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

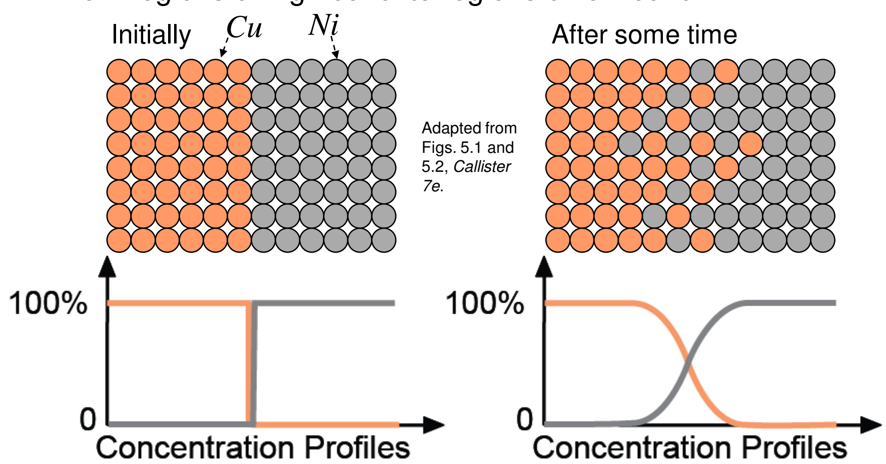
Diffusion - Mass transport by atomic motion

Mechanisms

- Gases & Liquids – random (Brownian) motion
- Solids – vacancy diffusion or interstitial diffusion

Diffusion

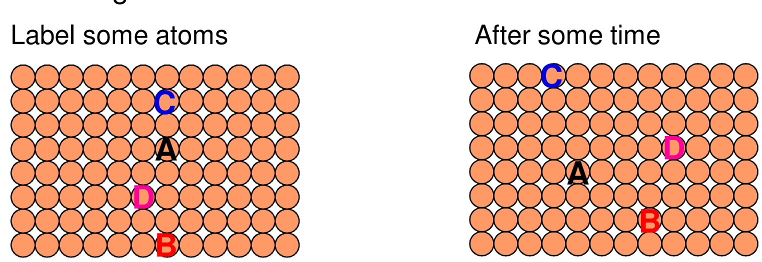
- Interdiffusion: In an alloy, atoms tend to migrate from regions of high conc. to regions of low conc.



Adapted from Figs. 5.1 and 5.2, *Callister 7e.*

Diffusion

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



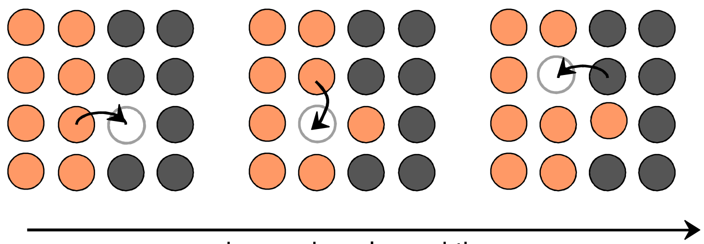
Diffusion is just a stepwise migration of atoms from lattice site to lattice site.

- *There must be an empty adjacent site.*
- *The atom must have sufficient energy to break bonds with its neighbor atoms and them cause some lattice distortion during the displacement.*

Diffusion Mechanisms

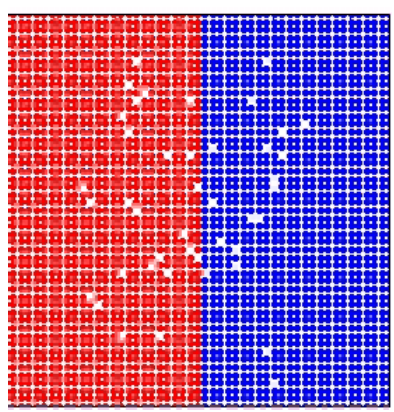
Vacancy Diffusion:

- atoms exchange with vacancies
- applies to substitutional impurities atoms
- 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.



