2018 Fall

“Phase Transformation *in* Materials”

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Contents for previous 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

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

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

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

  - Nonsteady-state diffusion – Fick's Second Law

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

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

  - For random walk in 3 dimensions,

  after n steps of length α

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

- **Effect of Temperature on Diffusivity**

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

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

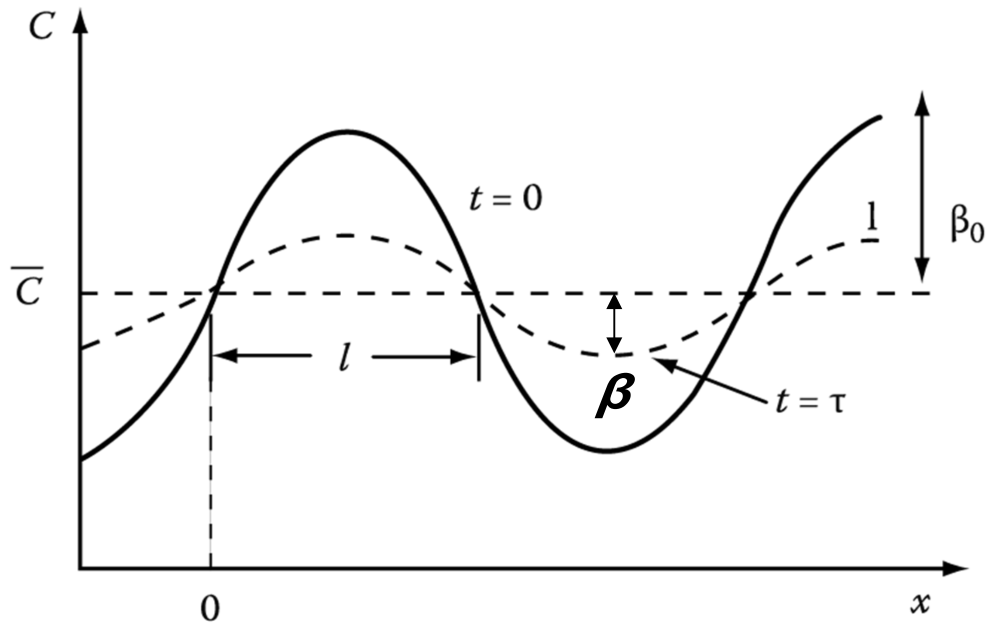


Fig. 2.10 The effect of diffusion on a sinusoidal variation of composition.

Initial or Boundary Cond.?

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

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

β_0 : the amplitude of the initial concentration profile

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

Using a method of variable separation

Let $C = XT \longrightarrow \boxed{\dfrac{\partial C}{\partial t} = D\dfrac{\partial^2 C}{\partial x^2}}$

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

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

$$\boxed{\begin{aligned} &\frac{1}{T}\frac{dT}{dt} = -\lambda^2 D \\ &\frac{d\ln T}{dt} = -\lambda^2 D \\ &T = T_0 e^{-\lambda^2 Dt} \end{aligned}}$$

$$\boxed{\begin{aligned} &\frac{d^2X}{dx^2} + \lambda^2 X = 0 \\ &X = A'\cos\lambda x + B'\sin\lambda x \\ &\boxed{X(x,0) \equiv \overline{C} + \beta_0 \sin\frac{\pi x}{l}} \end{aligned}}$$

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

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

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

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

($A_n = 0$ for all others)

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

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

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

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

Solutions to the diffusion equations

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

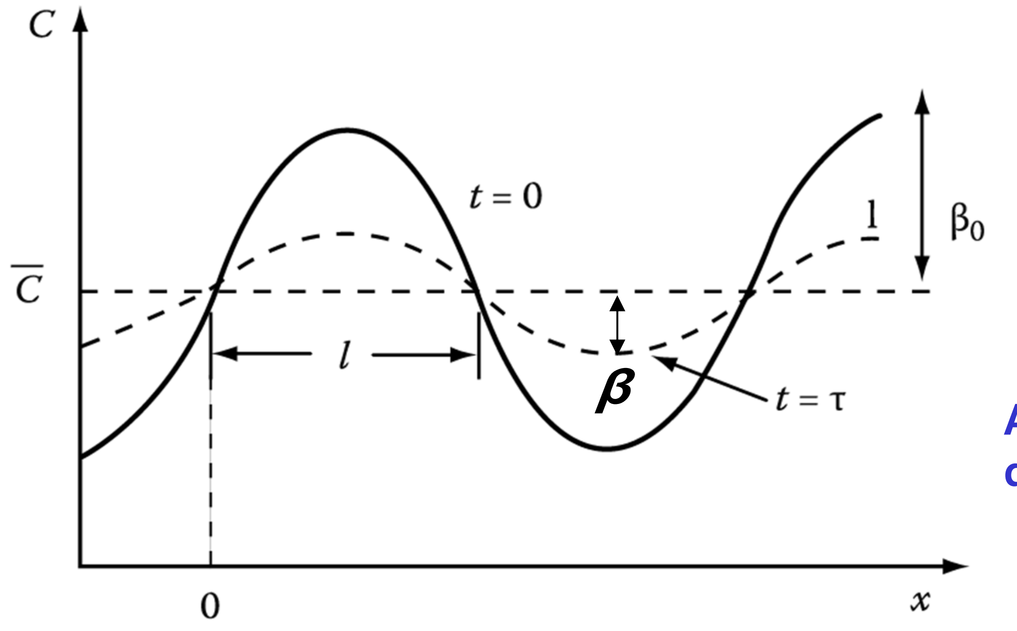


Fig. 2.10 The effect of diffusion on a sinusoidal variation of composition.

$$C = \bar{C} + \beta_0 \sin\frac{\pi x}{l}$$ **at t=0**

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

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

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

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

decide homogenization rate

The initial concentration profile will not usually be sinusoidal, but in general any concentration 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**.

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

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

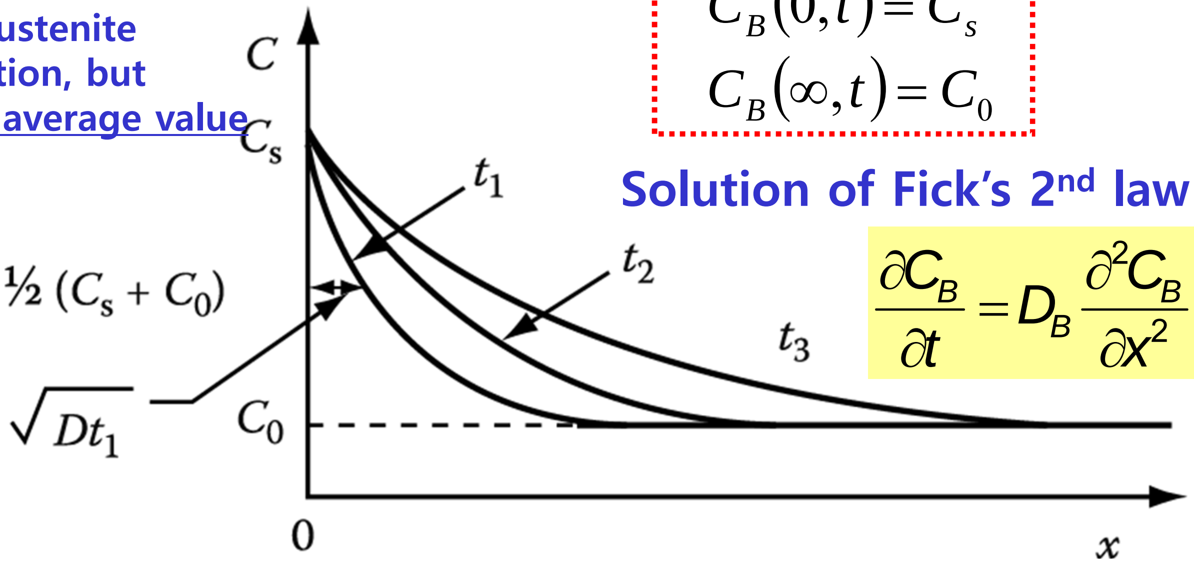


Fig. 2.11 Concentration profiles at successive times (t_3>t_2>t_1) for diffusion into a semi-infinite bar when the surface concentration Cs is maintained constant.

Error function

In mathematics, the error function (also called the Gauss error function) is a non-elementary function which occurs in probability, statistics and partial differential equations.

It is defined as:

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

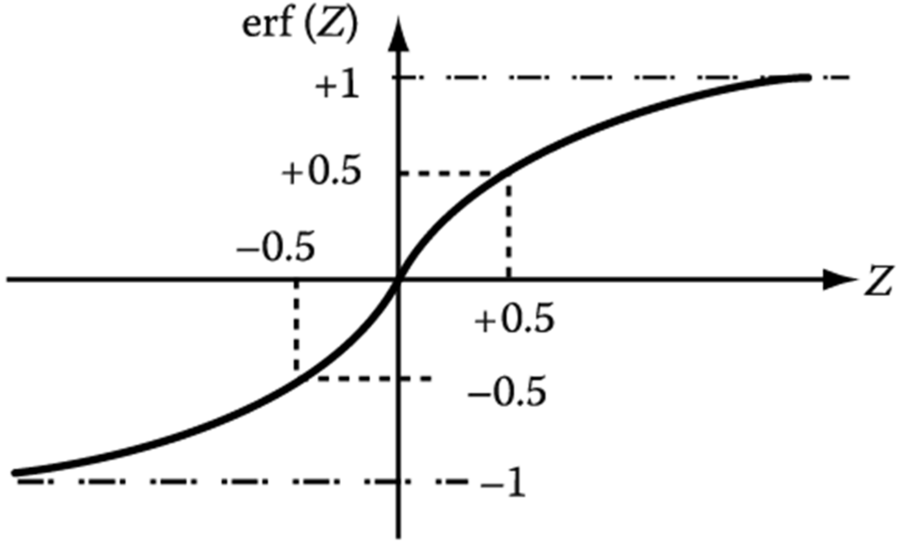
By expanding the right-hand side in a Taylor series and integrating, one can express it in the form

$$\operatorname{erf}(x) = \frac{2}{\sqrt{\pi}} \sum_{n=0}^{\infty} \frac{(-1)^n x^{2n+1}}{(2n+1)n!} = \frac{2}{\sqrt{\pi}} \left(x - \frac{x^3}{3} + \frac{x^5}{10} - \frac{x^7}{42} + \frac{x^9}{216} - \ \cdots \right)$$

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

Error function

$$\mathrm{erf}(z) = \frac{2}{\sqrt{\pi}} \int_{o}^{z} \exp(-y^2)\,dy$$



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

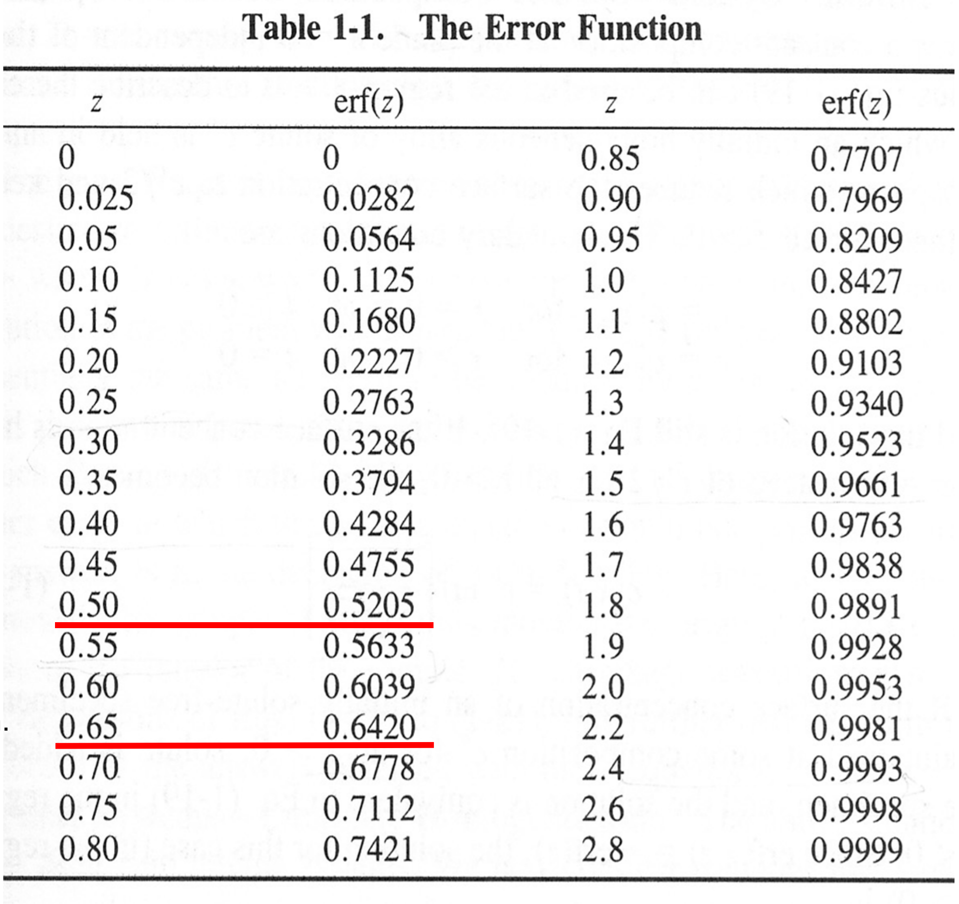


Table 1-1. The Error Function

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

*** Concentration profile : using boundary conditions**

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

⇨ **Solution of Fick's 2nd law**

The error function solution:

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

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

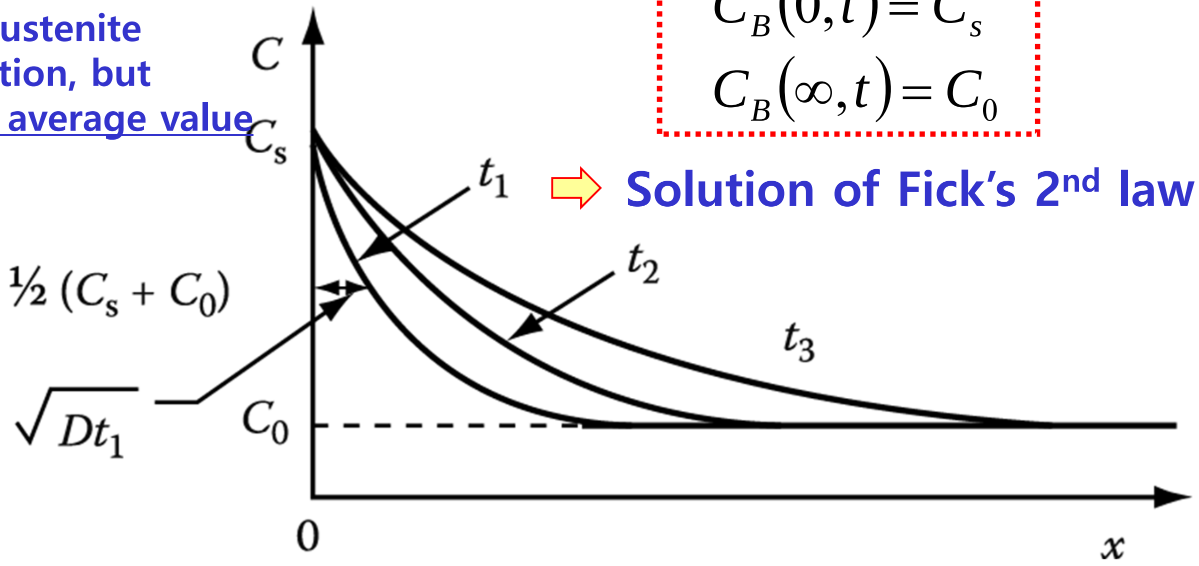


Fig. 2.11 Concentration profiles at successive times (t_3>t_2>t_1) for diffusion into a semi-infinite bar when the surface concentration Cs is maintained constant.

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

erf(0.5)≈0.5

$$C = \frac{C_s + C_0}{2}$$

- 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 $x \cong \sqrt{Dt}$ → **Depth of Carburization**

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?

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

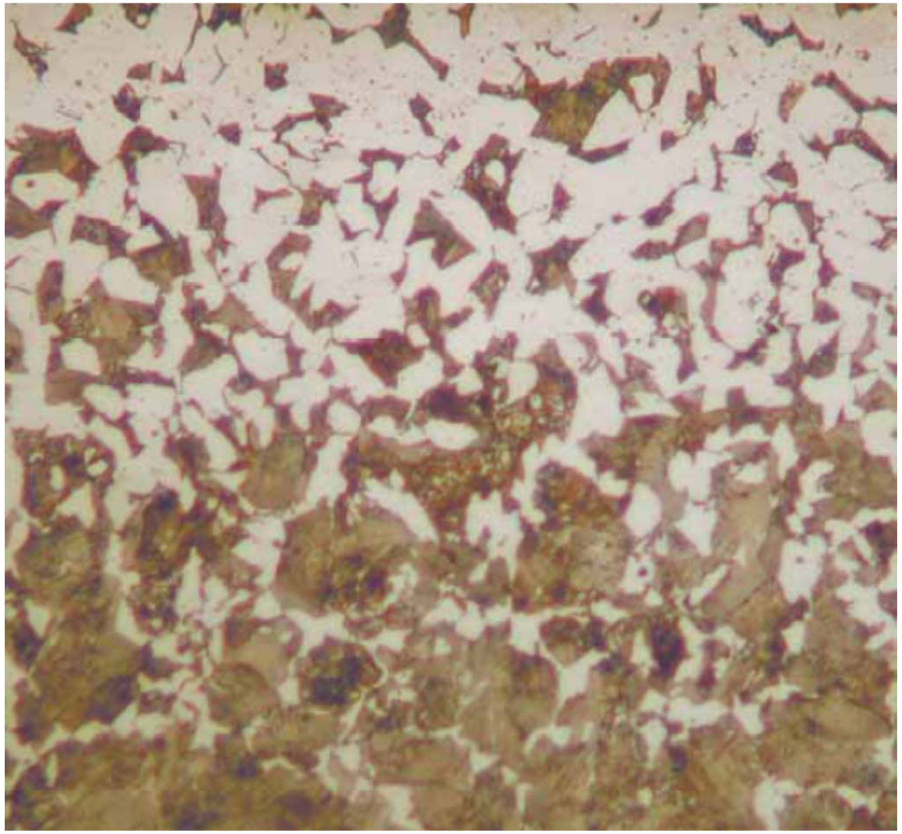
$$\updownarrow$$

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

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.

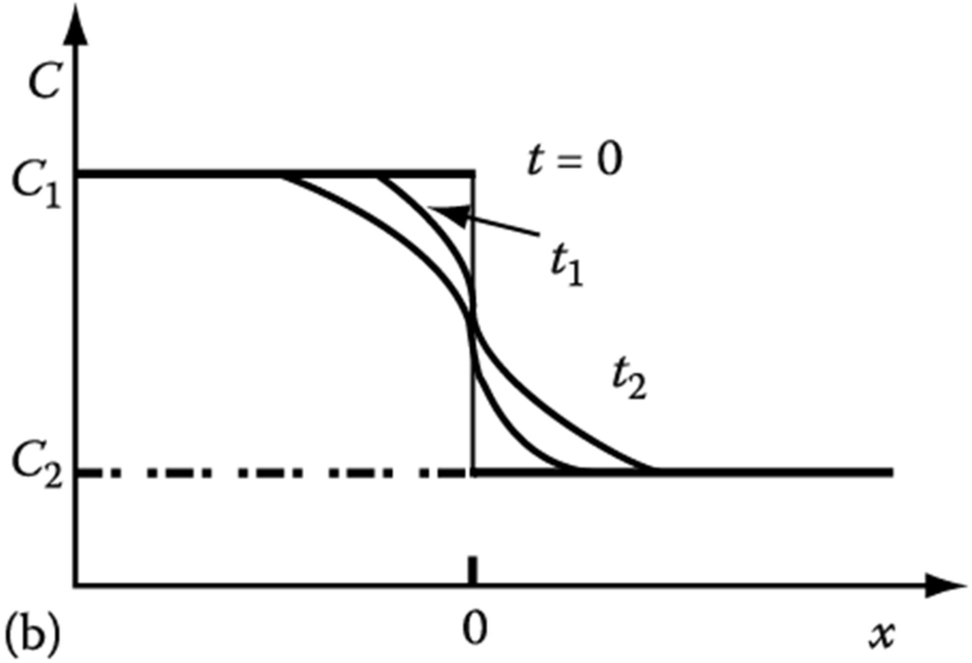


Fig. 2.12 (b) concentration profiles at successive times (t2>t1>0)
when two semi-infinite bars of different composition are annealed after welding.

Boundary conditions?

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

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

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

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

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

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	$C = C_S - (C_S - C_0)\,\mathrm{erf}\left(\frac{x}{2\sqrt{Dt}}\right)$ C_S = Surface concentration C_0 = Initial bulk concentration
Decarburization	$C = C_0\,\mathrm{erf}\left(\frac{x}{2\sqrt{Dt}}\right)$ 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

Contents for today's class

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.

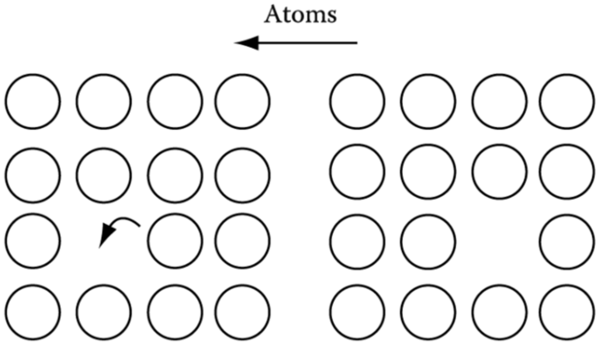
- In substitutional diffusion,

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 introducing 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.

Diffusion coefficient

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

Assumption
: unrelated to the previous jump

most likely to occur back into the same vacancy →

$$D_A^* = f\, D_A$$

(f : correlation factor)
close to unity

The next jump is not equally probable in all directions.

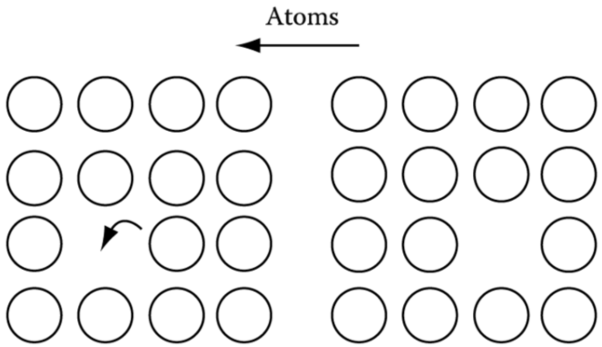
Q. Interstitial diffusion vs Substitutional diffusion

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

Substitutional diffusion

1. Self diffusion in pure material

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

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

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

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, $\alpha = a/\sqrt{2}$

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

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

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

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

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

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

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

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

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

$\because$ 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**

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?

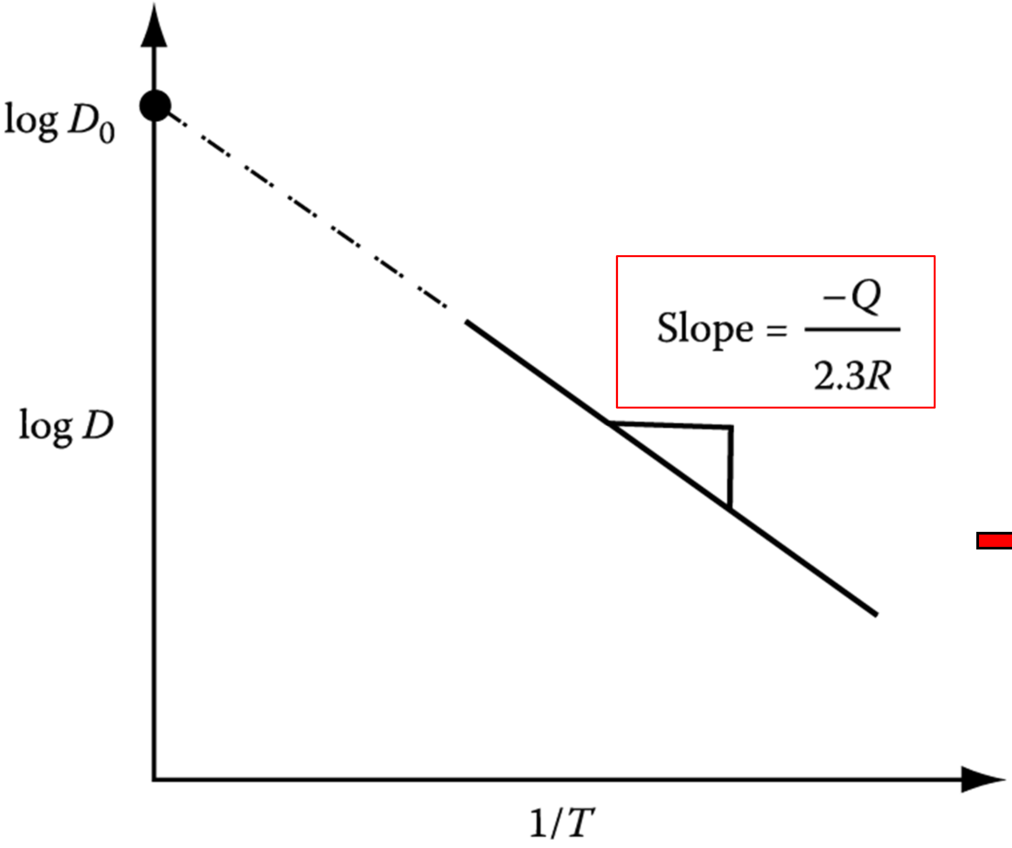


Fig. 2.7 The slope of log D v. 1/T gives the activation energy for diffusion Q.

