tions," NATO Inst. on Decomposition, Cambridge, England (1972).
Rose, D. J., and R. A. Willoughby (eds.), *Sparse Matrices and Their Applications,* Plenum Press, New York (1972).
Rosen, J. B., "The Gradient Projection Method for Non-linear Programming, Part I, Linear Constraints," *J. Soc. Ind. Appl. Math.,* 8, 181 (1960).
Rudd, D. F., and C. C. Watson, *Strategy of Process Engineering,* pp. 34-69, Wiley, New York (1968).
Sargent, R. W. H., and A. W. Westerberg, "'SPEED-UP' in Chemical Engineering Design," *Trans. Instn. Chem. Engrs.,* 42, T190 (1964).
Sauer, R. N., A. R. Colville, Jr., and C. W. Burwick, *Hydrocarbon Process. Petrol. Refiner,* 43, 84 (1964).
Van de Panne, C., and W. Popp, *Management Sci.,* 9, 405 (1963).
Westerberg, A. W., and F. C. Edie, "Computer Aided Design, Parts 1 and 2," *Chem. Eng. J.,* 2, 9, 17 (1971).
Westerberg, A. W., "Decomposition Methods for Solving Steady State Process Design Problems," NATO Inst. on Decomp., Cambridge, England (1972).
Wilde, D. J., and C. S. Beightler, *Foundations of Optimization,* p. 35, Prentice-Hall, Englewood Cliffs, N. J. (1967).

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Restricted Diffusion in Binary Solutions

Diffusion coefficients of binary solutions can be measured accurately by observation at long times of isothermal diffusion in a vertical cell closed at the ends (restricted diffusion). The present analysis, which accounts for the effects of solvent flux and variable solution properties, demonstrates that the experiment yields a well-defined, differential diffusion coefficient, even in concentrated solutions.

Observation is effected by Rayleigh interference optics, and results for aqueous potassium chloride solutions confirm the accuracy of the method.

JOHN NEWMAN and
THOMAS W. CHAPMAN

Inorganic Materials Research Division
Lawrence Berkeley Laboratory and
Department of Chemical Engineering
University of California, Berkeley, California

SCOPE

Accurate values of diffusion coefficients of binary mixtures, including their dependence on composition and temperature, are required to provide complete transport-property data (somewhat analogous to thermodynamic data like activity coefficients), to permit quantitative design of separation processes like distillation and electrochemical deposition, and to permit detailed comparison with theoretical results. Among theoretical results we have in mind, on the one hand, the treatment of simple systems where variable physical properties have been included in the analysis and, on the other hand, the theoretical prediction or correlation of transport properties on a molecular basis such as the Debye-Hückel theory.

For binary solutions of electrolytes, three methods are used to measure the diffusion coefficient: the magnetically stirred diaphragm cell, optical observation of diffusion from an initially sharp boundary, and (restricted) diffusion in a box of finite height with observation of the concentration distribution by measurement of the electrical conductivity at two positions in the box. The last method, developed by Harned beginning in 1949, appeals to the intuition because the maximum concentration difference in the system vanishes as the experiment progresses, and an absolute determination of the diffusion coefficient requires only the height of the box.

One question we raise is just what diffusion coefficient is measured and is this complicated by the reference velocity for the diffusion flux, the precise definition of transport properties for concentrated solutions, or the variation of physical properties with composition?

Harned's method is restricted to very dilute solutions of electrolytes because adequate resistance measurement with solutions of higher conductivity requires larger cell dimensions where free convection becomes a problem. The second question is how can the method be extended to concentrated solutions?

CONCLUSIONS AND SIGNIFICANCE

An analysis of the restricted diffusion process shows that the measurement yields the differential diffusion coefficient D at the final average concentration. This is the diffusion coefficient which appears in the flux Equations (13) (where Q can be set equal to zero) and is related to the fundamental diffusion coefficient $\mathfrak{D}$ by Equation (15). D is equivalent to the binary diffusion coefficient $\mathfrak{D}_{AB}$ used by Bird, Stewart, and Lightfoot.

The analysis with variable physical properties gives a new form, different from previous results, for the correction to the dominant behavior of the cell. This permits quantitative determination of the time after which this perturbation would become negligible. The detailed analysis also permits one to estimate how much the height of the liquid column changes during the course of the experiment due to volume changes on mixing (or diffusion).

T. W. Chapman is with the Department of Chemical Engineering, University of Wisconsin, Madison, Wisconsin 53706.

This relates to the uncertainty in the value to be used for the height of the box in the determination of the diffusion coefficient.

To overcome the restriction to dilute electrolytic solutions, apparatus was procured and adapted for observing the concentration profile by Rayleigh interference optics. The refractive index varies enough with composition for most liquid solutions to permit measurement with a conveniently sized cell. Solutions of nonelectrolytes are also subject to measurement, with some accuracy being lost at high dilutions or for solutes with low solubility.

