2017 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

- **Substitution Diffusion**

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

Probability of vacancy x probability of jump

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

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

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

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:

$$D_v = D_A / X_v^e$$

3. **Diffusion in substitutional alloys**

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

Contents for previous class

Q: Diffusion in substitutional alloys?

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

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

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

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

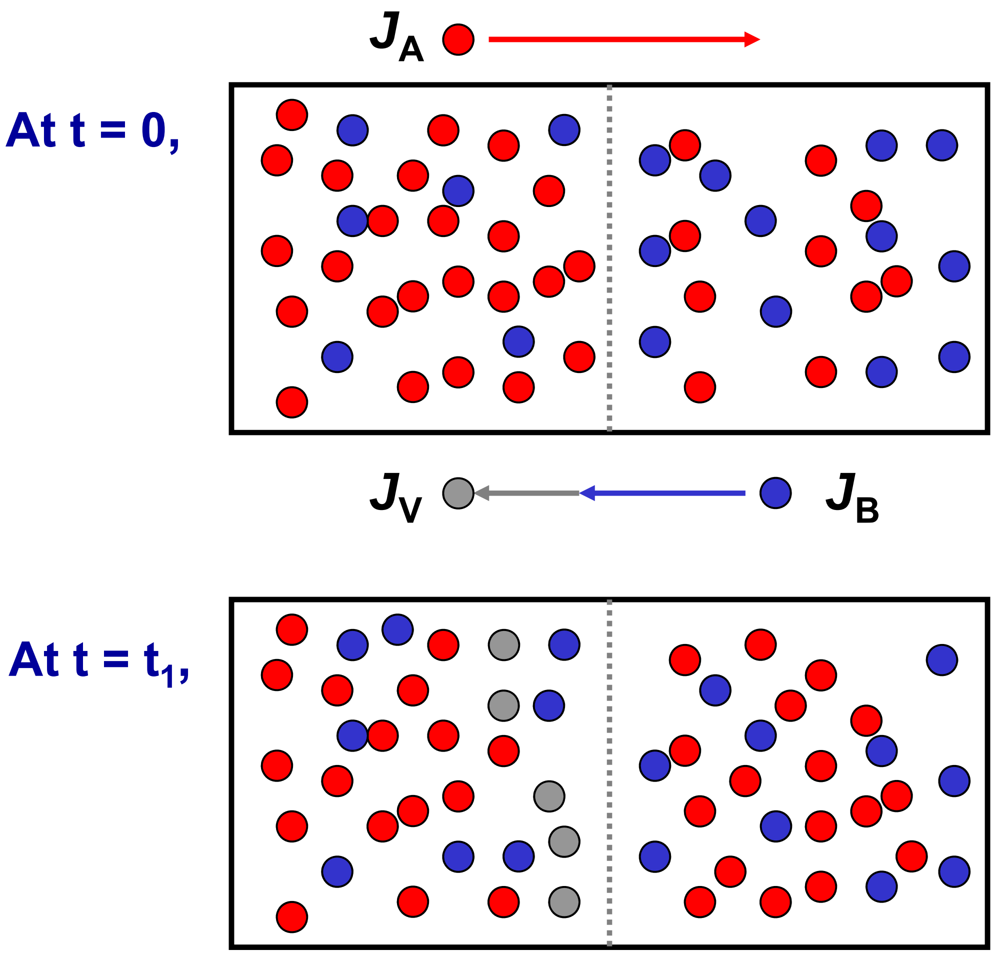
$$\boxed{\frac{\partial C_A}{\partial t} = \frac{\partial}{\partial x}\left(\tilde{D}\frac{\partial C_A}{\partial x}\right)}$$

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

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.**



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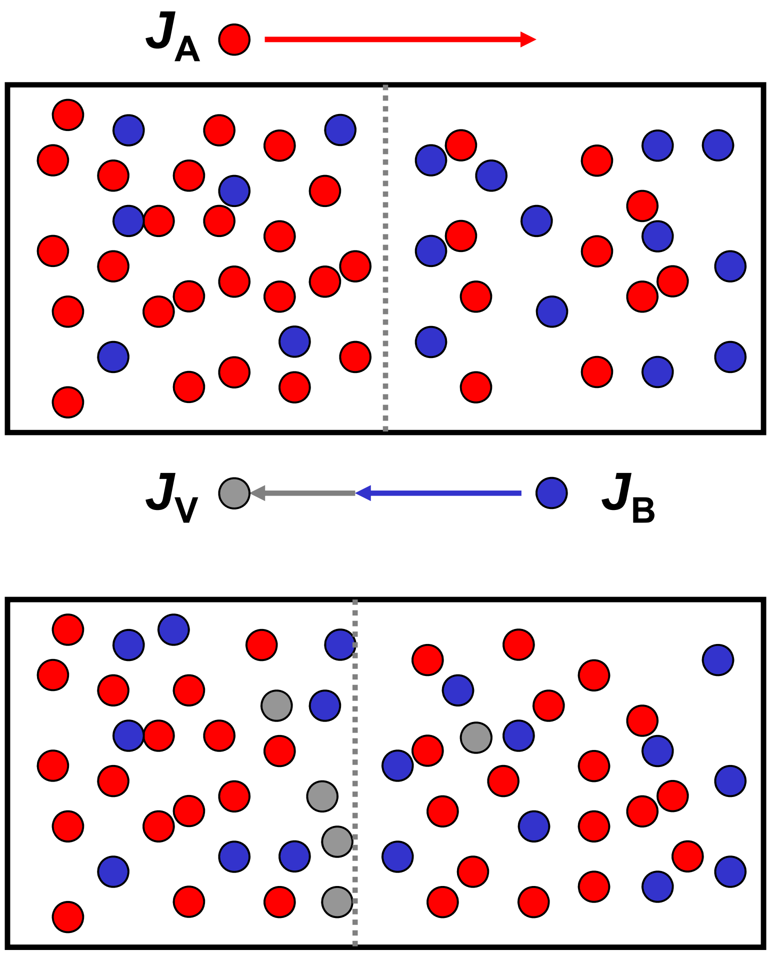
At t = 0,

At t = t_1,



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

Kirkendall effect

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

$$J_V = -J_A - J_B \quad \text{(a net flux of vacancies)}$$
$$= (D_A - D_B)\frac{\partial C_A}{\partial x}$$

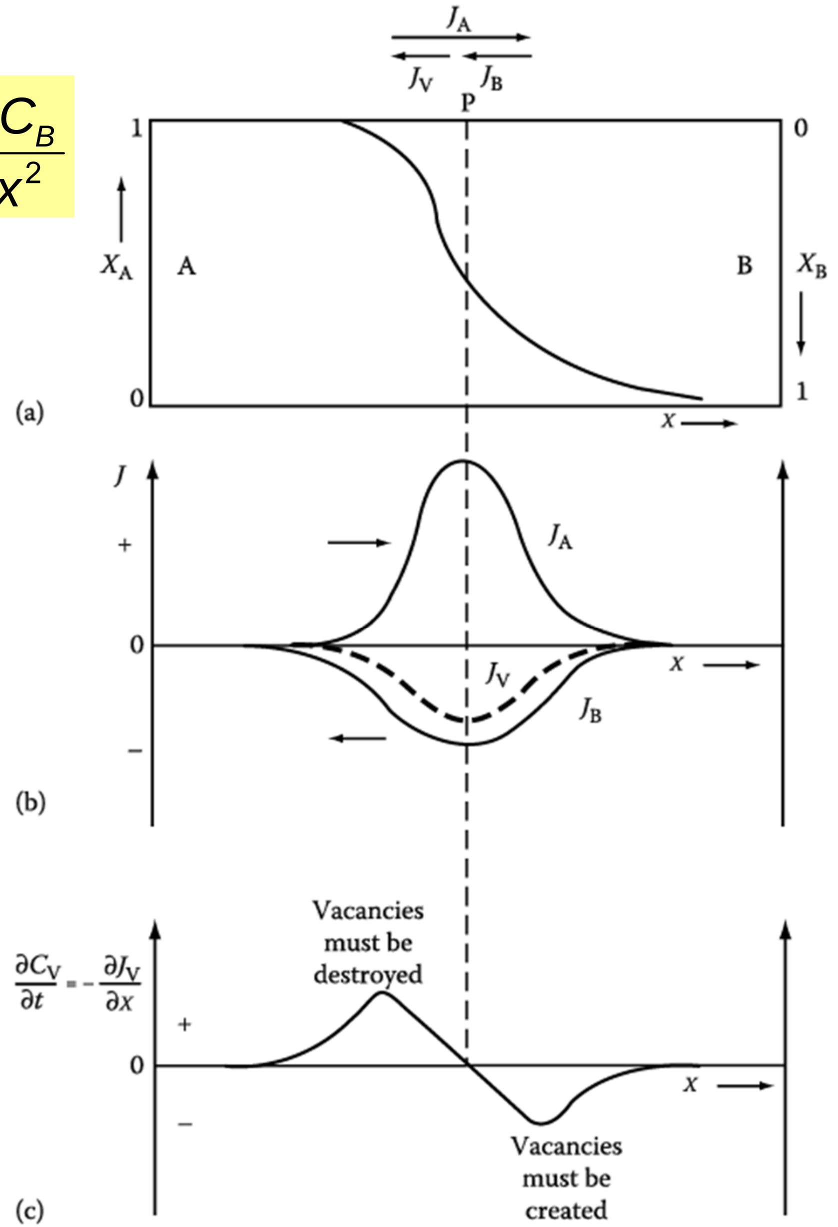
$$\frac{\partial C_B}{\partial t} = D_B \frac{\partial^2 C_B}{\partial x^2}$$

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

What would become of excess vacancy?

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

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



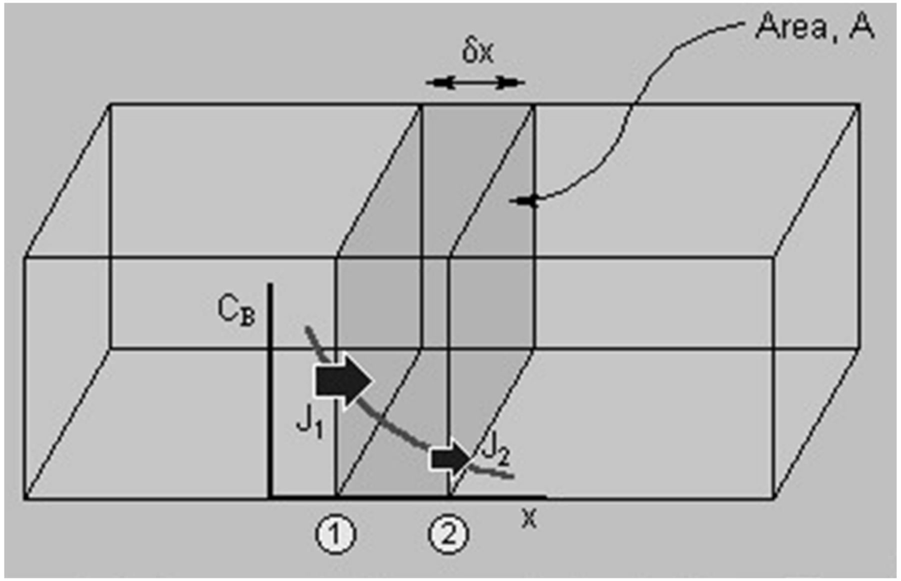
In order to maintain the vacancy concentration everywhere near equilibrium, vacancies must be created on the B-rich side and destroyed on the A-rich side.

