

$$\left(\frac{R_1}{R_2}\right) D_{12} = \frac{-[(\alpha_1)_1 - (\alpha_1)_{11}]\theta_1^2 + [(\alpha_1)_1(\mathfrak{D}_{4m}^2)_{11} - (\alpha_1)_{11}(\mathfrak{D}_{4m}^2)_1]}{[(\mathfrak{D}_{2m})_1 - (\mathfrak{D}_{2m})_{11}]} \quad (35)$$

$$\left(\frac{R_2}{R_1}\right) D_{21} = \frac{-[(\alpha_2)_1 - (\alpha_2)_{11}]\theta_2^2 + [(\alpha_2)_1(\mathfrak{D}_{4m}^2)_{11} - (\alpha_2)_{11}(\mathfrak{D}_{4m}^2)_1]}{[(\mathfrak{D}_{2m})_1 - (\mathfrak{D}_{2m})_{11}]} \quad (36)$$

$$D_{22} = \frac{[(\alpha_1)_1 - (\alpha_1)_{11}]\theta_2\theta_1 - [(\alpha_1)_1(\mathfrak{D}_{4m}^2)_{11} - (\alpha_1)_{11}(\mathfrak{D}_{4m}^2)_1]}{[(\mathfrak{D}_{2m})_1 - (\mathfrak{D}_{2m})_{11}]} \quad (37)$$

Experiments in which the concentration of one solute is the same on both sides of the boundary are of special interest because the value calculated for each D_{ij} is then influenced least by experimental uncertainty in the reduced moments. Further, such experiments can be used to evaluate R_1 and R_2 . According to equations 31 and 32, when $(\alpha_2)_1 = 0$ so that $(\alpha_1)_1 = 1$, and $(\alpha_1)_{11} = 0$ so that $(\alpha_2)_{11} = 1$

$$\theta_1 = (\mathfrak{D}_{2m})_1 \quad (38)$$

and

$$\theta_2 = (\mathfrak{D}_{2m})_{11} \quad (39)$$

For such experiments equations 34–37 reduce, after substitution of equations 31 and 32, to

$$D_{11} = \frac{(\mathfrak{D}_{4m}^2)_1 - (\mathfrak{D}_{2m})_1(\mathfrak{D}_{2m})_{11}}{(\mathfrak{D}_{2m})_1 - (\mathfrak{D}_{2m})_{11}} \quad (40)$$

$$\left(\frac{R_1}{R_2}\right) D_{12} = \frac{(\mathfrak{D}_{4m}^2)_{11} - (\mathfrak{D}_{2m})_{11}^2}{(\mathfrak{D}_{2m})_1 - (\mathfrak{D}_{2m})_{11}} \quad (41)$$

$$\left(\frac{R_2}{R_1}\right) D_{21} = \frac{(\mathfrak{D}_{4m}^2)_1 - (\mathfrak{D}_{2m})_1^2}{(\mathfrak{D}_{2m})_{11} - (\mathfrak{D}_{2m})_1} \quad (42)$$

$$D_{22} = \frac{(\mathfrak{D}_{4m}^2)_{11} - (\mathfrak{D}_{2m})_1(\mathfrak{D}_{2m})_{11}}{(\mathfrak{D}_{2m})_{11} - (\mathfrak{D}_{2m})_1} \quad (43)$$

The above equations may be used to calculate diffusion coefficients from measurements made with any diffusion apparatus which yields the reduced second and fourth moments of the refractive index gradient curve in free diffusion. In a companion paper measurements of \mathfrak{D}_{2m} and \mathfrak{D}_{4m}^2 with the Gouy diffusiometer are presented for two three-component systems with interacting flows.

Acknowledgments.—We would like to thank Dr. J. G. Kirkwood for valuable suggestions in connection with evaluating diffusion coefficients from the moments of the gradient curves, Dr. C. F. Curtiss for his helpful discussion of the flow equations, and Dr. J. W. Williams for support and encouragement of this work. This research was supported in part by the National Institutes of Health and by the Research Committee of the Graduate School from funds supplied by the Wisconsin Alumni Research Foundation.

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF WISCONSIN]

Interacting Flows in Liquid Diffusion: Expressions for the Solute Concentration Curves in Free Diffusion, and their Use in Interpreting Gouy Diffusiometer Data for Aqueous Three-component Systems

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RECEIVED MARCH 30, 1955

By using an extension of Fick's first law to represent interacting flows in three-component systems, series expansions are developed for the concentration of each solute as a function of time, position and four diffusion coefficients. These expressions converge rapidly when either of the two cross-term diffusion coefficients is small. From these series expansions, equations are derived relating the diffusion coefficients to the reduced height-area ratio, \mathfrak{D}_A , and to the fringe deviation graphs which provide a measure of deviations of the refractive index gradient curve from Gaussian shape. To test these relations, data are presented from several experiments with the Gouy diffusiometer in which lithium chloride and potassium chloride diffused simultaneously. An electrolyte system was chosen with the hope that it would exhibit greater interaction of flows than a non-electrolyte system through electrostatic coupling of the flows of ions of different mobility; assuming that the flow equations are valid, the series expansions are applicable to either case. In all experiments the mean concentration of a given solute was the same, but the ratio of their concentration increments across the boundary was varied from experiment to experiment. Values were chosen for the four diffusion coefficients which best fit the reduced moments (consult companion paper), reduced height-area ratios, and fringe deviation graphs of the several experiments. The results provide evidence for the validity of the flow equations. Data are also reported for the simultaneous diffusion of lithium and sodium chlorides in aqueous solution. The four diffusion coefficients for this system are calculated from reduced moments of the refractive index gradient curves: neither cross-term diffusion coefficient is small enough to permit use of the equations for the fringe deviation graphs.

Throughout the past one hundred years, diffusion measurements in liquid systems have been interpreted by means of Fick's first law.¹ This law may be regarded as a phenomenological equation expressing proportionality between the flow of a component and the first power of its concentration gradient, the proportionality coefficient being called the diffusion coefficient. Many careful studies of free, restricted and steady-state diffusion have established the validity of this law to describe the process of diffusion in liquid two-component

systems.² Furthermore, it has also been found adequate to describe the flow of each solute in certain three-component systems.^{3,4}

On the other hand, throughout the last several

(2) It should be noted that the diffusion coefficient may vary with concentration without invalidating Fick's first law. However, if the partial molal volume of the solute varies markedly with concentration, an additional term in the bulk flow must be added to the flow equation (see Onsager, ref. 13). The effects of such variations on the shape of the diffusing boundary can be diminished by reducing the concentration differences between the two solutions which are used to form the initial boundary.

(3) D. F. Akeley and L. J. Gosting, *THIS JOURNAL*, **75**, 5685 (1953).

(4) P. J. Dunlop, *ibid.*, **77**, 2994 (1955).

(1) A. Fick, *Pogg. Ann.*, **94**, 59 (1855).

decades numerous experiments have been reported which indicate that Fick's law cannot be generally valid for systems of three or more components. Perhaps the simplest way this has been shown was by allowing diffusion to proceed between two solutions originally containing one solute (the "test solute"⁵) at identical concentrations while the other solute (the "diffusing solute"⁵) was at different concentrations. After a period of diffusion, unequal concentrations of the "test solute" were found on the two sides of the initial boundary.⁶ Not only was this phenomenon noted when the two solutes were salts,^{3,7-11} but also when one was a salt and the other a non-electrolyte.^{9,12} Any mathematical representation of the "test solute's" flow when its concentration gradient is zero clearly requires a more general flow equation than Fick's first law. Therefore, it is important to recognize that the use of functions derived from Fick's first law (such as the Gaussian function for the case of free diffusion) to calculate a single "diffusion coefficient" for each solute in such systems is, at best, only an approximate procedure for representing the diffusion process.

Both Lamm^{13,14} and Onsager¹⁵ have proposed sets of generalized flow equations which are intended to describe flows in systems of three or more components. The equations we adopt are modifications of Onsager's set and constitute a direct phenomenological approach. Thus, the form of the flow equations is chosen so as to relate conveniently data from one diffusion experiment to the data from another in which the mean concentration of any given solute is the same in all experiments. Correlation of the measured diffusion coefficients with other data, such as activity coefficients or equivalent ionic conductances, is left for future investigation.

Theory: Solute Concentration Distributions

In this theoretical section, expressions for the solute concentrations in the freely diffusing boundary are derived, first for the case that one cross-term diffusion coefficient is zero and then when one of these coefficients is small. From these distributions an expression is next obtained for the refractive index curve which, in turn, is used to obtain an expression for the reduced height-area ratio. Equations which apply specifically to the Gouy diffusiometer are derived in the second theoretical section.

Flow Equations.—The derivations of equations in this article are based on flow equations which are also presented in the companion paper¹⁶ and dis-

(5) G. S. Walpole, *Biochem. J. (London)*, **9**, 132 (1915).

(6) Such effects might arise if the partial molal volumes of the solutes changed markedly with concentration, but the observed effects seem too large to be explained in this way.

(7) S. Arrhenius, *Z. physik. Chem.*, **10**, 51 (1892).

(8) J. Thovert, *Compt. rend.*, **134**, 826 (1902).

(9) W. A. Osborne and L. C. Jackson, *Biochem. J. (London)*, **8**, 246 (1914).

(10) J. W. McBain and C. R. Dawson, *THIS JOURNAL*, **56**, 52 (1934).

(11) L. J. Burrage and A. J. Allmand, *J. Phys. Chem.*, **41**, 887 (1937).

(12) J. W. McBain and T. H. Liu, *THIS JOURNAL*, **53**, 59 (1931).

(13) O. Lamm, *Arkiv Kemi, Mineral., Geol.*, **18A**, No. 2 (1944).

(14) O. Lamm, *J. Phys. Colloid Chem.*, **51**, 1063 (1947).

(15) L. Onsager, *Ann. N. Y. Acad. Sci.*, **46**, 241 (1945).

(16) R. L. Baldwin, P. J. Dunlop and L. J. Gosting, *THIS JOURNAL*, **77**, 5235 (1955).

cussed there in more detail. It may be helpful for the reader to refer to the section "Flow Equations" in that paper before proceeding further. To avoid rewriting a number of equations appearing in the companion article, we will refer directly to those equations, distinguishing them from the equations in this article by the suffix C.

