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ABSTRACT

The fruitful application of refined analytic techniques for treating mass transfer problems in electrochemical systems, whether these systems be experimental tools or industrial processes, requires accurate values of the transport properties of electrolytic solutions. We investigate here some problems in the definition, measurement, and correlation of these properties in concentrated solutions.

The flux expression which is usually used for describing mass transport in electrolytic solutions is inadequate at high concentrations and in multicomponent systems. We discuss a set of flux expressions which are generally applicable. These equations serve to define the proper number of independent transport properties which are state properties of a system and which have a more direct fundamental significance than those measured experimentally. To investigate the dependence of these transport properties on concentration and temperature, we calculate their values for the 32 systems for which sufficient data are available. The behavior of the calculated properties is much more systematic than that of the measured properties. We interpret the ionic diffusion coefficients defined by our general flux expression in terms of the effects of the various ions on the structure of water.

The concentrated-solution flux equations may also be used to analyze experimental measurements. Their application demonstrates that a restricted diffusion measurement yields a well-defined differential diffusion coefficient. We develop a restricted diffusion apparatus which uses Rayleigh interferometry to observe a concentration profile. The method appears to be accurate to 0.2 percent. It is used to measure the diffusivity of nitric acid in water at 25°C at concentrations up to 3 M. The results are consistent with qualitative generalizations drawn from the behavior of the transport properties calculated for other systems.

I. INTRODUCTION

Progress in the analysis, design, and control of most engineering systems requires an accurate description of the distribution and motion of various chemical species within the system. In electrochemical systems, in particular, rates of reactions are often determined by how fast the reactants and products, usually ionic species, are transported to and from the reaction sites, the electrode surfaces. Since the current passing through a cell is carried by ions, the resistance of the cell also depends upon the motion of the ions in solution. Mass transfer calculations in cases of practical interest usually require a knowledge of the diffusion coefficients of individual species, as well as the electrical conductance, in a multicomponent solution over a range of temperatures and concentrations. As the engineering techniques for analyzing such mass transfer problems become more refined, the lack of accurate data for the transport properties will become an increasingly serious drawback. This thesis is concerned with the investigation of the transport properties, and in particular, the measurement of diffusion coefficients in electrolytic solutions.

The complete, quantitative description of electrochemical systems is composed of a number of algebraic and partial differential equations, their parameters, and their boundary conditions. First of all, one can write a differential conservation equation for each species of the form:

$$\frac{\partial c_i}{\partial t} = - \nabla \cdot \underline{N}_i + R_i \qquad \text{(I-1)}$$

where c_i is the concentration of species i, t is time, $\underline{N}_i$ is the flux of species i, and R_i is the rate of generation of i in the homogeneous phase. The current density $\underline{i}$ through a solution is the algebraic summation of the fluxes of the various species times their charges:

$$\underline{i} = F \sum_i z_i \underline{N}_i \tag{I-2}$$

where F is Faraday's constant. An additional restriction in this situation is the condition of electroneutrality, expressed as

$$\sum_i z_i c_i = 0 \quad . \tag{I-3}$$

Because the solution is conducting, it can support no appreciable net charge density in the bulk phase.

The solution of these three equations requires the specification of an expression for the flux $\underline{N}_i$ and a sufficient number of boundary conditions for the various dependent variables. The nature of the boundary conditions depends on the particulars of the problem at hand, and often they involve problems in the area of electrode kinetics. We shall not consider these; it is the question of the flux expression with which we are particularly concerned.

The problem of describing the flux has two aspects. First, one must write equations which correctly relate the fluxes $\underline{N}_i$ to the driving forces for transport. Such equations define a number of parametric coefficients, the transport properties, which should be measurable state properties of the system depending only on pressure, temperature, and composition and independent of the gradients.

The second part of the problem is to systematize the experimental information about these properties and their variation. Ideally, the organization of data should be done within the framework of a theory soundly based on a knowledge of the microscopic structure of matter and molecular interactions. Resulting correlations provide a reliable basis for extrapolation and prediction of data. Since no such theory has been developed for electrolytic solutions,the organization of data must take the form of qualitative generalizations and strictly empirical correlations of available measurements.

In the investigation of transport properties, one must take care to distinguish between a state property and one which depends on the method by which it is measured. Transport properties, in general, depend upon concentration. A differential diffusion coefficient is a quantity well-defined by an appropriate flux expression and corresponds to one particular concentration. An integral diffusion coefficient, on the other hand, represents some sort of average of the differential diffusion coefficient over a region of varying concentration. Many experiments yield integral diffusion coefficients because their analyses involved the assumption that the transport properties are constants. Such experiments should be analyzed more carefully to determine the relationship between the measured quantities and the differential coefficient. Only then does one have confidence in interpreting the results theoretically or applying them to another situation.

In Chapter II of this discussion we present a summary of the relations which are useful for describing transport in dilute solutions. Although the flux expression discussed in that section is an approximation, it is one which has been used quite generally and has been successful in making tractable many very complicated problems. It also serves to define the transport properties which are measured and reported in the literature. Since all the microscopic theories of transport in electrolytic solutions are limited by the nature of their models to very dilute solutions, we include the discussion of these in Chapter II in conjunction with the macroscopic flux expression for dilute solutions.

In more concentrated solutions and particularly in multicomponent systems, the approximate transport relations described in Chapter II prove to be inadequate. It is necessary to construct a more complicated flux expression which takes into account the cross effects of the fluxes of various species on one another and the fact that the appropriate driving forces for the transport of charged species are gradients of electrochemical potential. In concentrated solutions the flux of the solvent must also be considered, and the question of a frame of reference resolved. A set of flux relations which encompasses these effects is described in Chapter III. The equations presented there provide unambiguous definitions of the transport properties which characterize the irreversible phenomena. It is such well defined quantities that one should consider in any attempt to construct a molecular theory of transport properties or even an empirical correlation for their prediction. Furthermore, the precise specification of the properties which are measured requires that the experimental methods be analyzed by means of these more general flux expressions.

Before it is possible to deal with the complicated problem of the properties of multicomponent solutions, for which data are practically nonexistent, we must first investigate the behavior of the transport properties of binary systems. In Chapter IV we summarize the available mass transport data for concentrated binary solutions for which it is possible to calculate the transport properties defined in Chapter III. Such calculations reveal the dependence of the defined quantities on temperature and composition. On the basis of these observations, we draw some tentative conclusions about the characteristics of ionic diffusion coefficients which may guide us in estimating values for systems where no measurements have yet been made.

In order to develop quantitative correlations, however, it is necessary to have much more diffusion coefficient and transference number data for concentrated solutions. In Chapter V we discuss the various methods now available for measuring diffusivity. Since none of these have been carefully analyzed for the case of concentrated solutions, we develop a new method for which this is possible. The new method is a hybrid of the restricted diffusion arrangement used with dilute solutions and an optical technique which makes it applicable to concentrated solutions. Thus, we create a tool for providing more of the requisite data.

In Chapter VI are described the apparatus and procedures which were used in the experimental work. The method was tested by measuring the diffusivity of concentrated potassium chloride at 25°C, the accepted standard; it was then used to study nitric acid, for which no values have been previously available.

Chapter VII presents the experimental results; these are discussed in Chapter VIII in relation to the qualitative generalizations suggested in Chapter IV. Also considered here are some of the problems of estimating the diffusion coefficients in multicomponent systems from binary solution data.

Since the problem of mass transport in electrolytic solutions is both vast and complicated, this thesis must be considered an exploratory study to determine what further work should be done to provide the necessary data for practical engineering calculations. Existing microscopic theories are not of any use in predicting values of technological interest. We are forced at this point to look at what experimental data there are, and to supplement these data, in order to discern what empirical correlations may exist and what general features of behavior must be accounted for by any future theoretical efforts. The conclusions of this study and recommendations for the direction of additional work in this area appear in Chapter IX.

II. MASS TRANSPORT IN DILUTE SOLUTIONS

To solve the equations given in Chapter I, one needs an expression for the flux of species i, $\underline{N}_i$. It is the usual practice with electrolytic solutions to write that[44]

$$N_i = z_i u_i F c_i \nabla\Phi - D_i \nabla c_i + c_i \underline{v} \qquad \text{(II-1)}$$

where z_i is the valence or charge number of species i, u_i is the mobility of species i, Φ is the electrostatic potential, D_i is the diffusion coefficient of species i, and $\underline{v}$ is the fluid velocity. Equation (II-1) states that the flow of a species is due to molecular diffusion, convection by the fluid motion, and electrical migration if the particles are charged. The first term defines the mobility, and the second, an expression of Fick's law, defines the diffusion coefficient. Since Eq. (II-1) involves the fluid velocity, it is also necessary in the description of mass transport to determine the function $\underline{v}$ from the fluid mechanical equations of continuity and motion.

In a binary electrolyte and in the absence of current, the condition of electroneutrality requires that both ions diffuse at the same rate.[45] It is then possible to write the flux expression for the salt,

$$N_s = -D \nabla c + c\underline{v} \; , \qquad \text{(II-2)}$$

where the diffusive flux is characterized by the diffusion coefficient of the salt, D, defined by

$$D = \frac{D_+ D_- (z_+ z_-)}{(z_+ D_+ - z_- D_-)} \; , \qquad \text{(II-3)}$$

and c is the concentration of the salt given by

$$c = \frac{c_+}{\nu_+} = \frac{c_-}{\nu_-} \quad . \tag{II-3a}$$

When there is an electric field but no concentration gradient in the solution, the current is given by

$$\underline{i} = -(F^2 \sum_i z_i^2 u_i c_i) \nabla\Phi \; . \tag{II-4}$$

By analogy with Ohm's law, the conductivity or specific conductance of the solution, κ, is identified as

$$\kappa = F^2 \sum_i z_i^2 u_i c_i \quad . \tag{II-5}$$

As a matter of convenience one defines the equivalent conductance of a solution Λ as

$$\Lambda = \frac{\kappa}{N} \tag{II-6}$$

where N is the normality of the solution given by

$$N = z_+ c_+ = -z_- c_- \quad . \tag{II-7}$$

The transference number of an ion j is defined as the fraction of the total current flowing in the solution which is carried by species j. That is, when $\nabla c_i = 0$ and $\underline{i} \neq 0$, the current carried by species j is

$$\begin{aligned} t_j \underline{i} &= -F^2 \, z_j u_j c_j \, \nabla\Phi \\ &= \frac{z_j^2 u_j c_j}{\sum_i z_i^2 u_i c_i} \, \underline{i} \quad , \end{aligned} \tag{II-8}$$

where t_j must be

$$t_j = \frac{z_j^2 u_j c_j}{\sum_i z_i^2 u_i c_i} \quad , \tag{II-9}$$

and

$$\sum_i t_i = 1.0 \quad . \tag{II-10}$$

The transport properties D, κ, and t_j are the ones which are measured experimentally, used in mass transfer calculations, and interpreted by microscopic theories.

In the interpretation of the transport properties one should first of all realize that the correct driving forces in linear phenomenological laws, such as the first two terms in Eq. (II-1), are gradients of thermodynamic potentials.[18] The true driving force for diffusion is not a concentration difference but a gradient of chemical potential. When the appropriate thermodynamic correction is made in Eq. (II-2), for instance, one finds[69] that the coefficient of theoretical interest takes the form of $D/\left(1 + \frac{d \ \ell n \ y}{d \ \ell n \ c}\right)$, where y is the activity coefficient of the salt on a concentration scale. It is found that this quantity is much more constant in very dilute solutions than is the quantity D by itself.

Since the mobility u_i can be defined in terms of the velocity a species attains resulting from a generalized force,[65] it can be related to the coefficient of the diffusion term in Eq. (II-1) when this term involves a thermodynamically appropriate driving force. At infinite dilution, where the activity equals concentration, such a force is $RT \nabla \ell n \ c_i$, and the resulting flux is $-u_i RT \nabla \ell n \ c_i$. Comparing this expression with the definition of D_i in Eq. (II-1), one obtains the

Nernst-Einstein relation,

$$D_i = u_i RT \; . \tag{II-11}$$

Note that this relation between u_i and D_i is true only at infinite dilution.

Kohlrausch's law of independent migration of ions states that the equivalent conductance at infinite dilution Λ° can be expressed as the sum of ionic contributions,

$$\Lambda^\circ = \lambda_+^\circ + \lambda_-^\circ \tag{II-12}$$

where the ionic limiting equivalent conductances λ_i° depend only on the nature of the individual ion, the solvent, and the temperature. The ions are so far apart that they do not influence one another. At infinite dilution the ionic transference numbers are given by

$$t_j(0) = \frac{\lambda_j^\circ}{\Lambda^\circ} \; . \tag{II-13}$$

The limiting mobilities u_i° are related to the λ_i° by

$$u_i^\circ = \frac{\lambda_i^\circ}{|z_i| F^2} \; , \tag{II-14}$$

and the ionic diffusion coefficients in the limit of zero concentration may be written as

$$D_i^\circ = \frac{\lambda_i^\circ RT}{|z_i| F^2} \; . \tag{II-15}$$

From the foregoing relations for infinitely dilute solutions and Eq. (II-3) one can derive the limiting value of the diffusion coefficient of a salt to be

$$D^\circ = \frac{RT}{F^2}\ \frac{z_+ - z_-}{-z_+ z_-}\ \frac{\lambda_+^\circ \lambda_-^\circ}{\lambda_+^\circ + \lambda_-^\circ}\ . \qquad \text{(II-16)}$$

This quantity is known as the Nernst limiting value. At very small but finite concentrations one may account for most of the concentration dependence of D by writing

$$D = D^\circ \left(1 + \frac{d\ \ell n\ y}{d\ \ell n\ c} \right) , \qquad \text{(II-17)}$$

which is known as the Nernst-Hartley relation.

Elaborate theoretical efforts to explain and to calculate the concentration dependence of the transport properties as they change from their limiting values have been made by Onsager and Fuoss.[60] Their work has been discussed at great length in a number of treatises[15,29,67] so we shall not attempt to describe it in any detail. Essentially, their model deals with two effects, the relaxation effect and the electrophoretic effect. The relaxation effect occurs in the phenomenon of ionic conductance. When oppositely charged ions are migrating in opposite directions, the equilibrium distribution functions of the ions, given by the Debye-Hückel theory, are distorted from spherical symmetry. This causes an electric field to be generated between the ions which opposes the applied field and thus retards the motion of the ions. Onsager's limiting expression for this effect on conductance is

$$\Lambda = \Lambda^\circ \left(1 + \frac{z_+ z_-}{(\epsilon kT)^{2/3}}\ \frac{q}{1+\sqrt{q}}\ (z_+ - z_-)^{1/2}\ (z_+ \nu_+)^{1/2}\ B\sqrt{c} \right) \qquad \text{(II-18)}$$

where

$$q = \frac{-z_+ z_-}{z_+ - z_-} \; \frac{\lambda_+^\circ + \lambda_-^\circ}{z_+ \lambda_+^\circ - z_- \lambda_-^\circ} \, , \quad B = \frac{e^3 \sqrt{4\pi}}{3} \qquad \text{(II-19)}$$

ϵ = the dielectric constant

and e = the electronic charge.

Higher order temrs in such an expression may be generated as the number of mathematical approximations in the analysis is reduced. Equation (II-18) has been definitely confirmed by extremely careful conductance measurements in very dilute solutions. One of the more perplexing problems in extending the theory to more concentrated solutions is the question of what effective dielectric constant applies as the ions get within a few water molecule's diameters of one another.

The concept of an electrophoretic effect is based on a hydrodynamic model and is therefore of dubious worth. The assumption that particles of the same dimensions as the solvent molecules follow the Stokes' flow equation for spheres in a viscous continuum is certainly untenable. Harned[27] was able to make precise diffusion coefficient measurements in very dilute solutions of many salts and claimed to verify the electrophoretic correction. Guggenheim,[24] however, has analyzed Harned's data for sodium chloride and potassium chloride very carefully and concluded that the calculated electrophoretic correction is no larger than the experimental error. Stokes[76] has also pointed out the inconsistency of the second electrophoretic term for unsymmetrical electrolytes with the linearized Boltzmann distribution. Since the calculated effect is small, particularly compared to the activity coefficient correction in diffusion, and claimed to be applicable in only very dilute solutions anyway, we shall not consider it further.* This is not to say that Harned's measurements are not important. They do serve to verify the validity of Eq. (II-17) in dilute solutions.

Other workers have endeavored to extend the microscopic theory of electrolytes to higher concentrations. Falkenhagen,[11] Pitts,[62] and Mirtskhulava[54] obtain slightly different forms for the higher terms in the conductance equation than do Onsager and Fuoss, but their results are not essentially different because they all base their work on the Debye-Hückel theory and the dilute solution flux formulation. Friedman[13] has developed a very elegant mathematical formulation along the lines of the Mayer cluster expansion method for calculating the concentration dependence of the ionic mobilities. Unfortunately, when he comes to the point of introducing an expression for the ion-solvent interactions, he is forced to use a hydrodynamic model; his final results, therefore, do not differ significantly from those of Onsager and Fuoss concerning the postulated electrophoretic effect.

At high concentrations few generalities may be made regarding the concentration dependence of the measured transport properties. Conductivities, transference numbers, and diffusion coefficients may increase, decrease, or remain constant in various concentration regions. The

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* Another confusing point about the derivation of the electrophoretic effect is that it predicts an enhancement of the sphere velocities due to interactions, whereas all other hydrodynamic work[26] on the interactions of spheres in Stokes flow predicts a net retardation. The Onsager and Fuoss derivation does not seem to be based soundly on hydrodynamic principles.

conductance is usually fit empirically by a power series in $c^{1/2}$. It has been suggested[32,70] that the diffusion coefficient may be represented by an expression such as Eq. (II-17), perhaps including the electrophoretic correction factor, with an additional factor of the viscosity of pure water divided by the viscosity of the solution. This ad hoc correction factor is based on a hydrodynamic concept of diffusion. It does account qualitatively for the observed behavior, but it has not been tested extensively and does not appear to be sufficiently accurate for satisfactory prediction.

Because of the lack of both sound theory and adequate data, even less can be said about the temperature dependence of the transport properties. The first step in resolving this question is to explain the temperature dependence of the limiting ionic mobilities. This would give the limits of the measured quantities to which any theory for the concentration dependence could then be applied. Based once again on a simple hydrodynamic model, one would expect the mobilities to correlate with the viscosity of water. Such a correlation is very rough and only qualitative.[66]

The only application of the principles of modern kinetic and statistical mechanical theories of dense phases to a problem remotely related to ionic mobilities in water is the work of Davis, Rice, and Meyer[10] on the mobilities of argon ions in liquid argon. Formally the results may be expressed in terms of integrals of molecular interaction potentials and radial distribution functions. If it were possible to characterize the ion-water interactions and the structure of water around an ion with a relatively small number of molecular and electrostatic parameters, it should be possible to make the integral expression for the mobility dimensionless to establish the basis for a corresponding states correlation.[33,63] We attempted such a correlation by considering only electrostatic ion-water interactions. Unfortunately, the situation is too complex for all the relevant parameters to be included in this way and no unified correlation could be discovered. This investigation did, however, reveal one interesting and useful fact. All the limiting equivalent ionic conductances exhibit a similar temperature dependence between 0° and 100°C which may be represented roughly as

$$\frac{\lambda_i^\circ}{T^{3/2}} = a_i + b_i T \quad . \tag{II-20}$$

The constant a_i is negative and of almost the same magnitude as $b_i T$. We shall give quantitative information regarding this behavior in Chapter IV.

If one attempts to apply Eq. (II-1) to the description of concentrated binary solutions or of multicomponent solutions, he encounters a number of difficulties. Since the Nernst-Einstein relation, Eq. (II-11), is rigorous only at infinite dilution, one must deal with more transport properties than he is able to measure. Furthermore, this equation does not take into account the flux of one species due to a concentration gradient of another, and it does not clearly account for the flux of solvent. Which velocity should be used in the convective term has not been specified. Finally, as Guggenheim has pointed out,[23,25] it is not possible to define thermodynamically the electrostatic potential in a medium of varying concentration.

The formulation of the microscopic theory has been somewhat confused by its basis on Eq. (II-1). The Nernst-Einstein relation is implicitly assumed so that the theory is directed at calculating the concentration dependence of two properties, the two ionic mobilities. The change in the effective force on an ion due to the presence and motion of other ions is calculated and then related to the ionic mobility through a linear relation between the ion's velocity and its driving force. Interactions of fluxes are thus neglected. Since the two calculated mobility expressions are then applied to the three observed phenomena, conductance, diffusion, and transference, the ionic mobility takes on a different character depending on the phenomenon in which the ion is involved.

Because of these difficulties, both theoretical and practical, it is necessary to use a more general flux equation than that given previously. Such a flux expression is discussed in Chapter III.

III. MASS TRANSPORT IN CONCENTRATED SOLUTIONS

The shortcomings of the flux expression, Eq. (II-1), which limit its applicability to dilute solutions have been indicated in the last chapter. To avoid these difficulties and to imporve the treatment of concentrated solutions Newman, Bennion, and Tobias[57] have proposed the use of a set of generally applicable* flux relations of the form

$$c_i \nabla \mu_i = RT \sum_j \frac{c_i c_j}{c_T \mathscr{D}_{ij}} (\underline{v}_j - \underline{v}_i) , \qquad \text{(III-1)}$$

where μ_i is the electrochemical potential of species i and $\mathscr{D}_{ij}$ are the transport properties defined by this equation. This equation is analogous to the Stefan-Maxwell equation for dilute gas mixtures[3] and is equivalent to one** developed by Onsager.[58] Equations of a similar form have also been discussed by Laity,[41] Klemm,[40] Burgers,[5] Lamm,[42] Truesdell,[81] and Lightfoot, Cussler, and Rettig[47] have applied Eq. (III-1) to liquid solutions.

Equation (III-1) may be regarded as a force balance. The term $c_i \nabla \mu_i$ is the driving force per unit volume acting on species i. As species i moves through the fluid it experiences an equal and opposite drag from the other components; the force per unit volume exerted by species j on species i as a result of their relative motion is assumed to be proportional to the difference in their velocities and is expressed as

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* This equation in the form presented is limited to isothermal systems. It may be extended to include the effects of temperature gradients.[56] We shall not consider this complication, however, and shall limit our present investigation to systems at constant temperature and pressure.

** Equation (14), page 245, in reference (59).

$$RT \frac{c_i c_j}{c_T \mathscr{D}_{ij}} (\underline{v}_j - \underline{v}_i) .$$

By the symmetry of this term and Newton's third law of motion $\mathscr{D}_{ij} = \mathscr{D}_{ji}$. Because the $\mathscr{D}_{ij}$ coefficients have the dimensions of cm^2/sec, we shall refer to them as multicomponent diffusion coefficients. Since we must consider the motion of the individual charged species, a binary electrolytic solution is already in a sense a multicomponent system.

The number of independent equations of the form (III-1) is one less than the number of species present. When the equations of this form for all species are added, an identity results. The sum of the terms on the left side is zero by the Gibbs-Duhem equation, and the terms on the right all cancel because $\mathscr{D}_{ij} = \mathscr{D}_{ji}$.

In order to make use of Eq. (III-1) in Eq. (I-1) it is necessary to invert them and thus to obtain explicit expressions for $\underline{N}_i$. When one performs this inversion, he has a choice to make regarding the reference velocity. Depending on this choice the resulting flux expressions take slightly different forms.

For example, if the velocity of the solvent $\underline{v}_o$ is taken as the reference velocity, the fluxes of the various species in a binary electrolytic solution appear as follows:

$$\underline{N}_+ = c_+ \underline{v}_+ = - \frac{\nu_+ c_T/c_o}{\nu \quad RT} \mathscr{D} c \nabla \mu_e + \frac{t_+^o \, \underline{i}}{F \, z_+} + c_+ \underline{v}_o , \qquad \text{(III-2)}$$

$$\underline{N}_- = c_- \underline{v}_- = - \frac{\nu_- c_T/c_o}{\nu \quad RT} \mathscr{D} c \nabla \mu_e + \frac{t_-^o \, \underline{i}}{F \, z_-} + c_- \underline{v}_o , \qquad \text{(III-3)}$$

and

$$\underline{N}_o = c_o \underline{v}_o , \tag{III-4}$$

where the diffusion coefficient is

$$\mathscr{D} = \frac{\mathscr{D}_{o+}\mathscr{D}_{o-}(z_+ - z_-)}{z_+\mathscr{D}_{o+} - z_-\mathscr{D}_{o-}} , \tag{III-5}$$

the transference number is

$$t_+^o = 1 - t_-^o = \frac{z_+\mathscr{D}_{o+}}{z_+\mathscr{D}_{o+} - z_-\mathscr{D}_{o-}} , \tag{III-6}$$

and

$$\mu_e = \nu_+\mu_+ + \nu_-\mu_- \tag{III-7}$$

is the chemical potential of the electrolyte.

If the diffusion is considered with respect to the molar average velocity, $\underline{v}^*$, these expressions take the slightly different forms

$$\underline{N}_+ = c_+ \underline{v}_+ = - \frac{\nu_+\mathscr{D}}{\nu RT} c\nabla\mu_e + \frac{t_+^* \underline{i}}{F z_+} + c_+ \underline{v}^* , \tag{III-8}$$

$$\underline{N}_- = c_- \underline{v}_- = - \frac{\nu_-\mathscr{D}}{\nu RT} c\nabla\mu_e + \frac{t_-^* \underline{i}}{F z_-} + c_- \underline{v}^* , \tag{III-9}$$

and

$$N_o = c_o \underline{v}_o = - \frac{\mathscr{D}}{RT} c_o \nabla\mu_o - \frac{i}{F}\left(\frac{t_+^*}{z_+} + \frac{t_-^*}{z_-}\right) + c_o \underline{v}^* . \tag{III-10}$$

The molar average velocity is defined as

$$\underline{v}^* = \frac{1}{c_T} \sum_i c_i \underline{v}_i \tag{III-11}$$

where c_T is the total solution concentration. The quantity t_j^o we call the transference number with respect to the solvent, and t_j^* is that with respect to the molar average velocity; the two are related by

$$t_+^* = 1 - t_-^* = \frac{c_-}{c_T} + \frac{c_o}{c_T} t_+^o \quad . \qquad \text{(III-12)}$$

Another possibly convenient form of the flux equations is the one taken with respect to the mass average velocity $\underline{v}$, which appears in the equations of motion. In this case the fluxes are written as

$$\underline{n}_+ = \rho_+ \underline{v}_+ = - \frac{\nu_+ M_+ M_o}{\nu M} \mathscr{D} \frac{c \nabla \mu_e}{RT} + \frac{M_+ t_+}{F z_+} \underline{i} + \rho_+ \underline{v} , \qquad \text{(III-13)}$$

$$\underline{n}_- = \rho_- \underline{v}_- = - \frac{\nu_- M_- M_o}{\nu M} \mathscr{D} \frac{c \nabla \mu_e}{RT} + \frac{M_- t_-}{F z_-} \underline{i} + \rho_- \underline{v} , \qquad \text{(III-14)}$$

and

$$\underline{n}_o = \rho_o \underline{v}_o = - \frac{M_s M_o}{\nu M} \mathscr{D} \frac{c_o \nabla \mu_o}{RT} - \frac{\underline{i}}{F} \left(\frac{M_+ t_+}{z_+} + \frac{M_- t_-}{z_-} \right) + \rho_o \underline{v} , \qquad \text{(III-15)}$$

where

$$M_s = \nu_+ M_+ + \nu_- M_- \qquad \text{(III-16)}$$

and

$$M = x_+ M_+ + x_- M_- + x_o M_o = \rho / c_T \quad , \qquad \text{(III-17)}$$

and M_i and x_i are molecular weights and mole fractions, respectively. The quantity t_j is the transference number with respect to the mass average velocity.

In the above equations μ_e and μ_o are chemical potentials of electrolyte and solvent, respectively. The quantities ν_i and ν are stoichiometric coefficients such that

$$\nu = \nu_+ + \nu_- \quad , \tag{III-18}$$

and ρ_i is the mass density of species i.

In order to talk about conductance it is necessary to define an unambiguous and measurable potential in the solution for use as a driving force for the current. Newman[56] has accomplished this by taking it to be the difference in potential between two suitable reference electrodes, one of which is located at a fixed point in the solution with the other at the point in question. Application of thermodynamic principles to such an arrangement yields for a binary electrolyte

$$s_-\nabla\mu_- + s_+\nabla\mu_+ + s_o\nabla\mu_o = nF\nabla\Phi \tag{III-19}$$

for the reversible electrode reaction given by

$$s_-[\text{Anion}]^{z_-} + s_+[\text{Cation}]^{z_+} + s_o[\text{Solvent}] \rightarrow ne^- \quad .$$

Rearrangement of Eq. (III-19) and substitution of an appropriate set of flux expressions such as Eqs. (III-2) and (III-3) give the explicit relation for the current

$$\underline{i} = -\kappa\nabla\Phi - \frac{\kappa}{Fz_+\nu_+}\nabla\mu_e\left[\frac{z_+s_+}{n} + \frac{z_+\mathcal{D}_{o+}}{z_+\mathcal{D}_{o+} - z_-\mathcal{D}_{o-}} - \frac{s_oz_+c_+}{n\,c_o}\right], \tag{III-20}$$

where as the coefficient of $\nabla\Phi$, the conductivity κ, has been identified as

$$\kappa = -\frac{z_+z_-F^2c_T}{RT}\;\frac{(c_-\mathcal{D}_{o+} + c_+\mathcal{D}_{o-})\,\mathcal{D}_{+-}}{c_-\mathcal{D}_{o+} + c_+\mathcal{D}_{o-} + c_o\mathcal{D}_{+-}} \quad . \tag{III-21}$$

When concentration and temperature are uniform, $\nabla\mu_e = 0$, and Eq. (III-20) is the same as Eq. (II-4). Therefore the conductivity defined here is the same as that which is usually measured.

Since experimental measurements of diffusion coefficients in binary solutions are always based on an equation of the form (II-2),

$$\underline{N}_s = -D\nabla c + c\,\underline{v}\,, \tag{II-2}$$

it is interesting to obtain an equation of this form from the flux expression valid for concentrated solutions. In the absence of current the fluxes of salt and solvent in a binary solution become, according to Eqs. (III-2) through (III-4),

$$\underline{N}_s = \frac{\underline{N}_+}{\nu_+} = \frac{\underline{N}_-}{\nu_-} = -\frac{c_T/c_o}{\nu RT}\mathcal{D}c\nabla\mu_e + c\,\underline{v}_o \tag{III-22}$$

and

$$\underline{N}_o = c_o\,\underline{v}_o\,. \tag{III-4}$$

At constant temperature and pressure, the gradient of chemical potential may be expressed as

$$\nabla\mu_e = \nu RT\,\nabla\ell n(yc) = \frac{\nu RT}{c}\left(1 + \frac{c\,d\,\ell n\,y}{dc}\right)\nabla c\,. \tag{III-23}$$

Substituting this relation into Eq. (III-22) and comparing the result with Eq. (II-2), we obtain

$$D = \mathcal{D}\frac{c_T}{c_o}\left(1 + \frac{d\,\ell n\,y}{d\,\ell n\,c}\right). \tag{III-24}$$

We have chosen to use here the set of inverted flux expressions which yields the solvent velocity as the frame of refernce. Alternative forms may be used, and a frequent choice for the frame of reference is the volume average velocity. (See Hartley and Crank[32] and Harned and Owen.[30])

When Eqs. (III-22) and (III-4) are substituted into the conservation Eq. (I-1), these become

$$\frac{\partial c_o}{\partial t} = - c_o \nabla \cdot \underline{v}_o - \underline{v}_o \cdot \nabla c_o \qquad \text{(III-25)}$$

and

$$\frac{\partial c}{\partial t} = \nabla \cdot D \nabla c - c \nabla \cdot \underline{v}_o - \underline{v}_o \cdot \nabla c \quad , \qquad \text{(III-26)}$$

and these may be rewritten as

$$\frac{\partial c}{\partial t} = \frac{\nabla \cdot D \nabla c}{1 - \dfrac{c}{c_o} \dfrac{dc_o}{dc}} - \underline{v}_o \cdot \nabla c \qquad \text{(III-27)}$$

and

$$c_o \left(1 - \frac{c}{c_o} \frac{dc_o}{dc} \right) \nabla \cdot \underline{v}_o + \frac{dc_o}{dc} \nabla \cdot D \nabla c = 0 \ . \qquad \text{(III-28)}$$

The equations are put into this form because it is a particularly convenient one for the analysis of experimental methods for measuring diffusivity in binary electrolytes. For this purpose it is also convenient to define another diffusion coefficient D_M as

$$D_M = c_o \bar{V}_o D = D \Big/ \left(1 - \frac{c}{c_o} \frac{dc_o}{dc} \right) = \mathscr{D} \frac{c_T}{c_o} \left(1 + \frac{d \ \ell n \ \gamma}{d \ \ell n \ m} \right) , \qquad \text{(III-29)}$$

where $\bar{V}_o$ is the partial molar volume of the solvent, γ is the activity coefficient on the molality scale, and m is the molality. Because of the approximations to Eqs. (II-27) and (III-28) which are commonly in use, D_M is the quantity usually measured and reported as the differential diffusion coefficient. It is also identical to the diffusion coefficient employed in the works by Bird, Stewart, and Lightfoot[4] and by Chapman and Cowling.[7] We note that there is only one independent diffusion coefficient and that in dilute solutions these subtle refinements are irrelevant because at infinite dilution

$$\mathcal{D} = D = D_M \ .$$

The activity coefficient "correction" factor (in Eqs. (III-24) and (III-29)) has arisen naturally from the use of $\nabla\mu_e$ as the driving force for diffusion (cf. Eq. (II-17)). The additional factor of c_T/c_o occurs because D is referred to the solvent velocity; it is a sort of drift factor resulting from the view of diffusion through a stagnant solvent.

Thus we see that a number of different diffusion coefficients and transference numbers may be defined and measured in concentrated solutions according to the particular choice of the flux expressions. It requires great care and detailed analysis to determine exactly what quantity is obtained from a particular experimental arrangement and also what quantity should be used in the treatment of a particular mass transfer problem. Furthermore, because of the correction factors appearing in the concentrated-solution flux equations, the complete investigation of these problems requires, in addition to the transport property data, accurate thermodynamic data for the density and activity coefficients of solutions.

In Chapter V and in Appendix B, we apply Eqs. (III-27) and (III-28) to analyze diffusion of a concentrated solution with variable properties in two particular configurations and thus demonstrate ways in which a well-defined differential diffusion coefficient may be obtained.

In a binary electrolytic solution there are three independent transport properties, which are measured and reported as the conductance, the diffusion coefficient, and the transference number. Provided these are sufficiently well defined, it is possible to calculate from them the quantities $\mathcal{D}_{+o}$, $\mathcal{D}_{-o}$, and $\mathcal{D}_{+-}$ according to relations given above. In any form the three independent transport properties are generally functions of temperature, pressure, and composition; only in certain forms such as the $\mathcal{D}_{ij}$ representation, are the data dependent on these variables alone and not on any other property of the system. For this reason the greatest hope for finding order and simplicity in the correlation and theoretical interpretation of transport data lies with the investigation of information reduced to the latter, more fundamental form.

Because of the prevalence of the dilute solution equations and because all the microscopic theories treat these equations, it is important to see the relation of the concentrated solution equations to them. Let us consider Eq. (III-1) for one of the ions i in a dilute solution. In this case $c_i \ll c_o$, the total concentration c_T is essentially c_o, and the equation may be approximated by

$$c_i \nabla \mu_i = \frac{RT}{\mathcal{D}_{oi}} \left(c_i \underline{v}_o - c_i \underline{v}_i \right) , \tag{III-30}$$

or after rearrangement

$$\underline{N}_i = - \mathcal{D}_{oi} \frac{c_i \nabla \mu_i}{RT} + c_i \underline{v}_o \quad . \tag{III-31}$$

This equation is to be compared with Eqs. (II-1). The driving forces for both diffusion and migration are included in one term by the use of the electrochemical potential as the proper thermodynamic driving force. The Nernst-Einstein relation (II-14) therefore arises automatically if one chooses to separate $\nabla \mu_i$ into a concentration term and an electrostatic potential term. (Such separation can be accomplished unambiguously only at the limit of zero concentration where the activity coefficients may all be taken as unity.) Identifying $\mathscr{D}_{oi}$ in this equation with the coefficients of Eq. (II-4), we find that in the limit of infinite dilution

$$\mathscr{D}^{\circ}_{oi} = D^{\circ}_{i} = \frac{\lambda^{\circ}_{i} RT}{|z_i| F^2} . \qquad \text{(III-32)}$$

The limits of the $\mathscr{D}_{oi}$ coefficients are thus related to the limiting ionic equivalent conductances.

We present from Newman[56] Table I which compares the expressions for the three transport properties as they arise from the dilute and concentrated solution flux formulations. The Nernst-Einstein relation has been used in the dilute solution case in order to bring out the similarities. Equation (III-21) for κ has been rearranged.

Table I. Comparison of transport property expressions for a binary electrolyte

Dilute solutions	Concentrated solutions
$D = \dfrac{D_+ D_-(z_+ - z_-)}{z_+ D_+ - z_- D_-} .$	$\mathscr{D} = \dfrac{\mathscr{D}_{o+} \mathscr{D}_{o-}(z_+ - z_-)}{z_+ \mathscr{D}_{o+} - z_- \mathscr{D}_{o-}} .$
$t_+ = \dfrac{z_+ D_+}{z_+ D_+ - z_- D_-} .$	$t^{\circ}_+ = \dfrac{z_+ \mathscr{D}_{o+}}{z_+ \mathscr{D}_{o+} - z_- \mathscr{D}_{o-}} .$
$\dfrac{1}{\kappa} = \dfrac{-RT}{c_o z_+ z_- F^2} \left(\dfrac{c_o t_-}{c_+ D_-} \right) .$	$\dfrac{1}{\kappa} = \dfrac{-RT}{c_T z_+ z_- F^2} \left(\dfrac{1}{\mathscr{D}_{+-}} + \dfrac{c_o t^{\circ}_-}{c_+ \mathscr{D}_{o-}} \right) .$

We see that in dilute solutions the quantities D_+ and D_- correspond directly to $\mathscr{D}_{0+}$ and $\mathscr{D}_{0-}$, respectively. In the dilute solution formulation no quantity arises which corresponds to $\mathscr{D}_{+-}$; the latter represents interactions between the ionic fluxes, and these are neglected in the macroscopic dilute solution formulation. The Onsager-Fuoss theory of the relaxation effect in conductance does, however, take the electrostatic forces between the ions into account, and thus it introduces the quantity $\mathscr{D}_{+-}$ implicitly in the conductance. Comparison of the concentrated solution expression for the conductance with the Onsager limiting law, Eq. (II-18), reveals the concentration dependence of $\mathscr{D}_{+-}$ at very high dilution to be predicted on the basis of electrostatic forces and the Debye-Hückel distribution function to be

$$\mathscr{D}_{+-} = \frac{(\epsilon kT)^{3/2}(1+\sqrt{q})(z_+\mathscr{D}_{0+}-z_-\mathscr{D}_{0-})\sqrt{c}}{c_0 z_+^2 z_-^2 \, q(z_+-z_-)^{1/2}(z_+\nu_+)^{1/2}E} \, , \qquad \text{(III-33)}$$

where $E = B\sqrt{N_0}$ and N_0 is Avogadro's number. We have taken the liberty of substituting the quantities $\mathscr{D}_{0i}$ at the concentration of interest for the limiting mobilities which appear in the Onsager equation, because with the concentrated solution theory we have the three independent transport properties at our disposal. In the derivation these mobilities are supposed to represent the facility with which the ions move through the solvent so that $\mathscr{D}_{0i}(c)$ is the appropriate parameter. Equation (III-33) indicates that $\mathscr{D}_{+-}$ vanishes at zero concentration and in the limit exhibits a $c^{1/2}$ dependence.

In the preceding chapter we indicated little confidence in aspects of the microscopic theory other than the relaxation effect. We are thus left with practically no theoretical basis for considering the behavior of the coefficients $\mathscr{D}_{oi}$. The concentrated solution formulation has, however, accomplished the distinction and separation of the effects of ion-ion interactions and ion-solvent interactions. The problem of calculating the $\mathscr{D}_{oi}$ coefficients is therefore in form the same as the problem of calculating diffusion coefficients in solutions of nonelectrolytes. That is, it can be stated formally in terms of correlations of molecular motions, intermolecular forces, and radial distribution functions. To be sure, it is much more complicated in detail because of the complex structure of water, the orientation of the water molecules, and the rather long-range nature of the ion-dipole interaction, but one might hope that, as the kinetic theory of liquids becomes more highly developed, it will offer some clue to the problem of diffusion in electrolytes. At the same time one can hardly expect to make very significant progress by methods simpler and more heuristic than those required for problems with non-electrolytes. In the meantime, however, a qualitative investigation of these quantities is in order.

In the next chapter we report on a survey of the literature for existing data in binary electrolytic solutions from which the quantities $\mathscr{D}_{o+}$, $\mathscr{D}_{o-}$, and $\mathscr{D}_{+-}$ may be calculated. The results are interpreted in terms of the microscopic structure of solutions, and we consider the possibility of predicting $\mathscr{D}_{ij}$ coefficients where no measurements are available.

IV. A SURVEY OF THE TRANSPORT PROPERTY DATA FOR BINARY ELECTROLYTIC SOLUTIONS

The investigation of the behavior of the α_{ij} coefficients in a binary electrolytic solution requires values of diffusivity, transference number, conductance, and activity coefficients for the system. Since different concentration scales are in use, it is necessary to have density data to put them all on the same basis. It has often been suggested that the ionic mobility is related to the solution viscosity[77] so it is interesting to investigate this property as well. An attempt was made to obtain all the existing data for diffusion coefficients and transference numbers, the scarcest data, for binary aqueous electrolytic solutions. At the same time data were also collected for density, viscosity, conductance, and activity coefficients.

Most of the data were located with the help of the Chemical Abstracts indices and were taken from the original sources. The search for transport number data was facilitated by a recent review on the measurement of these properties by Kaimakov.[35] Many conductance and transport number measurements are summarized in Landolt-Börnstein.[43] Older density, viscosity, and conductance data are available in the International Critical Tables[83] and in Timmerman's compilations.[79] Since the activity coefficient data must be differentiated, it is desirable to have a smooth and consistent set of data. For this reason most of these data, at least at 25°C, were taken from the Appendix of Robinson and Stokes[71] or chosen from what appeared to be the best single source. In some cases the derivatives of the activity coefficient were available in the literature. All the data collected and their sources are given in a separate report.[8]

The systems for which data on all these properties are available, the temperature, and maximum concentration are listed in Table II. Since the transference numbers of ammonium nitrate and potassium iodide are near 0.5, the values for dilute solutions were assumed to be constant and extrapolated to higher concentrations for the purpose of these calculations. To determine the properties of interest for the systems in Table II, we wrote a computer program which takes all the experimental data for a system, converts concentration and each property to consistent scales, fits the various properties with empirical equations for interpolation, differentiates the activity coefficient data, and calculates the $\mathcal{L}_{ij}$ coefficients. Since the conductivity data are usually most abundant and also show the greatest variation with concentration, they were not interpolated for the calculations but were used as the points where calculations were made. The equations used to fit the experimental data for the various systems are summarized in Appendix A. For viscosity and conductance the equations given in the Appendix are in most cases accurate only at high concentrations because the data values at higher concentrations are much larger than in dilute solutions and bias the fit.

Miller[53a] has previously investigated the data for the various chlorides at 25°C and calculated two other sets of transport properties equivalent to those defined here but defined somewhat differently. He does not, however, attempt any physical interpretation of the results. We believe that the form chosen here lends itself more readily to such interpretation than those discussed by Miller.

Table II Aqueous electrolytic solutions for which all transport data are available

Solute	Temperature (°C)	Maximum concentration (moles/liter)
Ammonium chloride	25.00	.20
Ammonium nitrate	25.00	8.00
Barium chloride	25.00	1.24
Cadmium sulfate	25.00	.50
Calcium chloride	25.00	.96
Cupric sulfate	25.00	.55
Hydrochloric acid	25.00	4.00
Lanthanum chloride	25.00	.05
Lithium chloride	25.00	3.00
Lithium chloride	35.00	8.31
Lithium chloride	50.00	3.00
Lithium nitrate	25.00	6.92
Phosphoric acid	25.00	11.00
Potassium bromide	25.00	3.00
Potassium chloride	0.00	1.00
Potassium chloride	18.00	3.54
Potassium chloride	25.00	4.00
Potassium chloride	35.00	3.54
Potassium chloride	50.00	3.51
Potassium iodide	25.00	3.50
Potassium sulfate	25.00	.25
Silver nitrate	25.00	3.03
Sodium chloride	0.00	4.03
Sodium chloride	18.00	4.00
Sodium chloride	25.00	5.00
Sodium chloride	35.00	4.42
Sodium chloride	50.00	5.00

Table II (continued)

Solute	Temperature (°C)	Maximum Concentration (moles/liter)
Sodium hydroxide	25.00	1.11
Sodium iodide	25.00	1.00
Sodium sulfate	25.00	.20
Sulfuric acid	25.00	5.38
Zinc sulfate	25.00	.25

The smoothed experimental data as well as the calculated quantities for the systems listed in Table II are presented in the same order in Tables III through XXXIV. In these tables concentration is given in moles per liter of solution, viscosity is in centipoise, and the equivalent conductance is in cm^2/ohm-equiv. The diffusion coefficient D_M is in cm^2/sec. The activity coefficient correction $(1 + d\ \ell n\gamma / d\ \ell n\ m)$ is dimensionless. The three $\mathcal{D}_{ij}$ coefficients are all given in cm^2/sec. The quantity G, which will be introduced in Eq. (IV-1), is expressed in $(°K)^{3/2}/(\text{mole}/\ell)^{1/2}$. The quantities $\mathcal{D}_{+-}$ and G are presented in standard digital computer notation for a floating point variable where the number following E is the exponent of 10 in scientific notation. Since the interpolation formulae given in Appendix A are not very reliable in dilute solutions, properties in Tables III to XXXIV at concentrations below one molar are obtained from linear interpolation of the experimental data. Values given for zero concentration are consistent with the properties of water and the limiting values of the transport properties. Values of G are not given for concentrations below which experimental conductance data are available.

Some of the results in Tables III to XXXIV and in Appendix A are less reliable than others. The data are particularly questionable for the diffusivities of cadmium, sodium, and potassium sulfates and for the transference number of phosphoric acid. See Ref. 8 for the raw data and their sources.

Some results for $\mathcal{D}_{ij}$ representative of those in the tables are presented in logarithmic plots in Figs. 1 through 9. The systems presented graphically are ammonium nitrate at 25°C, calcium chloride at

25°C, cupric sulfate at 25°C, hydrochloric acid at 25°C, lithium nitrate at 25°C, potassium chloride at 0°C, 25°C, and 50°C, and sodium chloride at 25°C.

We first of all confirmed by our calculations the advantage of considering the diffusion coefficient based on an activity driving force rather than the experimentally measured one. Whereas the measured diffusivity may increase, decrease, or show multiple maxima and minima in various concentration regions, the thermodynamic diffusion coefficient shows a much smaller concentration dependence, particularly in dilute solutions, because most of the variation is accounted for by the concentration dependence of the activity coefficient. In most solutions the thermodynamic diffusion coefficient is nearly constant or increases slightly up to a concentration of a few tenths to one molar. At higher concentrations, thermodynamic diffusion coefficients decrease with increasing concentration.