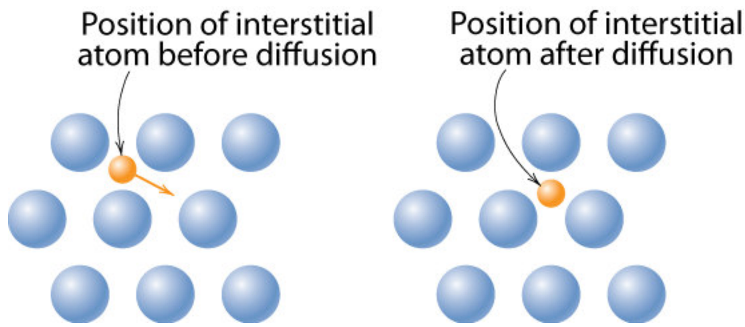
http://www.phys.au.dk/camp/m-t/

(Courtesy P.M. Anderson)

http://www.physics.leidenuniv.nl/sections/cm/ip/projects/dynamics/incopper/incopper.htm

Diffusion Mechanisms

- Interstitial diffusion – smaller atoms can diffuse between atoms.



Adapted from Fig. 5.3 (b), *Callister 7e.*

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 is a case hardened gear.

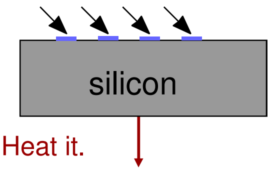
Adapted from chapter-opening photograph, Chapter 5, *Callister 7e.* (Courtesy of Surface Division, Midland-Ross.)

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

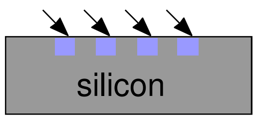
Processing Using Diffusion

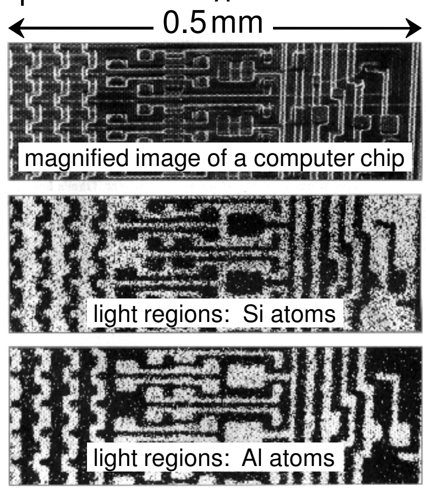
- Doping silicon with phosphorus for *n*-type semiconductors:
- Process:

1. Deposit P rich layers on surface.



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





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

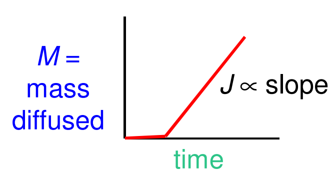
Diffusion

- 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

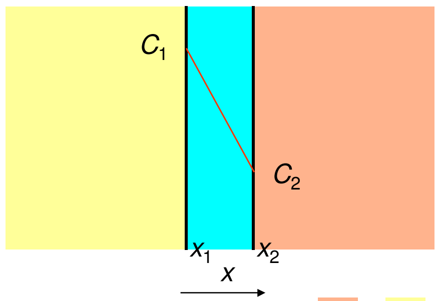
$$J = \frac{M}{At} = \frac{l}{A}\frac{dM}{dt}$$



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

Driving Force---concentration gradient

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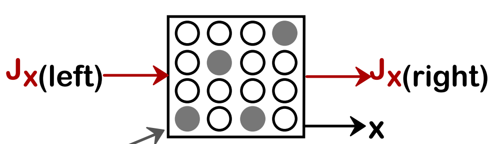
Steady-state diffusion

- **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** $\left(\frac{dC}{dx}\right)_{left} = \left(\frac{dC}{dx}\right)_{right}$
- **Result: the slope, dC/dx, must be constant (i.e., slope doesn't vary with position)!**

From Callister 6e resource CD.

