

2009 fall

Phase Transformation of Materials

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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)

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

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

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

2. **Vacancy diffusion**

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

Comparing D_v with the self-diffusion coefficient of A, D_A , $D_v = D_A / X_v^e$

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:

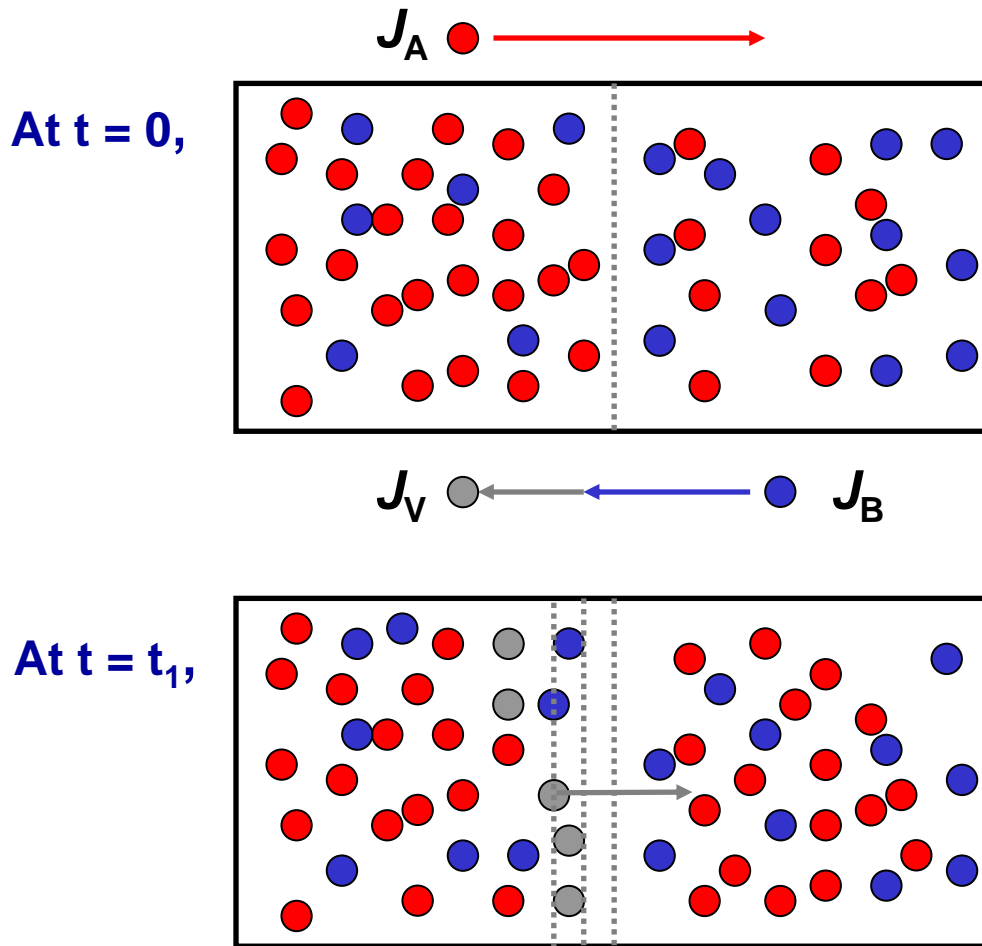
Process	Solution
Carburisation	$C = C_s - (C_s - C_0) \operatorname{erf}\left(\frac{x}{2\sqrt{Dt}}\right)$ <p>C_s = Surface concentration C₀ = Initial bulk concentration</p>
Decarburisation	$C = C_0 \operatorname{erf}\left(\frac{x}{2\sqrt{Dt}}\right)$ <p>C₀ = Initial bulk concentration</p>
Diffusion 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>C₁ = Concentration of steel 1 C₂ = Concentration of steel 2</p>
Homogenisation	$C = C_{\text{mean}} + \beta_0 \sin\left(\frac{\pi x}{l}\right) \exp\left(-\frac{t}{\tau}\right)$ <p>C_{mean} = Mean concentration b₀ = Initial concentration amplitude l = half-wavelength of cells t = relaxation time</p>

