Chemical Engineering 378

Science of Materials Engineering

Lecture 9

Steady-State Diffusion

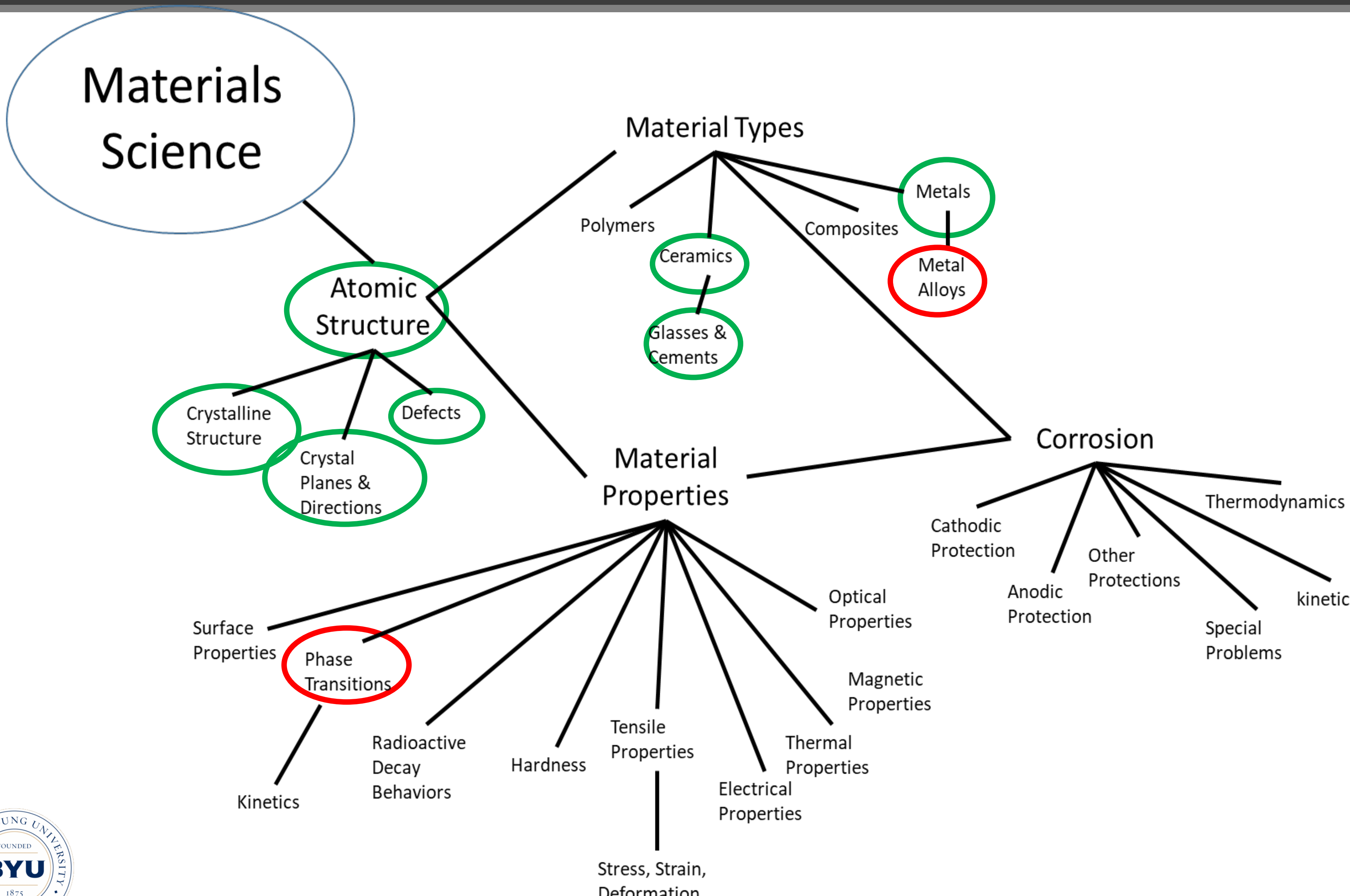
Spiritual Thought

Alma 34:17-18

17 Therefore may God grant unto you, my brethren, that ye may begin to exercise your faith unto repentance, that ye begin to call upon his holy name, that he would have mercy upon you;

