of maximum density of the pure solvents. The latter property is an indication of the relative structural strengths of the two liquids.

The suggestion has been made by Harned and Embree[61] that comparisons of acid strength should be made at θ rather than at some arbitrary temperature like 298°. There appears to be no advantage in this so far as pK_θ values are concerned, and comparisons of $\Delta F^0_\theta = -2.3026R\theta(pK_\theta)$ are not at all as favorable as those at some constant temperature because of the variable factor θ. The entropy change at θ shows the same behavior as pK_θ (or even pK_{298}) since $\Delta S^0_\theta = 2.3026R(pK_\theta)$.[60] Thus

(61) H. S. Harned and N. D. Embree, THIS JOURNAL, **56**, 1050 (1934).

chain branching and lengthening effects all but disappear when entropy changes are compared at $\theta°$. At 298.16°K. the entropy of ionization of acetyl-DL-alanine is 1.8 units more negative than that of acetylglycine. At 277.4°K. the temperature of maximum ionization constant for the branched chain acid, the ice-like ordered structure of the solvent predominates and less change in orientation of water can be produced as a result of ionization. The entropy of ionization of acetylalanine at this temperature therefore is less negative than that at 298.16° and differs from that of acetylglycine at its temperature of maximum ionization (294.3°) by only 0.13 unit.

NEW YORK, N. Y.

An Exact Solution of the Equations for Free Diffusion in Three-component Systems with Interacting Flows, and its Use in Evaluation of the Diffusion Coefficients

BY HIROSHI FUJITA[1] AND LOUIS J. GOSTING

A rigorous solution of the differential equations for one-dimensional free diffusion is obtained for a three-component system in which the solute flows interact; the only assumptions are that the volume change on mixing and the concentration dependence of the diffusion coefficients are negligibly small. Based on this solution, a general procedure is developed for computing the four diffusion coefficients from data for the reduced height–area ratios, $\mathfrak{D}_A$, and reduced second moments, $\mathfrak{D}_{2m}$, of the refractive index gradient curves of two or more experiments. An additional procedure for calculating the coefficients is devised which depends primarily on measurements of $\mathfrak{D}_A$ and the fringe deviation graphs obtained with the Gouy diffusiometer. These procedures are applied to recently reported data for free diffusion in aqueous solutions of mixtures of (1) LiCl and KCl and (2) LiCl and NaCl. New values for the four diffusion coefficients of each system are reported and compared with those obtained using the previous methods of calculation.

In general, the diffusion of either solute in a solution containing three components depends on the concentration gradients of both solutes, four diffusion coefficients being required to describe the system. This interaction or coupling of flows is conveniently represented by a modified form[2,3] of Onsager's[4] phenomenological flow equations. Data illustrating such interaction in two electrolyte systems have recently[3] been obtained using the Gouy diffusiometer.

In recent papers two procedures were developed for computing the four diffusion coefficients, but they are subject to certain limitations. A general method[2] utilizing reduced second and fourth moments, $\mathfrak{D}_{2m}$ and $\mathfrak{D}^2_{4m}$, of the refractive index gradient curves from two experiments is limited because of experimental inaccuracy in the reduced fourth moments. A second procedure[3] in which values of the diffusion coefficients are selected to reproduce best the observed fringe deviation graphs and reduced height–area ratios, $\mathfrak{D}_A$, of at least two experiments gives good results when it is applicable; however, it is based on series expansions for the concentration curves which are applicable only when one cross-term diffusion coefficient is sufficiently small.

(1) On leave from the Department of Fisheries, Faculty of Agriculture, Kyoto University, Maizuru, Japan.

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

(3) P. J. Dunlop and L. J. Gosting, *ibid.*, **77**, 5238 (1955).

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

Using the exact solutions derived below for the solute concentration distributions in free diffusion, new procedures are devised for calculating the four diffusion coefficients. The general method utilizing values of $\mathfrak{D}_A$ and $\mathfrak{D}_{2m}$ should be more accurate than the earlier procedure utilizing $\mathfrak{D}_{2m}$ and $\mathfrak{D}^2_{4m}$, because $\mathfrak{D}_A$ can be measured much more accurately than $\mathfrak{D}^2_{4m}$. The new second method, which depends primarily on values of $\mathfrak{D}_A$ and the fringe deviation graphs, has the advantage that neither cross-term diffusion coefficient need be small.

Theory

Basic Equations.—The equations for one-dimensional diffusion in a three-component system are written[5]

$$\frac{\partial C_1}{\partial t} = D_{11}\frac{\partial^2 C_1}{\partial x^2} + D_{12}\frac{\partial^2 C_2}{\partial x^2} \qquad (1)$$

$$\frac{\partial C_2}{\partial t} = D_{21}\frac{\partial^2 C_1}{\partial x^2} + D_{22}\frac{\partial^2 C_2}{\partial x^2} \qquad (2)$$

in which solute concentrations C_1 and C_2 are functions of position x and time t, D_{11} and D_{22} are the main diffusion coefficients, and D_{12} and D_{21} are the cross-term diffusion coefficients. For free diffu-

(5) These equations are obtained by substituting the flow equations 1 and 2 of ref. 3 into the continuity equations. It is here assumed that the diffusion coefficients are all independent of concentration and that no volume change occurs on mixing. These conditions may be approached experimentally by making the concentration differences across the initial boundary sufficiently small. The reader is referred to refs. 2 and 3 for a more detailed description of the flow equations and the conditions under which they are valid.

sion a sharp boundary is formed at $t = 0$ between solutions A and B which are above and below, respectively, the position $x = 0$. Therefore the initial conditions for the two solutes ($i = 1,2$) are

$$C_i = \bar{C}_i + \Delta C_i/2 \quad \text{for } x > 0, t = 0 \quad (3)$$
$$C_i = \bar{C}_i - \Delta C_i/2 \quad \text{for } x < 0, t = 0 \quad (4)$$

while the boundary conditions are

$$C_i \longrightarrow \bar{C}_i + \Delta C_i/2 \quad \text{for } x \longrightarrow \infty, t > 0 \quad (5)$$
$$C_i \longrightarrow \bar{C}_i - \Delta C_i/2 \quad \text{for } x \longrightarrow -\infty, t > 0 \quad (6)$$

Here

$$\bar{C}_i = [(C_i)_A + (C_i)_B]/2 \quad (7)$$

is the mean concentration of each solute and

$$\Delta C_i = (C_i)_B - (C_i)_A \quad (8)$$

is the concentration difference of solute i across the diffusing boundary.