The accuracy of this system is 0.1 to 0.2% on the basis of the internal consistency and the reproducibility of the data and also from comparison with results of free diffusion from an initially sharp boundary. The system is thus capable of providing accurate data for a variety of binary systems of chemical-engineering importance over a range of composition and temperature.

A number of years ago, Onsager (see Harned and French, 1945) devised an ingenious technique for measuring quite accurately the diffusion coefficients of electrolytes in solution at concentrations as low as 10^{-3} molar. In the following decade, Harned and co-workers reported results for many electrolytes. The great significance of this work was that the experimental results for many systems verified, for the first time, the theoretical Nernst (1888) limiting value of the diffusion coefficient at infinite dilution and permitted comparison with the theoretical concentration dependence at high dilutions.

The essential features of Harned's method are that it involves a cell of finite length such that diffusion is of the restricted type (Longsworth, 1945) and that the decay of an initial concentration gradient with time is monitored by a conductivity difference between two points in the cell. Although the conductivity measurement limits applicability of the method to dilute solutions, the upper limits of Harned's measurements for several systems agree quite well with the low concentration measurements of the Gouy optical method as developed by Gosting (1950). The accuracies of these two methods thus appear to be comparable and are claimed to be about one- or two-tenths of a percent. Furthermore, these two absolute methods are complimentary in their ranges of applicability, and together they provide the data necessary to calibrate the third important method for diffusion-coefficient measurement, the diaphragm cell, as refined by Stokes (1950a, b, 1951).

The analyses of these three experimental methods on the basis of transport relations valid only in the limit of infinite dilution and with constant physical properties leave unanswered the question of just what diffusion coefficient is measured. The strong concentration dependence of physical properties might show up in dilute solution, and the nonzero solvent flux might manifest itself in more concentrated solutions. A significant concentration difference is always present in the Gouy free-diffusion measurements and in the diaphragm-cell measurements. On the other hand, the concentration difference disappears in restricted diffusion at long times, permitting an unambiguous measurement of the differential diffusion coefficient. Furthermore, the present analysis provides a quantitative expression of the distortion of the concentration profile due to these nonideal effects.

SIMPLIFIED ANALYSIS OF RESTRICTED DIFFUSION

For a dilute, constant-property solution, Fick's second law in one dimension takes the form

$$\frac{\partial c}{\partial t} = D \frac{\partial^2 c}{\partial y^2} \tag{1}$$

and its solution for an enclosed column of height a is a Fourier series (Harned and French, 1945):

$$c = c^\infty + \sum_{n=1}^{\infty} A_n \exp\left(-\frac{n^2 \pi^2 D t}{a^2} \right) \cos \frac{n \pi y}{a} \tag{2}$$

where D is the diffusion coefficient, y is the distance from the bottom of the cell, t is time, and c^∞ is the uniform solute concentration at infinite time. The coefficients A_n depend upon the initial distribution of solute in the cell.

The experimentalists always look at the difference in concentration between $y = a/6$ and $y = 5a/6$. Because a number of terms cancel or vanish, the expression for this concentration difference becomes

$$\Delta c = c\left(\frac{a}{6}\right) - c\left(\frac{5a}{6}\right) = 2A_1 \exp\left(-\frac{D t \pi^2}{a^2} \right) \cos \frac{\pi}{6} + 2A_5 \exp\left(-25 \frac{D t \pi^2}{a^2} \right) \cos \frac{5\pi}{6} + \ldots \tag{3}$$

Because of the factor 25 in the exponent of the second term, this series converges very rapidly with time, and at sufficiently large times a plot of ln (Δc) versus time is linear with a slope of $-D\pi^2/a^2$. The same time constant holds for any property which is linear in concentration.

As the concentration variations get smaller with increasing time, the conductivity of the solution in the cell can be well approximated as a linear function of the concentration. Harned placed two pairs of electrodes in his cell 1/6 of the distance from each end and thus was able to determine the diffusion coefficient from the change in the difference of conductivity between these two locations over a period of days.

Since Harned's analysis was based on the dilute-solution equations with constant properties, the identification of a well-defined, differential diffusion coefficient rests on the assumption that the concentration differences during measurement are sufficiently small to justify the constant-property approximation. It remains to show how generally a restricted-diffusion experiment yields meaningful results. A more complete analysis of the problem based on general concentrated-solution flux equations will elucidate the nature of the diffusion coefficient which is measured in this type of experiment.

