2015 Fall

"Phase Transformation *in* Materials"

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Contents in Phase Transformation

Background to understand phase transformation

(Ch1) Thermodynamics and Phase Diagrams

(Ch2) Diffusion: Kinetics

(Ch3) Crystal Interface and Microstructure

Representative Phase transformation

(Ch4) Solidification: Liquid → Solid

(Ch5) Diffusional Transformations in Solid: Solid → Solid

(Ch6) Diffusionless Transformations: Solid → Solid

Contents for previous class

- **Diffusion** : **Movement of atoms to reduce its chemical potential μ.**

  ⟹ **driving force: Reduction of G**

  Down-hill diffusion movement of atoms from a high C_B region to low C_B region.
  Up-hill diffusion movement of atoms from a low C_B region to high C_B region.

- **Interstitial Diffusion** / **Substitution Diffusion**

  - Steady-state diffusion – Fick's First Law

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

  ⟹ **Concentration varies with position.**   **(atoms m^{-2} s^{-1})**

  - Nonsteady-state diffusion – 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.**

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

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

- **Effect of Temperature on Diffusivity**

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

3

Contents for today's class

- ## Interstitial Diffusion / Substitutional Diffusion

- Steady-state diffusion– Fick's First Law
➡ **Concentration varies with position.**

- Non-steady-state diffusion: Fick's Second Law
➡ **Concentration varies with time and position.**

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

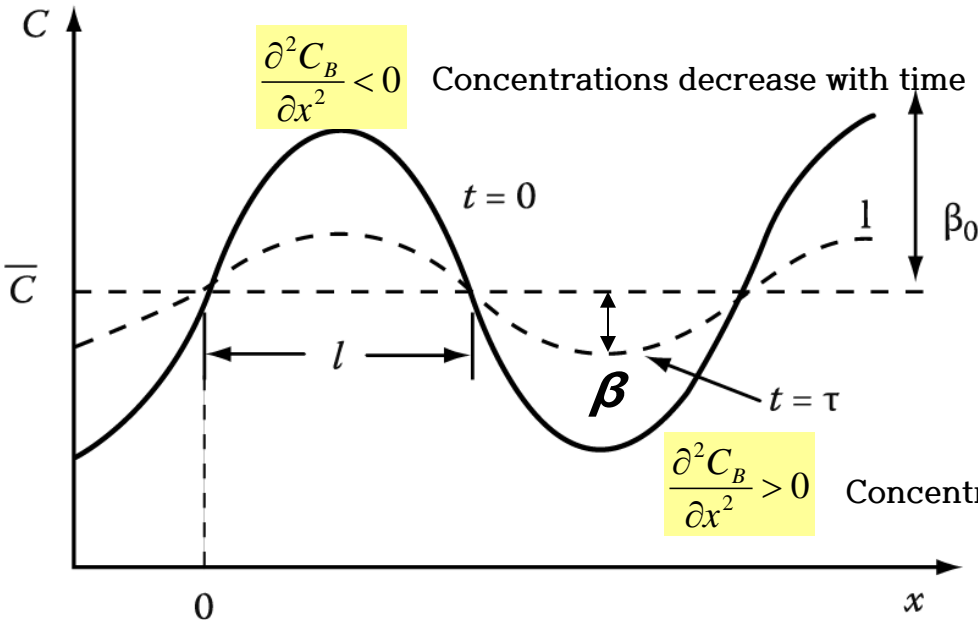# Q. How to solve the diffusion equations?

: Application of Fick's 2nd law

homogenization, carburization, decarburization, diffusion across a couple

Solutions to the diffusion equations (Application of Fick's 2nd law)

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

Ex1. Homogenization
of **sinusoidal varying composition**
in the **elimination of segregation in casting**

$\frac{\partial^2 C_B}{\partial x^2} < 0$ Concentrations decrease with time

$t = 0$

β_0

l

β

$t = \tau$

$\frac{\partial^2 C_B}{\partial x^2} > 0$ Concentrations increase with time.

Initial or Boundary Cond.?

$$C = \overline{C} + \beta_0 \sin \frac{\pi x}{l} \quad \text{at t=0}$$

Fig. 2.10 The effect of diffusion on a sinusoidal variation of composition.

$\overline{C}$: the mean composition l : **half wavelength**

β_0 : the amplitude of the initial concentration profile

6

Rigorous solution of $\dfrac{\partial C}{\partial t} = D\dfrac{\partial^2 C}{\partial x^2}$ for $C(x,0) = \overline{C} + \beta_0 \sin\dfrac{\pi x}{l}$

Using a method of variable separation

Let $C = XT$

$$X\frac{dT}{dt} = DT\frac{d^2 X}{dx^2}$$

$$\frac{1}{DT}\frac{dT}{dt} = \frac{1}{X}\frac{d^2 X}{dx^2} \equiv -\lambda^2$$

$$\frac{1}{T}\frac{dT}{dt} = -\lambda^2 D$$

$$\frac{d\ln T}{dt} = -\lambda^2 D$$

$$T = T_0 e^{-\lambda^2 Dt}$$

$$\frac{d^2 X}{dx^2} + \lambda^2 X = 0$$

$$X = A'\cos\lambda x + B'\sin\lambda x$$

$$X(x,0) \equiv \overline{C} + \beta_0 \sin\frac{\pi x}{l}$$

$$\therefore C = \left(A\cos\lambda x + B\sin\lambda x\right)e^{-\lambda^2 Dt}$$

$$\therefore C = A_0 + \sum_{n=1}^{\infty}\left(A_n \sin\lambda_n x + B_n \cos\lambda_n x\right)$$

$$t = 0 \rightarrow C \equiv \overline{C} + \beta_0 \sin\frac{\pi x}{l} \qquad \lambda = \frac{\pi}{l}$$

$$; A_0 = \overline{C}, B_n = 0, A_1 = \beta_0$$

$(A_n = 0$ for all others$)$

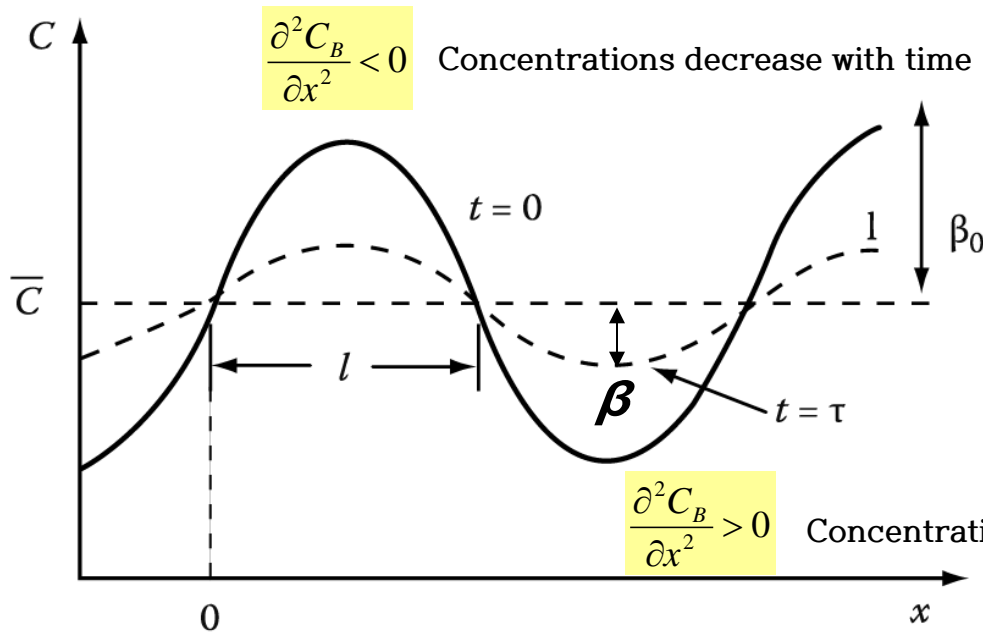$$\therefore C \equiv \overline{C} + \beta_0 \sin\frac{\pi x}{l}\, e^{-\frac{t}{l^2/\pi^2 D}}$$

$$C = \overline{C} + \beta_0 \sin\frac{\pi x}{l}\exp\left(\frac{-t}{\tau}\right)$$

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

$$\beta = \beta_0 \exp(-t/\tau) \quad at \quad x = \frac{l}{2}$$

7

Solutions to the diffusion equations

Ex1. Homogenization of sinusoidal varying composition
in the elimination of segregation in casting

$$\frac{\partial^2 C_B}{\partial x^2} < 0$$ Concentrations decrease with time

$$\frac{\partial^2 C_B}{\partial x^2} > 0$$ Concentrations increase with time.

