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A Kinetic Approach to the Theory of Conductance of Infinitely Dilute Solutions, Based on the "Cage" Model of Liquids

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Attention is called to the disparity between the hydrodynamic model of an electrolytic solution and its physical counterpart. The "cage" theory of liquids is reviewed, and some of its equations developed with the purpose of bringing to the surface the underlying assumptions. A quantitative comparison is carried out between the behavior of an ion subject to Brownian motion and that of the placidly moving ion of the hydrodynamic theory. The conclusion is drawn that the tremendous difference between the two models casts doubt upon the validity of the hydrodynamic equations. The possibility is mentioned that the hydrodynamic theory, while giving fortuitously approximately correct values of ionic radii, may still be incorrect in its theoretical implications. Stress is laid on the desirability of a kinetic theory of electrolytic con-

ductance. An approach to a kinetic theory is made, based on the cage model of liquids. In this method, the ionic migration is considered as the cumulative effect of a feeble, sporadic, but directed perturbation of the violent but random Brownian movement. The method leads to an experimentally substantiated relation between the diffusion and the conductivity of an electrolyte. It offers a plausible explanation of the high temperature coefficient of the slow-moving ions. For the ions of an infinitely dilute aqueous solution of potassium chloride, the method yields the following data: Heat of activation for a cage-to-cage jump, 4230 calories; frequency of cage-to-cage jumps, $1.12 \times 10^{11} \text{ sec.}^{-1}$; frequency of oscillation within the cage, $8.3 \times 10^{13} \text{ sec.}^{-1}$; average number of oscillations in each cage, 740.

THE hydrodynamic theory of electrolytic conductance treats the ion as a charged sphere moving with a steady velocity in the direction of the field. The Brownian movement of the ion is treated as an unimportant, self-canceling perturbation of the rectilinear motion. The object of the present paper is to compare the behavior of the hydrodynamic model with the model of an ion offered by the latest theories of liquid structure; to discuss the validity of the hydrodynamic equations; and to offer an approach to a *kinetic* theory of conductance, in which the migration of the ion along the field is considered as the result of a rather feeble but persistent perturbation of the vigorous Brownian movement.

I. THE HYDRODYNAMIC THEORY

In 1888 Nernst¹ derived a theoretical relation between the diffusion coefficient of a salt and the mobilities of its ions. Nernst assumed that a diffusing ion is acted upon by a force which in solution theory was called osmotic pressure. He assumed that the ion moves at a constant ve-

locity because of the resistance offered by the medium. He further assumed that the same friction coefficient operates to restrict to a steady velocity the movement of an ion in an electric field. Eliminating the unknown friction coefficient from his diffusion and conductance equations, Nernst obtained the relation between the diffusion coefficient and the mobility of the ion. Eq. (1) is a modification of the Nernst relation:

$$v = (nE\epsilon D)/kT. \quad (1)$$

In this equation n is the valence of the ion, E is the intensity of the field, D is the diffusion coefficient of the ion, ϵ is the electronic charge, and kT is the Boltzmann constant multiplied by the absolute temperature. v is the absolute mobility of the ion in a field of unit intensity.

Nernst showed that in the case of a salt whose ions possess unequal mobilities u and v the diffusion of the slower ion will be accelerated by the faster ion; the diffusion of the latter will be retarded. The equation for the diffusion of a salt retains the simple form shown in Eq. (1) if v is replaced by an average mobility, equal to $2uv/(u+v)$. The agreement between observed diffusion coefficients and those calculated from the known mobilities is highly satisfactory (Taylor, reference 1, p. 1024).

¹ Nernst, *Zeits. f. physik. Chemie* 2, 613 (1888); Taylor, *Treatise on Physical Chemistry* (D. Van Nostrand Co., 1930), p. 690, 1022. For several further references, see Taylor, p. 690.

In 1905, Einstein,² assuming that a large Brownian particle is also subject to the influence of osmotic force, added the assumption that the friction coefficient is given by Stokes law. This led to the now familiar equation:

$$D = kT / (6\pi\eta r). \quad (2)$$

In this equation η is the ordinary macroscopic coefficient of viscosity of the medium, and r is the radius of the particle. The assumption that a suspended particle or molecule is subject to an "osmotic force" in the direction of the concentration gradient is somewhat disturbing. Einstein meets this possible objection as follows:³

"In this calculation osmotic pressure is treated as a force acting on the individual molecules, which evidently does not correspond with the conceptions of the kinetic-molecular theory, since, according to the latter, the osmotic pressure in the case under discussion must be thought of as a virtual force only. However, this difficulty vanishes if we reflect that (dynamic) equilibrium with the (virtual) osmotic forces, which correspond to the differences in concentration of the solution, can be established by the aid of a numerically equal force acting on single molecules in the opposite direction."

In 1910, Lorenz⁴ contributed the assumption that, despite the small size of an ion, its friction coefficient is given by the Stokes formula. He suggested that the extended Einstein-Stokes equation may be used for the determination of ionic radii in solution. Lorenz's equation, slightly modified, reads as follows:

$$v = n\epsilon E / (6\pi\eta r). \quad (3)$$

Eliminating Stokes friction coefficient from Eqs. (2) and (3), we obtain the modified form of Nernst's Eq. (1).

In conclusion, we may state briefly the nature of the model offered by the hydrodynamic theory of electrolytic conductance, as it is known at the present time:^{5, 6} When an electric field is turned

on, each ion begins to move under the influence of the force $n\epsilon E$. The resistance, $6\pi\eta r v$, increases with the velocity. Eventually, the ion reaches a steady velocity, given by Eq. (3).