It was furthermore found from these calculations that the behavior of the $\mathscr{D}_{ij}$ coefficients is much more systematic than that of the measured properties D, κ, and t_+. The quantity $\mathscr{D}_{+-}$ is zero at zero concentration and is found to increase over many orders of magnitude with increasing concentration. The zero-concentration limiting value of $\mathscr{D}_{oi}$ is proportional to the limiting ionic equivalent conductance of the ion i according to Eq. (III-32). This is a property of solvent, temperature, and ion only and is known for most ions over a wide range of temperatures. The variation of $\mathscr{D}_{oi}$ from its limiting value is not extreme. At high concentrations it seems almost invariably to decrease gradually with concentration, going to perhaps half, or at the worst, a third, of its

Table III. Ammonium chloride in water at 25°C.

c	ρ	μ	Λ	t_+°	$D_M\times10^5$	$1+\frac{d\ln\gamma}{d\ln m}$	c	$\mathcal{D}_{0+}\times10^5$	$\mathcal{D}_{0-}\times10^5$	$\mathcal{D}_{+-}$	G
0.	.9971	.8903	149.91	.4907	1.994	1.0000	0.	1.958	2.032	0.	---
.001	1.0005	.8903	128.80	.4906	1.973	.9876	.001	1.958	2.032	3.917E-09	---
.010	1.0037	.8903	128.80	.4905	1.933	.9637	.010	1.961	2.035	3.917E-08	---
.050	1.0068	.8902	128.80	.4900	1.880	.9297	.050	1.974	2.050	1.958E-07	---
.100	1.0097	.8900	128.80	.4907	1.855	.9113	.100	1.990	2.068	3.917E-07	7.387E+03
.200	1.0072	.8897	123.80	.4911	1.837	.8941	.200	2.004	2.077	6.008E-07	8.047E+03

Table IV. Ammonium nitrate in water at 25°C.

0.	.9971	.8903	145.00	.5072	1.929	1.0000	0.	1.957	1.902	0.	---
.001	.9971	.8933	142.00	.5130	1.910	.9866	.001	1.967	1.905	2.876E-08	9.563E+03
.010	.9974	.8894	136.20	.5140	1.872	.9598	.010	1.986	1.914	9.248E-08	9.478E+03
.050	.9978	.8885	128.00	.5140	1.817	.9178	.050	2.021	1.933	2.204E-07	9.029E+03
.100	.9980	.8823	122.70	.5140	1.785	.8909	.100	2.046	1.948	3.192E-07	8.903E+03
.200	.9984	.8814	117.00	.5140	1.750	.8580	.200	2.080	1.972	4.765E-07	8.624E+03
.300	.9987	.8779	113.52	.5140	1.730	.8359	.300	2.105	1.991	6.085E-07	8.399E+03
.500	.9987	.8698	108.60	.5140	1.707	.8049	.500	2.142	2.023	8.249E-07	8.218E+03
.700	.9983	.8663	105.23	.5140	1.693	.7820	.700	2.171	2.049	1.012E-06	8.114E+03
1.000	1.0286	.8576	101.43	.5144	1.679	.7553	1.000	2.205	2.082	1.254E-06	8.060E+03
1.500	1.0441	.8557	96.15	.5142	1.660	.7188	1.500	2.245	2.122	1.586E-06	8.212E+03
2.000	1.0594	.8584	91.76	.5139	1.639	.6874	2.000	2.271	2.148	1.858E-06	8.359E+03
2.500	1.0746	.8645	87.80	.5138	1.615	.6589	2.500	2.286	2.163	2.087E-06	8.632E+03
3.000	1.0896	.8756	84.07	.5138	1.589	.6328	3.000	2.290	2.167	2.280E-06	8.930E+03
3.500	1.1044	.8857	80.48	.5138	1.560	.6088	3.500	2.285	2.162	2.442E-06	9.264E+03
4.000	1.1192	.9013	76.97	.5139	1.530	.5867	4.000	2.272	2.149	2.577E-06	9.604E+03
4.500	1.1358	.9206	73.51	.5141	1.499	.5668	4.500	2.249	2.126	2.688E-06	1.001E+04
5.000	[illegible]	[illegible]	70.09	.5142	1.463	.5490	5.000	2.218	2.096	2.777E-06	1.041E+04
6.000	1.1771	1.0104	63.36	.5143	1.412	.5205	6.000	2.151	2.012	2.895E-06	1.132E+04
7.000	1.2094	1.1058	56.75	.5142	1.365	.5025	7.000	2.010	1.898	2.943E-06	1.219E+04
8.000	1.2533	1.2318	50.34	.5137	1.332	.4969	8.000	1.855	1.756	2.927E-06	1.320E+04

Table V. Barium chloride in water at 25°C.

c	ρ	μ	Λ	t_+°	$D_M \times 10^5$	$1+\frac{d\ln\gamma}{d\ln m}$	c	$\mathcal{D}_{0+} \times 10^5$	$\mathcal{D}_{0-} \times 10^5$	$\mathcal{D}_{+-}$	G
0.	.9971	.8937	140.14	.4546	1.387	1.0000	0.	.848	2.034	0.	---
.001	.9971	.8941	132.10	.4522	1.338	.9528	.001	.850	2.085	8.971E-09	4.212E+03
.010	.9971	.8970	119.09	.4500	1.257	.8791	.010	.848	2.173	3.164E-08	3.840E+03
.050	.9972	.9069	105.19	.4483	1.174	.8166	.050	.827	2.266	8.789E-08	3.109E+03
.100	.9973	.9178	98.56	.4444	1.150	.8096	.100	.800	2.288	1.437E-07	2.659E+03
.200	.9975	.9383	91.55	.4419	1.148	.8353	.200	.754	2.269	2.421E-07	2.161E+03
.300	.9982	.9634	94.23	.4405	1.158	.8717	.300	.715	2.225	4.154E-07	1.491E+03
.500	.9980	1.0096	80.50	.4390	1.173	.9413	.500	.650	2.126	4.886E-07	1.534E+03
.700	.9989	1.0617	75.58	.4381	1.177	1.0001	.700	.596	2.030	6.270E-07	1.332E+03
1.000	1.1751	1.1488	77.59	.3578	1.171	1.0919	1.000	.528	1.891	1.101E-06	1.164E+03
1.500	1.2610	1.3226	73.12	.3389	1.186	1.3067	1.500	.419	1.664	1.965E-06	3.011E+03

Table VI. Cadmium sulfate in water at 25°C.

0.	.9971	.8937	118.01	.3984	.753	1.0000	0.	.626	.945	0.	---
.001	.9971	.8946	105.50	.3840	.826	.8050	.001	.852	1.291	7.361E-10	1.292E+04
.010	.9971	.9011	70.30	.3890	.847	.6437	.010	1.084	1.671	2.560E-09	1.511E+04
.050	.9971	.9272	48.75	.3890	.666	.5297	.050	1.012	1.653	7.746E-09	1.082E+04
.100	.9971	.9577	41.70	.3970	.545	.4964	.100	.863	1.496	1.311E-08	8.022E+03
.200	.9971	1.0126	34.62	.3840	.543	.5174	.200	.831	1.587	2.061E-08	7.427E+03
.300	.9972	1.0894	31.45	.3880	.621	.5388	.300	.837	1.742	2.712E-08	7.392E+03
.500	.9972	1.2080	27.00	.3890	.396	.4072	.500	.678	1.611	3.857E-08	8.439E+03

Table VII. Calcium chloride in water at 25°C.

c	ρ	μ	Λ	t_+°	$D_M \times 10^5$	$1+\frac{d\ell n\gamma}{d\ell nm}$	c	$\mathcal{D}_{o+}\times10^5$	$\mathcal{D}_{o-}\times10^5$	$\mathcal{D}_{+-}$	G
0.	.9971	.8937	135.86	.4380	1.335	1.0000	0.	.792	2.032	0.	---
.001	1.0016	.8940	128.20	.4380	1.294	.9631	.001	.793	2.057	9.736E-09	3.710E+03
.010	1.0079	.8966	115.60	.4363	1.219	.9008	.010	.787	2.112	3.357E-08	3.430E+03
.050	1.0087	.9082	102.46	.4363	1.128	.8376	.050	.754	2.207	9.193E-08	2.795E+03
.100	1.2072	.9228	92.00	.4342	1.091	.8250	.100	.715	2.274	1.290E-07	2.785E+03
.200	1.3166	.9514	84.40	.4342	1.076	.8486	.200	.654	2.344	2.080E-07	2.400E+03
.300	1.3239	.9796	80.45	.4326	1.086	.8960	.300	.602	2.384	2.813E-07	2.116E+03
.500	1.3531	1.0384	75.49	.4326	1.129	1.0205	.500	.517	2.407	4.155E-07	1.732E+03
.700	1.3582	1.0986	67.69	.4307	1.178	1.1653	.700	.462	2.323	4.925E-07	1.348E+03
1.000	1.0830	1.2078	60.89	.2586	1.243	1.3886	1.000	.381	2.184	6.011E-07	7.721E+02

Table VIII. Cupric sulfate in water at 25°C.

0.	.9971	.8937	133.38	.4030	.854	1.000	0.	.715	1.060	0.	---
.001	.9971	.8948	108.30	.3472	.792	.8599	.001	.762	1.163	1.037E-09	8.236E+03
.010	.9971	.9007	72.25	.3237	.688	.6647	.010	.841	1.346	3.100E-09	9.902E+03
.050	.9972	.9257	50.50	.3055	.584	.5033	.050	.920	1.561	8.309E-09	9.371E+03
.100	.9972	.9571	43.60	.3040	.549	.4582	.100	.933	1.660	1.345E-08	8.560E+03
.200	.9972	1.0198	38.20	.4342	.530	.4418	.200	.900	1.759	2.252E-08	7.412E+03
.300	.9972	1.0848	33.82	.4326	.520	.4441	.300	.850	1.805	2.901E-08	7.043E+03
.500	.9972	1.2390	29.00	.4326	.488	.4491	.500	.765	1.755	4.038E-08	6.203E+03
.700	.9972	1.4065	31.38	.4307	.445	.4483	.700	.703	1.550	6.263E-08	6.084E+03

Table IX. Hydrochloric acid in water at 25°C.

c	ρ	μ	Λ	t_+°	$D_M\times10^5$	$1+\frac{d\ln\gamma}{d\ln m}$	c	$\ell_{0+}\times10^5$	$\ell_{0-}\times10^5$	ℓ_{+-}	G
0.	.9971	.8937	426.12	.8208	3.336	1.0000	0.	9.308	2.032	9.	---
.001	1.0016	.8938	421.24	.8210	3.279	.9893	.001	9.260	2.018	3.534E-07	2.266E+03
.010	1.0038	.8943	411.88	.8214	3.177	.9692	.010	9.196	1.994	9.671E-07	2.599E+03
.050	1.0072	.8968	398.97	.8220	3.060	.9452	.050	9.190	1.960	1.946E-06	2.877E+03
.100	1.0073	.9000	391.20	.8224	3.020	.9382	.100	9.244	1.941	2.595E-06	3.062E+03
.200	1.0118	.9060	381.49	.8240	3.022	.9448	.200	9.355	1.913	3.466E-06	3.266E+03
.300	1.0122	.9117	372.53	.8240	3.061	.9630	.300	9.420	1.886	4.072E-06	3.381E+03
.500	1.0158	.9224	360.86	.8250	3.173	1.0152	.500	9.477	1.832	5.149E-06	3.490E+03
.700	1.0173	.9342	349.04	.8251	3.298	1.0795	.700	9.394	1.771	6.092E-06	3.447E+03
1.000	1.0146	.9498	334.70	.8445	3.488	1.1912	1.000	9.068	1.673	7.485E-06	3.233E+03
1.500	1.0231	.9755	306.78	.8461	3.787	1.4112	1.500	8.253	1.504	1.127E-05	2.680E+03
2.000	1.0316	1.0009	281.93	.8443	4.067	1.6669	2.000	7.312	1.347	1.478E-05	2.090E+03
2.500	1.0399	1.0263	259.41	.8401	4.339	1.9437	2.500	6.413	1.218	1.745E-05	1.619E+03
3.000	1.0482	1.0519	238.80	.8339	4.614	2.2095	3.000	5.668	1.130	1.883E-05	1.372E+03
3.500	1.0563	1.0779	219.85	.8263	4.901	2.4140	3.500	5.166	1.091	1.861E-05	1.478E+03
4.000	1.0644	1.1044	202.36	.8175	5.209	2.5060	4.000	4.973	1.109	1.651E-05	2.090E+03

Table X. Lanthanum chloride in water at 25°C.

0.	.9971	.8937	146.07	.4769	1.293	1.0000	0.	.618	2.033	0.	---
.001	.9971	.8951	131.16	.4705	1.175	.8976	.001	.617	2.090	5.527E-09	2.243E+03
.010	.9971	.9016	111.25	.4681	1.068	.7991	.010	.617	2.185	2.006E-08	1.985E+03
.050	.9971	.9251	94.95	.4598	1.118	.8810	.050	.571	2.125	6.630E-08	1.700E+03

Table XI. Lithium chloride in water at 25°C.

c	ρ	μ	Λ	t°_{+}	$D_M \times 10^5$	$1 + \frac{d \ln \gamma}{d \ln m}$	c	$\mathcal{D}_{0+} \times 10^5$	$\mathcal{D}_{0-} \times 10^5$	$\mathcal{D}_{+-}$	G
0.	.9971	.8937	115.62	.3337	1.368	1.0000	0.	1.027	2.050	0	---
.001	.9980	.8938	112.37	.3357	1.356	.9898	.001	1.025	2.065	1.693E-08	1.296E+04
.010	.9994	.8952	107.28	.3345	1.332	.9718	.010	1.019	2.093	6.255E-08	1.117E+04
.050	.9996	.9011	100.13	.3339	1.298	.9516	.050	1.002	2.127	1.608E-07	9.783E+03
.100	1.0015	.9086	95.83	.3380	1.280	.9461	.100	.984	2.141	2.467E-07	9.011E+03
.200	1.0021	.9235	90.20	.3289	1.264	.9515	.200	.953	2.141	3.766E-07	8.280E+03
.300	1.0072	.9384	85.31	.3289	1.259	.9655	.300	.928	2.121	4.817E-07	7.803E+03
.500	1.0087	.9682	81.40	.3288	1.262	1.0047	.500	.877	2.081	6.919E-07	6.849E+03
.700	1.0150	.9980	77.50	.3289	1.273	1.0521	.700	.832	2.024	8.714E-07	6.239E+03
1.000	1.0210	1.0329	73.03	.2855	1.295	1.1320	1.000	.772	1.933	1.120E-06	5.528E+03
1.500	1.0325	1.1038	66.76	.2777	1.336	1.2817	1.500	.683	1.778	1.486E-06	4.658E+03
2.000	1.0436	1.1802	61.51	.2707	1.375	1.4473	2.000	.606	1.632	1.795E-06	4.068E+03
2.500	1.0546	1.2621	56.83	.2634	1.409	1.6272	2.500	.537	1.501	2.050E-06	3.681E+03
3.000	1.0655	1.3511	52.54	.2554	1.437	1.8204	3.000	.475	1.386	2.251E-06	5.279E+02

Table XII. Lithium chloride in water at 35°C.

c	ρ	μ	Λ	t°_+	$D_M\times10^5$	$1+\frac{d\ln\gamma}{d\ln m}$	c	$\sigma_{o+}\times10^5$	$\sigma_{o-}\times10^5$	σ_{+-}	G
0.	.9941	.7194	140.18	.3423	1.736	1.0000	0.	1.320	2.536	0.	--
.010	1.0507	.7195	82.10	.2570	1.721	.9883	.001	1.319	2.536	1.303E-09	--
.010	1.0800	.7205	82.10	.2290	1.691	.9681	.001	1.316	2.533	1.303E-08	--
.050	1.1068	.7249	82.10	.1980	1.649	.9472	.050	1.303	2.524	6.513E-08	--
.100	1.1314	.7304	82.10	.1680	1.626	.9430	.100	1.287	2.512	1.303E-07	--
.200	1.1562	.7413	82.10	.1400	1.605	.9522	.200	1.253	2.488	2.605E-07	--
.300	1.1712	.7523	82.10	.1320	1.598	.9702	.300	1.220	2.464	3.908E-07	--
.500	1.1857	.7743	82.10	.1310	1.600	1.0173	.500	1.154	2.417	6.513E-07	--
.700	1.1999	.7962	82.10	.1300	1.611	1.0721	.700	1.087	2.369	9.118E-07	--
1.000	1.0177	.8558	81.74	.2910	1.634	1.1551	1.000	.963	2.353	1.352E-06	5.073E+03
1.500	1.0291	.8106	77.29	.2809	1.678	1.3128	1.500	.841	2.154	1.894E-06	4.890E+03
2.000	1.0403	.8531	72.44	.2706	1.720	1.4800	2.000	.740	1.992	2.257E-06	4.421E+03
2.500	1.0513	.9438	67.50	.2599	1.756	1.6535	2.500	.655	1.860	2.483E-06	3.975E+03
3.000	1.0622	1.0581	62.64	.2489	1.784	1.8315	3.000	.581	1.751	2.600E-06	4.000E+03
3.500	1.0730	1.1818	57.91	.2377	1.804	2.0128	3.500	.517	1.659	2.634E-06	4.026E+03
4.000	1.0838	1.3070	53.35	.2264	1.815	2.1972	4.000	.461	1.579	2.604E-06	4.061E+03
4.500	1.0945	1.4309	49.00	.2153	1.818	2.3855	4.500	.412	1.506	2.527E-06	4.238E+03
5.000	1.105	1.5539	44.86	.2043	1.812	2.5796	5.000	.367	1.436	2.418E-06	4.414E+03
6.000	1.1262	1.8098	37.24	.1835	1.775	3.0039	6.000	.290	1.291	2.147E-06	4.829E+03
7.000	1.1472	2.1166	30.50	.1648	1.706	3.5435	7.000	.222	1.119	1.874E-06	5.288E+03
8.000	1.1581	2.5337	24.65	.1491	1.604	4.4055	8.000	.159	.902	1.662E-06	5.748E+03
10.000	1.2037	3.9852	15.47	.1290	1.310	18.4220	10.000	.029	.269	1.620E-06	6.666E+03

Table XIII. Lithium chloride in water at 50°C.

c	ρ	μ	Λ	t°_{+}	$D_M\times10^5$	$1+\frac{d\ell n\gamma}{d\ell nm}$	c	$\mathcal{D}_{o+}\times10^5$	$\mathcal{D}_{o-}\times10^5$	$\mathcal{D}_{+-}$	G
0.	.9881	.5467	179.84	.3477	2.353	1.0000	0.	1.804	3.384	0.	--
.001	1.2040	.5468	123.20	.2510	2.333	.9835	.001	1.803	3.383	2.458E-09	--
.010	1.2230	.5476	123.20	.2480	2.296	.9555	.010	1.799	3.379	2.458E-08	--
.050	1.2410	.5513	123.20	.2460	2.242	.9275	.050	1.782	3.359	1.229E-07	--
.100	1.2450	.5558	123.20	.2450	2.213	.9223	.100	1.760	3.335	2.458E-07	--
.200	1.2560	.5649	123.20	.2450	2.187	.9346	.200	1.715	3.287	4.917E-07	--
.300	1.2610	.5740	123.20	.1320	2.178	.9583	.300	1.671	3.238	7.375E-07	--
.500	1.2690	.5923	123.20	.1310	2.179	1.0201	.500	1.583	3.141	1.229E-06	7.012E+03
.700	1.2770	.6105	115.87	.1300	2.191	1.0921	.700	1.470	3.009	1.639E-06	6.108E+03
1.000	1.0128	.6384	110.38	.3164	2.218	1.2025	1.000	1.301	2.810	2.236E-06	4.752E+03
1.500	1.0246	.6518	100.31	.3010	2.267	1.4152	1.500	1.085	2.520	3.236E-06	3.614E+03
2.000	1.0362	.6940	92.16	.2883	2.311	1.6407	2.000	.920	2.271	4.143E-06	2.883E+03
2.500	1.0477	.7524	84.95	.2781	2.345	1.8676	2.500	.794	2.060	4.896E-06	2.152E+03
3.000	1.0590	.8200	78.37	.2699	2.367	2.0830	3.000	.697	1.886	5.447E-06	1.421E+03

Table XIV. Lithium nitrate in water at 25°C.

c	ρ	μ	Λ	t_+°	$D_M \times 10^5$	$1+\frac{d\ell n\gamma}{d\ell nm}$	c	$\mathscr{D}_{o+} \times 10^5$	$\mathscr{D}_{o-} \times 10^5$	$\mathscr{D}_{+-}$	G
0.	.9971	.8937	110.16	.3512	1.336	1.0000	0.	1.030	1.902	0.	--
.001	1.0010	.8941	102.79	.3210	1.320	.9869	.001	1.028	1.908	6.064E-09	--
.010	1.0022	.8982	102.75	.3320	1.292	.9637	.010	1.018	1.961	6.051E-08	1.105E+04
.050	1.0026	.8991	92.95	.3580	1.256	.9382	.050	1.002	1.999	1.331E-07	1.043E+04
.100	1.0029	.9053	91.56	.3760	1.241	.9309	.100	.983	2.046	2.229E-07	9.660E+03
.200	1.0034	.9142	82.59	.4100	1.233	.9353	.200	.961	2.044	3.166E-07	9.218E+03
.300	1.0040	.9233	79.60	.1320	1.235	.9487	.300	.939	2.043	4.103E-07	8.776E+03
.500	1.0050	.9433	77.20	.1310	1.249	.9850	.500	.896	2.041	5.976E-07	7.892E+03
.700	1.0057	.9647	73.58	.1300	1.267	1.0260	.700	.860	2.005	7.496E-07	7.311E+03
1.000	1.0388	.9940	69.86	.2954	1.291	1.0911	1.000	.810	1.928	9.742E-07	6.616E+03
1.500	1.0586	1.0554	63.78	.2925	1.322	1.1988	1.500	.738	1.783	1.248E-06	5.991E+03
2.000	1.0779	1.1223	58.22	.2921	1.338	1.3036	2.000	.673	1.633	1.455E-06	5.423E+03
2.500	1.0970	1.1949	53.13	.2932	1.341	1.4045	2.500	.616	1.487	1.609E-06	5.053E+03
3.000	1.1159	1.2745	48.48	.2954	1.334	1.5011	3.000	.563	1.347	1.719E-06	4.665E+03
3.500	1.1346	1.3628	44.21	.2983	1.317	1.5929	3.500	.516	1.217	1.789E-06	4.466E+03
4.000	1.1531	1.4618	40.29	.3018	1.293	1.6790	4.000	.474	1.097	1.825E-06	4.335E+03
4.500	1.1715	1.5735	36.69	.3058	1.263	1.7583	4.500	.436	.988	1.830E-06	4.234E+03
5.000	1.1898	1.7001	33.38	.3103	1.230	1.8290	5.000	.402	.891	1.807E-06	4.166E+03
6.000	1.2263	2.0065	27.55	.3204	1.155	1.9348	6.000	.347	.734	1.684E-06	3.729E+03
7.000	1.2625	2.3986	22.65	.3320	1.078	1.9740	7.000	.309	.627	1.472E-06	2.065E+03

Table XV. Phosphoric acid in water at 25°C.

c	ρ	μ	Λ	t°_+	$D_M\times10^5$	$1+\frac{d\ell n\gamma}{d\ell nm}$	c	$\ell_{0+}\times10^5$	$\ell_{00}\times10^5$	ℓ_{+-}	G
0.	.9971	.8903	383.86	.8950	1.920	1.0000	0.	9.143	1.073	0.	--
.001	.9997	.8923	336.38	.9005	1.809	.9641	.001	8.703	1.051	1.974E-08	3.509E+04
.010	1.0012	.9106	223.00	.8880	1.589	.8888	.010	7.916	1.007	3.203E-08	6.260E+04
.050	1.0025	.9026	133.05	.9040	1.261	.7639	.050	6.907	.935	5.830E-08	6.772E+04
.100	1.0026	.9142	104.05	.9063	1.068	.6823	.100	6.389	.888	8.071E-08	6.433E+04
.200	1.0058	.9524	83.01	.9090	.861	.5879	.200	5.891	.829	1.188E-07	5.737E+04
.300	1.0075	.9610	73.60	.8770	.748	.5340	.300	5.643	.790	1.525E-07	5.261E+04
.500	1.0101	1.0127	64.71	.8700	.637	.4825	.500	5.447	.739	2.158E-07	4.579E+04
.700	1.0103	1.0623	60.82	.8970	.597	.4701	.700	5.348	.699	2.791E-07	4.212E+04
1.000	1.0487	.9983	60.15	.8906	.593	.4881	1.000	5.406	.660	4.026E-07	3.732E+04
1.500	1.0742	1.2617	59.71	.9000	.646	.5589	1.500	5.615	.609	5.647E-07	3.389E+04
2.000	1.0995	1.5901	58.31	.9078	.717	.6461	2.000	5.749	.567	7.158E-07	3.108E+04
2.500	1.1246	1.9306	56.36	.9141	.783	.7341	2.500	5.777	.529	8.552E-07	2.924E+04
3.000	1.1495	2.2597	54.07	.9191	.837	.8174	3.000	5.707	.493	9.820E-07	2.850E+04
3.500	1.1743	2.5703	51.58	.9231	.875	.8945	3.500	5.553	.458	1.096E-06	2.702E+04
4.000	1.1989	2.8652	48.95	.9264	.897	.9654	4.000	5.335	.423	1.195E-06	2.617E+04
4.500	1.2233	3.1535	46.25	.9291	.905	1.0307	4.500	5.071	.389	1.280E-06	2.553E+04
5.000	1.2476	3.4488	43.52	.9316	.900	1.0916	5.000	4.778	.356	1.350E-06	2.511E+04
6.000	1.2956	4.1274	38.07	.9364	.855	1.2048	6.000	4.172	.290	1.443E-06	2.431E+04
7.000	1.3430	5.0528	32.79	.9420	.775	1.3167	7.000	3.633	.227	1.471E-06	2.410E+04
8.000	1.3897	6.3942	27.78	.9495	.674	1.4437	8.000	3.259	.169	1.432E-06	2.480E+04
10.000	1.4812	11.0406	18.89	.9735	.450	1.8793	10.000	3.334	.072	1.144E-06	3.382E+04
12.000	1.5702	19.5212	11.81	1.0142	.260	3.1599	12.000	4.948	.010	5.657E-07	4.743E+04

Table XVI. Potassium bromide in water at 25°C.

c	ρ	μ	Λ	t_+°	$D_M\times10^5$	$1+\frac{d\ln\gamma}{d\ln m}$	c	$\mathscr{D}_{0+}\times10^5$	$\mathscr{D}_{0}\times10^5$	$\mathscr{D}_{+-}$	G
0.	.9971	.8937	151.80	.4847	2.018	1.0000	0.	1.958	2.082	0.	--
.001	.9972	.8938	148.78	.4933	1.995	.9868	.001	1.967	2.079	3.400E-08	8.450E+03
.010	.9975	.8937	143.15	.4933	1.952	.9618	.010	1.982	2.077	1.119E-07	8.146E+03
.050	.9979	.8926	135.44	.4923	1.898	.9281	.050	2.003	2.081	2.743E-07	7.488E+03
.100	.9988	.8908	131.19	.4850	1.875	.9111	.100	2.012	2.089	4.163E-07	7.022E+03
.200	1.0013	.8873	126.59	.4834	1.863	.8973	.200	2.019	2.104	6.458E-07	6.456E+03
.300	1.0055	.8840	122.50	.4913	1.867	.8934	.300	2.019	2.114	8.077E-07	6.352E+03
.500	1.0064	.8774	120.35	.4873	1.891	.8961	.500	2.017	2.128	1.200E-06	5.582E+03
.700	1.0140	.8706	117.76	.4863	1.923	.9047	.700	2.010	2.128	1.516E-06	5.277E+03
1.000	1.0806	.8647	115.44	.4847	1.974	.9233	1.000	1.999	2.125	1.967E-06	4.876E+03
1.500	1.1217	.8578	112.31	.4854	2.056	.9561	1.500	1.976	2.095	2.655E-06	4.546E+03
2.000	1.1624	.8556	109.45	.4865	2.132	.9904	2.000	1.944	2.052	3.258E-06	4.216E+03
2.500	1.2030	.8581	106.56	.4864	2.205	1.0260	2.500	1.903	2.009	3.772E-06	3.886E+03
3.000	1.2433	.8658	103.52	.4839	2.278	1.0635	3.000	1.849	1.972	4.193E-06	3.556E+03

Table XVII. Potassium chloride in water at 0°C.

0.	.9999	1.7870	81.70	.4982	.996	1.0000	0.	.992	1.000	0.	--
.001	1.0083	1.7869	80.30	.4962	.985	.9864	.001	.993	1.004	1.818E-08	6.822E+03
.010	1.0134	1.7855	77.40	.4943	.965	.9611	.010	.994	1.013	5.690E-08	6.930E+03
.050	1.0005	1.7796	73.90	.4953	.939	.9275	.050	.995	1.026	1.480E-07	6.008E+03
.100	1.0227	1.7723	71.50	.4957	.927	.9111	.100	.995	1.033	2.196E-07	5.758E+03
.200	1.0307	1.7576	69.10	.4890	.919	.8985	.200	.993	1.039	3.437E-07	5.234E+03
.300	1.0092	1.7429	67.71	.4957	.919	.8957	.300	.991	1.039	4.599E-07	4.866E+03
.500	1.0326	1.7134	66.60	.4880	.928	.9022	.500	.985	1.038	6.924E-07	4.129E+03
.700	1.0180	1.6840	65.81	.4880	.941	.9150	.700	.975	1.028	9.269E-07	3.392E+03
1.000	1.0426	1.6654	65.23	.4863	.963	.9417	1.000	.960	1.014	1.278E-06	2.286E+03
1.500	1.0672	1.6437	62.59	.4862	1.003	.9973	1.500	.926	.979	1.920E-06	4.432E+02

Table XVIII. Potassium chloride in water at 18°C.

c	ρ	μ	Λ	t°_+	$D_M\times10^5$	$1+\frac{d\,\ell n\gamma}{d\,\ell n m}$	c	$\mathcal{D}_{o+}\times10^5$	$\mathcal{D}_{o-}\times10^5$	$\mathcal{D}_{+-}$	G
0.	.9986	1.0530	129.87	.4919	1.687	1.0000	0.	1.660	1.715	0.	--
.001	.9987	1.0514	127.26	.4870	1.667	.9858	.001	1.661	1.722	2.679E-08	8.644E+03
.010	.9986	1.0514	102.60	.4870	1.631	.9599	.010	1.661	1.722	4.483E-08	8.587E+03
.050	.9987	1.0513	100.41	.4870	1.584	.9270	.050	1.657	1.720	1.250E-07	8.334E+03
.100	1.0034	1.0511	100.13	.4860	1.562	.9124	.100	1.652	1.717	2.253E-07	8.017E+03
.200	1.0034	1.0487	100.00	.4860	1.547	.9037	.200	1.643	1.712	4.258E-07	7.384E+03
.300	1.0043	1.0461	99.95	.4860	1.546	.9047	.300	1.633	1.707	6.263E-07	6.751E+03
.500	1.0051	1.0422	99.92	.4860	1.556	.9171	.500	1.614	1.696	1.027E-06	5.484E+03
.700	1.0081	1.0382	99.84	.4850	1.573	.9350	.700	1.595	1.685	1.427E-06	4.253E+03
1.000	1.0446	1.0371	98.15	.4863	1.601	.9665	1.000	1.555	1.642	1.940E-06	3.618E+03
1.500	1.0683	1.0355	94.91	.4859	1.649	1.0214	1.500	1.486	1.572	2.800E-06	3.052E+03
2.000	1.0910	1.0370	92.40	.4853	1.697	1.0782	2.000	1.420	1.506	3.645E-06	2.629E+03
2.500	1.1123	1.0422	90.48	.4848	1.747	1.1374	2.500	1.358	1.444	4.449E-06	2.361E+03
3.000	1.1317	1.0523	88.63	.4847	1.802	1.1999	3.000	1.302	1.385	5.195E-06	2.081E+03
3.500	1.1492	1.0690	86.29	.4852	1.866	1.2668	3.500	1.253	1.329	5.868E-06	2.112E+03
4.000	1.1645	1.0937	82.93	.4867	1.941	1.3387	4.000	1.212	1.276	6.454E-06	2.171E+03

Table XIX. Potassium chloride in water at 25°C.

c	ρ	μ	Λ	t°_+	$D_M \times 10^5$	$1 + \frac{d\ell n\gamma}{d\ell nm}$	c	$\mathcal{D}_{o+} \times 10^5$	$\mathcal{D}_{o-} \times 10^5$	$\mathcal{D}_{+-}$	G
0.	.9971	.8937	149.83	.4905	1.993	1.0000	0.	1.956	2.032	0.	--
.001	.9971	.8938	146.95	.4902	1.970	.9859	.001	1.960	2.037	3.323E-08	8.542E+03
.010	.9971	.8941	141.32	.4902	1.926	.9594	.010	1.968	2.047	1.071E-07	8.419E+03
.050	.9971	.8941	133.33	.4901	1.870	.9237	.050	1.981	2.062	2.591E-07	7.848E+03
.100	.9972	.8940	128.90	.4900	1.844	.9058	.100	1.988	2.071	3.930E-07	7.356E+03
.200	.9972	.8933	124.50	.4900	1.827	.8907	.200	1.994	2.080	6.220E-07	6.615E+03
.300	.9973	.8929	120.89	.4897	1.825	.8856	.300	1.994	2.082	7.989E-07	6.313E+03
.500	.9973	.8919	117.90	.4896	1.839	.8865	.500	1.992	2.082	1.160E-06	5.660E+03
.700	..9975	.8917	115.11	.4898	1.861	.8931	.700	1.984	2.076	1.460E-06	5.334E+03
1.000	1.0428	.8919	111.81	.4886	1.896	.9082	1.000	1.968	2.060	1.866E-06	4.988E+03
1.500	1.0649	.8946	108.35	.4884	1.953	.9354	1.500	1.931	2.023	2.520E-06	4.588E+03
2.000	1.0867	.8996	105.60	.4882	2.005	.9645	2.000	1.886	1.978	3.105E-06	4.220E+03
2.500	1.1082	.9080	102.98	.4881	2.055	.9960	2.500	1.836	1.926	3.625E-06	3.907E+03
3.000	1.1294	.9211	100.17	.4879	2.104	1.0314	3.000	1.780	1.868	4.079E-06	3.754E+03
3.500	1.1504	.9403	97.01	.4877	2.157	1.0725	3.500	1.719	1.806	4.463E-06	3.690E+03
4.000	1.1712	.9671	93.39	.4876	2.215	1.1210	4.000	1.655	1.739	4.778E-06	3.596E+03

Table XX. Potassium chloride in water at 35°C.

c	ρ	μ	Λ	t_+°	$D_M \times 10^5$	$1+\frac{d\ell n\gamma}{d\ell nm}$	c	$\mathscr{D}_{0+} \times 10^5$	$\mathscr{D}_{0-} \times 10^5$	$\mathscr{D}_{+-}$	G
0.	.9941	.7194	180.27	.4889	2.478	1.0000	0.	2.424	2.534	0.	--
.001	.9942	.7195	176.89	.4880	2.454	.9855	.001	2.436	2.548	3.779E-08	9.869E+03
.010	.9943	.7199	169.92	.4886	2.409	.9593	.010	2.454	2.570	1.213E-07	9.804E+03
.050	.9945	.7206	140.50	.4885	2.349	.9269	.050	2.446	2.564	2.274E-07	9.571E+03
.100	.9950	.7213	136.70	.4870	2.318	.9130	.100	2.435	2.556	3.587E-07	9.271E+03
.200	.9959	.7226	134.79	.4885	2.293	.9054	.200	2.414	2.539	6.213E-07	8.672E+03
.300	.9964	.7233	134.16	.4860	2.286	.9074	.300	2.393	2.522	8.838E-07	8.072E+03
.500	.9987	.7258	133.65	.4888	2.292	.9216	.500	2.350	2.488	1.409E-06	6.873E+03
.700	1.0003	.7297	133.43	.4850	2.310	.9410	.700	2.308	2.454	1.934E-06	5.674E+03
1.000	1.0394	.7307	132.28	.4832	2.343	.9744	1.000	2.243	2.398	2.662E-06	4.313E+03
1.500	1.0614	.7374	126.29	.4830	2.402	1.0310	1.500	2.132	2.282	3.695E-06	3.625E+03
2.000	1.0830	.7465	121.74	.4831	2.460	1.0881	2.000	2.030	2.173	4.644E-06	3.196E+03
2.500	1.1043	.7586	117.79	.4830	2.516	1.1473	2.500	1.932	2.067	5.510E-06	2.929E+03
3.000	1.1253	.7740	113.64	.4826	2.571	1.2112	3.000	1.832	1.963	6.290E-06	2.778E+03
3.500	1.1461	.7929	108.61	.4818	2.625	1.2839	3.500	1.727	1.857	6.981E-06	2.348E+03
4.000	1.1667	.8154	102.11	.4804	2.680	1.3700	4.000	1.613	1.748	7.580E-06	1.850E+03

Table XXI. Potassium chloride in water at 50°C.

c	ρ	μ	Λ	t_+°	$D_M \times 10^5$	$1 + \frac{d\ell n\gamma}{d\ell nm}$	c	$\mathcal{D}_{o+} \times 10^5$	$\mathcal{D}_{o-} \times 10^5$	$\mathcal{D}_{+-}$	G
0.	.9881	.5467	228.26	.4860	3.289	1.0000	0.	3.200	3.384	0.	--
.001	1.0006	.5467	199.64	.4850	3.259	.9857	.001	3.201	3.386	7.285E-09	--
.010	1.0034	.5469	199.64	.4850	3.201	.9598	.010	3.212	3.399	7.285E-08	1.063E+04
.050	1.0140	.5477	197.00	.4840	3.119	.9277	.050	3.260	3.458	3.332E-07	1.154E+04
.100	1.0185	.5487	194.59	.4840	3.075	.9138	.100	3.255	3.457	6.144E-07	8.857E+03
.200	1.0296	.5507	186.51	.4840	3.034	.9063	.200	3.224	3.431	9.930E-07	7.707E+03
.300	1.0320	.5528	181.13	.4830	3.019	.9084	.300	3.187	3.396	1.328E-06	7.003E+03
.500	1.0440	.5568	174.14	.4830	3.018	.9231	.500	3.110	3.320	1.960E-06	6.019E+03
.700	1.0580	.5626	169.18	.4830	3.034	.9435	.700	3.037	3.246	2.554E-06	5.373E+03
1.000	1.0329	.5679	161.57	.4831	3.072	.9758	1.000	2.935	3.141	3.278E-06	4.702E+03
1.500	1.0542	.5802	155.66	.4829	3.145	1.0326	1.500	2.785	2.983	4.580E-06	4.120E+03
2.000	1.0754	.5936	149.92	.4828	3.216	1.0886	2.000	2.650	2.839	5.753E-06	3.607E+03
2.500	1.0964	.6081	143.88	.4826	3.281	1.1447	2.500	2.520	2.702	6.781E-06	3.312E+03
3.000	1.1175	.6238	137.69	.4823	3.336	1.2036	3.000	2.388	2.563	7.651E-06	3.065E+03
3.500	1.1386	.6410	131.65	.4818	3.383	1.2691	3.500	2.249	2.419	8.354E-06	2.831E+03
4.000	1.1599	.6603	126.11	.4810	3.421	1.3464	4.000	2.096	2.264	8.880E-06	3.395E+03

Table XXII. Potassium iodide in water at 25°C.

c	ρ	μ	Λ	t°_{+}	$D_M\times10^5$	$1+\frac{d\ln\gamma}{d\ln m}$	c	$\mathcal{D}_{o+}\times10^5$	$\mathcal{D}_{o-}\times10^5$	$\mathcal{D}_{+-}$	G
0.	.9971	.8903	150.46	.4889	2.001	1.0000	0.	1.958	2.046	0.	--
.001	1.1204	.8902	136.85	.4883	1.975	.9878	.001	1.958	2.047	6.863E-09	--
.010	1.2279	.8896	136.85	.4882	1.929	.9646	.010	1.959	2.049	6.863E-08	5.912E+03
.050	1.3257	.8867	134.97	.4883	1.880	.9339	.050	1.964	2.058	2.995E-07	6.758E+03
.100	1.3976	.8832	131.11	.4887	1.866	.9196	.100	1.978	2.072	4.467E-07	6.464E+03
.200	1.5040	.8776	126.89	.4900	1.872	.9105	.200	2.001	2.093	6.757E-07	6.134E+03
.300	1.5458	.8721	124.51	.4900	1.892	.9110	.300	2.018	2.108	8.761E-07	5.865E+03
.500	1.6395	.8609	121.58	.4900	1.943	.9228	.500	2.039	2.126	1.238E-06	5.457E+03
.700	1.7013	.8497	119.68	.4900	1.995	.9403	.700	2.047	2.131	1.577E-06	5.134E+03
1.000	1.1183	.8328	117.51	.4903	2.067	.9560	1.000	2.043	2.124	2.071E-06	4.742E+03
1.500	1.1766	.8175	114.89	.4904	2.170	.9993	1.500	2.013	2.092	2.860E-06	4.273E+03
2.000	1.2343	.8088	112.37	.4902	2.259	1.0407	2.000	1.971	2.050	3.546E-06	3.979E+03
2.500	1.2917	.8066	109.61	.4899	2.345	1.0778	2.500	1.934	2.013	4.096E-06	3.871E+03
3.000	1.3490	.8111	106.49	.4897	2.435	1.1088	3.000	1.909	1.989	4.486E-06	3.947E+03
3.500	1.4064	.8225	102.99	.4898	2.536	1.1315	3.500	1.905	1.985	4.696E-06	4.024E+03

Table XXIII. Potassium sulfate in water at 25°C.

0.	.9971	.8937	153.53	.4788	1.529	1.0000	0.	1.956	1.065	0.	--
.001	.9971	.8943	144.50	.4818	1.456	.9254	.001	2.019	1.092	8.192E-09	5.315E+03
.010	.9972	.8967	127.50	.4829	1.342	.8258	.010	2.099	1.118	2.820E-08	5.026E+03
.050	.9971	.9051	109.25	.4848	1.231	.7525	.050	2.130	1.111	7.866E-08	4.041E+03
.100	.9972	.9150	101.15	.4870	1.186	.7261	.100	2.126	1.103	1.272E-07	3.521E+03
.200	.9972	.9342	93.09	.4890	1.126	.6801	.200	2.142	1.112	2.035E-07	3.150E+03
.300	.9974	.9541	84.40	.4910	1.070	.6372	.300	2.170	1.122	2.398E-07	2.978E+03

Table XXIV. Silver nitrate in water at 25°C.

c	ρ	μ	Λ	t_+°	$D_M\times10^5$	$1+\frac{d\ell n\gamma}{d\ell nm}$	c	$\ell_{o+}\times10^5$	$\ell_{o-}\times10^5$	ℓ_{+-}	G
0.	.9971	.8937	133.33	.4642	1.765	1.0000	0.	1.647	1.901	0.	--
.001	.9978	.8939	130.47	.4648	1.749	.9869	.001	1.654	1.908	2.505E-08	1.010E+04
.010	.9985	.8947	124.72	.4648	1.713	.9588	.010	1.669	1.921	7.943E-08	1.015E+04
.050	.9992	.8970	115.20	.4652	1.647	.9092	.050	1.696	1.936	1.763E-07	1.036E+04
.100	.9999	.8995	109.10	.4652	1.595	.8725	.100	1.715	1.943	2.511E-07	1.037E+04
.200	1.0041	.9046	91.73	.4664	1.521	.8210	.200	1.734	1.939	3.103E-07	1.047E+04
.300	1.0112	.9102	85.94	.4664	1.463	.7817	.300	1.754	1.936	3.694E-07	1.056E+04
.500	1.0111	.9213	81.31	.4687	1.371	.7197	.500	1.793	1.930	4.878E-07	1.075E+04
.700	1.0112	.9346	79.32	.4676	1.297	.6697	.700	1.831	1.924	6.061E-07	1.094E+04
1.000	1.1373	.9513	77.94	.4968	1.205	.6108	1.000	1.890	1.914	7.832E-07	1.122E+04
1.500	1.2060	.9979	70.04	.5101	1.084	.5317	1.500	1.969	1.891	9.258E-07	1.206E+04
2.000	1.2742	1.0506	64.08	.5232	.989	.4704	2.000	2.048	1.866	1.030E-06	1.289E+04
2.500	1.3420	1.1079	59.26	.5364	.912	.4214	2.500	2.126	1.838	1.108E-06	1.373E+04
3.000	1.4096	1.1697	55.21	.5499	.849	.3818	3.000	2.205	1.804	1.170E-06	1.457E+04
3.500	1.4770	1.2364	51.69	.5640	.796	.3496	3.500	2.284	1.765	1.221E-06	1.540E+04

Table XXV. Sodium chloride in water at 0°C.

c	ρ	μ	Λ	t_+°	$D_M \times 10^5$	$1+\frac{d\ln\gamma}{d\ln m}$	c	$\mathscr{D}_{0+}\times 10^5$	$\mathscr{D}_{0-}\times 10^5$	$\mathscr{D}_{+-}$	G
0.	.9999	1.7940	67.53	.3926	.785	1.0000	0.	.646	1.000	0.	--
.001	1.0001	1.7943	67.20	.3702	.775	.9861	.001	.644	1.009	3.373E-08	3.044E+03
.010	1.0003	1.7953	61.70	.3690	.757	.9609	.010	.639	1.026	2.810E-08	1.164E+04
.050	1.0008	1.7978	58.20	.3675	.731	.9298	.050	.628	1.046	8.323E-08	8.836E+03
.100	1.0021	1.8009	56.30	.3660	.717	.9170	.100	.619	1.052	1.362E-07	7.630E+03
.200	1.0044	1.8064	54.00	.3660	.705	.9114	.200	.605	1.050	2.249E-07	6.479E+03
.300	1.0049	1.8126	53.54	.3650	.700	.9157	.300	.593	1.041	3.410E-07	5.127E+03
.500	1.0088	1.8280	50.80	.3641	.698	.9354	.500	.573	1.017	4.707E-07	4.723E+03
.700	1.0095	1.8492	50.13	.3625	.701	.9614	.700	.555	.990	7.029E-07	3.579E+03
1.000	1.0432	1.8713	47.66	.3574	.708	1.0068	1.000	.528	.949	7.924E-07	3.530E+03
1.500	1.0636	1.9462	43.66	.3556	.721	1.0907	1.500	.486	.881	9.897E-07	3.209E+03
2.000	1.0834	2.0486	39.85	.3536	.735	1.1866	2.000	.446	.814	1.237E-06	3.036E+03
2.500	1.1028	2.1755	36.54	.3516	.748	1.2999	2.500	.405	.747	1.595E-06	2.863E+03
3.000	1.1218	2.3233	34.02	.3496	.760	1.4407	3.000	.364	.676	2.108E-06	2.691E+03
3.500	1.1405	2.4881	32.53	.3480	.773	1.6246	3.500	.321	.602	2.807E-06	2.518E+03
4.000	1.1590	2.6659	32.27	.3470	.788	1.8791	4.000	.278	.522	3.717E-06	2.345E+03
4.500	1.1772	2.8529	33.44	.3469	.803	2.2563	4.500	.233	.436	4.857E-06	2.172E+03

Table XXVI. Sodium chloride in water at 18°C.

c	ρ	μ	Λ	t°_+	$D_M\times10^5$	$1+\frac{d\ln\gamma}{d\ln m}$	c	$\mathcal{D}_{0+}\times10^5$	$\mathcal{D}_{0-}\times10^5$	$\mathcal{D}_{+-}$	G
0.	.9986	1.0600	108.84	.3934	1.350	1.0000	0.	1.113	1.716	0.	--
.001	1.0032	1.0601	106.49	.3822	1.336	.9874	.001	1.112	1.726	2.031E-08	9.564E+03
.010	1.0029	1.0610	101.95	.3800	1.308	.9644	.010	1.109	1.744	6.698E-08	9.218E+03
.050	1.0075	1.0649	95.71	.3800	1.269	.9364	.050	1.097	1.765	1.697E-07	8.166E+03
.100	1.0071	1.0691	92.02	.3753	1.249	.9253	.100	1.084	1.770	2.614E-07	7.483E+03
.200	1.0195	1.0630	89.20	.3750	1.229	.9220	.200	1.060	1.763	4.515E-07	6.070E+03
.300	1.0193	1.0825	84.97	.3723	1.222	.9281	.300	1.039	1.744	5.694E-07	5.993E+03
.500	1.0401	1.1934	80.94	.3700	1.219	.9517	.500	.996	1.707	7.983E-07	5.224E+03
.700	1.0391	1.1224	77.69	.3680	1.222	.9820	.700	.958	1.659	1.039E-06	4.670E+03
1.000	1.0396	1.1459	74.41	.3627	1.233	1.0339	1.000	.902	1.586	1.377E-06	4.012E+03
1.500	1.0591	1.2035	69.11	.3592	1.253	1.1322	1.500	.818	1.459	1.816E-06	3.375E+03
2.000	1.0782	1.2674	64.60	.3567	1.271	1.2435	2.000	.739	1.333	2.309E-06	2.728E+03
2.500	1.0969	1.3400	60.49	.3547	1.286	1.3710	2.500	.664	1.207	2.920E-06	2.297E+03
3.000	1.1154	1.4249	56.59	.3529	1.298	1.5212	3.000	.592	1.084	3.693E-06	1.885E+03
3.500	1.1337	1.5262	52.81	.3513	1.309	1.7044	3.500	.521	.962	4.658E-06	1.440E+03
4.000	1.1517	1.6482	49.12	.3496	1.318	1.9373	4.000	.452	.841	5.840E-06	9.954E+02

