Diffusion in Solids

Diffusion

Diffusion - Mass transport by atomic motion

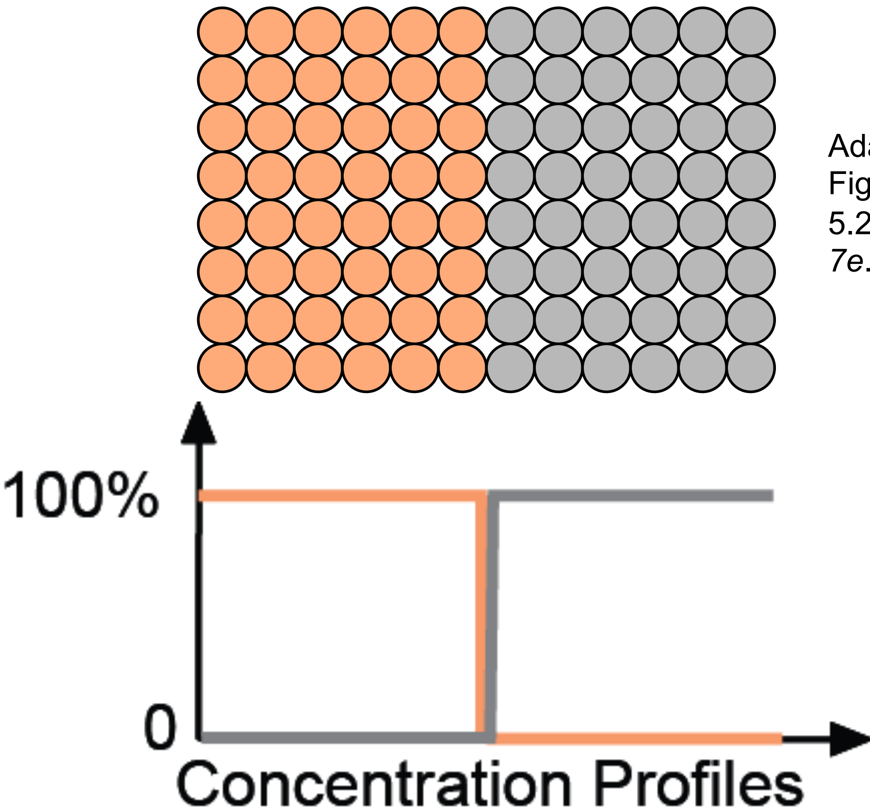
Mechanisms

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

Diffusion

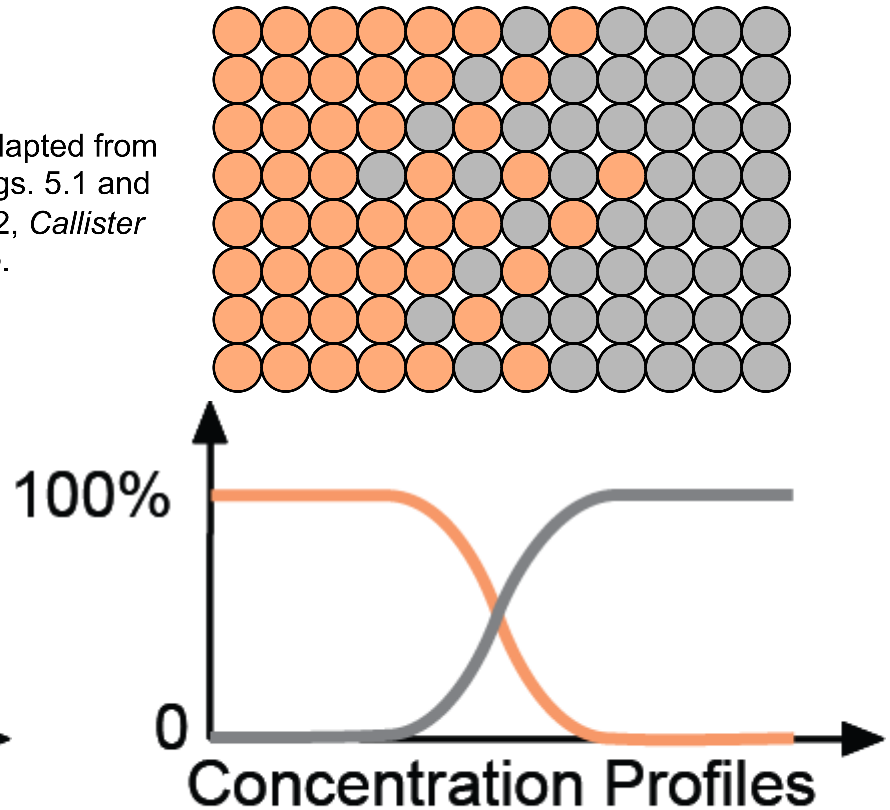
- Interdiffusion: In an alloy, atoms tend to migrate from regions of high conc. to regions of low conc.

