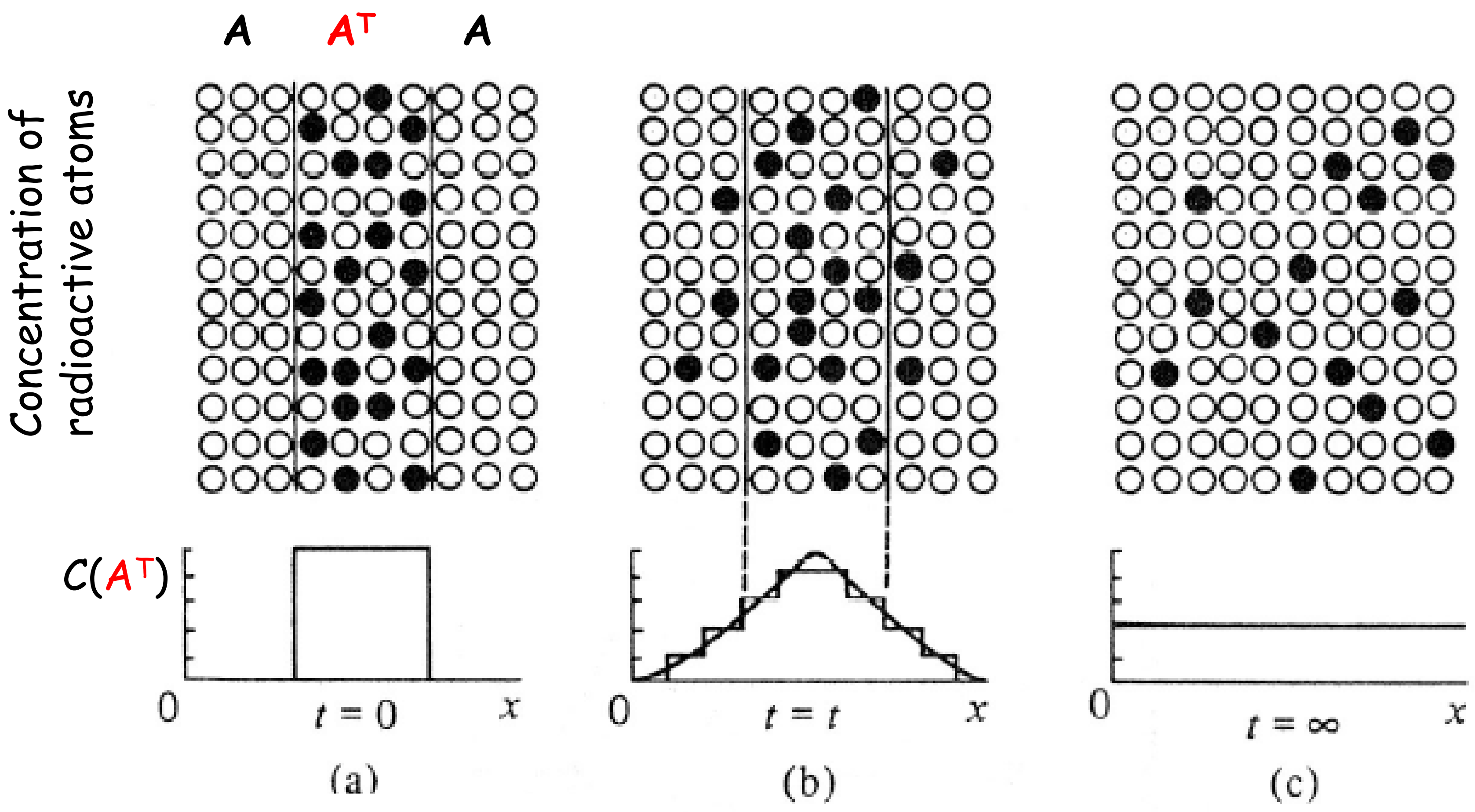
Atomic Theory of Diffusion

Self Diffusion



(a) (b) (c)

O A normal atom

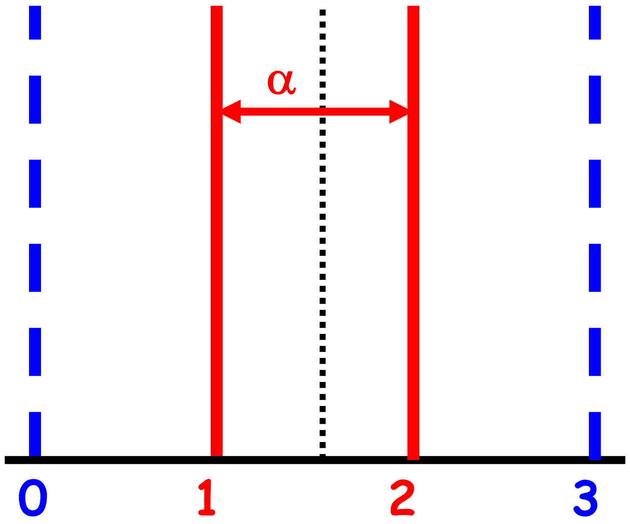
● A^T radioactive atom

Isotope is an element with the same number of protons but different number of neutrons

Atomic Theory of Diffusion

Reference: Shewmon, Diffusion in Solids, Chap.2

Q: How does atomic mobility relate to D?



- Crystal with concentration gradient in x-direction
- Assuming atoms jump left and right only
- Planes 1 and 2 are adjacent atomic planes
- N_1: diffusing atoms/unit area on plane 1
  N_2: diffusing atoms/unit area on plane 2
- Γ: random jump frequency (jumps/second)
- $\Gamma_{12} = \Gamma_{21}$ (1→2 and 2→1)

$$N_1\Gamma\delta t = (N_1\Gamma_{12} + N_1\Gamma_{10})\delta t$$

$$N_2\Gamma\delta t = (N_2\Gamma_{21} + N_2\Gamma_{23})\delta t$$

Net flux from 1→2

$$\begin{aligned} J_{net} &= J_{12} - J_{21} \\ &= N_1\Gamma_{12} - N_2\Gamma_{21} \\ &= \frac{1}{2}\Gamma(N_1 - N_2) \\ &= \frac{1}{2}\alpha\Gamma(C_1 - C_2) \end{aligned}$$

Random jump

$$\begin{aligned} \because 2\Gamma_{12} &= 2\Gamma_{21} = \Gamma \\ &= ZP_{v2}w_{12} = 2P_{v2}w_{12} \\ &= 2P_v w \end{aligned}$$

- Number of atoms jumping out of plane in $\underline{\delta t}$

$$N_1\Gamma\delta t = (\frac{1}{2}N_1\Gamma_{12} + \frac{1}{2}N_1\Gamma_{10})\delta t$$

$$N_2\Gamma\delta t = (\frac{1}{2}N_2\Gamma_{21} + \frac{1}{2}N_2\Gamma_{23})\delta t$$

Net flux from 1→2

$$\begin{aligned} J_{net} &= J_{12} - J_{21} \\ &= \frac{1}{2}N_1\Gamma_{12} - \frac{1}{2}N_2\Gamma_{21} \\ &= \frac{1}{2}\Gamma(N_1 - N_2) \\ &= \frac{1}{2}\alpha\Gamma(C_1 - C_2) \end{aligned}$$

Random jump

$$\boxed{\because \Gamma_{12} = \Gamma_{21} = \Gamma}$$

$$\therefore C_i = \frac{N_i}{\alpha}$$

$$C_1 - C_2 \approx -\alpha \frac{\partial C}{\partial x}$$

c.f.

$$J_{net} = \frac{1}{2}\alpha\Gamma\left(-\alpha\frac{\partial C}{\partial x}\right) = \frac{-1}{2}\alpha^2\Gamma\frac{\partial C}{\partial x}$$

$$J_{net} = -D\frac{\partial C}{\partial x}$$

$$D = \frac{1}{2}\alpha^2\Gamma$$ α : jump distance

Diffusion in 3-Dimension $D = \frac{1}{6}\alpha^2\Gamma$

Example 1: Carbon in α-Fe at 900℃

$D_C = 10^{-6}$ cm^2/sec, $\alpha = 10^{-8}$ cm

-> **$\Gamma = 10^{10}$ sec^{-1}**

Debye frequency $= 10^{13}$ sec^{-1}, therefore

$$\frac{10^{10}}{10^{13}} = \frac{1}{1000}$$

(atom changes position only one out of 1000 oscillations)

Example 2: FCC and HCP metals near their MPs.

$D = 10^{-8}$ cm^2/sec, $\alpha = 10^{-8}$ cm

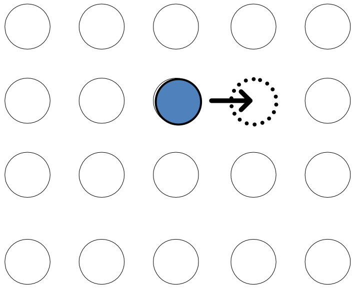
→ **$\Gamma = 10^{8}$ sec^{-1}**

$$\frac{10^{8}}{10^{13}} = \frac{1}{100000}$$

(most of time, the atom oscillates about its equilibrium position)

Diffusion Mechanism in Solids - Atomic Approach

Vacancy mechanism: atom passing from an occupied site to an adjacent unoccupied site



$$N_V = \exp(-\frac{\Delta G_V}{RT})$$
$$= \exp(\frac{\Delta S_V}{R})\exp(-\frac{\Delta H_V}{RT})$$

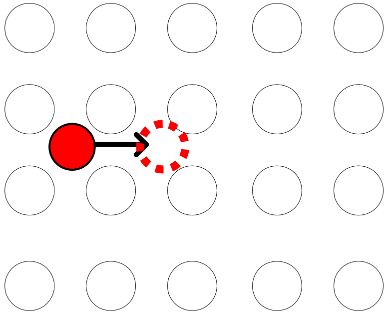
ΔG_V : the vacancy formation energy

Vacancy formation energy (kJ/mol)

Au	Al	Ag	Cu	BeO	MgO	NaCl	CaO
92.5	72.5	105	96	576	576	220	570

Al: $N_v(873K) = 4.6\times10^{-5}$
Al_2O_3: $N_v(1873K) = 8.6\times10^{-17}$

Interstitial Mechanism: atom moving through the crystal by jumping directly from one interstitial site to another



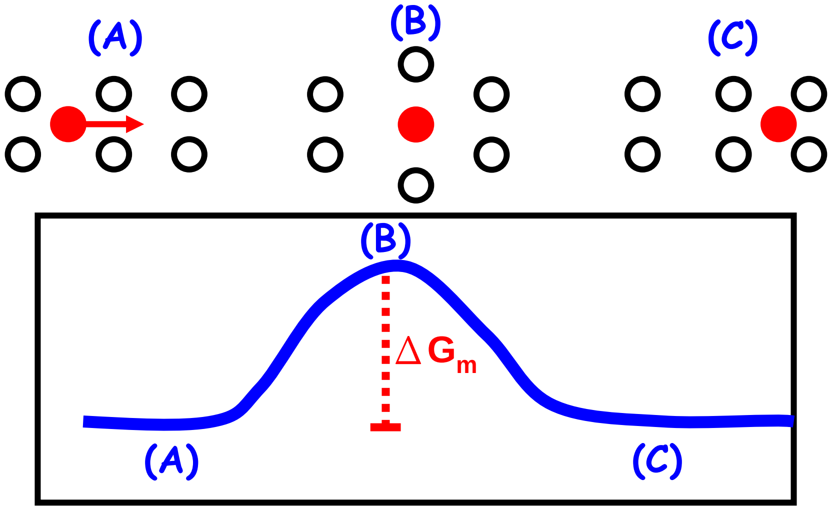
Question: How are Γ and α related to D in real crystals with different diffusion mechanisms?

Definition

ν : vibration frequency
ω : possible jump frequency
Γ : successful jump frequency

ν : **atomic vibration frequency at its lattice**
Debye frequency $\approx 10^{12} \sim 10^{13}\ \mathrm{sec}^{-1}$

ω : **possible jump frequency which is an activated process and can be calculated by**

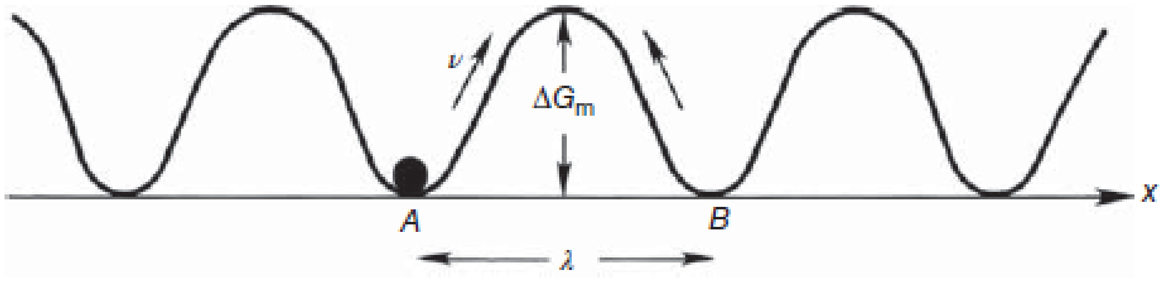


$$\omega = \upsilon \exp\left(-\frac{\Delta G_m}{RT}\right)$$

$$\Gamma = Z\omega P_v$$

Z: coordination number
ω: possible jump frequency
P_v: the probability to find a vacancy, which is equivalent to the concentration of vacancy $= N_v$

Diffusion without a driving force $\omega = \upsilon \exp(-\frac{\Delta G_m}{RT})$



Diffusion with a driving force

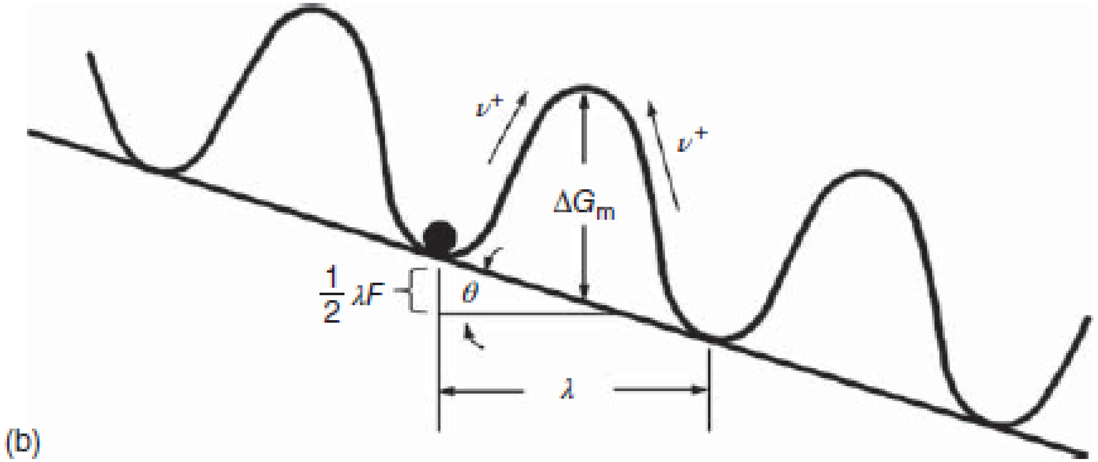
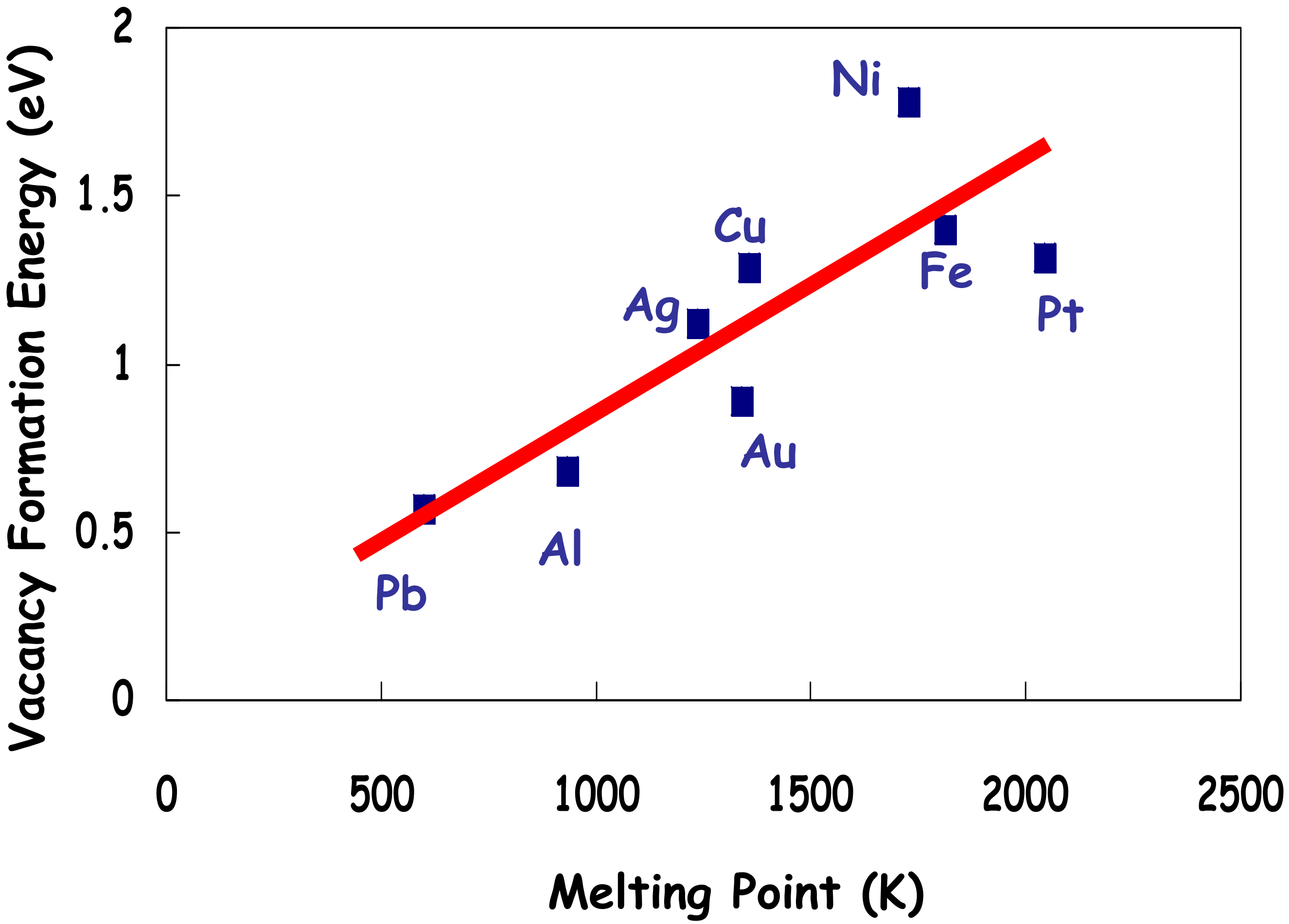


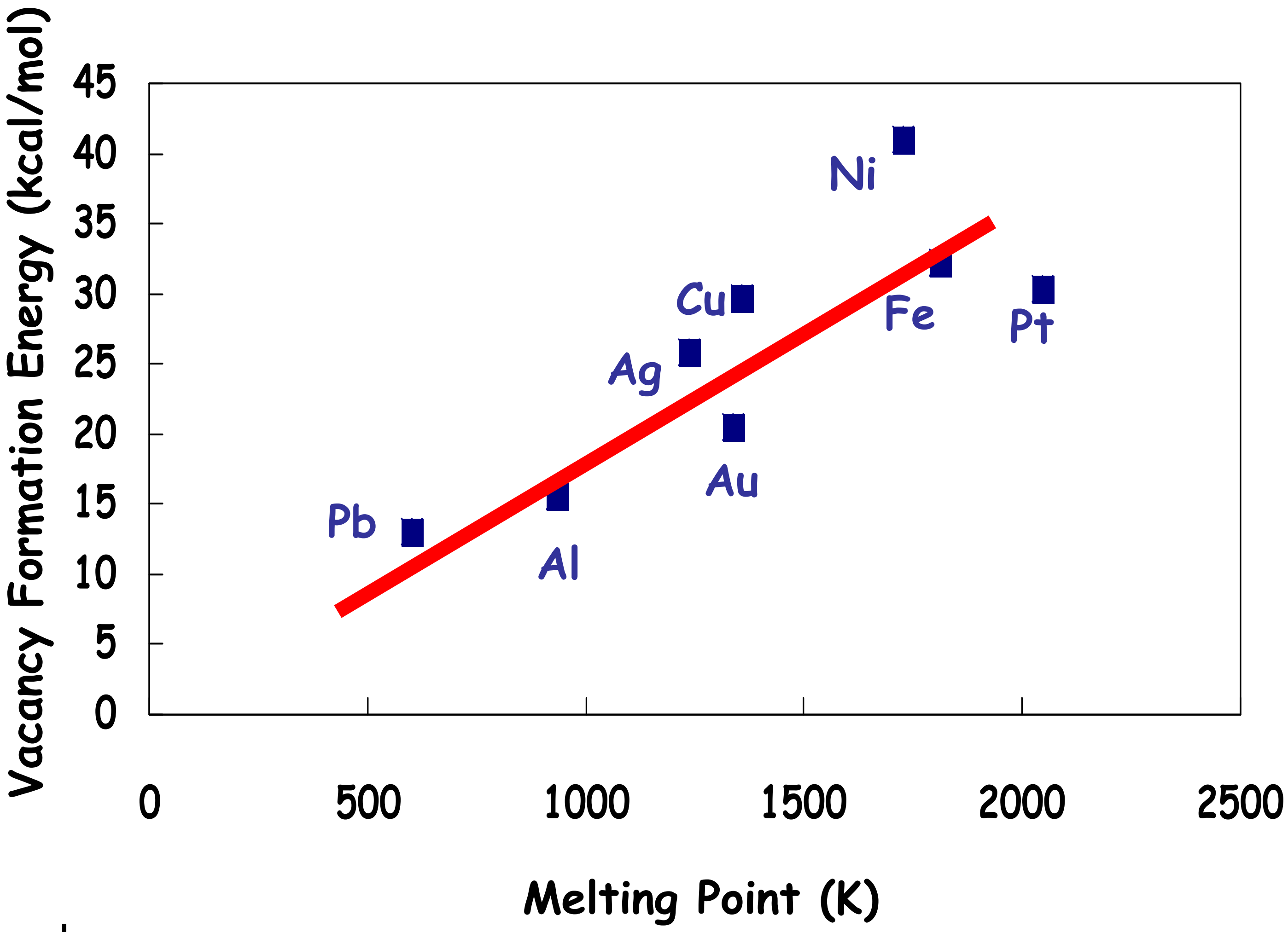
Figure 2.1 (a) Schematic diagram of a simple one-dimensional case representing the pair potential energy of a row of atoms by combining the pair potential curves between every two atoms. (b) To have a directional diffusion, we must introduce a driving force to drive the diffusion in a given direction. This can be represented by tilting the base line of the potential energy. The tilting introduces a gradient of the potential energy, which is the driving force of diffusion.

Vacancy formation enthalpy versus melting point for various metals



1 eV=23 kcal/mol

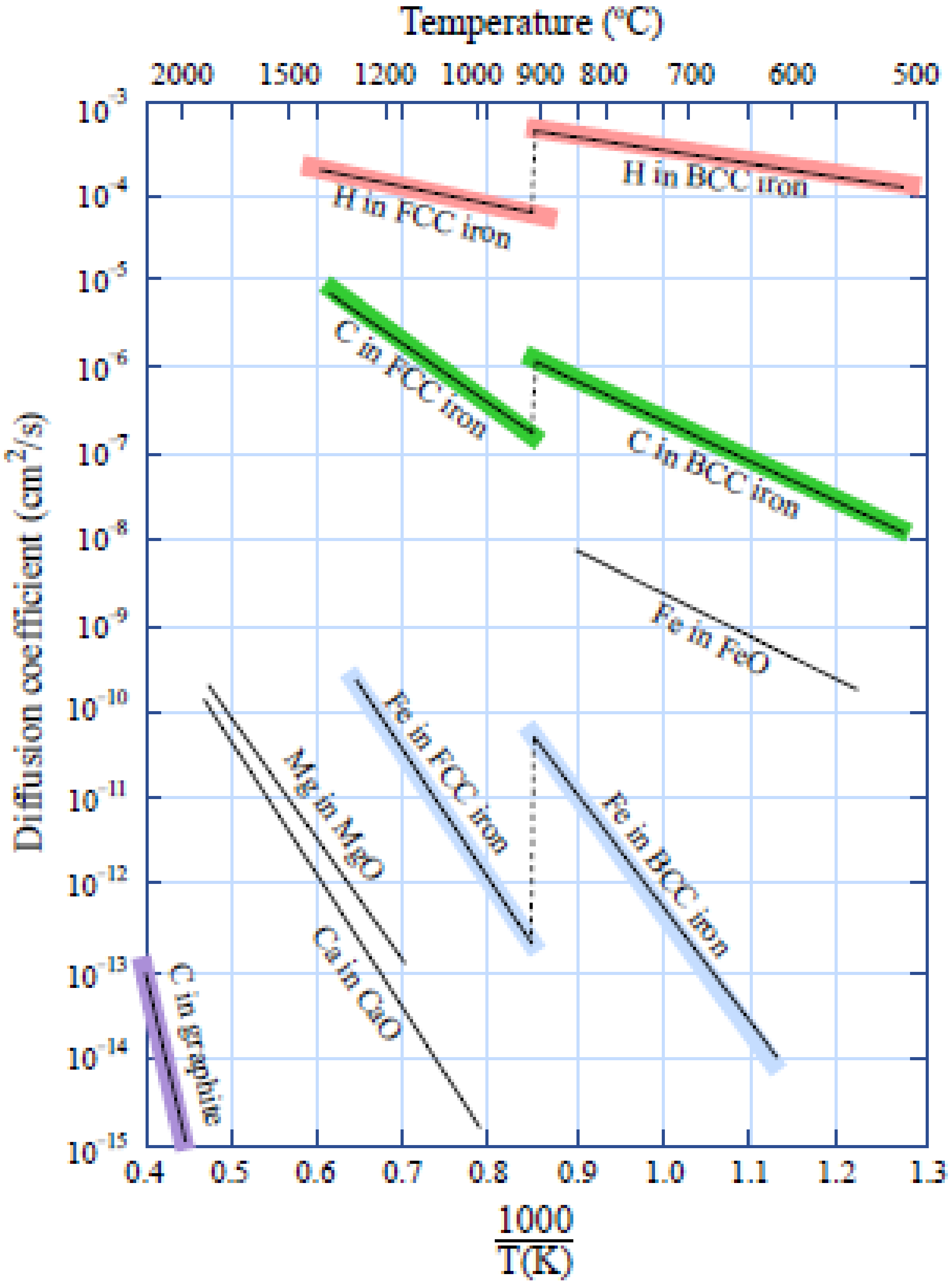
Vacancy formation enthalpy versus melting point for various metals

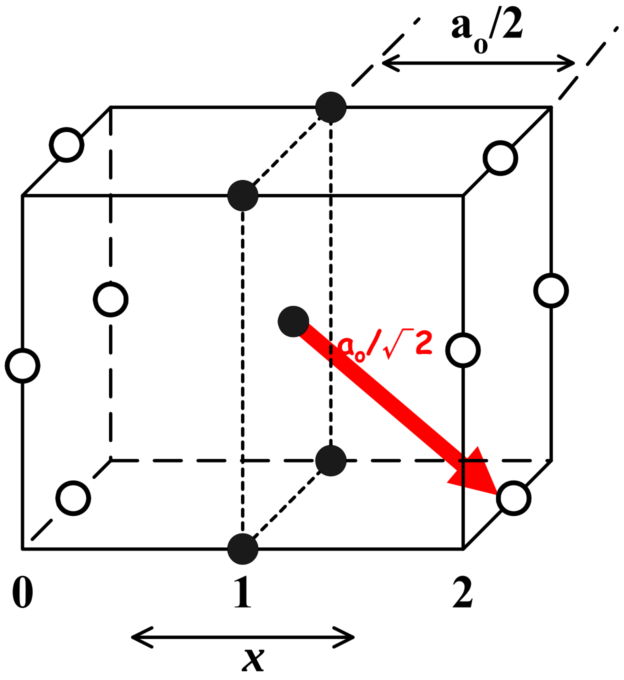


1 eV=23 kcal/mol

Effects of diffuser atom size on diffusion in Fe (Interstitial diffusivity)

Diffuser	Radius (A)	BCC @800°C (cm^2/sec)	FCC @1100°C (cm^2/sec)
H	0.46	2.7×10^{-4}	1.9×10^{-4}
C	0.77	1.7×10^{-6}	6.7×10^{-7}
N	0.71	7.3×10^{-7}	3.8×10^{-7}
B	0.97	------	6.1×10^{-7}


Temperature (°C)
2000
1500
1200
1000
900
800
700
600
500
Diffusion coefficient (cm^2/s)
10^{-3}
10^{-4}
10^{-5}
10^{-6}
10^{-7}
10^{-8}
10^{-9}
10^{-10}
10^{-11}
10^{-12}
10^{-13}
10^{-14}
10^{-15}
H in BCC iron
H in FCC iron
C in FCC iron
C in BCC iron
Fe in FeO
Mg in MgO
Fe in FCC iron
Fe in BCC iron
Ca in CaO
C in graphite
0.4
0.5
0.6
0.7
0.8
0.9
1.0
1.1
1.2
1.3
$\frac{1000}{T(K)}$



Ex. Vacancy mechanism in FCC

-motion only along x direction

-only 4 out of 12 nearest neighbors are on plane 2

$$J_{12} = 4n_1 P_{v2}\omega_{12}$$

$$J_{21} = 4n_2 P_{v1}\omega_{21}$$

$$J_{net} = J_{12} - J_{21}$$

$$= 4P_v\omega(n_1 - n_2)$$

$$\because \omega_{12} = \omega_{21} = \omega$$

$$\because P_{v1} = P_{v2} = P_v$$

Random Jump

$$J_{net} = 4P_v\omega \cdot \frac{a_o}{2}\left(\frac{n_1}{\frac{a_0}{2}} - \frac{n_2}{\frac{a_0}{2}}\right)$$

$$= 4P_v\omega \cdot \frac{a_o}{2}(C_1 - C_2)$$

$$= 4P_v\omega \cdot \frac{a_o}{2}\left(-\frac{a_o}{2}\frac{\partial C}{\partial x}\right)$$

$$= -P_v\omega a_0^2\frac{\partial C}{\partial x} = -D\frac{\partial C}{\partial x}$$

$$\therefore D = P_v\omega a_0^2$$

Note:

$$D = \frac{1}{6}\alpha^2\Gamma \quad \& \quad \alpha = a_0/\sqrt{2} \quad (FCC)$$

$$D = \frac{1}{6}\left(\frac{a_0}{\sqrt{2}}\right)^2\Gamma = a_0^2 P_v\omega$$

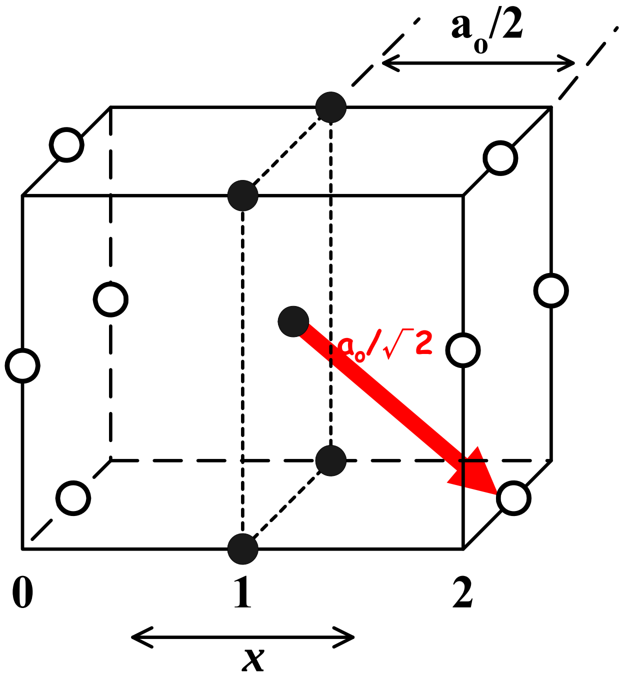
$$\Rightarrow \Gamma = 12P_v\omega \quad (Z = 12)$$

$$\Gamma = ZP_v\omega$$

Ex. Vacancy mechanism in FCC

-motion only along x direction

-only 4 out of 12 nearest neighbors are on plane 2



$$\Gamma = ZP_v w = 8P_v w$$

$$\Gamma_{12} = \Gamma_{21} = \frac{1}{2}\Gamma = \frac{1}{2}(8P_v w) = 4P_v w$$

$$J_{12} = n_1\Gamma_{12} = n_1(4P_v w) = \frac{1}{2}n_1\Gamma$$

$$J_{21} = n_2\Gamma_{21} = n_2(4P_v w) = \frac{1}{2}n_2\Gamma$$

$$J_{net} = J_{12} - J_{21} = 4P_v\omega(n_1 - n_2)$$

$$\because \omega_{12} = \omega_{21} = \omega \qquad \because P_{v1} = P_{v2} = P_v$$

$$J_{net} = 4P_v\omega\cdot\frac{a_o}{2}\left(\frac{n_1}{\frac{a_0}{2}} - \frac{n_2}{\frac{a_0}{2}}\right) = 4P_v\omega\cdot\frac{a_o}{2}(C_1 - C_2)$$

$$= 4P_v\omega\cdot\frac{a_o}{2}\left(-\frac{a_o}{2}\frac{\partial C}{\partial x}\right) = -P_v\omega a_0^2\frac{\partial C}{\partial x} = -D\frac{\partial C}{\partial x}$$

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Note:

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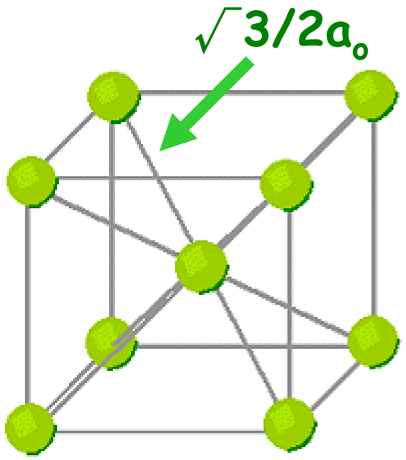
$$\Rightarrow \Gamma = 12P_v\omega \quad (Z = 12)$$

$$\Gamma = ZP_v\omega$$

BCC



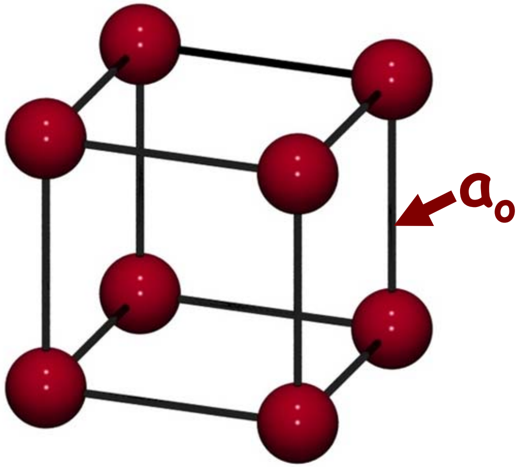
$$D = \frac{1}{6}\alpha^2\Gamma$$

$$\alpha = \sqrt{3}/_2\, a_0$$

$$\Gamma = 8N_v\omega$$

$$D = \frac{1}{6}\left(\frac{\sqrt{3}}{2}a_0\right)^2(8N_v\omega) = \omega N_v a_0^2$$

