THE QUANTITATIVE ASPECT OF DIFFUSION IN ELECTROLYTE SOLUTIONS

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CONTENTS

I. INTRODUCTION

There are few domains of physical science in which so much experimental effort over nearly a century has yielded so little accurate data as the field of diffusion in liquid systems. The numerical difficulties inherent in the computation of the diffusion coefficients from rate measurements, the elimination of turbulent flow, the very accurate control of temperature, and the analytical accuracy required are all contributing obstacles to the attainment of high accuracy.

In general, the theory of diffusion in liquid systems is undeveloped. It is difficult and complicated and, owing to the scarcity of experimental results of fundamental nature, has not made great progress. However, electrolytes possess certain properties which have made possible the development of an exact theory for very dilute solutions. As the concentrations of strong electrolytes approach zero, the properties of the ions and in particular the mobilities approach additivity. This behavior was utilized by Nernst (71) to compute the limiting value of the diffusion coefficient from the knowledge of the ionic mobilities at infinite dilution. On the other hand, the diffusion coefficient varies with the electrolyte concentration. In dilute solutions, this variation may be theoretically computed because of the fortunate fact that the character of the force between ions is known. The theory of concentrated solutions is obscure because the short-range forces of interaction between the ions and the forces between the ions and the solvent are such that the net influences of all these factors cannot be predicted by Coulombic interaction alone.

In recent years, the diffusion of molecules in liquid media has been the subject of numerous reviews both in journals and in books (13, 19, 30, 72, 107). The modern theory of diffusion of electrolytes and an analysis of the most accurate determinations of diffusion coefficients up to 1943 has been presented in a systematic but specialized form by Harned and Owen (41). More recently, at a colloquium under the auspices of the New York Academy of Sciences on "The Diffusion of Electrolytes and Macromolecules in Solution" (1), a number of specialists have considered many of the aspects of the subject. All of these contributions are devoted to restricted phases of the field and none includes the fundamental theory of irreversible processes.

In this review, as indicated by the preceding table of contents, we shall strive

to coördinate into a logical and reasonably complete treatment the scattered contributions to the theory. Since diffusion comes under the same class of flow phenomena as electrical conductance and heat flow, we shall begin with the general theory of irreversible processes as a necessary foundation for the discussion of electrolytic conductance and diffusion (77, 78). Then, after the introduction of some necessary relations from the interionic attraction theory (17, 18), we shall develop the present theory of the diffusion of electrolytes (79, 80) and finally derive the "dissipation function" for electrolytic conductance and diffusion. This procedure will bring together for the first time the somewhat scattered literature of this subject and provide a phenomenological and theoretical background for the experimental part of the review.

Of the many experimental methods, we shall describe in some detail only those which have led to good numerical results. Fortunately we shall be able to establish values for the differential diffusion coefficient of potassium chloride in dilute aqueous solution (39, 40) which can be used in establishing the theory at concentrations from 0.001 to 0.01 normal and also as a standard for the calibration of diaphragm cells. It is important to note that this makes possible a new field of investigation, since no previous measurements of differential diffusion coefficients of high accuracy have been reported below 0.05 normal concentration.

We conclude with some general considerations concerning the extension of theory to systems of more than two components and with a summary of the present status of the quantitative aspect of the subject.

II. FUNDAMENTAL THEORY AND DEFINITIONS[1]

1. Fick's first law

Although diffusion in liquid solutions was observed by Parrot (81) as early as 1815, the first measurements of consequence were made by Graham (34, 35) and the first theoretical contribution by Adolph Fick (23) in 1855. If the quantity of solute which diffuses through unit area in unit time is $\mathbf{J}$, hereafter denoted "the flow," then Fick's first law takes the form

$$\mathbf{J} \equiv n\mathbf{v} = -\mathfrak{D}\nabla n = -\mathfrak{M}\nabla\mu \qquad (1)$$

where n is the number of molecules of diffusing component per cubic centimeter, $\mathbf{v}$ its velocity, $\mathfrak{D}$ the diffusion coefficient of the solute, and μ its chemical potential. ∇ is the operator "del", and consequently ∇n and $\nabla\mu$ are the gradients of the concentration and chemical potential, respectively.

The flow is usually defined relative to a fixed plane of reference. This is sufficient for many applications, but is not valid for the general theory of the diffusion of electrolytes, since volume changes result from the mixing of the components. This difficulty may be remedied by defining the flow of a component relative to a frame of reference moving with the solvent (80). A bulk velocity defined by

$$\mathbf{v} \equiv \Sigma \mathbf{J}_i \bar{V}_i = \Sigma n_i \mathbf{v}_i \bar{V}_i \qquad (2)$$

[1] As far as possible, the symbols used are those of Harned and Owen (41).

where $\bar{V}_0$, $\bar{V}_1$, $\cdots$ are the partial volumes of the components, may be employed in the general treatment of this phenomenon. For the present, we shall consider only the simpler case where the partial volume effect is omitted.

The form of Fick's law as stated by the last expression on the right of equation 1, which recognizes that the "force" causing diffusion is the gradient of the chemical potential of the diffusing substance, was first suggested by Hartley (42) and is a necessary basis for all our subsequent derivations.[2] Obviously,

$$\mathfrak{D} = \left(\frac{\partial \mu}{\partial n}\right)_{P,T} \mathfrak{M} \tag{3}$$

If the diffusion is restricted to motion in the x-direction only, then Fick's first law assumes the familiar form:

$$\mathbf{J} = -\mathfrak{D}\,\frac{\partial n}{\partial x} \tag{4}$$

This fundamental law for the flow of matter has the same form as that of the flow of electricity (Ohm's law) or the flow of heat (Fourier's law). Here the gradient of the concentration is analogous to the electromotive force and to the gradient of the temperature. In the discussion of the theory of simultaneous irreversible processes, we shall make full use of this analogy and refer to the gradients of concentration, electrical potential, and temperature as "forces" in a generalized sense.

We shall now introduce the relation which defines the activity coefficient ($\zeta \equiv a/n$):

$$\mu = \mu^0 + kT \ln \zeta n \tag{5}$$

where k is the gas constant per molecule, μ is the chemical potential of the diffusing substance, μ^0 is its chemical potential in a standard state, and n is the number of molecules per cubic centimeter. For a real solution, it follows from equations 3 and 5 that

$$n\mathfrak{D} = kT\mathfrak{M}\left[1 + n\,\frac{\partial \ln \zeta}{\partial n}\right] \tag{6}$$

In the limit when n approaches zero and ζ unity

$$\mathfrak{D} = \frac{kT}{n}\,\mathfrak{M} \tag{7}$$

The units in which the above equations have been expressed were chosen because they are convenient for theoretical developments.[3] To convert to more familiar units, we let

$$n = N\bar{n}; \qquad \mu N = \bar{\mu} \tag{8}$$

[2] Nernst's derivations assumed that the "force" which causes migration is the gradient of the osmotic pressure. Later, Schreiner (87) substituted a function of the activity for osmotic pressure.

[3] We draw attention to this rather confusing situation at this juncture so that the reader will have it in mind when more complicated derivations are involved.

where N is Avogadro's number and $\bar{n}$ is in mols per cubic centimeter. With these changes, equation 1 becomes

$$\bar{J} = \bar{n}\mathbf{v} = -\overline{\mathfrak{M}}\nabla\bar{\mu} = -\left(\frac{\mathfrak{M}}{N^2}\right)\nabla\mu \qquad (9)$$

where $\bar{J}$ is the flow in mols per cubic centimeter per second. Further,

$$\mathfrak{D} = \frac{\partial\bar{\mu}}{\partial\bar{n}}\overline{\mathfrak{M}} = 1000\overline{\mathfrak{M}}\frac{\partial\bar{\mu}}{\partial c} \qquad (10)$$

where c is the concentration in mols per liter. For an electrolyte dissociating into ν ions, equation 5 becomes

$$\mu = \mu^0 + \nu kT \ln \zeta_{\pm} n_{\pm} \qquad (11)$$

and

$$c\frac{\partial\bar{\mu}}{\partial c} = \nu RT\left(1 + c\frac{\partial\ln y_{\pm}}{\partial c}\right) \qquad (12)$$

where $y_{\pm}$ is the conventional mean activity coefficient defined on the molar scale (41). In these units the diffusion coefficient is related to $\overline{\mathfrak{M}}$ according to the equation:

$$\mathfrak{D} = \nu 1000 RT \frac{\overline{\mathfrak{M}}}{c}\left(1 + c\frac{\partial\ln y_{\pm}}{\partial c}\right) \qquad (13)$$

2. Fick's second law

By substituting the value of $n\mathbf{v}$ given by equation 1 in the equation of continuity

$$\frac{\partial n}{\partial t} + \nabla\cdot(n\mathbf{v}) = 0 \qquad (14)$$

where $\nabla\cdot$ is recognized as the divergence, we obtain

$$\frac{\partial n}{\partial t} = \nabla\cdot\mathfrak{D}\nabla n \qquad (15)$$

in general and for unidirectional flow

$$\frac{\partial n}{\partial t} = \frac{\partial}{\partial x}\mathfrak{D}\frac{\partial n}{\partial x} \qquad (16)$$

This is the law for the differential diffusion coefficient as defined by equation 1. If $\mathfrak{D}$ is independent of the concentration, then

$$\frac{\partial n}{\partial t} = \mathfrak{D}\frac{\partial^2 n}{\partial x^2} \qquad (17)$$

the familiar expression for Fick's second law.

3. Differential and integral diffusion coefficients

In general $\mathfrak{D}$ is a function of the concentration, so that it is necessary to distinguish between differential ($\mathfrak{D}$) and integral ($\mathfrak{D}_i$) diffusion coefficients.

The integral coefficient is an average value over a concentration range and is given by the integral

$$\mathfrak{D}_i = \frac{1}{n_2 - n_1} \int_{n_1}^{n_2} \mathfrak{D} \, dn \qquad (18)$$

Of these two quantities, the differential diffusion coefficient is the one required by theory. Unfortunately, most measurements in the past yielded integral coefficients and true differential coefficients were rarely determined. Gordon (32) has aptly described the situation: "The resulting confusion has had some unfortunate consequences, since the 'diffusion constant' is usually only a constant in the Pickwickian sense of the term. Thus, one finds the quantity determined in an experiment in which a solution, initially decinormal, is allowed to diffuse into water, referred to as the 'diffusion constant for 0.1 N.' The fact that it could, with equal justice, be spoken of as the value at infinite dilution is conveniently ignored." We shall have occasion later to discuss Gordon's contribution to the clarification of this situation.

If measurements of sufficient accuracy can be obtained in the later stages of diffusion when $(n_2 - n_1)$ becomes small, the value of $\mathfrak{D}_i$ will approach closely the value of $\mathfrak{D}$ (58). Later, we shall discuss conductance measurements which take full advantage of this fact.

III. GENERAL THEORY OF IRREVERSIBLE PROCESSES (77, 78)

A detailed presentation of the theory of diffusion of electrolytes requires an exposition of the fundamental principles which underlie the behavior of combined irreversible processes. As illustrations of phenomena in which two or more irreversible processes may proceed simultaneously, we cite thermoelectric phenomena (Peltier effect), heat conduction in anisotropic media, and transport processes in electrolytic solutions. In the Peltier effect, the flow of electric current in a system of conductors of different metals will produce heat, and conversely, if the metallic junctions are maintained at different temperatures, electricity will flow. In anisotropic media, temperature gradients and the corresponding "flows" of heat will be different along the three space coördinates required to express the phenomena. General equations for this problem will involve combined relations of the flows in three directions. In electrolytic diffusion where two or more ions are present, interactions between the individual transport of the ions occur. The general theory of the reciprocal relations in such combined processes has been developed by Onsager (77, 78). It forms an essential background for the theory of electrolytic conductance and diffusion. A general but abbreviated presentation of this theory will be sufficient for our immediate purpose.

A. RECIPROCAL RELATIONS IN IRREVERSIBLE PROCESSES (THEORY OF ONSAGER)

1. Introduction to phenomenological relations

The earliest reciprocal relation of the coupled processes involved in thermoelectric phenomena (Peltier effect) was recognized by Thomson (Lord Kelvin)

(95). In the thermoelectric circuit let $\mathbf{J}_1$ be the electric current and $\mathbf{J}_2$ the heat flow. Let $\mathbf{X}_1$ equal the electromotive force which drives the electric current and $\mathbf{X}_2$ the "force" in corresponding units which causes the flow of heat and will be proportional to the gradient of the temperature. Then

$$\mathbf{X}_2 = -\frac{1}{T}\nabla T \tag{19}$$

where T is the absolute temperature. If the flows of current and heat happen to be independent, then

$$\mathbf{X}_1 = R_1\,\mathbf{J}_1$$
$$\mathbf{X}_2 = R_2\,\mathbf{J}_2 \tag{20}$$

where R_1 and R_2 are the electrical and thermal resistances, respectively. However, since the thermal and electrical processes may interact, it seemed probable to Thomson that the more complicated phenomenological equations

$$\mathbf{X}_1 = R_{11}\,\mathbf{J}_1 + R_{12}\,\mathbf{J}_2$$
$$\mathbf{X}_2 = R_{21}\,\mathbf{J}_1 + R_{22}\,\mathbf{J}_2 \tag{21}$$

must be employed. He also thought it plausible that the assumption of the reciprocal relation

$$R_{21} = R_{12} \tag{22}$$

was correct. This assumption has been generally accepted, since it has been confirmed by the best available measurements.

Thermoelectric phenomena in electrolytes investigated by Eastman (21) are examples of a situation where three simultaneous processes are superimposed on thermodynamic equilibrium. Imagine two chemically identical reversible electrodes connected by a solution of a suitable electrolyte and let these be immersed in thermostats at two different temperatures. An electromotive force will be generated and electric current $\mathbf{J}_1$ will flow. Simultaneously, diffusion of matter and transfer of heat will occur. If $\mathbf{J}_2$ is the flow of matter and $\mathbf{J}_3$ that of heat, the extension of the previous result for coupled processes will lead to the three phenomenological equations

$$\mathbf{J}_1 = L_{11}\mathbf{X}_1 + L_{12}\mathbf{X}_2 + L_{13}\mathbf{X}_3$$
$$\mathbf{J}_2 = L_{21}\mathbf{X}_1 + L_{22}\mathbf{X}_2 + L_{23}\mathbf{X}_3 \tag{23}$$
$$\mathbf{J}_3 = L_{31}\mathbf{X}_1 + L_{32}\mathbf{X}_2 + L_{33}\mathbf{X}_3$$

and reciprocal relations of the type

$$L_{12} = L_{21}; \qquad L_{13} = L_{31}; \qquad L_{23} = L_{32} \tag{24}$$

may be expected to occur.

Diffusion of s kinds of ions in a liquid medium is another phenomenon which may be expected to follow a similar pattern, provided interactions take place between ions of different kinds. In this case, equation 23 may be written in the general form

$$\mathbf{J}_i = -\sum_{k=1}^{s} \mathfrak{M}_{ik}\nabla\mu_k \tag{25}$$

where $\nabla\mu_k$, the gradient of the chemical potential of each ion, is the analogue of the force $\mathbf{X}_k$, and $\mathfrak{M}_{ik}$ corresponds to L_{ik}.   Here again, we suspect that

$$\mathfrak{M}_{ik} = \mathfrak{M}_{ki} \tag{26}$$

All these considerations suggest that there may be a general class of reciprocal relations in irreversible processes which may be derived from fundamental considerations of molecular mechanics.

2. Reciprocal relations in chemical reactions

Consideration of a triangular monomolecular chemical reaction in which three forms A, B, C of a substance exist simultaneously in the same phase yields analogous results.   In this case, represented by the scheme

$$\begin{array}{c} A \\ \diagup \quad \diagdown \\ C \rightleftharpoons B \end{array}$$

each of the forms may change into either of the others.   According to the simple mass action law, the fraction of A molecules which changes into B in the short time Δt will be $k_{BA}\Delta t$, where k_{BA} is the proportionality constant.   The rates of change of the concentrations n_A, n_B, n_C will be given by

$$\frac{dn_A}{dt} = -(k_{BA} + k_{CA})n_A + k_{AB}n_B + k_{AC}\,\bar{n}_C$$

$$\frac{dn_B}{dt} = k_{BA}\,n_A - (k_{AB} + k_{CB})n_B + k_{BC}n_C \tag{27}$$

$$\frac{dn_C}{dt} = k_{CA}\,n_A + k_{CB}n_B - (k_{AC} + k_{BC})n_C$$

If all the coefficients are $\gtrless 0$, then at equilibrium finite concentrations $\bar{n}_A$, $\bar{n}_B$, $\bar{n}_C$ are assured and these are given by relations of the type

$$\frac{d\bar{n}_A}{dt} = -(k_{BA} + k_{CA})\bar{n}_A + k_{AB}\bar{n}_B + k_{AC}\bar{n}_C = 0 \tag{28}$$

and

$$\bar{n}_A + \bar{n}_B + \bar{n}_C = n_A + n_B + n_C = n \tag{29}$$

In addition to these restrictions, physical chemists have assumed that when equilibrium is reached each individual reaction must be balanced microscopically. Thus, every transition from A to B will occur as frequently as the reverse transition from B to A.   If then the equilibrium concentrations $\bar{n}_A$, $\bar{n}_B$, and $\bar{n}_C$ are known, three further relations

$$k_{BA}\bar{n}_A = k_{AB}\bar{n}_B$$

$$k_{CB}\bar{n}_B = k_{BC}\bar{n}_C \tag{30}$$

$$k_{AC}\bar{n}_C = k_{CA}\bar{n}_A$$

are imposed. These correspond to the reciprocal relations in the phenomeno-logical equation (equation 23) and lead to one relation between the velocity constants:

$$k_{AC}k_{CB}k_{BA} = k_{AB}k_{BC}k_{CA} \tag{31}$$

Now this relation is not necessary to meet the thermodynamic requirement which will be satisfied when equilibrium is established by any set of positive values of the velocity constants. Indeed, other mechanisms can be postulated in which the detailed balancing of all the reactions does not occur. But these other mechanisms are not in accord with the idea that molecular mechanics and the dynamics of ordinary mechanics of conservative systems are fundamentally similar. With the exception of cases which involve Coriolis forces and external magnetic fields, the law of dynamic reversibility requires that if all the velocities of all the particles of a conservative dynamical system are reversed, the particles will retrace their former paths, thus reversing the previous succession of configurations. Applied to molecular mechanics, the assumption of dynamic reversibility implies that, if we wait until equilibrium is established, then every type of motion has a probability equal to that of its reverse. This implies the assumption made above that when the molecule A changes a given number of times to molecule B, the reverse transition of B to A takes place just as often.

