Chapter 5: Diffusion

- 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

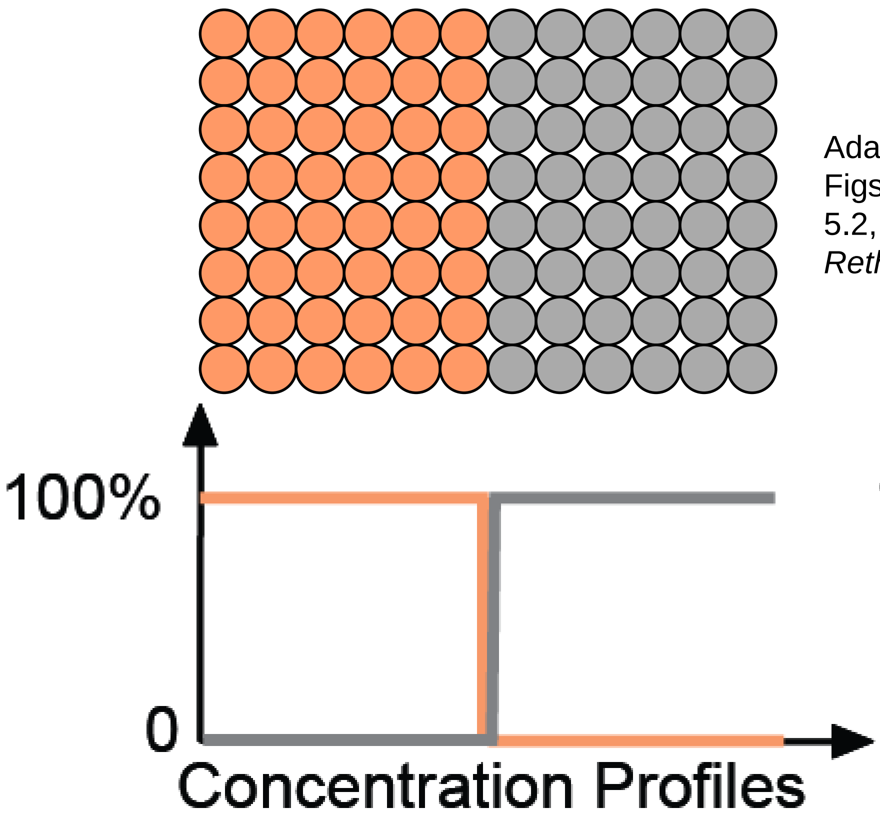
Mechanisms

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

Diffusion

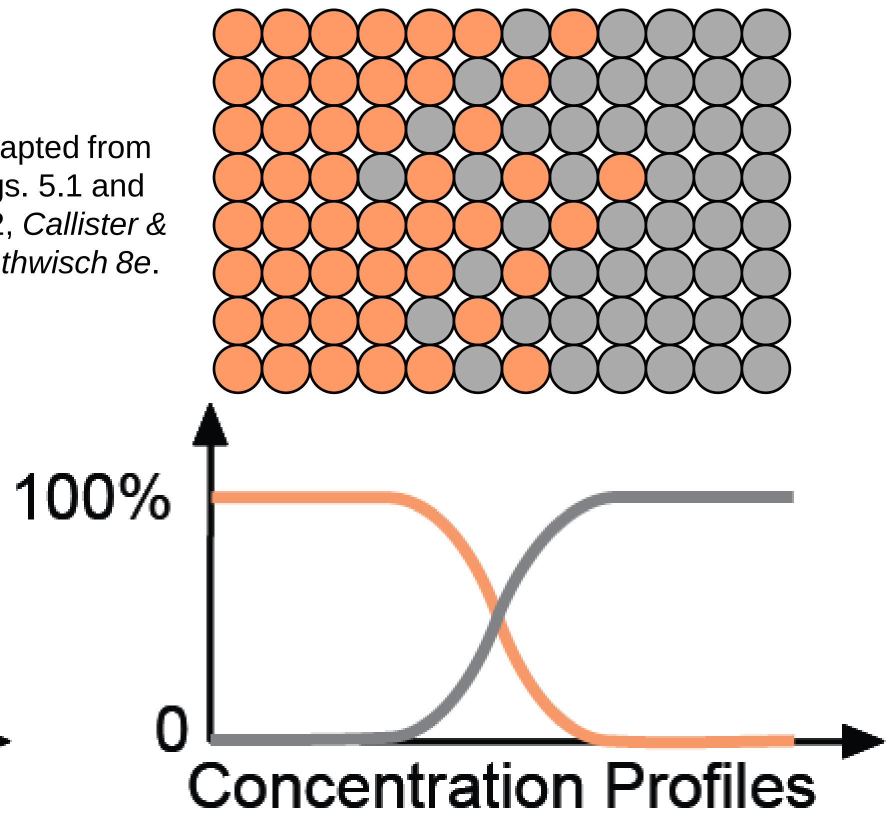
- Interdiffusion: In an alloy, atoms tend to migrate from regions of high conc. to regions of low conc.

