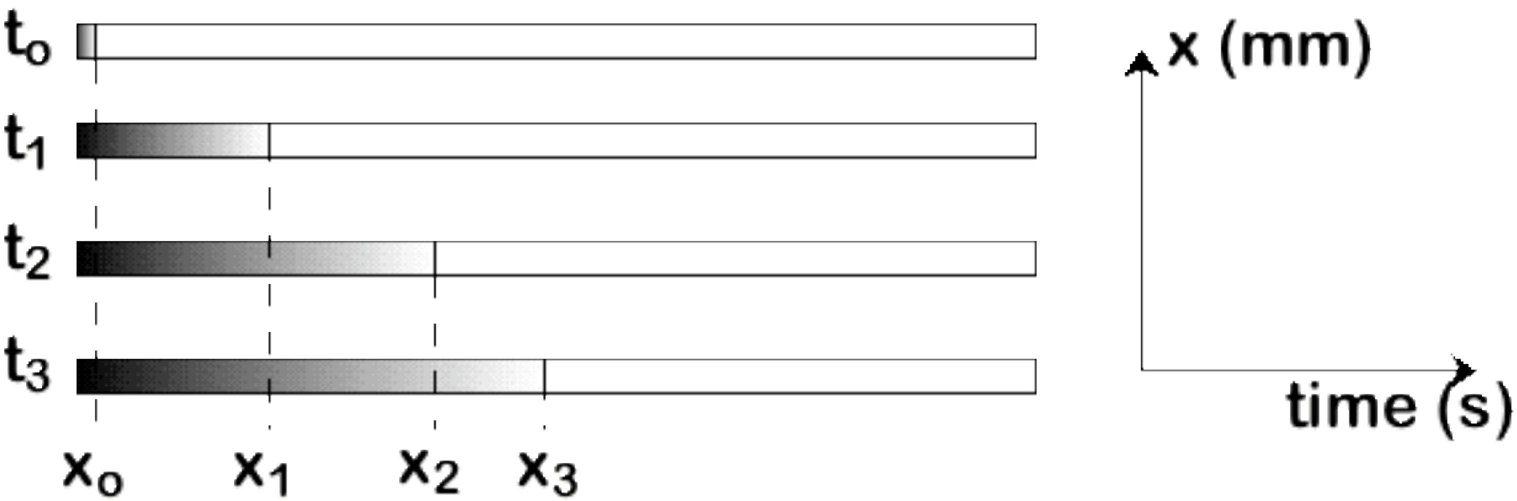
CHAPTER 5:
DIFFUSION IN SOLIDS

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 DEMO

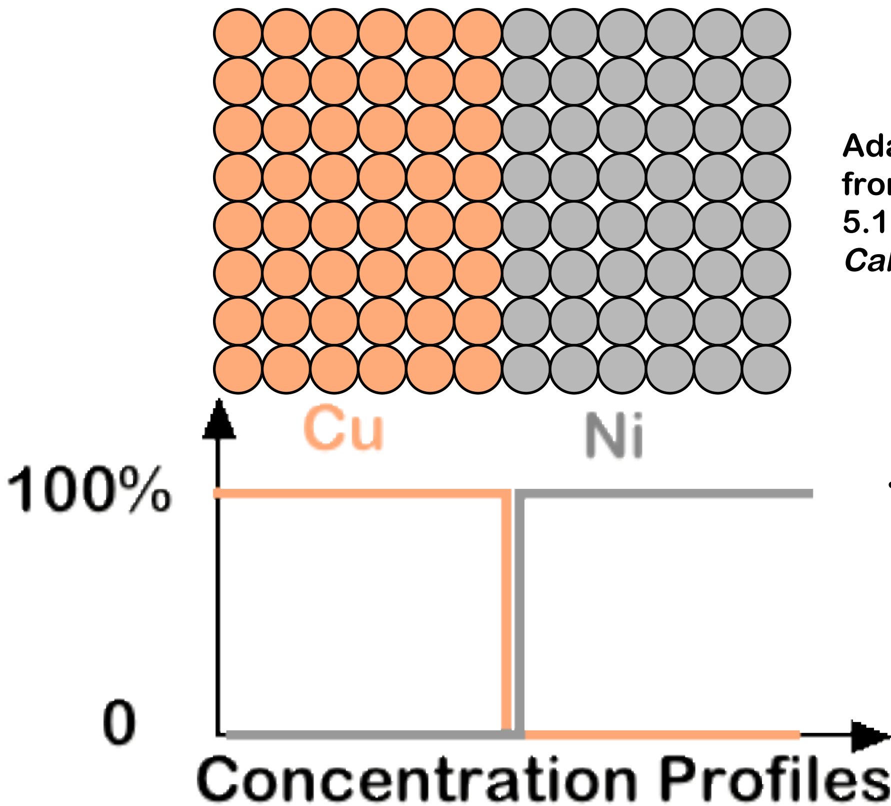
- Glass tube filled with water.
- At time t = 0, add some drops of ink to one end of the tube.
- Measure the diffusion distance, x, over some time.
- Compare the results with theory.