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

Nonsteady-state diffusion

In most practical situations steady-state conditions are not established, i.e. concentration varies with both distance and time, and Fick's 1st law can no longer be used.

How do we know the variation of C_B with time? → Fick's 2nd law



The number of interstitial B atoms that diffuse into the slice across plane (1) in a small time interval d*t* :

→ $J_1 A\, dt$ Likewise : $J_2 A\, dt$

Sine $J_2 < J_1$, the concentration of B within the slice will have increased by

Due to mass conservation

$$(J_1 - J_2)A\delta t = \delta C_B A \delta x \qquad \delta C_B = \frac{(J_1 - J_2)A\delta t}{A\delta x}$$

Nonsteady-state diffusion

$$J_2 = J_1 + \frac{\partial J}{\partial x}\delta x$$ **(δx is small)**

as δt → 0

$$\delta C_B = \frac{(J_1 - J_2)A\delta t}{A\delta x}$$

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

substituting Fick's 1st law gives

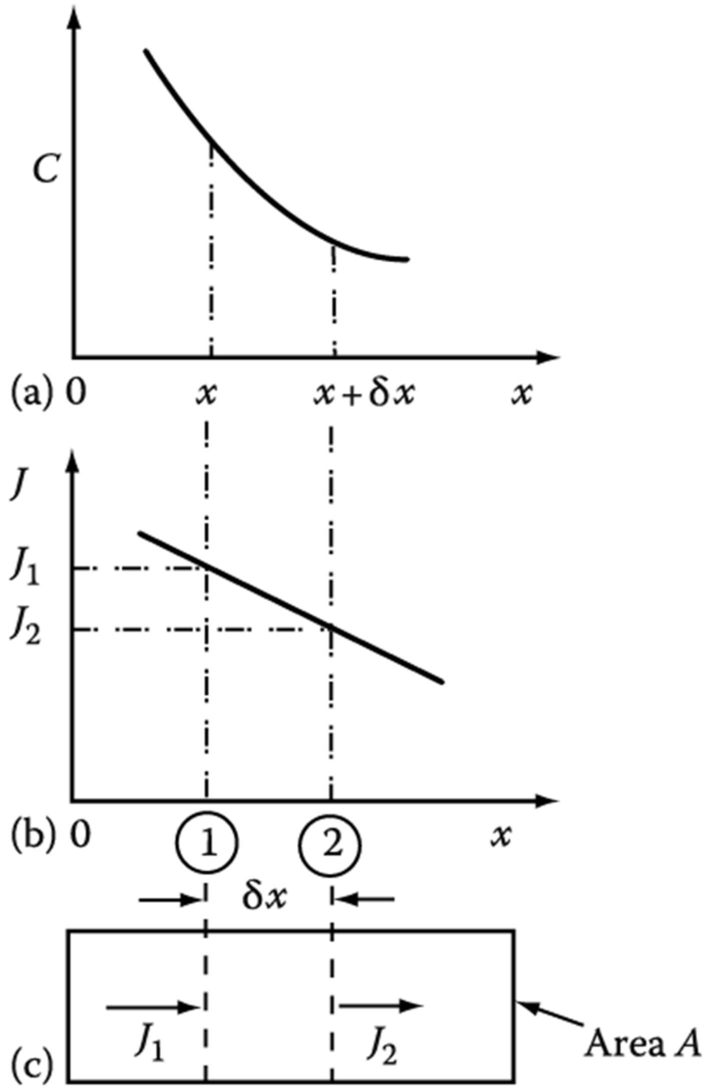
$$J_B = -D\frac{\partial C_B}{\partial x}$$

$$\frac{\partial C_B}{\partial t} = \frac{\partial}{\partial x}\left(D_B\frac{\partial C_B}{\partial x}\right)$$

If variation of D with concentration can be ignored,

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

Fick's Second Law



Fick's Second Law

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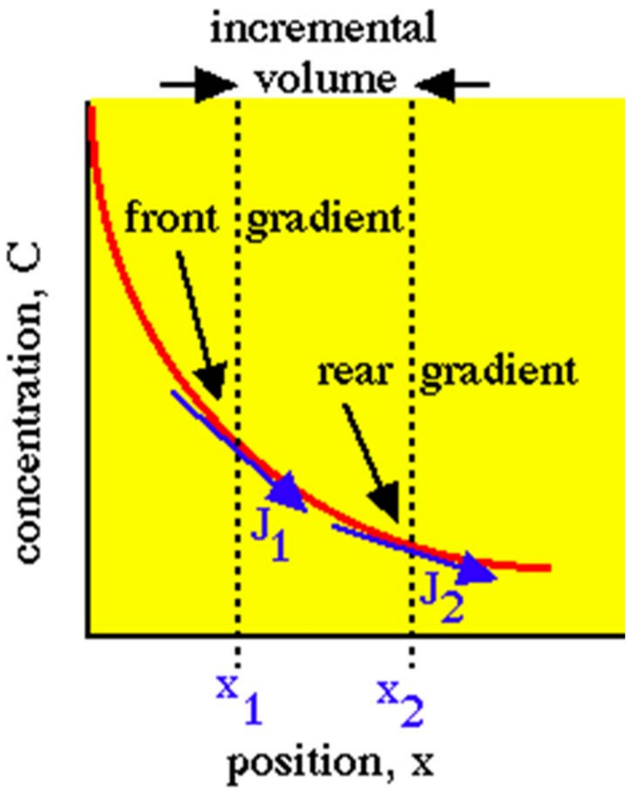
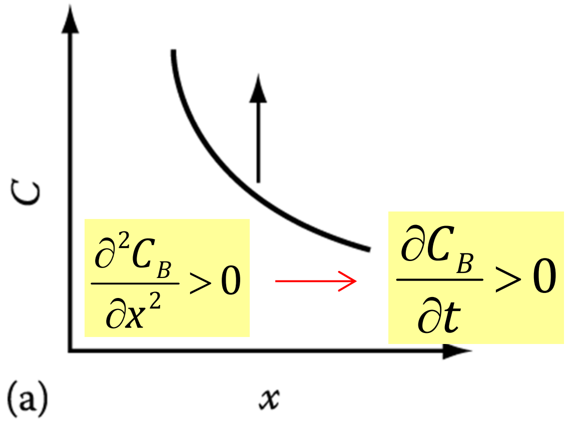


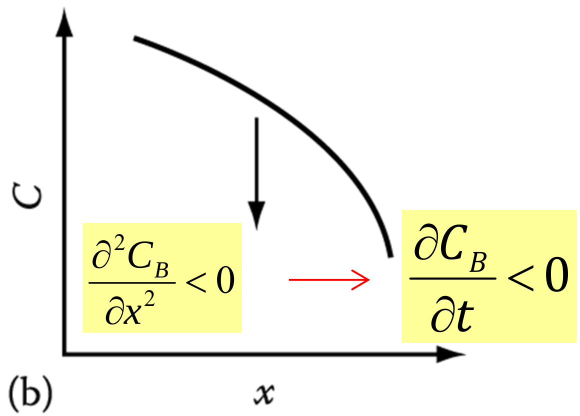
➡ **Concentration varies with time and position.**

$$\frac{\partial^2 C_B}{\partial x^2} = ?$$

Note that $\frac{\partial^2 C_B}{\partial x^2}$ **is the <u>curvature</u> of the C_B versus x curve.**



All concentration increase with time



All concentration decrease with time

$$J_V = -J_A - J_B \quad \text{(a net flux of vacancies)}$$
$$= (D_A - D_B)\frac{\partial C_A}{\partial x}$$

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

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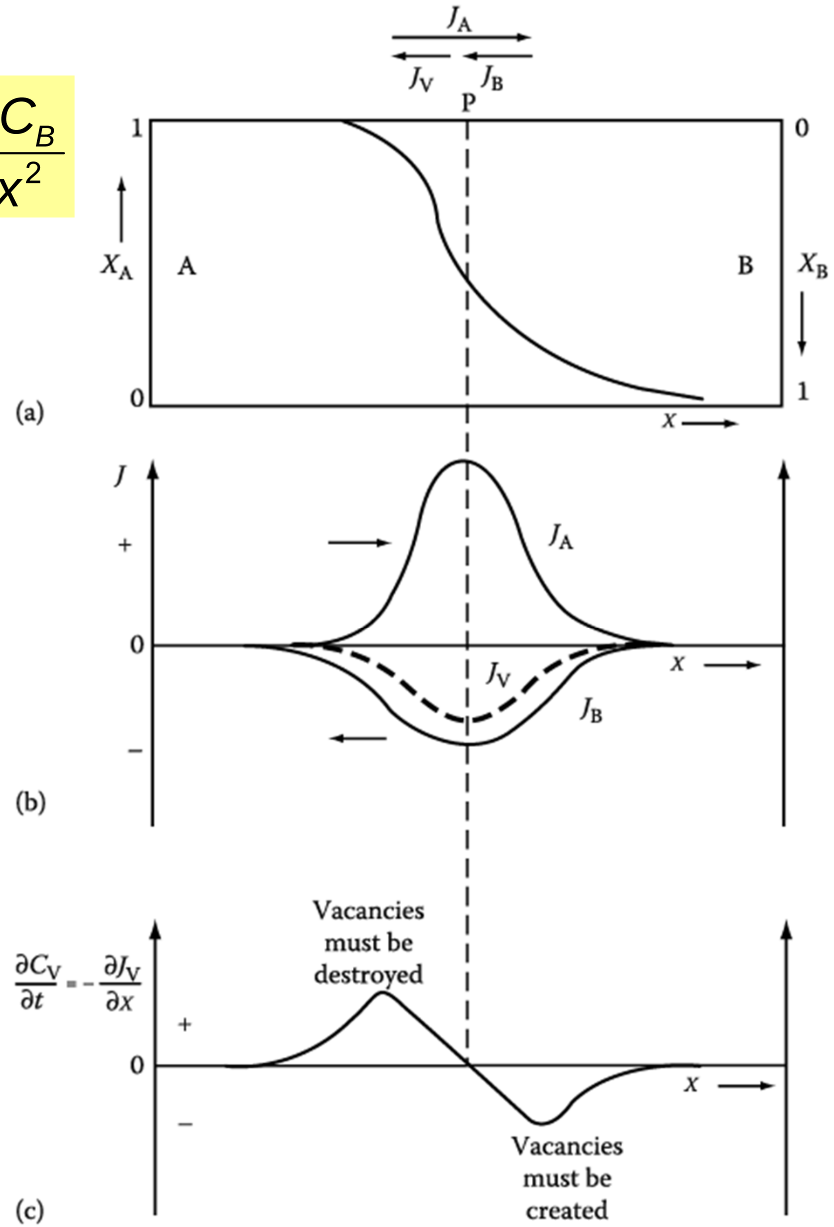
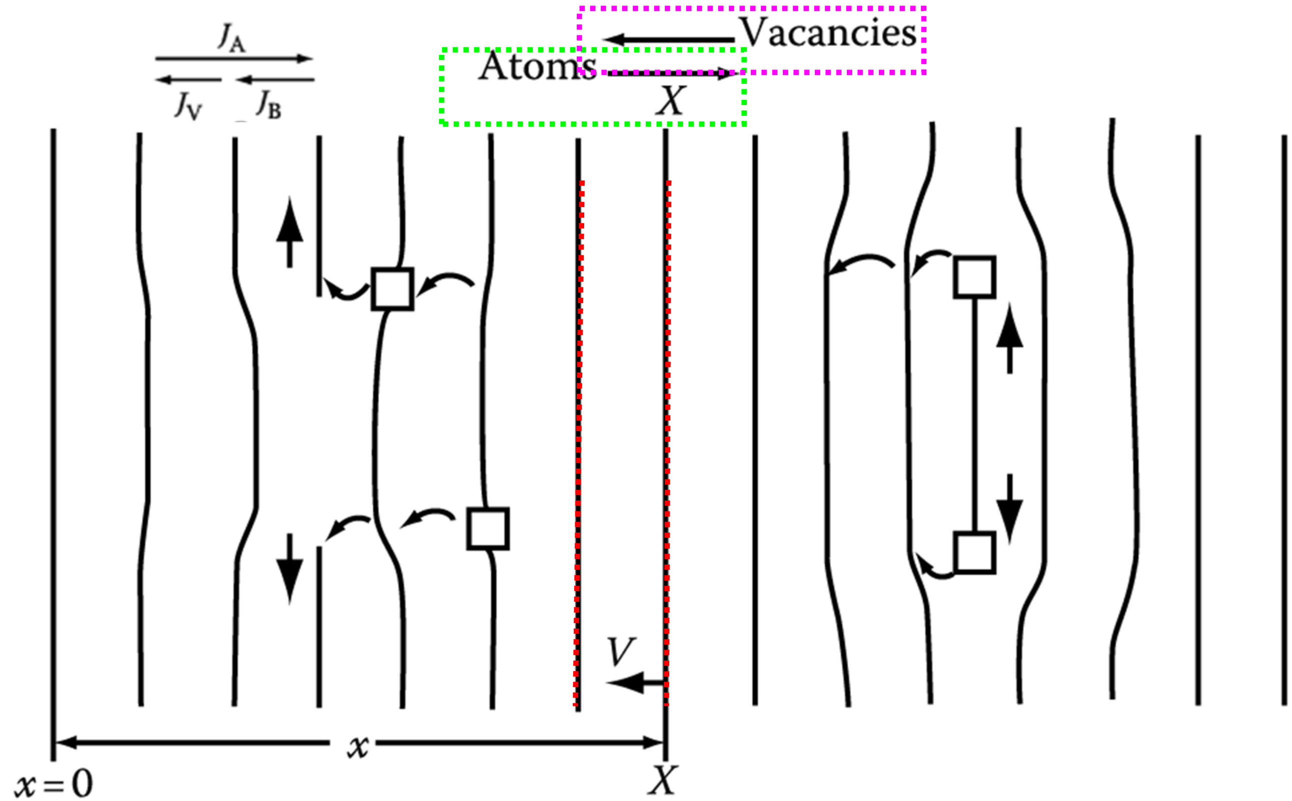