Initially



Adapted from Figs. 5.1 and 5.2, *Callister & Rethwisch 8e*.

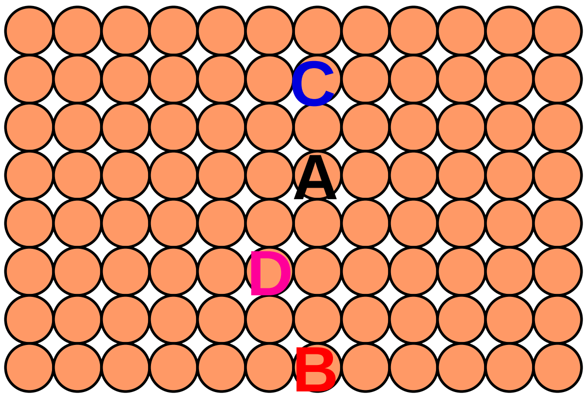
After some time



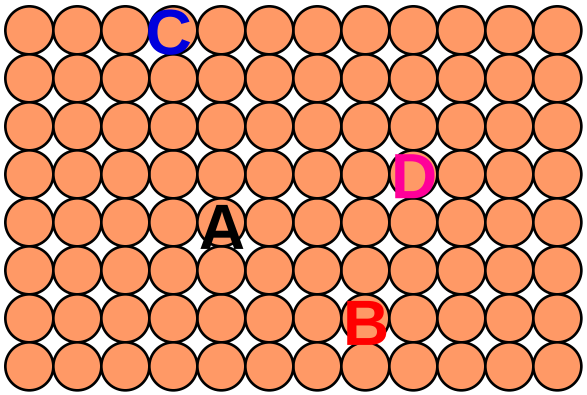
Diffusion