Initially



Adapted from Figs. 5.1 and 5.2, *Callister 7e*.

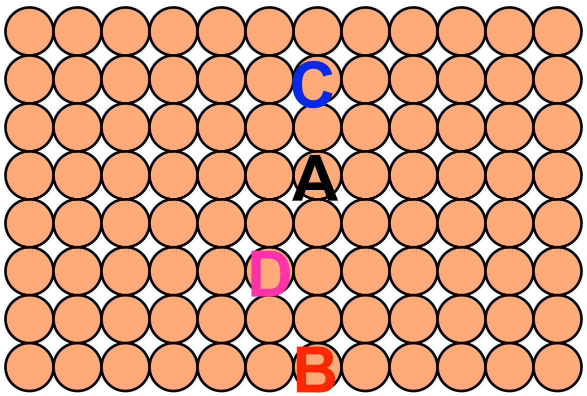
After some time



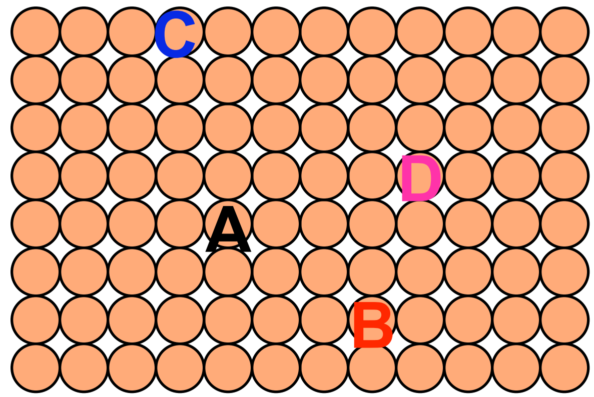
Diffusion

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

Label some atoms



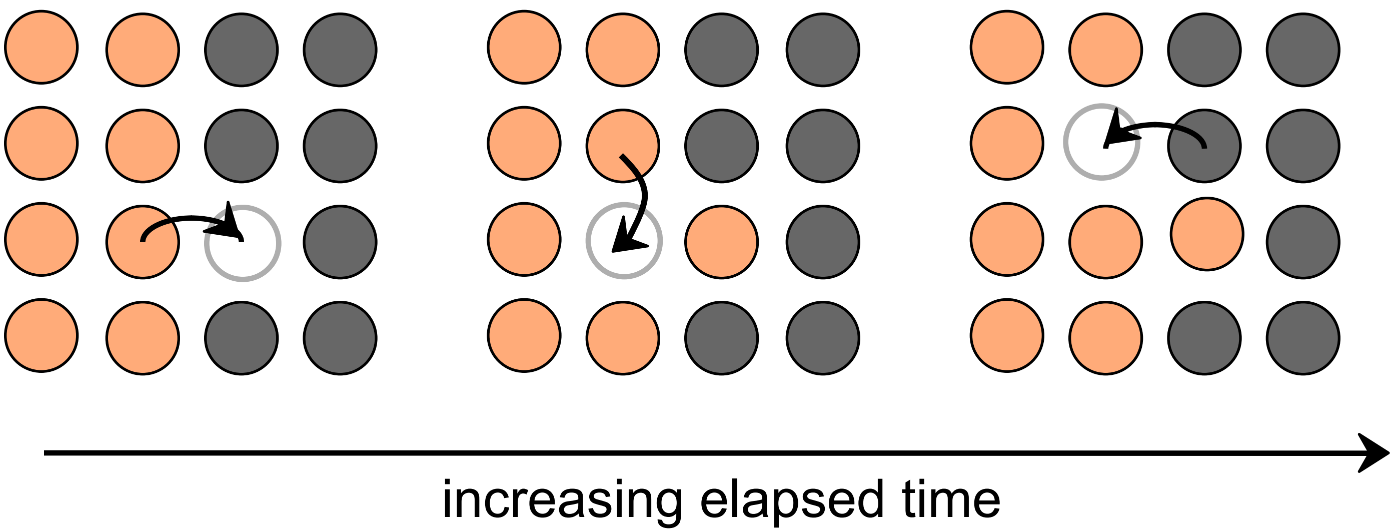
After some time



Diffusion Mechanisms

Vacancy Diffusion:

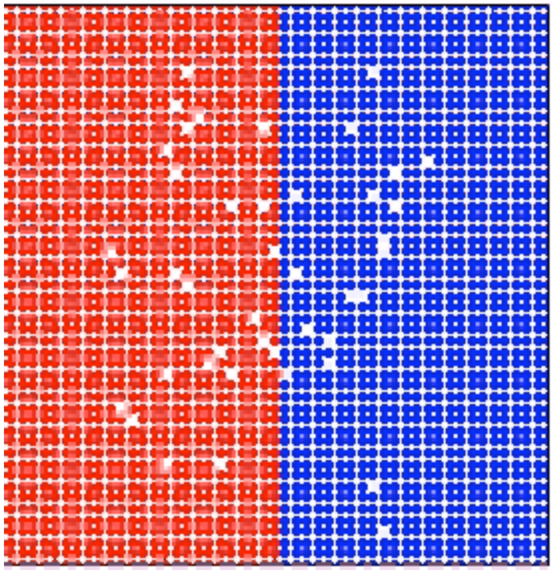