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

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

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.**

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

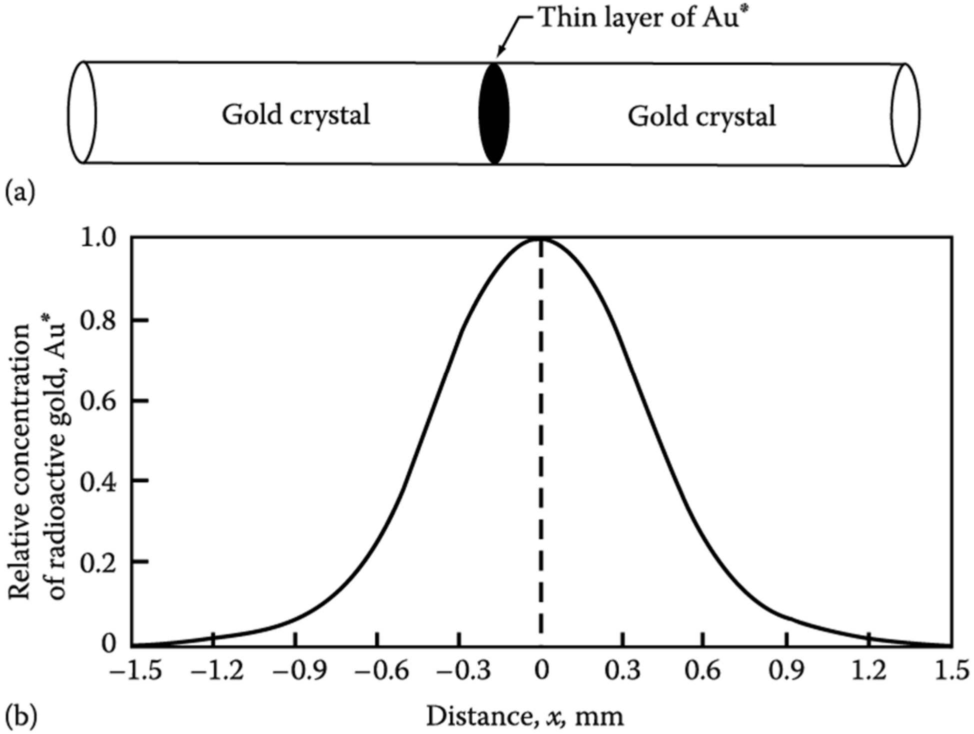
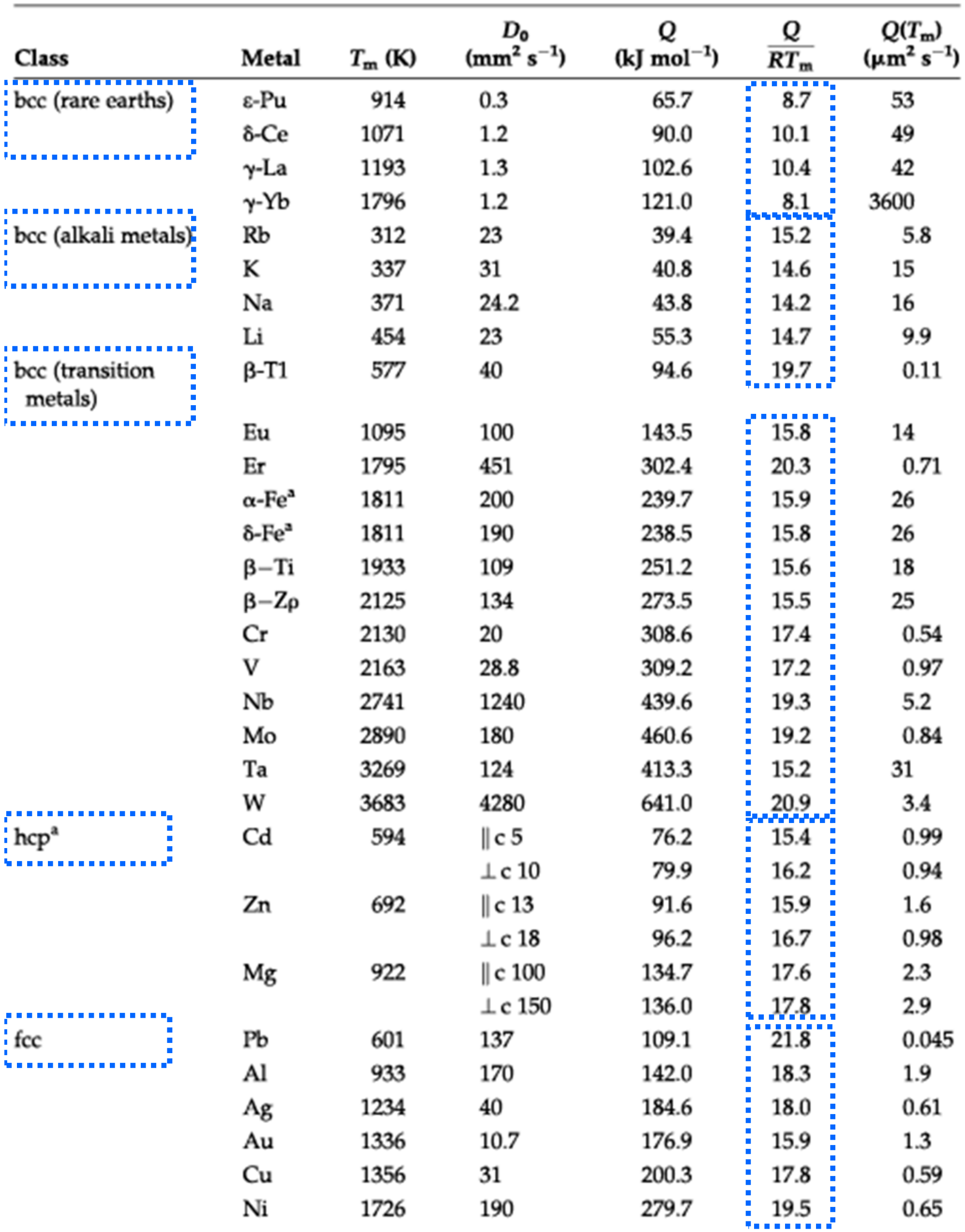


Fig. 2.14 Illustration of the principle of tracer diffusion and of the planar source method for determining the self-diffusion coefficient of gold. (a) Initial diffusion couple with planar source of radioactive gold Au*
(b) Distribution of Au* after diffusion for 100h at 920℃

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})	$\frac{Q}{RT_m}$	$Q(T_m)$ (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;

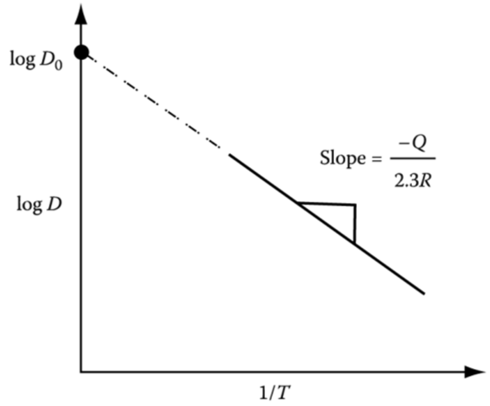
⇨ Q is roughly proportional to T_m.

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) ~ constant**

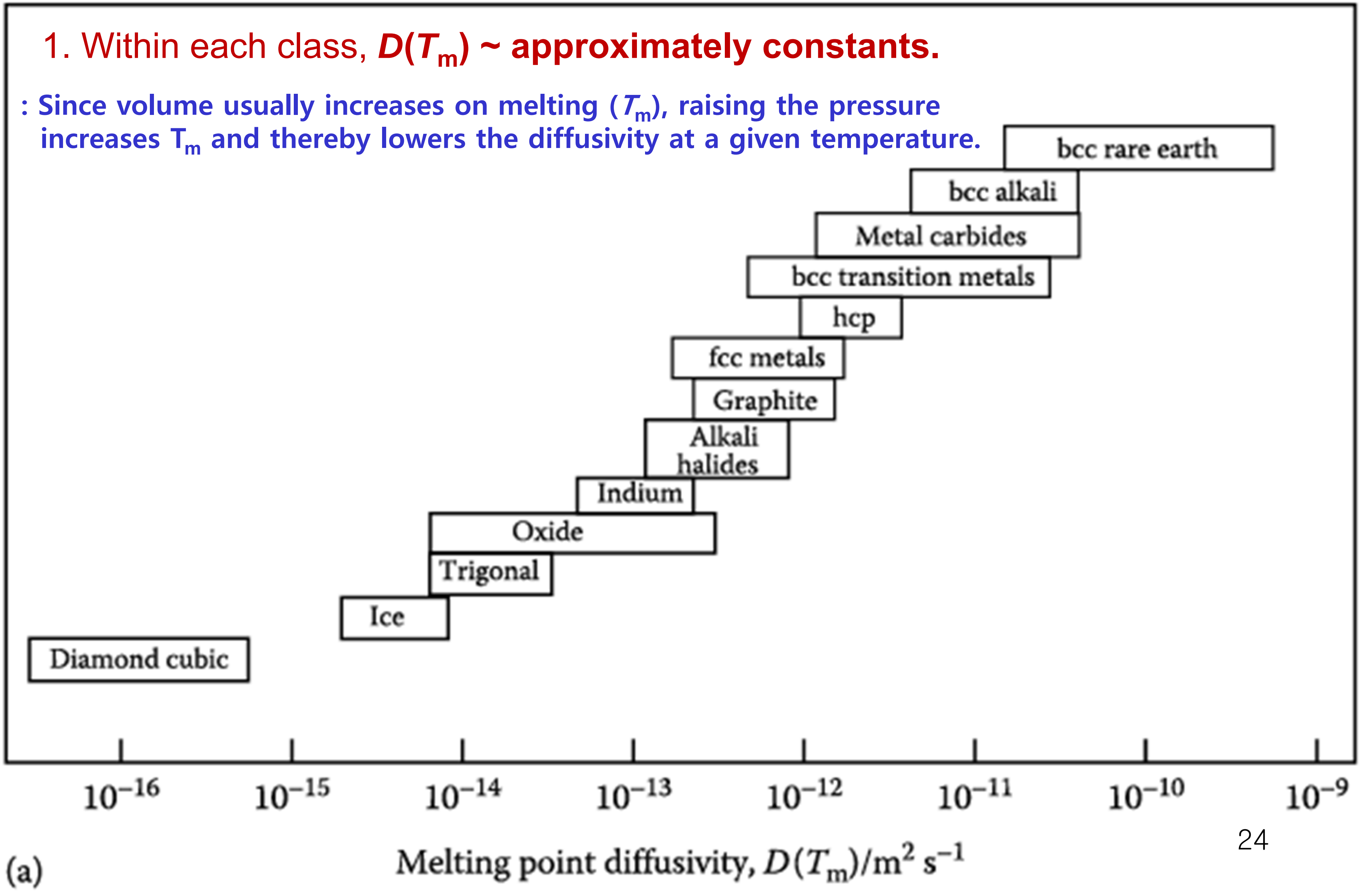
T/T_m : homologous temperature

* 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.

