

The theory of electrolytes. I. Freezing point depression and related phenomena

Written by *P. Debye & E. Hückel (1923)*; Translated and Typeset by *Michael J. Braus (2019)*

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Translator's Preface

This document is an English translation and complete typesetting of a seminal paper in the field of electrolyte chemistry, written by Peter Debye and Erich Hückel in 1923, published in the journal *Physikalische Zeitschrift*. Researchers in the field of electrolyte chemistry may have read this paper in English, because there exists an extant English translation found in the collected papers of Debye, published in 1954 (Interscience Publishers, New York) and reprinted in 1988 (Ox Bow Press, Woodbridge, CT), that was completed by an unknown translator. That translation, unfortunately, contained several errors, somewhat outdated language, and both unclear terminology and inconsistent mathematical symbols. For example, v vs. ν appear to represent different variables, and the original typesetting has been maintained despite the symbol v being similar in shape to ν . In the case of x vs. χ , their similarity caused minor confusion but are now more clearly distinguishable here.

However, in the case of x vs. κ , there is a serious typesetting error, after which the κ symbol carried forward in the literature but never appeared in the original work. The two figures below depict a comparison of the existing documents (1923 German on left, 1954 English translation on right) and show both the symbol κ not corresponding to the original German (pagination 199) and not even corresponding to a centrally typeset equation (44') nearby in the same document (pagination 248). Below this figure, the corrected text provided in this document is shown for direct comparison. Dotted-line boxes and arrows have been added.

<p>Darin hat der rechts stehende Faktor von ψ die Dimension eines reziproken Quadrates einer Länge. Wir setzen</p> $\kappa^2 = \frac{8\pi n \epsilon^2}{DkT}, \quad (11)$ <p>so daß κ eine reziproke Länge ist und (10') wird zu</p> $\Delta\psi = \kappa^2\psi. \quad (12)$ <p>Die somit eingeführte Länge</p> $\frac{1}{\kappa} = \sqrt{\frac{DkT}{8\pi n \epsilon^2}}$ <p>ist die wesentlichste Größe unserer Theorie und ersetzt die mittlere Entfernung der Ionen in der von uns abgelehnten Ghoshschen Betrachtung. Setzt man Zahlenwerte ein (vgl. später) und mißt die Konzentration wie gebräuchlich in Mol pro Liter Lösung, so wird, wenn die so gemessene Konzentration mit γ bezeichnet wird</p> $\frac{1}{\kappa} = \frac{3,06}{\sqrt{\gamma}} 10^{-8} \text{ cm}$ <p>für Wasser bei 0° C. Die charakteristische Länge erreicht also bei einer Konzentration $\gamma = 1$ (1 Mol pro Liter) molekulare Dimensionen.</p>	<p>In this equation, the factor of ψ on the right hand side has the dimension of the reciprocal of the square of a length. We put:</p> $\kappa^2 = \frac{8\pi n \epsilon^2}{DkT} \quad (11)$ <p>so that κ is the reciprocal of a length, and equation (10') becomes:</p> $\Delta\psi = \kappa^2\psi \quad (12)$ <p>The length, introduced in this way:</p> $\frac{1}{\kappa} = \sqrt{\frac{DkT}{8\pi n \epsilon^2}}$ <p>is the essential quantity in our theory and replaces the average distance between ions in Ghosh's consideration. If numerical values are inserted (see later) and the concentration is measured, as usual, in moles per liter solution, then, if this concentration is denoted by γ,</p> $\frac{1}{\kappa} = \frac{3,06}{\sqrt{\gamma}} 10^{-8} \text{ cm}$ <p>for water at 0°C. The characteristic length reaches molecular dimensions for a concentration of $\gamma = 1$ (1 mole per liter).</p>
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Here the factor ψ on the right side has the dimension of the reciprocal of the square of a length. We set

$$x^2 = \frac{8\pi n \varepsilon^2}{DkT}, \quad (11)$$

so x is the reciprocal length, and equation (10') becomes

$$\Delta\psi = x^2\psi. \quad (12)$$

The length introduced as

$$\frac{1}{x} = \sqrt{\frac{DkT}{8\pi n \varepsilon^2}}$$

is the most significant quantity in our theory and replaces the mean distance between the ions in the deprecated approach of Ghosh. If one uses numerical values (see later) and if the concentration is as usual in moles per liter of solution, then, if the measured concentration is denoted by γ ,

$$\frac{1}{x} = \frac{3.06}{\sqrt{\gamma}} 10^{-8} \text{cm}$$

for water at 0°C . The characteristic length therefore reaches molecular dimensions when $\gamma = 1$ (1 mole per liter).

The erroneous symbol κ can be found in-line throughout the 1954 translation. Below is another such example of the κ symbol being used in the 1954 English translation (pagination 199), where x was intended. The complete original 1923 German text and 1954 English text have been provided in the final sections of this document for the reader to review themselves.

$$\log f_a = \frac{\varepsilon^2 x}{6DkT} \sum_{i=1}^i \left\{ 2\mu_i z_i^2 \chi_i + \mu_i (z_i^2 - \nu_i \sum_{j=1}^i n_j z_j^2) \frac{\sum_{j=1}^i n_j z_j^2 \frac{d(x\chi_j)}{dx}}{\sum_{j=1}^i n_j z_j^2} \right\} \quad (43)$$

According to this formula it is, of course, possible to provide a special activity coefficient for each atom or molecule taking part in the reaction by putting:

$$\log f_a = \mu_1 \log f_a^1 + \dots \\ \mu_i \log f_a^i + \dots \mu_i \log f_a^i \quad (44)$$

with:

$$\log f_a^i = \frac{\varepsilon^2 x}{6DkT} \left\{ 2 z_i^2 \chi_i + (z_i^2 - \nu_i \sum_{j=1}^i n_j z_j^2) \frac{\sum_{j=1}^i n_j z_j^2 \frac{d(x\chi_j)}{dx}}{\sum_{j=1}^i n_j z_j^2} \right\} \quad (44')$$

Then, however, as equation (44') indicates by the appearance of κ , this coefficient referred to a definite type of molecule does not solely depend on quantities which are related to this type of atom.

The use of x was indeed the desired symbol of the authors, as evidenced in citations of Debye & Hückel's paper by their peers, such as the following snippet of work by Schärer (1924, "Theorie der Löslichkeitsbeeinflussung bei starken Elektrolyten", pagination 7).

die ungleichnamigen. Berechnet man nach dem Maxwell-Boltzmannschen Prinzip die Verteilung aller vorhandenen Ionen um dieses eine hervorgehobene Ion, so erzeugt diese Verteilung im Zentrum ein Potential ψ_i vom Betrag¹⁾

$$\psi_i = - \frac{z_i \varepsilon \cdot z}{D} \frac{1}{1 + \kappa a_i}.$$

Dabei bedeutet κ (von der Dimension einer reziproken Länge) ein Maß für die exponentielle Abnahme der elektrischen Dichte der Ionenatmosphäre nach außen und ist definiert durch

$$\kappa^2 = \frac{4 \pi \varepsilon^2}{D k T} \sum_{i=1}^s n_i z_i^2. \quad (9)$$

Dabei ist D die Dielektrizitätskonstante des Lösungsmittels, k die Boltzmannsche Konstante, T die absolute Temperatur und n_i die Anzahl der Ionen der i^{ten} Sorte pro cm^3

$$n_i = \frac{N_i}{V}$$

¹⁾ P. Debye, Physik. Zeitschr. **24**, 185, 1923.

All figures have been presented as they were printed in 1923 but enlarged and increased in exposure to improve legibility, and all tables have been reprinted from the 1954 English translation and checked for accuracy to the original data. Where necessary, a corresponding German (italicized) term has been provided adjacent to its translation in square brackets, which became important to interpreting the very pithy first paragraph of Section 3 Part (b).

Overall, this document provides a corrected and updated English translation of Debye & Hückel's great work, with the additional intent of expressing as accurately as possible their desired scientific meaning and bright tone. The theories and ideas presented will certainly continue to offer further use and insight to ongoing scientific research and the historical record of investigation of the physicochemical phenomena of the natural world.

- Michael J. Braus, 2019

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Frontmatter

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ORIGINAL COMMUNICATION

The theory of electrolytes.

1. Freezing point depression and related phenomena

By P. Debye and E. Huckel [1].

1. Introduction

As we know, Arrhenius' hypothesis of dissociation explains the abnormally large values of osmotic pressure, freezing point depression, etc., observed in electrolyte solutions, because the existence of ions goes hand in hand with an increase in the number of individual

particles. The quantitative theory is based on the extension of the laws of ideal gases, which van't Hoff introduced, to dilute solutions for the calculation of their osmotic pressure. Because it is possible to justify this extension via thermodynamics, there is no doubt as to the general validity of these fundamentals.

At finite concentrations, however, values for freezing point depression, conductivity, etc. are smaller than would be expected at first consideration in the presence of complete dissociation of the electrolytes into ions. Let, for instance, P_k be osmotic pressure, which results from van't Hoff's classical law for perfect dissociation, the actual osmotic pressure observed is smaller, such that

$$P = f_o P_k,$$

in agreement with Bjerrum [2], where the "osmotic coefficient" f_o thus introduced is intended to measure those deviations and is observable as a function of concentration, pressure, and temperature. In reality, such observations are not directly related to the osmotic pressure itself but to freezing point depression or boiling point elevation, both deducible for thermodynamic reasons using the same osmotic coefficient f_o from their limiting values according to van't Hoff's law for complete dissociation.

The most obvious assumption to explain the presence of this osmotic coefficient is the classical one, according to which not all molecules are dissociated into ions, but an equilibrium exists between dissociated and undissociated molecules that depends on the total concentration, as well as on pressure and temperature. The number of free individual particles is therefore variable, and indeed it would have to be set directly proportional to f_o . The quantitative theory of these dependencies, as far as it relates to the concentration, relies on Guldberg-Waage's law of mass action; the dependence on temperature and pressure of the equilibrium constant appearing in this law is to be determined thermodynamically according to van't Hoff. The whole complex of dependencies, including Guldberg-Waage's approach, can be grounded in thermodynamics, as Planck showed.

Because the electrical conductivity is determined solely by the ions and, according to the classical theory, the number of ions immediately follows from f_o , this theory requires the well-known relationship between the two properties that depend on concentration, conductivity on the one hand and osmotic pressure on the other.

A large group of electrolytes, the strong acids, bases, and their salts, grouped under the name of "strong" electrolytes, shows pronounced deviations demanded by the classical theory, which, remarkably, are all the clearer the more dilute the solutions are [3]. Therefore, as it was realized in the course of its development, it is possible only with a certain amount of approximation from f_o demanded by the classical theory to infer the dependence of the conductivity on the concentration. Furthermore, the dependence of the osmotic coefficient f_o itself on the concentration is quite incorrectly represented. For heavily diluted solutions, f_o approaches 1; if we now plot $1 - f_o$ as a function of the concentration c , the classical theory for binary electrolytes, such as KCl , requires that this curve intersects with the origin [*Nullpunkt*] with a finite tangent (determined by the equilibrium constant K). If the molecule of the electrolyte generally dissociates into ν ions, then, according to the law of mass action, small concentrations result:

$$1 - f_o = \frac{\nu - 1}{\nu} \frac{c^{\nu-1}}{K},$$

such that in cases where the dissociation occurs in more than 2 ions, the curve in question must have an even higher order of contact with the abscissa axis. The complex of these dependencies constitutes Wilhelm Ostwald's law of dilution.

Actually, observations of strong electrolytes show quite a different behavior. The experimental curve leaves the origin at a right angle [4] to the abscissa axis, independent of the number of ions, ν . All proposed practical interpolation formulas attempt to model this behavior by setting $1 - f_o$ to be proportional to a fractional power (less than 1, about 1/2 or 1/3) of the concentration. The same phenomenon is repeated in the extrapolation of the conductivity to infinite dilution, which according to Kohlrausch is to be done using a power of 1/2.

It is clear that, under these circumstances, the classical theory cannot be maintained. On the contrary, all experimental material clearly indicates that it can also be abandoned in its fundamental features, and, in particular, an equilibrium cannot be calculated on the basis of Gulberg-Waage's approach and correspond to the real phenomena.

W. Sutherland [5] in 1907 attempted to establish the theory of electrolytes on the assumption of complete dissociation. His work contains some good thoughts. N. Bjerrum [6] is probably the one who first came to a correctly delineated formulation of that hypothesis. He has clearly stated and argued that in the case of the strong electrolytes, there is no apparent equilibrium between dissociated and undissociated molecules and that there are compelling reasons for considering such electrolytes to be dissociated to ions in their entirety up to high concentrations. Only when considering weak electrolytes do undissociated molecules occur again. Therefore the classical explanation falls short as the sole basis for the variability of, for instance, the osmotic coefficient, and the task arises to search for a hitherto overlooked effect of the ions, which, despite the absence of an association, could explain the decrease of f_o with increasing concentration.

More recently, under the influence of Bjerrum, it has been suggested that the consideration of the electrostatic forces that the ions exert, and which, because the relatively enormous size of the electric elementary charge should be strongly important, must provide the desired explanation. Such forces are not mentioned in the classical theory, which rather treats the ions as completely independent components. The theory as it was conceived corresponds approximately to the step one takes when van der Waals passes from the ideal to those of the real gases. However, we must resort to completely different remedies, because the electrostatic forces between the ions decrease only with the squares of the distance and thus differ substantially from the molecular forces, which disappear much more rapidly with increasing distance.

For osmotic coefficients there exists a calculation by Milner [7]. It is flawless in its structure but has mathematical difficulties that are not completely overcome and reaches its result only in the form of a graphically determined curve for the relation between $1 - f_o$ and the concentration. Moreover, it will be seen from the following that the comparison with the experience of Milner supersedes the admissibility of his negligence of excessively high concentrations, for which the individual properties of the ions, which Milner does not take into account, play a very important role. Still, it would be unjustified to discount Milner's calculations in favor of the recent accounts of J. Ch. Ghosh [8]. In what follows, we shall have to return to the reason why we cannot agree with Ghosh's calculations in their application to conductivity nor their somewhat more transparent application to osmotic pressure. We are even forced to call his calculation of the electrostatic energy of an ionized electrolyte, which underlies all his further conclusions, fundamentally wrong.

Quite similar to the calculations of osmotic coefficients are the calculations of conductivity. Again, the theory must strive to understand the mutual electrostatic influence of the ions with respect to their mobility. An attempt in this direction comes from P. Hertz [9]. He transcribes the methods of kinetic gas theory and actually finds a mutual interference of the ions. In the meantime, the transfer of those methods, and in particular the use of terms that correspond to the free path of dilute gases, seems to have profound consequences in the case of free ions between the molecules of the solvent. Indeed, the final result by Hertz of small concentrations are irreconcilable with the experimental results.

In this first article, we will deal exclusively with the “osmotic coefficient f_o ” and a similar one used by Bjerrum [10] of “activity coefficient f_a ” stressing its significance. Even with such (weak) electrolytes, where a significant number of undissociated molecules is present, it cannot simply be modeled after Gulberg-Waage’s approach

$$c_1^{\mu_1} c_2^{\mu_2} \dots c_n^{\mu_n} = K$$

(c_1, c_2, \dots, c_n concentrations, K equilibrium constant). Rather, one has to write, with respect to the electrostatic forces of the ions, instead of K ,

$$f_a K,$$

introducing an activity coefficient [11] f_a . This coefficient, like f_o , will depend on the concentration of ions. Although Bjerrum has a thermodynamically related relationship between f_a and f_o , the relationships of the two coefficients to concentration are different.

The lengthy discussion of conductivity we will reserve for a future article, a classification, which is internally justified. Whereas the determination of f_o and f_a can be done by using only reversible processes, the calculation of mobilities leads to essentially irreversible processes in which there is no longer a direct connection to fundamental thermodynamic laws.

2. Fundamentals

It is known in thermodynamics that the properties of a system are fully known if one of the many possible thermodynamic potentials is given as a function of the properly chosen variables. Correspond to the form in which the terms based on the mutual electric effects will appear, we consider the quantity [12]

$$G = S - \frac{U}{T} \quad (1)$$

(S = entropy, U = energy, T = absolute temperature) to be the basic function. As variables here (in addition to the concentration) we have volume and temperature, of course, because

$$dG = \frac{p}{T} dV + \frac{U}{T^2} dT. \quad (1')$$

The calculations to be carried out below differ from the classical ones in that the electrical effects of the ions are taken into account. Accordingly, we divide U into two components, a classical component U_k and an additional electrical energy U_e

$$U = U_k + U_e.$$

Considering that, according to equation (1),

$$T^2 \frac{\partial G}{\partial T} = U \quad (2)$$

and also divide the potential G into two parts:

$$G = G_k + G_e,$$

we find that, according to equation (2)

$$G_e = \int \frac{U_e}{T^2} dT. \quad (3)$$

Our main task is to determine the electrical energy U_e of an ionic solution. For practical purposes, however, the potential G is not as suitable as Planck's preferred function

$$\Phi = S - \frac{U + pV}{T}. \quad (4)$$

As the differential form of the definition

$$d\Phi = -\frac{V}{T} dp + \frac{U + pV}{T^2} dT \quad (4')$$

shows, the variables important to the potential Φ are pressure and temperature, and, because the vast majority of experiments are performed at constant pressure (and not at constant volume), Φ is preferable. A comparison of equations (4) with (1) yields

$$\Phi = G - \frac{pV}{T}; \quad (5)$$

if G above is known, then we must find and add the term $-pV/T$ as a function of p and T . Considering equation (1'), we can conclude that

$$\frac{p}{T} = \frac{\partial G}{\partial V} = \frac{\partial G_k}{\partial V} + \frac{\partial G_e}{\partial V},$$

and so have obtained the equation of state that relates pressure, volume, and temperature for the ionic solution. It can be interpreted by assuming that, as a consequence of the electric effect of the ions, added to the external pressure p is an electric pressure p_e , to be calculated from the relation

$$p_e = -\frac{\partial G_e}{\partial V}. \quad (6')$$

We will later have the opportunity [13] to determine this electrical pressure p_e ; it applies only about 20 atmospheres to an aqueous solution, for example, of KCl at a concentration of 1 mole per liter. Strictly speaking, it is not correct to use the classical approach for V (as a function of p and T) without considering the electrical effects of the ions, because the pressure p_e also causes a change in volume. However, understand that the compressibility of the water is so low that 20 atmospheres can cause only a relative volume change of 0.001, so most applications the electrical addition to V (as a function of p and T) can be neglected. Furthering this observation, we will also break down Φ into a classical part and an additional electric component

$$\Phi = \Phi_k + \Phi_e \quad (7)$$

and, following equation (3), we can set

$$\Phi_e = G_e = \int \frac{U_e}{T^2} dT \quad (7')$$

The classical component Φ_k is, according to Planck's form:

$$\Phi_k = \sum_0^s N_i (\varphi_i - k \log c_i), \quad (7'')$$

where

$$N_o, N_1, \dots, N_i, \dots, N_s$$

signify the numbers of individual particles in the solution, and N_o should refer specifically to the solvent [14]. Next is the thermodynamic potential referring to the single particle

$$\varphi_i = s_i - \frac{u_i + pv_i}{T}$$

a quantity independent of the concentration; k is the Boltzmann constant, $k = 1.346 * 10^{-16}$ erg and c_i signifies the concentration of particle i , such that

$$c_i = \frac{N_i}{N_o + N_1 + \dots + N_i + \dots + N_s},$$

from which the relation

$$\sum_0^s c_i = 1$$

follows.

Having completed these preliminary remarks on thermodynamics, we come to the discussion of the main task: calculation of the electrical energy U_e .

At first glance, it seems as if this energy would be obtained directly in the following way. If, in the solvent with the dielectric constant D , there are two electric charges of magnitudes ε and $-\varepsilon$ at a distance r , then their mutual potential energy is

$$-\frac{1}{D} \frac{\varepsilon^2}{r}$$

For simplicity, consider a binary electrolyte such as KCl that has completely dissociated into ions such that there exist, in the volume V of the solution, $N_1 = N$ K -ions with the charge $+\varepsilon$ and an equal number $N_2 = N$ Cl -ions with the charge $-\varepsilon$. It can then be imagined that the mean distance r , which is used in the energy calculation, equals the mean distance between the ions, and because the volume associated with one ion is equal to $V/2N$, we write

$$r = \left(\frac{V}{2N}\right)^{1/3}.$$

By using this value for r , one would estimate the electrical energy of the solution to be

$$U_e = -N \frac{\varepsilon^2}{D} \left(\frac{2N}{V}\right)^{1/3}$$

In fact, J. Ch. Ghosh [15] proceeds in this way. This approach, however, is fundamentally wrong, and the entire theory built upon it (practically characterized by the introduction of the cube root of concentration) must be rejected.

The (negative) electrical energy of an ionic solution results from the fact that, when one looks at any one ion in the environment described above, often dissimilar ions of the same name are found, an immediate consequence of the electrostatic forces acting between the ions. An exemplary case is crystals, such as $NaCl$, KCl , etc., in which, according to Bragg's investigations, each atom (which also occurs here as an ion) is immediately surrounded by dissimilar atoms. As true as it is in this case (in accordance with the precise calculations of M. Born) to estimate the electric energy of the crystal with the distance of two neighboring dissimilar atoms, it is a mistake to overstate the analogy using the mean distance $(\frac{V}{2N})^{1/3}$ in the case of a solution. In fact, a very different length is appropriate here, because the ions are free to move and therefore can only maintain the length due to the evaluation of differences in the probability of residence times of similar and dissimilar ions in the same voxel [*Volumelement*] near a specific ion. From this it follows that the thermally induced movement [*Temperaturbewegung*] has an essential role to play in the calculation of U_e .

In terms of dimensions, one can only conclude that, assuming the size of the ions need not be taken into account for large dilutions [16], one energy is the expression already given above

$$\frac{\varepsilon^2}{D} \left(\frac{2N}{V}\right)^{1/3}.$$

However, another energy, measured by kT , plays an equal role in the thermally induced movement. It is therefore to be expected that U_e will take the form

$$U_e = -N \frac{\varepsilon^2}{D} \left(\frac{2N}{V} \right)^{1/3} f \left(\frac{\varepsilon^2}{D} \left(\frac{2N}{V} \right)^{1/3} / kt \right), \quad (8)$$

where f is a function of the ratio of the two energies over which we cannot make claims *a priori* [17].

Investigation of the limiting case of high temperatures also leads to the same conclusion. If the energy of the thermally induced movement is large, and if one considers a voxel in the vicinity of an ion handpicked for this consideration, then the probability that an ion of the same name is found there is the same as the probability for a dissimilar one. So in the high temperature limit, U_e must disappear, i.e. the expression for U_e also contains T as an essential parameter at medium temperatures.

3. Calculation of the Electric Energy of an Ionic Solution of an Uni-univalent Salt.

In a volume V , N molecules of a uni-univalent salt (for example, KCl) are dissociated into ions; if the absolute value of the charge of an ion is ε ($4.77 * 10^{-10}$ electrostatic units), let the dielectric constant be D . We consider one of these ions with the charge $+\varepsilon$ and intend to determine its potential energy u relative to the surrounding ions. The direct calculation, as attempted by Milner, taking into account every possible arrangement of the ions and allowing for their probability according to Boltzmann's principle, has proved to be too difficult mathematically. We therefore replace it with another consideration, in which the calculation from the outset is guided toward the mean value of the electric potential generated by the ions.

At a point P in the vicinity of the specific ion, let the mean electrical potential be ψ with respect to time; if one brings a positive ion to that location, then the work required is $+\varepsilon\psi$, while for a negative ion the work $-\varepsilon\psi$ is required. In a voxel dV at this point with respect to time, therefore, we will find a mean value, according to the Boltzmann principle,

$$n e^{-\frac{\varepsilon\psi}{kT}} dV$$

positive and

$$n e^{+\frac{\varepsilon\psi}{kT}} dV$$

negative ions, setting $n = \frac{N}{V}$. In fact, in the limit for $T = \infty$, the distribution of the ions must become uniform, such that the factor before the exponential function is equal to $\frac{N}{V}$, i.e. must be set equal to the number of ions of one kind per cm^2 of the solution. For the time being, however, nothing can be said with these data, because the potential ψ of the point P is still unknown. According to Poisson's equation, however, the potential must sufficiently satisfy the condition

$$\Delta\psi = -\frac{4\pi}{D}\varrho,$$

if the electricity with the density ϱ in the medium is affected by the dielectric constant D . On the other hand, after the above

$$\varrho = n\varepsilon(e^{-\frac{\varepsilon\psi}{kT}} - e^{+\frac{\varepsilon\psi}{kT}}) = -2n\varepsilon\mathfrak{Gin}\frac{\varepsilon\psi}{kT}; \quad (9)$$

so ψ can be determined as the equation's solution

$$\Delta\psi = \frac{8\pi n\varepsilon}{D}\mathfrak{Gin}\frac{\varepsilon\psi}{kT}. \quad (10)$$

The further one moves away from the specified ion, the smaller will be the potential ψ , and for larger distance the sufficient approximation $\mathfrak{Gin}\frac{\varepsilon\psi}{kT}$ can replace $\frac{\varepsilon\psi}{kT}$. If one does that, equation (10) takes on the much simpler form [18]

$$\Delta\psi = \frac{8\pi n\varepsilon^2}{DkT}\psi. \quad (10')$$

Here the factor ψ on the right side has the dimension of the reciprocal of the square of a length. We set

$$x^2 = \frac{8\pi n\varepsilon^2}{DkT}, \quad (11)$$

so x is the reciprocal length, and equation (10') becomes

$$\Delta\psi = x^2\psi. \quad (12)$$

The length introduced as

$$\frac{1}{x} = \sqrt{\frac{DkT}{8\pi n\varepsilon^2}}$$

is the most significant quantity in our theory and replaces the mean distance between the ions in the deprecated approach of Ghosh. If one uses numerical values (see later) and if the concentration is as usual in moles per liter of solution, then, if the measured concentration is denoted by γ ,

$$\frac{1}{x} = \frac{3.06}{\sqrt{\gamma}}10^{-8}\text{cm}$$

for water at 0°C . The characteristic length therefore reaches molecular dimensions when $\gamma = 1$ (1 mole per liter).

We now wish to interrupt this course of thought in order to explore the physical meaning of the characteristic length.

In an electrolyte solution of potential 0, immerse an electrode whose surface has a potential difference ψ to this solution. The transition from ψ to 0 will then take place in a layer of finite thickness given the above considerations. If we use equation (12) and designate z as a coordinate perpendicular to the electrode surface, then we find

$$\psi = \Psi e^{-xz}$$

a function that satisfies equation (1). Because the right-hand term of equation (12), in the sense of Poisson's equation, signifies $-\frac{4\pi}{D}\varrho$, the charge density associated with the given potential is

$$\varrho = -\frac{Dx^2}{4\pi}\psi e^{-xz}.$$

According to this formula, $\frac{1}{x}$ signifies the length at which the electrical density of the ionic atmosphere decreases to the e th part. Our characteristic length $\frac{1}{x}$ is a measure of the thickness of such an ionic atmosphere (i.e., of the widely known Helmholtz double layer); according to equation (11) it depends on the concentration, temperature, and dielectric constant of the solvent [19].

Now that the meaning of the length $\frac{1}{x}$ has been clarified, let us now use equation (12) to determine the potential and density distribution in the environment of the specified ion with the charge $+\varepsilon$. We call the distance from this ion r and introduce spatial polar coordinates to equation (12). Then equation (12) becomes

$$\frac{1}{r^2} \frac{d}{dr} \left(r^2 \frac{d\psi}{dr} \right) = x^2 \psi \quad (12')$$

and this equation has the general solution

$$\psi = A \frac{e^{-xr}}{r} + A' \frac{e^{xr}}{r}. \quad (13)$$

Because ψ disappears at infinity, it must be that $A' = 0$; the constant A , on the other hand, must be determined from the conditions in the vicinity of the ion. We want to carry out this determination in two steps, (a) and (b), while under (a) assume that the dimensions of the ion have no effect; under (b) consider the ion to have a finite size. Considerations under (a) then provide the boundary law for large dilutions, while (b) provides the changes that are to be made to this boundary law for larger concentrations.

(a) Infinitesimal Ion Diameter.

The potential of a single point charge ε in a medium of dielectric constant D would be

$$\psi = \frac{\varepsilon}{D} \frac{1}{r},$$

if no other ions are present in the medium. Our potential in equation (13) must agree with this expression for infinitesimally small distances, so we write

$$A = \frac{\varepsilon}{D}$$

and the desired potential will be:

$$\psi = \frac{\varepsilon}{D} \frac{e^{-xr}}{r} = \frac{\varepsilon}{D} \frac{1}{r} - \frac{\varepsilon}{D} \frac{1 - e^{-xr}}{r}. \quad (14)$$

We have subsequently divided the potential into two components, the first of which represents the potential unaffected by the surrounding ions, and the second of which represents the potential originating from the ionic atmosphere. For small values of r , the value of this latter potential becomes equal to

$$-\frac{\varepsilon}{D}x;$$

the potential energy u , which contains the specified ion $+\varepsilon$ relative to its surroundings, is therefore [20]

$$u = -\frac{\varepsilon^2}{D}x. \quad (15)$$

If one now has a series of charges e_i and the potential at the respective location of a charge is ψ_i , according to the laws of electrostatics, the total potential energy

$$U_e = \frac{1}{2} \sum e_i \psi_i.$$

In our case, where N positive ions are present, each of which has the potential difference $-\frac{\varepsilon}{D}x$ relative to its surroundings, and N negative ions with a potential difference of $+\frac{\varepsilon}{D}x$ are added, then the desired potential energy [21]

$$U_e = \frac{N\varepsilon}{2} \left(-\frac{\varepsilon x}{D}\right) - \frac{N\varepsilon}{2} \left(+\frac{\varepsilon x}{D}\right) = -\frac{N\varepsilon^2 x}{D}. \quad (16)$$

At the same time, x is given as a function of the concentration by equation (11), so the potential energy of the ionic solution is proportional to the square root of concentration and not, as in Ghosh, proportional to the cube root of the same quantity.

(b) Finite Ion Diameter.

We noted earlier that the characteristic length $\frac{1}{x}$ at concentrations of 1 mole per liter reaches the scale of molecular dimensions. At such concentrations, it is therefore inadmissible for the ion of finite molecular size to be replaced by a point charge, as was done under (a). It would not correspond to the meaning of our calculation, based on Poisson's equation, if

one wanted to introduce detailed concepts about the distances of mutual approach of ions. Rather, we will now utilize an image [*Bild*] that considers an ion to be a sphere of radius a , whose interior is to be treated as a medium with the dielectric constant D , and at the center of which is the charge $+\varepsilon$ or $-\varepsilon$, as a point charge. The magnitude of a then does not evidently represent the ion radius but measures a length that is the mean distance up to which the surroundings, both positive and negative ions, can approach the specified ion. Accordingly, with positive and negative ions of exactly equal size, a would be, for example, expected to be of the same order of magnitude as the ion diameter. In general, this ion diameter cannot yet to be regarded as the diameter of the real ion, because ions are expected to be surrounded according to their hydration by a firmly adhered layer of water molecules. Therefore, with the assistance of the length a , we can only approximate reality with the schematic provided above. However, the discussion of practical cases (see below) will show that this approximation is fairly extensive [*recht weitgehende*].

The potential for a specified ion remains

$$\psi = A * \frac{e^{-xr}}{r}, \quad (17)$$

except the constant A must now be determined differently. According to our assumptions, inside the ion sphere (for a positive ion) we set

$$\psi = \frac{\varepsilon}{D} \frac{1}{r} + B. \quad (17')$$

The constants A and B are to be determined from the boundary conditions at the surface of the sphere. There, for $r = a$, the potentials ψ as well as the field strengths $-\frac{d\psi}{dr}$ continuously merge together.

Accordingly

$$\left. \begin{aligned} A \frac{e^{-xa}}{a} &= \frac{\varepsilon}{D} \frac{1}{a} + B, \\ A * e^{-xa} \frac{1+xa}{a^2} &= \frac{\varepsilon}{D} \frac{1}{a^2}, \end{aligned} \right\} (18)$$

consequently

$$A = \frac{\varepsilon}{D} \frac{e^{xa}}{1+xa}, \quad B = -\frac{\varepsilon x}{D} \frac{1}{1+xa}. \quad (18')$$

The value of B represents the potential generated at the center of the ion sphere by the ionic atmosphere; accordingly, one obtains the expression for the potential energy of a positive ion relative to its surroundings

$$u = -\frac{\varepsilon^2 x}{D} \frac{1}{1+xa}. \quad (19)$$

As the comparison with equation (15) shows, the effect of the ion size is represented by the factor $1/(1+xa)$ only. For low concentrations (n small) x is also small following equation

(11), and the energy approaches the value given above for infinitely small ions. For large concentrations (x large), on the other hand, u gradually approaches the quantity

$$-\frac{\varepsilon^2}{Da},$$

such that the importance of our characteristic length $\frac{1}{x}$ lessens compared to the new length measuring the ionic size a .

With the aid of equation (19), the expression is similar to that under (a) for the total electrical energy of the ion solution

$$U_e = -\frac{N \varepsilon^2 x}{2 D} \left[\frac{1}{1 + xa_1} + \frac{1}{1 + xa_2} \right], \quad (20)$$

if we clearly characterize the positive ions by a radius a_1 and the negative ones by another radius a_2 . We could now use equations (16) or (20) directly to determine our thermodynamic function as explained in Section 2. In the meantime, let us first derive equation (20) as an expression for the energy of any ionic solution, by eliminating the restriction to uni-univalent salts introduced for the sake of clarity.

4. The Potential Energy of Any Ionic Solution.

In a solution there exist

$$N_1 \dots N_i \dots N_s$$

various ions with the charges

$$z_1 \dots z_i \dots z_s$$

such that the integers $z_1 \dots z_i \dots z_s$, can measure the valences and be positive and negative. Because the total charge is zero,

$$\sum N_i z_i = 0$$

must be true. In addition to the total numbers N_i , the ion numbers per cm^3

$$n_1 \dots n_i \dots n_s$$

are also introduced.

Again, any ion can be specified, and in its vicinity the potential is determined according to Poisson's equation

$$\Delta\psi = -\frac{4\pi}{D}\varrho.$$

The density of the i th ion of this type is provided by Boltzmann's principle

$$n_i e^{-z_i \frac{\varepsilon\psi}{kT}},$$

such that

$$\varrho = \varepsilon \sum n_i z_i e^{-z_i \frac{\varepsilon\psi}{kT}},$$

and the fundamental equation becomes

$$\Delta\psi = -\frac{4\pi\varepsilon}{D} \sum n_i z_i e^{-z_i \frac{\varepsilon\psi}{kT}}. \quad (21)$$

If we use the expansion of the exponential function in the previous paragraph, then equation (21) practically becomes the equation

$$\Delta\psi = \frac{4\pi\varepsilon^2}{DkT} \sum n_i z_i^2 \psi \quad (21')$$

because the condition

$$\sum n_i z_i = 0$$

causes the first term of the expansion to disappear. In the general case, therefore, the square of our characteristic length $\frac{1}{x^2}$ is to be defined by the equation [22]

$$x^2 = \frac{4\pi\varepsilon^2}{DkT} \sum n_i z_i^2, \quad (22)$$

while the equation for potential maintains its former form

$$\Delta\psi = x^2\psi.$$

Again, any ion is specified and the potential ψ in its vicinity is determined. In accordance with the statements of the previous paragraph,

$$\psi = A \frac{e^{-xr}}{r}$$

for the field outside the ion.

If the ion has the charge $z_i\varepsilon$ and has an approach distance of a_i , then the inside of the ion sphere becomes

$$\psi = \frac{z_i \varepsilon}{D} \frac{1}{r} + B,$$

while the constants A and B are

$$A = \frac{z_i \varepsilon}{D} \frac{e^{x a_i}}{1 + x a_i}, \quad B = -\frac{z_i \varepsilon x}{D} \frac{1}{1 + x a_i}.$$

The given value of B corresponds to the potential energy

$$u = -\frac{z_i^2 \varepsilon^2 x}{D} \frac{1}{1 + x a_i}$$

of the ion specified ion relative to its ionic atmosphere, while the total electrical energy of the ion solution, as can be readily seen, is

$$U_e = -\sum \frac{N_i z_i^2}{2} \frac{\varepsilon^2 x}{D} \frac{1}{1 + x a_i}. \quad (23)$$

The inverse length x is defined in the general case by equation (22) [23].

5. The Additional Electrical Term to Thermodynamic Potential.

In Section 2 we came to the conclusion that the additional term originating in the potential from the mutual effect of the ions

$$G = S - \frac{U}{T}$$

is determined from the equation

$$G_e = \int \frac{U_e}{T^2} dT.$$

If we now use the expression given in equation (23) for U_e to address the general case, it must be remembered when integrating that according to equation (22) the reciprocal length in this expression contains the temperature. The calculation becomes clearer when we first conclude from equation (22) that

$$2x dx = -\frac{4\pi \varepsilon^2}{Dk} \sum n_i z_i^2 \frac{dT}{T^2},$$

where D is considered to be temperature-independent [24], and then use x as the integration variable, not T . So the result is

$$G_e = \frac{k}{4\pi \sum n_i z_i^2} \sum N_i z_i^2 \int \frac{x^2 dx}{1 + xa_i}. \quad (24)$$

If one applies the abbreviation

$$xa_i = x_i,$$

one finds that

$$\int^{x=x} \frac{x^2 dx}{1 + xa_i} = \frac{1}{a_i^3} \int^{u=x_i} \frac{u^2 du}{1 + u} = \frac{1}{a_i^3} \left\{ \text{const} + \log(1 + x_i) - 2(1 + x_i) + \frac{1}{2}(1 + x_i)^2 \right\}.$$

The constant of integration is determined in such a way that the electrical addition G_e to the total potential disappears from the limit for infinite dilution. Because x in equation (22) is proportional to $\sqrt{\sum n_i z_i^2}$, $x = 0$ corresponds to the case of infinite dilution. Accordingly, the constant in the curly brace must be determined such that for $x = 0$ the parenthetical expression also disappears, and within that limit

$$\log(1 + x_i) - 2(1 + x_i) + \frac{1}{2}(1 + x_i)^2$$

the value $-\frac{3}{2}$ means

$$\text{const.} = \frac{3}{2}$$

Then

$$\int \frac{x^2 dx}{1 + xa} = \frac{1}{a_i^3} \left\{ \frac{3}{2} + \log(1 + x_i) - 2(1 + x_i) + \frac{1}{2}(1 + x_i)^2 \right\}$$

and

$$G_e = \frac{k}{4\pi \sum n_i z_i^2} \sum \frac{N_i z_i^2}{a_i^3} \left\{ \frac{3}{2} + \log(1 + x_i) - 2(1 + x_i) + \frac{1}{2}(1 + x_i)^2 \right\}. \quad (26)$$

The function in the curly brace, when expanded with powers of x_i , takes the form

$$\frac{3}{2} + \log(1 + x_i) - 2(1 + x_i) + \frac{1}{2}(1 + x_i)^2 = \frac{x_i^3}{3} - \frac{x_i^4}{4} + \frac{x_i^5}{5} - \frac{x_i^6}{6} + \dots;$$

this is why one sets the abbreviation

$$\chi_i = \chi(x_i) = \frac{3}{x_i^3} \left\{ \frac{3}{2} + \log(1 + x_i) - 2(1 + x_i) + \frac{1}{2}(1 + x_i)^2 \right\}, \quad (27)$$

therefore χ approaches the value 1 for small concentrations and can be expanded to

$$\chi_i = 1 - \frac{3}{4}x_i + \frac{3}{5}x_i^2 - \dots \quad (27')$$

By introducing this function and considering the definition in equation (22) of x^2 , our addition to the thermodynamic potential can be reduced to the form [25]

$$G_e = \sum N_i \frac{z_i^2 \varepsilon^2 x}{DT} \chi_i, \quad (28)$$

where, for the sake of clarity, according to equation (22) for x ,

$$x^2 = \frac{4\pi\varepsilon^2}{DkT} \sum n_i z_i^2$$

is explicitly repeated again here.

