2009 fall

Phase Transformation of Materials

10.06.2009

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Contents for previous class

- **Solutions to the diffusion equations**

  : Application of Fick's 2nd law

- **Interstitial Diffusion / Substitution Diffusion**

1. **Self diffusion in pure material (방사성동위원소)**

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

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

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

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**

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:

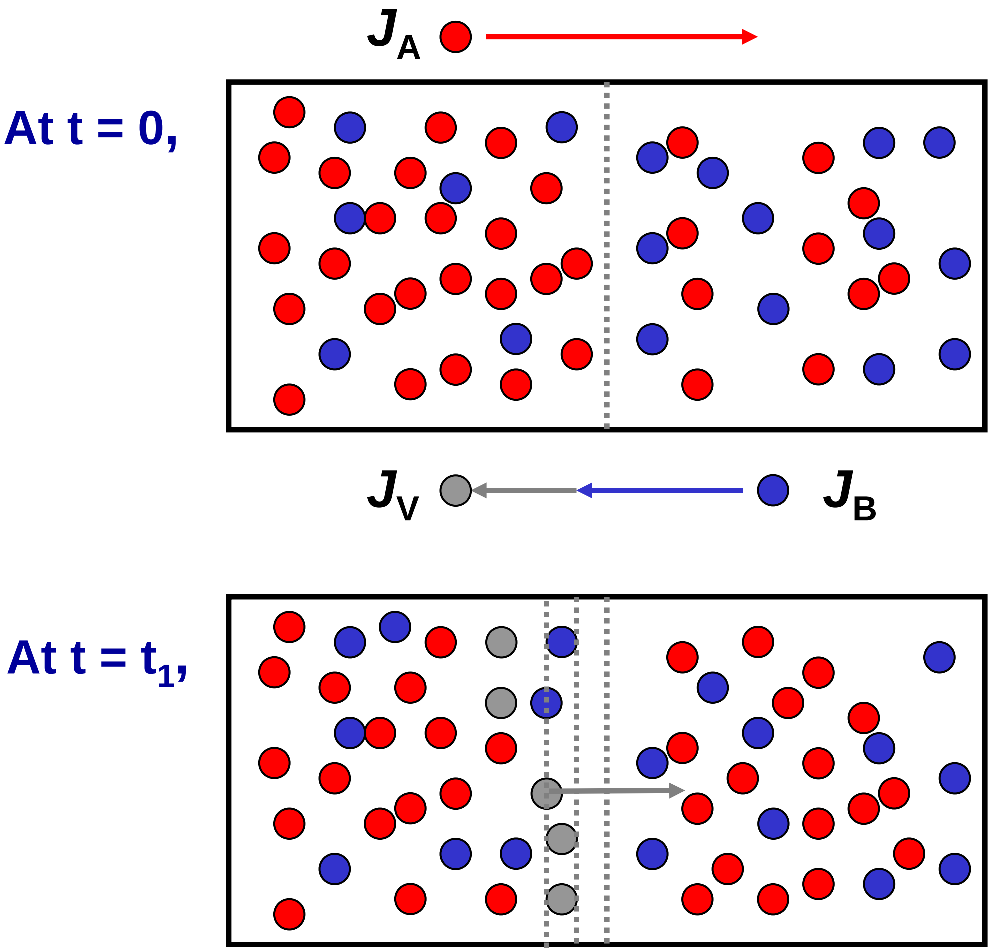
Process	**Solution**
Carburisation	$C = C_S - (C_S - C_0)\,\mathrm{erf}\left(\frac{x}{2\sqrt{Dt}}\right)$ **C_S = Surface concentration** **C_0 = Initial bulk concentration**
Decarburisation	$C = C_0\,\mathrm{erf}\left(\frac{x}{2\sqrt{Dt}}\right)$ C_0 = Initial bulk concentration
Diffusion Couple	$C = \left(\frac{C_1 + C_2}{2}\right) - \left(\frac{C_1 - C_2}{2}\right)\mathrm{erf}\left(\frac{x}{2\sqrt{Dt}}\right)$ C_1 = Concentration of steel 1 C_2 = Concentration of steel 2
Homogenisation	$C = C_{\mathrm{mean}} + \beta_0 \sin\left(\frac{\pi x}{l}\right)\exp\left(-\frac{t}{\tau}\right)$ C_{mean} = Mean concentration b_0 = Initial concentration amplitude l = half-wavelength of cells t = relaxation time

Contents for today's class

- Interstitial Diffusion / Substitution Diffusion
    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

