

# Thermodynamic Parameters for the Solvation of Monatomic Ions in Water

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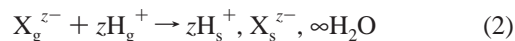
The estimation of solvation parameters for monatomic ions is reviewed and new values for the Gibbs energy, enthalpy, and entropy of solvation are given on the basis of the most recent thermodynamic data. The results for alkali metal and alkaline earth metal cations, and for the halide anions together with the sulfide anion, are examined within the context of a model based on the mean spherical approximation (MSA) for the Gibbs energy of ion–solvent interactions.

## Introduction

Solvation parameters for monatomic ions in water were collected and discussed by Rosseinsky in a review published more than 30 years ago.<sup>1</sup> The quantities involved are the enthalpy, entropy, and Gibbs energy of solvation of the ion which relate to the process in which a given ion in the gas phase is transferred to an aqueous solution under conditions of infinite dilution, that is, in the limit that ion–ion interactions are absent. Solvation parameters are of fundamental interest in assessing ion–solvent interactions and in estimating other important thermodynamic quantities such as redox potentials. Since the solvation of a single ion cannot be studied experimentally in the classical sense, they are reported on a scale relative to the proton. Thus, the solvation parameters for a cation of charge  $+z$  are those for the exchange reaction



in which the unsolvated cation in the gas phase replaces  $z$  protons from an aqueous solution at infinite dilution. In the case of an anion of charge  $-z$ , the reaction involves the solvation of  $z$  protons and the anion, that is



The thermodynamic quantities  $\Delta_s H$ ,  $\Delta_s S$ , and  $\Delta_s G$  associated with reactions 1 and 2 can be found from experimental data for aqueous solutions together with data for the formation of ions in the gas phase. In the case of the entropy of gas-phase ions, a suitable model based on the translational partition function of an ideal monatomic gas and information about the electronic energy levels of the ion are required. Rosseinsky's tabulated values of  $\Delta_s H$ ,  $\Delta_s S$ , and  $\Delta_s G$  were based on data given in the National Bureau of Standards, Circular 500, published in 1952.<sup>2</sup> These data were updated with a change to SI units and adjustment of the gas-phase standard state from 1 atm to 1 bar in 1982.<sup>3</sup> Improved values of the electron affinities for monatomic atoms were published in 1985.<sup>4</sup> Thus, a reevaluation of these important quantities seems worthwhile.

From a theoretical point of view, there is considerable interest in estimating absolute values of the solvation parameters. Conway<sup>5</sup> reviewed various extrathermodynamic assumptions for estimating the absolute values of  $\Delta_s H$  and  $\Delta_s S$  and concluded that the best values of these quantities for the proton are  $-1104$

$\text{kJ mol}^{-1}$  and  $-131 \text{ J K}^{-1} \text{ mol}^{-1}$ , respectively. The corresponding value of  $\Delta_s G(\text{abs})$  at 25 °C and 1 atm pressure is  $-1066 \text{ kJ mol}^{-1}$ . An important way of estimating  $\Delta_s G(\text{abs})$  for the proton is from measurements of its real potential in an experiment such as that carried out by Randles.<sup>6</sup> The real potential is the negative value of the work function to remove the ion from an electrolyte solution phase under conditions that the condensed phase carries no net charge on its surface. It differs from the absolute Gibbs energy of ion solvation by the work done in crossing the gas/solution interface at which a potential difference may exist due to the orientation of solvent dipoles and the nonequivalent distribution of electrolyte ions near the interface.<sup>7</sup> Farrell and McTigue<sup>8</sup> carefully repeated the Randles experiments in 1982 and obtained a value of the real potential for  $H^+$  at infinite dilution in water equal to  $-1088 \pm 2 \text{ kJ mol}^{-1}$ . Assuming that the surface potential of water is  $80 \pm 60 \text{ mV}$ ,<sup>9</sup> the corresponding estimate of the absolute Gibbs energy of solvation is  $-1096 \pm 6 \text{ kJ mol}^{-1}$ .