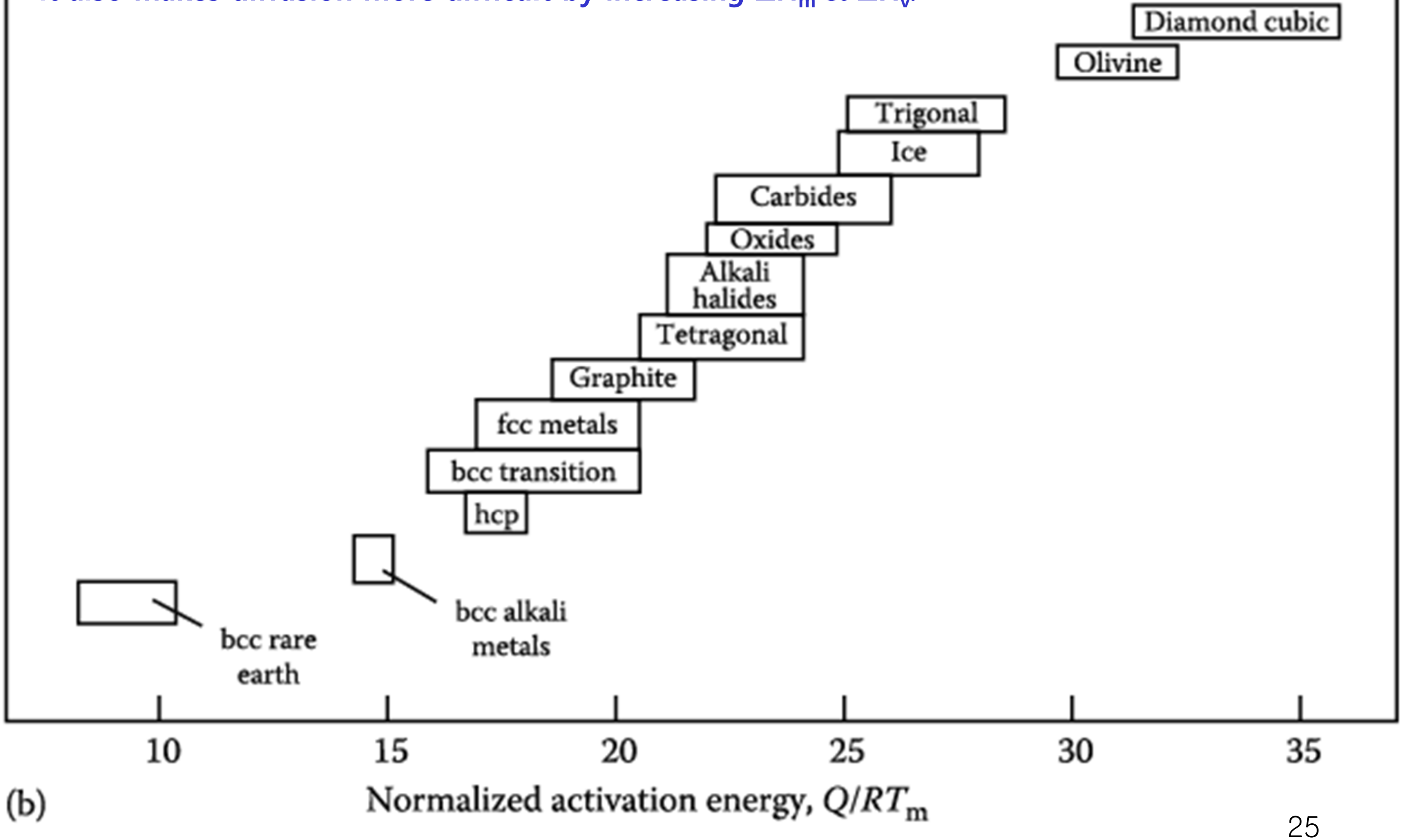
1. Within each class, **$D(T_m)$ ~ approximately constants.**

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



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.



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

ex) At 800°C, D_{Cu}= 5 × 10^{-9} mm^2s^{-1}, α = 0.25 nm Γ_{Cu} : ?

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

$$\Gamma_{Cu} = 5\times 10^5 \; jumps \; s^{-1}$$

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

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?

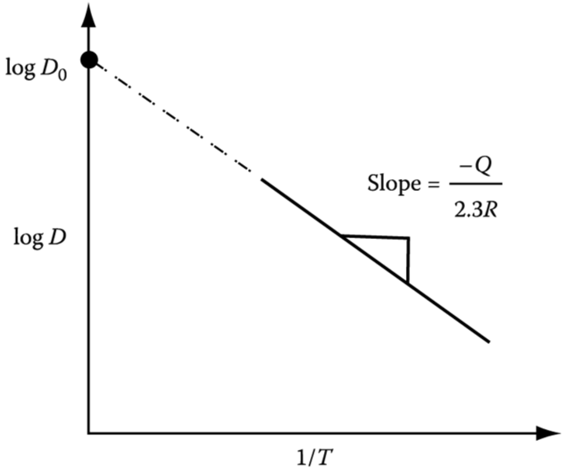


Fig. 2.7 The slope of log D v. 1/T gives the activation energy for diffusion Q.

At 20°C, D_{Cu}~ 10^{-34} mm^2s^{-1}

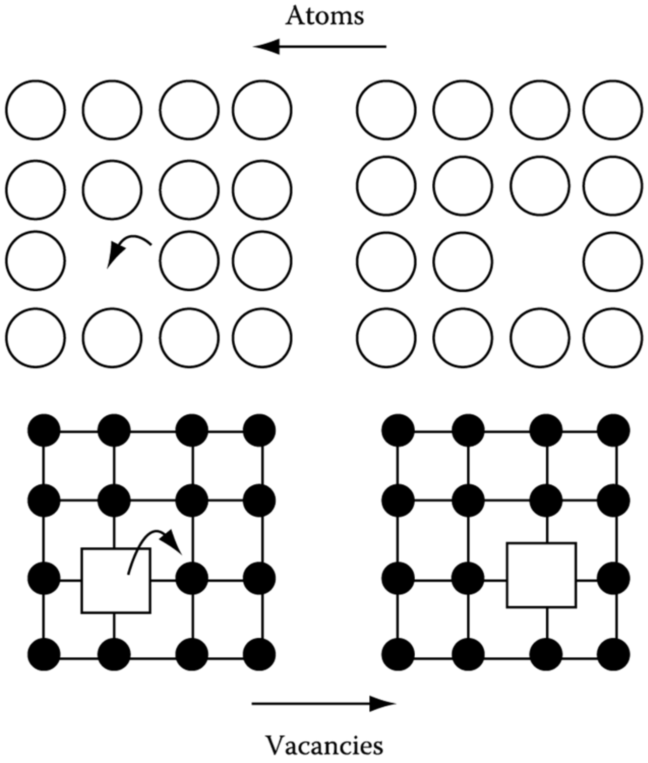
$$\Gamma_{Cu} \sim 10^{-20} \; jumps \;\; s^{-1}$$

→ Each atom would make one jump every 10^{12} 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.

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

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

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

$$\boxed{D_v = D_A / X_v^e}$$

This shows in fact that the diffusivity of vacancy (D_v) is many orders of magnitude greater than the diffusivity of substitutional atoms (D_A).

Q: Diffusion in substitutional alloys?

