Chapter 5
DIFFUSION IN SOLIDS

ISSUES TO ADDRESS...

1. How does diffusion occur?

2. Why is it an important of processing?

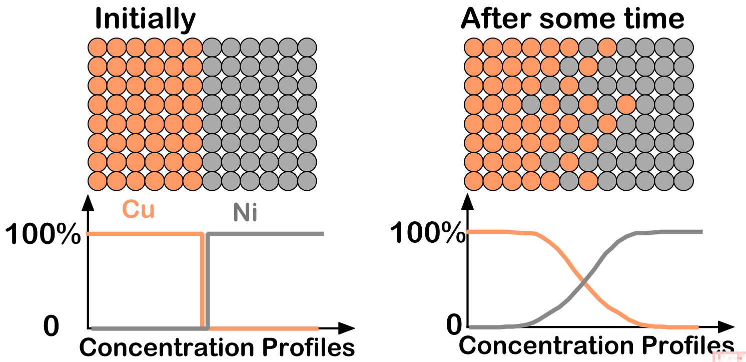
3. How can the rate of diffusion be predicted for some simple cases?

from Materials Science: A Multimedia Approach by John C. Russ.

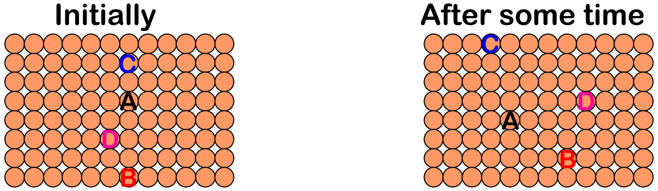
4. How does diffusion depend on structure and temperature?

DIFFUSION: THE PHENOMENON

- **Interdiffusion**: in a solid with more than one type of element (an alloy), atoms tend to migrate from regions of large concentration.

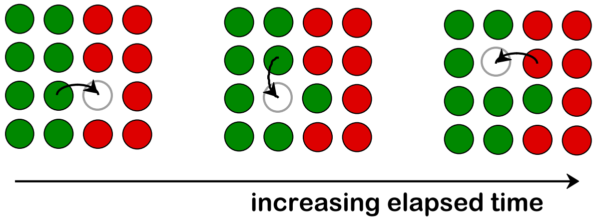


- **Self-diffusion**: In an **elemental solid**, atoms also migrate.

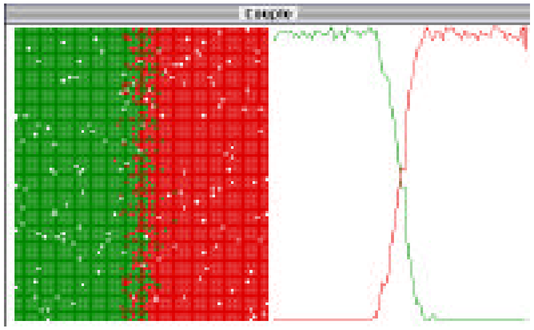


DIFFUSION MECHANISMS

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



DIFFUSION COUPLE MOVIE

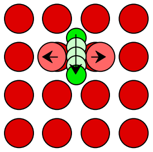


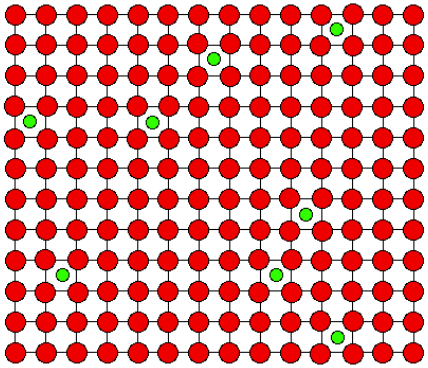
From Materials Science:
A Multimedia Approach,
by John C. Russ

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

Note: Authorware called “Couple” in Materials Science: A Multimedia Approach demonstrates this well.

