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# THE INTER-IONIC ATTRACTION THEORY OF IONIZED SOLUTES. I. CRITICAL PRESENTATION OF THE THEORY

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## Purpose of these Articles

There seems to be good reason to hope that the recent papers of Milner[1,2] and of Debye and Hückel,[3,4] may furnish for the first time a satisfactory explanation of the deviations of largely ionized substances from the laws of perfect solutions, at any rate up to moderate concentrations, and thus bring to a certain measure of fruition the innumerable researches made upon this subject during the last thirty-five years. The great importance of this new "inter-ionic attraction" theory has led me to prepare these articles.

The fundamental idea underlying the treatments of Milner and of Debye and Hückel is that, owing to the electrical attraction between the positive and negative ions, there are on an average in the neighborhood of any ion more ions of unlike sign than of like sign; and that consequently, when a solution is diluted, the separation of the ions involves doing internal work against this electrical attraction and a corresponding increase in the energy content of the solution. Evidently, in case this theory proves to account fully for the deviations of the behavior of ions from that of perfect solutes, it will confirm the view, recently supported by several investigators,[5] that most of the largely ionized substances are practically completely ionized up to moderate concentrations.

The treatment of Milner involved mathematical considerations so difficult as to make it scarcely available to chemists or physicists with ordinary mathematical training. The more recent derivation of Debye and Hückel, on the other hand, is based on a few fundamental physical principles whose application presents no serious mathematical difficulties.

I am greatly indebted to many of my colleagues in the chemistry and physics departments of this Institute for suggestions and criticisms as to the theoretical treatment; also to the Carnegie Institution of Washington, whose financial grants made possible the long series of experimental researches carried out in this field under my direction.

[1] Milner, *Phil. Mag.*, **23**, 551 (1912).

[2] Milner, *ibid.*, **25**, 742 (1913).

[3] Debye and Hückel, *Physik. Z.*, **24**, 185 (1923).

[4] Debye, *ibid.*, **24**, 334 (1923); also in *Rec. trav. chim.*, **42**, 597 (1923).

[5] See especially, (a) Bjerrum, *Z. Elektrochem.*, **24**, 231 (1918); (b) *Z. anorg. Chem.*, **109**, 275 (1920); also (c) Noyes and Sherrill, "Chemical Principles," Macmillan Co., N. Y., **1922**, pp. 123–126, 153, 172; (d) Lewis and Randall, "Thermodynamics," McGraw-Hill Book Co., N. Y., **1923**, pp. 317–319; and (e) Brönsted, THIS JOURNAL, **42**, 761 (1920); **44**, 877, 938 (1922); **45**, 2903 (1923).

## Derivation of the Energy Effect Due to Electrical Forces between the Ions

The derivation of Debye and Hückel of the relation mentioned in the heading is based on two general principles. One, the so-called Boltzmann's principle, is borrowed from the kinetic theory; and the other, known as Poisson's equation, is derived from the laws of electrostatics and involves Coulomb's law. They apply these principles in the first place to determine the distribution of the ions of opposite charges around any selected ion, and to evaluate the potential that prevails around that ion in consequence of its own charge and of the unequal distribution which it produces in the surrounding ions. The following considerations will become clearer by reference to Fig. 1. In this figure the dot at the center represents an ion of valence $\pm\nu$ and charge $\pm \nu e$; and this produces in any shell of volume $dv$ located between the distances $r$ and $r + dr$ a potential P and a density of electric charge D.

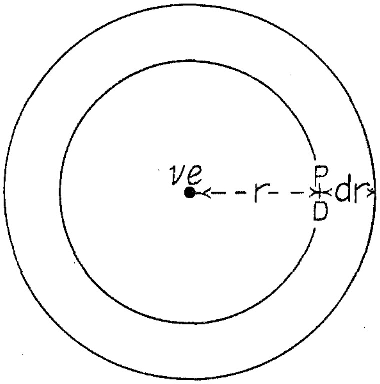

Fig. 1.

The Boltzmann principle[6] may be stated as follows. When a large number of molecules possessing an average kinetic energy $\frac{3}{2}\,kT$ are distributed throughout a region in which there prevail at different points different fields of force (and therefore, different electric potentials) whereby any kind of molecule $A$ in any given volume-element $dv$ acquires a potential energy $E$, the number of such molecules will equal the number $n_{\mathrm{A}}$ per unit volume in a place where this energy is zero, multiplied by the factor $\mathrm{e}^{-E/kT}$ and by the volume $dv$. We apply this principle to determine the distribution of ions in a solution containing per unit volume $n_{\mathrm{A}}$ positive ions of A with valence $\nu_{\mathrm{A}}$ and charge $+\nu_{\mathrm{A}}e$, $n_{\mathrm{B}}$ negative ions of B with valence $\nu_{\mathrm{B}}$ and charge $-\nu_{\mathrm{B}}e$, $n_{\mathrm{C}}$ positive ions of C with valence $\nu_{\mathrm{C}}$ and charge $+\nu_{\mathrm{C}}e$, $n_{\mathrm{D}}$ negative ions of D with valence $\nu_{\mathrm{D}}$ and charge $-\nu_{\mathrm{D}}e, \ldots$ Since the potential energy $E$ of any ion is $\pm\nu e\mathrm{P}$, there are evidently the following numbers of these ions in any volume element $dv$ in which an electric potential P prevails:

$$n_{\mathrm{A}}\,\mathrm{e}^{-\frac{\nu_{\mathrm{A}}e\mathrm{P}}{kT}}\,dv;\; n_{\mathrm{B}}\,\mathrm{e}^{\frac{\nu_{\mathrm{B}}e\mathrm{P}}{kT}}\,dv;\; n_{\mathrm{C}}\,\mathrm{e}^{-\frac{\nu_{\mathrm{C}}e\mathrm{P}}{kT}}\,dv;\; n_{\mathrm{D}}\,\mathrm{e}^{\frac{\nu_{\mathrm{D}}e\mathrm{P}}{kT}}\,dv;\; \ldots \tag{1}$$

Developing the exponential quantities in a series (by the formula $\mathrm{e}^x = 1 + x + \frac{1}{2}x^2 + \ldots$), and neglecting all terms after the second,[7] this

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[6] For an elementary derivation of this principle, see Jäger, "Fortschritte der kinetischen Gastheorie," Vieweg und Sohn, Braunschweig, **1919**, pp. 67–70.