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**

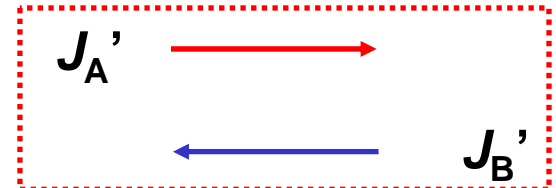
3. Diffusion in substitutional alloys

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



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

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



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

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

1) INTERDIFFUSION

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

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

**Fluxes of A and B atoms
across a given lattice plane**

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

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

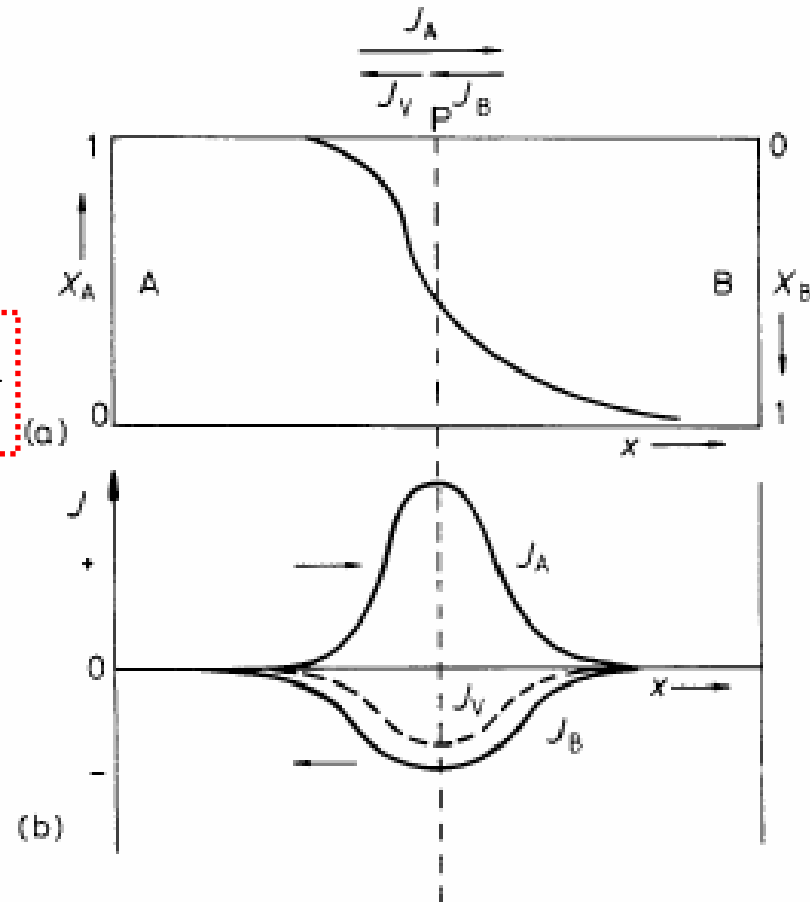
$$J_A \rightarrow J_{V,A} = -J_A \quad J_B \rightarrow J_{V,B} = -J_B$$

