Chapter 7: 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**?

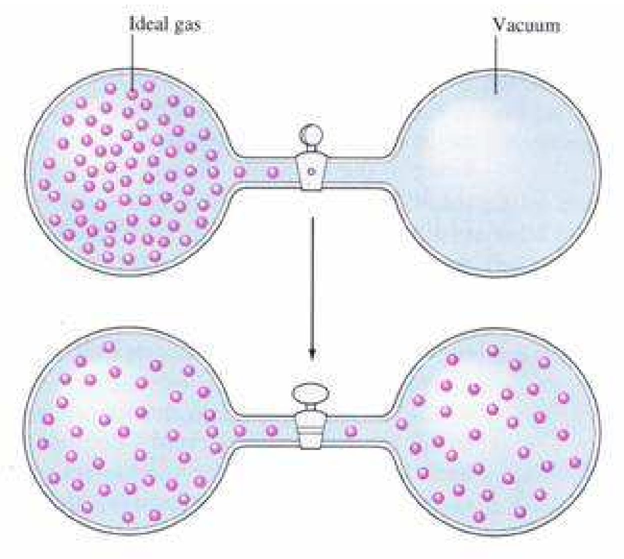
Case Hardening
表面硬化

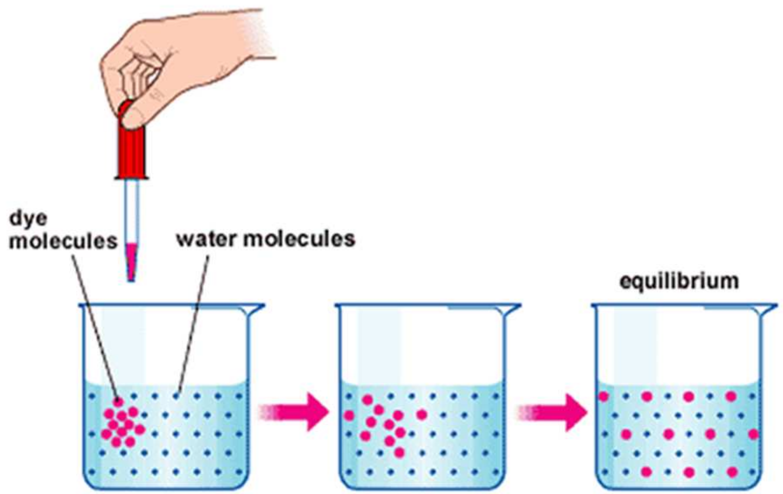
Diffusion

Diffusion - Mass transport by atomic motion

Mechanisms

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





http://www.ch.ntu.edu.tw/~jtchen/course/genchem/2002/Entropy%20&%20Free%20Energy.html

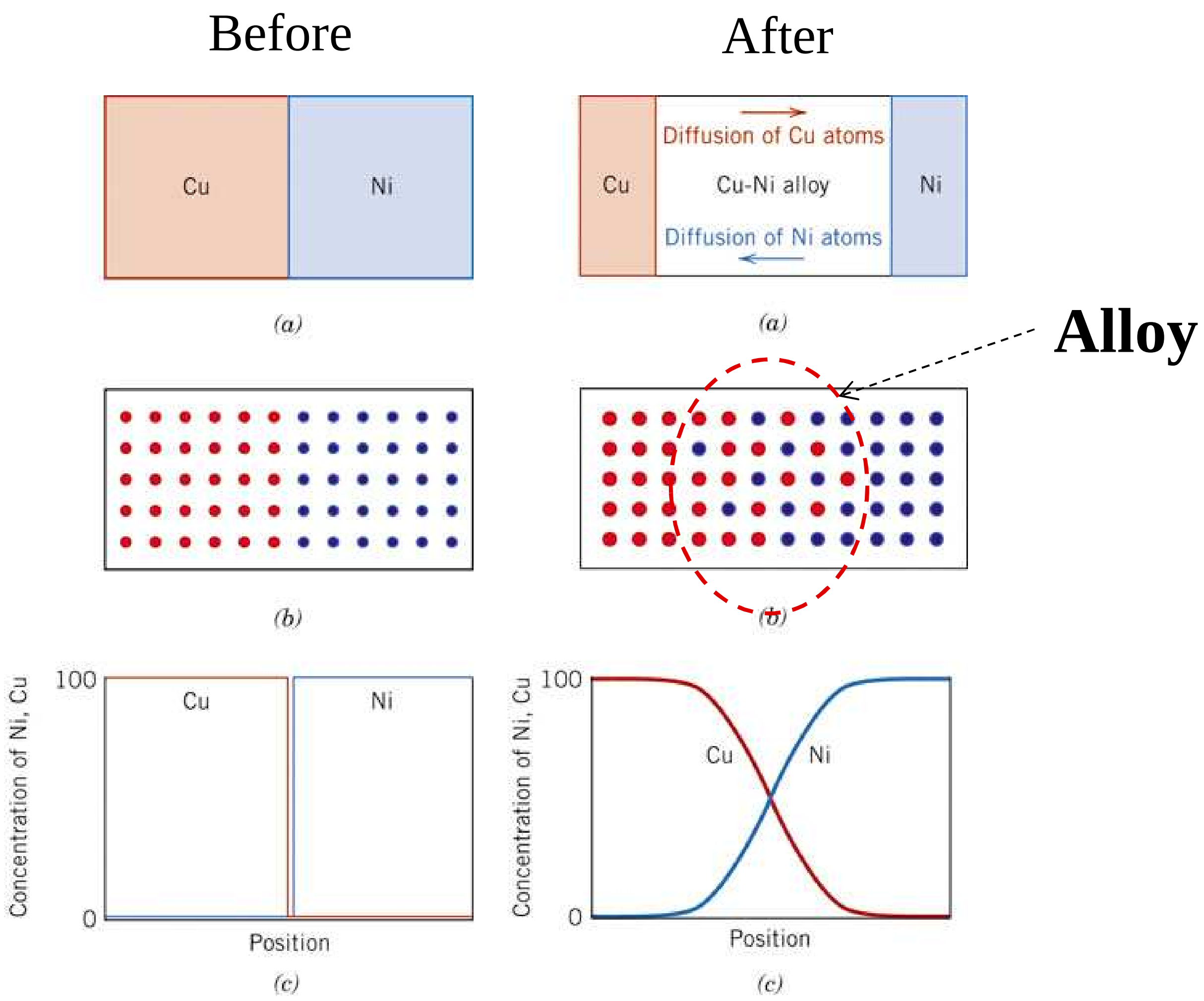
http://solarwiki.ucdavis.edu/@api/deki/files/137/diffusion_1.png