[7] The authors state that they have considered the effect of neglecting these higher terms and find it to be negligible, except at fairly high concentrations.

equation becomes

$$n_{\mathrm{A}}\left(1-\frac{\nu_{\mathrm{A}}e\mathrm{P}}{kT}\right)dv;\ n_{\mathrm{B}}\left(1+\frac{\nu_{\mathrm{B}}e\mathrm{P}}{kT}\right)dv;\ n_{\mathrm{C}}\left(1-\frac{\nu_{\mathrm{C}}e\mathrm{P}}{kT}\right)dv;\ n_{\mathrm{D}}\left(1+\frac{\nu_{\mathrm{D}}e\mathrm{P}}{kT}\right)dv;\ \ldots \quad (2)$$

The Poisson equation applied to a case where the potential $\mathrm{P}$ changes with the distance $r$ by the same amount in all radial directions from a central point[8] has the following form, in which $\mathrm{D}$ denotes the density of electricity at distance $r$, and $\mathrm{K}$ is the dielectric constant of the medium

$$\frac{1}{r^2}\frac{d}{dr}\left(r^2\frac{d\mathrm{P}}{dr}\right)=\frac{d^2\mathrm{P}}{dr^2}+\frac{2}{r}\frac{d\mathrm{P}}{dr}=-\frac{4\pi\mathrm{D}}{\mathrm{K}} \quad (3)$$

This differential equation evidently shows how the potential gradient or field strength $d\mathrm{P}/dr$ varies with the electric density $\mathrm{D}$ and the distance $r$. In order to solve it for $\mathrm{P}$ in terms of $r$, we must express the density $\mathrm{D}$ as a function of the potential $\mathrm{P}$ or of the distance $r$. Debye and Hückel show that the former can be done in the following manner. By multiplying the number of ions of each kind present in any volume-element $dv$ (as shown by Expression 2 above) by their respective charges $\nu_{\mathrm{A}}e$, $-\nu_{\mathrm{B}}e$, $\nu_{\mathrm{C}}e$, $-\nu_{\mathrm{D}}e$, .., summing, dividing by $dv$, and noting that $n_{\mathrm{A}}\nu_{\mathrm{A}}+n_{\mathrm{C}}\nu_{\mathrm{C}}\ldots = n_{\mathrm{B}}\nu_{\mathrm{B}}+n_{\mathrm{D}}\nu_{\mathrm{D}}\ldots$ (since the average number of equivalents of positive and negative ions are equal), we evidently get for the electric density $\mathrm{D}$ in that volume-element the following expression

$$\mathrm{D}=-\frac{e^2\mathrm{P}}{kT}(n_{\mathrm{A}}\nu_{\mathrm{A}}^2+n_{\mathrm{B}}\nu_{\mathrm{B}}^2+n_{\mathrm{C}}\nu_{\mathrm{C}}^2+n_{\mathrm{D}}\nu_{\mathrm{D}}^2+\ldots)=-\frac{e^2\mathrm{P}}{kT}\Sigma(n\nu^2) \quad (4)$$

We now substitute this value of $\mathrm{D}$ in Equation 3, and write a single constant $B^2$ in place of the resulting coefficient of $\mathrm{P}$; namely, we put

$$B^2=\frac{4\pi e^2\cdot\Sigma(n\nu^2)}{\mathrm{K}\,kT} \quad (5)$$

The differential equation can then be solved, the general solution being

$$\mathrm{P}=I\,\frac{\mathrm{e}^{-Br}}{r}+I'\,\frac{\mathrm{e}^{Br}}{r} \quad (6)$$

In this expression $I$ and $I'$ are integration constants to be determined from the limiting conditions in our special case. The constant $I'$ must evidently be equal to zero, since otherwise $\mathrm{P}$ would approach infinity (instead of zero) as $r$ approaches infinity. The value of the constant $I$ is determined by Debye and Hückel for the two cases that the central ion may be regarded as a point, and as a sphere of definite radius. In the former case, which will alone be considered here, its value is $\pm\nu e/\mathrm{K}$, if $\pm\nu e$ denotes the charge on the central positive or negative ion of valence $\nu$ under consideration and $\mathrm{K}$ is the dielectric constant of the medium. This value follows from the fact that, when the concentration of the surrounding ions is negligible (so that $\Sigma(n\nu^2)=0$ and $B=0$), the expression for the potential

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[8] See Houston, "Introduction to Mathematical Physics," Longmans, Green and Co., London and N. Y., **1912**, p. 24.

must reduce to that caused by a point charge in an ion-free medium, namely, to $\pm\nu e/\mathrm{K}r$. This conclusion may also be derived, as is done by Debye and Hückel, from the consideration that it must hold true as $r$ approaches zero, since in the region around the central ion the number of other ions present is negligible. Hence we get for the potential P at the distance $r$ from a positive or negative ion of valence $\pm\nu$ the expression

$$\mathrm{P} = \frac{\pm\nu e}{\mathrm{K}}\,\frac{\mathrm{e}^{-Br}}{r} \tag{7}$$

From this point on, we may proceed in two ways. Debye and Hückel employ the following method. They resolve the expression for the potential P into two terms, as follows

$$\mathrm{P} = \frac{\pm\nu e}{\mathrm{K}r} - \frac{\pm\nu e}{\mathrm{K}r}(1 - \mathrm{e}^{-Br}) \tag{8}$$

The first term evidently represents the potential at the distance $r$ that would be caused by the central ion if there were no surrounding ions, and the second term therefore represents the potential at that distance that arises from the "ion-atmosphere," that is, from the unequal distribution of the positive and negative ions in the surroundings. This last term, however, has the same value for all small values of $r$ (since for such values the parenthesis reduces to $Br$ upon developing it in a series). This is also the potentials $\mathrm{P}_0$ at distance zero, and therefore the potential of the ion itself in so far as this arises from its ion-atmosphere. Its value for an ion of charge $\pm\nu e$ is seen to be

$$\mathrm{P}_0 = \mp\frac{\nu eB}{\mathrm{K}} \tag{9}$$

The increase $\delta U$ in the energy of such an ion with charge $\pm\nu e$ caused by removing it from its ion-atmosphere is therefore

$$\delta U = \frac{\nu^2e^2B}{\mathrm{K}} \tag{10}$$

For the removal from the influence of their ion-atmospheres of all the ions in any given solution the energy increase may evidently be found by summing the $\delta U$ values for all the separate ions and dividing the result by 2 (since otherwise the effect from separating any given pair of ions would be counted twice). In view of the additivity of the energy effects, we may, moreover, distribute this sum among the different kinds of ions. Thus, the energy-increase $\Delta U$ attending the removal of $\tilde{n}$ molecules (constituting one mole) of any particular kind of ion of valence $\nu$ is given by the following expression; it being understood that all the other ions present in the solution are simultaneously removed and that their removal is attended by other energy effects.

