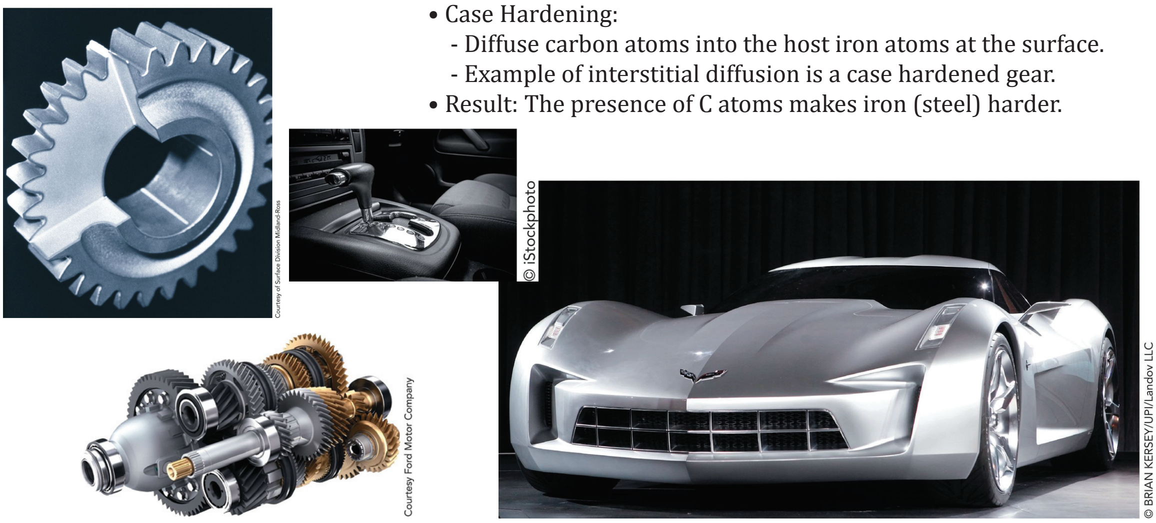
Chapter 7: Diffusion

- **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?



- 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.

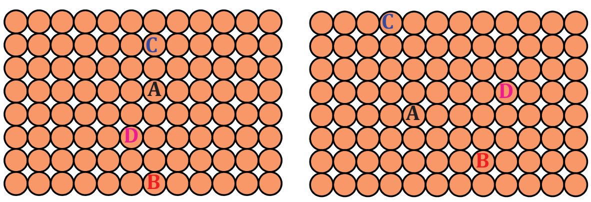
7.1 Introduction to Diffusion

- **Diffusion: Material transport by atomic motion**

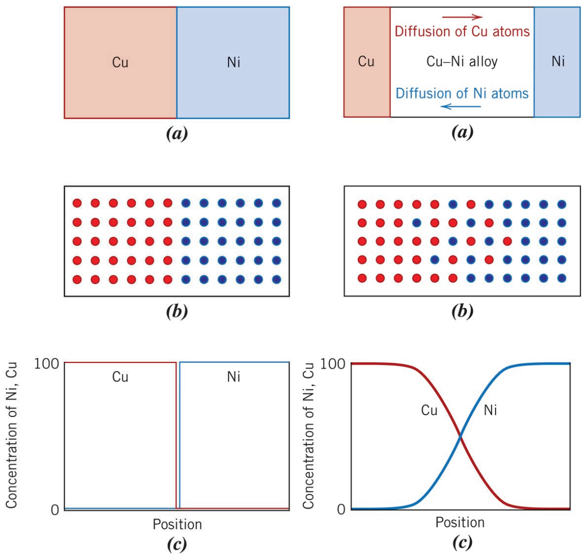
- **Mechanisms**
  - Gases & Liquids – random (Brownian) motion
  - Solids – vacancy diffusion or interstitial diffusion

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

Label some atoms After some time



- **Interdiffusion: In an alloy, atoms tend to migrate from regions of high concentration to regions of low concentration.**