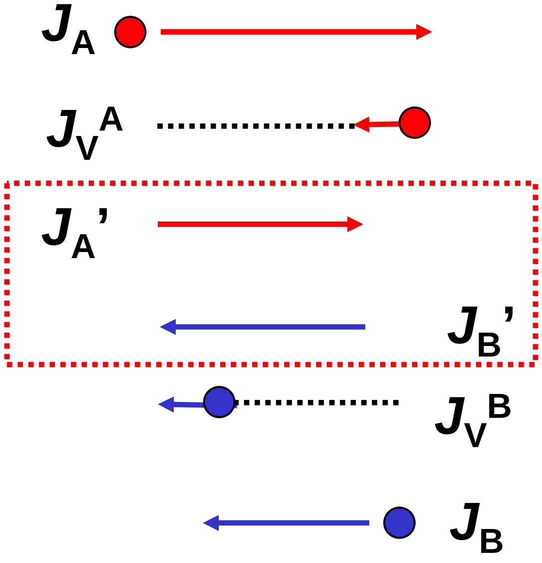
3. Diffusion in substitutional alloys

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



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

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



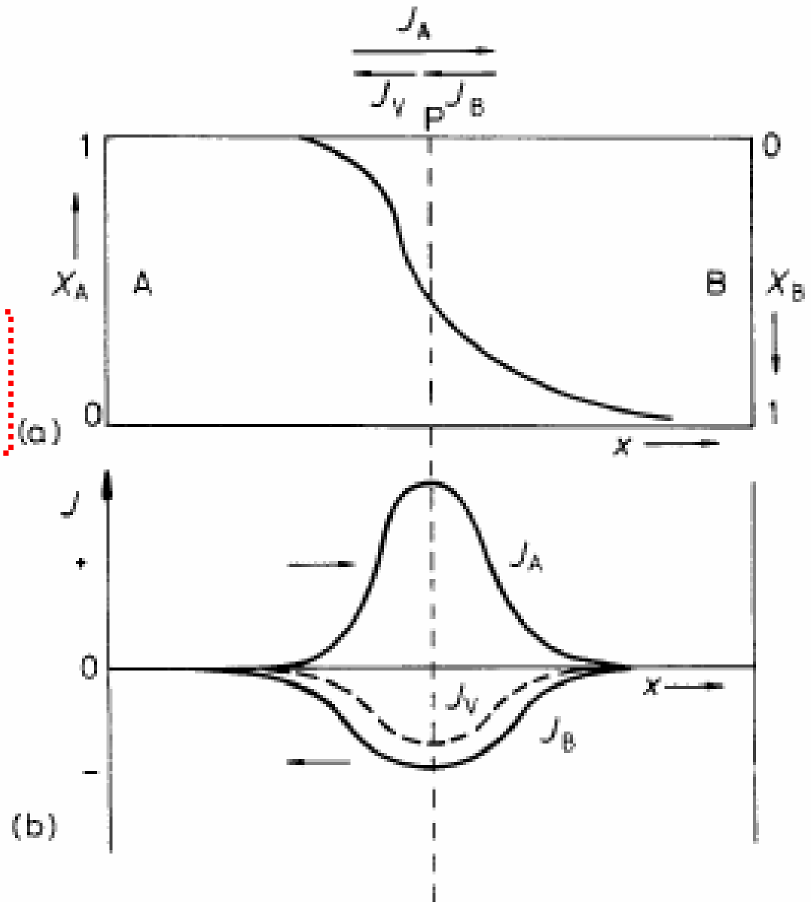
$$J'_B = J_B + J_B^v = -\tilde{D}\frac{\partial C_B}{\partial x}$$

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

1) INTERDIFFUSION

Assume that C_0: total number of atoms (A, B) per unit volume 일정/ 조성에 무관

$$C_o=C_A+C_B \qquad \frac{\partial C_A}{\partial x} = -\frac{\partial C_B}{\partial x}$$



Fluxes of A and B atoms across a given lattice plane

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

Due to the difference in diffusivities,

a flux difference is created.