Fig. 2.10 The effect of diffusion on a sinusoidal variation of composition.

$$C = \overline{C} + \beta_0 \sin \frac{\pi x}{l} \quad \text{at t=0}$$

$$C = \overline{C} + \beta_0 \sin \frac{\pi x}{l} \exp\left(\frac{-t}{\tau}\right)$$

$$\beta = \beta_0 \exp(-t/\tau) \quad at \quad x = \frac{l}{2}$$

Amplitude of the concentration profile (β) decreases exponentially with time, $C \Rightarrow \overline{C}$

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

decide homogenization rate

The initial concentration profile will not usually be sinusoidal, but in general any con-centration profile can be considered as the sum of an infinite series of sine waves of varying wavelength and amplitude, and each wave decays at a rate determined by its own "τ". Thus, the short wavelength terms die away very rapidly and the homogenization will ultimately be determined by τ for the longest wavelength component.

8

Solutions to the diffusion equations

Ex2. Carburization of Steel

The aim of carburization is to increase the carbon concentration in the surface layers of a steel product in order to achiever a harder wear-resistant surface.

1. Holding the steel in CH_4 and/or Co at an austenitic temperature.

2. By controlling gases the concentration of C at the surface of the steel can be maintained at a suitable constant value.

3. At the same time carbon continually diffuses from the surface into the steel.

Carburizing of steel

Depth of Carburization?

1) Specimen ~ infinitely long.
2) Diffusion coefficient of carbon in austenite increases with increasing concentration, but an approximate solution: Taking an average value

The error function solution:

$$C = C_s - (C_s - C_0) erf\left(\frac{x}{2\sqrt{Dt}}\right)$$

$$erf(Z) = \frac{2}{\sqrt{\pi}} \int_0^Z e^{-y^2} dy$$

* Concentration profile
: using boundary conditions

$$C_B(0,t) = C_s$$
$$C_B(\infty,t) = C_0$$

Solution of Fick's 2nd law

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

Fig. 2.11 Concentration profiles at successive times ($t_3 > t_2 > t_1$) for diffusion into a semi-infinite bar when the surface concentration Cs is maintained constant.

$$\frac{C_s - C}{C_s - C_0} = erf\left(\frac{x}{2\sqrt{Dt}}\right) \qquad \textbf{erf(0.5)≈0.5} \qquad C = \frac{C_s + C_0}{2}$$

- Since erf(0.5)≈0.5, the depth at which the carbon concentration is midway between C_s and C_0 is given $(x/2\sqrt{Dt}) \cong 0.5$

  that is $\boxed{x \cong \sqrt{Dt}}$ → **Depth of Carburization**

10
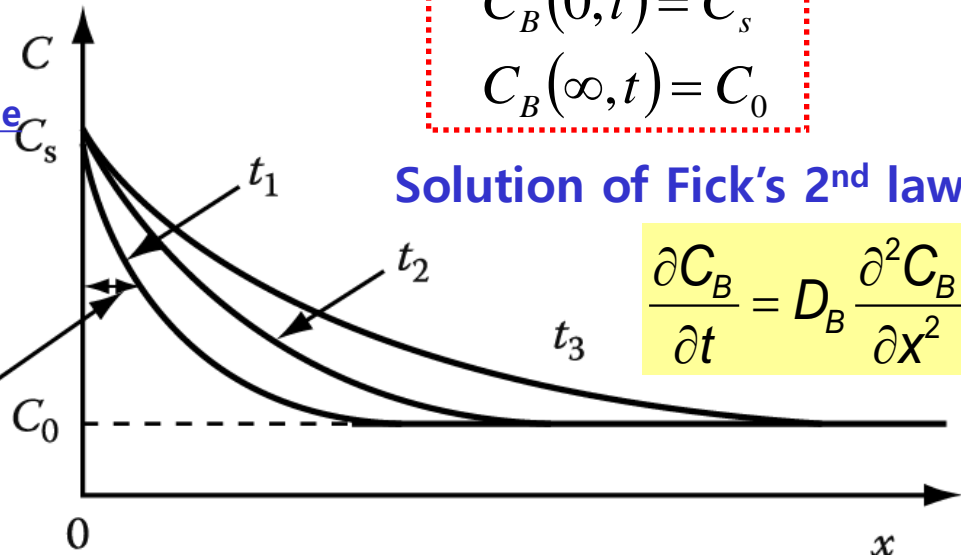
Error function

In mathematics, the error function (also called the <u>Gauss error function</u>) is a non-elementary function which occurs in probability, statistics and partial differential equations.
It is defined as:

$$\mathrm{erf}(x) = \frac{2}{\sqrt{\pi}} \int_0^x e^{-t^2}\, dt.$$

By expanding the right-hand side in a Taylor series and integrating, one can express it in the form
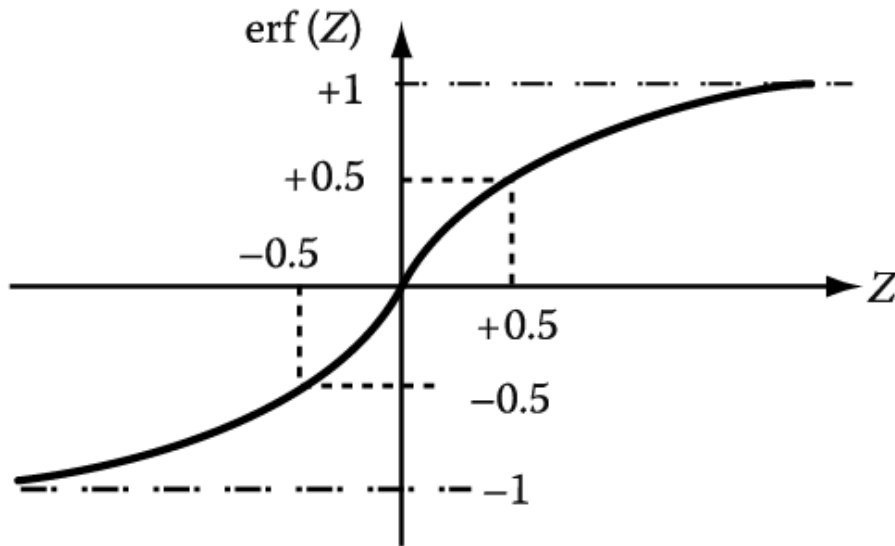
$$\mathrm{erf}(x) = \frac{2}{\sqrt{\pi}} \sum_{n=0}^{\infty} \frac{(-1)^n x^{2n+1}}{(2n+1)n!} = \frac{2}{\sqrt{\pi}} \left(x - \frac{x^3}{3} + \frac{x^5}{10} - \frac{x^7}{42} + \frac{x^9}{216} - \cdots \right)$$

for every real number x.   (From Wikipedia, the free encyclopedia)

Error function

$$erf(z) = \frac{2}{\sqrt{\pi}} \int_O^z exp(-y^2)dy$$

erf (Z)

(a) Schematic diagram illustrating the main features of the error function.

Table 1-1.   The Error Function

z	erf(z)	z	erf(z)
0	0	0.85	0.7707
0.025	0.0282	0.90	0.7969
0.05	0.0564	0.95	0.8209
0.10	0.1125	1.0	0.8427
0.15	0.1680	1.1	0.8802
0.20	0.2227	1.2	0.9103
0.25	0.2763	1.3	0.9340
0.30	0.3286	1.4	0.9523
0.35	0.3794	1.5	0.9661
0.40	0.4284	1.6	0.9763
0.45	0.4755	1.7	0.9838
0.50	0.5205	1.8	0.9891
0.55	0.5633	1.9	0.9928
0.60	0.6039	2.0	0.9953
0.65	0.6420	2.2	0.9981
0.70	0.6778	2.4	0.9993
0.75	0.7112	2.6	0.9998
0.80	0.7421	2.8	0.9999

Carburizing of steel

Depth of Carburization?