TRANSPORT RELATIONS FOR CONCENTRATED ELECTROLYTES

A completely consistent description of isothermal diffusion requires the use of a set of flux equations of the type

$$c_i \nabla \mu_i = RT \sum_j \frac{c_i c_j}{c_T \mathfrak{D}_{ij}} \left(\underline{v}_j - \underline{v}_i \right) \tag{4}$$

where μ_i is the electrochemical potential of species i, and $\mathfrak{D}_{ij}$, the transport coefficients defined by these equations, are functions of temperature, pressure, and composition only, being independent of the fluxes and the gradients.

This equation is analogous to the Stefan-Maxwell equations for diffusion in mixtures of gases. It may be viewed as a force balance and by Newton's third law of motion $\mathcal{D}_{ij} = \mathcal{D}_{ji}$. This particular set of flux equations has been proposed by Newman et al. (1965) and discussed by Newman (1967). It is consistent with the principles of irreversible thermodynamics and is equivalent to flux laws discussed by Onsager (1945) and others.

Equations of this form may be written for each ionic species as well as for the solvent, although one of these equations will be redundant. To apply such equations in differential material balances for mass-transfer or diffusion calculations, one must invert them and express the fluxes in terms of the forces. This inversion requires a choice of the frame of reference for the fluxes. For example, if the solvent velocity $\underline{v}_0$ is chosen as the reference velocity, one obtains for a binary salt solution the flux expressions (Newman, 1967)

$$\left.\begin{aligned} \underline{N}_+ &= c_+\underline{v}_+ = -\frac{\nu_+\mathcal{D}c_T}{\nu RT\,c_0}c\nabla\mu_e + \frac{t_+{}^0\underline{i}}{Fz_+} + c_+\underline{v}_0 \\ \underline{N}_- &= c_-\underline{v}_- = -\frac{\nu_-\mathcal{D}c_T}{\nu RT\,c_0}c\nabla\mu_e + \frac{t_-{}^0\underline{i}}{Fz_-} + c_-\underline{v}_0 \\ N_0 &= c_0\,v_0 \quad , \end{aligned}\right\} \tag{5}$$

where

$$\mathcal{D} = \frac{\mathcal{D}_{0+}\mathcal{D}_{0-}(z_+ - z_-)}{z_+\mathcal{D}_{0+} - z_-\mathcal{D}_{0-}} \tag{6}$$

is the diffusion coefficient

$$t_+{}^0 = 1 - t_-{}^0 = \frac{z_+\mathcal{D}_{0+}}{z_+\mathcal{D}_{0+} - z_-\mathcal{D}_{0-}} \tag{7}$$

is the cation transference number relative to the solvent and

$$\mu_e = \nu_+\mu_+ + \nu_-\mu_- \tag{8}$$

is the chemical potential of the electrolyte.

Transport equations using the molar-average velocity or the mass-average velocity for the frame of reference are given by Newman et al. (1965) or by Newman (1967). In those cases, the mole fraction or the mass fraction becomes the natural way to express concentration. In the present work, we shall illustrate how to use the so-called "volume-average velocity" (Bird et al., 1960a)

$$v^{\blacksquare} = c_0\overline{V}_0\,\underline{v}_0 + c_+\overline{V}_+\,\underline{v}_+ + c_-\overline{V}_-\,\underline{v}_- \tag{9}$$

For electrolytic solutions we generally avoid using the volume-average velocity because the partial molar volumes $\overline{V}_i$ of individual ionic species are not accessible to experimental determination. Here we require $\overline{V}_+$ and $\overline{V}_-$ to yield the partial molar volume of the electrolyte $\overline{V}_e$ according to

$$\overline{V}_e = \nu_+\overline{V}_+ + \nu_-\overline{V}_- \tag{10}$$

In addition, we shall let Q represent the quantity

$$Q = \frac{t_+{}^0}{z_+}\overline{V}_+ + \frac{t_-{}^0}{z_-}\overline{V}_- \tag{11}$$

This quantity cannot be measured independently, and it can arbitrarily be taken to be zero, in which case

$$t_+{}^0\nu_+\overline{V}_+ = t_-{}^0\nu_-\overline{V}_- \tag{12}$$

In other words, the transference numbers of the ions are assumed to be inversely proportional to their partial molar volumes. However, this choice is based solely on convenience, and no physical significance should be attached to it.

