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Assignment of Individual Ionic Contributions to Properties of Aqueous Ions

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Properties of aqueous ions are usually based upon the convention that hydrogen ion has zero values for those properties. If the properties of neutral species of the same size can be estimated, data for large singly charged monoatomic cations and anions can be extrapolated to determine absolute properties of aqueous hydrogen ion and hence to assign absolute contributions to other ions. A previous application to free energies of hydration has been modified to recognize possible bulk electrostatic potentials of water and to include surface free energy effects. The internal consistency of the data has been greatly improved by employing revised electron affinities of gaseous halogen atoms, and it is hoped that absolute free energies of ions of charge z can be assigned with an uncertainty no more than about $2z$ kcal./mole. Inclusion of surface effects has rather little influence on previous estimates of absolute ionic contributions to entropy and enthalpy. The peculiar nature of the hydrated proton is emphasized by the conclusion that it contributes only 1.5 ml./mole of the 23.3 ml./mole electrostriction associated with the self-ionization of water; the remaining electrostriction is associated with hydroxide ion. This conclusion indicates extreme differences in solvent structure around cations and anions and warns of dangers in treatments like the Taft attempt to separate polar and steric contributions to ionic reactions. The properties heat capacity, compressibility, and thermal expansibility are not accurately known at present and are related to second derivatives of the dielectric constant; better data will be needed to improve on the tentative assignments of ionic contributions to these properties.

Introduction

In dilute aqueous solutions, individual ionic species make additive contributions to thermodynamic properties. However, the requirement that any real solution be electrically neutral prevents any truly thermodynamic assignment of properties to individual ions. It is customary to adopt a convention assigning the properties of some ion (usually hydrogen ion) and thereby permitting experimental data to be used to assign values to corresponding properties of all other ions. Such values can be used in many self-consistent thermodynamic calculations, but they cannot be compared directly with conventional values for nonionic species.

A recent publication¹ on hydration of gaseous ions employed procedures that are here extended to treat properties of aqueous ions directly. The following development supercedes and slightly modifies the nomenclature of that paper, which failed to consider electrostatic potentials across interfaces. The importance of such potentials is discussed in Appendix B.

Let \bar{Y}^0_{con} be the standard state partial molal value of some extensive property Y for an ion calculated with the use of the convention that \bar{Y}^0_{con} is zero for aqueous hydrogen ion. Let \bar{Y}^0_{H} be the true standard state partial molal value of Y for aqueous hydrogen ion on the same scale as is valid for neutral chemical species. Then \bar{Y}^0 , the true standard state partial molal value of Y for an aqueous ion of absolute charge z electronic units, is

$$\bar{Y}^0 = \bar{Y}^0_{\text{con}} + z\bar{Y}^0_{\text{H}} \quad (\text{cation}) \quad (1)$$

$$\bar{Y}^0 = \bar{Y}^0_{\text{con}} - z\bar{Y}^0_{\text{H}} \quad (\text{anion}) \quad (2)$$

Although \bar{Y}^0_{con} is susceptible to direct experimental

measurement, \bar{Y}^0 and \bar{Y}^0_{H} are not determinable by any method employing only thermodynamic reasoning.

It is also possible to write

$$\bar{Y}^0 = \bar{Y}^0_{\text{neut}} + \bar{Y}^0_{\text{el}} \quad (3)$$

where \bar{Y}^0_{neut} is the partial molal value of Y^0 for a neutral species the same size as the ion and \bar{Y}^0_{el} is the electrostatic contribution associated with the effect of the charge in the solvent dielectric medium.

If this type of argument were applied to a macroscopic charged sphere of radius r , \bar{Y}^0_{el} would generally be inversely proportional to r , and we could write

$$\bar{Y}^0_{\text{theo}} = Q_Y/r \quad (4)$$

where \bar{Y}^0_{theo} is the computed value of \bar{Y}^0_{el} and Q_Y is calculable from the macroscopic dielectric properties of the medium.

For spheres of molecular dimensions, \bar{Y}^0_{el} can be expanded as a power series in $1/r$ that reduces to \bar{Y}^0_{theo} for large r . Values of the coefficients will depend only on the signs and magnitudes of ionic charges. For singly charged cations and anions, the nomenclature can be illustrated by the equations

$$\bar{Y}^0_{\text{neut}} - \bar{Y}^0_{\text{con}} = \bar{Y}^0_{\text{H}} - Q_Y/r - C_{2Y}/r^2 - C_{3Y}/r^3 - \dots = \bar{Y}^0_{\text{H}} - \bar{Y}^0_{\text{el}} \quad (z = +1) \quad (5)$$

$$\bar{Y}^0_{\text{con}} - \bar{Y}^0_{\text{neut}} = \bar{Y}^0_{\text{H}} + Q_Y/r + A_{2Y}/r^2 + A_{3Y}/r^3 + \dots = \bar{Y}^0_{\text{H}} + \bar{Y}^0_{\text{el}} \quad (z = -1) \quad (6)$$

Plots of the left sides of these equations against $1/r$ for singly charged ions with the same electronic structure should give two curves diverging from a common intercept with calculable initial slopes that are equal in magnitude but opposite in sign. If the expansions consider no terms beyond those in $1/r^2$, a three-parameter least-squares treatment can be used to evaluate \bar{Y}^0_{H} , C_{2Y} , and A_{2Y} .

(1) R. M. Noyes, *J. Am. Chem. Soc.*, **84**, 513 (1962).

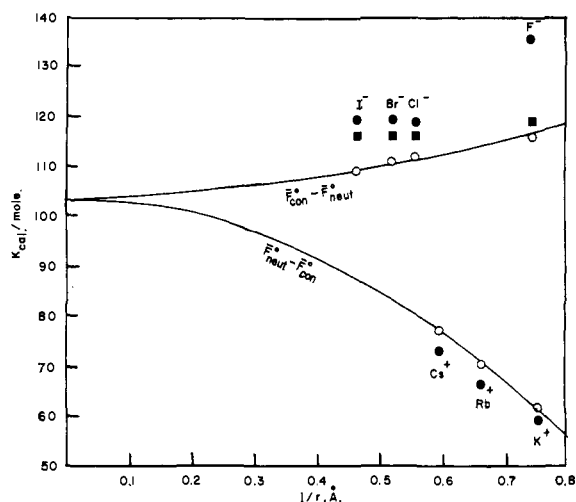


Fig. 1.—Application of eq. 5 and 6 to free energies. Filled designations use $\Delta F^0_{\text{neut}} = 1.325$ kcal./mole as in reference 1; circles are based on anion data from the Bureau of Standards,⁴ and squares are based on the revised electron affinities of Berry and Reimann.³ Open circles use eq. 10 with $J_F = 1.58$ kcal./Å.² mole. Curves use parameters associated with eq. 11.

The ionic contributions to the extensive properties free energy, entropy, enthalpy, volume, heat capacity, compressibility, and thermal expansibility can be related to the dielectric constant of the medium and to its first and second derivatives with respect to temperature and pressure. The present paper considers the extent to which available data permit individual ionic contributions to be assigned to these properties for aqueous ions at 25°. Although the first three properties were discussed previously,¹ a brief reconsideration is justified by the recent careful study of the dielectric properties of water by Owen, Miller, Milner, and Cogan² and by the improved determination of the electron affinities of gaseous halogen atoms by Berry and Reimann.³

The above discussion probably defines the various terms sufficiently clearly for most persons who will use these concepts. However, past work in this field has suffered because quantities called single ionic properties were not always clearly defined. It is hoped that the development in Appendix A will remove any ambiguity as to the intended meanings of the symbols in the above equations.

Ionic Free Energies

The electrostatic contribution to the partial molal free energy of an aqueous ion is given by

$$\bar{F}^0_{\text{el}} = z^2 e^2 / 2r \epsilon_{\text{eff}} \quad (7)$$

Owen, *et al.*,² quote $\epsilon = 78.358$ for water at 25°. Then

$$\bar{F}^0_{\text{theo}} = Q_F / r = 2.12z^2 / r \text{ kcal. } \text{Å.} / \text{mole} \quad (8)$$

Figure 1 illustrates a free energy plot of eq. 5 and 6. The filled circles are based on data from reference 4; they are computed with the zero energy assumption¹ that

$$\Delta \bar{F}^0_{\text{neut}} = 1.325 \text{ kcal./mole} \quad (9)$$

for transfer of a neutral species from gas at 1 atmosphere to 1 M solution. The best fit to these points indicates that $\Delta \bar{F}^0_{\text{Hf}}$ is 103.32 kcal./mole where $\Delta \bar{F}^0_{\text{Hf}}$ is the standard free energy of formation of aqueous hydrogen ion by process γ of Appendix A. If the standard

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

(3) R. S. Berry and C. W. Reimann, *J. Chem. Phys.*, **38**, 1540 (1963).

