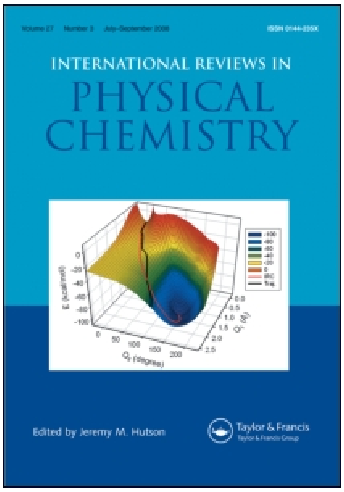

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A thermodynamic analysis of the first solvation shells of alkali and halide ions in liquid water and in the gas phase

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A thermodynamic analysis of the first solvation shells of alkali and halide ions in liquid water and in the gas phase

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Let n denote the number of water molecules in the nearest-neighbour shell (NS) of an ion $J^{\pm}$ in liquid water, and denote $J^{\pm}\cdot nH_2O$ in the gas phase by $J^{\pm}\cdot$NSG (g). The standard free energy of hydration ΔG^0_{hyd} ($J^{\pm}\cdot$NSG) can then be deduced by a thermodynamic cycle involving ΔG^0_n for the formation of $J^{\pm}\cdot$NSG (g) and ΔG^0_{hyd} for the transfer of $J^{\pm}$ (g) to water. Values of ΔG^0_{hyd} ($J^{\pm}\cdot$NSG) for alkali and halide ions are substantial, ranging from 48% to 86% of ΔG^0_{hyd}. The values of ΔG^0_{hyd} ($J^{\pm}\cdot$NSG) can be accounted for largely by the calculated work—electrostatic (ΔW_{elec}) and surface (ΔW_{surf})—in the process $J^{\pm}\cdot$NSG (g) $\rightarrow J^{\pm}$ (aq). ΔW_{elec} is the major contributor. ΔW_{surf} depends on whether (i) $J^{\pm}\cdot$NSG (g) can be represented by a cluster consisting of the ion and n separate water molecules, or (ii) there is some molecular complex formation within that cluster. In fact, $\Delta W_{surf} < 20$ kJ mol^{-1} for the alkali ions and of the order of 100 kJ mol^{-1} for the halide ions. A reasonable case can be built that the alkali ions and some of the n water molecules form molecular complexes while the anions are better represented by case (i).

1. Introduction

One approach to ionic hydration is to study the stepwise association of the ion with water molecules in the gas phase—for instance in the case of alkali ions (M^+),

$$M^+(g) + w\,H_2O(l) \rightarrow M^+\cdot(H_2O)_w(g); \quad \Delta G^0_w(M^+) \tag{1}$$

and allow w to grow large enough to represent a macroscopic liquid cluster. This approach is exemplified by the elegant work of Kebarle and co-workers (Dzidic and Kebarle 1970, Arshadi *et al.* 1970). Another approach is to measure ΔG^0_{hyd} for the transfer of an electrically neutral combination—for instance, $M^+ + X^-$, from the gas phase to liquid water, and use the Born equation, or some modification of it (for references see table 3), to dissect the measurement into additive terms for the separate ionic species, $\Delta G^0_{hyd}(M^+ + X^-) = \Delta G^0_{hyd}(M^+) + \Delta G^0_{hyd}(X^-)$, where

$$M^+(g) + aq \rightarrow M^+(aq); \quad \Delta G^0_{hyd}(M^+) \tag{2}$$

In equation (2) and the following, 'aq' denotes an unspecified amount of liquid water, and M^+ (aq) denotes the solvated alkali ion at equilibrium in liquid water. More generally in what follows we shall represent the alkali or halide ions by a common symbol $J^{\pm}$.