$$|J_A| > |J_B|$$

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

$$J_V + \quad J_B \; = \; -J_A$$

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

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

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

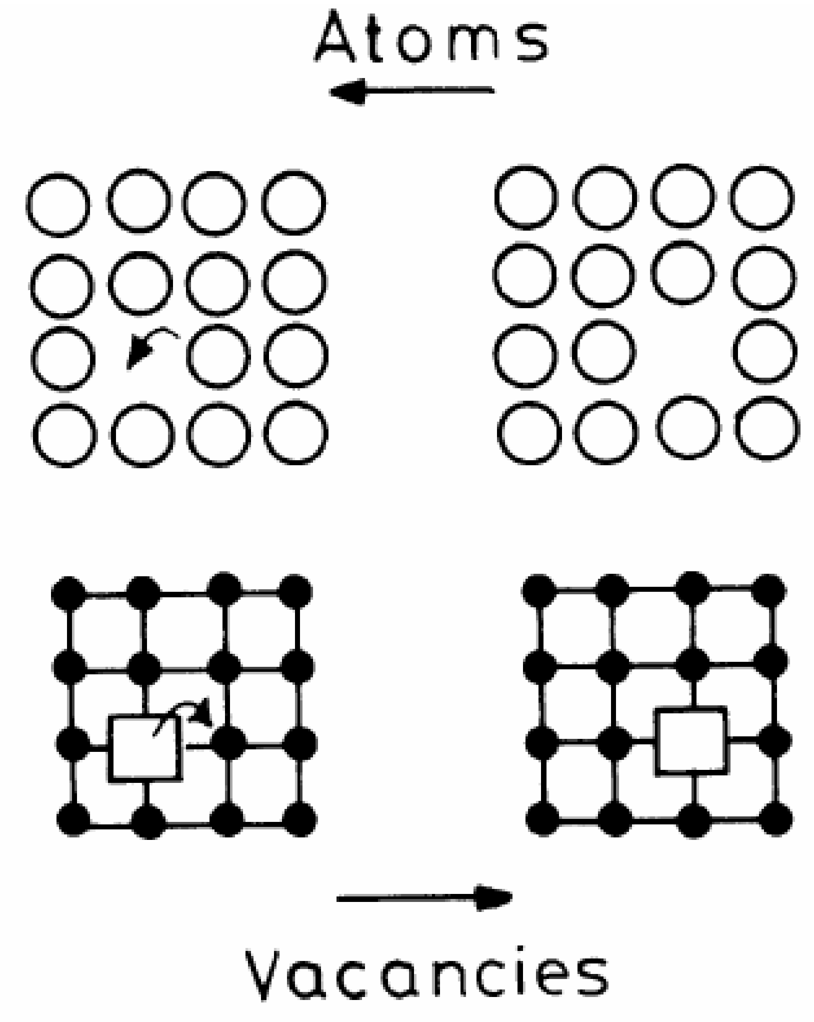


Fig. 2.16 The jumping of atoms in one direction can be considered as the jumping of vacancies in the other direction.

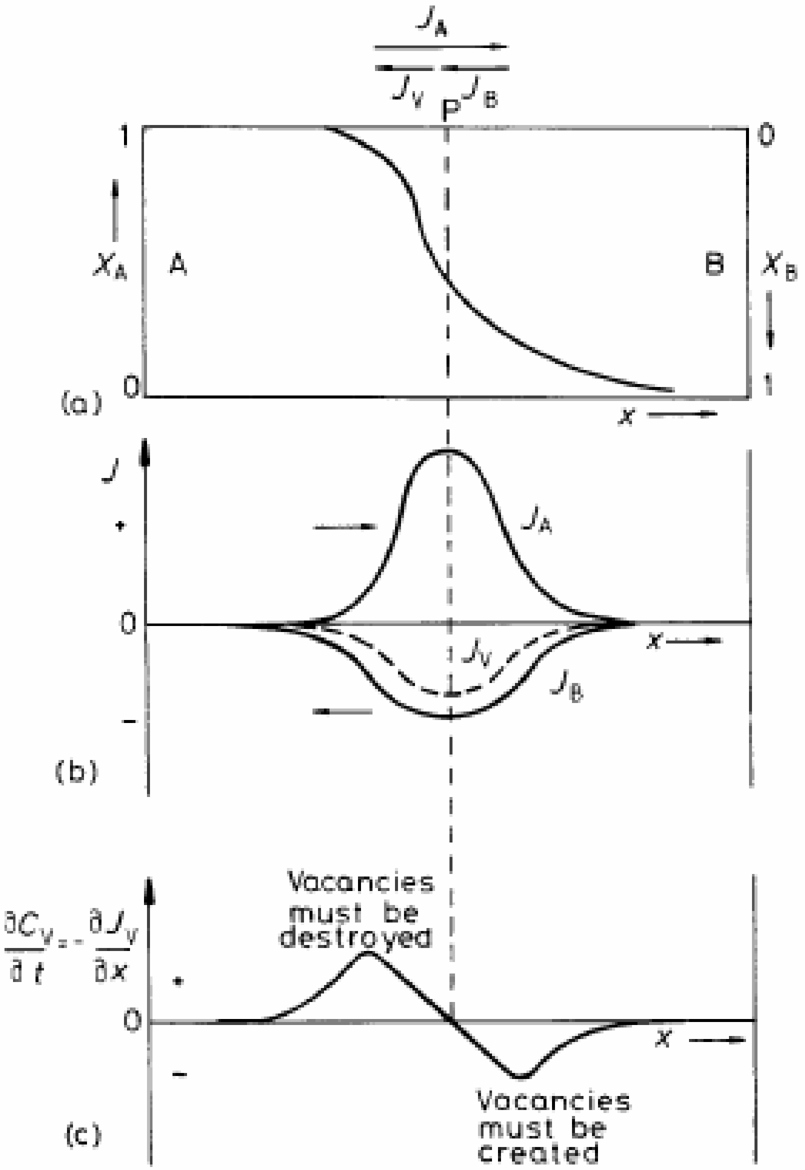
$$\frac{\partial C_v}{\partial t} = -\frac{\partial J_v}{\partial x} \text{ vs. } x\,?$$

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

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.