Diffusion - Introduction

Why do we care about diffusion?

- Impurities can diffuse into a material
- Diffusion is important during the solidification process
- Diffusion can be purposely used to introduce impurities that affect the **mechanical properties**

A copper-nickel diffusion couple after a high-temperature heat treatment.

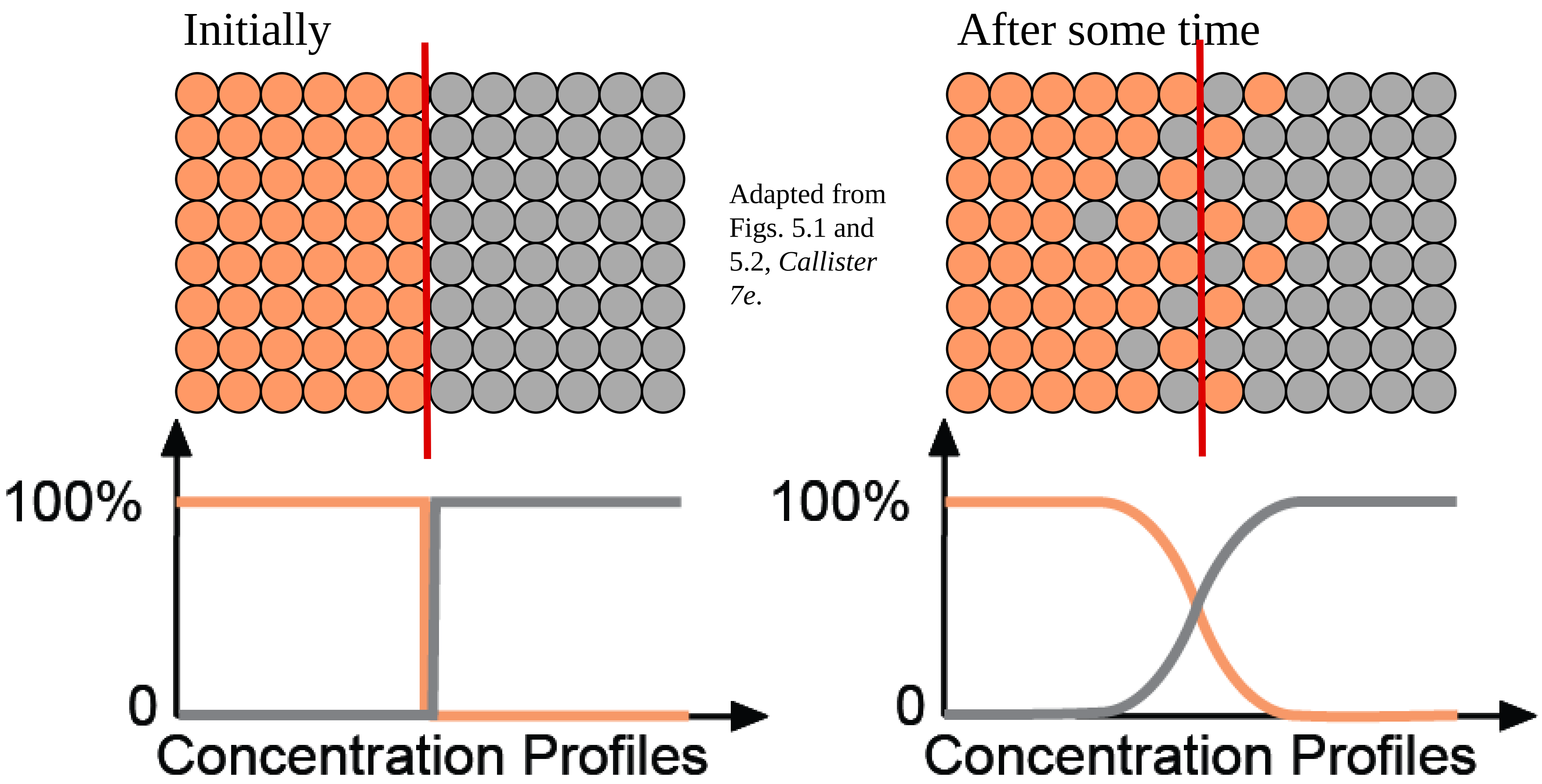


Concentrations of copper and nickel as a function of position across the couple

→ **Interdiffusion** or **impurity diffusion**

Diffusion process I

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

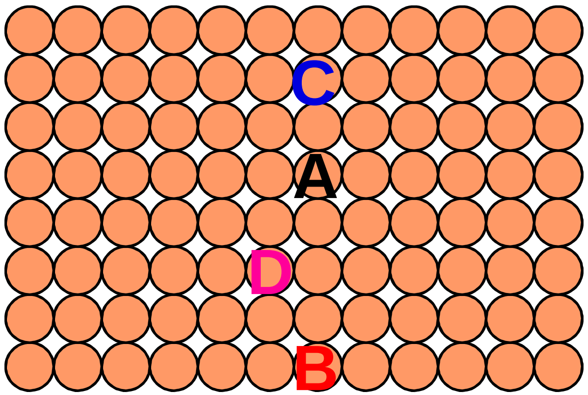


Adapted from Figs. 5.1 and 5.2, *Callister 7e.*

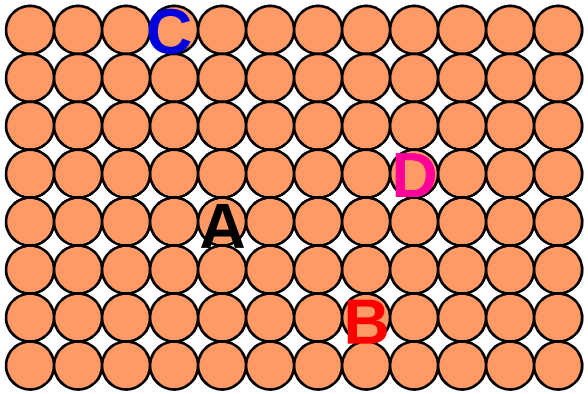
Diffusion process II

- **Self-diffusion:** Diffusion also occurs for pure metal

