

## Electrolyte Diffusion into Water

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The diffusion coefficient  $D(C)$  for a very dilute aqueous electrolyte is represented, in a first approximation, by  $D(C) = D(0)(1 - k\sqrt{C})$ , where  $C$  is the electrolyte concentration and  $k$  is a positive parameter. For the experimental setup in which, initially, a sharp boundary is formed between an electrolyte solution and pure water, the Gosting–Fujita method is not applicable for solving free diffusion with this concentration-dependent  $D$ , because  $D$  is not regular at  $C = 0$ . In this paper, another perturbation method which uses  $k$  as a perturbation parameter is applied to solve this diffusion problem correct up to second order in  $k$ , and the apparent diffusion coefficient  $D_j$  defined in the Rayleigh fringe method for measuring transport processes in solutions is calculated as a function of the position in the diffusion boundary. It is shown that the result does not support Albright and Miller's finding from numerical solutions that the position at which  $D_j$  agrees with  $\bar{D}$  is independent of  $k$ . Here,  $\bar{D}$  is the  $D$  value at the mean concentration.

### Introduction

Diffusion of an electrolyte in very dilute aqueous solutions is governed by the diffusion coefficient  $D(C)$  which, in a first approximation, is represented by

$$D(C) = D(0)(1 - k\sqrt{C}) \quad (1.1)$$

where  $C$  is the concentration of the electrolyte, and  $D(0)$  and  $k$  are system-dependent (positive) parameters. The dependence of  $D$  on  $\sqrt{C}$  is usually considered to make the diffusion boundary considerably skew from the ideal situation in which  $D$  is constant, and the skewness has been the subject of theoretical and experimental interest in the studies of liquid diffusion.

Albright and Miller<sup>1</sup> approached both analytically and numerically the one-dimensional diffusion equation with  $D(C)$  given by eq 1.1 under the experimental setup that, initially, a dilute electrolyte solution is separated by a sharp boundary from water in an infinitely long cell. For the analytical treatment they applied the perturbation method of Gosting and Fujita,<sup>2</sup> which uses the fact that the diffusion boundary tends to be ideal with the diffusion coefficient  $D(\bar{C})$  as a dimensionless variable  $\Delta C/2\bar{C}$  goes to zero. Here,  $\bar{C} = (C_B + C_T)/2$  and  $\Delta C = C_B - C_T$ , with  $C_B$  and  $C_T$  denoting the initial concentrations of the bottom and top layers of solution. Thus, this method views deviations of the diffusion boundary from the ideal one by a concentration dependence of  $D(C)$  as perturbations due to nonzero  $\Delta C/2\bar{C}$ . After expanding  $D(C)$  in powers of  $C - \bar{C}$  about  $C = \bar{C}$ , it expresses  $C$  as a power series of  $\Delta C/2\bar{C}$  and successively determines from the diffusion equation the coefficients of the series as functions of time  $t$  and position  $x$  (actually, of a combined single variable  $x/\sqrt{t}$ ). In the Albright–Miller problem,  $C_T$  is zero, so that  $\Delta C/2\bar{C} = 1$ , which is the worst case for the convergence of the Gosting–Fujita method. However, more important is the fact that the  $D(C)$  of eq 1.1 is not a regular function of  $C$  at  $C = 0$ , since  $dD/dC$  diverges there. Hence, the expansion of  $D$  in powers of  $C - \bar{C}$  fails to be valid at  $C = 0$ . This means that formal application of the Gosting–Fujita

perturbation approach as it stands may not hold when  $D$  depends on  $\sqrt{C}$  and  $C_T = 0$ .

In reality, eq 1.1 should be regarded as a limiting form of  $D$  as  $C$  approaches zero. It is more practical to add at least one term linear in  $C$  to its right-hand side. Albright and Miller<sup>3</sup> worked out this case again using the Gosting–Fujita perturbation method for the analytic treatment. However, for the above reason the solution they present seems to have no theoretical value when  $C_T = 0$ .

In the present paper, the Albright–Miller problem is attacked by another perturbation method which utilizes the idea that the diffusion boundary tends to be ideal with the diffusion coefficient  $D(0)$  as  $k$  diminishes to zero, so that deviations of the diffusion boundary from the ideal one by a concentration dependence of  $D(C)$  may be treated as perturbations due to nonzero  $k$ . Thus, it expands  $C$  in powers of  $k$  (actually,  $k\sqrt{C_B}$ ) and successively determines the expansion coefficients from the diffusion equation. It should be noted that though both are perturbation methods the present method differs from the Gosting–Fujita one in the basic idea.

