Chapter 6: 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

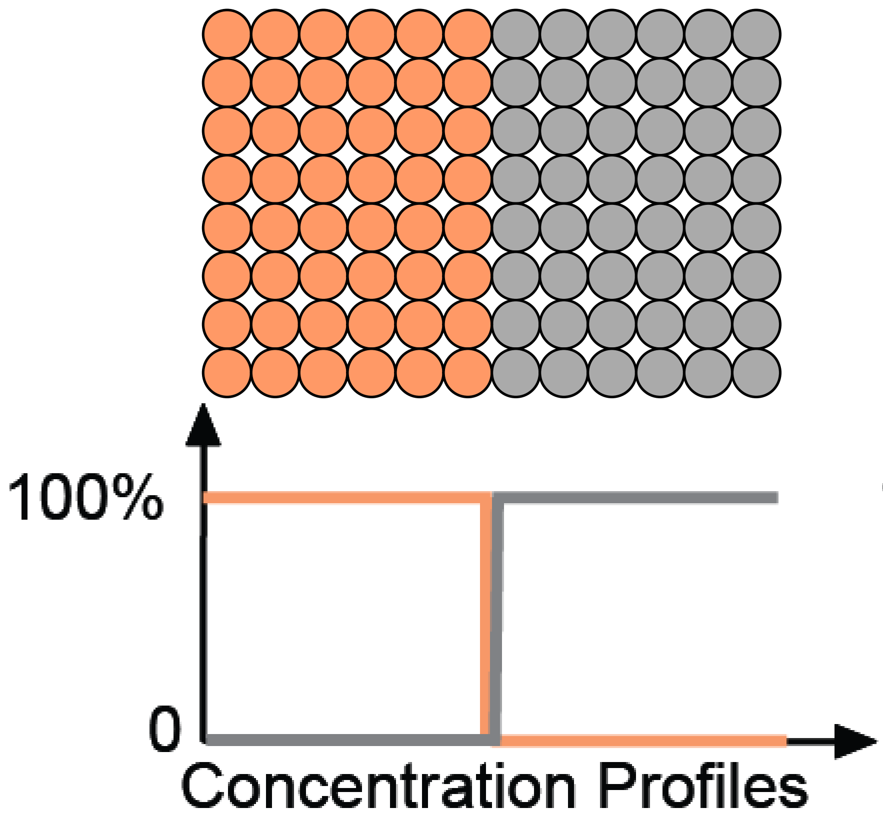
Mechanisms

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

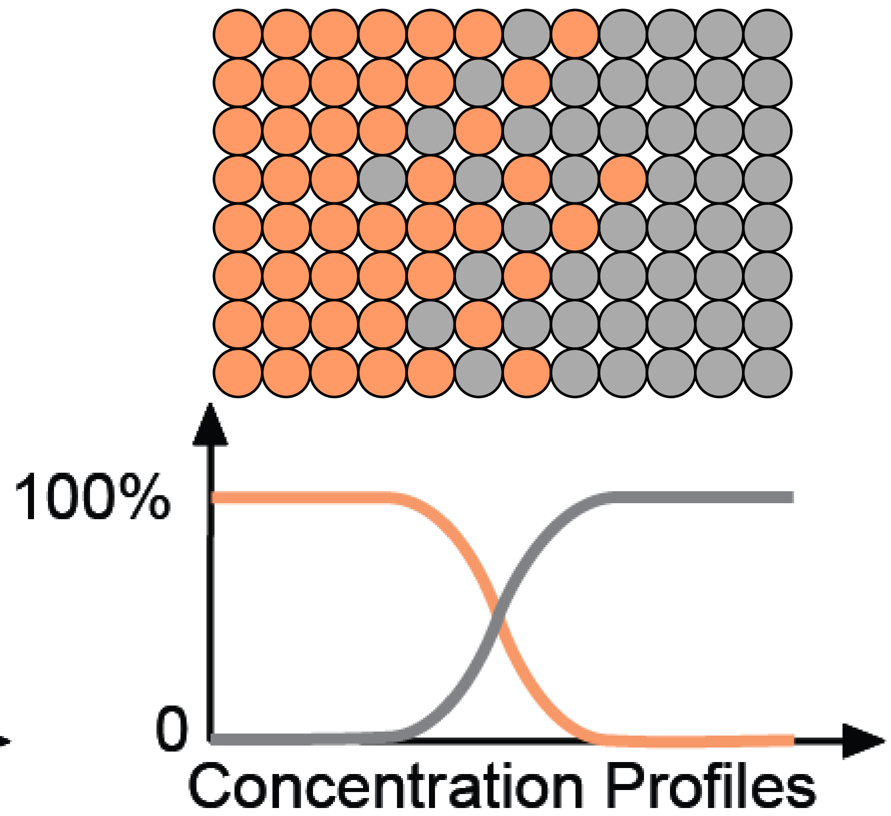
Diffusion

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

Initially



After some time

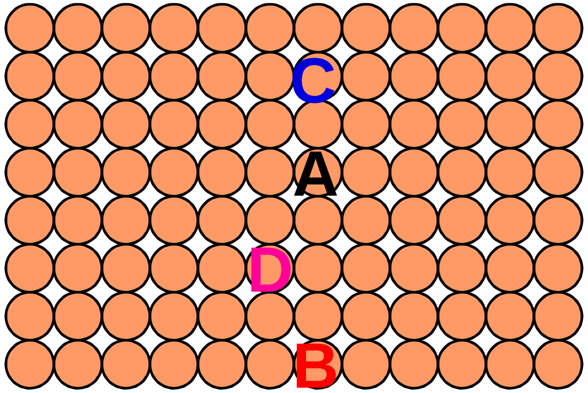


From Figs. 6.1 and 6.2
Callister's Materials Science and Engineering, Adapted Version.

