2009 fall

Phase Transformation of Materials

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Contents for previous class

- **Effect of Temperature on Solid Solubility**

$$X_B^e = A\exp\left\{-\frac{Q}{RT}\right\}$$

- **Equilibrium Vacancy Concentration**

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

- **Influence of Interfaces on Equilibrium**

$$\Delta G = \frac{2\gamma V_m}{r}$$ **Gibbs-Thomson effect**

- **Gibbs-Duhem Equation:** Be able to calculate the change in chemical potential that result from a change in alloy composition.

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

- **Ternary Equilibrium: Ternary Phase Diagram**

Contents in Phase Transformation

상변태를 이해하는데 필요한 배경

- **(Ch1) 열역학과 상태도: Thermodynamics**
- **(Ch2) 확산론: Kinetics**
- **(Ch3) 결정계면과 미세조직**

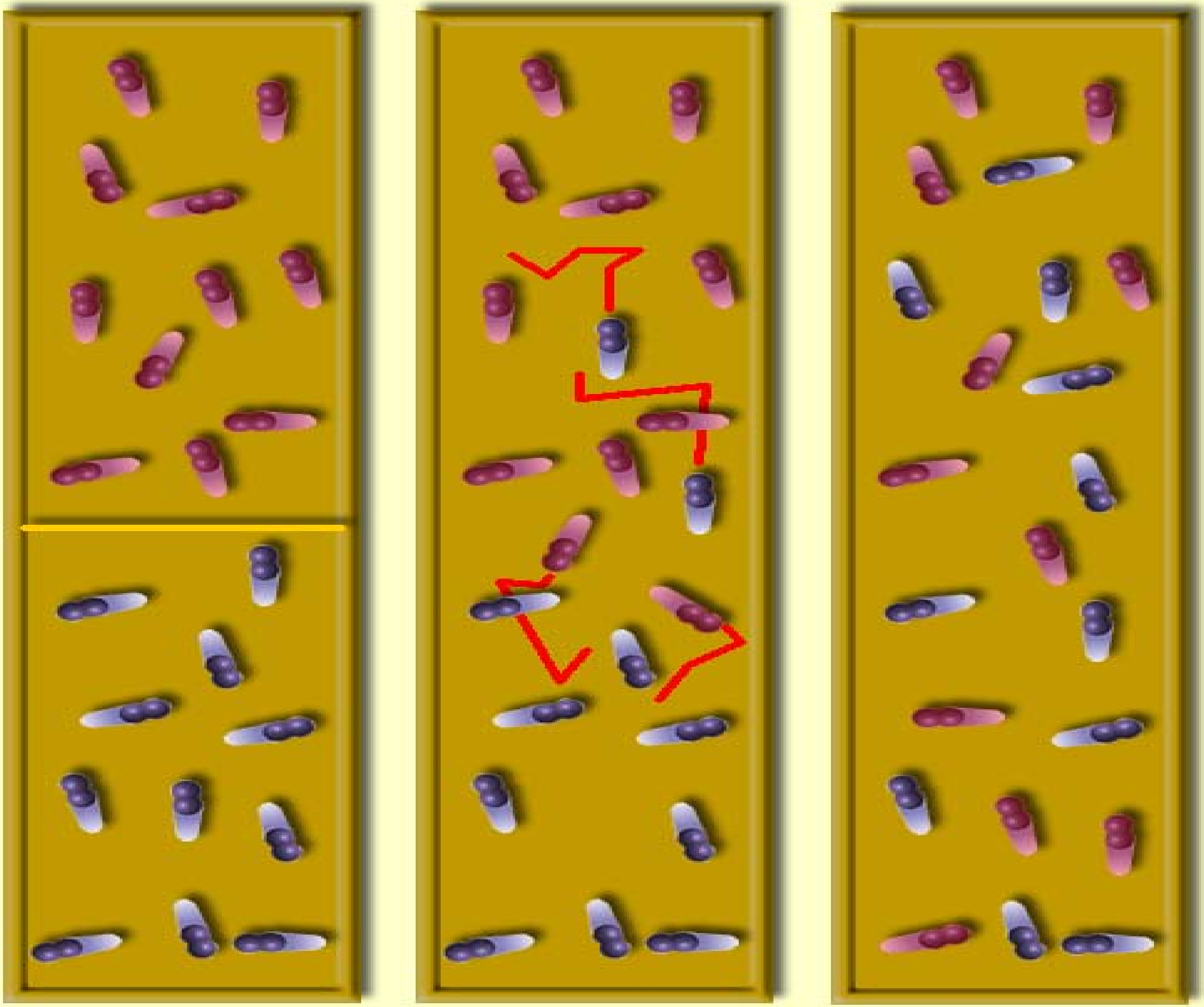
대표적인 상변태

- **(Ch4) 응고: Liquid → Solid**
- **(Ch5) 고체에서의 확산 변태: Solid → Solid (Diffusional)**
- **(Ch6)고체에서의 무확산 변태: Solid → Solid (Diffusionless)**

Contents for today’s class

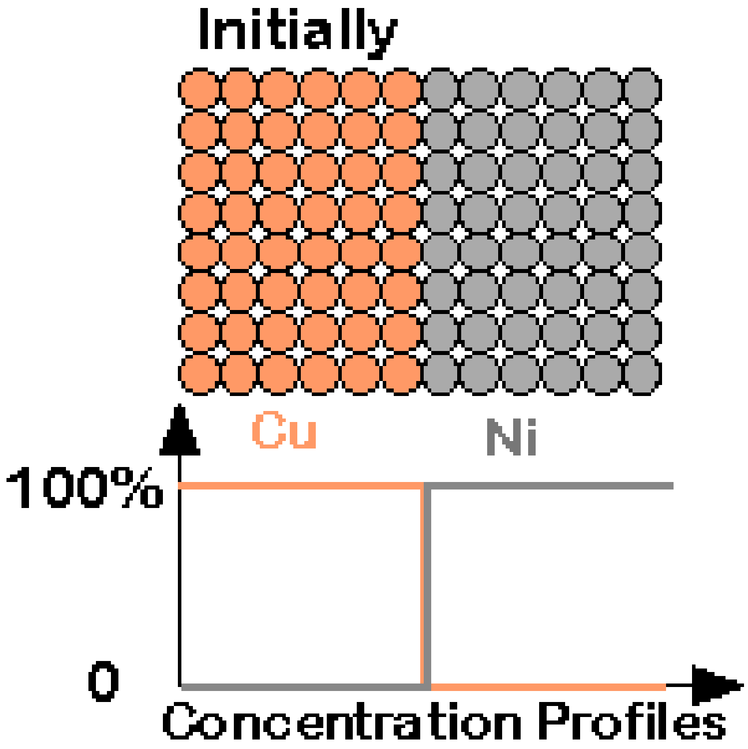
- Diffusion
- Interstitial Diffusion – Fick’s First Law
- Effect of Temperature on Diffusivity
- Nonsteady-state diffusion – Fick’s Second Law

Diffusion

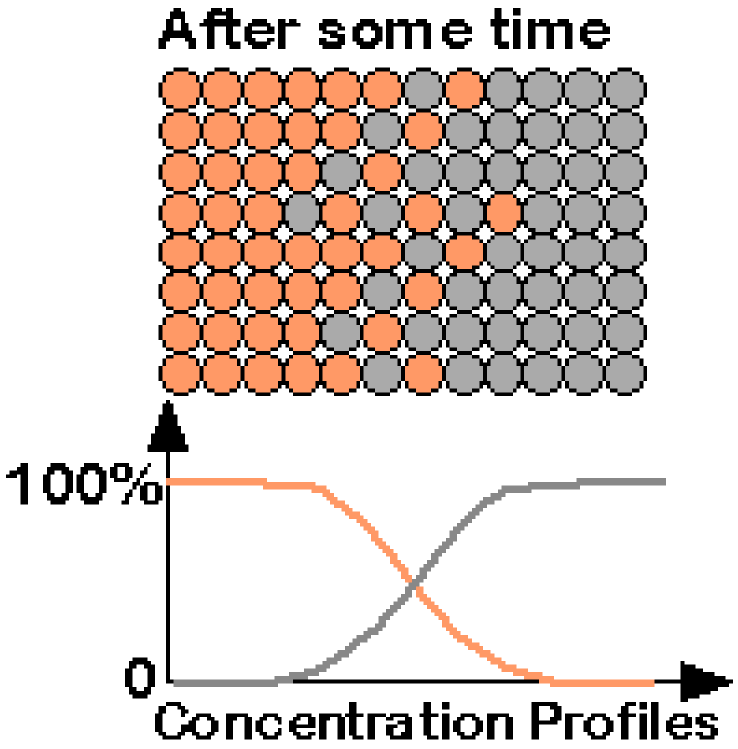


Diffusion: THE PHENOMENON

- **Interdiffusion**: in a solid with more than one type of element (an alloy), atoms tend to migrate from regions of large concentration.



