wave was masked by the wave for the anodic dissolution of mercury. Monodentate ligands tend to favor the stepwise reduction while bi- or polydentate ligands favor the direct reduction. This enhanced stability of the copper(II) complex relative to copper(I) is reasonable when one considers that two linear sp bonds with copper(I) often appear to be more stable than four sp^3 bonds.

Monodentate amines are as effective as dangling polydentate amines for forming these linear sp complexes. Copper(II) tends to form four square dsp^2 bonds so the copper(II) complexes with bidentate ligands are very stable. Consequently their reduction waves occur at more negative potentials than those of any of the possible intermediate sp linear copper(I) complexes.

Thermodynamics of Ion Hydration as a Measure of Effective Dielectric Properties of Water

BY RICHARD M. NOYES

An improved method has been developed for evaluating the changes in thermodynamic properties associated with hydration of individual species of gaseous monatomic ions. Application of the method to entropy data leads to consistent results only by neglecting the contributions observed during solvation of neutral atoms of the same size. The partial molal entropy of hydrogen ion at 25° is estimated to be -3.3 cal./mole deg. in satisfactory agreement with thermocell calculations. For cations having the electronic structure of an inert gas, the free energies of hydration indicate effective dielectric constants that depend only on size of ion and are virtually independent of charge. These effective dielectric constants can be used to estimate local dielectric constant as a function of distance from the center of a cation, but the data are not sensitive enough to permit extrapolation beyond the radius of the largest cation studied. Cations not having an inert gas structure show larger absolute enthalpies and free energies of hydration as predicted by ligand field theory. The singly charged d^{10} ions Cu^+, Ag^+, and Au^+ exhibit extreme solvation effects that are not observed for any other ions, including the isoelectronic species Zn^{2+}, Cd^{2+}, and Hg^{2+}. Thermodynamic properties change more during the hydration of anions than for cations of the same size, and the few available data do not exhibit the monotonic variation with ionic size that is observed with cations.

Introduction

If a charge q is reversibly transferred from a conducting sphere of radius r in a vacuum to an identical sphere in a medium of dielectric constant ϵ, the change in electrostatic free energy is

$$\Delta F^0_{el} = -\frac{q^2}{2r}\left(1 - \frac{1}{\epsilon}\right) \qquad (1)$$

Also

$$\Delta S^0_{el} = -\left(\frac{\partial \Delta F^0_{el}}{\partial T}\right)_P = \frac{q^2}{2rT\epsilon}\left(\frac{\partial \ln \epsilon}{\partial \ln T}\right)_P \qquad (2)$$

These equations are unquestionably valid for spheres of macroscopic dimensions. If they are applied to ions of absolute charge ze dissolved in water at 25° (for which[1] $\epsilon = 78.30$ and $(\partial \ln \epsilon)/\partial \ln T)_P = -1.357$), they predict the theoretical values

$$\Delta F^0_{theo} = -163.89 \frac{z^2}{r/\text{Å}} \text{ kcal./mole} \qquad (3)$$

$$\Delta S^0_{theo} = -9.649 \frac{z^2}{r/\text{Å}} \text{ cal./mole deg.} \qquad (4)$$

The absolute free energy changes observed for hydration of real ions are less than those predicted by equation 3. Latimer, Pitzer and Slansky[2] showed that an empirical fit with theory could be obtained by adding a constant factor to the crystallographic radii of the ions. Little attempt has been made to adopt an alternative treatment of experimental data by assuming that ion sizes are known and constant but that dielectric saturation effects occur in the neighborhood of solvated ions.
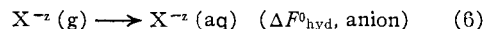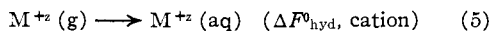
(1) C. G. Malmberg and A. A. Maryott, J. Res. Nat. Bur. Standards, 56, 1 (1956).

(2) W. M. Latimer, K. S. Pitzer and C. M. Slansky, J. Chem. Phys., 7, 108 (1939).

Near the surface of an ion, the electrostatic potential gradient is of the order of millions of volts per cm. Such an intense field causes extreme polarization of the solvent, and it has long been recognized that it must be a very poor approximation to assume that the bulk dielectric constant of the medium can be used to describe effects at distances of the order of molecular dimensions. The purpose of the present paper is to show that thermodynamic measurements on solvated ions can be used to calculate effective dielectric properties of solvent in the neighborhood of these ions.

Formulation of Problem

Let monatomic cations and anions be represented by M^{+z} and X^{-z}, respectively. Let the hydration reaction be the transfer of ions from gas phase at a standard state of one atmosphere fugacity to aqueous solution at a standard state of one molal activity. Then

$$M^{+z} (g) \longrightarrow M^{+z} (aq) \quad (\Delta F^0_{hyd}, \text{cation}) \qquad (5)$$

$$X^{-z} (g) \longrightarrow X^{-z} (aq) \quad (\Delta F^0_{hyd}, \text{anion}) \qquad (6)$$

where the parentheses represent a convention to be followed in this paper to permit easy reference to reactions defining the subscripts applied to various changes in thermodynamic properties.

Let A be a monatomic inert species of the same radius as an ion of interest. The hydration of this neutral species is represented by

$$A(g) \longrightarrow A(aq) \quad (\Delta F^0_{neut}) \qquad (7)$$
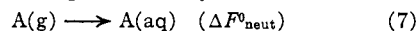
The hydration of an ion can be conceived to proceed by discharging the gaseous ion, hydrating the resulting neutral species, and then recharging it. Then we can write

$$\Delta F^0_{hyd} = \Delta F^0_{neut} + \Delta F^0_{el} \quad (\text{cation or anion}) \qquad (8)$$

where ΔF^0_{el} is the electrostatic free energy change to be compared to the theoretical quantity mentioned in the Introduction.
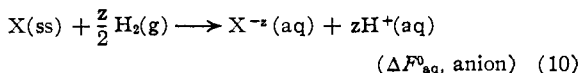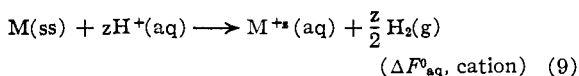
If ΔF^0_{el} can be calculated from experimental data, equation 1 can be used to determine the effective dielectric constant associated with the reversible charging of a solvated atom to an ion. Although ΔF^0_{neut} can be estimated with considerable confidence, ΔF^0_{hyd} is not directly measurable because no experiment can study an ionic transfer process unless equal quantities of positive and negative charge are involved.

This difficulty about properties of individual ions is conventionally resolved by assigning zero values to the free energy, enthalpy, and entropy of hydrated protons in a standard state of one molal activity. Zero values are also conventionally assigned to the free energies and enthalpies of the elements in their standard states, but tabulated entropies are usually based on applications of the third law.

The above set of conventions can be used in self-consistent fashion for any balanced chemical equation provided there is no change in the net charge on hydrated ions. If there is a net change, application of tabulated data will fail to satisfy the thermodynamic relationship $\Delta F^0 = \Delta H^0 - T\Delta S^0$. Part of the potential ambiguity has been recognized by Rossini,[3] but neither the Bureau of Standards tabulation[4] nor Latimer[5] provides adequate warning of the inconsistencies that can arise when tabulated data are applied to problems like those considered here. The matter has been discussed further in another paper submitted to this Journal.

In the present paper, "conventional" thermodynamic properties have been calculated by assigning zero values to the free energies and enthalpies of aqueous hydrogen ion and of the elements in their standard states at 25°. Standard entropy changes were then computed from the changes in free energy and enthalpy and do not agree with values computed from tabulated values for entropies of aqueous ions.