SC



$$D = \frac{1}{6}\alpha^2\Gamma$$

$$\alpha = a_0$$

$$\Gamma = 6N_v\omega$$

$$D = \omega N_v a_0^2$$

Interstitial Diffusion

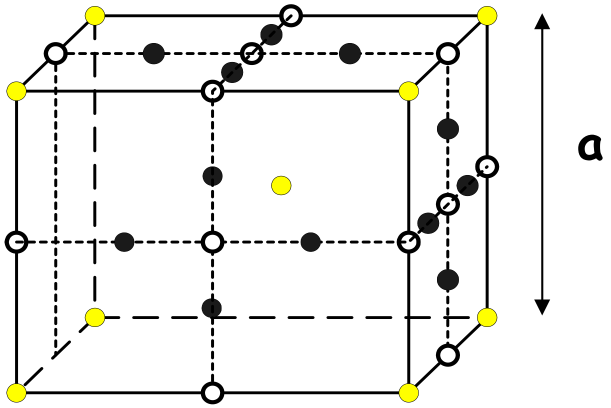
$$D = \gamma w a_o^2$$

$$P_i = 1$$

γ : **Structural factor**

Interstitial Diffusion

BCC



○ : Octahedral Site
● : Tetrahedral Site

Octahedral Site

$$D = \frac{1}{6}\alpha^2\Gamma = \frac{1}{6}\left(\frac{a}{2}\right)^2(4\omega) = \frac{1}{6}\omega a^2$$

$$\gamma = \frac{1}{6}$$

Tetrahedral Site

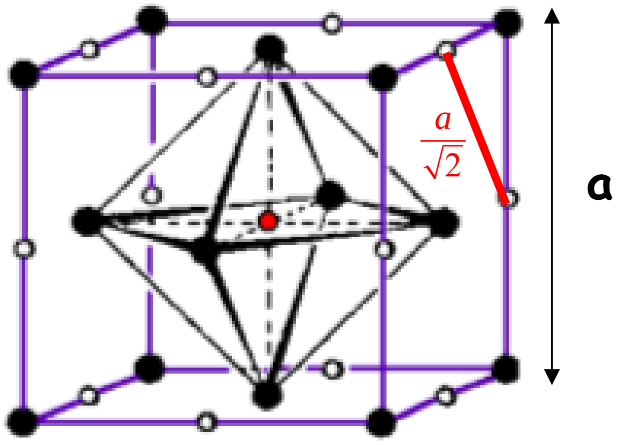
$$D = \frac{1}{6}\alpha^2\Gamma$$

$$\alpha^2 = \left(\frac{1}{4}a\right)^2 + \left(\frac{1}{4}a\right)^2 \rightarrow \alpha = \frac{1}{2\sqrt{2}}a$$

$$D = \frac{1}{6}\left(\frac{1}{2\sqrt{2}}a\right)^2(4\omega) = \frac{1}{12}\omega a^2$$

$$\gamma = \frac{1}{12}$$

FCC



Octahedral Site

$$D = \frac{1}{6}\alpha^2\Gamma$$

$$\Gamma = 12\omega$$

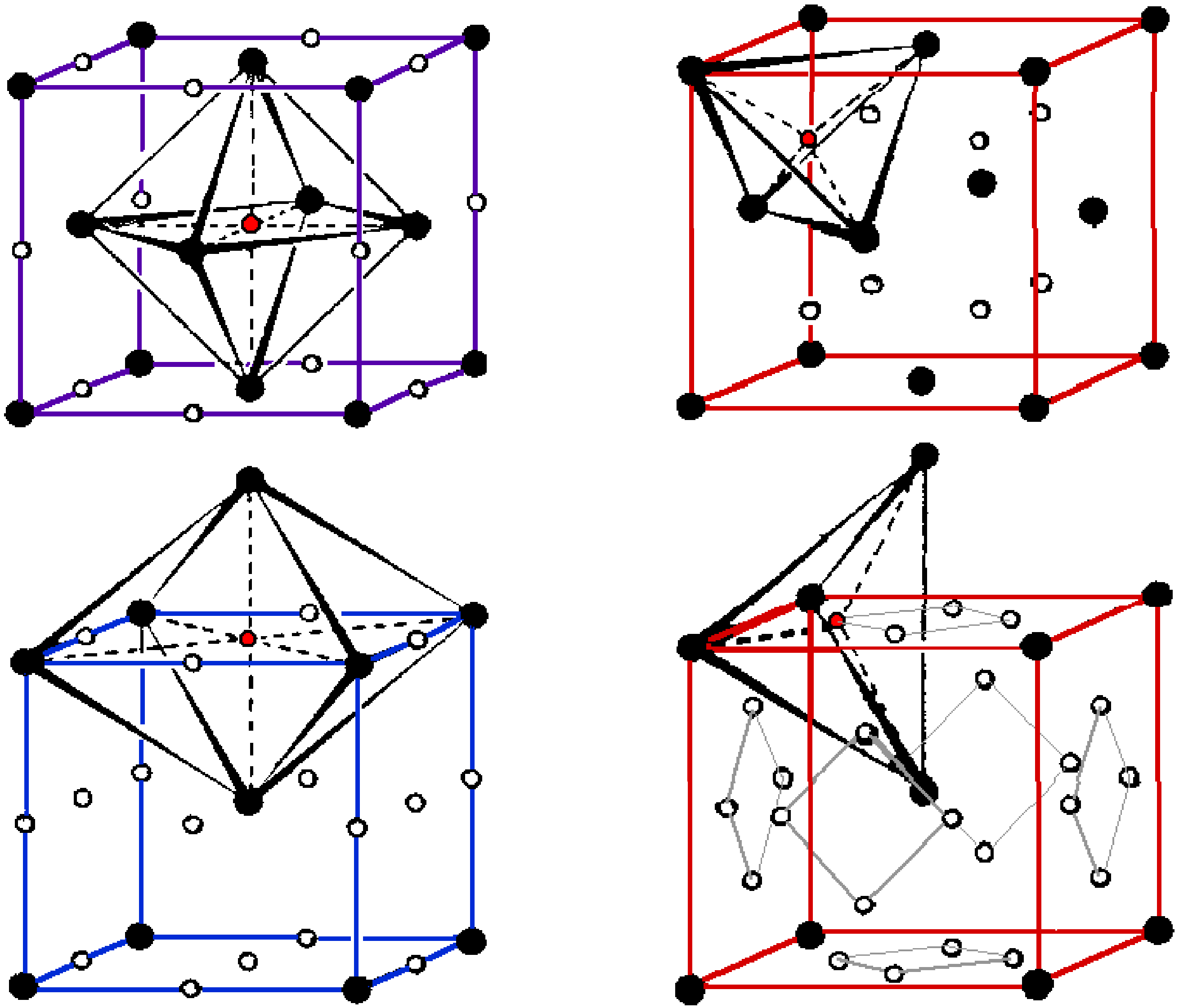
$$D = \frac{1}{6}\left(\frac{a}{\sqrt{2}}\right)^2(12\omega) = \omega a^2$$

$$\gamma = 1$$

O Sites **T Sites**

FCC

BCC



$$D = \omega N_v a_0^2$$

$$N_V = \exp(-\frac{\Delta G_v}{RT})$$: thermodynamic equilibrium

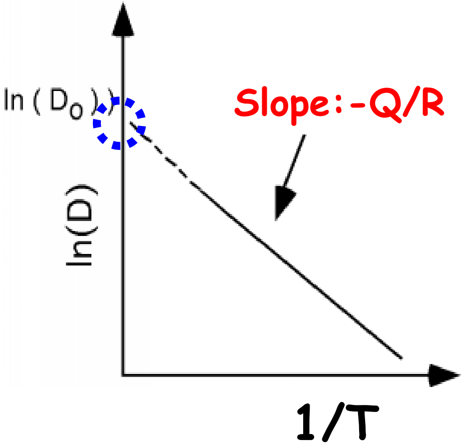
$$= \exp(\frac{\Delta S_v}{R})\exp(-\frac{\Delta H_v}{RT})$$

ΔG_v:the vacancy formation free energy

$$\omega = \nu \exp(-\frac{\Delta G_m}{RT})$$

ΔG_m:the migration activation energy

Arrhenius Activation Analysis



Vacancy Mechanism

$$D = a_0^2 \nu \exp(-\frac{\Delta G_v}{RT})\exp(-\frac{\Delta G_m}{RT})$$

$$= a_0^2 \nu \exp(\frac{\Delta S_v + \Delta S_m}{R})\exp(-\frac{(\Delta H_v + \Delta H_m)}{RT})$$

$$= D_0 \exp(-\frac{Q}{RT})$$

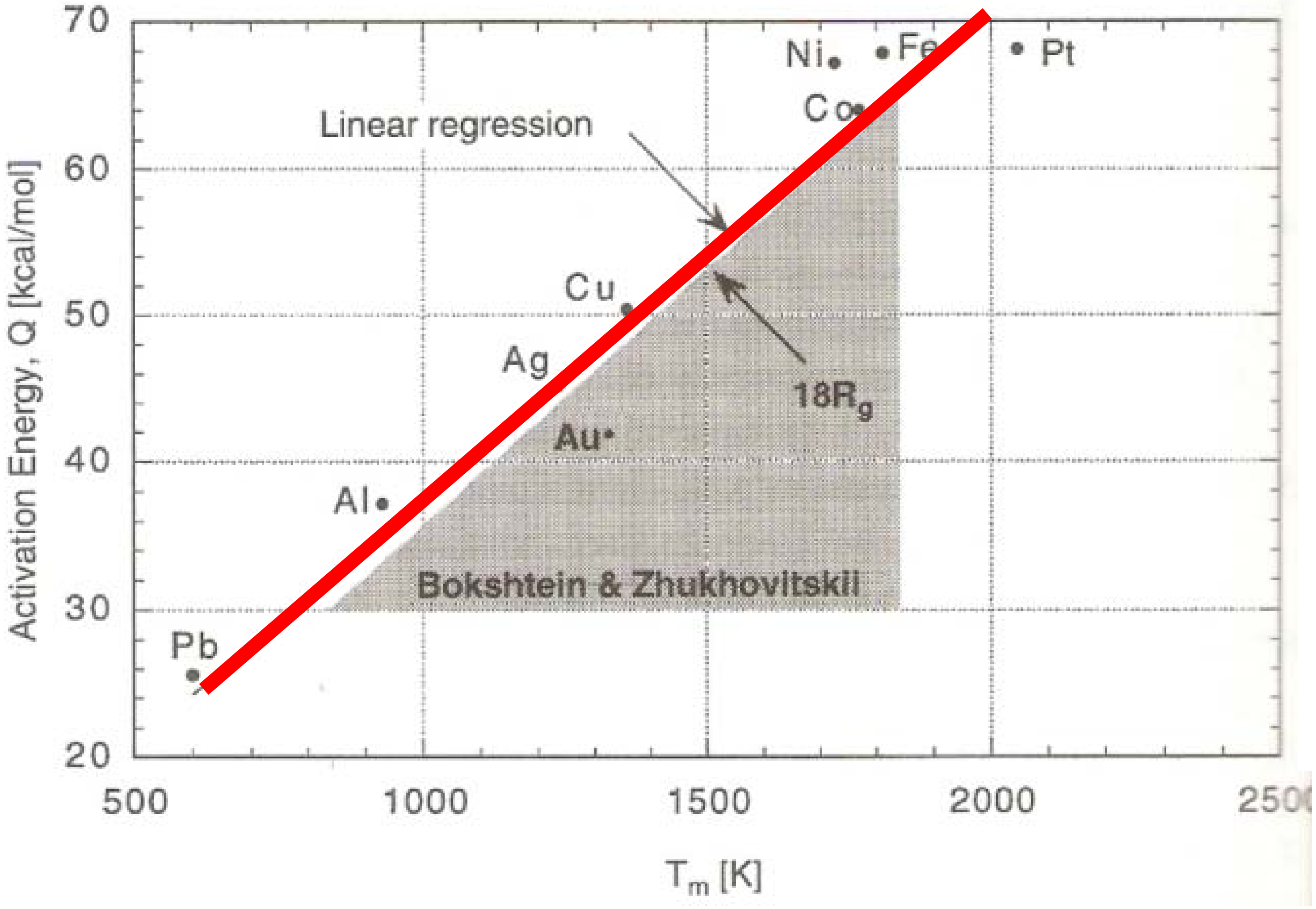
Interstitial Mechanism

$$D = \gamma a_0^2 \nu \exp(-\frac{\Delta G_m}{RT})$$

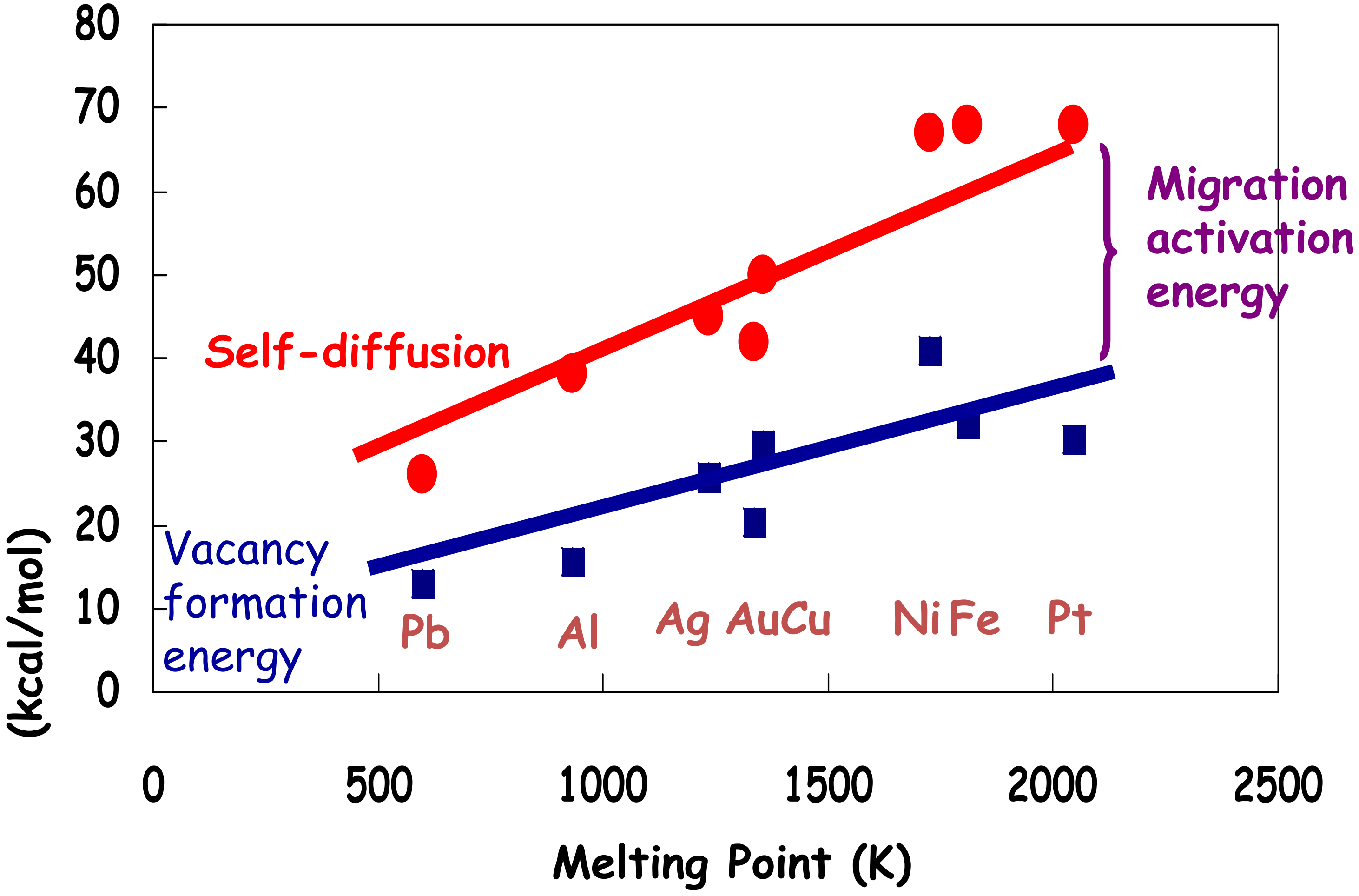
$$= \gamma a_0^2 \nu \exp(\frac{\Delta S_m}{R})\exp(-\frac{\Delta H_m}{RT})$$

$$= D_0 \exp(-\frac{Q}{RT})$$

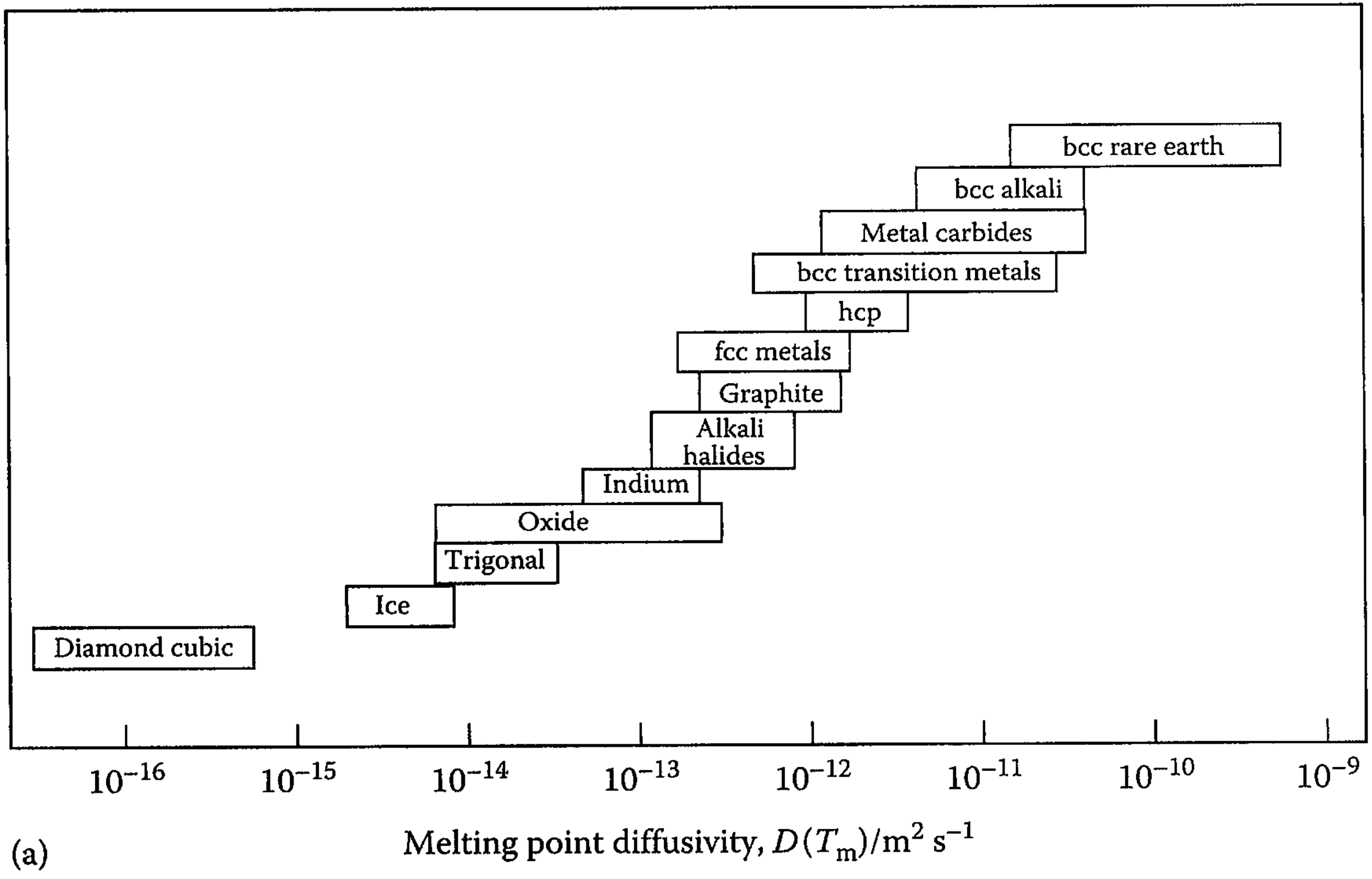
Activation energy for self-diffusion versus melting point for various metals



Activation energy for self-diffusion versus melting point for various metals



Self Diffusion



Diffusivity at melting point

Self-diffusion

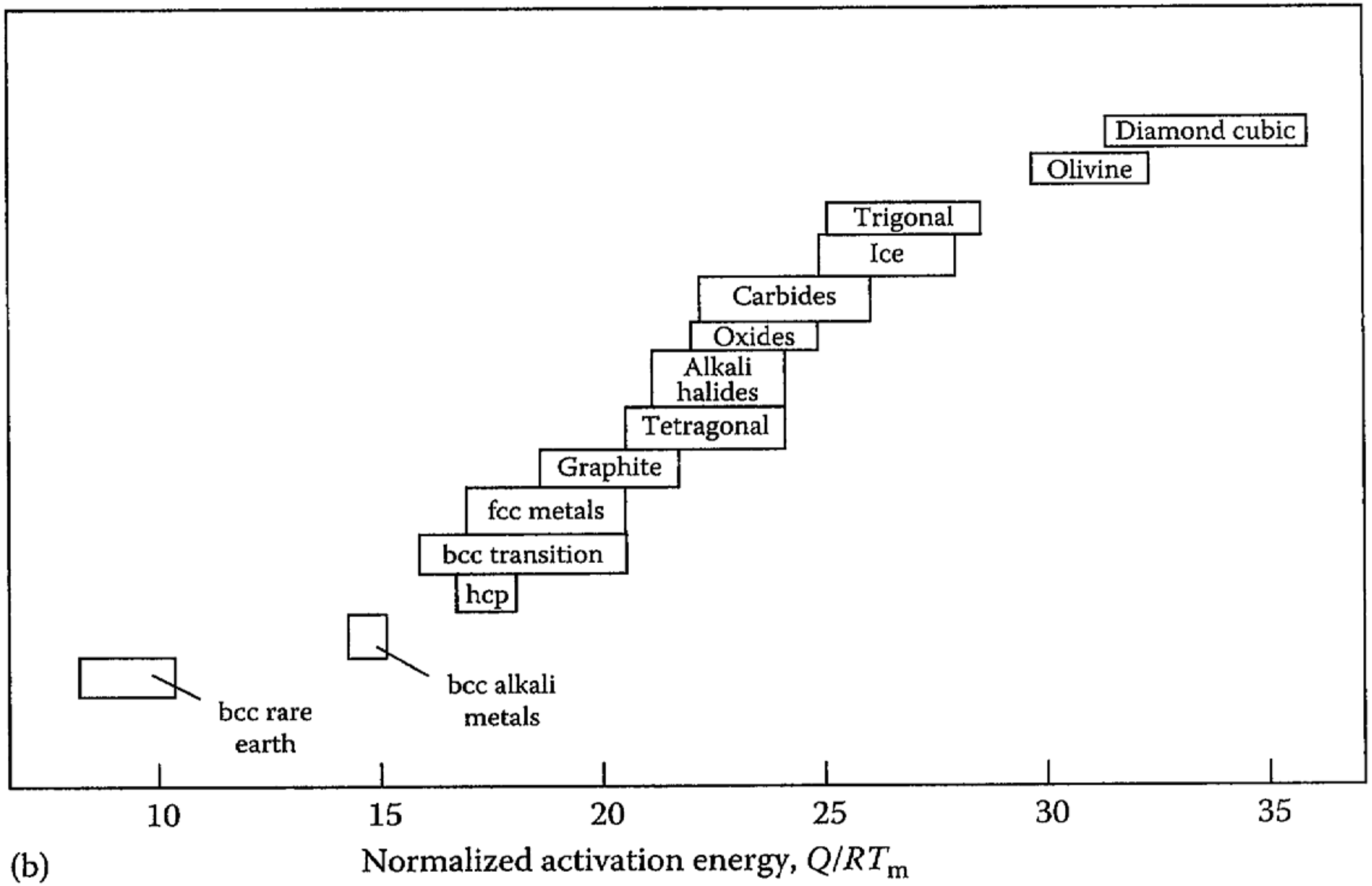
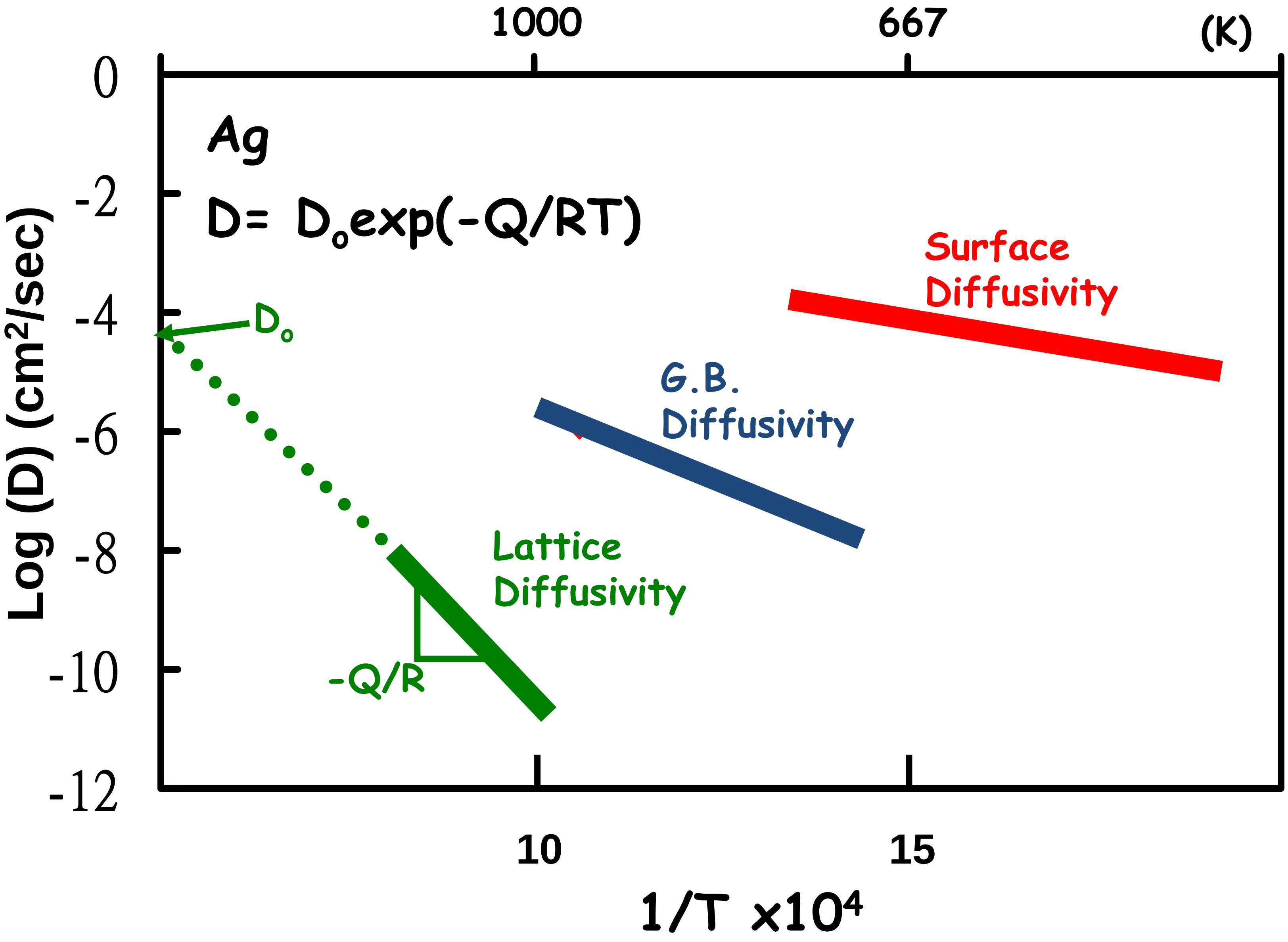


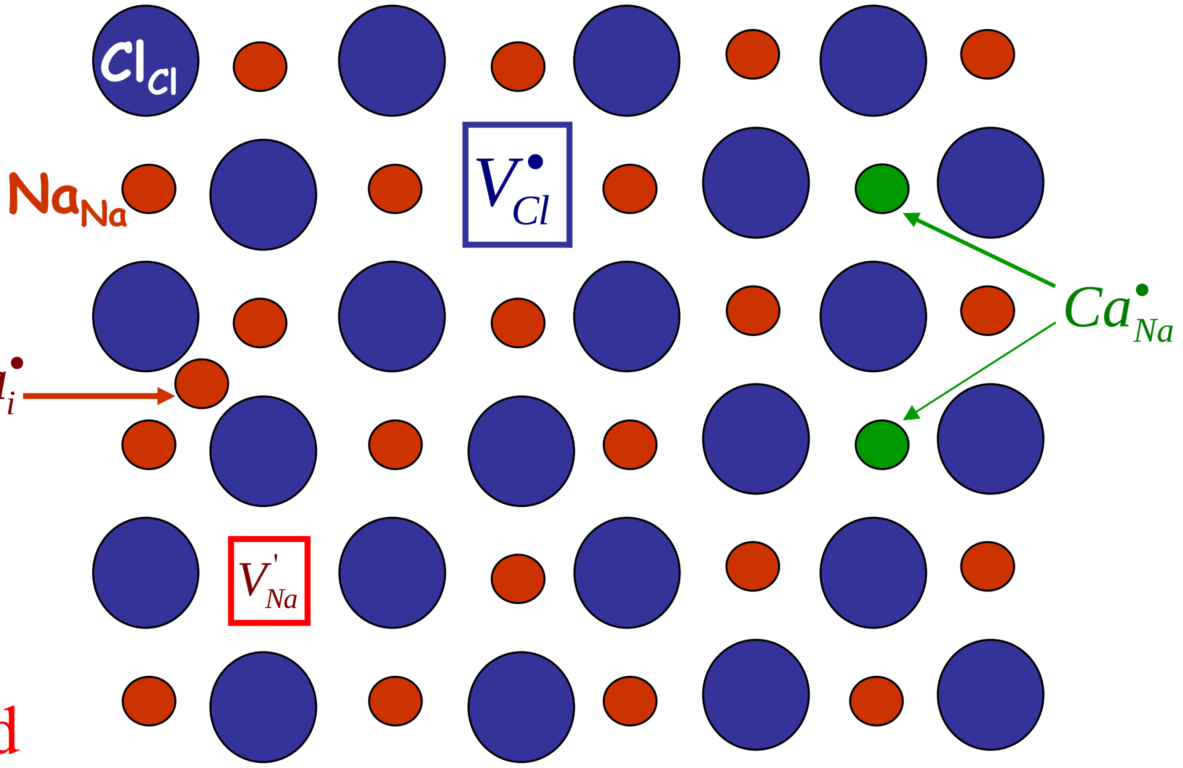
FIGURE 2.13
(a) Melting point diffusivities and (b) normalized activation energies for various classes of materials. (After Brown, A.M. and Ashby, M.F., *Acta Metall.*, 28, 1085, 1980.)

Diffusivities of Ag



Diffusion in Ionic Compounds

Summary of Kroger-Vink Notation



$V_{Cl}^{\bullet}$: Positively Charged

$V_{Na}^{'}$: Negatively Charged

$Na_i^{\bullet}$: Positively Charged

$Ca_{Na}^{\bullet}$: Positively Charged

Defect chemistry in ionic compounds must follow the following principles:

(1) Mass balance
(2) Charge balance
(3) Site balance

Example

(1) $$2MgO \xrightarrow{Al_2O_3} 2Mg_{Al}^{'} + 2O_O + V_O^{\bullet\bullet}$$

(2) $$CaCl_2 \xrightarrow{NaCl} Ca_{Na}^{\bullet} + 2Cl_{Cl} + V_{Na}^{'}$$

e.g., **Diffusion of Na in NaCl**

$$D_{Na} = \gamma a_o^2 w[V_{Na}^{'}]$$

γ : Structural factor

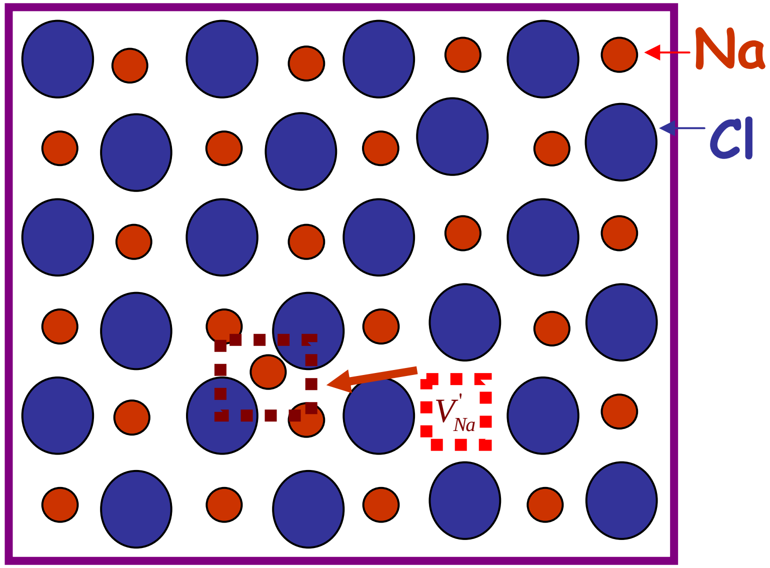
a_o : Lattice constant

w : Possible jump frequency

$[V_{Na}^{'}]$: Vacancy concentration of Na

Concentration of Intrinsic (Thermally Induced) Defects

Frenkel Defect



$$Na_{Na} \overset{K_F}{\rightleftarrows} Na_i^{\bullet} + V_{Na}'$$

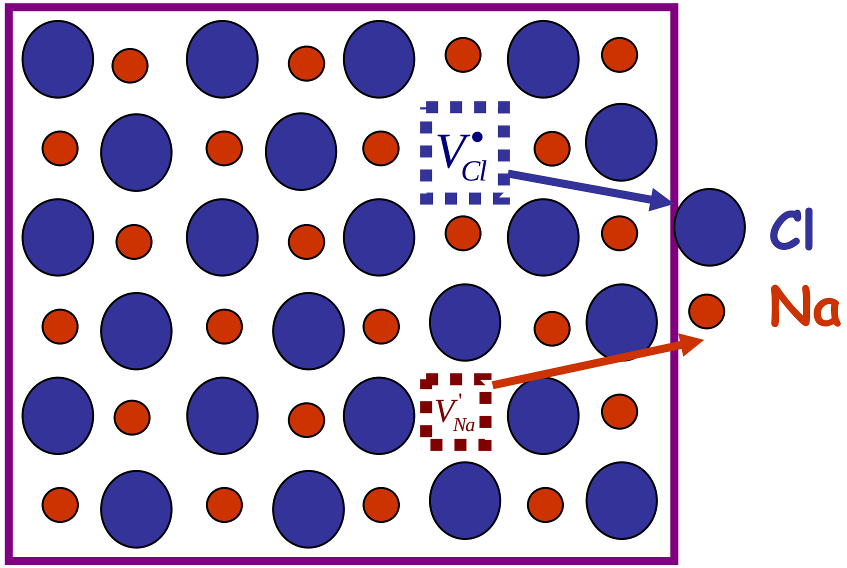
$$K_F = \frac{[Na_i^{\bullet}][V_{Na}']}{[Na_{Na}]} = [Na_i^{\bullet}][V_{Na}']$$

$$= \exp(-\frac{\Delta G_F}{RT}) \qquad \because [Na_{Na}] = 1$$

$$[Na_i^{\bullet}] = [V_{Na}'] = K_F^{1/2} = \exp(-\frac{\Delta G_F}{2RT})$$

ΔG_F : Formation energy of Frenkel Defect

Schottky Defect



$$Null \overset{K_S}{\rightleftarrows} V_{Na}' + V_{Cl}^{\bullet}$$

$$K_S = [V_{Na}'][V_{Cl}^{\bullet}] = \exp(-\frac{\Delta G_S}{RT})$$

$$[V_{Na}'] = [V_{Cl}^{\bullet}] = K_S^{1/2} = \exp(-\frac{\Delta G_S}{2RT})$$

ΔG_S : Formation energy of
Schottky Defect

Table 2.1 Defect Concentration at Different Temperatures

$$\frac{n}{N} = \exp\left[-\frac{\Delta g}{2kT}\right] = \exp\left[\frac{\Delta s}{2k}\right]\exp\left[-\frac{\Delta h}{2kT}\right] \approx \exp\left(-\frac{\Delta h}{2kT}\right)$$

Defect Concentration	1eV[a]	2eV	4eV	6eV	8eV
n / N at 100°C	2×10^{-7}	3×10^{-14}	1×10^{-27}	3×10^{-41}	1×10^{-54}
n / N at 500°C	6×10^{-4}	3×10^{-7}	1×10^{-13}	3×10^{-20}	8×10^{-27}
n / N at 800°C	4×10^{-3}	2×10^{-5}	4×10^{-10}	8×10^{-15}	2×10^{-19}
n / N at 1000°C	1×10^{-2}	1×10^{-4}	1×10^{-8}	1×10^{-12}	1×10^{-16}
n / N at 1200°C	2×10^{-2}	4×10^{-4}	1×10^{-7}	5×10^{-11}	2×10^{-19}
n / N at 1500°C	4×10^{-2}	1×10^{-4}	2×10^{-6}	3×10^{-9}	4×10^{-12}
n / N at 1800°C	6×10^{-2}	4×10^{-3}	1×10^{-5}	5×10^{-8}	2×10^{-10}
n / N at 2000°C	8×10^{-2}	6×10^{-3}	4×10^{-5}	2×10^{-7}	1×10^{-9}

[a] 1eV = 23.05 kcal/mole.