<u>In order to maintain the vacancy concentration everywhere near equilibrium</u>, **vacancies must be created on the B-rich side and destroyed on the A-rich side.**

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



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.

3. Diffusion in substitutional alloys

*** During self-diffusion, all atoms are chemically identical.**
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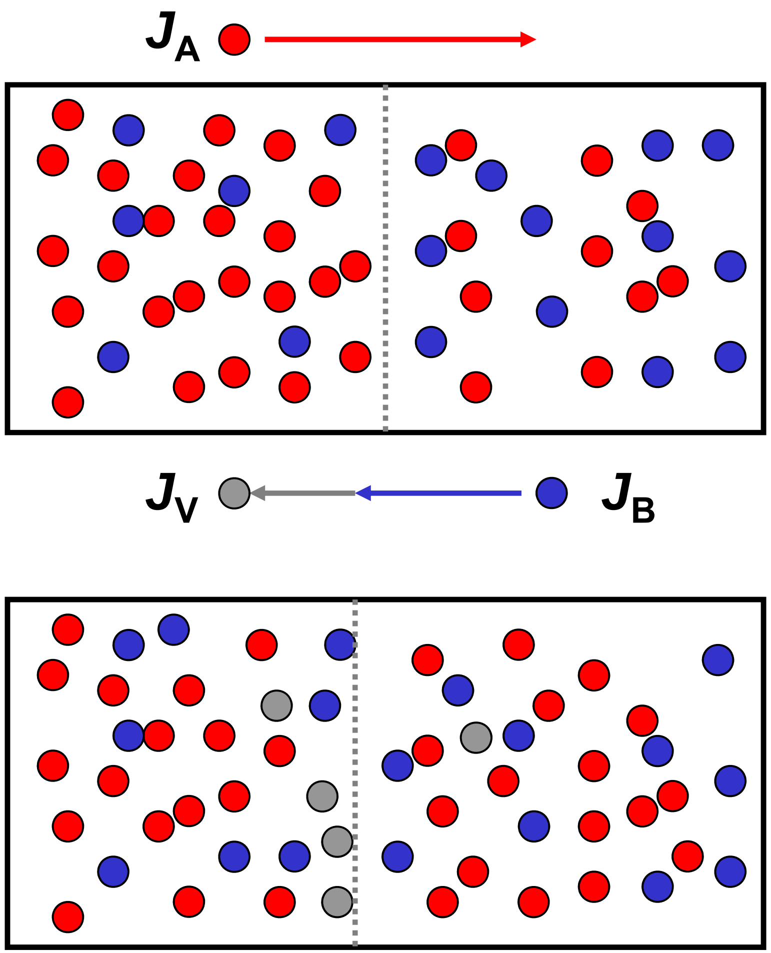
*** In binary substitutional alloys, each atomic species must be given its own intrinsic diffusion coefficient D_A or D_B.**

At t = 0,

At t = t_1,



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

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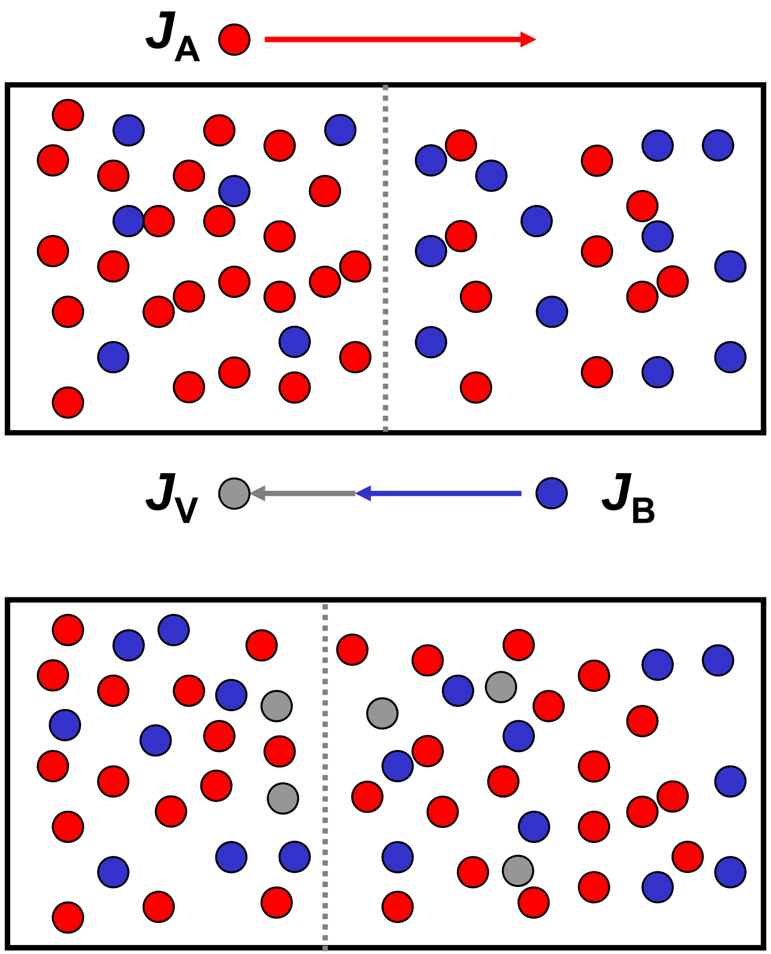
At t = 0,

At t = t_2,



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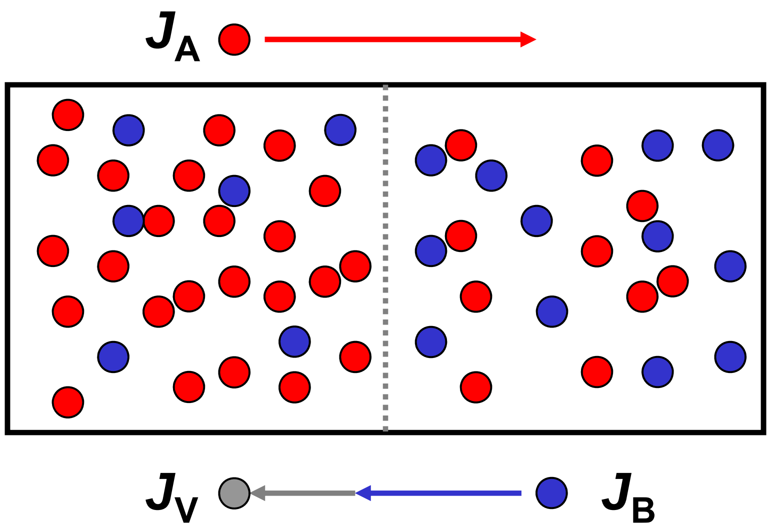
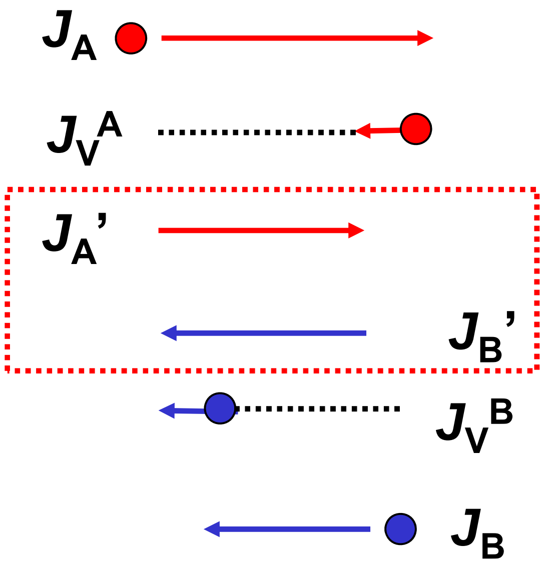
$$\boxed{\frac{\partial C_A}{\partial t} = \frac{\partial}{\partial x}\left(\tilde{D}\frac{\partial C_A}{\partial x}\right)}$$

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

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

At t = 0,

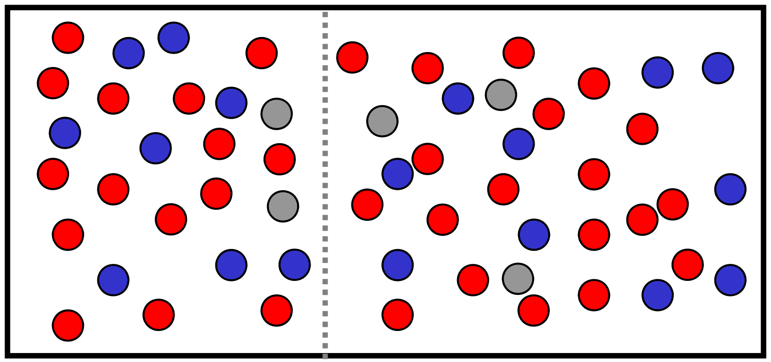




$$J'_B = J_B + J^v_B = -\tilde{D}\frac{\partial C_B}{\partial x}$$

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

At t = t_2,



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

Q: How can we determine D_A and D_B?

in substitutional alloys?