In order to complete the analogy between the reciprocal relations (relations 24) and the phenomenological equations (equations 23), we must find the expressions analogous to J_1, J_2, J_3 and X_1, X_2, X_3. To this end we employ the thermodynamic equation for the free energy at constant temperature and pressure of a single reaction in a perfect gas system, namely:

$$F_{P,T} = F^0_{P,T} + RT\left[n_A \ln\frac{n_A}{\bar{n}_A} + n_B \ln\frac{n_B}{\bar{n}_B} + n_C \ln\frac{n_C}{\bar{n}_C}\right] \tag{32}$$

According to the condition specified by equation 29, it follows that:

$$\delta F_{P,T,n} = RT\left[\left(\ln\frac{n_A}{\bar{n}_A}\right)\delta n_A + \left(\ln\frac{n_B}{\bar{n}_B}\right)\delta n_B + \left(\ln\frac{n_C}{\bar{n}_C}\right)\delta n_C\right] \tag{33}$$

Let

$$x_A = n_A - \bar{n}_A, \text{ etc.} \tag{34}$$

and write δF in the form

$$\delta F = -X_A\delta x_A - X_B\delta x_B - X_C\delta x_C \tag{35}$$

To obtain proportionality between the "forces" X_A, X_B, and X_C and the displacements x_A, x_B, and x_C, it is necessary to impose the restriction that the system is nearly in equilibrium. Thus

$$x_A << \bar{n}_A \text{ etc.} \tag{36}$$

in which case

$$\mathbf{X}_A = -RT \ln \frac{n_A}{\bar{n}_A} \sim - \frac{RT}{\bar{n}_A} x_A$$

$$\mathbf{X}_B \sim - \frac{RT}{\bar{n}_B} x_B \tag{37}$$

$$\mathbf{X}_C \sim - \frac{RT}{\bar{n}_C} x_C$$

From equations 28 and 36, it follows that

$$\dot{x}_A = \frac{dx_A}{dt} = -(k_{BA} + k_{CA})x_A + k_{AB}x_B + k_{AC}x_C \tag{38}$$

or finally by application of equations 37:

$$\dot{x}_A = (k_{BA} + k_{CA}) \frac{\bar{n}_A}{RT} \mathbf{X}_A - \frac{k_{AB}\bar{n}_B}{RT} \mathbf{X}_B - \frac{k_{AC}\bar{n}_C}{RT} \mathbf{X}_C$$

$$\dot{x}_B = - \frac{k_{BA}\bar{n}_A}{RT} \mathbf{X}_A + (k_{AB} + k_{CB}) \frac{\bar{n}_B}{RT} \mathbf{X}_B - \frac{k_{BC}\bar{n}_C}{RT} \mathbf{X}_C \tag{39}$$

$$\dot{x}_C = - \frac{k_{CA}\bar{n}_A}{RT} \mathbf{X}_A - \frac{k_{CB}\bar{n}_B}{RT} \mathbf{X}_B + (k_{AC} + k_{BC}) \frac{\bar{n}_C}{RT} \mathbf{X}_C$$

If this be compared to equation 23, it is obvious that the analogy is complete, including all the reciprocal relations given by equations 24 and 30. Here $\dot{x}_A$, $\dot{x}_B$, $\dot{x}_C$ and the coefficients of $\mathbf{X}_A$, $\mathbf{X}_B$, $\mathbf{X}_C$ correspond to J_1, J_2, J_3 and L_{11}, L_{12}, $\cdots L_{ik} \cdots L_{33}$, respectively.

This conclusion suggests forcibly that general reciprocal relations may be deduced upon the basis of the principle of microscopic reversibility. To this end it is necessary to develop the theory by a method which involves no special mechanism. The only way in which this result can be achieved is by considering the *fluctuations* in a system which is in a normal state of thermodynamic equilibrium.

B. THE DERIVATION OF RECIPROCAL RELATIONS IN IRREVERSIBLE PROCESSES FROM THE GENERAL THEORY OF FLUCTUATIONS[4]

1. Formulation of the problem

By utilizing the fundamental equation of Boltzmann, relating entropy S and probability W

$$S = k \log W + \text{constant} \tag{40}$$

and by considering fluctuations in a set of variables α_1, α_2, $\cdots \alpha_n$ which measure displacements of matter, heat, and electricity, reciprocal relations in the simul-

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[4] We have not included in this review Onsager's derivation of reciprocal relations for the conduction of heat in anisotropic (triclinic) crystals.

taneous transport of these quantities will be derived by means of the principle of microscopic reversibility as applied to these fluctuations.

We shall first define the quantities which correspond to the "flow" $\mathbf{J}$ and the "force" $\mathbf{X}$ and the coefficients in the phenomenological equation (equation 23). We start with the fundamental thermodynamic equation

$$\delta S = \frac{1}{T} (\delta E - \delta A) - \frac{\mu}{T} \delta m \tag{41}$$

where E, A, and m are the energy, work content, and mass of substance, respectively, and μ is the Gibbs chemical potential. The entropy will be determined by the heat displacements, α_1, α_2, α_3, so that

$$S = \sigma(\alpha_1, \alpha_2, \alpha_3) \tag{42}$$

Now, if there exists a uniform gradient of $1/T$ in the r-direction, a quantity of heat $\delta Q = (\delta E - \delta A)$ will be transferred a distance Δx_r

$$\delta S = \delta Q \cdot \Delta \left(\frac{1}{T}\right) = \delta Q \cdot \Delta x_r \frac{\partial (1/T)}{\partial x_r} = \delta \alpha_r \frac{\partial (1/T)}{\partial x_r} \tag{43}$$

and

$$\frac{\partial \sigma}{\partial x_r} = \frac{\partial (1/T)}{\partial x_r} \tag{44}$$

Similarly, if α is the displacement of matter

$$\frac{\partial \sigma}{\partial \alpha} = - \frac{\partial (\mu/T)}{\partial x} \tag{45}$$

and, if α is a displacement of electrical charge and $\mathbf{X}$ is the electrical field intensity:

$$\frac{\partial \sigma}{\partial \alpha} = \frac{\mathbf{X}}{T} \tag{46}$$

We note that the right members of these equations all correspond to the "forces" in equation 23 or equal $\mathbf{X}_1$, $\mathbf{X}_2$, $\mathbf{X}_3$, divided by T.

Now, the flows of heat, matter, and electricity are proportional to the gradients of the corresponding potentials. Thus,

$$\mathbf{J} \sim -\operatorname{grad} T = -\nabla T \tag{47}$$

$$\mathbf{J} \sim \mathbf{X} \tag{48}$$

$$\mathbf{J} \sim -\nabla \mu \tag{49}$$

for the transport of heat, electricity, and matter, respectively. In general, these relations are given by

$$\frac{d\alpha_r}{dt} = \dot{\alpha}_r \sim \frac{\partial S}{\partial \alpha_r} \tag{50}$$

where $\dot{\alpha}_r$ is the flow J except for a volume factor. When different transport processes (n in number) interfere with each other, the flow is a function of the different kinds of displacements ($\alpha_1, \alpha_2, \cdots \alpha_n$) and

$$\dot{\alpha}_r = G_{r1} \frac{\partial \sigma}{\partial \alpha_1} + \cdots + G_{rn} \frac{\partial \sigma}{\partial \alpha_n} \quad (r = 1, 2, \cdots n) \tag{51}$$

and $S = \sigma(\alpha_1, \alpha_2, \cdots \alpha_n)$. We shall proceed to show that general reciprocal relations

$$G_{rs} = G_{sr} \tag{52}$$

can be deduced by application of the principle of microscopic reversibility.

2. General theory of fluctuations

Statistical mechanics applied to molecules provides an explanation of thermodynamic equilibrium as a statistical equilibrium of elementary processes among large numbers of molecules. The fundamental relation of Boltzmann

$$S = k \log W + \text{constant} \tag{53}$$

relating the entropy S with the thermodynamic probability W, is the most suitable as a basis for a theory of fluctuations from the state of equilibrium. W is the number of ways in which a given thermodynamic state may be realized and for a state of thermodynamic equilibrium is in general a very large number. Thus, a thermodynamic equilibrium state, specified by the energy and external variables (pressure, volume, etc.), is incompletely determined by molecular theory.

The Boltzmann constant k is 1.380×10^{-16} ergs per degree, so the probability of a deviation involving a change in entropy ΔS,

$$e^{\Delta S/k} \tag{54}$$

is appreciable when ΔS and k are of the same order of magnitude. Fluctuations of this order have been observed in a few favorable cases, as with liquids near the critical point and the Brownian movement of particles in liquids. To compute W, a complete molecular theory of the system is required. If the molecules of the system obey the laws of classical mechanics, W equals a gross extension in phase-space.

Consider a system of constant energy in which the external parameters (volume, pressure, etc.) and the number of atoms and molecules are fixed. If this system is isolated for a sufficient length of time to reach equilibrium, then we expect that it will have passed through all the states $\Gamma^1, \Gamma^2, \cdots \Gamma^l$ consistent with the conditions of isolation. Over a long time period t the system will spend a time t_r in the state Γ^r, and we may expect that $t_1, t_2, \cdots t_l$ will be proportional to the phase regions, $W_1, W_2, \cdots W_l$, respectively. Upon this assumption $W_1, W_2, \cdots$ are defined as proportional to $t_1/t, t_2/t \cdots$. Boltzmann's principle then may be stated in the form

$$S_r = k \log (t_r/t) + \text{constant} \tag{55}$$

where S_r is the entropy of the state Γ^r and t_r/t is the probability of this state.

It is necessary to define the probability in terms of the measurable variables $\alpha_1, \ \alpha_2, \ \cdots \ \alpha_n$. For this purpose, we introduce the distribution function $f(\alpha_1, \ \alpha_2, \ \cdots \ \alpha_n)$ and to meet the statistical requirements the probability of the state Γ^r will be equal to the integral of this function over the region

$$\alpha'^{(r)}_1 < \alpha_1 < \alpha'^{(r)}_1 + \Delta\alpha_1$$
$$\bullet$$
$$\bullet$$
$$\bullet$$
$$\alpha'^{(r)}_n < \alpha_n < \alpha'^{(r)}_n + \Delta\alpha_r$$

Equation 55 then becomes

$$S_r = k \log f(\alpha'^{(r)}_1, \alpha'^{(r)}_2, \cdots \alpha'^{(r)}_n) + k \log \Delta\alpha_1, \Delta\alpha_2, \cdots \Delta\alpha_n + \text{constant} \quad (56)$$

The magnitudes $\Delta\alpha$ should be of the same order as the fluctuations, in which case the product, $\Delta\alpha_1 \Delta\alpha_2 \cdots \Delta\alpha_n$, varies so little for a change of entropy $S' - S''$ that the quantity $k \log [(\Delta\alpha'_1 \cdots \Delta\alpha'_n)/(\Delta\alpha''_1 \cdots \Delta\alpha''_n)]$ is negligible in comparison to $k \log [f(\alpha'_1, \alpha'_2, \cdots \alpha'_n)/f(\alpha''_1, \alpha''_2, \cdots \alpha''_n)]$. Consequently, equation 56 may be written

$$S_r = k \log f(\alpha'^{(r)}_1, \alpha'^{(r)}_2, \cdots \alpha'^{(r)}_n) + \text{constant} \quad (57)$$

Up to the present, an actual thermodynamic state is defined completely by the variables $\alpha_1, \alpha_2, \cdots \alpha_n$. Einstein (22) pointed out that the Boltzmann relation is valid for cases when this definition is not complete and may be applied to fluctuations from this equilibrium state. The probabilities of the different states will be of different magnitudes. Of these, a chosen thermodynamic state given by a set of variables, $\alpha_1, \alpha_2, \cdots \alpha_n$, will occur much more frequently than all the other states. Thus, we adopt the convention that the greatest entropy occurs when the variables have the values $\alpha'_1, \alpha'_2, \cdots \alpha'_n$ and this we denote by

$$\sigma_{1\cdots n}(\alpha'_1, \alpha'_2, \cdots \alpha'_n) \quad (58)$$

The corresponding thermodynamic state will be specified by

$$\Gamma_{1\cdots n}(\alpha'_1, \alpha'_2, \cdots \alpha'_n) \quad (59)$$

Then

$$\sigma_{1\cdots n}(\alpha'_1, \alpha'_2, \cdots \alpha'_n) = k \log f(\alpha'_1, \alpha'_2, \cdots \alpha'_n) + \text{constant} \quad (60)$$

measures the probability for finding the variables $\alpha_1, \cdots \alpha_n$ with the values $\alpha'_1, \cdots \alpha'_n$.

For a single variable α_p, we may write

$$\sigma_p(\alpha_p) = k \log f_p(\alpha_p) + \text{constant} \quad (61)$$

where $\sigma(\alpha'_p)$ is the greatest possible entropy when $\alpha_p = \alpha'_p$. Upon differentiation of this relation, we obtain

$$k \frac{df_p(\alpha_p)}{d\alpha_p} = f_p(\alpha_p) \frac{d\sigma_p}{d\alpha_p} \quad (62)$$

Further

$$\int_{-\infty}^{\infty} f_p(\alpha_p) \, \mathrm{d}\alpha_p = 1 \tag{63}$$

Now let the entropy $\sigma_p(\alpha_p)$ be a maximum when α_p equals α_p^0 and assume that $(\alpha_p - \alpha_p^0)f_p(\alpha_p)$ approaches zero for large values of $|\alpha_p - \alpha_p^0|$. If this latter assumption is not true, the function must have an infinite number of maxima. With these premises, an important result is obtained by evaluating the average

$$\overline{(\alpha_p - \alpha_p^0) \, \mathrm{d}\sigma_p/\mathrm{d}\alpha_p} = \int_{-\infty}^{\infty} (\alpha_p - \alpha_p^0)(\mathrm{d}\sigma_p/\mathrm{d}\alpha_p)f(\alpha_p) \, \mathrm{d}\alpha_p$$

$$= k \int_{-\infty}^{\infty} (\alpha_p - \alpha_p^0)(\mathrm{d}f(\alpha_p)/\mathrm{d}\alpha_p) \, \mathrm{d}\alpha_p$$

$$= k[(\alpha_p - \alpha_p^0)f_p(\alpha_p)]_{-\infty}^{\infty} - k \int_{-\infty}^{\infty} f_p(\alpha_p) \, \mathrm{d}\alpha_p \tag{64}$$

upon integration by parts. The first term vanishes and since the whole integral is unity

$$\overline{(\alpha_p - \alpha_p^0)\mathrm{d}\sigma_p/\mathrm{d}\alpha_p} = -k \tag{65}$$

Similarly, it can be shown

$$\overline{(\alpha_q - \alpha_q^0)\partial\sigma_{1\cdots n}/\partial\alpha_p} = \begin{cases} -k; & p = q \\ 0; & p \neq q \end{cases} \tag{66}$$

These averages involving the fluctuations $(\alpha_p - \alpha_p^0)$ are important in the subsequent derivations.

3. The regression of fluctuations

From an empirical point of view, the initial thermodynamic state has been employed to predetermine the course of an irreversible process according to definite laws, such as those for the flows of heat, electricity, and matter. Since molecular theory cannot completely define a thermodynamic state, it cannot completely predetermine an irreversible process. Nevertheless, the predictions of irreversible process from empirical laws may be interpreted statistically and with practical certainty from averages of a large number of cases of processes starting from the same initial state of thermodynamic equilibrium.

Now, consider the fluctuations of the variables of an isolated system over a long period of time. Whenever $\alpha_1, \alpha_2, \cdots \alpha_n$ have the values $\alpha_1', \alpha_2', \cdots \alpha_n'$, we record their values τ seconds later, and denote their averages by

$$\bar{\alpha}_1(\tau, \alpha_1', \cdots \alpha_n'), \cdots \bar{\alpha}_n(\tau, \alpha_1', \cdots \alpha_n') \tag{67}$$

Almost every time when $\alpha_1 = \alpha_1', \cdots \alpha_n = \alpha_n'$, the system will be in the phenomenological state

$$\Gamma'(1 \cdots n) = \Gamma(\alpha_1', \cdots \alpha_n') \tag{68}$$

and the average course of an irreversible process following this state, and described by the averages

$$\bar{\alpha}_1'(\tau, \Gamma_{1\cdots n}'), \cdots \bar{\alpha}_n(\tau, \Gamma_{1\cdots n}') \tag{69}$$

will be known from macroscopic experiments and may be regarded as properties of the state $\Gamma_{1\cdots n}'$. The "normal" properties corresponding to $\alpha_1', \cdots \alpha_n'$ of the fluctuating quantities $\alpha_1, \cdots \alpha_n$ are certainly those of the state $\Gamma_{1\cdots n}'$. Whether these "normal" and average values are interchangeable must be determined from consideration of each case. If this interchange is assumed, the relation

$$\bar{\alpha}_i(\tau, \alpha_1', \cdots \alpha_n') = \bar{\alpha}_i(\tau, \Gamma_{1\cdots n}'), \qquad i = 1, \cdots n \tag{70}$$

may be employed as a rule for predicting the average regression of fluctuations from the laws of irreversible processes.

4. The derivation of reciprocal relations from the theory of microscopic reversibility applied to fluctuations

We define the function A_{ji} by the equation

$$A_{ji}(\tau) \equiv \overline{\alpha_j(t)\alpha_i(t + \tau)} = \overline{\alpha_j'(t)\alpha_i(\tau, \alpha_j')} \tag{71}$$

Thus, whenever $\alpha_j = \alpha_j'$, we record α_i τ seconds later and denote it by $\alpha_i(t + \tau)$. $A_{ji}(\tau)$ may also be defined by the time integral

$$A_{ji}(\tau) \equiv \lim_{t'' \to \infty} \frac{1}{t'' - t'} \int_{t'}^{t''} \alpha_j(t)\alpha_i(t + \tau)\, \mathrm{d}t \tag{72}$$

We shall now assume that the variables $\alpha_1, \alpha_2, \cdots \alpha_n$ represent deviations from the state of equilibrium in which their average values $\bar{\alpha}_1, \cdots \bar{\alpha}_n$ as well as their normal values α_j^0 vanish, or

$$\bar{\alpha}_i = \alpha_i^0 = 0, \qquad (i = 1, \cdots n) \tag{73}$$

This will be consistent with the evaluation of the averages given by equations 65 and 66, which depend upon the Boltzmann equation.

Now, if α_j and α_i are suitable "reversible" variables, the principle of microscopic reversibility requires that

$$A_{ji} = \overline{\alpha_j(t)\alpha_i(t + \tau)} = \overline{\alpha_i(t)\alpha_j(t + \tau)} = A_{ij} \tag{74}$$

This means that the event $\alpha_j = \alpha_j'$ followed τ seconds by $\alpha_i(t + \tau)$ occurs just as frequently as the event $\alpha_i = \alpha_i'$ followed τ seconds later by $\alpha_j(t + \tau)$.

Now, consider the type of irreversible process starting from the state $\Gamma_{1\cdots n}$ which can be described by the linear differential equations

$$\frac{\mathrm{d}\bar{\alpha}_i}{\mathrm{d}t} = \dot{\alpha}_i = \sum_{r=1}^{n} G_{ir} \frac{\partial \sigma_{1\cdots n}(\alpha_1, \alpha_2, \cdots \alpha_n)}{\partial \alpha_r}; \qquad (i = 1, \cdots n) \tag{75}$$

previously expressed by equation 51. Introducing relation 70 between average and normal values, we obtain

$$\bar{\alpha}_i(\tau, \alpha'_j) = \bar{\alpha}_i(\tau, \Gamma'_j) \tag{76}$$

in which Γ'_j is the state of maximum entropy for a given value of α'_j, characterized by the relations

$$\alpha_j = \alpha'_j \tag{77}$$

$$\frac{\partial \sigma_{1\cdots n}}{\partial \alpha_r} = 0; \qquad (r \neq j) \tag{78}$$

and consequently,

$$\frac{\partial \sigma_{1\cdots n}}{\partial \alpha_j} = \left[\frac{d\sigma_j}{d\alpha_j}\right]_{\alpha_j = \alpha'_j} \tag{79}$$

For a short time integral, equation 75 leads to

$$\bar{\alpha}_i(\Delta t, \alpha'_j) = \bar{\alpha}_i(0, \alpha'_j) + \dot{\alpha}_i \Delta t$$
$$= \bar{\alpha}_i(0, \alpha'_j) + \sum_{r=1}^{n} G_{ir} \frac{\partial \sigma_{1\cdots n}}{\partial \alpha_r} \Delta t \tag{80}$$

whence from equations 77, 78, and 79:

$$\bar{\alpha}_i(\Delta t, \alpha'_j) = \bar{\alpha}_i(0, \alpha'_j) + G_{ij} \frac{d\sigma(\alpha'_j)}{d\alpha_j} \Delta t \tag{81}$$

Therefore, $A_{ji}(\Delta t)$ (equation 71) may be written

$$A_{ji}(\Delta t) = \overline{\alpha'_j(t)\alpha_i(t + \Delta t)} = \overline{\alpha'_j \alpha_i(0, \alpha'_j)} + G_{ij}\Delta t \overline{\alpha_j \frac{d\sigma_j}{d\alpha_j}} \tag{82}$$

Since α_j is a small fluctuation from the equilibrium, it corresponds to $\overline{(\alpha_p - \alpha_p^0)}$ in equation 65 and consequently $\overline{\alpha_j d\sigma_j/d\alpha_j} = -k$. Hence,

$$A_{ji}(\Delta t) = A_{ji}(0) - k\Delta t G_{ij} \tag{83}$$

and, similarly,

$$A_{ij}(\Delta t) = A_{ij}(0) - k\Delta t G_{ji} \tag{84}$$

The condition of microscopic reversibility, $A_{ji} = A_{ij}$, leads immediately to the general reciprocal relation

$$G_{ji} = G_{ij} \tag{85}$$

From this derivation, the importance of considering fluctuations from the thermodynamic equilibrium state becomes clear. The use of the Boltzmann relation leads to the simple introduction of the constant k in the above relations.