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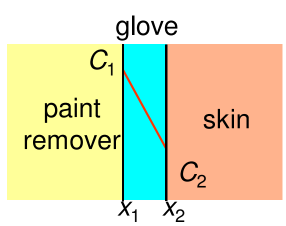
Example: Chemical Protective Clothing (CPC)

- 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: $D = 110 \times 10^{-8}\ \text{cm}^2/\text{s}$
  - surface concentrations: $C_1 = 0.44\ \text{g/cm}^3$, $C_2 = 0.02\ \text{g/cm}^3$

Example (cont).

- Solution – assuming linear conc. gradient



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

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

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

Factors That Influence Diffusion

- **Diffusing Species & Temperature**

  example: carbon _α iron

  self-diffusion: $D = 3 \times 10^{-21}$ m²/s

  interdiffusion: $D = 2.4 \times 10^{-12}$ m²/s

Table 5.2 A Tabulation of Diffusion Data

Diffusing Species	*Host Metal*	$D_0(m^2/s)$	*Activation Energy Q_d* kJ/mol	eV/atom	*Calculated Values* T(°C)	$D(m^2/s)$
Fe	α-Fe (BCC)	2.8×10^{-4}	251	2.60	500 900	3.0×10^{-21} 1.8×10^{-15}
Fe	γ-Fe (FCC)	5.0×10^{-5}	284	2.94	900 1100	1.1×10^{-17} 7.8×10^{-16}
C	α−Fe	6.2×10^{-7}	80	0.83	500 900	2.4×10^{-12} 1.7×10^{-10}
C	γ-Fe	2.3×10^{-5}	148	1.53	900 1100	5.9×10^{-12} 5.3×10^{-11}
Cu	Cu	7.8×10^{-5}	211	2.19	500	4.2×10^{-19}
Zn	Cu	2.4×10^{-5}	189	1.96	500	4.0×10^{-18}
Al	Al	2.3×10^{-4}	144	1.49	500	4.2×10^{-14}
Cu	Al	6.5×10^{-5}	136	1.41	500	4.1×10^{-14}
Mg	Al	1.2×10^{-4}	131	1.35	500	1.9×10^{-13}
Cu	Ni	2.7×10^{-5}	256	2.65	500	1.3×10^{-22}

Source: E. A. Brandes and G. B. Brook (Editors), *Smithells Metals Reference Book*, 7th edition, Butterworth-Heinemann, Oxford, 1992.

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]

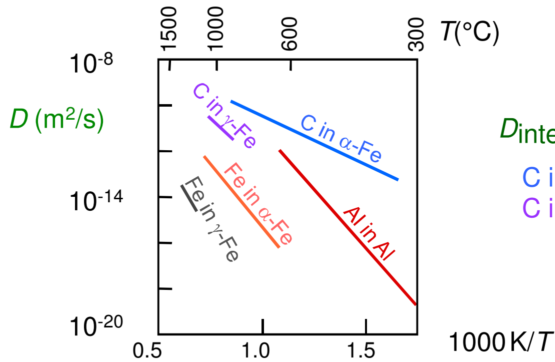
Q_d = activation energy [J/mol or eV/atom]

R = gas constant [8.314 J/mol-K]

T = absolute temperature [K]

Diffusion and Temperature

D has exponential dependence on *T*



$D_{\text{interstitial}} >> D_{\text{substitutional}}$

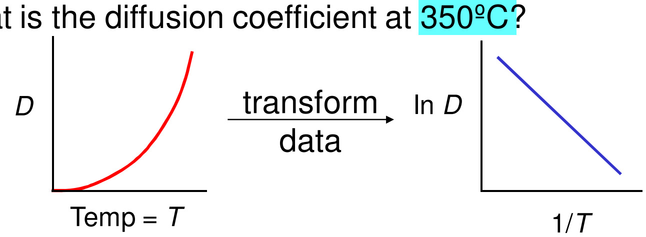
C in α-Fe	Al in Al
C in γ-Fe	Fe in α-Fe
	Fe in γ-Fe

Adapted from Fig. 5.7, *Callister 7e.* (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.)

