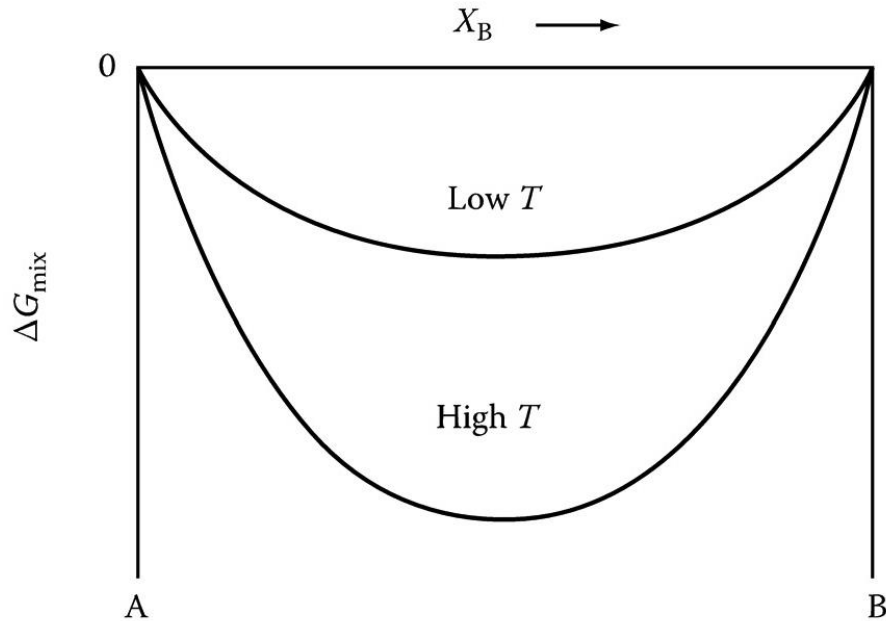# 1.3.2 Ideal solution

$$\Delta H_{mix} = 0 \quad \text{(no interaction)}$$

$$\Delta S_{mix} = 0 \quad \Rightarrow \text{random statistics}$$

$$S = k \ln \omega$$

k: Boltzmann constant
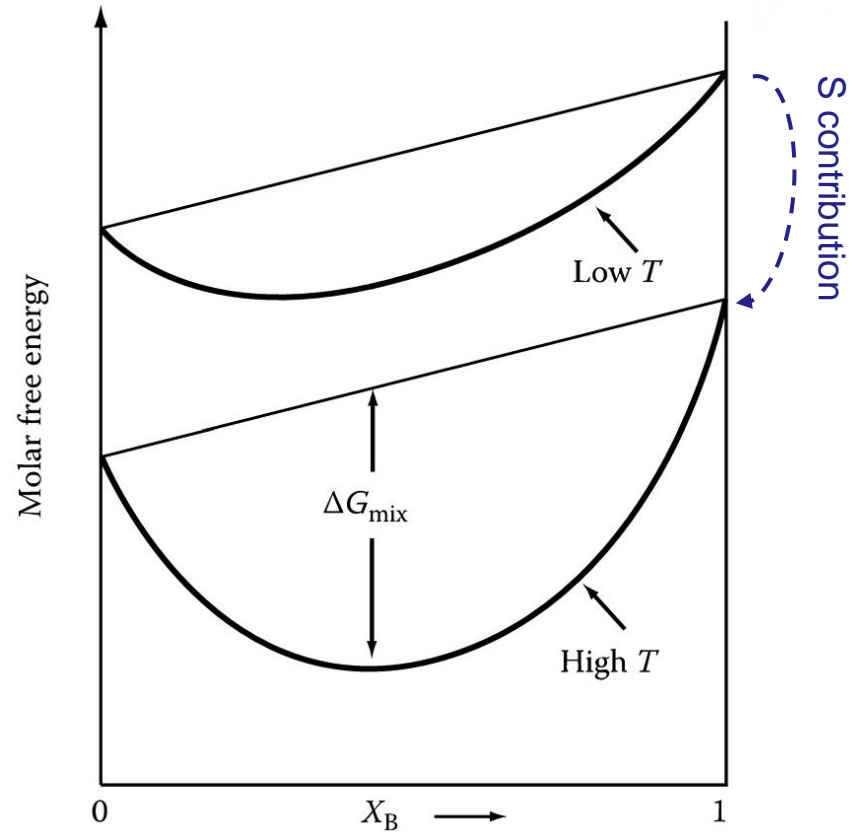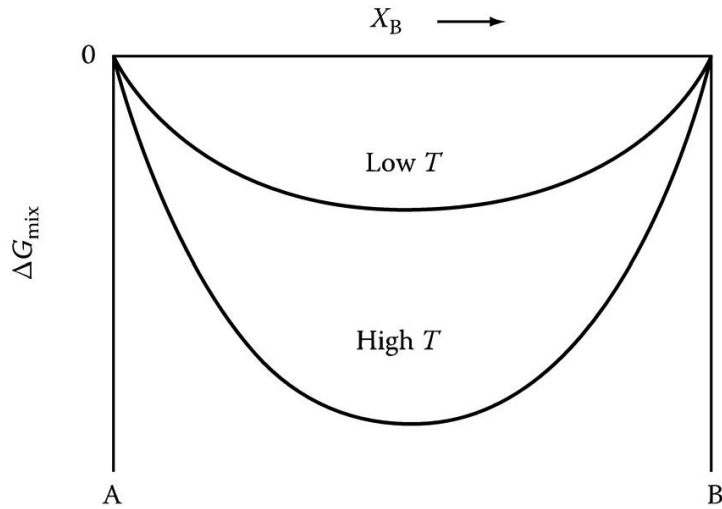ω: measure of randomness

$$\omega = \frac{(N_A + N_B)!}{N_A! \, N_B!}$$

$$< 0$$

$$\Delta S_{mix} = -R(\overbrace{X_A \ln X_A + X_B \ln X_B}) \quad > 0$$

$$\therefore \Delta G^M = -RT \ln(X_A \ln X_A + X_B \ln X_B) \quad < 0$$

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1.3.2 Ideal solution

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

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1.3 Binary solution

❖ 1.3.4. Chemical Potential

Partial molar quantity (아주 작은 양이 add 되었을 때 변하는 성질)

$$\bar{Q}_i = \left(\frac{\partial Q_i}{\partial n_i}\right)_{T,P,n_j}$$

Partial Molar Quantity of Free energy → Chemical Potential

Whole System

$$\mu_A = \left(\frac{\partial G'}{\partial n_A}\right)_{T,P,n_B} \quad G : \text{molar free } E \text{ (independent of size)}$$

For binary solution at T, P, const. $\quad dG' = \mu_A dn_A + \mu_B dn_B$

If T, P change & multi components

$$dG' = -SdT + VdP + \mu_A dn_A + \mu_B dn_B + \mu_C dn_C + \dots$$

For molar quantity

$$G = \mu_A X_A + \mu_B X_B \ (Jmol^{-1})$$

$(\because 1 \ mol \text{ of original phase, } X_A \ mol, X_B \ mol. \ dn_A : dn_B = X_A : X_B)$

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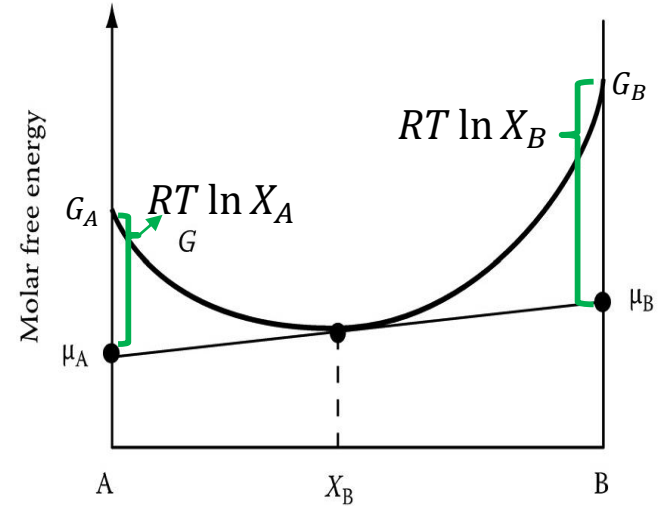Device Materials Lab.**