1) Specimen ~ infinitely long.
2) Diffusion coefficient of carbon in austenite increases with increasing concentration, but an approximate solution: Taking an average value

The error function solution:

$$C = C_s - (C_s - C_0) erf\left(\frac{x}{2\sqrt{Dt}}\right)$$

$$erf(Z) = \frac{2}{\sqrt{\pi}}\int_0^Z e^{-y^2} dy$$

* Concentration profile
: using boundary conditions

$$C_B(0,t) = C_s$$
$$C_B(\infty,t) = C_0$$

⟹ **Solution of Fick's 2nd law**

½ $(C_s + C_0)$

$\sqrt{Dt_1}$

Fig. 2.11 Concentration profiles at successive times ($t_3 > t_2 > t_1$) for diffusion into a semi-infinite bar when the surface concentration Cs is maintained constant.

$$\frac{C_s - C}{C_s - C_0} = erf\left(\frac{x}{2\sqrt{Dt}}\right) \qquad \textbf{erf(0.5)≈0.5} \qquad C = \frac{C_s + C_0}{2}$$

- Since erf(0.5)≈0.5, the depth at which the carbon concentration is **midway between C$_s$ and C$_0$** is given $(x/2\sqrt{Dt}) \cong 0.5$

  that is $\boxed{x \cong \sqrt{Dt}}$ → **Depth of Carburization**

13
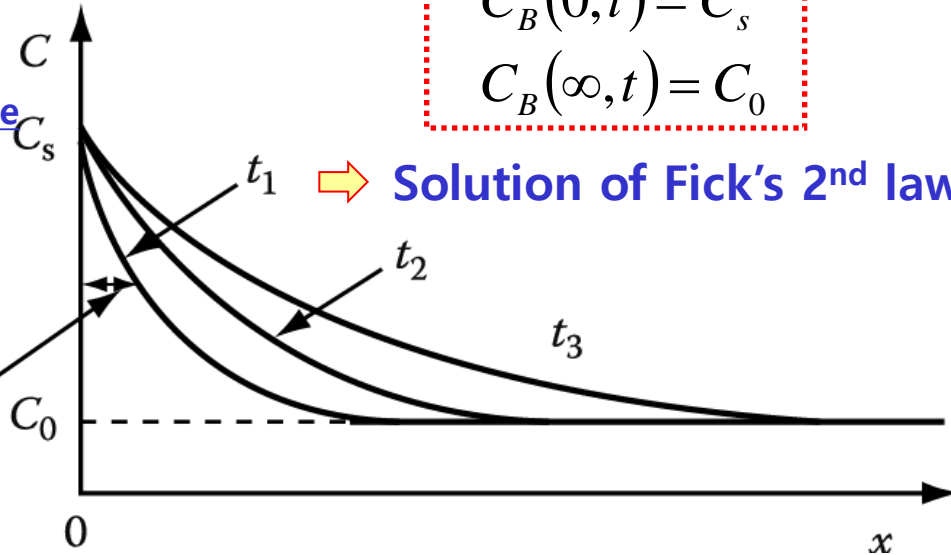
Carburizing of steel

Thus the thickness of the carburized layer is $\cong \sqrt{Dt}$.

Note also that the depth of any is concentration line is directly proportion to $\sqrt{Dt}$, i.e. *to obtain a twofold increase in penetration requires a fourfold increase in time.*

(2배의 침투 깊이 → 4배의 시간)

Ex.3 Decarburization of Steel?

$$C = C_0 erf\left(\frac{x}{2\sqrt{Dt}}\right)$$

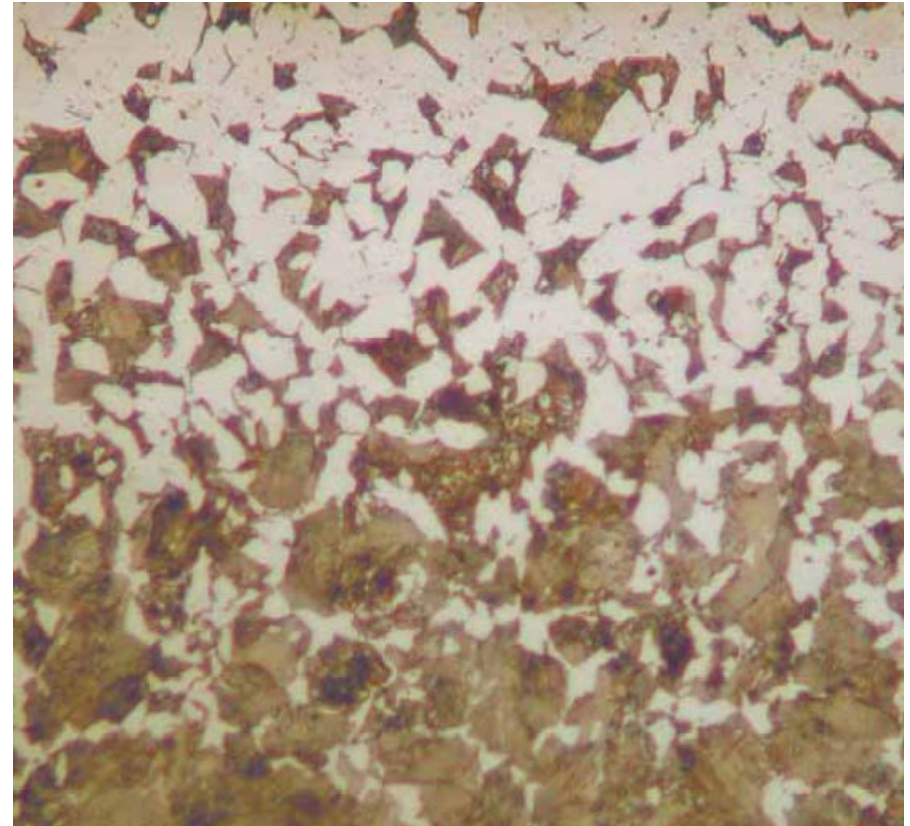$$C = C_s - (C_s - C_0)erf\left(\frac{x}{2\sqrt{Dt}}\right)$$

Carburization

$$erf(Z) = \frac{2}{\sqrt{\pi}}\int_0^Z e^{-y^2}\,dy$$

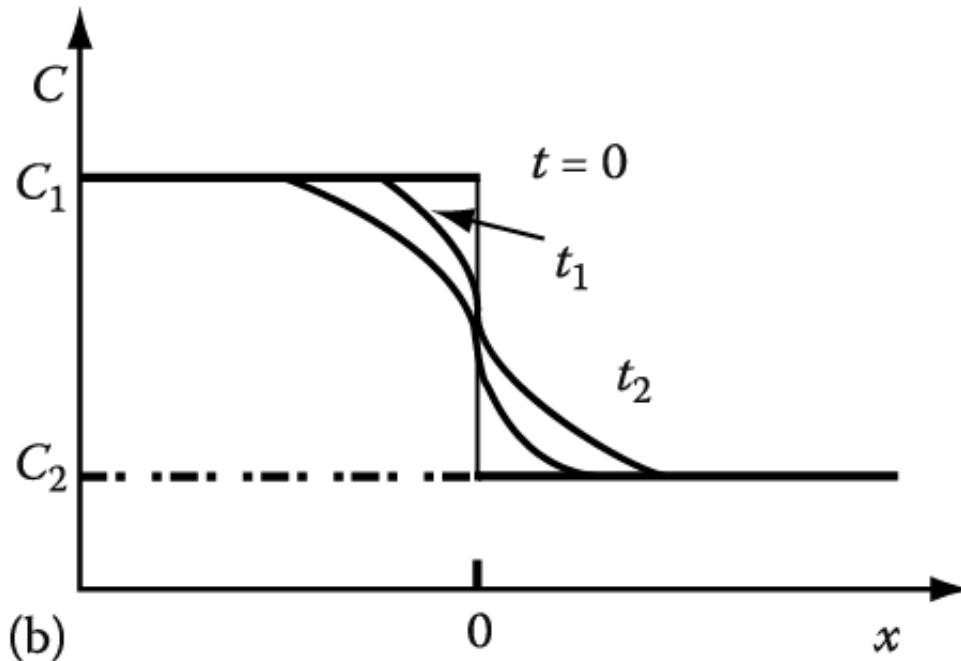C_S = Surface concentration
C_0 = Initial bulk concentration

Solutions to the diffusion equations

Ex4. Diffusion Couple

Joining of two semi-infinite specimens of compositions C_1 and C_2 ($C_1 > C_2$)

Draw C vs. x with time t = 0 and t > 0.   **Boundary conditions?**

(b)

Fig. 2.12 (b) concentration profiles at successive times (t2>t1>0)
when two semi-infinite bars of different composition are annealed after welding.

$$C = C_1 \quad t = 0, \ -\infty < x < 0$$

$$C = C_2 \quad t = 0, \ 0 < x < \infty$$

$$C = C_1 \quad x = -\infty, \ 0 < t < \infty$$

$$C = C_2 \quad x = \infty, \ 0 < t < \infty$$

$$C = \left(\frac{C_1 + C_2}{2} \right) - \left(\frac{C_1 - C_2}{2} \right) erf \left(\frac{x}{2\sqrt{Dt}} \right)$$

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

Q. Interstitial diffusion vs Substitutional diffusion

1. **Self diffusion in pure material**
2. **Vacancy diffusion**
3. **Diffusion in substitutional alloys**

• Interstitial Diffusion / Substitutional Diffusion

- Diffusion in dilute interstitial alloys ~ relatively simple
because the diffusing atoms are <u>always surrounded by vacant sites</u> to which they can jump whenever they have enough to overcome the energy barrier for migration.

