

discrete crystalline and amorphous phases, all of the diluent being confined to the amorphous phase. These lines represent the change in temperature required for maintenance of equilibrium as the composition of the amorphous phase is altered by transfer of polymer from one phase to the other in the course of melting.

This calculation has been performed on the basis of the familiar relationship<sup>7,27</sup>

$$1/T - 1/T_m^* = (R/\Delta H_u)(V_u/V_1)[v_1 - (BV_1/RT)v_1^2] \quad (7)$$

where  $T_m^*$  is the melting point of the undiluted polymer,<sup>28</sup> 410.2°K. in this instance;  $V_u/V_1$  denotes the ratio of molar volumes of the structural unit ( $C_2H_4$ ) and the diluent, its value being 0.2415, with negligible dependence on temperature;  $\Delta H_u = 1940$  cal. mole<sup>-1</sup> is the heat of fusion per unit,  $B = 1.5$  cal. cc.<sup>-1</sup> represents the polymer-diluent interaction<sup>29</sup> and  $v_1$  is the volume fraction of diluent in the amorphous phase coexisting in equilibrium with crystalline polymer. In compliance with the assumption introduced above, we take

$$v_1 = v_1^0/[v_1^0 + (1 - v_1^0)\lambda] \quad (8)$$

$\lambda$  being that fraction of the polymer which occurs in the amorphous phase;  $v_1^0$  is the nominal volume fraction of diluent calculated from the weights and specific volumes of the two components. Substitution of eq. 8 in 7 provides a relationship between  $T$  and the degree of crystallinity  $1 - \lambda$ . The thus calculated (theoretical) degrees of crystallinity are readily translated to specific volumes using eq. 3 and assuming additivity of volumes with respect to the diluent. The dashed lines in Fig. 3 have been deduced in this manner.

It is to be noted that  $T_m^*$  and  $\Delta H_u$  are independently known. The value of  $B$  rests on application

(28) Inasmuch as the melting points for the polymer samples vary somewhat, being generally slightly less than  $T_m^0$  for the precisely linear polymer of infinite chain length, we introduce the symbol  $T_m^*$  to represent the melting point of a given pure polymer sample in absence of diluent.

(29) The values of  $\Delta H_u$  and  $B$  originally reported by Quinn and Mandelkern<sup>9</sup> were subject to a numerical error. We are indebted to Quinn and Mandelkern for communicating the corrected values which are quoted here. See also ref. 6.

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## Free Diffusion in a Two-component System in which There Is a Volume Change on Mixing

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For one-dimensional free diffusion in two-component systems in which volume changes occur on mixing, a formal series solution to the diffusion equation is obtained correct up to terms of order  $(\Delta c)^2$ , where  $\Delta c$  is the difference in concentration across the initial sharp boundary. Equations are derived by which observed data for the reduced height-area ratio and reduced second moment of the refractive index gradient curves can be used to evaluate the correct dependence on concentration of the diffusion coefficient. For this calculation separate data are required for the partial specific volume of the solute and the refractive index of the solution, both as functions of solute concentration.

### Introduction

Assuming that the Fick first law is valid, Gosting and Fujita<sup>2</sup> and Creeth and Gosting<sup>3</sup> have recently

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of eq. 7 to the melting points  $T_m$  of the mixtures, *i.e.*, to the temperatures for completion of melting where  $v_1 = v_1^0$ . Thus, given  $T_m$  for one mixture (as required for evaluation of  $B$ ), the broken lines are prescribed by the dictates of phase equilibrium as embodied in eq. 7. Excellent agreement up to degrees of crystallinity  $1 - \lambda$  in excess of 0.5 is evident. It is thus established that phase equilibrium is by no means confined to very low degrees of crystallinity. Deviations from equilibrium at temperatures far below  $T_m$  nevertheless are to be expected.

**Conclusions.**—An interspersed of crystalline and amorphous regions which fails to meet the criteria for representation as two discrete phases may indeed be of common occurrence in polymers rapidly crystallized by uncontrolled cooling from the melt. In addition to being imperfectly ordered, the crystalline regions in such systems may be separated from adjoining amorphous material by ill-defined boundaries. Whether or not this is the case is largely a matter of conjecture. Marked departures from equilibrium, however, are demonstrated unequivocally in polymers thus crystallized by their susceptibility to recrystallization upon raising the temperature and by their broad melting ranges.

