Chapter 4

Diffusion with a Chemical Concentration Gradient

1. (a) Schematic composition, flux and vacancy profiles are shown in figure 4.1. In the first sample (graphs on left) we see that the Zn flux to the left out of the sample. In the second sample the Zn flux is to the right into the sample.

(b) The gradient of the flux gives an indication of the loss of atoms, and since we know Zn is the fast diffuser, it is leaving faster than Cu is replacing it in the first sample. Hence near the minimum in the vacancy source term there will be voids created in this sample. In the second sample there will be no voids created.
Figure 4.1: Schematic composition, flux and vacancy source profiles for Cu-Zn diffusion couples. On the left are graphs for 30% Zn held in vacuum and on the right are graphs for Cu with surface held at 30% Zn. The depth is in units of $\sqrt{4Dt}$, the flux is in units of $D/(VA\sqrt{4Dt})$, and the vacancy source is in units of $1/(VA4t)$. 
2. (a) The force due to the acceleration $a$ on an $i$ atom with mass $m_i$ is:

$$F_i = (\langle m \rangle - m_i)a$$

where $\langle m \rangle$ is the local average mass given by:

$$\langle m \rangle = x_A m_A + x_B m_B$$

The jump frequency for atoms jumping against the force will be less than for those jumping with the force. These jump frequencies are given by:

$$\nu_{\pm}^i = \nu (1 \pm \epsilon_i)$$

where the $+$ sign is for jumps with the force (forward jumps) and the $-$ sign is for jumps against the force (backward jumps), $\nu$ is the jump frequency in the absence of the force, and $\epsilon_i$ is given by:

$$\epsilon_i = \frac{F_i \Delta z}{2kT}$$

Hence the difference between forward and backward jumps is:

$$\Delta \nu^i = 2\epsilon_i \nu$$
(b) The condition of steady state implies that:
\[
\frac{\partial c_i}{\partial t} = - \frac{\partial J_i}{\partial z} = 0
\]

and since the flux at the ends of the rod is zero, the the flux of each component is zero everywhere. Let’s consider the \( B \)-atom flux:
\[
J_B = -D_B \frac{\partial c_B}{\partial z} + \frac{D_B c_B F_B}{kT} = 0
\]

Rewriting this in terms of \( x_B = c_B/c \) we find:
\[
\frac{dx_B}{dz} = \frac{x_B F_B}{kT}
\]

where we have also changed the partials into total derivatives, since there is no time dependence. This is a differential equation for the concentration as a function of position. We can write the force \( F_B \) as:
\[
F_B = (\langle m \rangle - m_B)a = [(1 - x_B)m_A + x_B m_B - m_B]a = x_A(m_A - m_B)a = (1 - x_B)a \Delta m
\]

where \( \Delta m = m_A - m_B \). The differential equation now becomes:
\[
\frac{dx_B}{dz} = \frac{x_B(1 - x_B)a \Delta m}{kT}
\]

On rearranging we find:
\[
\int_{x_B^0}^{x_B} \frac{dx_B}{x_B(1 - x_B)} = \frac{a \Delta m}{kT} z
\]

where \( x_B^0 \) is the atomic fraction of \( B \) atoms at \( z = 0 \). Performing the integral we find:
\[
\ln \left( \frac{x_B}{1 - x_B} \right) - \ln \left( \frac{x_B^0}{1 - x_B^0} \right) = \frac{a \Delta m}{kT} z
\]
which can be rearranged to yield:

\[
\frac{x_B}{1 - x_B} = \frac{x_B^0}{1 - x_B^0} \exp \left( \frac{a \Delta m z}{kT} \right)
\]

Solving for \(x_B\) gives:

\[
x_B = \frac{x_B^0}{1 - x_B^0} \left( \frac{\exp \left( \frac{a \Delta m z}{kT} \right)}{1 + \frac{x_B^0}{1 - x_B^0} \exp \left( \frac{a \Delta m z}{kT} \right)} \right)
\]

To find the constant \(x_B^0\) we apply the condition that the total number of \(B\) atoms is constant. Since the initial value of the integral of \(x_B\) \(dz\) over the length of the bar was \(L/2\), where \(L\) is the length of the bar, we have:

\[
\int_0^L x_B \, dz = \frac{L}{2}
\]

Performing this integral and solving for \(x_B^0\) we find:

\[
x_B^0 = \frac{\exp \left( \frac{a \Delta m L}{2kT} \right) - 1}{\exp \left( \frac{a \Delta m L}{kT} \right) - 1}
\]

Inserting this into our equation for \(x_B\) we find:

\[
x_B = \frac{\exp \left( \frac{a \Delta m z}{kT} \right)}{\exp \left( \frac{a \Delta m L}{2kT} \right) + \exp \left( \frac{a \Delta m z}{kT} \right)}
\]
3. (a) The vacancy-atom exchange rate can be found by examining the schematic shown in figure 4.2. Each of the first three jumps increases the number of anti-site defects by one. This has a formation free energy cost of $\Delta G'_{AS}$. Hence the effective energy barrier is $\Delta G'_M + \Delta G'_AS/2$. The jumping rate for these jumps is then:

$$\nu^{(1,2,3)} \equiv \nu^+ = \nu_0 e^{-\Delta G'_M/kT} e^{-\Delta G'_{AS}/2kT}$$

Similarly, the last three jumps each remove an anti-site defect and so have an an effective jump frequency of:

$$\nu^{(4,5,6)} \equiv \nu^- = \nu_0 e^{-\Delta G'_M/kT} e^{-\Delta G'_{AS}/2kT}$$

For the case of a strongly ordering system, where the anti-site defect formation energy is relatively large, the frequency for jumps which create an anti-site defect will be much smaller than that for jumps which remove one.

