Chapter 6: Diffusion

ISSUES TO ADDRESS...

- What is diffusion?
- By what atomic mechanisms does diffusion occur?
- What are examples of diffusion in materials processing?
- What equations do we use to solve diffusion problems?
- How does the rate of diffusion depend on temperature?

Diffusion 擴散

依原子運動作質量傳遞

Diffusion - Mass transport by atomic motion

- Diffusion Mechanisms

  隨機布朗運動

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

  間質

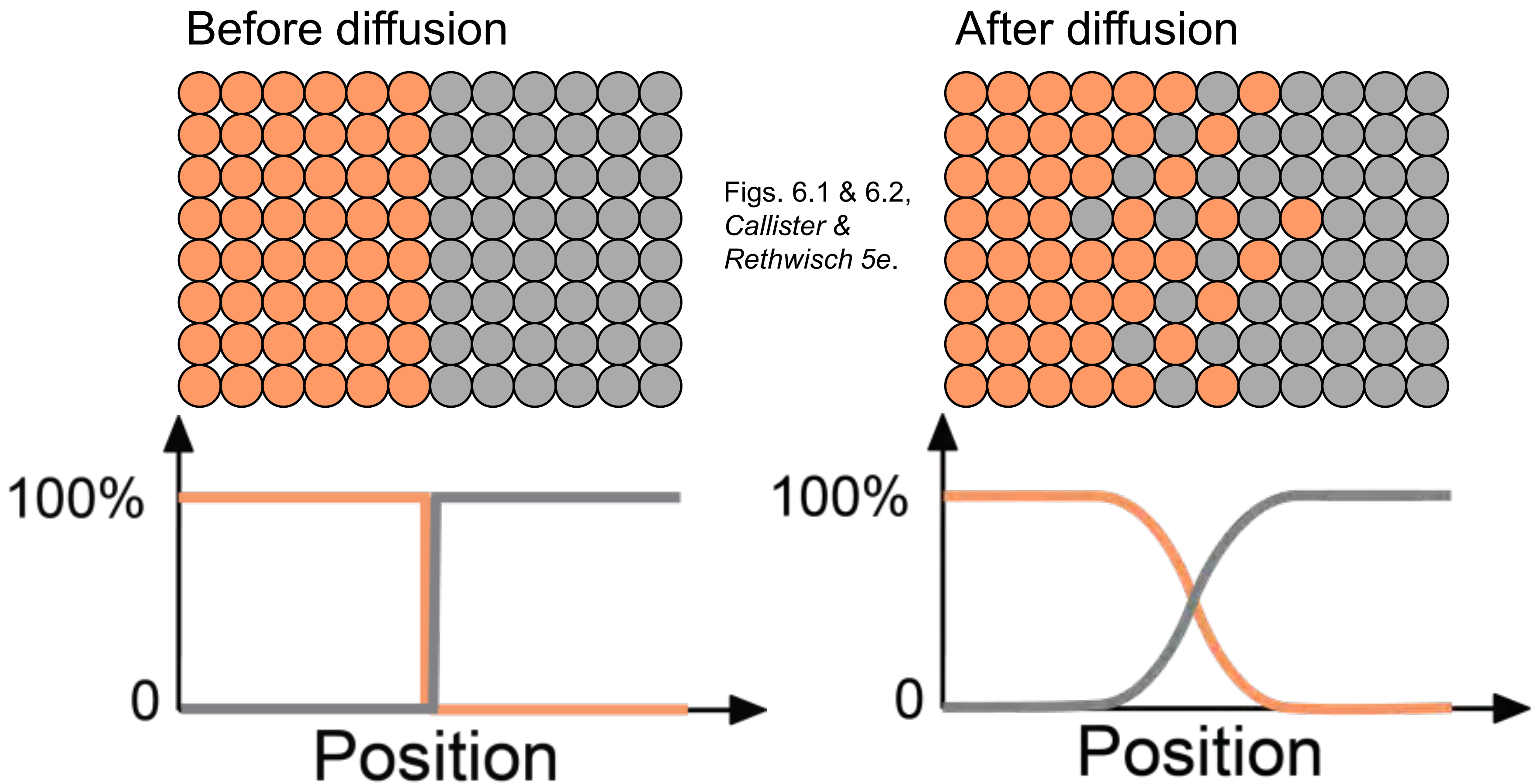
- Interdiffusion - diffusion of atoms of one material into another material

  相互擴散

- Self-diffusion – atomic migration in a pure metal

Diffusion

- Atoms tend to migrate from regions of high concentration to regions of low concentration.



Figs. 6.1 & 6.2, *Callister & Rethwisch 5e*.

