On Electrolytes in Media of Low Dielectric Constant

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A conductance function derived by Halpern and Gross is compared with experimental data for what they consider to be the most favorable case: slight dissociation in a solvent of very low dielectric constant, at concentrations near that of the minimum in conductance. Such comparison shows that the functional form required by their equation is not satisfied by the data for tetraisoamylammonium picrate in benzene over the concentration range $1 \times 10^{-6} - 2 \times 10^{-4} N$. It is pointed out that the Bjerrum radius is not of decisive importance in the interpretation of conductance data.

IN a recent number of this journal, Halpern and Gross[1] present a theoretical treatment of electrolytic solutions, which is based on "ion-dipole" interaction, and in a succeeding paper in the same number of the journal, Gross and Halpern[2] undertake a "theoretical interpretation of the experimental results obtained by Fuoss and Kraus," this interpretation being made in the light of their theory. They criticize our own interpretation[3] of our experimental results in terms of "ion association" and conclude that "the formulae of Kraus and Fuoss can only be considered to be empirical laws," while they hold that their own theory reproduces "quantitatively several features of the conductivity phenomena." It will be unnecessary for us to offer any criticisms of the theoretical foundations of the Halpern-Gross theory since, as we shall show, it does not reproduce the experimental data. We must take exception, however, to their statement that our formulae are merely empirical laws, since they have obviously arrived at their conclusions through misinterpretation of the physical picture underlying our description.

To consider first the applicability of the Gross-Halpern theory to the experimental data, we consider their Eq. (9), which they use "to explain conductivity phenomena in media of low dielectric constant" and for which they claim "that the agreement is best for very low dielectric constants and near the minimum of dissociation." The equation is

$$\log \gamma^2 c = A + Bc. \tag{1}$$

Our limiting conductance equation, for which we make the same claims, is

$$\Lambda \sqrt{c} = \alpha + \beta c. \tag{2}$$

Gross and Halpern show a plot of Eq. (1) applied to our data for the conductance of tetraisoamylammonium nitrate in dioxane.[4] If the equation is applicable, the plot should be linear. At best, the plot is linear for a concentration ratio of 1 : 3 and if the plot is carefully constructed, it is evident that it exhibits curvature over the whole range. A much more conclusive test of the equation could have been obtained by applying it to the conductance of tetraisoamylammonium picrate in benzene,[5] for which we have published data to concentrations as low as $10^{-6} N$. In Fig. 1 are plotted Halpern and Gross' function (1) and our own function (2) for solutions of the picrate in benzene for the concentration interval 1×10^{-6} to 2×10^{-4}. Inspection of the figure will show that, while our Eq. (2) yields a linear plot over the entire concentration range, the Halpern and Gross Eq. (1) shows a marked curvature over the entire range. At best, their equation might be applicable in the case of very small concentrations, because it can readily be shown that (1) and (2) have the same form at concentrations well below that of the minimum. An extrapolation of their function from the concentration range where it approximates linearity is shown by the dotted line in the figure. The conclusion of Gross and Halpern that their formula "gives satisfactory results principally for the region close to the minimum-conductivity" is clearly untenable. On the plot, the position of the

[1] Halpern and Gross, J. Chem. Phys. **2**, 184 (1934).

[2] Gross and Halpern, J. Chem. Phys. **2**, 188 (1934).

[3] Fuoss and Kraus, J. Am. Chem. Soc. **55**, 476, 1019, 2387 (1933).

[4] Kraus and Fuoss, J. Am. Chem. Soc. **55**, 21 (1933).

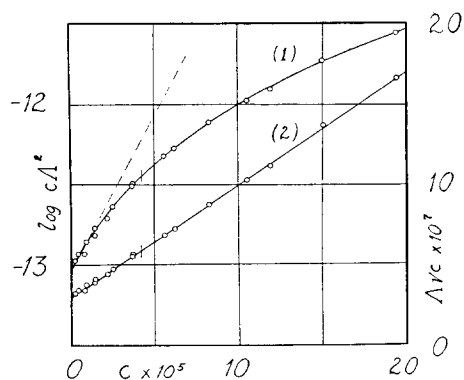[5] Fuoss and Kraus, J. Am. Chem. Soc. **55**, 3614 (1933).

