Chapter 5: Diffusion
(Mass transport by atomic motion)

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?

1

Diffusion

•Many reactions and processes that are important in the treatment of materials rely on the transfer of mass either within a specific solid or from a liquid, a gas, or another solid phase.

•This is necessarily accomplished by **diffusion**, the phenomenon of material transport by atomic motion

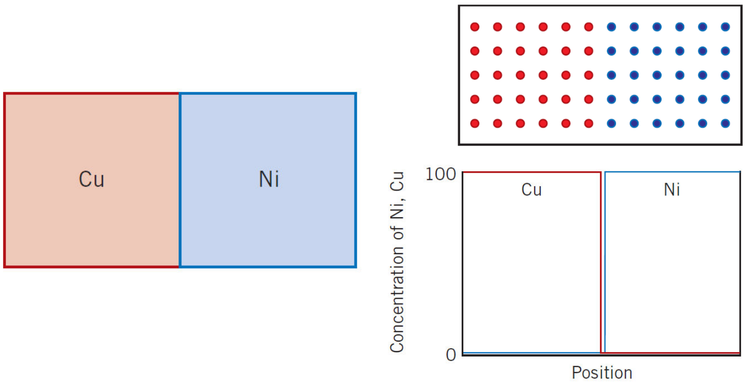
Diffusion - Mass transport by atomic motion

Mechanisms
•Gases & Liquids – random motion
•Solids – vacancy diffusion or interstitial diffusion

2

Diffusion

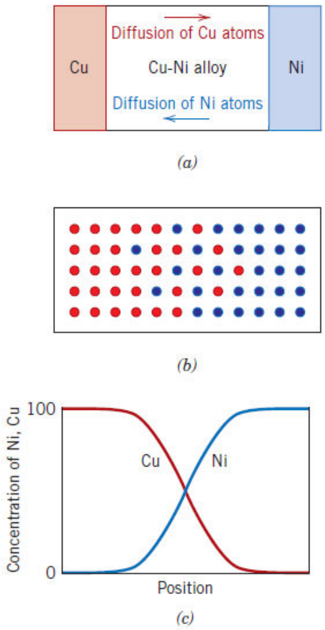
•The phenomenon of diffusion may be demonstrated with the use of a diffusion couple, which is formed by joining bars of two different metals together so that there is intimate contact between the two faces;



Diffusion

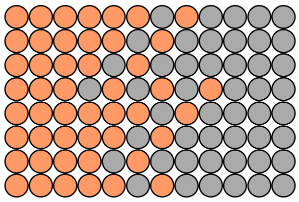
•This couple is heated for an extended period at an elevated temperature (but below the melting temperature of both metals), and cooled to room temperature.

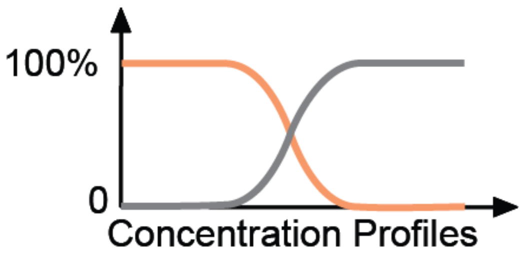
•Chemical analysis will reveal a condition similar to that, pure copper and nickel at the two extremities of the couple, separated by an alloyed region.



Diffusion

•Concentrations of both metals vary with position. This result indicates that copper atoms have migrated or diffused into the nickel, and that nickel has diffused into copper.
•There is a net drift or transport of atoms from high- to low-concentration regions.
•This process, whereby atoms of one metal diffuse into another, is termed **interdiffusion**, or **impurity diffusion**.

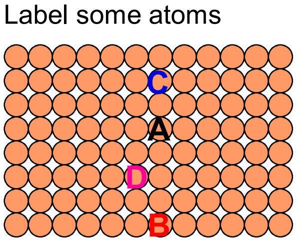


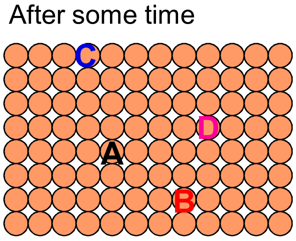


5

Diffusion

Self-diffusion:
•diffusion also occurs for pure metals,
•but all atoms exchanging positions are of the same type.





In an elemental solid, atoms also migrate.