- In substitutional diffusion,
An atom can only jump if there happens to be vacant site at one of the adjacent lattice positions

<u>Probability of vacancy</u> x probability of jump

⟶ **amenable to a simple atomic model: self-diffusion** (순금속의 자기확산)

1. Self diffusion in pure material

The rate of self-diffusion can be measured experimentally by intro-ducing a **few radioactive A atoms** (A*) into pure A and measuring the rate at which penetration occurs at various temperatures. Since A* and A atoms are chemically identical their jump frequencies are almost identical.

Atoms
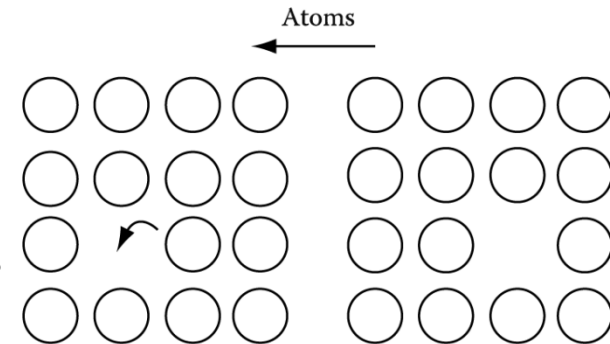
Diffusion coefficient

most likely to occur back into the same vacancy

$$D_A^* = \quad D_A = \frac{1}{6}\Gamma_A \alpha^2 \quad \longrightarrow \quad D_A^* = f\, D_A \quad (f : \text{correlation factor})$$

close to unity
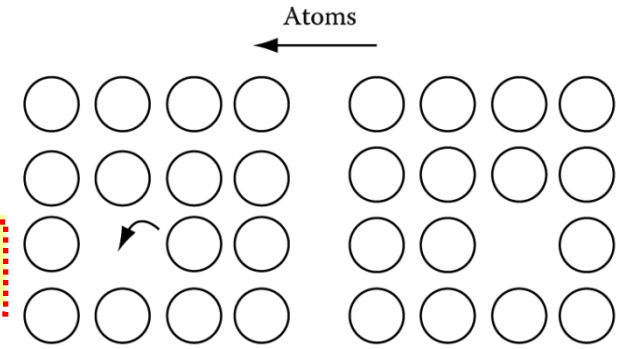
Assumption
: unrelated to the previous jump

The next jump is not equally probable in all directions.

Q. Interstitial diffusion vs Substitutional diffusion

1. **Self diffusion in pure material**
2. Vacancy diffusion
3. Diffusion in substitutional alloys

Substitutional diffusion

1. Self diffusion in pure material

Atoms ←

Probability of vacancy x probability of jump

What would be the jump frequency in substitutional diffusion?

An atom next to a vacancy can make a jump provided

it has enough thermal energy to overcome ΔG_m. $\rightarrow \exp(-\Delta G_m/kT)$

The probability that an adjacent site is vacant $\rightarrow zX_v$

Z= # of nearest neighbours

Jump frequency

$$cf)\ \Gamma = \nu z \exp\frac{-\Delta G_m}{RT}$$
for interstitials

$$\rightarrow \Gamma = \nu z X_V \exp\frac{-\Delta G_m}{RT}$$

In thermodynamic equilibrium,

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

$$D_A = \frac{1}{6}\Gamma_A \alpha^2$$

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

For most metals: $\nu \sim 10^{13}$, fcc metals : z = 12, $\alpha = a/\sqrt{2}$

20

Z=number of nearest neighbors/ ν= temperature independent frequency

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

$$\Delta G = \Delta H - T\Delta S$$

$$D_A = \frac{1}{6}\alpha^2 z\nu \exp\frac{\Delta S_m + \Delta S_V}{R}\exp(-\frac{\Delta H_m + \Delta H_V}{RT})$$

Z=number of nearest neighbors/ ν= temperature independent frequency

For most metals: $\nu \sim 10^{13}$, fcc metals : z = 12, $\alpha = a/\sqrt{2}$

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

$$D_0 = \frac{1}{6}\alpha^2 z\nu \exp\frac{\Delta S_m + \Delta S_V}{R}$$

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

∵ self-diffusion requires the presence of vacancies

~Same with interstitial diffusion except that the activation energy for self-diffusion has an extra term

* interstitial diffusion

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**
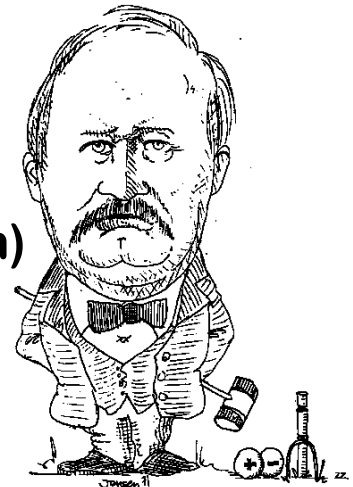
Δ**G**$_m$: **activation energy for moving**

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

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

$$\Delta H_m \equiv Q_{ID}$$
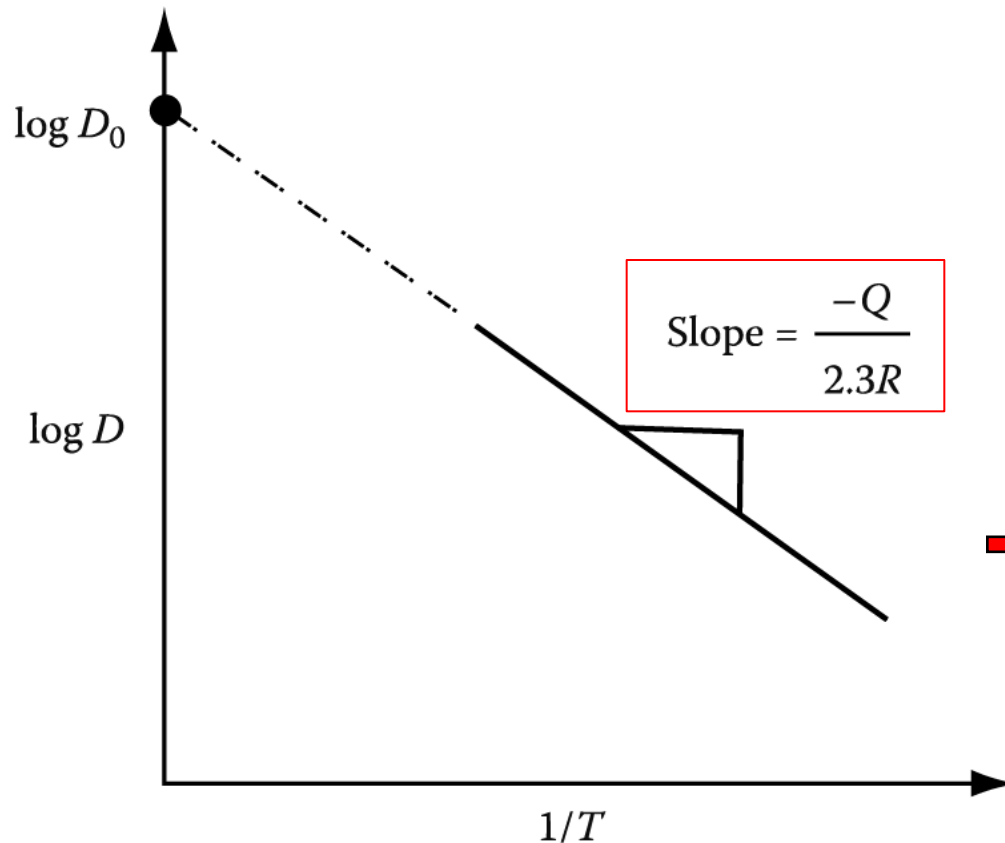
$$D_B = D_{B0} \exp\frac{-Q_{ID}}{RT}$$ **(Arrhenius-type equation)**

Temperature Dependence of Diffusion

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

How to determine Q_{ID} experimentally?