- atoms exchange with vacancies
- applies to substitutional impurities atoms
- rate depends on:
  - --number of vacancies
  - --activation energy to exchange.



Diffusion Simulation

- Simulation of interdiffusion across an interface:

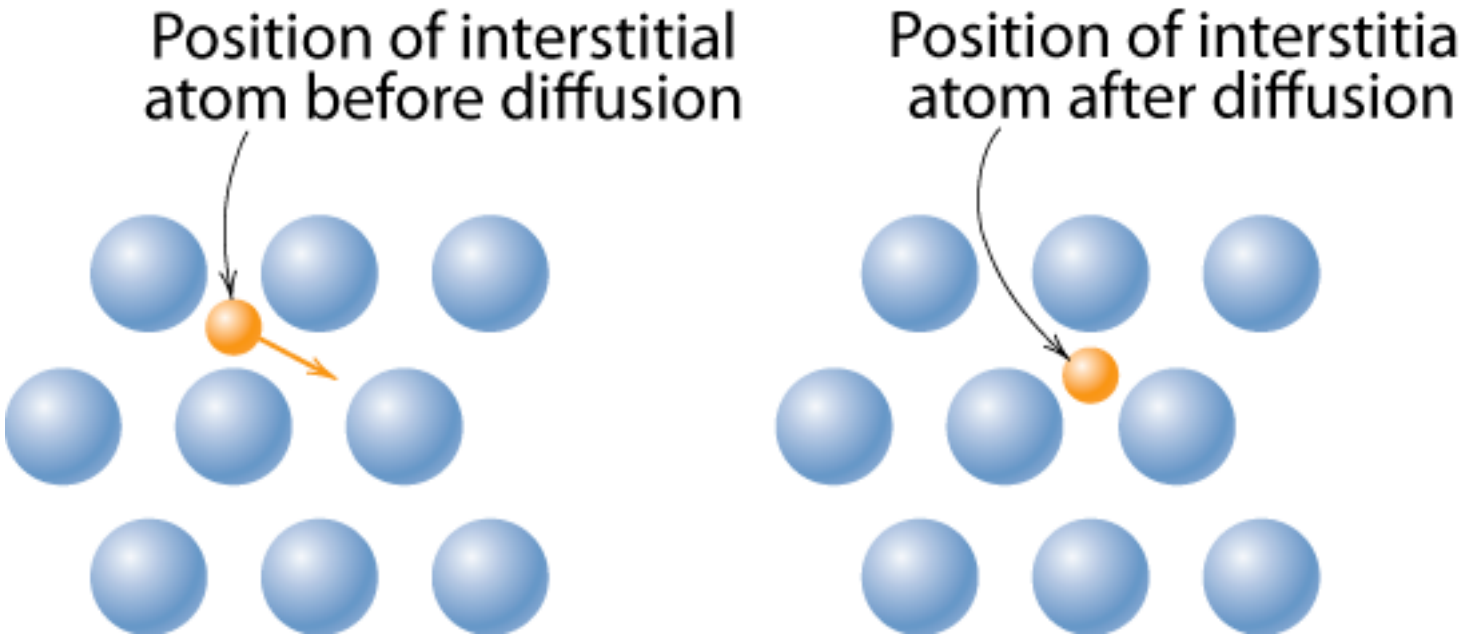
- Rate of substitutional diffusion depends on:
  --vacancy concentration
  --frequency of jumping.