II. THE RELATION BETWEEN THE ASSUMPTIONS OF THE HYDRODYNAMIC THEORY AND THE VALIDITY OF THE DERIVED EQUATIONS

We have seen that the hydrodynamic theory calls for an initial period of acceleration. The question may be raised: Why is the conductivity of an electrolyte in an alternating electric field independent of the frequency of the field? This question is taken up in some of the reference books. Ulich (reference 6, p. 224) estimates that the period of acceleration is of the order of magnitude of 10^{-13} sec. and is much shorter than the periods of the fields ordinarily used. Newman,⁷ discussing the same question, gives the following equations in support of the statement that the period of acceleration must be extremely short:

$$\begin{aligned} m \frac{dv}{dt} &= n\epsilon E - 6\pi\eta r v; \\ v &= \frac{n\epsilon E}{6\pi\eta r} (1 - e^{-6\pi\eta r t / m}). \end{aligned} \quad (4)$$

It is obvious that for large values of t Eq. (4) is reduced to Eq. (3). To check Ulich's estimate, we shall calculate the value of t at which v will have reached 90 percent of its maximum velocity. Solving the equation: $e \exp(-6\pi\eta r t / m) = 0.1$, and assuming a molecular weight 100 for the ion, $\eta = 0.01$, $r = 3 \times 10^{-8}$ cm, we find that $t = 6.7 \times 10^{-14}$ sec., in fair agreement with Ulich's value.

If the frictional force were absent, the freely accelerated ion would have acquired in the same time interval a velocity 2.303 times as great as its steady limiting velocity given by Eq. (4). In other words, the velocity of the ion at the end of an interval of 6.7×10^{-14} second is $0.9/2.303$, or 39 percent of the value it would have had if friction were completely absent. This last calculation, which does not appear in reference books on electrolytic conductance, leads to a very

² Einstein, *Ann. d. Physik* **17**, 549 (1905).

³ Einstein, *Investigations of the Theory of the Brownian Movement*, edited by Fürth, translated by Cowper (Methuen & Co., London, 1926), p. 58.

⁴ Lorenz, *Zeits. f. physik. Chemie* **73**, 252 (1910).

⁵ Baars, *Handbuch der Physik*, Vol. XIII (Julius Springer, Berlin, 1928), p. 399, 437.

⁶ Ulich, Eucken-Wolf's *Hand- und Jahrbuch der chemischen Physik*, Vol. VI (Leipzig, Akademische Verlagsgesellschaft, 1933), pp. 152-181.

⁷ Newman, *Electrolytic Conduction* (Wiley, 1931), p. 367.

puzzling conclusion. The absolute velocity of an ion in a field of 1 volt/cm is of the order of magnitude of 1×10^{-3} cm/sec. Therefore, in 6.7×10^{-14} sec. the distance covered by the accelerated ion is less than 6.7×10^{-17} cm. We find, then, that, while the ion covered this distance, frictional forces operated to give it a velocity which was only 39 percent of the velocity it would have acquired in the absence of friction!

This is a startling conclusion. We are accustomed to think that the distance between the particles of a liquid are of the order of magnitude of 10^{-9} cm. How could the friction of the solvent affect the ion while it was moving through a distance equal to approximately one-ten-millionth of its mean free path?

The difficulty may be resolved in one of two ways. First, we may try to apply the Heisenberg principle of uncertainty. The momentum of the ion moving at full speed is approximately 16.5×10^{-26} . Since we are trying to define the momentum of the ion within 10 percent of this value, or 1.65×10^{-26} , we can localize its position with an uncertainty equal to $h/1.65 \times 10^{-26}$, or 0.386 cm. (Taylor, reference 1, p. 1354). We could say that the problem should have been approached with the methods of quantum mechanics. This, however, would be too much like changing the rules of the game after the cards had been dealt. Since we have been using classical dynamics, it is desirable to discover, with the use of simple ideas of classical dynamics, the contradiction which has crept into our discussion of the problem.

The alternative explanation is based upon an inherent weakness of any model intended to represent a complicated physical system. To be amenable to theoretical treatment, the model must be simpler than the system it represents, and therefore different from it. Any calculation in which the difference between the system and its model is of crucial importance is apt to bring contradictory results. Stokes law is based on the assumption that the sphere is moving in a continuous viscous medium, the latter extending from the very surface of the sphere. In Lorenz's model of an electrolytic solution the coarse-grained solvent was replaced by a viscous, placid, continuous medium. The restless ions were replaced by steadily moving charged spheres. It

should be clear that any argument based on the coarse-grained structure of the solution is almost bound to conflict with the deductions based on the Lorenz model. In the opinion of the writer, it is not unfair to the hydrodynamic theory to state that it cannot give the correct answer to the question of initial acceleration of ions in a real solution. As a matter of fact, in a subsequent section it will be shown that this question, perfectly definite as it is when applied to a Lorenz model, is meaningless when applied to a real solution.

The paradox discussed in this section represents one case in which the difference between a solution and its hydrodynamic model is of enough importance to invalidate the conclusions of the theory. In the light of this example it would be desirable to carry out a careful quantitative comparison between the behavior of ions in solution and that of ions in the hydrodynamic model, with a view to examining critically the validity of the hydrodynamic equations. In some discussions of the hydrodynamic theory the Brownian movement of the ions is mentioned parenthetically. In others, it is mentioned with real concern. In all cases, however, it is assumed that the randomness of the movement operates to leave unimpaired the applicability of Stokes law. In this paper the writer intends to reopen this discussion in the light of a *quantitative* comparison between the behavior of a Lorenz ion and its physical counterpart. This quantitative treatment is made possible by recent progress in the theory of liquids. Some of the latest developments of the theory will be discussed in the next two sections, after which it will be possible to return to the main subject of this paper.

III. THE "CAGE" MODEL OF LIQUIDS AND SOLUTIONS

In 1926, Frenkel⁸ called attention to an important aspect of the motion of molecules and of ions in a liquid. He pointed out that the particles do not "crawl" past each other; that they oscillate about an equilibrium position; and that they jump from one equilibrium position to another on infrequent occasions. The same idea was ad-

⁸ Frenkel, *Zeits. f. Physik* **35**, 652 (1926).

vanced by the writer in 1932.⁹ Bradley¹⁰ brought forth the same idea in his interesting paper on the rate of reactions in solution. Since then several papers appeared which deal, in whole or in part, with the idea of "caged" molecules.¹¹⁻¹⁶

To quote from the writer's earlier paper: "There is good evidence that molecules in the liquid phase are fairly closely packed. Thus, if we calculate the molecular diameters of molecules in the liquid phase on the assumption of close packing, we obtain values which are in fair agreement with those obtained by other methods.¹⁷ It follows from what has been said that the application of the gas-kinetic formula to the case of solutions may be incorrect not only in degree but also in kind.