18 Yea, cry unto him for mercy; for **he is mighty to save**.

Materials Roadmap



Diffusion

Diffusion - Mass transport by atomic motion

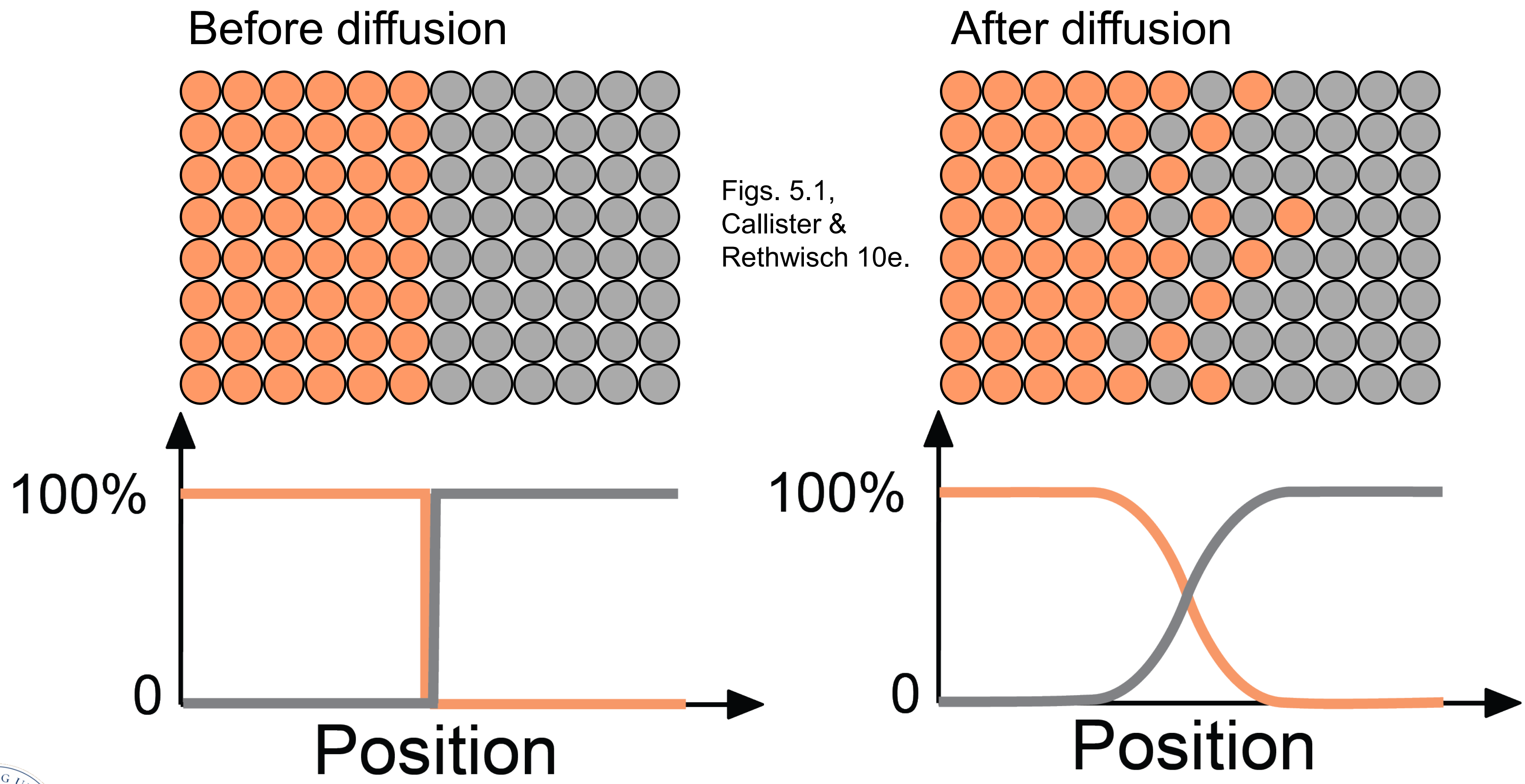
- Diffusion Mechanisms
  - Gases & Liquids – random (Brownian) motion
  - Solids – vacancy diffusion and interstitial diffusion