(4) "Selected Values of Chemical Thermodynamic Properties," Circular of the National Bureau of Standards No. 500, U. S. Government Printing Office, Washington, D. C., 1952.

free energy of elementary hydrogen is assumed to be zero, $\Delta \bar{F}^0_{\text{Hf}}$ is numerically equal to \bar{F}^0_{H} defined in the same way as the other thermodynamic properties of this paper. The distinction is introduced to avoid potential inconsistencies discussed elsewhere.⁵

The quantity called ΔF^0_{H} in reference 1 and defined by a different process from γ was really $\Delta \bar{F}^0_{\text{Hf}}$; the previous treatment failed to recognize possible interfacial potentials.

The correct numerical value for $\Delta \bar{F}^0_{\text{Hf}}$ differs by $5/2 RT$ from the value quoted for ΔF^0_{H} in reference 1 because it was only subsequently⁶ realized that tabulated⁴ enthalpies of gaseous ions include a term for the electrons associated with their formation.

Berry and Reimann³ have recently redetermined the electron affinities of gaseous halogen atoms. The filled squares for anions in Fig. 1 use their values and also use eq. 9 for ΔF^0_{neut} . The best fit gives $\Delta \bar{F}^0_{\text{Hf}} = 110.38$ kcal./mole with about the same standard deviation for individual points as with the filled circles. This value cannot be correct. It leads to values of ϵ_{eff} that are greater for multiply charged cations than for singly charged cations of the same size. No model for dielectric saturation could lead to such a conclusion.

For reasons that will become more apparent below, the data were also fitted with the relation

$$\Delta F^0_{\text{neut}} = J_F r^2 + 1.325 \text{ kcal./mole} \quad (10)$$

where J_F is an empirical constant selected to give the best fit to the data. This term effectively assigns to a neutral species a surface free energy proportional to the area of that species. The best fit was obtained for $J_F = 1.58$ kcal./Å.² mole and gave

$$\Delta \bar{F}^0_{\text{Hf}} = 103.81 \text{ kcal./mole} \quad (11)$$

with C_{2F} and A_{2F} values of 71.12 and 19.79 kcal. Å.²/mole, respectively. The fit from this treatment is shown with the open circles in Fig. 1, and the curves are drawn with these parameters. The maximum deviation of any of the seven points is 0.26 kcal./mole, and the standard deviation is 0.25 kcal./mole computed for three degrees of freedom.

The conclusions from this model were used to calculate ϵ_{eff} , the effective dielectric constant, for a number of ions. The results are presented in Table I, and their significance is discussed later.

TABLE I
REVISED FREE ENERGY AND ENTROPY DATA

Ion	r , Å.	\bar{F}^0_{el} , kcal./mole	ϵ_{eff}	\bar{S}^0_{el} , cal./mole deg.	\bar{S}^0_{theo} , cal./mole deg.	$10^4 \frac{\partial \ln \epsilon_{\text{eff}}}{\partial T}$, P.
Li ⁺	0.60	154.53	1.791	-23.7	1.46	-1.53
Na ⁺	0.95	75.51	2.315	-17.1	1.67	-2.26
K ⁺	1.33	41.96	2.975	-9.8	1.34	-2.34
Rb ⁺	1.48	33.73	3.327	-7.6	1.16	-2.25
Cs ⁺	1.69	26.43	3.719	-7.8	1.36	-2.95
Ag ⁺	1.26	15.30	8.615	-19.44	2.52	-12.71
Be ²⁺	0.31	1560.5	1.373	-84	0.67	-0.54
Mg ²⁺	.65	567.7	1.800	-60.3	1.01	-1.06
Ca ²⁺	.99	290.63	2.308	-47.6	1.21	-1.64
Sr ²⁺	1.13	246.9	2.380	-46.6	1.35	-1.89
Ba ²⁺	1.35	176.0	2.795	-36	1.25	-2.05
Ra ²⁺	1.40	166	2.857	-28	1.01	-1.69
Cd ²⁺	0.97	254.98	2.685	-52.0	1.30	-2.04
Al ³⁺	.50	1888.7	1.582	-108.2	0.62	-0.57
Sc ³⁺	.81	906.4	2.035	-91	.84	-1.10
Y ³⁺	.93	747.6	2.149	-86	.91	-1.05
La ³⁺	1.15	519.8	2.499	-84	1.10	-1.62
F ⁻	1.36	12.18	10.02	-32.3	4.52	-26.5
Cl ⁻	1.81	7.38	12.42	-20.78	3.87	-28.2
Br ⁻	1.95	6.41	13.28	-17.87	3.58	-27.9
I ⁻	2.16	5.03	15.28	-13.65	3.03	-27.1
S ²⁻	1.84	47.16	7.653	-27.3	1.29	-5.79
Macroscopic		$2.12z^2/r$	78.358	$-9.720z^2/r$	1.000	-45.88

(5) R. M. Noyes, *J. Chem. Educ.*, **40**, 2 (1963).

(6) R. M. Noyes, *ibid.*, **40**, 116 (1963).

Ionic Entropies

As has been shown elsewhere⁵ the convention of assigning zero entropy to aqueous hydrogen ion leads to thermodynamic inconsistencies when it is applied to some hypothetical processes. However, the convention is satisfactory for the purposes of the present paper, and entropies for individual ions obtained by this treatment will be consistent with the other thermodynamic properties obtained similarly.

The electrostatic contribution to the entropy of aqueous ions is given by

$$\bar{S}_{el}^0 = - \left(\frac{\partial \bar{F}_{el}^0}{\partial T} \right)_P = \frac{z^2 e^2}{2r \epsilon_{eff}} \left(\frac{\partial \ln \epsilon_{eff}}{\partial T} \right)_P \quad (12)$$

Owen, *et al.*,² quote $(\partial \ln \epsilon / \partial T)_P = -45.88 \times 10^{-4}$ deg.⁻¹ for water at 25°. Then

$$\bar{S}_{theo}^0 = Q_S/r = -9.720z^2/r \text{ cal. } \text{Å.}/\text{mole deg.} \quad (13)$$

where the coefficient does not differ significantly from the -9.649 used in reference 1.

Figure 2 illustrates an entropy plot of eq. 5 and 6. The filled circles use the equivalent of the zero energy assumption¹ that

$$\bar{S}_{neut}^0 = \bar{S}_{ig}^0 \quad (14)$$

where \bar{S}_{ig}^0 is the entropy calculated by standard procedures for ions in a standard state of ideal gas at 1 mole per liter.

As was discussed previously,¹ the plots with filled circles do not extrapolate well to a common intercept. The cation data were used alone to estimate \bar{S}_H^0 as -3.3 cal./mole deg.

If neutral species exert effects proportional to surface area, we can also write

$$\bar{S}_{neut}^0 = \bar{S}_{ig}^0 + J_S r^2 \quad (15)$$

where J_S is an empirical constant. The best fit was obtained for $J_S = 1.48$ cal./Å.² mole deg. and gave

$$\bar{S}_H^0 = -1.17 \text{ cal./mole deg.} \quad (16)$$

with C_{2S} and A_{2S} values of -3.99 and -47.25 cal. Å.²/mole deg., respectively. The fit from this treatment is shown with the open circles in Fig. 2, and the curves are drawn with these parameters. The maximum deviation of any point is 1.0 cal./mole deg., and the standard deviation is 1.1 cal./mole deg. for three degrees of freedom. The data for a number of ions are presented in Table I and combined with ϵ_{eff} values in that table to obtain $(\partial \ln \epsilon_{eff} / \partial T)_P$.

An alternative method for estimation of \bar{S}_H^0 could use data for large anions of equal size but different charge type. If ions are large enough that dielectric saturation effects are essentially absent or constant for different electronic charges, eq. 2 and 3 can be rearranged to give

$$\bar{Y}_{con}^0 = \bar{Y}_{neut}^0 + z\bar{Y}_H + z^2 U_Y \quad (17)$$

where U_Y is related to effective dielectric properties.

