THE INTERIONIC ATTRACTION THEORY OF ELECTRICAL CONDUCTANCE

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I. INTRODUCTION AND DEFINITIONS

The nature of solutions is unquestionably one of the main objects of modern chemistry. It has been customary to define a solution in terms of its concentration. However, it is now a familiar fact that when it is necessary to investigate chemical equilibria such a definition will suffice only when the solutions in question are of such dilution that the ideal gas laws may be utilized to describe the properties of the dissolved substance. For representing deviations from the ideal state the conception of the thermodynamic function called the activity, first defined by G. N. Lewis (1), has proven to be of great importance. It has proven to be of particular value in the study of the marked deviations from ideality which occur in aqueous solutions of strong electrolytes. The idea as developed empirically by Lewis led to the hypothesis (2) that "In dilute solutions of electrolytes the activity coefficient of an ion depends only on the total ionic strength of the solution," the ionic strength of a solution being defined by the expression

$$I = \frac{1}{2} \Sigma c_i z_i^2 \qquad (1)$$

where I = ionic strength.
c_i = concentration in moles per 1000 grams of water.
z_i = valence.

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Brönsted (3) showed, also in an empirical manner, that in the region of sufficiently dilute solutions, in which the behavior of the electrolyte was determined only by its valence type, that in the case of a uni-univalent salt its activity could be expressed by the relation

$$\log f = -3\,\alpha \sqrt{\gamma} \tag{2}$$

where α = constant dependent on the temperature.
γ = concentration in moles per liter of solution.

In short, the change of the activity coefficient of the ions with concentration in highly dissociated solutions can be represented by a square root law. Equation 2 has more recently been written in a general form which is valid for any valence ion, as follows:

$$\log f = -3\,\alpha\, z_i^2 \sqrt{I} \tag{2a}$$

In the limiting case, therefore, the activity coefficient depends only upon the square root of the ionic strength and the valence of the ion in question.

The interionic attraction theory of activity, first developed by Milner (4), and later in simpler form by Debye and Hückel and by Debye (5), gives an adequate theoretical explanation of these empirical laws, based on the fact that the thickness of the ionic atmosphere of mean charge surrounding each ion has to be proportional to the square root of the concentration, if the principal forces between ions are the ordinary Coulomb forces.

However, it is not the purpose of this article to treat the activity problem;[3] rather it is its purpose to show in the first part how these fundamental ideas have been applied by Debye and his co-workers to show that the square-root law, found experimentally by Kohlrausch, is the correct one to explain the change in electrical conductance of dilute solutions of electrolytes with

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[3] The activity problem has been the subject of a number of reviews. The following articles may be mentioned in this connection:

Brönsted: Trans. Faraday Soc. Symposium on Strong Electrolytes, April, 1927.
Hückel: Ergebnisse d. exakt. Naturwiss. III, 199 (1924).
LaMer: Trans. Am. Electrochem. Soc. **41**, 507 (1927).
Noyes: J. Am. Chem. Soc. **46**, 1080, 1098 (1924).

concentration, and in the second part, to show how these ideas have led to the prediction of an electrical conductance which is dependent on the frequency used to measure it.

Definitions

In treating the quantitative problem of the electrical conductance of solutions of strong electrolytes it is necessary to define carefully a number of quantities. For the elementary quantities (in electrostatic units), specific conductance, molar conductance, and equivalent conductance the symbols, λ, Λ, and Λ^*, respectively, will be used. Further, the molecular concentration and equivalent concentration are given by the symbols γ and γ^*, respectively. According to the familiar definitions of physical chemistry,

$$\Lambda = \frac{1000\,\lambda}{\gamma};\ \Lambda^* = \frac{1000\,\lambda}{\gamma^*} \tag{3}$$

Also,

$$\gamma = \gamma^*_{.}m \tag{4}$$

where m is the valence factor defined for a given ion by the relation

$$m = \nu_i\, z_i$$

where ν_i is the number of ions formed from one molecule.

Therefore the relation between molar conductance and equivalent conductance is

$$\Lambda^* = \frac{\Lambda}{m} \tag{5}$$

It is customary in physical chemistry to use the practical system of units, i.e., for $\bar{\Lambda}$ the unit OHM^{-1} CM^2. In this article the quantities which are given in practical units are designated by a bar over the symbol which represents the quantity in question, thus

$$\bar{\Lambda} = \frac{\Lambda}{9 \times 10^{11}} \tag{6}$$

The mobility of an ion of the i^{th} kind will be designated by the symbol $\overline{L}_i$. If a molecule is dissociated into ions of the number $\nu_1 \ldots \nu_i \ldots \nu_s$, of charge $e_1 \ldots e_i \ldots e_s$, with valences $z_1 \ldots z_i \ldots z_s$ and friction coefficients $\rho_1 \ldots \rho_i \ldots \rho_s$, then the molecular conductance at infinite dilution is written

$$\overline{\Lambda}_\infty = \Sigma\, \nu_i\, \overline{L}_i \tag{7}$$

where $\overline{L}_i = \dfrac{N\epsilon^2}{9 \times 10^{11}} \cdot \dfrac{z_i^2}{\rho_i}$

$N = 6.06 \times 10^{23}$

$\epsilon = 4.774 \times 10^{-10}$ e.s.u.

Between the mobilities, $\overline{L}_i$ and the friction coefficients, ρ_i there exists the relation

$$\overline{L}_i = \frac{15.34}{\rho_i}\, z_i^2 \times 10^{-8} \tag{8}$$

The mobilities, $\overline{L}_i$, used in this article are related to the mobilities usually found in tables of physical constants, $\bar{l}_i$, by the simple relation

$$\overline{L}_i = z_i\, l_i \tag{9}$$

Further, the ionic strength to be used in this article is the one defined by Bjerrum rather than the Lewis quantity referred to above. This ionic strength is given by the equation

$$I^1 = \Sigma\, \gamma_i\, z_i^2 \tag{10}$$

A purely arbitrary method of referring to electrolytes of the various valence types has been adopted. Those electrolytes which give two different kinds of ions are called *simple* electrolytes. The simple electrolytes are further subdivided into *symmetrical* and *unsymmetrical* electrolytes depending on whether the ions formed have equal or unequal valences. Thus an electrolyte of the type 1–1 or 2–2 is said to be symmetrical, while one of the type 1–2 or 2–3 is unsymmetrical.