For systems of three components, we propose equations for each solute flow, J_i , ($i = 1, 2$) of the following form¹⁷ (see equation 3C).

$$J_1 = -D_{11}(\partial C_1/\partial x)_t - D_{12}(\partial C_2/\partial x)_t \quad (1)$$

$$J_2 = -D_{21}(\partial C_1/\partial x)_t - D_{22}(\partial C_2/\partial x)_t \quad (2)$$

As indicated in the companion paper, the differential diffusion coefficients D_{11} , D_{12} , D_{21} and D_{22} defined by these equations differ from those defined by Onsager.¹⁵ Equations of this type were chosen because it is convenient in experimental work to measure, at a given level x and time t , the solute concentrations, C_i , or concentration gradients, $(\partial C_i/\partial x)_t$, rather than corresponding quantities for the solvent ($i = 0$). Consideration of systems with 4, 5, etc., components, requiring 9, 16, etc., diffusion coefficients for their description,¹⁵ is left for future investigation. For convenience the coefficients D_{12} and D_{21} will be referred to as *cross-term diffusion coefficients*. It should be noted that, in general, $D_{12} \neq D_{21}$; however, because of the principle of microscopic reversibility, a relation exists among the four measured diffusion coefficients of a three-component non-electrolyte system.¹⁵

Differential Equations for the Solute Concentrations.—These relations are obtained by substituting equations 1 and 2, separately, into the equation of continuity

$$(\partial C_i/\partial t)_x = -(\partial J_i/\partial x)_t \quad (3)$$

Because only free diffusion will be considered, we may utilize the fact, first recognized by Boltzmann,¹⁸ that the variables x and t always occur¹⁹ in the ratio x/\sqrt{t} , provided t is the time of diffusion from a sharp initial boundary. Defining

$$y = x/(2\sqrt{t}) \quad (4)$$

and assuming that each diffusion coefficient is constant throughout the boundary region, we obtain from equations 1-4 the desired differential equations

(17) Here we consider only the case of one-dimensional diffusion in a vertical cell of uniform cross-section. The x coordinate is defined as fixed relative to the cell and increasing in the downward direction, with its origin at the position of the sharp initial boundary between the two starting solutions A and B. Flows J_1 and J_2 are expressed as moles of components 1 and 2, respectively, which cross a unit area at some level x per unit of time, t ; they are considered positive in the direction of increasing x . The concentrations are expressed as moles per unit volume of solution. Because no term for bulk flow is included in these equations, we are assuming that all concentration differences, ΔC_i , between solutions A and B are made so small that variations with concentration of the partial molal volumes, V_i , of each component can be neglected. Use of small values of ΔC_i also reduces variations within the cell of the diffusion coefficients, D_{11} , D_{12} , D_{21} and D_{22} and of the differential refractive increments, K_i (equation 7C). This permits us to consider these quantities as constants, and simplifies the derivation of the equations in this section.

(18) L. Boltzmann, *Wied. Ann.*, **53**, 959 (1894).

(19) That this relationship is valid even when the flows interact is indicated by equation 24C and also by the experimental observations reported below: *i.e.*, the product of the downward displacement of each Gouy fringe and the square root of the time was independent of time (after making the small starting time correction, Δt).

$$-2y(dC_1/dy) = D_{11}(d^2C_1/dy^2) + D_{12}(d^2C_2/dy^2) \quad (5)$$

and

$$-2y(dC_2/dy) = D_{22}(d^2C_2/dy^2) + D_{21}(d^2C_1/dy^2) \quad (6)$$

These equations must now be solved for the case of free diffusion subject to the following boundary conditions for each solute ($i = 1, 2$): when $t = 0$

$$C_i = \bar{C}_i + (\Delta C_i/2) \text{ for } x > 0 \quad (7)$$

$$C_i = \bar{C}_i - (\Delta C_i/2) \text{ for } x < 0 \quad (8)$$

and when $t > 0$

$$C_i = \bar{C}_i + (\Delta C_i/2) \text{ for } x = +\infty \quad (9)$$

$$C_i = \bar{C}_i - (\Delta C_i/2) \text{ for } x = -\infty \quad (10)$$

Here the mean concentration of each solute is denoted by

$$\bar{C}_i = [(C_i)_A + (C_i)_B]/2 \quad (11)$$

and each concentration difference across the boundary between solutions A and B is

$$\Delta C_i = [(C_i)_B - (C_i)_A] \quad (12)$$

Equations for the Solute Concentrations when One Cross-Term Diffusion Coefficient is Zero.—

Inspection of equations 5 and 6 shows that when either D_{12} or D_{21} is zero, these equations uncouple and allow solution for both C_1 and C_2 in closed form. For example, if $D_{21} = 0$ then equation 6 may be integrated directly after multiplying by the integrating factor, $e^{+y^2/D_{22}}$. Evaluation of the integration constants from equations 9 and 10 then yields the familiar concentration distribution for free diffusion without interacting flows

$$C_2 = \bar{C}_2 + (\Delta C_2/2)H(z_{22}) \quad (13)$$

In this and subsequent equations the notation is simplified by the definitions

$$z_{11} = y/\sqrt{D_{11}} \quad (14)$$

$$z_{22} = y/\sqrt{D_{22}} \quad (15)$$

$$H(z_{11}) = (2/\sqrt{\pi}) \int_0^{z_{11}} e^{-\beta^2} d\beta \quad (16)$$

$$H(z_{22}) = (2/\sqrt{\pi}) \int_0^{z_{22}} e^{-\beta^2} d\beta \quad (17)$$

The second derivative of equation 13

$$\frac{d^2C_2}{dy^2} = \frac{1}{D_{22}} \frac{d^2C_2}{dz_{22}^2} = \frac{\Delta C_2}{2D_{22}} H''(z_{22}) \quad (18)$$

is now substituted into equation 5 which is then integrated after multiplication by the integrating factor $e^{+y^2/D_{11}}$. Use of equations 9 and 10 to evaluate the constants gives

$$C_1 = \bar{C}_1 + \left(\frac{\Delta C_1}{2}\right)H(z_{11}) + \frac{D_{12}}{D_{11} - D_{22}} \left(\frac{\Delta C_2}{2}\right)[H(z_{11}) - H(z_{22})] \quad (19)$$

If D_{12} , instead of D_{21} , is set equal to zero, then corresponding integrations of equations 5 and 6 lead to the results

$$C_1 = \bar{C}_1 + (\Delta C_1/2)H(z_{11}) \quad (20)$$

and

$$C_2 = \bar{C}_2 + \left(\frac{\Delta C_2}{2}\right)H(z_{22}) + \frac{D_{21}}{D_{22} - D_{11}} \left(\frac{\Delta C_1}{2}\right)[H(z_{22}) - H(z_{11})] \quad (21)$$

Series Expansions for the Solute Concentrations when One Cross-Term Diffusion Coefficient is

Small.—When D_{21} is not zero but is small, equation 19 is an approximate solution for C_1 . Similarly, equation 21 is an approximate solution for C_2 when D_{12} is small. Thus, when neither D_{12} nor D_{21} is zero, the next term in an expansion for C_1 or C_2 , respectively, can be obtained using equation 21 to approximate d^2C_2/dy^2 for equation 5 and equation 19 to approximate d^2C_1/dy^2 for equation 6. Subsequent integration of these forms of equations 5 and 6, and evaluation of the constants from the boundary conditions 9 and 10 yields the desired relations

$$C_1 = \bar{C}_1 + \left(\frac{\Delta C_1}{2}\right)H(z_{11}) + \frac{D_{12}}{D_{11} - D_{22}} \left[\left(\frac{\Delta C_2}{2}\right)[H(z_{11}) - H(z_{22})] - \frac{D_{21}}{D_{11} - D_{22}} \left(\frac{\Delta C_1}{2}\right)\{H(z_{11}) - H(z_{22})\} + \frac{z_{11}(D_{11} - D_{22})}{2D_{11}} H'(z_{11})\} + \dots\right] \quad (22)$$

$$C_2 = \bar{C}_2 + \left(\frac{\Delta C_2}{2}\right)H(z_{22}) + \frac{D_{21}}{D_{22} - D_{11}} \left[\left(\frac{\Delta C_1}{2}\right)[H(z_{22}) - H(z_{11})] - \frac{D_{12}}{D_{22} - D_{11}} \left(\frac{\Delta C_2}{2}\right)\{H(z_{22}) - H(z_{11})\} + \frac{z_{22}(D_{22} - D_{11})}{2D_{22}} H'(z_{22})\} + \dots\right] \quad (23)$$

Higher terms in these series could be obtained by repeating this procedure of successive approximations, but such extensions will not be considered.²⁰

A Series Expression for the Refractive Index

Curve.—The series expansions for the solute concentrations will now be used to obtain a relation between refractive index and position in the cell. As in equation 5C, we assume that the dependence of refractive index on solute concentrations, throughout the diffusing boundary, is adequately represented by the first three terms of a Taylor expansion

$$n = n_{\bar{c}} + R_1(C_1 - \bar{C}_1) + R_2(C_2 - \bar{C}_2) + \dots \quad (24)$$

Here $n_{\bar{c}}$ is the refractive index of a solution in which the solutes are at the mean concentrations, \bar{C}_1 and \bar{C}_2 , and the differential refractive increments, R_i , are defined by equation 7C. Solute fractions on the basis of refractive index are defined by

$$\alpha_1 = R_1 \Delta C_1 / \Delta n \quad (25)$$

and

$$\alpha_2 = R_2 \Delta C_2 / \Delta n \quad (26)$$

where Δn is the total difference in refractive index across the boundary

$$\Delta n = R_1 \Delta C_1 + R_2 \Delta C_2 \quad (27)$$

Substitution of equations 22 and 23 for C_1 and C_2 into equation 24 and use of equations 25 and 26 leads to the required expression for the refractive index

⁽²⁰⁾ Equations 22 and 23 can also be derived by first expressing each concentration, C_i , as a Taylor expansion in its cross-term diffusion coefficient, D_{ij} . Substitution of these expansions into the corresponding differential equations (5 and 6) yields a separate differential equation for each coefficient in the expansions; these are then integrated subject to the boundary conditions for free diffusion. If systems containing more than two solutes were being considered, this approach might be more convenient than the one followed above.