As the results of the present investigation demonstrate, stringent measures may be required to achieve close approach to conditions of equilibrium in semi-crystalline polymer systems. Requirements in this regard are much more severe than in substances consisting of small molecules. This is a consequence of the long relaxation times for diffusive processes involving long polymer chains. Yet, it is noteworthy that even in monomeric substances the characteristic discontinuity at the first order transition may be obscured by rapid cooling to frozen-in states of non-equilibrium, by imperfect mixing, or by adventitious retention of impurities. The difference in comparison with polymers is one of degree. Departures from the precise requirements for phase equilibrium in semi-crystalline polymers are more plausibly attributable to inadequacies of experimental procedure than to any inhomogeneity of substances consisting of macromolecular chains.

discussed the effects of concentration dependence of the diffusion coefficient and of non-linear concentration dependence of the refractive index of

(2) L. J. Gosting and H. Fujita, *J. Am. Chem. Soc.*, **79**, 1359 (1957).  
(3) J. M. Creeth and L. J. Gosting, *J. Phys. Chem.*, **62**, 58 (1958).

the solution upon optical measurements of free diffusion in two-component systems (solvent + solute). The volume change which occurs on mixing of the two components was neglected in these treatments. A differential equation for describing one-dimensional diffusion in a binary system which exhibits a volume change on mixing has been derived by Prager,<sup>4</sup> but it appears that no solution of this equation has yet been given. More recently, Kirkwood, *et al.*,<sup>5</sup> have derived flow equations for one-dimensional free diffusion in multi-component systems where volume changes occur on mixing. The flow equation of Prager is shown to be included as a special case of these more general equations of Kirkwood, *et al.*

The purpose of the present article is to incorporate the volume change factor in the previous development of Gosting and Fujita<sup>2</sup> for binary solutions on the basis of the flow equation of Kirkwood, *et al.* It is shown that observed data for the reduced height-area ratio and reduced second moment of the refractive index gradient curves can be corrected for the volume change effect to determine the dependence on concentration of the diffusion coefficient referred to the volume-fixed frame.

### Theory

**The Basic Equation.**—For the development given below we adopt a form of the flow equation of Kirkwood, *et al.*,<sup>5</sup> as the starting equation. When it is substituted in the continuity equation we have

$$\frac{\partial c}{\partial t} = \frac{\partial}{\partial x} \left[ D_V \frac{\partial c}{\partial x} + c \int_{-\infty}^x \left( \frac{\partial \bar{v}}{\partial c} \right) \frac{D_V}{1 - \bar{v}c} \left( \frac{\partial c}{\partial x} \right)^2 dx \right] \quad (1)$$

Here  $x$  is the space coordinate taken along the length of the diffusion cell (its positive direction is upward because equation 1 was derived assuming that the flow vanishes at negative infinity of  $x$ ),  $t$  is the time variable,  $c$  is the concentration of the solute expressed in weight per unit volume of solution,  $\bar{v}$  is the partial specific volume of the solute and  $D_V$  is the diffusion coefficient of the system defined in terms of the volume-fixed frame of reference.<sup>6</sup> When  $\bar{v}$  is constant, equation 1 reduces to the ordinary diffusion equation for which detailed studies may be found in ref. 2 and 3. Thus the second term in the right-hand side of equation 1 represents the effect arising from volume changes on mixing.

The initial condition chosen here corresponds to that considered previously,<sup>2</sup> *i.e.*

$$c(x, 0) = c_B \quad (-\infty < x < 0) \quad (2)$$

$$c(x, 0) = c_A \quad (0 < x < \infty) \quad (3)$$

In practice, it is necessary to place the less dense solution above the more dense one so that gravitational stability will be maintained during the experiment. Hence for most cases  $\Delta c \equiv c_B - c_A > 0$ .

It is assumed that  $D_V$  is a function of  $c$  only and can be expanded in powers of  $c - \bar{c}$  about the

(4) S. Prager, *J. Chem. Phys.*, **21**, 1344 (1953); see also J. Crank, "The Mathematics of Diffusion," Oxford Univ. Press, London, 1956, pp. 236-237.

(5) J. G. Kirkwood, R. L. Baldwin, P. J. Dunlop, L. J. Gosting and G. Kegeles, *J. Chem. Phys.*, **33**, 1505 (1960).