More recently, Tissandier et al.<sup>10</sup> have described a new method of estimating the absolute values of the solvation parameters for simple inorganic ions in water on the basis of cluster-ion solvation data.<sup>11–13</sup> Using mass spectrometry, values of the Gibbs energy and enthalpy of formation of clusters containing simple inorganic ions such as  $Na^+$  and  $Cl^-$  in water have been obtained as a function of the number of water molecules ranging from one to six per cluster. The analysis leads to the conclusion that  $\Delta_s G(\text{abs})$  for  $H^+$  is  $-1104.5 \text{ kJ mol}^{-1}$  and  $\Delta_s H(\text{abs})$  is  $-1150 \text{ kJ mol}^{-1}$ .<sup>10</sup> When these estimates are compared with previous estimates,<sup>5</sup> it is clear that  $\Delta_s G(\text{abs})$  agrees very well with the value estimated from the real potential.<sup>8</sup>

In the present paper, revised estimates of the solvation parameters for monatomic ions in water on the conventional scale are presented on the basis of up-to-date thermodynamic data. The variation in  $\Delta_s G(\text{abs})$  with ion size is examined using a model for ion solvation based on the mean spherical approximation (MSA).<sup>14,15</sup> The significance of the results is then discussed with respect to structural studies of ion solvation in water.

## Thermodynamic Parameters for Monatomic Ions in the Gas Phase

The enthalpies of formation of monatomic ions in the gas phase are available in the NBS tables.<sup>3</sup> They may also be

**TABLE 1: Gas Phase Enthalpy ( $H_g$ ) and Entropy ( $S_g$ ) of Monatomic Ions formed from Main Group Elements**

ion	$H_g/\text{kJ mol}^{-1}$	$S_g/\text{J K}^{-1} \text{mol}^{-1}$
H <sup>+</sup>	1530.00	108.95
Li <sup>+</sup>	679.59	133.02
Na <sup>+</sup>	603.16	147.95
K <sup>+</sup>	508.06	154.58
Rb <sup>+</sup>	483.90	164.33
Cs <sup>+</sup>	451.76	169.84
Be <sup>2+</sup>	2980.83	178.24
Mg <sup>2+</sup>	2336.10	148.65
Ca <sup>2+</sup>	1913.50	154.89
Sc <sup>2+</sup>	1778.14	164.64
Ba <sup>2+</sup>	1647.98	170.25
Al <sup>3+</sup>	5464.57	149.95
Ga <sup>3+</sup>	5798.00	161.79
In <sup>3+</sup>	5303.40	168.02
Tl <sup>+</sup>	771.56	175.21
Tl <sup>3+</sup>	5620.60	175.21
Sn <sup>2+</sup>	2422.40	168.43
Pb <sup>2+</sup>	2360.93	175.38
F <sup>-</sup>	-249.01	145.58
Cl <sup>-</sup>	-227.32	153.36
Br <sup>-</sup>	-212.72	163.49
I <sup>-</sup>	-188.34	169.26
S <sup>2-</sup>	534.39	152.10