$$n = n_{\bar{c}} + \left(\frac{\Delta n}{2}\right) \left\{ \Gamma_1 H(z_{11}) + \Gamma_2 H(z_{22}) + \frac{D_{12}D_{21}}{D_{22} - D_{11}} \left[\alpha_1 \left(\frac{z_{11}}{2D_{11}}\right) H'(z_{11}) - \alpha_2 \left(\frac{z_{22}}{2D_{22}}\right) H'(z_{22}) \right] + \dots \right\} \quad (28)$$

in which

$$\Gamma_1 = \alpha_1 + \alpha_2 \frac{(R_1/R_2)D_{12}}{D_{11} - D_{22}} + \alpha_1 \frac{(R_2/R_1)D_{21}}{D_{11} - D_{22}} + (\alpha_2 - \alpha_1) \frac{D_{12}D_{21}}{(D_{11} - D_{22})^2} + \dots \quad (29)$$

$$\Gamma_2 = \alpha_2 + \alpha_1 \frac{(R_2/R_1)D_{21}}{D_{22} - D_{11}} + \alpha_2 \frac{(R_1/R_2)D_{12}}{D_{22} - D_{11}} + (\alpha_1 - \alpha_2) \frac{D_{21}D_{12}}{(D_{22} - D_{11})^2} + \dots \quad (30)$$

An important property of these functions which will be useful later is

$$\Gamma_1 + \Gamma_2 = 1 \quad (31)$$

The Reduced Height-Area Ratio.—The series expression for the refractive index, equation 28, will now be used to relate the four diffusion coefficients to an accurately measurable quantity, \mathfrak{D}_A , which we call the *reduced height-area ratio*

$$\mathfrak{D}_A \equiv \frac{(\Delta n)^2}{4\pi t [(\partial n/\partial x)_t]_{\max}^2} \quad (32)$$

This equation is the basis for the "maximum height-area method"²¹⁻²³ used to analyze refractive index gradient curves in free diffusion. It seems desirable to give a distinctive name and symbol to this experimental quantity because, when the flows interact, the number calculated using equation 32 represents neither the diffusion coefficient of a single solute nor a simple average diffusion coefficient.²⁴ A series relation between \mathfrak{D}_A and the four diffusion coefficients is derived by using equations 4, 14 and 15 to obtain the expression

$$\left(\frac{\partial n}{\partial x}\right)_t = \frac{1}{2\sqrt{t}} \frac{dn}{dy} = \frac{1}{2\sqrt{t}} \left[\frac{1}{\sqrt{D_{11}}} \left(\frac{\partial n}{\partial z_{11}}\right)_{z_{22}} + \frac{1}{\sqrt{D_{22}}} \left(\frac{\partial n}{\partial z_{22}}\right)_{z_{11}} \right] \quad (33)$$

Substitution of the derivatives of n with respect to z_{11} and z_{22} from equation 28 yields an equation for $(\partial n/\partial x)_t$. Because we have assumed that each D_{ij} is constant throughout the boundary, this expression is found to be an even function of x . Finally, an expression for $[(\partial n/\partial x)_t]_{\max}$ is obtained by setting²⁵ $x = z_{11} = z_{22} = 0$, and after substitut-

(21) O. Wiener, *Wied. Ann.*, **49**, 105 (1893).

(22) O. Lamm, *Nova Acta Regiae Soc. Sci. Upsaliensis*, Series IV, **10**, No. 6 (1937).

(23) O. Quensel, Dissertation, Uppsala, 1942.

(24) The reader will note that the script symbol, \mathfrak{D} , is reserved for quantities which are defined directly in terms of measurable properties of the refractive index gradient curve for free diffusion. Thus equation 32 defines the reduced height-area ratio, \mathfrak{D}_A , and equations 29C and 30C define the reduced second moment, \mathfrak{D}_{2m} , and the reduced fourth moment, \mathfrak{D}_{4m} , respectively. The form of other equations relating these quantities to the actual diffusion coefficients for the system depend on the nature of the system, *i.e.*, whether there are two or more components and whether the flows interact (see equation 34, equation 10 of ref. 3 and equations 27a and 28a of the companion paper).

(25) This condition for a maximum in the $(\partial n/\partial x)_t$ versus x curve is obtained because our discussion is limited to those curves for which $(\partial^2 n/\partial x^2)_t = 0$ at only one point in the region $-\infty < x < +\infty$. Without this limitation equation 32 would have to be more carefully

ing it into equation 32 we obtain the desired relation

$$\mathfrak{D}_A = \left\{ \frac{1}{\sqrt{D_{11}}} \left[\Gamma_1 + \alpha_1 \frac{D_{12}D_{21}}{2D_{11}(D_{22} - D_{11})} + \dots \right] + \frac{1}{\sqrt{D_{22}}} \left[\Gamma_2 + \alpha_2 \frac{D_{21}D_{12}}{2D_{22}(D_{11} - D_{22})} + \dots \right] \right\}^{-2} \quad (34)$$

Theory: Gouy Diffusimeter

Throughout the above derivations, equations were presented in forms which, after some specialization, are of use for any apparatus measuring free diffusion with sufficient accuracy. These and other relevant expressions will now be used to obtain equations which apply to the Gouy diffusimeter.^{3,26-28}

Reduced Height-Area Ratio.—For this apparatus equation 32 becomes²⁶⁻²⁹

$$\mathfrak{D}_A \equiv \frac{(j_m \lambda b)^2}{4\pi C_t^2 t} \quad (35)$$

In this equation, which is basic for Gouy diffusimeter measurements, j_m is the total number of fringes

$$j_m = a \Delta n / \lambda \quad (36)$$

a is the distance between the cell windows, and λ is the wave length of the monochromatic light. Measurements of the optical lever arm,^{27,30} b , are referred to the refractive index of air as unity, provided the value of λ is also referred to air. An extrapolation procedure for obtaining the greatest downward displacement of light, C_t , predicted by geometrical optics at the time t , is described below. Values of \mathfrak{D}_A obtained from equation 35 are related to the four diffusion coefficients by equation 34, provided that one of the two cross-term diffusion coefficients is sufficiently small to insure satisfactory convergence of this series expression.

Fringe Deviation Graphs.—Deviations of a (symmetrical) refractive index gradient curve from Gaussian shape can be represented conveniently by a fringe deviation graph which is independent of time. As in the case of non-interacting flows,³ the first step in obtaining such a graph is to calculate the reduced fringe numbers³¹

$$f(j) = \frac{\left(j + \frac{3}{4} + \dots\right)}{j_m} \simeq \frac{Z_j}{j_m} \quad (37)$$

for several fringe minima, j ($j = 0, 1, 2, \dots$ counting from the bottom of the Gouy pattern upward). Provided the boundaries are symmetrical as assumed, the light intensity is zero at each minimum. The Airy integral approximation³² Z_j , for the series

defined. An interesting diffusion photograph of a refractive index gradient curve with two maxima was published by Longworth ("Electrochemical Constants," National Bureau of Standards Circular 524, 1951). In that experiment one diffusing solute had a large negative concentration gradient.

(26) L. G. Longworth, *THIS JOURNAL*, **69**, 2510 (1947).

(27) G. Kegeles and L. J. Gosting, *ibid.*, **69**, 2516 (1947).

(28) L. J. Gosting and L. Onsager, *ibid.*, **74**, 6066 (1952).

(29) This relation may be obtained by substituting equation 36 and the definition of C_t (equation 39e) into equation 32.

(30) See footnote 27 of ref. 3.

(31) The function $f(\zeta)$ is defined (equation 12 of ref. 27) by

$$f(\zeta) = \frac{2}{\sqrt{\pi}} \left[\int_0^\zeta e^{-\beta^2} d\beta - \zeta e^{-\zeta^2} \right] \quad (37a)$$

(32) L. J. Gosting and M. S. Morris, *THIS JOURNAL*, **71**, 1998 (1949).

($j + \frac{3}{4} + \dots$) is adequate when j_m is large.^{38,33} Numerical evaluation of the dependent variable, ζ , is unnecessary; by means of tables, one obtains from $f(\zeta_j)$ an "ideal" reduced fringe displacement, $e^{-\zeta_j^2}$, corresponding to a Gaussian refractive index gradient curve with the same number of fringes, j_m , as the boundary under consideration. From this quantity and the actual downward displacement, Y_j , of fringe j , the relative (*i.e.*, reduced) deviation

$$\Omega_j \equiv (e^{-\zeta_j^2} - Y_j/C_t) \quad (38)$$

of that fringe is easily computed and several such values plotted against $f(\zeta_j)$ to obtain the desired fringe deviation graph.

Series expansions relating these graphs to the diffusion coefficients have been derived³ for the case of non-interacting flows. With the restriction that one cross-term diffusion coefficient must be small, similar relations will now be obtained between these graphs and the diffusion coefficients for three-component systems with interacting flows. Substitution of equation 28 for the refractive index into the general interference condition for fringe minima yields the result^{34,35}

$$f(\zeta_j) = [\Gamma_1 f(z_{11})_j + \Gamma_2 f(z_{22})_j + \dots] = \frac{(j + 3/4 + \dots)}{j_m} \simeq \frac{Z_j}{j_m} \quad (39)$$

and the reduced fringe displacement for this case becomes³⁵

$$\frac{Y_j}{C_t} = \frac{[(\Gamma_1/\sqrt{D_{11}})e^{-(z_{11})_j^2} + (\Gamma_2/\sqrt{D_{22}})e^{-(z_{22})_j^2} + \dots]}{[(\Gamma_1/\sqrt{D_{11}}) + (\Gamma_2/\sqrt{D_{22}}) + \dots]} \quad (40)$$

(33) See footnote 25 of ref. 3.

(34) The first equality is included only to emphasize the definition of $f(\zeta_j)$, equation 37; the second equality is the desired interference condition.