Both approaches can focus on the nearest-neighbour shell (NS) to the ion. Stepwise association in the gas phase can allow w to increase up to the number, n, of water molecules in the NS of $J^{\pm}$ *in liquid water*. The result, $J^{\pm}(H_2O)_n$, will be denoted by $J^{\pm}\cdot$NSG; it represents a hydrated ion in the gas phase with an equilibrium water shell which is isomeric, but perhaps not identical, with that of the nearest-neighbour shell of the ion in liquid water. The latter we shall designate NSL. Since the water structure in the NS should be mainly controlled by the central ion, we shall at present assume that NSG = NSL. In figure 1 we denote ΔG^0 for the formation of $J^{\pm}\cdot$NSG (g) from $J^{\pm}$ (g) and nH_2O (l) by ΔG^0_n ($J^{\pm}$).

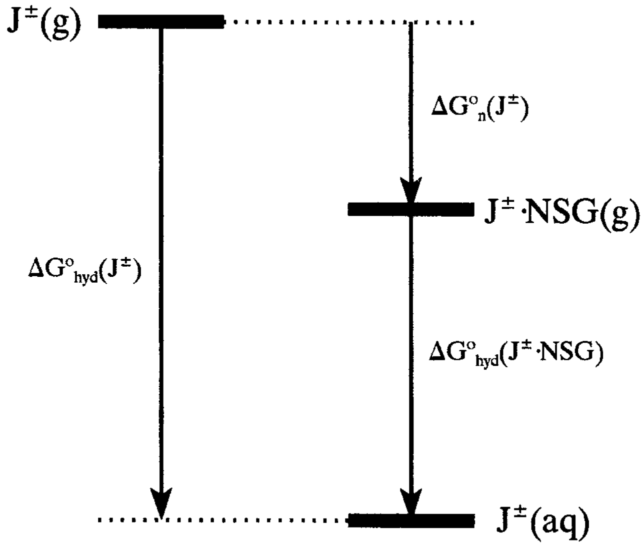

Figure 1. Relationship between the free energy of hydration of the 'bare' ion, $J^{\pm}$ (g), and the ion with water filling its nearest-neighbour shell, $J^{\pm}\cdot$NSG (g).

Kebarle and co-workers plotted cation–cation differences and anion–anion differences $\delta\Delta G^0_w$ versus w. As w becomes large, such plots approach the corresponding values of $\delta\Delta G^0_{hyd}$, thus satisfying a condition for thermodynamic consistency between gas-phase and liquid-phase hydration. In this paper, on the other hand, we intercompare cations with anions and examine the absolute hydration free energies of the gaseous ion hydrates, ΔG^0_{hyd} ($J^{\pm}\cdot$NSG). We find that the latter are very substantial, varying from 48% to 86% of ΔG^0_{hyd} ($J^{\pm}$), the hydration free energy of the 'bare' ion.

In the following we shall use the symbol W for *calculated* work (electrostatic or surface) done on the system. Thus, for example, if W_{elec} (g) is the work done in creating the electrical field associated with $J^{\pm}\cdot$NSG (g) and W_{elec} (aq) is the work done in creating the field associated with $J^{\pm}$ (aq), then $\Delta W_{elec} = W_{elec}\,(aq) - W_{elec}\,(g)$, with a similar definition for ΔW_{surf}. This means that ΔG^0_{hyd} ($J^{\pm}\cdot$NSG) $= \Delta W_{elec} + \Delta W_{surf}$. We shall show that for $J^{\pm}\cdot$NSG (g), the electrostatic part of the hydration free energy, ΔW_{elec}, is within the scope of the Born equation (1920). Surface work must also be considered because the species $J^{\pm}\cdot$NSG (g) may be considered as a water 'droplet' with a high surface/volume ratio. The ability to use classical equations for the surface free energy of a droplet of the dimensions of $J^{\pm}\cdot$NSG (g) is open to question and we shall say more about this later in the paper.

Let us assume that the number n of water molecules in the NS can be predicted. Then ΔG^0_n ($J^{\pm}$) can be obtained from the papers of Kebarle *et al.* after converting the starting state from H_2O (g) to H_2O (l). ΔG^0_{hyd} (M^+) and ΔG^0_{hyd} (X^-) are known from the dissection of experimental values of ΔG^0_{hyd} for the neutral combinations of ions. Figure 1 then shows how this information can be used to determine ΔG^0_{hyd} ($J^{\pm}\cdot$NSG). Figure 2, which will be discussed in greater detail later, displays the species shown in figure 1 more pictorially.

