

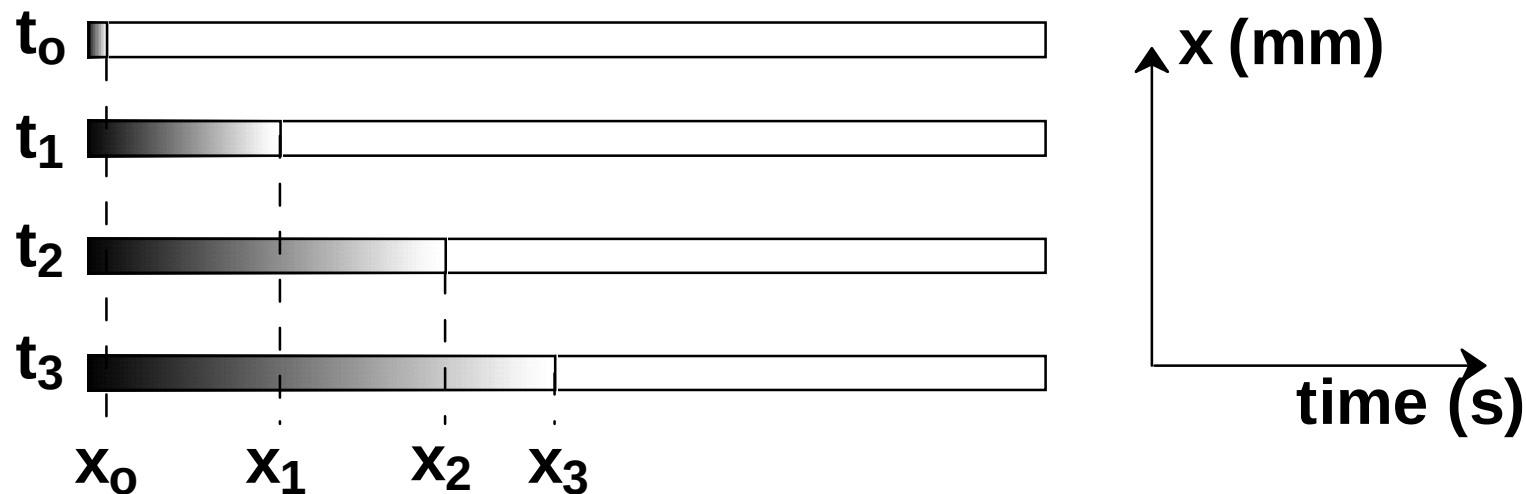
CHAPTER 5: DIFFUSION IN SOLIDS

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?**

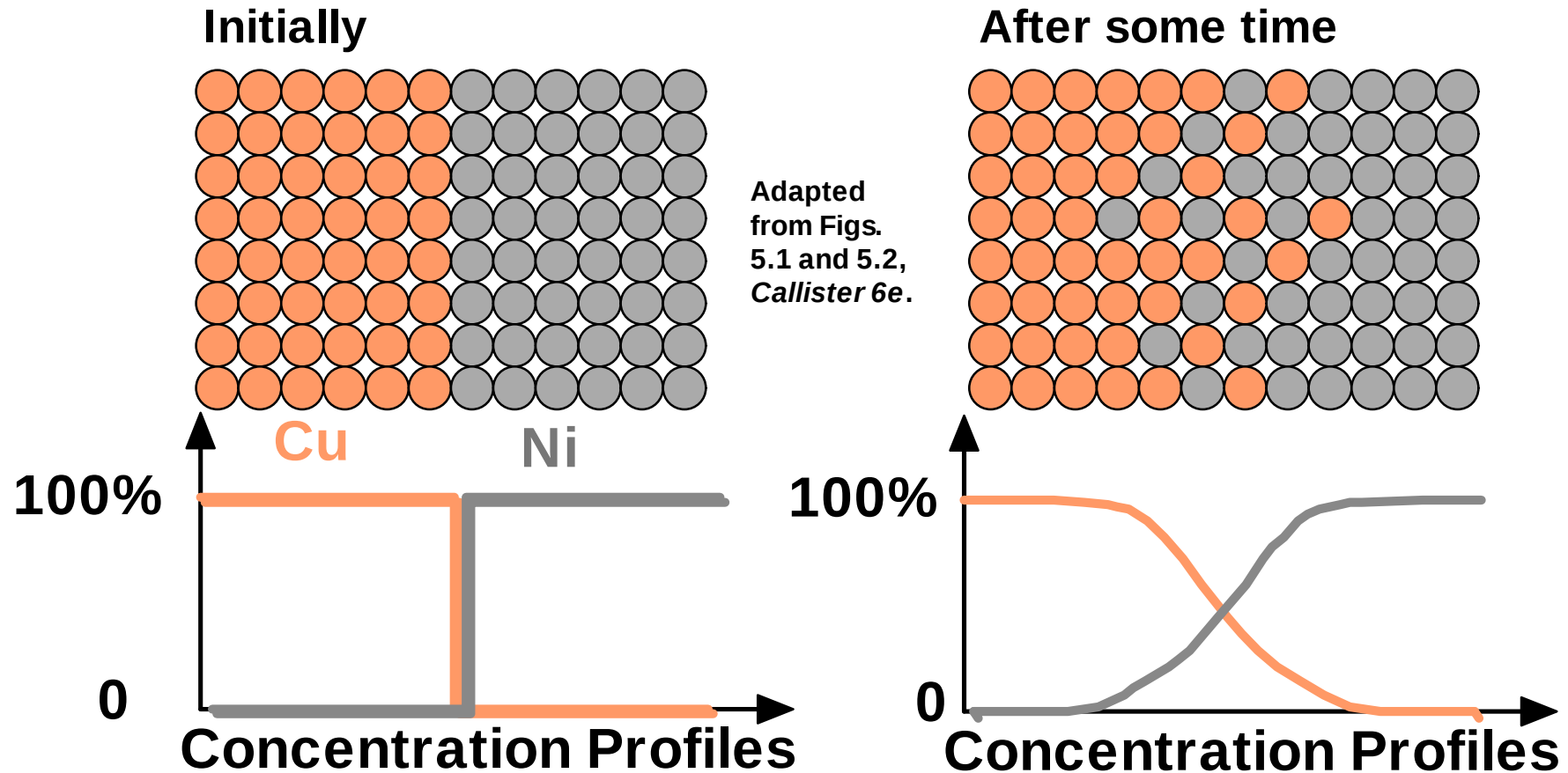
DIFFUSION DEMO

- 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)