$$\Delta U = \frac{\tilde{n}\,e^2\nu^2B}{2\mathrm{K}}$$

Resubstituting also the expression for the constant $B$ given by (5), we get for this molal energy of dilution

$$\Delta U = \frac{\sqrt{\pi}\, e^3 \tilde{n}\, \nu^2 \sqrt{\Sigma\,(n\,\nu^2)}}{\mathrm{K}^{1.5}\,(kT)^{0.5}} \tag{11}$$

We may also derive Equation 11 from Expressions 1 to 7 by the following considerations, which seem worthy of presentation, since the treatment from a different viewpoint affords a certain confirmation of the result and may serve to make the matter clearer.

We will consider each ion to be separately removed from all the other ions in the solution against the forces prevailing between it and those ions and formulate the resulting change in energy. Consider first any volume-element $dv$ around any selected ion of charge $\pm\nu\, e$ in the form of a spherical shell of radius $r$ and thickness $dr$, and therefore of volume $4\pi r^2 dr$ (see Fig. 1). The number of ions of the various kinds located in any such volume-element is shown by Expression 2, and the resultant charge upon them is given by Equation 4 multiplied by $dv$. The energy-increase $\delta U$ attending the removal of the selected ion from these ions is evidently equal to minus the product of this charge by its own charge $\pm\nu\, e$ divided by the quantity $\mathrm{K}r$. It is therefore given by the following equations, the last of which results from the first by substituting for $\mathrm{P}$ its value given by Equation 7:

$$\delta U = \frac{\pm\nu\, e}{\mathrm{K}r}\,\frac{e^2\mathrm{P}}{kT}\,\Sigma(n\nu^2)\cdot 4\pi r^2 dr = \frac{4\pi e^4\nu^2}{\mathrm{K}^2 kT}\,\Sigma(n\nu^2)\cdot \mathrm{e}^{-Br}\,dr \tag{12}$$

To get the total energy-increase attending the removal of the selected ion from all the ions we must evidently sum the separate effects for all the concentric shells surrounding it; in other words, integrate Equation 12 for values of $r$ between zero and infinity. Carrying out this integration, there results

$$\frac{4\pi e^4\nu^2}{\mathrm{K}^2 kTB}\,\Sigma(n\nu^2) \tag{13}$$

To find the energy increase attending infinite dilution of the solution or the removal of all the ions in it from one another, we must evidently multiply Expression 13 by the number of ions of each particular kind present, sum the products for all the kinds of ions, and divide the result by 2 (so as to avoid counting the effect for each pair of ions twice). Correspondingly, the molal energy of dilution, $\Delta U$, for any kind of ion of valence $\pm\nu$ is evidently obtained simply by multiplying (13) by half the mole-molecule number $\tilde{n}$. Doing this and substituting the value of $B$ given by 5, we get

$$\Delta U = \frac{\sqrt{\pi}\, e^3 \tilde{n}\, \nu^2 \sqrt{\Sigma(n\nu^2)}}{\mathrm{K}^{1.5}\,(kT)^{0.5}} \tag{14}$$

This equation will be seen to be identical with Equation 11.

Substituting in Equation 11 or 14 $\tilde{n}c$ for $n$ (where $n$ denotes the number of molecules per cubic centimeter and $c$ the number of moles per cubic centimeter) and writing $R$ for $\tilde{n}k$, the following equation results

$$\Delta U = \frac{\sqrt{\pi}\, e^3\, \tilde{n}^2\, \nu^2 \sqrt{\Sigma\,(c\nu^2)}}{\kappa^{1.5}\,(RT)^{0.5}} = \frac{A\, \nu^2 \sqrt{\Sigma\,(c\nu^2)}}{\kappa^{1.5}\, T^{0.5}} \tag{15}$$

As is done in the last member of (15), we shall hereafter write a single letter $A$ for the product of the universal constants, whose value is found, by putting $\pi = 3.142$, $R = 8.315 \times 10^7$, $\tilde{n} = 6.06 \times 10^{23}$ and $e = 4.774 \times 10^{-10}$, to be as follows

$$A = e^3\, \tilde{n}^2 \sqrt{\pi/R} = 7.77 \times 10^{15} \text{ in c.g.s. units} \tag{16}$$

In Equation 15 $\Delta U$ denotes the difference in the energy-content of one mole of ions of valence $\pm\nu$, when present at temperature $T$ in an infinitely dilute solution and when present in a solution containing these and other ions at such concentrations that the sum of the products of the concentration $c$ of each kind of ion by the square of its valence $\nu$ is $\Sigma(c\nu^2)$; the dielectric constant of the solution being $\kappa$. It should be noted, however, that this constant is that which prevails in the immediate neighborhood of the ions and that its value, owing to electrostriction,[9] will be somewhat greater than that of the solvent as a whole.

In the general case where $N_{\mathrm{A}}$ moles of ion A, $N_{\mathrm{B}}$ moles of ion B,... are present in the solution, the difference between their energy-contents in the infinitely dilute and in the more concentrated solution is evidently given by the following expression (which corresponds to the result of Debye and Hückel[10] when the size of the ions is neglected):

$$\Sigma\,(N\cdot \Delta U) = \frac{A\cdot\Sigma(N\nu^2)\cdot\sqrt{\Sigma(c\nu^2)}}{\kappa^{1.5}\, T^{0.5}} \tag{17}$$

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[9] See Drude and Nernst, *Z. physik Chem.*, **15**, 79 (1894), also Drude, "Physik des Aethers," [Ferdinand Enke, Stuttgart, **1912**] p. 127. These authors show thermodynamically that the electric field around an ion exerts a pressure upon the solvent, whereby its density is increased. Falchenberg [*Ann. Phys.*, **61**, 159 (1920)] has shown experimentally that for water up to 200 atmospheres the dielectric constant increases linearly with the increase in density. Assuming that this proportionality continues up to higher pressures and using the compressibility data of Bridgman, the general magnitudes of these effects are calculated to be a pressure of 9000 atm. and a 18% increase in the density and dielectric constant at a distance $10^{-8}$ cm. from a univalent ion considered as a point charge, and 1000 atm. and a 4% increase at a distance of $1.7 \times 10^{-8}$ cm. A correction for these effects might be applied to the interionic attraction theory; but this will not be attempted here. These results serve, however, to show that the electrostriction might cause a decrease of many per cent. in the calculated energy of dilution (especially in the case of the hydrogen ion, which can perhaps be treated as a point charge).