For small concentrations, therefore, in G_e , each ion has a contribution proportional to x , i.e. proportional to the square root of the concentration. If the finite dimensions of the ions were neglected, then, according to equations (27') and (25), χ_i would be equal to 1, and this dependency would appear to be valid for all concentrations. The dependence on the ion's size, which takes into account the individual properties of the ions, is therefore measured by the function χ given equations (27) or (27'). In the limit for large dilutions, however, this influence disappears, and the ions only differ as far as their valences are different.

6. Osmotic Pressure, Vapor Pressure Depression, Freezing Point Depression, Boiling Point Elevation.

According to Section 2 regarding equations (7), (7'), and (7''), the thermodynamic function Φ of the solution is represented by the expression

$$\Phi = \sum_0^s N_i (\varphi_i - k \log c_i) + \sum_1^\varepsilon N_i \frac{z_i^2 \varepsilon^2 x}{3D T} \chi_i. \quad (29)$$

In this case, for the electrical addition to Φ , equation (28) is used, in which $\chi_i = \chi(x_i) = \chi(x a_i)$ is provided by equation (27) and, as explained in the previous paragraph, approaches the value of 1 (unity) in the limit for infinitesimal concentrations. x is our reciprocal characteristic length, defined by equation (22),

$$x^2 = \frac{4\pi\varepsilon^2}{DkT} \sum n_i z_i^2.$$

According to the method used in Planck's textbook on thermodynamics [possibly *Vorlesungen über Thermodynamik (1897)*], the laws of the phenomena named in the heading can all be deduced by differentiation of equation (29). The condition for equilibrium in the

transition of a quantity of δN_o -molecules of the solvent from the solution to the respective other phase is known,

$$\delta\Phi + \delta\Phi' = 0,$$

if Φ' signifies the thermodynamic potential of that second phase. We set

$$\Phi' = N'_o\varphi'_o \quad (30)$$

and wish to account for the case of equilibrium between the solution and the frozen solvent, bearing in mind that the most extensive and reliable measurements for freezing point depression are as a function of concentration. We now let N_o vary by δN_o and N'_o vary by $\delta N'_o$ and then immediately find that

$$\delta(\Phi + \Phi') = \varphi'_o\delta N'_o + (\varphi_o - k \log c_o)\delta N_o + \sum_1^s N_i \frac{z_i^2 \varepsilon^2}{3DT} \frac{d(x\chi_i)}{dx} \frac{\partial x}{\partial N_o} \delta N_o, \quad (31)$$

as it is easily apparent

$$\sum_0^s N_i \delta \log c_i = \sum_0^s N_i \frac{\partial \log c_i}{\partial N_o} \delta N_o$$

has the value zero.

Because

$$\delta N'_o = -\delta N_o$$

the condition for equilibrium is

$$\varphi'_o - \varphi_o = -k \log c_o + \sum_1^s N_i \frac{z_i^2 \varepsilon^2}{3DT} \frac{d(x\chi_i)}{dx} \frac{\partial x}{\partial N_o}; \quad (32)$$

it could be utilized in this form for all the phenomena named in the heading and represents a relation between pressure, temperature, and concentrations.

In the definition of x , n_i represents the number of ions of the i th type per unit volume, such that

$$n_i = \frac{N_i}{V}$$

On the other hand, the whole formulation, like that of Planck for volume V , is based on the linear approach

$$V = \sum_0^s n_i v_i = n_o v_o + \sum_1^s n_i v_i$$

Accordingly, equation (22) becomes

$$2x \frac{\partial x}{\partial N_o} = -\frac{4\pi\epsilon^2}{DkT} \sum z_i^2 \frac{N_i v_o}{V^2} = -\frac{4\pi\epsilon^2}{DkT} \frac{v_o}{V} \sum n_i z_i^2;$$

according to this equation of definition one therefore finds

$$\frac{\partial x}{\partial N_o} = -\frac{x v_o}{2 V},$$

and our condition for equilibrium takes the form:

$$\varphi_o - \varphi'_o = k \log c_o + v_o \sum_1^s n_i \frac{z_i^2 \epsilon^2}{6DT} x \frac{d(x\chi_i)}{dx}. \quad (32')$$

The function for concentration characterizing the effects in question

$$\frac{d(x\chi_i)}{dx}$$

can easily be calculated from equation (27). If we designate it as σ_i , it follows while keeping the abbreviation

$$x_i = xa_i$$

to

$$\sigma_i = \frac{d(x\chi_i)}{dx} = \frac{3}{x_i^3} \left[(1 + x_i) - \frac{1}{1 + x_i} - 2 \log (1 + x_i) \right]. \quad (33)$$

For small values of x_i , the expansion is

$$\sigma_i = 1 - \frac{3}{2}x_i + \frac{9}{5}x_i^2 - 2x_i^3 + \dots = \sum_{\nu=0}^{v=s} 3 \frac{\nu+1}{\nu+3} x_i^\nu,$$

such that σ_i approaches the value 1 (unity) for small concentrations; for large concentrations, σ_i disappears as $3/x_i^2$. Table 1 contains numerical values for σ as a function of $x = xa$; Fig. 1 presents the trend of the function graphically.

Table I

x	$\sigma(x)$	x	$\sigma(x)$	x	$\sigma(x)$	x	$\sigma(x)$
0	1.000	0.4	0.598	0.9	0.370	3.0	0.1109
0.05	0.929	0.5	0.536	1.0	0.341	3.5	0.0898
0.1	0.855	0.6	0.486	1.5	0.238	4.0	0.0742
0.2	0.759	0.7	0.441	2.0	0.176	4.5	0.0628
0.3	0.670	0.8	0.403	2.5	0.136	5.5	0.0540

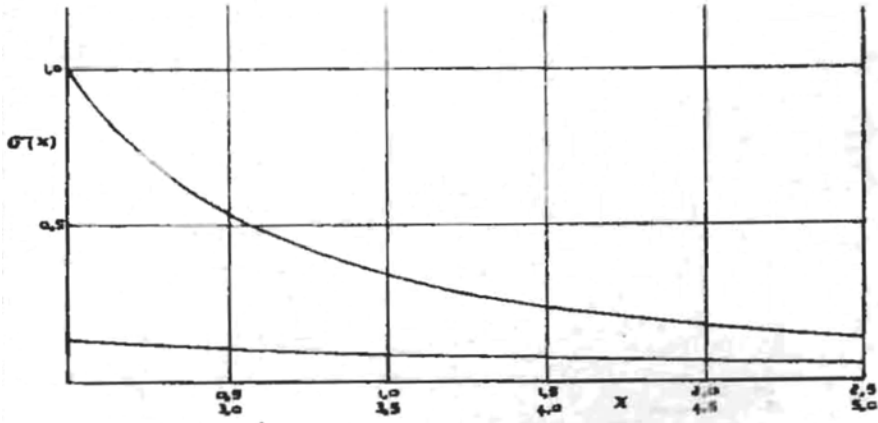


Fig. 1.

Because we will later take the opportunity to address the freezing point of concentrated solutions, it is advisable to calculate the magnitude of depression from equation (32') without first introducing all the simplifications that are permitted in very dilute solutions. The freezing point of the pure solvent is T_o , the freezing point of the solution $T_o - \Delta$, the heat of fusion of the frozen solvent q , the specific heat of the liquid solvent at constant pressure c_p , and the same quantity for the frozen solvent c'_p . The three latter quantities should always be related to a real molecule, such that they represent the typical molar masses divided by Loschmidt's number. Then, according to the equation that defines φ ,

$$\varphi_o - \varphi'_o = -\frac{\Delta}{T_o} \frac{q}{T_o} + \frac{\Delta^2}{T_o^2} \left[(c_p - c'_p) - \frac{2q}{kT_o} \right].$$

For c_o we can set

$$c_o = 1 - \sum_1^s c_i$$

Continuing, we set

$$\frac{d(x\chi_i)}{dx} = \sigma_i$$

it finally follows that

$$\frac{\Delta}{T_o} \frac{q}{kT_o} - \frac{\Delta^2}{T_o^2} \left(\frac{c_p - c'_p}{2k} - \frac{q}{kT_o} \right) = -\log \left(1 - \sum_1^s c_i \right) - \frac{\varepsilon^2 x}{6DkT} \sum_1^s v_o n_i z_i^2 \sigma_i.$$

If Loschmidt's number is called N , then

$$Nq = Q$$

is the melting heat of a mole,

$$Nk = R$$

is the gas constant, and

$$Nc_p = C_p \text{ and } Nc'_p = C'_p$$

the specific heat per mole of liquid or solid solvent, respectively, such that you can also write

$$\frac{\Delta}{T_o} \frac{Q}{RT_o} - \frac{\Delta^2}{T_o^2} \left(\frac{C_p - C'_p}{2R} - \frac{Q}{RT_o} \right) = -\log \left(1 - \sum_1^s c_i \right) - \frac{\varepsilon^2 x}{6DkT} \sum_1^s v_o n_i z_i^2 \sigma_i. \quad (34)$$

For small concentrations first Δ^2/T_o^2 then Δ/T_o can be neglected, second,

$$-\log \left(1 - \sum_1^s c_i \right) = \sum_1^s c_i$$

becomes true, and third, the total volume can be identified with the volume of water by considering the number of dissolved ions as infinitesimal relative to the number of water molecules. It is identical when we set

$$v_o n_i = \frac{v_o}{V} N_i = \frac{V_i}{N_o} = \frac{N_i}{N_o + \sum_1^s v_i N_i} = c_i.$$

With these approximations you find [26]

$$\frac{\Delta}{T_o} \frac{Q}{RT_o} = \sum_1^s c_i \left(1 - \frac{\varepsilon^2 x}{6DkT} z_i^2 \sigma_i \right), \quad (35)$$

whereas under the same assumptions, the classical formula would be

$$\frac{\Delta}{T_o} \frac{Q}{RT_o} = \sum_1^s c_i. \quad (35')$$

7. The Freezing Point Depression of Dilute Solutions.

The characteristics of the electric effect of the ions are particularly evident in the limiting laws for large dilutions, as represented by equation (35). We therefore wish to treat the formulas and laws for this limiting case separately. Equation (35) is applicable to the general case of a mixture of a variety of electrolytes that may also have only partially dissociated into ions. Here we consider the special case of a single species of molecule in solution. The molecule is completely dissociated into ions and consists of s -ion species, numbered 1, i , s , such that

$$\nu_1, \dots, \nu_i, \dots, \nu_s$$

ions of the species 1, ..., i , ..., s compose the molecule. The charges associated with each of these ions are

$$z_i \varepsilon, \dots, z_i \varepsilon, \dots, z_s \varepsilon.$$

(For H_2SO_4 , this would be dissociated into the ions H and SO_4 , for example,

$$\nu_1 = 2, \nu_2 = 1, z_1 = +1, z_2 = -2,$$

if the superscript index 1 is related to the H -ions and the superscript index 2 to the SO_4 -ions.)

Because the molecule as a whole is uncharged, it is true that

$$\sum_1^s \nu_i z_i = 0.$$

The solution now consists of N_o molecules of solvent and N molecules of the added electrolyte, where N is considered small relative to N_o . Then,

$$c_i = \frac{N_i}{N_o + \sum_1^s N_i} = \frac{N_i}{N_o}.$$

Considering that

$$N_i = \nu_i N$$

and designates c as the concentration of the dissolved species, in the approximation used here

$$c = \frac{N}{N_o},$$

so will

$$c_i = \nu_i c.$$

Equation (35) for the freezing point depression then becomes

$$\frac{\Delta Q}{T_o RT_o} = f_o \sum c_i = f_o c \sum \nu_i \quad (36)$$

with

$$f_o = 1 - \frac{\varepsilon^2 x}{6DkT} \frac{\sum \nu_i z_i^2 \sigma_i}{\sum \nu_i}. \quad (37)$$

The quantity f_o is the osmotic coefficient mentioned in the introduction, because $f_o = 1$ would correspond to the transition to classical theory, as shown by equation (35'). If one calls Δ_k the freezing point depression calculated according to the classical theory, then

$$\frac{\Delta}{\Delta_k} = f_o$$

or

$$1 - f_o = \frac{\Delta_k - \Delta}{\Delta_k}.$$

The relation in equation (37) therefore shows, qualitatively for the moment, that the actual depression of the freezing point must be smaller than expected under classical theory, a result that is consistently confirmed for dilute electrolyte solutions. The quantities x and σ occurring in equation (37) are determined by equations (22) and (33) (the latter with the associated table). As explained in the previous section, σ_i measures the influence of the ionic size and disappears at very low concentrations, because then σ tends to value 1. Accordingly, if we deal first with the limiting law, which should be valid for goose large dilutions, then in the limiting case we find

$$f_o = 1 - \frac{\varepsilon^2 x}{6DkT} \frac{\sum \nu_i z_i^2}{\sum \nu_i}. \quad (38)$$

On the other hand, according to equation (22)

$$x^2 = \frac{4\pi\varepsilon^2}{DkT} \sum n_i z_i^2 ;$$

however, because

$$n_i = \nu_i \frac{N}{V} = \nu_i n$$

with the introduction of the volume concentration n of the dissolved molecules, so too

$$x^2 = \frac{4\pi n \varepsilon^2}{DkT} \sum \nu_i z_i^2.$$

It follows that for very low concentrations,

$$f_o = 1 - \frac{\varepsilon^2}{6DkT} \sqrt{\frac{4\pi\varepsilon^2}{DkT} n} \sum \nu_i \left(\frac{\sum \nu_i z_i^2}{\sum \nu_i} \right)^{3/2}, \quad (38')$$

where $n \sum \nu_i$ represents the total number of ions per cm^3 of the solution, and

$$w = \left(\frac{\sum \nu_i z_i^2}{\sum \nu_i} \right)^{3/2} \quad (39)$$

is to be called the valence factor, because it measures the influence of the ion valences z_i on the phenomena. It is best not to consider f_o itself but the deviation from 1 (unity) and so write for very low concentrations:

$$1 - f_o = w \frac{\varepsilon^2}{6DkT} \sqrt{\frac{4\pi\varepsilon^2}{DkT} n \sum \nu_i}. \quad (40)$$

Firstly, with this formula expressing how the deviations $1 - f_o$ depend on the concentration, namely, it states in this regard:

Theorem 1.

For all electrolytes, in the limit for low concentrations, the percentage deviation of the freezing point depression from the classical value is proportional to the square root of the concentration.

It is possible to state this law as a general law because all the electrolytes for large dilutions can be considered as completely dissociated into ions. Of course, only the strong electrolytes practically reach that area of complete dissociation.

Secondly, equation (39) makes a statement about the influence of ion valence, which can be formulated as follows:

Theorem 2.

If the dissolved molecule dissociates into $\nu_1, \dots, \nu_i, \dots, \nu_s$ different ions of types 1, \dots, i, \dots, s with the valences $z_1, \dots, z_i, \dots, z_s$, then, for low concentrations, the percentage deviation of the freezing point depression from the classical value is proportional to a valence factor w , which is calculated from

$$w = \left(\frac{\sum \nu_i z_i^2}{\sum \nu_i} \right)^{3/2}.$$

As an example for the calculation of this valence factor, Table 2 is presented, where in the left column an example of the type of salt is given, and in the right column the value of w is given:

Table II

Type	Valence factor, w
KCl	$1 \cdot 1$
$CaCl_2$	$2 \sqrt{2} = 2.83$
$CuSO_4$	$4 \sqrt{4} = 8$
$AlCl_3$	$3 \sqrt{3} = 5.20$
$Al_2(SO_4)_3$	$6 \sqrt{6} = 16.6$

The influence of the ions therefore increases considerably with increasing valence, which also corresponds to the qualitative findings.

Thirdly, the solvent has an influence, in the sense of Nernst's well-known suggestion for explaining the ionizing force of solvents with a high dielectric constant. Following equation (40), one finds

Theorem 3.

For low concentrations, the percent deviation of the freezing point depression from the classical value is inversely proportional to the 3/2th power of the dielectric constant of the solvent.

The remaining constants in equation (40) are the charge of the elementary electric quantum $\varepsilon = 4.77 \cdot 10^{-10}$ e.s.u., Boltmann's constant $k = 1.346 \cdot 10^{-16}$ erg, and the temperature T , the latter of which occurs both explicitly and implicitly, because the dielectric constant D varies with T .

If one deals with dilute solutions in the conventional sense, then σ can no longer be replaced by 1 (unity), and equation (37) comes into effect, which is explicit:

$$1 - f_o = w \frac{\varepsilon^2}{6DkT} \sqrt{\frac{4\pi\varepsilon^2}{DkT} n \sum \nu_i \frac{\sum \nu_i z_i^2 \sigma_i}{\sum \nu_i z_i^2}}. \quad (41)$$

As Table 1 shows, as well as equation (33), upon which it is based, σ_i continuously decreases with increasing concentration, and ultimately

$$\frac{3}{x_i^2} = \frac{3}{x^2 a_i^2},$$

i.e. inversely proportional to the concentration, because x is proportional to the square root of this quantity. Therefore, according to equation (41), the deviation $1 - f_o$ must first increase proportional to the square root of the concentration for very low concentrations but then increase with increasing concentration in view of the influence of σ , i.e. the deviation will reach a maximum and finally decrease again inversely proportional to the square root of the concentration. Although this statement contains a poorly justified extrapolation to larger concentrations of equation (41), which is specialized for dilute solutions, the statement remains qualitatively valid even on closer examination of more concentrated solutions (see Section 9). In fact, the measurements also show a maximum of deviation of $1 - f_o$ as a characteristic of the curves for the freezing point depression. However, we believe that the phenomenon of hydration (see the concluding section) also significantly

influence the production of the maximum. A numerical comparison of the theory with empirical knowledge will be provided in Section 9.

8. The Dissociation Equilibrium.

If one does not restrict oneself only to strong electrolytes, there will be an equilibrium of dissociation between undissociated molecules and ions. However, this equilibrium will not be calculated according to the classical formula, because otherwise the mutual electrical forces of the ions will interfere. The way in which this happens according to our quantitative theory will be calculated here. We start again from equation (29) for the thermodynamic potential Φ of the solution

$$\Phi = \sum_0^s N_i(\varphi_i - k \log c_i) + \sum_1^s N_i \frac{z_i^2 \varepsilon^2}{3DT} x \chi_i;$$

the individual particles present in the solution are both charged and uncharged. For the latter we simply set $z_i = 0$. The solvent will be provided with the superscript index o . Now we introduce a variation of the number N_i in the well-known manner and calculate the corresponding change of the potential. This results in

$$\delta\Phi = \sum_{i=0}^{i=s} \delta N_i(\varphi_i - k \log c_i) + \sum_{i=1}^{i=s} \delta N_i \frac{z_i^2 \varepsilon^2}{3DT} x \chi_i + \sum_{i=1}^{i=s} N_i \frac{z_i^2 \varepsilon^2}{3DT} \frac{d(x\chi_i)}{dx} \sum_{j=1}^{j=s} \frac{\partial x}{\partial N_j} \delta N_j,$$

taking into account that, according to the definition-equation (22),

$$x^2 = \frac{4\pi\varepsilon^2}{DkT} \sum_{l=1}^{l=s} n_l z_l^2 = \frac{4\pi\varepsilon^2}{DkT} \sum_{l=1}^{l=s} \frac{N_l z_l^2}{V}$$

the quantity x may depend on all numbers $N_1 \dots N_s$. If one exchanges the indices of summation i and j in the third sum, then $\delta\Phi$ may also be reduced to the form:

$$\delta\Phi = \delta N_o(\varphi_o - k \log c_o) + \sum_{i=1}^{i=s} \delta N_i \left[\varphi_i - k \log c_i + \frac{\varepsilon^2}{3DT} \left(z_i^2 x \chi_i + \sum_{j=1}^{j=s} N_j z_j^2 \frac{d(x\chi_i)}{dx} \frac{\partial x}{\partial N_i} \right) \right].$$

However, following the definition of x , $\frac{\partial x}{\partial N_i}$ can be calculated. If, for the volume, the linear approach is maintained,

$$\frac{\partial x}{\partial N_i} = \frac{x}{2 \sum_1^s n_l z_l^2} * \frac{z_i^2 - v_i \sum_1^s n_l z_l^2}{V}.$$

Making the conventional assumption that the following proportion holds in a chemical reaction in the solution

$$\delta N_1 : \delta N_2 : \dots : \delta N_i : \dots : \delta N_s = \mu_1 : \mu_2 : \dots : \mu_i : \dots : \mu_s ,$$

the condition for equilibrium follows from the variation of the potential

$$\sum_{i=1}^{i=s} \mu_i \log c_i = \sum_{i=1}^{i=s} \frac{\mu_i \varphi_i}{k} + \frac{\varepsilon^2 x}{6DkT} \sum_{i=1}^{i=s} \left\{ 2\mu_i z_i^2 \chi_i + \mu_i (z_i^2 - v_i \sum_1^s n_j z_j^2) \frac{\sum_{j=1}^{j=s} n_j z_j^2 \frac{d(x\chi_j)}{dx}}{\sum_{j=1}^{j=s} n_j z_j^2} \right\}. \quad (42)$$

This differs from the classical condition by the additional term on the right-hand side. If one introduces the activity coefficient f_a , as was done in the introduction, one sets

$$\sum_1^s \mu_i \log c_i = \log(f_a K),$$

where K is the classical equilibrium constant, the activity coefficient is defined by the relationship

$$\log f_a = \frac{\varepsilon^2 x}{6DkT} \sum_{i=1}^{i=s} \left\{ 2\mu_i z_i^2 \chi_i + \mu_i (z_i^2 - v_i \sum_1^s n_j z_j^2) \frac{\sum_{j=1}^{j=s} n_j z_j^2 \frac{d(x\chi_j)}{dx}}{\sum_{j=1}^{j=s} n_j z_j^2} \right\}. \quad (43)$$

According to this formula, it is of course possible to provide each atom participating in the reaction or molecule with its own activity coefficient by setting

$$\log f_a = \mu_i \log f_a^1 + \dots \mu_i \log f_a^i + \dots \mu_s \log f_a^s \quad (44)$$

with

$$\log f_a^i = \frac{\varepsilon^2 x}{6DkT} \left\{ 2z_i^2 \chi_i + (z_i^2 - v_i \sum_1^s n_j z_j^2) \frac{\sum_1^s n_j z_j^2 \frac{d(x\chi_j)}{dx}}{\sum_1^s n_j z_j^2} \right\}. \quad (44')$$

Then, however, as shown by equation (44') by the appearance of x , this coefficient referring to a particular species of molecule will not be applicable solely to quantities related to that type of atom.

Again, simplifications are possible when limited to smaller concentrations. In that case,

$$v_i \sum_1^s n_j z_j^2$$

can be neglected compared to z_i^2 ; when this is the case, the volume of the dissolved substance is regarded as vanishing with respect to the volume of the whole solution. Therefore,

$$\log f_a^i = \frac{\varepsilon^2 x}{6DkT} z_i^2 \left\{ 2 \chi_i + \frac{\sum_1^s n_j z_j^2 \frac{d(x\chi_j)}{dx}}{\sum_1^s n_j z_j^2} \right\}. \quad (45)$$

Finally, the limit can be specified for the activity coefficient for maximally dilute solutions. In this limit, where the effect of ion's size vanishes, $\chi = 1$ can be set to obtain

$$\log f_a^i = \frac{\varepsilon^2 x}{2DkT} z_i^2. \quad (45')$$

Because x depends on the properties of all ions (affected by their valence), even in this limit, coefficient f_a^i is not simply a function of the properties of the i th ion. We refrain from discussing the limiting law in detail and only comment again that, in the limit, $\log f_a$ is proportional to the square root of the concentration.

9. Comparison of Freezing Point Depression with Experimental Empirical Knowledge.

Fig. 2 depicts the characteristic behavior of strong electrolytes. On the horizontal axis, the variable $\nu\gamma$, which measures the ion concentration, is plotted against γ , which, as stated earlier, is the concentration of the electrolyte in moles per liter [27], while $\nu = \sum \nu_i$ represents the number of ions into which one molecule of the salt dissociates. The four representatives KCl , K_2SO_4 , $La(NO_3)_3$ and $MgSO_4$ were selected from the four types distinguished by their ionic valences. KCl dissociates into two univalent ions, K_2SO_4 into one univalent and two bivalent ions, $La(NO_3)_3$ into three univalent and one trivalent ions, and $MgSO_4$ into two divalent ions. If we designate the freezing point depression with Δ_k that is expected in the case of complete dissociation according to the classical theory, and the real observed freezing point depression with Δ , the expression is

$$\Theta = \frac{\Delta_k - \Delta}{\Delta_k}, \quad (46)$$

i.e. the percentage deviation from the classical value was found and plotted as ordinate. Following Section 7 we also set

$$\Theta = 1 - f_o ; \quad (46')$$

as shown, Θ indicates the deviation of the osmotic coefficient from its limiting value 1. Because, in an aqueous solution,

$$\Delta_k = \nu\gamma * 1.860^\circ \quad (47)$$

for all electrolytes, a point on the axis of abscissa corresponds to a concentration that should always produce the same freezing point depression disregarding the mutual forces. We have plotted the observed values alone without the corresponding curve to avoid any interference. This method, however, was only made possible by the fact that some American researchers have recently carried out very excellent measurements of freezing point depression at low concentrations. The measurements of Fig. 2 are from Adams and Hall and Harkins [28].

It is evident that the deviation Θ does not increase, as the law of mass action would require, for small concentrations proportional to the first or even a higher power of the concentration.

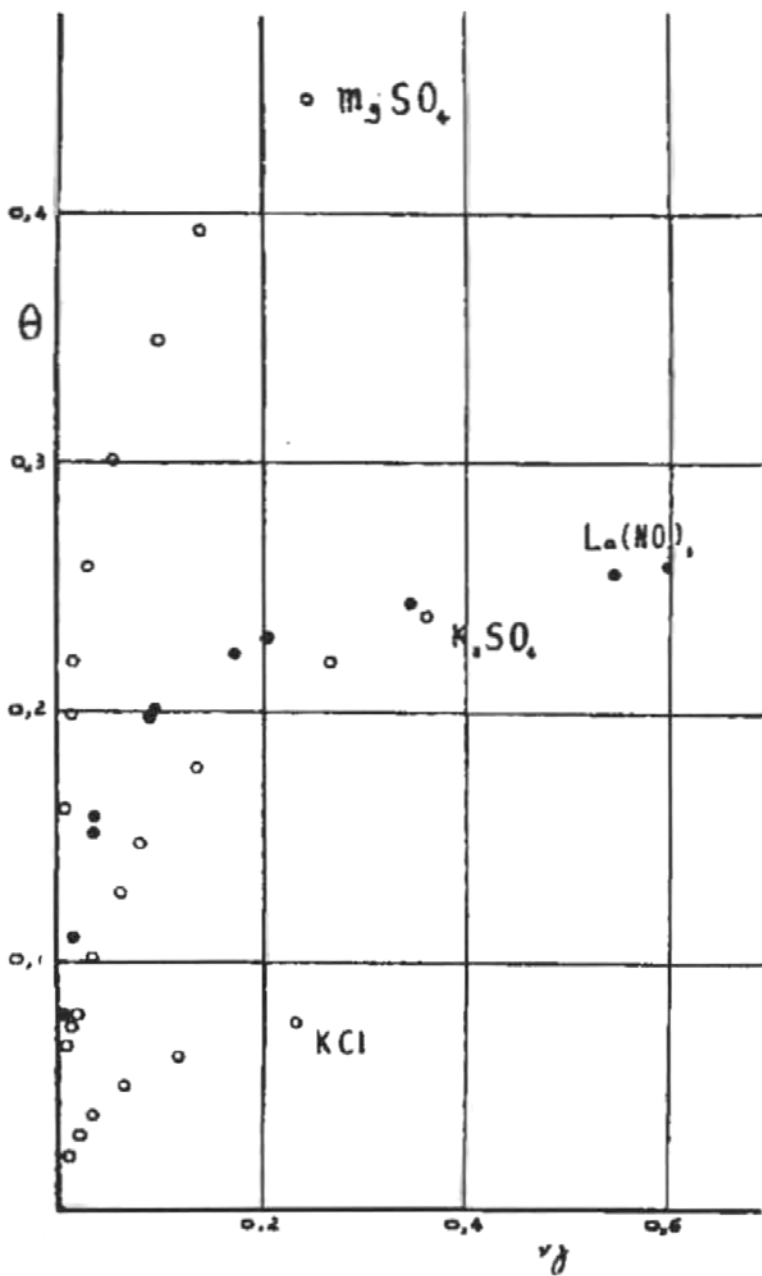


Fig. 2.

Additionally, the curves demonstrate the strong influence of ion valence.

Our theory now requires that, at very low concentrations, the percentage deviation Θ be proportional to the square root of the concentration, with a factor of proportionality that depends substantially on the valence of the ions. According to equations (39) and (40) (if the molecule dissociate into $\nu_1 \dots \nu_i \dots \nu_s$ ions with valences $z_1 \dots z_i \dots z_s$)

$$\Theta = 1 - f_o = w \frac{\varepsilon^2}{6DkT} \sqrt{\frac{4\pi\varepsilon^2}{DkT} n \sum \nu_i} \quad (48)$$

with the valence factor

$$w = \left(\frac{\sum \nu_i z_i^2}{\sum \nu_i} \right)^{3/2}. \quad (49)$$

We must now express the number of ions n per cm^2 in concentration γ , measured in moles per liter. We assume the value $6.06 * 10^{23}$ for Loschmidt's number, then

$$n = 6.06 * 10^{20} \gamma.$$

Further, it is assumed that $\varepsilon = 4.77 * 10^{-10}$ e.s.u., $k = 1.346 * 10^{-16}$ erg, and, because the following deals with freezing points of aqueous solutions, $T = 273$ [sic]. For the dielectric constant of water, we take the formula of interpolation calculated by Drude from measurements, according to which [29], for 0°C ,

$$D = 88.23 .$$

Using these figures (setting $\sum \nu_i = \nu$),

$$\sqrt{\frac{4\pi\varepsilon^2}{DkT} n \nu} = 0.231 * 10^8 \sqrt{\nu \gamma} \frac{1}{\text{cm}}$$

and therefore

$$\Theta = 0.270 w \sqrt{\nu \gamma}. \quad (50)$$

The quantity x becomes, using the above numerical values,

$$x = 0.231 * 10^8 \sqrt{\nu \gamma} \sqrt{\frac{\sum \nu_i z_i^2}{\nu} \frac{1}{\text{cm}}}. \quad (51)$$

In Fig. 3, observed values [30] of Θ were plotted against the abscissa $\sqrt{\nu \gamma}$, and the observed points have been connected by straight lines.

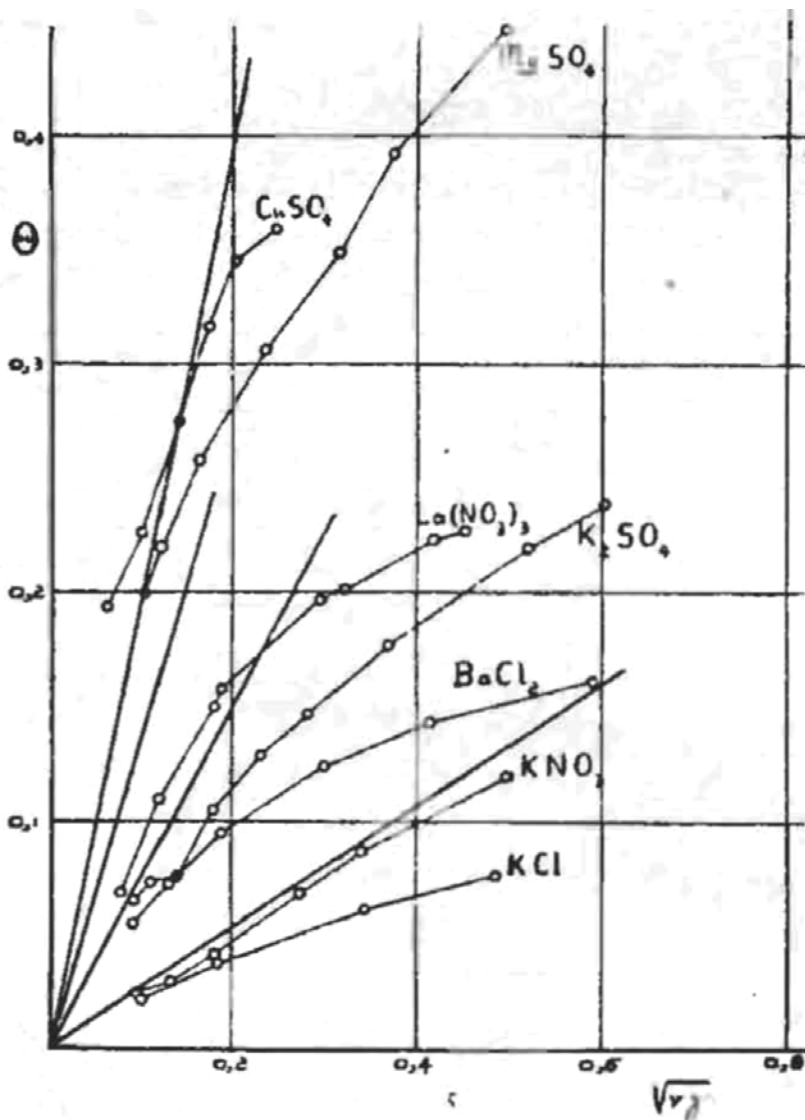


Fig. 3.

Additionally, in the figure, four straight lines radiating from the origin are depicted, which represent the limiting law of equation (50). The four types of salt in the figure have the valence factors

$$w = 1, w = 2\sqrt{2}, w = 3\sqrt{3}, w = 8,$$

corresponding to the aforementioned straight lines. It is apparent that the straight lines are approximated for small concentrations, such that the limiting law with the square root from the concentration evidently corresponds to the facts. The absolute values of the slope (as expressed by the factor $0.270 w$ in equation (50)), calculated using the dielectric constant 88.23, and otherwise theoretically distinguished only by the valence factor, are confirmed by the experiment. However, Fig. 3 shows that deviations from the limiting law begin early. This agrees with the considerations of Section 3 and equation (51), according to which, even in the case of uni-univalent electrolytes, the characteristic length $1/x$ is on the order

of magnitude of the ion diameter already at $\gamma = 1$, and it is therefore no longer permissible to neglect it. We have now based our theory on the simplified form of equation (21'), of the potential equation. This too could have an effect. However, we pointed out (see note 18) that this latter effect is theoretically relatively small. The experimental results also indicate that the deviation from the limiting law are caused by the individual properties of the ions. To show this, we present Fig. 4.

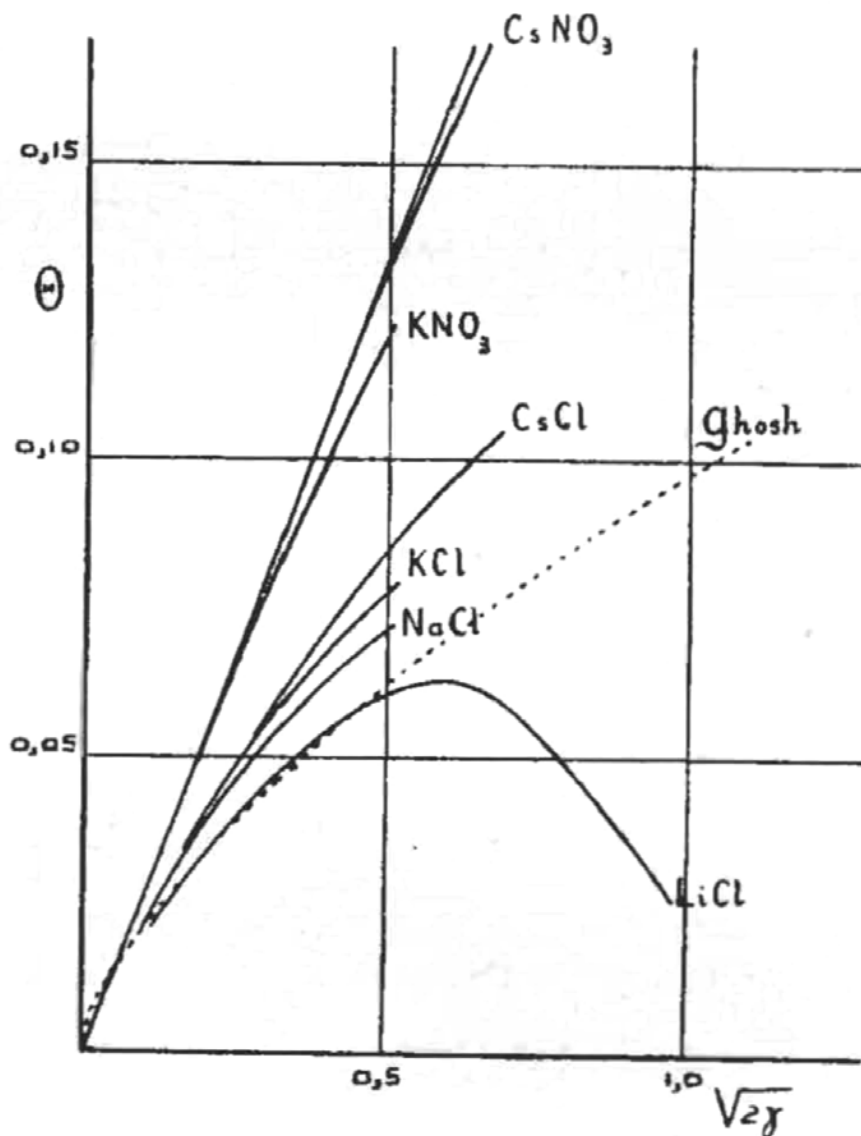


Fig. 4.

These observations are entered only for uni-univalent salts [31] as a function of $\sqrt{2\gamma}$ (because $\nu = 2$ here). The straight line represents the limiting law discussed above. The deviations are very different in magnitude and remarkably, in the case of the chloride salts, are ordered as *Cs*, *K*, *Na*, and *Li*. This is the same sequence that results when alkali ions are ordered by decreasing mobility, an order that contradicts the assumed size of the ions and, more recently from Born [32], was considered to be correlated with the relaxation time of water for electric polarization according to dipole theory. In order to allow an orientation towards

work by Ghosh, the curve for Θ is provided as a dashed line in the figure, as it results from that theory. It should simultaneously apply to all salts and also goes to the origin with a vertical tangent.

The question then arises as to how far our theory, which has been improved with regard to ionic dimensions, is able to account for the individual deviations. The relationships are illustrated in Fig 5.