FIG. 1. Conductance of tetraisoamylammonium picrate in benzene at 25°; (1) Halpern and Gross function $\log c\gamma^2 = A + Bc$; (2) Fuoss and Kraus function $\Lambda\sqrt{c} = \alpha + \beta c$.

minimum is indicated by vertical lines crossing the curves.

In passing, we may point out that in attempting to fit their theory to our experimental data, they have found it necessary to assume for their "molecules" a value of the moment $\mu = 5.8 \times 10^{-18}$. This value is of the same order of magnitude as that of ordinary neutral polar molecules. The values found by Kraus and Hooper[6] for electrolytes are several times larger. This discrepancy seems serious, because the parameter μ appears as an exponent in the coefficient of c in their formula (8).

On the theoretical side, the criticisms of Gross and Halpern are largely concerned with the hypothesis of ion association and center around the Bjerrum radius R. Actually, the Bjerrum radius R is not fundamental to our theory, as one of us has already shown;[7] it is merely a convenience introduced for the purpose of approximate calculation and, if necessary, can be dispensed with altogether.[8] However, since the criticisms of Gross and Halpern are directed at our use of the Bjerrum radius, we may be permitted to develop this picture and to indicate how the criticisms of Gross and Halpern fail to apply. Detailed discussions will be found in papers already published or in papers which will appear shortly.

In solvents of high dielectric constant and at low concentrations, it is possible to account for many of the properties of electrolytic solutions by means of the time average potential of the ionic atmosphere as proposed by Debye and Hückel. As the dielectric constant of the solvent is decreased, the potential energy of a given pair of ions at contact increases, and when it becomes equal to and greater than kT, we may expect that ion pairs will have a finite chance of existing as stable structures. We assumed that such pairs are non-conductors (unless a third ion is present at short distances, which will produce a triple ion) and have shown that by means of this simple picture it is possible to account quantitatively for conductance data over a wide range of all variables.[9]

We then sought a plausible mechanism for the assumed reaction

$$A^+ + B' \rightleftharpoons AB$$
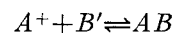
and found that the Coulomb force law was sufficient[10] to account for the observed energies of dissociation as calculated from experimental K values, provided some device were introduced to force convergence of the phase integral. Breaking the integral at the Bjerrum limit $R = \epsilon^2/2Dkt$ was chosen as the simplest method; this step is, however, a numerical approximation and is not an essential element in our theory. When two ions are far apart, other molecules and ions between screen the ions so that their effects on each other decrease integrably.[11]

In any case, when the dielectric constant of the solvent is small, the principal contribution to our calculated K values are due to the exponential peak near $r = a$ (contact) and the integral is numerically *independent* of the upper limit, so long as it is not of order infinity.

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[6] Kraus and Hooper, Proc. Nat. Acad. Sci. **19**, 939 (1933).

[7] Fuoss, Phys. Zeits. **35**, 59 (1934).

[8] We might point out that elimination of the Bjerrum radius will not "invalidate the application of the theory to media of low dielectric constants." Our variation of K with DT comes from the limit $r = a$ in our integration, as inspection of Eq. (7) of our third paper (J. Am. Chem. Soc. **55**, 1019 (1933)) will show.

[9] Fuoss and Kraus, J. Am. Chem. Soc. **55**, 476 (1933).

[10] Fuoss and Kraus, J. Am. Chem. Soc. **55**, 1019 (1933).

[11] Fuoss, Phys. Zeits. **35**, 59 (1934). Further work on this problem is in progress; and in a forthcoming publication (J. Am. Chem. Soc. **56**, 1027 (1934)), a method is given for the calculation of osmotic properties of an associated electrolyte, which is independent of the Bjerrum radius. The convergence problem is also discussed in some detail in the papers mentioned in this footnote.

Extending our physical picture along the same lines, we next assumed the triple ion equilibrium[12] as the interaction of next order of importance, and found that it quantitatively accounted for the minimum in conductance. We again used the analogue of the Bjerrum radius, but are able to show that the precise value of the upper[13] limit is unimportant.