It is well known[6,7] that under these initial and boundary conditions a new variable

$$y = x/(2\sqrt{t}) \quad (9)$$

may be introduced to reduce equations 1 and 2 to a set of ordinary differential equations.

$$- 2y \frac{dC_1}{dy} = D_{11} \frac{d^2 C_1}{dy^2} + D_{12} \frac{d^2 C_2}{dy^2} \quad (10)$$

$$- 2y \frac{dC_2}{dy} = D_{21} \frac{d^2 C_1}{dy^2} + D_{22} \frac{d^2 C_2}{dy^2} \quad (11)$$

Furthermore, conditions 3–6 reduce to

$$C_i \longrightarrow \bar{C}_i + \Delta C_i/2 \quad \text{for } y \longrightarrow \infty \quad (12)$$
$$C_i \longrightarrow \bar{C}_i - \Delta C_i/2 \quad \text{for } y \longrightarrow -\infty \quad (13)$$

The Exact Solution for the Solute Concentrations.—First we let

$$\alpha = D_{11} \frac{dC_1}{dy} + D_{12} \frac{dC_2}{dy} \quad (14)$$

$$\beta = D_{21} \frac{dC_1}{dy} + D_{22} \frac{dC_2}{dy} \quad (15)$$

and

$$\eta = y^2 \quad (16)$$

Providing that the determinant

$$|D_{ij}| \equiv \begin{vmatrix} D_{11} & D_{12} \\ D_{21} & D_{22} \end{vmatrix} = D_{11}D_{22} - D_{12}D_{21} \quad (17)$$

is not zero, equations 14 and 15 are readily solved for dC_1/dy and dC_2/dy to give

$$\frac{dC_1}{dy} = H\alpha - F\beta \quad (18)$$

$$\frac{dC_2}{dy} = -G\alpha + E\beta \quad (19)$$

in which

$$E = D_{11}/|D_{ij}| \quad (20)$$
$$F = D_{12}/|D_{ij}| \quad (21)$$
$$G = D_{21}/|D_{ij}| \quad (22)$$
$$H = D_{22}/|D_{ij}| \quad (23)$$

Substitution of equations 18 and 19 (and their first derivatives with respect to y) into equations 10 and

11, and utilization of equation 16 yields the relations

$$H\alpha - F\beta = -\frac{d\alpha}{d\eta} \quad (24)$$

$$G\alpha - E\beta = \frac{d\beta}{d\eta} \quad (25)$$

which may be solved to obtain a set of differential equations of the second order for α and β.

$$\frac{d^2\alpha}{d\eta^2} + (E + H)\frac{d\alpha}{d\eta} + (EH - FG)\alpha = 0 \quad (26)$$

$$\frac{d^2\beta}{d\eta^2} + (E + H)\frac{d\beta}{d\eta} + (EH - FG)\beta = 0 \quad (27)$$

The general solutions of this set of equations are[8]

$$\alpha = P_+ e^{-\sigma_+ \eta} + P_- e^{-\sigma_- \eta} \quad (28)$$
$$\beta = Q_+ e^{-\sigma_+ \eta} + Q_- e^{-\sigma_- \eta} \quad (29)$$

where P_+, P_-, Q_+ and Q_- are integration constants to be determined and

$$\sigma_+ = \frac{1}{2}\{H + E + [(H - E)^2 + 4FG]^{1/2}\} \quad (30)$$

$$\sigma_- = \frac{1}{2}\{H + E - [(H - E)^2 + 4FG]^{1/2}\} \quad (31)$$

If either D_{12} or D_{21} is zero, these equations for σ_+ and σ_- reduce to simple expressions: for example, if $D_{22} > D_{11}$, they become

$$\sigma_+ = 1/D_{11} \quad (32)$$
$$\sigma_- = 1/D_{22} \quad (33)$$

Relations between P_+ and Q_+, and P_- and Q_-, in equations 28 and 29 are obtained by substituting these equations into either equation 24 or 25. Then because in general $\sigma_+ \neq \sigma_-$, we obtain

$$Q_+ = \left(\frac{H - \sigma_+}{F}\right)P_+ = \left(\frac{G}{E - \sigma_+}\right)P_+ \quad (34)$$

$$Q_- = \left(\frac{H - \sigma_-}{F}\right)P_- = \left(\frac{G}{E - \sigma_-}\right)P_- \quad (35)$$

Substitution of equations 28, 29, 34, 35 and 16 into equations 18 and 19, integration, and application of boundary conditions 12 and 13 permits determination of P_+ and P_-

$$P_+ = \frac{1}{\sqrt{\pi\sigma_+}}\left[\frac{(\sigma_+ - E)\Delta C_1 - F\Delta C_2}{\sigma_+ - \sigma_-}\right] \quad (36)$$

$$P_- = \frac{1}{\sqrt{\pi\sigma_-}}\left[\frac{(\sigma_- - E)\Delta C_1 - F\Delta C_2}{\sigma_- - \sigma_+}\right] \quad (37)$$

and also the constants of integration. Thus the desired exact solutions for the solute concentrations become[9]

$$C_1 = \bar{C}_1 + K_1^+ \Phi(\sqrt{\sigma_+}y) + K_1^- \Phi(\sqrt{\sigma_-}y) \quad (38)$$
$$C_2 = \bar{C}_2 + K_2^+ \Phi(\sqrt{\sigma_+}y) + K_2^- \Phi(\sqrt{\sigma_-}y) \quad (39)$$

in which

$$\Phi(q) = \frac{2}{\sqrt{\pi}}\int_0^q e^{-q^2} dq \quad (40)$$

---

(6) L. Boltzmann, *Wied. Ann.*, **53**, 959 (1894), or see W. Jost, "Diffusion in Solids, Liquids, Gases," Academic Press, Inc., New York, N. Y., 1952, p. 31.

(7) The applicability of this relation to systems in which the flows interact is discussed briefly in footnote 19 of ref. 3.

(8) See, for example, H. Margenau and G. M. Murphy, "The Mathematics of Physics and Chemistry," D. Van Nostrand Co., Inc., New York, N. Y., 1950, p. 48 ff.

(9) When either D_{12} or D_{21} is sufficiently small, equations 38 and 39 can be expanded to give the series solutions derived previously (equations 22 and 23 of ref. 3).

and[10]

$$K_1^+ = \frac{(\sigma_+ - E)\Delta C_1 - F\Delta C_2}{2(\sigma_+ - \sigma_-)} \quad (41)$$

$$K_1^- = \frac{(\sigma_- - E)\Delta C_1 - F\Delta C_2}{2(\sigma_- - \sigma_+)} \quad (42)$$

$$K_2^+ = \frac{(\sigma_+ - H)\Delta C_2 - G\Delta C_1}{2(\sigma_+ - \sigma_-)} \quad (43)$$

$$K_2^- = \frac{(\sigma_- - H)\Delta C_2 - G\Delta C_1}{2(\sigma_- - \sigma_+)} \quad (44)$$

It should be noted that the equation thus obtained for each solute concentration is a linear combination of two probability integrals (plus a constant term), the characteristics of each term depending on ΔC_1, ΔC_2 and the four diffusion coefficients.