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

Label some atoms



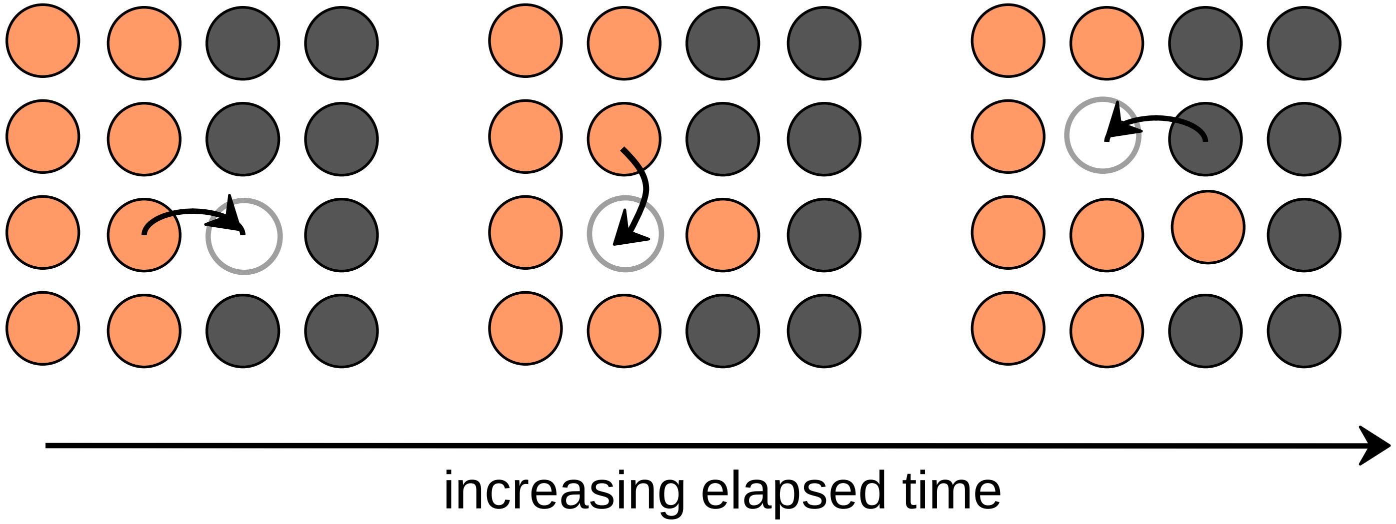
After some time



Diffusion Mechanisms

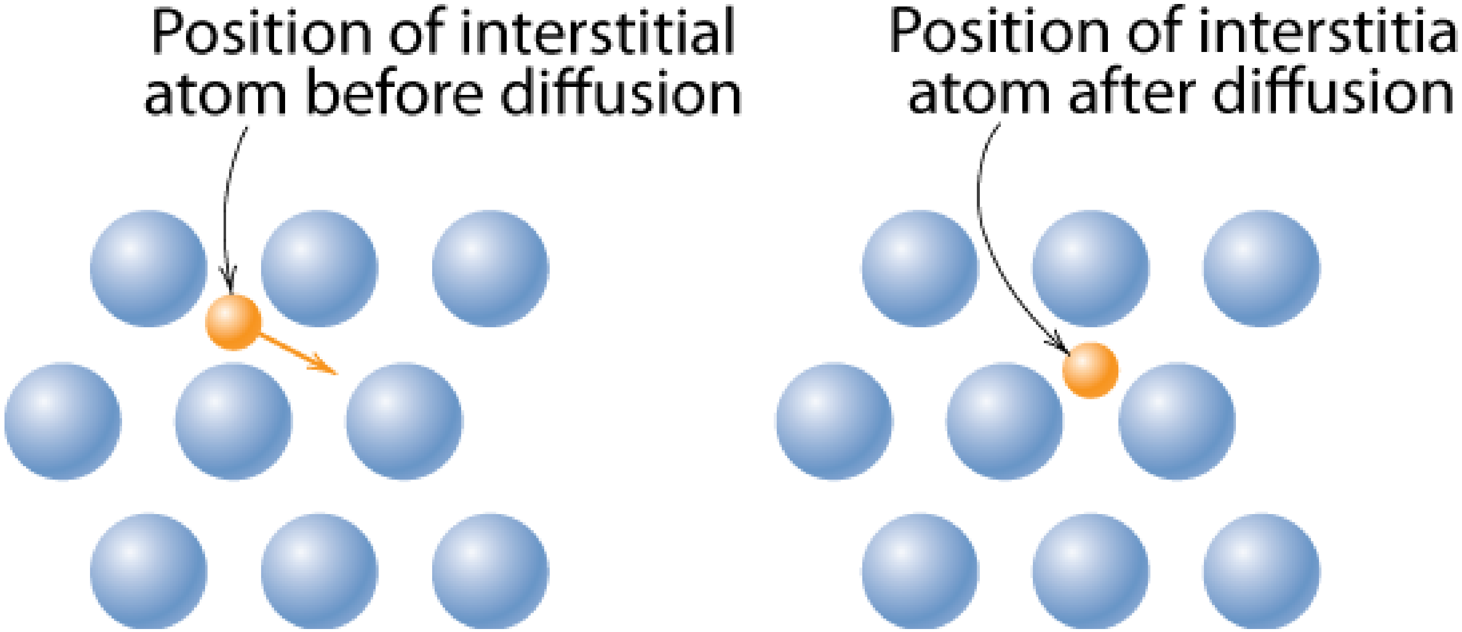
Vacancy Diffusion:

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



Diffusion Mechanisms

- Interstitial diffusion – smaller atoms can diffuse between atoms.



Adapted from Fig. 5.3(b), *Callister & Rethwisch 8e*.

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.

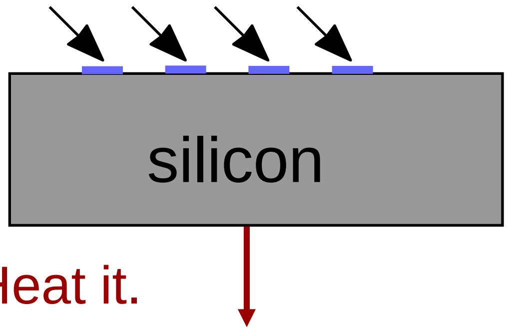
Adapted from chapter-opening photograph, Chapter 5, *Callister & Rethwisch 8e.* (Courtesy of Surface Division, Midland-Ross.)

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

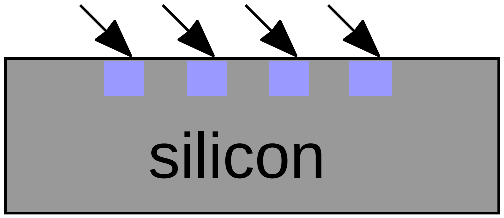
Processing Using Diffusion

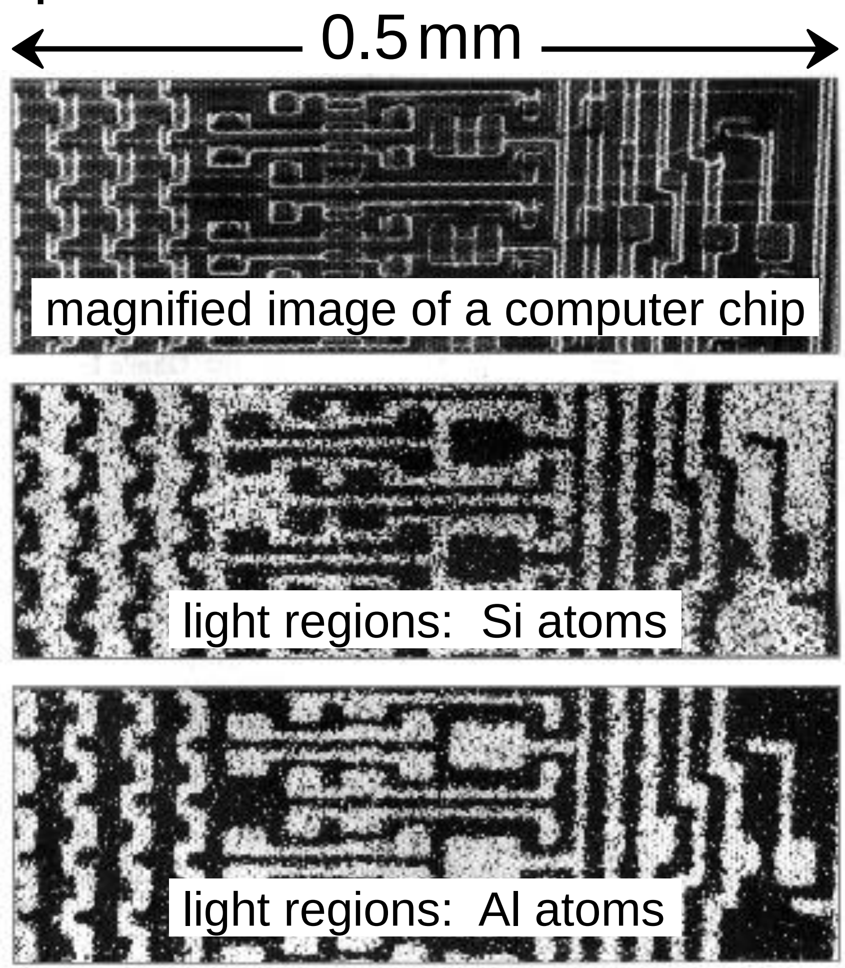
- Doping silicon with phosphorus for *n*-type semiconductors:
- Process:

1. Deposit P rich layers on surface.



2. Heat it.
3. Result: Doped semiconductor regions.





Adapted from Figure 18.27, *Callister & Rethwisch 8e.*

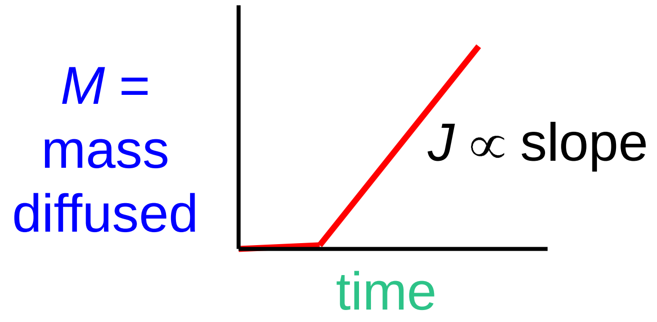
Diffusion

- 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

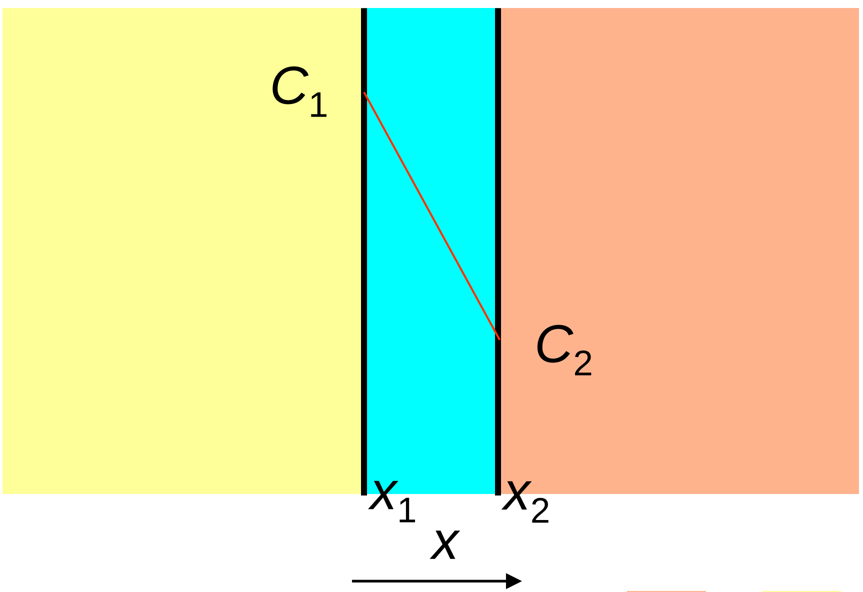
$$J = \frac{M}{At} = \frac{l}{A}\frac{dM}{dt}$$



Steady-State Diffusion

Rate of diffusion independent of time

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



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

Fick's first law of diffusion

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

$D \equiv$ diffusion coefficient

Example: Chemical Protective Clothing (CPC)