DIFFUSION: THE PHENOMENA (1)

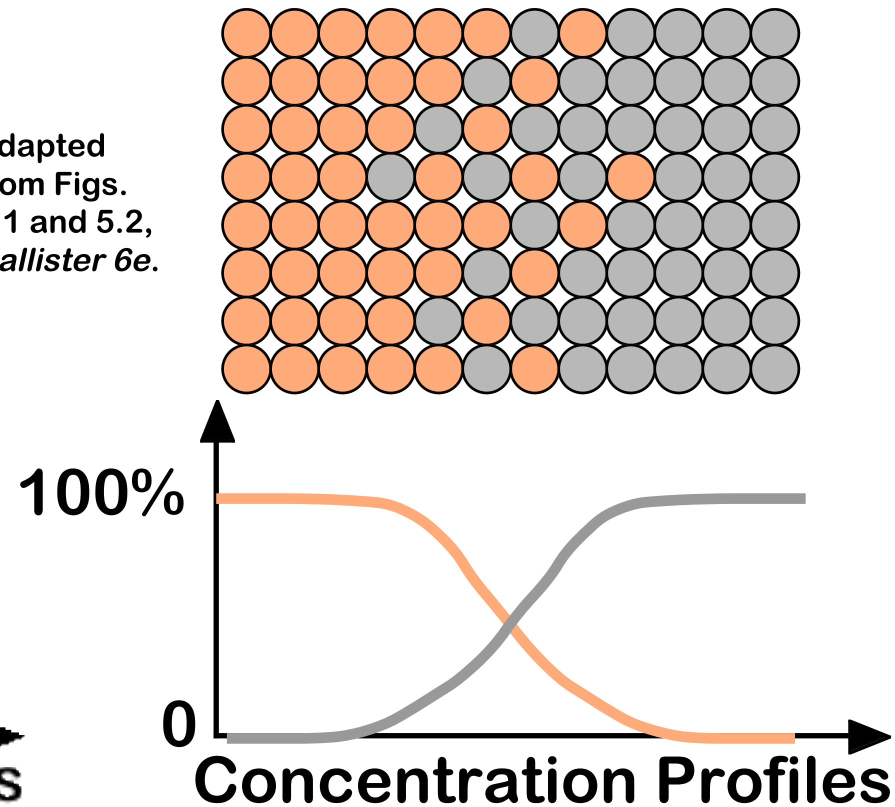
- **Interdiffusion**: In an alloy, atoms tend to migrate from regions of large concentration.

Initially



Adapted from Figs. 5.1 and 5.2, *Callister 6e.*

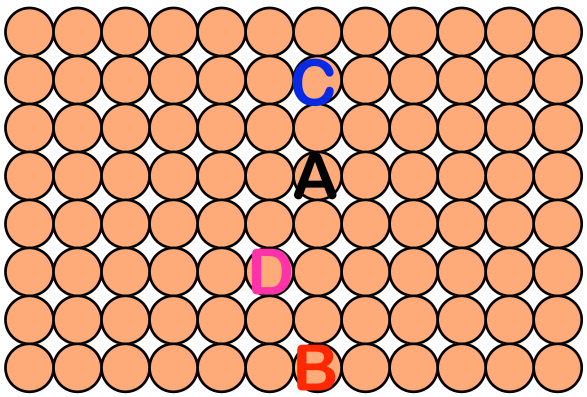
After some time



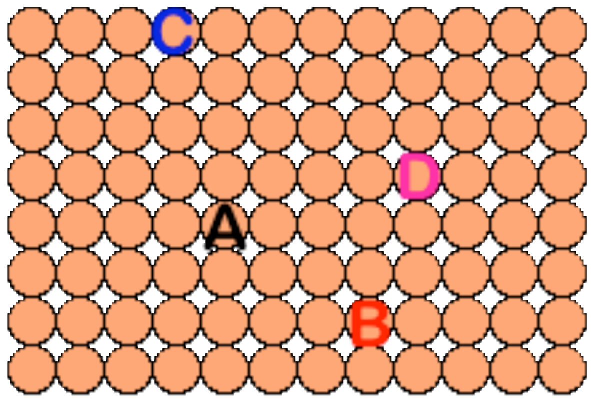
DIFFUSION: THE PHENOMENA (2)

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

Label some atoms



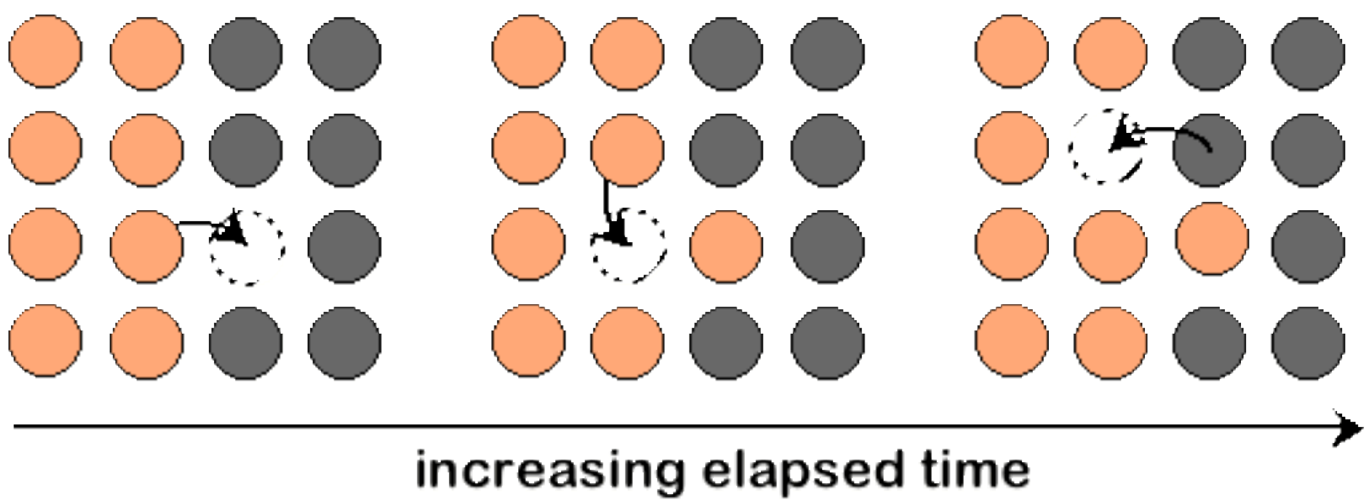
After some time



DIFFUSION MECHANISMS

Substitutional Diffusion:

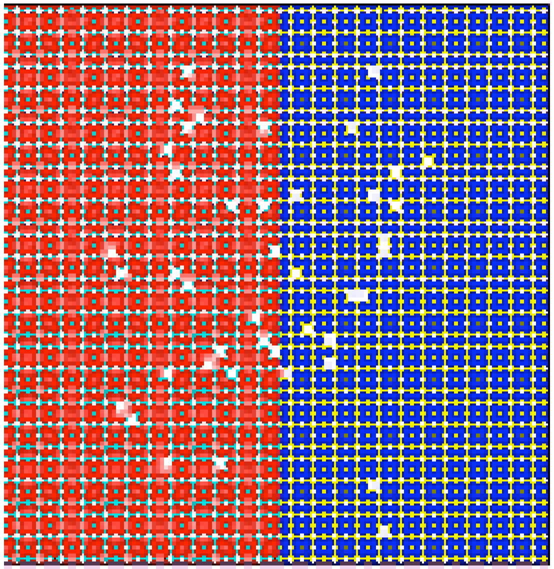
- applies to substitutional impurities
- atoms exchange with vacancies
- rate depends on:
  - --number of vacancies
  - --activation energy to exchange.



DIFFUSION SIMULATION

- Simulation of interdiffusion across an interface:

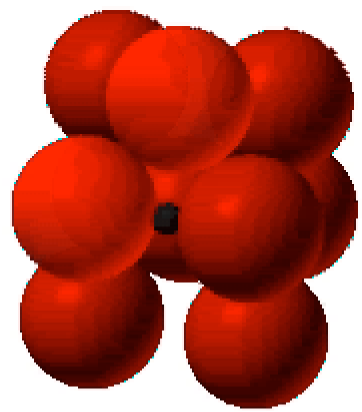
- Rate of substitutional diffusion depends on:
  --vacancy concentration
  --frequency of jumping.



(Courtesy P.M. Anderson)

INTERSTITIAL SIMULATION

- Applies to interstitial impurities.
- More rapid than vacancy diffusion.
- Simulation:
  --shows the jumping of a smaller atom (gray) from one interstitial site to another in a BCC structure. The interstitial sites considered here are at midpoints along the unit cell edges.



(Courtesy P.M. Anderson)

PROCESSING USING DIFFUSION (1)

- Case Hardening:
  --Diffuse carbon atoms into the host iron atoms at the surface.
  --Example of interstitial diffusion is a case hardened gear.

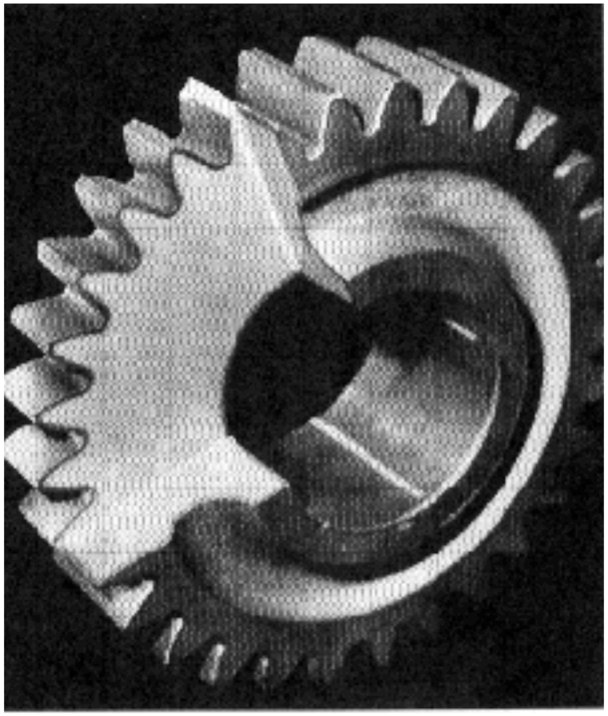
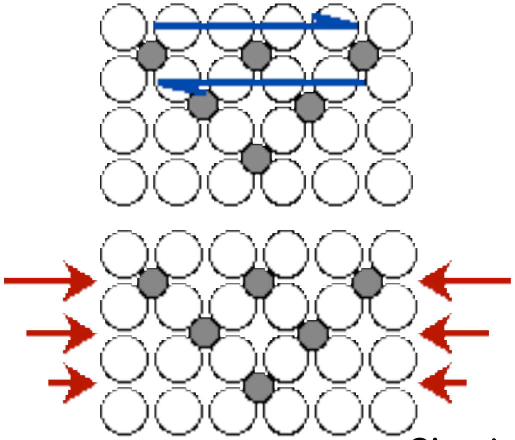


Fig. 5.0, *Callister 6e*. (Fig. 5.0 is courtesy of Surface Division, Midland-Ross.)

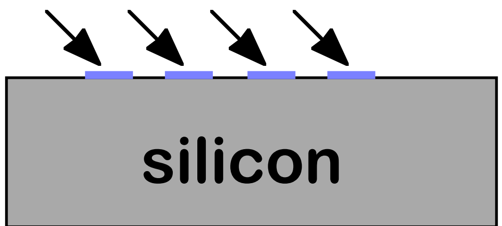
- Result: The "Case" is
  --hard to deform: C atoms "lock" planes from shearing.
  --hard to crack: C atoms put the surface in compression.