Substitutional diffusion



Interstitial diffusion

Mechanism of Solid-State Diffusion

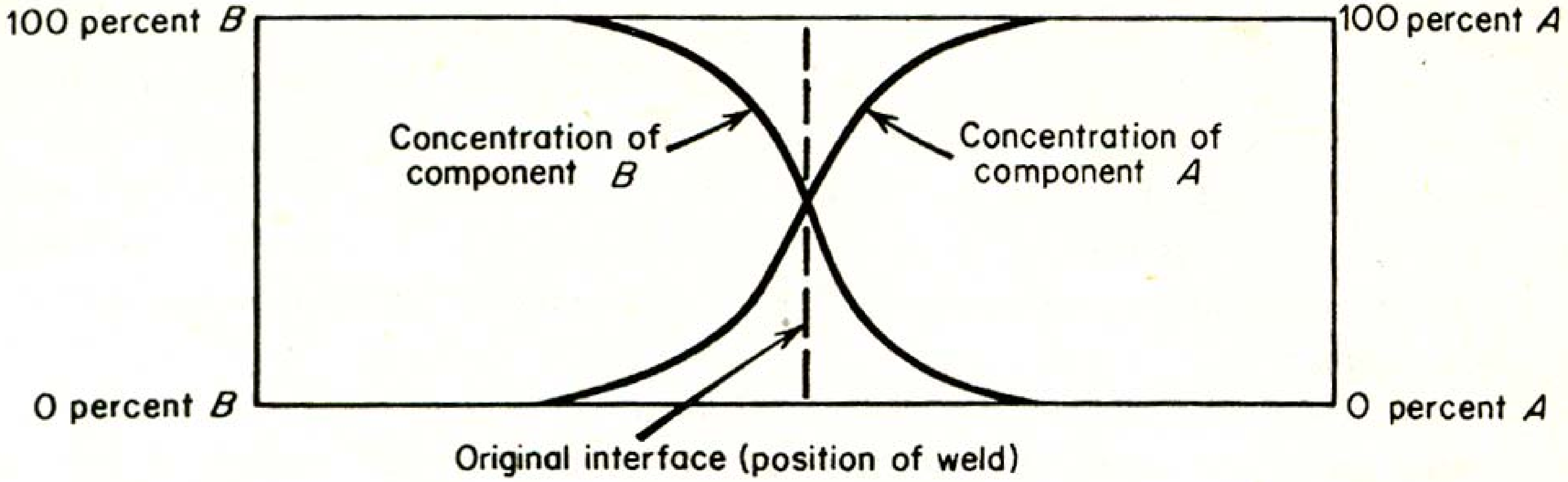
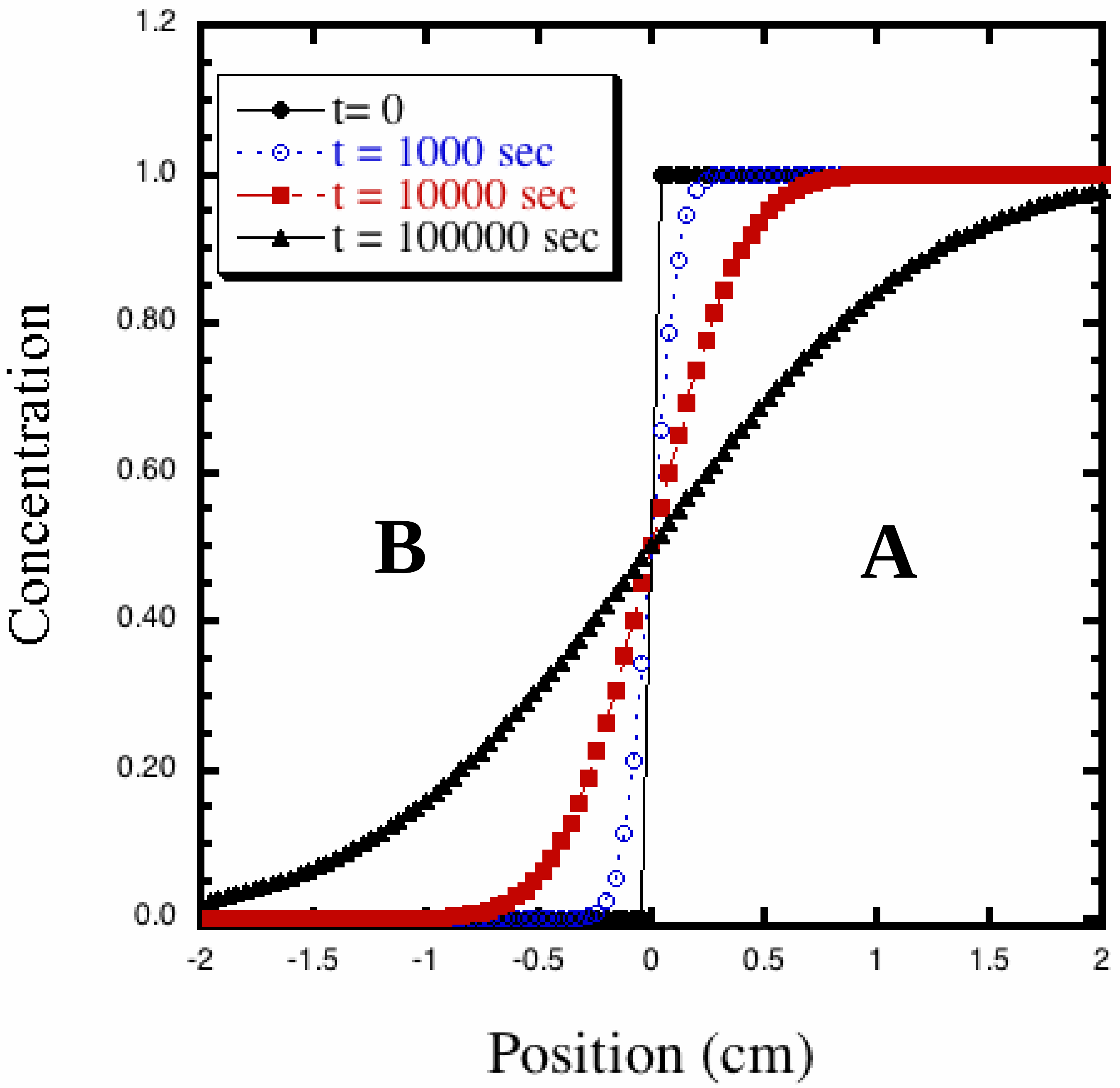


Fig. 10.6 Curves showing concentration as a function of distance along a diffusion couple. Curves of this type are usually called *penetration curves.*

R.E. Reed-Hill, Physical Metallurgy Principles


1.2
1.0
0.80
0.60
0.40
0.20
0.0
Concentration
t= 0
t = 1000 sec
t = 10000 sec
t = 100000 sec
B
A
-2
-1.5
-1
-0.5
0
0.5
1
1.5
2
Position (cm)

Diffusion

Movement of atoms to reduce its chemical potential μ.