II. THE LIMITING LAW OF THE ELECTRICAL CONDUCTANCE OF SOLUTIONS OF STRONG ELECTROLYTES. STATIONARY CASE

As the fundamental ideas underlying the treatment of the conductance problem are the same as those mentioned for the treatment of the activity problem, it is well to consider them in some detail at this point. In the first place Coulomb's law as used here, i.e., to measure the forces between the ions, states that these forces are inversely proportional to the square of the distance between them. As a result of the presence of these Coulomb forces a completely random distribution of ions in an electrolyte solution is impossible. The probability that two oppositely charged ions will come near to each other is greater than the probability that like charged ions will find themselves in the same position. To describe these deviations from a random arrangement of ions the conception of an "ionic atmosphere" has been introduced. This ionic atmosphere may be conveniently described in terms of two of its characteristic properties, 1, its thickness and 2, its time of relaxation.

1. Thickness, $\frac{1}{\kappa}$

If a straight line of length r, is considered with a given ion attached to one end and an element of volume at the other, it is found that sometimes there is an excess of positive and at other times an excess of negative electricity in the element of volume. The time integral of this charge divided by the time of observation gives its mean charge. The density of the ionic atmosphere is the mean charge divided by the volume of the element. The density in the ionic atmosphere is of opposite sign to the charge carried by the ion, and decreases as the length r is increased. It is possible to show that the significant factor in representing this decrease in density with distance is the exponential $e^{-\kappa r}$, where κ has the dimension of a reciprocal length and is given by the formula

$$\kappa^2 = \frac{4\pi}{DkT} \Sigma n_i e_i^2 \tag{11}$$

Where D = dielectric constant of the solvent
k = Boltzmann's constant = 1.372×10^{-16} erg/degree.
T = absolute temperature
N_i = number of ions of the i^{th} kind in 1 cc.
e_i = charge on ion of the i^{th} kind.

The order of magnitude of κ in centimeters is

$$\frac{1}{\kappa} = \frac{10^{-8}}{\sqrt{\gamma}} \text{ cm.} \tag{12}$$

where γ is the concentration in moles per liter. It is further suggested by table 1 which gives the values of the thickness $\frac{1}{\kappa}$ in centimeters for γ = 0.001 in water at 18°C.

TABLE 1

TYPE OF ELECTROLYTE	THICKNESS
	cm.
1-1	96.6×10^{-8}
1-2	55.9×10^{-8}
2-2	48.3×10^{-8}
1-3	39.5×10^{-8}
1-4	30.7×10^{-8}
2-4	27.8×10^{-8}

The characteristic dependence of the thickness on the concentration $\gamma^{\frac{1}{2}}$, is explanation for the fact of the proportionality of the change of the logarithm of the activity coefficient with the square root of the concentration and therefore with the square root of the ionic strength, the latter containing both a concentration and valence term. As will be seen it is also explanation for the law of conductance found by Kohlrausch.

2. Time of relaxation, θ

The influence of this property of the ionic atmosphere is extremely important in the consideration of the irreversible process of conduction. The ionic atmosphere can neither be destroyed nor created in an infinitely small period of time. If an ion is suddenly separated from the solution, the regularity in its neighborhood will cease to exist because it owes its presence only to the force field of the central ion. The transfer to the regular orientation with reference to the point where the ion was will take place gradually. The time necessary for this change is the time of relaxation, and is dependent on a number of factors. It is dependent on the quantities which characterize the thickness of the ionic atmosphere, also it is dependent on the mobility of the ions. Its order of magnitude in seconds has been shown to be

$$\theta = \frac{10^{-10}}{\gamma} \text{ seconds} \qquad (13)$$

TABLE 2

ELECTROLYTE	TIME OF RELAXATION	CORRESPONDING WAVE LENGTHS
	seconds	*meters*
KCl	0.553×10^{-7}	16.6
HCl	$.189 \times 10^{-7}$	5.67
$MgCl_2$	$.324 \times 10^{-7}$	9.72
$CdSO_4$	$.315 \times 10^{-7}$	9.45
$LaCl_3$	$.162 \times 10^{-7}$	4.86

The values of θ for $\gamma = 0.001$ in water at 18°C. for several electrolytes are given in table 2. There have also been included in this table corresponding wave lengths whose significance will be recognized in Part III.

In the following pages it will be shown that the dissymmetry of the ionic atmosphere caused by this time of relaxation, though small, is sufficient to cause an additional (resisting) force on an ion as it passes through the solution. This force is appreciable because of the relatively large value of the charge carried by an ion.

According to present views electrical conductance in solutions of electrolytes is explained in the following manner. Due to the influence of the outer electric field each ion, because of its charge, is subjected to a force. This force gives to the ion a velocity which is proportional to this force. Its velocity is also dependent upon the forces which resist the passage of the ions through the solution, namely, the frictional forces; but these may be neglected for the moment. At this point we shall consider only the velocity which the ion assumes under the influence of the outer electric field at infinite dilution. The resulting electrical force E_i is proportional to this field-strength because otherwise Ohm's law would not be obeyed. If $z_i\epsilon$ is the charge of the ion and X the outer field-strength then

$$E_i = z\,\epsilon\,X = \rho_i\,v_{i_\infty} \tag{14}$$

where ρ_i specifies that outer electric force which gives to the ion a velocity of 1 cm. per second, and $\rho_i\,v_{i\infty}$ is a measure of the resisting forces which the ion meets when it moves with the velocity $v_{i\infty}$ under the influence of the outer field strength X.

At finite concentrations equation 14 is no longer strictly obeyed, since it fails to take into account the forces of relaxation and electrophoresis which are about to be discussed. The absolute value of the velocity which an ion has under the influence of a unit outer field is called its mobility, u_i. This mobility u_i is related to the mobility $\bar{l}_i$ in the following manner:

$$\bar{u}_i = \tfrac{1}{300}\,u_i$$

$$\bar{l}_i = 96{,}500\,\bar{u}_i.$$

$$u_i = \frac{|v_i|}{X} \text{ (absolute electrostatic units)} \tag{15}$$

The connection between electrical field-strength and current density follows directly. If a molecule of the salt is dissociated on solution into ions $\nu_1 \ldots \nu_i \ldots \nu_s$, with valences $z_1 \ldots z_i \ldots z_s$, number present per cubic centimeter $n_1 \ldots n_i \ldots n_s$, and quantities $\rho_1 \ldots \rho_i \ldots \rho_s$, which measure the resisting forces of the passage of the ions, then the current density j (current strength per square centimeter cross-section) is given by the expression

$$\begin{aligned} j &= \epsilon\,\Sigma\,n_i\,z_i\,v_i \\ &= \epsilon\,\Sigma\,n_i\,|\,z_i\,|\,u_i\,X \end{aligned} \tag{16}$$

The specific conductance λ is defined as the current density for unit field-strength. Therefore,

$$\lambda = \frac{j}{X} = \epsilon \Sigma n_i |z_i| u_i \tag{17}$$

From formula (17) the expression for the specific conductance at infinite dilution can now be written

$$\lambda_\infty = \epsilon^2 \Sigma \frac{n_i z_i^2}{\rho_i} \tag{17,a}$$

For finite concentrations the mobilities u_i are necessary to calculate the specific conductance, or any of the conductances derived from it, again using equation 17.