The Refractive Index Distribution.—To derive equations for use with the several optical methods for studying free diffusion, it is assumed that the refractive index, n, in the three-component system is adequately represented by

$$n = n_{\bar{c}} + R_1(C_1 - \bar{C}_1) + R_2(C_2 - \bar{C}_2) \quad (45)$$

Here $n_{\bar{c}}$ is the refractive index of a solution in which the solute concentrations are $\bar{C}_1$ and $\bar{C}_2$, while R_1 and R_2 are the differential refractive index increments[11] of the solutes in that solution. Solute fractions on the basis of refractive index are defined by

$$\alpha_1 = R_1\Delta C_1/\Delta n \quad (46)$$

$$\alpha_2 = R_2\Delta C_2/\Delta n \quad (47)$$

where Δn is the total refractive index change across the diffusing boundary.

$$\Delta n = R_1\Delta C_1 + R_2\Delta C_2 \quad (48)$$

Equations 38 and 39 are then substituted into equation 45 to give the desired expression for the refractive index distribution curve

$$n = n_{\bar{c}} + (\Delta n/2) [\Gamma_+ \Phi(\sqrt{\sigma_+}y) + \Gamma_- \Phi(\sqrt{\sigma_-}y)] \quad (49)$$

where

$$\Gamma_+ = (2/\Delta n)(R_1 K_1^+ + R_2 K_2^+)$$
$$= \frac{[\sigma_+ - E - (R_2/R_1)G]\alpha_1 + [\sigma_+ - H - (R_1/R_2)F]\alpha_2}{\sigma_+ - \sigma_-} \quad (50)$$

$$\Gamma_- = (2/\Delta n)(R_1 K_1^- + R_2 K_2^-)$$
$$= \frac{[\sigma_- - E - (R_2/R_1)G]\alpha_1 + [\sigma_- - H - (R_1/R_2)F]\alpha_2}{\sigma_- - \sigma_+} \quad (51)$$

---

(10) In terms of the four diffusion coefficients, equations 41 and 42 become

$$K_1^+ = \frac{\{(D_{22} - D_{11}) + [(D_{22} - D_{11})^2 + 4D_{12}D_{21}]^{1/2}\}\Delta C_1 - 2D_{12}\Delta C_2}{4[(D_{22} - D_{11})^2 + 4D_{12}D_{21}]^{1/2}} \quad (41a)$$

$$K_1^- = -\frac{\{(D_{22} - D_{11}) - [(D_{22} - D_{11})^2 + 4D_{12}D_{21}]^{1/2}\}\Delta C_1 - 2D_{12}\Delta C_2}{4[(D_{22} - D_{11})^2 + 4D_{12}D_{21}]^{1/2}} \quad (42a)$$

Expressions for K_2^+ and K_2^- are obtained from K_1^+ and K_1^-, respectively, simply by interchanging subscripts 1 and 2 throughout. Equations 30 and 31 may be written

$$\sigma_+ = \frac{1}{2} \left\{ \frac{(D_{22} + D_{11}) + [(D_{22} - D_{11})^2 + 4D_{12}D_{21}]^{1/2}}{D_{11}D_{22} - D_{12}D_{21}} \right\} \quad (30a)$$

$$\sigma_- = \frac{1}{2} \left\{ \frac{(D_{22} + D_{11}) - [(D_{22} - D_{11})^2 + 4D_{12}D_{21}]^{1/2}}{D_{11}D_{22} - D_{12}D_{21}} \right\} \quad (31a)$$

In these equations the square root term is seen to be invariant to exchange of subscripts 1 and 2.

(11) See equation 7 of ref. 2 for an equation defining R_1 and R_2.

Because equation 49 has the same mathematical form as the refractive index expression for the case of two solutes diffusing independently, and because

$$\Gamma_+ + \Gamma_- = 1 \quad (52)$$

which follows from equations 50 and 51, all of the equations relating to refractive index measurements which have been derived for the case of independent diffusion in three-component systems may be applied to the present case by making a simple redefinition of terms.[12]

Evaluation of the Diffusion Coefficients from Measurements of the Reduced Height–Area Ratios and Reduced Second Moments.—The reduced height–area ratio[3] is defined by[13]

$$\mathfrak{D}_A \equiv \frac{(\Delta n)^2}{4\pi t[(\partial n/\partial x)_t]^2_{max}} \quad (53)$$

and the reduced second moment[2] by

$$\mathfrak{D}_{2m} \equiv \frac{m_2}{2t} \quad (54)$$

where m_2 is the second moment of the refractive index gradient curve at time t. Substitution of the maximum value of the first derivative of equation 49 with respect to x into equation 53 yields

$$1/\sqrt{\mathfrak{D}_A} = \Gamma_+ \sqrt{\sigma_+} + \Gamma_- \sqrt{\sigma_-} \quad (55)$$

which, by making use of the obvious relation $\alpha_1 + \alpha_2 = 1$, may be written

$$1/\sqrt{\mathfrak{D}_A} = I_A + S_A\alpha_1 \quad (56)$$

Thus, a graph of $1/\sqrt{\mathfrak{D}_A}$ versus α_1 is a straight line with slope S_A, intercept I_A at $\alpha_1 = 0$, and intercept L_A at $\alpha_1 = 1$.

$$S_A = \frac{H + (R_1/R_2)F - E - (R_2/R_1)G}{\sqrt{\sigma_+} + \sqrt{\sigma_-}} \quad (57)$$

$$I_A = \frac{\sqrt{\sigma_+\sigma_-} + E - (R_1/R_2)F}{\sqrt{\sigma_+} + \sqrt{\sigma_-}} \quad (58)$$

$$L_A = I_A + S_A = \frac{\sqrt{\sigma_+\sigma_-} + H - (R_2/R_1)G}{\sqrt{\sigma_+} + \sqrt{\sigma_-}} \quad (59)$$

Similarly, it is shown[14] that $\mathfrak{D}_{2m}$ is a linear function of α_1.

$$\mathfrak{D}_{2m} = I_{2m} + S_{2m}\alpha_1 \quad (60)$$

where the slope S_{2m} is

$$S_{2m} = D_{11} + (R_2/R_1)D_{21} - D_{22} - (R_1/R_2)D_{12} \quad (61)$$

and the intercept I_{2m} at $\alpha_1 = 0$ is

$$I_{2m} = D_{22} + (R_1/R_2)D_{12} \quad (62)$$

The intercept at $\alpha_1 = 1$ is

$$L_{2m} = I_{2m} + S_{2m} = D_{11} + (R_2/R_1)D_{21} \quad (63)$$

Because it follows from equations 30, 31 and 17 that

$$\sigma_+\sigma_- = EH - FG = |D_{ij}|^{-1} \quad (64)$$

and

$$(\sqrt{\sigma_+} + \sqrt{\sigma_-})^2 = (D_{11} + D_{22} + 2\sqrt{|D_{ij}|})/|D_{ij}| \quad (65)$$

(12) The deviation from this principle which was observed in the higher terms in equations in ref. 3 resulted because in that derivation probability integrals occurred in the form $\Phi(y/\sqrt{D_{11}})$, instead of $\Phi(\sqrt{\sigma_+}y)$, etc.

(13) This definition is restricted to the simple case in which the refractive index gradient curve has only one maximum; see footnote 25 of ref. 3.