The ions ClO_4^- , SO_4^{2-} , and PO_4^{3-} have \bar{S}_{con}^0 values of 43.5, 4.1, and -52 cal./mole deg., respectively. Masses, radii, and vibrational contributions to entropy are sufficiently similar to attempt to estimate \bar{S}_H^0 by application to eq. 17 and solution of three simultaneous equations. The result of -14.4 cal./mole deg. is clearly inconsistent with the extrapolations from monatomic singly charged species. The data can be made consistent if U_S becomes more negative with increasing ionic charge.

Ionic Enthalpies

Equations 8 and 13 can be combined to give

$$\bar{H}_{theo}^0 = Q_H/r = -0.80z^2/r \text{ kcal. } \text{Å.}/\text{mole} \quad (18)$$

Since enthalpy data are easily calculable from those for free energies and entropies, no plot is presented. The treatments used for the open circle points in Fig. 1

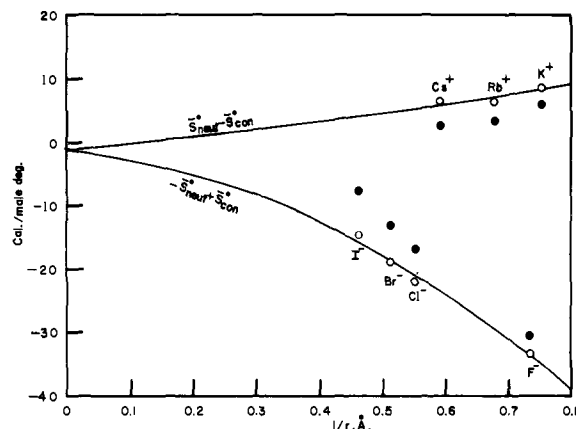


Fig. 2.—Application of eq. 5 and 6 to entropies. Filled circles use $\bar{S}_{neut}^0 = \bar{S}_{ig}^0$, and open circles use eq. 15 with $J_S = 1.48$ cal./Å.² mole deg. Curves use parameters associated with eq. 16.

and 2 lead to a best fit for $J_H = 2.02$ kcal./Å.² mole and give

$$\Delta \bar{H}_{Hf}^0 = 98.83 \text{ kcal./mole} \quad (19)$$

Values of C_{2H} and of A_{2H} are 70.01 and 5.67 kcal. Å.²/mole, respectively.

The fit given by these parameters is astoundingly good and obviously somewhat fortuitous. Except for one deviation of 0.20 kcal./mole, no other deviation is more than 0.08 kcal./mole, and the standard deviation for three degrees of freedom is 0.13 kcal./mole.^{6a}

Enthalpy data are not as easily related to effective dielectric properties of solvent as are data for the other properties, and they add no additional principles of importance.

Ionic Volumes

Table II contains values of \bar{V}_{con}^0 for a number of monatomic aqueous ions at 25°. The values for the alkali and halide ions were computed from the results tabulated by Harned and Owen⁷; the other values are from the review by Owen and Brinkley.⁸ The radii assigned the ions are those quoted by Pauling.⁹

The electrostatic contribution to the partial molal volume is given by

$$\bar{V}_{el}^0 = \left(\frac{\partial \bar{F}_{el}^0}{\partial P} \right)_T = - \frac{z^2 e^2}{2r \epsilon_{eff}} \left(\frac{\partial \ln \epsilon_{eff}}{\partial P} \right)_T \quad (20)$$

At 25°, Owen, *et al.*,² quote $(\partial \ln \epsilon / \partial P)_T = 47.10 \times 10^{-6}$ bar⁻¹. Then the theoretical contribution computed from the macroscopic dielectric properties is

$$\bar{V}_{theo}^0 = Q_V/r = -4.175z^2/r \text{ ml. } \text{Å.}/\text{mole} \quad (21)$$

Figure 3 illustrates a volume plot of eq. 5 and 6. The filled circles use the obvious equation

$$\bar{V}_{neut}^0 = (4\pi/3)Nr^3 = 2.523r^3 \text{ ml./Å.}^3 \text{ mole} \quad (22)$$

where N is the Avogadro number. The two curves obviously fail to extrapolate to a common intercept, although the slopes are of the sign and approximate magnitude anticipated from eq. 21.

(6a) NOTE ADDED IN PROOF.—C. E. Vanderzee and J. D. Nutter, [*J. Phys. Chem.*, **67**, 2521 (1963)] have just raised the enthalpy of formation of aqueous chloride ion by 0.10 kcal./mole. This change cuts in half the deviation of this ion from the computed curve, and a recalculation with the new value would lead to slightly revised parameters fitting the experimental points even more closely than the excellent fit reported here!

(7) H. S. Harned and B. B. Owen, "The Physical Chemistry of Electrolytic Solutions," Third Ed., Reinhold Publishing Corp., New York, N. Y., 1958, p. 361.

(8) B. B. Owen and S. R. Brinkley, Jr., *Chem. Rev.*, **29**, 461 (1941).

(9) L. Pauling, "The Nature of the Chemical Bond and the Structure of Molecules and Crystals," 3rd. Ed., Cornell University Press, Ithaca, N. Y., 1960, p. 514.

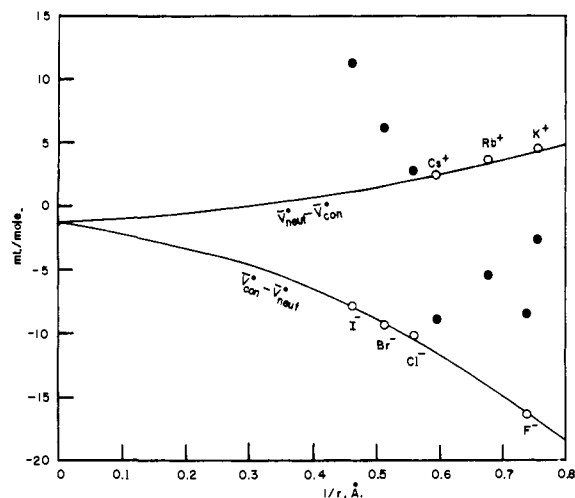


Fig. 3.—Application of eq. 5 and 6 to volumes. Filled circles use eq. 22 for \bar{V}_{neut}^0 , and open circles use eq. 23 with $J_V = 4.09$ ml./ \AA^2 mole. Curves use parameters associated with eq. 24.

As with the previous properties, the data can be fitted empirically to the desired model by adding a term proportional to surface area. Then

$$\bar{V}_{\text{neut}}^0 = J_V r^2 + 2.523 r^3 \text{ ml./}\text{\AA}^3 \text{ mole} \quad (23)$$

The best fit was obtained for $J_V = 4.09$ ml./ \AA^2 mole and gave

$$\bar{V}_{\text{H}}^0 = -1.49 \text{ ml./mole} \quad (24)$$

with C_{2V} and A_{2V} values of -4.75 and -21.30 ml./ \AA^2 /mole, respectively. The excellent fit from this treatment is shown with the open circles and curves in Fig. 3. The maximum deviation of any point is 0.13 ml./mole, and the standard deviation is 0.09 ml./mole for three degrees of freedom. The model clearly fits the data to within the experimental uncertainties of the individual points.