$$J_V + J_B = -J_A$$

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

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

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



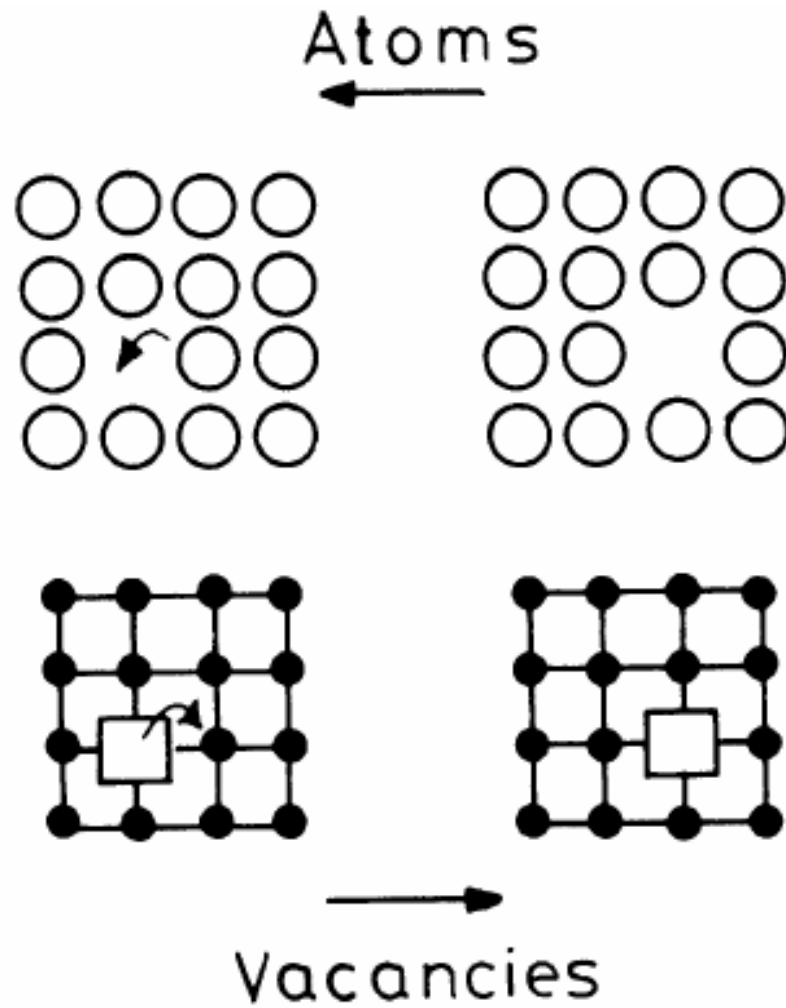


Fig. 2.16 The jumping of atoms in one direction can be considered as the jumping of vacancies in the other direction.