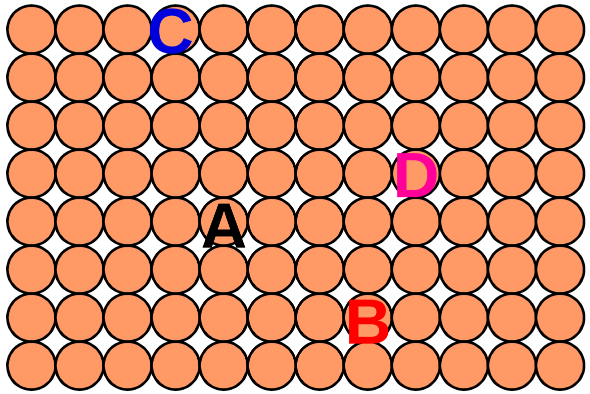
Diffusion

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

Label some atoms



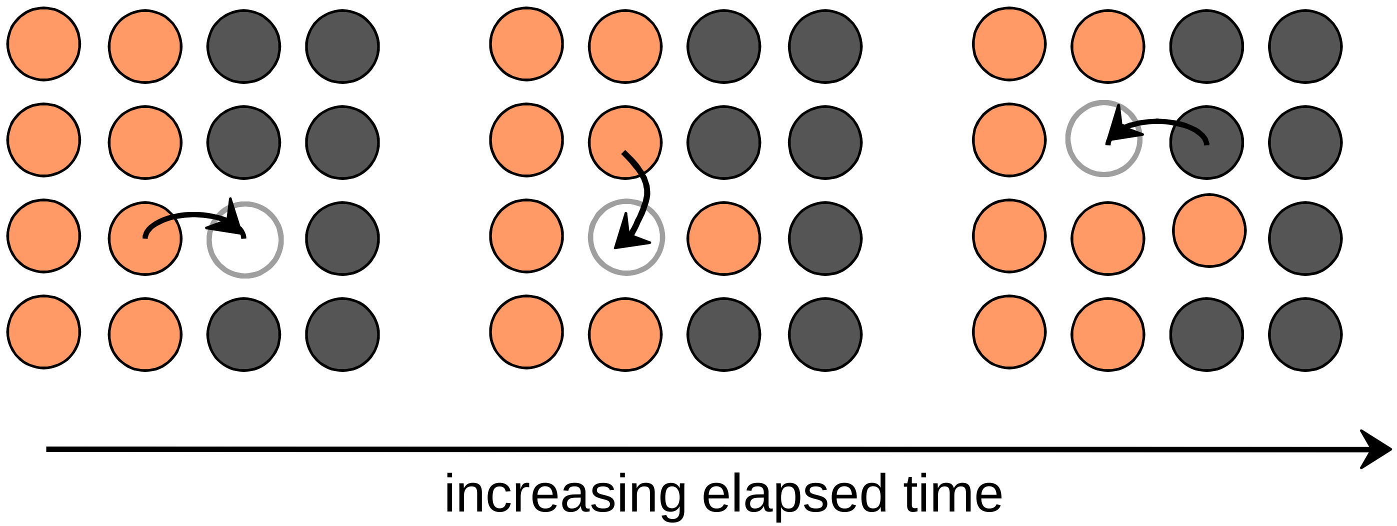
After some time



Diffusion Mechanisms

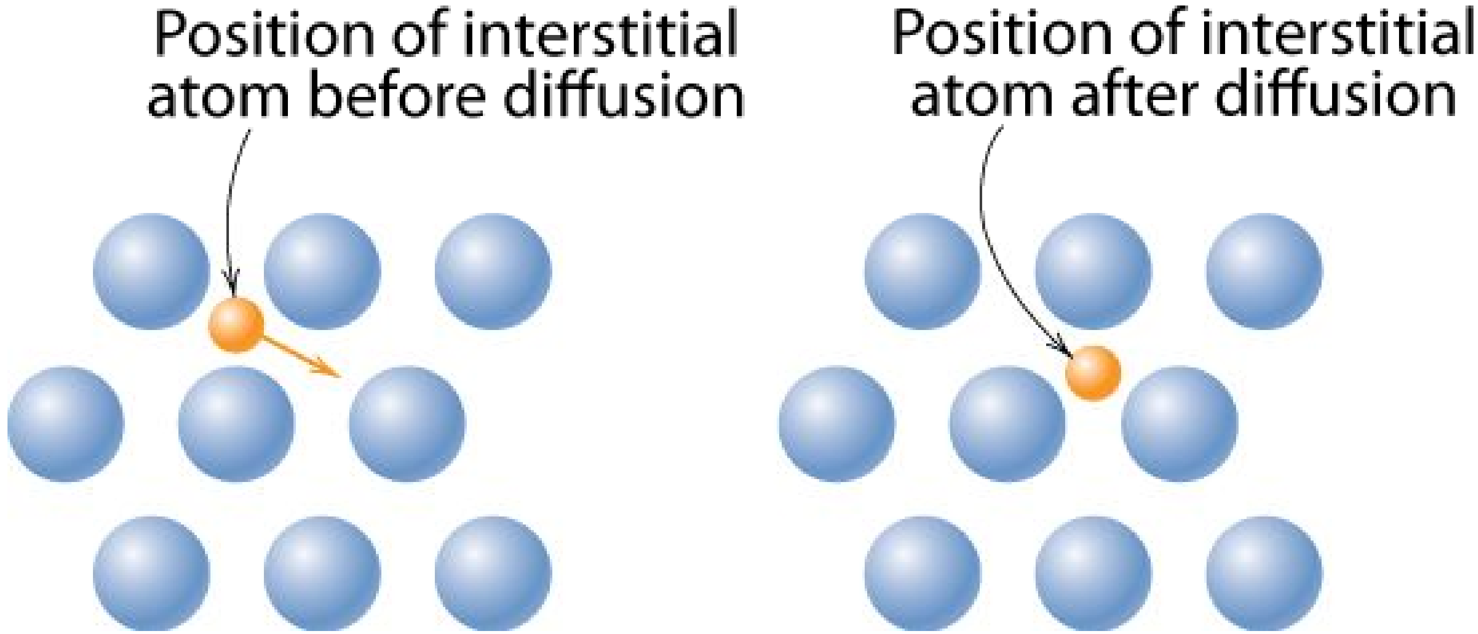
Vacancy Diffusion:

- 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.



From Fig. 6.3 (b)
Callister's Materials Science and Engineering, Adapted Version.

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.

From chapter-opening photograph, Chapter 6, *Callister's Materials Science and Engineering, Adapted Version.*

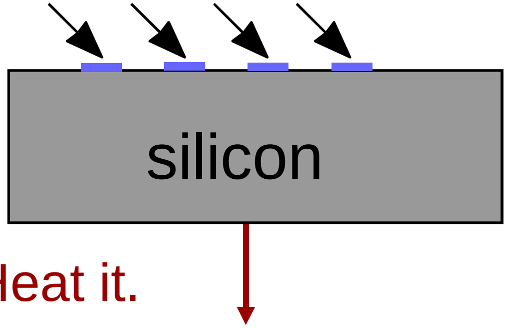
(Courtesy of Surface Division, Midland-Ross.)

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

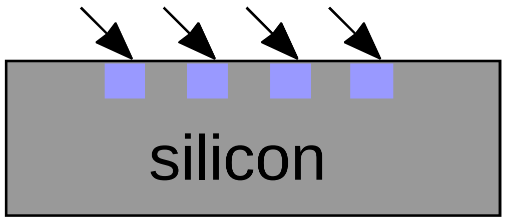
Processing Using Diffusion

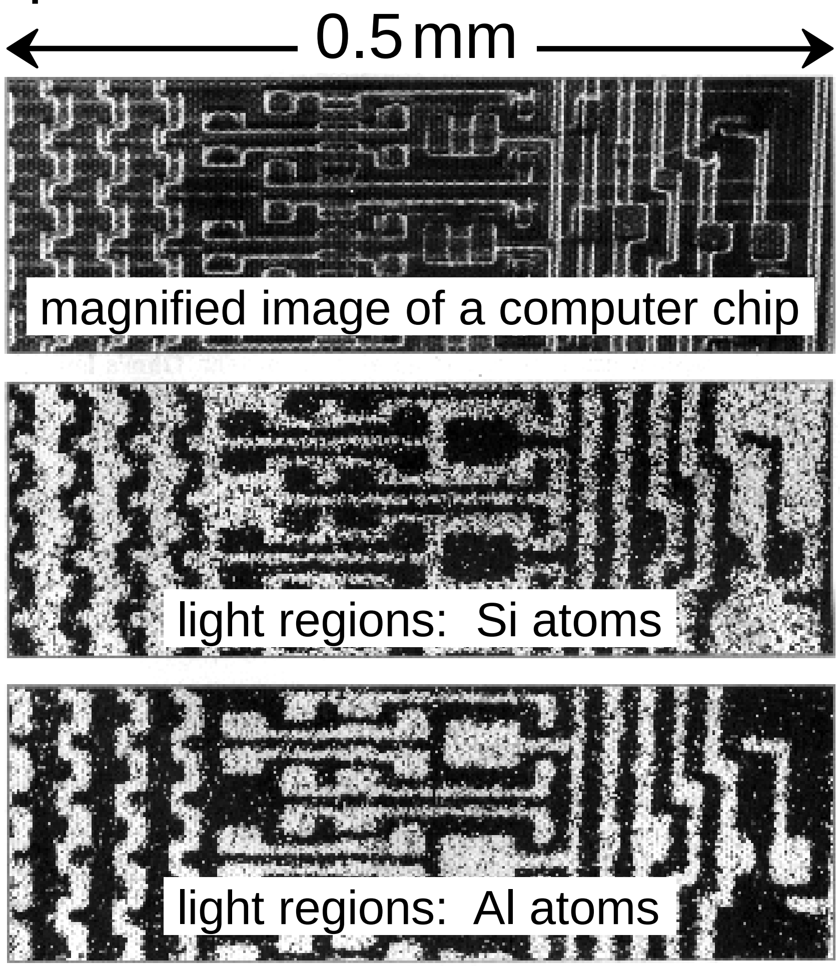
- Doping silicon with phosphorus for *n*-type semiconductors:
- Process:

1. Deposit P rich layers on surface.



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





From chapter-opening photograph, Chapter 17
Callister's Materials Science and Engineering, Adapted Version.

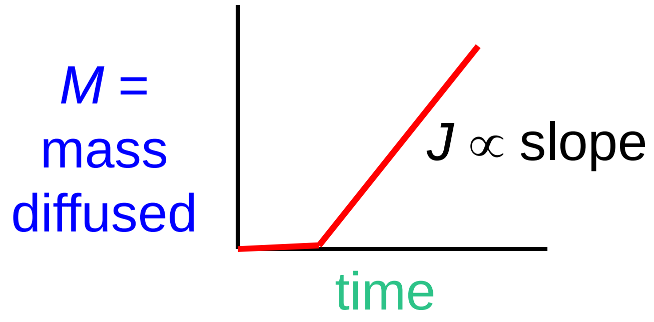
Diffusion

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

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

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

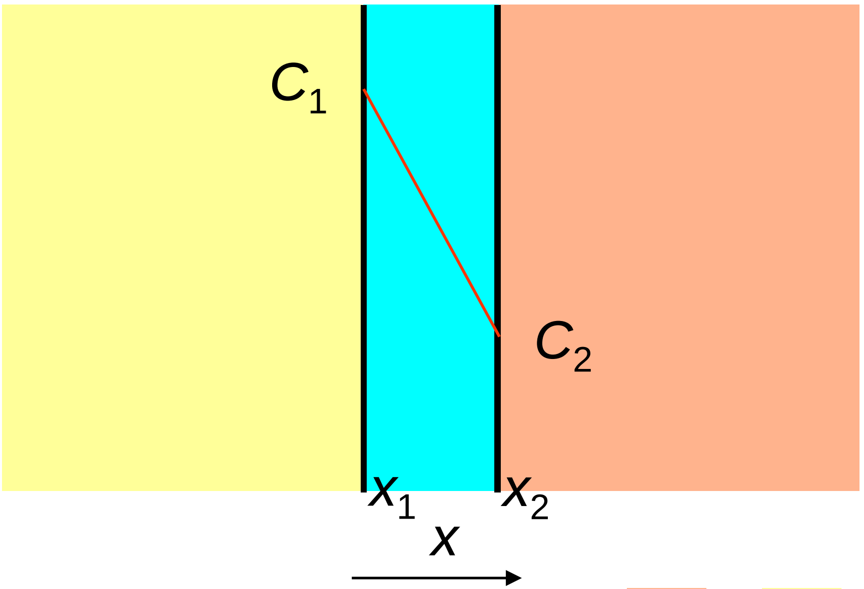
$$J = \frac{M}{At} = \frac{l}{A}\frac{dM}{dt}$$