This treatment is equivalent to defining ΔF^0_{aq}, the free energy of formation of an aqueous ion, as being determined by one of the reactions

$$M(ss) + zH^+(aq) \longrightarrow M^{+z}(aq) + \frac{z}{2}H_2(g)$$
$$(\Delta F^0_{aq}, \text{ cation}) \quad (9)$$

$$X(ss) + \frac{z}{2}H_2(g) \longrightarrow X^{-z}(aq) + zH^+(aq)$$
$$(\Delta F^0_{aq}, \text{ anion}) \quad (10)$$

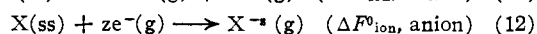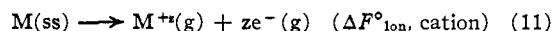where ss in parentheses refers to the appropriate standard state of the element.

No similar convention is generally adopted for discussing the thermodynamics of gaseous ions. We shall create one by assigning zero free energy and enthalpy to electrons in some standard state.

(3) F. D. Rossini, "Chemical Thermodynamics," John Wiley and Sons, Inc., New York, N. Y., 1950, p. 375.

(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.

(5) W. M. Latimer, "The Oxidation States of the Elements and their Potentials in Aqueous Solutions," 2nd Ed., Prentice-Hall, Inc., New York. N. Y., 1952.

This standard state can conveniently be chosen as one atmosphere fugacity, but the conclusions of this paper are all independent of the electronic standard state selected provided it is applied consistently. This convention defines ΔF^0_{ion}, the free energy of formation of a gaseous ion, by one of the reactions

$$M(ss) \longrightarrow M^{+z}(g) + ze^-(g) \quad (\Delta F^0_{ion}, \text{ cation}) \quad (11)$$

$$X(ss) + ze^-(g) \longrightarrow X^{-z}(g) \quad (\Delta F^0_{ion}, \text{ anion}) \quad (12)$$

The quantities ΔF^0_{aq} and ΔF^0_{ion} are experimentally accessible in terms of the assumed conventions, and available data are sufficient to calculate them for many ions. However, they cannot be used to calculate ΔF^0_{hyd} because the conventions for gaseous and for hydrated species are different.

Let us define an additional hypothetical change of state

$$\frac{1}{2}H_2(g) \longrightarrow H^+(aq) + e^-(g) \quad (\Delta F^0_H) \quad (13)$$
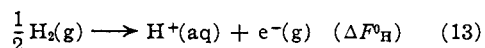
where no assumption is made about thermodynamic properties of H^+. Of course ΔF^0_H is not measurable directly, but we shall show below that it can be estimated with considerable confidence. Then

$$\Delta F^0_{hyd} = \Delta F^0_{aq} - \Delta F^0_{ion} + z\Delta F^0_H \quad (\text{cation}) \quad (14)$$

$$\Delta F^0_{hyd} = \Delta F^0_{aq} - \Delta F^0_{ion} - z\Delta F^0_H \quad (\text{anion}) \quad (15)$$

The problem of interest can be defined in terms of these quantities. The free energy changes ΔF^0_{aq} and ΔF^0_{ion} are measurable for a particular ionic species, and ΔF^0_{neut} is estimable. If ΔF^0_H also can be estimated, ΔF^0_{el} can be computed for the hydration of the ion. The results obtained for a number of ions can be used to indicate effects of ionic charge and of ionic radius on the dielectric properties of the solvating medium.

Calculation of ΔF^0_{aq} and ΔF^0_{ion}.—Standard thermodynamic references[4,5] tabulate the enthalpies of formation from the elements of gaseous ions and of hydrated ions in dilute solution; they also tabulate free energies of formation of hydrated ions at one molal activity. These tabulated quantities are ΔH^0_{ion}, ΔH^0_{aq} and ΔF^0_{aq} in terms of the conventions adopted above.

The same references also tabulate enthalpies and free energies of formation of neutral gaseous atoms from the elements. The reactions defining these quantities are

$$M(ss) \longrightarrow M(g) \quad (\Delta F^0_{atom}) \quad (16)$$

$$X(ss) \longrightarrow X(g) \quad (\Delta F^0_{atom}) \quad (17)$$
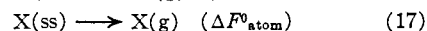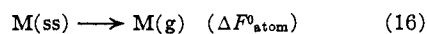
Free energies of formation of gaseous ions are not usually tabulated, but they are calculable from the other quantities by the equation

$$\Delta F^0_{ion} = \Delta F^0_{atom} + \Delta H^0_{ion} - \Delta H^0_{atom} - RT \ln(Q_{ion}/Q_{atom}) \quad (18)$$

where the Q's are electronic partition functions for the appropriate species.

If all of these quantities are known, it is easy to calculate ΔF^0_{con} the conventional expression for the free energy of hydration of an ion, defined by the equation

$$\Delta F^0_{con} = \Delta F^0_{aq} - \Delta F^0_{ion} \quad (\text{cation or anion}) \quad (19)$$

Of course ΔF^0_{con} differs by $z\Delta F^0_H$ from the desired ΔF^0_{hyd}.

TABLE I

THERMODYNAMICS OF HYDRATION OF IONS AT 25°

Ion	r, Å.	ΔF^0_{con}, kcal./mole	ΔS^0_{con}, cal./mole deg.	ΔF^0_{el}, kcal./mole	ΔH^0_{el}, kcal./mole	ΔS^0_{el}, cal./mole deg.
		Singly charged cations				
Li^+	0.60	−225.61	−12.76	−122.13	−129.67	−25.36
Na^+	0.95	−201.84	− 4.88	− 98.36	−103.55	−17.48
K^+	1.33	−184.06	3.19	− 80.58	− 83.37	− 9.41
Rb^+	1.48	−179.00	6.0	− 75.52	− 77.5	− 6.6
Cs^+	1.69	−171.31	6.7	− 67.83	− 69.6	− 5.9
Cu^+	0.96	−239.8	−28.8	−136.3	−148.7	−41.4
Ag^+	1.26	−217.97	− 6.67	−114.49	−120.22	−19.27
Au^+	1.37	−248.6	...	−145.1	...	...
Tl^+	1.40	−185.52	4.23	− 82.04	− 84.52	− 8.37
H^+	...	−363.985	−10.407	−260.50	−267.35	−23.01
		Doubly charged cations				
Be^{2+}	0.31	−790.6	−55	−582.3	−608	−86
Mg^{2+}	.65	−662.5	−32.5	−454.2	−473.29	−63.9
Ca^{2+}	.99	−587.76	−18.95	−379.46	−394.50	−50.35
Sr^{2+}	1.13	−548.0	−34.0	−339.7	−359.22	−65.4
Ba^{2+}	1.35	−522.3	− 7.0	−314.0	−325.47	−38.4
Ra^{2+}	1.40	−514	0	−306	−315	−31
Zn^{2+}	0.74	−691.58	−32.70	−483.28	−502.42	−64.10
Cd^{2+}	0.97	−637.42	−23.48	−429.12	−445.51	−54.88
Hg^{2+}	1.10	−643.23	−15.90	−434.93	−449.06	−47.30
Ti^{2+}	0.90	−634	...	−426	...	...
V^{2+}	.88	−649	...	−441	...	...
Cr^{2+}	.84	−653.1	− 6.0	−444.8	−456.0	−37.4
Mn^{2+}	.80	−644.7	−30.5	−436.4	−454.9	−61.9
Fe^{2+}	.76	−660.1	−28.9	−451.8	−472.8	−70.3
Co^{2+}	.74	−689	−49.6	−481	−504.9	−81.0
Ni^{2+}	.72	−701.1	−50.3	−492.8	−517.2	−81.7
Cu^{2+}	...	−704.46	−34.44	−496.16	−515.82	−65.84
Pd^{2+}	.86	−681	...	−573	...	...
Sn^{2+}	1.12	−579.7	−13.8	−371.4	−384.9	−45.2
Pb^{2+}	1.20	−564.83	− 5.60	−356.53	−367.6	−37.00
		Multiply charged cations				
Al^{3+}	0.50	−1413.6	−64.4	−1100.5	−1134.7	−114.8
Sc^{3+}	.81	−1251.6	−47	− 938.5	− 967.5	− 97
Y^{3+}	.93	−1172.1	−41	− 859.0	− 886.2	− 91
La^{3+}	1.15	−1091.9	−39.9	− 778.8	− 805.7	− 90.3
Ga^{3+}	0.62	−1416.5	−75.1	−1103.4	−1140.8	−125.5
In^{3+}	.81	−1293.0	−55.3	− 979.9	−1011.4	−105.7
Tl^{3+}	.95	−1289.0	−101.3	− 975.9	−1021.1	−151.7
Ti^{3+}	.76	−1280	...	− 967	...	...
Cr^{3+}	.69	−1350	−70	−1037	−1073	−120
Fe^{3+}	.64	−1346	−64	−1033	−1067	−114
Ce^{3+}	1.11	...	...	...	− 870	...
Ce^{4+}	1.01	...	...	...	−1579	...
		Anions				
F^-	1.36	16.6	−53.0	−89.5	−97.8	−27.8
Cl^-	1.81	30.0	−39.2	−76.1	−80.3	−14.0
Br^-	1.95	36.9	−35.2	−69.2	−72.2	−10.0
I^-	2.16	45.8	−30.2	−60.3	−61.8	− 5.0
S^{2-}	1.84	−96.5	−62.7	−307.4	−313.0	−18.5