Table 2.2 Some Defect Energies of Formation

Compound	Reaction	Energy of Formation Δh (eV)
AgCl	$\mathrm{Ag}_{\mathrm{Ag}}^{x} \Leftrightarrow \mathrm{Ag}_{i}^{\bullet} + V_{\mathrm{Ag}}'$	1.1
NaCl	null $\Leftrightarrow V_{\mathrm{Na}}' + V_{\mathrm{Cl}}^{\bullet}$	2.2 – 2.4
KCl	null $\Leftrightarrow V_{\mathrm{K}}' + V_{\mathrm{Cl}}^{\bullet}$	2.6
LiF	null $\Leftrightarrow V_{\mathrm{Li}}' + V_{\mathrm{F}}^{\bullet}$	2.4 – 2.7
CsCl	null $\Leftrightarrow V_{\mathrm{Cs}}' + V_{\mathrm{Cl}}^{\bullet}$	1.86
BeO	null $\Leftrightarrow V_{\mathrm{Be}}'' + V_{\mathrm{O}}^{\bullet}$	~ 6
MgO	null $\Leftrightarrow V_{\mathrm{Mg}}'' + V_{\mathrm{O}}^{\bullet\bullet}$	7.7
CaO	null $\Leftrightarrow V_{\mathrm{Ca}}'' + V_{\mathrm{O}}^{\bullet\bullet}$	~ 6
BaO	null $\Leftrightarrow V_{\mathrm{Ba}}'' + V_{\mathrm{O}}^{\bullet\bullet}$	3.4
MnO	null $\Leftrightarrow V_{\mathrm{Mn}}'' + V_{\mathrm{O}}^{\bullet\bullet}$	4.6
FeO	null $\Leftrightarrow V_{\mathrm{Fe}}'' + V_{\mathrm{O}}^{\bullet\bullet}$	6.5
ZnO	$\mathrm{O}_{\mathrm{O}}^{x} \Leftrightarrow \mathrm{O}_{i}'' + V_{\mathrm{O}}^{\bullet\bullet}$	2.51
$\mathrm{Li_2O}$	$\mathrm{Li}_{\mathrm{Li}}^{x} \Leftrightarrow \mathrm{Li}_{i}^{\bullet} + V_{\mathrm{Li}}'$	2.28
$\mathrm{CaF_2}$	$\mathrm{F}_{\mathrm{F}}^{x} \Leftrightarrow V_{\mathrm{F}}^{\bullet} + \mathrm{F}_{i}'$	2.3 – 2.8
	$\mathrm{Ca}_{\mathrm{Ca}}^{x} \Leftrightarrow V_{\mathrm{Ca}}'' + \mathrm{Ca}_{i}^{\bullet\bullet}$	~ 7
	null $\Leftrightarrow V_{\mathrm{Ca}}'' + 2V_{\mathrm{F}}^{\bullet}$	~ 5.5
$\mathrm{UO_2}$	$\mathrm{O}_{\mathrm{O}}^{x} \Leftrightarrow \mathrm{O}_{i}'' + V_{\mathrm{O}}^{\bullet\bullet}$	5.1
	$\mathrm{U}_{\mathrm{U}}^{x} \Leftrightarrow V_{\mathrm{U}}'''' + \mathrm{U}_{i}^{\bullet\bullet\bullet\bullet}$	~ 9.5
	null $\Leftrightarrow V_{\mathrm{U}}'''' + 2V_{\mathrm{O}}^{\bullet\bullet}$	~ 6.4
$\mathrm{TiO_2}$ (rutile)	null $\Leftrightarrow V_{\mathrm{Ti}}'''' + 2V_{\mathrm{O}}^{\bullet\bullet}$	5.2
	$\mathrm{O}_{\mathrm{O}}^{x} \Leftrightarrow \mathrm{O}_{i}'' + V_{\mathrm{O}}^{\bullet\bullet}$	8.7
	$\mathrm{Ti}_{\mathrm{Ti}}^{x} \Leftrightarrow \mathrm{Ti}_{i}^{\bullet\bullet\bullet\bullet} + V_{\mathrm{Ti}}''''$	12
$\alpha-\mathrm{Al_2O_3}$	null $\Leftrightarrow 2V_{\mathrm{Al}}''' + 3V_{\mathrm{O}}^{\bullet\bullet}$	20.1 – 25.7 (4.2 – 5.1 eV/defect)
	$\mathrm{Al}_{\mathrm{Al}}^{x} \Leftrightarrow \mathrm{Al}_{i}^{\bullet\bullet\bullet} + V_{\mathrm{Al}}'''$	10.4 – 14.2 (5.2 – 7.1 eV/defect)
	$\mathrm{O}_{\mathrm{O}}^{x} \Leftrightarrow \mathrm{O}_{i}'' + V_{\mathrm{O}}^{\bullet\bullet}$	7.6 – 14.5 (3.8 – 8.3 eV/defect)
$\mathrm{MgAl_2O_4}$	null $\Leftrightarrow V_{\mathrm{Mg}}'' + 2V_{\mathrm{Al}}''' + 4V_{\mathrm{O}}^{\bullet\bullet}$	29.1 (4.15 eV/defect)

Pure stoichiometric NaCl doped with $CaCl_2$

Assuming Schottky defects dominated

$$CaCl_2 \xrightarrow{NaCl} Ca_{Na}^{\bullet} + V_{Na}^{'} + 2Cl_{Cl}$$

$$null \xrightarrow{K_s} V_{Na}^{'} + V_{Cl}^{\bullet}$$

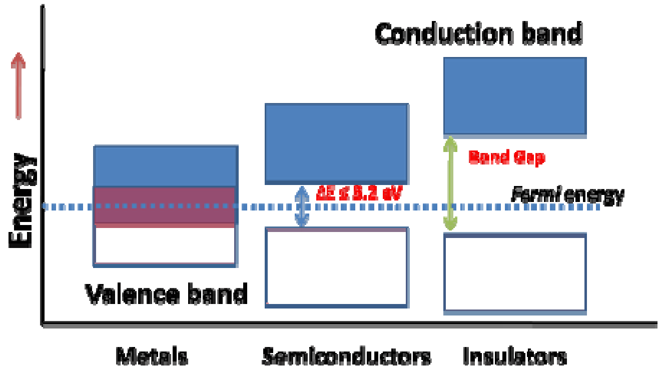
$$null \xrightarrow{K_i} e^{'} + h^{\bullet}$$

$$[V_{Na}^{'}] + [e^{'}] = [Ca_{Na}^{\bullet}] + [h^{\bullet}] + [V_{Cl}^{\bullet}]$$

$$K_s = [V_{Na}^{'}][V_{Cl}^{\bullet}]$$

$$K_i = [e^{'}][h^{\bullet}]$$

$$if\ \ K_i << K_s \ \ \rightarrow [e^{'}]\ and\ \ [h^{\bullet}]\ \text{can be ignored}$$



$$[V_{Na}^{'}] = [Ca_{Na}^{\bullet}] + [V_{Cl}^{\bullet}]$$

$$[V_{Na}^{'}] = [Ca_{Na}^{\bullet}] + \frac{K_s}{[V_{Na}^{'}]}$$

$$or\ \ [V_{Na}^{'}]^2 - [Ca_{Na}^{\bullet}][V_{Na}^{'}] - K_s = 0$$

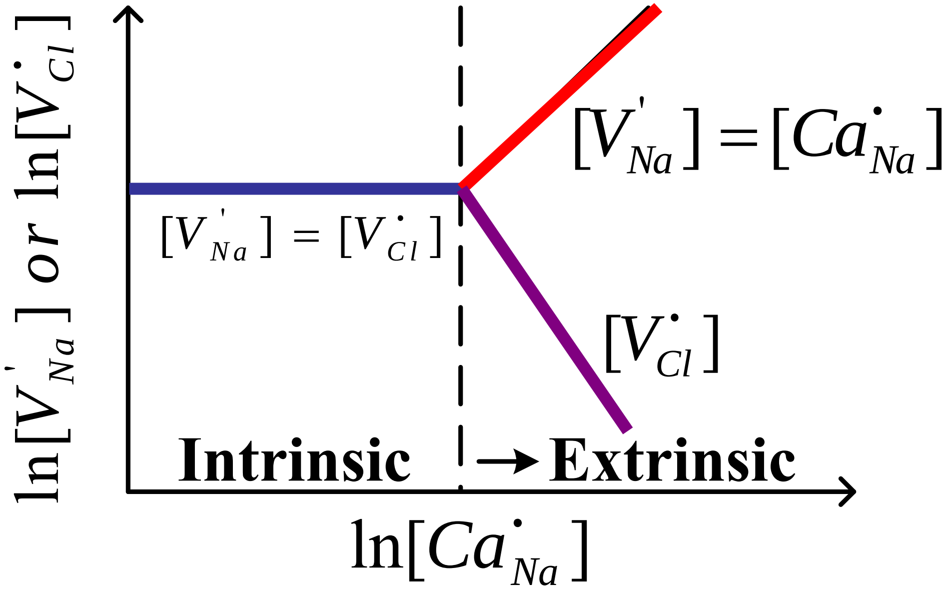
$$\text{The solution is}\ \ [V_{Na}^{'}] = \frac{[Ca_{Na}^{\bullet}] + ([Ca_{Na}^{\bullet}]^2 + 4K_s)^{1/2}}{2}$$

$$[V'_{Na}] = \frac{[Ca^{\bullet}_{Na}] + ([Ca^{\bullet}_{Na}]^2 + 4K_s)^{1/2}}{2}$$

Intrinsic area:

-The vacancy is induced thermally

$$[V'_{Na}] = K_S^{1/2} = [V^{\bullet}_{Cl}] >> [Ca^{\bullet}_{Na}]$$

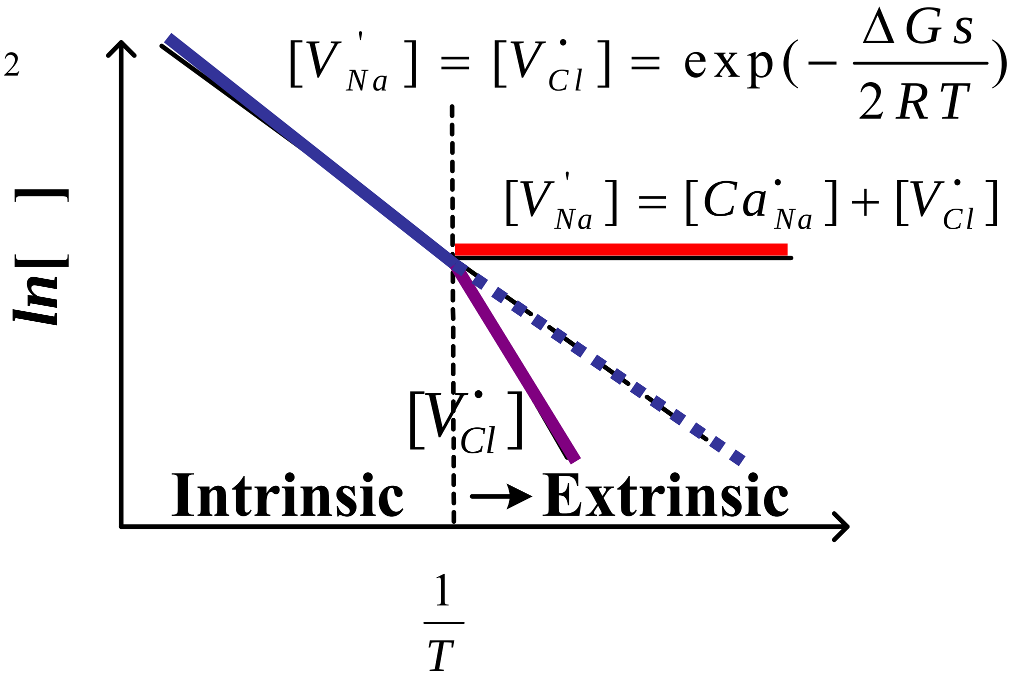


Extrinsic area:

-The vacancy is induced by dopants

$$[V'_{Na}] \approx [Ca^{\bullet}_{Na}] \qquad \because [Ca^{\bullet}_{Na}] >> K_S^{1/2}$$

$$[V^{\bullet}_{Cl}] = \frac{K_S}{[V'_{Na}](=[Ca^{\bullet}_{Na}])}$$



Diffusivity of Na in NaCl doped with $CaCl_2$

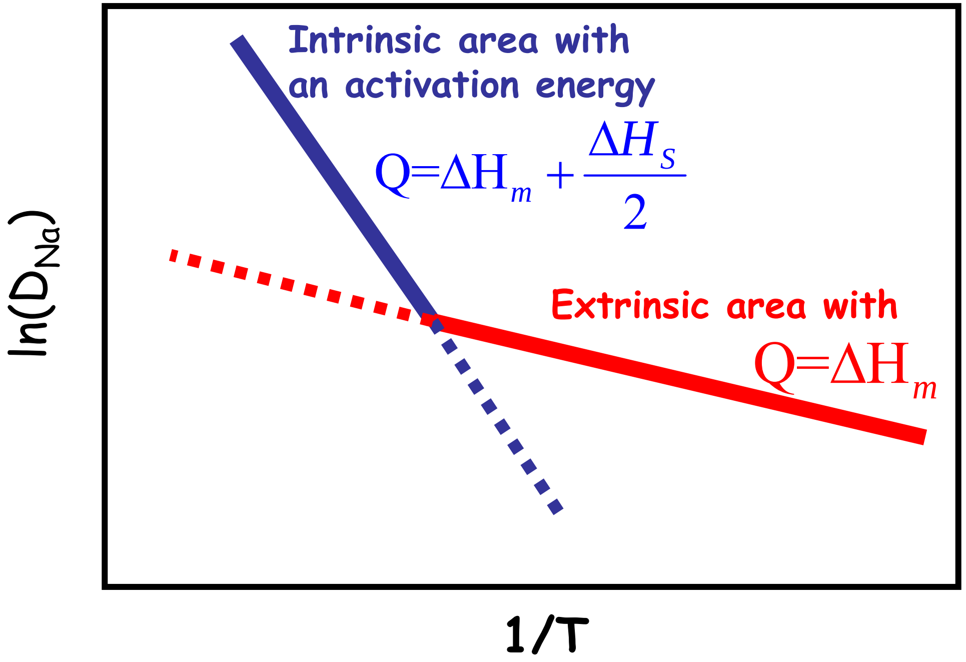
$$CaCl_2 \xrightarrow{NaCl} Ca^{\bullet}_{Na} + V'_{Na} + 2Cl_{Cl}$$

$$D_{Na} = \gamma a_o^2 w[V'_{Na}]$$

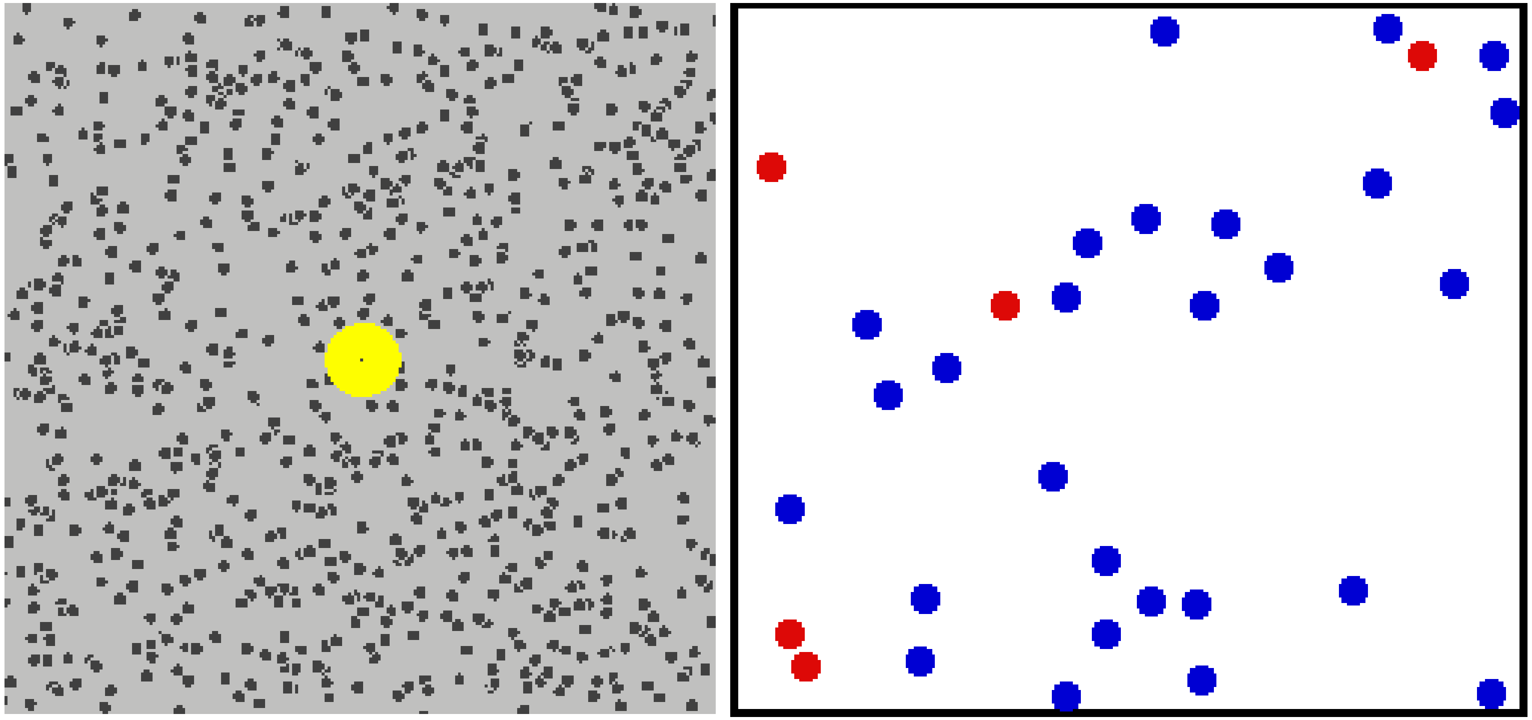
$$= \gamma a_o^2 \nu \exp(-\frac{\Delta G_m}{RT}) \exp(-\frac{\Delta G_s}{2RT}) \quad \rightarrow \text{Intrinsic}$$

$$D_{Na} = \gamma a_o^2 w[V'_{Na}]$$

$$= \gamma a_o^2 \nu \exp(-\frac{\Delta G_m}{RT})[CaCl_2] \quad \rightarrow \text{Extrinsic}$$



Brownian Motion



Brownian Motion

$$\overline{x}^2 = \frac{4kTK_m t}{3\pi\eta D_p}$$

$\overline{x}^2$: statistical average of linear displacement

K_m : correction factor depending upon medium

η : viscosity of medium, D_P : diameter of particle, t : time

* Displacement in one second for powders with a density of 2 g/cm^3

D_P (μm)	B_{air} (μm)	G_{air}	B_{water}	G_{water}
10	1.75	1550	0.236	55.4
1	5.91	69.6	0.745	0.35
0.1	29.4	1.7	2.36	0.005

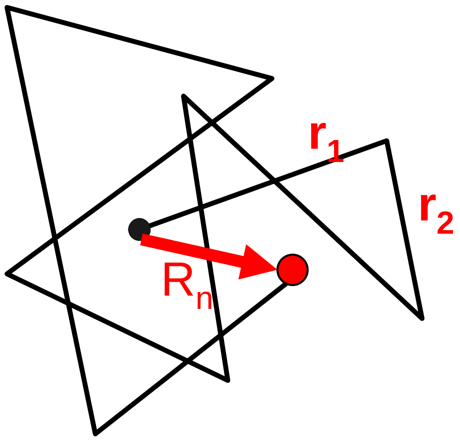
B : Displacement due to Brownian motion
G: Displacement due to Gravitational movement

$\because \eta_{water} > \eta_{air}$

Random-Walk Problem

No assumptions of

(1) randomness of the jumps
(2) length of the successive jumps
(3) allowable values of $\theta_{i,\ i+j}$
(4) number of dimensions in which the atom is jumping



one atom has n jumps and each one is independent

The vector connecting the origin and final positions of an atom will be designated as R_n, which is given by

$$R_n = r_1 + r_2 + \ldots\ldots r_n = \sum_{n=1}^{n} r_i$$

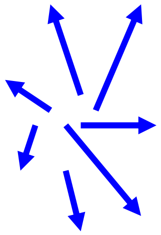
where r_i are vectors representing the various jumps.

$$\because \langle R_n \rangle = 0$$

$$\langle R_n \rangle = \frac{\sum_{N=1}^{N=N} (R_n)_N}{N} = 0$$

N particles

n jumps



To obtain the magnitude of R_n, we square both sides

$$R_n \cdot R_n = r_1 r_1 + r_1 r_2 + \ldots\ldots + r_1 r_n + r_2 r_1 + r_2 r_2 + \ldots\ldots$$
$$+ r_2 r_n + \ldots\ldots\ldots\ldots + r_n r_1 + r_n r_2 + \ldots\ldots + r_n r_n$$

$$R_n^2 = \sum_{i=1}^{n} r_i r_i + 2\sum_{i=1}^{n-1} r_i r_{i+1} + 2\sum_{i=1}^{n-2} r_i r_{i+2} + \ldots\ldots$$

$$= \sum_{i=1}^{n} r_i^2 + 2\sum_{j=1}^{n\text{-}1}\sum_{i=1}^{n\text{-}j} r_i r_{i+j}$$

Define
$$r_i \cdot r_{i+j} = |r_i||r_{i+j}|\cos\theta_{i,i+j}$$

where $\theta_{i,i+j}$ is the angle between two vectors

$$R_n^2 = \sum_{i=1}^{n} r_i^2 + 2\sum_{j=1}^{n-1}\sum_{i=1}^{n-j}|r_i||r_{i+j}|\cos\theta_{i,i+j}$$

For crystal with cubic symmetry, all the jump vectors will be the same in magnitude

$$R_n^2 = nr^2 + 2r^2\sum_{j=1}^{n-1}\sum_{i=1}^{n-j}\cos\theta_{i,i+j}$$

$$= nr^2\left(1+\frac{2}{n}\sum_{j=1}^{n-1}\sum_{i=1}^{n-j}\cos\theta_{i,i+j}\right)$$

N particles → n jumps → average $\overline{R_n^2}$

$$\overline{R_n^2} = \frac{\sum_{N=1}^{N=N}(R_n^2)_N}{N} = nr^2\left(1+\frac{2}{n}\overline{\sum_{j=1}^{n-1}\sum_{i=1}^{n-j}\cos\theta_{i,i+j}}\right)$$

- nr^2 will be the same for each particle
- If each jump direction is independent of the direction of the jumps which proceed it, and each jump vector and its negative are equally probable, then positive and negative values of any given $\cos\theta_{i,i+j}$ will occur with equal frequency, and the average value of the term involving the double sum will be zero.

$$\therefore \overline{R_n^2} = n r^2$$

$$\sqrt{\overline{R_n^2}} = \sqrt{n}\,|r|$$

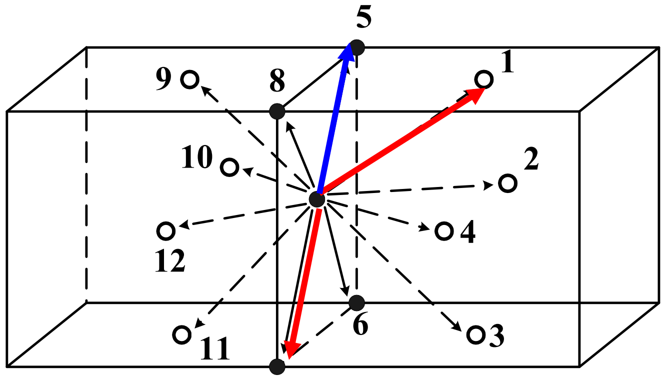
The root-mean-square displacement is proportional to the square root of the number of jumps.

Example: At carburizing temperature of 950℃, carbon atoms make 10^{10} jumps per second, and each jump distance is 10^{-10} m.

*The distance for each atom travels in one second is
10^{10} jumps/sec*10^{-10} m/jump = 1 m/sec
Three hours will be 1 (m/sec)x10^4 (sec)=**10^4 m**

* $total\ jumps: n = 10^{10}\ jump/\sec\cdot 10^{4} \sec = 10^{14}\ jumps$

$$\sqrt{\overline{R_n^2}} = \sqrt{n}\,|r| = \sqrt{10^{14}}\cdot 10^{-10} = 10^{-3}\ m$$



The arrows show 12 possible jump vector in an FCC lattice

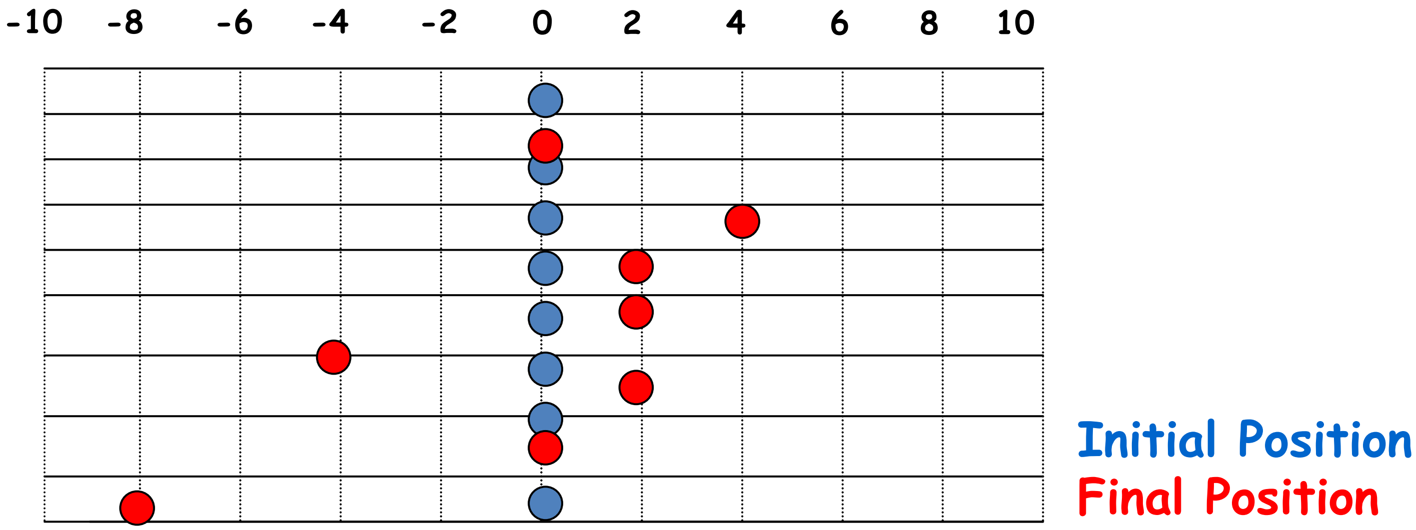
FCC

$$\sum_{j=1}^{12} \mathbf{r}_i \cdot \mathbf{r}_j = r^2 \sum_{j=1}^{12} \cos\theta_{i,j} = 0$$

$$e.g.,\quad r_i r_7 + r_i r_5 = r_i r_7 - r_i r_7 = 0$$

$$\therefore \overline{R_n^2} = n r^2$$

One-dimension Random Walk



n: number of random jumps (n=16)
N: number of particles (N=8)

$$\sqrt{\overline{R_n^2}} = \sqrt{n}\,|r| = \sqrt{16}\cdot r = 4r \text{ (expected RMS displacement)}$$

RMS: Root-Mean-Square

$$\sqrt{\overline{R_n^2}} = \left(\frac{\Sigma R_n^2}{N}\right)^{1/2}\cdot r$$

$$= \left[\frac{((-8)^2 + 0^2 + 2^2 + (-4)^2 + 2^2 + 2^2 + 4^2 + 0^2)}{8}\right]^{1/2}\cdot r$$

$$= 3.67r$$

One-dimension Random Walk

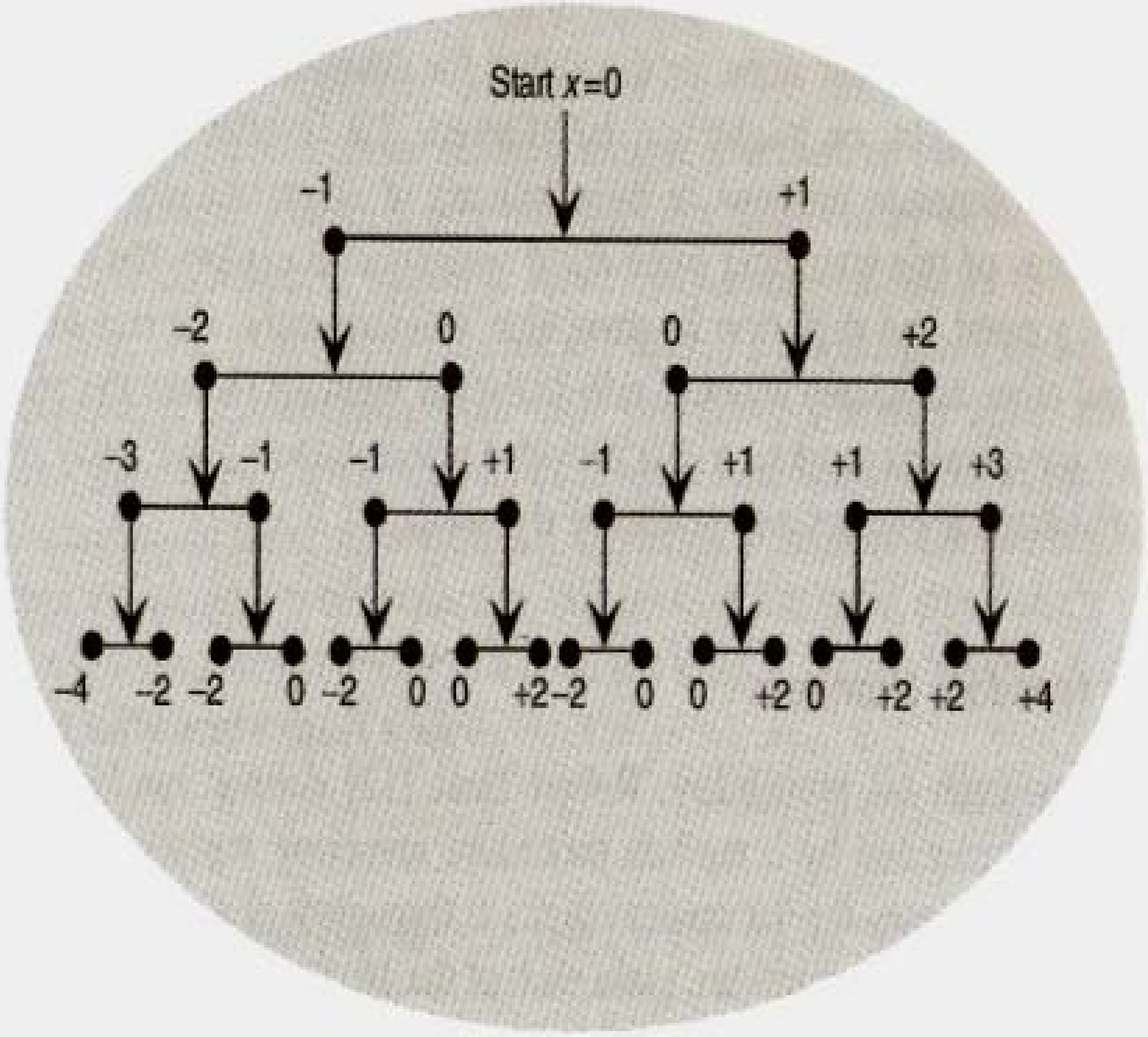


FIGURE 12.1 Four levels of a symmetric one-dimensional random walk.

TABLE 12.1 Random walk sequence

n	Sequence	Displacement, λ_k	Square Displacement, λ_k^2	Root-Mean-Square Displacement $\sqrt{\sum_k \lambda_k^2} = \sqrt{\mathbf{n}}\lvert\mathbf{r}\rvert$
1	+1	+1	1	$[(\frac{1}{2})(2)(1)]^{1/2} = 1$ N=2 coins,
	−1	−1	1	n=1 time
2	+1, +1	+2	4	$[(\frac{1}{4})(2(4)+2(0))]^{1/2} = (2)^{1/2}$
	+1, −1	0	0	N=4 coins,
	−1, +1	0	0	n=2 times
	−1, −1	−2	4	
3	+1, +1, +1	+3	9	$[(\frac{1}{8})(2(9)+6(1))]^{1/2} = (3)^{1/2}$
	+1, +1, −1	+1	1	
	+1, −1, +1	+1	1	N=8 coins,
	−1, +1, +1	+1	1	
	−1, −1, +1	−1	1	n=3 times
	−1, +1, −1	−1	1	
	+1, −1, −1	−1	1	
	−1, −1, −1	−3	9	
4	+1, +1, +1, +1	+4	16	$[(\frac{1}{16})(2(16)+8(4)$
	+1, +1, +1, −1	+2	4	$+6(0))]^{1/2} = (4)^{1/2}$
	+1, +1, −1, −1	0	0	
	+1, −1, −1, −1	−2	4	N=16 coins,
	−1, −1, −1, −1	−4	16	n=4 times
	−1, −1, −1, +1	−2	4	
	−1, −1, +1, +1	0	0	
	−1, +1, +1, +1	+2	4	
	−1, +1, −1, +1	0	0	
	−1, +1, +1, −1	0	0	
	+1, −1, −1, +1	0	0	
	−1, +1, −1, −1	−2	4	
	+1, −1, +1, +1	2	4	
	+1, −1, +1, −1	0	0	
	−1, −1, +1, −1	−2	4	
	+1, +1, −1, +1	+2	4	

$$\sqrt{\overline{R_n^2}} = \sqrt{n}\lvert r\rvert = \sqrt{4}\cdot r = 2r$$

$$\sqrt{\overline{R_n^2}} = (\frac{\Sigma R_n^2}{N})^{1/2}\cdot r$$

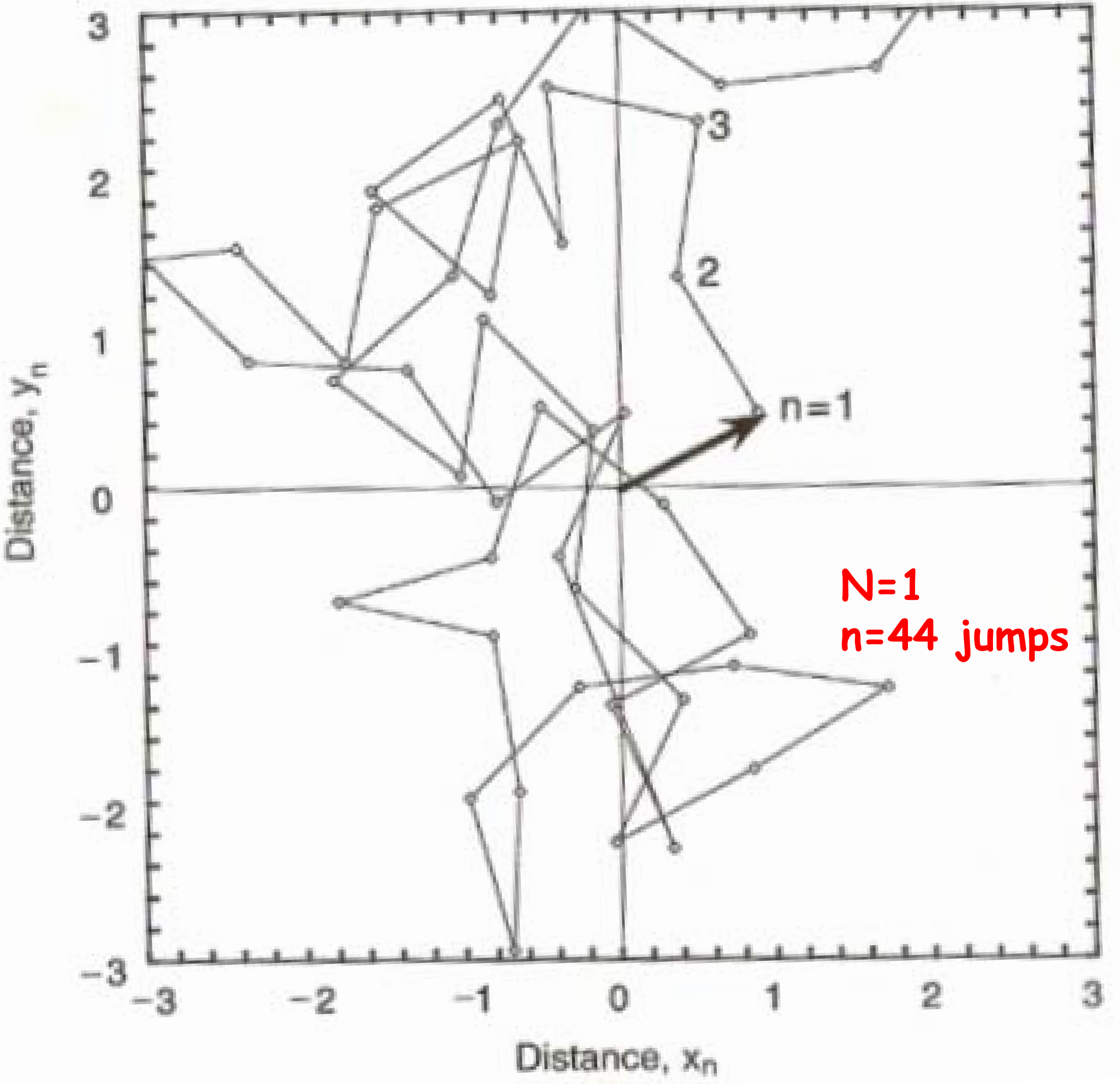
$$= [\frac{16+4+0+4+16+4+0+4+0+0+0+4+4+0+4+4}{16}]^{1/2}\cdot r$$

$$= [\frac{64}{16}]^{1/2} r = \sqrt{4}\cdot r = 2r$$

$$\Sigma(\lambda_g)=0$$

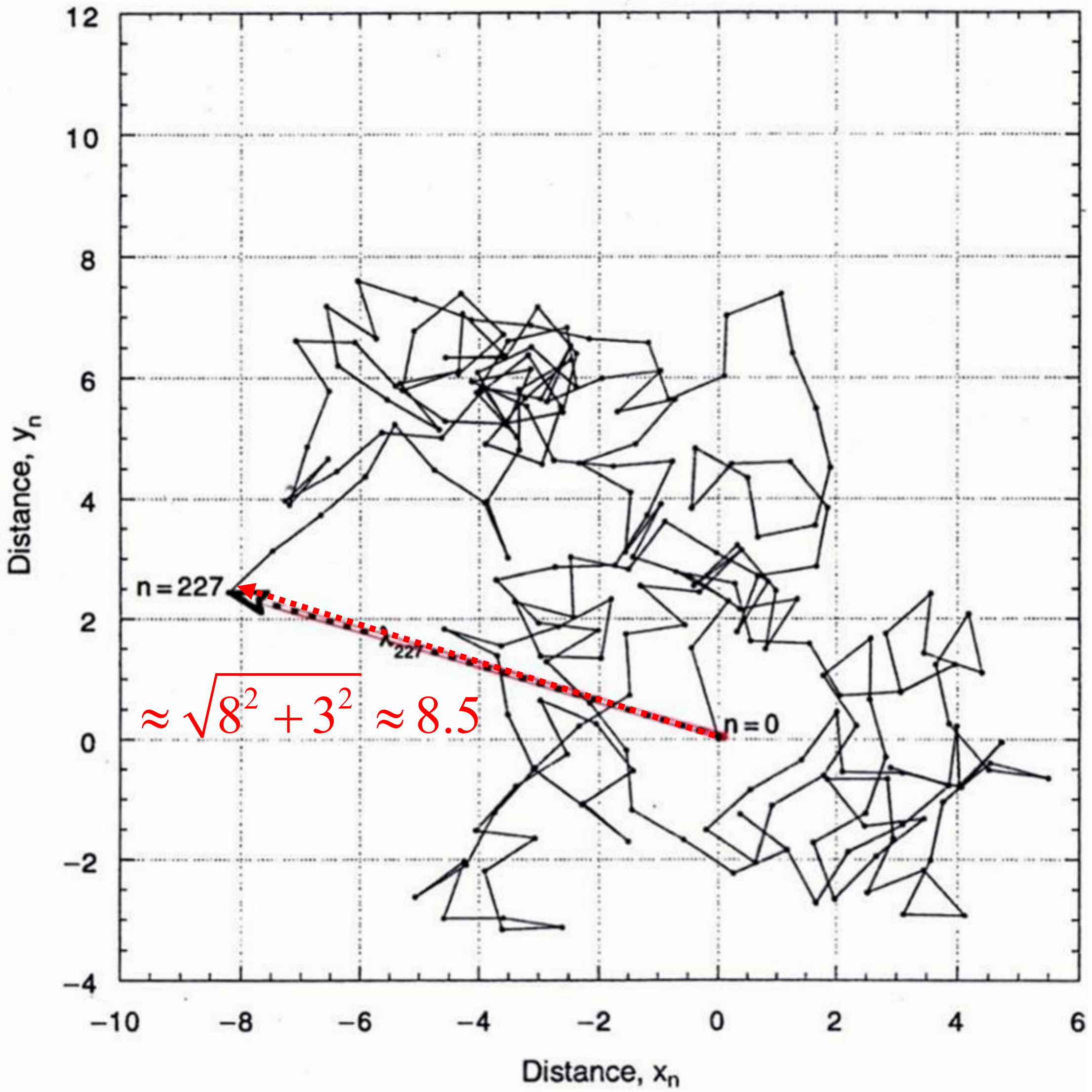
$$\Sigma(R_n)=0$$

Two-dimension Random Walk



N=1
n=44 jumps

Two-dimension Random Walk



$\approx \sqrt{8^2 + 3^2} \approx 8.5$

FIGURE 12.3 A 227-step random walk in two dimensions.