TABLE II
PARTIAL MOLAL VOLUMES AT 25°

Ion	r , Å	\bar{V}_{con}^0 , ml./ mole	\bar{V}^0 , ml./ mole	\bar{V}_{el}^0 , ml./mole	$\frac{\bar{V}_{\text{el}}^0}{\bar{V}_{\text{theo}}^0}$	10^6 ($\partial \ln \epsilon_{\text{eff}} / \partial P$) _T , bar ⁻¹
H ⁺	...	0.000	-1.49	(-1.49)
Li ⁺	0.60	-0.94	-2.43	-4.44	0.64	0.69
Na ⁺	0.95	-1.46	-2.95	-8.80	2.00	2.79
K ⁺	1.33	8.78	7.29	-5.89	1.88	3.35
Rb ⁺	1.48	13.77	12.28	-4.86	1.72	3.45
Cs ⁺	1.69	21.17	19.68	-4.18	1.69	3.78
Ag ⁺	1.26	-1.0	-2.5	-14.0	4.23	21.9
Mg ²⁺	0.65	-20.9	-23.9	-26.3	1.02	1.11
Ca ²⁺	0.99	-17.7	-20.7	-27.1	1.61	2.23
Sr ²⁺	1.13	-18.2	-21.2	-30.0	2.03	2.90
Ba ²⁺	1.35	-12.3	-15.3	-28.9	2.33	3.92
Cd ²⁺	0.97	-13	-16	-22	1.28	2.06
La ³⁺	1.15	-38.3	-42.8	-52.0	1.60	2.40
F ⁻	1.36	-2.14	-0.65	-14.57	4.75	28.6
Cl ⁻	1.81	18.07	19.56	-8.80	3.81	28.4
Br ⁻	1.95	25.01	26.50	-7.76	3.63	29.0
I ⁻	2.16	36.57	38.06	-6.42	3.33	30.6
Macroscopic	$-4.175z^2/r$	1.000	47.10

Equation 24 can be combined with eq. 1 and 2 to estimate absolute partial molal volumes of ions. They are presented in Table II along with values of \bar{V}_{el}^0 calculated from eq. 3 and 23. The values of $\bar{V}_{\text{el}}^0 / \bar{V}_{\text{theo}}^0$ are based on eq. 21 and compare the observed electrostrictions with those predicted from macroscopic dielectric properties. The final column contains ($\partial \ln \epsilon_{\text{eff}} / \partial P$)_T values from eq. 20 with the use of ϵ_{eff} values from Table I. The last line presents predictions from macroscopic dielectric properties.

As is discussed below, these conclusions require remarkably different electrostrictions about the H₃O⁺

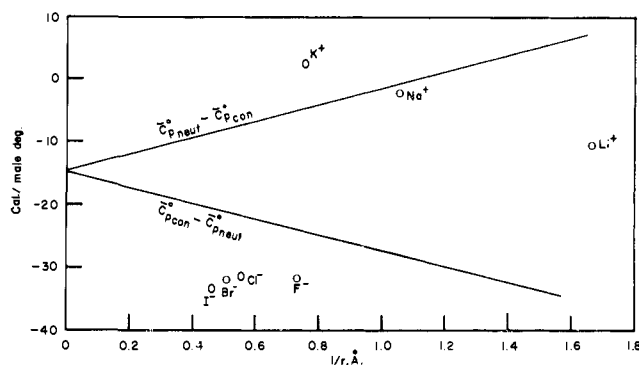


Fig. 4.—Application of eq. 5 and 6 to heat capacities. Points are computed for $\bar{C}_{\text{pneut}}^0 = 3R/2$. Lines fit predictions of theoretical eq. 26 assuming equal electrostatic contributions for K⁺ and F⁻.

and OH⁻ ions produced in the self-ionization of water. Equal contribution from these ions would require the curves in Fig. 3 to extrapolate to approximately -12 ml./mole. The effects of two alternative models for \bar{V}_{neut}^0 were examined. The use of $\bar{V}_{\text{neut}}^0 = 2.523(r + \Delta)^3$ ml./ \AA^3 mole gave the best fit for $\Delta = 0.45$ Å, and $\bar{V}_{\text{H}}^0 = -1.26$ ml./mole; the fit was almost but not quite as good as for eq. 23. The use of $\bar{V}_{\text{neut}}^0 = L_V r^3$ gave the best fit for $L_V = 4.38$ ml./ \AA^3 mole and $\bar{V}_{\text{H}}^0 = -2.09$ ml./mole; the fit was distinctly poorer than for the other models. Since all three functions for \bar{V}_{neut}^0 give values of \bar{V}_{H}^0 within 1 ml./mole of each other, it is very doubtful that any other plausible one parameter function would give a good fit extrapolating to \bar{V}_{H}^0 10 ml./mole more negative.

Use of the "experimental" radii proposed by Blandamer and Symons¹⁰ would raise all of the filled circles in Fig. 3 and presumably make any extrapolated value of \bar{V}_{H}^0 more positive. No attempt was made to get a quantitative fit.

The method of eq. 17 could not be applied to oxyanion data because \bar{V}_{con}^0 does not appear to have been measured for PO₄³⁻. Data for ClO₄⁻ and SO₄²⁻ suggested the same type of discrepancy as was observed with entropy values and indicated that dielectric saturation effects cause electrostriction to increase more rapidly than with the square of the charge on ions of the same size.

Ionic Heat Capacities

Table III contains values of \bar{C}_{pcon}^0 for a number of monatomic aqueous ions at 25°. The values are taken in part from Harned and Owen¹¹ and in part from the Bureau of Standards tables.⁴ Just as is the case with entropies, the convention of assigning zero heat capacity to aqueous hydrogen ion can lead to thermodynamic inconsistencies.⁵ However, no difficulty is associated with using this convention for the present purpose.

The electrostatic contribution to the heat capacity is given by

$$\begin{aligned} \bar{C}_{\text{pel}}^0 &= T \left(\frac{\partial \bar{S}_{\text{el}}^0}{\partial T} \right)_P = -T \left(\frac{\partial^2 \bar{F}_{\text{el}}^0}{\partial T^2} \right)_P \\ &= \frac{z^2 e^2 T}{2r \epsilon_{\text{eff}}} \left[\left(\frac{\partial^2 \ln \epsilon_{\text{eff}}}{\partial T^2} \right)_P - \left(\frac{\partial \ln \epsilon_{\text{eff}}}{\partial T} \right)_P^2 \right] \quad (25) \end{aligned}$$

At 25°, Owen, *et al.*,² quote $(\partial^2 \ln \epsilon / \partial T^2)_P = 54 \times 10^{-3}$ deg.⁻². Then the theoretical contribution computed from the macroscopic dielectric properties is

$$\bar{C}_{\text{theo}}^0 = Q_{C_p} / r = -12.96z^2 / r \text{ cal. } \text{\AA} / \text{mole deg.} \quad (26)$$

(10) M. J. Blandamer and M. C. R. Symons, *J. Phys. Chem.*, **67**, 1304 (1963).

(11) Reference 7, p. 354.

For simple gaseous ions, \bar{C}_{pneut}^0 should be $3R/2$, and this value has been used in preparing Fig. 4. The plot shows complete failure of the simplified model in that the apparent slopes of the curves are opposite in sign to those predicted by macroscopic properties.

Since data are not available for the large cations Rb⁺ and Cs⁺, it has not seemed profitable to attempt a quantitative treatment involving surface tension effects. An empirical treatment would obviously have to invoke negative values of \bar{C}_{pneut}^0 .

A tentative evaluation of \bar{C}_{pH}^0 has been attempted by assigning the same \bar{C}_{pel}^0 to the ions K⁺ and F⁻ which are almost equal in size. This procedure was suggested by Kortüm and Bockris¹²; the approximation must be very crude in view of the large differences in the electrostatic contributions to other properties of these ions.

Application of this approximation gives

$$\bar{C}_{\text{pH}}^0 = -14.5 \text{ cal./mole deg.} \quad (27)$$

The solid lines in Fig. 4 illustrate application of this value to eq. 5 and 6 combined with the predictions from macroscopic dielectric properties. Table III uses the above-indicated values of various quantities combined with effective dielectric properties from Table I.

