

‘The theory of electrolytes. I. Freezing point depression and related phenomena’ (Debye & Hückel, 1923)

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Translator's Preface

This document is an English translation and complete typesetting of one of the seminal papers 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 the original German or in English, because there exists an extant English translation found in the collected papers of Debye. That translation was published in 1954 by Interscience Publishers, New York, and reprinted in 1988 after acquisition of the copyright by Ox Bow Press, Woodbridge, CT. The 1954 translation was completed by an unknown translator, and that document unfortunately contained several typesetting errors of inconsistent mathematical symbols, somewhat outdated language, and unclear terminology. For example, v and ν are similar but represent different variables, and the definition of v was somewhat nebulous. In the case of \varkappa , κ , x , and χ , their similarities caused confusion but are now more clearly distinguishable in this edition.

Briefly, x and κ were uncannily similar in the German edition and later made inconsistent in the English edition, which was an unacceptable typesetting error. In fact, an earlier version of this translation mistook \varkappa for x and x for χ , which has been corrected. Fortunately, the κ symbol carried forward in the literature, and it is the most easily distinguishable from \varkappa , x , and χ . The figure below depicts the symbols used in the original German publication (left) and the 1954 English translation (right). Readers will notice in the English edition that the lower-case kappa symbol is typeset in the fixed-width print font in the body's text but typeset in the cursive font in the indented equations.

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

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

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

$$A\psi = \chi^2 \psi. \quad (12)$$

Die somit eingeführte Länge

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

ist die wesentliche Größe unserer Theorie und ersetzt die mittlere Entfernung der Ionen in der von uns abgelehnten Ghosh'schen 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

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

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

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:

$$\chi^2 = \frac{8\pi n \epsilon^2}{DkT} \quad (11)$$

so that χ is the reciprocal of a length, and equation (10') becomes:

$$A\psi = \chi^2 \psi \quad (12)$$

The length, introduced in this way:

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

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 ,

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

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

The use of \varkappa 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⁾

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

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

$$\varkappa^2 = \frac{4\pi \varepsilon^2}{DkT} \sum_{i=1}^s n_i z_i^2. \quad (9)$$

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.

It is my sincere wish that further confusion can be avoided, and this publication has been paired with a detailed summary and guide to understanding each section or theorem. 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 italicized German term has been provided adjacent to its translation in square brackets, which became especially 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 from 1923, 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, 2020

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Frontmatter

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ORIGINAL COMMUNICATION

The theory of electrolytes. [*Zur Theorie der Elektrolyte.*]

1. Freezing point depression and related phenomena [*I. Gefrierpunktserniedrigung und verwandte Erscheinungen.*]

By P. Debye and E. Hückel¹.

¹The 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 on it in the winter of 1921 in the local colloquium. Under the active assistance of my assistant Dr. E. Hückel, the detailed discussion of the results and their summary took place in the winter of 1922. - P. Debye

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. If we let, for instance, P_k be osmotic pressure, which results from van't Hoff's classical law for perfect dissociation, then the actual osmotic pressure observed is smaller, such that

$$P = f_o P_k,$$

in agreement with Bjerrum², 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 of 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

²N. Bjerrum, Zeischr. f. Elektrochemie 24, 231, 1918.

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 are³. 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 angle⁴ 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. Sutherland⁵ in 1907 attempted to establish the theory of electrolytes on the assumption of complete dissociation. His work contains some good thoughts. N. Bjerrum⁶ is

³A summary of this subject was reported by L. Ebert, “Research on the anomalies of strong electrolytes (Forschungen ueber die Anomalien starker Electrolyte),” Jahrb. Rad. u. Elektr. 18, 134, 1921.

⁴See Fig. 2.

⁵W. Sutherland, Phil. Mag. 14, 1, 1907.

⁶Proceedings of the seventh international congress of applied chemistry, London May 27th to June 2nd, 1909, Section X: A

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 into 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 Milner⁷. 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. Ghosh⁸. 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

new form for the electrolytic dissociation theory.