In terms of the volume-average velocity, Equations (5) become

$$\left.\begin{aligned} \underline{N}_+ &= -D\nabla c_+ + \frac{\underline{i}}{F}\left(\frac{t_+{}^0}{z_+} - c_+Q\right) + c_+\underline{v}^{\blacksquare} \\ \underline{N}_- &= -D\nabla c_- + \frac{\underline{i}}{F}\left(\frac{t_-{}^0}{z_-} - c_-Q\right) + c_-\underline{v}^{\blacksquare} \\ \underline{N}_0 &= -D\nabla c_0 - \frac{\underline{i}}{F}c_0Q + c_0\,\underline{v}^{\blacksquare}\ , \end{aligned}\right\} \tag{13}$$

since

$$\frac{\mathcal{D}c_T\overline{V}_0}{\nu RT}c\nabla\mu_e = D\nabla c = -D\frac{\overline{V}_0}{\overline{V}_e}\nabla c_0 \tag{14}$$

where (Newman et al., 1965; Newman, 1967)

$$D = \mathcal{D}\frac{c_T}{c_0}\left(1 + \frac{d\ln\gamma}{d\ln m}\right) \tag{15}$$

For each species in the solution, the conservation law is (Bird et al., 1960b)

$$\frac{\partial c_i}{\partial t} = -\nabla\cdot\underline{N}_i \tag{16}$$

provided there are no homogeneous reactions. Substitution of Equations (13) and rearrangement gives three important relations for a solution of a binary electrolyte:

$$\nabla\cdot\underline{i} = 0 \tag{17}$$

$$\nabla\cdot\left(\underline{v}^{\blacksquare} - \frac{\underline{i}Q}{F}\right) + \overline{V}_e\frac{\underline{i}\cdot\nabla t_+{}^0}{z_+\nu_+F} = -D\frac{\nabla c\cdot\nabla\overline{V}_e}{c_0\overline{V}_0} \tag{18}$$

$$\frac{\partial c}{\partial t} + \left(\underline{v}^{\blacksquare} - \frac{\underline{i}Q}{F}\right)\cdot\nabla c + c\nabla\cdot\left(\underline{v}^{\blacksquare} - \frac{\underline{i}Q}{F}\right) = \nabla\cdot(D\nabla c) - \frac{\underline{i}\cdot\nabla t_+{}^0}{z_+\nu_+F} \tag{19}$$

Equation (17), saying that the divergence of the current density is zero, is an expression of conservation of charge in an electrically neutral solution (Newman, 1967). Equation (18) is an overall conservation equation, expressing perhaps conservation of volume. Note that the divergence of the volume-average velocity is not exactly zero, as one might expect. Equation (19) is a material balance for the electrolyte and should be compared to equations (26), (72), (81), and (82) given by Newman (1967). The volume-average velocity is ambiguous to the extent that Q is undefined. Equations (18) and (19) show that it is convenient to set Q equal to zero. When the current density is zero, one is not concerned at all with Q, and the anions and cations diffuse together as though they were a single solute, the electrolyte.

ANALYSIS OF RESTRICTED DIFFUSION IN CONCENTRATED BINARY SOLUTIONS

The continuity equations have been put into the above form [Equations (17) to (19)] because it is a particularly convenient one for the analysis of experimental measurements of diffusion coefficients in binary solutions. The diffusion coefficient D given by Equation (15) is the quantity usually measured and reported as the differential diffusion coefficient. This statement anticipates the result of the following analysis, but it is convenient to simplify the mathematical expressions and important to emphasize that only one experimental diffusion coefficient need be defined, although it can be used in a variety of flux expressions (Newman, 1967; Bird et al., 1960c). The diffusion coefficient $\mathcal{D}$, based on a thermodynamic driving force, is convenient in the correlation and theoretical interpretation of transport properties (Newman et al., 1965; Bird et al., 1960d), although its definition does depend on the assumed state of dissociation of the electrolyte (Newman, 1973). In very dilute solutions, these subtle refinements are irrelevant because $\mathcal{D} = D$ at infinite dilution. In more concentrated solutions, however, one must take care to identify exactly which coefficient he is measuring.

Micka (1968) has suggested a disagreement with the relationship 15 between the experimental diffusion coefficient D and the diffusion coefficient $\mathcal{D}$ based on a thermodynamic driving force. However, to us it appears possible to derive this result from Micka's equations (5), (14), (21), (28), and (41) without any assumption about the value of the transference number.

In the restricted-diffusion process, as it occurs in the experiments of Harned, no current flows, and Equations (18) and (19) are to be solved for the decay of a one-dimensional concentration gradient in a column of solution of height a, subject to the boundary conditions

$$v^{\blacksquare} = 0 \quad \text{and} \quad \frac{\partial c}{\partial y} = 0 \quad \text{at} \quad y = 0 \tag{20}$$

(at the bottom of the cell)

$$\frac{\partial c}{\partial y} = 0 \quad \text{at} \quad y = a \tag{21}$$

(at the free surface). At the bottom of the cell, the fluxes are all zero, while at the top of the column the fluxes are supposed to be zero relative to the interface, which may actually be moving as the volume changes on mixing. To stipulate further the condition at the top, we can use an overall mass balance or a balance on the solute:

$$\int_0^a c\,dy = c^{\infty} a^{\infty} \tag{22}$$

The total amount of electrolyte in the column remains constant. The superscript infinity (∞) will be used to denote quantities evaluated after a long time, when the concentration will have become uniform in the cell.