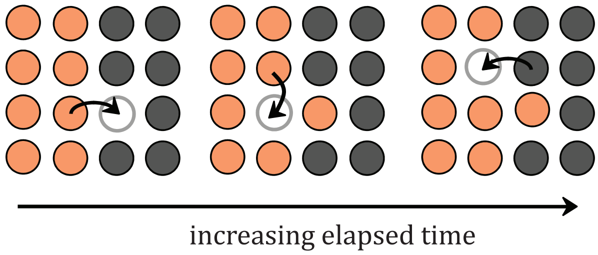


Figs. 7.1 & 7.2, Callister & Rethwisch 9e.

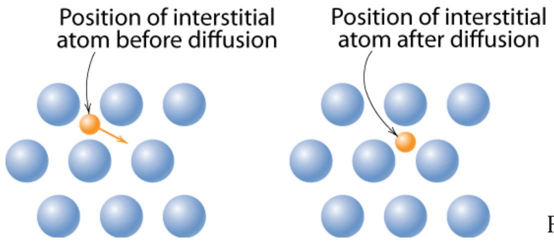
7.2 Diffusion Mechanisms

- **Diffusion: Stepwise migration of atoms from lattice site to lattice site. For this,**
  (1) there must be an empty adjacent site, and
  (2) the atom must have sufficient energy to break bonds with its neighbor atoms.

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



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



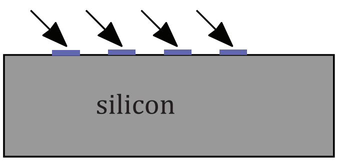
- Ex: hydrogen, carbon, nitrogen, oxygen, etc.
- More rapid than vacancy diffusion

Fig. 7.3 (b), Callister & Rethwisch 9e.

Processing Using Diffusion

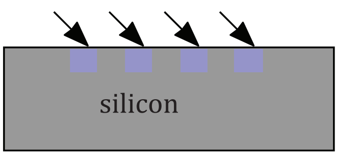
- **Doping silicon with phosphorus for n-type semiconductors:**
- **Process:**

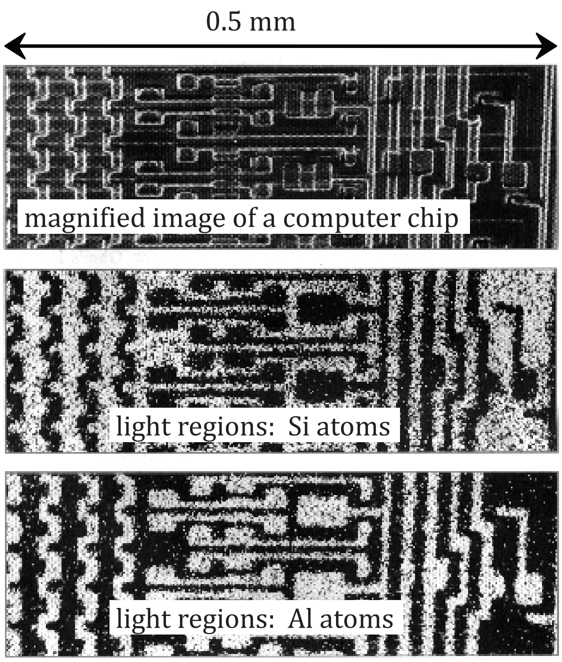
1. Deposit P rich layers on surface.



2. Heat it.

3. Result: Doped semiconductor regions.





Adapted from Figure 19.27, Callister & Rethwisch 9e.