"The question may be raised as to the nature of the process whereby molecules in a closely packed system change position and neighbors. The answer will probably be supplied by the statistical theory of fluctuations. As long as the molecules are not solidly packed, there is room for fluctuation in density. The density fluctuation in a system consisting of a large number of molecules is very small. However, in a system consisting of from ten to fifty molecules the fluctuation may be violent enough to allow individual molecules a frequent change of neighbors and position."

The present view is that in a liquid each particle is surrounded by a "cage" consisting of approximately 12 molecules and that the central molecule or ion cannot escape from this "cage" unless it possesses energy of activation of the order of magnitude of 5000 calories. Since a great portion of the discussion in this paper will depend on the assumption of caged molecules, it will be of interest to form an estimate of the distance between the molecules in a liquid.

⁹ Polissar, J. Am. Chem. Soc. **54**, 3105 (1932).

¹⁰ Bradley, J. Chem. Soc. 1910 (1934). Bradley was unaware of the two papers published earlier, just as the author was unaware in 1932 of Frenkel's paper published 6 years earlier.

¹¹ Wheeler, Proc. Ind. Acad. Sci. **1**, 795 (1935); **4**, 291, 298, 466 (1936); Trans. Nat'l. Inst. of Sci. of India **1**, 333 (1938).

¹² Rabinowitch and Wood, Trans. Faraday Soc. **32**, 1381 (1936).

¹³ Eyring, J. Chem. Phys. **4**, 283 (1936).

¹⁴ Bradley, Trans. Faraday Soc. **33**, 1185 (1937).

¹⁵ Rabinowitch, Trans. Faraday Soc. **33**, 1225 (1937).

¹⁶ Fowler and Slater, Trans. Faraday Soc. **34**, 81 (1937).

¹⁷ Jeans, *The Dynamical Theory of Gases* (Cambridge University Press, 1925), p. 332.

Lorenz,¹⁸ after a careful study of the available data, estimated that the volumes of an "average" liquid, at its melting point and at its boiling point, are 21 percent and 41 percent, respectively, greater than the extrapolated volume at 0°K. Volume expansions in the ratios 1.21 and 1.41 correspond to linear expansions in the ratios 1.065 and 1.120, respectively. This means that in an "average" liquid the average distance between the surfaces of two adjacent molecules is equal to something like 6.5 percent to 12 percent of the molecular diameter. It seems plausible that under such conditions a molecule or an ion must possess more than its average share of kinetic energy before it can squeeze through a "gate" or exchange places with one of its neighbors.

IV. CALCULATION OF THE FREQUENCY OF CAGE-TO-CAGE JUMPS

The calculations in this section will be based on the following assumptions and definitions: (1) In an ordinary liquid or solution each particle (molecule or ion) is oscillating in a cage made up of the surrounding particles, approximately twelve in number. (2) When the central particle has suddenly changed positions in such a way as to exchange about half or more of its former neighbors, we shall say that it has made a cage-to-cage jump. We need not specify the precise mechanism of the process. The molecule may exchange places with one of the cage molecules; it may occupy a hole created by the departure of one of the cage molecules; it may squeeze past two of the cage particles. (3) We shall assume that long jumps are extremely rare and that the average distance between two successive equilibrium positions is of the order of magnitude of the average distance between the centers of two neighboring particles.

Suppose we fix our attention on a single particle and study its progress through space in the course of n cage-to-cage jumps. Its vector-displacement will be given by the following vector equation:

$$\mathbf{S}_n = \sum_{p=1 \dots n} \mathbf{L}_p, \quad (5)$$

¹⁸ R. Lorenz, *Raumerfüllung und Ionenbeweglichkeit* (Leopold Voss, Leipzig, 1922.)

where \mathbf{L}_p is the vector displacement in jump number p . Taking the dot product of each side against itself, we obtain the following equations:

$$\mathbf{S}_n \cdot \mathbf{S}_n = S_n^2 = \sum_{\substack{p=1 \dots n \\ q=1 \dots n}} \mathbf{L}_p \cdot \mathbf{L}_q = \sum_{p=1 \dots n} \mathbf{L}_p^2 + \sum_{p \neq q} \mathbf{L}_p \cdot \mathbf{L}_q \quad (6)$$

If we repeat the experiment m times, where m is a very large number, we obtain m equations similar to Eq. (6). On adding the left sides of the m equations and dividing by m , we shall obtain the average of the square of the vector displacement after n jumps. The sum of the right sides of the m equations, divided by m , will be equal to $n\bar{L}^2$, where \bar{L}^2 is the average of the square of a cage-to-cage displacement¹

$$\bar{S}_n^2 = n\bar{L}^2. \quad (7)$$

The terms of the type $\mathbf{L}_p \cdot \mathbf{L}_q$ will add up to zero, since the cosine of the angle between the two vectors has an equal chance of being positive or negative. This last statement is dependent on the reasonable assumption, to be verified later, that in each cage the particle completes several oscillations, thus making the directions of two successive jumps completely independent of each other.

Let j be the number of cage-to-cage jumps per second. Then the average of the square of the displacement after a time t is given by the following equation:

$$\bar{S}_t^2 = jt\bar{L}^2. \quad (8)$$

The relations between L , S , and the components of the latter along three mutually perpendicular directions are given by the following equations:

$$S^2 = X^2 + Y^2 + Z^2; \quad \bar{S}_t^2 = 3\bar{X}_t^2; \quad \bar{X}_t^2 = (jt\bar{L}^2)/3. \quad (9)$$

Einstein² has derived the following equation, in which D is the coefficient of diffusion of a particle:

$$\bar{X}_t^2 = 2Dt. \quad (10)$$

This equation is completely independent of any physical assumptions, such as the application of Stokes law to molecules, except the assumption of

* Because of typographical difficulties the overbar does not extend beyond the letter. In this and in the other equations, \bar{A}^2 is to be taken as the average of the square of A and not as the square of the average of A .

completely random motion. Combining Eqs. (9) and (10), we obtain the following relation:

$$j = 6D/\bar{L}^2. \quad (11)$$

Equation (11) makes it possible to calculate the value of j in terms of the diffusion coefficient. It is applicable to neutral molecules of a solute, to molecules of a solvent (in which case D is the coefficient of self-diffusion), and to electrolytes, such as potassium chloride, whose ions possess equal mobilities.

