MOLAL VOLUMES. V

THERMODYNAMIC PROPERTIES OF ELECTROLYTES AT INFINITE DILUTION[1]

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The extent of the validity of Born's equation for the electrical part of the free energy of an ion at infinite dilution is not yet definitely known. Clearly this equation has failed in several respects. While the ionic radius is to be considered merely an empirical parameter, Born's expression might still be useful to relate various thermodynamic properties of solutions of electrolytes at infinite dilution. Subject to this restriction, Born's equation is confirmed within the narrow limits of experimental errors by a comparison of heat capacities with new data on molal volumes of acetic acid. New experimental data confirm the limiting law relating the apparent molal volumes of electrolytes and the concentration.

As old as Arrhenius' theory are the attempts to derive from electrostatics the influence exerted by the electric charges of the ions on their thermodynamic properties. That the dependence of the free energy on concentration differed from the laws of the perfect solution was recognized by Planck and van't Hoff in 1887 (*cf.* 1), and the first quantitative theory of electrostatic interaction was developed by Malmström (23) in 1905. The electric influence of polar substituents on the strength of acids was studied by Wegscheider (38) in 1902. The electric part of the free energy of an ion at infinite dilution, explicitly derived by Born (6), was involved in the derivation of the electrostriction effect (1894) by Drude and Nernst (8). The theories which started from these three points are well known.

Although the electric parts of *all* thermodynamic properties can be derived from Born's equation[3] by straightforward thermodynamics (*cf.* 11), most of the consequences have been discussed only in recent times. The obvious reason of this delay is the uncertainty, from a theoretical viewpoint, of Born's equation itself, and of the additional assumptions required to isolate the electric part of any property.

Webb (37) used a more elaborate model for the purpose of replacing Born's equation. However, Webb uses the classical formula of the inner field, which

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[3] Born's equation represents the electric part of the *free* energy of the solution, not of the energy or heat content. This is to be concluded from Gross and Halpern's discussion (12) of the analogous problem involved in the theory of Debye and Hückel. The equation represents the electric part of the Gibbs free energy as well as of the Helmholtz free energy, the reference states of the solution of discharged ions being different in the two cases (*cf.* 27).

requires that the Lorentz–Lorenz term does not depend on pressure, a condition not even approximately satisfied by a dipole liquid like water (*cf.* also 3). To expect a good approximation in spite of this simplification would be the less justified, as high pressures are involved in the vicinity of an ion.

The dipole character of water was taken into account by Ingold (16). However, there is still no way to estimate the effect of the depolymerization of water in the neighborhood of an ion. It must be concluded from Onsager's discussion (25) of the dielectric constant that this effect is essential. An expression for the free energy of an ion in a non-associated dipole solvent probably may be derived from Onsager's theory; however, there still appears no way of a consistent treatment of aqueous solutions.

On the other hand, there is some experimental evidence that Born's equation, in spite of the weakness of its theoretical basis, represents in some respects a good approximation (3, 13, 21). As even a restricted validity will be useful, a thorough experimental test appears to be worthwhile.

Several restrictions must be stated from the start. It can be concluded from the investigations of Webb and Ingold, and it is demonstrated by available experimental data, that the Born ionic radii are far too small and hardly more than arbitrary parameters. The non-electric parts of F, ΔF, H, ΔH, C_p, V (Δ indicating ionization) must not be neglected. Thus, if any, the non-electric parts of only the following properties may be expected to be small compared with the electric terms: ΔC_p, ΔV, and the variation of C_p and V with temperature, pressure, and the composition of the solvent.

Born's equation was first tested by Scatchard (33) with respect to the variation of the free energy with the dielectric constant of the solvent, and similar tests have been carried out by other authors (2, 5, 7, 14, 21, 24, 26, 41). The somewhat diverging results may be summed up in the statement that the influence of the electrostatic term is more or less noticeable but frequently cannot account for the whole change,—not a surprising result as the non-electric part cannot be supposed to be independent of the solvent.

Kritschewsky (20) obtained satisfactory results testing the pressure dependence of the molal volume.

The temperature dependence of the ionization constant, discussed by Gurney (13) and Baughan (3), has been carefully tested in the case of acetic acid by La Mer and Brescia (21). This test is equivalent to a comparison of the ionic radii calculated from ΔC_p and the variation of this quantity with temperature.

A similar test can be carried out by means of the expansibility and its temperature coefficient in the following way: As a consequence of the formula of Drude and Nernst (8), the quotient

$$[\phi^0(t_1) - \phi^0(t_2)]/[\phi^0(t_2) - \phi^0(t_3)]$$

where ϕ^0 denotes the apparent molal volume at infinite dilution, should be independent of the nature of the electrolyte and equal to a similar quotient in terms of $1/D^2 \cdot (\mathrm{d}D/\mathrm{d}P)$. As discussed later, the value of $\mathrm{d}D/\mathrm{d}P$ can be calculated from the variation of the apparent molal volume with concentration. Using the data of Baxter and Wallace (4) for fifteen alkali halides, we found the same order of magnitude for these quotients. Considering the uncertainty of the data, extremely magnified in the involved calculation, a detailed report of the results is hardly justified.

The sensitivity of these methods of testing is greatly impaired by the fact that they are based upon derivatives of the measured properties. Much more sensitive, and therefore decisive, is a test which compares the two quantities which immediately can be measured: namely, ΔC_p and ΔV. In the following this test is discussed for acetic acid.

A TEST OF BORN'S EQUATION

The harmonic mean ionic radius r of a weak electrolyte can be derived independently and with considerable accuracy from the change of heat capacity, ΔC_p, and the change of volume ΔV, accompanying ionization. If Born's equation is valid within the restrictions discussed in the preceding section, and if the non-electric parts of these two properties are negligible, the two values of r should coincide within the experimental error.

In order to discuss ΔC_p, we start, following the procedure of La Mer and Brescia (21), from Born's equation, a thermodynamic relation, and an empirical formula of Åkerlöf as used by Wyman and Ingalls (40):

$$F_\epsilon = \frac{N\epsilon^2}{Dr}; \quad C_p = -T\frac{\partial^2 F}{\partial T^2}; \quad D = ae^{-bT} \tag{1}$$

(F_ϵ = electric part of the free energy; N = Avogadro's constant; ϵ = elementary electric charge; D = dielectric constant of water). The change of heat capacity is represented by

$$\Delta C_p = -\frac{N\epsilon^2 b^2 T}{Dr} \tag{2}$$

or, with the numerical values $N = 6.03 \times 10^{23}$, $\epsilon = 4.796 \times 10^{-10}$, $b = 2.303 \times 0.00198$, and $D = 78.54$ (40),

$$\begin{aligned}\Delta C_p &= -109.5/r \text{ (joules}\cdot\text{degree}^{-1}\cdot\text{mole}^{-1}) \\ &= -26.2/r \text{ (calories}\cdot\text{degree}^{-1}\cdot\text{mole}^{-1}) \quad (25°\text{C.})\end{aligned} \tag{3}$$

r being expressed in Ångström units.

From the variation with temperature of the ionization constant, La Mer and Brescia derive $r = 0.704$, corresponding to $\Delta C_p = -37.2$ calories·degree^{-1}·mole^{-1}.[4] From the same experimental material, Harned and Owen (15) found $\Delta C_p = -41.3$, the difference illustrating the uncertainty involved in the computation of a second derivative.

A reliable value of ΔC_p can be calculated with the aid of the heat capacities of acetic acid solutions determined by Richards and Gucker (31). Table 1 contains the molality m, the apparent molal heat capacities $\phi(C_p)$ at the tem-

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[4] La Mer and Brescia give -39.9, which value, however, is not in accord with their other data.

peratures of measurement, the values for 25°C. found by parabolic extrapolation, and the values $\phi_u(C_p)$ of the undissociated acid obtained by adding $-\alpha\Delta C_p$, where the degree of ionization, α, was computed from the ionization constant given by MacInnes (22). The limiting value for infinite dilution $\phi_u^0(C_p) = 174 \pm 4$ joules·degree^{-1}·mole^{-1} was found, the uncertainty being due mainly to the temperature correction.

With Rossini's (32) value $\phi_i^0(C_p) = 17$ joules·degree^{-1}·mole^{-1} for the ions $H^+ + Ac^-$, we obtain

$$\Delta C_p = -157 \pm 5 \text{ joules}\cdot\text{degree}^{-1}\cdot\text{mole}^{-1} = -37.6 \pm 1.2 \text{ calories}\cdot\text{degree}^{-1}\cdot\text{mole}^{-1} \quad (4)$$

$r = 0.697 \pm 0.023$, in excellent agreement with La Mer and Brescia.

The application of the electrostriction formula of Drude and Nernst (8)

$$\Delta V = \frac{\partial \Delta F_e}{\partial P} = -\frac{N\epsilon^2}{D^2 r}\cdot\frac{\partial D}{\partial P} \quad (5)$$

requires the knowledge of the pressure coefficient of the dielectric constant. The direct determinations of this coefficient were discussed in the fourth paper of this series (29). A much more reliable value can be derived from the limiting value $d\phi/dc^{1/2} = k = 1.86$ (25°C.; ϕ, apparent molal volume; c, concentration in moles per liter), meanwhile confirmed by new measurements (30). According to a relation previously derived (27), we obtain (25°C.)

TABLE 1

Apparent molal heat capacities of acetic acid solutions in joules/degree mole

m	$\phi\ (C_p)$ 16°C.	$\phi\ (C_p)$ 18°C.	$\phi\ (C_p)$ 20°C.	$\phi\ (C_p)$ EXTRAPOLATED 25°C.	$\phi_u\ (C_p)$ 25°C.
0.0695	160.1	160.0	161.3	170.9	173.3
0.139	161.9	162.5	164.5	174.3	176.0
0.278	161.5	161.8	163.8	175.2	176.4
0.555	160.20	161.03	162.61	170.3	171.2
1.11	157.42	158.22	159.86	167.6	168.2
2.22	152.37	153.18	154.83	162.8	163.2

$$\frac{1}{D}\cdot\frac{\partial D}{\partial P} = \frac{\beta}{3} + \frac{k}{2 \times 2.303RTh} = (47.7 \pm 0.3) \times 10^{-6} \text{ atm.}^{-1} \quad (6)$$

with $\beta = 45.0 \times 10^{-6}$ atm.$^{-1}$ (compressibility) and $h = 0.5056$ (coefficient of the Debye–Hückel law). Thus

$$\Delta V = -\frac{8.31 \pm 0.06}{r} \text{ cc. per mole} \quad (7)$$

To determine with the desired accuracy the volume change of ionization, i.e., of the reaction

$$\text{HAc} + \text{NaCl} = \text{HCl} + \text{NaAc}$$

in the limit of infinite dilution, new measurements of the molal volumes of acetic acid, sodium acetate, and hydrochloric acid were required, because the insufficient precision of earlier data in the dilute range caused a large uncertainty of extrapolation. A report of the experimental work will be given in the next papers of this series (30). The molal volume of sodium chloride is well established by the work of Geffcken, Beckmann, and Kruis (10) and of Wirth (39). The values of the apparent or the partial molal volumes at infinite dilution are (in milliliters per mole):

HAc	51.942 ± 0.01	HCl	17.830 ± 0.01
NaCl	16.60 ± 0.03	NaAc	39.244 ± 0.03

so that

$$\Delta V = -11.47 \pm 0.05 \text{ cc. per mole};\ r = 0.725 \pm 0.006\ \text{Å}. \qquad (8)$$

The two values of r, equation 4 and 8, derived from Born's equation by means of independent experimental data, agree within the limits of error. The main source of uncertainty, the temperature correction applied to the data of Richards and Gucker, is apt to result in too low a value of r. The agreement is, therefore, very satisfactory.

Of course, extensive experimental material will be required before a general conclusion as to the validity of Born's equation within restricted limits can be drawn. The present result appears to justify further experimental work in this direction.

ON THE VALIDITY OF THE LIMITING LAW OF THE MOLAL VOLUME

The discussion presented in the preceding section makes use of the limiting law of the apparent molal volume of electrolytes (27, 28) in a twofold way. First, the extrapolation of the molal volumes to infinite dilution and the uncertainty involved in this extrapolation depend on the validity of this law. Second, the method of calculating[5] the value of dD/dP would be entirely unjustified if the limiting law did not hold true.

It was believed that the experimental material available ten years ago was sufficient to support the limiting law. In addition, some more recent data of high precision reviewed in the fourth paper of this series (29) confirmed this law. Still, some objections were raised meanwhile which made a further investigation necessary, especially since the experimental basis was admittedly small.

Stewart (35, 36) examined the density data given for one hundred and ninety-seven strong electrolytes in the *International Critical Tables* and the Landolt-Börnstein *Tabellen*, and concluded that the limiting law was not valid. In six cases even a decrease of the molal volume with increasing concentration was found, strictly contrary to theory. Stewart's negative result is, in general, a consequence of the use of data obtained for too high concentrations, and in some cases of secondary effects like hydrolysis or incomplete ionization. In

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[5] This method has previously been used in unpublished work by Professor M. Randall.

some cases, e.g., potassium chlorate, the negative result was to be explained only by gross mistakes in the data.

Our results (30) for potassium chlorate are represented in figure 1, in which the apparent molal volume is plotted against the square root of the concentration $c^{1/2}$.

Scatchard (34) has pointed out that the square root of the molality should be used rather than $c^{1/2}$ in the limiting law of the activity coefficient. However, for the sake of easier comparison with earlier data, we prefer to keep $c^{1/2}$ until a general revision of the available experimental material has been made.

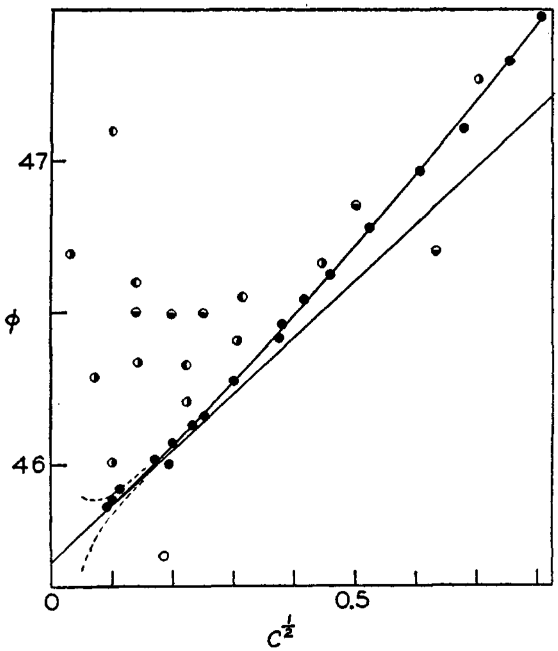

FIG. 1. Apparent molal volumes of potassium chlorate. ○, *International Critical Tables* Vol. III (25°C.); ◒ Joy and Wolfenden (19) (interpolated to 25°C.); ◐, Jones and Talley (17) (25°C.); ◑, Jones and Ray (18) (25°C.); ●, this paper (24.81°C.).

The curve in figure 1 represents the equation

$$\phi = 45.677 + 1.86c^{1/2} + 0.418c \quad (\text{KClO}_3 \text{ at } 24.81°\text{C.}) \tag{9}$$

the straight line corresponds to the limiting slope 1.86 previously derived. The broken lines indicate the influence of an error of $\pm 3 \times 10^{-7}$ in the density, which corresponds to the sensitivity of our reading device.

The limiting slope is fully confirmed by these data. Our results definitely cannot be represented by a straight line with a different slope, according to Masson's rule rather than to the theoretical limiting law.

The data of some earlier observers (17, 19) have been included in the diagram.

A number of other data are outside the ordinate range. The results of Jones and Ray (18), published after our measurements were finished, agree above $c^{1/2} = 0.25$ within a few hundredths with ours, if the difference of temperature is corrected for.

Only the lowest point of the data given in the *International Critical Tables* falls within the ordinate range of figure 1. Obviously these data, which indicate a negative slope, are grossly erroneous.

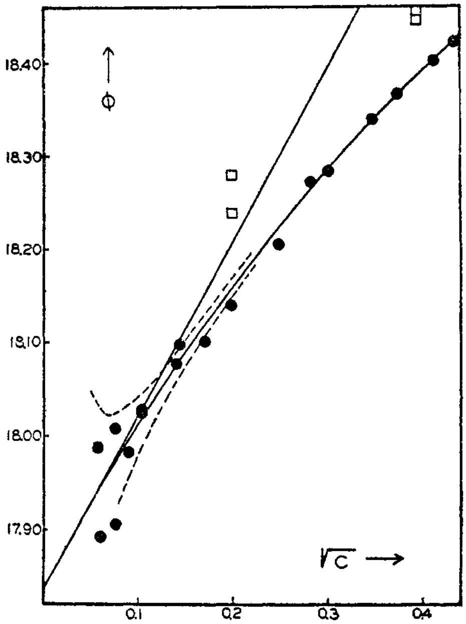

FIG. 2. Apparent molal volumes of hydrochloric acid at 25.00°C. □, Wirth (39); ●, this paper.

Hydrochloric acid offered a serious problem, for the following reasons: Wirth's precise data (39) resulted in a linear relationship of the apparent molal volume with the square root of the concentration, but the coefficient was only one-half of the universal value $k = 1.86$. Thus Wirth's results in this case are in strict disagreement with the theory. As the limiting law has been confirmed so far only for salts, a decisive test of an acid was particularly desirable. In addition, accurate data were required for the test discussed in the preceding section.

Figure 2 represents the lowest points of Wirth and our results, which tend to approach Wirth's data at higher concentrations, except for a small systematic discrepancy. The curve corresponds to the equation

$$\phi = 17.830 + 1.86c^{1/2} - 1.15c \quad \text{(HCl at 25.00°C.)} \tag{10}$$

The agreement with the predicted limiting slope is perfect.

A RELATIONSHIP INVOLVING THE MOLAL VOLUME AT INFINITE DILUTION

A relationship of some sort between the value ϕ^0 of the apparent or partial molal volume at infinite dilution and the coefficient of the first-power term in equations like 9 or 10 may be expected. This coefficient, which we shall denote by B, represents a measure of the deviations from the limiting law at moderate concentrations and corresponds to a term of the extended Debye–Hückel law. The quantity ϕ^0 may be split into a non-electric or "true" volume and an electrostriction term, as given by the formula of Drude and Nernst. Each of these three terms,—namely, the coefficient B, the "true" volume, and the electrostriction term,—can be represented by means of an "ionic radius." Unfortunately, these ionic radii are little more than arbitrary parameters, so that they must not be identified with one another. Still, they are somehow related to one another, and the same may therefore be expected of ϕ^0 and B.

Indeed, a striking parallelism between ϕ^0 and B has already been mentioned ten years ago (28) in the second paper of this series. This parallelism has been found both by an inspection of the variation with temperature of these two quantities and by a comparison of the values for different alkali halides. Recently Fajans (9) stated a similar relationship between the electric part of ϕ^0 and the individual deviations from the limiting law at moderate concentrations.

The parallelism between ϕ^0 and B explains an empirical relationship found by Stewart (36). It can easily be seen in a purely formal way that Stewart's structural parameter h corresponds to the volume of the solution, and the quantity dh/dm, therefore, to the partial molal volume or, within Stewart's experimental error, to ϕ^0. Thus the parallelism between dh/dm and the deviations of ϕ from the limiting law at moderate concentrations, as found by Stewart, represents just the relationship discussed above.

SUMMARY

Previous tests of Born's equation are discussed, and a restricted range of possible applicability is stated.

A test of Born's equation is based on a comparison of two independent sets of experimental data: namely, the change of heat capacity and the change of volume accompanying ionization. Data available for acetic acid agree with Born's equation within the narrow limits of experimental uncertainty.

The limiting law of the apparent molal volume of electrolytes, used in this test, is fully confirmed by new determinations of the density of dilute solutions of potassium chlorate and hydrochloric acid, contrary to earlier data.

A qualitative relationship between the apparent molal volume of electrolytes at infinite dilution and the deviations of this property from the limiting law at moderate concentrations is discussed.

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