The calculation here is made up to second order in  $k\sqrt{C_B}$ . The solution obtained is used to calculate  $D_j$  as a function of the position in the diffusion boundary, and the result is compared with that obtained by Albright and Miller<sup>1</sup> from numerical integrations. Here,  $D_j$  is an apparent diffusion coefficient appearing in the Rayleigh fringe method<sup>4</sup> for measuring diffusion in solutions (see below for its definition).

### Basic Equations

The diffusion equation to be solved is

$$\frac{\partial C}{\partial t} = \frac{\partial}{\partial x} \left[ D(0)(1 - k\sqrt{C}) \frac{\partial C}{\partial x} \right] \quad (2.1)$$

and the associated initial and boundary conditions are

$$C = C_B \quad (t = 0; 0 < x < \infty), \quad C = 0 \quad (t = 0; -\infty < x < 0) \quad (2.2)$$

$$C = C_B \quad (t > 0; x = \infty), \quad C = 0 \quad (t > 0; x = -\infty) \quad (2.3)$$

If a dimensionless concentration  $c$  is introduced by

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$$c = C/C_B \quad (2.4)$$

and a dimensionless variable  $z$  by<sup>5</sup>

$$z = x/(2\sqrt{D(0)t}) \quad (2.5)$$

eq 2.1 changes to an ordinary differential equation

$$\frac{d}{dz} \left[ (1 - \epsilon\sqrt{c}) \frac{dc}{dz} \right] + 2z \frac{dc}{dz} = 0 \quad (2.6)$$

and the initial and boundary conditions are reduced to

$$c = 1 \quad (z = \infty), \quad c = 0 \quad (z = -\infty) \quad (2.7)$$

where  $\epsilon$  is defined by

$$\epsilon = k\sqrt{C_B} \quad (2.8)$$

and can be taken as smaller than unity to meet the physical requirement that  $D$  be positive. We note that Albright and Miller<sup>1</sup> used  $\bar{D}$  for  $D(0)$  in defining the variable  $z$ , where  $\bar{D}$  is the  $D$  value at the mean concentration  $c = 1/2$ , i.e.,

$$\bar{D} = D(0)(1 - 0.7071\epsilon) \quad (2.9)$$

The ordinary differential equation derived from eq 2.1 with  $z$  thus defined is different in form from eq 2.6. Hence, our solutions presented below do not hold as they stand if the  $z$  in them are simply replaced by Albright and Miller's  $z = x/(2\sqrt{\bar{D}t})$ .

We begin with the substitution

$$n = \sqrt{c} \quad (2.10)$$

Then eq 2.6 changes to

$$\frac{d}{dz} \left[ n(1 - \epsilon n) \frac{dn}{dz} \right] + 2zn \frac{dn}{dz} = 0 \quad (2.11)$$

and eq 2.7 to

$$n = 1 \quad (z = \infty), \quad n = 0 \quad (z = -\infty) \quad (2.12)$$

Equation 2.10 removes nonregularity from eq 2.6, but introduces the problem that the coefficient of the highest derivative in eq 2.11, i.e.,  $n(1 - \epsilon n)$ , vanishes at  $n = 0$  and  $n = 1/\epsilon$ . Fortunately, however,  $c = 0$  occurs at  $z = -\infty$  and  $n = 1/\epsilon$  is located outside the interested range of  $n$  ( $0 < n < 1$ ) because  $\epsilon < 1$ . Therefore, we may treat eq 2.11 by the ordinary perturbation method, in which an independent variable is expanded in powers of a small parameter contained in the equation considered.

We express  $n(z)$  as

$$n(z) = n_0(z) + n_1(z) + n_2(z)\epsilon + n_2(z)\epsilon^2 + \dots \quad (2.13)$$

Then, eq 2.10 gives

$$c(x,t) = u_0(z) + 2u_1(z)\epsilon + u_2(z)\epsilon^2 + \dots \quad (2.14)$$

with

$$u_0(z) = n_0(z)^2 \quad (2.15)$$

$$u_1(z) = n_0(z) n_1(z) \quad (2.16)$$

$$u_2(z) = 2n_0(z) n_2(z) + n_1(z)^2 \quad (2.17)$$

which indicates that  $c(x,t)$  can be determined up to second order in  $\epsilon$  by calculating  $u_0(z)$ ,  $u_1(z)$ , and  $u_2(z)$ .

