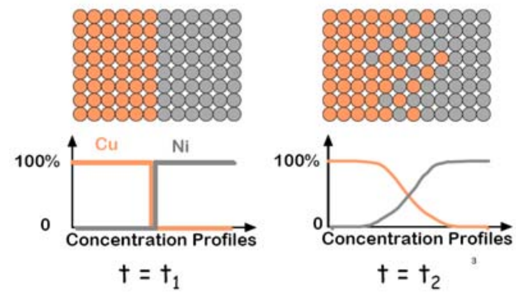
Diffusion in Solids

- 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?

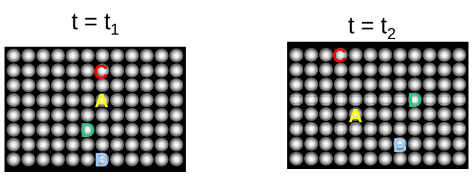
Diffusion

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



Diffusion

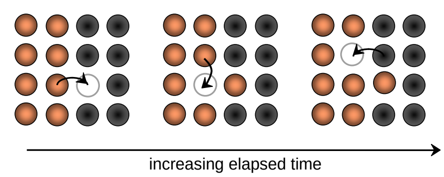
Self-diffusion: In an elemental solid, atoms also migrate.



Diffusion Mechanisms

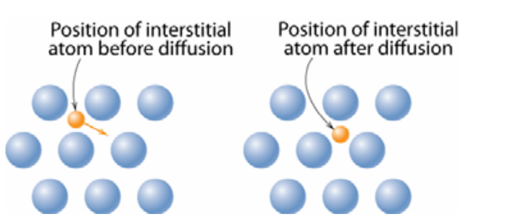
Vacancy Diffusion:

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



Diffusion Mechanisms

Interstitial diffusion: smaller atoms can diffuse between atoms.



More rapid than vacancy diffusion

Processing Using Diffusion

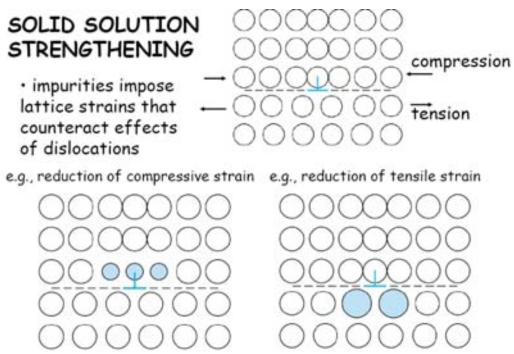
- **Case Hardening:**
  Diffuse carbon atoms into the host iron atoms at the surface.

  Example of interstitial diffusion: case hardened gear.

Carburization of iron at surface:
Liquid: NaCl: NaCN: $NaCO_3$ molten salt 900 C, ~10 min.
Gas: CH_4 in N_2 900 C, hours
Plasma: CH_4 + H_2, 500V, part as cathode

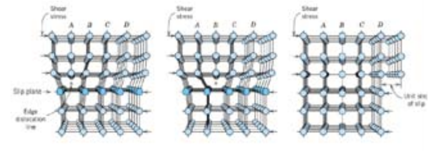
Result: The presence of C atoms makes iron (steel) harder.

Processing Using Diffusion



Processing Using Diffusion

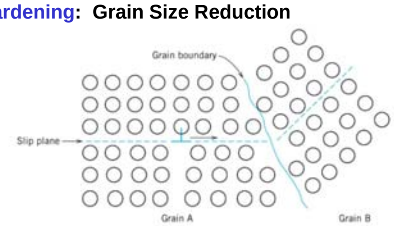
Work Hardening: Diffusion of defects and their mutual immobilization.