1.3.2 Ideal solution

❖ **For molar quantity**

$$G = \mu_A X_A + \mu_B X_B$$

$$\left(\frac{\partial G}{\partial X_A}\right)_{T,P,X_B} = \mu_A$$

❖ For ideal solution,

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

$$\mu_A = \left(\frac{\partial G}{\partial X_A}\right)_{T,P,X_B} = G_A + RT \ln X_A$$

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

Phase Transformation in Materials

1.3 Binary solution

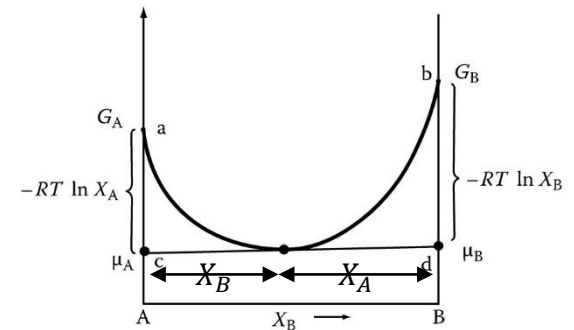$$\left(\frac{\partial G}{\partial X_A}\right)_{T,P,X_B} = \mu_A = G_A + RTlnX_A$$

$$\mu_B = G_B + RTlnX_B$$

- $dG' = -SdT + VdP + \sum \mu_i \, dn_i$
- $dG^M = \mu_A dX_A + \mu_B dX_B$ - ①
- $G^M = X_A \mu_A + X_B \mu_B$ - ②
- $\frac{dG^M}{dX_A} = \mu_A - \mu_B$ - ③ $\left(\frac{dG^M}{dX_B} = \mu_B - \mu_A\right)$
- ③ $\times X_B \rightarrow X_B \frac{\partial G^M}{\partial X_A} = \mu_A X_B - \mu_B X_B$ - ④
- ② +④ $\rightarrow G^M + X_B \frac{\partial G^M}{\partial X_A} = \mu_A(X_A + X_B) = \mu_A$ - ⑤
- $\mu_A = G^M + X_B \frac{\partial G^M}{\partial X_A}$ - ⑥
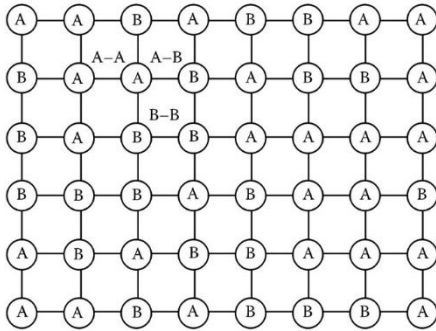- $\mu_B = G^M + X_A \frac{\partial G^M}{\partial X_B}$ - ⑦

(intercept at $X_B = 1$) $= G^M_{at \, X_B} + X_A \cdot slope = G^M + X_A \frac{\partial G^M}{\partial X_B}$

$from \; ⑦ = \mu_B$

$by \; ③'$ intercept at $X_B = 0$

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1.4 Regular solutions (Quasi- chemical model)

$$\Delta H^M = 0 \qquad \text{Ideal}$$

$$\Delta H^M > 0 \qquad \text{Endothermic}$$

$$\Delta H^M < 0 \qquad \text{Exothermic}$$

❖ Quasi- chemical approach

✓ ΔH^M is only due to the bonding E.

$(\Delta V^M = 0, \text{ vol of A} \cong \text{B})$

✓ Interatomic bonding E, distance maintained the same

A-A $\quad \varepsilon_{AA}$

B-B $\quad \varepsilon_{BB}$

A-B $\quad \varepsilon_{AB}$

# of A-B pair

$$E = P_{AB}\varepsilon_{AB} + P_{AA}\varepsilon_{AA} + P_{AB}\varepsilon_{AB}$$

Internal energy of solution

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1.3.3. Regular solutions

❖ **when A&B are mixed:**

$$\Delta H_{Mix} = P_{AB}\left[\varepsilon_{AB} - \frac{1}{2}(\varepsilon_{AA} + \varepsilon_{BB})\right] = P_{AB}\varepsilon$$

ε: difference between A-B to aveg. of AA. BB

① $\varepsilon = 0$ $\Delta H^M = 0$ Ideal solution

# of bonds   # atom

$$P_{AB} = N_A Z X_A X_B \text{ (random solution)}$$

Avogadro's #

② $\varepsilon > 0$ $\Delta H^M > 0$ P_{AB} ↑, 다른 종류의 atom이 둘려 쌓여지길 선호함

③ $\varepsilon < 0$ $\Delta H^M < 0$ P_{AB} ↓, 같은 종류의 atom이 둘려 쌓여지길 선호함
(less random)

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1.3.3. Regular solutions (Quasi-chemical model)
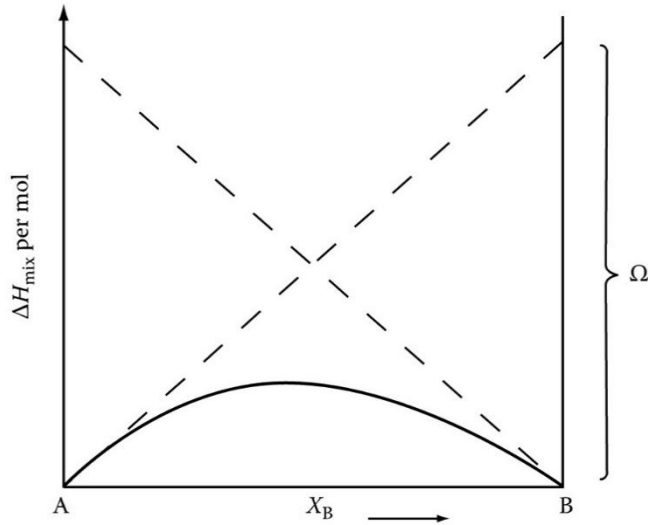
$|\varepsilon|$가 작으면 $P_{AB} = N_A Z X_A X_B$ 가 성립.

$$\boxed{\Delta H_{Mix} = \Omega X_A X_B}$$

$\Rightarrow$ regular solution

$$\Omega = N_A Z \varepsilon$$

$$\Delta H_{Mix} = \Omega X_A X_B \quad = \quad \Omega(X_B - (X_B)^2)$$

$$(X_A = 1 - X_B)$$

$$\Delta G_{Mix} = \Omega X_A X_B + RT(X_A \ln X_A + X_B \ln X_B)$$

ΔH_{mix} $-T\Delta S_{mix}$

$\Delta G_{Mix}, always\ decrease\ for\ small\ X_B$

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❖ The Effect of ΔH_{mix} and T on ΔG_{mix}