(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.

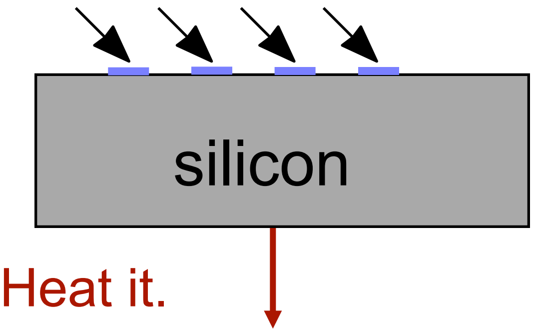
Adapted from chapter-opening photograph, Chapter 5, *Callister 7e.* (Courtesy of Surface Division, Midland-Ross.)

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

Processing Using Diffusion

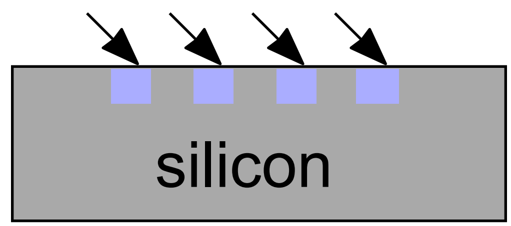
- Doping silicon with phosphorus for *n*-type semiconductors:
- Process:

1. Deposit P rich layers on surface.



2. Heat it.

3. Result: Doped semiconductor regions.



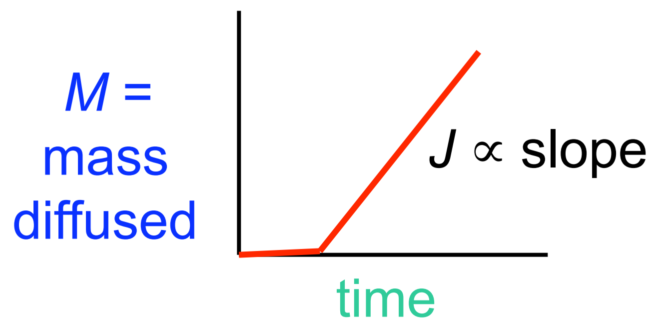
Diffusion

- 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

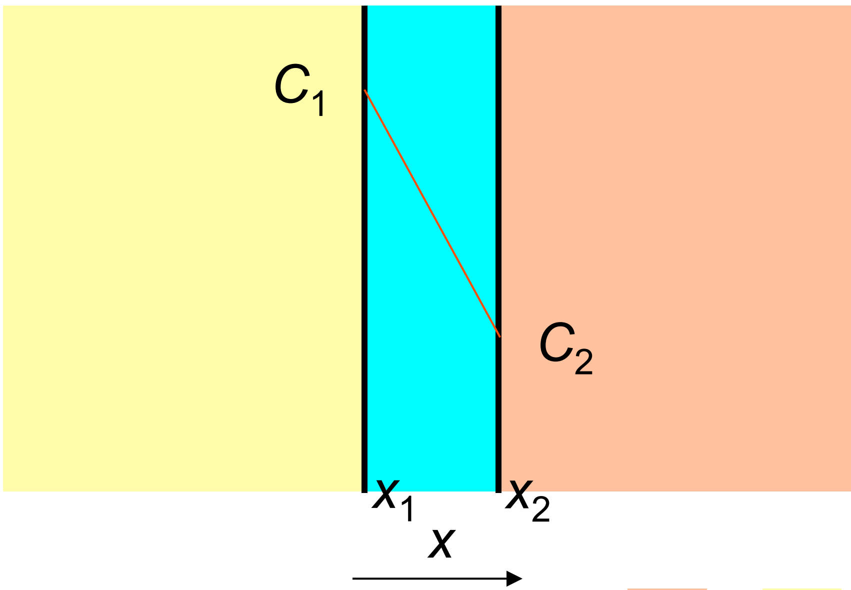
$$J = \frac{M}{At} = \frac{1}{A}\frac{dM}{dt}$$