Label some atoms



After some time

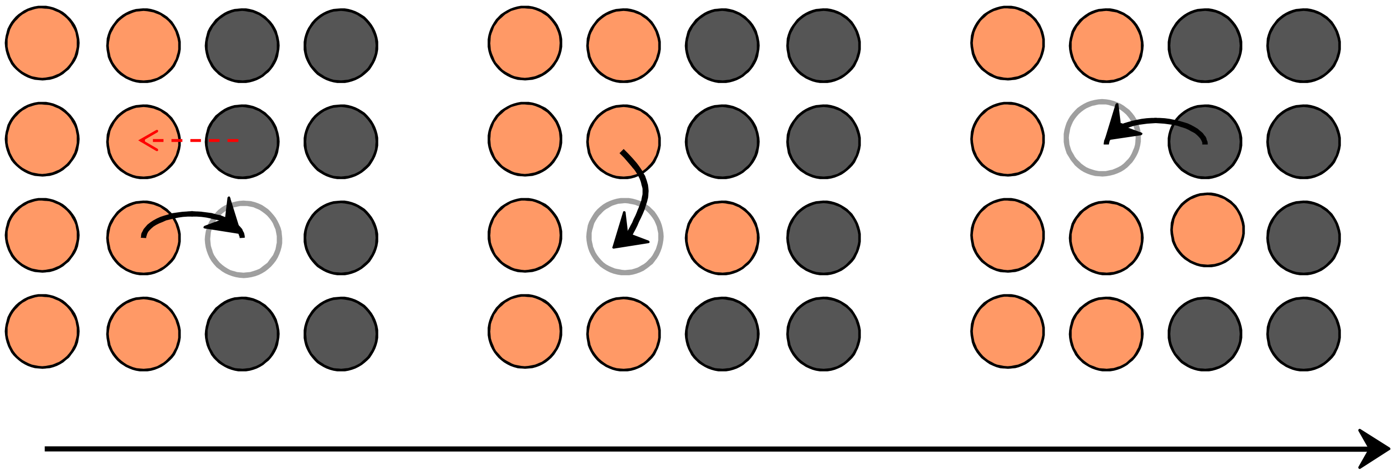


All atoms exchanging positions are of the same type.
→ not subject to observation by noting compositional changes

Diffusion Mechanisms

The atoms in the **solid** materials:

- There must be an empty adjacent site
- The atom must have sufficient energy
  → break bonds with its neighbor atoms.
  → some distortion during displacement.
- Rising Temperature
  → the fraction of the atoms having sufficient energy increase.



increasing elapsed time

http://wenwen.sogou.com/z/q175298563.htm

Diffusion Mechanisms

Vacancy Diffusion:

- atoms exchange with vacancies
- applies to substitutional impurities atoms
- rate depends on:
  --number of vacancies
  --activation energy to exchange .
  --both are related to temperature (T).