Again, we chose the four electrolytes from the four types mentioned above and plotted the observed values for Θ as a function of $\sqrt{\nu\gamma}$. According to equation (41), considering the ionic size (after entering the numerical values),

$$\Theta = 1 - f_o = 0.270w\sqrt{\nu\gamma} \frac{\sum \nu_i z_i^2 \sigma_i}{\sum \nu_i z_i^2}, \quad (52)$$

where σ_i represents the formula of the argument $x_i = xa_i$ tabulated in Table 1 and given by equation (33), where a_i is the length of the size of the i th ion relative to its surroundings. It seemed to us appropriate, in the present situation, not to investigate the individual sizes of ions, but to calculate with a mean diameter a that is the same for all ions of an electrolyte. Then all σ_i become equal to each other and one obtains the expression for Θ

$$\Theta = 0.270 w \sqrt{\nu\gamma} \sigma(xa). \quad (53)$$

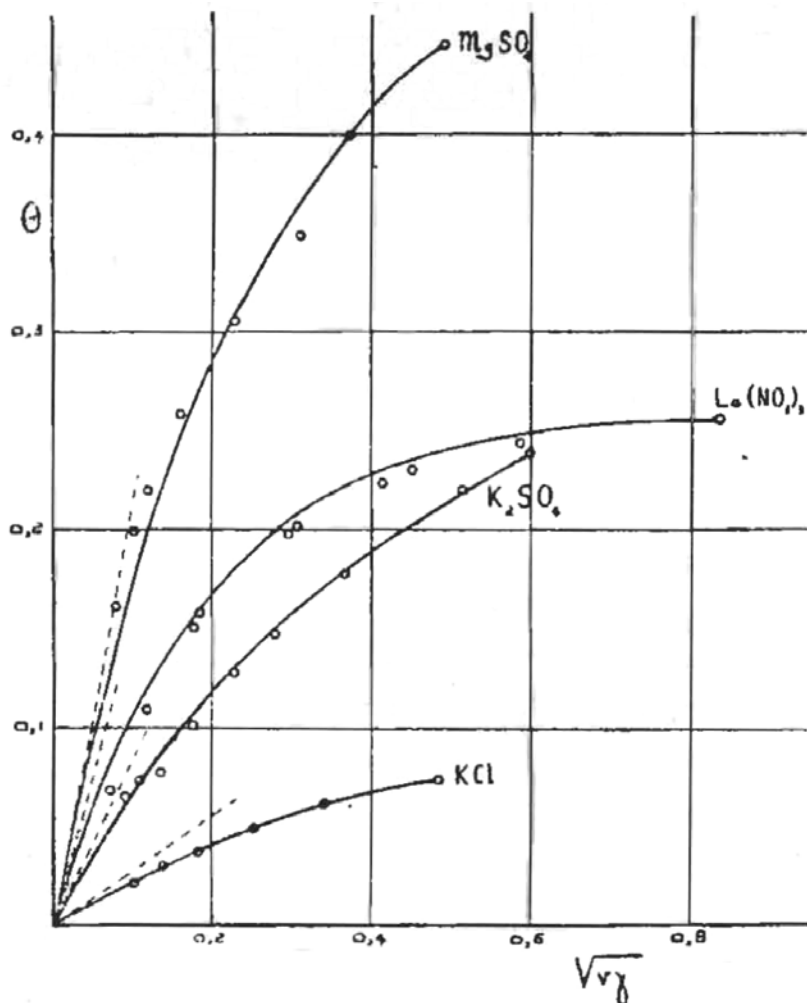


Fig. 5.

For the determination of the magnitude of a , we chose only one, namely the point observed at the highest concentration, and then plotted the curve, with a determined according to the theoretical equation (53), in the figure. Four dashed straight lines radiate from the origin (the tangents of the curves) representing the limiting law equation (50) for large dilutions. The agreement with the observations is a very good one, especially in terms of the determination of the constant from a single observation point [33]. The figure is supplemented by the following tables:

Table III.
 $KCl (a = 3.76 \times 10^{-8} \text{cm})$

2γ	$\sqrt{2\gamma}$	θ observed	θ calculated
0.0100	0.100	0.0214	0.0237
0.0193	0.139	0.0295	0.0313
0.0331	0.182	0.0375	0.0392
0.0633	0.252	0.0485	0.0499
0.116	0.341	0.0613	0.0618
0.234	0.484	0.0758	---

Table IV.

 $K_2SO_4(a = 2.69 \times 10^{-8} \text{ cm})$

$3\gamma'$	$\sqrt{3\gamma'}$	Θ observed	Θ calculated
0.00722	0.0906	0.0647	0.0612
0.0121	0.110	0.0729	0.0724
0.0185	0.136	0.0776	0.0871
0.0312	0.176	0.101	0.108
0.0527	0.229	0.128	0.132
0.0782	0.280	0.147	0.152
0.136	0.369	0.178	0.183
0.267	0.516	0.220	0.217
0.361	0.600	0.238	---

Table V.

 $La(NO_3)_3(a = 4.97 \times 10^{-8} \text{ cm})$

$4\gamma'$	$\sqrt{4\gamma'}$	Θ observed	Θ calculated
0.00528	0.0728	0.0684	0.0828
0.0142	0.119	0.110	0.121
0.0322	0.179	0.151	0.157
0.0343	0.185	0.158	0.161
0.0889	0.298	0.197	0.204
0.0944	0.308	0.201	0.207
0.173	0.418	0.223	0.230
0.205	0.453	0.229	0.235
0.346	0.588	0.243	0.248
0.599	0.836	0.255	---

Table VI.

 $MgSO_4(a = 3.35 \times 10^{-8} \text{ cm})$

$2\gamma'$	$\sqrt{2\gamma'}$	Θ observed	Θ calculated
0.00640	0.0800	0.160	0.147
0.0107	0.103	0.199	0.179
0.0149	0.122	0.220	0.203
0.0262	0.162	0.258	0.248
0.0534	0.231	0.306	0.311
0.0976	0.312	0.349	0.368
0.138	0.372	0.392	0.400
0.242	0.493	0.445	---

In the first column, the respective ion concentration [34] $\nu\gamma$, in the second column the abscissa $\sqrt{\nu\gamma}$ of Fig. 5, in the third column the observed value of Θ [34], and in the fourth column the value of the same quantity calculated from equations (53) and (51). The number corresponding to the largest concentration is not listed here, because it was used to calculate the value of the mean diameter a stated in the heading of the tables.

Finally, Fig. 6 provides a plot of the theory and observation of aqueous KCl solutions. In discussing this figure, our primary goal is to make some remarks regarding the behavior of concentrated solutions; in addition, we intend to show how large the deviations are between the separate results given in the literature by individual observers with purportedly great accuracy. For this purpose, the figure contains all the observations we have found of KCl solutions since the year 1900 [35].

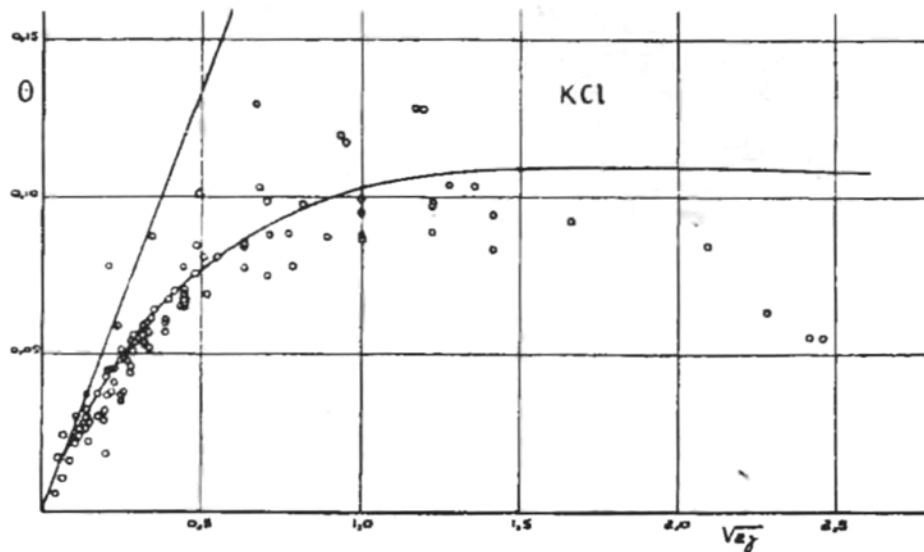


Fig. 6.

As an abscissa, as previously, $\sqrt{2\gamma}$ is chosen, where γ is by definition the concentration in moles per liter of solution. All data referring to differently measured concentrations have been converted to those concentrations using measured densities [36] of *KCl* solutions. The ordinate is again referred to as Θ but does not exactly represent the previous expression

$$\frac{\Delta_k - \Delta}{\Delta_k}.$$

In fact, the classical theory, when it comes to concentrated solutions, no longer shows proportionality of freezing point depression and concentration. The first reason for this is that $\log(1 - c)$ appears in the classical equation, not the concentration c itself. Second, the difference between the thermodynamic potentials of ice and water is no longer accurately represented by the first term of the Taylor series, proportional to Δ , and the second member, incorporating Δ^2 , must be retained. Accordingly, in this case, we have to use the full equation (34). In the case of *KCl*, $n_1 = n_2 = n$ and $z_1 = -z_2 = 1$ are to be set, and we wish to replace the two ion diameters a_1 and a_2 by a mean value a . Then equation (34) can be arranged as follows

$$\frac{1}{2nv_o} \left[\frac{\Delta}{T_o} \frac{Q}{RT_o} - \frac{\Delta}{T_o^2} \left(\frac{C_p - C'_p}{2R} - \frac{Q}{RT_o} \right) + \log(1 - 2c) \right] = -\frac{\varepsilon^2 x}{6Dkt} \sigma. \quad (54)$$

The left-hand term is now calculated for different concentrations. For this, we set $C_p - C'_p = 3.6$, corresponding to an approximate value for $C'_p = 14.4$, as extrapolated from Nernst's measurements [37] of the specific heat of ice at 273° . For the calculation it is still necessary to know the molar concentration c and the volume concentration γ . With the aid of the observed density of the solution, this relation can be readily established; however, both here and in the derivation of the equation itself, the molecular weight of the water has a certain influence. As a first approximation, this influence disappears, but the second-order members are not free from this influence. Insofar as this effect only influences the second

order, its influence is greatly suppressed, so we have consistently used the simple expected molecular weight 18. The quantity $2nv_o$ in the denominator can finally be equal to

$$2nv_o = 2\Omega_o \frac{\gamma}{1000}$$

if Ω_o signifies the molar volume of water. If no mutual electrical effect of the ions were present, the left-hand term would have to be zero at the onset of the observed depression of the freezing point. In fact, it gives a finite value, and we call that value $-\Theta$. Then, according to the theory, this difference Θ must be represented by the right-hand term, such that

$$\Theta = \frac{\varepsilon^2 x}{6DkT} \sigma(xa) = 0.270\sqrt{2\gamma} \sigma(xa) \quad (55)$$

should hold. Moreover, it is confirmed that the definition of Θ obeyed here agrees with the limit given above for low concentrations.

The points, which are plotted in the figure, have the ordinates calculated from the observations using the outlined method. The curve in the figure represents the right-hand term of equation (55), assuming $a = 3.76 * 10^{-8}$ cm. This value of a was determined from an observation by Adams, according to which the experimental value $\Theta = 0.0758$ pertains to $\gamma = 0.117$. The straight line, which is also plotted in the figure, again represents the limiting law for extreme dilution corresponding to $\sigma = 1$. It can be claimed that the observations are representative up to concentrations of about 1 mol/liter. At higher concentrations, the observations show a maximum for Θ . Although the theoretical curve has a maximum, but this is, as the figure shows, so flat that it is hardly indicated. We would like to regard this difference at high concentrations as real and make several remarks in the next section.

10. General Remarks.

It may be concluded from the preceding sections that it is inadmissible from the theoretical as well as the experimental standpoint to consider the electrical energy of an ionic solution essentially determined by the mean mutual distance of the ions. Rather, the characteristic length is a quantity that measures the thickness of the ionic atmosphere, or, to refer to a more familiar concept, the thickness of a Helmholtz double-layer. Because this thickness depends on the concentration of the electrolyte, the electrical energy of the solution also becomes a function of this quantity. The fact that this thickness is inversely proportional to the square root of the concentration results from the fact that the limiting laws for large dilutions owe their characteristic nature to that $1/2$ power. We must therefore refrain from discussing a lattice structure of the electrolyte in the popular sense, and, as the development of the subject has shown, although taking this image too literally will lead to impermissible errors, a kernel of truth is contained in it. To make this clear, we will perform the following two thought experiments. First, take a space unit and think of moving it many times in succession to any point of the electrolyte. It is clear that, in a binary electrolyte, one will encounter equally often a positive as a negative ion. Second, however, take the same space unit and place it in the electrolyte many times in succession, not quite arbitrarily but always such that it, for example, is always removed by a certain distance (of several

angstrom) from a randomly selected positive ion. Now, one will no longer encounter both positive and negative charges but more frequently the negative ones. Therefore, in the immediate vicinity of each ion, the oppositely charged ions predominate in number, and one can rightly see an analogy to the crystal structure of the *NaCl* type, where every *Na*-ion is directly surrounded by 6 *Cl*-ions and every *Cl*-ion by 6 *Na*-ions. However, it is important to note an essential characteristic of the electrolyte solution is that the measure of order is determined by the thermal equilibrium between attractive forces and thermally induced movement, while it is predetermined in the crystal.

The calculations and the comparison with empirical knowledge were carried out such that the ambient solvent was expected to have its usual dielectric constant. The success proves the validity of this assumption, but in itself this procedure is justified at low concentrations and should lead to errors at large concentrations. In fact, it follows from dipole theory that dielectrics at high field strengths [*Feldstärken*] must exhibit saturation phenomena that are similar to the known magnetic saturation. The recent experiments by Herweg [38] can be regarded as an experimental confirmation of this theoretical requirement. Because a field strength of approximately 200 000 volt/cm can be expected at a distance of 10^{-7} cm from a singly charged ion, one should be prepared to observe some of these saturation phenomena. It would, of course, be very interesting if it were possible to extract that effect from these observations, the more such that nature makes available to us field strengths of a magnitude that would otherwise be difficult to attain by ordinary experimental means.

But, in other ways, more concentrated solutions must exhibit special behavior. If there are many ions in the surroundings of each individual, this may be considered a change of the surrounding medium in electrical terms, an effect that has not been considered in the preceding theory. Whatever it may be, let it emerge from the following consideration. Take an ion that is held captive and one that is mobile, approximately oppositely charged, and investigate the work required to remove the mobile ion. This work can then be regarded as consisting of two parts: firstly, the ion will consume some work to remove it, but secondly, one will gain work by subsequently filling the space previously occupied by the ion with the solvent. Now, experiments on the heat of dilution actually provide an indication of the real existence of such conditions. If, for example, a solution of *HNO*₃ of initially low concentration is used and it is diluted with a large amount of water (that is, so much that dilution would no longer produce a thermal effect), then cooling takes place, i.e., work must be done in the sense of the prior considerations to further separate the ions from each other. However, if the starting solution has a larger concentration, heat will be generated in the same experiment, i.e., work is gained by liberating the surroundings of each ion from enough other ions and replacing them with water molecules. In conventional terms, this means that hydration of the ions predominantly occurs, and this process is considered to be an exothermic process. Obviously, the above considerations aim to interpret this so-called hydration with purely electrical methods. In fact, it is possible to make an approximate calculation that theoretically gives Berthelot's rules for the dependence of the heat of dilution on the initial concentration, which makes knowable the order of magnitude of the numerical coefficients as they are found in practice. For the freezing point observations, these considerations are meaningful in that they suggest the possibility of calculating why and to what extent the curves found for the percent deviation Θ (see the case of *KCl*) bend downwards at higher concentrations and even cross the abscissa axis, provided the concentration is high enough. In this case, the freezing point depression is greater than that which is classically expectable (and also, explicitly stated, if the classical theory is used in its unabridged form). Until then, one had been contented to speak of hydration in

such instances.

However, before the conditions for concentrated solutions can be investigated, it must first be shown that the irreversible process of conduction of the current in dilute strong electrolytes can be quantitatively controlled from the standpoint taken here. We reserve the detailed statements on this subject for the following article, in which one will find their mathematical execution. Here we content ourselves with a presentation of the basic ideas. If an ion in the liquid moves under the influence of an external field strength, the surrounding ions must constantly rearrange in order to be able to form the ion atmosphere. If one now assumes a charge has suddenly arisen in the interior of the electrolyte, then the ionic atmosphere requires a certain relaxation time for its formation. Similarly, for the moving ion, the surrounding atmosphere will not be able to achieve its equilibrium distribution [*Gleichgewichtsverteilung*], so it will not be calculable on the basis of the Boltzmann-Maxwell principle. However, their determination can be properly carried out with the equations for Brownian motion. It can already be qualitatively estimated in what sense this effect can have an effect based on the presence of a finite relaxation time. At a point in front of the moving ion (i.e., a point toward which it moves), the electrical density of the ionic atmosphere must increase with time; for a point behind the ion, it must decrease. Owing to the effect of the relaxation time, however, the density before the ion will be somewhat smaller than its equilibrium values, but behind it will not have dropped to its equilibrium value. As a result, during movement there is always a slightly larger electrical density of the atmosphere behind the ion than in front of the ion. Because charge density and ion charge always carry opposite signs, a force occurs that slows the ion in its motion, regardless of its sign, and that obviously must increase with increasing concentration.

This is one effect that works in the same sense as the decrease of the degree of dissociation, which is otherwise calculated on the basis of Ostwald's law of dilution. But there is a second effect that must also be considered. In the vicinity of one ion there exist predominantly ions of opposite sign, which, of course, move in the opposite direction under the influence of the external field. These ions will drag with them the surrounding solvent to some extent. This means, therefore, that the individual ion considered does not have to move relative to a stationary solvent but rather relative to a solvent moving in the opposite direction. Because, apparently, this effect increases with increasing concentration, one has a second effect, which acts in the same sense as a decrease of the degree of dissociation. Quantitatively calculated, the effect may be based on the same principles that Helmholtz has applied for the treatment of electrophoresis.

The common factor of the two effects mentioned is, as the calculations show, that both are directly related to the thickness of the ionic atmosphere, and therefore the forces generated are proportional to the square root of the concentration of the electrolyte, at least in the limit of very low concentrations. Therefore, according to the observation material of Kohlrausch [39], at low concentrations, the percentage deviation of the molecular conductivity from its limiting value is proportional to the square root of the concentration. The proportionality factor naturally receives a molecular interpretation.

Anticipating the detailed presentation of the conditions of electrolytic conduction in the following article, we can conclude, as a result of the whole account, that the notion, according to which the strong electrolytes are completely dissociated, is entirely supported.

Zurich, February 1923.

(Received February 27, 1923.)

Notes

- 1) The present considerations were inspired by a lecture by E. Bauer in the local Physical Society based on Ghosh's works. The general points of view, which are used here to calculate freezing point depression and conductivity, led me, among other things, to the limiting law using the square root of concentration. I was able to report about it in the winter of 1921 in the local colloquium. Under the active assistance of my assistant Dr. E. Huckel, the detailed discussion of the results and their summary took place in the winter of 1922. – P. Debye
- 2) N. Bjerrum, *Zeitschr. f. Elektrochemie* 24, 231, 1918.
- 3) A summary of this subject was reported by L. Ebert, "Research on the anomalies of strong electrolytes (Forschungen ueber die Anomallen starker Electrolyte)," *Jahrb. Rad. u. Elektr.* 18, 134, 1921.
- 4) See Fig. 2.
- 5) W. Sutherland, *Phil. Mag.* 14, 1, 1907.
- 6) Proceedings of the seventh international congress of applied chemistry, London May 27th to June 2nd, 1909, Section X: A new form for the electrolytic dissociation theory.
- 7) Milner, *Phil. Mag.* 23, 551, 1912; 25, 743, 1913.
- 8) J. Ch. Ghosh, *Chem. Soc. Journ.* 113, 449, 627, 707, 790, 1918; *Zeitschr. f. phys. Chem.* 98, 211, 1921.
- 9) P. Hertz, *Ann. d. Phys.* (4) 37, 1, 1912.
- 10) N. Bjerrum, *l.c. und Zeitschr. f. anorgan. Chem.* 109, 275, 1920.
- 11) The activity coefficient f_a introduced here is not completely identical to that introduced by Bjerrum. Namely, Bjerrum splits our coefficient f_a into a product of coefficients, each of which is unique to the individual ionic species. (See Section 8.)
- 12) The potential G differs from the Helmholtz free energy $F = U - TS$ only by the factor $-\frac{1}{T}$. By itself, this difference is negligible; we define, as it appears in the text, a direct connection to Planck's thermodynamics.
- 13) See note 25.
- 14) Our relation differs from Planck's in that we do not count the number of moles but the actual number of particles, which proves to be more suited to our purposes. This corresponds to the occurrence of the Boltzmann constants k instead of the gas constant R . An essential difference from Planck is, of course, not caused by the above formulation.
- 15) See note 8.
- 16) It will be shown below that this assumption is true.

- 17) The considerations of O. Klein agree with this discussion of dimensions: Meddelanden från K. Vetenskapsakademiens Nobelinstitut 5, Nr. 6, 1919 (A commemoration of the 60th birthday of S. Arrhenius).
- 18) We have also investigated the influence of the following terms in the development of $\mathfrak{G} \ln \frac{\varepsilon \psi}{kT}$ and found that their influence on the final result is very small. For the sake of brevity, the communication of these calculations will be omitted.
- 19) The agreement of the above results regarding the bilayer with calculations of M. Gouy was subsequently shown. Journ. de phys. (4), 9, 457, 1910 on the theory of the capillary electrometer. Perhaps we may point out that in this case equation (10) enables a simple solution.
- 20) Apart from the graphical result mentioned in the introduction, Milner's work contains a footnote (Phil. Mag. 23, 575, 1912), according to which, in the case of the above text, in our notation

$$u = -\frac{\varepsilon^2}{D} x \sqrt{\frac{\pi}{2}}.$$

A derivative of this formula is missing. It differs from our resultant by the factor $\sqrt{\frac{\pi}{2}}$.

- 21) Because we are concerned only with the mutual potential energy, ψ_i must not take the value of the whole potential but only the part resulting from the surrounding charges, always calculated for the point at which the potential charge e_i is located.
- 22) Because, for monovalent salts, $n_1 = n_2 = n$ and $z_1 = z_2 = 1$, the general equation (22) for x^2 agrees with the earlier one (see equation (11)) given for this special case.
- 23) By the expression given for U_e , we are immediately able to derive to the heat of dilution. We convinced ourselves that the theoretical value corresponds to the observations.
- 24) In fact, a direct kinetic theory of osmotic pressure, reported elsewhere (*Recueil des travaux chimique des Pays-Bas et de la Belgique*), shows the validity of the final expression for G_e independent of this assumption. For a discussion of the thermodynamic calculation we can refer to B. A. M. Cavanagh, Phil. Mag. 43, 606, 1922.
- 25) The additional electric pressure p_e , which was mentioned in Section 2, equation (6'), results from this formula. The numerical value given there was calculated in this way.
- 26) There is no need to make a distinction between ions and uncharged molecules; if both occur, you simply have to set $z_i = 0$ for the latter. If all particles are uncharged, naturally equations (35) and (35') become identical.
- 27) For the salts K_2SO_4 , $La(NO_3)_3$, $MgSO_4$, instead of γ , the concentration γ' is used in moles per 1000 g of water, as given by the authors cited below, because, in the absence of measurements of the density of these salt solutions at 273°, a conversion into moles per liter was not executable; this means only an insignificant deviation among the low concentrations considered here.
- 28) L.H. Adams, Journ. Amer. Chem. Soc. 37, 481, 1915 (KCl); L.E. Hall u. W.D. harkins, ibid. 38, 1658, 1916 (K_2SO_4 , $La(NO_3)_3$, $MgSO_4$).
- 29) Ann. d. Phys. 59, 61, 1896.

- 30) L. H. Adams, l.c. (KNO_3 , KCl); R. E. Hall u. W. D. Harkins, l.c. (K_2SO_4 , $La(NO_3)_3$, $MgSO_4$, $BaCl_2$); T. G. Bedford, Proc. of the Royal Soc. A 83, 454, 1909 ($CuSO_4$) [Concentration in mol per liter at KCl , $CuSO_4$; a mole per 1000 g of water at KNO_3 , $BaCl_2$, K_2SO_4 , $La(NO_3)_3$].
- 31) In addition to the references cited, measurements by H. Jahn, Ztschr. F. Phys. Ch. 50, 129, 1905; 59, 31, 1907 ($LiCl$, $CsCl$); E.W. Washburn et al. MacInnes, Journ. Amer. Chem. Soc. 33, 1686, 1911 ($LiCl$, $CsNO_3$); W.H. Harkins u. W.A. Roberts, ibid. 38, 2658, 1916 ($NaCl$) [concentration partly in moles per liter, partly in moles per 1000 g of water].
- 32) M. Born, Zeitschr. f. Phys. 1, 221, 1920.
- 33) The method for determining a is explained in detail using the example of $La(NO_3)_3$. For $\gamma' = 0.17486$ was observed $\Theta' = 0.2547$; because $\nu = 4$, the abscissa becomes $\sqrt{\nu\gamma'} = 0.836$. According to the limiting law equation (50) for extreme dilution, if $w = 3\sqrt{3}$ (as $\nu_1 = 1$, ν_2 , $z_1 = 3$, $z_2 = -1$ corresponding to equation (49)) then $\Theta = 1.173$, the value actually observed is derived from this limit by multiplication by 0.216. This factor is equal to σ according to equation (53). From Fig. 1 one now finds the ordinate $\sigma = 0.216$ has the abscissa $x = xa = 1.67$; on the other hand, according to equation (51), $\sqrt{\nu\gamma'} = 0.836$ is the value of $x = 0.336 * 10^{-8} \text{cm}^{-1}$. So the observed value is the diameter
- $$a = \frac{x}{\chi} = 4.97 * 10^{-8} \text{cm.}$$
- [For the salts K_2SO_4 , $La(NO_3)_3$, $MgSO_4$, the concentration γ' is given in moles per 1000 g of water and was used instead of γ for the determination of Θ , which is therefore designated Θ' . For the low concentrations considered here, the deviations are very slight; a conversion from γ' to γ observed no appreciable change in the values for the Θ' observed, the Θ' calculated, and the a yielded.]
- 34) See the previous note.
- 35) J. Barnes, Trans. Nova Scot. Inst. of Science 10, 139, 1900; C. Hebb, ibid. 10, 422, 1900; H. J. Jones, J. Barnes u. E. P. Hyde, Americ. Chem. Journ. 27, 22, 1902; H. B. Jones u. Ch. G. Carroll, ibid. 28, 284, 1902; W. Biltz, Zeitschr. f. phys. Chem. 40, 185, 1902; Th. W. Richards, ibid. 44, 563, 1903; S. W. Young u. W. H. Sloan, Journ. Americ. Chem. Soc. 26, 919, 1904; H. Jahn, l.c.; T. G. Bedford, l.c.; F. Flügel, Zeischr. f. physl. Chem. 79, 577, 1912; L. H. Adams, l.c.; W. H. Rodenbusch, Journ. Americ. Chem. Soc [sic] 40, 1204, 1918.
- 36) Baxter u. Wallace, Journ. Americ. Chem. Soc. 38, 18, 1916.
- 37) W. Nernst, Berl. Ber. 1910, 1, 262.
- 38) Zeischr. f. Phys. 3, 36, 1920 and 8, 1, 1922.
- 39) F. Kohlrausch u. L. Holborn, The Conductivity of Electrolytes, 2nd ed., Leipzig 1916, p. 108 and 112.

[END OF TRANSLATION]

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ORIGINALMITTEILUNGEN.

Zur Theorie der Elektrolyte.

I. Gefrierpunktserniedrigung und verwandte Erscheinungen.

Von P. Debye und E. Hückel¹⁾.

§ 1. Einleitung.

Bekanntlich deutet die Arrheniussche Dissoziationshypothese die bei den Elektrolytlösungen beobachteten abnormal großen Werte von osmotischem Druck, Gefrierpunktserniedrigung usw., durch die Existenz freier Ionen und der damit Hand in Hand gehenden Vermehrung der Zahl der Einzelteilchen. Die quantitative Theorie stützt sich auf die von van't Hoff herrührende Übertragung der Gesetze idealer Gase auf die verdünnten Lösungen zur Berechnung ihres osmotischen Druckes. Da es möglich ist, diese Übertragung thermodynamisch zu begründen, so besteht kein Zweifel an der Gültigkeit der Grundlagen im allgemeinen.

Bei endlicher Konzentration aber ergeben sich für Gefrierpunktserniedrigung, Leitfähigkeit usw. Werte, welche kleiner sind, als man auf den ersten Blick beim Vorhandensein einer vollkommenen Dissoziation der Elektrolyte in Ionen erwarten müßte. Ist z. B. P_k der osmotische Druck, welcher sich nach dem klassischen van't Hoff'schen Gesetz für vollkommene Dissoziation ergibt, so ist der tatsächlich zu beobachtende osmotische Druck kleiner, so daß

$$P = f_0 P_k,$$

wobei in Übereinstimmung mit Bjerrum²⁾ der

1) Angeregt wurde ich zu den vorliegenden Überlegungen durch einen Vortrag von E. Bauer in der hiesigen Physikalischen Gesellschaft über die Ghosh'schen Arbeiten. Die allgemeinen Gesichtspunkte, von denen hier zur Berechnung von Gefrierpunktserniedrigung, sowie der Leitfähigkeit ausgegangen wird, führten mich unter anderem zu dem Grenzgesetz mit der zweiten Wurzel der Konzentration. Ich konnte darüber im Winter 1921 im hiesigen Kolloquium berichten. Unter der tätigen Mithilfe meines Assistenten Dr. E. Hückel fand dann im Winter 1922 die eingehende Diskussion der Ergebnisse und ihre Zusammenfassung statt. P. Debye.

2) N. Bjerrum, Zeitschr. f. Elektrochemie 24, 231, 1918.

hiermit eingeführte „osmotische Koeffizient“ f_0 , unabhängig von jeder Theorie, jene Abweichungen messen soll und als Funktion von Konzentration, Druck und Temperatur beobachtbar ist. In Wirklichkeit beziehen sich solche Beobachtungen nicht unmittelbar auf den osmotischen Druck selber, sondern auf Gefrierpunktserniedrigung, bzw. Siedepunktserhöhung, welche beide aus thermodynamischen Gründen mit Hilfe desselben osmotischen Koeffizienten f_0 aus ihren nach dem van't Hoff'schen Gesetz für vollkommene Dissoziation folgenden Grenzwerten ableitbar sind.

Die nächstliegende Annahme zur Erklärung des Auftretens jenes osmotischen Koeffizienten ist die klassische, wonach nicht alle Moleküle in Ionen dissoziiert sind, sondern zwischen dissoziierten und undissoziierten Molekülen ein Gleichgewicht besteht, welches von der Gesamtkonzentration, sowie von Druck und Temperatur abhängt. Die Zahl der freien Einzelteilchen ist dementsprechend variabel, und zwar würde sie direkt proportional f_0 zu setzen sein. Die quantitative Theorie dieser Abhängigkeiten, soweit sie sich auf die Konzentration beziehen, stützt sich auf den Guldberg-Waageschen Ansatz, die Abhängigkeit der in diesem Ansatz auftretenden Gleichgewichtskonstanten von Temperatur und Druck ist nach van't Hoff auf thermodynamischem Wege zu bestimmen. Auch der ganze Komplex von Abhängigkeiten, mit Einschluß des Guldberg-Waageschen Ansatzes kann, wie Planck zeigte, thermodynamisch begründet werden.

Da die elektrische Leitfähigkeit nur durch die Ionen bedingt wird und nach der klassischen Theorie aus f_0 die Zahl der Ionen ohne weiteres folgt, so erhebt diese Theorie die Forderung des unmittelbaren, bekannten Zusammenhanges zwischen den beiden Abhängigkeiten von Leitfähigkeit einerseits, osmotischem Druck andererseits von der Konzentration.

Eine große Gruppe von Elektrolyten, die starken Säuren, Basen und die Salze derselben, zusammengefaßt unter dem Namen der „starken“

Elektrolyte, zeigt nun von den nach der klassischen Theorie geforderten Abhängigkeiten ausgesprochene Abweichungen, welche bemerkenswerterweise umso klarer hervortreten, je verdünnter die Lösungen sind¹⁾. So ist es, wie im Laufe der Entwicklung erkannt wurde, nur mit einer gewissen Annäherung möglich, aus f_0 , auf dem nach der klassischen Theorie geforderten Wege, auf die Abhängigkeit der Leitfähigkeit von der Konzentration zu schließen. Aber auch die Abhängigkeit des osmotischen Koeffizienten f_0 selber von der Konzentration wird ganz unrichtig wiedergegeben. Bei stark verdünnten Lösungen nähert sich f_0 dem Werte 1; trägt man nun $1 - f_0$ als Funktion der Konzentration c auf, so verlangt die klassische Theorie für binäre Elektrolyten, wie etwa KCl , daß diese Kurve in den Nullpunkt einmündet mit einer endlichen (durch die Gleichgewichtskonstante K bestimmten) Tangente. Zerfällt das Molekül des Elektrolyten allgemein in ν Ionen, so ergibt sich nach dem Massenwirkungsgesetz für kleine Konzentrationen:

$$1 - f_0 = \frac{\nu - 1}{\nu} \frac{c^{\nu-1}}{K},$$

so daß in Fällen, wo der Zerfall in mehr als 2 Ionen stattfindet, die fragliche Kurve sogar eine Berührung höherer Ordnung mit der Abszissenachse aufweisen müßte. Den Komplex dieser Abhängigkeiten stellt das Ostwaldsche Verdünnungsgesetz dar.

Tatsächlich zeigen die Beobachtungen an starken Elektrolyten ein ganz abweichendes Verhalten. Die experimentelle Kurve verläßt den Nullpunkt unter einem rechten Winkel²⁾ mit der Abszissenachse, unabhängig von der Ionenzahl ν . Alle vorgeschlagenen, praktischen Interpolationsformeln versuchen dieses Verhalten darzustellen, indem sie $1 - f_0$ einer gebrochenen Potenz (kleiner als 1, etwa $1/2$ oder $1/3$) der Konzentration proportional setzen. Dieselbe Erscheinung wiederholt sich bei der Extrapolation der Leitfähigkeit auf unendliche Verdünnung, welche nach Kohlrausch unter Benutzung einer Potenz $1/2$ erfolgen soll.

Es ist klar, daß unter diesen Umständen die klassische Theorie nicht beibehalten werden kann. Das ganze experimentelle Material weist vielmehr deutlich darauf hin, daß sie auch in ihren Grundzügen zu verlassen ist, und insbesondere nicht ein auf Grund des Guldberg-Waageschen Ansatzes berechenbares Gleichgewicht den wirklichen Erscheinungen entspricht.

1) Eine zusammenfassende Darstellung über diesen Gegenstand verfaßte L. Ebert, Forschungen über die Anomalien starker Elektrolyte. Jahrb. d. Rad. u. Elektr. 18, 134, 1921.

2) Vgl. Fig. 2.

W. Sutherland¹⁾ hat 1907 die Theorie der Elektrolyte überhaupt auf der Annahme einer vollkommenen Dissoziation aufbauen wollen. Seine Arbeit enthält manche gute Gedanken. N. Bjerrum²⁾ ist aber wohl derjenige, der zuerst zu einer richtig abgegrenzten Formulierung jener Hypothese gekommen ist. Er hat klar ausgesprochen und begründet, daß bei den starken Elektrolyten von einem Gleichgewicht zwischen dissoziierten und undissoziierten Molekülen überhaupt nichts bemerkbar ist, daß vielmehr zwingende Gründe bestehen, solche Elektrolyte bis zu großen Konzentrationen als vollständig in Ionen zerfallen anzusehen. Erst beim Übergang zu schwachen Elektrolyten treten undissoziierte Moleküle wieder auf. Damit fällt die klassische Erklärung als alleinige Grundlage für die Veränderlichkeit z. B. des osmotischen Koeffizienten dahin und es entsteht die Aufgabe nach einer bis dahin übersehenen Wirkung der Ionen zu suchen, welche trotz Abwesenheit einer Assoziation die Verminderung von f_0 mit zunehmender Konzentration erklären könnte.

In neuerer Zeit hat sich unter dem Einflusse von Bjerrum der Eindruck befestigt, daß die Berücksichtigung der elektrostatischen Kräfte, welche die Ionen aufeinander ausüben und welche infolge der relativ enormen Größe des elektrischen Elementarquantums stark ins Gewicht fallen sollten, die gesuchte Erklärung liefern muß. Von solchen Kräften ist in der klassischen Theorie nicht die Rede, sie behandelt vielmehr die Ionen als voneinander ganz unabhängige Bestandteile. Die gedachte Theorie entspricht etwa dem Schritte, den man macht, wenn man mit van der Waals von den Gesetzen der idealen zu denen der wirklichen Gase übergeht. Nur wird sie ganz andere Hilfsmittel heranzuziehen haben, weil die elektrostatischen Kräfte zwischen den Ionen nur mit dem Quadrate des Abstandes abnehmen und sich dadurch wesentlich unterscheiden von den Molekularkräften, welche mit zunehmendem Abstände viel schneller verschwinden.

Für den osmotischen Koeffizienten existiert eine Rechnung im angedeuteten Sinne von Milner³⁾. Sie ist in ihrem Aufbau einwandfrei, führt aber über mathematische Schwierigkeiten, welche nicht ganz überwunden werden und erreicht ihr Resultat nur in Form einer graphisch bestimmten Kurve für die Abhängigkeit zwischen $1 - f_0$ und der Konzentration.

1) W. Sutherland, Phil. Mag. 14, 1, 1907.

2) Proceedings of the seventh international congress of applied chemistry, London May 27th to June 2nd, 1909, Section X: A new form for the electrolytic dissociation theory.

3) Milner, Phil. Mag. 23, 551, 1912; 25, 743, 1913.

Überdies wird aus dem Folgenden hervorgehen, daß der Vergleich mit der Erfahrung, den Milner anstellt, die Zulässigkeit seiner Vernachlässigungen bei viel zu hohen Konzentrationen supponiert, bei denen tatsächlich die von Milner nicht in Rechnung gestellten individuellen Eigenschaften der Ionen schon eine sehr wesentliche Rolle spielen. Trotzdem wäre es ungerecht, wollte man die Milnerschen Rechnungen zurückstellen hinter den Rechnungen neueren Datums von J. Ch. Ghosh¹⁾ über denselben Gegenstand. Wir werden im Folgenden darauf zurückzukommen haben, warum wir den Ghoshschen Rechnungen weder in ihrer Anwendung auf die Leitfähigkeit noch in ihrer immerhin durchsichtigeren Anwendung auf den osmotischen Druck beipflichten können. Wir sind sogar gezwungen, seine Berechnung der elektrostatischen Energie eines ionisierten Elektrolyten, welche allen seinen weiteren Schlüssen zugrunde liegt, als prinzipiell verfehlt zu bezeichnen.

Ganz ähnlich wie für den osmotischen Koeffizienten liegen die Verhältnisse bei der Berechnung der Leitfähigkeit. Auch hier muß die Theorie die gegenseitige elektrostatische Beeinflussung der Ionen in bezug auf ihre Beweglichkeit zu fassen suchen. Ein Versuch in dieser Richtung rührt von P. Hertz²⁾ her. Er überträgt die Methoden der kinetischen Gastheorie und findet tatsächlich eine gegenseitige Behinderung der Ionen. Indessen scheint uns die Übertragung jener Methoden und insbesondere das Operieren mit Begriffen, welche der freien Weglänge bei verdünnten Gasen entsprechen, auf den Fall freier Ionen mitten zwischen den Molekülen des Lösungsmittels schwerwiegenden Bedenken Platz zu lassen. Tatsächlich ist denn auch das Endresultat von Hertz für kleine Konzentrationen unvereinbar mit den experimentellen Ergebnissen.