We can now calculate the approximate value of the frequency, j , of cage-to-cage jumps in ordinary liquids. D is of the order of magnitude of 10^{-5} cm²/sec.; \bar{L}^2 is of the order of magnitude of 10^{-15} cm²; j must be of the order of magnitude of 6×10^{10} sec.⁻¹.^a

^a Note: Equation (11) has been used by preceding writers on the subject. Bradley (reference 9, 13) used the familiar method of derivation involving two planes separated by a distance L . Rabinowitch (reference 14) employed a method similar to that given here. His equations involve an error of a factor of 3, caused by the use of \bar{X}^2 in place of \bar{S}^2 . The complete derivation of Eq. (7) is given here, since it is not given in any of the papers perused by the writer. The purpose is twofold: First, to show that it can be used with equal rigor for any value of n , from $n=1$ and up; secondly, to bring to the surface all the underlying assumptions.

To start with, we may note that the derivation is independent of the shape of the molecule. It is also independent of the mechanism of the cage-to-cage jump, as long as \bar{L}^2 is recognized as the weighted average of the squares of the possible single displacements. The derivation is based on the assumption that the directions of two successive jumps are mutually independent. This assumption does not hold true in the case of an ion jumping in the vicinity of another ion. It holds true for the ions of an infinitely dilute solution.

There is one hidden assumption which should be discussed at this point. In the derivation of Eq. (7) it has been assumed that the vector displacement S was due solely to the cage-to-cage jumps of the particle. This need not necessarily be correct and is most probably incorrect to a small extent. To make this point clear, we shall assume the extreme case of a hypothetical liquid containing semi-crystalline molecular swarms. In such a liquid an individual molecule may be buried in a single cage for a relatively long time, while the swarm is subject to Brownian motion. The Brownian motion of the swarm and not the cage-to-cage jumps of the molecule would serve as the chief contributor to the diffusion of the molecule, and Eq. (11) would be incorrect.

Even in a liquid with no localized rigid structure, the whole cage must be subject to Brownian movement, because of fluctuations in density of the environment. In a loosely packed liquid, this motion would be more violent than in a tightly packed one. But in a loosely packed liquid the frequency of jumps would be greater than in a tightly packed one. For this reason, the relative importance of the two types of displacement would be roughly the same in all liquids. Furthermore, the Brownian displacement of a group of molecules must be smaller than that of a single one.

There cannot be any doubt that Eq. (11) will give the correct order of magnitude of the value of j , despite the neglect of the Brownian movement of the cage as a whole.

V. A COMPARISON BETWEEN THE HYDRODYNAMIC MODEL OF AN ELECTROLYTIC SOLUTION AND ITS PHYSICAL COUNTERPART

In carrying out a comparison between the behavior of an electrolytic solution in an electrical field and that of its hydrodynamic model, it would be desirable to avoid a discussion of those differences which are not essential to the validity of the hydrodynamic equations. In order to provide both direction and emphasis to our line of inquiry, we shall consider the differences in the light of the assumptions underlying the derivation and the use of Stokes law. We need not consider all the assumptions.¹⁹ Two of them are of particular interest in the present case: The motion of the sphere must be steady; and there must be no slipping at the surface of the sphere. It will be most pertinent to the present discussion to quote Herzfeld and Smallwood's interpretation, given in Taylor's treatise (reference 1, p. 183). After showing that a small particle subject to a constant force will move through a gas with a speed which is inversely proportional to the *square* of its radius, they state that a large particle will obey Stokes law. Their explanation follows:

"The physical difference between the two cases is as follows: In the case of *small* particles (or ions), it was assumed that the motion of the particle had no effect on the motion of the molecules in front of it prior to the actual collision. . . . In Stokes' case, however, the motion of the gas molecules is changed throughout the entire surrounding region by the motion of the particle. That is to say, so many molecules are reflected from the particle that they might be said to prepare the molecules in front of them, due to their altered distribution of velocities. The entire body of gas in front of the particle has therefore a component of velocity parallel to the velocity of the particle."

The hydrodynamic model satisfies all the requirements underlying the use of Stokes equa-

It is highly probable that this equation is satisfactory within an error of a very few percent. This assumption is supported by the fact that equations derived in a later section and based on Eq. (11) are in agreement with experimental observations.

¹⁹ For a list of assumptions, see Ulich, reference 6, p. 152, or Millikan, *Electrons* (The University of Chicago Press, 1935), p. 95.

tion. In examining the behavior of an actual solution, we shall attempt to answer the following questions: Is the motion of the ion steady? Is there slippage at the surface? Is the motion of the ion under the influence of the field a dominating factor in the region surrounding the ion?

For the sake of concreteness we shall study the behavior of potassium ions in a dilute solution of potassium chloride, at 18°C, in a field of 1 volt/cm. This electrolyte has the convenient, but unessential, characteristic that its ions possess approximately equal mobilities. For the convenience of the reader, the data and derived quantities are assembled in Table I.

(1) We shall estimate the number of jumps per second. The diffusion coefficient in very dilute solutions cannot be much different from that of a 0.001-molal solution (1.69×10^{-5} cm²/sec.). The value of L will be taken quite arbitrarily as 3×10^{-8} cm. This value is certainly correct as to order of magnitude. No effort is made to obtain a more accurate value, since none of the arguments of this paper are based on the exact value of L . Substituting in Eq. (11), we get: $j = 1.12 \times 10^{11}$ jumps per second.

(2) We shall compare the migration velocity of the ion with its kinetic velocity. The former is 6.75×10^{-4} cm/sec.; the latter is of the order of magnitude of 300 meters/sec. The ratio of these two quantities is approximately 4.5×10^7 . It would seem, then, that the introduction of a field of 1 volt/cm would not affect greatly the behavior of the ion.

(3) We shall compare the energy acquired by the ion as it moves along the field with the mean thermal energy per degree of freedom. We shall make the usual assumption that the ion picks up energy while it is free to move with the field. Assuming that the ion can cover even as large a distance as 3×10^{-8} cm without losing its energy, we find that the energy so acquired is 3×10^{-8} volt-electron, or 4.77×10^{-20} erg. The value of kT is 3.99×10^{-14} erg. The ratio of these two quantities is 8.35×10^5 . This is another indication that the electrical field cannot be very effective in helping the ion to batter its way through the surrounding molecules!

