Chapter 7: Diffusion

ISSUES TO ADDRESS...

• How does diffusion occur?
• Why is it an important part of processing?
• How can the rate of diffusion be predicted for some simple cases?
• How does diffusion depend on structure and temperature?
Diffusion

Diffusion - Mass transport by atomic motion

Mechanisms
• Gases & Liquids – random (Brownian) motion
• Solids – vacancy diffusion or interstitial diffusion
Diffusion

- **Interdiffusion**: In an alloy, atoms tend to migrate from regions of high concentration to regions of low concentration.

Initially

After some time

Figs. 7.1 & 7.2, *Callister & Rethwisch 9e.*
Diffusion

- **Self-diffusion**: In an elemental solid, atoms also migrate.

Label some atoms

After some time
Diffusion Mechanisms

Vacancy Diffusion:

- atoms exchange with vacancies
- applies to substitutional impurities atoms
- rate depends on:
  -- number of vacancies
  -- activation energy to exchange.

increasing elapsed time
Diffusion Mechanisms

- **Interstitial diffusion** – smaller atoms can diffuse between atoms.

More rapid than vacancy diffusion

Fig. 7.3 (b), Callister & Rethwisch 9e.
Processing Using Diffusion

• **Case Hardening:**
  -- Diffuse carbon atoms into the host iron atoms at the surface.
  -- Example of interstitial diffusion is a case hardened gear.

• Result: The presence of C atoms makes iron (steel) harder.
Processing Using Diffusion

• **Doping** silicon with phosphorus for *n*-type semiconductors:

  • **Process:**
    1. Deposit *P* rich layers on surface.
    2. Heat it.
    3. Result: Doped semiconductor regions.

Adapted from Figure 19.27, *Callister & Rethwisch 9e.*
Diffusion

- How do we quantify the amount or rate of diffusion?

\[ J \equiv \text{Flux} \equiv \frac{\text{moles (or mass) diffusing}}{(\text{area})(\text{time})} = \frac{\text{mol}}{\text{cm}^2 \text{s}} \text{ or } \frac{\text{kg}}{\text{m}^2 \text{s}} \]

- Measured empirically
  - Make thin film (membrane) of known cross-sectional area
  - Impose concentration gradient
  - Measure how fast atoms or molecules diffuse through the membrane

\[ J = \frac{M}{At} = \frac{I}{A} \frac{dM}{dt} \]

\[ M = \text{mass diffused} \]

\[ J \propto \text{slope} \]

\[ \text{time} \]
Steady-State Diffusion

Rate of diffusion independent of time

Flux proportional to concentration gradient = \( \frac{dC}{dx} \)

Fick’s first law of diffusion

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

\( D \equiv \) diffusion coefficient

if linear

\[ \frac{dC}{dx} \approx \frac{\Delta C}{\Delta x} = \frac{C_2 - C_1}{x_2 - x_1} \]
Example: Chemical Protective Clothing (CPC)

- Methylene chloride is a common ingredient of paint removers. Besides being an irritant, it also may be absorbed through skin. When using this paint remover, protective gloves should be worn.
- If butyl rubber gloves (0.04 cm thick) are used, what is the diffusive flux of methylene chloride through the glove?

Data:
- diffusion coefficient in butyl rubber: \( D = 110 \times 10^{-8} \text{ cm}^2/\text{s} \)
- surface concentrations: \( C_1 = 0.44 \text{ g/cm}^3 \)
  \( C_2 = 0.02 \text{ g/cm}^3 \)
Example (cont).

- Solution – assuming linear conc. gradient

\[ J = -D \frac{dC}{dx} \approx -D \frac{C_2 - C_1}{x_2 - x_1} \]

Data:

- \( D = 110 \times 10^{-8} \text{ cm}^2/\text{s} \)
- \( C_1 = 0.44 \text{ g/cm}^3 \)
- \( C_2 = 0.02 \text{ g/cm}^3 \)
- \( x_2 - x_1 = 0.04 \text{ cm} \)

\[ J = -(110 \times 10^{-8} \text{ cm}^2/\text{s}) \frac{(0.02 \text{ g/cm}^3 - 0.44 \text{ g/cm}^3)}{(0.04 \text{ cm})} = 1.16 \times 10^{-5} \frac{\text{g}}{\text{cm}^2\text{s}} \]
Diffusion and Temperature

