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

Interacting Flows in Liquid Diffusion: Equations for Evaluation of the Diffusion Coefficients from Moments of the Refractive Index Gradient Curves

BY ROBERT L. BALDWIN, PETER J. DUNLOP AND LOUIS J. GOSTING

RECEIVED MARCH 30, 1955

For systems of three or more components, flow equations of a more general form than Fick's first law may be required to describe the process of diffusion. Generalized flow equations for liquid systems are proposed which are purely phenomenological and which follow from certain considerations of Onsager. Using these flow equations, expressions for the moments of refractive index gradient curves observed in free diffusion are derived in closed form and for any number of components. The four diffusion coefficients which appear in the flow equations for a three-component system are then expressed in terms of the second and fourth moments for two experiments. Providing that both the specific refractive increments and the diffusion coefficients do not vary appreciably across the diffusing boundary (as assumed in the derivations), it is shown that the refractive index gradient curves are symmetrical about the position of the initially sharp boundary.

In some liquid systems the flows produced by diffusion are not adequately represented by Fick's first law,[1] and more general flow equations[2,3] are required to describe experimental results within the error of measurement. Data for two such systems are presented in a companion article.[4] The purpose of this paper is to show how the diffusion coefficients which appear in the following general flow equations can be evaluated from moments of the refractive index gradient curves observed in free diffusion experiments.

Flow Equations.—We may divide liquid systems into three classes according to the complexity of the flow equations required to interpret diffusion experiments. In the first class are all systems of two components, wherein diffusion of either component is completely described by Fick's first law.[1,5]

$$J_i = -D(\partial C_i/\partial x)_t \quad (i = 0,1) \qquad (1)$$

In this equation J_i is the flow[5] of component i, and $(\partial C_i/\partial x)_t$ its concentration gradient, at position x and time t; the same diffusion coefficient, D, applies to both components.[2,3,6]

A second class may be defined operationally as those systems of $q + 1$ components ($q \geqslant 2$) in which the flows of all but one are given separately by relations of the form

$$J_i = -D_i(\partial C_i/\partial x)_t \quad (i = 1, \ldots, q) \qquad (2)$$

Equations of this type have long been used to describe diffusion in dilute solutions of two or more solutes,[7-11] but satisfactory tests of their adequacy were difficult and seem to have awaited the development of modern interferometric techniques.[12-21] Recent studies[22,23] with a Gouy diffusiometer have shown that in certain dilute aqueous solutions these relations are adequate to describe the Gouy fringe positions (and hence the refractive index gradient curve) for free diffusion with an accuracy of about 0.02% of the maximum fringe displacement. In those cases, equation 2 was used to describe each solute flow, leaving the flow of solvent, component 0, unspecified.[24] It can be seen later that equation 2 is only a special case of equation 3 in which each cross-term diffusion coefficient is zero ($D_{ij} = 0$ for $i \neq j$); when somewhat greater experimental accuracy becomes available, many systems which can now be considered in this second class must be moved to class three and described by equations 3.

In the third class we consider the general case, that is, systems of three or more components in which the flows interact: the flow of each solute depends not only on its concentration gradient but also on other concentration gradients. Onsager formulated a description of this case by expressing the flow of each component as the sum of every concentration gradient multiplied by a diffusion coefficient (equation 3 of ref. 3), thus introducing $(q + 1)^2$ diffusion coefficients for a system of $q + 1$ components. He then showed that only q^2 diffusion coefficients are necessary to describe the

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

[2] O. Lamm, *Arkiv Kemi, Mineral., Geol.*, **18B**, No. 2 (1944); *J. Phys. Colloid Chem.*, **51**, 1063 (1947).

[3] L. Onsager, *Ann. N. Y. Acad. Sci.*, **46**, 241 (1945).

[4] P. J. Dunlop and L. J. Gosting, THIS JOURNAL, **77**, 5238 (1955).