- Interdiffusion - diffusion of atoms of one material into another material

- Self-diffusion – atomic migration in a pure metal

Diffusion

- Atoms tend to migrate from regions of high concentration to regions of low concentration.

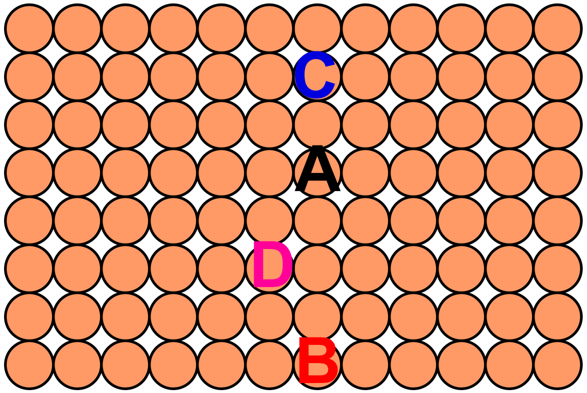


Concentration Profiles

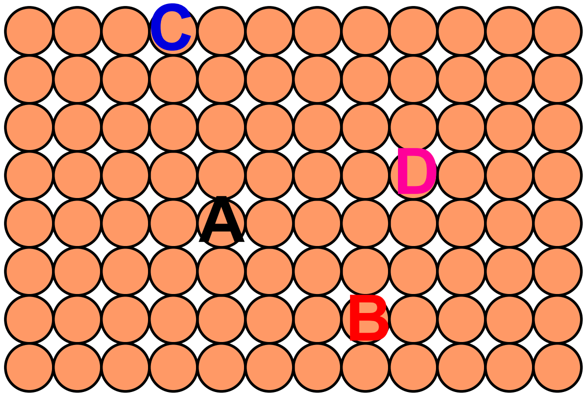
Diffusion

- Self-diffusion: Migration of host atoms in pure metals

Locations of 4 labeled atoms before diffusion



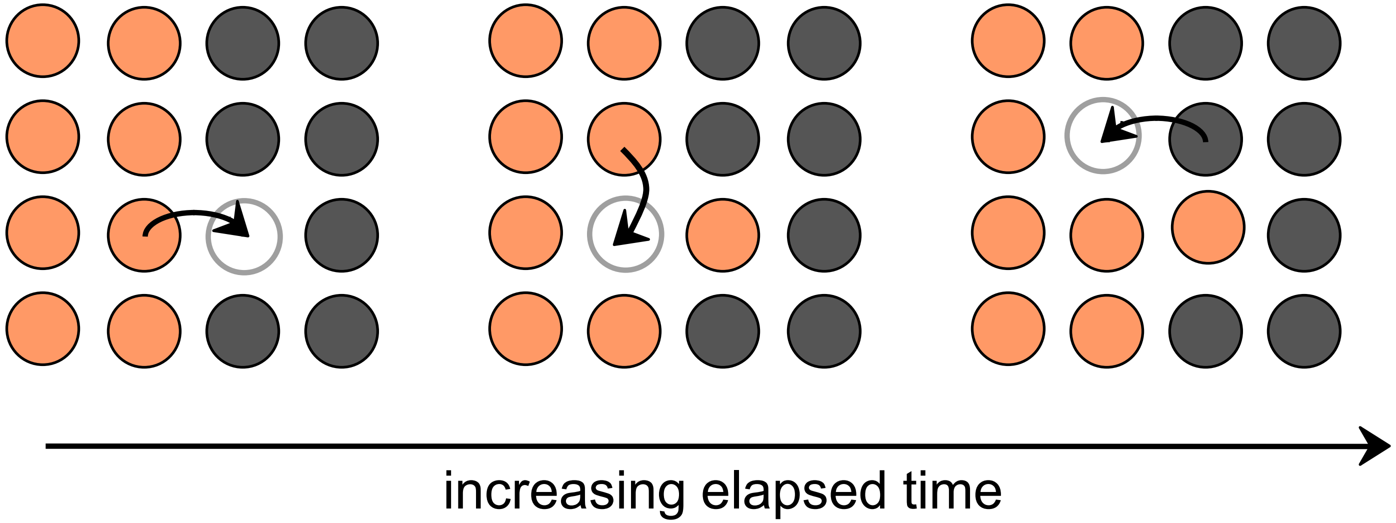
Locations of 4 labeled atoms after diffusion