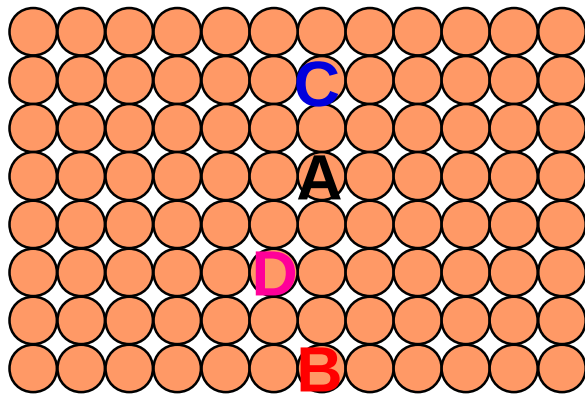
- **Interdiffusion:** In an alloy, atoms tend to migrate from regions of large concentration.



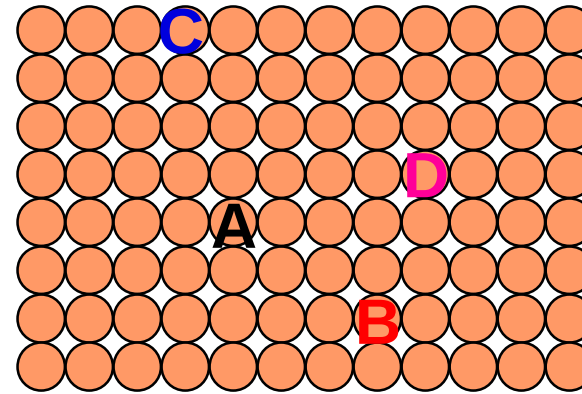
DIFFUSION: THE PHENOMENA (2)