(4) It will be even more significant to compare the activation effected by the electrical field with the energy of activation needed for a cage-to-cage

jump. This latter quantity is calculated in a later section and is equal to 4230 calories per mole, or 2.92×10^{-13} erg per ion. The ratio between this and the activation energy of the field is 6.12×10^6 . The electric field supplies only one-six-millionth, approximately, of the energy needed to push the ion from one cage to another.

(5) The migration velocity of the ion is 6.75×10^{-4} cm/sec. This is equivalent to 22,500 jumps per second along the field. Although the absolute number is large, it should be compared with the total number of jumps per second (paragraph 1). The ratio is 5×10^6 . In the absence of an electrical field the average numbers of jumps in two opposite directions must be equal. Our calculations show that in the presence of a field of 1 volt/cm, the net gain along the field is only one for every five million jumps.

(6) It will be of interest to compare the average Brownian displacement in the line of the field with the average gain along the field. It takes the ion 4.45×10^{-5} second to make a net gain of 3×10^{-8} cm along the field. During this time, the average Brownian displacement along the line of the field (given by the equation: $\bar{X}^2 = 2Dt$) is equal to 3.87×10^{-5} cm. The Brownian displacement along the field is 1290 times as large as the net gain. (The distance along the zig-zag path is 5×10^6 times as large, as shown in the preceding paragraph.)

(7) Since the net gain along the field is proportional to the time, whereas the Brownian displacement is proportional to the square root of the time, the relative magnitude of the Brownian displacement decreases with time. For use in a subsequent discussion, it will be of interest to calculate how long the ion must be "under observation" before its average Brownian displacement is only 1 percent of the gain along the field. Solving the equation: $v^2 t^2 = 10,000 \bar{X}^2 = 20,000 Dt$, we find $t = 7.41 \times 10^5$ sec., or 206 hours.

We have seen that for the validity of Stokes law it was necessary to ascribe a dominant role to the moving ion. The ion was supposed to plow its way through the surrounding medium, pushing it out of the way and in turn being retarded by it. From a consideration of the behavior of an ion in solution we learned that the role of the electrical field is much more humble than the hydrodynamic theory assumes it to be. An

TABLE I. Some of the symbols used and the values of these quantities in a dilute solution of potassium chloride, at 18°C, and under a potential gradient of 1 volt per centimeter.

1. $T = 291^\circ \text{K.}$	
2. E : Intensity of electrical field $E = 1$ volt/cm.	
3. e : Electronic charge; $e = 4.77 \times 10^{-10}$ e.s.u.	
4. n : Valence of ion.	
5. S : Vector displacement of ion.	
6. η : Viscosity of solvent. $\eta = 0.0106$ poise.	
7. D : Diffusion coefficient of ion. $D = 1.69 \times 10^{-5}$ cm ² /sec.	
8. r : Hydrodynamic value of the ionic radius. $r = 1.18 \times 10^{-8}$ cm.	
9. Crystal theory value of the radius of potassium ion: $r' = 1.33 \times 10^{-8}$ cm. ($r'/r = 1.13$, despite hydration!).	
10. Approximate time necessary for "hydrodynamic" ion to reach 90 percent of migration velocity: $t_{0.9} = 6.7 \times 10^{-14}$ sec.	
11. Distance covered in that time: $S_{0.9} = 6.7 \times 10^{-17}$ cm, approx.	
12. Compare with mean free path of ion: $F = 0.1$ to 3×10^{-9} cm. ($S_{0.9}/F = 6.7 \times 10^{-7}$, approx.!).	
13. L : Cage-to-cage distance. $L = 3 \times 10^{-8}$ cm, approx.	
14. v : Migration velocity of ion. $v = 6.75 \times 10^{-4}$ cm/sec.	
15. This corresponds to a net gain of j_{Field} jumps per second along the field: $j_{\text{Field}} = 22,500$ sec. ⁻¹	
16. j : Total number of cage-to-cage jumps per second. $j = 1.12 \times 10^{11}$ sec. ⁻¹ ($j/j_{\text{Field}} = 5 \times 10^6$).	
17. 1 volt-electron = 1.59×10^{-12} erg.	
18. Q_E : Activation due to field operating through a distance L . $q_E = 4.77 \times 10^{-20}$ erg/electron $Q_E = 6.91 \times 10^{-4}$ calorie/faraday.	
19. kT : Thermal energy per degree of freedom. $kT = 3.99 \times 10^{-14}$ erg. $RT = 578$ calories ($kT/q_E = 8.35 \times 10^6$).	
20. Q : Energy of activation for a cage-to-cage jump. $q = 2.92 \times 10^{-13}$ erg. per ion $Q = 4230$ calories per mole ($Q/Q_E = 6.12 \times 10^6$).	
21. Time in which ion migrates through distance L : $t_L = 4.45 \times 10^{-5}$ sec.	
22. Brownian displacement along the field in the same time: $X_L = 3.87 \times 10^{-5}$ cm. ($X_L/L = 1290$).	
23. Distance covered along field in 206 hours: $v \cdot t = 500$ cm. Average Brownian displacement in the same time: ($2Dt$) ^{1/2} = 5.00 cm, or 1 percent of former.	
24. Temperature Coefficient of mobility: Simple hydrodynamic theory: 2.54% per degree for all ions. Lindemann's theory: 0.13% per degree for potassium ion. Observed values: 2.65% for lithium ion 2.17% for potassium ion 2.12% for cesium ion.	
25. $A/2$: Frequency of oscillation within the cage. $A/2 = 8.3 \times 10^{13}$ sec. ⁻¹ , approx.	
26. Average number of oscillations per cage: $A/2j = 740$ (for potassium ion).	

imaginary observer deriving his information by watching an individual ion would hardly be able to detect any change on the introduction of a potential gradient of 1 volt/cm. Only by keeping

his records to an accuracy of seven significant figures, would he be able to observe that in every five million jumps there is a discrepancy of one, between the number of jumps with the field and the number of jumps against it.