• Diffusion coefficient increases with increasing $T$

$$D = D_0 \exp\left(-\frac{Q_d}{RT}\right)$$

$D =$ diffusion coefficient [m$^2$/s]

$D_0 =$ pre-exponential [m$^2$/s]

$Q_d =$ activation energy [J/mol or eV/atom]

$R =$ gas constant [8.314 J/mol-K]

$T =$ absolute temperature [K]
Diffusion and Temperature

$D$ has exponential dependence on $T$

$$\frac{1000}{T}$$

$D$ (m$^2$/s)

$D$ interstitial $>>$ $D$ substitutional

Adapted from Fig. 7.7, Callister & Rethwisch 9e.
(Data for Fig. 7.7 taken from E.A. Brandes and G.B. Brook (Ed.) Smithells Metals Reference Book, 7th ed., Butterworth-Heinemann, Oxford, 1992.)
Example: At 300°C the diffusion coefficient and activation energy for Cu in Si are

\[ D(300°C) = 7.8 \times 10^{-11} \text{ m}^2/\text{s} \]
\[ Q_d = 41.5 \text{ kJ/mol} \]

What is the diffusion coefficient at 350°C?

\[
\ln D_2 = \ln D_0 - \frac{Q_d}{R} \left( \frac{1}{T_2} \right) \quad \text{and} \quad \ln D_1 = \ln D_0 - \frac{Q_d}{R} \left( \frac{1}{T_1} \right)
\]

\[
\therefore \quad \ln D_2 - \ln D_1 = \ln \frac{D_2}{D_1} = - \frac{Q_d}{R} \left( \frac{1}{T_2} - \frac{1}{T_1} \right)
\]
Example (cont.)

\[ D_2 = D_1 \exp \left[ - \frac{Q_d}{R} \left( \frac{1}{T_2} - \frac{1}{T_1} \right) \right] \]

\[ T_1 = 273 + 300 = 573 \text{K} \]
\[ T_2 = 273 + 350 = 623 \text{K} \]

\[ D_2 = (7.8 \times 10^{-11} \text{ m}^2/\text{s}) \exp \left[ -\frac{41,500 \text{ J/mol}}{8.314 \text{ J/mol-K}} \left( \frac{1}{623 \text{ K}} - \frac{1}{573 \text{ K}} \right) \right] \]

\[ D_2 = 15.7 \times 10^{-11} \text{ m}^2/\text{s} \]
Non-steady State Diffusion

- The concentration of diffusing species is a function of both time and position \( C = C(x,t) \)
- In this case **Fick’s Second Law** is used

\[
\frac{\partial C}{\partial t} = D \frac{\partial^2 C}{\partial x^2}
\]
Non-steady State Diffusion

- Copper diffuses into a bar of aluminum.

B.C. at \( t = 0 \), \( C = C_0 \) for \( 0 \leq x \leq \infty \)

at \( t > 0 \), \( C = C_S \) for \( x = 0 \) (constant surface conc.)

\( C = C_0 \) for \( x = \infty \)

Fig. 7.5, Callister & Rethwisch 9e.
Solution:

\[
\frac{C(x,t) - C_o}{C_s - C_o} = 1 - \text{erf}\left(\frac{x}{2\sqrt{Dt}}\right)
\]

\(C(x,t) = \text{Conc. at point } x \text{ at time } t\)

\(\text{erf}(z) = \text{error function}\)

\[
\text{erf}(z) = \frac{2}{\sqrt{\pi}} \int_0^z e^{-y^2} dy
\]

\(\text{erf}(z) \text{ values are given in Table 7.1}\)

Fig. 7.5, Callister & Rethwisch 9e.
Non-steady State Diffusion

• Sample Problem: An FCC iron-carbon alloy initially containing 0.20 wt% C is carburized at an elevated temperature and in an atmosphere that gives a surface carbon concentration constant at 1.0 wt%. If after 49.5 h the concentration of carbon is 0.35 wt% at a position 4.0 mm below the surface, determine the temperature at which the treatment was carried out.