(6) R. P. Wendt and L. J. Gosting, *J. Phys. Chem.*, **63**, 1287 (1959).

mean concentration  $\bar{c}$  of the starting solutions. Thus

$$D_V(c) = D_V(\bar{c}) [1 + k_1(c - \bar{c}) + k_2(c - \bar{c})^2 + \dots] \quad (4)$$

where

$$\bar{c} = (c_A + c_B)/2 \quad (5)$$

In equation 4,  $D_V(\bar{c})$  is the value of  $D_V$  at  $c = \bar{c}$  and the coefficients  $k_1, k_2, \text{etc.}$  stand for

$$k_1 = [(1/D_V)(dD_V/dc)]_{c=\bar{c}}, \quad k_2 = [(1/2!D_V)(d^2D_V/dc^2)]_{c=\bar{c}}, \dots \quad (6)$$

These coefficients generally vary with  $\bar{c}$ .

The partial specific volume  $\bar{v}(c)$  as a function of  $c$  may also be expanded in powers of  $c - \bar{c}$ , giving

$$\bar{v}(c) = \bar{v}(\bar{c}) [1 + m_1(c - \bar{c}) + m_2(c - \bar{c})^2 + \dots] \quad (7)$$

Here  $\bar{v}(\bar{c})$  is the value of  $\bar{v}$  at  $c = \bar{c}$  and the coefficients  $m_1, m_2, \text{etc.}$ , are defined by

$$m_1 = [(1/\bar{v})(d\bar{v}/dc)]_{c=\bar{c}}, \quad m_2 = [(1/2!\bar{v})(d^2\bar{v}/dc^2)]_{c=\bar{c}}, \dots \quad (8)$$

In general, these  $m_i$  ( $i = 1, 2, \dots$ ) are functions of  $\bar{c}$ .

Thus the problem is to solve equation 1 subject to conditions 2 and 3 with the functional forms of  $D_V$  and  $\bar{v}$  given, respectively, by equations 4 and 7.

**A Series Solution of Equation 1.**—As in the case previously treated by Gosting and Fujita,<sup>2</sup> equation 1 may be integrated by using the method of successive approximations. To do this we first introduce the Boltzmann variable  $z$  defined by

$$z = x/2[D_V(\bar{v})t]^{1/2} \quad (9)$$

Then equation 1, after substituting for  $D_V$  and  $\bar{v}$  from equations 4 and 7, is shown to become

$$-2z \frac{d\phi}{dz} = \frac{d}{dz} \left\{ [1 + q_1\beta\phi + q_2\beta^2\phi^2 + \dots] \frac{d\phi}{dz} + \beta\gamma\rho_1(1 + \beta\phi) \int_{-\infty}^z \frac{(1 + q_1\beta\phi + \dots)[1 + (2\rho_2/\rho_1)\beta\phi + \dots]}{1 - \gamma(1 + \beta\phi)(1 + \rho_1\beta\phi + \dots)} \left( \frac{d\phi}{dz} \right)^2 dz \right\} \quad (10)$$

where  $\phi$  is the reduced concentration defined as

$$\phi = 2(c - \bar{c})/\Delta c \quad (11)$$

and  $\beta, \gamma, \text{etc.}$ , are the dimensionless parameters defined as

$$\beta = \Delta c/2\bar{c} \quad (12)$$

$$\gamma = \bar{v}(\bar{c})\bar{c} \quad (13)$$

$$\rho_1 = m_1\bar{c} \quad (14)$$

$$\rho_2 = m_2\bar{c}^2 \quad (15)$$

$$q_1 = k_1\bar{c} \quad (16)$$

$$q_2 = k_2\bar{c}^2 \quad (17)$$

In terms of  $\phi$  and  $z$  conditions 2 and 3 may be expressed as

$$\phi(z) \rightarrow 1 \quad (z \rightarrow -\infty) \quad (18)$$

$$\phi(z) \rightarrow -1 \quad (z \rightarrow \infty) \quad (19)$$

If the magnitude of  $\Delta c$  is sufficiently small, the desired solution for  $\phi$  may be expanded in powers of  $\Delta c$ . This is equivalent to assuming that  $\phi$  may be expressed as a power series in  $\beta$  as

$$\phi(z) = \phi_0(z) + \beta\phi_1(z) + \beta^2\phi_2(z) + \dots \quad (20)$$

where each  $\phi_i(z)$  ( $i = 0, 1, \dots$ ) is a function of  $z$  to be determined from equation 10 and accompanying boundary conditions 18 and 19. Introducing equation 20 into equation 10, expanding both sides of the resulting expression in powers of