TABLE III
PARTIAL MOLAL HEAT CAPACITIES AT 25°

Ion	r , Å.	\bar{C}_{pcon}^0 , cal./mole deg.	\bar{C}_{p}^0 , cal./mole deg.	\bar{C}_{pel}^0 , cal./mole deg.	\bar{C}_{ptheo}^0	$10^8(\partial^2 \ln \epsilon_{\text{eff}}/\partial T^2)_P$, deg. ⁻²
H ⁺	..	0.000	-14.5	-17.5
Li ⁺	0.60	13.57	-0.9	-3.9	0.18	-6
Na ⁺	0.95	5.4	-9.1	-12.1	0.89	-49
K ⁺	1.33	0.2	-14.3	-17.3	1.78	-133
Ag ⁺	1.26	9.0	-5.5	-8.5	0.83	-26
Ba ²⁺	1.35	-15.96	-30.5	-33.5	0.87	-59
F ⁻	1.36	-28.7	-14.2	-17.2	1.81	229
Cl ⁻	1.81	-29.20	-14.7	-17.7	2.46	-6
Br ⁻	1.95	-29.7	-15.2	-18.2	2.76	-182
I ⁻	2.16	-30.4	-15.9	-18.9	3.15	-523
Macroscopic	-12.96z ² /r	1.000	54

Ionic Compressibilities

Table IV contains values of \bar{K}_{con}^0 for a number of monatomic aqueous ions at 25°. The quantity \bar{K}_{con}^0 is defined by

$$\bar{K}_{\text{con}}^0 = -(\partial \bar{V}_{\text{con}}^0/\partial P)_T \quad (28)$$

and the data are taken from the review by Owen and Brinkley.⁸

The electrostatic contribution to the compressibility is obtained by application of eq. 20 to eq. 28 and becomes

$$\bar{K}_{\text{el}}^0 = \frac{z^2 e^2}{2r \epsilon_{\text{eff}}} \left[\left(\frac{\partial^2 \ln \epsilon_{\text{eff}}}{\partial P^2} \right)_T - \left(\frac{\partial \ln \epsilon_{\text{eff}}}{\partial P} \right)_T^2 \right] \quad (29)$$

At 25°, Owen, *et al.*,² quote $(\partial^2 \ln \epsilon/\partial P^2)_T = -71.53 \times 10^{-10} \text{ bar}^{-2}$. Then the theoretical contribution computed from the macroscopic dielectric properties is

$$\bar{K}_{\text{theo}}^0 = Q_K/r = -8.307 \times 10^{-4} z^2/r \text{ ml. Å./bar mole} \quad (30)$$

Figure 5 illustrates a compressibility plot of eq. 5 and 6. The filled circles use $\bar{K}_{\text{neut}}^0 = 0$. The open circles use

$$\bar{K}_{\text{neut}}^0 = L_K r^3 \quad (31)$$

where L_K is an empirical constant. The best fit was obtained for $L_K = 2.50 \times 10^{-4} \text{ ml./Å.}^3 \text{ bar mole}$ and gave

$$\bar{K}_{\text{H}}^0 = 30.6 \times 10^{-4} \text{ ml./bar mole} \quad (32)$$

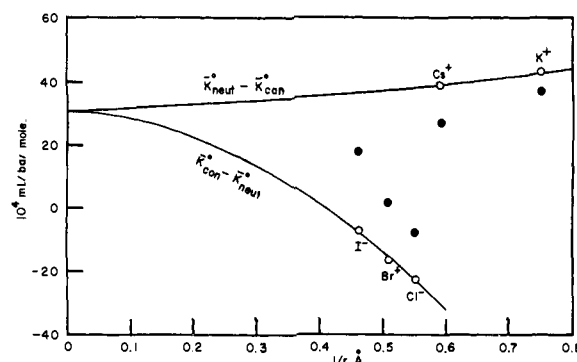


Fig. 5.—Application of eq. 5 and 6 to compressibilities. Filled circles use $\bar{K}_{\text{neut}}^0 = 0$, and open circles use eq. 31 with $L_K = 2.50 \times 10^{-4} \text{ ml./Å.}^3 \text{ bar mole}$. The curves use parameters associated with eq. 32.

with C_{2K} and A_{2K} values of -10.5×10^{-4} and $-160.9 \times 10^{-4} \text{ ml. Å.}^2/\text{bar mole}$, respectively. Since five points are being fitted with four parameters, the small deviations are not necessarily indicative of a proper choice of model.

The only other model examined used $\bar{K}_{\text{neut}}^0 = Dr^6/n$, suggested by a compressibility proportional both to reciprocal electron density in an ion and to its volume. This model gave a poorer fit than did eq. 31 but led to $\bar{K}_{\text{H}}^0 = 30.2 \times 10^{-4} \text{ ml./bar mole}$. The value of this quantity is obviously very insensitive to the model function chosen for \bar{K}_{neut}^0 .

The entries in Table IV are computed similarly to those for other properties.

TABLE IV
PARTIAL MOLAL COMPRESSIBILITIES AT 25°

Ion	r , Å.	$10^4 \bar{K}_{\text{con}}^0$, ml./bar mole	$10^4 \bar{K}_{\text{el}}^0$, ml./bar mole	\bar{K}_{theo}^0	$(\partial^2 \ln \epsilon_{\text{eff}}/\partial P^2)_T$, bar ⁻²
H ⁺	..	0.00	31
Li ⁺	0.60	-34	-3	-4	-0.6
Na ⁺	0.95	-42	-11	-14	-4.1
K ⁺	1.33	-37	-6	-12	-7.0
Cs ⁺	1.69	-27	4	-9	-7.4
Be ²⁺	0.31	-23	38	38	-0.4
Mg ²⁺	.65	-83	-22	-22	-0.8
Ca ²⁺	.99	-71	-10	-12	-1.1
Ba ²⁺	1.35	-99	-38	-44	-5.9
Cu ²⁺	..	-62	-1
Zn ²⁺	0.74	-70	-9	-10	0.2
Cd ²⁺	0.97	-57	4	2	0.3
Ce ³⁺	1.11	-152	-60	-64	..
Cl ⁻	1.81	-8	-39	-53	11.6
Br ⁻	1.95	2	-29	-47	11.1
I ⁻	2.16	18	-13	-38	9.8
Macroscopic	-8.307z ² /r	1.000	-71.53

Ionic Thermal Expansibilities

The partial molal expansibility, \bar{E}_{con}^0 , is defined

$$\bar{E}_{\text{con}}^0 = (\partial \bar{V}_{\text{con}}^0/\partial T)_P \quad (33)$$

Quoted values for this quantity show surprising variations. The first column of figures in Table V contains values for a few monatomic ions based on entries by Harned and Owen¹³ and supplemented by measurements by Gibson and Kincaid¹⁴ and by Gibson and Loeffler.¹⁵ The next column contains values calculated from tabulated and graphical information by Fajans and Johnson.¹⁶ The deviations suggested that \bar{E}_{con}^0 is scarcely known to the first significant figure.

The electrostatic contribution to the expansibility is obtained by application of eq. 20 to eq. 33 and becomes

(13) Reference 7, p. 373.

(14) R. E. Gibson and J. F. Kincaid, *J. Am. Chem. Soc.*, **59**, 25 (1937).

(15) R. E. Gibson and O. H. Loeffler, *ibid.*, **63**, 443 (1941).

(16) K. Fajans and O. Johnson, *ibid.*, **64**, 668 (1942).

(12) G. Kortüm and J. O'M. Bockris, "Textbook of Electrochemistry," Elsevier Publishing Co., New York, N. Y., 1951, p. 123.

$$\bar{E}_{e1}^0 = -\frac{z^2 e^2}{2r\epsilon_{eff}} \left[\frac{\partial^2 \ln \epsilon_{eff}}{\partial T \partial P} - \left(\frac{\partial \ln \epsilon_{eff}}{\partial T} \right)_P \left(\frac{\partial \ln \epsilon_{eff}}{\partial P} \right)_T \right] \quad (34)$$

At 25°, Owen, *et al.*,² quote $\partial^2 \ln \epsilon / \partial T \partial P = 9.27 \times 10^{-8}$ bar⁻¹ deg.⁻¹. Then the theoretical contribution computed from the macroscopic dielectric properties is

$$\bar{E}_{theo}^0 = Q_E/r = -0.02742z^2/r \text{ ml. } \text{Å.}/\text{deg. mole} \quad (35)$$

Available data provide little basis for estimating \bar{E}_{neut}^0 , although Gucker and Moser¹⁷ found the partial molal expansibility of urea in water to be 0.0645 ml./deg. mole and hence comparable to the values observed for electrolytes. The procedure employed was to assume

$$\bar{E}_{neut}^0 = L_E r^3 \quad (36)$$

similar to eq. 31.

The data from references 13–15 include too few ions to use the procedure employed for other properties. It was assumed that electrostatic contributions were given by eq. 35, and the best fit of the data was obtained for $L_E = 0.013 \text{ ml./}\text{Å.}^3 \text{ deg. mole}$ and $\bar{E}_H^0 = -0.038 \text{ ml./deg. mole}$. The fit is illustrated by the filled circles and dashed lines in Fig. 6.