Diffusion Mechanism I

Vacancy Diffusion

- atoms and vacancies exchange positions
- applies to host and substitutional impurity atoms
- diffusion rate depends on:
  -- number of vacancies
  -- activation energy to exchange.



Diffusion Mechanism II

Interstitial Diffusion

- Small, interstitial atoms move from one interstitial position to an adjacent one

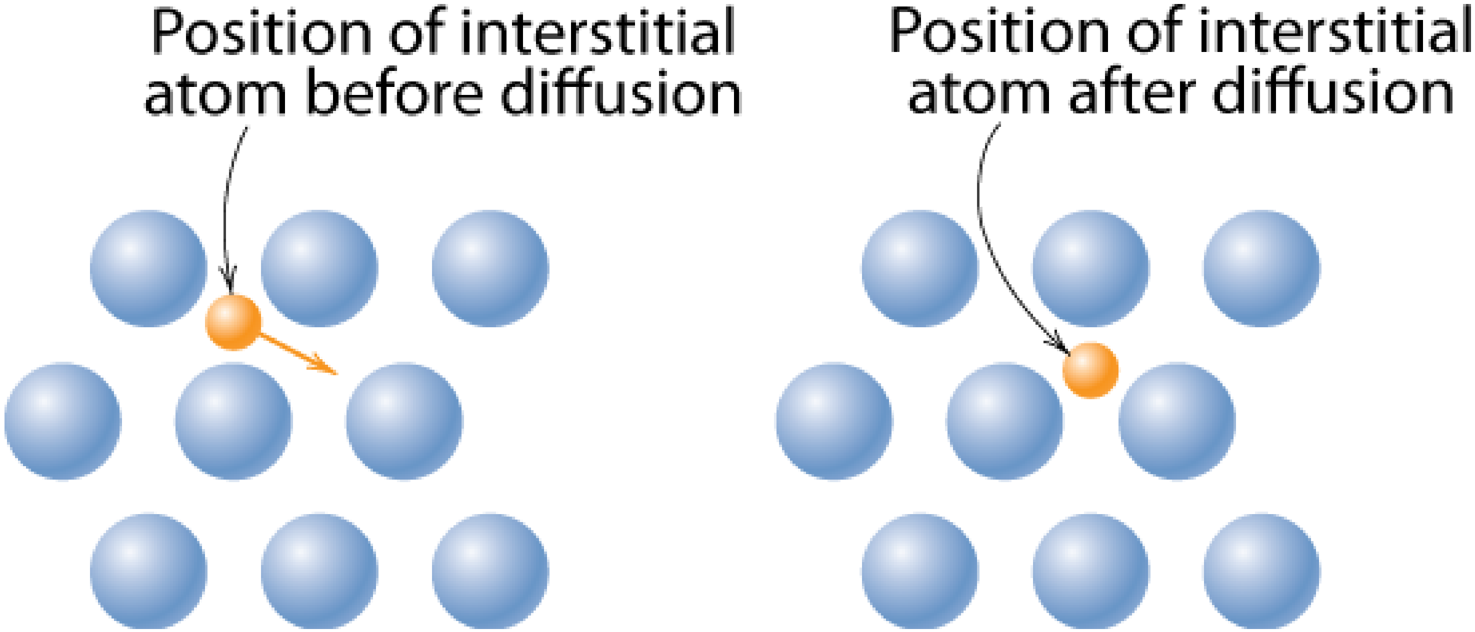


Fig. 5.2 (b), Callister & Rethwisch 10e.

More rapid than vacancy diffusion

Processing Using Diffusion

- Case Hardening:
  - Example of interstitial diffusion
  - Outer surface selectively hardened by diffusing carbon atoms into surface
  - Presence of C atoms makes iron (steel) harder

- Example: Case hardened gear
  - Case hardening improves wear resistance of gear
  - Resulting residual compressive stresses improve resistance to fatigue failure