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

Label some atoms



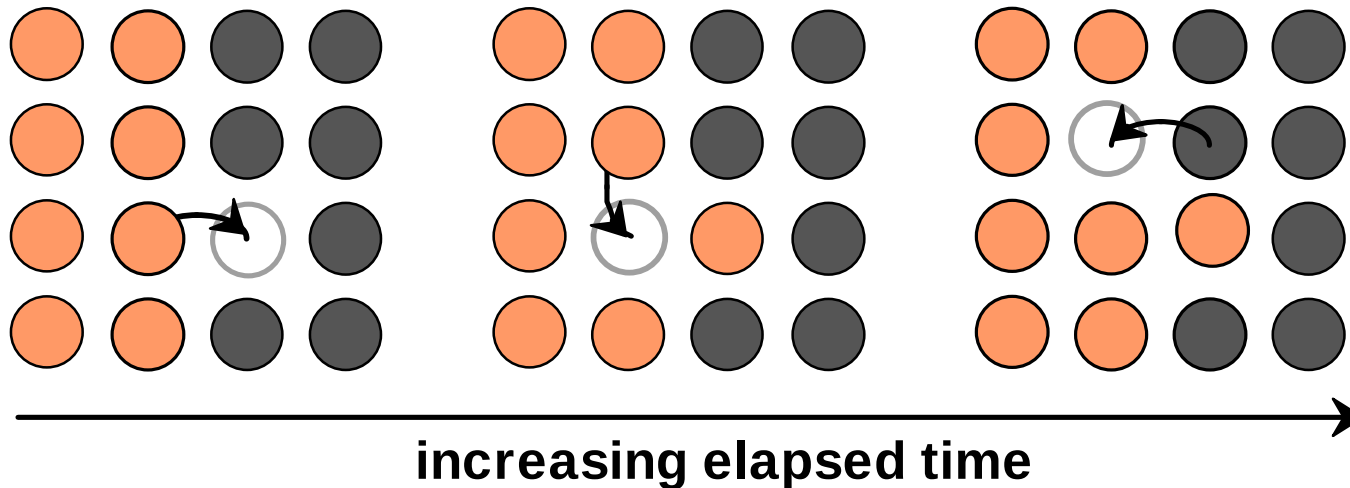
After some time



DIFFUSION MECHANISMS

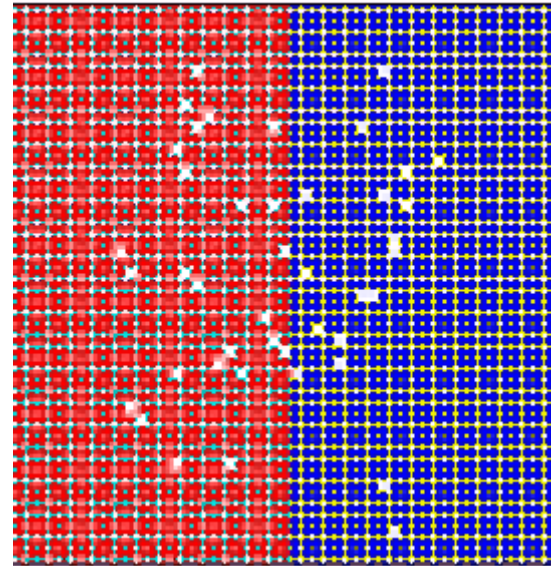
Substitutional Diffusion:

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



DIFFUSION SIMULATION

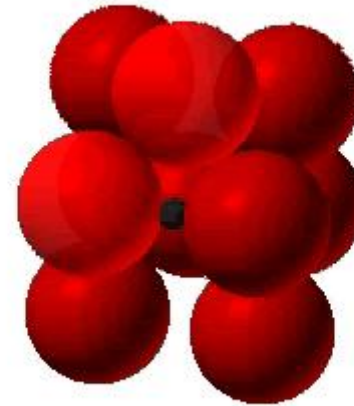
- Simulation of interdiffusion across an interface:
- Rate of substitutional diffusion depends on:
 - vacancy concentration
 - frequency of jumping.



(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.



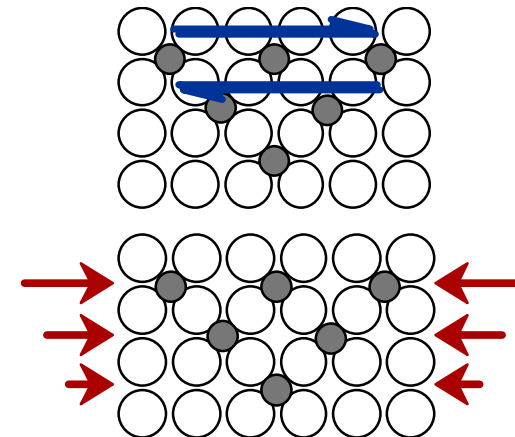
(Courtesy P.M. Anderson)

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



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

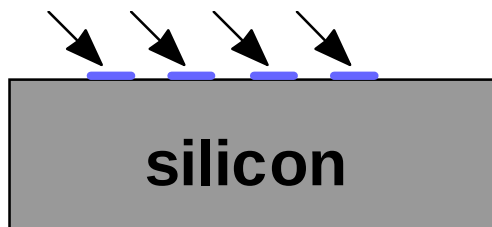


PROCESSING USING DIFFUSION (2)