(14) By eliminating α_2 from equation 27 of ref. 2 using $\alpha_2 = 1 - \alpha_1$.

equations 57 and 61 can be combined to give

$$|D_{ij}|(D_{11} + D_{22} + 2\sqrt{|D_{ij}|}) - (S_{2m}/S_A)^2 = 0 \quad (66)$$

and similarly equations 57, 58, 61 and 62 give

$$D_{11} + D_{22} = I_{2m} - I_A(S_{2m}/S_A) - \sqrt{|D_{ij}|} \quad (67)$$

Elimination of $D_{11} + D_{22}$ from these relations leads to a cubic equation

$$(\sqrt{|D_{ij}|})^3 + [I_{2m} - I_A(S_{2m}/S_A)](\sqrt{|D_{ij}|})^2 - (S_{2m}/S_A)^2 = 0 \quad (68)$$

from which $|D_{ij}|$ may be evaluated either numerically or graphically.

Combination of equations 62, 63 and 17 gives

$$I_{2m}D_{11} + L_{2m}D_{22} = |D_{ij}| + I_{2m}L_{2m} \quad (69)$$

As the value of $|D_{ij}|$ is now known, equations 67 and 69 are readily solved for D_{11} and D_{22}.

$$D_{11} = - [|D_{ij}| + L_{2m}\sqrt{|D_{ij}|} + L_{2m}I_A S_{2m}/S_A]/S_{2m} \quad (70)$$

$$D_{22} = [|D_{ij}| + I_{2m}\sqrt{|D_{ij}|} + I_{2m}L_A S_{2m}/S_A]/S_{2m} \quad (71)$$

Substitution of these results into equations 62 and 63 permits solution for D_{12} and D_{21} providing that the value of R_1/R_2 has been measured.

Evaluation of the Cross-Term Diffusion Coefficients from Gouy Fringe Deviation Graphs.— The method described above for calculation of the four diffusion coefficients is self-contained from the theoretical point of view and is useful for practical purposes. It should be noted, however, that experimental values of $\mathfrak{D}_{2m}$ are usually less accurate than those of $\mathfrak{D}_A$, so that the diffusion coefficient values obtained by that method may be subject to some uncertainty. Therefore, another calculation method is developed which is based primarily on the values of $\mathfrak{D}_A$ and the fringe deviation graphs[8,15] measured directly with the Gouy diffusiometer. This method consists of two parts: first the cross-term diffusion coefficients are evaluated using either method "a" or "b" below; then the procedure described in the following section is employed to determine the main diffusion coefficients.

When σ_-/σ_+ is close to unity, the fringe deviation graphs, Ω versus $f(\zeta)$, are described by the relation[16]

$$\Omega(\zeta) = \zeta^2 e^{-\zeta^2}\Gamma_+\Gamma_-\left(\sqrt{\frac{\sigma_-}{\sigma_+}} - 1\right)^2\left\{1 + \frac{1}{3}\left(\sqrt{\frac{\sigma_-}{\sigma_+}} - 1\right)[1 - 8\Gamma_- - 2\zeta^2(1 - 2\Gamma_-)] + O\left(\sqrt{\frac{\sigma_-}{\sigma_+}} - 1\right)^2\right\} \quad (72)$$

Here $\Omega(\zeta)$ is the reduced fringe deviation corresponding to a modified cell coördinate ζ. In practice only the reduced fringe number, $f(\zeta)$, is evaluated; the functional form of $f(\zeta)$ has been given previously.[17] At a value of $\zeta = \sqrt{2}$, for which $f(\zeta) = 0.73854$, equation 72 simplifies to

$$\Omega(\sqrt{2}) = 2e^{-2}\left(2 - \sqrt{\frac{\sigma_-}{\sigma_+}}\right)\Gamma_+\Gamma_-\left(\sqrt{\frac{\sigma_-}{\sigma_+}} - 1\right)^2 \quad (73)$$

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

(16) Because equation 49 is identical in form with the corresponding relations for the case in which no interaction of solute flows occurs, the equations in ref. 15 are completely applicable to Gouy fringe measurements on three-component systems with interacting flows by simply replacing α_1, α_2, $1/D_1$, $1/D_2$ and r_2 in those equations by Γ_+, Γ_-, σ_+, σ_- and σ_-/σ_+, respectively (when $D_{22} > D_{11}$). In this way equation 72 was obtained from equation 27 of ref. 15.

(17) See equation 12 of G. Kegeles and L. J. Gosting, THIS JOURNAL, **69**, 2516 (1947), or footnote 24 of ref. 15.

if terms higher than the first order of $(\sqrt{\sigma_-/\sigma_+} - 1)$ may be neglected in comparison with unity. Use of equations 50 and 51 to express the product $\Gamma_+\Gamma_-$ in terms of α_1 and α_2, and simplification by means of equations 17, 30, 31, 57, 61 and 64, and the relation $\alpha_1 + \alpha_2 = 1$, leads finally to

$$\Gamma_+\Gamma_-\left(\sqrt{\frac{\sigma_-}{\sigma_+}} - 1\right)^2 = \frac{S_A^2}{S_{2m}\sigma_+}\left[S_{2m}\alpha_1\alpha_2 + \left(\frac{R_1}{R_2}\right)D_{12}\alpha_2 - \left(\frac{R_2}{R_1}\right)D_{21}\alpha_1\right] \quad (74)$$

Equation 73 may therefore be written

$$\Omega(\sqrt{2}) = - N\{S_{2m}\ \alpha_1\alpha_2 + (R_1/R_2)D_{12} - [(R_1/R_2)D_{12} + (R_2/R_1)D_{21}]\alpha_1\} \quad (75)$$

in which

$$N = -2e^{-2}\left(2 - \sqrt{\frac{\sigma_-}{\sigma_+}}\right)\frac{S_A^2}{S_{2m}\sigma_+} \quad (76)$$

1. Method a.—Denoting the value of $\Omega(\sqrt{2})$ at $\alpha_1 = 0$ by $\Omega^0(\sqrt{2})$, equation 75 is written in the form

$$\frac{\Omega(\sqrt{2}) - \Omega^0(\sqrt{2})}{\alpha_1} = N\left[\left(\frac{R_1}{R_2}\right)D_{12} + \left(\frac{R_2}{R_1}\right)D_{21} - S_{2m}\right] + NS_{2m}\alpha_1 \quad (77)$$

Thus a plot of $[\Omega(\sqrt{2}) - \Omega^0(\sqrt{2})]/\alpha_1$ versus α_1 should be a straight line with slope S_Ω and intercept L_Ω at $\alpha_1 = 1$.

$$S_\Omega = NS_{2m} \quad (78)$$

$$L_\Omega = N[(R_1/R_2)D_{12} + (R_2/R_1)D_{21}] \quad (79)$$

Since

$$\Omega^0(\sqrt{2}) = - N(R_1/R_2)D_{12} \quad (80)$$

from equation 75, $(R_1/R_2)D_{12}$ is obtained by substitution of the value of N calculated from equation 78. A value of $(R_2/R_1)D_{21}$ is then calculated from equation 79.

It should be noted that for this method a value of S_{2m} is the only datum required in addition to fringe deviation graphs at several values of α_1. This method is both self-contained and simple to use; however, in practice it was found (see "Application") that accurate values of the cross-term diffusion coefficients can be obtained only for systems with large, and hence accurate, values of S_Ω.