Driving force: Reduction of G

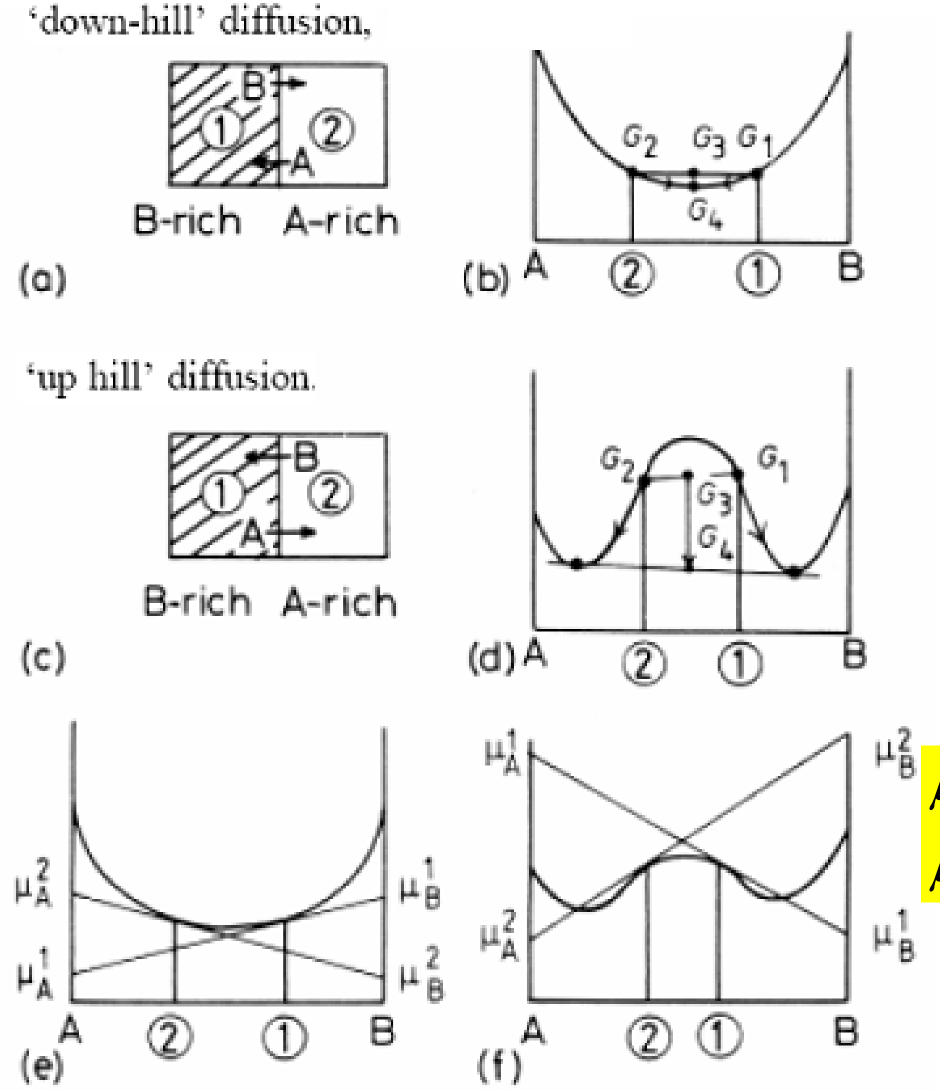
Down-hill diffusion

movement of atoms from a high concentration region to low concentration region.

Up-hill diffusion

movement of atoms from a low concentration region to high concentration region

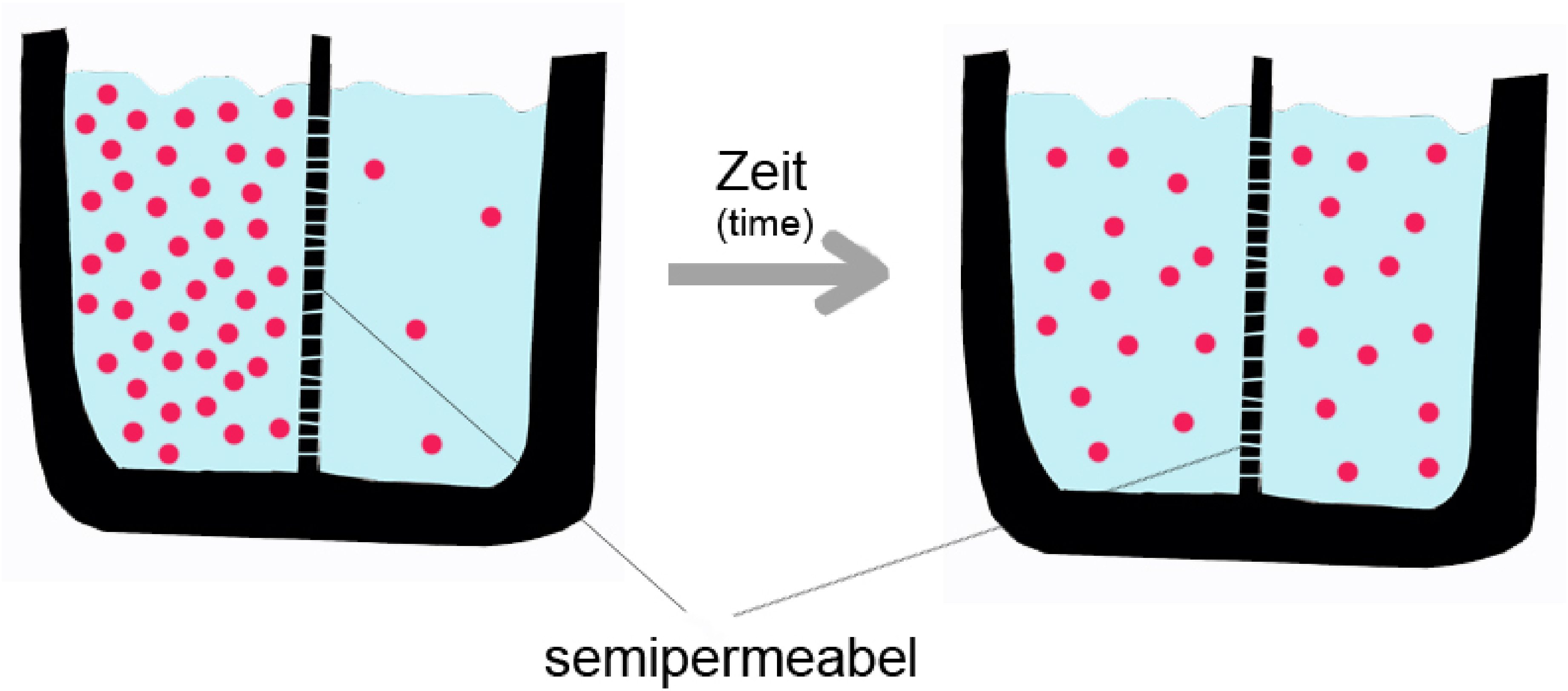
$$\mu_A^1 < \mu_A^2$$
$$\mu_B^1 > \mu_B^2$$



$$\mu_A^1 > \mu_A^2$$
$$\mu_B^1 < \mu_B^2$$

Down-hill diffusion

movement of atoms from a high concentration region to low concentration region.