Table XXVII. Sodium chloride in water at 25°C.

c	ρ	μ	Λ	t_+°	$D_M\times10^5$	$1+\frac{d\ell n\gamma}{d\ell nm}$	c	$\mathcal{L}_{0+}\times10^5$	$\mathcal{L}_{0-}\times10^5$	$\mathcal{L}_{+-}$	G
0.	.9971	.8937	126.45	.3962	1.610	1.0000	0.	1.333	2.032	0.	--
.001	.9971	.8939	123.70	.3951	1.591	.9869	.001	1.332	2.041	2.485E-08	9.640E+03
.010	.9973	.8950	118.51	.3947	1.556	.9626	.010	1.330	2.059	8.199E-08	9.285E+03
.050	.9972	.8985	111.06	.3930	1.510	.9314	.050	1.322	2.084	1.997E-07	8.575E+03
.100	.9975	.9025	106.74	.3918	1.487	.9172	.100	1.314	2.095	3.022E-07	8.026E+03
.200	.9972	.9104	101.71	.3918	1.468	.9086	.200	1.297	2.101	4.664E-07	7.344E+03
.300	.9979	.9185	98.37	.3919	1.463	.9097	.300	1.281	2.097	6.058E-07	6.896E+03
.500	.9974	.9348	93.62	.3918	1.465	.9231	.500	1.247	2.076	8.475E-07	6.283E+03
.700	.9991	.9522	90.04	.3919	1.473	.9428	.700	1.212	2.045	1.060E-06	5.852E+03
1.000	1.0367	.9788	85.74	.3684	1.488	.9786	1.000	1.161	1.990	1.345E-06	5.356E+03
1.500	1.0560	1.0287	79.82	.3634	1.510	1.0440	1.500	1.076	1.884	1.758E-06	4.774E+03
2.000	1.0750	1.0857	74.71	.3595	1.527	1.1147	2.000	.995	1.770	2.106E-06	4.352E+03
2.500	1.0936	1.1514	70.02	.3566	1.539	1.1911	2.500	.917	1.654	2.395E-06	4.016E+03
3.000	1.1120	1.2270	65.59	.3547	1.550	1.2741	3.000	.845	1.538	2.631E-06	3.750E+03
3.500	1.1302	1.3138	61.33	.3536	1.561	1.3651	3.500	.778	1.424	2.813E-06	3.535E+03
4.000	1.1482	1.4127	57.23	.3535	1.574	1.4656	4.000	.717	1.313	2.945E-06	3.369E+03
4.500	1.1659	1.5246	53.27	.3544	1.591	1.5767	4.500	.662	1.207	3.025E-06	3.248E+03
5.000	1.1834	1.6504	49.45	.3564	1.613	1.6989	5.000	.614	1.106	3.055E-06	3.171E+03

Table XXVIII. Sodium chloride in water at 35°C.

c	ρ	μ	Λ	t_+°	$D_M \times 10^5$	$1+\frac{d\ell n\gamma}{d\ell nm}$	c	$\mathcal{D}_{o+} \times 10^5$	$\mathcal{D}_{o-} \times 10^5$	$\mathcal{D}_{+-}$	G
0.	.9941	.7440	153.80	.4003	2.031	1.0000	0.	1.693	2.537	0.	--
.001	1.0285	.7439	150.38	.3893	2.011	.9892	.001	1.691	2.548	3.109E-08	1.020E+04
.010	1.1367	.7433	143.49	.3880	1.973	.9699	.010	1.684	2.568	9.943E-08	1.011E+04
.050	1.1585	.7403	107.21	.3880	1.920	.9472	.050	1.671	2.560	1.586E-07	9.920E+03
.100	1.0566	.7366	102.67	.3853	1.891	.9388	.100	1.656	2.549	2.326E-07	9.689E+03
.200	1.0566	.7332	100.40	.3826	1.863	.9380	.200	1.625	2.526	3.806E-07	9.225E+03
.300	1.0661	.7419	99.65	.3832	1.852	.9449	.300	1.594	2.504	5.287E-07	8.762E+03
.500	1.1010	.7593	99.04	.3830	1.848	.9679	.500	1.532	2.460	8.247E-07	7.835E+03
.700	1.1169	.7767	98.78	.3797	1.854	.9960	.700	1.470	2.416	1.121E-06	6.908E+03
1.000	1.0804	.7930	98.78	.3690	1.870	1.0408	1.000	1.376	2.351	2.082E-06	5.518E+03
1.500	1.0935	.8407	92.86	.3649	1.902	1.1242	1.500	1.264	2.200	2.257E-06	4.615E+03
2.000	1.1002	.8952	87.66	.3619	1.930	1.2169	2.000	1.158	2.043	2.442E-06	3.873E+03
2.500	1.1047	.9563	82.68	.3594	1.953	1.3240	2.500	1.052	1.876	2.904E-06	3.389E+03
3.000	1.1096	1.0237	77.77	.3572	1.970	1.4553	3.000	.944	1.698	3.829E-06	2.840E+03
3.500	1.1171	1.0966	72.90	.3551	1.981	1.6272	3.500	.829	1.505	5.357E-06	2.267E+03
4.000	1.1286	1.1744	68.08	.3530	1.987	1.8693	4.000	.708	1.296	7.595E-06	1.572E+03
4.500	1.1455	1.2561	63.34	.3509	1.988	2.2426	4.500	.576	1.068	1.063E-05	8.609E+02

Table XXIX. Sodium chloride in water at 50°C.

c	ρ	μ	Λ	t°_{+}	$D_M\times10^5$	$1+\frac{d\ell n\gamma}{d\ell nm}$	c	$\mathcal{D}_{0+}\times10^5$	$\mathcal{D}_{0-}\times10^5$	$\mathcal{D}_{+-}$	G
0.	.9882	.5467	196.69	.4035	2.731	1.0000	0.	2.289	3.384	0.	--
.001	.9962	.5530	172.35	.4010	2.711	.9877	.001	2.289	3.386	6.265E-09	--
.010	1.0079	.5530	172.35	.3950	2.672	.9655	.010	2.292	3.407	6.265E-08	--
.050	1.0275	.5530	172.35	.3890	2.613	.9390	.050	2.302	3.501	3.133E-07	1.060E+04
.100	1.0643	.5530	165.26	.3890	2.578	.9289	.100	2.281	3.512	4.825E-07	9.726E+03
.200	1.0928	.5532	156.66	.3857	2.541	.9272	.200	2.230	3.495	7.596E-07	8.649E+03
.300	1.1351	.5620	151.27	.3825	2.522	.9351	.300	2.176	3.458	1.015E-06	7.815E+03
.500	1.1568	.5794	143.41	.3800	2.507	.9622	.500	2.073	3.362	1.481E-06	6.696E+03
.700	1.1771	.5918	137.52	.3793	2.506	.9972	.700	1.975	3.254	1.922E-06	5.899E+03
1.000	1.0277	.6081	130.35	.3735	2.516	1.0521	1.000	1.840	3.085	2.678E-06	5.010E+03
1.500	1.0466	.6410	120.66	.3688	2.545	1.1625	1.500	1.641	2.810	3.566E-06	3.958E+03
2.000	1.0652	.6789	112.42	.3655	2.577	1.2848	2.000	1.468	2.551	4.426E-06	3.242E+03
2.500	1.0835	.7224	104.98	.3631	2.606	1.4176	2.500	1.316	2.311	5.364E-06	2.686E+03
3.000	1.1016	.7714	98.12	.3611	2.629	1.5614	3.000	1.180	2.088	6.452E-06	2.239E+03
3.500	1.1194	.8251	91.78	.3592	2.645	1.7176	3.500	1.057	1.883	7.743E-06	1.863E+03
4.000	1.1371	.8825	85.94	.3573	2.654	1.8885	4.000	.944	1.694	9.279E-06	1.540E+03
4.500	1.1546	.9426	80.62	.3551	2.654	2.0785	4.500	.838	1.521	1.109E-05	1.247E+03
5.000	1.1719	1.0042	75.87	.3526	2.646	2.2936	5.000	.738	1.362	1.322E-05	9.791E+02

Table XXX. Sodium hydroxide in water at 25°C.

c	ρ	μ	Λ	t_+°	$D_M\times10^5$	$1+\frac{d\ln\gamma}{d\ln m}$	c	$\mathscr{D}_{0+}\times10^5$	$\mathscr{D}_{0-}\times10^5$	$\mathscr{D}_{+-}$	G
0.	.9971	.8937	248.22	.2017	2.127	1.0000	0.	1.332	5.273	0.	--
.001	.9971	.8940	244.05	.1970	2.100	.9824	.001	1.339	5.295	5.736E-08	8.127E+03
.010	.9971	.8969	238.47	.1890	2.046	.9537	.010	1.340	5.368	2.125E-07	7.080E+03
.050	.9971	.9097	227.80	.1830	1.966	.9261	.050	1.311	5.537	4.726E-07	7.247E+03
.100	.9971	.9257	221.17	.1770	1.919	.9201	.100	1.273	5.650	6.943E-07	7.076E+03
.200	.9971	.9577	212.93	.1690	1.866	.9257	.200	1.213	5.713	1.084E-06	6.412E+03
.300	.9972	.9897	207.06	.1630	1.835	.9370	.300	1.169	5.657	1.470E-06	5.706E+03
.500	.9972	1.0536	197.12	.3800	1.795	.9603	.500	1.106	5.415	2.228E-06	4.650E+03
.700	.9973	1.1176	188.49	.3793	1.770	.9798	.700	1.061	5.207	2.840E-06	4.139E+03
1.000	1.0400	1.2220	177.71	.1629	1.744	1.0045	1.000	1.002	5.150	3.177E-06	3.564E+03
1.500	1.0599	1.3508	160.54	.1118	1.716	1.0478	1.500	.853	6.349	2.019E-06	2.606E+03

Table XXXI. Sodium iodide in water at 25°C.

0.	.9971	.8903	127.08	.3947	1.616	1.0000	0.	1.335	2.047	0.	--
.001	1.2973	.8903	124.25	.3840	1.599	.9868	.001	1.337	2.058	2.332E-08	1.034E+04
.010	1.4749	.8905	119.24	.1890	1.570	.9638	.010	1.339	2.077	8.063E-08	9.518E+03
.050	1.6842	.8915	112.79	.1830	1.536	.9395	.050	1.335	2.103	2.117E-07	8.169E+03
.100	1.7075	.8928	108.78	.1770	1.525	.9335	.100	1.327	2.113	3.244E-07	7.557E+03
.200	1.8710	.8952	104.98	.1690	1.527	.9399	.200	1.311	2.112	5.387E-07	6.459E+03
.300	.9972	.8976	102.34	.1630	1.540	.9494	.300	1.295	2.103	7.226E-07	5.858E+03
.500	.9972	.9016	98.83	.3800	1.574	.9832	.500	1.265	2.071	1.053E-06	5.120E+03
.700	.9973	.9068	95.79	.3793	1.613	1.0208	.700	1.240	2.019	1.377E-06	4.607E+03
1.000	1.1112	.9156	92.66	.3840	1.670	1.0846	1.000	1.204	1.932	1.836E-06	3.836E+03

Table XXXII. Sodium sulfate in water at 25°C.

c	ρ	μ	Λ	t°_{+}	$D_M \times 10^5$	$1+\frac{d\ln\gamma}{d\ln m}$	c	$\mathcal{D}_{o+}\times10^5$	$\mathcal{D}_{o-}\times10^5$	$\mathcal{D}_{+-}$	G
0.	.9971	.8937	130.11	.3850	1.230	1.0000	0.	1.333	1.065	0.	--
.001	.9972	.8945	119.07	.3836	1.180	.9424	.001	1.356	1.082	6.669E-09	5.272E+03
.010	.9974	.8986	106.52	.3829	1.103	.8486	.010	1.406	1.125	2.293E-08	5.465E+03
.050	.9977	.9137	89.91	.3828	1.036	.7561	.050	1.475	1.189	5.677E-08	5.242E+03
.100	.9983	.9328	81.63	.3828	1.017	.7260	.100	1.505	1.213	8.684E-08	4.956E+03
.200	.9992	.9726	72.75	.1690	1.000	.7100	.200	1.505	1.214	1.354E-07	4.500E+03
.300	1.0003	1.0136	68.13	.1630	.980	.7040	.300	1.480	1.206	1.781E-07	4.069E+03

Table XXXIII. Sulfuric acid in water at 25°C.

0.	.9971	.8937	429.67	.8138	2.599	1.0000	0.	9.305	1.065	0.	--
.001	1.0104	.8941	390.80	.8190	2.473	.9368	.001	9.509	1.080	1.732E-08	5.945E+03
.010	1.0169	.8981	185.40	.8190	2.244	.8272	.010	9.861	1.106	1.507E-08	2.252E+03
.050	1.0234	.9054	251.20	.8132	1.954	.7007	.050	10.228	1.132	1.295E-07	6.020E+03
.100	1.0300	.9120	147.05	.8190	1.826	.6504	.100	10.284	1.136	1.024E-07	1.086E+04
.200	1.0330	.9283	140.14	.8150	1.745	.6258	.200	10.103	1.123	2.053E-07	7.888E+03
.300	1.0367	.9451	164.61	.8080	1.743	.6351	.300	9.811	1.101	4.044E-07	7.140E+03
.500	1.0434	.9789	211.00	.7930	1.813	.6874	.500	9.170	1.052	9.845E-07	2.488E+03
.700	1.0502	1.0141	206.50	.7760	1.908	.7553	.700	8.562	1.003	1.415E-06	1.886E+03
1.000	1.0551	1.0131	201.36	.8046	2.046	.8633	1.000	7.677	.929	2.113E-06	1.387E+03
1.500	1.0856	1.1165	182.89	.7963	2.224	1.0387	1.500	6.446	.825	2.898E-06	1.028E+03
2.000	1.1164	1.2540	164.62	.7882	2.341	1.1998	2.000	5.473	.739	3.484E-06	8.148E+02
2.500	1.1472	1.4096	147.35	.7800	2.420	1.3509	2.500	4.696	.666	3.896E-06	7.567E+02
3.000	1.1779	1.5746	131.33	.7713	2.485	1.5033	3.000	4.061	.604	4.152E-06	7.053E+02
3.500	1.2084	1.7443	116.62	.7620	2.558	1.6743	3.500	3.523	.548	4.266E-06	6.792E+02
4.000	1.2387	1.9169	103.19	.7516	2.657	1.8880	4.000	3.041	.496	4.250E-06	6.603E+02
4.500	1.2685	2.0921	91.00	.7402	2.799	2.1789	4.500	2.582	.446	4.112E-06	6.397E+02
5.000	1.2980	2.2710	79.97	.7274	2.998	2.6021	5.000	2.117	.395	3.861E-06	6.422E+02
6.000	1.3555	2.6480	61.10	.6974	3.614	4.3671	6.000	1.072	.285	3.047E-06	6.422E+02

Table XXXIV. Zinc sulfate in water at 25°C.

c	ρ	μ	Λ	t°_+	$D_M\times10^5$	$1+\frac{d\ell n\gamma}{d\ell nm}$	c	$\ell_{o+}\times10^5$	$\ell_{o-}\times10^5$	ℓ_{+-}	G
0.	.9971	.8937	132.82	.3975	.846	1.000	0.	.702	1.065	0.	—
.001	.9971	.8948	106.00	.3826	.760	.8570	.001	.734	1.120	1.067E-09	7.713E+03
.010	.9972	.9007	73.25	.3830	.686	.6536	.010	.862	1.343	3.158E-09	9.801E+03
.050	.9972	.9301	52.50	.3890	.688	.5375	.050	1.028	1.689	8.490E-09	1.006E+04
.100	.9972	.9668	45.00	.3920	.650	.5221	.100	.979	1.692	1.392E-08	8.537E+03
.200	.9972	1.0403	38.64	.3890	.551	.5088	.200	.887	1.663	2.318E-08	8.014E+03
.300	.9973	1.1138	36.14	.3799	.682	.4885	.300	.842	1.708	3.184E-08	8.634E+03

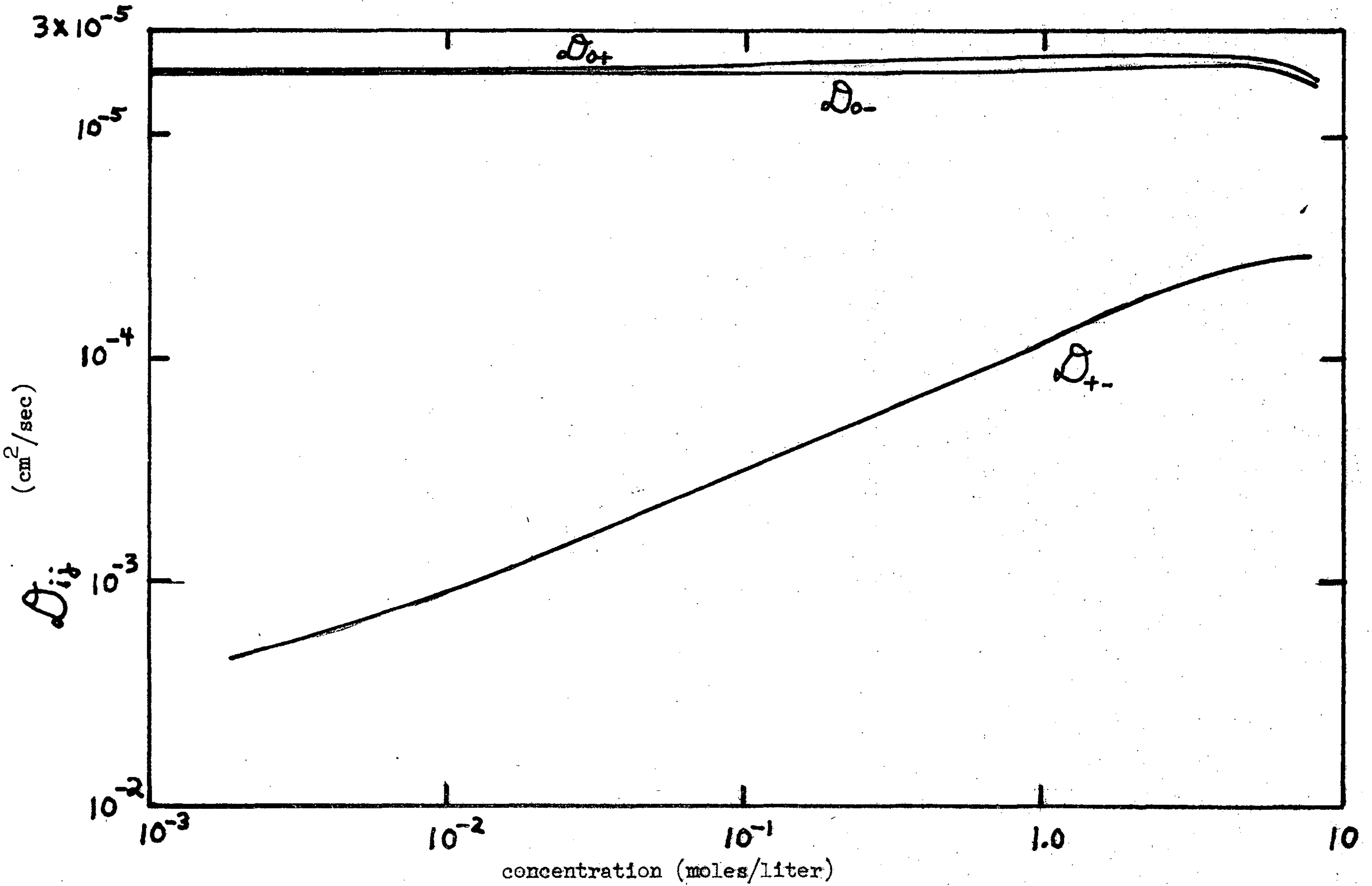


Fig. 1 The multicomponent diffusion coefficients of ammonium nitrate in water at 25°C

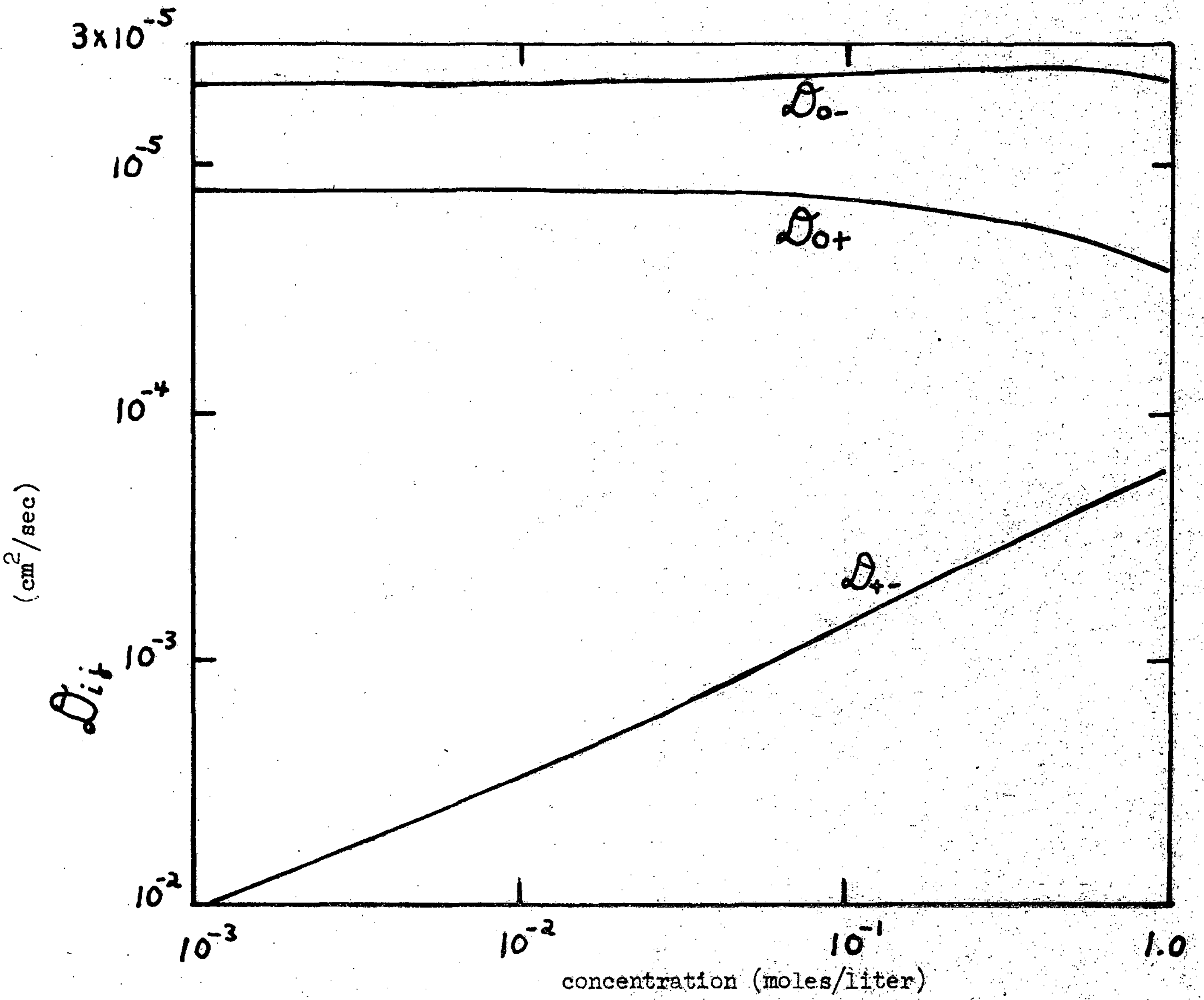


Fig. 2 The multicomponent diffusion coefficients of calcium chloride in water at 25°C

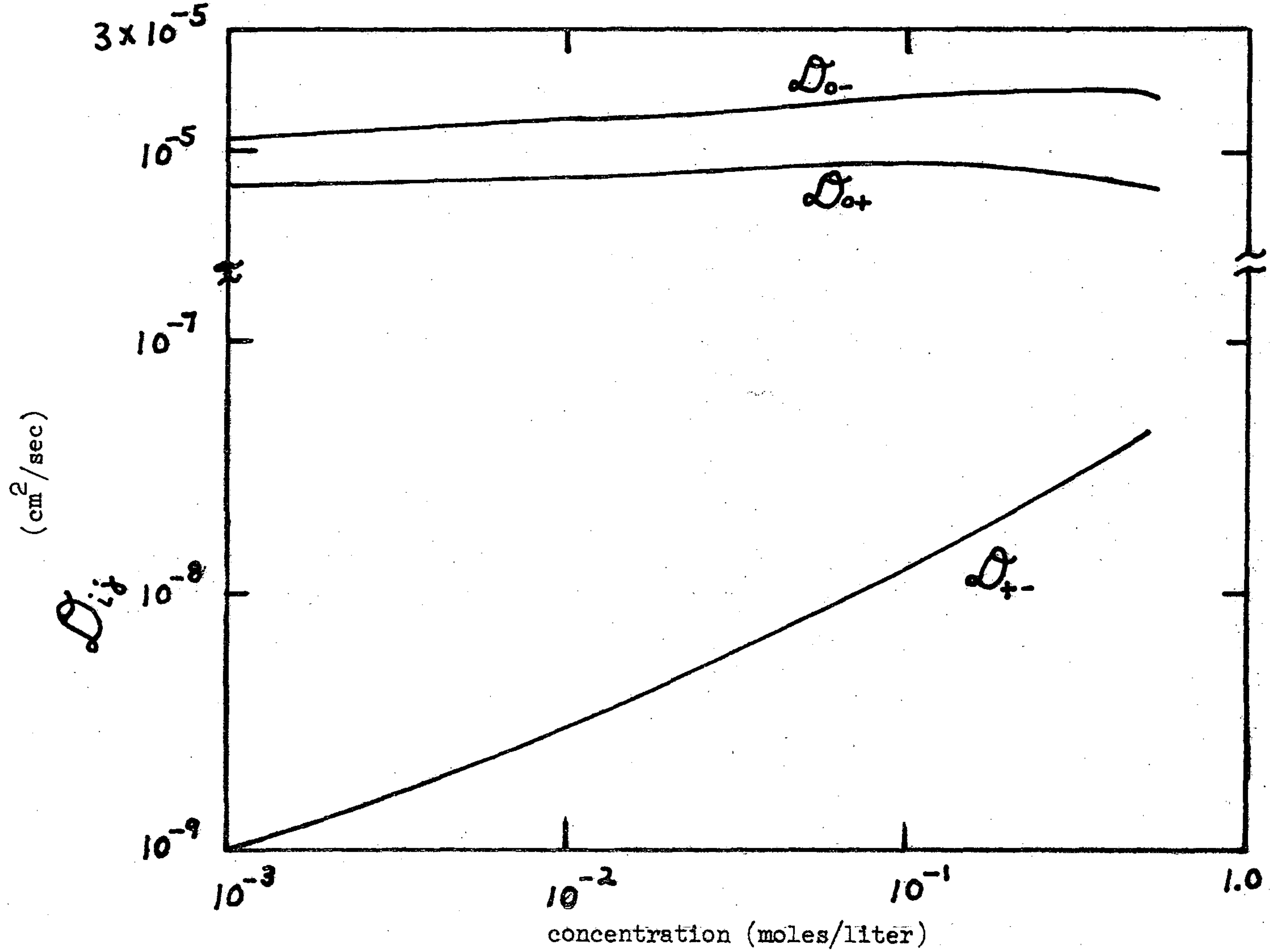


Fig. 3 The multicomponent diffusion coefficients of cupric sulfate in water at 25°C

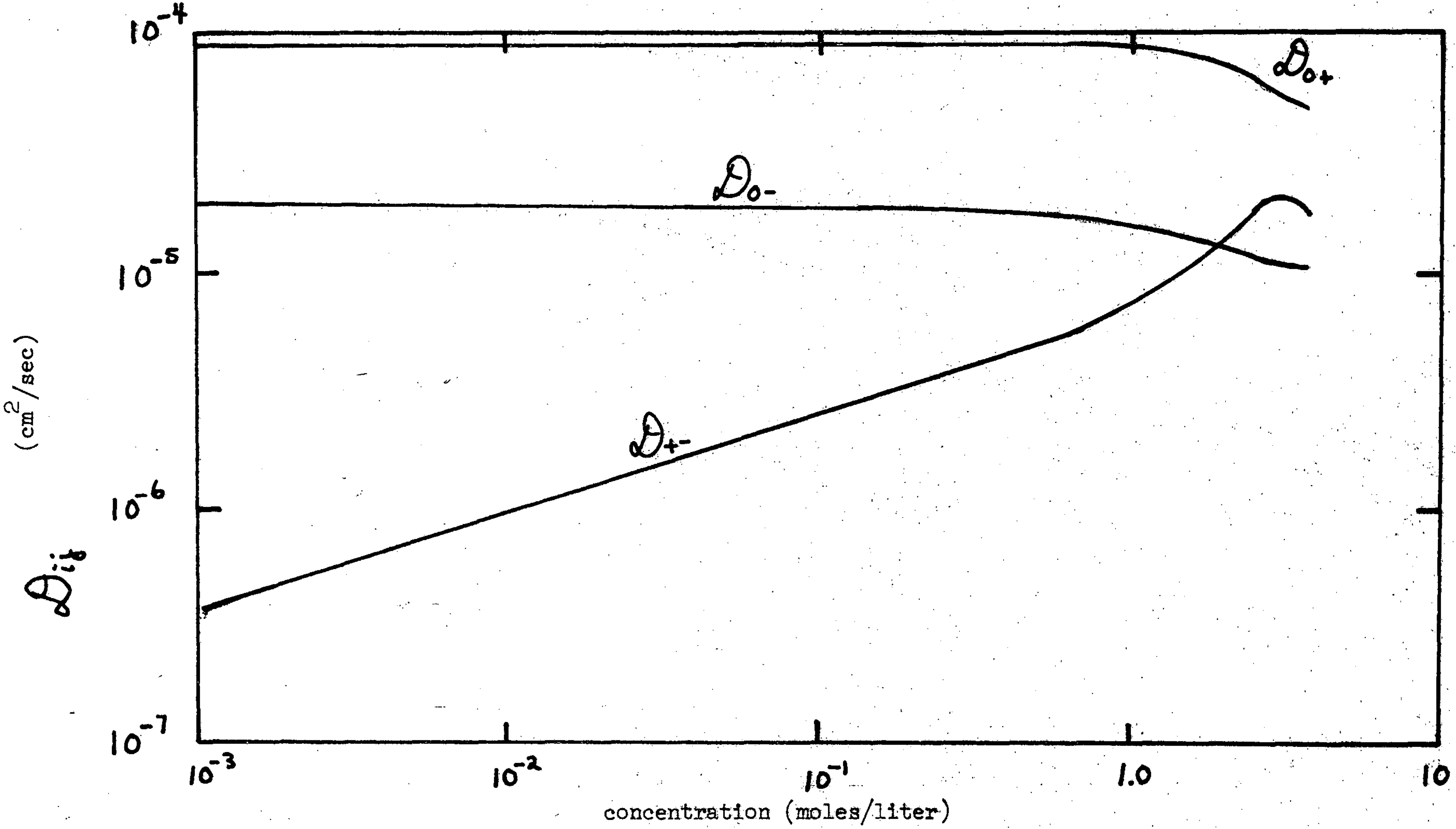


Fig. 4 The multicomponent diffusion coefficients of hydrochloric acid in water at 25°C

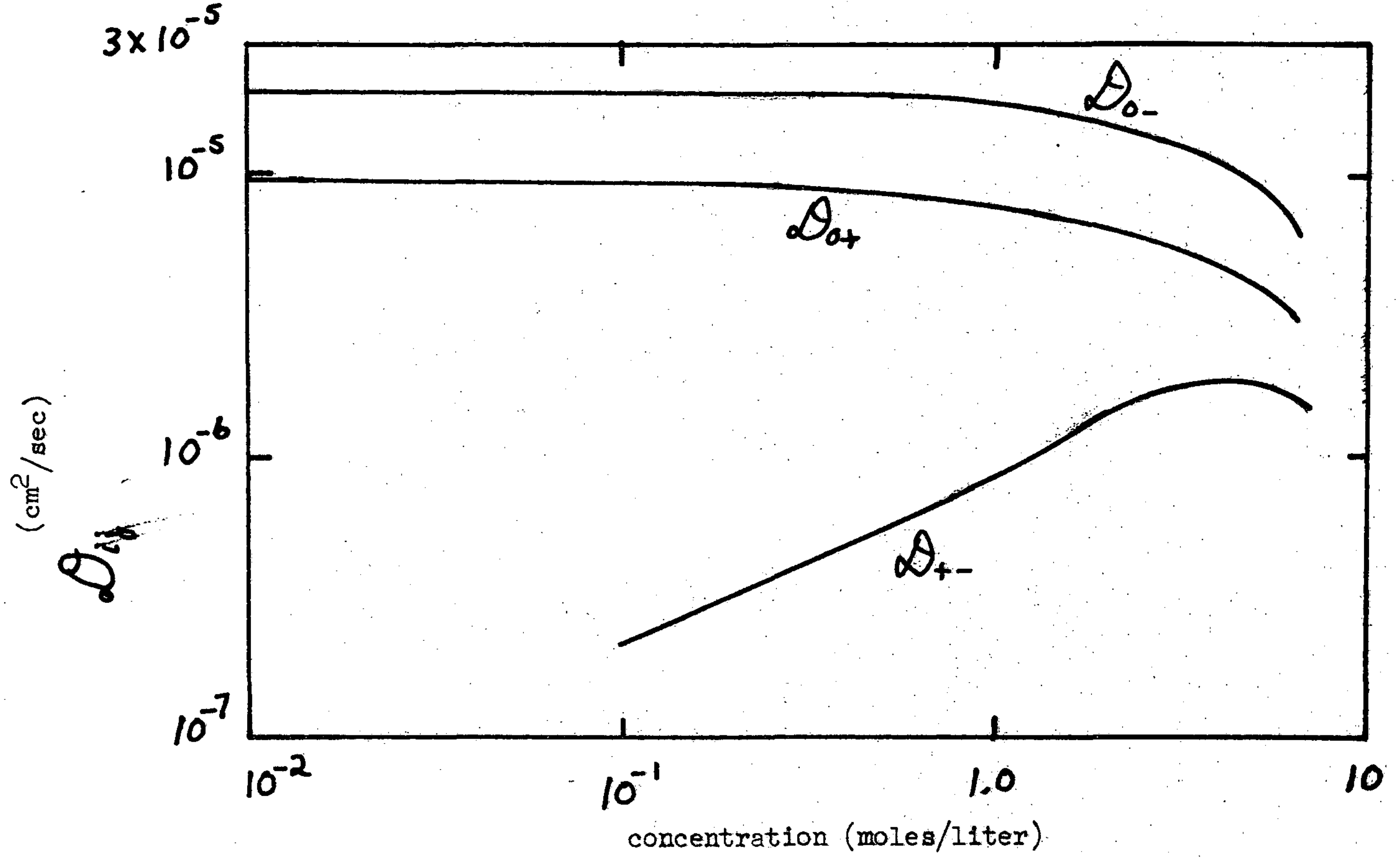


Fig. 5 The multicomponent diffusion coefficients of lithium nitrate in water at 25°C

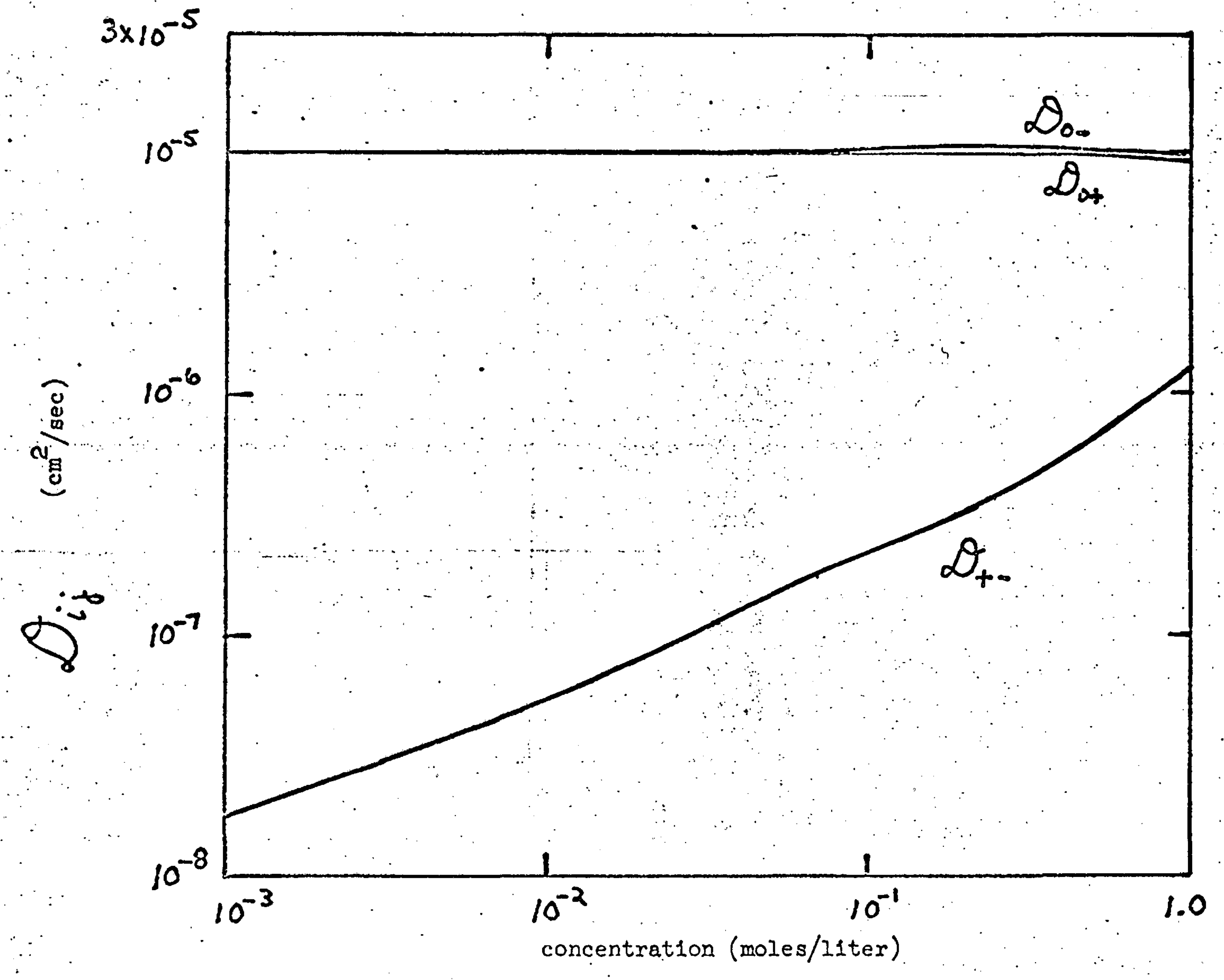


Fig. 6 The multicomponent diffusion coefficients of potassium chloride in water at 0°C

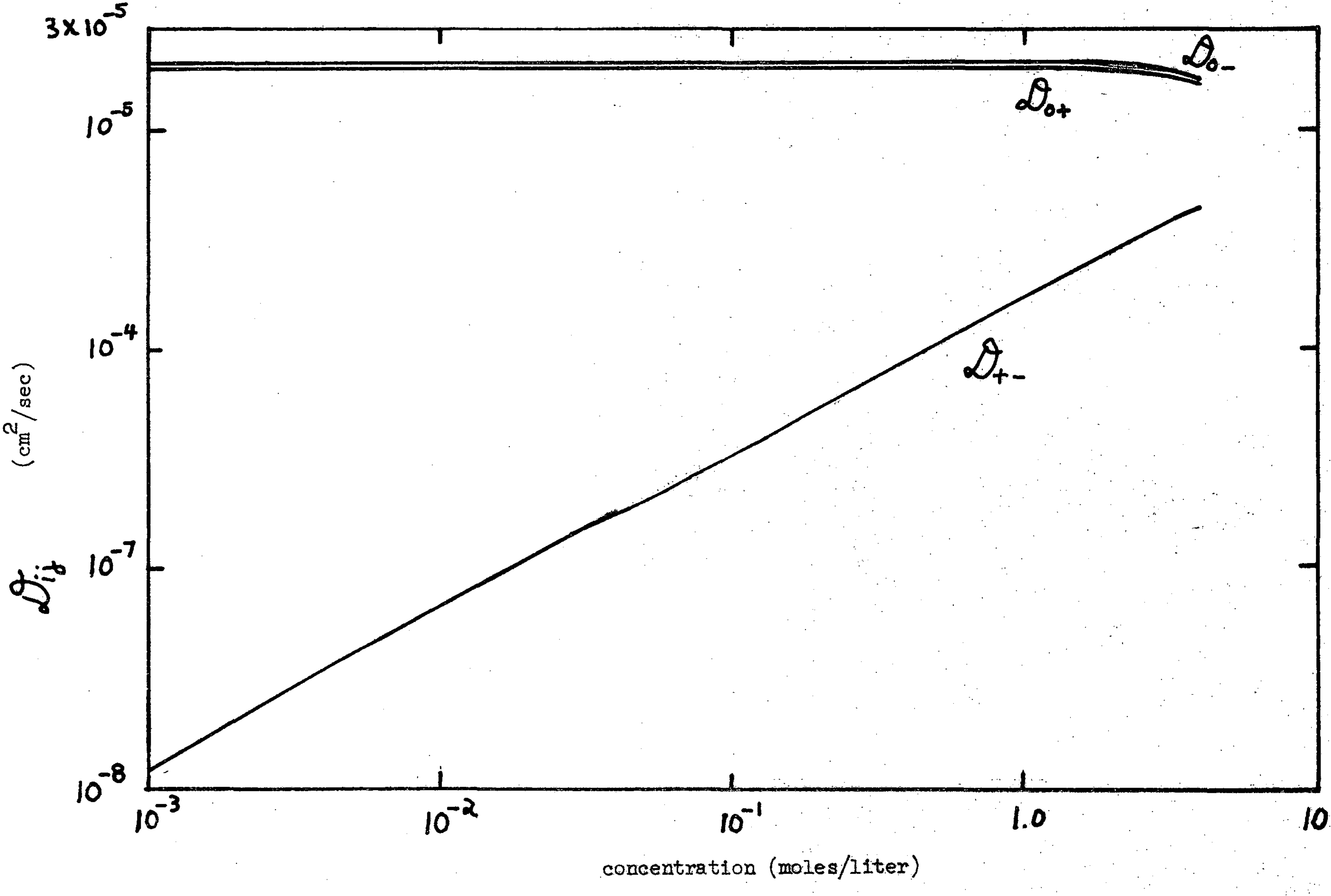


Fig. 7 The multicomponent diffusion coefficients of potassium chloride in water at 25°C

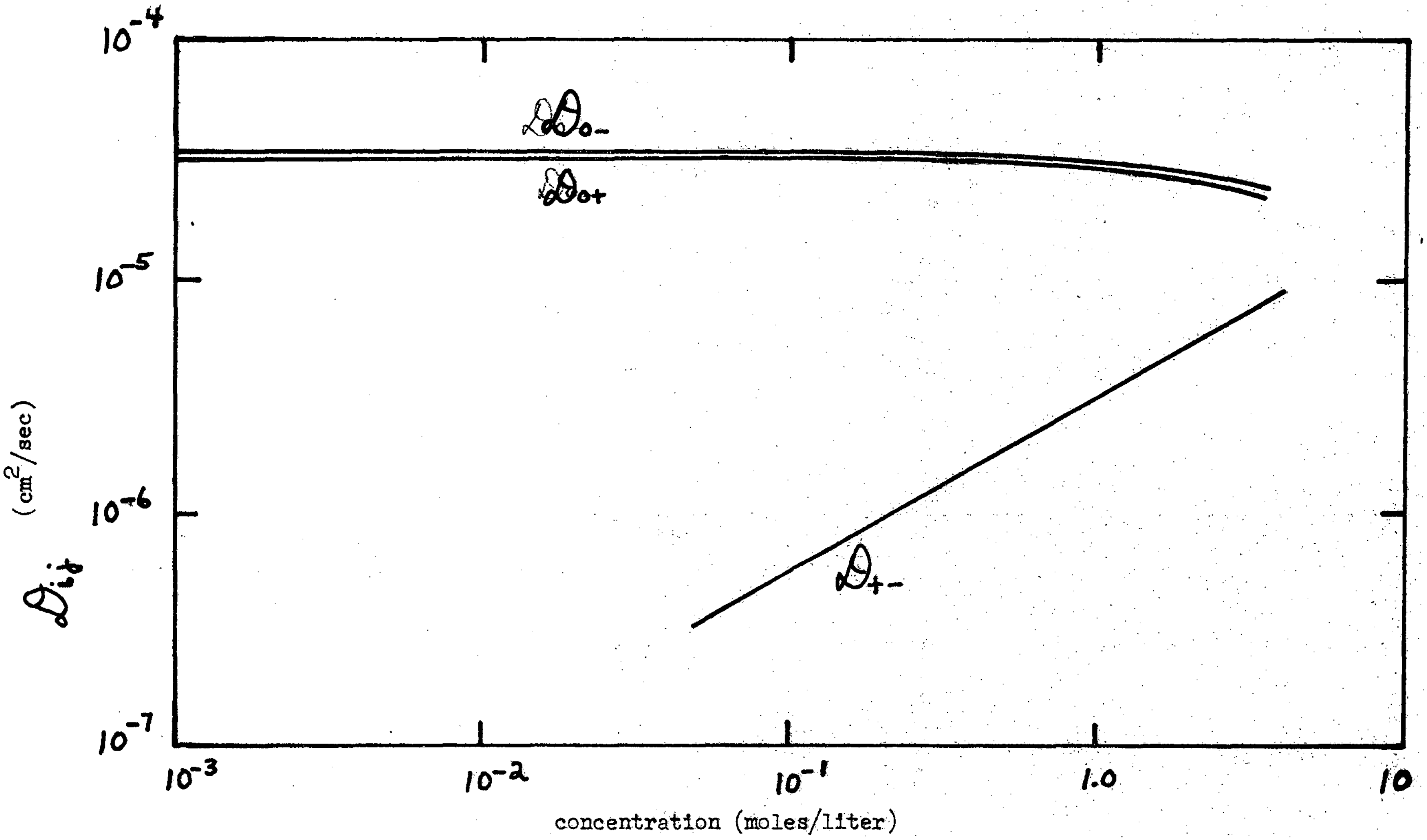


Fig. 8 The multicomponent diffusion coefficients of potassium chloride in water at 50°C

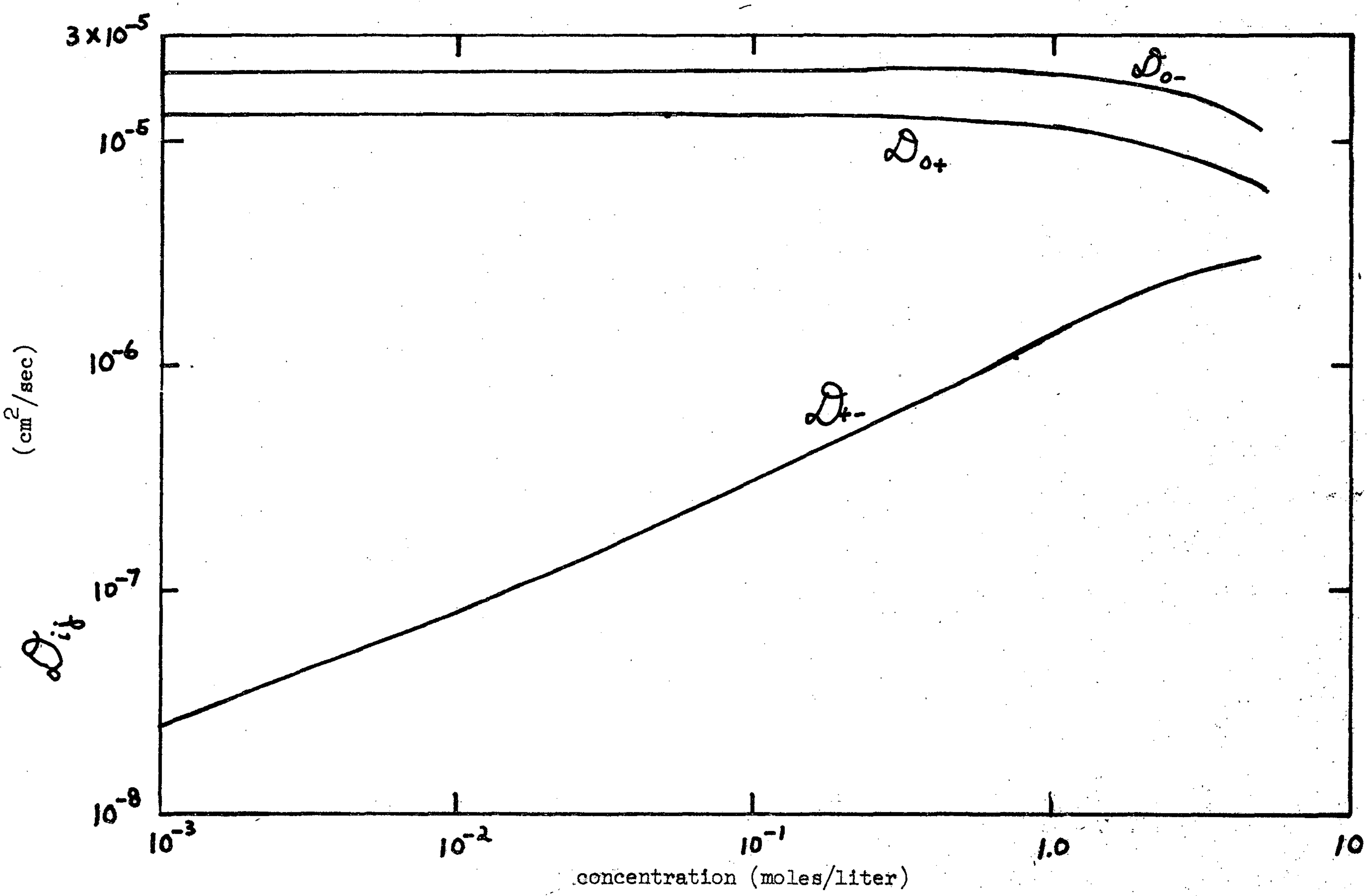


Fig. 9 The multicomponent diffusion coefficients of sodium chloride in water at 25°C

original value. An exception is sulfuric acid, in which $\mathscr{D}_{0+}$ decreases almost an order of magnitude.