**TABLE 2: Gas Phase Enthalpy ( $H_g$ ) and Entropy ( $S_g$ ) of Monatomic Transition Metal Ions<sup>a</sup>**

ion	ground state term symbol	$H_g/\text{kJ mol}^{-1}$	$S_g/\text{J K}^{-1} \text{mol}^{-1}$
Sc <sup>3+</sup>	<sup>1</sup> S <sub>0</sub>	4633.71	156.32
V <sup>2+</sup>	<sup>4</sup> F <sub>3/2</sub>	2578.46	182.01
V <sup>3+</sup>	<sup>3</sup> F <sub>2</sub>	5406.00	177.68
Cr <sup>2+</sup>	<sup>5</sup> D <sub>0</sub>	2643.31	181.69
Cr <sup>3+</sup>	<sup>4</sup> F <sub>3/2</sub>	5629.80	179.00
Mn <sup>2+</sup>	<sup>6</sup> S <sub>5/2</sub>	2507.29	173.72
Mn <sup>3+</sup>	<sup>5</sup> D <sub>0</sub>	5757.80	179.57
Fe <sup>2+</sup>	<sup>5</sup> D <sub>4</sub>	2737.53	180.26
Fe <sup>3+</sup>	<sup>6</sup> S <sub>5/2</sub>	5694.20	173.92
Co <sup>2+</sup>	<sup>4</sup> F <sub>9/2</sub>	2831.80	179.45
Co <sup>3+</sup>	<sup>5</sup> D <sub>4</sub>	6064.10	179.32
Ni <sup>2+</sup>	<sup>3</sup> F <sub>4</sub>	2918.99	177.98
Cu <sup>+</sup>	<sup>1</sup> S <sub>0</sub>	1083.79	160.64
Cu <sup>2+</sup>	<sup>2</sup> D <sub>5/2</sub>	3041.67	175.54
Ag <sup>+</sup>	<sup>1</sup> S <sub>0</sub>	1015.53	167.24
Zn <sup>2+</sup>	<sup>1</sup> S <sub>0</sub>	2770.38	160.99
Cd <sup>2+</sup>	<sup>1</sup> S <sub>0</sub>	2611.14	167.75
Hg <sup>2+</sup>	<sup>1</sup> S <sub>0</sub>	2878.07	174.97

<sup>a</sup> The data used to estimate the electronic contribution to the entropy were obtained in refs 16 and 17.

calculated from the standard enthalpy of formation of the corresponding atom from the element in its standard state at 25 °C and 1 bar pressure together with the ionization potential in the case of cations or the electron affinity in the case of anions. The latter route does not consider the enthalpy of the electron involved in the reaction and therefore is based on a standard state of the electron as an ideal gas at 0 K. The heat of formation given in the NBS tables<sup>3</sup> is based on a standard state of the electron as an ideal gas at 25 °C and 1 bar pressure. This leads to a contribution of  $5RT/2$  per electron. The values given in Tables 1 and 2 use an electronic standard state at 0 K.

Ionic entropies in the gas phase are not given in the NBS tables.<sup>3</sup> However, they can be calculated in a straightforward fashion with consideration of the translational and electronic contributions to the entropy. The former is found using the Sackur–Tetrode equation, which is based on the translational partition function for an ideal gas. The latter requires spectroscopic data giving the electronic energy levels and term symbols for the ion, which have been tabulated by Moore.<sup>16</sup> The Sackur–

Tetrode equation is

$$S_{\text{trans}} = R \ln \left[ \left( \frac{2\pi M k T}{1000 N_0 h^2} \right)^{3/2} \frac{k T}{P} \right] + \frac{5R}{2} \quad (3)$$

where  $M$  is the atomic weight of the ion in g,  $P$  is the pressure (1 bar) expressed in pascals,  $N_0$  is the Avogadro constant, and the other symbols have their usual meaning. Substituting for the constants at 25 °C, one obtains

$$S_{\text{trans}} = 108.8555 + 12.4716 \ln M \quad (4)$$

The electronic contribution to the entropy is given by

$$S_{\text{elec}} = R \ln q_{\text{elec}} + RT \frac{d \ln q_{\text{elec}}}{dT} \quad (5)$$

and the electronic partition function by

$$q_{\text{elec}} = \sum_{i=0}^n (2J_i + 1) e^{-\epsilon_i/kT} \quad (6)$$

where  $\epsilon_i$  is the energy of the  $i$ th electronic level and  $J_i$  is the associated quantum number for the total angular momentum. For most ions from elements of the main group, only the ground electronic state with an energy  $\epsilon_i = 0$  needs to be considered because all higher energy levels give a negligible contribution to the electronic partition function. Furthermore, these ions usually have a closed shell electronic structure with the term symbol <sup>1</sup>S<sub>0</sub> signifying that  $J$  is 0. This means that  $q_{\text{elec}}$  is equal to 1 and the electronic contribution to the entropy is 0.

Values of the enthalpy and entropy of gas-phase ions from the main group elements are summarized in Table 1. In the case of cations the enthalpies were taken from ref 3 but corrected for the change in standard state of the electron as described above. The enthalpies for the anions were calculated from the enthalpies of formation of the gas-phase atom given in ref 3 and the electron affinities given in ref 4. Gas-phase entropies were calculated from the Sackur–Tetrode equation. Since all ions in this table have a ground-state electronic configuration equivalent to <sup>1</sup>S<sub>0</sub> and no low-lying energy levels, the electronic contribution to the entropy is zero in all cases.

