

Materials Science

ME 274

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Chapter 5: 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

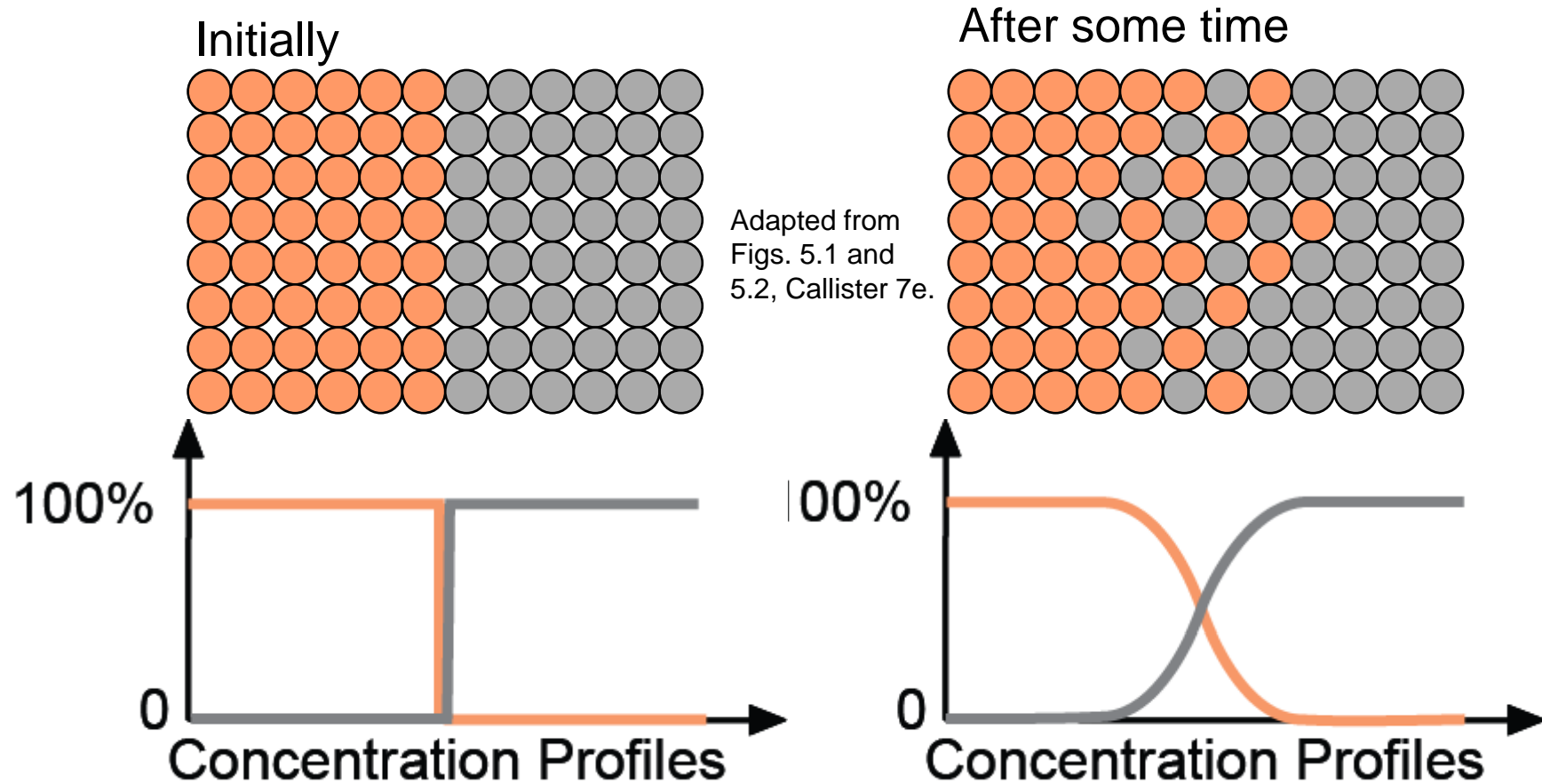
Diffusion - Mass transport by atomic motion