(35) Derivation of this interference condition from the general theory of the Gouy method, ref. 28, may be outlined as follows. The notation in ref. 28 will be used without further definition, and equations in it will be referred to directly by including a letter T with the equation number. Starting with equation 46T for the light intensity distribution in Gouy fringes from any symmetrical refractive index gradient curve (having a single maximum, see ref. 25), we obtain intensity minima by setting $I(Y)$ equal to zero as before. However, the general maximized phase function $\Phi(x_2)$ is retained, so by using equations 35T and 42T we may solve for a general interference condition

$$\frac{1}{\pi} \Phi(x_2) = j + \frac{3}{4} - \frac{W_2}{\pi V_2} + \frac{1}{3\pi} \left(\frac{W_2}{V_2}\right)^3 - \dots \quad (39a)$$

instead of condition 59T for a Gaussian boundary. Then an expression for $\Phi(x_2)$ in terms of n is obtained by first setting the first derivative of $\Phi(x)$, equation 4T, equal to zero

$$Y = ab(\partial n/\partial x)_t \quad (39b)$$

which is one derivation of the ray optical relation for light displacement by a refractive index gradient. Substitution of this relation into equation 4T yields the maximized phase function

$$\frac{1}{\pi j_m} \Phi(x_2) = \left(\frac{2}{\Delta n}\right) \left[(n - n\bar{c}) - x \left(\frac{\partial n}{\partial x}\right)_t \right]_{x=x_2} \quad (39c)$$

By combining equations 39a and 39c, and associating $x = x_2$ with j , we obtain the interference condition

$$\left(\frac{2}{\Delta n}\right) \left[(n - n\bar{c}) - x \left(\frac{\partial n}{\partial x}\right)_t \right]_j = \left(j + \frac{3}{4} + \dots\right) / j_m \simeq \frac{Z_j}{j_m} \quad (39d)$$

Dividing equation 39b by the definition

$$C_t = ab[(\partial n/\partial x)_t]_{\max} \quad (39e)$$

provides an expression for the reduced fringe displacement

$$\frac{Y_j}{C_t} = \frac{[(\partial n/\partial x)_t]_j}{\{(\partial n/\partial x)_t\}_{\max}} \quad (39f)$$

Equations 39 and 40 are then obtained by substituting first equation 33, and then equation 28, into equations 39d and 39f, respectively.

In these equations higher terms (represented by $+\dots$) of the three series in brackets correspond to the two terms of order $D_{12}D_{21}$

$$\frac{D_{12}D_{21}}{D_{22} - D_{11}} \left[\alpha_1 \left(\frac{z_{11}}{2D_{11}}\right) H'(z_{11}) - \alpha_2 \left(\frac{z_{22}}{2D_{22}}\right) H'(z_{22}) \right] \quad (41)$$

and to some of the higher terms, in equation 28. Neglecting the terms not shown in equations 39 and 40, these equations become identical in form with the two corresponding relations for three-component systems without interacting flows (equations 8 and 6 of ref. 3). The previous expressions³ derived for Ω_j then become applicable to the present case by simply replacing α_1 and α_2 by Γ_1 and Γ_2 (since $\Gamma_1 + \Gamma_2 = 1$, equation 31) and D_1 and D_2 by D_{11} and D_{22} . Thus equations 13 and 23 of that theory become

$$r_2 = D_{11}/D_{22} \quad (42)$$

and

$$\Omega = \Gamma_2 F(\zeta, r_2) - \Gamma_2^2 G(\zeta, r_2) + \dots \quad (43)$$

The subscript j has been omitted because we are interested in the general functional dependence of Ω on ζ , rather than consideration of a particular fringe. This series expression is useful when Γ_2 is small because then it converges rapidly. The functions $F(\zeta, r_2)$ and $G(\zeta, r_2)$ were tabulated previously.³⁶ If Γ_1 , instead of Γ_2 , is small, we obtain a rapidly convergent expression for Ω by simply replacing 2 by 1 and 1 by 2 in equations 42 and 43.

$$r_1 = D_{22}/D_{11} \quad (44)$$

$$\Omega = \Gamma_1 F(\zeta, r_1) - \Gamma_1^2 G(\zeta, r_1) + \dots \quad (45)$$

Further, equation 27 of the previous theory³ becomes, for the present case of interacting flows

$$\Omega = \Gamma_2(1 - \Gamma_2)\zeta^2 e^{-\zeta^2} (\sqrt{r_2} - 1)^2 + \frac{1}{3} \Gamma_2(1 - \Gamma_2)[(1 - 8\Gamma_2) - 2\zeta^2(1 - 2\Gamma_2)] \zeta^2 e^{-\zeta^2} (\sqrt{r_2} - 1)^3 + \dots \quad (46)$$

This expression is useful whenever r_2 is near unity because then it converges rapidly regardless of the values of Γ_1 and Γ_2 .

Extrapolation Procedure for Obtaining C_t .

The procedure for obtaining³ C_t when the solute flows do not interact is equally applicable when the two solute flows do interact, provided higher terms are not required in equations 39 and 40; that is, provided the terms in expression 41, as well as higher terms, can be neglected in equation 28. Thus each C_t is obtained by extrapolating a plot of $Y_j/e^{-\zeta_j^2}$ versus $Z_j^{2/3}$ to $Z_j^{2/3} = 0$. When equation 28 does not converge satisfactorily this extrapolation still provides a convenient empirical method for obtaining C_t ; however, its validity for this case must not be considered proven.

Moments.—In a companion paper¹⁶ relations are derived (equations 34C-37C) for computing the four diffusion coefficients from values of the reduced second and fourth moments measured in two free diffusion experiments. In both experiments the mean concentration of a given solute must be identical. A general procedure has already been given³ for evaluating these moments from \mathfrak{D}_A and the fringe deviation graph. To be consistent with the present notation, the previous expressions³⁷ for the r th even moment ($r = 2, 4, \dots$) are rewritten

(36) Tables I and II of ref. 3.

(37) Equations 38 and 39 of ref. 3.

$$\mathfrak{D}_{r_m}^{r/2} = \mathfrak{D}_A^{r/2} \left\{ 1 + \frac{2\pi^{r/2-1} \left(\frac{r}{2}\right)!}{r!} \int_0^1 \left(\frac{2}{\sqrt{\pi}} \zeta\right)^{r-2} \left[H\left(\zeta, \frac{r}{2}\right) - 1 \right] d\zeta + \frac{\pi^{r/2} \left(\frac{r}{2}\right)!}{r!} \int_{\zeta=\infty}^0 \left(\frac{2}{\sqrt{\pi}} \zeta\right)^{r+2} e^{-\zeta^2} H\left(\zeta, \frac{r}{2}\right) d\left[\frac{d\Omega}{df(\zeta)}\right] \right\} \quad (47)$$

in which

$$H\left(\zeta, \frac{r}{2}\right) = \frac{\left(1 - \frac{\Omega}{e^{-\zeta^2}}\right)}{\left[1 + \left(\frac{2}{\sqrt{\pi}} \zeta\right) \frac{d\Omega}{df(\zeta)}\right]^{r+2}} \quad (48)$$

The integrals, which are small compared to unity, are evaluated graphically from the heights and slopes of the curve Ω versus $f(\zeta)$. The functions of ζ required for $r = 2$ and $r = 4$ have been tabulated.³⁸

Experimental

The Gouy diffusimeter described previously^{39,40} was used for all experiments. Measurements were made with the 5460.7 Å. mercury line isolated from a G.E. A-H4 lamp with a Wratten 77A filter. Because the design of cell holders was improved during the course of these diffusion measurements, three different cell holders, each with a separate Tiselius cell 9 cm. in height, were employed. Values for the cell dimensions, a , and the optical lever arms, b , are tabulated below. The values for b are relative to gage blocks

TABLE I

OPTICAL CONSTANTS FOR THE APPARATUS		
Cell ^a	a , cm.	b , cm.
GA	2.4862	307.88
SB	2.5103	306.86
SD	2.5062	306.86

^a For each cell, the arm of better optical quality was used throughout.

which had been calibrated at 68°F. as had also the Gaertner M2001RS toolmaker's microscope used to measure the photographic plates. In all experiments six sets of photographs were employed to determine the reference correction^{32,41} δ . The fused silica cells SB and SD were mounted in improved cell holders, which maintained the center section of the cell in a fixed position relative to the cell holder and mask assembly. These two cells gave more reproducible values of δ than did the glass cell GA, which was mounted so that (when opening the cell) its center section was moved relative to the cell holder and masks. Previous papers^{3,26,40,41} have described experimental procedures which are now used to obtain the reduced height-area ratios, \mathfrak{D}_A (equation 35), the fringe deviation graphs³ (equation 38) and the second and fourth reduced moments, \mathfrak{D}_{2m} and \mathfrak{D}_{4m} (equation 47, and equations 29C and 30C, C denoting the companion paper¹⁶). In no experiment was the starting time correction,³⁵ Δt , greater than 19 sec. Using a series form of the Stokes-Einstein relation

$$(\mathfrak{D}_A)_{25} = (\mathfrak{D}_A)_T [1 + 0.0264(25 - T) + \dots] \quad (49)$$

the values of \mathfrak{D}_A were corrected to 25.000° using temperatures, T , read from mercury-in-glass thermometers which had been calibrated against a certified platinum resistance thermometer. During each experiment, which was allowed to proceed until $\mathfrak{D}_A t \approx 0.15$, the temperature did not differ from 25° by more than 0.005° and was constant to $\pm 0.002^\circ$.

Materials.—Three strong electrolytes, potassium, sodium and lithium chlorides, were used in these experiments. The

(38) Table IV of ref. 3.

(39) L. J. Gosting, E. M. Hanson, G. Negeles and M. S. Morris, *Rev. Sci. Instruments*, **20**, 209 (1949).

(40) P. J. Dunlop and L. J. Gosting, *THIS JOURNAL*, **75**, 5073 (1953).

(41) L. J. Gosting, *ibid.*, **72**, 4418 (1950).

sodium chloride, reagent grade, was precipitated once by the addition of hydrogen chloride gas to a saturated solution of the salt in conductance water. The potassium and lithium chlorides, also reagent grade, were once recrystallized from conductance water by making use of the change in solubility of the salts with temperature.⁴² All three salts were then drained centrifugally and dried *in vacuo* at 80°. The potassium and sodium chloride samples were fused in a platinum crucible and broken up in an agate mortar. Because of the deliquescent nature of the lithium chloride, each portion used to make up solutions was dried, at the time of weighing, to constant weight *in vacuo* at 80°.