It should now be emphasized that these general reciprocal relations apply to systems whose macroscopic laws may be derived from initial thermodynamic conditions. Consequently, they are generally valid for laminar flow of liquids, conductance of heat, conductance of electricity, and the flow of matter in which no turbulence occurs. They are not valid for irreversible processes involving

Coriolis forces and the presence of external magnetic fields where it is known that the principle of dynamic reversibility no longer holds.

5. The principle of the least dissipation of energy. The dissipation function

It is now possible to define a dissipation function for irreversible processes which has a statistical significance similar to that of the entropy. Equation 75 may be written

$$\frac{\partial \sigma_{1 \cdots n}(\alpha_1, \alpha_2, \cdots \alpha_n)}{\partial \alpha_i} = \sum_{r=1}^{n} \rho_{ir} \dot{\alpha}_r ; \qquad (i = 1, 2, \cdots n) \tag{86}$$

where ρ_{ij} and G_{ij} are related by the well-known equation

$$\sum_{r=1}^{n} \rho_{ir} G_{rj} = \sum_{r=1}^{n} G_{ir} \rho_{rj} = \delta_{ij} = \begin{cases} 1, & (i = j) \\ 0, & (i \neq j) \end{cases} \tag{87}$$

The coefficients ρ_{ij} form the inverse matrix of G_{ij}. The symmetry conditions expressed by equation 85 become

$$\rho_{ij} = \rho_{ji}; \qquad (i = 1, 2, \cdots n) \tag{88}$$

We now define the *dissipation function* by

$$\Phi(\dot{\alpha}, \dot{\alpha}) \equiv \tfrac{1}{2} \sum_{i,j} \rho_{ij} \dot{\alpha}_i \dot{\alpha}_j \tag{89}$$

Utilizing the symmetry condition, $\rho_{ij} = \rho_{ji}$, we find from equations 86 and 89 that

$$\frac{\partial \sigma_{1 \cdots n}(\alpha_1, \cdots \alpha_n)}{\partial \alpha_i} = \frac{\partial \Phi(\dot{\alpha}, \dot{\alpha})}{\partial \dot{\alpha}_i} \tag{90}$$

Further, we define $\dot{S}(\alpha, \dot{\alpha})$ by

$$\dot{S}(\alpha, \dot{\alpha}) \equiv \sum_{r=1}^{n} \frac{\partial \sigma_{1 \cdots n}}{\partial \alpha_r} \dot{\alpha}_r \tag{91}$$

for the rate of increase of entropy.

If we adopt the convention that the velocities, $\dot{\alpha}_1, \dot{\alpha}_2, \cdots \dot{\alpha}_n$, are the only variables, we may obtain a variation principle in the form

$$\delta[\dot{S}(\alpha, \dot{\alpha}) - \Phi(\dot{\alpha}, \dot{\alpha})] = 0 \tag{92}$$

for according to equation 90,

$$\delta[\dot{S}(\alpha, \dot{\alpha}) - \Phi(\dot{\alpha}, \dot{\alpha})] = \sum_{i=1}^{n} \left(\frac{\partial \sigma_{1 \cdots n}}{\partial \alpha_i} - \frac{\partial \Phi}{\partial \dot{\alpha}_i} \right) \delta\dot{\alpha}_i = 0 \tag{93}$$

This is a generalization of Lord Rayleigh's "principle of the least dissipation of energy." The dissipation function according to equations 86, 87, and 88 equals one-half the rate of increase of entropy

$$2\Phi(\dot{\alpha}, \dot{\alpha}) = \dot{S}(\alpha, \dot{\alpha}) \tag{94}$$

and

$$\Phi(\dot{\alpha}, \dot{\alpha}) = \frac{1}{2} \sum_{i,j} \rho_{ij} \dot{\alpha}_i \dot{\alpha}_j = \frac{1}{2} \sum_i \dot{\alpha}_i \frac{\partial \Phi}{\partial \dot{\alpha}_i} \tag{95}$$

Since according to thermodynamics $\dot{S} \geqq 0$, $\Phi(\dot{\alpha}, \dot{\alpha})$ is positive, and therefore the variation given by equation 92 is the condition for a maximum. Thus,

$$\dot{S}(\alpha, \dot{\alpha}) - \Phi(\dot{\alpha}, \dot{\alpha}) = \text{maximum} \tag{96}$$

This quantity is similar to the entropy in reversible processes, and it is clear from the preceding discussion that it depends on the existence of reciprocal relations.

6. Condensed summary and formulation

We have noted that the quantities $\partial\sigma/d\alpha$ as expressed by equations 44, 45, and 46 correspond to "the forces" $\mathbf{X}_1$, $\mathbf{X}_2$, and $\mathbf{X}_3$ in the phenomenological equations with which we introduced the subject, and that $\dot{\alpha}_r$ corresponds to the "flows" $\mathbf{J}_1$, $\mathbf{J}_2$, $\mathbf{J}_3$. If ρ_{ir} be replaced by R_{ir}, then equation 86 for three processes may be written in the expanded form

$$\mathbf{X}_1 = R_{11} \mathbf{J}_1 + R_{12} \mathbf{J}_2 + R_{13} \mathbf{J}_3$$

$$\mathbf{X}_2 = R_{21} \mathbf{J}_1 + R_{22} \mathbf{J}_2 + R_{23} \mathbf{J}_3 \tag{97}$$

$$\mathbf{X}_3 = R_{31} \mathbf{J}_1 + R_{32} \mathbf{J}_2 + R_{33} \mathbf{J}_3$$

where R_{11} etc. are related to L_{11} etc. in equation 23 by the transformation equations

$$\sum_{m=1}^{3} L_{im} R_{mk} = \sum_{m=1}^{3} R_{im} L_{mk} = \delta_{ik} = \begin{cases} 1, & i = k \\ 0, & i \neq k \end{cases} \tag{98}$$

and where the reciprocal relations

$$R_{12} = R_{21}; \qquad R_{13} = R_{31}; \qquad R_{32} = R_{23} \tag{99}$$

$$L_{12} = L_{21}; \qquad L_{13} = L_{31}; \qquad L_{32} = L_{23} \tag{100}$$

are valid. The dissipation function becomes

$$2\Phi(\mathbf{J}, \mathbf{J}) \equiv \frac{1}{T} \sum_{i,k} R_{ik} \mathbf{J}_i \mathbf{J}_k \tag{101}$$

Although these symmetry conditions have not been tested experimentally, the preceding argument and experiments on thermoelectric phenomena, cells with liquid junction, etc. lend confidence to their fundamental correctness. If these reciprocal relations are valid for a given combination of processes, then the dissipation function may be expressed by equation 101 and the function $\dot{S}(\alpha, \dot{\alpha}) - \Phi(\dot{\alpha}, \dot{\alpha})$ will be a maximum as required by equation 96. For the process of diffusion in a system of any number of components, the reciprocal relation $\mathfrak{M}_{ik} = \mathfrak{M}_{ki}$ (equation 26) may be assumed with confidence. In Section IV we shall derive a detailed formula for the dissipation function for combined

conductance and diffusion of a single electrolyte in dilute solution. Onsager and Fuoss (80) have treated the more general case of systems containing more than two components. These relations are indeed important, although no direct determination of the dissipation function has been made up to the present time.

A general statistical theory of transport processes which goes further than the treatment of Onsager has been developed recently by Kirkwood (51a). A generalized treatment of Brownian motion is obtained in which relations between friction constants and intermolecular forces are deduced for the first time. Important progress in this direction is to be anticipated. Another contribution by Leaf (57a), who has succeeded in obtaining a general phenomenological theory of transport processes in liquids from the equations of thermodynamics and hydrodynamics, deserves serious consideration. Expressions for the flow of entropy and the flows of masses as well as reciprocal relations between the coefficients in these processes are derived.

IV. Theory of Electrolytic Diffusion

1. General considerations and force relations (80)

The quantitative theory of electrolytes depends on two fundamental facts. (1) To a first approximation, the properties of electrolytic solutions are additive and to a great extent they are functions of the individual ions. On this fact depend the law of Kohlrausch, of the additivity of ionic conductances at infinite dilution, and the law of Nernst (71), which permits the computation of the diffusion coefficients of electrolytes at infinite dilution from electrical properties derived from other measurements. These behaviors and the fact that deviations from additivity in electrolytic solutions increase slowly with increasing concentration of solute are advantages which electrolytic solutions possess and which are not characteristic of molecular solutions.

(2) The deviations from additivity may be explained by the interactions between ions as charged particles and between ions and the solvent molecules. Fortunately, the law of attraction between charged particles is known, which makes possible a highly developed theory of the properties of ionic solutions of sufficient dilution so that solvent interaction is a higher order effect. In concentrated solutions, little progress has been achieved towards a detailed theory nor may we expect quantitative results until we know the structure of the solvent and the laws of the forces between all the constituents of the solution.

A treatment of the motion of ions in homogeneous media and fields of forces sufficiently general to include a basis for a detailed theory of conductance and diffusion of electrolytes may be expressed in a simple form. For, suppose the forces $\mathbf{k}_1$, $\mathbf{k}_2$, $\cdots$ $\mathbf{k}_s$ act on the ions, 1, 2, $\cdots$ s, and that these are balanced by necessity by a compensating force $\mathbf{k}_0$ acting on the molecules of the solvent. Then

$$n_0 \mathbf{k}_0 + \sum_{i=1}^{s} n_i \mathbf{k}_i = 0 \qquad (102)$$

This system of forces is produced by a combination of electrical fields, $-\nabla e_i \psi$ acting on each ion, where ψ is the electrical potential, with the concentration gradients, ∇n_1, ∇n_2, $\cdots$ ∇n_s. The required condition of electrical neutrality is

$$\sum_{i=1}^{s} e_i \nabla n_i \equiv \nabla \sum_{i=1}^{s} n_i e_i = \nabla(0) = 0 \tag{103}$$

That these relations are consistent with thermodynamics is proved by the following reasoning. Equilibrium may be maintained with these electrical forces and gradients by superimposed forces of opposite signs and of different kinds, $-\mathbf{k}_0$, $-\mathbf{k}_1$, $\cdots$ $-\mathbf{k}_s$ designated by

$$\mathbf{k}_i = -\nabla \bar{\mu}_i = -\nabla(\mu_i + e_i \psi) \tag{104}$$

where μ_i is the Gibbs chemical potential. Here we employ the quantity $\bar{\mu}_i$, which Brønsted (7) and Guggenheim (38) denoted the "electrochemical potential." In addition to these relations, thermodynamics imposes the Gibbs-Duhem equation:

$$\sum_{i=0}^{s} n_i \, \mathrm{d}\mu_i = 0 \tag{105}$$

From equations 102, 103, and 104 we obtain

$$n_0 \nabla \mu_0 + \sum_{i=1}^{s} n_i \nabla \mu_i + \nabla \sum_{i=1}^{s} n_i e_i \psi = 0 \tag{106}$$

whence by equation 105

$$\nabla \sum_{i=1}^{s} n_i e_i \psi = 0 \tag{107}$$

and consequently

$$\nabla \sum_{i=1}^{s} n_i e_i = 0 \tag{108}$$

the required condition of electrical neutrality.

2. The limiting value of the diffusion coefficient of a simple electrolyte. Extension of Nernst's equation

We shall now consider the case of diffusion of a simple electrolyte dissociating into ν_1 cations and ν_2 anions and omit all the effects of interactions between ions. In diffusion, the condition of the absence of electric current requires that the ions migrate with the same velocity:

$$\mathbf{v} = \mathbf{v}_1 = \mathbf{v}_2 \tag{109}$$

The flows are given by

$$\mathbf{J}_1 = n_1 \mathbf{v}_1; \qquad \mathbf{J}_2 = n_2 \mathbf{v}_2 \tag{110}$$

Further, the velocities are related to the forces and the electrochemical potentials according to

$$\mathbf{v} = \mathbf{k}_1\omega_1 = \mathbf{k}_2\omega_2 = -\omega_1\nabla\bar{\mu}_1 = -\omega_2\nabla\bar{\mu}_2 \tag{111}$$

where ω_1 and ω_2 are the mobilities, or velocities in unit force fields. Now

$$\bar{\mu}_1 + \bar{\mu}_2 = \mu_1 + \mu_2 + \psi(e_1 + e_2) = \mu_1 + \mu_2 \tag{112}$$

since $e_1 = -e_2$ and their sum is zero. Therefore we write

$$\mathbf{k} = \nu_1\mathbf{k}_1 + \nu_2\mathbf{k}_2 = -\nabla\mu \tag{113}$$

From these equations

$$\mathbf{k}_2 = \mathbf{k}_1 \frac{\omega_1}{\omega_2} = \mathbf{k}_1 \frac{\rho_2}{\rho_1} \tag{114}$$

where $\rho = 1/\omega$ denotes a coefficient of friction. From the last two relations

$$\mathbf{k}_1 = -\frac{\omega_2}{\nu_1\omega_2 + \nu_2\omega_1} \nabla\mu = -\frac{\rho_1}{\nu_1\rho_1 + \nu_2\rho_2} \nabla\mu \tag{115}$$

and

$$\mathbf{v} = -\frac{\omega_1\omega_2}{\nu_1\omega_2 + \nu_2\omega_1} \nabla\mu \tag{116}$$

If the solution is ideal

$$\mu = \mu^0 + (\nu_1 + \nu_2) kT \ln n$$

where μ^0 represents the standard state of chemical potential and n is the number of mols of electrolyte per cubic centimeter. Then

$$\nabla\mu = (\nu_1 + \nu_2)kT \frac{\nabla n}{n} \tag{117}$$

and

$$\mathbf{J} = n\mathbf{v} = -\frac{(\nu_1 + \nu_2)\omega_1\omega_2}{\nu_1\omega_2 + \nu_2\omega_1} kT\nabla n = -\mathfrak{D}\nabla n \tag{118}$$

Consequently, the diffusion coefficient is given by

$$\mathfrak{D}_0 = \mathfrak{D}_{n\to 0} = \frac{(\nu_1 + \nu_2)\omega_1\omega_2}{\nu_1\omega_2 + \nu_2\omega_1} kT \tag{119}$$

which is the famous limiting equation of Nernst (71) valid at infinite dilution of electrolyte.

If we introduce the real value of μ, then

$$\nabla\mu = (\nu_1 + \nu_2)kT \nabla \ln \zeta_{\pm} n \tag{120}$$

$$\mathbf{J} = n\mathbf{v} = -\frac{\omega_1\omega_2}{\nu_1\omega_2 + \nu_2\omega_1} (\nu_1 + \nu_2)kT \left(1 + n \frac{\partial \ln \zeta_{\pm}}{\partial n}\right) \nabla n \tag{121}$$

and

$$\mathfrak{D} = \frac{(\nu_1 + \nu_2)\omega_1\omega_2}{\nu_1\omega_2 + \nu_2\omega_1} kT \left(1 + n \frac{\partial \ln \zeta_{\pm}}{\partial n}\right) \tag{122}$$

or according to equation 6

$$\mathfrak{D} = (\nu_1 + \nu_2) \frac{\mathfrak{M}}{n} kT \left(1 + n \frac{\partial \ln \zeta_\pm}{\partial n} \right) \qquad (123)$$

Thus, if the variation of $\mathfrak{D}$ with concentration depended entirely on the term in parenthesis representing the deviation from the ideal solution, $\mathfrak{M}/n$ would be constant. This is not the case, nor is it to be expected on theoretical grounds because the velocities of the ions in diffusion will be affected by various interactions. $\mathfrak{M}/n$ is seen to be a mobility term, or a velocity under unit potential gradient caused by a force $\mathbf{k} = -\nabla\mu$. We shall now undertake the theoretical evaluation of $\mathfrak{M}/n$.

3. Elements of the interionic attraction theory of Debye required for the theory of diffusion

In an ionic solution, the electrostatic forces tend to bring the ions of opposite sign together while the thermal force acts contrariwise. Combination of these two effects was shown by Debye (17, 18) to lead to the formation of ionic atmospheres whereby each positive ion, by inducing a negative charge density in its neighborhood, will be surrounded by an "atmosphere" which contains on the average more negative and less positive ions than the bulk of the solution. Similarly, a negative ion will be surrounded by a positive atmosphere.

When the system is undisturbed or at equilibrium, the potential $\psi_j^0(r)$ of the central ion, j, and its atmosphere at a distance r from it is given by

$$\psi_j^0(r) = Ae^{-\kappa r}/r \qquad (124)$$

where A is an integration constant and κ is defined by

$$\kappa^2 \equiv \frac{4\pi\epsilon^2}{DkT} \sum_{i=1}^{s} n_i z_i^2 \qquad (125)$$

This quantity has the dimensions of a reciprocal distance, and $1/\kappa$ is related to the potential of the ionic atmosphere ψ_j^{0*} in exactly the same way as the distance r from a charge e is related to the potential produced at this distance. Here ϵ is the electronic charge, D the dielectric constant, z_i the valence of the ions surrounding the j ion, and k the gas constant per molecule. The summation is over all the kinds of ions in the solution. It is to be noted that z_i carries the sign of the charge. We shall use the customary symbolism of vertical bars $|z_i|$ when magnitude is represented.

The constant A in equation 124 is found to be

$$A = \frac{e_j}{D} \frac{e^{\kappa a}}{1 + \kappa a} \qquad (126)$$

where a is the parameter which represents the mean distance of approach of ions positive or negative. By substituting this value of A in equation 124, we obtain

$$\psi_j^0(r) = \frac{e_j}{D} \frac{e^{\kappa a} e^{-\kappa r}}{(1 + \kappa a)r} \tag{127}$$

This is one of the relations required for our subsequent derivations (41).

We shall also use the Maxwell–Boltzmann equation for the number of ions of one kind in the neighborhood of another ion, namely:

$$n_{ji} = n_i e^{-(e_i \psi_j^0/kT)} \simeq n_i \left[1 - \frac{e_i \psi_j^0}{kT} + \frac{1}{2} \left(\frac{e_i \psi_j^0}{kT} \right)^2 - \cdots \right] \tag{128}$$

We observe that $\psi_j^0 e_i$ is the potential energy, the work required to bring an i ion of charge e_i from infinity to a distance r from the j ion in a field derivable from the potential ψ_j^0.

For the computation of the activity coefficient term in an equation corresponding to equation 123 we shall use the relation

$$\log y_\pm = -\frac{\mathcal{S}_{(f)} \sqrt{c}}{1 + A' \sqrt{c}} + B2c + D'c^2 - \log \left[\frac{d + 0.001c[2M_1 - M_2]}{d_0} \right] \tag{129}$$

where $y_\pm$ is the mean activity coefficient of electrolyte on the mol per liter scale, $\mathcal{S}_{(f)}$ is the Debye and Hückel constant, A' is the parameter containing the mean distance of approach of the ions, B and D' are empirical constants, and c is in mols per liter (41). The last term on the right is the relation required for converting $\log y_\pm$ to $\log f_\pm$, where $f_\pm$ is the "rational" activity coefficient. In this term d is the density of the solution, d_0 the density of the solvent, M_1 the molecular weight of electrolyte, and M_2 that of solvent (41).

4. Preliminary theory of the action of forces which cause the migration of ions

When the ions of a system in thermodynamic equilibrium are subjected to certain forces, the ion atmospheres are disturbed. If the perturbing force is removed, the displaced ions will return to their original state of distribution. This will require a finite time which is denoted the time of relaxation τ and is expressed by

$$\tau = \frac{1}{\kappa^2 kT \overline{1/\rho}} \tag{130}$$

where

$$\overline{1/\rho} = \frac{\sum\limits_{i=1}^{s} n_i e_i^2/\rho_i}{\sum\limits_{i=1}^{s} n_i e_i^2} \tag{131}$$

If we let $\rho_1 = \rho_2 = \cdots \rho_i$, then

$$\tau = \frac{\rho_i}{\kappa^2 kT} \tag{132}$$

a simplified result which is sufficient for our purpose. Comparison with the derivations (Section IV, 2) will show that kT/ρ_i is really the diffusion coefficient of an ion.