Mechanisms

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

Diffusion

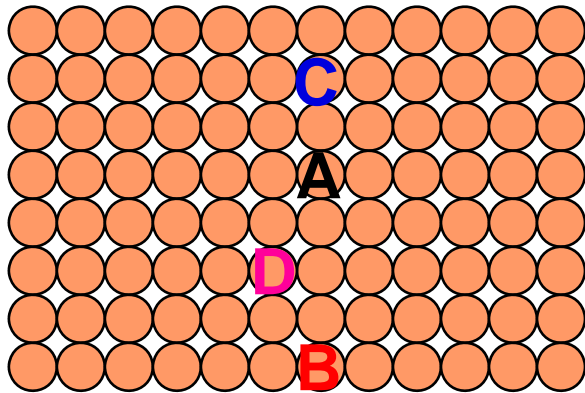
- **Interdiffusion:** In an alloy, atoms tend to migrate from regions of high conc. to regions of low conc.



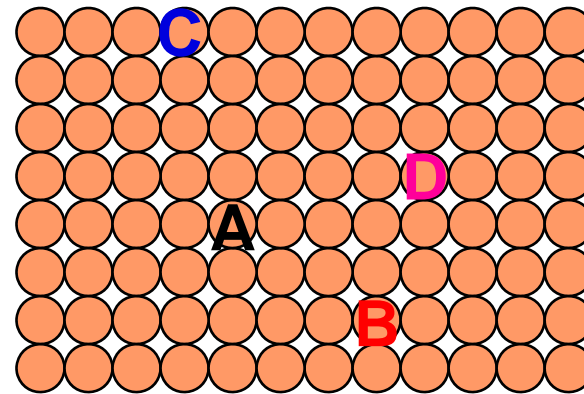
Diffusion

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

Label some atoms



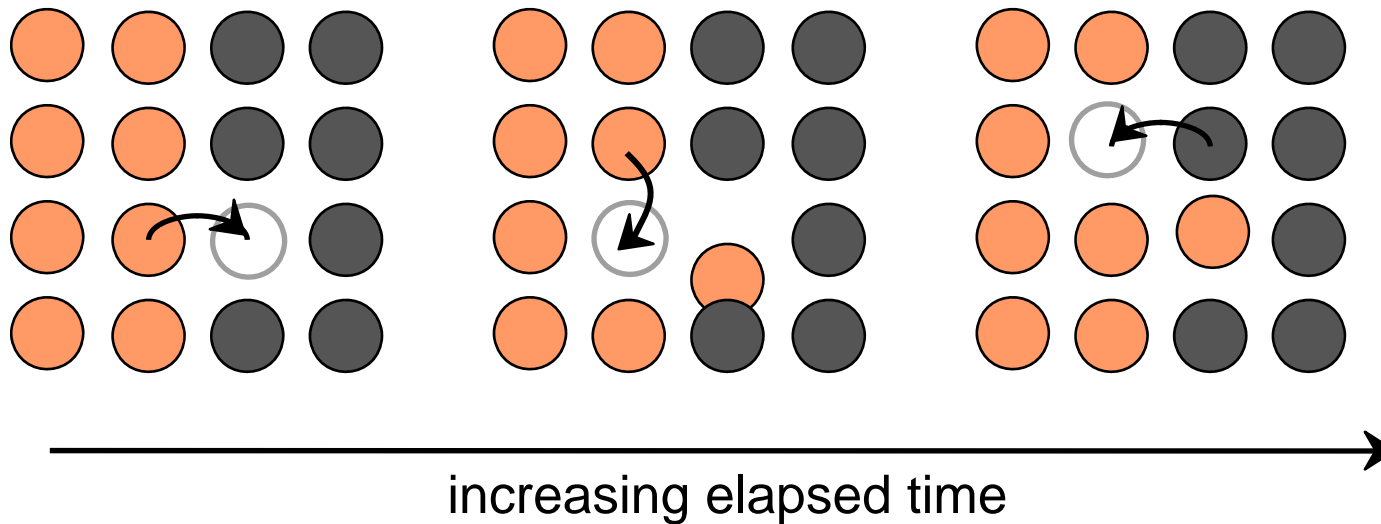
After some time



Diffusion Mechanisms

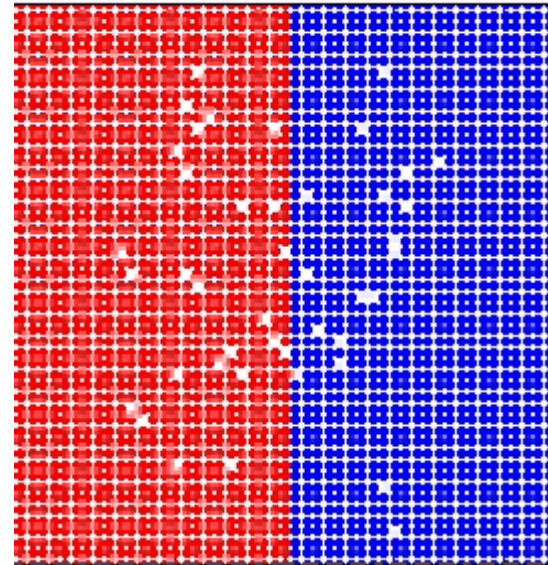