$\beta$  and equating the coefficients of equal powers of  $\beta$ , we obtain a set of differential equations.

$$\frac{d^2\phi_0}{dz^2} + 2z \frac{d\phi_0}{dz} = 0 \quad (21)$$

$$\frac{d^2\phi_1}{dz^2} + 2z \frac{d\phi_1}{dz} = -\frac{q_1}{2} \frac{d^2}{dz^2} (\phi_0)^2 - \lambda p_1 \left( \frac{d\phi_0}{dz} \right)^2 \quad (22)$$

$$\begin{aligned} \frac{d^2\phi_2}{dz^2} + 2z \frac{d\phi_2}{dz} = & -q_1 \frac{d^2}{dz^2} (\phi_0\phi_1) - \frac{q_2}{3} \frac{d^2}{dz^2} (\phi_0)^3 - \\ & \lambda p_1 \left\{ \frac{d}{dz} \left[ \phi_0 \int_{-\infty}^z \left( \frac{d\phi_0}{dz} \right)^2 dz \right] + 2 \frac{d\phi_0}{dz} \frac{d\phi_1}{dz} + \lambda (1 + \right. \\ & \left. p_1) \phi_0 \left( \frac{d\phi_0}{dz} \right)^2 \right\} - \lambda (\lambda p_1 q_1 + 2p_2) \phi_0 \left( \frac{d\phi_0}{dz} \right)^2 \quad (23) \end{aligned}$$

Here  $\lambda$  is a dimensionless parameter defined by

$$\lambda = \gamma/(1 - \gamma) \quad (24)$$

Differential equations for  $\phi_i$  of higher orders may be derived, but in the present treatment we shall be interested in evaluating the expression of  $\phi$  correct up through the term  $\phi_2$ . It should be noted that in the previous work of Gosting and Fujita<sup>2</sup> for diffusion involving no volume change on mixing a similar calculation was extended up to the term corresponding to  $\phi_3$  in the expansion 20.

The boundary conditions for the  $\phi_i(z)$  are derived by substituting equation 20 into equations 18 and 19 and observing that these relations must be satisfied regardless of the value of  $\beta$ . The results are

$$\begin{aligned} \phi_0(z) &\rightarrow 1 \quad (z \rightarrow -\infty) \\ \phi_0(z) &\rightarrow -1 \quad (z \rightarrow \infty) \end{aligned} \quad (25)$$

$$\begin{aligned} \phi_j(z) &\rightarrow 0 \quad (z \rightarrow -\infty) \\ \phi_j(z) &\rightarrow 0 \quad (z \rightarrow \infty) \end{aligned} \quad (j \geq 1) \quad (26)$$

The above set of ordinary differential equations of the second order for  $\phi_i(z)$  may be solved successively from top to bottom under the boundary conditions given by equations 25 and 26. The results of these calculations are

$$\phi_0(z) = -\Phi \quad (27)$$

$$d\phi_0(z)/dz = -\Phi' \quad (28)$$

$$\phi_1(z) = -\frac{(q_1/4)[2\Phi^2 + 2z\Phi\Phi' + (\Phi')^2 - 2] + (\lambda p_1/2)(1 - \Phi^2)}{\lambda p_1\Phi\Phi'} \quad (29)$$

$$d\phi_1(z)/dz = -\frac{(q_1/2)\Phi'[(3 - 2z^2)\Phi - z\Phi'] - \lambda p_1\Phi\Phi'}{\lambda p_1\Phi\Phi'} \quad (30)$$

