



Diffusion

Atoms movements in materials

Movement of atoms in **solids**, liquids and gases is very **important**

Examples: Hardening steel, chrome-plating, gas reactions, Si wafers .. etc.

We will study:

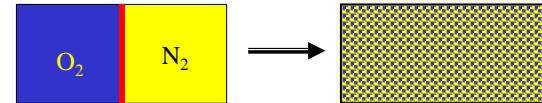
- Atomic mechanisms of diffusion
- Mathematics of diffusion
- Factors affecting diffusion
- Examples
- Steady state diffusion
- Nonsteady state diffusion
- Summary



Diffusion

- diffusion is the mass transport through atomic motion at high temperature
- can have *self-diffusion* or *interdiffusion* between two materials
 - Self-diffusion occurs in pure elements

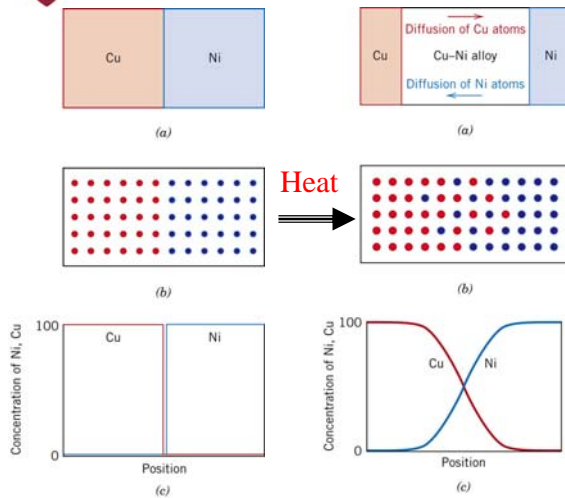
Example: Two chambers, each containing a different gas, separated by a removable barrier; when the barrier is pulled away, *interdiffusion* occurs



driving force is the chemical or *concentration gradient* through materials or *diffusion couple*



Diffusion in Solid Materials



temperature should be high enough to overcome energy barriers to atomic motion.

Heat causes atoms to vibrate

- Vibration amplitude increases with temperature
- Melting occurs when vibrations are sufficient to rupture bonds

The process of substitutional diffusion requires the presence of vacancies (Vacancies give the atoms a place to move)

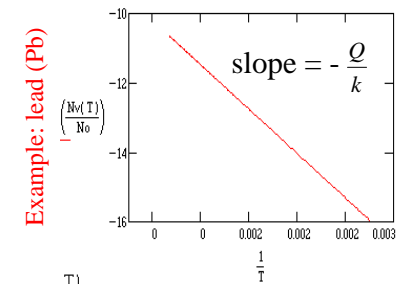
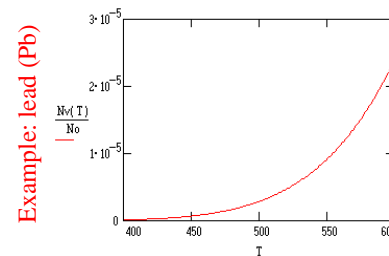


Recall Arrhenius equation

$$N_v = N_o \exp\left(-\frac{Q}{kT}\right)$$

where

- N_v = equilibrium # of vacancies
- N_o = total number of lattice sites
- k = Boltzman's constant
- Q = activation energy for vacancy formation

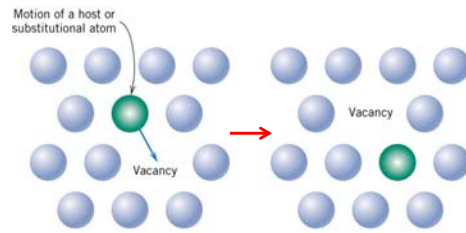


As $T \uparrow$, number of vacancies \uparrow , and energy \uparrow , so diffusion is faster