[5] This and the following flow equations are written in terms of the x coördinate only, rather than for three dimensions, because derivations in this paper are restricted to the case of diffusion in one dimension in a cell of uniform cross-section. The flow is defined as positive in the direction of increasing x, and it is expressed as mass (or moles) of component i crossing unit area per second when C_i is the mass (or moles) of component i per unit volume of solution. It is supposed that no volume change occurs on mixing, so that this coördinate system may be taken as fixed relative to the cell. This condition is met in experimental work by making every concentration difference within the cell sufficiently small that the partial molal volume of each component can be taken as constant throughout the cell. Correspondingly, taking small concentration differences also decreases variation of the diffusion coefficients.

[6] G. S. Hartley and J. Crank, *Trans. Faraday Soc.*, **45**, 801 (1949).

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

[8] N. Gralen, *Kolloid-Z.*, **95**, 188 (1941); Dissertation, Uppsala, 1944.

[9] O. Quensel, Dissertation, Uppsala, 1942.

[10] H. Neurath, *Chem. Revs.*, **30**, 357 (1942).

[11] E. M. Bevilacqua, E. B. Bevilacqua, M. M. Bender and J. W. Williams, *Ann. N. Y. Acad. Sci.*, **46**, 309 (1945).

[12] L. G. Longsworth, THIS JOURNAL, **69**, 2510 (1947).

[13] G. Kegeles and L. J. Gosting, *ibid.*, **69**, 2516 (1947).

[14] C. A. Coulson, J. T. Cox, A. G. Ogston and J. St. L. Philpot, *Proc. Roy. Soc. (London)*, **A192**, 382 (1948).

[15] A. G. Ogston, *ibid.*, **A196**, 272 (1949).

[16] P. A. Charlwood, *J. Phys. Chem.*, **57**, 125 (1953).

[17] E. Calvet, *Compt. rend.*, **220**, 597 (1945); **221**, 403 (1945); *Rev. opt.*, **29**, 35 (1950).

[18] J. St. L. Philpot and G. H. Cook, *Research*, **1**, 234 (1948).

[19] H. Svensson, *Acta Chem. Scand.*, **3**, 1170 (1949); **4**, 399 (1950); **5**, 72 (1951).

[20] L. G. Longsworth, THIS JOURNAL, **74**, 4155 (1952).

[21] G. Scheibling, *J. chim. phys.*, **47**, 689 (1950); **48**, 559 (1951).

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

[23] P. J. Dunlop, *ibid.*, **77**, 2994 (1955).

[24] The solvent flow, J_0, is specified indirectly since the partial molal volume, $\bar{V}_i$, of each component is assumed constant (ref. 5). Therefore, J_0 is given by equation 3a.

flows.[3,25] For convenience, because solute rather than solvent concentrations are usually measured, we choose to omit the concentration gradient of the solvent (or major component), and also its flow equation,[24,25] from the set of flow relationships. The equation for the flow of any solute, i, may then be written

$$J_i = -\sum_{j=1}^{q} D_{ij}(\partial C_j/\partial x)_t \quad (i = 1,\ldots,q) \tag{3}$$

This set of flow equations defines q^2 diffusion coefficients for a system of $q + 1$ components, as required by Onsager's theory; however, these coefficients differ from those defined by Onsager.[3] They are related to certain combinations of his $(q + 1)^2$ coefficients and the various partial molal volumes. In the accompanying article the coefficients, D_{ij}, of equation 3 are evaluated for two systems; equations for obtaining them from even moments of the refractive index gradient curve in free diffusion will now be derived.