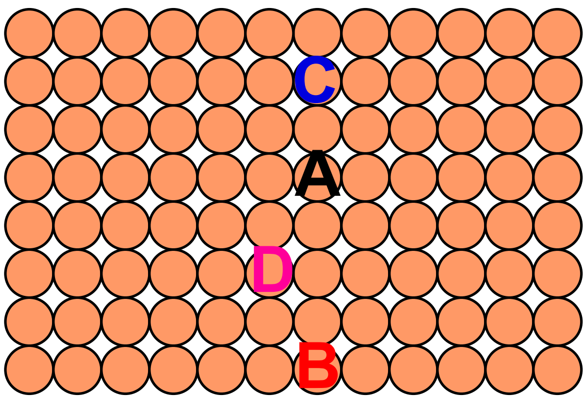
Concentration Profiles

Diffusion

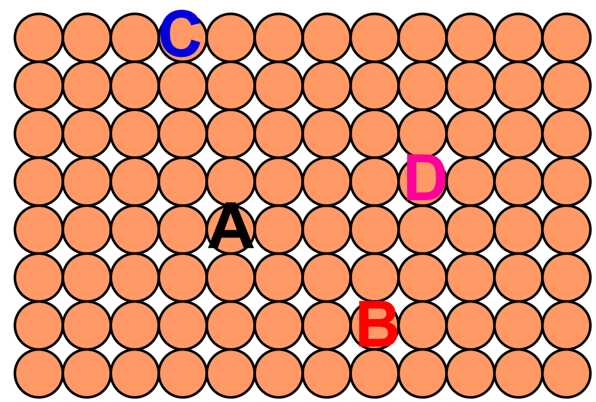
- Self-diffusion: Migration of host atoms in pure metals

都在純物質內發生運動

Locations of 4 labeled atoms before diffusion



Locations of 4 labeled atoms after diffusion



布朗運動

空氣中分子間距離大
可以運動的空間相對大
固體的限制最多
14:53

Diffusion Mechanism I

空缺擴散

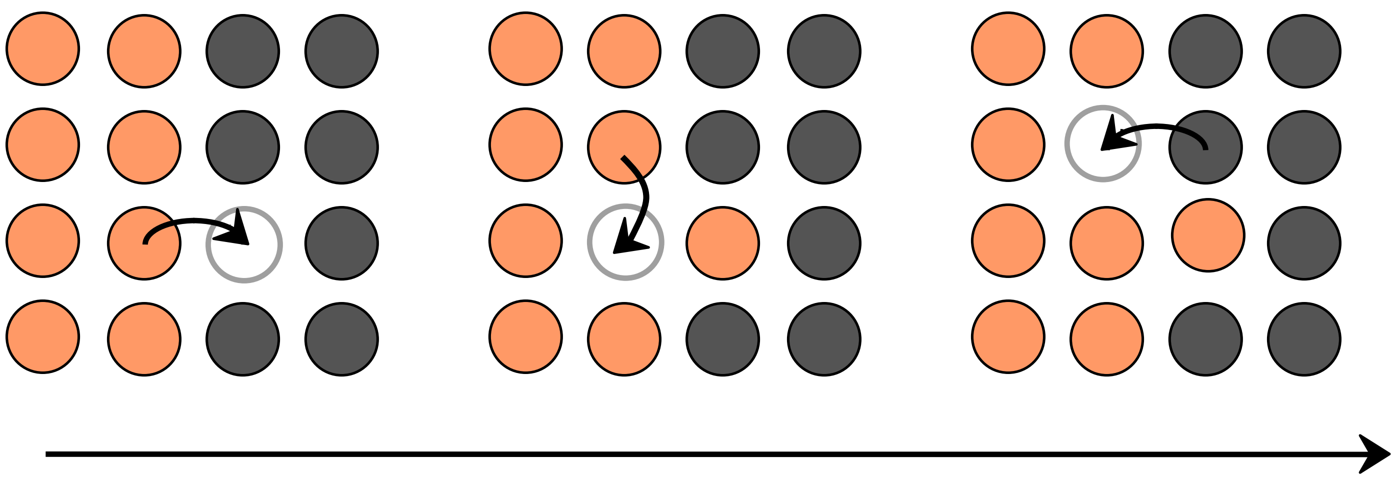
間隙擴散

Vacancy Diffusion

原子和空缺的交互作用

- atoms and vacancies exchange positions
- applies to host and substitutional impurity atoms
- diffusion rate depends on:
  - -- number of vacancies 空缺
  - -- activation energy to exchange.