These conventional changes in thermodynamic properties of hydration for a number of ions at 25° are reported in Table I. Most of the data came from Bureau of Standards Circular No. 500[4], but a few additional entries were taken from Latimer's[5] compilation. The electronic partition functions were computed when appropriate from energy levels and term assignments in Bureau of Stand-ards Circular No. 467.[6] No energy level data were available for the ions of cerium, and for no ion were the conclusions of this paper seriously affected by application of these corrections for electronic structure.

(6) "Atomic Energy Levels," Circular of the National Bureau of Standards No. 467, U. S. Government Printing Office, Washington, D. C., 1948–1958.

Ionic radii also are presented in Table I. The values quoted are those of Pauling.[7]

Estimation of ΔF^0_{neut}.—The quantity ΔF^0_{neut} refers to the process when a mole of neutral gaseous species at 1 atmosphere fugacity dissolves in water to an ideal 1 molal solution under a pressure of 1 atmosphere. Two assumptions seem appropriate for estimating this quantity.

The *zero energy assumption* applies if there is no energy of hydration so that the enthalpy and entropy changes are just those calculable from the change in volume associated with the change of state. At 25° the volume of the gas is 24.47 liters, and the appropriate quantities are

$$\Delta S^0_{neut} = -R \ln 24.47 = -6.350 \text{ cal./mole deg.} \quad (20)$$

$$\Delta H^0_{neut} = -23.47 \text{ liter atm./mole} =$$
$$-0.568 \text{ kcal./mole} \quad (21)$$

$$\Delta F^0_{neut} = 1.325 \text{ kcal./mole} \quad (22)$$

The *inert gas assumption* evaluates ΔF^0_{neut} as equal to the experimentally measured value for an inert gas molecule of the same size. The solubility data on these gases have been reviewed by Lawrence.[8] Table II contains a reasonably self-con-

TABLE II

THERMODYNAMICS OF HYDRATION OF INERT GASES AT 25°

Gas	r, Å.	Bunsen coefficient, β	ΔF^0_{neut}, kcal./mole	ΔH^0_{neut}, kcal./mole	ΔS^0_{neut}, cal./mole deg.
He	1.78	0.0083	4.68	−0.85	−18.55
Ne	1.60	.0150	4.33	−2.36	−22.44
Ar	1.91	.033	3.86	−2.73	−22.10
Kr	2.01	.056	3.55	−3.45	−23.48
Xe	2.21	.110	3.15	−5.04	−27.47
Rn	..	.200	2.80	−4.82	−25.56

sistent tabulation of results that often show considerable discrepancy from one investigator to another. The solubility is quoted as the Bunsen coefficient, β, defined as the volume of gas (calculated at 0°C. and 760 mm.) dissolved by one volume of water at the temperature of interest when the gas pressure is 1 atmosphere; its temperature dependence can be related to ΔH^0_{neut} in identically the same way as can the temperature dependence of an equilibrium constant.

The radii listed in Table II are half the interatomic distances calculated from crystallographic data.[9] The value for helium is not consistent with the other entries in the table, and presumably either the reported structure is in error or the properties of this peculiar solid cannot be related to properties of gas molecules in the same way as for the other gases.

The data for the four gases from neon to xenon, inclusive, were fitted empirically to obtain the linear equations

$$\Delta F^0_{neut} = 0.16 + 6.76/r \text{ kcal./mole} \quad (23)$$

$$\Delta H^0_{neut} = -10.83 + 14.13/r \text{ kcal./mole} \quad (24)$$

$$\Delta S^0_{neut} = -36.86 + 24.70/r \text{ cal./mole deg.} \quad (25)$$

These equations were used to estimate these quantities for the application of the inert gas assumption to calculations for ions.

The zero energy assumption is appropriate to the macroscopic situation of the Introduction if there are no surface tension effects during solvation. It essentially assumes that a neutral atom is introduced into the solvent without disturbing the surrounding molecules and that all of the influences of ions on solvent structure are associated with the charging process. The inert gas assumption gives the appearance of greater validity, but we shall see below that the experimental data are more consistent with the zero energy assumption.

Estimation of ΔF^0_H.—The method of estimation for ΔF^0_H was developed in principle before it was realized that Verwey[10] had used a somewhat similar approach.

Equations 3 and 4 are valid for the hydration of charged spheres that are large enough for macroscopic dielectric properties of water to be applicable. For smaller spheres, dielectric saturation effects will make ΔF^0_{el} smaller in absolute magnitude and will make ΔS^0_{el} more negative. If measurements are restricted to singly charged ions having an inert gas structure, it may be permissible to assume that these saturation effects can be approximated by a single additional term of a series expansion in $1/r$. Then we can write

$$\Delta F^0_{el} = -163.89/r + B/r^2 \quad \text{(cation)} \quad (26)$$

$$\Delta F^0_{el} = -163.89/r + C/r^2 \quad \text{(anion)} \quad (27)$$

$$\Delta S^0_{el} = -9.649/r - D/r^2 \quad \text{(cation)} \quad (28)$$

$$\Delta S^0_{el} = -9.649/r - E/r^2 \quad \text{(anion)} \quad (29)$$

where B, C, D and E are constants. We shall see later that moderate failure of these approximations does not seriously affect the estimation of ΔF^0_H.

