Chapter 5: Diffusion

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

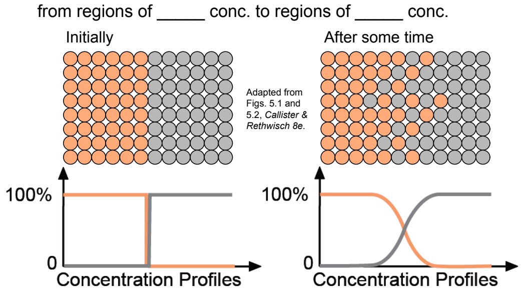
Diffusion - Mass transport by atomic motion

____

- Gases & Liquids – random (___________) motion
- Solids – ________ diffusion or __________ diffusion

Diffusion

- __________: In an alloy, atoms tend to __________ from regions of _____ conc. to regions of _____ conc.

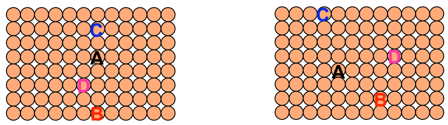


Adapted from Figs. 5.1 and 5.2, *Callister & Rethwisch 8e.*

Diffusion

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

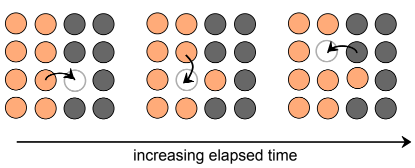
Label some atoms | After some time



Diffusion Mechanisms

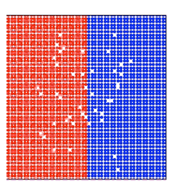
Vacancy Diffusion:

- _______ exchange with __________
- applies to ____________ impurities atoms
- rate depends on:
  - --number of _________
  - --activation _________ to exchange.



Diffusion Simulation

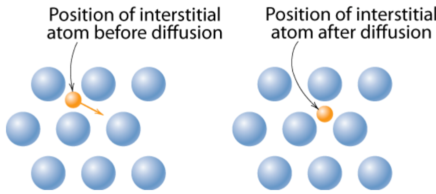
- Simulation of interdiffusion across an interface:
- Rate of ____________ diffusion depends on:
  - -- ___________concentration
  - -- frequency of ___________.



(Courtesy P.M. Anderson)

Diffusion Mechanisms

- ____________ diffusion – smaller atoms can diffuse between __________.



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

More rapid than ___________ diffusion

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Processing Using Diffusion

- Case ___________:
  - -- 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: ________________ atoms makes iron (steel) harder.

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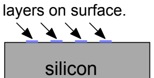
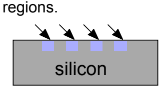
Processing Using Diffusion

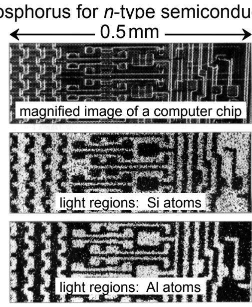
- ______silicon with phosphorus for *n*-type semiconductors:
- Process:

1. Deposit __ rich layers on surface.



2. ________
3. Result: Doped ________ regions.





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

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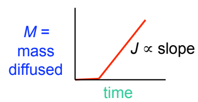
Diffusion

- 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 (__________) of known surface area
  - Impose ____________ gradient
  - Measure how fast atoms or molecules diffuse through the membrane

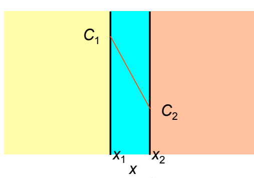
$$J = \frac{M}{At} = \frac{l}{A}\frac{dM}{dt}$$



Steady-State Diffusion

Rate of ___________ independent of time

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



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

___________ of diffusion

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

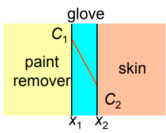
$D \equiv$ diffusion coefficient

Example: Chemical Protective Clothing (CPC)

- _________________ 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 (____ cm thick) are used, what is the diffusive flux of _______________ through the glove?
- Data:
  - diffusion coefficient in butyl rubber:
    $D =$ ________________
  - surface concentrations: $C_1 = 0.44$ g/cm^3
    $C_2 = 0.02$ g/cm^3

Example (cont).

- Solution – assuming ___________ conc. gradient



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

Data: D = ___________
C_1 = ___________
C_2 = 0.02 g/cm^3
$x_2 - x_1$ = 0.04 cm

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

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Diffusion and Temperature

- Diffusion coefficient increases with increasing _____.

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

D = _________ coefficient [m^2/s]
D_o = pre-exponential [m^2/s]
Q_d = _________ energy [J/mol or eV/atom]
R = gas constant [_______________]
T = absolute temperature [K]

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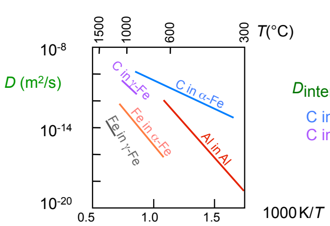
Diffusion and Temperature

D has _______________ dependence on T



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

C in α-Fe
C in γ-Fe

Al in Al
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.)