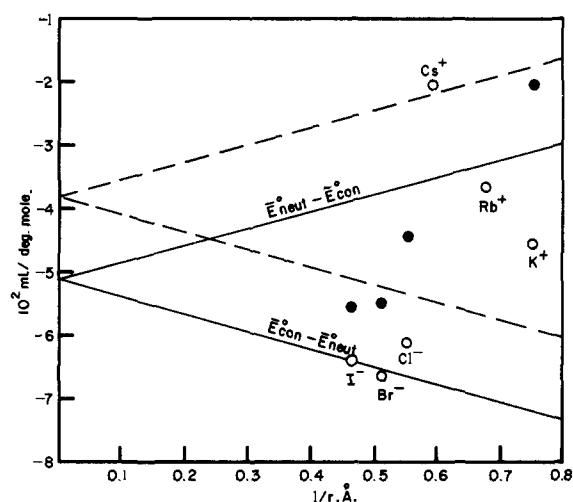


Fig. 6.—Application of eq. 5 and 6 to thermal expansibilities. Dashed lines and filled circles illustrate best fit of eq. 35 and 36 to data from references 13–15. Solid lines and open circles illustrate best fit to data from reference 16.

The data from reference 16 include more ions, but the points do not fit well to curves of the types shown for other properties. When the treatment of the preceding paragraph was used, the best fit was obtained for $L_E = 0.010 \text{ ml./}\text{Å.}^3 \text{ deg. mole}$ and gave

$$\bar{E}_H^0 = -0.051 \text{ ml./deg. mole} \quad (37)$$

The fit is illustrated by the open circles and solid lines in Fig. 6.

In view of the deviations of values for individual ions, the two sets of data give remarkably similar values for L_E and \bar{E}_H^0 . Since the data from reference 16 involve more ions, these data were used to compute the remaining entries in Table V. The calculations also involve values of ϵ_{eff} and its derivatives reported previously.

Discussion

General Considerations.—If neutral conducting spherical species could be dissolved in water and then charged by a hypothetical process, \bar{Y}_{e1}^0 is the change in value of the molar property Y associated with the charging process. If the spheres are of macroscopic dimensions, \bar{Y}_{e1}^0 can indubitably be calculated from the macroscopic dielectric properties of water. Moreover,

TABLE V
PARTIAL MOLAL EXPANSIBILITIES AT 25°

Ion	$r, \text{Å.}$	$10^3 \bar{E}_{con}^0$		$10^3 \bar{E}_{e1}^0$		$\frac{\bar{E}_{e1}^0}{\bar{E}_{theo}^0}$	$10^{10} \left(\frac{\partial^2 \ln \epsilon_{eff}}{\partial T \partial P} \right)$
		ml./mole deg. Ref. 13-15	ml./mole deg. Ref. 16	ml./mole deg. Ref. 13-15	ml./mole deg. Ref. 16		
H ⁺	...	0.00	0.00	-5.1
Li ⁺	0.60	-0.9	1	-4.1	-4.3	0.9	63
Na ⁺	0.95	5.9	10	4.9	4.0	-1.4	-134
K ⁺	1.33	5.1	7	1.9	-0.5	0.2	16
Rb ⁺	1.48	...	7	1.9	-1.4	0.8	97
Cs ⁺	1.69	...	7	1.9	-3.1	1.9	267
Mg ²⁺	0.65	...	4	-6.2	-6.5	0.4	27
Sr ²⁺	1.13	...	12	1.8	0.3	-0.03	-8
Ba ²⁺	1.35	6.4	18	7.8	5.3	-7.8	-85
Cl ⁻	1.81	3.4	0	5.1	-1.0	.7	-458
Br ⁻	1.95	4.2	1	6.1	-1.5	1.1	-232
I ⁻	2.16	7.6	4	9.1	-1.3	1.0	-227
Macroscopic	-2.742z ² /r	1.000	927	

the effects for a given low surface density of charge will be the same whether that charge is positive or negative.

If the spheres are of molecular dimensions, the surface charge densities are so great that neighboring solvent molecules undergo profound rearrangements that may be very different for charge densities of equal magnitude but opposite sign. The phenomenological approach used here ignores the details of these rearrangements and formally relates changes in Y to effective values of appropriate dielectric properties.

If such a procedure were restricted to *average* values for electrolytes containing equal concentrations of positive and negative charge, the procedure would be as unexceptionable as the measurement of a mean ionic activity coefficient. The additional assumption introduced here is that \bar{Y}_{e1}^0 for ions of a single charge type is a continuous monotonic function when extrapolated to macroscopic dimensions from the largest singly charged ions accessible to measurement.

The treatments of the properties free energy, entropy, and volume involve fitting seven independent observations with four empirical parameters. Such a procedure is acceptable only if the fit is exceptionally good and if the magnitudes of the parameters are reasonable. These problems are considered below.

Free Energies.—The three-parameter treatment of reference 1 was based on previously reported⁴ properties of gaseous anions. It led to a value of 103.32 kcal./mole for $\Delta \bar{F}_{HF}^0$ and gave rather peculiar behavior of computed effective dielectric constants.

Berry and Reimann³ have since obtained apparently definitive values for electron affinities of gaseous halogen atoms. Use of their data causes a dramatic improvement in fit. The standard deviation from the curves in Fig. 1 is only one-ninth the deviation for the best four-parameter fit to the former⁴ data. The deviations of individual points are now well within the range to be anticipated from uncertainties in conventional ionic free energies and crystallographic radii.

Although $\Delta \bar{F}_{HF}^0$ is only shifted to 103.81 kcal./mole, the modified equation for \bar{F}_{neut}^0 changes effective dielectric constants. Values of ϵ_{eff} in Table I are somewhat larger for singly charged cations than for multiply charged cations of the same size; hence there is a small increase in dielectric saturation when the ionic charge is increased from +1 to +2 but little additional effect when it is increased to +3. The ϵ_{eff} values for singly charged anions now increase with increasing ionic size as would be anticipated and contrary to values in reference 1. Finally, the values for the equally-sized ions Cl⁻ and S²⁻ now illustrate an increase in dielectric saturation with increasing charge, while the values in reference 1 could hardly have been explained by any model.

(17) F. T. Gucker and C. E. Moser, *J. Am. Chem. Soc.*, **61**, 1558 (1939).

Even singly charged cations obviously form a highly ordered primary hydration sphere and thereby virtually saturate the possible orientation polarization of the surrounding medium. Increasing cationic charge can cause little more than electronic polarization. Since the water molecule contains two protons that cannot both be directed toward an anion, changes in anionic charge density can have more effect on molecular orientation than is the case with cations, and the effective dielectric constant around an anion is considerably greater than around a cation.

The treatment requires that \bar{F}^0_{neut} contain a surface free energy of $1.58r^2$ kcal./Å.² mole. This purely empirical term corresponds to a surface free energy of 87 erg/cm.² in remarkably close agreement with the experimental surface tension of water against its vapor of 71.97 dyne/cm. (erg/cm.²). One could hardly expect the microscopic surface free energy around a dissolved atom to be more than superficially related to the macroscopic surface free energy against a gas. If \bar{F}^0_{neut} were computed with a J_F value based on the macroscopic surface tension, $\Delta\bar{F}^0_{\text{Hf}}$ would only be shifted to 104.98 kcal./mole.

In spite of the above consistency, a minor caveat is provided by solubility data for the elementary aerogens.¹⁸ Results presented in reference 1 show that solubility in water *increases* with increasing size of the dissolving atoms, whereas surface free energy effects should cause it to decrease. Other factors such as polarizability and specific water structure undoubtedly contribute to the solubility of neutral species. The reason for the discrepancy is not apparent, but if \bar{F}^0_{neut} decreases with increasing size of the dissolved species, any treatment of experimental data on aqueous ions will extrapolate very poorly to the known behavior of macroscopic charged spheres.

The results of this treatment are reasonably consistent with previous attempts to estimate the same quantity. Halliwell and Nyburg¹⁹ have recently reviewed the literature and have concluded that $\Delta\bar{H}^0$ is -260.7 ± 2.5 kcal./mole for the hydration of a gaseous proton. Since the enthalpy of formation of this species is 365.60 kcal./mole (when the enthalpy of the accompanying electron is not included⁶), their treatment gives 104.9 kcal./mole for $\Delta\bar{H}^0_{\text{Hf}}$ in contrast to the 98.8 kcal./mole of eq. 19. The internal consistency of the treatment used here gives reason to hope that $\Delta\bar{H}^0_{\text{Hf}}$ is known to within about 1 kcal./mole and that the uncertainty in $\Delta\bar{F}^0_{\text{Hf}}$ is not much more than 2 kcal./mole. An impressive number of independent evaluations lie within a range that does not exceed these estimated limits by more than a factor of three.