No. of defects

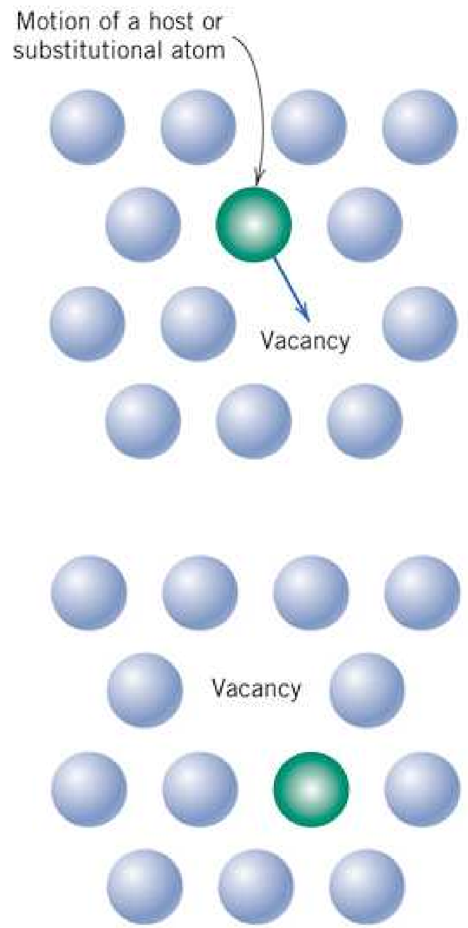
Activation energy

$$\frac{N_v}{N} = \exp\frac{-Q_v}{kT}$$

No. of total atomic sites

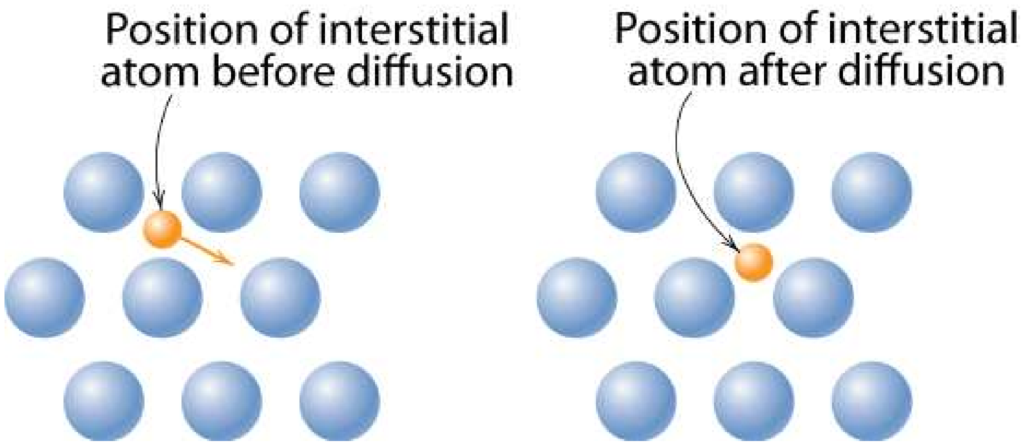
Temperature

Boltzmann's constant



Diffusion Mechanisms

- Interstitial diffusion – smaller atoms can diffuse between atoms.
- This mechanism is found for the atoms such as **hydrogen (H)**, **carbon (C)**, **nitrogen (N)** and **oxygen (O)**, which are small enough to fit into interstitial position.



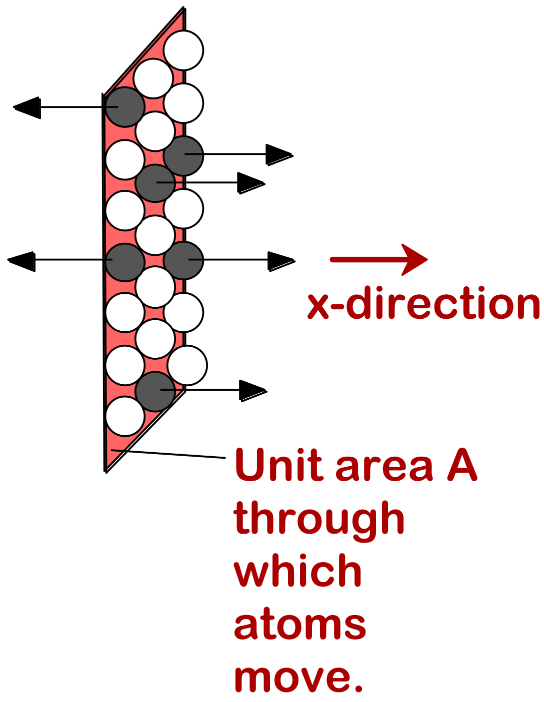
Adapted from Fig. 5.3 (b), *Callister 7e*.

More rapid than vacancy diffusion !

Diffusion Flux

- Diffusion is a time-dependent process.
- How do we quantify the amount or rate of diffusion?