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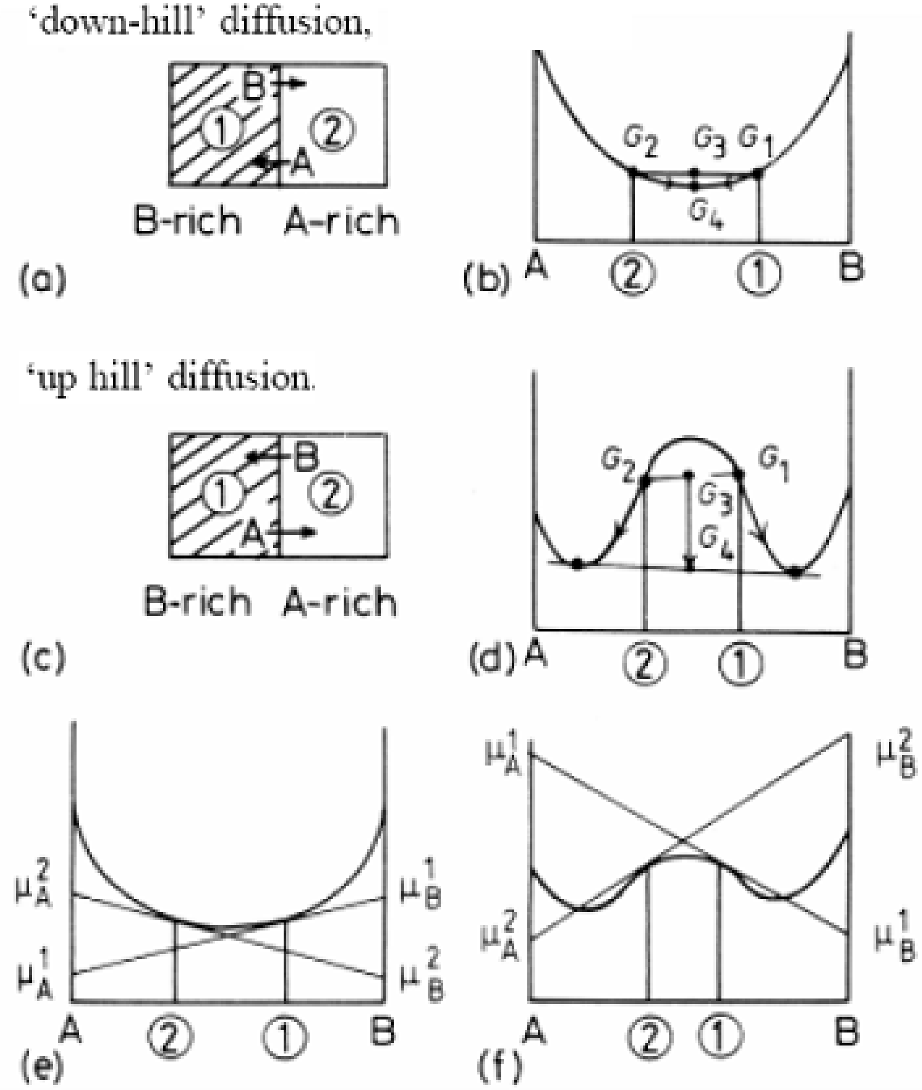
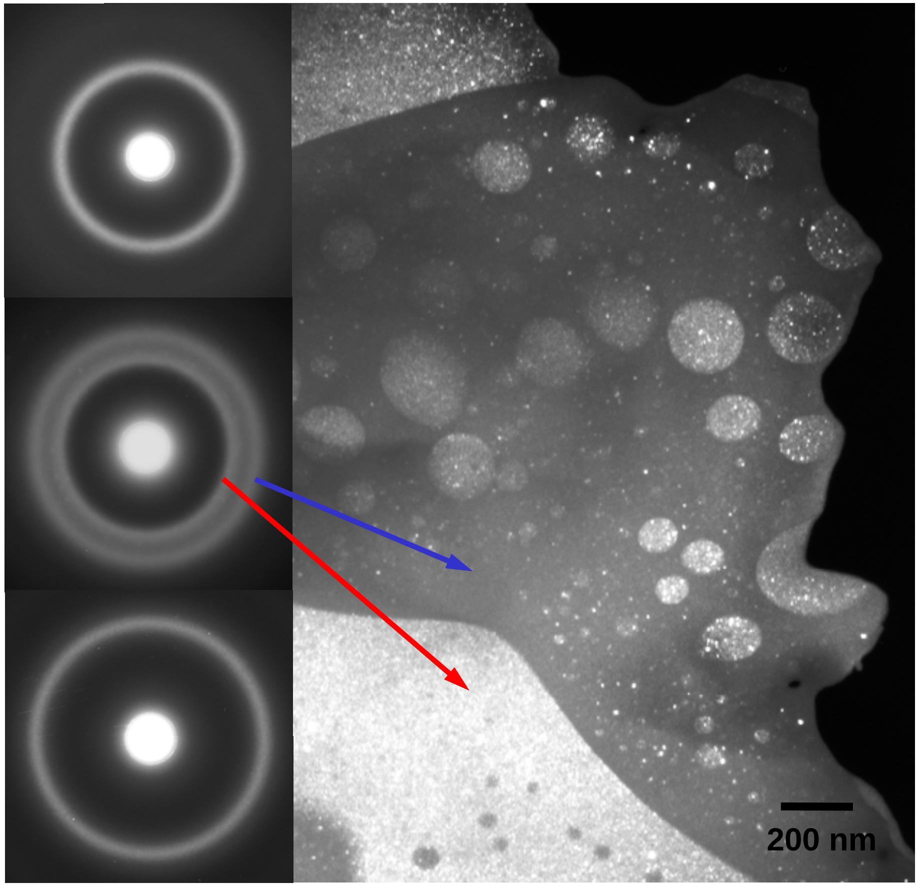


$$\mu_A^1 > \mu_A^2$$
$$\mu_B^1 < \mu_B^2$$

Phase separation in metallic glasses



$Nd_{60}Al_{10}Co_{30}$
2.91 Å

$Nd_{30}Zr_{30}Al_{10}Co_{30}$

2.37 Å, 2.99 Å

$Zr_{60}Al_{10}Co_{30}$
2.40 Å

TEM results for $Nd_{30}Zr_{30}Al_{10}Co_{30}$ alloy

Diffusion

Diffusion : Mechanism by which matter transported through matter

What is the driving force for diffusion?

⇒ a concentration gradient (x)

⇒ a chemical potential (o)

But this chapter will explain with “concentration gradients for a convenience”.