2. Method b.—In this method equation 75 is written in the form

$$\frac{\Omega(\sqrt{2})}{N} + S_{2m}\alpha_1\alpha_2 = - \left(\frac{R_1}{R_2}\right)D_{12} + \left[\left(\frac{R_1}{R_2}\right)D_{12} + \left(\frac{R_2}{R_1}\right)D_{21}\right]\alpha_1 \quad (81)$$

The constant N is computed from equation 76 using data for $\mathfrak{D}_A$ and $\mathfrak{D}_{2m}$ to obtain diffusion coefficients for approximate evaluation of σ_+ and σ_-. If the value of N so obtained is correct, a plot of $[\Omega(\sqrt{2})/N] + S_{2m}\alpha_1\alpha_2$ versus α_1 is a straight line giving directly the values of $-(R_1/R_2)D_{12}$ and $(R_2/R_1)D_{21}$ at the intercepts $\alpha_1 = 0$ and $\alpha_1 = 1$, respectively. Usually the value of N computed by the above procedure is more accurate than the values of $\Omega(\sqrt{2})$. If it is not, use of this method in conjunction with the following method for evaluating D_{11} and D_{22} allows an improved value of N to be computed by a procedure of successive approximations.

Evaluation of the Main Diffusion Coefficients from the Cross-Term Diffusion Coefficients and Reduced Height-Area Ratios.

—Although the main diffusion coefficients, D_{11} and D_{22}, are readily evaluated from equations 62 and 63 when the cross-term diffusion coefficients are known, the values so obtained may not be of satisfactory accuracy because of uncertainty in the experimental values of the reduced second moments. More reliable values may be obtained from the accurately measurable reduced height-area ratios by simultaneous solution of equations 57 and 58. In general this operation is very involved, and it is more convenient to resort to the following method of successive approximations.

Using equations 17, 64 and 65, equation 57 is first converted to

$$S_A^2 |D_{ij}| [D_{11} + D_{22} + 2\sqrt{|D_{ij}|}] = [D_{22} - D_{11} + (R_1/R_2)D_{12} - (R_2/R_1)D_{21}]^2 \quad (82)$$

while equations 58 and 59 are combined to give

$$L_A D_{11} - I_A D_{22} + S_A \sqrt{|D_{ij}|} = L_A (R_1/R_2) D_{12} - I_A (R_2/R_1) D_{21} \quad (83)$$

Into these equations we substitute

$$D_{11} = D_{11}^0 (1 + \epsilon_1) \quad (84)$$

$$D_{22} = D_{22}^0 (1 + \epsilon_2) \quad (85)$$

where D_{11}^0 and D_{22}^0 are approximate values of D_{11} and D_{22}. After neglecting terms of higher orders than ϵ_1 and ϵ_2, we obtain

$$A_1 \epsilon_1 + A_2 \epsilon_2 = U \quad (86)$$

$$B_1 \epsilon_1 + B_2 \epsilon_2 = V \quad (87)$$

in which

$$A_1 = \frac{S_A D_{11}^0 D_{22}^0}{2\sqrt{|D_{ij}|^0}} + L_A D_{11}^0 \quad (88)$$

$$A_2 = \frac{S_A D_{11}^0 D_{22}^0}{2\sqrt{|D_{ij}|^0}} - I_A D_{22}^0 \quad (89)$$

$$B_1 = D_{11}^0 D_{22}^0 (D_{11}^0 + D_{22}^0 + 3\sqrt{|D_{ij}|^0}) + D_{11}^0 |D_{ij}|^0 - \frac{2D_{11}^0}{S_A^2} \left[D_{11}^0 - D_{22}^0 + \left(\frac{R_2}{R_1}\right) D_{21} - \left(\frac{R_1}{R_2}\right) D_{12} \right] \quad (90)$$

$$B_2 = D_{11}^0 D_{22}^0 (D_{11}^0 + D_{22}^0 + 3\sqrt{|D_{ij}|^0}) + D_{22}^0 |D_{ij}|^0 + \frac{2D_{22}^0}{S_A^2} \left[D_{11}^0 - D_{22}^0 + \left(\frac{R_2}{R_1}\right) D_{21} - \left(\frac{R_1}{R_2}\right) D_{12} \right] \quad (91)$$

$$U = L_A \left(\frac{R_1}{R_2}\right) D_{12} - I_A \left(\frac{R_2}{R_1}\right) D_{21} + I_A D_{22}^0 - L_A D_{11}^0 - S_A \sqrt{|D_{ij}|^0} \quad (92)$$

$$V = \frac{1}{S_A^2} \left[D_{11}^0 - D_{22}^0 + \left(\frac{R_2}{R_1}\right) D_{21} - \left(\frac{R_1}{R_2}\right) D_{12} \right]^2 - (D_{11}^0 + D_{22}^0) |D_{ij}|^0 - 2(\sqrt{|D_{ij}|^0})^3 \quad (93)$$

and

$$|D_{ij}|^0 = D_{11}^0 D_{22}^0 - D_{12} D_{21} \quad (94)$$

Although any reasonable values may be used for the zeroth approximations, D_{11}^0 and D_{22}^0, in practice it is convenient to obtain these values from equations 70 and 71. Equations 86 and 87 are then solved for values of ϵ_1 and ϵ_2, which are in turn substituted into equations 84 and 85 to yield the first approximations, D_{11}^1 and D_{22}^1, to the main diffusion coefficients. Using D_{11}^1 and D_{22}^1 values in place of D_{11}^0 and D_{22}^0 in equations 88–94, new values of ϵ_1 and ϵ_2 are computed and used to obtain the second

approximations to the main diffusion coefficients. This procedure may be repeated until the desired accuracy is obtained.

Application

The above procedures for calculating diffusion coefficients will now be illustrated by applying them to Gouy diffusiometer data which were obtained recently[3] for the two systems, LiCl–KCl–H$_2$O and LiCl–NaCl–H$_2$O. Subscripts 1 and 2 will be used to denote LiCl and KCl, respectively, for the first system, while they denote LiCl and NaCl for the second system. For each system the solute fractions on the basis of refractive index, α_1 and α_2, were varied from experiment to experiment, while $\bar{C}_1$, as well as $\bar{C}_2$, was made the same in all the experiments in order to have the same diffusion coefficients and specific refractive increments throughout.

Evaluation of Diffusion Coefficients from the Reduced Height-Area Ratios and Reduced Second Moments.—Figures 1 and 2 show, respectively, graphs of the experimental values of $1/\sqrt{\mathfrak{D}_A}$ versus α_1 and $\mathfrak{D}_{2m}$ versus α_1 for the two systems, which are seen to be linear in accordance with equations 56 and 60. Straight lines were drawn through each set of points on large scale graphs and their slopes and intercepts are presented in Table I. After substitution of these values into equation 68 and solution for $|D_{ij}|$, the values for D_{11} and D_{22} shown below in Table II, method iii, were obtained from equations 70 and 71. Equations 62 and 63 were then solved for $(R_1/R_2)D_{12}$ and $(R_2/R_1)D_{21}$, which were converted to the values of D_{12} and D_{21} shown in the same line of Table II by using the factors $R_1/R_2 = 0.908_6$ for the LiCl–KCl–H$_2$O system and $R_1/R_2 = 0.900_3$ for the LiCl–NaCl–H$_2$O system.