6

Diffusion Mechanisms

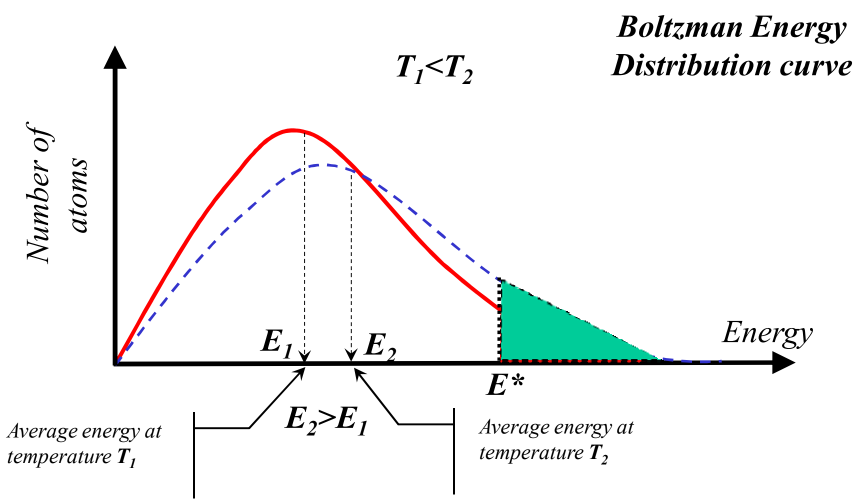
•Diffusion is just the stepwise migration of atoms from lattice site to lattice site. In fact, the atoms in solid materials are in constant motion, rapidly changing positions. For an atom to make such a move, two conditions must be met:

(1) there must be an empty adjacent site
(2) the atom must have sufficient energy to break bonds with its neighbor atoms and then cause some **lattice distortion** during the displacement.

At a specific temperature some small fraction of the total number of atoms is capable of diffusive motion, depending on the magnitudes of their vibrational energies. This fraction increases with rising temperature.

7

Diffusion Mechanisms

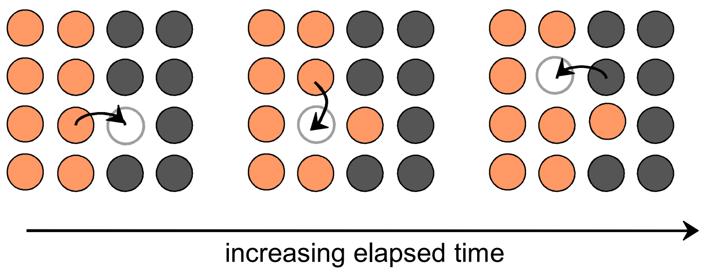


8

Diffusion Mechanisms

Vacancy Diffusion:

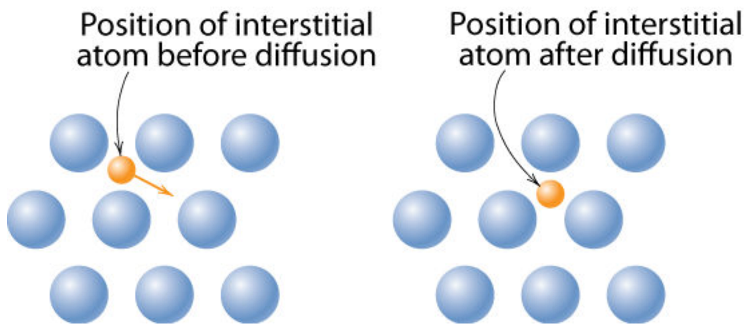
- atoms exchange with vacancies
- applies to substitutional impurities atoms
- rate depends on:
  - -- number of vacancies
  - -- activation energy to exchange.



9

Diffusion Mechanisms

- Interstitial diffusion – smaller atoms can diffuse between atoms.



Adapted from Fig. 5.3(b), *Callister & Rethwisch 8e.*

More rapid than vacancy diffusion

10

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 & Rethwisch 8e.* (Courtesy of Surface Division, Midland-Ross.)

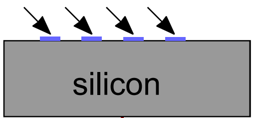
• Result: The presence of C atoms makes iron (steel) harder.