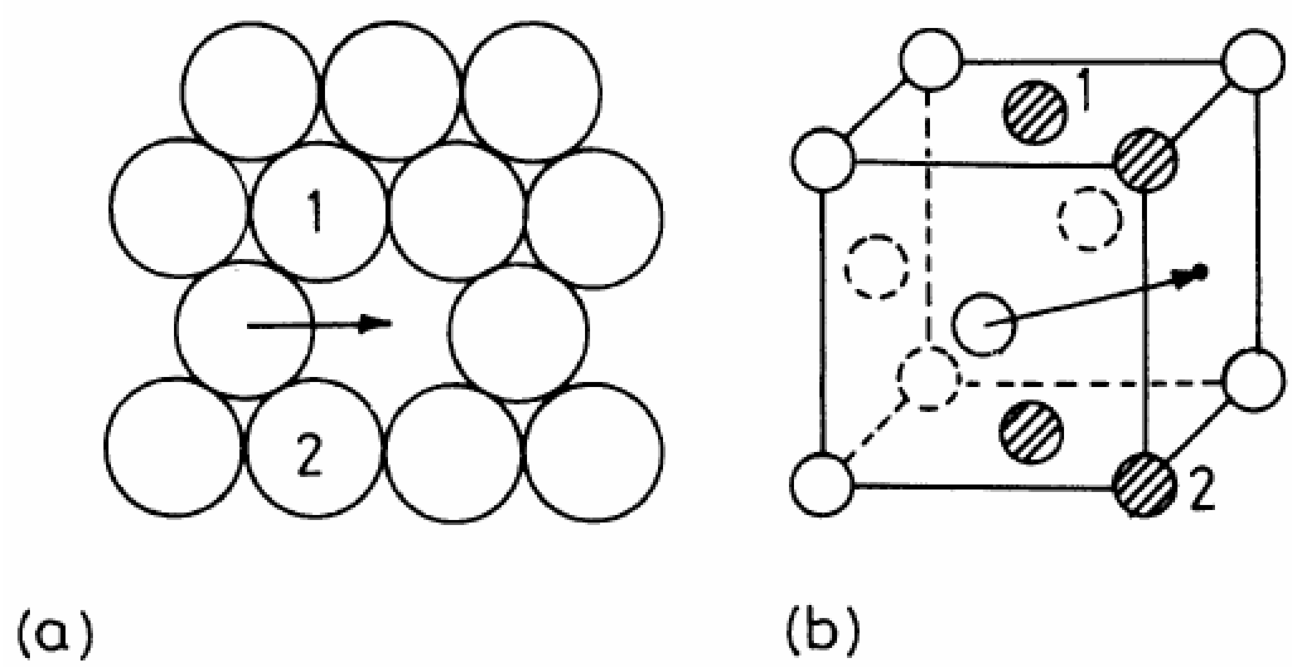
Atomic mechanisms of diffusion

Substitutional vs. Interstitial diffusion

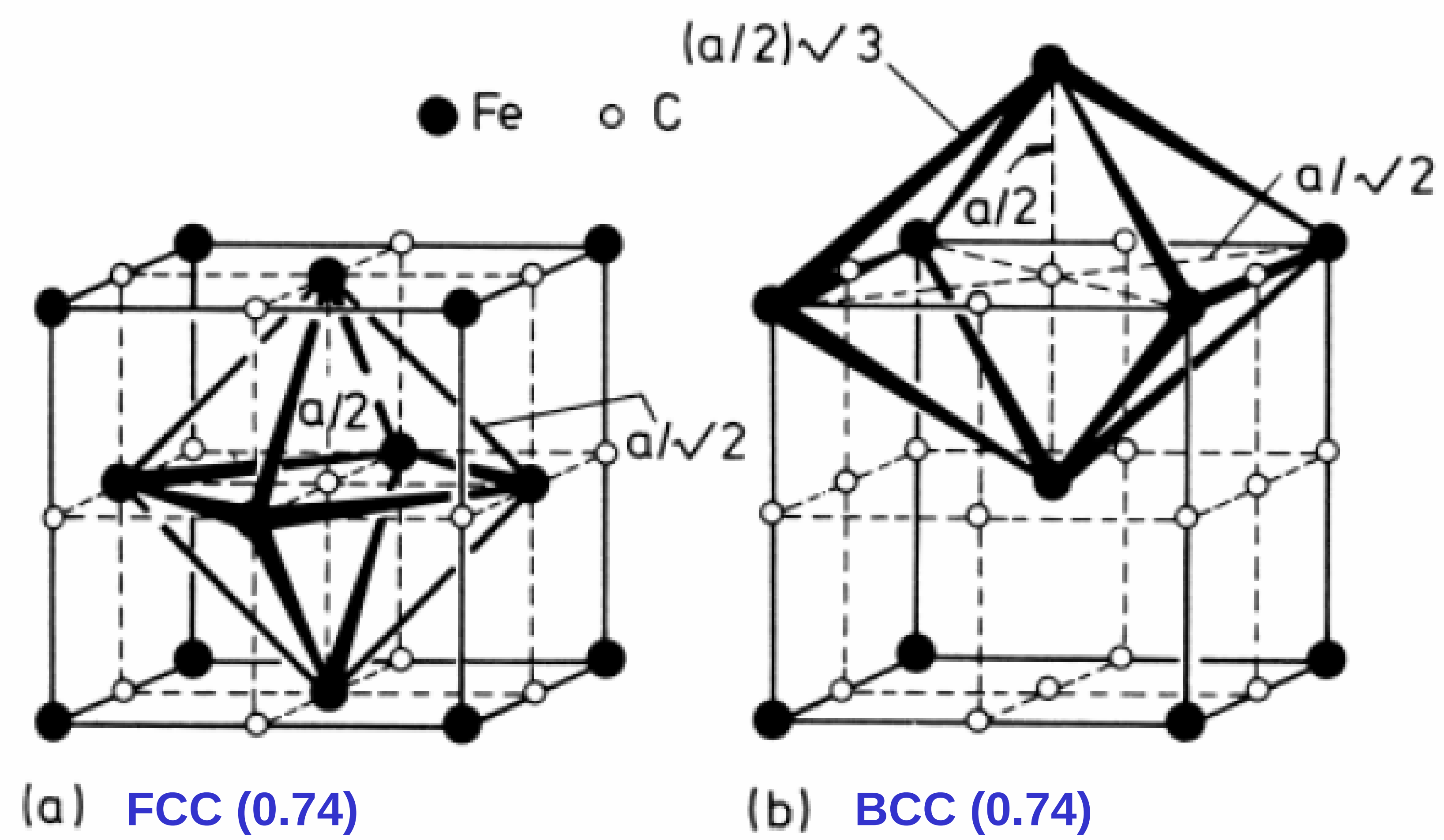
The mean vibrational energy is **3kT**, therefore the amplitude of thermal oscillation of an atom increases markedly with temperature. If a neighboring atom site is vacant, then the oscillation atom can change site with a certain probability (**atom jumping**). The probability consists of creation of the vacant site and movement of a neighboring atom into the site.

Substitutional diffusion

FCC



Interstitial diffusion

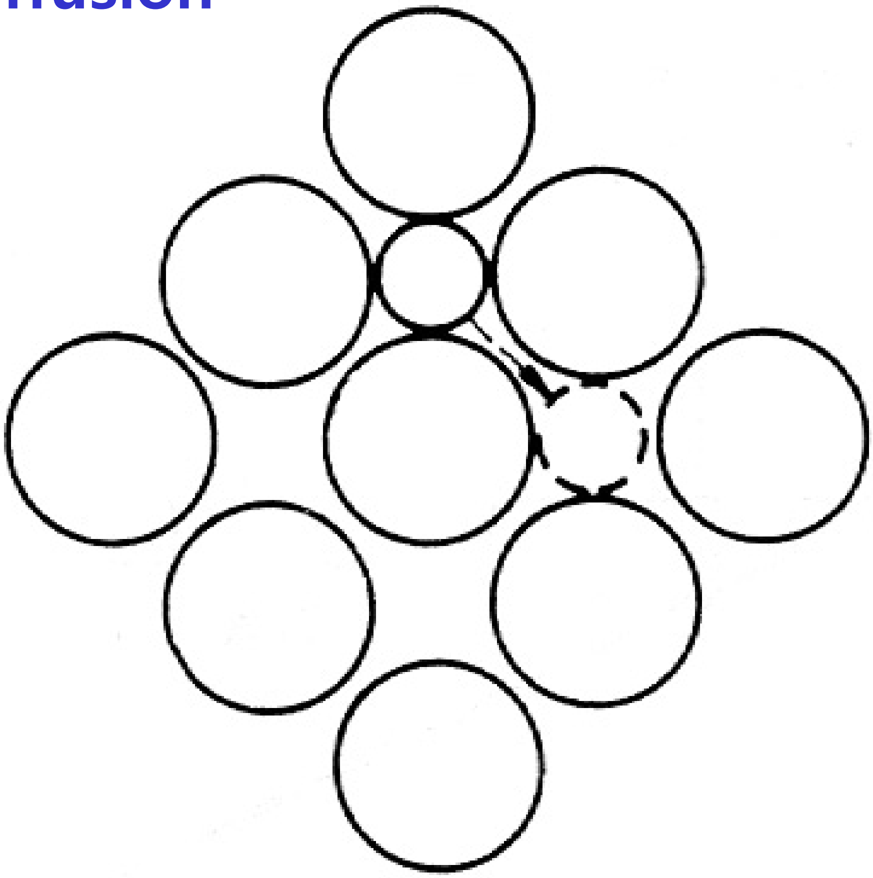


FCC (0.74)

BCC (0.74)

Fig. 2.3 (a) Octahedral interstices (0) in an fcc crystal. (b) Octahedral interstices in a bcc crystal. (After P. Haasen, *Physical Metallurgy*, Cambridge University Press, Cambridge, 1978.)

Interstitial diffusion



How interstitial diffusion differs from substitutional diffusion?

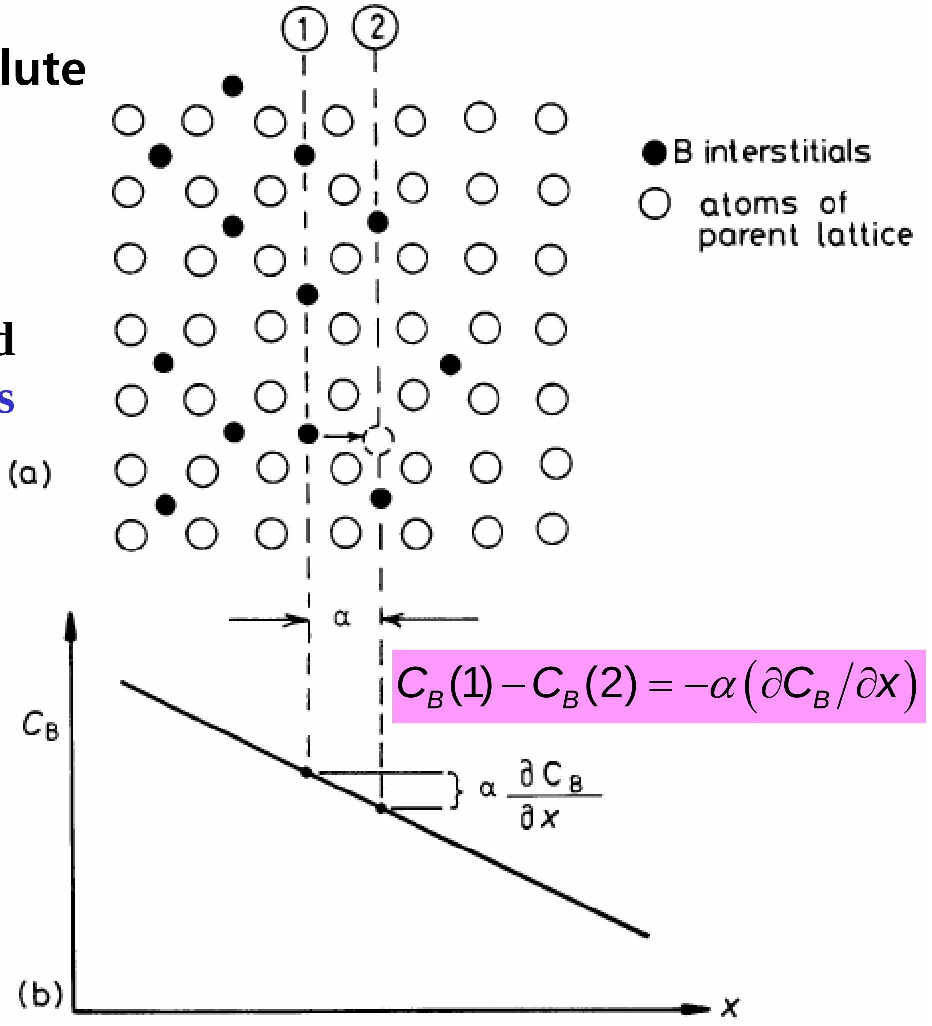
Interstitial diffusion

Random jump of solute B atoms in a dilute solid solution of a simple cubic lattice

Assume that there is no lattice distortion and also that there are always six vacant sites around the diffusion atom.

$$\boxed{J_B = \frac{1}{6}\Gamma_B n_1 - \frac{1}{6}\Gamma_B n_2}$$

J_B : Flux of B atom
Γ_B : Average jump rate of B atoms
n_1 : # of atoms per unit area of plane 1
n_2 : # of atoms per unit area of plane 2



$$C_B(1) - C_B(2) = -\alpha\left(\partial C_B / \partial x\right)$$

Fig. 2.5 Interstitial diffusion by random jumps in a concentration gradient.