⁷Milner, Phil. Mag. 23, 551, 1912; 25, 743, 1913.

⁸J. Ch. Ghosh, Chem. Soc. Journ. 113, 449, 627, 707, 790, 1918; Zeitschr. f. phys. Chem. 98, 211, 1921.

the ions with respect to their mobility. An attempt in this direction comes from P. Hertz⁹. 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 Bjerrum¹⁰ 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 coefficient¹¹ 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. Corresponding to the form in which the terms based on the mutual

⁹P. Hertz, Ann. d. Phys. (4) 37, 1, 1912.

¹⁰N. Bjerrum, I.c. und Zeitschr. f anorgan. Chem. 109, 275, 1920.

¹¹The 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.)

electric effects will appear, we consider the quantity¹²

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

(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

¹²The 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.

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 opportunity¹³ 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

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

¹³See note 25.

signify the numbers of individual particles in the solution, and N_o should refer specifically to the solvent¹⁴. Next is the thermodynamic potential referring to the single particle

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

is 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. Ghosh¹⁵ proceeds in this way. This approach, however, is fundamentally wrong, and the entire theory built upon it (practically characterized by the introduction

¹⁴Our 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.

¹⁵See note 8.

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 dilutions¹⁶, 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.

¹⁶It will be shown below that this assumption is true.

¹⁷The 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).

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 ($4.77 \cdot 10^{-10}$ 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,

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

positive and

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

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

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

so ψ can be determined as the equation's solution

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

The further one moves away from the specified ion, the smaller will be the potential ψ , and for larger distance the sufficient approximation $\text{Sin}^{\frac{\varepsilon\psi}{kT}}$ can replace $\frac{\varepsilon\psi}{kT}$. If one does that, equation (10) takes on the much simpler form¹⁸

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

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

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

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

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

The length introduced as

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

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 ,

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

for water at $0^\circ C$. 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

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

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

¹⁸We have also investigated the influence of the following terms in the development of $\text{Sin}^{\frac{\varepsilon\psi}{kT}}$ 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.

given potential is

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

According to this formula, $\frac{1}{\kappa}$ signifies the length at which the electrical density of the ionic atmosphere decreases to the e th part. Our characteristic length $\frac{1}{\kappa}$ 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 solvent¹⁹.

Now that the meaning of the length $\frac{1}{\kappa}$ 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

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

and this equation has the general solution

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

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

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

¹⁹The 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.

and the desired potential will be:

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

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

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

the potential energy u , which contains the specified ion $+\varepsilon$ relative to its surroundings, is therefore²⁰

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

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 $-\frac{\varepsilon}{D} \kappa$ relative to its surroundings, and N negative ions with a potential difference of $+\frac{\varepsilon}{D} \kappa$ are added, then the desired potential energy²¹

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

At the same time, κ 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 $\frac{1}{\kappa}$ 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

²⁰Apart 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

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

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

²¹Because 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.

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

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

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

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

consequently

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

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

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

As the comparison with equation (15) shows, the effect of the ion size is represented by the factor $1/(1 + \kappa a)$ only. For low concentrations (n small) κ is also small following equation (11), and the energy approaches the value given above for infinitely small ions. For large concentrations (κ large), on the other hand, u gradually approaches the quantity

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

such that the importance of our characteristic length $\frac{1}{\kappa}$ 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

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

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 valances 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 $\frac{1}{\kappa^2}$ is to be defined by the equation²²

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

while the equation for potential maintains its former form

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

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

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

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

²²Because, for monovalent salts, $n_1 = n_2 = n$ and $z_1 = z_2 = 1$, the general equation (22) for κ^2 agrees with the earlier one (see equation (11)) given for this special case.

ion sphere becomes

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

while the constants A and B are

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

The given value of B corresponds to the potential energy

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

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

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

The inverse length κ 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

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

²³By 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.

where D is considered to be temperature-independent²⁴, and then use κ as the integration variable, not T . So the result is

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

If one applies the abbreviation

$$\kappa a_i = x_i,$$

one finds that

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

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 κ in equation (22) is proportional to $\sqrt{\sum n_i z_i^2}$, $\kappa = 0$ corresponds to the case of infinite dilution. Accordingly, the constant in the curly brace must be determined such that for $x_i = 0$ 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

$$\int \frac{\kappa^2 d\kappa}{1 + \kappa a} = \frac{1}{a_i^3} \left\{ \frac{3}{2} + \log(1 + x_i) - 2(1 + x_i) + \frac{1}{2}(1 + x_i)^2 \right\}$$

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

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

²⁴In 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.