TABLE I

SLOPES AND INTERCEPTS OF REDUCED HEIGHT-AREA AND SECOND MOMENT DATA FOR TWO SYSTEMS WITH INTERACTING FLOWS

$T = 25°$, c.g.s. units

	⌐LiCl-KCl-H$_2$O⌐	⌐LiCl-NaCl-H$_2$O⌐
	$\bar{C}_1 \equiv \bar{C}_{LiCl} = 0.25$[a]	$\bar{C}_1 \equiv \bar{C}_{LiCl} = 0.25$
	$\bar{C}_2 \equiv \bar{C}_{KCl} = 0.2$	$\bar{C}_2 \equiv \bar{C}_{NaCl} = 0.2$
I_A	235.0$_8$	262.7$_8$
S_A	40.1$_2$	14.3$_7$
L_A	275.2$_0$	277.1$_5$
$I_{2m} \times 10^5$	1.810	1.442
$S_{2m} \times 10^5$	−0.444	−0.124
$L_{2m} \times 10^5$	1.366	1.318
$|D_{ij}| \times 10^{10}$	2.090$_8$	1.508$_1$

[a] Concentrations are expressed in moles of solute per liter of solution.

Evaluation of the Cross-term Diffusion Coefficients from Gouy Fringe Deviation Graphs.—Smooth curves were drawn through the average fringe deviations[18] of the several experiments and values of $\Omega(\sqrt{2})$ were read off the curves at $f(\zeta) = 0.7385$. The method "a" of calculation is illustrated in Fig. 3, in which values of $[\Omega(\sqrt{2}) - \Omega^0(\sqrt{2})]/\alpha_1$ are plotted against α_1 for the two sys-

(18) The curves were drawn through the crosses in Figs. 2, 2a and 3 of ref. 3.
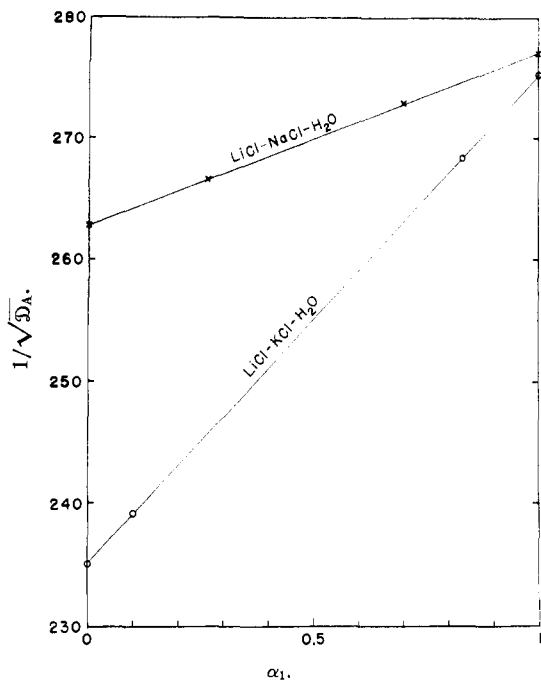
Fig. 1.—Linear relations of the reciprocal square root of reduced height–area ratio, $1/\sqrt{\mathfrak{D}_A}$, against the refractive fraction of LiCl, α_1, for the two systems
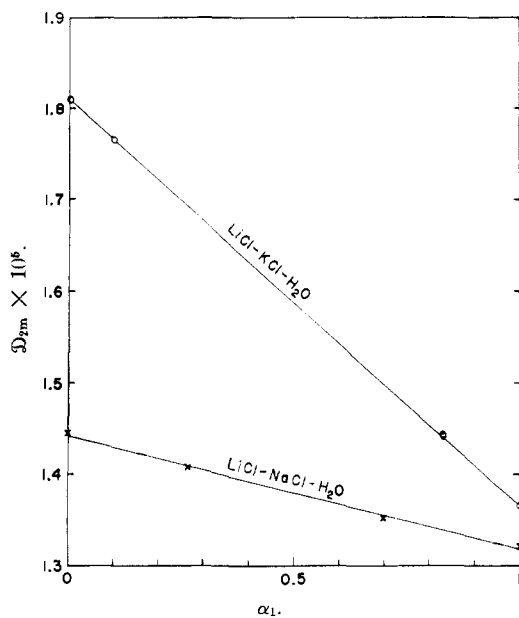

Fig. 2.—Linear relations of the reduced second moment, $\mathfrak{D}_{2m}$, against the refractive fraction of LiCl, α_1, for the two systems.

tems. An error of $\pm 1 \times 10^{-4}$ in $[\Omega(\sqrt{2}) - \Omega^0 \cdot (\sqrt{2})]$ is represented by the length of the vertical segments through the experimental points. Because the slope of these data for the LiCl–NaCl–H$_2$O system is so small, reliable diffusion coefficients cannot be evaluated; therefore, this method of analysis will be applied only to the LiCl–KCl–H$_2$O system. The slope and intercept of a straight line through these points were found to be $S_\Omega = -63.6 \times 10^{-4}$ and $L_\Omega = 32.0 \times 10^{-4}$, respectively.
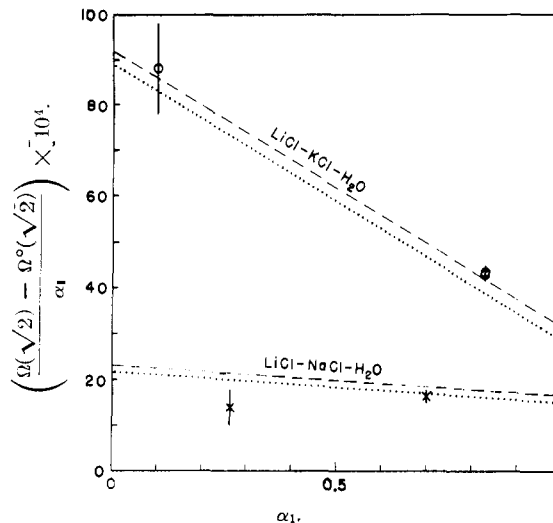

Fig. 3.—Graphs for evaluation of the cross-term diffusion coefficients from the fringe deviation graphs, method "a": . . . ., computed using D_{ij} values from method iii, Table II; – – –, computed using D_{ij} values from method iv, Table II.

Substituting this S_Ω value into equation 78, together with the value of S_{2m} from Table I, we obtain $N = 1430$. Because $\Omega^0(\sqrt{2}) = 0._0 \times 10^{-4}$ a value of $0.00_0 \times 10^{-5}$ is then obtained for $(R_1/R_2)D_{12}$ from equation 80, and insertion of L_Ω into equation 79 allows solution for $(R_2/R_1)D_{21} = 0.22_4 \times 10^{-5}$. For comparison with the experimental points dotted and dashed lines corresponding to the diffusion coefficient values obtained from methods iii and iv, respectively (Table II), were computed from equations 76, 78 and 79.