The corresponding data for the transition metal ions are summarized in Table 2. For these ions, the enthalpy reported is that from ref 3 with correction for the contribution from the electrons formed on ionization of the gas-phase atom. The main contribution to the entropy comes from the translational contribution (eq 3). In addition, many of these ions have an electronic contribution to the entropy. This usually involves a degenerate ground state and low-lying electronic states. The number of low-lying states is normally given by the value of  $2S + 1$  in the term symbol except for Mn<sup>2+</sup> and Fe<sup>3+</sup>, which have no low-lying energy levels. Although Mn<sup>2+</sup> and Fe<sup>3+</sup> have a degenerate ground state, the fact that they are d<sup>5</sup> systems means that the next available electronic levels have sufficiently high energy that they need not be considered in evaluating  $S_{\text{elec}}$ . The energy levels and degeneracies were taken from the updated compilations of Sugar et al.<sup>17,18</sup>

The above data are now used to obtain improved estimates of the solvation parameters for monatomic ions in water.

### Thermodynamic Solvation Parameters for Monatomic Ions on the Conventional Scale

To complete the calculation of the thermodynamic solvation parameters according to eqs 1 and 2, the enthalpy and entropy

**TABLE 3: Solvation Parameters for Monatomic Ions in Water at 25 °C and 1 bar Pressure on the Conventional Scale<sup>a</sup>**

ion	$\Delta_s H/\text{kJ mol}^{-1}$	$\Delta_s S/\text{J K}^{-1} \text{mol}^{-1}$	$\Delta_s G/\text{kJ mol}^{-1}$
Cations from Main Group Elements			
H <sup>+</sup>	0	0	0
Li <sup>+</sup>	571.9	−10.7	575.1
Na <sup>+</sup>	686.7	20.0	680.8
K <sup>+</sup>	769.6	56.9	752.6
Rb <sup>+</sup>	794.9	66.1	775.2
Cs <sup>+</sup>	820.0	72.2	798.4
Be <sup>2+</sup>	−303.6	−48.1	−289.3
Mg <sup>2+</sup>	257.1	−68.8	277.6
Ca <sup>2+</sup>	603.7	9.9	600.7
Sr <sup>2+</sup>	736.1	20.7	729.9
Ba <sup>2+</sup>	874.4	57.3	857.3
Al <sup>3+</sup>	−1405.6	−144.8	−1362.4
Ga <sup>3+</sup>	−1419.7	−165.9	−1370.2
In <sup>3+</sup>	−818.4	7.9	−820.7
Tl <sup>+</sup>	763.8	59.3	746.1
Tl <sup>3+</sup>	−834.0	−40.3	−822.0
Sn <sup>2+</sup>	628.8	32.5	619.1
Pb <sup>2+</sup>	697.4	53.0	681.6
Transition Metal Cations			
Sc <sup>3+</sup>	−657.9	−84.5	−632.7
Cr <sup>2+</sup>	273.2	−9.5	276.0
Cr <sup>3+</sup>	−1282.7	−174.4	−1230.7
Mn <sup>2+</sup>	332.0	−29.4	340.7
Fe <sup>2+</sup>	232.5	−64.0	251.5
Fe <sup>3+</sup>	−1153.2	−125.5	−1115.8
Co <sup>2+</sup>	170.0	−74.6	192.2
Ni <sup>2+</sup>	87.0	−89.0	113.5
Cu <sup>+</sup>	517.9	−11.1	521.2
Cu <sup>2+</sup>	83.1	−57.2	100.2
Ag <sup>+</sup>	620.1	14.4	615.8
Zn <sup>2+</sup>	135.7	−55.2	152.2
Cd <sup>2+</sup>	373.0	−23.1	379.8
Hg <sup>2+</sup>	353.0	10.7	349.8
Anions from Main Group Elements			
F <sup>−</sup>	−1613.6	−268.3	−1533.6
Cl <sup>−</sup>	−1469.8	−205.8	−1408.5
Br <sup>−</sup>	−1438.8	−190.1	−1382.2
I <sup>−</sup>	−1396.9	−166.9	−1347.1
S <sup>2−</sup>	−3561.3	−384.6	−3446.6