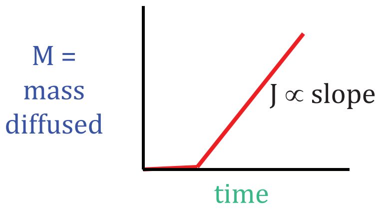
7.3 Steady-State Diffusion

- **How do we quantify the amount or rate of diffusion?**

$$J \equiv \text{Diffusion flux} \equiv \frac{\text{moles (or mass) diffusing}}{\text{(area)(time)}} = \frac{\text{mol}}{\text{cm}^2\text{s}} \text{ or } \frac{\text{kg}}{\text{m}^2\text{s}}$$

- **Measured empirically**
  - Make thin film (membrane) of known cross-sectional area
  - Impose concentration gradient
  - Measure how fast atoms or molecules diffuse through the membrane

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



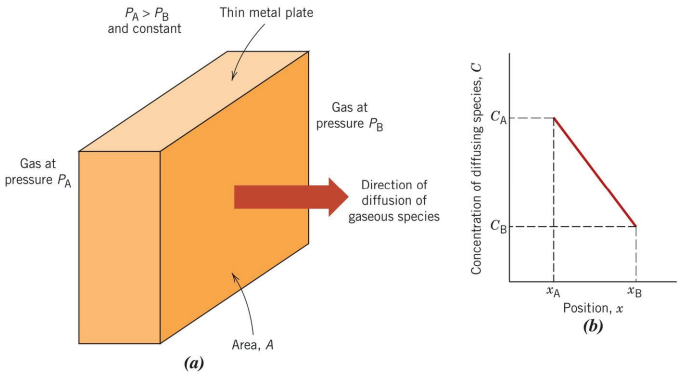
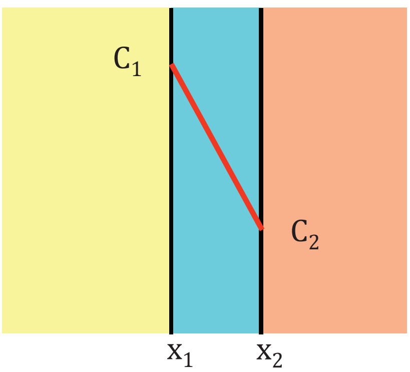


Fig. 7.4, Callister & Rethwisch 9e.

7.3 Steady-State Diffusion

- **Rate of diffusion is independent of time**
- **Flux is proportional to concentration gradient =** $\frac{dC}{dx}$



Fick's first law of diffusion

$$J = -D\frac{dC}{dx}$$

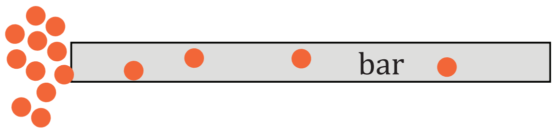
$D \equiv$ diffusion coefficient [m^2/s]

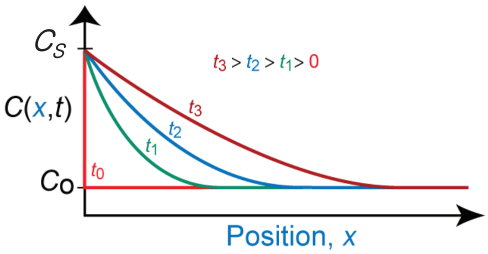
if linear $\frac{dC}{dx} \cong \frac{\Delta C}{\Delta x} = \frac{C_2 - C_1}{x_2 - x_1}$

- **Concentration gradient is the driving force of diffusion**

7.4 Nonsteady-State Diffusion

- **The concentration of diffusing species is a function of both time and position, that is, $C = C(x,t)$.**
- **Fick's Second Law:** $$\frac{\partial C}{\partial t} = \frac{\partial}{\partial x}\left(D\frac{\partial C}{\partial x}\right)$$ or $$\frac{\partial C}{\partial t} = D\frac{\partial^2 C}{\partial x^2}$$ for constant D
- **Example: Copper diffuses into a bar of aluminum.**
  - C_o = pre-existing concentration of Cu atoms
  - C_S = Surface concentration, of Cu atoms





Boundary Conditions

at t = 0, $C = C_o$ for $0 \le x \le \infty$

at t > 0, $C = C_S$ (constant) for $x = 0$

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

Fig. 7.5, Callister & Rethwisch 9e.

