calcd[b]	Exptl[c]	Calcd[b]	Exptl[c]	Calcd[d]	Exptl[d]
Li^+	5	2.188	64.7	64.7	10.3	52.6	111.7	161.8	73.6	83.4	110.3	122.1	127.9	132.1	17.6	10.0
Na^+	4	2.076	46.6	46.6	8.2	42.1	69.1	105.6	77.6	86.2	91.9	98.2	103.1	106.0	11.2	7.8
K^+	4	2.180	25.5	25.5	8.2	42.1	39.1	72.4	73.9	82.4	79.3	80.6	87.2	85.8	7.9	5.2
Rb^+	4	2.245	19.2	19.2	8.2	42.1	31.6	63.4	71.7	80.2	75.8	75.5	82.2	79.8	6.4	4.3
Cs^+	4	2.320	17.5	17.5	8.2	42.1	25.0	55.5	69.3	77.7	68.6	67.8	73.6	72.0	5.0	4.2
Mg^{2+}	5	2.188	288.6	288.6	10.3	52.6	434.8	486.7	298.3	312.0	434.2	455.5	457.5	477.6	23.3	22.1
Ca^{2+}	5	2.237	177.8	177.8	10.3	52.6	270.9	321.1	291.7	305.4	374.5	380.8	396.1	398.8	21.6	18.0
Sr^{2+}	4	2.158	114.2	114.2	8.2	42.1	161.2	198.4	302.5	315.0	341.3	345.9	357.1	363.5	15.9	17.6
Ba^{2+}	4	2.219	95.9	95.9	8.2	42.1	131.1	167.1	294.1	306.5	321.1	315.1	335.6	329.5	14.5	14.4
Al^{3+}	6	2.301	1192.8	1192.8	12.3	63.1	1649.6	1714.4	639.6	660.7	1084.2	1103.3	1119.2	1141.0	35.0	37.7
Sc^{3+}	6	2.319	790.4	790.4	12.3	63.1	1062.4	1127.1	634.6	655.6	894.4	929.3	929.2	962.7	34.9	33.4
Y^{3+}	6	2.340	597.7	597.7	12.3	63.1	813.8	878.3	629.1	650.0	833.0	859.5	867.5	891.5	34.6	32.0
La^{3+}	6	2.400	314.7	314.7	12.3	63.1	509.5	572.1	613.4	634.0	795.8		828.2	811.9	32.4	
F^-	5	2.312	37.9	37.9	10.3	52.6	70.3	116.0	69.6	79.3	91.7	103.8	104.8	113.3	13.1	9.5
Cl^-	4	2.406	18.0	18.0	8.2	42.1	29.9	60.9	66.8	75.2	70.5	75.8	76.0	81.3	5.5	5.5
Br^-	3	2.383	12.5	12.5	6.2	31.6	20.6	41.5	67.5	74.5	69.4	72.5	72.0	77.9	2.6	5.4
I^-	3	2.553	10.3	10.3	6.2	31.6	14.7	34.4	62.9	69.8	61.1	61.4	62.4	64.1	1.3	2.7

[a] $\Delta G°$, $\Delta H°$, and $T\Delta S°$ in kcal mol^{-1}. [b] Calculated with eq 29 and 30. [c] Taken from ref 28 and 29. [d] Calculated by $T\Delta S_t° = \Delta H_t° - \Delta G_t°$.

as a regular octahedron, respectively. Within each of these configurations, for a particular ion, the primary water molecules are electrostatically equivalent. Values of $\Delta G_3°$ and $\Delta H_3°$ for $n = 5$ were interpolated from the values of $\Delta G_t°$ and $\Delta H_t°$ (Table IV) for $n = 4$ and 6. It was found through preliminary calculations that primary hydration numbers (n) greater than 6 did not result in satisfactory values for the thermodynamic transfer functions. This was found to be due to the repulsion term (E_{1a}) in eq 13, which becomes relatively larger as n increases beyond **6**.