In a regular crystal lattice, defects can propagate easily; immobilisation of dislocations means that you increase the irregularity of the crystal structure, such that dislocations block each other from propagating. (like a traffic jam)

Processing Using Diffusion

Work Hardening: Grain Size Reduction

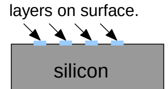


- changing directions at a grain boundary can immobilise the dislocation
- smaller grains = greater total grain boundary area
  - ➢ harder and stronger materials
- **GRAIN SIZE REDUCTION** is achieved by controlling alloy composition and cooling

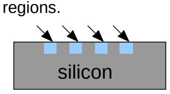
Processing Using Diffusion

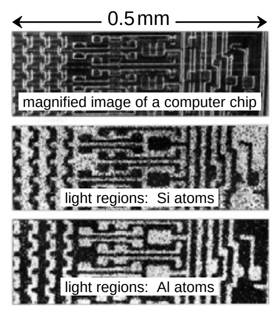
- Doping silicon with phosphorus for *n*-type semiconductors:
- Process:

1. Deposit P rich layers on surface.



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





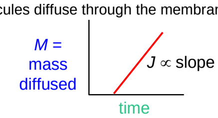
Adapted from chapter-opening photograph, Chapter 18, *Callister 7e.*

Diffusion

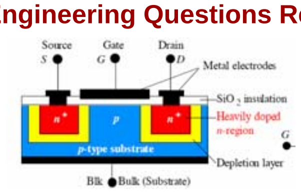
- How do we quantify the amount or rate of diffusion?

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

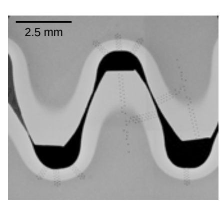
- Measured empirically
  - Make thin film (membrane) of known surface area
  - Impose concentration gradient
  - Measure how fast atoms or molecules diffuse through the membrane



Engineering Questions Related to Diffusion



How will the dimensions and electrical properties of this MOSFET be achieved?



How hard will the surface of the carburized gear be?

How long will the coffee retain its flavor?

Steady-State Diffusion

- **Consider a gas flowing through a membrane:**
  - ***J*: diffusive flux**
  - ***M*: mass diffused**
  - ***A*: cross-sectional area**
  - ***t*: time**

$$J \equiv \frac{1}{A}\frac{dM}{dt}$$

- Concentration gradient:

$$\frac{\Delta C}{\Delta x} = \frac{C_A - C_B}{x_A - x_B}$$

C = mass per unit volume

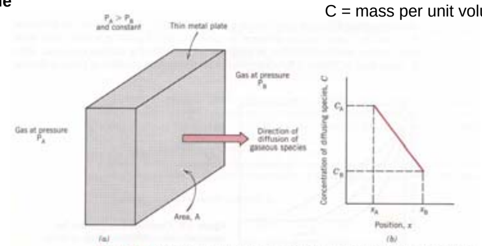


Figure 5.4 (*a*) Steady-state diffusion across a thin plate. (*b*) A linear concentration profile for the diffusion situation in (*a*).

Fick's First Law

Steady-State Diffusion

Fick's First Law:

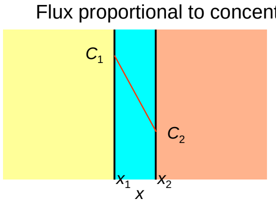
$$J = -D\frac{dC}{dx}$$

where J = flux of atoms/unit area/unit time
D = Diffusion coefficient
C = concentration of diffusing atoms
x = distance

Steady-State Diffusion

Rate of diffusion independent of time

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



Fick's first law of diffusion

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

$D \equiv$ diffusion coefficient

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

Diffusion and Temperature

- **Diffusion coefficient increases with increasing *T*.**

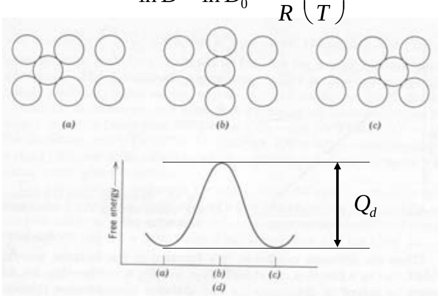
$$D = D_o \exp\left(-\frac{Q_d}{RT}\right)$$

D **= diffusion coefficient [m²/s]**
D_o **= pre-exponential [m²/s]**
Q_d **= activation energy [J/mol or eV/atom]**
R **= gas constant [8.314 J/mol-K]**
T **= absolute temperature [K]**