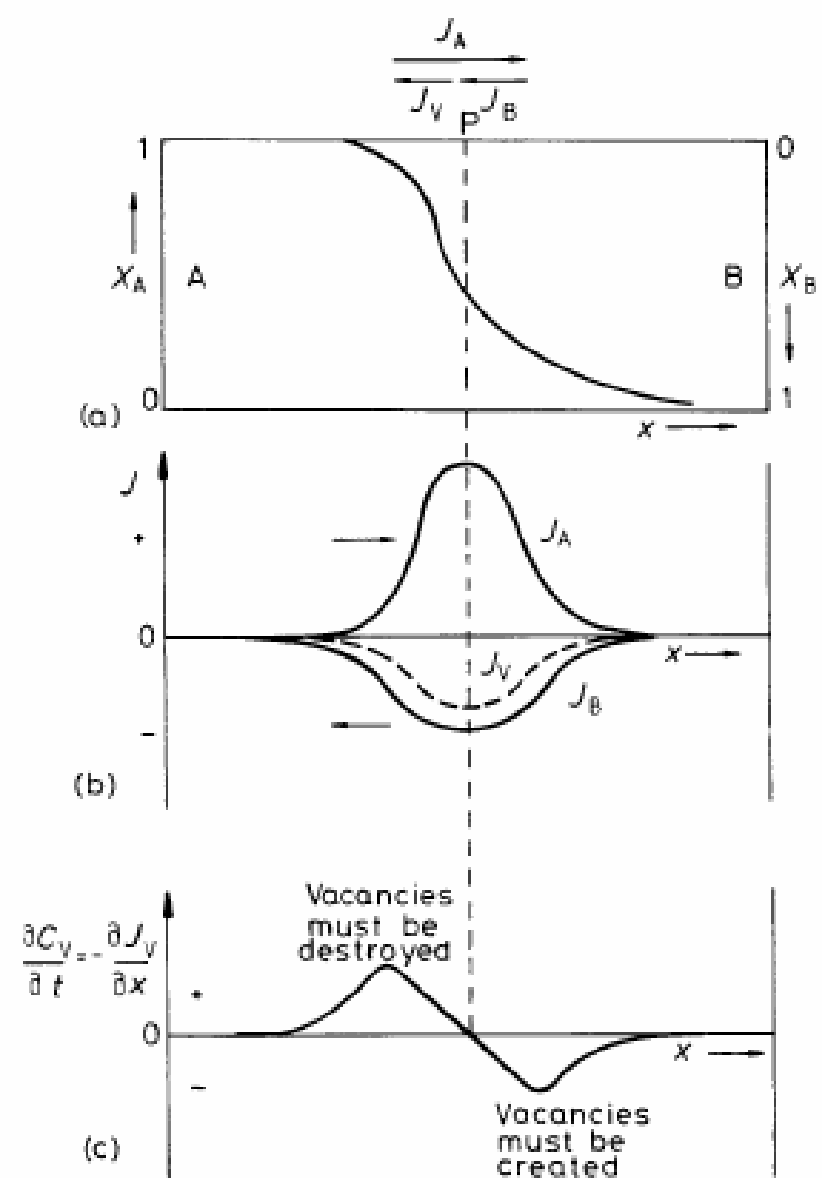
$$\frac{\partial C_V}{\partial t} = -\frac{\partial J_V}{\partial x} \text{ vs. } x?$$

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

What would become of
excess vacancy?