Let us look more closely at the behavior of the $\mathscr{D}_{+-}$ coefficients. These coefficients for various systems have qualitatively similar behavior. Over the concentration range 10^{-3} to above one molar the function increases somewhat more rapidly than the predicted $c^{1/2}$ dependence. For most of the 1-1 electrolytes the values are close to one another, but the $\mathscr{D}_{+-}$ values for 2-2 electrolytes are more than an order of magnitude lower, and acids are considerably higher. Values for 1-2 electrolytes fall somewhat below those for 1-1 electrolytes. The $\mathscr{D}_{+-}$ coefficients increase with temperature by about a factor of 1.5 or 2.0 from 0°C to 50°C according to the data for sodium and potassium chlorides.

Equation (III-33) may be rearranged to the form

$$G = \left[\frac{(1 + \sqrt{q})(z_+ \mathscr{D}_{0+} - z_- \mathscr{D}_{0-}) \sqrt{c} \ z_+ \nu_+}{c_0 \ z_+^2 z_-^2 q (z_+ - z_-)^{1/2} (z_+ \nu_+)^{1/2} \mathscr{D}_{+-}} \right] T^{3/2} \qquad \text{(IV-1)}$$

where G should be inversely proportional to the 3/2 power of the dielectric constant and at infinite dilution equal $2858.5 \ [(^\circ K)^3 \ \ell/\text{mole}]^{1/2}$. The quantity G was calculated for the systems listed in Table II. Some of the results are shown in Fig. 10. Although G is not a constant, it is found to vary less than an order of magnitude, with most of the variation occurring at high dilution and to be a similar function of concentration for almost all the substances considered; furthermore, it appears to be relatively insensitive to temperature. This means that the appearance of the charge numbers, ionic diffusion coefficients, $c^{1/2}$ and temperature in the theoretical equation (IV-1) is appropriate to the extent that these variables partially account for the gross differences in σ_{+-} of the various systems and its variation over many orders of magnitude. Part of the concentration dependence of G results from the appearance of σ_{oi} in Eq. (IV-1); if the constant limiting values σ_{oi}^{o} are used, however, there is no substantial change in the appearance of Fig. 10.

Unfortunately the values of G at low concentrations do not extrapolate to the theoretical value or even converge to the same value for different substances. The values are actually closer together and closer to the theoretical value at higher concentrations. It is difficult to determine σ_{+-} or G very accurately in dilute solutions because σ_{+-} is a small difference between two large experimental quantities. Conversely, a rough estimate of G might be satisfactory for predicting σ_{+-} values with Eq. (IV-1) because the magnitude of σ_{+-} is significant only at concentrations where G appears to be fairly constant.

The function G may be interpreted as a catch-all quantity which includes the effects of the many inadequacies of the idealized theory. The value of G (in $(°K)^{3/2}/(\text{moles}/l)^{1/2}$) for most electrolytes is between 7000 and 10,000 in very dilute solutions. With increasing concentrations it drops to between 4000 and 5000 above one molar and may drop even more in very concentrated solutions. The only exceptions to this general behavior are ammonium nitrate and silver nitrate. These two systems appear to be anomalous in that G increases with concentration and becomes considerably higher than in other cases.

The values for hydrochloric acid are particularly low in dilute solutions but remain near 2000 at higher concentrations. Sodium hydroxide, however, does not appear to behave differently from other, more typical

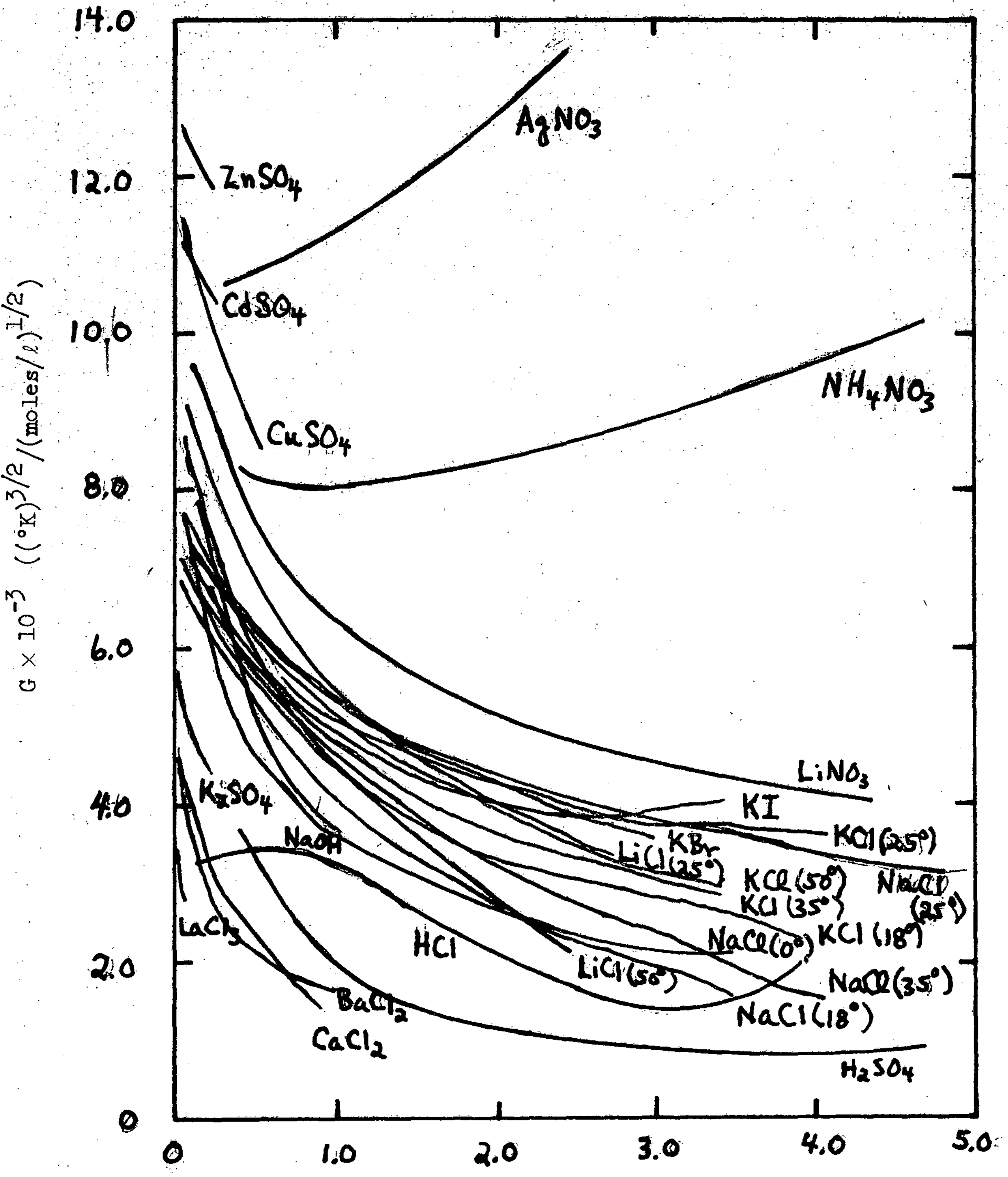


Fig. 10 The empirical function G for various systems

electrolytes.

In general, the values of G for uni-univalent electrolytes fall within a band characterized by the following limits:

at c = 0.5 M, G = 6000 ± 1000 ;

at c = 1.0 M, G = 4500 ± 1000 ;

at c = 2.0 M, G = 3500 ± 1000 ;

at c = 3.0 M and above, G = 3000 ± 1000 .

The temperature dependence of G for sodium, potassium, and lithium chloride is not great. All values between 0° and 50°C fall within the limits given above. Since data at higher concentrations and various temperatures are often not as accurate as one would like, it is difficult to say how reliable the observed variations in G are. Although the G values for a system at different temperatures do not coincide, there is no systematic trend in their variation with temperature.

Divalent symmetrical electrolytes were found to exhibit higher values of G. For copper sulfate these are 10,000 at 0.25 M and 8500 at 0.5 M. Cadmium sulfate appears to be quite similar and zinc sulfate is even higher.

Values of G calculated for the unsymmetrical electrolytes $BaCl_2$, $CaCl_2$, and $LaCl_3$ as well as H_2SO_4 are lower than those for symmetrical electrolytes. Barium and calcium chlorides are near 2250 at 0.5 M and 1500 at 1.0 M. Lanthanum chloride appears to fall even lower. Potassium sulfate, on the other hand, is somewhat higher, and sodium sulfate is only slightly lower than the typical G values for uni-univalent electrolytes.

Rewriting Eq. (IV-1), we obtain the expression for $\mathscr{D}_{+-}$:

$$\mathscr{D}_{+-} = \frac{\sqrt{c}\ (z_+\mathscr{D}_{o+} - z_-\mathscr{D}_{o-})(1+\sqrt{q})\ T^{3/2}\ (z_+\nu_+)^{1/2}}{G\ c_o(z_+ - z_-)^{1/2}\ z_+^2\ z_-^2 q} . \qquad \text{(IV-2)}$$

If it is necessary to estimate a value of $\mathscr{D}_{+-}$ where no data are available or to extrapolate limited data, one could choose a value for G, depending upon the type of electrolyte being considered, from the range of values we have calculated here.

It is unfortunate that the variation of G cannot be interpreted in terms of the Onsager-Fuoss-Debye-Hückel model. Since G should be inversely proportional to $\epsilon^{3/2}$, one would expect it to increase with increasing concentration, an effect quite opposite to that observed. It appears, then, that the theory is inadequate for solutions of concentrations where $\mathscr{D}_{+-}$ is of significant magnitude. Even at very low concentrations the electrostatic model breaks down because the $\mathscr{D}_{+-}$ coefficients become chemically specific. (At infinite dilution all the values of G should approach a common value, $e^3 \sqrt{4\pi N_o}/3\ (\epsilon k)^{3/2}$ =

$$2.858.5 \times 10^3\ (°K)^{3/2}/(\text{mole}/\ell)^{1/2}) .$$

Since the limit of the diffusion coefficient of an ion $\mathscr{D}_{oi}$ in the solvent is given by its limiting equivalent conductance, it is interesting to investigate how $\mathscr{D}_{oi}$ varies from its limit at finite concentrations in various solutions. The ion which has been studied most extensively is chloride. The diffusion coefficients of the chloride ion in various solutions are shown in Fig. 11. In every case except hydrochloric acid, $\mathscr{D}_{H_2O\text{-}Cl^-}$ initially increases with concentration, goes through a maximum,

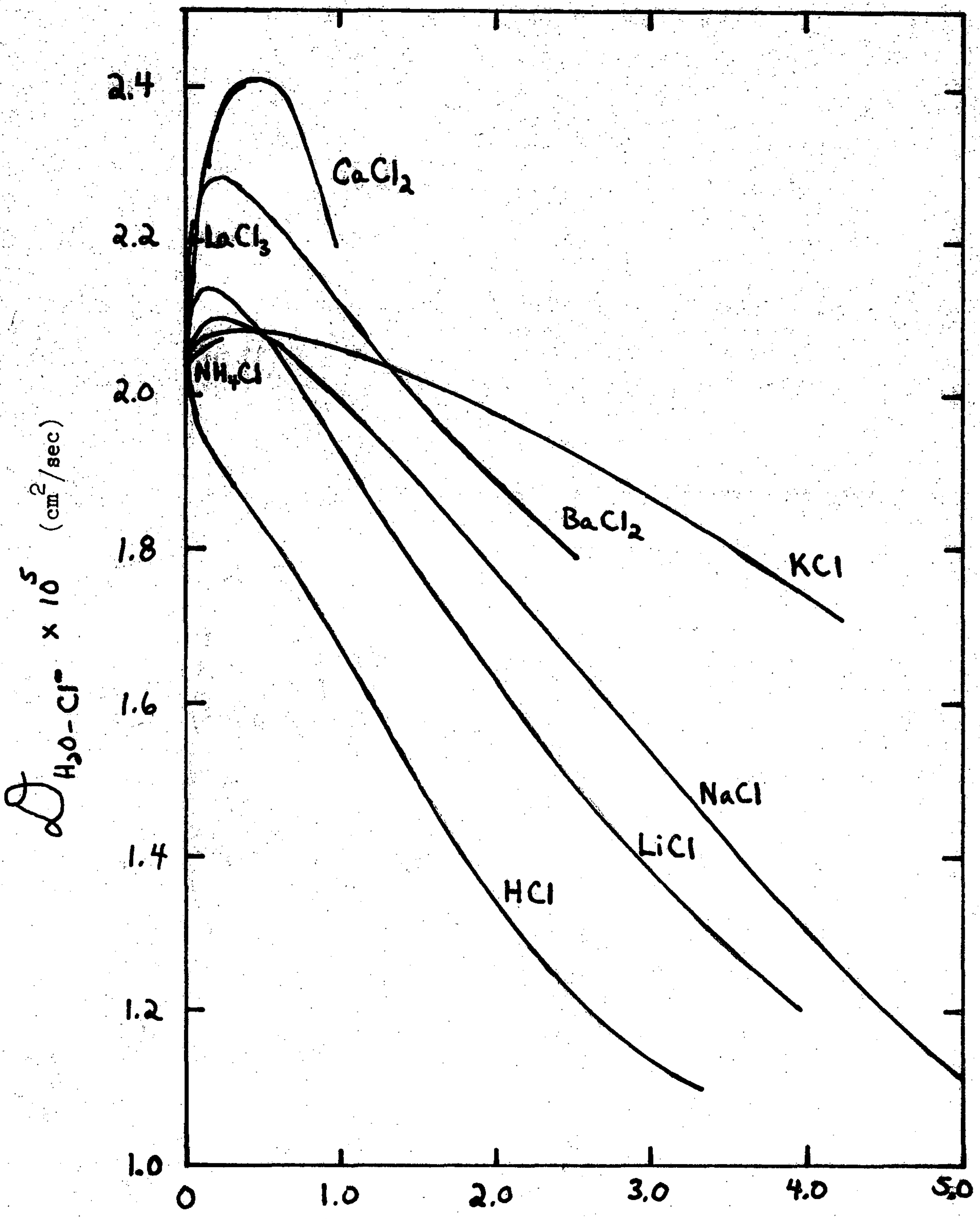


Fig. 11 The diffusion coefficient of chloride ion in various aqueous solutions at 25°C

and decreases at higher concentrations. The largest increase observed, almost 20 percent, occurs with calcium. The next largest effect is caused by barium, and the available data for lanthanum indicate a similarly large increase.

Of the other halides, data are available only for potassium bromide, sodium iodide, and potassium iodide, all at 25°C. The diffusion coefficients of these halide ions all exhibit a maximum with concentration, as shown in Fig. 12. The iodide maxima are slightly larger than those of the corresponding chlorides. As in the chlorides, the potassium salt maximum appears at a higher concentration than that of the sodium salt, but in this latter case the potassium iodide maximum is somewhat greater than for the sodium salt. The maximum for bromide is very similar to, but slightly larger than, that for the corresponding chloride and is almost identical to that for potassium iodide.

The behavior of the nitrate ion in silver, lithium, and ammonium nitrates is similar to that of the halide ions in that these systems exhibit maxima in $\mathcal{D}_{H_2O-NO_3^-}$, which are shown in Fig. 13. With lithium, the nitrate ion diffusion coefficient drops off at high concentrations, whereas with silver and ammonium its value does not change greatly in concentrated solutions.

The behavior of several alkali metal ions is shown in Fig. 14. In lithium chloride and lithium nitrate $\mathcal{D}_{H_2O-Li^+}$ decreases smoothly with increasing concentration. The cation coefficient in sodium chloride and sodium hydroxide decreases uniformly, but it exhibits a slight increase in dilute solutions of sodium iodide before decreasing, and it increases very rapidly in sodium sulfate. In potassium salt solution $\mathcal{D}_{H_2O-K^+}$

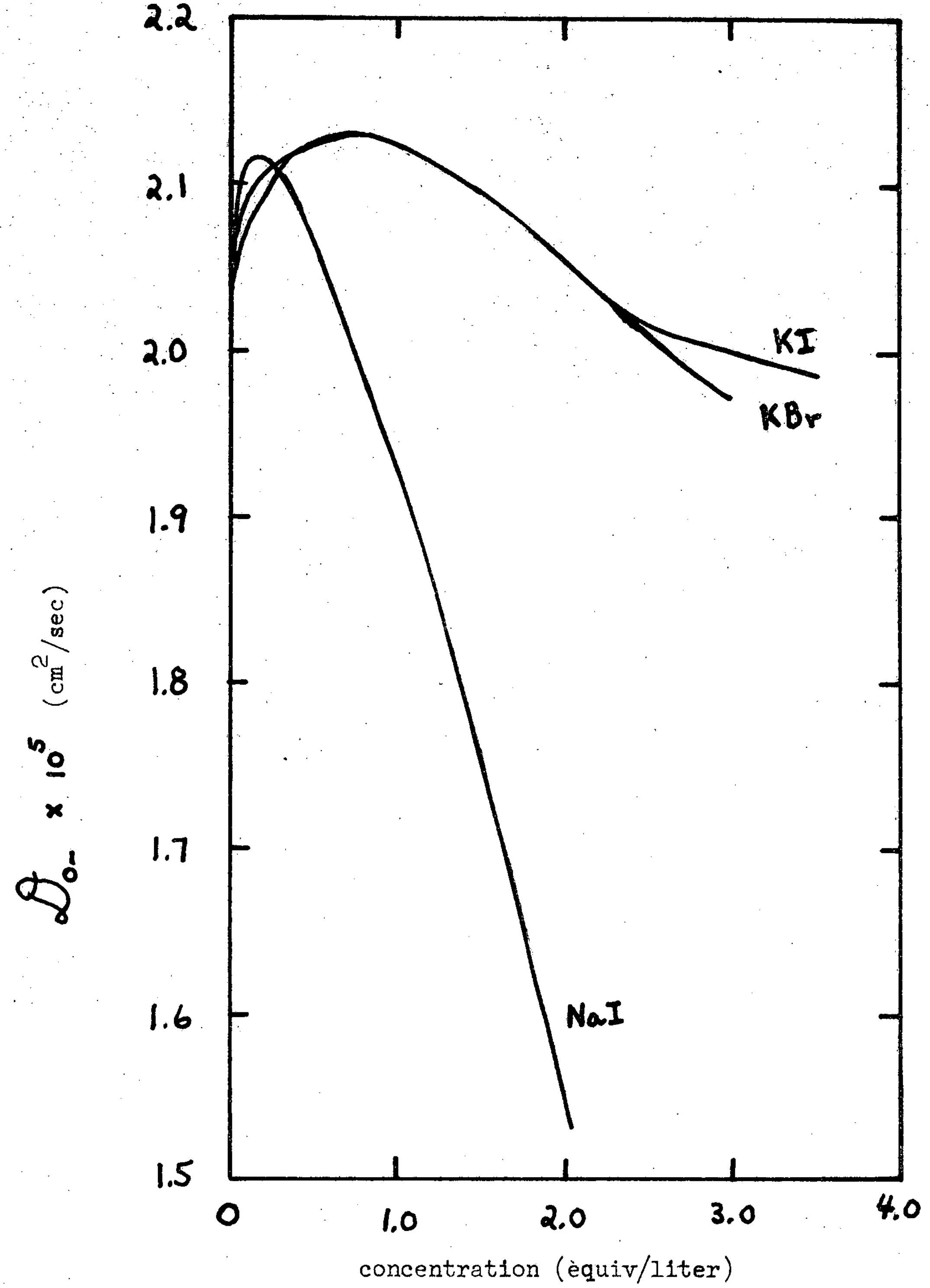


Fig. 12 Halide ion diffusion coefficients at 25°C

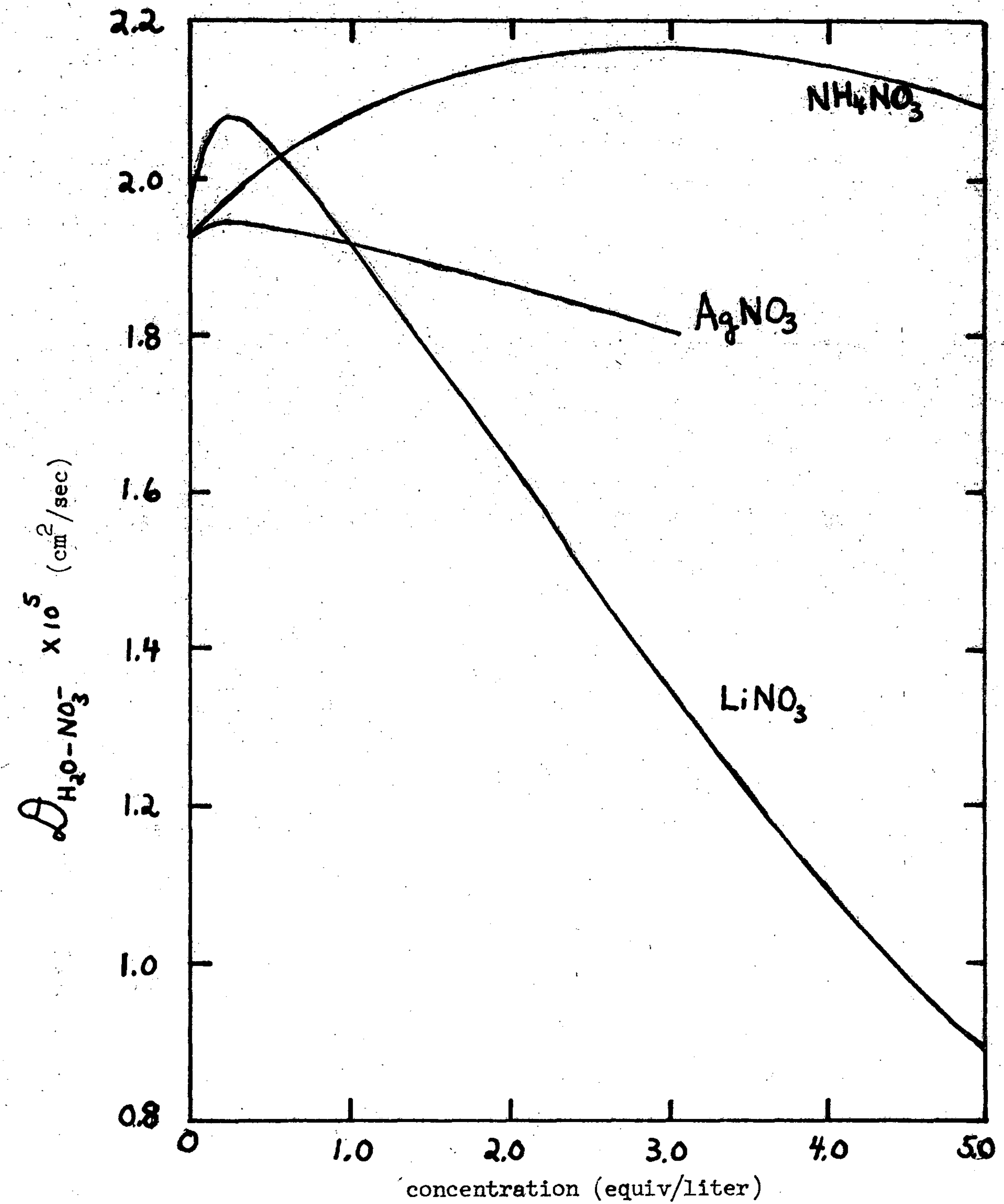


Fig. 13 Nitrate ion diffusion coefficients at 25°C

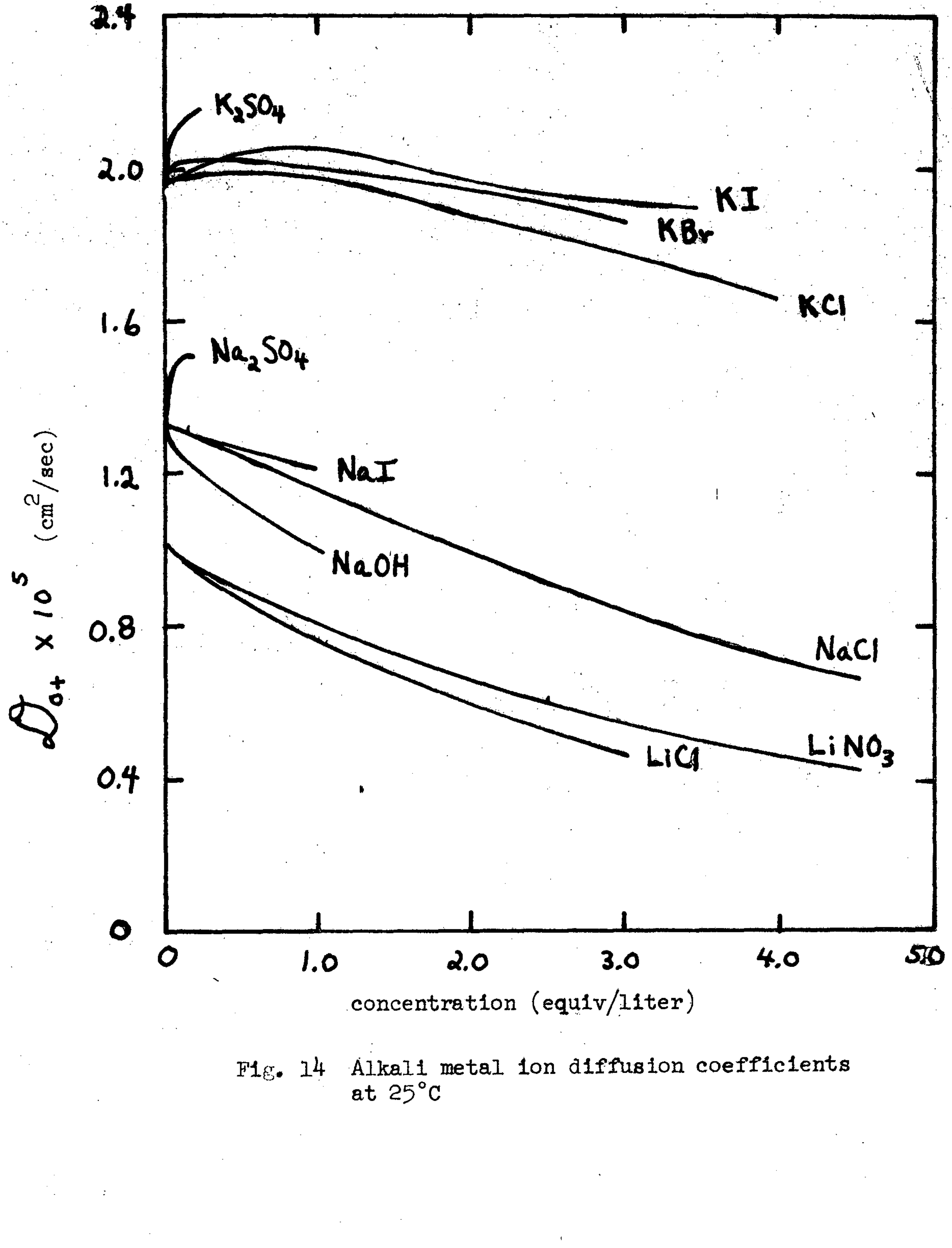


Fig. 14 Alkali metal ion diffusion coefficients at 25°C

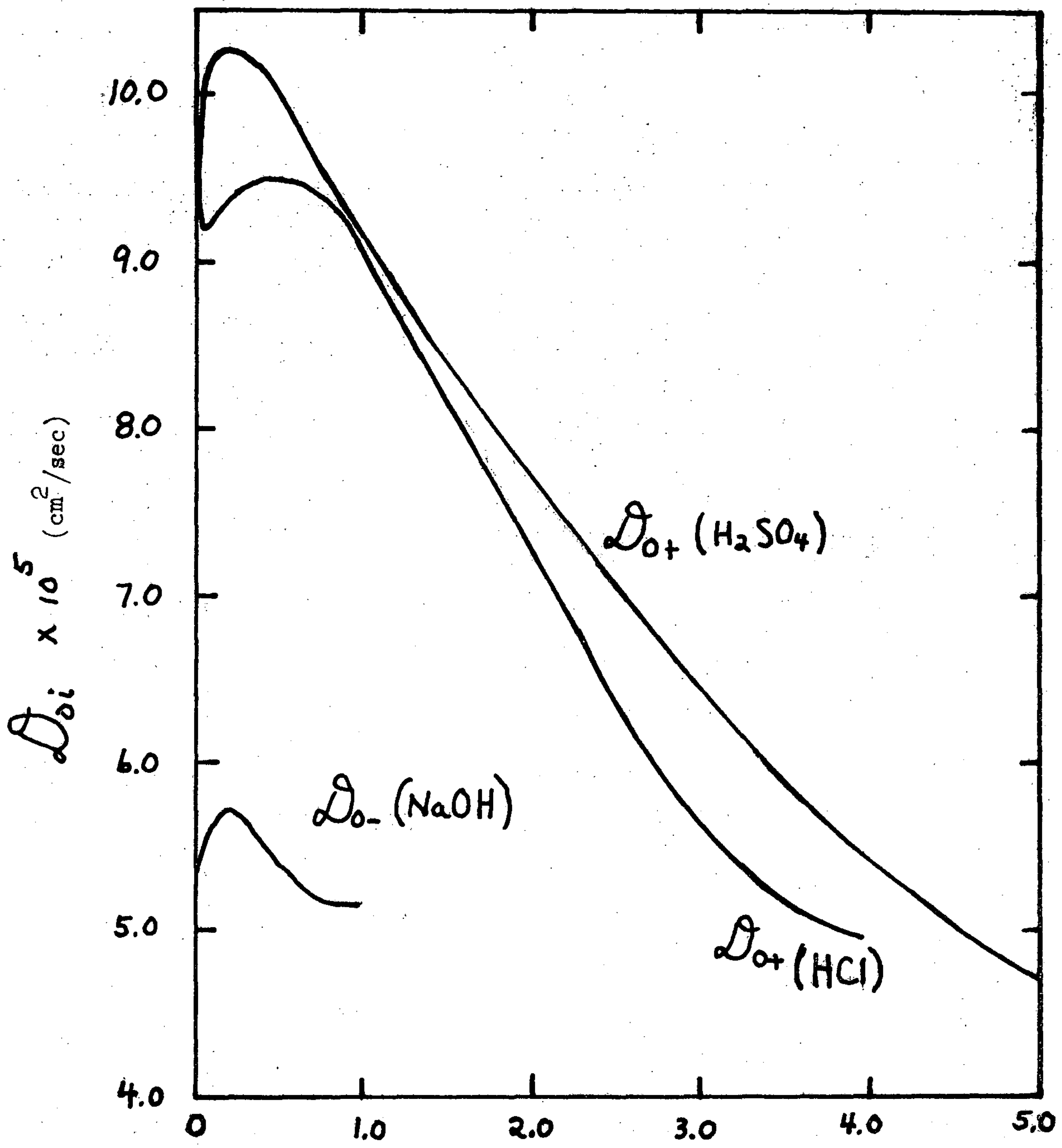
goes through about a 2 or 3 percent maximum before decreasing in concentrated solutions. With sulfate the potassium ion diffusion coefficient increases very rapidly at low concentrations.

The calculations for hydrochloric and sulfuric acids yield the diffusion coefficients for hydrogen ion shown in Fig. 15. $\mathcal{D}_{H_2O-H^+}$ in sulfuric acid goes through a simple maximum, whereas that in hydrochloric acid behaves rather strangely, going through a minimum and then a maximum before decreasing at higher concentrations in a manner quite similar to that in sulfuric acid. Calculations with the phosphoric acid data which were summarized in Table XV indicate that the hydrogen ion diffusion coefficient drops off from its limiting value very rapidly with concentration. These calculations are in doubt, however, because the experimental diffusion data do not appear to extrapolate to the Nernst value; also there is considerable divergence of several sets of data for the transference number.

The diffusion coefficient of hydroxide ion in sodium hydroxide is also shown in Fig. 15. It is seen to exhibit a maximum of about 10 percent near .2 molar and then to decrease with increasing concentration up to one molar.

According to Tables III and IV, the diffusion coefficient of ammonium ion in ammonium chloride and ammonium nitrate also increases in dilute solutions. The maximum in ammonium nitrate, however, occurs near 3 molar, which is much higher than for other ions. The subsequent decrease of $\mathcal{D}_{H_2O-NH_4^+}$ at higher concentrations is not rapid.

The only other ion for which appreciable data are available is sulfate. $\mathcal{D}_{H_2O-SO_4^=}$ is shown in Fig. 16 for solutions of sulfuric acid,



concentration (equiv/liter)

Fig. 15 Ionic diffusion coefficients of hydrogen and hydroxide at 25°C

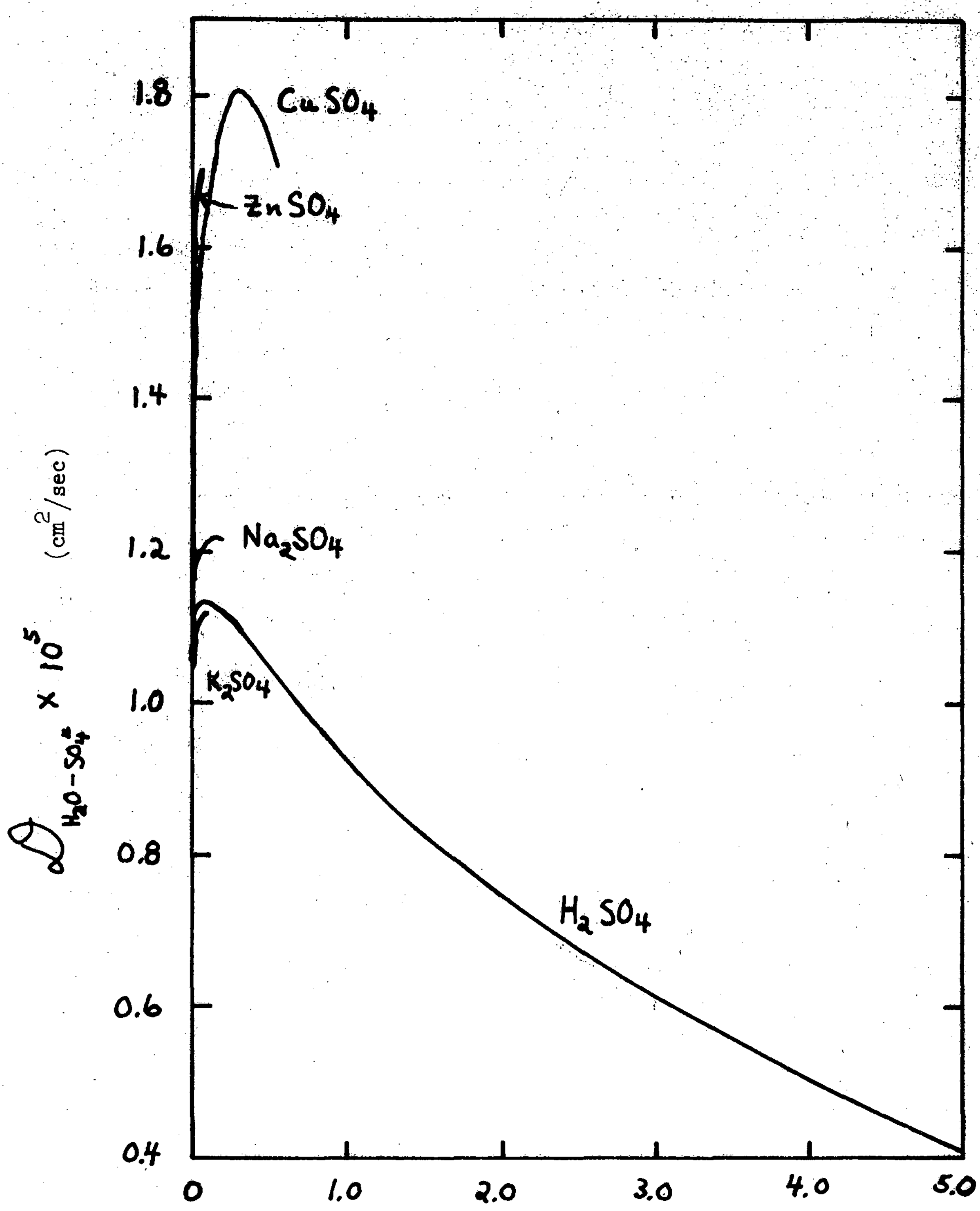


Fig. 16 Sulfate ion diffusion coefficients at 25°C

copper sulfate, zinc sulfate, sodium sulfate, and potassium sulfate. In all cases this coefficient increases with concentration in dilute solutions. The increase is greatest with zinc and copper; the maximum increase over the limiting value in cupric sulfate is almost 90 percent. The increase in sulfuric acid amounts to about 5 percent before $\mathcal{D}_{H_2O-SO_4^=}$ decreases gradually with concentration up to 5.5 molar.

Of the other ions which are included in Tables III through XXXIV, the diffusion coefficients of zinc and copper in sulfate solutions both go through rather sharp maxima at low concentrations. The $\mathcal{D}_{oi}$ coefficients for barium, calcium, and lanthanum in chloride solutions do not exhibit maxima but decrease continuously with increasing concentration. Silver ion, on the other hand, increases from its limiting value and continues to increase up to 3 molar.

Since the diffusion coefficients, transference numbers, and other pertinent properties of potassium, sodium, and lithium chlorides have been measured over a range of temperatures, we may also investigate the temperature dependence of the ionic diffusion coefficients. In Chapter III we indicated that the limiting diffusion coefficients of various ions all follow a similar dependence on temperature. According to Eq. (III-32) the limiting diffusion coefficients $\mathcal{D}_{oi}$ at various temperatures may be calculated from the limiting ionic equivalent conductances tabulated in the Appendix of Robinson and Stokes.[72] For the purposes of interpolation the results can be fit by an equation of the form

$$\mathcal{D}^{\circ}_{oi} = aT^{3/2} + bT^{2} + cT^{5/2} \, . \qquad \text{(IV-3)}$$

This equation follows from Eq. (II-20) except for the term in T^2, which was introduced to make the fit more accurate over a temperature range of 100°C. Coefficients of Eq. (IV-3) and values of $\mathcal{D}_{oi}$ at 25°C for various ions are given in Table XXXV. The fit is generally within a percent or two over the entire range.

In order to investigate the temperature dependence of the ionic diffusion coefficients at finite concentrations, we have plotted the quantity $\mathcal{D}_{oi}/\mathcal{D}^{\circ}_{oi}$ at various temperatures versus concentration for the ions of sodium, potassium, and lithium chloride solutions in Figs. 17 through 22. It is found that the concentration dependence at different temperatures is roughly the same and that most of the temperature dependence is accounted for by that of $\mathcal{D}^{\circ}_{oi}$.

The diffusion data for these systems were all obtained by Vitagliano[82] by the Gouy method. He also provides the activity coefficient correction based on data of Caramazza.[6] It is seen in the figures that values based on these data for potassium and sodium chlorides all fall below the well-corroborated values for 25°C. One might suspect that some inconsistency has arisen in the measurements because the values of $\mathcal{D}_{oi}/\mathcal{D}^{\circ}_{oi}$ at 0°, 18°, 35°, and 50°C for the various ions all differ less among themselves than they do from the values for 25°C. Assuming that Vitagliano's data are consistent among themselves, one might conclude that there is a slight temperature effect on the concentration dependence of the $\mathcal{D}_{oi}$; values of $\mathcal{D}_{oi}/\mathcal{D}^{\circ}_{oi}$ seem to decrease more rapidly at higher temperatures than at lower temperatures. This effect, however, seems to be very small, and in sodium chloride there is an inversion of the order of the 18° and 35° curves between the 0° and 50° curves.