Steady-State Diffusion

Rate of diffusion independent of time

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



Fick's first law of diffusion

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

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

$D \equiv$ 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:
    $D = 110 \times 10^{-8}\ cm^2/s$
  - surface concentrations: $C_1 = 0.44\ g/cm^3$
    $C_2 = 0.02\ g/cm^3$

Example (cont).

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]

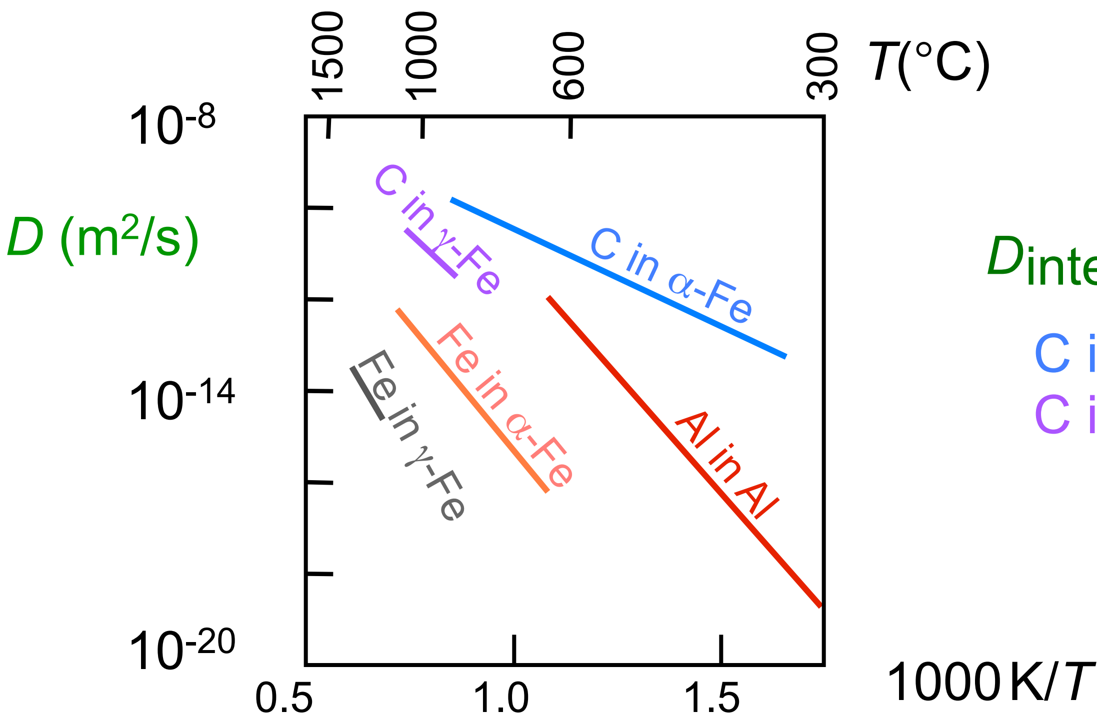
Q_d = activation energy [J/mol or eV/atom]

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

T = absolute temperature [K]

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 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.)