Chapter-opening photograph, Chapter 5, Callister & Rethwisch 10e. (Courtesy of Surface Division, Midland-Ross.)

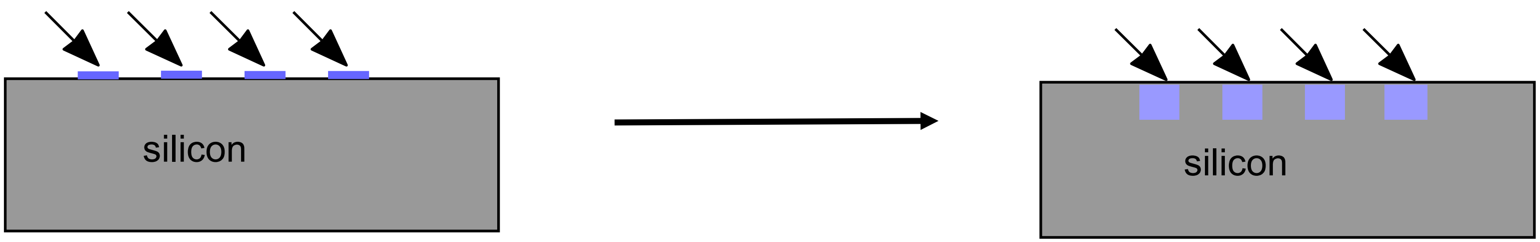
Processing Using Diffusion

Diffusion in Semiconducting Devices

- Doping – Diffusion of very small concentrations of atoms of an impurity (e.g., P) into the semiconductor silicon.

- Process:

1. Deposit P rich layers on surface
2. Heat treat the sample to drive in P
3. Result is P doped semiconductor regions



2 Main Objectives

1. Calculate steady state diffusion (flux, concentration, thickness)
2. Evaluate impact of temperature on diffusion and diffusion coefficient

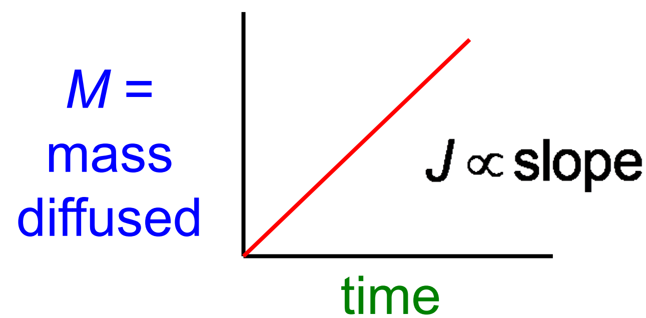
Rate of Diffusion

- Diffusion is a time-dependent process.
- Rate of Diffusion- expressed as diffusion flux, *J*

$$J \equiv \text{Flux} \equiv \frac{\text{mass of diffused species}}{\text{(area)(time)}} = \frac{M}{At} \left(\frac{\text{kg}}{\text{m}^2\text{-s}}\right)$$