As with the calibration step, $\Delta H_3°$ is calculated with eq 4 and 5. The quantities E, $\Sigma_i\omega_i$, and $(\partial \ln Q'/\partial T)_P$ were calculated as previously described; the values of the parameters δ_1, δ_2, and δ_3 (eq 13 and 21) for trigonal, tetrahedral, and octahedral hydration are entered in Table II. The repulsion constant B (eq 14) was recalculated for each ion and for each value of n.

The values of $\Delta G_3°$ were calculated by

$$\Delta G_3° = \Delta H_3° - T\Delta S_3° = \\ \Delta H_3° - T[(\Delta S°_{\text{trans}})_3 + (\Delta S°_{\text{rot}})_3 + (\Delta S°_{\text{vib}})_3] \quad (32)$$

The values of the entropy changes needed for the calculation of $\Delta G_3°$ were obtained as described below. From

$$S = R \ln Q + RT(\partial \ln Q/\partial T)_V \quad (33)$$

together with the conventional equation for the partition function of an ideal gas at 1 atm, it follows that

$$(\Delta S°_{\text{trans}})_3 = \\ R\left[1.5 \ln \frac{M_{I\cdot n\text{H}_2\text{O}}}{(M_I)(M_{\text{H}_2\text{O}})^n} - 2.5n \ln T\right] + 2.314n \quad (34)$$

As before, we also assume here that each of the bound water molecules in the gaseous hydrate rotates freely about its dipole axis. Hence, the rotational partition function of the gaseous hydrate is given by eq 18. The principal moments of inertia I_A, I_B, and I_C of the hydrate were calculated by considering each of the bound water molecules to be a mass point. The formulas thus derived for the products $(I_AI_BI_C)$ for each configuration are entered in Table II, column 6. Combining eq 18 and 33

$$(S°_{\text{rot}})_{\text{hydrate}} = R\left[\ln (Q_{\text{rot}})_{\text{hydrate}} + \frac{3+n}{2}\right] \quad (35)$$

The rotational partition function for each of the free water molecules is

$$Q_w = (1/\pi\sigma)(8\pi^3(I_aI_bI_c)^{1/3}kT/h^2)^{3/2} \quad (36)$$

Substitution of the values $\sigma = 2$, $(I_aI_bI_c)_w = 5.797 \times 10^{-120}$ g^3 cm^6,[36] and combination of eq 36 and 33 gives

$$(S°_{\text{rot}})_w = R(1.5 \ln T - 3.287) \quad (37)$$

Hence

$$(\Delta S°_{\text{rot}})_3 = \\ R\left[\ln (Q_{\text{rot}})_{\text{hydrate}} + \frac{3+n}{2} - 1.5n \ln T + 3.287n\right] \quad (38)$$

The frequencies required for the vibrational entropy change in step 3, Cycle I, were calculated with the equal frequency approximation and the two fundamental torsional oscillations. Thus

$$(\Delta S°_{\text{vib}})_3 = (5n - 5)R\left(\frac{X_f}{e^{X_f} - 1} - \ln (1 - e^{-X_f})\right) + \\ R\left(\frac{X_a}{e^{X_a} - 1} - \ln (1 - e^{-X_a})\right) + \\ R\left(\frac{X_c}{e^{X_c} - 1} - \ln (1 - e^{-X_c})\right) \quad (39)$$

Numerical values of the relevant quantities which enter into the calculations of $\Delta G_3°$ and $\Delta H_3°$ are given in Table III for four sample ions.

Step 4, Cycle I. There has been some controversy in the past[15,16] as to whether or not a separate energy term of the form $ze\chi$, where χ represents the surface potential of water, need be considered to account for the passage through the surface of water of single ions. Whereas this effect undoubtedly occurs in the measurement of so-called "real" transfer free energies,[41,42]

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(41) J. E. B. Randles, *Trans. Faraday Soc.*, **52**, 1573 (1956).
(42) B. Case and R. Parsons, *ibid.*, **63**, 1224 (1967).

it is our view that it does not enter into the calculation of transfer functions in which the transfer is from one hypothetical standard state to another. In the present work, the standard state of the single ions in solution is chosen as the hypothetical 1 *m* solution. Since this standard state contains no reference to the surface/volume ratio of the solution, any surface effects operative in the standard state need not be considered. In the present work, the thermodynamic transfer functions are calculated from differences in G and H between final and initial standard states. Consequently, we do not in the present treatment include a surface potential term.

