Diffusion

Atoms movements in materials

Movement of atoms in **solids**, liquids and gases is very important.

Examples: Hardening steel, chrome-plating, gas reactions, Si wafers .. etc.

We will study:
- Atomic mechanisms of diffusion
- Mathematics of diffusion
- Factors affecting diffusion
- Examples

• Steady state diffusion
• Nonsteady state diffusion
• Summary

Self-diffusion or interdiffusion between two materials:
- Self-diffusion occurs in pure elements
- Interdiffusion occurs through materials or diffusion couple

Diffusion is the mass transport through atomic motion at high temperature.

Example:
- Two chambers, each containing a different gas, separated by a removable barrier; when the barrier is pulled away, interdiffusion occurs

Recall Arhenius equation

\[ N_v = N_o \exp \left( - \frac{Q}{kT} \right) \]

where
- \( N_v \) = equilibrium # of vacancies
- \( N_o \) = total number of lattice sites
- \( k \) = Boltzman’s constant
- \( Q \) = activation energy for vacancy formation

As \( T \) \( \uparrow \), number of vacancies \( \uparrow \), and energy \( \uparrow \), so diffusion is faster

Example: lead (Pb)

- Slope = \( -\frac{Q}{k} \)

The process of substitutional diffusion requires the presence of vacancies (Vacancies give the atoms a place to move).

Heat causes atoms to vibrate:
- Vibration amplitude increases with temperature
- Melting occurs when vibrations are sufficient to rupture bonds.
**Diffusion Mechanisms**

- Atoms are constantly in motion and vibrating.
  - Change of atomic position requires:
    - vacant site
    - energy to break atomic bonds
- Two types of diffusion mechanism:
  - vacancy diffusion
  - interstitial diffusion
- Movement of vacancies in one direction is equivalent to atomic movement in the opposite direction.

**Diffusion**

- Diffusion is a process. Rate of diffusion is important.
  - diffusion flux \( J \) is defined as the mass, \( M \), diffusing through unit area, \( A \), per unit time, \( t \):
    \[ J = \frac{M}{At} \quad \text{or} \quad J = \frac{1}{A} \frac{dM}{dt} \]
  - If flux does not change with time: ………………

**INTERSTITIAL DIFFUSION**

- Interstitial atom moves from one interstitial site to another (empty).
- Energy needed, again to squeeze past atoms.
- Example: ………….  
- Usually much faster because many more empty interstitial sites and no vacancies are required.

**Steady-State Diffusion**

- Concentration gradient:
  \[ \frac{dC}{dx} \]
- Fick’s 1st law:
  \[ J = -D \frac{dC}{dx} \]
  Where \( D \) is the diffusion coefficient (diffusivity) or speed of diffusion (\( m^2/s \)).
- Because atoms diffuse down concentration gradient.
- Example of steady-state diffusion is gas diffusing through a metal plate (gas pressure constant).
Example

The purification of H₂ (gas) by diffusion through a Pd sheet was discussed in Callister 5.3. Compute the number of kilograms of hydrogen that pass per hour through a 5 mm thick sheet of Pd having an area of 0.20 m² at 500°C. Assume a diffusion coefficient of 1.0x10⁻⁸ m²/s, that the concentrations at the high and low pressure sides of the plate are 2.4 and 0.6 kg of H₂ per m³ of Pd, and that steady state conditions have been attained.

Recall, flux is mass per unit time per unit area. Thus, multiplying J by area and time will give total mass.

Case Hardening

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

• Result: The "Case" is
  - hard to deform: C atoms "lock" planes from shearing.
  - hard to crack: C atoms put the surface in compression.

Steady State Diffusion: Summary

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

  Steady State:

  \[ J_x(\text{left}) = J_x(\text{right}) \]

  Concentration, C, in the box doesn’t change w/time.

• Apply Fick’s First Law:

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

• If \( J_x_{\text{left}} = J_x_{\text{right}} \), then \( \frac{dC}{dx}_{\text{left}} = \frac{dC}{dx}_{\text{right}} \)

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

Non-steady State Diffusion

• In most real situations diffusion is not ..............
  • Flux and concentration gradient vary with time

  • The changes of the concentration profile is given in this case by a differential equation, ........ second law:

  \[ \frac{\partial C}{\partial t} = \frac{\partial}{\partial x} \left( D \frac{\partial C}{\partial x} \right) \]

  • If diffusion coefficient is independent of composition then:

  \[ \frac{\partial C}{\partial t} = D \frac{\partial^2 C}{\partial x^2} \]

  Solution of this equation is concentration profile as function of time, ........
Fick’s Second Law

\[ \frac{\partial C}{\partial t} = D \frac{\partial^2 C}{\partial x^2} \]

- Solution requires boundary conditions.
  - A useful solution is for a semi-infinite solid when the surface concentration remains constant.
  - What is semi-infinite solid?
    - semi infinite bar: If none of the diffusing atoms reaches the bar end during the time over which the diffusion takes place.
    - \( l > 10 \sqrt{Dt} \), where \( l \): bar length, \( D \): diffusion coefficient and \( t \): time