- Measured experimentally
  - Use thin sheet (or membrane) – cross-sectional area *A*
  - Impose concentration gradient across sheet
  - Measure mass of diffusing species (*M*) that passes through the sheet over time period (*t*)

$$J = \frac{M}{At} = \frac{1}{A}\frac{dM}{dt}$$



SS Diffusion: Fick's First Law

$\underline{\mathbf{J}} = -D_{AB}\underline{\nabla} c_A$ (mole flux with respect to mole average velocity) where:

$$\underline{\nabla} c_A = \frac{\partial c_A}{\partial x}\underline{\mathbf{i}} + \frac{\partial c_A}{\partial y}\underline{\mathbf{j}} + \frac{\partial c_A}{\partial z}\underline{\mathbf{k}} \qquad \text{(rectangular)}$$

$$= \frac{\partial c_A}{\partial r}\underline{\mathbf{i}} + \frac{1}{r}\frac{\partial c_A}{\partial \theta}\underline{\mathbf{j}} + \frac{\partial c_A}{\partial z}\underline{\mathbf{k}} \qquad \text{(cylindrical)}$$

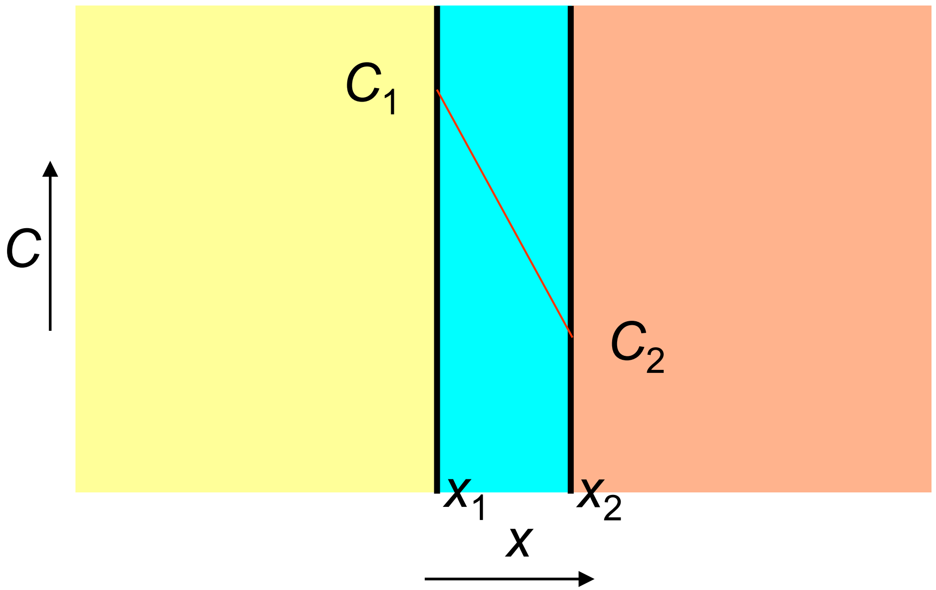
$$= \frac{\partial c_A}{\partial r}\underline{\mathbf{i}} + \frac{1}{r}\frac{\partial c_A}{\partial \theta}\underline{\mathbf{j}} + \frac{1}{r\sin\theta}\frac{\partial c_A}{\partial \phi}\underline{\mathbf{k}} \qquad \text{(spherical)}$$