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

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

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

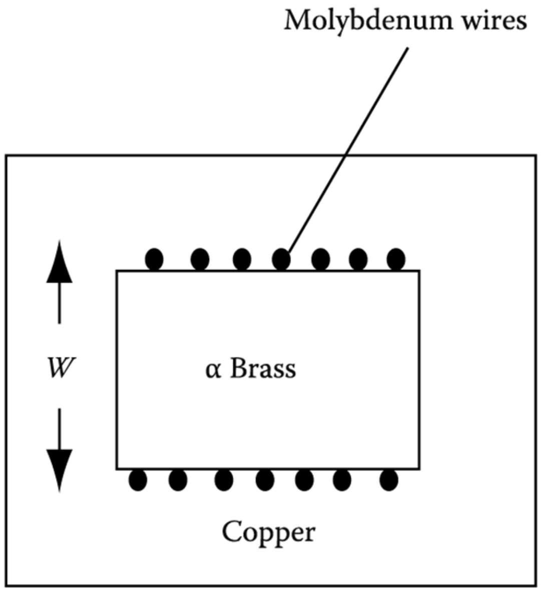
How can we determine D_A and D_B?

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

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

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.**

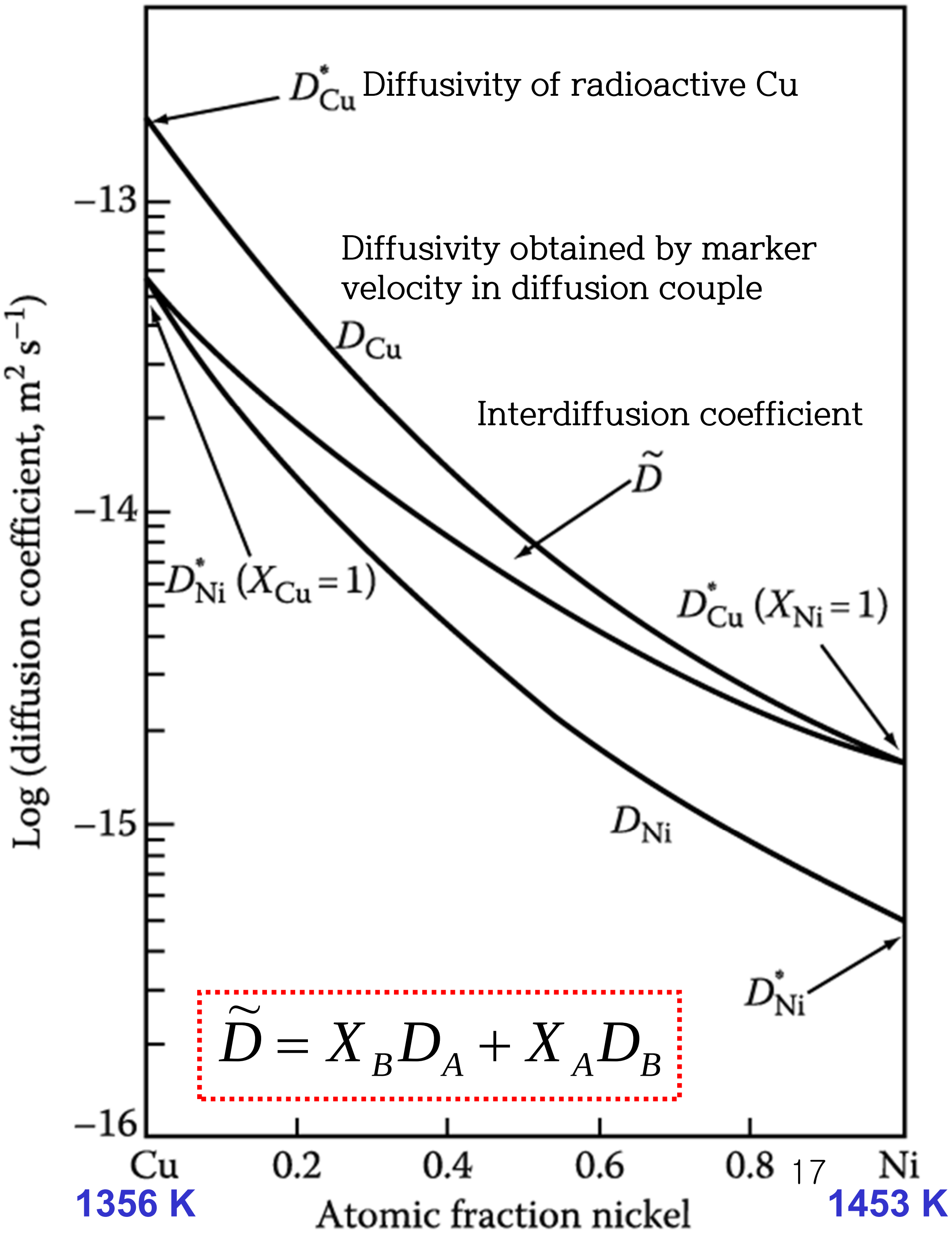
$$D_{Zn} > D_{Cu}$$

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.



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

- 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.

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

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^α / D_C^γ ~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

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

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

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.

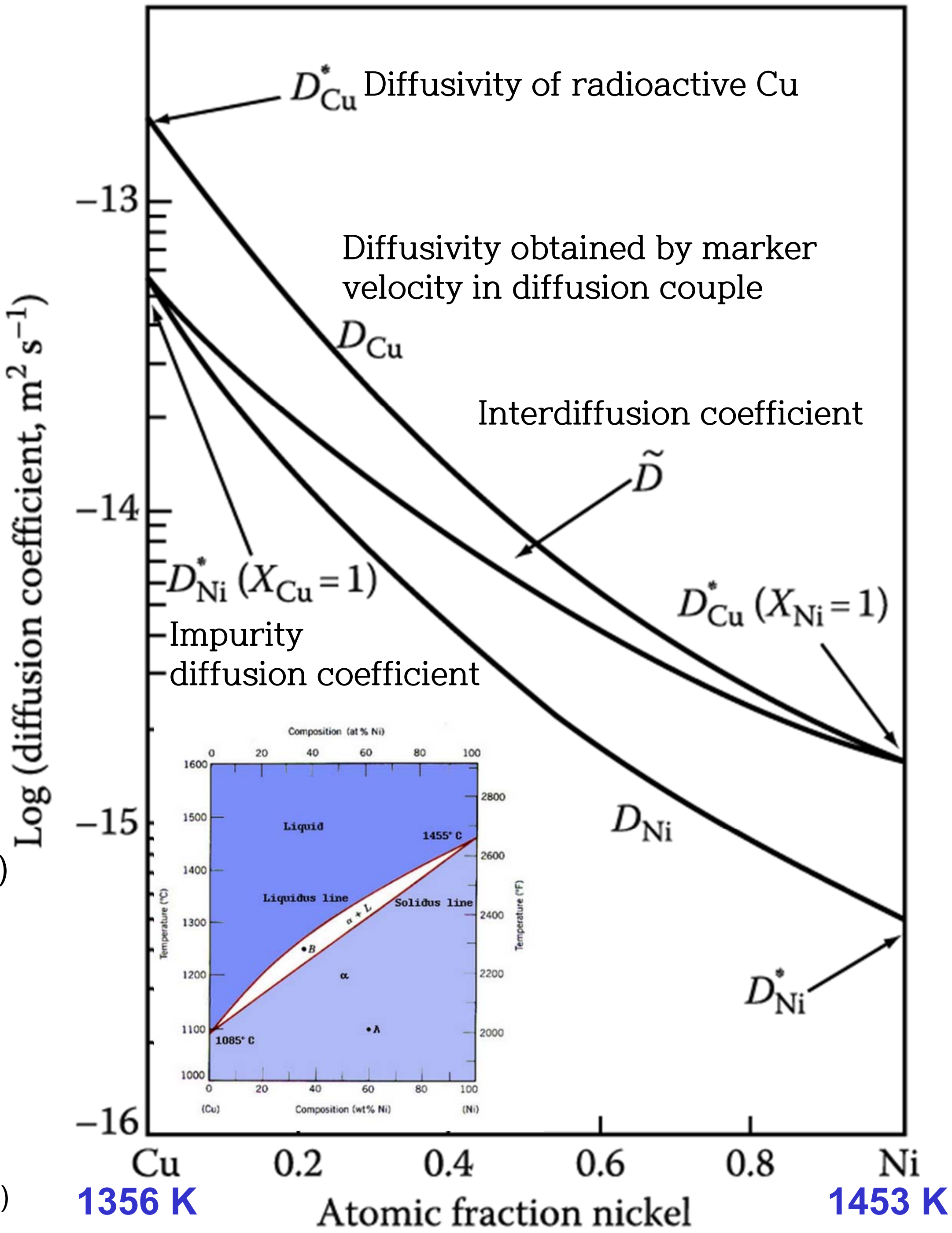
* Concentration of A & B at any x after t

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

- 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

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

(가정: 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 ∞ ***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)