In dieser ersten Notiz werden wir uns ausschließlich beschäftigen mit dem „osmotischen Koeffizienten f_0 “ und einem ähnlichen von Bjerrum benutzten³⁾ und in seiner Bedeutung hervorgehobenen „Aktivitätskoeffizienten f_a “. Auch bei solchen (schwachen) Elektrolyten nämlich, bei denen eine merkliche Zahl von undissoziierten Molekülen vorhanden ist, kann dieselbe nicht einfach nach dem Guldberg-Waageschen Ansatz in seiner klassischen Form

$$c_1^{\mu_1} c_2^{\mu_2} \dots c_n^{\mu_n} = K$$

(c_1, c_2, \dots, c_n Konzentrationen, K Gleichgewichts-

konstante) bestimmt werden. Man wird vielmehr mit Rücksicht auf die elektrostatischen Kräfte der Ionen untereinander statt K zu schreiben haben

$$f_a K,$$

unter Einführung eines Aktivitätskoeffizienten¹⁾ f_a . Dieser Koeffizient wird ebenso wie f_0 von der Ionenkonzentration abhängen. Zwar besteht nach Bjerrum zwischen f_a und f_0 ein thermodynamisch zu begründender Zusammenhang, aber die Abhängigkeit der beiden Koeffizienten von der Konzentration ist eine verschiedene.

Die ausführliche Behandlung der Leitfähigkeit behalten wir einer folgenden Notiz vor, eine Einteilung, welche innerlich begründet ist. Während nämlich die Bestimmung von f_0 und f_a geschehen kann unter alleiniger Heranziehung reversibler Prozesse, führt die Berechnung der Beweglichkeit über wesentlich irreversible Prozesse, bei denen ein unmittelbarer Zusammenhang mit den thermodynamischen Grundgesetzen nicht mehr besteht.

§ 2. Grundlagen.

Bekanntlich wird in der Thermodynamik gezeigt, daß die Eigenschaften eines Systems völlig bekannt sind, falls einer der vielen möglichen thermodynamischen Potentiale als Funktion der richtig gewählten Variablen gegeben ist. Der Form, in der die auf den gegenseitigen elektrischen Wirkungen beruhenden Glieder erscheinen, würde es entsprechen, wenn wir als Grundfunktion die Größe²⁾

$$G = S - \frac{U}{T} \quad (1)$$

(S = Entropie, U = Energie, T = absolute Temperatur) wählen würden. Als Variable sind hier (neben den Konzentrationen) Volumen und Temperatur naturgemäß, da

$$dG = \frac{p}{T} dV + \frac{U}{T^2} dT. \quad (1')$$

Die Rechnungen, welche im Folgenden auszuführen sind, unterscheiden sich von den klassischen durch die Berücksichtigung der elektrischen

1) Der hier eingeführte Aktivitätskoeffizient f_a ist nicht ganz identisch mit dem von Bjerrum eingeführten. Bjerrum zerlegt nämlich unsern Koeffizienten f_a in ein Produkt von Koeffizienten, welche den einzelnen Ionenarten als charakteristisch zugehören sollen. (Vgl. § 8.)

2) Das Potential G unterscheidet sich von der Helmholtzschen freien Energie $F = U - TS$ nur durch den Faktor $-\frac{1}{T}$. An sich ist dieser Unterschied ganz unwesentlich; wir definieren so, wie es im Text geschieht, um den direkten Anschluß an die Plancksche Thermodynamik zu haben.

1) J. Ch. Ghosh, Chem. Soc. Journ. 113, 449, 627, 707, 790, 1918; Zeitschr. f. phys. Chem. 98, 211, 1921.

2) P. Hertz, Ann. d. Phys. (4) 37, 1, 1912.

3) N. Bjerrum, l. c. und Zeitschr. f. anorgan. Chem. 109, 275, 1920.

Ionenwirkungen. Dementsprechend zerlegen wir U in zwei Bestandteile, einen klassischen Anteil U_k und eine elektrische Zusatzenergie U_e :

$$U = U_k + U_e.$$

Bedenkt man, daß nach (1)

$$T^2 \frac{\partial G}{\partial T} = U, \quad (2)$$

und zerlegt das Potential G ebenfalls in zwei Teile:

$$G = G_k + G_e,$$

so findet man nach (2)

$$G_e = \int \frac{U_e}{T^2} dT. \quad (3)$$

Unsere Hauptaufgabe besteht also darin, die elektrische Energie U_e einer Ionenlösung zu bestimmen. Für die praktische Verwertung ist aber das Potential G nicht so gut geeignet, wie die auch von Planck bevorzugte Funktion

$$\Phi = S - \frac{U + pV}{T}. \quad (4)$$

Wie die Differentialform dieser Definition

$$d\Phi = -\frac{V}{T} dp + \frac{U + pV}{T^2} dT \quad (4')$$

zeigt, sind nämlich beim Potential Φ Druck und Temperatur die naturgemäßen Variablen, und da die überwiegende Mehrzahl der Versuche bei konstantem Druck (und nicht bei konstantem Volumen) ausgeführt wird, ist Φ vorzuziehen. Ein Vergleich von (4) mit (1) ergibt

$$\Phi = G - \frac{pV}{T}; \quad (5)$$

ist also nach dem obigen G bekannt, so handelt es sich noch darum, das Zusatzglied $-pV/T$ als Funktion von p und T zu finden und hinzuzufügen. Mit Rücksicht auf (1') kann man schließen

$$\frac{p}{T} = \frac{\partial G}{\partial V} = \frac{\partial G_k}{\partial V} + \frac{\partial G_e}{\partial V}, \quad (6)$$

und hat so die Zustandsgleichung erhalten, welche bei der Ionenlösung Druck, Volumen und Temperatur miteinander verknüpft. Dieselbe kann so interpretiert werden, daß infolge der elektrischen Ionenwirkungen zum äußeren Druck p noch ein elektrischer Zusatzdruck p_e hinzugekommen ist, zu berechnen nach der Beziehung

$$p_e = -\frac{\partial G_e}{\partial V}. \quad (6')$$

Wir werden später nebenbei¹⁾ Gelegenheit haben, diesen elektrischen Druck p_e zu bestimmen, er beträgt für eine wäßrige Lösung z. B. von KCl bei einer Konzentration von 1 Mol pro Liter

1) Vgl. Anmerkung 1, S. 194.

nur etwa 20 Atm. Es ist also streng genommen nicht richtig, wenn wir für V (als Funktion von p und T) den klassischen Ansatz ohne Berücksichtigung der elektrischen Ionenwirkungen benutzen, da der Druck p_e auch eine Volumänderung hervorruft. Mit Rücksicht darauf aber, daß die Kompressibilität des Wassers so gering ist, daß 20 Atm. nur eine relative Volumänderung von 0,001 hervorrufen, kann für die meisten Anwendungen der elektrische Zusatz zu V (als Funktion von p und T) vernachlässigt werden. Im Sinne dieser Bemerkung werden wir auch Φ zerlegen in einen klassischen Teil und einen elektrischen Zusatzbestandteil

$$\Phi = \Phi_k + \Phi_e \quad (7)$$

und können nach (3)

$$\Phi_e = G_e = \int \frac{U_e}{T^2} dT \quad (7')$$

setzen. Der klassische Bestandteil Φ_k hat nach Planck die Form:

$$\Phi_k = \sum_0^s N_i (\varphi_i - k \log c_i), \quad (7'')$$

wobei

$$N_0, N_1, \dots, N_i, \dots, N_s$$

die Zahlen der Einzelteilchen in der Lösung bedeuten und N_0 sich speziell auf das Lösungsmittel beziehen soll¹⁾. Weiter ist das auf das Einzelteilchen bezogene thermodynamische Potential

$$\varphi_i = s_i - \frac{u_i + p v_i}{T}$$

eine von den Konzentrationen unabhängige Größe; k ist die Boltzmannsche Konstante $k = 1,346 \cdot 10^{-16}$ erg und c_i steht für die Konzentration der Teilchenorte i , so daß

$$c_i = \frac{N_i}{N_0 + N_1 + \dots + N_i + \dots + N_s},$$

was die Beziehung

$$\sum_0^s c_i = 1$$

nach sich zieht.

Nach Erledigung dieser thermodynamischen Vorbemerkungen kommen wir zur Besprechung der Hauptaufgabe: der Berechnung der elektrischen Energie U_e .

Auf den ersten Blick scheint es, als ob diese Energie unmittelbar auf folgendem Wege

1) Unsere Bezeichnung weicht insofern von der Planckschen ab, als wir nicht mit den Molzahlen, sondern mit den wirklichen Teilchenzahlen rechnen, was sich mit Rücksicht auf das Folgende zweckmäßiger erweist. Dem entspricht das Auftreten der Boltzmannschen Konstanten k an Stelle der Gaskonstante R . Ein irgendwie wesentlicher Unterschied gegen Planck wird natürlich durch die obige Formulierung nicht bedingt.

zu erhalten wäre. Befinden sich im Lösungsmittel mit der Dielektrizitätskonstanten D zwei elektrische Ladungen von der Größe ϵ und $-\epsilon$ im Abstände r , so ist ihre gegenseitige potentielle Energie

$$-\frac{1}{D} \frac{\epsilon^2}{r}.$$

Es sei nun der Einfachheit wegen bei dieser allgemeinen Überlegung an einen binären Elektrolyten wie etwa KCl gedacht, der vollständig in Ionen zerfallen ist, so daß im Volumen V der Lösung $N_1 = N$ Ionen K mit der Ladung $+\epsilon$ und gleichviel $N_2 = N$ Ionen Cl mit der Ladung $-\epsilon$ vorhanden sind. Man kann sich dann vorstellen, daß der mittlere Abstand r , der für die Energieberechnung eine Rolle spielt, dem mittleren Abstände der Ionen voneinander gleichkommt, und da das einem Ion zukommende Volumen gleich $V/2N$ ist, dafür setzen

$$r = \left(\frac{V}{2N}\right)^{1/3}.$$

Indem man für r diesen Wert benutzt, würde man die elektrische Energie der Lösung schätzen zu

$$U_e = -N \frac{\epsilon^2}{D} \left(\frac{2N}{V}\right)^{1/3}.$$

Tatsächlich geht J. Ch. Ghosh¹⁾ in dieser Weise vor. Die Überlegung aber ist prinzipiell verfehlt, und die ganze hierauf aufgebaute (durch die Einführung der dritten Wurzel aus der Konzentration praktisch gekennzeichnete) Theorie ist zu verwerfen.

Die (negative) elektrische Energie einer Ionenlösung kommt dadurch zustande, daß, wenn man irgendein Ion ins Auge faßt, in dessen Umgebung im Mittel öfter ungleichnamige als gleichnamige Ionen gefunden werden, eine unmittelbare Folge der zwischen den Ionen wirkenden elektrostatischen Kräfte. Ein charakteristisches Beispiel für einen äußerlich ähnlich liegenden Fall bilden die Kristalle wie $NaCl$, KCl usw., bei denen nach den Bragg'schen Untersuchungen jedes (auch hier als Ion auftretende) Atom unmittelbar von ungleichnamigen umgeben ist. So richtig es hier ist (in Übereinstimmung mit den genauen Rechnungen von M. Born) die elektrische Energie des Kristalls zu schätzen unter Einsetzung des Abstandes zweier benachbarter ungleichnamiger Atome, so fehlerhaft ist die Überwertung dieses Bildes als Analogiefall, wenn man bei der Lösung den mittleren Abstand $\left(\frac{V}{2N}\right)^{1/3}$ die entsprechende Rolle spielen läßt. Tatsächlich hat hier eine ganz andere Länge für die Energie eine Be-

deutung, da die Ionen frei beweglich sind und die gesuchte Länge demnach erst folgen kann auf Grund der Bewertung von Unterschieden in der Wahrscheinlichkeit der Verweilzeiten gleichnamiger und ungleichnamiger Ionen in demselben Volumelement in der Nähe eines hervorgehobenen Ions. Schon hieraus folgt, daß die Temperaturbewegung eine wesentliche Rolle bei der Berechnung von U_e zu spielen hat.

Rein dimensionsmäßig kann man nicht mehr wie folgendes schließen: Angenommen die Größe der Ionen brauche für große Verdünnungen nicht berücksichtigt zu werden¹⁾, dann ist eine Energie der oben schon angegebene Ausdruck

$$\frac{\epsilon^2}{D} \left(\frac{2N}{V}\right)^{1/3}.$$

Daneben aber spielt die andere durch kT gemessene Energie der Wärmebewegung eine gleichberechtigte Rolle. Es steht also zu erwarten, daß U_e die Form annehmen wird

$$U_e = -N \frac{\epsilon^2}{D} \left(\frac{2N}{V}\right)^{1/3} f\left(\frac{\epsilon^2}{D} \left(\frac{2N}{V}\right)^{1/3} / kT\right), \quad (8)$$

wobei f eine Funktion des Verhältnisses jener beiden Energien ist, über die man a priori nichts aussagen kann²⁾.

Auch die Betrachtung des Grenzfalles hoher Temperaturen führt zu demselben Schluß. Ist nämlich die Energie der Temperaturbewegung eine große und betrachtet man ein Volumelement in der Nähe eines für die Betrachtung besonders hervorgehobenen Ions, so ist die Wahrscheinlichkeit, daß dort ein gleichnamiges Ion gefunden wird gleich groß wie dieselbe Wahrscheinlichkeit für ein ungleichnamiges. In der Grenze für hohe Temperaturen muß also U_e verschwinden, d. h. der Ausdruck für U_e enthält T auch bei mittleren Temperaturen als wesentlichen Parameter.

§ 3. Berechnung der elektrischen Energie einer Ionenlösung eines ein-einwertigen Salzes.

In einem Volumen V seien N -Moleküle eines ein-einwertigen Salzes (Beispiel KCl) in Ionen zerfallen vorhanden; der Absolutwert der Ladung eines Ions sei ϵ ($4,77 \cdot 10^{-10}$ e. s. E.), die Dielektrizitätskonstante des Lösungsmittels sei D . Wir fassen eines dieser Ionen mit der Ladung $+\epsilon$ ins Auge und beabsichtigen dessen potentielle Energie u relativ zu den umgebenden Ionen

1) Im Folgenden wird gezeigt werden, daß diese Annahme tatsächlich zutrifft.

2) In Übereinstimmung mit dieser Dimensionsbetrachtung stehen die Überlegungen von O. Klein: Meddelanden från K. Vetenskapsakademiens Nobelinstitut 5, Nr. 6, 1919 (Festschrift zum 60. Geburtstage von S. Arrhenius).

1) l. c.

zu bestimmen. Die direkte Berechnung, wie sie von Milner versucht wurde, indem er jede mögliche Anordnung der Ionen in Betracht zieht und mit ihrer, dem Boltzmannschen Prinzip entsprechenden Wahrscheinlichkeit in die Rechnung eingehen läßt, hat sich als mathematisch zu schwierig erwiesen. Wir ersetzen sie deshalb durch eine andere Betrachtung, bei der die Rechnung von vornherein auf den Mittelwert des von den Ionen erzeugten elektrischen Potentials abzielt.

In einem Punkte P in der Umgebung des hervorgehobenen Ions herrsche im zeitlichen Mittel das elektrische Potential ψ ; bringt man ein positives Ion dorthin, so ist die Arbeit $+\varepsilon\psi$, für ein negatives Ion dagegen die Arbeit $-\varepsilon\psi$ zu leisten. In einem Volumelement dV an dieser Stelle wird man deshalb im zeitlichen Mittel nach dem Boltzmannschen Prinzip

$$ne^{-\frac{\varepsilon\psi}{kT}} dV$$

positive und

$$ne^{+\frac{\varepsilon\psi}{kT}} dV$$

negative Ionen finden, wenn $n = \frac{N}{V}$ gesetzt wird. In der Tat muß in der Grenze für $T = \infty$ die Verteilung der Ionen gleichmäßig werden, so daß der Faktor vor der Exponentialfunktion gleich $\frac{N}{V}$, d. h. gleich der Zahl der Ionen einer Sorte pro cm^3 der Lösung gesetzt werden muß. Mit jenen Angaben ist indessen vorläufig noch nichts zu erreichen, da das Potential ψ des Punktes P noch unbekannt ist. Nach der Poissonschen Gleichung muß aber jenes Potential der Bedingung

$$\Delta\psi = -\frac{4\pi}{D}\rho$$

genügen, wenn die Elektrizität mit der Dichte ρ im Medium von der Dielektrizitätskonstante D verteilt ist. Andererseits ist nach dem Obigen

$$\rho = n\varepsilon \left(e^{-\frac{\varepsilon\psi}{kT}} - e^{+\frac{\varepsilon\psi}{kT}} \right) = -2n\varepsilon \text{Cin} \frac{\varepsilon\psi}{kT}; \quad (9)$$

also kann ψ bestimmt werden als Lösung der Gleichung

$$\nabla^2\psi = \Delta\psi = \frac{8\pi n\varepsilon}{D} \text{Cin} \frac{\varepsilon\psi}{kT}. \quad (10)$$

Je weiter man sich von dem hervorgehobenen Ion entfernt, um so kleiner wird das Potential ψ werden, für größere Entfernung wird man demnach mit genügender Näherung $\text{Cin} \frac{\varepsilon\psi}{kT}$ durch

$\frac{\varepsilon\psi}{kT}$ ersetzen können. Tut man das, so nimmt (10) die viel einfachere Form an¹⁾

$$\Delta\psi = \frac{8\pi n\varepsilon^2}{DkT} \psi. \quad (10')$$

Darin hat der rechts stehende Faktor von ψ die Dimension eines reziproken Quadrates einer Länge. Wir setzen

$$\kappa^2 = \frac{8\pi n\varepsilon^2}{DkT}, \quad (11)$$

so daß κ eine reziproke Länge ist und (10') wird zu

$$\Delta\psi = \kappa^2\psi. \quad (12)$$

Die somit eingeführte Länge

$$\frac{1}{\kappa} = \sqrt{\frac{DkT}{8\pi n\varepsilon^2}}$$

ist die wesentlichste Größe unserer Theorie und ersetzt die mittlere Entfernung der Ionen in der von uns abgelehnten Ghoshschen Betrachtung. Setzt man Zahlenwerte ein (vgl. später) und mißt die Konzentration wie gebräuchlich in Mol pro Liter Lösung, so wird, wenn die so gemessene Konzentration mit γ bezeichnet wird

$$\frac{1}{\kappa} = \frac{3,06}{\sqrt{\gamma}} 10^{-8} \text{ cm}$$

für Wasser bei 0°C . Die charakteristische Länge erreicht also bei einer Konzentration $\gamma = 1$ (1 Mol pro Liter) molekulare Dimensionen.

Wir wollen nunmehr den Gang der Überlegungen unterbrechen, um die physikalische Bedeutung der charakteristischen Länge näher zu beleuchten.

Es sei in eine Elektrolytlösung vom Potential ϕ eine Elektrode eingetaucht, deren Oberfläche gegen diese Lösung eine Potentialdifferenz ψ besitzt. Der Übergang von ψ auf ϕ wird dann stattfinden in einer Schicht von endlicher Dicke, welche durch die obigen Überlegungen gegeben wird. Benutzen wir (12) und nennen wir z eine Koordinate senkrecht zur Elektrodenoberfläche, so ist nämlich

$$\psi = \Psi e^{-\kappa z}$$

ein Ansatz, der (12) befriedigt. Da das rechte Glied von (12) im Sinne der Poissonschen

Gleichung $-\frac{4\pi}{D}\rho$ bedeutet, so ist also die mit dem angegebenen Potential verknüpfte Ladungsdichte

1) Wir haben auch den Einfluß der folgenden Glieder in der Entwicklung von $\text{Cin} \frac{\varepsilon\psi}{kT}$ untersucht und konnten dabei feststellen, daß dieser Einfluß auf das Endresultat sehr geringfügig ist. Der Kürze halber wird von der Mitteilung dieser Rechnungen Abstand genommen.

$$\rho = -\frac{D\kappa^2}{4\pi} \psi e^{-\kappa r}.$$

Nach dieser Formel mißt demnach $\frac{1}{\kappa}$ diejenige Länge, auf der die elektrische Dichte der Ionenatmosphäre auf den e ten Teil abnimmt. Unsere charakteristische Länge $\frac{1}{\kappa}$ ist ein Maß für die Dicke einer solchen Ionenatmosphäre, (d. h. der bekannten Helmholtzschen Doppelschicht); nach (11) ist dieselbe abhängig von Konzentration, Temperatur und Dielektrizitätskonstante des Lösungsmittels¹⁾.

Nachdem die Bedeutung der Länge $\frac{1}{\kappa}$ klar gestellt ist, soll nunmehr (12) benutzt werden, um die Potential- und Dichteverteilung in der Umgebung des hervorgehobenen Ions mit der Ladung $+\varepsilon$ zu bestimmen. Wir nennen den Abstand von diesem Ion r und führen in (12) räumliche Polarkoordinaten ein. Dann wird (12)

$$\frac{1}{r^2} \frac{d}{dr} \left(r^2 \frac{d\psi}{dr} \right) = \kappa^2 \psi, \quad (12')$$

und diese Gleichung hat die allgemeine Lösung

$$\psi = A \frac{e^{-\kappa r}}{r} + A' \frac{e^{\kappa r}}{r}. \quad (13)$$

Da ψ im Unendlichen verschwindet, muß $A' = 0$ sein; die Konstante A dagegen muß aus den Verhältnissen in der Nähe des Ions bestimmt werden. Diese Bestimmung wollen wir in zwei Schritten a) und b) ausführen, indem wir unter a) die Annahme machen, daß die Dimensionen des Ions keine Rolle spielen; unter b) die endliche Größe der Ionen in Betracht ziehen. Die Überlegungen unter a) liefern dann das Grenzesetz für große Verdünnungen, während unter b) die Änderungen fallen, welche an diesem Grenzesetz für größere Konzentrationen vorzunehmen sind.

a) Ionendurchmesser verschwindend.

Das Potential einer einzigen Punktladung ε in einem Medium von der Dielektrizitätskonstante D wäre

$$\psi = \frac{\varepsilon}{D r},$$

falls in dem Medium keine andern Ionen vorhanden sind. Mit diesem Ausdruck muß unser

1) Es zeigte sich nachträglich die Übereinstimmung der obigen Resultate über die Doppelschicht mit Rechnungen von M. Gouy. Journ. de phys. (4), 9, 457, 1910 zur Theorie des Kapillarelektrometers. Vielleicht dürfen wir noch darauf aufmerksam machen, daß in diesem Falle die unverkürzte Gleichung (10) eine einfache Lösung zuläßt.

Potential (13) für unendlich kleine Entfernungen übereinstimmen, also ist

$$A = \frac{\varepsilon}{D}$$

zu setzen und das gesuchte Potential wird:

$$\psi = \frac{\varepsilon}{D} \frac{e^{-\kappa r}}{r} = \frac{\varepsilon}{D} \frac{1}{r} - \frac{\varepsilon}{D} \frac{1 - e^{-\kappa r}}{r}. \quad (14)$$

Wir haben gleich das Potential in zwei Bestandteile zerlegt, von denen das erste das durch die umgebenden Ionen unbeeinflusste Potential ist, und von denen der zweite Teil das von der Ionenatmosphäre herrührende Potential darstellt. Für kleine Werte von r wird der Wert dieses letzteren Potentials gleich

$$-\frac{\varepsilon}{D} \kappa;$$

die potentielle Energie u , welche das hervorgehobene Ion $+\varepsilon$ gegen seine Umgebung besitzt, beträgt also¹⁾

$$u = -\frac{\varepsilon^2}{D} \kappa. \quad (15)$$

Hat man nun eine Reihe von Ladungen e_i und trägt das Potential jeweilig am Orte einer Ladung ψ_i , so ist nach den Gesetzen der Elektrostatik die gesamte potentielle Energie

$$U_e = \frac{1}{2} \sum e_i \psi_i.$$

In unserm Falle, wo N positive Ionen vorhanden sind, von denen jedes gegen seine Umgebung die Potentialdifferenz $-\frac{\varepsilon}{D} \kappa$ hat, und außerdem N -negative Ionen mit der Potentialdifferenz $+\frac{\varepsilon}{D} \kappa$ hinzukommen, wird demnach die gesuchte potentielle Energie²⁾

$$U_e = \frac{N\varepsilon}{2} \left(-\frac{\varepsilon \kappa}{D} \right) - \frac{N\varepsilon}{2} \left(+\frac{\varepsilon \kappa}{D} \right) = -\frac{N\varepsilon^2 \kappa}{D}. \quad (16)$$

Dabei ist κ als Funktion der Konzentration durch (11) gegeben, so daß die potentielle Energie der Ionenlösung der zweiten Wurzel aus der Konzentration und nicht wie bei Ghosh

1) Außer dem in der Einleitung erwähnten graphischen Resultat enthält die Milnersche Arbeit eine Fußnote (Phil. Mag. 23, 575, 1912), wonach im Falle des obigen Textes in unserer Bezeichnungsweise

$$u = -\frac{\varepsilon^2}{D} \kappa \sqrt{\frac{\pi}{2}}.$$

Eine Ableitung dieser Formel fehlt, sie unterscheidet sich von unserem Resultat durch den Faktor $\sqrt{\frac{\pi}{2}}$.

2) Da es uns nur um die gegenseitige potentielle Energie zu tun ist, muß für ψ_i nicht der Wert des ganzen Potentials, sondern nur der Teil, der von den umgebenden Ladungen herrührt, genommen werden, stets berechnet für den Punkt, in dem sich die Ladung e_i befindet.

der dritten Wurzel derselben Größe proportional wird.

b) Ionendurchmesser endlich.

Wir bemerkten früher, daß die charakteristische Länge $\frac{1}{\kappa}$ bei Konzentrationen von 1 Mol pro Liter die Kleinheit molekularer Dimensionen erreicht. Es muß deshalb bei solchen Konzentrationen unstatthaft sein, das Ion endlicher, molekularer Größe durch eine Punktladung zu ersetzen, so wie das unter a) geschah. Dem Sinne unserer auf der Poissonschen Gleichung aufgebauten Rechnung würde es nicht entsprechen, wollte man detaillierte Vorstellungen über die gegenseitigen Annäherungsabstände der Ionen einführen. Wir wollen vielmehr im Folgenden ein Bild zugrunde legen, wonach ein Ion angesehen wird als eine Kugel vom Radius a , deren Inneres zu behandeln ist wie ein Medium mit der Dielektrizitätskonstante D und in deren Mittelpunkt die Ladung $+\varepsilon$, oder $-\varepsilon$ als Punktladung vorhanden ist. Die Größe a mißt dann offenbar nicht den Ionenradius, sondern steht für eine Länge, welche einen Mittelwert bildet für den Abstand bis auf welchen die umgebenden, sowohl positiven, wie negativen Ionen an das hervorgehobene Ion herankommen können. Dementsprechend wäre a bei völlig gleichdimensionierten positiven und negativen Ionen z. B. von der Größenordnung des Ionendurchmessers zu erwarten. Dabei ist im allgemeinen dieser Ionendurchmesser noch nicht als Durchmesser des wirklichen Ions anzusehen, da die Ionen voraussichtlich ihrer Hydratation entsprechend von einer fest haftenden Schicht Wassermoleküle umgeben zu denken sind. Wir können also durch die oben auseinandergesetzte schematische Berücksichtigung mit Hilfe der Länge a nur eine Näherung an die Wirklichkeit erreichen. Die Diskussion praktischer Fälle (vgl. später) wird allerdings zeigen, daß diese Näherung praktisch eine recht weitgehende ist.

Für das Potential um ein hervorgehobenes Ion ist nach wie vor zu setzen

$$\psi = A \cdot \frac{e^{-\kappa r}}{r}, \quad (17)$$

nur muß die Konstante A jetzt anders bestimmt werden. Nach unseren Voraussetzungen wird im Inneren der Ionenkugel (für ein positives Ion)

$$\psi = \frac{\varepsilon}{D} \frac{1}{r} + B \quad (17')$$

zu setzen sein. Die Konstanten A und B sind aus den Grenzbedingungen an der Oberfläche der Kugel zu bestimmen. Dort, d. h. für $r=a$, müssen sowohl die Potentiale ψ , wie auch die

Feldstärken $-\frac{d\psi}{dr}$ stetig ineinander übergehen.

Danach wird

$$\left. \begin{aligned} A \frac{e^{-\kappa a}}{a} &= \frac{\varepsilon}{D} \frac{1}{a} + B, \\ A \cdot e^{-\kappa a} \frac{1 + \kappa a}{a^2} &= \frac{\varepsilon}{D} \frac{1}{a^2}. \end{aligned} \right\} (18)$$

somit

$$A = \frac{\varepsilon}{D} \frac{e^{\kappa a}}{1 + \kappa a}, \quad B = -\frac{\varepsilon \kappa}{D} \frac{1}{1 + \kappa a}. \quad (18')$$

Der Wert von B stellt das Potential dar, das im Mittelpunkt der Ionenkugel von der Ionenatmosphäre erzeugt wird; demnach erhält man für die potentielle Energie eines positiven Ions gegen seine Umgebung den Ausdruck

$$u = -\frac{\varepsilon^2 \kappa}{D} \frac{1}{1 + \kappa a}. \quad (19)$$

Wie der Vergleich mit (15) zeigt, kommt die Berücksichtigung der Ionengröße lediglich in dem Faktor $1/(1 + \kappa a)$ zum Ausdruck. Für kleine Konzentrationen (κ klein) wird nach (11) auch κ klein und die Energie nähert sich ihrem früher für unendlich kleine Ionen angegebenen Wert. Für große Konzentrationen (κ groß) dagegen, nähert sich u allmählich der Größe

$$-\frac{\varepsilon^2}{D a},$$

so daß unsere charakteristische Länge $\frac{1}{\kappa}$ ihren Einfluß einbüßt, gegen die neue, die Ionengröße messende Länge a .

Mit Hilfe von (19) ergibt sich ähnlich wie unter a) für die gesamte elektrische Energie der Ionenlösung der Ausdruck

$$U_e = -\frac{N}{2} \frac{\varepsilon^2 \kappa}{D} \left[\frac{1}{1 + \kappa a_1} + \frac{1}{1 + \kappa a_2} \right], \quad (20)$$

wenn wir, wie das offenbar angezeigt ist, die positiven Ionen durch einen Radius a_1 , die negativen aber durch einen andern Radius a_2 charakterisieren. Wir könnten nun (16) oder (20) sofort benutzen, um gemäß den Ausführungen in § 2 unsere thermodynamische Funktion zu bestimmen. Indessen wollen wir zuerst den (20) entsprechenden Ausdruck für die Energie einer beliebigen Ionenlösung angeben, indem wir die im Interesse der Übersichtlichkeit eingeführte Beschränkung auf ein-einwertige Salze nunmehr aufheben.

§ 4. Die potentielle Energie einer beliebigen Ionenlösung.

In einer Lösung seien vorhanden

$$N_1 \dots N_i \dots N_s$$

Ionen verschiedener Art mit den Ladungen

$$z_1 \dots z_i \dots z_s,$$

so daß die ganzen Zahlen $z_1 \dots z_i \dots z_s$ die Wertigkeiten messen und sowohl positiv wie negativ sein können. Da die Gesamtladung Null ist, muß

$$\sum N_i z_i = 0$$

sein. Neben den Gesamtzahlen N_i seien außerdem die Ionenzahlen pro cm^3

$$n_1 \dots n_i \dots n_s$$

eingeführt.

Es wird wieder irgendein Ion hervorgehoben und um dieses das Potential bestimmt nach der Poissonschen Gleichung

$$\Delta \psi = -\frac{4\pi}{D} \rho.$$

Die Dichte der Ionen i ter Art ergibt sich nach dem Boltzmannschen Prinzip zu

$$n_i e^{-z_i \frac{e\psi}{kT}},$$

so daß

$$\rho = \epsilon \sum n_i z_i e^{-z_i \frac{e\psi}{kT}},$$

und die Grundgleichung wird

$$\Delta \psi = -\frac{4\pi\epsilon}{D} \sum n_i z_i e^{-z_i \frac{e\psi}{kT}}. \quad (21)$$

Benutzen wir wieder die Entwicklung der Exponentialfunktion des vorigen Paragraphen, so wird statt (21) praktisch die Gleichung

$$\Delta \psi = \frac{4\pi\epsilon^2}{DkT} \sum n_i z_i^2 \psi \quad (21')$$

zugrunde zu legen sein, da wegen der Bedingung

$$\sum n_i z_i = 0$$

das erste Entwicklungsglied verschwindet. Im allgemeinen Falle ist also das Quadrat $\frac{1}{\alpha^2}$ unserer charakteristischen Länge zu definieren durch die Gleichung¹⁾

$$\alpha^2 = \frac{4\pi\epsilon^2}{DkT} \sum n_i z_i^2, \quad (22)$$

während die Potentialgleichung ihre frühere Form

$$\Delta \psi = \alpha^2 \psi$$

beibehält.

Nun werde wieder irgendein Ion hervorgehoben und das Potential ψ in dessen Umgebung bestimmt. In Übereinstimmung mit den Ausführungen des vorhergehenden Paragraphen wird wieder

1) Da für ein-einwertige Salze $n_1 = n_2 = n$ und $z_1 = -z_2 = 1$, so stimmt der allgemeine Ausdruck (22) für α^2 mit dem früher (vgl. II) für diesen Spezialfall angegebenen überein.

$$\psi = A \frac{e^{-\alpha r}}{r}$$

für das Feld außerhalb des Ions.

Hat das Ion die Ladung $z_i \epsilon$ und kommt für dieses ein Annäherungsabstand a_i in Frage, so wird im Innern der Ionenkugel

$$\psi = \frac{z_i \epsilon}{D} \frac{1}{r} + B,$$

während die Konstanten A und B sich ergeben zu

$$A = \frac{z_i \epsilon}{D} \frac{e^{\alpha a_i}}{1 + \alpha a_i}, \quad B = -\frac{z_i \epsilon \alpha}{D} \frac{1}{1 + \alpha a_i}.$$

Dem angegebenen Werte von B entspricht die potentielle Energie

$$u = -\frac{z_i^2 \epsilon^2 \alpha}{D} \frac{1}{1 + \alpha a_i}$$

des hervorgehobenen Ions gegen seine Ionenatmosphäre, während die gesamte elektrische Energie der Ionenlösung, wie leicht ersichtlich, den Betrag

$$U_e = -\sum \frac{N_i z_i^2 \epsilon^2 \alpha}{2 D} \frac{1}{1 + \alpha a_i} \quad (23)$$

erreicht. Die reziproke Länge α ist dabei im allgemeinen Falle durch (22) definiert¹⁾.

§ 5. Das elektrische Zusatzglied zum thermodynamischen Potential.

In § 2 kamen wir zum Resultat, daß das von der gegenseitigen Wirkung der Ionen herführende Glied im Potential

$$G = S - \frac{U}{T}$$

zu bestimmen war nach der Gleichung

$$G_e = \int \frac{U_e}{T^2} dT.$$

Benutzen wir nun für U_e , um gleich den allgemeinen Fall zu erledigen, den in (23) angegebenen Ausdruck, so ist bei der Integration zu bedenken, daß nach (22) die in diesem Ausdruck vorkommende reziproke Länge die Temperatur enthält. Übersichtlicher wird die Rechnung, wenn zunächst aus (22) geschlossen wird

$$2\alpha d\alpha = -\frac{4\pi\epsilon^2}{Dk} \sum n_i z_i^2 \frac{dT}{T^2},$$

wobei D als temperaturunabhängig angesehen wird²⁾, und dann als Integrationsvariable nicht T , sondern α benutzt wird. So ergibt sich

1) Aus dem angegebenen Ausdruck für U_e kann unmittelbar auf die Verdünnungswärme geschlossen werden. Wir überzeugten uns, daß der theoretische Wert den Beobachtungen entspricht.

2) Tatsächlich ergibt eine direkte kinetische Theorie des osmotischen Druckes, über welche an anderer Stelle (Recueil des travaux chimiques des Pays-Bas et de la Belgique) berichtet wird, die Gültigkeit des endgültigen Ausdrucks für G_e unabhängig von dieser Annahme. Für eine Diskussion der thermodynamischen Rechnung können wir verweisen auf B. A. M. Cavanagh, Phil. Mag. 43, 606, 1922.

$$G_e = \frac{k}{4\pi \sum n_i z_i^2} \sum N_i z_i^2 \int \frac{x^2 dx}{1 + xa_i} \quad (24)$$

Setzt man abkürzend die Zahl

$$xa_i = x_i, \quad (25)$$

so findet man

$$\int \frac{x^2 dx}{1 + xa_i} = \frac{1}{a_i^3} \int \frac{u^2 du}{1 + u} = \frac{1}{a_i^3} \left\{ \text{const} + \log(1 + x_i) - 2(1 + x_i) + \frac{1}{2}(1 + x_i)^2 \right\}.$$

Die Integrationskonstante ist so zu bestimmen, daß in der Grenze für unendliche Verdünnung der elektrische Zusatz G_e zum Gesamtpotential verschwindet. Da x nach (22) proportional $\sqrt{\sum n_i z_i^2}$ ist, so entspricht $x = 0$ dem Falle der unendlichen Verdünnung. Dementsprechend muß die Konstante in der geschweiften Klammer so bestimmt werden, daß für $x_i = 0$ der Klammerausdruck ebenfalls verschwindet, und da in dieser Grenze

$$\log(1 + x_i) - 2(1 + x_i) + \frac{1}{2}(1 + x_i)^2$$

den Wert $-\frac{3}{2}$ annimmt, so ist

$$\text{const.} = \frac{3}{2}$$

zu setzen. Damit wird dann

$$\int \frac{x^2 dx}{1 + xa} = \frac{1}{a_i^3} \left\{ \frac{3}{2} + \log(1 + x_i) - 2(1 + x_i) + \frac{1}{2}(1 + x_i)^2 \right\}$$

und

$$G_e = \frac{k}{4\pi \sum n_i z_i^2} \sum \frac{N_i z_i^2}{a_i^3} \left\{ \frac{3}{2} + \log(1 + x_i) - 2(1 + x_i) + \frac{1}{2}(1 + x_i)^2 \right\}. \quad (26)$$

Die Funktion in der geschweiften Klammer hat nach Potenzen von x_i entwickelt die Form

$$\frac{3}{2} + \log(1 + x_i) - 2(1 + x_i) + \frac{1}{2}(1 + x_i)^2 = \frac{x_i^3}{3} - \frac{x_i^4}{4} + \frac{x_i^5}{5} - \frac{x_i^6}{6} + \dots;$$

setzt man deshalb abkürzend

$$\chi_i = \chi(x_i) = \frac{3}{x_i^3} \left\{ \frac{3}{2} + \log(1 + x_i) - 2(1 + x_i) + \frac{1}{2}(1 + x_i)^2 \right\}, \quad (27)$$

so nähert sich χ für kleine Konzentrationen dem Werte 1 und ist entwickelbar in der Form

$$\chi_i = 1 - \frac{2}{3}x_i + \frac{2}{5}x_i^2 - \dots \quad (27')$$

Unter Einführung dieser Funktion und Berücksichtigung der Definitionsgleichung (22) für x^2 , läßt sich unser Zusatz zum thermodynamischen Potential auch auf die Form bringen¹⁾

$$G_e = \sum N_i \frac{z_i^2 \varepsilon^2}{DT} \frac{x}{3} \chi_i, \quad (28)$$

wobei der Übersichtlichkeit wegen der Ausdruck (22) für x , wonach

1) Der elektrische Zusatzdruck p_e , von dem in § 2 Gleichung (6') die Rede war, ergibt sich aus dieser Formel. Der dort angegebene Zahlenwert wurde in dieser Weise berechnet.

$$x^2 = \frac{4\pi \varepsilon^2}{DkT} \sum n_i z_i^2$$

ist, noch einmal auch hier explizite wiederholt sei.