The action of forces which cause the ions to move leads to two effects which are subject to quantitative treatment. The first of these is the "time of relaxation" effect, whereby the applied force causes the ion to move away from its atmosphere. This ion will attract the lagging atmosphere and cause the original spherical distribution of the ions in the atmosphere to assume an assymetry. The net effect will be the retardation of the motion of the ion. The time of relaxation effect has been treated in detail by Onsager (80). The second effect, that of electrophoresis, is due to the fact that the ion migrates in one direction while its atmosphere and the solvent move in the opposite direction. This counterwise motion has the effect of retarding the motion of the ion.

5. The time-of-relaxation effect

Under the influence of a force $\mathbf{k}_j$ an ion will migrate with a velocity

$$\mathbf{v}_j = \frac{\mathbf{k}_j}{\rho_j} \tag{133}$$

When a force is applied, the ion will move away from its atmosphere and will be ahead of its lagging atmosphere by a distance

$$\mathbf{v}_j \tau = \frac{\tau \mathbf{k}_j}{\rho_j} \tag{134}$$

The ratio of this distance to $1/\kappa$ (the radius of the atmosphere), or $\tau \mathbf{k}_j \kappa / \rho_j$, will be a measure of the asymmetry of the atmosphere. The directed force $\Delta \mathbf{k}_j$ due to this effect will be given roughly by multiplying this quantity by the Coulombic force between the ion and its atmosphere, $e_j^2 \kappa^2 / D$, whence

$$\Delta \mathbf{k}_j = \frac{-e_j^2 \kappa^2}{D} \frac{\kappa \tau}{\rho_j} \mathbf{k}_j = -\frac{e_j^2 \kappa \mathbf{k}_j}{DkT} \tag{135}$$

after eliminating τ by means of equation 132. This result differs from Onsager's final result by a numerical factor which can only be computed by an elaborate method. Its derivation, however, shows the essential characteristics of the theory.

It is sufficient for our purpose of calculating the dissipation function for simultaneous diffusion and electrical conductance of ions to omit the complicated calculation of the effect of a superimposed electrical field and simply state the required results of the theory. If $\mathbf{X}$ is the x-component of the external electrical field, then $\Delta \mathbf{X}$, the field caused by the asymmetry of the ionic atmospheres for an electrolyte dissociating into two ions, is given by

$$\Delta \mathbf{X} = \Delta \mathbf{X}_1 = \Delta \mathbf{X}_2 = \frac{e_1 e_2 \kappa}{3DkT} \left(\frac{q^*}{1 + \sqrt{q^*}} \right) \mathbf{X} \tag{136}$$

where

$$q^* = \frac{n_1 e_1^2 \omega_1 + n_2 e_2^2 \omega_2}{(n_1 e_1^2 + n_2 e_2^2)(\omega_1 + \omega_2)} \tag{137}$$

The forces $\mathbf{k}_1$ and $\mathbf{k}_2$ are equal to $\mathbf{X}e_1$ and $\mathbf{X}e_2$, respectively, so that $\mathbf{X}$ may be expressed by

$$\mathbf{X} = \frac{\omega_2 \mathbf{k}_2 - \omega_1 \mathbf{k}_1}{e_2 \omega_2 - e_1 \omega_1} \tag{138}$$

Upon elimination of $\mathbf{X}$ and rearranging we readily obtain

$$\Delta \mathbf{X}_1 = \Delta \mathbf{X}_2 = \frac{e_1 e_2 \kappa}{3DkT} \frac{(1 - \sqrt{q^*})n_2 e_2}{n_1 e_1^2 \omega_2 + n_2 e_2^2 \omega_1} (\omega_2 \mathbf{k}_2 - \omega_1 \mathbf{k}_1) \tag{139}$$

the relation we shall use later to compute the dissipation function.

From this equation a very important conclusion in relation to the theory of diffusion is apparent. In the process of diffusion of a simple electrolyte, both kinds of ions travel with the same velocity and in the same direction. Thus

$$\mathbf{v}_1 = \omega_1 \mathbf{k}_1 = \omega_2 \mathbf{k}_2 = \mathbf{v}_2 \tag{140}$$

whence by equation 139 the *time-of-relaxation effect vanishes and the ionic atmospheres retain their original spherical symmetry*. In conductance, not only do the ionic velocities differ but positive and negative ions move in opposite directions, which leads to an additive contribution to the current.

6. Electrophoresis

For conductance, where the force $\mathbf{k}_j$ is proportional to the charge on an ion, e_j,

$$\mathbf{k}_0 = 0; \quad \mathbf{k}_j = e_j \mathbf{X}; \quad j = 1, 2, \cdots s \tag{141}$$

the effect of electrophoresis is easily computed. The ionic atmosphere will possess a charge, $-e_j$, and will be subjected to the force $-e_j \mathbf{X}$, which will cause the atmosphere and the solvent containing it to migrate in a direction opposite to the motion of the ion. Therefore the ion moves in a counter-current of solvent which has the net effect of retarding its velocity. As pointed out by Debye (18), the velocity of the counter-current may be computed by assuming that the entire charge, $-e_j$, is at a distance $1/\kappa$ from the central ion and distributed over a sphere of radius $1/\kappa$. Further, it is assumed that Stokes law applies to the motion of this sphere and therefore the velocity of the electrophoretic effect is given by

$$\Delta \mathbf{v}_j = -\frac{\mathbf{k}_j \kappa}{6\pi\eta} = -\frac{\mathbf{X}e_j \kappa}{6\pi\eta} \tag{142}$$

where η is the viscosity of the medium.

The velocity of the ion during electrical current flow under a field $\mathbf{X}$ may be expressed in the following manner. If the ion possessed no atmosphere, its velocity in a field $\mathbf{X}$ would be $\mathbf{X}e_j\omega_j$; but owing to its lagging atmosphere it is subjected to an additional force in the opposite direction, $-\omega_j \Delta \mathbf{k}_j$, and the electrophoretic effect $\Delta \mathbf{v}_j$. Therefore, the net velocity becomes

$$\mathbf{v}_j = \omega_j \mathbf{X} e_j - \omega_j \Delta \mathbf{k}_j - \frac{\mathbf{X}e_j \kappa}{6\pi\eta} \tag{143}$$

When an electrolyte diffuses into a solvent, both ions travel with the same velocity, a phenomenon required by electrical neutrality. In this case, electrophoresis occurs because as the ions move in one direction, they take positions previously occupied by the water molecules which in a system at constant volume must move in the opposite direction. The calculation of the electrophoretic effect will require therefore an estimate of the volume force acting on the water molecules.

According to equation 102

$$n_0\mathbf{k}_0 + \sum_{i=1}^{s} n_i\mathbf{k}_i = 0 \tag{144}$$

the forces acting on the ions must be balanced by a compensating force acting on the water molecules. For simplicity, we shall let the subscript σ represent summation. Then

$$n_0\mathbf{k}_0 + n_\sigma\mathbf{k}_\sigma = 0 \tag{145}$$

Now, the presence of a j ion influences the average concentration of the ions in a given volume element dV at a distance r from it. The volume force becomes $n_{j\sigma}\mathbf{k}_\sigma\,dV$ and the net force on the volume element will be

$$(n_{j\sigma}\mathbf{k}_\sigma + n_0\mathbf{k}_0)dV = (n_{j\sigma} - n_\sigma)\mathbf{k}_\sigma dV \tag{146}$$

In spherical coördinates, the force acting on a spherical shell at the distance, r, from the j ion will be

$$\mathcal{F}dr = 4\pi r^2(n_{j\sigma} - n_\sigma)\mathbf{k}_\sigma dr \tag{147}$$

and is distributed over the shell of radius r. This force will cause the points within the sphere to move with a velocity, $\mathbf{v}$, given by Stokes law:

$$\mathbf{v} = \frac{\mathcal{F}}{6\pi\eta r} \tag{148}$$

Now $(n_{ji} - n_i)$ may be obtained from the Boltzmann equation (equation 128) and ψ_j^0 may be eliminated from this expression by means of equation 127. Substituting this result in equation 147, the force acting on the spherical shell is found to be

$$\mathcal{F}\,dr = 4\pi r^2\left\{-\frac{e_j e_\sigma}{DkT}\frac{e^{\kappa a}}{(1+\kappa a)}\frac{e^{-\kappa r}}{r} + \frac{1}{2}\left(\frac{e_j e_\sigma}{DkT}\frac{e^{\kappa a}}{(1+\kappa a)}\right)^2\frac{e^{-2\kappa r}}{r^2}\right\}n_\sigma\mathbf{k}_\sigma\,dr \tag{149}$$

or more simply

$$\mathcal{F}dr = 4\pi(-A_1 re^{-\kappa r} + A_2 e^{-2\kappa r})\,dr \tag{150}$$

Upon substituting in Stokes equation

$$d\mathbf{v}_i = \frac{\mathcal{F}\,dr}{6\pi\eta r} = \frac{2}{3\eta}\left(-A_1 e^{-\kappa r} + \frac{A_2 e^{-2\kappa r}}{r}\right)dr \tag{151}$$

is obtained and upon integration from a to ∞, the total velocity $\Delta\mathbf{v}_j$ is found to be

$$\Delta\mathbf{v}_j = \frac{2}{3\eta}\left(-\frac{A_1 e^{-\kappa a}}{\kappa} + A_2 Ei(2\kappa a)\right) \tag{152}$$

where $Ei(2\kappa a)$ is the well-known exponential integral function

$$Ei(x) = \int_x^\infty e^{-t}\frac{dt}{t} = -0.5772 - \ln x + x - \frac{x^2}{2\underline{|2}} + \cdots \tag{153}$$

Introducing A_1 and A_2, the final result is

$$\Delta\mathbf{v}_j = -\frac{2}{3\eta}\frac{e_j e_\sigma n_\sigma \mathbf{k}_\sigma}{DkT\kappa(1+\kappa a)} + \frac{1}{3\eta}\left(\frac{e_j}{DkT}\frac{e_\sigma e^{\kappa a}}{(1+\kappa a)}\right)^2 n_\sigma \mathbf{k}_\sigma Ei(2\kappa a) \tag{154}$$

At low concentrations when κa is negligible, and when the force, $\mathbf{k}_i = \mathbf{X}e_i$, is proportional to the charge,

$$\Delta\mathbf{v}_j = -\frac{2}{3\eta}\frac{e_j\mathbf{X}\sum_{i=1}^s n_i e_i^2}{DkT\kappa} \tag{155}$$

From the equation which defines κ, we find that

$$\sum_{i=1}^s n_i e_i^2 = \frac{DkT\kappa^2}{4\pi} \tag{156}$$

whence

$$\Delta\mathbf{v}_j = -\frac{1}{6}\frac{\mathbf{X}e_j\kappa}{\pi\eta} \tag{157}$$

which is the simple result for the electrophoretic effect previously obtained for the case of conductance.

It is well to note that in the derivation of equation 154, the Debye and Hückel calculation of the Coulombic force effect and their second approximation to include the effect of the mean distance of approach of the ions were employed. Consequently, this estimate of the electrophoretic effect can only be expected to approach validity at low concentrations of electrolytes. Deviations due to ion–solvent and other short-range ionic interactions may be expected at higher concentrations and at the present time there exists no means of computing their magnitudes.

7. Extension of the theory of the diffusion of a simple electrolyte to include electrophoresis

Now the effect of electrophoresis is to alter the forces, $\mathbf{k}_1$ and $\mathbf{k}_2$, acting upon the ions of an electrolyte by decreasing the velocities. Thus

$$\mathbf{k}_j = \rho_j(\mathbf{v} - \Delta\mathbf{v}_j); \quad j = 1, 2 \tag{158}$$

which when introduced in equation 113 gives

$$-\nabla\mu = \mathbf{k} = \nu_1\rho_1(\mathbf{v} - \Delta\mathbf{v}_1) + \nu_2\rho_2(\mathbf{v} - \Delta\mathbf{v}_2) \tag{159}$$

For the electrophoretic terms, equation 154 yields

$$\Delta \mathbf{v}_j = \mathbf{v}\left[-\frac{2}{3\eta}\,(n_1 e_1 \rho_1 + n_2 e_2 \rho_2)\,\frac{e_j}{DkT\kappa(1+\kappa a)} \right.$$

$$\left. +\frac{1}{3\eta}\,(n_1 e_1^2 \rho_1 + n_2 e_2^2 \rho_2)\left(\frac{e_j}{DkT}\right)^2 \phi(\kappa a) \right] \quad (160)$$

where

$$\phi(\kappa a) = e^{2\kappa a} Ei(2\kappa a)/(1 + \kappa a)^2 \quad (161)$$

Upon substituting the values of $\Delta \mathbf{v}_1$ and $\Delta \mathbf{v}_2$ in equation 159 and using the relations $n_1 e_1 = -n_2 e_2$ and $\nu_1 e_1 = \nu_2 e_2$, we obtain for the gradient of the chemical potential:

$$-\nabla \mu = \mathbf{v}\left[\nu_1 \rho_1 + \nu_2 \rho_2 + (\rho_1 - \rho_2)^2\,\frac{\nu_1 \nu_2}{\nu_1 + \nu_2}\,\frac{\kappa}{6\pi\eta(1+\kappa a)} \right.$$

$$\left. -\left(\frac{\nu_2 \rho_1 + \nu_1 \rho_2}{\nu_1 + \nu_2}\right)^2 \frac{\kappa^4 \phi(\kappa a)}{48\pi^2 \eta n} \right] \quad (162)$$

$\nabla \mu$ is the force per molecule of solute when the concentration is expressed in molecules per cubic centimeter. The electrophoretic effect is seen to depend on the changes in frictional forces caused by the action of the Coulomb forces. The third term on the right is the first-order electrolytic effect which depends on the factor $\rho_1^2 - 2\rho_1 \rho_2 + \rho_2^2$, whose terms correspond to cation–cation, cation–anion, and anion–anion effects, respectively. The last term of this equation is of the order $n \log n$.

If this equation be solved for $\mathbf{v}$ and multiplied by n, and higher order terms be discarded as negligible, we obtain the flow, $\mathbf{J}$. Thus

$$\mathbf{J} = n\mathbf{v} = -\mathfrak{M}\nabla\mu = -\left(\frac{n\omega_1 \omega_2}{\nu_1 \omega_2 + \nu_2 \omega_1} + \Delta\mathfrak{M}\right)\nabla\mu \quad (163)$$

where

$$\Delta\mathfrak{M} = -\left(\frac{\omega_1 - \omega_2}{\nu_1 \omega_2 + \nu_2 \omega_1}\right)^2 \left(\frac{\nu_1 \nu_2}{\nu_1 + \nu_2}\right)\frac{\kappa n}{6\pi\eta(1+\kappa a)}$$

$$+\left(\frac{\nu_1 \omega_1 + \nu_2 \omega_2}{\nu_1 \omega_2 + \nu_2 \omega_1}\right)^2 \frac{1}{(\nu_1 + \nu_2)^2}\frac{\kappa^4 \phi(\kappa a)}{48\pi^2 \eta} \quad (164)$$

It is now necessary to convert this equation into a form convenient for practical computations. To this end, we recall that

$$n = N\bar{n} = Nc/1000 \quad (165)$$

where $\bar{n}$ and c are the concentrations in mols per cubic centimeter and mols per liter, respectively. Further

$$\mu N = \bar{\mu} \quad (166)$$

and consequently

$$\mathbf{J} = \bar{n}\mathbf{v} = -\overline{\mathfrak{M}}\nabla\bar{\mu} = -\left(\frac{\mathfrak{M}}{N^2}\right)\nabla\mu \quad (167)$$

Now, the equivalent conductance of an ion, λ_i, is equal to the current at a potential gradient of one volt per centimeter produced by 1 gram-equivalent. Thus

$$\lambda_i = 96{,}500\ \bar{u}_i = 96{,}500 \mid e_i \mid \omega_i \tag{168}$$

If $\bar{u}_i$ is expressed in volts per centimeter and u_i in electrostatic units, then

$$\omega_i = u_i / \mid z_i \mid \epsilon = 300\ \bar{u}_i / \mid z_i \mid \epsilon \tag{169}$$

$$= \frac{300\ \lambda_i}{96{,}500 \mid z_i \mid \epsilon} \tag{170}$$

Using this relation to eliminate ω_1 and ω_2 from equation 164, and taking into consideration the relations given by equations 165 and 166, we find that

$$\overline{\mathfrak{M}} = 1.0748 \times 10^{-20} \frac{\lambda_1^0 \lambda_2^0 c}{\nu_1 \mid z_1 \mid \Lambda^0} + \Delta\overline{\mathfrak{M}}' + \overline{\mathfrak{M}}'' \tag{171}[5]$$

where the superscript signifies limiting equivalent conductance and $\Lambda^0 = \lambda_1^0 + \lambda_2^0$. The number of cations and anions into which an electrolyte dissociates are ν_1 and ν_2, respectively, and $\mid z_1 \mid$ and $\mid z_2 \mid$ are the magnitudes of their valences. Making use of the relations $\nu_1 \mid z_1 \mid = \nu_2 \mid z_2 \mid$, $\nu_2 = \mid z_1 \mid$, and $\nu_1 = \mid z_2 \mid$, $\Delta\overline{\mathfrak{M}}'$ and $\Delta\overline{\mathfrak{M}}''$ are given by

$$\Delta\overline{\mathfrak{M}}' = -\frac{(\mid z_2 \mid \lambda_1^0 - \mid z_1 \mid \lambda_2^0)^2}{\mid z_1 z_2 \mid (\nu_1 + \nu_2)\Lambda^{02}} \frac{3.1322 \times 10^{-19}}{\eta_0(DT)^{\frac{1}{2}}} \frac{c\sqrt{\Gamma}}{(1 + \kappa a)} \tag{172}$$

$$\Delta\overline{\mathfrak{M}}'' = \left(\frac{z_2^2 \lambda_1^0 + z_1^2 \lambda_2^0}{\Lambda^0}\right)^2 \frac{9.304 \times 10^{-18}}{\eta_0(DT)^2} c^2 \phi(\kappa a) \tag{173}$$

The coefficient of diffusion in terms of these quantities is expressed by

$$\mathfrak{D} = \mathfrak{M} \frac{\partial\mu}{\partial n} = \overline{\mathfrak{M}} \frac{\partial\bar{\mu}}{\partial\bar{n}} = 1000\overline{\mathfrak{M}} \frac{\partial\bar{\mu}}{\partial c} \tag{174}$$

and, since

$$c \frac{\partial\bar{\mu}}{\partial c} = (\nu_1 + \nu_2)RT \left(1 + c \frac{\partial \ln y_\pm}{\partial c}\right) \tag{175}$$

we find that

$$\mathfrak{D} = (\nu_1 + \nu_2)1000RT \left(\frac{\overline{\mathfrak{M}}}{c}\right)\left(1 + c \frac{\partial \ln y_\pm}{\partial c}\right) \tag{176}$$

Here, the activity coefficient is mean activity divided by the molar concentration. For an electrolyte dissociating into two ions

$$\mathfrak{D} = 16.629 \times 10^{10}\ T \frac{\overline{\mathfrak{M}}}{c} \left(1 + c \frac{\partial \ln y_\pm}{\partial c}\right) \tag{177}$$

[5] The numerical values in this and the following equations have been computed from the fundamental constants given by R. T. Birge (Rev. Modern Phys. 13, 233 (1941).

and equations 171, 172, and 173 reduce to a convenient form

$$\left(\frac{\mathfrak{M}}{c}\right)10^{20} = \frac{1.0748}{z}\left(\frac{\lambda_1^0\lambda_2^0}{\Lambda^0}\right) - \frac{0.4404}{\mathring{a}\eta_0}\left(\frac{\lambda_1^0 - \lambda_2^0}{\Lambda^0}\right)^2 \frac{\kappa a}{1 + \kappa a}$$
$$+ \left(\frac{z}{\mathring{a}}\right)^2 \frac{36790}{\eta_0 DT}(\kappa a)^2 \phi(\kappa a) \quad (178)$$

where $\mathring{a}$ is the mean distance of approach of the ions in Ångström units. Another useful form for 1-1 type electrolytes is

$$\left(\frac{\mathfrak{M}}{c}\right)10^{20} = 1.0748\left(\frac{\lambda_1^0\lambda_2^0}{\Lambda^0}\right) - \frac{22.148}{\eta_0(DT)^{\frac{1}{2}}}\left(\frac{\lambda_1^0 - \lambda_2^0}{\Lambda^0}\right)^2 \frac{\sqrt{c}}{1 + A'\sqrt{c}}$$
$$+ \frac{9.304 \times 10^7}{\eta_0(DT)^2}c\phi(A'\sqrt{c}) \quad (179)$$

Here

$$\kappa a = A\sqrt{\Gamma} = A'\sqrt{c} \quad (180)$$

$$A = \mathring{a}\frac{35.559}{(DT)^{\frac{1}{2}}} \quad (181)$$

For convenience in utilizing these equations, values of $\phi(\kappa a)$ and $(\kappa a)^2\phi(\kappa a)$ as a function of κa are recorded in table 1.