$\Omega < 0$

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

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

$\Omega > 0$

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

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

Phase Transformation in Materials

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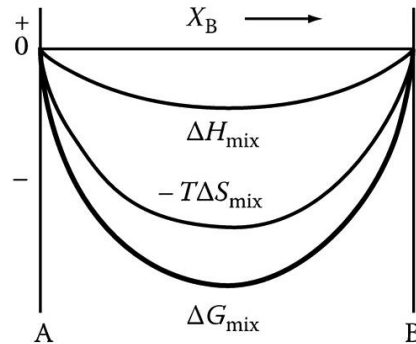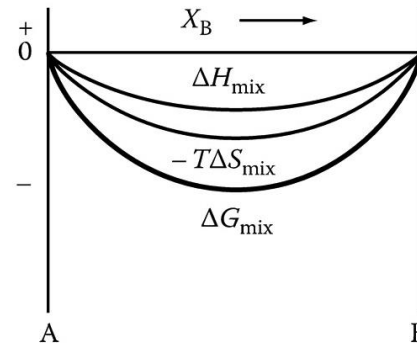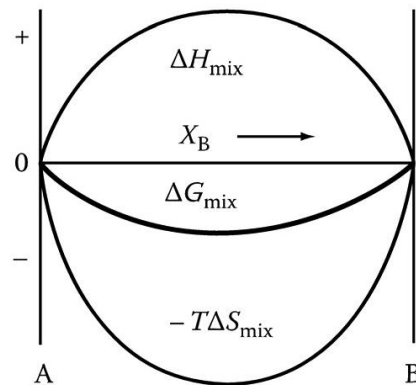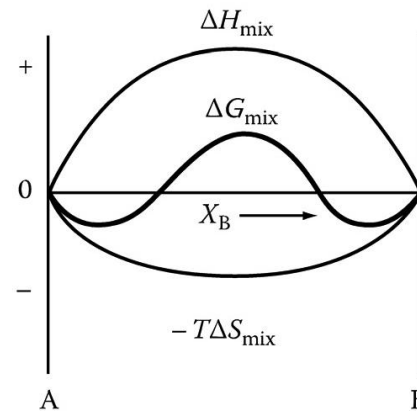
1.3.5 Regular solution
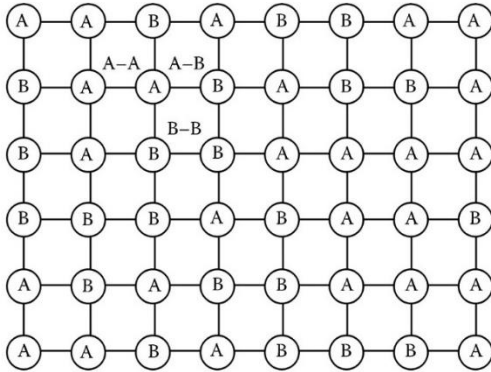
Total free energy of alloy (1-39)

$$G^M$$

$$= \overbrace{X_A G_A^\circ + X_B G_B^\circ}^{} + \overbrace{\Omega X_A X_B + RT(X_A \ln X_A + X_B \ln X_B)}^{}$$

$$= X_A \left[G_A^\circ + \Omega(1 - X_A)^2 + RT\ln X_A \right]$$

$$+ X_B \left[G_B^\circ + \Omega(1 - X_B)^2 + RT\ln X_B \right]$$

$$(X_A X_B = X_A^2 X_B + X_B^2 X_A)$$

$$= \mu_A X_A + \mu_B X_B$$
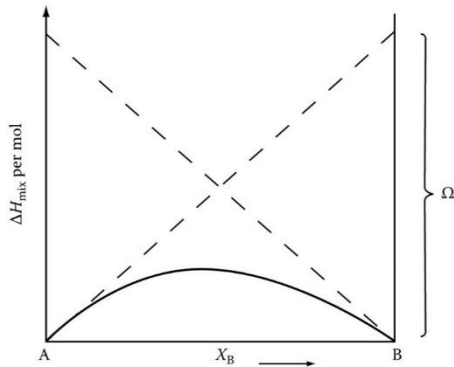
$$\therefore \begin{cases} \mu_A = G_A^\circ + \Omega(1 - X_A)^2 + RT\ln X_A \\ \mu_B = G_B^\circ + \Omega(1 - X_B)^2 + RT\ln X_B \end{cases}$$

Phase Transformation in Materials

1.3 Binary Solutions

❖ Activity

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

for regular solution

$$\gamma_A = \frac{a_A}{X_A}$$

: activity coefficient

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

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

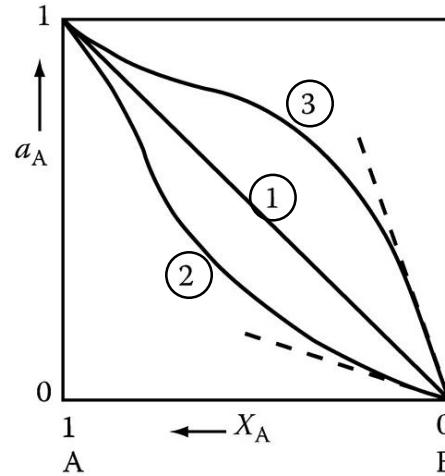$$RT\ln\gamma_A = \Omega X_B^2$$
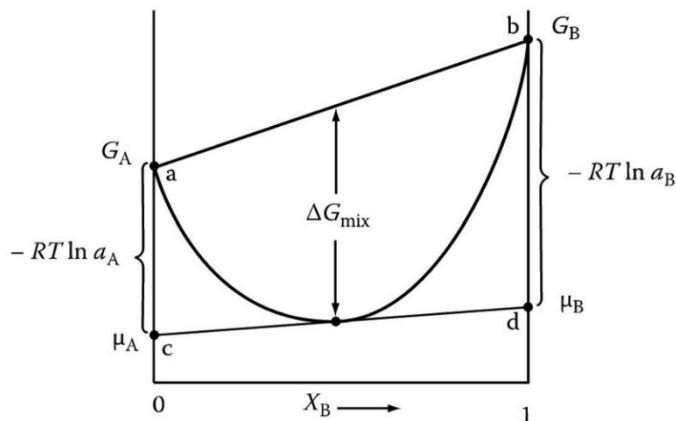
1.3 Binary Solutions
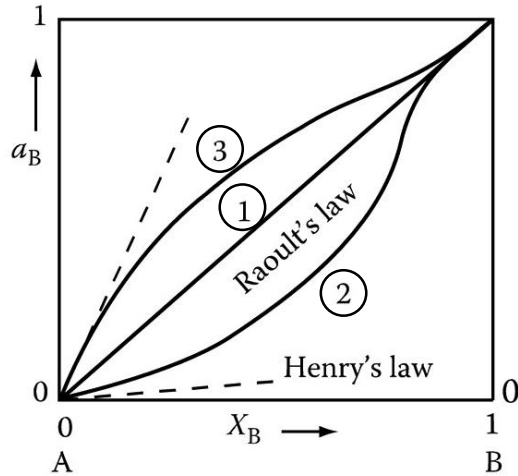
(a)   (b)

① Ideal Solution ($a_A = X_A, a_B = X_B$)

② $\Delta H_{mix} < 0$

③ $\Delta H_{mix} > 0$

❖ Activity related to <u>chemical potential.</u> $\boxed{\mu_A = G_A + RT \ln a_A}$

→measure of the tendency of atom to leave the solution

Ex) a or μ is low.   → Reluctant to leave the solution.

→ ε_{AB} preferred.

❖ For dilute solution.
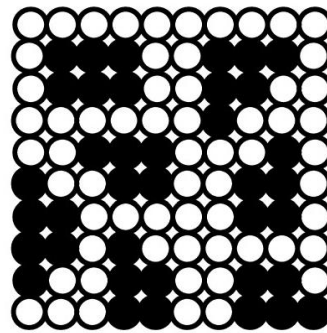
$\gamma_B = \dfrac{a_B}{X_B} = const$ (Henry's law)

$\gamma_A = \dfrac{a_A}{X_A} = 1$ (Raoult's law)

1.3.6 Real Solutions
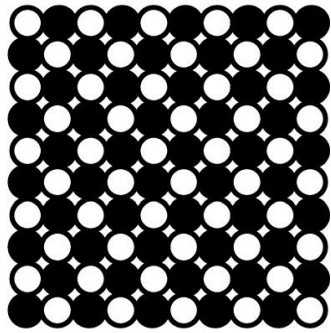
(a)	(b)	(c)
Ordered substitutional	**Clustering**	**Random interstitial**
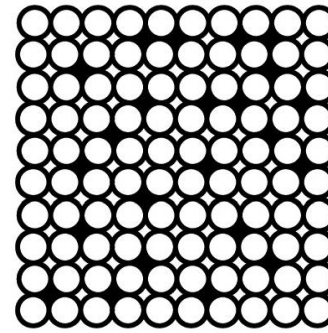
❖ Actual arrangement in real solution

