Chapter 5: Diffusion (1)

Diffusion - Mass transport by random, atomic (or molecular-scale) motion

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**

- **Interdiffusion**: when joining different metals (or in other materials system), atoms (or other species) tend to migrate from regions of high conc. to regions of low conc.

Initially

![Initial Concentration Profiles]

After some time

![Concentration Profiles]

Adapted from Figs. 5.1 and 5.2, *Callister & Rethwisch 8e.*
**Self-diffusion**: Even in a pure elemental solid, atoms also migrate randomly via self-diffusion process.

Label some atoms

Before:

- A
- B
- C
- D

After some time:

- A
- B
- C
- D
Examples of (Inhibiting) Diffusion

• Different packaging for food to preserve freshness, e.g.,
  – $\text{CO}_2$ diffuses out from bottles
  – $\text{O}_2$ diffuses into the bottles

• Paints applied to metal surface to prevent corrosion
  – $\text{O}_2$, $\text{H}_2\text{O}$, and salt diffuse through the paint layer (even undamaged) to corrode metals underneath

Diffusion Mechanisms (1)

**Interstitial diffusion**

**Smaller** atoms/molecules can diffuse through the interstitial sites between larger atoms/molecules.

![Diagram of interstitial diffusion](image)

Adapted from Fig. 5.3(b), *Callister & Rethwisch 8e.*
Diffusion Mechanisms (2)

Substitutional Diffusion via vacancy exchange
For pure elements or alloys with similar sized atoms (e.g., Ni-Cu)
• atoms exchange with vacancies
• applies to substitutional impurities atoms and also self diffusion
• rate depends on:
  -- vacancies concentration
  -- activation energy to exchange.

Increasing elapsed time

Substitutional diffusion via exchange with vacancy usually much slower than interstitial diffusion
Simulation of Vacancy Diffusion

- Simulation of interdiffusion across an interface:

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

This slide contains an animation that requires Quicktime and a Cinepak decompressor. Click on the message or image below to activate the animation.

(Courtesy P.M. Anderson)
Example of **Case Hardening**: The surface of a metal gear needs to be hard (for wear resistance) while the inside needs to be tough (not brittle)

**Approach:**
- Diffuse carbon (atoms) into the surface of the steel (iron) gear via heat treatment in a carbon-rich atmosphere
- Carbon atoms are much smaller than Fe atoms – interstitial diffusion mechanism

**Result:** The presence of C atoms in the surface makes the surface of steel (iron) harder and wear resistant while inside remains low in carbon content and tough (not brittle)
Doping silicon with phosphorus for *n*-type semiconductors:

**Process:**

1. Deposit \( P \) rich layers on surface.

2. Heat it.

Diffusional Flux

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

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

\[ J = \frac{1}{A} \frac{dM}{dt} \]
Fick’s 1\textsuperscript{st} Law about Diffusion

Fick’s first law of diffusion for 1D: Flux

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

\( D \equiv \text{diffusion coefficient} \), in unit of \( \text{cm}^2/\text{sec} \) or similar
\( C \equiv \text{concentration} \), in unit of \( \text{mole/cm}^3 \) or similar
\( x \equiv \text{distance} \), in unit of \( \text{cm} \) or similar
\( \frac{dC}{dx} \) \text{concentration gradient} along \( x \) direction

If linear

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

\( C_1 \) \( C_2 \)
Other 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 if assuming linear concentration distribution?

Given:

- diffusion coefficient in butyl rubber: $D = 110 \times 10^{-8}$ cm$^2$/s

- surface concentrations: 
  - $C_1$ (outside glove) = 0.44 g/cm$^3$
  - $C_2$ (inside glove) = 0.02 g/cm$^3$
Example: Chemical Protective Clothing (CPC) (cont).

- **Solution** – linear conc. gradient

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

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

\[ J = -\left(110 \times 10^{-8} \text{ cm}^2/\text{s}\right) \frac{(0.02 \text{ g/cm}^3 - 0.44 \text{ g/cm}^3)}{(0.04 \text{ cm})} = 1.16 \times 10^{-5} \frac{\text{g}}{\text{cm}^2\text{s}} \]
Diffusion Coefficient and Temperature (1)

• Diffusion coefficient increases “exponentially” with increasing temperature \( T \).

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

- \( D \) = diffusion coefficient \([m^2/s]\)
- \( D_o \) = pre-exponential \([m^2/s]\)
- \( Q_d \) = activation energy \([J/mol]\)
- \( R \) = gas constant \([8.314 \, J/mol\cdot K]\)
- \( T \) = absolute temperature \([K]\)
Diffusion Coefficient and Temperature (2)

$D$ has “exponential” dependence on $T$: higher $T \rightarrow$ much higher $D$

Adapted from Fig. 5.7, *Callister & Rethwisch 8e*. (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 $300^\circ$C the diffusion coefficient and activation energy for Cu in Si are

$$D_1(300^\circ$C) = 7.8 \times 10^{-11} \text{ m}^2/\text{s}$$
$$Q_d = 41.5 \times 10^3 \text{ J/mol}$$

What is the diffusion coefficient at $350^\circ$C?

Solution

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

Knowing

$$D_1 = D_0 \exp\left(-\frac{Q_d}{RT_1}\right)$$

Wanting to know

$$D_2 = D_0 \exp\left(-\frac{Q_d}{RT_2}\right)$$
Example (cont.)

\[
\frac{D_2}{D_1} = \frac{\exp\left(- \frac{Q_d}{RT_2}\right)}{\exp\left(- \frac{Q_d}{RT_1}\right)}
\]

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

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

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

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

\[
D_2 = 15.7 \times 10^{-11} \text{ m}^2/\text{s}
\]
Summary

Diffusion is mass transport by random walking of atoms/molecules.

Mechanism of diffusion include interstitial diffusion mechanism and vacancy diffusion mechanism.

For 1D, Fick’s 1st Law gives $J = -D \frac{dC}{dx}$ that relates diffusion flux $J$ and concentration gradient $dC/dx$ via a material/system property of diffusion coefficient $D$.

Diffusion coefficient $D$ increases “exponentially” with temperature $T$ following:

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