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 κ^2 , our addition to the thermodynamic potential can be reduced to the form²⁵

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

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

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

is explicitly repeated again here.

For small concentrations, therefore, in G_e , each ion has a contribution proportional to κ , 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

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

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

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

²⁵The 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.

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

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

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

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

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 κ , 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

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

according to this equation of definition one therefore finds

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

and our condition for equilibrium takes the form:

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

The function for concentration characterizing the effects in question

$$\frac{d(\kappa \chi_i)}{d\kappa}$$

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

$$x_i = \kappa a_i$$

to

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

For small values of x_i , the expansion is

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

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 $x = \kappa a$; 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

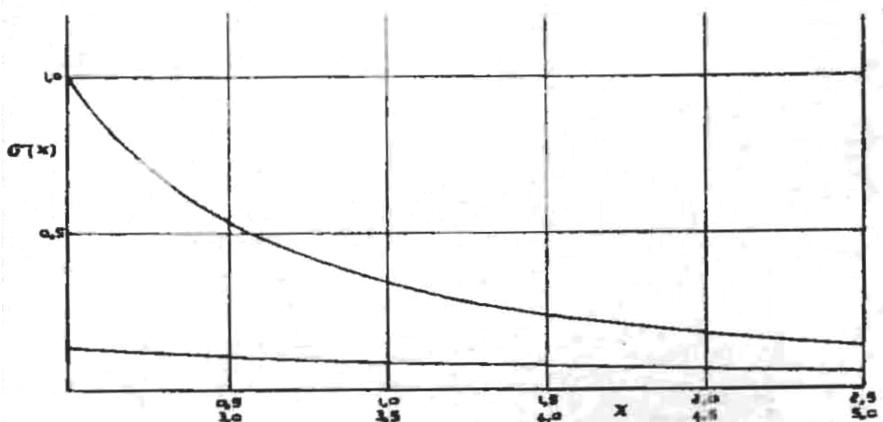


Fig. 1.

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

$$\frac{d(\kappa\chi_i)}{d\kappa} = \sigma_i$$

it finally follows that

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

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

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

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

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

With these approximations you find²⁶

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

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

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

²⁶There 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.

ions of the species $1, \dots, i, \dots, s$ 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

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

with

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

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 κ 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 very large dilutions, then in the limiting case we find

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

On the other hand, according to equation (22)

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

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

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

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 concentra-

tion, 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, ...i, ...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

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

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 * 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 $\varepsilon = 4.77 * 10^{-10}$ e.s.u., Boltmann's constant $k = 1.346 * 10^{-16}$ 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

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

i.e. inversely proportional to the concentration, because κ 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

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

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

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

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

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

the quantity κ 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:

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

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

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

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

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

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

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

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

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

with

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

Then, however, as shown by equation (44') by the appearance of κ , 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,

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

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

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

Because κ 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 liter²⁷, 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 Harkins²⁸.

It is evident that the deviation Θ does not increase, as the law of mass action would

²⁷For 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.

²⁸L.H. Adams, Journ. Amer. Chem. Soc. 37, 481, 1915 (KCl); L.E. Hall u. W.D. Harkins, ibid. 38, 1658, 1916 (K_2SO_4 , $La(NO_3)_3$, $MgSO_4$).

require, for small concentrations proportional to the first or even a higher power of the concentration.