It is evident that there are two possible methods in which the change of conductance with concentration may be explained, as follows:

First, the number of ions n_i may be considered to be variable. This is the method of the classical theory in which a thermodynamic equilibrium between undissociated molecules and the dissociated ions is assumed. The method of treatment is that by which the number n_i is decreased by multiplication by a factor α, the "degree of dissociation," as the concentration increases. This is familiar as the classical theory and will not be discussed further.

Second, the conductance may change with concentration because of variations in the mobilities, u_i. This possibility involves the assumption of complete dissociation, or that the number of ions n_i is always exactly proportional to the total concentration. This assumption is the one which had to be made in the treatment of the activity problem; furthermore it is the one which is used by Debye and Hückel to explain the deviations of the proportionality between the conductance and concentration and which is used throughout the work reviewed in this article.

When an outer field-strength is applied to a solution of finite concentration each ion will no longer move with the same velocity as it did in the infinitely dilute solution because now other forces between the ions come into play, since each ion finds itself in the presence of others. In other words, the mobility u_i at finite concentration will differ from that at infinite dilution u_{i_∞}. In the first place the distribution of the ions in the solution is such that on the average in the neighborhood of an ion of given sign there are more ions of unlike than of like sign. Each ion is surrounded by an ionic atmosphere, the properties of which have been suggested above. This ionic atmosphere is built symmetrically about a stationary ion, but if the ion is caused to move through the liquid with the velocity v, the ionic atmosphere about it can no longer be symmetrical. It is true that the interionic forces tend to restore the symmetry of the ionic atmosphere, but as has been shown, this requires a definite period of time—the time of relaxation. Since the ion is moving, the symmetry of the ionic atmosphere is never completely restored; however, there will be built about each moving ion a stationary ionic atmosphere which moves with the ion to which it belongs. This ionic atmosphere will be unsymmetrical in the direction of the motion of the ion. Before the ion there will be more ions of like charge and behind it more ions of opposite charge than was the case when the ion was not moving. The electrical forces will not be able to build up the static ionic atmosphere before the ion, while a definite period of time is necessary to restore the ionic atmosphere behind it. This granted, it is evident that each moving ion, positive or negative, is subjected to a force which decreases its mobility, since bodies charged alike repel each other and bodies charged unlike attract each other. This force will be called the electrical force of relaxation in the sections to follow.

As a result of the characteristic properties of the ionic atmosphere this electrical force of relaxation is dependent on a number of circumstances. In the first place, the greater the velocity of the ion the greater the additional electrical force will be, because the ionic atmosphere will deviate more and more from that of the stationary case, at least for small velocities. If the friction constants of the ions ρ_i are larger the electrical forces of relaxation are increased because the adjustment of the ionic atmosphere is more difficult. If the temperature is decreased, the electrical forces of relaxation are again increased, again because the adjustment of the ionic atmosphere is more difficult. In short, the mobility is modified by the ionic atmosphere. Therefore, the ionic atmosphere with its characteristic thickness, which is also a function of the (ionic) concentration plays a very important part in the determination of the magnitude of this force which resists the passage of an ion (6). The problems which confronted Debye and Hückel at this point were, first, to find an expression for the space distribution of ions, taking into account its variation with time, and second, to calculate the stationary dissymmetry around an ion moving with a constant velocity v in the direction of the external field. Their solution, the details of which are given in the original article, was found in the general equations which describe the Brownian movement, and leads to the result that the passage of an ion through the solution is subjected to an additional electrical force of relaxation, E_i', in the direction opposite to its velocity,

$$E_i' = -\tfrac{1}{6}\frac{\rho\, v_i}{DkT}\,\kappa\,\epsilon^2\, z_i^2 \tag{18}$$

where the mean friction constant of the solution $\rho = \dfrac{\Sigma n_i \epsilon_i^2 \rho_i}{\Sigma n_i \epsilon_i^2}$

Thus, if only the electrical forces acting on an ion are considered the total force is the algebraic sum of the two which have been evaluated.

$$E = E_i + E_i' = z_i\,\epsilon\, X - \tfrac{1}{6}\frac{\rho\, v_i}{DkT}\,\kappa\,\epsilon^2\, z_i^2 \tag{19}$$

For a steady state of motion these electrical forces must be in equilibrium with other forces. These other forces are frictional in nature as has already been suggested in equation (14)

$$F_i = \rho_i\, v_i$$

which expresses the frictional force on the ions exerted by the impacts of the surrounding molecules. The force may also be expressed in terms of Stokes law as follows:

$$F_i = 6\,\pi\,\eta\, b_i\, v \tag{20}$$

where η is the internal friction constant of the liquid. In a solution of finite concentration the apparent frictional constant will vary from the limiting value, ρ_i, again because of the distribution of ions about the one in question. In such a solution all the positive ions are moving towards the cathode, while all the negative ions are moving in the opposite direction. But in the vicinity of a given ion there are on the average more ions of unlike than of like sign. Since the ions carry with them a certain amount of the solvent the given ion may be considered to be moving in a medium that is moving in a direction opposite to its motion rather than in a stationary medium, so that a decrease in the mobility results from this force. This effect is the simple electrophoretic effect, and is calculated in a manner similar to that utilized by Helmholtz in earlier studies of this phenomenon. The electrophoretic effect was shown by Debye and Hückel to be given by the expression

$$F_i^1 = \epsilon z_i \kappa b_i X \tag{21}$$

where b_i is the radius of the ion of the i^{th} kind.