Diffusion: a Thermally Activated Process

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

$$\ln D = \ln D_0 - \frac{Q_d}{R}\left(\frac{1}{T}\right)$$



Diffusion: a Thermally Activated Process

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

$$\ln D = \ln D_0 - \frac{Q_d}{R}\left(\frac{1}{T}\right)$$

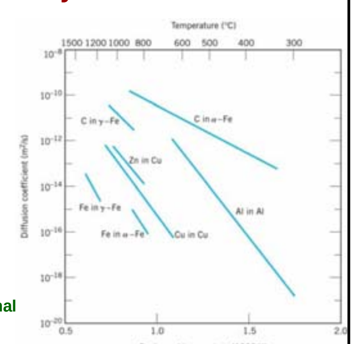
intercept (ln D_0), slope ($\frac{Q_d}{R}$)

on a plot of ln *D* vs. 1/*T*

$D_{interstitial} >> D_{substitutional}$

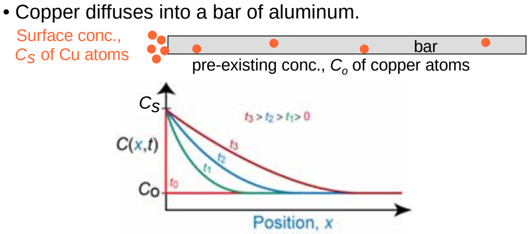
C in α-Fe
C in γ-Fe

Al in Al
Fe in α-Fe
Fe in γ-Fe



Non-steady State Diffusion

- Copper diffuses into a bar of aluminum.

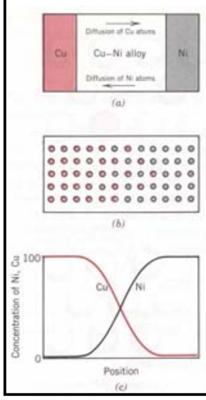


B.C. at $t = 0$, $C = C_o$ for $0 \leq x \leq \infty$

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

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

Examples of Nonsteady-State Diffusion



- **Cu and Ni form a complete solid solution**
- **Put the two metals in direct contact at high T**

⇒both will diffuse from high concentration to low — *diffusive alloying*

Cu diffuses from left to right
⇒ accumulation of Cu in Ni
Ni diffuses from right to left
⇒ accumulation of Ni in Cu

Examples of Nonsteady-State Diffusion

- **Other examples of diffusion into a solid from another phase:**
  - **Carburization of steels**
  - **Diffusion of dopants into semiconductors**
  - **Concentration gradient changes in time**

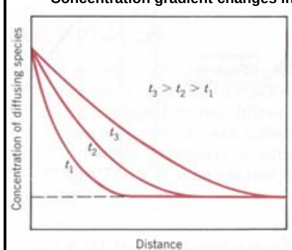


Figure 5.5 Concentration profiles for nonsteady-state diffusion taken at three different times, t_1, t_2, and t_3.

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 applies:

Fick's Second Law: $$\frac{\partial C}{\partial t} = D\frac{\partial^2 C}{\partial x^2}$$

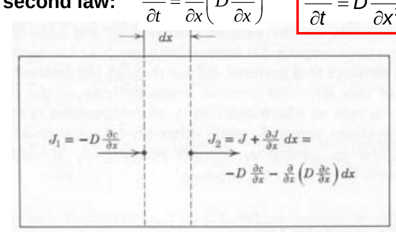
Nonsteady-State Diffusion

- **Conservation of mass: [what stays there] = [what goes in] – [what comes out]**

Flux at plane 1: $J_1 = -D\frac{\partial C}{\partial x}$ **Flux at plane 2:** $J_2 = J_1 + \frac{\partial J}{\partial x}dx$

Accumulation: $\frac{\partial C}{\partial t} = \frac{J_1 - J_2}{\partial x} = \frac{-\partial J}{\partial x} = \frac{\partial}{\partial x}\left(D\frac{\partial C}{\partial x}\right)$

Fick's second law: $\frac{\partial C}{\partial t} = \frac{\partial}{\partial x}\left(D\frac{\partial C}{\partial x}\right)$ $\quad \frac{\partial C}{\partial t} = D\frac{\partial^2 C}{\partial x^2}$



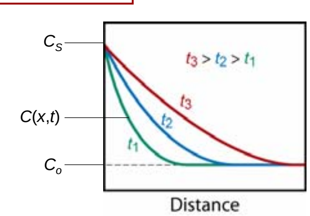
Solution: Fick's 2nd Law

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

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

erf (z) = error function

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



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