**Fundamentals of Diffusion**

**Diffusion:** Transport in a solid, liquid, or gas driven by a concentration gradient (or, in the case of mass transport, a chemical potential gradient). Diffusion does not necessarily apply to transport of mass. Consider, for example, thermal diffusion, or transport of phonons – heat quanta.

**Example:** Two chambers, each containing a different gas, separated by a removable barrier; when the barrier is pulled away, *interdiffusion* occurs.

Initially, a plot of concentration of each species would look like the following:
After a time, the concentration profiles would look like this:

![Graph showing concentration profiles](image)

And after a *long* time, the concentration of the two gasses would be everywhere the same:

![Graph showing concentration profiles after long time](image)

We see essentially the same process in solids, as seen in the case of Cu and Ni: (note, diffusion in the gaseous state does not require an activation energy as it does in solids)
The process of substitutional diffusion requires the presence of *vacancies*.

(Vacancies give the atoms a place to move)
Diffusion tends to equalize concentration gradients.

Note the presence of vacancies in the material.
Recall, the fraction of vacancies is temperature dependent:

\[
\frac{N_v}{N_o} = \frac{Q_v}{kT} \quad \text{e}^{\frac{Q_v}{kT}}
\]

\[
\therefore \text{diffusion is a temperature-dependent process}
\]

In the example of a Cu-Ni diffusion couple, diffusion of Ni into Cu occurs at a faster rate than Cu in Ni.

Why is this?

\[T_m(\text{Ni}) = 1451^\circ\text{C}, \quad T_m(\text{Cu}) = 1083^\circ\text{C} \Rightarrow \text{larger fraction of vacancies in Cu at a given temperature than in Ni.}\]

Mathematically, we would write

\[
\left(\frac{N_v}{N_o}\right)_{\text{Cu}} > \left(\frac{N_v}{N_o}\right)_{\text{Ni}}
\]

(We say that Cu is at a higher homologous temperature than Ni)

Diffusion tends to equalize compositional gradients (if all other factors are equal - sometimes “kinetics” do not favor diffusional equilibration. That is, some diffusional processes occur so slowly as to be imperceptible.)

Factors that affect solid state diffusion:

**Diffusion occurs at a higher rate…**

- at higher temperatures
  atoms have more energy to overcome “barrier” to diffusion
  greater probability of activation over the energy barriers

- with smaller atoms
  smaller atoms can “squeeze” in between host atoms more easily

- in lower melting point host material
  lower \(T_m\) \Rightarrow weaker bonds (easier to push apart)

- in lower packing density host material
  easier to migrate with fewer bonds to expand

- in grain boundaries
  more disordered than bulk material (lower bond density)
Steady state diffusion is described in terms of a **flux** and a **concentration gradient**:

(Steady state means the concentration gradient does not change with time, or that the flux into a unit area is equal to the flux leaving the area – no accumulation or loss)

**Flux** = number (or mass) of atoms passing through an area per unit time

Units: \[rac{\text{atoms}}{\text{cm}^2 \cdot \text{sec}} \quad \text{or} \quad \frac{\text{grams}}{\text{cm}^2 \cdot \text{sec}} \quad \text{('could also be moles, Kg; the main thing is to just be consistent)}
\]
Flux is usually denoted by the letter “J”

\[ J \propto \frac{\Delta C}{\Delta x} \]

- or -

\[ J = D \frac{dC}{dx} \]

where the constant of proportionality (D) is called the diffusion coefficient

units of the diffusion coefficient: \( \text{length}^2/\text{time} \) (cm\(^2\)/s or m\(^2\)/s)

the diffusion coefficient is a “thermally activated” quantity:

\[ D = D_o e^{\frac{-Q_d}{RT}} \]

- or -

\[ D = D_o e^{\frac{-q_d}{kT}} \]

where \( Q_d \) and \( q_d \) are activation energies for diffusion

per mole per atom
Since D increases exponentially with temperature, diffusion rates increase with temperature:
Typical values for preexponential ($D_o$) and activation energy:
(after Kittel, “Solid State Physics” 5th ed.)

\[ D = D_o \exp\{-q/k_B T\} \]

<table>
<thead>
<tr>
<th>Host crystal</th>
<th>Atom</th>
<th>$D_o$ (cm$^2$/s)</th>
<th>$q_d$ (eV/atom)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cu</td>
<td>Cu</td>
<td>0.20</td>
<td>2.04</td>
</tr>
<tr>
<td>Cu</td>
<td>Zn</td>
<td>0.34</td>
<td>1.98</td>
</tr>
<tr>
<td>Ag</td>
<td>Ag</td>
<td>0.40</td>
<td>1.91</td>
</tr>
<tr>
<td>Ag</td>
<td>Au</td>
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<td>1.98</td>
</tr>
<tr>
<td>Ag</td>
<td>Cu</td>
<td>1.2</td>
<td>2.00</td>
</tr>
<tr>
<td>Ag</td>
<td>Pb</td>
<td>0.22</td>
<td>1.65</td>
</tr>
<tr>
<td>U</td>
<td>U</td>
<td>0.002</td>
<td>1.20</td>
</tr>
<tr>
<td>Si</td>
<td>Al</td>
<td>8.0</td>
<td>3.47</td>
</tr>
<tr>
<td>Si</td>
<td>Ga</td>
<td>3.6</td>
<td>3.51</td>
</tr>
<tr>
<td>Si</td>
<td>In</td>
<td>16.0</td>
<td>3.90</td>
</tr>
</tbody>
</table>