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

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

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

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

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

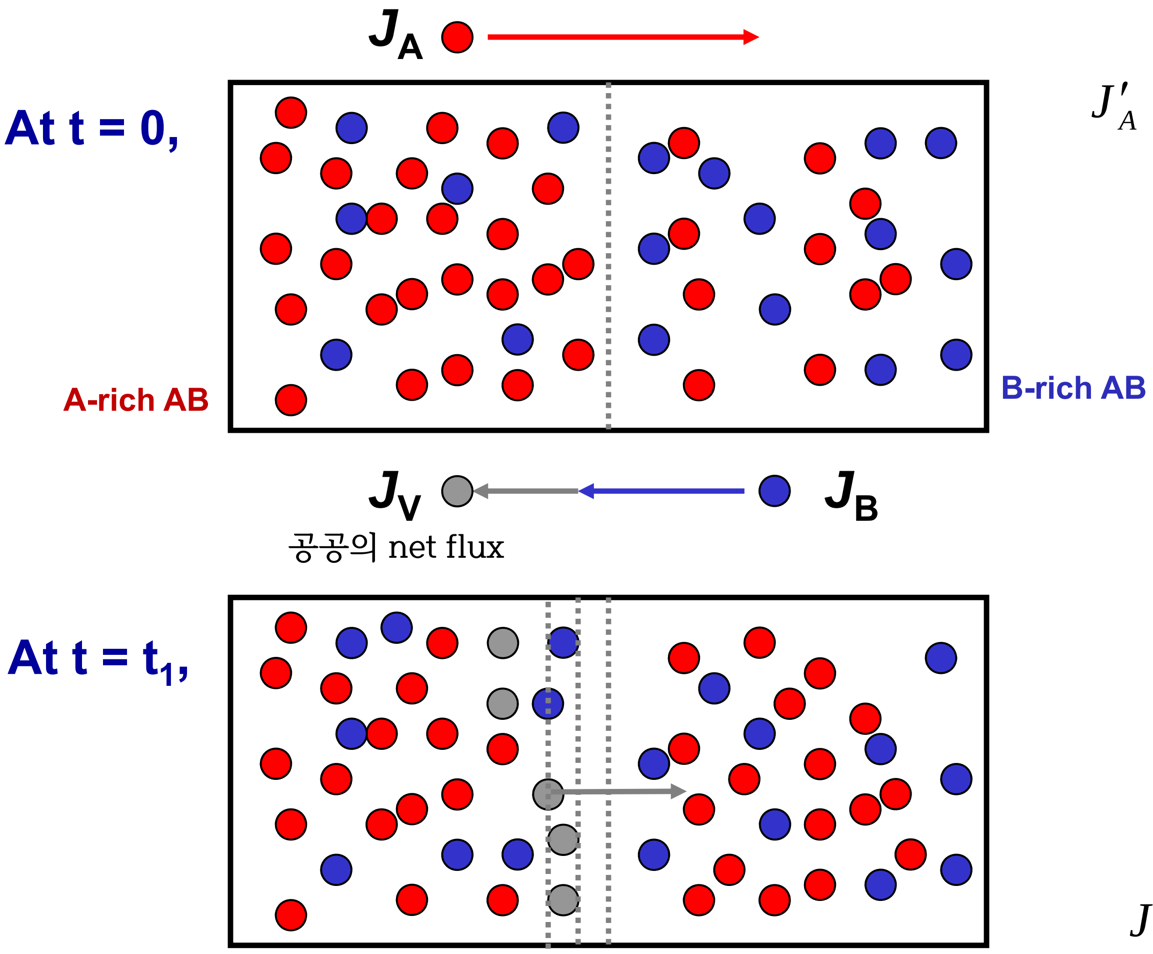
Fick's 1st law for substitutional alloy

Fick's 2nd law for substitutional alloy

침입형 확산에서 Fick의 법칙 고정된 격자면의 이동 고려

3. Diffusion in substitutional alloys

: A원자/B원자의 상호확산을 통한 격자면의 이동 고려



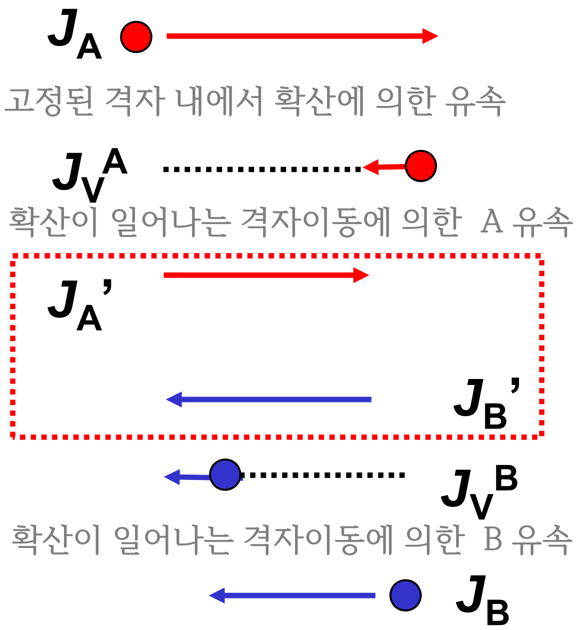
A원자와 B원자가 서로 다른 속도로 도약 →

농도 구배에 의한 속도 + 격자면 이동에 의한 속도

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

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

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



고정된 격자 내에서 확산에 의한 유속

확산이 일어나는 격자이동에 의한 A 유속

확산이 일어나는 격자이동에 의한 B 유속

고정된 격자 내에서 확산에 의한 유속

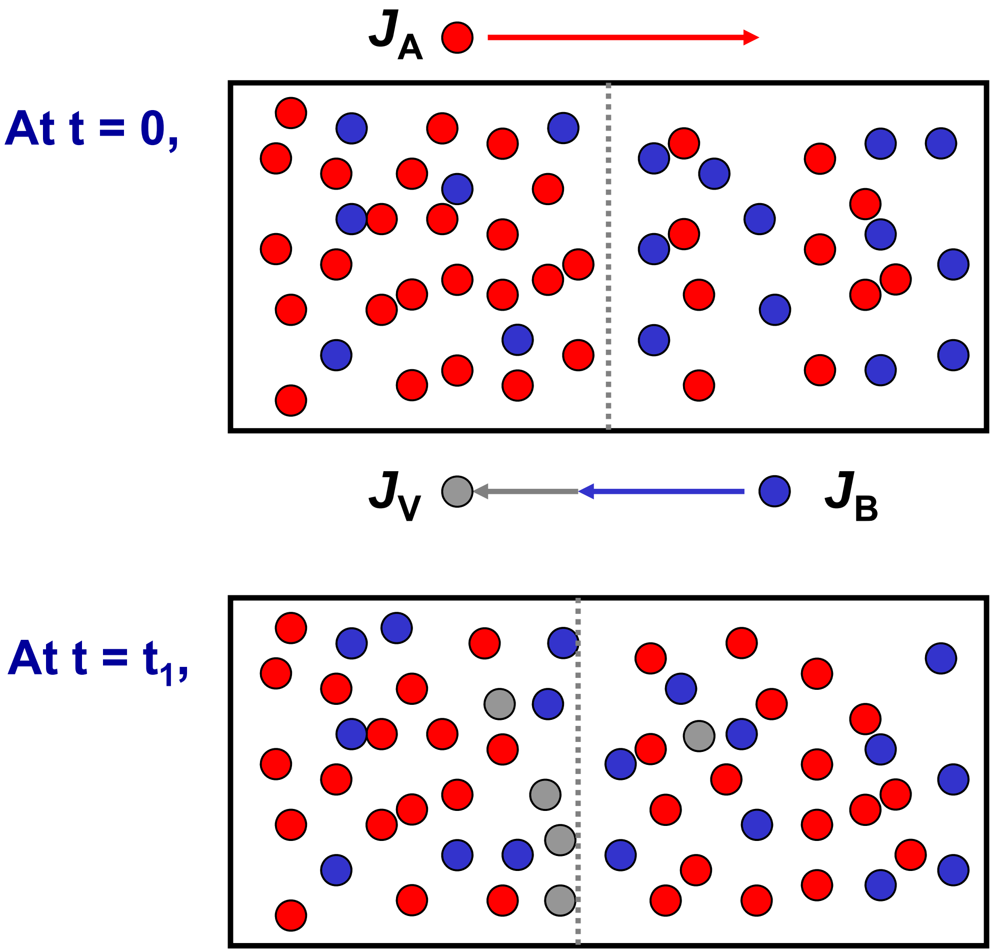
$$J'_B = J_B + J_v^B = J_B + vC_B = -\tilde{D}\frac{\partial C_B}{\partial x}$$

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

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.**



Kirkendall effect

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

Whole planes of atoms will be ‘eaten’ away **Extra atomic planes will be introduced**

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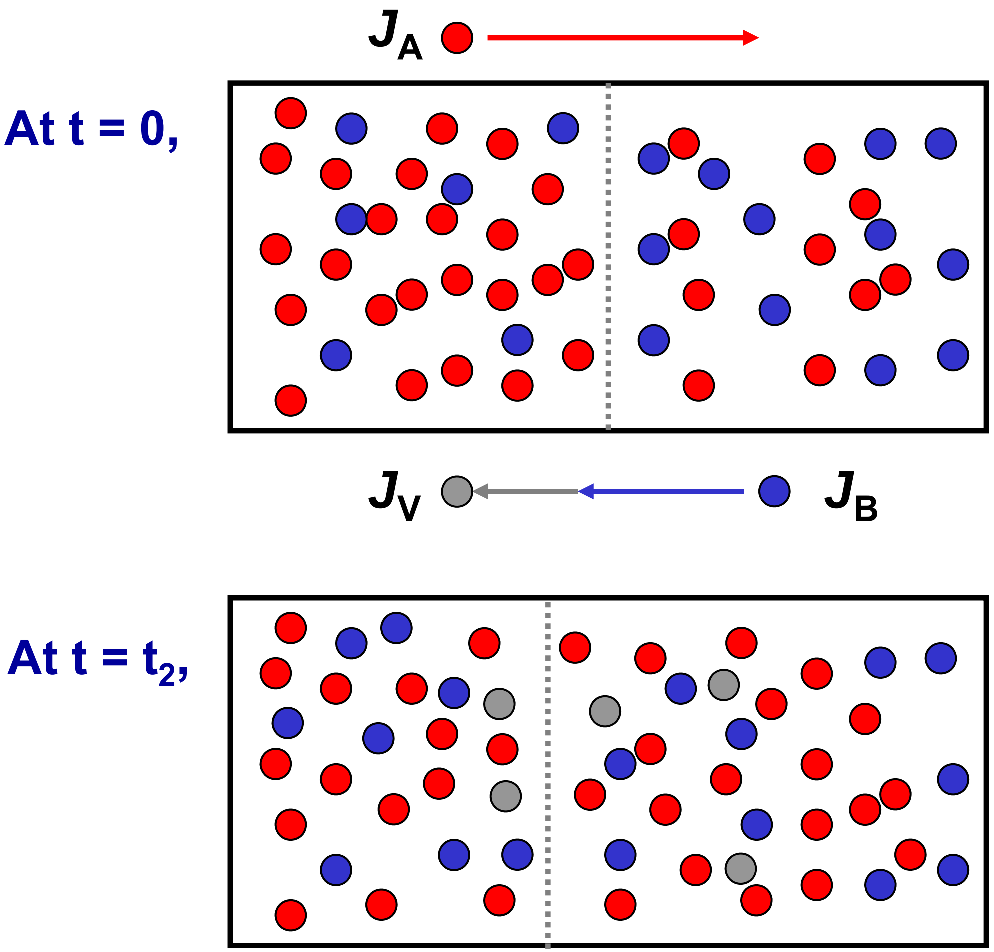

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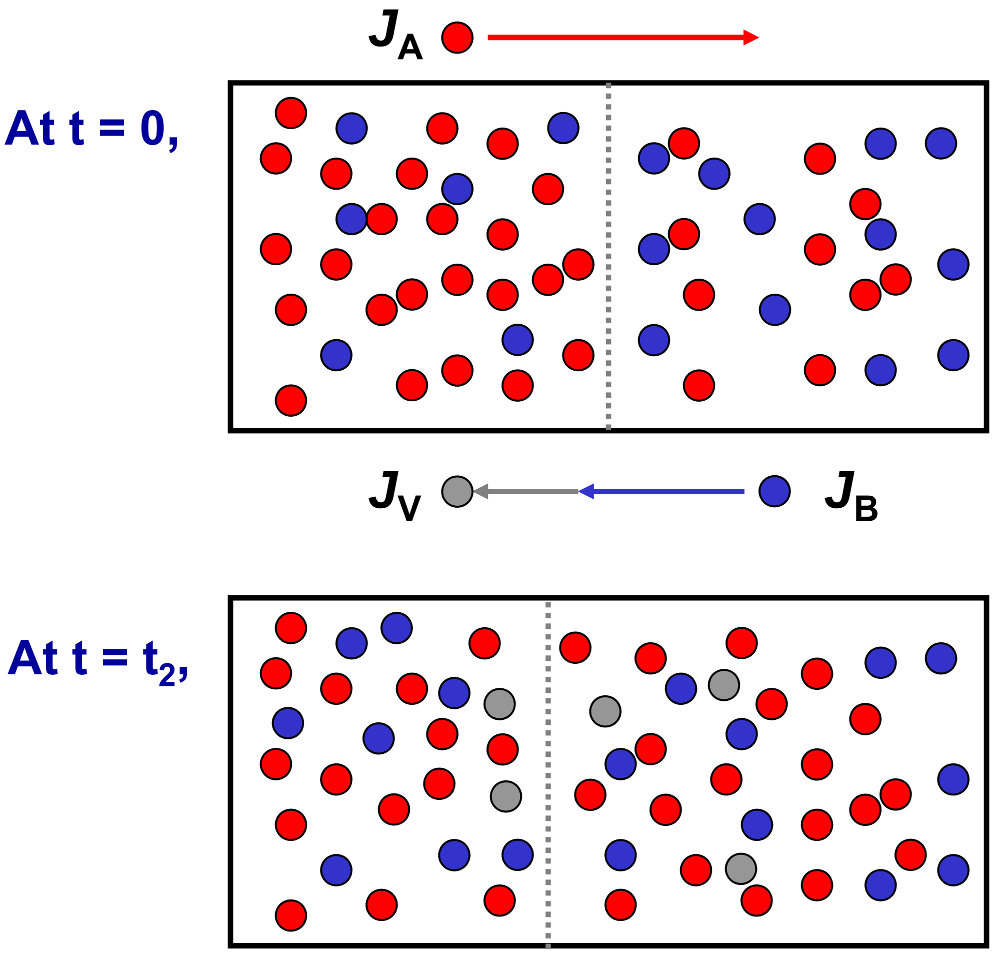
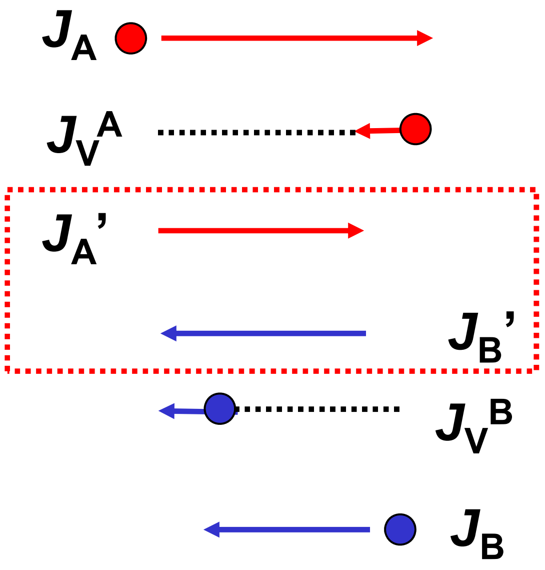


Whole planes of atoms will be 'eaten' away   Extra atomic planes will be introduced

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

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

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



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

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

1) INTERDIFFUSION

Assume that C_0: total number of atoms (A, B) per unit volume = constant, independent of composition

$C_o = C_A + C_B$ **and** $\dfrac{\partial C_A}{\partial x} = -\dfrac{\partial C_B}{\partial x}$