Für kleine Konzentrationen entfällt daher in G_e auf jedes Ion ein Beitrag, der pro-

portional x , d. h. proportional der Wurzel aus der Konzentration ist. Würde man die endlichen Abmessungen der Ionen vernachlässigen, so wäre nach (27') und (25) χ_i durchweg gleich 1 zu setzen und jene Abhängigkeit würde als für alle Konzentrationen gültig erscheinen. Die ganze Abhängigkeit von der Ionengröße, welche den individuellen Eigenschaften der Ionen Rechnung trägt, wird also durch die Funktion χ nach (27) oder (27') gemessen. In der Grenze für große Verdünnungen verschwindet aber dieser Einfluß, und die Ionen unterscheiden sich nur mehr sofern ihre Wertigkeit verschieden ist.

§ 6. Osmotischer Druck, Dampfdruckerniedrigung, Gefrierpunktserniedrigung, Siedepunktserhöhung.

Nach den Ausführungen des § 2, mit Rücksicht auf (7), (7') und (7'') wird die thermodynamische Funktion Φ der Lösung dargestellt durch den Ausdruck

$$\Phi = \sum_0^s N_i (\varphi_i - k \log c_i) + \sum_1^e N_i \frac{z_i^2 \varepsilon^2}{3D} \frac{x}{T} \chi_i. \quad (29)$$

Dabei ist für den elektrischen Zusatz zu Φ die Gleichung (28) benutzt, in der $\chi_i = \chi(x_i) = \chi(xa_i)$ durch (27) gegeben ist und, wie im vorigen Paragraphen auseinandergesetzt wurde, in der Grenze für unendlich kleine Konzentrationen dem Werte 1 zustrebt. x ist unsere reziproke charakteristische Länge, definiert durch (22), wonach

$$x^2 = \frac{4\pi \varepsilon^2}{DkT} \sum n_i z_i^2.$$

Nach dem im Planckschen Lehrbuch der Thermodynamik eingeschlagenen Verfahren können nun die Gesetze der in der Überschrift genannten Erscheinungen alle durch Differentiation aus (29) erschlossen werden. Die Bedingung für das Gleichgewicht beim Übergang einer Menge δN_0 -Moleküle des Lösungs-

mittels aus der Lösung in die jeweilige andere Phase lautet bekanntlich

$$\delta\Phi + \delta\Phi' = 0,$$

wenn Φ' das thermodynamische Potential jener zweiten Phase bedeutet. Wir setzen

$$\Phi' = N_0' \varphi_0' \quad (30)$$

und wollen die Rechnung ausführen für den Fall des Gleichgewichtes zwischen Lösung und ausgefrorenem Lösungsmittel, mit Rücksicht auf die Tatsache, daß für die Gefrierpunktserniedrigung als Funktion der Konzentration die ausgedehntesten und zuverlässigsten Messungen vorliegen. Wir lassen nun N_0 um δN_0 und N_0' um $\delta N_0'$ variieren und erhalten dann sofort

$$\delta(\Phi + \Phi') = \varphi_0' \delta N_0' + (\varphi_0 - k \log c_0) \delta N_0 + \sum_1^i N_i \frac{z_i^2 \varepsilon^2}{3DT} \frac{d(x\chi_i)}{dx} \frac{\partial x}{\partial N_0} \delta N_0, \quad (31)$$

da wie leicht ersichtlich

$$\sum_0^i N_i \delta \log c_i = \sum_0^i N_i \frac{\partial \log c_i}{\partial N_0} \delta N_0$$

den Wert Null hat.

Da nun

$$\delta N_0' = -\delta N_0$$

ist, so lautet die Gleichgewichtsbedingung

$$\varphi_0' - \varphi_0 = -k \log c_0 + \sum_1^i N_i \frac{z_i^2 \varepsilon^2}{3DT} \frac{d(x\chi_i)}{dx} \frac{\partial x}{\partial N_0}; \quad (32)$$

sie wäre in dieser Form für alle in der Überschrift genannten Erscheinungen zu verwenden und stellt eine Beziehung dar zwischen Druck, Temperatur und Konzentrationen.

In der Definition von x stellt n_i die Ionenzahl i ter Art pro Volumeneinheit dar, so daß

$$n_i = \frac{N_i}{V}$$

ist, andererseits ist der ganzen Formulierung wie bei Planck für das Volumen V der lineare Ansatz

$$V = \sum_0^s n_i v_i = n_0 v_0 + \sum_1^s n_i v_i$$

zugrunde gelegt. Nach (22) wird demnach

$$2x \frac{\partial x}{\partial N_0} = -\frac{4\pi \varepsilon^2}{DkT} \sum z_i^2 \frac{N_i v_0}{V^2} = -\frac{4\pi \varepsilon^2 v_0}{DkT V} \sum n_i z_i^2;$$

unter nochmaliger Heranziehung dieser Definitionsgleichung hat man also

$$\frac{\partial x}{\partial N_0} = -\frac{x v_0}{2V},$$

und unsere Gleichgewichtsbedingung nimmt die Form an:

$$\varphi_0 - \varphi_0' = k \log c_0 + v_0 \sum_1^i n_i \frac{z_i^2 \varepsilon^2}{6DT} x \frac{d(x\chi_i)}{dx}. \quad (32')$$

Die für die fraglichen Effekte charakteristische Konzentrationsfunktion

$$\frac{d(x\chi_i)}{dx}$$

läßt sich leicht nach (27) berechnen. Nennen wir sie σ_i , so ergibt sie sich unter Beibehaltung der Abkürzung

$$x_i = x a_i$$

zu

$$\sigma_i = \frac{d(x\chi_i)}{dx} = \frac{3}{x_i^3} \left[(1+x_i) - \frac{1}{1+x_i} - 2 \log(1+x_i) \right]. \quad (33)$$

Für kleine Werte von x_i gilt die Entwicklung

$$\sigma_i = 1 - \frac{3}{2} x_i + \frac{9}{8} x_i^2 - 2 x_i^3 + \dots = \sum_{\nu=0}^{\nu=\infty} 3 \frac{\nu+1}{\nu+3} x_i^\nu,$$

so daß σ_i für kleine Konzentrationen dem Werte 1 zustrebt; für große Konzentrationen verschwindet σ_i wie $3/x_i^2$. Die folgende Tabelle enthält Zahlenwerte für σ als Funktion von $x = x a$; Fig. 1 stellt den Verlauf der Funktion graphisch dar.

Tabelle I.

x	σ(x)	x	σ(x)	x	σ(x)	x	σ(x)
0	1,000	0,4	0,598	0,9	0,370	3,0	0,1109
0,05	0,929	0,5	0,536	1,0	0,341	3,5	0,0898
0,1	0,855	0,6	0,486	1,5	0,238	4,0	0,0742
0,2	0,759	0,7	0,441	2,0	0,176	4,5	0,0628
0,3	0,670	0,8	0,403	2,5	0,136	5,5	0,0540

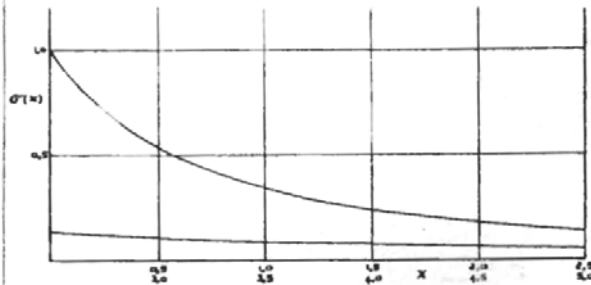


Fig. 1.

Weil wir später Gelegenheit nehmen müssen, auch auf die Gefrierpunktserniedrigung konzentrierter Lösungen einzugehen, so empfiehlt es sich, die Werte jener Erniedrigung aus (32') zu berechnen, ohne zunächst alle Vereinfachungen einzuführen, welche bei ganz verdünnten Lösungen gestattet sind. Die Gefriertertemperatur des reinen Lösungsmittels sei T_0 , die Gefriertertemperatur der Lösung $T_0 - \Delta$, die Schmelzwärme des gefrorenen Lösungsmittels q , die spezifische Wärme des flüssigen Lösungsmittels

bei konstantem Druck c_p und dieselbe Größe für das gefrorene Lösungsmittel c_p' . Dabei sollen die drei letzteren Größen durchweg je auf ein wirkliches Molekül bezogen sein, so daß sie die gebräuchlichen Molgrößen, dividiert durch die Loschmidtsche Zahl darstellen. Nach der Definitionsgleichung für φ wird dann

$$\varphi_0 - \varphi_0' = -\frac{\Delta}{T_0} \frac{q}{T_0} + \frac{\Delta^2}{T_0^2} \left[(c_p - c_p') - \frac{2q}{kT_0} \right]$$

Für c_0 kann

$$c_0 = 1 - \sum_1^s c_i$$

eingesetzt werden. Da weiter

$$\frac{d(x\chi_i)}{dx} = \sigma_i$$

gesetzt wurde, folgt schließlich

$$\begin{aligned} \frac{\Delta}{T_0} \frac{q}{kT_0} - \frac{\Delta^2}{T_0^2} \left(\frac{c_p - c_p'}{2k} - \frac{q}{kT_0} \right) &= \\ &= -\log \left(1 - \sum_1^s c_i \right) - \frac{\varepsilon^2 x}{6DkT} \sum_1^s v_0 n_i z_i^2 \sigma_i. \end{aligned}$$

Wird die Loschmidtsche Zahl N genannt, so ist

$$Nq = Q$$

die Schmelzwärme eines Mols,

$$Nk = R$$

die Gaskonstante und

$$Nc_p = C_p \text{ bzw. } Nc_p' = C_p'$$

die spezifische Wärme pro Mol flüssiges, bzw. festes Lösungsmittel, so daß man auch schreiben kann

$$\left. \begin{aligned} \frac{\Delta}{T_0} \frac{Q}{RT_0} - \frac{\Delta^2}{T_0^2} \left(\frac{C_p - C_p'}{2R} - \frac{Q}{RT_0} \right) &= \\ = -\log \left(1 - \sum_1^s c_i \right) - \frac{\varepsilon^2 x}{6DkT} \sum_1^s v_0 n_i z_i^2 \sigma_i. \end{aligned} \right\} \quad (34)$$

Für kleine Konzentrationen kann erstens Δ^2/T_0^2 neben Δ/T_0 vernachlässigt werden, zweitens kann

$$-\log \left(1 - \sum_1^s c_i \right) = \sum_1^s c_i$$

gesetzt werden, und drittens kann das Gesamtvolumen mit dem Volumen des Wassers identifiziert werden, indem die Zahl der gelösten Ionen als unendlich klein gegen die Zahl der Wassermoleküle angesehen wird. Dem entspricht es, wenn gesetzt wird

$$v_0 n_i = \frac{v_0}{V} N_i = \frac{N_i}{N_0} = \frac{N_i}{N_0 + \sum_1^s v_i N_i} = c_i$$

Mit diesen Vernachlässigungen erhält man¹⁾

1) Es ist nicht nötig, zwischen Ionen und ungeladenen Molekülen einen Unterschied zu machen; kommen beide vor, so hat man für letztere einfach $z_i = 0$ zu setzen. Sind alle Einzelheiten ungeladen, dann werden naturgemäß (35) und (35') identisch.

$$\frac{\Delta}{T_0} \frac{Q}{RT_0} = \sum_1^s c_i \left(1 - \frac{\varepsilon^2 x}{6DkT} z_i^2 \sigma_i \right), \quad (35)$$

wogegen unter denselben Annahmen die klassische Formel

$$\frac{\Delta}{T_0} \frac{Q}{RT_0} = \sum_1^s c_i \quad (35')$$

lautet.

§ 7. Die Gefrierpunktserniedrigung verdünnter Lösungen.

Das Charakteristische der elektrischen Wirkung der Ionen tritt besonders deutlich hervor in den Grenzesetzen für große Verdünnungen, wie sie durch (35) dargestellt werden. Wir wollen deshalb die Formeln und Gesetze für diesen Grenzfall besonders behandeln. Die Formel (35) ist anwendbar auf den allgemeinen Fall, daß ein Gemisch von mehreren Elektrolyten vorliegt, die außerdem eventuell nur teilweise in Ionen zerfallen sind. Wir betrachten hier den besonderen Fall, daß eine einzige Molekülart gelöst wurde. Das Molekül sei vollständig in Ionen zerfallen und bestehe aus s -Ionenarten, numeriert mit $1, \dots, i, \dots, s$, sodaß

$$v_1, \dots, v_i, \dots, v_s$$

Ionen der Arten $1, \dots, i, \dots, s$ das Molekül aufbauen. Die mit jedem dieser Ionen verbundenen Ladungen seien

$$z_1 e, \dots, z_i e, \dots, z_s e.$$

(Bei H_2SO_4 , zerfallen in den Ionen H und SO_4 , wäre z. B.

$$v_1 = 2, \quad v_2 = 1, \quad z_1 = +1, \quad z_2 = -2,$$

wenn der Index 1 auf die H -Ionen und der Index 2 auf die SO_4 -Ionen bezogen wird.)

Da das Molekül als Ganzes ungeladen ist, gilt

$$\sum_1^s v_i z_i = 0.$$

Die Lösung bestehe nun aus N_0 -Molekülen Lösungsmittel und N -Molekülen des zugesetzten Elektrolyten, wobei N als klein gegen N_0 angesehen wird. Dann ist

$$c_i = \frac{N_i}{N_0 + \sum_1^s N_i} = \frac{N_i}{N_0}$$

Bedenkt man, daß

$$N_i = v_i N$$

ist, und nennt die auf die gelöste Molekülart bezogene Konzentration c , sodaß in der hier benutzten Näherung

$$c = \frac{N}{N_0}$$

so wird

$$c_i = \nu_i c.$$

Die Gleichung (35) für die Gefrierpunktserniedrigung wird dann

$$\frac{\Delta}{T_0} \frac{Q}{RT_0} = f_0 \sum c_i = f_0 c \sum \nu_i \quad (36)$$

mit

$$f_0 = 1 - \frac{\epsilon^2 \alpha}{6 D k T} \frac{\sum \nu_i z_i^2 \sigma_i}{\sum \nu_i}. \quad (37)$$

Die Größe f_0 ist der in der Einleitung erwähnte osmotische Koeffizient, denn $f_0 = 1$ würde dem Übergang zur klassischen Theorie entsprechen, wie (35') zeigt. Nennt man noch Δ_k die nach der klassischen Theorie berechnete Gefrierpunktserniedrigung, so ist

$$\frac{\Delta}{\Delta_k} = f_0$$

oder

$$1 - f_0 = \frac{\Delta_k - \Delta}{\Delta_k}.$$

Die Beziehung (37) zeigt also zunächst in qualitativer Hinsicht, daß die wirkliche Gefrierpunktserniedrigung kleiner sein muß, als die nach der klassischen Theorie zu erwartende, ein Resultat, das sich für verdünnte Elektrolytlösungen durchweg bestätigt. Die in (37) vorkommenden Abkürzungen α und σ sind durch die Formeln (22) und (33) (letztere nebst zugehöriger Tabelle) bestimmt. Wie im vorigen Paragraphen auseinandergesetzt wurde, mißt σ_i den Einfluß der endlichen Ionengröße und dieser verschwindet bei ganz geringen Konzentrationen, da dann σ dem Werte 1 zustrebt. Beschäftigen wir uns demnach zunächst mit dem Grenzgesetz, das für ganz große Verdünnungen Gültigkeit haben sollte, so gilt in diesem Grenzfall

$$f_0 = 1 - \frac{\epsilon^2 \alpha}{6 D k T} \frac{\sum \nu_i z_i^2}{\sum \nu_i}. \quad (38)$$

Andrerseits gilt nach (22)

$$\alpha^2 = \frac{4 \pi \epsilon^2}{D k T} \sum n_i z_i^2;$$

da aber

$$n_i = \nu_i \frac{N}{V} = \nu_i n$$

ist, unter Einführung der Volumenkonzentration n der gelösten Moleküle, so ist auch

$$\alpha^2 = \frac{4 \pi n \epsilon^2}{D k T} \sum \nu_i z_i^2.$$

Für ganz geringe Konzentrationen folgt demnach

$$f_0 = 1 - \frac{\epsilon^2}{6 D k T} \sqrt{\frac{4 \pi \epsilon^2}{D k T} n \sum \nu_i \left(\frac{\sum \nu_i z_i^2}{\sum \nu_i} \right)^{3/2}}, \quad (38')$$

wobei $n \sum \nu_i$ die Gesamtionenanzahl im cm^3 der Lösung darstellt und

$$w = \left(\frac{\sum \nu_i z_i^2}{\sum \nu_i} \right)^{3/2} \quad (39)$$

als Wertigkeitsfaktor bezeichnet werden soll, da er den Einfluß der Ionenwertigkeiten z_i auf die Erscheinungen mißt. Am besten ist es, wenn man nicht f_0 selber, sondern die Abweichung von 1 der Betrachtung unterzieht und so für ganz geringe Konzentrationen schreibt:

$$1 - f_0 = w \frac{\epsilon^2}{6 D k T} \sqrt{\frac{4 \pi \epsilon^2}{D k T} n \sum \nu_i}. \quad (40)$$

Diese Formel drückt nun erstens aus, wie die Abweichungen $1 - f_0$ von der Konzentration abhängen, und zwar behauptet sie in dieser Hinsicht:

Satz 1.

Für alle Elektrolyte sind in der Grenze für geringe Konzentrationen die prozentualen Abweichungen der Gefrierpunktserniedrigung vom klassischen Wert der Wurzel aus der Konzentration proportional.

Daß es möglich ist, dieses Gesetz als allgemeines Gesetz auszusprechen, rührt daher, daß alle Elektrolyten für große Verdünnungen als völlig in Ionen zerfallen angesehen werden können. Freilich sind es nur die starken Elektrolyte, bei denen jenes Gebiet des vollständigen Zerfalls praktisch erreicht wird.

An zweiter Stelle macht (39) eine Aussage über den Einfluß der Ionenwertigkeit, die folgendermaßen formuliert werden kann:

Satz 2.

Zerfällt das gelöste Molekül in $\nu_1, \dots, \nu_i, \dots, \nu_s$ Ionen verschiedener Art 1, ..., i, ..., s mit den Wertigkeiten $z_1, \dots, z_i, \dots, z_s$, so sind für geringe Konzentrationen die prozentualen Abweichungen der Gefrierpunktserniedrigung vom klassischen Wert einem Wertigkeitsfaktor w proportional, welcher sich berechnet zu

$$w = \left(\frac{\sum \nu_i z_i^2}{\sum \nu_i} \right)^{3/2}.$$

Als Beispiel für die Berechnung dieses Wertigkeitsfaktors gelte die folgende Tabelle, bei der in der linken Spalte der Typus des Salzes durch ein Beispiel festgelegt, und in der rechten Spalte der Wert von w angegeben ist:

Tabelle II.

Typus	Wertigkeitsfaktor w
KCl	1 = 1
CaCl ₂	$2\sqrt{2} = 2,83$
CuSO ₄	$4\sqrt{4} = 8$
AlCl ₃	$3\sqrt{3} = 5,20$
Al ₂ (SO ₄) ₃	$6\sqrt{6} = 16,6$

Der Einfluß der Ionen wächst also beträchtlich mit zunehmender Wertigkeit, was ebenfalls dem qualitativen Befunde entspricht.

An dritter Stelle hat schließlich das Lösungsmittel einen Einfluß, und zwar im Sinne der bekannten Nernstschen Anregung zur Erklärung der ionisierenden Kraft von Lösungsmitteln großer Dielektrizitätskonstante. Nach (40) hat man

Satz 3.

Für geringe Konzentrationen sind die prozentualen Abweichungen der Gefrierpunktserniedrigung vom klassischen Wert umgekehrt proportional der $3/2$ ten Potenz der Dielektrizitätskonstanten des Lösungsmittels.

Die übrigen noch in (40) vorkommenden Konstanten sind die Ladung des elektrischen Elementarquantums $e = 4,77 \cdot 10^{-10}$ e. s. E., die Boltzmannsche Konstante $k = 1,346 \cdot 10^{-16}$ erg und die Temperatur T , wobei letztere sowohl explicite wie implicite auftritt, da die Dielektrizitätskonstante D mit T variiert.

Hat man nun mit verdünnten Lösungen im gewöhnlichen Sinne zu tun, dann kann σ nicht mehr durch 1 ersetzt werden, und es tritt die Gleichung (37) in Kraft, welche explicite lautet:

$$1 - f_0 = w \frac{e^2}{6DkT} \sqrt{\frac{4\pi e^2}{DkT} n \sum v_i \frac{\sum v_i z_i^2 \sigma_i}{\sum v_i z_i^2}} \quad (41)$$

Wie die Tabelle I, sowie die ihr zugrunde liegende Formel (33) zeigt, nimmt σ_i mit zunehmender Konzentration immer weiter ab, und zwar schließlich wie

$$\frac{3}{x_i^2} = \frac{3}{x^2 a_i^2},$$

d. h. umgekehrt proportional der Konzentration, da x der Wurzel dieser Größe proportional ist. Nach (41) muß also die Abweichung $1 - f_0$ zunächst für ganz geringe Konzentrationen proportional der Wurzel aus der Konzentration steigen, dann aber bei steigender Konzentration mit Rücksicht auf den Einfluß von σ , d. h. mit Rücksicht auf die endlichen Durchmesser der Ionen ein Maximum erreichen und endlich wieder umgekehrt proportional der Wurzel aus der Konzentration abnehmen. Wenn auch in

dieser Aussage eine nicht ganz berechtigte Extrapolation auf größere Konzentrationen der für verdünnte Lösungen spezialisierten Formel (41) enthalten ist, so bleibt die Aussage auch bei näherer Betrachtung konzentrierterer Lösungen (vgl. § 9) qualitativ bestehen. Tatsächlich haben auch die Messungen ein Maximum der Abweichungen $1 - f_0$ als charakteristisches Merkmal der Kurven für die Gefrierpunktserniedrigung ergeben. Allerdings glauben wir, daß die Erscheinungen der Hydratation (vgl. den Schlußparagraphen) ebenfalls einen wesentlichen Einfluß auf die Erzeugung des Maximums besitzen. Ein zahlenmäßiger Vergleich der Theorie mit der Erfahrung wird in § 9 gegeben werden.

§ 8. Das Dissoziationsgleichgewicht.

Beschränkt man sich nicht nur auf starke Elektrolyte, so wird ein Dissoziationsgleichgewicht zwischen ungespaltenen Molekülen und Ionen bestehen. Aber auch dieses Gleichgewicht wird nicht nach der klassischen Formel zu berechnen sein, weil hier ebenfalls die gegenseitigen elektrischen Kräfte der Ionen störend eingreifen werden. In welcher Weise das nach unserer Theorie quantitativ geschieht, soll hier berechnet werden. Wir gehen wieder aus von dem Ausdruck (29) für das thermodynamische Potential Φ der Lösung

$$\Phi = \sum_0^s N_i (\varphi_i - k \log c_i) + \sum_1^s N_i \frac{z_i^2 e^2}{3D} \frac{x}{T} \chi_i;$$

unter den Einzelteilchen, welche in der Lösung vorhanden sind, befinden sich dann sowohl geladene wie ungeladene. Für letztere ist einfach $z_i = 0$ zu setzen. Das Lösungsmittel sei mit dem Index 0 versehen. Nun nehmen wir in der bekannten Weise eine Variation der Zahlen N_i vor und berechnen die zugehörige Änderung des Potentials. Diese ergibt sich zu

$$\delta \Phi = \sum_{i=0}^s \delta N_i (\varphi_i - k \log c_i) + \sum_{i=1}^s \delta N_i \frac{z_i^2 e^2}{3DT} x \chi_i + \sum_{i=1}^s N_i \frac{z_i^2 e^2}{3DT} \frac{d(x \chi_i)}{dx} \sum_{j=1}^s \frac{\partial x}{\partial N_j} \delta N_j,$$

wenn man berücksichtigt, daß nach der Definitionsgleichung (22)

$$x^2 = \frac{4\pi e^2}{DkT} \sum_{l=1}^s n_l z_l^2 = \frac{4\pi e^2}{DkT} \sum_{l=1}^s \frac{N_l z_l^2}{V}$$

die Größe x von allen Zahlen $N_1 \dots N_s$ abhängen kann. Vertauscht man in der dritten Summe die Summationsindizes i und j , so kann $\delta \Phi$ auch auf die Form gebracht werden:

$$\delta \Phi = \delta N_0(\varphi_0 - k \log c_0) + \sum_{i=1}^{i=s} \delta N_i \left[\varphi_i - k \log c_i + \frac{\varepsilon^2}{3DT} \left(z_i^2 \chi_i + \sum_{j=1}^{j=s} N_j z_j^2 \frac{d(\chi_i)}{dx} \frac{\partial x}{\partial N_i} \right) \right].$$

Nach der Definition von χ kann aber $\frac{\partial \chi}{\partial N_i}$ ausgerechnet werden. Man erhält, falls für das Volumen der lineare Ansatz beibehalten wird,

$$\frac{\partial \chi}{\partial N_i} = \frac{\chi}{2 \sum_1^s n_j z_j^2} \cdot \frac{z_i^2 - v_i \sum_1^s n_j z_j^2}{V}.$$

Nimmt man nun in üblicher Weise an, daß in der Lösung eine chemische Reaktion stattfinden kann, bei welcher die Proportion besteht

$$\delta N_1 : \delta N_2 : \dots : \delta N_i : \dots : \delta N_s = \mu_1 : \mu_2 : \dots : \mu_i : \dots : \mu_s,$$

so folgt aus dem angegebenen Wert der Variation des Potentials die Gleichgewichtsbedingung

$$\sum_{i=1}^{i=s} \mu_i \log c_i = \sum_{i=1}^{i=s} \frac{\mu_i \varphi_i}{k} + \frac{\varepsilon^2 \chi}{6DkT} \sum_{i=1}^{i=s} \left\{ 2 \mu_i z_i^2 \chi_i + \mu_i (z_i^2 - v_i \sum_1^s n_j z_j^2) \frac{\sum_{j=1}^{j=s} n_j z_j^2 \frac{d(\chi_i)}{dx}}{\sum_{j=1}^{j=s} n_j z_j^2} \right\}. \quad (42)$$

Von der klassischen unterscheidet sich diese Bedingung durch das Zusatzglied rechter Hand. Führt man den Aktivitätskoeffizienten f_a ein, wie in der Einleitung, indem man setzt

$$\sum_1^s \mu_i \log c_i = \log (f_a K),$$

wobei K die klassische Gleichgewichtskonstante bedeutet, so ist der Aktivitätskoeffizient definiert durch die Beziehung

$$\log f_a = \frac{\varepsilon^2 \chi}{6DkT} \sum_{i=1}^{i=s} \left\{ 2 \mu_i z_i^2 \chi_i + \mu_i (z_i^2 - v_i \sum_1^s n_j z_j^2) \frac{\sum_{j=1}^{j=s} n_j z_j^2 \frac{d(\chi_i)}{dx}}{\sum_{j=1}^{j=s} n_j z_j^2} \right\}. \quad (43)$$

Nach dieser Formel ist es natürlich möglich, jedes an der Reaktion beteiligte Atom bzw. Molekül mit einem eigenen Aktivitätskoeffizienten zu versehen, indem man setzt

$$\log f_a = \mu_1 \log f_a^1 + \dots + \mu_i \log f_a^i + \dots + \mu_s \log f_a^s \quad (44)$$

mit

$$\log f_a^i = \frac{\varepsilon^2 \chi}{6DkT} \left\{ 2 z_i^2 \chi_i + (z_i^2 - v_i \sum_1^s n_j z_j^2) \frac{\sum_1^s n_j z_j^2 \frac{d(\chi_i)}{dx}}{\sum_1^s n_j z_j^2} \right\}. \quad (44')$$

Es wird dann aber, wie (44') durch das Auftreten von χ zeigt, dieser auf eine bestimmte Atomart bezogene Koeffizient nicht nur von Größen abhängig, welche sich auf jene Atomart allein beziehen.

Auch hier sind wieder Vereinfachungen möglich bei Beschränkung auf kleinere Konzentrationen. In diesem Falle ist nämlich

$$v_i \sum_1^s n_j z_j^2$$

zu vernachlässigen neben z_i^2 ; man hat, wenn so verfahren wird, das Volumen der gelösten Substanz als verschwindend angesehen gegenüber dem Volumen der ganzen Lösung. So wird

$$\log f_a^i = \frac{\varepsilon^2 \chi}{6DkT} z_i^2 \left\{ 2 \chi_i + \frac{\sum_1^s n_j z_j^2 \frac{d(\chi_i)}{dx}}{\sum_1^s n_j z_j^2} \right\}. \quad (45)$$

Schließlich kann dann noch der Grenzwert angegeben werden, dem der Aktivitätskoeffizient

zustrebt bei größten Verdünnungen. In dieser Grenze, wo der Einfluß der Ionengröße verschwindet, kann $\chi = 1$ gesetzt werden und man erhält

$$\log f_a^i = \frac{\varepsilon^2 \chi}{2DkT} z_i^2. \quad (45')$$

Da χ von den Eigenschaften aller Ionen abhängt (durch ihre Wertigkeit beeinflusst wird), so ist auch noch in diesem Grenzfall der Einzel-

koeffizient f_a^i nicht nur Funktion der Eigenschaften des i ten Ions. Wir verzichten darauf, das Grenzgesetz ausführlich zu diskutieren und bemerken nur, daß auch hier wieder in der Grenze Proportionalität von $\log f_a$ mit der zweiten Wurzel aus der Konzentration besteht.

§ 9. Vergleich mit der experimentellen Erfahrung über Gefrierpunktserniedrigung.

In Fig. 2 geben wir zunächst eine Darstellung zur Veranschaulichung des charakteristischen

Verhaltens starker Elektrolyte. Auf der horizontalen Achse ist eine Größe $\nu\gamma$ aufgetragen, welche die Ionenkonzentration mißt, indem γ , wie schon früher ausgeführt, die Konzentration des Elektrolyten in Mol pro Liter ist¹⁾, während $\nu = \sum \nu_i$ die Anzahl Ionen bedeutet, in welche ein Molekül des Salzes zerfällt. Es wurden vier Vertreter KCl , K_2SO_4 , $La(NO_3)_3$ und $MgSO_4$ von vier durch ihre Ionenwertigkeiten unterschiedenen Typen gewählt. KCl zerfällt in zwei einwertige, K_2SO_4 in zwei ein- und ein zweiwertiges, $La(NO_3)_3$ in drei ein- und ein dreiwertiges, $MgSO_4$ in zwei zweiwertige Ionen. Bezeichnen wir die nach der klassischen Theorie bei vollständiger Dissoziation zu erwartende Gefrierpunktserniedrigung mit Δ_k und die wirklich beobachtete mit Δ , so ist der Ausdruck

$$\theta = \frac{\Delta_k - \Delta}{\Delta_k}, \quad (46)$$

d. h. die prozentuale Abweichung vom klassischen Wert gebildet und als Ordinate aufgetragen worden. Nach § 7 kann auch

$$\theta = 1 - f_0 \quad (46')$$

gesetzt werden; θ mißt, so dargestellt, die Abweichung des osmotischen Koeffizienten von seinem Grenzwerte 1. Da in wässriger Lösung

$$\Delta_k = \nu\gamma \cdot 1,860^0 \quad (47)$$

ist, entspricht ein Punkt der Abszissenachse für alle Elektrolyte einer Konzentration, die ohne Berücksichtigung der gegenseitigen Kräfte stets dieselbe Gefrierpunktserniedrigung erzeugen sollte. Wir haben die beobachteten Werte allein eingetragen, ohne die entsprechenden Punkte durch eine Kurve zu verbinden, um jede Beeinflussung zu vermeiden. Dieses Verfahren ist indessen nur dadurch ermöglicht worden, daß in neuerer Zeit einige amerikanische Forscher ganz vorzügliche Messungen der Gefrierpunktserniedrigung bei geringen Konzentrationen ausgeführt haben. Die Messungen der Fig. 2 stammen von Adams und Hall und Harkins²⁾.

Es kommt klar zum Ausdruck, daß die Abweichung θ nicht, wie es das Massenwirkungsgesetz verlangen würde, für kleine Konzentrationen proportional der ersten oder sogar einer höheren Potenz der Konzentration steigt. Außer-

1) Bei den Salzen K_2SO_4 , $La(NO_3)_3$, $MgSO_4$ ist statt γ die Konzentration γ' in Mol pro 1000 g Wasser eingesetzt, wie sie von den unten zitierten Autoren angegeben ist, da mangels Messungen der Dichte dieser Salzlösungen bei 273⁰ eine Umrechnung in Mol pro Liter nicht ausführbar war; dies bedeutet bei den hier in Betracht gezogenen geringen Konzentrationen eine nur un erhebliche Abweichung.

2) L. H. Adams, Journ. Amer. Chem. Soc. 37, 481, 1915 (KCl); L. E. Hall u. W. D. Harkins, ibid. 38, 2658, 1916 (K_2SO_4 , $La(NO_3)_3$, $MgSO_4$).

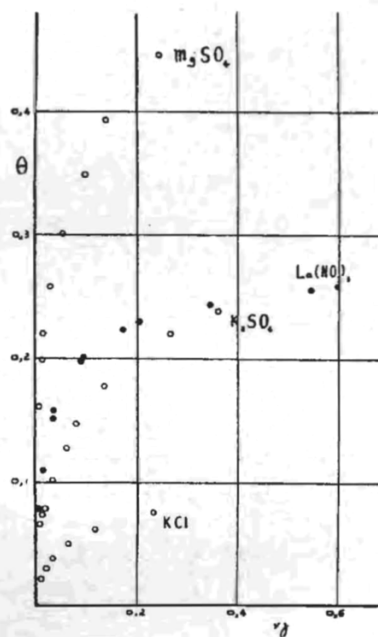


Fig. 2.

dem demonstrieren die Kurven den starken Einfluß der Ionenwertigkeit.

Unsere Theorie verlangt nun, daß bei ganz geringen Konzentrationen die prozentuale Abweichung θ der zweiten Wurzel aus der Konzentration proportional wird, mit einem Proportionalitätsfaktor, der wesentlich von der Wertigkeit der Ionen abhängt. Nach (39) und (40) ist (wenn das Molekül zerfällt in $\nu_1 \dots \nu_i \dots \nu_s$ Ionen mit den Wertigkeiten $z_1 \dots z_i \dots z_s$)

$$\theta = 1 - f_0 = w \frac{\epsilon^2}{6DkT} \sqrt{\frac{4\pi\epsilon^2}{DkT} n \sum \nu_i} \quad (48)$$

mit dem Wertigkeitsfaktor

$$w = \left(\frac{\sum \nu_i z_i^3}{\sum \nu_i} \right)^{3/2}. \quad (49)$$

Einmal soll nun die Anzahl Ionen n pro cm^3 in der Konzentration γ , gemessen in Mol pro Liter, ausgedrückt werden. Wir nehmen für die Loschmidtsche Zahl den Wert $6,06 \cdot 10^{23}$ an, dann ist

$$n = 6,06 \cdot 10^{20} \gamma.$$

Weiter wird angenommen $\epsilon = 4,77 \cdot 10^{-10}$ e.s.E., $k = 1,346 \cdot 10^{-16}$ erg, und da es sich im folgenden um Gefrierpunkte wässriger Lösungen handelt, $T = 273$. Für die Dielektrizitätskonstante des Wassers nehmen wir die von Drude aus den Messungen berechnete Interpolationsformel, wonach bei 0⁰ C

$$D = 88,23$$

wird¹⁾. Unter Benutzung dieser Zahlen wird ($\sum \nu_i = \nu$ gesetzt)

1) Ann. d. Phys. 59, 61, 1896.

$$\sqrt{\frac{4\pi\epsilon^2}{DkT}} n\nu = 0,231 \cdot 10^8 \sqrt{\nu\gamma} \frac{1}{\text{cm}}$$

und damit

$$\Theta = 0,270 w \sqrt{\nu\gamma}. \quad (50)$$

Die Größe α von früher ist unter Einsetzung der obigen Zahlenwerte

$$\alpha = 0,231 \cdot 10^8 \sqrt{\nu\gamma} \sqrt{\frac{\sum \nu_i z_i^2}{\nu}} \frac{1}{\text{cm}}. \quad (51)$$

In Fig. 3 sind Beobachtungen¹⁾ über Θ jetzt im Gegensatz zu früher aufgetragen zu der

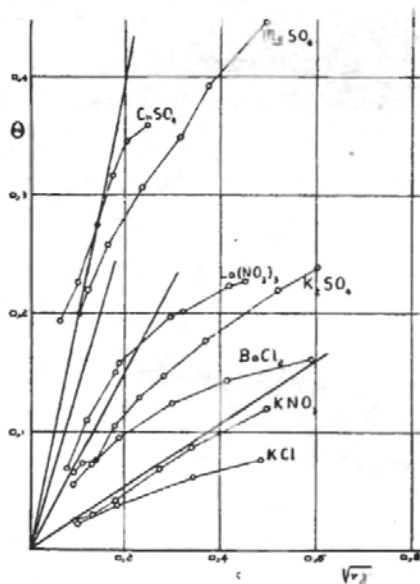


Fig. 3.

Abszisse $\sqrt{\nu\gamma}$, die Beobachtungspunkte wurden jeweilig durch gerade Striche verbunden. Außerdem sind in der Figur vier vom Nullpunkt ausstrahlende gerade Linien eingetragen, welche das Grenzgesetz (50) darstellen. Die vier Salztypen der Figur haben die Wertigkeitsfaktoren

$$w = 1, \quad w = 2\sqrt{2}, \quad w = 3\sqrt{3}, \quad w = 8,$$

diesen Werten entsprechen die genannten Geraden. Man sieht, daß tatsächlich die Annäherung an die geraden Linien für kleine Konzentrationen stattfindet, daß also das Grenzgesetz mit der zweiten Wurzel aus der Konzentration offenbar den Tatsachen entspricht. Überdies aber werden die mit Hilfe der Dielektrizitätskonstante 88,23 berechneten, im übrigen theoretisch nur durch den Wertigkeitsfaktor unterschiedenen

1) L. H. Adams, l. c. (KNO_3 , KCl); R. E. Hall u. W. D. Harkins, l. c. (K_2SO_4 , $La(NO_3)_3$, $MgSO_4$, $BaCl_2$); T. G. Bedford, Proc. of the Royal Soc. A 83, 454, 1909 ($CuSO_4$) [Konzentration im Mol pro Liter bei KCl , $CuSO_4$; in Mol pro 1000 g Wasser bei KNO_3 , $BaCl_2$, K_2SO_4 , $La(NO_3)_3$].