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

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

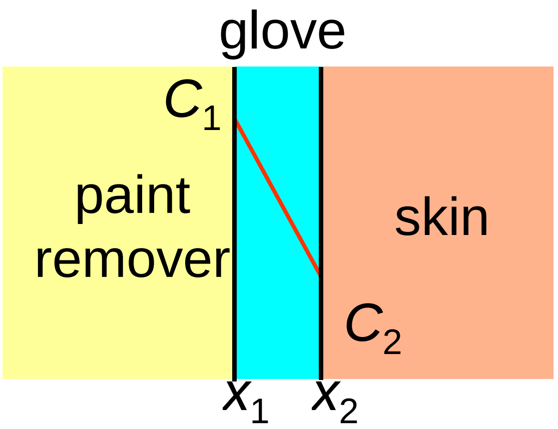
$D \equiv$ diffusion coefficient

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:

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

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

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

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

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

Diffusion and Temperature

- Diffusion coefficient increases with increasing *T*.

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

D = diffusion coefficient [m^2/s]

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

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

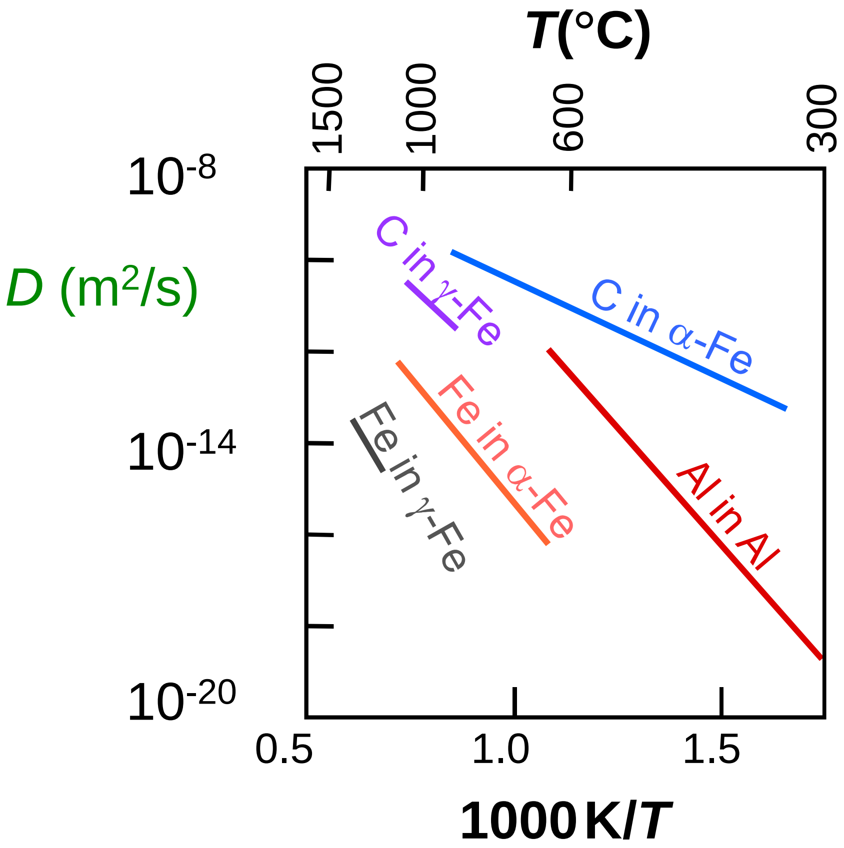
R = gas constant [8.314 J/mol-K]

T = absolute temperature [K]

- The activation energy may be thought of as the energy required to produce the diffusive motion of one mole of atom

