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

Marvin Appel

December 1967

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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 literature¹⁻⁴ 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

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

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

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

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 give⁴

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

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 function⁵ 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,⁵ since δ⁽ⁿ⁾(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

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

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

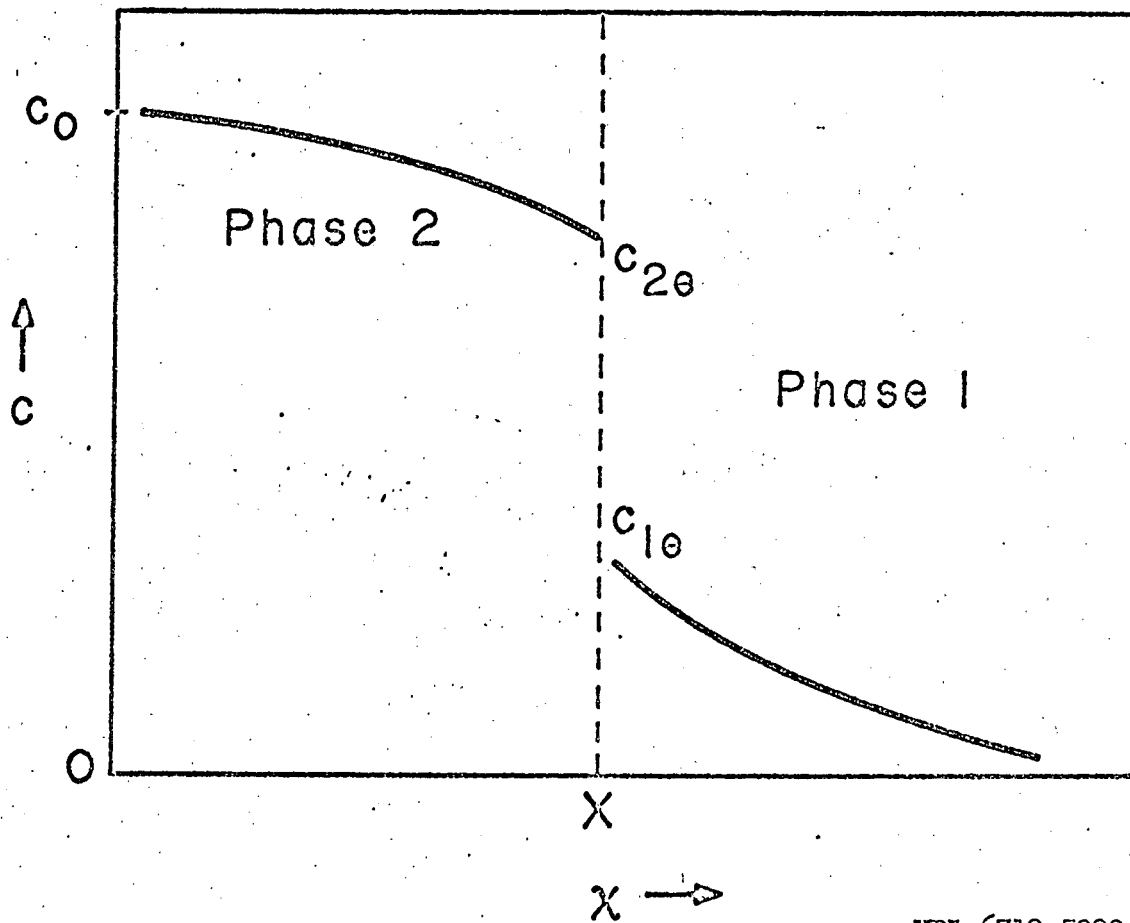
and the derivation proceeds exactly as before.

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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REFERENCES

1. L. Boltzmann, Ann. Physik, 53, 939 (1894).
2. C. Matano, Japanese J. Phys., 8, 109 (1933).
3. J. Crank, The Mathematics of Diffusion, Chap. 9 (1956).
4. P. G. Shewmon, Diffusion in Solids, Chap. 1 (1963).
5. B. Friedman, Principles and Techniques of Applied Mathematics, Chap. 3 (1956).



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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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