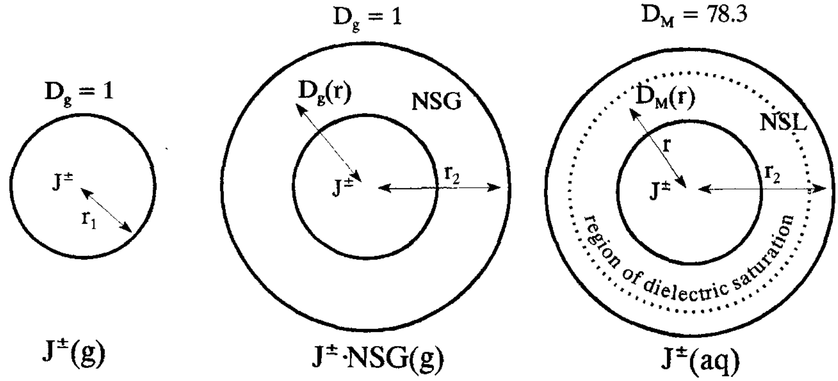

Figure 2. Schematic of (*a*) a 'bare' ion, $J^{\pm}$ (g), (*b*) an ion with its nearest-neighbour shell (NS) filled with water, $J^{\pm}\cdot$NSG (g), and (*c*) an ion dissolved in water, $J^{\pm}$ (aq). In (*c*) $D_M(r)$ is the dielectric constant of the surrounding medium at distance *r* from the centre of the ion. Beyond NS, $D_M(r)$ is close to its low-field value of 78·3 (water). In (*b*), beyond NS, $D_g(r)$ is close to 1, but this is not so inside NS. Inside the NS of (*b*) and (*c*) we may expect $D_M(r) \sim D_g(r)$.

2. Comparison with stepwise hydration in the gas phase

Experimental results for ΔG^0_w ($J^{\pm}$) (equation (1)) for alkali and halide ions are listed on the left side of table 1. The values are those reported by Dzidic and Kebarle (1970) and by Arshadi, Yamdagni and Kebarle (1970) but have been corrected by us for the standard free energy of condensation of water, since figure 1 requires H_2O (l) rather than H_2O (g) as reactant. The stepwise hydration numbers *w* go up to 4, 5, or 6. Measurement beyond the highest reported *w* was impractical.

For comparison with the nearest-neighbour shell (NS) of the ion in liquid water, we need ΔG^0_n ($J^{\pm}$), where *n* is the number of water molecules in the NS in liquid water. The thickness of the nearest-neighbour shell (NS) is close to 2·4 Å, obtained by adding the radius of the water molecule, 1·4 Å, to half the distance between the first and second peak in the radial distribution function of liquid water (Narten and Levy 1969). Thus $r_2 = r_1 + 2{\cdot}4$ Å, where r_1 is the hard-sphere radius of the ion. Values of r_1 and r_2 for alkali and halide ions are listed in table 2. Given these values, letting $V_{H_2O} = 18$ mL mol^{-1}, and assuming that the electrostriction of the water around an ion is localized in the NS, we calculate *n* as the integer nearest to the value of *f* in equations (3).

$$f = [4\pi N_A(r_2^3 - r_1^3)/3 + \Delta V_{\text{electrostric}}]/18 \tag{3a}$$

$$\Delta V_{\text{electrostric}} = (4/3)\pi N_A r_1^3/0{\cdot}55 - V_{\text{ion}}. \tag{3b}$$

In (3*b*) the first term on the right estimates the ionic volume in the absence of electrostriction, using a filling factor of 0·55. V_{ion} is the ionic partial molar volume as given in the review by Marcus (1994). Values of 18*f* range from 80 to 220 mL mol^{-1}; those of $\Delta V_{\text{electrostric}}$ range from 4 to 12 mL mol^{-1}. The results for *n* are included in table 1.

For Li^+ and Na^+, *n* is within the experimental range of Dzidic and Kebarle (1970), and ΔG^0_n is an experimental number. For the other ions, extrapolation of the experimental ΔG^0_w to $w = n$ is required. Fortunately the extrapolation is small. To make the extrapolation as smooth as possible, we fitted the available ΔG^0_w to the empirical equation, $\Delta G^0_w = a + bw + cw^{-1/5}$ (where *a*, *b*, *c* are parameters of fit), and extrapolated to $w = n$. The results are listed in table 1. For consistency, we fitted the data for Li^+ and Na^+ similarly and interpolated at $w = n$. As can be seen from figure

Table 1. Stepwise hydration of gaseous ions at 298 K.[a]

Ion	$-\Delta G_1^0$	$-\Delta G_2^0$	$-\Delta G_3^0$	$-\Delta G_4^0$	$-\Delta G_5^0$	$-\Delta G_6^0$	n	$-\Delta G_n^0(J^\pm)$
Li^+	98	169	216	238	249	250	5	249
Na^+	65	112	142	160	168	171	6	173
K^+	39	68	86	95	100	101	8	105
Rb^+	32	52	65	72	75		8	84
Cs^+	24	40	50	54	57		9	61
F^-	67	105	128	142	163		7	190
Cl^-	26	44	54	60			10	76
Br^-	21	35	44	47			11	57
I^-	14	23	27	(30·5)			12	39

[a] All free energies in kJ mol^{-1}.

Table 2. Ion parameters and ionic free energies of hydration at 298 K[d]

Ion	Radius of NS (Å)[b] Inner (r_1)[c]	outer (r_2)	$-\Delta G^0_{hyd}(J^\pm)$[a,c]	$-\Delta G^0_{hyd}(J^\pm\cdot NSG)$
Li^+	0·69	3·09	475	226
Na^+	1·02	3·42	365	192
K^+	1·38	3·78	295	190
Rb^+	1·49	3·89	275	191
Cs^+	1·70	4·10	250	189
F^-	1·33	3·73	465	275
Cl^-	1·81	4·21	340	264
Br^-	1·96	4·36	315	258
I^-	2·20	4·60	275	236

[a] These values use the same concentration units in gas and liquid phase and are independent of concentration units.
[b] $r_2 = a + 2{\cdot}4$ Å.
[c] Data tabulated by Marcus (1994).
[d] All energies in kJ mol^{-1}.

1, these values together with the values of $\Delta G^0_{hyd}(J^\pm)$ from table 2 allow the determination of $\Delta G^0_{hyd}(J^\pm\cdot NSG)$, whose values are given in table 2. The first point to notice is that *these ions still have very substantial free energies of hydration, ranging from 48% to as much as 86% of the hydration free energy of the 'bare' ions*. Also for similar values of r_2, the magnitude of $\Delta G^0_{hyd}(X^-\cdot NSG)$ exceeds that of $\Delta G^0_{hyd}(M^+\cdot NSG)$ by about 100 kJ mol^{-1}. We shall now see if we can account for these results.

3. Calculation of hydration free energies

3.1. *Electrical work and the Born equation*

The dissection of measured standard free energies of hydration for neutral *pairs*, $M^+ + X^-$, into separate terms for M^+ and X^- has been giving robust results (within 20 kJ mol^{-1}) since feasibility was demonstrated in a classic paper by Latimer, Pitzer and Slansky (1939). Key methods and results are shown in table 3. All of the treatments are inspired by the Born equation, but they differ in approach and detail. The approaches include elements of electrostatics, electrochemistry, physical chemistry, and physical–organic chemistry.

Table 3. ΔG^0 and ΔH^0 for H^+ (g, atm) $\rightarrow$ H^+ (aq, molal).

Date	Source	ΔG^0 (kJ mol^{-1})	ΔH^0 (kJ mol^{-1})
1920	Born, citing Fajans		$\Delta U - 1100$
1939	Latimer *et al.*, Born equation with adjusted radii	-1050 ± 10	$-1100 \pm 101{\cdot}5$
1962	Noyes, Born equation with dielectric saturation	-108_5	-1110
1963	Halliwall and Nyburg, dominant charge-quadrupole interaction		-1090 ± 10
1978	Conway, review of various methods	-1070 ± 20	-1100 ± 20
1985	Reiss and Heller, electrochemical (abs. potential of H_2/H^+ electrode)	-1080 ± 10	
1987	Marcus, physical organic ($Ph_4As^+ = Ph_4B^-$)		-1100 ± 10
1994	Marcus, review, average	-1060	-109_5
Standard deviation of these dissections		12	6

All available data for $\Delta G^0_{\mathrm{hyd}}$ for neutral pairs can be separated into ionic terms $\Delta G^0_{\mathrm{hyd}}$ ($J^\pm$) if a single absolute value for an ionic species can be deduced; that is, there is just one parameter. In table 3 this parameter is chosen to be $\Delta G^0_{\mathrm{hyd}}$ (H^+), an essential ingredient for basicity and hydronium–hydrate reactivity in the gas phase (Hierl *et al.* 1988, Koppel *et al.* 1994, Smith *et al.* 1980). Because of the concordance of the largely independent approaches and because, save for one parameter, the material is experimental, we think of the values of $\Delta G^0_{\mathrm{hyd}}$ ($J^\pm$) as essentially experimental values, with a determinate error that is probably within 20 kJ mol^{-1}. Of course, 20 kJ mol^{-1} is large on the scale of RT, but it is small compared to the magnitude of the values obtained for $\Delta G^0_{\mathrm{hyd}}$ ($J^\pm$). In the following we shall use the values listed in table 2, which are based on the Marcus review (1994); they differ little from the values reported by Latimer *et al.* (1939).

The difference in energy stored in the electric fields (E) associated with a solution phase (M) and a gas phase (g) system is given by

$$\Delta W_{\mathrm{elec}} = \frac{N_A \varepsilon_0}{2} \int [D_M(E)\, E_M^2 - D_g(E)\, E_g^2]\, \mathrm{d}V, \qquad (4a)$$

where ε_0 is the permittivity of free space, N_A is Avogadro's number, and D is the dimensionless dielectric constant or relative permittivity (Böttcher 1952). In the particular case of interest where the fields are associated with an ion having spherical symmetry and charge q_J, for which $E = q_J/[4\pi\varepsilon_0 D(E) r^2]$, equation (4*a*) becomes

$$\Delta W_{\mathrm{elec}} = \frac{q_J^2 N_A}{8\pi\varepsilon_0} \int \left[\frac{1}{D_M(r)} - \frac{1}{D_g(r)}\right] \frac{\mathrm{d}r}{r^2}. \qquad (4b)$$

In principle D is a function of the electric field and thus in the case of the spherical ion

D is also a function of r, the distance from the centre of the ion. Note also that by electrostatic definition, q_J is the free charge and $q_J/D(r)$ is the net charge. That is, $q_J/D(r)$ is the difference between the free charge and the screening charge (which will also have spherical symmetry) resulting from the polarization of the dielectric around the ion.

The application of equation (4*b*) to the determination of the electrical part of the hydration free energy of $J^{\pm}\cdot$NSG can be seen with the aid of figure 2. Because of dielectric saturation at distances close to r_1, $D_M(r)$ will not yet have reached its conventional low-field value, ($D_M = 78{\cdot}3$ for water). However if electrical saturation is nearly complete for $r \geqslant r_2$, then beyond NS $D_M \approx 78{\cdot}3$. Also, since we are assuming for now that the structures NSG and NSL are the same, when $r < r_2$, $D_g(r) = D_M(r)$, while $D_g(r) = 1$ for $r > r_2$. In this case equation (4*b*) becomes

$$\Delta W_{elec} = \frac{q_J^2 N_A}{8\pi\varepsilon_0}\left[\int_{r_1}^{r_2}\left(\frac{1}{D_M(r)} - \frac{1}{D_g(r)}\right)\frac{dr}{r^2} + \int_{r_2}^{\infty}\left(\frac{1}{D_M} - 1\right)\frac{dr}{r^2}\right] \qquad (5a)$$

$$= \Delta W_{elec,\,inner} + \frac{694{\cdot}5}{r_2}\left[1 - \frac{1}{D_M}\right] \qquad (5b)$$

where $\Delta W_{elec,\,inner}$ should be equal to zero when NSG = NSL. In equation (5*b*) r_2 is measured in Å. But before using this equation we have to show that electrical saturation is indeed nearly negligible when $r \geqslant r_2$.

The smallest r_2 in table 2 is 3·09 Å for $Li^+\cdot$NSG. The local dielectric constant in an electric field at a distance of 3·09 Å from the centre of a univalent ion in water is calculated conveniently by the method of Booth (1951), who introduced a Langevin factor for dielectric saturation into Oster and Kirkwood's model (1943) for the dielectric constant of water. Within that framework, Booth's calculation of $D(E)$ is a close approximation. The range of electrical saturation in water is shorter than originally predicted by Debye (1945). After minor adjustment of the dipole moment of the water molecule to fit $D = 78{\cdot}3$ in low electric fields at 298 K, $D(r)$ at a distance r from the ionic centre was calculated from Booth's $D(E)$ and the relation $r^2 D_M(r) = r^2\cdot D_M(E) = q_J/4\pi\varepsilon_0 E$. For the smallest r of interest, 3·09 Å, $D_M(r) = 68$. Accordingly, the factor $(1 - 1/D_M)$ in the Born equation varies between $(1 - 1/68) = 0{\cdot}985$, and $(1 - 1/78{\cdot}3) = 0{\cdot}987$. The error of neglecting this variation in Born integrals is less than 0·2%.

A different way of suggesting that the bulk dielectric constant, 78·3, is a plausible choice when $r > r_2$, is to interpret the dissection method first used by Latimer *et al.* in 1939 for ions $J^{\pm}$. If D_M was constant (= 78·3) for all radii up to the ionic radius and if ΔW_{elec} was the only contributor to the hydration free energy, then we would immediately have from equation (4*b*),

$$\Delta G^0_{hyd}\,(M^+ + X^-)/\mathrm{kJ\,mol^{-1}} = 694{\cdot}5(1/78{\cdot}3 - 1)(1/r_{1+} + 1/r_{1-}),\ \text{with } r \text{ in Å}. \qquad (6a)$$

Latimer *et al.* (1939) found that this gave poor agreement with the experimental data; when the r_{1+} and r_{1-} where chosen as the Pauling ionic crystal radii, the calculated values of ΔG^0_{hyd} were much too large. However, agreement was greatly improved when the above equation was replaced by

$$\Delta G^0_{hyd}\,(M^+ + X^-) = 694{\cdot}5(1/78{\cdot}3 - 1)[1/(r_{1+} + \delta_+) + 1/(r_{1-} + \delta_-)]. \qquad (6b)$$

In this modified equation, δ_+ was a constant parameter for all cations and δ_- was constant for all anions. They reported $\delta_+ \approx 0{\cdot}85$ Å and $\delta_- \approx 0{\cdot}1$ Å. $\Delta G^0_{hyd}\,(M^+)$ is then

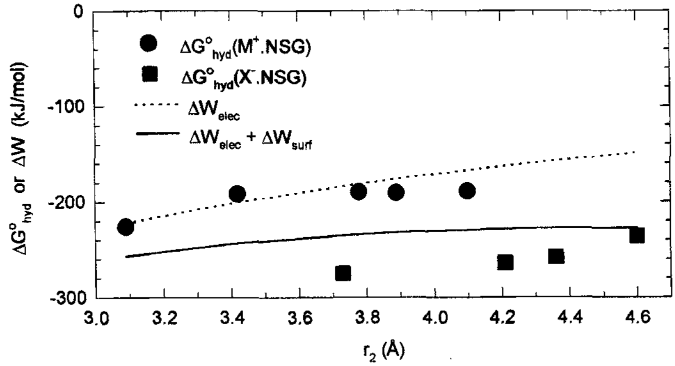

Figure 3. Hydration free energies of alkali (●) and halide ions (■) in comparison with the calculated free energies (electrostatic and surface) associated with the process, $J^{\pm}$ (g) → $J^{\pm}\cdot$NSG (g).

assigned the value $694{\cdot}5(1/78{\cdot}3-1)(1/(r_{1+}+\delta_{+}))$ and $\Delta G^{0}_{\text{hyd}}(\mathrm{X}^{-})$ the value $694{\cdot}5(1/78{\cdot}3-1)(1/(r_{1-}+\delta_{-})$. The δs are notably smaller than the thickness, 2·4 A, of the nearest-neighbour shell. In carrying out the integration demanded by (4*b*), it is clear that we only have to integrate over volume elements in which D_{M} differs from D_{g}.

3.2. *Surface work*

Consider a spherical droplet of radius r. Let r be small enough so that the thickness t of the surface 'phase' around the droplet is significant, and let $(r-t)$ be the radius of the interior liquid. Let f_{int} denote the fraction of $(4/3)\pi r^{3}$, the total volume, that belongs to the interior. Then $f_{\text{int}} = (1-t/r)^{3}$, and $f_{\text{surf}} = (1-f_{\text{int}})$. Let γ_{r} denote the surface tension, which is a function of r defined so that it applies when the surface area $A = 4\pi r^{2}$.

The surface work now consists of two parts. The fraction f_{surf} of the droplet has its free energy raised by $4\pi r^{2}\gamma_{r}$. The surface tension γ_{r} in turn compresses the interior, and the pressure increase, as predicted by the Kelvin equation, is $\delta P = 2\gamma_{r}/r$. The fraction f_{int} of the droplet therefore has its free energy raised by $V_{\text{int}}\,\delta P$, or $(4/3)\pi(r-t)^{3}\,(2\gamma_{r}/r)$. The total work *per mole* of droplets is given by

$$\Delta W_{\text{surf}} = N_{A} f_{\text{surf}}\cdot 4\pi r^{2}\gamma_{r} + N_{A} f_{\text{int}}\cdot(8\pi/3)\,\gamma_{r}(r-t)^{3}/r. \tag{7}$$

There are two limiting cases. (a) When $t \ll r$, f_{surf} is negligible and $\Delta W_{\text{surf}} = N_{A}(8\pi/3)\,\gamma_{r}\,r^{2}$. This is the Kelvin equation for macroscopic droplets. (b) When $t \approx r$, f_{int} is negligible, the droplet is so small that $f_{\text{surf}} \approx 1$ and $\Delta W_{\text{surf}} = 4\pi N_{A}\gamma_{r} r^{2}$. Cases (a) and (b) differ by only $\frac{2}{3}$. For the species $J^{\pm}\cdot$NSG that we are considering, case (b) applies. Also, as r decreases, it is likely that γ_{r} decreases somewhat below γ (Lewis and Randall 1961, Boruvka *et al.* 1985), the conventional surface tension for a flat surface. In the following figure 3, we have assumed that for the species $J^{\pm}\cdot$NSG, $\gamma_{r}/\gamma = \frac{2}{3}$.

4. Interpretation

Calculated values for ΔW_{elec} and ΔW_{surf}, using equations (5*b*) and (7; case (b)), together with the data for $\Delta G^{0}_{\text{hyd}}$ ($J^{\pm}\cdot$NSG) are displayed in figure 3. The plotted points and smooth relationships confirm that the hydration free energies are significant and are mostly accounted for by the Born term (dotted curve), with surface tension amounting to less than one-third of the total for the halide ions, and less than one-tenth for the alkali ions. The calculated values of $(\Delta W_{\text{elec}} + \Delta W_{\text{surf}})$ (solid curve) differ from $-\Delta G^0_{hyd}$ ($J^{\pm}\cdot$NSG) by an average of 35 kJ mol^{-1}, the calculated values being too negative for the cations and not negative enough for the anions.