The first term on the right of equation 179 is a constant and never greater than $\Lambda^0/4$. Since $(\lambda_1^0 - \lambda_2^0)$ is small for many salts, the second term is frequently negligible. As a glance at table 1 will show, $c\phi(A'\sqrt{c})$, which equals $(1/A')^2(\kappa a)^2\phi(\kappa a)$, is nearly constant at high concentrations and is never greater than 0.1. As a result, the variation of the diffusion coefficient is governed to a greater extent by the factor $[1 + c(\partial \ln y_\pm/\partial c)]$ than by $(\mathfrak{M}/c)$.

This term may be evaluated for 1-1 electrolytes from equation 129

$$\log y_\pm = \frac{-S_{(f)}\sqrt{c}}{1 + A'\sqrt{c}} + 2Bc + D'c^2 - \log\left[\frac{d + 0.001c(2M_1 - M_2)}{d_0}\right] \quad (182)$$

in which case

$$\left(1 + c\frac{\partial \ln y_\pm}{\partial c}\right) = 1 - \frac{1.1514 S_{(f)}\sqrt{c}}{(1 + A'\sqrt{c})^2} + 4.606Bc + 4.606D'c^2 - c\psi(d) \quad (183)$$

where

$$\psi(d) \equiv \frac{\partial d/\partial c + 0.001(2M_1 - M_2)}{d + 0.001c(2M_1 - M_2)} \quad (184)$$

Values of parameters of this equation for a number of important 1-1 electrolytes at 25°C. are given by Harned and Owen (41).

Observing that $c\phi(A'\sqrt{c})$ and its derivative with respect to c approach zero as c approaches zero, the limiting equation

$$\mathfrak{D} = \mathfrak{D}_0 - S_{(\mathfrak{D})}\sqrt{c} \quad (185)$$

is obtained where

$$\mathfrak{D}_0 = 17.872 \times 10^{-10} T \left(\frac{\lambda_1^0 \lambda_2^0}{\Lambda^0} \right) \qquad (185)$$

and

$$\mathfrak{S}_{(\mathfrak{D})} = \frac{3.754 \times 10^{-3}}{D^{\frac{1}{2}} T^{\frac{1}{2}}} \left(\frac{\lambda_1^0 \lambda_2^0}{\Lambda^0} \right) + \frac{3.683 \times 10^{-3}}{\eta_0 D^{\frac{1}{2}} T^{-\frac{1}{2}}} \left(\frac{\lambda_1^0 - \lambda_2^0}{\Lambda^0} \right)^2 \qquad (187)$$

The result obtained for $\mathfrak{D}_0$, the diffusion coefficient at infinite dilution, is of course the same as that obtained by Nernst and derived previously.

TABLE 1

Values of the functions $\phi(\kappa a)$ and $(\kappa a)^2 \phi(\kappa a)$ for use in equations 178 and 179 (41)

κa	$\phi(\kappa a)$	$(\kappa a)^2 \phi(\kappa a)$	κa	$\phi(\kappa a)$	$(\kappa a)^2 \phi(\kappa a)$
0.000	∞	0	0.5	0.2651	0.06628
0.010	3.3550	0.00034	0.6	0.2054	0.07344
0.025	2.4695	0.00154	0.7	0.16304	0.07989
0.05	1.8273	0.00457	0.8	0.13194	0.08444
0.10	1.2342	0.01234	0.9	0.10844	0.08784
0.15	0.9245	0.02080	1.0	0.09033	0.09033
0.20	0.7277	0.02911	1.2	0.06477	0.09327
0.25	0.5907	0.03692	1.4	0.04813	0.09433
0.30	0.4899	0.04409	1.6	0.03676	0.09411
0.35	0.4130	0.05059	1.8	0.02876	0.09318
0.40	0.3527	0.05643	2.0	0.02292	0.09168
0.45	0.3044	0.06164	2.5	0.01391	0.08694
0.50	0.2651	0.06628	3.0	0.00908	0.08172

8. The dissipation function of a simple electrolyte for diffusion and conductance

In order to compute the dissipation function for the combined processes of electrical conductance and diffusion, we employ the electrochemical potential, $\bar{\mu}_i$, and the force, $\mathbf{k}_i$; obtained from its gradient.   Thus

$$\bar{\mu}_i = \mu_i + e_i \psi \qquad (188)$$

$$\mathbf{k}_i = - \nabla \bar{\mu}_i = - \nabla \mu_i + e_i \nabla \psi = - \nabla \mu_i + e_i \mathbf{X} \qquad (189)$$

The equation relating the forces $\mathbf{k}_i$ to the flows $\mathbf{J}_k$ is

$$\mathbf{k}_i = \sum_{k=1}^{s} R_{ik} \mathbf{J}_k ; \quad (i = 1, 2) \qquad (190)$$

which corresponds to equation 97 and where

$$R_{ik} = R_{ki} \qquad (191)$$

The dissipation function (equation 101) is given by

$$2F(\mathbf{J}, \mathbf{J}) = \sum_{i,k=1}^{s} R_{ik} \mathbf{J}_i \mathbf{J}_k = 2\phi(\mathbf{J}, \mathbf{J}) \qquad (192)$$

and as a result of the above relations

$$\frac{\partial F}{\partial \mathbf{J}_i} = -\operatorname{grad} \bar{\mu}_i = -\nabla \bar{\mu}_i = \mathbf{k}_i \tag{193}$$

For a simple electrolyte $(s = 2)$,

$$\begin{aligned}
\mathbf{k}_1 &= R_{11}\mathbf{J}_1 + R_{12}\mathbf{J}_2 \\
\mathbf{k}_2 &= R_{21}\mathbf{J}_1 + R_{22}\mathbf{J}_2 \\
2F &= R_{11}\mathbf{J}_1^2 + 2R_{12}\mathbf{J}_1\mathbf{J}_2 + R_{22}\mathbf{J}_2^2
\end{aligned} \tag{194}$$

from which the operation given by equation 193 is seen to be valid.

In order to compute the dissipation function we first gather the detailed expression for the force $\mathbf{k}_j$. In the limit as the concentration approaches zero

$$\mathbf{k}_j = \rho_j \mathbf{v}_j = \mathbf{v}_j/\omega_j = \mathbf{J}_j/n_j\omega_j \tag{195}$$

At finite concentrations, owing to the time-of-relaxation effect and electrophoresis, $\Delta \mathbf{k}_j$,

$$\mathbf{k}_j = \rho_j \mathbf{v}_j - e_j \Delta \mathbf{X}_j - \rho_j \Delta \mathbf{v}_j \tag{196}$$

Upon introducing the detailed expression for ΔX_j from equation 139 and $\Delta \mathbf{v}_j$ given by equation 154 we obtain:

$$\mathbf{k}_j = \rho_j \mathbf{v}_j - e_j \left(\frac{e_1 e_2 \kappa}{3DkT} \cdot \frac{(1-\sqrt{q^*})n_2 e_2}{(n_1 e_1^2 \omega_2 + n_2 e_2^2 \omega_1)} \right)(\omega_2 \mathbf{k}_2 - \omega_1 \mathbf{k}_1)$$
$$+ \frac{2}{3\eta}\frac{\rho_j e_j e_\sigma n_\sigma \mathbf{k}_\sigma}{DkT\kappa(1+\kappa a)} - \frac{1}{3\eta}\left(\frac{\rho_j^{\frac{1}{2}} e_j e_\sigma e^{\kappa a}}{DkT(1+\kappa a)}\right)^2 n_\sigma \mathbf{k}_\sigma \, Ei(\kappa a) \tag{197}$$

Now

$$n_2 e_2(\omega_2 \mathbf{k}_2 - \omega_1 \mathbf{k}_1) = n_2 e_2 \omega_2 \mathbf{k}_2 - n_1 e_1 \omega_1 \mathbf{k}_1$$
$$= (e_2 \mathbf{J}_2 + e_1 \mathbf{J}_1) \tag{198}$$

$$n_1 \mathbf{k}_1 = \mathbf{J}_1 \rho_1; \qquad n_2 \mathbf{k}_2 = \mathbf{J}_2 \rho_2 \tag{199}$$

$$\phi(\kappa a) = \frac{e^{2\kappa a}}{(1+\kappa a)^2} Ei(\kappa a) \tag{200}$$

and

$$\omega_1 = \frac{1}{\rho_1}; \qquad \omega_2 = \frac{1}{\rho_2} \tag{201}$$

Utilizing these relations, we obtain for a 1-1 electrolyte

$$\mathbf{k} = \mathbf{k}_1 + \mathbf{k}_2 = \mathbf{J}_1 \rho_1/n_1 + \mathbf{J}_2 \rho_2/n_2$$
$$- \frac{e_1 e_2 \kappa}{3DkT}\frac{\rho_1 \rho_2(1-\sqrt{q^*})}{(n_1 e_1^2 \rho_1 + n_2 e_2^2 \rho_2)}(e_1 + e_2)(e_1 \mathbf{J}_1 + e_2 \mathbf{J}_2)$$
$$+ \frac{2}{3\eta DkT\kappa(1+\kappa a)}(\rho_1 e_1 + \rho_2 e_2)(e_1 \rho_1 \mathbf{J}_1 + e_2 \rho_2 \mathbf{J}_2)$$
$$- \frac{\phi(\kappa a)}{3\eta(DkT)^2}(\rho_1 e_1^2 + \rho_2 e_2^2)(e_1^2 \rho_1 \mathbf{J}_1 + e_2^2 \rho_2 \mathbf{J}_2) \tag{202}$$

The dissipation function takes the form

$$2F = R_{11}J_1^2 + 2R_{12}J_1J_2 + R_{22}J_2^2$$

$$= (\rho_1/n_1)J_1^2 + (\rho_2/n_2)J_2^2 - \frac{e_1e_2\kappa}{3DkT} \frac{\rho_1\rho_2(1 - \sqrt{q^*})}{(n_1e_1^2\rho_1 + n_2e_2^2\rho_2)} [e_1J_1 + e_2J_2]^2$$

$$+ \frac{2}{3\eta DkT(1 + \kappa a)\kappa} [e_1\rho_1J_1 + e_2\rho_2J_2]^2 - \frac{\phi(\kappa a)}{3\eta(DkT)^2} [e_1^2\rho_1J_1 + e_2^2\rho_2J_2]^2 \quad (203)$$

The correctness of this expression may be proved by differentiation with respect to J_1 and J_2 according to equation 193 and comparing the result with the preceding expression for k.

The first two terms of this equation represent the dissipation function when the effects of Coulombic forces are neglected. The second is the time-of-relaxation effect which, as previously shown, vanishes in the case of diffusion alone when both ions migrate with the same velocity. The last two terms represent the electrophoretic effect.

For diffusion

$$\mathbf{v} = \mathbf{v}_1 = \mathbf{v}_2 = J_1/n_1 = J_2/n_2 \quad (204)$$

and

$$2F = \left[n_1\rho_1 + n_2\rho_2 + \frac{2e_1^2n_1^2}{3\eta DkT} \frac{(\rho_1 - \rho_2)^2}{(1 + \kappa a)\kappa} - \frac{\phi(\kappa a)(e_1n_1)^2(\rho_1e_1 - \rho_2e_2)^2}{3\eta(DkT)^2} \right] \mathbf{v}^2 \quad (205)$$

We note that for an electrolyte dissociating into two ions, the electrophoretic terms will vanish if the frictional coefficients of the ions are identical.

V. EXPERIMENTAL METHODS FOR THE MEASUREMENT OF DIFFUSION COEFFICIENTS[6]

A. BOUNDARY CONDITIONS AND ADAPTATIONS OF FICK'S LAWS FOR THE MEASUREMENT OF DIFFUSION COEFFICIENTS

The experimental methods for measuring diffusion coefficients may be arranged under three classes, which depend on whether or not a steady state is reached or whether the entire solution is maintained in a closed system. The application of Fick's laws then depends on the experimentally imposed boundary conditions.

1. Free diffusion

Free diffusion refers to diffusion from an initially sharp boundary between two solutions at different concentrations, or between solution and solvent, in a vertical apparatus in which the composition of the liquid media at the top and bottom remain constant. In order to adapt equations 16 or 17 for practical

[6] For this part of the review, the author is particularly indebted to Dr. Lewis G. Longsworth of the Rockefeller Institute for Medical Research, whose paper (61) on the theory of measurement of diffusion coefficients has been used as a basis for this discussion and who has kindly permitted the reproduction of some of the figures employed in describing the optical methods.

calculations, use is made of the fact, first observed by Boltzmann (5), that the variables x and t always occur in the ratio x^2/t. Consequently, since $x = 0$ when $t = 0$, we may let $y = x/t^{\frac{1}{2}}$ and introduce this new variable in the differential equations. Thus, equation 16 becomes

$$\frac{y}{2}\frac{dn}{dy} = -\frac{d}{dy}\,\mathfrak{D}\,\frac{dn}{dy} \tag{206}$$

and

$$-\mathfrak{D} = \frac{dy}{dn}\int_0^n \frac{y}{2}\,dn = \frac{1}{2t}\frac{dx}{dn}\int_0^n x\,dn$$

$$= \frac{1}{2t}\frac{dx}{dn}\int_{-\infty}^x x\,\frac{dn}{dx}\,dx \tag{207}$$

This equation has been employed as a basis for computing $\mathfrak{D}$ by the float method (29). Also, since dn/dx is usually very nearly proportional to the refractive-index gradient, it is the basic relation for the development of the optical methods of evaluating $\mathfrak{D}$. If $\mathfrak{D}$ is assumed to be independent of y, equation 206 becomes:

$$\frac{y}{2}\frac{dn}{dy} = -\mathfrak{D}\frac{d^2n}{dy^2}. \tag{208}$$

Upon integration and resubstitution of x and t,

$$\frac{dn}{dx} = \frac{1}{It^{\frac{1}{2}}}e^{-x^2/4\mathfrak{D}t} \tag{209}$$

where I is a constant of integration. Now

$$\int_{-\infty}^{\infty}\frac{dn}{dx}\,dx = n_1 - n_0 \tag{210}$$

which is the total area under the curve of dn/dx versus x. Therefore the concentration difference of the two ends of the diffusion column is given by

$$n_1 - n_0 = \frac{1}{It^{\frac{1}{2}}}\int_{-\infty}^{\infty}e^{-x^2/4\mathfrak{D}t}\,dx$$

$$= \frac{2}{It^{\frac{1}{2}}}\int_0^{\infty}e^{-x^2/4\mathfrak{D}t}\,dx$$

$$= \frac{2}{It^{\frac{1}{2}}}\sqrt{\pi\mathfrak{D}t} \tag{211}$$

and

$$I = \frac{2\sqrt{\pi\mathfrak{D}}}{n_1 - n_0} \tag{212}$$

Upon eliminating I from equation 209 we obtain Wiener's equation (105)

$$\frac{dn}{dx} = \frac{(n_1 - n_0)}{2\sqrt{\pi\mathfrak{D}t}}e^{-x^2/4\mathfrak{D}t} \tag{213}$$

from which

$$n = \frac{(n_1 - n_0)}{2\sqrt{\pi \mathfrak{D} t}} \int_{-\infty}^{x} e^{-x^2/4\mathfrak{D}t}\, \mathrm{d}x \qquad (214)$$

These equations, which give the distribution of solute as a function of height, x, find their principal application in the use of optical methods for the determination of diffusion coefficients of macromolecules. Although it was recognized that the gradient of the refractive index could be used to measure a concentration gradient (33), the first optical system used quantitatively for this purpose was constructed by Wiener (105). Important technical advances were made some years later by Thovert (96, 97) and others (45, 83, 104), who used optical methods for measuring diffusion coefficients. The three modern methods, the absorption, the "schlieren", and the scale, have been developed to a high degree of precision at the Chemical Institute of Upsala by Svedberg (93), Tiselius (98), and Lamm (37, 52–56). The investigations of Longsworth (60–66), who is responsible for the "schlieren scanning" method, are the last word in precision technique by optical methods of this nature.

These experimental procedures have found their principal application in determining diffusion coefficients of macromolecules and in electrophoretic analysis. With the exception of Clack's researches (9, 10), very few accurate diffusion coefficients of electrolytes have been determined by optical means. On the other hand, these procedures can be carried out in a short time as compared with that usually required for the study of the slow process of diffusion and for this reason may prove important in future studies.

In addition to the optical methods, the microindicator method (25–28, 84, 99, 108) and the float method of Gerlach (29, 106) have been employed for the determination of diffusion coefficients from systems undergoing free diffusion. These have not yielded nor do they promise to yield as accurate results as other methods and will not be mentioned further.

2. Steady-state diffusion

The diffusion upwards in a vertical column from a reservoir at the bottom containing a solution at one concentration into a reservoir at the top containing solution at another lower concentration, or into pure solvent, ultimately attains a steady state in which, at each height in the column, the flow J is constant. With such a column Clack (9, 10), with an accurate series of measurements of some salt solutions in water, was able to determine both the flow J and the concentration gradient $\mathrm{d}n/\mathrm{d}x$. From these, he was able to compute the differential diffusion coefficient by Fick's first law:

$$\mathfrak{D} = - J(\mathrm{d}n/\mathrm{d}x)^{-1} \qquad (215)$$

These results are among the very few direct determinations of differential diffusion coefficients and their accuracy at concentrations of 0.05 N and higher are estimated to be within 1.5 per cent. These results constitute one of the few important contributions to our knowledge of electrolytic diffusion but were not obtained at sufficiently low concentrations to afford an accurate test of

theory. Clack (9) also used a gravitational method in a system in a steady state
of diffusion to determine integral diffusion coefficients.

The diaphragm method of McBain (67, 68, 101) and Northrup (74), which
permits a solute on one side of a sintered-glass membrane to diffuse into water
or a more dilute solution on the other side of the membrane, approaches the
steady condition if the solutions employed are sufficiently large. Under this
condition, the diaphragm method can be treated as a steady-state problem, since
the concentrations on the two sides of the membrane will not alter appreciably.
This method has been shown by McBain (67) and Dawson (16), and particu-
larly by Hartley and Runnicles (43) and Gordon (31, 32), to yield accurate
relative results.

3. Restricted diffusion

When diffusion from an initially sharp boundary takes place in a solution
which completely fills a vessel and is permitted to proceed for a sufficient length
of time, the concentrations at all heights in the apparatus will change continu-
ally. In a vertical column of height a, the flow J will be zero when $x = 0$ and
$x = a$, since the solute is confined within the vessel. In this case, the differen-
tial equation

$$\frac{\partial n}{\partial t} = -\mathfrak{D}\,\frac{\partial^2 n}{\partial t^2} \tag{216}$$

with boundary conditions

$$\frac{\partial n}{\partial x} = 0 \quad \text{for} \quad \begin{cases} x = 0 \\ x = a \end{cases}$$

$$n = f(x) \quad \text{for} \quad t = 0$$

$$n \neq \infty \quad \text{for} \quad t = \infty \tag{217}$$

may be satisfied by a solution arranged in a Fourier series. Thus

$$n = n_0 + \sum_{m=1}^{\infty} A_m e^{-m^2\pi^2\mathfrak{D}t/a^2} \cos\frac{m\pi x}{a} \tag{218}$$

where

$$n_0 = \frac{1}{a}\int_0^a f(x)\,\mathrm{d}x; \qquad A_m = \frac{2}{a}\int_0^a f(x)\cos\frac{m\pi x}{a}\,\mathrm{d}x \tag{218a}$$

Obviously, $n = n_0$ when $t = \infty$, in agreement with the condition that no solute
can enter or leave the system. As an example of restricted diffusion, we cite
the layer analysis method, used by many investigators from the very beginning
of the study of diffusion and culminating in the precise study of the diffusion of
potassium chloride in water by Cohen and Bruins (12). Among these inves-
tigations we mention particularly the extensive series of results of Öholm (75,
76). Unfortunately, determinations like those of Cohen and Bruins yield
integral diffusion coefficients and, as pointed out by Gordon (32), it is difficult
to compare such results with the integral values obtained by the diaphragm-cell
method.