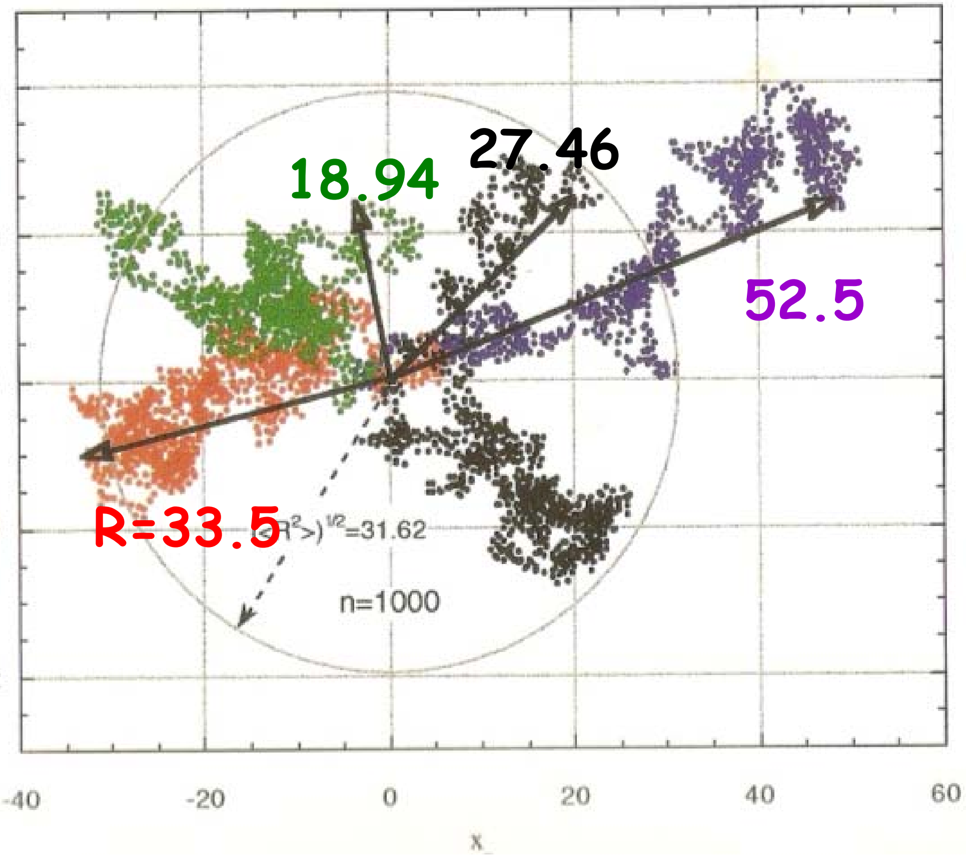
Expected RMS Displacement
N=1, n=227

$$\sqrt{\overline{R_n^2}} = \sqrt{n}\,|r|$$

$$= \sqrt{227} \cdot r$$

$$= 15.06\, r$$

Two-dimension Random Walk



N=4
n=1000

$$n = 1000 \qquad \sqrt{\overline{R_n^2}} = \sqrt{n}\left|r\right| = \sqrt{1000}\cdot r = 31.6r$$

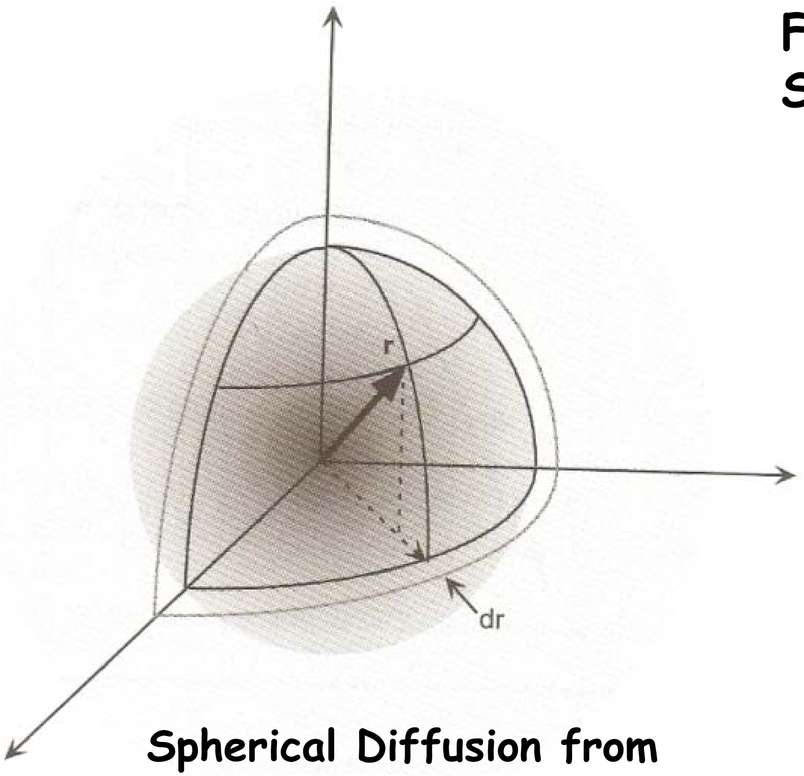
$$N = 4 \qquad \sqrt{\overline{R_n^2}} = \left(\frac{\Sigma R_n^2}{N}\right)^{1/2}\cdot r$$

$$= \left[\frac{33.5^2 + 18.9^2 + 27.5^2 + 52.5^2}{4}\right]^{1/2}\cdot r$$

$$= 35.4r$$

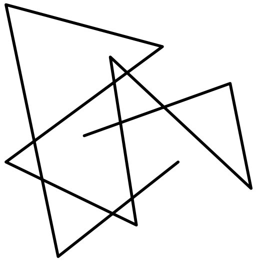
Relation of D to Random Walk : Diffusion taking place under equilibrium condition

$$\overline{R_n^2} = n\alpha^2$$ (α = r = jump distance)



Spherical Diffusion from a Point Source

Fick's 2nd law
Spherical approach in 3-D



$$D\nabla^2 C = \frac{\partial C}{\partial t}$$

$$C(r,t) = \frac{A}{t^{3/2}} \exp\left(-\frac{r^2}{4Dt}\right)$$ (A: constant)

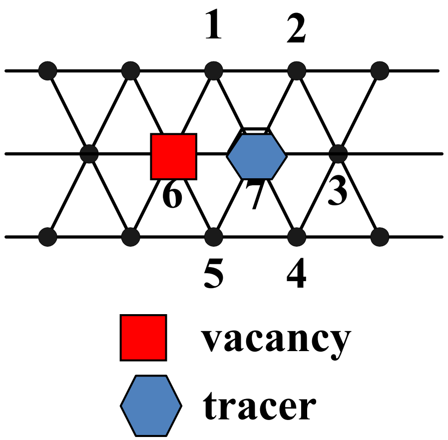
$$\frac{\int r^2 C(r,t)dr}{\int C(r,t)dr} = \overline{r^2} = 6Dt$$

$$\overline{R_n^2} = n\alpha^2 = \overline{r^2} = 6Dt$$

$$D = \frac{1}{6}\frac{n}{t}\alpha^2 = \frac{1}{6}\Gamma\alpha^2$$: Self diffusivity

$$\because \frac{n}{t} = \Gamma$$

Correlation Effect



Initially the tracer locates at #6. After jumping from #6→#7, its next most probable jump is to jump back to the original position #7→#6 → it is not random.

Correlation factor (f): relate probability of preferred exchange of tracer and vacancy

$$\overline{R_n^2}(t) < \overline{R_n^2}(v)$$

Tracer's mean-square displacement is less than that of vacancy.

$$f = \lim_{n\to\infty} \frac{\overline{R_n^2}(t)}{\overline{R_n^2}(v)}$$

$$\because \overline{R_n^2} = n\alpha^2 \ \text{and} \ \overline{X^2} \ \alpha \ Dt$$

$$f = \frac{D_A^* t_n(A^*)}{D_v t_n(v)}$$

3-D

$$\boxed{\overline{R_n^2} = n\alpha^2 = \overline{r^2} = 6Dt}$$

$t_n(t)$ is the time for n jumps of species i.

Since vacancy concentration is small

$$\frac{C_v}{C_A} << 1$$

average jump frequency

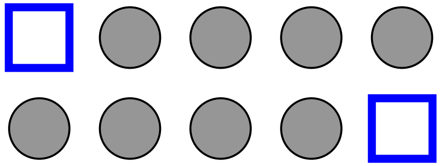
$$\Gamma_A = \Gamma_v \frac{C_v}{C_A} \rightarrow \Gamma_A = \Gamma_v \cdot N_v$$

$$D_A = D_v \cdot N_v$$

$$f = \frac{D_A^* \frac{n}{\Gamma_A}}{D_v \frac{n}{\Gamma_v}} = \frac{D_A^* (\frac{n}{\Gamma_v})(\frac{C_A}{C_v})}{D_v \frac{n}{\Gamma_v}}$$

$$= \frac{D_A^*}{D_v \frac{C_v}{C_A}} = \frac{D_A^*}{D_v \cdot N_v} = \frac{D_A^*}{D_A}$$

where D_A= self diffusivity
D_A^*= tracer diffusivity



$$C_v = \frac{1}{5}, \quad C_A = \frac{4}{5}$$

$$\Gamma_v \cdot C_v = \Gamma_A \cdot C_A$$

$$4 \cdot \frac{1}{5} = 1 \cdot \frac{4}{5}$$

Approximation of correlation factor (*f*)

- Probability that tracer jumps back into vacancy:1/Z (Z: coordination number of v, A, A*)
-Pair of jumps resulting in no net displacement of A* (6→7, 7→6)

$$f \approx 1 - \frac{2}{z}$$

f=0, completely correlated
(back and forth
completely)
f=1, completely random

Lattice	Z	1-2/Z	*f* (calculated)
FCC	12	0.83	0.78
BCC	8	0.75	0.72

$$\overline{R_n^2} = n\alpha^2[1+\frac{2}{n}\sum_{j=1}^{n-1}\sum_{i=1}^{n-j}\overline{\cos\theta_{i,i+j}})$$

$$\overline{R_n^2} = n\alpha^2$$ because all allowed values of θ are equally probable

$$f = 1+\frac{2}{n}\sum_{j=1}^{n-1}\sum_{i=1}^{n-j}\overline{\cos\theta_{i,i+j}}$$

All tracer-vacancy pairs that have just completed an exchange are indistinguishable, aside from their orientations. Thus, the value of $\overline{\cos\theta_{i,i+j}}$ is the same for each value of i.
i.e., i→i+1 and n→n+1 have the same angle

$$f = \lim_{n\to\infty}[1+\frac{2}{n}\sum_{j=1}^{n-1}(n-j)\overline{\cos\theta_j}]$$

$$n \to \infty \quad \frac{n-j}{n} = 1$$

$$f = 1+2\overline{\cos\theta_1}+2\overline{\cos\theta_2}+\ldots\ldots.$$

$\overline{\cos\theta_1}$: the mean value of cosine of the angle between the ith and the (i+1)th jump vector.

$$\overline{\cos\theta_2} = (\overline{\cos\theta_1})^2$$

……

$$\overline{\cos\theta_n} = (\overline{\cos\theta_1})^n$$

(Compaan and Haven)

$$f = 1 + 2(\overline{\cos\theta_1}) + 2(\overline{\cos\theta_1})^2 + 2(\overline{\cos\theta_1})^3 + \ldots\ldots$$

$$= \frac{1+\overline{\cos\theta_1}}{1-\overline{\cos\theta_1}}$$

Lattice	**Z**	$f \approx 1 - \frac{2}{Z}$	$f = \frac{1+\overline{\cos\theta_1}}{1-\overline{\cos\theta_1}}$
FCC	12	0.833	0.781
BCC	8	0.750	0.727
SC	6	0.667	0.653
Diamond	4	0.500	0.500

$$\overline{\text{Cos}\,\theta}_1 = p_1\cos\theta_{76}+p_2\cos\theta_{71}+p_3\cos\theta_{72}+ p_4\cos\theta_{73}+p_5\cos\theta_{74}+p_6\cos\theta_{75}$$

$P_1 = 1/Z$

$\text{Cos}\,\theta_{76} = -1$

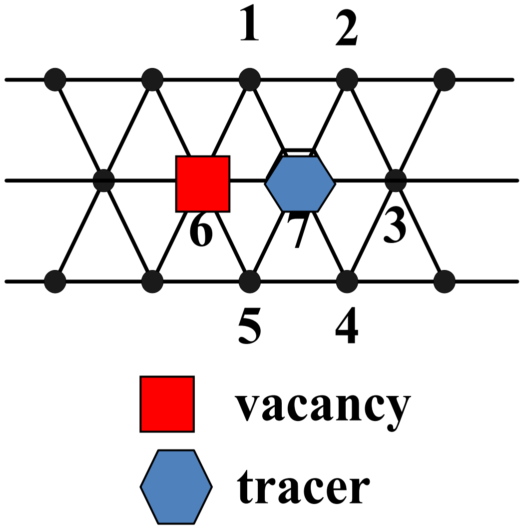
$P_2=P_3=P_4=P_5=P_6=0$

$\rightarrow \overline{\text{Cos}\,\theta}_1 = -1/Z$

$$f=\frac{1+\overline{\cos\theta_1}}{1-\overline{\cos\theta_1}}=\frac{1-{}^{1}\!/_{Z}}{1+{}^{1}\!/_{Z}}$$

$$=\frac{Z-1}{Z+1}=1-\frac{2}{Z+1}\approx 1-\frac{2}{Z}$$

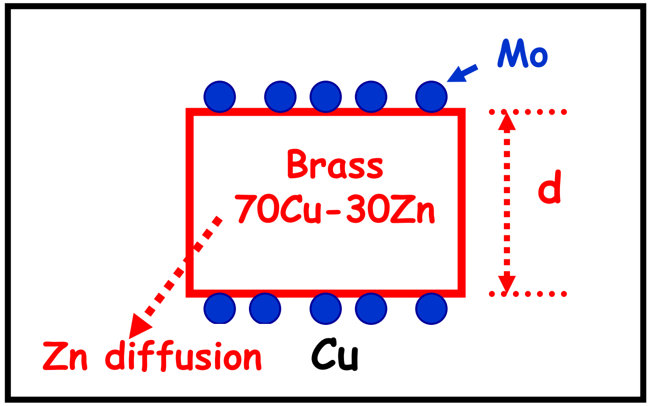
Correlation Effect



Diffusion in a Concentrated Solution

Reference: Shewmon, Diffusion in Solids, Chap.4

Kirkendall experiment



- Mo insoluble in Cu and brass
- Annealed at t time, the d decreases monotonically with time

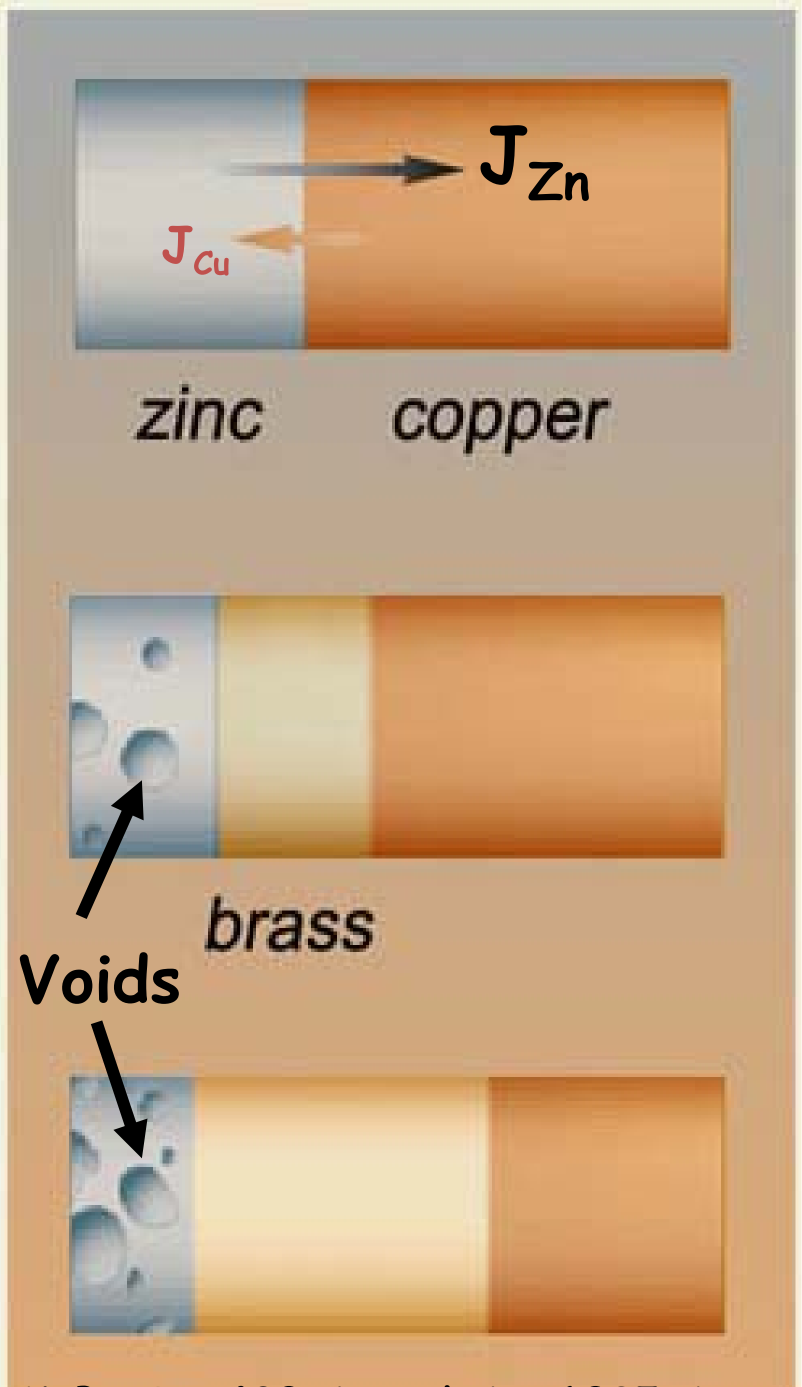
(1) marker displacement → net flow of matter
(2) matter flow compensated by vacancy flow
(3) matter flow arises because $D_{Cu} \neq D_{Zn}$
(4) evidence of vacancy mechanism for diffusion
(5) evidence of maintaining equilibrium of vacancy

Darken's analysis of Kirkendall experiment

e.g., The migration of ink on the river includes

(1) Ink diffusion
(2) Stream movement

Vacancy Diffusion



M.P.: Zn:420°C, and Cu: 1085°C.

Mechanisms of Substitutional Atom Diffusion

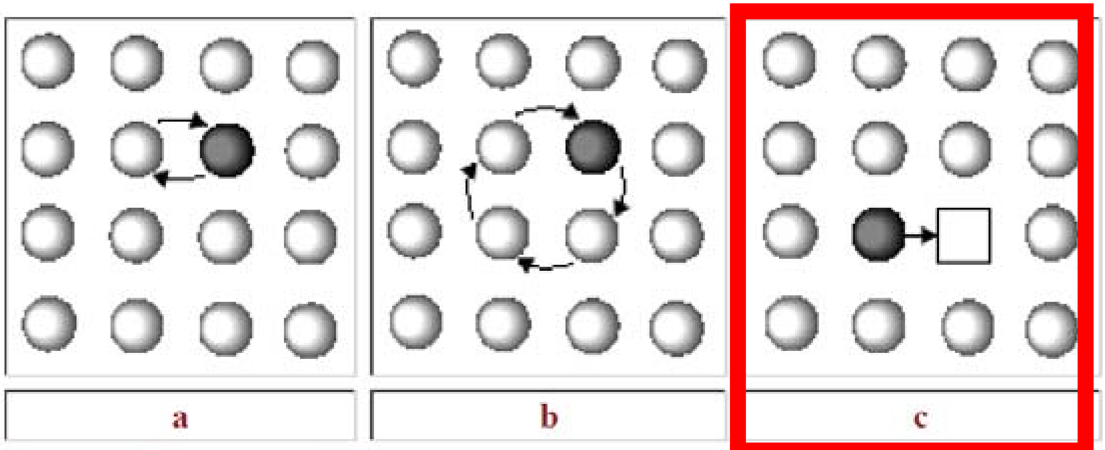
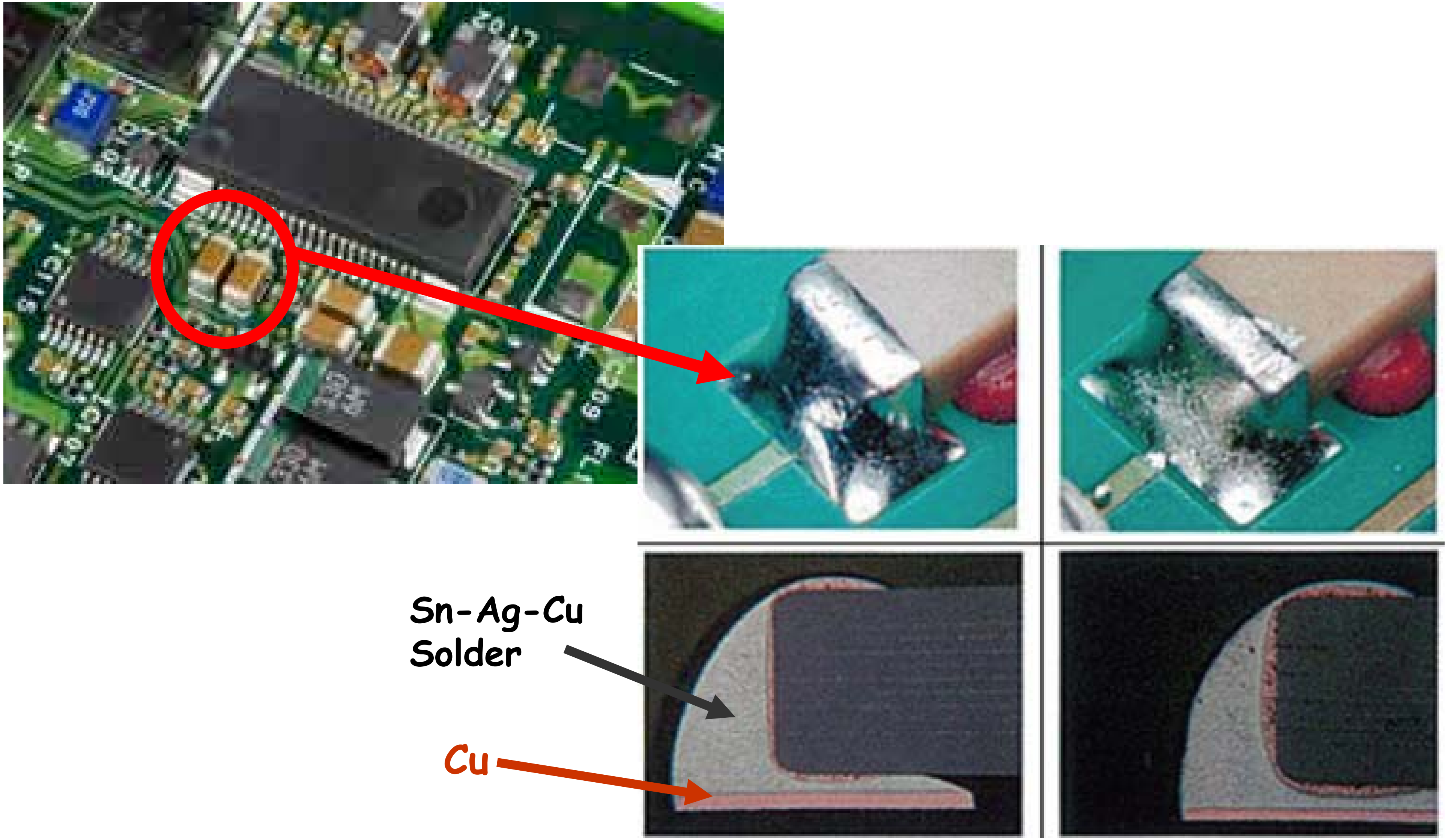


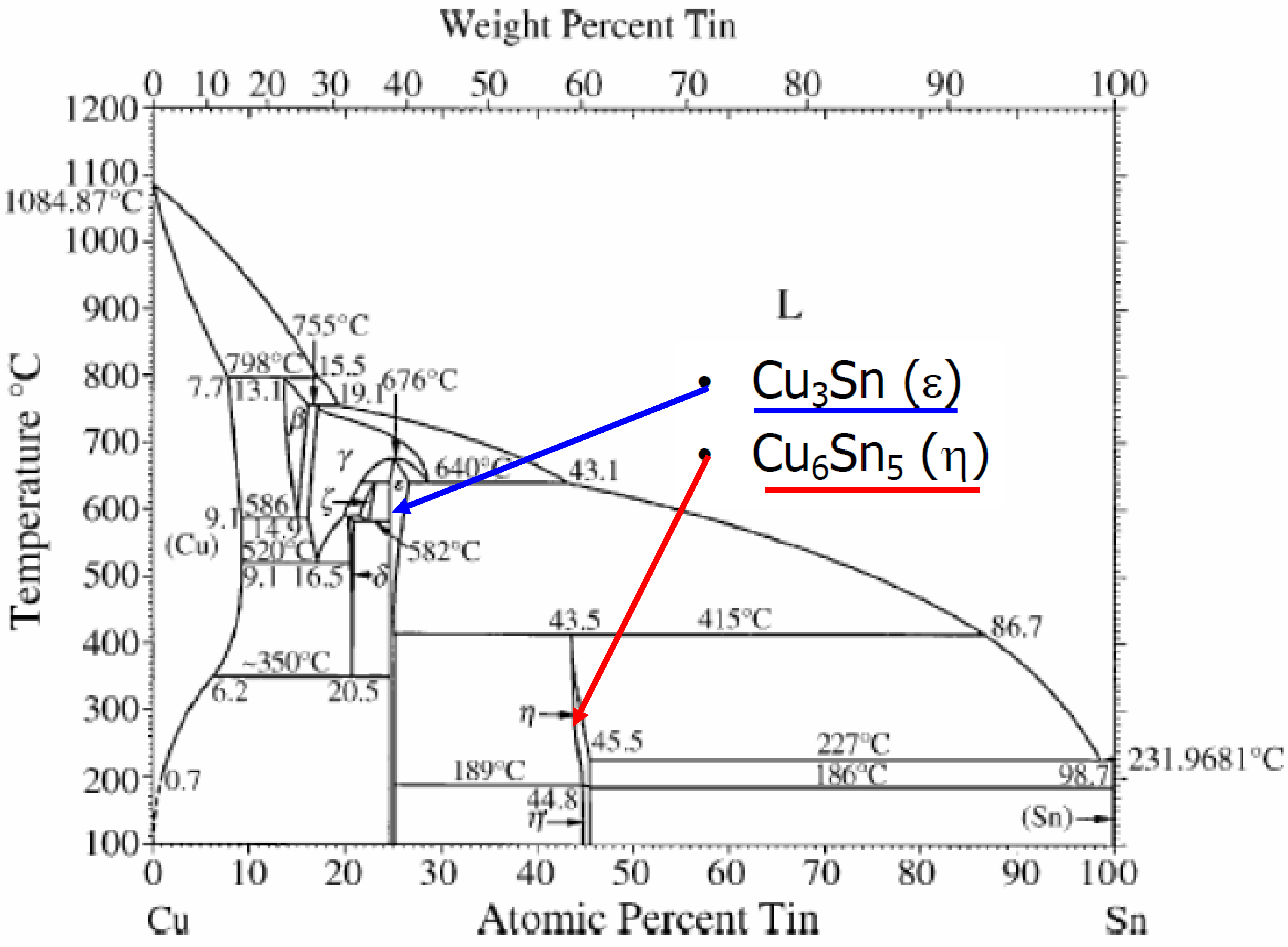
Figure 1. The atomic diffusion mechanism showing (a) a direct exchange mechanism, (b) ring mechanism, and (c) vacancy mechanism.

$$J_{Zn} >> J_{Cu}$$

Only happening by a vacancy mechanism. A direct exchange or ring mechanism does not allow different fluxes.

Surface Mount Technology (SMT)





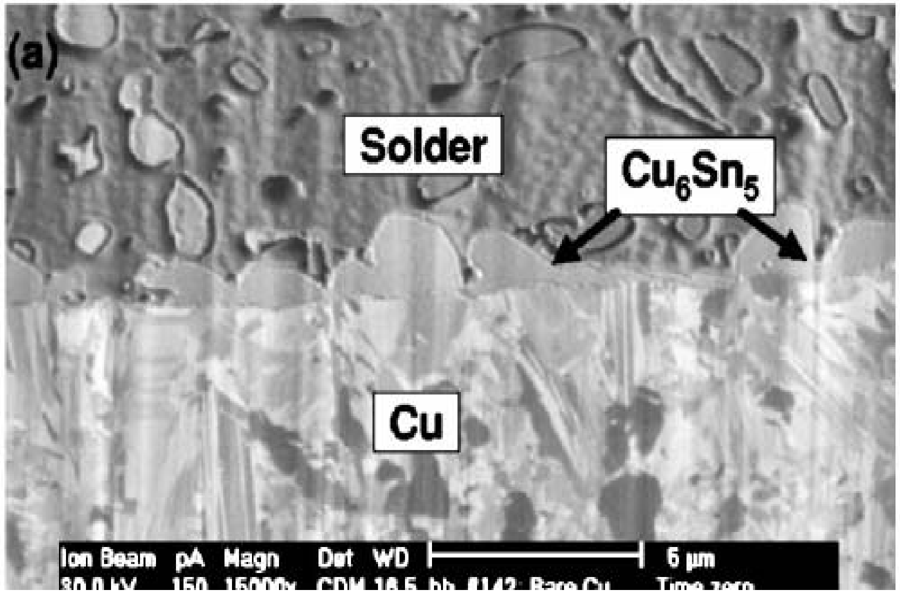
- Cu_3Sn (ε)
- Cu_6Sn_5 (η)

Fig. 1. Cu–Sn binary phase diagram [65].

<u>Soldering</u>: solid Cu dissolves in liquid Sn (supersaturised locally)

formation of Cu_6Sn_5 (η) , scallop-like uniphase

formation of Cu_3Sn (ε), requires long contact times, thickness limited



t=0

Zeng et al. J.Appl.Phys. 97, 2005

SnPb solder - electrodeposited Cu

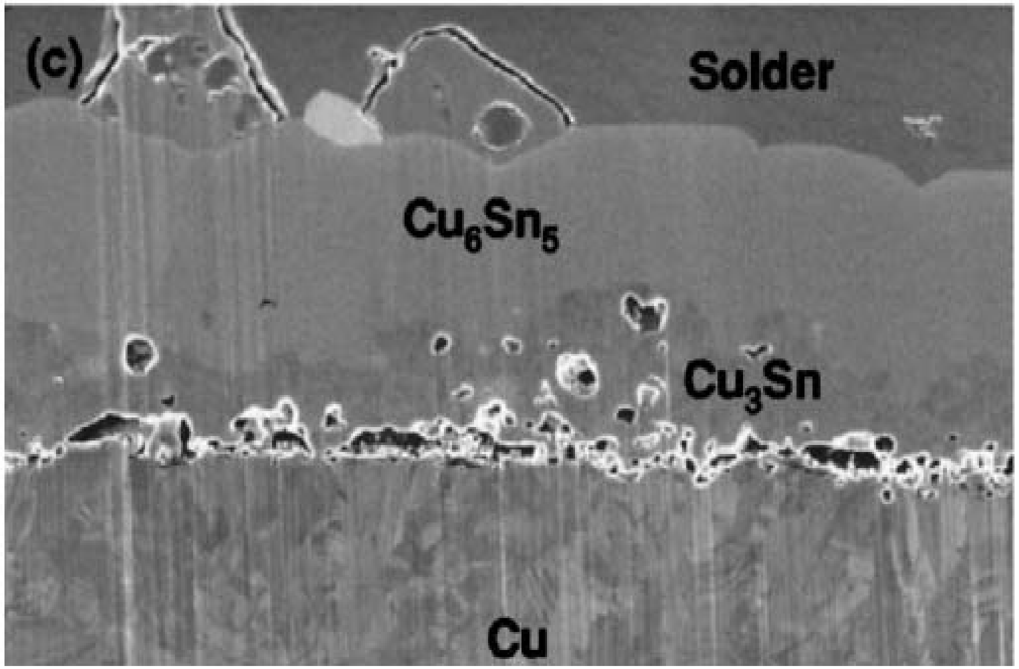
Case: diffusion couple Sn-Cu

Annealing:

Thickness of IMC increases **(IMC: Intermetallic Compound)**

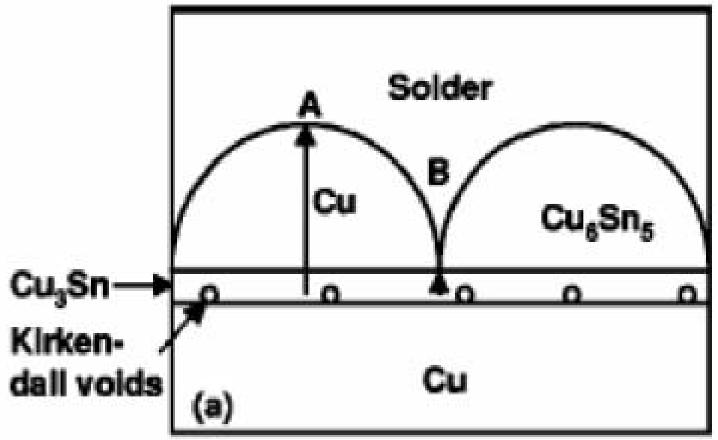
Cu_6Sn_5 (η), uniform

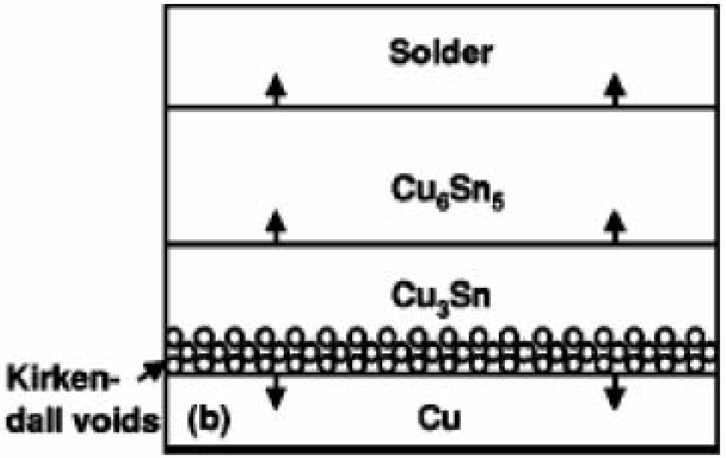
Cu_3Sn (ε), Sn diffusion exceeds Cu diffusion at higher T