Entropies.—The four-parameter treatment of entropies does not come quite as close as the treatments for enthalpies and volumes do to fitting available data within estimated errors. Perhaps the tabulated conventional entropy of one or more of the aqueous ions is in error by about 1 cal./mole deg. The somewhat anomalous $S^0_{\text{el}}/S^0_{\text{theo}}$ value for Cs⁺ suggests this ion as a candidate for experimental verification of its conventional entropy.

The empirical parameter J_S of 1.48 cal./Å.² mole deg. corresponds to a surface entropy of 0.082 erg/cm.² deg. The temperature derivative of the macroscopic surface tension indicates a surface entropy of 0.156 erg/cm.² deg. for water at 25°. The agreement to within a factor of two is encouraging. If J_S were computed from the macroscopic surface behavior, the value of

S^0_{H} given by the method of this paper would be -6.7 cal./mole deg.

In this case also, entropies of solution of inert atoms become more *negative* with increasing size in contrast both to the necessities of the present treatment and to the macroscopic surface properties of water.

The treatment used here certainly indicates that S^0_{H} lies in the range 0 to -5 cal./mole deg.; this conclusion is consistent with the interpretation of thermocel measurements²⁰ based on a different procedure.

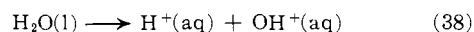
Treatment of Volumes.—The four-parameter treatment of volumes fits available data remarkably well. The empirical parameter J_V of 4.09 ml./Å.² mole indicates that external pressure increases the surface free energy of water by 0.00540 erg/cm.² bar.

If water could be compressed by an inert gas that was completely insoluble, these results indicate that the surface tension should be increased about 1 dyne/cm. by a pressure of 200 atm. Rice²¹ has pointed out that $(\partial\gamma/\partial P)_T$ should indeed be positive because the density of material in a surface is almost certainly less than that in bulk liquid, but that data in real systems will be complicated by adsorption of the compressing gas in the surface.

For volumes also, the available solubility data are contrary to the predictions of the present treatment. Thus Némethy and Scheraga²² point out that hydrocarbons dissolve with a *contraction* in the volume occupied by surrounding water molecules. An examination of the filled circles in Fig. 3 indicates that the data cannot extrapolate with any plausibility unless \bar{V}^0_{neut} is *larger* than the volume of the dissolved ion, and use of the radii proposed by Blandamer and Symons¹⁰ would make the discrepancy even worse.

The treatment of this paper seems consistently to require that \bar{V}^0_{neut} contains a surface term of the magnitude predicted from the macroscopic surface properties of water, while data on solubilities of inert neutral species are consistent with surface effects of opposite sign. It may be that solution of real neutral species involves effects in the structure of water that are reversed during the charging process when an ion is formed. This interpretation implies that \bar{V}^0_{neut} refers to a hypothetical state in which the neutral species dissolves without affecting the solvent except for the creation of new surface. For the moment, the comparison of theory and experiment must be admitted to contain some paradoxes.

Volumes of Specific Ions.—Undoubtedly the most interesting and unexpected conclusion of this paper is the value of -1.5 ml./mole for \bar{V}^0_{H} . Since \bar{V}^0_{con} is -5.3 ml./mole for OH⁻, and since the molar volume of water is 18.0 ml./mole, $\Delta V = -23.3$ ml./mole for the process



Since gaseous H₃O⁺ and OH⁻ ions must be very nearly equal in size, it has generally been assumed that they contributed approximately equally to the electrostriction associated with the self-ionization of water. The present analysis indicates that if isolated H₂O and OH⁻ species differ little in absolute volume, then 21.8 ml./mole of the observed electrostriction is associated with hydroxide ion and only 1.5 ml./mole with the hydrated proton.

If H₃O⁺ and OH⁻ contributed equally to electrostriction in water, the curves in Fig. 3 would have to extrapolate to about -12 ml./mole with the same limiting slopes shown in that figure. No possible set of

(18) R. M. Noyes, *J. Am. Chem. Soc.*, **85**, 2202 (1963).

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

(20) J. C. Goodrich, F. M. Goyan, E. E. Morse, R. G. Preston, and M. B. Young, *J. Am. Chem. Soc.*, **72**, 4411 (1950).

(21) O. K. Rice, *J. Chem. Phys.*, **15**, 333 (1947).

(22) G. Némethy and H. A. Scheraga, *ibid.*, **36**, 3401 (1962).

values for \bar{V}^0_{neut} could make the cation and anion curves extrapolate to -12 ml./mole as monotonic functions of $1/r$. For large spheres, \bar{V}^0_{el} becomes less negative as r increases; for singly charged ions with radii between 1.3 and 2.2 Å., \bar{V}^0_{el} also clearly becomes less negative as r increases. It seems implausible that there is an intermediate range of sizes such that for negatively charged spheres \bar{V}^0_{el} becomes greatly *more* negative as r increases; yet such a situation would have to exist if the data in Fig. 3 were to extrapolate to the neighborhood of -12 ml./mole.

Further support is provided by the comparison of Fig. 2 and 3. Changes of entropy and volume often behave similarly for series of reactions involving ions, and the two figures are almost superimposable if a volume ordinate of 1 ml./mole is equated to an entropy ordinate of about 2 cal./mole deg. The two figures agree that S^0_{el} and \bar{V}^0_{el} for the larger alkali ions are not much more dependent upon radius than would be predicted from macroscopic dielectric properties, while for the halide ions the dependence on radius is much greater. Figure 5 indicates that ionic compressibilities show the same qualitative behavior. The point of extrapolation for entropy in Fig. 2 agrees with a completely independent²⁰ method of estimating S^0_{H} . These facts all further support the conclusion that \bar{V}^0_{H} is about -1 rather than -10 ml./mole.

Of course the hydrated proton can best be described by the formula H_3O^+ or H_9O_4^+ . The species H_3O^+ can form hydrogen bonds to only three water molecules whose dipoles are oriented in the field of the ion. Probably only one other water molecule can be present as a nearest neighbor, and its dipole moment would cause it to orient with its protons away from rather than toward the remaining electron pair of the H_3O^+ . This rather open structure with only four water molecules around the H_3O^+ could explain the low electrostriction. Figure 3 suggests that an electrostriction of only 1.5 ml./mole would be associated with a cation of radius about 3 Å. or distinctly more than that of H_3O^+ , and the difference reflects a particularly open structure.

The 21.8 ml./mole electrostriction around OH^- is somewhat greater in absolute magnitude than Fig. 3 indicates for the isoelectronic F^- ion. However, the effect of OH^- on the surrounding solvent is not greatly different from that of a similar ion with symmetrical charge distribution.

These very different behaviors of cations and anions may make it necessary to reconsider some treatments that have assumed electrostrictions to be comparable for ions of equal charge density but opposite sign. Thus Taft²³ has noted that the transition states for acidic and alkaline hydrolysis of carboxylate esters are opposite in sign but differ structurally only by the presence or absence of two protons. He has then used relative rates of acidic and basic hydrolyses to assign polar and steric contributions to substituents near the active center in the reaction. If the hydration of positive and negative ions differs as much as the present paper suggests, Taft's treatment may not have separated steric effects as cleanly as was hoped.

A few other ions exhibit interesting behavior. Table II shows that \bar{V}^0_{el} goes through a pronounced minimum for Na^+ ion, and the electrostriction around Li^+ is smaller in magnitude than for the larger ions in spite of the very large electrostriction predicted by simple extrapolation. The anomalously small electrostriction around the hydrated proton is thus only a magnification of an effect already strongly evidenced by Li^+ . The corresponding entropy effect exists but is much less pronounced; the S^0_{el} of -20.8 cal./mole deg. for H^+ is

almost as large in magnitude as the value of -23.7 for Li^+ .

These effects can be rationalized by examining values of $S^0_{\text{el}}/S^0_{\text{theo}}$ and $\bar{V}^0_{\text{el}}/\bar{V}^0_{\text{theo}}$ in Tables I and II. These functions reach maxima for cationic radii in the region of 1.0–1.3 Å. and decrease for both larger and smaller radii. This behavior presumably reflects a change in coordination number of primary water of hydration, and the smaller ions do not reduce entropy and volume as much as might be expected from their charge densities because they cannot coordinate as many water molecules. This interpretation justifies the decision to make K^+ the smallest cation used in the calculations of this paper.