Absolutwerte der Neigung [so wie sie durch den Faktor $0,270 w$ in (50) zum Ausdruck kommen] durch das Experiment bestätigt. Die Fig. 3 zeigt aber, daß schon bald Abweichungen von dem Grenzgesetz einsetzen. Das steht in Übereinstimmung mit den Überlegungen des § 3 und Gleichung (51), wonach sogar bei ein-einwertigen Elektrolyten schon bei $\gamma = 1$ die charakteristische Länge $1/\alpha$ von der Größenordnung der Ionen-durchmesser wird, es also nicht mehr statthaft ist, diese zu vernachlässigen. Unserer Theorie

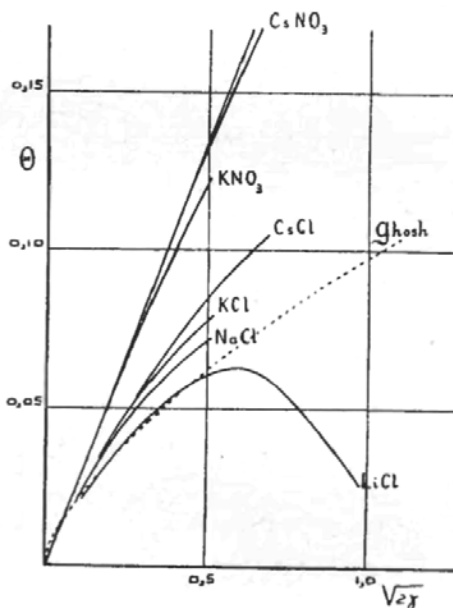


Fig. 4.

haben wir nun außerdem die vereinfachte Form (21') der Potentialgleichung zugrunde gelegt. Auch dieses könnte einen Einfluß haben. Indessen machten wir S. 190 (Fußnote) darauf aufmerksam, daß der letztere Einfluß theoretisch verhältnismäßig geringfügig ist. Aber auch die experimentellen Ergebnisse deuten darauf hin, daß die Abweichungen vom Grenzgesetz durch die individuellen Eigenschaften der Ionen bedingt werden. Um das zu zeigen, bringen wir Fig. 4. In dieser sind Beobachtungen nur an ein-einwertigen Salzen eingetragen¹⁾ als Funktion von $\sqrt{2\gamma}$ (da hier $\nu = 2$ ist). Die gerade Linie stellt das oben diskutierte Grenzgesetz dar, alle Kurven streben bei kleinen Konzentrationen dieser Geraden zu. Die Abweichungen

1) Außer den bereits zitierten sind hier noch benützt Messungen von H. Jahn, Ztschr. f. phys. Ch. 50, 129, 1905; 59, 31, 1907 ($LiCl$, $CsCl$); E. W. Washburn u. Mac Innes, Journ. Amer. Chem. Soc. 33, 1686, 1911 ($LiCl$, $CsNO_3$); W. H. Harkins u. W. A. Roberts, ibid. 38, 2658, 1916 ($NaCl$) [Konzentration z. T. in Mol pro Liter, z. T. in Mol pro 1000 g Wasser].

sind aber sehr verschieden groß und gehen bemerkenswerterweise z. B. bei den Chlorsalzen in der Reihenfolge *Cs, K, Na, Li*. Das ist dieselbe Reihenfolge, welche sich ergibt, wenn man die Alkaliionen ordnet nach abnehmender Beweglichkeit, eine Reihenfolge, die mit der anzunehmenden Größe der Ionen im Widerspruch steht und erst neuerdings von Born¹⁾ mit der aus der Dipoltheorie folgenden Relaxationszeit des Wassers für die elektrische Polarisation in Zusammenhang gebracht wurde. Um auch eine Orientierung gegenüber den Ghoshschen Arbeiten zu ermöglichen, ist in der Figur die Kurve für Θ gestrichelt eingetragen, so wie sie sich aus jener Theorie ergibt. Sie sollte für alle Salze gleichzeitig gelten und geht außerdem mit senkrechter Tangente in den Nullpunkt ein.

Es fragt sich nun, inwieweit unsere mit Rücksicht auf die Ionenabmessungen verbesserte Theorie imstande ist, von den individuellen Abweichungen Rechenschaft zu geben. Die Verhältnisse sollen durch Fig. 5 illustriert werden.

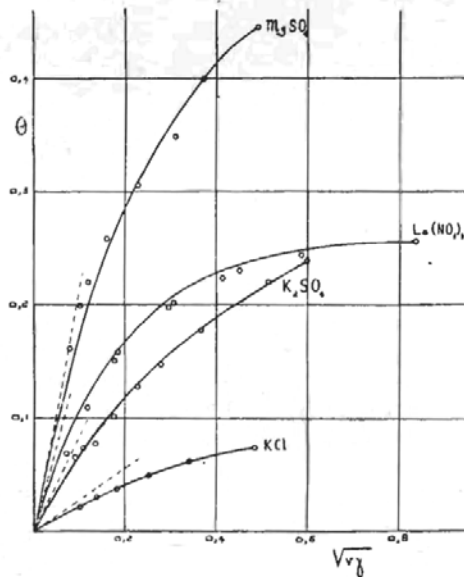


Fig. 5.

Wir haben wieder die vier Elektrolyte von den eingangs erwähnten vier Typen gewählt und die beobachteten Werte für Θ als Funktion von $\sqrt{\nu\gamma}$ aufgetragen. Nach (41) hat man mit Berücksichtigung der Ionengröße (nach Einsetzung der Zahlenwerte)

$$\Theta = 1 - f_0 = 0,270 w \sqrt{\nu\gamma} \frac{\sum \nu_i z_i^2 \sigma_i}{\sum \nu_i z_i^2}, \quad (52)$$

in der σ_i die S. 195 tabellierte und in (33) durch eine Formel dargestellte Funktion des Argu-

1) M. Born, Zeitschr. f. Phys. 1, 221, 1920.

mentes $x_i = \kappa a_i$ bedeutet, wobei a_i die Länge ist, welche die Größe des i ten Ions gegenüber seiner Umgebung zu messen hat. Es schien uns nun angezeigt, bei der heutigen Sachlage nicht auf die einzelnen Ionengrößen einzugehen, sondern mit einem mittleren für die Ionen eines Elektrolyten gleichen Durchmesser a zu rechnen. Dann werden alle σ_i untereinander gleich und man erhält für Θ den Ausdruck

$$\Theta = 0,270 w \sqrt{\nu\gamma} \sigma(\kappa a). \quad (53)$$

Zur Bestimmung der Größe a wählten wir jeweilig nur einen, und zwar den bei der größten Konzentration beobachteten Punkt und haben dann die sich mit dem so bestimmten a nach der theoretischen Formel (53) ergebende Kurve in der Figur eingetragen. Vom Nullpunkt strahlen noch vier gestrichelt gezeichnete gerade Linien aus (die Tangenten der Kurven), welche das Grenzesetz (50) für große Verdünnungen darstellen. Die Übereinstimmung mit den Beobachtungen ist eine sehr gute, besonders in Anbetracht der Konstantenbestimmung aus einem einzigen Beobachtungspunkt¹⁾. Die Figur ergänzen wir durch die folgenden Tabellen:

Tabelle III.
KCl ($a = 3,76 \cdot 10^{-8}$ cm)

2γ	$\sqrt{2\gamma}$	Θ beobachtet	Θ berechnet
0,0100	0,100	0,0214	0,0237
0,0193	0,139	0,0295	0,0313
0,0331	0,182	0,0375	0,0392
0,0633	0,252	0,0485	0,0499
0,116	0,341	0,0613	0,0618
0,234	0,484	0,0758	—

1) Das Verfahren zur Bestimmung von a sei im einzelnen am Beispiel des $La(NO_3)_3$ erläutert. Für $\gamma' = 0,17486$ ist beobachtet $\Theta' = 0,2547$; da $\nu = 4$ ist, wird die Abszisse $\sqrt{\nu\gamma'} = 0,836$. Nach dem Grenzesetz (50) für äußerster Verdünnung würde sich mit $w = 3\sqrt{3}$ (wie es $\nu_1 = 1$, $\nu_2 = 3$, $z_1 = 3$, $z_2 = -1$ nach (49) entspricht) für Θ der Wert $\Theta = 1,173$ ergeben, der wirklich beobachtete Wert geht aus diesem Grenzwerte hervor durch Multiplikation mit 0,216. Dieser Faktor ist nach (53) dem Werte von σ gleichzusetzen. Aus Fig. 1 (S. 195) liest man nun ab, daß zur Ordinate $\sigma = 0,216$ die Abszisse $x = \kappa a = 1,67$ gehört; andererseits ist nach (51) unter Einsetzung von $\sqrt{\nu\gamma'} = 0,836$ der Wert von $\kappa = 0,336 \cdot 10^{-8} \text{ cm}^{-1}$. Also entspricht dem Beobachtungswert der Durchmesser

$$a = \frac{x}{\kappa} = 4,97 \cdot 10^{-8} \text{ cm.}$$

[Bei den Salzen K_2SO_4 , $La(NO_3)_3$, $MgSO_4$ ist die Konzentration γ' in Mol pro 1000 g Wasser angegeben und statt γ zur Bestimmung von Θ benutzt, das deshalb mit Θ' bezeichnet ist. Bei den hier nur in Betracht gezogenen geringen Konzentrationen sind die dadurch bedingten Abweichungen ganz geringfügig; eine Umrechnung von γ' in γ würde keine merkliche Änderung an den Werten für Θ' beobachtet, Θ berechnet und a ergeben.]

Tabelle IV.
 $K_2SO_4 (a = 2,69 \cdot 10^{-8} \text{ cm})$

$3\gamma'$	$\sqrt{3\gamma'}$	θ' beobachtet	θ' berechnet
0,00722	0,0906	0,0647	0,0612
0,0121	0,110	0,0729	0,0724
0,0185	0,136	0,0776	0,0871
0,0312	0,176	0,101	0,108
0,0527	0,229	0,128	0,132
0,0782	0,280	0,147	0,152
0,136	0,369	0,178	0,183
0,267	0,516	0,220	0,217
0,361	0,600	0,238	—

 Tabelle V.
 $La(NO_3)_3 (a = 4,97 \cdot 10^{-8} \text{ cm})$

$4\gamma'$	$\sqrt{4\gamma'}$	θ' beobachtet	θ' berechnet
0,00528	0,0728	0,0684	0,0828
0,0142	0,119	0,110	0,121
0,0322	0,179	0,151	0,157
0,0343	0,185	0,158	0,161
0,0889	0,298	0,197	0,204
0,0944	0,308	0,201	0,207
0,173	0,418	0,223	0,230
0,205	0,453	0,229	0,235
0,346	0,588	0,243	0,248
0,599	0,836	0,255	—

 Tabelle VI.
 $MgSO_4 (a = 3,35 \cdot 10^{-8} \text{ cm})$

$2\gamma'$	$\sqrt{2\gamma'}$	θ' beobachtet	θ' berechnet
0,00640	0,0800	0,160	0,147
0,0107	0,103	0,199	0,179
0,0149	0,122	0,220	0,203
0,0262	0,162	0,258	0,248
0,0534	0,231	0,306	0,311
0,0976	0,312	0,349	0,368
0,138	0,372	0,392	0,400
0,242	0,493	0,445	—

In der ersten Kolonne steht jeweilig die Ionenkonzentration¹⁾ $\nu\gamma$, in der zweiten die Abszisse $\sqrt{\nu\gamma}$ der Fig. 5, in der dritten der beobachtete Wert von θ' und in der vierten Kolonne der nach (53) und (51) berechnete Wert derselben Größe. Die der größten Konzentration entsprechende Zahl ist hier nicht aufgeführt, da mit ihrer Hilfe der in der Überschrift der Tabellen jeweilig angegebene Wert des mittleren Durchmessers a berechnet wurde.

Schließlich wird in Fig. 6 eine Darstellung von Theorie und Beobachtung an wässrigen KCl -Lösungen gegeben. Wir verfolgen mit der Diskussion dieser Figur hauptsächlich das Ziel, einige Andeutungen zu machen bezüglich des

1) Siehe die vorige Anmerkung.

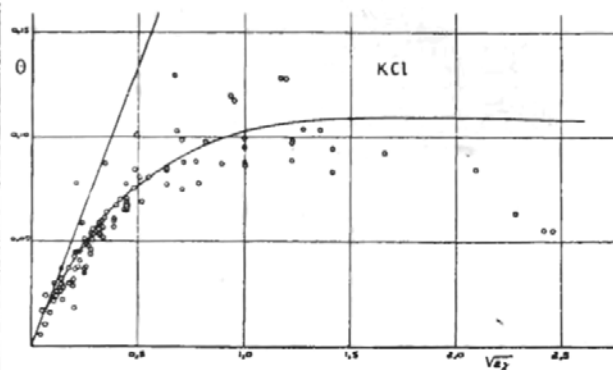


Fig. 6.

Verhaltens konzentrierter Lösungen; nebenbei soll sie zeigen, wie groß die Abweichungen untereinander der in der Literatur von den einzelnen Beobachtern mit scheinbar großer Genauigkeit angegebenen Einzelresultate ist. Sie enthält zu diesem Zwecke alle von uns aufgefundenen Beobachtungen an KCl -Lösungen seit dem Jahre 1900¹⁾. Als Abszisse ist wie früher $\sqrt{2\gamma}$ gewählt. Dabei ist γ unserer Definition nach die Konzentration in Mol pro Liter Lösung. Alle Angaben, die sich auf anders gemessene Konzentrationen bezogen, sind hier auf jene Konzentrationen umgerechnet worden unter Benutzung der gemessenen Dichten²⁾ von KCl -Lösungen. Die Ordinate ist wieder mit θ bezeichnet, stellt aber nicht mehr genau den früheren Ausdruck

$$\frac{\Delta_k - \Delta}{\Delta_k}$$

dar. Tatsächlich ergibt nämlich schon die klassische Theorie, wenn man zu konzentrierten Lösungen übergeht, nicht mehr Proportionalität zwischen Gefrierpunktniedrigung und Konzentration. Das hat einmal seinen Grund darin, daß nicht die Konzentration c selber, sondern $\log(1-c)$ in der klassischen Gleichung vorkommt. Zweitens ist die Differenz zwischen den thermodynamischen Potentialen von Eis und Wasser nicht mehr genau genug dargestellt durch das erste, Δ proportionale Glied der

1) J. Barnes, Trans. Nova Scot. Inst. of Science 10, 139, 1900; C. Hebb, ibid. 10, 422, 1900; H. J. Jones, J. Barnes u. E. P. Hyde, Americ. Chem. Journ. 27, 22, 1902; H. B. Jones u. Ch. G. Carroll, ibid. 28, 284, 1902; W. Biltz, Zeitschr. f. phys. Chem. 40, 185, 1902; Th. W. Richards, ibid. 44, 563, 1903; S. W. Young u. W. H. Sloan, Journ. Americ. Chem. Soc. 26, 919, 1904; H. Jahn, l. c.; T. G. Bedford, l. c.; F. Flügel, Zeitschr. f. phys. Chem. 79, 577, 1912; L. H. Adams, l. c.; W. H. Rodebusch, Journ. Americ. Chem. Soc. 40, 1204, 1918.

2) Baxter u. Wallace, Journ. Americ. Chem. Soc. 38, 18, 1916.

Taylor-Entwicklung, auch das zweite mit A^2 behaftete Glied muß beibehalten werden. Dementsprechend haben wir in diesem Falle die vollständige Gleichung (34) zu benutzen. Für den Fall des KCl ist darin $n_1 = n_2 = n$ und $z_1 = -z_2 = 1$ zu setzen, außerdem wollen wir wieder die beiden Ionendurchmesser a_1 und a_2 durch einen mittleren a ersetzen. Dann kann (34) folgendermaßen geordnet werden

$$\frac{1}{2nv_0} \left[\frac{A}{T_0} \frac{Q}{RT_0} - \frac{A}{T_0^2} \left(\frac{C_p - C_p'}{2R} - \frac{Q}{RT_0} \right) + \log(1 - 2c) \right] = - \frac{\epsilon^2 \kappa}{6DkT} \sigma. \quad (54)$$

Das links stehende Glied wurde nun für die verschiedenen Konzentrationen berechnet. Hierzu wurde $C_p - C_p' = 3,6$ gesetzt, entsprechend einem ungefähren Wert für $C_p' = 14,4$, wie man ihn aus den Nernstschen Messungen¹⁾ der spezifischen Wärme des Eisens für 273° etwa extrapoliert. Zur Berechnung ist es noch nötig, den Zusammenhang zu kennen zwischen der molekularen Konzentration c und der Volumkonzentration γ . Mit Hilfe der beobachteten Dichte der Lösung ist dieser Zusammenhang ohne weiteres angebar, indessen spielt sowohl hier wie bei der Ableitung der Gleichung selbst das Molekulargewicht des Wassers eine gewisse Rolle. In erster Näherung verschwindet zwar dieser Einfluß, die Glieder zweiter Ordnung aber sind von ihm nicht zu befreien. Dadurch aber, daß dieser Effekt erst in zweiter Ordnung eine Rolle spielt, wird sein Einfluß außerordentlich stark herabgedrückt, deshalb haben wir durchweg mit dem einfachen Molekulargewicht 18 gerechnet. Die Größe $2nv_0$ im Nenner schließlich kann gleich

$$2nv_0 = 2\Omega_0 \frac{\gamma}{1000}$$

gesetzt werden, falls Ω_0 das Molekularvolumen des Wassers bedeutet. Wäre nun kein gegenseitiger elektrischer Einfluß der Ionen vorhanden, so müßte das linke Glied bei Einsetzen der beobachteten Gefrierpunktniedrigung den Wert Null ergeben. Tatsächlich ergibt es aber einen endlichen Wert und diesen Wert bezeichnen wir mit $-\Theta$. Der Theorie nach muß dann diese Differenz Θ durch das rechte Glied dargestellt werden, so daß

$$\Theta = \frac{\epsilon^2 \kappa}{6DkT} \sigma(\kappa a) = 0,270 \sqrt{2\gamma} \sigma(\kappa a) \quad (55)$$

sein sollte. Im übrigen bestätigt man, daß die hier befolgte Definition von Θ mit der oben für geringe Konzentrationen angegebenen in der Grenze übereinstimmt.

Die Punkte, welche in der Figur eingetragen sind, haben die auf dem skizzierten Wege aus

den Beobachtungen berechneten Ordinaten. Die Kurve der Figur stellt das rechte Glied von (55) dar unter der Annahme $a = 3,76 \cdot 10^{-8}$ cm. Dieser Wert von a wurde bestimmt aus der einen Beobachtung von Adams, wonach zu $\gamma = 0,117$ der experimentelle Wert $\Theta = 0,0758$ gehört. Die gerade Linie, welche außerdem in der Figur eingetragen ist, gibt wieder das Grenzwertgesetz für äußerste Verdünnung entsprechend

$\sigma = 1$. Man kann wohl sagen, daß bis zu Konzentrationen von etwa 1 Mol/Liter die Beobachtungen dargestellt werden. Bei höheren Konzentrationen zeigen die Beobachtungen ein Maximum in Θ . Zwar hat auch die theoretische Kurve ein Maximum, aber dieses ist, wie die Figur zeigt, so flach, daß es kaum angedeutet ist. Wir möchten diesen Unterschied bei großen Konzentrationen als reell ansehen und im nächsten Paragraphen einiges dazu bemerken.

§ 10. Allgemeine Bemerkungen.

Aus dem Vorhergehenden darf wohl geschlossen werden, daß es sowohl vom theoretischen wie vom experimentellen Standpunkte aus unzulässig ist, die elektrische Energie einer Ionenlösung als wesentlich durch den mittleren gegenseitigen Abstand der Ionen bestimmt anzusehen. Vielmehr erweist sich als charakteristische Länge eine Größe, welche die Dicke der Ionenatmosphäre oder, um an Altbekanntes anzuknüpfen, die Dicke einer Helmholtzschen Doppelschicht mißt. Dadurch, daß diese Dicke von der Konzentration des Elektrolyten abhängt, wird auch die elektrische Energie der Lösung eine Funktion jener Größe. Dem Umstande, daß diese Dicke der zweiten Wurzel aus der Konzentration umgekehrt proportional ist, verdanken die Grenzwertgesetze für große Verdünnungen ihr charakteristisches, jener Potenz $1/2$ angepaßtes Gepräge. Trotzdem wir es somit ablehnen müssen, von einer Gitterstruktur des Elektrolyten im landläufigen Sinne zu sprechen und es, wie die Entwicklung des Gegenstandes gezeigt hat, zu unzulässigen Fehlern führt, falls man das Bild zu wörtlich nimmt, ist doch ein Kern von Wahrheit in ihm enthalten. Um dieses klar zu machen, führe man die folgenden zwei Gedankenexperimente aus. Erstens nehme man ein Raumelement und denke sich dieses viele Male hintereinander an beliebige Stellen des Elektrolyten verlegt. Es ist klar, daß man dann bei einem binären Elektrolyten ebensooft ein positives wie ein negatives Ion in ihm vorfinden wird. Zweitens aber nehme man dasselbe Raumelement und lege es wieder viele

1) W. Nernst, Berl. Ber. 1910, I, 262.

Male hintereinander in den Elektrolyten hinein, nun aber nicht ganz beliebig, sondern immer so, daß es z. B. von einem übrigens jeweilig beliebig gewählten positiven Ion stets um eine bestimmte Strecke (von einigen Å-Einheiten) entfernt ist. Nunmehr wird man nicht mehr gleich oft positive wie negative Ladungen vorfinden, sondern es werden die negativen an Zahl überwiegen. Darin, daß also in der unmittelbaren Umgebung jedes Ions die entgegengesetzt geladenen im Mittel an Zahl überwiegen, kann man mit Recht eine Analogie zum Kristallbau des $NaCl$ -Typus sehen, wo jedes Na -Ion unmittelbar von 6 Cl -Ionen und jedes Cl -Ion von 6 Na -Ionen umgeben ist. Nur ist als wesentlicher Punkt bei der Elektrolytlösung zu beachten, daß das Maß jener Ordnung bestimmt wird durch das thermische Gleichgewicht zwischen anziehenden Kräften und Temperaturbewegung, während es beim Kristall fest vorgegeben ist.

Die Rechnungen und der Vergleich mit der Erfahrung wurden so ausgeführt, daß für das umgebende Lösungsmittel mit seiner gewöhnlichen Dielektrizitätskonstante gerechnet wurde. Der Erfolg zeigt die Berechtigung dieser Annahme, aber an sich ist dieses Vorgehen zwar bei geringen Konzentrationen berechtigt, sollte jedoch bei größeren Konzentrationen doch zu Fehlern Veranlassung geben. In der Tat folgt aus der Dipoltheorie, daß Dielektrika bei großen Feldstärken Sättigungserscheinungen aufweisen müssen, welche Ähnlichkeit haben mit der bekannten magnetischen Sättigung. Die neueren Versuche von Herweg¹⁾ können als eine experimentelle Bestätigung dieser theoretischen Forderung angesehen werden. Da nun in einem Abstände 10^{-7} cm von einem einfach geladenen Ion eine Feldstärke von etwa 200000 Volt/cm zu erwarten ist, sollte man sich darauf gefaßt machen, etwas von diesen Sättigungserscheinungen zu bemerken. Es wäre natürlich sehr interessant, wenn es gelingen würde, aus den Beobachtungen jenen Effekt in seiner Wirkung herauszuschälen, um so mehr, als die Natur uns hier Feldstärken zur Verfügung stellt von einer Größe, welche sonst mit gewöhnlichen experimentellen Mitteln kaum erreichbar wären.

Aber noch in anderer Hinsicht müssen konzentriertere Lösungen ein besonderes Verhalten zeigen. Befinden sich nämlich viele Ionen in der Umgebung jedes einzelnen, so kann das etwa aufgefaßt werden als eine Änderung des umgebenden Mediums in elektrischer Hinsicht, ein Effekt, welcher in der vorstehenden Theorie nicht berücksichtigt worden ist. In welchem Sinne derselbe wirksam sein kann, möge aus

folgender Überlegung hervorgehen. Man nehme ein Ion, das festgehalten wird und ein bewegliches, etwa entgegengesetzt geladenes und frage nach der Arbeit, die nötig ist, um das bewegliche Ion zu entfernen. Diese Arbeit kann dann als aus zwei Teilen bestehend angesehen werden: erstens wird das Ion zu seiner Entfernung eine gewisse Arbeit verbrauchen, zweitens aber wird man eine Arbeit gewinnen, indem man den Raum, den das Ion vorher eingenommen hat, nachträglich mit dem Lösungsmittel ausfüllt. Nun ergeben Versuche über die Verdünnungswärme tatsächlich einen Hinweis auf die reale Existenz solcher Verhältnisse. Nimmt man etwa eine HNO_3 -Lösung von zunächst geringer Konzentration und verdünnt dieselbe mit sehr viel Wasser (d. h. so weit, daß weitere Verdünnung keinen Wärmeeffekt mehr hervorbringen würde), dann findet eine Abkühlung statt, d. h. es muß ganz im Sinne der früheren Überlegungen Arbeit geleistet werden, um die Ionen weiter voneinander zu entfernen. Hat aber die Ausgangslösung eine größere Konzentration, dann tritt bei demselben Versuch eine Wärmeentwicklung ein, d. h. man gewinnt Arbeit, wenn man die Umgebung jedes Ions von genügend vielen andern Ionen befreit und sie durch Wassermoleküle ersetzt. Im üblichen Sprachgebrauche heißt das, es tritt überwiegend eine Hydratation der Ionen ein und dieser Vorgang ist als exothermer Prozeß anzusehen. Offenbar bezwecken die vorstehenden Überlegungen eine Deutung dieser sogenannten Hydratation auf rein elektrischem Wege. Tatsächlich kann man eine Näherungsrechnung ausführen, welche die auf diesem Gebiete geltenden Berthelotschen Regeln für die Abhängigkeit der Verdünnungswärme von der Anfangskonzentration theoretisch ergibt und deren praktisch gefundenen Zahlenkoeffizienten der Größenordnung nach verständlich macht. Für die Gefrierpunktsbeobachtungen haben diese Überlegungen insofern eine Bedeutung, als sie die Möglichkeit nahelegen, zu berechnen, warum und in welchem Grade die für die prozentuale Abweichung θ gefundenen Kurven (vgl. den Fall der KCl) sich bei größeren Konzentrationen nach unten krümmen und die Abszissenachse sogar schneiden können, wenn die Konzentration groß genug gemacht werden kann. In diesem Falle ist die Gefrierpunktserniedrigung größer als die klassisch zu erwartende (auch wie ausdrücklich bemerkt sei, wenn die klassische Theorie in ungekürzter Form zur Verwendung kommt). Man hat sich bis dahin damit begnügt, in solchen Fällen von einer Hydratation zu sprechen.

Bevor indessen die Verhältnisse bei konzentrierten Lösungen untersucht werden können,

1) Zeitschr. f. Phys. 3, 36, 1920 und 8, 1, 1922.

muß zunächst gezeigt werden, daß auch der irreversible Vorgang der Stromleitung bei verdünnten starken Elektrolyten vom hier eingenommenen Standpunkte aus quantitativ beherrscht werden kann. Die ausführlichen Darlegungen zu diesem Thema behalten wir einer folgenden Notiz vor. Hier begnügen wir uns mit der Angabe der Grundgedanken, welche dort ihre mathematische Ausführung finden werden. Bewegt sich unter der Einwirkung einer äußeren Feldstärke ein Ion in der Flüssigkeit, so werden sich die umgebenden Ionen, um die Ionenatmosphäre bilden zu können, dauernd umlagern müssen. Denkt man sich nun eine Ladung im Innern der Elektrolyten plötzlich entstanden, so braucht die Ionenatmosphäre eine gewisse Relaxationszeit zu ihrer Entstehung. Ähnlich wird beim bewegten Ion die umgebende Atmosphäre nicht ihre Gleichgewichtsverteilung aufweisen können, wird also nicht auf Grund des Boltzmann-Maxwellschen Prinzips berechenbar sein. Ihre Bestimmung kann aber einwandfrei geschehen auf Grund einer nahe liegenden Interpretation der Gleichungen für die Brownsche Bewegung. Von vornherein kann schon qualitativ abgeschätzt werden, in welchem Sinne dieser auf dem Vorhandensein einer endlichen Relaxationszeit beruhende Effekt wirken kann. In einem Punkte vor dem bewegten Ion (d. h. ein Punkt, nach dem es sich hinbewegt) muß die elektrische Dichte der Ionenatmosphäre zeitlich zunehmen; für einen Punkt hinter dem Ion muß sie abnehmen. Infolge der Wirkung der Relaxationszeit wird aber die Dichte vor dem Ion etwas kleiner sein, als es ihrem Gleichgewichtswerte entsprechen würde, hinten dagegen wird sie noch nicht auf ihren Gleichgewichtswert abgefallen sein. Infolgedessen besteht während der Bewegung hinter dem Ion stets eine etwas größere elektrische Dichte der Atmosphäre als vor dem Ion. Da nun Ladungsdichte und Ionenladung stets entgegengesetztes Vorzeichen haben, tritt eine Kraft auf, welche das Ion in seiner Bewegung bremst, unabhängig von seinem Vorzeichen und welche offenbar mit zunehmender Konzentration auch zunehmen muß.

Das ist der eine Effekt, welcher im selben Sinne wirkt, wie die sonst auf Grund des Ostwaldschen Verdünnungsgesetzes rechnerisch bestimmte Verminderung des Dissoziationsgrades. Aber noch ein zweiter Effekt ist vorhanden, der ebenfalls berücksichtigt werden muß. In der Umgebung von einem Ion befinden sich vorzugsweise Ionen entgegengesetzten Vorzeichens, die sich unter der Einwirkung des äußeren Feldes natürlich in entgegengesetzter Richtung bewegen. Diese werden das umgebende Lösungsmittel bis zu gewissem Grade mitschleppen, be-

dingen also, daß das betrachtete Einzelion sich nicht relativ zu einem ruhenden, sondern relativ zu einem in entgegengesetztem Sinne bewegten Lösungsmittel zu bewegen hat. Da offenbar diese Wirkung mit zunehmender Konzentration zunimmt, hat man hier einen zweiten Effekt, der im selben Sinne wirkt wie eine Verminderung des Dissoziationsgrades. Quantitativ berechnet kann der Effekt werden nach denselben Prinzipien, die Helmholtz angewandt hat, um die Elektrophorese zu behandeln.

Das Gemeinsame der beiden genannten Einflüsse besteht, wie die Rechnung zeigt, darin, daß beide mit der Dicke der Ionenatmosphäre in unmittelbarem Zusammenhang stehen und deshalb die erzeugten Kräfte der zweiten Wurzel aus der Konzentration des Elektrolyten proportional werden, wenigstens in der Grenze für sehr geringe Konzentrationen. So ergibt sich dann ein vor vielen Jahren auf Grund des Beobachtungsmaterials von Kohlrausch¹⁾ gefundenes Gesetz, wonach bei geringen Konzentrationen die prozentuale Abweichung der molekularen Leitfähigkeit von ihrem Grenzwerte bei unendlicher Verdünnung der zweiten Wurzel aus der Konzentration proportional ist. Auch der Proportionalitätsfaktor bekommt natürlich so seine molekulare Bedeutung.

Indem wir der für die folgende Notiz in Aussicht genommenen ausführlichen Darstellung der Verhältnisse bei der elektrolytischen Leitung vorgreifen, können wir als Gesamtergebnis feststellen, daß die Ansicht, wonach die starken Elektrolyte vollständig dissoziiert sind, sich vollkommen bewährt.

¹⁾ F. Kohlrausch u. L. Holborn, Das Leitvermögen der Elektrolyte, 2. Aufl., Leipzig 1916, S. 108 u. 112.

Zürich, Februar 1923.

(Eingegangen 27. Februar 1923.)

Vorlesungsverzeichnis für das Sommersemester 1923.

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Translated Text (English, 1954)

ON THE THEORY OF ELECTROLYTES. I. FREEZING POINT
DEPRESSION AND RELATED PHENOMENA.*
(Zur Theorie der Elektrolyte. I. Gefrierpunktserniedrigung
und verwandte Erscheinungen)

P. Debye and E. Hückel**

Translated from
Physikalische Zeitschrift, Vol. 24, No. 9, 1923, pages 185-206

I. Introduction

It is known that the dissociation hypothesis by Arrhenius explains the abnormally large values of osmotic pressure, freezing point depression, etc., observed for solutions of electrolytes, by the existence of free ions and the associated increase in the number of separate particles. The quantitative theory relies on the extension, introduced by van't Hoff, of the laws for ideal gases to diluted solutions for the computation of their osmotic pressure. Since it is possible to justify this extension on the basis of thermodynamics, there can be no doubt regarding the general validity of these fundamentals.

*Submitted February 27, 1923.

**The present considerations were stimulated by a lecture by E. Bauer on Ghosh's works, held at the Physikalische Gesellschaft. The general viewpoints taken as the basis for the computation of the freezing point depression as well as of the conductivity lead me, among other things, to the limiting law involving the square root of the concentration. I could have reported on this during the winter of 1921 at the "Kolloquium." With the active assistance of my assistant, Dr. E. Hückel, a comprehensive discussion of the results and their collection took place during the winter of 1922.

ELECTROLYTES

However, for finite concentrations we obtain smaller values for freezing point lowering, conductivity, etc. than one would expect on first consideration, in the presence of a complete dissociation of the electrolyte into ions. Let P_k , for instance, be the osmotic pressure resulting from the classical law by van't Hoff for complete dissociation, then the actually observed osmotic pressure will be smaller, so that:

$$P = f_o P_k$$

where, according to Bjerrum,¹ the "osmotic coefficient" f_o thus introduced is intended to measure this deviation independent of any theory—and can be observed as a function of concentration, pressure, and temperature. In fact, these observations do not relate directly to the osmotic pressure but to freezing point lowering, and boiling point rise, respectively, which can both be derived on the basis of thermodynamics, and by means of the same osmotic coefficient f_o , from their limiting value following from van't Hoff's law for complete dissociation.

The most evident assumption to explain the presence of the osmotic coefficient is the classical assumption, according to which not all molecules are dissociated into ions, but which assumes an equilibrium between dissociated and undissociated molecules which depend on the over-all concentration, as well as on pressure and temperature. The number of free, separate particles is thus variable, and would have to be made directly proportional to f_o . The quantitative theory of this dependence, as far as it relates to the concentration, relies on the mass action law of Guldberg-Waage; the dependence on temperature and pressure of the constant of equilibrium appearing in this law can be determined thermodynamically, according to van't Hoff. The complete aggregate of dependencies, including the Guldberg-Waage law, can be proved by thermodynamics, as is shown by Planck.

Since, the electric conductivity is determined exclusively by the ions, and since, according to the classical theory the number of ions follows immediately from f_o , the theory requires the well known relation between the dependence on the concentration of the conductivity on the one hand and of the osmotic pressure on the other hand.

A large group of electrolytes, the strong acids, bases, and their salts, collectively designated as "strong" electrolytes, exhibits definite deviations from the dependencies demanded by the classical theory. It is especially noteworthy that these deviations are the more pronounced the more the solutions are diluted.* Thus, as was recognized in the course of developments and following

*A summary presentation of this subject was given by L. Ebert, "Forschungen ueber die Anomalien starker Elektrolyte," *Jahrb. Rad. u. Elektr.*, 18, 134 (1921).

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the classical theory, it is possible only with a certain degree of approximation to draw a conclusion from f_0 as to the dependence of the conductivity on the concentration. Moreover the dependence of the osmotic coefficient f_0 on the concentration is also represented entirely incorrectly. For strongly diluted solutions, f_0 approaches the value 1; if $1-f_0$ is plotted as a function of the concentration c , classical theory requires for binary electrolytes, such as KCl, that this curve meets the zero point with a finite tangent (determined by the constant of equilibrium, K). In the general case, provided the molecule of the electrolyte splits into ν ions, we obtain from the law of mass action for low concentrations:

$$1 - f_0 = \frac{\nu - 1}{\nu} \frac{c^{\nu-1}}{K}$$

so that in cases where splitting into more than two ions occurs, the curve in question should present even a higher order of contact with the abscissa. The complex of these dependencies constitutes Ostwald's dilution law.

Actually observations on strong electrolytes show an entirely different behavior. The experimental curve starts from the zero point at a right angle (cf. Figure 2) to the abscissa, independent of the number of ions, ν . All proposed, practical interpolation formulas attempt to represent this behavior by assuming $1-f_0$ to be proportional to a fractional power (smaller than 1, such as 1/2 or 1/3) of the concentration. The same remark holds with regard to the extrapolation of the conductivity to infinite dilutions which, according to Kohlrausch, requires the use of the power $\frac{1}{2}$.

It is clear that under these circumstances the classical theory can not be retained. All experimental material indicates that its fundamental starting point should be abandoned, and that, in particular, an equilibrium calculated on the basis of the mass action law does not correspond to the actual phenomena.

W. Sutherland,² in 1907, intended to build the theory of the electrolytes on the assumption of a complete dissociation. His work contains a number of good ideas. N. Bjerrum³ is, however, the first to have arrived at a distinct formulation of the hypothesis. He clearly stated and proved that, for strong electrolytes, no equilibrium at all is noticeable between dissociated and undissociated molecules, and that, rather, convincing evidence exists which shows that such electrolytes are completely dissociated into ions up to high concentrations. Only in considering weak electrolytes, undissociated molecules reappear. Thus the classical explanation as an exclusive basis for the variation of, for instance, the osmotic coefficient, has to be abandoned and the task ensues to search for an effect of the ions, heretofore overlooked, which explains, in the absence of association, a decrease in f_0 with an increase in concentration.

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Recently, under the influence of Bjerrum, the impression gained strength that consideration of the electrostatic forces, exerted by the ions on one another and of considerable importance because of the comparatively enormous size of the elementary electric charge, must supply the desired explanation. Classical theory does not discuss these forces, rather, it treats the ions as entirely independent elements. A new interaction theory has to be analogous in some respects to van der Waals' generalization of the law of ideal gases to the case of real gases. However, it will have to resort to entirely different expedients, since the electrostatic forces between ions decrease only as the square of the distance and thus are essentially different from the intermolecular forces which decline much more rapidly with an increase in distance.

Milner⁴ computed the osmotic coefficient along such lines. His computation can not be objected to as regards its outline, but it leads to mathematical difficulties which are not entirely overcome, and the final result can only be expressed in the form of a graphically determined curve for the relation between $1-f_0$ and the concentration. From the following it will further emerge that the comparison with experience, carried through by Milner, supposes the admission of his approximations for concentrations which are much too high and for which, in fact, the individual properties of the ions, not taken into account by Milner, already play an important part. In spite of this, it would be unjust to discard Milner's computation in favor of the more recent computations by Ghosh⁵ on the same subject. We shall have to revert, in the following, to the reason why we can not agree to Ghosh's calculations, neither in their application to the conductivity nor in their more straightforward application to the osmotic pressure. We will even have to reject entirely his calculation of the electrostatic energy of an ionized electrolyte, which is the basis for all his further conclusions.

The circumstances to be considered in the computation of the conductivity are very similar to those for the osmotic coefficient. Here also the new interaction theory has to make an attempt at understanding the mutual electrostatic effect of the ions with regard to its influence on their mobility. An earlier attempt was made in this direction by Hertz.⁶ He transcribes the methods of the kinetic theory of gases, and, in fact, finds a mutual interference of the ions. However, the transcription of this classical method, and particularly the use of concepts like that of the free path length of a molecule in a gas for the case of free ions surrounded by the molecules of the solvent, does not seem to be very reliable. The final result obtained by Hertz cannot, in fact, be reconciled with the experimental results.