Table XXXV. Limiting ionic diffusion coefficients in water at 25°C and the coefficients of Eq. (IV-3) representing their temperature dependence

Ion	z_i	$\mathcal{D}^{\circ}_{oi}$ (25°C)×10^5 (cm^2/sec)	(a) ($cm^2/sec(°K)^{3/2}$)	(b) ($cm^2/sec(°K)^2$)	(c) ($cm^2/sec(°K)^{5/2}$)
Acetate	-1	1.0884	-2.23492 E-08	+1.44415 E-09	-1.58715 E-12
Ammonium	+1	1.9573	-4.25901 E-08	+3.13303 E-09	-2.57595 E-11
Barium	+2	0.84666	2.69722 E-08	-4.02517 E-09	+1.48163 E-10
Beryllium	+2	0.59877	--	--	--
Bromide	-1	2.0795	1.64023 E-08	-3.93244 E-09	+1.86298 E-10
Calcium	+2	0.79171	1.51031 E-08	-2.62609 E-09	+1.06624 E-10
Cerium	+3	0.61917	--	--	--
Cesium	+1	2.0560	2.02209 E-08	-4.20989 E-09	+1.89362 E-10
Chlorate	-1	1.7926	1.38440 E-08	-3.33957 E-09	+1.58686 E-10
Chloride	-1	2.0318	1.03570 E-08	-3.24800 E-09	+1.66650 E-10
Cobalt	+2	0.73183	--	--	--
Cupric	+2	0.71320	--	--	--
Fluoride	-1	1.4743	--	--	--
Hydrogen	+1	9.3091	-4.14093 E-07	+4.26060 E-08	-1.01781 E-09
Hydroxide	-1	5.2772	-1.97281 E-07	+1.81433 E-08	-3.54824 E-10
Iodide	-1	2.0449	1.03310 E-08	-3.19709 E-09	+1.63840 E-10
Lanthanum	+3	0.61828	1.19921 E-08	-2.10208 E-09	+8.55552 E-11
Lead	+2	0.92477	--	--	--
Lithium	+1	1.0294	-4.05971 E-10	-1.16844 E-09	+7.58604 E-11

Table XXXV (continued)

Ion	z_i	$\mathcal{D}^{\circ}_{oi}$ (25°C)×10^5 (cm^2/sec)	(a) ($cm^2/sec(°K)^{3/2}$)	(b) ($cm^2/sec(°K)^2$)	(c) ($cm^2/sec(°K)^{5/2}$)
Magnesium	+2	0.70588	2.91534 E-08	-4.11630 E-09	+1.45178 E-10
Nitrate	-1	1.9017	2.06960 E-08	-4.18107 E-09	+1.85124 E-10
Potassium	+1	1.9560	-2.22478 E-09	-1.60418 E-09	+1.13170 E-10
Rubidium	+1	2.0707	1.71488 E-08	-3.88494 E-09	+1.80915 E-10
Silver	+1	1.6473	1.82639 E-08	-3.78099 E-09	+1.68455 E-10
Sodium	+1	1.3333	4.30925 E-09	-1.96743 E-09	+1.08304 E-10
Strontium	+2	0.79104	1.77859 E-08	-2.91201 E-09	+1.14144 E-10
Sulfate	-2	1.0647	4.24746 E-08	-6.14640 E-09	+2.20452 E-10
Thallium	+1	1.9879	--	--	--
Zinc	+2	0.70256	--	--	--

Ions for which constants are not given have not been measured over a range of temperatures

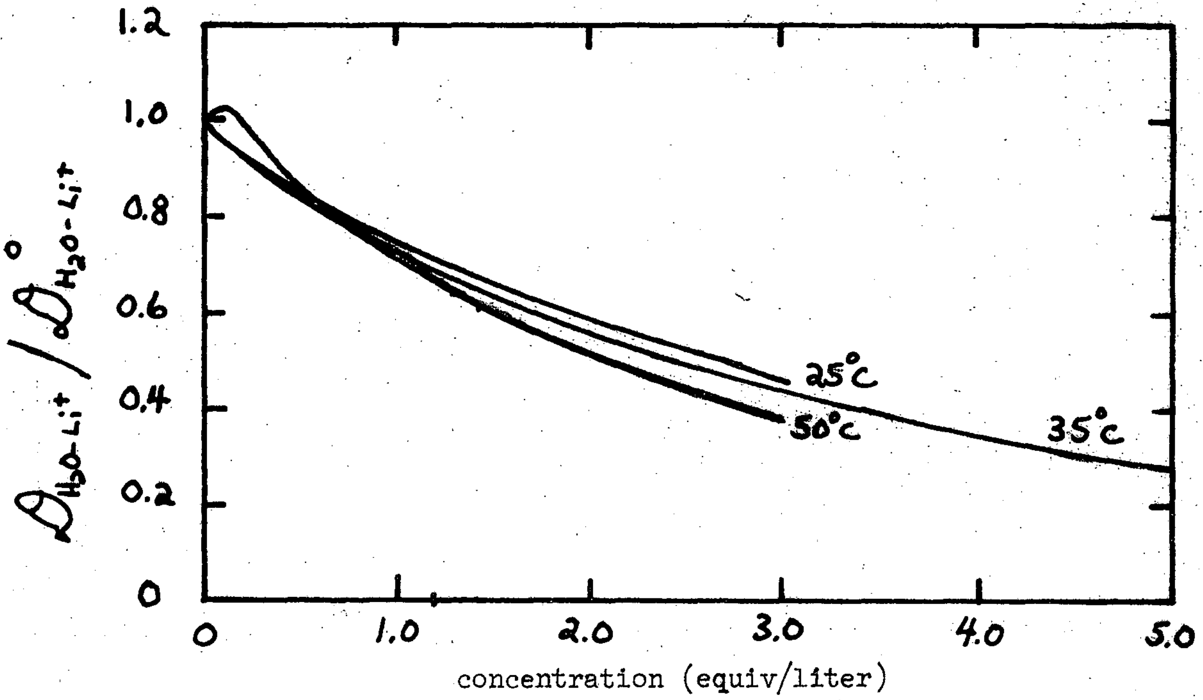


Fig. 17 Lithium ion diffusion coefficients in lithium chloride solutions at various temperatures

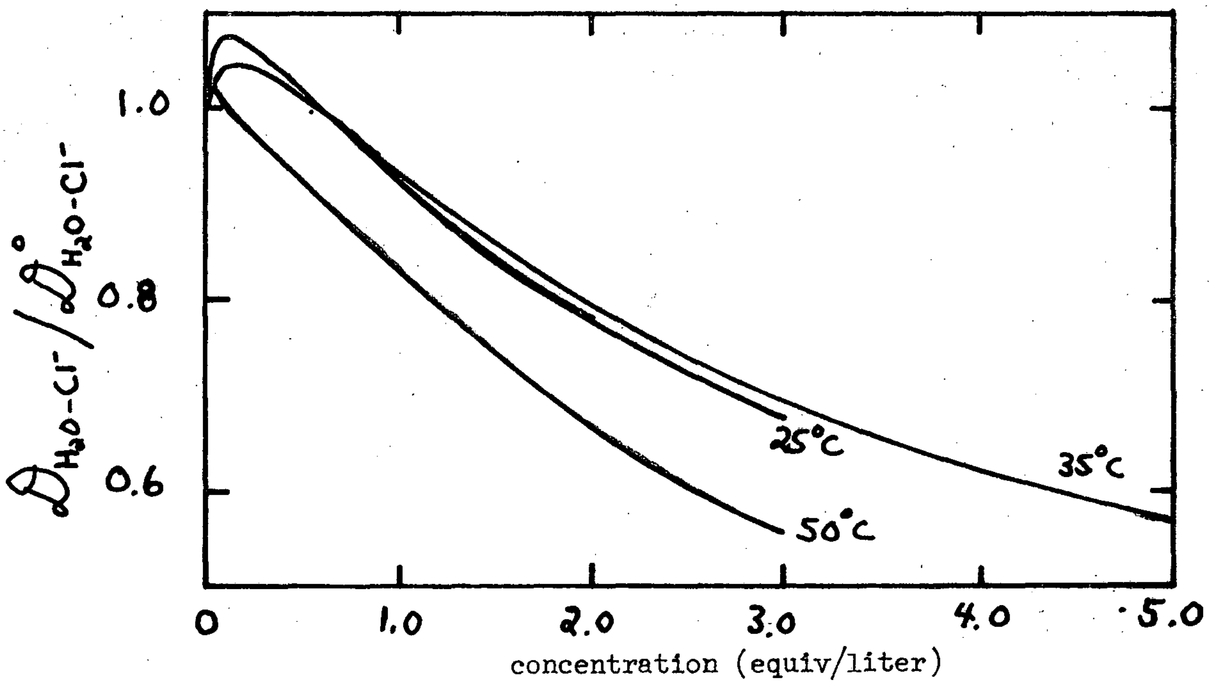
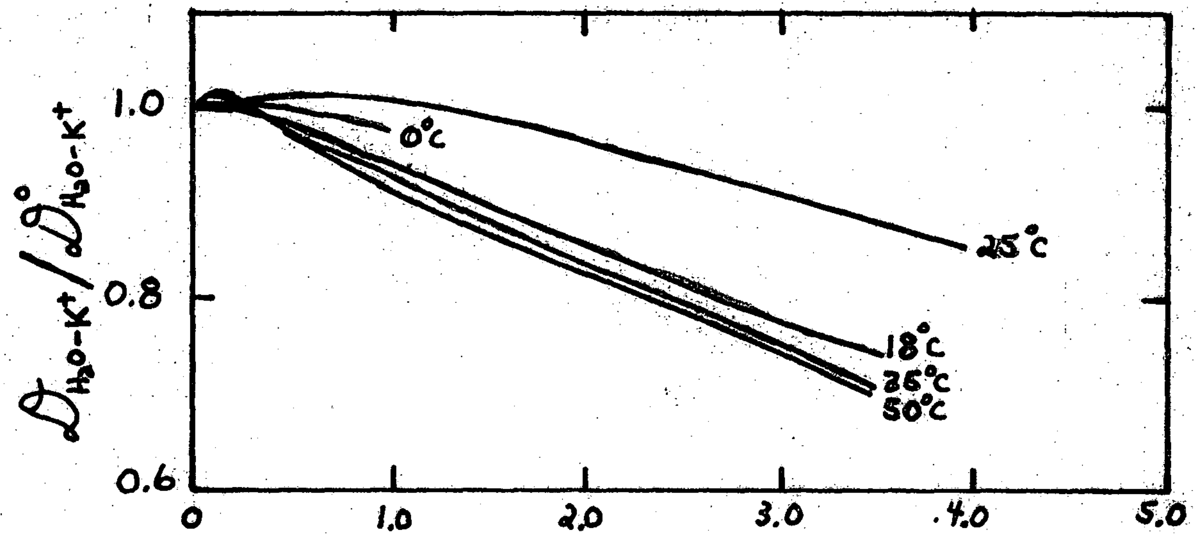
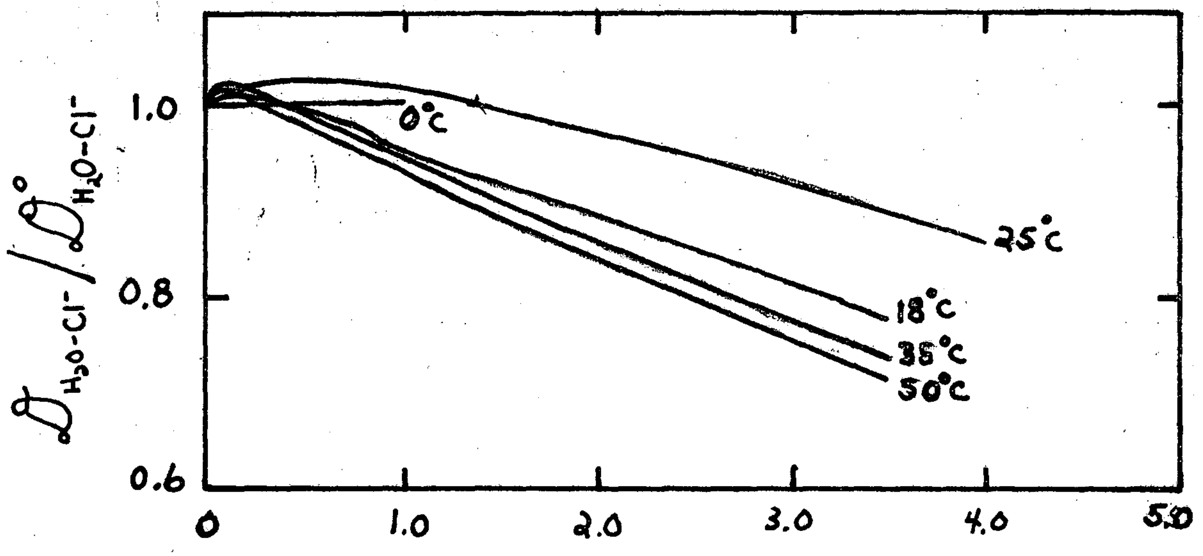


Fig. 18 Chloride ion diffusion coefficients in lithium chloride solutions at various temperatures



concentration (equiv/liter)

Fig. 19 Potassium ion diffusion coefficients in potassium chloride solutions at various temperatures



concentration (equiv/liter)

Fig. 20 Chloride ion diffusion coefficients in potassium chloride solutions at various temperatures

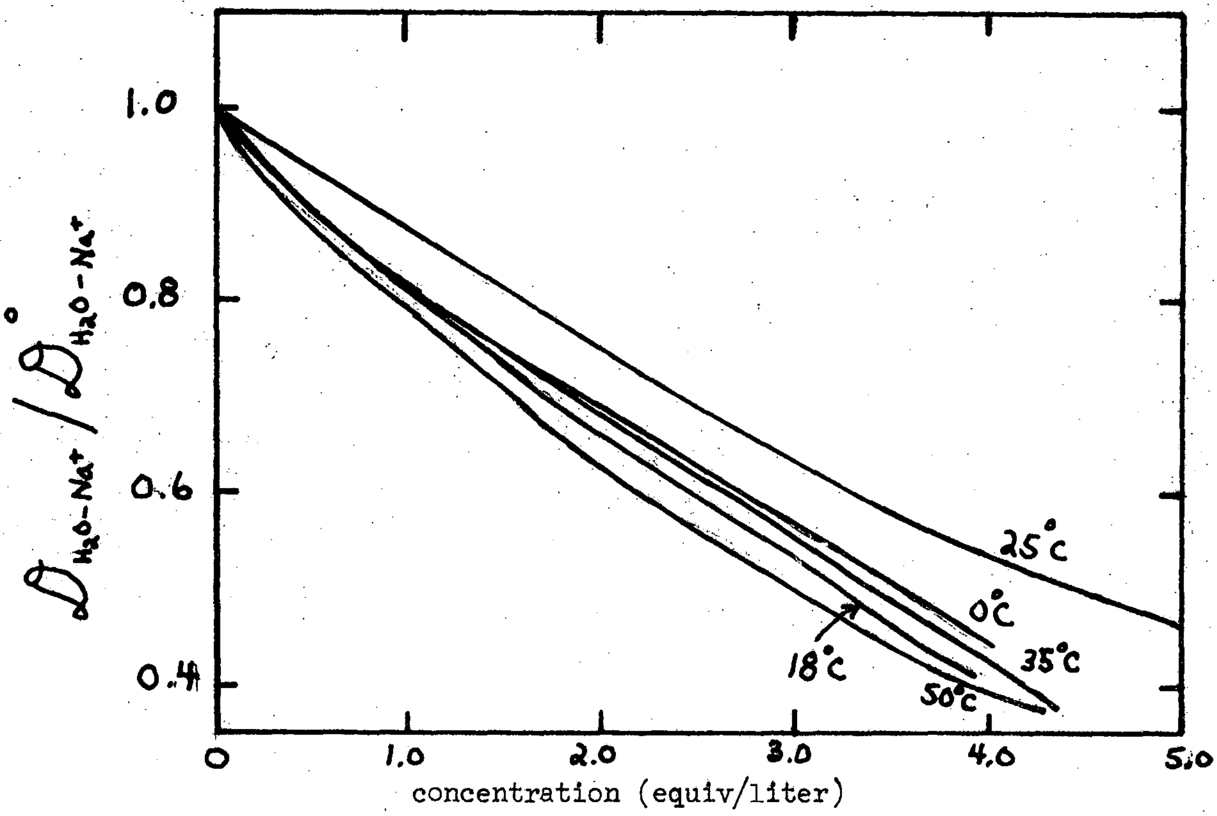


Fig. 21 Sodium ion diffusion coefficients in sodium chloride solutions at various temperatures

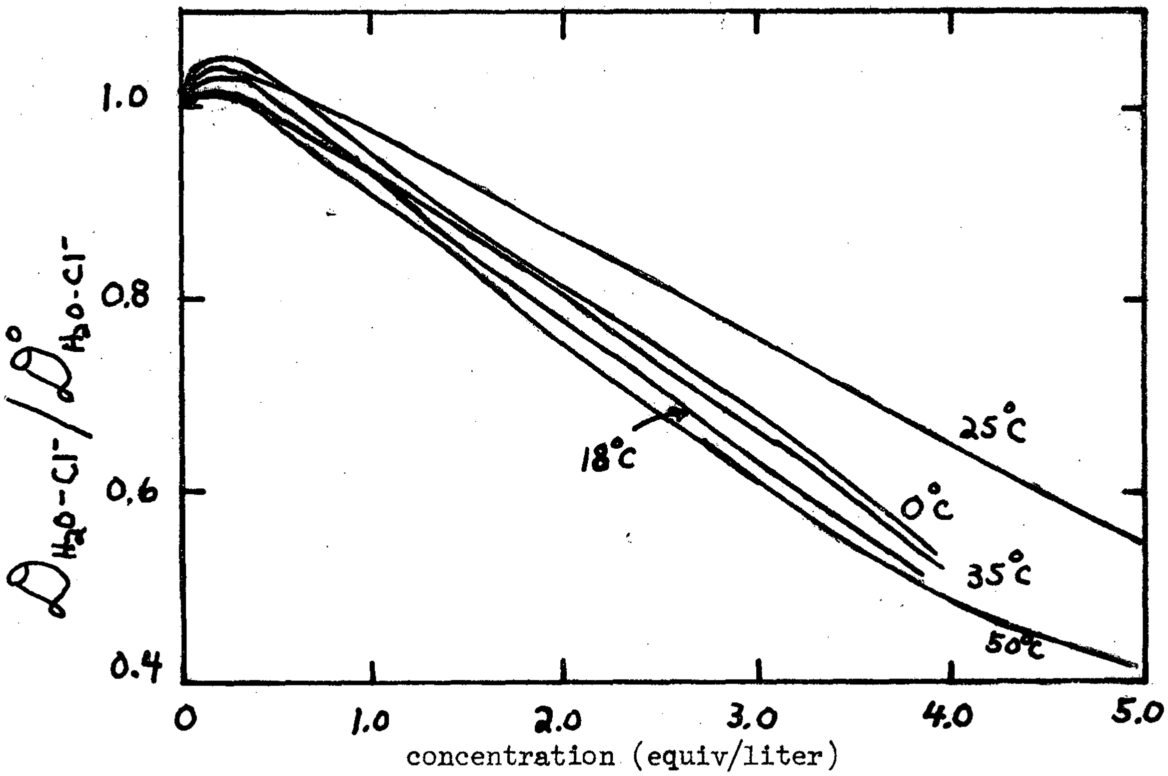


Fig. 22 Chloride ion diffusion coefficients in sodium chloride solutions at various temperatures

A number of qualitative generalizations may be made regarding the concentration dependence of the ionic diffusion coefficients. The variation from the limiting value depends on the nature of both the diffusing ion and the counter ion present. The value of $\mathcal{D}_{oi}$ may gradually decrease from its limiting value as it does in the majority of cases for sodium and lithium; it may exhibit a small maximum in the region of several tenths molar and then decrease at higher concentrations as is the case for most halide ions and nitrate; or it may increase very rapidly at low concentrations, go through an appreciable maximum, and then decrease at higher concentrations as appears to happen for both ions whenever sulfate is present. For all ions for which concentrated solution data are available, except silver in silver nitrate, the diffusion coefficients decrease at higher concentrations.

These observations may be interpreted in terms of the structure of aqueous ionic solutions. Modern theories of the structure of water[12,36,64] indicate that at lower temperatures the water molecules are rather loosely arranged in a hydrogen-bonded tetrahedral structure. When an ion is introduced into this structure, it may alter it by virtue of its size as well as by its ability to orient the polar water molecules in its vicinity. It is believed that some ions have a structure-enhancing effect and that some destroy the water structure. Evidence for these effects comes from considerations of viscosity of electrolytic solutions, thermodynamic properties such as entropies and heat capacities of ions in solution, variation of dielectric constant with concentration, and nuclear magnetic resonance studies in electrolytic solutions (see references 36 and 64). It is supposed that a small ion with a large charge has the ability to impose a structure on the water around it because of the high electric field at its surface. A large ion, on the other hand, disrupts the natural water structure by breaking up the continuing tetrahedral configuration of water molecules in the volume it occupies.

In general we should expect that structure-breaking ions would increase the diffusion coefficients by effectively decreasing the local viscosity, that is, by reorienting the water molecules so that the constraining intermolecular forces are reduced. Structure-making ions, on the other hand, would be expected to decrease the diffusivity with increasing concentration by orienting the water molecules such that the effective intermolecular forces are enhanced.

At concentrations above one molar the ions of an electrolytic solute are so close together (less than 10 Å on the average) that almost all the water molecules must be trapped in a particular orientation by the fields of the ions. The increased forces in this configuration (both ion-solvent and ion-ion) must be responsible for the high viscosities of electrolytic solutions, and, in particular, the same strong ion-solvent forces must cause the observed decrease in ionic diffusion coefficients at high concentrations. At low and intermediate concentrations there is a region where most of the water molecules are only partially and indirectly affected by the presence of ions. It is in this concentration range that a viscosity minimum is observed for some solutions and where the ionic diffusion coefficients may increase to a maximum.

If an ion is intrinsically structure-breaking, it should even at the limit of zero concentration exhibit a higher diffusivity than one which is structure making. This general scheme works reasonably well in the interpretation of the ionic diffusion data. The halide ions, Cl^-, I^-, and Br^-, have relatively high diffusion coefficients, in general exhibit maxima, and are therefore believed to be structure-breaking. This is in agreement with the fact that a number of halide solutions cause a minimum in the viscosity of aqueous solutions. Of the alkali metal ions investigated, only potassium consistently shows a maximum; it also has a relatively high limiting diffusivity so it must be structure-breaking. Lithium and sodium are structure-making. Nitrate behaves similarly to the halide ions and is taken to be structure-breaking.

Sulfate ion has been found to cause large increases in its own diffusivity as well as that of its counter-ions in solutions of low concentrations, so that it must be structure-breaking by virtue of its size. It does not have quite as high a limiting diffusivity as the halide ions or nitrate, but this may be due to its larger mass.

The monatomic, polyvalent ions of barium, calcium, and lanthanum would be expected to be structure-making and are found to possess continuously decreasing diffusion coefficients. Zinc and cupric ions, on the other hand, exhibit unexpected maxima, but these may be due to the very strong effect of the sulfate ion on the structure of the solution.

The interpretation of the diffusion coefficients in strong acids and bases is somewhat more difficult. The high mobilities of these species is attributed to fast proton transfer between water molecules and the hydronium or hydroxide ions. This mechanism is both acid- and base-catalyzed so that the increase of diffusivity with concentration may be related to the rate of the proton exchange. At high concentrations there are relatively fewer water molecules present, and because of the effect of the counter-ion on their structure, these are apparently not in as favorable a configuration to accomplish the proton transfer. Thus, the mobility or diffusion coefficient decreases in concentrated solutions.

We also observed that the presence of hydrogen ions decreases the effect of anions in breaking the structure so that the usually large increase of the sulfate ion diffusivity is minimal and that of chloride ion does not occur. The presence of the extra proton in these solutions is believed to intensify the strength of the hydrogen bonds in water, and there is even spectroscopic evidence[37] for the existence of a stable species $H_9O_4^+$. The hydrogen ion, therefore, is strongly structure-making and opposes the effects of the structure-breaking anions.

The somewhat anomalous behavior of the ammonium ion, in that its diffusivity does not decrease greatly in concentrated solutions, may be related to this ion's unique similarity to water. Since it is of the same size and mass as the water molecule and able to form hydrogen bonds of about the same strength, it is believed to be only slightly structure-breaking.[38] Even at higher concentrations it apparently does not act very strongly to change the solution structure.

It is difficult to translate these qualitative explanations of the behavior of ionic diffusion coefficients into accurate quantitative correlations from which unknown values may be estimated. The situation is very complex with a large number of physical parameters entering into the problem. Looking at the data in this way, however, does point out the qualitative effects for which any satisfactory microscopic theory or correlation must be able to account.

Few suggestions have been made regarding the prediction of transport properties. As indicated earlier, Hartley and Crank[32] have suggested that the relative viscosity be employed in the estimation of diffusion coefficients. Wendt[84] realized the existence of the three independent transport properties, but he was willing to neglect $\mathscr{D}_{+-}$ and to assume that the $\mathscr{D}_{oi}$ coefficients are constant. These approximations are valid only at very low concentrations.

Newman et al.[57] tentatively proposed that $\mathscr{D}_{oi}$ is inversely proportional to viscosity. This approximation is equivalent to that of Hartley and Crank and has several unsatisfactory implications. First of all, it requires that all transference numbers be constant, which is definitely not the case in most systems. Furthermore, such a form cannot account for the varied behaviors described above, particularly the large maxima in $\mathscr{D}_{oi}$. One reason that a simple viscosity correction to $\mathscr{D}_{oi}$ does not work better may be that the viscosity of a solution results from the microscopic transport of momentum by both ion-solvent and ion-ion interactions, whereas the diffusion coefficient $\mathscr{D}_{oi}$ is related directly only to the ion-solvent interactions.

No single, simple quantitative relation can possibly account for the complicated behavior of the ionic diffusion coefficients. At concentrations around one molar and above there is generally a decrease of $\mathscr{D}_{oi}$ which corresponds to an increase in the viscosity. In very few cases, however, are these properties inversely proportional. In many cases $\mathscr{D}_{oi}$ in this concentration range drops off as rapidly as viscosity to the -4 power, and the decrease may be even more severe. Therefore, if one wishes to estimate an ionic diffusion coefficient, he is probably on safer ground to look at the behavior of the particular ion or of similar ions in some other systems and then to guess a reasonable value on the basis of the arguments given above. Since high accuracy in the value of σ_{+-} is important only in very concentrated solutions, the estimation of σ_{+-} based on Eq. (IV-2) and the empirical function G(c) illustrated in Fig. 10 is a slightly more satisfactory situation.

In order to develop more reliable schemes for estimating both the ionic diffusion coefficients and the σ_{+-} coefficients it is necessary to have more data to establish the patterns of behavior of many other ions as well as the relative effects of various counter-ions. In the following chapters we develop a method for measuring diffusion coefficients which is soundly based on the equations of Chapter III.

V. MEASUREMENT OF DIFFUSIVITY

From the summary of the transport data given above, one can see that values of diffusion coefficients and transference numbers in concentrated solutions are still relatively scarce. Because of the need for more extensive accurate data, both for direct practical application and as a basis for a successful theory or correlation for concentrated and multicomponent solutions, we decided to develop the necessary means for measuring accurately diffusion coefficients in concentrated binary solutions. In conjunction with this, a program of transference number measurement has been undertaken concurrently by one of our co-workers.*

A. Experimental Methods for Measuring Diffusivity

In deciding what experimental method would be chosen for the diffusion studies, we considered all the techniques which are presently available. Since a number of thorough reviews[2,34,48,68] on the methods for measuring diffusivity have appeared over the last twenty-five years, no detailed discussion of these seems necessary or desirable here.** Also, since the vast majority of the modern work in diffusion has been done by a relatively small number of men, it is suggested that the original papers be consulted. We shall simply outline the several general categories of methods which have been shown to be reasonably accurate and note the particularly relevant advantages and disadvantages of each.

1. Optical Methods

Most of the popular optical methods are based on the solution of Fick's

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* Paul Millios, of this laboratory, is working to develop a moving boundary experiment to measure the transference number of ammonium nitrate.

** A particularly complete discussion of the measurement of diffusivity has been given recently by Geddes and Pontius.[16]

law for free diffusion.[17] That is, diffusion takes place from an initially sharp boundary in an effectively infinite column of solution. Most of these methods use interferometry or Schlieren analysis to observe the gradient of the index of refraction as it changes with time. Such a measurement can be made quite accurately. Unfortunately, the analysis of these experiments requires the assumption of a constant diffusion coefficient, or, at best, a specified concentration dependence. Therefore it is necessary to start with a very small concentration difference, which minimizes the favorable density gradient acting to stabilize the solution against convection. Furthermore the analysis of the measurements depends rather critically on the initial condition. One must be very careful to make the initial concentration boundary as sharp as possible; it is necessary in any case to make a zero time correction, which detracts from the elegance of the method.

Such methods do offer the advantage of affording measurements in a relatively short time. In spite of the various difficulties, several investigators, notably Gosting,[21] and Longsworth,[49] have succeeded in developing the Gouy method to an accuracy of 0.2 percent, and as a result a large portion of the reliable data, particularly in concentrated solutions, has been obtained by this technique. Recently it has been developed for the study of multicomponent solutions as well.[9,14,39]

2. Diaphragm Cell

A method which is not as accurate as most of the optical methods but which is more convenient to use for approximate measurements, is the diaphragm cell as developed to its modern form by Stokes.[73] The cell employs pseudo-steady state diffusion through a porous diaphragm which separates two closed volumes of solution. The method is not absolute, and each diaphragm must be calibrated with some substance of known diffusivity.

This cell measures an integral diffusion coefficient, that is, a complicated average of diffusivity over the concentration difference in the diaphragm and over the duration of the run, but an analysis has been developed which makes it possible to calculate approximately the differential coefficient from the measured values.[74] It appears that under the best circumstances an accuracy of half a percent is possible with the diaphragm cell. Because chemical analysis of the solutions is involved, this type of experiment offers a means for studying multicomponent diffusion.

It seems that the primary disadvantage of this method, aside from its limited accuracy, is that one may make measurements without being aware of a sizable systematic error. For example, the effective diffusion path length which is determined by calibration may change from solution to solution because changes in density or viscosity may alter the hydrodynamics at the faces of the diaphragm. (For further comments on the diaphragm cell method and an investigation of its analysis see Appendix B.)

3. Conductometric Method

A method has been developed by Harned[27] which has made it possible to measure diffusivities of electrolytes at concentrations as low as 10^{-3} molar where the values may be readily extrapolated to the Nernst limiting value. The results obtained for many systems have been gratifying in verifying the theory of the Nernst limit and the activity coefficient correction as well as indicating high experimental accuracy. The upper limits of Harned's measurements for several systems also agree quite well with the results of the Gouy optical method, and thus his method appears to be accurate to one or two tenths of a percent.

The essential features of Harned's cell are that it is of finite length such that diffusion is of the restricted type and that the decay of a concentration gradient with time is monitored by a conductivity difference between two points in the cell.

The solution of Fick's second law for an enclosed column of solution of height a and with constant properties takes the form of a Fourier series:

$$c = c_o + \sum_{n=1}^{\infty} A_n e^{-n^2\pi^2 D/a^2\, t} \cos n\pi x/a \qquad \text{(V-1)}$$

where D is the diffusion coefficient, x is distance from the bottom of the cell, t is time, and c_o is the uniform concentration at infinite time. The coefficients A_n depend upon the initial distribution of solute in the cell. Measurement of the difference in concentration between two symmetrical points in the cell causes the even terms in the series to vanish:

$$\begin{aligned} c(\zeta) - c(a-\zeta) &= 2A_1 e^{-\pi^2 Dt/a^2} \cos \pi\zeta/a \\ &+ 2A_3 e^{-9\pi^2 Dt/a^2} \cos 3\pi\zeta/a \\ &+ 2A_5 e^{-25\pi^2 Dt/a^2} \cos 5\pi\zeta/a \qquad \text{(V-2)} \\ &+ \ldots\ldots \quad . \end{aligned}$$

Harned chose ζ to be a/6 so that the second term in the above equation also vanishes, and

$$\begin{aligned} c(a/6) - c(5a/6) &= 2A_1 e^{-Dt(\pi/a)^2} \cos (\pi/6) \\ &+ 2A_5 e^{-25Dt(\pi/a)^2} \cos (5\pi/6) + \ldots . \qquad \text{(V-3)} \end{aligned}$$

Because of the factor of 25 in the exponent in the second term this series converges very rapidly with time, and at sufficiently large times a plot of $\ell n\ [c(a/6) - c(5a/6)]$ versus time is linear with a slope of $-D(\pi/a)^2$. The same exponential form holds for any property which is proportional to concentration. Harned placed two pairs of electrodes in his cell at $a/6$ from each end and thus was able to determine the diffusivity from the change in the difference of conductivity between these two locations over a period of days. Because this analysis is independent of the initial concentration profile in the cell, the special care which is required in setting up the free-diffusion experiments is not necessary in this case.

Of the various methods for measuring diffusion coefficients the Harned approach demonstrates the greatest finesse in treating the problem. It is therefore unfortunate that this technique is not directly applicable in concentrated solutions. In many solutions the conductance can not be used to monitor the concentration difference accurately because it is not a linear function at higher concentrations and may even exhibit a maximum as in the cases of potassium hydroxide, sulfuric acid, and lithium chloride. Furthermore, in order to obtain a conductivity cell constant of reasonable magnitude the diffusion channel must be made fairly wide. For Harned's measurements in dilute solutions the electrode spacing was 3/8 inch. (The height of his cell was about two inches, and the depth was at least two centimeters, since electrodes of this length were used in some cases.)[28] With the most concentrated solutions measured by Harned, .5276 N KCl, the electrode size was reduced to a one millimeter diameter circle, which must be close to the practical lower limit of this experimental variable. Solutions of higher conductivity would require a wider cell. Already at a spacing of 3/8 inch Harned had to take major precautions to avoid the induction of convection in his cell. To make the cell wider would almost surely make the prevention of convection impossible. The extension of this approach for use in concentrated solutions requires that another means of observing the concentration distribution in the cell be devised. Preferably the new method will allow the cell to be made smaller in cross section to diminish the possibility of convection.

Before considering these experimental difficulties, one should ask several theoretical questions regarding the possibility of extending Harned's method to concentrated solutions without losing the accuracy he achieved at high dilution. Since Harned's analysis was based on the dilute solution equations with constant properties, it remains to show that the method will give a well-defined differential diffusion coefficient in concentrated solutions. For that matter, it has been only an assumption that Harned's dilute solution values are differential coefficients because his concentration differences are so small. A more complete analysis of the problem based on the concentrated solution equations will elucidate the nature of the diffusion coefficient which is measured in this type of an experiment.

B. Analysis of Restricted Binary Diffusion in Concentrated Solutions

In Chapter III we presented the flux expressions for solute and solvent which are appropriate in concentrated binary solutions. These were used with the conservation equations to derive the analog of Fick's second law, Eqs. (III-27) and (III-28):

$$\frac{\partial c}{\partial t} = c_o\overline{V}_o\nabla\cdot D\nabla c - \underline{v}_o\cdot\nabla c \qquad \text{(III-27)}$$

and

$$\nabla \cdot \underline{v}_o + \bar{V}_o \frac{dc_o}{dc} \nabla \cdot D \nabla c = 0. \tag{III-28}$$

Let us use these equations to analyze the decay of a one-dimensional concentration gradient in a column of solution of height a.

At infinite time the concentration will become uniform in the cell. Let us then call the concentration, the density, and the height of the column c^∞, ρ^∞, and a^∞, respectively. At the bottom of the cell the fluxes are zero which means that

$$v_o \Big|_{y=0} = 0 \tag{V-4}$$

and

$$\frac{\partial c}{\partial y} \Big|_{y=0} = 0. \tag{V-5}$$

At the top of the liquid column the fluxes vanish also so that

$$\frac{\partial c}{\partial y} \Big|_{y=a} = 0. \tag{V-6}$$

Since the mass in the system remains constant, another boundary condition is that

$$\int_o^a \rho \, dy = \int_o^{a^\infty} \rho^\infty \, dy = a^\infty \rho^\infty . \tag{V-7}$$

We solve these equations by assumint that all the variables can at large times be expanded in singular perturbation expansion series of the type

$$c = c^\infty + \epsilon c^{(1)} + \epsilon^2 c^{(2)} + \dots , \tag{V-8}$$

$$a = a^\infty + \epsilon a^{(1)} + \epsilon^2 a^{(2)} + \dots , \tag{V-9}$$

and

$$v_o = \epsilon v_o^{(1)} + \epsilon v_o^{(2)} + \dots , \tag{V-10}$$

where ϵ is a function of time and goes to zero as t goes to infinity. v_o is the solvent velocity. The coefficients $c^{(i)}$, $a^{(i)}$, and $v_o^{(i)}$ are independent of time; $c^{(i)}$ and $v_o^{(i)}$ then depend only on position.

For convenience we apply the definition

$$D_M \equiv c_o \overline{V}_o D \ , \tag{V-11}$$

and for use in the solution of Eqs. (III-27) and (III-28) we express this quantity as its Taylor series around c^∞:

$$D_M = D_M^\infty + \left.\frac{dD_M}{dc}\right|_{c^\infty} (c-c\;) + \frac{1}{2} \left.\frac{d^2 D_M}{dc^2}\right|_{c^\infty} (c-c_\infty)^2 + \ldots \tag{V-12}$$

where $D_M^\infty = D_M(c^\infty)$. Substitution of Eqs. (V-8) through (V-11) into Eqs. (III-27), (III-28), and (V-4) through (V-7) and equating terms of equal order in ϵ yield a hierarchy of differential equations with boundary conditions from which ϵ and the coefficients $c^{(i)}$, $a^{(i)}$, and $v_o^{(i)}$ can be determined. The ability to generate these necessary equations justifies the assumptions expressed in Eqs. (V-8), (V-9), and (V-10).

The results of these manipulations are very complicated. The equations which were solved and the various functions obtained are given in Appendix C. The important conclusions are that

$$\epsilon = e^{-D_M^\infty t (\pi/a^\infty)^2} \ , \tag{V-13}$$

and the difference in concentration between points one-sixth of the overall length from each end of the cell is given by

$$\Delta c = c(a/6) - c(5a/6) = A_1\sqrt{3}\ e^{-D_M^\infty t(\pi/a)^2} + \left\{ K\sqrt{3} + L(3\sqrt{3}/4) - \frac{a}{3} M \right\} e^{-3D_M^\infty t(\pi/a)^2} + \ldots \tag{V-14}$$

where A_1 depends upon the initial condition, and the constants K, L, and M depend on the concentration derivatives of the properties of the solution. Explicit expressions for K, L, and M are given in Appendix C. Since it was found that $a^{(1)} = 0$ and that $a^{(2)}$ is very small,* we no longer distinguish between the height of the cell and the actual height of the liquid column.

It is seen in Eq. (V-14) that the second term in this series is of order ϵ^3 rather than ϵ^{25} as suggested by Harned's Fourier series solution. Nevertheless at sufficiently large times the first term predominates, and the Harned-type measurement yields the differential value D_M corresponding to the concentration c^∞.

It is interesting to investigate the order of magnitude of the coefficient of this second term. For an initially sharp boundary at the center of the cell, the value of A_1 is $2(\Delta c)_o/\pi$. (It seems worthwhile to approximate this condition experimentally since it will minimize the non-symmetrical coefficients of higher terms and hasten the approach of the concentration profile to the symmetrical cosine form expressed by the leading term.) From Eqs. (C-24) and (C-25) it can be shown that K and L are proportional to A_1^3 and therefore to $(\Delta c)_o^3$. The ratio of the second term in Δc to the first term is therefore proportional to

$$(\Delta c)_o^2 \quad e^{-2D_M^\infty t(\pi/a)^2} .$$

Since a is usually about 6 centimeters and D_M^∞ is about 2×10^{-5} cm^2/sec, this ratio is

$$(\Delta c)_o^2 \quad e^{-.36\ t}$$

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* See Appendix C.

where t is here expressed in hours. The duration of a run is several days so that the exponential term rapidly becomes very small. The use of a small initial concentration difference also helps to minimize the magnitude of the second term in relation to the first. The fact that the second term is of order ϵ^3 rather than ϵ^{25} as Harned states is therefore unimportant. The method is nevertheless valid and yields a well-defined, differential diffusion coefficient even in concentrated solutions.*

C. An Experimental Method for the Observation of a Concentration Profile in Concentrated Solutions - Rayleigh Interferometry

We have discussed above the reasons why Harned's conductometric analysis is limited to dilute solutions. The extension of the restricted diffusion approach requires the application of some other method for observing the concentration difference Δc in the cell as it changes with time. An obvious solution to this problem is the use of one of the many optical techniques which lend themselves so readily to in situ analysis of concentration gradients and have already been developed for work on free diffusion experiments. Rather than the Gouy method, which yields the gradient of refractive index, we chose instead Rayleigh interferometry, which gives a mapping of the refractive index directly. Since over small concentration ranges the refractive index is very nearly linear with concentration for most electrolytes, a map of index of refraction is essentially a map of concentration. This approximation becomes increasingly good as the concentration gradient gets smaller and smaller; and it is such a situation that prevails when the measurements are to be made in a restricted diffusion experiment.

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* Since the concentration dependence of the diffusion coefficient D_M is most severe at low concentrations the coefficients of the second term of Eq. (V-14) are actually more important in dilute solutions. Therefore the evidence that Harned's results are accurate lends support to our conclusion that the method is valid in concentrated solutions.

The Rayleigh interference method for observing concentration gradients and boundaries in liquids has been developed by a number of workers for applications in electrophoresis, ultracentrifugation, and free diffusion. The modern modification of the Rayleigh refractometer such that it yields a concentration profile was devised by Philpot and Cook.[61] Their addition of a cylindrical lens set up a one-to-one correspondence between the refractive index at a point in a vertical cell and the interference pattern on only one horizontal line on the horizontally extended image of the cell. This principle was also discovered independently by Svensson.[78] The actual application of the method in physico-chemical measurements has been accomplished primarily by Longsworth[50] and by Moore.[55] Excellent examples of the patterns one observes are given in photographs by the latter.

The type of cell used by Longsworth and Moore is also directly applicable to the study of restricted diffusion. Essentially it is a Tiselius cell, which is the standard apparatus for electrophoresis studies. It is about 7.9 cm high in the center section, and the channel has a cross section of 2 mm × 9 mm. These smaller cross-sectional dimensions are an improvement over the Harned cell with regard to the avoidance of convection. The top and bottom sections of the cell contact the center section on greased ground glass flanges. They can be displaced by sliding in the flanges to close off the center section and to leave an enclosed column of solution of exactly the height of the center section. If a concentration disturbance is introduced in the cell, and the center channel is then closed off and observed optically, the rate of change of the concentration difference between the two points in the cell, $a/6$ and $5a/6$, can be determined from the change in the interference pattern, and the diffusion coefficient can be calculated according to Eq. (V-14) when terms higher than the first are negligible.

D. Analysis of Rayleigh Interference Patterns

The basic principle of what is called the Rayleigh interferometer is the ability of two coherent beams of light to interfere constructively or destructively depending on the phase difference of their waves. For example, if coherent light passes through two parallel slits in a mask as shown in Fig. 23, the two beams are in phase at points A and B. When light from the two slits reaches a point M on screen S they may be still in phase or out of phase, depending on the distance each has traveled. If d is the spacing between slits, R is the distance between the mask and the screen, and y is the distance from the center point L on S and the point in question M, the difference in the paths from A and B is $d \sin \theta$, where $\theta = \tan^{-1}(y/R)$. When $d \sin \theta$ is an integral number m of wavelengths λ, the beams are in phase at M, and the intensity of light at that point is a maximum. As y increases from M to N, where $d \sin \theta = (m+1)\lambda$, the two beams get out of phase, and the intensity decreases. At the point where $d \sin \theta = (m+1/2)\lambda$ they are exactly 180° out of phase, and their opposite amplitudes cancel to cause an intensity minimum. At N another intensity maximum appears. Therefore a pattern of light and dark bands or fringes appears on the screen S.

Now if the beam passing through the mask at B is initially out of phase with that from A, the positions of the bright fringes on the screen are shifted according to the relation

$$d \sin \theta_m = m\lambda - \delta\lambda \qquad \text{(V-15)}$$

where δ is the fraction of a wave that the beams at A and B are out of phase, and the angles θ_m, for which m is an integer, are the angles at which the maxima appear. The reason for two beams of light from a common source to be out of phase at points A and B is that they have already traversed different optical path lengths, and $\delta\lambda$ in Eq. (V-15) represents

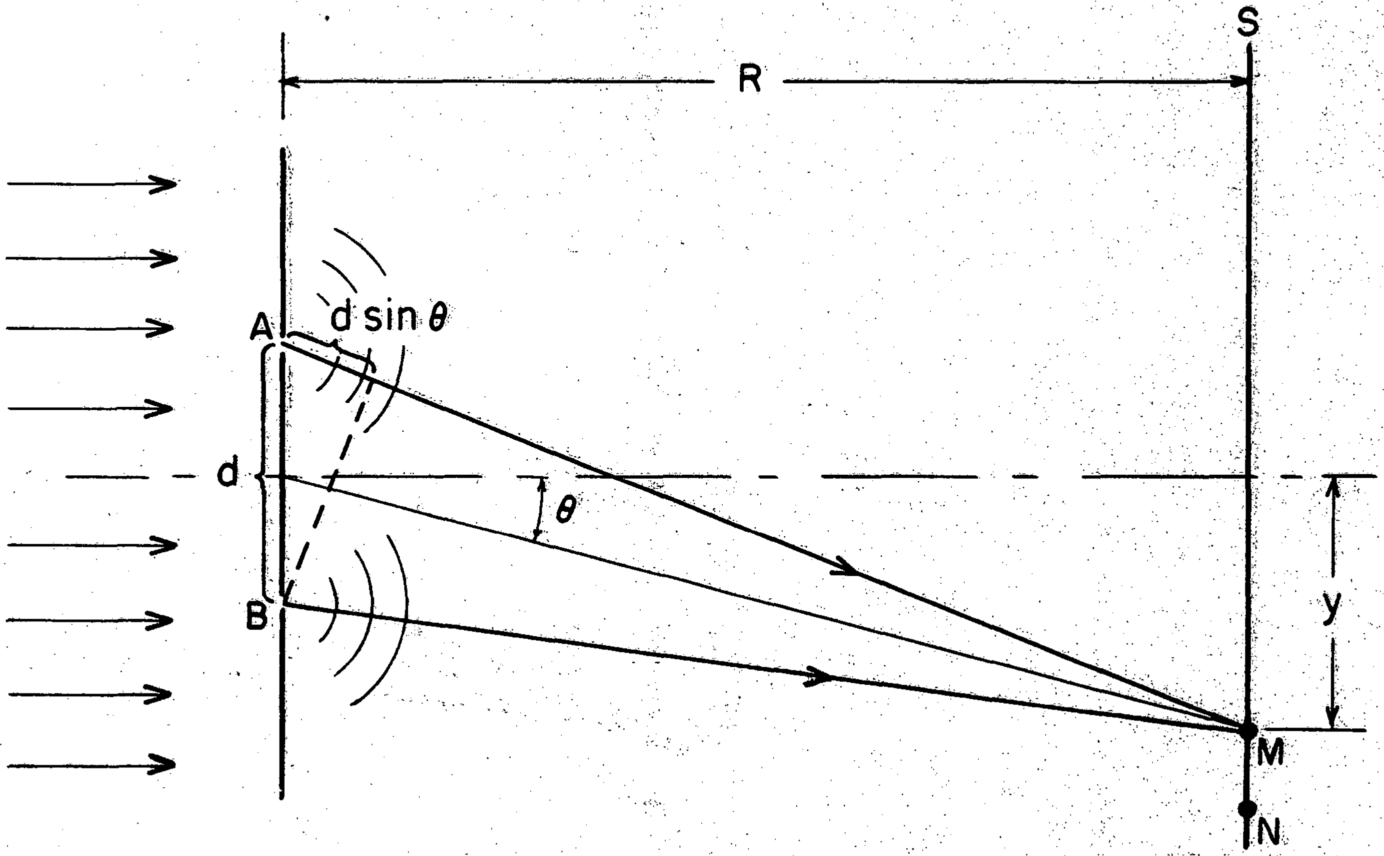

Fig. 23 Diagram showing interference of coherent light from two slits

this path difference. Since the optical path length in a medium is the product of actual distance ℓ times the refractive index μ of the medium, this path difference can result from a difference in μ of the medium adjacent to A or B as well as a difference in ℓ.

Suppose that different media of thicknesses ℓ_A and ℓ_B and refractive indices μ_A and μ_B are placed behind slits A and B, respectively. If $\mu_A \ell_A = \mu_B \ell_B$, $\delta\lambda = 0$. In general,

$$\delta\lambda = \mu_A \ell_A - \mu_B \ell_B. \tag{V-16}$$

Let us take $\ell_A = \ell_B$. The condition for interference on S in this situation can be written as

$$d \sin \theta_m + \ell(\mu_A - \mu_B) = m\lambda . \tag{V-17}$$

Now as $(\mu_A - \mu_B)$ changes, the value of θ_m, and therefore the position of the interference fringe of order m, must also change. A difference in refractive index difference between media at slits A and B causes a shift of the entire interference fringe pattern.

Let us now consider the point M again where there is an intensity maximum when $\mu_A = \mu_B$. If μ_B is constant but μ_A is changed,

$$\ell \Delta\mu_A = \lambda \Delta m \tag{V-18}$$

at the point M; the order m of the interference at M depends upon the change in μ_A. Only when $\Delta\mu_A$ is such that Δm is an integer does an intensity maximum appear at M. Equation (V-18) is the condition which applied when one uses a Rayleight interferometer to determine a concentration change. A change in refractive index $\Delta\mu_A$ in a sample solution is identified by the number of fringe shifts Δm.

The important contribution of Philpot and Svensson was to take the essentially two-dimensional Rayleigh refractometer described above and to make it a three-dimensional self-plotting interferometer. They did this by adding a cylindrical lens to the system. If two cells, one with a one-dimensional concentration gradient and one which serves as a comparison path, are placed adjacent to the vertical slits A and B, and the cylindrical lens is inserted between the mask and the screen, this lens serves to focus the images of the cells, or rather their vertical extent, on the screen without distorting the interference patterns which exist on every horizontal line. Since the vertical dimension of the interference pattern corresponds to the vertical dimension of the sample cell, a gradual change in refractive index in the cell with position is related to gradual shifting or bending of the fringes along a vertical trace according to the condition of Eq. (V-18).

A diagram of such an arrangement is shown in Fig. 24. Monochromatic light from a point source P is focused at point F on the screen S by lens L. Now the cell C and the reference cell C' along with the mask M are placed in this beam. The interference patterns formed by the two slits in M are all located near F. They are spread horizontally around F because of the diffraction by the slits, but contributions from various locations in the cell all fall on top of one another. When the cylindrical lens K is inserted, the image is extended vertically on the screen such that the interference pattern corresponding to the refractive index difference at the top of the cell appears at the bottom of the screen, and vice versa. When the concentration in the cell C is uniform, the interference fringes are straight and vertical. But when a concentration gradient exists, the loci of maxima and minima at each horizontal level are displaced by a differential increment to give a pattern of curved fringes of the same shape as the

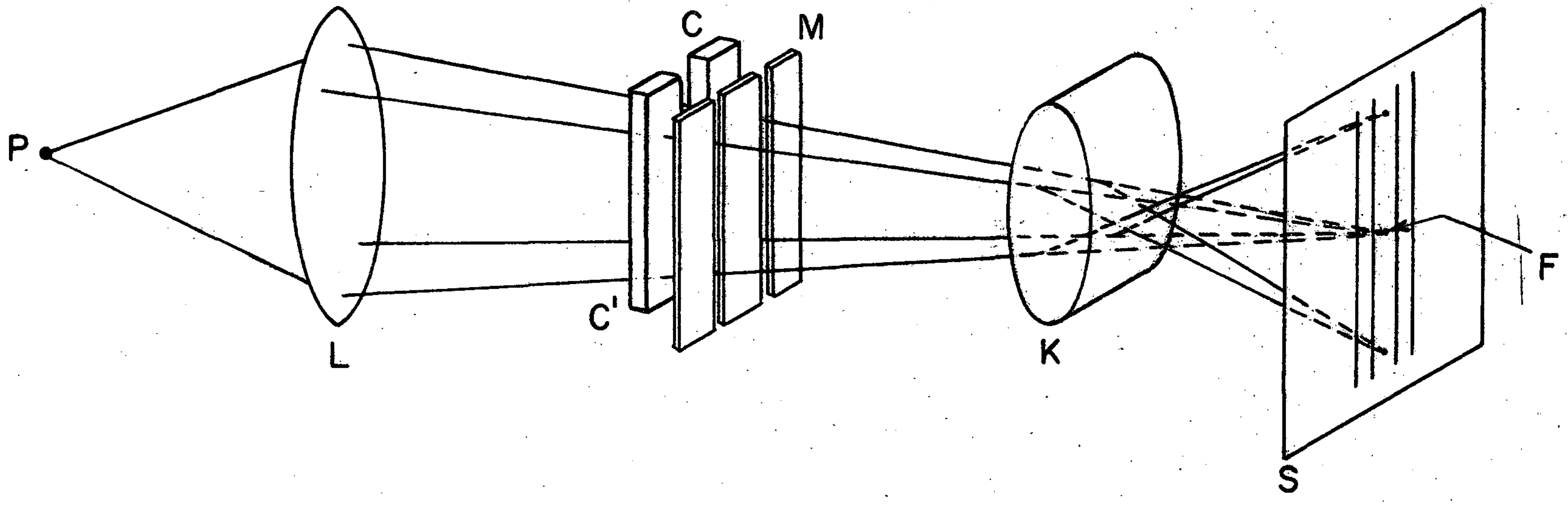

Fig. 24 A simplified Rayleigh interferometer

concentration profile. The change in refractive index or concentration between two points in the cell is proportional to the number of fringe shifts between corresponding levels on the interference pattern.