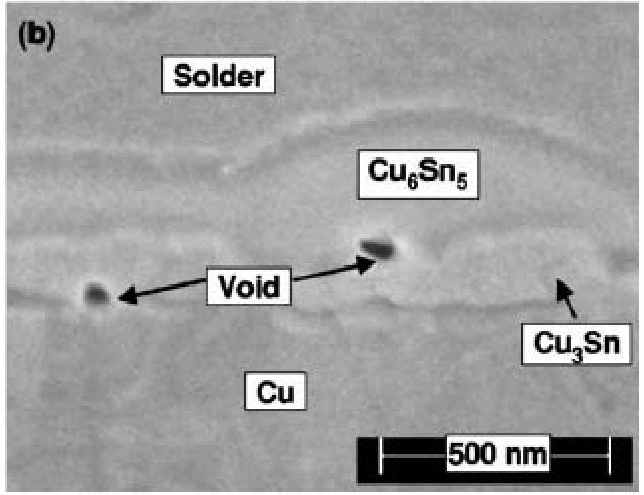


t=20days, T=150 °C

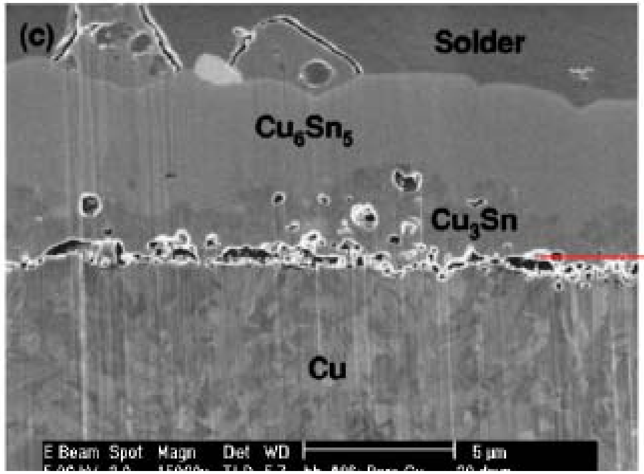
Case: diffusion couple Sn-Cu







t=0

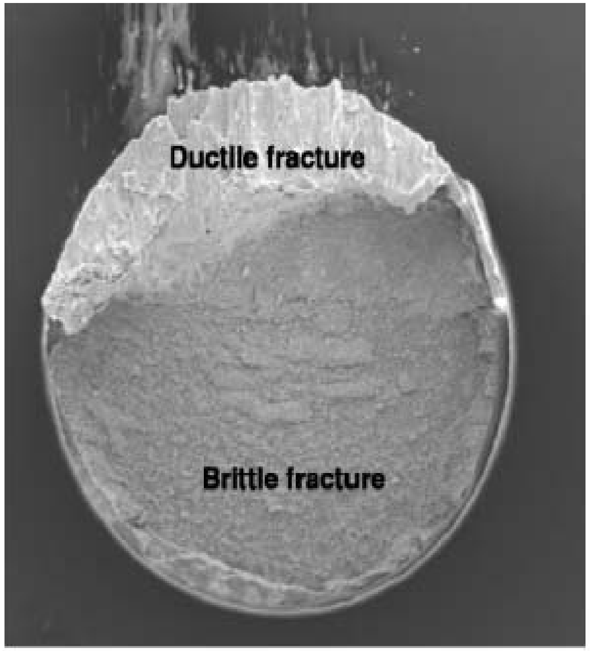


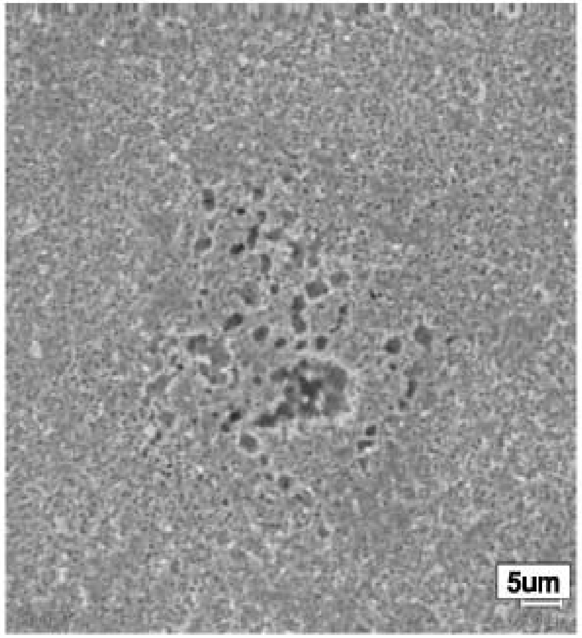
t=20days,
T=150 °C

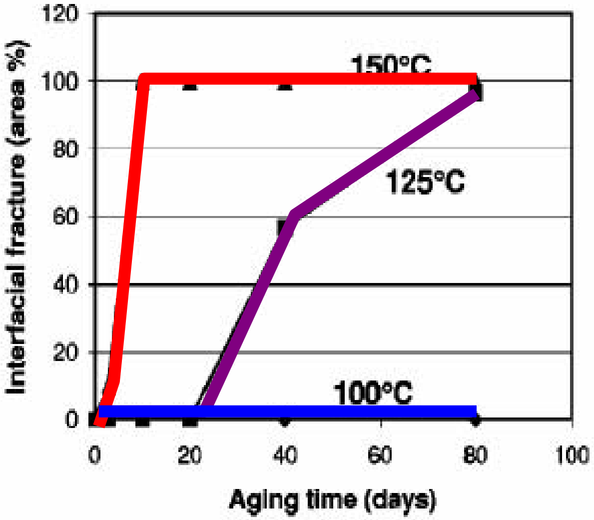
Voids influence diffusion

Case: diffusion couple Sn-Cu

- Pull and <u>shear</u> testing



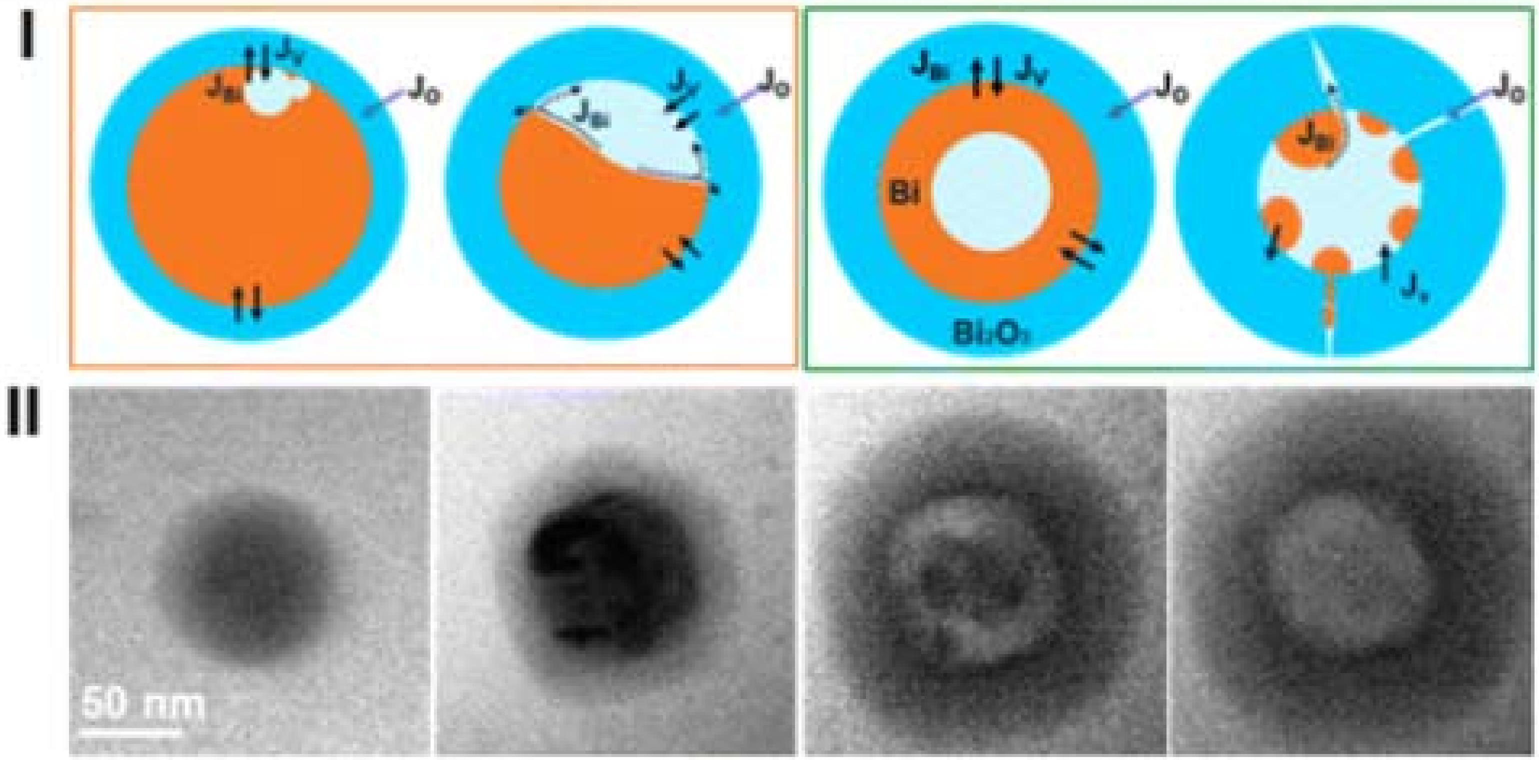




Pad side

t=40days, T=125 °C

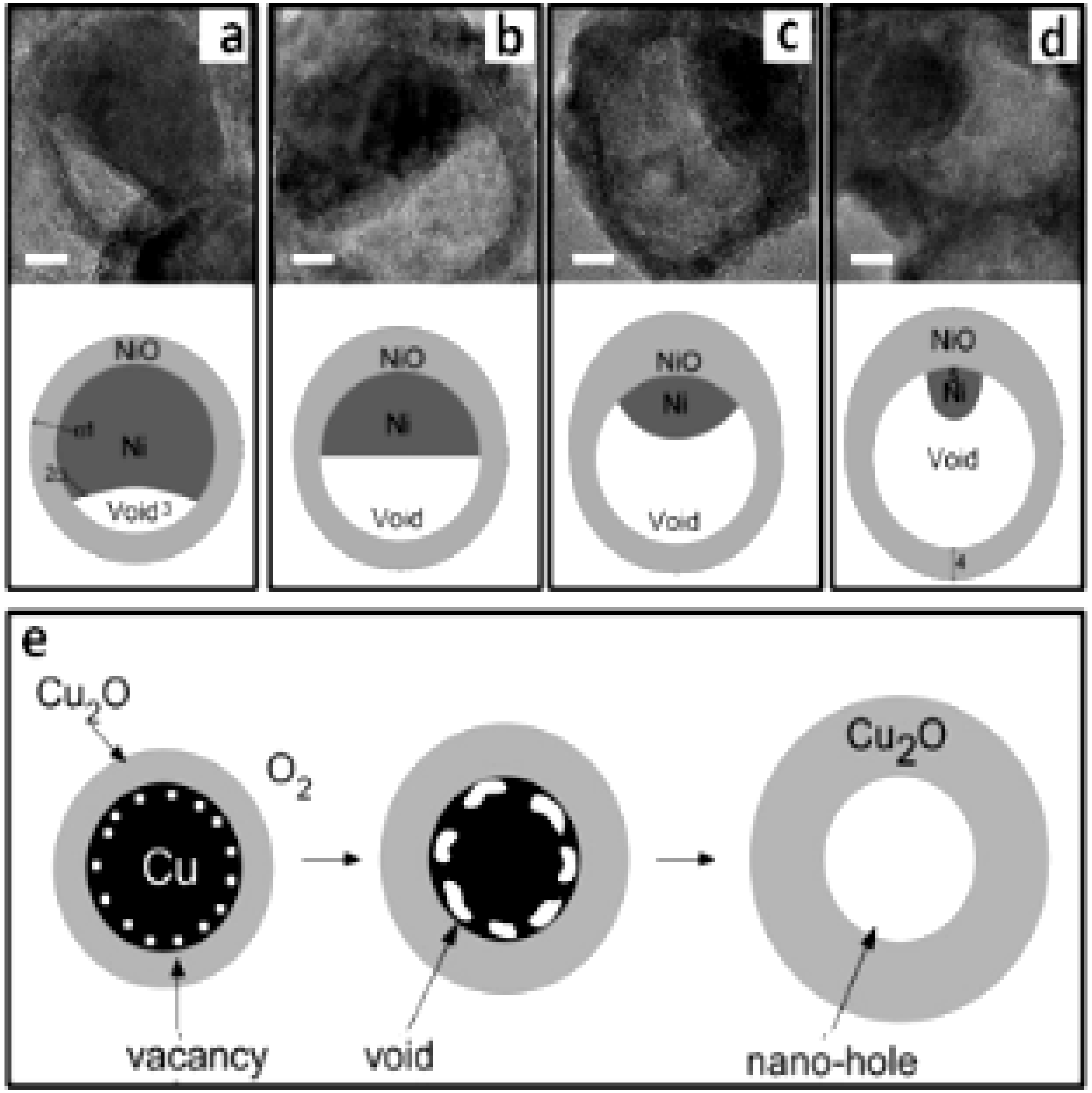
Kirkendall Effect

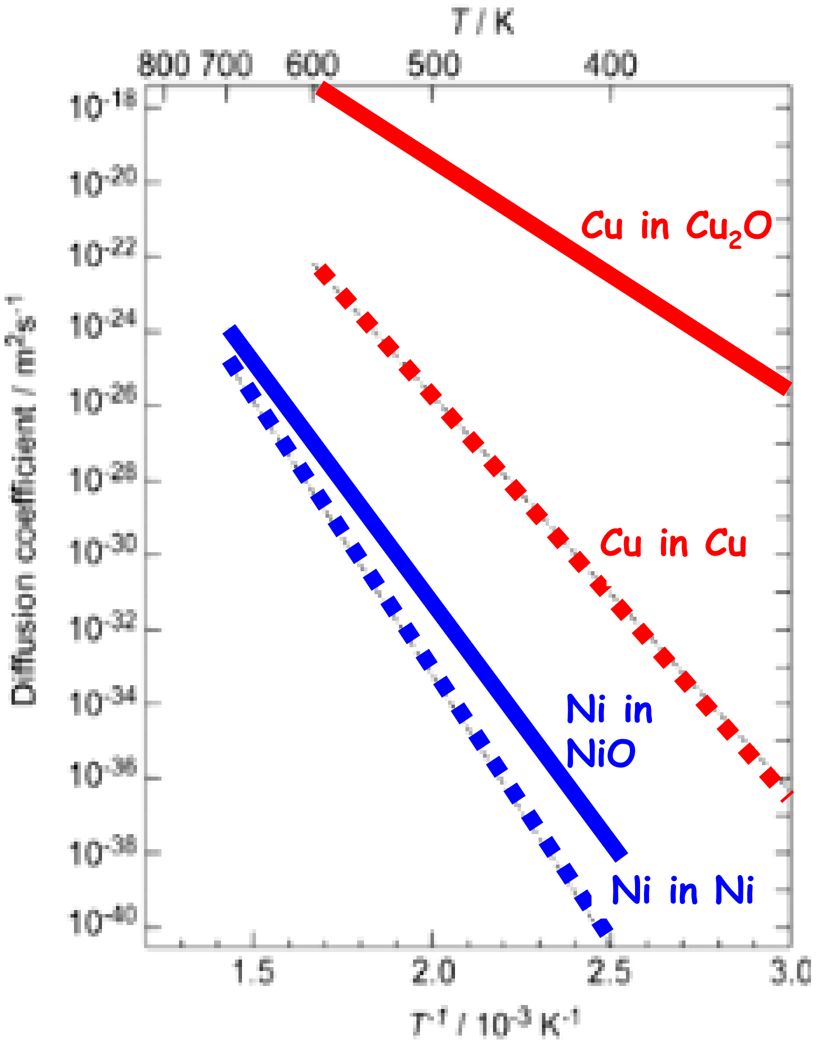


Diffusivity:

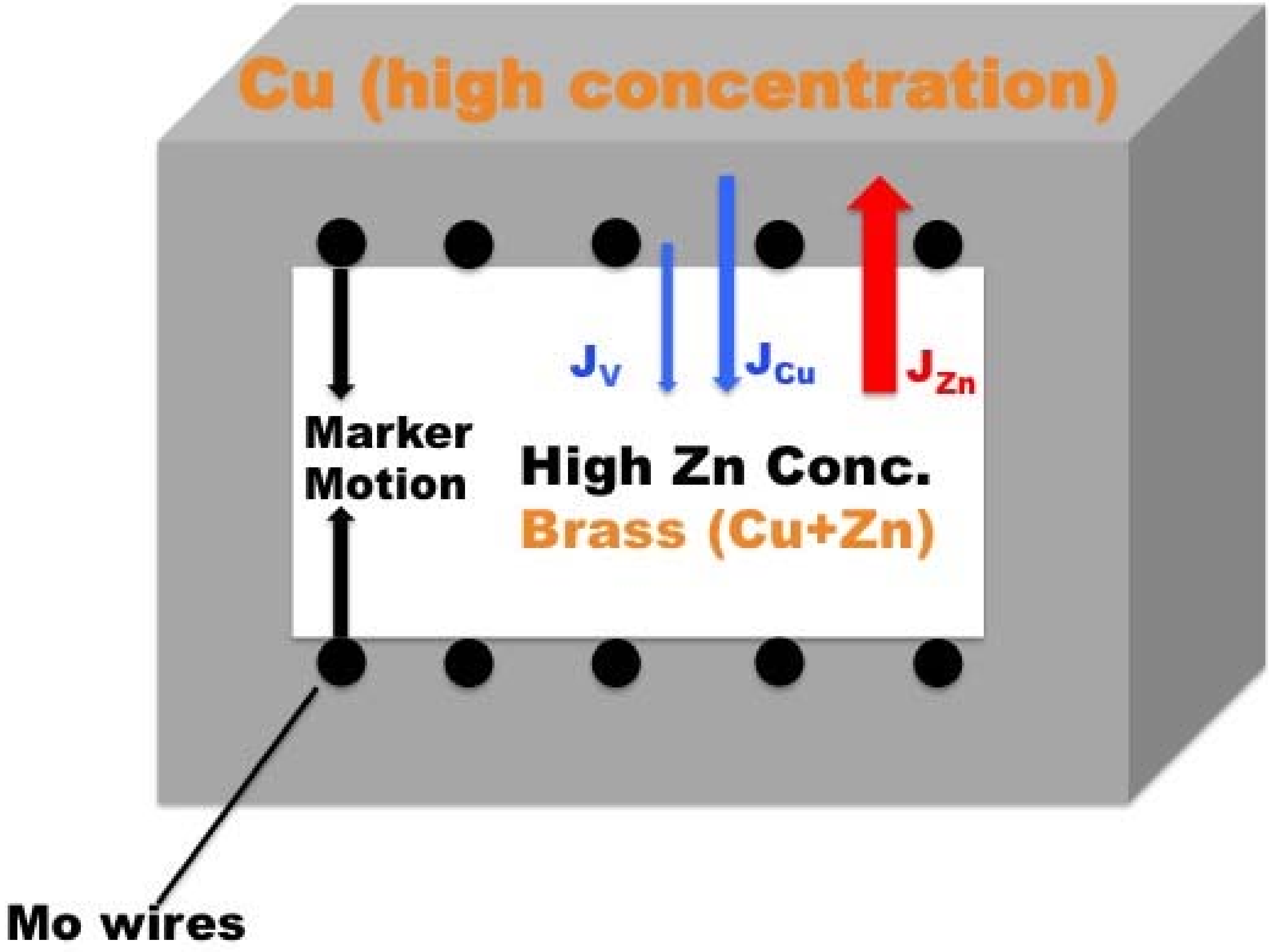
Bi in Bi_2O_3 >> Bi in Bi

Kirkendall Effect

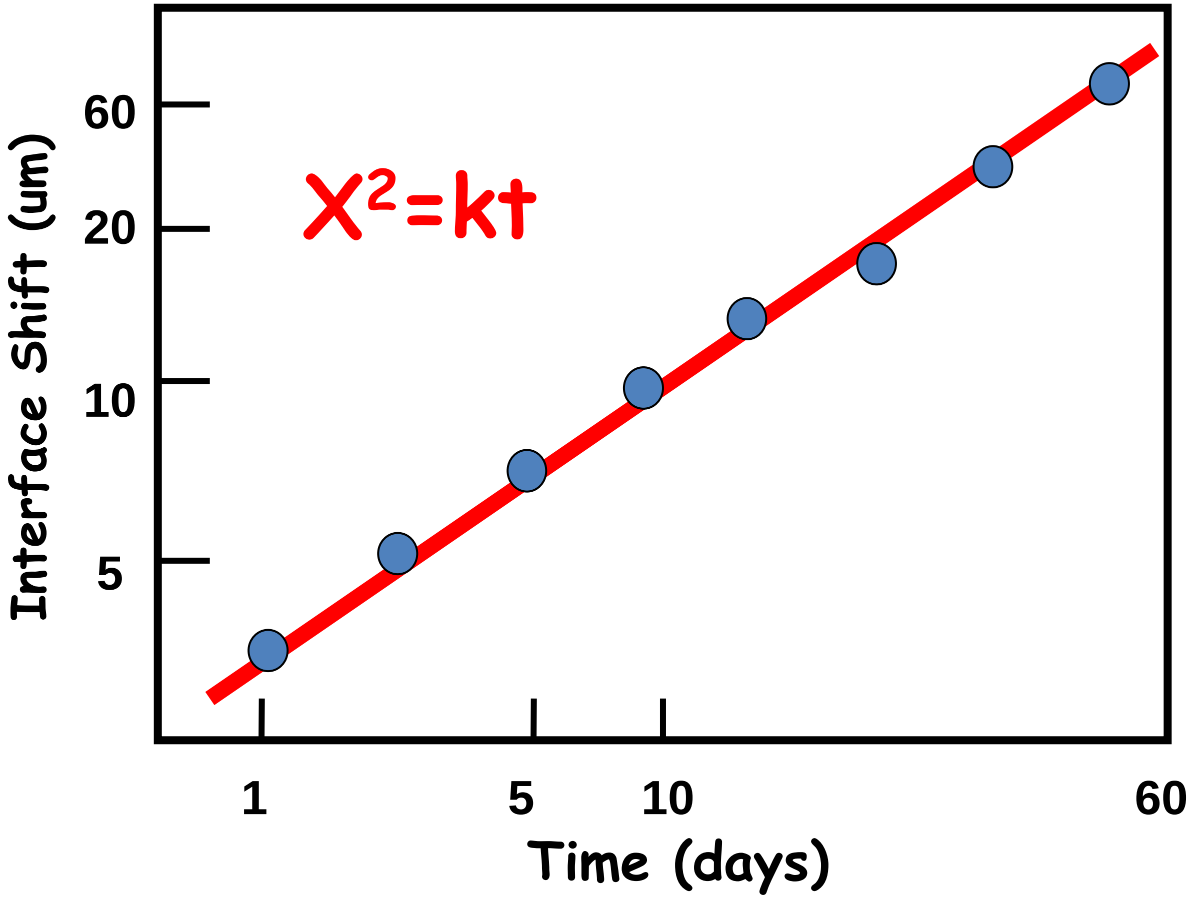




Kirkendall experiment



Kirkendall Effect



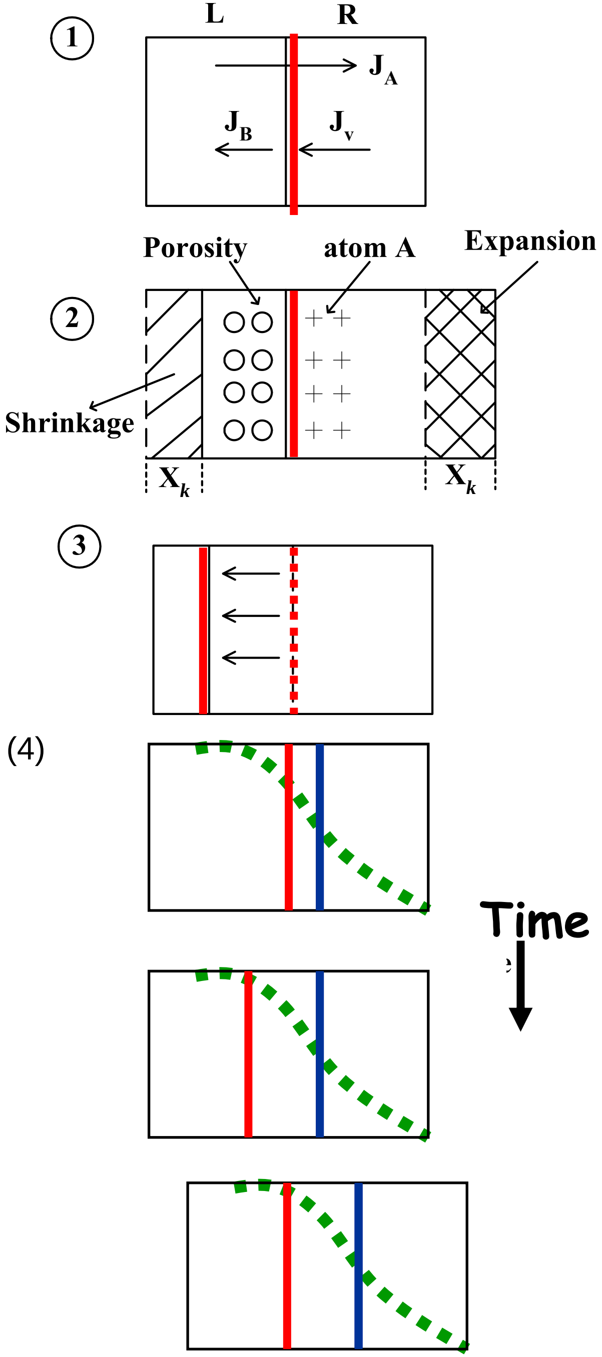
$$\because x_{\text{marker}} = \eta\sqrt{t}$$

$$v = \frac{dx_{\text{marker}}}{dt} = \frac{\eta}{2t^{1/2}} = \frac{x_{\text{marker}}}{2t}$$

In an infinite couple any given composition shifts as $C = f(\eta) = f\left(\frac{x}{2\sqrt{Dt}}\right)$, so the markers stay at the same composition.

Kirkendall-Smigelskas experiment showing inert Mo wires shift versus time (log-log scales used)

Kirkendall or Lattice Shift: atomic mechanism of marker motion



$D_A > D_B$

*$j_A > j_B$. If the plane containing the marker is held in a fixed position, the crystal moves to the right with a distance of X_k

*If the crystal is held in a fixed position (volume is the same), marker will move to the left

* $j_A + j_B + j_v = 0$ (conservation of lattice sites)

$$j_v = -(j_A + j_B)$$

$$|j_A| > |j_B|$$

j_B and j_v are positive, but j_A is negative

$j_B \parallel j_v$

the direction of marker's movement // j_v

*Matano interface moves to - j_v relative to marker, but doesn't move with respect to the end of crystal, i.e., Matano interface doesn't move.

Matano interface is defined where

$$\int_0^{C_0} x\,dC = 0 \rightarrow x = 0$$

$$\because x_{\mathrm{marker}} = \eta\sqrt{t}$$

$$\mathrm{v} = \frac{dx_{\mathrm{marker}}}{dt} = \frac{\eta}{2t^{1/2}} = \frac{x_{\mathrm{marker}}}{2t}$$

$x = 0 \Rightarrow v = 0$ →doesn't move relative to the end of crystal

1. For moving coordinate, e.g., marker or lattice

$$j_A = -D_A^I \frac{\partial C_A}{\partial x}$$

$$\frac{\partial C_A}{\partial t} = \frac{\partial}{\partial x}\left(D_A^I \frac{\partial C_A}{\partial x}\right)$$

D_A^I: Intrinsic diffusivity

:Diffusivity under concentration gradient

or non-equilibrium condition

2. For stationary coordinate, e.g., Matano interface, end of crystal or observer.

$$J_A = -D_A^I \frac{\partial C_A}{\partial x} + vC_A = -\tilde{D}\frac{\partial C_A}{\partial x}$$

$$J_B = -D_B^I \frac{\partial C_B}{\partial x} + vC_B = -\tilde{D}\frac{\partial C_B}{\partial x}$$

v: Velocity of lattice flow or velocity of marker

$\tilde{D}$: Chemical diffusivity or interdiffusion coefficient

detrmined by Boltzmann-Matano analysis

(1) Stationary Coordinate:

The atomic flux including **diffusion** and **lattice flow**

$$J_A = -D_A^I \frac{\partial C_A}{\partial x} + vC_A = -\tilde{D}\frac{\partial C_A}{\partial x}$$

where v: velocity of lattice flow or marker

$$J_B = -D_B^I \frac{\partial C_B}{\partial x} + vC_B = -\tilde{D}\frac{\partial C_B}{\partial x}$$

$$J(\text{Net flux}) = J_A + J_B = -D_A^I \frac{\partial C_A}{\partial x} + vC_A - D_B^I \frac{\partial C_B}{\partial x} + vC_B$$

$$= -D_A^I \frac{\partial C_A}{\partial x} - D_B^I \frac{\partial C_B}{\partial x} + v(C_A + C_B)$$

$$= -D_A^I \frac{\partial C_A}{\partial x} - D_B^I \frac{\partial C_B}{\partial x} + vC$$

$$\text{since } X_A + X_B = 1 \rightarrow C(X_A + X_B) = C \rightarrow CX_A + CX_B = C \rightarrow C_A + C_B = C$$

where *C* is the total number of atom per unit volume. If we assume that the atomic volume is Ω, we have $C\Omega=1$. As *C* is constant, it implies that

$$\frac{\partial C}{\partial x} = \frac{\partial (C_A + C_B)}{\partial x} = 0 \rightarrow \frac{\partial C_A}{\partial x} = -\frac{\partial C_B}{\partial x} \rightarrow \frac{\partial X_A}{\partial x} = -\frac{\partial X_B}{\partial x}$$

$$\frac{\partial C}{\partial t} = -\frac{\partial J}{\partial x} = \frac{\partial}{\partial x}[D_A^I \frac{\partial C_A}{\partial x} + D_B^I \frac{\partial C_B}{\partial x} - vC]$$

$$\text{since C is constant, } \frac{\partial C}{\partial t} = 0$$

$$D_A^I \frac{\partial C_A}{\partial x} + D_B^I \frac{\partial C_B}{\partial x} - vC = k = \text{constant}$$

To determine the constant *k*, we consider the end of the sample, where no interdiffusion occurs, and the concentrations of C_A and C_B are constant, and their concentration gradients are zero. Thus, there is no lattice flow, so v=0. The constant of *k* is then zero, and the net flux (J) in the stationary coordinate is zero, so $J = J_A + J_B = 0$ and $J_A = -J_B$.

(2) Moving Coordinate :

Only diffusion flux considered

$$j_A = -D_A^I \frac{\partial C_A}{\partial x};\ j_B = -D_B^I \frac{\partial C_B}{\partial x}$$

$$\text{Since } J(\text{Net flux}) = J_A + J_B = -D_A^I \frac{\partial C_A}{\partial x} - D_B^I \frac{\partial C_B}{\partial x} + vC = j_A + j_B + vC = 0$$

$$j_A + j_B = -vC = -j_V$$ where vacancy flux (j_V) is to balance the difference between j_A and j_B.

Lattice flow velocity = Marker velocity (v):

$$v = \frac{1}{C}[D_A^I \frac{\partial C_A}{\partial x} + D_B^I \frac{\partial C_B}{\partial x}] = D_A^I \frac{\partial X_A}{\partial x} + D_B^I \frac{\partial X_B}{\partial x} = (D_B^I - D_A^I)\frac{\partial X_B}{\partial x}$$

$$J_B = j_B + C_B v = -D_B^I \frac{\partial C_B}{\partial x} + C_B (D_B^I - D_A^I)\frac{\partial X_B}{\partial x}$$

$$= -\frac{C_A + C_B}{C} D_B^I \frac{\partial C_B}{\partial x} + \frac{C_B}{C}(D_B^I - D_A^I)\frac{\partial C_B}{\partial x}$$

$$= -\frac{C_A}{C} D_B^I \frac{\partial C_B}{\partial x} - \frac{C_B}{C} D_A^I \frac{\partial C_B}{\partial x}$$

$$= -\frac{1}{C}(C_A D_B^I + C_B D_A^I)\frac{\partial C_B}{\partial x}$$

$$= -(X_A D_B^I + X_B D_A^I)\frac{\partial C_B}{\partial x} = -\widetilde{D}\frac{\partial C_B}{\partial x}$$

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

Since $J_A = -J_B$ and $\frac{\partial C_A}{\partial x} = -\frac{\partial C_B}{\partial x} \rightarrow J_A = -\widetilde{D}\frac{\partial C_A}{\partial x}$

$$J_A = j_A + C_A v$$

In Darken's analysis, the vacancy is at equilibrium due to lattice shift. Since there is no vacancy super-saturation, no void is formed. However, if the vacancy flux can not be absorbed by lattice shift, it will lead to vacancy super-saturation and the nucleation of voids.

Kirkendall (Frenkel) voiding without lattice shift

$$J(\text{Net flux}) = J_A + J_B = -D^I_A \frac{\partial C_A}{\partial x} - D^I_B \frac{\partial C_B}{\partial x} + vC$$

$$= j_A + j_B + vC = 0$$

$$j_A + j_B = -vC = -j_V$$

$$j_V = vC = C(D^I_B - D^I_A)\frac{\partial X_B}{\partial x} = (D^I_B - D^I_A)\frac{\partial C_B}{\partial x}$$

Number of vacancy transported = $j_v At$

where A is cross section area and t is time. If the atomic volume of a single vacancy is Ω,

Total volume of vacancy transported = $j_v At\Omega$.

Total volume of vacancy transported ($V_{vacancy}$)= $j_V A t \Omega$

$$j_V = vC = \frac{x}{2t} C = \frac{\eta\sqrt{t}}{2t} C = \frac{C\eta}{\sqrt{t}}$$

$$V_{vacancy} = A\Omega \int_0^t j_V \, dt = A\Omega C \int_0^t \frac{\eta}{\sqrt{t}} dt = A\Omega C\eta\sqrt{t} = A\frac{1}{C}Cx = xA$$

where

x : marker shift distance

A: the cross section area of diffusion

Ω: atomic volume of a single vacancy

C: total concentration $=C_A+C_B=1/\Omega$

v: velocity of marker

t: time

$$j_A + j_B + j_v = 0$$

$$j_v = -(j_A + j_B) = \mathrm{C}\mathrm{v}$$

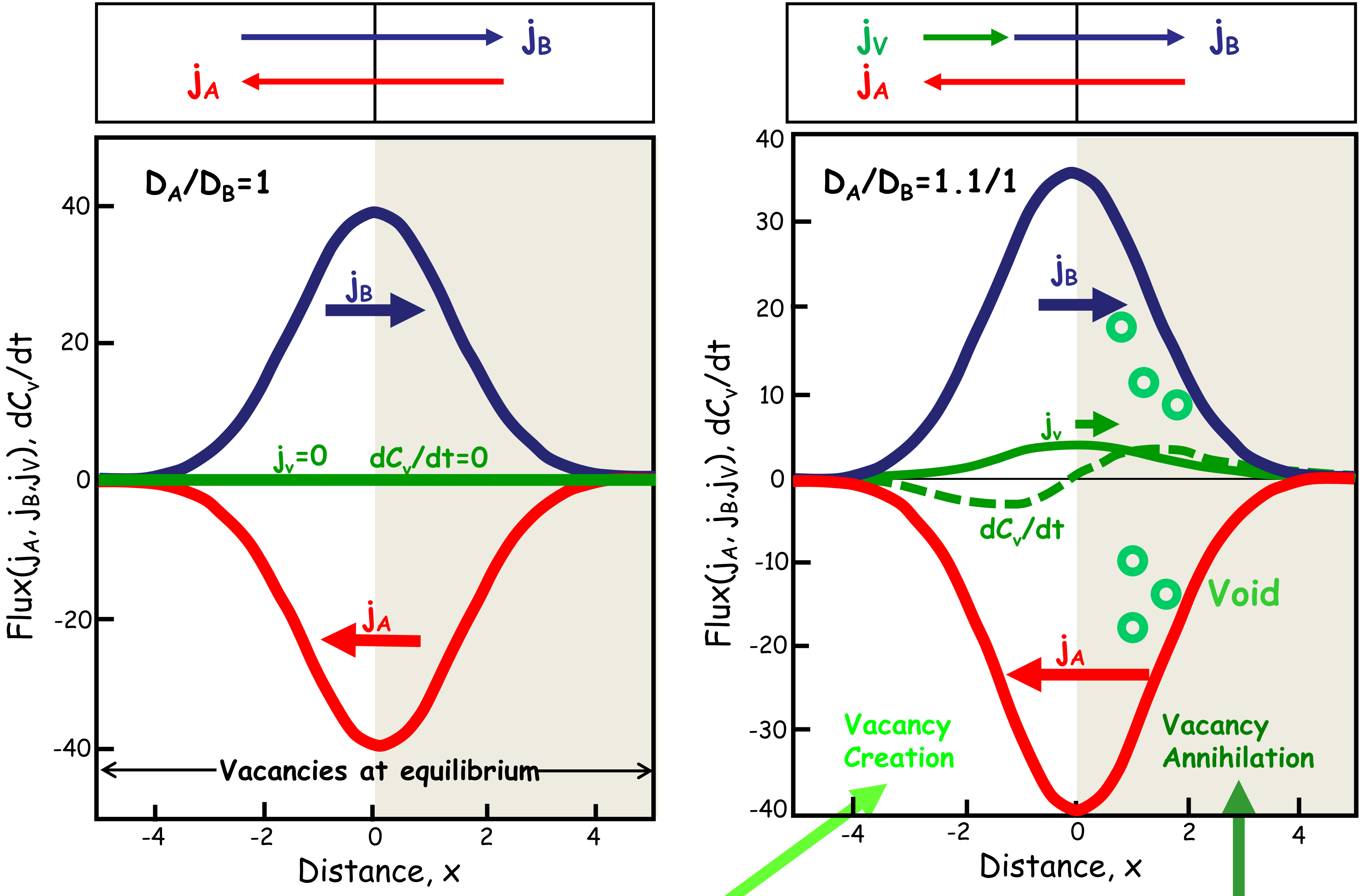
$$j_v = D^I_A \frac{\partial C_A}{\partial x} + D^I_B \frac{\partial C_B}{\partial x}$$

$$= (D^I_A - D^I_B)\frac{\partial C_A}{\partial x} = \mathrm{C}\mathrm{v}$$

$$\mathrm{v} = \frac{1}{C}(D^I_A - D^I_B)\frac{\partial C_A}{\partial x} = (D^I_A - D^I_B)\frac{\partial X_A}{\partial x}$$

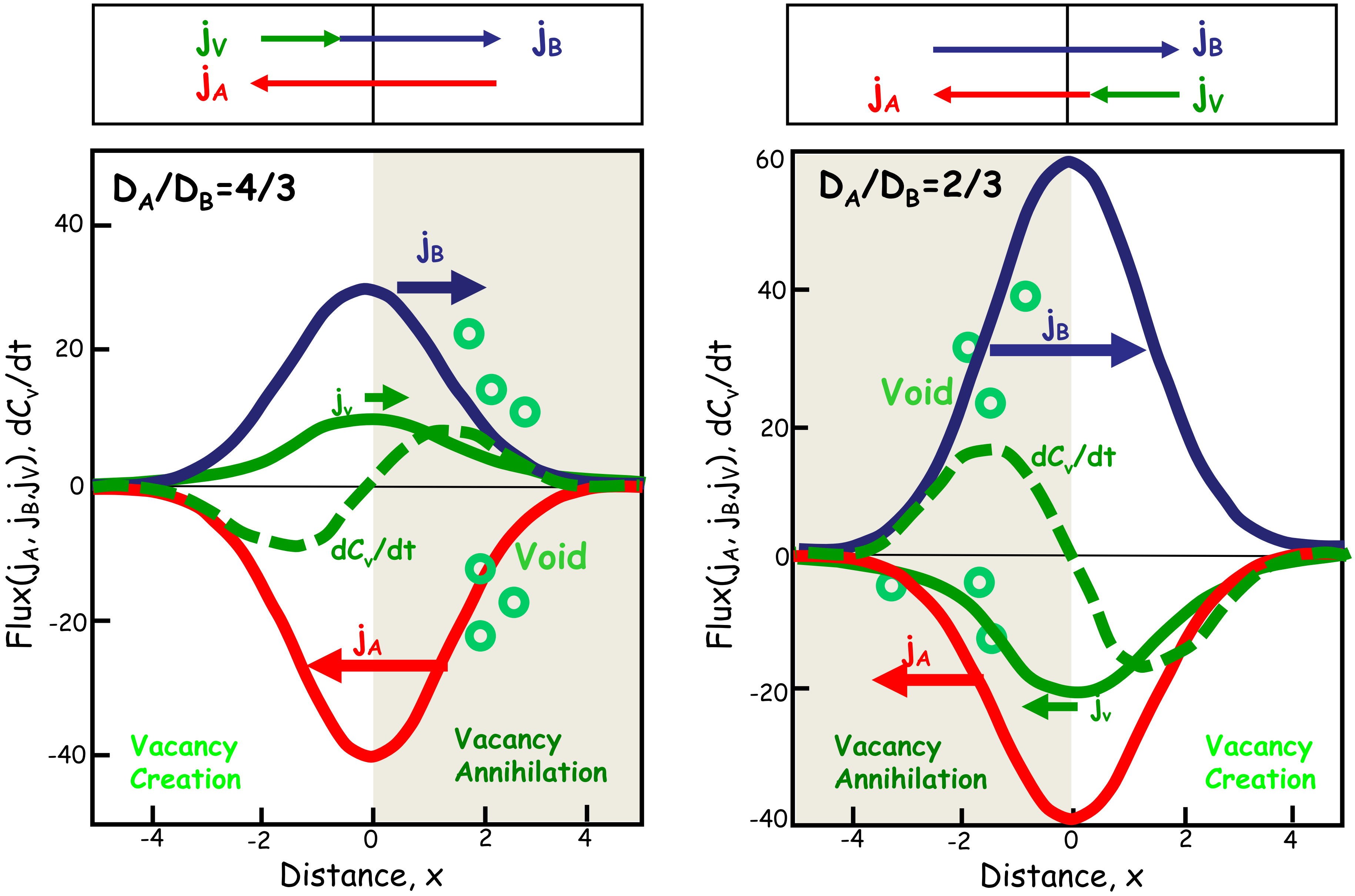
v: velocity of lattice flow or marker

Fick's 2nd Law: $-\frac{\partial \mathrm{j}_\mathrm{v}}{\partial x} = \frac{\partial C_\mathrm{v}}{\partial t}$