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

- **Process:**

1. Deposit **P** rich layers on surface.



2. **Heat it.**

3. Result: Doped semiconductor regions.

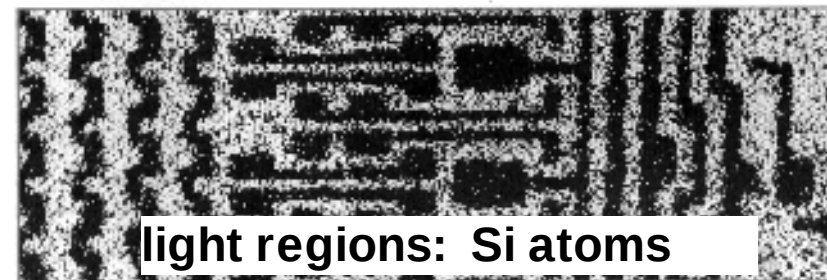
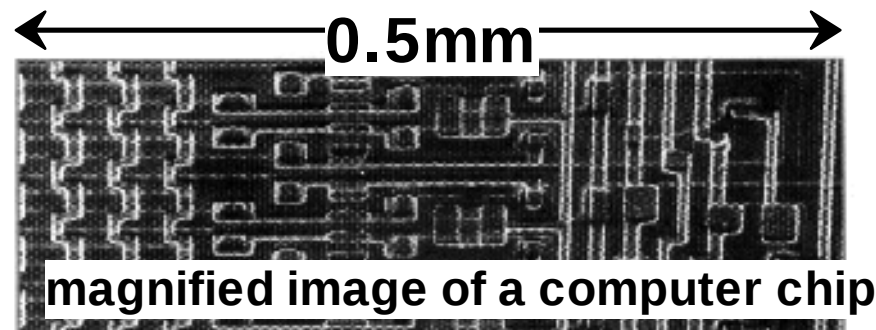
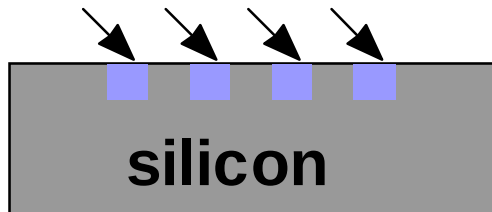


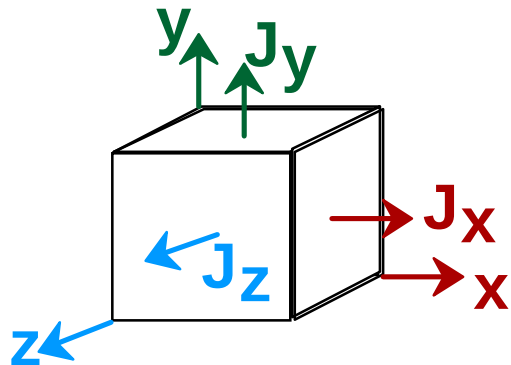
Fig. 18.0,
Callister 6e.