2 primary mechanisms that affect flux:

- Diffusion coefficient (temperature)
- Slope of concentration gradient

$D_o$ and $Q_d$ (or $q_d$) can be found by plotting $\ln(D)$ vs. $\frac{1}{T}$

Then,

\[ \text{Slope} = -Q/R \quad (or \quad -q/k_B) \]

\[ \text{Intercept} = \ln(D_o) \]

Reciprocal temperature (1000/K)
We usually don’t have steady state; more often, the concentration versus position curve changes with time (non-steady state)

In this case, we must use another relationship → Fick’s second law:

(we are interested in the **time rate of change of the concentration**…)

\[ \delta C = \frac{\Delta (\text{# atoms})}{\text{volume}} = \frac{(J_1 - J_2)A\delta t}{A\delta x}, \text{ simplifying, we have } \frac{\delta C}{\delta t} = \frac{\Delta J}{\Delta x} \]

- or \[ \frac{dC}{dt} = \frac{dJ}{dx} = \frac{d}{dx} \left( \frac{DC}{dx} \right) \approx D \frac{d^2C}{dx^2}, \text{ assuming } D \text{ is independent of position!} \]

Fick’s 2\textsuperscript{nd} law is: \[ \frac{dC}{dt} = D \frac{d^2C}{dx^2} \]

Which describes diffusion in cases where the concentration profile changes with time

Think of as the **curvature** of the concentration profile
Example:

Consider diffusion of C into $\gamma$-Fe (this is one example of carburization)

In carburization, we diffuse C atoms into the surface of low C steels, heated to $\sim 1000^\circ$C (FCC structure)

![Graph showing carbon concentration profile](image)

(The profile above is consistent with an initial carbon concentration of $\sim 0$. Steels, by definition, always have a non-zero carbon content, $w_o$.

Solution to Fick’s 2nd law:

Employing appropriate boundary conditions, Fick’s 2nd law can be solved, with the solution written in a useful form for metallurgical applications:

$$\frac{C_x - C_o}{C_s - C_o} = 1 - \text{erf} \left( \frac{x}{2\sqrt{Dt}} \right)$$

where $C_x$ = carbon concentration at any point “x” in the steel during diffusion, $C_o$ = initial (uniform) carbon concentration in the steel (at $t = 0$), $C_s$ = surface concentration of carbon during diffusion (we can control this)

$\text{erf}()$ = “error” function (a mathematical expression: $-1 < \text{erf}(x) < 1$ )

While not strictly true, for this class we will assume $\text{erf}(x) \approx x$. 

12
(The assumption that \( \text{erf}(x) \approx x \) isn’t too bad for \( x < 0.7 \). In situations where \( x > 0.7 \) or where \( \text{erf}(x) > 0.65 \), you should really use the correct value. The following table may be of help. Remember to interpolate to obtain values between those listed.)

<table>
<thead>
<tr>
<th>( z )</th>
<th>( \text{erf}(z) )</th>
<th>( z )</th>
<th>( \text{erf}(z) )</th>
<th>( z )</th>
<th>( \text{erf}(z) )</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>0</td>
<td>0.55</td>
<td>0.5633</td>
<td>1.3</td>
<td>0.9340</td>
</tr>
<tr>
<td>0.025</td>
<td>0.0282</td>
<td>0.60</td>
<td>0.6039</td>
<td>1.4</td>
<td>0.9523</td>
</tr>
<tr>
<td>0.05</td>
<td>0.0564</td>
<td>0.65</td>
<td>0.6420</td>
<td>1.5</td>
<td>0.9661</td>
</tr>
<tr>
<td>0.1</td>
<td>0.1125</td>
<td>0.70</td>
<td>0.6778</td>
<td>1.6</td>
<td>0.9763</td>
</tr>
<tr>
<td>0.15</td>
<td>0.1680</td>
<td>0.75</td>
<td>0.7112</td>
<td>1.7</td>
<td>0.9838</td>
</tr>
<tr>
<td>0.2</td>
<td>0.2227</td>
<td>0.80</td>
<td>0.7421</td>
<td>1.8</td>
<td>0.9891</td>
</tr>
<tr>
<td>0.25</td>
<td>0.2763</td>
<td>0.85</td>
<td>0.7707</td>
<td>1.9</td>
<td>0.9928</td>
</tr>
<tr>
<td>0.3</td>
<td>0.3286</td>
<td>0.90</td>
<td>0.7970</td>
<td>2.0</td>
<td>0.9953</td>
</tr>
<tr>
<td>0.35</td>
<td>0.3794</td>
<td>0.95</td>
<td>0.8209</td>
<td>2.2</td>
<td>0.9981</td>
</tr>
<tr>
<td>0.4</td>
<td>0.4284</td>
<td>1.0</td>
<td>0.8427</td>
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<td>0.9993</td>
</tr>
<tr>
<td>0.45</td>
<td>0.4755</td>
<td>1.1</td>
<td>0.8802</td>
<td>2.6</td>
<td>0.9998</td>
</tr>
<tr>
<td>0.5</td>
<td>0.5205</td>
<td>1.2</td>
<td>0.9103</td>
<td>2.8</td>
<td>0.9999</td>
</tr>
</tbody>
</table>