活化能

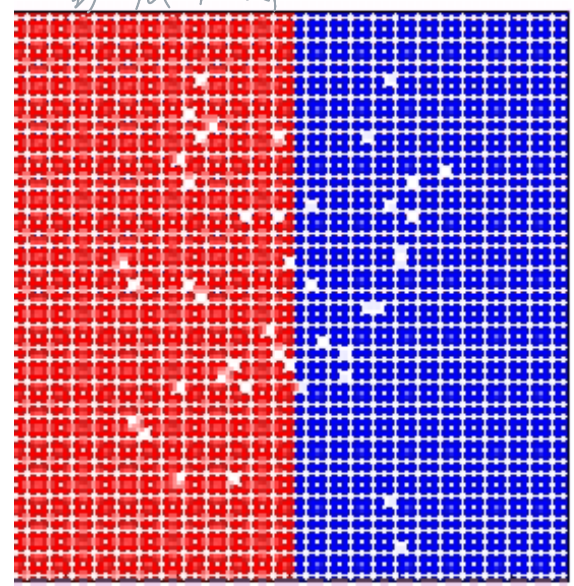


increasing elapsed time

Diffusion Simulation

- Simulation of
  vacancy interdiffusion
  across an interface

動態平衡



(Courtesy P.M. Anderson)

Diffusion Mechanism II

Interstitial Diffusion

- Small, interstitial atoms move from one interstitial position to an adjacent one

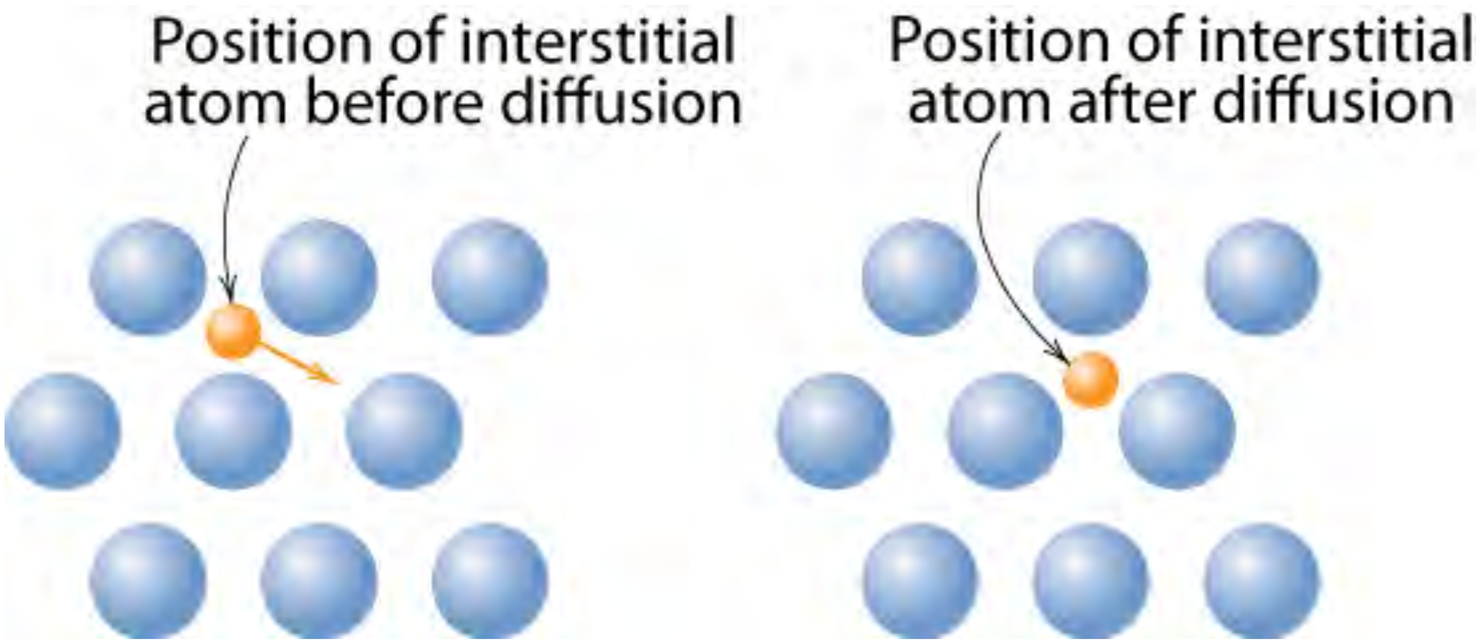


Fig. 6.3 (b), *Callister & Rethwisch 5e*.

More rapid than vacancy diffusion 比空缺擴散快

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Processing Using Diffusion

表面硬化

- Case Hardening:
  - Example of interstitial diffusion
  - Outer surface selectively hardened by diffusing carbon atoms into surface
  - Presence of C atoms makes iron (steel) harder

C擴散至表面

- Example: Case hardened gear
  - Case hardening improves wear resistance of gear
  - Resulting residual compressive stresses improve resistance to fatigue failure

Case hardened region

Chapter-opening photograph, Chapter 6, *Callister & Rethwisch 5e.* (Courtesy of Surface Division, Midland-Ross.)

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Processing Using Diffusion

Diffusion in Semiconducting Devices

小質量的原子

- Doping – Diffusion of very small concentrations of atoms of an impurity (e.g., P) into the semiconductor silicon.