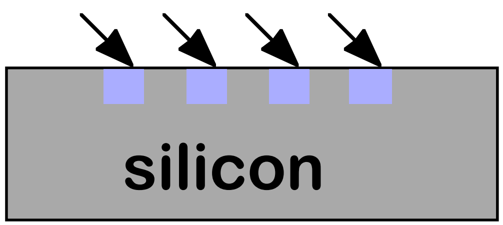
PROCESSING USING DIFFUSION (2)

- Doping Silicon with P for n-type semiconductors:
- Process:

1. Deposit P rich layers on surface.



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



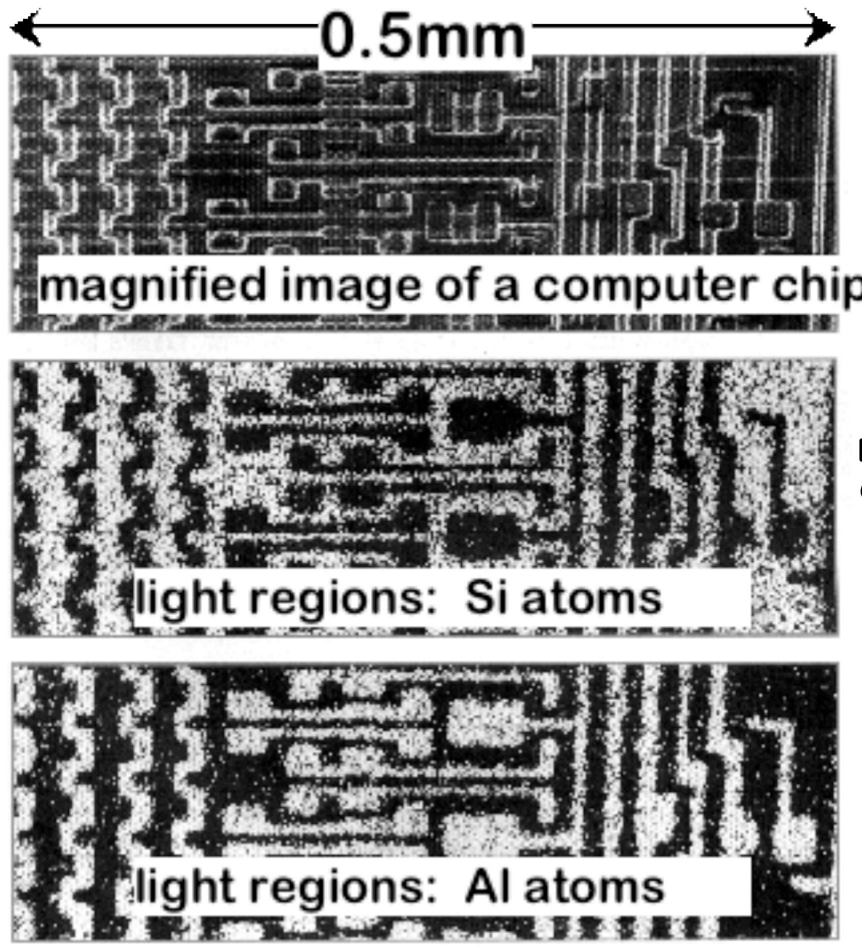
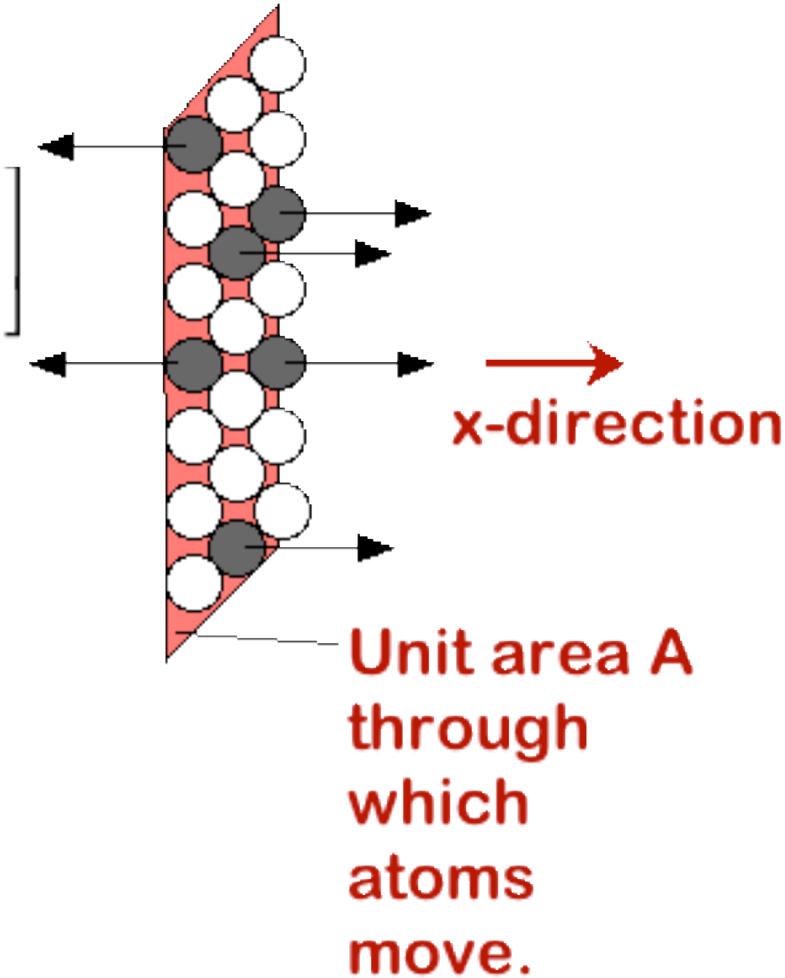


Fig. 18.0, *Callister 6e*.