Vacancies need to be created to restore equilibrium

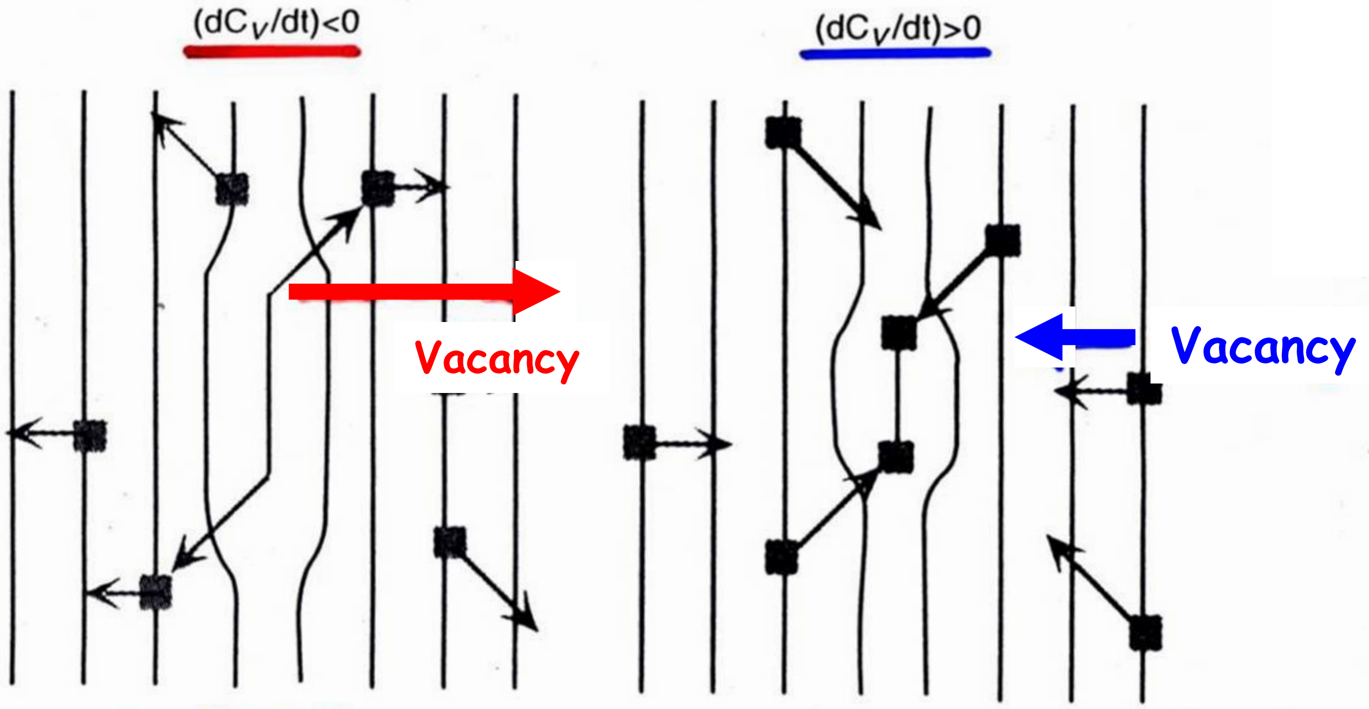
Vacancies need to be destroyed to maintain equilibrium



j_V
j_B
j_A
$D_A/D_B=4/3$
40
20
0
-20
-40
-4
-2
0
2
4
Flux(j_A, j_B,j_V), dC_v/dt
j_B
j_v
dC_v/dt
Void
j_A
Vacancy Creation
Vacancy Annihilation
Distance, x
j_B
j_A
j_V
$D_A/D_B=2/3$
60
40
20
0
-20
-40
-4
-2
0
2
4
Flux(j_A, j_B,j_V), dC_v/dt
j_B
Void
dC_v/dt
j_A
j_v
Vacancy Annihilation
Vacancy Creation
Distance, x

Vacancy Creation

Vacancy Annihilation



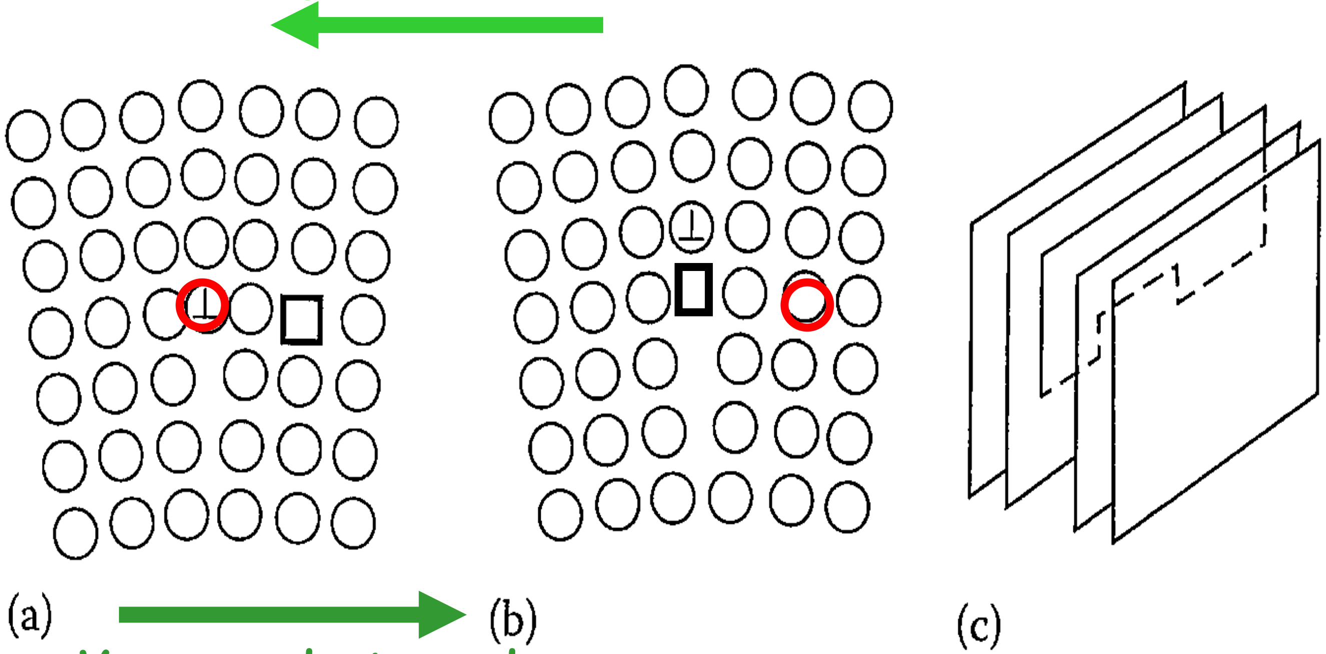
Create Lattice Plane

Remove Lattice Plane

■ Vacancy

More vacancies are created due to unequal diffusivities, which yields a non-equilibrium system. Therefore, excessive vacancies need to be destroyed by removing lattice plane to bring the system back to equilibrium.

Vacancy created
(negative climb)



Vacancy destroyed
(positive climb)

FIGURE 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.

1. For moving coordinate, e.g., marker or the lattice

$$j_A = -D_A^I \frac{\partial C_A}{\partial x}$$

$$\frac{\partial C_A}{\partial t} = -\frac{\partial j_A}{\partial x} = \frac{\partial}{\partial x}\left(D_A^I \frac{\partial C_A}{\partial x}\right)$$

D_A^I: Intrinsic diffusivity

:Diffusivity under concentration gradient

or non-equilibrium condition

2. For stationary coordinate, e.g., Matano interface, end of crystal or observer.

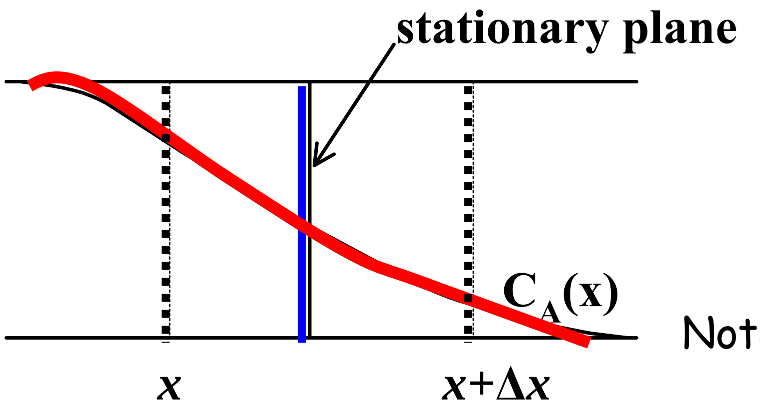
$$J_A = -D_A^I \frac{\partial C_A}{\partial x} + vC_A = -\tilde{D}\frac{\partial C_A}{\partial x}$$

$$J_B = -D_B^I \frac{\partial C_B}{\partial x} + vC_B = -\tilde{D}\frac{\partial C_B}{\partial x}$$

v: Velocity of lattice flow or velocity of marker

$\tilde{D}$: Chemical diffusivity or interdiffusion coefficient

detrmined by Boltzmann-Matano analysis



$$\Delta x\left(\frac{\partial C_A}{\partial t}\right) = (J_A)_x - (J_A)_{x+\Delta x}$$

$$\Delta x \to 0$$

$$\frac{\partial C_A}{\partial t} = -\frac{\partial J_A}{\partial x}$$

Note: J_A: flux relative to the stationary coordinate
j_A: flux relative to the moving coordinate

$$\frac{\partial C_A}{\partial t} = \frac{\partial}{\partial x}\left(D_A^I \frac{\partial C_A}{\partial x} - vC_A\right) \qquad (*)$$

$$\frac{\partial C_B}{\partial t} = \frac{\partial}{\partial x}\left(D_B^I \frac{\partial C_B}{\partial x} - vC_B\right)$$

If the vacancy concentration within the unit volume is constant (constant volume)

$$\frac{\partial C}{\partial t} = \frac{\partial C_A}{\partial t} + \frac{\partial C_B}{\partial t} = 0$$

$$\therefore \frac{\partial}{\partial x}\left(D_A^I \frac{\partial C_A}{\partial x} - vC_A\right) + \frac{\partial}{\partial x}\left(D_B^I \frac{\partial C_B}{\partial x} - vC_B\right) = 0$$

$$v = \frac{1}{C_A + C_B}\left(D_A^I \frac{\partial C_A}{\partial x} + D_B^I \frac{\partial C_B}{\partial x}\right)$$

$$= \frac{1}{C}\left(D_A^I - D_B^I\right)\left(\frac{\partial C_A}{\partial x}\right) \qquad (**)$$

$$\because C = C_A + C_B = const., \quad \frac{\partial C_A}{\partial x} = -\frac{\partial C_B}{\partial x}$$

Eq.(**)→Eq.(*)

$$\frac{\partial C_A}{\partial t} = \frac{\partial}{\partial x}\left[D_A^I \frac{\partial C_A}{\partial x} - \frac{C_A}{C}(D_A^I - D_B^I)\frac{\partial C_A}{\partial x}\right]$$

$$= \frac{\partial}{\partial x}\left[\left(\left(1-\frac{C_A}{C}\right)D_A^I + \frac{C_A}{C}D_B^I\right)\frac{\partial C_A}{\partial x}\right] = \frac{\partial}{\partial x}\left[(X_B D_A^I + X_A D_B^I)\frac{\partial C_A}{\partial x}\right]$$

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

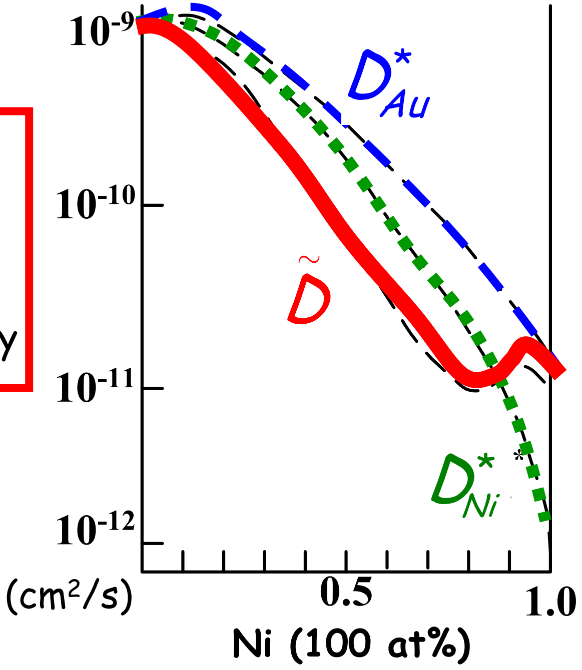
$$J_A = -\tilde{D}\frac{\partial C_A}{\partial x}$$

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

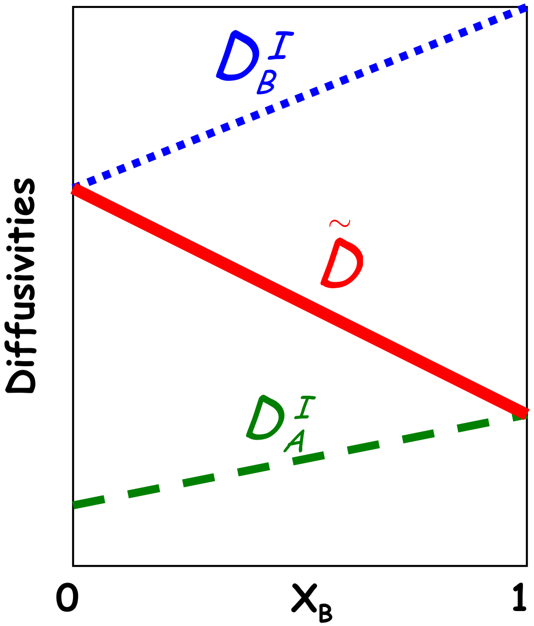
Darken's equation

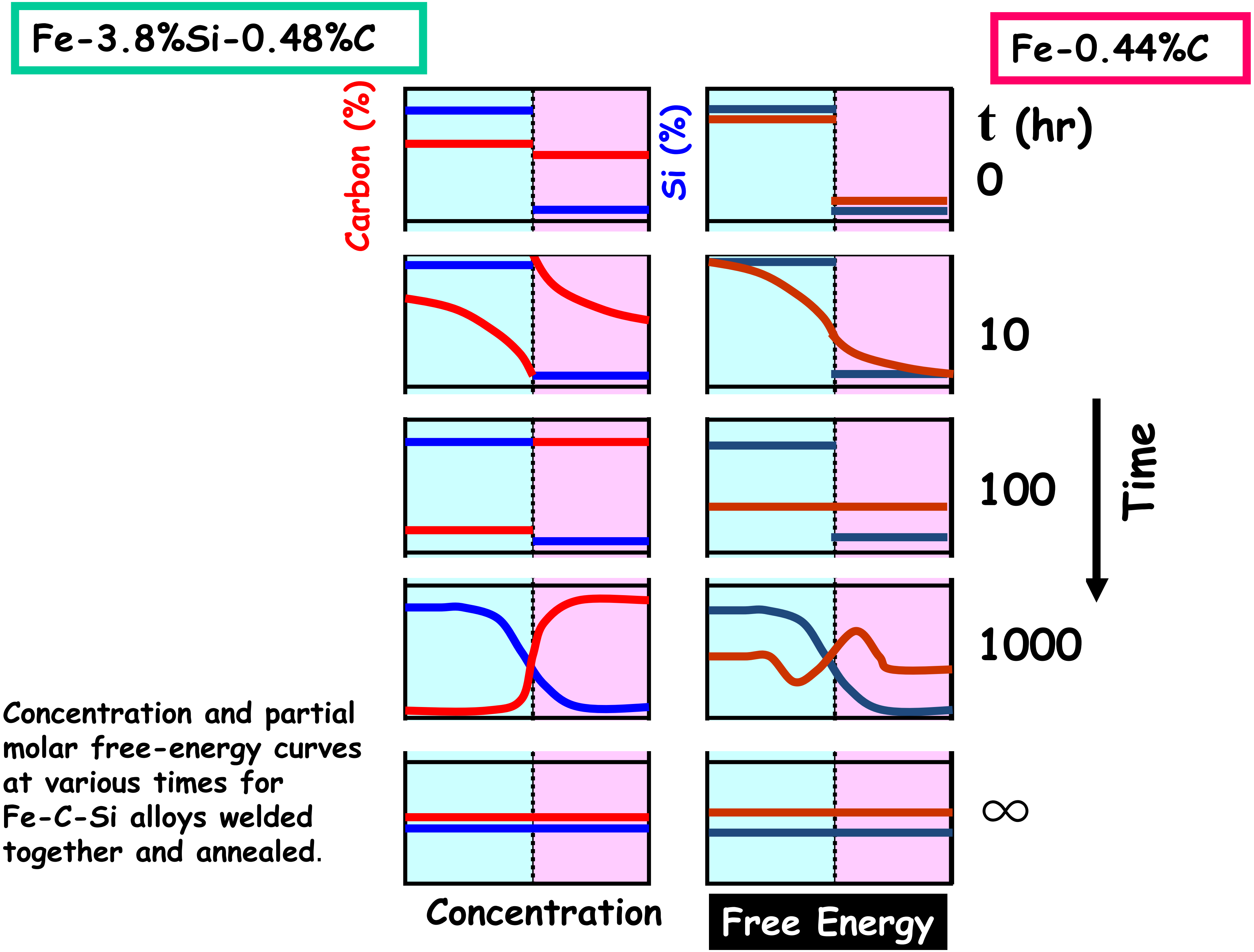
$$\tilde{D} \neq X_{Ni} D^*_{Au} + X_{Au} D^*_{Ni}$$

D^*_{Au}, D^*_{Ni} : Tracer diffusivity

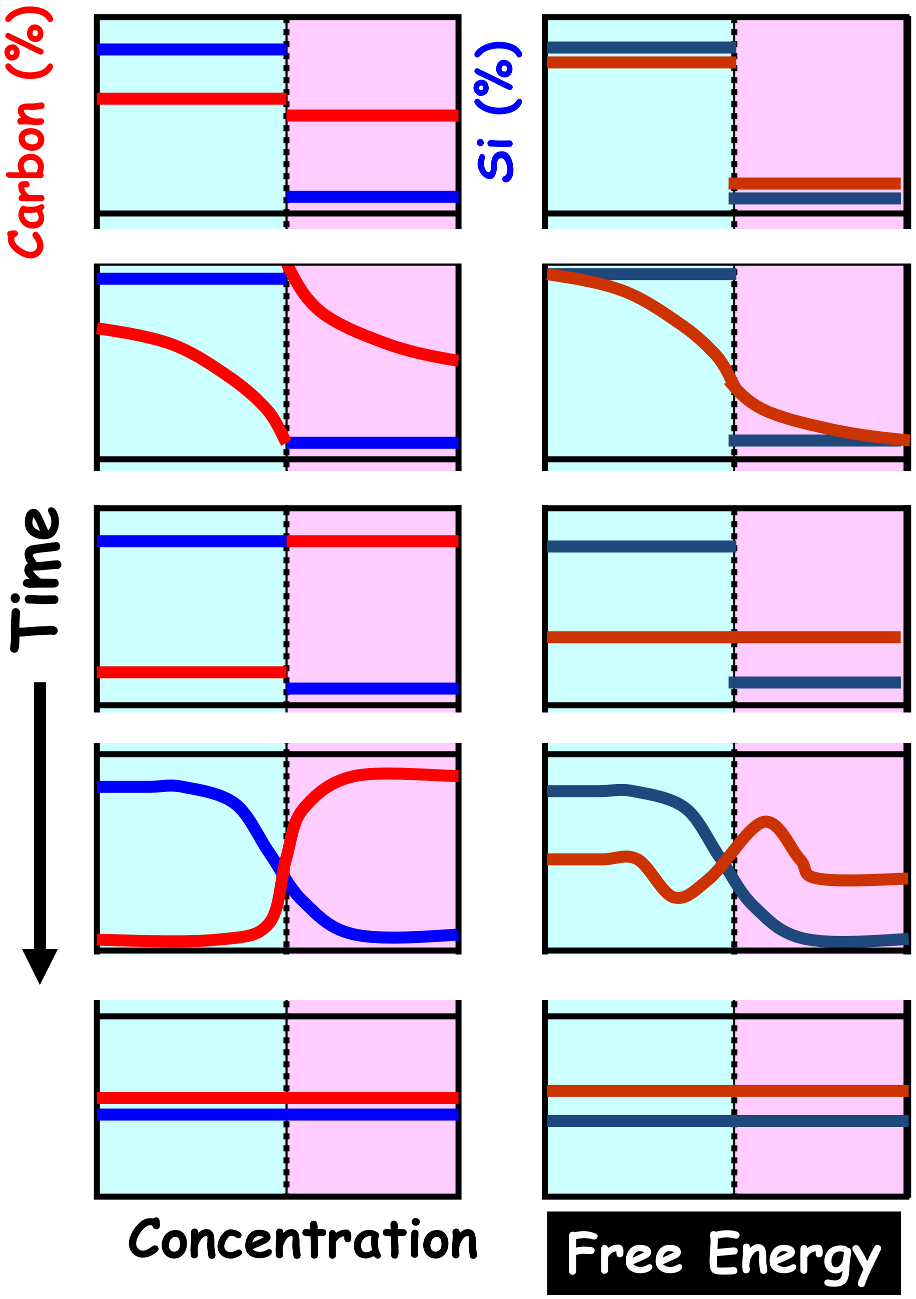


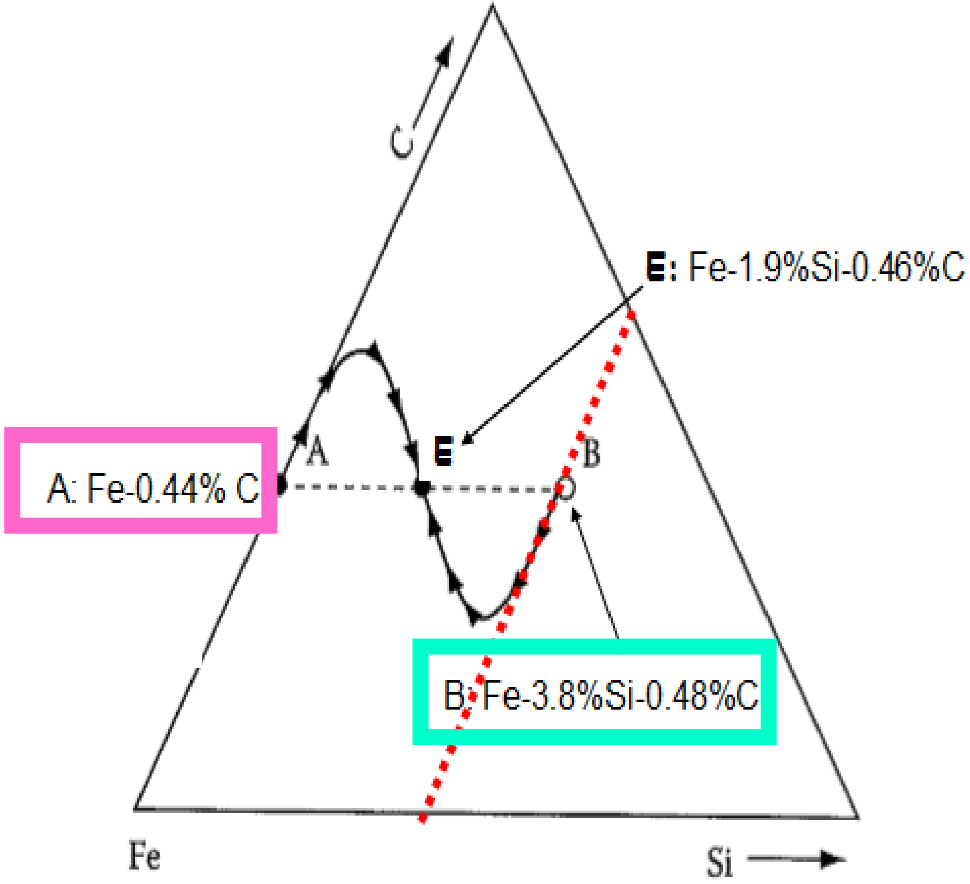
$$\tilde{D} = X_B D_A^I + X_A D_B^I$$





Concentration and partial molar free-energy curves at various times for Fe-C-Si alloys welded together and annealed.





The change in composition of two points A and B on opposite sides of diffusion Couple; E is the final equilibrium concentration of the whole bar.

Force acting on an atom of species A

$$F = -\frac{\partial \mu}{\partial x} \qquad \mu = \frac{G}{N}$$

$$F = -\frac{1}{N_0}\left(\frac{\partial \overline{G_A}}{\partial x}\right)$$

$$\mathbf{v_A = B_A F = -\frac{B_A}{N_0}\left(\frac{\partial \overline{G_A}}{\partial x}\right)}$$

B_A: mobility of species A under a force of F

$$J = C_A \cdot \mathrm{v}_A = C_A \cdot B_A \cdot F = -C_A \frac{B_A}{N_0}\left(\frac{\partial \overline{G_A}}{\partial x}\right)$$

$$= -\frac{B_A}{N_0} RT\left(\frac{\partial \ln a_A}{\partial x}\right) C_A \equiv -D_A^I \frac{\partial C_A}{\partial x}$$

$$\because \overline{G_A} = G_A^\circ + RT \ln a_A$$

$$\frac{\partial \overline{G_A}}{\partial x} = RT \frac{\partial \ln a_A}{\partial x}$$

$$\frac{B_A}{N_0} RT \frac{\partial \ln a_A}{\partial x} = D_A^I \frac{\partial \ln C_A}{\partial x}$$

$$\therefore \mathbf{D}_A^I = \mathbf{B_A \cdot k_B \cdot T \frac{\partial \ln a_A}{\partial \ln C_A}}$$

$$k_B = \frac{R}{N_0} = 1.38 \times 10^{-23}\ J \cdot \deg^{-1}$$

$$\partial \ln a_A = \partial \ln X_A \cdot \gamma_A; \quad \partial \ln C_A = \partial \ln X_A \cdot C = \partial \ln X_A$$

$$D_A^I = B_A \cdot k_B T \frac{\partial \ln X_A \gamma_A}{\partial \ln X_A}$$

$$= B_A \cdot k_B T \left(1 + \frac{\partial \ln \gamma_A}{\partial \ln X_A}\right)$$

: Intrinsic diffusivity of species A under the influence of its own free energy gradient

Ideal Solution: $\gamma = 1$

$$D_A^I = B_A \cdot k_B T$$ →Nernst-Einstein Equation

$$X_1 d\overline{G_1} + X_2 d\overline{G_2} + \ldots + X_n d\overline{G_n} = 0 \longrightarrow$$ Gibbs-Duhem Equation

$$\frac{\partial \ln a_B}{\partial \ln X_B} = \frac{\partial \ln a_A}{\partial \ln X_A}$$

$$\therefore \tilde{D} = (X_A B_B k_B T + X_B B_A k_B T)\left(\frac{\partial \ln a_A}{\partial \ln X_A}\right)$$

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

if $B_A = B_A^*$ and $B_B = B_B^*$ (Intrinsic mobility = Tracer mobility)

$$\tilde{D} = (X_A D_B^* + X_B D_A^*)\left(\frac{\partial \ln a_A}{\partial \ln X_A}\right)$$

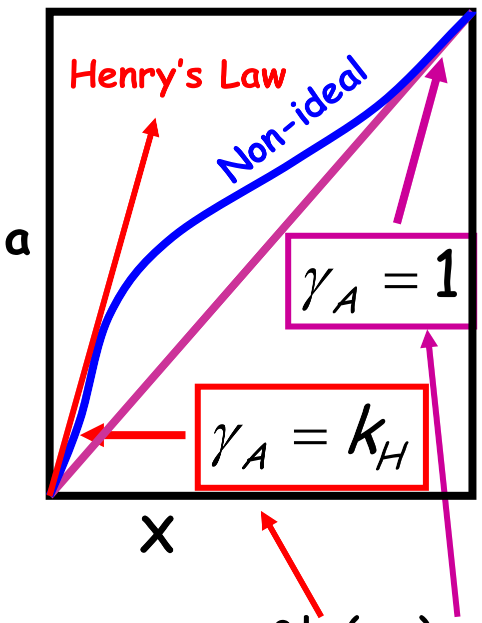
$$= (X_A D_B^* + X_B D_A^*)\left(1 + \frac{\partial \ln \gamma_A}{\partial \ln X_A}\right)$$

$$\tilde{D} = (X_A D_B^* + X_B D_A^*)\left[1 + \frac{\partial \ln(\gamma_A)}{\partial \ln(X_A)}\right]$$

$X_A D_B^* + X_B D_A^*$: transport or kinetic factor

$\dfrac{\partial \ln \gamma_A}{\partial \ln X_A}$: thermodynamic factor

Activity vs. Molar Fraction



$$\frac{\partial \ln(\gamma_A)}{\partial \ln(X_A)} = 0$$

I. For the case of an **ideal solution** (Raoultian) or an ideal dilute (Henryan) solution, γ_i is constant (=1 or K_H), and the thermodynamic factor becomes zero. Therefore, for an ideal solution

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

For the case of very **dilute solution** with $X_B \to 0$ and $X_A \to 1$

$$\tilde{D} = D_B^*$$

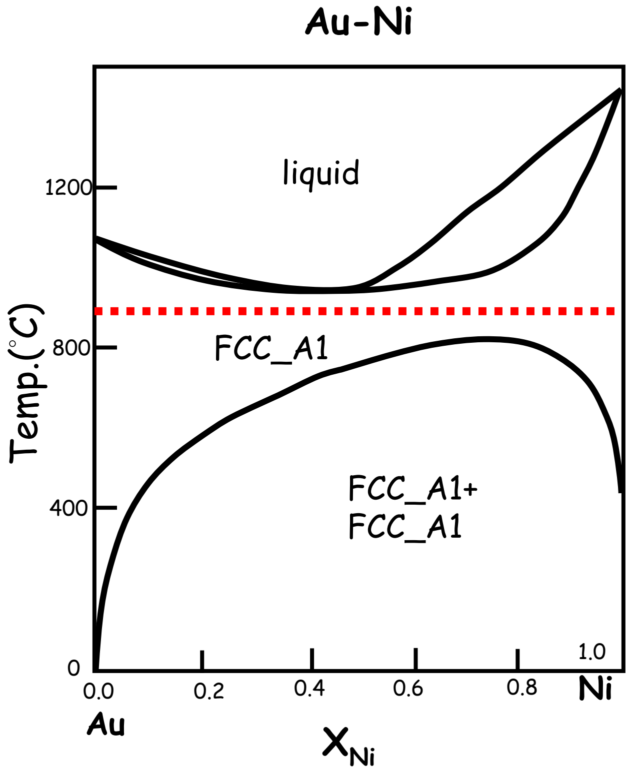
→chemical diffusivity = tracer diffusivity of solute

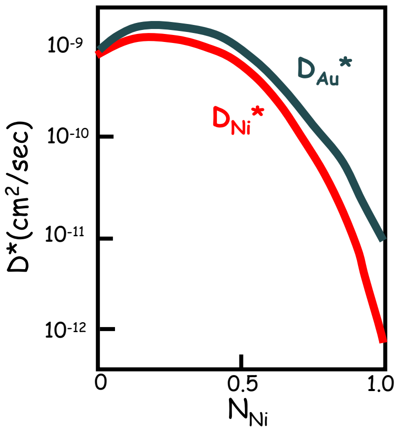
II. For the case of **Regular Solution**

$$\frac{\partial \ln \gamma_A}{\partial \ln X_A} = (-)\frac{2\Omega X_A X_B}{RT}$$

$$1 + \frac{\partial \ln \gamma_A}{\partial \ln X_A} = 1 - \frac{2\Omega X_A X_B}{RT}$$

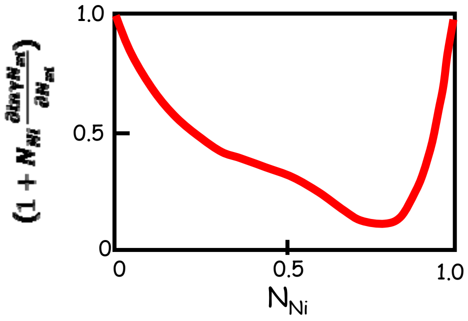
($\Omega < 0 \rightarrow$ A+B > A-A + B-B → D increasing)





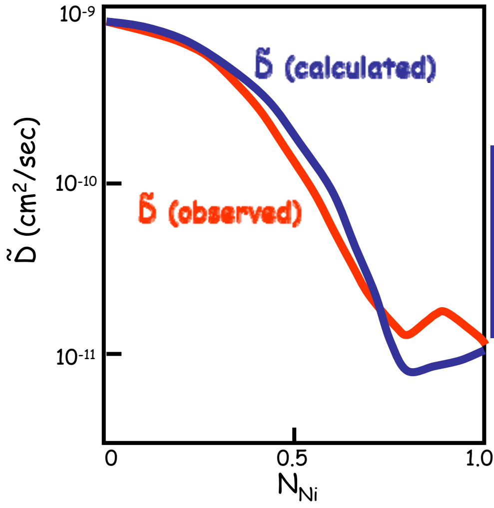
$$\boxed{(X_{Au}D_{Ni}^* + X_{Ni}D_{Au}^*)}$$

x

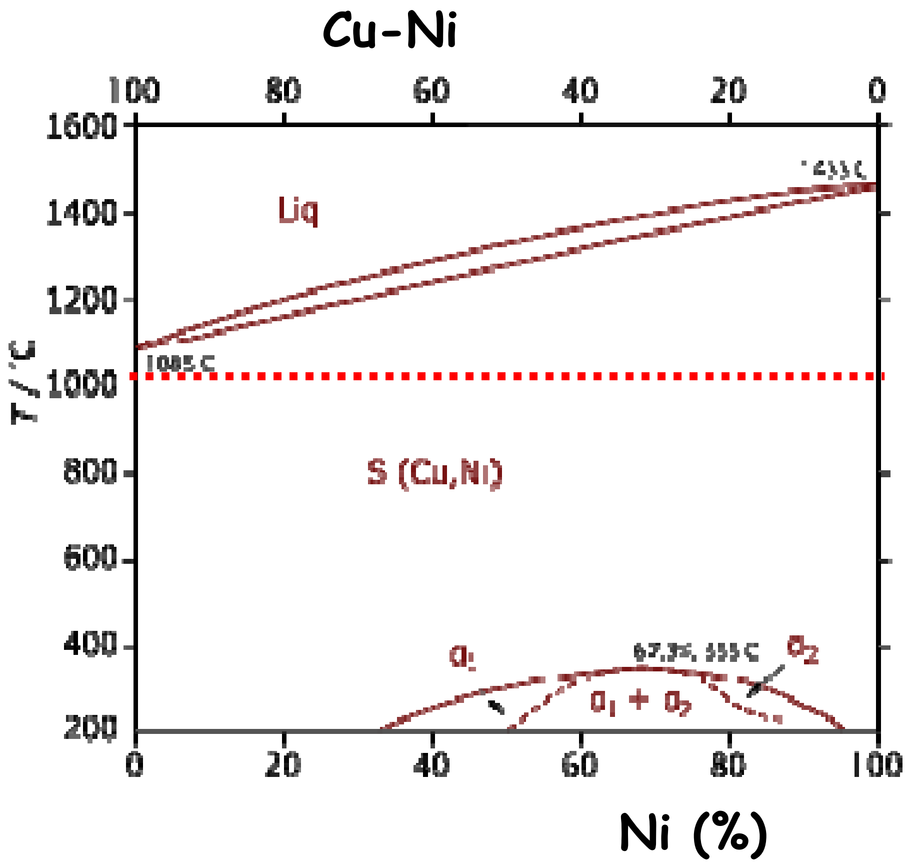


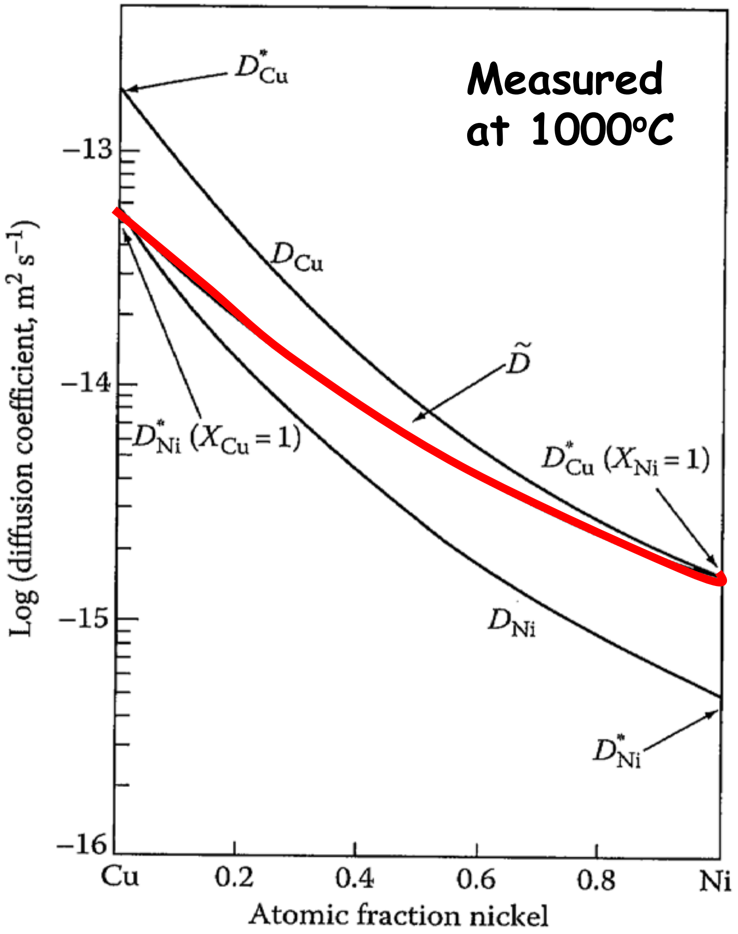
$$\boxed{(1 + \frac{\partial \ln(\gamma_{Ni})}{\partial \ln(X_{Ni})})}$$