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

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

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

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

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

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

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

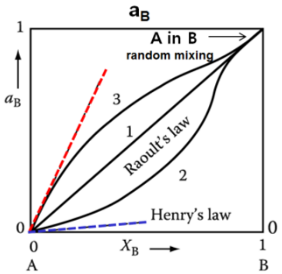
$$\boxed{C_B} = \frac{n_B}{V} = \frac{n_B}{(n_A + n_B)V_m} = \frac{X_B}{V_m}$$

$$D_B = M_B RTF$$

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

For ideal or dilute solutions,

near $X_B \approx 0$, γ_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.**

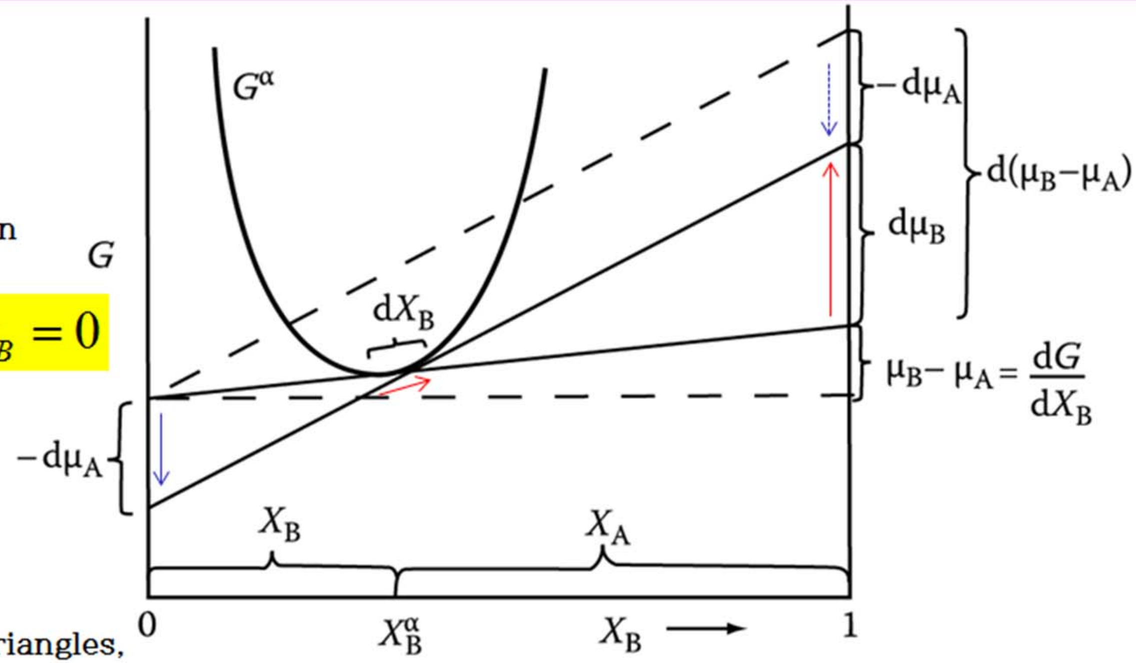
Additional Thermodynamic Relationships for Binary Solutions

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_AX_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. $d\mu_A$, $d\mu_B$

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, ∂E/∂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.

$$\boxed{\mu_B = G_B + RT\ln\gamma_B X_B + E} \Rightarrow \boxed{J_B = -D_B \cdot \frac{\partial C_B}{\partial x} - \frac{D_B C_B}{RT} \cdot \frac{\partial E}{\partial x}}$$

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 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.

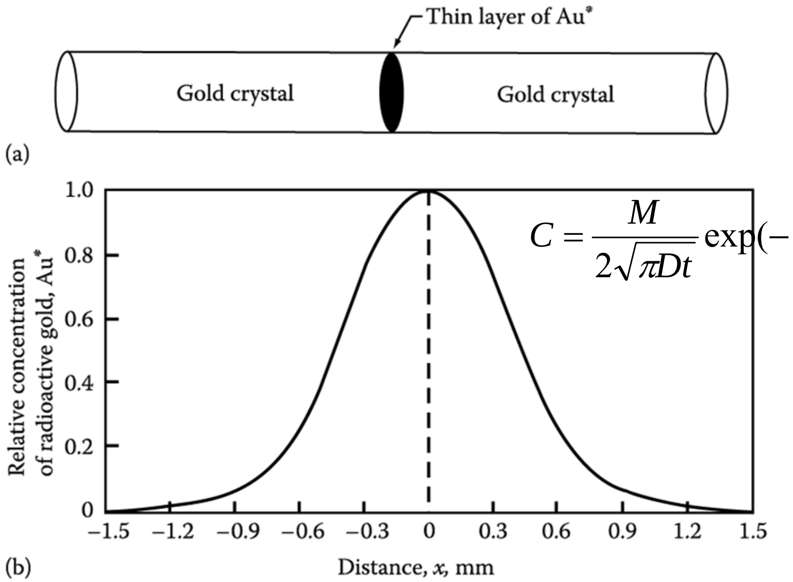
Thermodynamic factor

$$\boxed{\tilde{D} = X_B D_A + X_A D_B = F\left(X_B D_A^* + X_A D_B^*\right)} \qquad F = \left(1 + \frac{d\ln \gamma_B}{d\ln X_B}\right)$$

순금속에서 자기확산 & 합금원소의 고유확산계수 → 방사성 추적자의 확산을 이용하여 결정

2.5 Tracer diffusion in binary alloys

1) Au* in Au or Au/X alloy



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

Tracer diffusion coefficient (D^*_{Au}) in pure metal

& Intrinsic diffusion coefficients (D_{Au}) in an alloy

: possible to determine by radioactive tracers

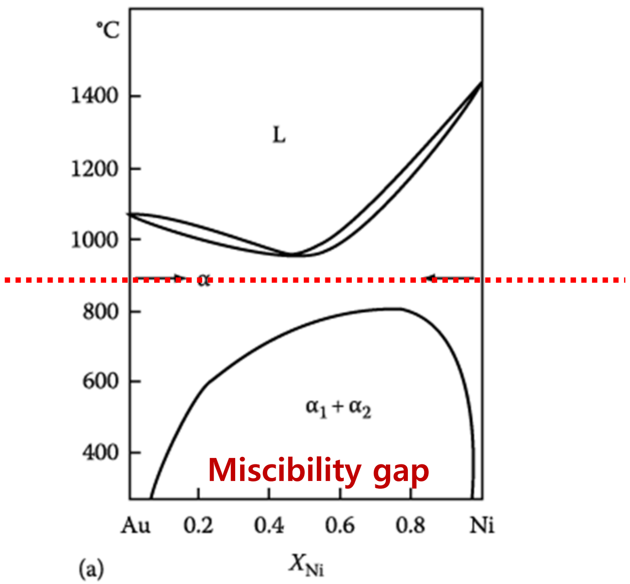
How does D^*_{Au} differ from D_{Au} ?

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

2) Au* in Au-Ni



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.

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

F : Thermodynamic Factor

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

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

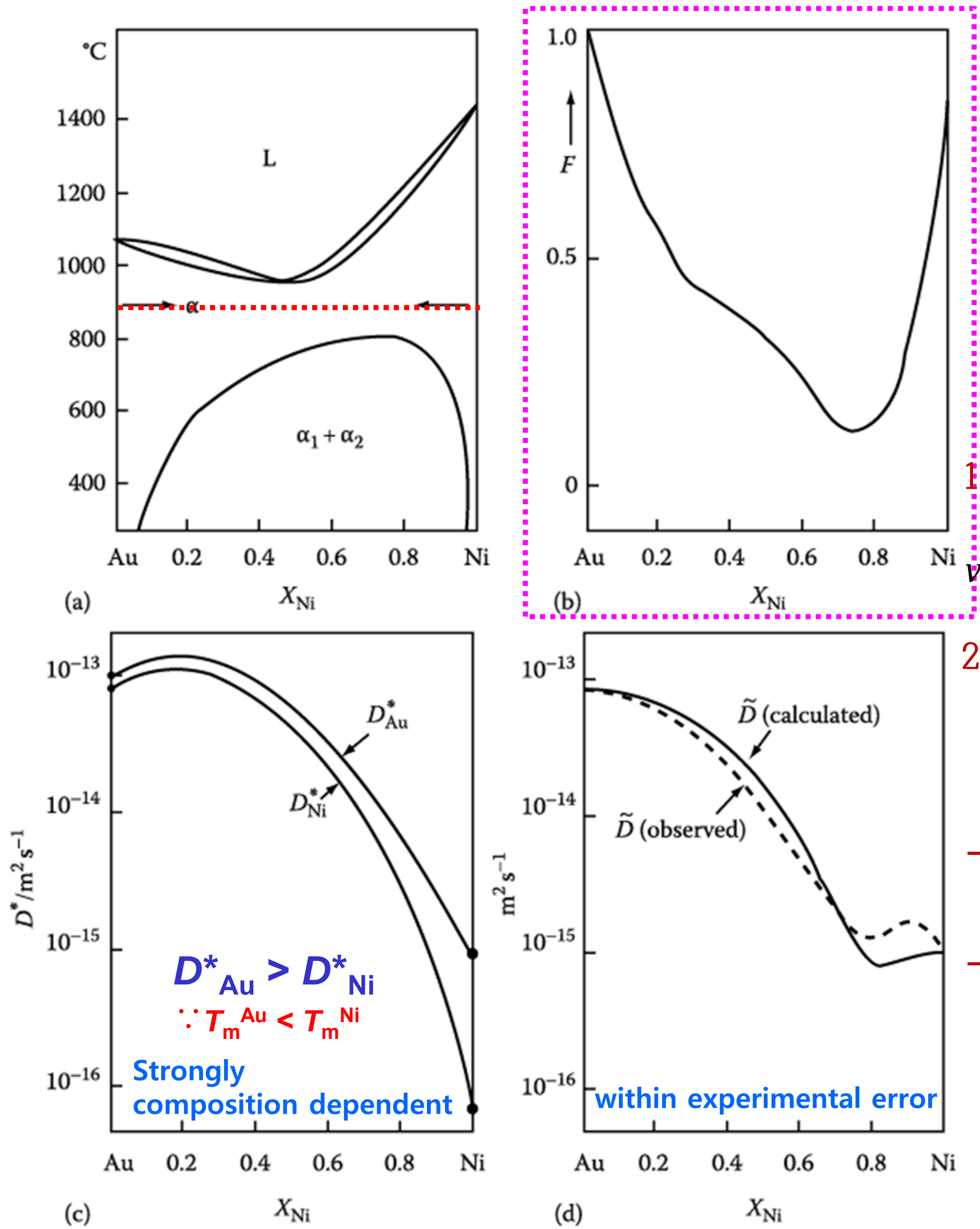


Fig. 2.22 Inter-diffusion in Au-Ni alloys at 900 ℃ (a) Au-Ni phase diagram, (b) the thermodynamic factor, F, at 900 ℃, (c) experimentally measured tracer diffusivities At 900 ℃ (d) experimentally measured inter-diffusion coefficients compared with values calculated from (b) and (c).