One can solve Equations (18) and (19) subject to these boundary conditions and an arbitrary initial condition by assuming that the unknown functions can at large times be represented by perturbation expansion series of the form

$$c = c^{\infty} + \epsilon c^{(1)} + \epsilon^2 c^{(2)} + \ldots, \tag{23}$$

$$a = a^{\infty} + \epsilon a^{(1)} + \epsilon^2 a^{(2)} + \ldots, \tag{24}$$

and

$$v^{\blacksquare} = \epsilon v^{(1)} + \epsilon^2 v^{(2)} + \ldots, \tag{25}$$

where ϵ is a function of time and goes to zero at infinite time. Equation (2) is a special case of this form. The coefficients $c^{(i)}$, $a^{(i)}$, and $v^{(i)}$ should be independent of time if this scheme is valid; $c^{(i)}$ and $v^{(i)}$ then depend only on position y.

For convenience we employ the definition of D given above to simplify the equations. Furthermore, we account for the concentration dependence of D formally by expressing this quantity as its Taylor expansion around the value at c^{∞}:

$$\begin{aligned} D = D^{\infty} &+ \left.\frac{dD}{dc}\right|_{c^{\infty}} (c - c^{\infty}) \\ &+ \frac{1}{2} \left.\frac{d^2D}{dc^2}\right|_{c^{\infty}} (c - c^{\infty})^2 + \ldots \end{aligned} \tag{26}$$

where $D^{\infty} = D(c^{\infty})$. Substitution of Equations (23) through (26) into Equations (18) and (19) and the boundary conditions (20) through (22) and equating terms of like order in ϵ accomplishes a separation of variables for this problem by yielding a hierarchy of differential equations with boundary conditions from which ϵ and all the coefficients $c^{(i)}$, $a^{(i)}$, and $v^{(i)}$ can be determined. The ability to generate these necessary equations justifies the assumptions expressed in Equations (23) to (25).

The results of these manipulations can be rather complicated and are laid out by Chapman (1967). The significant results are that

$$\epsilon = e^{-D^{\infty} t (\pi / a^{\infty})^2} \tag{27}$$

and that the difference in concentration between points 1/6 of the overall length from each end of the cell, as previously estimated by Equation (3), is given more completely by

$$\begin{aligned} \Delta c = c\left(\frac{a^{\infty}}{6}\right) - c\left(\frac{5a^{\infty}}{6}\right) &= 2A_1 e^{-D^{\infty} t (\pi/a^{\infty})^2} \cos(\pi/6) \\ &+ Be^{-3D^{\infty} t (\pi/a^{\infty})^2} + \ldots, \end{aligned} \tag{28}$$

where the coefficient A_1 depends on the initial condition and the coefficient B is a complicated function of the initial condition and concentration derivatives of the physical properties

$$\begin{aligned} B = A_1^3 \frac{\pi}{12} \left(\frac{\overline{V}_0}{M_0} \frac{d^2\rho}{dc^2}\right)^{\infty} &+ \frac{\sqrt{3}}{16} A_1^3 \left[\frac{1}{D} \frac{d^2D}{dc^2} \right. \\ &- 2\left(\frac{1}{D}\frac{dD}{dc}\right)^2 - 3\frac{c}{D}\frac{dD}{dc}\frac{\overline{V}_0}{M_0}\frac{d^2\rho}{dc^2} \\ &\left. + 6\left(\frac{c\overline{V}_0}{M_0}\frac{d^2\rho}{dc^2}\right)^2 + 2c\frac{\overline{V}_0}{M_0}\frac{d^3\rho}{dc^3} + 7\frac{\overline{V}_0}{M_0}\frac{d^2\rho}{dc^2} \right]^{\infty} \end{aligned} \tag{29}$$

Furthermore, it was found that $a^{(1)}$ and $v^{(1)}$ are both zero and that $a^{(2)}$ is very small,

$$a^{(2)} = -\frac{A_1^2 a^{\infty}}{4} \left(\frac{\overline{V}_0}{M_0} \frac{d^2\rho}{dc^2}\right)^{\infty} \tag{30}$$

so that it is not necessary in practice to recognize the variation in solution volume.

EXPERIMENTAL SYSTEM

Because a conductimetric method fails with conductivities of appreciable magnitude, we developed an optical arrangement for measuring the concentration difference Δc in the cell, using the Rayleigh interferometer of a commercial electrophoresis apparatus manufactured by Perkin-Elmer Corporation. The glass diffusion cell shown in Figure 1 had dimensions 79 mm by 9 mm by 2 mm, which were small enough to prevent convection. The length of the cell was measured accurately, and fine lines were scribed on the cell face one sixth of the distance from either end.