Then, the (somewhat oversimplified) solution becomes:

\[
C(x) \approx C_o + \left( C_s - C_o \right) \left[ 1 - \frac{x}{2\sqrt{Dt}} \right]
\]

(x in cm, t in sec, D in cm\(^2\)/s, C1, Co, Cx all in wt. %)

Next, some example problems…
The purification of $H_2$ (gas) by diffusion through a Pd sheet was discussed in Section 5.3. Compute the number of kilograms of hydrogen that pass per hour through a 5-mm thick sheet of Pd having an area of 0.20 m$^2$ at 500°C. Assume a diffusion coefficient of $1.0 \times 10^{-8}$ m$^2$/s, that the concentrations at the high- and low-pressure sides of the plate are 2.4 and 0.6 kg of $H_2$ per m$^3$ of Pd, and that steady state conditions have been attained.

This problem calls for the mass of hydrogen per hour that diffuses through a Pd sheet. It first becomes necessary to employ both Equations (5.1a) and (5.3). Combining these expressions and solving for the mass yields

$$M = JAt = -DAt \frac{DC}{Dx}$$

$$= -(1.0 \times 10^{-8} \text{ m}^2/\text{s})(0.2 \text{ m}^2)(3600 \text{ s/h}) \left[ \frac{0.6 - 2.4 \text{ kg/m}^3}{5 \times 10^{-3} \text{ m}} \right]$$

$$= 2.6 \times 10^{-3} \text{ kg/h}$$

An FCC Fe-C alloy initially containing 0.35 wt. % C is exposed to an oxygen-rich (and carbon-free) atmosphere at 1400 K (1127°C). Under these conditions the carbon in the alloy diffuses toward the surface and reacts with the oxygen in the atmosphere; that is, the carbon concentration at the surface is maintained essentially at 0 wt. % C. (This process of carbon depletion is termed decarburization.) At what position will the carbon concentration be 0.15 wt. % after a 10-hour treatment. The value of $D$ at 1400 K is $6.9 \times 10^{-11}$ m$^2$/s.
This problem asks that we determine the position at which the carbon concentration is 0.15 wt% after a 10-h heat treatment at 1400 K when \( C_0 = 0.35 \) wt% C. From Equation (5.5)

\[
\frac{C_x - C_0}{C_s - C_0} = \frac{0.15 - 0.35}{0 - 0.35} = 0.5714 = 1 - \text{erf} \left( \frac{x}{2 \sqrt{Dt}} \right)
\]

Thus,

\[
\text{erf} \left( \frac{x}{2 \sqrt{Dt}} \right) = 0.4286
\]

Since we are assuming \( \text{erf}(z) \approx z \), we will simply let \( z = 0.4 \):

Which means that

\[
\frac{x}{2 \sqrt{Dt}} = 0.4
\]

And, finally

\[
x = 2(0.4)\sqrt{Dt} = (0.8004)\sqrt{(6.9 \times 10^{-11} \text{ m}^2/\text{s})(3.6 \times 10^4 \text{ s})}
\]

\[
= 1.3 \times 10^{-3} \text{ m} = 1.3 \text{ mm}
\]

III. Callister 5. 26.

At approximately what temperature would a specimen of \( \gamma\)-Fe have to be carburized for 2 hours to produce the same diffusion result as at 900°C for 15-hours?

To solve this problem it is necessary to employ Equation (5.7) \((Dt = \text{constant})\) which takes on the form

\[
(Dt)_{900} = (Dt)_T
\]

(the hint is that the problem stated “the same diffusion result,” meaning that we want the same specific carbon concentration in both cases)

At 900°C, and using the data from Table 5.2
\[
D_{900} = (2.3 \times 10^{-5} \text{ m}^2/\text{s}) \exp\left[ -\frac{148000 \text{ J/mol}}{(8.31 \text{ J/mol-K})(900 + 273 \text{ K})} \right] = 5.9 \times 10^{-12} \text{ m}^2/\text{s}
\]

Thus,
\[
(5.9 \times 10^{-12} \text{ m}^2/\text{s})(15 \text{ h}) = D_T(2 \text{ h})
\]

And
\[
D_T = 4.43 \times 10^{-11} \text{ m}^2/\text{s}
\]

Solving for \( T \) from Equation (5.9a)
\[
T = -\frac{Q_d}{R(\ln D_T - \ln D_0)} = \frac{148000 \text{ J/mol}}{(8.31 \text{ J/mol-K})[\ln (4.43 \times 10^{-11}) - \ln (2.3 \times 10^{-5})]} = 1353 \text{ K} = 1080^\circ \text{C}
\]

Next topic: mechanical properties of materials