The very negative partial molal volume of silver ion is consistent with the anomalous free energy and entropy behavior of this species discussed previously.¹

Other Properties.—The properties heat capacity, compressibility, and thermal expansibility can only be measured as derivatives of other properties and are related to second derivatives of the dielectric constant of the medium. Moreover, for none of these properties are data available for all seven of the ions used in the other extrapolation procedures. It is hardly surprising that these properties show rather poor fit to the anticipated relations.

Only for compressibility did the treatment employed differentiate between \bar{V}^0_{el} values for cations and anions of the same size, and only for this property do the entries in the last column of the appropriate table show even a modest tendency to extrapolate toward macroscopic values as r increases. The conclusions of the present paper must be regarded as crude approximations for these properties, and individual ionic contributions cannot be assigned with any confidence until better data are available for more ions.

Some of this material was presented at the 144th National Meeting of the American Chemical Society in Los Angeles, Calif., April, 1963.

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Appendix A

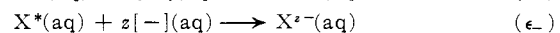
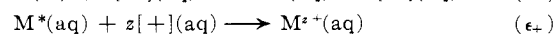
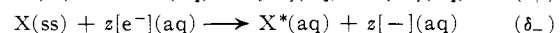
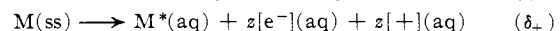
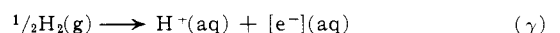
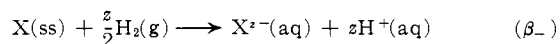
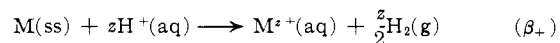
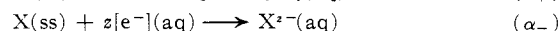
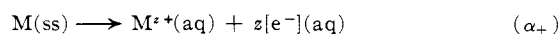
Definitions of Ionic Properties.—Equations 1–3 are concerned with contributions to properties of aqueous ions M^{z+} and X^{z-} . Definitions of these contributions involve certain real and hypothetical states of matter. The symbols ss, g, and aq refer to standard state of element, to gas phase, and to dilute aqueous solution, respectively. The symbols M^* and X^* refer to neutral species that differ from the ions M^{z+} and X^{z-} only in the lack of charge; they are not neutral atoms of M and X.

The symbol $[\text{e}^-](\text{aq})$ refers to one mole of electrons distributed in water at the bulk electrostatic potential of the solvent but without interaction with it; the state is defined to have zero values for entropy, free energy, and similar thermodynamic properties. The symbols $[\text{+}]$ and $[\text{-}]$ refer to one faraday of positive or negative charge dispersed in the indicated medium at an indefinitely great distance from any other species of interest.

Of course these hypothetical states are not realizable experimentally. However, processes involving them are conceptually useful for defining electrostatic contributions to thermodynamic properties. Since thermodynamics is concerned only with initial and final

states of a system, experimentally observable changes of state can be discussed consistently in terms of processes proceeding through unattainable states.

Let us define the processes



For reasons explained in Appendix B, the above processes are defined to involve no net transport of charge across a phase boundary.

The quantities used in the Introduction can be defined by the following relations where Y_{ss}^0 is the value of Y for the element in its standard state and the other subscripts refer to the above processes. Absence of a sign in the subscript means that the equation is valid for both cations and anions.

$$\bar{Y}^0 = Y_{ss}^0 + \Delta\bar{Y}_{\alpha}^0 \quad (A1)$$

$$\bar{Y}_{\text{con}}^0 = Y_{ss}^0 + \Delta\bar{Y}_{\beta_+}^0 - (z/2)Y_{H_2}^0 \quad (\text{cation}) \quad (A2)$$

$$\bar{Y}_{\text{con}}^0 = Y_{ss}^0 + \Delta\bar{Y}_{\beta_-}^0 + (z/2)Y_{H_2}^0 \quad (\text{anion}) \quad (A3)$$

$$\bar{Y}_{H}^0 = \frac{1}{2}Y_{H_2}^0 + \Delta\bar{Y}_{\gamma}^0 \quad (A4)$$

$$\bar{Y}_{\text{neut}}^0 = Y_{ss}^0 + \Delta\bar{Y}_{\delta}^0 \quad (A5)$$

$$\bar{Y}_{e1}^0 = \Delta\bar{Y}_{\epsilon}^0 \quad (A6)$$

The processes are also defined to satisfy the equations

$$\alpha_+ = \beta_+ + z\gamma \quad (A7)$$

$$\alpha_- = \beta_- - z\gamma \quad (A8)$$

$$\alpha = \delta + \epsilon \quad (A9)$$

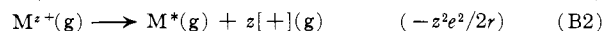
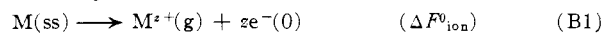
Hence eq. 1-3 in the Introduction follow directly.

Appendix B

Treatment of Interfacial Potentials.—Special problems arise when the above equations are applied to the properties free energy and enthalpy. Estimation of \bar{F}_{neut}^0 and \bar{H}_{neut}^0 from experimental data seems to require use of properties of gaseous ions.

Let $e^{-}(l)$ refer to gaseous electrons in a hypothetical state having zero values for kinetic energy, entropy, and free energy. Let Z be the electrostatic potential of an aqueous phase relative to a gas in contact with it. Frumkin²⁴ has suggested that orientation of water dipoles will make Z negative by some tenths of a volt, but no really satisfactory method of experimental measurement is known.

Process δ_+ can be separated into the following component processes. Free energy changes are given in parentheses, and ΔF_{ion}^0 and ΔF_{neut}^0 have been defined previously.¹

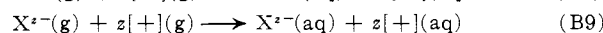
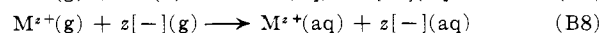
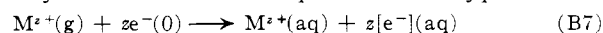


Similar component processes can be written to define process δ_- involving an anion.

The ionic hydration process is usually written



The above equations indicate that the electrostatic contribution to the free energy of this process contains a term involving an unknown interfacial potential in addition to the usual terms involving dielectric properties of the medium. These effects can be eliminated if eq. B6 is avoided and if hydration of gaseous ions is always defined to involve a process of the type



(24) A. Frumkin, *J. Chem. Phys.*, **7**, 552 (1939).

[CONTRIBUTION FROM THE DEPARTMENT OF PHYSICAL AND INORGANIC CHEMISTRY OF THE UNIVERSITY OF NEW ENGLAND, ARMIDALE, N.S.W., AUSTRALIA]

The van der Waals Radii of Gaseous Ions of the Noble Gas Structure in Relation to Hydration Energies

BY R. H. STOKES

RECEIVED SEPTEMBER 6, 1963

In comparing experimental free energies of hydration of ions with calculations from electrostatic models, the self energy of the gaseous ion is the dominant term. The crystal radius is not appropriate for the calculation of this term. The van der Waals radius calculated from that of the isoelectronic noble gas by the quantum mechanical scaling principle is a reasonable alternative and leads to excellent agreement with the experimental data for ions of the noble gas structure. The model used for the ion in solution is consistent with the known dielectric properties of water.

Notation

μ , chemical potential of ionic species
 $\Delta\mu_h$, Gibbs free energy of hydration per mole
 ϵ , dielectric constant (relative permittivity)
 $e1$, electrostatic contribution
 r_E , "equivalent electrostatic radius" of ion
 r_V , van der Waals radius
 r_C , crystal radius (Pauling)
 z , valency of ion (signed)
 Z , atomic number of ion
 S , screening constant for outermost electron shell of ion or noble gas atom
 ΔF^0 , standard free energy change

Introduction

The failure of the Born equation

$$-\Delta\mu_{h1} = \frac{Nz^2e^2}{2r} \left(1 - \frac{1}{\epsilon}\right) \quad (1)$$

to represent the electrostatic contribution to observed free energies of hydration of ions is well known. Using the crystal radius of the ion for r , agreement can be produced only by either: (a) reducing the value of ϵ to values much lower than the expected value for "irrotationally bound" water. Thus the work of Hasted,