Gross and Halpern, however, seem to read into our papers the statement that nearly all of the ion pairs consist of ions at a distance of $R = \epsilon^2/2Dkt$ from each other, thus: "The 'molecules' in Bjerrum's theory of ionic association have a 'radius' R which for media of low dielectric constant (e.g. dioxane $D = 2.2$) takes a value 1.3×10^{-6} cm. Since almost all the salt dissolved is forming 'molecules' the volume accessible to the 'free ions' becomes very much reduced (sometimes even negative); the free energy of the ions therefore is very much increased as compared with the value it would take if the total volume were accessible to the ions." We point out the fact that the ratio p of the probability that two ions are at contact to the probability that they are at a distance R from each other is

$$p = (a^2/R^2) \exp (\epsilon^2/aDkT - \epsilon^2/RDkT)$$

In dioxane, with $a = 6 \times 10^{-8}$ and $R = 127 \times 10^{-8}$,

$$p = (36/16,100)e^{42.3-2} = 2.24 \times 10^{-3}e^{40.3} = 7 \times 10^{14}.$$

It therefore appears that ions at contact are enormously more probable configurations than "molecules" containing ions at $r = R$. In dilute solutions in solvents of low dielectric constant, ions will either be in contact, or if they are free, they will be at distances greater than R from other free ions, except for a very small number of transition cases. Suppose we *do* assign a

[12] Fuoss and Kraus, J. Am. Chem. Soc. 55, 2387 (1933).

[13] Since the details of this investigation will be published shortly, it seems unnecessary to reproduce them here.

[14] The editor informs us that the original statement of Gross and Halpern contains a misprint, and that it should read "a thousandth normal solution." We therefore have made the correction in the quotation. It is unfortunate that the misprint was not noticed in proof, because it gives the impression that we expect our formulas to apply to normal solutions. Our present equations cover concentrations only up to the neighborhood of the minimum in conductance, which for tetraisoamylammonium nitrate in dioxane appears at about $3 \times 10^{-5}N$.

volume $v = (4\pi R^3/3)$ to each ion, and assert that an ion pair will form if two such spheres intersect. For $R = 1.27 \times 10^{-6}$ cm, $v = 8.6 \times 10^{-18}$ cm^3. If we had Gross and Halpern's "actual case of practical interest: a (*thousandth*) normal[14] solution of tetraisoamylammonium nitrate in dioxane," and *if* the salt existed completely in the form of such "molecules," then the volume excluded would be $Nv = 5000$ cc. As a matter of fact, we applied our limiting equations to dioxane solutions of concentrations of the order of $10^{-4}N$, where the degree of dissociation was about $3 \times 10^{-5}/100 = 3 \times 10^{-7}$ (if we use round values: $\Lambda = 3 \times 10^{-5}$, $\Lambda_0 = 100$), so that the free ion concentration is about 3×10^{-11}. This corresponds to an excluded volume of $3 \times 10^{-11} \times Nv = 2 \times 10^{-4}$ cc per liter of $10^{-4}N$ solution. To this, we add a volume of 10^{-4} $N.2. (4\pi a^3/3) \approx 0.11$ cc corresponding to the ion pairs assumed to be pairs at contact. Gross and Halpern would have us exclude a volume v for each ion pair, while the probability calculation made above indicates that ion pairs are predominantly ions in contact.

We wish also to correct several erroneous statements appearing in the paper by Gross and Halpern. They state ". . . they (Fuoss and Kraus) have to assume for example that a molecule and an ion are bound to a triple ion even though the binding energy in some cases is smaller than kT . . . ." We are unable to find any binding energies for triple ions that are less than kT. In Table III of our fourth paper, the smallest (numerical) value of log $_{10}k_3$ is 1.56 which corresponds to log nat $k_3 = 3.58$. This is equivalent to a dissociation energy of about $3kT$ per triple ion, that is, twice the average kinetic energy. In this case the dissociation of triple ions was so nearly complete that we were unwilling to assign an experimental value to the constant. Again, quoting: "the main points which Fuoss and Kraus consider as experimental verification of Bjerrum's ionic association may be enumerated as follows: (a) with a suitably chosen value a_1 for the minimum distance of approach between the ions it is possible to calculate the variation of the logarithm of the molecular dissociation constant for changes in the dielectric constant of the medium; the following relation is found to hold:

$$\log K_1 \sim 1/D."$$

And again: "The fact that the logarithm of the dissociation constant varies proportional to $1/D$, and that this variation is implied in Bjerrum's picture cannot be thought to corroborate the latter." Reference to Eq. (7) of our third paper will show that the logarithm is not proportional to $1/D$ but that

$$\log K \sim \log D + A/D.$$

This formula covers a range of experimental data to which the simple equation cited by Gross and Halpern does not apply.

In conclusion, we wish to point out that our formulation of the problem of electrolytic solutions provides a simple and consistent picture of these solutions which reproduces the experimental data over a wide range of conditions. In contrast, the theory of Halpern and Gross fails to reproduce experimental observations even in a narrow range of concentration, and in solvents of lowest dielectric constant.

Heat Capacity Curves of the Simpler Gases. VI. Rotational Heat Capacity Curves of Molecular Deuterium and of Deuterium Hydride. The Equilibrium Between the Ortho and Para Forms of Deuterium. Free Energy, Total Energy, Entropy, Heat Capacity and Dissociation of H^2H^2 and of H^1H^2, to 3000°K[1]

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Heat capacities, entropies, free energies, total energies and dissociation constants have been calculated for H^2H^2 and for H^1H^2, to 3000°K, by reliable methods and are listed in tabular form. The ortho-para equilibrium in H^2H^2 has been considered for both the gaseous and the solid states. The solid state equilibrium has been discussed from the point of view of its bearing on the application of the third law of thermodynamics. The rotational heat capacity curves of the various forms of H^2H^2 and that of H^1H^2 are shown graphically and are compared with the rotational heat capacity curve of ordinary hydrogen and with the hypothetical rotational specific heats of gaseous nitrogen. The heavy molecules, H^2H^2 and H^1H^2, dissociate to only about one-half the extent of H^1H^1 below 3000°K. The three hydrogen molecules are compared with respect to the influences of molecular stretching and of anharmonic vibration in the high temperature heat capacities. We also include tables which show the distributions of molecules among the vibrational levels as a function of the temperature.

THE growing importance of deuterium and its compounds, and its increasing availability, warrant the preparation of accurate and extensive tables of its thermodynamic properties. Particular interest also attaches to the rotational heat capacity curves of molecular deuterium, which possesses ortho and para modifications, and of deuterium hydride, which exists in only one form.

We have carried out accurate calculations of this character by the summation method[1] which Davis and Johnston[1] have shown is, for the special case of hydrogen, *more rapid* than approximation methods.[2]

The discrete energies, E_i, were calculated by the equation

* Charles A. Coffin Research Fellow, 1933–34.

[1] Previous papers in this series have been published in the Journal of the American Chemical Society. These include calculations on NO [Johnston and Chapman, J. Am. Chem. Soc. **55**, 153 (1933)], on O_2 [Johnston and Walker, ibid. **55**, 172, 187 (1933)], on neutral OH [Johnston and Dawson, ibid. **55**, 2744 (1933)], on CO and N_2 [Johnston and Davis, ibid. **56**, 271 (1934)] and on ordinary H_2 [Davis and Johnston, ibid. **56**, 1045 (1934)]. The equations appropriate to the exact summation method, and the labor saving use of "corrected approximations," in obtaining sums for the excited vibrational levels, used again in this paper, are discussed in the paper by Johnston and Chapman. As we do not wish to employ space to repeat details of that treatment, the reader is referred to these earlier papers.

[2] Giauque and Overstreet, J. Am. Chem. Soc. **54**, 1731 (1932); Johnston and Davis, ibid. **55**, 271 (1934); Kassel, J. Chem. Phys. **1**, 576 (1933); Gordon and Barnes, ibid. **1**, 297 (1933).