

Chapter 5

Moving Boundary Problems in Mass Diffusion

1 Introduction

At equilibrium, the values of *chemical potential* of each substance in a multicomponent system are the same in all constituent phases of the system. For instance, in a binary system consisting of two substances A and B and existing in two phases α and β , the equilibrium conditions are

$$\mu_A^\alpha = \mu_A^\beta$$

and

$$\mu_B^\alpha = \mu_B^\beta$$

Sometimes it is more convenient to state the equilibrium conditions in terms of the *activities* of the various substances, i.e.

$$a_A^\alpha = a_A^\beta = a_A^*$$

and

$$a_B^\alpha = a_B^\beta = a_B^*$$

If for some reason, gradients in the chemical potentials of constituent substances develop, the system naturally changes in such a way that the gradients disappear. The mechanism by which chemical potential gradients are reduced is atomic transport of substance from regions of high potential to regions of low potential. This is entirely analogous to the situation encountered in heat conduction where thermal energy is transported from regions at high temperature toward regions at low temperature in a natural attempt by the system to reduce temperature gradients. .

An interesting and commonly encountered situation in multicomponent multiphase systems in equilibrium is the coexistence of different phases with different concentrations of

substance (at the same chemical potential). For instance, for the same binary system above the equilibrium concentrations of the two components may be given by

$$c_A^\alpha = c_A^{\alpha*} \neq c_A^\beta = c_B^{\beta*}$$

and

$$c_B^\alpha = c_B^{\alpha*} \neq c_B^\beta = c_B^{\beta*}$$

Therefore, if such a system is taken out of equilibrium thus introducing gradients in the chemical potentials of the constituent substances, the natural response of the system is the atomic displacement (diffusion) of the constituent substances in an attempt to bring the system back into equilibrium conditions. In this process the relative amounts of phases α and β may change with time. This is a phase transformation process and a typical moving boundary problem, the boundary being the interface separating the two coexisting phases.

The mathematical formulation of these problems requires the statement of diffusion equations for the phases involved, specification of necessary initial and boundary conditions and a description of conditions at the interface between the phases. Since the position of the interface is not known in advance and must be determined as part of the solution, the problem is nonlinear.

Consider the problem of phase transformation in a semiinfinite region $0 < x < \infty$ of a binary system initially all β and at uniform potential of the constituent substances. We will consider only the case where the atomic mobilities of the component substances are significantly different so that only the diffusion of the fastest moving species needs to be examined and the subscripts A and B can be omitted. Therefore, let the activity and concentration of this substance be a and c , respectively. Let the initial condition of the system be given by $a^\beta(x, 0) = a_i > a^*$ where a^* is the value of the activity of the substance in question at equilibrium of the phases α and β (in terms of concentration $c^\beta(x, 0) = c_i$). We shall also assume that although $a^\alpha = a^\beta = a^*$, the concentrations $c^\alpha = c^{\alpha*} < c^\beta = c^{\beta*}$.

Now let the activity at its boundary $x = 0$ be fixed to a value $a_0(0, t) < a^*$ (concentration $c(0, t) = c_0 < c^{\alpha*}$). As a result, a layer of α phase forms at the surface and the interface separating the α and β phases $\xi(t)$, moves along the positive x direction. It is commonly assumed that equilibrium conditions are quickly reached at the interface so that there (and only there) $c_- = c^{\alpha*}$ and $c_+ = c^{\beta*}$. This is the *condition of local equilibrium* at the interface.

The formulation of the problem requires finding functions $c^\alpha(x, t)$, $c^\beta(x, t)$ and $\xi(t)$ such that

$$\frac{\partial^2 c^\alpha}{\partial x^2} = \frac{1}{D^\alpha} \frac{\partial c^\alpha}{\partial t}$$

in $0 < x < \xi(t)$,

$$\frac{\partial^2 c^\beta}{\partial x^2} = \frac{1}{D^\beta} \frac{\partial c^\beta}{\partial t}$$

in $\xi(t) < x < \infty$, subject to

$$c^\alpha(0, t) = c_0$$

at $x = 0$,

$$c^\beta \rightarrow c_i$$

as $x \rightarrow \infty$.

At the interface $x = \xi(t)$ one has the local equilibrium condition

$$a^\alpha(\xi, t) = a^\beta(\xi, t) = a^*$$

(or, equivalently

$$c^\alpha = c^{\alpha*}; c^\beta = c^{\beta*}$$

and the interfacial mass balance

$$D^\alpha \frac{\partial c^\alpha}{\partial x} - D^\beta \frac{\partial c^\beta}{\partial x} = (c^{\beta*} - c^{\alpha*}) \frac{d\xi}{dt} = (c^{\beta*} - c^{\alpha*}) v$$

Here $(c^{\beta*} - c^{\alpha*})$ is the jump in concentration at the interface and $v = d\xi/dt$ is the velocity of advancement of the $\alpha - \beta$ interface.

In 3D systems, the corresponding form of the mass balance at the interface is

$$D^\alpha \frac{\partial c^\alpha}{\partial n} - D^\beta \frac{\partial c^\beta}{\partial n} = (c^{\beta*} - c^{\alpha*}) v_n$$

where v_n is the interface velocity in the normal direction.