MODELING DIFFUSION: FLUX

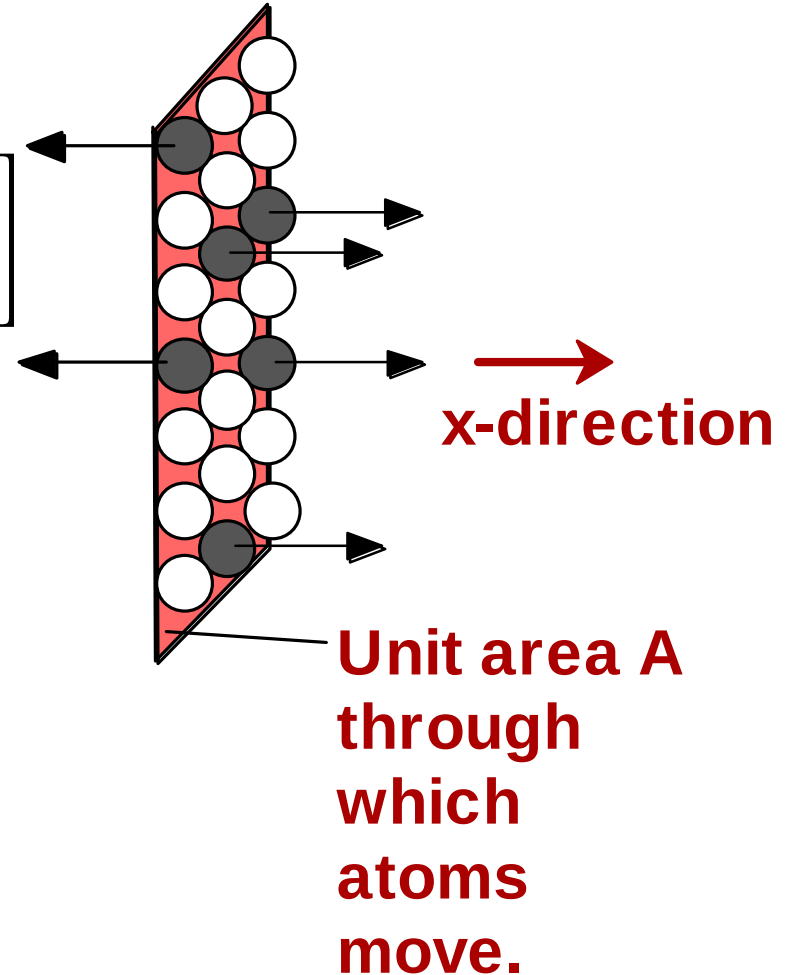
- **Flux:**

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

- **Directional Quantity**

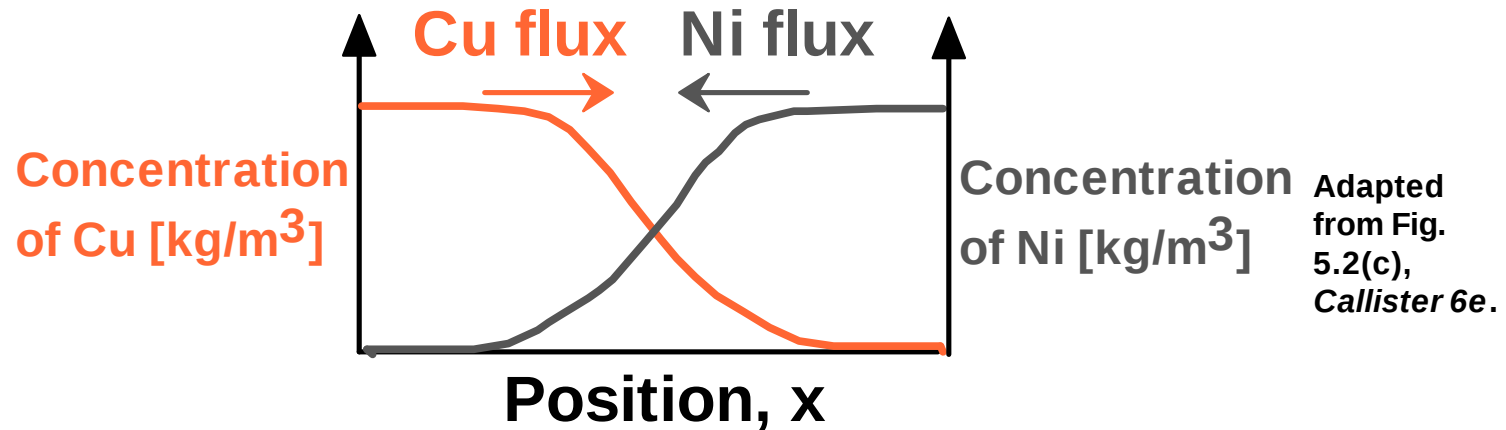


- Flux can be measured for:
 - vacancies
 - host (A) atoms
 - impurity (B) atoms



CONCENTRATION PROFILES & FLUX

- **Concentration Profile, $C(x)$: [kg/m³]**



- **Fick's First Law:**

flux in x-dir. [kg/m²-s] $\rightarrow$ $J_x = -D \frac{dC}{dx}$

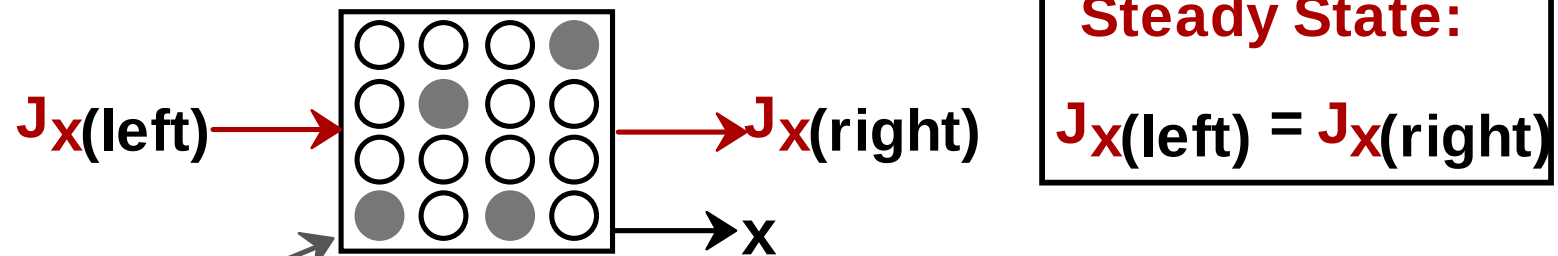
Diffusion coefficient [m²/s] $\rightarrow$ D