Temperature control was to within 0.01°C. The interferometer served to generate an interference, or fringe, pattern which plots very precisely the profile of concentration versus position in the cell. After a boundary was formed and the cell was closed off at both ends, photographs of the fringe pattern were taken every few hours for a period of several days. Figures 2 and 3 correspond to times just after forming the boundary and toward the end of an experiment, respectively. Provided that the refractive index is linearly dependent upon concentration, as is normally the case over a narrow concentration range, the displacement of a fringe is proportional to Δc, and the measured fringe displacements can be used directly in Equation (28) to determine the diffusion coefficient from the time constant of their decay.

As a test for the method, measurements were made on solutions of potassium chloride at 25°C, the system which has been studied most extensively and is accepted as a standard for diffusion measurements. It was found that after our experimental techniques were perfected, our values agreed within 0.2% of the literature values, as shown in Figure 4. Furthermore, statistical analyses of the fit of measured fringe displacements with time yielded a standard deviation in the slope which corresponds to about 0.1 or 0.2% of the diffusion coefficient. Thus, it was concluded that the method is valid and that our apparatus is capable of measurements comparable in accuracy to the other modern methods for measuring diffusion coefficients.

DISCUSSION AND CONCLUSIONS

It is seen in Equation (28) that the second term in the complete series for Δc is of order ϵ^3 rather than ϵ^{25}, as indicated by the approximate Fourier series solution in Equation (3). Although the effect is no longer demonstrated so dramatically, it is clear that at sufficiently large times the first term necessarily dominates, and the Harned-type measurement and calculation of the decay time constant (from the slope of a semilogarithmic plot of Δc versus time) yield the differential value of the diffusion coefficient D corresponding to the concentration c^∞.

Thus, consideration of the complete continuity equations for concentrated, variable-property binary solutions demonstrates that a restricted diffusion experiment is generally valid. The method does indeed yield a well-defined, differential diffusion coefficient even in concentrated solutions

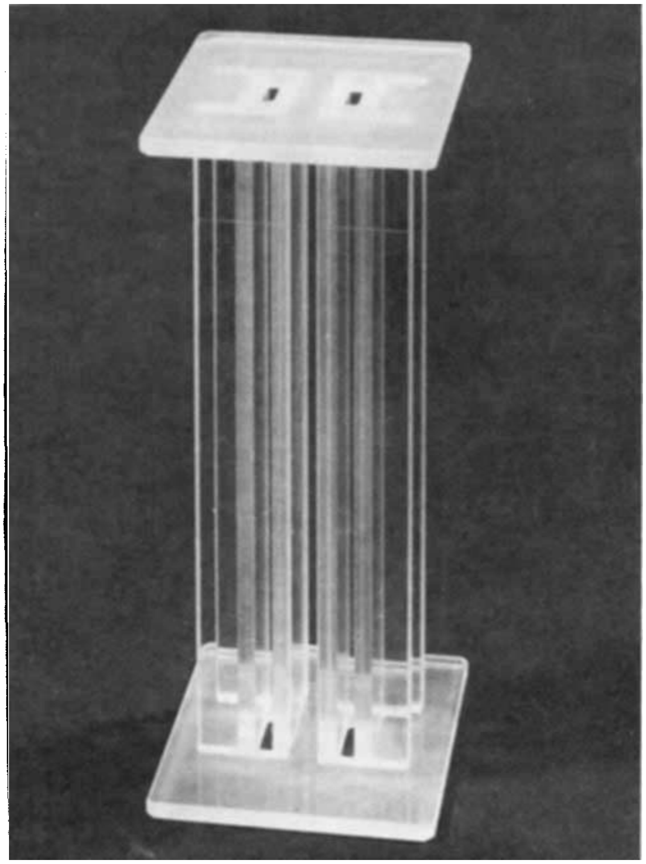

Fig. 1. Optical cell.

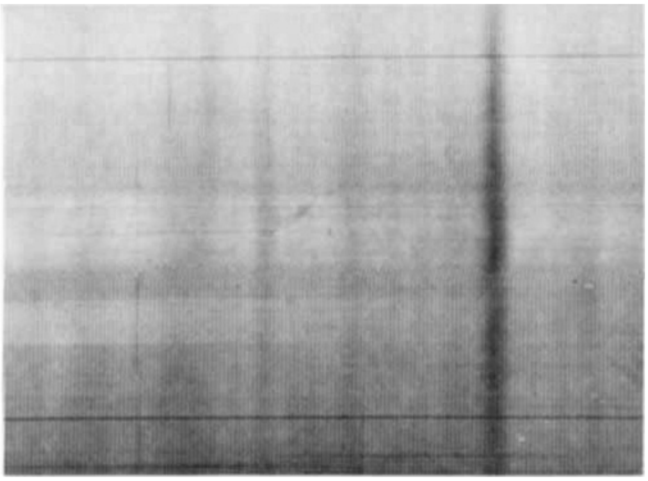

Fig. 2. Fringe pattern about half an hour after the formation of the boundary. The fringes cannot yet be distinguished in the boundary. The scribed marks show up as horizontal lines.

