

2021 Fall

“Phase Transformation *in* Materials”

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Eun Soo Park

Office: 33-313

Telephone: 880-7221

Email: espark@snu.ac.kr

Office hours: by an appointment

Contents for previous class

• **Interstitial Diffusion** / Substitutional Diffusion

- Steady-state diffusion– Fick's First Law

➔ Concentration varies with position.

- Non-steady-state diffusion: Fick's Second Law

➔ Concentration varies with time and position.

1. Self diffusion in pure material
2. Vacancy diffusion
3. Diffusion in substitutional alloys

• Atomic Mobility

• Tracer Diffusion in Binary Alloys

• High-Diffusivity Paths

1. Diffusion along Grain Boundaries and Free Surface
2. Diffusion Along Dislocation

• Diffusion in Multiphase Binary Systems

Contents for previous class

- **Diffusion** : Movement of atoms to reduce its chemical potential μ .
  **driving force: Reduction of G**

Down-hill diffusion movement of atoms from a high C_B region to low C_B region.

Up-hill diffusion movement of atoms from a low C_B region to high C_B region.

- **Interstitial Diffusion / Substitution Diffusion**

- **Steady-state diffusion – Fick's First Law**

$$J_B = \frac{1}{6} \Gamma_B (n_1 - n_2) = - \left(\frac{1}{6} \Gamma_B \alpha^2 \right) \frac{\partial C_B}{\partial x} = -D_B \frac{\partial C_B}{\partial x}$$

 **Concentration varies with position.** (atoms $\text{m}^{-2} \text{s}^{-1}$)

- **Nonsteady-state diffusion – Fick's Second Law**

$$\frac{\partial C_B}{\partial t} = D_B \frac{\partial^2 C_B}{\partial x^2}$$

 **Concentration varies with time and position.**

- **For random walk in 3 dimensions,**
after n steps of length α

$$r = \alpha \sqrt{(\Gamma t)} = f(D) = 2.4 \sqrt{Dt}$$

- **Effect of Temperature on Diffusivity**

$$\log D = \log D_0 - \frac{Q}{2.3R} \left(\frac{1}{T} \right)$$

The section is completed with **4 example solutions to Fick's 2nd law:**
carburisation, decarburisation, diffusion across a couple and homogenisation.

The solutions given are as follows:

Process	Solution
Homogenization	$C = C_{\text{mean}} + \beta_0 \sin\left(\frac{\pi x}{l}\right) \exp\left(-\frac{t}{\tau}\right)$ <p> C_{mean} = Mean concentration β_0 = Initial concentration amplitude l = half-wavelength of cells t = relaxation time </p>
Carburization	$C = C_s - (C_s - C_0) \operatorname{erf}\left(\frac{x}{2\sqrt{Dt}}\right)$ <p> C_s = Surface concentration C_0 = Initial bulk concentration </p>
Decarburization	$C = C_0 \operatorname{erf}\left(\frac{x}{2\sqrt{Dt}}\right)$ <p> C_0 = Initial bulk concentration </p>
Diffusion Couple	$C = \left(\frac{C_1 + C_2}{2}\right) - \left(\frac{C_1 - C_2}{2}\right) \operatorname{erf}\left(\frac{x}{2\sqrt{Dt}}\right)$ <p> C_1 = Concentration of steel 1 C_2 = Concentration of steel 2 </p>

Contents for today's class

Q. Interstitial diffusion vs Substitutional diffusion

1. **Self diffusion in pure material**
2. **Vacancy diffusion**
3. **Diffusion in substitutional alloys**

• Interstitial Diffusion / Substitutional Diffusion

- Diffusion in dilute interstitial alloys ~ relatively simple

because the diffusing atoms are always surrounded by vacant sites to which they can jump whenever they have enough to overcome the energy barrier for migration.

- In substitutional diffusion,

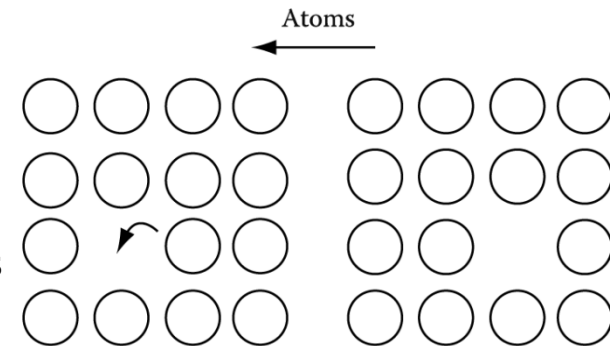
An atom can only jump if there happens to be vacant site at one of the adjacent lattice positions

Probability of vacancy x probability of jump

→ amenable to a simple atomic model: self-diffusion (순금속의 자기확산)

1. Self diffusion in pure material

The rate of self-diffusion can be measured experimentally by introducing a **few radioactive A atoms** (A^*) into pure A and measuring the rate at which penetration occurs at various temperatures. Since A^* and A atoms are chemically identical their jump frequencies are almost identical.



Diffusion coefficient

$$D_A^* = D_A = \frac{1}{6} \Gamma_A \alpha^2$$

most likely to occur back into the same vacancy



$$D_A^* = f D_A \quad (f: \text{correlation factor})$$

close to unity

Assumption

: **unrelated to the previous jump**

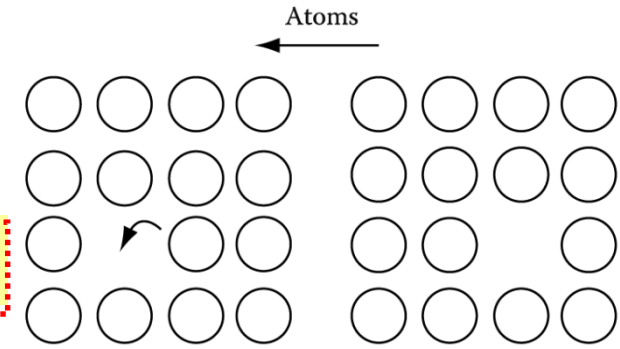
The next jump is not equally probable in all directions.

Q. Interstitial diffusion vs **Substitutional diffusion**

1. **Self diffusion in pure material**
2. Vacancy diffusion
3. Diffusion in substitutional alloys

Substitutional diffusion

1. Self diffusion in pure material



Probability of vacancy x probability of jump

What would be the jump frequency in substitutional diffusion?

An atom next to a vacancy can make a jump provided

it has enough thermal energy to overcome ΔG_m .

$$\rightarrow \exp(-\Delta G_m/kT)$$

The probability that an adjacent site is vacant

$$\rightarrow zX_v$$

Jump frequency

$$\rightarrow \Gamma = \nu z X_v \exp\left(\frac{-\Delta G_m}{RT}\right)$$

$Z = \#$ of nearest neighbours

In thermodynamic equilibrium,

$$X_v = X_v^e = \exp\left(\frac{-\Delta G_v}{RT}\right)$$

cf) $\Gamma = \nu z \exp\left(\frac{-\Delta G_m}{RT}\right)$
for interstitials

$$D_A = \frac{1}{6} \Gamma_A \alpha^2$$

$$D_A = \frac{1}{6} \alpha^2 z \nu \exp\left(\frac{-(\Delta G_m + \Delta G_v)}{RT}\right)$$

For most metals: $\nu \sim 10^{13}$, fcc metals : $z = 12$, $\alpha = a/\sqrt{2}$

$Z = \text{number of nearest neighbors} / \nu = \text{temperature independent frequency}$

$$D_A = \frac{1}{6} \alpha^2 z \nu \exp\left(-\frac{(\Delta G_m + \Delta G_v)}{RT}\right)$$

$$\Delta G = \Delta H - T\Delta S$$

$$D_A = \frac{1}{6} \alpha^2 z \nu \exp\left(\frac{\Delta S_m + \Delta S_v}{R}\right) \exp\left(-\frac{\Delta H_m + \Delta H_v}{RT}\right)$$

Z=number of nearest neighbors/ ν = temperature independent frequency

For most metals: $\nu \sim 10^{13}$, fcc metals : $z = 12$, $\alpha = a/\sqrt{2}$

$$D_A = D_0 \exp\left(-\frac{Q_{SD}}{RT}\right)$$

$$D_0 = \frac{1}{6} \alpha^2 z \nu \exp\left(\frac{\Delta S_m + \Delta S_v}{R}\right)$$

$$Q_{SD} = \Delta H_m + \Delta H_v$$

\therefore self-diffusion requires the presence of vacancies

~Same with interstitial diffusion except that the activation energy for self-diffusion has an extra term

* interstitial diffusion

Thermally activated process *jump frequency* Γ_B ?

$$\Gamma_B = Z \nu \exp(-\Delta G_m / RT)$$

Z : nearest neighbor sites

ν : vibration frequency

ΔG_m : activation energy for moving

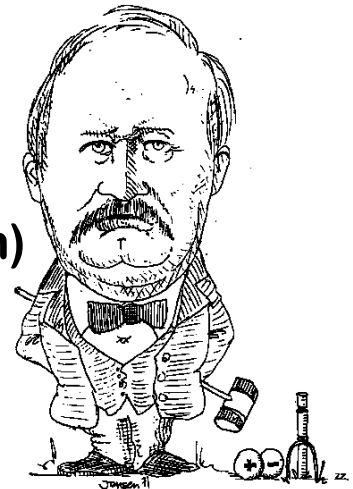
$$\left\{ \Delta G_m = \Delta H_m - T \Delta S_m, D_B = \frac{1}{6} \Gamma_B \alpha^2 \right\}$$

$$D_B = \left[\frac{1}{6} \alpha^2 Z \nu \exp(\Delta S_m / R) \right] \exp(-\Delta H_m / RT)$$

$$\Delta H_m \equiv Q_{ID}$$

$$D_B = D_{B0} \exp \frac{-Q_{ID}}{RT}$$

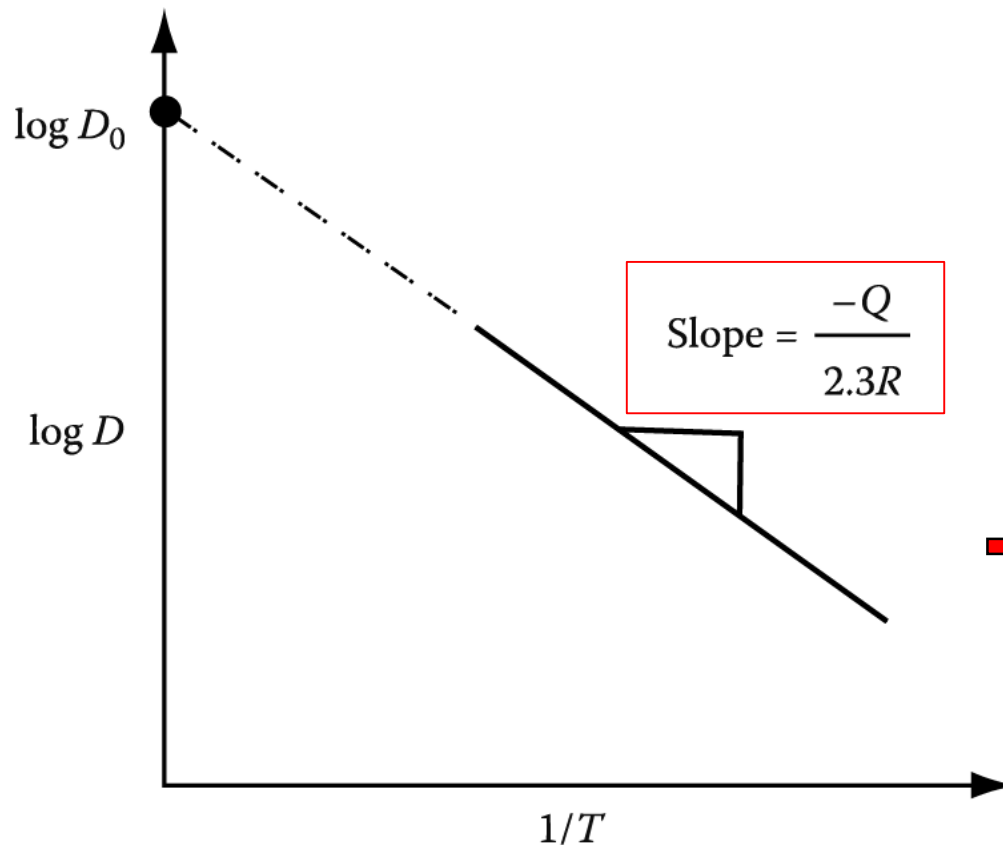
(Arrhenius-type equation)



Temperature Dependence of Diffusion

$$D_B = D_{B0} \exp \frac{-Q_{ID}}{RT}$$

How to determine Q_{ID} experimentally?



$$\log D = \log D_0 - \frac{Q}{2.3R} \left(\frac{1}{T} \right)$$

➔ Therefore, from the slope of the D -curve in an $\log D$ vs $1/T$ coordinate, the activation energy may be found.

Fig. 2.7 The slope of $\log D$ v. $1/T$ gives the activation energy for diffusion Q .

Experimental Determination of D

- Deposit a known quantity (M) of a radioactive isotope A*

$$\frac{\partial C_B}{\partial t} = D_B \frac{\partial^2 C_B}{\partial x^2} \quad (2.18)$$

- 1) Solution for the **infinite boundary condition**

$$C = \frac{M}{2\sqrt{\pi Dt}} \exp\left(-\frac{x^2}{4Dt}\right)$$

M : quantity·m⁻²/ C : quantity·m⁻³

- 2) Solution for the **semi-infinite B.C.**

$$C = \frac{2M}{\sqrt{\pi Dt}} \exp\left(-\frac{x^2}{4Dt}\right)$$

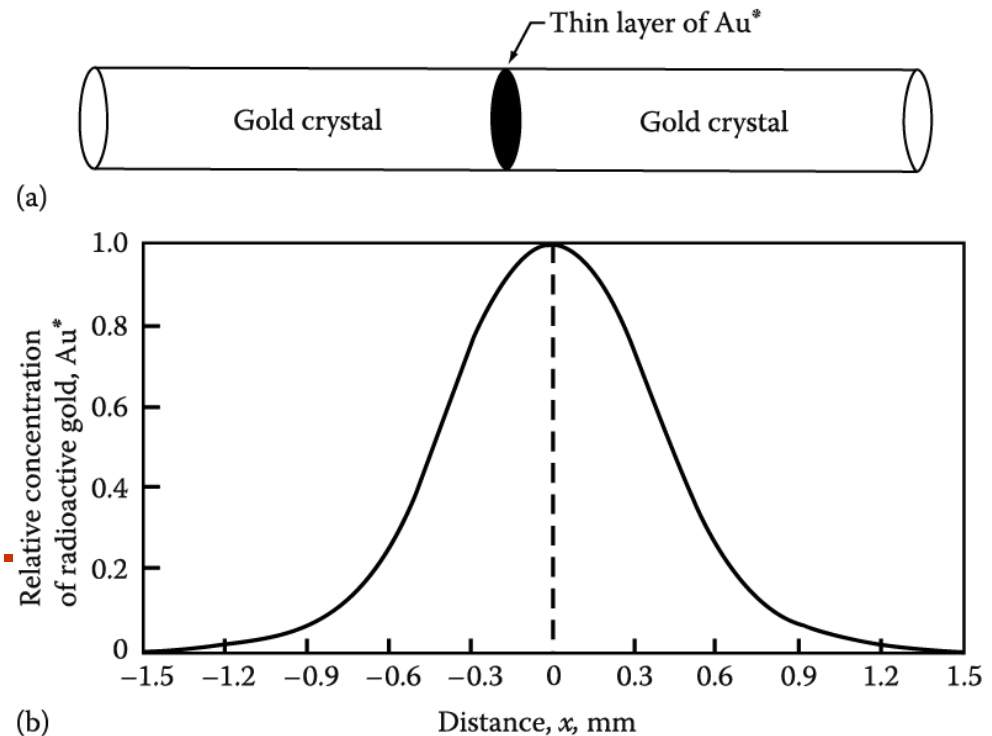


Fig. 2.14 Illustration of the principle of tracer diffusion and of the planar source method for determining the self-diffusion coefficient of gold. (a) Initial diffusion couple with planar source of radioactive gold Au* (b) Distribution of Au* after diffusion for 100h at 920°C

Table 2.2 Experimental Data for Substitutional Self-Diffusion in Pure Metals at Atmospheric Pressure

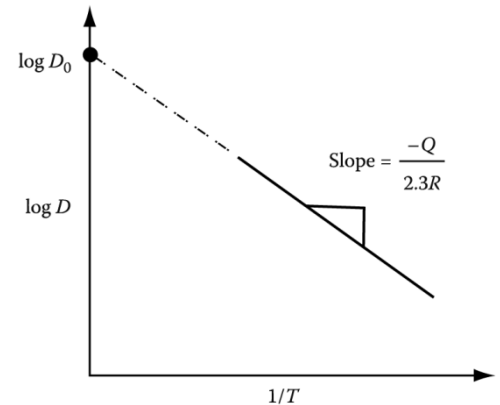
Class	Metal	T_m (K)	D_0 ($\text{mm}^2 \text{s}^{-1}$)	Q (kJ mol^{-1})	$\frac{Q}{RT_m}$	$Q(T_m)$ ($\mu\text{m}^2 \text{s}^{-1}$)	
bcc (rare earths)	ϵ -Pu	914	0.3	65.7	8.7	53	
	δ -Ce	1071	1.2	90.0	10.1	49	
	γ -La	1193	1.3	102.6	10.4	42	
	γ -Yb	1796	1.2	121.0	8.1	3600	
bcc (alkali metals)	Rb	312	23	39.4	15.2	5.8	
	K	337	31	40.8	14.6	15	
	Na	371	24.2	43.8	14.2	16	
bcc (transition metals)	Li	454	23	55.3	14.7	9.9	
	β -Tl	577	40	94.6	19.7	0.11	
	Eu	1095	100	143.5	15.8	14	
	Er	1795	451	302.4	20.3	0.71	
	α -Fe ^a	1811	200	239.7	15.9	26	
	δ -Fe ^a	1811	190	238.5	15.8	26	
	β -Ti	1933	109	251.2	15.6	18	
	β -Zr	2125	134	273.5	15.5	25	
	Cr	2130	20	308.6	17.4	0.54	
	V	2163	28.8	309.2	17.2	0.97	
	Nb	2741	1240	439.6	19.3	5.2	
	Mo	2890	180	460.6	19.2	0.84	
	Ta	3269	124	413.3	15.2	31	
	W	3683	4280	641.0	20.9	3.4	
	hcp ^a	Cd	594	\parallel c 5	76.2	15.4	0.99
			\perp c 10	79.9	16.2	0.94	
		Zn	692	\parallel c 13	91.6	15.9	1.6
fcc	Mg	\perp c 18	96.2	16.7	0.98		
		\parallel c 100	134.7	17.6	2.3		
	\perp c 150	136.0	17.8	2.9			
	Pb	601	137	109.1	21.8	0.045	
Al	933	170	142.0	18.3	1.9		
Ag	1234	40	184.6	18.0	0.61		
Au	1336	10.7	176.9	15.9	1.3		
Cu	1356	31	200.3	17.8	0.59		
Ni	1726	190	279.7	19.5	0.65		

For a given structure and bond type, Q/RT_m is roughly constant;

⇒ Q is roughly proportional to T_m .

Within each class, $D(T_m)$ and D_0 are approximately constants.

Most close-packed metals
 ex) for fcc and hcp, $Q/RT_m \sim 18$ and $D(T_m) \sim 1 \mu\text{m}^2\text{s}^{-1}$ ($10^{-12} \text{m}^2\text{s}^{-1}$)



For a given structure and bond type, $D(T/T_m) \sim \text{constant}$

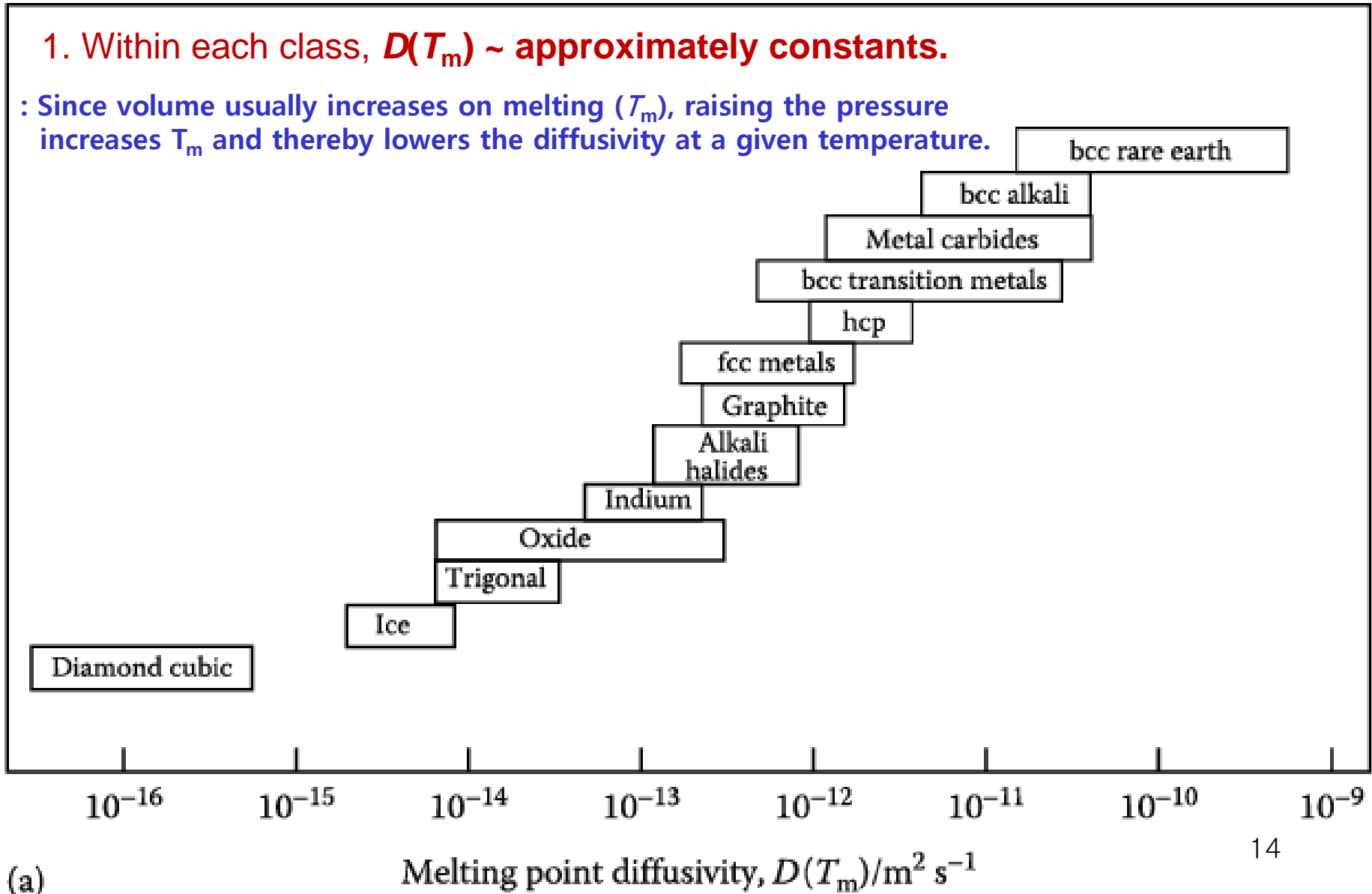
T/T_m : homologous temperature

* Melting point diffusivities for various classes of materials:

: The diffusion coefficients of all materials with a given crystal structure and bond type will be approximately the same at the same fraction of their melting temperature, i.e. $D(T/T_m) = \text{const.}$

1. Within each class, $D(T_m) \sim$ approximately constants.

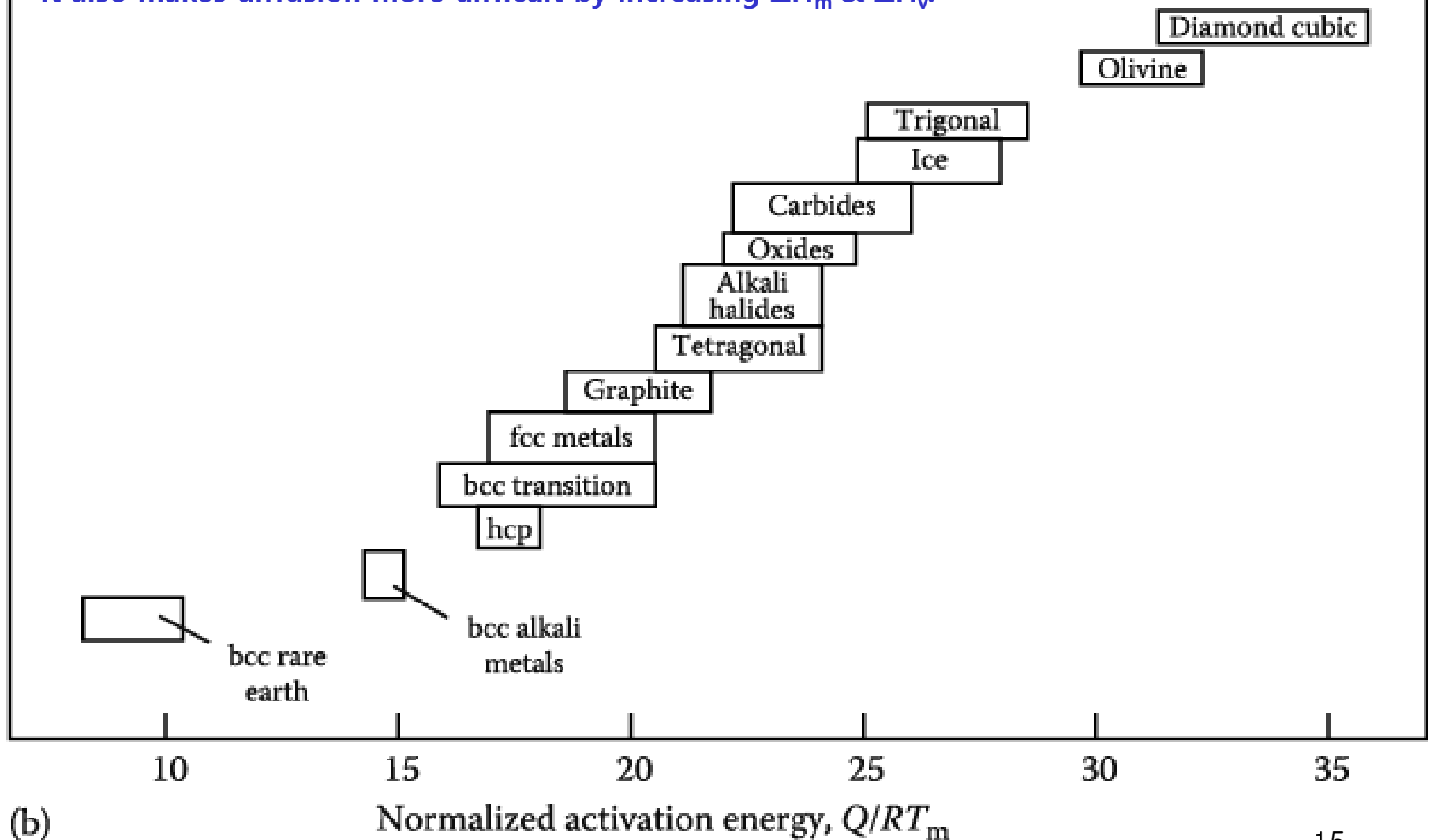
: Since volume usually increases on melting (T_m), raising the pressure increases T_m and thereby lowers the diffusivity at a given temperature.



(a)

For a given structure and bond type, Q/RT_m is roughly constant;

: Q and T_m exhibit rough linear correlation because increasing the interatomic bond strength makes the process of melting more difficult; that is, T_m is raised. It also makes diffusion more difficult by increasing ΔH_m & ΔH_v .



Consider the effect of temperature on self-diffusion in Cu:

ex) At 800°C, $D_{Cu} = 5 \times 10^{-9} \text{ mm}^2\text{s}^{-1}$, $\alpha = 0.25 \text{ nm}$ $\Gamma_{Cu} : ?$

$$D_B = \frac{1}{6} \Gamma_B \alpha^2$$

$$\Gamma_{Cu} = 5 \times 10^5 \text{ jumps s}^{-1}$$

After an hour, diffusion distance (x)? $\sqrt{Dt} \sim 4 \mu\text{m}$

How do we determine D_{Cu} at low temperature such as 20°C?

Hint) From the data in Table 2.2, how do we estimate D_{Cu} at 20°C?

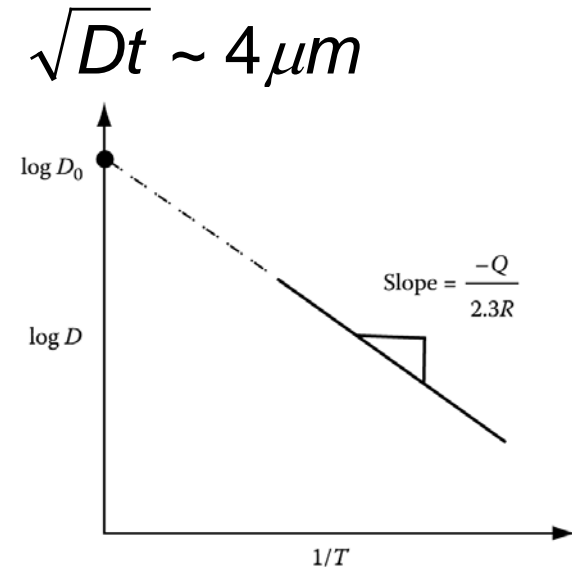


Fig. 2.7 The slope of $\log D$ v. $1/T$ gives the activation energy for diffusion Q .

At 20°C, $D_{Cu} \sim 10^{-34} \text{ mm}^2\text{s}^{-1}$

$$\Gamma_{Cu} \sim 10^{-20} \text{ jumps s}^{-1}$$

→ Each atom would make one jump every 10^{12} years!

Q. Interstitial diffusion vs **Substitutional diffusion**

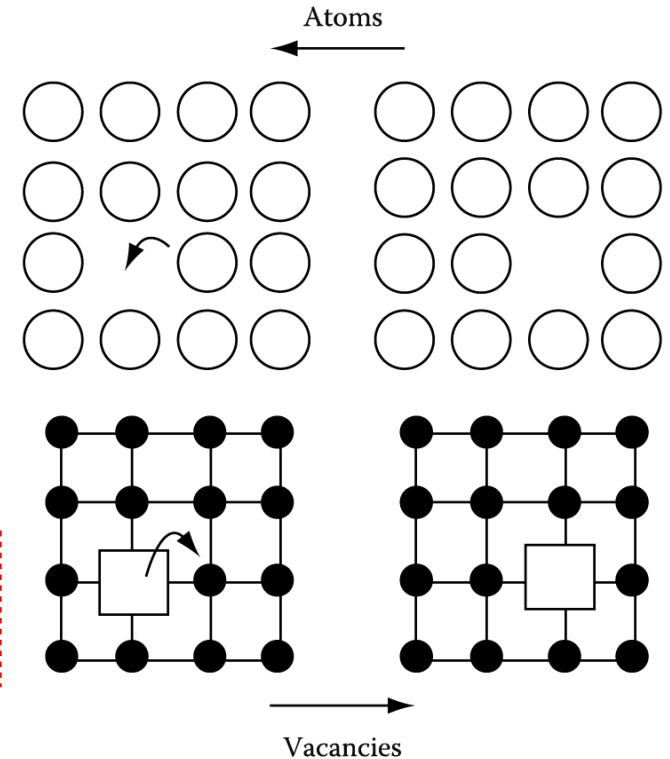
1. Self diffusion in pure material
2. **Vacancy diffusion**
3. Diffusion in substitutional alloys

2. Vacancy diffusion

All the surrounding atoms are possible jump sites of a vacancy, which is analogous to interstitial diffusion.

$$D_v = \frac{1}{6} \alpha^2 \Gamma_v$$

$$= \frac{1}{6} \alpha^2 z v \exp(\Delta S_m / R) \exp(-\Delta H_m / RT)$$



Comparing D_v with the self-diffusion coefficient of A, D_A ,

$$D_v = D_A / X_v^e$$

This shows in fact that the diffusivity of vacancy (D_v) is many orders of magnitude greater than the diffusivity of substitutional atoms (D_A).

Q: Diffusion in substitutional alloys?

$$\tilde{D} = X_B D_A + X_A D_B$$

$$\therefore J'_B = -J'_A$$

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

$$J'_A = J_A + J_A^v = -\tilde{D} \frac{\partial C_A}{\partial x} = \tilde{D} \frac{\partial C_B}{\partial x}$$

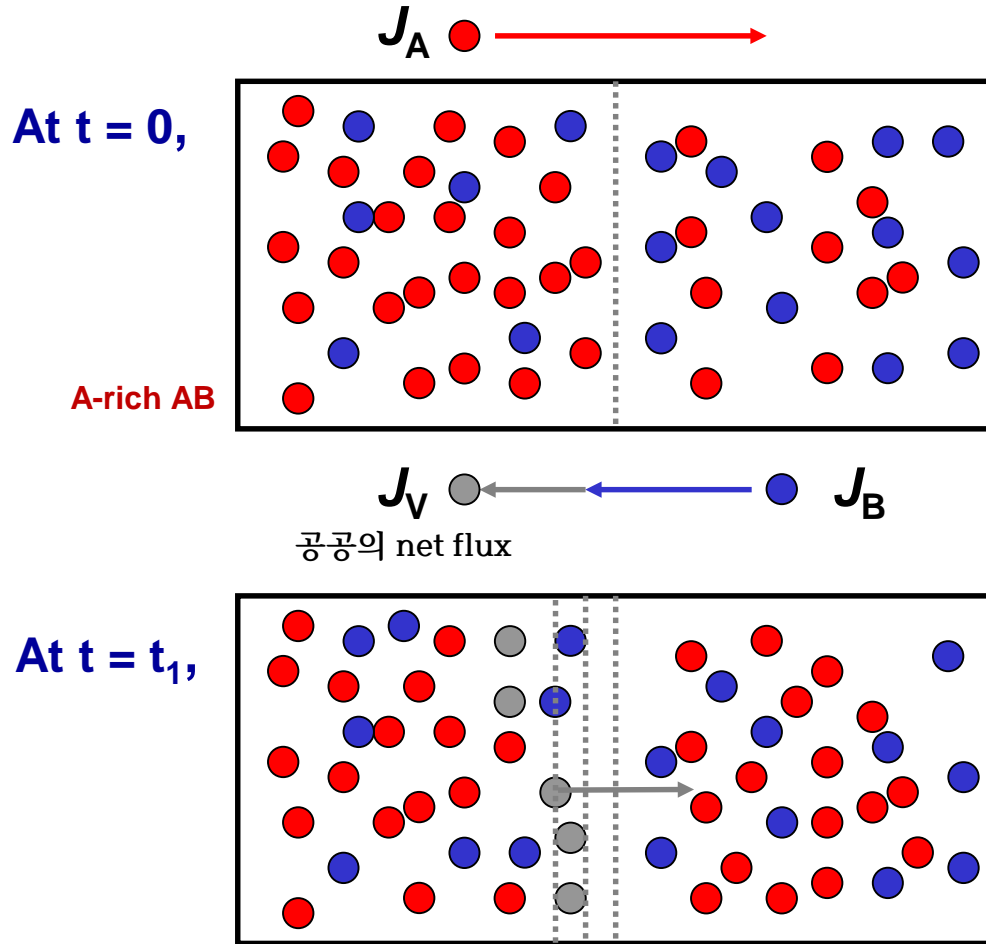
$$J'_B = J_B + J_B^v = -\tilde{D} \frac{\partial C_B}{\partial x} = \tilde{D} \frac{\partial C_A}{\partial x}$$

Fick's 1st law for substitutional alloy Fick's 2nd law for substitutional alloy

침입형 확산에서 Fick의 법칙 고정된 격자면의 이동 고려

3. Diffusion in substitutional alloys

: A원자/B원자의 상호확산을 통한 격자면의 이동 고려



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

$$\tilde{D} = X_B D_A + X_A D_B$$

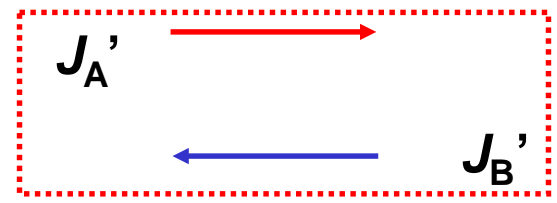
$$J'_A = J_A + J_v^A = J_A + v C_A = -\tilde{D} \frac{\partial C_A}{\partial x}$$



고정된 격자 내에서 확산에 의한 유속



확산이 일어나는 격자이동에 의한 A 유속



J_v^B (dotted arrow) ←

확산이 일어나는 격자이동에 의한 B 유속



고정된 격자 내에서 확산에 의한 유속

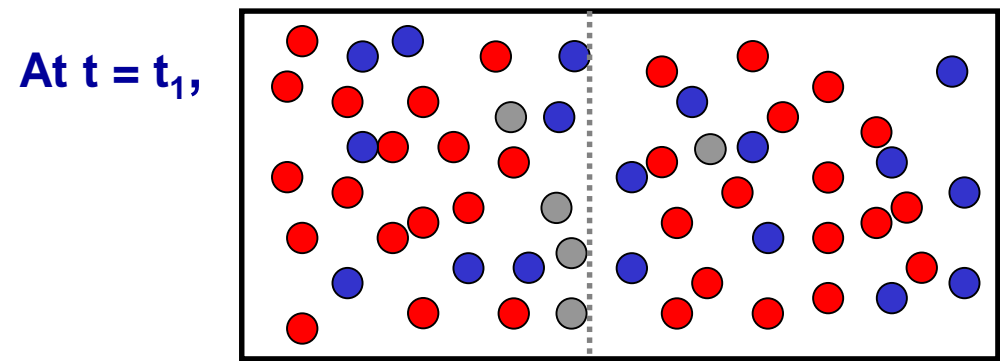
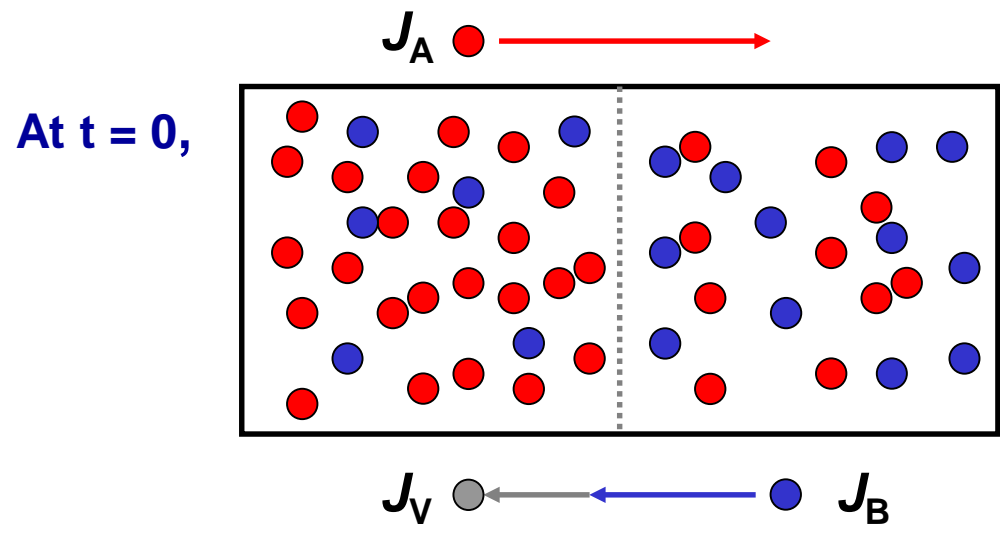
$$J'_B = J_B + J_v^B = J_B + v C_B = -\tilde{D} \frac{\partial C_B}{\partial x}$$

$$\therefore J'_B = -J'_A$$

A원자와 B원자가 서로 다른 속도로 도약 →
농도 구배에 의한 속도 + 격자면 이동에 의한 속도

3. Diffusion in substitutional alloys

- * During self-diffusion, all atoms are chemically identical.
: probability of finding a vacancy and jumping into the vacancy ~ equal
- * In binary substitutional alloys, each atomic species must be given its own intrinsic diffusion coefficient D_A or D_B .

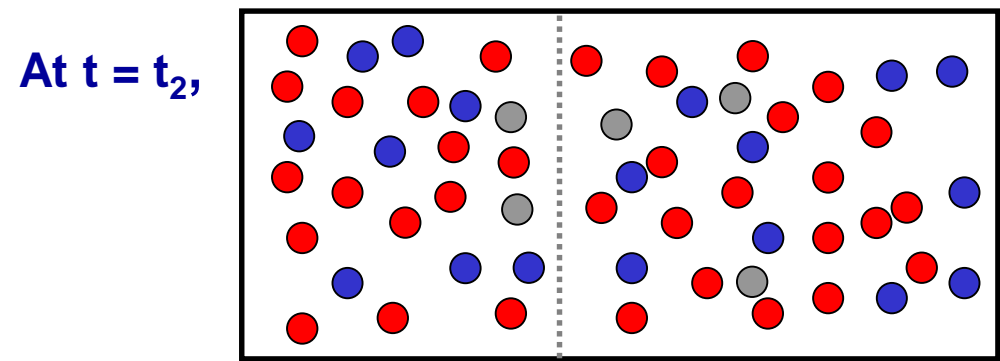
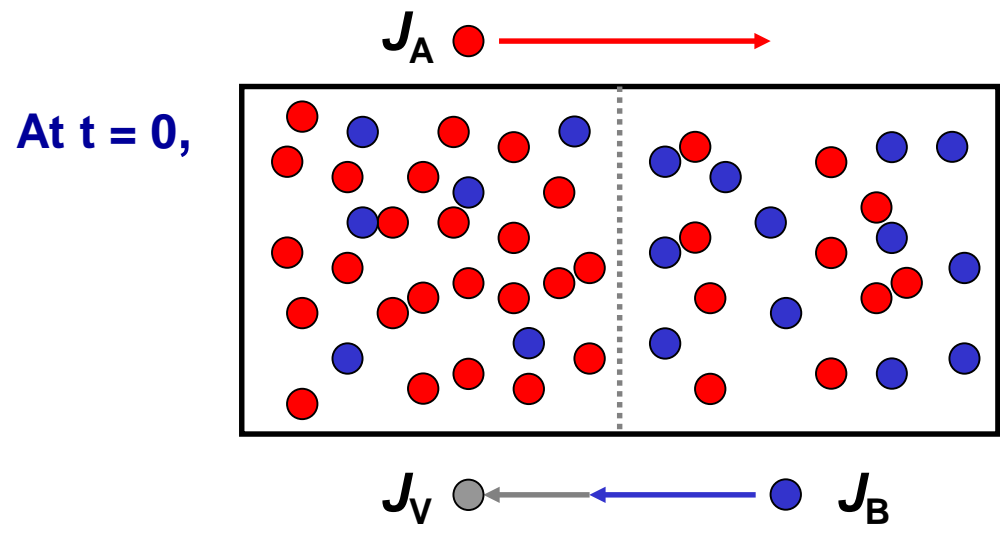


Kirkendall effect
Creation/destruction of vacancies
is accomplished by *dislocation climb*.

Whole planes of atoms will be 'eaten' away Extra atomic planes will be introduced

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3. Diffusion in substitutional alloys

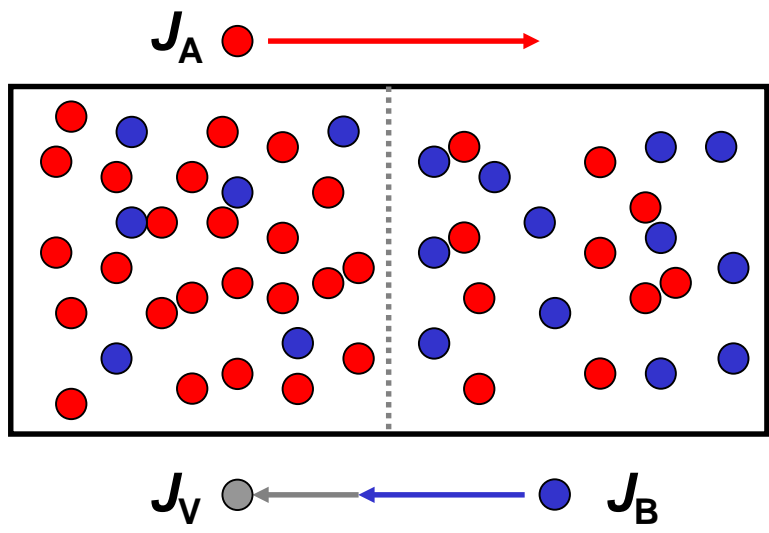
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: probability of finding a vacancy and jumping into the vacancy ~ equal
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$$\frac{\partial C_A}{\partial t} = \frac{\partial}{\partial x} \left(\tilde{D} \frac{\partial C_A}{\partial x} \right)$$

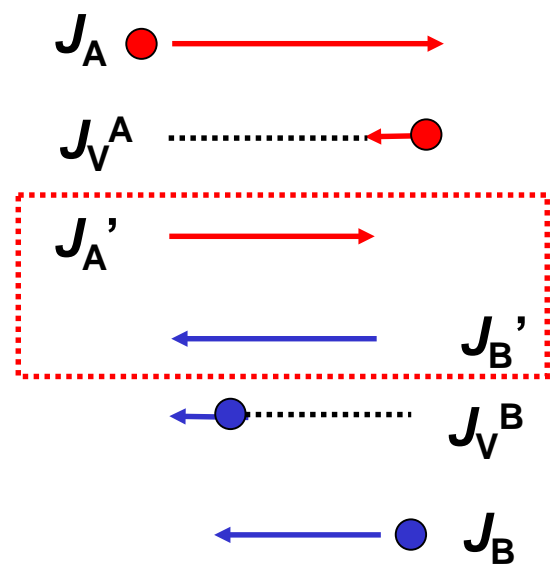
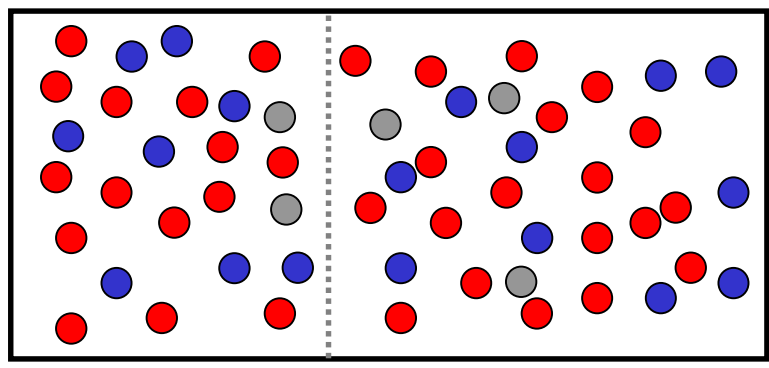
$$\tilde{D} = X_B D_A + X_A D_B$$

$$J'_A = J_A + J_A^v = -\tilde{D} \frac{\partial C_A}{\partial x}$$

At $t = 0$,



At $t = t_2$,



$$J'_B = J_B + J_B^v = -\tilde{D} \frac{\partial C_B}{\partial x}$$

$$\therefore J'_B = -J'_A$$

Whole planes of atoms will be 'eaten' away Extra atomic planes will be introduced

1) INTERDIFFUSION

Assume that C_0 : total number of atoms (A, B) per unit volume = constant, independent of composition

$$C_0 = C_A + C_B \quad \text{and} \quad \frac{\partial C_A}{\partial x} = -\frac{\partial C_B}{\partial x} \quad \rightarrow$$

* If the couple is annealed at a high enough temp., a concentration profile will develop as shown.

Fluxes of A and B atoms across a given lattice plane ~ equal

$$J_A = -D_A \frac{\partial C_A}{\partial x} \quad J_B = -D_B \frac{\partial C_B}{\partial x} = D_B \frac{\partial C_A}{\partial x}$$

Due to the difference in diffusivities, a flux difference is created. $|J_A| > |J_B|$

Flux of vacancies

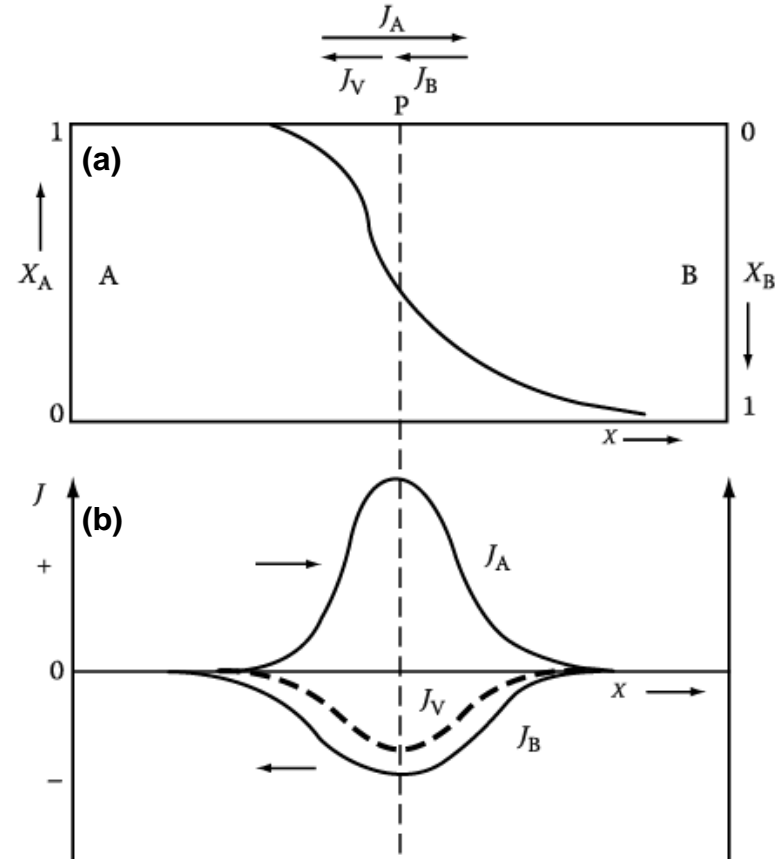
$$J_A \rightarrow J_{V,A} = -J_A \quad J_B \rightarrow J_{V,B} = -J_B$$

$$J_V + J_B = -J_A$$

$$J_V = -J_A - J_B \quad (\text{a net flux of vacancies})$$

$$= (D_A - D_B) \frac{\partial C_A}{\partial x}$$

$$\therefore J_B = -D_B \frac{\partial C_B}{\partial x} = D_B \frac{\partial C_A}{\partial x}$$



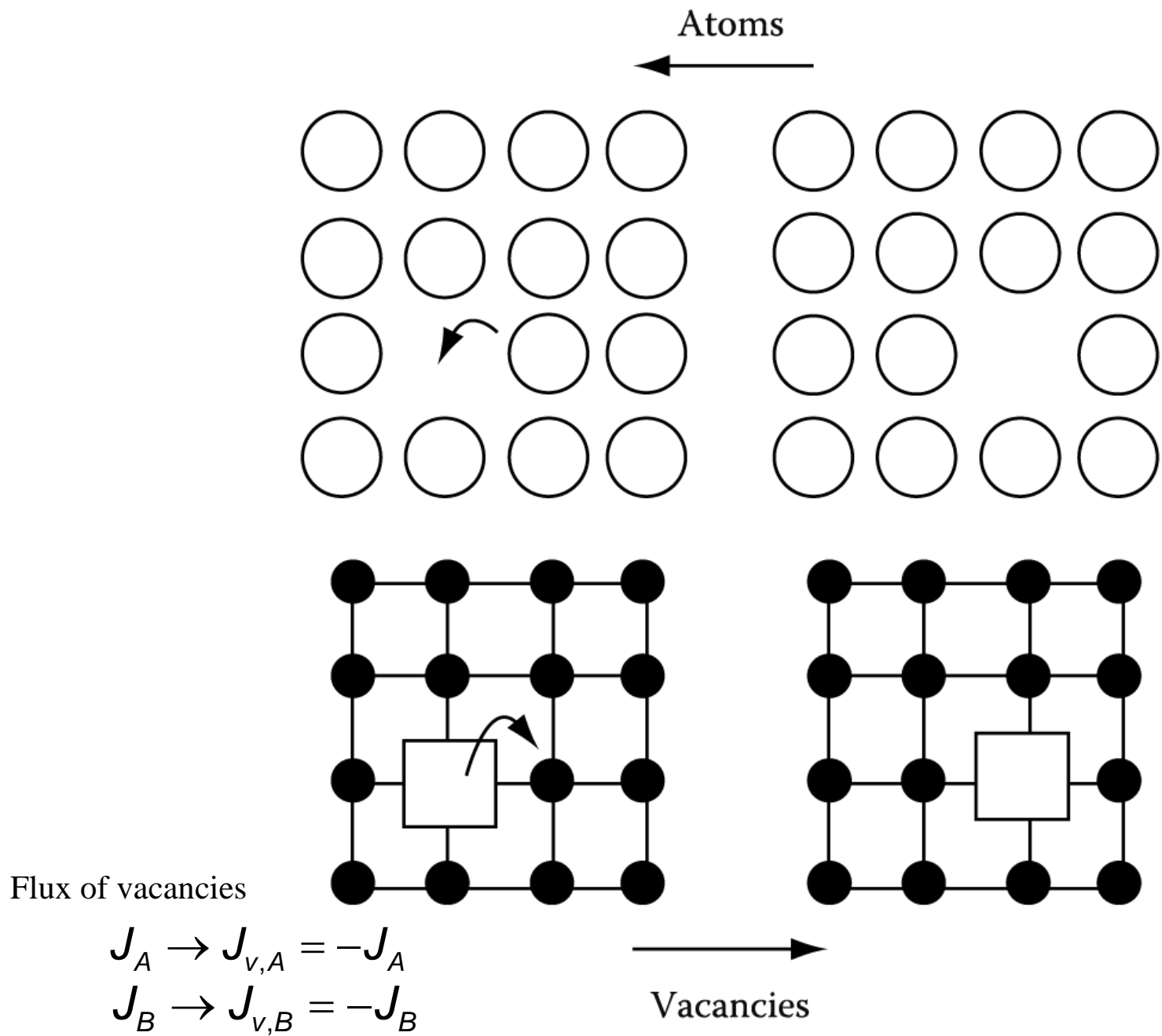


Fig. 2.16 **The jumping of atoms in one direction can be considered as the jumping of vacancies in the other direction.**

$$J_V = -J_A - J_B \text{ (a net flux of vacancies)}$$

$$= (D_A - D_B) \frac{\partial C_A}{\partial x}$$

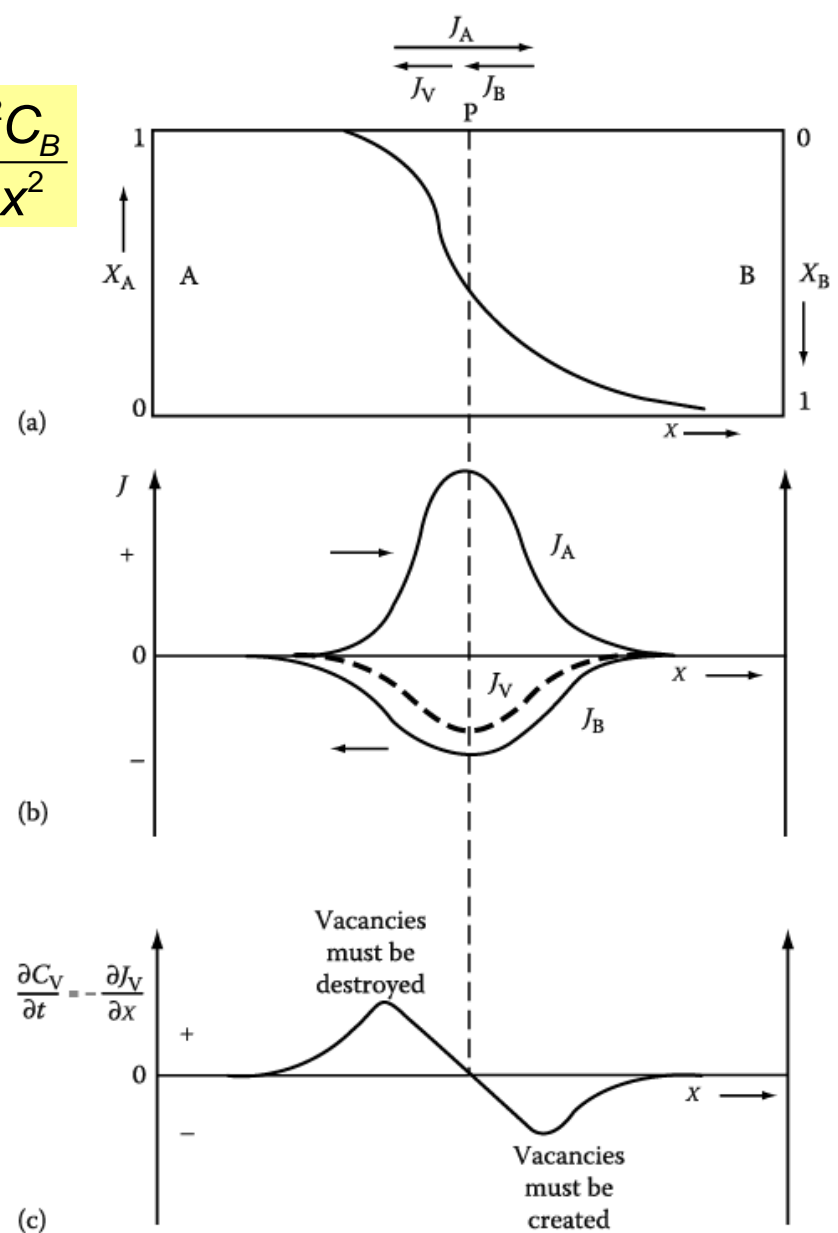
$$\frac{\partial C_B}{\partial t} = D_B \frac{\partial^2 C_B}{\partial x^2}$$

$$\frac{\partial C_V}{\partial t} = -\frac{\partial J_V}{\partial x} \text{ vs. } x?$$

What would become of excess vacancy?

$$\partial C_V / \partial t = -\partial J_V / \partial x \text{ (Fig. 2. 15c)}$$

$$\text{cf) } \frac{\partial C_B}{\partial t} = -\frac{\partial J_B}{\partial x}$$



In order to maintain the vacancy concentration everywhere near equilibrium, vacancies must be created on the B-rich side and destroyed on the A-rich side.

* Net flux of vacancies across the middle of the diffusion couple → “Movement of lattice”

Kirkendall effect

Creation/destruction of vacancies is accomplished by *dislocation climb*.

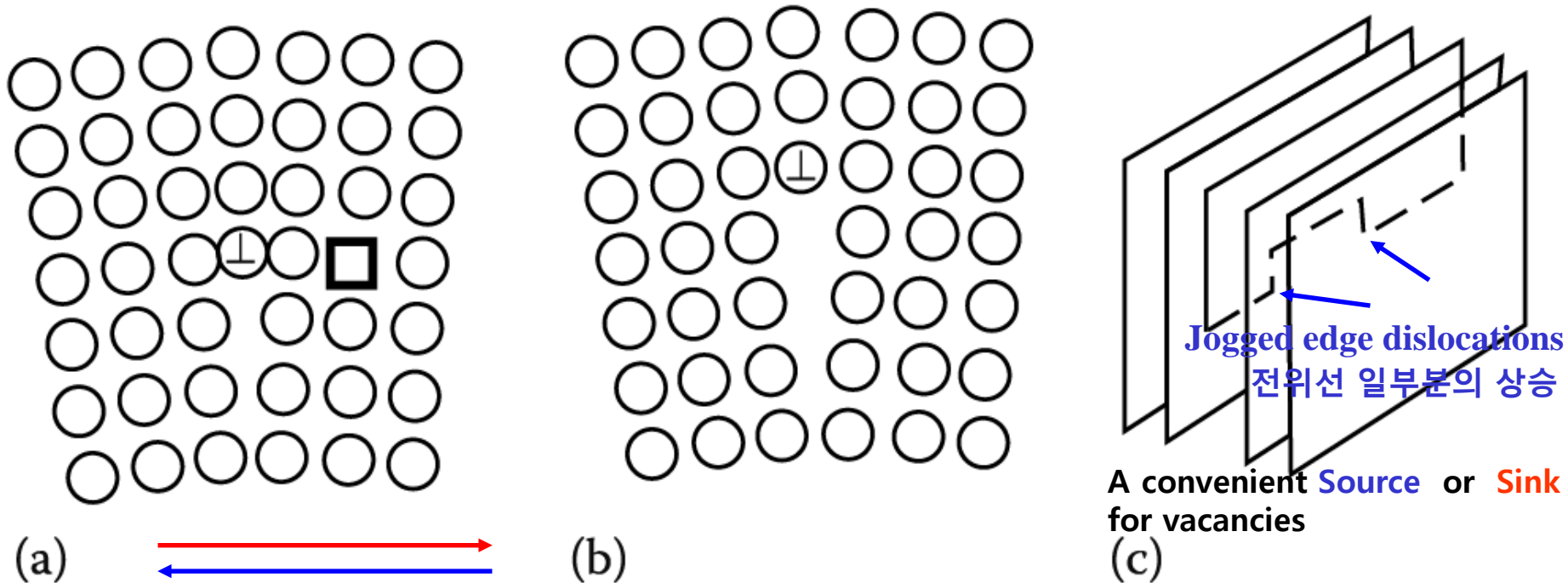
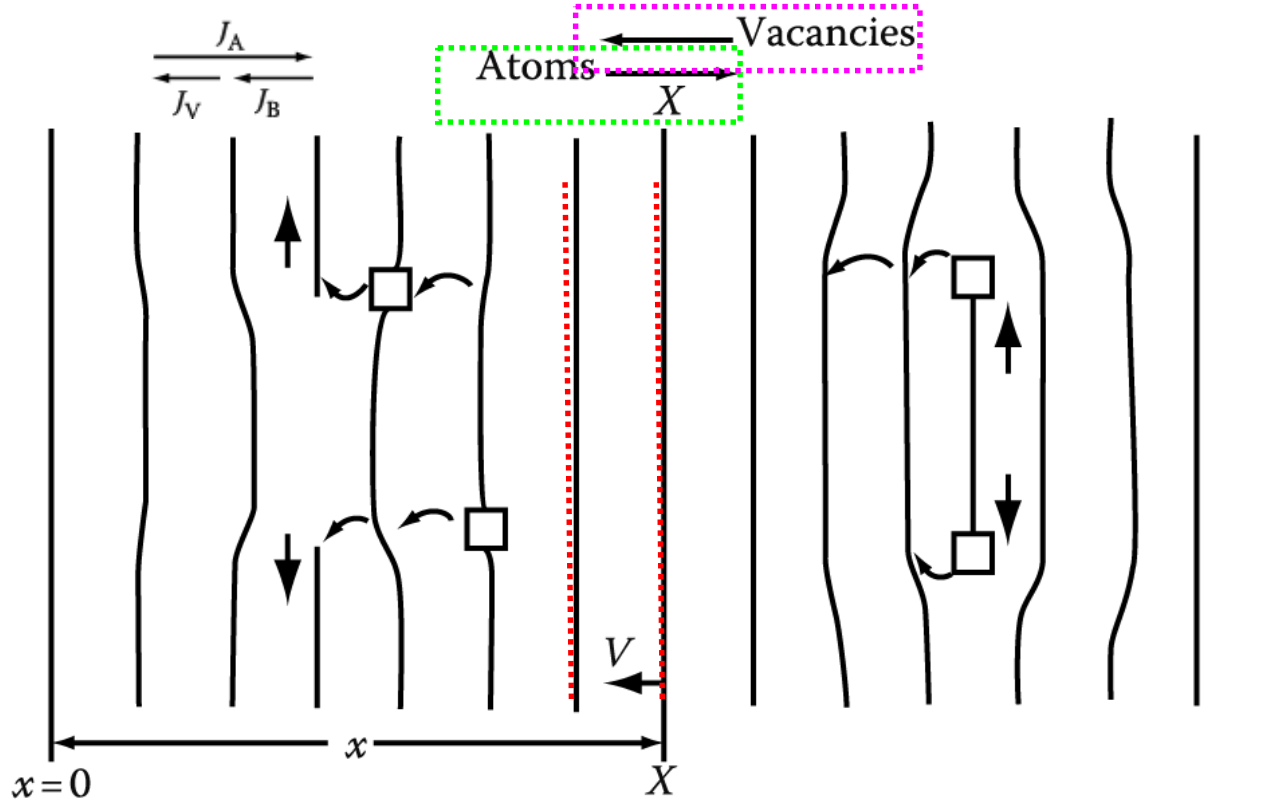


Fig. 2.17 (a) before, (b) after: a vacancy is absorbed at a jog on an edge dislocation (positive climb).
(b) before, (a) after: a vacancy is created by negative climb of an edge dislocation.
(c) Perspective drawing of a jogged edge dislocation.

If dislocation climbs continue to occur, what would happen?



Whole planes of atoms will be 'eaten' away

Extra atomic planes will be introduced

Fig. 2.18 A flux of vacancies causes the atomic planes to move through the specimen.

2) **velocity of the movement of the lattice plane** is related to the net flux of vacancies across the middle of the diffusion couple, such that

$$Av \cdot \delta t \cdot C_0 = J_v A \cdot \delta t \longrightarrow J_v = C_0 v$$

of removed atoms # of vacancies crossing the plane

$$v = \frac{1}{C_0} (D_A - D_B) \frac{\partial C_A}{\partial x} = (D_A - D_B) \frac{\partial X_A}{\partial x}$$

X_A : mole fraction of A atoms, v : marker velocity (velocity of the lattice plane)

In practice, internal movement of lattice planes are usually not directly of interest. More practical questions concern **how long** homogenization of an alloy takes, or **how rapidly** the composition will change at a fixed position relative to the ends of a specimen.

(균질화 시간 혹은 확산쌍의 위치에 따른 조성 변화)

➔ Derivation of the **Fick's 2nd law** for substitutional alloys

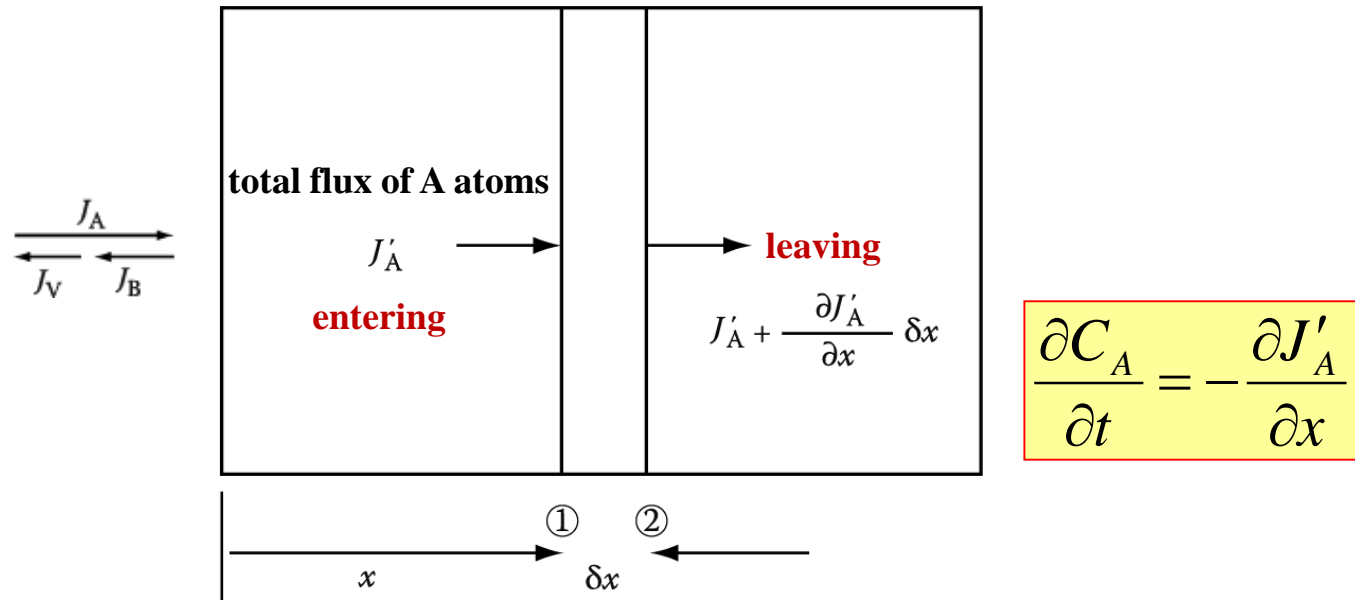


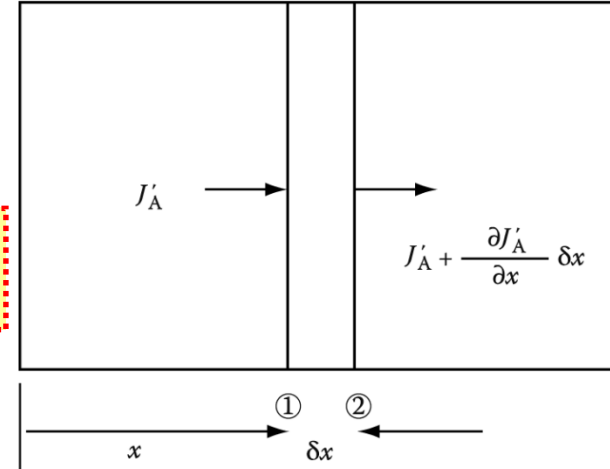
Fig. 2.19 Derivation of Fick's second law for interdiffusion. (See text for details.)

J'_A : total flux of A atoms across a stationary plane with respect to the specimen

3) Derivation of the Fick's 2nd law for substitutional alloys

J'_A : total flux of A atoms across a stationary plane with respect to the specimen

$$\frac{\partial C_A}{\partial t} = -\frac{\partial J'_A}{\partial x}$$



**A Diffusive flux due to diffusion relative to the lattice +
A flux due to the velocity of the lattice**

$$J'_A = J_A + vC_A$$

$$= -D_A \frac{\partial C_A}{\partial x} + vC_A$$

$$v = \frac{1}{C_0} (D_A - D_B) \frac{\partial C_A}{\partial x} = (D_A - D_B) \frac{\partial X_A}{\partial x} \quad X_A = C_A / C_0$$

$$= -(X_B D_A + X_A D_B) \frac{\partial C_A}{\partial x}$$

Fick's 1st law for substitutional alloy

$$= -\tilde{D} \frac{\partial C_A}{\partial x}$$

$$\tilde{D} = X_B D_A + X_A D_B$$

$$J'_B = -\tilde{D} \frac{\partial C_B}{\partial x} = \tilde{D} \frac{\partial C_A}{\partial x}$$

(Darken's equation, **interdiffusion coefficient**)

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

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$$\frac{\partial C_B}{\partial t} = D_B \frac{\partial^2 C_B}{\partial x^2}$$

**Only difference with ID
: diffusion coefficient**

$$\therefore J'_B = -J'_A$$

Q: How can we determine D_A and D_B ? in substitutional alloys?

By measuring velocity of a lattice (v) and interdiffusion coefficient (\tilde{D})

$$v = (D_A - D_B) \frac{\partial X_A}{\partial x} = (D_B - D_A) \frac{\partial X_B}{\partial x} \quad \Rightarrow \quad \tilde{D} = X_B D_A + X_A D_B$$

The interdiffusion coefficient (\tilde{D}) can be **experimentally measured** by determining the variation of X_A and X_B after annealing a diffusion couple.

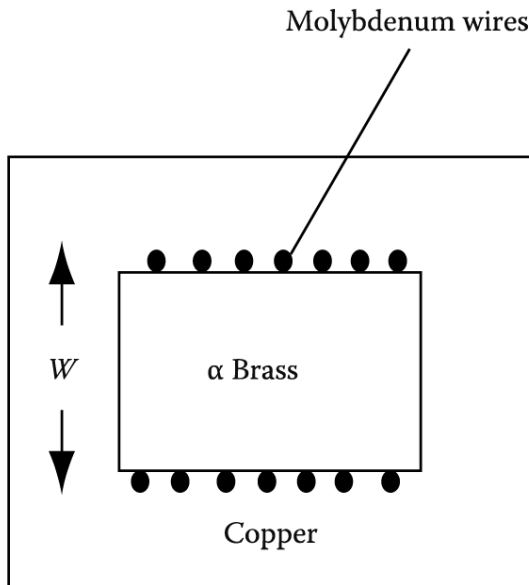
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When the velocity of a lattice (v) and interdiffusion coefficient (\tilde{D}) are known, D_A and D_B for the composition at the markers can be calculated.

How can we determine the velocity of a lattice (v)?



The displacement of wires during diffusion was first observed by Smigelskas and Kirkendall in 1947 and is usually known as the **Kirkendall effect**.

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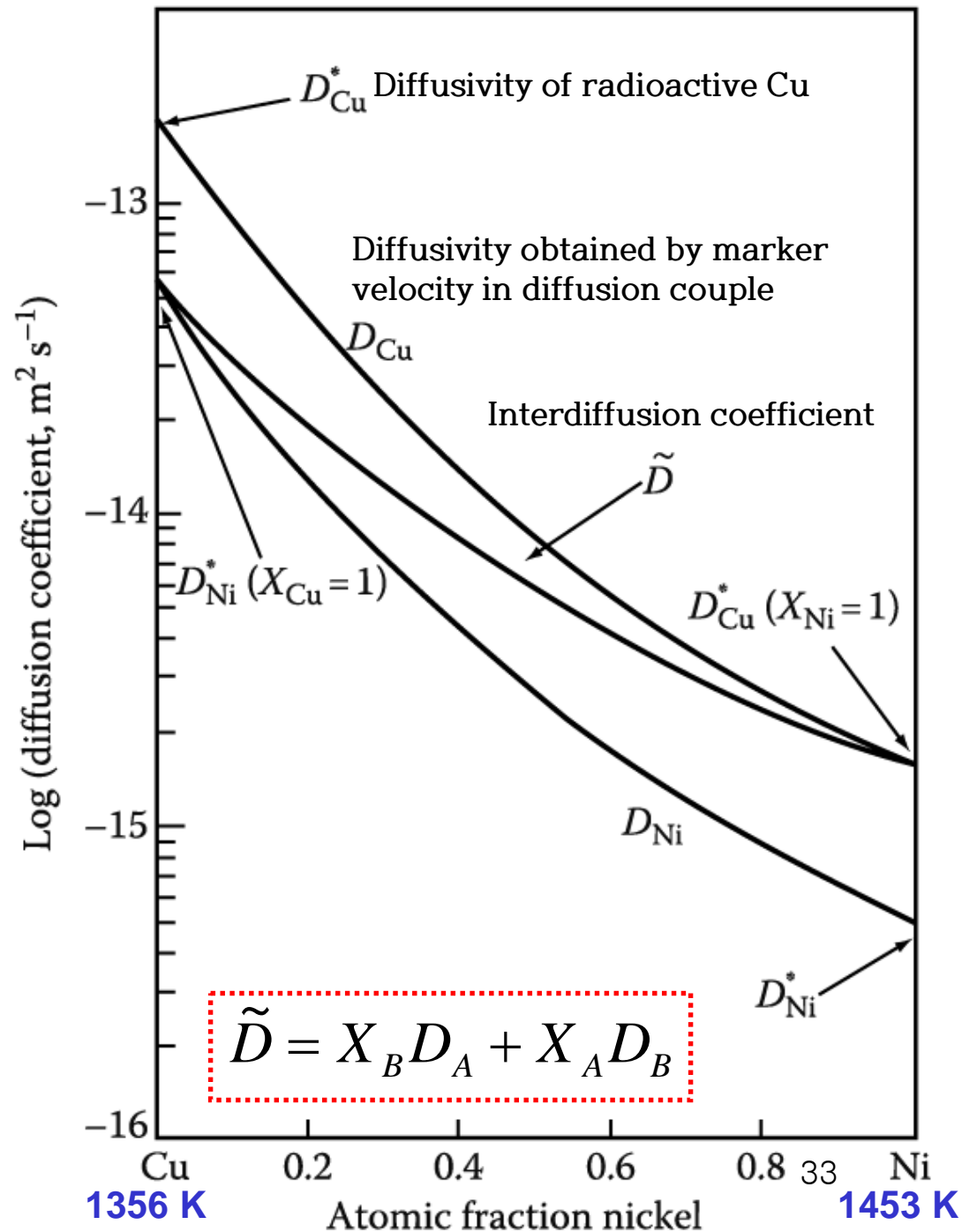
$$D_{Zn} > D_{Cu}$$

After annealing at a high temperature, it was found that the separation of the markers (w) had decreased. ³²

The relationship between the various diffusion coefficients in the Cu-Ni system at 1273 K.

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D_{Cu} , D_{Ni} , (\tilde{D}) are all composition dependent, increasing as X_{Cu} increases.



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$$\tilde{D} = X_B D_A + X_A D_B$$

(interdiffusion coefficient)

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$$\text{if } X_A \approx 1, \tilde{D} = D_B$$

The rate of homogenization in dilute alloys is controlled by how fast the solute (B) atoms can diffuse.

In this case, D_B is called 'impurity diffusion coefficient'.

~ can be measured by using radioactive tracers like self-diffusion

* D_B in a dilute solution of B in A is greater than D_A .

- The reason for this is that the solute atoms can attract vacancies so that there is more than a random probability of finding a vacancy next to a solute atom with the result that they can diffuse faster than solvent.
- This is caused by the **larger size or higher valency of the B atoms** compared to those of A atoms.
- If the **binding energy** is very large, the vacancy will be unable to escape from the solute atom. In this case the solute-vacancy pair can diffuse through the lattice together.

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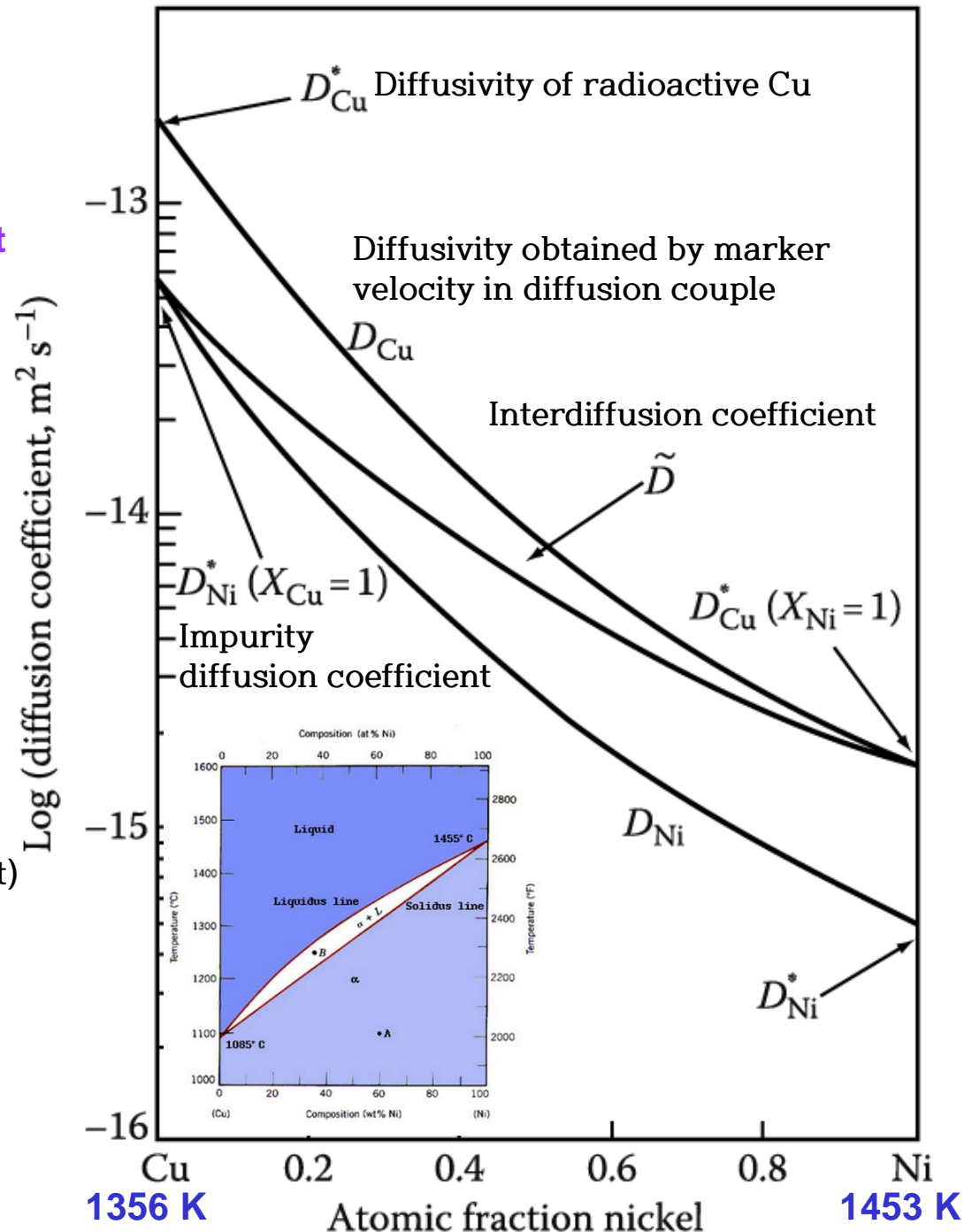
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By solving (2.53) with appropriate BCs, \rightarrow Possible to obtain $C_A(x, t)$ and $C_B(x, t)$

Characteristic relaxation time for an Homogenization anneal

$$\tau = \frac{l^2}{\pi^2 \tilde{D}} \quad \tau : \text{relaxation time}$$

(The range of composition is small enough that any effect of composition on \tilde{D} can be ignored)



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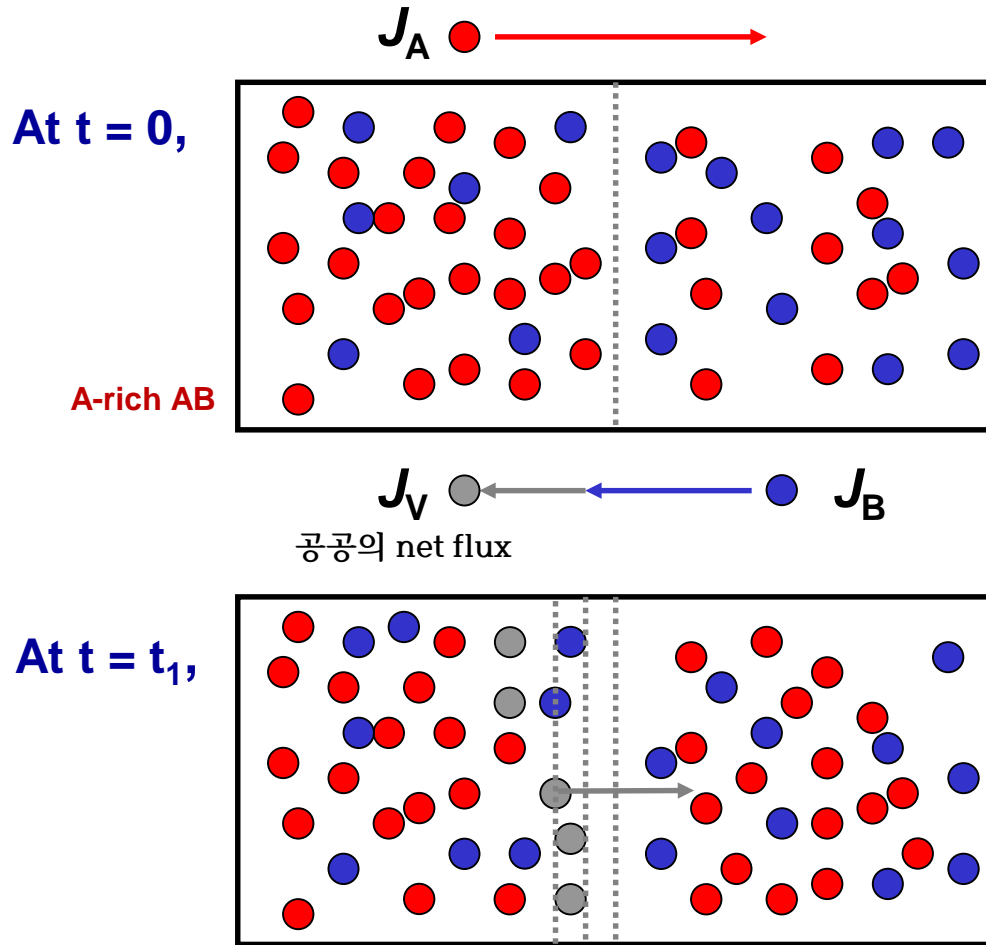
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$$X_v = X_v^e = \exp\left(\frac{-\Delta G_v}{RT}\right)$$

침입형 확산에서 Fick의 법칙 고정된 격자면을 통한 이동

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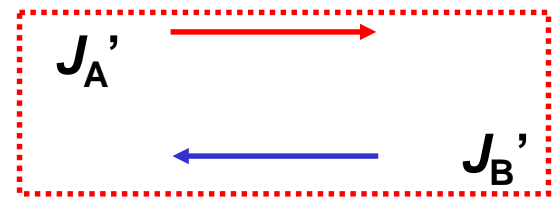
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고정된 격자 내에서 확산에 의한 유속



확산이 일어나는 격자이동에 의한 A 유속



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고정된 격자 내에서 확산에 의한 유속

$$J'_B = J_B + J_v^B = J_B + v C_B = -\tilde{D} \frac{\partial C_B}{\partial x}$$

$$\therefore J'_B = -J'_A$$

A원자와 B원자가 서로 다른 속도로 도약 →
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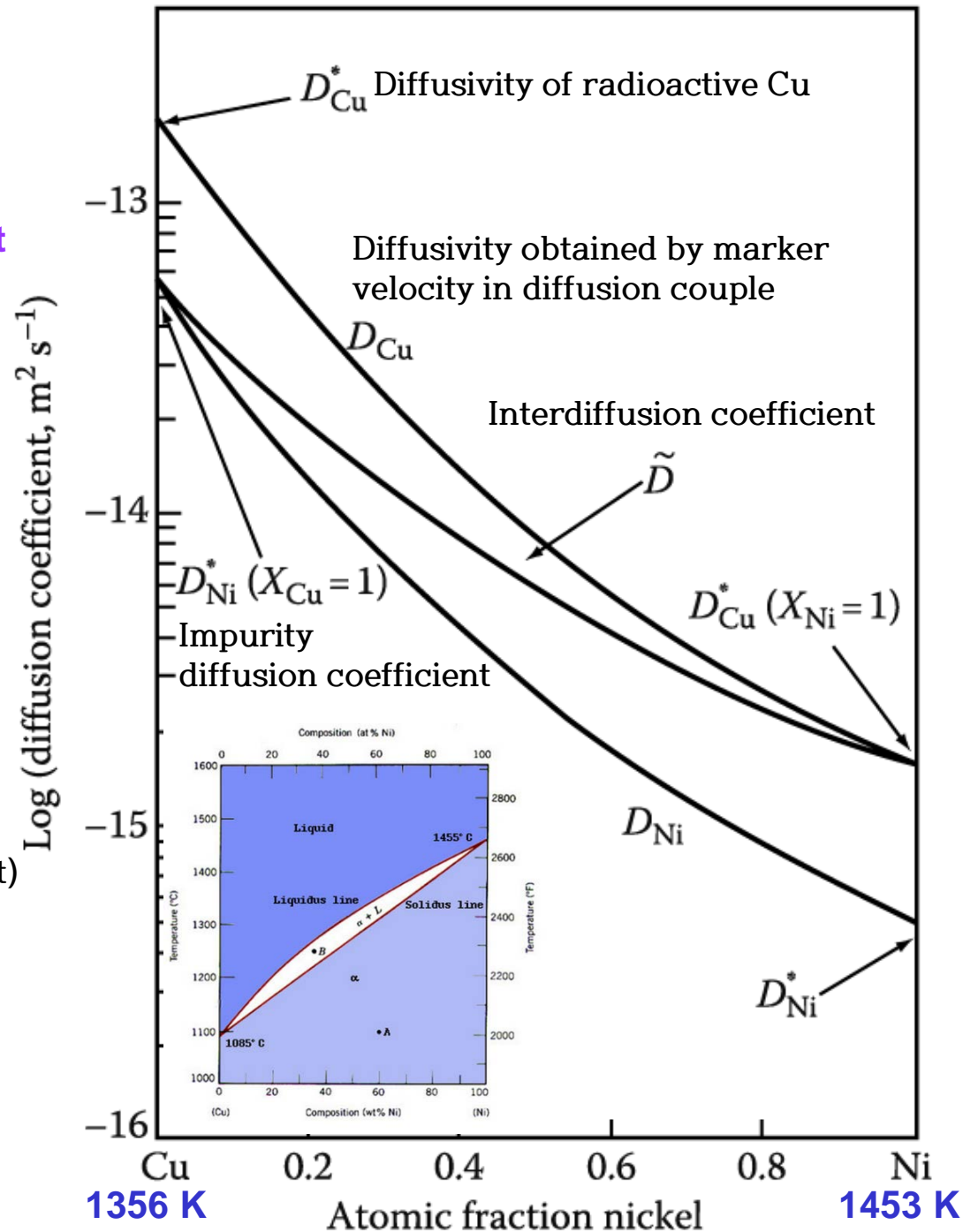
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2021 Fall

“Phase Transformation *in* Materials”

10th lecture

Eun Soo Park

Office: 33-313

Telephone: 880-7221

Email: espark@snu.ac.kr

Office hours: by an appointment

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Q: Diffusion in substitutional alloys?

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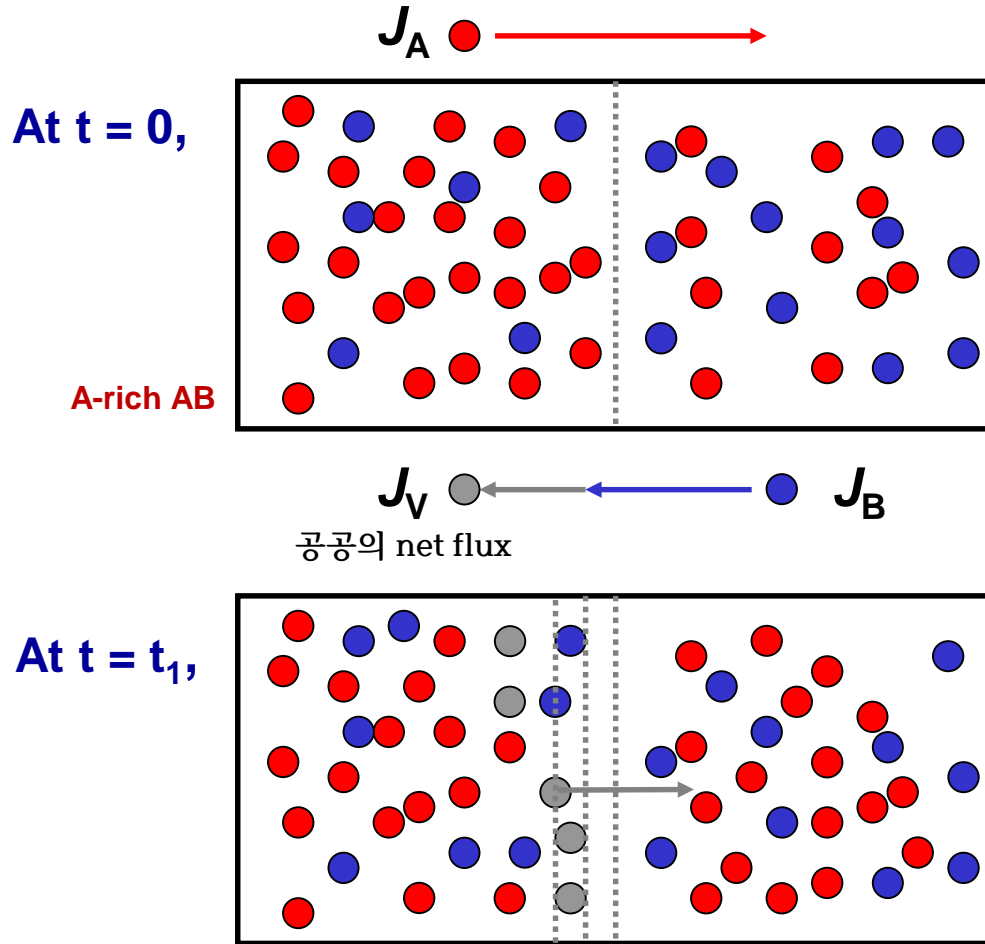
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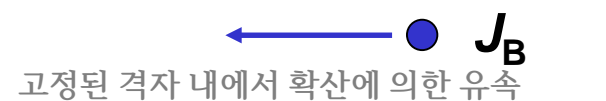
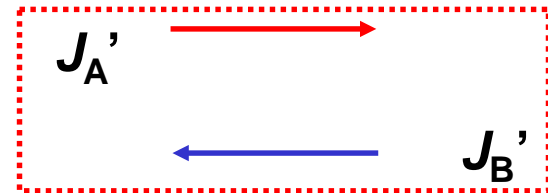
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A원자와 B원자가 서로 다른 속도로 도약 →
농도 구배에 의한 속도 + 격자면 이동에 의한 속도

1) INTERDIFFUSION

Assume that C_0 : total number of atoms (A, B) per unit volume = constant, independent of composition

$$C_0 = C_A + C_B \quad \text{and} \quad \frac{\partial C_A}{\partial x} = -\frac{\partial C_B}{\partial x} \quad \rightarrow$$

* If the couple is annealed at a high enough temp., a concentration profile will develop as shown.

Fluxes of A and B atoms across a given lattice plane ~ equal

$$J_A = -D_A \frac{\partial C_A}{\partial x} \quad J_B = -D_B \frac{\partial C_B}{\partial x} = D_B \frac{\partial C_A}{\partial x}$$

Due to the difference in diffusivities, a flux difference is created. $|J_A| > |J_B|$

Flux of vacancies

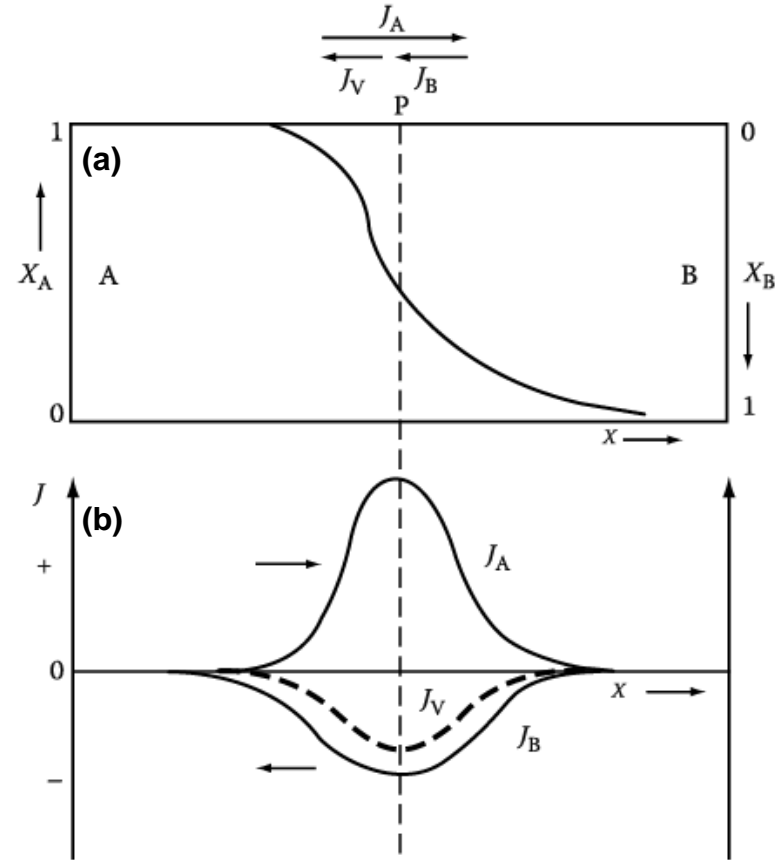
$$J_A \rightarrow J_{V,A} = -J_A \quad J_B \rightarrow J_{V,B} = -J_B$$

$$J_V + J_B = -J_A$$

$$J_V = -J_A - J_B \quad (\text{a net flux of vacancies})$$

$$= (D_A - D_B) \frac{\partial C_A}{\partial x}$$

$$\therefore J_B = -D_B \frac{\partial C_B}{\partial x} = D_B \frac{\partial C_A}{\partial x}$$



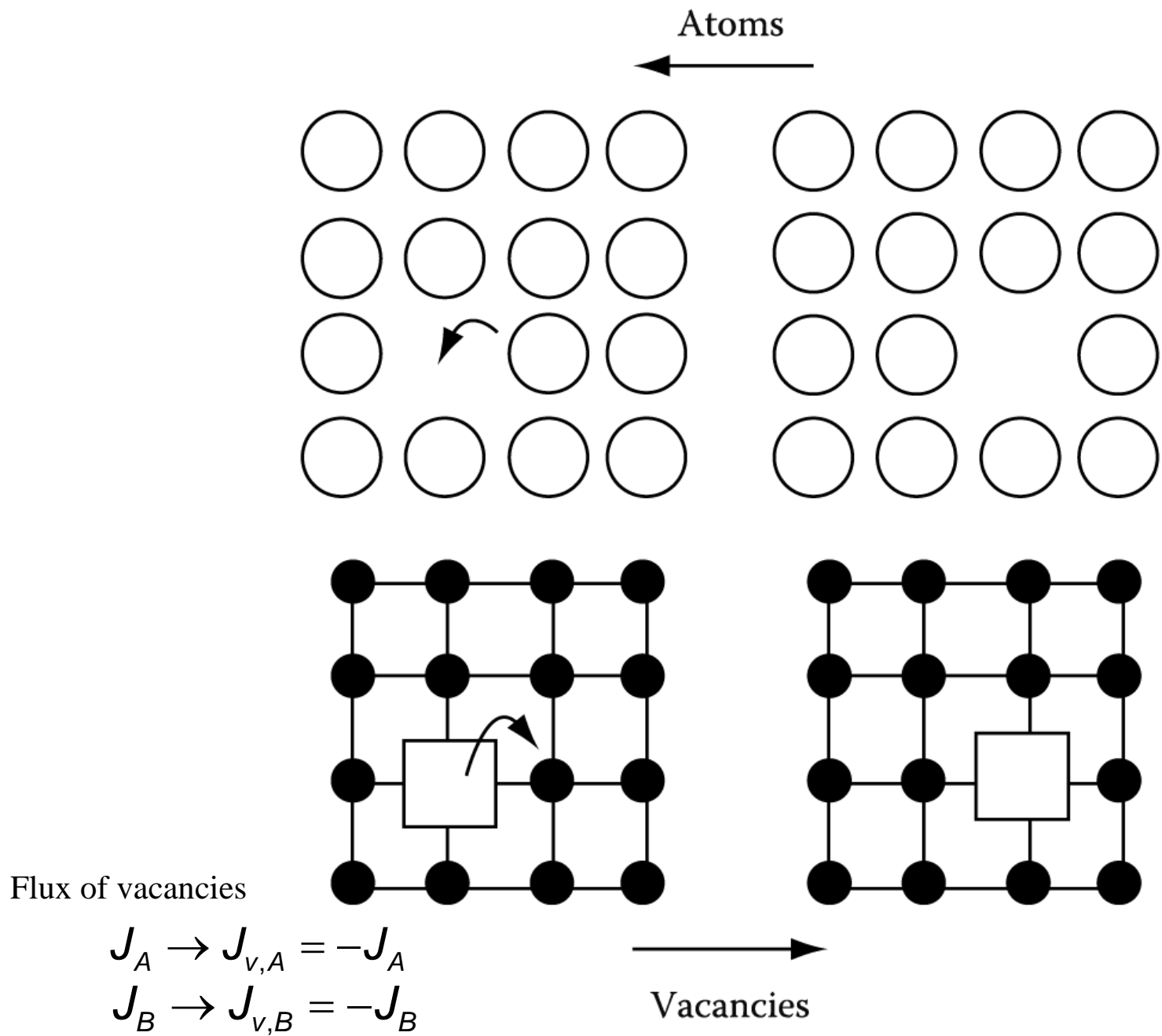


Fig. 2.16 **The jumping of atoms in one direction can be considered as the jumping of vacancies in the other direction.**

$$J_V = -J_A - J_B \text{ (a net flux of vacancies)}$$

$$= (D_A - D_B) \frac{\partial C_A}{\partial x}$$

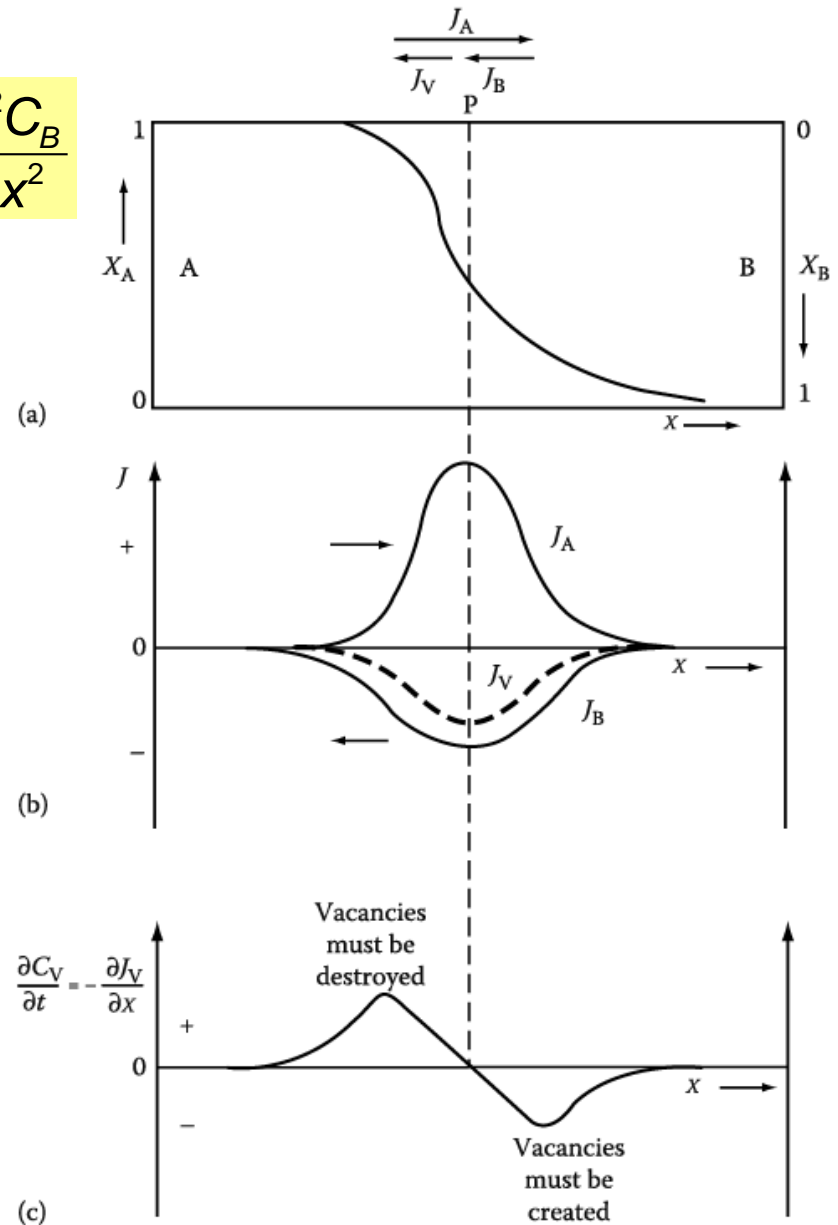
$$\frac{\partial C_B}{\partial t} = D_B \frac{\partial^2 C_B}{\partial x^2}$$

$$\frac{\partial C_V}{\partial t} = -\frac{\partial J_V}{\partial x} \text{ vs. } x?$$

What would become of excess vacancy?

$$\partial C_V / \partial t = -\partial J_V / \partial x \text{ (Fig. 2. 15c)}$$

$$\text{cf) } \frac{\partial C_B}{\partial t} = -\frac{\partial J_B}{\partial x}$$



In order to maintain the vacancy concentration everywhere near equilibrium, vacancies must be created on the B-rich side and destroyed on the A-rich side.

* Net flux of vacancies across the middle of the diffusion couple \rightarrow "Movement of lattice"

Kirkendall effect

Creation/destruction of vacancies is accomplished by *dislocation climb*.

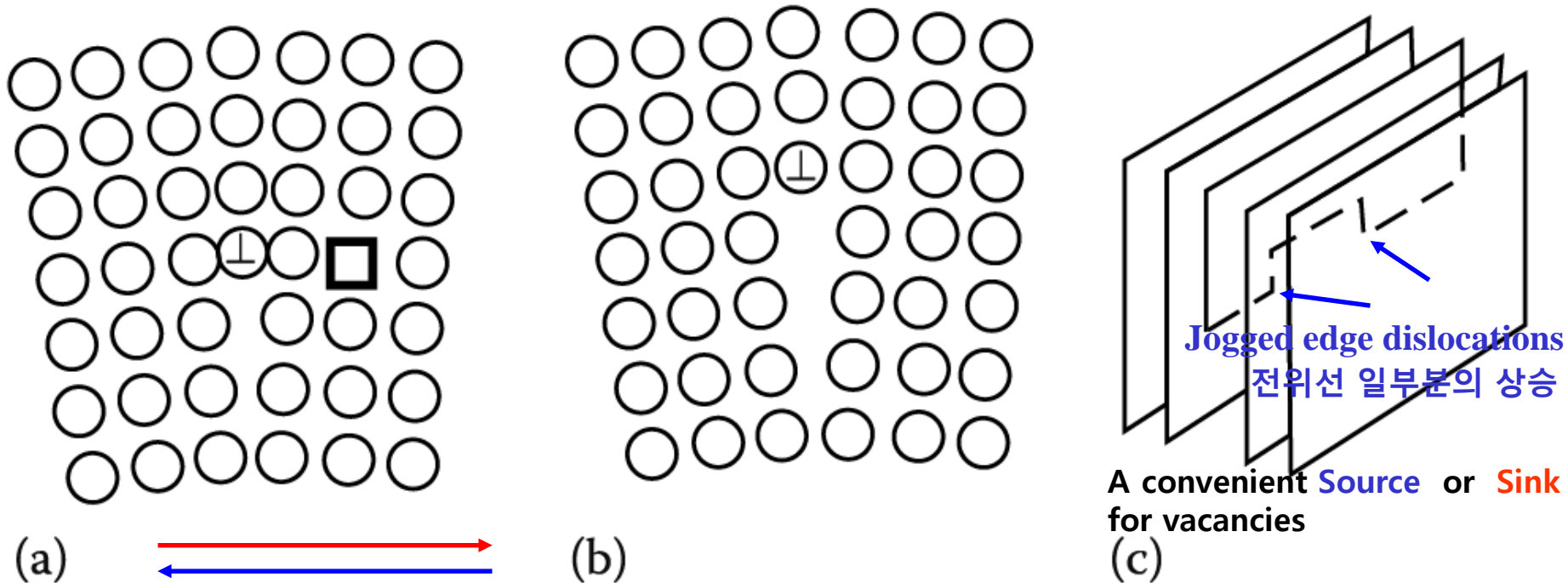
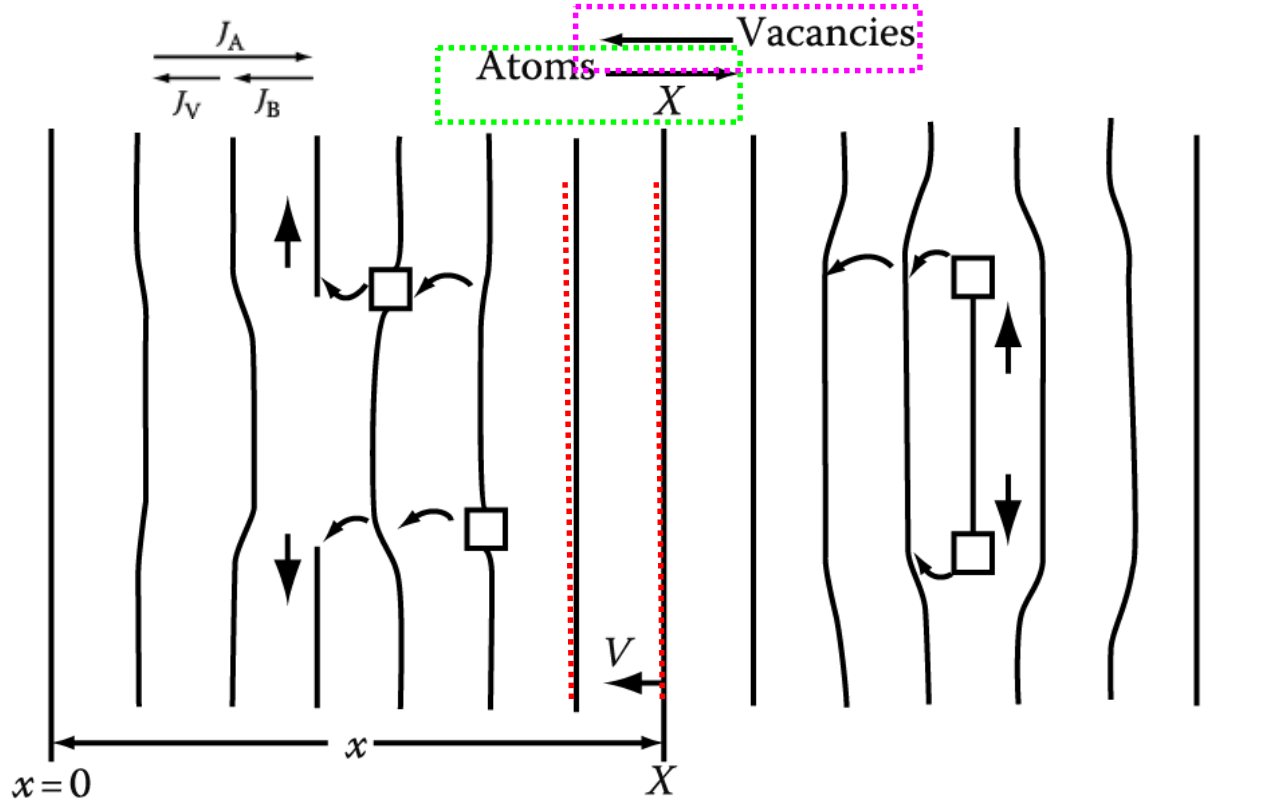


Fig. 2.17 (a) before, (b) after: a vacancy is absorbed at a jog on an edge dislocation (positive climb).
(b) before, (a) after: a vacancy is created by negative climb of an edge dislocation.
(c) Perspective drawing of a jogged edge dislocation.

*** Homework 3 : Kirkendall effect?**

If dislocation climbs continue to occur, what would happen?



Whole planes of atoms will be 'eaten' away

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$$\begin{aligned}
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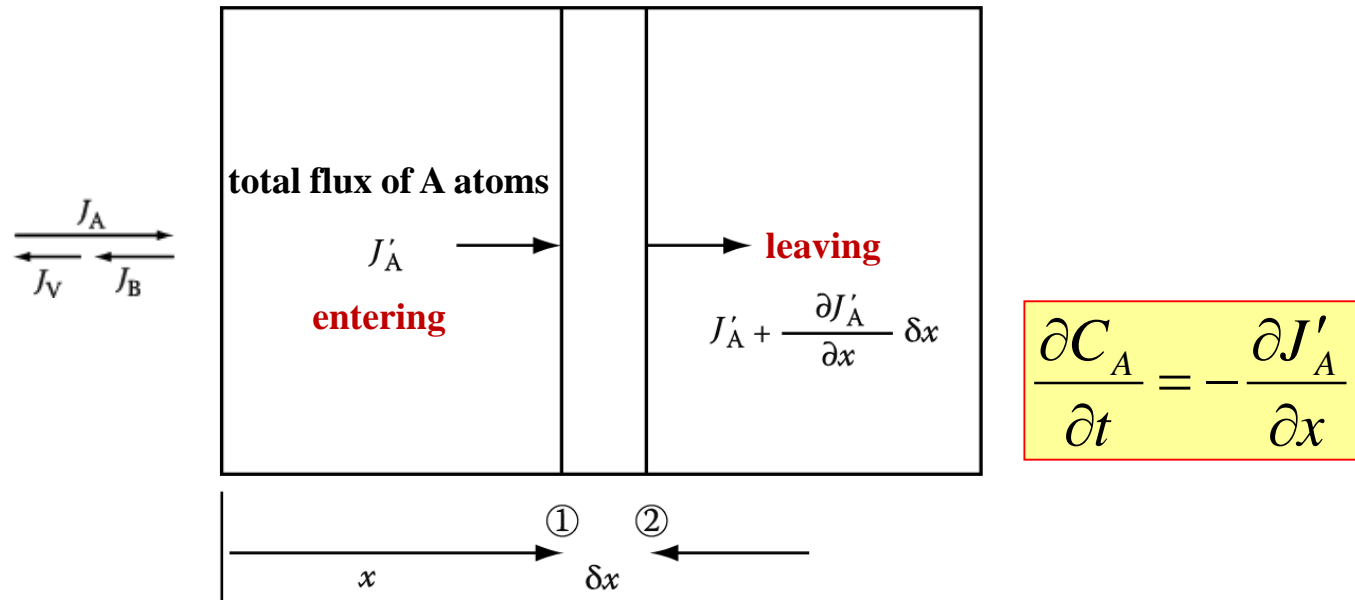


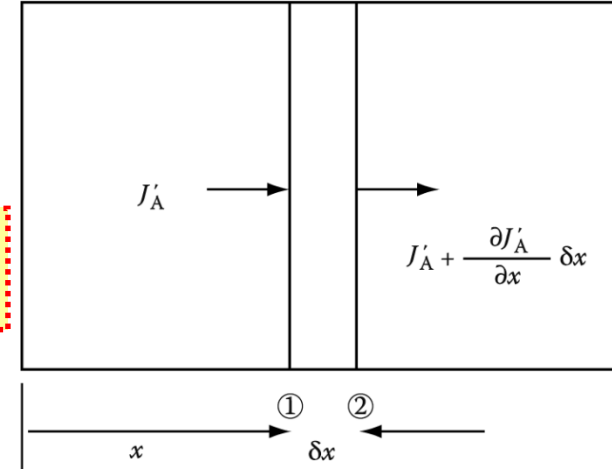
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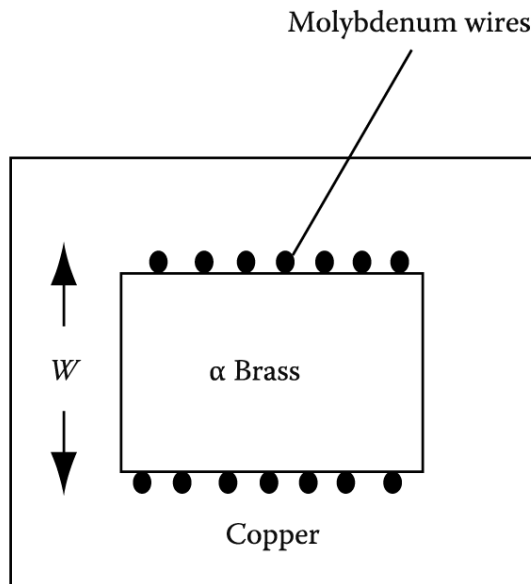
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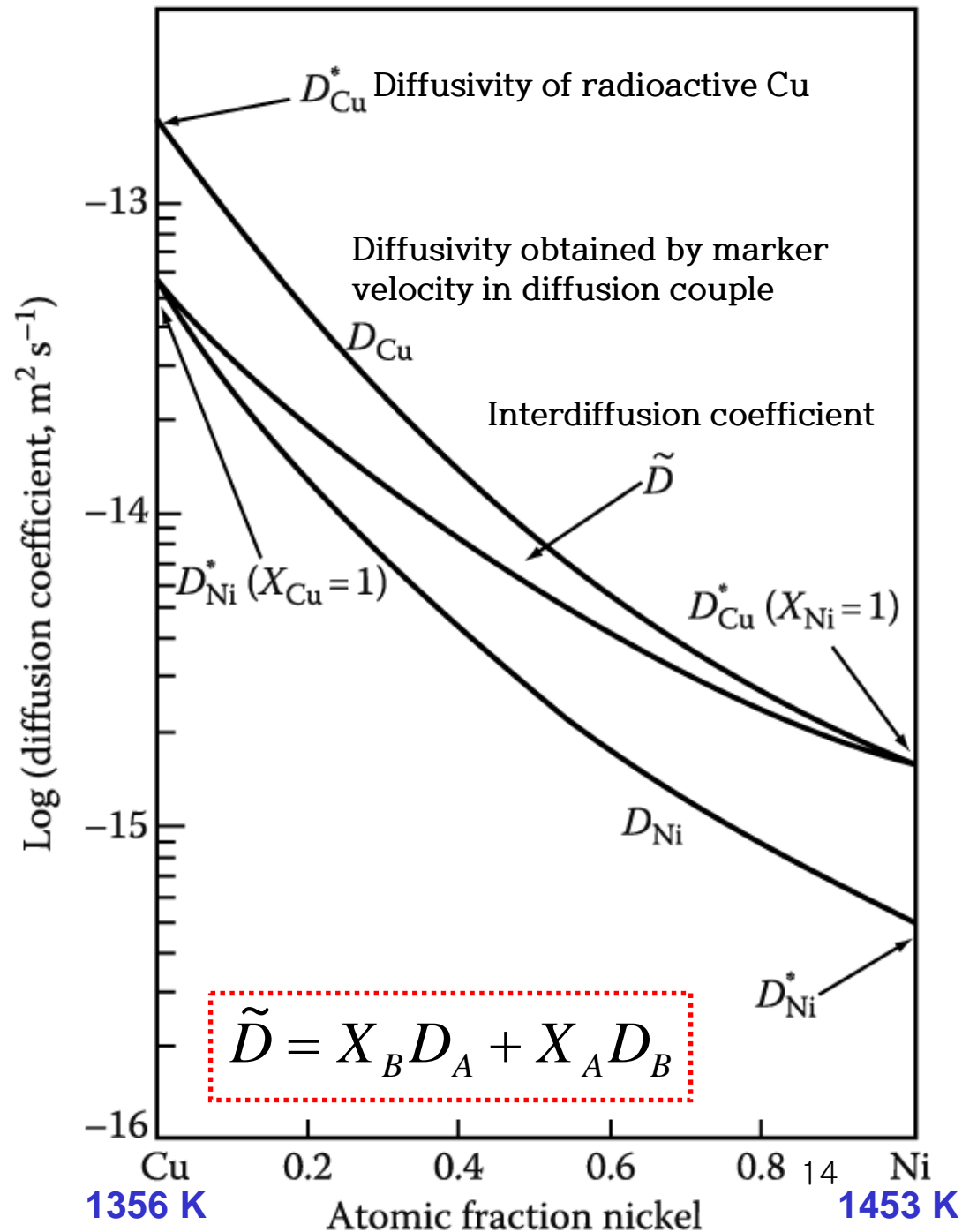
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~ can be measured by using radioactive tracers like self-diffusion

* D_B in a dilute solution of B in A is greater than D_A .

- The reason for this is that the solute atoms can attract vacancies so that there is more than a random probability of finding a vacancy next to a solute atom with the result that they can diffuse faster than solvent.
- This is caused by the **larger size or higher valency of the B atoms** compared to those of A atoms.
- If the **binding energy** is very large, the vacancy will be unable to escape from the solute atom. In this case the solute-vacancy pair can diffuse through the lattice together.

The relationship between the various diffusion coefficients in the Cu-Ni system at 1273 K.

Atoms with the lower melting point possess a higher D .

D_{Cu} , D_{Ni} , (\tilde{D}) are all composition dependent, increasing as X_{Cu} increases.

* Concentration of A & B at any x after t

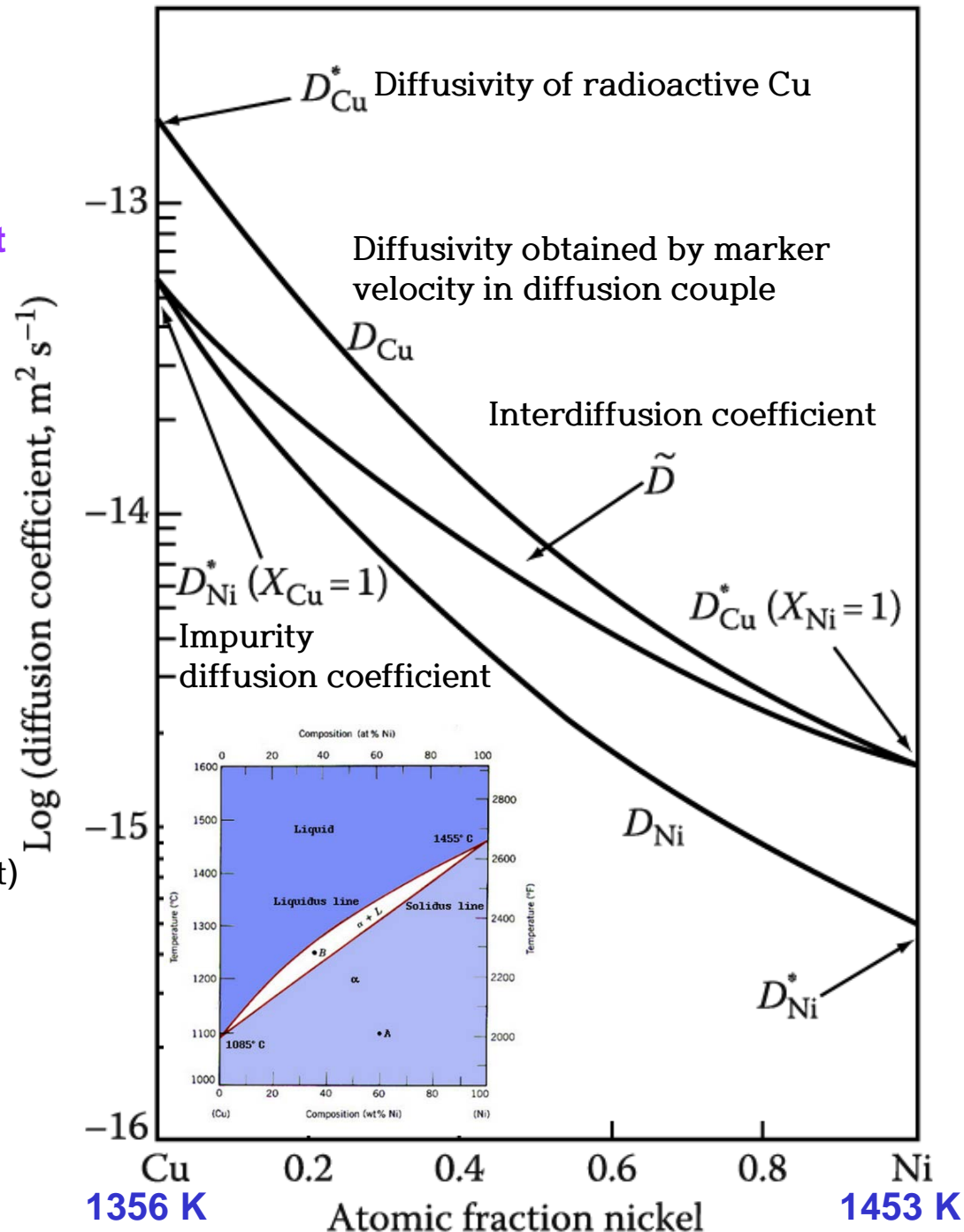
$$\frac{\partial C_A}{\partial t} = \frac{\partial}{\partial x} \left(\tilde{D} \frac{\partial C_A}{\partial x} \right) \quad \text{Eq. (2.53)}$$

By solving (2.53) with appropriate BCs, \rightarrow Possible to obtain $C_A(x, t)$ and $C_B(x, t)$

Characteristic relaxation time for an Homogenization anneal

$$\tau = \frac{l^2}{\pi^2 \tilde{D}} \quad \tau : \text{relaxation time}$$

(The range of composition is small enough that any effect of composition on \tilde{D} can be ignored)



Contents for today's class

- Interstitial Diffusion / Substitution Diffusion
- **Atomic Mobility**
- **Tracer Diffusion in Binary Alloys**
- **High-Diffusivity Paths**
 1. Diffusion along Grain Boundaries and Free Surface
 2. Diffusion Along Dislocation
- **Diffusion in Multiphase Binary Systems**

Q: How the mobility of an atom is related to its diffusion coefficient?

$$D_B = M_B RTF$$

Thermodynamic factor

$$F = \left(1 + \frac{d \ln \gamma_B}{d \ln X_B}\right)$$

2.4 Atomic mobility

- **Fick's first law**: assume that diffusion eventually stops when the concentration is the same everywhere → never true in practice due to lattice defect (농도구배만 고려)
 - **Higher concentrations in the vicinity of the “defect”**
→ Diffusion in the vicinity of these defects is affected by **both the concentration gradient and the gradient of the interaction energy.**(결함과의 상호작용에너지의 구배)
- ⇒ **Fick's law alone ~ insufficient**
to describe how to concentration will vary with distance and time.

e.g. Too big or too small solute atom

- relatively high potential energy due to the “strain” in the surrounding matrix
- However, this strain energy can be reduced if the atom is located in a position where it **better matches the space available**, i.e., near dislocations and in boundaries, where the matrix is already distorted.

2.4 Atomic mobility

- **“Segregation”** of atoms occur at crystal defects where the strain energy can be reduced. Segregation causes problems like **temper embrittlement** and **dynamic strain aging**. Fundamental kinetics of phase transformation are also affected by segregation.

→ The problem of atom migration can be solved by considering the **thermodynamic condition for equilibrium**; namely that the **chemical potential of an atom must be the same everywhere**. In general the **1) flux of atoms** at any point in the lattice is proportional to the **chemical potential gradient**: diffusion occurs down the slope of the chemical potential. Fick’s first law is merely a special case of this more general approach. (“previous approach”) $J_B = -D_B \frac{\partial C_B}{\partial x}$

무질서한 도약에 의한 순 표류속도



$$J_B = v_B C_B$$

2) A diffusion flux ~ a net drift velocity superimposed on the **random jumping motion** of each diffusing atom,

: remove differences in chemical potential \propto *chemical potential gradient*

$$v_B = -M_B \frac{\partial \mu_B}{\partial x}$$

– $\frac{\partial \mu_B}{\partial x}$: ① chemical force causing atom to migrate

“**M_B**”: mobility of B atoms, a constant of proportionality



$$J_B = -M_B C_B \frac{\partial \mu_B}{\partial x}$$

How the mobility of an atom is related to its diffusion coefficient?

Relationship between M_B and D_B

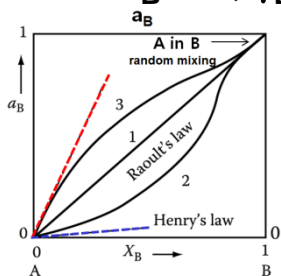
(원자이동도와 원자확산계수간 관계)

$$J_B = -M_B C_B \frac{\partial \mu_B}{\partial x}$$

$$\begin{aligned} \therefore J_B &= -M_B \frac{X_B}{V_m} \frac{RT}{X_B} \left(1 + \frac{\partial \ln \gamma_B}{\partial \ln X_B}\right) \frac{\partial X_B}{\partial x} \\ &= -M_B RT F \frac{\partial C_B}{\partial x} = -D_B \frac{\partial C_B}{\partial x} \end{aligned}$$

$$D_B = M_B RT F$$

For ideal or dilute solutions,
near $X_B \approx 0$, $\gamma_B = \text{const.}$ with respect to X_B



$$\therefore F = 1$$

$$D_B = M_B RT$$

$$\mu_B = G_B + RT \ln a_B = G_B + RT \ln \gamma_B X_B$$

$$\frac{\partial \mu_B}{\partial x} = \frac{\partial}{\partial x} (G_B^0 + RT \ln \gamma_B X_B)$$

$$= RT \left(\frac{\partial \ln \gamma_B}{\partial x} + \frac{\partial \ln X_B}{\partial x} \right)$$

$$= RT \left(1 + \frac{\partial \ln \gamma_B}{\partial \ln X_B} \right) \frac{\partial \ln X_B}{\partial x}$$

$$C_B = \frac{n_B}{V} = \frac{n_B}{(n_A + n_B)V_m} = \frac{X_B}{V_m}$$

$$F = \left\{ 1 + \frac{d \ln \gamma_A}{d \ln X_A} \right\} = \left\{ 1 + \frac{d \ln \gamma_B}{d \ln X_B} \right\} = \frac{X_A X_B}{RT} \frac{d^2 G}{dX^2}$$

For non-ideal concentrated solutions,
thermodynamic factor (F) must be included.

→ Related to the curvature of the molar
free energy-composition curve.

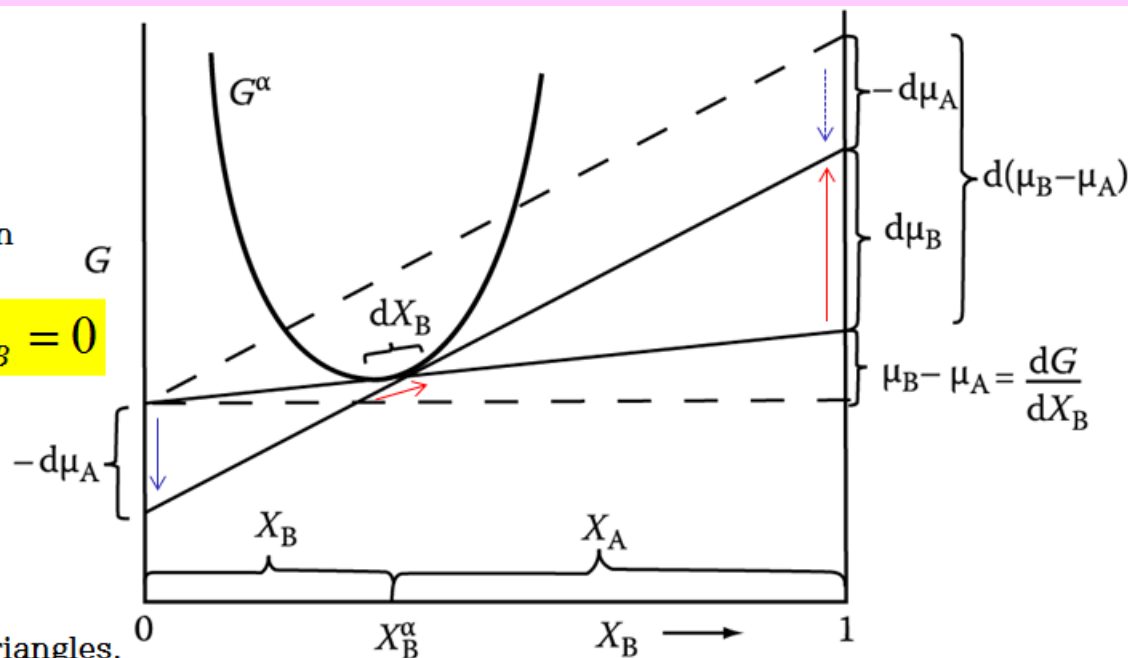
Additional Thermodynamic Relationships for Binary Solutions

The Gibbs-Duhem Equation 합금조성의 미소변화 (dX)로 인한 화학퍼텐셜의 미소변화(dμ)를 계산

be able to calculate the change in chemical potential (dμ) that result from a change in alloy composition (dX).

Gibbs-Duhem equation for a binary solution

$$X_A d\mu_A + X_B d\mu_B = 0$$



Comparing two similar triangles,

$$-\frac{d\mu_A}{X_B} = \frac{d\mu_B}{X_A} = \frac{d(\mu_B - \mu_A)}{1} \quad \leftarrow \quad \frac{dG}{dX_B} = \frac{\mu_B - \mu_A}{1} \quad , \quad \frac{d^2G/dX^2}{d^2G/dX_B^2} = d^2G/dX_A^2$$

Substituting right side Eq. & Multiply $X_A X_B$

$$-X_A d\mu_A = X_B d\mu_B = X_A X_B \frac{d^2G}{dX^2} dX_B \quad \text{Eq. 1.65}$$

“Gibbs-Duhem Equation”

X_A, X_B vs. $d\mu_A, d\mu_B$

γ_A, γ_B

a_A, a_B

$$X_A X_B \frac{d^2G}{dX^2} = RT \left\{ 1 + \frac{d \ln \gamma_A}{d \ln X_A} \right\} = RT \left\{ 1 + \frac{d \ln \gamma_B}{d \ln X_B} \right\}$$

② The diffusive flux is also affected by the **gradient of strain energy, $\partial E/\partial x$.**

변형 E 구배도 확산에 영향

Ex) The expression for the chemical potential can be modified to include the effect of an **“elastic strain energy term”**, **E** depends on the position (x) relative to a dislocation.

$$\mu_B = G_B + RT \ln \gamma_B X_B + E$$



$$J_B = -D_B \cdot \frac{\partial C_B}{\partial x} - \frac{D_B C_B}{RT} \cdot \frac{\partial E}{\partial x}$$

Concentration gradient & strain E gradient

③ Atoms diffusing towards regions of high concentration can be found

a. when diffusion occurs in the **presence of an electric field or a temperature gradient.**

b. when the free energy curve has a negative curvature, which is known as **spinodal decomposition.**

Q: How does D_{Au}^* differ from D_{Au} ?

Tracer diffusion coefficient

Intrinsic diffusion coefficients

D_{Au}^* gives the rate at which Au* (or Au) atoms diffuse in a chemically homogeneous alloy, whereas D_{Au} gives the diffusion rate of Au when concentration gradient is present.

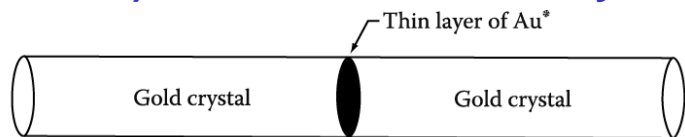
$$\tilde{D} = X_B D_A + X_A D_B = F (X_B D_A^* + X_A D_B^*)$$

Thermodynamic factor

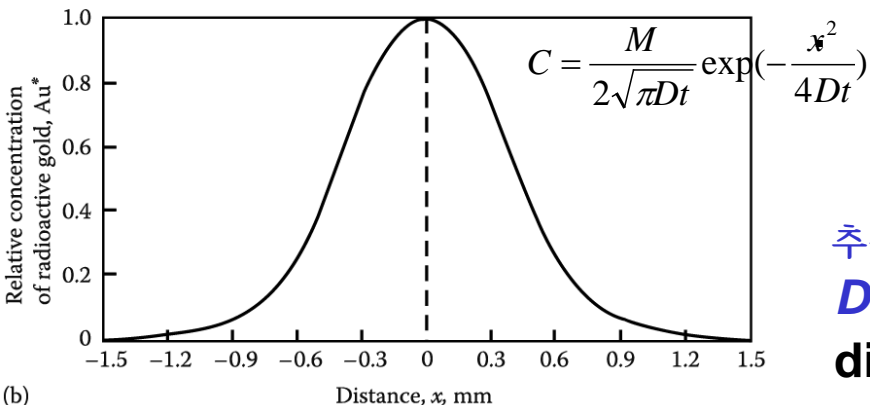
$$F = \left(1 + \frac{d \ln \gamma_B}{d \ln X_B}\right)$$

2.5 Tracer diffusion in binary alloys

1) Au* in Au or Au/X alloy

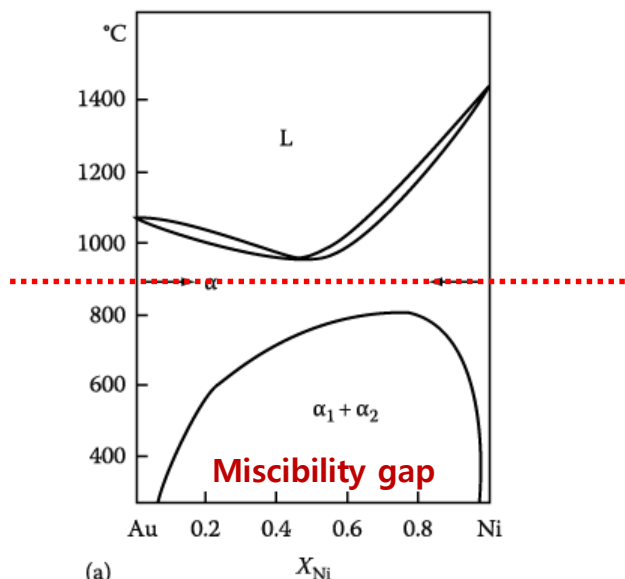


(a)



(b)

2) Au* in Au-Ni



(a)

Tracer diffusion coefficient (D_{Au}^*) in pure metal & **Intrinsic diffusion coefficients (D_{Au})** in an alloy : possible to determine by radioactive tracers

$$D = D_{Au}^* \text{ (tracer diffusion coefficient)}$$

How does D_{Au}^* differ from D_{Au} ?

추적자 확산계수: 원자의 도약확률이 모든방향에서 일정

D_{Au}^* gives the rate at which Au* (or Au) atoms diffuse in a **chemically homogeneous** alloy, whereas D_{Au} gives the diffusion rate of Au when **concentration gradient** is present.

고유 확산계수: 원자의 도약확률 농도구배의 영향

If concentration gradient exhibit,

$$\Delta H_{mix} > 0 \rightarrow D_{Au} < D_{Au}^* \quad D_{Ni} < D_{Ni}^*$$

Au-Ni: 'dislike' each other

the rate of homogenization will therefore be slower.

Ex) Probability for the jumps made by Au atoms

in Ni-rich regions ↓ → "slower diffusivity"

D^* versus D : On the other hand,

Since the **chemical potential gradient** is the driving force for diffusion in both types of experiment, it is reasonable to suppose that the atomic mobility are not affected by the concentration gradient. ($M^*=M$)

What would be the relation between the intrinsic chemical diffusivities D_B and tracer diffusivities D_B^* in binary alloys?

추적자 원소의 함량 매우 적음

In the tracer diffusion experiment, the tracer essentially forms a **dilute solution** in the alloy.

$$D_B^* = M_B^* RT = M_B RT \quad \leftarrow \quad D_B = M_B RT \left\{ 1 + \frac{d \ln \gamma_B}{d \ln X_B} \right\} = F M_B RT$$

$$\begin{aligned} D_A &= F D_A^* \\ D_B &= F D_B^* \end{aligned} \quad \rightarrow \quad \tilde{D} = X_B D_A + X_A D_B = F (X_B D_A^* + X_A D_B^*)$$

F : Thermodynamic Factor

Additional Thermodynamic Relationships for Binary Solution:

Variation of chemical potential ($d\mu$) by change of alloy compositions (dX)

Eq.(1.71)

$$X_A X_B \frac{d^2 G}{dX^2} = RT \left\{ 1 + \frac{d \ln \gamma_A}{d \ln X_A} \right\} = RT \left\{ 1 + \frac{d \ln \gamma_B}{d \ln X_B} \right\}$$

$$\rightarrow F = \left\{ 1 + \frac{d \ln \gamma_A}{d \ln X_A} \right\} = \left\{ 1 + \frac{d \ln \gamma_B}{d \ln X_B} \right\} = \frac{X_A X_B}{RT} \frac{d^2 G}{dX^2}$$

2.5 Tracer diffusion in binary alloys

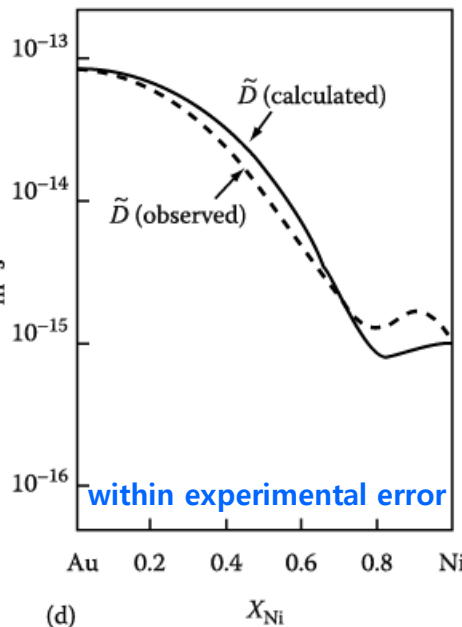
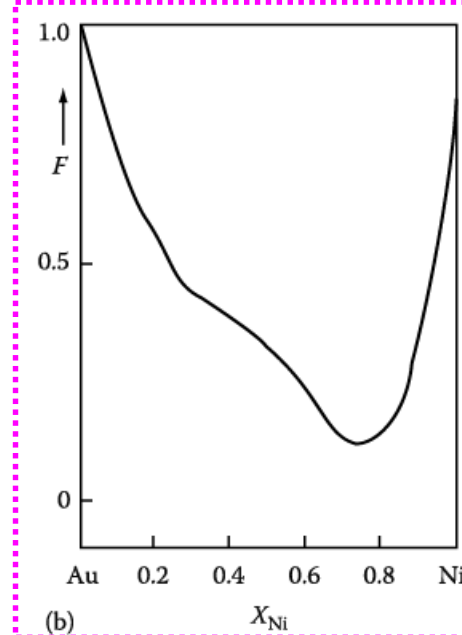
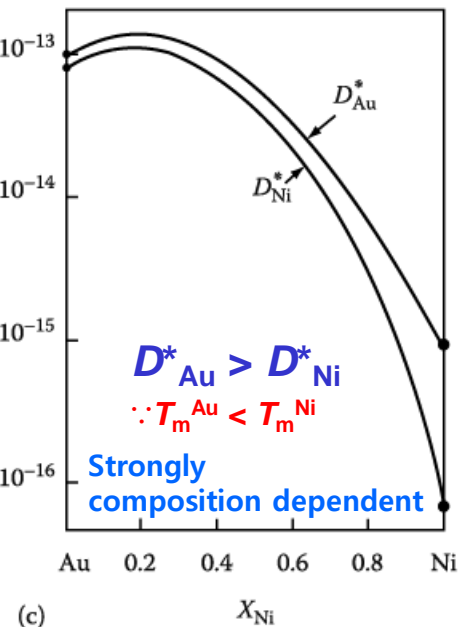
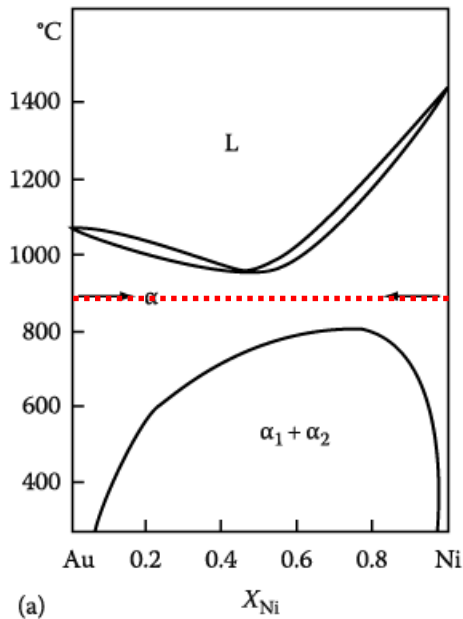


Fig. 2.22 Inter-diffusion in Au-Ni alloys at 900°C (a) Au-Ni phase diagram, (b) the thermodynamic factor, F , at 900°C, (c) experimentally measured tracer diffusivities At 900°C (d) experimentally measured inter-diffusion coefficients compared with values calculated from (b) and (c).

1) Measured by diffusion couple experiment in Au-Ni: \tilde{D}

$$v = (D_A - D_B) \frac{\partial X_A}{\partial X} = (D_B - D_A) \frac{\partial X_B}{\partial X} \Rightarrow \tilde{D} = X_B D_A + X_A D_B$$

2) Calculated by tracer diffusion coefficient D^*_{Au} & D^*_{Ni} :

$$\tilde{D} = F (X_B D_A^* + X_A D_B^*)$$

→ The agreement is within the experimental error.

→ Strong composition dependent, $Ni \uparrow \rightarrow \tilde{D} \downarrow$

$$\because T_m^{Au} < T_m^{Ni}$$

Q: How do the compositions of ternary A and B alloys of diffusion couple change with time?

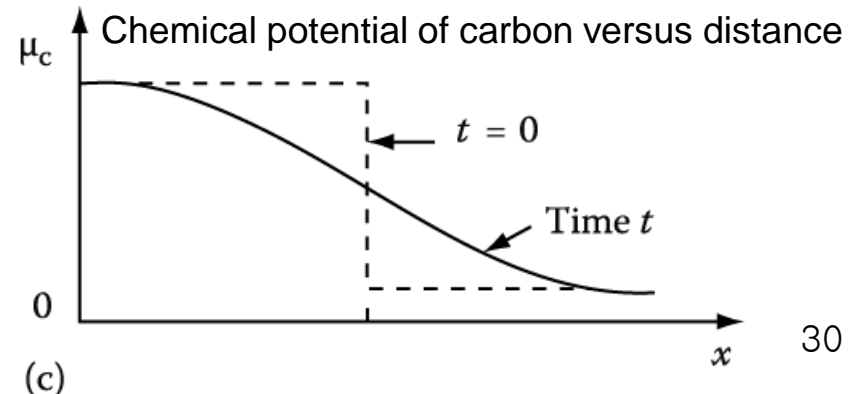
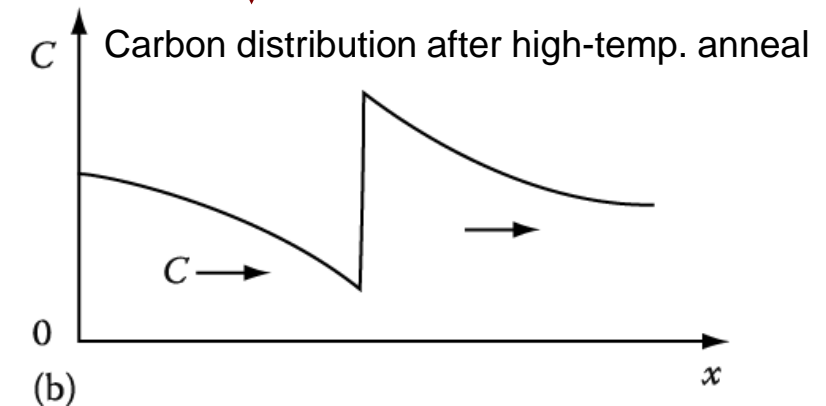
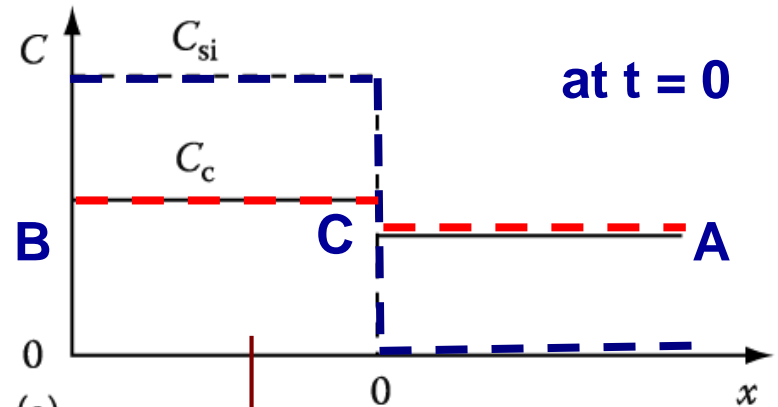
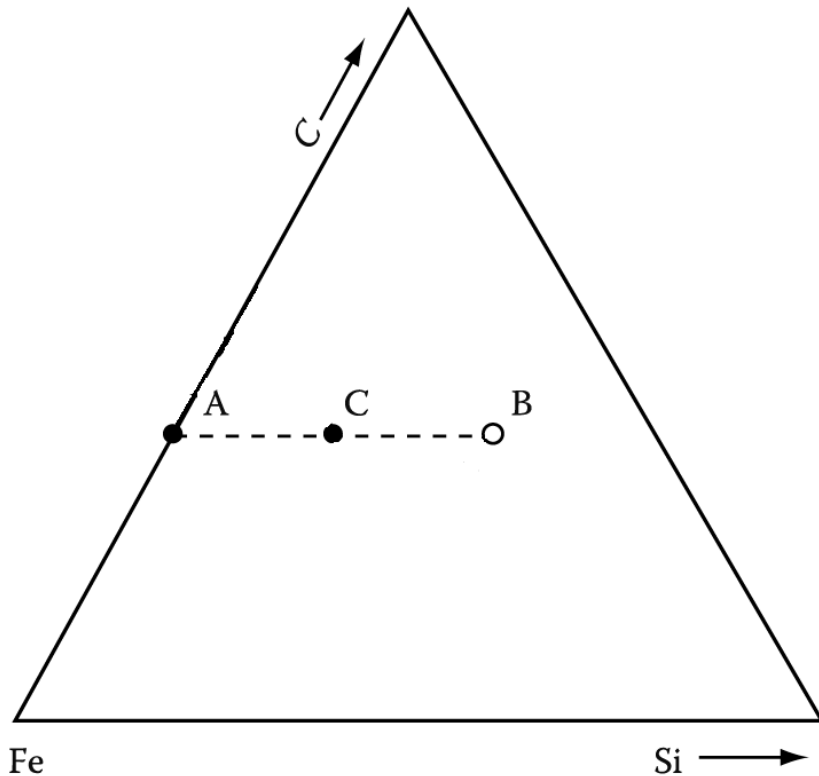
2.6 Diffusion in ternary alloys: Additional Effects

Example) Fe-Si-C system (Fe-3.8%Si-0.48%C) vs. (Fe-0.44%C) at 1050°C

- ① Si raises the μ_C in solution.
(chemical potential of carbon)

C 이동: 고농도 → 저농도 영역 & Si-rich → Si 적은 영역

- ② $M_{Si} \text{ (sub.)} \ll M_C \text{ (interstitial solute)}$,
(M : mobility)



How do the compositions of A and B change with time?

- 1) Carbon atom migration $B \rightarrow A$**
 - ~ equilibrate the activity, or chemical potential, of carbon in both sides
 - ~ only partial equilibrium of chemical potential of the carbon & not for the silicon
- 2) Silicon atom migration $B \rightarrow A$**
 - ~ over sufficient time
 - ~ the carbon atoms will continually redistribute themselves to maintain a constant chemical potential.
- 3) The concentrations of carbon and silicon are uniform everywhere. C**

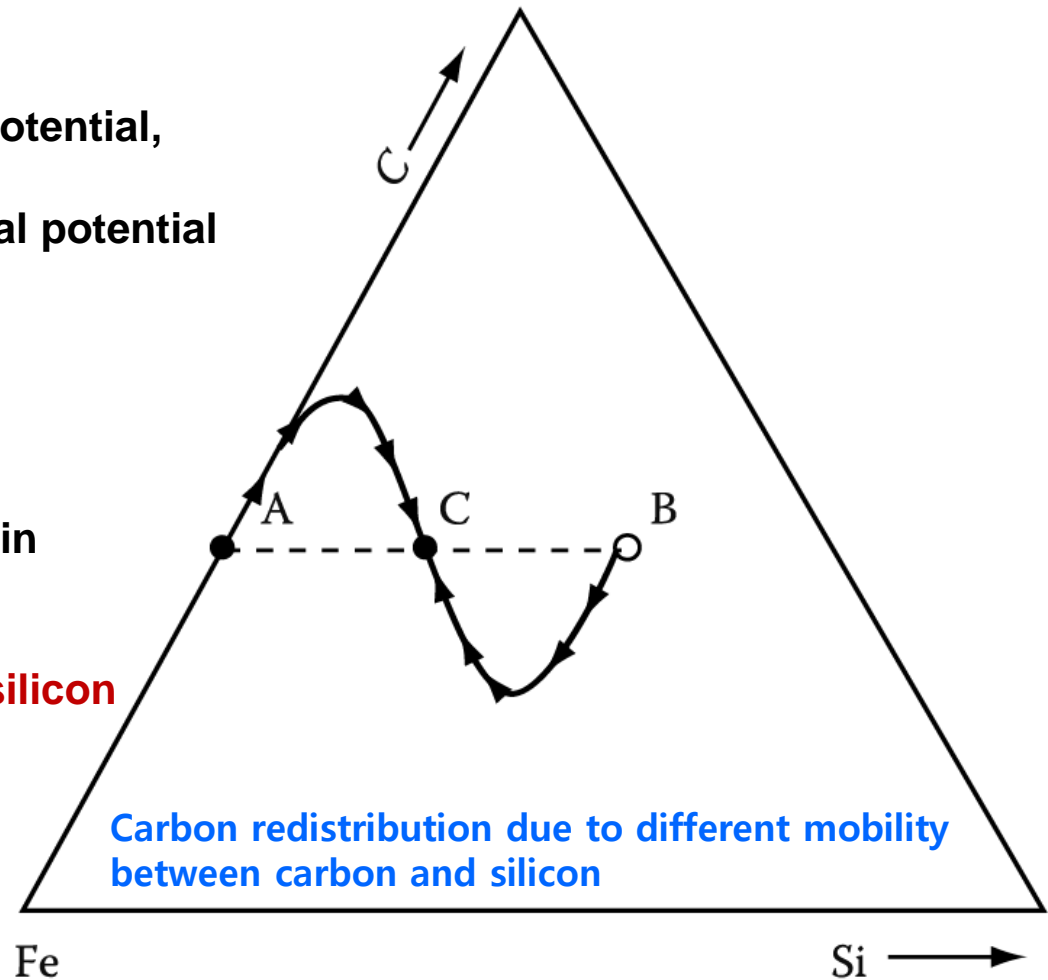


Fig. 2.24. Schematic diagram showing the change in composition of two points (A and B) on opposite sides of the diffusion couple

Q: What conditions high-diffusivity paths' (grain boundary, dislocation) diffusion is important?

$$D_s > D_b > D_l \longleftrightarrow A_l > A_b > A_s$$

1. Diffusion along Grain Boundaries and Free Surface

Grain boundary diffusion makes a significant contribution

only when $D_b \delta > D_l d$. ($T < 0.75 \sim 0.8 T_m$)

$$D_{app} = D_l + D_b \frac{\delta}{d}$$

2. Diffusion Along Dislocation

At low temperatures, ($T < \sim 0.5 T_m$)

gD_p/D_l can become so large that the apparent diffusivity is entirely due to diffusion along dislocation.

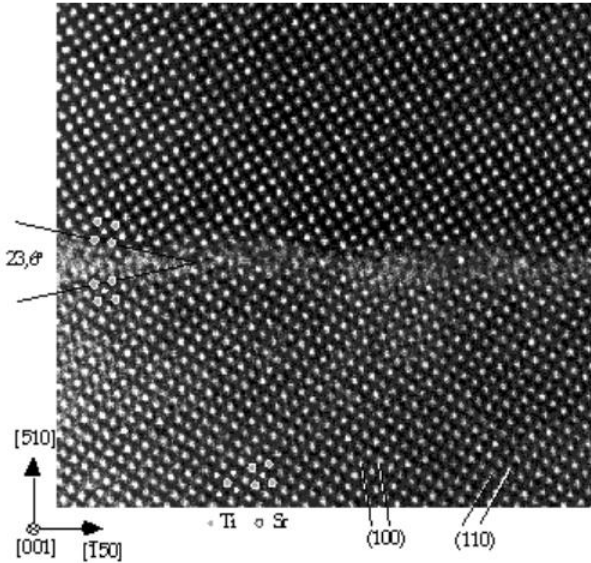
2.7.1 High-diffusivity paths

Real materials contain **defects**.

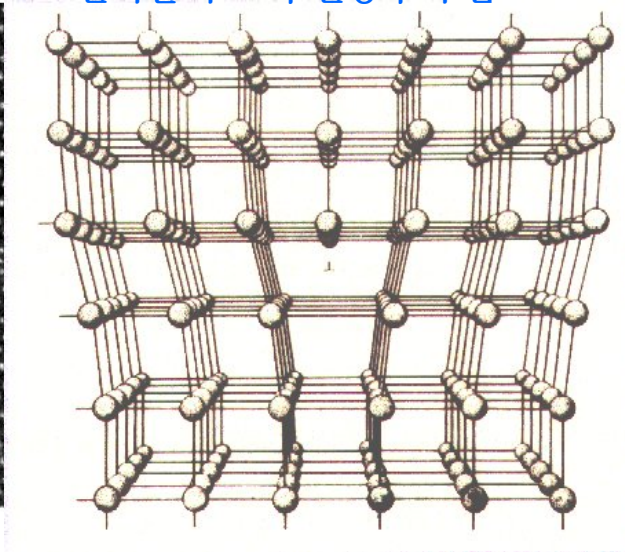
= more open structure → fast diffusion path.

원자들의 도약 진동수가 큼

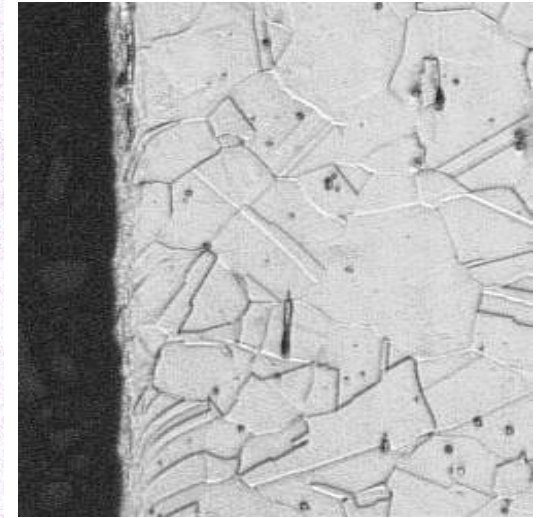
확산의 주요한 행로



Grain boundary



dislocation



surface

$$D_s > D_b > D_l$$

Diff. along lattice

$$D_l = D_{l0} \exp\left(-\frac{Q_l}{RT}\right)$$

Diff. along grain boundary

$$D_b = D_{b0} \exp\left(-\frac{Q_b}{RT}\right)$$

Diff. along free surface

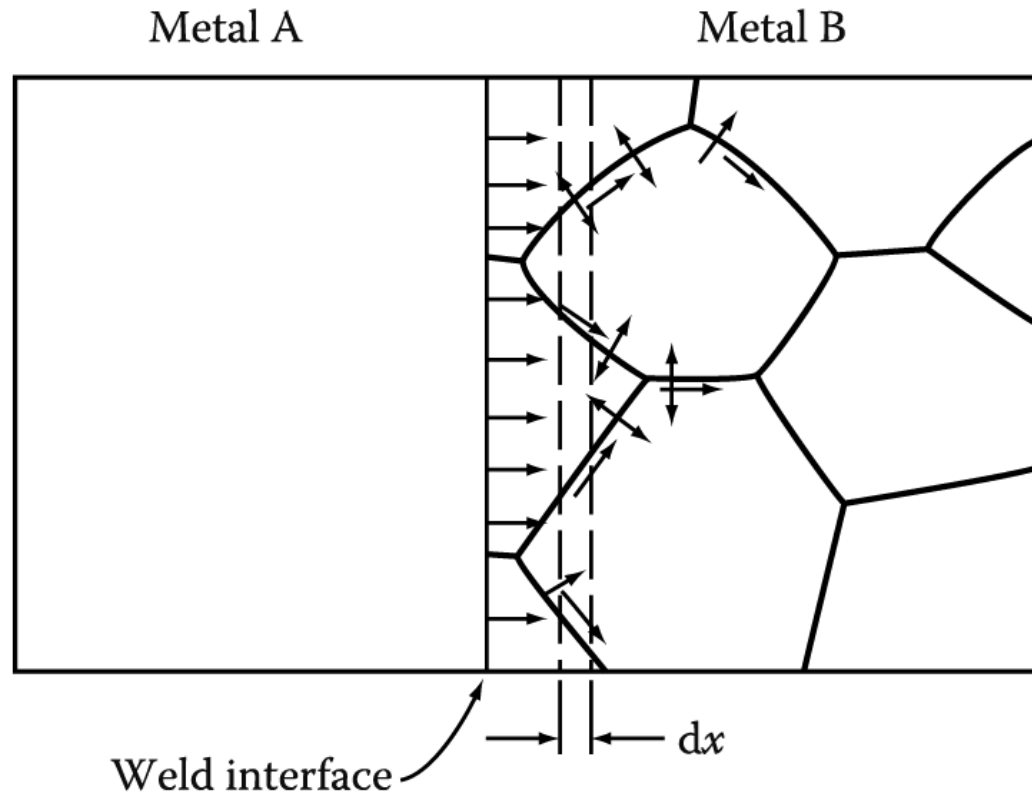
$$D_s = D_{s0} \exp\left(-\frac{Q_s}{RT}\right)$$

But area fraction → **lattice** > **grain boundary** > **surface**

Diffusion along grain boundaries

Atoms diffusing along the boundary will be able to **penetrate much deeper** than atoms which only diffuse through the lattice.

In addition, as the concentration of solute builds up in the boundaries, atoms will also **diffuse from the boundary into the lattice**.



Weld interface

Composite between plastic matrix and a continuous network of Al sheets

Fig. 2.25. The effect of grain boundary diffusion combined with volume diffusion.

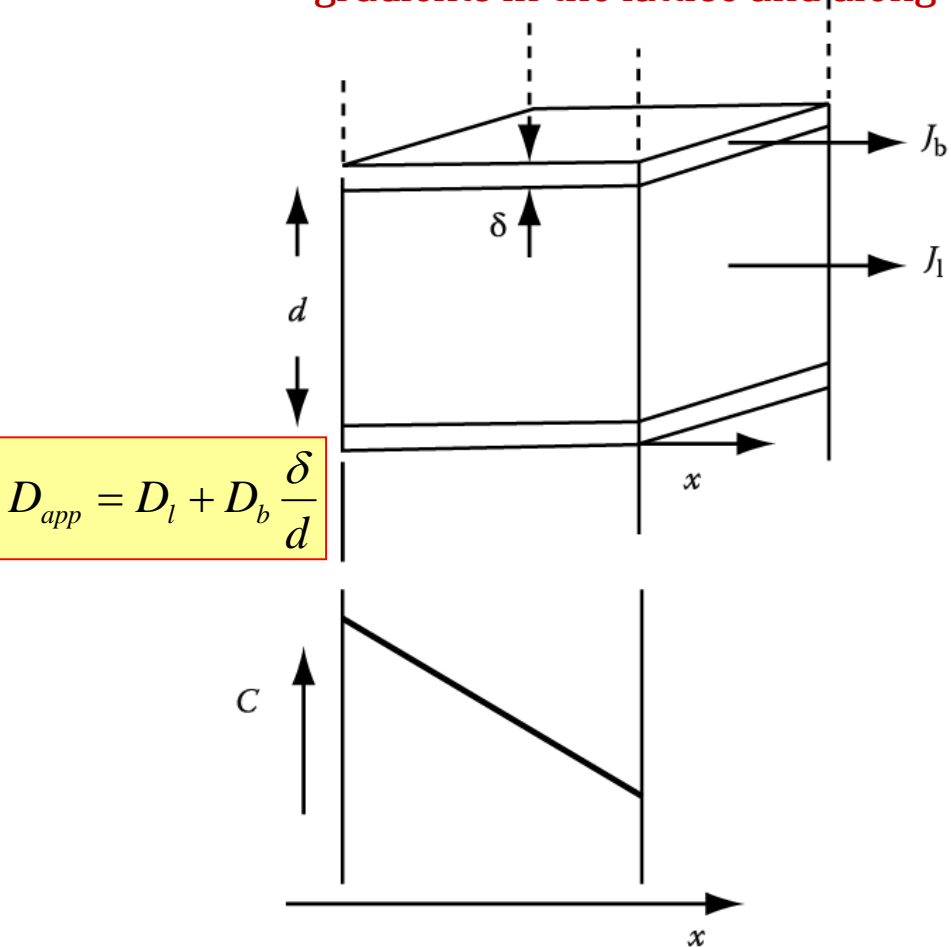
: Rapid diffusion along the grain boundaries

→ increase in the apparent diffusivity in the materials as a whole

Combined diffusion of grain boundary and lattice

: What conditions grain boundary diffusion is important?

Assumption: GBs are perpendicular to the sheet, steady-state diffusion, Concentration gradients in the lattice and along the GB are identical,



$$J_l = -D_l \frac{dC}{dx}$$

$$J_b = -D_b \frac{dC}{dx}$$

$$J = (J_b \delta + J_l d) / d = -D_{app} \frac{dC}{dx}$$

δ : grain boundary thickness $\approx 0.5\text{nm}$

d : grain size

D_{app} : apparant diffusivity

$$D_{app} = D_l + D_b \frac{\delta}{d}$$

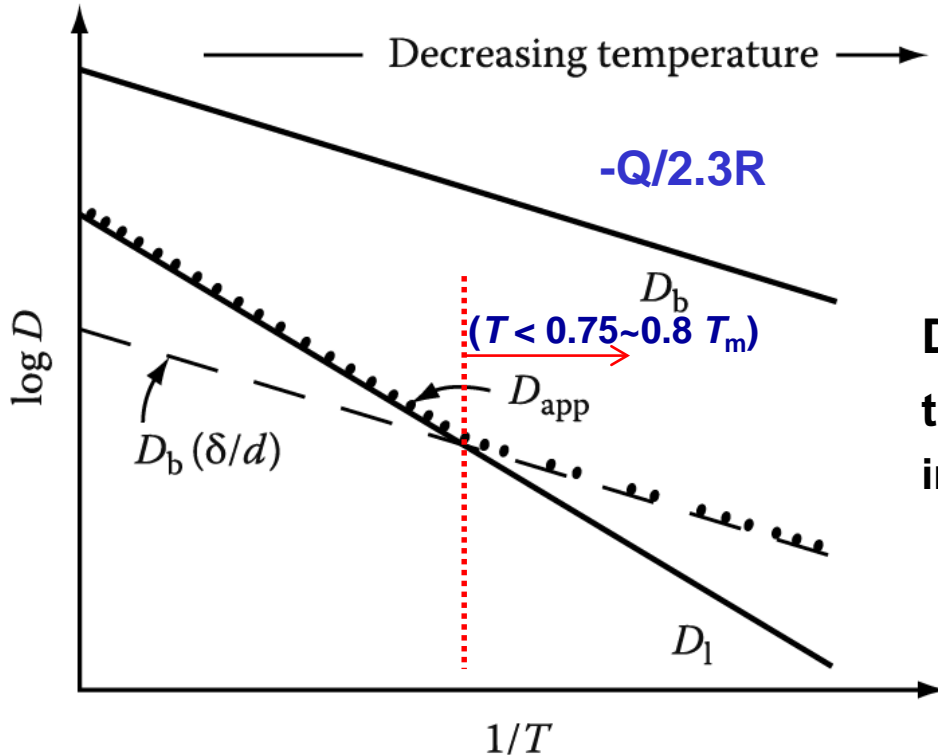
Fig. 2.26 Combined lattice and boundary fluxes during steady-state diffusion through a thin slab of material.

Thus, grain boundary diffusion makes a significant contribution

only when $D_b \delta > D_l d$.

The relative magnitudes of $D_b\delta$ and $D_l d$ are most sensitive to **temperature**.

$$D_b = D_{b0} \exp\left(-\frac{Q_b}{RT}\right) \quad D_l = D_{l0} \exp\left(-\frac{Q_l}{RT}\right)$$



$D_b > D_l$ at all temp.

Due to $Q_b < Q_l$, ($Q_b = 0.5Q_l$)
 the curves for D_l and $D_b\delta/d$ cross
 in the coordinate system of $\ln D$ versus $1/T$.

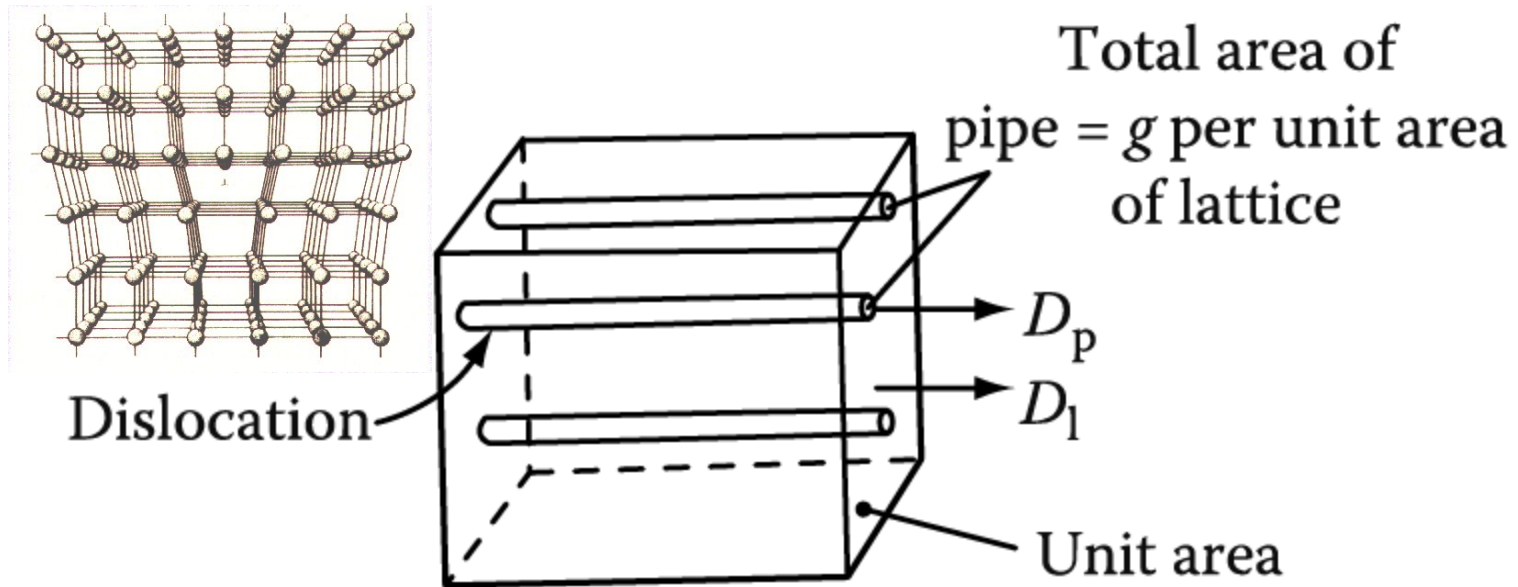
Fig. 2.27 Diffusion in a polycrystalline metal.

➔ Therefore, the grain boundary diffusion becomes predominant at temperatures lower than the crossing temperature.

$$(T < 0.75 \sim 0.8 T_m)$$

The diffusion rate depends on the atomic structure of the individual boundary = orientation of the adjoining crystals and the plane of the boundary. Also, the diffusion coefficient can vary with direction within a given boundary plane.

2.7.2 Diffusion along dislocations



Composite between plastic matrix and Al wires

Fig. 2.28. Dislocations act as a high conductivity path through the lattice.

$D_{app} = ?$ hint) 'g' is the cross-sectional area of 'pipe' per unit area of matrix.
 파이프와 기지의 횡단면적

$$D_{app} = D_l + g \cdot D_p \quad \rightarrow \quad \frac{D_{app}}{D_l} = 1 + g \cdot \frac{D_p}{D_l}$$

ex) annealed metal $\sim 10^5$ disl/mm²; one dislocation(\perp) accommodates 10 atoms in the cross-section; matrix contains 10^{13} atoms/mm².

$$g = \frac{10^5 * 10}{10^{13}} = \frac{10^6}{10^{13}} = 10^{-7}$$

g = cross-sectional area of 'pipe' per unit area of matrix

At high temperatures,

diffusion through the lattice is rapid and gD_p/D_l is very small so that the dislocation contribution to the total flux of atoms is very small.

Due to $Q_p < Q_l$,

the curves for D_l and gD_p/D_l cross in the coordinate system of $\ln D$ versus $1/T$.

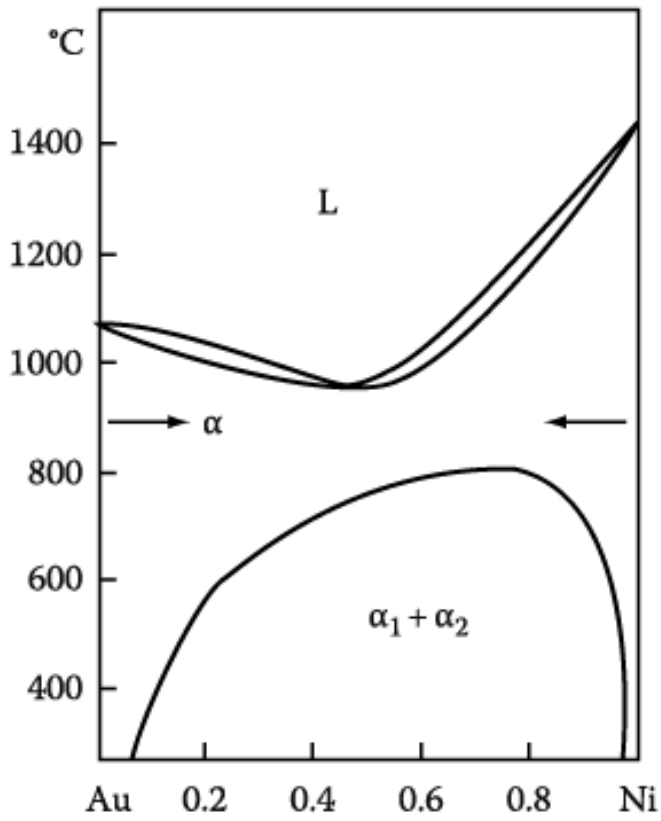
At low temperatures, ($T < \sim 0.5 T_m$)

gD_p/D_l can become so large that the apparent diffusivity is entirely due to diffusion along dislocation.

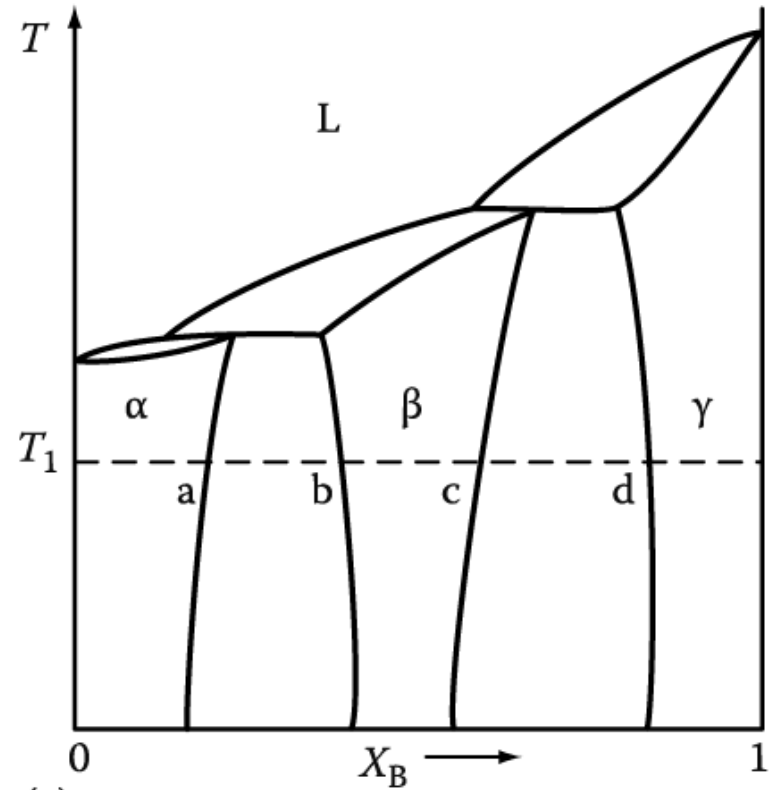
Q: How can we formulate the interface (α/β , β/γ) velocity in multiphase binary systems?

$$v = \frac{dx}{dt} = \frac{1}{(C_B^\beta - C_B^\alpha)} \left\{ \tilde{D}(\alpha) \frac{\partial C_B^\alpha}{\partial x} - \tilde{D}(\beta) \frac{\partial C_B^\beta}{\partial x} \right\} \quad \text{(velocity of the } \alpha/\beta \text{ interface)}$$

2.8 Diffusion in multiphase binary systems (다상 2원계의 확산)



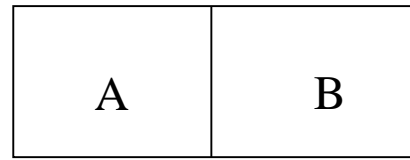
(a) X_{Ni}



(a)

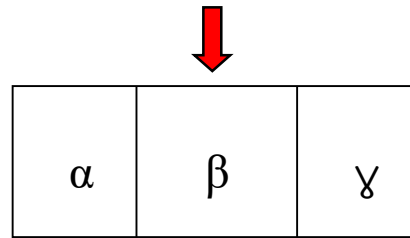
2.8 Diffusion in multiple binary system

A diffusion couple made by welding together pure A and pure B

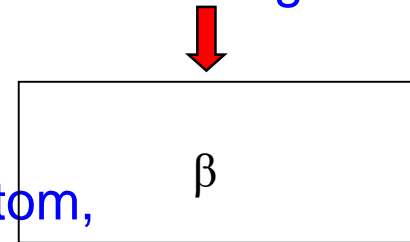


What would be the microstructure evolved after annealing at T_1 ?

→ a layered structure containing α , β & γ .



Draw a phase distribution and composition profile in the plot of distance vs. X_B after annealing at T_1 .

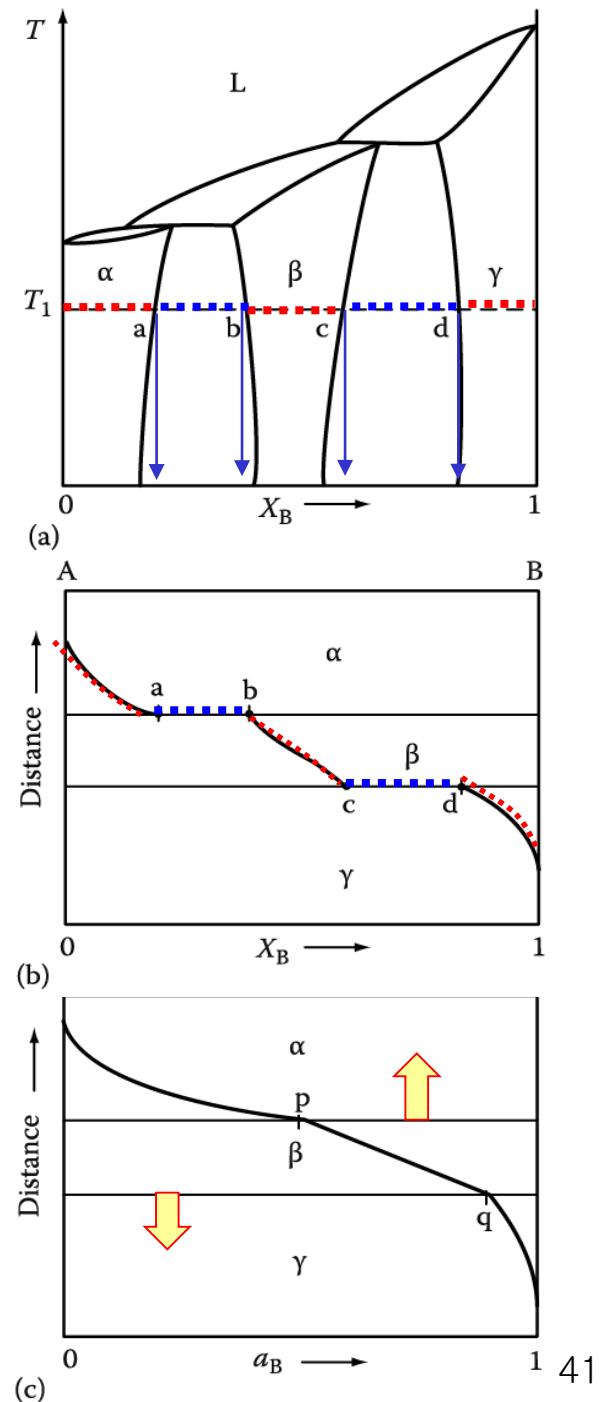


Draw a profile of activity of B atom, in the plot of distance vs. a_B after annealing at T_1 .

A or B atom → easy to jump interface (local equil.)

→ $\underline{\mu_A^\alpha = \mu_A^\beta, \mu_A^\beta = \mu_A^\gamma}$ at interface

$(a_A^\alpha = a_A^\beta, a_A^\beta = a_A^\gamma)$



Local equilibrium is assumed.

a flux of B towards the interface from the β phase

$$J_B^\beta = -\tilde{D}(\beta) \frac{\partial C_B^\beta}{\partial x}$$

a flux of B away from the interface into the α phase

$$J_B^\alpha = -\tilde{D}(\alpha) \frac{\partial C_B^\alpha}{\partial x}$$

In a time dt , there will be an accumulation of B atoms given by

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



$$\frac{\partial C}{\partial t} = -\frac{\partial J}{\partial x}$$

$$- [J_B - J_A] dt$$

$$dC dx$$

$$\left\{ - \left(\tilde{D}(\beta) \frac{\partial C_B^b}{\partial x} \right) - \left(-\tilde{D}(\alpha) \frac{\partial C_B^a}{\partial x} \right) \right\} dt = (C_B^b - C_B^a) dx$$

Accumulation of B atoms during dt

$$v = \frac{dx}{dt} = \frac{1}{(C_B^b - C_B^a)} \left\{ \tilde{D}(\alpha) \frac{\partial C_B^a}{\partial x} - \tilde{D}(\beta) \frac{\partial C_B^b}{\partial x} \right\}$$

(velocity of the α/β interface)

Contents for today's class

Thermodynamic factor

$$F = \left(1 + \frac{d \ln \gamma_B}{d \ln X_B}\right)$$

- Atomic Mobility

$$D_B = M_B RTF$$

- Tracer Diffusion in Binary Alloys

$$\tilde{D} = X_B D_A + X_A D_B = F(X_B D_A^* + X_A D_B^*)$$

D_{Au}^* gives the rate at which Au* (or Au) atoms diffuse in a **chemically homogeneous** alloy, whereas D_{Au} gives the diffusion rate of Au when **concentration gradient** is present.

- High-Diffusivity Paths

$$D_s > D_b > D_l$$



$$A_l > A_b > A_s$$

1. Diffusion along Grain Boundaries and Free Surface

Grain boundary diffusion makes a significant contribution

only when $D_b \delta > D_l d$. ($T < 0.75 \sim 0.8 T_m$)

$$D_{app} = D_l + D_b \frac{\delta}{d}$$

2. Diffusion Along Dislocation

At low temperatures, ($T < \sim 0.5 T_m$)

gD_p/D_l can become so large that the apparent diffusivity is entirely due to diffusion along dislocation.

- Diffusion in Multiphase Binary Systems

$$v = \frac{dx}{dt} = \frac{1}{(C_B^\beta - C_B^\alpha)} \left\{ \tilde{D}(\alpha) \frac{\partial C_B^\alpha}{\partial x} - \tilde{D}(\beta) \frac{\partial C_B^\beta}{\partial x} \right\}$$

(velocity of the α/β interface)

*** Homework 4 : Exercises 2 (pages 111-114)**

until 1st exam

1st exam : October 17, 2021 6 pm – 8 pm

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Good Luck!!