Figure 4 illustrates method "b" of calculation, equation 81, in which values of $[\Omega(\sqrt{2})/N] +$
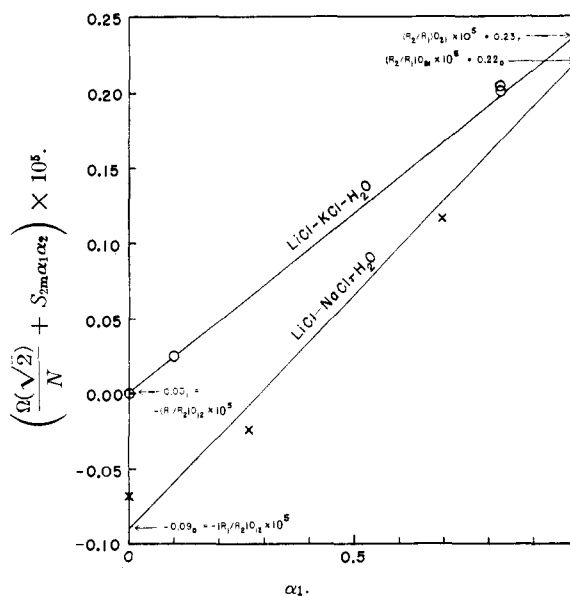

Fig. 4.—Graphs for evaluation of the cross-term diffusion coefficients from the fringe deviation graphs, method "b"; ——, the straight lines which were drawn to fit best the experimental points.
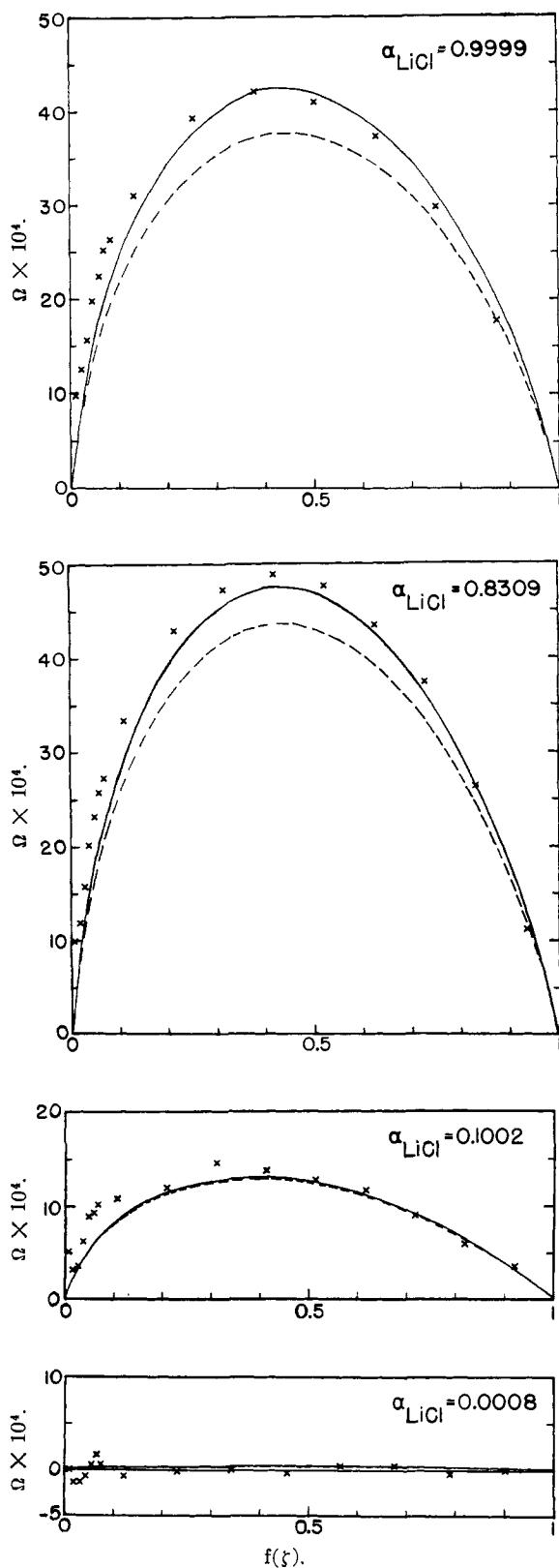
Fig. 5.—Comparison of calculated with experimental Gouy fringe deviations for the LiCl–KCl–H₂O system: X, average experimental values from ref. 3; — — — —, calculated using D_{ij} values from method iii, Table II; ————, calculated using D_{ij} values from method iv, Table II.
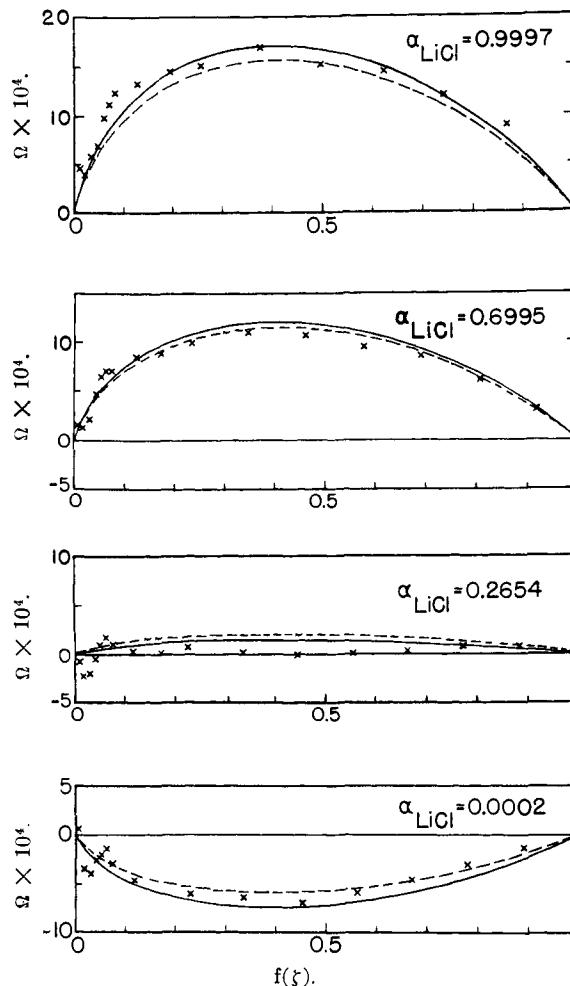

Fig. 6.—Comparison of calculated with experimental Gouy fringe deviations for the LiCl–NaCl–H₂O system: X, average experimental values from ref. 3; — — — —, calculated using D_{ij} values from method iii, Table II; ————, calculated using D_{ij} values from method iv. Table II.

$S_{2m}\alpha_1\alpha_2$ are plotted *versus* α_1 to give $-(R_1/R_2)D_{12}$ as the intercept at $\alpha_1 = 0$ and $(R_2/R_1)D_{21}$ as the intercept at $\alpha_1 = 1$. To calculate the ordinates of this graph, the value of S_{2m} was taken from Table I and N, equation 76, was approximated using the diffusion coefficients calculated from $\mathfrak{D}_A$ and $\mathfrak{D}_{2m}$, method iii of Table II. It should be noted that such approximations to S_{2m} and N do not introduce appreciable errors into this calculation because both S_{2m} and N are usually known more accurately than the values of $\Omega(\sqrt{2})$. From the intercepts in Fig. 4, and the values of R_1/R_2 for both systems, the cross-term diffusion coefficients were evaluated and recorded in Table II, method iv.