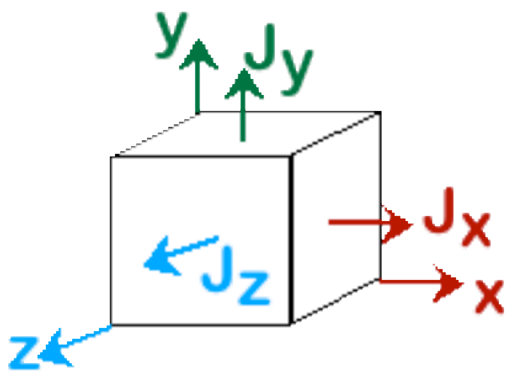
MODELING DIFFUSION: FLUX

• **Flux**:

$$J = \frac{1}{A}\frac{dM}{dt} \Rightarrow \left[\frac{kg}{m^2 s}\right] \text{ or } \left[\frac{atoms}{m^2 s}\right]$$



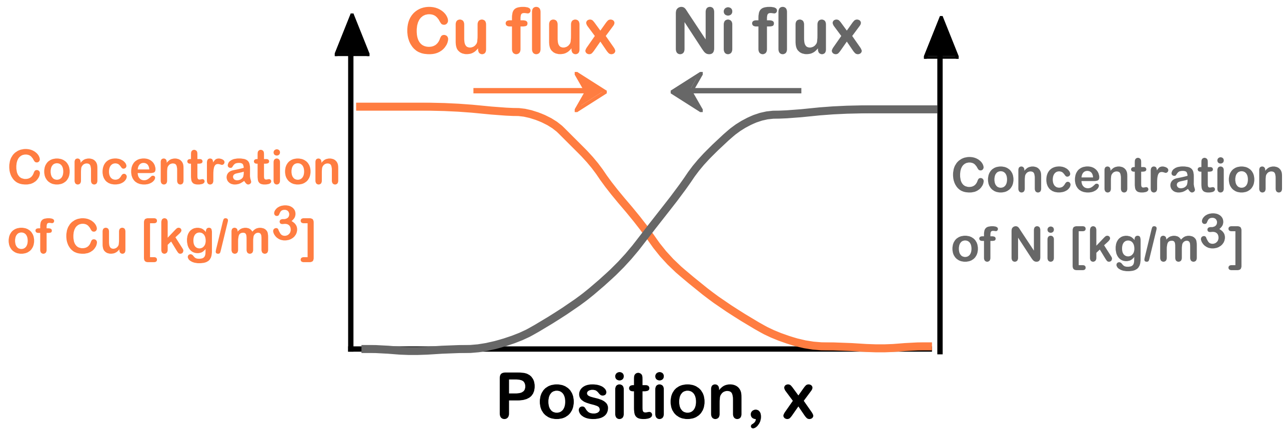
• Directional Quantity



• Flux can be measured for:
--vacancies
--host (A) atoms
--impurity (B) atoms

CONCENTRATION PROFILES & FLUX

- Concentration Profile, C(x): [kg/m^3]



Adapted from Fig. 5.2(c), *Callister 6e.*

- Fick's First Law:

flux in x-dir. [kg/m^2-s]

Diffusion coefficient [m^2/s]

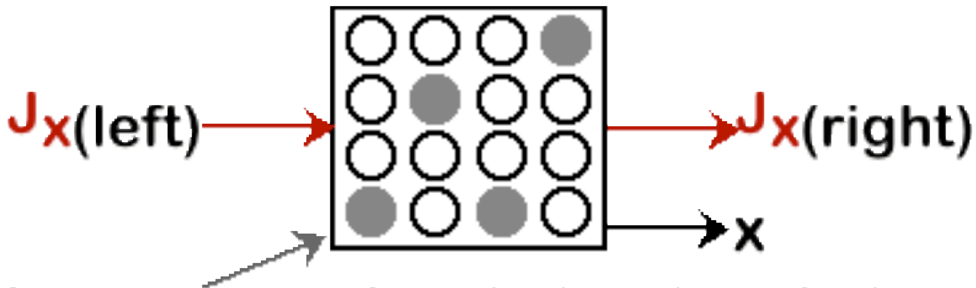
$$J_x = -D \frac{dC}{dx}$$

concentration gradient [kg/m^4]

- The steeper the concentration profile, the greater the flux!

STEADY STATE DIFFUSION

- **Steady State**: the concentration profile doesn't change with time.



Concentration, C, in the box doesn't change w/time.

Steady State:

$J_x(\text{left}) = J_x(\text{right})$

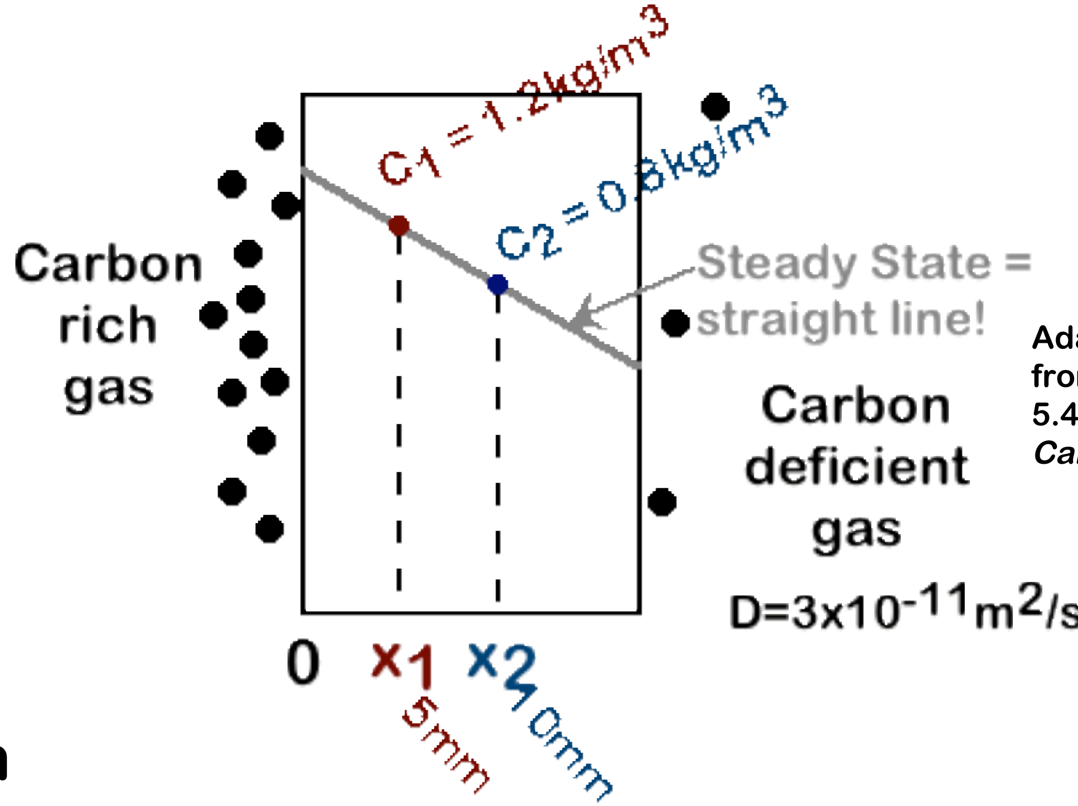
- Apply Fick's First Law: $J_x = -D\dfrac{dC}{dx}$

- If $J_x)_{left} = J_x)_{right}$, then $\left(\dfrac{dC}{dx}\right)_{left} = \left(\dfrac{dC}{dx}\right)_{right}$

- Result: the slope, dC/dx, must be constant (i.e., slope doesn't vary with position)!

EX: STEADY STATE DIFFUSION

- Steel plate at 700C with geometry shown:



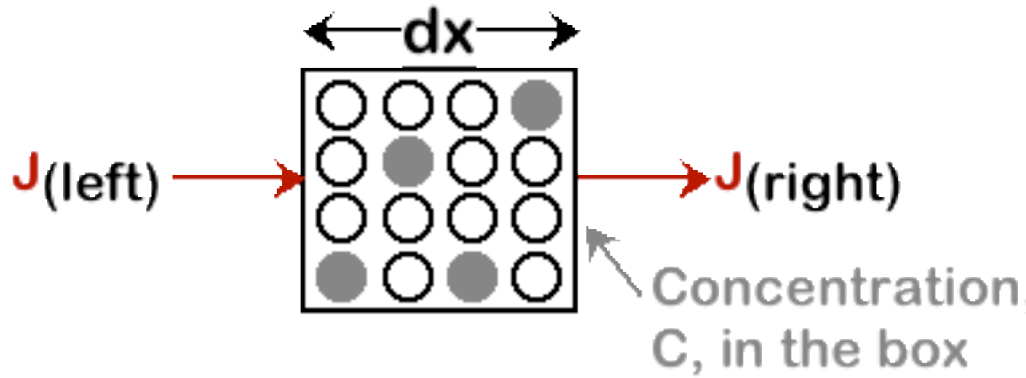
Adapted from Fig. 5.4, *Callister 6e.*

- Q: How much carbon transfers from the rich to the deficient side?

$$J = -D\frac{C_2 - C_1}{x_2 - x_1} = 2.4 \times 10^{-9} \frac{kg}{m^2 s}$$

NON STEADY STATE DIFFUSION

- Concentration profile, C(x), changes w/ time.



- To conserve matter:

$$\frac{J(\text{right}) - J(\text{left})}{dx} = -\frac{dC}{dt}$$

$$\frac{dJ}{dx} = -\frac{dC}{dt}$$

- Fick's First Law:

$$J = -D\frac{dC}{dx} \quad \text{or}$$

$$\frac{dJ}{dx} = -D\frac{d^2C}{dx^2}$$

(if D does not vary with x)