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

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

B　　　　A　austenitized

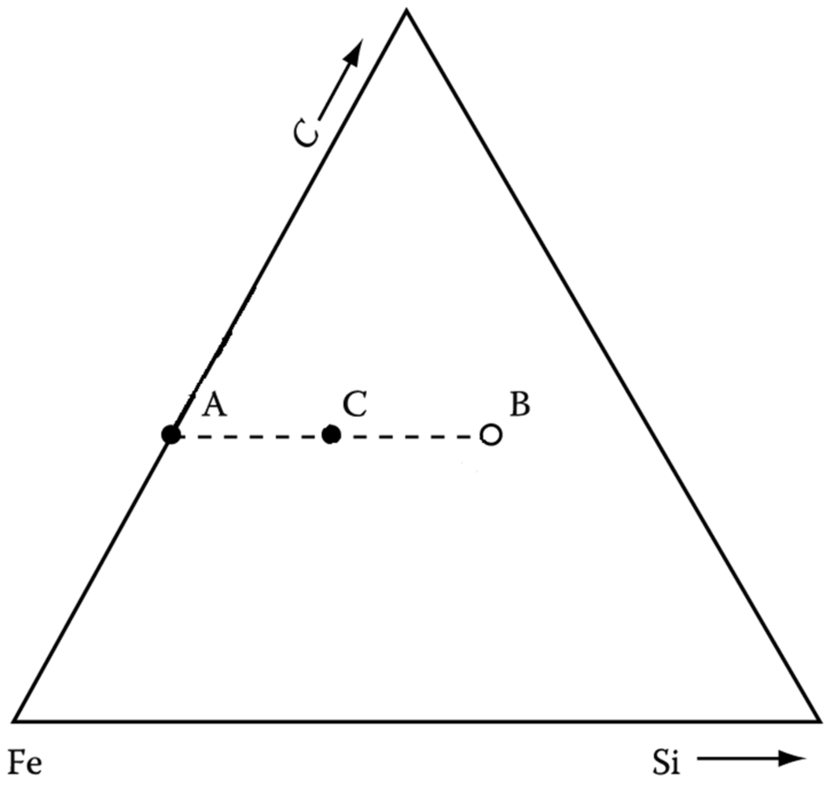
① **Si raises the μ_C in solution.**

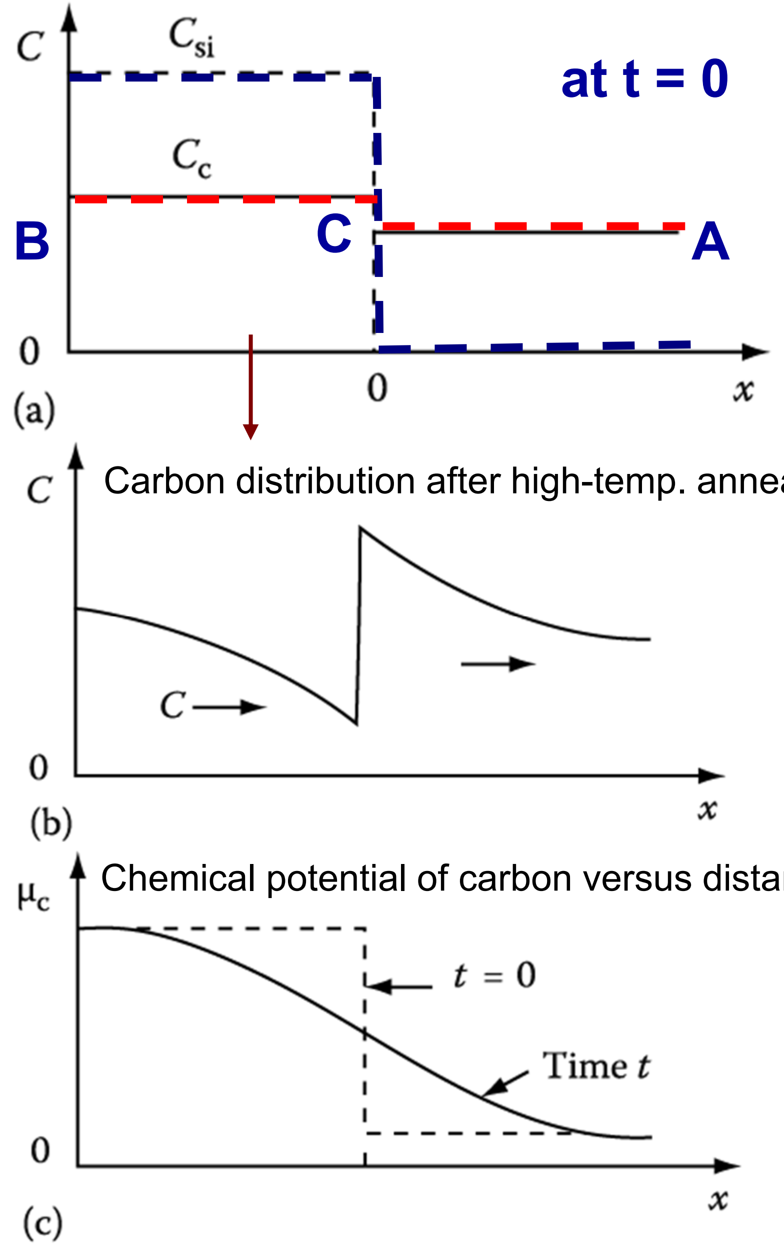
(chemical potential of carbon)

C 이동: 고동도→ 저농도 영역 & Si-rich→Si 적은 영역

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

(M : mobility)





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**

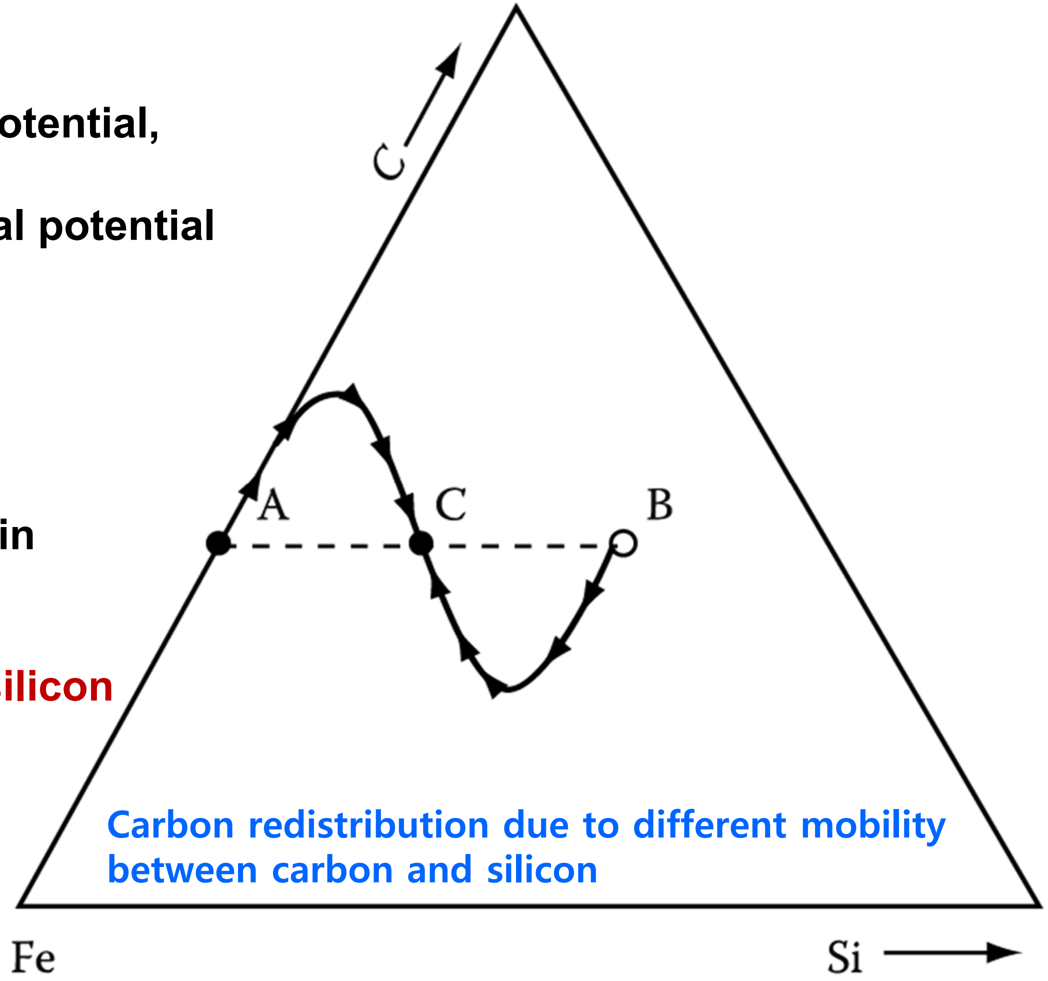


Fig. 2.24. Schematic diagram showing the change in composition of two points (A and B) on opposite sides of the diffusion couple

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

$$\boxed{D_s > D_b > D_l} \Longleftrightarrow \boxed{A_l > A_b > A_S}$$

1. Diffusion along Grain Boundaries and Free Surface

Grain boundary diffusion makes a significant contribution

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

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

2. Diffusion Along Dislocation

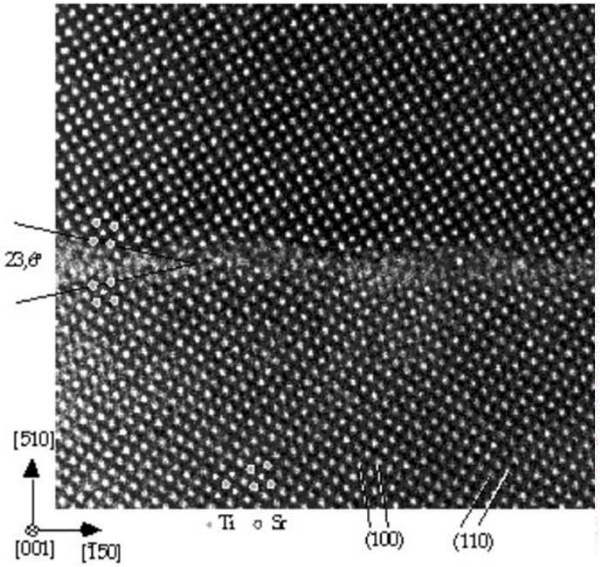
At low temperatures, **(T < ~0.5 T_m)**
gD_p/D_l can become so large that the apparent diffusivity is entirely due to diffusion along dislocation.

2.7.1 High-diffusivity paths

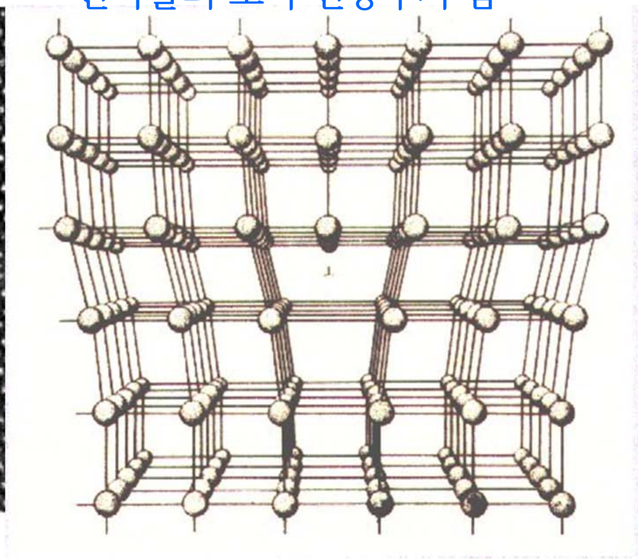
Real materials contain defects.

= more open structure ➡ fast diffusion path.