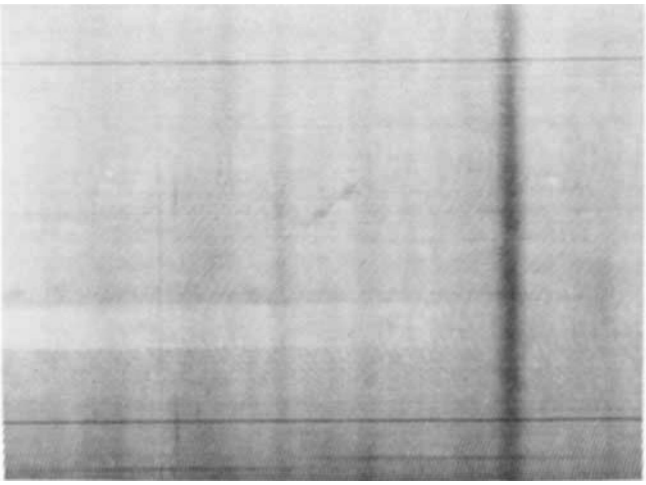

Fig. 3. Fringe pattern toward the end of the run.

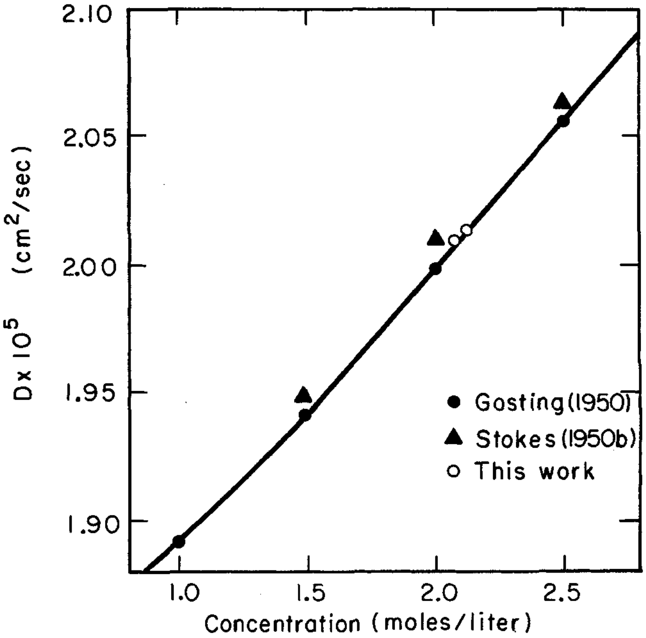

Fig. 4. The diffusion coefficient of potassium chloride in water at 25°C and high concentrations.

provided that an analytical technique suitable for measuring Δc in such solutions is used. Since the analysis of restricted diffusion presented here is more thorough than any available for free diffusion or the diaphragm cell method, and since it is equally valid for nonelectrolytic solutions as for electrolytes, we suggest that more extensive experimental implementation of the restricted diffusion method should be considered.

A new optical, restricted-diffusion method has been developed and has been shown to yield accurate diffusion coefficients in concentrated solutions. Restricted diffusion is an absolute method, requiring no calibration. Only the height a^∞ of the liquid column need be measured with great accuracy. The initial concentration distribution within the cell is not critical. Any concentration variations perpendicular to the long dimension of the cell will decay very rapidly, leaving only the desired one-dimensional profile.

Any velocity disturbances generated in the cell by the boundary formation would be expected to decay exponentially with a time constant depending upon the kinematic viscosity rather than the diffusion coefficient. Since the kinematic viscosity of liquid solutions is about three orders of magnitude greater than the diffusion coefficient, any small convective velocities should vanish long before the concentration profile does.

The nature of restricted diffusion at long times eliminates several other potential sources of error. Δc does not need to be made between points exactly 1/6 of the way from either end of the cell. The optical system does not need to be perfect. Distortion from the nonzero gradients of refractive index and a nonuniform temperature from the heat of mixing also become higher order effects at long times. The scale between the cell and the film image and the scale in the direction of the fringe shifts are also irrelevant as long as they are constant throughout a run.