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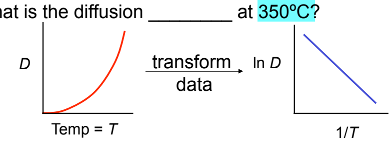
Example: At 300ºC the diffusion coefficient and activation ___________ for _____________ are

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

What is the diffusion ________ at 350ºC?



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

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

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Example (cont.)

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

$T_1 = 273 + 300 = 573\text{K}$

$T_2 = 273 + 350 = 623\text{K}$

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

D_2 = _______________

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Non-steady State Diffusion

- The ___________ of diffusing species is a function of both time and position $C = C(x,t)$
- In this case ________________ Law is used

____________ Law $$\frac{\partial C}{\partial t} = D\frac{\partial^2 C}{\partial x^2}$$

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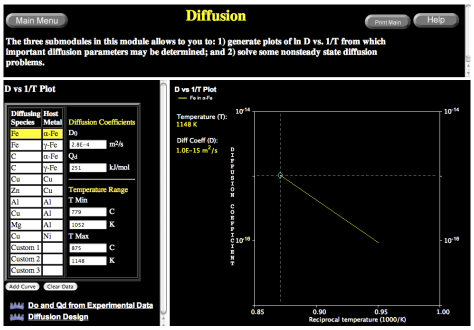
VMSE: Student Companion Site
Diffusion Computations & Data Plots



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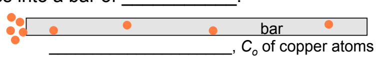
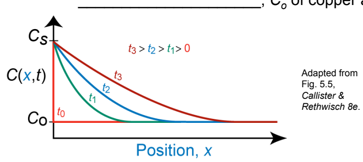
Non-steady State Diffusion

- Copper diffuses into a bar of ___________.

Surface conc., C_s of Cu atoms



___________________, C_o of copper atoms



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

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

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

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

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Solution:

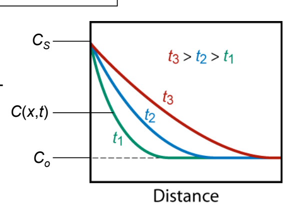
$$\frac{C(x,t) - C_o}{C_s - C_o} = 1 - \text{erf}\left(\frac{x}{2\sqrt{Dt}}\right)$$

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

erf (z) = error __________

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

erf(z) values are given in Table ______



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

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Non-steady State Diffusion

- Sample Problem: An FCC iron-carbon alloy initially containing ___________ is carburized at an elevated temperature and in an atmosphere that gives a surface carbon concentration constant at 1.0 wt%. If after _____ the concentration of carbon is 0.35 wt% at a position _____ below the surface, determine the temperature at which the treatment was carried out.
- Solution: use Eqn. 5.5 $\frac{C(x,t)-C_o}{C_s-C_o}=1-\text{erf}\left(\frac{x}{2\sqrt{Dt}}\right)$

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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 = ________

x = ________
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) = ______

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

$$\therefore D=\left(\frac{x^2}{4z^2t}\right)=\frac{(4\times10^{-3}\text{m})^2}{(4)(0.93)^2(49.5\text{ h})}\frac{1\text{h}}{3600\text{ s}}=2.6\times10^{-11}\text{ m}^2/\text{s}$$

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Solution (cont.):

- To solve for the temperature at which D has the 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

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

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

T = 1300 K = _______

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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 ___________ through skin. When using this paint remover, protective gloves should be worn.
- If butyl rubber gloves (_______________) are used, what is the breakthrough time (t_b), i.e., how long could the gloves be used before methylene _________ reaches the hand?
- Data (from Table 22.5)
  - diffusion coefficient in butyl rubber:

    $D = 110 \times 10^{-8}\ cm^2/s$

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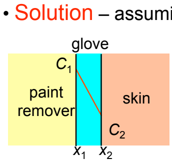
CPC Example (cont.)

- Solution – assuming linear conc. _____________



Breakthrough time = t_b

$$t_b = \frac{\ell^2}{6D}$$

Equation from online CPC Case Study 5 at the Student Companion Site for *Callister & Rethwisch 8e* (www.wiley.com/college/callister)

$\ell = x_2 - x_1 = 0.04$ cm

$D = 110 \times 10^{-8}\ cm^2/s$

$$t_b = \frac{(0.04\ cm)^2}{(6)(110 \times 10^{-8}\ cm^2/s)} = 240\ s = 4\ min$$

Time required for ___________ ca. 4 min

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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

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