concentration gradient [kg/m⁴] $\rightarrow$ $\frac{dC}{dx}$

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

STEADY STATE DIFFUSION

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

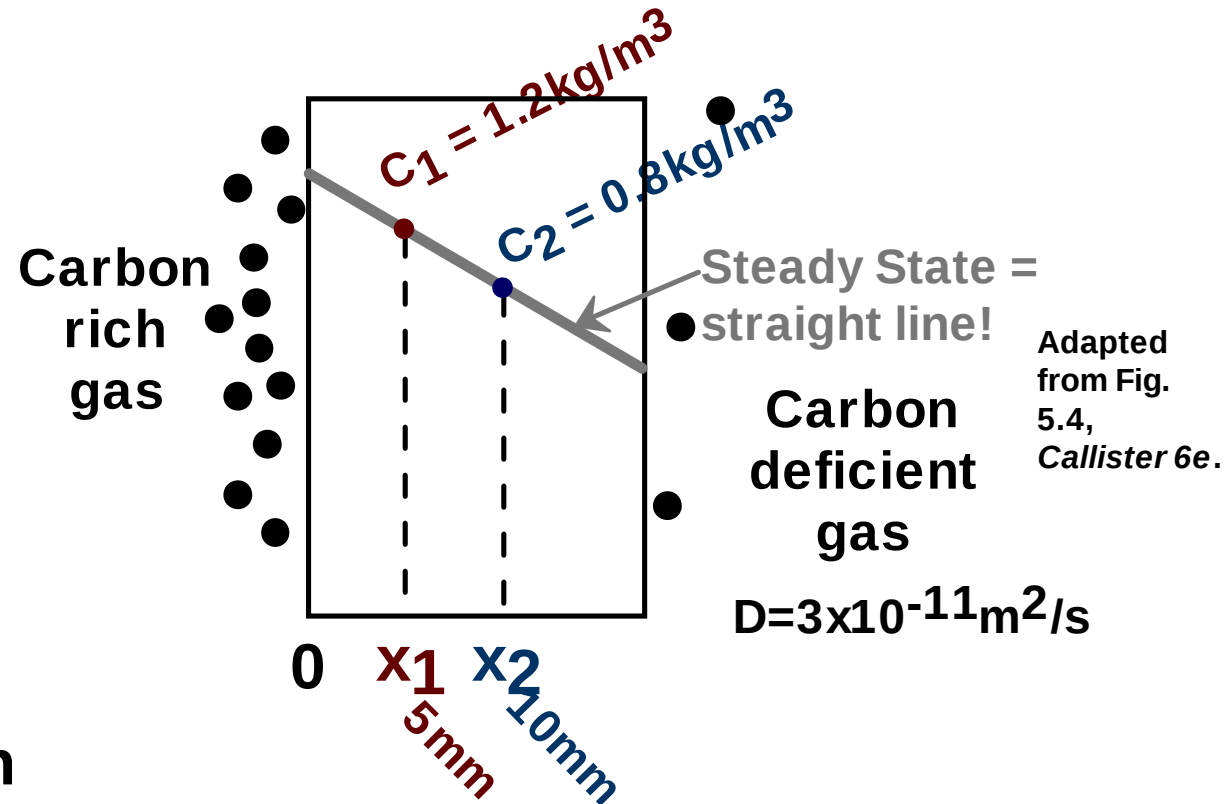


Concentration, C , in the box doesn't change w/time.

- Apply Fick's First Law: $J_x = -D \frac{dC}{dx}$
- If $J_x(\text{left}) = J_x(\text{right})$, then $\left(\frac{dC}{dx} \right)_{\text{left}} = \left(\frac{dC}{dx} \right)_{\text{right}}$
- 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:

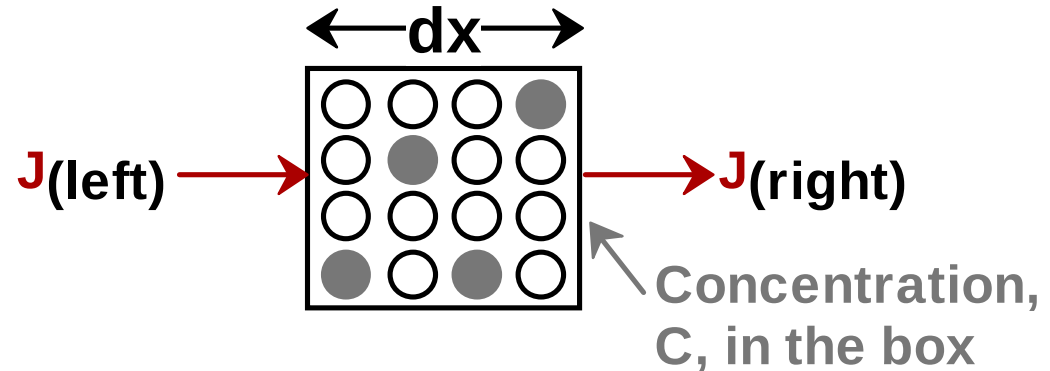


- Q: How much carbon transfers from the rich to the deficient side?