Steady-State Diffusion

Rate of diffusion (or flux) independent of time

Flux (J) proportional to concentration gradient: $J \propto \frac{dC}{dx}$

C = concentration
x = diffusion direction



Fick's first law of diffusion

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

D = diffusion coefficient

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

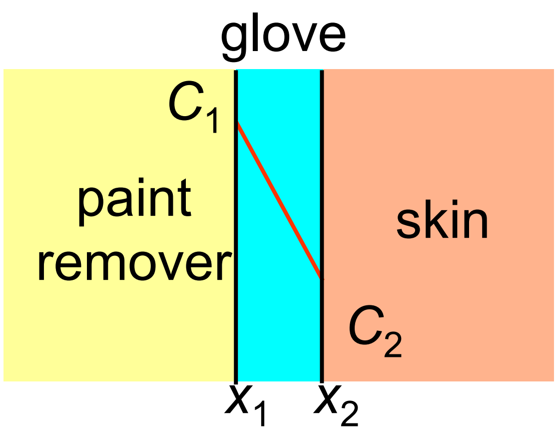
Diffusion Example

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.
- Let's investigate whether butyl rubber gloves (0.04 cm thick) commonly found in the kitchen can be used as protective gloves.
- Note: The maximum allowable flux for a 150 lb person is less than 3.5×10^{-7} g/cm^2/s
- Compute the diffusion flux of methylene chloride through the gloves.

CPC Example (cont.)

- Solution – diffusion flux of methylene chloride assume linear conc. gradient



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

Data:

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

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

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

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

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

Note: this is more than 30 times the allowable flux.
Unsafe to use these gloves for paint removal.

Influence of Temperature on Diffusion

- Diffusion coefficient increases with increasing T

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

D = diffusion coefficient [m²/s]

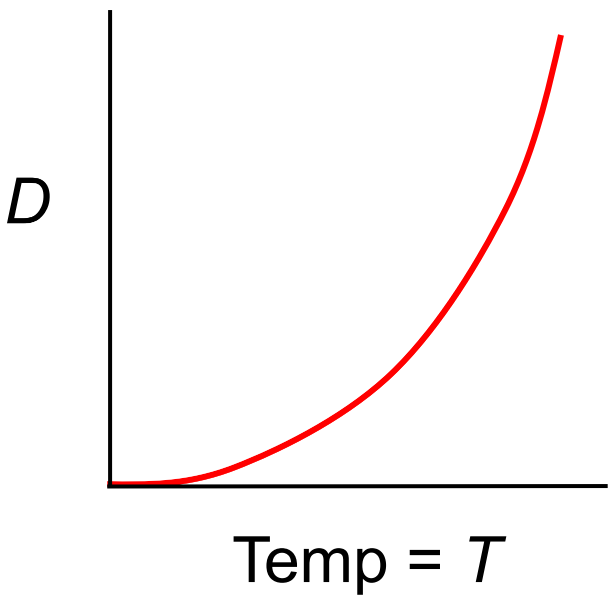
D_o = pre-exponential [m²/s]

Q_d = activation energy [J/mol]

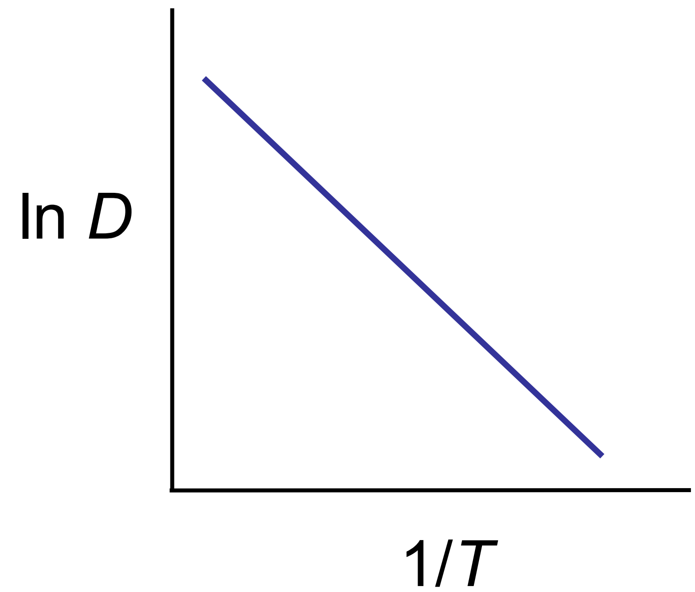
R = gas constant [8.314 J/mol-K]

T = absolute temperature [K]

Influence of Temperature on Diffusion (cont.)