- Process:

磷

1. Deposit P rich 沉積 layers on surface

2. Heat treat the sample to drive in P

3. Result is P doped semiconductor regions

質傳現象與應用

Rate of Diffusion

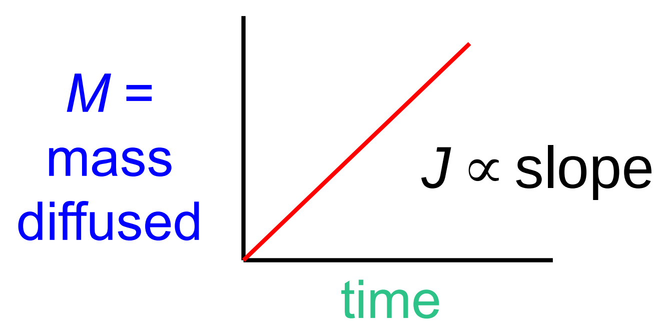
- Diffusion is a time-dependent process.
- Rate of Diffusion - expressed as diffusion flux, J

$$J \equiv \text{Flux} \equiv \frac{\text{mass of diffused species}}{(\text{area})(\text{time})} = \frac{M}{At} \left(\frac{\text{kg}}{\text{m}^2\text{-s}}\right)$$

- Measured experimentally
  - Use thin sheet (or membrane) – cross-sectional area A
  - Impose concentration gradient across sheet
  - Measure mass of diffusing species (M) that passes through the sheet over time period (t)

one

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

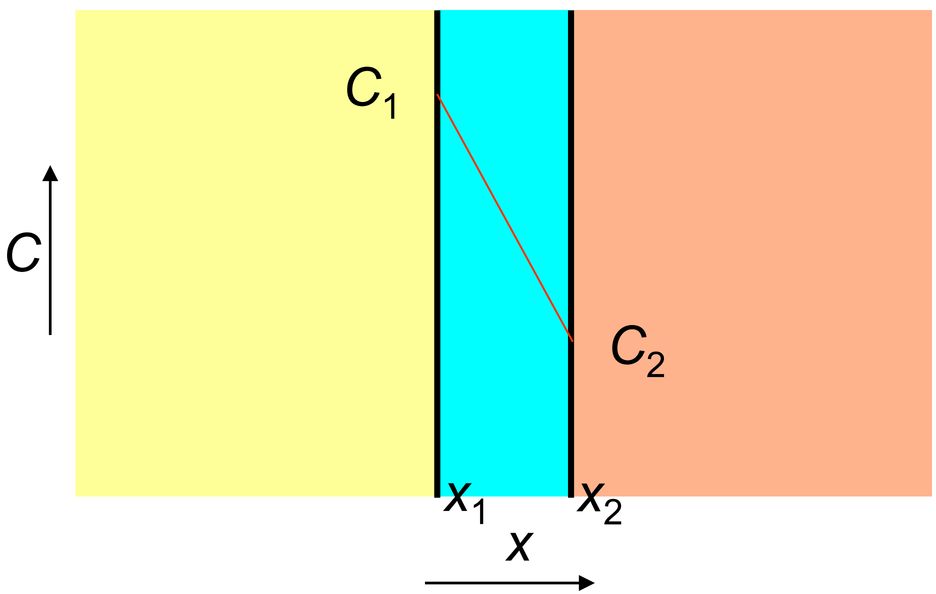


Steady-State Diffusion

Rate of diffusion (or flux) independent of time

Flux (J) proportional to concentration gradient: $J \propto \dfrac{dC}{dx}$

C = concentration
x = diffusion direction



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

Fick's first law of diffusion

考

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

D = diffusion coefficient

係數

Diffusion Example

Chemical Protective Clothing (CPC)

- Methylene chloride (二氯甲烷) 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.

  移除油漆

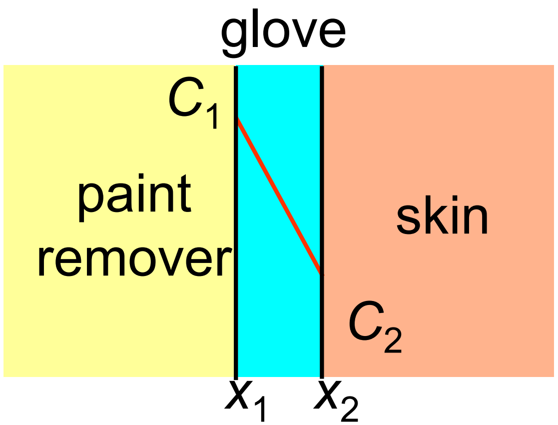
  要護手

- Lets investigate whether butyl rubber gloves (0.04 cm thick) commonly found in the kitchen can be used as protective gloves.
- Note: The maximum allowable flux for a 150 lb person is less than 3.5×10^{-7} $g/cm^2/s$
- Compute the diffusion flux of methylene chloride through the gloves.

CPC Example (cont.)