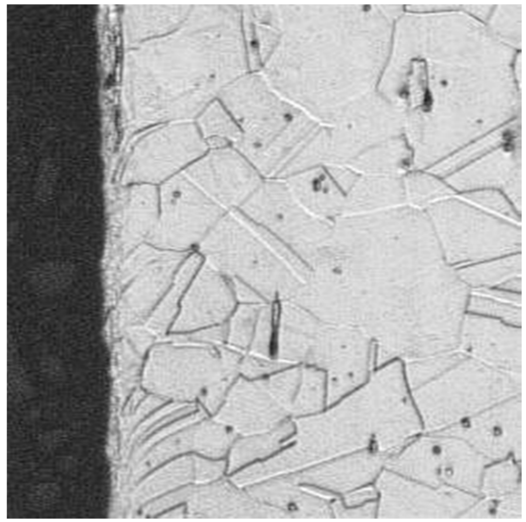
원자들의 도약 진동수가 큼 　 확산의 주요한 행로



Grain boundary



dislocation



surface

Diff. along lattice

$$D_l = D_{lo} \exp(-\frac{Q_l}{RT})$$

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

Diff. along grain boundary

$$D_b = D_{bo} \exp(-\frac{Q_b}{RT})$$

Diff. along free surface

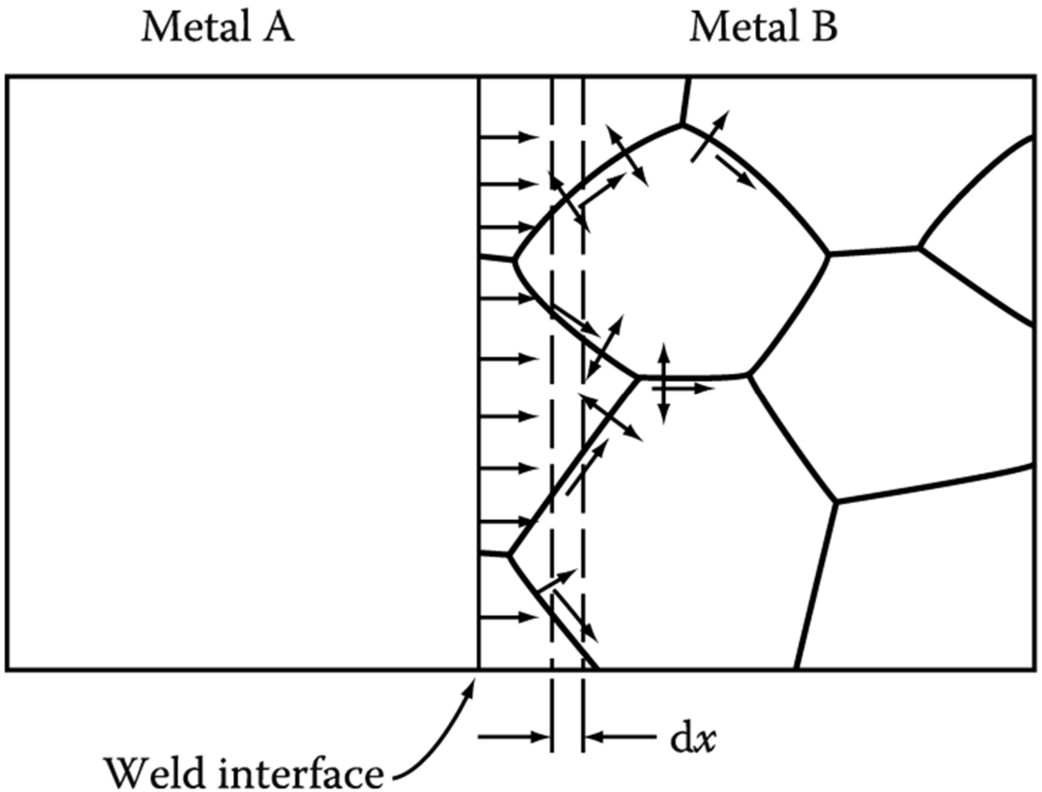
$$D_s = D_{so} \exp(-\frac{Q_s}{RT})$$

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

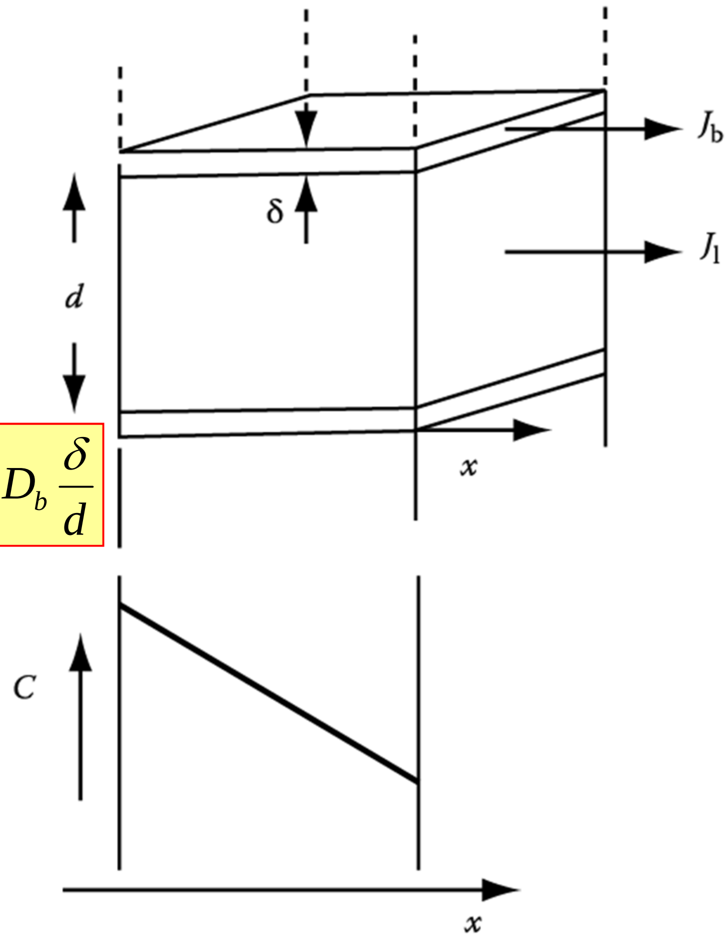
Combined diffusion of grain boundary and lattice

: 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,

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

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



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

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

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

δ : grain boundary thickness ≈ 0.5nm

d : grain size

D_{app} : apparant diffusivity

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

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.

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

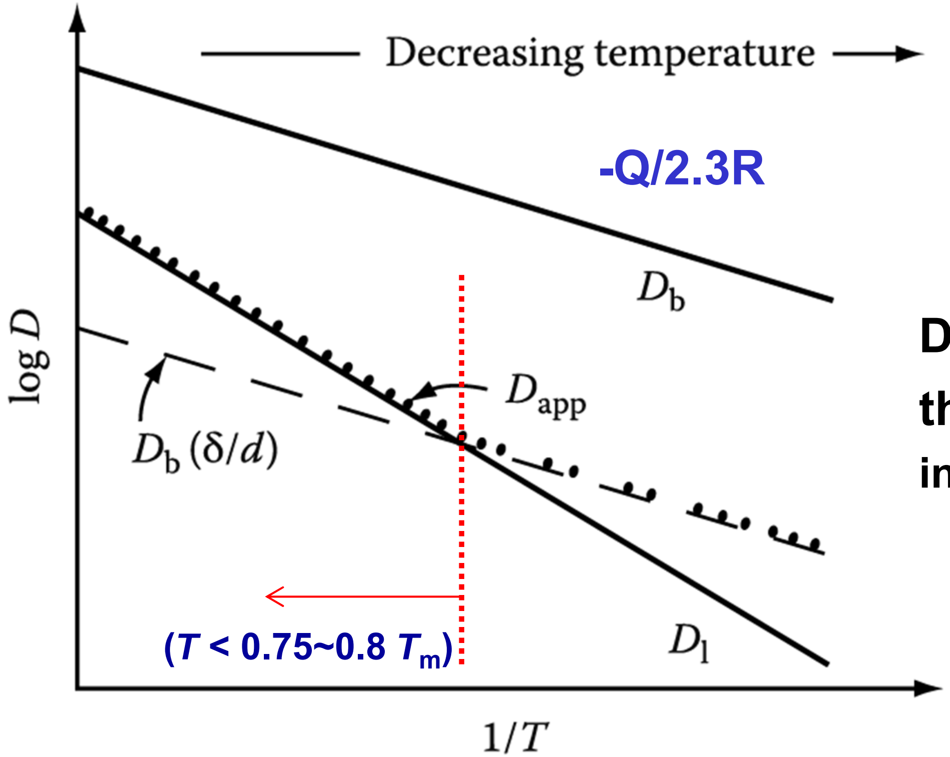


Fig. 2.27 Diffusion in a polycrystalline metal.

$D_b > D_l$ at all temp.

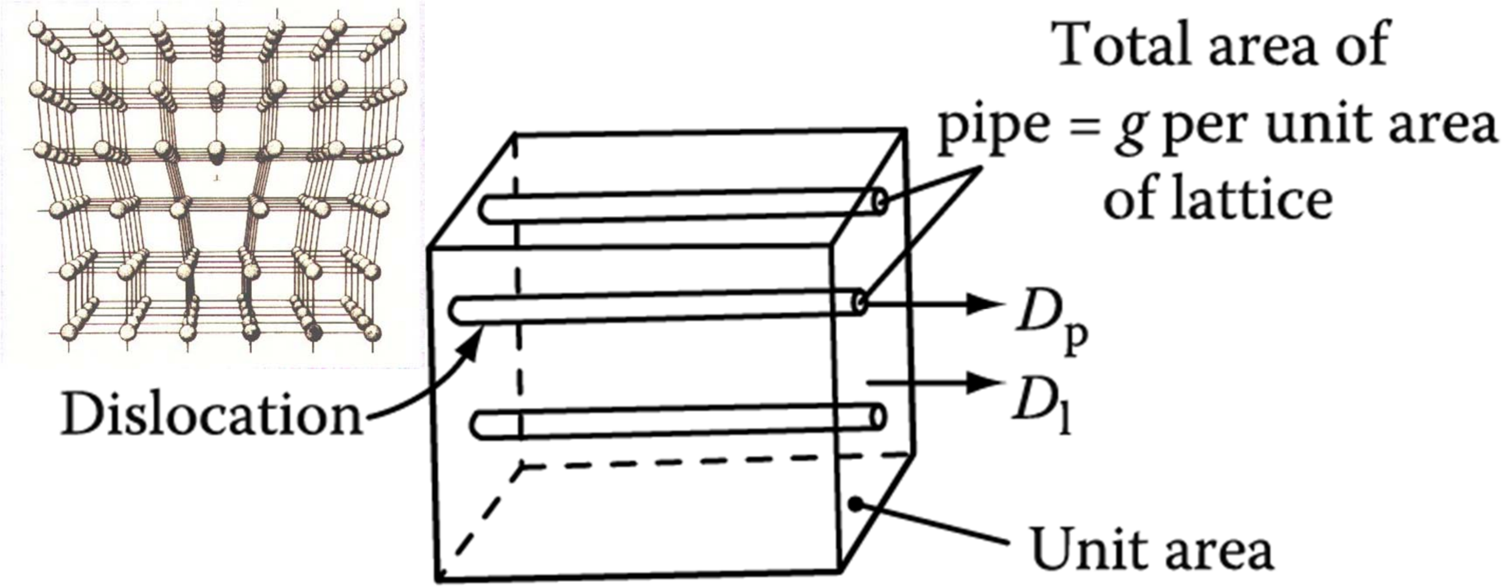
Due to $Q_b < Q_l$, ($Q_b = 0.5 Q_l$)
the curves for D_l and $D_b\delta/d$ cross in the coordinate system of lnD versus 1/T.

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

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

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 ~ 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.