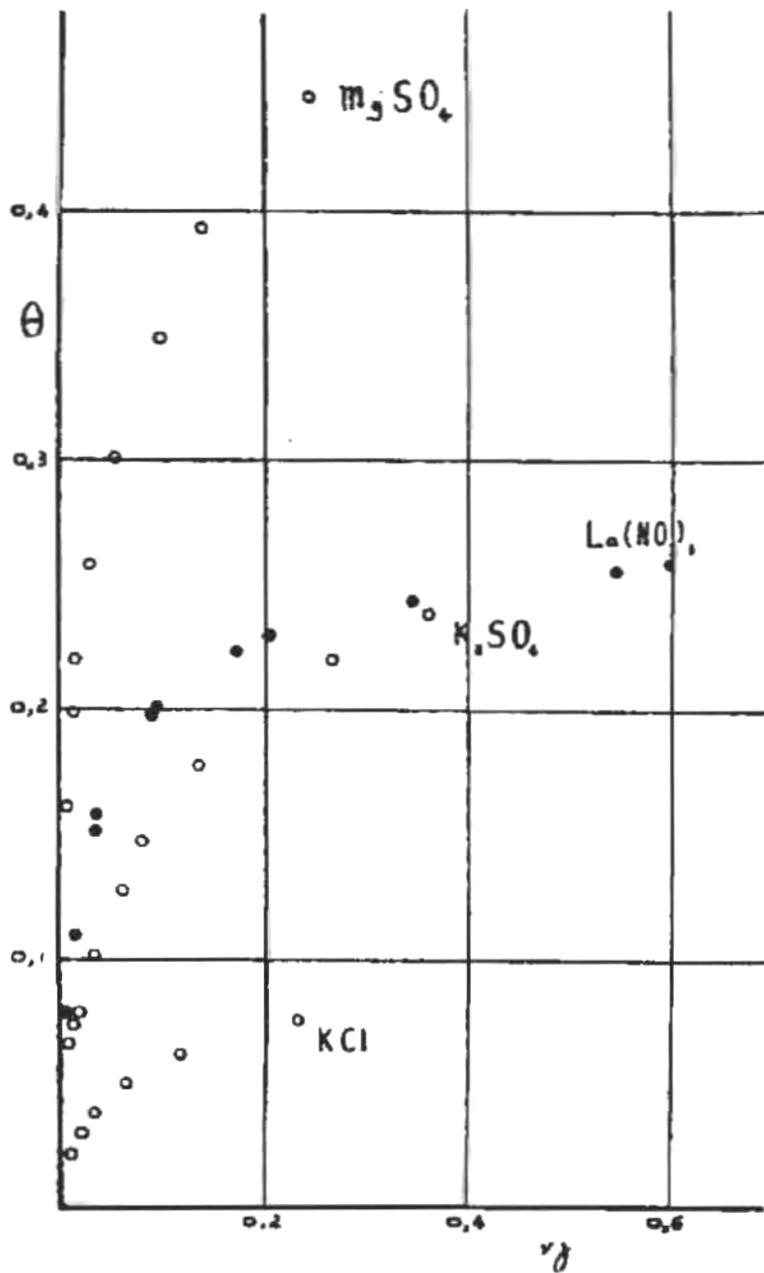


Fig. 2.

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 $\varepsilon = 4.77 * 10^{-10}$ electrostatic units, $k = 1.346 * 10^{-16}$ 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 which²⁹, for $0^\circ C$,

$$D = 88.23 .$$

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 κ becomes, using the above numerical values,

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

In Fig. 3, observed values³⁰ of Θ were plotted against the abscissa $\sqrt{\nu \gamma}$, and the observed points have been connected by straight lines.

²⁹Ann. d. Phys. 59, 61, 1896.

³⁰L. 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 , $La(NO_3)_3$].