Therefore the purely frictional forces are given by the algebraic sum

$$F = F_i + F_i^1 = \rho_i v_i + \epsilon z_i \kappa b_i X \tag{22}$$

As already indicated, for a steady state of motion the two sets of forces must be in equilibrium

Therefore,

$$E_i + E_i' = F_i + F_i',$$

That is,

$$\epsilon z_i X - \frac{1}{6} \frac{\rho v_i}{DkT} \kappa \epsilon^2 z_i^2 = \rho_i v_i + \epsilon z_i \kappa b_i X$$

or

$$v_i = \epsilon z_i X \cdot \frac{1 - \kappa b_i}{\rho_i + \frac{1}{6} \frac{\rho}{DkT} \epsilon^2 z_i^2 \kappa} \tag{23}$$

For the mobility u_i this equation may be written

$$u_i = \frac{v_i}{X} = u_{i_\infty}\left[1 - \left(\frac{1}{6}\,\frac{\rho}{\rho_i}\,\frac{\epsilon^2 z_i^2}{DkT} + b_i\right)\kappa\right] \tag{24}$$

where

$$u_{i_\infty} = \frac{\epsilon\, z_i}{\rho_i}$$

Thus, in the region of small concentration the mobility is proportional to the square root of the concentration, since the factor κ is proportional to this quantity. Thus the law found empirically by Kohlrausch is explained.

From this expression others giving the molar conductance, the equivalent conductance, and the so-called conductance coefficient of Bjerrum (7) may be written. For example, the molar conductance of a simple electrolyte in sufficiently dilute solution may be given by an expression of the form

$$\Lambda = \Lambda_\infty - \Lambda_\infty\left[\frac{K_1}{D^{\frac{3}{2}}}\,w_1 + \frac{K_2}{D^{\frac{1}{2}}}\,b\right]\sqrt{2\,\gamma} \tag{25}$$

where K_1 and K_2 are constants varying only with the temperature,

$$w_1 = \frac{1}{2}\left(\frac{u_{1_\infty}}{u_{2_\infty}} + \frac{u_{2_\infty}}{u_{1_\infty}}\right)$$

$u_{1,\infty}$ $u_{2,\infty}$ = mobilities of anion and cation
b = harmonic mean of the ionic radii
and γ = molecular concentration

It may be further simplified to

$$\Lambda = \Lambda_\infty - \alpha\sqrt{\gamma} \tag{25,a}$$

where α = numerical factor.

Debye and Hückel tested this equation by making a survey of the existing conductance data for dilute aqueous solutions. They found in practically every case the linear relation between the equivalent conductance and the square-root of the concentration demanded by the equation. It is, as suggested above, in exactly the form of the expression found empirically by Kohlrausch to hold for very dilute aqueous solutions.

The experimental verification of the equation in non-aqueous solutions is more difficult for several reasons of which the following may be mentioned.

1. The experimental data are incomplete, and in a number of cases where they have been reported they must be considered as unreliable.

2. Since the theory is applicable only when the electrolyte in solution is completely dissociated, measurements in non-aqueous solutions have to be made at greater dilutions even than in the case of the aqueous solutions. In non-aqueous solvents the presence of undissociated molecules even in dilute solutions is a much more common phenomenon than in water. It goes without saying then, that the experimental difficulties may become very great.

In spite of these difficulties Fraser and Hartley (8) have shown that the square-root law is satisfied by the conductance data for a number of uni-univalent salts dissolved in methyl alcohol up to a concentration of $\gamma = 0.002$. These experiments were conducted with extreme care and the results must be considered to be among the most accurate conductance data available at the present time. Walden, Ulich and Busch (9) tested the theoretical relation with their data, and found it to be obeyed for a number of salts dissolved in acetone up to a concentration of $\gamma = 0.0005$. In the more dilute solutions the data of Franklin and Kraus (10) and of Kraus and Bishop (11) for certain of the alkali-halides dissolved in liquid ammonia may be represented by the equation given above.

The development of the theory by Onsager

To this point the numerical factor α in equation (25a) has not been considered. Unfortunately the equations lead to a numerical factor which is more complicated than the corresponding factor in the activity theory which is made up of universal constants only. The factor of the conductance equation has to be calculated for each individual case from the conductance measurements themselves, because one of the terms from which it is obtained contains the ionic radius—a distance not accurately known at present. Also, if this distance is calculated from the mobility of the ion, using Stokes Law, and the result used to calculate α it is found that the calculated decrease in conductance as the concentration is increased is always somewhat large.

On investigation of these difficulties Onsager (12) was able to improve the theory in several respects. In the first place he was able to calculate the effect due to electrophoresis in such a way that in the region of small concentrations it was entirely independent of the ionic radius. The result is given by the expression

$$F_i' = \frac{\epsilon\, z_i\, X\, \kappa}{6\, \pi\, \eta} \tag{26}$$

This expression is essentially the one found previously by Debye and Hückel (equation 21), since it may be obtained from the latter by the simple substitution of the equivalent of the ionic radius given by Stokes Law. Therefore, although the calculation of the factor α was simplified in this manner, the difficulty concerning its magnitude was not removed.

Onsager showed further that the method used by Debye and Hückel to calculate the electrical force of relaxation upon an ion passing through a solution needed some modification. The original Debye expression

$$E_i' = -\tfrac{1}{6}\, \frac{\rho\, v_i}{DkT}\, \kappa\, \epsilon^2\, z_i^2 \tag{18}$$

was obtained by considering the ion to be moved in a given direction with a constant velocity, which, according to Onsager, cannot be strictly true. The ion, in addition to its mean motion in the given direction, possesses an irregular motion, due to its Brownian movement, which will have an effect on the dissymmetry of the ionic atmosphere. Introducing this conception it is found that the resistance to the passage of an ion is lower than was indicated by the earlier treatment. The calculation is also modified due to the fact that the diffusion of two ions in relation to one another causes a combined relaxation of both ionic atmospheres. The additional electrical force of relaxation is calculated to be

$$E_i'' = \frac{\epsilon^2}{3\,DkT} \frac{\kappa'^2}{\kappa + \kappa'} X \tag{27}$$

where

$$\kappa'^2 = \frac{4\,\pi}{DkT} \frac{\Sigma \frac{n_i\,\epsilon^2}{\rho_i}}{\Sigma \frac{1}{\rho_i}}$$

n_i and ρ_i being the number and frictional coefficients, respectively of the various ions in the solution, as before.