If these equations are combined with equations 8, 14, 15 and 19, we obtain

$$\Delta F^0_H + 163.89/r - B/r^2 = -\Delta F^0_{con} + \Delta F^0_{neut}$$
$$\text{(cation)} \quad (30)$$

$$\Delta F^0_H - 163.89/r + C/r^2 = \Delta F^0_{con} - \Delta F^0_{neut}$$
$$\text{(anion)} \quad (31)$$

$$\Delta S^0_H + 9.649/r + D/r^2 = -\Delta S^0_{con} + \Delta S^0_{neut}$$
$$\text{(cation)} \quad (32)$$

$$\Delta S^0_H - 9.649/r - E/r^2 = \Delta S^0_{con} - \Delta S^0_{neut}$$
$$\text{(anion)} \quad (33)$$

Figure 1 illustrates plots of the right sides of equations 30 and 31 for halide ions and for the three alkali ions having radii greater than 1 Å. The equations predict that the plotted points should lie on two curves having a common intercept and diverging from this intercept with slopes of absolute magnitude 163.89 kcal. Å./mole. A three-parameter least squares technique can then be used to evaluate the three quantities ΔF^0_H, B and C. If ΔF^0_{neut} is computed by the zero energy assumption, the values of these parameters are

$$\Delta F^0_H = 104.81 \text{ kcal./mole} \quad (34)$$

$$B = 78.05 \text{ kcal. Å.}^2/\text{mole} \quad (35)$$

$$C = 57.22 \text{ kcal. Å.}^2/\text{mole} \quad (36)$$

If ΔF^0_{neut} is computed by the inert gas assumption,

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

(8) J. H. Lawrence, *J. Physiol. (London)*, **105**, 197 (1946).

(9) Landolt-Börnstein, "Zahlenwerte und Funktionen aus Physik, Chemie, Astronomie, Geophysik und Technik," Sechste Auflage, 1955. Band I, Teil 4, p. 89.

(10) E. J. W. Verwey, *Chem. Weekblad*, **37**, 530 (1940).

Fig. 1.—Application of equations 30 and 31 to estimation of ΔF^0_H: open circles represent zero energy assumption, and filled circles represent inert gas assumption. Point marked V is value computed by method of Verwey,[10] and point marked K & B is value computed from K^+ and F^- by method of Kortüm and Bockris[11]
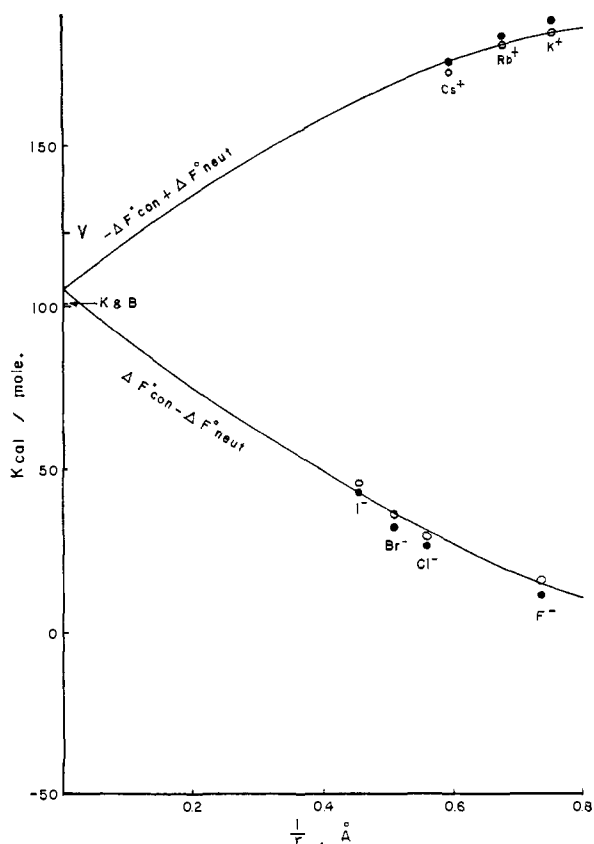

Fig. 2.—Application of equations 32 and 33 to estimation of ΔS^0_H. Open circles represent zero energy assumption, and filled circles represent inert gas assumption. Point marked K & B is value computed from K^+ and F^- for zero energy assumption by method of Kortüm and Bockris.[11]

the corresponding value of ΔF^0_H is 104.32 kcal./mole. Individual points fit these curves with a maximum deviation of 3.28 kcal./mole, and all seven points fit each pair of curves to the accuracy expected if ΔF^0_{el} were known exactly, but errors in r exhibited a standard deviation of 0.09 Å.

Some additional calculations were made for other situations such as omitting the point for fluoride (the smallest anion) or adding the points for the smaller cations sodium and lithium. The results suggested that the B/r^2 term of equation 26 over-corrects the deviations of small cations from the predictions of theory, but the extrapolated value of ΔF^0_H can hardly be in error by more than a very few kcal./mole.

Two points on the ordinate in Fig. 1 illustrate alternative ways of assigning experimental free energies to individual ions. Verwey[10] used linear extrapolations for the largest cations and anions; his technique with these data gives $\Delta F^0_H = 123$ kcal./mole. Kortüm and Bockris[11] noted that K^+ and F^- have almost identical crystallographic radii and postulated that they would have equal free energies of hydration. This postulate gives $\Delta F^0_H = 100.3$ kcal./mole.

(11) G. Kortüm and J. O'M. Bockris, "Textbook of Electrochemistry," Elsevier Publishing Co., New York, N. Y., 1951, p. 123.
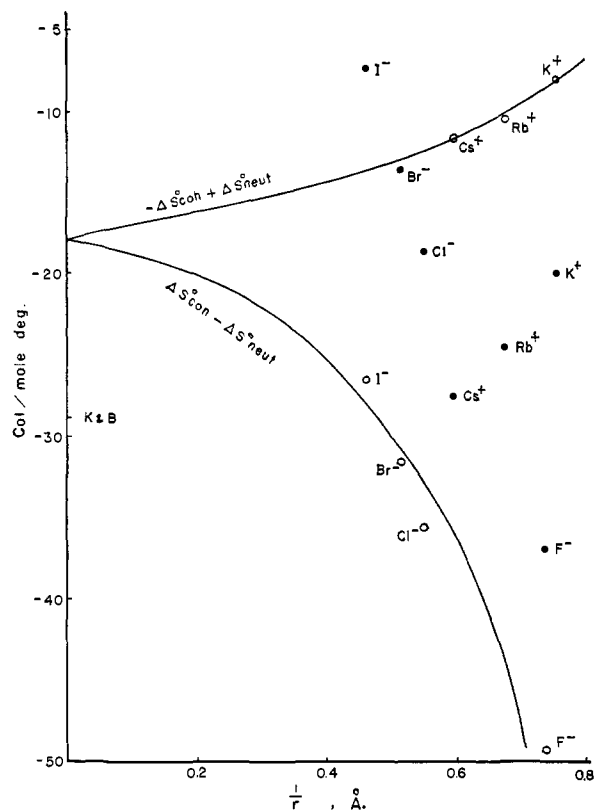
Figure 2 illustrates similar plots for the right sides of equations 32 and 33. The solid circles in this figure were computed with the use of the inert gas assumption. They cannot possibly be extrapolated to a common intercept and indicate that this intuitively plausible assumption is wholly inapplicable to the problem of interest.

Even the open circles based on the zero energy assumption cannot be fitted reasonably to the left sides of equations 32 and 33. The curves in Fig. 2 were computed by introducing terms in $1/r^3$ and assuming that D and E were equal. When equation 32 was rearranged and $-\Delta S^0_{con} + \Delta S^0_{neut} - 9.649/r$ for the cations was extrapolated to $1/r = 0$, the data suggested

$$\Delta S^0_H = -18.9 \text{ cal./mole deg.} \tag{37}$$

This result is not inconsistent with a similar treatment of equation 33, and the subsequent discussion indicates why the cation extrapolation appears more apt to be reliable.