11

Processing Using Diffusion

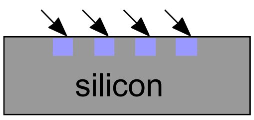
• Doping silicon with phosphorus for *n*-type semiconductors:
• Process:

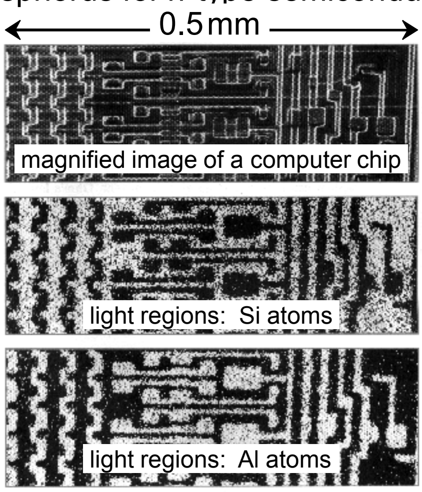
1. Deposit P rich layers on surface.



2. Heat it.

3. Result: Doped semiconductor regions.





Adapted from Figure 18.27, *Callister & Rethwisch 8e.*

12

Diffusion

- How do we quantify the amount or rate of diffusion?
- Diffusion is a time-dependent process
- In a macroscopic sense, the quantity of an element that is transported within another is a function of time.

Diffusion Flux: The mass (or, equivalently, the number of atoms) M diffusing through and perpendicular to a unit cross-sectional area of solid per unit of time.

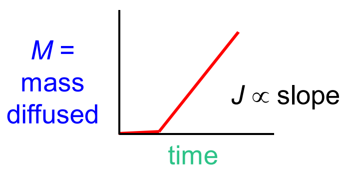
$$J \equiv \text{Flux} \equiv \frac{\text{moles (or mass) diffusing}}{(\text{surface area})(\text{time})} = \frac{\text{mol}}{\text{cm}^2\text{s}} \text{ or } \frac{\text{kg}}{\text{m}^2\text{s}}$$

13

Diffusion

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

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



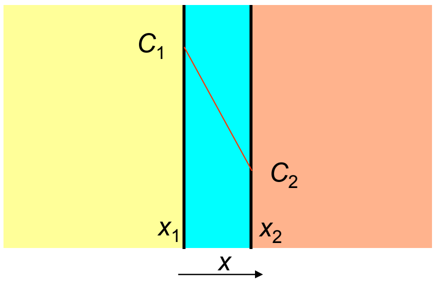
The units for J are kilograms or atoms per meter squared per second: (kg/m^2-s or atoms/m^2-s)

14

i) Steady-State Diffusion

•Rate of diffusion independent of time: "Diffusion flux does not change with time".

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



Fick's first law of diffusion

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

$D \equiv$ diffusion coefficient
(*constant of proportionality*)

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

15

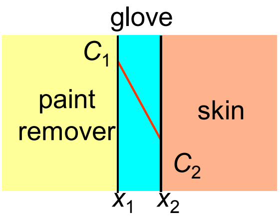
Example: Chemical Protective Clothing (CPC)

- 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 = 110x10^{-8} cm^2/s
  – surface concentrations: C_1 = 0.44 g/cm^3
    C_2 = 0.02 g/cm^3

16

Example (cont).

- Solution – assuming linear conc. gradient



$$J = -D\frac{dC}{dx} \cong -D\frac{C_2 - C_1}{x_2 - x_1}$$

Data: $D = 110 \times 10^{-8}\ \text{cm}^2/\text{s}$
$C_1 = 0.44\ \text{g/cm}^3$
$C_2 = 0.02\ \text{g/cm}^3$
$x_2 - x_1 = 0.04\ \text{cm}$

$$J = -(110 \times 10^{-8}\ \text{cm}^2/\text{s})\frac{(0.02\ \text{g/cm}^3 - 0.44\ \text{g/cm}^3)}{(0.04\ \text{cm})} = \boxed{1.16 \times 10^{-5}\ \frac{\text{g}}{\text{cm}^2\text{s}}}$$

17

Diffusion and Temperature

- Diffusion coefficient increases with increasing T.

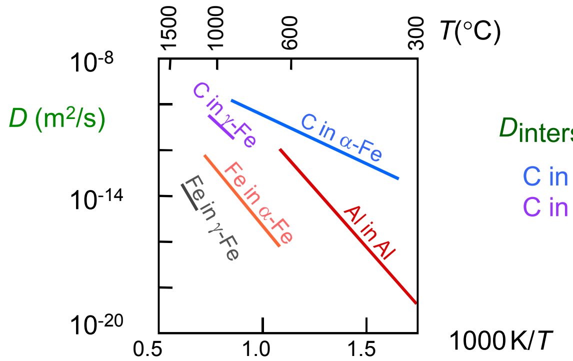
$$D = D_o \exp\left(-\frac{Q_d}{RT}\right)$$

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]