In the configuration just described the interferogram is rather narrow, being located within the horizontally diffracted image of the point source. A major improvement has been achieved, following the suggestion of Zernike,[85] by the use of a multipoint source. Provided that the points are properly spaced to reinforce one another, this gives a much wider and more intense pattern. The result is effectively to place beside on another many patterns of the type illustrated in Fig. 24. The bright center fringe from one point source is made to coincide with the second, less intense fringes of its adjacent point sources. This gives a wide field of sharpened, parallel fringes.

The only question remaining about the use of such a method for our purposes is how precisely a concentration difference can be measured. According to Eq. (V-18), the change in refractive index for a shift of one fringe is equal to (λ/ℓ). If $\lambda = 5000$ Å and $\ell = 1.7$ cm,* $(\Delta\mu/\Delta m) = 2.8 \times 10^{-5}$. As a typical case potassium chloride exhibits a nearly linear refractive index-concentration relation; the derivative $(d\mu/dc)$ at 25°C is roughly $10^{-2}/(\mathrm{mol}/\ell)$. Therefore, $(\Delta c/\Delta m)$ is about 3×10^{-3} (mol/ℓ)/fringe. Since it seems quite likely that the fringe pattern can be measured to some small fraction of a fringe, the precision in the measurement of Δc should be considerably better than 10^{-3} mol/ ℓ.

Thus we have shown that a restricted diffusion experiment yields a well-defined differential diffusion coefficient and that a Rayleigh interferometer

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* This value of ℓ is chosen because in our experiments the optical arrangement was such that the light passed twice through a 9 mm cell. See Chapter VI.

used with a Tiselius cell of the proper dimensions should be well suited to the measurement of concentration differences necessary for the calculation of the diffusion coefficient according to Eq. (V-14). In the next chapter we describe the apparatus which was assembled and the experiments which were performed to test these conclusions and to measure new diffusivity data.

VI. EXPERIMENTAL APPARATUS AND PROCEDURE

From our investigation of the transport properties of binary electrolytes we concluded that more extensive accurate diffusion coefficient data for concentrated solutions are desirable. In the last chapter we suggested a method by which such data may be obtained. In this chapter are described the apparatus and procedures for implementing these suggestions and the experiments which were carried out.

A. Optical Apparatus

It was a considerable convenience that interferometers as well as Tiselius cells meeting the specifications of the desired apparatus are commercially available as laboratory electrophoresis apparatus. Primarily on the basis of cost we decided to purchase the Model 238 Tiselius Electrophoresis Apparatus from the Perkin-Elmer Corporation.* Since the instrument offers a choice between a Schlieren optical arrangement and a Rayleigh interferometer making use of the same optics, the optics are necessarily somewhat different from the interferometer described in the previous chapter. The net effect, however, is the same. The configuration for generating Rayleigh interference is shown in Fig. 25.

A mercury vapor lamp H emits monochromatic light ($\lambda = 5461\text{Å}$), which is channeled by the condenser and field lenses A and B through the multipoint source horizontal slit P, and to the mirror F, whence it is directed through a wide-slit mask E and the Schlieren lens L. Lens L makes the diverging beams from B, P, and F parallel for their passes through the cell. These parallel beams pass through the window W of a liquid constant

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* Similar items varying somewhat in design and flexibility are available from Beckman and American Instruments as well as from Strübin and Co. in Switzerland.

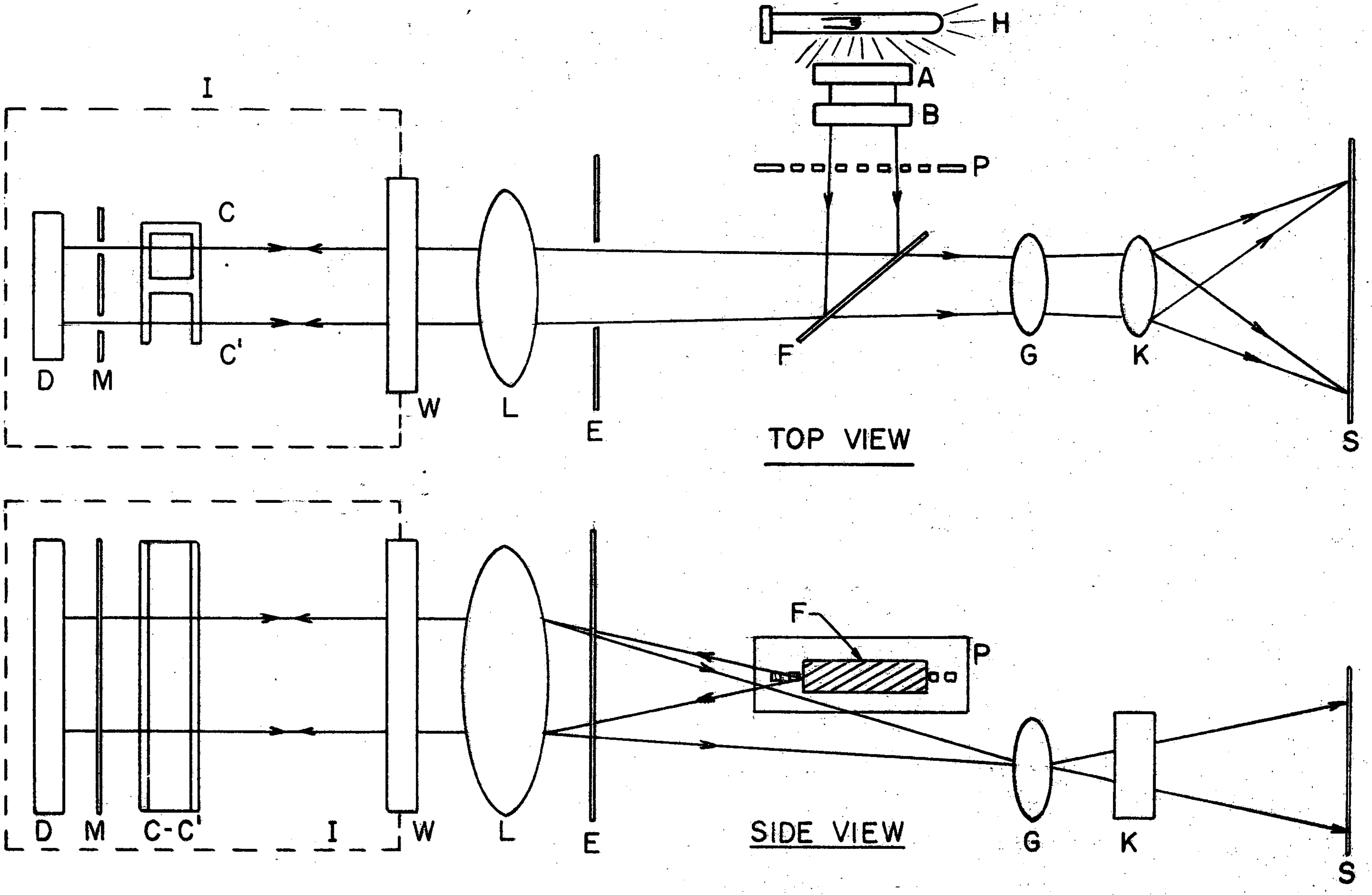

Fig. 25 Schematic diagram of the optical apparatus

temperature bath and through the cell C-C'. In the channel of the cell C is contained the vertically diffusing solution. The windows of the cell are extended fo form C', a space in which the thermostat bath fluid circulates are thus serves as the comparison medium of uniform refractive index. The cell windows are extended to be included in the reference path because the optical path difference, $\delta\lambda$ in Eq. (V-15), must be kept small. Because of the pressure broadening of the mercury vapor radiation, coherence of the light is short-lived and lost completely if $\delta\lambda$ is too large. If the coherence is lost, interference is impossible.

As the light passes from the cell it encounters two vertical slits in mask M, one adjacent to C and one to C'. These are the slits which generate the interference. Behind the cell and the mask is another mirror D, which reverses the direction of the light back through whence it came. The effective thickness of the cell is thus doubled by the two passes.

Lens L refocuses the beams. These beams do not retrace their original path exactly, however, because mirror D is tilted downward slightly to cause them to pass under the narrow mirror F on their return. Lens G is a camera lens which focuses the images of the slits in mask M, and for all practical purposes the fluid in the cell, on the photographic plate S. The images of the point sources in P passing through the slits in M are at this stage not in focus but are encompassed in the images of these latter slits. The introduction finally of the cylindrical lens K with its axis vertical spreads and focuses the light in each of these images horizontally over the entire field of S and thus accomplishes their interference after the cell has already been imaged in the vertical direction by the camera lens.

The results is as in the simpler case of Fig. 24 to generate a field of vertical interference fringes, now equally spaced because of the equally spaced multipoint sources. When there is no variation of refractive index in the vertical cell C, the fringes are straight. Changes in the refractive index cause the interference pattern to shift horizontally according to Eq. (V-18). Since the vertical coordinate on the photographic plate is unaffected by this shift, the resulting pattern represents a mapping of refractive index versus position.

The Perkin-Elmer Model 238 unit contains a built-in insulated constant temperature bath as indicated by the walls I in Fig. 25. On one wall of the bath is installed a thermoelectric cooling plate, which is designed for constant operation to maintain the bath at 0°C for electrophoresis experiments. For fluid circulation there is a small centrifugal pump, which takes bath fluid from near the bottom of the cooling plate and injects it as a steady, gentle stream in the direction of the cell in the center of the bath. The small motor which runs the pump is mounted on rubber shock absorbers to prevent vibrations from being transmitted through the optical bench to the cell. The instrument itself was placed on one-inch-thick hard rubber pads on a laboratory bench.

To attain temperatures other than 0°C, a 125-watt resistance heater reduced to 50 percent of its power was installed in the bath very near the cooling plate. This heater was controlled in an on-off fashion by means of a mercury contact thermometer in conjunction with an electronic relay. To improve mixing in the bath a variable speed stirrer was placed in the corner of the bath farthest from the pump outlet and operated at about 90 rpm. The stand on which the stirrer was mounted rested on the same laboratory bench as the instrument, but it was weighted heavily and sat upon one-inch-thick rubber cushions. During a run the bath was covered with a 3/8-inch-thick sheet of lucite. The temperature of the bath fluid was measured with a Beckman thermometer and found to be constant within ±0.005°C; all measurements were made at 25.00°C.

In most experiments the bath fluid was distilled water. With very concentrated sample solutions, however, the refractive index of the two fluids differed too greatly to maintain the interference. Longsworth[50] resolved this difficulty by placing additional pieces of flat glass in the reference beam at C'. We found it more convenient simply to alter the refractive index of the bath fluid by adding a sufficient amount of ethylene glycol to the bath water to match approximately the index of refraction of the sample solution.

An example of fringes obtained with 3.5 N nitric acid (refractive index ≈ 1.355) in the cell and pure water (refractive index ≈ 1.333) in the bath is shown in Fig. 26. These fringes are fuzzy and of very poor quality. When about 30 percent ethylene glycol solution was placed in the bath, the fringes appear as in Fig. 27. They are much sharper under these circumstances.

B. Optical Cells and Cell Holders

The cells used in these experiments were also purchased from Perkin-Elmer Corporation. They are patterned after the original Tiselius cell as modified by Longsworth.[51] A picture of the center part of the cell is shown in Fig. 28. It consists simply of two legs or channels, rectangular parallelepipeds in shape, between flat ground-glass flanges. As indicated previously, the faces of the cell are extended to the sides to be included

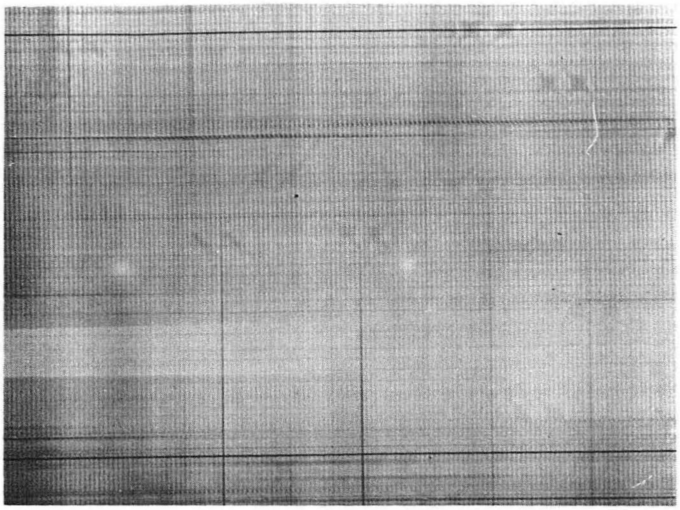

Fig. 26 Fringe pattern with a considerable difference of refractive index between the cell solution and the comparison path.

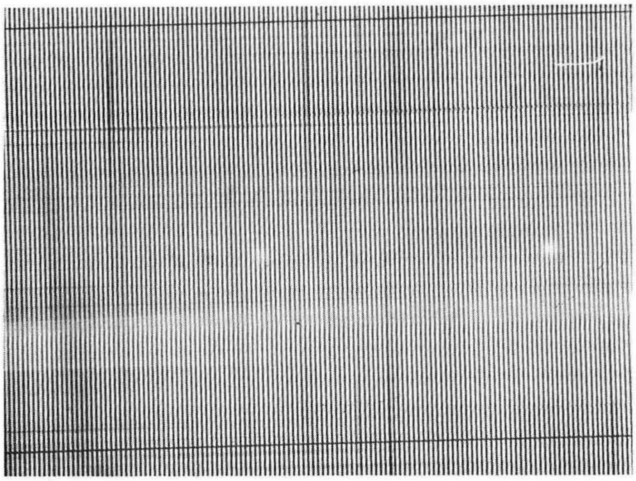

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Fig. 27 Fringe pattern with the bath solution adjusted to about the same refractive index as the cell solution.

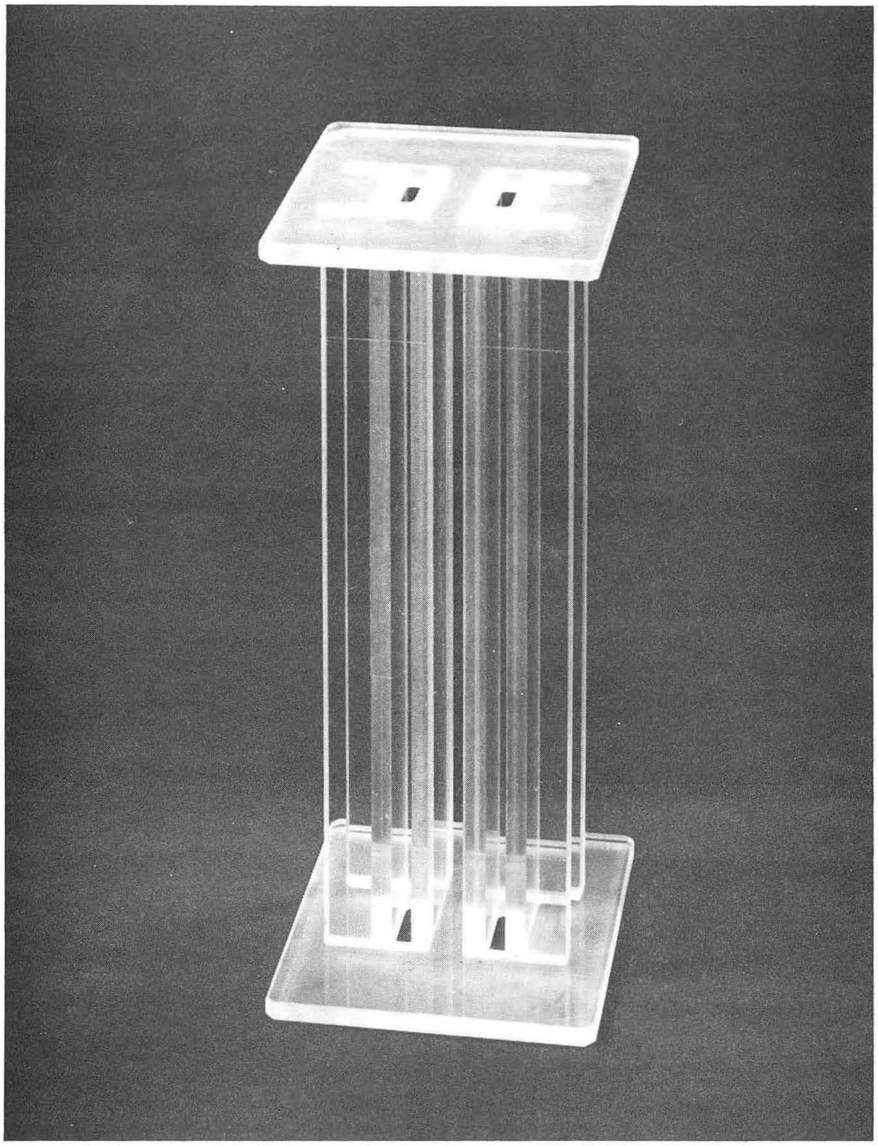

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Fig. 28 Central optical cell

in the optical reference path.

When the center section is closed off from the rest of the cell by flanges sliding over the ends of the channels, the height of the column of diffusing liquid is the overall length of this piece. Since this quantity enters into Eq. (V-14) in a very critical way, it must be known as exactly as possible. The Precision Shop of the Lawrence Radiation Laboratory measured the cells which were used and reported their lengths to 0.03 percent. These lengths were on the order of 7.9 cm. The cross section of a channel was, as suggested before, 2 mm by 9 mm along the optical path.

To avoid any difficulties in the measurement of fringes resulting from geometrical distortions in the optical system or shrinkage of film, the Precision Shop also scribed very fine markings on one face of the cell at exactly one-sixth of the overall length from each end of the cell. These scratches appeared as fine lines across the photographs of the fringe patterns and thus served as a reliable frame of reference for both the vertical position as well as the orientation of the fringes.

The entire cell when assembled and in its holder is shown in Fig. 29. The bottom section is simply a flat ground glass flange with a small box on the bottom which closes a U between the two legs of the cell through holes in the flange. The top section also consists of a flat ground glass flange with two holes through which the channels of the center section are extended and open at the top. The extended channels in the top section open to the sides through short tubes to which rubber or tygon tubing may be attached. These provide connections to the two solution reservoirs.

The cell holders, which are an integral accessory to the instrument, were also purchased from Perkin-Elmer. The cell is held by being clamped

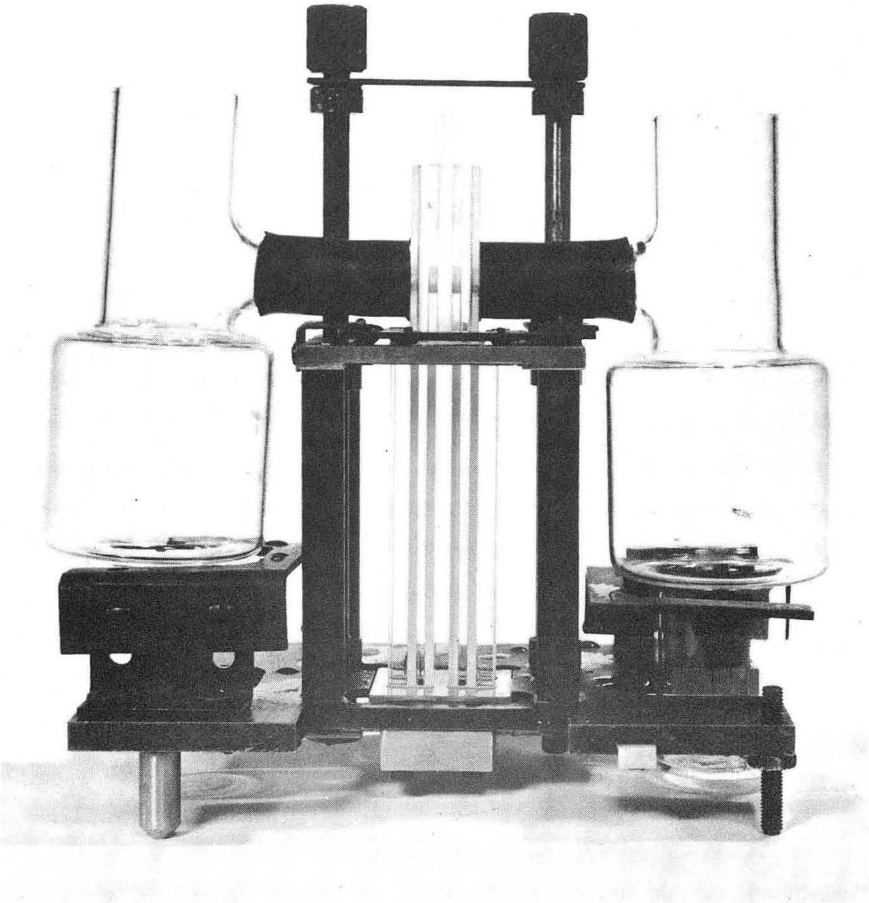

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Fig. 29 Optical cell with accoutrements in cell holder.

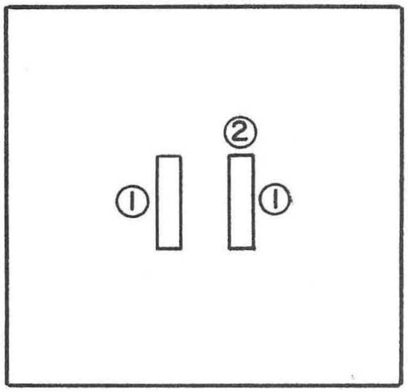
from the outside flanges; that is, it rests on the bottom one while spring tension is applied on the top. There are mechanical linkages which allow both the top and the bottom sections to be displaced from the center section by manipulation at the top of the holder. This allows the center section, which is stationary, to be closed off at the outer surfaces of its flanges by the opposing flange surfaces.

Since these cells are designed for use in electrophoresis experiments, they are primarily meant to be used with all channels aligned. When we made our first diffusion experiments, we found that small amounts of solution could leak between the contacting flange interfaces when the channels were displaced. This was possible because the cells were not mounted very solidly in the holder, and the tension holding the flanges together was not uniform. Several modifications in the cell holder design were necessary to eliminate these difficulties.

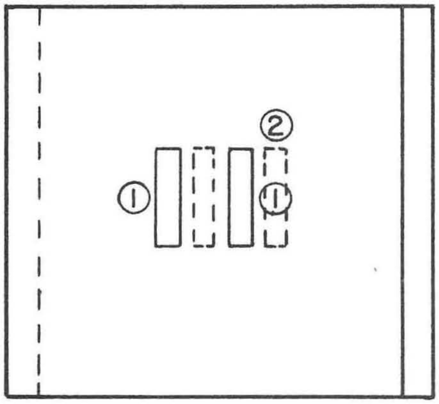
In the original design the cell rested at the bottom on two small pegs on two plates mounted independently to the holder base. These were replaced by four flat and coplanar pegs on a single block which was mounted across the base of the holder.

At the top of the holder the piece which constrained the cell laterally contacted it on only two sides. This piece was modified to be thicker and to contain the contacting flanges at the top on all four sides except for a shallow notch on one side to allow the top piece to be displaced.

The vertical tension on the cell was supplied by two flat springs contacting the top flange at the points illustrated in Fig. 30. The original springs apply pressure at points marked by a ① . When the top was displaced, the applied tension was shifted off center and thus created



a. TOP ALIGNED.



b. TOP DISPLACED.

Fig. 30 Diagram of placement of spring holders on the cell top a torque on the cell. The tension was made more uniform by the installation of a stationary flat spring which touches the flange at the point marked ②.

Finally, notches in the top and bottom plates were made slightly wider to allow the maximum displacement of the channels as indicated by the configuration in Fig. 30b.

C. Miscellaneous Apparatus

Time was measured by an electric timer. Photographs of the fringe patterns were taken on Polaroid Type 46L 3-1/4 in. by 4-1/4 in. transparencies. The speed of the film and the intensity of the fringes were such that exposure times of about twnety seconds were required. A trap-door type shutter operated by a knob located on the front panel of the instrument was used to control the exposure time.

D. Experimental Procedure

The first step in making a run was to prepare the cell. The glass pieces were washed in a solution of Alconox and rinsed several times in distilled water to remove the soap. They were then rinsed with cyclohexane for drying. If necessary, any dirt or grease inside the chennels was removed during the washing by use of a pipe cleaner, one end of which was bent into a swirl so that the wire tip was not exposed.

To seal and to lubricate the contacting ground glass surfaces between sections, chemically inert Apiezon Type N vacuum grease was used. This lubricant was found superior to silicon grease because it flowed more readily to seal the flange surfaces, and it could be removed from the glass more readily when the cell was disassembled because it is soluble in cyclohexane.. A light coat of this grease was applied to the flanges of the top and bottom sections. Areas about a millimeter or two wide around the perimeters of channel openings were left bare to avoid getting excess grease into the channels. The top and bottom sections were one at a time pressed against the center section to seal the flanges together with the grease. The glass solution reservoirs were then connected to the top section by means of short lengths of rubber tubing. The assembled cell was slipped into the holder, and the springs were put into place against the top flange.

The face of the cell on which the reference marks were made was oriented in the holder such that it would be closest to the mirror D in the instrument. (See Fig. 25) If it were located on the far side, refraction of the light on it passes through the cell would make the images of these marks excessively wide or even double. The mask M containing the vertical slits was a metal sheet which clamped onto this face of the cell. When the holder and cell were placed in the bath, they were positioned such that the mask was in contact with the mirror D.

To fill the cell all channels were aligned. A 10 cc syringe with a 6-in. 18 gauge needle was filled with the more concentrated solution of two which had been prepared. With the cell tilted for air to escape, the needle was inserted into one of the channels and to the very bottom of the U. Solution was slowly injected until the entire cell up to the reservoir inlets was filled with no bubbles remaining. The needle was then withdrawn, and the bottom section was displaced.

To distinguish between the two branches of the center section let us call one leg A and the other leg B. Most of the solution in leg A as well as any solution which had overflowed into the reservoir on that side was removed by means of the syringe. The reservoir on side B was filled with the same solution as that in leg B. The syringe was then used to inject a less concentrated solution into leg A. The reservoir on that side was also filled with this solution. When inserting the syringe needle into the cell, one must take care to avoid picking up any grease at the flange joints and smearing it onto the windows of the cell.

The liquid levels in the cell were adjusted such that the solution on side B was slightly higher than that on side A. Thus when the bottom section was aligned, the boundary between the two solutions flowed up into leg A with the more concentrated, and hence more dense, solution on the bottom. Since we wished to form the initial diffusion boundary more carefully and to assure that it was located near the center of the cell, the syringe needle was inserted into leg A once again and the solution was slowly withdrawn from a region near the center until about 5 cc had been removed. This served to form a very sharp boundary. The needle was then carefully removed, and the top and bottom sections were displaced to close off the diffusion channel.

Although it would be theoretically desirable to start the experiment with as small a concentration difference as could be measured with sufficient precision, it seemed more prudent to form the boundaries between solutions of appreciable concentration differences so that a large density difference would be acting to stabilize the system against convection during the boundary forming procedures. Therefore, initial concentration differences of one half to one molar were usually employed. The decay of such a difference required several days before the concentration difference could be measured; large concentration differences cause so many fringe shifts that the bending fringes are too close together to be resolved. This situation was exploited by the employment of two cells. While one cell was being measured, the other was set aside for its steep concentration gradient to decay. A three or four day decay period also gave the initial concentration distribution time to attain the symmetrical form required by the first term of Eqs. (V-3) or (V-14).

Any velocity disturbances generated in the cell by the boundary formation would be expected to damp out according to an exponential form analogous to Eq. (V-14) with the time constant depending on the kinematic viscosity rather than the diffusion coefficient. Since the kinematic viscosity of liquid solutions is about three orders of magnitude greater than the diffusivity, any small convective velocities should vanish long before the concentration profile does.

Even after the concentration gradient in a cell reached a convenient magnitude, precisely measurable concentration differences persisted for quite a long time. Actual measurements on a run were made over a period of from 3000 to 4000 minutes. Temperature readings and photographs were taken about every two to three hours except over the night when the interval reached ten hours. The precision of the measurements and the rate of change were such that more frequent observations were not deemed necessary.

At the termination of a run the cell was removed from the bath, and the solution in the reservoir and top section on side A was drained. The top of the cell was then aligned, and the solution in the diffusion channel was transferred by syringe to a small stoppered flask. From there 1.00 cc of solution was taken up by pipette and titrated to determine the value of c^{∞}. Since in most cases the diffusion coefficient varies rather gradually with concentration in concentrated solutions, great precision is not required in this chemical analysis for corresponding values of concentration and diffusivity to be of comparable accuracy. For example, in the case of potassium chloride at high concentrations an error of one percent in concentration corresponds to an error of only 0.1 percent in the diffusion coefficient.

E. Measurement of Fringes

Typical fringe patterns during the course of a run are shown in Figs. 31 through 34. In Fig. 31 the boundary had been formed about 30 minutes earlier. Figure 32 shows the boundary several hours later. The fringes in the boundary are too close together to be resolved, but we have included a superimposed Schlieren pattern, which plots the refractive index gradient, to indicate the shape of the boundary. Figures 33 and 34 show the fringes much later in the run when measurements are being made.

The two horizontal lines across these patterns result from the reference marks on the cell. Each of the fringes crossing these lines represents the refractive index profile. According to Eq. (V-18) the refractive index difference between the two reference lines is proportional to the number of fringes which are displaced across a vertical line between them. Since the fringes are equally spaced as a result of the multipoint source, the refractive index difference is also proportional to the horizontal distance which any particular fringe is displaced between the two lines.

A Jarrell-Ash Recording Microphotometer was used to measure the location of fringes on the transparent photographs. This instrument has the capability of measuring the intensity of light transmitted by an area of a transparent photograph as small as one micron by 0.1 mm. The photograph is placed on a traveling stage with precision motor-driven or manual drive

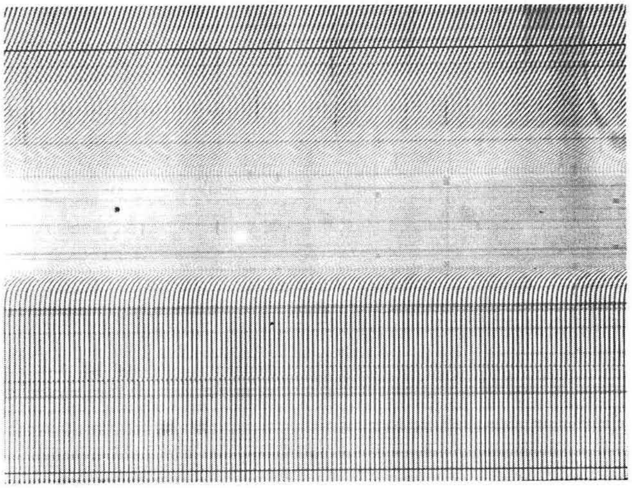


Fig. 31 Fringe pattern about half an hour after the formation of the boundary. The fringes cannot yet be distinguished in the boundary.

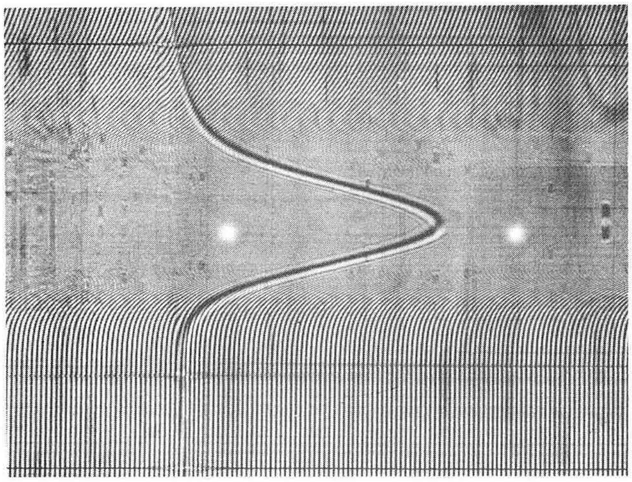


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Fig. 32 Fringe pattern about 2 hours after the formation of the boundary. A Schlieren pattern, proportional to the concentration gradient, is superposed on the fringe pattern.

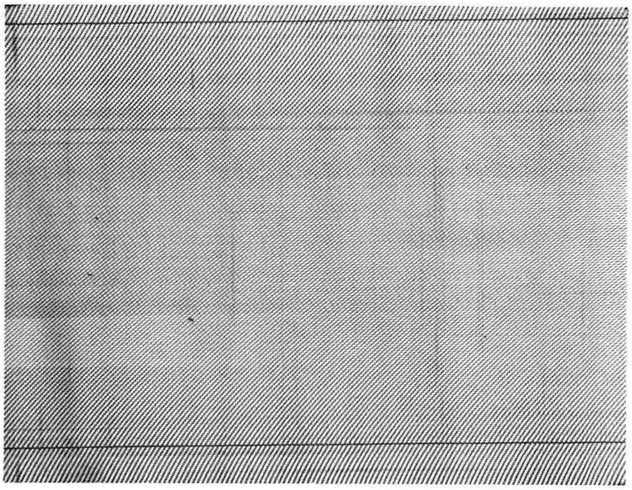

Fig. 33 Fringe pattern after the fringes can be distinguished.

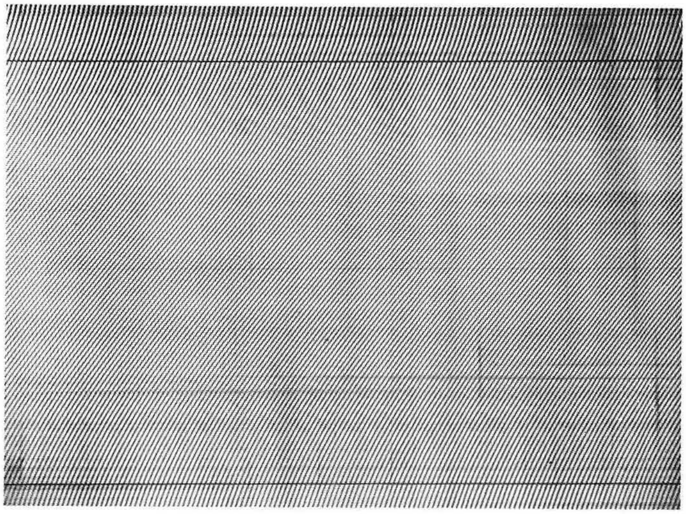

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Fig. 34 Fringe pattern toward the end of the run.

and a vernier scale for measuring the position of the stage to 0.01 mm in the longitudinal direction. The stage may also be moved manually in the transverse direction. A beam of light passing through the specimen is magnified and projected onto a small adjustable slit. Behind the slit is a photoelectric cell, the signal from which is plotted on a chart recorder. The glass on which the specimen is placed is mounted in an aluminum holder which may be rotated to any orientation as well as being translated by the two independent drive mechanisms.

One way to measure the interference patterns would be to place the photograph on the stage with the reference lines perpendicular to the longitudinal drive direction. As the stage carried the fringes through the analyzing beam, intensity peaks corresponding to each fringe crossed would be recorded on the chart. This would in effect magnify the pattern to facilitate the counting of fringes. It would require, however, the determination of fractional portions of fringes at the intersections with the reference lines. Such interpolation cannot be made very precisely so a more accurate method for measuring the fringe shifts was chosen.

The transparent Polaroid photograph was placed on the stage with a 5/8-in. by 3-in. by 4-in. optical quality glass plate on top of it to hold it flat. The stage was then rotated until the reference lines were parallel to the direction of longitudinal travel of the stage. The position of the stage was adjusted such that the analyzing slit corresponded to a locus just inside one of the reference marks. The manual longitudinal drive and the intensity indicator were used to locate the position of an intensity minimum, that is, a dark fringe. The intensity minimum was chosen because it seemed to be slightly sharper than an intensity maximum. The reading on the vernier scale on the stage was recorded.

Now the stage was slowly moved by manually turning the driving knobs as the projection of the chosen fringe was followed visually across the screen until the other reference line came into view. The intersection of this fringe with the reference line was brought to fall upon the analyzing slit, and the exactly longitudinal coordinate of the fringe just inside the reference line was determined as at the other end. The displacement of the fringe between these two points was equal to the difference in the stage scale readings.

The measurement of the fringe location be means of the intensity minimum was found to be reproducible within 0.06 mm. Since the fringe spacing was about 0.59 mm, this precision corresponds to one-tenth of a fringe. Also since the total displacement of a fringe was on the order of thirty to seventy millimeters, this precision in a single measurement amounts to about 0.2 percent.

To ascertain that there were no imperfections in the cell or in the optics which would require a zero correction to the fringe measurements, we took a photograph of the uniform concentration profile in the cell before the boundary was formed in each run. Such a pattern was shown in Fig. 27. In every case the fringes were straight and vertical within the precision of the measurement.

F. Treatment of Data

Equation (V-14) indicates that at large times the logarithm of the concentration difference between our two reference lines should vary linearly with time and exhibit a slope of $-D_M^{\infty}(\pi/a)^2$. Because of the nature of the logarithmic function, any property which is linearly proportional to concentration will follow the same time dependence. For most electrolytes the refractive index is roughly proportional to concentration. A typical example is potassium chloride; its refractive index behavior is shown in Fig. 35. Although there is some curvature, a linear dependence is followed quite closely over any narrow concentration range, such as is encountered in the restricted diffusion cell during the period of measurement. According to our earlier estimates of the concentration change per fringe shift in potassium chloride, the concentration difference when the fringes become less measurable than one-tenth molar. Since refractive index is linear over such a range, and since the distance a fringe is displaced is in turn proportional to the refractive index difference, the logarithm of the measured fringe shift should vary as $-D_M^\infty(\pi/a)^2 t$.

The measurements of fringe displacement Δ versus time t were fit by an equation of the form

$$\ell n\, \Delta = a - b\, t \tag{VI-1}$$

by the least squares method on a CDC 6600 digital computer. There were usually about twenty points, and time range was about 3000 or 4000 minutes. The variance in b due to scatter in Δ was computed according to a standard statistical formula.[53] The value of the diffusion coefficient was calculated from the relation

$$D_M^\infty = \frac{b\, a^2}{\pi^2}\ . \tag{VI-2}$$

If the residual of the fit function at a data point greatly exceeded the estimated experimental error, the corresponding photograph was remeasured at least twice. This was rarely necessary, but when it was, the subsequent measurements usually conformed satisfactorily with the fit equation. As might be inferred from the appearance of Fig. 33, an occasional

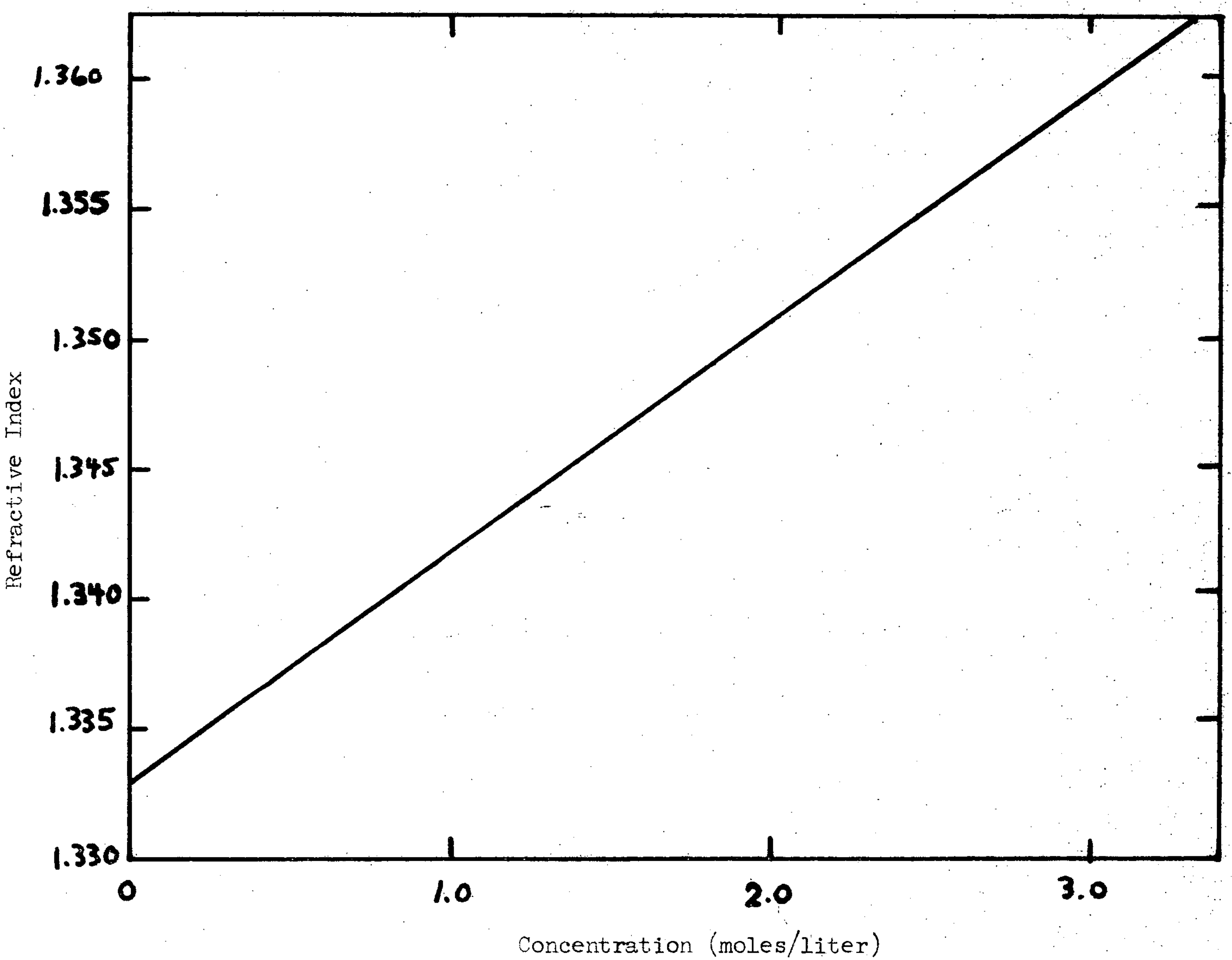

Fig. 35. The Refractive Index of Aqueous Potassium Chloride Solutions at 25°C.

mistake is likely while tracing a fringe across the pattern. In a few of our earlier runs a point or two at either the small time or the large time end of the curve did not conform. At small times and large concentration differences such deviations may result from contributions or higher order terms in Eq. (V-14). The deviations that occasionally appeared at long times were invariably below the fit line, which would indicate an enhancement of mass transfer. These were probably the result of convection induced by vibrations in the system when the density gradient became too small to prevent it. Such points at either end were discarded because an accurate value of the diffusion coefficient can be determined only from a set of data taken over a period of time when the system is obeying an equation of the form (VI-1).

G. Selection and Preparation of Materials

The electrolytic solution whose diffusivity has been studied most thoroughly is aqueous potassium chloride at 25°C. Harned[28] investigated dilute solutions by his conductometric method, and Gosting[20] made measurements over the entire concentration range with the Gouy interferometer. Where these two sets of data overlap, the agreement is within 0.2 percent. Stokes[75] used these data to calibrate his diaphragm cell and then in subsequent runs at different concentrations found agreement with the absolute method measurements within the precision of his experiments, half a percent.

In order to test our apparatus and to determine its accuracy, we measured the diffusion coefficients of several concentrated potassium chloride solutions at 25°C. Baker reagent grade potassium chloride was used to make a saturated solution in distilled, degassed water. The water which was used had a conductivity of about 5×10^{-6} ohm^{-1} cm^{-1}. Since we were working with concentrated salt solutions, no higher purity was believed necessary. The saturated solution was kept in glass under vacuum and mixed with more water to prepare sample solutions of the desired concentrations. The final concentrations after diffusion were determined by titration with Van Waters and Rogers, Inc., standardized 0.0282 N silver nitrate solutions; potassium chromate was dissolved in the chloride solution to indicate the end point by precipitation of brightly colored silver chromate.

Of the many electrolytes whose diffusion coefficients have not been measured, one of the more interesting, theoretically, scientifically, and technologically, is nitric acid. Its thermodynamic properties have been studied quite thoroughly, and its other transport properties are known to moderately high concentrations. We therefore decided to determine its diffusion coefficient at various concentrations.

Baker reagent grade 71.0 percent nitric acid solution, which is about 15.8 molar, was mixed with degassed distilled water to obtain solutions of the desired concentrations for the boundary formation. The final acid concentration was determined by titration with standardized 0.1000 N sodium hydroxide solution to the phenolthalein end point. The carbonate-free hydroxide solution was prepared from a concentrate supplied by the Hartman-Leddon Company.

Tests were made prior to these experiments to confirm that concentrated nitric acid does not react appreciably with the Apierzon grease used to lubricate the cell. It was necessary with nitric acid to use a glass-tipped syringe and a platinum needle for the transfer of solutions in order to avoid needle corrosion and unwanted reaction products in the solutions.

The refractive index of nitric acid solutions has been measured at 25°C by Lühdemann.[52] Unfortunately this function passes through a maximum at very high concentrations (about 37 mole percent) so that our experimental method will not work there. Nevertheless, the function is nearly linear over a considerable range of concentration, and measurements at concentrations corresponding to the existing transference number data could be made.

A summary of the runs performed and the experimental results are given in the next chapter.

VII. EXPERIMENTAL RESULTS

A number of runs were made with aqueous solutions of potassium chloride at 25°C during which the experimental procedure and the improvements in the cell holder design were developed. In most of these experiments the final solution concentration was determined by measuring its conductance. Unfortunately, the conductance cell which was used for this purpose was found to behave nonlinearly so that the measured conductances and therefore the concentrations of the more concentrated solutions were incorrect.

After titration was adopted as the analytical method, two runs were made at concentrations near 2 molar. At final concentrations 2.075 M and 2.125 M, the diffusion coefficients were calculated to be 2.0113×10^{-5} cm^2/sec and 2.0149×10^{-5} cm^2/sec, respectively. The analysis of one of these runs is shown in Table XXXVI where the fringe displacements calculated by the fit equation are compared with the measured values. They are found to agree within the reproducibility of the measurement, which indicates that the assumption is valid that terms higher than the first in Eq. (V-14) are negligible at these large times. The standard deviation of the estimated error in the diffusion coefficient calculated from the slope, which is a statistical quantity for expressing the confidence level of a least squares slope, is 0.19 percent and 0.21 percent of the measured diffusion coefficient in the two cases.

The results for potassium chloride are to be compared with values interpolated from Gosting's Guoy measurements.[20] As shown in Fig. 36, agreement is within 0.2 percent and 0.1 percent for the two cases. Stokes'

Table XXXVI. Summary of results of fringe measurements and data analysis for diffusion of potassium chloride in water at 25°C and c^{∞} = 2.075 M.

Height of cell = 7.9045 cm

Time (Min)	Fringe displacement (mm) Measured	Calculated
0	49.35	49.42
126.0	48.20	48.25
266.5	46.89	46.97
752.5	42.66	42.82
1458.5	37.58	37.43
1649.0	36.11	36.09
1800.5	35.28	35.06
1952.5	34.06	34.06
2166.0	32.80	32.70
2808.0	28.90	28.94
2959.0	28.21	28.12
3178.0	26.93	26.97
3276.0	26.51	26.47
3495.0	25.26	25.39
3626.0	24.69	24.75

Diffusion coefficient equals 2.0113X10** -5 sq cm/sec .

Standard deviation of the estimated error in the diffusion coefficient = 3.7677 = -08 sq cm/sec.