[10] Ref. 3, p. 193, Equations 22 and 23.

For the special case that only two kinds of ions of equal valence $\nu$ are present at the same molal concentration $c$, these equations become

$$2\Delta U = \frac{2A\nu^2\sqrt{2c\nu^2}}{\kappa^{1.5}T^{0.5}} \tag{18}$$

Here $2\Delta U$ evidently denotes the energy change attending infinite dilution of that volume of solution containing one mole of each of these ions.

Milner had previously determined the energy effect corresponding to the inter-ionic attraction for the case of a single salt with ions of equal valence by a very different method from that used by Debye and Hückel. It is therefore important to compare the results of the two treatments.

Milner also makes use of the Boltzmann principle of the non-uniform distribution of the ions resulting from the electrical potential due to their attractions and repulsions. But, instead of employing the Poisson equation expressing a relation between potential gradient and density of space charge, he determines the energy change corresponding to this electric effect by summing, in the case of a particular configuration of the ions, for each pair of ions which can be formed out of all those in the solution the product of their mutual electrical force into the distance between them, multiplying this sum by the probability of the occurrence of this configuration, and summing for every possible configuration of the ions in the solution.[11] The intricate character of these operations is evident from this statement; and the apparently successful treatment of them may well excite admiration.

Milner by this method derives the following expression[12] (using the notation of this article) for the energy-increase $2\Delta U$ attending the infinite dilution at temperature $T$ of a solution containing one mole of positive ions and one mole of negative ions, each of valence $\nu$ and at concentration $c$:

$$2\Delta U = -RT\,h{\cdot}f(h), \text{ where } h = \left(\frac{8\pi\tilde{n}c}{3}\right)^{\frac{1}{3}}\frac{e^2\nu^2\tilde{n}}{\kappa RT} \tag{19}$$

In this equation $f(h)$ is a function for which an algebraic expression could not be obtained, but for which numerical values were calculated up to moderate concentrations.

In order to make this equation become completely identical with Equation 18, it is necessary to assume that $h{\cdot}f(h) = -\sqrt{3h^3}$. To show how closely this is fulfilled, the values of $-h{\cdot}f(h)$ calculated by Milner for various values of $h$ (and therefore for certain values at 0° of the concentration $c$ and valence $\nu$), are given in Table I, together with the corresponding values of the ratio $-h{\cdot}f(h)/\sqrt{3h^3}$ (which must equal unity to make Equations 18

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[11] Ref. 1, p. 552.

[12] Ref. 2, pp. 745–746.

and 19 identical).[13] The concentration $c$ is here expressed in moles per liter.

TABLE I

COMPARATIVE VALUES OF MILNER'S FUNCTION

| $c\,\nu^6$ | $h$ | $-h.f(h)$ | $-h.f(h)/\sqrt{3h^3}$ |
|---|---|---|---|
| 0.0001 | 0.0559 | 0.0168 | 0.734 |
| .001 | .120 | .0525 | .728 |
| .002 | .152 | .0735 | .715 |
| .005 | .206 | .114 | .704 |
| .01 | .259 | .159 | .696 |
| .02 | .327 | .222 | .685 |
| .05 | .443 | .345 | .675 |
| .10 | .559 | .486 | .670 |
| .20 | .704 | .672 | .656 |

It will be observed that the ratio does not change very rapidly with the concentration. Hence there would be a comparatively small error in regarding the ratio as having the constant value 0.667 between the upper limit of concentration (say $c\,\nu^6 = 0.20$) up to which Milner considers the calculation of $f(h)$ reasonably accurate and the lower limit (say $c\,\nu^6 = 0.0001$) below which the value of $h.f(h)$, and therefore the electrical effect, becomes relatively insignificant (thus only 2.5% of what it is at $c\,\nu^6 = 0.20$). Milner's expression for the energy change $2\Delta U$ attending infinite dilution of a solution containing one mole of positive ions and one mole of negative ions of the same valence is, therefore, approximately two-thirds of that required by Equation 18.

There seems to be no possibility of reconciling this divergence between the result of Milner and that of Debye and Hückel except by a detailed reconsideration of Milner's derivation by a competent mathematician. For the present it seems therefore best to adopt the more simply derived expression of Debye and Hückel, and this will be done in the following discussions of this article. It should, however, be realized that the divergence is of relatively minor significance, and that the general concordance of the two results, involving as they do elaborate kinetic considerations of molecular effects, is more striking than their disagreement.

It may next be pointed out that the energy quantity calculated by Milner or by Debye and Hückel differs in significance from that commonly considered in free-energy considerations. Namely, these authors have in substance derived the energy change attending the infinite *dilution* of a solution containing one mole of positive and one mole of negative ions of

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[13] Milner makes a statement in a footnote of his first article (p. 575), without presenting its derivation, that "it may be shown that as an approximation and when $h$ is very small" the relation becomes that expressed by the equation $h{\cdot}f(h) = -\sqrt{3h^3\pi/2} = -1.253\sqrt{3h^3}$. This does not seem, however, to accord with his computed values reproduced in the above table; but it may do so in case the ratio increases very rapidly at extremely small concentrations.

valence $\nu$, each at concentration $c$, while in free-energy considerations there is involved the energy-change or heat-content change attending the *transfer* of one mole of each of these ions from an infinite volume of such a solution to an infinite volume of a very dilute solution. These two energy quantities are, however, not identical, but are related to each other in a way that will now be shown.