Kirkendall effect

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

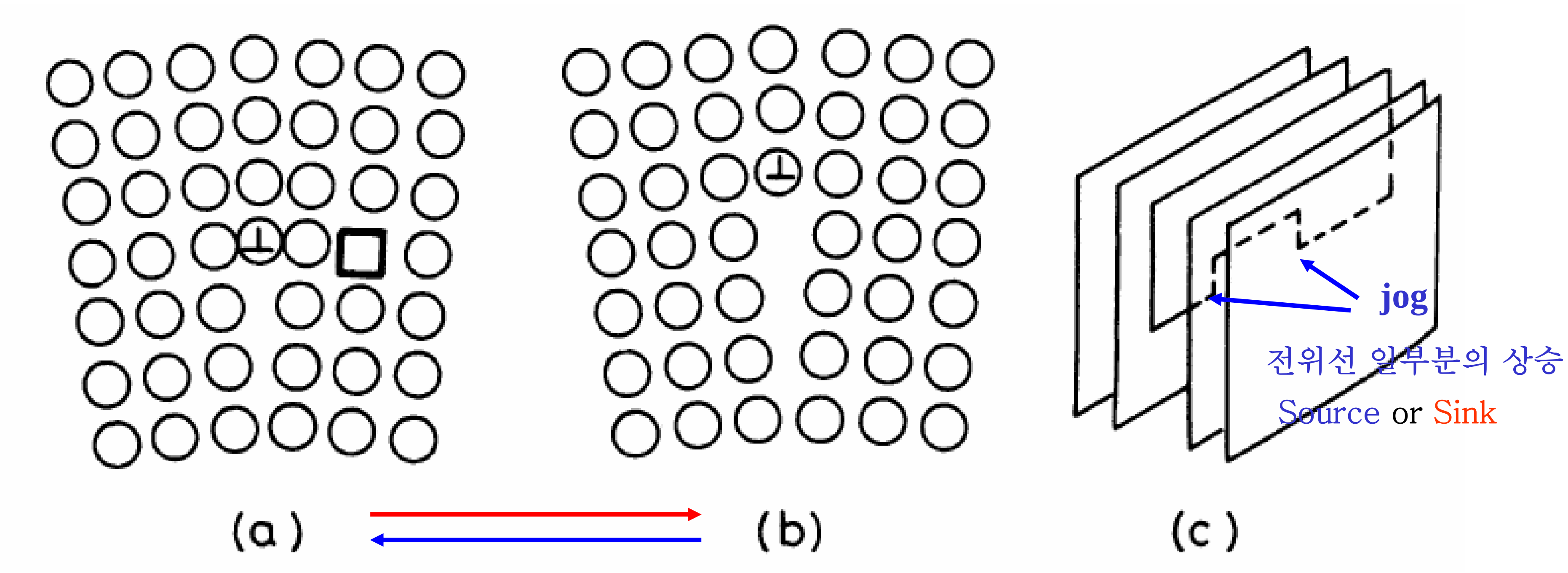


Fig. 2.17 (a) before, (b) after: a vacancy is absorbed at a jog on an edge dislocation (positive climb). (b) before, (a) after: a vacancy is created by negative limb of an edge dislocation. (c) Perspective drawing of a jogged edge dislocation.

If dislocation climbs continue to occur, what would happen?

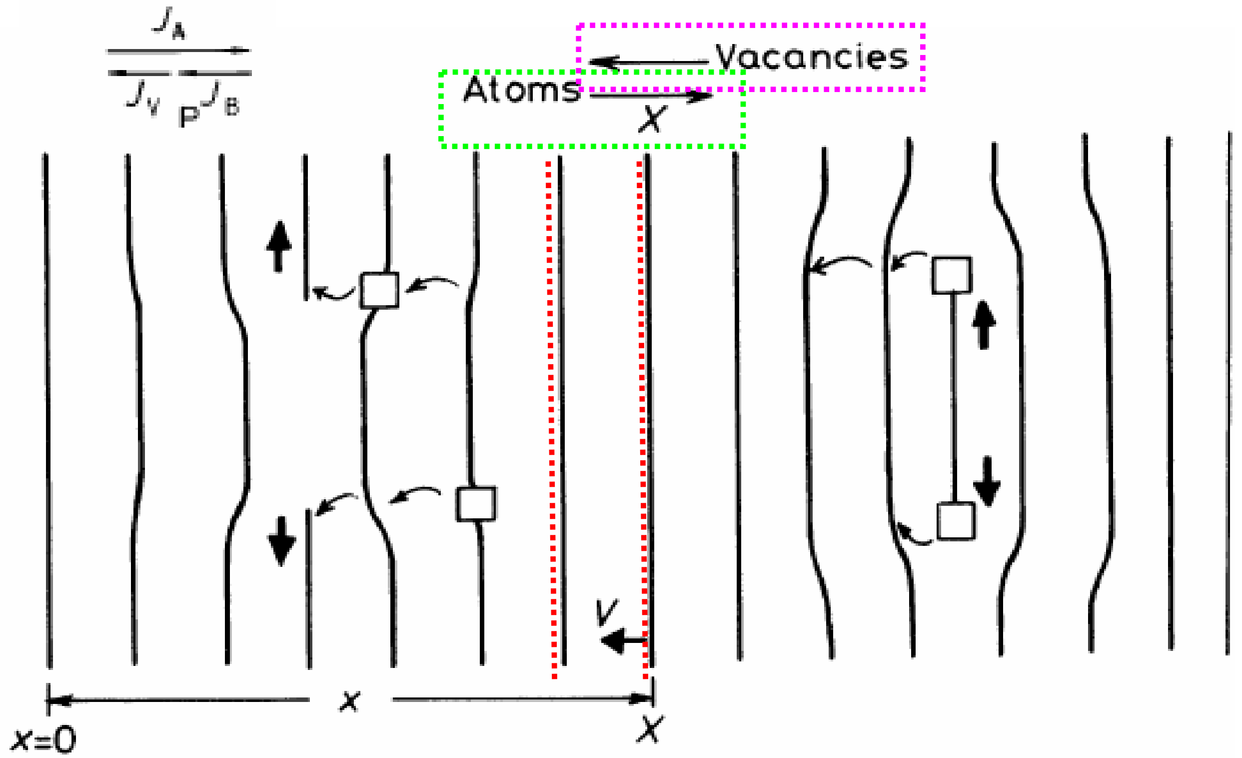


Fig. 2.18 A flux of vacancies causes the atomic planes to move through the specimen.