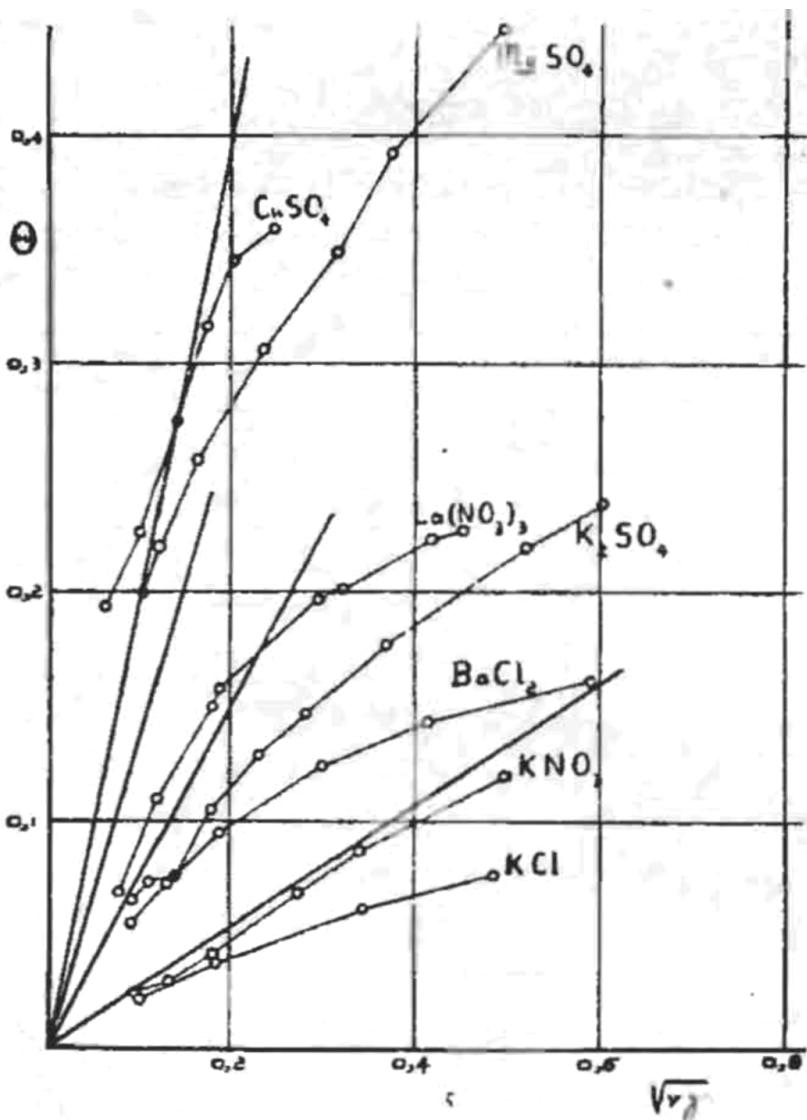


Fig. 3.

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 $1/\kappa$ 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.