The motion of the ion is admittedly not constant and rarely in the direction of the field. If the idea of "caged" molecules is approximately correct, then the motion is not even smooth and continuous, but intermittent and jerky. Furthermore, the electric field, while acting on the ion all the time, succeeds in influencing the direction of the jump on extremely rare occasions. This is contrary to one of the assumptions underlying Stokes law, namely that the force operates continuously on the moving sphere. This assumption is so obvious that it is never even mentioned in a discussion of the applicability of Stokes law.

The question as to whether there is any slippage at the surface of the moving ion would appear to be meaningless. Furthermore, the question as to the time interval during which the ion is accelerated to its "steady" velocity, discussed in Section II, also loses physical significance.

VI. A CRITICAL DISCUSSION OF THE VALIDITY OF THE HYDRODYNAMIC EQUATION

The conclusions reached in the preceding section are not such as to inspire confidence in the validity of Eqs. (2) and (3) when applied to ions. Whereas, to the best of the writer's knowledge, the quantitative comparison is here carried out for the first time, the qualitative objections lying in the way of acceptance of the hydrodynamic theory have been taken up before. It is not improbable that the hydrodynamic equations would not have gained acceptance if it were not for the fact that they are supported, more or less accurately, by experimental results. For this reason, before taking up the theoretical arguments adduced in support of these equations, we shall consider the nature of the experimental evidence.

Lorenz⁴ compared several ionic radii obtained from Eq. (3) with the Reinganum values. He found that, whereas individual values showed high discrepancies, the two averages of all the radii agreed to within 2.5 percent. When one considers the tremendous simplification of model offered by the hydrodynamic theory, it is amazing

to find that the calculated radii are correct as to order of magnitude, let alone to an accuracy of a few percent.

Ulich,⁶ who is a supporter of the hydrodynamic theory, devotes about twenty-five pages to a discussion of the applicability of the Stokes friction coefficient to the diffusion of ions and molecules and to the conductance of ions. He cites numerous cases in which the calculated radii are correct to within a few percent. On the other hand, among those listed there are quite a few where the value is correct only as to order of magnitude.

The fact that Eq. (3) gives approximately correct values of the radii of many ions cannot be taken as so many independent verifications of the equation. The sizes of ordinary ions do not vary greatly. It is to be expected that larger ions migrate more slowly. Under such circumstances it is almost unavoidable that if the equation gives fortuitously an approximately correct value for one ion, it will also give approximately correct values for all other ions, with a good correlation between the values so obtained and those obtained by other means.

There is no doubt at the present time that Eq. (3) gives approximately correct ionic radii. Controversy arises when an attempt is made to give this equation a strict interpretation, namely, to assume that it is correct to, say, 5 percent and that all the theoretical implications deduced from this equation are correct. Serious objections must be met before such a conclusion can be accepted. For instance, aside from the discrepancy between the values of ionic radii obtained with the use of Eq. (3) and those obtained by other means, there is the question of temperature coefficient of mobility.²⁰ If Eq. (3) is correct, then the temperature coefficients of mobility of all ions should be equal to the coefficient of fluidity, which for water is 0.0254 per degree, at 18°C. Actually, the slow ions show this coefficient, whereas the faster ones exhibit lower coefficients, the faster the ion, the lower the temperature coefficient. To account for this fact it was necessary to assume that the degree of solvation of the fast ions *increases* with increase in temperature.

Herein lies the importance of a critical examination of the validity of Eq. (3). Whereas addi-

²⁰ Davies, *The Conductivity of Solutions* (John Wiley & Sons, New York, 1933), p. 210.

tional assumptions are needed to bring the theory in alignment with the experimental facts, once the equation is accepted as essentially correct, the very assumptions used for its support become far-reaching conclusions based on an accepted theory. In this connection, it is of interest to mention that Kraus²¹ after considering the various assumptions necessary to square the theory with observed values, concludes that the Einstein-Stokes equation should be applied with caution to systems of particles of molecular dimensions.

We shall now consider the theoretical arguments adduced in support of the application of the Einstein-Stokes equation to ions. It will suffice to refer to Ulich's review.⁶ Two of the difficulties offered by the coarse-grained structure are listed: (1) The ion may be able to slip between the molecules of the solvent. (2) The velocity of the medium may fall off discontinuously. The errors introduced by these two factors are opposite in sign, and the assumption is made that they will cancel each other. It should be pointed out that this assumption need not necessarily be correct. As a matter of fact, a similar assumption is definitely incorrect in the case of a Brownian particle falling through a gas. Millikan and his co-workers found (reference 19, p. 115) that when the size of the particle is equal to the mean free path of the gaseous molecule, the friction coefficient in Stokes' formula must be multiplied by the factor 1/1.874.

In support of the assumption that the Brownian motion of the ion does not invalidate the applicability of Stokes law, Ulich⁶ cites the experimental work of Fürth²² on the rate of fall of microscopic particles through water and the rate of movement of charged metallic particles through a gas, in an electric field. To this evidence we may add the work Fletcher and Millikan (reference 19, p. 154), who verified the applicability of Stokes law to large particles falling through a gas. Unfortunately, this evidence is not convincing when applied to a molecular system. Millikan states quite definitely that in these experiments the irregular Brownian

displacements were much smaller than the orderly displacement of the falling particle. On the other hand, the calculations given in Section V, paragraphs 6 and 7, show that ordinarily the Brownian displacement of an ion is very much greater than its displacement along the field. A potassium ion, moving in a field of one volt per centimeter would have to be "under observation" for 206 hours before its displacement along the field is one hundred times as great as its irregular Brownian displacement.

In conclusion, we must state that the validity of the hydrodynamic equation is still in doubt. We must recognize the existence of two possibilities: Either Eq. (3) yields approximately correct values of ionic radii fortuitously, through a favorable set of cancellations of errors: or the equation is correct, through the operation of an even more magnificent set of cancellations of error. In either case the hydrodynamic model is admittedly very much different from its physical counterpart. The writer is of the opinion that it would not be unscientific to accept the simpler alternative, namely, that the agreement is fortuitous.^a

VII. AN APPROACH TO A KINETIC THEORY OF ELECTROLYTIC CONDUCTANCE

Independently of whether the strict interpretation of the Einstein-Stokes-Lorenz equation is correct, it would be desirable to develop a theory of electrolytic conductance based on a model which resembles the kinetic theory picture of a liquid much more closely than the hydrodynamic model does. The desirability of such an approach has been expressed by others who doubted the validity of the hydrodynamic equation.²³ The theories of Lindemann²⁴ and of

²¹ Kraus, *Properties of Electrically Conducting Systems* (The Chemical Catalog Co., New York, 1922), p. 202.