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

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:

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

$$\frac{dJ}{dx} = -D \frac{d^2C}{dx^2} \quad (\text{if } D \text{ does not vary with } x)$$

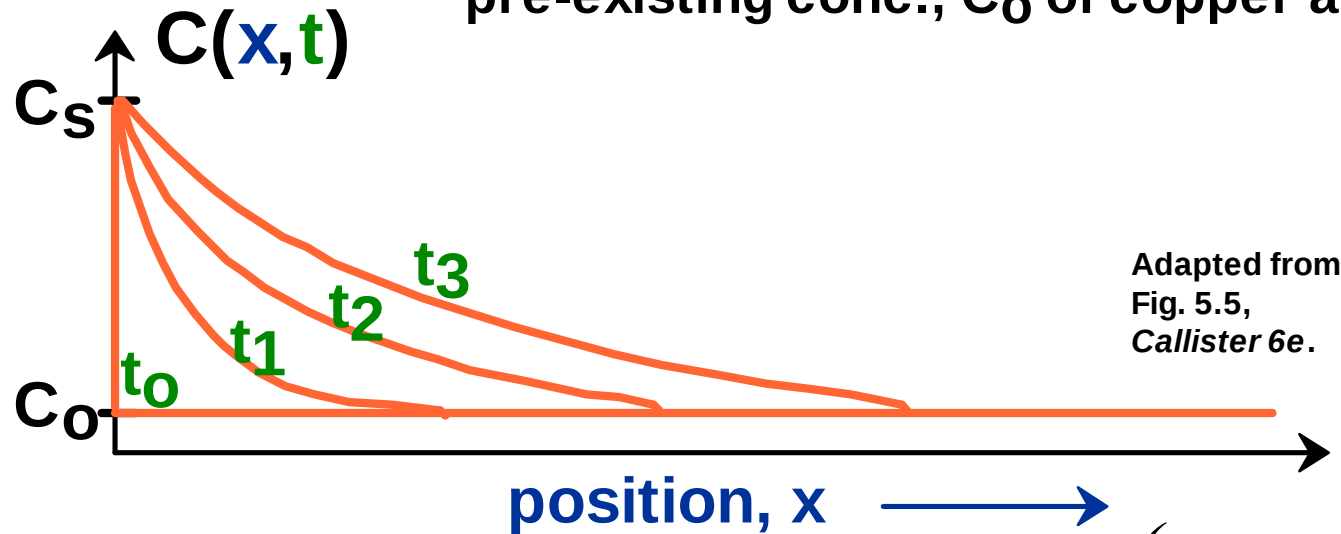
equate

- Governing Eqn.:

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

EX: NON STEADY STATE DIFFUSION

- Copper diffuses into a bar of aluminum.



- General solution:

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

"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.

$$\frac{C(x, t) - C_o}{C_s - C_o} = 1 - \operatorname{erf}\left(\frac{x}{\sqrt{2Dt}}\right) \rightarrow (Dt)_{500^\circ\text{C}} = (Dt)_{600^\circ\text{C}}$$

• Answer: $t_{500} = \frac{(Dt)_{600}}{D_{500}} = 110 \text{ hr}$

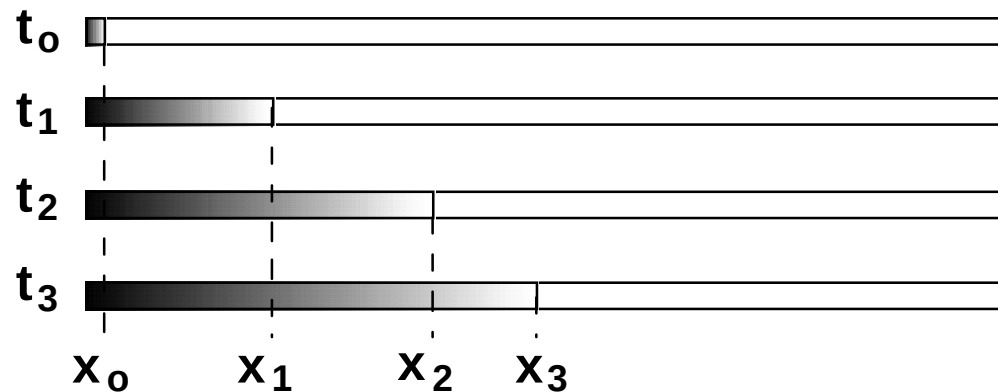
Annotations for the equation above:

- $5.3 \times 10^{-13} \text{ m}^2/\text{s}$ points to $(Dt)_{600}$
- 10 hrs points to $(Dt)_{600}$
- $4.8 \times 10^{-14} \text{ m}^2/\text{s}$ points to D_{500}

Note: values of D are provided here.