• Solution: use Eqn. 7.5

\[
\frac{C(x,t) - C_o}{C_s - C_o} = 1 - \text{erf}\left(\frac{x}{2\sqrt{Dt}}\right)
\]
Solution (cont.): 

\[ \frac{C(x,t) - C_o}{C_s - C_o} = 1 - \operatorname{erf} \left( \frac{x}{2\sqrt{Dt}} \right) \]

- \( t = 49.5 \) h
- \( C_x = 0.35 \) wt%
- \( C_o = 0.20 \) wt%
- \( x = 4 \times 10^{-3} \) m
- \( C_s = 1.0 \) wt%

\[ \frac{C(x,t) - C_o}{C_s - C_o} = \frac{0.35 - 0.20}{1.0 - 0.20} = 1 - \operatorname{erf} \left( \frac{x}{2\sqrt{Dt}} \right) = 1 - \operatorname{erf}(z) \]

\[ \therefore \operatorname{erf}(z) = 0.8125 \]
Solution (cont.):

We must now determine from Table 7.1 the value of \( z \) for which the error function is 0.8125. An interpolation is necessary as follows:

<table>
<thead>
<tr>
<th>( z )</th>
<th>( \text{erf}(z) )</th>
<th>( \frac{z - 0.90}{0.95 - 0.90} = \frac{0.8125 - 0.7970}{0.8209 - 0.7970} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.90</td>
<td>0.7970</td>
<td></td>
</tr>
<tr>
<td>( z )</td>
<td>0.8125</td>
<td></td>
</tr>
<tr>
<td>0.95</td>
<td>0.8209</td>
<td></td>
</tr>
</tbody>
</table>

\[ z = 0.93 \]

Now solve for \( D \)

\[
D = \frac{x^2}{4z^2t}
\]

\[
D = \left(\frac{4 \times 10^{-3} \text{m}}{4(0.93)^2(49.5 \text{ h})}\right) \frac{1 \text{ h}}{3600 \text{ s}} = 2.6 \times 10^{-11} \text{ m}^2/\text{s}
\]
Solution (cont.):

• To solve for the temperature at which $D$ has the above value, we use a rearranged form of Equation (8.9a);

from Table 8.2, for diffusion of C in FCC Fe

\[ D_o = 2.3 \times 10^{-5} \text{ m}^2/\text{s} \quad Q_d = 148,000 \text{ J/mol} \]

\[ T = \frac{Q_d}{R(\ln D_o - \ln D)} \]

\[ \therefore \quad T = \frac{148,000 \text{ J/mol}}{(8.314 \text{ J/mol-K})(\ln 2.3 \times 10^{-5} \text{ m}^2/\text{s} - \ln 2.6 \times 10^{-11} \text{ m}^2/\text{s})} \]

\[ T = 1300 \text{ K} = 1027^\circ \text{ C} \]
Example: Chemical Protective Clothing (CPC)

• Methylene chloride is a common ingredient of paint removers. Besides being an irritant, it also may be absorbed through skin. When using this paint remover, protective gloves should be worn.

• If butyl rubber gloves (0.04 cm thick) are used, what is the breakthrough time ($t_b$), i.e., how long could the gloves be used before methylene chloride reaches the hand?

• Data
  – diffusion coefficient in butyl rubber: $D = 110 \times 10^{-8} \text{ cm}^2/\text{s}$
CPC Example (cont.)

• Solution – assuming linear conc. gradient

Breakthrough time = $t_b$

$D = 110 \times 10^{-8}$ cm$^2$/s

$\ell = x_2 - x_1 = 0.04$ cm

$t_b = \frac{\ell^2}{6D}$

Equation from online CPC
Case Study 5 at the Student Companion Site for Callister & Rethwisch 9e (www.wiley.com/college/callister)

Time required for breakthrough ca. 4 min
## Summary

<table>
<thead>
<tr>
<th>Diffusion FASTER for...</th>
<th>Diffusion SLOWER for...</th>
</tr>
</thead>
<tbody>
<tr>
<td>- open crystal structures</td>
<td>- close-packed structures</td>
</tr>
<tr>
<td>- materials w/secondary bonding</td>
<td>- materials w/covalent bonding</td>
</tr>
<tr>
<td>- smaller diffusing atoms</td>
<td>- larger diffusing atoms</td>
</tr>
<tr>
<td>- lower density materials</td>
<td>- higher density materials</td>
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</tbody>
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