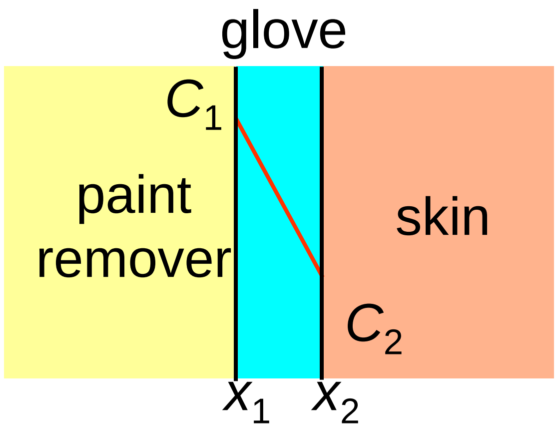
- Methylene chloride is a common ingredient of paint removers. Besides being an irritant, it also may be absorbed through skin. When using this paint remover, protective gloves should be worn.
- If butyl rubber gloves (0.04 cm thick) are used, what is the diffusive flux of methylene chloride through 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*.

$$D = D_o \exp\left(-\frac{Q_d}{R\,T}\right)$$

D = diffusion coefficient [m^2/s]

D_o = temperature independent pre-exponential [m^2/s]

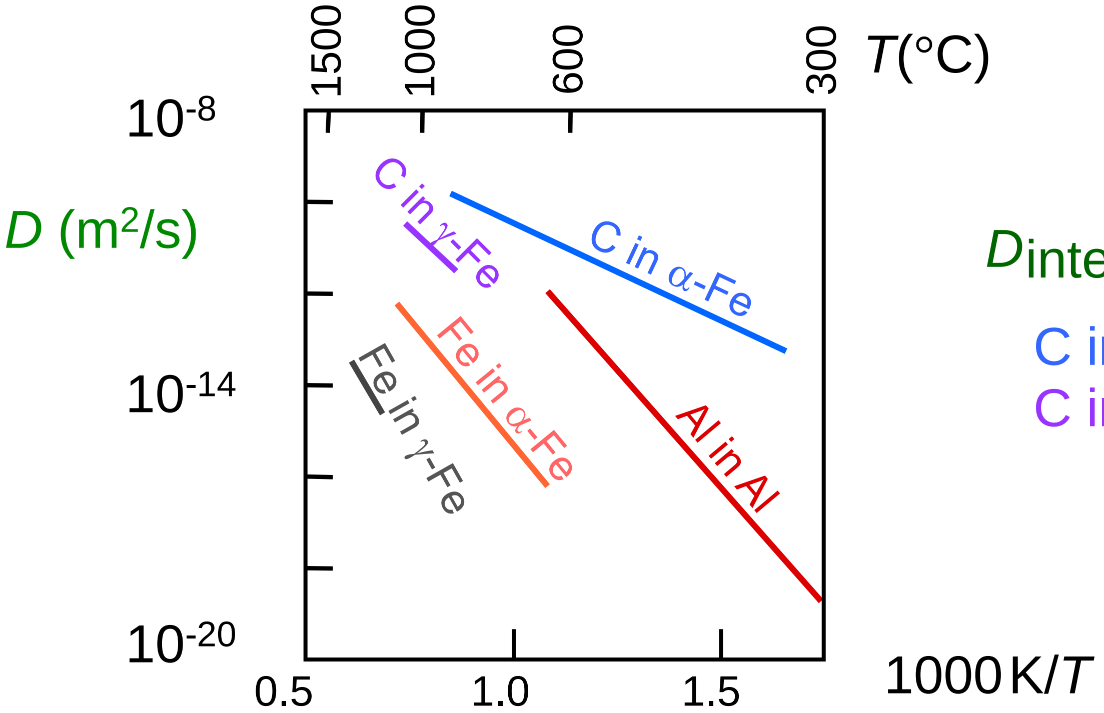
Q_d = activation energy for diffusion [J/mol or eV/atom]