Electromotive-force measurements (82, 85, 89, 103) and conductance measurements (44, 56, 73) have also been applied to measure diffusion coefficients in vessels in which restricted diffusion occurred. We shall describe in some detail a method which involves the measurement of electrical resistance at the top and bottom of a carefully designed vertical cell. By such a technique (39, 40), the diffusion coefficient of potassium chloride in water from 0.001 N to 0.01 N has been determined with an accuracy of the order of 0.1 per cent. These results serve for the first time to prove the validity of the limiting equation of Nernst (71) and to test the theory of Onsager and Fuoss (80).

B. FREE DIFFUSION. A GENERAL SURVEY OF OPTICAL SYSTEMS USED FOR DETERMINATION OF DIFFUSION COEFFICIENTS[7]

A general idea of how a concentration gradient in a solution deflects light from the normal path is clearly illustrated by figure 1. A horizontal slit to the left
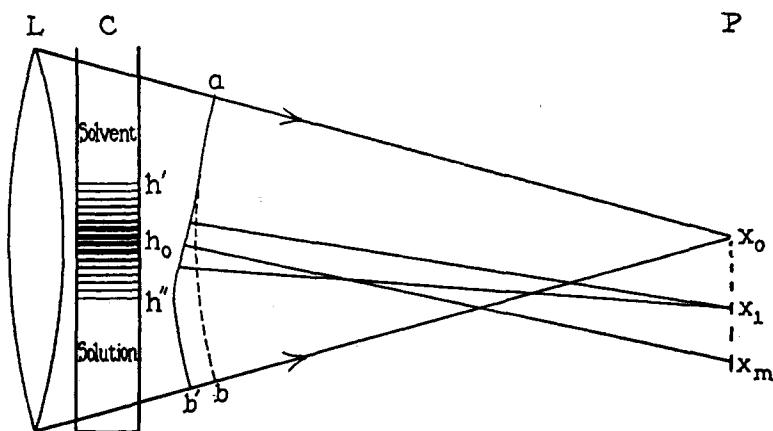

FIG. 1. Diagram illustrating the interference phenomena accompanying the deflection of light by gradients of refractive index in a freely moving boundary (Longsworth).

of lens L is focussed by this lens in the plane P. If the cell G contains a homogeneous liquid or solution, the wave front may be represented by the circular arc ab and the image of the slit will be focussed at x_0. Now suppose that free diffusion takes place at a sharp boundary between solution at the bottom and solvent at the height h_0. After a period of time, concentration gradients of magnitudes indicated by the intensity of the shading will be present and the new wave front will have the form ah_0b'. Since the refractive index of the more concentrated solution is the greater, the velocity of light will be less in the lower portion and $h''b'$ will be retarded relative to ah'. However, the light passing through these regions will still converge at x_0. On the other hand, the light which passes through the portion $h'h_0h''$ will converge at x_1, as indicated by the lines drawn normal to the wave front, and if the diffusion is not affected by turbulence or other disturbing factors will form a series of light and dark bands,

[7] See reference 1, which contains a review of optical methods.

which depend on the phase relations of the light. These bands increase in width from x_0 to x_m, at which level a diffuse band appears corresponding to the normal of the inflection point of the wave front.

In figure 2 a photograph of such a system of bands taken by Longsworth (61) is reproduced. He suggested that a quantitative theory of the distribution of these bands for the case of ideal free diffusion would be of considerable value for the application of optical methods.[8]
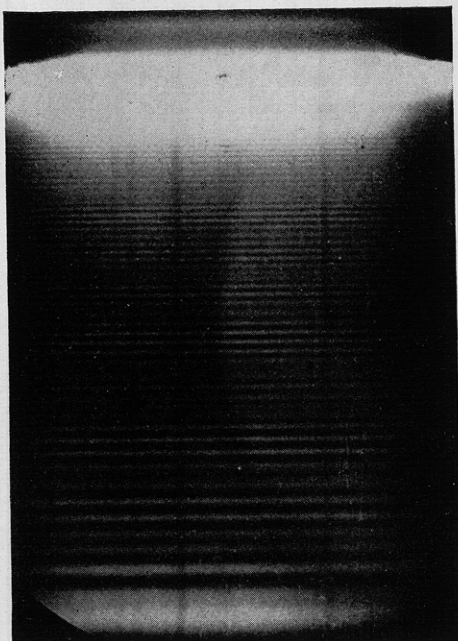

FIG. 2. Photograph at the schlieren diaphragm (Longsworth)

1. The "schlieren" method for the observation of boundaries and bands

The adaptation of Toepler's schlieren (shadow) method by Tiselius (98) for the observation of boundaries formed during the electrophoresis of macromolecules inaugurated an important development in the modern optical technique of measuring concentration gradients. By this method, a graph of a gradient of the refraction index dn/dx *versus* the vertical distance x in the cell may be constructed.[9] The method of Tiselius has been greatly improved in accuracy and ease of manipulation by Longsworth (60–66), who devised the

[8] In a private communication, Dr. Longsworth has informed me that as a result of this suggestion, Dr. Gerson Kegeles at the University of Wisconsin has developed a theory of this phenomenon by means of which the diffusion coefficient for ideal diffusion may be computed from the spacing of the bands.

[9] In this section n has been used to denote refractive index, in conformity with common usage.

"schlieren scanning" method by which a photograph of the plot of dn/dx against x can be obtained directly.[10]

A simple diagram of the optical system is shown in figure 3. An image of a horizontal slit is brought to focus in the plane at P by the lens D. At P an opaque diaphragm with a sharp horizontal upper edge is placed. This can be moved vertically. We note that the schlieren diaphragm is at the same position as the plane P in figure 1, so that the photograph (figure 2) was taken at this position. The objective lens O serves to focus the image of the cell E upon the photographic plate G.

If gradients of the refractive index are present in the cell, the light through these will be deflected downward as shown in figure 1. If the diaphragm is placed so as to intercept these deflected pencils, dark horizontal bands appear at the photographic plate. These shadows are known as the schlieren bands, which with electrophoretic boundaries can be made sharp by suitable lenses and a sufficiently narrow slit S. The displacement of the diaphragm from the position of the undeviated to the deviated image is proportional to the gradients of the refractive index in the cell conjugate to the edges of the bands.
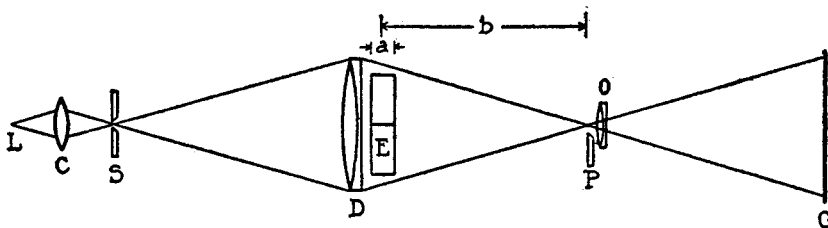

FIG. 3. Schematic diagram of the optical system employed in the schlieren method (Longsworth).

The facility with which the schlieren method can be applied has been greatly increased by Longsworth. A vertical slit is placed at the photographic plate and the latter is moved horizontally past the slit. Simultaneously, the schlieren diagram is moved vertically until the position of the undeviated slit image is reached. By this method a transparent area caused by the interception of the deviated pencils of light appears on the plate. The contour line of this area is a graph of the gradient dn/dx against the vertical position x.

The theory of the deflection of light by an inhomogeneous liquid system shows that if δ is the displacement of the schlieren diaphragm

$$\delta = ab\, dn/dx \qquad (219)$$

where a is thickness of the liquid in the cell and b is the optical distances indicated in figure 3. Lamm's (54) recent contribution to this subject contains detailed considerations of the optics of the scale and schlieren methods with particular emphasis upon the scale method. The theory of ray deflection is developed exhaustively.

[10] Special attention is suggested to the article by Longsworth (64), which is a masterpiece of description of this experimental method.

Now the integral which equals the area under the plot derived from the schlieren scanning photographs is

$$\int \delta \, dx = \int ab \frac{dn}{dx} \, dx = ab\Delta n \tag{220}$$

This equation has proved of importance in the study of electrophoresis, where a substance is concentrated in a thin layer. For this case, the increment in refractive index, Δn, is nearly proportional to the concentration of substance. Consequently the schlieren scanning method can be used conveniently to estimate the total concentration of the substance and the distribution of concentration through the boundary.

2. The scale method of Lamm (54)

The optical system of the scale method consists of a lens by means of which a scale is focussed on a plane photographic plate. A vertical cell with parallel sides is placed between the scale and the lens at a distance b from the scale. The scale is first photographed through a distance a of a homogeneous solvent or solution. It is photographed again later through the inhomogeneous media produced by the diffusing substances or electrophoretic boundary. The refractive-index gradients cause deviations in the images of the lines of the scale on the photographic plate which can be determined by comparison with the normal scale-line positions. For this purpose a comparator is used. In this optical system the deviated line is somewhat out of focus, but this condition can be remedied to a large extent by employing a lens with a long focal length.

Lamm (54) has made a very careful and exhaustive theoretical and experimental investigation of the scale method, and his dissertation should be read by all those seriously interested in the subject. Geometric optics shows that the displacement of a line from its normal position on the photographic plate is given by the equation

$$Z = Gab \, dn/dx \tag{221}$$

where a and b are the distances mentioned above and G is a magnification factor (photographic enlargement).

The photographic deviation Z and scale reading z are arbitrary but depend on the refractive-index gradient dn/dx, which we shall denote by X, and the x-dimension in the cell. The projection factor is dx/dz or F, which when introduced in equation 22 yields

$$dn = \frac{F}{Gab} Z \, dz \tag{222}$$

and the integral

$$n - n_0 = \frac{F}{Gab} \int_{z_{n_0}}^{z_n} Z \, dz \tag{223}$$

In order to determine the diffusion coefficient from these measurements of free diffusion, we resort to equation 213, which was derived by Wiener (105).

Thus

$$X = dn/dx = \frac{n_1 - n_0}{2\sqrt{\pi \mathfrak{D} t}} e^{-x^2/4\mathfrak{D} t} = \frac{\Phi}{2\sqrt{\pi \mathfrak{D} t}} e^{-x^2/4\mathfrak{D} t} \qquad (224)$$

where Φ is the area under the (X, x) graph. This relation is recognized to have the form of the error or probability law, and its general validity in the case of pure free diffusion is well illustrated by the diagram of Wiener's optical system in figure 4. The illuminated slit at an angle of $45°$ is focussed upon a screen (G) by a lens of large focal length. If the solution in the cell (C) is homogeneous, the image of the slit is the straight dashed line. If a diffusion gradient is produced from an originally sharp boundary at h_0 between a solution at the bottom and solvent at the top, the light rays are bent downward and the image upon G has the characteristic form of the error function, $ab'c$. Somewhat later Thovert, by interposing a cylindrical lens between the cell and a photograph,
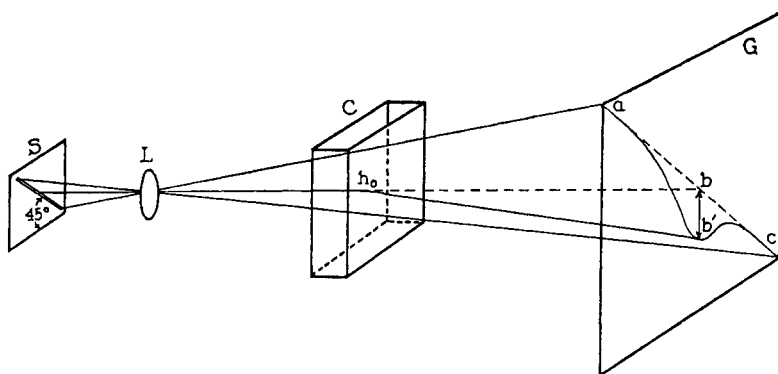

FIG. 4. The optical system of Wiener (Longsworth)

obtained a horizontal image. One of his photographs of an experiment in which 0.85 N sodium chloride is diffusing into water is shown in figure 5. The three curves correspond to different times during the diffusion process.

The actual experimental observations in the scale method are deviations of the scale lines on the photograph, Z, and the distances of the scale lines, z, from some arbitrary origin. Since these results depend on equation 224, which has the form of a Gauss distribution function, they may be computed by the methods of mathematical statistics.[11] To this end, the experimental values of the ordinates Z are plotted against the abscissae z. The z-axis is then divided into a large number of equal parts of length w, and the scale values corresponding to each of these divisions are obtained from the ordinates of the graph. From an arbitrary origin $(s = 0)$ the divisions are numbered $1, 2$, etc. to the right and $-1, -2$, etc. to the left of this arbitrary origin.

The ideal frequency curve $S = f(s)$ of Charlier (11)

[11] K. Pearson (Trans. Roy. Soc. (London) **A185**, 71 (1894)). For a simple textbook treatment see B. H. Camp, *The Mathematical Part of Elementary Statistics*, Heath and Company, New York (1934).

$$S = \frac{N\omega}{\sigma\sqrt{2\pi}}\, e^{-(s-\beta)^2\omega^2/2\sigma^2} \tag{225}$$

is suitable for this computation.   In this relation, S is the frequency of a given statistical element, N is the total number of statistical elements, s is the class number, ω is the class breadth, σ is the standard deviation, and β is the distance of the arbitrary origin from the centroid.
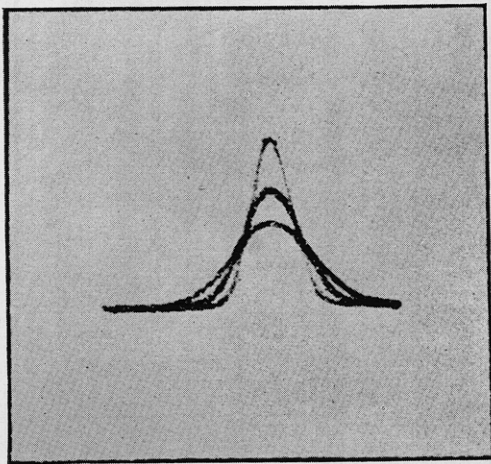

FIG. 5. Photograph obtained by Thovert of 0.85 N sodium chloride diffusing into water (Longsworth).

This equation becomes analogous to equation 213

$$X = \frac{dn}{dx} = \frac{\Phi}{2\sqrt{\pi\mathfrak{D}t}}\, e^{-x^2/4\mathfrak{D}t} \tag{226}$$

upon substituting

$$x = (s - \beta)\omega \tag{227}$$

$$\Phi = N\omega = \text{area} \tag{228}$$

$$\sigma^2 = 2\mathfrak{D}t \tag{228}$$

The quantities N, β, and σ/ω are determined from the theory by the relations

$$N = \Sigma S \tag{230}$$

$$\beta = \frac{\Sigma S s}{\Sigma S} \tag{231}$$

and

$$\left(\frac{\sigma}{\omega}\right)^2 = \frac{\Sigma s^2 S}{\Sigma S} - \left(\frac{\Sigma S s}{\Sigma S}\right)^2 \tag{232}$$

The latter equation is derived from consideration of the area and the second

moment. The maximum value of the frequency S_m occurs when $(S - \beta)\omega$ is zero, whence

$$S_m = \frac{N\omega}{\sigma\sqrt{2\pi}} = \frac{(\Sigma S)\omega}{\sigma\sqrt{2\pi}} \tag{233}$$

These later equations yield

$$\mathfrak{D} = \left[\frac{\Sigma s^2 S}{\Sigma S} - \left(\frac{\Sigma S s}{\Sigma S}\right)^2\right]\frac{\omega^2}{2t} \tag{234}$$

and

$$\mathfrak{D} = \frac{(\Sigma S)^2}{S_m^2}\frac{\omega^2}{4\pi t} \tag{235}$$

which have been frequently employed for the evaluation of the diffusion coefficient. Since the calculations are made from the Z, z graph, the projection constants of the apparatus must be employed for determining ω and N. In order to obtain the mean position of the boundary or to change the origin to the centroid, $\beta\omega$ is added to the s readings.

Further, in order to compare the frequency curve with the corresponding normal ideal Gauss curve, let

$$\xi = \frac{(s - \beta)\omega}{2\sigma} \tag{236}$$

and

$$\Xi = \frac{5\sigma}{N\omega}S \tag{237}$$

whence

$$\Xi = \frac{5}{\sqrt{2\pi}}e^{-2\xi^2} \tag{238}$$

The numbers 5 and 2 are arbitrary and are chosen for convenience in drawing the graph.

The free diffusion of a pure solute into a solvent has been shown in many instances to conform to the theory. Consequently, agreement with theory has been interpreted as proving that the solute is a homogeneous substance and that deviations from the ideal curve indicate that the diffusing substance is a mixture. The principal application of this latter reasoning has found the basis for numerous studios of diffusion of polydisperse systems containing macromolecules (3, 4).

That the real diffusion graph conforms to the ideal normal Gauss distribution is illustrated by figure 6. These are plots of Lamm's results for the diffusion of 0.1 N potassium chloride into water at 20°C. The bottom curve is the plot of the photographic displacements Z versus the distances z on the arbitrary scale with origin corresponding to the maximum of the graph. The top curve shows the same results in normal coördinates, Ξ and ξ. The agreement between the experimental and theoretical results is good.

Lamm (54) computed the diffusion coefficient for this case by a number of methods involving the mathematical properties of these curves and obtained values of 1.44 to 1.47 cm.^{2} per day or 1.67 to 1.70 $\times$ 10^{-5} cm.^{2} per second. This agrees closely with the result, 1.448 cm.^{2} per day, obtained by Cohen and Bruins (12) by the layer analysis method. However, this agreement must be taken cautiously, since it is difficult to interpret exactly results obtained by the layer analysis method (see Section V, D, 1).
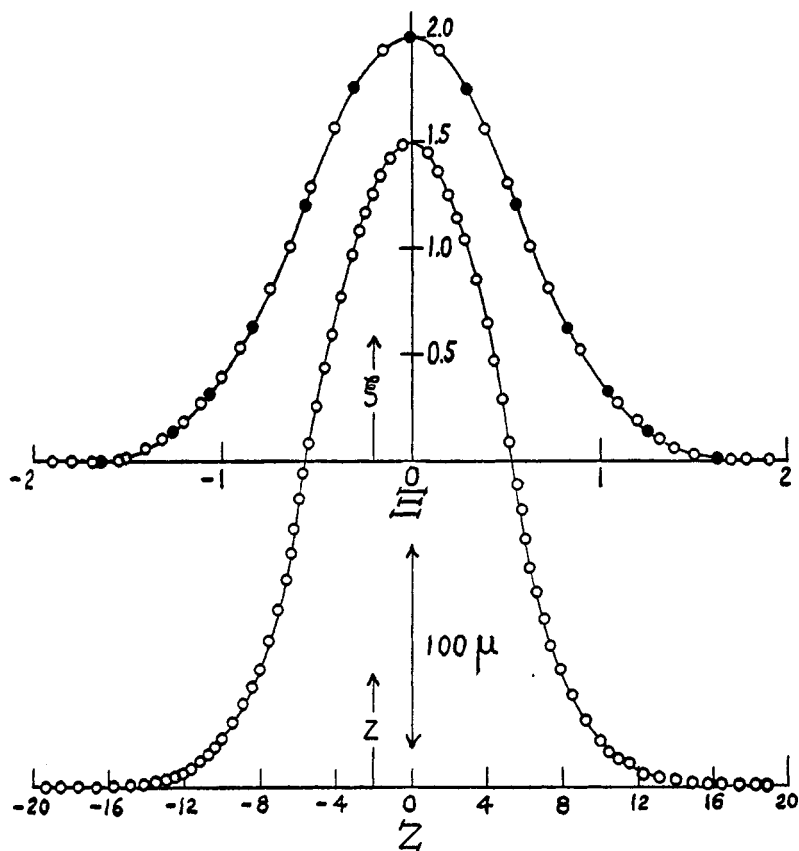
FIG. 6. Z,z and Ξ,ξ plots employed for the calculation of the diffusion coefficient by the scale method.

