Introduction to Materials Science and Engineering

Chapter 5. Diffusion in Solids

- How does diffusion occur?
- Why is it important for synthesis?
- How can the rate of diffusion be predicted?
- How does the diffusivity depend on the structure and temperature?

Activation Energy for Diffusion

In basketball, smaller players can "diffuse" through the open spaces between bigger players. (Courtesy of Getty Images)

Introduction

- Diffusion demo (in liquid and gas)

http://www.class1air.com/facts.htm

Contents

Introduction

- Atoms and molecules can be quite mobile in both liquids and solids, especially at high temperature.
  - √ Drop of ink in a beaker of water
    - → spread, water evenly colored.
  - √ Intermixing at molecular level → **Diffusion**
- Continuous motion of H_2O molecules in water at R.T.
  - → **Self diffusion**
- Atomic-scale motion (diffusion) in liquids is relatively rapid and easy to visualize.
- More difficult to visualize diffusion in rigid solids, but it does occur.

Diffusion

- Diffusion is related to the **internal atom movements**.

- Heat treatments alter the properties of materials.

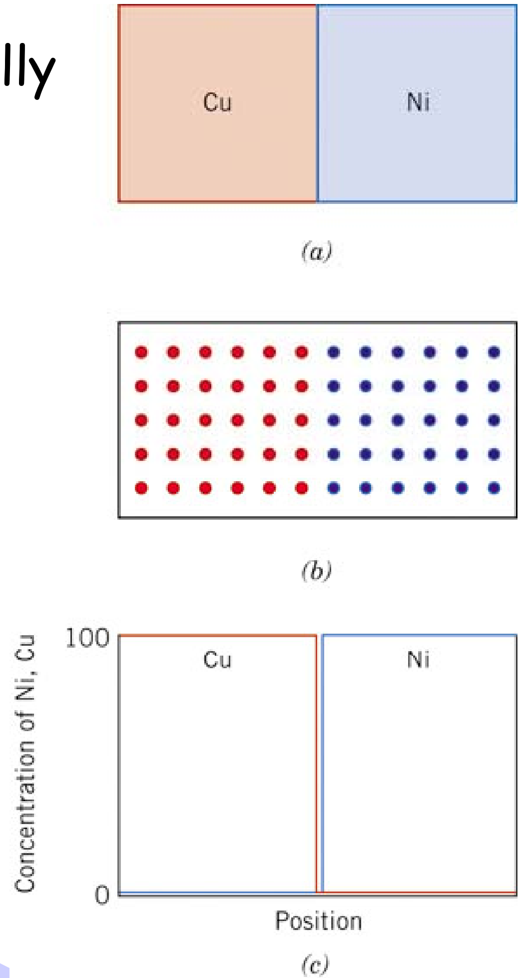
Internal structure of material changes ← Only possible by atom movement

- Diffusion required for:
  - √ Synthesis of transistors and solar cells
  - √ Heat treatment of metals
  - √ Manufacture of ceramics
  - √ Solidification of materials
  - √ Electrical conductivity of ceramic materials

Diffusion-Phenomenon (1)

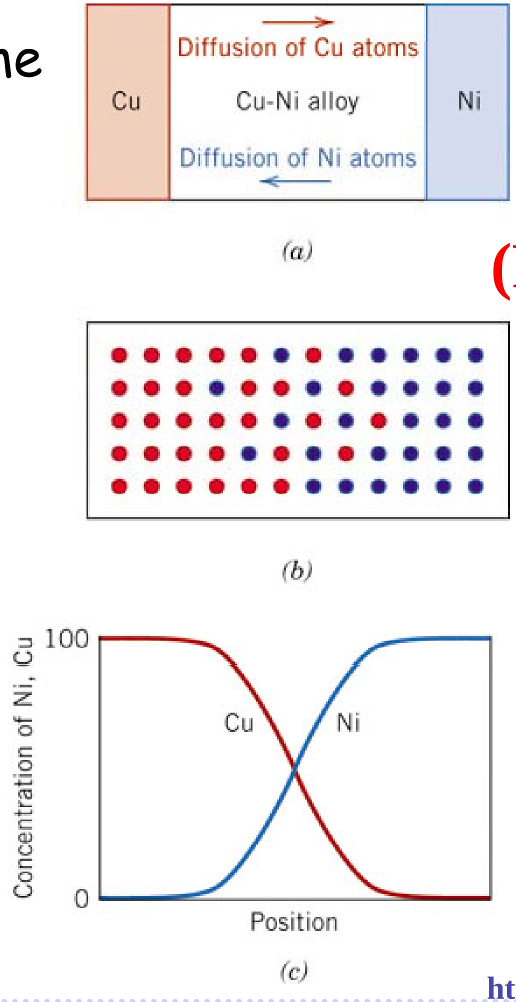
- **Interdiffusion** in diffusion couple
  - Atoms migrate from high to low-concentration regions

Initially



(Fig. 5-1)

After some time



(Fig. 5-2)

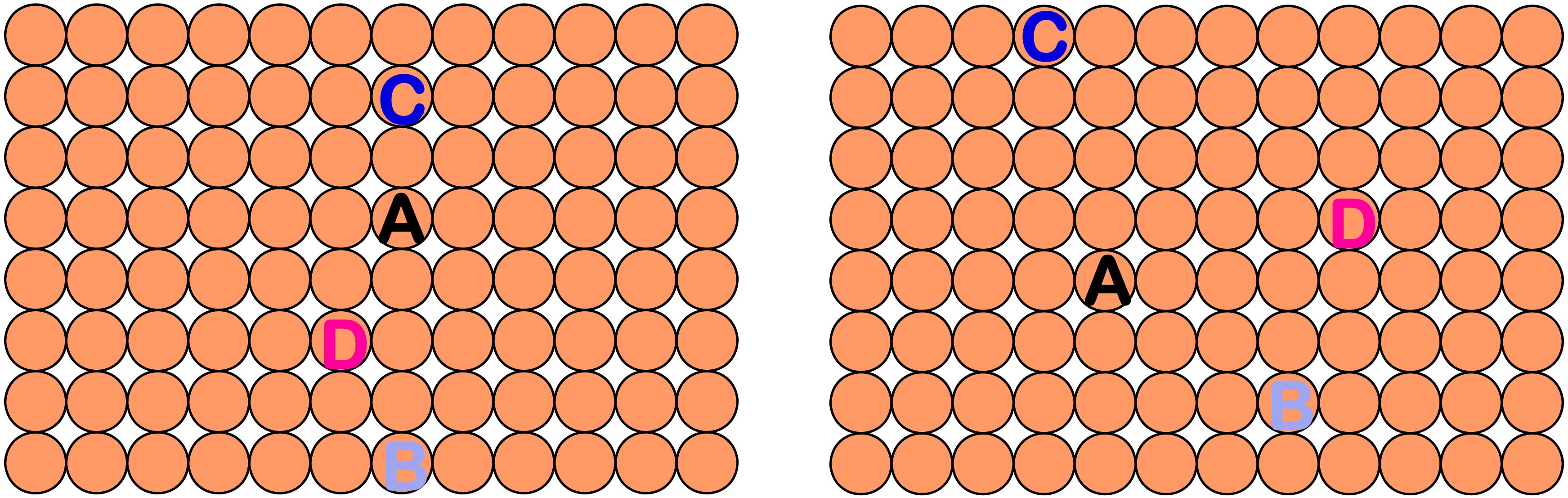
Diffusion-Phenomenon (2)

- Self diffusion:

  All atoms exchanging positions are of the same type

Label some atoms

After some time



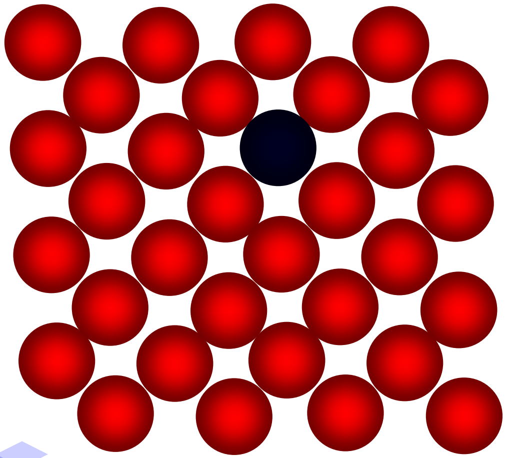
* Labeling by isotope (tracer diffusion)

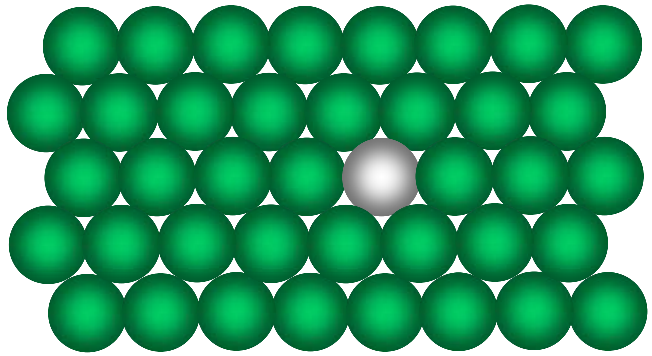
Contents

Diffusion

- The slower diffusion rate in the solid state than in the liquid state.
- **Tight atomic structure** of atoms has an impact on the diffusion of atoms or ions within the solid.
- The **energy required** to squeeze most atoms or ions through a **perfect crystal** structure are so high that diffusion is nearly impossible.

(Fig. 5-3)

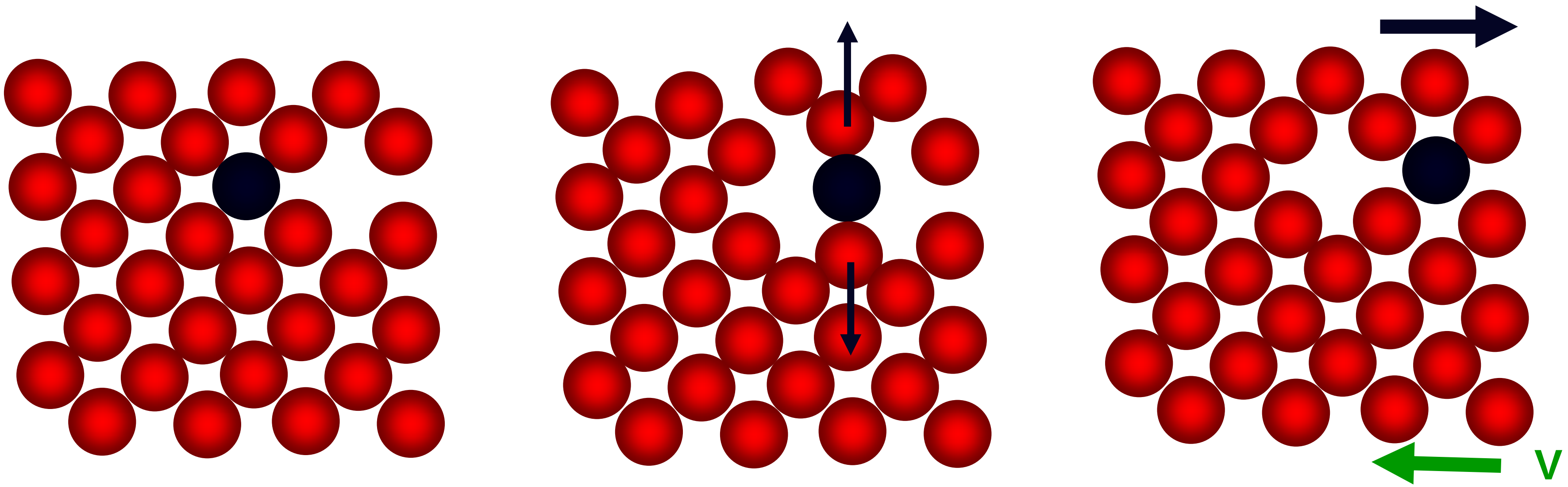




Substitutional Diffusion (Vacancy Diffusion)

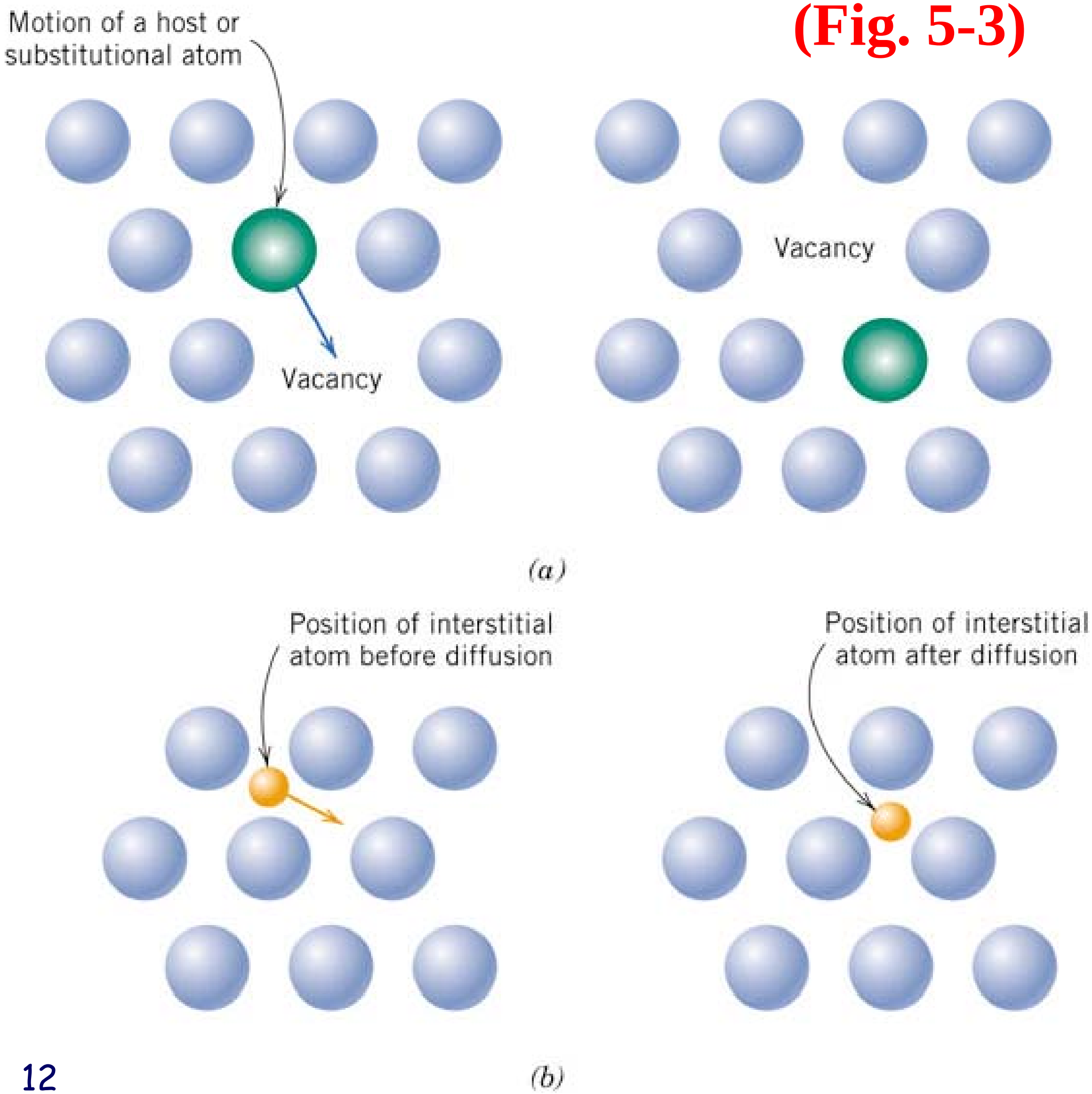
- What is needed to make solid-state diffusion practical? → **POINT DEFECTS**

(Fig. 5-3)



Vacancy vs. Interstitial Diffusion

(Fig. 5-3)



- Atom *interchange* from a normal lattice position to an adjacent vacant lattice site.

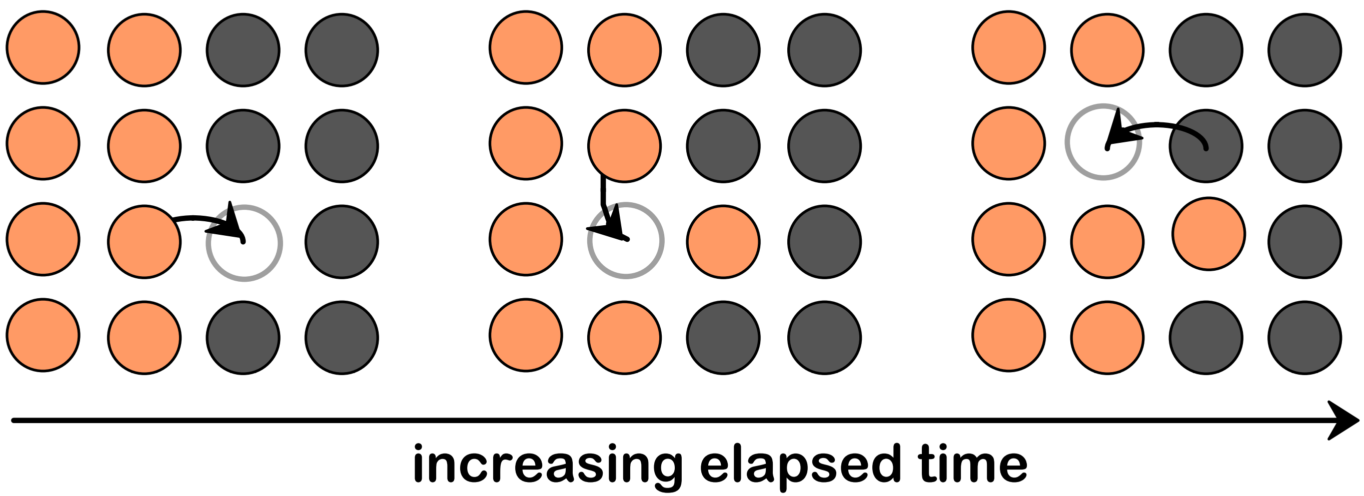
- The extent of vacancy diffusion is controlled by the concentration of these defects.

- The direction of vacancy motion is opposite to the direction of diffusing atoms.

- Both self-diffusion and interdiffusion occur by this mechanism.

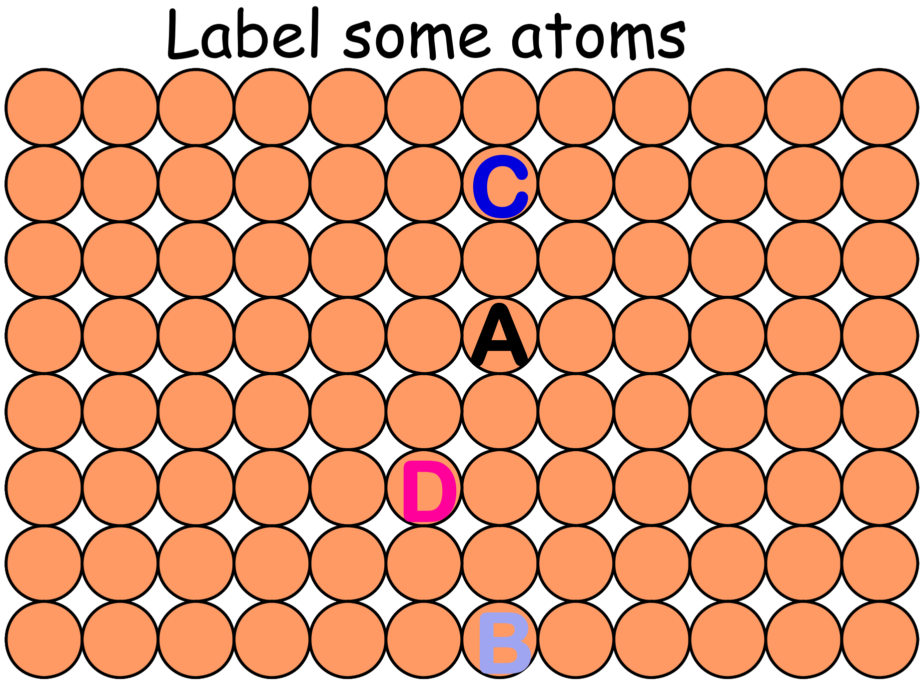
Substitutional Diffusion

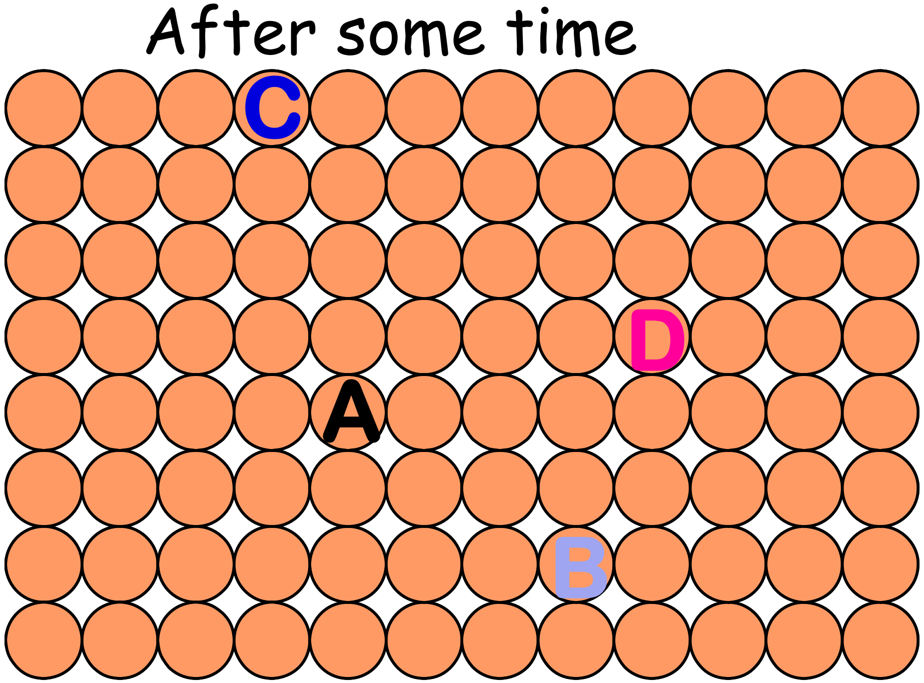
- Applies to substitutional solutes (impurities)
- Atoms exchange with vacancies
- Rate depends on:
  - √ number of vacancies
  - √ activation energy to migrate



Self Diffusion

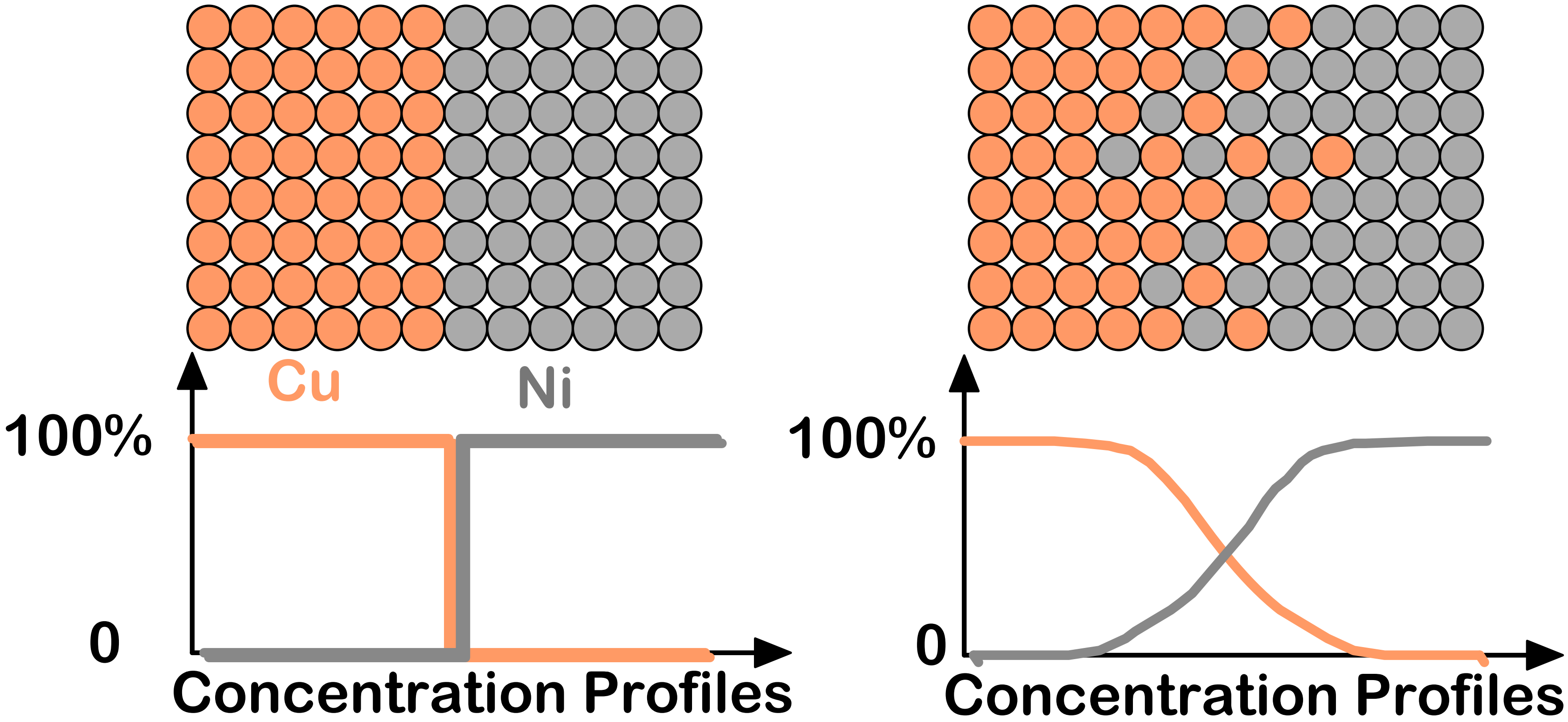
- In an elemental solid, atoms also migrate.



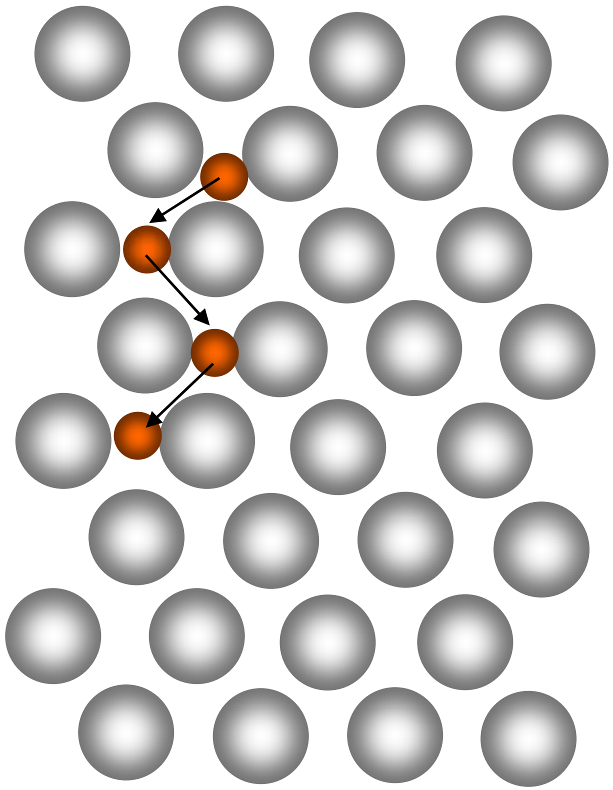


Interdiffusion

- In an alloy, atoms tend to migrate from regions of large concentration.



Interstitial Diffusion

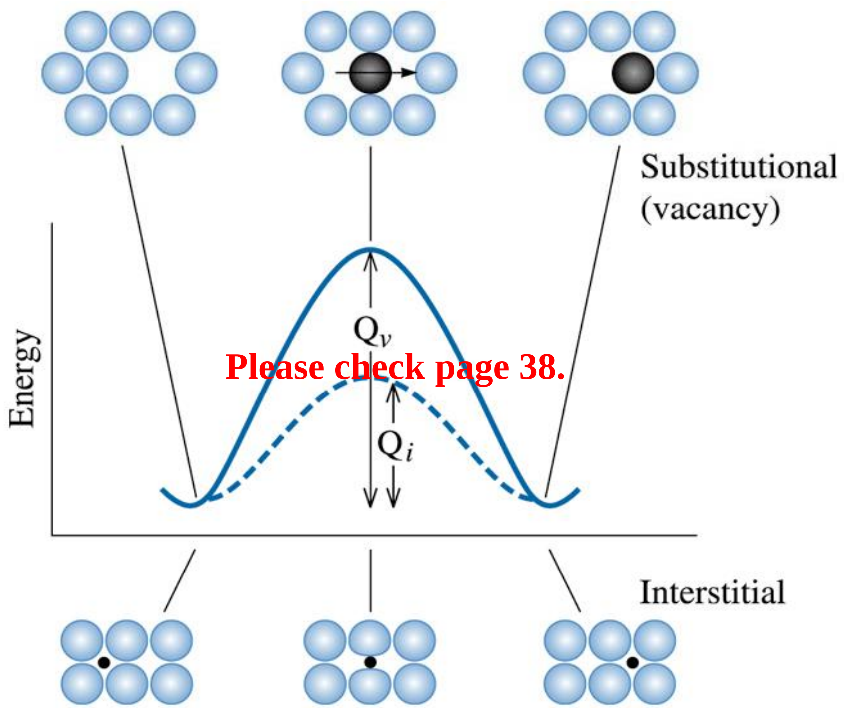


- Migration of interstitial atoms from an interstitial position to an adjacent empty site.
- Typical interstitial atoms: *hydrogen, carbon, nitrogen, or oxygen.*
- In most solids, interstitial diffusion occurs much more rapidly than vacancy diffusion.

Activation Energy for Diffusion

- **Conditions for atom migration:**
  - empty adjacent site
  - atom must have enough energy to break bonds and cause lattice distortion during displacement.
- **Diffusive motion influenced by**

  atom vibrational energies (*$k_B T$*) or phonon.



(Eq. 5-8)

Diffusion

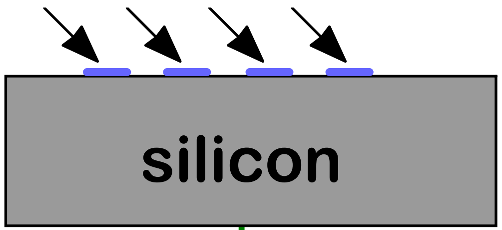
- Substitutional Diffusion (Vacancy Diffusion)
  - √ Self diffusion
  - √ Interdiffusion

- Interstitial Diffusion

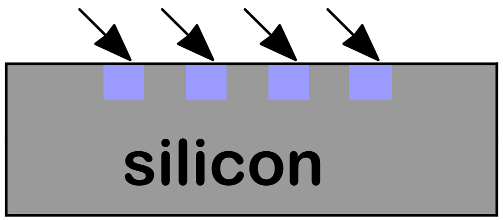
Processing Using Diffusion (2)

- Doping Silicon with P for *n*-type semiconductors
- Process

1. Deposit P rich layers on surface



2. Heat it
3. Result: Doped semiconductor regions



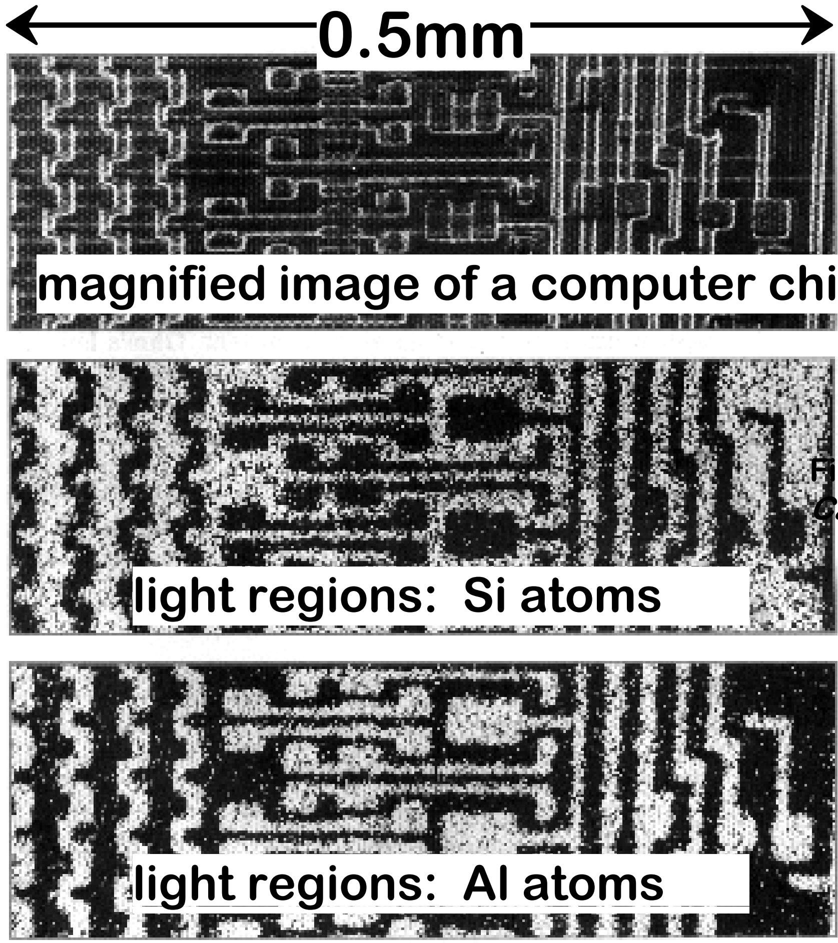
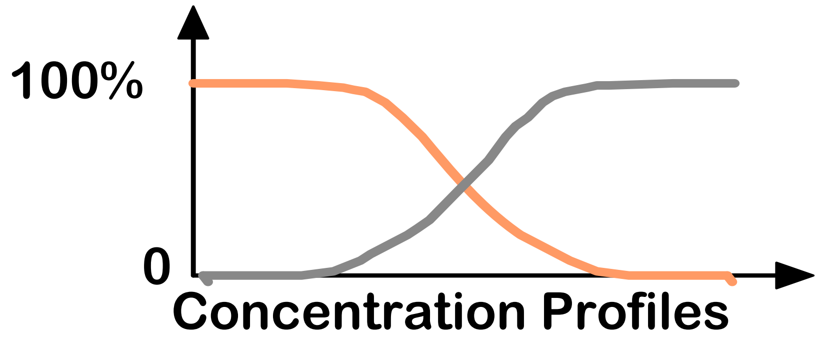


Fig. 18.0, *Callister 6e.*

Contents

Steady State Diffusion

- Concentration Profile, $C(x)$: [atoms/cm^3]



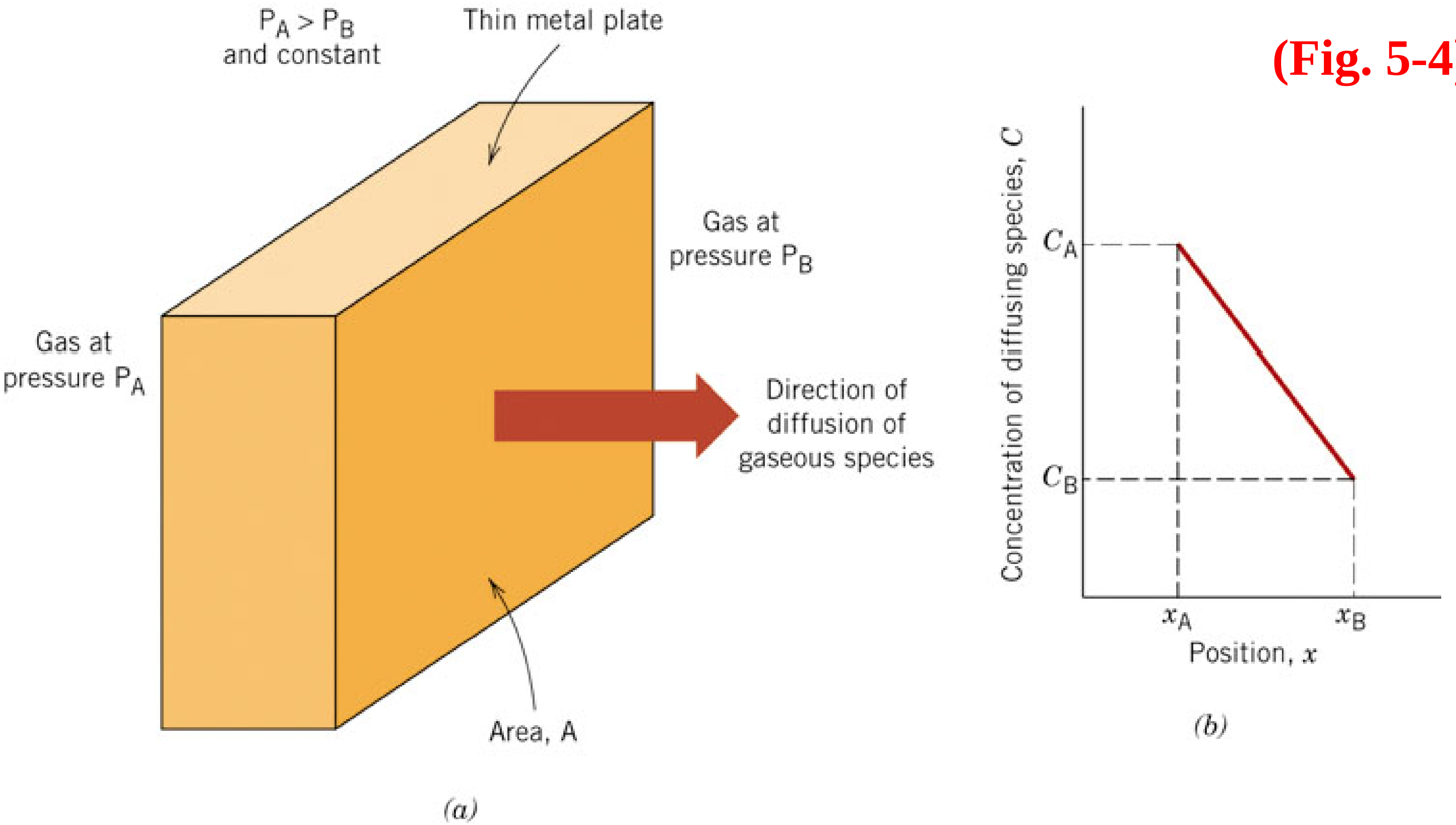
- Fick's First Law

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

- The steeper the concentration profile, the greater the flux!

Steady State Diffusion

(Fig. 5-4)

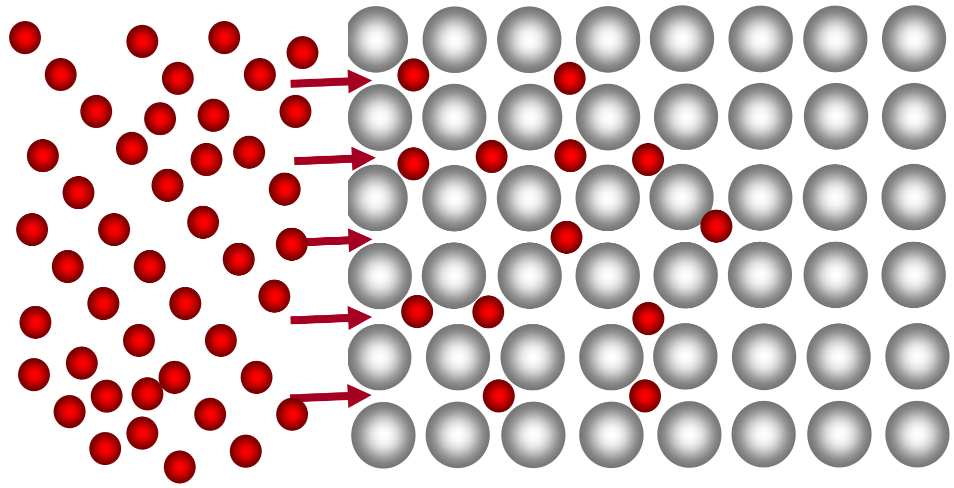


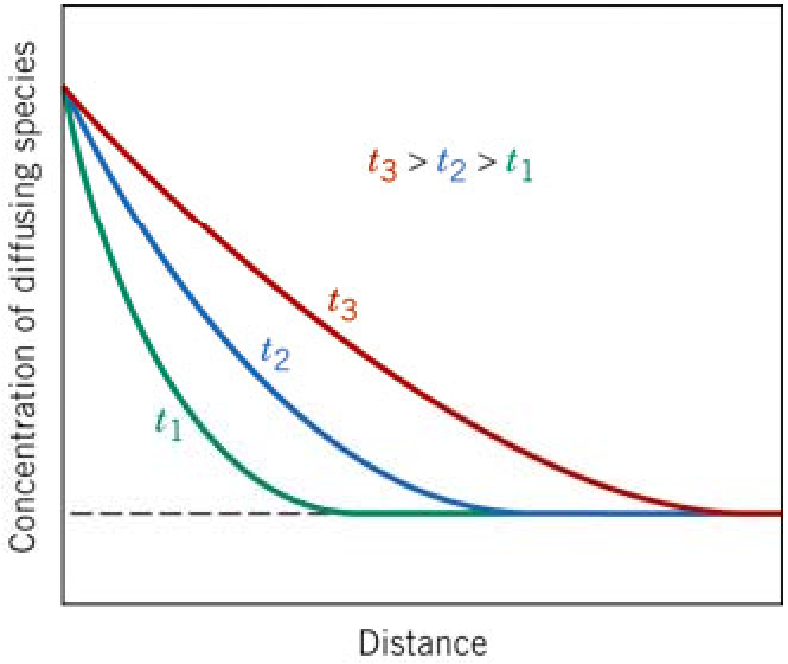
Contents

Nonsteady-State Diffusion

- Steady-state diffusion not commonly encountered in engineering materials.
- In most cases the concentration of solute atoms at any point in the material changes with time ➔ **Nonsteady-state diffusion**

(Fig. 5-5)





Fick's Second Law

Fick's 2nd law applies for nonsteady-state cases.

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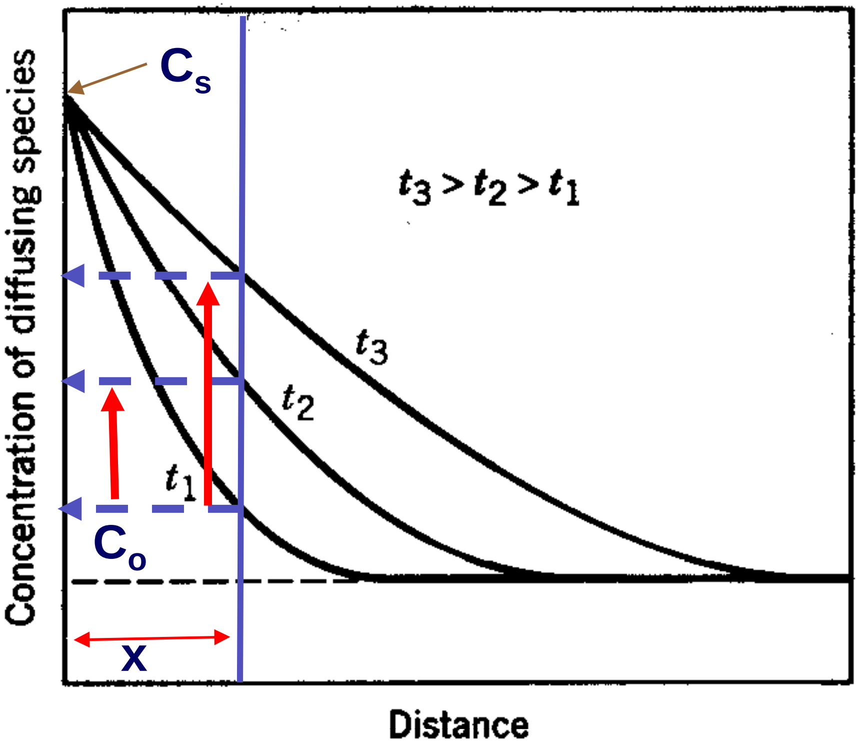
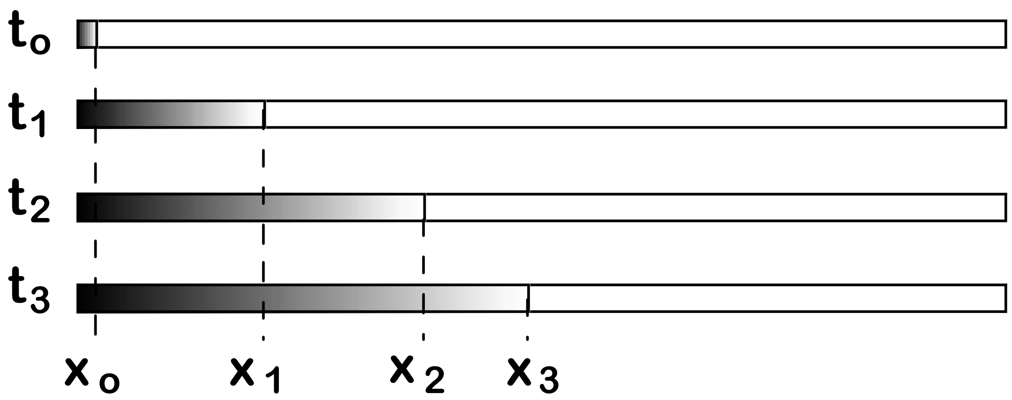


$$\frac{\partial C}{\partial t} = \frac{\partial}{\partial x}\left(D \frac{\partial C}{\partial x} \right)$$

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

Diffusion Demo: Analysis

- The experiment: combinations of *t* and *x* that kept *C* constant, were recorded.



- **(Diffusion Length)^2 = *Dt***

Diffusion Coefficient

(Fig. 5-7)

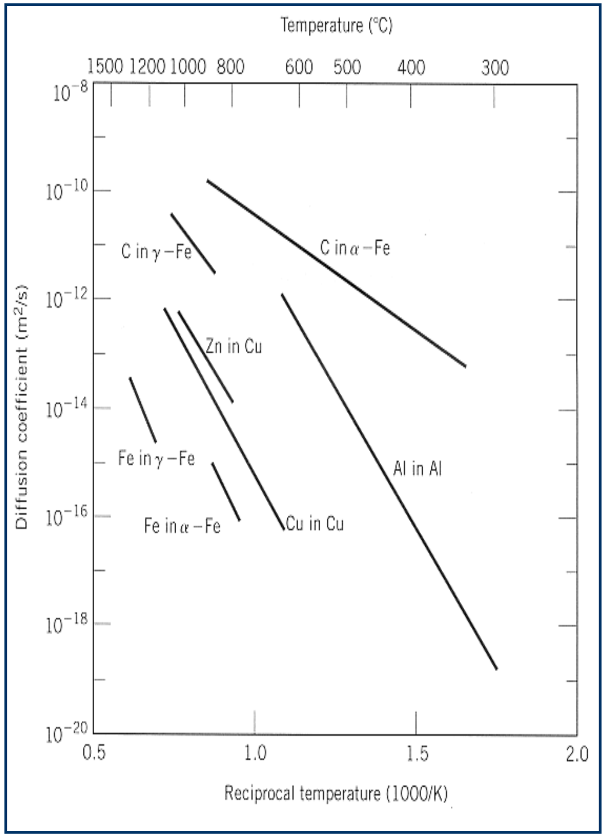


Table 5.2 A Tabulation of Diffusion Data

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	3.0×10^{-21}
					900	1.8×10^{-15}
Fe	γ-Fe (FCC)	5.0×10^{-5}	284	2.94	900	1.1×10^{-17}
					1100	7.8×10^{-16}
C	α-Fe	6.2×10^{-7}	80	0.83	500	2.4×10^{-12}
					900	1.7×10^{-10}
C	γ-Fe	2.3×10^{-5}	148	1.53	900	5.9×10^{-12}
					1100	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}

Contents

Factors influencing diffusion

- Temperature
  - Diffusion is thermally activated processes.

$$D = D_o \exp(-\frac{Q_d}{k_B T})$$

(Eq. 5-8)

D_o : temperature independent preexponential (cm^2/s)

Q_d : activation energy for diffusion (eV/atom)

k_B : Boltzman's constant $= 8.617 \times 10^{-5}$ eV/K

T : absolute temperature (K)

Factors influencing diffusion

➢ Diffusing Species

(Table. 5-2)

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	3.0×10^{-21}
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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.

Example: Determine D_{cu} in Ni at 500°C.

Q_d = 2.5 eV/atom

$D_O = 2.7 \times 10^{-1}\ cm^2/sec$

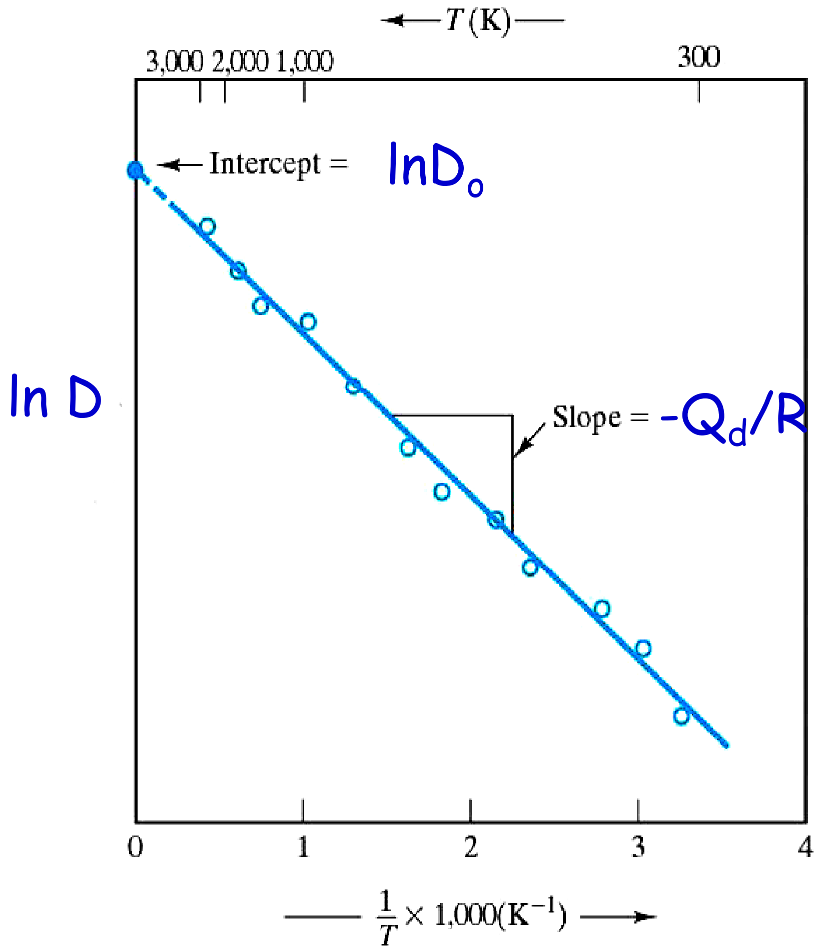
$T = 500 + 273 = 773$ K

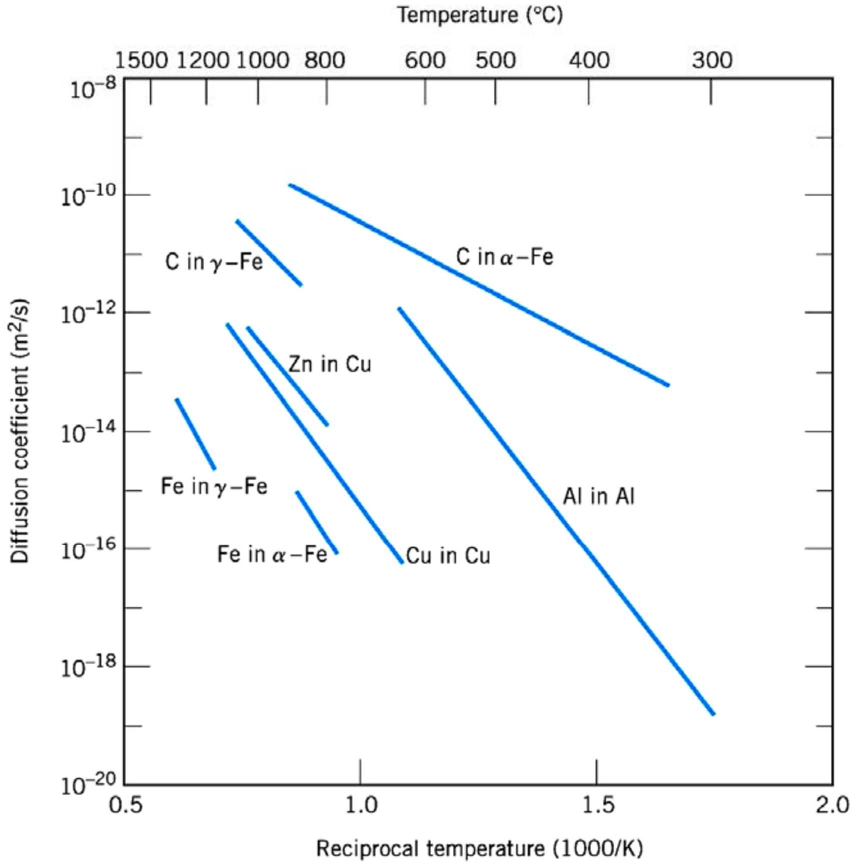
$k_B = 8.617 \times 10^{-5}$ eV/atom·K

$D = 1.33 \times 10^{-18}\ cm^2/sec$

Factors influencing diffusion

- Temperature

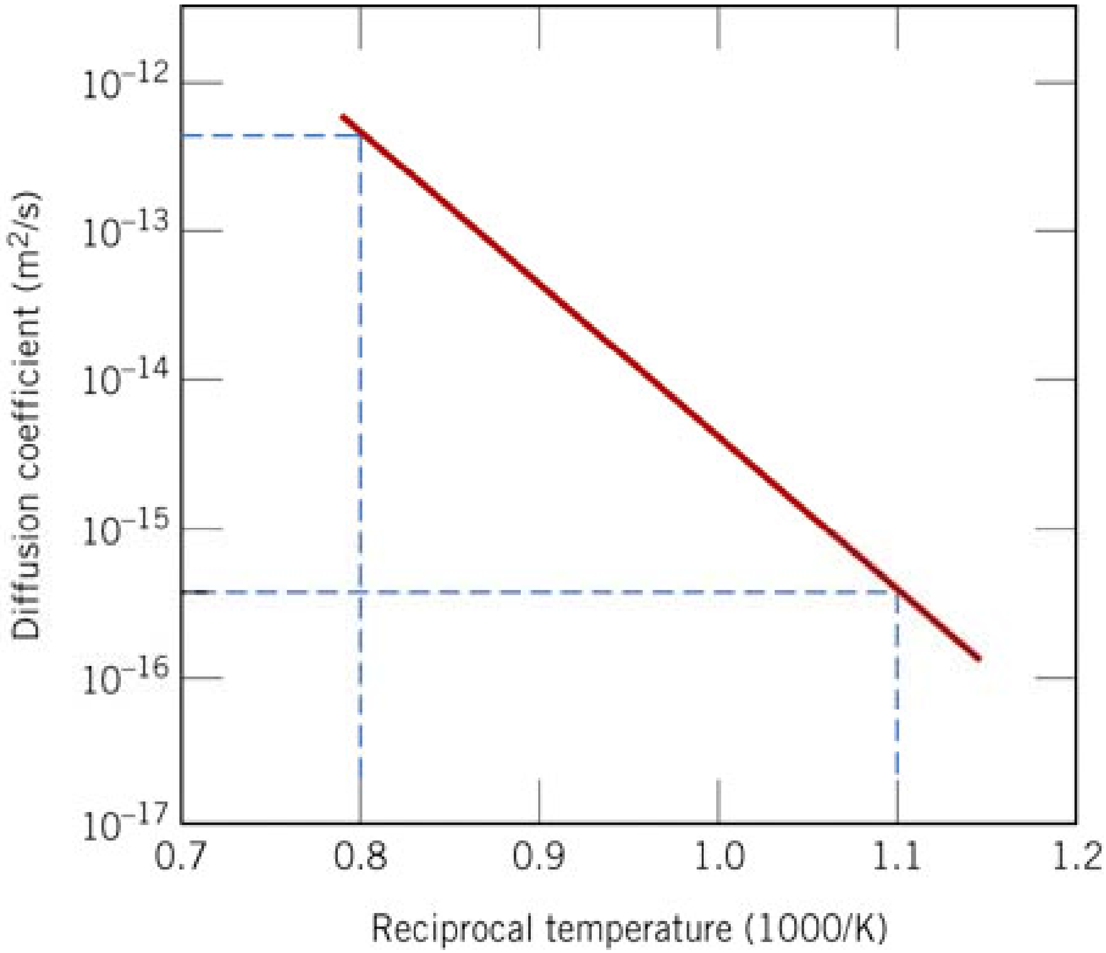




- Arrhenius plot of relationship between diffusion coefficient and reciprocal of temperature for different elements.

Factors influencing diffusion

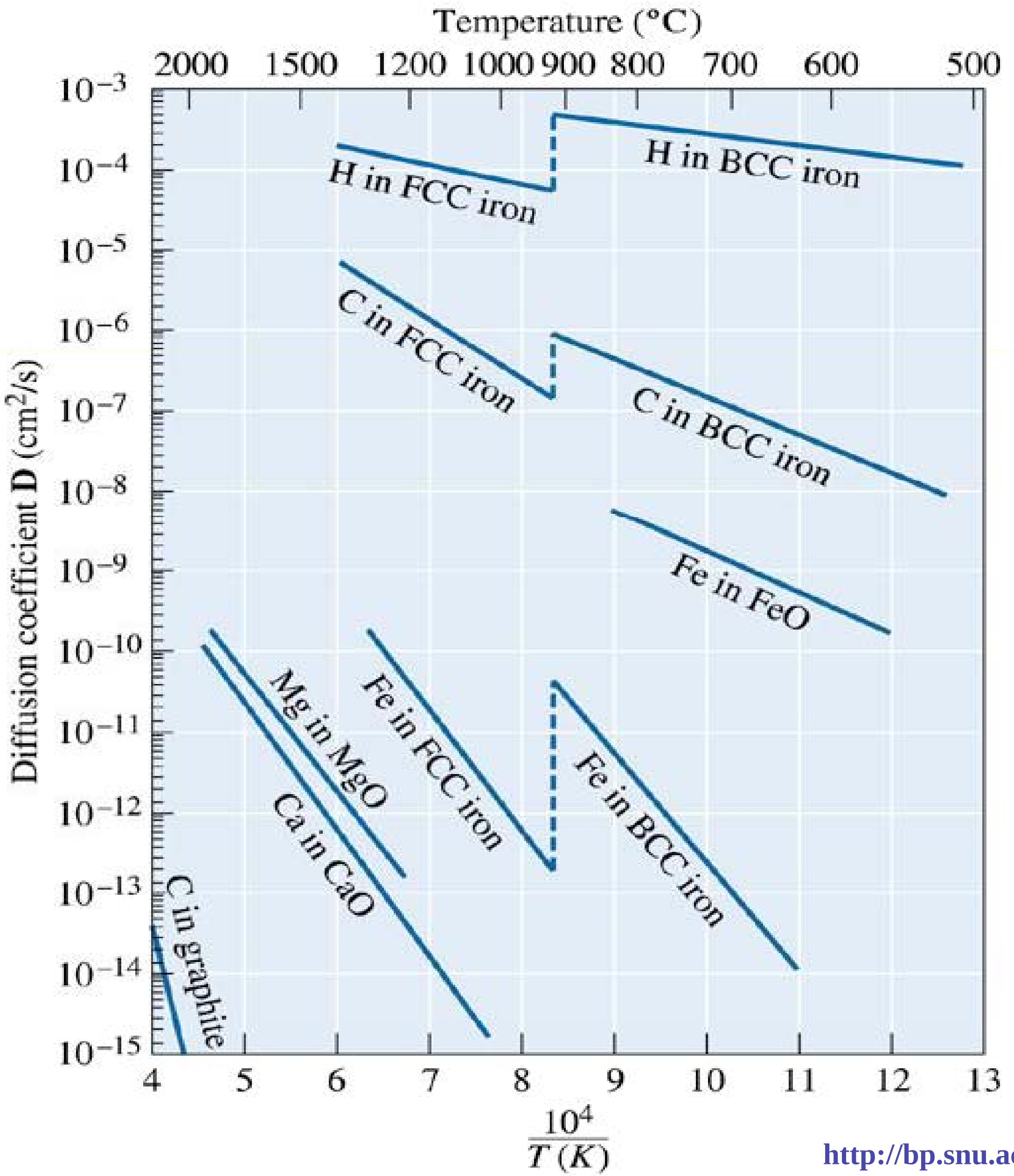
➢ Determination of activation energy



(Fig. 5-8)

Factors influencing diffusion

➢ Crystal structure

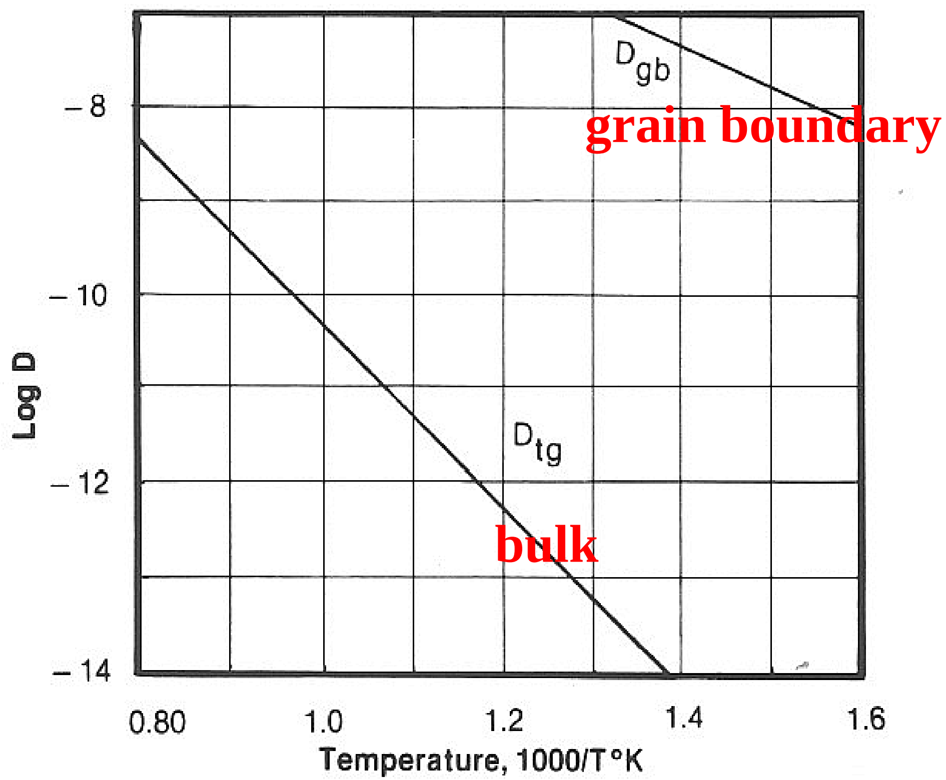


Factors influencing diffusion

➢ **Grain boundary** - Diffusion is faster along the grain boundaries than through the grain:

√ More open structure at grain boundaries than the interior grain.

√ Much lower activation energy for diffusion along the grain boundaries



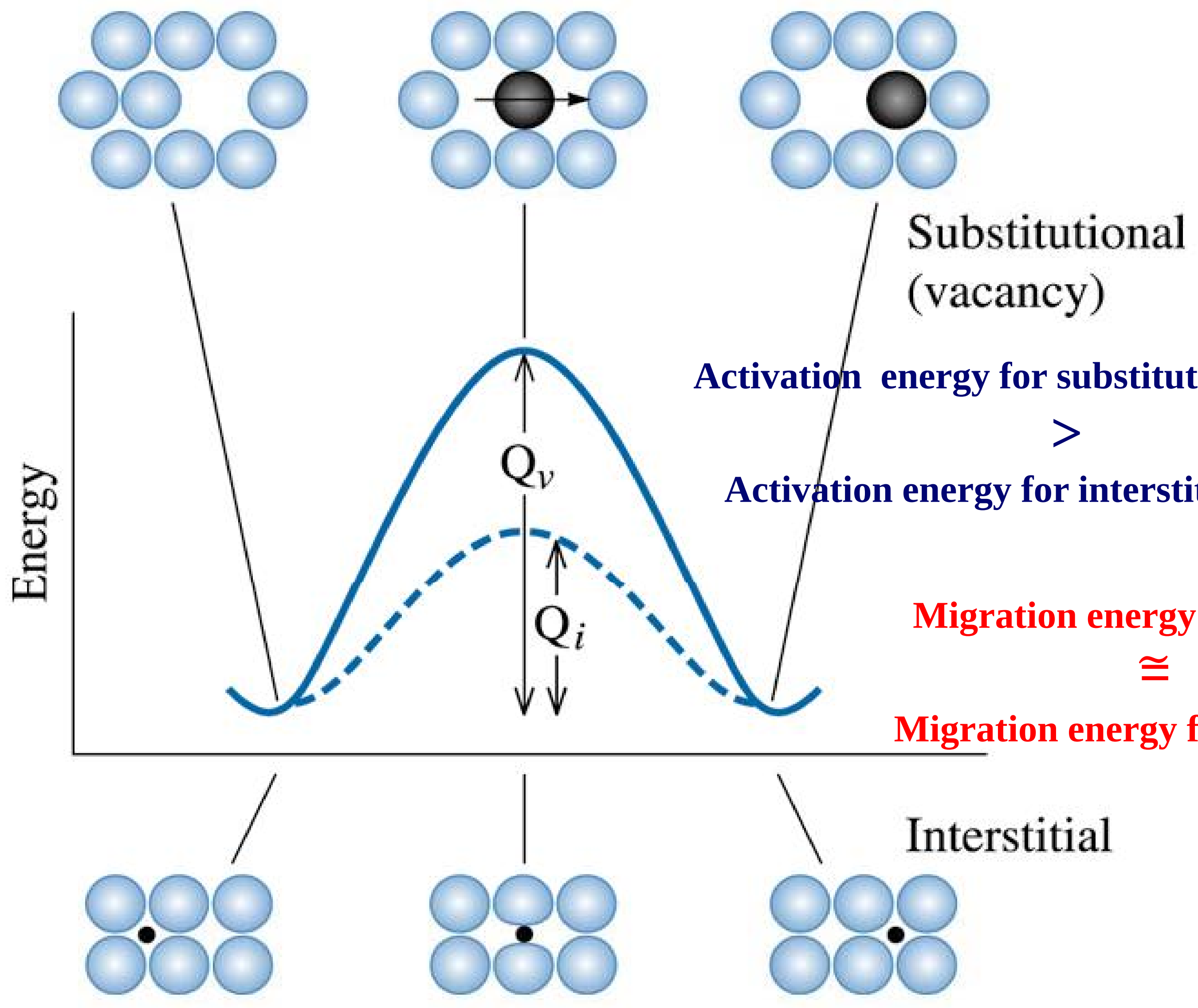
Diffusion Concepts

- Stepwise migration of atoms from a lattice point to another.
- Diffusive motion: influenced by atom vibrational energies (temperature).
- Conditions for atomic migration:
  - √ Empty adjacent site.
  - √ Atom must have enough energy to break bonds, and cause lattice distortion at the activated state.

SUMMARY: Structure & Diffusion

Diffusion ***FASTER*** *for...*	*Diffusion* ***SLOWER*** *for...*
Open crystal structures	Close-packed structures
Lower melting *T* materials	Higher melting *T* materials
Materials with metallic or secondary bonding	Materials with covalent bonding
Smaller diffusing atoms	Larger diffusing atoms

Substitutional vs. Interstitial Diffusion



Activation energy for substitutional diffusion

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Activation energy for interstitial diffusion

Migration energy for Vacancy

≅

Migration energy for Interstitial

Activation Energy for Diffusion

Problems from Chap. 5

http://bp.snu.ac.kr

Prob. 5-1 Prob. 5-2 Prob. 5-3 Prob. 5-5 Prob. 5-10
Prob. 5-17 Prob. 5-19 Prob. 5-22 Prob. 5-23