DIFFUSION DEMO: ANALYSIS

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

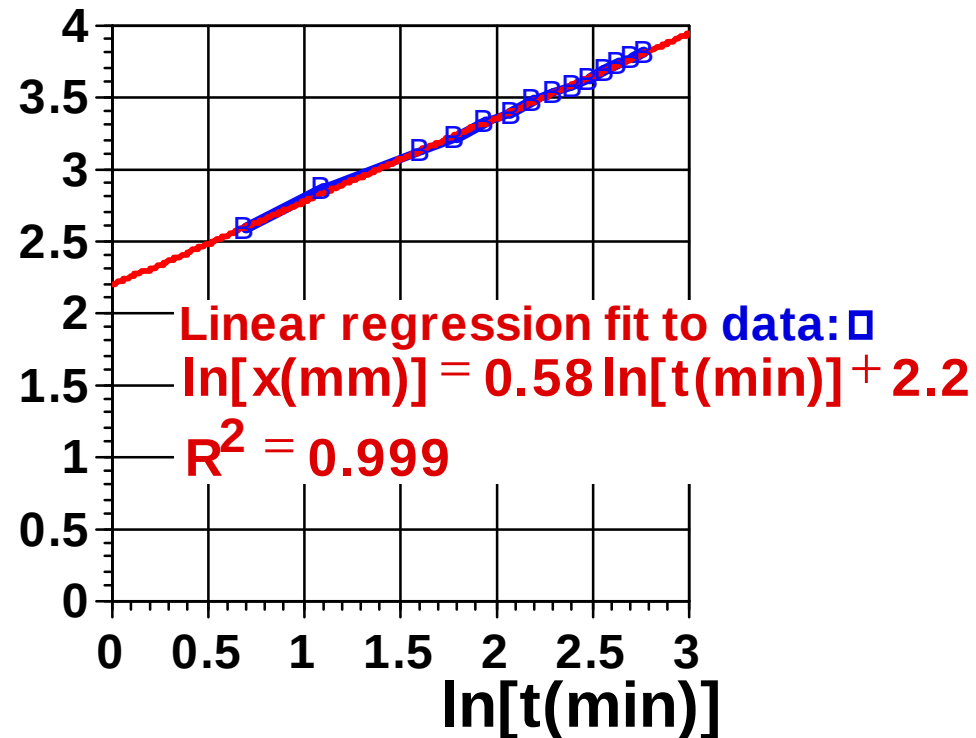


$$\frac{C(x_i, t_i) - C_0}{C_S - C_0} = 1 - \operatorname{erf} \left(\frac{x_i}{2\sqrt{Dt_i}} \right) = \text{(constant here)}$$

- 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.

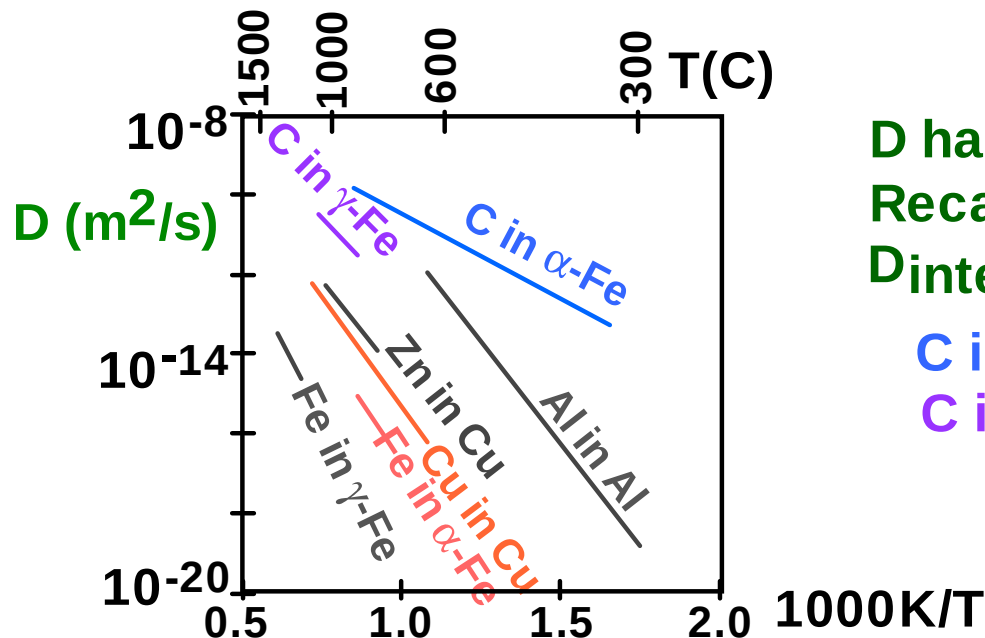
diffusivity $D = D_0 \exp \left(-\frac{Q_d}{RT} \right)$

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

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

gas constant [8.31 J/mol-K]

- Experimental Data:



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

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