C. STEADY-STATE DIFFUSION

1. The measurement of the differential diffusion coefficient according to Clack (9, 10)

The experiments of Clack which led to the determination of the differential diffusion coefficients of potassium and sodium chlorides and potassium nitrate from 0.05 N to high concentrations are one of the most important contributions to this field. Clack's apparatus is represented in figure 7. A salt from a

saturated solution is allowed to diffuse upward into water in the cell C until a steady state of diffusion is reached. The refractive index and its gradient are measured by an optical system consisting of a horizontal slit S focussed by the lenses L_1 and L_2 upon an ocular E. A screen B with a compound slit Y is interposed between the lens L_1 and the cell. This screen can be moved vertically along the column. Clack found that the interference pattern formed by the double slit in the ocular yielded a sharply defined central band. The displacement of the pencil of rays produced by the refractive-index gradient in the cell from its normal position can be measured by moving the ocular in a vertical direction.
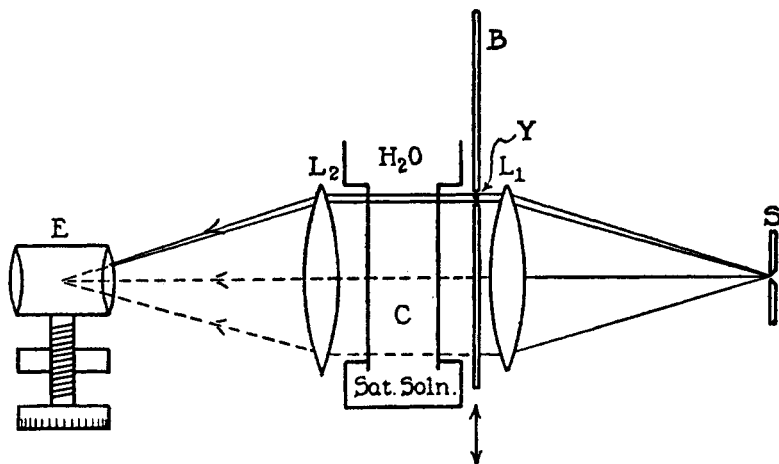

FIG. 7. The optical system used by Clack for the determination of differential diffusion coefficients (Longsworth).

As in the previous optical methods, this displacement δ is given by the equation

$$\delta = ab \, dn/dx \qquad (239)$$

where a is the distance through which the light passes in the liquid, b is the distance from C to E, and x is position in the cell at the height of the slit Y. Knowing these dimensions and δ, dn/dx at any height z may be determined, and if n is known as a function of the concentration c, both c and dc/dx may be evaluated at the position x.

In order to evaluate the differential diffusion coefficient by this method, it is necessary to determine the solute flow J, and also to make a correction for the solvent counterflow. With this in mind, we write Fick's first law

$$\mathfrak{D} = - J_1 \phi (dc/dx)^{-1} \qquad (240)$$

where ϕ is the frame-of-reference factor. In Clack's final experiments, the lower reservoir of the cell contained solid salt in equilibrium with its saturated solution. When the steady state is attained, the flow J_1 is a constant and the

lower reservoir loses J_1 grams of salt and gains J_0 grams of water per unit cross section in unit time. The quantities J_1 and J_0 can be computed from the weight of salt dissolved, the density of the salt, and the concentration and density of the saturated solution.

We have pointed out that the flow has usually been defined relative to a fixed plane of reference and have indicated by equation 2, which defines a bulk velocity, how the flow can be defined relative to a frame of reference moving with the solvent. It is clear that in dilute solutions when extremely small volume changes are involved there will be no appreciable difference between results obtained upon these two frames of reference. On the other hand, in Clack's cell the concentration of salt through the column varies from that of the saturated solution to zero, so that the results obtained at a reference fixed with respect to the apparatus must be corrected for solvent counterflow and volume changes. Clack derived expressions for this correction.

2. The diaphragm-cell method

The use of sintered-glass diaphragm cells for measuring diffusion coefficients has been shown by McBain (67) and especially by Gordon (14, 32) and Hartley and Runnicles (43) to be convenient and accurate. Since the diffusion process is slow, measurements in vessels without diaphragms are most sensitive to any factors which, like local gradients of temperatures or initial stirring, may cause convection. In the diaphragm cell, the diffusion is confined to the pores of a sintered-glass or an alundum diaphragm, so that errors caused by agitation by thermal or mechanical means are reduced to a minimum.

The apparatus used by McBain and Liu (68) and Gordon (14, 32) consisted of a bell-shaped vessel with a stopcock at the top and a flat diaphragm of sintered glass at the bottom. This (inner) vessel is filled with the more concentrated solution and is suspended in such a way that the diaphragm just touches the surface of a weaker (outer) solution. The diaphragm must be adjusted horizontally and must be in contact with the outer solution over its entire surface. The whole apparatus is placed in an air thermostat. In this form of apparatus only density stirring can take place.

Mouquin and Cathcart (69) have described a glass cell containing a sintered-glass diaphragm at the middle, which was stirred by rotating end over end. Hartley and Runnicles (43) obtained stirring by rotation of their cell about its axis at an angle inclined to the vertical. The upper solution was stirred by a glass sphere resting on the diaphragm, and the lower solution by a lighter glass sphere which pressed against the bottom surface of the diaphragm. The concentration in the inner compartment of the apparatus was measured by conductance.

The obvious disadvantage of the diaphragm-cell method consists in the fact that each cell possesses a cell constant which must be evaluated by employing a solution containing a solute with a known diffusion coefficient. Up to very recently, no determination of a diffusion coefficient of an electrolyte could be relied on to within a few per cent, so that no really satisfactory cell-constant calibration could be made.

On the other hand, by careful experimentation resulting from critical analysis of the sources of error, it has been shown that diaphragm-cell measurements are capable of high accuracy and reproducibility. The theory of the method, originally developed by Northrup and Anson (74) and McBain and Liu (68), is very simple. The diaphragm is assumed to be made up of a large number of parallel pores of a length l and of an effective cross-sectional area, A. The solutions on both sides of the diaphragm are assumed to have uniform composition and the transfer of matter from the inner to the outer solution occurs only by the process of diffusion. The membrane must be such that any stream-lined flow is prohibited. If c' and c'' change slowly, the solute distribution throughout the diaphragm will approach that of a steady-state process. The concentration gradient across the diaphragm if $\mathfrak{D}$ is independent of the concentration will be $(c' - c'')$ and will be constant throughout the diaphragm. If the quantity, dq, of solute diffuses in the time dt, then

$$dq = \frac{\mathfrak{D}A}{l} (c' - c'') \, dt \tag{241}$$

which is the differential form of equation for the diaphragm cell. The concentrations c', c'' and the quantity dq/dt may be measured, but A/l is not known and must be determined from the known diffusion coefficient of some solute. Northrup and Anson used this differential form of equation. There are obvious practical advantages of extending the measurements over longer time intervals and most of these measurements have employed the result obtained by integration. The change in the quantity of solute in one compartment in a time dt must equal the amount which has diffused in or out of this compartment. If V' and V'' are the volumes of the inner and outer solutions, respectively, then

$$V'dc' + (\mathfrak{D}A/l)(c' - c'') \, dt = 0$$
$$V''dc'' + (\mathfrak{D}A/l)(c'' - c') \, dt = 0 \tag{242}$$

where dc' and dc'' are the concentration changes. Upon subtracting the second of these equations from the first and writing Δc for $(c' - c'')$, we obtain:

$$\frac{d(\Delta c)}{\Delta c} + \beta \mathfrak{D} \, dt = 0 \tag{243}$$

where the cell factor constant β is given by

$$\beta = \frac{A}{l} \left(\frac{1}{V'} + \frac{1}{V''} \right) \tag{243a}$$

Assuming that $\mathfrak{D}$ is not a function of c, and that the cell remained constant during an experiment, equation 243 can be integrated from the initial concentrations c_0', c_0'' to the final concentration c_f', c_f'' to yield

$$\ln \frac{\Delta c_f}{\Delta c_0} = -\beta \mathfrak{D} t \tag{244}$$

the equation most frequently used in determining the diffusion coefficient by this method.

An analytical and critical survey of the diaphragm-cell technique has been made by Gordon (32). In addition to the discussion of the sources of errors and their elimination, he has shown that the density-stirred method yields results which agree with those obtained by mechanical stirring. He also shows that the diaphragm-cell method may be safely treated as a steady-state process. We shall reserve for a later section the discussion of the selection of a standard diffusion coefficient required for the calibration of the cell.

Gordon (32) has made an important contribution in showing how the differential diffusion coefficient can be evaluated from diaphragm-cell measurements. Let us assume that $\mathfrak{D}$ is a function of the concentration so that

$$\mathfrak{D}/\mathfrak{D}_0 = 1 + f(c) \tag{245}$$

where $\mathfrak{D}_0$ is the value of $\mathfrak{D}$ at infinite dilution. If this is the case, then the derivation of equation 244 is incorrect. Now for convenience, an integral diffusion coefficient $\mathfrak{D}_i$ may be defined by equation 244, since ΔC_f, ΔC_0, and β are known. By the following procedure, one may find the concentration c_i at which $\mathfrak{D}_i$ equals the differential diffusion coefficient $\mathfrak{D}$. For a steady-state process at a given time, the flow $\mathfrak{D}\partial c/\partial x$ is constant from the top ($x = 0$) to the bottom ($x = l$) of the membrane, for if this were not the case the transport of matter would be unequal at different areas on the diaphragm. At this instant, let the inner and outer concentrations be c' and c'' and define an "effective" diffusion coefficient $\mathfrak{D}'$ by

$$- \mathfrak{D}'(c' - c'')/l = \mathfrak{D}\partial c/\partial x \tag{246}$$

If this equation be multiplied by dx and integrated from $x = 0$ to $x = l$

$$\mathfrak{D}'/\mathfrak{D}_0 = 1 + \frac{1}{\Delta c} \int_{c''}^{c'} f(c) \, dc \tag{247}$$

where $\Delta c = (c' - c'')$. Since $\mathfrak{D}'$ changes as the diffusion proceeds, equation 243 becomes

$$\frac{d(\Delta c)}{\Delta c} + \beta \mathfrak{D}' \, dt = 0 \tag{248}$$

and if $F(c', c'')$ be defined by

$$\mathfrak{D}_0/\mathfrak{D}' = 1 + F(c', c'') \tag{249}$$

its integration can be effected by means of the equation

$$\ln \frac{\Delta c_f}{\Delta c_0} + \int_{\Delta c_0}^{\Delta c_f} \frac{F(c', c'')}{\Delta c} \, d(\Delta c) = -\beta \mathfrak{D}_0 t \tag{250}$$

but since by definition

$$\ln \frac{\Delta c_f}{\Delta c_0} \equiv -\beta \mathfrak{D}_i t \tag{251}$$

$$\mathfrak{D}_i/\mathfrak{D}_0 = 1 + \left(\frac{1}{\beta} \mathfrak{D}_0 t\right) \int_{\Delta c_0}^{\Delta c_f} \frac{F(c', c'')}{\Delta c} \, d(\Delta c) \tag{252}$$

Recalling that c_i is the concentration at which $\mathfrak{D}_i = \mathfrak{D}$, the second term on the right of this equation must equal $f(c_i)$, because of the original assumption expressed by equation 245.

If $\mathfrak{D}$ is known as a function of c, $\mathfrak{D}'$ can be readily calculated by graphical or analytical integration from the known values of c' and c'' by equation 247. Then equation 252 can be used to evaluate $\mathfrak{D}_i$, since for every value of $(c' - c'')$, $F(c', c'')$ can be computed. The more important reverse calculation of $\mathfrak{D}$ from $\mathfrak{D}_i$ requires a short series of approximations. If, as is usually the case, the inner and outer solution volumes are the same, $\mathfrak{D}$ is identified with $\mathfrak{D}_i$ at the mean of the initial concentrations of the inner and outer solution. These values of $\mathfrak{D}$ may be represented by the empirical equation

$$\mathfrak{D}/\mathfrak{D}_0 = 1 - A\sqrt{c} + Bc \qquad (253)$$

where A and B are empirical constants. Then by means of equations 244, 247, and 252 a second series of values of $\mathfrak{D}_i$ is computed. The next step is to substitute these values of $\mathfrak{D}_i$ in equation 253 and to calculate the corresponding values of c_i. The second approximation consists in adjusting the constants A and B with these values of c so that they are identified with the observed integral values $\mathfrak{D}_i$. We shall have occasion to reconsider this method of calculation when actual diffusion coefficients by the conductance and diaphragm-cell methods are compared.

D. RESTRICTED DIFFUSION

1. The layer analysis method

The method of layer analysis in which a solute diffuses upward in a closed vertical cell and, after a known time, equal portions of the solution at suitable heights are analyzed is in the category of restricted diffusion. The early measurements of Scheffer (86) and Arrhenius (2), the extended results of "Öholm (75, 76), and the precision study of Cohen and Bruins (12) were made by the method of layer analysis. The best technique was effected in cells in which a shearing mechanism was employed, first to form an initial sharp boundary and secondly for removing the layers for analysis (8, 20, 36, 47, 75, 76, 88, 92, 102). The most precise measurements of this kind were made by Cohen and Bruins, who allowed $0.1 \ N$ potassium chloride at 20°C. to diffuse from the lower compartment in an accurately machined apparatus divided into four compartments. After 36 hr. the four compartments were separated by a shearing mechanism and the solutions analyzed by a liquid interferometer.

On the assumption that the diffusion coefficient is not a function of the concentration, its determination may be obtained from the solution of the differential equation of Fick's second law for restricted diffusion given by equation 218. If a is the height of each of the four compartments and n_0 the initial concentration of the solute in the lowest compartment, then when $t = 0$,

$$n = n^0 \text{ from } x = 0 \text{ to } x = a; n = 0 \text{ for } x = a \text{ to } x = 4a$$

and at all times

$$\frac{\partial n}{\partial x} = 0 \quad \text{for} \quad x = 0 \quad \text{and} \quad x = 4a \tag{254}$$

With these conditions, equation 218 becomes

$$n = \frac{n^0}{4} + \frac{2n^0}{\pi} \sum_{m=1}^{\infty} \frac{1}{m} \sin \frac{m\pi}{4} \cos \frac{m\pi x}{4a} e^{-(m^2\pi^2 \mathfrak{D}t)/16a^2} \tag{255}$$

At a time t, the quantity of solute in each of the four equal layers may be obtained by the integrals

$$Q_p = A \int_{(p-1)a}^{pa} n \, \mathrm{d}x \tag{256}$$

where A is the cross-sectional area of the cell.

This method has been thoroughly investigated by Stefan (91) and Kawalki (51), who constructed tables which were regarded by the earlier investigators as suitable for the computation of $\mathfrak{D}$. These give the percentage of the total quantity of solute in each of the layers as a function of $\mathfrak{D}$, t, and a: namely, $\mathfrak{D}t/(\Delta a/2)^2$. Thus, by matching the experimental results with those in the tables, a value of $\mathfrak{D}$ may be obtained.

As shown by Cohen and Bruins (12), this experiment may be carried out with great precision but unfortunately, the values of $\mathfrak{D}$ are not differential diffusion coefficients nor are they the same as integral diffusion coefficients corresponding to a concentration of one-fourth the initial concentration. Further, Gordon (31, 32) showed that the $\mathfrak{D}$ of Cohen and Bruins was not the same as the integral coefficient obtained from diaphragm-cell measurements. Hartley and Runnicles (43) examined the matter in greater detail and came to the conclusion that the coefficient of Cohen and Bruins, obtained by diffusing 0.1 N potassium chloride into three-fourths the volume of water, was approximately the integral coefficient which would be obtained in a diaphragm cell if 0.06 N potassium chloride were allowed to diffuse into pure water. Both Gordon, and Hartley and Runnicles, are of the opinion that the result of Cohen and Bruins is high, owing to mixing when the apparatus is separated into layers.

2. A conductance method for the differential diffusion coefficient

The possibility of utilizing conductance measurements for determining the diffusion coefficient of electrolytes has naturally occurred to many investigators, but only very recently has it been carefully developed. Niemöller (73), over fifty years ago, measured the change in conductance through a capillary tube containing a solution of a diffusing electrolyte. Haskell (44) employed a diffusing column 50 cm. in length and 5 cm. wide and recorded the conductance at various heights. Lamm (57) has recently developed a method and described a cell for the determination of the differential diffusion coefficient by this method. Lamm develops the theory of an apparatus in which free diffusion occurs. This method is more complicated than the method based upon restricted diffusion employed by Harned and French (39). The latter demonstrated that

their apparatus was capable of yielding differential diffusion coefficients of potassium chloride at concentrations between 0.002 and 0.005 N with an accuracy of the order of 0.9 per cent. As a result of their experience, they stated that with a new design of cell and with some technical improvements this accuracy could be greatly increased. This has proved to be the case (40) and there seems to be little doubt that this method is well calculated to solve experimentally the fifty-year-old problem of diffusion coefficients of electrolytes in very dilute solutions.

The most important feature of the method consists in designing a cell in such a way that mathematical complications are reduced to a minimum and the interpretation of the measurements is simple and direct. The simplest possible form of cell is a rectangular parallelepiped of height a, completely filled with liquid in which an electrolyte is allowed to diffuse upward. This process belongs
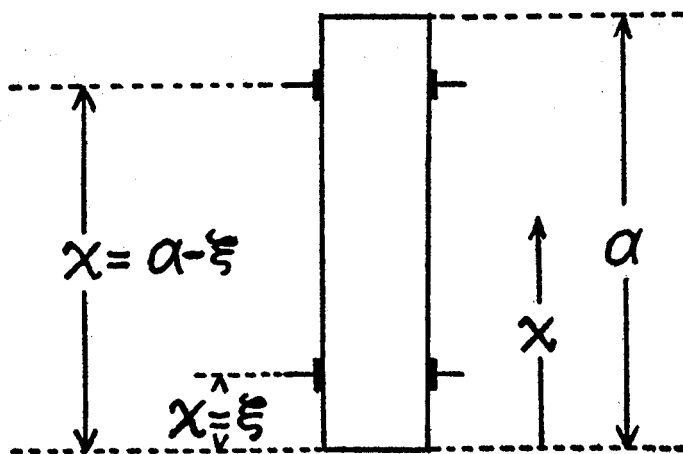

FIG. 8. Vertical cross-section of conductance cell showing quantities involved in the theoretical derivations.

to the category of restricted diffusion. The calculations are greatly simplified by measuring the difference of conductance between two electrodes near the bottom and two electrodes near the top of the cell, their exact position to be determined by theory. For this idea, we are indebted to Professor Lars Onsager.