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

$D(300ºC) = 7.8 \times 10^{-11}$ m²/s
$Q_d = 41.5$ kJ/mol

What is the diffusion coefficient at 350ºC?



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

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

Example (cont.)

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

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

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

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

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

Concept Check

- **Rank the magnitudes of the diffusion coefficients from greatest to least for the following systems:**

  N in Fe at 700°C

  Cr in Fe at 700°C

  N in Fe at 900°C

  Cr in Fe at 900°C

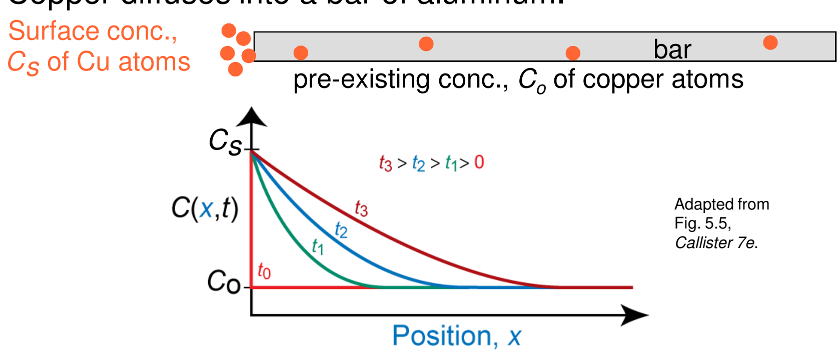
Non-steady State Diffusion

- The concentration of diffucing 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
$$\frac{\partial C}{\partial t} = D\frac{\partial^2 C}{\partial x^2}$$

Non-steady State Diffusion

- Copper diffuses into a bar of aluminum.



Adapted from Fig. 5.5, *Callister 7e.*

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

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

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

Solution:

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

$C(x,t)$ = 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 in Table 5.1

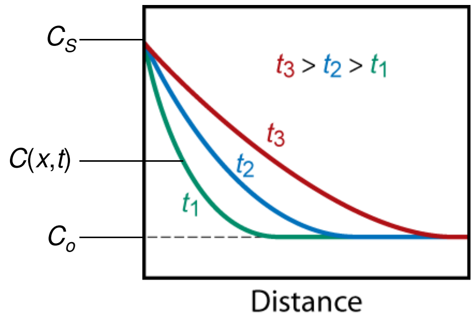


Table 5.1 Tabulation of Error Function Values

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

interpolation

Non-steady State Diffusion

- Sample Problem: An FCC iron-carbon 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: use Eqn. 5.5 $\frac{C(x,t)-C_o}{C_s-C_o}=1-\text{erf}\left(\frac{x}{2\sqrt{Dt}}\right)$

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

- 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%

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

$\therefore$ erf(z) = 0.8125

Solution (cont.):

We must now determine from Table 5.1 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

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

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

Solution (cont.):

- To solve for the temperature at which D has above value, we use a rearranged form of Equation (5.9a);

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

from Table 5.2, for diffusion of C in FCC Fe

D_o = 2.3 x 10^{-5} m^2/s Q_d = 148,000 J/mol

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

$$T = 1300 \text{ K} = 1027°\text{C}$$

Example Problem 5.2 and 5.3

- Consider one Fe-C alloy that has a uniform carbon concentration of 0.25 wt% and is to be treated at 950°C. If the concentration of C at the surface is suddenly brought to and maintained at 1.2wt%, how long will it take to achieve a carbon content of 0.8wt% at a position 0.5mm below the surface? The diffusion coefficient for C in Fe at this temperature is $1.6x10^{-11} m^2/s$; assume that the steel piece is semi-infinite.

- The diffusion coefficient for copper in aluminum at 500 and 600°C are $4.8x10^{-14}$ and $5.3x10^{-13} m^2/s$, respectively. Determine the approximate time at 500°C that will produce the same diffusion result (in terms of concentration of Cu at some specific point in Al) as a 10-h heat treatment at 600°C.

Solution

- 5.2:

Erf(z)=0.4210, z=0.392, t=7.1

- 5.3:

Dt=constant

t_{500}=110.4h

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