The result of the calculations of Onsager may be given quite simply by means of the relation

$$\bar{\Lambda} = \bar{\Lambda}_\infty - \bar{\Lambda}_{Io} - \bar{\Lambda}_{II} \tag{28}$$

where $\bar{\Lambda}_\infty$ = ordinary conductance at infinite dilution

$\bar{\Lambda}_{Io} = \frac{|\epsilon_1\,\epsilon_2|}{3\,DkT}\,\kappa\,\bar{\Lambda}_\infty \frac{q}{1 + \sqrt{q}}$ = electrical force of relaxation expressed as conductance. (28,a)

$\bar{\Lambda}_{II} = \frac{n_1\,\epsilon_1^2 + n_2\,\epsilon_2^2}{6\,\pi\,\eta} \frac{1000}{\gamma} \frac{1}{9 \times 10''} \cdot \kappa$ = electrophoretic force expressed as conductance. (28,b)

$$\kappa^2 = \frac{4\,\pi}{DkT} \frac{\epsilon^2\,N}{1000}\,\gamma\,\Sigma\,\nu_i\,z_i^2 \tag{28,c}$$

For water at 18°C.:

$$\kappa^2 = 0.05342 \times 10^{16}\,\gamma\,\Sigma\,\nu_i\,z_i^2$$

For water at 25°C.:

$$\kappa^2 = 0.05385 \times 10^{16}\,\gamma\,\Sigma\,\nu_i\,z_i^2$$

Equation 28 shows at a glance that the molecular conductance, $\bar{\Lambda}$, is equal to the familiar molecular conductance at infinite dilution, $\bar{\Lambda}_\infty$, minus the effect of the two additional forces, which have been under discussion, namely the electrical force of relaxation and the force due to electrophoresis. These forces are, of course, expressed as molecular conductances.

The quantity, q, depends only on the valences and mobilities. It is given by the relation

$$q = \frac{\bar{L}_1 z_2 + \bar{L}_2 z_1}{(z_1 + z_2)\,(\bar{L}_1 z_2^2 + \bar{L}_2 z_1^2)} \cdot z_1 z_2 \tag{29}$$

Introducing the universal constants the expression for the molecular conductance of a simple electrolyte takes the following form

$$\bar{\Lambda} = \bar{\Lambda}_\infty - \left(\frac{0.985 \times 10^6}{(DT)^{\frac{3}{2}}}\, w\, \bar{\Lambda}_\infty \sqrt{\Sigma\, \nu_i\, z_i^2} + \frac{29.0}{(DT)^{\frac{1}{2}}\, \eta}\, (\sqrt{\Sigma\, \nu_i\, z_i^2})^3\right) \sqrt{\gamma} \tag{30}$$

where

$$w = \frac{2\,q}{1 + \sqrt{q}}$$

The molar conductance, $\bar{\Lambda}$, is therefore given by an expression of the form

$$\bar{\Lambda} = \bar{\Lambda}_\infty - \alpha \sqrt{\gamma} \tag{30a}$$

where

$$\alpha = \left(\frac{0.985 \times 10^6}{(DT)^{\frac{3}{2}}}\, w\, \bar{\Lambda}_\infty \sqrt{\Sigma \nu_i\, z_i^2} + \frac{29.0}{(DT)^{\frac{1}{2}}\, \eta}\, (\sqrt{\Sigma\, \nu_i\, z_i^2})^3\right)$$

The corresponding expression for the equivalent conductance (the quantity used exclusively by Onsager) is

$$\bar{\Lambda}^* = \bar{\Lambda}^*_\infty - \left(\frac{0.985 \times 10^6}{(DT)^{\frac{3}{2}}}\, w\, \bar{\Lambda}^*_\infty + \frac{29.0\,(z_1 + z_2)}{(DT)^{\frac{1}{2}}\, \eta}\right) \sqrt{(z_1 + z_2)\,\gamma^*} \tag{31}$$

This equation is of the form

$$\bar{\Lambda}^* = \bar{\Lambda}^*_\infty - \alpha^* \sqrt{(z_1 + z_2)\,\gamma^*} \tag{31a}$$

where

$$\alpha^* = \frac{0.985 \times 10^6}{(DT)^{\frac{3}{2}}}\, w\, \bar{\Lambda}^*_\infty + \frac{29.0\,(z_1 + z_2)}{(DT)^{\frac{1}{2}}\, \eta}$$

The limiting law for the equivalent conductance may be written in still simpler form when the ionic strength, I', given by equation 10, is introduced. It may be written

$$\bar{\Lambda}^* = \bar{\Lambda}^*_\infty - \alpha^* \sqrt{I'} \tag{32}$$

where α^* has the value given above.

The above general equations contain, besides universal constants, only the valences of the ions in question and their velocities of migration at infinite dilution. According to these equations, the decrease in conductance with increasing concentration takes place more rapidly the higher the valences are, and the greater the ionic mobilities at infinite dilution are. The valence effect predominates because it occurs in both members of the term which gives the numerical factor.

Considerable progress has already been made in the verification of the theory.

For solvent water at 18°C., using the values of Drude for the dielectric constant of water

$$\alpha^* = 0.270\ w\ \bar{\Lambda}^*_\infty + 17.85\ (z_a + z_c)$$

For solvent water at 25°C.

$$\alpha^* = 0.274\ w\ \bar{\Lambda}^*_\infty + 21.14\ (z_a + z_c)$$

That the experimental data of Kohlrausch (13) for salts of the valence types 1–1, and 1–2, as well as for acids of the type 1–1 may be represented by the equation of Onsager is indicated in tables 3 and 4. In practically every case the deviations are within the limit of the experimental error. The fact that the differences between experiment and theory are somewhat greater in the case of the uni-bivalent salts is explained by the fact that only five values of the molar conductance, corresponding to the concentrations $\gamma^* = 0.0001, 0.0002, 0.0005, 0.001$, and 0.002 could be used. In the case of the uni-univalent salts the concentrations used were $\gamma^* = 0.0001, 0.0002, 0.0005, 0.001, 0.002$ and 0.005.