The free-energy and enthalpy changes which occur upon transfer of the hydrated ion from the gas to the solution are each written as a sum of electrostatic and nonelectrostatic terms

$$\Delta G_4{}^\circ = (\Delta G_4{}^\circ)_e + (\Delta G_4{}^\circ)_{ne} \tag{40}$$

$$\Delta H_4{}^\circ = (\Delta H_4{}^\circ)_e + (\Delta H_4{}^\circ)_{ne} \tag{41}$$

The electrostatic terms $(\Delta G_4{}^\circ)_e$ and $(\Delta H_4{}^\circ)_e$ are the changes on transfer of the hydrated ion which result from the charge on the central ion. It is assumed that a continuum model for the solvent is appropriate beyond the primary hydration shell, and moreover that the bulk dielectric constant of pure water is applicable there. In other words, the effect of dielectric saturation on solvation is negligible beyond the primary hydration shell. This supposition is supported by several investigations.[12,14,20] One recent study,[17] however, suggests the contrary, namely that dielectric saturation extends for a considerable distance from the ion into the solution. This conclusion, however, seems to be based on an error in the derivation of the dielectric saturation equation. Specifically, Millen and Watts[17] substitute the equation $E_f = q/Dr$ (their eq 6) rather than $E_f = q/Dr^2$ into their eq 5. By the application of a Born continuum treatment for the transfer of the hydrated ion from the gas to the solution

$$(\Delta G_4{}^\circ)_e(\text{kcal}) = \frac{166z^2}{r_e}\left(\frac{1}{78.30} - 1\right) = \frac{-163.88z^2}{r_e} \tag{42}$$

$$(\Delta H_4{}^\circ)_e\,(\text{kcal}) = (\Delta G_4{}^\circ)_e - T\frac{\partial}{\partial T}[(\Delta G_4{}^\circ)_e] = \frac{-166.76z^2}{r_e} \tag{43}$$

with r_e in ångströms. The numerical coefficient in eq 43 was derived with the value[43] of -1.357 for $\partial \ln D/\partial T$. The quantity r_e represents the effective radius (both in the gas and the solution) of the ion together with its primary hydration shell.

The Born equation[3] may be derived from the relation[32c]

$$W = \int_V \mathrm{d}W = \int_V(\mathbf{E}_f\cdot\mathbf{D}\ \mathrm{d}V/8\pi) \tag{44}$$

where

$$\mathbf{D} \equiv D\mathbf{E}_f;\ E_f = \begin{cases} \dfrac{(ze)}{Dr^2} & r > r_e \\ 0 & r < r_e \end{cases}$$

The Born equation results upon integrating eq 44 over all space, taking D to be invariant with r. Since the field within the hydrated ion is taken as zero, integration of the element of work $(\mathbf{E}_f\cdot\mathbf{D}\ \mathrm{d}V/8\pi)$ is performed only outside of the volume occupied by the hydrated ion. Consequently, the effective radius of the hydrated ion is taken to be that of a uniform sphere, equal in volume to the volume of the hydrated ion, that is

$$r_e\,(\text{Å}) = [r_c{}^3 + (1.26)^3 n]^{1/3} \tag{45}$$

The values of r_e calculated with eq 45 are entered in Table IV, column 3.

The nonelectrostatic terms $(\Delta G_4{}^\circ)_{ne}$ and $(\Delta H_4{}^\circ)_{ne}$ refer to the changes in G and H which occur upon the transfer of the discharged hydrated species $(\mathrm{I}\cdot n\mathrm{H_2O})^0$ from the gas to water. It is assumed here that hydrogen bonding of the primary water molecules with the surrounding bulk water and the effect of the change in volume associated with the transfer are the only terms which significantly contribute to the nonelectrostatic effect. Each bound primary water molecule is assumed to form one hydrogen bond with the surrounding solvent, and we use Némethy and Scheraga's enthalpy value[44] (ice to unbonded liquid transition) of -1.32 kcal mol^{-1} for the hydrogen bond formation. This value is quite close to Muirhead-Gould and Laidler's estimate[27] of -1.60 kcal for this quantity. The corresponding free energy (G) of hydrogen bonding is very difficult to estimate, but a comparison of the free energy and enthalpy of condensation of water (-2.05 and -10.52 kcal, respectively) suggests that ΔG of hydrogen bonding is probably small relative to -1.32 kcal. Consequently we assume ΔG of hydrogen bonding to be zero, and therefore $(\Delta G_4{}^\circ)_{ne}$ consists only of the free-energy change associated with the change in volume in step 4, Cycle I. Thus

