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SOLUTION FOR FICK'S 2ND LAW WITH VARIABLE DIFFUSIVITY IN A MULTI-PHASE SYSTEM

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

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

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<sup>1-4</sup> 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<sup>1,2</sup> 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

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

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

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

so that

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

The initial conditions

$$c = c_0 \text{ for } x < 0, \text{ at } t = 0 \quad (4a)$$

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

transform to

$$c = c_0 \text{ at } \eta = -\infty \quad (4c)$$

$$c = 0 \text{ at } \eta = +\infty \quad (4d)$$

From Eq. (3)

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

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

$$-\frac{1}{2} xdc = d \left( Dt \frac{dc}{dx} \right) \quad (6)$$

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  $0 < c' < c_0$ , to give<sup>4</sup>

$$-\frac{1}{2} \int_0^{c'} xdc = t \left[ D \frac{dc}{dx} \right]_{c=0}^{c=c'} \quad (7)$$

But

$$\left. \frac{dc}{dx} \right|_{c=0} = \left. \frac{dc}{dx} \right|_{c=c_0} = 0, \text{ so } D(c') = -\frac{1}{2t} \left( \frac{dx}{dc} \right)_{c=c'} \int_0^{c'} xdc \quad (8)$$

$$\text{and } \int_0^{c_0} xdc = 0, \quad (9)$$

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,

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

where H(x-X) is the Heaviside unit step function<sup>5</sup> and is defined so that

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

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

where

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

and

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

Now, g(x) is a continuous function with continuous derivatives of all orders,<sup>5</sup> since δ<sup>(n)</sup>(x-X) is continuous for all n. g(x) is amenable to the mathematical operations of integration and differentiation and

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



Integrating over all  $x$  gives  $\int_{g(c=0)}^{g(c=c_0)} x dg =$

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

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

$$I_1 = \int_0^{c_{1e}} x dc + \int_{c_{2e}}^{c_0} x dc \quad (17)$$

$$I_2 = \int_{-\infty}^{X-\epsilon} x \delta(x-X) dx + \int_{X-\epsilon}^{X+\epsilon} x \delta(x-X) dx + \int_{X+\epsilon}^{\infty} x \delta(x-X) dx \quad (18)$$

where  $\epsilon > 0$  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

$$I_2 = \lim_{\epsilon \rightarrow 0} \int_{X-\epsilon}^{X+\epsilon} x \delta(x-X) dx = X \quad (19)$$

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.

$$\int_0^{c_{1e}} xdc + \int_{c_{2e}}^{c_0} xdc - (c_{2e} - c_{1e}) X = 0 \quad (20)$$

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

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

$$D(c') = -\frac{1}{2t} \left( \frac{dx}{dc} \right)_{c=c'} \left[ \int_0^{c_{1e}} xdc + \int_{c_{2e}}^{c'} xdc - (c_{2e} - c_{1e}) X \right]$$

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

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

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

$$\dots - \left( c_{(2n-2)e} - c_{(2n-3)e} \right) H(x - X_{n-1}) \quad (22)$$

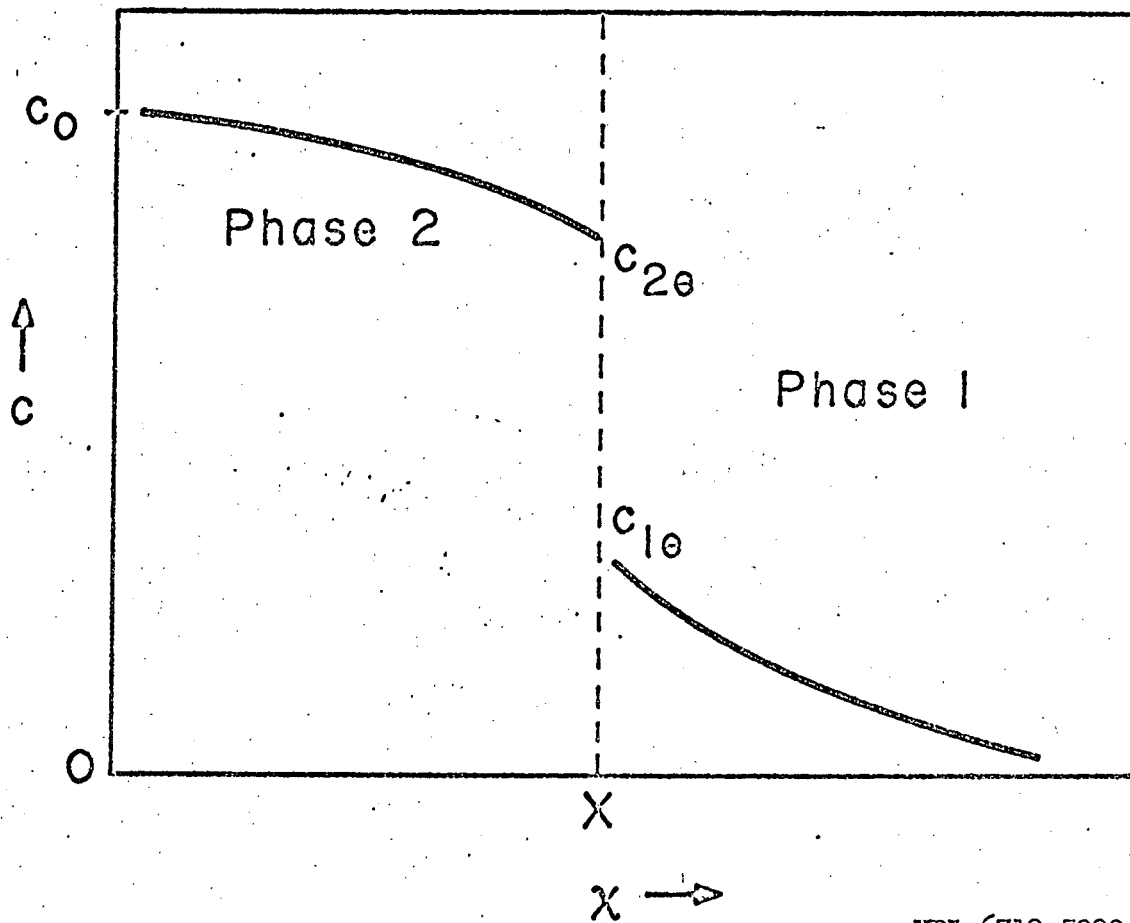
and the derivation proceeds exactly as before.

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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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.

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