*** If the couple is annealed at a high enough temp., a concentration profile will develop as shown.**

Fluxes of A and B atoms across a given lattice plane ~ equal

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

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

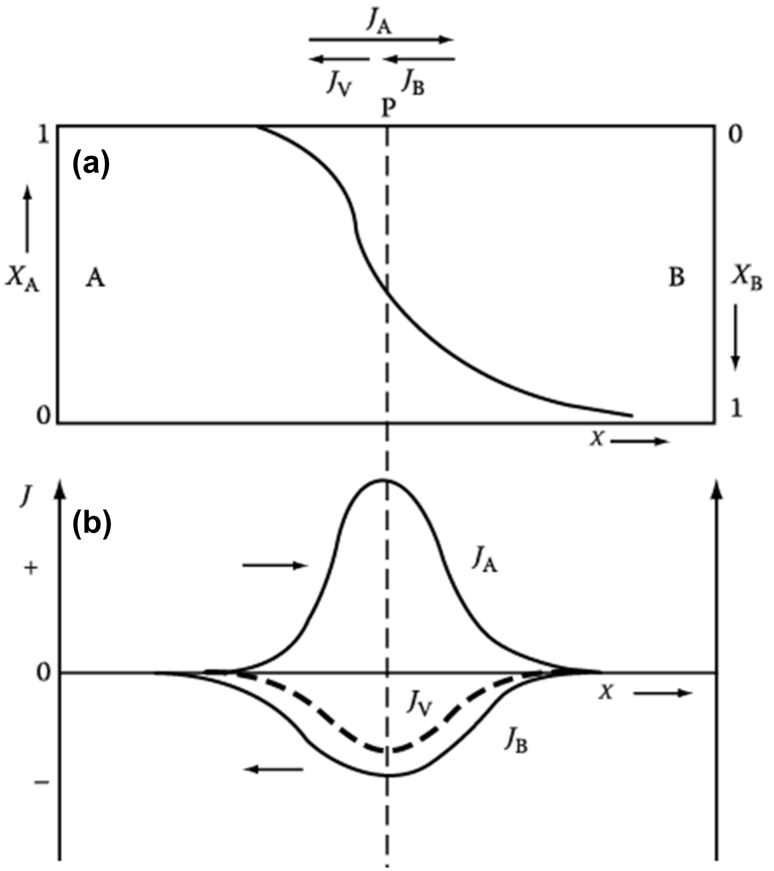
Flux of vacancies

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

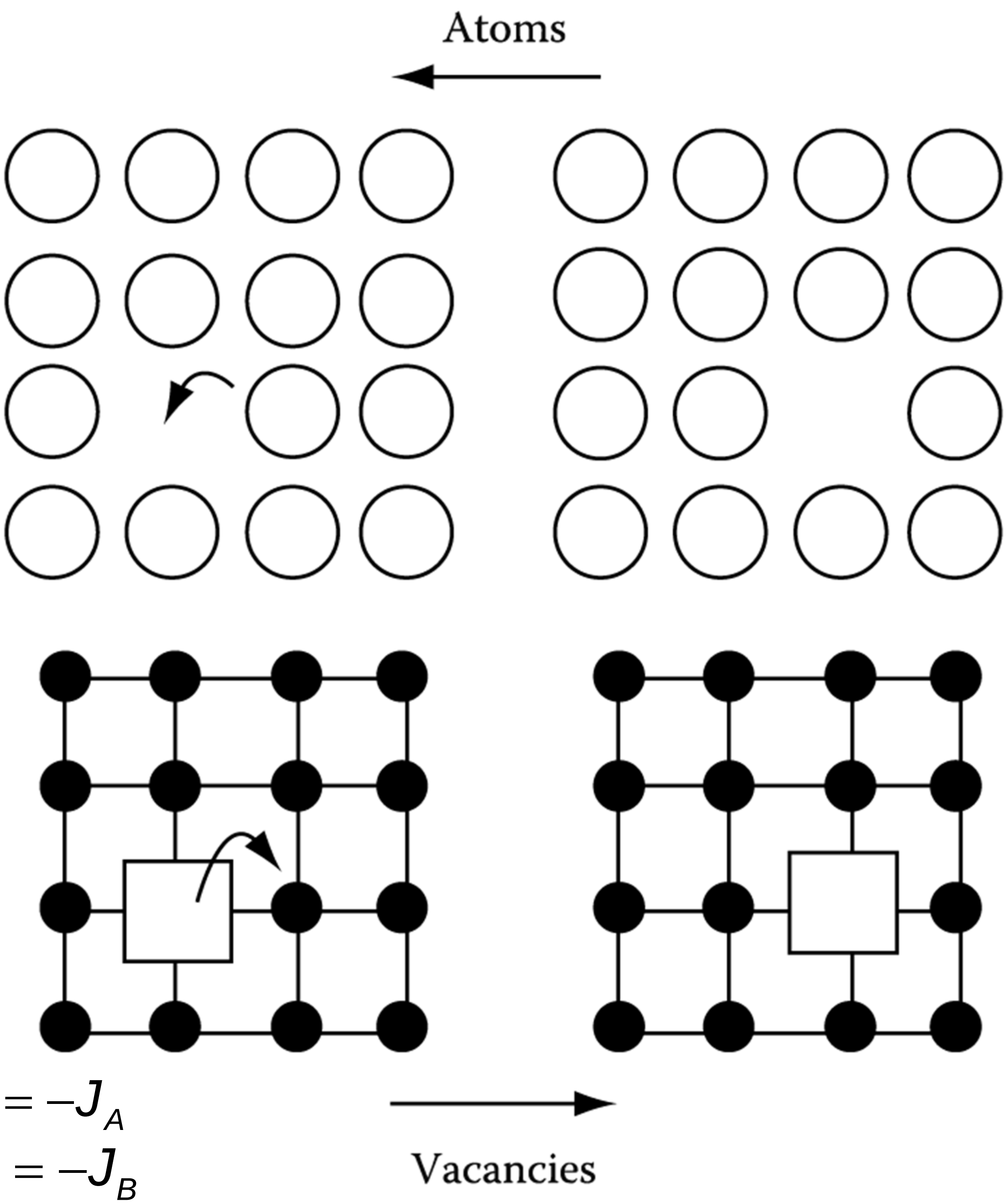
$$J_V + J_B = -J_A$$

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

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



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



Flux of vacancies

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

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

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

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

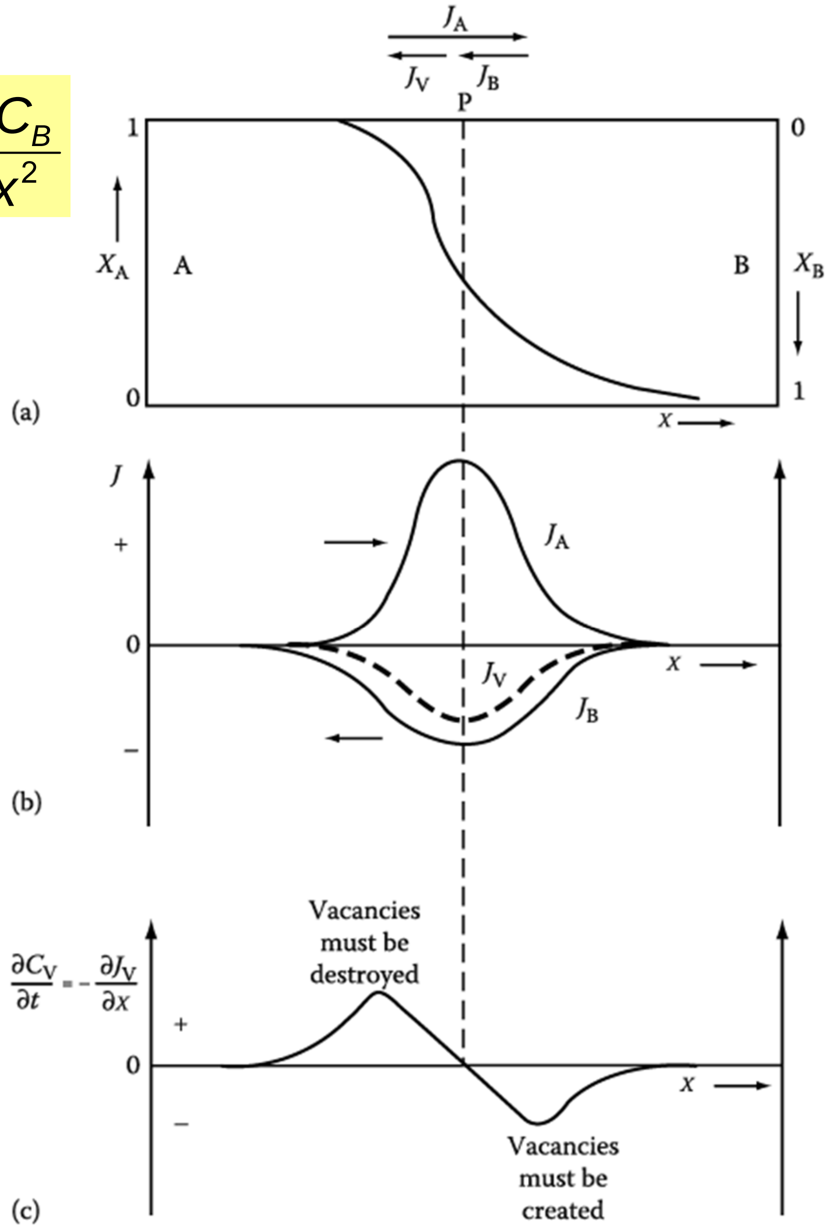
$$\frac{\partial C_B}{\partial t} = D_B \frac{\partial^2 C_B}{\partial x^2}$$

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

What would become of excess vacancy?

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

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

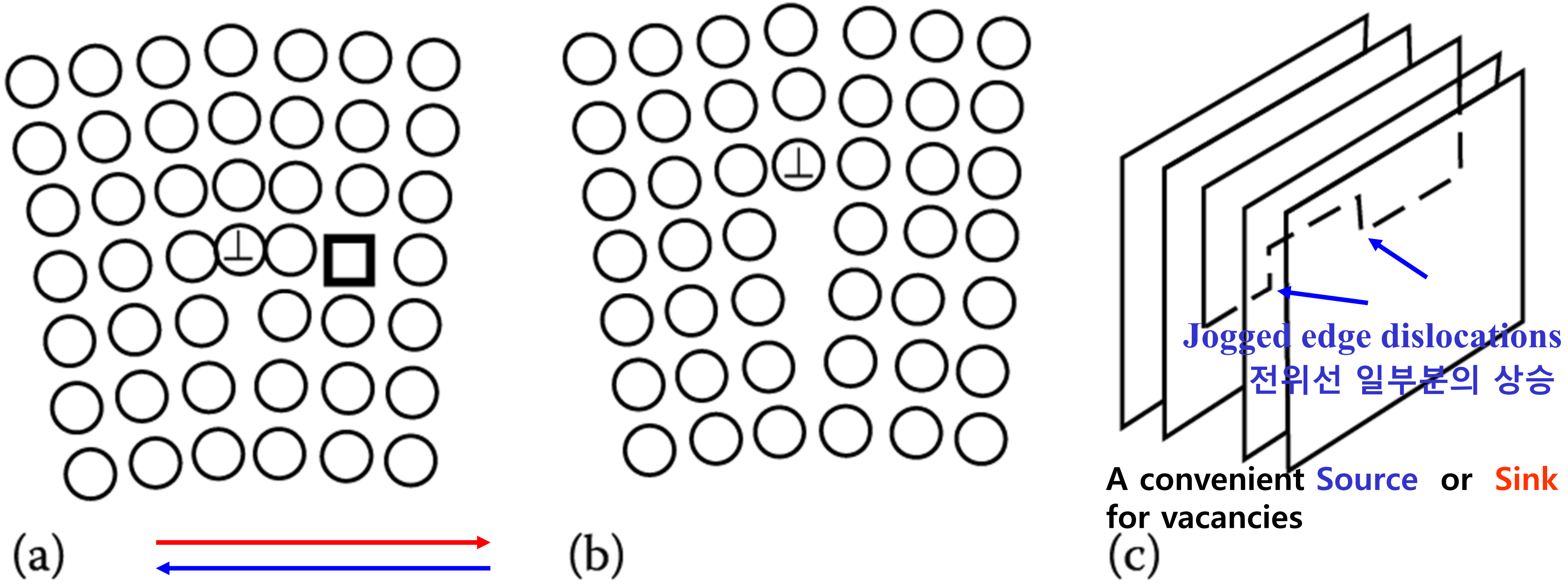


In order to maintain the vacancy concentration everywhere near equilibrium, **vacancies must be created on the B-rich side and destroyed on the A-rich side.**