In the case of the salts of the higher valence types the conductance values at the highest dilutions for which data exist are represented by a square-root law, but the values of the limiting slope, α^*, are much higher than that demanded by the theory. This is indicated in table 5 which, like tables 3 and 4, has been adopted from the article of Onsager (12). The values of α^* were calculated from the conductance data of Kohlrausch at the concentrations $\gamma^* = 0.0001, 0.0002, 0.0005, 0.001$ and 0.002. It

TABLE 3

Conductance data for electrolytes of type 1–1. Solvent water

$$\alpha^*_{\text{theor.}} = 35.7 + 0.159\bar{\Lambda}_\infty$$

ELECTROLYTE	$\bar{\Lambda}^*_\infty$	$\alpha^*_{\text{exp.}}$	$\alpha^*_{\text{theor.}}$	$\alpha^*_{\text{exp.}} - \alpha^*_{\text{theor.}}$
LiCl	98.9	57.4	51.4	6.0
$LiIO_3$	67.4	48.3	46.4	1.9
$LiNO_3$	35.2	56.3	50.9	5.4
NaCl	108.9	54.7	53.0	1.7
$NaIO_3$	77.4	51.4	48.0	3.4
$NaNO_3$	105.3	58.3	52.5	5.8
KCl	129.9	59.9	56.4	3.5
KBr	132.0	62.2	56.7	5.5
KI	130.5	51.5	56.5	−5.0
KIO_3	98.4	54.2	51.4	2.8
$KClO_3$	119.5	58.2	54.7	3.5
KNO_3	126.4	65.7	55.8	9.9
KCNS	121.0	54.1	55.0	−0.9
CsCl	133.1	53.8	56.9	−3.2
$AgNO_3$	115.8	62.4	54.1	8.3
$TlNO_3$	127.6	63.4	56.0	7.4

TABLE 4

Conductance data for electrolytes of type 1–2. Solvent water

$$\alpha^*_{\text{theor.}} = 53.55 + 1.084 \frac{q}{1 + \sqrt{q}} \bar{\Lambda}^*_\infty$$

ELECTROLYTE	$\bar{\Lambda}^*_\infty$	$\alpha^*_{\text{exp.}}$	$\alpha^*_{\text{theor.}}$	$\alpha^*_{\text{exp.}} - \alpha^*_{\text{theor.}}$
$Ba(NO_3)_2$	117.0	92.8	86.9	5.9
$Sr(NO_3)_2$	113.4	97.8	85.5	12.3
$CaCl_2$	116.7	88.0	86.1	1.9
$Ca(NO_3)_2$	113.6	97.4	85.6	11.8
$MgCl_2$	110.9	83.2	84.1	−0.9
K_2SO_4	132.2	81.0	92.1	−11.1

appears as if the experiments had not as yet been carried out at high enough dilutions to be able to apply the limiting law, since the extrapolation to $\gamma^* = 0$ gives a value for which $\bar{\Lambda}^*_\infty$ is always too large.

TABLE 5

Conductance data for electrolytes of type 2–2. Solvent water

$$\alpha^*_{\text{theor.}} = 71.4 + 0.636\,\bar{\Lambda}^*_\infty$$

ELECTROLYTE	$\bar{\Lambda}_\infty$	$\alpha^*_{\text{exp.}}$	$\alpha^*_{\text{theor.}}$	$\alpha^*_{\text{exp.}} - \alpha^*_{\text{theor.}}$
$MgSO_4$	114.7	242.7	144.4	98.3
$CdSO_4$	115.8	270.7	145.1	125.6

TABLE 6

Conductance data for electrolytes of type 1–1. Solvent methyl alcohol

$$\alpha^*_{\text{theor.}} = 109 + 0.626\,\bar{\Lambda}^*_\infty$$

ELECTROLYTE	$\bar{\Lambda}^*_\infty$	$\alpha^*_{\text{exp.}}$	$\alpha^*_{\text{theor.}}$	$\alpha^*_{\text{exp.}} - \alpha^*_{\text{theor.}}$
LiCl	90.9	158	166	−8
NaCl	97.0	163	170	−7
KCl	105.1	185	175	10
RbCl	108.7	199	177	12
CsCl	113.6	200	180	20
KF	94.0	167	168	−1
KBr	109.4	185	178	7
KI	114.9	184	181	3
NH_4Cl	111.0	187	179	8
HCl	193.5	260	231	29
$LiNO_3$	100.3	177	172	5
$NaNO_3$	106.5	204	177	27
KNO_3	114.6	244	181	63
$RbNO_3$	118.2	251	183	68
$CsNO_3$	123.0	268	186	82
$AgNO_3$	113.0	319	180	139
NaBr	101.5	170	173	−3
$NaOCH_3$	98.4	157	171	−14
$NaClO_4$	115.1	198	181	17

For the solvent methyl alcohol at 25°C. (Dielectric Constant = 30) the coefficient becomes

$$\alpha^* = 1.07\, w\, \bar{\Lambda}^*_\infty + 54.5\,(z_a + z_c)$$

The data of Fraser and Hartley (8) have been used by Onsager for the verification of the limiting conductance expression. The range of concentration considered was $\gamma^* = 0.0001$ to 0.002 as in the case of the aqueous solutions. The comparison of the experimental results with the theoretical is given in table 6. Many of the differences at least must be considered as real deviations from the limiting law. It seems probable that in the region of concentration studied many of the electrolytes are associated to a certain degree, and that if the data were available for the region $\gamma^* = 0.00001$ to 0.0001 a better agreement with the theory might be expected.

Examining the work of Walden, Ulich and Busch in the solvent acetone it is found that the change of conductance in the dilute solutions may be represented by a square-root law. However, simple calculations carried out by the present authors indicate that the values for the constant α^* determined from the experimental data are much greater than that given by the theory, again indicating a certain degree of association of the ions.

The authors believe that satisfactory experimental verification of the theory in any solvent having a dielectric constant much below that of water will only be possible in solutions which are more dilute than any which have as yet been studied. The same thing is true in the case of aqueous solutions of salts of the higher valence types.

Thus the present position of the conductance theory may be compared to that of the activity theory which, although it has been amply verified in aqueous solutions, cannot as yet be said to have been proven satisfactorily in solvents of considerably lower dielectric constant. It is true that several attempts have been made in this direction using electromotive force measurements (14). More recently one of us (15) has published data which indicate that the activity theory is obeyed for salts of the type 1–1 and 1–2 in methyl alcohol in sufficiently dilute solution. The activity coefficients were determined by means of the effect of suitable solvent salts on the solubility of highly insoluble complex cobaltammine salts in that solvent. The solubility of the saturating salts in methyl alcohol is considerably less than it is in water. Since the same salts and salts of similar solubility had previously been used to verify the theory in aqueous solution (16), it is probable that if the necessary measurements can be made on sufficiently dilute solutions a verification will be possible.