Application of the method of Kortüm and Bockris[11] gives a value of -28.2 as indicated in Fig. 2, and there does not seem to be any simple way to apply the method of Verwey[10] to these entropy data. If ΔS^0_{neut} were actually somewhat less negative than the value calculated from the zero energy assumption (rather than being still more negative as predicted by the inert gas assumption), the value of ΔS^0_H might be a few cal./mole deg. less negative than the value in equation 37. A more negative

TABLE III

EFFECTIVE DIELECTRIC PROPERTIES OF SOLVENT AROUND IONS

Ion	r, Å	$\dfrac{\Delta H^0{}_{el}}{\Delta H^0{}_{theo}}$	$\dfrac{\Delta S^0{}_{el}}{\Delta S^0{}_{theo}}$	$r_{eff} - r$, Å	ε_{eff}	$-\left(\dfrac{\partial \ln \varepsilon_{eff}}{\partial \ln T}\right)_P$
			Singly charged cations			
Li$^+$	0.60	0.4664	1.577	0.74	1.790	0.0489
Na$^+$	0.95	.5897	1.720	.72	2.287	.0682
K$^+$	1.33	.6648	1.297	.70	2.821	.0634
Rb$^+$	1.48	.6874	1.012	.69	3.058	.0536
Cs$^+$	1.69	.7050	1.033	.73	3.228	.0578
Cu$^+$	0.96	.8557	4.118	.24	4.716	.3365
Ag$^+$	1.26	.9079	2.515	.17	7.610	.3317
Au$^+$	1.37	...	...	$-$ .24	($-$5.069)	...
Tl$^+$	1.40	.7098	1.215	.60	3.248	.0684
H$^+$	...	...	...	...	...	...
			Doubly charged cations			
Be^{2+}	0.31	0.2826	0.691	0.82	1.389	0.0166
Mg^{2+}	.65	.4612	1.076	.79	1.800	.0336
Ca^{2+}	.99	.5855	1.292	.74	2.303	.0515
Sr^{2+}	1.13	.6085	1.915	.80	2.370	.0786
Ba^{2+}	1.35	.6587	1.343	.74	2.765	.0644
Ra^{2+}	1.40	.6611	1.125	.74	2.818	.0549
Zn^{2+}	0.74	.5574	1.229	.62	2.167	.0462
Cd^{2+}	.97	.6478	1.379	.56	2.679	.0640
Hg^{2+}	1.10	.7406	1.348	.41	3.578	.0836
Ti^{2+}	0.90	...	...	.64	2.366	...
V^{2+}	.88	...	...	.61	2.407	...
Cr^{2+}	.84	.5742	0.814	.63	2.287	.0323
Mn^{2+}	.80	.5455	1.283	.70	2.109	.0469
Fe^{2+}	.76	.5387	1.384	.69	2.071	.0497
Co^{2+}	.74	.5601	1.553	.62	2.155	.0580
Ni^{2+}	.72	.5582	1.524	.61	2.147	.0567
Cu^{2+}	...	...	...	...	...	...
Pd^{2+}	.86	...	...	.28	3.878	...
Sn^{2+}	1.12	.6463	1.312	.65	2.677	.0609
Pb^{2+}	1.20	.6613	1.150	.64	2.812	.0561
			Multiply charged cations			
Al^{3+}	0.50	0.3780	0.661	0.84	1.583	0.0181
Sc^{3+}	.81	.5221	.905	.76	2.036	.0319
Y^{3+}	.93	.5491	.975	.79	2.149	.0363
La^{3+}	1.15	.6173	1.196	.74	2.497	.0517
Ga^{3+}	0.62	.4712	0.896	.72	1.845	.0286
In^{3+}	.81	.5458	.986	.70	2.133	.0364
Tl^{3+}	.95	.6463	1.659	.56	2.635	.0758
Ti^{3+}	.76	...	...	.77	1.968	...
Cr^{3+}	.69	.4933	0.954	.73	1.919	.0317
Fe^{3+}	.64	.4550	.840	.79	1.794	.0261
Ce^{3+}	1.11	.6434	...	...	...	...
Ce^{4+}	1.01	.5977	...	...	...	...
			Anions			
F$^-$	1.36	0.7978	3.920	0.47	3.752	0.2549
Cl$^-$	1.81	.8723	2.629	.34	5.897	.2686
Br$^-$	1.95	.8440	2.020	.42	5.336	.1868
I$^-$	2.16	.8004	1.119	.56	4.641	.0900
S^{2-}	1.84	.8633	0.882	.29	6.745	.1031

value seems harder to accommodate to the data. The experimental values of $\Delta S^0{}_{con}$ do not suggest any better method of treatment than the one employed here.

Equations 34 and 37 can be combined to give

$$\Delta H^0{}_H = 99.17 \text{ kcal./mole} \qquad (38)$$

Calculation of $\Delta F^0{}_{el}$.—As a result of all the combinations of data discussed above, values of $\Delta F^0{}_{el}$,

$\Delta H^0{}_{el}$ and $\Delta S^0{}_{el}$ were computed for the hydration of the ions for which data are available. The computations used the zero energy assumption for solvation of neutral atoms. The results are presented in Table I along with the conventional values for ionic hydration.

Table III contains the ratios of $\Delta H^0{}_{el}$ and $\Delta S^0{}_{el}$ to the theoretical values computed for ions of the same size with the use of equations 3 and 4.

Discussion

Comparison with Previous Estimates.—It is interesting to compare these conclusions with other attempts to determine individual ionic contributions to experimentally measurable hydration energies. The method of Kortüm and Bockris[11] assumes that ions of equal size but opposite charge will have equal free energies of hydration. They chose K$^+$ and F$^-$ for their calculations. Since the cation and anion curves in Fig. 1 have different slopes, the Kortüm and Bockris value depends on the accident that the ions chosen had radii of 1.33 Å. The entropy data of Fig. 2 show much greater slope differences in the curves for cations and anions, and the method of Kortüm and Bockris is much more strongly dependent upon the specific ionic size chosen for the comparison.

The method of Verwey[10] makes an extrapolation that assumes the slope difference observed for cations and anions would continue to be observed for very large ions. However, we would expect that for these large ions the free energy of hydration would be independent of sign of charge for ions of identical size, and the macroscopic dielectric properties of the solvent tell us what the limiting slopes in Figs. 1 and 2 should be.

The approach of this paper gives predictions intermediate between those of the other two methods, and we believe that it combines the validity of the Kortüm and Bockris postulate for large ions with the Verwey recognition that slopes for cations and anions are different for sizes accessible to measurement.

"Absolute" Entropy of Hydrogen Ion.—The above discussion selected -18.9 cal./mole deg. as the best value for $\Delta S^0{}_H$. Half of the standard molal entropy of hydrogen gas at 25° is 15.606 cal./mole deg. If the electron is assigned an entropy of zero, these data indicate that aqueous hydrogen ion has a standard partial molal entropy of -3.3 cal./mole deg. in terms of the usual third law convention. Thermocell measurements[12] led to values of the same quantity from -2.1 to -3.4 cal./mole deg., while the same authors interpret the paper of Latimer, Pitzer, and Slansky[2] to predict a value of -1.5. Eley and Evans[13] quote previous thermocell data leading to a value of -4.6 cal./mole deg. Certainly the value given by the present method is consistent with previous attempts to estimate this important quantity.