→ Compromise between ΔE & ΔS for min G

$$\begin{cases} \varepsilon < 0 & G \downarrow \text{ by increasing A} - \text{B bonds} & \rightarrow \textbf{\textcolor{red}{ordering}} \\ \varepsilon > 0 & G \uparrow \text{ by increasing A} - \text{A, B} - \text{B bonds} & \rightarrow \textbf{\textcolor{red}{clustering}} \end{cases}$$

- Ordering & clustering tendency ↓ as T ↑
- $\Delta V^M \neq 0$ (size dependence)
  Size difference → interstitial solid solution

Strong chemical bonding force → <u>intermediate phase</u> formation

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1.3 Binary Solutions

❖ 1.3.7. Ordered Phases - SPO parameter
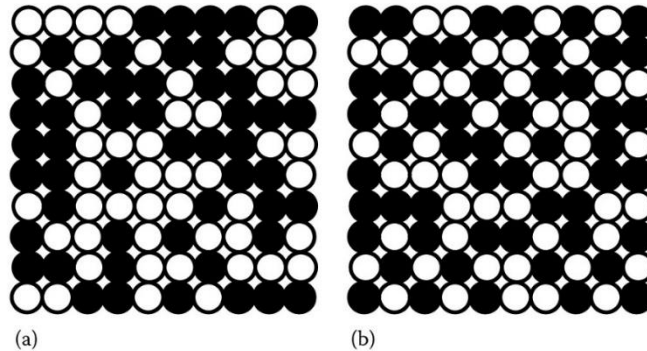
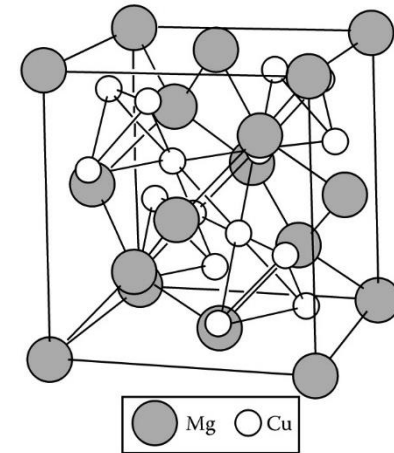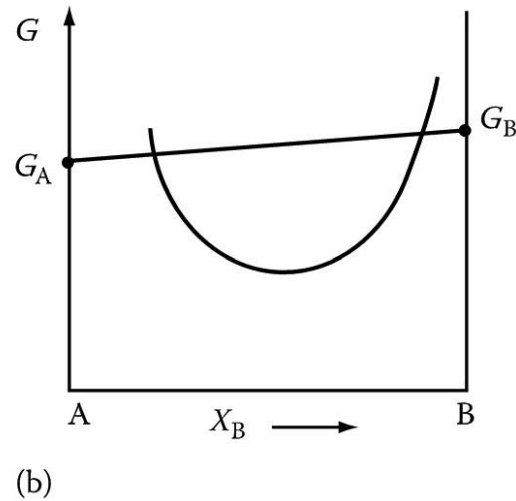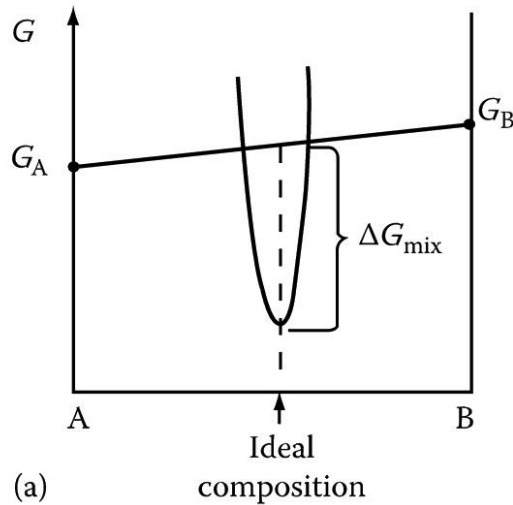(a) Random A-B solution with a total of 100 atoms and $X_A = X_B = 0.5, P_{AB} \sim 100, S = 0$.

(b) Same alloy with short-range order $P_{AB} = 132, P_{AB}(\max) \sim 200, S = 0.32$.

If $\Omega < 0$, and # P_{AB} is greater. $\rightarrow$ short range order (S) (vs. long range order)

$$S = \frac{P_{AB} - P_{AB}(random)}{P_{AB}(max) - P_{AB}(random)}$$

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1.3 Binary Solutions

❖ 1.3.8. Intermediate Phases

❖ When small composition deviation cause rapid rise of G

→ intermetallic compound.
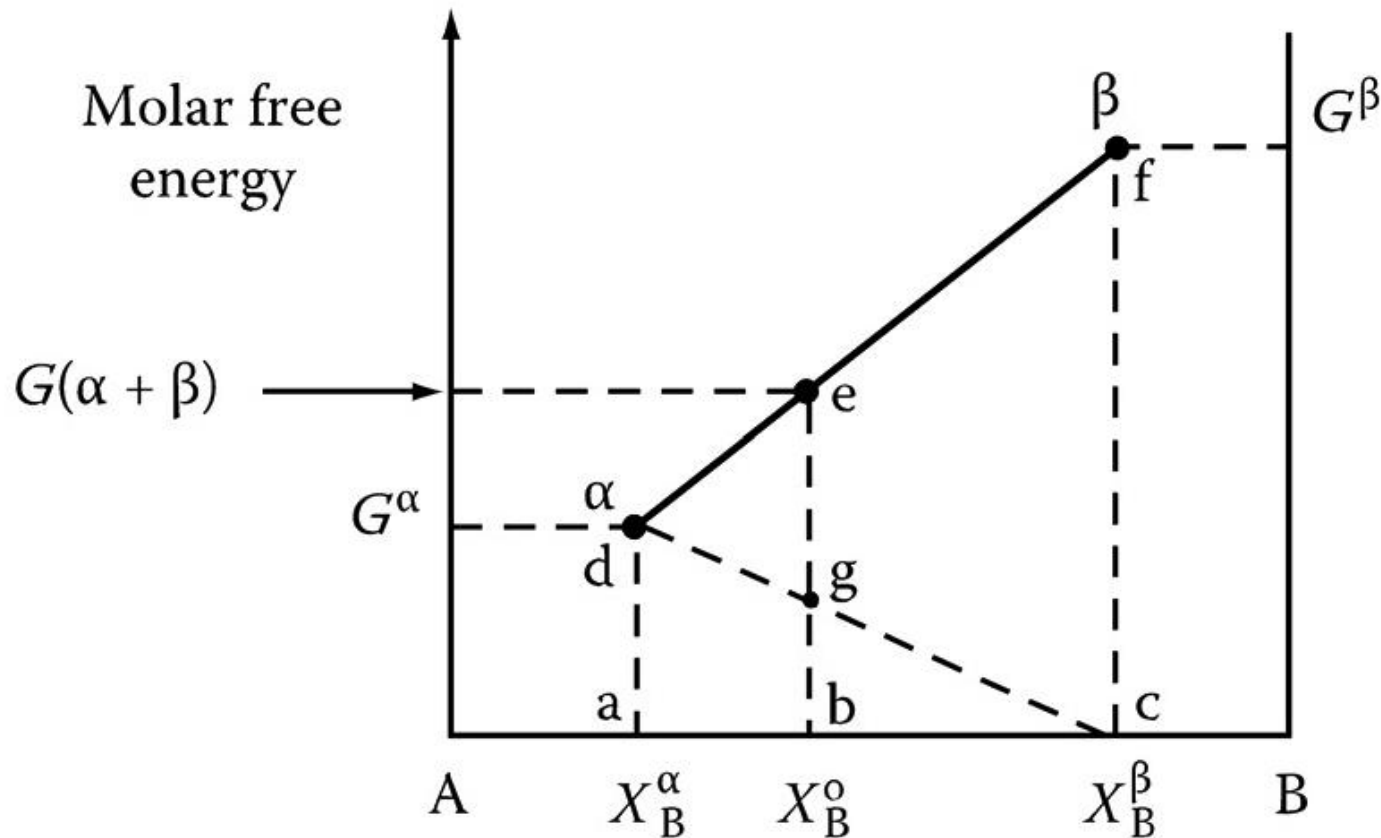
Usually stoichiometric $\qquad A_m B_n \ (m, n :\text{integer})$