A Relation between the Time Derivative of the *r*th Moment and the Flows.—The rth moment of the refractive index gradient curve, $(\partial n/\partial x)_t$ *versus* x, is defined by

$$m_r \equiv (1/\Delta n) \int_{-\infty}^{\infty} x^r(\partial n/\partial x)_t\, \mathrm{d}x \quad (r = 0,1,2,\ldots) \tag{4}$$

where Δn is the total change in refractive index across the freely diffusing boundary. In order to relate $(\partial n/\partial x)_t$ to the solute flows, we first express this derivative in terms of the q solute concentration gradients. For this purpose it is assumed that the dependence of refractive index, n, on solute concentrations, C_i, expressed per unit volume of solution, may be adequately represented by the first $q + 1$ terms of a Taylor expansion

$$n = n_{\bar{C}} + \sum_{i=1}^{q} R_i(C_i - \bar{C}_i) + \ldots \tag{5}$$

Here $n_{\bar{C}} = n(\bar{C}_1, \ldots, \bar{C}_q)$ is the value of n when the concentration of each solute is the mean concentration

$$\bar{C}_i = [(C_i)_A + (C_i)_B]/2 \tag{6}$$

Solutions A and B are, respectively, the upper and lower solutions used to form the initially sharp boundary at time $t = 0$. In general, each differential refractive increment

$$R_i = |[\partial n(C_1,\ldots,C_q)/\partial C_i]_{T,P,C_{j\neq i}}|_{C_1=\bar{C}_1,\ldots,C_q=\bar{C}_q} \tag{7}$$

depends on the temperature, T, pressure, P, and the nature and concentrations of each of the q solutes present. It follows from equation 5 that the total change in refractive index across the boundary may be written

$$\Delta n = \sum_{i=1}^{q} R_i \Delta C_i \tag{8}$$

where

$$\Delta C_i = [(C_i)_B - (C_i)_A] \tag{9}$$

and for convenience we define solute fractions on the basis of refractive index by

$$\alpha_i = R_i \Delta C_i/\Delta n \tag{10}$$

Differentiation of equation 5 with respect to x and substitution of the result into equation 4 yields, after rearrangement[26]

$$m_r = (1/\Delta n) \sum_{i=1}^{q} R_i \int_{-\infty}^{\infty} x^r (\partial C_i/\partial x)_t\, \mathrm{d}x \tag{11}$$

To facilitate the derivation we define an rth moment of each concentration gradient curve by

$$(m_r)_i = (R_i/\Delta n) \int_{-\infty}^{\infty} x^r(\partial C_i/\partial x)_t\, \mathrm{d}x \tag{12}$$

so that summation yields the rth moment of the refractive index gradient curve, which is a measurable quantity.

$$m_r = \sum_{i=1}^{q} (m_r)_i \tag{13}$$

The flows, J_i, are now introduced from the continuity equation

$$(\partial C_i/\partial t)_x = -(\partial J_i/\partial x)_t \tag{14}$$

by first differentiating equation 12 with respect to time and then inverting the order of differentiation with respect to t and x.

$$\frac{\mathrm{d}(m_r)_i}{\mathrm{d}t} = \frac{R_i}{\Delta n} \int_{-\infty}^{\infty} x^r \left[\frac{\partial}{\partial x}\left(\frac{\partial C_i}{\partial t}\right)_x\right]_t \mathrm{d}x \tag{15}$$

These operations are permissible whenever the derivatives $[\partial(\partial C_i/\partial t)_x/\partial x]_t$ and $[\partial(\partial C_i/\partial x)_t/\partial t]_x$ are both continuous.[27,28] Substituting equation 14 into equation 15, and integrating once the right-hand side by parts, yields

$$\frac{\mathrm{d}(m_r)_i}{\mathrm{d}t} = \frac{rR_i}{\Delta n} \int_{-\infty}^{\infty} x^{r-1} \left(\frac{\partial J_i}{\partial x}\right)_t \mathrm{d}x \tag{16}$$

since, for free diffusion, $(\partial J_i/\partial x)_t$ is zero at the limits $x = \pm\infty$. Another integration by parts, remembering that J_i is also zero at $x = \pm\infty$, gives

$$\frac{\mathrm{d}(m_r)_i}{\mathrm{d}t} = -\frac{r(r-1)R_i}{\Delta n} \int_{-\infty}^{\infty} x^{r-2} J_i\, \mathrm{d}x \tag{17}$$

Equation 16 is useful when $r = 1$ while equation 17 will be used when $r \geqslant 2$.