²² Fürth, *Ann. d. Physik* **59**, 409 (1919); **60**, 77 (1919); **63**, 521 (1920).

^a It is of interest to note that the theory of solutions offers another case in which an erroneous hypothesis yields theoretical equations which are in good agreement with experimental results. The hypothesis that the osmotic pressure of a solution is due to the pressure of the solute, considered as a gas, with the solvent merely supplying the space, will give correct equations for dilute solutions. According to Hildebrand (*Solubility*, Second edition, (1936), p. 21), the limitations of the van't Hoff law were clearly stated by van't Hoff himself; yet the failure of later writers to recognize these limitations obscured certain important aspects of solutions and retarded progress in the theory of solutions.

²³ Davies, reference 20, p. 211; Baars, reference 5, p. 437.
²⁴ Lindemann, *Zeits. f. physik. Chemie* **110**, 394 (1924); reference 20, p. 211.

Magnus²⁵ offered a step in the right direction, and will be discussed later.

The cage model of pure liquids and of solutions offers a simple method of attack of this problem. The temperature coefficient of diffusion is of the order of magnitude of 2 percent to 3 percent per degree. This is much larger than the temperature coefficient of T (0.34 percent at 18°) or of \bar{L}^2 ($\frac{2}{3}$ of the coefficient of expansion of the solvent, or, for water, approximately 0.014 percent per degree.) On inspection of Eq. (11), we must conclude that j is the chief contributor to the high value of the temperature coefficient of diffusion. We shall therefore, follow the procedure, quite customary in chemical kinetics, of ascribing the high temperature coefficient to a need for a high heat of activation. In accordance with this well-established practice, we shall represent j in the form of an Arrhenius equation:

$$j = Ae^{-Q/RT}. \quad (12)$$

The physical interpretation of Eq. (12) is as follows: Q is the energy of activation per mol necessary to break through the walls of the cage. A is twice the frequency of oscillation within the cage (since the ion may break through twice in a complete oscillation, each time it reaches the wall). The exponential term gives the fraction of collisions with the wall in which the energy is sufficient to break through it.

Suppose a potential gradient, E , is established in the solution along the X direction in such a sense as to tend to propel the positive ions to the right. It was shown in Section V that the activation effected by the field is exceedingly small as compared with the energy of activation needed for a cage-to-cage jump. Thus, the effect of the field will be wasted on all but two very small classes of ions. There will be a small class of ions whose oscillatory motion is carrying them to the right and whose energy is just a trifle smaller than that necessary to carry them over the summit of the potential barrier. These ions will be carried across the barrier, thanks to the contribution of the electrical field. There will be another class of ions, moving to the left, with only a trifle more energy than that necessary to carry them across the potential barrier. These ions will be

prevented by the field from crossing the barrier. The net result will be a very slow migration of each positive ion in the direction of the field. Using modern terminology, we shall state that the introduction of an electrical field lowers slightly the height of the potential barrier for positive ions moving to the right, and raises slightly the height of the barrier for those ions which jump to the left. In each case the change in energy is equal to the product of the force, neE , by the distance from the average position of the ion in the cage to the summit of the barrier. This distance, for reasons of symmetry, must be equal to $L/2$.

To carry out a quantitative calculation, we shall make the simplifying assumption that one-third of all the ions jump in the X direction and that all the others jump in the plane of $Y-Z$. A more careful analysis, allowing for distribution amongst all possible directions leads to the same final result. We have, then, in the absence of the field:

$$j_{+X} = j_{-X} = \frac{Ae^{-Q/RT}}{6} = \frac{j}{6}. \quad (13)$$

When the field is turned on, the following equations hold:

$$\begin{aligned} j_{+X} &= \frac{Ae^{(-Q+0.5nN\epsilon EL)/RT}}{6}; \\ j_{-X} &= \frac{Ae^{(-Q-0.5nN\epsilon EL)/RT}}{6}. \end{aligned} \quad (14)$$

The difference between the two expressions of Eq. (14) gives the net gain along the field, or the net number of jumps per second along the field:

$$j_{+X} - j_{-X} = j_{\text{Field}} = j(neEL)/6kT. \quad (15)$$

In the expansion of the exponentials, the higher terms were disregarded. R/N was replaced by the Boltzmann constant. Multiplying the number of jumps along the field by the length of a jump, L , we obtain the absolute velocity of the ion along the field:

$$v = j(neEL^2)/6kT. \quad (16)$$

^a There may be some ambiguity in this derivation whether the numerator of the right side of Eq. (16) should contain the average of the square of L or the square of the average of L . In a gas, where the mean free paths vary greatly, the ratio of these two quantities is equal to 2. In a liquid, where the jumps do not vary greatly, the two quantities would be more nearly equal. Nevertheless, to avoid any ambiguity,

²⁵ Magnus, *Zeits. f. physik. Chemie* **174A**, 262 (1935).

Combining Eq. (16) with Eq. (11), we arrive at Eq. (1), obtained by Nernst in 1888 with the use of a hydrodynamic model! The application of the cage method to the more general case of a uni-univalent salt whose ions possess different mobilities leads to Nernst's more general equation:

$$2uv/(u+v) = (E\epsilon D)/kT. \quad (18)$$

Nernst and others have tested Eq. (18) and have found that it agrees with experimental observations to within a very few percent (Taylor, reference 1, p. 1024). A casual consideration of Eqs. (1), (2), and (3) may lead to the conclusion that the validity of Eq. (1) serves as an indirect proof of the validity of the other two, since the former can be obtained directly from the latter by elimination of the friction coefficient. It should be pointed out, however, that even if the friction coefficient were incorrect as to order of magnitude, its elimination from Eqs. (2) and (3) would leave Eq. (1) unaffected.