<sup>a</sup> The enthalpy and entropy of formation of the ions in aqueous solution were taken from ref 3 except in the cases of Cr<sup>18</sup> and Fe<sup>19</sup>.

of formation of the ions are required in an infinitely dilute aqueous solution. These parameters were taken from ref 3 except in the cases of Cr and Fe for which more recent data are available.<sup>19,20</sup> The results of the present compilation are given in Table 3.

The results recorded in Table 3 may be compared directly with the Rosseinsky results, which were tabulated in SI units by Parsons.<sup>21</sup> First of all, the present compilation is more extensive. This is quite simply due to the fact that more data have been obtained in the 35 years since the Rosseinsky review was published. Furthermore, there are significant differences between the results presented earlier and those given here. This is especially true for the entropy of solvation  $\Delta_s S$ . As a result, some differences are also found for the Gibbs energy of solvation  $\Delta_s G$ .

The data in Table 3 are easily converted to absolute values. If one accepts the results of Tissandier et al.,<sup>10</sup> the absolute values of  $\Delta_s H$ ,  $\Delta_s S$ , and  $\Delta_s G$  for the proton are  $−1150.1 \text{ kJ mol}^{-1}$ ,  $−152.9 \text{ J K}^{-1} \text{mol}^{-1}$ , and  $−1104.5 \text{ kJ mol}^{-1}$ , respectively. By adding the thermodynamic parameter for the proton to the corresponding value for the conventional parameter in Table 3, one obtains the absolute value. The absolute scale based on these results is considerably more negative than those

proposed earlier. Conway<sup>5</sup> concluded that the absolute Gibbs energy of solvation for the proton is  $−1066 \text{ kJ mol}^{-1}$ , that is,  $39 \text{ kJ mol}^{-1}$  more positive. Marcus<sup>22</sup> concluded that this quantity is equal to  $−1056 \text{ kJ mol}^{-1}$ . On the basis of the mass spectrometric analysis<sup>10</sup> and the real potential data of Randles<sup>9</sup> and Farrell and McTigue,<sup>8</sup> it is clear that these estimates are too low in magnitude. Tissandier et al.<sup>10</sup> claimed that their estimate of the absolute thermodynamic parameters for the proton does not involve an extrathermodynamic assumption. However, their analysis is clearly subject to the experimental error in the mass spectrometric data.<sup>11</sup>

Gas-phase data for transition metal ions are reported in Table 2 for ions that are not included in Table 3. When the necessary solution-phase thermodynamic data become available, it would be a simple matter to estimate the solvation parameters for these systems. Redox couples based on transition metal ions are important in electrochemistry, and these data would make valuable additions to our knowledge of this subject.

## Discussion

It is interesting to examine the absolute values of the solvation parameters for simple monatomic monovalent ions on the basis of the models used for ion solvation. The most well-known but much criticized theory is the Born model, according to which the Gibbs energy of solvation is found from the difference in work done to charge up the discharged ion in a vacuum and in the pure solvent. The resulting expression for  $\Delta_s G$  is

$$\Delta_s G_i = \frac{-N_0 z_i^2 e_0^2}{8\pi\epsilon_0 r_i} \left(1 - \frac{1}{\epsilon_s}\right) \quad (7)$$

where  $z_i e_0$  is the charge on ion  $i$ ,  $r_i$  its radius,  $\epsilon_s$  the relative permittivity of the pure solvent, and  $\epsilon_0$ , the permittivity of free space. The only quantity needed to estimate  $\Delta_s G_i$  is the ionic radius  $r_i$ . The entropy of solvation is found by taking the derivative of  $\Delta_s G_i$  with respect to temperature so that

$$\Delta_s S_i = \frac{N_0 z_i^2 e_0^2}{8\pi\epsilon_0 \epsilon_s^2 r_i} \frac{d\epsilon_s}{dT} \quad (8)$$

where  $d\epsilon_s/dT$  is the temperature derivative of  $\epsilon_s$ . The values of  $\epsilon_s$  and  $d\epsilon_s/dT$  for water at 25 °C are 78.46 and  $−0.360 \text{ K}^{-1}$ , respectively.