We may consider the transfer of ions to be made as follows: (1) cut off the volume containing one mole of positive and one mole of negative ions at concentration $c$ from a volume of the solution containing a very large number $(N + 1)$ of moles of each of these ions, and add to the remaining solution an equal volume of water; (2) dilute the cut-off solution (containing one mole of each of the ions) with enough water to make the inter-ionic attraction negligible and the ions perfect solutes; (3) unite this solution with an infinite volume of an equally dilute solution, and remove from the latter a volume of water equal to that added. The energy-change attending Step 3 is zero since the ions then act as perfect solutes; that attending Step 2 is the energy of dilution $2\,\Delta U$ given by Equation 18; and that attending Step 1 may be found as follows. Replacing all the quantities except the concentration $c$ in Equation 18 by a single factor $2G$, and writing for $\Delta U$ the difference $U_0 - U$ in the energies of the ions at concentrations 0 and $c$, we get for the energy-increase attending Step 2:

$$2U_0 - 2U = 2G\,c^{0.5} \tag{20}$$

Differentiating this equation, we get $2\,dU = -G\,dc/c^{0.5}$, where $2\,dU$ denotes the energy increase attending such dilution of a solution containing one mole of each of the ions as causes a concentration-decrease, $-dc$. In Step 1, however, a solution containing $N$ moles of each ion is so diluted, and the concentration decrease, $-dc$, is equal to $c/(N + 1)$. Substituting this value in the differential equation just given, multiplying by $N$, and noting that $N/(N+1)$ approaches unity as $N$ increases, the energy-change attending Step 1 is found to be $2\,N\,dU = G\,c^{0.5}$. This is seen to be one-half the energy-change attending the dilution in Step 2 as given by Equation 20. The total energy-increase attending all three steps, or the energy attending the *transfer* is, therefore, three-halves times as great as that attending the *dilution*. This energy of transfer, representing its value for one mole of any ion by $\Delta H$ and taking that of $\Delta U$ from Equation 15, is therefore given by the expression

$$\Delta H = 1.5\,\Delta U = \frac{1.5A\nu^2\sqrt{\Sigma(c\nu^2)}}{\kappa^{1.5}\,T^{0.5}} \tag{21}$$

This energy-increase attending the transfer is substantially identical with the corresponding heat-content increase, more commonly employed in chemical thermodynamics. For the two quantities differ only by the change $\Sigma(pv)$ in the product of the volume times the pressure of the system in its initial and final states,[14] and this difference is negligible in the case of the dilution of dilute solutions or of the transfer of solutes between them. For this reason the symbol $\Delta H$ has been here adopted. It is used in this article, however, primarily to distinguish the process of transfer from that of dilution.

## Thermodynamic Relation between the Energy and Free-Energy Effects

Before any conclusion can be drawn from the energy effect derived above as to the osmotic pressure, freezing point, or other molal property of solutions of largely ionized substances, or as to the activity of their ions, it is necessary to determine what relation that change in energy bears to the maximum work or to the change in free energy attending the same change in state.

From the principles of thermodynamics there can be derived directly from the energy-change the temperature coefficient of the maximum work or of the free-energy change. For this purpose we may use, as do in substance both Milner and Debye and Hückel, the following familiar second-law equation,[15]

$$d\left(\frac{-\Delta A}{T}\right) = \frac{\Delta U}{T^2}\,dT \tag{22}$$

In this equation if $\Delta U$ denotes as above the increase in energy in one mole of an ion when removed at temperature $T$ from a solution having a concentration $c$ of such a magnitude that the inter-ionic attraction is appreciable but other causes of deviation are still negligible, to a solution having a concentration $c_0$ so small that the attraction is negligible, then $-\Delta A$ denotes the corresponding decrease in the work content, which is equal to the maximum work producible.

Noting that for perfect solutes $\Delta U$ is zero and that even the concentration $c$ is to be so small that other deviations than that arising from the inter-ionic attraction are negligible, we may substitute in this equation the value of $\Delta U$ given by Equation 18. We obtain thus for one mole of an ion of valence $\nu$ the expression

$$d\left(\frac{-\Delta A}{T}\right) = \frac{A\nu^2\sqrt{\Sigma\,(c\nu^2)}}{\kappa^{1.5}\,T^{2.5}}\,dT \tag{23}$$

This equation can evidently be integrated between definite temperature limits provided the dielectric constant $\kappa$ can be expressed as an empirical function of the temperature between those limits, as is the case, for example, with water between 0° and 76°.

From a purely thermodynamic standpoint, however, this is all that can be attained. To obtain an absolute value of the work content at any temperature, it is necessary to find the indefinite integral of Equation

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[14] Ref. 5 c, p. 210.

[15] Ref. 5 c, p. 284.

23 and to evaluate the integration constant. Milner and also Debye and Hückel carry out this integration by assuming that the dielectric constant $\kappa$ does not vary with the temperature. If this assumption be made, the following expression, in which $I$ is the integration-constant, results:

$$-\Delta A = IT - \frac{2A\nu^2\sqrt{\Sigma(c\nu^2)}}{3\,\kappa^{1.5}\,T^{0.5}} \tag{24}$$

The integration constant $I$ is determined by the fact that, as $\Sigma(c\nu^2)$ approaches zero, the electrical effect expressed by the last term becomes negligible, and the free-energy decrease must become that for a perfect solute, namely, $RT\,ln(c/c_0)$. Substituting this value, we get

$$-\Delta A = RT\,ln\,\frac{c}{c_0} - \frac{2A\nu^2\sqrt{\Sigma(c\nu^2)}}{3\,\kappa^{1.5}\,T^{0.5}} \tag{25}$$

By starting with the second-law free-energy equation, which differs from (22) only in that the work-content decrease $-\Delta A$ is replaced by the free-energy decrease $-\Delta F$, and the energy increase $\Delta U$ by the heat-content increase $\Delta H$, substituting for the latter the expression given by (21), and proceeding exactly as before, the following expressions are obtained for the free-energy decrease attending the *transfer* of one mole of an ion of valence $\nu$ from an infinite volume of a solution in which its concentration is $c$ and in which it and other ions are present at such concentrations as correspond to $\Sigma(c\nu^2)$, to an infinite volume of a solution in which its concentration is $c_0$ and which is so dilute that all the ions present behave as perfect solutes.

$$d\left(\frac{-\Delta F}{T}\right) = \frac{1.5A\nu^2\sqrt{\Sigma(c\nu^2)}}{\kappa^{1.5}\,T^{2.5}}\,dT \tag{26}$$

$$-\Delta F = RT\,ln\,\frac{c}{c_0} - \frac{A\nu^2\sqrt{\Sigma(c\nu^2)}}{\kappa^{1.5}\,T^{0.5}} \tag{27}$$

By comparing (25) with (15) and (27) with (21), it is seen that the effect of the inter-ionic attraction is to diminish the work-content decrease or the free-energy decrease in the case of perfect solutes by an amount equal to two-thirds of the energy of dilution or of the heat of transfer, respectively.