Vacancy Diffusion:

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



Diffusion Simulation

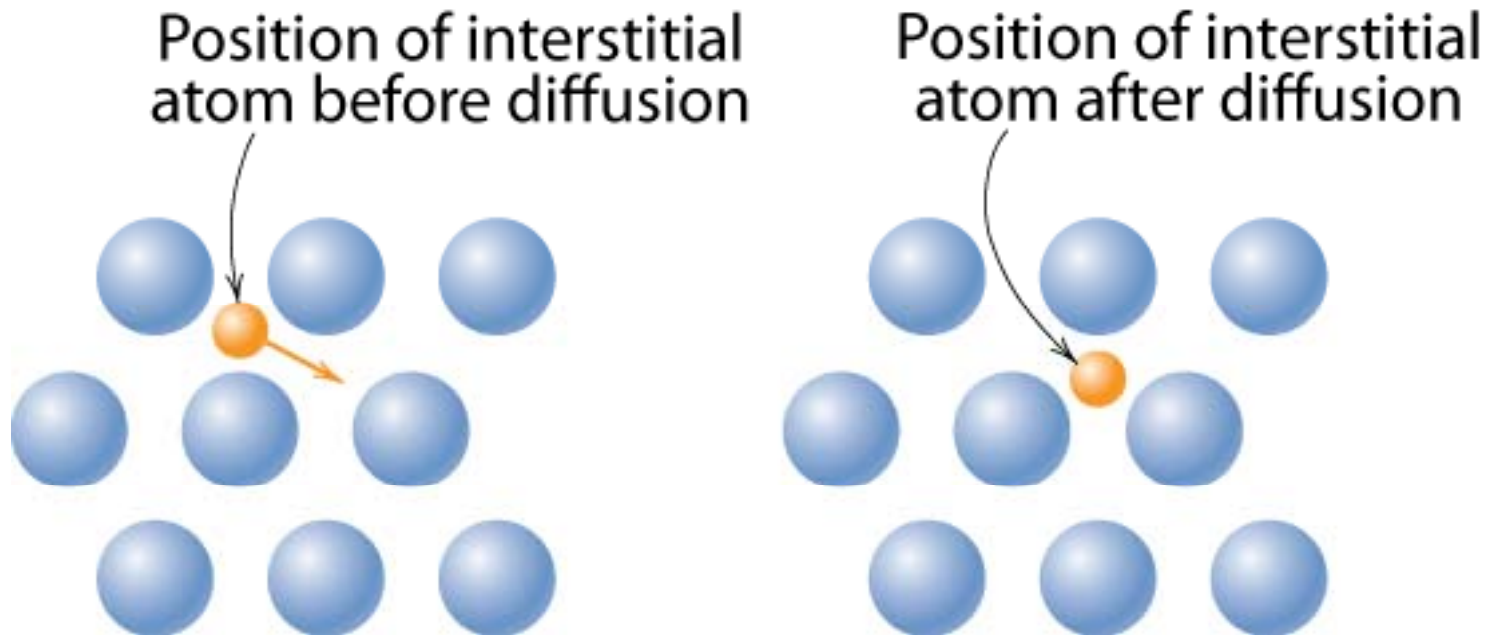
- Simulation of interdiffusion across an interface:
- Rate of substitutional diffusion depends on:
 - vacancy concentration
 - frequency of jumping.



(Courtesy P.M. Anderson)

Diffusion Mechanisms

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



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.