The experimental data in the various solvents which have been utilized above in the verification of the simple conductance theory are for the most part for solutions whose lowest concentration is not less than 0.0001 mol per liter, and whose highest concentration is not greater than 0.005 mol per liter. The figures seem to indicate that 0.0001 mol per liter is sufficient dilution only in the case of the conductance effect of salts of the simpler valence types in water. In the case of the activity theory the straight line relationship between the logarithm of the activity coefficient and the square root of the ionic strength, and with the correct slope, has been shown to hold in many cases up to concentrations of the order of magnitude of 0.01 mol per liter. The difficulties of verification of the simple conductance theory are therefore greater than in the case of the activity theory. One reason is, without doubt, that it is necessary to use a number of complicating assumptions in calculating the limiting slope in the case of the conductance theory. It may be suggested here that with improvements in the technic of conductance measurements at high dilutions, at least certain of the difficulties which the theory has met will be overcome.

III. THE DEPENDENCE OF THE ELECTRICAL CONDUCTANCE ON FREQUENCY

In the preceding section the theory which describes the conductance of dilute solutions of strong electrolytes for the usual type of conductance measurement has been reviewed. It will be recalled that for this measurement the Vreeland oscillator, the ordinary vacuum tube generator, the induction coil, or the Washburn generator are standard sources of the alternating current which are used to reduce electrolytic disturbances and polarization effects to a minimum. These instruments are styled in textbooks as sources of "high-frequency" current. In the discussion given for this type of conductance it was recognized that the thickness of the ionic atmosphere was of primary importance.

The purpose of the present section is to show that as a necessary consequence of the existence of a finite time of relaxation, an electrical conductance which is dependent on the frequency must result. From the examples to be given it will be apparent that the frequencies of the sources mentioned in the paragraph above are not high enough to cause any appreciable effect on the conductance of the solution. In other words, to measure the predicted effect it will be necessary to resort to such sources as the Holborn sender or especially built vacuum tube generators which will operate to give waves of length of the order of magnitude 1 to 10 meters.

Consider an ion, surrounded by its ionic atmosphere, to be suddenly removed from the solution. The regular distribution of the ions in the neighborhood of this ion can no longer exist, because the central force field which is the cause of the regular distribution has been removed. The change of the distribution of the charges of the ionic atmosphere to a random distribution with respect to the point where the central ion was will take place gradually. The disappearance of this equilibrium position has been given both mathematically and in the form of a graph in the original articles (17). In the first article this process which is described above was treated only for the case of a symmetrical electrolyte whose ions possessed equal mobilities and neglecting the effect of their Brownian movements. The general case of an unsymmetrical electrolyte, taking into consideration the Brownian movements of the ions is considered in the second article. To summarize the results of these calculations, the statement may be made that the *time of relaxation* is a measure for the disappearance of the equilibrium condition. It has already been shown that it is of the order of magnitude $\frac{10^{-10}}{\gamma}$ seconds.

The reason why a dispersion or frequency dependence of the electrical conductance must exist may be explained in the following manner. If an ion is in motion due to the action of an external electrical field, then, as we have seen in Part II, there will be a density of charge (of opposite sign) which is too small before and too large behind any ion upon which attention is fixed. Therefore, there will be a dissymmetry of the ionic atmosphere which becomes more and more important the greater the average velocity of the ion is. The result is the resisting force which has been called the electrical force of relaxation in Part II. This electrical force of relaxation appears in the calculation (as is shown by equation (28)) as a decrease in the mobility of the ion.

It must be emphasized that the calculation of the dissymmetry can give an approximation only for small ionic velocities. In the usual cases an approximation is sufficient but the case is different when one, as has been done by Wien (18) in his recent experiments, causes the existence of abnormally large ionic velocities by great field strengths. The order of magnitude of the ionic velocities in the Wien experiments was 1 meter per second contrasted to the usual velocities of the order of magnitude 0.01 mm. per second. It can be readily shown that ions which have these high velocities will travel many times the thicknesses of their ionic atmospheres in the time of relaxation. Under these conditions, then, the ionic atmosphere can hardly be built. Therefore, in very strong fields the force which has been termed the additional electrical force of relaxation is of little or no consequence, and the conductance will approach that value found at infinite dilution. This deviation from Ohm's law is exactly the effect discovered experimentally by Wien and explained in a more or less quantitative manner by Joos and Blumentritt (19). This effect has also been discussed in some detail from the standpoint of the interionic attraction theory by the authors (20). It has been introduced at this point merely to assist the reasoning which leads to the explanation of the dispersion effect.

To return to the point in question, it may be said that if the experiments of Wien can be explained in the manner which has been given, and the explanation is certainly beyond reasonable doubt the correct one, then the existence of an electrical conductance which is dependent on the frequency must be suspected. If it be assumed that an outer electrical field of oscillation frequency ω acts on the ions in the solution, then apart from their Brownian movements the ions must acquire a back and forth, or periodic movement. For the ordinary frequencies it can be shown that the ionic atmosphere will have in each moment a dissymmetry of distribution of charges which corresponds to the momentary velocity of the ion. In other words, the decrease in the conductance of a solution due to the electrical force of relaxation will be independent of frequency until the extreme case where the frequency of the field is extraordinarily great compared to $\frac{1}{\theta}$, is reached. Under these conditions it may be shown (17), (20) that the dissymmetry of the ionic atmosphere cannot be built. If the frequency is made high enough, it should then be possible to almost completely destroy this electrical force of relaxation. Since this force is one which in the case of the frequencies ordinarily used for the measurement of conductance operates to resist the passage of an ion, it is evident that an increase in conductance will appear when such high frequencies are used that this force disappears. It is, therefore, predicted (17) that for sufficiently high frequencies an electrical conductance which is dependent on the frequency will result.

The results of the original calculations for the general case of an unsymmetrical electrolyte, taking into consideration the Brownian movement of the ions are given below. The molecular conductance, ¯, as a function of the frequency may be written:

$$\bar{\Lambda} = \bar{\Lambda}_\infty - \bar{\Lambda}_{Iw} - \bar{\Lambda}_{II} \tag{33}$$

where $\bar{\Lambda}_\infty$ = molecular conductance at infinite dilution.

$$\bar{\Lambda}_{Iw} = \frac{|\epsilon_1 \ \epsilon_2|}{3\ DkT} \kappa \, \bar{\Lambda}_\infty \, \overline{\mathrm{X}} \, (\omega\, \theta,\ q) \tag{33,a}$$

= electrical force of relaxation for frequency ω.