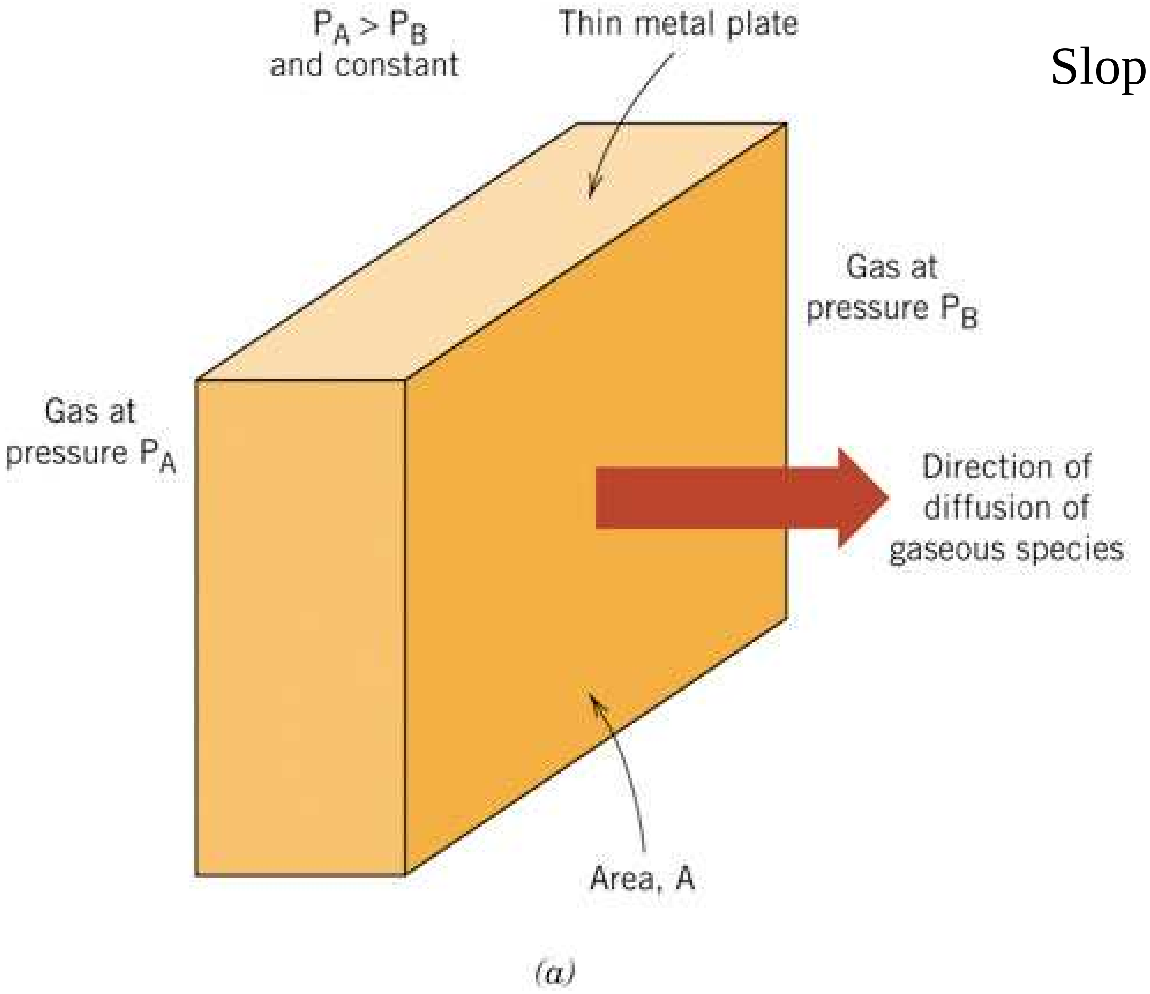
$$J = \frac{M}{At} = \frac{1}{A}\frac{dM}{dt} \qquad \left(\frac{\text{atoms}}{\text{m}^2\text{s}} \text{ or } \frac{\text{kg}}{\text{m}^2\text{s}}\right)$$



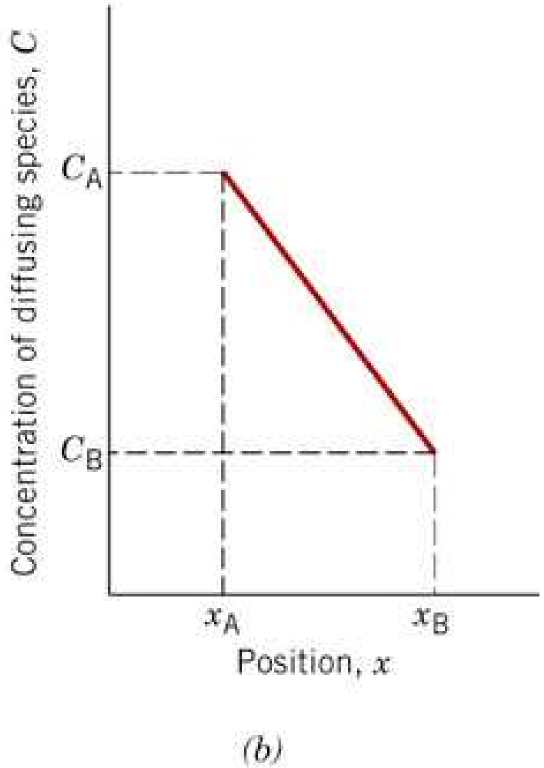
- Mass or the number of atoms diffusing through and perpendicular to a unit cross-sectional area of solid per unit of time.

- If the diffusion flux (J is fixed) does not change with time → **steady-state diffusion**

- One common example of steady state diffusion is the diffusion of atoms of a gas through a plate of metal for which concentrations (or pressure) of the diffusion species on both surface of the plate are held constant.