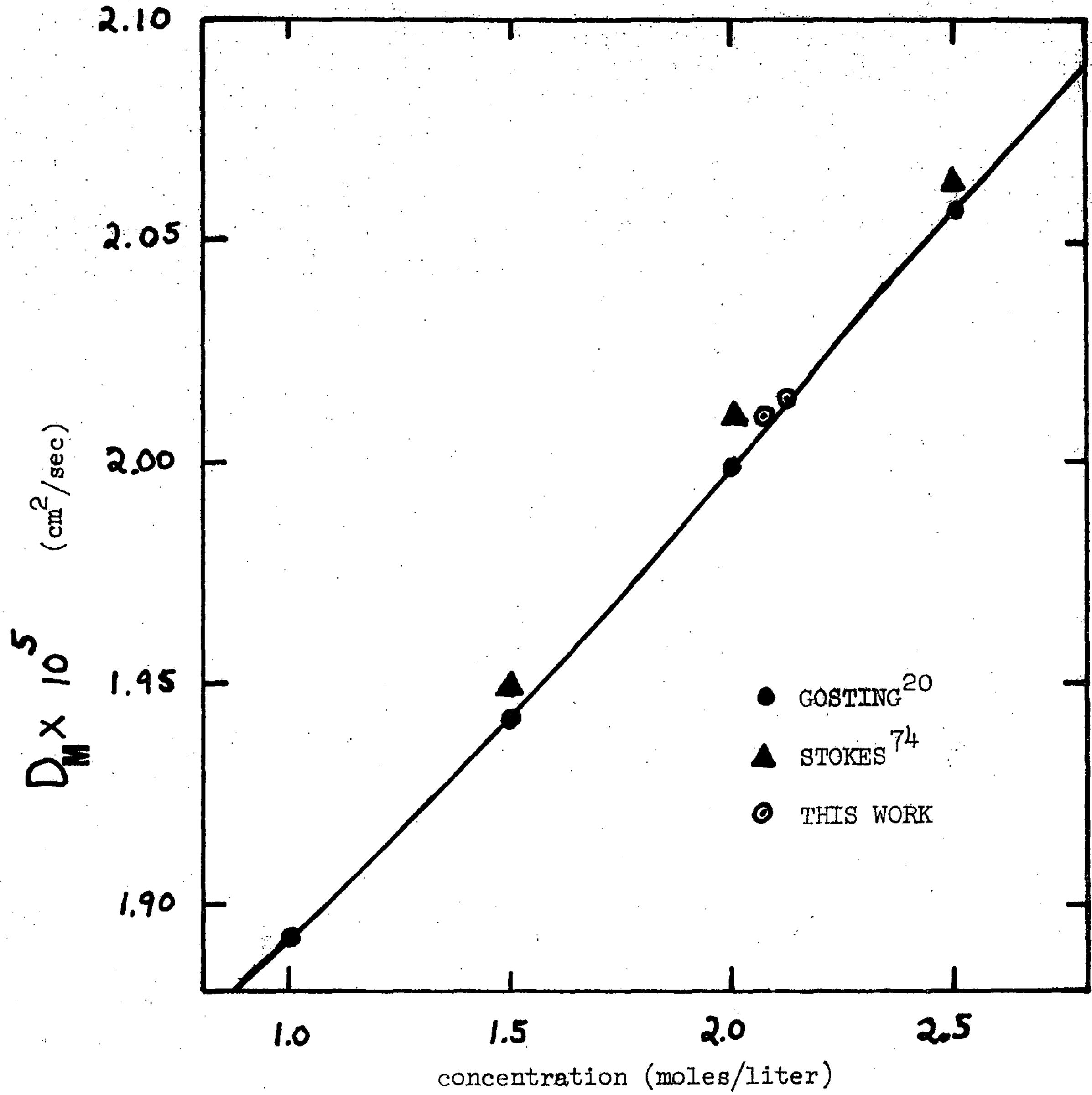

Fig. 36 The diffusion coefficient of potassium chloride in water at 25°C and high concentrations

Table XXXVII The diffusion coefficient of nitric acid in water at 25°C

c (moles/ℓ)	$D_M \times 10^5$ (cm^2/sec)	Standard deviation of estimated error[53] in D_M (percent)
0	3.158*	---
0.456	2.842	0.08
1.005	2.979	0.07
2.155	3.180	0.07
3.040	3.312	0.17

* Calculated from Eq. (III-5) and values in Table XXXV

results[74] in this range are also included in the figure for comparison. The statistical evidence for high precision and the close agreement with Gosting's values indicate that the method used here is valid and capable of accuracy at least comparable to that of the other modern methods for measuring diffusivity.

Measurements were made with nitric acid at four final concentrations and 25°C. The results are summarized in Table XXXVII. The measured diffusion coefficient is found to go through a shallow minimum in dilute solution and then to increase gradually with concentration. In every run except one the standard deviation of the estimated error in D_M is less than 0.08 percent.

VIII. DISCUSSION OF RESULTS

From the diffusivity measurements and from data for other properties available in the literature it is possible to calculate the multicomponent diffusion coefficients $\mathcal{D}_{ij}$ of nitric acid in water. The results are given in Table XXXVIII. Values of the quantity G defined in Chapter IV are also presented in this table. It is found that the function G for nitric acid is quite similar to that for the other acids, HCl and H_2SO_4, being lower than those for other 1-1 electrolytes. An assumption of G based on the values presented in Chapter IV would therefore yield a rough but approximately correct value for $\mathcal{D}_{+-}$ for nitric acid.

The behavior of $\mathcal{D}_{H_2O-H^+}$ and $\mathcal{D}_{H_2O-NO_3^-}$ is also qualitatively in agreement with the observations of Chapter IV regarding the effects of these ions in other systems. The nitrate ion is believed to be structure-breaking in a manner similar to chloride, but the presence of the structure-making hydrogen ion, as in the case of hydrochloric acid, causes the diffusion coefficient of nitrate to decrease monotonically with concentration. The hydrogen ion diffusion coefficient behaves similarly to those in hydrochloric and sulfuric acid, exhibiting a small maximum at low concentrations and then diminishing considerably at higher concentrations.

From the complicated and varied results of our investigation of many different systems in Chapter IV, it appears that no general quantitative correlation of the transport properties of electrolytic solutions is possible at this time. By looking at the $\mathcal{D}_{ij}$ representation of the data, we have been able to discover a consistent qualitative scheme of behavior which is not at all obvious in the measured transport properties. All the $\mathcal{D}_{+-}$ coefficients increase with concentration according to Eq. (IV-2), where G is a function much less concentration dependent than $\mathcal{D}_{+-}$ and may be estimated from Fig. 10;

Table XXXVIII. Nitric acid in water at 25°C.

c	ρ	μ	Λ	t_+	$D_M \times 10^5$	$1+\frac{d\ln\gamma}{d\ln m}$	c	$\mathcal{D}_{o+} \times 10^5$	$\mathcal{D}_{o-} \times 10^5$	$\mathcal{D}_{+-}$	G
0.	.9971	.8937	420.50	.8300	3.158	1.0000	0.	9.288	1.902	0.	--
.001	1.0040	.8937	414.80	.8371	3.103	.9919	.001	9.284	1.882	2.076E-07	3.592E+03
.010	1.0051	.8938	406.00	.8392	3.003	.9764	.010	9.283	1.843	6.763E-07	3.696E+03
.050	1.0054	.8942	393.30	.8438	2.881	.9559	.050	9.290	1.795	1.655E-06	3.369E+03
.100	1.0134	.8946	385.00	.8392	2.829	.9475	.100	9.286	1.771	2.420E-06	3.255E+03
.200	1.0096	.8956	376.10	.8416	2.802	.9457	.200	9.242	1.749	3.781E-06	2.937E+03
.300	1.0096	.8965	365.39	.8388	2.808	.9522	.300	9.137	1.736	4.830E-06	2.783E+03
.500	1.0181	.8984	356.80	.8411	2.850	.9755	.500	8.926	1.710	6.955E-06	2.465E+03
.700	1.0236	.9003	344.89	.8380	2.903	1.0057	.700	8.630	1.681	8.847E-06	2.235E+03
1.000	1.0303	.8811	341.72	.8332	2.978	1.0579	1.000	8.141	1.629	1.184E-05	1.960E+03
1.500	1.0470	.8854	308.08	.8266	3.081	1.1573	1.500	7.272	1.524	1.777E-05	1.513E+03
2.000	1.0635	.8917	280.13	.8201	3.162	1.2681	2.000	6.433	1.411	2.379E-05	1.121E+03
2.500	1.0799	.9002	256.03	.8139	3.232	1.3859	2.500	5.697	1.306	2.956E-05	8.866E+02
3.000	1.0961	.9111	234.79	.8078	3.306	1.5027	3.000	5.113	1.217	3.486E-05	7.805E+02
3.500	1.1120	.9244	215.81	.8018	3.392	1.6049	3.500	4.714	1.154	3.951E-05	7.632E+02

it appears to be practically independent of temperature.

The temperature dependence of the $\mathfrak{D}_{oi}$ coefficients is accounted for primarily by the temperature dependence of the limiting values. The latter is represented by Eq. (IV-3) with the coefficients for various ions given in Table XXXV.

The concentration dependence of $\mathfrak{D}_{oi}$ depends on the nature of the ion itself as well as the identity of the counter-ion. This dependence can not be quantitatively related to the viscosity of the solution, but it can be explained qualitatively on the basis of the effects of the ions on the structure of the solution. Rough estimates of values may be made from a knowledge of the behavior in similar systems. For example, the behavior of hydrogen ions in other strong acids might be expected to be quite close to that in hydrochloric, sulfuric, and nitric acids, and the behavior of the other alkali metal ions may be inferred from the behavior of Li^+, Na^+, and K^+. The larger ions Rb^+ and Cs^+ are probably structure-breaking so that their diffusion coefficients should increase initially with concentration and not decrease very rapidly at high concentrations.

The effect of the counter-ion on the diffusion coefficient may also be estimated qualitatively on the basis of its effect on the solution structure. For example, since sodium and lithium are structure-making, the diffusivities of chloride and iodide drop off much more in concentrated solutions with these cations than they do with structure-breaking potassium. According to the results for chlorides, lithium has a slightly stronger structure-making ability than does sodium, but not nearly as great as does hydrogen. The results for potassium indicate iodide is a stronger structure-breaker than bromide, which is in turn a more effective structure-breaker than chloride. Since nitrate is a slightly stronger structure-breaker with lithium than is chloride, it must fall in somewhere with the other halides.

The quantitative characterization of these effects is a complicated one which will require a detailed mathematical theory of the microscopic structure of solutions. Such a theory seems at the present time to be far from our grasp. It is hoped that the effects elucidated here may help guide the eventual development of a successful theory.

In order to determine more completely the properties of various ions and their effects on the properties of other ions, as well as to provide a more sound basis for an empirical correlation, it is necessary to have more extensive experimental data. We have developed a new apparatus for the measurement of diffusivity in concentrated binary solutions. It is hoped that this apparatus will be used in a systematic investigation of the behavior of ions which have not yet been studied as well as in a thorough study of certain specific systems to determine more clearly what physical parameters are important in affecting the transport properties.

Since the statistical analysis of the fringe measurements indicates such a high precision in the determination of the diffusion coefficient, the limit of the accuracy of the method at this time may be the chemical analysis of the solution. With barely more than one cubic centimeter of solution available, titration can not be extremely accurate. It is recommended that a more precise method for the analysis of the sample be devised.

Both the analysis of diffusion data in the manner suggested here and the application of estimated $\mathcal{D}_{oi}$ coefficients in mass transfer problems require values of the activity coefficient correction. For the most part activity coefficient data are available only at 0°C from freezing point depression measurements or at 25°C from E.M.F. or isopiestic measurements. It appears that the most convenient method for obtaining necessary values for concentrated solutions where no data are available is an isopiestic measurement.[46] Provided that thermodynamic data are available for some system A at a particular temperature, the required activity coefficient term for an unknown system B may be determined by comparing the concentrations of the two solutions which are in equilibrium with the same partial pressure of water vapor. The condition for this equilibrium is

$$\phi_B = R\phi_A \tag{VIII-1}$$

where ϕ is the osmotic coefficient and

$$R = \frac{\nu_A m_A}{\nu_B m_B} \tag{VIII-2}$$

where m_A and m_B are the molalities of the two solutions. Furthermore,

$$\ln \gamma_B = {}_B - 1 + \int_o^{m_B} (\phi_B - 1)\, d \ln m_B \,. \tag{VIII-3}$$

Differentiation of Eq. (VIII-3) and substitution of Eqs. (VIII-1) and (VIII-2) yield the desired expression

$$\left[1 + \frac{d \ln \gamma}{d \ln m}\right]_B = \frac{d}{dm_B} \left[\frac{\nu_A m_A \phi_A}{\nu_B}\right] \tag{VIII-4}$$

for the activity coefficient correction of solution B.

For the complete description of mass transport in a multicomponent electrolytic solution containing n ions, one needs values for $n(n-1)/2$ $\mathscr{D}_{+-}$ coefficients and n $\mathfrak{D}_{oi}$ coefficients; that is, $n(n+1)/2$ independent transport properties, which are functions of composition and temperature. The specification of this large amount of information requires a tremendous experimental effort, and no complete set of data for any system has yet been obtained.[53b] It would therefore be desirable to have some means for estimating these transport properties theoretically. One might hope that information about binary systems could be used in the estimation of the multicomponent transport properties.

Lightfoot et al.[47] have suggested that $\mathcal{D}_{oi}$ for an ion in a binary solution be used as its value in a multicomponent system. This procedure should be valid when all ions are present in very low concentrations. Since we have discovered that these coefficients are concentration dependent as well as dependent upon what other ions are present in the solution, the value of $\mathcal{D}_{oi}$ when any ions in the system are present in high concentrations will probably be changed considerably from its zero-concentration limiting value. The direction and extent of the change will depend upon the effects of all the ions present on the structure of the solution. These might be estimated qualitatively on the basis of the arguments presented above for binary solutions. Some careful experimental work in multicomponent systems will be required to determine whether these suppositions are valid.

In a multicomponent system the condition of electroneutrality no longer requires that the ions all diffuse at the same rate. In this case, the quantity $\mathcal{D}_{+-}$ for various pairs of ions can become important in diffusion as well as conductance. It is therefore more important in these cases to be able to estimate values of $\mathcal{D}_{ij}$. As a first approximation one might attempt to use a form such as Eq. (IV-2). The manner in which the ionic concentrations enter into such an equation for multicomponent solutions is not clear, nor is the concentration upon which the factor G should depend. It is therefore desirable to investigate the forms of the ionic distribution functions in multicomponent systems and to calculate from them the limiting law for $\mathcal{D}_{ij}$ on the basis of a relaxation effect. A complete calculation of this type should also allow for some specific effects on $\mathcal{D}_{ij}$ by the ions through their influence on the structure of water. It will then be necessary to have some experimental data to determine empirically the behavior of a correction factor analogous to G which accounts for the deviations from the theoretical limiting expression.

IX. CONCLUSIONS AND RECOMMENDATIONS

We have discussed a set of generally applicable flux equations which define the transport properties necessary for the complete description of mass transport in electrolytic solutions. The transport properties so defined are related to those usually measured, but they are more easily interpreted in terms of molecular interactions. It is, therefore, these properties which should be the easiest to correlate and which should be treated directly by any microscopic theory of electrolytic solutions.

There are essentially two kinds of transport properties in this situation: those which are related to ion-ion interactions, $\mathscr{D}_{+-}$, and those which are determined by ion-solvent interactions, $\mathscr{D}_{oi}$. From an investigation of the available data on mass transport in binary solutions, we discovered that the formed are very small in dilute solutions but increase over many orders of magnitude and are appreciable in concentrated solutions. Based on the relaxation term of the limiting law for electrolytic conductance, a crude empirical correlation of $\mathscr{D}_{+-}$ data was suggested which takes into account most of the dependence of $\mathscr{D}_{+-}$ on concentration and temperature for a system.

The ionic diffusion coefficients $\mathscr{D}_{oi}$ were found to vary from their limiting values in a way characteristic of the ions present in the solution. In general, if the ions present are large, they initially tend to break the structure of water such that $\mathscr{D}_{oi}$ goes through a maximum before decreasing at higher concentrations. Smaller and multivalent ions impose additional structure on the solution, and $\mathscr{D}_{oi}$ decreases monotonically from its limiting value. A qualitative estimate of the variation of an ionic diffusion coefficient from its limiting value may be made on the basis of this scheme by investigaging the behavior of a similar system. Most of the temperature dependence of the $\mathcal{D}_{oi}$ coefficients is accounted for by the variation of its limiting value.

The development of a reliable quantitative correlation of the transport properties in electrolytic solutions will require much more extensive data, as well as valid quantitative theories of the structure of solutions and molecular interactions, to elucidate what physical parameters are important in determining the observed behavior. In order to provide some of the requisite data, we have developed an optical restricted-diffusion method for measuring diffusion coefficients in concentrated binary solutions. From measurements with potassium chloride in water, the method was found to agree with the Gouy method within the estimated accuracy of 0.2 percent. The new method has the advantages that its mathematical analysis involves fewer approximations than any other method and that experimentally it does not require an initially sharp boundary between two solutions. One disadvantage is that the time required for each data point is several days.

The diffusion coefficient of nitric acid in water at 25°C and at concentrations up to 3 molar was measured. The ionic diffusion coefficients were found to behave consistently with the qualitative scheme suggested on the basis of the effects of various ions on the structure of water. The diffusivity of nitrate in nitric acid decreases much more rapidly than in other nitrate solutions because of the strong effect of hydrogen ions on the solution structure. The diffusivity of hydrogen increases initially because of the catalytic effect of pH on the rapid proton transfer, but it decreases rapidly at concentrations above .1 molar in a manner similar to the hydrogen in HCl and H_2SO_4.

The problem of relating the transport porperties of multicomponent solutions to those in the binary systems is even more complicated than the quantitative description of binary solutions. It would be desirable to have complete sets of transport property data in some multicomponent solutions so that an investigation of the behavior of the σ_{ij} coefficients would be possible.

Of the many theoretical problems which need to be solved, there are two which may be within the reach of the current theories of the liquid state. The first is the explanation of the values as well as the temperature dependence of the limiting ionic diffusion coefficients. Consideration of this particular problem in electrolytes minimizes the number of factors which need to be taken into account. Its solution should elucidate the types of forces which are most important in the ion-solvent interactions. It would also serve as a quantitative basis for describing subsequent changes in the structure and effective forces as the concentration is increased.

Another important problem to be treated is a derivation of the relaxation effect consistent with Eq. (III-1) rather than one based on the dilute solution formulation. Such a development is primarily a problem in electrostatics. A more sophisticated solution of this problem should shed light on the nature of the empirical factor G or offer a more satisfactory form than Eq. (IV-2) for the correlation of σ_{+-}. It should, furthermore, be a sufficiently general formulation so that it will treat the ionic distribution functions in multicomponent solutions and indicate the manner in which σ_{ij} in these systems depend on the concentrations and might be related to the ionic interaction coefficients in binary electrolytes.

The investigation of transport properties in the forms suggested in this discussion has been found to be quite advantageous. It has revealed a qualitatively systematic behavior of the σ_{ij} coefficients which was not obvious in the measured properties. Since the general behavior of the ionic diffusion coefficients may be interpreted in terms of the effects of various ions on the structure of water and of long range ion-ion interactions, there is promise that a general correlation of them will become possible as progress is made in the quantitative description of the structure of water and molecular interactions in electrolytic solutions. Conversely, the observations made in this study should be valuable guides in the development of a successful microscopic theory by providing qualitative information about the structure of electrolytic solutions. It is hoped that the experimental apparatus developed here will be used to obtain additional data in a wide variety of systems and thus increase our knowledge of the complex liquid state.

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APPENDIX A

Functions Used to Fit Properties and Values of the Parameters for Various Systems

To interpolate the experimental data to the concentrations where calculations were made, we fit all the values for a property to an analytic representation. Experimental density data, after being converted to gm/cm^3, were represented by

$$\rho = \rho_{H_2O} + a_1 c + a_2 c^{3/2} + a_3 c^2 \quad . \tag{A-1}$$

With this equation any concentration values on other scales could be converted to moles/liter. Values of the coefficients in Eq. (A-1) for various systems are given in Table A-1.

Viscosity data were fit by the form

$$\mu = \mu_{H_2O} + b_1 c^{1/2} + b_2 c + b_3 c^{3/2} + b_4 c^2 + b_5 c^{5/2} \quad . \tag{A-2}$$

The coefficients of this equation are given in Table A-2.

The conductivity was represented by

$$\kappa = d_1 c + d_2 c^{3/2} + d_3 c^2 + d_4 c^{5/2} + d_5 c^3 \quad . \tag{A-3}$$

The coefficients are presented in Table A-3.

The cation transference number data were fit by the form

$$t_+^\circ = t_+^\circ(0) + e_1 c^{1/2} + e_2 c + e_3 c^{3/2} + e_4 c^2 \quad . \tag{A-4}$$

The limiting value $t_+^\circ(0)$ may be calculated from Eq. (III-6) and the values of $\mathscr{D}^\circ_{oi}$ given by Eq. (IV-3) and Table XXXV. The parameters e_i are given in Table A-4.

The experimental diffusion coefficients were fit by the form

$$D_M = D^\circ + f_1 c^{1/2} + f_2 c + f_3 c^{3/2} + f_4 c^2 \quad . \qquad \text{(A-5)}$$

The Nernst limiting value D may be calculated from Eq. (III-5) and the $\mathcal{D}^\circ_{oi}$ values given by Eq. (IV-3) and Table XXXV. The parameters f_i are given in Table A-5.

For the differentiation of the activity coefficient data we fit the log of these data by

$$\ln\gamma = \frac{g_1 m^{1/2}}{(1+m^{1/2})} + g_2 m + g_3 m^{3/2} + g_4 m^2 + g_5 m^2 + g_6 m^3 \quad . \qquad \text{(A-6)}$$

The coefficients g_i are presented in Table A-6.

The fit of D_M was not used for the calculations of the $\mathcal{D}_{oi}$ coefficients. The experimental diffusivity points were used to calculate the thermodynamic diffusion coefficient, which was then fit by

$$\mathcal{D} = D^\circ + h_1 c^{1/2} + h_2 c + h_3 c^{3/2} + h_4 c^2 \quad , \qquad \text{(A-7)}$$

and this equation was used in the subsequent calculations. The values of the coefficients h_i are given in Table A-7.

The interpolation of equivalent conductance and viscosity by these equations is inaccurate in very dilute solutions for some systems. When there were insufficient data at low concentrations, the large variation at high concentrations biased the fit. For the other properties the fit was within the experimental error or within the scatter of values from different experimenters.

The calculated ionic diffusion coefficients $\mathcal{D}_{oi}$ were fit quite accurately by an equation of the form

$$\mathcal{D}_{0i} = \mathcal{D}^{\circ}_{0i} + k_1 c^{1/2} + k_2 c + k_3 c^{3/2} + k_4 c^2 \quad . \qquad \text{(A-8)}$$

The limiting values are given by Eq. (IV-3) and Table XXXV. The coefficients k_i for $\mathcal{D}_{0+}$ and $\mathcal{D}_{0-}$ in various systems are given by Tables A-8 and A-9, respectively.

The ionic interaction diffusion coefficient is represented accurately by the form

$$\mathcal{D}_{+-} = \ell_1 c^{1/2} + \ell_2 c + \ell_3 c^{3/2} + \ell_4 c^2 \quad . \qquad \text{(A-9)}$$

The coefficients ℓ_1 are given in Table A-9.

In some cases Eqs. (A-2), (A-3), and (A-10) are not accurate in dilute solutions because the predominance of data at high concentrations biases the fit. The inaccuracy is particularly blatant for the conductance of $LaCl_3$, LiCl at 35°C, $LiNO_3$, H_3PO_4, KCl at 18°C, KCl at 35°C, and H_2SO_4, where d_2 is positive and for $\mathcal{D}_{+-}$ of $BaCl_2$, LiCl at 35°C, NaCl at 0°C and 50°C, and H_2SO_4, for which ℓ_i is negative.

Table A-1. Values of density equation parameters for aqueous electrolytic solutions

Solute	Temp. (°C)	a_1	a_2	a_3
Ammonium chloride	25.00	1.5268E-02	4.2267E-04	-3.8344E-04
Ammonium nitrate	25.00	3.2426E-02	-7.5583E-04	-9.5159E-05
Barium chloride	25.00	1.8152E-01	1.3507E-03	-4.8312E-03
Cadmium sulfate	25.00	1.7083E-01	-1.7484E-02	9.0769E-03
Calcium chloride	25.00	8.4592E-02	4.6483E-03	-3.2862E-03
Cupric sulfate	25.00	1.6319E-01	-8.8629E-03	-1.1939E-04
Hydrochloric acid	25.00	1.7957E-02	-3.2003E-04	-1.2209E-04
Lanthanum chloride	25.00	2.2929E-01	-1.1470E-02	-3.5067E-04
Lithium chloride	25.00	2.6117E-02	-2.4564E-03	3.1902E-04
Lithium chloride	35.00	2.5410E-02	-1.9625E-03	2.3639E-04
Lithium chloride	50.00	2.6342E-02	-1.7390E-03	1.0080E-04
Lithium nitrate	25.00	4.5565E-02	-4.4676E-03	5.9611E-04
Nitric acid	25.00	3.2061E-02	2.1099E-03	-9.0324E-04
Phosphoric acid	25.00	5.2204E-02	-3.1817E-04	-2.7830E-04
Potassium bromide	25.00	8.5851E-02	-2.5499E-03	2.1722E-04
Potassium chloride	0.00	2.8447E-02	1.8256E-02	-3.9529E-03
Potassium chloride	18.00	3.3102E-02	2.1511E-02	-8.6615E-03
Potassium chloride	25.00	4.7830E-02	-2.0471E-03	-5.4033E-05
Potassium chloride	35.00	4.7485E-02	-2.0650E-03	-5.1796E-05
Potassium chloride	50.00	4.9976E-02	-6.7865E-03	1.6357E-03
Potassium iodide	25.00	1.3203E-01	-1.3936E-02	3.1413E-03
Potassium sulfate	25.00	1.4180E-01	-1.1383E-02	-8.0789E-04
Silver nitrate	25.00	1.4567E-01	-6.4757E-03	1.0150E-03
Sodium chloride	0.00	4.7817E-02	-4.9601E-03	4.6814E-04
Sodium chloride	18.00	4.4389E-02	-3.7295E-03	3.3908E-04
Sodium chloride	25.00	4.1137E-02	-1.2339E-03	-2.2432E-04
Sodium chloride	35.00	2.3348E-01	-1.9429E-01	4.7185E-02
Sodium chloride	50.00	4.2015E-02	-2.7096E-03	1.5638E-04
Sodium hydroxide	25.00	4.7791E-02	-4.9148E-03	6.4046E-05
Sodium iodide	25.00	1.1761E-01	-4.1864E-03	7.0349E-04
Sodium sulfate	25.00	1.3836E-01	-2.5404E-02	5.2724E-03
Sulfuric acid	25.00	5.0346E-02	1.0344E-02	-2.6583E-03
Zinc sulfate	25.00	1.1681E-01	6.9285E-02	-3.0404E-02

Table A-2. Values of viscosity equation parameters for aqueous electrolytic solutions

Solute	Temp. (°C)	b_1	b_2	b_3	b_4	b_5
Ammonium chloride	25.00	-1.045E-01	3.723E-01	-4.717E-01	2.424E-01	-4.257E-02
Ammonium nitrate	25.00	3.795E-02	-2.136E-01	2.186E-01	-9.147E-02	1.574E-02
Barium chloride	25.00	1.256E-02	1.912E-01	3.291E-03	2.306E-02	2.492E-02
Cadmium sulfate	25.00	4.851E-02	2.366E-01	9.559E-01	-1.113E+00	6.500E-01
Calcium chloride	25.00	4.515E-01	-1.945E+00	3.689E+00	-2.548E+00	6.669E-01
Cupric sulfate	25.00	4.089E-02	9.554E-02	1.452E+00	-1.464E+00	6.668E-01
Hydrochloric acid	25.00	-7.686E-06	6.921E-02	-1.846E-02	5.635E-03	-2.712E-04
Lanthanum chloride	25.00	2.628E-02	5.322E-01	-1.753E-01	3.120E-01	6.380E-02
Lithium chloride	25.00	1.468E-01	-2.702E-01	4.265E-01	-2.053E-01	4.142E-02
Lithium chloride	35.00	3.487E+00	-7.681E+00	6.124E+00	-2.049E+00	2.538E-01
Lithium chloride	50.00	1.132E+00	-2.496E+00	2.085E+00	-7.255E-01	9.598E-02
Lithium nitrate	25.00	5.813E-02	-1.333E-01	2.918E-01	-1.483E-01	3.199E-02
Nitric acid	25.00	-8.033E-02	1.471E-01	-1.251E-01	5.269E-02	-6.971E-03
Phosphoric acid	25.00	2.227E+00	-7.169E+00	+7.743E+00	-3.152E+00	4.592E-01
Potassium bromide	25.00	2.854E-03	-5.882E-02	3.460E-02	-1.261E-02	4.962E-03
Potassium chloride	0.00	-5.864E+00	1.643E+01	-1.718E+01	7.793E+00	-1.294E+00

Table A-2 (continued)

Solute	Temp. (°C)	b_1	b_2	b_3	b_4	b_5
Potassium chloride	18.00	2.445E-02	-1.338E-01	1.647E-01	-9.318E-02	2.186E-02
Potassium chloride	25.00	1.783E-02	-8.427E-02	1.195E-01	-7.344E-02	1.856E-02
Potassium chloride	35.00	2.550E-03	1.740E-02	-1.976E-02	1.102E-02	9.118E-05
Potassium chloride	50.00	2.109E-02	-4.870E-02	7.974E-02	-3.869E-02	7.729E-03
Potassium iodide	25.00	1.287E-02	-1.415E-01	1.000E-01	-3.835E-02	9.534E-03
Potassium sulfate	25.00	-3.303E-02	8.451E-01	-2.273E+00	2.867E+00	-1.191E+00
Silver nitrate	25.00	7.105E-02	-2.377E-01	3.508E-01	-1.542E-01	2.767E-02
Sodium chloride	0.00	1.313E-04	1.331E-01	-2.453E-01	2.348E-01	-4.549E-02
Sodium chloride	18.00	3.826E-02	-1.529E-01	3.708E-01	-2.251E-01	5.500E-02
Sodium chloride	25.00	-1.681E-02	1.247E-01	-4.168E-02	1.342E-02	5.383E-03
Sodium chloride	35.00	-1.263E-01	2.977E-01	-2.149E-01	1.094E-01	-1.684E-02
Sodium chloride	50.00	-4.781E-02	2.440E-01	-2.449E-01	1.317E-01	-2.167E-02
Sodium hydroxide	25.00	2.781E-01	1.396E-02	-4.013E-02	8.108E-02	-4.781E-03
Sodium iodide	25.00	-1.123E-01	4.721E-01	-6.178E-01	3.411E-01	-5.783E-02
Sodium sulfate	25.00	4.926E-02	-2.023E-02	9.995E-01	-9.684E-01	4.404E-01
Sulfuric acid	25.00	8.167E-01	-2.132E+00	2.075E+00	-7.392E-01	9.809E-02
Zinc sulfate	25.00	-1.919E-01	4.073E+00	-7.775E+00	5.732E+00	-1.059E+00

Table A-3

Values of Conductivity Equation Parameters for Aqueous Electrolytic Solutions

Solute	Temp. (°C)	d_1	d_2	d_3	d_4	d_5
Ammonium chloride	25.00	1.430E-01	-5.633E-02	3.479E-02	-1.113E-02	9.129E-02
Ammonium nitrate	25.00	1.354E-01	-5.132E-02	2.577E-02	-9.551E-03	1.094E-03
Barium chloride	25.00	2.290E-01	-3.619E-02	-1.536E-01	1.668E-01	-5.095E-02
Cadmium sulfate	25.00	1.763E-01	-5.283E-01	1.011E+00	-9.637E-01	3.451E-01
Calcium chloride	25.00	2.716E-01	-4.268E-01	6.065E-01	-3.802E-01	5.057E-02
Cupric sulfate	25.00	1.736E-01	-4.462E-01	7.069E-01	-5.391E-01	1.517E-01
Hydrochloric acid	25.00	4.196E-01	-3.969E-02	-5.602E-02	1.077E-02	8.233E-07
Lanthanum chloride	25.00	2.728E-01	6.877E-01	-3.290E+00	4.718E+00	-2.234E+00
Lithium chloride	25.00	1.086E-01	-4.888E-02	2.047E-02	-8.365E-03	1.180E-03
Lithium chloride	35.00	7.512E-02	3.503E-02	-3.423E-02	5.980E-03	-1.724E-04
Lithium chloride	50.00	2.010E-01	-1.730E-01	1.305E-01	-5.755E-02	9.396E-03
Lithium nitrate	25.00	8.168E-02	7.488E-03	-2.555E-02	6.749E-03	-5.095E-04
Nitric acid	25.00	4.994E-01	-1.471E-01	-1.551E-02	8.246E-03	-6.517E-04
Phosphoric acid	25.00	4.369E-02	3.256E-02	-1.655E-02	1.085E-04	3.438E-04
Potassium bromide	25.00	1.462E-01	-6.437E-02	5.375E-02	-2.337E-02	3.223E-03
Potassium chloride	0.00	8.118E-02	-3.060E-02	2.722E-02	7.175E-03	-1.066E-03
Potassium chloride	18.00	4.333E-02	2.046E-01	-2.555E-01	1.300E-01	-2.421E-02
Potassium chloride	25.00	1.438E-01	-5.327E-02	2.593E-02	-3.473E-03	-1.243E-03

Table A-3 (continued)

Solute	Temp. (°C)	d_1	d_2	d_3	d_4	d_5
Potassium chloride	35.00	1.208E-01	1.137E-01	-1.878E-01	1.080E-01	-2.244E-02
Potassium chloride	50.00	2.486E-01	-2.211E-01	2.265E-01	-1.115E-01	1.913E-02
Potassium iodide	25.00	1.433E-01	-5.643E-02	4.565E-02	-1.780E-02	1.714E-03
Potassium sulfate	25.00	2.893E-01	-4.315E-01	6.435E-01	-4.958E-01	1.292E-01
Silver nitrate	25.00	1.299E-01	-7.083E-02	2.355E-02	-5.218E-03	4.879E-04
Sodium chloride	0.00	6.603E-02	-4.022E-02	5.087E-02	-3.843E-02	9.418E-03
Sodium chloride	18.00	1.049E-01	-4.3181E-02	1.933E-02	-7.544E-03	8.468E-04
Sodium chloride	25.00	1.200E-01	-5.087E-02	2.683E-02	-1.203E-02	1.742E-03
Sodium chlrodie	35.00	1.448E-01	-8.563E-02	6.396E-02	-2.853E-02	4.185E-03
Sodium chloride	50.00	1.924E-01	-1.010E-01	6.442E-02	-3.074E-02	5.237E-03
Sodium hydroxide	25.00	2.432E-01	-7.951E-02	4.145E-02	-3.461E-02	7.165E-03
Sodium iodide	25.00	1.218E-01	-4.815E-02	3.225E-02	-1.570E-02	2.469E-03
Sodium sulfate	25.00	2.582E-01	-5.496E-01	1.216E+00	-1.633E+00	8.960E-01
Sulfuric acid	25.00	3.744E-01	2.759E-01	-3.310E-01	9.129E-02	-7.874E-03
Zinc sulfate	25.00	1.895E-01	-5.657E-01	1.091E+00	-1.040E+00	3.718E-01

Table A-4

Values of Cation Transference Number Equation Parameters for Aqueous Electrolytic Solutions.

Solute	Temp. (°C)	e_1	e_2	e_3	e_4
Ammonium chloride	25.00	-1.794E-04	5.332E-03	-7.306E-02	1.487E-01
Ammonium nitrate	25.00	2.243E-02	-2.390E-02	1.019E-02	-1.507E-03
Barium chloride	25.00	-1.799E-01	1.728E-01	-1.145E-01	2.482E-02
Cadmium sulfate	25.00	-1.432E-02	-3.850E-01	3.593E-01	-1.065E-01
Calcium chloride	25.00	-7.180E-02	-4.104E-01	4.089E-01	-1.061E-01
Cupric sulfate	25.00	-2.147E+00	8.837E-01	-2.147E+00	1.583+00
Hydrochloric acid	25.00	5.701E-03	5.033E-02	-3.766E-02	5.330E-03
Lanthanum chloride	25.00	-2.513E-01	8.428E-01	-1.761E+00	1.191E+00
Lithium chloride	25.00	-6.425E-02	1.322E-02	8.512E-03	-5.660E-03
Lithium chloride	35.00	-9.345E-02	8.142E-02	-4.677E-02	7.469E-03
Lithium chloride	50.00	4.072E-02	-1.128E-01	4.658E-02	-5.765E-03
Lithium nitrate	25.00	-1.009E-01	5.560E-02	-1.221E-02	1.728E-03
Nitric acid	25.00	5.042E-02	-6.941E-02	2.654E-02	-4.364E-03
Phosphoric acid	25.00	-9.210E-02	1.392E-01	-6.049E-02	8.900E-03
Potassium bromide	25.00	4.790E-02	-1.225E-01	1.021E-01	-2.739E-02
Potassium chloride	0.00	-3.450E-02	3.737E-02	-1.794E-02	3.184E-03
Potassium chloride	18.00	-2.930E-02	5.042E-02	-3.496E-02	8.210E-03
Potassium chloride	25.00	-3.006E-03	1.220E-03	-4.576E-05	-9.020E-05

Table A-4 (Continued)

Solute	Temp. (°C)	e_1	e_2	e_3	e_4
Potassium chloride	35.00	-3.825E-03	-1.138E-02	1.350E-02	-3.963E-03
Potassium chloride	50.00	-2.567E-03	-3.911E-03	5.198E-03	-1.615E-03
Potassium iodide	25.00	-5.992E-03	1.793E-02	-1.384E-02	3.263E-03
Potassium sulfate	25.00	4.715E-02	1.340E-01	-7.827E-01	8.458E-01
Silver nitrate	25.00	3.558E-03	4.045E-02	-1.609E-02	4.648E-03
Sodium chloride	0.00	-1.012E-01	1.160E-01	-6.169E-02	1.165E-02
Sodium chloride	18.00	-5.030E-02	2.587E-02	-6.789E-03	4.793E-04
Sodium chloride	25.00	-4.037E-02	2.439E-02	-1.626E-02	4.412E-03
Sodium chloride	35.00	-4.502E-02	1.585E-02	-1.600E-03	-4.913E-04
Sodium chloride	50.00	-2.784E-02	-1.447E-02	1.631E-02	-3.946E-03
Sodium hydroxide	25.00	1.593E-02	-4.255E-01	7.400E-01	-3.691E-01
Sodium iodide	25.00	-2.808E-02	-3.261E-03	7.842E-03	1.280E-02
Sodium sulfate	25.00	1.970E-02	-3.501E-01	1.283E+00	-1.396E+00
Sulfuric acid	25.00	3.731E-02	-7.723E-02	3.988E-02	-9.182E-03
Zinc sulfate	25.00	-4.732E-02	-2.004E-01	1.382E-01	-3.083E-02

Table A-5

Values of Experimental Diffusion Coefficient Equation Parameters for Aqueous Electrolytic Solutions.

Solute	Temp. (°C)	f_1	f_2	f_3	f_4
Ammonium chloride	25.00	-6.936E-06	9.007E-06	-3.147E-06	3.369E-07
Ammonium nitrate	25.00	-6.290E-06	6.354E-06	-3.021E-06	4.586E-07
Barium chloride	25.00	-1.662E-05	3.946E-05	-3.730E-05	1.230E-05
Cadmium sulfate	25.00	3.161E-05	-2.844E-04	6.704E-04	-4.830E-04
Calcium chloride	25.00	-1.367E-05	2.216E-05	-1.077E-05	1.376E-06
Cupric sulfate	25.00	-2.133E-05	5.342E-05	-5.893E-05	2.220E-05
Hydrochloric acid	25.00	-1.908E-05	3.364E-05	-1.637E-05	3.333E-06
Lanthanum chloride	25.00	-5.092E-05	5.205E-05	-3.082E-03	7.229E-03
Lithium chloride	25.00	-4.021E-06	4.175E-06	-8.172E-07	-7.027E-08
Lithium chloride	35.00	-5.025E-06	5.269E-06	-1.247E-06	-1.620E-08
Lithium chloride	50.00	-6.384E-06	6.728E-06	-1.645E-06	-4.619E-08
Lithium nitrate	25.00	-5.208E-06	8.097E-06	-3.868E-06	5.339E-07
Nitric acid	25.00	-1.828E-05	2.998E-05	-1.700E-05	3.506E-06
Phosphoric acid	25.00	-3.627E-05	3.2866E-05	-1.107E-05	1.214E-06
Potassium bromide	25.00	-7.779E-06	1.197E-05	-5.761E-06	1.114E-06
Potassium chloride	0.00	-3.636E-06	5.333E-06	-2.594E-06	5.717E-07
Potassium chloride	18.00	-6.523E-06	9.671E-06	-5.125E-06	1.118E-06
Potassium chloride	25.00	-7.771E-06	1.136E-05	-5.664E-06	1.101E-06

Table A-5 (Continued)

Solute	Temp. (°C)	f_1	f_2	f_3	f_4
Potassium chloride	35.00	-7.808E-06	9.941E-06	-4.205E-06	7.198E-07
Potassium chloride	50.00	-9.866E-06	1.075E-05	-3.368E-06	3.123E-07
Potassium iodide	25.00	-8.794E-06	1.721E-05	-9.928E-06	2.169E-06
Potassium sulfate	25.00	-2.545E-05	7.861E-05	-1.248E-04	6.968E-05
Silver nitrate	25.00	-5.052E-06	-1.233E-06	7.553E-07	-7.074E-08
Sodium chloride	0.00	-3.214E-06	3.894E-06	-1.769E-06	3.141E-07
Sodium chloride	18.00	-4.741E-06	5.546E-06	-2.325E-06	3.486E-07
Sodium chloride	25.00	-6.170E-06	8.487E-06	-4.331E-06	7.929E-07
Sodium chloride	35.00	-6.457E-06	7.172E-06	-2.617E-06	2.947E-07
Sodium chloride	50.00	-6.459E-06	5.447E-06	-1.077E-06	-6.384E-08
Sodium hydroxide	25.00	-8.992E-06	9.114E-06	-5.131E-06	1.180E-06
Sodium iodide	25.00	-5.589E-06	1.005E-05	-4.906E-06	9.811E-07
Sodium sulfate	25.00	-1.743E-05	5.472E-05	-7.797E-05	3.832E-05
Sulfuric Acid	25.00	-4.172E-05	6.532E-05	-3.610E-05	6.974E-06
Zinc sulfate	25.00	-3.465E-05	2.525E-04	-7.311E-04	6.856E-04

Table A-6

Values of Activity Coefficient Equation Parameters for Aqueous Electrolytic Solutions.

Solute	Temp. (°C)	g_1	g_2	g_3	g_4	g_5	g_6
Ammonium chloride	25.00	-1.131E+00	1.496E-01	-1.783E-01	1.219E-01	-3.861E-02	4.476E-03
Ammonion nitrate	25.00	-1.226E+00	-3.813E-02	-6.071E-02	3.215E-02	-5.961E-03	3.902E-04
Barium chloride	25.00	-3.499E+00	2.216E+00	-1.918E+00	-5.684E-02	9.574E-01	-3.631E-01
Cadmium sulfate	25.00	-1.205E+01	1.816E+01	-3.810E+01	3.697E+01	-1.726E+01	3.110E+00
Calcium chloride	25.00	-3.487E+00	2.638E+00	-3.033E+00	1.928E+00	-5.339E-01	5.223E-02
Curpic sulfate	25.00	-1.066E+01	1.272E+01	-2.632E+01	2.652E+01	-1.360E+01	2.854E+00
Hydrochloric acid	25.00	-1.311E+00	1.446E+00	-2.302E+00	1.839E+00	-6.226E-01	7.535E-02
Lanthanun chloride	25.00	-8.794E+00	3.703E+01	-2.044E+02	5.535E+02	-4.065E+02	-4.979E+02
Lithium chloride	25.00	-1.216E+00	6.642E-01	-5.373E-01	2.810E-01	-5.962E-02	4.267E-03
Lithium chloride	35.00	----	----	-----	----	----	----
Lithium chloride	50.00	----	----	-----	----	----	----
Lithium nitrate	25.00	-1.137E+00	4.324E-01	-2.663E-01	1.373E-01	-3.538E-02	3.307E-03
Nitric acid	25.00	-1.094E+00	3.414E-01	-5.287E-02	-1.158E-01	1.015E-01	-2.253E-02
Phosphoric acid	25.00	----	----	-----	----	----	----
Potassium bromide	25.00	-1.140E+00	2.145E-01	-2.412E-01	1.533E-01	-4.504E-02	5.012E-03
Potassium chloride	0.00	----	----	-----	----	----	----
Potassium chloride	18.00	----	----	-----	----	----	----
Potassium chloride	25.00	-1.172E+00	2.975E-01	-4.553E-01	3.387E-01	-1.158E-01	1.516E-02
Potassium chloride	35.00	----	----	-----	----	----	----

Table A-6 (Continued)

Solute	Temp. (°C)	g_1	g_2	g_3	g_4	g_5	g_6
Potassium chloride	50.00	----	----	----	----	----	---
Potassium iodide	25.00	-1.145E+00	4.003E-01	-5.188E-01	3.637E-01	-1.203E-01	1.493E-02
Potassium sulfate	25.00	-2.278E+01	-1.160E+01	4.997E+01	-9.021E+01	7.428E+01	-2.276E+01
Silver nitrate	25.00	-1.153E+00	-3.534E-01	8.577E-02	-1.015E-03	-1.776E-03	1.478E-04
Sodium chloride	0.00	----	----	----	----	----	---
Sodium chloride	18.00	----	----	----	----	----	---
Sodium chloride	25.00	-1.151E+00	3.775E-01	-4.318E-01	2.827E-01	-8.301E-02	9.384E-03
Sodium chloride	35.00	----	----	----	----	----	---
Sodium chloride	50.00	----	----	----	----	----	---
Sodium hydroxide	25.00	-1.329E+00	6.953E-01	-6.831E-01	3.102E-01	-4.829E-02	7.432E-04
Sodium iodide	25.00	-1.140E+00	3.677E-01	-1.930E-02	-2.085E-01	1.553E-01	-3.199E-02
Sodium sulfate	25.00	-3.655E+00	-8.023E-01	5.983E+00	-9.948E+00	6.617E+00	-1.580E+00
Sulfuric acid	25.00	-6.743E+00	4.550E+00	-5.834E+00	3.549E+00	-1.033E+00	1.166E-01
Zinc sulfate	25.00	-1.0549E+01	1.234E+01	-2.249E+01	1.856E+01	-7.322E+00	1.129E+00

Table A-7

Values of Thermodynamic Diffusion Coefficient Equation Parameters for Aqueous Electrolytic Solutions.

Solute	Temp. (°C)	h_1	h_2	h_3	h_4
Ammonium chloride	25.00	1.131E-06	1.441E-07	-9.401E-07	2.173E-07
Ammonium nitrate	25.00	2.0597E-06	1.705E-07	4.376E-08	-1.473E-07
Barium chloride	25.00	6.208E-06	-2.212E-05	1.789E-05	-5.682E-06
Cadmium sulfate	25.00	1.0398E-04	-5.864E-04	1.162E-03	-7.565E-04
Calcium chloride	25.00	3.083E-06	-1.352E-05	6.564E-06	-9.906E-07
Cupric sulfate	25.00	2.255E-05	-4.796E-05	3.800E-05	-1.314E-05
Hydrochloric acid	25.00	-7.306E-06	1.580E-05	-1.923E-05	5.626E-06
Lanthanum chloride	25.00	5.530E-06	-2.040E-05	1.806E-04	-1.010E-03
Lithium chloride	25.00	6.371E-07	-4.382E-06	1.161E-06	-6.664E-08
Lithium chloride	35.00	1.825E-06	-8.577E-06	3.514E-06	-4.801E-07
Lithium chloride	50.00	6.842E-06	-2.042E-05	9.064E-06	-1.223E-06
Lithium nitrate	25.00	6.850E-07	-3.121E-06	4.306E-07	5.771E-08
Nitric acid	25.00	-9.953E-06	1.814E-05	-1.697E-05	4.341E-06
Phosphoric acid	25.00	-1.428E-05	1.031E-05	-4.038E-06	5.194E-07
Potassium bromide	25.00	1.0296E-06	2.659E-07	-1.092E-06	2.228E-07
Potassium chloride	0.00	8.276E-07	-8.817E-07	1.015E-07	-1.430E-07
Potassium chloride	18.00	1.409E-06	-2.632E-06	2.429E-07	8.300E-08
Potassium chloride	25.00	1.519E-06	-1.223E-06	-5.202E-08	-4.362E-08

Table A-7 (Continued)

Solute	Temp. (°C)	h_1	h_2	h_3	h_4
Potassium chloride	35.00	4.173E-06	-9.374E-06	4.552E-06	-9.541E-07
Potassium chloride	50.00	5.843E-06	-1.443E-05	7.717E-06	-1.715E-06
Potassium iodide	25.00	-7.516E-07	6.671E-06	-7.008E-06	1.908E-06
Potassium sulfate	25.00	1.669E-05	-9.018E-05	1.916E-04	-1.373E-04
Silver nitrate	25.00	2.318E-06	-2.115E-06	1.570E-06	-4.037E-07
Sodium chloride	0.00	4.190E-07	-2.177E-06	9.203E-07	-2.322E-07
Sodium chloride	18.00	9.451E-07	-3.866E-06	1.101E-06	-1.785E-07
Sodium chloride	25.00	8.094E-07	-1.865E-06	-6.419E-07	2.596E-07
Sodium chloride	35.00	8.605E-07	-5.989E-06	2.968E-06	-7.916E-07
Sodium chloride	50.00	4.772E-06	-1.303E-05	4.581E-06	-5.786E-07
Sodium hydroxide	25.00	3.863E-06	-2.347E-05	2.235E-05	-7.253E-06
Sodium iodide	25.00	1.619E-06	-4.175E-06	1.741E-06	-5.087E-07
Sodium sulfate	25.00	6.965E-06	2.519E-06	-3.469E-05	2.802E-05
Sulfuric acid	25.00	1.394E-05	-2.881E-05	1.355E-05	-2.240E-06
Zinc sulfate	25.00	6.433E-06	2.294E-04	-1.017E-03	1.112E-03

Table A-8

Values of $_{o+}$ Equation Parameters for Aqueous Electrolytic Solutions.

Solute	Temp. (°C)	k_1	k_2	k_3	k_4
Ammonium chloride	25.00	-2.960E-03	2.526E-02	-7.103E-02	6.561E-02
Ammonium nitrate	25.00	3.009E-06	-7.605E-07	4.401E-07	-2.094E-07
Barium chloride	25.00	9.128E-07	-1.016E-05	9.127E-06	-3.073E-06
Cadmium sulfate	25.00	8.559E-05	-4.881E-04	9.577E-04	-6.183E-04
Calcium chloride	25.00	8.236E-07	-1.423E-05	1.404E-05	-4.752E-06
Cupric sulfate	25.00	1.570E-05	-3.210E-05	1.145E-05	5.576E-06
Hydrochloric acid	25.00	-1.999E-05	8.383E-05	-9.014E-05	2.390E-05
Lanthanum chloride	25.00	-3.325E-07	7.523E-07	5.732E-05	-4.313E-04
Lithium chloride	25.00	6.371E-07	-4.382E-06	1.161E-06	-6.664E-08
Lithium chloride	35.00	-1.026E-07	-5.438E-06	2.274E-06	-3.011E-07
Lithium chloride	50.00	6.639E-06	-2.005E-05	9.969E-06	-1.576E-06
Lithium nitrate	25.00	-1.116E-06	-1.203E-06	6.442E-08	6.077E-08
Nitric acid	25.00	2.231E-06	4.562E-06	-2.781E-05	9.466E-06
Phosphoric acid	25.00	-1.285E-04	1.453E-04	-6.316E-05	8.918E-06
Potassium bromide	25.00	2.853E-06	-4.468E-06	2.862E-06	-8.327E-07
Potassium chloride	0.00	1.423E-07	-1.493E-07	-2.317E-07	-8.410E-08
Potassium chloride	18.00	4.509E-07	-1.012E-06	-8.210E-07	3.269E-07
Potassium chloride	25.00	1.374E-06	-1.157E-06	-4.884E-08	-4.613E-08

Table A-8

Solute	Temp. (°C)	k_1	k_2	k_3	k_4
Potassium chloride	35.00	3.891E-06	-9.647E-06	5.043E-06	-1.103E-06
Potassium chloride	50.00	5.499E-06	-1.421E-05	7.782E-06	-1.715E-06
Potassium iodide	25.00	-9.729E-07	7.241E-06	-7.410E-06	1.997E-06
Potassium sulfate	25.00	2.314E-05	-1.086E-04	2.091E-04	-1.370E-04
Silver nitrate	25.00	2.256E-06	-6.021E-07	9.125E-07	-1.406E-07
Sodium chloride	0.00	-7.270E-07	-4.564E-07	4.447E-08	-4.769E-08
Sodium chloride	18.00	-1.635E-07	-2.586E-06	7.812E-07	-1.366E-07
Sodium chloride	25.00	-1.798E-07	-1.159E-06	-6.288E-07	2.415E-07
Sodium chloride	35.00	-5.842E-07	-4.258E-06	2.292E-06	-6.248E-07
Sodium chloride	50.00	2.767E-06	-1.103E-05	4.4096E-06	-6.340E-07
Sodium hydroxide	25.00	2.599E-06	-2.114E-05	2.558E-05	-1.033E-05
Sodium iodide	25.00	7.205E-07	-3.579E-06	1.861E-06	-3.077E-07
Sodium sulfate	25.00	8.010E-06	-5.458E-06	-7.742E-06	-1.977E-06
Sulfuric acid	25.00	6.951E-05	-1.444E-04	7.030E-05	-1.164E-05
Zinc sulfate	25.00	5.112E-06	1.808E-04	-8.215E-04	9.047E-04

Table A-9

Values of $_{o}$- Equation Parameters for Aqueous Electrolytic Solutions.

Solute	Temp. (°C)	k_1	k_2	k_3	k_4
Ammonium chloride	25.00	-2.960E-03	2.526E-02	-7.103E-02	6.560E-02
Ammonium nitrate	25.00	1.179E-06	1.037E-06	-3.269E-07	-8.895E-08
Barium chloride	25.00	1.757E-05	-3.788E-05	2.631E-05	-7.445E-06
Cadmium sulfate	25.00	1.328E-04	-7.411E-04	1.504E-03	-9.937E-04
Calcium chloride	25.00	7.963E-06	5.066E-07	-3.598E-06	-3.351E-06
Cupric sulfate	25.00	3.594E-05	-8.517E-05	1.257E-04	-8.129E-05
Hydrochloric acid	25.00	-4.566E-06	8.240E-06	-1.039E-05	3.130E-06
Lanthanum chloride	25.00	1.946E-05	-6.080E-05	3.474E-04	-1.712E-03
Lithium chloride	25.00	4.964E-06	-6.791E-06	1.908E-07	4.607E-07
Lithium chloride	35.00	1.225E-05	-2.291E-05	1.045E-05	-1.628E-06
Lithium chloride	50.00	4.923E-06	-1.466E-05	4.103E-06	-9.094E-08
Lithium nitrate	25.00	7.112E-06	-7.708E-06	6.387E-07	2.154E-07
Nitric acid	25.00	-7.135E-06	1.259E-05	-1.090E-05	2.708E-06
Phosphoric acid	25.00	-7.134E-06	4.515E-06	-1.723E-06	2.191E-07
Potassium bromide	25.00	-9.931E-07	5.514E-06	-5.478E-06	1.394E-06
Potassium chloride	0.00	1.524E-06	-1.548E-06	3.225E-07	-1.519E-07
Potassium chloride	18.00	2.441E-06	-4.372E-06	1.387E-06	-1.798E-07
Potassium chloride	25.00	1.674E-06	-1.292E-06	-5.649E-08	-4.062E-08

Table A-9 (Continued)

Solute	Temp. (°C)	k_1	k_2	k_3	k_4
Potassium chloride	35.00	4.475E-06	-9.039E-06	3.983E-06	-7.825E-07
Potassium chloride	50.00	6.217E-06	-1.465E-05	7.622E-06	-1.625E-06
Potassium iodide	25.00	-5.093E-07	6.043E-06	-6.562E-06	1.808E-06
Potassium sulfate	25.00	1.053E-05	-6.611E-05	1.526E-04	-1.165E-04
Silver nitrate	25.00	2.342E-06	-3.928E-06	2.286E-06	-5.688E-07
Sodium chloride	0.00	3.251E-06	-5.870E-06	2.698E-06	-5.865E-07
Sodium chloride	18.00	3.469E-06	-6.011E-06	1.440E-06	-1.978E-07
Sodium chloride	25.00	3.022E-06	-3.064E-06	-6.230E-07	2.508E-07
Sodium chloride	35.00	4.020E-06	-8.715E-06	3.863E-06	-1.031E-06
Sodium chloride	50.00	8.490E-06	-1.506E-05	3.861E-06	-2.825E-07
Sodium hydroxide	25.00	3.747E-06	7.090E-05	1.708E-04	9.499E-05
Sodium iodide	25.00	3.487E-06	-4.680E-06	9.874E-07	-9.480E-07
Sodium sulfate	25.00	5.438E-06	1.271E-05	-6.847E-05	6.589E-05
Sulfuric acid	25.00	5.219E-06	-1.079E-05	5.052E-06	-8.352E-07
Zinc sulfate	25.00	8.575E-06	3.112E-04	-1.328E-03	1.441E-03

Table A-10

Values of $_{+-}$ Equation Parameters for Aqueous Electrolytic Solutions.

Solute	Temp. (°C)	ℓ_1	ℓ_2	ℓ_3	ℓ_4
Ammonium chloride	25.00	2.255E-06	-5.140E-06	4.045E-06	6.460E-06
Ammonium nitrate	25.00	8.357E-07	6.137E-07	-1.975E-07	1.932E-09
Barium chloride	25.00	-1.555E-07	3.564E-06	-4.846E-06	2.539E-06
Cadmium sulfate	25.00	1.478E-08	1.240E-07	-1.583E-07	8.798E-08
Calcium chloride	25.00	3.303E-07	1.106E-07	8.119E-07	-6.518E-07
Cupric sulfate	25.00	2.131E-08	1.073E-07	-1.612E-07	1.185E-07
Hydrochloric acid	25.00	1.589E-05	-3.492E-05	3.747E-05	-1.096E-05
Lanthanum chloride	25.00	6.533E-08	3.737E-06	-2.545E-05	5.952E-05
Lithium chloride	25.00	6.206E-07	3.867E-07	2.625E-07	-1.497E-07
Lithium chloride	35.00	-2.084E-06	6.096E-06	-3.119E-06	4.589E-07
Lithium chloride	50.00	1.870E-06	-2.427E-06	4.114E-06	-1.321E-06
Lithium nitrate	25.00	2.974E-07	1.099E-06	-4.502E-07	2.703E-08
Nitric acid	25.00	3.977E-05	-8.813E-05	8.033E-05	-2.078E-05
Phosphoric acid	25.00	1.647E-07	1.565E-07	1.327E-07	-5.139E-08
Potassium bromide	25.00	1.138E-06	3.580E-07	8.127E-07	-3.417E-07
Potassium chloride	0.00	5.331E-07	4.107E-07	2.473E-07	8.727E-08
Potassium chloride	18.00	1.309E-06	-7.629E-07	1.928E-06	-5.337E-07
Potassium chloride	25.00	1.065E-06	4.769E-07	5.547E-07	-2.311E-07

Table A-10 (Continued)

Solute	Temp. (°C)	ℓ_1	ℓ_2	ℓ_3	ℓ_4
Potassium chloride	35.00	1.104E-06	1.175E-06	6.806E-07	-2.985E-07
Potassium chloride	50.00	1.372E-06	1.005E-06	1.536E-06	-6.359E.07
Potassium iodide	25.00	1.601E-06	-1.163E-06	2.496E-06	-8.631E-07
Potassium sulfate	25.00	2.442E-07	3.666E-07	9.286E-07	-1.548E-06
Silver nitrate	25.00	7.569E-07	1.963E-07	-2.105E-07	4.048E-08
Sodium chloride	0.00	-2.537E-07	3.117E-06	-3.112E-06	1.040E-06
Sodium chloride	18.00	5.836E-08	3.281E-06	-3.000E-06	1.037E-06
Sodium chloride	25.00	7.747E-07	5.713E-07	1.085E-07	-1.099E-07
Sodium chloride	35.00	-2.878E-06	1.509E-05	-1.438E-05	4.254E-06
Sodium chloride	50.00	-7.340E-07	7.265E-06	-5.416E-06	1.563E-06
Sodium hydroxide	25.00	2.620E-06	-5.721E-06	1.630E-05	-1.003E-05
Sodium iodide	25.00	6.986E-07	1.073E-06	1.515E-07	-8.796E-08
Sodium sulfate	25.00	2.248E-07	1.404E-08	7.009E-07	-7.686E-07
Sulfuric acid	25.00	-9.229E-07	4.672E-06	-1.698E-06	6.206E-08
Zinc sulfate	25.00	3.509E-08	-6.259E-08	4.432E-07	-4.767E-07

APPENDIX B

Binary Diffusion in a Diaphragm Cell

As a result of the work of Stokes[73-75] on the problems outlined by Gordon[19] the diaphragm cell method has been developed into one of the few reliable techniques for determining liquid phase diffusion coefficients (see Chapter V). Its accuracy under careful operation is estimated to be about 0.5 percent from a comparison of results with measurements by the Gouy method. There nevertheless remain several theoretical questions to be answered concerning the analysis of diffusion in a diaphragm cell.

Since the classical analysis is based upon the dilute solution flux equation, the diffusion coefficient which is measured in a concentrated solution has not yet been precisely defined in terms of a frame of reference. The existing analysis also assumes that the volume change of mixing in the solution over the course of the diffusion experiment is negligible. In order to minimize the effect of errors in chemical analysis, experiments are made with as great a concentration difference as possible. For this reason the assumption of no volume change may contribute significantly to the experimental error in the determination of diffusion coefficients in concentrated solutions. To investigate these questions we have applied the equations of Chapter III to achieve a more complete analysis of binary diffusion in a diaphragm cell.

Analysis of the Method

We consider a cell of the type employed by Stokes. Two well-stirred volumes of solution are separated by a porous diaphragm of thickness L. Properties of the lower, more concentrated solution are denoted by the superscript ‡ and those of the upper solution by the superscript °.

The volume of the lower compartment $V^{\ddagger}$ is fixed, but the upper volume V° may change to allow for any volume changes of mixing since it is vented through a capillary. The effective cross-sectional area for diffusion through the diaphragm is A. Toor[80] has justified the application of a one-dimensional model for diffusion in the complex pore geometry. The assumption of a quasi-steady state in the diaphragm, which has been justified by Barnes[1] and Gordon,[19] will be maintained here.

The equations which govern the diffusion of a concentrated solution in the diaphragm are (III-22) with (III-23) and (III-29), (III-4), and (I-1):

$$\underline{N}_s = - D_M \left(1 - \frac{d\,\ell n\, c_o}{d\,\ell n\, c}\right) \nabla c + c\,\underline{v}_o \tag{B-1}$$

$$\underline{N}_o = c_o\,\underline{v}_o \tag{B-2}$$

$$\frac{\partial c}{\partial t} = - \nabla\cdot\underline{N}_s \tag{B-3}$$

and

$$\frac{\partial c_o}{\partial t} = - \nabla\cdot\underline{N}_o \tag{B-4}$$

where ∇ becomes $\frac{\partial}{\partial y}$ where y is the distance through the diaphragm measured from the bottom surface. Since the density is given by

$$\rho = M_s c + M_o c_o , \tag{B-5}$$

another condition which applies is

$$\frac{\partial \rho}{\partial t} = M_s \frac{\partial c}{\partial t} + M_o \frac{\partial c_o}{\partial t} \; . \tag{B-6}$$

Equation (B-6) may be rewritten as

$$\nabla\cdot\underline{N}_s \left(\frac{\partial \rho}{\partial c} - M_s\right) = M_o\; \nabla\cdot\underline{N}_o \; . \tag{B-7}$$

Since the bottom volume is constant,

$$V^{\ddagger} \frac{dc^{\ddagger}}{dt} = - A N_s \tag{B-8}$$

and

$$V^{\ddagger} \frac{dc_o^{\ddagger}}{dt} = - A N_o \tag{B-9}$$

at y = 0. By means of Eqs. (B-6) and (B-8), Eq. (B-9) may be rewritten as

$$N_s \left(\frac{d\rho}{dc} - M_s \right) = -N_o M_o \quad . \tag{B-10}$$

In the top compartment, material balances give

$$\frac{d(c^{\circ}V^{\circ})}{dt} = A N_s \tag{B-11}$$

and

$$\frac{d(c_o^{\circ}V^{\circ})}{dt} = A N_o \tag{B-12}$$

at y = L. These may be rearranged to the following forms:

$$\rho \left(1 - \frac{d \ \ell n \ \rho}{d \ \ell n \ c} \right) \frac{dV^{\circ}}{dt} = A \left[\left(M_s - \frac{d\rho}{dc} \right) N_s + M_o \ N_o \right] \tag{B-13}$$

and

$$\frac{V^{\circ}\rho}{c} \left(1 + \frac{d \ \ell n}{d \ \ell n \ c} \right) \frac{dc}{dt} = A \left[\left(\frac{\rho}{c} - M_s \right) N_s - M_o \ N_o \right] \tag{B-14}$$

at y = L. Equations (B-8), (B-10), (B-13), and (B-14) constitute the necessary boundary conditions for solution of the problem.

Initially the concentrations in the two compartments are known,

$$c^{\ddagger} = c^{\ddagger} \ (0) \tag{B-15}$$

and

$$c^{\circ} = c^{\circ} \ (0) \tag{B-16}$$

at t = 0, and a steady concentration profile is already established. This latter condition is accomplished experimentally by allowing a prediffusion period before a run is started. The usual quasi-steady state approximation which is made is that the volumes V° and $V^{\ddagger}$ are sufficiently large compared to AL that c° and $c^{\ddagger}$ change very slowly and a steady diffusion problem applies in the diaphragm; N_s and N_o are therefore assumed to be constant throughout the diaphragm at any time. Accordingly we seek solutions of the forms

$$c = c^{(1)} + (AL/V^{\ddagger})\, c^{(2)} + \dots \tag{B-17}$$

$$N_s = N_s^{(1)} + (AL/V^{\ddagger})\, N_s^{(2)} + \dots \tag{B-18}$$

$$N_o = N_o^{(1)} + (AL/V^{\ddagger})\, N_o^{(2)} + \dots \tag{B-19}$$

We assume V° is of the same order as $V^{\ddagger}$ so that, as the parameter $(AL/V^{\ddagger})$ goes to zero, the situation becomes a true steady state problem. Application of this limit to Eqs. (B-3) and (B-4) after the series (B-17), (B-18) and (B-19) are substituted indicates that $N_s^{(1)}$ and $N_o^{(1)}$ must be independent of position and therefore represent the quasi-steady state solution. We proceed to solve for $c^{(1)}$, $N_s^{(1)}$, and $N_o^{(1)}$. The superscripts will be dropped with the understanding that N_s and N_o are henceforth taken to be independent of y.

Substituting Eq. (B-2) into Eq. (B-1) and making use of the relation between N_s and N_o, Eq. (B-10), we obtain an expression for the flux:

$$N_s = -D_M \left[\frac{1 - \dfrac{d\,\ln c_o}{d\,\ln c}}{1 - \dfrac{c}{\rho}\left(\dfrac{d\rho}{dc}\right)^{\ddagger}} \right] \frac{c_o M_o}{\rho}\, \frac{dc}{dy} \ . \tag{B-20}$$

Integrated from y = 0 to y = L this becomes

$$N_s L = \int_{c^\circ}^{c^\ddagger} \left[\frac{1 - \frac{d\ \ell n\ c_o}{d\ \ell n\ c}}{1 - \frac{c}{\rho}\left(\frac{d\rho}{dc}\right)^\ddagger} \right] \frac{c_o M_o}{\rho}\ D_M dc \quad . \tag{B-21}$$

The integral diffusion coefficient D^* is defined by the equation

$$\ell n \left(\frac{(c^\ddagger - c^\circ)_{t=0}}{(c^\ddagger - c^\circ)_t} \right) = \left(\frac{1}{V^\ddagger} + \frac{1}{V^\circ_{t=0}} \right) \frac{A}{L}\ D^* t \quad . \tag{B-22}$$

The quantity $\left(\frac{1}{V^\ddagger} + \frac{1}{V^\circ_{t=0}} \right) \frac{A}{L}$ is called the cell constant β and is determined experimentally by measuring the concentration changes in the cell of a solution whose diffusivity is known. The integral diffusion coefficient used for the determination of β must be calculated from the known diffusivity-concentration function. In experiments with other solutions β, a geometrical property of the cell, should be unchanged so that D^* may be calculated from Eq. (B-22). To calibrate the cell as well as to determine the appropriate diffusivity values in systems being measured, it is then necessary to have a relation between D^* and the differential coefficient D_M.

It is convenient to work with the integral diffusion coefficient for a run of vanishingly short duration. Subtraction of Eq. (B-14) from Eq. (B-8) and integration yield

$$\ell n \left(\frac{(c^\ddagger - c^\circ)_{t=0}}{(c^\ddagger - c^\circ)_t} \right) = \int_0^t \frac{AN_s}{(c^\ddagger - c^\circ)} \left[\frac{1}{V^\ddagger} + \frac{1}{V^\circ} \frac{1 - \frac{c^\circ}{\rho^\circ}\left(\frac{d\rho}{dc}\right)^\ddagger_\circ}{1 - \left(\frac{d\ \ell n\ \rho}{d\ \ell n\ c}\right)} \right] dt \tag{B-23}$$

We consider a run of vanishingly short duration and take the limit of Eq. (B-23) as $t \to 0$ to obtain by comparison with Eq. (B-22)

$$D^*_{t=0} = \frac{N_s L}{(c^\ddagger - c^\circ)} \; \frac{\left[\dfrac{1}{V^\ddagger} + \dfrac{1}{V^\circ_{t=0}} \; \dfrac{1 - \dfrac{c^\circ}{\rho^\circ}\left(\dfrac{d\rho}{dc}\right)^\ddagger}{1 - \left(\dfrac{d\,\ell n\,\rho}{d\,\ell n\,c}\right)^\circ}\right]}{\left(\dfrac{1}{V^\ddagger} + \dfrac{1}{V^\circ_{t=0}}\right)} \, . \qquad \text{(B-24)}$$

Substitution of Eq. (B-21) yields:

$$D^*_{t=0} = \frac{\left[\dfrac{1}{V^\ddagger} + \dfrac{1}{V^\circ_{t=0}} \; \dfrac{1 - \dfrac{c^\circ}{\rho^\circ}\left(\dfrac{d\rho}{dc}\right)^\ddagger}{1 - \left(\dfrac{d\,\ell n\,\rho}{d\,\ell n\,c}\right)^\circ}\right] \displaystyle\int_{c^\circ}^{c^\ddagger} \left[\frac{1 - \dfrac{d\,\ell n\,c_o}{d\,\ell n\,c}}{1 - \dfrac{c}{\rho}\left(\dfrac{d\rho}{dc}\right)^\ddagger}\right] \frac{c_o M_o}{\rho} D_M dc}{(c^\ddagger - c^\circ)\left(\dfrac{1}{V^\ddagger} + \dfrac{1}{V^\circ_{t=0}}\right)} \qquad \text{(B-25)}$$

Finally, differentiation of this expression with respect to $c^\ddagger$ gives the desired relation between $D^*_{t=0}$ and D_M:

$$(c^\ddagger - c^\circ)\,\frac{dD^*_{t=0}}{dc^\ddagger} + D^*_{t=0} = \left[\int_{c^\circ}^{c^\ddagger} \frac{c\,D_M(c)}{\rho^2\left[1 - \dfrac{c}{\rho}\left(\dfrac{d\rho}{dc}\right)^\ddagger\right]^2} \, dc\right] \times$$

$$\left\{R\left(\frac{d^2\rho}{dc^2}\right)^\ddagger - T\left(\frac{d^2\rho}{dc^2}\right)^\ddagger\left(\frac{d\rho}{dc}\right)^\ddagger\right\} - T\left(\frac{d^2\rho}{dc^2}\right)^\ddagger \int_{c_o}^{c^\ddagger} \frac{D_M(c)\,dc}{\rho - c\left(\dfrac{d\rho}{dc}\right)^\ddagger} \; +$$

$$\left\{R - T\left(\frac{d\rho}{dc}\right)^\ddagger\right\}\left[\frac{D_M(c^\ddagger)}{\rho^\ddagger - c^\ddagger\left(\dfrac{d\rho}{dc}\right)^\ddagger}\right] \, . \qquad \text{(B-26)}$$

where

$$R = \left\{ \frac{V^{\circ}_{t=0}\left[1 - \left(\frac{d\ell n\ \rho}{d\ell n\ c}\right)^{\circ}\right] + V^{\ddagger}}{\left(V^{\circ}_{t=0} + V^{\ddagger}\right)\left[1 - \left(\frac{d\ \ell n\ \rho}{d\ \ell n\ c}\right)^{\circ}\right]} \right\} c_o^{\ddagger}\ M_o \left(1 - \frac{d\ \ell n\ c_o}{d\ \ell n\ c}\right)^{\ddagger} \qquad \text{(B-27)}$$

and

$$T = \frac{-V^{\ddagger}\ \frac{c^{\circ}}{\rho^{\circ}}\ M_o c_o^{\ddagger}\left(1 - \frac{d\ \ell n\ c_o}{d\ \ell n\ c}\right)^{\ddagger}}{\left(V^{\circ}_{t=0} + V^{\ddagger}\right)\left[1 - \left(\frac{d\ \ell n\ \rho}{d\ \ell n\ c}\right)^{\circ}\right]} \ . \qquad \text{(B-28)}$$

Equation (B-26) is to be compared with the expression

$$(c^{\ddagger} - c^{\circ})\ \frac{dD^{*}_{t=0}}{dc^{\ddagger}} + D^{*}_{t=0} = D_M(c^{\ddagger}) \quad , \qquad \text{(B-29)}$$

which is used by Stokes to determine the differential diffusion coefficient. Before making this comparison, however, we note that Stokes recommends that $c^{\circ}(0)$ be zero to maximize the precision of the method. Under these circumstances, $T = 0$, $R = \rho^{\ddagger} - c^{\ddagger}\ (\frac{d\rho}{dc})^{\ddagger}$, and Eq. (B-26) becomes

$$c^{\ddagger}\ \frac{dD^{*}_{t=0}}{dc} + D^{*}_{t=0} = R\left(\frac{d^2\rho}{dc^2}\right)^{\ddagger} \int_{0}^{c^{\ddagger}} \frac{c\ D_M(c)\ \ dc}{\rho^2\left[1 - \frac{c}{\rho}\left(\frac{d\rho}{dc}\right)^{\ddagger}\right]^2} + D_M(c^{\ddagger}) \qquad \text{(B-30)}$$

Comparison of Eq. (B-30) with Eq. (B-29) now demonstrates the nature of the approximations made in the classical analysis. Exact agreement requires that

$$\left(\frac{d^2\rho}{dc^2}\right)^{\ddagger} = 0$$

since the additional term is of the order of

$$\left(\frac{d^2\rho}{dc^2}\right)\frac{(c^{\ddagger})^2}{2\rho} \quad DM .$$

An estimate of the extra term for KCl with $c^{\ddagger} = 2M$ indicates a magnitude of 1.5×10^{-3} D_M. This approximation may therefore account for some considerable portion of the inaccuracy of this method. We note the great simplification of Eq. (B-26) accomplished by making $c^{\circ}_{t=0}=0$.

The problem remains to relate the measured integral diffusion coefficients for runs of finite duration to $D^{*}_{t=0}$. Stokes accomplished this by replacing the time integral in Eq. (B-23) by the use of mean values of $c^{\ddagger}$ and c° in the integrand. Such a procedure is not rigorous, but it is difficult to avoid severe mathematical complications otherwise. Another way to obtain $D^{*}_{t=0}$ from the data would be to repeat the same run (i.e., with the same initial concentrations) for various lengths of time and to extrapolate D^{*} to t=0. This would require excessive experimental effort. Also measurements at short times becomes increasingly imprecise.

The integral diffusion coefficient is in general given by

$$D^{*} = \frac{1}{t}\int_{0}^{t} \frac{\left[\dfrac{1}{V^{\ddagger}}\,\dfrac{1}{V^{\circ}_{t}} \quad \dfrac{1-\dfrac{c^{\circ}}{\rho^{\circ}}\left(\dfrac{d\rho}{dc}\right)^{\ddagger}}{1-\left(\dfrac{d\ \ell n\ \rho}{d\ \ell n\ c}\right)^{\circ}}\right]}{(c^{\ddagger}-c^{\circ})\left(\dfrac{1}{V^{\ddagger}}+\dfrac{1}{V^{\circ}_{t}}\right)} \int_{c^{\circ}}^{c^{\ddagger}} \left[\frac{1-\dfrac{d\ \ell n\ c_{o}}{d\ \ell n\ c}}{1-\dfrac{c}{\rho}\left(\dfrac{d\rho}{dc}\right)^{\ddagger}}\right]$$

$$\frac{c_{o}M_{o}}{\rho}\ D_{M}dc\ dt \qquad \text{(B-32)}$$

where c°, $c^{\ddagger}$, and V° are functions of time. This equation may be differentiated with respect to time, and the concentration integral may be separated into two definite integrals, each having 0 as one limit. These integrals may then, according to Eq. (B-25), be replaced by terms in

$D^*_{t=0}(c^\ddagger)$ and $D^*_{t=0}(c^\circ)$. Equation (B-22) may be used to eliminate t. The time derivative of D^* may be written in terms of the partial concentration derivatives of D^* and the time derivatives of the concentrations. The former of these are available from Eq. (B-32), and the latter are given by Eqs. (B-13) and (B-14) and related through Eqs. (B-21) and (B-25) to $D^*_{t=0}(c^\ddagger)$ and $D^*_{t=0}(c^\circ)$. The result of these manipulations is an equation, analogous to one of Stokes,* which relates $D^*(c^\ddagger(t), c^\circ(t), c^\ddagger(o))$ to $D^*_{t=0}(c^\ddagger)$ and $D^*_{t=0}(c^\circ)$. According to the results of Stokes, one might expect an iterative procedure for calculating the $D^*_{t=0}$ function from D^* data to converge readily and rapidly.

Thus we find that the use of the complete flux equations given in Chapter III makes it possible to analyze diffusion in a diaphragm cell and to eliminate the assumption of no volume change of mixing. It also provides the necessary equations for relating the measured integral diffusion coefficients to the differential diffusion coefficient more rigorously than has been done in the past.

Experimental Application

Because of its technological importance, we had intended to measure the diffusion coefficient of potassium hydroxide in water. Since these solutions are known to attack glass, we were hesitant to put them into our optical cells. Therefore we decided to construct a diaphragm cell of corrosion-resistant materials for the purpose of studying this system.

A suitable material for the diaphragm was chosen to be sintered zirconium to take the place of the usual porous glass disk. This material has very favorable corrosion-resisting properties and is available commercially with the same pore sizes (about 10 to 15 microns) as are used

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* Equation (8) of reference 74 .

in the glass cells. We purchased a circle of porous zirconium 1-7/8 inches in diameter and 0.10 inch thick welded in a 3.5 inch ring of zircalloy from Clevite Corporation. This plate was sandwiched between two cups, each about 35 cc in volume, machined from lucite. The access hole in each end of the cell was closed by a teflon plug in which there was drilled a capillary hole. The bottom one could be sealed, and the top was left open as a vent. Stirring on the faces of the diaphragm was accomplished by two teflon-coated stirrers. The one on the top was a permanent magnet and the lower one was a nail, which was held up against the diaphragm by the magnet. The latter was driven at 60 rpm by means of permanent magnets which were rotated externally around the cell.

This apparatus was operated in the manner described by Stokes, and measurements were made with potassium chloride solutions in an attempt to determine the cell constant. It was found that a cell constant reproducible within less than several percent could not be obtained.

It is felt that the reason for this failure was that the diaphragm was too thin. The measured cell constant was on the order of 1.5 cm^{-1}. This means that runs must be of about 12 hours duration to maintain a reasonable concentration difference. With such a short run the times involved in setting the cell up and sampling at the end became appreciable, and the run duration was not known precisely. Also the initial condition of a steady state concentration profile in the diaphragm becomes increasingly critical for shorter run durations. Stokes' experiments lasted several days so that these effects were minimal. Another possible problem with a thin diaphragm is that convective velocities caused by the stirrers may reach into the pores for a significant fraction of the diaphragm thickness.

Since in other respects the porous zirconium diaphragm performed satisfactorily, it is felt that such an apparatus can be developed to yield diffusion data of better than one percent accuracy in corrosive systems. It is therefore recommended that a similar zirconium diaphragm, at least 0.3 inch thick, be obtained, tested with potassium chloride solutions, and used to measure diffusivity in strong alkali solutions.

APPENDIX C

Detailed Results of the Analysis of Restricted Diffusion

In Chapter V we have indicated the procedure for solving Eqs. (III-27) and (III-28). When the appropriate substitutions are carried out and terms of equal order in ϵ equated, the following equations result.

From Eq. (III-27),

$$\frac{d\epsilon}{dt}\, c^{(1)} = D_M^{\infty}\, \epsilon\, \frac{d^2c^{(1)}}{dy^2}\,, \qquad \text{(C-1)}$$

$$2c^{(2)}\epsilon\, \frac{d\epsilon}{dt} = D_M^{\infty}\epsilon^2\, \frac{d^2c^{(2)}}{dy^2} + \left(\frac{dD_M}{dc}\right)^{\infty} \epsilon^2 c^{(1)}\, \frac{d^2c^{(1)}}{dy^2} + \qquad \text{(C-2)}$$

$$\left(c_o\bar{V}_o\, \frac{dD}{dc}\right)^{\infty} \epsilon^2 \left(\frac{dc^{(1)}}{dy}\right)^2 - \epsilon^2 v_o^{(1)}\, \frac{dc^{(1)}}{dy}\,,$$

$$3c^{(3)}\epsilon^2\, \frac{d\epsilon}{dt} = D_M^{\infty}\, \epsilon^3\, \frac{d^2c^{(3)}}{dy^2} + \left(\frac{dD_M}{dc}\right)^{\infty} \left[\epsilon^3 c^{(2)}\, \frac{d^2c^{(1)}}{dy^2} + \qquad \text{(C-3)}\right.$$

$$\left.\epsilon^3 c^{(1)}\, \frac{d^2c^{(2)}}{dy^2}\right] + \frac{1}{2}\left(\frac{d^2D_M}{dc^2}\right)^{\infty} \epsilon^3 \left(c^{(1)}\right)^2 \frac{d^2c^{(1)}}{dy^2} +$$

$$2\left(c_o\bar{V}_o\, \frac{dD}{dc}\right)^{\infty} \epsilon^3 \left(\frac{dc^{(2)}}{dy}\right)\left(\frac{dc^{(1)}}{dy}\right) + \left[\frac{d}{dc}\left(c_o\bar{V}_o\, \frac{dD}{dc}\right)\right]^{\infty} \times$$

$$\epsilon^3 c^{(1)} \left(\frac{dc^{(1)}}{dy}\right)^2 - \epsilon^3 v_o^{(1)}\, \frac{dc^{(2)}}{dy} - \epsilon^3 v_o^{(2)}\, \frac{dc^{(1)}}{dy}\,,$$

etc. From Eq. (III-28)

$$\epsilon \frac{dv_o^{(1)}}{dy} + \left(\bar{V}_o \frac{dc_o}{dc} D\right)^\infty \epsilon \frac{d^2c^{(1)}}{dy^2} = 0 , \qquad (C-4)$$

$$\epsilon^2 \frac{dv_o^{(2)}}{dy} + \left(\bar{V}_o \frac{dc_o}{dc} D\right)^\infty \epsilon^2 \frac{d^2c^{(2)}}{dy^2} + \left(\bar{V}_o \frac{dc_o}{dc} \frac{dD}{dc}\right)^\infty \epsilon^2 \frac{d}{dy}\left(c^{(1)} \frac{d^2c^{(1)}}{dy}\right)$$

$$+ \left[D \frac{d}{dc} (\bar{V}_o \frac{dc_o}{dc})\right]^\infty \epsilon^2 c^{(1)} \frac{d^2c^{(1)}}{dy^2} = 0 , \qquad (C-5)$$

etc. And from the boundary conditions,

$$\frac{dc^{(i)}}{dy} \Bigg|_{y=0} =0 , \qquad (C-6)$$

$$v_o^{(i)} \Bigg|_{y=0} =0 , \qquad (C-7)$$

$$\epsilon \left(\frac{dc^{(1)}}{dy}\right)_{y=a^\infty} =0 , \qquad (C-8)$$

$$\epsilon^2 \left(\frac{dc^{(2)}}{dy}\right)_{a^\infty} + \epsilon^2 a^{(1)} \left(\frac{d^2c^{(1)}}{dy^2}\right)_{a^\infty} = 0, \qquad (C-9)$$

$$\epsilon^3 \left(\frac{dc^{(3)}}{dy}\right)_{a^\infty} + \epsilon^3 \left(\frac{d^2c^{(1)}}{dy^2}\right)_{a^\infty} a^{(2)} +$$

$$\epsilon^3 a^{(1)} \left(\frac{d^2c^{(2)}}{dy^2}\right)_{a^\infty} + \frac{1}{2} \epsilon^3 \left(\frac{d^3c^{(1)}}{dy^3}\right)_{a^\infty} \left(a^{(1)}\right)^2 = 0 , \qquad (C-10)$$

$$\rho^\infty \epsilon a^{(1)} + \epsilon \left(\frac{d\rho}{dc}\right)^\infty \int_0^{a^\infty} c^{(1)} dy = 0 , \qquad (C-11)$$

$$\epsilon^2 \rho^\infty a^{(2)} + \left(\frac{d\rho}{dc}\right)^\infty c^{(1)}_{(a^\infty)} \epsilon^2 a^{(1)} + \epsilon^2 \left(\frac{d\rho}{dc}\right)^\infty .$$

$$\int_0^{a^\infty} c^{(2)} dy + \frac{\epsilon^2}{2} \left(\frac{d^2\rho}{dc^2} \right)^\infty \int_0^{a^\infty} {c^{(1)}}^2 dy = 0 \ , \qquad (C\text{-}12)$$

etc.

Equation (C-1) yields ϵ and $c^{(1)}$ to be

$$\epsilon = e^{-D_M^\infty t(\pi/a^\infty)^2} \qquad (C\text{-}13)$$

and

$$c^{(1)} = A_1 \cos (\pi y/a^\infty) \ . \qquad (C\text{-}14)$$

The constant A_1 depends upon the initial concentration distribution.

Now that ϵ and $c^{(1)}$ are known, the remaining equations may be solved one by one. Several of the resulting functions are given below.

$$c^{(2)} = \frac{Q}{2} \left[N + P \cos^2 (\pi y/a^\infty) \right] , \qquad (C\text{-}15)$$

$$c^{(3)} = K \cos (\pi y/a^\infty) + L \cos^3 (\pi y/a^\infty) + My \sin (\pi y/a^\infty). \qquad (C\text{-}16)$$

Also,

$$a^{(1)} = 0 \qquad (C\text{-}17)$$

$$a^{(2)} = - \frac{A_1^2 a^\infty}{4} \left(\frac{\bar{V}_o}{M_o} \quad \frac{d^2\rho}{dc^2} \right)^\infty , \qquad , \ (C\text{-}18)$$

$$v_o^{(1)} = A_1 (\pi/a^\infty) \left(\bar{V}_o \ \frac{dc_o}{dc} D \right)^\infty \sin (\pi y/a^\infty), \qquad (C\text{-}19)$$

and

$$v_o^{(2)} = \sin\left(\pi y/a^{\infty}\right) \cos\left(\pi y/a^{\infty}\right) \left[(J-B) \frac{a^{\infty}}{2\pi} \right] +$$

$$y\frac{(B+J)}{2} - \frac{1}{2} A_1^2 \frac{\pi}{a^{\infty}} \left(\bar{V}_o \frac{dc_o}{dc} \frac{dD}{dc}\right)^{\infty} \left(\frac{\pi y}{a^{\infty}} - \sin \frac{\pi y}{a^{\infty}} \cos \frac{\pi y}{a^{\infty}}\right) . \qquad \text{(C-20)}$$

The various constants appearing above depend upon the properties of the system in the following way:

$$Q = \frac{A_1^2}{D^{\infty}_{M}} , \qquad \text{(C-21)}$$

$$N = \left(\frac{dD_M}{dc}\right)^{\infty} , \qquad \text{(C-22)}$$

$$P = \left[\left(c_o D \frac{d\bar{V}_o}{dc}\right)^{\infty} - 2 \left(\frac{dD_M}{dc}\right)^{\infty} \right] , \qquad \text{(C-23)}$$

$$K = \frac{1}{4} \left\{ \frac{A_1 Q}{D^{\infty}_{M}} \left(\frac{dD_M}{dc}\right)^{\infty} [N + 3P] + \frac{A_1^3}{D^{\infty}_{M}} \left(\frac{d^2 D_M}{dc^2}\right)^{\infty} + \right.$$

$$\left. A_1^{\,3} \left(\frac{D}{D_M} \frac{d\bar{V}_o \frac{dc_o}{dc}}{dc}\right)^{\infty} \right\} , \qquad \text{(C-24)}$$

$$L = \frac{-A_1}{6D_M^{\infty}} \left\{ 5\left(\frac{dD_M}{dc}\right)^{\infty} \frac{PQ}{2} + 2PQ \left(c_o \bar{V}_o \frac{dD}{dc}\right)^{\infty} + \right.$$

$$A_1^2 \left[\frac{d\left(c_o \bar{V}_o \frac{dD}{dc}\right)^{\infty}}{dc}\right] + 2 \left(\bar{V}_o \frac{dc_o}{dc} D\right)^{\infty} PQ +$$

$$\left. \frac{1}{2} A_1^2 \left[\frac{d\left(\bar{V}_o \frac{dc_o}{dc} D\right)^{\infty}}{dc}\right] + \frac{A_1^2}{2} \left(\frac{d^2 D_M}{dc^2}\right)^{\infty} + \frac{A_1^2}{2} \left(\bar{V}_o \frac{dc_o}{dc} \frac{dD}{dc}\right)^{\infty} \right\} \qquad \text{(C-25)}$$

$$M = \frac{-A_1^3 \pi}{4a^\infty} R^\infty , \quad \text{(C-26)}$$

$$B = -S^\infty QP(\pi/a^\infty)^2 , \quad \text{(C-27)}$$

$$J = \left[\left(\frac{dS}{dc} \right)^\infty \left(\frac{\pi A_1}{a^\infty} \right)^2 - B \right] , \quad \text{(C-28)}$$

$$R = \frac{\overline{V}_o}{M_o} \frac{d^2\rho}{dc^2} , \quad \text{(C-29)}$$

and

$$S = \overline{V}_o \frac{dc_o}{dc} D . \quad \text{(C-30)}$$

For an initially sharp boundary at the center of the cell,

$$A_1 = \frac{2(\Delta c)_o}{\pi} . \quad \text{(C-31)}$$

For that initial condition, $a^{(2)}$ may be approximated by

$$a^{(2)} = -\frac{(\Delta c)_o^2 a^\infty}{\pi^2} \left(\frac{\overline{V}_o}{M_o} \frac{d^2\rho}{dc^2} \right)^\infty . \quad \text{(C-32)}$$

For a typical case, 3.0 M KCl in water at 25°C, $(d^2\rho/dc^2) \approx 6\times10^{-4}$ $(\mathrm{gm/cm^3})/(\mathrm{mol^2}/\ell^2)$, and $\overline{V}_o \approx 27\ \mathrm{cm^3/mole}$. Since $(\Delta c)_o$ would be at the most 1.0 mol/ℓ , the magnitude of $a^{(2)}/a^\infty$ would be smaller than 10^{-4}. The variation in "a" is therefore negligible.

NOMENCLATURE

A	effective cross-sectional area in diaphragm (cm^2)
A_n	coefficients of series expression for concentration in restricted diffusion cell
a	height of restricted diffusion cell (cm)
a,b,c	empirical constants introduced in Eq. (IV-3)
$a_i,b_i,d_i,e_i,f_i,g_i,h_i,l_i$	empirical constants given in Appendix A to represent concentration dependence of properties
B	constant identified after Eq. (II-18)
B,J,K,L,M,N,P,Q,R,S	abbreviations for terms arising in Appendix C
c_i	concentration of species i ($moles/cm^3$)
c	concentration of binary electrolyte $= \frac{c_+}{\nu_+} = \frac{c_-}{\nu_-}$ ($moles/cm^3$).
c_o	concentration of solvent
c_T	total solution concentration
D	molecular diffusion coefficient of binary electrolyte (cm^2/sec)
D_i	diffusion coefficient of species i (cm^2/sec)
D_m	diffusion coefficient of electrolyte defined by Eq. (III-29) (cm^2/sec)
D^*	integral diffusion coefficient (cm^2/sec)
$D^*_{t=0}$	diaphragm cell integral diffusion coefficient for a run of vanishingly short duration (cm^2/sec)
D	diffusion coefficient of electrolyte (Chapter III)(cm^2/sec)
D_{ij}	diffusion coefficient for binary interactions (cm^2/sec)
E	constant defined following Eq. (III-33)
e	electronic charge (coulombs)
F	Faraday's constant (coulomb/equiv)

G	function defined by Eq. (IV-1) $((°K)^{3/2}/(\text{mole/liter})^{1/2})$
$\underline{i}$	current density (amp/cm^2)
k	Boltzmann's constant (erg/deg molecule)
L	effective length of pores in diaphragm (cm)
ℓ	thickness of medium through which light passes to generate interence (cm)
M	ρ/c_T, average molecular weight of solution (Chapter III)
M	abbreviation for molarity, i.e., moles/liter
M_i	molecular weight of species i
m	order of interference fringe
N	normality (equiv/cm^3)
$\underline{N}_i$	flux of species i (moles/cm^2 sec)
n	number of electrons involved in electrode reaction
$\underline{n}_i$	flux of species i relative to mass-average velocity (moles/cm^2 sec)
q	constant defined in Eq. (II-19)
R	universal gas constant (joule/mole-deg)
R_i	rate of homogeneous generation of species i (moles/cm^3 sec)
R, T	abbreviations for terms arising in Appendix B
s_i	stoichiometric coefficient of species i for electrode reaction
T	Temperature (deg K)
t	time (sec)
t_j	transference number of species j (in particular, with respect to mass-average velocity)
t_j^o	transference number of species j with respect to the solvent
t_j^*	transference number of species j with respect to molar-average velocity
u_i	mobility of species i (cm^2-mole/joule sec)

V	volume of compartment of diaphragm cell (cm^3)
$\bar{V}_o$	partial molar volume of solvent (cm^3/mole)
$\underline{v}$	fluid velocity (specifically mass-average velocity)(cm/sec)
$\underline{v}_o$	velocity of solvent (cm/sec)
$\underline{v}_i$	velocity of species i (cm/sec)
$\underline{v}^*$	molar average velocity (cm/sec)
x_i	mole fraction of species i
y	mean activity coefficient on concentration scale
y	position coordinate in diffusion cells (cm)
z_i	valence or charge number of species i
β	diaphragm cell constant (cm^{-1})
γ	mean molal activity coefficient
ϵ	dielectric constant (Chapters II-IV)
ϵ	perturbation parameter introduced in Eq. (V-8)
κ	specific conductance (ohm/cm)
Λ	equivalent conductance (cm^2/ohm equiv)
λ_i	ionic equivalent conductance (cm^2/ohm equiv)
λ	wavelength of light (cm)
μ	viscosity (centipoise)
μ	refractive index (Chapter V)
μ_i	electrochemical potential of species i (joule/mole)
μ_e	chemical potential of salt in binary electrolyte (joule/mole)
ν	$\nu_+ + \nu_-$
ν_+ , ν_-	numbers of cations and anions produced by dissociation of one molecule of electrolyte

ρ	density of solution (gm/cm^3)
ρ_i	mass density of species i (gm/cm^3)
Φ	electrostatic potential (volts)

Superscripts

∞	indicates values at infinite time, i.e., uniform concentration
(i)	identifies coefficients of terms in singular perturbation expansion series, Eq. (V-8) and following
o	indicates properties at infinite dilution
o	indicates properties in top compartment of diaphragm cell (Appendix B)
$\ddagger$	indicates properties in bottom compartment of diaphragm cell (Appendix B)

Subscripts

o	indicates property of solvent
$+, -$	indicate properties of cations and anions
e	indicates properties of electrolyte
$t=0, 0$	indicate values at zero time

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