18

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

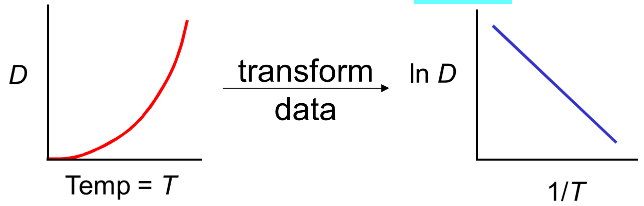
Adapted from Fig. 5.7, *Callister & Rethwisch 8e*. (Date for Fig. 5.7 taken from E.A. Brandes and G.B. Brook (Ed.) *Smithells Metals Reference Book*, 7th ed., Butterworth-Heinemann, Oxford, 1992.)

19

Example: At 300ºC the diffusion coefficient and activation energy for **Cu** in **Si** are

$D(300ºC) = 7.8 \times 10^{-11}$ m^2/s
Q_d = 41.5 kJ/mol

What is the diffusion coefficient at 350ºC?



$$\ln D_2 = \ln D_0 - \frac{Q_d}{R}\left(\frac{1}{T_2}\right) \quad \text{and} \quad \ln D_1 = \ln D_0 - \frac{Q_d}{R}\left(\frac{1}{T_1}\right)$$

$$\therefore \quad \ln D_2 - \ln D_1 = \ln\frac{D_2}{D_1} = -\frac{Q_d}{R}\left(\frac{1}{T_2} - \frac{1}{T_1}\right)$$

20

Example (cont.)

$$D_2 = D_1 \exp\left[-\frac{Q_d}{R}\left(\frac{1}{T_2} - \frac{1}{T_1}\right)\right]$$

$T_1 = 273 + 300 = 573\,K$

$T_2 = 273 + 350 = 623\,K$

$$D_2 = (7.8 \times 10^{-11}\ m^2/s)\exp\left[\frac{-41{,}500\ J/mol}{8.314\ J/mol\text{-}K}\left(\frac{1}{623\,K} - \frac{1}{573\,K}\right)\right]$$

$$\boxed{D_2 = 15.7 \times 10^{-11}\ m^2/s}$$

21

ii) Non-steady State Diffusion

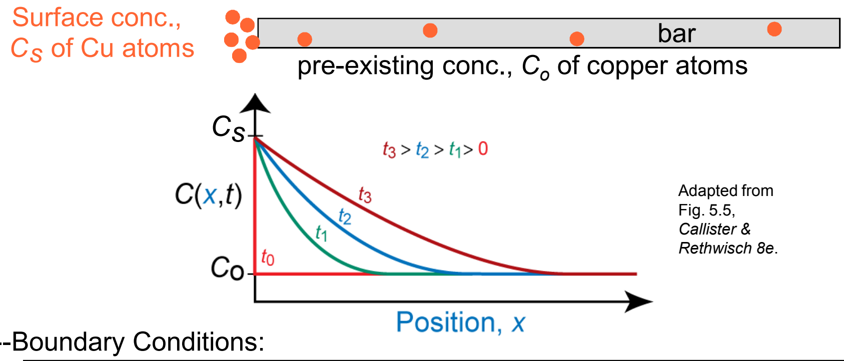
- Most practical diffusion situations are nonsteady-state ones.
- The "diffusion flux" and the "concentration gradient" at some particular point in a solid vary with time, with a net accumulation or depletion of the diffusing species resulting.
- The concentration of diffusing species is a function of both time and position $C = C(x,t)$
- In this case Fick's Second Law is used

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

22

Non-steady State Diffusion

- Copper diffuses into a bar of aluminum.



Adapted from Fig. 5.5, *Callister & Rethwisch 8e.*

---Boundary Conditions:

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

at $t > 0$, $C = C_S$ for $x = 0$ (constant surface conc.)

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

23

Solution:

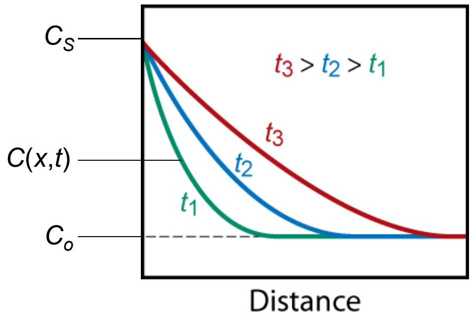
$$\frac{C(x,t) - C_o}{C_s - C_o} = 1 - \text{erf}\left(\frac{x}{2\sqrt{Dt}}\right)$$

$C(x,t)$ = 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 on next slide.