There seems, however, to be no sufficient *a priori* justification[16] for carrying out the integration under the assumption that the dielectric constant of the solvent does not vary with the temperature; and it is also clearly inadmissible to evaluate the indefinite integral by introducing an empirical temperature function of the dielectric constant valid only through a limited temperature range. Hence, the only conclusion that can in

[16] Milner (Ref. 2, p. 748), to be sure, suggests that the assumption of a non-variable dielectric constant may be justified by the fact that this assumption was implicitly made in determining the electrical effect, since otherwise the electrical force between two ions would depend on their kinetic energies as well as on their positions.

strictness be drawn from thermodynamic considerations alone as to the difference between the free-energy change $\Delta F$ and that $\Delta F_0$ which would result if the ions were perfect solutes is that given by the following equation

$$\Delta F - \Delta F_0 = A \cdot f\,(T, \kappa) \cdot \nu_A{}^2 \sqrt{\Sigma\,(c\nu^2)} \qquad (28)$$

In this equation $A$ is a numerical factor consisting of universal constants and $f(T, \kappa)$ is an unknown temperature function, which is constant for solutions in any definite solvent at any definite temperature.

Even if this result were all that could be attained, it would be of great importance since it shows how the deviation of the free energy arising from the inter-ionic attraction varies at any definite temperature with the concentration and valence of the ions. It will be shown, however, in the following sections that kinetic considerations lead to a complete solution of the problem.

## Kinetic Derivations of the Osmotic Pressure and Free Energy of Ions

The foregoing considerations have made it clear that, although a purely thermodynamic treatment of the inter-ionic attraction leads to important functional relations (those expressed by Equations 26 and 28) showing the variation of the free energy of the ions with the temperature and its variation at any definite temperature with their concentration and valence, yet it does not furnish a conclusive means of determining the absolute value of the free energy at any concentration and temperature. For further development of the theory we must therefore resort to kinetic or molecular considerations. Since the mechanism of the inter-ionic attraction, as derived from the underlying hypothesis, is clearly defined in terms of molecular electrical attractions, it is to be expected that such considerations properly worked out will lead to a definite result.

Milner[17] obtained, in fact, directly from kinetic considerations an expression for osmotic pressure by substituting his value of the energy of the ions in the virial equation[18] of Clausius. This equation, as derived for gases, is as follows

$$p\,v = \tfrac{1}{3}\,nmu^2 - \tfrac{1}{3}\,\Sigma\,(f{\cdot}r) \qquad (29)$$

In this expression $\Sigma(f \cdot r)$, called the virial, denotes the sum (for all the pairs of the $n$ molecules in volume $v$ of the gas) of the products of the force $f$ between the molecules of each pair and their distance $r$ apart. When the force function is of the form $f = X/r^2$ (so that $f \cdot r = X/r$), the virial is evidently the difference between the energy which the molecules possess in a perfect gas (where they may be considered to be at an infinite distance) and that in the actual gas. This corresponds, however, to the energy of

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[17] Ref. 2, p. 747.

[18] See Jäger, Ref. 6, pp. 56–58, 85–86.

the ions as calculated by Milner and by Debye and Hückel. If, therefore, we may assume that the virial equation is applicable also to solutions when the osmotic pressure is replaced by the gas pressure, we can at once derive, as Milner did, an expression for the osmotic pressure. Namely, by substituting for $\Sigma(f \cdot r)$ in (29) the expression for $2\,\Delta U$ given by Equation 18, and writing $2RT$ for $\frac{1}{3}nmu^2$, we get the following expression for the osmotic pressure $P$ of a solution containing one mole of positive ions and one mole of negative ions of valence $\nu$ in the volume $v$ (each at concentration $c$).

$$P\,v = 2RT - \frac{2A\nu^2\sqrt{2c\nu^2}}{3\mathrm{K}^{1.5}\,T^{0.5}} \tag{30}$$

Substituting $1/c$ for $v$ and transforming, we get

$$P = 2cRT - \frac{2Ac\nu^2\sqrt{2c\nu^2}}{3\mathrm{K}^{1.5}\,T^{0.5}} \tag{31}$$

From this we can derive an expression for the free-energy decrease $-\Delta F$ attending the transfer of one mole of positive ions and one mole of negative ions from a solution of osmotic pressure $P$ in which each of the ions has a concentration $c$ to a solution of osmotic pressure $P_0$ in which each has a concentration $c_0$ so small that the inter-ionic attraction is negligible, by means of the general thermodynamic relation:[19]

$$-\Delta F = \int_{\mathrm{P}_1}^{\mathrm{P}_2} -v dP;\ \text{which in this case becomes} - 2\,\Delta F = \int_{\mathrm{P}_0}^{\mathrm{P}} \frac{dP}{c} \tag{32}$$

Differentiating (31) with respect to $c$, we find

$$dP = 2RT\,dc - \frac{A\sqrt{2}\,\nu^3 c^{0.5}}{\mathrm{K}^{1.5}\,T^{0.5}}\,dc \tag{33}$$

Dividing this expression by $c$, substituting it in (32), integrating between $c_0$ and $c$, and noting that the last term containing the limit $c_0$ is negligible, we get

$$-2\,\Delta F = 2RT\,ln\frac{c}{c_0} - \frac{2A\nu^2\sqrt{2c\nu^2}}{\mathrm{K}^{1.5}\,T^{0.5}} \tag{34}$$

This result is seen to correspond completely with Equation 27 which was derived thermodynamically under the assumption that the dielectric constant does not vary with the temperature.