Introducing eq 2.13 into eq 2.11, rearranging the result in powers of  $\epsilon$ , and equating the coefficients of successive terms to zero, we obtain the following set of equations for  $u_0(z)$ ,  $u_1(z)$ , and  $u_2(z)$ :

$$d^2 u_0/dz^2 + 2z du_0/dz = 0 \quad (2.18)$$

$$d^2 u_1/dz^2 + 2z du_1/dz = (1/3) d^2 u_0^{3/2}/dz^2 \quad (2.19)$$

$$d^2 u_2/dz^2 + 2z du_2/dz = 2 d^2 (u_0^{1/2} u_1)/dz^2 \quad (2.20)$$

The associated boundary conditions are

$$u_0(\infty) = 1, \quad u_1(\infty) = u_2(\infty) = 0 \quad (2.21)$$

$$u_0(-\infty) = u_1(-\infty) = u_2(-\infty) = 0 \quad (2.22)$$

### Solutions

Solving the above set of equations is just standard mathematical exercises, so only the important consequences are presented below.

First, as is well documented in textbooks,<sup>5</sup>  $u_0(z)$  is given by

$$u_0(z) = E(z)/2 \quad (3.1)$$

with

$$E = 1 + \Phi(z) \quad (3.2)$$

where  $\Phi(z)$  is the error function defined by

$$\Phi(z) = \frac{2}{\sqrt{\pi}} \int_0^z \exp(-w^2) dw \quad (3.3)$$

Equation 3.1 gives

$$du_0/dz = (2/\sqrt{\pi}) \exp(-z^2) \quad (3.4)$$

which is graphed in Figure 1.

Next,  $u_1(z)$  is represented by

$$u_1(z) = -\frac{1}{\sqrt{2\pi}} \int_{-\infty}^z \exp(-w^2) f(w) dw + \frac{1}{\sqrt{2}} [E(z)]^{3/2} - 0.309E(z) \quad (3.5)$$

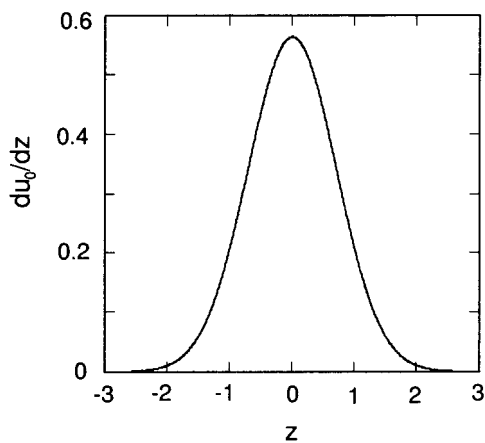
where

$$f(z) = \int_{-\infty}^z w\sqrt{E(w)}dw \quad (3.6)$$

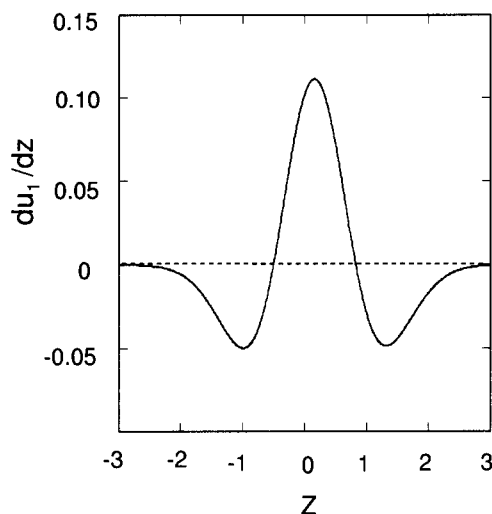
It follows from eq 3.5 that

$$du_1/dz = \exp(-z^2) [-(1/\sqrt{2\pi})f(z) + (1/2\sqrt{2\pi})\sqrt{E(z)} - 0.349] \quad (3.7)$$

which is graphed in Figure 2. The curve consists of a sharp positive peak accompanying a pair of nearly symmetric negative troughs on both sides of it. It should be noted that the maximum is not much shifted from  $z = 0$  and its height is only about one-fifth of the maximum of  $du_0/dz$ .