Slope ： concentration gradient



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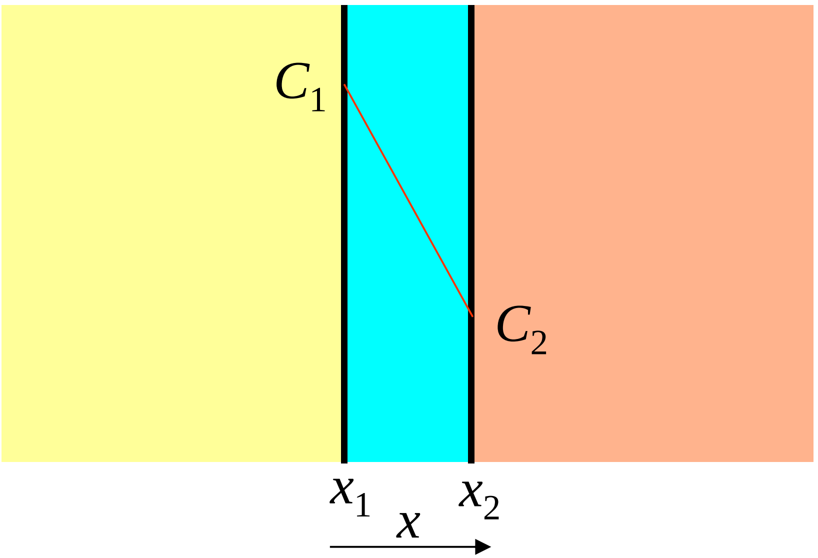
Steady-State Diffusion

- Rate of diffusion independent of time
- Flux proportional to concentration gradient = $\dfrac{dC}{dx}$



Fick's first law of diffusion

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

(Driving force ：concentration gradient)

$D \equiv$ diffusion coefficient

(Diffusion coefficient ：physical constant depends on molecule size and other properties of the diffusing substance)

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

(kg/m^3 or g/cm^3)

Example: Chemical Protective Clothing (CPC)

二氯甲烷

- 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:

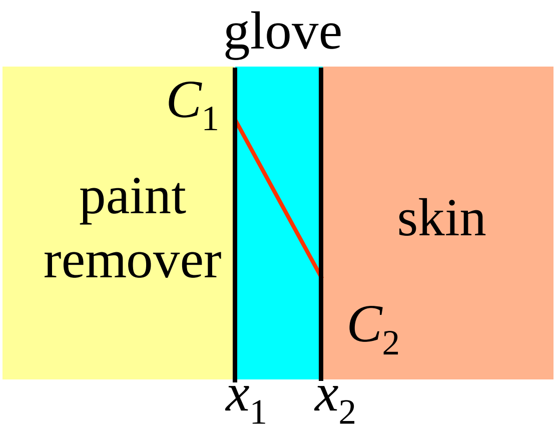
    $$D = 110\text{x}10^{-8}\ \text{cm}^2/\text{s}$$

  - 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:

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

$C_1 = 0.44 \text{ g/cm}^3$

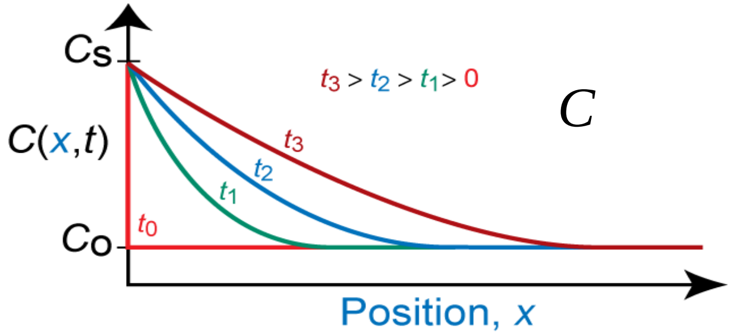
$C_2 = 0.02 \text{ g/cm}^3$

$x_2 - x_1 = 0.04 \text{ cm}$

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

Non-steady State Diffusion

- The diffusion flux and concentration gradient vary with time.