$$\begin{aligned} d\phi_2(z)/dz = & -\frac{(q_1^2/8)\Phi'[(21 - 24z^2 + 4z^4)\Phi^2 - \\ & z(10 - 4z^2)\Phi\Phi' + (1 + z^2)(\Phi')^2 + 4z^2 - (6 - \\ & 6\sqrt{3}/\pi)] + (q_2/12)\Phi'[(18 - 12z^2)\Phi^2 - 12z\Phi\Phi' - \\ & 3(\Phi')^2 - (4 - 12\sqrt{3}/\pi)] + (\lambda p_1/12)\Phi'[6(1 + \lambda - \\ & \lambda p_1)\Phi^2 + 12\sqrt{2}/\pi z\Phi(\sqrt{2}z) + 3(\Phi')^2 + 12\sqrt{2}/\pi z - \\ & 2(1 + \lambda - \lambda p_1 + 6\sqrt{3}/\pi)] - (\lambda p_1 q_1/24)\Phi'[(66 - \\ & 36z^2)\Phi^2 - 12z\Phi\Phi' + 3(\Phi')^2 + 12z^2 + (12\sqrt{3}/\pi - \\ & 22)] - (\lambda p_2/3)\Phi'(1 - 3\Phi^2) \quad (31) \end{aligned}$$

Here

$$\Phi = (2/\sqrt{\pi}) \int_0^z \exp(-z^2) dz \quad (32)$$

$$\Phi' = (2/\sqrt{\pi}) \exp(-z^2) \quad (33)$$

The expression for  $\phi_2$  is not shown here because it is not required in deriving subsequent equations.

**The Refractive Index Gradient Distribution.**—As in the previous paper of Gosting and Fujita,<sup>2</sup> we assume that the refractive index,  $n$ , of the solution as a function of solute concentration  $c$  can be expressed in a series form as

$$n(c) = n(\bar{c}) + R(c - \bar{c})[1 + a_1(c - \bar{c}) + a_2(c - \bar{c})^2 + \dots] \quad (34)$$

where

$$R = (dn/dc)_{c=\bar{c}}$$

$$a_1 = \{[1/(2!R)](d^2n/dc^2)\}_{c=\bar{c}}$$

$$a_2 = \{[1/(3!R)](d^3n/dc^3)\}_{c=\bar{c}}, \dots \quad (35)$$

In general these coefficients vary with  $\bar{c}$  and their values can be determined from direct optical measurements or as auxiliary data from optical diffusion experiments.

Equation 34 may be written in terms of  $\phi$  by using equation 11

$$n(c) = n(\bar{c}) + R(\Delta c/2)[\phi + \beta A_1\phi^2 + \beta^2 A_2\phi^3 + \dots] \quad (36)$$

where

$$A_1 = a_1\bar{c}, A_2 = a_2\bar{c}^2, \text{ etc.} \quad (37)$$

These  $A_1, A_2, \text{ etc.}$ , are dimensionless quantities. Introduction of equation 20 into equation 36 and rearrangement of the resulting equation in powers of  $\beta$  yields

$$\begin{aligned} n(c) = n(\bar{c}) + R(\Delta c/2)[\phi_0 + \beta(\phi_1 + A_1\phi_0^2) + \\ \beta^2(\phi_2 + 2A_1\phi_0\phi_1 + A_2\phi_0^3) + \dots] \quad (38) \end{aligned}$$

Differentiation of this equation with respect to  $x$  gives the expression for the refractive index gradient distribution along the length of the diffusion cell (for fixed values of  $\bar{c}$  and  $\Delta c$ ). In terms of  $z$  it may be written

$$\begin{aligned} \frac{\partial n}{\partial x} = \frac{R\Delta c}{4[D_v(\bar{c})t]^{1/2}} \left[ \frac{d\phi_0}{dz} + \beta \left( \frac{d\phi_1}{dz} + 2A_1\phi_0 \frac{d\phi_0}{dz} \right) + \right. \\ \left. \beta^2 \left( \frac{d\phi_2}{dz} + 2A_1\phi_0 \frac{d\phi_1}{dz} + 2A_1\phi_1 \frac{d\phi_0}{dz} + 3A_2\phi_0^2 \frac{d\phi_0}{dz} \right) + \dots \right] \quad (39) \end{aligned}$$

We see that the equation for  $\phi_2$  is not required for obtaining the refractive index gradient correct up to the order of  $(\Delta c)^2$ .