$$(\Delta H_4{}^\circ)_{ne}\,(\text{kcal mol}^{-1}) = \Delta(PV) - 1.32n = -(0.568 + 1.32n)$$

$$(\Delta G_4{}^\circ)_{ne}\,(\text{kcal mol}^{-1}) = -0.568 - RT\ln(1/24.47) = +1.325$$

The values of ΔG° and ΔH° for each of steps 1–4 of Cycle I are entered in Table IV, together with the respective sums of these quantities, that is, $\Delta G_t{}^\circ$ and $\Delta H_t{}^\circ$. The values of n entered in column 2, Table IV, are those which result in best agreement between $\Delta G_t{}^\circ$(calcd) and $\Delta G_t{}^\circ$(exptl), and between $\Delta H_t{}^\circ$(calcd) and $\Delta H_t{}^\circ$(exptl). It is seen that the values of n so obtained are both reasonable and consistent. For a particular ion in solution, the quantity n represents the number of water molecules around that ion which cannot, because of their interaction with the ion, be considered as part of a dielectric continuum. The value of n is determined partly by the electrostatic field and partly by the steric factors manifested by a particular ion. As the electrostatic field increases, either due to a decrease in ionic radius or an increase in valency, its perturbing effect on the surrounding solvent increases and therefore n increases. This tendency is offset, however, particularly in the case of the small trivalent ions, by the fact that the space available for primary hydration decreases as the ionic radius decreases.

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[43] C. G. Malmberg and A. A. Maryott, *J. Res. Nat. Bur. Stand.*, **56**, 1 (1956).

[44] G. Némethy and H. A. Scheraga, *J. Chem. Phys.*, **36**, 3382 (1962).

Conclusions

From an examination of columns 12 to 15 in Table IV, it is seen that the agreement between calculated and experimental values of ΔG_t° and ΔH_t° is good. The average absolute error for both ΔG_t° and ΔH_t° is less than 5%. The agreement between the values of $T\Delta S_t^\circ$ (columns 16 and 17) is not as good on a percentage basis, since these values, both experimental and calculated, are obtained as a difference of two large numbers. Nevertheless, for all the ions considered here, the calculated and experimental values for the standard entropy of transfer are of the same sign and the same order of magnitude and follow the same trends.

Insofar as the approach taken here yields reasonably good estimates of ΔG_t° and ΔH_t°, it is suggested that the foregoing calculations may be extended to obtain the hydration transfer functions for ions other than those considered here. Moreover, the off-centered dipole model is quite adaptable, so that these calculations may be extended to obtain values of the transfer functions for ions in nonaqueous solvents, provided that the requisite gas-phase data exist for calibration of the solvents. Experiments that will furnish single-ion gas-phase solvation data are currently under way.[45] When these are completed, the extension of these calculations to certain nonaqueous solvents will be possible.

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Appendix A

If the transfer free energy ΔG_t° of an ion is considered to consist of an electrostatic and a nonelectrostatic term

$$\bar{G}_e^\circ(\text{s}) = \Delta G_t^\circ + G_e^\circ(\text{g}) - \Delta G_{ne}^\circ \qquad (46)$$

where (1) $\Delta G_t^\circ \equiv$ the transfer free energy of 1 mol of ions from the standard state of an ideal gas at one atmosphere to the standard state of the hypothetical 1 m solution; (2) $\bar{G}_e^\circ(\text{s}) \equiv$ the electrostatic contribution to the partial molal free energy of the ions in their standard state in solution; this also represents the energy required to charge reversibly 1 mol of the ions when they are in their standard state in solution; (3) $G_e^\circ(\text{g}) \equiv$ the electrostatic contribution to the self energy of 1 mol of the ions in their gaseous standard state; it also represents the energy that is required to charge reversibly 1 mol of the ions when they are in their gaseous standard state; (4) $\Delta G_{ne}^\circ \equiv$ all contributions to ΔG_t° other than electrostatic.

