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Fick's second law of diffusion in the one-dimensional case may be written as

$$\frac{\partial c}{\partial t} = \frac{\partial}{\partial x}\left(D\frac{\partial c}{\partial x}\right) \qquad (1)$$

where c is the concentration as a function of distance, x, and time, t, and D is the diffusivity. If $D = D(c)$, the equation is inhomogeneous and a closed-form solution may be obtained only in some special cases. One case which has been treated extensively in the literature[1-4] is that of a pair of semi-infinite solids forming one phase, so that $c(x,t)$ is a continuous function with continuous derivatives for all $t>0$ and $-\infty<x<\infty$. No one, however, has treated the case of a pair of semi-infinite solids of two different phases with a moving boundary between them, so that $c(x,t)$ is discontinuous at the boundary.

A modification of the Boltzmann-Matano solution[1,2] will be made, which will allow a solution for the two-phase case. The results will then be generalized to show how a solution may be obtained for one-dimensional diffusion across any number of phases.

If the physical process is diffusion-controlled, $c = c\,(xt^{-1/2})$ only and, with the substitution, $\eta = xt^{-1/2}$, we have

$$\frac{\partial c}{\partial t} = \frac{\partial c}{\partial \eta}\frac{\partial \eta}{\partial t} = -\frac{x}{2t^{3/2}}\frac{dc}{d\eta} \tag{2a}$$

$$\frac{\partial c}{\partial x} = \frac{\partial c}{\partial \eta}\frac{\partial \eta}{\partial x} = \frac{1}{t^{1/2}}\frac{dc}{d\eta} \tag{2b}$$

$$\frac{\partial}{\partial x} = \frac{\partial}{\partial \eta}\frac{\partial \eta}{\partial x} = \frac{1}{t^{1/2}}\frac{d}{d\eta} \tag{2c}$$

so that

$$-\frac{\eta}{2}\frac{dc}{d\eta} = \frac{d}{d\eta}\left(D\frac{dc}{d\eta}\right) \tag{3}$$

The initial conditions

$$c = c_o \text{ for } x<0, \text{ at } t = 0 \tag{4a}$$

$$c = 0 \text{ for } x>0, \text{ at } t = 0 \tag{4b}$$

transform to

$$c = c_o \text{ at } \eta = -\infty \tag{4c}$$

$$c = 0 \text{ at } \eta = +\infty \tag{4d}$$

From Eq. (3)

$$-\frac{1}{2}\eta\, dc = d\left(D\frac{dc}{d\eta}\right) \tag{5}$$

Since c(x) is always determined for a given, fixed t,

$$-\frac{1}{2}\,x\,dc = d\left(Dt\frac{dc}{dx}\right) \tag{6}$$

Now, if c(x) is continuous with continuous derivatives over the entire range, $-\infty<x<\infty$, Eq. (6) may be integrated between the limits c = 0 and $c = c'$, where $0<c'<c_o$, to give[4]

$$-\frac{1}{2}\int_0^{c'} x\,dc = t\left[D\frac{dc}{dx}\right]_{c=0}^{c=c'} \tag{7}$$

But

$$\left.\frac{dc}{dx}\right|_{c=o} = \left.\frac{dc}{dx}\right|_{c=c_o} = 0, \text{ so } D(c') = -\frac{1}{2t}\left(\frac{dx}{dc}\right)_{c=c'}\int_0^{c'} x\,dc \tag{8}$$

and $$\int_0^{c_o} x\,dc = 0, \tag{9}$$

where $-\infty<x<\infty$.

Equation (9) determines the Boltzmann-Matano interface, x = 0, for the evaluation of the integral in Eq. (8). It represents the conservation of the diffusing species in the system; half the species is to the left of it and half is to the right.

If, however, c(x) is not continuous with continuous derivatives over the entire range, $-\infty<x<\infty$, Eq. (6) cannot be integrated as it stands and Eqs. (8) and (9) may not justifiably be used. This situation is illustrated in Fig. 1. Equations (6-9) will now be modified, so that they may be integrated and a solution for D(c') obtained.