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

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

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

Experimental Determination of D

- Deposit a known quantity (M) of a radioactive isotope A*

$$\frac{\partial C_B}{\partial t} = D_B \frac{\partial^2 C_B}{\partial x^2} \quad \textbf{(2.18)}$$

1) Solution for the **infinite boundary condition**

$$C = \frac{M}{2\sqrt{\pi D t}} \exp\left(-\frac{x^2}{4Dt}\right)$$

M : quantity·m^{-2}/ C : quantity·m^{-3}

2) Solution for the **semi-infinite B.C.**

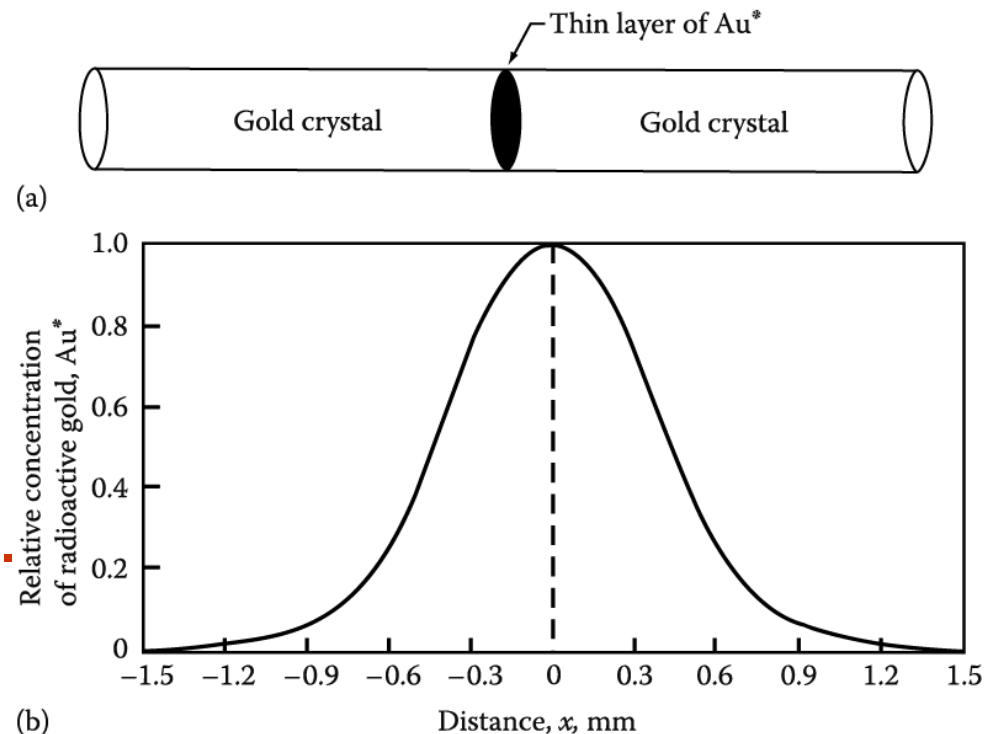$$C = \frac{2M}{\sqrt{\pi D t}} \exp\left(-\frac{x^2}{4Dt}\right)$$

Fig. 2.14 Illustration of the principle of tracer diffusion and of the planar source method for determining the self-diffusion coefficient of gold. (a) Initial diffusion couple with planar source of radioactive gold Au* (b) Distribution of Au* after diffusion for 100h at 920℃

**Table 2.2 Experimental Data for Substitutional Self-Diffusion in Pure Metals at Atmospheric Pressure**

Class	Metal	T_m (K)	D_0 (mm^2 s^{-1})	Q (kJ mol^{-1})	$\dfrac{Q}{RT_m}$	$Q(T_m)$ (μm^2 s^{-1})
bcc (rare earths)	ε-Pu	914	0.3	65.7	8.7	53
	δ-Ce	1071	1.2	90.0	10.1	49
	γ-La	1193	1.3	102.6	10.4	42
	γ-Yb	1796	1.2	121.0	8.1	3600
bcc (alkali metals)	Rb	312	23	39.4	15.2	5.8
	K	337	31	40.8	14.6	15
	Na	371	24.2	43.8	14.2	16
	Li	454	23	55.3	14.7	9.9
bcc (transition metals)	β-T1	577	40	94.6	19.7	0.11
	Eu	1095	100	143.5	15.8	14
	Er	1795	451	302.4	20.3	0.71
	α-Fe[a]	1811	200	239.7	15.9	26
	δ-Fe[a]	1811	190	238.5	15.8	26
	β−Ti	1933	109	251.2	15.6	18
	β−Zρ	2125	134	273.5	15.5	25
	Cr	2130	20	308.6	17.4	0.54
	V	2163	28.8	309.2	17.2	0.97
	Nb	2741	1240	439.6	19.3	5.2
	Mo	2890	180	460.6	19.2	0.84
	Ta	3269	124	413.3	15.2	31
	W	3683	4280	641.0	20.9	3.4
hcp[a]	Cd	594	∥c 5	76.2	15.4	0.99
			⊥c 10	79.9	16.2	0.94
	Zn	692	∥c 13	91.6	15.9	1.6
			⊥c 18	96.2	16.7	0.98
	Mg	922	∥c 100	134.7	17.6	2.3
			⊥c 150	136.0	17.8	2.9
fcc	Pb	601	137	109.1	21.8	0.045
	Al	933	170	142.0	18.3	1.9
	Ag	1234	40	184.6	18.0	0.61
	Au	1336	10.7	176.9	15.9	1.3
	Cu	1356	31	200.3	17.8	0.59
	Ni	1726	190	279.7	19.5	0.65

For a given structure and bond type, Q/RT_m is roughly constant;

⇒ Q is roughly proportional to T_m.

Within each class, $D(T_m)$ and D_0 are approximately constants.