- **Interstitial** Diffusion:
  - -applies to interstitial impurities
  - -more rapid than vacancy diffusion





PROCESSING USING DIFFUSION

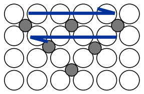
- **Case Hardening**

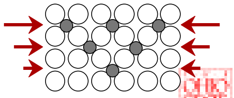
Diffuse carbon atoms into the host iron atoms at the surface

Interstitial diffusion

Callister
Fig. 5.0

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



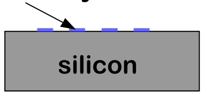


PROCESSING USING DIFFUSION

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

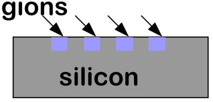
Doping process:

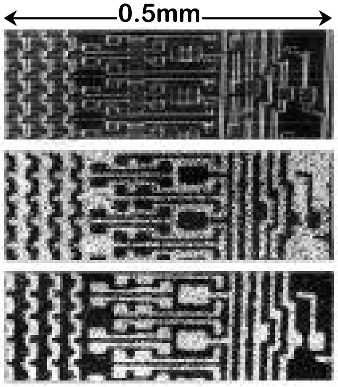
1. Surface deposit P rich layers



2. Heat it

3. Result: Doped semiconductor regions





magnified image of a computer chip

Light regions: silicon atoms

Light regions: aluminum atoms

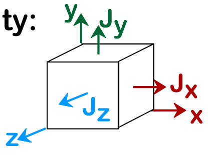
Figure 19.0, Callister

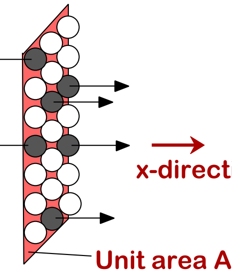
Modeling Diffusion: FLUX

- Definition

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

- Directional quantity:



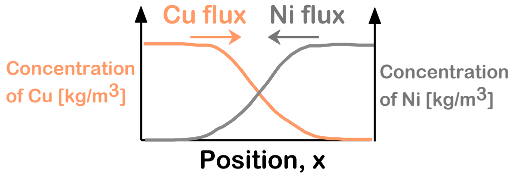


Unit area A through which atoms move.

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

CONCENTRATION PROFILES AND FLUX

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



- Fick's First Law:

Diffusion coefficient [m^2/s]

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

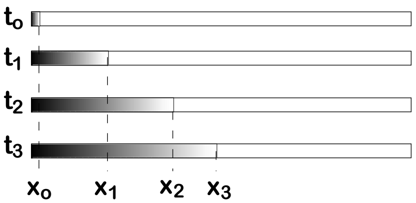
$$J_x = -D \boxed{\frac{dC}{dx}}$$

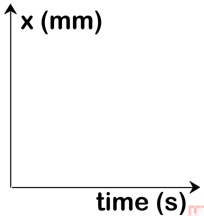
concentration gradient [kg/m^4]

The steeper the concentration profile, the greater the flux!

DIFFUSION DEMO

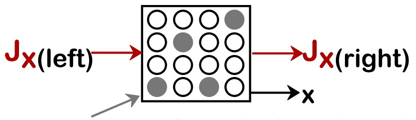
- Glass tube-filled with water
- At time = 0, add some drops of ink to one side.
- Measure the diffusion distance, x, over time.
- Compare the results with theory.





STEADY STATE DIFFUSION

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



Steady State:
J_x(left) = J_x(right)

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

- Apply Fick's First Law:

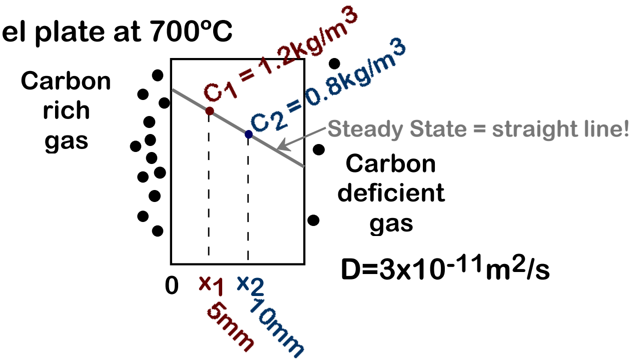
$$J_x = -D\frac{dC}{dx}$$

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

the slope, dC/dx, is constant.
(does not vary with position)!