Define a new function,

$$g(x) \equiv c(x) - (c_{2e} - c_{1e})\ H\ (x-X) \qquad (10)$$

where H(x-X) is the Heaviside unit step function[5] and is defined so that

$$H(x-X) = \begin{cases} 1 \text{ for } x>X \\ 0 \text{ for } x<X \end{cases} \qquad (11)$$

$$\frac{d}{dx} H(x-X) = \delta(x-X) \qquad (12)$$

where $$\delta(x-X) \begin{cases} \text{undefined for } x = X \\ 0 \text{ for all } x \neq X \end{cases} \qquad (13)$$

and $$\int_{-\infty}^{\infty} \delta(x-X)\ dx = 1 \qquad (14)$$

Now, g(x) is a continuous function with continuous derivatives of all orders,[5] since $\delta^{(n)}$ (x-X) is continuous for all n. g(x) is amenable to the mathematical operations of integration and differentiation and

$$xdg = x\left(\frac{dg}{dx}\right) dx = x\left(\frac{dc}{dx}\right)dx - x\ (c_{2e} - c_{1e})\ \delta(x-X)\ dx \qquad (15)$$

Integrating over all x gives $\int_{g(c\,=\,o)}^{g(c\,=\,c_o)} x\,dg =$

$$\int_{-\infty}^{\infty} x\left(\frac{dg}{dx}\right) dx = \int_{-\infty}^{\infty} x\left(\frac{dc}{dx}\right) dx - (c_{2e} - c_{1e}) \int_{-\infty}^{\infty} x\delta(x-X)\, dx =$$

$$I_1 - (c_{2e} - c_{1e})\, I_2 \tag{16}$$

$$I_1 = \int_{o}^{c_{1e}} x\, dc + \int_{c2e}^{c_o} x\, dc \tag{17}$$

$$I_2 = \int_{-\infty}^{X-\varepsilon} x\delta(x-X)\, dx + \int_{X-\varepsilon}^{X+\varepsilon} x\delta(x-X)\, dx + \int_{X+\varepsilon}^{\infty} x\delta(x-X)\, dx \tag{18}$$

where $\varepsilon>0$ and is vanishingly small. The first and third integrals in Eq. (18) are identically zero, since $\delta(x-X) \equiv 0$ for all $x \neq X$, so

$$I_2 = \lim_{\varepsilon\to 0} \int_{X-\varepsilon}^{X+\varepsilon} x\delta(x-X)\, dx = X \tag{19}$$

The conservation of the diffusing species requires that Eq. (16) equals zero. This is now the condition which determines the x = 0 interface, i.e.

$$\int_{o}^{c_{1e}} xdc + \int_{c_{2e}}^{c_o} xdc - (c_{2e} - c_{1e})\, X = 0 \qquad (20)$$

where X is measured from x = 0. This avoids the necessity of integrating over the discontinuity at c = c (X).

If $c' < c_{1e}$, c(x) is continuous with continuous derivatives over the entire interval $0 < c < c'$, and Eqs. (6) and (8) for D(c') may be integrated straightforwardly. For the portion of the concentration profile where $c' > c_{2e}$, however, the substitution of Eq. (10) must be made, and

$$D(c') = -\frac{1}{2t}\left(\frac{dx}{dc}\right)_{c = c'}\left[\int_{o}^{c_{1e}} xdc + \int_{c_{2e}}^{c'} xdc - (c_{2e} - c_{1e})\, X\right]$$

$$\text{for } c' > c_{2e} \qquad (21)$$

Notice that if these equations are applied to the one phase system, i.e., $c_{2e} = c_{1e}$, g(x) = c(x) and Eqs. (20) and (21) reduce to their one-phase counterparts, Eqs. (9) and (8) respectively.

The solution may be quite easily generalized to apply to an n-phase system. g(x) is now defined as

$$g(x) \equiv c(x) - (c_{2e} - c_{1e})\, H\,(x - X_1) - (c_{4e} - c_{3e})\, H\,(x - X_2) -$$

$$\cdots\cdots - \left(c_{(2n-2)e} - c_{(2n-3)e}\right) H\,(x - X_{n-1}) \qquad (22)$$

and the derivation proceeds exactly as before.