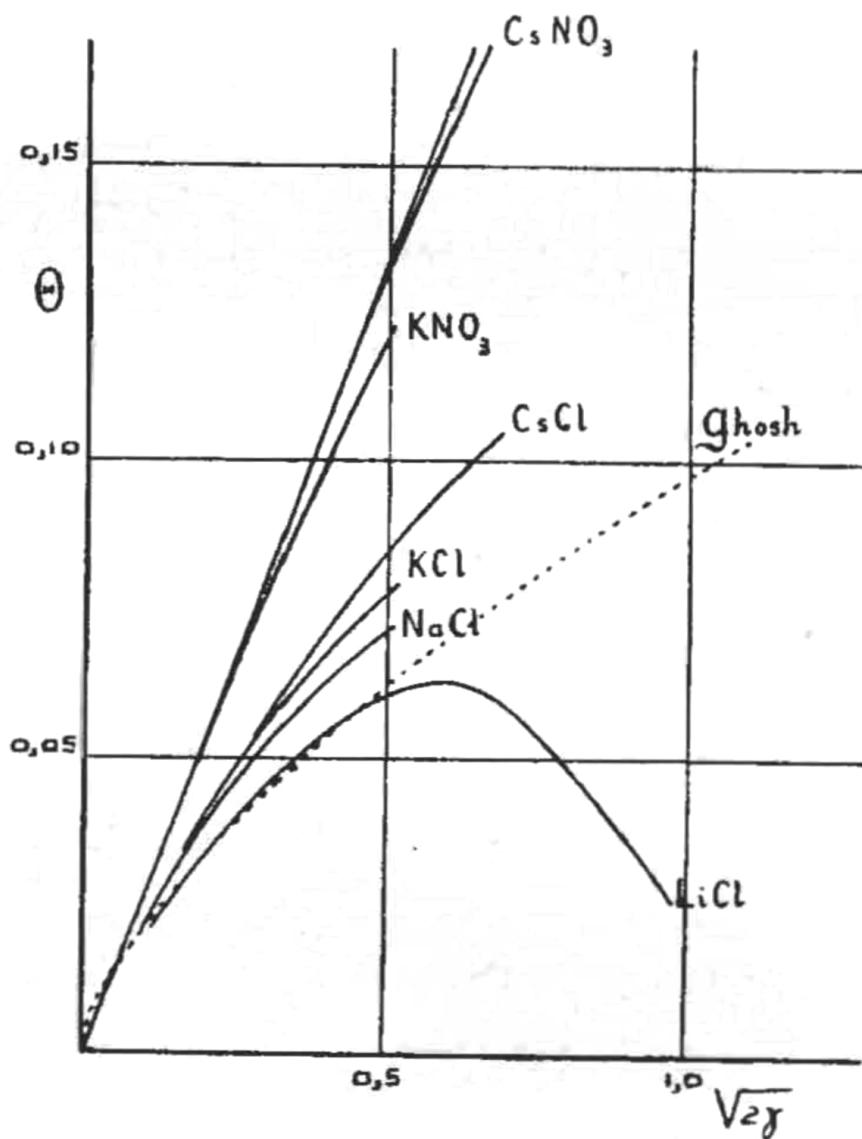


Fig. 4.

These observations are entered only for uni-univalent salts³¹ 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 Born³², 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),

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

where σ_i represents the formula of the argument $x_i = \kappa a_i$ 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

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

³¹In 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*, *CsNO₃*); 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].

³²M. Born, Zeitschr. f. Phys. 1, 221, 1920.