In this first note, we shall confine ourselves to the "osmotic coefficient f_0 " and to a similar "activity coefficient f_a ," used by

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Bjerrum⁷ and stressed in its significance. Even for such (weak) electrolytes, where a noticeable number of undissociated molecules is present, the equilibrium cannot simply be determined by the Guldberg-Waage formula in its classical form:

$$c_1^{\mu_1} c_2^{\mu_2} \dots c_n^{\mu_n} = K$$

(c_1, c_2, \dots, c_n , are the concentrations, K the constant of equilibrium). It will be necessary, in view of the mutual electrostatic forces between the ions, to write:

$$f_a K$$

instead of K , introducing the activity coefficient* f_a . This coefficient, just as f_o , will depend on the concentration of the ions. Though, according to Bjerrum, a relation to be proved by thermodynamics exists between f_a and f_o , their dependence on the concentration is different for the two coefficients.

The detailed treatment of conductivity shall be reserved for a later note. This division seems justified, since the determination of f_o and f_a requires solely a consideration of reversible processes, whereas the computation of mobilities has to do with essentially irreversible processes for which no direct relation to the fundamental laws of thermodynamics exists.

II. Fundamentals

As is well known, it is shown in thermodynamics that the properties of a system are completely known, provided one of the many possible thermodynamic potentials is given as a function of the correctly chosen variables. In view of the form in which the terms based on the mutual electric effects will appear we chose the quantity:**

*The activity coefficient f_a introduced here is not identical with that introduced by Bjerrum. Bjerrum splits our coefficient f_a in order to give a produce of coefficients each of which is associated with a separate ion type. (Compare section 8).

**The potential G differs from Helmholtz' free energy $F = U - TS$ only by the factor $-1/T$. This difference is not essential at all; we define it as in the text: to have immediate connection with Planck's thermodynamics.

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$$G = S - \frac{U}{T} \quad (1)$$

(S = entropy, U = energy, T = absolute temperature) as basic functions. As variables in this case (besides the concentration) we have, naturally, volume and temperature, since:

$$dG = \frac{p}{T} dV + \frac{U}{T^2} dT \quad (1')$$

The computations which follow differ from the classical computations in that the electrical effects of the ions are taken into account. Accordingly, we divide U into two parts, a classical part U_k and an additional electrical energy U_e :

$$U = U_k + U_e$$

If we consider that, according to equation (1):

$$T^2 \frac{\partial G}{\partial T} = U \quad (2)$$

and divide the potential G also into two parts:

$$G = G_k + G_e$$

we find that, according to equation (2):

$$G_e = \int \frac{U_e}{T^2} dT \quad (3)$$

It is our main assignment to determine the electric energy U_e of an ionic solution. For practical evaluations, however, the potential G is not as suitable as the function:

$$\Phi = S - \frac{U + pV}{T} \quad (4)$$

also preferred by Planck. As shown by the differential form of this definition:

$$d\Phi = -\frac{V}{T} dp + \frac{U + pV}{T^2} dT \quad (4')$$

the variables pertaining to the potential Φ are pressure and temperature, and since a large majority of the experiments are carried through at constant pressure (and not at constant volume), Φ is

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preferable. A comparison between (4) and (1) results in:

$$\Phi = G - \frac{pV}{T} \quad (5)$$

if, according to the above, G is known, it remains to find the additional term $-pV/T$ as a function of p and T , and to add it. In view of (1') we can conclude that:

$$\frac{p}{T} = \frac{\partial G}{\partial V} = \frac{\partial G_k}{\partial V} + \frac{\partial G_e}{\partial V} \quad (6)$$

and so have obtained the equation of state which relates pressure, volume, and temperature for the ionic solution. It can be interpreted by assuming that, as a consequence of the electric effect of the ions, an additional, electric pressure p_e , is added to the external pressure p ; the electric pressure is to be computed from the relation:

$$p_e = - \frac{\partial G_e}{\partial V} \quad (6')$$

Later we shall, incidentally,* have occasion to determine this electric pressure p_e ; it amounts to approximately 20 atmospheres for an aqueous solution of, for instance, KCl at a concentration of 1 mole per liter. Strictly speaking, it is incorrect to use the classical expression for V (as function of p and T) without regard to the electric effect of the ions, since the pressure p_e causes also a change in volume. In view of the low compressibility of water which results in a relative change of volume of 0.001 for 20 atmospheres, the electric addition to V (as function of p and T) can be neglected for most applications. In the light of this remark, we shall also divide Φ in a classical part and an additional electric part:

$$\Phi = \Phi_k + \Phi_e \quad (7)$$

and can put, according to equation (3):

$$\Phi_e = G_e = \int \frac{U_e}{T^2} dT \quad (7')$$

The classical part, Φ_k , has, according to Planck, the form:

$$\Phi_k = \sum_0^i N_i (\varphi_i - k \log c_i) \quad (7'')$$

*Compare with footnote, page 237.

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where:

$$N_0, N_1, \dots, N_i, \dots, N_s$$

designate the number of separate particles in the solution, and N_0 refers to the solvent.* Further the thermodynamic potential referred to a single particle is equal to:

$$\varphi_i = s_i - \frac{u_i + \phi v_i}{T}$$

a quantity independent of the concentration; k is Boltzmann's constant, $k = 1.346 \times 10^{-16}$ erg, and c_i denotes the concentration of the i type particle so that:

$$c_i = \frac{N_i}{N_0 + N_1 + \dots + N_i + \dots + N_s}$$

of which the relation:

$$\sum_0 c_i = 1$$

is a consequence.

Upon completion of this thermodynamic introduction, we proceed to the discussion of the principal assignment: computation of the electric energy U_e .

At a first glance it appears as if this energy could be obtained directly in the following manner. In a solvent with dielectric constant D are located two electric charges of magnitudes ϵ and $-\epsilon$, respectively, at a distance r , so that their energy is given by:

$$-\frac{1}{D} \frac{\epsilon^2}{r}$$

For simplicity, in these general considerations, a binary electrolyte, such as KCl, is kept in mind which is completely split into

*Our relation deviates from that given by Planck in as much as we do not use the number of moles but rather the number of actual particles, which appears to be more suitable for our purpose. This corresponds to the appearance of Boltzmann's constant k instead of the gas constant R . An essential difference compared with Planck is, of course, not caused by this formulation.

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ions so that in a volume V of the solution $N_1 = N$ K ions with the charge $+e$ and an equal number $N_2 = N$ Cl ions with the charge $-e$ are present. It can then be imagined that the average distance r , which enters into the computation of energy, equals the average distance between the ions, and since the volume associated with one ion is equal to $V/2N$, we write:

$$r = \left(\frac{V}{2N}\right)^{1/3}$$

In using this value for r , the electric energy of the solution would be estimated to:

$$U_e = -N \frac{e^2}{D} \left(\frac{2N}{V}\right)^{1/3}$$

In fact, Ghosh⁵ proceeds in this manner. This consideration, however, is wrong, and the complete theory based on it (practically characterized by the introduction of the cube root of the concentration), is to be rejected.

The (negative) electric energy of an ionic solution originates from the fact that, considering any one ion, we shall find on the average more dissimilar than similar ions in its surroundings, an immediate consequence of the electrostatic forces effective between the ions. There is some similarity to the case of crystals, such as NaCl, KCl, etc., in which, according to Bragg's investigations, each atom (here also present as ion) has dissimilar ones as nearest neighbors. Though it is correct (in agreement with the exact calculations by Born) to estimate the electric energy of the crystal by inserting the distance of two neighboring dissimilar atoms, it is a mistake to overestimate the analogy, and to use the same average distance $(V/2N)^{1/3}$ in the case of solutions. In fact, here an entirely different length is of fundamental importance, since now the ions can move freely, and, consequently, the desired length can only follow on the basis of an evaluation of the difference in probability for the period of time spent by similar and dissimilar ions in the same volume element in the vicinity of a specified ion. From this alone it already follows that the temperature movement will be of importance in the calculation of U_e .

From dimensions alone, we can only conclude the following. Assuming that the size of the ions does not have to be taken into account* for high dilutions, then one energy is the expression given above:

*In the following it will be shown that this assumption actually holds.

$$\frac{\epsilon^2}{D} \left(\frac{2N}{V} \right)^{1/2}$$

Another energy, that of the temperature movement, measured by kT , is of equal importance. Thus it is to be expected that U_e will take the form:

$$U_e = -N \frac{\epsilon^2}{D} \left(\frac{2N}{V} \right)^{1/2} f \left(\frac{\epsilon^2}{D} \left(\frac{2N}{V} \right)^{1/2} / kT \right) \quad (8)$$

in which f is a function of the ratio of the two energies about which we can not make any *a priori* statements.*

A consideration of the limiting case of high temperatures leads to the same conclusion. If the energy of the temperature movement is large, and if we consider a volume element in the neighborhood of an ion singled out for this consideration, the probability of finding in it a similar ion is equal to the probability to find a dissimilar one. In the limit for high temperatures, U_e must disappear, i.e., the expression for U_e has T as essential parameter also for medium temperatures.

III. Computation of the Electric Energy of an Ionic Solution of a Uni-Univalent Salt

In a volume V , N molecules of a uni-univalent salt (for instance, KCl) are present disintegrated into ions; if the absolute value of the charge of an ion is ϵ (4.77×10^{-10} electrostatic units), the dielectric constant of the solvent is D . We follow one of these ions with the charge $+\epsilon$, and we intend to ascertain its potential energy u with respect to the surrounding ions. Direct calculation, as attempted by Milner, who considers each possible arrangement of ions and lets it enter into the computation with the probability corresponding to Boltzmann's principle, proved too difficult mathematically. We therefore replace it by another consideration, where the computation is, from the beginning directed toward the average of the electric potential generated by the ions.

At a point P in the surroundings of the specified ion, the average value of the electric potential with respect to time be ψ ; to transport a positive ion there, the work expended is $+\epsilon\psi$; for a negative ion, however, the work expended is $-\epsilon\psi$. Therefore, in

*The considerations by O. Klein are in agreement with this discussion on dimensions. *Meddel. från. K. Vetenskapsakad. Nobelinstitut*, 5, No. 6 (1919) (Article to celebrate the 60th birthday of S. Arrhenius).

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a volume element dV at this location, we shall find, as an average value with respect to time, according to Boltzmann's principle,

$$ne^{-\frac{\epsilon\psi}{kT}} dV$$

positive and:

$$ne^{+\frac{\epsilon\psi}{kT}} dV$$

negative ions, putting $n = N/V$. In fact, in the limit for $T = \infty$, the ion distribution must become uniform, so that the multiplying factor of the exponential function must be put equal to N/V , i.e., equal to the number of ions of one kind per cubic centimeter of solution. With these statements however, nothing can as yet be obtained, since the potential ψ of the point P is still unknown. However, according to Poisson's equation, this potential must satisfy the condition:

$$\Delta\psi = -\frac{4\pi}{D}\rho$$

if the electricity is distributed with a density ρ in a medium of dielectric constant D . On the other hand, from the above:

$$\rho = n\epsilon \left(e^{-\frac{\epsilon\psi}{kT}} - e^{+\frac{\epsilon\psi}{kT}} \right) = -2n\epsilon \text{sh} \frac{\epsilon\psi}{kT} \quad (9)$$

so that ψ can be determined as a solution of the equation:

$$\Delta\psi = \frac{8\pi n\epsilon}{D} \text{sh} \frac{\epsilon\psi}{kT} \quad (10)$$

The further we go from the specified ion, the smaller will be the potential ψ . For large distances we can then replace, with sufficient approximation, $\text{sinh}(\epsilon\psi/kT)$ by $\epsilon\psi/kT$. If this is done, equation (10) assumes the much simpler form:*

$$\Delta\psi = \frac{8\pi n\epsilon^2}{DkT} \psi \quad (10')$$

*We have also investigated the effect of the successive terms in the expansion of $\text{sinh}(\epsilon\psi/kT)$, and could establish that their effect on the final result is rather small. This computation is not presented.

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In this equation, the factor of ψ on the right hand side has the dimension of the reciprocal of the square of a length. We put:

$$\kappa^2 = \frac{8\pi n \epsilon^2}{DkT} \quad (11)$$

so that κ is the reciprocal of a length, and equation (10') becomes:

$$\Delta\psi = \kappa^2\psi \quad (12)$$

The length, introduced in this way:

$$\frac{1}{\kappa} = \sqrt{\frac{DkT}{8\pi n \epsilon^2}}$$

is the essential quantity in our theory and replaces the average distance between ions in Ghosh's consideration. If numerical values are inserted (see later) and the concentration is measured, as usual, in moles per liter solution, then, if this concentration is denoted by γ ,

$$\frac{1}{\kappa} = \frac{3.06}{\sqrt{\gamma}} 10^{-8} \text{ cm}$$

for water at 0°C. The characteristic length reaches molecular dimensions for a concentration of $\gamma = 1$ (1 mole per liter).

We shall now interrupt the course of the consideration in order to investigate the physical interpretation of our characteristic length.

If an electrode is immersed in an electrolytic solution of potential ϕ , the surface of the electrode compared with the solution have a potential difference ψ . The transition from ψ to ϕ will then take place within a layer of finite thickness which is given by the above considerations. Using equation (12) and designating by z a coordinate at right angles to the surface of the electrode, we obtain:

$$\psi = \Psi e^{-\kappa z}$$

a function which satisfies equation (12). Since the right term of equation (12), from Poisson's equation, stands for $-4\pi\rho/D$, the charge density related to the given potential is:

$$\rho = -\frac{D\kappa^2}{4\pi} \psi e^{-\kappa z}$$

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According to this formula, $1/\kappa$ measures the length within which the charge density of the ion atmosphere reduces to one e th part. Our characteristic length is a measure for the thickness of the ion atmosphere (i.e., of the well-known double layer by Helmholtz); according to equation (11), it depends on concentration, temperature, and dielectric constant of the solvent.*

Having clarified the significance of $1/\kappa$, we shall now use equation (12) to determine the potential distribution and the density distribution in the neighborhood of the singled-out ion with charge $+e$. We designate the distance from this ion by r , and introduce spatial polar coordinates in equation (12). Equation (12) then becomes:

$$\frac{1}{r^2} \frac{d}{dr} \left(r^2 \frac{d\psi}{dr} \right) = \kappa^2 \psi \quad (12')$$

and this equation has the general solution:

$$\psi = A \frac{e^{-\kappa r}}{r} + A' \frac{e^{\kappa r}}{r} \quad (13)$$

Since ψ disappears at infinity, A' must equal zero; the constant A , however, will have to be found from the conditions prevailing in the neighborhood of the ion. This determination shall be carried through in two steps, (a) and (b), assuming for (a) that the dimensions of the ion have no effect, and under (b) take the size of the ion into consideration. The trend of thought under (a) will then give the limiting law for high dilutions, while under (b) will fall the changes to be made in order to adapt this limiting law to larger concentrations.

(a) Ion Diameter Negligible

The potential of a single point charge e in a medium of dielectric constant D would be:

$$\psi = \frac{e}{D} \frac{1}{r}$$

assuming no other ions in the medium. Our potential, equation (13), must agree with this expression for infinitely small distances, consequently we must put;

*Agreement of the above results on the double layer with computations by M. Gouy, *J. Physik.* (4), 9, 457 (1910) on the theory of the capillary electrometer was subsequently established. We may, perhaps, point out that in this instance the original equation (10) permits a simple solution.

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$$A = \frac{\epsilon}{D}$$

and the desired potential becomes:

$$\psi = \frac{\epsilon e^{-\kappa r}}{D r} = \frac{\epsilon}{D r} - \frac{\epsilon}{D} \frac{1 - e^{-\kappa r}}{r} \quad (14)$$

We split the potential into two parts, the first part representing a potential which is undisturbed by the surrounding ions, and the second part representing the potential derived from the ion atmosphere. For small values of r , the value of this latter potential is equal to:

$$-\frac{\epsilon}{D} \kappa$$

the potential energy u of the singled-out ion $+e$ with respect to its surroundings amounts to:*

$$u = -\frac{\epsilon^2}{D} \kappa \quad (15)$$

If we have a series of charges e_i , and if the potential at the respective location of each charge is ψ_i , then, according to the laws of electrostatics, the total potential energy:

$$U_e = \frac{1}{2} \sum e_i \psi_i$$

In our case, where N positive ions are present, each of which at a potential difference $-\kappa/D$ against its surrounding, and further N negative ions with a potential difference of $+\kappa/D$, the desired potential energy** will be:

*Besides the graphical result mentioned in the preface, the article by Milner contains a footnote (*Phil. Mag.*, 24, 575, 1912), according to which in the case of the above text and in our terminology:

$$u = -\frac{\epsilon^2}{D} \kappa (\pi/2)^{\frac{1}{2}}$$

A derivation of this formula is not included. It differs from our result by the factor $(\pi/2)^{\frac{1}{2}}$.

**Since we are only concerned with the mutual potential energy, we have to take for ψ_i not the value of the total potential but only the part caused by the surrounding charges, always calculated for the point at which the charge e_i is located.

$$U_i = \frac{N\varepsilon}{2} \left(-\frac{\varepsilon\kappa}{D} \right) - \frac{N\varepsilon}{2} \left(+\frac{\varepsilon\kappa}{D} \right) = -\frac{N\varepsilon^2\kappa}{D} \quad (16)$$

Since κ is given by equation (11) as a function of the concentration, the potential energy of the ion solution is proportional to the square root of the concentration and not, as according to Ghosh, to the cube root of this quantity.

(b) Ion Diameter is Finite

We observed, previously, that the characteristic length $1/\kappa$ reaches the magnitude of molecular dimensions for concentrations of 1 mole per liter. At such concentrations, it is therefore inadmissible to replace an ion of finite, molecular size by a point charge, as was done under (a). It would not be within the nature of our calculations, based on Poisson's equation, to introduce a detailed concept of the distances to which the ions approach one another. Rather we shall in the following visualize ions as spheres of radius a , the interior of which is to be treated as a medium of dielectric constant D , and in the center of which is located a point charge of value $+\varepsilon$ or $-\varepsilon$. Then the magnitude a , obviously, does not measure the radius of the ion but a length which constitutes the mean value for the distance to which the surrounding ions, positive as well as negative, can approach the singled-out ion. Correspondingly, for positive and negative ions of equal size, for instance, a would be expected to be of the order of magnitude of the ion diameter. In general, the ion diameter is not to be considered the diameter of the actual ion, since, most likely, the ions have to be imagined as surrounded by a firmly attached layer of water molecules. It is obvious that the introduction of such a length a cannot be expected to be more than a rough approximation. The discussion of practical cases (compare later) will show that, in practice, this approximation is rather good.

As before, we express the potential surrounding a singled-out ion by:

$$\psi = A \cdot \frac{e^{-\kappa r}}{r} \quad (17)$$

only the constant A must now be determined differently. According to our assumptions, we have to write:

$$\psi = \frac{\varepsilon}{D} \frac{1}{r} + B \quad (17')$$

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for the interior of the ion sphere (for a positive ion). Constants A and B must be determined from the boundary conditions on the surface of the sphere. There, that is, for $r = a$, the potentials ψ as well as the field strengths $-d\psi/dr$ must be continuous. From this it follows that:

$$\left. \begin{aligned} A \frac{e^{-\kappa a}}{a} &= \frac{\epsilon}{D} \frac{1}{a} + B \\ A \cdot e^{-\kappa a} \frac{1 + \kappa a}{a^2} &= \frac{\epsilon}{D} \frac{1}{a^2} \end{aligned} \right\} (18)$$

hence:

$$A = \frac{\epsilon}{D} \frac{e^{\kappa a}}{1 + \kappa a}, \quad B = -\frac{\epsilon \kappa}{D} \frac{1}{1 + \kappa a} \quad (18')$$

The value of B represents the potential generated by the ion atmosphere in the center of the ion sphere; from this we obtain for the potential energy of a positive ion with respect to its surroundings the expression:

$$u = -\frac{\epsilon^2 \kappa}{D} \frac{1}{1 + \kappa a} \quad (19)$$

As shown by comparison with equation (15), the effect of the size of the ion is expressed by the factor $1/(1 + \kappa a)$ only. For low concentrations (n small) κ is also small, according to equation (11), and the energy approaches the value given previously for infinitely small ions. For large concentrations (κ large), however, u gradually approaches the value:

$$-\frac{\epsilon^2}{Da}$$

so that our characteristic length, $1/\kappa$, loses its effect in favor of the new length a which measures the size of the ions.

By means of equation (19) we obtain, as under (a), for the total electric energy of the ion solution the expression:

$$U_e = -\frac{N}{2} \frac{\epsilon^2 \kappa}{D} \left[\frac{1}{1 + \kappa a_1} + \frac{1}{1 + \kappa a_2} \right] \quad (20)$$

provided - as appears to be indicated - the positive ions are characterized by a radius a_1 and the negative ions by another radius a_2 . We could use (16) or (20) directly for the determination of the thermodynamic function in accordance with the discussion in section II. However, we shall first derive the expression for the energy, corresponding to (20), for any ionic solution, by eliminating the restriction to uni-univalent salts introduced in the interest of brevity.

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IV. The Potential Energy of an Arbitrary Ion Solution

A solution contains:

$$N_1 \dots N_i \dots N_s$$

different ions with charges:

$$z_1 \dots z_i \dots z_s$$

such that the integers $z_1 \dots z_i \dots z_s$ measure the valencies and may assume positive as well as negative values. Since the total charge is equal to zero,

$$\sum N_i z_i = 0$$

must hold. In addition to the total numbers N_i , the number of ions per cubic centimeter:

$$n_1 \dots n_i \dots n_s$$

be introduced.

Again any one of the ions is singled out, and the potential in its surroundings is determined from Poisson's equation:

$$\Delta\psi = -\frac{4\pi}{D}\rho$$

From Boltzmann's principle, the density of the i th ion type is given by:

$$n_i e^{-z_i \frac{e\psi}{kT}}$$

so that:

$$\rho = e \sum n_i z_i e^{-z_i \frac{e\psi}{kT}}$$

and the fundamental equation is given by:

$$\Delta\psi = -\frac{4\pi e}{D} \sum n_i z_i e^{-z_i \frac{e\psi}{kT}} \quad (21)$$

If we use again the expansion of the exponential function, as in the previous paragraph, the equation:

$$\Delta\psi = \frac{4\pi e^2}{DkT} \sum n_i z_i^2 \psi \quad (21')$$

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instead of (21) will be the basic equation, since, because of the condition:

$$\sum n_i z_i = 0$$

the first term of the expansion disappears. Thus, in the general case, the square of the characteristic length $1/\kappa^2$ is to be defined by the equation:*

$$\kappa^2 = \frac{4\pi\epsilon^2}{DkT} \sum n_i z_i^2 \quad (22)$$

while the equation for the potential retains its previous form:

$$\Delta\psi = \kappa^2\psi$$

Again an ion shall be singled out, and the potential ψ in its vicinity be determined. In concordance with the discussion in the preceding paragraph,

$$\psi = A \frac{e^{-\kappa r}}{r}$$

is obtained for the field outside the ion.

Provided the ion carries a charge $z_i\epsilon$ and a distance of approach to it equal to a_i is to be considered, then we have for the interior of the ion sphere:

$$\psi = \frac{z_i\epsilon}{D} \frac{1}{r} + B$$

while the constants A and B are evaluated to:

$$A = \frac{z_i\epsilon}{D} \frac{e^{\kappa a_i}}{1 + \kappa a_i}, \quad B = -\frac{z_i\epsilon\kappa}{D} \frac{1}{1 + \kappa a_i}$$

To the given value of B corresponds the potential energy:

$$u = -\frac{z_i^2\epsilon^2\kappa}{D} \frac{1}{1 + \kappa a_i}$$

of the singled-out ion with respect to its ion atmosphere, while the total electric energy of the ion solution, as will readily be seen, assumes the value:

$$U_e = -\sum \frac{N_i z_i^2 \epsilon^2 \kappa}{2} \frac{1}{D} \frac{1}{1 + \kappa a_i} \quad (23)$$

*Since for uni-univalent salts $n_1 = n_2 = n$ and $z_1 = -z_2 = 1$, the general expression (22) for κ^2 agrees with the one (compare equation 11) given for this special case.

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The inverse length κ is, in the general case, defined by equation (22).*

V. The Additional Electric Term to the Thermodynamic Potential

In section II we arrived at the result that the additional term to the thermodynamic potential:

$$G = S - \frac{U}{T}$$

resulting from the mutual effect of the ions, should be found from the equation:

$$G_e = \int \frac{U_e}{T^2} dT$$

To take care of the general case, let us take the expression (23) for U_e , then, when integrating, we have to consider that, according to (22), the reciprocal length in this expression depends on the temperature. The computation becomes clearer, if we first conclude from (22) that:

$$\kappa dx = - \frac{4\pi\epsilon^2}{Dk} \sum n_i z_i^2 \frac{dT}{T^2}$$

where D is assumed independent of temperature,** and then use κ and not T as variable of integration. Thus results:

$$G_e = \frac{k}{4\pi \sum n_i z_i^2} \sum N_i z_i^2 \int \frac{\kappa^2 dx}{1 + \kappa a_i} \quad (24)$$

If we introduce the abbreviation:

$$\kappa a_i = x_i \quad (25)$$

find:

*From the expression for U_e , we can immediately derive the heat of dilution. We established that the theoretical value agrees with the experiments.

**In fact a direct, kinetic theory of the osmotic pressure, reported in *Recueil des travaux chimiques des Pays-Bas et de la Belgique*, proves the validity of the final expression for G_e independent of this assumption. For a discussion of the thermodynamic computation we may refer to B. A. M. Cavanagh, *Phil. Mag.*, 43, 606 (1922).

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$$\int_{1+x_i}^{x=x} \frac{x^2 dx}{1+x_i} = \frac{1}{a_i^3} \int_{1+u}^{u=x_i} \frac{u^2 du}{1+u} = \frac{1}{a_i^3} \left\{ \text{const} + \log(1+x_i) - 2(1+x_i) + \frac{1}{2}(1+x_i)^2 \right\}$$

The constant of integration must be so determined that in the limit for infinite dilution the electrical addition G_e to the total potential disappears. Since according to (22), κ is proportional to:

$$\sqrt{\sum n_i z_i^2}$$

$\kappa = 0$ corresponds to infinite dilution. Consequently the constant in the bracket must be so determined that for $x_i = 0$ the expression in the bracket is also equal to zero. Since at this limit:

$$\log(1+x_i) - 2(1+x_i) + \frac{1}{2}(1+x_i)^2$$

assumes the value $-3/2$, our constant is $3/2$. Then:

$$\int \frac{x^2 dx}{1+xa} = \frac{1}{a_i^3} \left\{ \frac{3}{2} + \log(1+x_i) - 2(1+x_i) + \frac{1}{2}(1+x_i)^2 \right\}$$

and:

$$G_e = \frac{k}{4\pi \sum n_i z_i^2} \sum \frac{N_i z_i^2}{a_i^3} \left\{ \frac{3}{2} + \log(1+x_i) - 2(1+x_i) + \frac{1}{2}(1+x_i)^2 \right\} \quad (26)$$

If expanded with respect to powers of x_i the function in the bracket takes the form:

$$\begin{aligned} \frac{3}{2} + \log(1+x_i) - 2(1+x_i) + \frac{1}{2}(1+x_i)^2 &= \\ &= \frac{x_i^3}{3} - \frac{x_i^4}{4} + \frac{x_i^5}{5} - \frac{x_i^6}{6} + \dots \end{aligned}$$

If we, therefore, introduce the abbreviation:

$$\begin{aligned} \chi_i &= \chi(x_i) = \\ &= \frac{3}{x_i^3} \left\{ \frac{3}{2} + \log(1+x_i) - 2(1+x_i) + \frac{1}{2}(1+x_i)^2 \right\} \end{aligned} \quad (27)$$

χ will, for small concentration, approach unity, and can be expanded into:

$$\chi_i = 1 - \frac{2}{3}x_i + \frac{3}{5}x_i^2 - \dots \quad (27')$$

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By introduction of this function and consideration of the equation (22) defining κ^2 , the addition to the thermodynamic potential can now be presented in the form:*

$$G_e = \sum N_i \frac{z_i^2 \epsilon^2}{DT} \frac{\kappa}{3} \chi_i \quad (28)$$

where, for clarity, the expression (22) for κ according to which:

$$\kappa^2 = \frac{4\pi\epsilon^2}{DkT} \sum n_i z_i^2$$

be repeated explicitly.

For small concentrations, therefore, an amount of G_e proportional to κ , i.e., proportional to the square root of the concentration, is associated with each ion. If the finite dimensions of the ions are neglected, then, according to (27') and (25), χ_i would be equal to 1 throughout, and this dependency would appear to be valid for all concentrations. The dependence on the size of the ions, which accounts for the individual properties of the ions, is, then, measured by the function χ , given by (27) or (27'). In the limit for high dilutions, however, this influence disappears, and the ions can only be distinguished if their valencies are different.

**VI. Osmotic Pressure, Vapor Pressure Depression,
Freezing Point Depression, Boiling Point Increase**

In accordance with the discussion of section II and in view of equations (7), (7'), and (7''), the thermodynamic function Φ of the solution is given by the expression:

$$\Phi = \sum_0^s N_i (\varphi_i - k \log c_i) + \sum_1^k N_i \frac{z_i^2 \epsilon^2}{3D} \frac{\kappa}{T} \chi_i \quad (29)$$

Here equation (28) has been used for the additional electric term to Φ , where:

$$\chi_i = \chi(x_i) = \chi(\kappa a_i)$$

is given by (27), and, as explained in the preceding paragraph, approaches unity in the limit for infinitely small concentrations. κ is our characteristic reciprocal length, defined by equation (22),

*The additional electric pressure p_e , mentioned in section II, equation (8'), results from this formula. The numerical value given there was computed in this way.

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$$\alpha^2 = \frac{4\pi\epsilon^2}{DkT} \sum n_i z_i^2$$

By the method followed in Planck's *Lehrbuch der Thermodynamik*, the rules for the description of the phenomena mentioned in the heading can all be derived by differentiation of equation (29). The condition for equilibrium of a transition of a quantity δN_0 molecules of the solvent from the solution to the appropriate other phase is, as is well known,

$$\delta\Phi + \delta\Phi' = 0$$

where Φ' designates the thermodynamic potential of the second phase. We put:

$$\Phi' = N_0' \varphi_0' \quad (30)$$

We wish to carry out the computations for the case of equilibrium between the solution and the frozen solvent, in view of the fact that the most extensive and the most reliable measurements are available for the freezing point depression as a function of concentration. We let N_0 vary by the amount δN_0 and N_0' by the amount $\delta N_0'$, and obtain immediately:

$$\begin{aligned} \delta(\Phi + \Phi') &= \varphi_0' \delta N_0' + (\varphi_0 - k \log c_0) \delta N_0 + \\ &+ \sum_1^i N_i \frac{z_i^2 \epsilon^2}{3DT} \frac{d(\alpha \chi_i)}{d\alpha} \frac{\partial \alpha}{\partial N_0} \delta N_0 \quad (31) \end{aligned}$$

since, as will readily be seen:

$$\sum_0^i N_i \delta \log c_i = \sum_0^i N_i \frac{\partial \log c_i}{\partial N_0} \delta N_0$$

assumes the value zero.

Since:

$$\delta N_0' = -\delta N_0$$

the condition for equilibrium reads:

$$\varphi_0' - \varphi_0 = -k \log c_0 + \sum_1^i N_i \frac{z_i^2 \epsilon^2}{3DT} \frac{d(\alpha \chi_i)}{d\alpha} \frac{\partial \alpha}{\partial N_0} \quad (32)$$

As presented here, it may be applied to all the phenomena mentioned in the heading, and it constitutes a relation between pressure, temperature, and concentrations.

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In the definition of κ , n_i designates the number of ions of the i th type per unit volume so that:

$$n_i = \frac{N_i}{V}$$

and, as in Planck's treatment, the method is based on the linear relation for the volume:

$$V = \sum_0^i n_i v_i = n_0 v_0 + \sum_1^i n_i v_i$$

According to equation (22),

$$\begin{aligned} 2x \frac{\partial x}{\partial N_0} &= -\frac{4\pi\epsilon^2}{DkT} \sum z_i^2 \frac{N_i v_0}{V^2} = \\ &= -\frac{4\pi\epsilon^2}{DkT} \frac{v_0}{V} \sum n_i z_i^2 \end{aligned}$$

Again using the equation defining κ , we obtain:

$$\frac{\partial x}{\partial N_0} = -\frac{x v_0}{2V}$$

and our condition for equilibrium assumes the form:

$$\varphi_0 - \varphi_0' = k \log c_0 + v_0 \sum_1^i n_i \frac{z_i^2 \epsilon^2}{6DT} x \frac{d(x\chi_i)}{dx} \quad (32')$$

The function of the concentration:

$$\frac{d(x\chi_i)}{dx}$$

characterizing the phenomena considered, can be computed easily from equation (27). Let us designate it by σ_i , then, retaining the abbreviation:

$$x_i = x a_i$$

we obtain:

$$\begin{aligned} \sigma_i &= \frac{d(x\chi_i)}{dx} = \\ &= \frac{3}{x_i^3} \left[(1+x_i) - \frac{1}{1+x_i} - 2 \log(1+x_i) \right] \quad (33) \end{aligned}$$

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For small values of x_i , the expansion:

$$\begin{aligned} \sigma_i &= 1 - \frac{1}{2} x_i + \frac{2}{3} x_i^2 - 2 x_i^3 + \dots = \\ &= \sum_{\nu=0}^{\infty} 3 \frac{\nu+1}{\nu+3} x_i^{\nu} \end{aligned}$$

is valid so that σ_i approaches unity for small concentrations; for large concentrations σ_i approaches zero as $3/x_i^2$. Table I contains numerical values for σ as a function of $x = \kappa a$.

Table I

x	$\sigma(x)$	x	$\sigma(x)$	x	$\sigma(x)$	x	$\sigma(x)$
0	1.000	0.4	0.598	0.9	0.370	3.0	0.1109
0.05	0.929	0.5	0.536	1.0	0.341	3.5	0.0898
0.1	0.855	0.6	0.486	1.5	0.238	4.0	0.0742
0.2	0.759	0.7	0.441	2.0	0.176	4.5	0.0628
0.3	0.670	0.8	0.403	2.5	0.136	5.5	0.0540

In Figure 1 a plot of this function is presented.

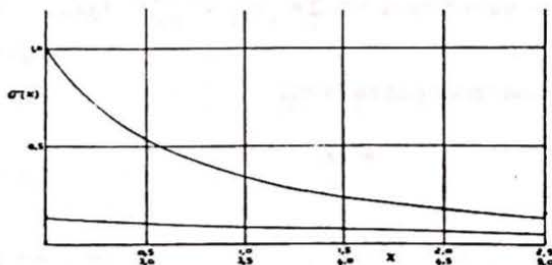


Figure 1

Since we shall have occasion to treat the freezing point depression of more concentrated solutions, it is advisable to calculate the amount of this depression from equation (32'), without introducing all simplifications permissible for highly diluted solutions. Let the freezing point of the pure solvent be T_0 , the freezing point of the solution $T_0 - \Delta$, the heat of fusion of the frozen solvent q , the specific heat at constant pressure of the liquid solvent c_p , and the same quantity for the frozen solvent c_p' , where the three last mentioned quantities be referred to an actual molecule so that they constitute the conventional quantities for one mole divided by Loschmidt's number. According to the equa-

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tion defining φ , we then have:

$$\varphi_0 - \varphi_0' = -\frac{\Delta}{T_0} \frac{q}{T_0} + \frac{\Delta^2}{T_0^2} \left[(c_p - c_p') - \frac{2q}{kT_0} \right]$$

For c_0 we can put:

$$c_0 = 1 - \sum_1^i c_i$$

Since further we abbreviated:

$$\frac{d(x\chi_i)}{dx} = \sigma_i$$

it finally follows that:

$$\begin{aligned} \frac{\Delta}{T_0} \frac{q}{kT_0} - \frac{\Delta^2}{T_0^2} \left(\frac{c_p - c_p'}{2k} - \frac{q}{kT_0} \right) &= \\ &= -\log \left(1 - \sum_1^i c_i \right) - \frac{\varepsilon^2 x}{6DkT} \sum_1^i v_0 n_i z_i^2 \sigma_i \end{aligned}$$

If Loschmidt's number is designated by N ,

$$Nq = Q$$

the heat of fusion of one mole,

$$Nk = R$$

the gas constant, and:

$$Nc_p = C_p \text{ e.g. } Nc_p' = C_p'$$

the specific heat per mole of the liquid and solid solvent, respectively, so that we can also write:

$$\left. \begin{aligned} \frac{\Delta}{T_0} \frac{Q}{RT_0} - \frac{\Delta^2}{T_0^2} \left(\frac{C_p - C_p'}{2R} - \frac{Q}{RT_0} \right) &= \\ &= -\log \left(1 - \sum_1^i c_i \right) - \frac{\varepsilon^2 x}{6DkT} \sum_1^i v_0 n_i z_i^2 \sigma_i \end{aligned} \right\} \quad (34)$$

For low concentrations we can (1) neglect Δ^2/T_0^2 compared with Δ/T_0 ,
(2) put:

$$-\log \left(1 - \sum_1^i c_i \right) = \sum_1^i c_i$$

and (3) the total volume can be identified with the volume of the water, considering the number of the dissolved ions as infinitely

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small compared with the number of the water molecules. This corresponds to:

$$v_0 n_i = \frac{v_0}{V} N_i = \frac{N_i}{N_0} = \frac{N_i}{N_0 + \sum_1^s v_i N_i} = c_i$$

With these approximations, we obtain:*

$$\frac{\Delta}{T_0} \frac{Q}{RT_0} = \sum_1^s c_i \left(1 - \frac{\epsilon^2 x}{6DkT} z_i^2 \sigma_i \right) \quad (35)$$

whereas the classical formula for the same assumptions reads:

$$\frac{\Delta}{T_0} \frac{Q}{RT_0} = \sum_1^s c_i \quad (35')$$

VII. Freezing Point Depression of Diluted Solutions

The characteristics of the electric effect of the ions are particularly clear in the limit for highly diluted solutions as expressed in equation (35). We shall therefore treat the laws for this limiting case separately. The formula (35) applies to the general case of a mixture of several electrolytes which, moreover, may be only partially dissociated into ions. We consider the special case of one type of molecule in solution. The molecule be completely dissociated into ions, and consist of s types of ions, numbered $1, \dots, i, \dots, s$, so that:

$$\nu_1, \dots, \nu_i, \dots, \nu_s$$

ions of the type $1, \dots, i, \dots, s$ constitute the molecule. If the charges associated with each of these ions are:

$$z_1 \epsilon, \dots, z_i \epsilon, \dots, z_s \epsilon$$

(For H_2SO_4 , dissociated into the ions H and SO_4 , for instance,

$$\nu_1 = 2, \nu_2 = 1, z_1 = +1, z_2 = -2$$

*It is not necessary to distinguish between ions and neutral molecules; if both are present, we imply have to put $z_i = 0$ for the latter. If all separate particles are neutral, then, naturally, equations (35) and (35') become identical.

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provided subscript 1 refers to the H ions and subscript 2 to the SO₄ ions.)