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

Kirkendall effect

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

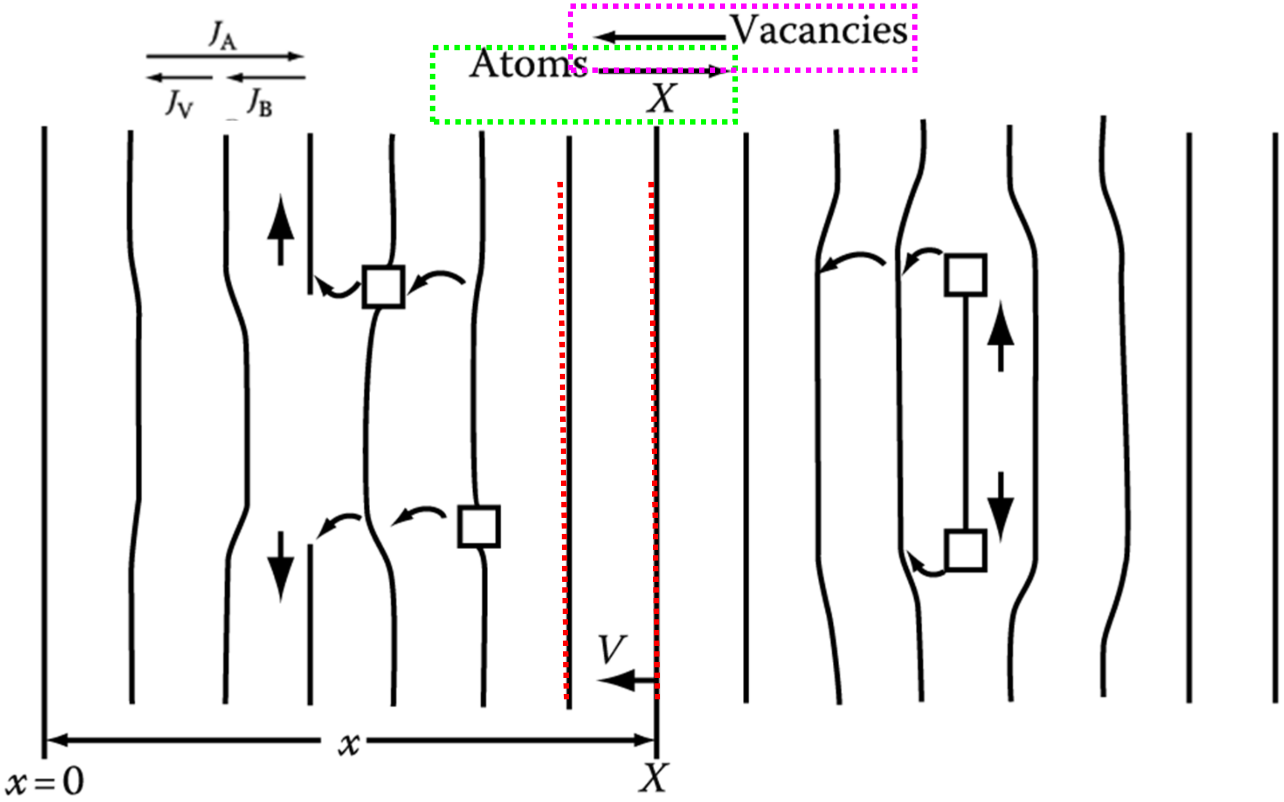


Jogged edge dislocations
전위선 일부분의 상승

A convenient Source or Sink for vacancies

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 climb of an edge dislocation.
(c) Perspective drawing of a jogged edge dislocation.

If dislocation climbs continue to occur, what would happen?



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.

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

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

# of removed atoms

# of vacancies crossing the plane

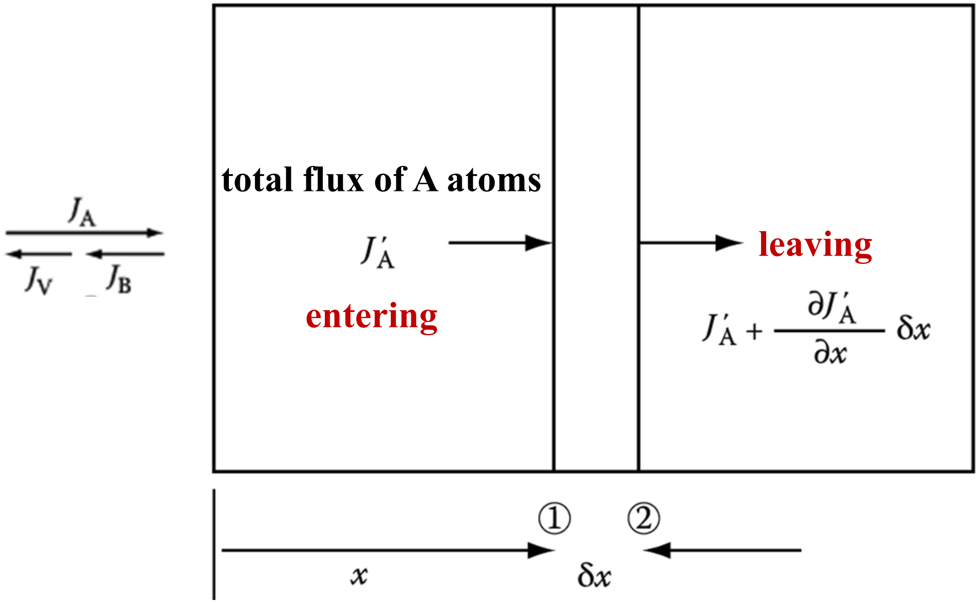
$$v = \frac{1}{C_0}\boxed{(D_A - D_B)\frac{\partial C_A}{\partial x}} = (D_A - D_B)\frac{\partial X_A}{\partial x}$$

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.

(균질화 시간 혹은 확산쌍의 위치에 따른 조성 변화)

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



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

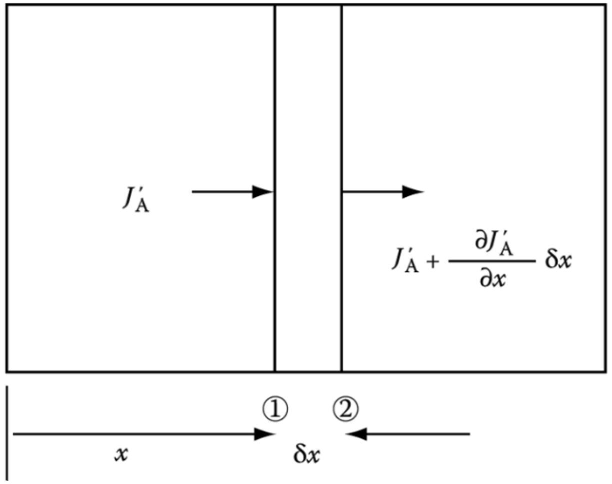
Fig. 2.19 Derivation of Fick's second law for interdiffusion. (See text for details.)

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

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

$$= -D_A \frac{\partial C_A}{\partial x} + vC_A$$

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

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

Fick's 1st law for substitutional alloy

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

(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 ⟷

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

Only difference with ID
: diffusion coefficient

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

Q: How can we determine D_A and D_B? in substitutional alloys?

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

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

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

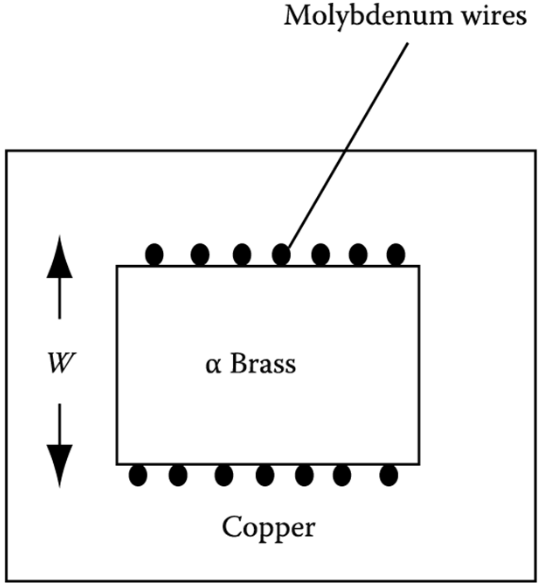
How can we determine D_A and D_B?

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

⇨ $\tilde{D} = X_B D_A + X_A D_B$

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.**

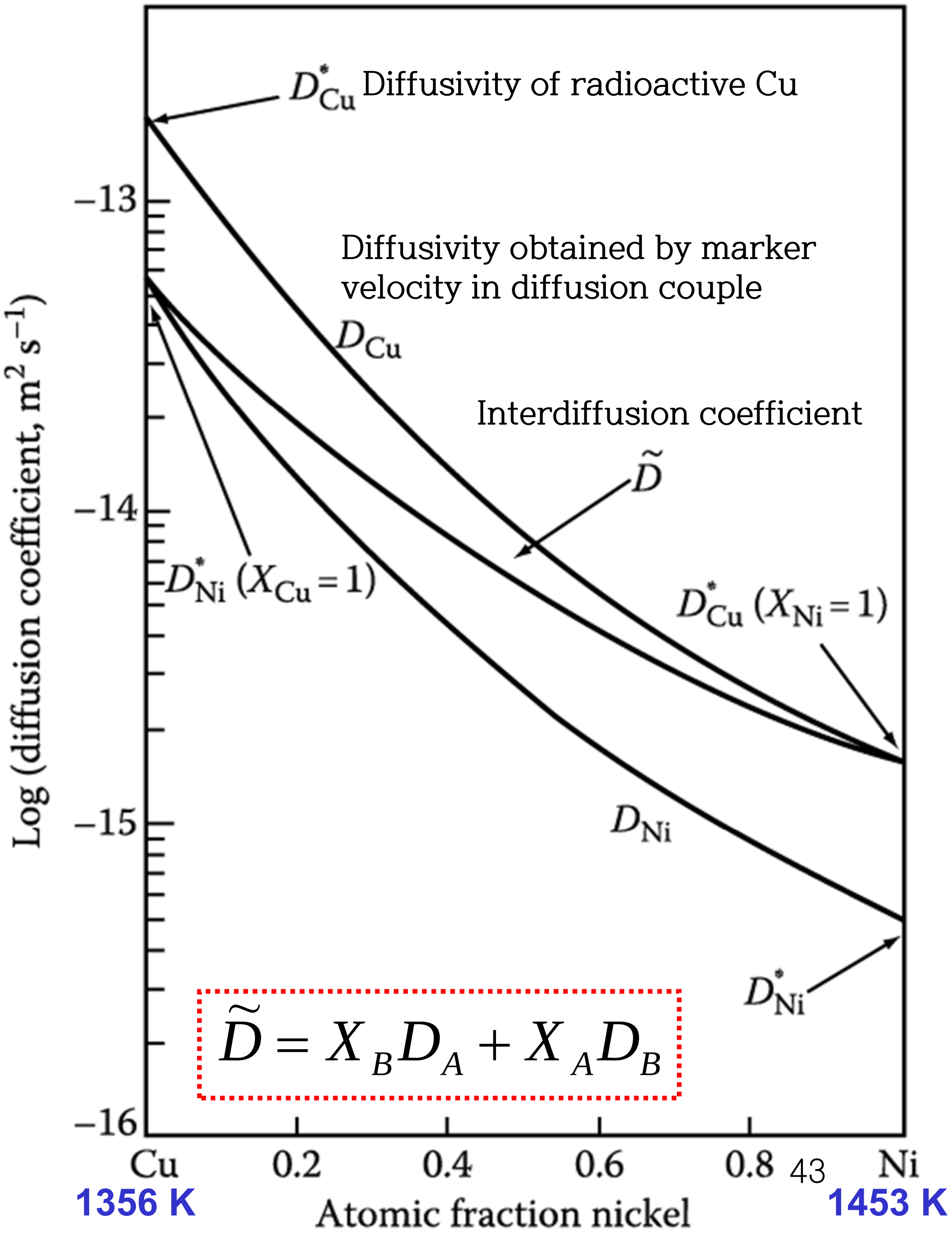
$D_{Zn} > D_{Cu}$

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.

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

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).