For the purpose of this appendix we have chosen the standard free energy of transfer of neon to represent ΔG_{ne}° of the fluoride ion. Neon is chosen because it is isoelectronic with the fluoride ion and of approximately the same size. Substitution of the relevant values for the fluoride ion [$\Delta G_t^\circ = -103.8$ kcal (Table IV, column 13); $G_e^\circ(\text{g}) = +166.0/r_g = +87.0$ kcal, $\Delta G_{ne}^\circ = +4.3$ kcal[15]] into eq 46 results in $\bar{G}_e^\circ(\text{s}) = -21.1$ kcal.

If a continuum model for the solvent is assumed to apply up to the surface of the ion in solution

$$\bar{G}_e^\circ(\text{s}) = \int_0^{ze}\int_{r_s}^{\infty} \frac{q}{D(r,q)r^2}\,\text{d}r\text{d}q \qquad (47)$$

where $D(r,q)$ represents the dielectric constant of the solvent, assumed variable with r and q throughout the charging process. Equation 47 represents the energy required to charge reversibly the ions in this medium of variable dielectric constant. Regardless of the model adopted for dielectric saturation, $D(r,q)$ is always positive. Therefore, eq 47 will always result in a positive value for $\bar{G}_e^\circ(\text{s})$ and thus cannot in principle account for the value of $\bar{G}_e^\circ(\text{s}) = -21.1$ kcal for the fluoride ion.

By treating the primary hydration shell as a discrete set of water molecules, as is done in the present work, negative values of $\bar{G}_e^\circ(\text{s})$ can be accounted for.

Appendix B

Buckingham[20] defines the permanent electrical quadrupole moment of water as the second-order tensor

$$\textcircled{H}_{\alpha\beta} = \sum_i e_i r_{i\alpha} r_{i\beta} \qquad (48)$$

and then defines the quadrupole function

$$(\textcircled{H}_a + \textcircled{H}_b) = 2\textcircled{H}_{zz} - (\textcircled{H}_{xx} + \textcircled{H}_{yy}) \qquad (49)$$

in terms of the principal quadrupole moments $\textcircled{H}_{xx}$, $\textcircled{H}_{yy}$, and $\textcircled{H}_{zz}$, where these moments are so chosen that $\textcircled{H}_{\alpha\beta} = 0$ if $\alpha \neq \beta$. From Glaeser and Coulson's[21] theoretical calculations, based on a modified electron-pair wave function, the values of the principal quadrupole moments of water (relative to oxygen as the center of the coordinate system) are $\textcircled{H}_{zz} = -5.496 \times 10^{-26}$ esu, $\textcircled{H}_{xx} = -6.554 \times 10^{-26}$ esu, $\textcircled{H}_{yy} = -5.157 \times 10^{-26}$ esu, or $(\textcircled{H}_a + \textcircled{H}_b) = +0.719 \times 10^{-26}$ esu. The value of $(\textcircled{H}_a + \textcircled{H}_b)$ is essentially independent of which set of $\textcircled{H}_{xx}$, $\textcircled{H}_{yy}$, and $\textcircled{H}_{zz}$ is chosen from Glaeser and Coulson's values.

In order to account for the difference in the hydration enthalpies of the potassium and the fluoride ions, Buckingham required that $(\textcircled{H}_a + \textcircled{H}_b)$ be $+3.9 \times 10^{-26}$ esu, that is, a factor of ~5.4 larger than the value obtained from Glaeser and Coulson's results. This disparity is, in the present work, taken to indicate that the quadrupole moments of water alone cannot account for possible differences in the hydration enthalpies of positive and negative ions of the same size and valency, and also that the effect of the quadrupole moment of water on primary hydration is relatively small.

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(45) P. Kebarle, private communication.