**The Reduced Height-Area Ratio and Reduced Second Moment of the Refractive Index Gradient Distribution.**—The reduced height-area ratio,  $\mathfrak{D}_A$ , of the refractive index gradient curve is defined by<sup>2</sup>

$$\mathfrak{D}_A = \frac{(n_B - n_A)^2}{4\pi t \left[ \frac{\partial n}{\partial x} \right]_{\max}^2} \quad (40)$$

Here  $n_B - n_A$  represents the refractive index difference between the starting solutions of concentrations  $c_A$  and  $c_B$ ; by using equation 36 and remembering conditions 18 and 19 we have

$$n_B - n_A = R(\Delta c)[1 + \beta^2 A_2 + O(\beta^4)] \quad (41)$$

The value of  $x$  at which  $|\partial n/\partial x|$  reaches its maximum,  $[\partial n/\partial x]_{\max}$ , can be obtained in the form of a power series in  $\beta$  by using the procedure described previously.<sup>2</sup> The result is

$$z_* = (\beta\sqrt{\pi})(q_1 + \lambda p_1 - 2A_1) - (\lambda p_1/\sqrt{2\pi})\beta^2 + O(\beta^3) \quad (42)$$

where  $z_*$  is the value of  $z$  corresponding to the value of  $x$  in question. From equation 42 one finds that when  $\bar{c}$  varies with  $c$ , there appears a second order (in  $\Delta c$ ) shift in the position of the maximum refractive index gradient from the initial boundary position ( $x = 0$ ). The maximum refractive index gradient can be obtained by introducing equation 42 into equation 39, yielding

$$\left. \frac{\partial n}{\partial x} \right|_{\max} = \frac{R\Delta c}{2[\pi D_V(\bar{c})t]^{1/2}} \left\{ 1 + \frac{\beta^2}{\pi} \left[ 4.41^2 + \right. \right. \\ (\pi - 6)A_1q_1 + \frac{(6 + 3\sqrt{3} - 3\pi)}{4}q_1^2 + \\ \frac{(3 - 3\sqrt{3} + \pi)}{3}q_2 + \frac{\lambda[6\sqrt{3} - 6 + \pi(1 + \lambda)]}{6}p_1 + \\ \left. \frac{\lambda^2(6 - \pi)}{6}p_1^2 + \lambda(\pi - 4)p_1A_1 + \right. \\ \left. \frac{\lambda(6\sqrt{3} + 30 - 11\pi)}{12}p_1q_1 + \frac{\lambda\pi}{3}p_2 \right] + O(\beta^3) \right\} \quad (43)$$

The desired expression for  $\mathfrak{D}_A$  then is obtained by substituting equations 41 and 43 into equation 40. In the form of a power series in  $\Delta c$  (instead of  $\beta$ ) it reads

$$\mathfrak{D}_A = D_V(\bar{c}) \{ 1 - K(\Delta c)^2 + O[(\Delta c)^3] \} \quad (44)$$

where

$$K = K_D + K_V + K_R + K_M \quad (45)$$

with

$$K_D = [(6 + 3\sqrt{3} - 3\pi)/8\pi]k_1^2 + \\ [(\pi - 3\sqrt{3} + 3)/6\pi]k_2 \quad (46)$$

$$K_V = \{ \lambda[\pi(1 + \lambda) + 6\sqrt{3} - 6]/12\pi \} (m_1/\bar{c}) + \\ [\lambda^2(6 - \pi)/12\pi]m_1^2 + (\lambda/6)m_2 \quad (47)$$

$$K_R = (2/\pi)a_1^2 - (1/2)a_2 \quad (48)$$

$$K_M = [(\pi - 6)/2\pi]a_1k_1 + [\lambda(\pi - 4)/2\pi]a_1m_1 + \\ [\lambda(6\sqrt{3} + 30 - 11\pi)/24\pi]k_1m_1 \quad (49)$$

The first three of these four coefficients represent the individual contributions to  $K$  from the concentration dependences of  $D_V$ , of  $\bar{v}$  and of  $n$ , respectively while the last one gives the contribution from the first order couplings of these three factors.