Most close-packed metals

ex) for fcc and hcp, $Q/RT_m \sim 18$ and $D(T_m) \sim 1\ \mu m^2 s^{-1}$ ($10^{-12}\ m^2 s^{-1}$)
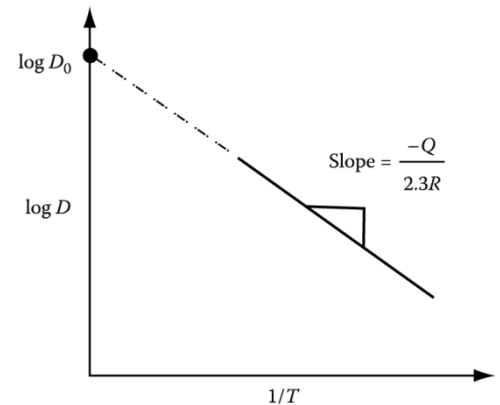
For a given structure and bond type, $D(T/T_m) \sim$ **constant**
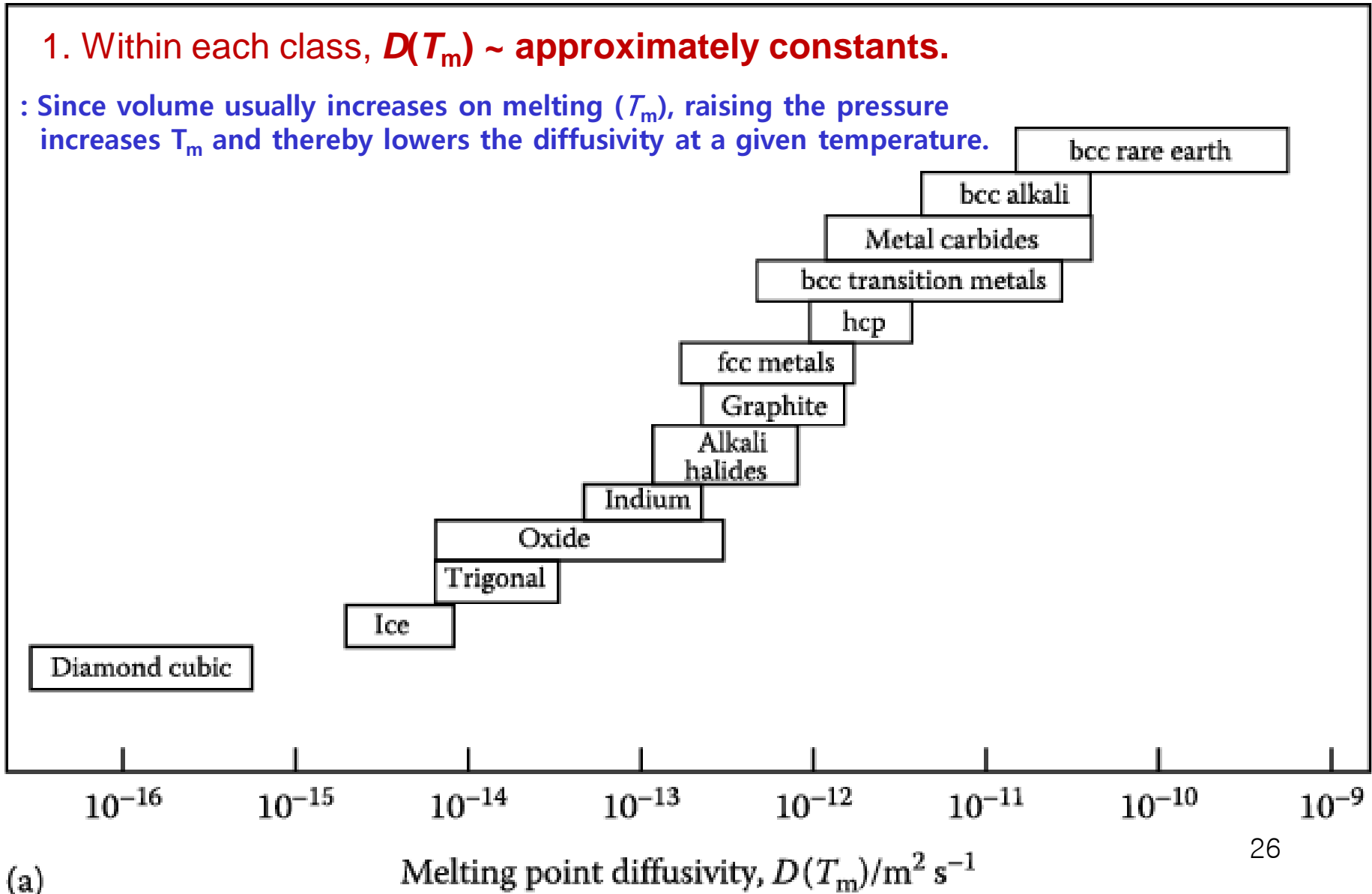
T/T_m : **homologous temperature**

25

* Melting point diffusivities for various classes of materials:

: The diffusion coefficients of all materials with a given crystal structure and bond type will be approximately the same at the same fraction of their melting temperature, i.e. $D(T/T_m)$ = const.

1. Within each class, $D(T_m)$ ~ **approximately constants.**

: Since volume usually increases on melting (T_m), raising the pressure increases T_m and thereby lowers the diffusivity at a given temperature.

bcc rare earth
bcc alkali
Metal carbides
bcc transition metals
hcp
fcc metals
Graphite
Alkali halides
Indium
Oxide
Trigonal
Ice
Diamond cubic

10^{-16} $\quad$ 10^{-15} $\quad$ 10^{-14} $\quad$ 10^{-13} $\quad$ 10^{-12} $\quad$ 10^{-11} $\quad$ 10^{-10} $\quad$ 10^{-9}

Melting point diffusivity, $D(T_m)/\text{m}^2\,\text{s}^{-1}$

(a)

# For a given structure and bond type, Q/RT_m is roughly constant;

: Q and T_m exhibit rough linear correlation because increasing the interatomic bond strength makes the process of melting more difficult; that is, T_m is raised.
It also makes diffusion more difficult by increasing ΔH_m & ΔH_v.

(b) Normalized activation energy, Q/RT_m
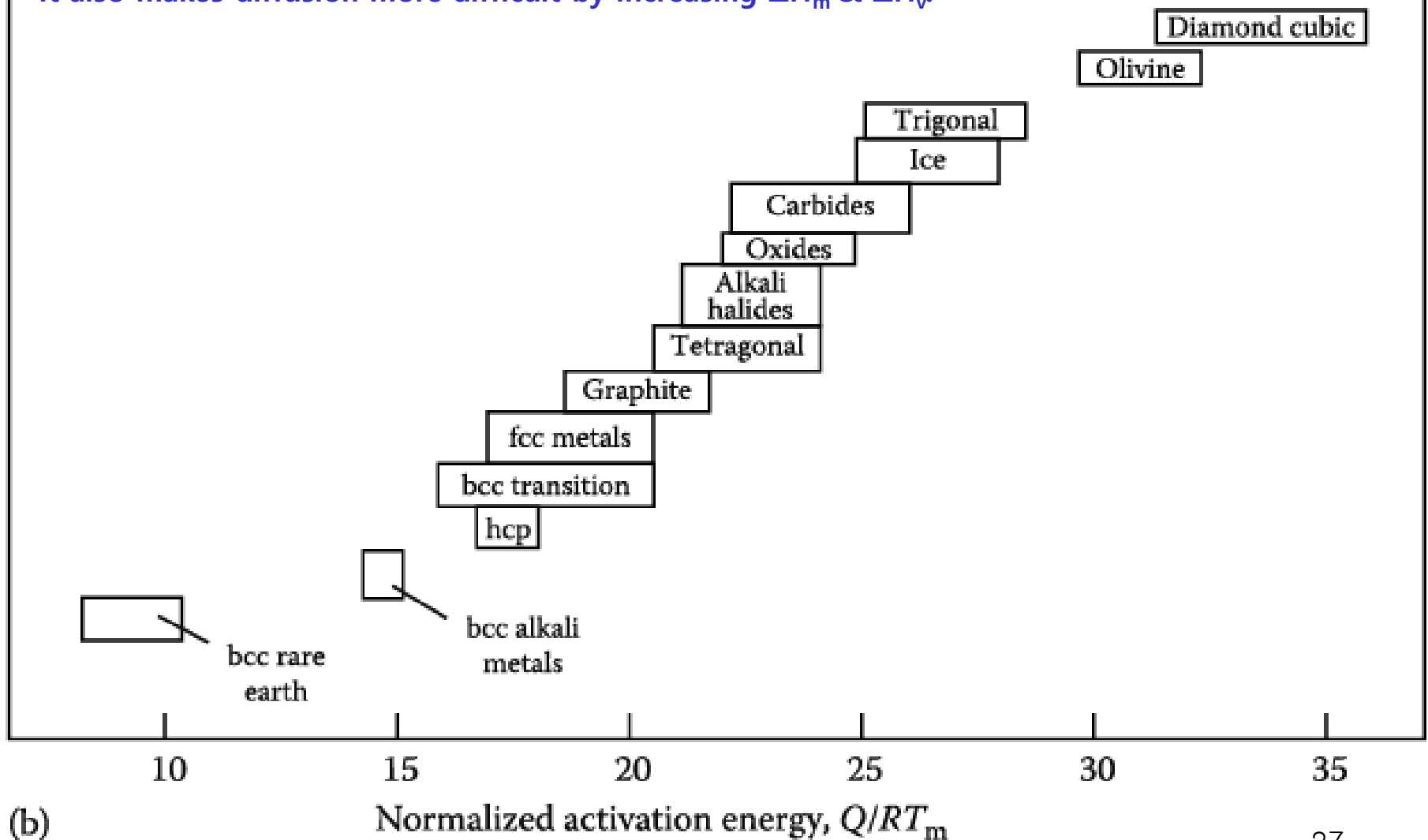
$$\frac{L}{RT_E} = \ln \frac{A_M}{A_F}$$

b) $A_M \sim 1$ for all liquid, A_F depends on crystal structure

- **Metallic structure** (FCC, C.P.H, and BCC, "less localized bonding") ~ good relationship compared with the structures which are covalently bonded ("specific directional bonds").