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

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



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.⁸

Kirkendall effect

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

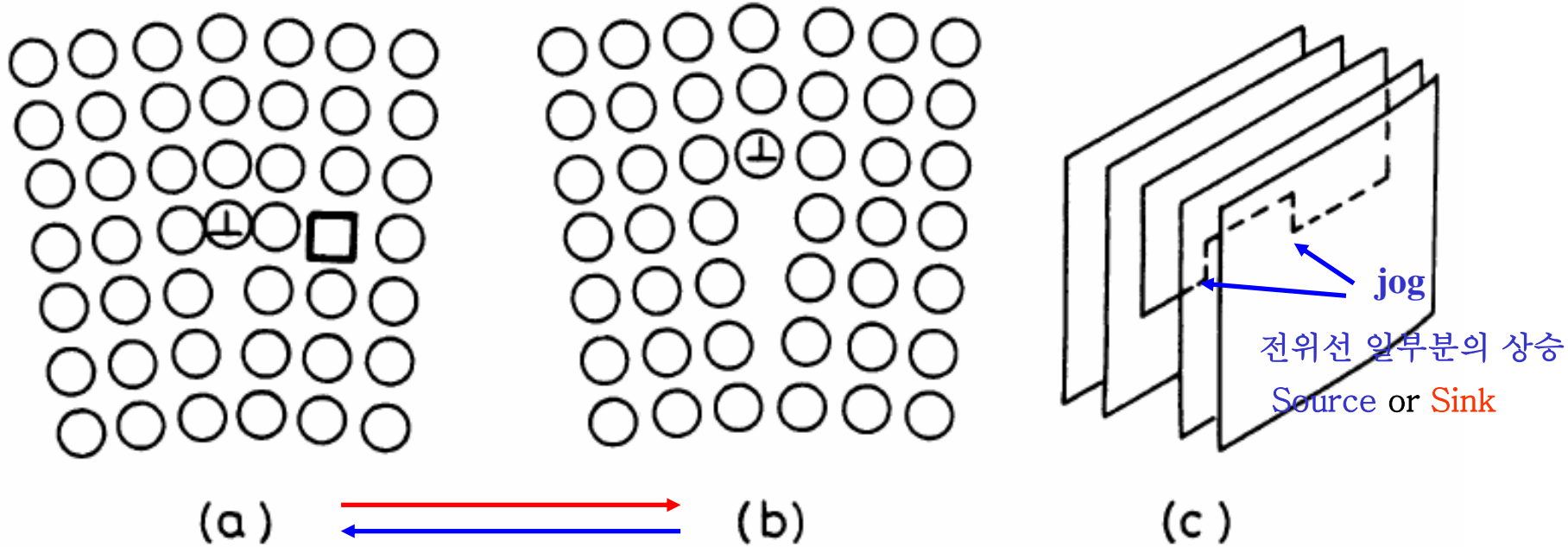


Fig. 2.17 (a) before, (b) after: a vacancy is absorbed at a jog on an edge dislocation (positive climb). (b) before, (a) after: a vacancy is created by negative limb of an edge dislocation. (c) Perspective drawing of a jogged edge dislocation.

If dislocation climbs continue to occur, what would happen? 9

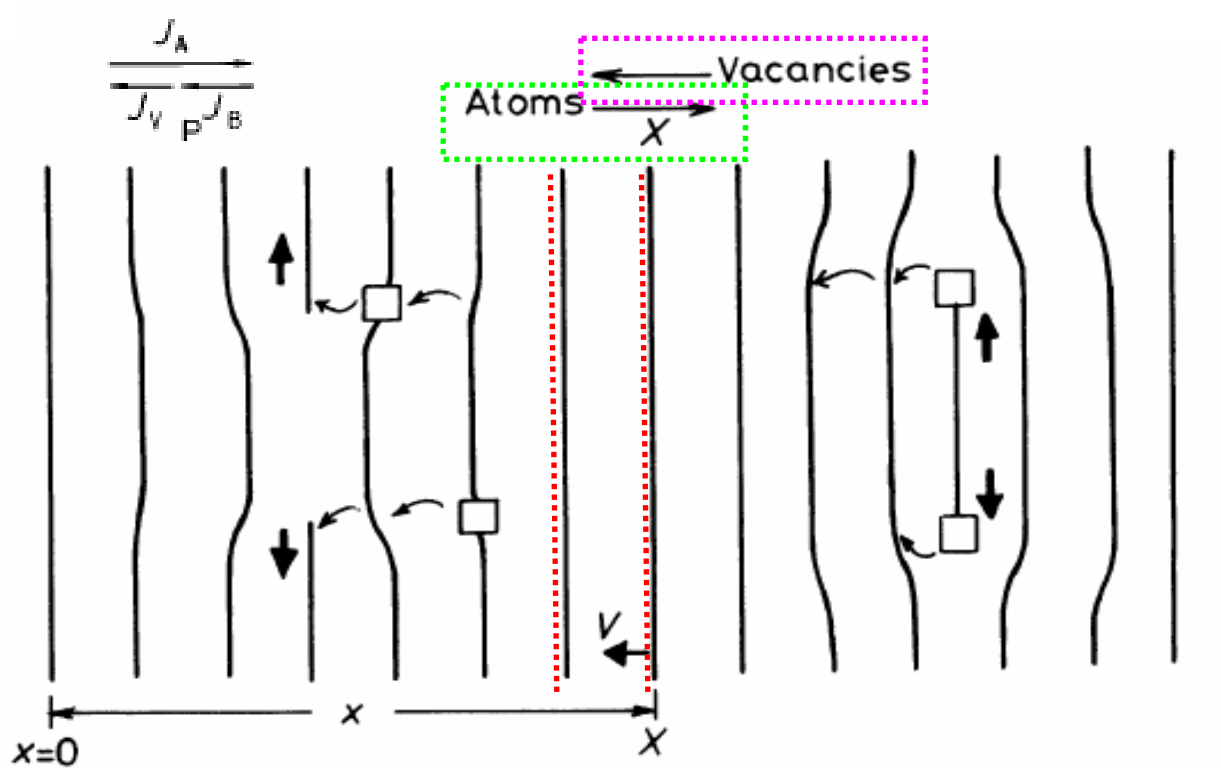


Fig. 2.18 A flux of vacancies causes the atomic planes to move through the specimen.