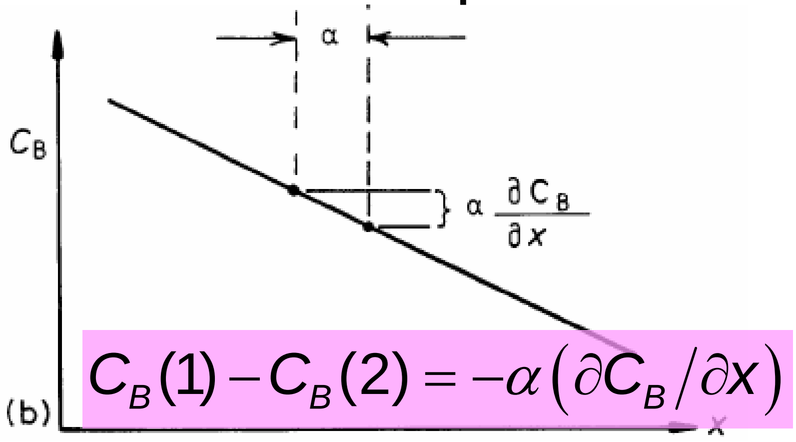
Fick's First Law of Diffusion

$$J_B = \frac{1}{6}\Gamma_B n_1 - \frac{1}{6}\Gamma_B n_2 = \frac{1}{6}\Gamma_B \left(n_1 - n_2\right)$$

$$C_B(1) = n_1/\alpha,\ C_B(2) = n_2/\alpha$$

$$\left(n_1 - n_2\right) = \alpha\left(C_B(1) - C_B(2)\right)$$

α: Jump distance



$$C_B(1) - C_B(2) = -\alpha\left(\partial C_B/\partial x\right)$$

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

(atoms $m^{-2}\ s^{-1}$)

➡ Concentration varies with position.

D_B: Intrinsic diffusivity or

Diffusion coefficient of B

⇒ depends on

microstructure of materials

Magnitude of D in various media

Gas : $D \approx 10^{-1}\ cm^2/s$

Liquid : $D \approx 10^{-4} \sim 10^{-5}\ cm^2/s$

Solid : Materials near melting temp. $D \approx 10^{-8}\ cm^2/s$

Elemental semiconductor (Si, Ge) $D \approx 10^{-12}\ cm^2/s$

Estimate the jump frequency of a carbon atom in γ-Fe (FCC) at 1000 °C.

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

lattice parameter of γ-Fe : ~0.37 nm

$$\alpha = 0.37/\sqrt{2} = 0.26\, nm \qquad D_C = 2.5\times10^{-11} m^2 s^{-1}$$

$$\Gamma = 2\times10^9\ jumps\ s^{-1}$$

the vibration frequency of carbon : ~ 10^{13}

If the crystal structure is not cubic, then the probability of jump is anisotropic. For example the probability of jumps along the basal direction and the axial direction of hcp crystal are different.

D_B, in general, is concentration-dependent.

For example, in γ-Fe at 1000 °C,

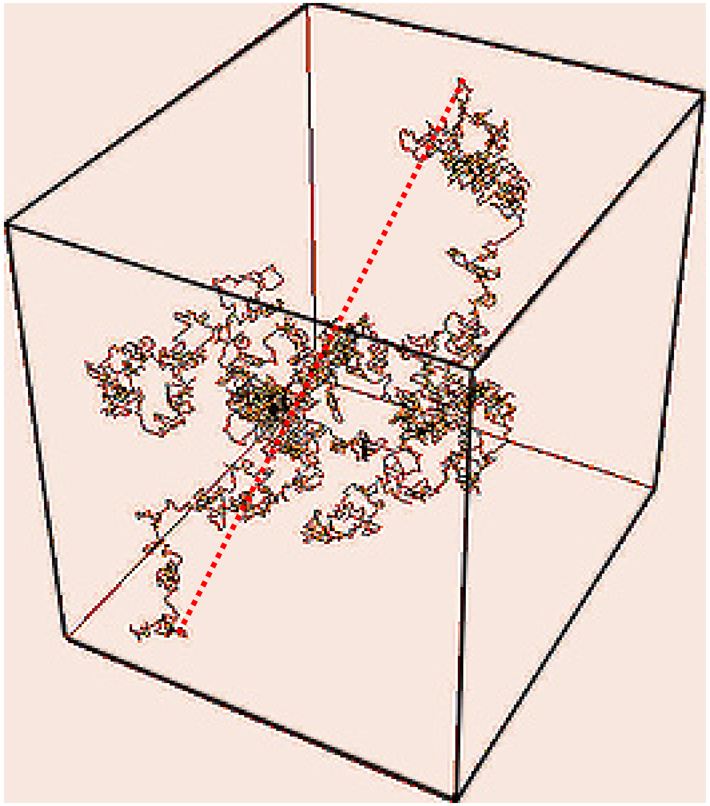
$D_c = 2.5 \times 10^{-11} m^2 s^{-1}$, when $C_c = 0.15$ wt%

$D_c = 7.7 \times 10^{-11} m^2 S^{-1}$, when $C_c = 1.4$ wt%

$$C_c \uparrow \rightarrow D_C \uparrow$$

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

$$\rightarrow \alpha\sqrt{n}$$



During random walk,
an atom will move in time (t)
a radial distance (r) from the origin

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

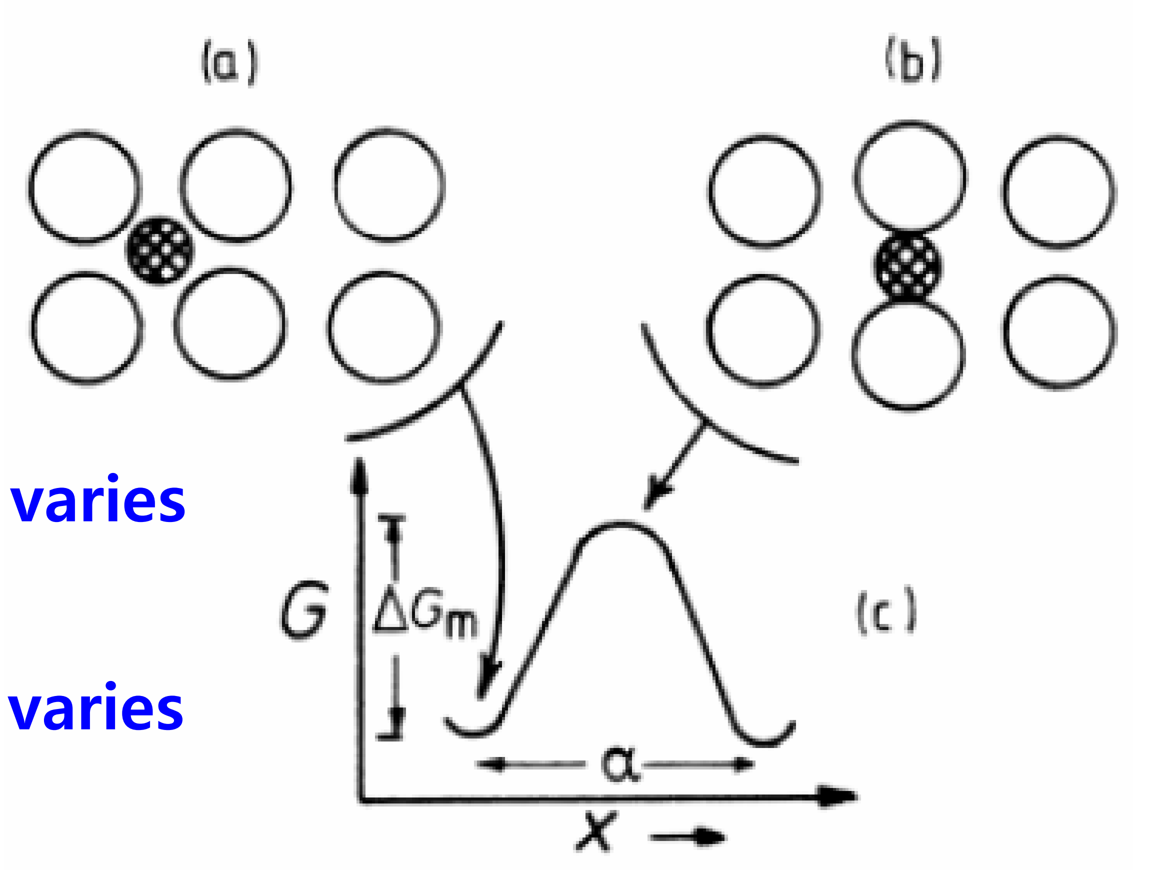
$$\boxed{r = \alpha\sqrt{(\Gamma t)} = f(D) = 2.4\sqrt{Dt}}$$

$$\because \Gamma = \frac{6D}{\alpha^2} \rightarrow r = \sqrt{6}\sqrt{Dt}$$

In 1 s, each carbon atom will move a total distance of ~ 0.5 m
→ a net displacement : ~ 10 μm.