The total diffusion rate will be a function of the anti-site formation energy since formation of these sites is necessary for diffusion to take place and the anti-site formation energy acts as a potential barrier for diffusive jumps.

(b) The jump probability can be found by dividing the atom-vacancy exchange rate for a given jump by the sum of the exchange rates for all possible vacancy jumps. For example, the probability that the vacancy jumps to the selected tracer atom in the first jump is given by:

$$p^{(1)} = \frac{\nu^+}{4\nu^+} = \frac{1}{4}$$
In a similar way we find for the remaining jumps:

\[
\begin{align*}
p^{(2)} &= \frac{\nu^+}{3\nu^+ + \nu^-} \\
p^{(3)} &= \frac{\nu^+}{3\nu^+ + \nu^-} \\
p^{(4)} &= \frac{\nu^-}{2\nu^+ + 2\nu^-} \\
p^{(5)} &= \frac{\nu^-}{3\nu^+ + \nu^-} \\
p^{(6)} &= \frac{\nu^-}{3\nu^+ + \nu^-}
\end{align*}
\]
4. (a) The boundary conditions are determined by equating the chemical potentials at the interface. Outside the membrane the chemical potential for the water is

$$\mu_O = \mu_0 + k_B T \ln 1 = \mu_0$$

Just inside the membrane at this interface the chemical potential is

$$\mu_O^M = \mu_0 + k_B T \ln a^M = \mu_0 + k_B T (\ln x_O^M + \ln \gamma^M)$$
Figure 4.5: Vacancy fraction as a function of position for several different values of normalized potential gradient $k$, which is given by $k = q^* \nabla V h / k_B T$.

Equating these two we find:

$$x_M^O = \frac{1}{\gamma_M^O}$$

So the concentration on the outer surface of the membrane is

$$c_M^O = \frac{1}{\gamma_M^O V_A}$$

Similarly, inside the cell the water chemical potential is

$$\mu_I = \mu_0 + k_B T \ln x$$

Just inside the membrane at this interface the chemical potential is

$$\mu_I^M = \mu_0 + k_B T \ln a^M = \mu_0 + k_B T (\ln x_I^M + \ln \gamma^M)$$

Equating these two we find:

$$x_I^M = \frac{x}{\gamma^M}$$

So the concentration on the inner surface of the membrane is

$$c_I^M = \frac{x}{\gamma^M V_A}$$
(b) The diffusion in the membrane wall occurs quickly and so reaches
a steady-state concentration profile much faster than the concen-
tration inside the cell (and hence the interior boundary condition)
changes. For this case the concentration within the membrane follows
\[
\frac{\partial c}{\partial t} = 0
\]
Hence from Ficks second law, we have
\[
\frac{dc^M}{dz} = \text{constant}
\]
Applying the boundary conditions we find
\[
c^M = c^M_I + \frac{z}{h} (c^M_O - c^M_I) = \frac{\gamma M V_A}{h} \left[ x + \frac{z}{h} (1 - x) \right]
\]
(c) The flux through the membrane is given by
\[
J = -D^M \frac{dc^M}{dz} = -D^M \frac{(1 - x)}{h \gamma M V_A}
\]
(d) For simplicity we write the flux magnitude as
\[
J = \kappa [1 - x(r)]
\]
where we have put in the dependence of the solution concentration
on the cell radius \( r \). Conserving the non-water molecules inside
the cell we find
\[
(1 - x)r^3 = (1 - x_0)r_0^3
\]
From which we find:
\[
x = 1 - (1 - x_0) \left( \frac{r_0}{r} \right)^3
\]
The rate of change of the cell volume is due to the flux of molecules,
so
\[
\frac{dV}{dt} = 4\pi r^2 \frac{dr}{dt} = 4\pi r^2 J V_A
\]
Inserting $x(r)$ into our expression for $J$ we find:

\[
\frac{dr}{dt} = V_A J \\
= V_A \kappa [1 - x(r)] \\
= V_A \kappa (1 - x_0) \left( \frac{r_0}{r} \right)^3
\]

Integrating we find:

\[
r = \left[ r_0^4 + V_A \kappa (1 - x_0) r_0^3 t \right]^{1/4}
\]

This is linear in $t$ for small $t$ and goes like $t^{1/4}$ for large $t$. We can insert this into our expression for $x(r)$ to find the cell solution concentration as a function of time.

Cells with compliant walls will expand until they rupture when placed in fresh water.