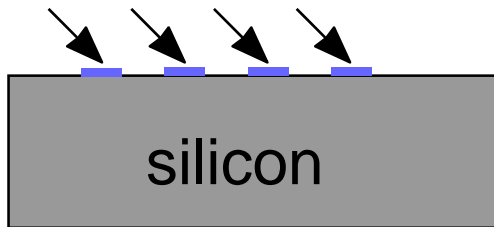
Adapted from chapter-opening photograph, Chapter 5, Callister 7e. (Courtesy of Surface Division, Midland-Ross.)

- **Result:** The presence of C atoms makes iron (steel) harder.

Processing Using Diffusion

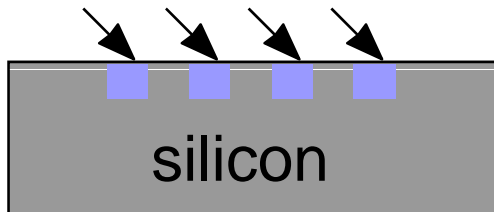
- **Doping** silicon with phosphorus for n-type semiconductors:
- Process:

1. Deposit P rich layers on surface.

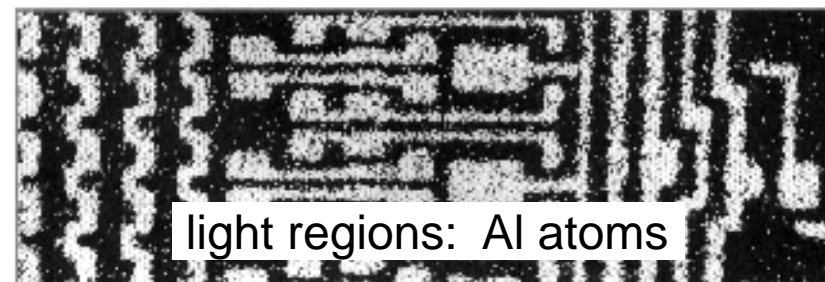
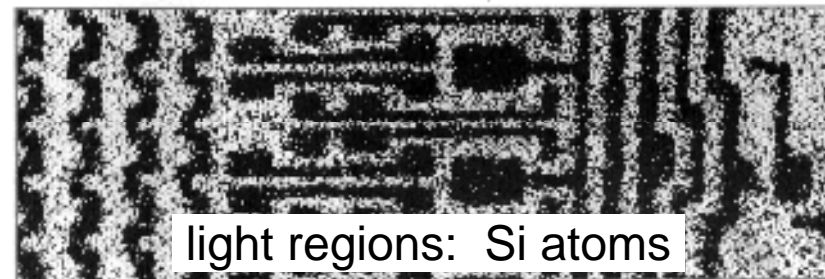
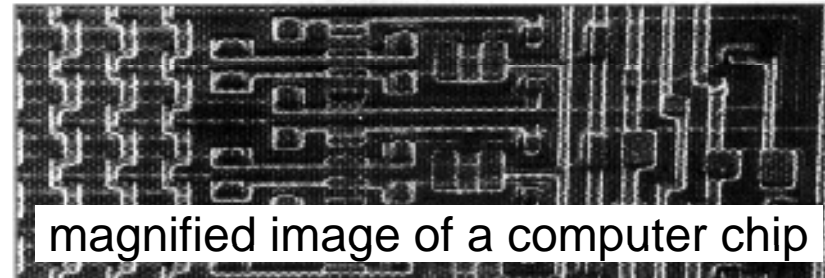


2. Heat it.

3. Result: Doped semiconductor regions.



← 0.5 mm →



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

Diffusion

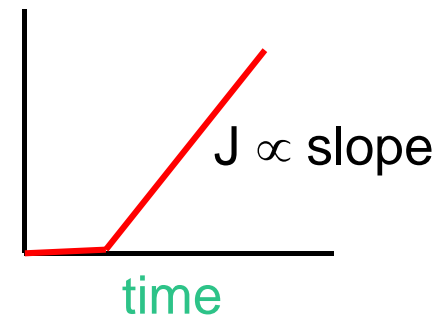
- How do we quantify the amount or rate of diffusion?