EFFECT OF TEMPERATURE on Diffusivity

Thermal Activation



How D varies with T?

How Γ varies with T?

Fig. 2.6 Interstitial atom, (a) in equilibrium position, (b) at the position of maximum lattice distortion. (c) Variation of the free energy of the lattice as a function of the position of interstitial. (After P.G. Shewmon, in *physical Metallurgy, 2nd edn.*, R.W. Cahn (Ed.), North-Holland, Amsterdam, 1974.)

Thermally activated process *jump frequency* Γ_B ?

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

Z : **nearest neighbor sites**

ν : **vibration frequency**

ΔG_m : activation energy for moving

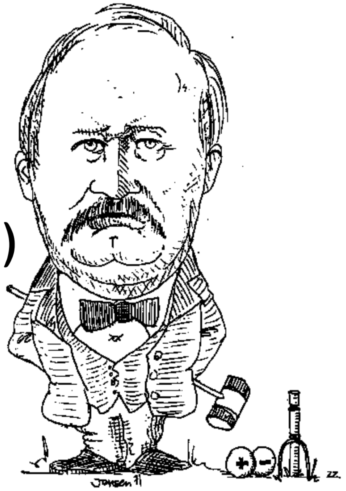
$$\left\{ \Delta G_m = \Delta H_m - T\Delta S_m \ , \ D_B = \frac{1}{6}\Gamma_B \alpha^2 \right\}$$

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

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

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

(Arrhenius-type equation)



Temperature Dependence of Diffusion

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

How to determine Q_{ID} experimentally?

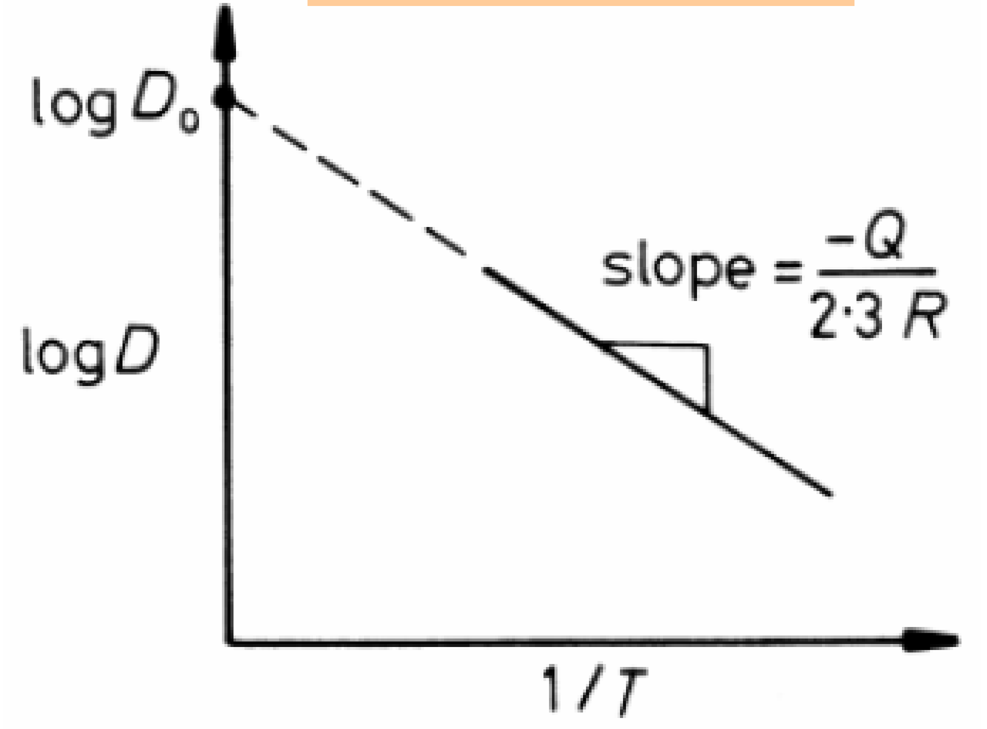


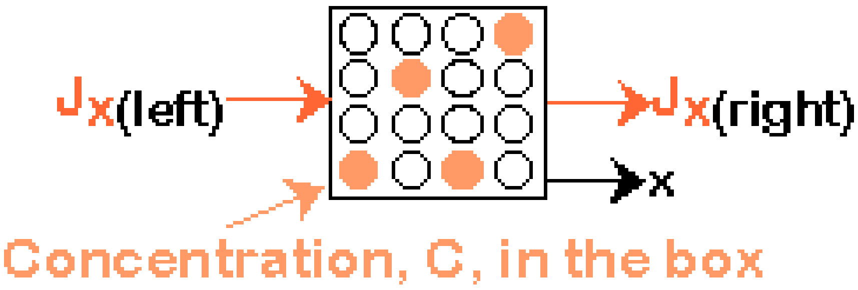
Fig. 2.7 The slope of log D v. 1/T gives the activation energy for diffusion Q.

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

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

Steady-state diffusion

The simplest type of diffusion to deal with is when the concentration at every point does not change with time.



Steady State:

$J_{x(\text{left})} = J_{x(\text{right})}$

- Apply Fick's First Law:

$$J_x = -D\frac{dC}{dx}$$

If $J_{x(\text{left})} = J_{x(\text{right})}$, then

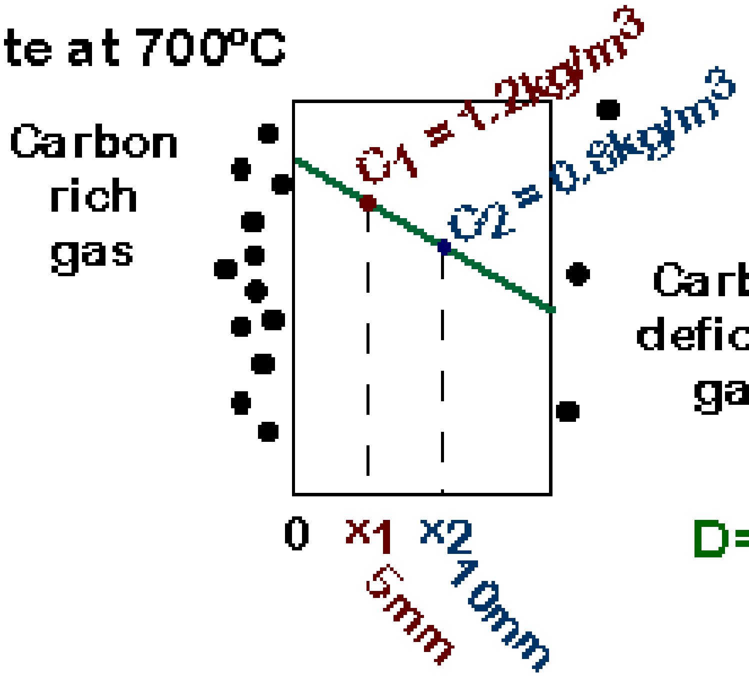
$$\left.\frac{dC}{dx}\right|_{(\text{left})} = \left.\frac{dC}{dx}\right|_{(\text{right})}$$

$\Rightarrow$ the slope, dC/dx, is constant (does not vary with position)!

Steady-state diffusion

The simplest type of diffusion to deal with is when the concentration at every point does not change with time.