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

T = absolute temperature [K]

Diffusion and Temperature

D has exponential dependence on *T*



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

C in α-Fe	Al in Al
C in γ-Fe	Fe in α-Fe
	Fe in γ-Fe

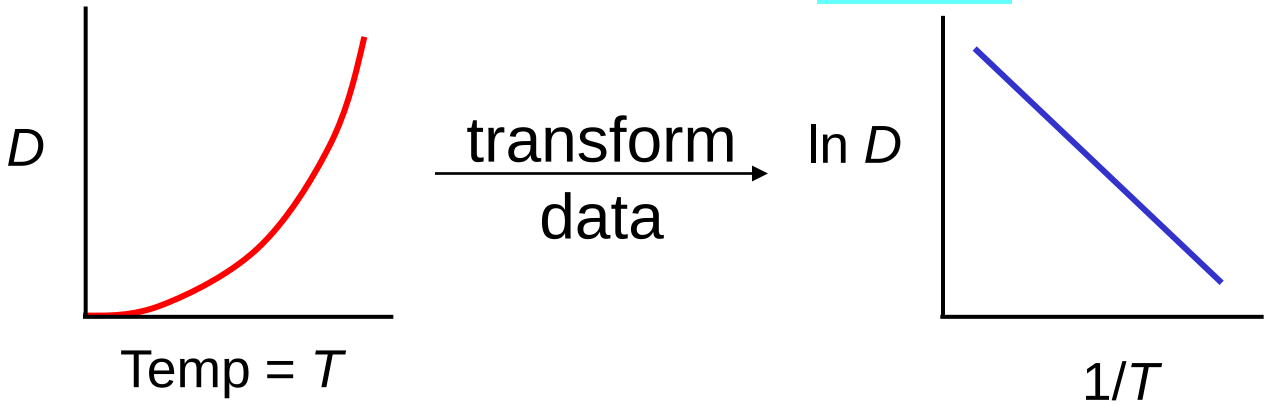
Adapted from Fig. 5.7, *Callister & Rethwisch 8e*. (Date for Fig. 5.7 taken from E.A. Brandes and G.B. Brook (Ed.) *Smithells Metals Reference Book*, 7th ed., Butterworth-Heinemann, Oxford, 1992.)

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

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

$Q_d = 41.5$ kJ/mol

What is the diffusion coefficient at 350ºC?



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

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

Example (cont.)

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

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

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

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

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

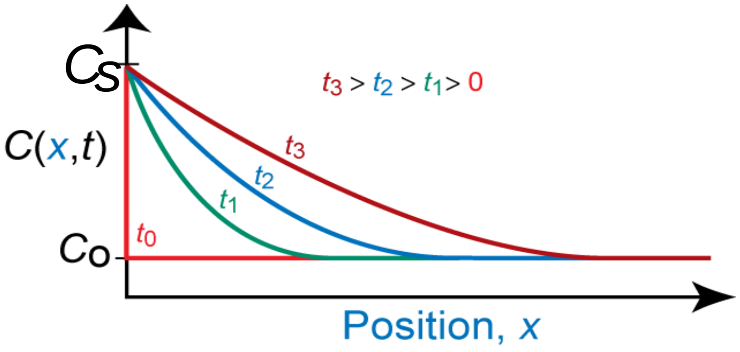
Non-steady State Diffusion

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

Solution:

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



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

- t = 49.5 h
- C_x = 0.35 wt%
- C_o = 0.20 wt%

x = 4 x 10^{-3} m

C_s = 1.0 wt%

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

$\therefore$ 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	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*

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

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

Solution (cont.):

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

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

from Table 5.2, for diffusion of C in FCC Fe

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

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

$T = 1300\ \text{K} = 1027°\text{C}$

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