Solutions.—All solutions were prepared by weight using doubly-distilled water, saturated with air, as solvent. The weight fraction of each solute, corrected to vacuum, was converted to the corresponding molarity, C , using values of 74.557, 58.454 and 42.397 for the molecular weights of potassium, sodium and lithium chlorides, respectively. For solutions of single salts the required solution densities, d , at 25° were obtained using a value of 0.997075 g./ml. for the density of water and the following apparent molal volumes,⁴³ ϕ , in ml. per mole.

$$\phi_{KCl} = 26.52 + 2.327\sqrt{C} \quad (50)$$

$$\phi_{NaCl} = 16.40 + 2.153\sqrt{C} \quad (51)$$

$$\phi_{LiCl} = 17.00 + 1.488\sqrt{C} \quad (52)$$

Densities were measured for most of the mixed solute solutions. Three 30-ml. Pyrex pycnometers, filled to measured positions in their capillary necks, were employed in all cases. For all mixed solute solutions, densities were also computed from equations 50, 51 and 52 and the relationship for the volume, V

$$V = N_0 \bar{V}_0^\circ + \sum_{k=1}^2 N_k \phi_k \quad (53)$$

where N_k is the number of moles of each solute present in solution and \bar{V}_0° is the volume of a mole of the pure solvent at 25°. It was found that good agreement was obtained between the experimental and computed values of d only when each ϕ_k was calculated by substituting in equations 50–52 the sum ($C_1 + C_2$) of the salt concentrations, instead of each individual C_k value; this procedure was followed in calculating the values of d_{cal} in Tables III and IV.

Results

Single Solutes.—Diffusion experiments were performed with these lithium and sodium chloride samples, both at the same mean solute concentrations ($\bar{C}_{LiCl} = 0.25$, $\bar{C}_{NaCl} = 0.2$) and at the same mean ionic strengths ($\mu = 0.45$) used in the mixed electrolyte experiments. Similar data for potassium chloride are available elsewhere.⁴¹ It is hoped that with additional theoretical developments these data, presented in Table II, will eventually be useful for further interpretation of the mixed electrolyte experiments.

Although the diffusion coefficients for sodium chloride are in excellent agreement with those of Stokes,⁴⁴ the lithium chloride data are one per cent. lower than the results he reported.⁴⁴

Experiments I and II were performed with the same solutions but in two different cells and cell holders; the diffusion coefficients, D , and the molar refractive increments, $\Delta n/\Delta C$, are in excellent agreement. That the value of $\Delta n/\Delta C$ obtained in experiment III is 0.15% lower than the values in

(42) Analysis with a Beckman DU flame photometer with a photo-multiplier attachment showed the potassium chloride sample (prepared previously, ref. 3) to contain less than 0.05% of sodium. A similar analysis indicated that the lithium chloride contained less than 0.005% of sodium; potassium was not detected.

(43) H. S. Harned and B. B. Owen, "The Physical Chemistry of Electrolytic Solutions," 2nd Ed., Reinhold Publ. Corp., New York, N. Y., 1950, p. 253.

(44) R. H. Stokes, *THIS JOURNAL*, **72**, 2243 (1950).

TABLE II
DATA FOR THE SINGLE-SOLUTE DIFFUSION OF LITHIUM AND
SODIUM CHLORIDES IN AQUEOUS SOLUTION AT 25°

Exp. no. ^a	Cell	Solute	\bar{C} moles/l.	ΔC moles/l.	j_m	$\frac{\Delta n}{\Delta C}$ $\times 10^3$	$\frac{D}{\text{cm.}^2/\text{sec.}}$ $\times 10^3$
I	GA	LiCl	0.2498 ₀	0.2034 ₀	83.44	9.010	1.2561
II	SB	LiCl	.2498 ₀	.2034 ₀	84.26	9.011	1.2570
III	GA	LiCl	.2502 ₀	.1006 ₂	41.21	8.996	1.2551
VIII	GA	LiCl	.1499 ₈	.2000 ₀	82.88	9.102	1.2597
IX	SD	LiCl	.4500 ₂	.2000 ₅	81.58	8.886	1.263 ₀
XI	SB	NaCl	.1999 ₈	.1999 ₀	92.28	10.037	1.4787
XIV	SB	NaCl	.4499 ₆	.2000 ₇	90.31	9.819	1.4731

^a In this paper Roman numerals not only designate experiments but also indicate the order in which they were performed.

experiments I and II, with the same mean concentrations, is believed to be beyond the limit of experimental error and due to the smaller value of ΔC . This would indicate a small deviation from linearity in the dependence of n on C . Because this effect is relatively small, we will neglect it in the mixed solute experiments and use the symbol R_i for the differential refractive increments interchangeably with $\Delta n/\Delta C_i$ for the finite refractive increments.

Figure 1 shows fringe deviation graphs³ for these two solutes. In this and subsequent figures, dots indicate the individual experimental values of the reduced fringe deviations, Ω , (equation 38), obtained from the several Gouy photographs for each reduced fringe number $f(\zeta)$ (equation 37). The crosses represent the averages of the experimental points. That the average value of Ω , at each value of $f(\zeta)$, is approximately zero, indicates that the refractive index gradient curves were Gaussian within the error of measurement. A fringe deviation graph for the potassium chloride sample, used in the mixed solute experiments reported below, has been given previously.³

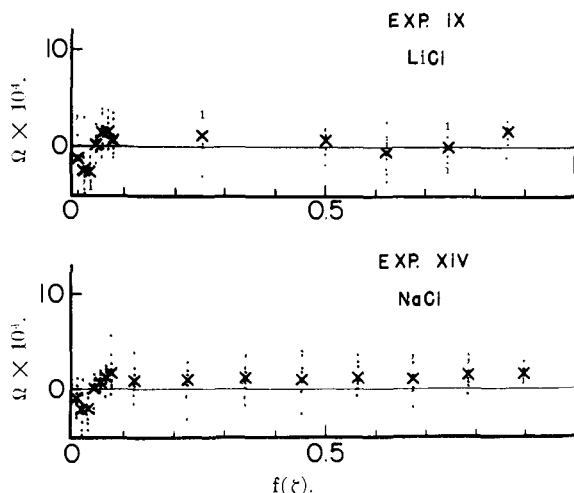


Fig. 1.—Fringe deviation graphs for the diffusion of LiCl and of NaCl.

Mixed Solutes with Interacting Flows.—Data are presented in Table III for a group of diffusion experiments in which lithium and potassium chlorides were both present in the upper and lower solutions, A and B, used to form the initial boundary. Similar data are reported in Table IV for a

second group of experiments in which lithium and sodium chlorides diffused simultaneously. Because the diffusion coefficients are expected to vary somewhat with concentration, the mean concentration, \bar{C}_1 , as well as \bar{C}_2 , was made the same in all experiments of each group. The experiments of each group differ primarily in their values of α_1 and α_2 , the fractional concentration increments on the basis of refractive index. Fringe deviation graphs for the experiments, Figs. 2, 2a and 3, provide a measure of the deviations of each refractive index gradient curve from Gaussian shape. As will be seen later, when either α_1 or α_2 (equations 25 and 26) is zero these graphs can be used directly to detect any interaction existing in the solute flows.

In the first line of each table are the experiment numbers; the cells used are recorded in the next line. Concentrations, C_i , and densities, d , of solutions A and B used in each experiment are reported in lines 3 to 10. Good agreement is seen to exist between the pycnometrically measured densities, $d_{exp.}$, and the values, $d_{calc.}$, computed from equations 50–53 as described in the experimental section. Values of \bar{C}_i and ΔC_i , lines 11–14, were obtained from the concentration data using equations 11 and 12. To calculate the α_i , lines 17 and 18, from the concentration differences ΔC_i , values were required for the differential refractive increments, R_i , equation 7C. The experiments best suited for these computations were VII, X, XII and XIII, in which the refractive index differences between solutions A and B were due almost entirely to one salt. The small amount contributed by the other salt to the total number of fringes, line 15, was easily approximated and subtracted from j_m . This gave a corrected j_m , line 15 in parentheses, due entirely to that salt with a large value of ΔC . Using equations 36 and 7C, each R_i shown at the bottom of each table was then computed from its corrected j_m . That these values of R_i are applicable within each group of experiments can be seen by comparing the experimental j_m values, line 15, with those calculated, line 16, by substituting the individual R_i and ΔC_i into equations 27 and 36.

To obtain the reduced height–area ratios, line 19, using equation 35, C_i was evaluated for each photograph by plotting $Y_j/e^{-\zeta^2}$ versus⁴⁵ $Z_j^{2/3}$ and extrapolating to $Z_j^{2/3} = 0$. This extrapolation procedure used previously for mixed solutes without interacting flows,³ was shown in the theoretical section “Extrapolation Procedure for Obtaining C_i ” to be valid for the case of interacting flows, provided all terms other than the first three terms of equation 28 are negligible. The experiments with mixtures of lithium and potassium chlorides, which satisfy this requirement, gave good straight lines in the extrapolations. It is of interest that the experiments with mixtures of lithium and sodium chlorides also gave straight lines within experimental error, even though the convergence of equations 29 and 30 is very poor. A representative extrapolation for this system is shown in Fig. 4. The reduced second moments and the reduced fourth moments, lines 20 and 21, were calculated using the values of \bar{C}_A , the fringe deviation graphs and equation 47.

(45) Values of $Z_j^{2/3}$ were given in Table 111 of ref. 3.