The choice of the ionic radii is an important question in estimating ion solvation parameters. Traditionally, the radii estimated by Pauling<sup>23</sup> have been used in this calculation. Gourary and Adrian<sup>24</sup> suggested an alternative way of dividing up the internuclear distance in ionic crystals, which was based on the minimum in electron density between two oppositely charged ions. On the basis of an extensive compilation of X-ray crystallographic data, Shannon and Prewitt<sup>25</sup> devised a set of *crystal radii* which are consistent with the results from electron density maps for the alkali metal halides.<sup>24</sup> These radii are generally regarded as the appropriate values by inorganic chemists.<sup>26</sup> It should be noted that Shannon and Prewitt<sup>25</sup> also give an alternate set of radii called *effective ionic radii*. These radii are close to the original Pauling results and are 14 pm smaller for cations and 14 pm larger for anions. In the following analysis, the Shannon and Prewitt crystal radii are used.

Values of  $\Delta_s G$  and  $\Delta_s S$  estimated by the Born model are compared in Table 4 with the experimental values on the absolute scale for the alkali metal cations and halide anions. In

**TABLE 4: Values of Gibbs Energy and Entropy of Solvation of Alkali Metal and Halide Ions Estimated Using the Born and MSA Models with the Shannon–Prewitt Crystal Radii**

ion	radius/pm	Gibbs energy, $\Delta_s G_i/\text{kJ mol}^{-1}$			entropy, $\Delta_s S_i/\text{J K}^{-1} \text{mol}^{-1}$		
		expt	Born	MSA	expt	Born	MSA
cations							
Li <sup>+</sup>	88	-529	-779	-483	-164	-46	-199
Na <sup>+</sup>	116	-424	-591	-403	-133	-35	-143
K <sup>+</sup>	152	-352	-451	-333	-96	-27	-101
Rb <sup>+</sup>	163	-329	-421	-316	-87	-25	-92
Cs <sup>+</sup>	184	-306	-373	-288	-81	-22	-78
anions							
F <sup>-</sup>	119	-429	-576	-396	-115	-34	-138
Cl <sup>-</sup>	167	-304	-379	-310	-53	-24	-89
Br <sup>-</sup>	182	-278	-377	-291	-37	-22	-79
I <sup>-</sup>	206	-243	-333	-264	-14	-20	-66

the case of  $\Delta_s G$ , the Born estimate is considerably higher than the experimental value. For the small Li<sup>+</sup> cation, the difference is 250 kJ mol<sup>-1</sup>, whereas for the large I<sup>-</sup> anion it is 90 kJ mol<sup>-1</sup>. In the case of the entropy of solvation, the Born estimates are too small in magnitude. The failure of the Born model is generally recognized to be due to its use of a dielectric continuum model for the solvent. Thus, it fails to take into account the disruptive nature of the ion on the structure of the solvent in its immediate vicinity. This is especially important in water, which is highly structured due to hydrogen bonding.

The MSA represents an attempt to describe ion solvation at the nonprimitive level with consideration of the molecular nature of the solvent. In this model, the ion is assumed to be a sphere of radius  $r_i$  with an embedded charge  $z_i e_0$ , and the solvent molecule as a sphere of radius  $r_s$  with an embedded point dipole  $p_s$ . The goal of the model is to develop expressions for the pair correlation functions using the Ornstein–Zernike integral equation.<sup>27</sup> The ion–solvent pair correlation function may then be used to estimate the contribution to the Gibbs solvation energy due to ion–solvent interactions. If the contribution of dipole–dipole interactions is neglected, the resulting expression for the Gibbs solvation energy is

$$\Delta_s S_i = \frac{-N_0 z_i^2 e_0^2}{8\pi\epsilon_0(r_i + \delta_s)} \left(1 - \frac{1}{\epsilon_s}\right) \quad (9)$$