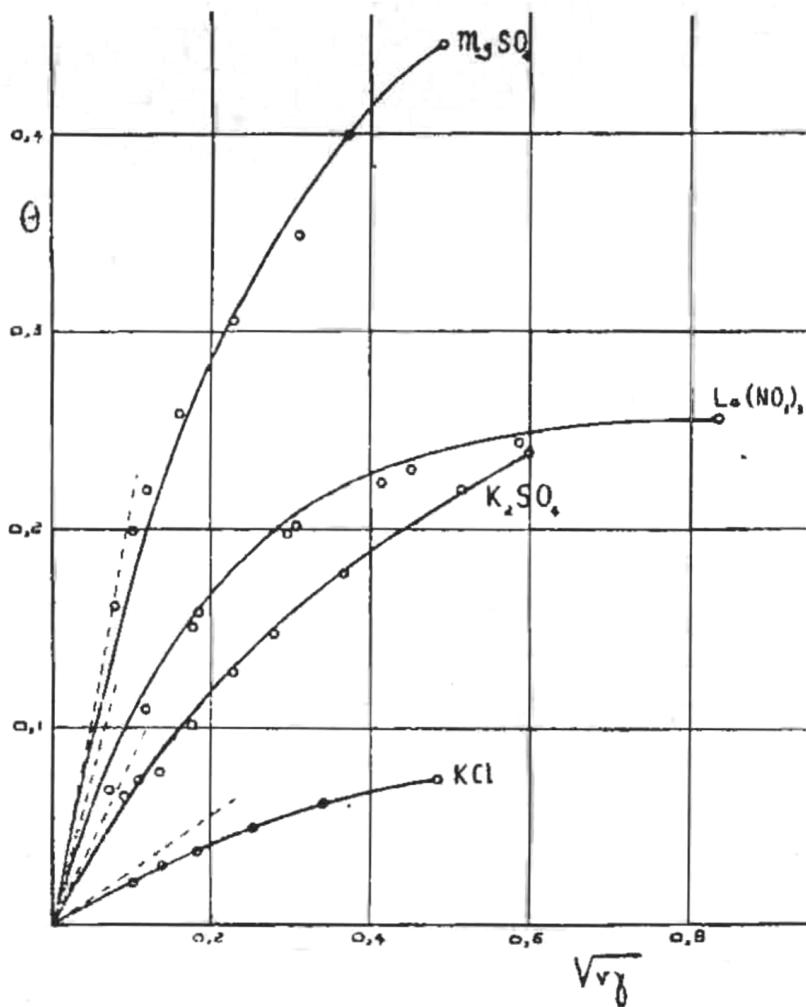


Fig. 5.

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 point³³. The figure

³³The 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 $\nu_1 = 1$, $\nu_2 = 3$, $z_1 = 3$, $z_2 = -1$ 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 $x = \kappa a = 1.67$; on the other hand, according to equation (51), $\sqrt{\nu\gamma'} = 0.836$ is the value of $\kappa = 0.336 * 10^{-8} \text{ cm}^{-1}$. So the observed value is the diameter

$$a = \frac{x}{\kappa} = 4.97 * 10^{-8} \text{ cm.}$$

[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

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	---

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	---

yielded.]

In the first column, the respective ion concentration³⁴ $\nu\gamma$, 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 1900³⁵.

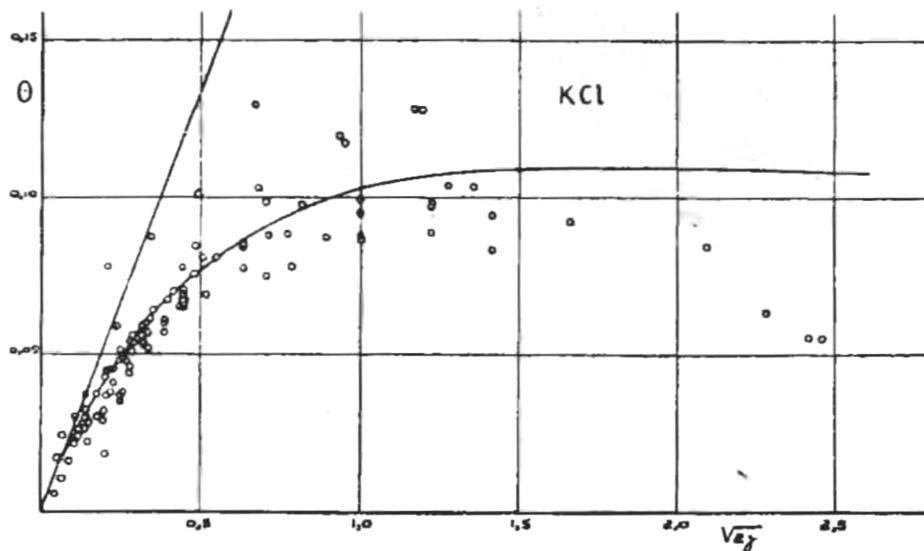


Fig. 6.

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 densities³⁶ 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

³⁴See the previous note.

³⁵J. 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, 1.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.

³⁶Baxter u. Wallace, Journ. Americ. Chem. Soc. 38, 18, 1916.

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

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

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 measurements³⁷ 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

$$\Theta = \frac{\varepsilon^2 \kappa}{6Dkt} \sigma(\kappa a) = 0.270 \sqrt{2\gamma} \sigma(\kappa a) \quad (55)$$

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 $\Theta = 0.0758$ per-

³⁷W. Nernst, Berl. Ber. 1910, 1, 262.

tains 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, 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 Herweg³⁸ 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

³⁸Zeischr. f. Phys. 3, 36, 1920 and 8, 1, 1922.

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 Kohlrauch³⁹, 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.

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³⁹F. Kohlrausch u. L. Holborn, *The Conductivity of Electrolytes*, 2nd ed., Leipzig 1916, p. 108 and 112.