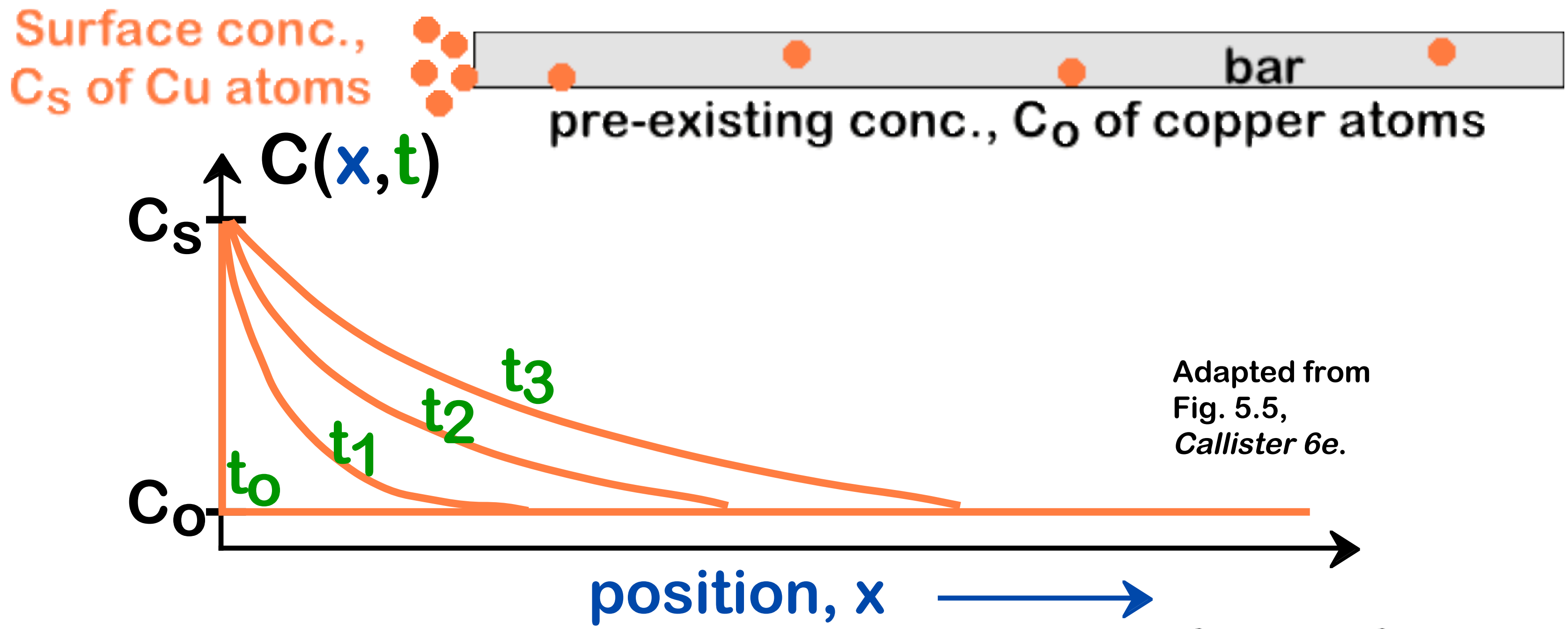
equate

- Governing Eqn.:

$$\frac{dC}{dt} = D\frac{d^2C}{dx^2}$$

EX: NON STEADY STATE DIFFUSION

- Copper diffuses into a bar of aluminum.



Adapted from Fig. 5.5, *Callister 6e.*

- General solution:

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

"error function"

Values calibrated in Table 5.1, *Callister 6e.*

PROCESSING QUESTION

- Copper diffuses into a bar of aluminum.
- 10 hours at 600C gives desired C(x).
- How many hours would it take to get the same C(x) if we processed at 500C?

Key point 1: $C(x,t_{500C}) = C(x,t_{600C})$.
Key point 2: Both cases have the same C_o and C_s.

- Result: Dt should be held constant.

$$\frac{C(x,t)-C_o}{C_s-C_o} = 1-\mathrm{erf}\left(\frac{x}{\sqrt{2Dt}}\right) \longrightarrow (Dt)_{500°C} = (Dt)_{600°C}$$

- Answer:

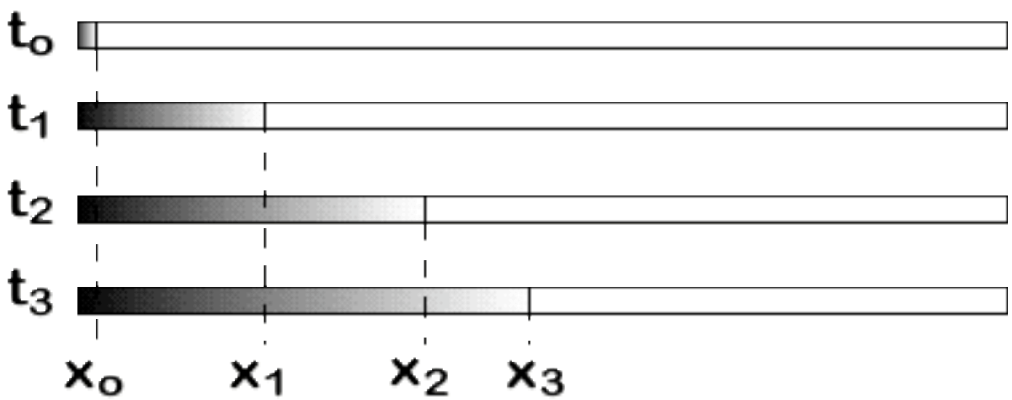
$$t_{500} = \frac{(Dt)_{600}}{D_{500}} = 110\,\mathrm{hr}$$

($D_{600} = 5.3\times10^{-13}\,\mathrm{m^2/s}$, $t_{600} = 10\,\mathrm{hrs}$, $D_{500} = 4.8\times10^{-14}\,\mathrm{m^2/s}$)

Note: values of D are provided here.

DIFFUSION DEMO: ANALYSIS

- The experiment: we recorded combinations of
  t and x that kept C constant.