Effective Dielectric Properties of Water.— Absolute values of $\Delta F^0{}_{el}$ are invariably *less* than those predicted by equation 1 for spheres of macro-

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

(13) D. D. Eley and M. G. Evans, *Trans. Faraday Soc.*, **34**, 1093 (1938).
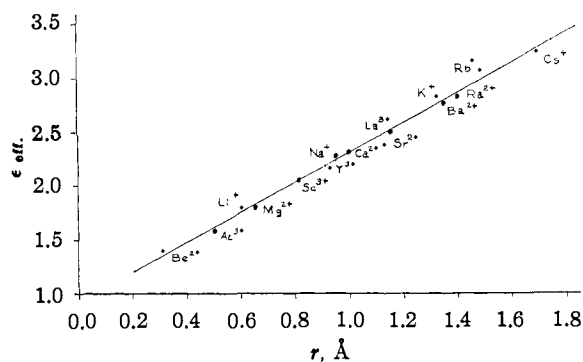
Fig. 3.—Effective dielectric constant as a function of size for cations having the electronic structure of an inert gas. Note extreme deviation from macroscopic dielectric constant of 78.30.

scopic dimensions. The discrepancy can be reconciled on an empirical basis either by using the macroscopic dielectric constant and assigning the ion an effective radius, r_{eff}, greater than the crystallographic radius, or else by using the crystallographic radius and assigning the solvent an effective dielectric constant, ϵ_{eff}, less than the macroscopic value. The results of both approaches are presented in Table III.

For many cations, including all those having the electronic structure of an inert gas, values of ΔF^0_{el} can be brought into excellent agreement with equation 1 by adding a constant value of about 0.75 Å. to the crystallographic radii. This is essentially the approach of Latimer, Pitzer and Slansky,[2] and it has considerable empirical validity. However, the absolute values of ΔS^0_{el} are almost invariably *greater* than those predicted by equation 2 for spheres of the crystallographic radius; any empirical increase in radius will magnify the discrepancy between theory and observation.

Since it is impossible to assign any ionic radius, such that data for both ΔF^0_{el} and ΔS_{el}^0 can be simultaneously accommodated to the macroscopic dielectric properties of water, it has seemed appropriate to assign crystallographic radii to the ions and to regard thermodynamic changes during hydration as measures of effective dielectric properties of solvent. Table III contains the values of ϵ_{eff} and of $(\partial \ln \epsilon_{eff}/\partial \ln T)_P$ necessary to satisfy equations 1 and 2 on the basis of this assumption.

In Fig. 3, values of ϵ_{eff} are plotted against r for those cations having the electronic structure of an inert gas. The surprising conclusion from Fig. 3 is that ϵ_{eff} is primarily a function only of the size of such a cation and is virtually independent of the charge on it. Thus the fifteen points in Fig. 3 can be fitted by the linear equation

$$\epsilon_{eff} = 1.000 + 1.376(r - 0.054) \qquad (39)$$

with a standard deviation of only 0.054 in ϵ_{eff} values. If free energy data were exact, the observed variations could be caused by standard deviations of 0.04 Å. in reported crystallographic radii.

Even the small deviations in Fig. 3 are not random. Thus the points for all $+1$ ions except Cs^+ lie above the line of equation 39, and the points for all $+3$ ions lie below this line. Ap-
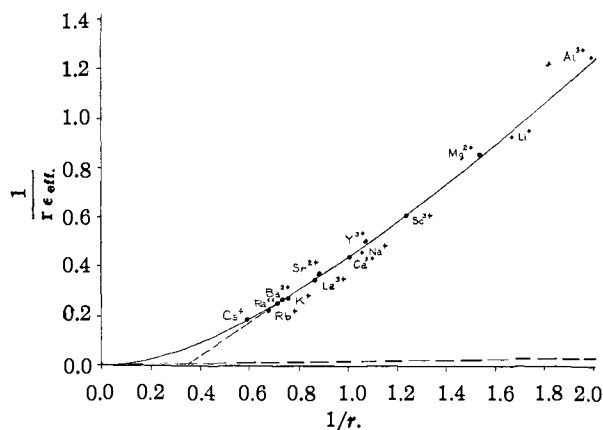

Fig. 4.—Plot for estimation of ϵ_{loc}: solid curve represents prediction of equation 43, and dashed alternative extension represents equation 44. Lower dashed line near axis represents prediction if macroscopic dielectric constant applied. The point for Be^{2+} (at $1/r\epsilon_{eff} = 2.323$ and $1/r = 3.226$) has been omitted so that the other features can be enlarged.

parently the effective dielectric constant is slightly reduced by increasing cationic charge, but data of extreme precision would be needed to define the charge dependence.

Of course the virtual independence of ϵ_{eff} from charge is a necessary consequence of the observation that the data can be fitted to the macroscopic ϵ by adding a constant increment to r. The quantity ϵ_{eff} is the average effective dielectric constant influencing the electrostatic forces as successive increments of charge are added to a neutral solvated atom. The data indicate that for a species of a particular radius almost the same effective dielectric constant would be involved in increasing the charge from 0 to 1, from 1 to 2 or from 2 to 3 electronic units. It seems to be inescapable that during the reversible charging of an initially neutral molecule, a small fraction of an electronic charge would polarize the surrounding solvent molecules and cause a reduced local dielectric constant; and that continued charging even to three electronic units would have very little influence on this local dielectric constant.

Estimation of Local Dielectric Constant.—The quantity ϵ_{eff} is a composite average. Let ϵ_{loc} be the local dielectric constant in the neighborhood of an ion; in principle it is a function of both the distance from the ion and the charge on that ion, Then for the reversible transfer of charge from vacuum to solvent we can write

$$\Delta F^0_{el} = -\frac{z^2 e^2}{2r} + \frac{z^2 e^2}{2r\epsilon_{eff}} - \frac{z^2 e^2}{2r} -$$
$$\int_0^{ze} \int_\infty^r \frac{q}{\epsilon_{loc} r'^2} dr' dq \qquad (40)$$

where r' is a distance greater than r. The experimental evidence from Fig. 3 indicates strongly that ϵ_{loc} is very little dependent on q. To the extent that this assumption is true, equation 40 becomes

$$\frac{1}{r\epsilon_{eff}} = -\int_\infty^r \frac{dr'}{\epsilon_{loc} r'^2} = \int_0^{1/r} \frac{d(1/r')}{\epsilon_{loc}} \qquad (41)$$

Equation 41 relates ϵ_{eff} to an integrated function of ϵ_{loc} but does not permit any estimate of individual values of ϵ_{loc} as long as measurements are restricted

to a single ion. We can go further if we treat the solvent as a dielectric continuum and postulate that ϵ_{loc} at a distance r' from the center of a cation is the same regardless of the size of the cation. This postulate is undoubtedly very good when r' is several Ångstroms. Since the solvent is composed of discrete molecules, we can question the validity of the postulate when r' becomes very nearly equal to r. However, the postulate is no worse than many that have been applied to ionic solutions, and it is interesting to explore its consequences. If we differentiate equation 41 when $r = r'$, we obtain

$$\frac{1}{\epsilon_{loc}} = \frac{d(1/r\epsilon_{eff})}{d(1/r)} \tag{42}$$

Figure 4 illustrates the data for the ions of Fig. 3 plotted as $1/r\epsilon_{eff}$ against $1/r$. If the postulate of the previous paragraph is valid, the reciprocal of ϵ_{loc} for any value of $1/r$ is equal to the local slope of the curve through the points of this figure. If ϵ_{eff} never differed from the macroscopic dielectric constant, the points would lie on the indicated dashed line passing through the origin with slope $1/78.30 = 0.01277$.

The data in Fig. 4 can be fitted reasonably in two ways. One way is to use equation 39 as derived from Fig. 3. Application of this equation to equation 42 gives

$$\epsilon_{loc} = \frac{(0.926 + 1.376r)^2}{0.926 + 2.752r} \tag{43}$$

The predictions of this equation have been used to draw the solid curve in Fig. 4.

Although this treatment fits the data very satisfactorily, it predicts that ϵ_{loc} increases approximately linearly with r and does not attain the macroscopic value of 78.30 until $r = 113$ Å. If dielectric saturation effects are significant for distances of this magnitude, the theory of ionic interactions in solution will be complicated indeed.