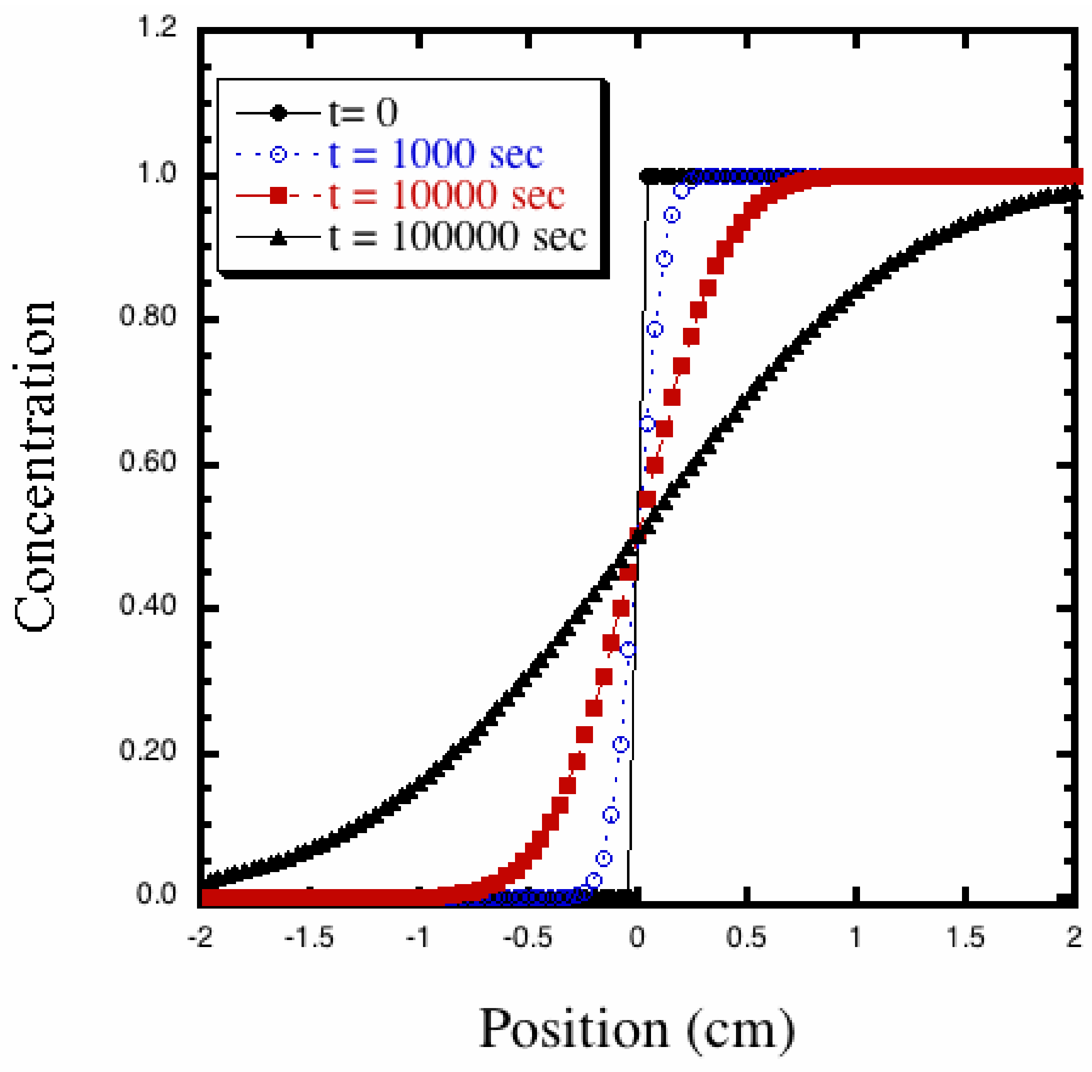


- In this case Fick's Second Law is used

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

If the diffusion coeff. is independent of composition

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

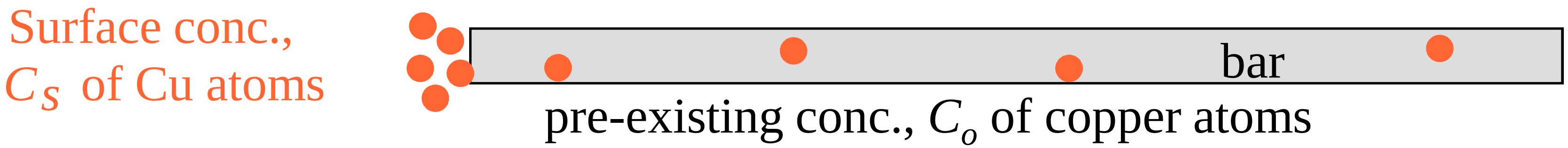


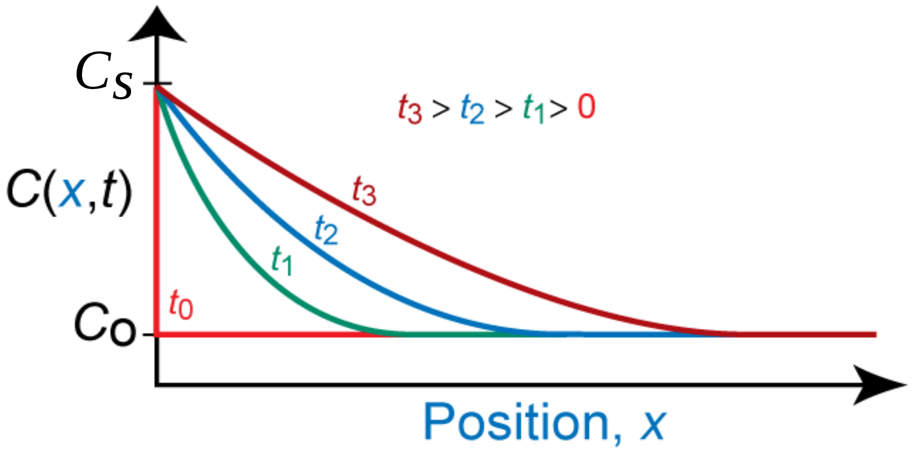
$$\frac{\partial C}{\partial t} = D\frac{\partial^2 C}{\partial x^2}$$

http://www.pojman.com/mg_materials/Diffusion/Diffusion.html

Non-steady State Diffusion

- Copper diffuses into a bar of aluminum.