Fick’s Second Law - Application

- Simple boundary condition is where the surface concentration is held constant,
  - e.g. gas phase with constant partial pressure at the surface
- Conditions are:
  - before diffusion, solute atom have a homogeneous concentration of \( C_0 \)
  - \( x \) is zero at the surface and increases with distance into the solid
  - time is zero just before diffusion begins
- Mathematically, for \( t = 0, C = C_0 \) at \( 0 \leq x \leq \infty \)
  \[ t > 0, C = C_s \text{ at } x = 0 \text{ and } C = C_0 \text{ at } x = \infty \]
  \( C_s \): constant surface concentration
- applying these boundary conditions gives:
  \[ \frac{C_x - C_0}{C_s - C_0} = 1 - \text{erf}\left( \frac{x}{2\sqrt{Dt}} \right) \]

Application of Fick’s Second Law

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

\( C_s \): Surface concentration which remains constant
\( C_0 \): Initial concentration in solid
\( C_x \): Concentration at distance \( x \) into sample after time \( t \).
\( D \): Diffusivity of solute in solvent, m\(^2\)s\(^{-1}\)
\( t \): Time, seconds
\( \text{erf} \): Gaussian error function, based on integration of the “bell shaped” curve

\[ \text{erf} (z) = \frac{1}{\sqrt{\pi}} \int_0^z \exp(-y^2) \, dy \]

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>
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<tr>
<td>0</td>
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<td>0.9340</td>
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<td>0.6039</td>
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<td>0.9523</td>
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<td>0.6420</td>
<td>1.5</td>
<td>0.9661</td>
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<td>1.6</td>
<td>0.9763</td>
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<td>0.9891</td>
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<tr>
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<td>0.85</td>
<td>0.7707</td>
<td>1.9</td>
<td>0.9928</td>
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<td>0.90</td>
<td>0.7970</td>
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<td>0.9953</td>
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<td>0.5205</td>
<td>1.2</td>
<td>0.9103</td>
<td>2.8</td>
<td>0.9999</td>
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</tbody>
</table>
**Factors Affecting Solid-State Diffusion**

- Diffusing species and host material are important
  - smaller atoms can “squeeze” in between host atoms more easily
  - in lower packing density host material ⇒ easier for atoms to migrate with fewer bonds to expand
    - eg faster in more open lattice (BCC faster than FCC) ([example 5.3](#))
  - in lower melting point host material ⇒ weaker bonds (easier to push apart)

- **Temperature** has a strong effect on diffusion rates:
  \[
  D = D_0 \exp \left( - \frac{Q_d}{RT} \right) 
  \]
  Where:
  - \( D_0 \) = temperature dependant pre-exponential constant
  - \( Q_d \) = activation energy for diffusion
  - \( R \) = gas constant (8.31 J/mol K)
  - \( T \) = absolute temperature

**Activation energy is the barrier to diffusion and controls the diffusion coefficient, D**

**Typical Diffusion Data**

<table>
<thead>
<tr>
<th>Host crystal</th>
<th>Atom</th>
<th>( D_0 ) (cm²/s)</th>
<th>( Q_d ) (eV/atom)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cu</td>
<td>Cu</td>
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</tr>
<tr>
<td>Cu</td>
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<td>1.98</td>
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<tr>
<td>Ag</td>
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<td>Au</td>
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<tr>
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<td>Cu</td>
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<tr>
<td>Ag</td>
<td>Pb</td>
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<td>U</td>
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<tr>
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</tr>
<tr>
<td>Si</td>
<td>Ga</td>
<td>3.6</td>
<td>3.51</td>
</tr>
<tr>
<td>Si</td>
<td>In</td>
<td>16.0</td>
<td>3.90</td>
</tr>
</tbody>
</table>

Typical values for preexponential (\( D_0 \)) and activation energy

*(after Kittel, “Solid State Physics” 5th ed.)*
An FCC Fe-C alloy initially containing 0.35 wt. % C is exposed to an oxygen-rich (and carbon-free) atmosphere at 1400 K (1127°C). Under these conditions, the carbon in the alloy diffuses toward the surface and reacts with the oxygen in the atmosphere; that is, the carbon concentration at the surface is maintained essentially at 0 wt. % C. (This process of carbon depletion is termed decarburization). At what position will the carbon concentration be 0.15 wt. % after a 10-hour treatment. The value of $D$ at 1400 K is $6.9 \times 10^{-11}$ m$^2$/s.

**Example**

### SUMMARY

<table>
<thead>
<tr>
<th>Diffusion FASTER for...</th>
<th>Diffusion SLOWER for...</th>
</tr>
</thead>
<tbody>
<tr>
<td>• ……… crystal structures</td>
<td>• …………………. structures</td>
</tr>
<tr>
<td>• ……… melting T materials</td>
<td>• ………. melting T materials</td>
</tr>
<tr>
<td>• materials with …………. bonding</td>
<td>• materials with ………….. bonding</td>
</tr>
<tr>
<td>• ……….. diffusing atoms</td>
<td>• …………. diffusing atoms</td>
</tr>
<tr>
<td>• ………… density materials</td>
<td>• ………….. density materials</td>
</tr>
</tbody>
</table>

Next topic:
Mechanical properties of materials