**Figure 1.** Distribution of  $du_0/dz$  over the  $z$  axis. This is a Gaussian distribution function.



**Figure 2.** Distribution of  $du_1/dz$  over the  $z$  axis. The area enclosed by the solid curve above and below the dashed line is zero because of the boundary conditions for  $u_1(z)$ .

Finally,  $u_2(z)$  is conveniently represented as the sum of three terms:

$$u_2(z) = -0.564p(z) + 0.167q(z) - 0.437r(z) \quad (3.8)$$

with

$$p(z) = \int_{-\infty}^z \exp(-w^2) \{ Ga(w) - [f(w)]^2 + f(w) E(w) - 2 \int_{-\infty}^w y Ga(y) dy + 0.986 \} dw \quad (3.9)$$

$$q(z) = [E(z)]^2 - 2.00E(z) - (8/\sqrt{\pi}) \int_{-\infty}^z \exp(-w^2) g(w) dw \quad (3.10)$$

$$r(z) = (6\sqrt{2}) \{ -(1/\sqrt{2\pi}) \int_{-\infty}^z (-w^2) f(w) dw + (\sqrt{2}/12) [E(z)]^{3/2} - 0.309E(z) \} \quad (3.11)$$

where

$$g(z) = \int_{-\infty}^z w E(w) dw \quad (3.12)$$

and

$$Ga(z) = -0.2[1 + \tanh(z + 0.2)] + 0.057[\Phi(z - 0.75) + \Phi(|z - 0.75|)] \quad (3.13)$$

The function  $Ga(z)$  is an approximation to  $G(z)$  defined by

$$G(z) = \frac{1}{\sqrt{\pi E(z)}} \int_{-\infty}^z \exp(-w^2) f(w) dw \quad (3.14)$$

and has been introduced to simplify the numerical evaluation of  $p(z)$ . Figure 3 compares  $Ga(z)$  with the exact  $G(z)$ . Though the agreement of the two functions leaves something to be desired, both give  $p(z)$  almost indistinguishable values over the entire range of  $z$ .

The derivatives  $dp/dz$ ,  $dq/dz$ , and  $dr/dz$  are given by

$$dp/dz = \exp(-z^2) \{ Ga(z) - [f(z)]^2 + f(z) E(z) - 2 \int_{-\infty}^z w Ga(w) dw + 0.986 \} \quad (3.15)$$

$$dq/dz = \exp(-z^2) [ (4/\sqrt{\pi}) E(z) - (8/\sqrt{\pi}) g(z) - 2.257 ] \quad (3.16)$$

$$dr/dz = (6/\sqrt{\pi}) \exp(-z^2) [ -f(z) + (1/2)\sqrt{E(z)} - 0.874 ] \quad (3.17)$$

Figure 4 shows the  $du_2/dz$  vs  $z$  plot calculated by inserting these three equations into

$$du_2/dz = -0.564(dp/dz) + 0.167(dq/dz) - 0.437(dr/dz) \quad (3.18)$$

It has a general feature similar to the  $du_1/dz$  curve, except that the two troughs have different depth. The height and location of the maximum are comparable to those of  $du_1/dz$ . This implies that the contribution of the  $\epsilon^2$  term to the concentration gradient  $dc/dz$  (and  $c$  as well) becomes significant with increasing  $\epsilon$ .

## Results and Discussion

### Concentration and Concentration Gradient Distributions.

With the substitution of the above analytical results into eq 2.14 and

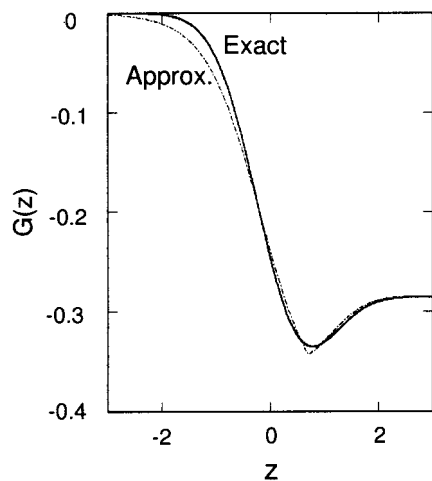
$$dc/dz = du_0/dz + 2\epsilon(du_1/dz) + \epsilon^2(du_2/dz) + \dots \quad (4.1)$$

the distributions of  $c$  and  $dc/dz$  over the  $z$  axis for a given  $\epsilon$  can be calculated. Figure 5 shows the  $dc/dz$  distributions for  $\epsilon = 0, 0.2, 0.4$ , and Figure 6 the corresponding  $c$  distributions. These graphs are meaningful only for  $\epsilon$  at which contributions of terms higher than  $\epsilon^2$  may be neglected. Thus, those for  $\epsilon = 0.4$  may be accepted with reservation until at least the order of magnitude of  $u_3$  is estimated.