- Steel plate at 700°C



$D=3x10^{-11} m^2/s$

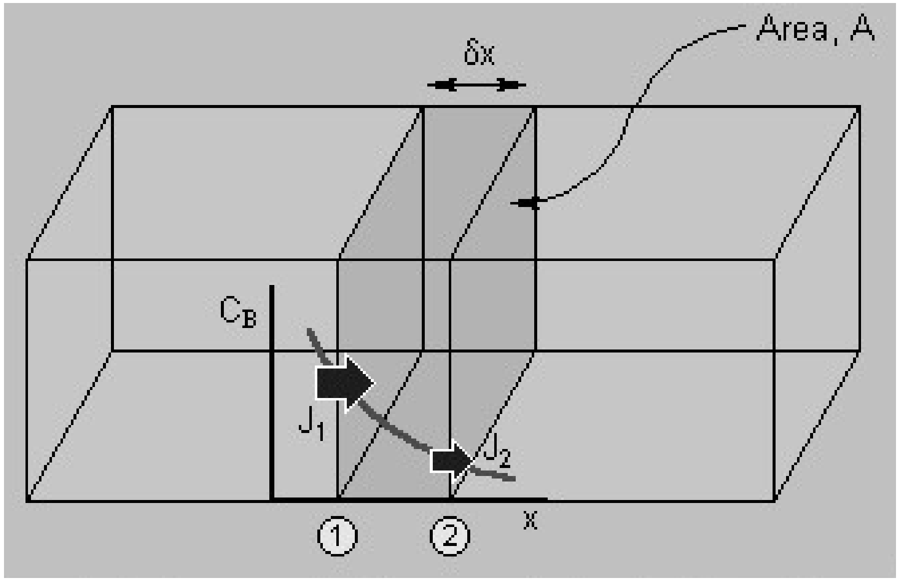
Q: How much carbon is transferring from the rich to deficient side?

$$J = -D\frac{C_2 - C_1}{x_2 - x_1} = 2.4 \times 10^{-9} \frac{kg}{m^2 s}$$

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 dt :

→ $J_1A\,dt$ **Likewise : $J_2A\,dt$**

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

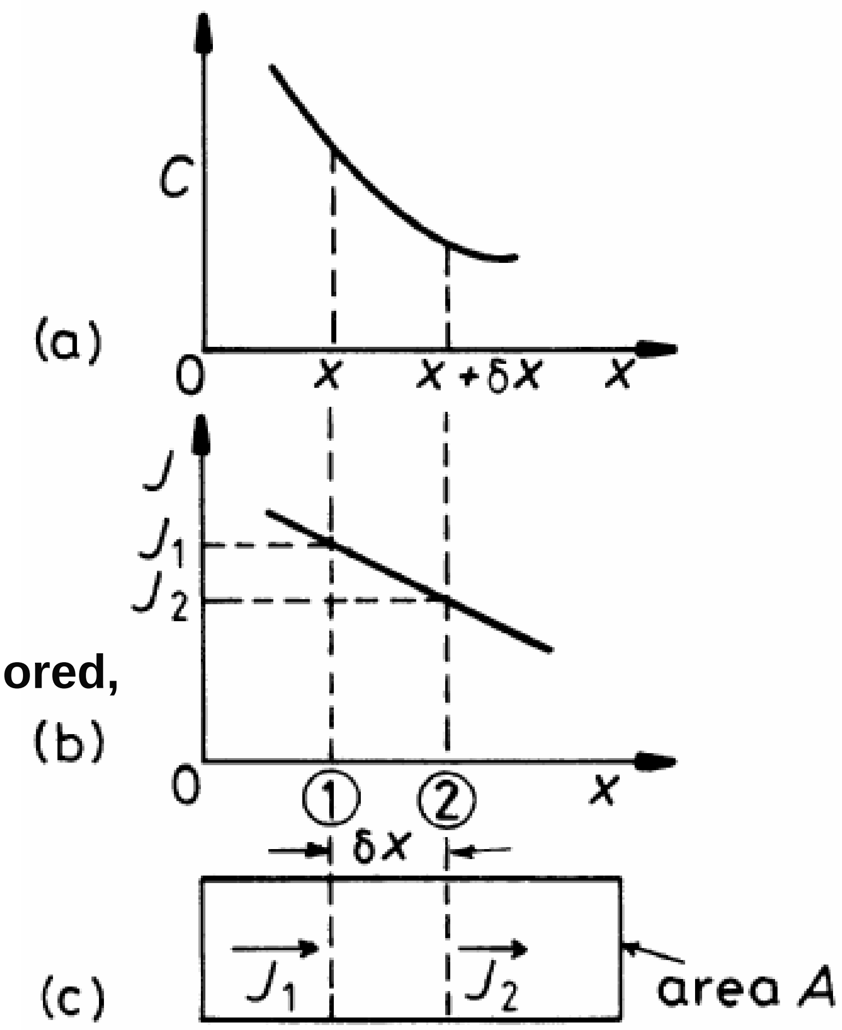
Due to mass conservation

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

Nonsteady-state diffusion

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

as δt => 0 $$\boxed{\frac{\partial C_B}{\partial t} = -\frac{\partial J_B}{\partial x}}$$



substituting Fick's 1st law gives

$$J_B = -D\frac{\partial C_B}{\partial x} \qquad \frac{\partial C_B}{\partial t} = \frac{\partial}{\partial x}\left(D_B \frac{\partial C_B}{\partial x}\right)$$

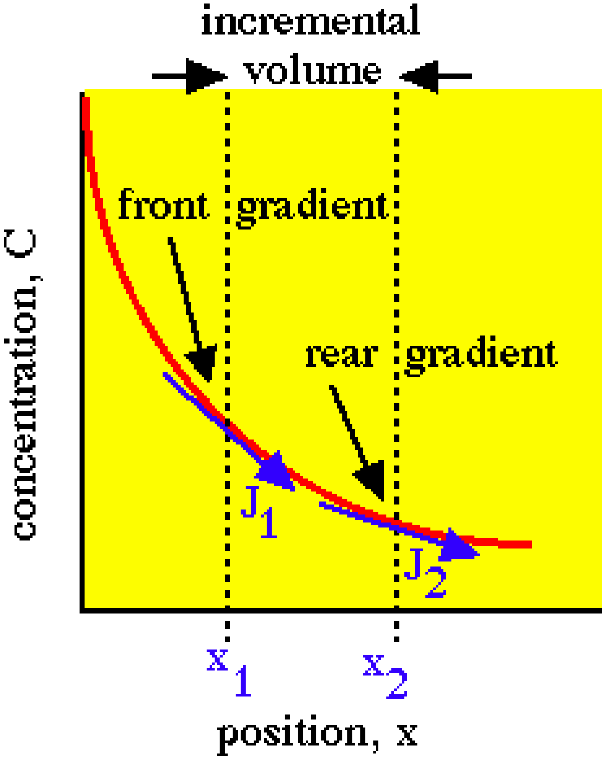
If variation of D with concentration can be ignored,

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

Fick's Second Law

Fick's Second Law

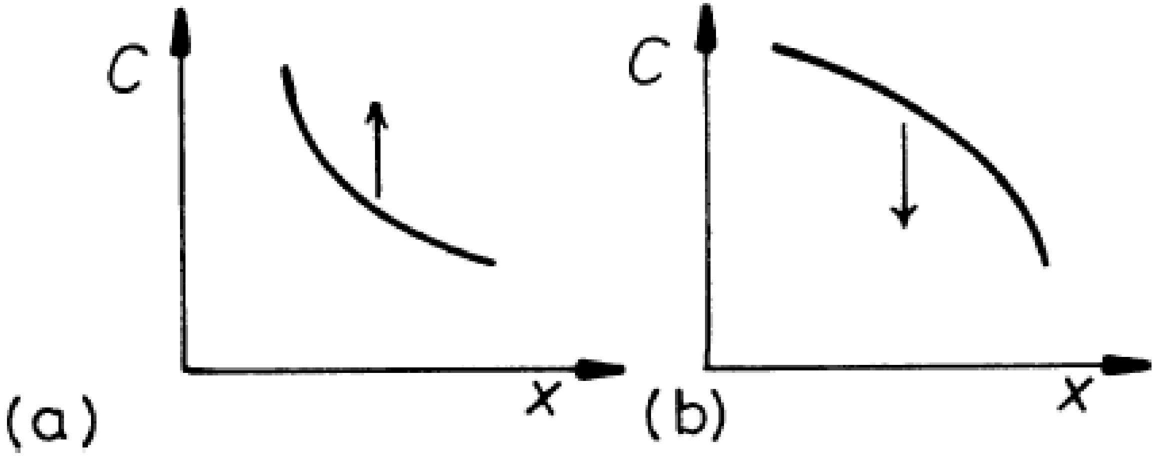
$$\frac{\partial C_B}{\partial t} = D_B \frac{\partial^2 C_B}{\partial x^2}$$



➡ **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 curvature.**



Diffusion