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 conc. to regions of low conc.

Initially $\text{Cu} \quad \text{Ni}$

- After some time

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

![](image1)

**Diffusion**

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

Label some atoms

- After some time

Diffusion is just a stepwise migration of atoms from lattice site to lattice site.

- There must be an empty adjacent site.
- The atom must have sufficient energy to break bonds with its neighbor atoms and them cause some lattice distortion during the displacement.
Diffusion Mechanisms

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

![Diffusion Mechanism Diagram](image)

increasing elapsed time

**Diffusion Simulation**
- Simulation of interdiffusion across an interface:
- Rate of substitutional diffusion depends on:
  -- vacancy concentration
  -- frequency of jumping.

http://www.phys.au.dk/camp/m-t/
http://www.physics.leidenuniv.nl/sections/cm/ip/projects/dynamics/incopper/incopper.htm

(Courtesy P.M. Anderson)
Diffusion Mechanisms

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

  More rapid than vacancy diffusion

  ![](image)

  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.

  ![](image)

  Adapted from chapter-opening photograph, Chapter 5, Callister 7e. (Courtesy of Surface Division, Midland-Ross.)

- 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.

Diffusion

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

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

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

  \[
  J = \frac{M}{A} = \frac{1}{A} \frac{dM}{dt}
  \]

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

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

Adapted from chapter-opening photograph, Chapter 18, Callister 7e.
Steady-State Diffusion

Rate of diffusion independent of time

Flux proportional to concentration gradient:

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

Fick’s first law of diffusion

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

if linear

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

Driving Force---concentration gradient

Steady-state diffusion

• **Steady State**: the concentration profile doesn’t change with time.

• **Steady State**: \( J_x(\text{left}) = J_x(\text{right}) \)

• Apply Fick’s First Law:

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

• If \( J_x(\text{left}) = J_x(\text{right}) \), then

\[
\left( \frac{dC}{dx} \right)_{\text{left}} = \left( \frac{dC}{dx} \right)_{\text{right}}
\]

• Result: the slope, \( dC/dx \), must be constant (i.e., slope doesn’t vary with position)!
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

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

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

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

• **Diffusing Species & Temperature**
  
  example: carbon _α_ iron
  
  self-diffusion: \( D = 3 \times 10^{-21} \text{ m}^2/\text{s} \)
  
  interdiffusion: \( D = 2.4 \times 10^{-12} \text{ m}^2/\text{s} \)

<table>
<thead>
<tr>
<th>Diffusing Species</th>
<th>Host Metal</th>
<th>( D_0 [\text{m}^2/\text{s}] )</th>
<th>Activation Energy ( Q_d [\text{kJ/mol or eV/atom}] )</th>
<th>Calculated Values</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fe α-Fe (BCC)</td>
<td>2.8 \times 10^{-4}</td>
<td>251</td>
<td>2.00</td>
<td>500</td>
</tr>
<tr>
<td>Fe γ-Fe (FCC)</td>
<td>5.0 \times 10^{-5}</td>
<td>284</td>
<td>2.04</td>
<td>900</td>
</tr>
<tr>
<td>C α-Fe</td>
<td>8.2 \times 10^{-7}</td>
<td>80</td>
<td>0.83</td>
<td>1100</td>
</tr>
<tr>
<td>C γ-Fe</td>
<td>2.3 \times 10^{-9}</td>
<td>148</td>
<td>1.53</td>
<td>900</td>
</tr>
<tr>
<td>Cu Cu</td>
<td>7.8 \times 10^{-7}</td>
<td>211</td>
<td>2.19</td>
<td>500</td>
</tr>
<tr>
<td>Zn Cu</td>
<td>2.4 \times 10^{-5}</td>
<td>189</td>
<td>1.06</td>
<td>500</td>
</tr>
<tr>
<td>Al Al</td>
<td>2.5 \times 10^{-5}</td>
<td>144</td>
<td>1.49</td>
<td>500</td>
</tr>
<tr>
<td>Cu Al</td>
<td>6.5 \times 10^{-4}</td>
<td>121</td>
<td>1.43</td>
<td>500</td>
</tr>
<tr>
<td>Mg Al</td>
<td>1.2 \times 10^{-4}</td>
<td>131</td>
<td>1.35</td>
<td>500</td>
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<tr>
<td>Cu Ni</td>
<td>2.7 \times 10^{-5}</td>
<td>256</td>
<td>2.65</td>
<td>500</td>
</tr>
</tbody>
</table>


Diffusion and Temperature

• Diffusion coefficient increases with increasing \( T \).

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

- \( D \) = diffusion coefficient [m²/s]
- \( D_o \) = pre-exponential [m²/s]
- \( Q_d \) = activation energy [kJ/mol or eV/atom]
- \( R \) = gas constant [8.314 J/mol-K]
- \( T \) = absolute temperature [K]
Diffusion and Temperature

$D$ has exponential dependence on $T$

![Graph showing diffusion coefficient ($D$) vs. temperature ($T$) with data for different elements such as C in α-Fe, Al in Al, etc.]

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

$D(300°C) = 7.8 \times 10^{-11}$ m²/s
$Q_d = 41.5$ 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

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

∴ $\ln D_2 - \ln D_1 = \ln \frac{D_2}{D_1} = -\frac{Q_d}{R} \left( \frac{1}{T_2} - \frac{1}{T_1} \right)$
Example (cont.)