Diffusion Mechanisms

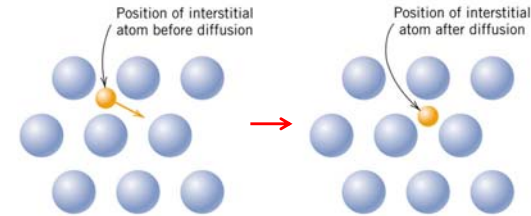
- Atoms are constantly in motion and vibrating
- change of atomic position requires:
 - vacant site
 - energy to break atomic bonds
- Two types of diffusion mechanism:
 - vacancy diffusion
 - interstitial diffusion
- movement of vacancies in one direction is equivalent to atomic movement in the opposite direction



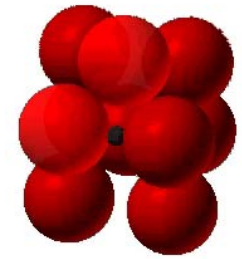
Vacancy diffusion



INTERSTITIAL DIFFUSION



Interstitial diffusion



- Interstitial atom moves from one interstitial site to another (*empty*)
- Energy needed, again to squeeze past atoms.
- Example:
- Usually much faster because many more empty interstitial sites and no vacancies are required

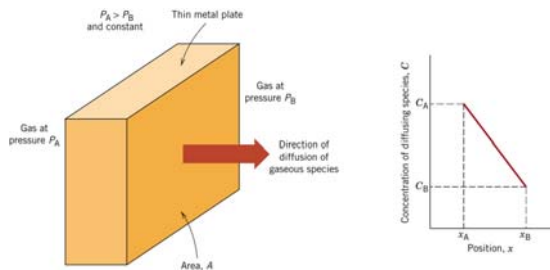


Diffusion

- Diffusion is a process
- ➔ rate of diffusion is important
- diffusion flux (J) is defined as the mass, M , diffusing through unit area, A , per unit time, t

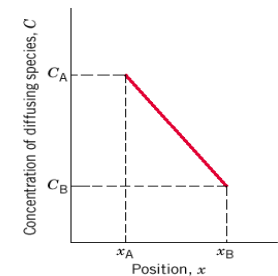
$$J = \frac{M}{At} \quad \text{or} \quad J = \frac{1}{A} \frac{dM}{dt}$$

If flux does not change with time:



Steady-State Diffusion

- Concentration gradient = $\frac{dC}{dx}$
- Fick's 1st law: $J = -D \frac{dC}{dx}$



Where D is the **diffusion coefficient** (diffusivity) or speed of diffusion (m^2/s).

-ve because atoms diffuse down concentration gradient

- Example of *steady-state diffusion* is gas diffusing through a metal plate (*gas pressure constant*).



Example

The purification of H₂ (gas) by diffusion through a Pd sheet was discussed in Callister 5.3. Compute the number of kilograms of hydrogen that pass per hour through a 5 mm thick sheet of Pd having an area of 0.20 m² at 500°C. Assume a diffusion coefficient of 1.0x10⁻⁸ m²/s, that the concentrations at the high and low pressure sides of the plate are 2.4 and 0.6 kg of H₂ per m³ of Pd, and that **steady state conditions** have been attained.

Recall, flux is mass per unit time per unit area. Thus, multiplying J by area and time will give total mass.



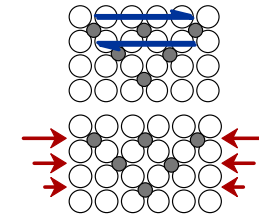
Case Hardening

Chapter 5
Callister 8e.
(courtesy of
Surface
Division,
Midland-
Ross.)



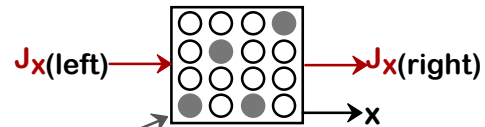
- Example of interstitial diffusion is a **case hardened gear**.
- Diffuse carbon atoms into the host iron atoms at the surface.

- Result: The "Case" is
 - **hard to deform**: C atoms "lock" planes from **shearing**.
 - **hard to crack**: C atoms put the surface in compression.