The schematic cross section of such a cell is shown in figure 8, in which the electrodes are at a distance, ξ, from the top and bottom. Solute in the solution from the bottom part of the cell diffuses upwards into the top part, so that as time elapses the concentrations at the top and bottom of the cell approach each other. We shall assume that this difference in concentration is small enough so that $\mathfrak{D}$ may be regarded as constant. Then, according to Fick's second law

$$\frac{\partial c}{\partial t} = \mathfrak{D}\,\frac{\partial^2 c}{\partial x^2}\,; \qquad \frac{\partial c}{\partial x} = 0 \quad \text{for} \quad \begin{cases} x = a \\ x = 0 \end{cases} \tag{275}$$

where c is the concentration in mols per liter. These conditions are satisfied

by the solution (equation 218) in the form

$$c = \sum_{m=1}^{\infty} A_m e^{-m^2 \pi^2 \mathfrak{D} t / a^2} \cos \frac{m\pi x}{a} + c_0 \tag{258}$$

where the Fourier coefficients are such as to satisfy the initial conditions of concentration. The difference in concentration at the bottom $c(\xi)$ and the top $c(a - \xi)$ is

$$c(\xi) - c(a - \xi) = 2A_1 e^{-\pi^2 \mathfrak{D} t / a^2} \cos \frac{\pi \xi}{a} + 2A_3 e^{-9\pi^2 \mathfrak{D} t / a^2} \cos \frac{3\pi \xi}{a}$$

$$+ 2A_5 e^{-25\pi^2 \mathfrak{D} t / a^2} \cos \frac{5\pi \xi}{a} + \cdots \tag{259}$$

We note immediately the great advantage in measuring the difference in concentrations at the bottom and top electrodes, since all even terms of the series vanish and, owing to the character of the experimental term, the series converges very rapidly. Now, if the electrodes are placed at a distance ξ from the top and bottom equal to one-sixth the total depth of the cell ($\xi = a/6$), then

$$c(\xi) - c(a - \xi) = 2A_1 e^{-\pi^2 \mathfrak{D} t / a^2} \cos \frac{\pi \xi}{a} + 2A_5 e^{-25\pi^2 \mathfrak{D} t / a^2} \cos \frac{5\pi \xi}{a} + \cdots \tag{260}$$

and only the first term of the series has significance after sufficient time has elapsed. Since ξ and a are constant,

$$\ln (c(\xi) - c(a - \xi)) = -\frac{\pi^2 \mathfrak{D} t}{a^2} + \text{constant} = -\frac{t}{\tau} + \text{constant} \tag{261}$$

where $\tau = a^2 / \pi^2 \mathfrak{D}$, $1/\tau$ becomes the slope of the plot of

$$\ln (c(\xi) - c(a - \xi)) \; versus \; t$$

and

$$\mathfrak{D} = \frac{a^2}{\pi^2} \frac{1}{\tau} \tag{262}$$

As a result of this design of cell, the equation of the diffusion process becomes one of the first order, so that if the concentration difference at the bottom and top be measured accurately, $\mathfrak{D}$ may be evaluated by the simple measurement of the depth of the cell.

For many electrolytes over the narrow ranges of concentration involved in this experiment the difference in concentrations, $c(\xi) - c(a - \xi)$, is proportional to the difference in conductance, $K_B - K_T$, so that

$$\ln [K_B - K_T] = -t/\tau + \text{constant} \tag{263}$$

When this is the case, the calculation of $\mathfrak{D}$ is considerably simplified.

It is apparent that this method is most direct and has the greatest theoretical simplicity. Only the measurements of the resistances at the top and bottom of

the cell at suitable times and the depth of the cell are required. It has the advantage of great accuracy in dilute solutions. Its only disadvantage is the length of time required to obtain suitable results.

The procedure of measuring concentrations at the top and bottom of an apparatus during restricted diffusion might be made the basis of an optical method. Two parallel beams of light could be passed through the cell at suitable positions at the top and bottom. By a proper arrangement of an optical sytem, the interference phenomena produced could be used to measure the difference in concentrations at the bottom and top as the diffusion proceeds. Such a method might prove to possess some advantages over other optical methods.

VI. EXPERIMENTAL RESULTS

1. The differential diffusion coefficient of potassium chloride in dilute aqueous solution

The conductance method described in the last section has provided the most accurate values of diffusion coefficients in dilute solutions. The second column of table 2 contains values of $\mathfrak{D} \times 10^5$ of potassium chloride in water recently determined by Harned and Nuttall (40). These results were obtained by an apparatus which differed somewhat from the one used by Harned and French (39) in their earlier measurements by this conductance method. This and other improvements in technique have reduced the error of the determination from ± 0.9 per cent to the order of ± 0.1 per cent.

Each of these determinations depends on three measurements,—differences in conductance between the bottom and top of the cell taken at suitable intervals over a period of 6 days, the times when these conductances were recorded, and the depth of the cell. Values of the diffusion coefficients were calculated from the first to second, second to third, etc. days from the slopes derived from 24-hr. differences in conductance. These values were constant to within narrow limits and, as shown by Harned and Nuttall, showed no trend over a period of 6 days. The results in the table represent the mean of all these individual determinations.

The fifth column contains values of $\mathfrak{D}$ computed by equation 176. All the factors involved are considered. In this concentration range, the calculation $\overline{\mathfrak{M}}/c$ for potassium chloride is comparatively simple. Since the equivalent conductances of the ions involved are so nearly equal, the second term on the right of equation 178 is negligible. The calculation of the activity term is also simple at low concentrations, since the term $\psi(d)$ in equation 184 may be neglected. Upon introducing the values: $\lambda_1^0 = 73.48$, $\lambda_2^0 = 76.34$ from the data of Shedlovsky (90), and Longsworth and MacInnes (65), $\eta_0 = 8.949 \times 10^{-3}$ and $D_0 = 78.54$, equation 179 becomes

$$\frac{\overline{\mathfrak{M}}}{c} \times 10^{20} = 40.254 + 18.96c\phi(A'\sqrt{c}) \tag{264}$$

from which the values of $\overline{\mathfrak{M}}/c$ in column three were obtained. The activity coefficient term in column four was computed by equation 183 upon substitution

of the parameters given by Harned and Owen (41): namely, $\mathfrak{S}_{(f)} = 0.5065$' $A' = 1.249$, and $B = 0.0202$. The term containing D' is negligible in solutions as dilute as those under consideration.

The agreement of the observed values with the theoretical ones is remarkable. This is illustrated most clearly by the results in the last column of the tables, in which the calculated values of $\mathfrak{D}_0 - \mathfrak{D}$ have been added to the experimental results. If the theory is valid, the resulting values of $\mathfrak{D}_0$ should be constant and equal the limiting value computed from conductance data. The mean value of these results is 1.997, a figure which confirms the limiting value of 1.996. In fact, as pointed out by Gordon (32), these are the first objective results of sufficient accuracy to confirm the limiting equation of Nernst for the differential diffusion coefficient at infinite dilution.

TABLE 2

The observed and calculated values of the differential diffusion coefficient of potassium chloride at 25° C.

c	$\mathfrak{D} \times 10^5$ (OBSERVED)	$\dfrac{\overline{\mathfrak{M}}}{c} \times 10^{20}$	$1 + c \dfrac{\partial \ln y_\pm}{\partial c}$	$\mathfrak{D} \times 10^5$ (THEORETICAL)	$\mathfrak{D}_0 \times 10^5$
0.00000		40.253	1.000	1.9958	
0.00125	1.961	40.301	0.981	1.9605	1.996
0.00194	1.954	40.317	0.977	1.953	1.997
0.00325	1.943	40.346	0.971	1.943	1.996
0.00585	1.931	40.395	0.963	1.929	1.997
0.00704	1.924	40.413	0.960	1.925	1.995
0.00980	1.918	40.449	0.955	1.916	1.999

The magnitudes of the electrophoretic contribution and the activity coefficient terms are illustrated by figure 9. The lowest plot represents the limiting law as calculated by equations 185, 186, and 187, which upon substitution of the experimental values indicated reduces to

$$\mathfrak{D} \times 10^5 = 1.9958 - 1.170\sqrt{c} \tag{265}$$

The dotted curve was computed by equation 177 by employing the limiting value of $\overline{\mathfrak{M}}/c$ and neglecting its change with concentration. This leads to the numerical equation

$$\mathfrak{D} \times 10^5 = 1.9958 \left(1 + c \frac{\partial \ln y_\pm}{\partial c}\right) \tag{266}$$

The graph at the top is the plot of the results of the complete theoretical computation given in the fifth column of table 2. The circles are the observed values from the second column of this table.

There is little doubt from the agreement between the theoretical and observed results that, in these dilute solutions, the term in equation 264 containing $\phi(A'\sqrt{c})$ is required. Indeed, this is the first experimental confirmation of the Onsager and Fuoss theory.

2. *Comparison with diaphragm-cell measurements*[12]

The only other measurements at low concentrations which can be compared with these results have been obtained by the diaphragm-cell method. In his recent contribution, Gordon (32) gives the results of his computation of the differential diffusion from the integral values by the method outlined in Section V, C. The experimental data of Hartley and Runnicles (43), McBain and Dawson (67), and Gordon were used. The selection of a standard for the calibration of the diaphragm cells depended on the semi-empirical equation of Gordon, which represented Clack's data at the higher concentrations and which extra-
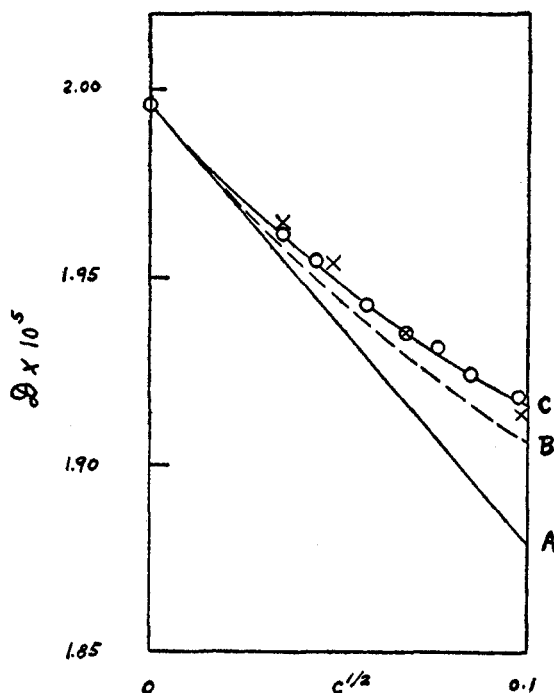

FIG. 9. The diffusion coefficient of potassium chloride in dilute aqueous solution at 25°C. O, conductance method; ×, diaphragm-cell method. A, limiting equation 265; B, equation 266; C, complete theoretical computation.

polated to the Nernst limiting value. The results at low concentrations fall closely to the dotted line in figure 9.

These results have now been revised by Gordon upon the basis of the new measurements given in table 2. This is much more satisfactory, since the calibration depends on objective evidence only. The data in this table are represented accurately by the empirical equation 253, which with numerical values becomes

$$\mathfrak{D} \times 10^5 = 1.996 - 1.065 \sqrt{c} + 2.75c \qquad (267)$$

[12] The subject matter and calculations of this section have been derived from a private communication from Professor A. R. Gordon of the University of Toronto.

On this basis and the method of computation described in Section V,C, the results in table 3 were obtained. The values of $\mathfrak{D}_i$ are differential diffusion coefficients at the concentration c_i, since c_i is the concentration at which $\mathfrak{D}$ and $\mathfrak{D}_i$ are equal. These results are plotted as crosses in figure 9. The value at 0.00468 represented by the circle and cross was used for calibration. The other results agree within 0.004 with those obtained by the conductance method. This agreement is probably within the experimental error, and nothing further need be said until further data are available in dilute and moderately dilute solution.

TABLE 3

The diffusion coefficient from diaphragm-cell measurements

$c_0'' = 0; V' = V''; \Delta c_f / \Delta c_0 = 0.5$

c_i'	$10^5 \mathfrak{D}_i$ (OBSERVED)	c_i
0.10	1.838	0.044
0.05	1.871	0.0225
0.025	1.904	0.0115
0.02	1.914	0.0093
0.01	(1.936)*	0.00468
0.005	1.954	0.00235†
0.0025	1.968	0.00118†

* Calibration of the diaphragm cell was based on this concentration.

† From the data of Hartley and Runnicles.

3. Comparison of experimental and theoretical results at high concentrations

The characteristics of the diffusion coefficient in concentrated solutions in relation to the theory are illustrated in figure 10, where $\mathfrak{D} \times 10^5$ for potassium chloride in water at 25°C. is plotted against $c^{1/2}$. Here the curves shown in figure 9 are extended to high concentrations. Curve A represents values computed by the limiting equation (265), curve B those given by equation 266, and curve C those obtained by a complete calculation of $(\overline{\mathfrak{M}}/c)$. In concentrated solutions, the term containing the function $\psi(d)$ in equation 183 contributes as large an amount as the $(\overline{\mathfrak{M}}/c)$ term.[13] The circles represent the conductance results shown in figure 9 and the crosses results computed by Gordon (32).

The existence of the minimum in this plot which corresponds closely to the minimum in the activity-coefficient function confirms the premise that the gradient of the thermodynamic potential is one of the important factors in concentrated solutions. This is confirmed by the data for other electrolytes. However, in the case of potassium chloride as well as all other electrolytes so

[13] This is also true for sodium chloride in aqueous solution at 18.5°C., as shown by Harned and Owen (41).

far examined, the experimental results above 0.01 N lie considerably below those resulting from theory. This is not surprising for, as pointed out in Section IV,6, the obscure ion–solvent interactions and any other short-range repulsive force interactions between the ions are not yet subject to quantitative treatment and were omitted in the development of the theory.

Onsager and Fuoss suggested that the change in viscosity caused by the electrolyte would have an appreciable effect on the $\overline{\mathfrak{M}}/c$ term in the more concentrated solutions and that as a first approximation should be inversely pro-
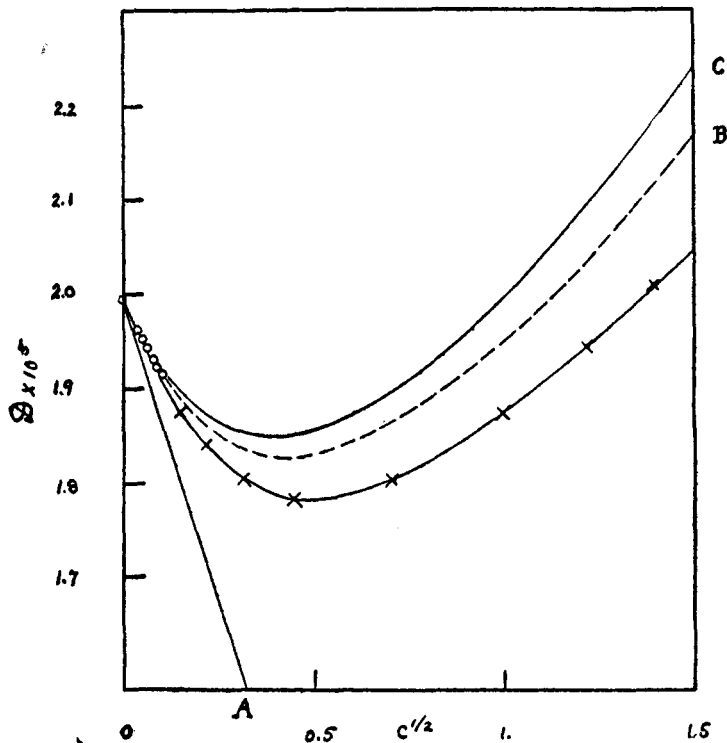

FIG. 10. The diffusion coefficient of potassium chloride at 25°C. O, conductance; × diaphragm cell. A, limiting equation 265; B, equation 266; C, complete theoretical computation.

portional to the macroscopic viscosity. Harned and Owen (41) have shown that for sodium chloride solutions at 18.5°C. multiplication of $\overline{\mathfrak{M}}/c$ by η_0/η causes the theoretical curve to approach the experimental at moderate concentration but overcorrects in solutions of higher concentrations. Deviations from the theory and the viscosity factor have been examined in considerable detail by Van Rysselberghe (100).

The empirical equation of Gordon (31) is

$$\mathfrak{D} = 2000RT \left[1.074 \times 10^{-20} \frac{\lambda_+^0 \lambda_-^0}{\Lambda^0} \frac{V}{n_1 \bar{V}_1} \frac{\eta_0}{\eta} \right] \left(1 + m \frac{\partial \ln \gamma_\pm}{\partial m} \right) \quad (268)$$

in which both the viscosity and the partial molal volume of the solvent are introduced in the mobility term. This reduces to the Nernst equation at the limit but leads to a result in dilute solutions lower than that obtained by the theoretical equation (equation 176). For sodium and potassium chlorides and for potassium nitrate in water, this equation fits the results of Clack (9, 10) from 0.05 to 2 N with considerable accuracy. This is interesting, since at 18°C. η_0/η is less than unity for sodium chloride and greater than unity for potassium chloride and nitrate solutions. For higher valence type electrolytes it does not represent the results as accurately.

VII. General Considerations, Critical Observations, and Summary

The preceding discussion has incorporated the fundamental theoretical derivations upon which criticism and further developments may be expected. The theory of reciprocal relations in irreversible processes has provided certain symmetry conditions which are fundamental to the specialized theories of conductance of electricity, heat, or matter in solutions. In his most recent paper, Onsager (79) has made a notable contribution to the theory of diffusion in systems of more than two components. For a system of this kind Fick's law may be generalized to

$$\mathbf{J}_i = - \Sigma_k D_{ik} \nabla c_k \qquad (269)$$

which defines a set of diffusion coefficients. Interrelations between members of this set are deduced, the equations for the dissipation function are stated, and relations between the diffusion coefficients and thermodynamic properties for a system of more than two components are discussed. For diffusion in electrolytic solutions of three or more components, Onsager (79) has introduced some new substitutions and expressed the part of the dissipation function due to the relaxation effect in a form which is simpler than that formerly obtained by Onsager and Fuoss (80), which required the solution of secular equations. Since there are no experimental data for multiple-component diffusion, these considerations go beyond the scope of this review.

Our descriptions of the methods of measurement have been limited to those which at present seem to be most promising. So far we have found that the Nernst limiting law has been verified by only one series of results on potassium chloride in water obtained by the conductance method. These results are also the only ones which indicate that part of the mobility term resulting from electrophoresis is required in interpreting the data in dilute solutions. We note that in this calculation the term in equation 179 which contains $(\lambda_1 - \lambda_2)^2$ is negligible, and consequently no evidence from any source is available to prove that this term is significant.

The only other results of comparable accuracy with these conductance measurements have been derived from diaphragm cells which have the disadvantage of being relative. It is interesting that for hydrochloric acid the limiting value of the diffusion coefficient as estimated by James and Gordon (49) from diaphragm-cell measurements differs by 6 per cent from the value computed by the Nernst equation.

Departures from the theoretical equation for potassium chloride occur in the neighborhood of 0.01 N and wide departures are found in concentrated solutions —where terms in powers of the concentration higher than $c^{1/2}$ become important. All measurements in both dilute and concentrated solutions confirm the importance of the activity coefficient term in the theoretical equations. In view of our lack of knowledge of concentrated solutions (e.g., ion–solvent etc. interactions), these deviations from the theory are inevitable. Indeed, much more data on electrolytes will be required to prove or disprove the general validity of the theory at very low concentrations. Further advances will depend on whether a quantitative statistical theory of such interactions can be developed.

Hermans (46) criticizes the theory of Onsager and Fuoss (80) on the grounds that it is illogical to employ a term of higher power than unity in the Boltzmann equation (128), while neglecting such a term in the Debye and Hückel theory (127). He allows no terms greater than a first power of $c^{1/2}$. This leads to the elimination of the term containing $\phi(A'\sqrt{c})$ in equation 179. In media of high dielectric constant, however, the effect of dropping the higher terms of the Debye and Hückel theory is small as compared to the $\phi(A'\sqrt{c})$ term, so that the Onsager and Fuoss procedure is justified. The diffusion coefficient of potassium chloride indicates definitely that this term is required, but it would be a mistake to rely solely on one series of measurements as final proof of a matter of this kind.

In addition to the data of Clack (9, 10) and Davies (15) in concentrated solutions, mention should be made of the work of James and Gordon (49) and Hollingshead and Gordon (48), who determined the differential diffusion coefficients of hydrochloric and sulfuric acids as a function of temperature. They find that the activation energy is a function of the concentration for hydrochloric acid above 0.2M but is not a function of the concentration for sulfuric acid from 0 to 1 M.

This review began with the statement that there are few fields of physical science which, for the effort made, have yielded so few experimental results of accuracy sufficient to test any part of the theory. This includes the limiting equation of Nernst, the validity of which has never been questioned but which with the exception of one series of results shown in figure 9 has never received experimental confirmation. By the use of the conductance method and the diaphragm-cell method in dilute solutions, it seems probable that many of the problems in very dilute solution may be solved. In more concentrated solutions optical methods may be easier and preferable. At present, there seems to be little chance of the development of a quantitative theory of concentrated solutions, but perhaps the nature of the deviations from theory in dilute solutions may prove a help to future advance.

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