7.4 Nonsteady-State Diffusion

$$\therefore \frac{C(x,t) - C_0}{C_S - C_0} = 1 - \text{erf}\left(\frac{x}{2\sqrt{Dt}}\right)$$

- C(x,t) = Conc. at point x at time t
- erf(z) = Gaussian error function
- $\text{erf}(z) = \frac{2}{\sqrt{\pi}}\int_0^z e^{-y^2}\,dy$
- erf(z) values are given in Table 7.1

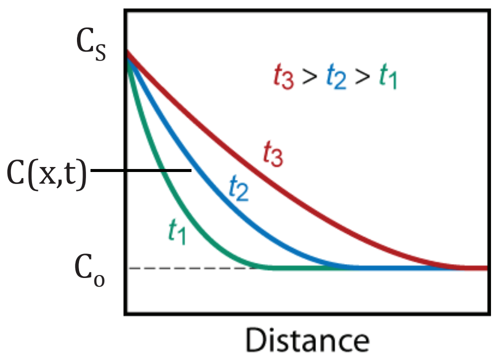


Fig. 7.5, Callister & Rethwisch 9e.

- **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.
  - Hint: Use Eq. 7.5

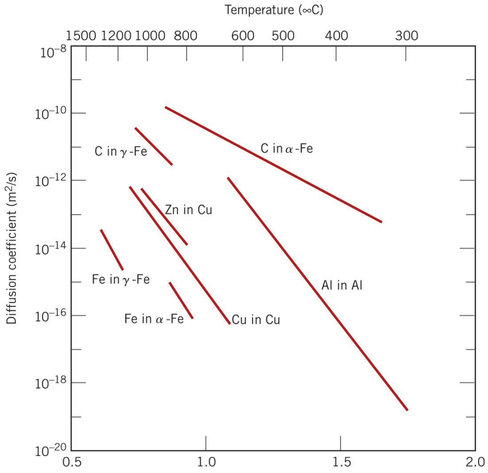
7.5 Factors That Influence Diffusion

- **Temperature has a profound influence on the coefficients and diffusion rates.**

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

  - Diffusion coefficient increases with increasing T.
  - D_0 = a temperature-independent preexponential (m^2/s)
  - Q_d = the activation energy for diffusion (J/mol or eV/atom)
  - R = the gas constant, 8.314 J/mol-K or 8.62×10-5 eV/atom-K
  - T = absolute temperature (K)

- **D has exponential dependence on T.**
- **$D_{interstitial} >> D_{substitutional}$**
  - Ex. of interstitial diffusion: C in α-Fe, C in γ-Fe, etc.
  - Ex. Of substitutional diffusion: Al in Al, Fe in α-Fe, Fe in γ-Fe, etc.



Data taken from E. A. Brandes and G. B. Brook (Editors), Smithells Metals Reference Book, 7th edition, Butterworth-Heinemann, Oxford, 1992.

Fig. 7.7, Callister & Rethwisch 9e

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Summary of Diffusion

- **Solid-state diffusion is a means of mass transport within solid materials by stepwise atomic motion.**
- **Two diffusion mechanisms:**
  - Vacancy diffusion
  - Interstitial diffusion
- **Fick's second law (diffusion equation):** $$\frac{\partial C}{\partial t} = D\left(\frac{\partial^2 C}{\partial x_1^2} + \frac{\partial^2 C}{\partial x_2^2} + \frac{\partial^2 C}{\partial x_3^2}\right)$$
- **Temperature has a profound influence on the coefficients and diffusion rates.**

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

➢ **Diffusion FASTER for...**

- open crystal structures
- materials with secondary bonding
- smaller diffusing atoms
- lower density materials

➢ **Diffusion SLOWER for...**

- close-packed structures
- materials with covalent bonding
- larger diffusing atoms
- higher density materials