Adapted from Fig. 5.5, *Callister & Rethwisch 8e.*

24

Tabulation of Error Function Values

z	$erf(z)$	z	$erf(z)$	z	$erf(z)$
0	0	0.55	0.5633	1.3	0.9340
0.025	0.0282	0.60	0.6039	1.4	0.9523
0.05	0.0564	0.65	0.6420	1.5	0.9661
0.10	0.1125	0.70	0.6778	1.6	0.9763
0.15	0.1680	0.75	0.7112	1.7	0.9838
0.20	0.2227	0.80	0.7421	1.8	0.9891
0.25	0.2763	0.85	0.7707	1.9	0.9928
0.30	0.3286	0.90	0.7970	2.0	0.9953
0.35	0.3794	0.95	0.8209	2.2	0.9981
0.40	0.4284	1.0	0.8427	2.4	0.9993
0.45	0.4755	1.1	0.8802	2.6	0.9998
0.50	0.5205	1.2	0.9103	2.8	0.9999

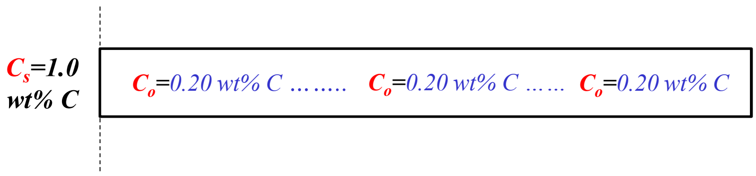
Non-steady State Diffusion

- **Sample Problem:** An FCC iron-carbon (Fe-C) 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.

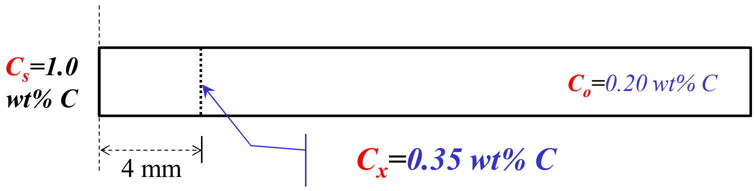
- Solution: Using Fick's 2nd Law: $\frac{C(x,t)-C_o}{C_s-C_o} = 1-\text{erf}\left(\frac{x}{2\sqrt{Dt}}\right)$

Solution (cont.):

•at *t=0*



•at *t=49.5 h*



27

Solution (cont.):

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

- t = 49.5 h
- C_x = 0.35 wt%
- C_o = 0.20 wt%

x = 4 x 10^{-3} m

C_s = 1.0 wt%

$$\frac{C(x,t)-C_o}{C_s-C_o}=\frac{0.35-0.20}{1.0-0.20}=1-\mathrm{erf}\left(\frac{x}{2\sqrt{Dt}}\right)=1-\mathrm{erf}(z)$$

$\therefore$ erf(z) = 0.8125

28

Solution (cont.):

We must now determine the value of z for which the error function is 0.8125. An interpolation is necessary as follows

z	erf(z)
0.90	0.7970
z	0.8125
0.95	0.8209

$$\frac{z - 0.90}{0.95 - 0.90} = \frac{0.8125 - 0.7970}{0.8209 - 0.7970}$$

$$z = 0.93$$

Now solve for D

$$z = \frac{x}{2\sqrt{Dt}} \Rightarrow D = \frac{x^2}{4z^2 t}$$

$$\therefore D = \left(\frac{x^2}{4z^2 t}\right) = \frac{(4 \times 10^{-3}\,\text{m})^2}{(4)(0.93)^2(49.5\,\text{h})} \frac{1\,\text{h}}{3600\,\text{s}} = 2.6 \times 10^{-11}\,\text{m}^2/\text{s}$$

29

Solution (cont.):

- To solve for the temperature at which D has the above value, we use a rearranged form of Equation shown on slide 18:

$$T = \frac{Q_d}{R(\ln D_o - \ln D)}$$

from Tables, for diffusion of C in FCC Fe

$D_o = 2.3 \times 10^{-5}\ \text{m}^2/\text{s}$ $\quad Q_d = 148{,}000$ J/mol

$$\therefore \quad T = \frac{148{,}000\ \text{J/mol}}{(8.314\ \text{J/mol-K})(\ln 2.3\text{x}10^{-5}\ \text{m}^2/\text{s} - \ln 2.6\text{x}10^{-11}\ \text{m}^2/\text{s})}$$

$$\boxed{T = 1300\ \text{K} = 1027^{\circ}\text{C}}$$

30

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

31