$$\bar{\Lambda}_{II} = \frac{n_1\ \epsilon_1^2 + n_2\ \epsilon_2^2}{6\ \pi\ \eta} \cdot \frac{1000}{\gamma} \ \frac{1}{9 \times 10^{11}} \cdot \kappa \tag{28,b}$$

$$\overline{\mathrm{X}} = \frac{\sqrt{q}}{\left(1 - \frac{1}{q}\right)^2 + \omega^2\, \theta^2} \left[\left(1 - \frac{1}{q}\right)\left(\bar{R} - \frac{1}{\sqrt{q}}\right) + \omega\, \theta \cdot \bar{Q}\right]$$

$$\overline{R} = \frac{1}{\sqrt{z}} \sqrt{\sqrt{1 + \omega^2 \theta^2} + 1}$$

$$\overline{Q} = \frac{1}{\sqrt{z}} \sqrt{\sqrt{1 + \omega^2 \theta^2} - 1}$$

$$\theta = \frac{z_1^2 z_2^2}{z_2^2 \overline{L}_1 + z_1^2 \overline{L}_2} \cdot \frac{15.34 \times 10^{-8}}{k T q \kappa^2}$$

κ^2 being given by equation 28,c

The dependence of the conductance on frequency appears in the term $\overline{X}$, which is in turn dependent on $\omega\theta$ and q. The values of θ in terms of the concentration for several electrolytes with the corresponding wave lengths in meters, have already been given in table 2. The frequency ω is controlled experimentally. It is evident from the equations (33) that in the case of ordinary frequencies the expression for the molecular conductance goes over to that given by equations (28). It is thereby assumed that the electrophoretic part of the conductance is independent of the frequency. The quantity, q, is given by equation (29).

Values of the quantity $\overline{\Lambda}_{I\omega}/\overline{\Lambda}_{Io}$, also dependent on $\omega\theta$ and q, have been used to demonstrate the magnitude of the effect of frequency on conductance (17), (21). In these articles a detailed description of the effect of such factors as concentration of the solution, mobilities and valences of the ions, dielectric constant of the medium, and temperature has been given. It is not our purpose to review this material here, it will be sufficient to include a single graph (fig. 1) to show the dispersion effect quantitatively. In this figure, which illustrates the effect of a change in the valences of the ions, values of the quantity $\overline{\Lambda}_{I\omega}/\overline{\Lambda}_{Io}$ are plotted against the wave lengths, for which a logarithmic scale has been used. Wave lengths for which the electrical force of relaxation has been reduced to one-half its usual value, i.e., when $\overline{\Lambda}_{I\omega}/\overline{\Lambda}_{Io} = 0.5$, may be read directly from the graph for each of the salts for which curves are given.

In order to indicate the magnitude of the effect under discussion we shall consider a 0.001 molal solution of cadmium sulfate. The molecular conductance at infinite dilution and 18°C. is

$$\bar{\Lambda}_\infty = 92 + 136.6 = 228.6$$

The calculated decrease in conductance due to the electrophoretic effect is, according to equation (28).

$$\bar{\Lambda}_{II} = 12.8 = 5.6 \text{ per cent of } \bar{\Lambda}_\infty$$

The calculated decrease in conductance due to the electrical force of relaxation for the ordinary frequencies is, also according to equation (28)

$$\bar{\Lambda}_{Io} = 13.0 = 5.7 \text{ per cent of } \bar{\Lambda}_\infty$$

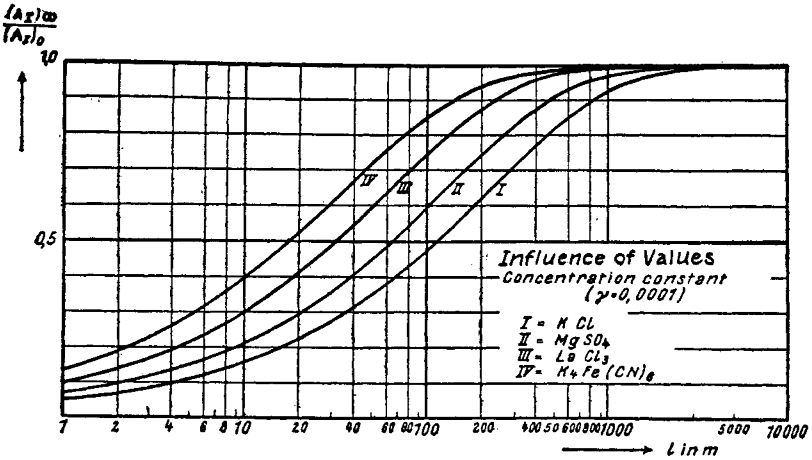

FIG. 1

At a wave length of 6.5 meters $\bar{\Lambda}_{Iw}/\bar{\Lambda}_{Io} = 0.5$, therefore,

$$\bar{\Lambda}_{Iw} = 6.5 = 2.85 \text{ per cent of } \bar{\Lambda}_\infty$$

Therefore, if a source of current having a frequency corresponding to a wave length of 6.5 meters is used to measure the conductance of a 0.001 molal solution of $CdSO_4$, its molecular conductance should be approximately 3 per cent higher than that measured using a frequency corresponding to a wave length of 300 meters, for example.

The example of $K_4Fe(CN)_6$ is similar. The molecular conductance at infinite dilution and 25°C. is

$$\bar{\Lambda}_{\infty} = 680$$

Further,

$$\bar{\Lambda}_{II} = 18.9 = 2.8 \text{ per cent of } \bar{\Lambda}_{\infty}$$

$$\bar{\Lambda}_{I_0} = 13.7 = 2.0 \text{ per cent of } \bar{\Lambda}_{\infty}$$

The total lowering of the molecular conductance is 4.8 per cent. An increase of approximately one per cent in the molecular conductance should be observed using the wave length, $l = 16.3$ meters, i.e., where $\bar{\Lambda}_{I_\omega}/\bar{\Lambda}_{I_0} = 0.5$. The curve for this salt is given in figure 1. The maximum dispersion effect, to be observed at extremely short wave lengths, would be of the order of magnitude of 2 per cent.

The predicted effect has been observed for the first time by Sack (22), working here in Debye's laboratory. This observation must, however, be considered to be one which is as yet but roughly qualitative in nature. A quantitative verification will of course consist in being able to show that a series of experimentally determined conductances for various short waves will give a curve which when properly plotted will coincide with the corresponding calculated curve. Such calculated curves are given in figure 1.

The effect in question is already finding application to chemical problems. For example, Nernst (23) has utilized it, in combination with the classical Arrhenius theory, to calculate a degree of dissociation for strong electrolytes in solution. Further, it now seems possible that the effect of the mutual association of the ions may be determined by a direct experiment. With the elimination of this factor a true degree of dissociation should be made accessible.

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