2 Exact Solutions

Consider the situation involving a semi-infinite sample of a binary system in single phase (α) state with a uniform initial concentration of diffusing substance $c(x, 0) = c_i$. At $t = 0$ the surface concentration is increased and therein maintained at a fixed value $c(0, t) = c_0 > c^{\beta*}$ (surface enrichment). As a result, a layer of β phase forms at the surface and its thickness increases with time with the interface $\alpha - \beta$ moving along the positive x -direction.

The mathematical formulation of the problem requires finding functions $c^\alpha(x, t)$, $c^\beta(x, t)$ and $\xi(t)$ such that

$$\frac{\partial^2 c^\beta}{\partial x^2} = \frac{1}{D^\beta} \frac{\partial c^\beta}{\partial t}$$

in $0 < x < \xi(t)$,

$$\frac{\partial^2 c^\alpha}{\partial x^2} = \frac{1}{D^\alpha} \frac{\partial c^\alpha}{\partial t}$$

in $\xi(t) < x < \infty$, subject to

$$c^\beta(0, t) = c_0$$

at $x = 0$,

$$c^\alpha(x, t) \rightarrow c_i$$

as $x \rightarrow \infty$, and

$$a^\alpha(\xi, t) = a^\beta(\xi, t) = a^*$$

(or, equivalently

$$c^\alpha = c^{\alpha*}, c^\beta = c^{\beta*}$$

and

$$D^\beta \frac{\partial c^\beta}{\partial x} - D^\alpha \frac{\partial c^\alpha}{\partial x} = (c^{\alpha*} - c^{\beta*}) \frac{d\xi}{dt}$$

at the interface boundary $x = \xi(t)$.

This problem is readily solved by assuming the solution can be expressed in terms of error functions. A solution of the form

$$c^\beta(x, t) = c_0 + B \times \operatorname{erf}\left[\frac{x}{2\sqrt{D^\beta t}}\right]$$

where the constant B is to be determined, satisfies the diffusion equation inside the β layer as well as the boundary condition at $x = 0$.

Satisfaction of the equilibrium condition at the $\alpha - \beta$ interface requires that

$$B = -\frac{c_0 - c^{\beta*}}{\operatorname{erf}(\lambda)}$$

where $\lambda = \xi/2\sqrt{D^\beta t}$ must be determined so as to satisfy the remaining condition at the interface.

Inside the α phase the appropriate form of the solution is

$$c^\alpha(x, t) = c_i + C \times \operatorname{erfc}\left[\frac{x}{2\sqrt{D^\alpha t}}\right]$$

where the constant C is determined by invoking the equilibrium condition at the interface.

Finally the required solution for the entire system thus becomes

$$\frac{c^\beta(x, t) - c_0}{c^{\beta*} - c_0} = \frac{\text{erf}[x/2\sqrt{D^\beta t}]}{\text{erf}(\lambda)}$$

in the β layer and

$$\frac{c^\alpha(x, t) - c_i}{c^{\alpha*} - c_i} = \frac{\text{erfc}[x/2\sqrt{D^\alpha t}]}{\text{erfc}(\lambda(D^\beta/D^\alpha)^{1/2})}$$

in the α interior.

The interface position is given by

$$\xi(t) = 2\lambda\sqrt{D^\beta t}$$

Finally, the required value of λ is the root of the transcendental equation

$$\frac{c_0 - c^{\beta*}}{\lambda\sqrt{\pi}\text{erf}(\lambda)}e^{-\lambda^2} - \frac{(c^{\alpha*} - c_i)e^{-\lambda^2\psi}}{\sqrt{\pi}\lambda\psi^{1/2}\text{erfc}(\lambda\psi^{1/2})} = c^{\beta*} - c^{\alpha*}$$

where

$$\psi = \frac{D^\beta}{D^\alpha}$$

The above solution can be applied to estimate the progress of oxidation of a pure metal ($c_i = 0$) where β is the oxide layer and oxygen is the diffusing substance.

Finally consider the problem involving a semiinfinite medium ($0 < x < \infty$), initially all β consisting of a pure substance B (i.e. $c_B^\beta = c^\beta = 1$ in atomic fraction units). This medium is then joined at time $t = 0$ with another semiinfinite medium ($-\infty < x < 0$) consisting of pure A (i.e. $c_A^\alpha = 1, c_B^\alpha = c^\alpha = 0$) in phase α . The two phases coexist in equilibrium over the concentration range from $c^{\alpha*}$ to $c^{\beta*}$. Finally, assume that the diffusivity of substance B is much larger than that of A in both phases so that $D_B^\alpha = D^\alpha$ and $D_B^\beta = D^\beta$.