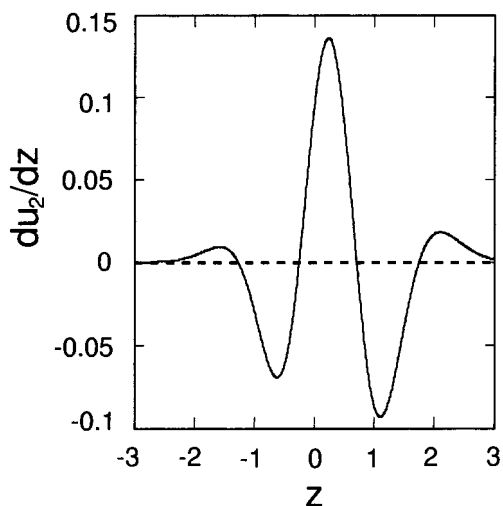
The curves for nonzero  $\epsilon$  reveal expected deviations from the ideal situation ( $\epsilon = 0$ ). Especially, those in Figure 5 show clearly enhanced sharpening with increasing  $\epsilon$ . We observe the  $c$  distribution for  $\epsilon = 0.5$  reported by Albright and Miller<sup>1</sup> to exhibit more marked downward deviations than ours on the side below  $c = 1/2$ .

### Apparent Diffusion Coefficient

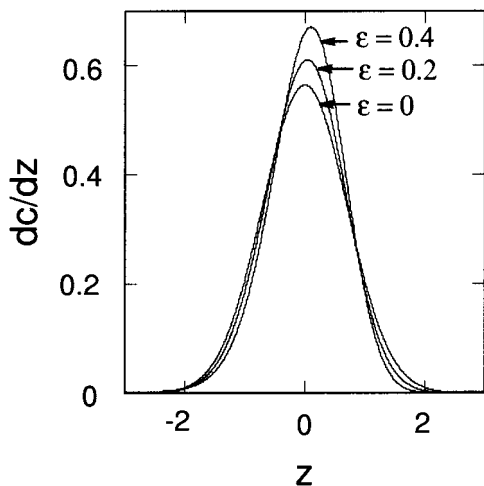
When the Rayleigh fringe method<sup>4</sup> is used to study free diffusion in solutions it is usual to evaluate an apparent diffusion coefficient  $D_j$  defined below. This is based on the expectation that  $D_j$  as a function of  $j$ , i.e., the position in the diffusion boundary, allows us to accurately estimate the diffusion coefficient at the mean concentration of a given solution. Albright and Miller<sup>1</sup> confirmed this with their numerical solutions to eq



**Figure 3.** Comparison of  $Ga(z)$  (dotted line) with  $G(z)$  (solid line).



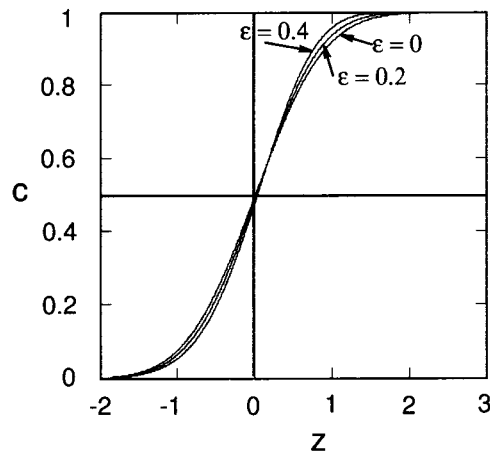
**Figure 4.** Distribution of  $du_2/dz$  over the  $z$  axis. The area enclosed by the solid curve above and below the dashed line is zero because of the boundary conditions for  $u_2(z)$ .