Since the molecule as a unit carries no charge, we have:

$$\sum_1^i \nu_i z_i = 0$$

The solution thus consists of N_0 molecules of the solvent and N molecules of the added electrolyte, where N may be considered small compared with N_0 . Then:

$$c_i = \frac{N_i}{N_0 + \sum_1^i N_i} = \frac{N_i}{N_0}$$

If we take into account that:

$$N_i = \nu_i N$$

and designate by c the concentration referred to the dissolved type of molecule so that, in the approximation here used,

$$c = \frac{N}{N_0}$$

then:

$$c_i = \nu_i c$$

Equation (35) for the freezing point depression then becomes:

$$\frac{\Delta}{T_0} \frac{Q}{RT_0} = f_0 \sum c_i = f_0 c \sum \nu_i \quad (36)$$

where:

$$f_0 = 1 - \frac{\epsilon^2 \kappa}{6 D k T} \frac{\sum \nu_i z_i^2 \sigma_i}{\sum \nu_i} \quad (37)$$

The quantity f_0 is the osmotic coefficient mentioned in the introduction, since $f_0 = 1$ represents the transition to classical theory as indicated by equation (35'). If Δ_k designates the freezing point depression calculated in accordance with classical theory, then:

$$\frac{\Delta}{\Delta_k} = f_0$$

or:

$$1 - f_0 = \frac{\Delta_k - \Delta}{\Delta_k}$$

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Relation (37) indicates qualitatively that the actual freezing point depression should be smaller than that expected from classical theory, a result which is consistently confirmed for diluted electrolytic solutions. The quantities κ and s which appear in equation (37) are determined by formulas (22) and (33) (the latter one with associated table). As explained in the preceding paragraph, σ_i is a measure for the effect of the finite size of the ions which disappears for very small concentrations, since σ then approaches unity. Therefore, if we first consider the limiting laws valid for highly diluted solutions, we have for this limiting case:

$$f_0 = 1 - \frac{\epsilon^2 \kappa}{6 D k T} \frac{\sum v_i z_i^2}{\sum v_i} \quad (38)$$

Further, from equation (22):

$$\kappa^2 = \frac{4 \pi \epsilon^2}{D k T} \sum n_i z_i^2$$

and since:

$$n_i = v_i \frac{N}{V} = v_i n$$

introducing the volume concentration, n , of the dissolved molecules, we have:

$$\kappa^2 = \frac{4 \pi n \epsilon^2}{D k T} \sum v_i z_i^2$$

It follows that for very low concentrations:

$$f_0 = 1 - \frac{\epsilon^2}{6 D k T} \sqrt{\frac{4 \pi \epsilon^2}{D k T} n \sum v_i \left(\frac{\sum v_i z_i^2}{\sum v_i} \right)^{3/2}} \quad (38')$$

where $n \sum v_i$ designates the number of total ions per cubic centimeter in the solution, and:

$$w = \left(\frac{\sum v_i z_i^2}{\sum v_i} \right)^{3/2} \quad (39)$$

shall be called the "valency factor," since it measures the effect of the valencies, z_i , on the phenomena. It is best not to consider f_0 , but its deviation from unity, and thus to write for very low concentrations:

$$1 - f_0 = w \frac{\epsilon^2}{6 D k T} \sqrt{\frac{4 \pi \epsilon^2}{D k T} n \sum v_i} \quad (40)$$

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First, this formula expresses the dependence of $1 - f_0$ on concentration, stating in this regard:

Law No. 1

For all electrolytes and in the limit for small concentrations, the percentage deviation of the freezing point depression from its classical value is proportional to the square root of the concentration.

It is possible to state this law as a general law, because, in highly diluted solutions, all electrolytes can be considered as completely dissociated into ions. However, the region of complete dissociation is, in practice, only reached by strong electrolytes.

Second, equation (39) makes a statement on the effect of the valencies of the ions which may be formulated as follows:

Law No. 2

If the dissolved molecule dissociates into $\nu_1, \nu_2, \dots, \nu_s$ different ions $1, \dots, i, \dots, s$ with the valencies $z_1, \dots, z_i, \dots, z_s$, then, for low concentrations, the percentage deviation of the freezing point depression from its classical value is proportional to a valency factor, w , which can be computed from:

$$w = \left(\frac{\sum \nu_i z_i^2}{\sum \nu_i} \right)^{3/2}$$

As an example for the calculation of this valency factor Table II is presented, where the type of the salt is determined by the example given in the left column, and the value of w is given in the right column:

Table II

Type	Valency factor, w
<i>KCl</i>	$1 \cdot 1$
<i>CaCl</i> ₂	$2 \sqrt{2} = 2.83$
<i>CuSO</i> ₄	$4 \sqrt{4} = 8$
<i>AlCl</i> ₃	$3 \sqrt{3} = 5.20$
<i>Al</i> ₂ (<i>SO</i> ₄) ₃	$6 \sqrt{6} = 16.6$

Thus the influence of the ions increases considerably with increasing valency which also is in accordance with the qualitative prediction.

Third, the solvent also has an effect in keeping with the well known suggestion by Nernst intended to explain the ionizing force of solvent with high dielectric constant. According to equation (40), we have:

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Law No. 3

For low concentrations the percentage deviation of the freezing point depression from the classical value is inversely proportional to the 3/2th power of the dielectric constant of the solvent.

The other constants appearing in equation (40) are the elementary charge $e = 4.77 \times 10^{-10}$ e.s.u., Boltzmann's constant $k = 1.346 \times 10^{-16}$ erg, and the temperature, T , which latter is present explicitly and implicitly, since the dielectric constant, D , varies with T .

If we deal with diluted solutions in the conventional sense, σ can no longer be replaced by unity, and equation (37) applies, which reads explicitly:

$$1 - f_0 = w \frac{e^2}{6DkT} \sqrt{\frac{4\pi e^2}{DkT} \frac{\sum v_i z_i^2 \sigma_i}{\sum v_i z_i^2}} \quad (41)$$

As shown by Table I, as well as by the formula (33) from which the table is derived, σ_i continuously decreases with increasing concentration and finally decreases as:

$$\frac{3}{x_i^2} = \frac{3}{\kappa^2 a_i^2}$$

i.e., inversely proportional to the concentration, since κ is proportional to the square root of this quantity. According to (41) the deviation $1 - f_0$ increases proportional to the square root of the concentration for very small concentrations, then, for higher concentrations, in view of the effect of σ , i.e., in view of the finite diameter of the ions, the deviation will reach a maximum, and finally decrease inversely proportionally to the square root of the concentration. Even though this statement contains an extrapolation to higher concentrations of equation (41) which is not entirely justified, it seems to describe the behavior of concentrated solutions (compare section IX). In fact, measurements show a maximum of $1 - f_0$ as a characteristic of the curves for the freezing point depression. However, we believe that the phenomenon of hydration (compare the last section) also contributes considerably to the formation of the maximum. A numerical comparison of theory and experiments will be given in section IX.

VIII. Dissociation Equilibrium

Not limiting our considerations to strong electrolytes only, a dissociation equilibrium will exist between undissociated molecules and ions. However, the equilibrium is not to be computed by means of the classical formula, because also in this instance the

mutual electric forces have a disturbing influence. How this can be taken into consideration in accordance with our theory shall now be computed. We start again with the expression (29) for the thermodynamic potential Φ of the solution:

$$\Phi = \sum_0^s N_i (\varphi_i - k \log c_i) + \sum_1^s N_i \frac{z_i^2 \epsilon^2}{3D} \frac{\kappa}{T} \chi_i$$

some of the particles present in the solution will carry an electric charge, while others will be electrically neutral. For the latter, we will have simply $z_i = 0$. The solvent shall be indicated by the subscript 0. We now undertake, in a well-known procedure, the variation of the numbers N_i , and calculate the associated changes in the potential. This leads to:

$$\begin{aligned} \delta\Phi &= \sum_{i=0}^{i=s} \delta N_i (\varphi_i - k \log c_i) + \sum_{i=1}^{i=s} \delta N_i \frac{z_i^2 \epsilon^2}{3DT} \kappa \chi_i \\ &+ \sum_{i=1}^{i=s} N_i \frac{z_i^2 \epsilon^2}{3DT} \frac{d(\kappa \chi_i)}{d\kappa} \sum_{j=1}^{j=s} \frac{\partial \kappa}{\partial N_j} \delta N_j \end{aligned}$$

If it is taken into account that, according to the defining equation (22):

$$\kappa^2 = \frac{4\pi\epsilon^2}{DkT} \sum_{l=1}^{l=s} n_l z_l^2 = \frac{4\pi\epsilon^2}{DkT} \sum_{l=1}^{l=s} \frac{N_l z_l^2}{V}$$

the quantity κ may depend on all numbers $N_1 \dots N_s$. If in the third sum the indices of summation, i and j , are interchanged, $\delta\Phi$ may be written in the form:

$$\delta\Phi = \delta N_0 (\varphi_0 - k \log c_0) + \sum_{i=1}^{i=s} \delta N_i \left[\varphi_i - k \log c_i + \frac{\epsilon^2}{3DT} \left(z_i^2 \kappa \chi_i + \sum_{j=1}^{j=s} N_j z_j^2 \frac{d(\kappa \chi_j)}{d\kappa} \frac{\partial \kappa}{\partial N_i} \right) \right]$$

However, $\partial \kappa / \partial N_i$ can be calculated from the definition of κ . We obtain, provided the linear relation regarding the volume is retained,

$$\frac{\partial \kappa}{\partial N_i} = \frac{\kappa}{2 \sum_1^s n_l z_l^2} \cdot \frac{z_i^2 - v_i \sum_1^s n_l z_l^2}{V}$$

If the conventional assumption is made that a chemical reaction may take place in the solution, where the proportions:

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$$\begin{aligned} \delta N_1: \delta N_2: \dots: \delta N_i: \dots: \delta N_s = \\ = \mu_1: \mu_2: \dots: \mu_i: \dots: \mu_s \end{aligned}$$

hold, the condition of equilibrium follows from the expression

$$\sum_{i=1}^{i=s} \mu_i \log c_i = \sum_{i=1}^{i=s} \frac{\mu_i \varphi_i}{k} + \frac{\varepsilon^2 z}{6DkT} \sum_{i=1}^{i=s} \left\{ 2\mu_i z_i^2 \chi_i + \mu_i (z_i^2 - v_i \frac{\sum_{j=1}^{j=s} n_j z_j^2}{\sum_{j=1}^{j=s} n_j z_j^2}) \frac{d(x\chi_i)}{dx} \right\} \quad (42)$$

for the variation of the potential. This condition is distinguished from the classical condition by the additional term on the righthand side. If the activity coefficient f_a is introduced, as was done in the introduction, by putting:

$$\sum_{i=1}^s \mu_i \log c_i = \log (f_a K)$$

where K represents the classical constant of equilibrium, the activity coefficient is defined by the relation:

$$\log f_a = \frac{\varepsilon^2 z}{6DkT} \sum_{i=1}^{i=s} \left\{ 2\mu_i z_i^2 \chi_i + \mu_i (z_i^2 - v_i \frac{\sum_{j=1}^{j=s} n_j z_j^2}{\sum_{j=1}^{j=s} n_j z_j^2}) \frac{d(x\chi_i)}{dx} \right\} \quad (43)$$

According to this formula it is, of course, possible to provide a special activity coefficient for each atom or molecule taking part in the reaction by putting:

$$\begin{aligned} \log f_a = \mu_1 \log f_a^1 + \dots \\ \mu_i \log f_a^i + \dots \mu_s \log f_a^s \end{aligned} \quad (44)$$

with:

$$\log f_a^i = \frac{\varepsilon^2 z}{6DkT} \left\{ 2 z_i^2 \chi_i + (z_i^2 - v_i \frac{\sum_{j=1}^{j=s} n_j z_j^2}{\sum_{j=1}^{j=s} n_j z_j^2}) \frac{d(x\chi_i)}{dx} \right\} \quad (44')$$

Then, however, as equation (44') indicates by the appearance of κ , this coefficient referred to a definite type of molecule does not solely depend on quantities which are related to this type of atom.

Here again simplifications are possible by limitation to lower concentrations. In this case:

$$v_i \sum_{j=1}^s n_j z_j^2$$

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is negligible compared with z_i^2 ; if this is done, the volume of the dissolved substance is considered negligible compared with the total volume. Thus:

$$\log f_a^i = \frac{\epsilon^2 \kappa}{6DkT} z_i^2 \left\{ 2\chi_i + \frac{\sum_1^i n_j z_j^2 \frac{d\chi_j}{dx}}{\sum_1^i n_j z_j^2} \right\} \quad (45)$$

Finally we can find the limiting value of the activity coefficient for increasingly diluted solutions. In this limit, where the effect due to the dimension of the ion vanishes, we can put $\kappa = 1$, and obtain:

$$\log f_a^i = \frac{\epsilon^2 \kappa}{2DkT} z_i^2 \quad (45')$$

Since κ depends on the properties of all ions (is affected by their valency), the special coefficient f_a^i is, not even in this limiting case, exclusively a function of the properties of the i th ion. We shall not discuss this limiting law in detail, and only observe that here again in the limit proportionality exists between $\log f_a$ and the square root of the concentration.

**IX. Comparison of Freezing Point Depression
with Experimental Results**

Figure 2 is a representation of the characteristic behavior of

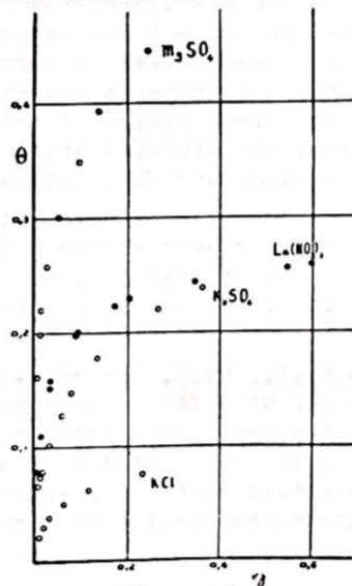


Figure 2

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strong electrolytes. A magnitude $\nu\gamma$ which measures the ion concentration is plotted on the horizontal axis, where γ , as indicated before, designates the concentration of the electrolyte in moles per liter,* while $\nu = \sum v_i$ represents the number of ions into which the molecule of the salt dissociates. Four representatives KCl , K_2SO_4 , $\text{La}(\text{NO}_3)_3$ and MgSO_4 were chosen from four types differing in the valencies of their ions. KCl dissociates into two univalent ions, K_2SO_4 in two univalent and one bivalent ion, $\text{La}(\text{NO}_3)_3$ in three univalent and one trivalent ion, and MgSO_4 in two bivalent ions. If we designate the freezing point depression expected from classical theory for complete dissociation with Δ_k , and the observed freezing point depression with Δ , the expression:

$$\theta = \frac{\Delta_k - \Delta}{\Delta_k} \quad (46)$$

i.e., the percentage deviation from the classical value was found and plotted as ordinate. According to section VII we can also put:

$$\theta = 1 - f_0 \quad (46')$$

thus represented, θ measures the deviation of the osmotic coefficient from its limiting value 1. Since in a solution with water as solvent:

$$\Delta_k = \nu\gamma \cdot 1.860^\circ \quad (47)$$

a point on the abscissa corresponds, for all electrolytes, to a concentration which should produce the same freezing point depression provided the mutual forces are disregarded. We plotted the observed values and omitted to connect corresponding points by a curve in order to avoid any preconceived interpretation. This method, however, is possible only because recent and excellent measurements by American research workers of the freezing point depression at low concentrations are available. The measurements in Figure 2 are taken from Adams and Hall and Harkins.⁹

It is evident that the deviation θ does not increase for low concentrations with the first or even higher powers of the concentration as required by the law of mass action. Further the curve demonstrates the strong effect of the ion valency.

*For the salts K_2SO_4 , $\text{La}(\text{NO}_3)_3$, MgSO_4 the concentration γ' in moles per 1000 g. water is substituted for γ , as given by the authors cited below, since in the absence of density measurements for these salt solutions at 273° , a conversion to moles per liter could not be carried out; this means only an insignificant deviation for the low concentrations considered here.

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Our theory requires that, for very low concentrations, the percentage deviation Θ be proportional to the square root of the concentration and that the factor of proportionality depend strongly on the valency of the ions. According to equations (39) and (40) we have (assuming the molecule dissociates into $\nu_1 \dots \nu_i \dots \nu_s$ ions with the valencies $z_1 \dots z_i \dots z_s$):

$$\Theta = 1 - f_0 = w \frac{\epsilon^2}{6DkT} \sqrt{\frac{4\pi\epsilon^2}{DkT} n \sum \nu_i} \quad (48)$$

with the valency factor:

$$w = \left(\frac{\sum \nu_i z_i^2}{\sum \nu_i} \right)^{3/2} \quad (49)$$

First we want to express the number of ions n per cc. as the concentration γ measured in moles per liter. We take the value 6.06×10^{23} for Loschmidt's number; then:

$$n = 6.06 \cdot 10^{20} \gamma$$

It is further assumed that $\epsilon = 4.77 \times 10^{-10}$ e. s. u., $k = 1.346 \times 10^{-16}$ erg, and since the following deals with the freezing point depression of solutions having water as a solvent, $T = 273$. The dielectric constant of water is calculated from the interpolation formula⁹ given by Drude. We find for $0^\circ\text{C}.$:

$$D = 88.23$$

Using these figures, we get (with $\sum \nu_i = \nu$):

$$\sqrt{\frac{4\pi\epsilon^2}{DkT} n \nu} = 0.231 \cdot 10^8 \sqrt{\nu \gamma} \frac{1}{\text{cm}}$$

and hence:

$$\Theta = 0.270 w \sqrt{\nu \gamma} \quad (50)$$

Our quantity κ becomes with the above numerical values:

$$\kappa = 0.231 \cdot 10^8 \sqrt{\nu \gamma} \sqrt{\frac{\sum \nu_i z_i^2}{\nu}} \frac{1}{\text{cm}} \quad (51)$$

In Figure 3 observed values¹⁰ of Θ have been plotted against a new abscissa $\sqrt{\nu \gamma}$, the experimental points have been interconnected by straight lines. Further, four straight lines starting at the origin are presented, which illustrate the limiting law expressed

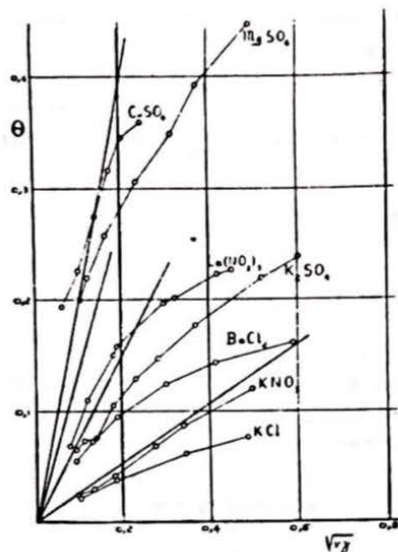


Figure 3

by equation (50). The four types of salts in the figure have the valency factors:

$$w = 1, w = 2\sqrt{2}, w = 3\sqrt{3}, w = 8$$

the straight lines correspond to these values. It will be seen that for low concentrations the straight lines are actually approximated, so that, apparently, the limiting law involving the square root of the concentration corresponds to the facts. Further the absolute values of the slope - computed by means of the dielectric constant equal to 88.23, and distinguished theoretically only by the valency factor (as expressed in equation (50) by the factor $0.270 w$) - are confirmed by experiment. However, Figure 3 indicates that early deviations from the limiting law take place. This is in agreement with the considerations in section III and equation (51), according to which, even for uni-univalent electrolytes, the characteristic length $1/\kappa$ is of the order of magnitude of the ion diameter already for $\gamma = 1$, so that it is no longer permissible to neglect it. We have further based our theory on the simplified version, equation (21'), of the potential equation. This also may have some effect. However, we pointed out (see footnote on page 227) that this latter effect is theoretically comparatively insignificant. The experimental results also indicate that the deviations from the limiting law are caused by the individual properties of

the ions. To show this, we present Figure 4. Here observations

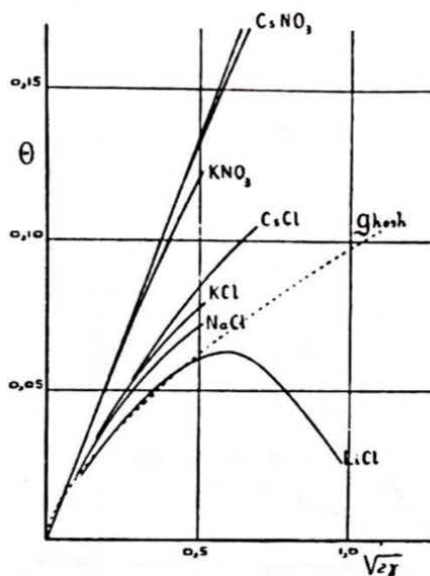


Figure 4

of uni-univalent ions, exclusively, are entered* as a function of $\sqrt{z\gamma}$ (since, here, $\nu = 2$). The straight line represents the limiting law discussed above; all curves approach this line for low concentrations. The deviations vary greatly in magnitude, and, it should be noted, are in the order Cs, K, Na, Li for the salts of chlorine. This is the same order as is obtained if the alkali ions are arranged according to decreasing mobility, an order which is in contradiction with the assumed dimension of the ions, and which was correlated only recently by Born¹¹ with the relaxation time of water for electric polarization following from dipole theory. To afford orientation with regard to the work by Ghosh, the curve for θ , as evaluated by this theory, is given in the figure by a dashed line. It should be valid for all salts, and, moreover, has a vertical tangent at the origin.

*Besides the measurements already cited, we used here measurements by H. Jahn, *Z. phys. Chem.*, 50, 129 (1905); 59, 31 (1907) (LiCl, CsCl); E. W. Washburn and MacInnes, *J. Am. Chem. Soc.*, 33, 1686 (1911) (LiCl, CsNO₃); W. H. Harkins and W. A. Roberts, *ibid.*, 38, 2658 (1916) (NaCl) (concentration partly in moles per liter, partly moles per 1000 g. water).

The question now is: to what extent can our theory, improved with regard to the ion dimensions, account for the individual deviations. The conditions are illustrated in Figure 5. We have

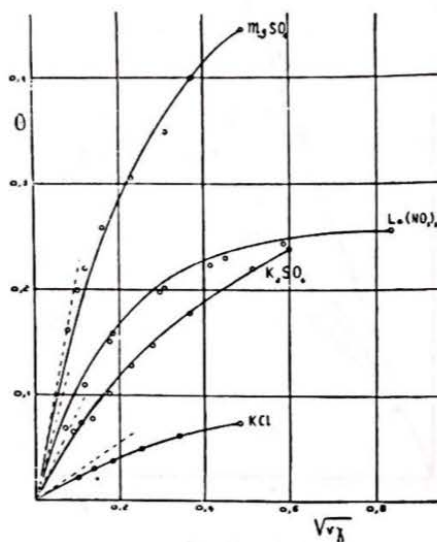


Figure 5

again chosen the four electrolytes of the four types previously mentioned, and plotted the observed values of Θ as a function of $\sqrt{v\gamma}$. According to equation (41) we obtain, taking into account the dimensions of the ions (upon introduction of the numerical values):

$$\Theta = 1 - f_0 = 0.270 w \sqrt{v\gamma} \frac{\sum v_i z_i^2 \sigma_i}{\sum v_i z_i^2} \quad (52)$$

where σ_i designates the function of the argument $x_i = \kappa a_i$ tabulated in Table I and given by formula (33), and where a_i denotes the length which measures the size of the i th ion with respect to its surroundings. At the present state of affairs, it did not appear advisable to us to study the separate ion dimensions, but to calculate with an average diameter a equal for all ions of one electrolyte. Then all σ_i become equal, and the expression:

$$\Theta = 0.270 w \sqrt{v\gamma} \sigma(\kappa a) \quad (53)$$

is obtained for Θ . For the determination of the magnitude of a , we chose, for the time, only one observed value, the one corresponding to the highest concentration, and then plotted the curve-

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resulting from the theoretical formula (53) with the a thus obtained-in the figure. Four dashed straight lines radiating from the origin (tangents to the curves) represent the limiting law (50) for strongly diluted solutions. Agreement with the observations is very good, particularly in view of the determination of constants from a single observed value.* The figure is supplemented by the following tables:

Table III.
KCl ($a = 3.76 \times 10^{-8}$ cm)

2γ	$\sqrt{2\gamma}$	Θ observed	Θ calculated
0.0100	0.100	0.0214	0.0237
0.0193	0.139	0.0295	0.0313
0.0331	0.182	0.0375	0.0392
0.0633	0.252	0.0485	0.0499
0.116	0.341	0.0613	0.0618
0.234	0.484	0.0758	---

In each first column is entered the ion concentration $v\gamma$, in the second column the value of the abscissa $\sqrt{v\gamma}$ in Figure 5, in

*The method for the determination of a is explained in detail for $\text{La}(\text{NO}_3)_3$ as an example. For $\gamma' = 0.17486$, $\Theta' = 0.2547$ was observed; since $v = 4$, the abscissa becomes $(v\gamma')^{\frac{1}{2}} = 0.836$. According to the limiting law (50) for extreme dilution, we would obtain with $\omega = 3\sqrt{3}$ (corresponding to equation 49 for $v_1 = 1$, $v_2 = 3$, $z_1 = 3$, $z_2 = -1$) a value of $\Theta = 1.173$, the actually observed value is obtained from this limiting value by multiplication with 0.216. According to equation (53) this factor is equal to σ . From Figure 1 we find that an abscissa $x = \kappa a = 1.67$ belongs to the ordinate $\sigma = 0.216$; further from equation (51) by substituting $\sqrt{v\gamma'} = 0.836$, the value of $\kappa = 0.336 \times 10^{-8} \text{ cm}^{-1}$. Consequently, a diameter

$$a = x/\kappa = 4.97 \times 10^{-8} \text{ cm.}$$

corresponds to the observed data.

(For the salts K_2SO_4 , $\text{La}(\text{NO}_3)_3$, MgSO_4 , the concentration γ' is given in moles per 1000 g. water and used for the determination of Θ which is, therefore, designated by Θ' . For the low concentrations considered here, the resulting deviations are very small; a conversion of γ' to γ would not give a noticeable change in the values for Θ' observed, Θ' calculated, and a .)

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Table IV.

K_2SO_4 ($a = 2.69 \times 10^{-8}$ cm)

$3\gamma'$	$\sqrt{3\gamma'}$	θ observed	θ calculated
0.00722	0.0906	0.0647	0.0612
0.0121	0.110	0.0729	0.0724
0.0185	0.136	0.0776	0.0871
0.0312	0.176	0.101	0.108
0.0527	0.229	0.128	0.132
0.0782	0.280	0.147	0.152
0.136	0.369	0.178	0.183
0.267	0.516	0.220	0.217
0.361	0.600	0.238	---

Table V.

$La(NO_3)_3$ ($a = 4.97 \times 10^{-8}$ cm)

$4\gamma'$	$\sqrt{4\gamma'}$	θ observed	θ calculated
0.00528	0.0728	0.0684	0.0828
0.0142	0.119	0.110	0.121
0.0322	0.179	0.151	0.157
0.0343	0.185	0.158	0.161
0.0889	0.298	0.197	0.204
0.0944	0.308	0.201	0.207
0.173	0.418	0.223	0.230
0.205	0.453	0.229	0.235
0.346	0.588	0.243	0.248
0.599	0.836	0.255	---

Table VI.

$MgSO_4$ ($a = 3.35 \times 10^{-8}$ cm)

$2\gamma'$	$\sqrt{2\gamma'}$	θ observed	θ calculated
0.00640	0.0800	0.160	0.147
0.0107	0.103	0.199	0.179
0.0149	0.122	0.220	0.203
0.0262	0.162	0.258	0.248
0.0534	0.231	0.306	0.311
0.0976	0.312	0.349	0.368
0.138	0.372	0.392	0.400
0.242	0.493	0.445	---

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the third column the observed value of Θ ,* and in the fourth column the value of the same quantity computed from equations (53) and (51). The figure corresponding to the highest concentration is not entered here, since from it, in each instance, the average diameter a , given in the title of the tables, was computed.

Finally, in Figure 6, is given a representation of the theory

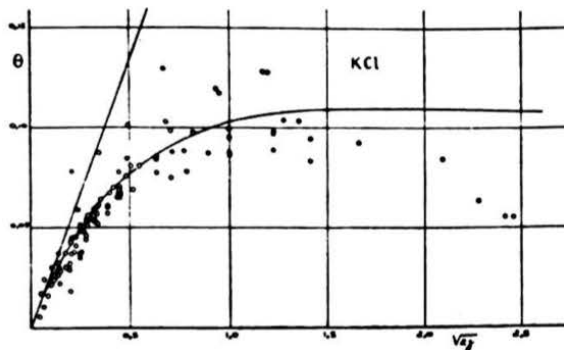


Figure 6

and observation of KCl solutions with water as solvent. In discussing this figure, it is our principal intention to present a few indications regarding the behavior of concentrated solutions; incidentally, we intend to show how large the discrepancies are between the separate results given in the literature in spite of high accuracy claimed by the individual observers. For this purpose the figure contains all observations on KCl solutions since 1900 that we found.¹² As abscissa is chosen, as before, $\sqrt{2\gamma}$, where γ denotes, according to our definition, the concentration in moles per liter solution. All information referring to concentrations measured differently, is here calculated for these concentrations by means of the measured densities¹³ of KCl solutions. The ordinate is again designated by Θ , it does not, however, exactly represent the previous expression:

$$\frac{\Delta_k - \Delta}{\Delta_k}$$

In fact, not even the classical theory prescribes proportionality between freezing point depression and concentration for concentrated solutions. First, this is so because $\log(1-c)$ and not the concentration itself appears in the classical equation. Second, the difference between the thermodynamic potentials of ice and water is no longer given with sufficient accuracy by the first

*See previous footnote.

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term of the Taylor expansion, proportional to Δ , the second term, involving Δ^2 , must be retained. Accordingly, in this instance, we have to use the complete equation (34). For KCl we have $n_1 = n_2 = n$ and $z_1 = z_2 = 1$, further we shall again replace the two ion diameters a_1 and a_2 by an average value a . Then equation 34 may be rearranged as follows:

$$\frac{1}{2nv_0} \left[\frac{\Delta Q}{T_0 RT_0} - \frac{\Delta}{T_0^2} \left(\frac{C_p - C_p'}{2R} - \frac{Q}{RT_0} \right) + \log(1 - 2c) \right] = -\frac{\epsilon^2 x}{6DkT} \sigma \quad (54)$$

The term on the left-hand side was now computed for different concentrations. For this purpose $C_p - C_p'$ was put equal to 3.6, corresponding to an approximate value for $C_p' = 14.4$, extrapolated from Nernst's measurements¹⁴ of the specific heat of ice at 273°. It is further required for the computation to know the relation between the molar concentration c and the volume concentration γ . By means of the observed density of the solution, this relation can be readily given, however, here as well as in the derivation of the equation, the molecular weight of water has a certain effect. Though this effect vanishes in the first approximation, it can not be eliminated from the second-order terms. Inasmuch as the effect is of second order only, its influence is considerably reduced; we have, therefore, used the simple molecular weight 18, throughout. Finally the quantity $2nv_0$ in the denominator can be put equal to:

$$2nv_0 = 2\Omega_0 \frac{\gamma}{1000}$$

where Ω_0 designates the molar volume of water. Provided no mutual electric effect of the ions was present, the left-hand term should give zero for substitution of the observed freezing point depression. Actually it gives a finite value, and we designate this finite value by $-\Theta$. Then, according to the theory, this difference Θ must be represented by the right-hand term so that:

$$\Theta = \frac{\epsilon^2 x}{6DkT} \sigma(xa) = 0.270 \sqrt{2\gamma} \sigma(xa) \quad (55)$$

should hold. It can be ascertained that the definition for Θ obeyed here is, in the limit, identical with the one given above for low concentrations.

The points entered in the figure have the ordinates calculated from the observations in the manner indicated. The curve in the figure represents the right-hand term of equation (55), under the assumption that $a = 3.76 \times 10^{-8}$ cm. This value of a was determined from one observation by Adams, according to which the experimental value $\Theta = 0.0758$ is associated with $\gamma = 0.117$. The straight line which is also given in the figure again represents

the limiting law for extreme dilution corresponding to $\sigma = 1$. It may be stated that, up to concentrations of approximately one mole per liter, the observations are well represented by the curve. For higher concentrations, the observations show a maximum for Θ . The theoretical curve also has a maximum; this is so flat, however, that it is hardly indicated, as shown by the figure. We are inclined to consider this discrepancy at high concentrations as factual, and wish to present a few pertinent remarks in the next section.

X. General Remarks

From the preceding discussion it may be concluded that it is inadmissible from a theoretical as well as from an experimental point of view to consider the electric energy of an ionic solution to be essentially determined by the average mutual distance of the ions. Rather, a quantity which measures the thickness of the ion atmosphere or, to connect with something known better, the thickness of a Helmholtz double-layer proves to be a characteristic length. In view of the fact that this thickness depends on the concentration of the electrolyte, the electric energy of the solution also becomes a function of this quantity. The fact that this thickness is inversely proportional to the square root of the concentration is responsible for the characteristic appearance of the limiting laws for highly diluted solutions. Though we must decline to talk in terms of a lattice structure of the electrolyte in the conventional sense, and though, as shown by the development of the subject, taking this image too literally leads to inadmissible mistakes, it still contains a grain of truth. To make this clear, the following two imaginary experiments are carried out. First, we take an element of space, and consider it placed, repeatedly, at arbitrary positions in the electrolyte. It is clear that, in a binary electrolyte, we shall find therein positive and negative ions with equal frequency. Second, we take the same spatial element, and again place it repeatedly in the electrolyte, now not arbitrarily, but always such that it is, for instance, located at a definite distance (of several angstrom units) from an arbitrarily selected positive ion. Now we shall not find positive and negative charges with equal frequency, the negative charges will prevail in number. In that the oppositely charged ions, on the average, prevail in number in the immediate surroundings of each ion, we can see, correctly, an analogy to the crystal structure of the NaCl type, where each Na ion is immediately surrounded by 6 Cl ions and each Cl ion by 6 Na ions. However, it is to be considered an essential characteristic of the electrolytic solution that the measure for this order is determined by the thermal equilibrium between attracting forces and temperature movement, while it is definitely predetermined for the crystal.

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The computations and comparison with experience were carried out by taking the conventional dielectric constant for the surrounding solvent. The success justifies this assumption. Though this procedure is justifiable for low concentrations, it should cause mistakes for higher concentrations. In fact, it follows from dipole theory that for high field intensities, dielectrics must show saturation phenomena similar to the known magnetic saturation. The recent experiments by Herweg¹⁵ may be taken as an experimental confirmation of this theoretical requirement. Since at a distance of 10^{-7} cm. from a singly charged ion, a field intensity of approximately 200,000 volt/cm. is to be expected, we should be prepared to observe something of these saturation phenomena. It would, of course, be very interesting if an attempt to separate this effect in its consequences from the observations were successful, the more so that nature puts at our disposal field intensities of a magnitude hardly attainable otherwise with conventional experimental means.

In another respect concentrated solutions should show a special behavior. If many ions are present in the surroundings of each single ion, this can be regarded as a change of the surrounding medium with respect to its electrical properties, an effect which has not been taken into account in the preceding theory. The manner in which this may become effective may be indicated by the following considerations. Let us consider one fixed ion and another mobile ion, oppositely charged, and investigate the amount of work required to remove the mobile ion. This work may be regarded as composed of two parts: (1) the ion will require a certain amount of work for its removal, and (2) we shall gain work by filling the space, previously taken up by the ion, with solvent. Experiments concerning the heat of dilution actually provide an indication of the existence of such conditions. Let us take, for example, a HNO_3 solution of initially low concentration and dilute it with a large quantity of water (i.e., so much that further dilution would not cause any heat effect), cooling will take place, i.e., work must be done in the sense of the previous considerations to separate the ions from one another. If the initial solution has a higher concentration, then, in the same experiment, heat is generated, i.e., work is obtained, if the surrounding of each ion is freed of a sufficient number of other ions which are replaced by water molecules. In conventional language, it is said that a predominant hydration of the ions occurs, and that this is to be regarded as an exothermic process. Obviously the above considerations intend an explanation of this so-called hydration on a purely electric basis. In fact an approximate computation can be carried through which gives theoretically Berthelot's rule, valid in this connection for the dependence of the heat of dilution from the initial concentration, and which makes plausible the order of magnitude of the experimentally determined numerical coefficient of this rule. These considerations have some bearing on the freezing point

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observations inasmuch as they suggest the possibility of computing why and to what extent the curves found for the percentage deviation Θ (compare the case of KCl) bend downward for higher concentrations and may even cross the abscissa provided the concentration is high enough. In this instance, the freezing point depression exceeds the one expected from classical theory (also, as may be stated explicitly, if the classical theory is used in its unabbreviated form). Until now, one has been resigned, in such cases, to talk about hydration.

However, before conditions for concentrated solutions can be investigated, it must be shown that the irreversible process of electric conduction in strong electrolytes can also be understood quantitatively from our point of view. We reserve the detailed presentation of this subject for a future article. Here only the basic ideas, which will be discussed more thoroughly in that paper, may be indicated. If an ion moving in a liquid is subjected to the influence of an external field, the surrounding ions will have to move constantly in order to form the ion atmosphere. If we now assume for a moment that a charge is suddenly generated in the electrolyte, an ion atmosphere will have to appear which requires a certain time of relaxation for its formation. Similarly, for a moving ion, the surrounding atmosphere will not attain its equilibrium distribution and thus cannot be computed on the basis of the Boltzmann-Maxwell principle. However, the determination of its charge distribution can be carried through on the basis of an obvious interpretation of the equations for the Brownian movement. It can be estimated qualitatively in which direction this effect, caused by the presence of a finite relaxation time, will be operative. At a point in front of the moving ion (i.e., a point toward which it moves) the electric density of the ion atmosphere must increase with time; it must decrease for a point behind the ion. As a consequence of the relaxation time, the density in front of the ion will be slightly smaller than its value at equilibrium; behind it, however, it will not yet have decreased to its equilibrium value. Consequently, during the movement there always exists a slightly larger electrical density of the ion atmosphere behind the ion than in front of it. Since charge density in the atmosphere and charge of the central ion always carry opposite signs, a force braking the ion movement will occur, independent of its sign, and obviously this force will increase with increasing concentration.

This is one effect which operates in the same sense as a decrease in dissociation calculated on the basis of Ostwald's dilution law. However, still another effect is present which must be taken into consideration. In the vicinity of an ion are predominantly ions of the opposite sign, which under the influence of the external field will, of course, move in the opposite direction. These ions will, to a certain degree, drag along the surrounding solvent, thus causing the considered single ion not to

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move relative to a stationary solvent but relative to a solvent moving in the opposite direction. Since, apparently, this effect increases with increasing concentration, we have a second effect operating in the same sense as a decrease in dissociation. The effect can be calculated quantitatively according to the principles used by Helmholtz for the treatment of electrophoresis.

The common factor of the two effects just mentioned consists, as is shown by the computations, in the fact that both are closely related to the thickness of the ion atmosphere, and that, therefore, the generated forces are proportional to the square root of the concentration of the electrolyte, at least in the limit for very low concentrations. Thus we obtain a law, found by Kohlrausch¹⁶ according to which for low concentrations the percentage deviation of the molecular conductivity from its limiting value at infinite dilution is proportional to the square root of the concentration. Also the proportionality factor thus finds a molecular interpretation.

Anticipating the detailed representation of electrolytic conductivity in prospect for a following article, we can state as an over-all result that the view, according to which strong electrolytes are completely dissociated, is entirely supported.

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