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

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

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

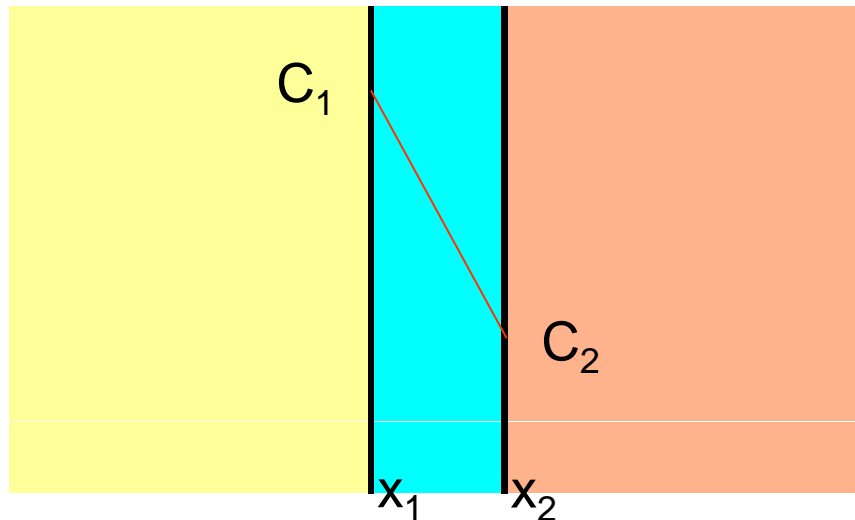
M =
mass
diffused



Steady-State Diffusion

Rate of diffusion independent of time

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



Fick's first law of diffusion

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

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

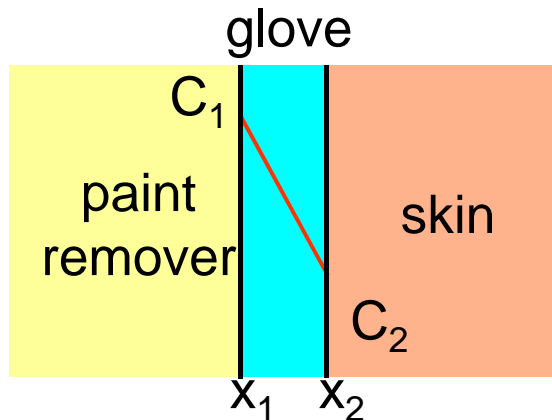
D \equiv diffusion coefficient

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



$$J = -D \frac{dC}{dx} \cong -D \frac{C_2 - C_1}{x_2 - x_1}$$

Data: $D = 110 \times 10^{-8} \text{ cm}^2/\text{s}$

$$C_1 = 0.44 \text{ g/cm}^3$$

$$C_2 = 0.02 \text{ g/cm}^3$$

$$x_2 - x_1 = 0.04 \text{ cm}$$

$$J = - (110 \times 10^{-8} \text{ cm}^2/\text{s}) \frac{(0.02 \text{ g/cm}^3 - 0.44 \text{ g/cm}^3)}{(0.04 \text{ cm})} = 1.16 \times 10^{-5} \frac{\text{g}}{\text{cm}^2\text{s}}$$

Diffusion and Temperature

- Diffusion coefficient increases with increasing T.

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

D = diffusion coefficient [m²/s]

D₀ = pre-exponential [m²/s]