**Figure 5.** Distributions of concentration gradient  $dc/dz$  for different  $\epsilon$ .

2.1. In what follows, we examine what happens to  $D_j$  when our perturbation solution is used.

In circumstances where concentration is proportional to refractive index, the following set of relations<sup>1</sup> is the basis for computing  $D_j$ :



**Figure 6.** Concentration distributions corresponding to Figure 5.

$$c(z_j) = j/J \quad (5.1)$$

$$c(z_j) - 1/2 = 1/2\Phi(z_j^*) \quad (5.2)$$

$$1/2 - c(z_{J-j}) = 1/2\Phi(z_j^*) \quad (5.3)$$

Here,  $J$  is the total number of Rayleigh fringes,  $j$  and  $J - j$  are the fringe numbers for Creeth's symmetric fringes<sup>4</sup> which define a pair of concentrations located above and below at an equal distance from  $c = 1/2$ , and  $z_j$  and  $z_{J-j}$  are the  $z$  coordinates at these fringes (in practice, since  $D(0)$  is unknown in advance, they are replaced by  $x_j/\sqrt{t}$  and  $x_{J-j}/\sqrt{t}$ ). Furthermore,  $z_j^*$  is a variable as a function of which  $D_j$  is to be evaluated.

When the concentration distribution is antisymmetric about the origin of  $z$  (or the concentration gradient distribution is symmetric about  $z = 0$ ), as observed in free diffusion of binary or multicomponent systems with constant diffusion coefficients (main-term and cross-term ones), we have  $z_{J-j} = -z_j$  so that eq 5.3 is not needed. This is the case that Albright and Sherill<sup>6</sup> have summarized methods for analyzing Rayleigh fringe data on liquid diffusion. However, since  $z_{J-j}$  may not be equal to  $-z_j$  for concentration-dependent diffusion, eq 5.3 must be retained. In this case,  $z_j$  and  $z_{J-j}$  determined as functions of  $z_j^*$  from eq 5.2 and 5.3 are used to calculate  $D_j$ , which is defined by

$$D_j = D(0) \left( \frac{z_j - z_{J-j}}{2z_j^*} \right)^2 \quad (5.4)$$

With the analytical expression for  $c(z)$  obtained above, this calculation can be carried through up to second order in  $\epsilon$ .

Because  $c(z)$  reduces to  $u_0(z)$  at  $\epsilon = 0$  (see eq 2.14), it follows from eq 3.1 and 5.2 that  $z_j$  tends to  $z_j^*$  as  $\epsilon \rightarrow 0$ . Thus, we start assuming the series

$$z_j = z_j^* + \epsilon v_1(z_j^*) + \epsilon^2 v_2(z_j^*) + \dots \quad (5.5)$$

Then, we find from eq 5.2 and 5.3 that  $z_{J-j}$  is represented by

$$z_{J-j} = -z_j^* + \epsilon v_1(-z_j^*) + \epsilon^2 v_2(-z_j^*) + \dots \quad (5.6)$$

so that eq 5.4 gives

$$D_j/D(0) = [1 + \epsilon V_1(z_j^*) + \epsilon^2 V_2(z_j^*) + \dots]^2 \quad (5.7)$$

with

$$V_1(z) = [v_1(z) - v_1(-z)]/(2z) \quad (5.8)$$

$$V_2(z) = [v_2(z) - v_2(-z)]/(2z) \quad (5.9)$$

To find the expressions for  $v_1(z)$  and  $v_2(z)$  we substitute eq 5.5 for  $z_j$  in  $c(z_j) = u_0(z_j) + 2\epsilon u_1(z_j) + \epsilon^2 u_2(z_j) + \dots$  (see eq 2.14), expand each term on the right-hand side in powers of  $\epsilon$ , and use the results to arrange the left-hand side of eq 5.2 as a power series of  $\epsilon$ . Comparison of both sides then yields

$$v_1(z_j^*)(du_0/dz)_{z=z_j^*} + 2u_1(z_j^*) = 0 \quad (5.10)$$

$$v_2(z_j^*)(du_0/dz)_{z=z_j^*} + (1/2)v_1(z_j^*)^2(d^2u_0/dz^2)_{z=z_j^*} + 2v_1(z_j^*)(du_1/dz)_{z=z_j^*} + u_2(z_j^*) = 0 \quad (5.11)$$

These allow  $v_1(z_j^*)$  and  $v_2(z_j^*)$ , and hence  $D_j/D(0)$  as a function of  $z_j^*$ , to be determined when the expressions for  $u_0$ ,  $u_1$ , and  $u_2$  are inserted.