- **Molecular liquid such as F_2, Cl_2 ~ extra condition for A_F**
($\because$ molecule must be correctly oriented in order to be accommodated.)
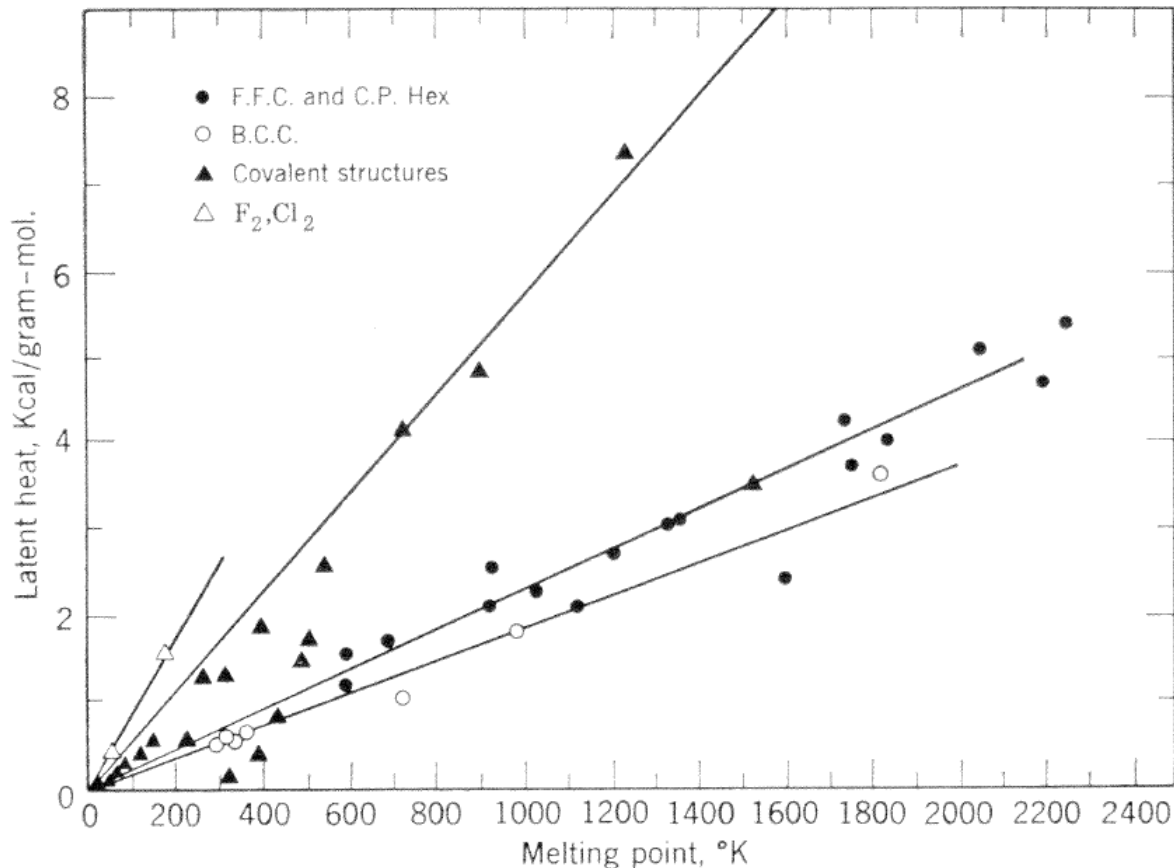
< Relationship between latent heat and melting point>

28

Consider the effect of temperature on self-diffusion in Cu:

ex) At 800°C, $D_{Cu} = 5 \times 10^{-9}$ mm²s⁻¹, α = 0.25 nm $\quad \Gamma_{Cu} : ?$

$$D_B = \frac{1}{6}\Gamma_B \alpha^2 \qquad \Gamma_{Cu} = 5 \times 10^5 \, jumps \, s^{-1}$$

After an hour, diffusion distance (x)? $\quad \sqrt{Dt} \sim 4\,\mu m$

How do we determine D_{Cu} at low temperature such as 20°C?

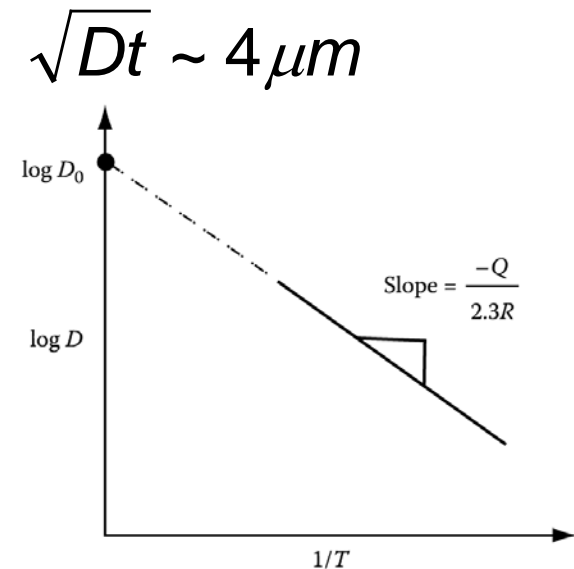Hint) From the data in Table 2.2,

how do we estimate D_{Cu} at 20°C?

log D_0

Slope = $\dfrac{-Q}{2.3R}$

log D

$1/T$

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

At 20°C, $D_{Cu} \sim 10^{-34}$ mm²s⁻¹ $\qquad \Gamma_{Cu} \sim 10^{-20} \, jumps \ s^{-1}$

→ Each atom would make one jump every 10¹² years!

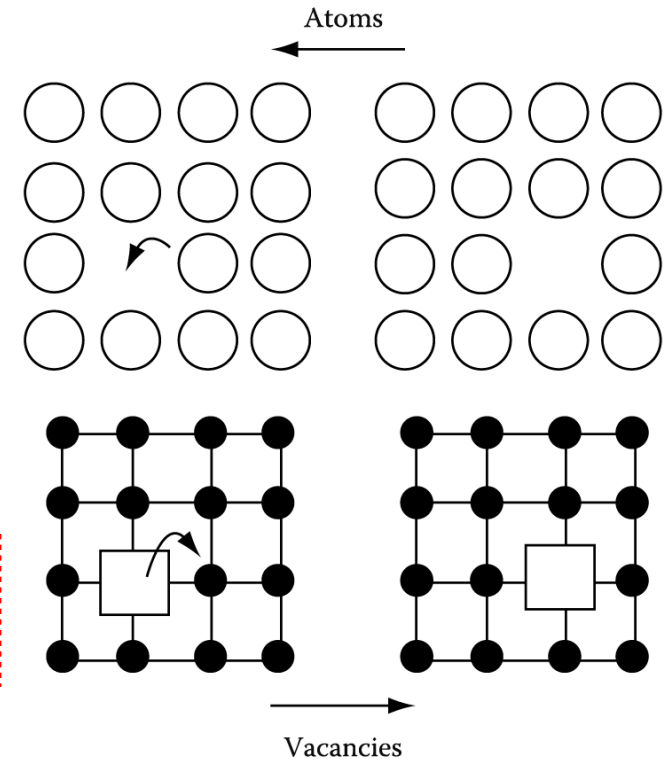# Q. Interstitial diffusion vs Substitutional diffusion

1. Self diffusion in pure material
2. **Vacancy diffusion**
3. Diffusion in substitutional alloys

2. Vacancy diffusion

All the surrounding atoms are possible jump sites of a vacancy, which is analogous to interstitial diffusion.

