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THERMAL EXPANSION AND THE DEBYE-HÜCKEL HEAT OF DILUTION

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The calculation of the heat of dilution from the Debye-Hückel theory has been based on the calculation^{1,2,3,4} of the energy U from the work content A by the Gibbs-Helmholtz equation, that is, through a differentiation *at constant volume*. However, the experimental data used are the change in heat content H , the dielectric constant and its temperature coefficient, all measured *at constant pressure*. The difference between the two heat quantities is small and can be determined, that between the two dielectric constants is probably also very small, but that between the temperature coefficients at constant pressure and at constant volume is generally more important. The difficulty is removed most simply by carrying out the calculations, like the experiments, at constant pressure. This involves the addition of a term dependent on the thermal expansion of the solution.

The present treatment will be limited to the case of a single electrolyte which does not change the dielectric constant of the solution. The fundamental equation of the Debye-Hückel theory, in the extended form of Gronwall, La Mer and Sandved,⁵ may be written

$$\psi_j = \frac{-KT}{\epsilon z_j} \sum_{m=1}^{\infty} \left(\frac{\epsilon^2 z_j^2}{-KTDa} \right)^m X_m(x) \quad (1)$$

where ψ_j is the potential at the distance a from the center of the j 'th ion, k is Boltzmann's constant, T the absolute temperature, ϵ the charge on the proton, z_j the valence of the j 'th ion (negative for a negative ion), D is the dielectric constant of the solvent, a the mean collision diameter of the ions, which we will assume to be the same for both ions. Each $X_m(x)$ is a function of the ratio z_1/z_2 and of x , which latter is defined by the equation

$$x = \kappa a = \sqrt{\frac{-4\pi N\epsilon^2\nu z_1 z_2 a^2 n}{1000 KTDV}} \quad (2)$$

where N is Avogadro's number, ν the number of ions formed from one molecule of electrolyte, n the number of moles of electrolyte in V liters of solution.

¹ Gross and Halpern, *Physik. Z.*, **26**, 403 (1926).

² E. Q. Adams, *THIS JOURNAL*, **48**, 621 (1926).

³ N. Bjerrum, *Z. physik. Chem.*, **119**, 145 (1926).

⁴ Lange and Meixner, *Physik. Z.*, **30**, 670 (1929).

⁵ Gronwall, La Mer and Sandved, *ibid.*, **29**, 358 (1928).

If we define a new variable as

$$Y_m(x) = \frac{1}{x^{2m}} \int_0^x y^{2m-1} X_m(y) dy \quad (3)$$

the work of charging all the ions reversibly at the same rate is

$$W_e = -NKTn \sum_{j=1}^2 \sum_{m=1}^{\infty} \nu_j \left(\frac{\epsilon^2 z_j^2}{-KTDa} \right)^m Y_m(x) \quad (4)$$

where ν_j is the number of ions of the j 'th kind formed from one molecule of electrolyte.

The electrical contribution to the heat content may be obtained by the Gibbs-Helmholtz equation at constant pressure written in the form

$$H_e = \frac{d(W_e/T)}{d(1/T)} \quad (5)$$

where W_e varies with the temperature directly, and also because of the temperature variation of D , V and a . All four of these quantities occur in x and therefore in each $Y_m(x)$. Gronwall, La Mer and Sandved give the relation

$$\frac{dY_m(x)}{dx} = \frac{X_m(x)}{x} - \frac{2mY_m(x)}{x} \quad (6)$$

The differentiation of x is obvious and

$$H_e = -NKTn \sum_{j=1}^2 \nu_j \sum_{m=1}^{\infty} \left(\frac{\epsilon^2 z_j^2}{-KTDa} \right)^m \left[\left(1 + \frac{d \ln D}{d \ln T} \right) \frac{X_m(x)}{2} + \frac{d \ln V}{d \ln T} \left(\frac{X_m(x)}{2} - mY_m(x) \right) - \frac{d \ln a}{d \ln T} (X_m(x) - 3mY_m(x)) \right] \quad (7)$$

The total heat of dilution to zero concentration per mole Q_c^0 is

$$Q_c^0 = (H_e - H_e^0)/n \quad (8)$$

where H_e^0 is the value of H_e when $x = 0$.

Let us consider the Debye-Hückel approximation ($m = 1$). Since

$$x_1(x) = 1/(1+x) \quad (9)$$

$$Q_c^0 = -NKT \sum_{j=1}^2 \frac{\epsilon^2 \nu_j z_j^2}{2KTDa} \left\{ \frac{x}{1+x} \left(1 + \frac{d \ln D}{d \ln T} \right) + \frac{1}{x^2} \left[1+x - \frac{1}{1+x} - 2 \ln(1+x) \right] \frac{d \ln V}{d \ln T} + \frac{2}{x^2} \left[\frac{x^2}{1+x} + \frac{x^2}{2} - 3x + 3 \ln(1+x) \right] \frac{d \ln a}{d \ln T} \right\} \quad (10)$$

$$= -NKT \sum_{j=1}^2 \frac{\epsilon^2 \nu_j z_j^2}{2KTD} \left[\left(1 + \frac{d \ln D}{d \ln T} + \frac{1}{3} \frac{d \ln V}{d \ln T} \right) \kappa - \left(1 + \frac{d \ln D}{d \ln T} + \frac{1}{2} \frac{d \ln V}{d \ln T} - \frac{1}{2} \frac{d \ln a}{d \ln T} \right) \right] \kappa^2 a + \dots \quad (11)$$

The earlier calculations all omit the term in $d \ln V/d \ln T$.⁶ Gross and Halpern¹ apparently used the rest of equation (10) although they

⁶ If the heat quantities on the left-hand side are energies rather than heat contents, and if the dielectric constant and its temperature coefficient are also measured at constant volume, the equations are correct with this omission.

did not publish their equation. Adams² gave the rest of the first term of equation (11) as the limiting law. Bjerrum³ gave the first term of equation (10) and Lange and Meixner⁴ gave the first term of equation (7). Bjerrum and Lange and Meixner drop the term in $d \ln a/d \ln T$ because this coefficient cannot be determined independently and because it does not appear in the limiting law. Since $X_m(x)$ and $Y_m(x)$ for m greater than one disappear at $x = 0$ (they do not even appear in the limiting law) the complete value of Q_c^0 may be obtained by adding to Q_c^0 for $m = 1$ the contribution of the higher terms to H_e .

We are particularly interested in the term in $d \ln V/d \ln T$ which has previously been omitted. We may note that it is in general, including the higher terms of equation (7), proportional to one minus the osmotic coefficient or to the j of Lewis and Randall. From the first term of equation (11) we see that it appears in the limiting law, and by comparing the two terms of this equation we see that for more concentrated solutions it increases less rapidly than the term in $(1 + d \ln D/d \ln T)$. A detailed study of the higher terms shows that its relative importance decreases with increasing values of m . The relative value of the two terms depends, of course, upon the two temperature coefficients. For water at 25° $\frac{1}{3} \frac{d \ln V}{d \ln T}$ is 0.0256, and Wyman's value⁷ for $(1 + d \ln D/d \ln T)$ is -0.371, so that the error in the limiting law due to the neglect of the thermal expansion is +7.2%. This is about the difference between $(1 + d \ln D/d \ln T)$ of Wyman and of Drude,⁸ and about the error of measurement of the heat of dilution in very dilute solutions.⁹ It is probable that in the near future both of these experimental uncertainties will be reduced. For other substances the measurements of the temperature coefficient of the dielectric constant are less certain. The values for ethyl alcohol given in the "International Critical Tables"¹⁰ indicate an error of 1.3% if the thermal expansion is neglected.

Summary

It is pointed out that it is incorrect to calculate the heat of dilution from the Debye-Hückel theory by differentiating at constant volume. The complete equation is derived for a solution containing a single electrolyte with the dielectric constant independent of the concentration. It is shown that neglect of the thermal expansion leads to a considerable error even in the limiting law.

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⁷ J. Wyman, *Phys. Review*, **35**, 623 (1930).

⁸ Drude, *Ann. phys.*, **59**, 48 (1896).

⁹ For references see Lange and Robinson, *Z. physik. Chem.*, **148A**, 97 (1930).

¹⁰ "International Critical Tables," Vol. VI, 1929, p. 85.