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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

\[ \frac{\partial c}{\partial t} = \frac{\partial}{\partial x} \left( D \frac{\partial c}{\partial x} \right) \]  

(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, \( c = c \left( xt^{-1/2} \right) \) only and, with the substitution, \( \eta = xt^{-1/2} \), we have
\[ \frac{\partial c}{\partial t} = \frac{\partial c}{\partial \eta} \frac{\partial \eta}{\partial t} = \frac{-x}{2t^{3/2}} \frac{dc}{d\eta} \]  

(2a)

\[ \frac{\partial c}{\partial x} = \frac{\partial c}{\partial \eta} \frac{\partial \eta}{\partial x} = \frac{1}{t^{1/2}} \frac{dc}{d\eta} \]  

(2b)

\[ \frac{\partial}{\partial x} = \frac{\partial}{\partial \eta} \frac{\partial \eta}{\partial x} = \frac{1}{t^{1/2}} \frac{d}{d\eta} \]  

(2c)

so that

\[ -\frac{n}{2} \frac{dc}{d\eta} = \frac{d}{d\eta} \left( d\frac{dc}{d\eta} \right) \]  

(3)

The initial conditions

\[ c = c_0 \text{ for } x < 0, \text{ at } t = 0 \]  

(4a)

\[ c = 0 \text{ for } x > 0, \text{ at } t = 0 \]  

(4b)

transform to

\[ c = c_0 \text{ at } \eta = -\infty \]  

(4c)

\[ c = 0 \text{ at } \eta = +\infty \]  

(4d)

From Eq. (3)

\[ -\frac{1}{2} \eta \frac{dc}{d\eta} = d \left( d\frac{dc}{d\eta} \right) \]  

(5)
Since \( c(x) \) is always determined for a given, fixed \( t \),

\[
- \frac{1}{2} \int x \, dc = d \left[ \frac{dc}{dx} \right]
\]

(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

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

(7)

But

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

(8)

and

\[
\int_0^{c_0} x \, dc = 0,
\]

(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,

$$g(x) = c(x) - (c_{2e} - c_{le}) H(x-X)$$  \hspace{1cm} (10)

where $H(x-X)$ is the Heaviside unit step function\(^5\) and is defined so that

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

$$\frac{d}{dx} H(x-X) = \delta(x-X)$$ \hspace{1cm} (12)

where $\delta(x-X)\begin{cases} \text{undefined for } x = X \\ 0 & \text{for all } x \neq X \end{cases}$ \hspace{1cm} (13)

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

$$xdg = x \left( \frac{dg}{dx} \right) \ dx = x \left( \frac{dc}{dx} \right) \ dx - x (c_{2e} - c_{le}) \delta(x-X) \ dx$$ \hspace{1cm} (15)
Integrating over all x gives
\[ \int g(c = c_0) x \, dg = g(c = 0) \]

\[ \int_{-\infty}^{\infty} x \left( \frac{dg}{dx} \right) \, dx = \int_{-\infty}^{\infty} x \left( \frac{dc}{dx} \right) \, dx - (c_{2e} - c_{1e}) \int_{-\infty}^{\infty} x \delta(x-X) \, dx = I_1 - (c_{2e} - c_{1e}) I_2 \tag{16} \]

\[ I_1 = \int_{0}^{c_{1e}} x \, dc + \int_{c_{2e}}^{c_0} x \, dc \tag{17} \]

\[ I_2 = \int_{-\infty}^{X-\epsilon} x \delta(x-X) \, dx + \int_{X-\epsilon}^{X+\epsilon} x \delta(x-X) \, dx + \int_{X+\epsilon}^{\infty} x \delta(x-X) \, dx \tag{18} \]

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

\[ I_2 = \lim_{\epsilon \to 0} \int_{X-\epsilon}^{X+\epsilon} x \delta(x-X) \, dx = X \tag{19} \]
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.

\[
\int_{0}^{c_{le}} x \, dc + \int_{c_{2e}}^{c_{o}} x \, dc - (c_{2e} - c_{le}) X = 0
\]

(20)

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

If $c' < c_{le}$, $c(x)$ 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

\[
D(c') = -\frac{1}{2t} \left( \frac{dx}{dc} \right)_{c = c'} \left[ \int_{0}^{c_{le}} x \, dc + \int_{c_{2e}}^{c'} x \, dc - (c_{2e} - c_{le}) X \right]
\]

for $c' > c_{2e}$

(21)

Notice that if these equations are applied to the one phase system, i.e., $c_{2e} = c_{le}$, $g(x) = c(x)$ 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
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

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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