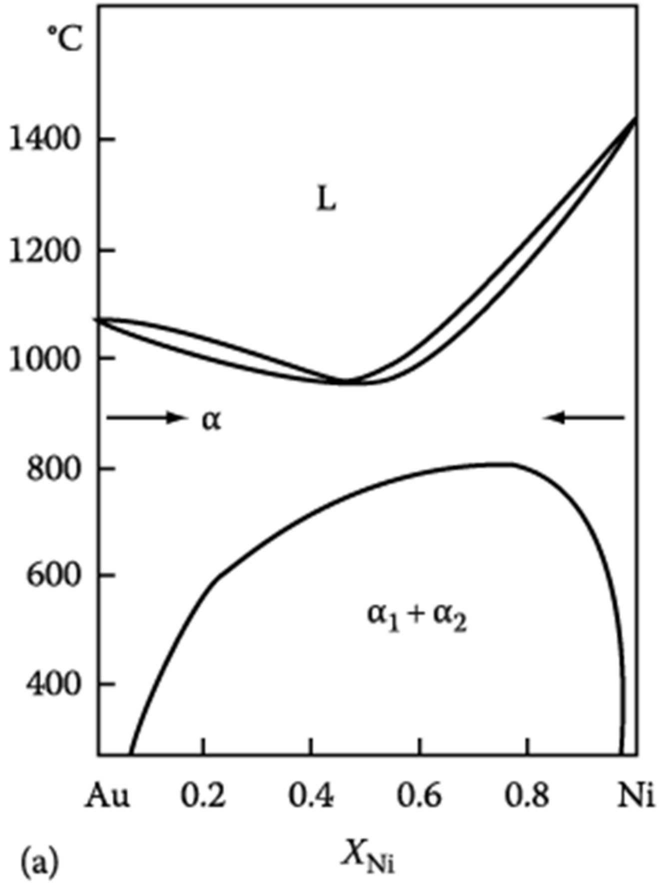
At low temperatures, **(T < ~0.5 T_m)**
gD_p/D_l can become so large that the apparent diffusivity is entirely due to diffusion along dislocation.

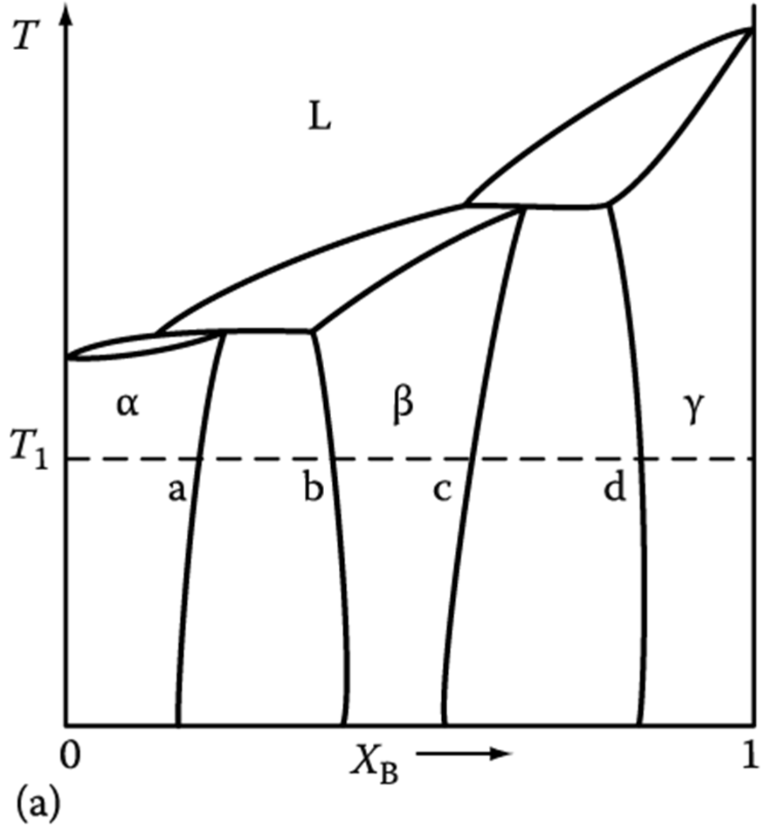
Q: How can we formulate the interface (α/β, β/γ) velocity in multiphase binary systems?

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

(velocity of the α/β interface)

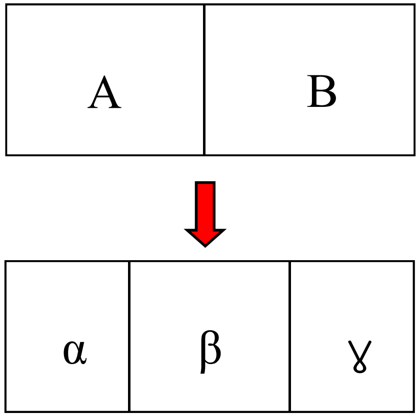
2.8 Diffusion in multiphase binary systems (다상 2원계의 확산)





2.8 Diffusion in multiple binary system

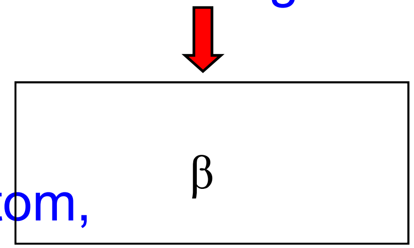
A diffusion couple made by welding together pure A and pure B



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.

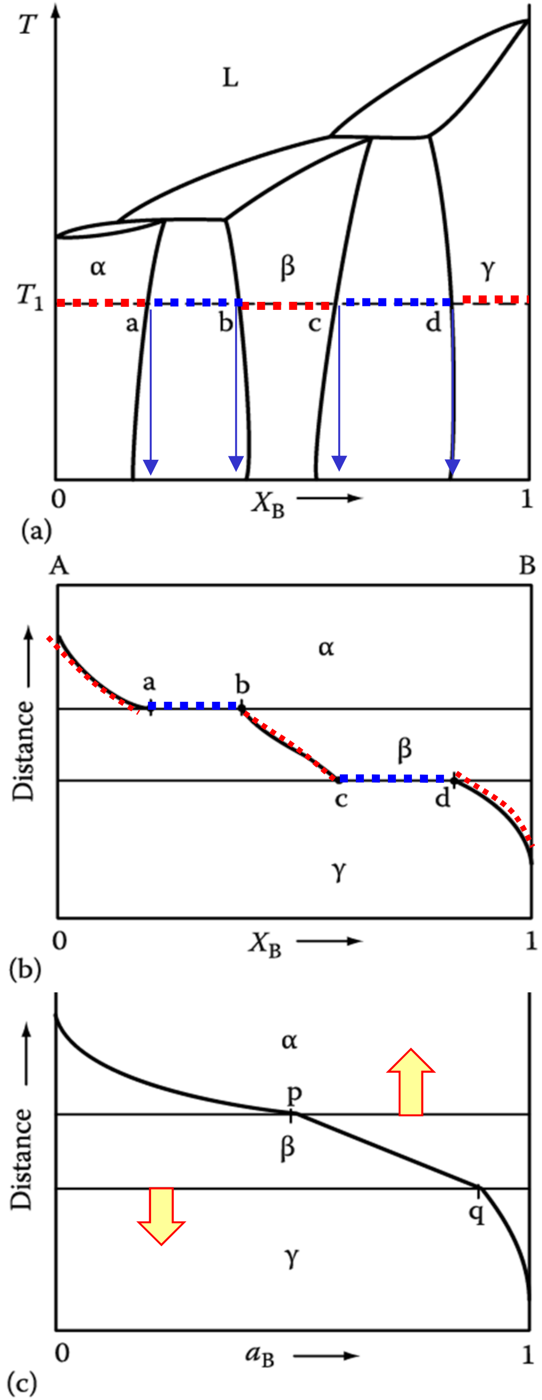


Draw a profile of activity of B atom, in the plot of distance vs. a_B after annealing at T_1.

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

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

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



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.

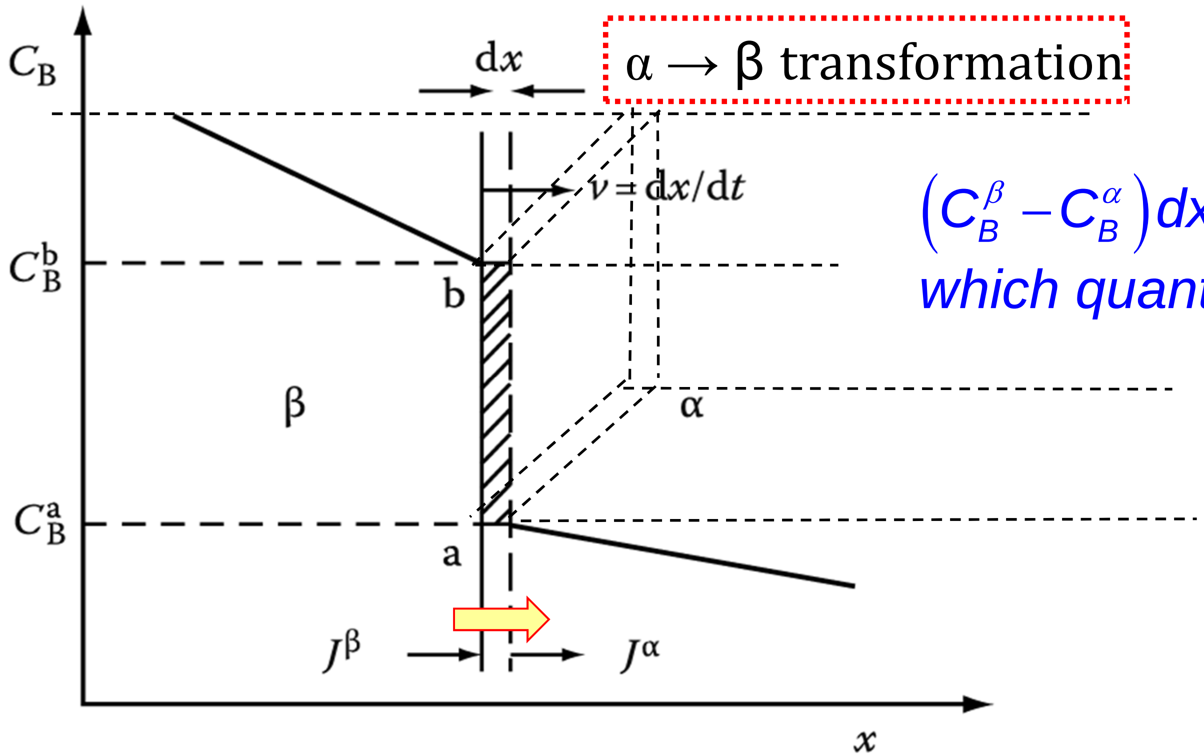
How can we formulate the interface (α/β, β/γ) velocity?

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

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

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

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

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

- $[J_B - J_A]\, dt$

$dCdx$

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

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 α/β interface)

Contents for today's class

Thermodynamic factor

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

- **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** $D_s > D_b > D_l \Leftrightarrow A_l > A_b > A_S$

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 $D_b\delta > D_l d$. **($T < 0.75\sim0.8\ T_m$)**

2. Diffusion Along Dislocation

At low temperatures, **($T < \sim0.5\ T_m$)**
gD_p/D_l can become so large that the apparent diffusivity is entirely due to diffusion along dislocation.

- **Diffusion in Multiphase Binary Systems**

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

(velocity of the α/β interface)

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

until 3rd November (before mid-term)

Good Luck!!