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1.3 Binary Solutions

❖ **Ordered structures in Cu-Au system**

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❖ **The Molar Free Energy of Two-phase Mixture**
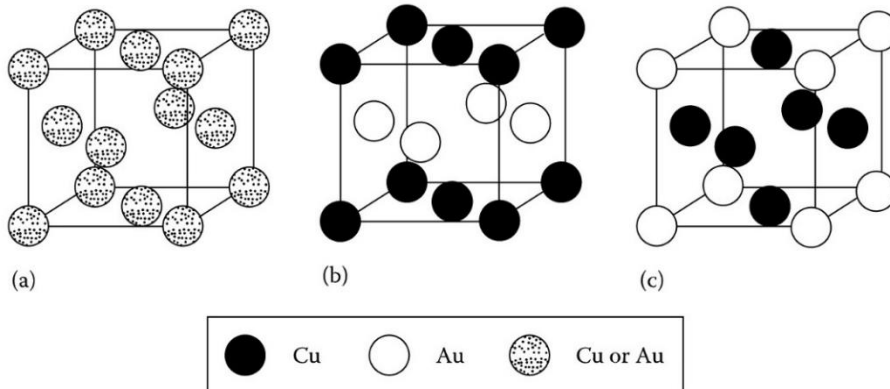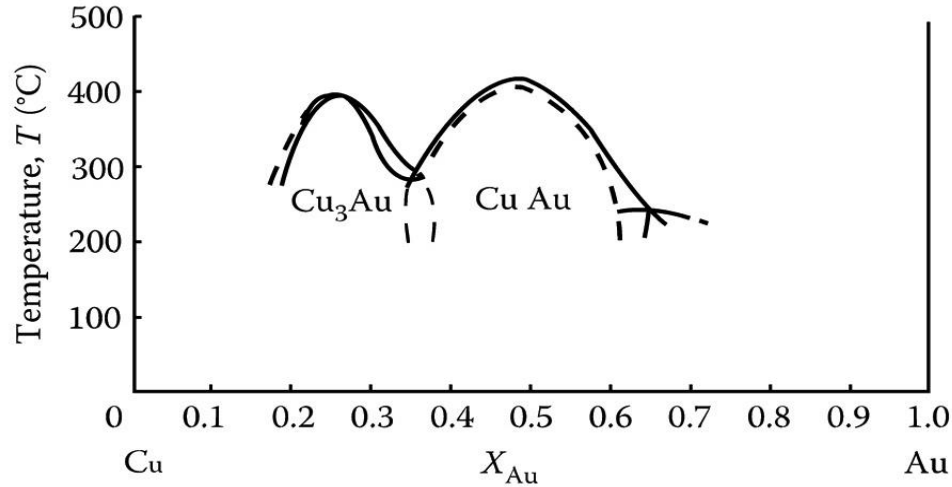
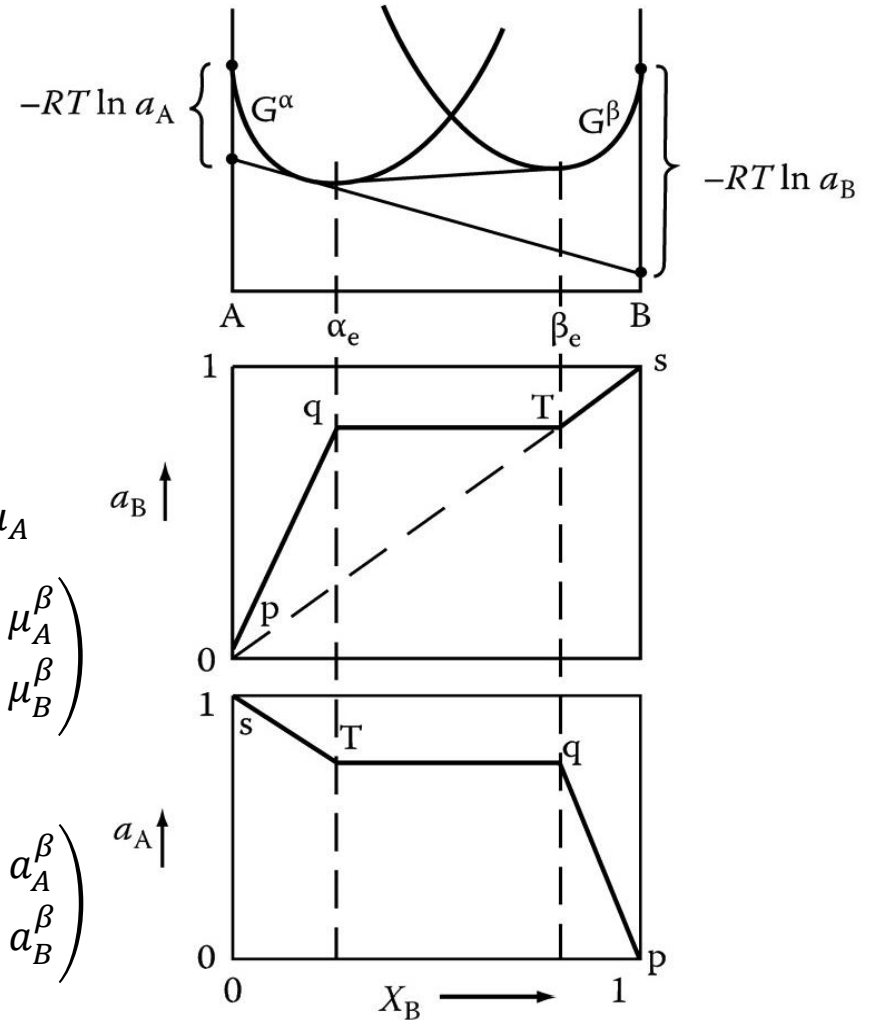# 1.4 Equilibrium in Heterogeneous Systems
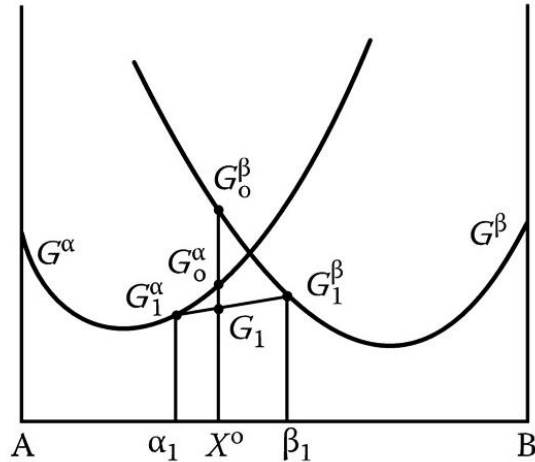
Equilibrium
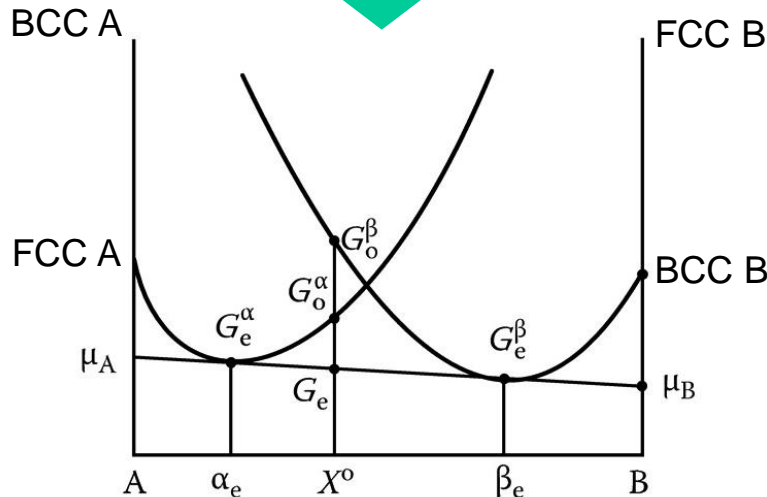
$$\mu_A^\alpha = \mu_A$$

$$\begin{pmatrix} \mu_A^\alpha = \mu_A^\beta \\ \mu_B^\alpha = \mu_B^\beta \end{pmatrix}$$