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

$$\boxed{Av\cdot\delta t\cdot C_0}=\boxed{J_vA\cdot\delta t}\longrightarrow\boxed{J_v}=C_0v$$

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

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.

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

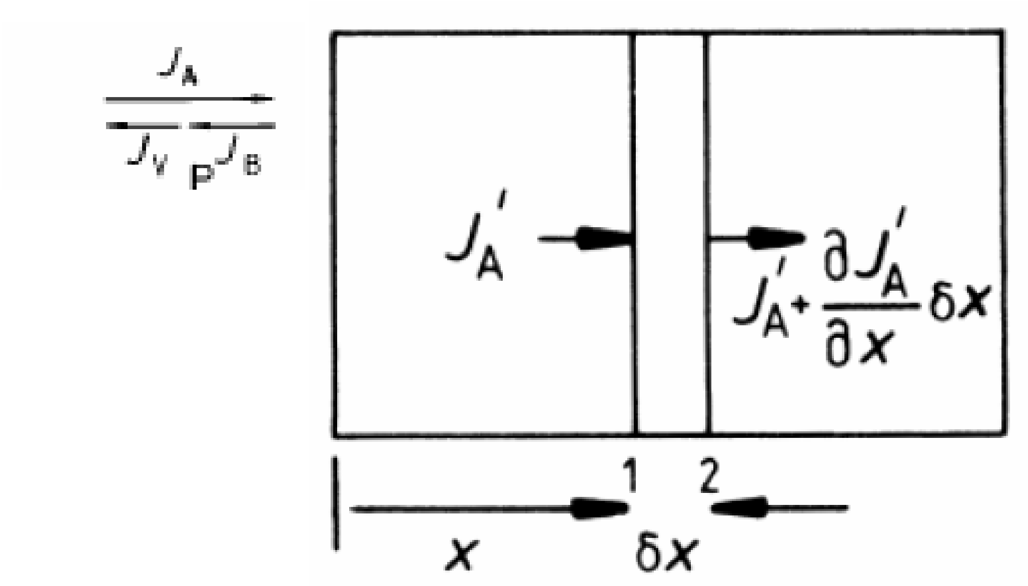


Fig. 2.19 Derivation of Fick's second law for interdiffusion. (See text for details.)

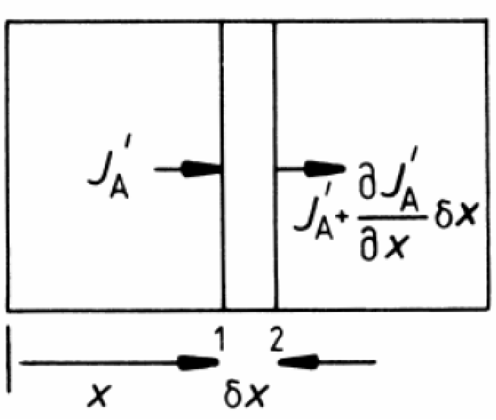
$$\boxed{\frac{\partial C_A}{\partial t} = -\frac{\partial J'_A}{\partial x}}$$

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

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

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

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

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

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

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

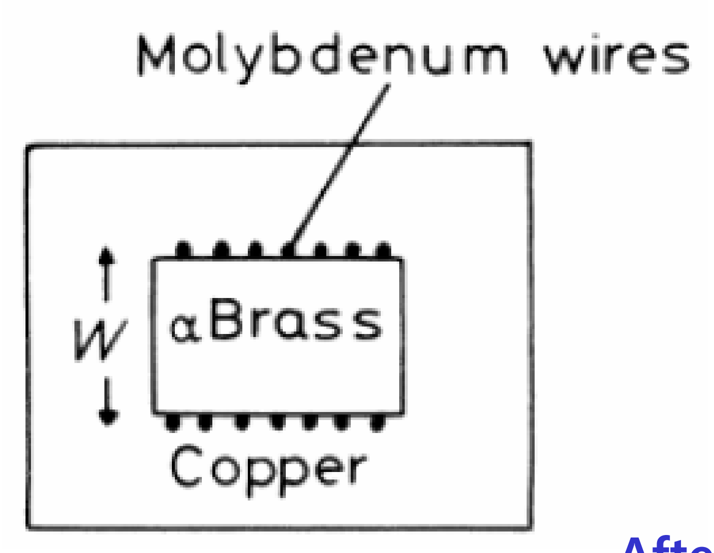
The interdiffusion coefficient $(\tilde{D})$ can be experimentally measured by determining the variation of X_A and X_B after annealing a diffusion couple.

How can we determine D_A and D_B?

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

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 know as the Kirkendall effect.