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

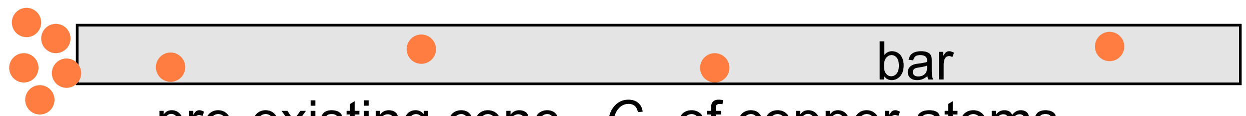
Fick's Second Law

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

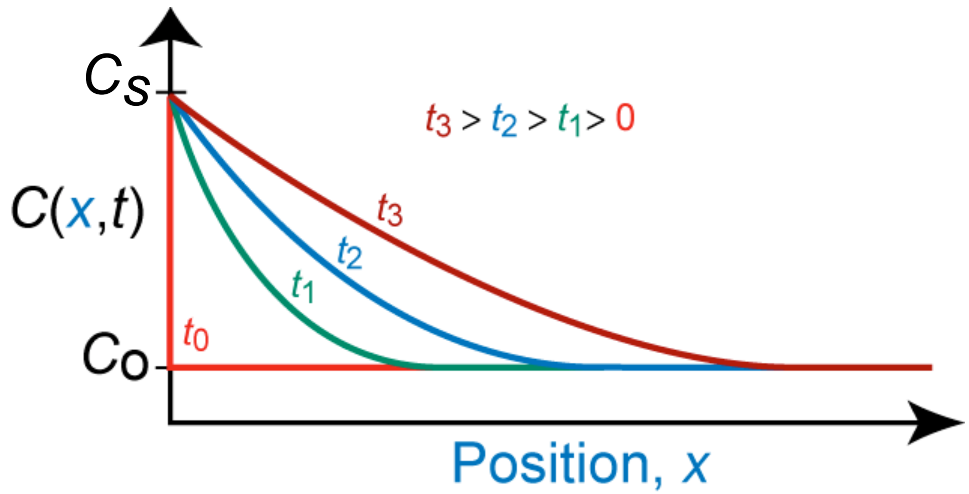
Non-steady State Diffusion

- Copper diffuses into a bar of aluminum.

Surface conc., C_S of Cu atoms



pre-existing conc., C_o of copper atoms



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:

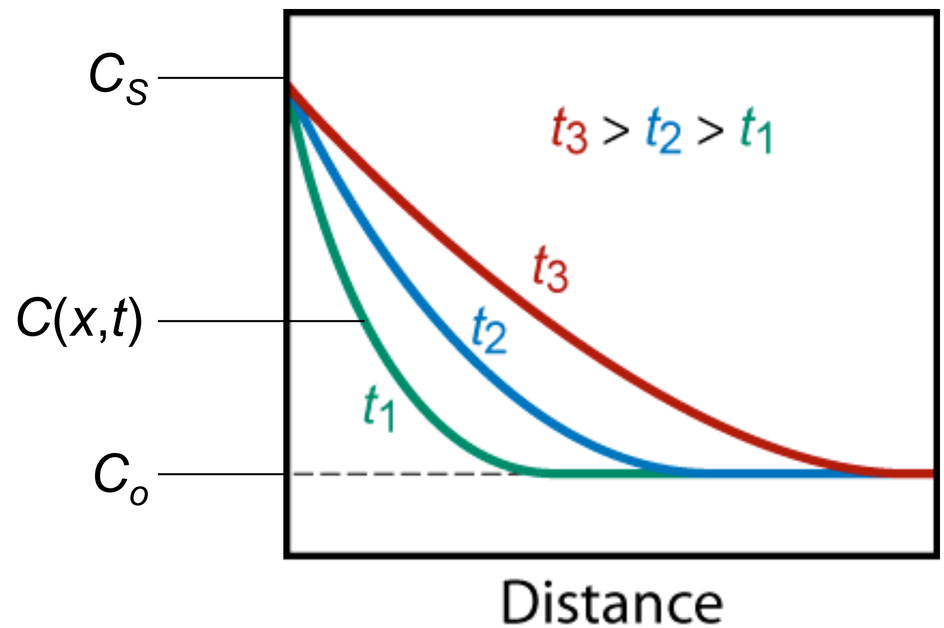
$$\frac{C(x,t)-C_o}{C_s-C_o}=1-\text{erf}\left(\frac{x}{2\sqrt{Dt}}\right)$$

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

erf (z) = error function

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

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.

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