Relation of the Moments to the Diffusion Coefficients.—We now substitute equation 3, describing the flow of each solute, into equation 17 and integrate the resulting equations in order to obtain expressions for the moments. To avoid serious complications in handling the equations, we restrict our discussion to experiments in which the concentration dependence of each diffusion coefficient may be neglected,[5] so that each D_{ij} may be taken outside the corresponding integral sign.

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[25] This was done by means of the conditions

$$\sum_{i=0}^{q} \bar{V}_i J_i = 0 \tag{3a}$$

$$\sum_{i=0}^{q} \bar{V}_i (\partial C_i/\partial x)_t = 0 \tag{3b}$$

where $\bar{V}_i$, the partial molal volume of component i, is constant throughout the cell.

[26] In taking R_i for each solute from under the integral sign we are assuming that the concentration differences, ΔC_i, are all so small that each R_i can be considered constant (see ref. 5).

[27] W. Kaplan, "Advanced Calculus," Addison-Wesley Publ. Co., Inc., Cambridge, Mass., 1953, p. 218.

[28] R. Courant, "Differential and Integral Calculus," Vol. II Blackie and Son Ltd., London and Glasgow, 1936, p. 55.

$$\frac{\mathrm{d}(m_r)_i}{\mathrm{d}t} = \frac{r(r-1)R_i}{\Delta n} \sum_{j=1}^{q} D_{ij} \int_{-\infty}^{\infty} x^{r-2} \left(\frac{\partial C_j}{\partial x}\right)_t \mathrm{d}x$$

$$= r(r-1) \sum_{j=1}^{q} (R_i/R_j) D_{ij} (m_{r-2})_j \qquad (18)$$

Equation 18 is seen to be a recursion formula relating the time derivative of any even moment (r) to a sum of the next lower ($r - 2$) even moments, and the time derivative of any odd moment to a sum of the next lower odd moments; its use depends on determining values for $(m_0)_j$ and $(m_1)_j$.

An expression for $(m_0)_j$ is obtained by integration of equation 12 and substitution of equation 10.

$$(m_0)_j = \alpha_j \qquad (19)$$

Integration of equation 16 for $r = 1$ leads to the result that the first moment of each concentration gradient curve is also independent of time

$$\frac{\mathrm{d}(m_1)_j}{\mathrm{d}t} = 0 \qquad (20)$$

since $J_j = 0$ at $x = \pm\infty$; hence the first moment coincides with the position of the initial boundary. For convenience the origin of x is now chosen to be the position of the initially sharp boundary, thus making the constant arising from integration of equation 20 equal to zero

$$(m_1)_j = 0 \qquad (21)$$

If now equation 18 is integrated for each successive odd value of r (after first substituting equation 21 into it for the case $r = 3$) it will be seen that every odd moment of each concentration gradient curve is zero. Thus we have the same result that is well known for systems without interacting flows: when all the diffusion coefficients (D_{ij}) and differential refractive increments (R_i) are independent of concentration, then every concentration gradient curve is an even function of x, and therefore the refractive index gradient curve is symmetrical about the position of the sharp initial boundary.

Expressions for the even moments are obtained by the same procedure. Thus, after substituting equation 19 for the case $r = 2$, equation 18 is integrated for each successive even value of r.

$$(m_2)_i = 2t \sum_{j=1}^{q} (R_i/R_j) D_{ij} \alpha_j \qquad (22)$$

$$(m_4)_i = 12t^2 \sum_{j=1}^{q} \sum_{k=1}^{q} (R_i/R_k) D_{ij} D_{jk} \alpha_k \qquad (23)$$