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

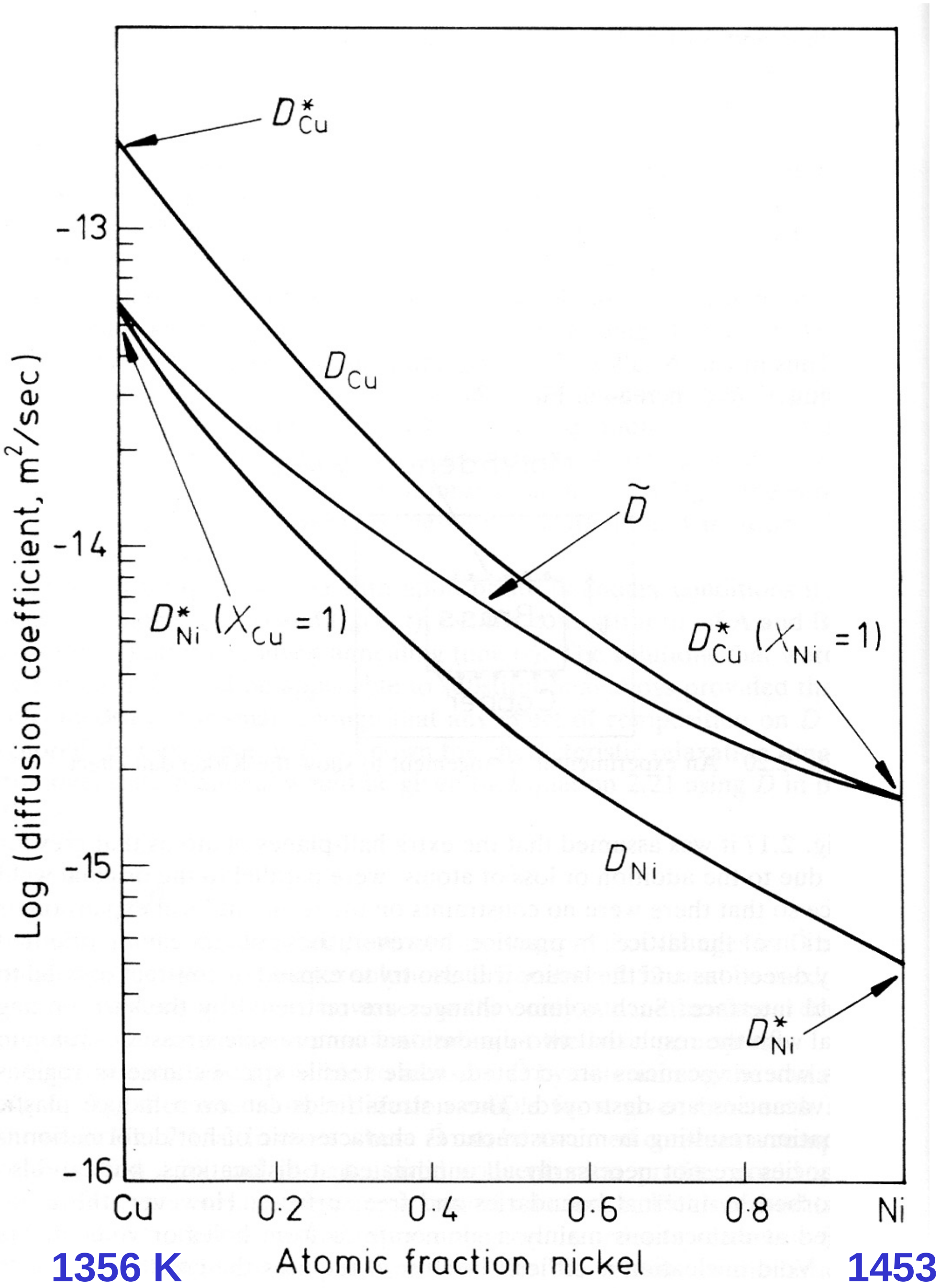
$$D_{Zn} > D_{Cu}$$

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.



1356 K **1453 K**

- 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).

Ferrite **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

➡ **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

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

In this case, D_B is called ‘impurity diffusion coefficient’.

- 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.