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 <u>'impurity diffusion coefficient'.</u>
~ can be measured by using radioactive tracers like self-diffusion

*** <u>D_B in a dilute solution of B in A is greater than D_A.</u>**

- The reason for this is that the <u>**solute atoms can attract vacancies**</u> so that there is more than a random probability of finding <u>a vacancy next to a solute atom</u> with the result that they can <u>**diffuse faster than solvent**</u>.
- 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 <u>solute-vacancy pair can diffuse through the lattice together.</u>

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

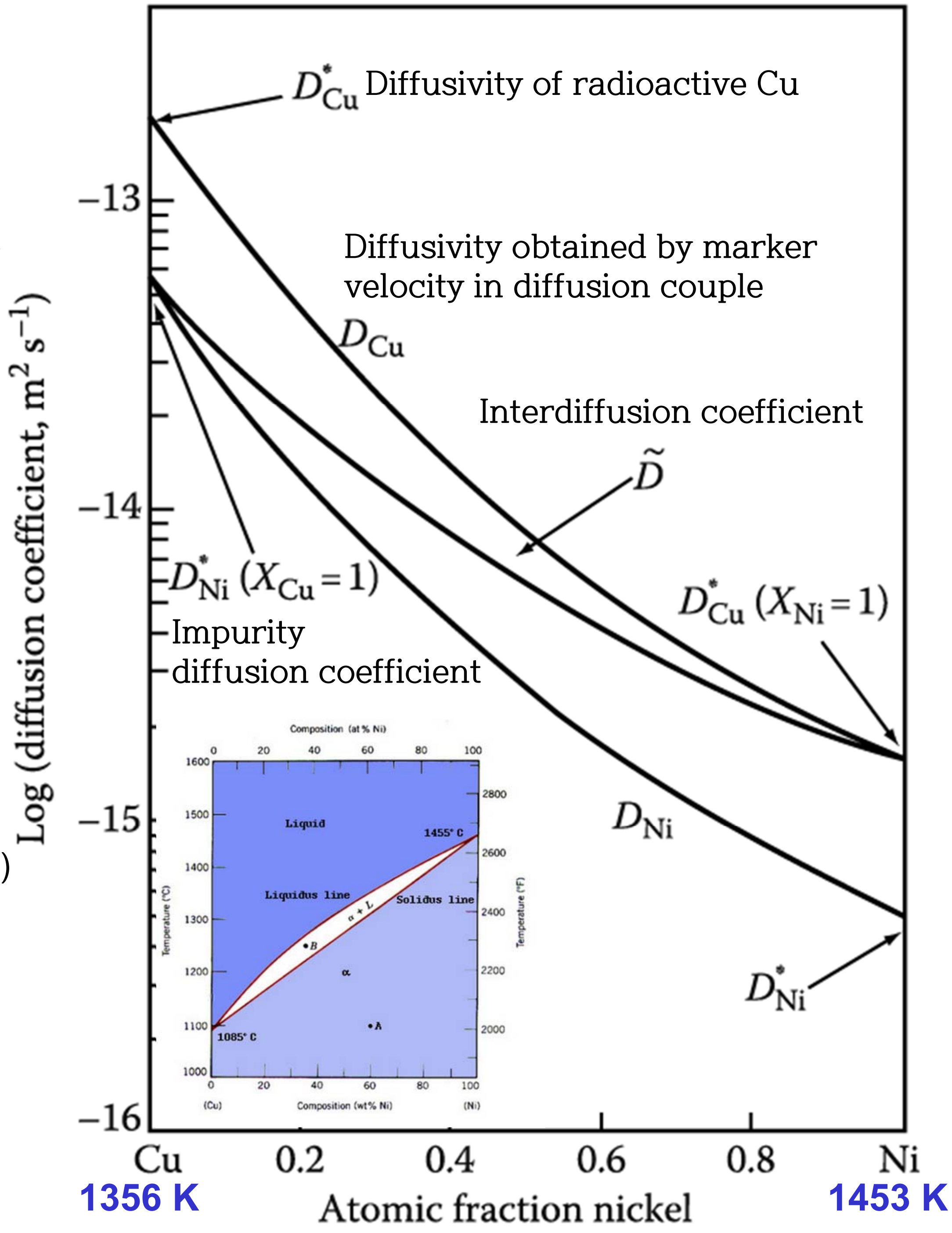
$$\boxed{\frac{\partial C_A}{\partial t} = \frac{\partial}{\partial x}\left(\tilde{D}\frac{\partial C_A}{\partial x}\right)} \quad \text{Eq. (2.53)}$$

⇨ 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

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

(The range of composition is small enough that any effect of composition on $\tilde{D}$ can be ignored)



1356 K **1453 K**

Contents for today's class

- **Substitution Diffusion**

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

Probability of vacancy x probability of jump

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

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

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

2. **Vacancy diffusion**

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

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

$$D_v = D_A / X_v^e$$

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

3. **Diffusion in substitutional alloys**

침입형 확산에서 Fick의 법칙 고정된 격자면을 통한 이동

3. Diffusion in substitutional alloys

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

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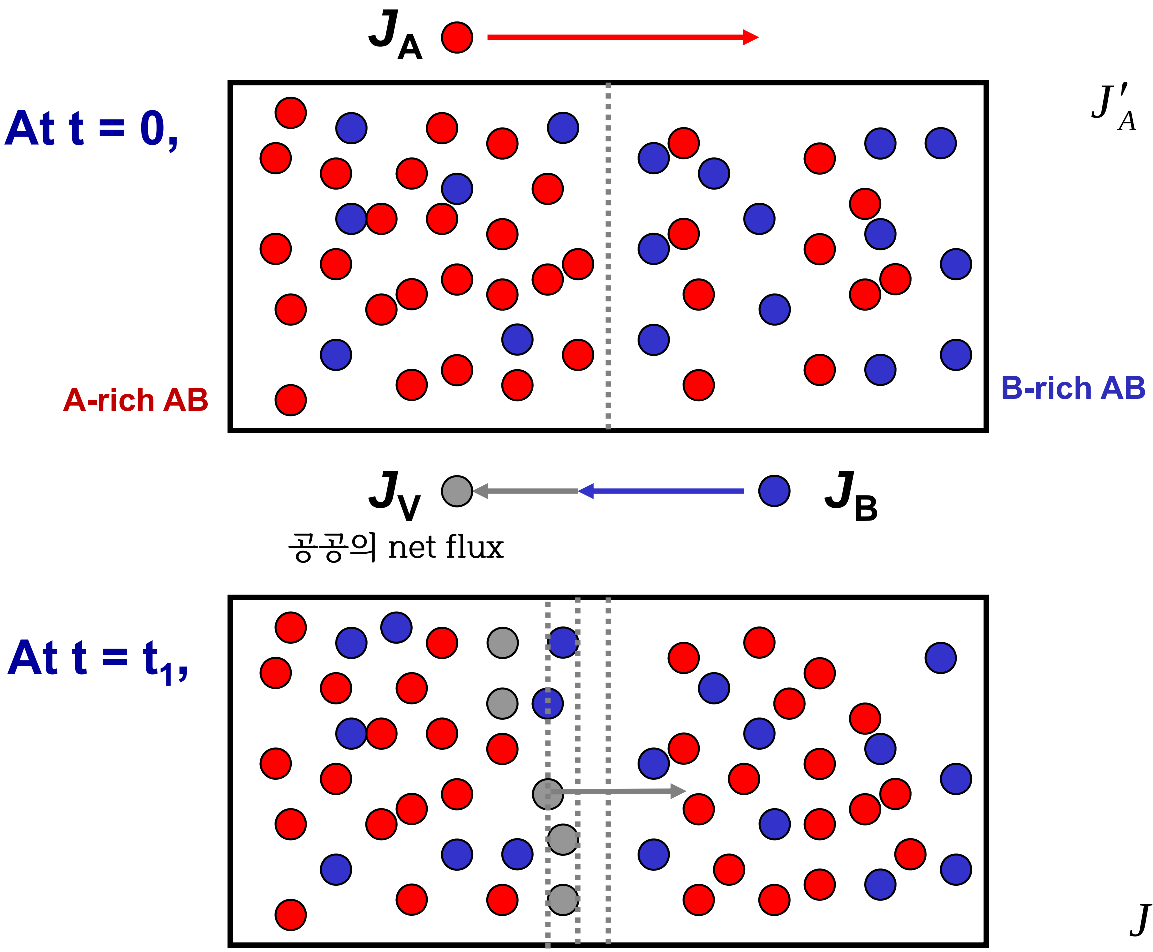

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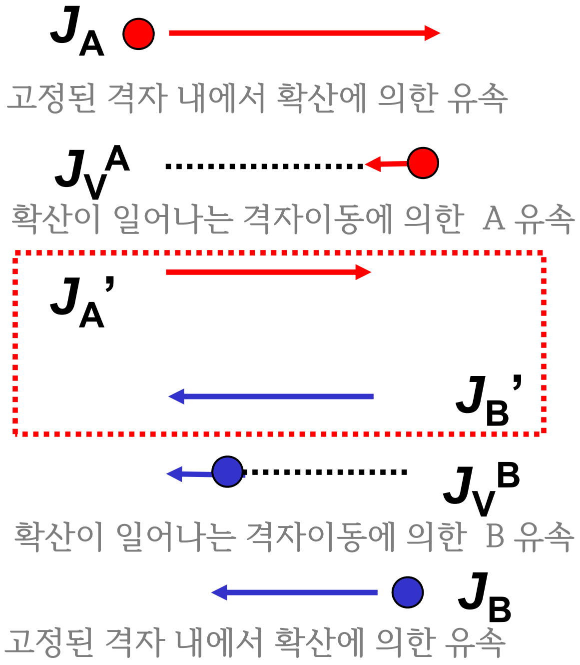

J_A: 고정된 격자 내에서 확산에 의한 유속

J_V^A: 확산이 일어나는 격자이동에 의한 A 유속

J_V^B: 확산이 일어나는 격자이동에 의한 B 유속

J_B: 고정된 격자 내에서 확산에 의한 유속

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

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

A원자와 B원자가 서로 다른 속도로 도약 →

농도 구배에 의한 속도 + 격자면 이동에 의한 속도

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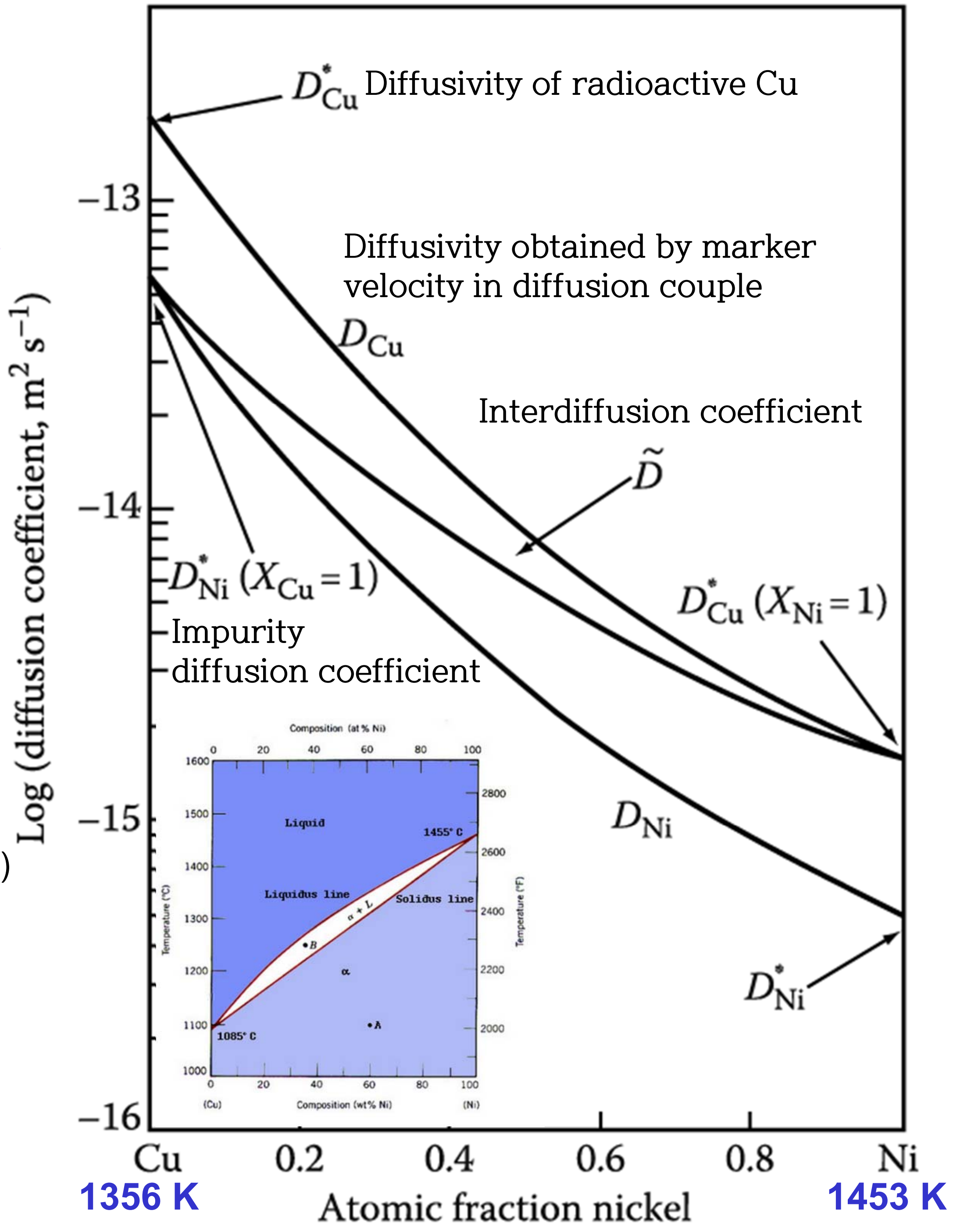

1356 K

1453 K