or, in general

$$(m_r)_{i_1} = \frac{(r)!\,t^{r/2}}{\left(\frac{r}{2}\right)!} \sum_{i_2=1}^{q} \sum_{i_3=1}^{q} \cdots \sum_{i_{\left(\frac{r+2}{2}\right)}=1}^{q} \frac{R_{i_1}}{R_{i_{\left(\frac{r+2}{2}\right)}}} D_{i_1 i_2} D_{i_2 i_3} \ldots D_{i_{\left(\frac{r}{2}\right)} i_{\left(\frac{r+2}{2}\right)}} \alpha_{i_{\left(\frac{r+2}{2}\right)}} \qquad (24)$$

where the running indices, i, j, k, etc., have been replaced, for simplicity, by i_1, i_2, i_3, etc.[29] Substitution of these expressions into equation 13 yields the desired equations for moments of the refractive index gradient curve in terms of the diffusion coefficients.

We restrict the remainder of this discussion to two-solute systems ($q = 2$) because it seems unlikely that, in the immediate future, systems with nine or more diffusion coefficients ($q \geqslant 3$) will be investigated by using optical methods to study free diffusion. For this case we denote two naturally occurring combinations of diffusion coefficients by

$$\theta_1 = D_{11} + (R_2/R_1) D_{21} \qquad (25)$$

and

$$\theta_2 = D_{22} + (R_1/R_2) D_{12} \qquad (26)$$

so that, when equations 22 and 23 are summed over all components by means of equation 13, the following important relations are obtained.[30]

$$\mathfrak{D}_{2\mathrm{m}} = \alpha_1\theta_1 + \alpha_2\theta_2 \qquad (27)$$

$$\mathfrak{D}_{4\mathrm{m}}^2 = \alpha_1[D_{11}\theta_1 + (R_2/R_1)D_{21}\theta_2] + \alpha_2[(R_1/R_2)D_{12}\theta_1 + D_{22}\theta_2] \qquad (28)$$

. . . .

Here the symbols

$$\mathfrak{D}_{2\mathrm{m}} \equiv m_2/2t \qquad (29)$$

$$\mathfrak{D}_{4\mathrm{m}}^2 \equiv m_4/12t^2 \qquad (30)$$

. . . .

denote experimentally measurable quantities which we choose to call, respectively, the *reduced second moment*, the *reduced fourth moment*, etc., of the refractive index gradient curve.

Equations for the Diffusion Coefficients in Terms of the Moments.—When $q = 2$, measurement of $\mathfrak{D}_{2\mathrm{m}}$ and $\mathfrak{D}_{4\mathrm{m}}^2$ for two diffusion experiments suffices to determine the four diffusion coefficients, provided R_1, R_2, α_1 and α_2 are known and provided that the same values of $\bar{C}_i$ (equation 6) are used in both experiments. Denoting the two experiments by subscripts I and II, we first solve equation 27 for θ_1 and θ_2.

$$\theta_1 = \frac{(\alpha_2)_{\mathrm{I}}(\mathfrak{D}_{2\mathrm{m}})_{\mathrm{II}} - (\alpha_2)_{\mathrm{II}}(\mathfrak{D}_{2\mathrm{m}})_{\mathrm{I}}}{(\alpha_2)_{\mathrm{I}} - (\alpha_2)_{\mathrm{II}}} \qquad (31)$$

$$\theta_2 = \frac{(\alpha_1)_{\mathrm{I}}(\mathfrak{D}_{2\mathrm{m}})_{\mathrm{II}} - (\alpha_1)_{\mathrm{II}}(\mathfrak{D}_{2\mathrm{m}})_{\mathrm{I}}}{(\alpha_1)_{\mathrm{I}} - (\alpha_1)_{\mathrm{II}}} \qquad (32)$$

Because these linear combinations of diffusion coefficients can be determined from the reduced second moments, without use of the less accurate reduced fourth moments, their values are more accurate than those which can be obtained for D_{11}, D_{12}, D_{21} and D_{22}.