where

$$\delta_s = r_s/\lambda_s \quad (10)$$

$\lambda_s$  is the Wertheim polarization parameter and can be calculated from the relative permittivity of the solvent using the equation

$$\lambda_s^2(1 + \lambda_s)^4 = 16\epsilon_s \quad (11)$$

The interesting result is that the MSA equation differs from the Born result only in that the ion radius must be corrected by an amount which depends on the properties of the solvent. Solving eq 11 for  $\lambda_s$ , its value for water at 25 °C is 2.65. The reciprocal of this parameter is related to the effective distance over which the ionic radius must be increased to account for disruption of solvent structure. In the case of water, a reasonable estimate of solvent radius is 142 pm.<sup>28</sup> It follows that the value of  $\delta_s$  is 54 pm.

The MSA expression for the entropy of solvation obtained by differentiating eq 9 is

$$\Delta_s S_i = \frac{N_0 z_i^2 e_0^2}{8\pi\epsilon_0} \left[ \frac{1}{\epsilon_s^2} \frac{1}{(r_i + \delta_s)} \frac{d\epsilon_s}{dT} - \frac{1}{(r_i + \delta_s)^2} \left(1 - \frac{1}{\epsilon_s}\right) \frac{d\delta_s}{dT} \right] \quad (12)$$

The temperature coefficient of  $\delta_s$  is given by

$$\frac{d\delta_s}{dT} = -\frac{r_s}{\lambda_s^2} \frac{d\lambda_s}{dT} \quad (13)$$

and that of  $\lambda_s$  by

$$\frac{d\lambda_s}{dT} = \left[ \frac{\lambda_s(1 + \lambda_s)}{3\lambda_s + 1} \right] \frac{1}{2\epsilon_s} \frac{d\epsilon_s}{dT} \quad (14)$$

Given that  $d\epsilon_s/dT$  for water is  $-0.360 \text{ K}^{-1}$ , the value of  $d\lambda_s/dT$  is  $-2.48 \times 10^{-3} \text{ K}^{-1}$  and that of  $d\delta_s/dT$  is  $0.050 \text{ pm K}^{-1}$ . With these parameters, the MSA estimates of  $\Delta_s S_i$  may also be calculated.

The MSA estimates of  $\Delta_s G_i$  and  $\Delta_s S_i$  are also given in Table 4. In the case of the cations, the MSA estimate of the Gibbs energy of solvation is quite good, the average MSA estimate being smaller than the experimental value. The estimates for the anions are quite close to the experimental values. The estimates of the entropy of solvation are quite close to experiment for the cations, but for anions they are too large in magnitude. In general, the MSA gives much better estimates of the solvation parameters than the Born model but it does not describe the experimental results in a completely satisfactory way. This conclusion is strengthened when one examines the changes in the calculated and experimental parameters with ionic radius.

One can identify two reasons why the MSA fails in the form presented here. The first is that the effect of dipole–dipole interactions were ignored in estimating  $\Delta_s G$  and  $\Delta_s S$ . Second, the mechanism of interaction of cations and anions with the solvent water is very different. Cations are stabilized by the electron density available from the lone electron pairs on the oxygen atom of the water molecule. On the other hand, anions are stabilized by hydrogen bonds formed with the hydrogen atoms on the water molecule. As a result, the representation of the solvent molecule as a hard sphere with a point dipole is inadequate.

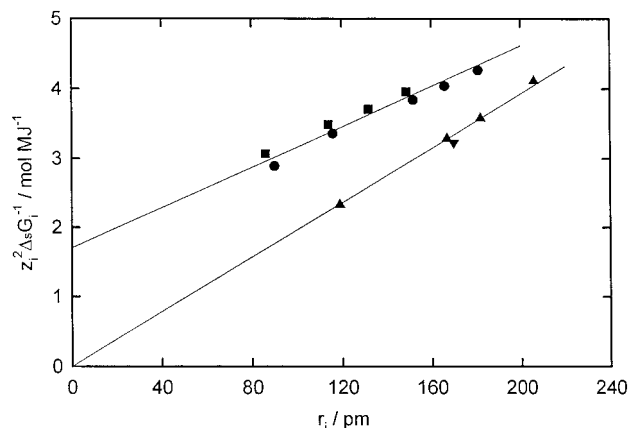
To examine these inadequacies further, the expression for  $\Delta_s G_i$  is rewritten as