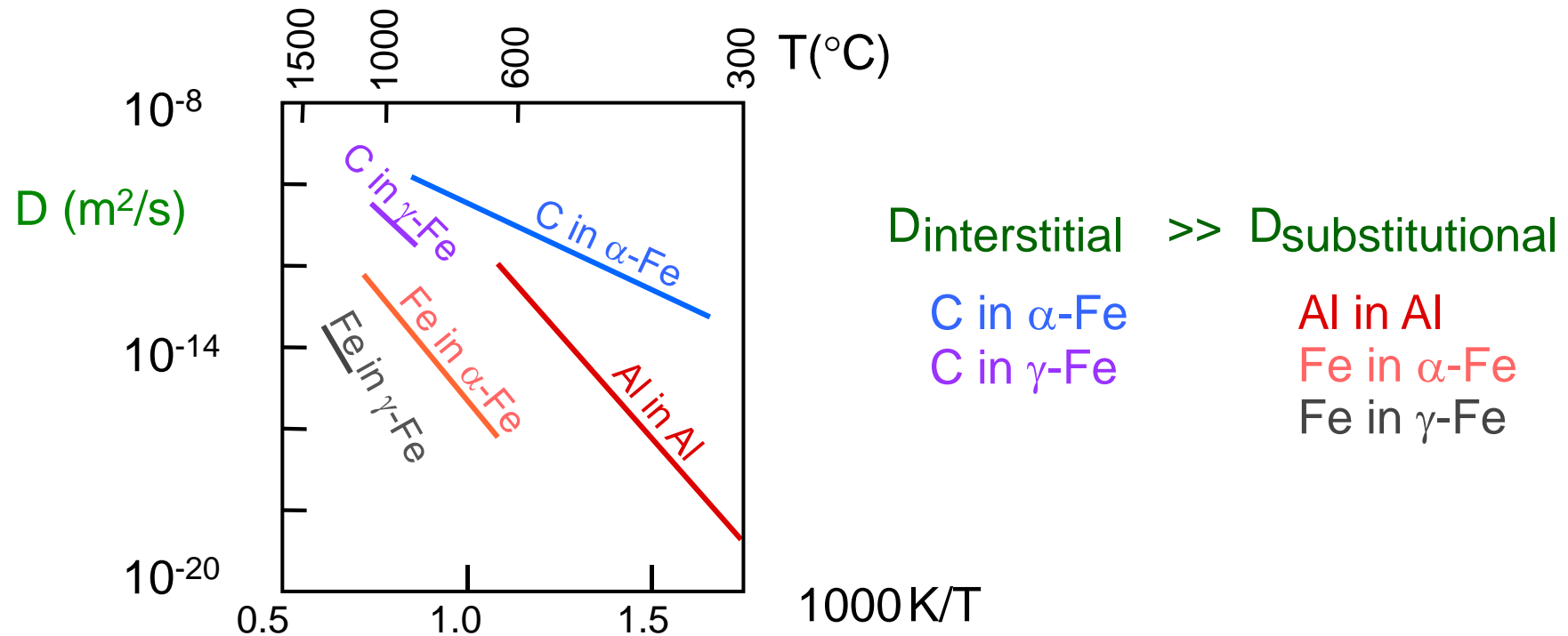
Q_d = activation energy [J/mol or eV/atom]

R = gas constant [8.314 J/mol-K]

T = absolute temperature [K]

Diffusion and Temperature

D has exponential dependence on T



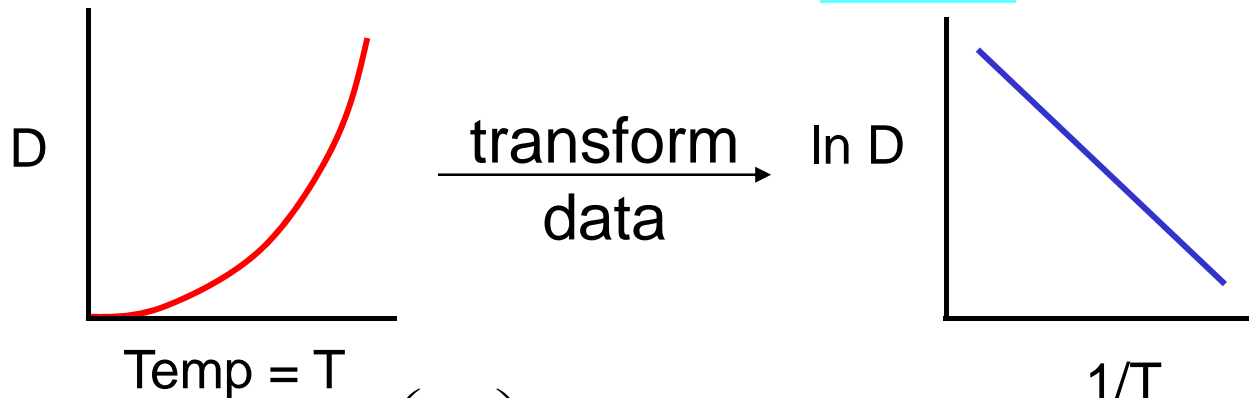
Adapted from Fig. 5.7, Callister 7e. (Date for Fig. 5.7 taken from E.A. Brandes and G.B. Brook (Ed.) Smithells Metals Reference Book, 7th ed., Butterworth-Heinemann, Oxford, 1992.)