TABLE III^a

DATA FROM EXPERIMENTS IN WHICH LiCl AND KCl DIFFUSED SIMULTANEOUSLY IN WATER AT 25°

1	Exp. no.	IV	V	VI	VII	X
2	Cell	GA	GA	GA	GA	SD
3	(C _{LiCl}) _B	0.26237	0.34978	0.35002	0.35000	0.25003
4	(C _{KCl}) _B	0.30002	0.21846	0.21861	0.20000	0.30004
5	(d _{exp.}) _B	1.01736	1.01569	1.01572	1.01489	1.01710
6	(d _{cal.}) _B ^b	1.01737	1.01571	1.01573	1.01488	1.01708
7	(C _{LiCl}) _A	0.23785	0.15006	0.15008	0.14998	0.24985
8	(C _{KCl}) _A	0.10000	0.18154	0.18147	0.19998	0.09997
9	(d _{exp.}) _A	1.00757	1.00922
10	(d _{cal.}) _A ^b	1.00760	1.00926	1.00925	1.01010	1.00788
11	\bar{C}_{LiCl}	0.25011	0.24992	0.25005	0.24999	0.24994
12	\bar{C}_{KCl}	0.20001	0.20000	0.20004	0.19999	0.20000
13	ΔC_{LiCl}	0.02452	0.19972	0.19994	0.20002	0.00018
14	ΔC_{KCl}	0.20002	0.03692	0.03714	0.00002	0.20007
15	$j_m(\text{exp.})$	98.67	96.89	97.09	80.67	89.58
16	$j_m(\text{cal.})$	98.66	96.92	97.11	(80.66) ^c	(89.51) ^c
17	α_{LiCl}	0.1002	0.8309	0.8303	0.9999	0.0008
18	α_{KCl}	0.8998	0.1691	0.1697	0.0001	0.9992
19	$\mathcal{D}_A \times 10^5$	1.7488	1.3891	1.3893	1.3194	1.8099
20	$\mathcal{D}_{2m} \times 10^5$	1.7651	1.4441	1.4421	1.3654	1.8099
21	$\mathcal{D}_{4m}^2 \times 10^{10}$	3.1366	2.1965	2.1853	1.9351	3.2757

$$R_{LiCl} = 8.857 \times 10^{-3}$$

$$R_{KCl} = 9.748 \times 10^{-3}$$

^a Units in Tables III and IV: concentrations, C , moles/l.; densities, d , g./ml.; reduced height-area ratios, \mathcal{D}_A , and reduced second moments, \mathcal{D}_{2m} , cm.²/sec.; reduced fourth moments, \mathcal{D}_{4m}^2 , (cm.²/sec.)². ^b Calculated using equation 53. ^c For experiments VII and X the values in parentheses have been corrected to ΔC_{KCl} and ΔC_{LiCl} , respectively, equal to zero (see text).

TABLE IV

DATA FROM EXPERIMENTS IN WHICH LiCl AND NaCl DIFFUSED SIMULTANEOUSLY IN WATER AT 25°

1	Exp. no.	XII	XIII	XV	XVI
2	Cell	SB	SB	SB	SB
3	(C _{LiCl}) _B	0.25004	0.35003	0.27974	0.32495
4	(C _{NaCl}) _B	0.29996	0.20006	0.27396	0.22903
5	(d _{exp.}) _B	1.01531	1.01371	1.01499	1.01424
6	(d _{cal.}) _B ^a	1.01531	1.01370	1.01498	1.01426
7	(C _{LiCl}) _A	0.25001	0.15001	0.22019	0.17499
8	(C _{NaCl}) _A	0.10004	0.20000	0.12554	0.17103
9	(d _{exp.}) _A	1.00730	1.00891	1.00760	1.00835
10	(d _{cal.}) _A ^a	1.00730	1.00893	1.00761	1.00836
11	\bar{C}_{LiCl}	0.25002	0.25002	0.24996	0.24997
12	\bar{C}_{NaCl}	0.20000	0.20003	0.19975	0.20003
13	ΔC_{LiCl}	0.00003	0.20002	0.05955	0.14996
14	ΔC_{NaCl}	0.19992	0.00006	0.14842	0.05800
15	$j_m(\text{exp.})$	90.54	81.57	91.52	87.39
16	$j_m(\text{cal.})$	(90.53) ^b	(81.54) ^b	91.48	87.40
17	α_{LiCl}	0.0002	0.9997	0.2654	0.6995
18	α_{NaCl}	0.9998	0.0003	0.7346	0.3005
19	$\mathcal{D}_A \times 10^5$	1.4482	1.3030	1.4075	1.3424
20	$\mathcal{D}_{2m} \times 10^5$	1.4447	1.3212	1.4075	1.3527
21	$\mathcal{D}_{4m}^2 \times 10^{10}$	2.0706	1.7790	1.9810	1.8466

$$R_{LiCl} = 8.868 \times 10^{-3} \quad R_{NaCl} = 9.850 \times 10^{-3}$$

^a Calculated using equation 53. ^b For experiments XII and XIII the values in parentheses have been corrected to ΔC_{LiCl} and ΔC_{NaCl} , respectively, equal to zero (see text).

Before discussing the relation of the diffusion coefficient D_{11} , D_{12} , D_{21} and D_{22} to the deviation graphs, numbers must be assigned to the components. When lithium and potassium chlorides were present together in solution we denote lithium chloride by 1 and potassium chloride by 2; when lithium chloride and sodium chloride were the solutes, lithium chloride is denoted by 1 and sodium chloride by 2. This notation will be used throughout the remainder of this paper.

By inspection of the fringe deviation graphs for experiments in which either concentration increment was zero, Figs. 2 and 3, it is possible to see whether interaction of the solute flows was significant. The solute with zero concentration increment does not diffuse unless the flows interact, in which case the fringe deviations measure flow interaction. In such experiments the algebraic signs of fringe deviations are directly related to the signs of the ratios $D_{12}/(D_{11} - D_{22})$ and $D_{21}/(D_{22} - D_{11})$, provided these ratios are small enough to ensure the applicability of the theory for the deviation graphs. Of the four experiments (VII, X, XII and XIII) for which either ΔC_1 or ΔC_2 was approximately zero, only X had fringe deviations equal to zero. This Gaussian refractive index gradient curve could have been produced only by diffusion of the potassium chloride alone, without any resulting flow of the lithium chloride; consequently for this system $D_{12} \approx 0$ in equation 1.

The fringe deviations for the other three experiments are not zero, indicating interaction of the flows. Interpretation of the algebraic signs of these fringe deviations is based on the quantities Γ_1 and Γ_2 defined by equations 29 and 30. The smaller of these two quantities for a given experiment has the same sign as the fringe deviations, as seen from either equation 43 or 45. From the definitions of Γ_1 and Γ_2 we then obtain the following rule for interpreting the deviation graphs assuming that R_1/R_2 is positive: when α_1 is zero $D_{12}/(D_{11} - D_{22})$ has the same algebraic sign as the fringe deviations; when α_2 is zero $D_{21}/(D_{22} - D_{11})$ has the same algebraic sign as the fringe deviations. Thus in experiment VII, for which the fringe deviations are positive and $\alpha_2 \approx 0$, we deduce that $D_{21}/(D_{22} - D_{11})$ should be

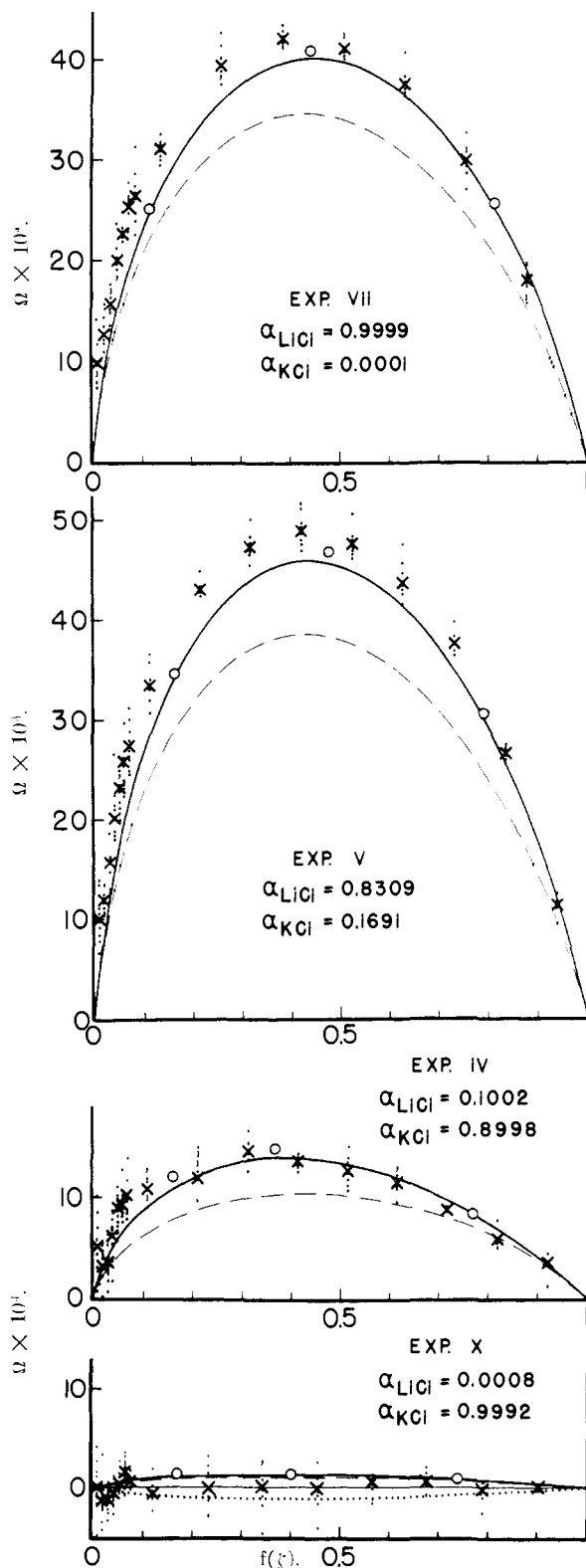


Fig. 2.—Fringe deviation graphs for the LiCl-KCl mixtures: \times , average experimental values. Curves were calculated from the values of the diffusion coefficients in Table VI: \cdots , first term of equation 46; $---$, both terms of equation 46; \circ , exact values from equation 38-40. For comparison, the dotted curve (exp. X) corresponds to $(R_1/R_2)D_{12} = +0.006 \times 10^{-2}$.

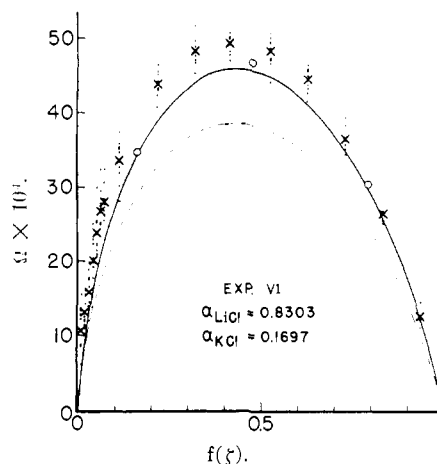


Fig. 2a.—Fringe deviation graph for an experiment designed to check experiment V.

positive, in agreement with the numerical results calculated below from the reduced moments and reduced height-area ratios. It should be noted that the signs of the cross-term diffusion coefficients, D_{12} and D_{21} , cannot be determined by inspection of the deviation graphs without independent knowledge of the relative magnitudes of D_{11} and D_{22} . It is of interest that the signs of $D_{12}/(D_{11} - D_{22})$ and $D_{21}/(D_{22} - D_{11})$ for experiments XII and XIII can also be predicted from the deviation graphs by using the above rule, even though these ratios are found later to be so large that the series expansions for Γ_1 and Γ_2 do not converge.