=



$$\boxed{\tilde{D} = (X_{Au}D_{Ni}^* + X_{Ni}D_{Au}^*)(1 + \frac{\partial \ln(\gamma_{Ni})}{\partial \ln(X_{Ni})})}$$


Cu-Ni
100
80
60
40
20
0
1600
1400
1200
1000
800
600
400
200
T / °C
1455 C
Liq
1085 C
S (Cu,Ni)
α_1
67.3%, 355 C
α_2
$\alpha_1 + \alpha_2$
0
20
40
60
80
100
Ni (%)


Measured at 1000°C
D^*_{Cu}
D_{Cu}
$\tilde{D}$
D^*_{Ni} ($X_{Cu}=1$)
D^*_{Cu} ($X_{Ni}=1$)
D_{Ni}
D^*_{Ni}
−13
−14
−15
−16
Log (diffusion coefficient, $m^2 s^{-1}$)
Cu
0.2
0.4
0.6
0.8
Ni
Atomic fraction nickel

Regular Solution

$$\Delta H_m \neq 0 \quad \& \quad \Delta S_m^{exc} = 0$$

$$(\text{Ideal Solution } \Delta H_m = 0 \quad \& \quad \Delta S_m^{exc} = 0)$$

$$\Delta H_m = \Omega X_A X_B \text{ where } \Omega = N_o Z \varepsilon \text{ and}$$

$$\varepsilon = \frac{1}{2}(\varepsilon_{AA} + \varepsilon_{BB}) - \varepsilon_{AB} \qquad \text{if } \varepsilon_{XX} > 0$$

$$\Delta S_m = -R(X_A \ln X_A + X_B \ln X_B)$$

$$\Delta G_m = \Delta H_m - T\Delta S_m$$

$$= \Omega X_A X_B + RT(X_A \ln X_A + X_B \ln X_B)$$

Regular Solution

$\Delta H_m = P_{AB}(1/2(\varepsilon_{AA} + \varepsilon_{BB}) - \varepsilon_{AB}) = P_{AB}\,\varepsilon$

$P_{AB} = ((1/2)ZN_o)(2X_AX_B)$

$= ZN_oX_AX_B$: Probability to form A-B bonds

$\Delta H_m = ZN_oX_AX_B\,\varepsilon = ZN_o\,\varepsilon\,X_AX_B = \Omega X_AX_B$

$\Omega = ZN_o\,\varepsilon$

$\Omega < 0 \rightarrow$ attraction between unlike ions

$\rightarrow 1/2(\varepsilon_{AA} + \varepsilon_{BB}) < \varepsilon_{AB}$

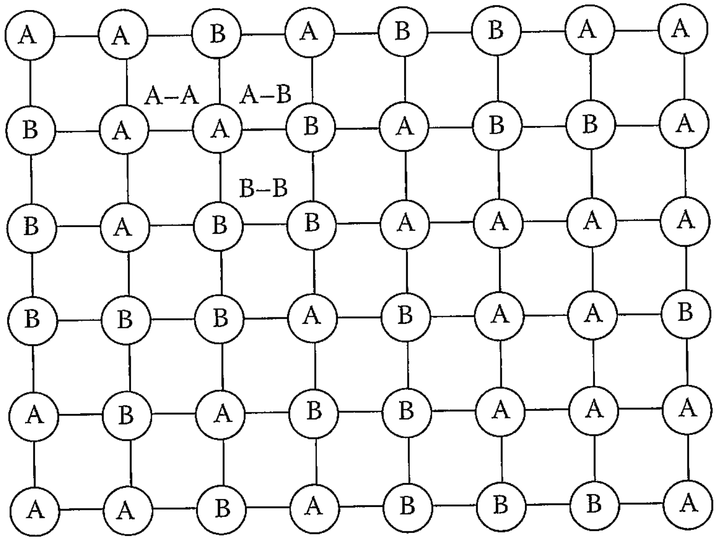
$\Omega > 0 \rightarrow$ repulsion between unlike ions

$\rightarrow 1/2(\varepsilon_{AA} + \varepsilon_{BB}) > \varepsilon_{AB}$

For Ideal Solution

$1/2(\varepsilon_{AA} + \varepsilon_{BB}) = \varepsilon_{AB}$

$\varepsilon = 0 \rightarrow \Omega = 0 \rightarrow \Delta H_m = 0$



$$N_o = N_A + N_B$$

$$X_A = \frac{N_A}{N_o}, X_B = \frac{N_B}{N_o}$$

Probability to have A-B: $X_A X_B$

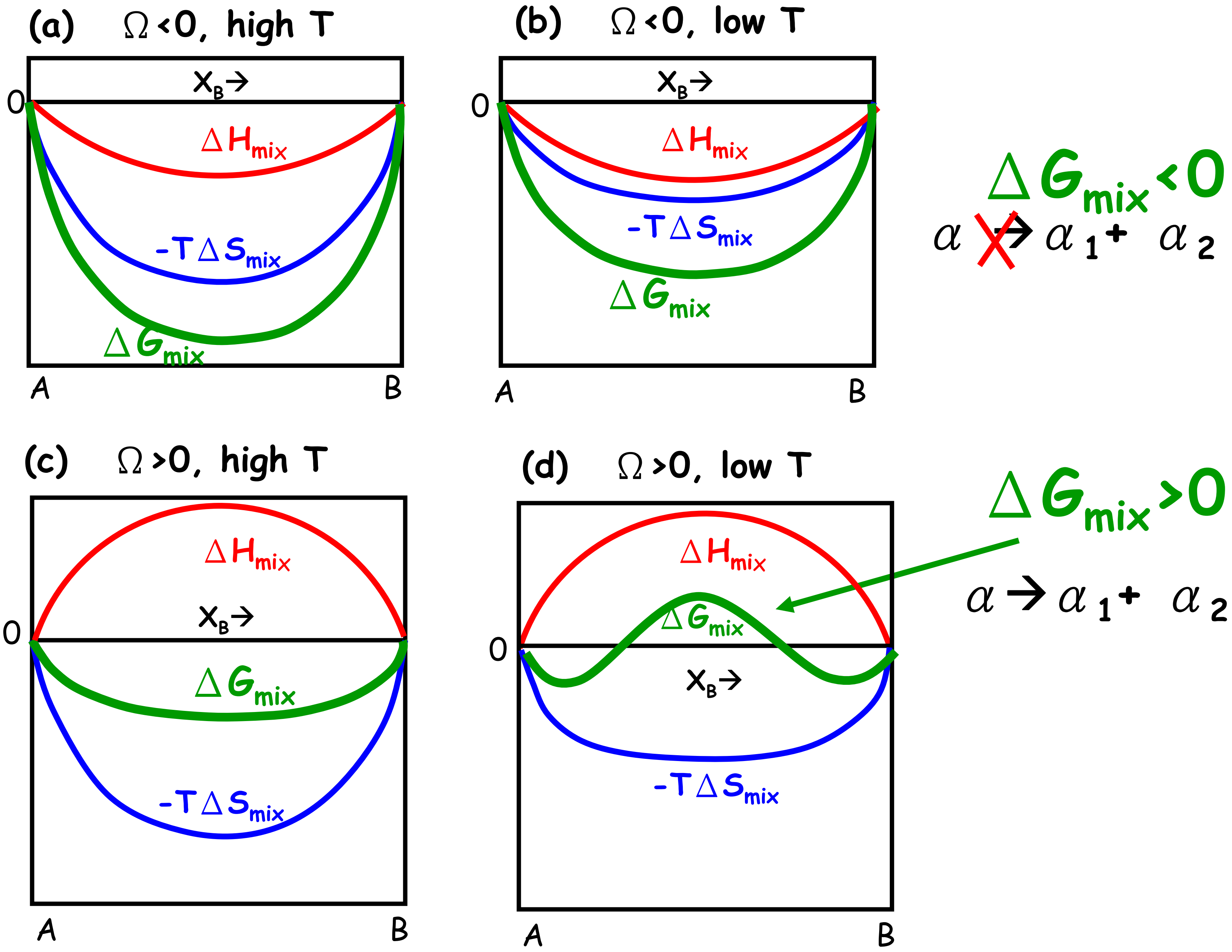
Probability to have B-A: $X_B X_A$

Probability for two sites with different atoms of A-B and B-A:

$$X_A X_B + X_B X_A = 2X_A X_B$$

Total number of pairs in the crystal: $\frac{1}{2} Z N_o$

P$_{AB}$(Total probability to form A-B pairs): $\frac{1}{2} Z N_o 2 X_A X_B = Z N_o X_A X_B$



(a) $\Omega < 0$, high T

(b) $\Omega < 0$, low T

(c) $\Omega > 0$, high T

(d) $\Omega > 0$, low T

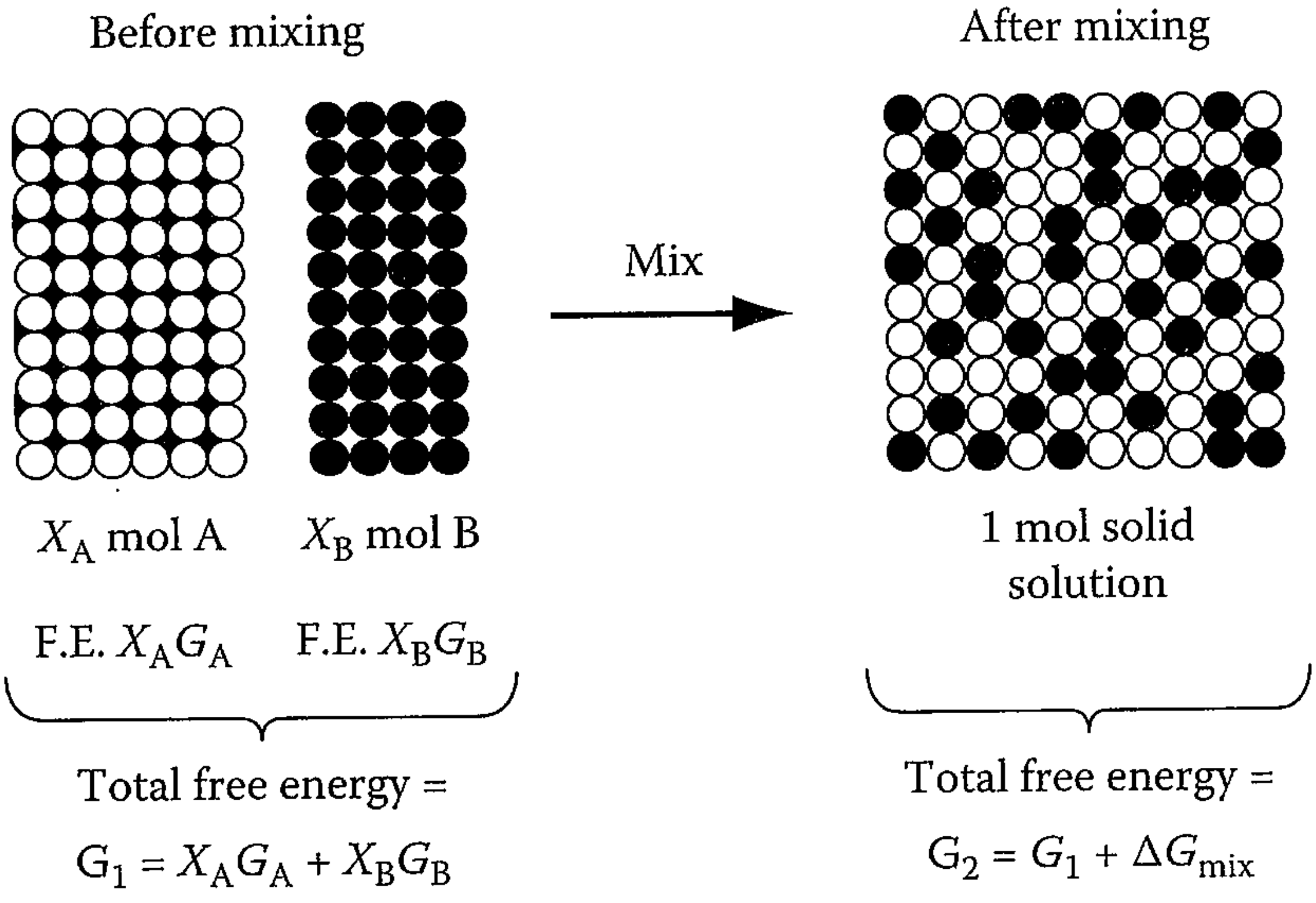
$\Delta G_{mix} < 0$

$\alpha \not\rightarrow \alpha_1 + \alpha_2$

$\Delta G_{mix} > 0$

$\alpha \rightarrow \alpha_1 + \alpha_2$

Gibbs Free Energy of Binary Solutions



Before mixing

After mixing

Mix

X_A mol A

X_B mol B

F.E. $X_A G_A$

F.E. $X_B G_B$

Total free energy =

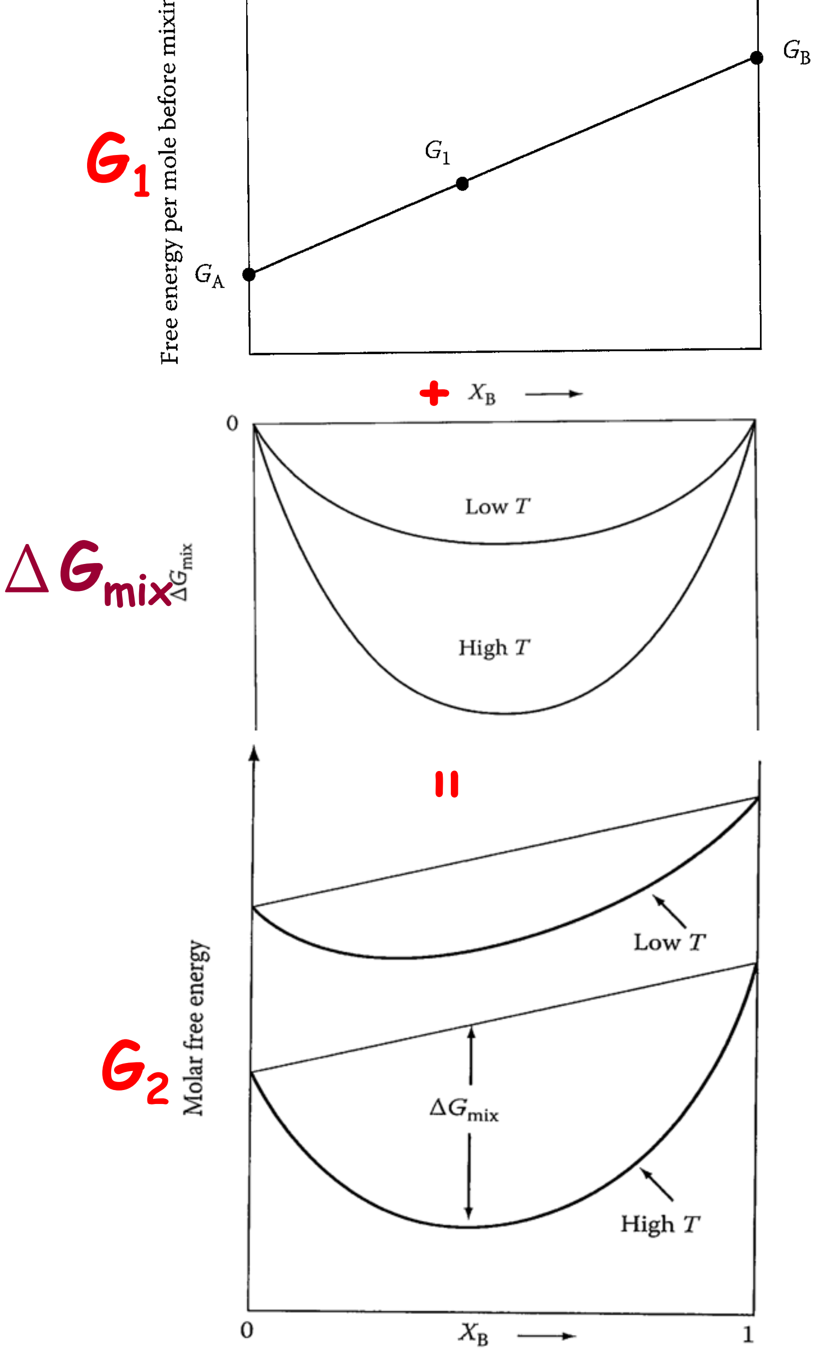
$G_1 = X_A G_A + X_B G_B$

1 mol solid solution

Total free energy =

$G_2 = G_1 + \Delta G_{mix}$

Ideal Solution



$$G_1=X_AG_A+X_BG_B$$

$$G_1=H_1-TS_1$$
$$G_2=H_2-TS_2$$
$$\Delta G_{mix}=G_2-G_1$$
$$=\Delta H_{mix}-T\Delta S_{mix}$$
$$\Delta H_{mix}=H_2-H_1$$
$$\Delta S_{mix}=S_2-S_1$$

Since $\Delta H_{mix}=0$ (ideal solution)

ΔG_{mix} (ideal solution)$= -T\Delta S_{mix}$

$$\Delta S_{mix} = -R(X_A\ln X_A+X_B\ln X_B)$$

$$G_2 =G_1+\Delta G_{mix}$$
$$=X_AG_A+X_BG_B-T\Delta S_{mix}$$
$$=X_A(G_A+RT\ln X_A)+$$
$$X_B(G_B+RT\ln X_B)$$

Ideal Solution

$$dG' = \mu_A dn_A \text{ (T,P, n}_B\text{:constant) (G':total free energy)}$$

$$\mu_A = \left(\frac{\partial G'}{\partial n_A}\right)_{\text{T,P, n}_B}$$

$$dG' = \mu_A dn_A + \mu_B dn_B$$

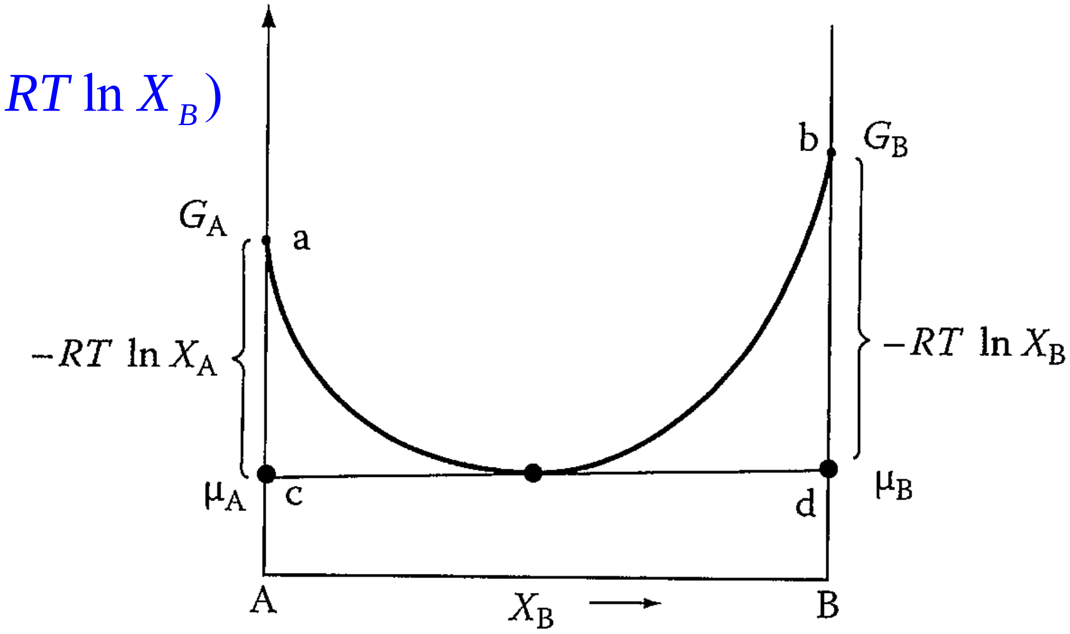
$$G' = \mu_A n_A + \mu_B n_B$$

$$G_2 = \frac{G'}{n_A + n_B} = \frac{\mu_A n_A + \mu_B n_B}{n_A + n_B} = \mu_A X_A + \mu_B X_B \text{ (molar free energy)}$$

$$G_2 = X_A(G_A + RT\ln X_A) + X_B(G_B + RT\ln X_B)$$

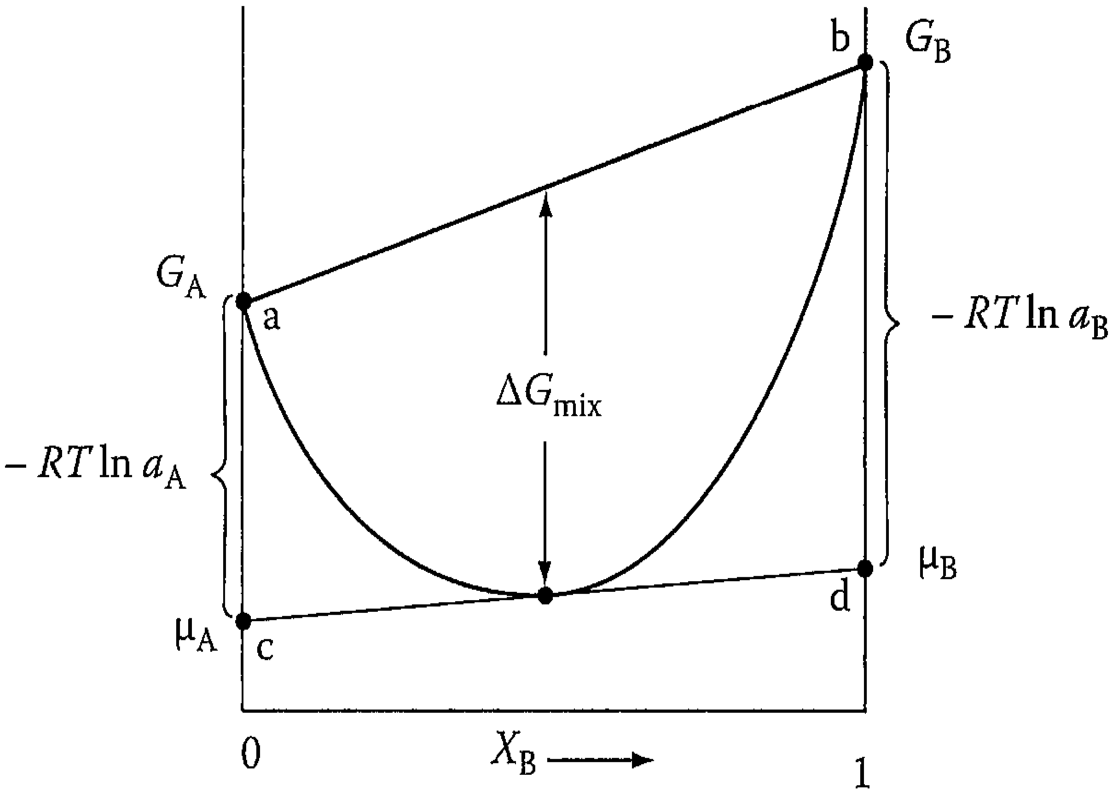
$$\mu_A = G_A + RT\ln X_A$$

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



$$\mu_A = G_A + RT\ln a_A$$

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



$$\begin{aligned}\Delta G_{mix} &= G_2 - G_1\\ &= (X_A\mu_A + X_B\mu_B) - (X_A G_A + X_B G_B)\\ &= RT(X_A\ln a_A + X_B\ln a_B)\end{aligned}$$

Regular Solution

$$\Delta G_{mix} = \Delta H_{mix} - T\Delta S_{mix}$$
$$= \Omega X_A X_B + RT(X_A \ln X_A + X_B \ln X_B)$$

$G_2=G_1+\Delta G_{mix}$

$=X_AG_A+X_BG_B+\Omega X_AX_B+RT(X_A\ln X_A+X_B\ln X_B)$ $(X_A+X_B=1)$

$=X_AG_A+X_BG_B+\Omega(X_A^2X_B+X_AX_B^2)+RT(X_A\ln X_A+X_B\ln X_B)$

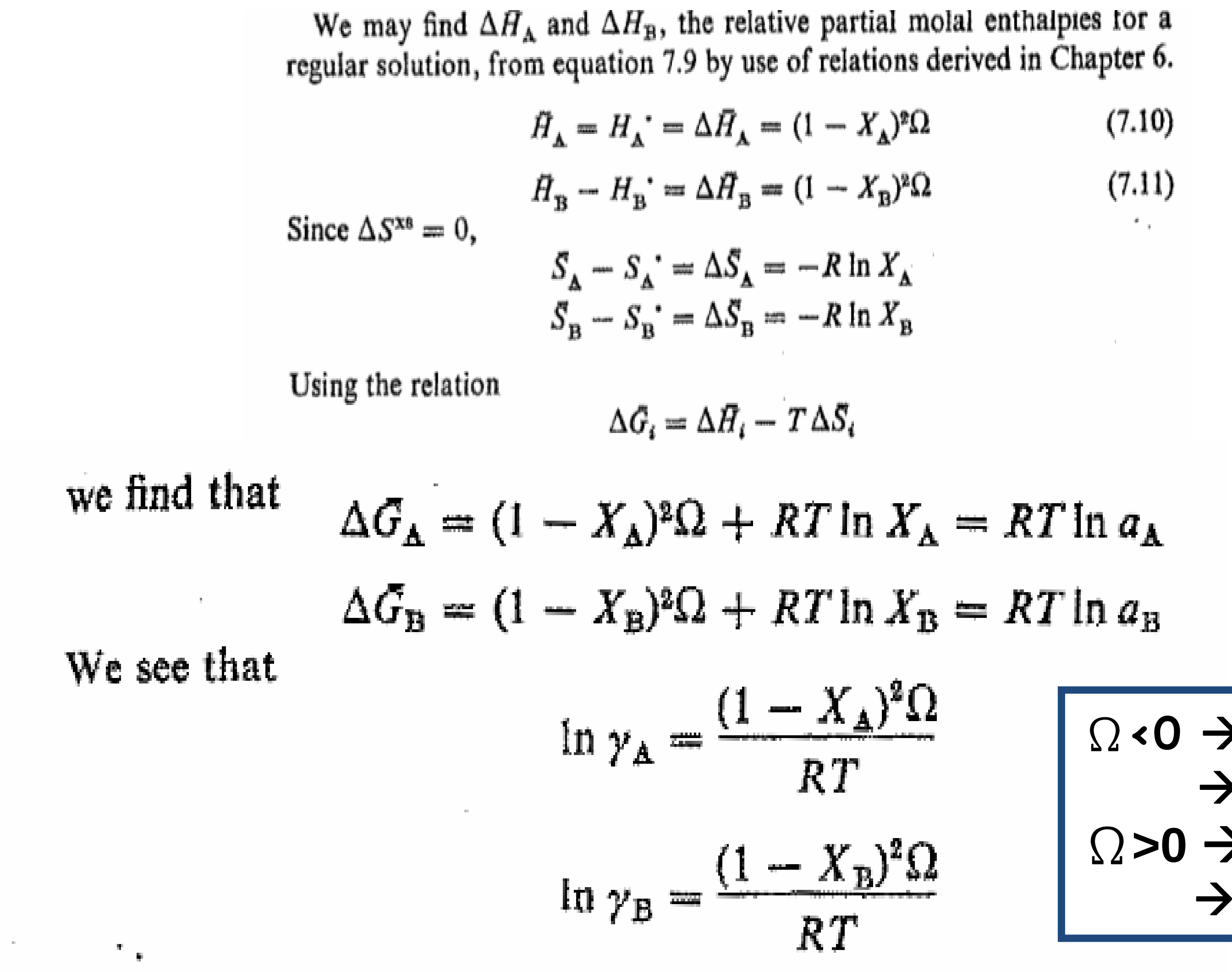
$=X_A\mu_A+X_B\mu_B$

$\mu_A = G_A+\Omega(1-X_A)^2+RT\ln X_A=G_A+RT\ln a_A \ =G_A+RT(\ln X_A+\ln\gamma_A)$

$\mu_B = G_B+\Omega(1-X_B)^2+RT\ln X_B=G_B+RT\ln a_B \ =G_B+RT(\ln X_B+\ln\gamma_B)$

$$\ln\gamma_A = \frac{(1-X_A)^2\Omega}{RT}$$

$$\ln\gamma_B = \frac{(1-X_B)^2\Omega}{RT}$$



We may find $\Delta\bar{H}_A$ and $\Delta\bar{H}_B$, the relative partial molal enthalpies for a regular solution, from equation 7.9 by use of relations derived in Chapter 6.

$$\bar{H}_A - H_A^\circ = \Delta\bar{H}_A = (1 - X_A)^2\Omega \qquad (7.10)$$

$$\bar{H}_B - H_B^\circ = \Delta\bar{H}_B = (1 - X_B)^2\Omega \qquad (7.11)$$

Since $\Delta S^{xs} = 0$,

$$\bar{S}_A - S_A^\circ = \Delta\bar{S}_A = -R\ln X_A$$

$$\bar{S}_B - S_B^\circ = \Delta\bar{S}_B = -R\ln X_B$$

Using the relation

$$\Delta\bar{G}_i = \Delta\bar{H}_i - T\Delta\bar{S}_i$$

we find that

$$\Delta\bar{G}_A = (1 - X_A)^2\Omega + RT\ln X_A = RT\ln a_A$$

$$\Delta\bar{G}_B = (1 - X_B)^2\Omega + RT\ln X_B = RT\ln a_B$$

We see that

$$\ln\gamma_A = \frac{(1 - X_A)^2\Omega}{RT}$$

$$\ln\gamma_B = \frac{(1 - X_B)^2\Omega}{RT}$$

$\Omega < 0$ → $\gamma_A < 1$

→ **Negative deviation**

$\Omega > 0$ → $\gamma_A > 1$

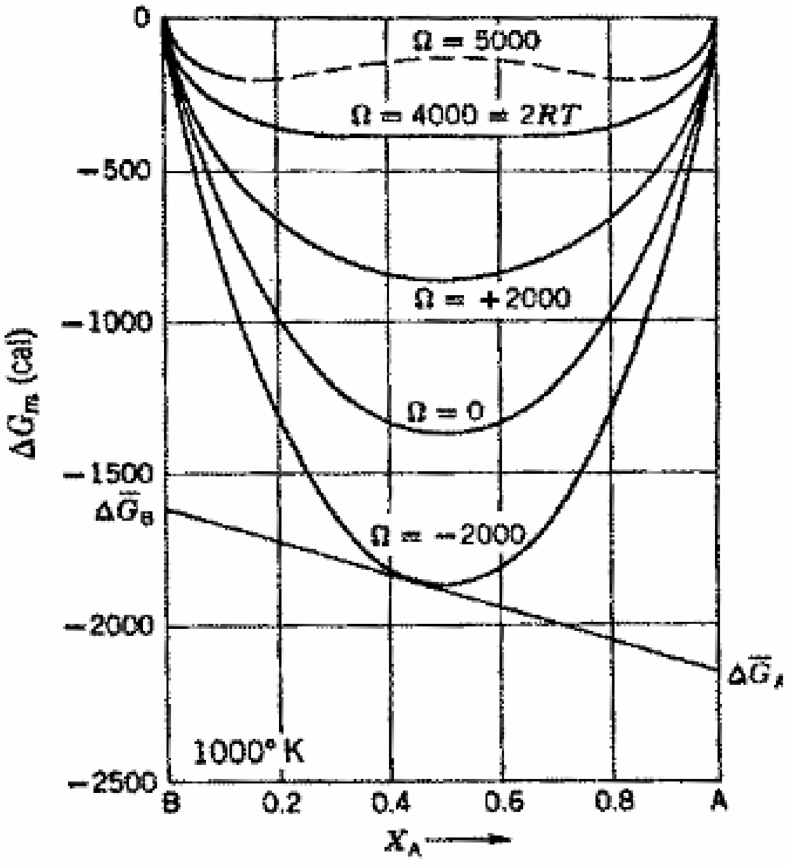
→ **Positive deviation**

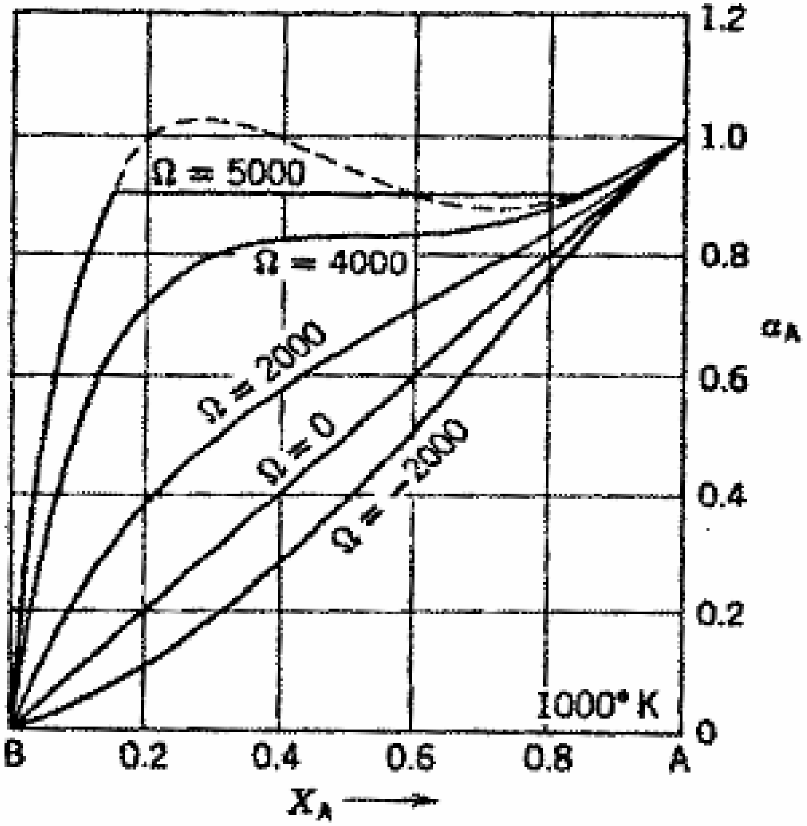
$$\boxed{\frac{\partial\ln(\gamma_A)}{\partial\ln(X_A)} = \frac{-2\Omega X_A X_B}{RT}}$$

$$\Delta G_{mix} = \Delta H_{mix} - T\Delta S_{mix}$$
$$= \Omega X_A X_B + RT(X_A \ln X_A + X_B \ln X_B)$$