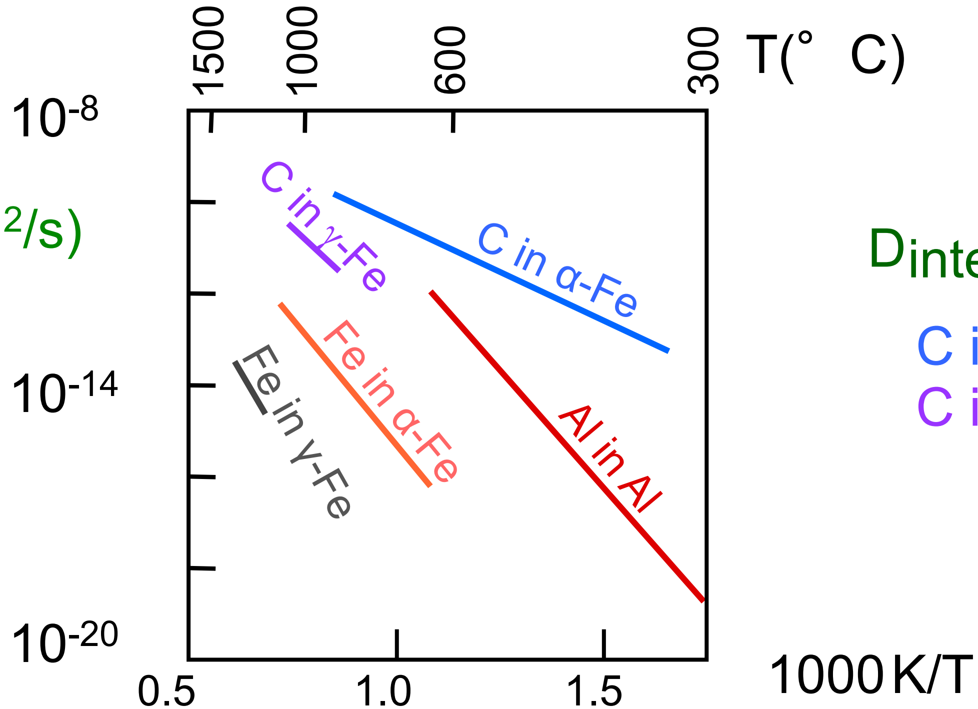
$\xrightarrow[\text{data}]{\text{transform}}$



$$D = D_0 \exp\left(-\frac{Q_d}{RT}\right) \xrightarrow[\text{of both sides}]{\text{take natural log}} \ln D = \ln D_0 - \frac{Q_d}{RT}$$

Influence of Temperature on Diffusion (cont.)

D has exponential dependence on T



$D_{interstitial} >> D_{substitutional}$

$D_{interstitial}$	$D_{substitutional}$
C in α-Fe	Al in Al
C in γ-Fe	Fe in α-Fe
	Fe in γ-Fe

Adapted from Fig. 5.6, Callister & Rethwisch 10e.
(Data for Fig. 5.7 taken from E.A. Brandes and G.B. Brook (Ed.) Smithells Metals Reference Book, 7th ed., Butterworth-Heinemann, Oxford, 1992.)

Influence of Temperature on Diffusion (cont.)

Derive an equation relating the diffusion coefficients at two temperature T_1 and T_2 using the equation derived on slide 19.

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

Subtracting equation at T_1 from equation at T_2

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

Take the exponential of each side to get the final equation

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

Example Diffusion Problem

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

$D_1(300°\ C) = 7.8 \times 10^{-11}\ m^2/s$
$Q_d = 41.5\ kJ/mol$

Compute the diffusion coefficient D_2 at 350° C?

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

$T_1 = 273 + 300 = 573\ K$

$T_2 = 273 + 350 = 623\ K$

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

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