A key assumption so far has been that NSG = NSL, which implies that $\Delta W_{elec, inner} = 0$. If this assumption were wrong and if the solid curve and points in figure 3 were error-free, $\Delta W_{elec, inner}$ would be measured by the distances of the points from the solid curve, and thus would be substantial. We do not believe that. While $\Delta W_{elec, inner}$ may not be zero, we would expect the structures NSG and NSL to be similar since they are both under the influence of the strong ion field.

Another intriguing aspect of figure 3 is that the values for ΔG^0_{hyd} ($J^{\pm}\cdot$NSG) clearly divide into two sets—one for anions and one for cations, with a separation of about 100 kJ mol^{-1}. A similar dispersion into two sets has long been known for ΔG^0_{hyd} ($J^{\pm}$) of the bare alkali and halide ions (Latimer *et al.* 1939), and one may wonder if such dispersion stems from a qualitative difference in the structure of nearest-neighbour shells. The evidence, like so much evidence in the field of hydration, is ambiguous. On the one hand, if there were a chemical origin, dispersion should show up also in a plot of ΔG^0_n for alkali and halide ions. A careful examination of all Kebarle's data (1970) for both ΔH^0_w and ΔG^0_w however offers no convincing evidence for such dispersion.

On the other hand, the surface work implied by the distances between the dotted curve for ΔW_{elec} and the points for ΔG^0_{hyd} in figure 3 may well supply a clue. Let us first ignore the solid curve because the estimate of ΔW_{surf} via equation (7; case (b)) is not reliably accurate for extremely small 'droplets' such as $M^+\cdot$NSG and $X^-\cdot$NSG. Surface tension is basically an intermolecular phenomenon whose existence requires the truncation of intermolecular interactions at the phase boundary (Millikan *et al.* 1937): when there are no intermolecular interactions, there is no surface tension. Suppose, for example, that the ion and the n adjacent water molecules form a molecular complex (rather than a cluster consisting of $n+1$ separate particles). The ion hydrate is then a single molecule, and whatever energy might be assigned to the surface of that molecule is part of the intrinsic energy of the molecule. There is no distinct, specifiable surface energy, and ΔW_{surf} accordingly is zero. Figure 3 shows that this description is a viable zeroth approximation for the alkali ions, especially for Li^+ and Na^+.

On the other hand, let the ion and the n adjacent water molecules exist as a cluster of $n+1$ separate particles. Now there are intermolecular interactions and ΔW_{surf} is non-zero. Following equation (7), the n water molecules are part of the surface layer, and the ion is in the interior; hence case (b) nearly applies. Assuming that $\gamma_r/\gamma = \frac{2}{3}$, we predict $\Delta W_{surf} = (8\pi/3)N_A \gamma r_2^2$, which yields the solid curve in figure 3. Making a reasonable allowance for the uncertainty in γ_r, figure 3 shows that the cluster hypothesis is a viable approximation for anions.

In conclusion, one can build a case that the pattern of the points in figure 3 can be rationalized if the alkali ions form molecular complexes with at least part of the 5–9 water molecules in the nearest-neighbour shells, while the halide ions and their surrounding water molecules remain separate molecules. This case is not definitive, but it is consistent with other evidence based on rather different properties. For instance, the ionic conductivities of Li^+ and Na^+ in solution are low, relative to the bare-ion size, in contrast to those of halide ions; for a recent example, see D'Aprano *et al.* (1995). The absorption mode in dielectric relaxation in aqueous salt solutions shows that some water molecules are irrotationally bound to alkali ions but not to halide ions (Haggis *et al.* 1952). There is thermodynamic and NMR evidence that alkali ions, but not halide ions, form complexes with organic solvent molecules in water–organic mixed solvents (Grunwald *et al.* 1960, Fratiello *et al.* 1968). And the hydration-shell water molecules of many di- or higher-valent cations reside next to the cations long enough to give discrete NMR spectra, while the authors know of no such evidence for di- or higher-valent anions (Gordon 1975).

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