Steady State Diffusion: Summary

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



Steady State:
 $J_x(\text{left}) = J_x(\text{right})$

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)!**



Non-steady State Diffusion

- In most real situations diffusion is not
- Flux and concentration gradient vary with time

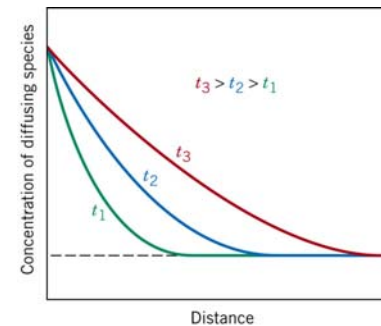


FIGURE 5.5 Concentration profiles for nonsteady-state diffusion taken at three different times, t_1 , t_2 , and t_3 .

- The changes of the concentration profile is given in this case by a differential equation,
- second law:*

$$\frac{\partial C}{\partial t} = \frac{\partial}{\partial x} \left(D \frac{\partial C}{\partial x} \right)$$

- If diffusion coefficient is independent of *composition* then:

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

Solution of this equation is concentration profile as function of time,



Fick's Second Law

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

▪ Solution requires boundary conditions.

• A useful solution is for a **semi-infinite** solid when the surface concentration remains constant.

• What is semi-infinite solid?

✓ **semi infinite bar**: If non of the diffusing atoms reaches the bar end during the time over which the diffusion takes place.

✓ $l > 10\sqrt{Dt}$, where l : bar length, D : diffusion coefficient and t : time



Fick's Second Law - *Application*

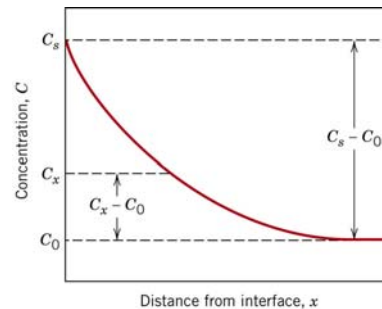
- Simple boundary condition is where the surface concentration is held constant,
 - e.g. gas phase with constant partial pressure at the surface
- Conditions are:
 - before diffusion, solute atom have a **homogeneous concentration** of C_0
 - x is zero at the surface and increases with distance into the solid
 - **time is zero just before diffusion begins**
- Mathematically, for $t = 0$, $C = C_0$ at $0 \leq x \leq \infty$
 $t > 0$, $C = C_s$ at $x = 0$ and $C = C_0$ at $x = \infty$
 $C_s =$ constant surface concentration
- applying these boundary conditions gives:

$$\frac{C_x - C_0}{C_s - C_0} = 1 - \operatorname{erf}\left(\frac{x}{2\sqrt{Dt}}\right)$$



Application of Fick's Second Law

$$\frac{C_x - C_0}{C_s - C_0} = 1 - \operatorname{erf}\left(\frac{x}{2\sqrt{Dt}}\right)$$



C_s = Surface concentration which remains constant

C_0 = Initial concentration in solid

C_x = Concentration at distance x into sample after time t .

D = Diffusivity of solute in solvent, m^2s^{-1}

t = Time, seconds

erf = Gaussian error function, based on integration of the "bell shaped" curve

$$\operatorname{erf}(z) = \frac{2}{\sqrt{\pi}} \int_0^z \exp(-y^2) dz \quad \left(\frac{x}{2\sqrt{Dt}}\right) = z$$



Tabulation of Error Function Values

Table 5.1 Tabulation of Error Function Values

z	$\operatorname{erf}(z)$	z	$\operatorname{erf}(z)$	z	$\operatorname{erf}(z)$
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

$$\frac{C_x - C_0}{C_s - C_0} = 1 - \operatorname{erf}(z) \quad \left(\frac{x}{2\sqrt{Dt}}\right) = z$$



Special case

- If it is desired to achieve a particular concentration of solute atoms in an alloy then:

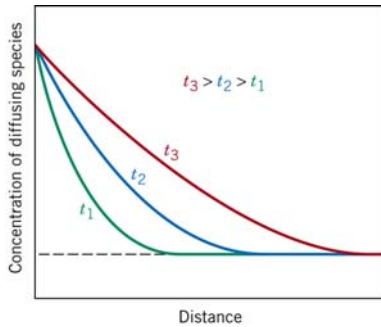


FIGURE 5.5 Concentration profiles for nonsteady-state diffusion taken at three different times, t_1 , t_2 , and t_3 .

$$\frac{C_1 - C_o}{C_s - C_o} = \dots\dots\dots$$

$$\text{and } \frac{x}{2\sqrt{Dt}} = \dots\dots\dots$$

$$\frac{x^2}{Dt} = \dots\dots\dots$$

- These equations facilitate the diffusion computation for this specific case (see example 5.3).



Factors Affecting Solid-State Diffusion

- Diffusing species and host material are important
 - smaller atoms can “squeeze” in between host atoms more easily
 - in lower packing density host material \Rightarrow easier for atoms to migrate with fewer bonds to expand
 - eg faster in more open lattice (BCC faster than FCC) (.....)
 - in lower melting point host material \Rightarrow weaker bonds (easier to push apart)
- Temperature** has a strong effect on diffusion rates:

Where:

- D_o = temperature dependant pre-exponential constant
- Q_d = activation energy for diffusion
- R = gas constant (8.31 J/mol K)
- T = absolute temperature

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

Activation energy is the barrier to diffusion and controls the diffusion coefficient, D



Typical Diffusion Data

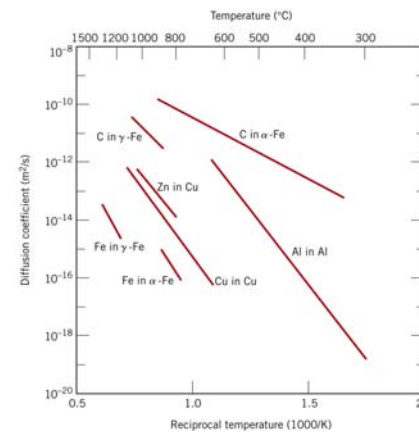
Host crystal	Atom	D_o (cm ² /s)	q_d (eV/atom)
Cu	Cu	0.20	2.04
Cu	Zn	0.34	1.98
Ag	Ag	0.40	1.91
Ag	Au	0.26	1.98
Ag	Cu	1.2	2.00
Ag	Pb	0.22	1.65
U	U	0.002	1.20
Si	Al	8.0	3.47
Si	Ga	3.6	3.51
Si	In	16.0	3.90

Typical values for preexponential (D_o) and activation energy

(after Kittel, “Solid State Physics” 5th ed.)



Experimental Determination of Activation Energy



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

- Taking logs:

$$\log D = \log D_o - \frac{Q_d}{2.3R} \left[\frac{1}{T} \right]$$

- plot $\log D$ vs. $1/T$
- slope =
- intercept =

FIGURE 5.7 Plot of the logarithm of the diffusion coefficient versus the reciprocal of absolute temperature for several metals.



Example

An FCC Fe-C alloy initially containing 0.35 wt. % C is exposed to an oxygen-rich (and carbon-free) atmosphere at 1400 K (1127°C). Under these conditions the carbon in the alloy diffuses toward the surface and reacts with the oxygen in the atmosphere; that is, the carbon concentration at the surface is maintained essentially at 0 wt. % C. (This process of carbon depletion is termed *decarburation*). At what position will the carbon concentration be 0.15 wt. % after a 10-hour treatment. The value of D at 1400 K is $6.9 \times 10^{-11} \text{ m}^2/\text{s}$.



SUMMARY

Diffusion **FASTER** for...

- crystal structures
- melting T materials
- materials with bonding
- diffusing atoms
- density materials

Diffusion **SLOWER** for...

- structures
- melting T materials
- materials with bonding
- diffusing atoms
- density materials



Next topic:
Mechanical properties of materials