To obtain expressions for the individual diffusion coefficients, equation 28 is written in the form

$$\mathfrak{D}_{4m}^2 = \alpha_1 D_{11}(\theta_1 - \theta_2) + \theta_1\theta_2 + \alpha_2 D_{22}(\theta_2 - \theta_1) \qquad (33)$$

After writing this equation for experiments I and II, solutions for D_{11} and D_{22} are readily obtained and simplified by means of equations 31 and 32; $(R_1/R_2)D_{12}$ and $(R_2/R_1)D_{21}$ are then obtained from equations 25 and 26.

$$D_{11} = \frac{[(\alpha_2)_{\mathrm{I}} - (\alpha_2)_{\mathrm{II}}]\theta_1\theta_2 - [(\alpha_2)_{\mathrm{I}}(\mathfrak{D}_{4\mathrm{m}}^2)_{\mathrm{II}} - (\alpha_2)_{\mathrm{II}}(\mathfrak{D}_{4\mathrm{m}}^2)_{\mathrm{I}}]}{[(\mathfrak{D}_{2\mathrm{m}})_{\mathrm{I}} - (\mathfrak{D}_{2\mathrm{m}})_{\mathrm{II}}]} \qquad (34)$$

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(29) This same approach has been used [R. L. Baldwin, *J. Phys. Chem.*, **58**, 1081 (1954)] to find expressions for the moments of the refractive index gradient curves observed in velocity ultracentrifuge experiments. The case considered was that in which $J_i = -D_i \cdot (\partial C_i/\partial x)_t + C_i s_i \omega^2 x$, where each diffusion coefficient, D_i, and each sedimentation coefficient, s_i, is constant.

(30) If there is no interaction of flows ($D_{ij} = 0$ for $i \neq j$) it is seen that equations 27 and 28 reduce to

$$\mathfrak{D}_{2\mathrm{m}} = \alpha_1 D_{11} + \alpha_2 D_{22} \qquad (27a)$$

$$\mathfrak{D}_{4\mathrm{m}}^2 = \alpha_1 D_{11}^2 + \alpha_2 D_{22}^2 \qquad (28a)$$

in agreement with earlier derivations (ref. 8). (Also see equation 33, ref. 22.)

$$\left(\frac{R_1}{R_2}\right) D_{12} = \frac{-[(\alpha_1)_{\mathrm{I}} - (\alpha_1)_{\mathrm{II}}]\theta_2^2 + [(\alpha_1)_{\mathrm{I}}(\mathfrak{D}^2_{4\mathrm{m}})_{\mathrm{II}} - (\alpha_1)_{\mathrm{II}}(\mathfrak{D}^2_{4\mathrm{m}})_{\mathrm{I}}]}{[(\mathfrak{D}_{2\mathrm{m}})_{\mathrm{I}} - (\mathfrak{D}_{2\mathrm{m}})_{\mathrm{II}}]} \quad (35)$$

$$\left(\frac{R_2}{R_1}\right) D_{21} = \frac{-[(\alpha_2)_{\mathrm{I}} - (\alpha_2)_{\mathrm{II}}]\theta_1^2 + [(\alpha_2)_{\mathrm{I}}(\mathfrak{D}^2_{4\mathrm{m}})_{\mathrm{II}} - (\alpha_2)_{\mathrm{II}}(\mathfrak{D}^2_{4\mathrm{m}})_{\mathrm{I}}]}{[(\mathfrak{D}_{2\mathrm{m}})_{\mathrm{I}} - (\mathfrak{D}_{2\mathrm{m}})_{\mathrm{II}}]} \quad (36)$$

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

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 $(\alpha_2)_{\mathrm{I}} = 0$ so that $(\alpha_1)_{\mathrm{I}} = 1$, and $(\alpha_1)_{\mathrm{II}} = 0$ so that $(\alpha_2)_{\mathrm{II}} = 1$

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

and

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

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

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

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

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

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

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 $\mathfrak{D}_{2\mathrm{m}}$ and $\mathfrak{D}^2_{4\mathrm{m}}$ 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.

MADISON, WISCONSIN

[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

BY PETER J. DUNLOP AND LOUIS J. GOSTING

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, $\mathfrak{D}_{\mathrm{A}}$, 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

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

[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. 15). 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).