PHYSICS OF MATERIALS

Physics School Autumn 2024

Series 5 Solution **1 November 2024**

Exercise 1 Steel carburizing

We use the equation defining the diffusion from the surface at a constant concentration (eq. 5.7 of the text).

$$\frac{C(x)-C_0}{C_s-C_0}=\left(1-erf\left(\frac{x}{2\sqrt{Dt}}\right)\right)$$

$$\frac{C(x)-C_0}{C_s-C_0}=\frac{0.5-0.02}{1-0.02}=0.49=\left(1-erf\left(\frac{x}{2\sqrt{Dt}}\right)\right)$$

Thus:

$$erf\left(\frac{x}{2\sqrt{Dt}}\right)=0.51$$

Looking up the erf function table, we get the following:

$$\frac{0.51-0.4755}{0.5205-0.4755}=\frac{z-0.45}{0.5-0.45}$$

$$z=\frac{x}{2\sqrt{Dt}}=0.483$$

From this, we get the following:

$$t=\frac{\left(10^{-3}[m]\right)^2}{4(0.483)^2\left(20\cdot 10^{-6}\left[m^2/s\right]\cdot \exp\left(\left(-142[kJ/mol]\right)/1273[K]\cdot 8.314[J/mol/K]\right)\right)^2}=9.96h$$

The diffusion coefficient used is for the f.c.c. phase and a temperature of 1000°C. The surface carburizing of the steels is classically made at about 1/10th of an mm per hour. The process is thus very precise but slow and, therefore, expensive.

Exercise 2 Conduction in an ionic crystal

All calculations are made in one dimension. For example, the electrical conductivity σ related to the electron flux is given by :

$$J_{el} = \sigma E$$

Let's calculate electron flux J_{el} :

$$J_{el} = \underbrace{C_i \mathrm{v}_i}_{J_i} q$$

where J_i is the flux of the ions.

Now, $\mathrm{v}_i = \frac{D_i F}{kT} = \frac{D_i q_i E}{kT}$

Therefore: $J_i = \frac{C_i D_i q_i^2 E}{kT}$ and the electrical conductivity is:

$$\sigma = \frac{C_i D_i q_i^2}{kT} = \frac{C_i q_i^2}{kT} D_{i0} \exp\left(\frac{-Q_i}{kT}\right)$$

If a concentration gradient is present, then:

$$J_{el} = J_i q_i = q_i \left(\frac{C_i D_i q_i E}{kT} - D_i \frac{\partial C_i}{\partial x} \right)$$

Exercise 3 Conduction in a two-component ionic crystal

An example of such a crystal could be a diffusion couple NaCl-KCl where only metal ions diffuse and the underlying Cl lattice remains steady.
Without any electrical field:

$$\boldsymbol{J_A = -D_A^* \frac{\partial C_A}{\partial x}}$$

$$\boldsymbol{J_B = -D_B^* \frac{\partial C_B}{\partial x}}$$

and

$$\boldsymbol{C_A + C_B} = \text{constant} \;\; \Rightarrow \;\; \frac{\partial \mathrm{C_A}}{\partial \mathrm{x}} = -\frac{\partial \mathrm{C_B}}{\partial \mathrm{x}}$$

Since $\boldsymbol{D_A^* \neq D_B^*}$ then $\boldsymbol{J_A \neq J_B}$, which would produce a total flux:

$$\boldsymbol{J = J_A + J_B = \left(D_A^* - D_B^*\right) \frac{\partial C_A}{\partial x}} \qquad (5.3.1)$$

However, the electrical neutrality implies that the total flux is zero, and an electric field $\boldsymbol{E}$ results. As calculated in exercise 2 above, the flux equations for ions A and B become:

$$\begin{aligned} J_A &= -D_A^* \frac{\partial C_A}{\partial x} + q_i E \frac{D_A^* C_A}{kT} \\ J_B &= -D_B^* \frac{\partial C_B}{\partial x} + q_i E \frac{D_B^* C_B}{kT} \end{aligned} \tag{5.3.2}$$

In this case, $J = J_A + J_B = 0$, which allows the calculation of $\boldsymbol{E}$:

$$E = \frac{kT}{q_i} \frac{D_A^* - D_B^*}{C_A D_A^* + C_B D_B^*} \frac{\partial C_A}{\partial x} \tag{5.3.3}$$

By inserting (5.3.3) in (5.3.2), the fluxes can be expressed as a function of concentration gradients:

$$\begin{aligned} J_A &= -\bar{D}_A \frac{\partial C_A}{\partial x} \\ J_B &= -\bar{D}_B \frac{\partial C_B}{\partial x} \end{aligned} \tag{5.3.4}$$

with

$$\bar{D} = \frac{D_A^* \cdot D_B^*}{X_A D_A^* + X_B D_B^*}$$

Beware not to confuse this coefficient of ionic interdiffusion with that of chemical interdiffusion $\tilde{D} = X_B D_A^* + X_A D_B^*$ obtained by the Boltzmann-Matano method.