Example: At 300°C the diffusion coefficient and activation energy for Cu in Si are

$$D(300^{\circ}\text{C}) = 7.8 \times 10^{-11} \text{ m}^2/\text{s}$$

$$Q_d = 41.5 \text{ kJ/mol}$$

What is the diffusion coefficient at 350°C ?



$$\ln D_2 = \ln D_0 - \frac{Q_d}{R} \left(\frac{1}{T_2} \right) \quad \text{and} \quad \ln D_1 = \ln D_0 - \frac{Q_d}{R} \left(\frac{1}{T_1} \right)$$

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

Example (cont.)

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

$$T_1 = 273 + 300 = 573 \text{ K}$$

$$T_2 = 273 + 350 = 623 \text{ K}$$

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

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

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

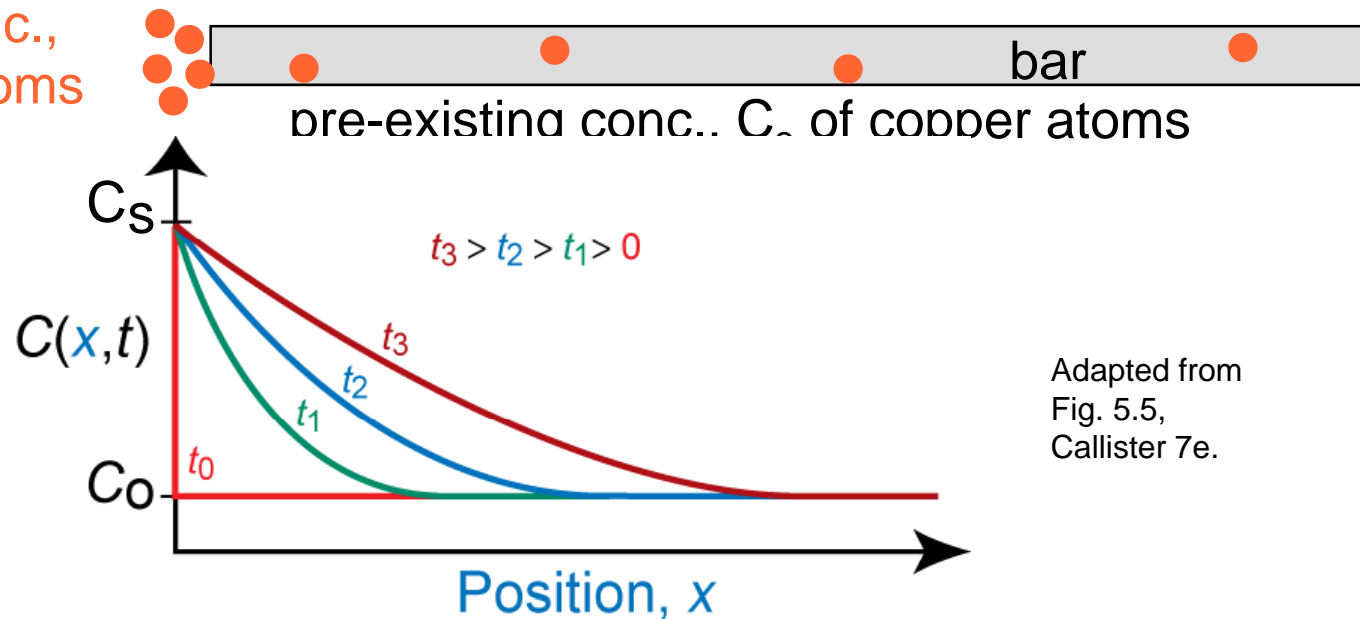
Fick's Second Law

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

Non-steady State Diffusion

- Copper diffuses into a bar of aluminum.

Surface conc.,
 C_S of Cu atoms



Adapted from
Fig. 5.5,
Callister 7e.

B.C. at $t = 0$, $C = C_0$ for $0 \leq x \leq \infty$

at $t > 0$, $C = C_S$ for $x = 0$ (const. surf. conc.)