The fringe deviation graphs also provide evidence for the assumption, made in the theory, that the variables x and t always occur in the ratio x/\sqrt{t} . In every experiment it was found that the values of Ω at each $f(\xi_j)$ showed no significant drift with time. Therefore each value of Y_j/C_i was time independent, and because $C_i\sqrt{t}$ was constant it follows that $Y_j\sqrt{t}$ for each fringe was also independent of time (subject to the validity of the small starting time correction, Δt). Hence, from equation 39b the quantity $[(\partial n/\partial x)_t]\sqrt{t} = dn/d(x/\sqrt{t})$ was constant for each fringe, thus supporting the assumption that the solute concentrations are functions of the variable x/\sqrt{t} .

(a) **The LiCl-KCl System.**—Two methods were employed to compute values of the diffusion coefficients corresponding to the mean solute concentrations. First they were obtained from the second and fourth reduced moments by use of the theory presented in the companion paper, and then they were also computed from the values of Ω_Δ , θ_1 , θ_2 and the fringe deviation graphs.

In columns 2 and 3 of Table V are reported values of θ_1 and θ_2 , the linear combinations of diffusion coefficients defined by equations 25C and 26C. They were computed by substituting the α_i and reduced moments, Table III, into equations 31C and 32C. To obtain reasonable accuracy, only those pairs of experiments indicated in column 1, for which $(\alpha_2)_{11} - (\alpha_2)_{11}' > 0.7$, were selected. Similarly, the values for D_{11} , $(R_1/R_2)D_{12}$, $(R_2/R_1)D_{21}$ and D_{22} were computed from the same pairs of experiments by substituting the individual values of θ_1 , θ_2 , α_1 ,

TABLE V

VALUES OF θ_1 , θ_2 AND THE FOUR DIFFUSION COEFFICIENTS CALCULATED FROM THE REDUCED MOMENTS FOR THE LiCl-KCl-H₂O SYSTEM $\bar{C}_{LiCl} = 0.25$, $\bar{C}_{KCl} = 0.2$; c.g.s. units; $T = 25^\circ$

1 Exps. used	2 $\theta_1 \times 10^5$	3 $\theta_2 \times 10^5$	4 $D_{11} \times 10^5$	5 $\left(\frac{R_1}{R_2}\right) D_{12} \times 10^5$	6 $\left(\frac{R_2}{R_1}\right) D_{21} \times 10^5$	7 $D_{22} \times 10^5$
VII:X	1.365 ± 0.003	1.810 ± 0.004	1.206 ± 0.042	0.000 ± 0.066	0.159 ± 0.039	1.810 ± 0.063
IV:VII	1.365 ± .003	1.810 ± .004	1.206 ± .042	.010 ± .076	.159 ± .039	1.800 ± .072
V:X	1.370 ± .004	1.810 ± .004	1.141 ± .064	.000 ± .067	.229 ± .060	1.810 ± .063
VI:X	1.367 ± .004	1.810 ± .004	1.155 ± .064	.000 ± .067	.212 ± .060	1.810 ± .063
IV:V	1.370 ± .004	1.809 ± .004	1.136 ± .066	.017 ± .080	.234 ± .062	1.792 ± .076
IV:VI	1.367 ± .004	1.809 ± .004	1.151 ± .066	.015 ± .079	.216 ± .061	1.794 ± .075
Av.	1.367	1.810	1.172	0.006	0.195	1.803

α_2 and the reduced moments into equations 34C-37C. The estimated maximum errors were calculated assuming that each reduced second moment

was known to $\pm 0.2\%$ and each reduced fourth moment to $\pm 0.5\%$. These simplified assumptions probably magnify the estimated maximum errors. Firstly, these errors may be too large for experiments with small fringe deviations (expts. X and XV); secondly, small errors in the experimental fringe deviation graphs would cause both second and fourth reduced moments to deviate in the same direction, not necessarily in the directions which give the maximum errors as assumed. However, since it is believed that a comparison of the errors within any given column is significant, the averages in the bottom line of Table V were obtained by weighting the data according to the reciprocals of the estimated errors. It should be noted that θ_1 and θ_2 are known much more accurately than the individual diffusion coefficients. Unfortunately, these values for the four diffusion coefficients do not reproduce the measured values of Ω_A and the fringe deviation graphs within experimental error. This difficulty is due to the high sensitivity of equations 34C-37C to small errors in the reduced moments, and the following method was employed to obtain a set of diffusion coefficients which better represent these data.

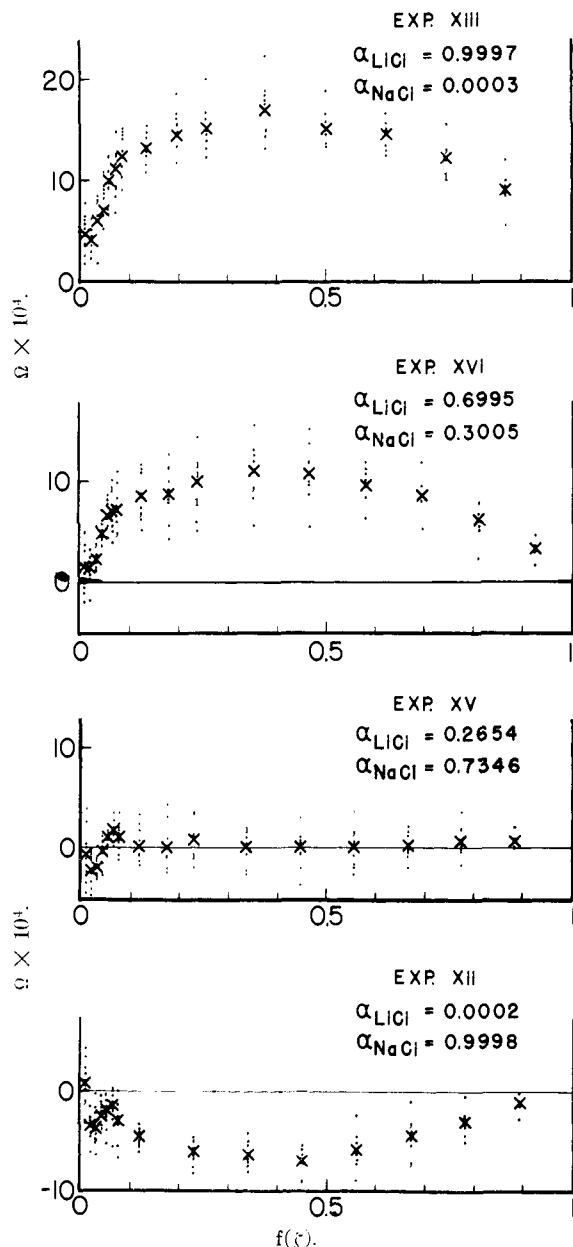


Fig. 3.—Fringe deviation graphs for the LiCl-NaCl mixtures.

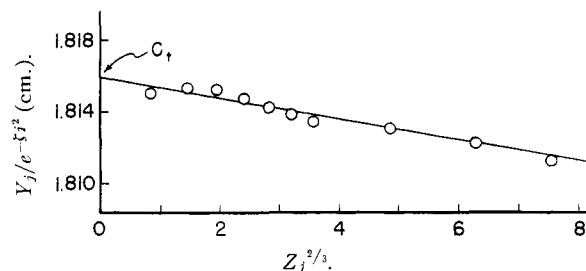


Fig. 4.—A typical extrapolation for obtaining C_t for the LiCl-NaCl system. Data are for $t = 3840$ sec., experiment XVI.

The first step in this calculation procedure was to estimate the uncertainty in $(R_1/R_2)D_{12}$ from the fringe deviations of experiment X. These values of Ω are so close to zero that this calculation was quite insensitive to D_{11} , D_{22} and $(R_2/R_1)D_{21}$; hence values for these quantities were taken from Table V. Assuming that the values of Ω do not exceed ± 0.0001 for this experiment, equation 46 (or 45) indicated that $-0.006 \leq (R_1/R_2)D_{12} \leq +0.006$. From this range, a value of -0.006 was chosen because it provided the greatest possible values of Ω_{max} for the other four experiments (the fringe deviations calculated for these experiments from the

diffusion coefficients in Table V were all too small). Values of 1.369×10^{-5} and 1.811×10^{-5} were next assigned to θ_1 and θ_2 . This small increase from the values in Table V is well within experimental error and was made in order to increase further the calculated values of Ω_{\max} . From equation 26C a value of 1.817×10^{-5} was then obtained for D_{22} . Using the three values of \mathfrak{D}_A from Table III for experiments V–VII, together with the values just presented for θ_1 , $(R_1/R_2)D_{12}$ and D_{22} , equations 25C and 34 were solved numerically to yield 1.148, 1.148 and 1.139, respectively, for $D_{11} \times 10^5$. Experiments IV and X were not used because they are not sensitive to D_{11} and $(R_2/R_1)D_{21}$. From θ_1 and the arithmetical average of these values of D_{11} , $(R_2/R_1)D_{21}$ was obtained from equation 25C. The results of this calculation procedure are summarized in Table VI. Included in brackets are values for D_{12} and D_{21} which were calculated by use of the differential refractive increments at the bottom of Table III.

TABLE VI

VALUES OF THE FOUR DIFFUSION COEFFICIENTS CHOSEN TO REPRESENT BEST THE FRINGE DEVIATION GRAPHS AND REDUCED HEIGHT-AREA RATIOS

$$\begin{aligned} \bar{C}_{\text{LiCl}} &= 0.25, \bar{C}_{\text{KCl}} = 0.2; \text{ c.g.s. units; } T = 25^\circ \\ \theta_1 &= 1.369 \times 10^{-5} & \theta_2 &= 1.811 \times 10^{-5} \\ D_{11} &= 1.145 \times 10^{-5} & D_{22} &= 1.817 \times 10^{-5} \\ (R_2/R_1)D_{21} &= 0.224 \times 10^{-5} & (R_1/R_2)D_{12} &= -0.006 \times 10^{-5} \\ [D_{21} &= 0.204 \times 10^{-5}] & [D_{12} &= -0.007 \times 10^{-5}] \end{aligned}$$

Estimation of the errors in the quantities in Table VI is difficult, but they are believed to be about $\pm 0.003 \times 10^{-5}$ for θ_1 and θ_2 and $\pm 0.01 \times 10^{-5}$ for the four diffusion coefficients.