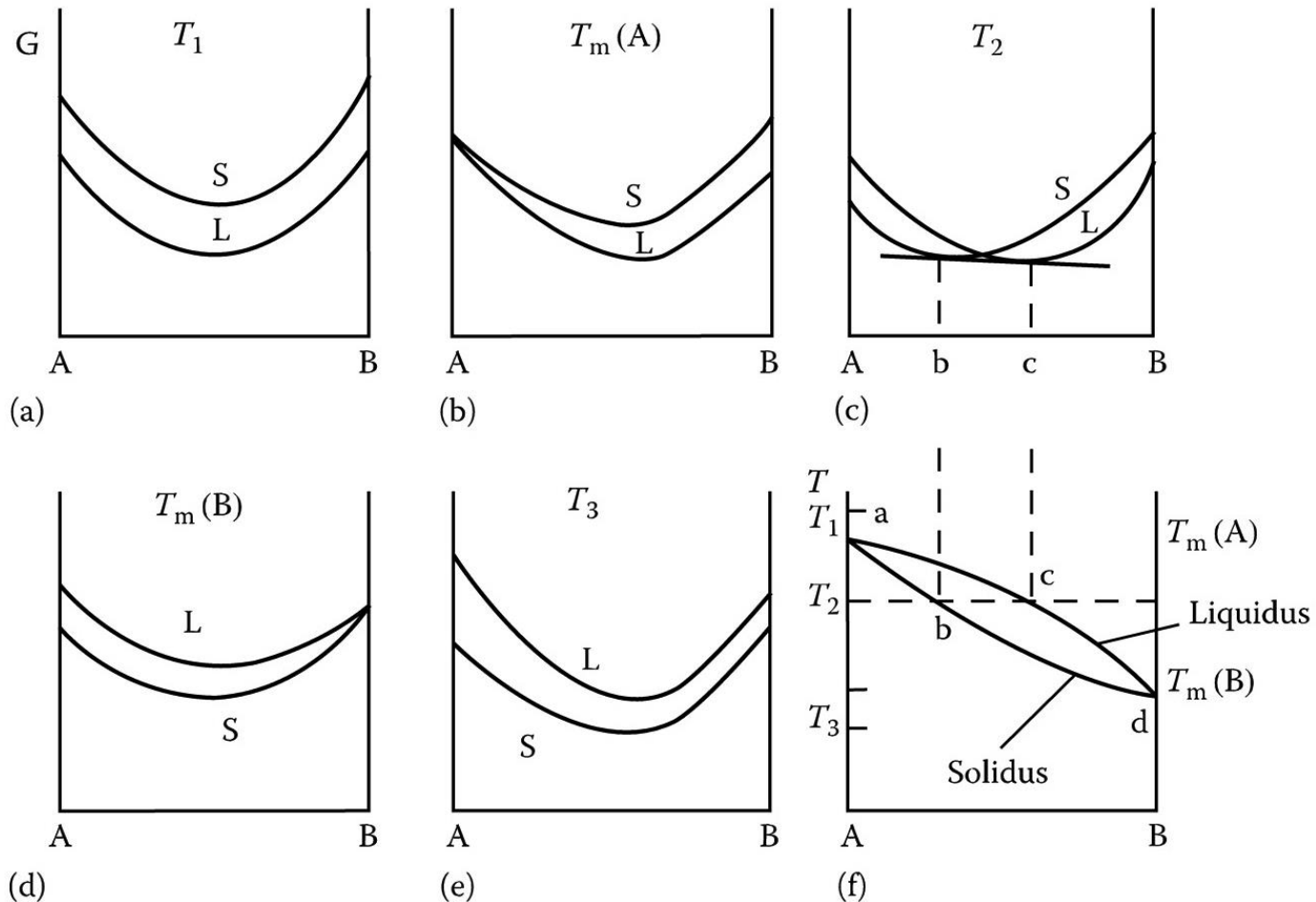$$\begin{pmatrix} a_A^\alpha = a_A^\beta \\ a_B^\alpha = a_B^\beta \end{pmatrix}$$

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1.5 Binary Phase Diagrams

❖ **A Simple Phase Diagram**

① Completely miscible

② Miscibility Gap
- Liquid phase (ideal)
- Solid phase ($\Delta H_{mix} > 0 \rightarrow$ A, B dislike)

③ Ordered Alloy
- $\Delta H_{mix} < 0$

④ Simple Eutectic
- Miscibility gap extend into liquid phase
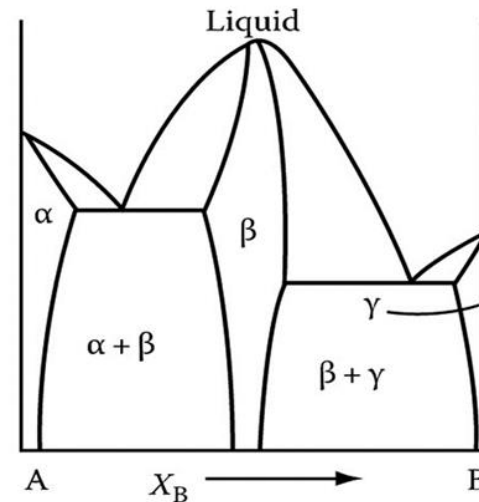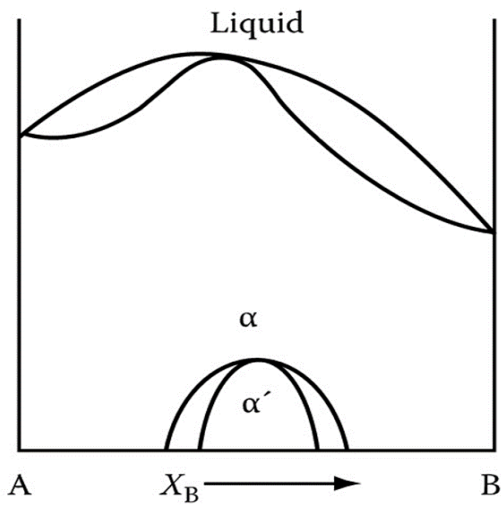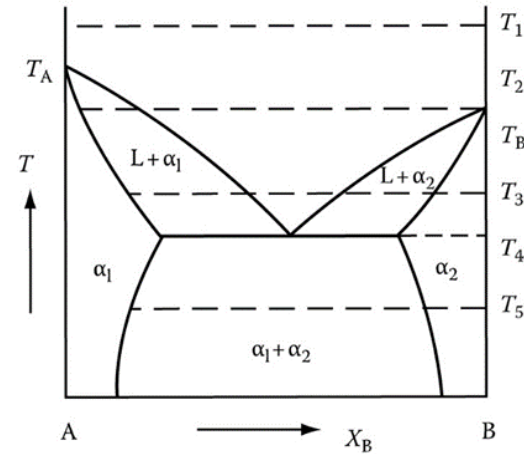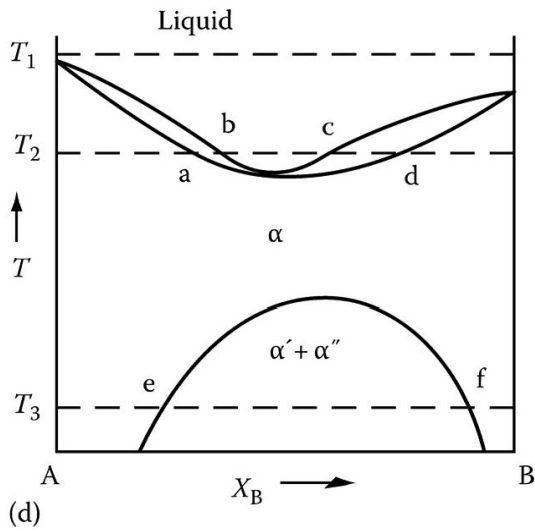
⑤ Phase diagram containing intermediate phase