$$D_v = \frac{1}{6}\alpha^2\Gamma_v$$

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

Atoms

Vacancies

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

$$D_v = D_A / X_v^e$$

This shows in fact that the diffusivity of vacancy ($\underline{D_v}$) is many orders of magnitude greater than the diffusivity of substitutional atoms ($\underline{D_A}$).
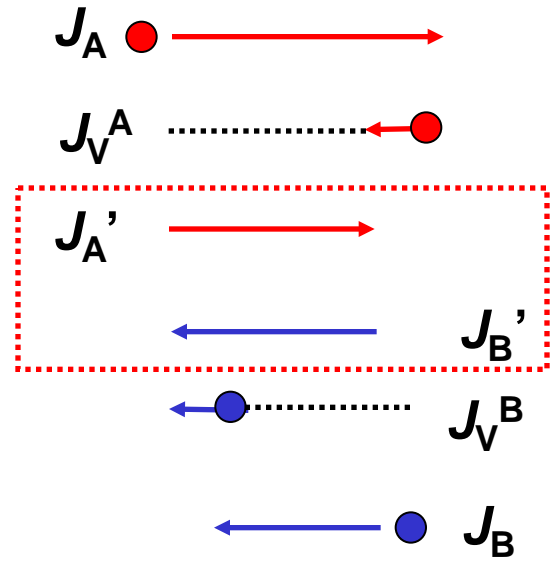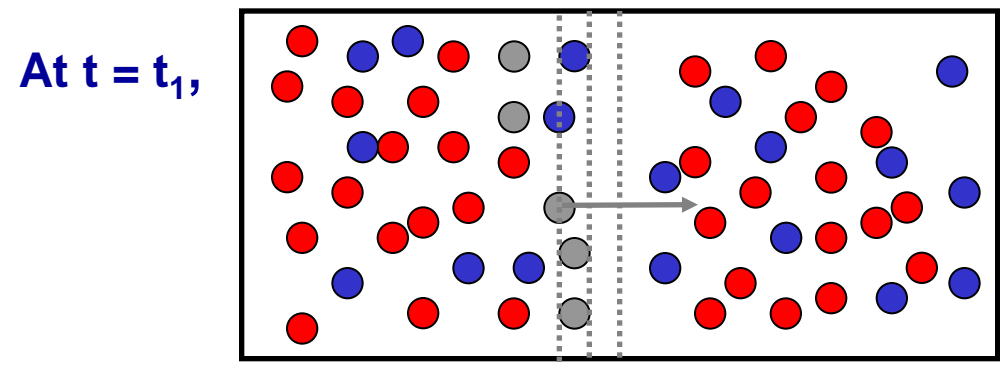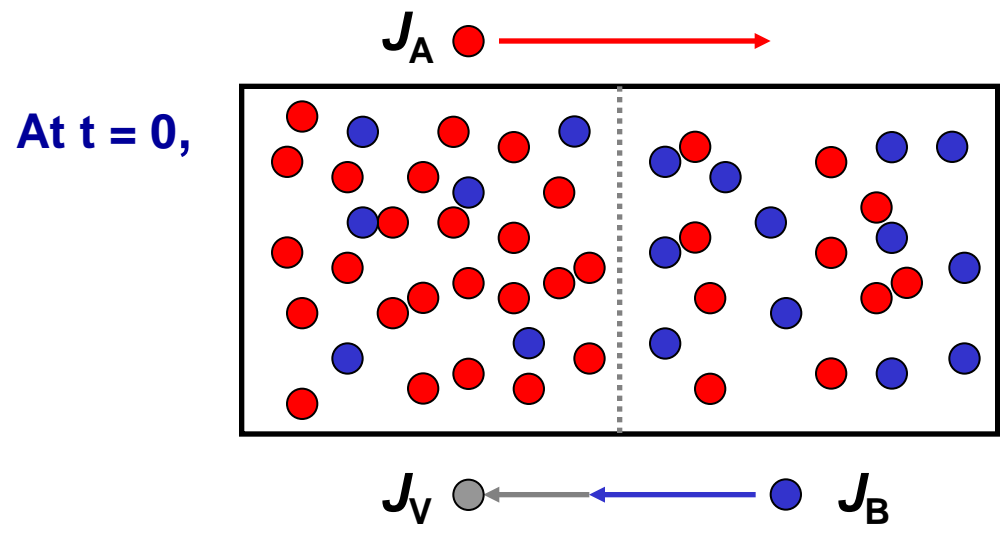
3. Diffusion in substitutional alloys

* **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.**

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

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

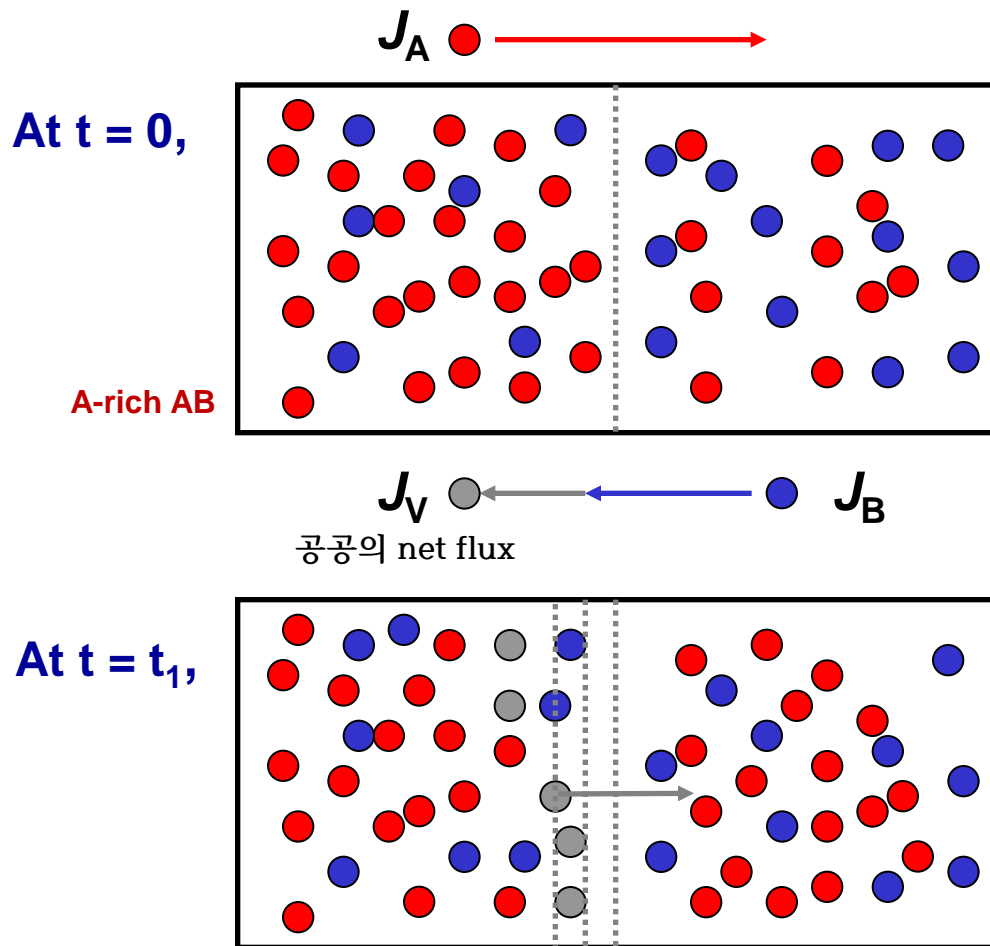$$J'_A = J_A + J^v_A = -\tilde{D}\frac{\partial C_A}{\partial x}$$

At t = 0,

J_A ⟶

J_V ⟵ J_B

At t = t₁,

J_A ⟶

J_V^A ⟵

J_A' ⟶

⟵ J_B'

⟵ J_V^B

⟵ J_B

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

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

32

침입형 확산에서 Fick의 법칙 고정된 격자면을 통한 이동

3. Diffusion in substitutional alloys

: A원자/B원자의 상호확산을 통한 격자면의 이동 고려

$$\frac{\partial C_A}{\partial t} = \frac{\partial}{\partial x}\left(\tilde{D}\frac{\partial C_A}{\partial x}\right)$$
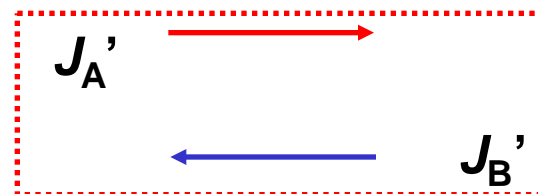
$$\tilde{D} = X_B D_A + X_A D_B$$

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

At t = 0,

A-rich AB

B-rich AB

J_A

J_V J_B

공공의 net flux

J_A

고정된 격자 내에서 확산에 의한 유속

$J_V{}^A$

확산이 일어나는 격자이동에 의한 A 유속

J_A'

J_B'

$J_V{}^B$

확산이 일어나는 격자이동에 의한 B 유속

J_B

고정된 격자 내에서 확산에 의한 유속

At t = t₁,

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

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

A원자와 B원자가 서로 다른 속도로 도약 →
농도 구배에 의한 속도 + 격자면 이동에 의한 속도

33