For comparison with Albright and Miller's report we have converted the calculated  $D_j/D(0)$  to  $D_j(z_j^*)/\bar{D}$  is defined by eq 2.9), and show the results for three  $\epsilon$  values in Figure 7. It is seen that as  $z_j^*$  increases,  $D_j/\bar{D}$  for a given  $\epsilon$  starts from a value slightly smaller than unity, rises, intersects the line for  $D_j/\bar{D} = 1$  (i.e., the line for  $\epsilon = 0$ ), reaches a maximum, and falls. This behavior is consistent with what Albright and Miller derived from numerical integrations, except that they found no maxima and the intersection with the line for  $\epsilon = 0$  to occur at the same  $z_j^* = 0.63$ , regardless of  $\epsilon$ . In the comparison, however, we must note that their  $z_j^*$  is not the same as ours, being larger by a constant factor of  $(1 - 0.7071\epsilon)^{1/2}$  than the latter. Our "cross points" read off Figure 7 are  $z_j^* = 0.722$ , 0.680, 0.625 for  $\epsilon = 0.1, 0.2, 0.3$ , respectively. When corrected for this difference, the Albright–Miller  $z_j^*$  values are about 0.75, 0.73, 0.71, which are definitely larger than 0.63. Thus, our analytical solution does not lend complete support to Albright and Miller's findings, but it confirms that  $D_j$  gives a very close approximation to  $\bar{D}$  (see Appendix).

As Figure 6 shows, the concentrations at  $|z_j^*|$  larger than 1.7 are almost indistinguishable from zero or unity. Since  $D_j$  at  $z_j^* > 1.7$  depends on them, its computation should suffer considerable errors unless they are determined very accurately. This fact may account for the presence of a maximum in  $D_j$  from our perturbation solution.

## Appendix

Albright and Miller<sup>1</sup> refer to their numerical investigation of the diffusion equation with a linearly concentration-dependent  $D$ :

$$D(c) = D(0)(1 - \beta c) \quad (A.1)$$

where  $\beta$  is a positive parameter corresponding to  $\epsilon$  above and  $c$  is a reduced concentration defined by eq 2.4. Though reported only for  $\beta = 0.5$  their  $D_j/\bar{D}$  starts from a value slightly above unity, decreases monotonically, and crosses the line for  $\epsilon = 0$  as  $z_j^*$  increases. Interestingly, this behavior is just opposite to what we observe for the  $\sqrt{c}$ -dependent  $D_j$ , and suggests that  $D_j$  not only gives a good approximation to  $\bar{D}$  but also is sensitive to the form of concentration dependence of  $D$ . In what follows, we examine what our perturbation method predicts for  $D_j$  when  $D$  is governed by eq A.1.

The problem is to solve the diffusion equation

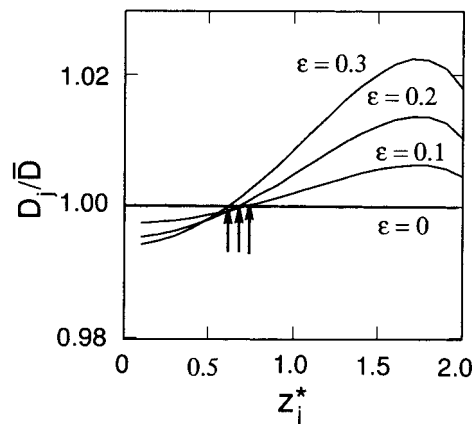


Figure 7. Variations of  $D_j/\bar{D}$  with  $z_j^*$  for small  $\epsilon$ . Arrows indicate cross points.

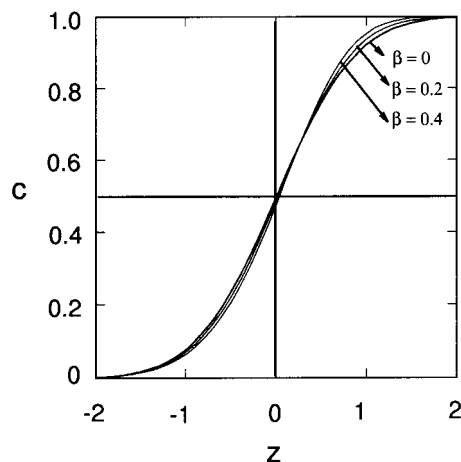


Figure 8. Concentration distributions for different  $\beta$ .