Phase Transformation in Materials

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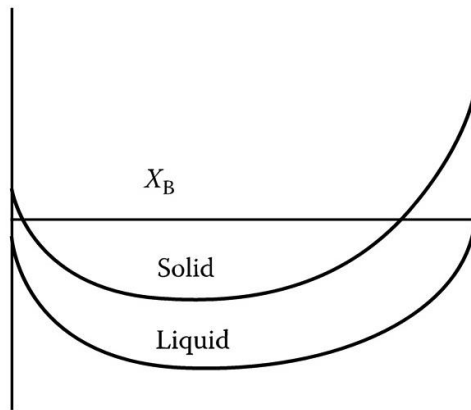
1.5 Binary Phase Diagrams

❖ A Simple Phase Diagram

Fig 1.29

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1.5 Binary Phase Diagrams(Summary)

Phase Transformation in Materials

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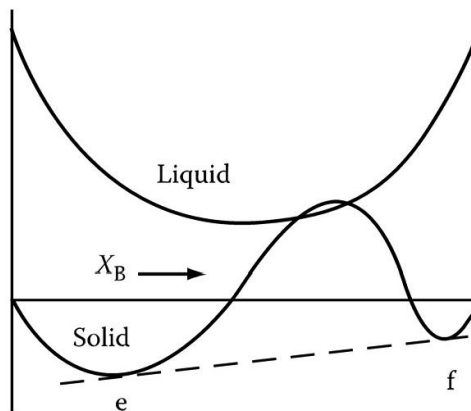
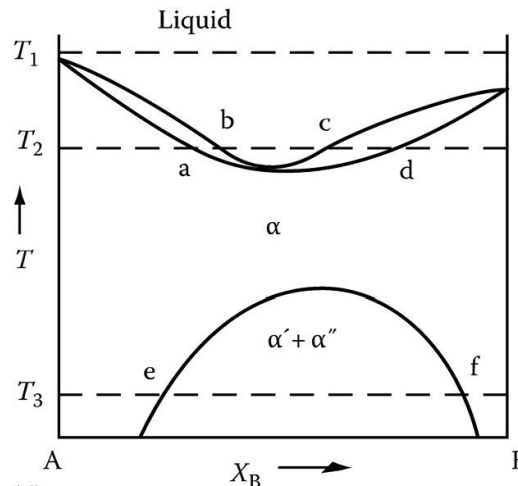❖ **System with a Miscibility Gap ($\Delta H_{mix}^{S} > \Delta H_{mix}^{L} = 0$)**
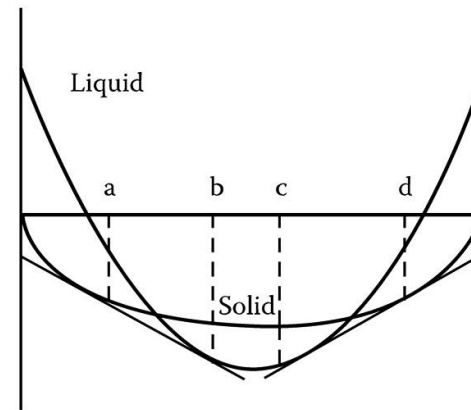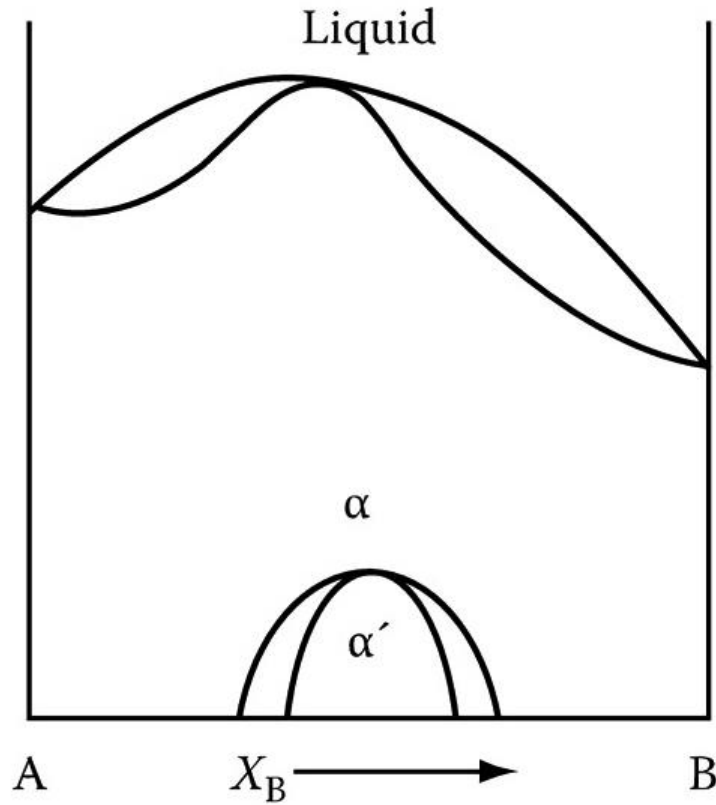
1.5 Binary Phase Diagrams

❖ Ordered Alloys ($\Delta H^S{}_{mix} < 0$)

(a)

(b)

Phase Transformation in Materials
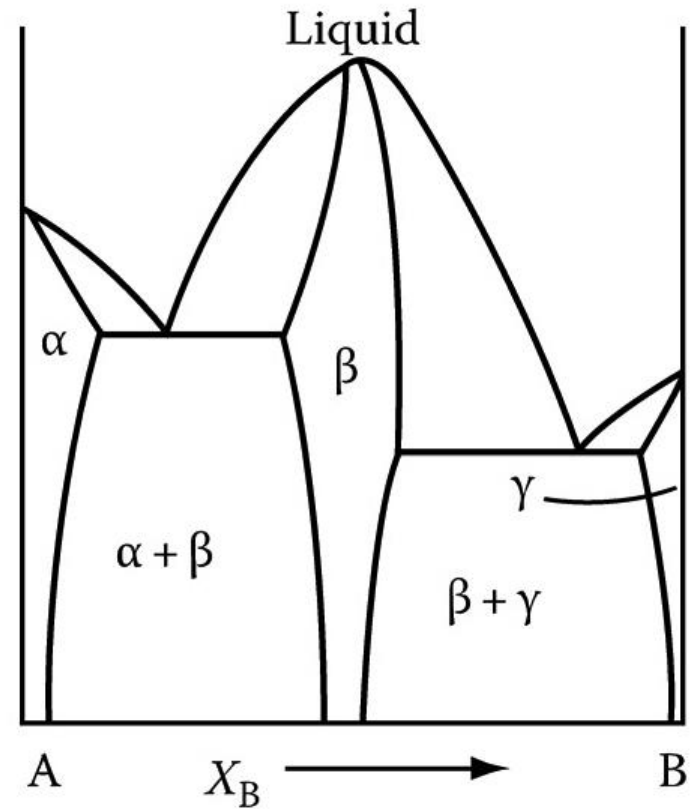
1.5 Binary Phase Diagrams

❖ **Eutectic Phase Diagram with Same Crystal Structure**

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❖ Eutectic Phase Diagram with Different Crystal Structure