Diffusion and Temperature

D has exponential dependence on *T*



$D_{\text{interstitial}} >> D_{\text{substitutional}}$

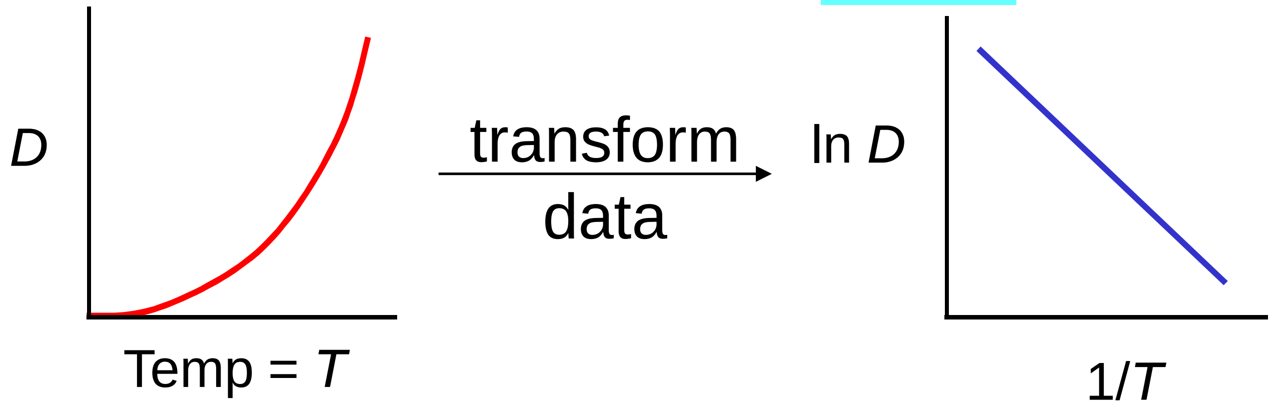
C in α-Fe	Al in Al
C in γ-Fe	Fe in α-Fe
	Fe in γ-Fe

From Fig. 6.7
Callister's Materials Science and Engineering, Adapted Version.
(Date for Fig. 6.7 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

$D(300ºC) = 7.8 \times 10^{-11}\ \mathrm{m^2/s}$
$Q_d = 41.5\ \mathrm{kJ/mol}$

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.)

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

$T_1 = 273 + 300 = 573\,K$

$T_2 = 273 + 350 = 623\,K$

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

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

Question*: Rank the magnitudes of the diffusion coefficients from greatest to least for the following systems:*

N in Fe at 700°C
Cr in Fe at 700°C

Answer*: Nitrogen is an interstitial impurity in Fe (on the basis of its atomic radius), whereas Cr is a substitutional impurity. Since interstitial diffusion occurs more rapidly than substitutional impurity diffusion,* $D_N > D_{Cr}$.

Non-steady State Diffusion

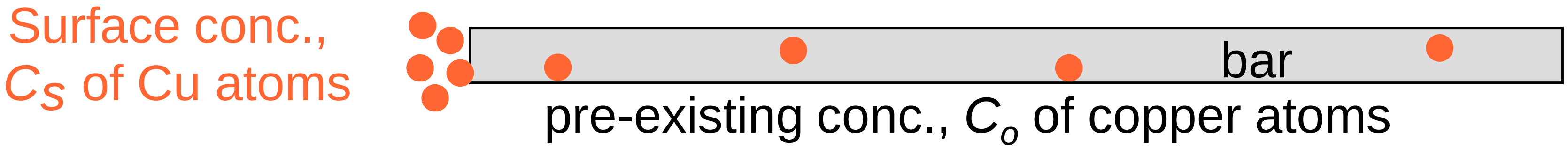
- The concentration of diffucing species is a function of both time and position $C = C(x,t)$
- In this case Fick's Second Law is used