ACKNOWLEDGMENT

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NOTATION

a = height of restricted diffusion cell or of liquid column, cm
A_n = coefficients of series expression for concentration in restricted diffusion cell
B = constant identified in Equation (29)
c = concentration of binary electrolyte = c_+/ν_+ = c_-/ν_-, mole/cm^3
Δc = concentration difference measured in diffusion cell
c_i = concentration of species i, mole/cm^3
c_0 = concentration of solvent
c_T = total solution concentration
D = experimental diffusion coefficient of binary electrolyte, cm^2/s
$\mathcal{D}$ = diffusion coefficient of electrolyte for thermodynamic driving force, cm^2/s
$\mathcal{D}_{ij}$ = diffusion coefficient for binary interactions, cm^2/s
F = Faraday's constant, 96,487 C/equiv
$\underline{i}$ = current density, amp/cm^2
M_0 = molecular weight of the solvent, g/mole
m = molality of electrolyte, mole/kg
$\underline{N}_i$ = flux of species i, mole/cm^2-s
Q = defined in Equation (11)
R = universal gas constant, J/mole-deg
T = absolute temperature, °K
t = time, s
t_j^0 = transference number of species j with respect to the solvent
$\overline{V}_e$ = partial molar volume of electrolyte, cm^3/mole
$\overline{V}_0$ = partial molar volume of solvent, cm^3/mole
$\underline{v}_0$ = velocity of solvent, cm/s
$\underline{v}_i$ = velocity of species i, cm/s
$\underline{v}^{\blacksquare}$ = volume average velocity, cm/s
y = position coordinate in diffusion cell, cm
z_i = valence or charge number of species i
γ = mean molal activity coefficient
ϵ = perturbation parameter, see Equation (27)
μ_i = electrochemical potential of species i, J/mole
μ_e = chemical potential of salt in binary electrolyte, J/mole
ν = $\nu_+ + \nu_-$
ν_+, ν_- = numbers of cations and anions produced by dissociation of one molecule of electrolyte
ρ = density of solution, g/cm^3

Superscripts

∞	indicates values at infinite time, that is, uniform concentration
(i)	identifies coefficients of terms in perturbation expansion series, Equation (23) and following

Subscripts

0	indicates property of solvent
$+, -$	indicates properties of cations and anions
e	indicates properties of electrolyte

LITERATURE CITED

Bird, R. B., Stewart, W. E., and Lightfoot, E. N., *Transport Phenomena*, p. 518, Wiley, New York (1960a).
———., *ibid.*, p. 556 (1960b).
———., *ibid.*, p. 502 and problem 16.I (1960c).
———., *ibid.*, p. 570 (1960d).
Chapman, T. W., *The Transport Properties of Concentrated Electrolytic Solutions.* Ph.D. thesis, Univ. California, Berkeley (1967).
Gosting, L. J., "A Study of the Diffusion of Potassium Chloride in Water at 25° with the Gouy Interference Method," *J. Am. Chem. Soc.*, **72**, 4418 (1950).
Harned, H. S., and D. M. French, "A Conductance Method for the Determination of the Diffusion Coefficients of Electrolytes," *Annals New York Acad. Sci.*, **46**, 267 (1945).
Longsworth, L. G., "The Diffusion of Electrolytes and Macromolecules in Solution: A Historical Survey," *ibid.*, 211.
Micka, K., "Mass Transfer in Concentrated Binary Electrolytes," *Ber. Bunsenges. physik. Chem.*, **72**, 60 (1968).
Nernst, W., "Zur Kinetik der in Lösung befindlichen Körper," *Zeit. physik. Chem.*, **2**, 613 (1888).
Newman, J., D. Bennion, and C. W. Tobias, "Mass Transfer in Concentrated Binary Electrolytes," *Ber. Bunsenges. physik. Chem.*, **69**, 608 (1965). For corrections, see *ibid.*, **70**, 493 (1966).
———., "Transport Processes in Electrolytic Solutions," *Adv. in Electrochem. Electrochem. Eng.*, **5**, 87 (1967).
———., *Electrochemical Systems*, problem 2-1, pp. 60-61, Prentice-Hall, Englewood Cliffs, N. J. (1973).
Onsager, L., "Theories and Problems of Liquid Diffusion," *Annals New York Acad. Sci.*, **46**, 241 (1945).
Stokes, R. H., "An Improved Diaphragm-cell for Diffusion Studies, and Some Tests of the Method," *J. Am. Chem. Soc.*, **72**, 763 (1950a).
———., "The Diffusion Coefficients of Eight Uni-univalent Electrolytes in Aqueous Solution at 25°," *ibid.*, 2243 (1950b).
———., "Integral Diffusion Coefficients of Potassium Chloride Solutions for Calibration of Diaphragm Cells," *ibid.*, **73**, 3527 (1951).

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