It should be re-emphasized that these solutions are only valid if the principal physical process involved is diffusion, so that $c = c\,(xt^{-1/2})$ only.

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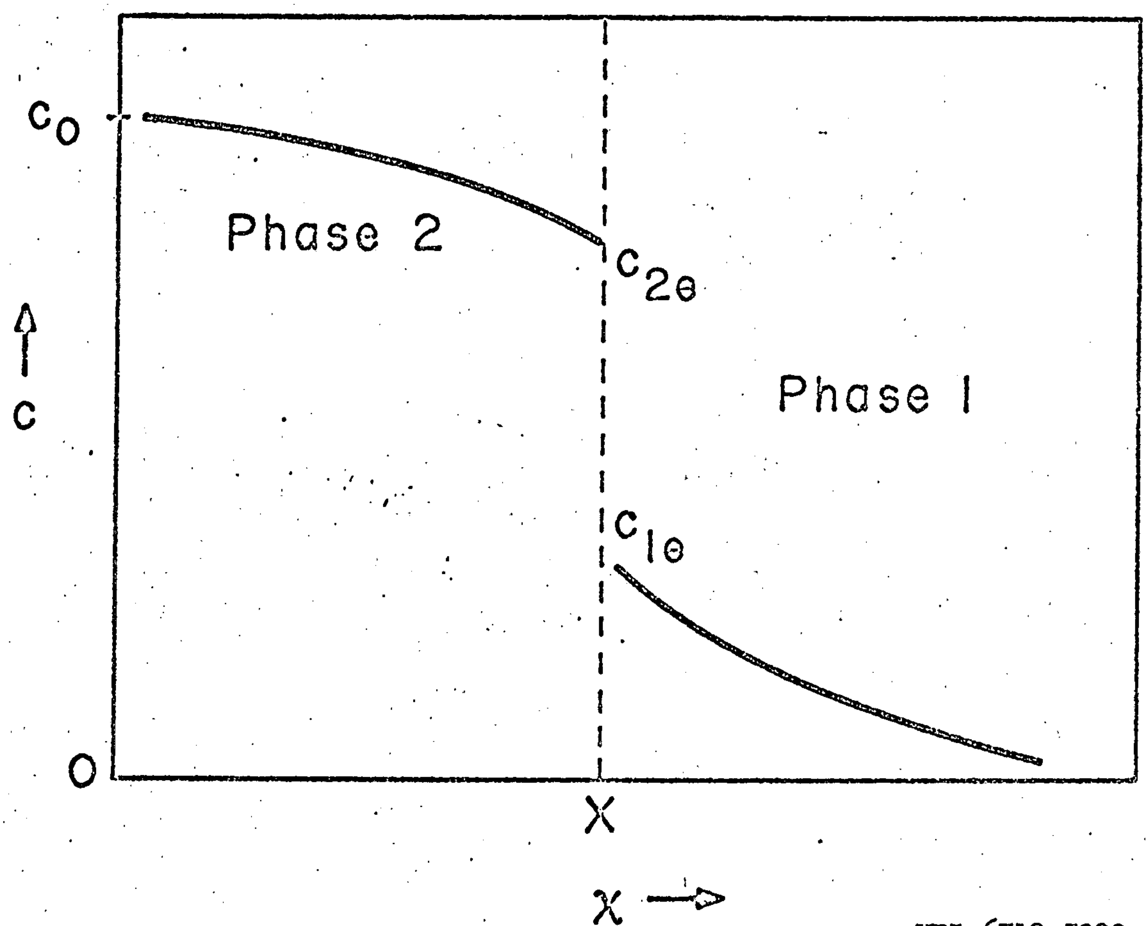

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Fig. 1 A discontinuous diffusion profile in one dimension. The position of the phase boundary, $x = X$, may or may not be changing with time. C_{2e} and C_{1e} are the respective equilibrium concentrations of the diffusing species in the two phases in contact.