$$\Delta_s G_i = \frac{-N_0 z_i^2 e_0^2 f_{dd}}{8\pi\epsilon_0(r_i + \delta_s)} \left(1 - \frac{1}{\epsilon_s}\right) \quad (15)$$

where  $f_{dd}$  is a fraction which describes the degree to which dipole–dipole interactions reduce the attractive effect of ion–dipole interactions. This is an approximate way of including the effect of dipole–dipole interactions which can be derived on the basis of a more detailed model.<sup>15</sup> The parameter  $\delta_s$  is now assumed to depend on whether cations or anions are involved in the solvation process. To test this equation with experimental data it is rearranged as follows:

$$-\frac{z_i^2}{\Delta_s G_i} = k_s(r_i + \delta_s) \quad (16)$$





**Figure 1.** Plot of  $z_i^2 \Delta_s G_i^{-1}$  for cations of the alkali metal (●) and alkaline earth metal groups (■) and for anions of the halide group (▲) and the sulfide ion (▼) against the ionic radius  $r_i$ . The plot for the cations is shifted vertically by one unit for the sake of clarity.

where

$$k_s = \frac{8\pi\epsilon_0\epsilon_s}{N_0 e_0^2 f_{dd}(\epsilon_s - 1)} \quad (17)$$

It follows that a plot of  $-z_i^2/\Delta_s G_i$  should be linear in the ionic radius  $r_i$  with the values of  $f_{dd}$  and  $\delta_s$  being determined from the slope and intercept, respectively.

Plots of experimental data for nine main group cations and five main group anions according to eq 16 are shown in Figure 1. Quite good linear plots are obtained in both cases. For the alkali metal and alkaline earth cations the slope gives a value of  $f_{dd}$  equal to unity and the intercept, a value of  $\delta_s$  equal to 49. The fact that  $f_{dd}$  is equal to 1 suggests that dipole–dipole interactions are not important in determining the solvation of cations. The value of  $\delta_s$  is somewhat smaller than that calculated on the basis of the point dipole model (54 pm). It emphasizes that cations are quite disruptive in water. In the case of the anions there are only five systems, namely, the four common monovalent halide ions and the divalent sulfide ion. The slope of the linear regression is significantly higher, yielding a value of  $f_{dd}$  equal to 0.74. In this case, dipole–dipole repulsive interactions are important and reduce the ion–dipole attractive energy by 26%. The value of  $\delta_s$  determined from the intercept is 0. This result demonstrates clearly that anions have a much less disruptive effect on water structure than cations.

When the MSA is applied in an empirical fashion as implied by eq 15, one gains considerable insight into the nature of the ion–solvent interactions in the solvation phenomenon in water. However, it must be emphasized that the analysis is strongly dependent on the choice of ionic radii. Smaller cations such as  $\text{Li}^+$  and  $\text{Mg}^{2+}$  have a coordination number with water which is closer to 4.<sup>29</sup> In this case, the radii given in Table 4 and used in Figure 1, which are for a coordination number of 6, are not appropriate. In addition, it should be noted that the above analysis does not yield reasonable results when the effective ionic radii of Shannon and Prewitt,<sup>25</sup> which are similar to the

Pauling values,<sup>23</sup> are used. These were used in a previous analysis<sup>30</sup> based on the absolute Gibbs energy of solvation estimated by Conway.<sup>5</sup> As stated earlier, Conway's estimates of  $\Delta_s G$  appear to be too low in magnitude for cations and too high in magnitude for anions by approximately 40 kJ mol<sup>-1</sup>.

In summary, the data presented in Table 3 provide an opportunity to update thermodynamic parameters such as redox potentials. When these results are examined for ions which interact with the solvent electrostatically, they provide confirmation of the MSA model for ion solvation.

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