VIII. TEMPERATURE COEFFICIENTS OF MOBILITY, OF DIFFUSION, AND OF THE FREQUENCY OF CAGE-TO-CAGE JUMPS. THE THEORIES OF LINDEMANN AND OF MAGNUS

With the use of Eqs. (1) and (12) we obtain the following relations between the various temperature coefficients and the energy of activation of a cage-to-cage jump:

$$\frac{dv}{v dT} = \frac{d \ln v}{dT} = \frac{d \ln D}{dT} - \frac{1}{T} = \frac{Q}{RT^2} - \frac{1}{T}. \quad (19)$$

In the derivation, the temperature coefficients of A and of L^2 were neglected. Eq. (19) offers a plausible explanation, both of the high temperature coefficients of mobility and of the difference between the temperature coefficients of slow and of fast ions. A large ion requires a higher energy of activation for a cage-to-cage jump than a small ion does. Therefore, the mobility of the former is smaller, but the temperature coefficient of mobility is larger.

The temperature coefficient of mobility of potassium ion is 2.17 percent per degree (Davies, reference 20, p. 205). Substituting this value in Eq. (19), we find that Q is 4230 calories.

It should be stated here that the more rigorous derivation of Eq. (16) demands the use of the mean-squared value of L .

We can now discuss the theories of Lindemann and of Magnus. Both writers emphasized the desirability of substituting the hydrodynamic model by a kinetic one. Since their models are essentially the same, the two theories may be discussed simultaneously. In the model adopted by each the ion moves in a zigzag path. The electrical field contributes a displacement component in the direction of the field in the course of every mean free path. Lindemann's further assumptions lead to a theoretical mobility which is proportional to the length of the free path and inversely proportional to the square root of the temperature. Magnus' assumptions lead to a mobility which is proportional to the square root of the mean free path.

If the behavior of an electrolytic solution approximates that of its cage model, then it follows that the effect of the electric field is wasted on all ions except the very small fraction which happens to reach the potential barrier summit with approximately zero energy. In this fundamental assumption the cage method differs radically from the Lindemann-Magnus methods. However, their approach to the problem need not be judged in the light of the cage theory. A more serious objection is that these two theories predict entirely too low temperature coefficients of mobility.

The mobility of a Lindemann ion is proportional to $L \cdot T^{-1/2}$, where L is the mean free path. These are the only temperature-variable quantities. According to Lindemann's own calculations, the temperature coefficient of L for potassium ion should be approximately 44 times the coefficient of linear expansion of water. The latter is approximately equal to 0.007 percent per degree, at 18°. Allowing for the variation of $T^{-1/2}$, we find that Lindemann's theory leads to the value 0.13 percent per degree for the temperature coefficient of the mobility of potassium ion. This is 16.5 times smaller than the observed coefficient. Magnus' theory would lead to approximately the same value as Lindemann's does.

IX. THE FREQUENCY OF OSCILLATION WITHIN THE CAGE. THE NUMBER OF OSCILLATIONS BETWEEN JUMPS

In Eq. (12), A is double the frequency of oscillation of the ion within a cage. Since j and Q are known, A can now be calculated. Substituting

$j = 1.12 \times 10^{11} \text{ sec.}^{-1}$ and $Q = 4230$ calories, we get: $A/2 = 8.3 \times 10^{13}$ oscillations per second. Since there is an approximately twofold uncertainty in the value of L , there is a fourfold uncertainty in the value of A .

It is possible to carry out a rough check of this calculation. The "mean free path" of the ion within its cage is given by the ratio of its mean thermal velocity and A . Assuming that the mean thermal velocity of potassium ion is the same as that of a gaseous ion ($M = 39$), its value at 18°C is $4.3 \times 10^4 \text{ cm/sec}$. The "mean free path" is equal to $4.3 \times 10^4 / 16.6 \times 10^{13}$, or $2.6 \times 10^{-10} \text{ cm}$. This value is approximately ten times smaller than the value one would be inclined to predict. However, allowing for the uncertainty in the value of A and for the crudity of the assumption regarding the mean thermal velocity, the agreement is fairly satisfactory.

The number of oscillations between jumps is given by $A/2j$. For potassium ion at 18° this number is 740. It follows that the assumption of complete independence between the directions of two successive jumps is justifiable.

CONCLUSIONS

When we attempt to discover the physical significance of the term "steady migration velocity," as applied to a real solution, we conclude that the term has no meaning, since the ions move violently to and fro and respond to the guiding influence of the electrical field during only a very short fraction of their turbulent existence. We suspect that the discussion of the rate of approach to a steady velocity is meaningless *a fortiori* (Table I, items 10, 11, 12).

When we consider the violence of the Brownian movement and compare it with the placid behavior of the hydrodynamic model (Table I, ratios 16, 19, 20, 22), we are apt to suspect that the violation of some of the fundamental assumptions underlying the derivation of Stokes law would tend to invalidate the conclusions of the hydrodynamic theory. Unfortunately, calculations based on Eq. (3) are not decisive. The computed ionic radii are neither so inaccurate as to discredit this equation, nor are they accurate enough to support it without the introduction of

additional assumptions. Under these circumstances, we have two courses open to us: We may make further attempts to strengthen our confidence in the validity of Eq. (3) by means of mathematical analysis, necessarily complicated. Or we may strike out in a different direction, attempting to build a theory based on a model which approximates more closely a real electrolytic solution. The cage model of liquids offers an approach to such a theory.

The hydrodynamic theory offered a promise of yielding the radii of ions. What promise does the cage model offer? First, the model conforms with the spirit of the times; instead of giving a definite description of the path of an ion, as the hydrodynamic theory does, it describes the migration of the ion in terms of its probable behavior in an electric field.

The hydrodynamic theory cannot possibly be depended on to shed any light on the Brownian movement of either the ion or the solvent molecules. The cage method, based on a recognition of the Brownian movement, offers a promise in this direction. It gives immediately the frequency of cage-to-cage jumps.

The cage method offers a plausible explanation of the high temperature coefficient of slow-moving ions. In hands more expert than the writer's, it may throw light on the nature of hydration and on the mechanism of solvent transport by an electric current. It offers the tempting prospect of discovering a kinetic theory approach to the calculation of the effects of inter-ionic attraction, to supplement the hydrodynamic method of the Debye-Hückel-Onsager theory.

If the present paper succeeds in accelerating even slightly the growing interest in the possibilities inherent in the cage model of liquids, it will have served its purpose.

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