Conversely, there can of course be derived from Equation 27 by combining it with (32) the same expression (31) for osmotic pressure that was obtained from the virial equation. Debye and Hückel in fact derived an

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[19] The *work of dilution*, $-2\,\Delta A$, is given by the corresponding integral of $Pdv$, and this is readily shown to have the value required by Equation 25. The *free energy of transfer* is given by the integral of $-vdP$, since in correspondence with the three steps in the process of transfer described above it includes the three quantities of osmotic work, $Pv$, $\int_V^{V_0} Pdv$ and $-P_0\,v_0$, where $v$ and $v_0$ denote the volumes of solvent containing two moles of ions when at the concentration $c$ and at the very small concentration $c_0$.

expression[20] for the freezing-point lowering by starting substantially with the work-content expression given by (25), which was derived by integrating the second-law equation under the assumption that the dielectric constant does not vary with the temperature and applying the thermodynamic-potential method of Planck. They thus obtained a result, valid at small concentrations and generalized for various kinds of ions differing in valence and concentration, which, in virtue of the proportionality up to moderate concentrations between freezing-point lowering and osmotic pressure, may be expressed in terms of the latter in our notation, as follows

$$P = \Sigma c \cdot RT - \frac{A(\Sigma c\nu^2)^{1.5}}{3\kappa^{1.5}T^{0.5}} \qquad (35)$$

This expression evidently becomes identical with Equation 31 when $\Sigma c = 2c$ and $\Sigma(c\nu^2) = 2c\nu^2$, which was the case involved in deriving (31) from the virial equation.

In a more recent article Debye[21] develops from purely kinetic considerations a new complete theory of osmotic pressure; and taking into account the inter-ionic attraction in ways similar to those followed by Debye and Hückel, he arrives at a formula for the osmotic pressure corresponding completely with Equations 31 and 35 and therefore also with Equations 34 and 27 for the free energy of transfer.

The independent kinetic derivations of the osmotic-pressure relation by Milner and by Debye are therefore fully in accord with each other, and they are also in accord with the thermodynamic derivation derived from the energy effect under the assumption that the dielectric constant does not vary with the temperature.

## Kinetic Derivation of the Free Energy of the Ions through Vapor-Pressure Considerations

Owing to the importance of the matter, it seems worth while to present here an independent kinetic derivation based on consideration of the vapor-pressure relations of the free-energy effect due to the inter-ionic attraction. For, as emphasized by G. N. Lewis,[22] vapor pressure (or fugacity) affords a far simpler treatment of the laws of solutions than does the concept of osmotic pressure.

According to the kinetic theory, the vapor pressure of a solvent at any temperature is determined by the following principles: (1) at equilibrium an equal number of molecules must pass in the two opposite directions through the surface layer intermediate between the liquid and gaseous phases; (2) all molecules reaching this layer from the gas side are caught and drawn into the liquid by the molecular attraction; (3) of the molecules

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[20] Their Equation 35, Ref. 3, p. 196.

[21] Ref. 4, pp. 334–338.

[22] Ref. 5d, p. 214.

reaching this layer from the liquid side, only those will pass through the layer into the gas phase which have a velocity component in a vertical direction greater than a certain limiting value $x$, sufficient to enable them to overcome the inward attraction of the surrounding molecules; and (4) the number of such "capable" molecules is determined by the Maxwell distribution law. Formulation of these principles leads to the following expression[23] for the vapor pressure $p$,

$$p = J'RTc_{\mathrm{L}}\,\mathrm{e}^{-(mx^2/2kT)} = JTc_{\mathrm{L}}\,\mathrm{e}^{-(E/RT)} \qquad (36)$$

In this expression $c_{\mathrm{L}}$ denotes the concentration of the liquid in moles per cubic centimeter, $J'$ is a function solely of this concentration, and $E$ is the (minimum) kinetic energy corresponding to the velocity $x$ which one mole of the molecules must possess to escape from the liquid.

An entirely similar expression must hold for the vapor pressure of a solute, its concentration being introduced in place of that of the liquid. In the case of a solute, however, the energy $E$ evidently consists at any very small concentration $c_0$ only of the energy $U_0$ corresponding to the separation of the molecules of the solute from those of the solvent; but at a higher concentration $c$ it includes in addition the energy $U$ of separation of the molecules of the solute from each other. For the two concentrations $c_0$ and $c$ Equation 36 therefore assumes the forms

$$\frac{p_0}{c_0} = JT\,\mathrm{e}^{-\frac{U_0}{RT}}, \text{ and } \frac{p}{c} = JT\,\mathrm{e}^{-\frac{U_0+U}{RT}} \qquad (37)$$

It is evident, however, that the quantities $J$ and $U_0$ will have substantially the same value in the two equations only in case the higher concentration $c$ is still so small that the concentration of the solvent can be regarded as practically the same in the two cases. We will consider that this is the case. Dividing the second of these equations by the first, and taking the natural logarithms of both members, we get

$$ln\,\frac{p/c}{p_0/c_0} = -\frac{U}{RT}; \text{ or } RT\,ln\frac{p}{p_0} = RT\,ln\frac{c}{c_0} - U \qquad (38)$$

Let us now apply this equation to solutions of any kind of ion, considering it to have appreciable vapor pressures $p_0$ and $p$ in the two solutions; and let us consider the case in which the concentration $c$ is still so small that the energy $U_0$ has substantially the same value as at the concentration $c_0$ and that the ordinary attraction between molecules of the solute, for example, of the un-ionized type, would still be negligible, but that the concentration $c$ is nevertheless large enough to produce in the case of ions a considerable inter-ionic attraction corresponding to a considerable energy $U$. This latter energy is evidently that denoted by $\Delta U$ in Equation 15. Substituting its value in the second form of (38), and noting that the first member of that equation is equal to the free-energy decrease

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[23] See Ref. 5c, p. 53.

attending the transfer of one mole of the ions from $c$ to $c_0$, we may write

$$-\Delta F = RT\,ln\frac{c}{c_0} - \frac{A\nu^2\sqrt{\Sigma(c\nu^2)}}{\kappa^{1.5}\,T^{0.5}} \tag{39}$$

This result will be seen to correspond with Equation 34, which was derived from two independent kinetic theories of osmotic pressure; also to be identical with Equation 27, which was derived thermodynamically from the energy effect by integrating the second-law equation under the assumption that the dielectric constant does not vary with the temperature. Why this assumption gives the correct result remains, however, entirely unexplained.