Because equation 43 predicts a local dielectric constant that increases surprisingly slowly, the points in Fig. 4 were also fitted by quadratic least squares. The equation is

$$\frac{1}{r\epsilon_{eff}} = -0.2129 + 0.6009/r + 0.0581/r^2 \tag{44}$$

The values of $1/r\epsilon_{eff}$ predicted by this formula agree to within 0.02 with those predicted by equation 43 for all $1/r$ values represented by points in Fig. 4. The two equations differ by 0.05 for Be^{2+} (not shown) at $1/r = 3.27$, but this deviation corresponds to an uncertainty of less than 0.01 Å. in the crystallographic radius of this ion.

The two equations differ greatly at very small values of $1/r$, and equation 44 is represented by a dashed curve in this region of Fig. 4.

Equation 44 leads to the prediction that

$\epsilon_{loc} = 78.30$ for $r > 2.86$ Å.

$$= \frac{1}{0.6009 + 0.1163/r} \text{ for } r < 2.86 \text{ Å.} \tag{45}$$

It may seem surprising that data as consistent as those in Fig. 3 cannot be extrapolated with enough confidence to distinguish between a model in which the local dielectric constant rises to its macroscopic value 2.86 Å. from the center of a cation from an alternative model in which the limit

is reached at 113 Å.! However, the experimentally measured ϵ_{eff} is primarily determined by the dielectric constant very close to the surface of an ion and is very little influenced by values of ϵ_{loc} only a short distance from that surface. A choice between the two models would require data for larger ions. It obviously will be impossible to find monatomic cations (except Fr^+) larger than Cs^+. Tests with tetraalkylammonium ions may be possible, but no data are available on the thermodynamic properties of these ions in gas phase.

Although standard state thermodynamic data obviously provide very little information about dielectric properties of solvent only a little distance from the surface of an ion, deviations of activity coefficients from the Debye–Hückel limiting law will be influenced by any dielectric saturation effects. Probably these deviations provide the best basis for interpreting effective dielectric properties of solvent, but the proper method for treating the data has not been developed.

Hydration Sphere Model. – The data for the larger ions in Fig. 4 can be fitted very satisfactorily by a straight line. This fact suggested a third model which assumes that a cation is surrounded by a coördination sphere of water molecules that can still undergo electronic polarization but no further orientation. Outside of this coördination sphere, the macroscopic dielectric constant applies.

This model essentially treats the ion as a conducting sphere immersed in a spherical shell of insulator having a smaller dielectric constant than the surrounding medium. If r_c is the radius of the coördination sphere, ϵ_w is the macroscopic dielectric constant of water, and ϵ_0 is the dielectric constant of the coördination shell, this model leads to

$$\frac{1}{r\epsilon_{eff}} = \frac{1}{r_c\epsilon_w} + \frac{1}{r\epsilon_0} - \frac{1}{r_c\epsilon_0} \tag{46}$$

This model is not satisfactory. For cations having the electronic structure of inert gases, it was not possible to find values of $r_c - r$ and of ϵ_0 that were consistent with all the data. If ϵ_0 was set equal to 1.777 (the square of the refractive index and the dielectric constant to be anticipated if only electronic polarization could occur), the data for cations greater than about 1 Å. radius could be fitted well by assuming $r_c = 3.7$ Å. independent of the actual size, and the three smallest anions could be fitted extremely well by assuming $r_c = 2.5$ Å. The smallest cations even have ϵ_{eff} less than 1.777 and cannot be fitted by this model at all. Around a small ion like Al^{3+} or Be^{2+}, even the electronic polarizability is being saturated by the intense field.

Significance of Entropy and Enthalpy Values. —The above discussion has been based on the results of *free energy* measurements. The results of *entropy* measurements are less revealing. Values of $\Delta S^0_{el}/\Delta S^0_{theo}$ quoted in Table III are directly proportional to $-(\partial \ln \epsilon_{eff}/\partial \ln T)_P/\epsilon_{eff}$. They tend to be somewhat greater than unity but do not show many significant features. Thus the anomalously large entropies of hydration of Na^+ and Sr^{2+} seem unlikely to be real. It may be significant that only Be^{2+} and some +3 ions have entropies of hydration much less than theoretical,
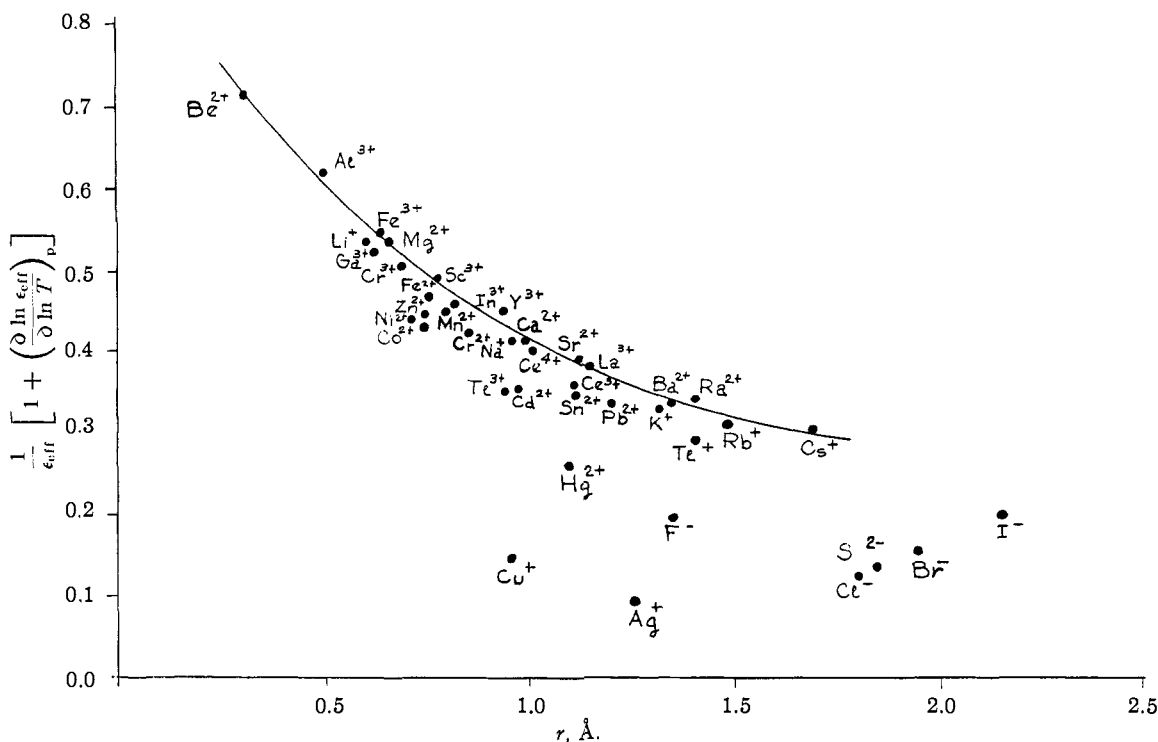
Fig. 5.—Comparison of enthalpy of hydration data for all monatomic ions for which data are available. If macroscopic dielectric properties were applicable, all points would lie below the axis and have the value −0.000456.

but Tl^{3+} has an unusually large entropy of hydration. The extreme values of Cu^+ and of Ag^+ are discussed below.