Using the four diffusion coefficients in Table VI and the values of α_1 and α_2 in Table III, equations 29, 30, 34, 27C and 28C were employed to calculate \mathfrak{D}_A , \mathfrak{D}_{2m} and \mathfrak{D}_{4m}^2 for each of the five experiments. These values are compared with the experimental results in lines 4 to 9 of Table VII; the agreement is seen to be satisfactory. The numbers in lines 2 and 3 of this table are included to indicate how much the values of Γ_2 , equation 30, differ from α_2 for these experiments.

TABLE VII

COMPARISON OF EXPERIMENTAL VALUES OF \mathfrak{D}_A , \mathfrak{D}_{2m} AND \mathfrak{D}_{4m}^2 WITH THOSE CALCULATED FROM THE FOUR DIFFUSION COEFFICIENTS IN TABLE VI

$\bar{C}_{\text{LiCl}} = 0.25, \bar{C}_{\text{KCl}} = 0.2; \text{ c.g.s. units; } T = 25^\circ$		IV	V	VI	VII	X
1	Exp. no.					
2	α_2	0.8998	0.1691	0.1697	0.0001	0.9992
3	Γ_2	0.9276	0.4425	0.4429	0.3304	0.9936
4	$(\mathfrak{D}_A \times 10^5)_{\text{calcd.}}$	1.749	1.388	1.389	1.321	1.809
5	$(\mathfrak{D}_A \times 10^5)_{\text{obsd.}}$	1.7488	1.3891	1.3893	1.3194	1.8099
6	$(\mathfrak{D}_{2m} \times 10^5)_{\text{calcd.}}$	1.767	1.444	1.444	1.369	1.811
7	$(\mathfrak{D}_{2m} \times 10^5)_{\text{obsd.}}$	1.7651	1.4441	1.4421	1.3654	1.8099
8	$(\mathfrak{D}_{4m}^2 \times 10^{10})_{\text{calcd.}}$	3.151	2.194	2.195	1.973	3.281
9	$(\mathfrak{D}_{4m}^2 \times 10^{10})_{\text{obsd.}}$	3.137	2.196	2.185	1.935	3.276

Fringe deviation graphs corresponding to the diffusion coefficients in Table VI were calculated for the five experiments by use of equations 42, 46, the values of Γ_2 in Table VII, and Table IV of a previous paper.³ The dashed lines in Figs. 2 and 2a represent the first term of order $(\sqrt{r_2} - 1)^2$ in equation 46, while the solid lines include the next term of order $(\sqrt{r_2} - 1)^3$. That the convergence of

equation 46 is adequate for this system is seen by comparing the solid lines with the circles, which were computed directly from equations 38–40 using arbitrary values of y . Although this numerical calculation procedure avoided the use of series expansions for Ω , it should be remembered that the terms containing $H'(z_{11})$ and $H'(z_{22})$ in equations 22 and 23 have been neglected in the derivation of equations 39 and 40; furthermore, any concentration dependence of the diffusion coefficients has not been considered. It is impossible at present to determine whether the small remaining discrepancies between calculated and observed fringe deviations in Figs. 2 and 2a are due to these omissions or to imperfect selection of values for the diffusion coefficients in Table VI. Equation 45 converges more rapidly than equation 46 for calculation of Ω for experiments IV and X, but equation 46 was employed since it converges satisfactorily for all five experiments.

(b) **The LiCl–NaCl System.**—Using the second and fourth reduced moments in Table IV, values for θ_1 , θ_2 , D_{11} , $(R_1/R_2)D_{12}$, $(R_2/R_1)D_{21}$ and D_{22} were computed as described above from those pairs of experiments for which $(\alpha_2)_I - (\alpha_2)_{II} > 0.4$. The results are listed in Table VIII; estimated maximum errors were calculated using the previous assumptions. As indicated above, the absolute values of these estimated errors are probably too large, but it is believed that their reciprocals provided suitable weighting factors for obtaining the averages in the bottom line of Table VIII.

Owing to the fact that both cross-term diffusion coefficients, D_{12} and D_{21} , are quite large for this system, equations 29 and 30 do not converge satisfactorily. Hence fringe deviation graphs cannot be calculated from the diffusion coefficients in Table VIII for comparison with the experimental graphs in Fig. 3, and the second calculation procedure used to obtain diffusion coefficients for the LiCl–KCl mixtures cannot be applied to this system. The non-zero deviation graphs for experiments XII and XIII, in which α_1 and α_2 were zero, respectively, show directly that interacting flows exist in this system. It is of interest to observe from the fringe deviation graph of experiment XV that, even in the presence of interacting flows and when neither value of α is close to unity, a Gaussian boundary may still be obtained within the error of measurement.

Discussion

We have purposely avoided considering the phenomenon of ionization in the above presentation of diffusion data for mixed electrolyte solutions. This was done to emphasize that diffusion in three-component systems is described by equations 1 and 2 for the case when two solutes dissociate into three ionic species, as well as when all components are non-electrolytes.

If, however, one wishes to relate the above diffusion coefficients to individual ion mobilities and solute activity coefficients, it is necessary to consider the flows of the individual ions. Quantitative relations of this kind will not be considered here, but a few qualitative correlations should be noted. For the LiCl–KCl mixtures the value of $D_{12} \approx 0$, and the resultant Gaussian refractive index gradient

TABLE VIII

VALUES OF θ_1 , θ_2 AND THE FOUR DIFFUSION COEFFICIENTS CALCULATED FROM THE REDUCED MOMENTS FOR THE LiCl-NaCl-H₂O SYSTEM; $\bar{C}_{\text{LiCl}} = 0.25$, $\bar{C}_{\text{NaCl}} = 0.2$; c.g.s. units; $T = 25^\circ$

1	2	3	4	5	6	7
Exps. used	$\theta_1 \times 10^5$	$\theta_2 \times 10^5$	$D_{11} \times 10^5$	$\left(\frac{R_1}{R_2}\right) D_{12} \times 10^5$	$\left(\frac{R_2}{R_1}\right) D_{21} \times 10^5$	$D_{22} \times 10^5$
XII:XIII	1.321 \pm 0.003	1.445 \pm 0.003	1.051 \pm 0.132	0.134 \pm 0.151	0.270 \pm 0.129	1.311 \pm 0.148
XII:XVI	1.313 \pm .005	1.445 \pm .003	1.116 \pm .229	0.126 \pm .142	0.197 \pm .224	1.319 \pm .139
XIII:XV	1.321 \pm .003	1.439 \pm .005	1.037 \pm .138	0.135 \pm .250	0.284 \pm .135	1.304 \pm .246
XV:XVI	1.315 \pm .007	1.441 \pm .006	1.118 \pm .300	0.106 \pm .302	0.197 \pm .293	1.335 \pm .295
Av.	1.319	1.443	1.069	0.127	0.250	1.316

curve for experiment X, Fig. 2, might be anticipated from the fact that the mobilities (or equivalent conductances) of K⁺ and Cl⁻ are nearly identical. Hence, no appreciable electrostatic potential gradient was created by the diffusion of potassium chloride, and the Li⁺ ions were not disturbed. In experiment VII the Cl⁻ ions tended to move faster than the Li⁺ ions because of their greater mobility. In the process a small proportion of K⁺ ions were transported with the Li⁺ ions by the resulting potential gradient, and a non-Gaussian refractive index gradient curve was produced. Interaction of flows occurred in both experiments XII and XIII with the LiCl-NaCl system because the mobilities of Li⁺ and Na⁺ differ from the mobility of Cl⁻. In experiment XIII a small proportion of Na⁺ was transported with the more rapidly moving Cl⁻, while some Li⁺ was transported with the Cl⁻ in experiment XII. These conclusions are supported by inspection of equations 22 and 23 after substitution of the appropriate numbers for the diffusion coefficients from Tables VI and VIII.

Previous descriptions of the diffusion process in electrolyte solutions, instead of using the phenomenological approach, have commonly been based on equations which relate the flow of each ion to the several ionic mobilities, concentrations and electrochemical potential gradients. In order to compute liquid junction potentials in cells with transference,⁴⁶ Taylor⁴⁷ used this approach to derive expressions for ionic concentrations in freely diffusing boundaries, but the series expressions he developed differ in form from equations 22 and 23. For a solution containing three ionic species his equations included terms corresponding to the variation of D_{11} ,

D_{12} , D_{21} and D_{22} with ionic concentrations, and they were not limited (as are equations 22 and 23) to the case in which one cross-term diffusion coefficient is small. However, his equations were sufficiently complex so that only the first correction to the Gaussian function could easily be evaluated, and approximations in his solution prevented the calculated values of the three ionic concentrations from satisfying the condition of electrical neutrality throughout the boundary. Our approach, while avoiding this difficulty by choosing as solute components the neutral salts, is not complete in that variations in the diffusion coefficients with solute concentrations have been neglected.

It is of interest that Taylor's flow equations have the same general form as equations 1 and 2, if we let the subscripts 1 and 2 denote the cations instead of neutral salts. Further studies should permit correlation of the phenomenological diffusion coefficients with terms in his flow equations, and with terms in the more general theories of Onsager and Fuoss⁴⁸ and Onsager.¹⁵ Besides increasing our knowledge of the fundamentals of diffusion in electrolyte solutions, these developments would aid in the interpretation of diffusion experiments with protein solutions at pH values other than their isoelectric points.

Acknowledgments.—It is a pleasure to thank Dr. R. L. Baldwin for helpful discussion throughout the course of this work and during the preparation of the manuscript. This research was supported in part by the Research Committee of the Graduate School from funds supplied by the Wisconsin Alumni Research Foundation.

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(46) D. A. MacInnes, "The Principles of Electrochemistry," Reinhold Publ. Corp., New York, N. Y., 1939, Chapter 13.

(47) P. B. Taylor, *J. Phys. Chem.*, **31**, 1478 (1927).

(48) L. Onsager and R. M. Fuoss, *ibid.*, **36**, 2689 (1932).