EXAMPLE: STEADY STATE DIFFUSION

- Steel plate at 700°C



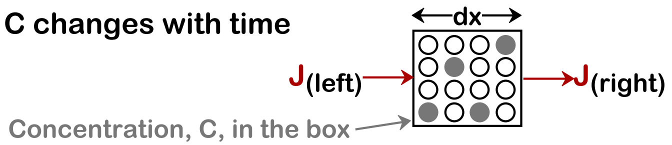
$D = 3\times10^{-11} m^2/s$

Q: How much carbon is transferring from the rich to deficient side?

$$J = -D\frac{C_2 - C_1}{x_2 - x_1} = 2.4\times10^{-9}\frac{kg}{m^2 s}$$

NON-STEADY STATE DIFFUSION

- C changes with time



- To conserve matter:

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

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

- Fick's First Law:

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

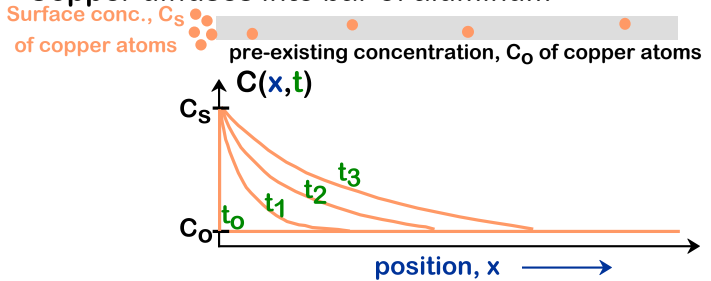
$$\boxed{\frac{dJ}{dx}} = -D\frac{d^2C}{dx^2}$$ (if D does not vary with x)

equate

- Governing Eqn: $$\boxed{\frac{dC}{dt} = D\frac{d^2C}{dx^2}}$$

EX: NON-STEADY STATE DIFFUSION

- Copper diffuses into bar of aluminum



- 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 tabulated in Callister, Table 5.1)

PROCESSING QUESTION

- Copper diffuses into bar of aluminum.
- 10 hrs at 600°C gives desired C(x).

Q: How many hours would it take to get the same C(x) if we processed at 500°C?

Key point 1: $C(x,t_{500°C}) = C(x,t_{600°C})$

Key point 2: Both cases have the same C_o and C_s

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

Values of D are given to you.

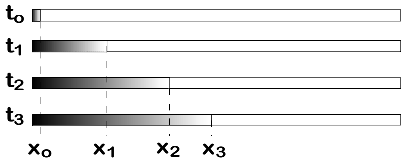
$5.3\times10^{-13} m^2/s$ 10hrs

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

$4.8\times10^{-14} m^2/s$

Analysis of Diffusion Demo

- The experiment: we recorded combinations of t_i, x_i that kept C constant.

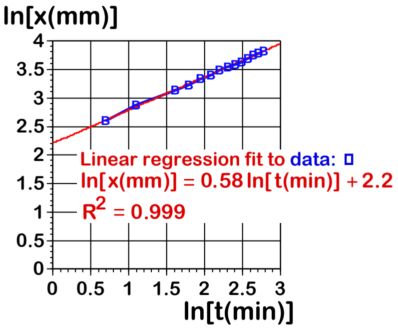


$$\frac{C(x_i, t_i) - C_o}{C_s - C_o} = 1 - \text{erf}\left(\frac{x_i}{2\sqrt{Dt_i}}\right)$$ (= a constant here)

- Diffusion Depth given by

$$x_i \quad \sqrt{Dt_i}$$

Data from Diffusion Demo



- Experimental results show $x \quad t^{0.58}$
- Theory predicts $x \quad t^{0.50}$
- Reasonable agreement!

Diffusion occurs faster at higher T

- Observed fit:

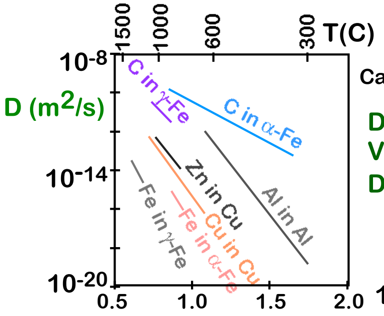
pre-exponential [m^2/s] (see Table 5.2)

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

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

gas constant [8.31J/mol-K]

- Experimental data:



Callister, Fig. 5.7

D has exp. dependence on T.
Vacancy conc. 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

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Structure Changes Diffusion

Diffusion FASTER for...	Diffusion SLOWER for...
Open crystal structures	Close packed structures
Lower melting temp. mat'ls	High melting temp. mat'ls
Mat'ls w/secondary bonding	Mat'ls w/covalent bonding
Cations	Anions
Smaller Diffusing atoms	Larger diffusing atoms
Lower density mat'ls	Higher density mat'ls