### Expressions for the Activation of the Ions

The expression may now be formulated to which the inter-ionic attraction theory leads for the activities of the ions in dilute solutions. For the simplest and most general method of expressing their deviations from the behavior of perfect solutes is to employ the concept, introduced by G. N. Lewis,[24] of the ion-activity coefficient which is defined as the empirical factor by which in free-energy and mass-action expressions of the forms holding for perfect solutes the concentration must be multiplied in order to make those expressions valid for the imperfect solute under consideration.

This definition of the activity coefficient, which may better be called the *activation*,[25] shows that the free-energy decrease attending the transfer of one mole of ions from a solution of concentration $c$ where the activation is $\alpha$ to one of concentration $c_0$ where the activation is unity, is

$$-\Delta F = RT\,ln\frac{c\alpha}{c_0} \tag{40}$$

Subtracting this equation from Equation 39 we get for the activation $\alpha$ of an ion of valence $\nu$ at temperature $T$ in a solvent of dielectric constant $\kappa$ in which this ion and other ions are present with such valences and at such concentrations as to give rise to the sum $\Sigma(c\nu^2)$ the following expression.

$$ln\ \alpha = -\frac{A\nu^2\sqrt{\Sigma(c\nu^2)}}{R\,(\kappa T)^{1.5}} \tag{41}$$

In this expression $R = 8.32 \times 10^7$; and by (16) $A = 7.77 \times 10^{15}$ when the concentrations are in moles per cubic centimeter.

### Summary and Discussion

There has first been presented (Equations 1–11), in as elementary a form as possible, the derivation given by Debye and Hückel of the energy effect corresponding to this inter-ionic attraction; and for a part of their

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[24] See Ref. 5 d, pp. 255–277.

[25] It seems highly desirable to substitute this term, which corresponds in form and relative significance to the quantitative use of the terms dissociation and ionization, for the awkward term "activity coefficient" heretofore used.

derivation a new alternative treatment (Equations 12–14) has also been given. For the difference $\Delta U$ in the energy possessed by one mole of an ion of valence $\nu$ at absolute temperature $T$ when present in two different solutions of dielectric constant $\kappa$, one of which is infinitely dilute and the other of which contains this ion and other ions of various valences $\nu$ at such molal concentrations $c$ as to give rise to the sum $\Sigma(c\nu^2)$, the following expression (Equations 15–16) was obtained.

$$\Delta U = \frac{A\nu^2\sqrt{\Sigma(c\nu^2)}}{\kappa^{1.5}\,T^{0.5}}$$

In this expression the factor $A$ is the product $e^3\tilde{n}^2\sqrt{\pi/R}$ of certain universal constants ($e$ being the electronic charge, $\tilde{n}$ the number of molecules per mole, and $R$ the gas constant), which has in c.g.s. units the numerical value $7.77 \times 10^{15}$, when the concentrations are expressed in moles per cubic centimeter.

It was then shown (Equation 19 and Table I) that the earlier derivation of Milner based on the same fundamental hypothesis, but employing an entirely different method of treatment leads, when his result is transformed, to this same expression, except for the minor difference that his numerical factor corresponding to $A$ in the foregoing equation varies somewhat with the concentration, and has a value of approximately $\frac{2}{3}\,A$ at moderate concentrations; thus one of $(0.67 \pm 0.03)\,A$ for $\Sigma(c\nu^2)$ between 0.01 and 0.40 $M$ for univalent ions.

It is then shown (Equations 20–21) that this difference $\Delta U$ in the energy of one mole of ions, which is equal to the energy increase that attends the dilution of a solution containing such ions with an infinite volume of solvent, differs in the ratio of $\frac{2}{3} : 1$ from the energy increase $\Delta H$ that attends the transfer of one mole of ions from an infinite volume of the more concentrated solution to an infinite volume of a very dilute solution. This energy quantity $\Delta H$ is substantially identical with the (partial) molal heat of transfer, which is commonly involved in free-energy considerations.

There is then derived (Equations 22–27), by substituting this value of $\Delta H$ in the general second-law free-energy equation and integrating it under the assumption employed by Milner and by Debye and Hückel that the dielectric constant does not vary with the temperature, the following expression (Equation 27) for the free-energy decrease $\Delta F$ attending the transfer of one mole of an ion of valence $\nu$ from a solution in which its concentration is $c$ and in which it and other ions of various valences are present at such concentrations as correspond to the sum $\Sigma(c\nu^2)$, to a solution in which its concentration is $c_0$ and which is so dilute in ions that the effect of the inter-ionic attraction is negligible:

$$-\Delta F = RT\,ln\,\frac{c}{c_0} - \frac{A\nu^2\sqrt{\Sigma c\nu^2}}{\kappa^{1.5}\,T^{0.5}}$$

It is pointed out, as was done by the earlier authors, that there is no *a priori* justification for the assumption of the invariability of the dielectric constant.

This free-energy expression is nevertheless identical with that obtained (Equations 29–35) from the kinetic derivations of the osmotic pressure of ionized substances by Milner's method employing the virial equation of Clausius and from Debye's new theory of osmotic pressure.

A new kinetic derivation based on simple vapor-pressure considerations is then presented (Equations 36–39), and this is shown to lead also to the same free-energy equation. And incidentally the logarithm ($ln\alpha$) of the activity coefficient $\alpha$ of an ion of valence $\nu$ in a solution in which the sum $\Sigma(c\nu^2)$ prevails is shown (Equations 40–41) to be equal to the last term of this free-energy equation divided by $RT$.

This equation has therefore been confirmed in so many independent ways that it may be unhesitatingly adopted as a correct expression of the inter-ionic attraction theory, provided the equation first cited in this summary, which is involved in all the free-energy derivations, correctly represents the corresponding energy effect. This energy equation, except for the minor divergence mentioned above, is, however, confirmed by the entirely independent treatments of Milner and of Debye and Hückel. Further inexactness may, however, be introduced in applying the equation, owing to the fact that the dielectric constant prevailing in the neighborhood of the ions may be somewhat larger than that of the solvent as a whole. Moreover, the derived expressions can be expected to be valid only when the ion concentrations are still so small that the size of the ions can be neglected in comparison with the distance between them, and that the other simplifications made in the mathematical treatments are insignificant.

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