Evaluation of the Main Diffusion Coefficients from the Cross-term Diffusion Coefficients and the Reduced Height–Area Ratios.—The basic data for this calculation were the values of I_A, S_A and L_A, Table I, and those of $(R_1/R_2)D_{12}$ and $(R_2/R_1)D_{21}$ obtained from the calculation method "b" above, Fig. 4. Values for D_{11} and D_{22} were computed from equations 84–94, using as the zeroth approximations to D_{11} and D_{22} the values obtained from $\mathfrak{D}_A$

TABLE II

COMPARISON OF VALUES OF THE DIFFUSION COEFFICIENTS COMPUTED BY FOUR DIFFERENT METHODS

$T = 25°$, c.g.s. units

| Method[d] | LiCl-KCl-H$_2$O[a] | | | | LiCl-NaCl-H$_2$O[b] | | | |
| | $\bar{C}_{LiCl} = 0.25$[c] | | $\bar{C}_{KCl} = 0.2$ | | $\bar{C}_{LiCl} = 0.25$ | | $\bar{C}_{NaCl} = 0.2$ | |
	$D_{11} \times 10^5$	$D_{12} \times 10^5$	$D_{21} \times 10^5$	$D_{22} \times 10^5$	$D_{11} \times 10^5$	$D_{12} \times 10^5$	$D_{21} \times 10^5$	$D_{22} \times 10^5$
i	1.172	0.007	0.177	1.80_3	1.06_9	0.141	0.22_5	1.31_6
ii	1.14_5	$-.007$	$.20_4$	1.817	...	...	...	...
iii	1.154	$-.002$	$.19_3$	1.81_2	1.11_3	$.08_1$	$.18_5$	1.36_9
iv	1.134	$-.00_1$	$.21_5$	1.81_1	1.09_9	$.10_0$	$.19_8$	1.35_1

[a] $R_1/R_2 = 0.9086$. Subscripts 1 and 2 denote LiCl and KCl, respectively. [b] $R_1/R_2 = 0.9003$. Subscripts 1 and 2 denote LiCl and NaCl, respectively. [c] Concentrations are expressed in moles of solute per liter of solution. [d] Method i is based on $\mathfrak{D}_{2m}$ and $\mathfrak{D}^2_{4m}$ (equations 34–37 in ref. 2). Method ii is based on $\mathfrak{D}_A$, $\mathfrak{D}_{2m}$ and Ω-graphs (ref. 3). Method iii is based on $\mathfrak{D}_A$ and $\mathfrak{D}_{2m}$ (equations 62, 63, 70 and 71). Method iv is based on $\mathfrak{D}_A$ and Ω-graphs (equations 81, 84–94).

TABLE III

COMPARISON OF COMPUTED AND EXPERIMENTAL VALUES OF $\mathfrak{D}_A$ AND $\mathfrak{D}_{2m}$

$T = 25°$, c.g.s. units

| Method[a] of computing D_{11}, etc. | | LiCl-KCl-H$_2$O | | | | | LiCl-NaCl-H$_2$O | | | |
		$\bar{C}_{LiCl} = 0.25$		$\bar{C}_{KCl} = 0.2$			$\bar{C}_{LiCl} = 0.25$		$\bar{C}_{NaCl} = 0.2$	
	α_{LiCl}[b]	0.0008	0.1002	0.8303	0.8309	0.9999	0.0002	0.2654	0.6995	0.9997
	$(\mathfrak{D}_A \times 10^5)_{obsd.}$	1.809_9	1.748_8	1.389_3	1.389_1	1.319_4	1.448_2	1.407_5	1.342_4	1.303_0
iii	$(\mathfrak{D}_A \times 10^5)_{calcd.}$	1.809_0	1.749_2	1.388_3	1.388_1	1.320_5	1.448_1	1.407_0	1.343_4	1.301_9
iv	$(\mathfrak{D}_A \times 10^5)_{calcd.}$	1.809_2	1.749_3	1.387_8	1.387_6	1.320_0	1.448_6	1.407_2	1.343_3	1.301_6
	$(\mathfrak{D}_{2m} \times 10^5)_{obsd.}$	1.809_9	1.765_1	1.442_1	1.444_1	1.365_4	1.444_7	1.407_5	1.352_7	1.321_2
iii	$(\mathfrak{D}_{2m} \times 10^5)_{calcd.}$	1.809_6	1.765_5	1.441_3	1.441_1	1.366_0	1.442_0	1.409_1	1.355_3	1.318_0
iv	$(\mathfrak{D}_{2m} \times 10^5)_{calcd.}$	1.809_6	1.766_0	1.445_5	1.445_2	1.371_0	1.441_0	1.408_6	1.355_7	1.319_0

[a] See Table II for numerical values of D_{ij}. [b] $\alpha_{LiCl} \equiv \alpha_1$.

and $\mathfrak{D}_{2m}$, Table I—method iii. Satisfactory convergence was obtained with the second approximation, and the results are given in Table II, method iv.

Discussion

The values of the four diffusion coefficients, D_{ij}, computed by four different methods for the two systems are compared in Table II. Here i and ii denote the two previous methods of calculation,[2,3] while iii and iv denote the methods developed in the present paper. It will be noted that for both systems the values obtained for each diffusion coefficient agree within 0.02×10^{-5}, providing that we ignore those from method i which are believed to be less accurate because of the uncertainty in evaluating the reduced fourth moments.

In order to test the reliability of the sets of D_{ij} values computed using methods iii and iv, two kinds of comparison were made. First, for each set, values of $\mathfrak{D}_A$ and $\mathfrak{D}_{2m}$ were computed from equations 56 and 60 and are compared with the experimental values in Table III. Both sets of D_{ij} values are seen to reproduce the experimental $\mathfrak{D}_A$ and $\mathfrak{D}_{2m}$ values satisfactorily, so that it is difficult to decide from this comparison which method, iii or iv, is better. Next, for each set, fringe deviation graphs were calculated from equation 72 and are plotted in Figs. 5 and 6 where the average experi-

mental deviations are represented by crosses. The dashed and solid lines represent the computed deviations corresponding to the D_{ij} values from methods iii and iv, respectively. It is seen that for the LiCl-KCl-H$_2$O system the values of D_{ij} obtained from method iv give the better agreement. For the LiCl-NaCl-H$_2$O system both sets of D_{ij} values reproduce the experimental results within the expected error of measurement.

Summarizing, it may be concluded that for these systems with σ_-/σ_+ close to unity, so that equation 72 is applicable, method iv yields somewhat better results than method iii. However, it should be remembered that the procedures involved in method iii are much simpler and less laborious than those in method iv. It is hoped that these methods for computing the diffusion coefficients in three-component systems will be subjected to further tests using other systems.

MADISON, WISCONSIN