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

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

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

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.

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

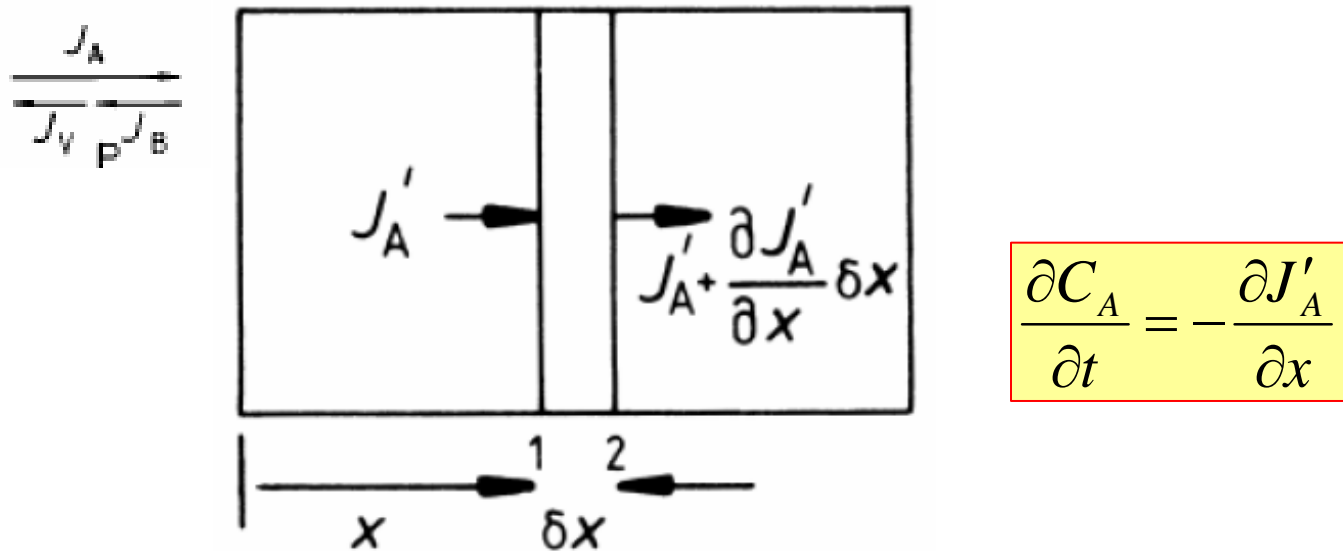


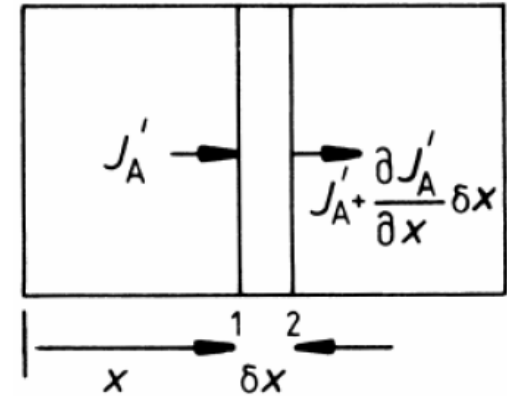
Fig. 2.19 Derivation of Fick's second law for interdiffusion. (See text for details.)

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

$$J'_A = J_A + vC_A$$

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

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

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

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

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

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

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

Fick's 2nd law for substitutional alloy

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

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