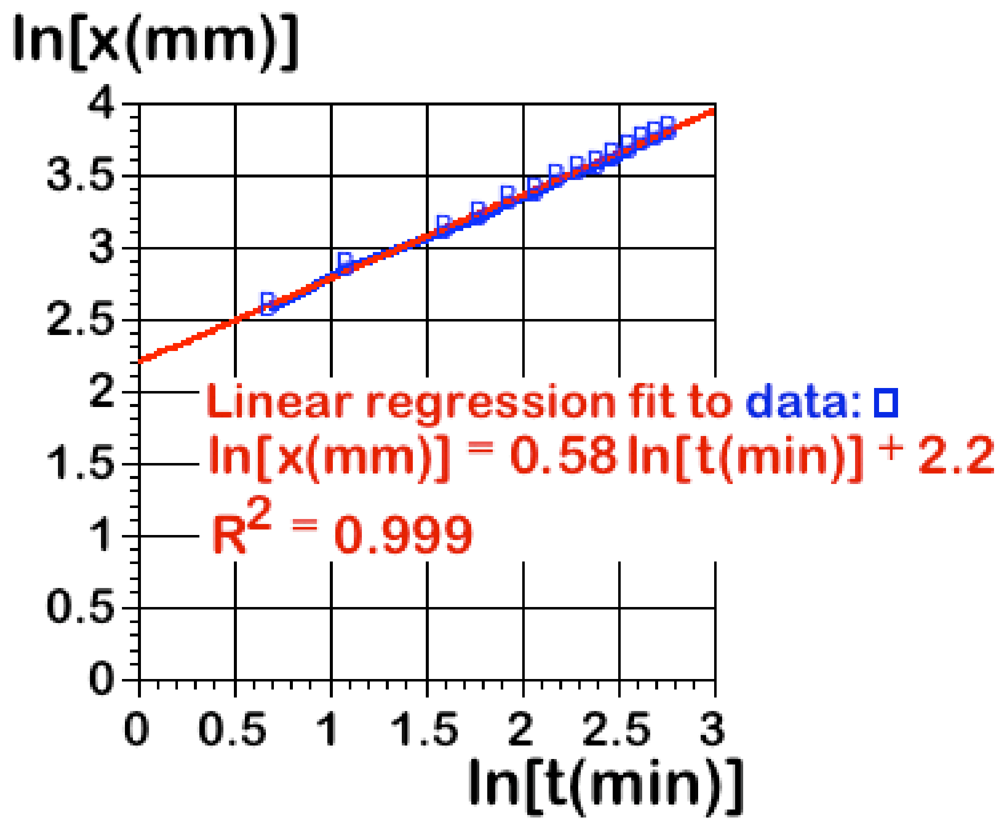


$$\frac{C(x_i,t_i) - C_o}{C_s - C_o} = 1 - \mathrm{erf}\left(\frac{x_i}{2\sqrt{Dt_i}}\right) = \text{(constant here)}$$

- Diffusion depth given by:

$$x_i \propto \sqrt{Dt_i}$$

DATA FROM DIFFUSION DEMO



- Experimental result: $x \sim t^{0.58}$
- Theory predicts $x \sim t^{0.50}$
- Reasonable agreement!

DIFFUSION AND TEMPERATURE

- Diffusivity increases with T.

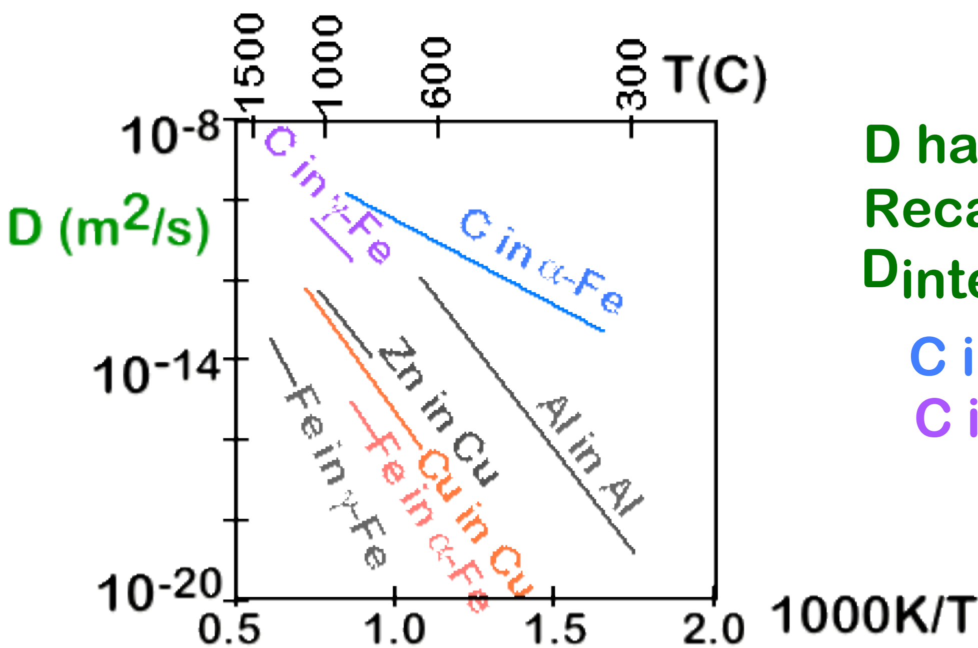
pre-exponential [m^2/s] (see Table 5.2, *Callister 6e*)

activation energy [J/mol],[eV/mol] (see Table 5.2, *Callister 6e*)

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

gas constant [8.31J/mol-K]

- Experimental Data:



D has exp. dependence on T
Recall: Vacancy does also!
$D_{interstitial} >> D_{substitutional}$

C in α-Fe
C in γ-Fe

Cu in Cu
Al in Al
Fe in α-Fe
Fe in γ-Fe
Zn in Cu

Adapted from Fig. 5.7, *Callister 6e*. (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.)

SUMMARY:
STRUCTURE & DIFFUSION

Diffusion FASTER for...

- open crystal structures
- lower melting T materials
- materials w/secondary bonding
- smaller diffusing atoms
- cations
- lower density materials

Diffusion SLOWER for...

- close-packed structures
- higher melting T materials
- materials w/covalent bonding
- larger diffusing atoms
- anions
- higher density materials

ANNOUNCEMENTS

Reading:

Core Problems:

Self-help Problems: