2018 Fall

# "Phase Transformation *in* Materials"

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# Contents for previous class

- **Substitution Diffusion**

1. **Self diffusion in pure material** (by radioactive element)

Probability of vacancy x probability of jump

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

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

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

2. **Vacancy diffusion**

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

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

$$D_v = D_A / X_v^e$$

$$X_V = X_V^e = \exp\frac{-\Delta G_V}{RT}$$

3. **Diffusion in substitutional alloys**

# Q: Diffusion in substitutional alloys?

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

$$\boxed{\therefore J'_B = -J'_A}$$

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

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

Fick's 1st law for substitutional alloy

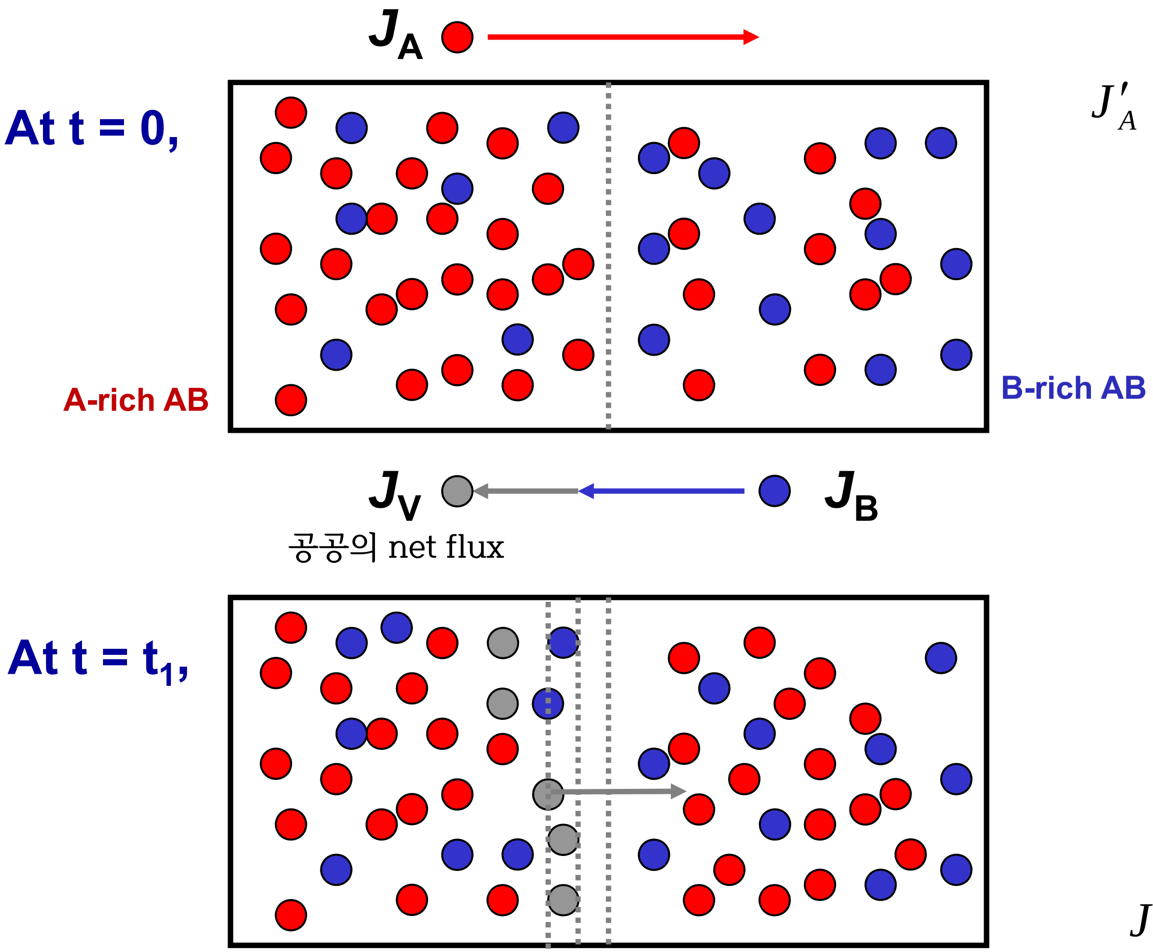
$$\boxed{\frac{\partial C_A}{\partial t} = \frac{\partial}{\partial x}\left(\tilde{D}\frac{\partial C_A}{\partial x}\right)}$$

Fick's 2nd law for substitutional alloy

침입형 확산에서 Fick의 법칙 고정된 격자면의 이동 고려

# 3. Diffusion in substitutional alloys

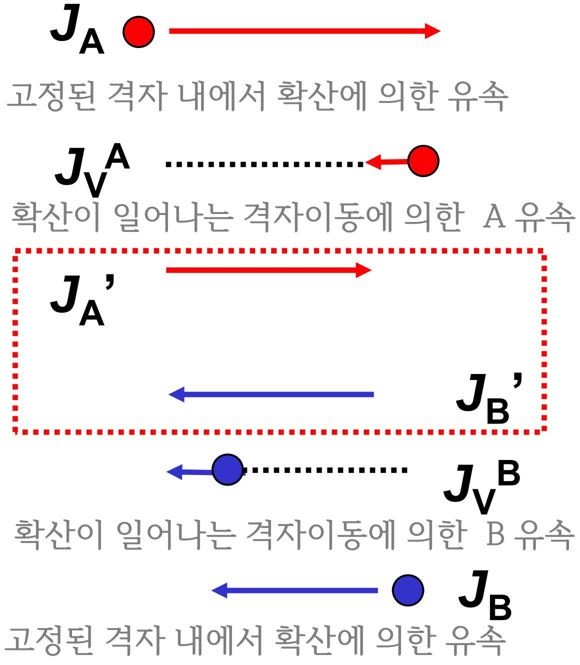
: A원자/B원자의 상호확산을 통한 격자면의 이동 고려



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

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

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



고정된 격자 내에서 확산에 의한 유속

확산이 일어나는 격자이동에 의한 A 유속

확산이 일어나는 격자이동에 의한 B 유속

고정된 격자 내에서 확산에 의한 유속

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

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

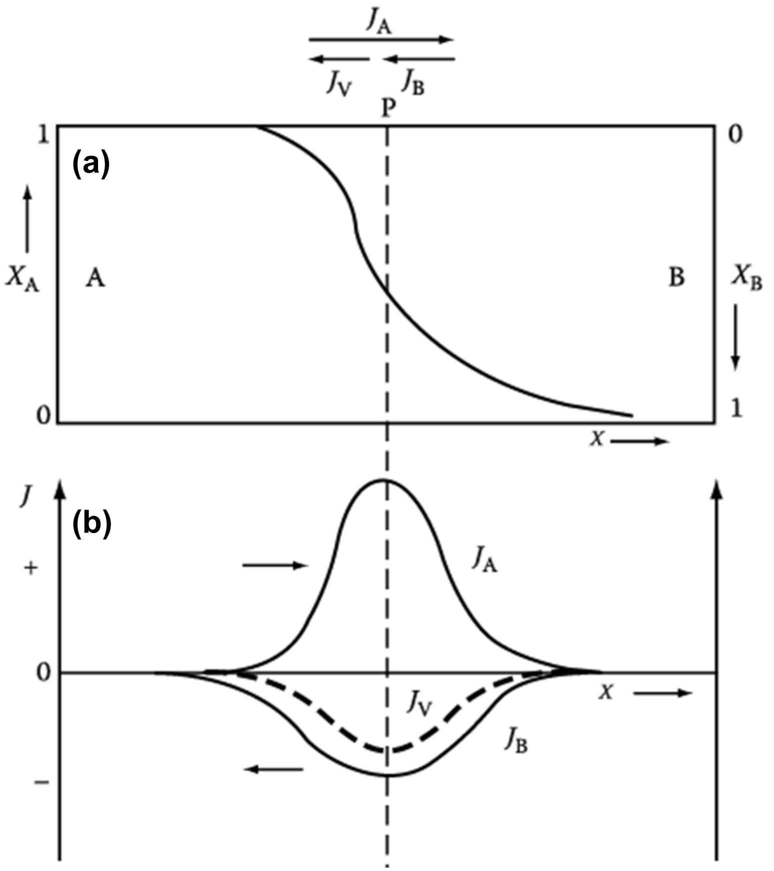
A원자와 B원자가 서로 다른 속도로 도약 →

농도 구배에 의한 속도 + 격자면 이동에 의한 속도

# 1) INTERDIFFUSION

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

**$C_o = C_A + C_B$ and** $\dfrac{\partial C_A}{\partial x} = -\dfrac{\partial C_B}{\partial x}$ ⇨ *** 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**

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

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

Flux of vacancies

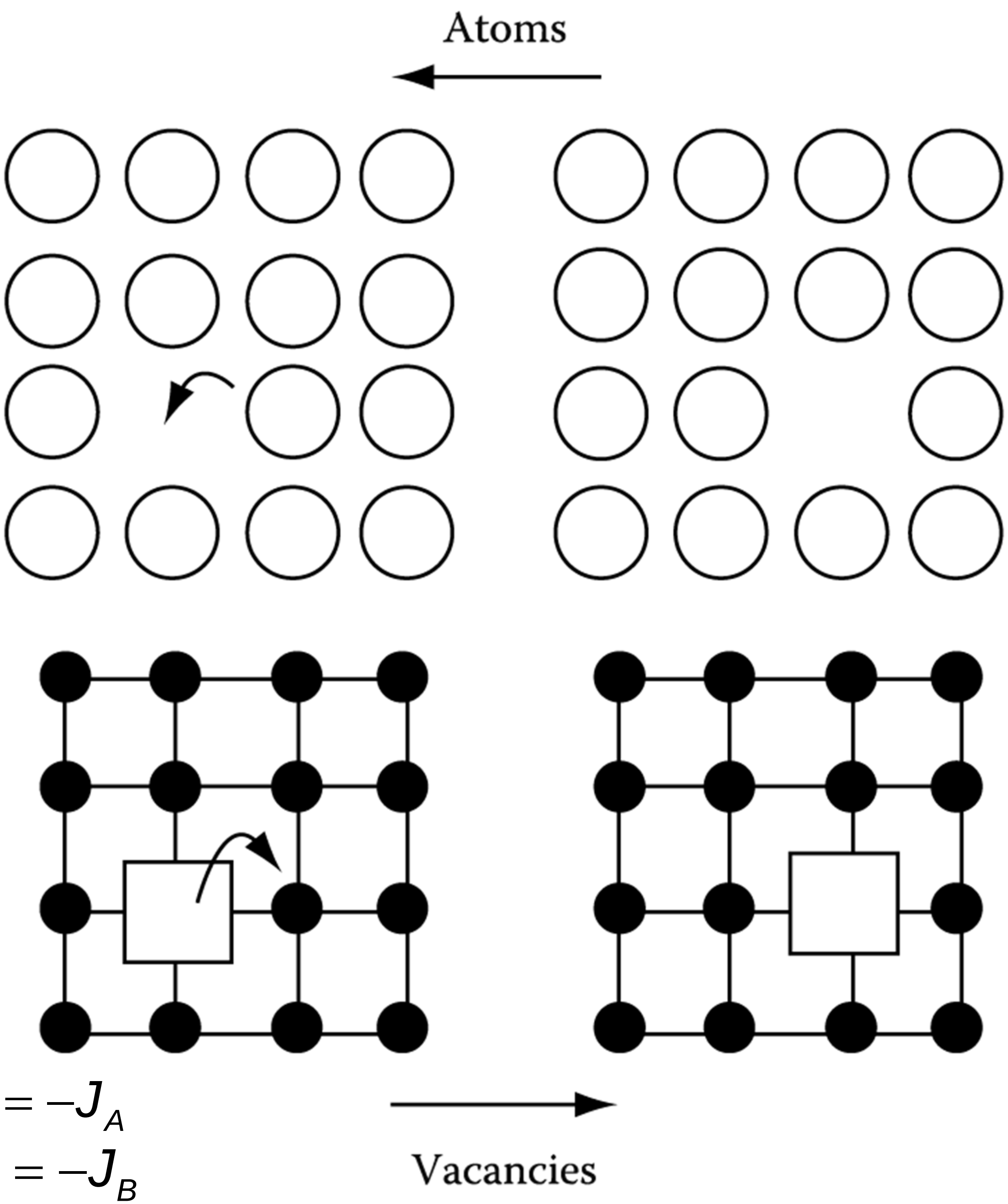
$$J_A \rightarrow J_{v,A} = -J_A \qquad J_B \rightarrow J_{v,B} = -J_B$$

$$J_V + J_B = -J_A$$

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

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

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



Flux of vacancies

$$J_A \rightarrow J_{v,A} = -J_A$$

$$J_B \rightarrow J_{v,B} = -J_B$$

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

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

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

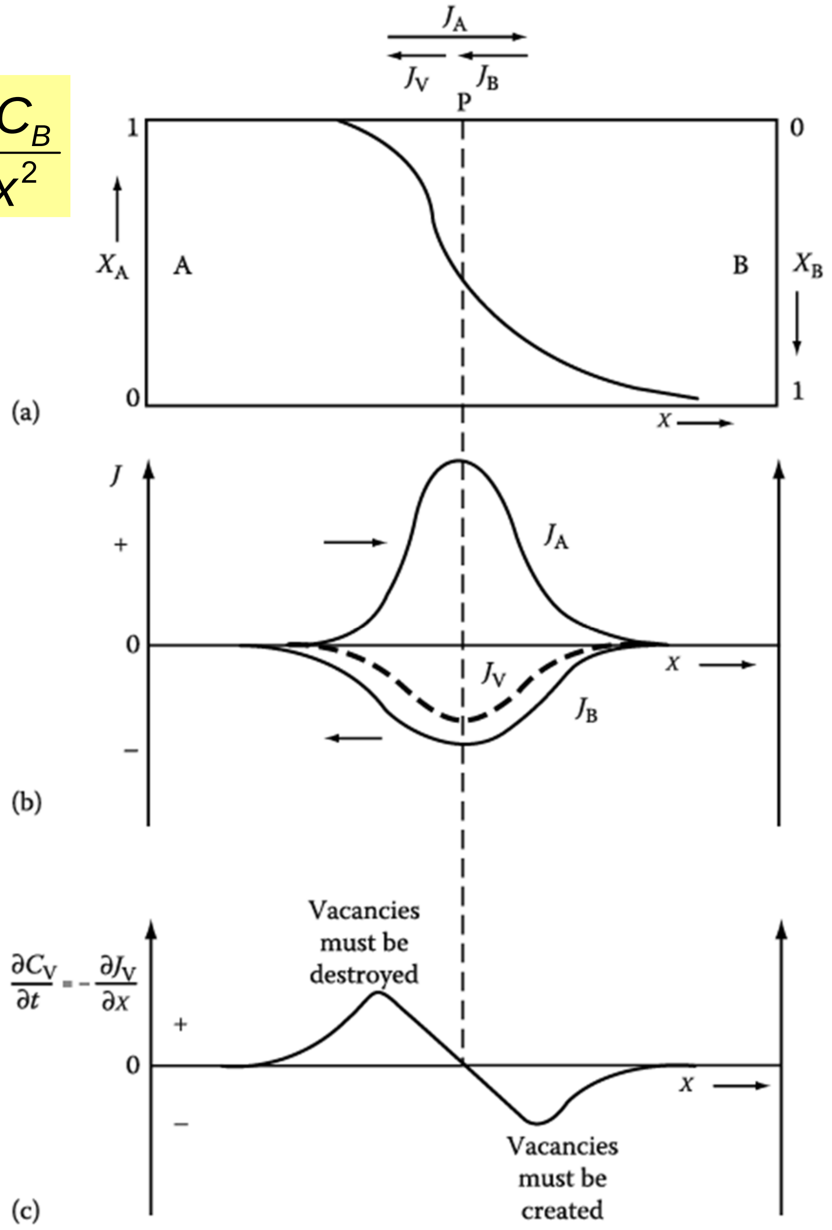
$$\frac{\partial C_B}{\partial t} = D_B \frac{\partial^2 C_B}{\partial x^2}$$

$$\frac{\partial C_v}{\partial t} = -\frac{\partial J_v}{\partial x} \quad vs.\ x\,?$$

**What would become of excess vacancy?**

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

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

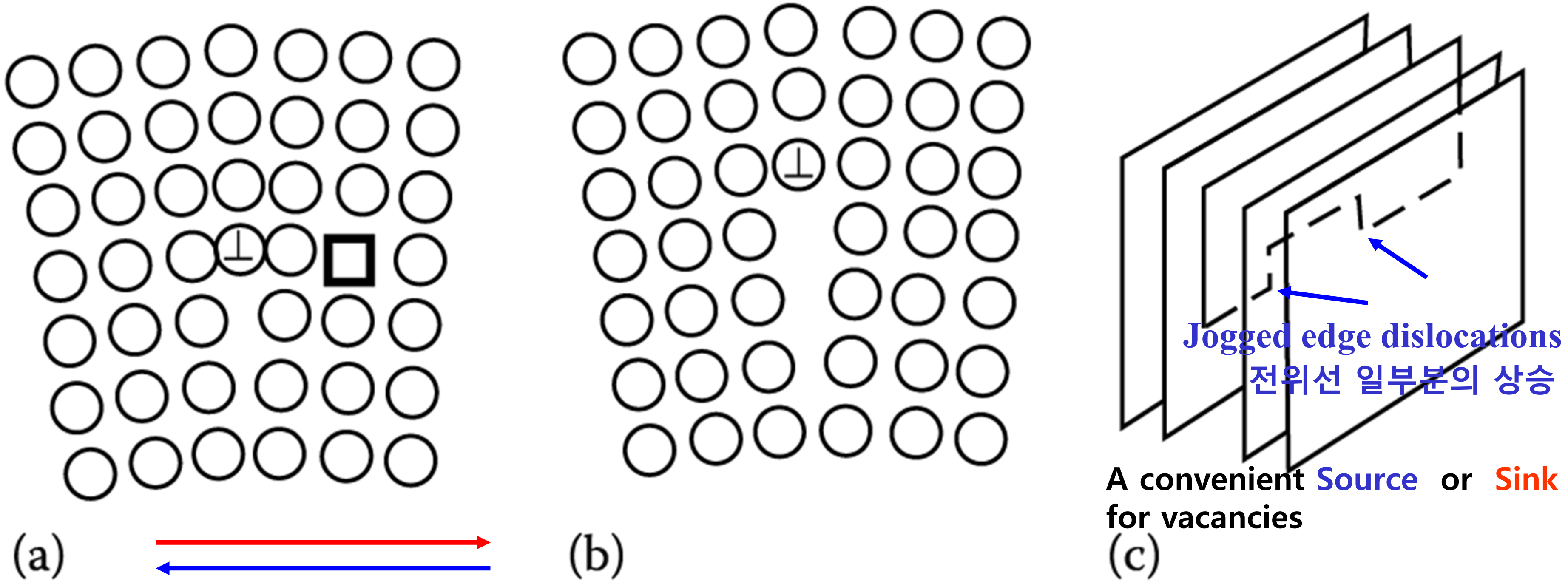


In order to maintain the vacancy concentration everywhere near equilibrium, vacancies must be created on the B-rich side and destroyed on the A-rich side.

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

**Kirkendall effect**

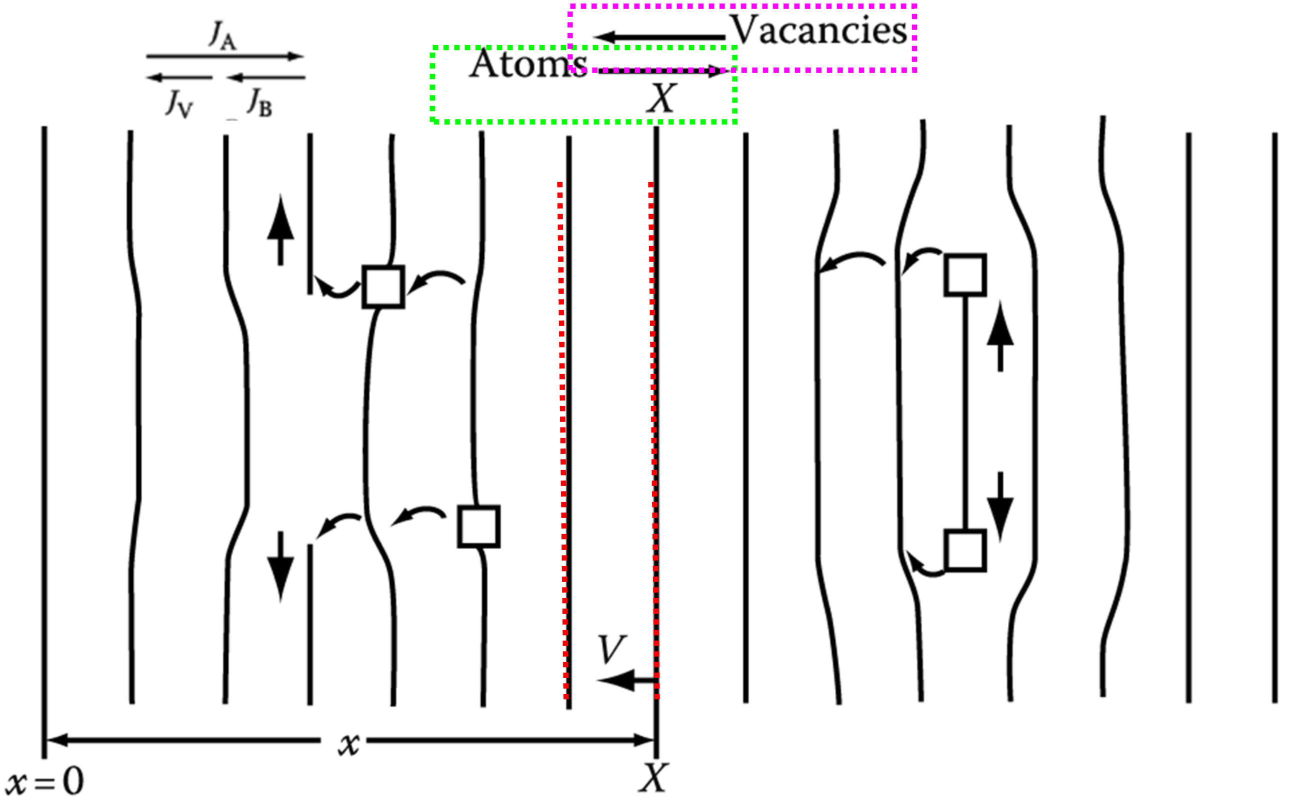
**Creation/destruction of vacancies is accomplished by *dislocation climb*.**



A convenient Source or Sink for vacancies

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**

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

**# of removed atoms**

**# of vacancies crossing the plane**

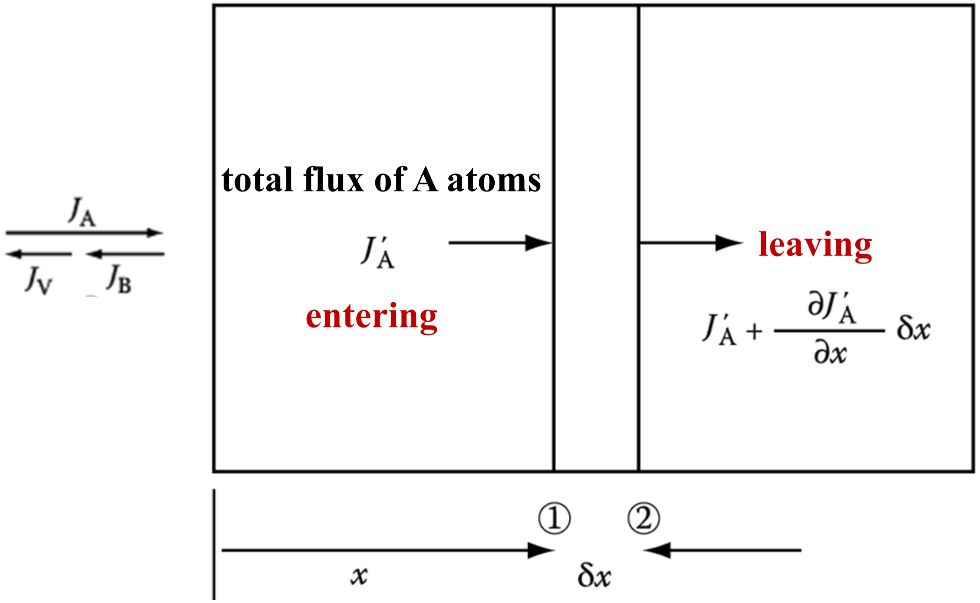
$$v = \frac{1}{C_0}\boxed{(D_A - D_B)\frac{\partial C_A}{\partial x}} = (D_A - D_B)\frac{\partial X_A}{\partial x}$$

**$X_A$: 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



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

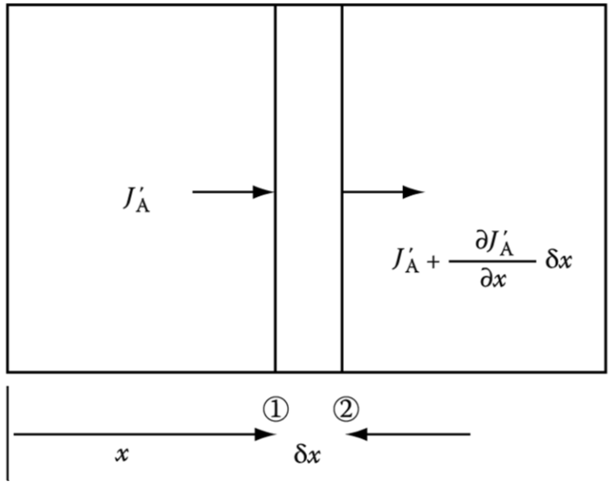
Fig. 2.19 Derivation of Fick's second law for interdiffusion. (See text for details.)

**$J'_A$ : 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**

$$J'_A = \boxed{J_A} + \boxed{vC_A}$$

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

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

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

Fick's 1st law for substitutional alloy

$$= -\tilde{D}\frac{\partial C_A}{\partial x} \qquad \tilde{D} = X_B D_A + X_A D_B \qquad J'_B = -\tilde{D}\frac{\partial C_B}{\partial x} = \tilde{D}\frac{\partial C_A}{\partial x}$$

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

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

Fick's 2nd law for substitutional alloy ⟺ $\boxed{\frac{\partial C_B}{\partial t} = D_B \frac{\partial^2 C_B}{\partial x^2}}$

**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 $(\tilde{D})$

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

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

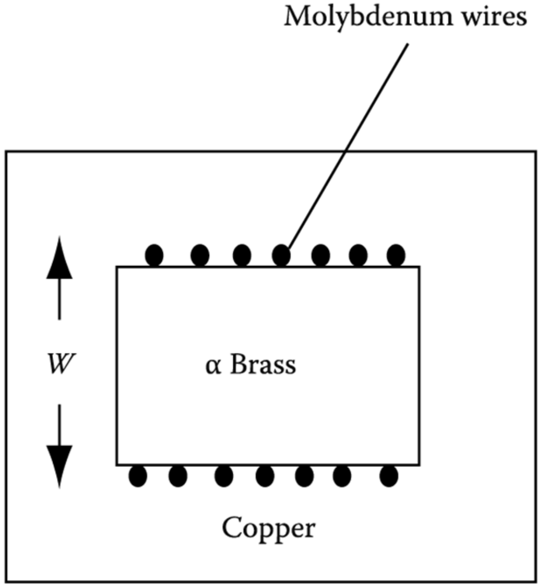
**How can we determine $D_A$ and $D_B$?**

$$\boxed{v = (D_A - D_B)\frac{\partial X_A}{\partial x} = (D_B - D_A)\frac{\partial X_B}{\partial x}}$$

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

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.**

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

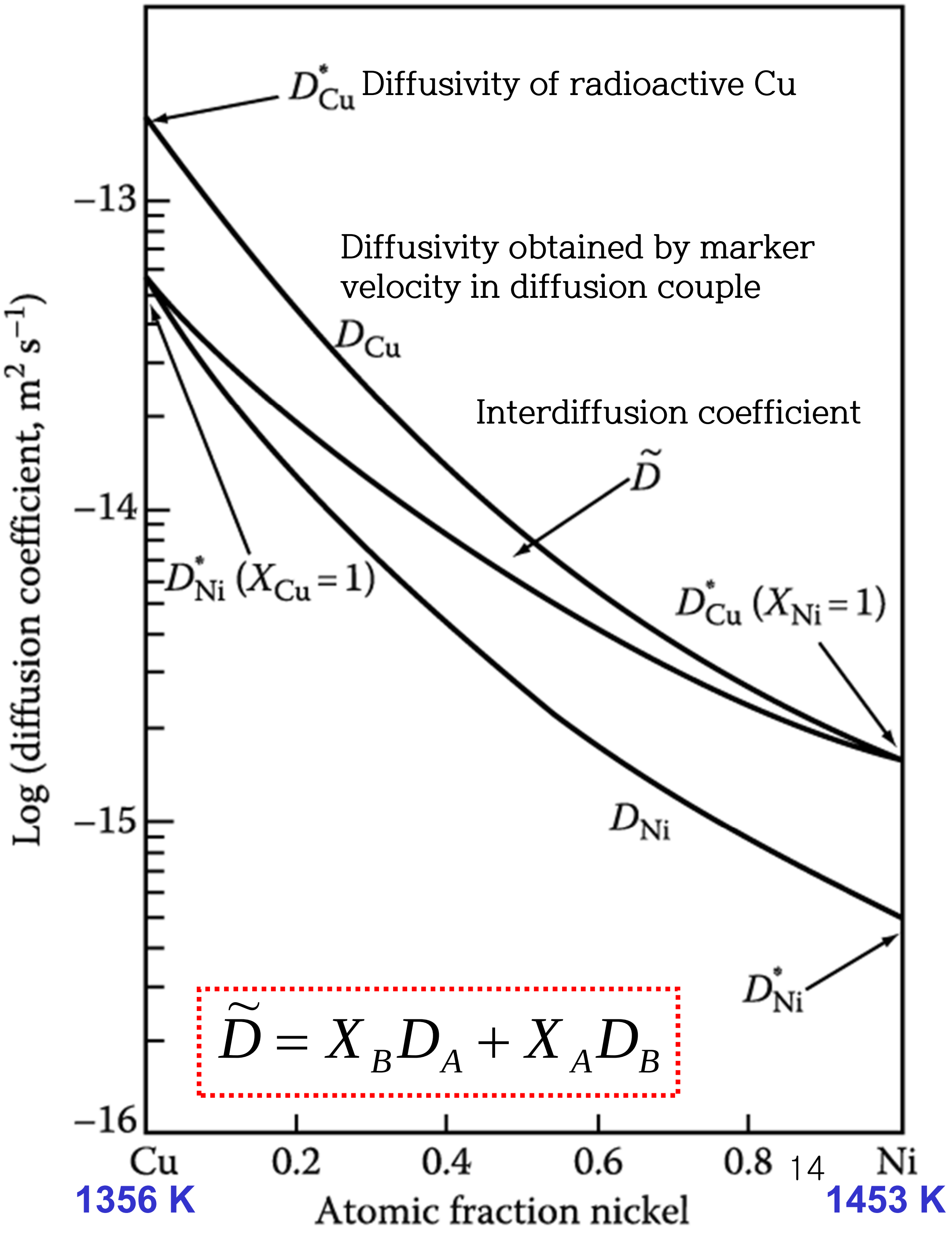
**$D_{Zn} > D_{Cu}$**

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

**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.**



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

- In concentrated alloys, the experimentally determined values of $\tilde{D}$, $D_A$ and $D_B$ are also found to show the same form of temperature dependence.

$$\boxed{\tilde{D} = \tilde{D}_0 \exp(-Q/RT)}$$

## Variation of $\tilde{D}$ with composition:

- ***For a given crystal structure, $\tilde{D}$ at $T_m$ is roughly constant.*** *Therefore if adding B to A decreases $T_m$, $\tilde{D}$ will increase at a given temperature, and vice verse.*
- *For both interstitial and substitutional alloys, diffusion is more rapid in bcc* (0.68) *than in a close-packed lattice* (FCC~0.74).

**α, Ferrite** **γ, Austenite**

Ex) diffusion of carbon in Fe at 1183 K, $D_C^\alpha / D_C^\gamma$ ~100

Self-diffusion coefficients for Fe at 1133 K, $D_{Fe}^\alpha / D_{Fe}^\gamma$ ~100

➡ **BCC_more open and less lattice distortion**

## 4) Diffusion in dilute substitutional alloy

$$\tilde{D} = X_B D_A + X_A D_B$$ **(interdiffusion coefficient)**

For Dilute Substitutional Alloys $$\text{if } X_A \approx 1, \quad \tilde{D} = D_B$$

**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.

## 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

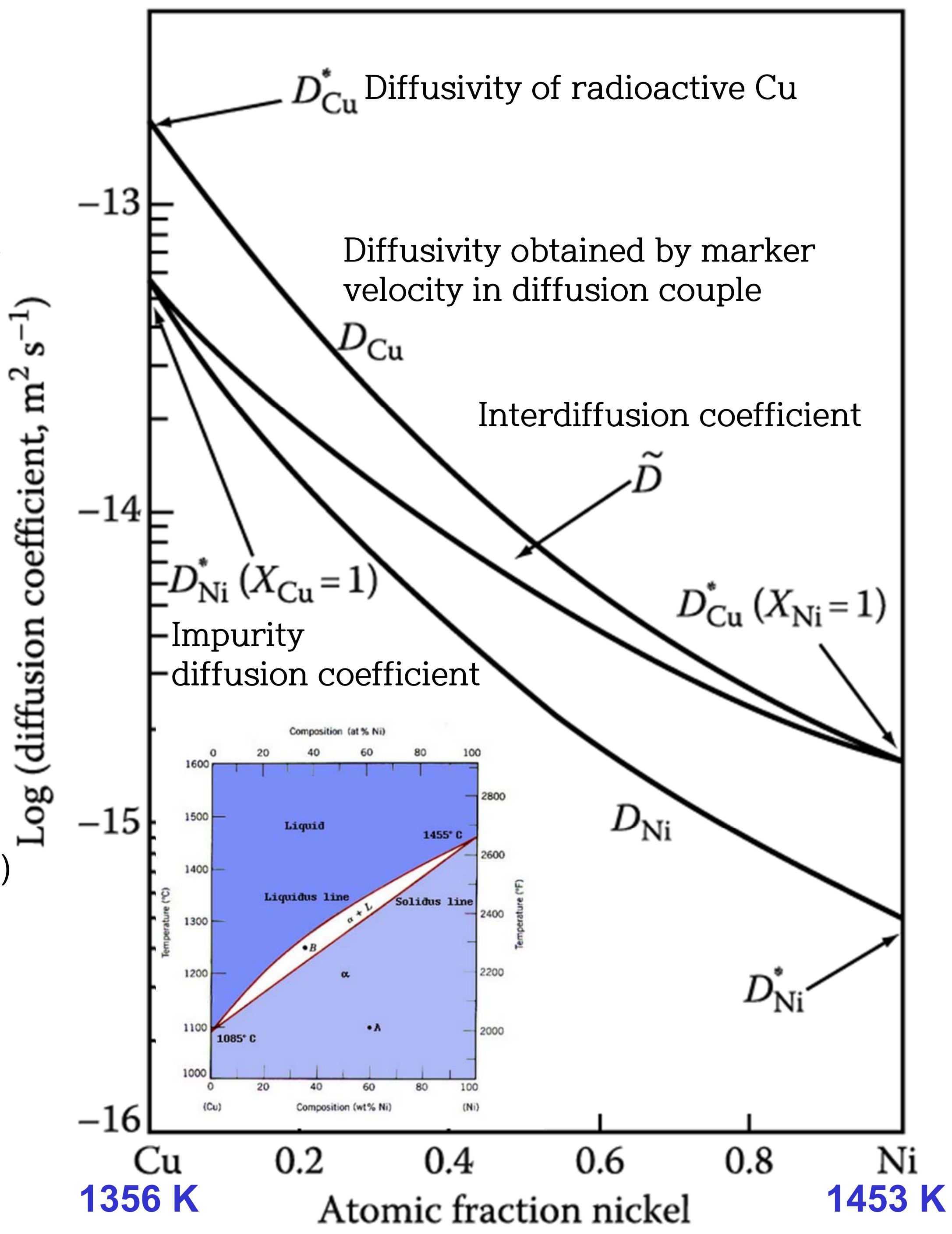
$$\boxed{\frac{\partial C_A}{\partial t} = \frac{\partial}{\partial x}\left(\tilde{D}\frac{\partial C_A}{\partial x}\right)} \qquad \text{Eq. (2.53)}$$

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

⇨ Characteristic relaxation time for an Homogenization anneal

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

(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”)

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

무질서한 도약에 의한 순 표류속도

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

**: remove differences in chemical potential ∞ *chemical potential gradient***

$$\boxed{J_B = v_B c_B}$$

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

$-\dfrac{\partial \mu_B}{\partial x}$ : ① chemical force causing atom to migrate

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

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

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

# Relationship between $M_B$ and $D_B$ (원자이동도와 원자확산계수간 관계)

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

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

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

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

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

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

$$\therefore J_B = -M_B \boxed{\frac{X_B}{V_m}}\boxed{\frac{RT}{X_B}\boxed{\left(1+\frac{\partial \ln\gamma_B}{\partial \ln X_B}\right)}\frac{\partial X_B}{\partial x}}$$

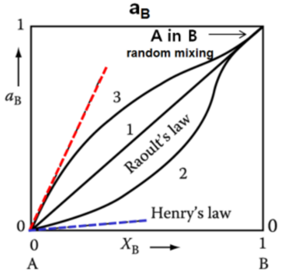
$$= -M_B RT\boxed{F}\frac{\partial C_B}{\partial x} = -D_B\frac{\partial C_B}{\partial x}$$

$$D_B = M_B RTF$$

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

**For ideal or dilute solutions,**

**near $X_B \approx 0$, $\gamma_B$ = const. with respect to $X_B$**



$$\therefore F = 1$$

$$D_B = M_B RT$$

**For non-ideal concentrated solutions,**

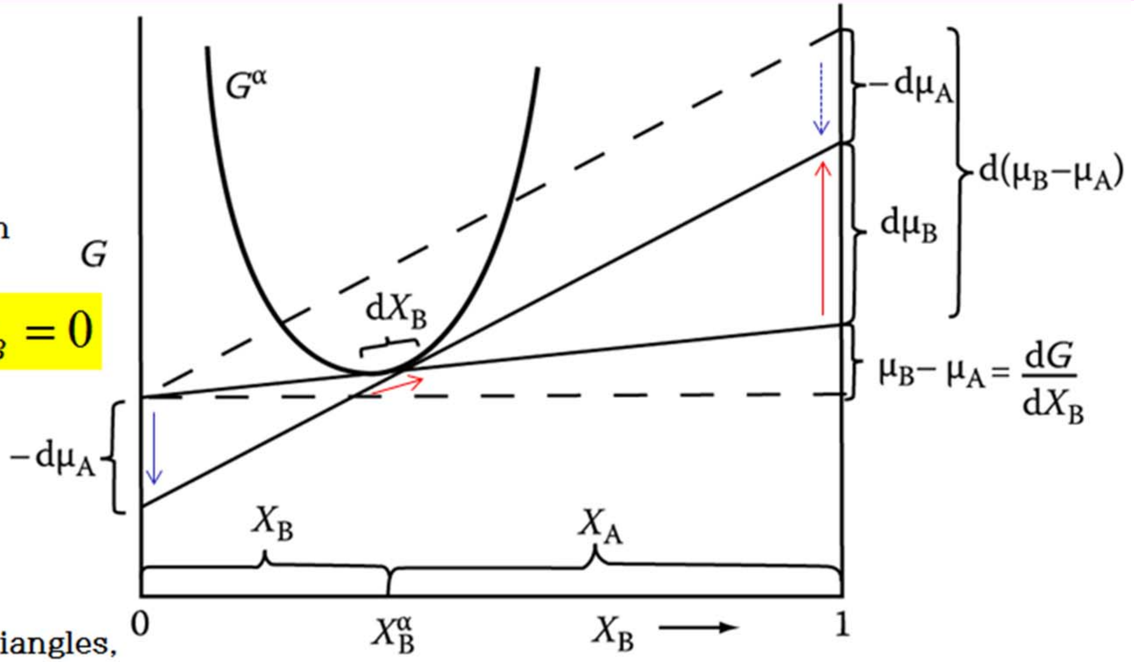
**thermodynamic factor (F) must be included.**

→ **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,

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

Substituting right side Eq.
& Multiply $X_A X_B$

$$-X_A d\mu_A = X_B d\mu_B = X_A X_B \frac{d^2G}{dX^2} dX_B$$

**Eq. 1.65**

**" Gibbs-Duhem Equation "**

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

**$\gamma_A$, $\gamma_B$**

**$a_A$, $a_B$**

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

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

변형 E 구배도 확산에 영향

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

$$\boxed{\mu_B = G_B + RT\ln\gamma_B X_B + E}$$

→

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

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 <u>negative curvature</u>, which is known as spinodal decomposition.**

# Q: How does $D^*_{\mathrm{Au}}$ differ from $D_{\mathrm{Au}}$?

**Tracer diffusion coefficient** **Intrinsic diffusion coefficients**

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

**Thermodynamic factor**

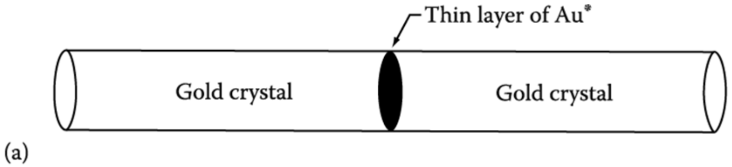
$$\boxed{\tilde{D} = X_B D_A + X_A D_B = F\left(X_B D_A^* + X_A D_B^*\right)}$$

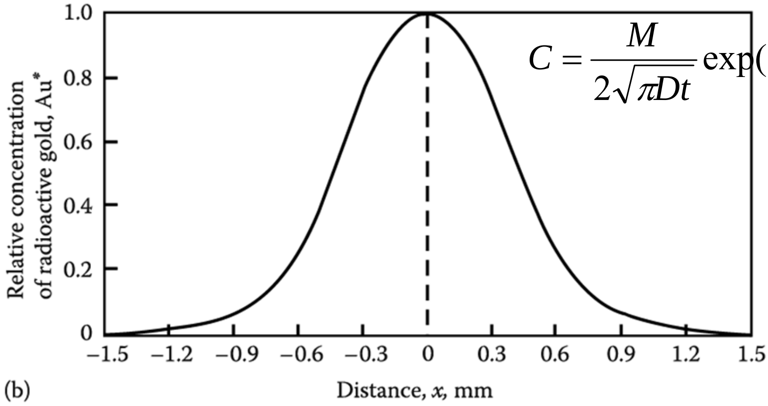
$$F = (1 + \frac{d \ln \gamma_B}{d \ln X_B})$$

순금속에서 자기확산 & 합금원소의 고유확산계수 → 방사성 추적자의 확산을 이용하여 결정

# 2.5 Tracer diffusion in binary alloys

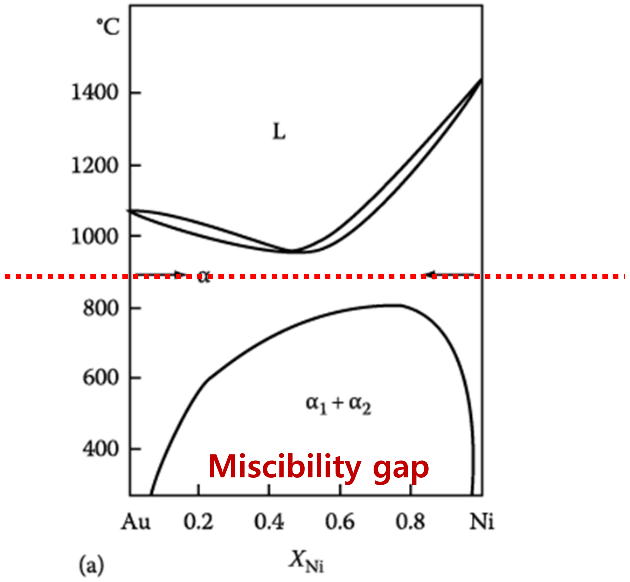
## 1) Au* in Au or Au/X alloy





$$C = \frac{M}{2\sqrt{\pi D t}} \exp\left(-\frac{x^2}{4Dt}\right) \longrightarrow$$ **$D = D^*_{Au}$ (tracer diffusion coefficient)**

## 2) Au* in Au-Ni



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

*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,**

$$\Delta H_{mix} > 0 \rightarrow \boxed{D_{Au} < D^*_{Au}}, \boxed{D_{Ni} < D^*_{Ni}}$$

**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.**

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

**F : Thermodynamic Factor**

$$\boxed{\begin{aligned} D_A &= F D_A^* \\ D_B &= F D_B^* \end{aligned}} \Rightarrow \boxed{\tilde{D} = X_B D_A + X_A D_B = F\left( X_B D_A^* + X_A D_B^* \right)}$$

**Additional Thermodynamic Relationships for Binary Solution:**
**Variation of chemical potential (dμ) by change of alloy compositions (dX)**
*Eq.*(1.71)

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

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

# 2.5 Tracer diffusion in binary alloys

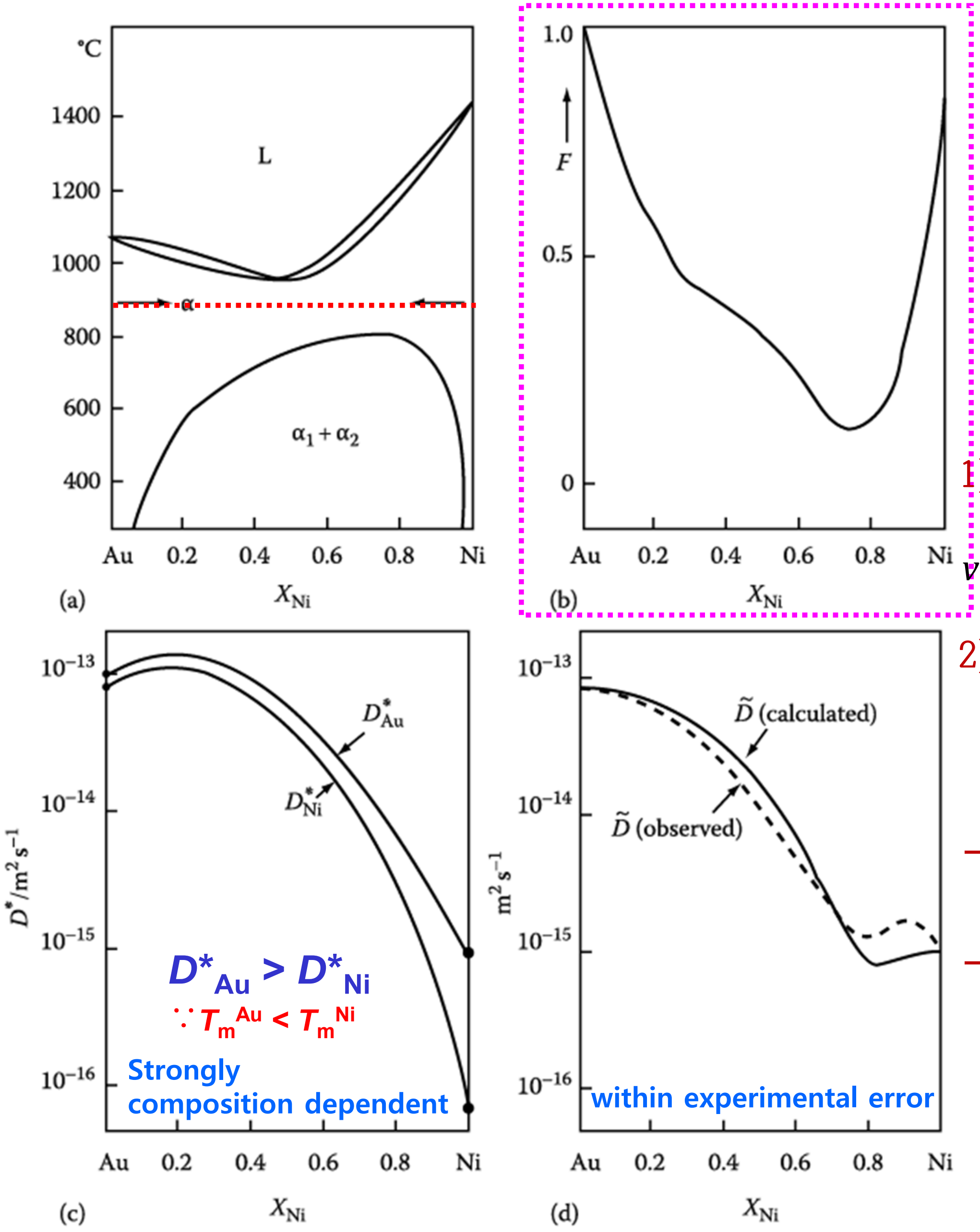


Fig. 2.22 Inter-diffusion in Au-Ni alloys at 900 ℃ (a) Au-Ni phase diagram, (b) the thermodynamic factor, F, at 900 ℃, (c) experimentally measured tracer diffusivities At 900 ℃ (d) experimentally measured inter-diffusion coefficients compared with values calculated from (b) and (c).

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 $D^*_{Au}$ & $D^*_{Ni}$:

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

→ The agreement is within the experimental error.

→ Strong composition dependent, **Ni ↑** → $\tilde{D}$↓

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

## 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

B A austenitized

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

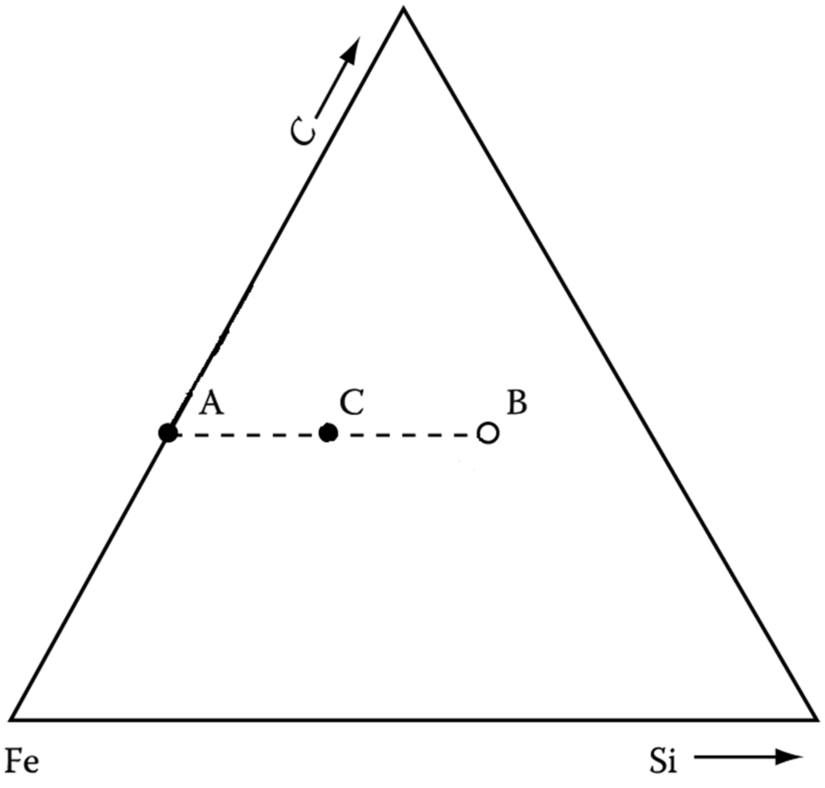
**① Si raises the $\mu_C$ in solution.**

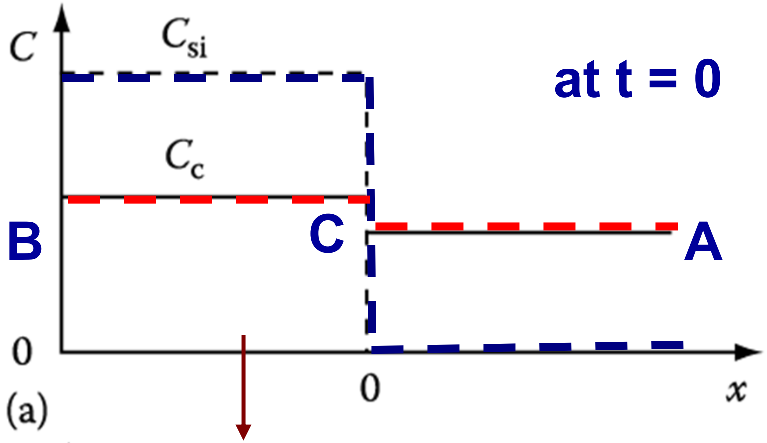
**(chemical potential of carbon)**

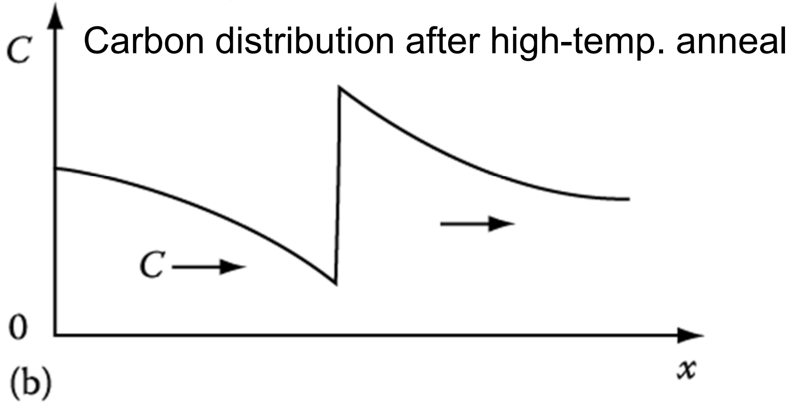
C 이동: 고농도→ 저농도 영역 & Si-rich→Si 적은 영역

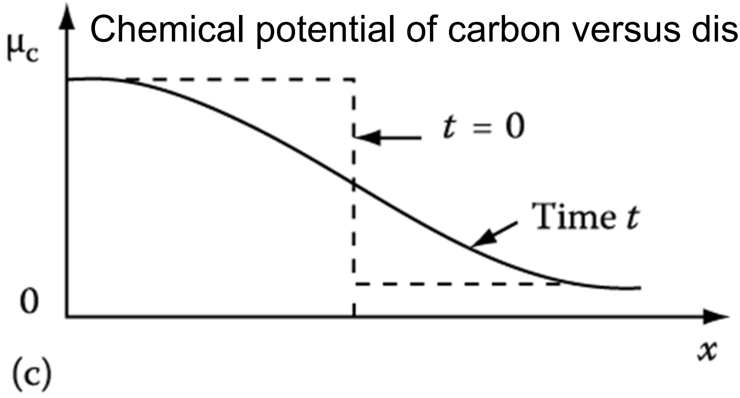
**② $M_{Si}$ (sub.) ≪ $M_C$ (interstitial solute),**

**(M : mobility)**






Carbon distribution after high-temp. anneal

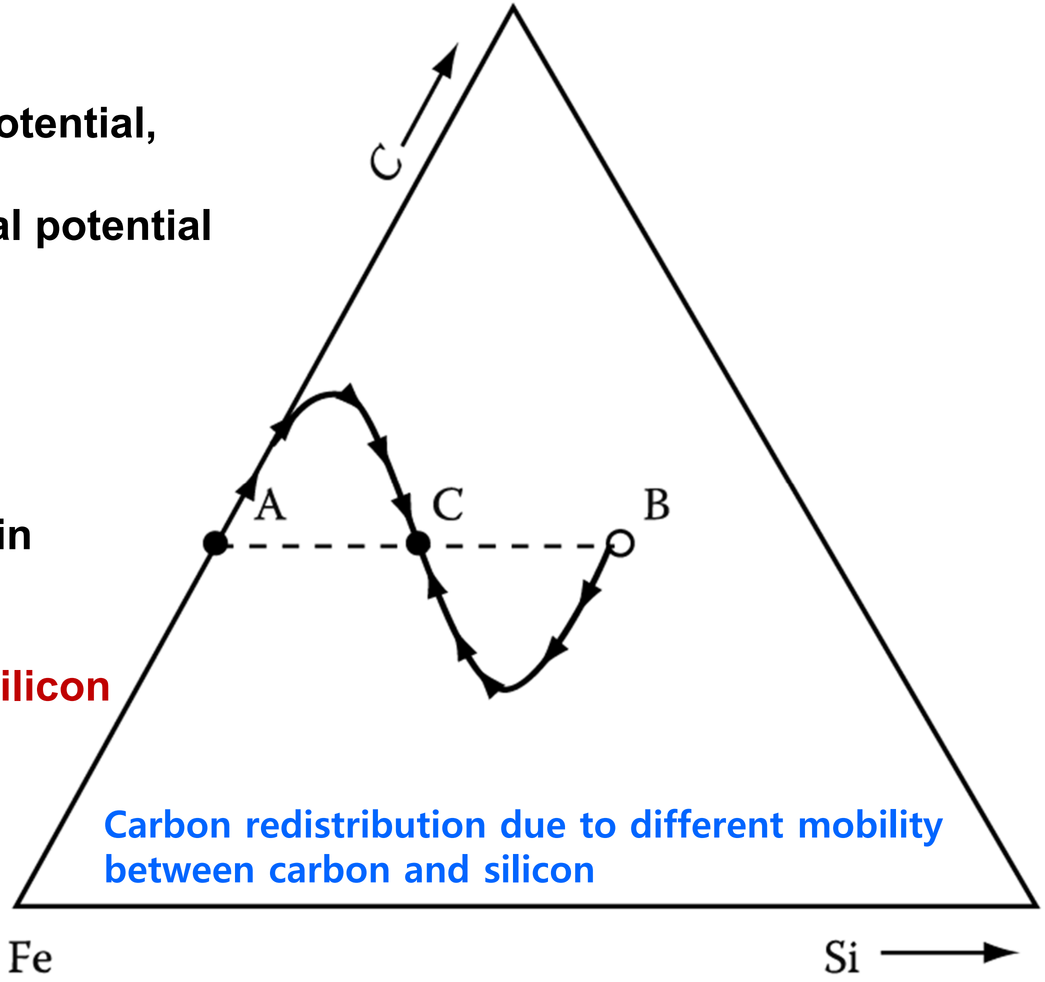

Chemical potential of carbon versus distance

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

1) **Carbon atom migration B → A**
   - ~ equilize 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 → 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**



Carbon redistribution due to different mobility between carbon and silicon

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?

$\mathrm{D_s > D_b > D_l}$ ⟺ $A_l > A_b > A_S$

## 1. Diffusion along Grain Boundaries and Free Surface

**Grain boundary diffusion makes a significant contribution**

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

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

## 2. Diffusion Along Dislocation

**At low temperatures**, **($T$ < ~0.5 $T_m$)**
**$gD_p/D_l$ can become so large** that the apparent diffusivity is entirely due to diffusion along dislocation.

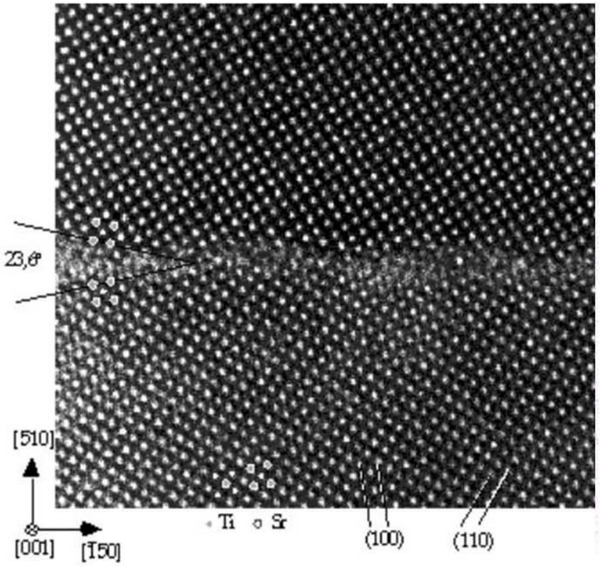
# 2.7.1 High-diffusivity paths

**Real materials contain defects.**

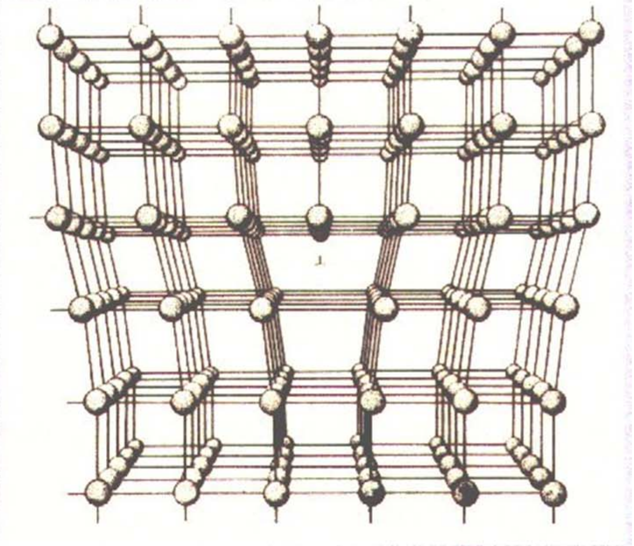
**= more open structure ➡ fast diffusion path.**

원자들의 도약 진동수가 큼

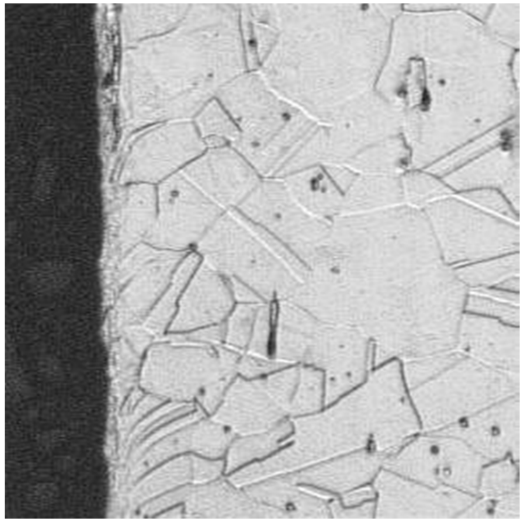
확산의 주요한 행로



**Grain boundary**



**dislocation**



**surface**

$$\boxed{D_s > D_b > D_l}$$

Diff. along lattice $$D_l = D_{lo} \exp(-\frac{Q_l}{RT})$$

Diff. along grain boundary $$D_b = D_{bo} \exp(-\frac{Q_b}{RT})$$

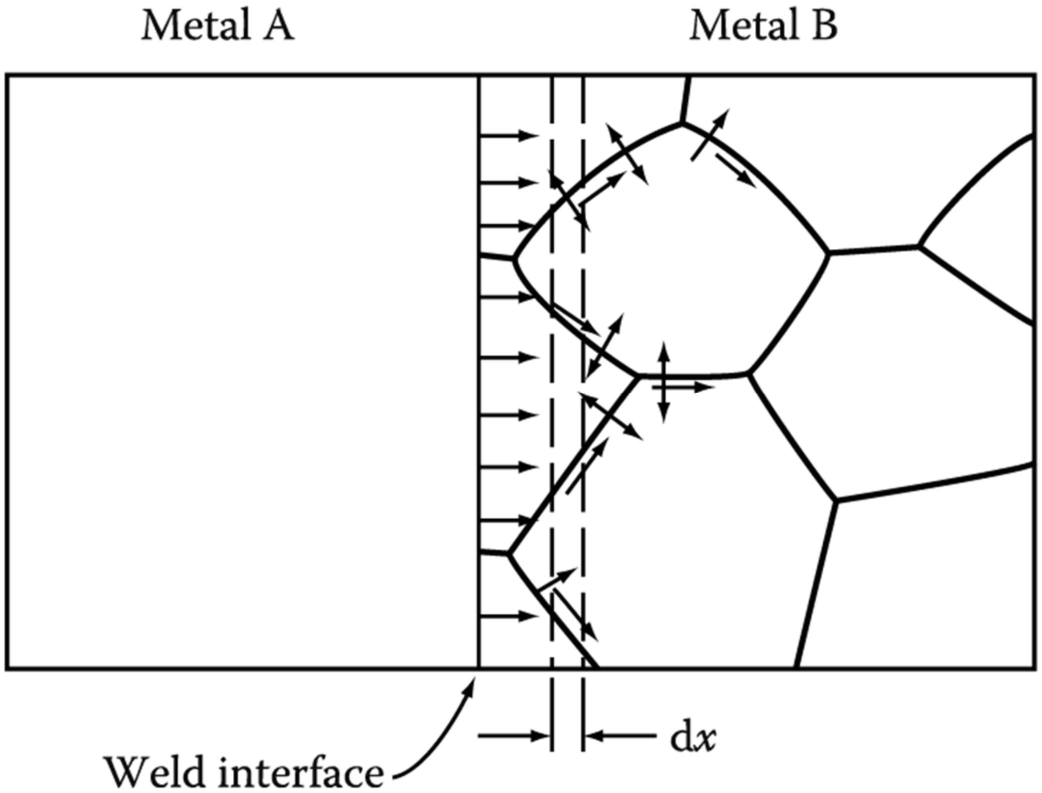
Diff. along free surface $$D_s = D_{so} \exp(-\frac{Q_s}{RT})$$

**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.**



**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 tot the sheet, steady-state diffusion, Concentration gradients in the lattice and along the GB are identical,

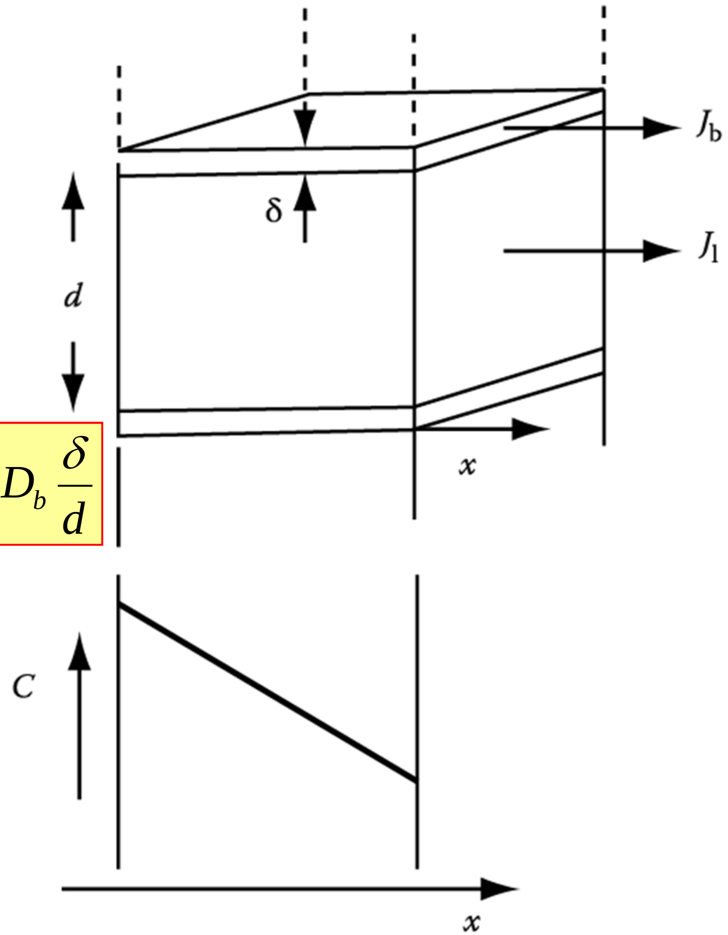


Fig. 2.26 Combined lattice and boundary fluxes during steady-state diffusion through a thin slab of material.

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

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

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

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

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

$d$ : grain size

$D_{app}$ : apparant diffusivity

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

**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.

$$D_b = D_{bo}\exp\left(-\frac{Q_b}{RT}\right) \qquad D_l = D_{lo}\exp\left(-\frac{Q_l}{RT}\right)$$

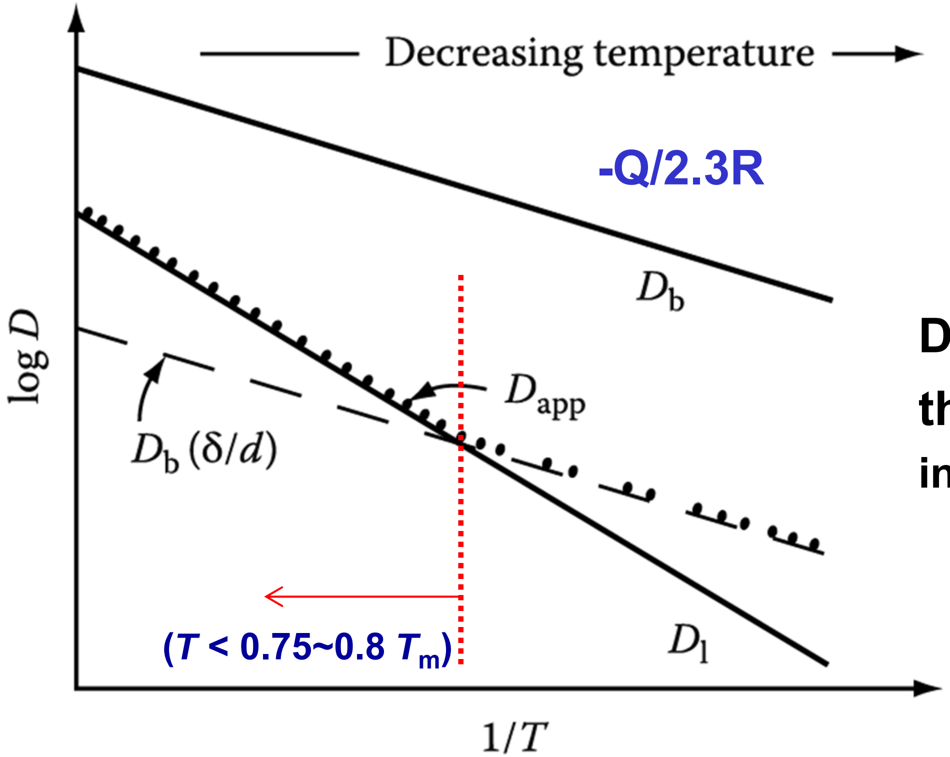


Fig. 2.27 Diffusion in a polycrystalline metal.

$D_b > D_l$ at all temp.

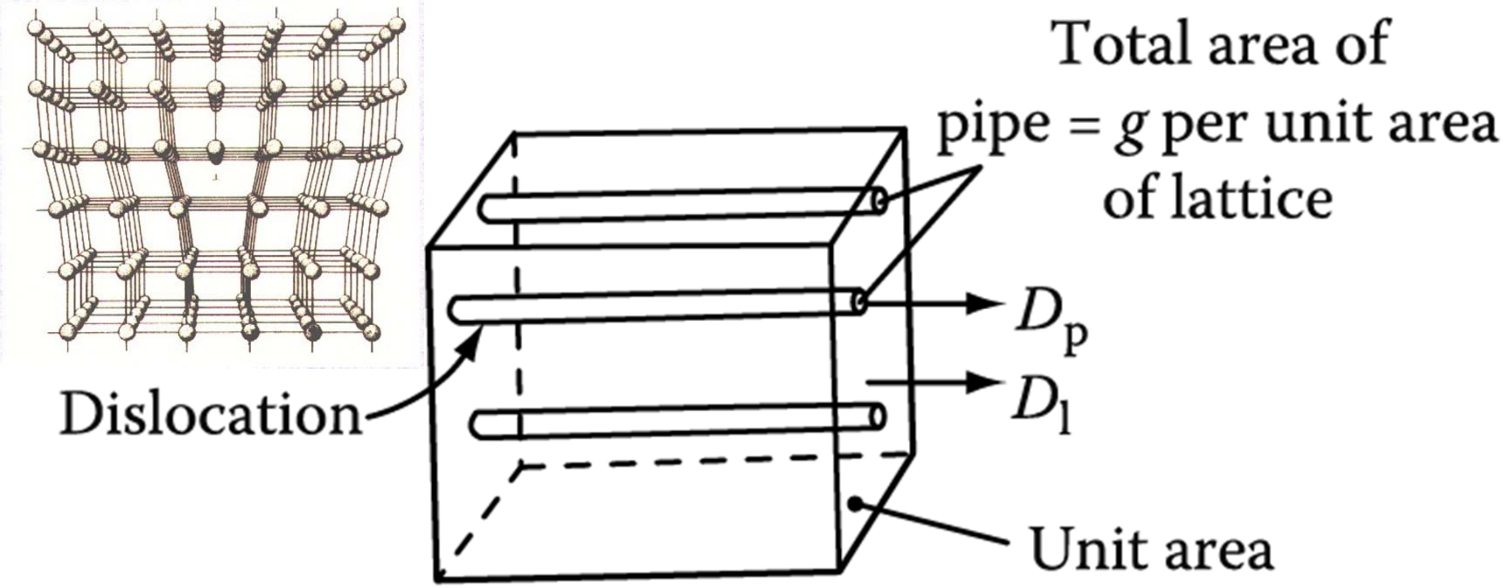
**Due to $Q_b < Q_l$, ($Q_b = 0.5Q_l$)**
**the curves for $D_l$ and $D_b\delta/d$ cross**
**in the coordinate system of lnD versus 1/T.**

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

**$(T < 0.75\sim0.8\ T_m)$**

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

$$\boxed{D_{app} = D_l + g \cdot D_p} \Rightarrow \boxed{\frac{D_{app}}{D_l} = 1 + g \cdot \frac{D_p}{D_l}}$$

ex) annealed metal ~ $10^5$ disl/mm$^2$; one dislocation($\perp$) accommodates 10 atoms in the cross-section; matrix contains $10^{13}$ atoms/mm$^2$.

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

**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** $\boxed{Q_p < Q_l}$,
**the curves for $D_l$ and $gD_p/D_l$ cross in the coordinate system of lnD versus 1/T.**

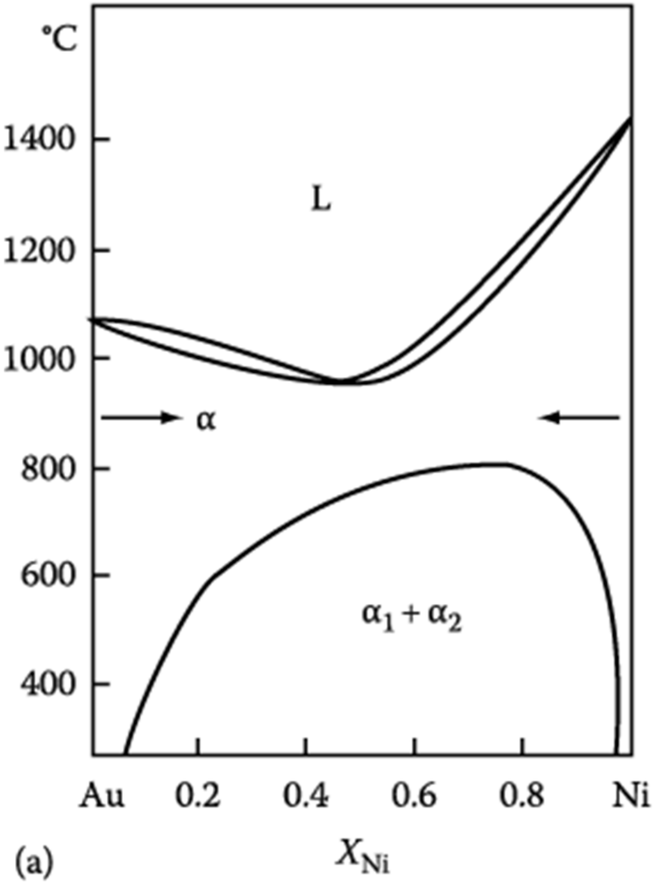
At low temperatures, **($T <$ ~$0.5\ T_m$)**
$gD_p/D_l$ can become so large that the apparent diffusivity is entirely due to diffusion along dislocation.

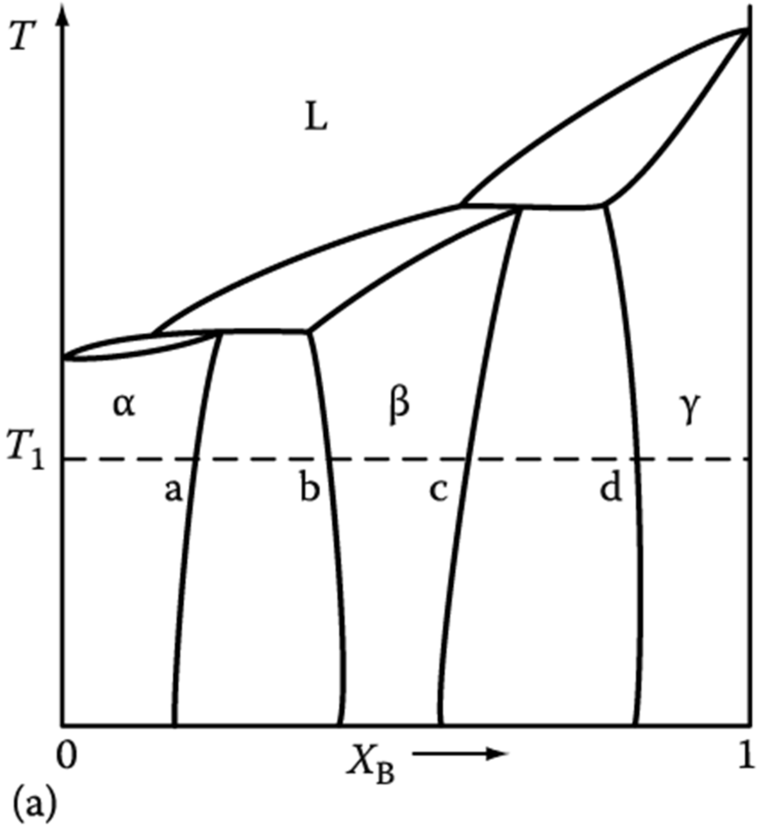
# Q: How can we formulate the interface (α/β, β/γ) velocity in multiphase binary systems?

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

**(velocity of the α/β interface)**

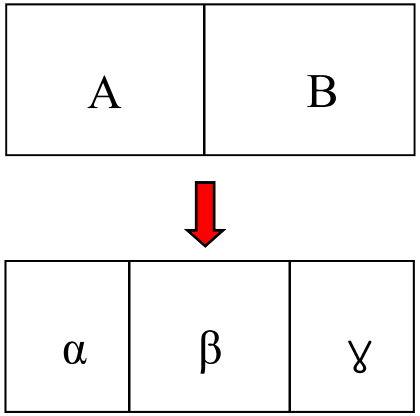
# 2.8 Diffusion in multiphase binary systems (다상 2원계의 확산)





# 2.8 Diffusion in multiple binary system

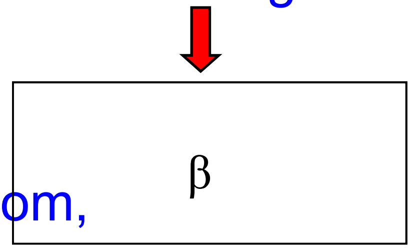
**A diffusion couple made by welding together pure A and pure B**



**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 $T_1$.

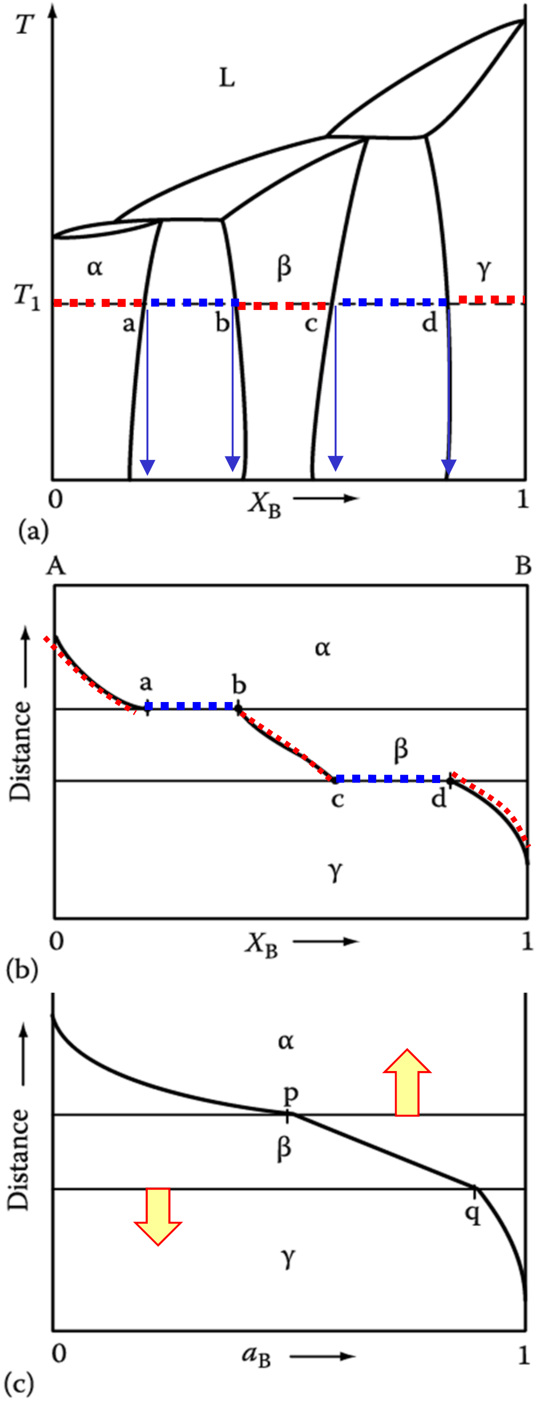


Draw a profile of activity of B atom, in the plot of distance vs. $a_B$ after annealing at $T_1$.

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

→ $\underline{\mu_A^\alpha = \mu_A^\beta,\ \mu_A^\beta = \mu_A^\gamma}$ <u>at interface</u>

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



Complete solution of the diffusion equations for this type of diffusion couple is complex.
However an expression for the rate at which the boundaries mover can be obtained as follows.

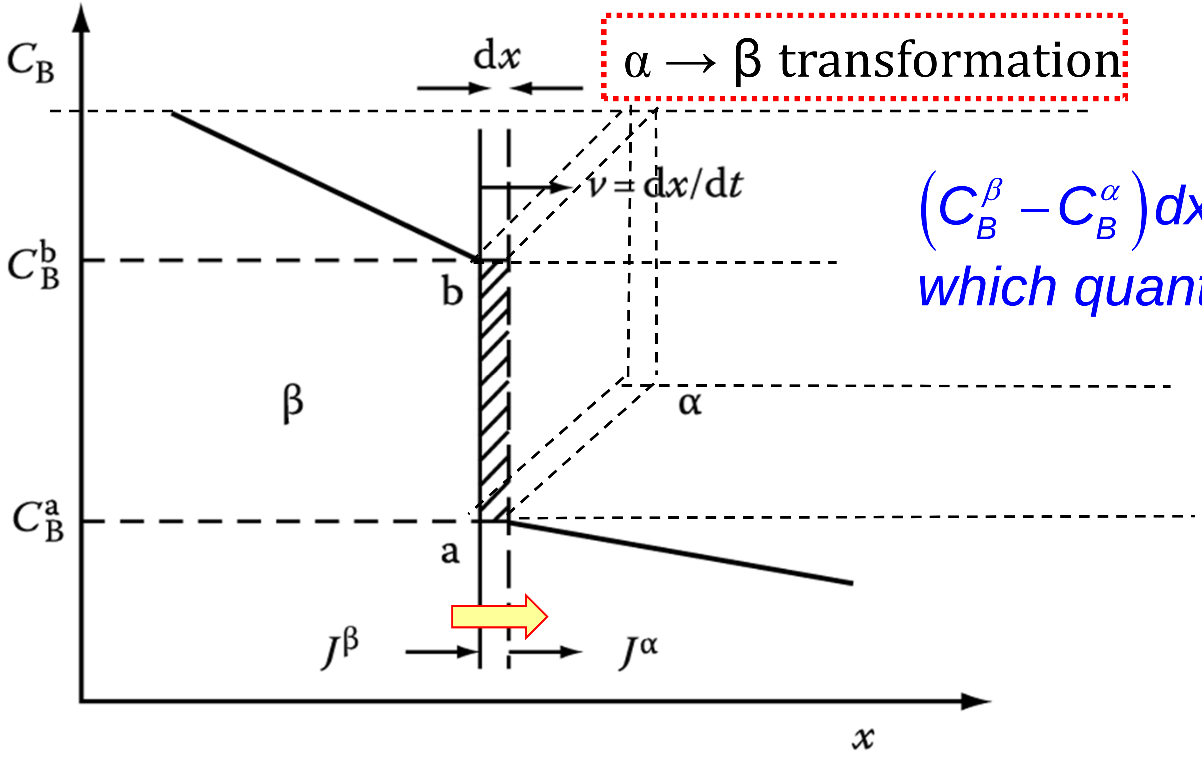
# How can we formulate the interface (α/β, β/γ) velocity?

If unit area of the interface moves a distance dx,
a volume (dx·1) will be converted
from α containing $C_B^{\alpha}$ atoms/m$^3$
to β containing $C_B^{\beta}$ atoms/m$^3$.

$C_B^{\alpha} < C_B^{\beta}$

$\left(C_B^{\beta} - C_B^{\alpha}\right)dx \rightarrow$ *shaded area*

α → β transformation



*$\left(C_B^{\beta} - C_B^{\alpha}\right)dx$ equal to which quantity?*

Fig. 2.30. Concentration profile across the α/β interface and its associated movement assuming diffusion control.

**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**

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

$- [J_B - J_A]\, dt$

$dCdx$

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

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 $\alpha/\beta$ 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** $\tilde{D} = X_B D_A + X_A D_B = F\left(X_B D_A^* + X_A D_B^*\right)$

**$D^*_{Au}$ 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** $D_s > D_b > D_l \Longleftrightarrow A_l > A_b > A_S$

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**At low temperatures**, **($T < \text{~}0.5\ T_m$)**
**$gD_p/D_l$ 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 3 : Exercises 2 (pages 111-114)**

**until 25 October**

**Good Luck!!**