Chapter 6: 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?
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.
• **Self-diffusion**: In an elemental solid, atoms also migrate.

Label some atoms

After some time
**Vacancy Diffusion:**

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

![Diagram showing diffusion of atoms through vacancies over increasing elapsed time](image-url)
Diffusion Mechanisms

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

More rapid than vacancy diffusion

From Fig. 6.3 (b)
*Callister’s Materials Science and Engineering, Adapted Version.*
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.

From chapter-opening photograph, Chapter 17
*Callister’s Materials Science and Engineering, Adapted Version.*
Diffusion

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

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

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

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

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

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

Chapter 6 - 9
Steady-State Diffusion

Rate of diffusion independent of time

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

Fick’s first law of diffusion

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

\( D \equiv \text{diffusion coefficient} \)

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:

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

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

• Diffusion coefficient increases with increasing $T$.

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

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

• The activation energy may be thought of as the energy required to produce the diffusive motion of one mole of atom
Diffusion and Temperature

$D$ has exponential dependence on $T$

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

$10^{-8}$

$10^{-14}$

$10^{-20}$

$T(°C)$

1500

1000

600

300

$1000K/T$

0.5

1.0

1.5

$D_{\text{interstitial}}$ $>> D_{\text{substitutional}}$

C in $\gamma$-Fe

Fe in $\alpha$-Fe

Al in Al

C in $\alpha$-Fe

C in $\gamma$-Fe

Fe in $\alpha$-Fe

Fe in $\gamma$-Fe

From Fig. 6.7

*Callister's Materials Science and Engineering, Adapted Version.*

(Date for Fig. 6.7 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?

\[
\ln D_2 = \ln D_0 - \frac{Q_d}{R} \left( \frac{1}{T_2} \right)
\]

and

\[
\ln D_1 = \ln D_0 - \frac{Q_d}{R} \left( \frac{1}{T_1} \right)
\]

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

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

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

\[ D_2 = 15.7 \times 10^{-11} \text{ m}^2/\text{s} \]
**Question:** Rank the magnitudes of the diffusion coefficients from greatest to least for the following systems:

- N in Fe at 700°C
- Cr in Fe at 700°C

**Answer:** Nitrogen is an interstitial impurity in Fe (on the basis of its atomic radius), whereas Cr is a substitutional impurity. Since interstitial diffusion occurs more rapidly than substitutional impurity diffusion, $D_N > D_{Cr}$. 
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

Fick’s Second Law

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

• Copper diffuses into a bar of aluminum.

Surface conc., $C_S$ of Cu atoms
pre-existing conc., $C_o$ of copper atoms

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:

\[
\frac{C(x,t) - C_0}{C_s - C_0} = 1 - \text{erf}\left(\frac{x}{2\sqrt{Dt}}\right)
\]

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

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

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

\[
C_s \quad t_3 > t_2 > t_1
\]

\[
C(x,t)
\]

\[
C_0
\]

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

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

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

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

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

We must now determine from the Table below 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>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 $D$

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

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

• To solve for the temperature at which $D$ has above value, we use a rearranged form of this equation:

$$ T = \frac{Q_d}{R(\ln D_0 - \ln D)} $$

It is given that for diffusion of C in FCC Fe

$$ D_0 = 2.3 \times 10^{-5} \text{ m}^2/\text{s} \quad Q_d = 148,000 \text{ J/mol} $$

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

$$ T = 1300 \text{ K} = 1027^\circ \text{C} $$
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