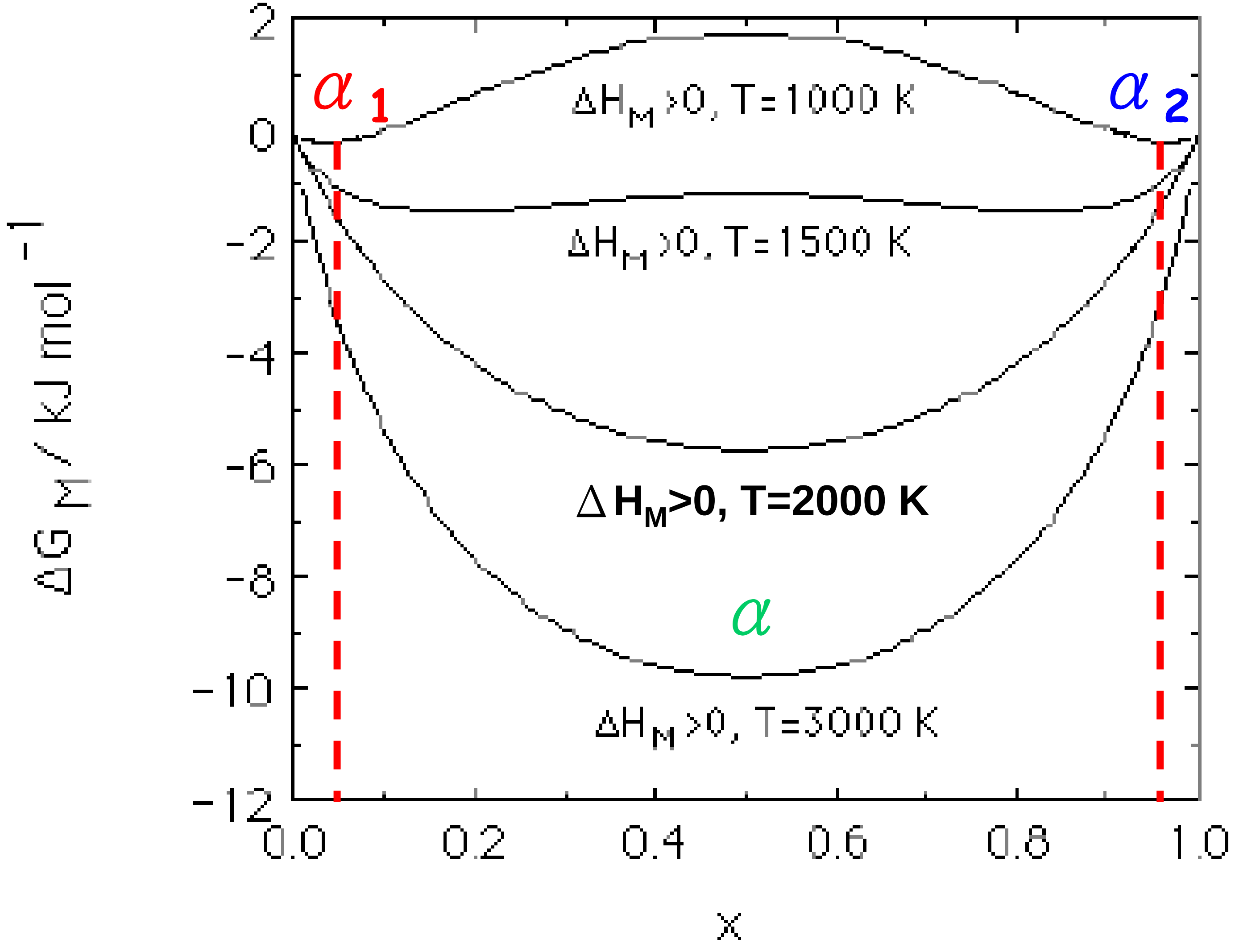
$$\ln \gamma_A = \frac{(1 - X_A)^2 \Omega}{RT}$$

$$\ln \gamma_B = \frac{(1 - X_B)^2 \Omega}{RT}$$



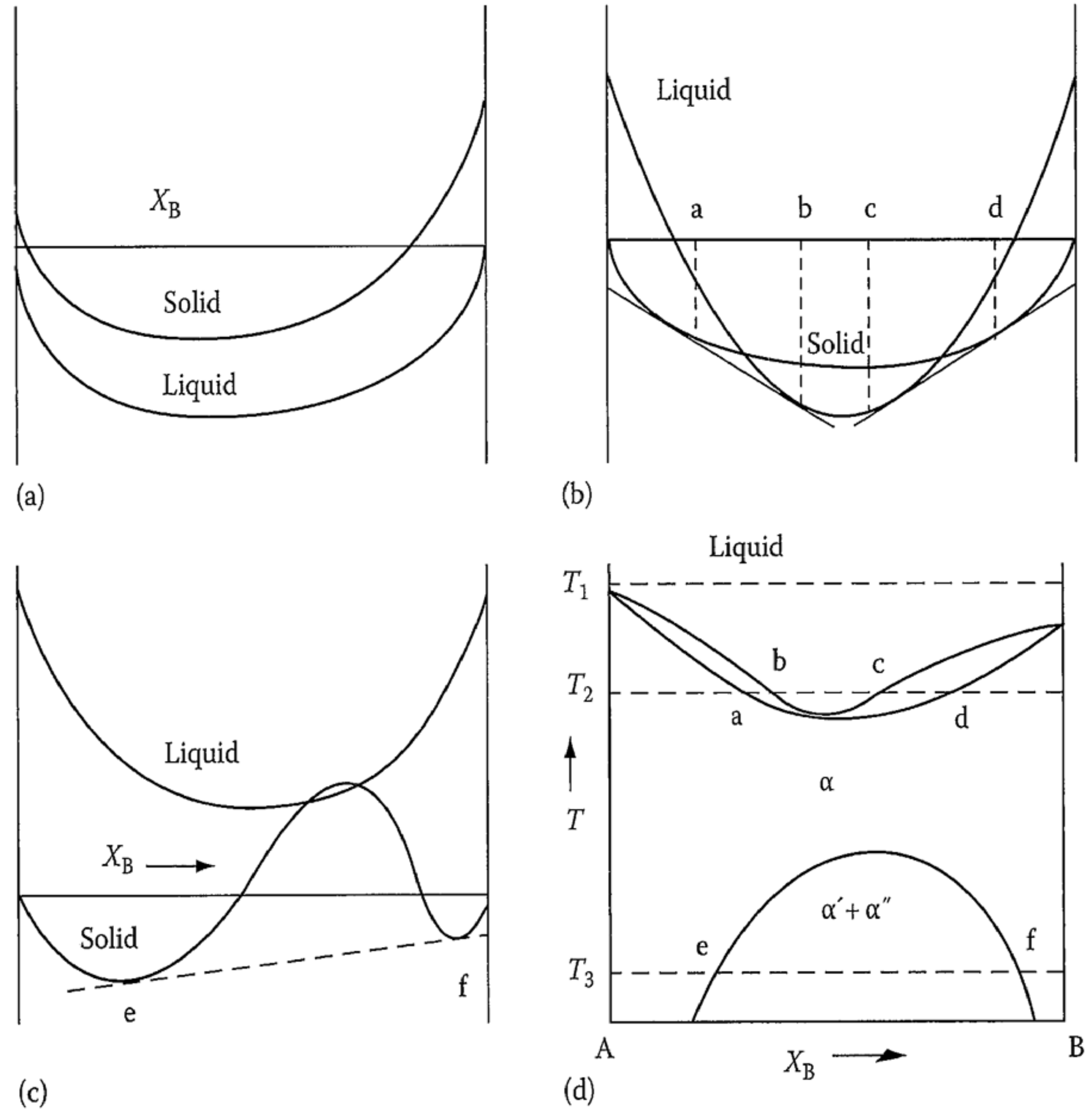


$\alpha \rightarrow \alpha_1 + \alpha_2$



$$\Delta G_m = \Delta H_m - T \Delta S_m$$

Systems with a Miscibility Gap



$$D_A^I = B_A^* RT\left(1 + \frac{\partial \ln \gamma_A}{\partial \ln X_A}\right)$$

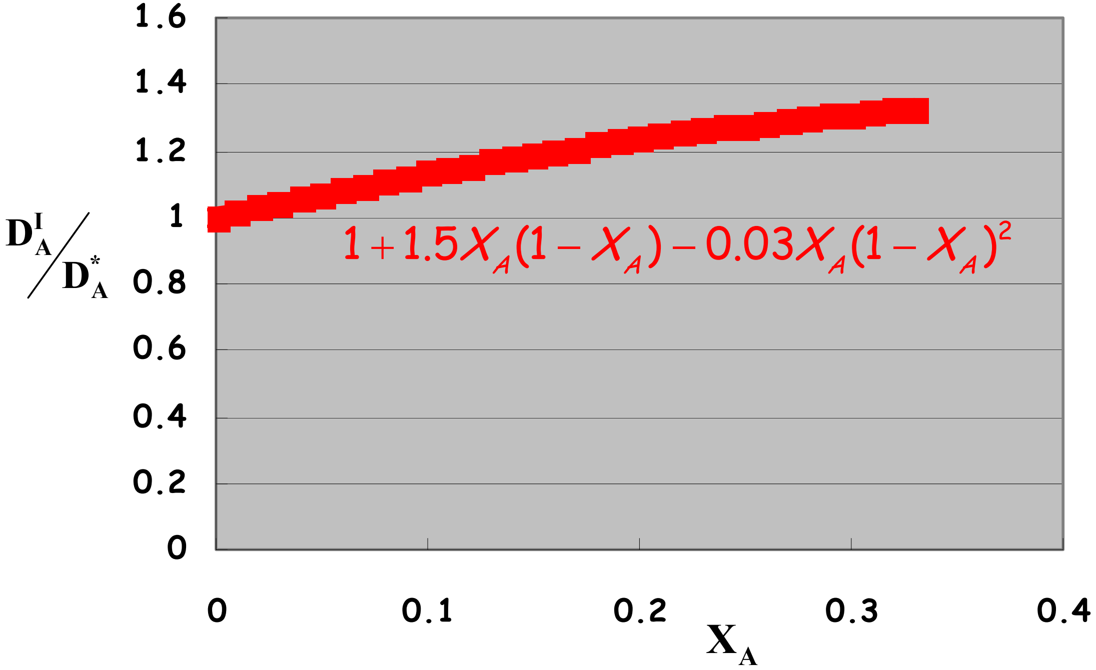
Example:

$$\ln \gamma_A = -0.75(1 - X_A)^2 + 0.01(1 - X_A)^3$$

$$\frac{\partial \ln \gamma_A}{\partial \ln X_A} = 1.5 X_A (1 - X_A) - 0.03 X_A (1 - X_A)^2$$

$$D_A^I = B_A^* RT[1 + 1.5 X_A (1 - X_A) - 0.03 X_A (1 - X_A)^2]$$

$$= D_A^* [1 + 1.5 X_A (1 - X_A) - 0.03 X_A (1 - X_A)^2]$$

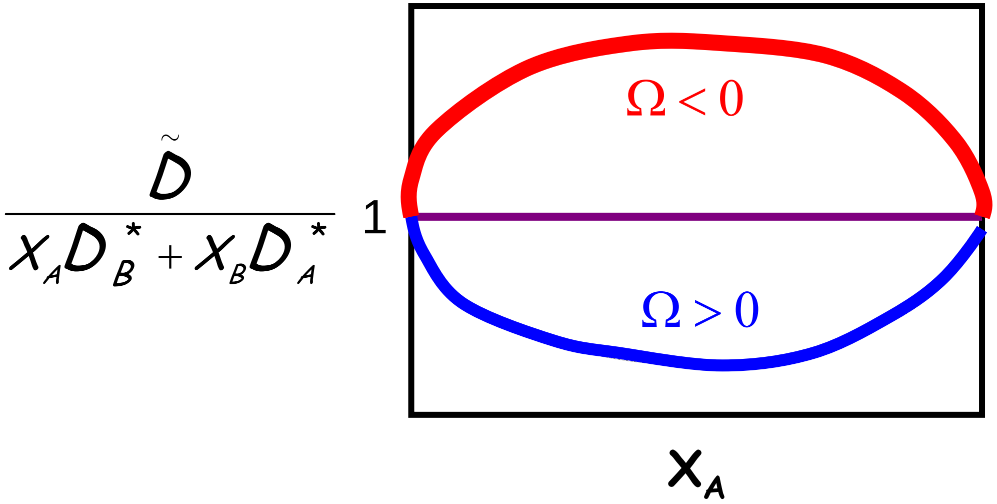


Regular Solution

$$\tilde{D} = (X_A D_B^I + X_B D_A^I)$$

$$= (X_A D_B^* + X_B D_A^*)\left(1 + \frac{\partial \ln \gamma_A}{\partial \ln X_A}\right)$$

$$= (X_A D_B^* + X_B D_A^*)\left(1 - \frac{2\Omega X_A X_B}{RT}\right)$$



Ideal solution $\rightarrow \Omega = 0$

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

$\Omega < 0 \Rightarrow \tilde{D} > 0 \Rightarrow$ *Downhill Diffusion*

$\Omega > 0$ *and* $1 < \frac{2\Omega X_A X_B}{RT} \Rightarrow \tilde{D} < 0$

$\Rightarrow$ *Uphill Diffusion*

$$\Delta G_m = \Delta H_m - T\Delta S_m$$

$$= \Omega X_A X_B + RT(X_A \ln X_A + X_B \ln X_B)$$

$$\frac{\partial \Delta G_m}{\partial X_B} = RT(-\ln X_A + \ln X_B) + \Omega(1 - 2X_B)$$

$$\frac{\partial^2 \Delta G_m}{\partial X_B^2} = RT\left(\frac{1}{X_A} + \frac{1}{X_B}\right) - 2\Omega = RT\left(\frac{X_A + X_B}{X_A X_B}\right) - 2\Omega = \frac{RT}{X_A X_B} - 2\Omega$$

$$\tilde{D} = (X_A D_B^I + X_B D_A^I)$$

$$= (X_A D_B^* + X_B D_A^*)\left(1 + \frac{\partial \ln \gamma_A}{\partial \ln X_A}\right)$$

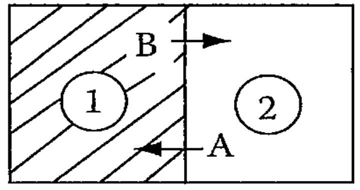
$$= (X_A D_B^* + X_B D_A^*)\left(1 - \frac{2\Omega X_A X_B}{RT}\right)$$

$$= (X_A D_B^* + X_B D_A^*)\frac{X_A X_B}{RT}\frac{\partial^2 \Delta G_m}{\partial X_B^2}$$

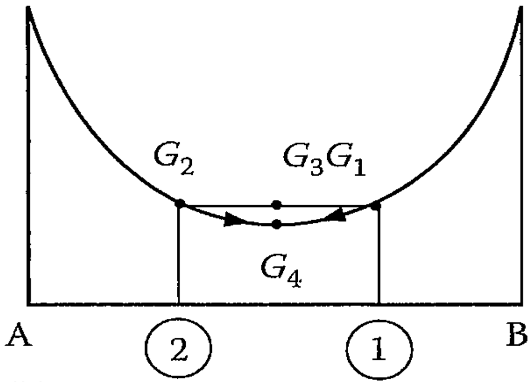
$$\frac{\partial^2 \Delta G_m}{\partial X_B^2} < 0 \Rightarrow \tilde{D} < 0 \Rightarrow \text{up-hill diffusion}$$

$$\frac{\partial^2 \Delta G_m}{\partial X_B^2} > 0 \Rightarrow \tilde{D} > 0 \Rightarrow \text{down-hill diffusion}$$

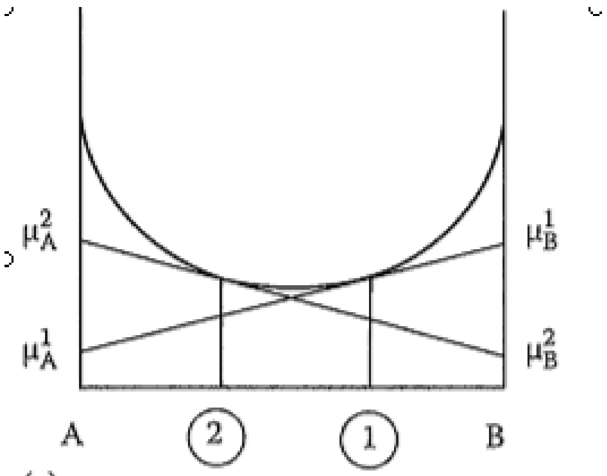
Down-Hill Diffusion



(a)

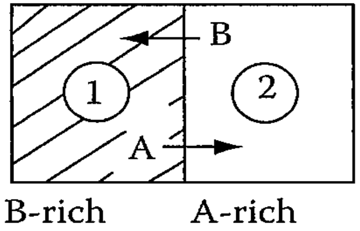


(b)

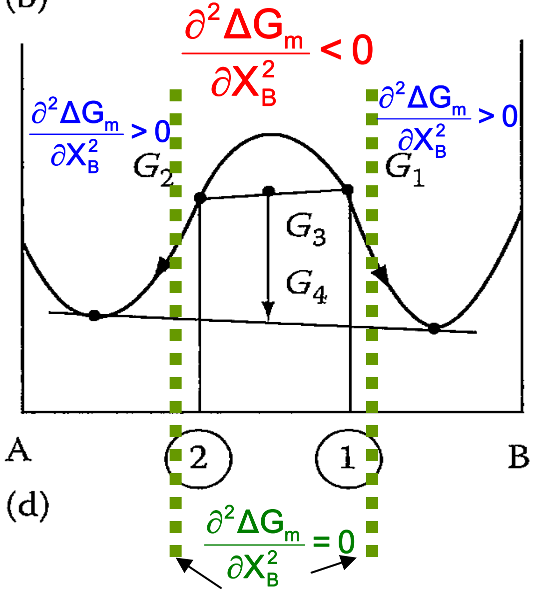


(e)

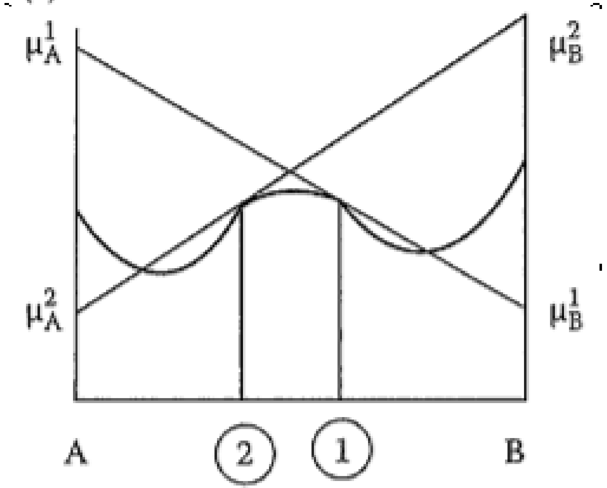
Up-hill Diffusion



(c)



(d)



(f)

$$Driving \quad force \quad \alpha \quad \frac{\partial \mu}{\partial x} \quad (not \frac{\partial C}{\partial x})$$

$$J = CV = C \cdot (B \cdot F) = C \cdot B(-\frac{\partial \mu}{\partial x})$$

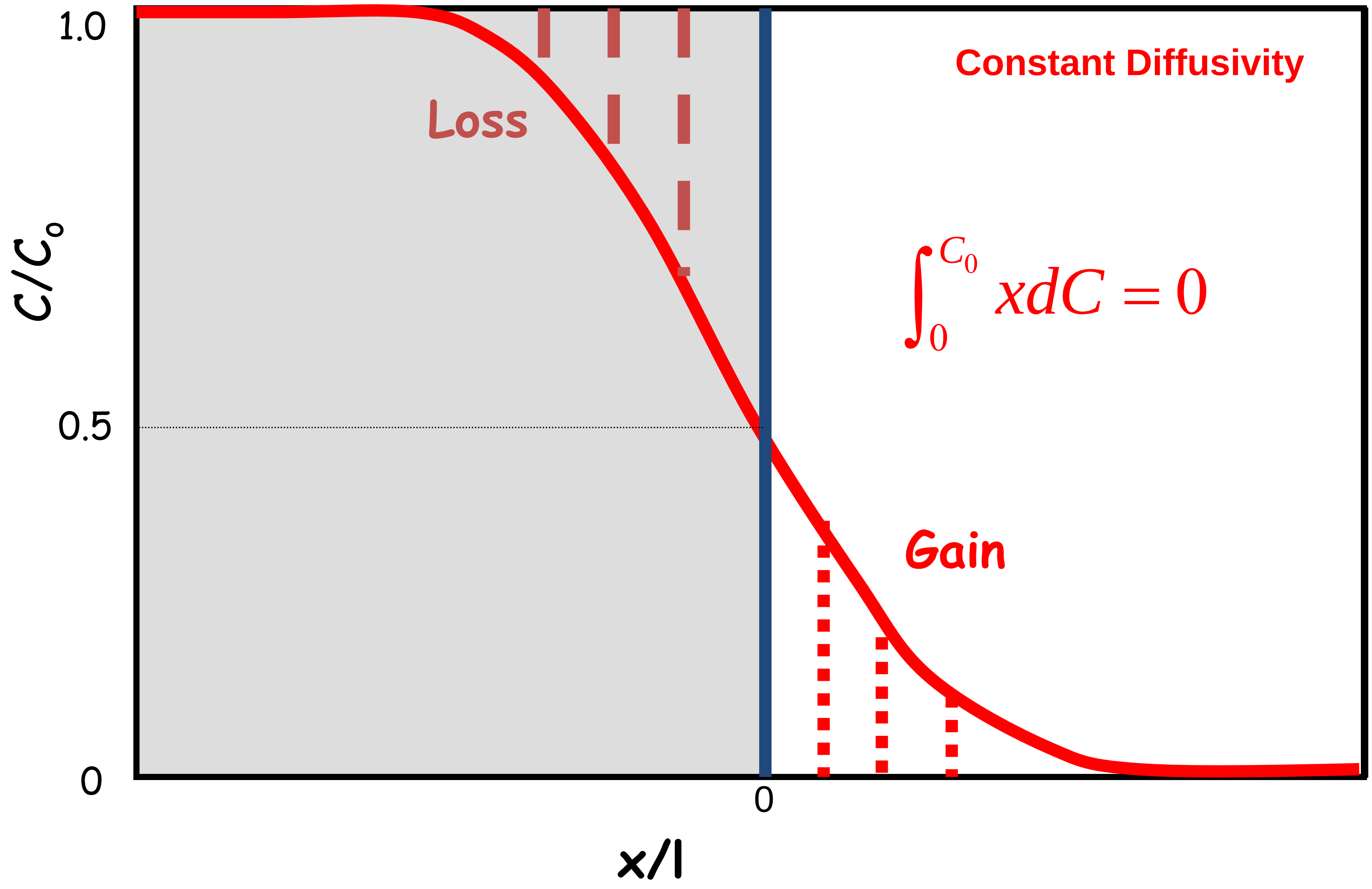
$$B : Mobility, \quad F : Force$$

Summary of Diffusivities

Symbol	Name/Nature	Equations	Coordi-nate
D^*	Self-diffusivity of a tracer in a chemically homogeneous material containing only one species	$D^* = f(\frac{1}{6}\alpha^2\Gamma)$ $D^* = B^* RT$	M=S (no net mass flow)
D_i^*	Self-diffusivity of a tracer in a chemically homogeneous material containing more than one species	$D_i^* = B_i^* RT$ $D_i^I = D_i^*(1+\frac{\partial \ln \gamma_i}{\partial \ln X_i})$	M=S (no net mass flow)
D_i^I	Composition-dependent intrinsic diffusivity of component i in a chemically inhomogeneous system.	$j_i^M = -D_i^I \nabla C_i$ $J_i^S = -D_i^I \nabla C_i + v_M C_i$	M S
$\tilde{D}$	Composition-dependent interdiffusivity in a chemically inhomogeneous system	$J_i^S = -\tilde{D} \nabla C_i$ $\tilde{D} = X_B D_A^I + X_A D_B^I$ $\tilde{D} = (X_B D_A^* + X_A D_B^*)(1+\frac{\partial \ln \gamma_A}{\partial \ln X_A})$	S S S

M: Moving and S: Stationary Coordinates

Error-Function Solution



$$\int_0^{C_0} x\,dC = 0$$

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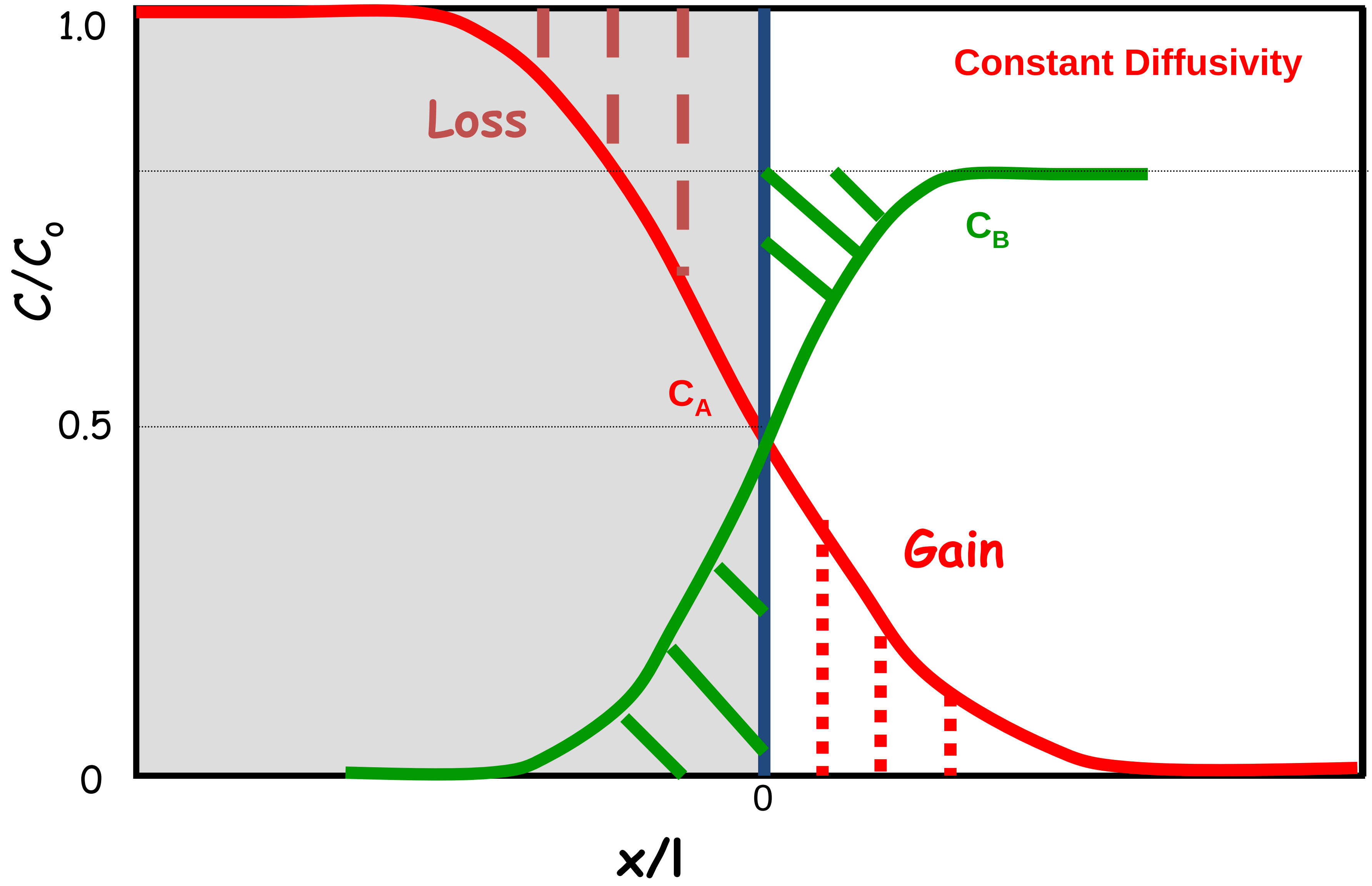
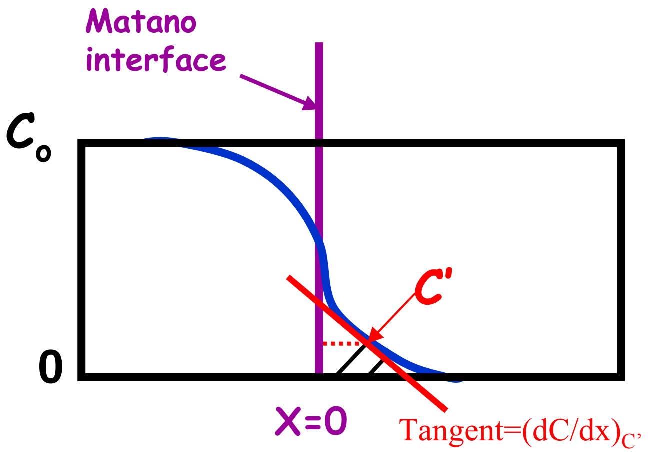


For an infinite system

$$\frac{dC}{dx}=0 \quad when \quad C=0 \quad or \quad C=C_o \qquad \therefore \frac{dC}{dx}\Big|_0^{C_0}=0$$



Therefore

$$-\frac{1}{2}\int_0^{C_0} xdC = Dt\frac{dC}{dx}\Big|_0^{C_0}$$

$$\because \frac{dC}{dx}\Big|_0^{C_0}=0$$

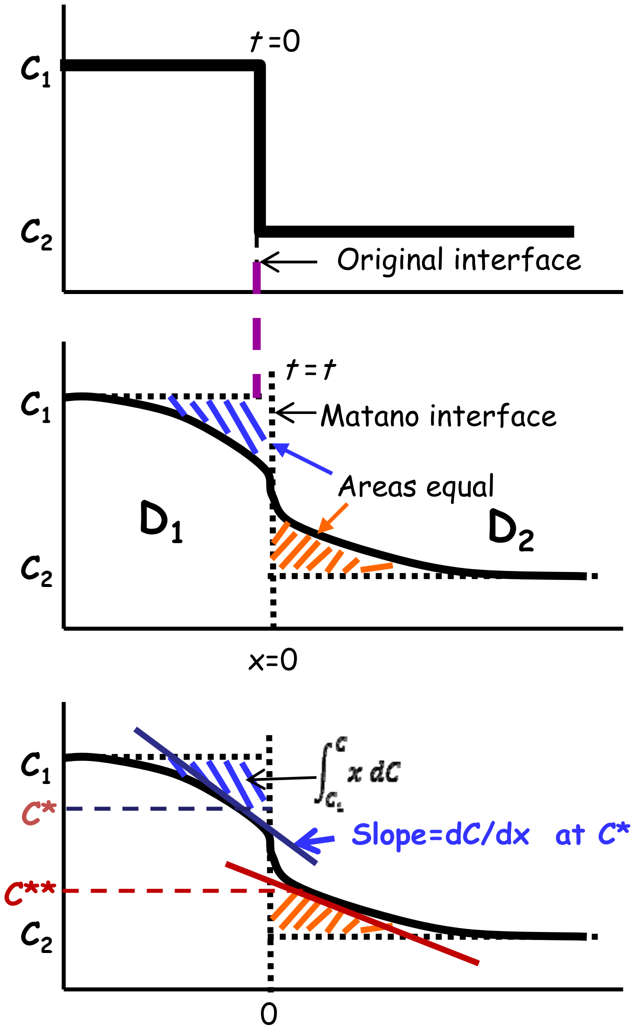
$$\therefore \int_0^{C_0} xdC = 0$$

which is an additional boundary condition and determines the location of Matano interface.

x=0 plane (Matano interface) determined by

$$\int_0^{C_0} xdC = 0$$

$$D(C^{'}) = \frac{-1}{2t}\left(\frac{dx}{dC}\right)_{C^{'}}\int_0^{C^{'}} xdC$$



$$D(C') = \frac{-1}{2t}\left(\frac{dx}{dC}\right)_{C'}\int_0^{C'} x\,dC$$

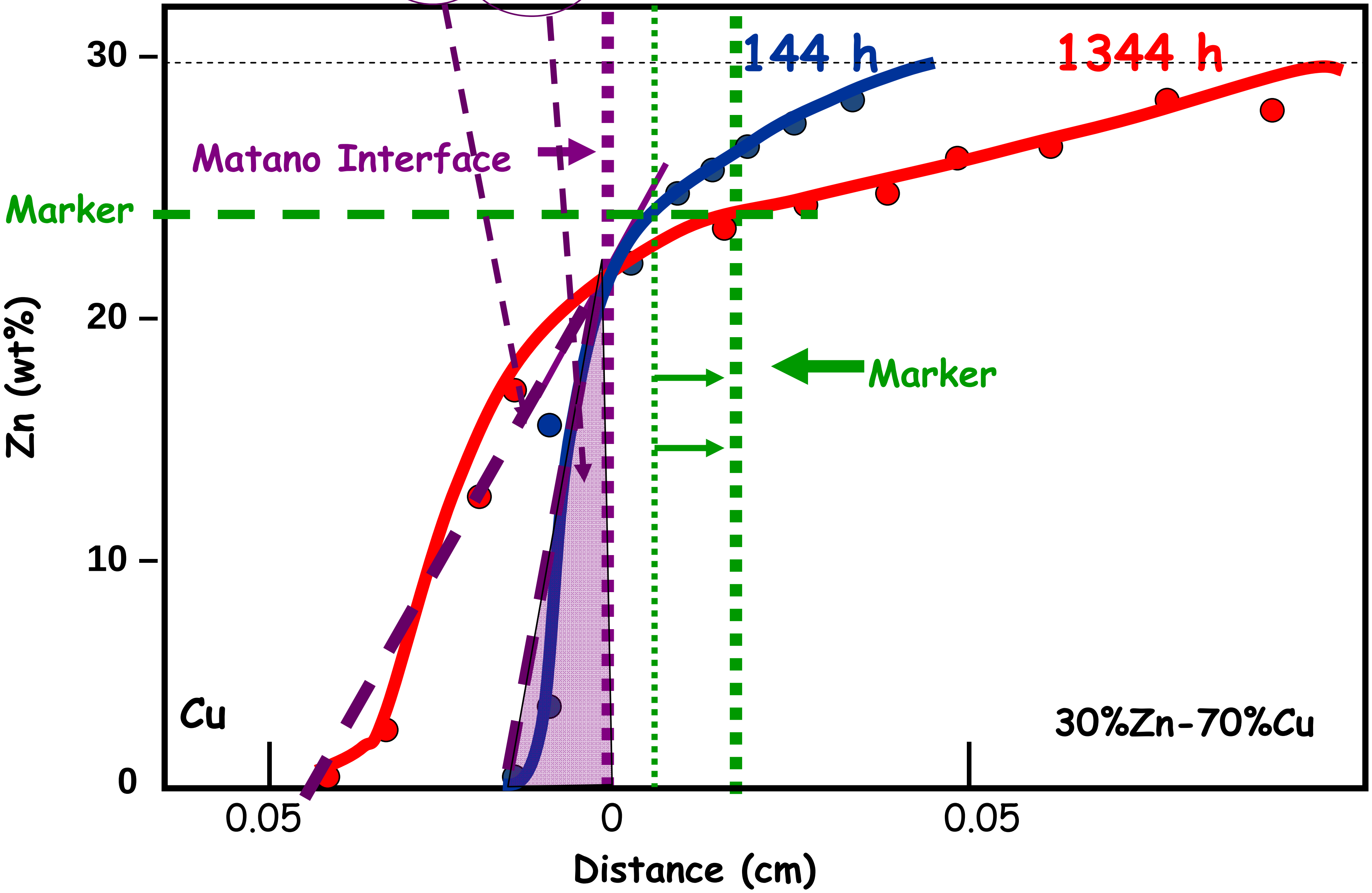
Slope : $\frac{\partial C}{\partial x}|_{C^*} > \frac{\partial C}{\partial x}|_{C^{**}}$

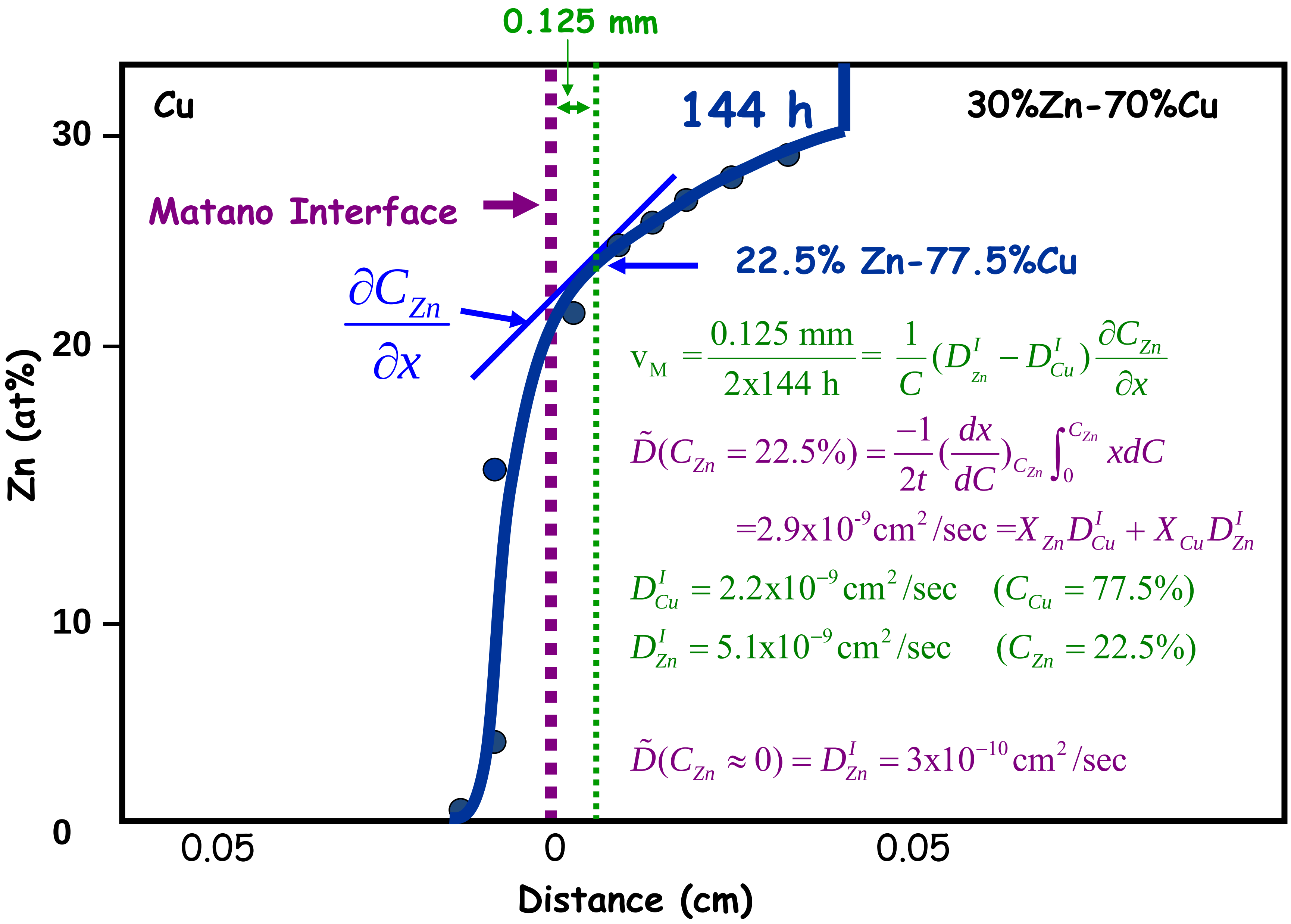
Diffusivity : $D_{C^*} < D_{C^{**}}$

Area : $\int_{C_1}^{C^*} x\,dC = \int_{C^{**}}^{C_2} x\,dC$

$$\int_0^{C_0} x\,dC = 0$$

$$\tilde{D}(C') = \frac{-1}{2t}\left(\frac{dx}{dC}\right)_{C'} \int_0^{C'} x\,dC \rightarrow \tilde{D} = X_B D_A^I + X_A D_B^I$$





$$v_M = \frac{0.125\text{ mm}}{2\text{x}144\text{ h}} = \frac{1}{C}(D^I_{Zn} - D^I_{Cu})\frac{\partial C_{Zn}}{\partial x}$$

$$\tilde{D}(C_{Zn} = 22.5\%) = \frac{-1}{2t}\left(\frac{dx}{dC}\right)_{C_{Zn}}\int_0^{C_{Zn}} x\,dC$$

$$= 2.9\text{x}10^{-9}\text{cm}^2/\text{sec} = X_{Zn}D^I_{Cu} + X_{Cu}D^I_{Zn}$$

$$D^I_{Cu} = 2.2\text{x}10^{-9}\text{cm}^2/\text{sec} \quad (C_{Cu} = 77.5\%)$$

$$D^I_{Zn} = 5.1\text{x}10^{-9}\text{cm}^2/\text{sec} \quad (C_{Zn} = 22.5\%)$$

$$\tilde{D}(C_{Zn} \approx 0) = D^I_{Zn} = 3\text{x}10^{-10}\text{cm}^2/\text{sec}$$