This is a model of a diffusion couple, an experimental system commonly used to investigate diffusional processes in solids. The problem can be solved as before by assuming a specific (error function) form for the concentration distributions and then determining the constants involved by enforcing the initial and boundary conditions. The final result for $-\infty < x < 0$ is

$$c^\alpha(x, t) = \frac{c^{\alpha*}}{1 + \text{erf}(\lambda)} \left[1 + \text{erf}\left(\frac{x}{2\sqrt{D^\alpha t}}\right) \right]$$

and for $0 < x < \infty$,

$$c^\beta(x, t) = \frac{1}{\operatorname{erfc}(\lambda/\psi^{1/2})} [c^{\beta*} - \operatorname{erf}(\lambda/\psi^{1/2}) + (1 - c^{\beta*})\operatorname{erf}(\frac{x}{2\sqrt{D^\beta t}})]$$

Further, the interface position is given by

$$\xi(t) = 2\lambda\sqrt{D^\beta t}$$

where λ is the root of

$$\frac{c^{\alpha*}e^{-\lambda^2}}{(c^{\beta*} - c^\alpha)\lambda\sqrt{\pi}(1 + \operatorname{erf}(\lambda))} - \frac{(1 - c^{\beta*})\psi^{1/2}e^{-\lambda^2/\psi}}{(c^{\beta*} - c^\alpha)\lambda\sqrt{\pi}\operatorname{erfc}(\lambda/\psi^{1/2})} = 1$$

where

$$\psi = \frac{D^\beta}{D^\alpha}$$

3 Numerical Methods

Numerical solution techniques for diffusion problems with phase change must account for the changing location of the phase boundary. As in the case of heat transfer, variable and fixed grid methods can be used. Since fixed grid methods are usually easier to implement we shall again focus on those here. The fixed grid method used for the numerical solution of moving boundary problems is based on the activity formulation.

Consider a slab of binary material in phase β with initial concentration of diffusing substance $c(x, 0) = c_i > c^{\beta*}$. At time $t = 0$, the concentration of diffusing substance at the boundaries of the slab is lowered and maintained at $c(0, t) = c_S < c^{\alpha*}$. As a result, layers of α form at the surface and $\alpha - \beta$ interfaces move towards the center of the slab. Instead of writing separate equations for the solid and liquid phases, the diffusion equation is written as follows:

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

where the concentration c is a step function of activity, i.e.

$$c = \begin{cases} \gamma^\alpha(a - a^*) + c^{\alpha*}; & a < a^* \\ \gamma^\beta(a - a^*) + \Delta c^*; & a > a^* \end{cases}$$

where $\Delta c^* = c^{\beta*} - c^{\alpha*}$.

Introduce now a fixed mesh in space (mesh spacing Δx) with $N + 1$ nodes located at x_i where $i = 1, 2, \dots, N + 1$ and a mesh in time (mesh spacing Δt) with nodes t_j where $j = 1, 2, 3, \dots$

Discretization of the heat equation by means of a simple explicit finite difference or finite volume schemes yields

$$\frac{c_{i,j+1} - c_{i,j}}{\Delta t} = \frac{D_{i+\frac{1}{2},j} \frac{a_{i+1,j} - a_{i,j}}{\Delta x} - D_{i-\frac{1}{2},j} \frac{a_{i,j} - a_{i-1,j}}{\Delta x}}{\Delta x}$$

where the two subscripts on the variables are needed to specify the mesh point where the quantity is to be evaluated.

The numerical calculation is carried out from an initial concentration condition by first computing values of concentration for all spatial nodes at the new time step ($c_{i,j+1}$) explicitly from the above expression. Activity values for all spatial nodes at the new time step are then calculated from the given concentration-activity relationship. The position of the moving boundary is determined by locating spatial nodes around a^* and interpolation. The calculation is then repeated to advance to the next time step. Since this is an explicit scheme, the mesh spacings must fulfill the CFL condition, namely

$$\Delta t = \frac{\Delta x^2}{2D}$$

where D is the smaller of D^α and D^β .

Alternatively, an implicit scheme may be employed but this will require implementation of an iterative process to advance the solution each time step.

4 Exercises

Exercise 1. Use the properties of the error function to verify that for the two phase binary system $\alpha - \beta$, the given expression for c^β satisfies the diffusion equation as well as the boundary condition at $x = 0$ while that for c^α satisfies the diffusion equation, the boundary condition at $x \rightarrow \infty$ as well as the initial condition.

Exercise 2. The surface of a large piece of pure iron is exposed to a carburizing atmosphere which fixes the surface concentration of carbon to $c_0 = 1$ percent. At the treatment temperature of 900 degrees Celsius a carbon rich austenite (γ) phase forms on the surface of the carbon lean ferrite (α) core. Estimate the advancement of the $\gamma - \alpha$ interface. Consider $D^\gamma = 5 \times 10^{-12}$, $D^\alpha = 5 \times 10^{-10}$ (both in m^2/s), $c^{\alpha*} = 0.001$, $c^{\gamma*} = 0.01$ (both in weight percent).

Exercise 3. A large sample of iron-carbon alloy contains 1 percent carbon. The sample is heated to 900 degrees Celsius (whence it becomes single phase - austenite or γ) and exposed

to an environment that lowers the surface concentration of carbon to 0. As a result, a layer of α phase forms on the surface and the $\alpha - \gamma$ interface moves towards the interior of the sample. Estimate the advancement of the interface using an explicit finite difference method.

5 References

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