The reduced second moment,  $\mathfrak{D}_{2m}$ , of the refractive index gradient curve is defined by<sup>2</sup>

$$\mathfrak{D}_{2m} = \frac{1}{2(n_B - n_A)} \int_{-\infty}^{\infty} \frac{\partial n}{\partial x} x^2 dx \quad (50)$$

Substitution of equations 39 and 41 and integration leads to

$$\mathfrak{D}_{2m} = D_V(\bar{c}) \{ 1 - L(\Delta c)^2 + O[(\Delta c)^3] \} \quad (51)$$

where

$$L = L_D + L_V + L_R + L_M \quad (52)$$

with

$$L_D = - (1/12)k_2 \quad (53)$$

$$L_V = + [\lambda(3 + \lambda)/4\pi\sqrt{3}] (m_1/\bar{c}) - \\ (\lambda^2/4\pi\sqrt{3})m_1^2 + (\lambda/2\pi\sqrt{3})m_2 \quad (54)$$

$$L_R = - (\sqrt{3}/2\pi)a_2 \quad (55)$$

$$L_M = - (1/6)a_1k_1 + (\lambda\sqrt{3}/2\pi)a_1m_1 \quad (56)$$

Thus, as in the corresponding coefficient  $K$  for  $\mathfrak{D}_A$ , the coefficient  $L$  for  $\mathfrak{D}_{2m}$  is separated into four factors; the first three of them represent the individual effects from the concentration dependences of  $D_V$ , of  $\bar{v}$  and of  $n$ , while the last one,  $L_M$ , is the contribution from the first order couplings of these three factors.

Finally, it should be remarked that the preceding equations for  $\mathfrak{D}_A$  and  $\mathfrak{D}_{2m}$  reduce to the cor-

responding equations derived in the previous paper<sup>2</sup> when  $m_1$  and  $m_2$  are set equal to zero, *i.e.*, when the concentration dependence of the partial specific volume of the solute is neglected. This is expected because the present calculation is based on the same method of solution as that employed previously.

### Discussion

Equations 44 and 51 indicate that for sufficiently small values of  $\Delta c$   $\mathfrak{D}_A$  and  $\mathfrak{D}_{2m}$  at a given value of  $\bar{c}$  vary linearly with the square of  $\Delta c$ . Similar types of dependence of  $\mathfrak{D}_A$  and  $\mathfrak{D}_{2m}$  on  $(\Delta c)^2$  have been obtained previously<sup>2</sup> for the case where no volume change occurs on mixing. Thus we see that to the degree of approximation up to the order of  $(\Delta c)^2$  the volume change on mixing does not affect the qualitative fashion in which both  $\mathfrak{D}_A$  and  $\mathfrak{D}_{2m}$  depend upon the concentration difference across the initial boundary. However, the slopes of the predicted straight lines are altered by the volume change effect, as seen from the expressions for  $K$  and  $L$  derived above.

As noted above, the values of  $a_1$  and  $a_2$  at the given value of  $\bar{c}$  may be obtained from direct optical measurements or as auxiliary data from optical diffusion experiments. The quantities  $\bar{v}(\bar{c})$  (and hence  $\lambda$ ),  $m_1$  and  $m_2$  may be evaluated from accurate density measurements over a range of concentration encompassing the given mean concentration. On the other hand, the values of  $D_V(\bar{c})$ ,  $K$  and  $L$  are determined from plots for  $\mathfrak{D}_A$  vs.  $(\Delta c)^2$  and  $\mathfrak{D}_{2m}$  vs.  $(\Delta c)^2$ , in accordance with equations 44 and 51; to obtain these plots diffusion experiments must be performed for several different values of  $\Delta c$  at the given value of  $\bar{c}$ . When the values of  $a_1$ ,  $a_2$ ,  $\lambda$ ,  $m_1$ ,  $m_2$ ,  $K$  and  $L$  so obtained are inserted into equations 45 and 52, we obtain a set of equations which may be solved for  $k_1$  and  $k_2$ . Substitution of these values of  $k_1$  and  $k_2$ , together with the value of  $D_V(\bar{c})$  obtained experimentally, into equation 4 then allows us to calculate  $D_V$  as a function of  $c$  throughout the range of  $c$  in which terms higher than the order of  $(c - \bar{c})^2$  may be neglected in comparison with unity. In this way the observed data for  $\mathfrak{D}_A$  and  $\mathfrak{D}_{2m}$  as functions of  $\Delta c$  (at a fixed  $\bar{c}$ ) may be used to determine the dependence of the diffusion coefficient (referred to the volume-fixed frame) upon solute concentration, even when the system exhibits volume change on mixing, provided that the data for  $\bar{v}(c)$  are available. It is hoped that the theory described in this paper will aid in more accurate evaluation of the diffusion coefficients for two-component systems from optical diffusion measurements.

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