$C = C_0$ for $x = \infty$

Solution

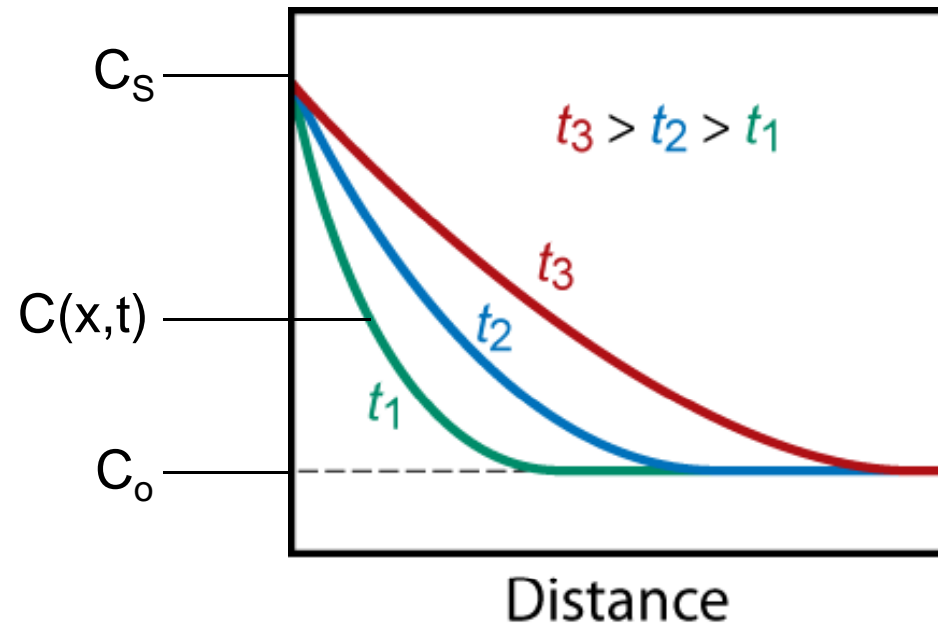
$$\frac{C(x,t) - C_o}{C_s - C_o} = 1 - \operatorname{erf}\left(\frac{x}{2\sqrt{Dt}}\right)$$

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

$\operatorname{erf}(z)$ = error function

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

$\operatorname{erf}(z)$ values are given in Table 5.1



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

Solution (cont.):

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

– $t = 49.5 \text{ h}$

$x = 4 \times 10^{-3} \text{ m}$

– $C_x = 0.35 \text{ wt\%}$

$C_s = 1.0 \text{ wt\%}$

– $C_o = 0.20 \text{ wt\%}$

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

$\therefore \operatorname{erf}(z) = 0.8125$

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

| z | $\text{erf}(z)$ |
|------|-----------------|
| 0.90 | 0.7970 |
| z | 0.8125 |
| 0.95 | 0.8209 |

$$\frac{z - 0.90}{0.95 - 0.90} = \frac{0.8125 - 0.7970}{0.8209 - 0.7970}$$

$$z = 0.93$$

Now solve for D

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

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

Solution (cont.):

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

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

from Table 5.2, for diffusion of C in FCC Fe

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

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

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

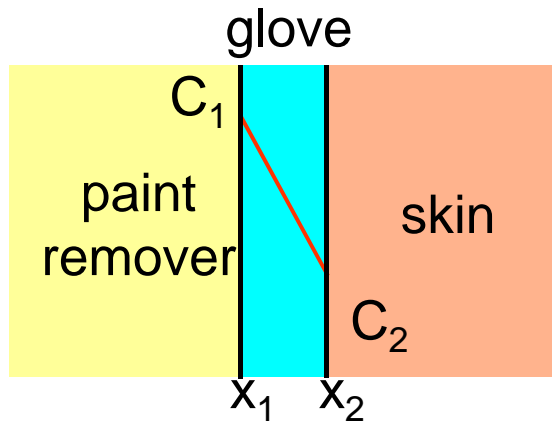
Example: Chemical Protective Clothing (CPC)

- 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 breakthrough time (t_b), i.e., how long could the gloves be used before methylene chloride reaches the hand?
- Data (from Table 22.5)
 - diffusion coefficient in butyl rubber:

$$D = 110 \times 10^{-8} \text{ cm}^2/\text{s}$$

Example (cont).

- **Solution** – assuming linear conc. gradient



$$t_b = \frac{l^2}{6D} \quad \text{Equation 22.24}$$

$$l = x_2 - x_1 = 0.04 \text{ cm}$$

$$D = 110 \times 10^{-8} \text{ cm}^2/\text{s}$$

$$t_b = \frac{(0.04 \text{ cm})^2}{(6)(110 \times 10^{-8} \text{ cm}^2/\text{s})} = 240 \text{ s} = \boxed{4 \text{ min}}$$

Time required for breakthrough ca. **4 min**

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