Diffusion in Solids

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?
Review: Types of solid solutions

- What are the atomic structures of the Cu-Ni solid solution?
- What about the Fe-Fe$_3$C solid solution (austenite)? Are these the same?
Solute atoms in Alloys

Two outcomes if impurity (B) added to host (A):

- Solid solution of \( B \) in \( A \) (i.e., random dist. of point defects)
  - Substitutional solid soln. (e.g., \( Cu \) in \( Ni \))
  - Interstitial solid soln. (e.g., \( C \) in \( Fe \))

- Solid solution of \( B \) in \( A \) plus particles of a new phase (usually for a larger amount of \( B \))

Second phase particle
  --different composition
  --often different structure.
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

Adapted from Figs. 5.1 and 5.2, *Callister 7e.*
Diffusion

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

Label some atoms

Before

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.

![Diagram showing the process of vacancy diffusion](image)
Diffusion Simulation

• Simulation of interdiffusion across an interface:

• Rate of substitutional diffusion depends on:
  --vacancy concentration
  --frequency of jumping.

(Courtesy P.M. Anderson)
Diffusion Mechanisms

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

Adapted from Fig. 5.3 (b), Callister 7e.

More rapid than vacancy diffusion
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.
• Surface hardness makes it harder to initiate cracks – better fatigue resistance
**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 chapter-opening photograph, Chapter 18, *Callister 7e.*
Diffusion

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

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

• Measured empirically
  – Make thin film (membrane) of known surface area
  – Impose concentration gradient
  – Measure how fast atoms or molecules diffuse through the membrane

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

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

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

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

Rate of diffusion independent of time

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

Fick’s first law of diffusion

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

if linear
\[ \frac{dC}{dx} \approx \frac{\Delta C}{\Delta x} = \frac{C_2 - C_1}{x_2 - x_1} \]

\( D \equiv \text{diffusion coefficient} \)
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 $T$.

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

$D =$ 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]

$k_B =$ Boltzmann’s constant $= R/N_A = 8.617 \times 10^{-5}$ eV/K

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

$D$ has exponential dependence on $1/T$

Adapted from Fig. 5.7, Callister 7e. (Date for Fig. 5.7 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 $t = 0$, $C = C_o$ for $0 \leq x \leq \infty$

at $t > 0$, $C = C_S$ for $x = 0$ (const. surf. conc.)

$C = C_o$ for $x = \infty$

Adapted from Fig. 5.5, Callister 7e.
Solution:

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

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

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

\[
= \frac{2}{\sqrt{\pi}} \int_0^z e^{-y^2} \, dy
\]

\( \text{erf}(z) \) values are given in Table 5.1
Solution:

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

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

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

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

\(\text{erf}(z)\) values are given in Table 5.1
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. 5.5

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

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

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

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

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

We must now determine from Table 5.1 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>
</tr>
</thead>
<tbody>
<tr>
<td>0.90</td>
<td>0.7970</td>
</tr>
<tr>
<td>( z )</td>
<td>0.8125</td>
</tr>
<tr>
<td>0.95</td>
<td>0.8209</td>
</tr>
</tbody>
</table>

\[
\frac{z - 0.90}{0.95 - 0.90} = \frac{0.8125 - 0.7970}{0.8209 - 0.7970}
\]

\[
z = 0.93
\]

Now solve for \( D \):

\[
z = \frac{x}{2\sqrt{Dt}} \quad \Rightarrow \quad D = \frac{x^2}{4z^2t}
\]

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

- To solve for the temperature at which $D$ has above value, we use a rearranged form of Equation (5.9a);

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

  from Table 5.2, for diffusion of C in FCC Fe

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

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

  \[ T = 1300 \text{ K} = 1027^\circ \text{C} \]
Summary

Diffusion **FASTER** for...

• open crystal structures
• materials w/secondary bonding
• smaller diffusing atoms
• lower density materials

Diffusion **SLOWER** for...

• close-packed structures
• materials w/covalent bonding
• larger diffusing atoms
• higher density materials