$$\partial c/\partial t = \partial/\partial x[D(0)(1 - \beta c)\partial c/\partial x] \quad (A.2)$$

under the same initial and boundary conditions as eqs 2.2 and 2.3 by expanding  $c$  in powers of  $\beta$  as

$$c(x,t) = c_0(z) + \beta c_1(z) + \beta^2 c_2(z) + \dots \quad (A.3)$$

where  $z$  is defined by eq 2.5. We have determined the solution up to second order in  $\beta$ . The results are

$$c_0(z) = E(z)/2 \quad (A.4)$$

$$c_1(z) = (1/2)E(z)^2 - E(z) - (4/\sqrt{\pi})\int_{-\infty}^z \exp(-z^2) g(z) dz \quad (A.5)$$

$$c_2(z) = (1/\sqrt{\pi})\int_{-\infty}^z \exp(-z^2) I(z) dz - (1/2\sqrt{\pi})\int_{-\infty}^z \exp(-z^2) J(z) dz + 0.0359E(z) \quad (A.6)$$

where

$$I(z) = F(z) - 2\int_{-\infty}^z zF(z) dz, \quad J(z) = E(z) g(z) - 2\int_{-\infty}^z zE(z) g(z) dz \quad (A.7)$$

with

$$F(z) = 1.5/[1 + \exp(-3z + 0.6)] \quad (A.8)$$

and  $E(z)$  and  $g(z)$  defined in the text.

Figure 8 shows the concentration distributions for three values of  $\beta$ . The skewness of the curve even for  $\beta = 0.4$  is not as marked as expected from Albright and Miller's curve for  $\beta = 0.5$ . Especially at  $c$  below  $c = 1/2$  the deviations from the ideal situation are unexpectedly small.

For the  $D$  under consideration eqs 5.10 and 5.12 must be replaced by

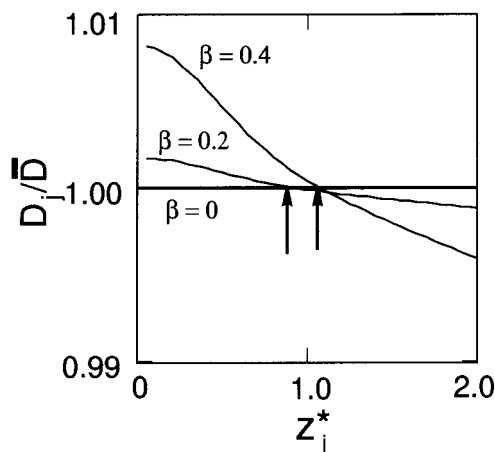
$$v_1(z_j^*)(du_0/dz)_{z=z_j^*} + c_1(z_j^*) = 0 \quad (\text{A.9})$$

$$v_2(z_j^*)(dc_0/dz)_{z=z_j^*} + (1/2)v_1(z_j^*)^2(d^2c_0/dz^2)_{z=z_j^*} + v_1(z_j^*)(dc_1/dz)_{z=z_j^*} + c_2(z_j^*) = 0 \quad (\text{A.10})$$

In Figure 9, the calculated  $D_j/\bar{D}$  for different  $\beta$  are plotted against  $z_j^*$ , where  $\bar{D}$  is the  $D$  value at the mean concentration  $c = 1/2$ , i.e.,

$$\bar{D} = 1 - (1/2)\beta \quad (\text{A.11})$$

For either nonzero  $\beta$  indicated,  $D_j/\bar{D}$  shows a variation with  $z_j^*$  very similar to that reported by Albright and Miller, but it crosses the line for  $\beta = 0$  at a  $z_j^*$  value which differs for different  $\beta$ . The crossover points read off Figure 9 are  $z_j^* = 1.07, 0.893$  for  $\beta = 0.2, 0.4$ , respectively. When corrected for the difference between our and Albright–Miller's  $z_j^*$ , 1.07 and



**Figure 9.** Variations of  $D_j/\bar{D}$  with  $z_j^*$  for small  $\beta$ . Arrows indicate cross points.

0.893 change to 1.18 and 1.12, respectively, which are as twice as larger than their  $z_j^*$  value that Albright and Miller found for  $\beta = 0.5$ .

#### References and Notes

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