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

Boundary conditions：

1) at $t = 0$, $C = C_o$ for $0 \le x \le \infty$

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

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

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

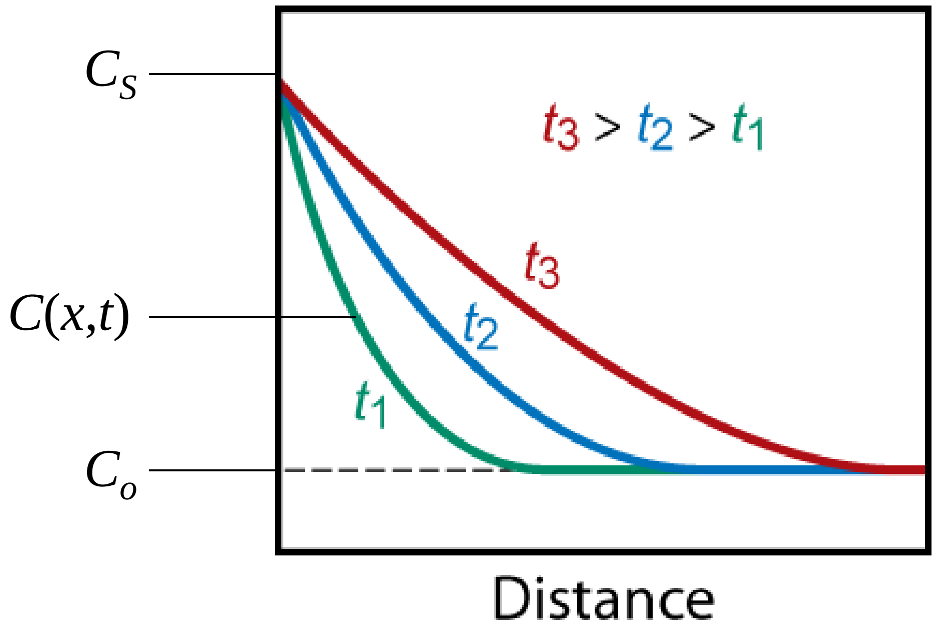
Solution:

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

$C(x,t)$ = 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

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

例題5.2

EXAMPLE PROBLEM 5.2

Nonsteady-State Diffusion Time Computation I

For some applications, it is necessary to harden the surface of a steel (or iron–carbon alloy) above that of its interior. One way this may be accomplished is by increasing the surface concentration of carbon in a process termed **carburizing**; the steel piece is exposed, at an elevated temperature, to an atmosphere rich in a hydrocarbon gas, such as methane (CH_4).

Consider one such alloy that initially has a uniform carbon concentration of 0.25 wt% and is to be treated at 950°C (1223 K). If the concentration of carbon at the surface is suddenly brought to and maintained at 1.20 wt%, how long will it take to achieve a carbon content of 0.80 wt% at a position 0.5 mm below the surface? The diffusion coefficient for carbon in iron at this temperature is 1.6×10^{-11} m^2/s; assume that the steel piece is semi-infinite.

Solution:

Solution

Because this is a nonsteady-state diffusion problem in which the surface composition is held constant, Equation 5.5 is used. Values for all the parameters in this expression except time t are specified in the problem as follows:

$$C_0 = 0.25 \text{ wt\% C}$$
$$C_s = 1.20 \text{ wt\% C}$$
$$C_x = 0.80 \text{ wt\% C}$$
$$x = 0.50 \text{ mm} = 5 \times 10^{-4} \text{ m}$$
$$D = 1.6 \times 10^{-11} \text{ m}^2/\text{s}$$

Thus,

$$\frac{C_x - C_0}{C_s - C_0} = \frac{0.80 - 0.25}{1.20 - 0.25} = 1 - \operatorname{erf}\left[\frac{(5 \times 10^{-4} \text{ m})}{2\sqrt{(1.6 \times 10^{-11} \text{ m}^2/\text{s})(t)}}\right]$$

$$0.4210 = \operatorname{erf}\left(\frac{62.5 \text{ s}^{1/2}}{\sqrt{t}}\right)$$

Solution:

We must now determine from Table 5.1 the value of z for which the error function is 0.4210. An interpolation is necessary, as

z	erf(z)
0.35	0.3794
z	0.4210
0.40	0.4284

$$\frac{z - 0.35}{0.40 - 0.35} = \frac{0.4210 - 0.3794}{0.4284 - 0.3794}$$

or

$$z = 0.392$$

Therefore,

$$\frac{62.5 \text{ s}^{1/2}}{\sqrt{t}} = 0.392$$

and solving for t,

$$t = \left(\frac{62.5 \text{ s}^{1/2}}{0.392}\right)^2 = 25{,}400 \text{ s} = 7.1 \text{ h}$$

Diffusion and Temperature

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.

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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]

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

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

What is the diffusion coefficient at 350ºC?

$$D = D_o \exp\left(-\frac{Q_d}{RT}\right) \longrightarrow \text{2邊取自然對數 ln}$$

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

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

Example (cont.)

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

$$T_1 = 273 + 300 = 573\,\mathrm{K}$$

$$T_2 = 273 + 350 = 623\,\mathrm{K}$$

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

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

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:

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