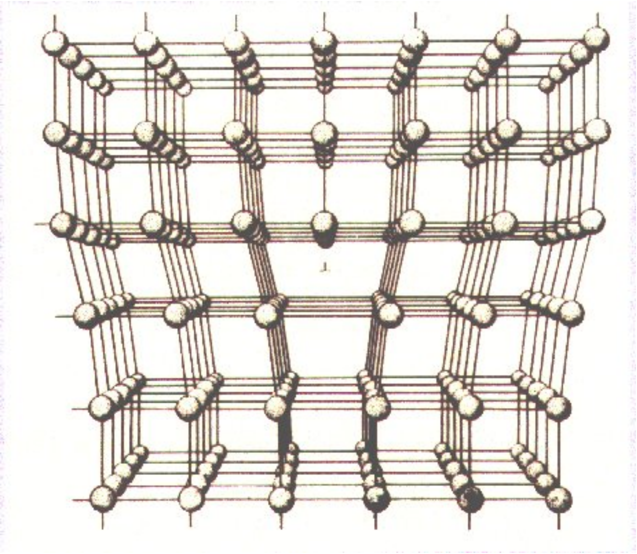
Atomic mobility

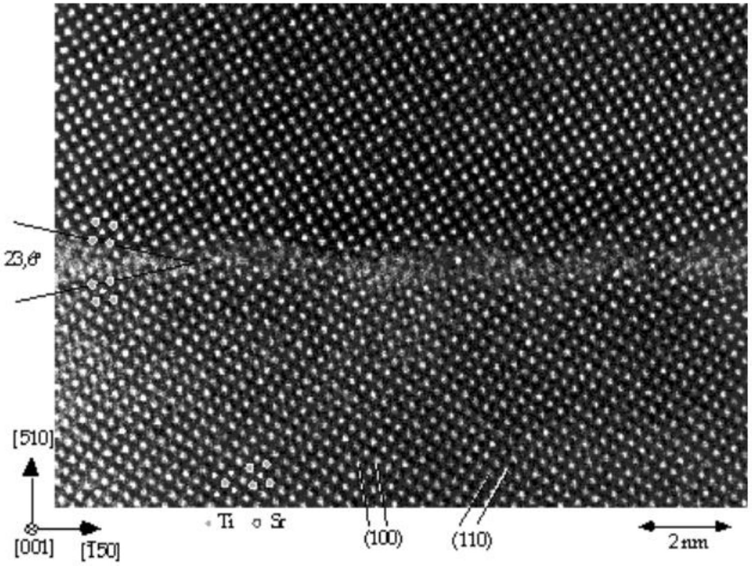
Ideal case, **Diffusion eventually stops, that is equilibrium is reached.**

➡ **Fick's first law**

Real materials contain <u>lattice defects</u>.

= more open structure = fast diffusion path.





➡ **Some atoms can lower their free energies if they migrate to such defects and at 'equilibrium' their concentrations will be higher in the vicinity of the defect than in the matrix.**

➡ **Fick's law alone is insufficient to describe how the concentration will vary with distance and time.**

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 aspects 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 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.

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

A **diffusion flux** is a combined **quantity of a drift velocity** and **random jumping motion.**

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

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

M_B : mobility of B atoms

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

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

Relationship between M_B and D_B

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

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

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

$$\boxed{D_B = M_B RTF}$$

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

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

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

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

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

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

For ideal or dilute solutions,

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

$$\therefore F = 1 \qquad D_B = M_B RT$$

For non-ideal concentrated solutions,

thermodynamic factor must be included.

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

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

Ex) Effect of E depends on the position (x) relative to a dislocation.

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

⇒

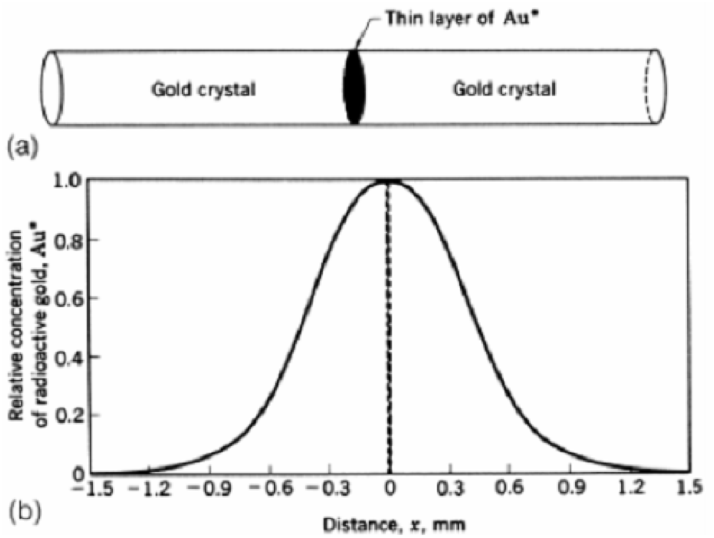
$$J_B = -D_B \cdot \frac{\partial C_B}{\partial x} - \frac{D_B C_B}{RT} \cdot \frac{\partial E}{\partial x}$$

Atoms diffusing towards regions of high concentration can be found

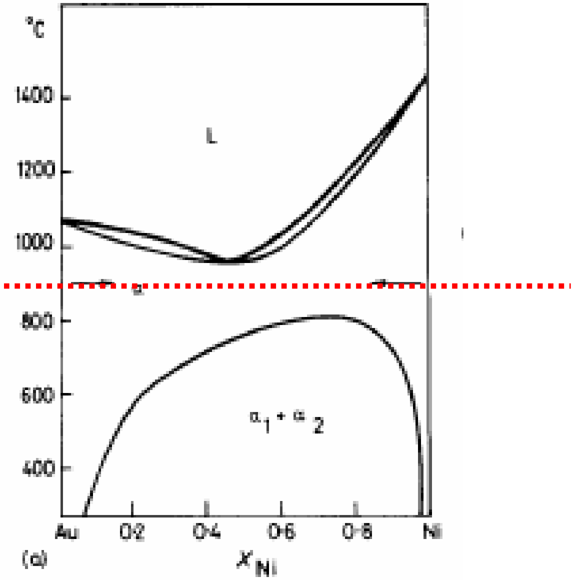
- **when diffusion occurs in the presence of an electric field or a temperature gradient.**
- **when the free energy curve has a negative curvature, which is known as spinodal decomposition.**

2.5 Tracer diffusion in binary alloys

1) Au* in Au



2) Au* in Au-Ni



It is possible to use radioactive tracers (D^*_{Au}) to determine the intrinsic diffusion coefficients (D_{Au}) of the components in an alloy .