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

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

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

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

Concept Check

- 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
  - N in Fe at 900°C
  - Cr in Fe at 900°C
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:

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

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

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

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

erf(z) values are given in Table 5.1

---

**Table 5.1 Tabulation of Error Function Values**

<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>0.025</td>
<td>0.0282</td>
<td>0.1</td>
<td>0.0916</td>
</tr>
<tr>
<td>0.025</td>
<td>0.0282</td>
<td>0.05</td>
<td>0.0564</td>
<td>0.15</td>
<td>0.1573</td>
</tr>
<tr>
<td>0.05</td>
<td>0.0564</td>
<td>0.1</td>
<td>0.1125</td>
<td>0.2</td>
<td>0.2227</td>
</tr>
<tr>
<td>0.1</td>
<td>0.1125</td>
<td>0.15</td>
<td>0.1680</td>
<td>0.25</td>
<td>0.2763</td>
</tr>
<tr>
<td>0.15</td>
<td>0.1680</td>
<td>0.2</td>
<td>0.2227</td>
<td>0.3</td>
<td>0.3286</td>
</tr>
<tr>
<td>0.2</td>
<td>0.2227</td>
<td>0.25</td>
<td>0.2763</td>
<td>0.35</td>
<td>0.3794</td>
</tr>
<tr>
<td>0.25</td>
<td>0.2763</td>
<td>0.3</td>
<td>0.3286</td>
<td>0.4</td>
<td>0.4284</td>
</tr>
<tr>
<td>0.3</td>
<td>0.3286</td>
<td>0.35</td>
<td>0.3794</td>
<td>0.45</td>
<td>0.4755</td>
</tr>
<tr>
<td>0.35</td>
<td>0.3794</td>
<td>0.4</td>
<td>0.4284</td>
<td>0.5</td>
<td>0.5205</td>
</tr>
<tr>
<td>0.4</td>
<td>0.4284</td>
<td>0.45</td>
<td>0.4755</td>
<td>0.55</td>
<td>0.5633</td>
</tr>
<tr>
<td>0.5</td>
<td>0.5205</td>
<td>0.55</td>
<td>0.5633</td>
<td>1.0</td>
<td>0.6321</td>
</tr>
<tr>
<td>0.55</td>
<td>0.5633</td>
<td>1.0</td>
<td>0.6321</td>
<td>1.3</td>
<td>0.7734</td>
</tr>
<tr>
<td>1.0</td>
<td>0.6321</td>
<td>1.3</td>
<td>0.7734</td>
<td>1.5</td>
<td>0.8686</td>
</tr>
<tr>
<td>1.3</td>
<td>0.7734</td>
<td>1.5</td>
<td>0.8686</td>
<td>1.7</td>
<td>0.9332</td>
</tr>
<tr>
<td>1.5</td>
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<td>1.7</td>
<td>0.9332</td>
<td>1.9</td>
<td>0.9664</td>
</tr>
<tr>
<td>1.7</td>
<td>0.9332</td>
<td>1.9</td>
<td>0.9664</td>
<td>2.0</td>
<td>0.9772</td>
</tr>
<tr>
<td>1.9</td>
<td>0.9664</td>
<td>2.0</td>
<td>0.9772</td>
<td>2.2</td>
<td>0.9916</td>
</tr>
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<td>0.9772</td>
<td>2.2</td>
<td>0.9916</td>
<td>2.4</td>
<td>0.9993</td>
</tr>
<tr>
<td>2.2</td>
<td>0.9916</td>
<td>2.4</td>
<td>0.9993</td>
<td>2.6</td>
<td>0.9998</td>
</tr>
<tr>
<td>2.4</td>
<td>0.9993</td>
<td>2.6</td>
<td>0.9998</td>
<td>2.8</td>
<td>0.9999</td>
</tr>
</tbody>
</table>

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

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

\[ \frac{C(x,t) - C_o}{C_s - C_o} = \frac{0.35 - 0.20}{1.0 - 0.20} = 1 - \text{erf} \left( \frac{4 \times 10^{-3}}{2\sqrt{Dt}} \right) \]

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

Now solve for $D$

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

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

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

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

from Table 5.2, for diffusion of C in FCC Fe

$D_o = 2.3 \times 10^{-5} \text{ m}^2/\text{s}$ \hspace{1cm} $Q_d = 148,000 \text{ J/mol}$

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

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

\[ T = 1300 \text{ K} = 1027 \text{ °C} \]
Example Problem 5.2 and 5.3

• Consider one Fe-C alloy that has a uniform carbon concentration of 0.25 wt% and is to be treated at 950°C. If the concentration of C at the surface is suddenly brought to and maintained at 1.2wt%, how long will it take to achieve a carbon content of 0.8wt% at a position 0.5mm below the surface? The diffusion coefficient for C in Fe at this temperature is $1.6 \times 10^{-11}$ m$^2$/s; assume that the steel piece is semi-infinite.

• The diffusion coefficient for copper in aluminum at 500 and 600°C are $4.8 \times 10^{-14}$ and $5.3 \times 10^{-13}$ m$^2$/s, respectively. Determine the approximate time at 500°C that will produce the same diffusion result (in terms of concentration of Cu at some specific point in Al) as a 10-h heat treatment at 600°C.

Solution

• 5.2:
$Erf(z)=0.4210$, $z=0.392$, $t=7.1$

• 5.3:
$Dt=constant$
$t_{500}=110.4h$
## 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>
</tr>
</tbody>
</table>