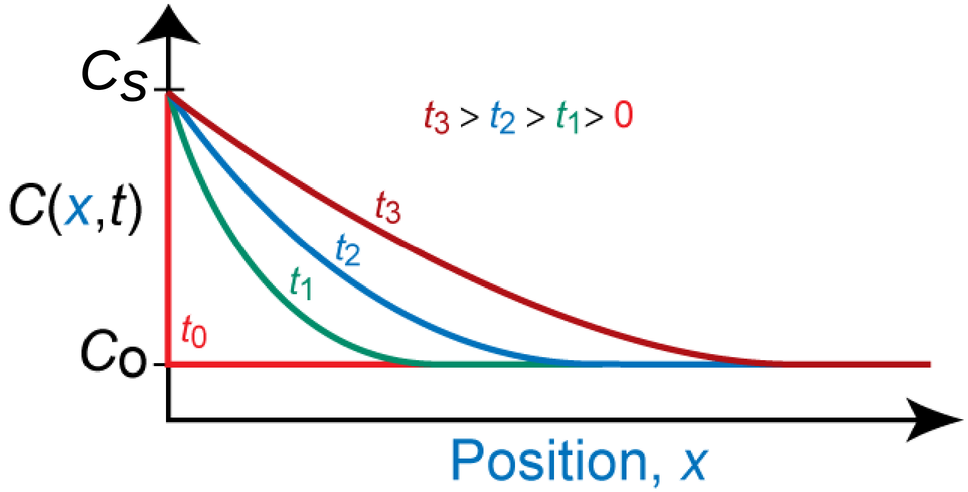
Fick's Second Law

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

Non-steady State Diffusion

- Copper diffuses into a bar of aluminum.





Adapted from Fig. 5.5, *Callister 7e*.

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

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

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

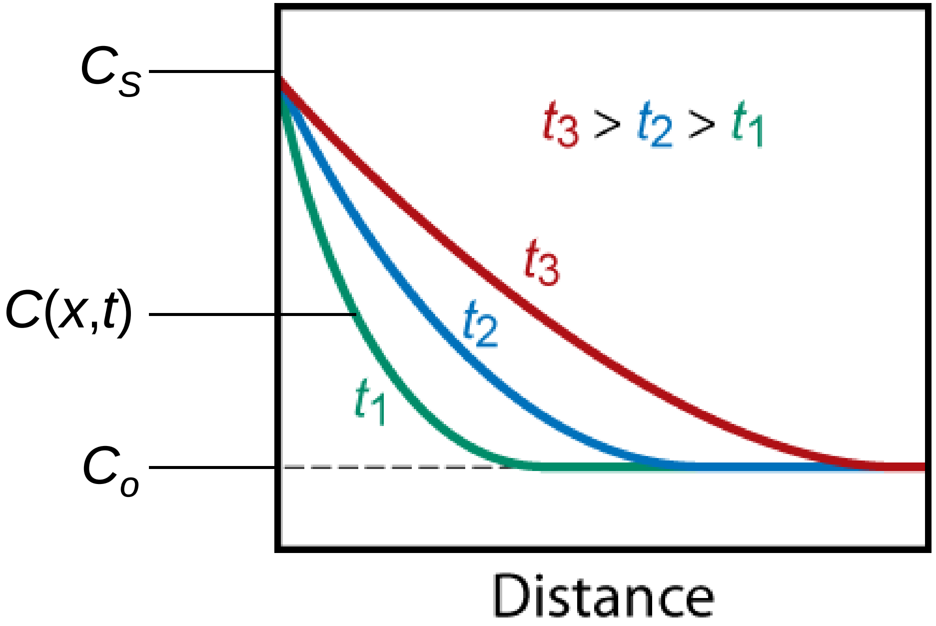
Solution:

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

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

erf (z) = error function

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



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

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

- 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%

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

$\therefore$ erf(z) = 0.8125

Solution (cont.):

We must now determine from the Table below 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*

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

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

Solution (cont.):

- To solve for the temperature at which D has above value, we use a rearranged form of this equation:

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

It is given that for diffusion of C in FCC Fe

D_o = 2.3 x 10^{-5} m^2/s Q_d = 148,000 J/mol

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

$$\boxed{T = 1300 \text{ K} = 1027°\text{C}}$$

Summary

Diffusion FASTER for...	Diffusion SLOWER for...
• open crystal structures	• close-packed structures
• materials w/secondary bonding	• materials w/covalent bonding
• smaller diffusing atoms	• larger diffusing atoms
• lower density materials	• higher density materials