- Solution – diffusion flux of methylene chloride

assume linear conc. gradient



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

Data:

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

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

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

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

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

Note: this is more than 30 times the allowable flux.
Unsafe to use these gloves for paint removal.

質傳現象與應用

Influence of Temperature on Diffusion

- Diffusion coefficient increases with increasing T

$D \propto \frac{1}{T}$

(活化能)
取決於物質的特性，也是T的修正項
constant

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

T的修正項

氣體常數

D = diffusion coefficient [m²/s]

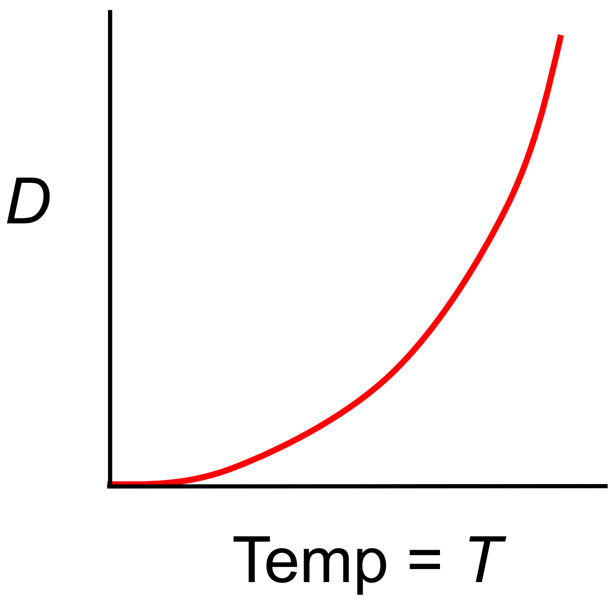
D_o = pre-exponential [m²/s]

Q_d = activation energy [J/mol]

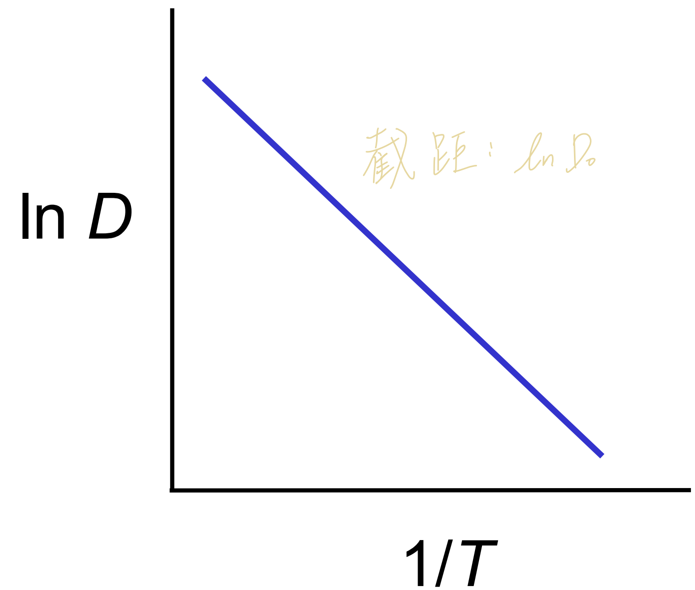
R = gas constant [8.314 J/mol-K]

T = absolute temperature [K]

Influence of Temperature on Diffusion (cont.)



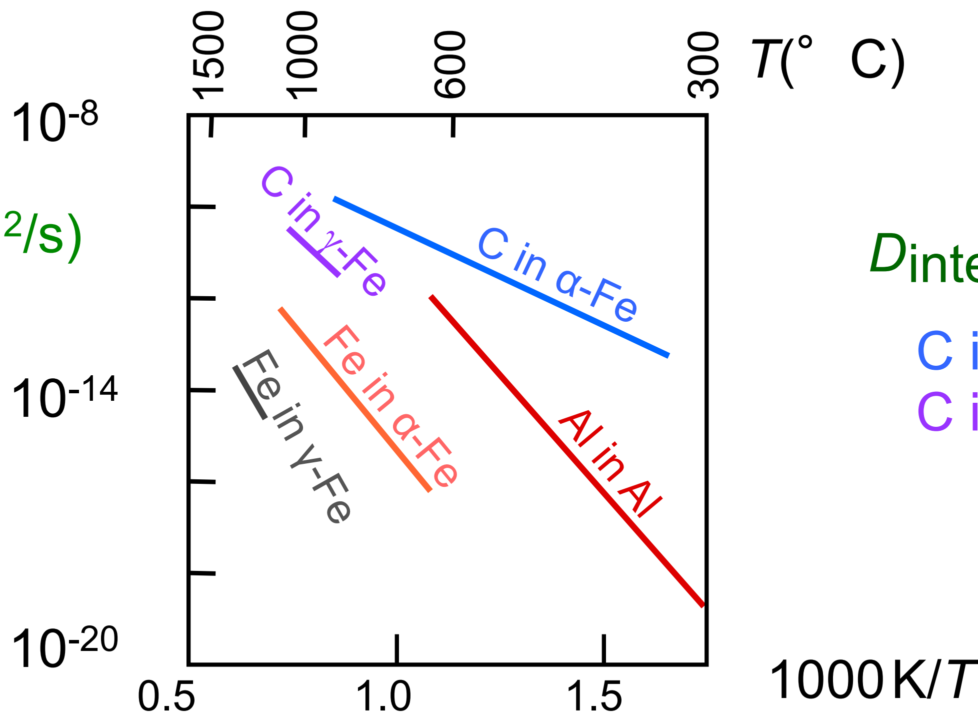
$$\xrightarrow[\text{data}]{\text{transform}}$$



$$D = D_0 \exp\left(-\frac{Q_d}{RT}\right) \xrightarrow[\text{of both sides}]{\text{take natural log}} \ln D = \ln D_0 - \frac{Q_d}{RT}$$

Influence of Temperature on Diffusion (cont.)

D has exponential dependence on *T*



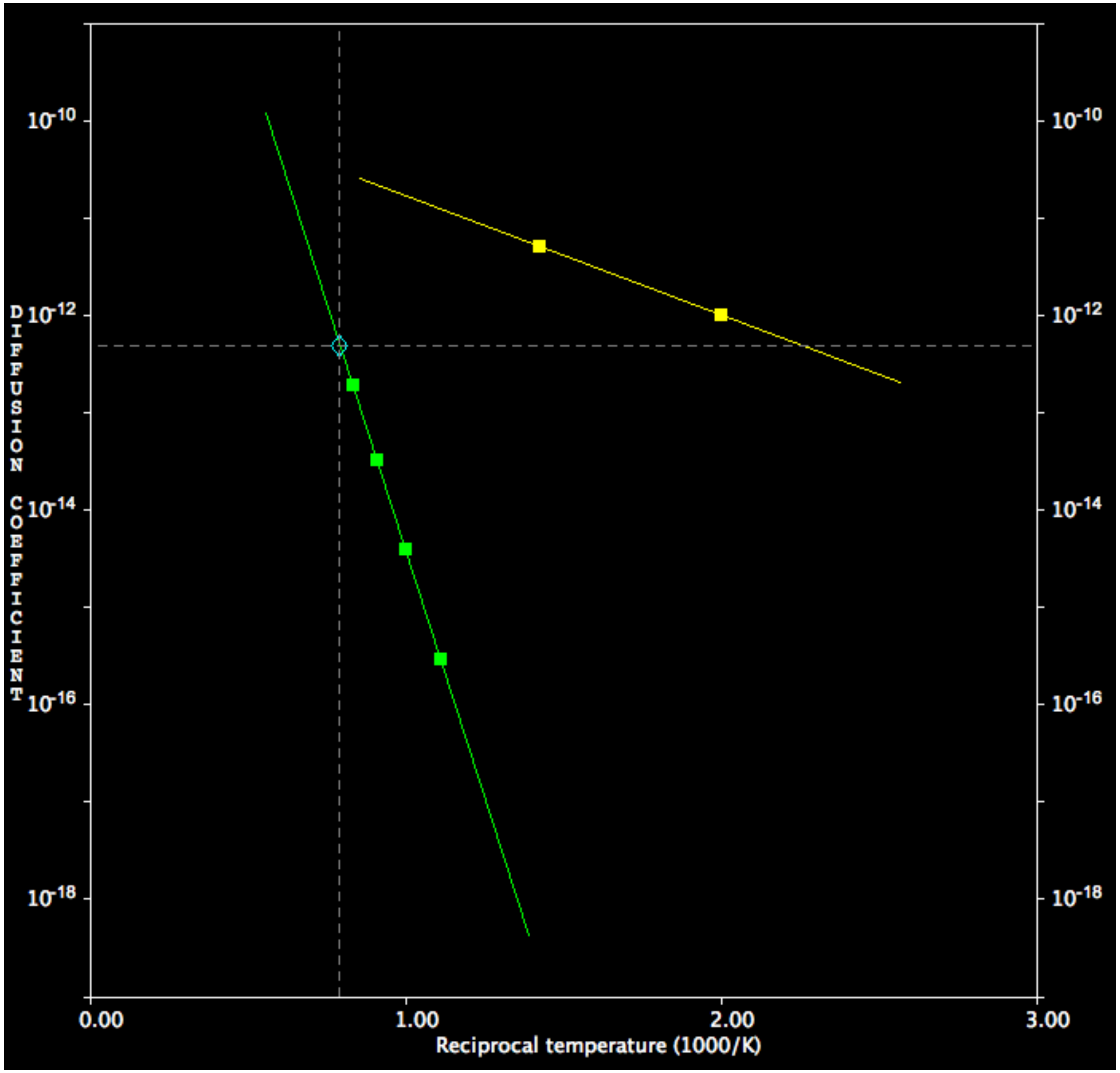
$D_{\text{interstitial}} >> D_{\text{substitutional}}$

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

$$\ln D = \ln D_0 - \frac{Q_d}{RT}$$

Adapted from Fig. 6.7, *Callister & Rethwisch 5e*.
(Data for Fig. 6.7 taken from E.A. Brandes and G.B. Brook (Ed.) *Smithells Metals Reference Book*, 7th ed., Butterworth-Heinemann, Oxford, 1992.)

VMSE: Screenshot of Diffusion Data Plots



Influence of Temperature on Diffusion (cont.)

Derive an equation relating the diffusion coefficients at two temperature T_1 and T_2 using the equation derived

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

(單位=K ℃+273=K)

Subtracting equation at T_1 from equation at T_2

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

Take the exponential of each side to get the final equation

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

300°C

$D_1 = 7.8 \times 10^{-11}$

$Q_d = 41.5 \ kJ/mol$

$D_2 \ (T = 350°C) = ?$

$$D_2 = \overset{7.8\times10^{-11}}{D_1} \exp\left[\frac{-\overset{41.5}{Q_d}}{R} \left(\frac{1}{T_2} - \frac{1}{T_1} \right) \right]$$

T_1: $273 + 300 = 573 \ K$

T_2: $273 + 350 = 623 \ K$

Non-steady State Diffusion

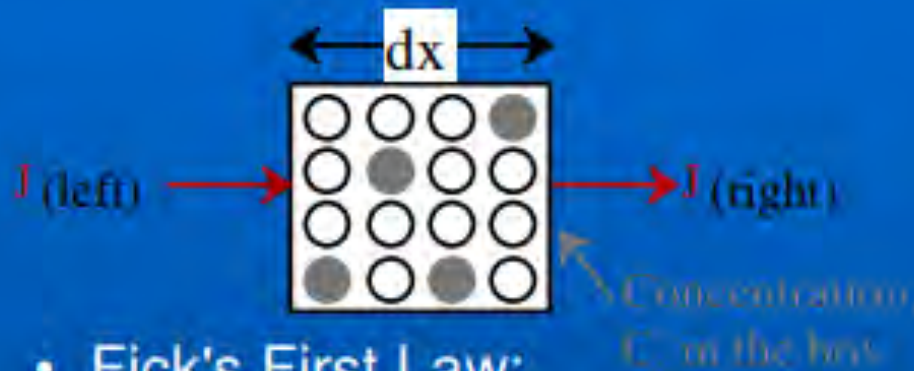
- The concentration of diffusing species is a function of both time and position $C = C(x,t)$ 濃度和時間位置有關
- For non-steady state diffusion, we seek solutions to Fick's Second Law

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

This form of the equation assumes D is independent of concentration

和濃度有關

- Concentration profile, C(x), changes w/ time.



- To conserve matter:
- Fick's First Law:

$$\boxed{\frac{J(\text{right}) - J(\text{left})}{dx}} = -\frac{dC}{dt}$$

$$J = -D\frac{dC}{dx} \quad \text{or}$$

$$\boxed{\frac{dJ}{dx}} = -\frac{dC}{dt}$$

$$\boxed{\frac{dJ}{dx}} = -D\frac{d^2C}{dx^2} \quad \text{(if D does not vary with x)}$$

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

equate

- Governing Eqn.:

$$\boxed{\frac{dC}{dt} = D\frac{d^2C}{dx^2}}$$

Non-steady State Diffusion

- Consider the diffusion of copper into a bar of aluminum

Surface conc., C_S of Cu atoms

pre-existing conc., C_o of copper atoms

$$\frac{dC}{dt} = D\frac{d^2C}{dx^2}$$

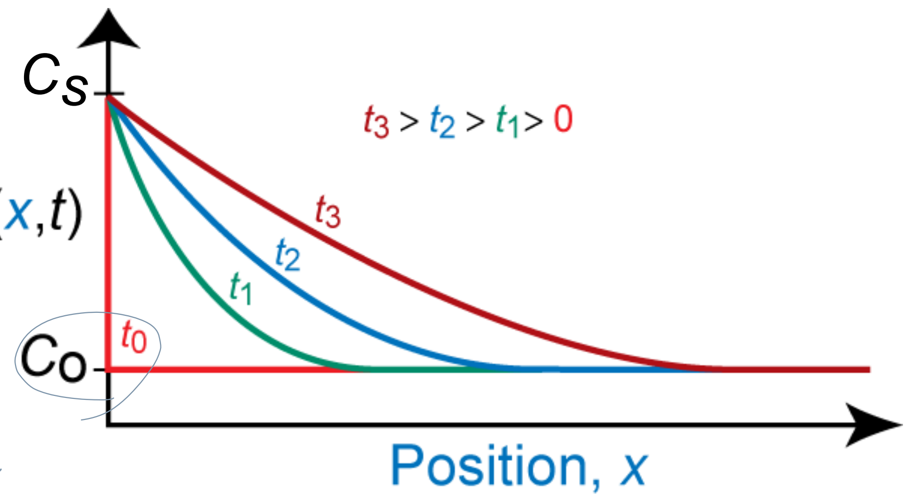


Fig. 6.5, *Callister & Rethwisch 5e*.

邊界條件

Boundary/Initial 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 $x = \infty$

$$\frac{C(x,t) - C_0}{C_s - C_0} = 1 - erf\left(\frac{x}{2\sqrt{Dt}}\right)$$

$t = 49.5\ h$

$C_x = 0.35\ wt\%$

$C_0 = 0.2\ wt\%$

$x = 4 \times 10^{-3}\ m$

$C_s = 1\ wt\%$

$$T = \frac{Q_d}{R(\ln D_0 - \ln D)}$$

Non-steady State Diffusion (cont.)

$$\frac{dC}{dt} = D\frac{d^2C}{dx^2}$$

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

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

$\mathrm{erf}(z)$ = error function

z and $\mathrm{erf}(z)$ values are given in Table

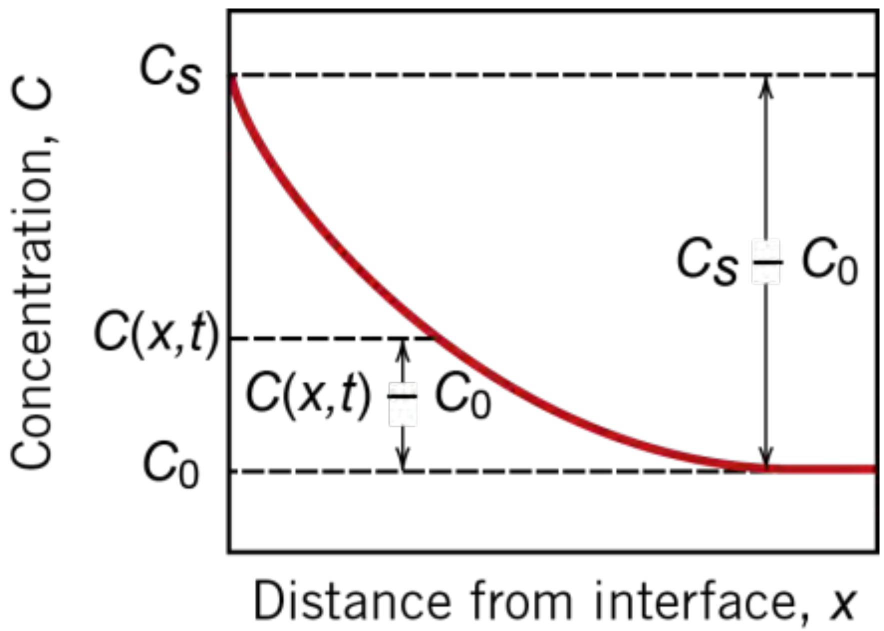


Fig. 6.6, *Callister & Rethwisch 5e*.

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Non-steady State Diffusion

Example Problem

An FCC iron-carbon alloy initially containing 0.20 C_o wt% C is carburized at an elevated temperature and in an atmosphere in which the surface carbon C_s concentration is maintained at 1.0 wt%. If, after t 49.5 h, the concentration of carbon is 0.35 wt% at a x position 4.0 mm below the surface, determine the temperature at which the treatment was carried out.

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

Example Problem (cont.):

Solution: use Eqn. 5.5 $$\frac{C(x,t)-C_o}{C_s-C_o}=1-\mathrm{erf}\left(\frac{x}{2\sqrt{Dt}}\right)$$

Data for problem tabulated as follows:

- 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%

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

erf(z) = 0.8125

Example Problem (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

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

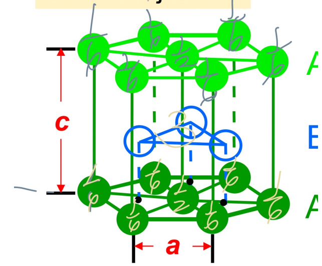
$$z = 0.93$$

Now solve for *D*

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

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

Example Problem (cont.):



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

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

As known, (Table), for diffusion of C in FCC Fe

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

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

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

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

D = diffusion coefficient [m^2/s]

D_o = pre-exponential [m^2/s]

Q_d = activation energy [J/mol]

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

T = absolute temperature [K]

Summary

- Solid-state diffusion is mass transport within solid materials by stepwise atomic motion

- Two diffusion mechanisms
  - Vacancy diffusion
  - Interstitial diffusion

- Fick's First Law of Diffusion

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

- Fick's Second Law of Diffusion
  - non-steady state diffusion

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

- Diffusion coefficient
  - Effect of temperature

$$D = D_0 \exp\left(-\frac{Q_d}{RT}\right)$$

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