$D^*_{Au} = D_{Au}$ (self diffusivity)

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

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.

If concentration gradient exhibit,

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

obtained by maker’s movement

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.

What would be the relation between the intrinsic chemical diffusivities D_B and tracer diffusivities D^*_B?

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

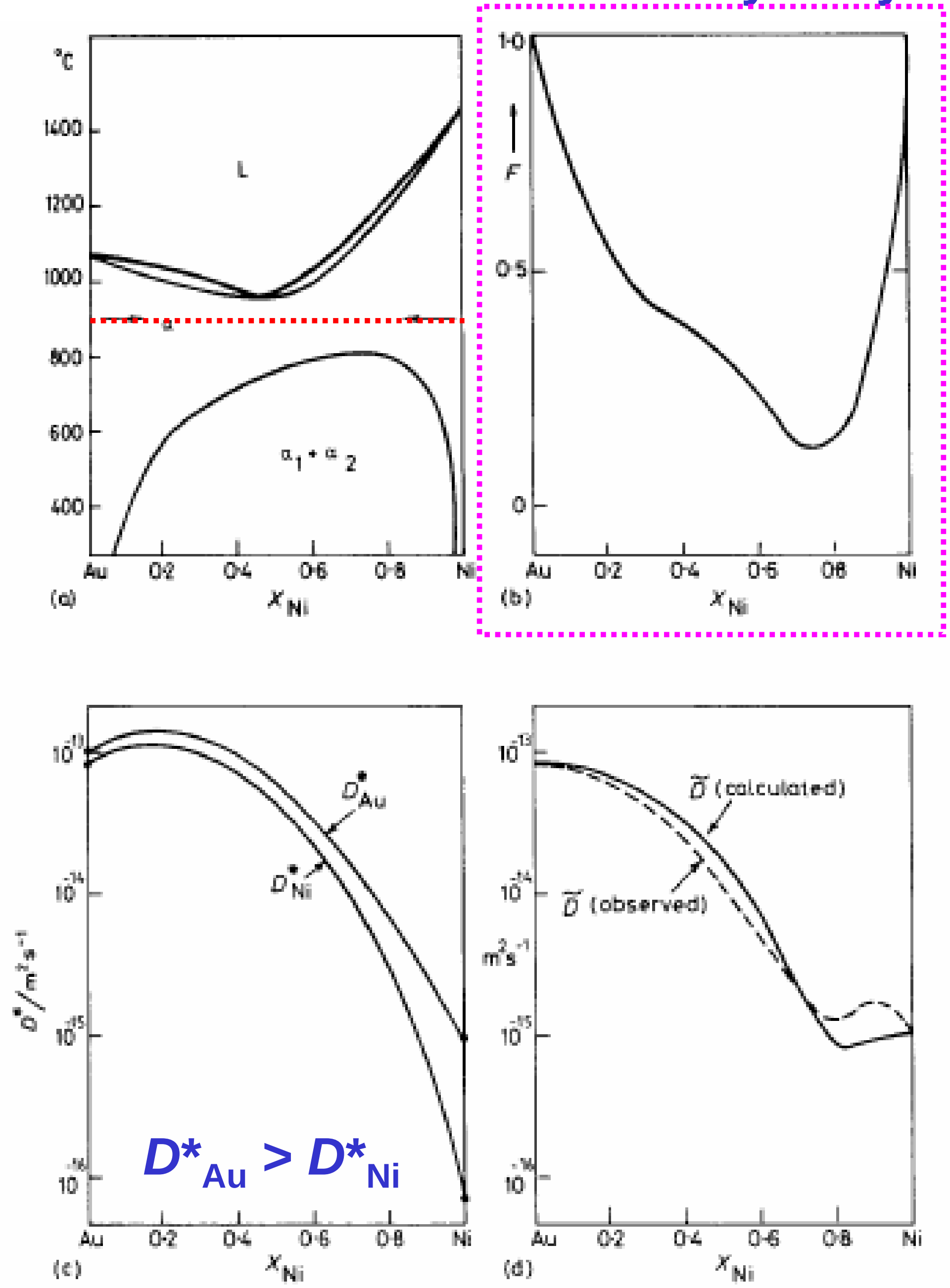
$$\boxed{\begin{aligned} D_A &= F D_A^* \\ D_B &= F D_B^* \end{aligned}} \Rightarrow \boxed{\tilde{D} = X_B D_A + X_A D_B = F\left(X_B D_A^* + X_A D_B^* \right)}$$

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

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

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

2.5 Tracer diffusion in binary alloys



$D^*_{Au} > D^*_{Ni}$

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

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

Fig. 2.22 Interdiffusion 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 interdiffusion coefficients compared with values calculated from (b) and (c). (From J.E. Reynolds, B.L. Averbach and Morris Cohen, *Acta Metallurgica*, 5 (1957) 29.)