Measurements of *enthalpy* can be used to determine $\dfrac{1}{\epsilon_{eff}}\left[1 + \left(\dfrac{\partial \ln \epsilon_{eff}}{\partial \ln T}\right)_P\right]$; this quantity never differs by more than 0.003 from $(1 - \Delta H^0_{el}/\Delta H^0_{theo})$ and is not recorded in Table III. Since this quantity has less obvious significance than the dielectric properties derivable from free energy and entropy measurements, it would not be considered were it not that the enthalpy measurements are probably more accurate than those of free energy or entropy, and they are the only data available for some ions. Figure 5 shows a plot of this quantity for most of the ions. The plot confirms the conclusion from Fig. 3 that around a cation having the structure of an inert gas the dielectric properties of the solvent depend upon the size of that ion but depend very little upon its charge. This statement applies even to Be^{2+} and Ce^{4+} for which charge densities are extreme. Points in Fig. 5 for multiply charged ions of inert gas type show a slight tendency to lie above those for the alkali ions, but the effect is never more than a few per cent and is barely significant.

If the cations having the electronic structure of an inert gas are taken to define the curve of Fig. 5, most of the other ions lie a small but significant amount below this curve. The free energy data on the same ions indicate values of ϵ_{eff} less than would have been expected. These deviations are associated with crystal field effects and involve more stable bonding of water than would be predicted from the crystallographic radius. Holmes and McClure[14] have discussed this type of situa-

tion. It is probably significant that Fe^{3+}, the only transition metal ion falling on or above the inert gas structure curve, is a highly charged weak field d^5 ion.

The d^{10} ions present problems of particular interest. The ions Zn^{2+} and Cd^{2+} show small but significant deviations from the curve of Fig. 5, while Hg^{2+} deviates by over 30%. The isoelectronic ions Cu^+ and Ag^+ show extreme deviations beyond those of any other ions in the figure. No enthalpy data are available for Au^+, but this ion is unique in that its free energy of hydration is *greater* in absolute magnitude than is predicted by equation 3. Hence the point for Au^+ undoubtedly lies below the axis in Fig. 5. It is not clear why the singly charged d^{10} cations should exhibit these extreme effects while only the large Hg^{2+} of the double charged d^{10} cations is at all comparable. The singly charged cations form linear divalent complexes with considerable covalent bond character, and the unusually large heats of solvation may reflect the formation of ions with very specific formulas like $Cu(H_2O)_2^+$ and $Ag(H_2O)_2^+$.

Measurements on Anions.—The above discussion has been concerned almost entirely with cations. Data are available for the hydration of only five monatomic anions. The absolute free energies and enthalpies of hydration of these ions are always somewhat greater than for cations of the same size and charge, and the absolute entropies of hydration are very much greater than for comparable cations.

Verwey[15] has discussed reasons why enthalpies of

(14) O. G. Holmes and D. S. McClure, *J. Chem. Phys.*, **26**, 1686 (1957).

(15) E. J. W. Verwey, *Rec. trav. chim.*, **61**, 127 (1942).

hydration should be greater for anions than for cations. The argument involves the orientation of water molecules and the possibility of additional motions. An additional energetic argument could be based on the fact that the center of positive charge in a dipolar water molecule is closer to the surface than is the center of negative charge, and the interaction with a negative ion will be stronger than with a positive ion.

The extreme entropy differences apparently involve additional configurational effects that undoubtedly are also reflected in the enthalpy values. Thus the anions plotted in Fig. 5 show irregular behavior not at all like that of the cations. These irregularities cannot be explained by uncertainties in electron affinities even though these quantities are known less well than the ionization energies needed for the cation data.

The discrete structure of solvent will be involved in any interpretation of these irregularities. One of the more surprising consequences of this work is the

observation that data for cations with an inert gas structure fall so nicely on a smooth curve despite a six-fold change in radius. The water molecules around a cation extend their protons outward, and apparently ions having a wide range of sizes lead to configurations that adapt themselves to the surrounding water structure. Anions require the hydrogens of the water molecules to be directed inward, and it may be that the possible configurations of the inner hydration spheres are more sharply dependent on the size of the central ion.

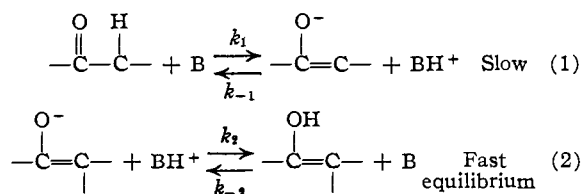[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, CORNELL UNIVERSITY, ITHACA, NEW YORK]

Deuterium Isotope and Solvent Effects on the Kinetics of the Keto-enol Interconversion of 2-Acetylcyclohexanone[1]

BY T. RILEY[2] AND F. A. LONG

The rate of enolization of 2-acetylcyclohexanone, as measured by its rate of bromination, exhibits general base catalysis (only) with a Brønsted β of 0.60. The datum for water as a base fits well with the data for other bases. The relative reactivity of the 2-monodeuterated ketone leads to a kinetic isotope effect of $k_{KH}/k_{KD} \simeq 5$ for reaction of the ketones with either of the catalysts water or acetate ion. For reactions of the ordinary ketone in the solvents H_2O and D_2O, $(k_{KH}{}^H/k_{KH}{}^D)_{OAc^-} = 1.2$, and $(k_{KH}{}^H/k_{KH}{}^D)_{water} = 1.4$, leading to the conclusion that the base strengths of the species H_2O and D_2O are in the ratio 1.2, i.e., not significantly different. Measurements of the keto–enol equilibrium and of the acid strength of the enol in the solvents H_2O and D_2O permit calculation of the relative rates of the reverse reactions. For the over-all ketonization, the relative rates k_H/k_D are again about 5 for the various catalysts. For the slow step, the attack of acid on the enolate ion, the ratios are $(k_E{}^{-H}/k_E{}^{-D})_{H_3O^+} = 1.7$ and $(k_E{}^{-H}/k_E{}^{-D})_{HOAc} = 5.9$. Both ratios are close to those for methyl acetylacetone, and it is concluded that the solvated proton is only about 1.5 times a better acid than is the solvated deuteron. Finally, these data, along with similar results for hydroxide ion, lead to the conclusion that the species H_2O is about a 5-fold stronger acid than is D_2O.

The reversible base-catalyzed transformation of β-diketones into their enolic forms is a reaction whose mechanism is well established[3,4]

$$-\overset{O}{\underset{}{\overset{\|}{C}}}-\overset{H}{\underset{}{\overset{|}{C}}}- + B \underset{k_{-1}}{\overset{k_1}{\rightleftarrows}} -\overset{O^-}{\underset{}{C}}=C- + BH^+ \quad \text{Slow} \quad (1)$$

$$-\overset{O^-}{\underset{|}{C}}=C- + BH^+ \underset{k_{-2}}{\overset{k_2}{\rightleftarrows}} -\overset{OH}{\underset{|}{C}}=C- + B \quad \begin{array}{c}\text{Fast}\\ \text{equilibrium}\end{array} \quad (2)$$

The rate of the forward reaction 1 can be conveniently measured by the rate of halogen uptake from solution since the enolate ion (E^-), once formed, reacts almost instantaneously with halogen. It is known that the enolization reaction is subject to general base catalysis[5-7] and that for β-diketones no

acid catalysis occurs.[8,9] A summary of the previous studies on hydrogen isotope effects for these has been given recently by Bell.[10] The evidence points to a general solvent effect which alone will cause the reaction to be 20–40 % slower in D_2O than in H_2O. If one neglects this effect, which is superimposed on all comparisons of rates in H_2O and D_2O, then H_2O appears to be 20–30 % more effective as a base than D_2O. Conversely OH^- (in H_2O) is 30–40 % less effective as a base than OD^- (in D_2O).[10,11] Long and Watson[12] concluded from a study similar to the present one that the acid strengths of the species H_3O^+ and D_3O^+ are almost identical. These facts taken together with the

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