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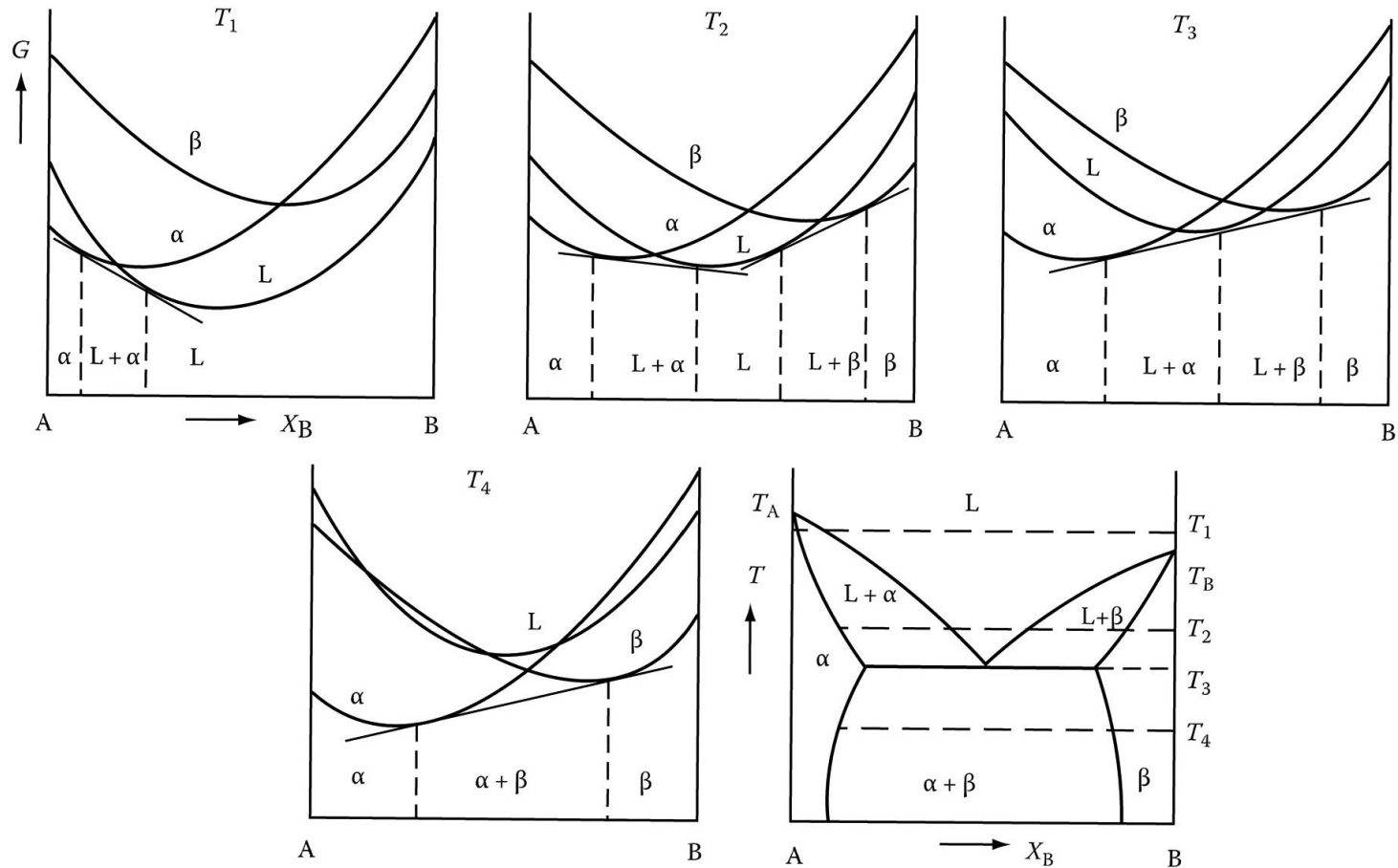
❖ More Complex Phase Diagram
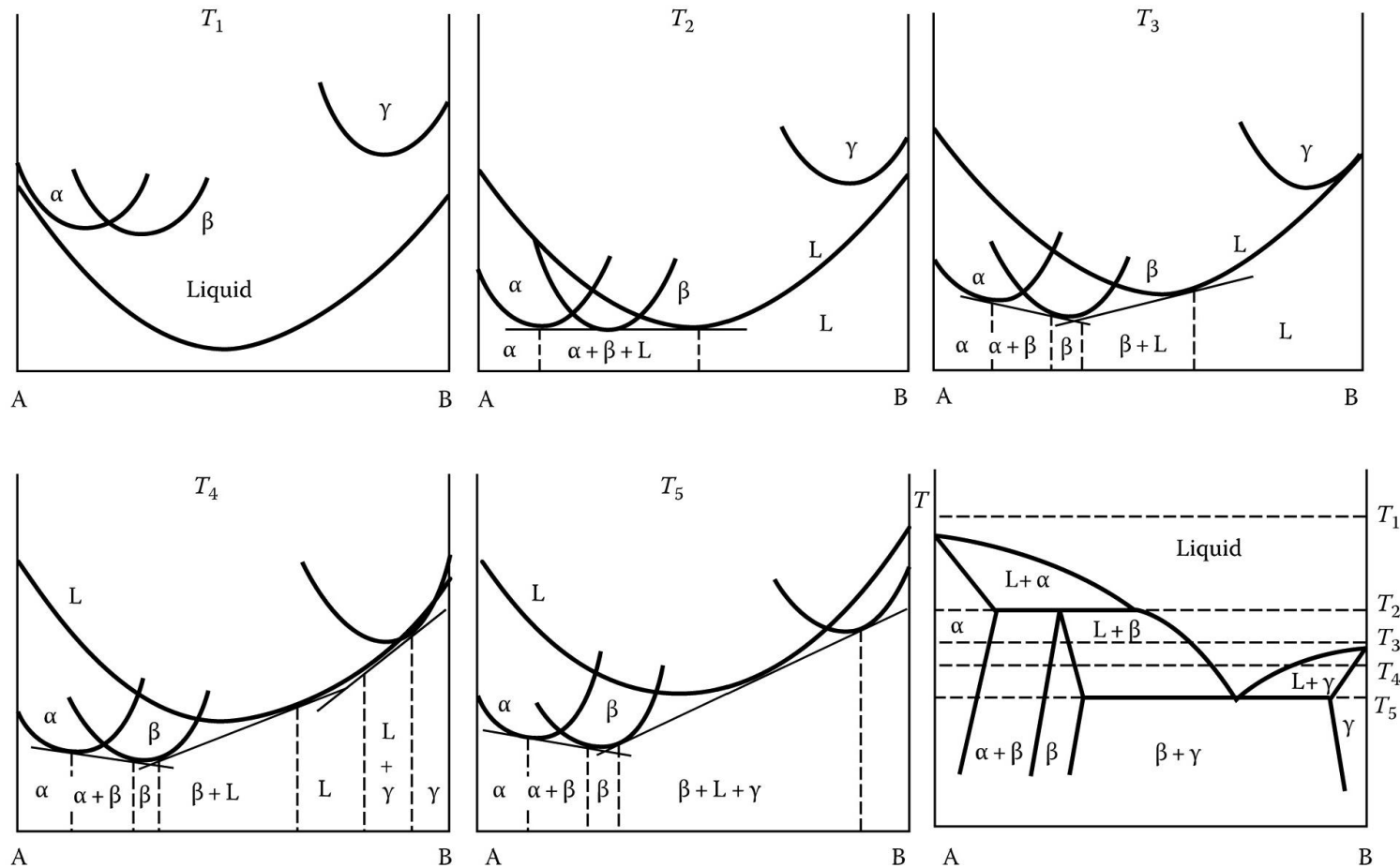
Phase Transformation in Materials

❖ **Phase Diagrams Containing Intermediate Phases**

G

α

β

γ

A

B

Stable compositions

Stoichiometric composition (A_mB_n)

Minimum G

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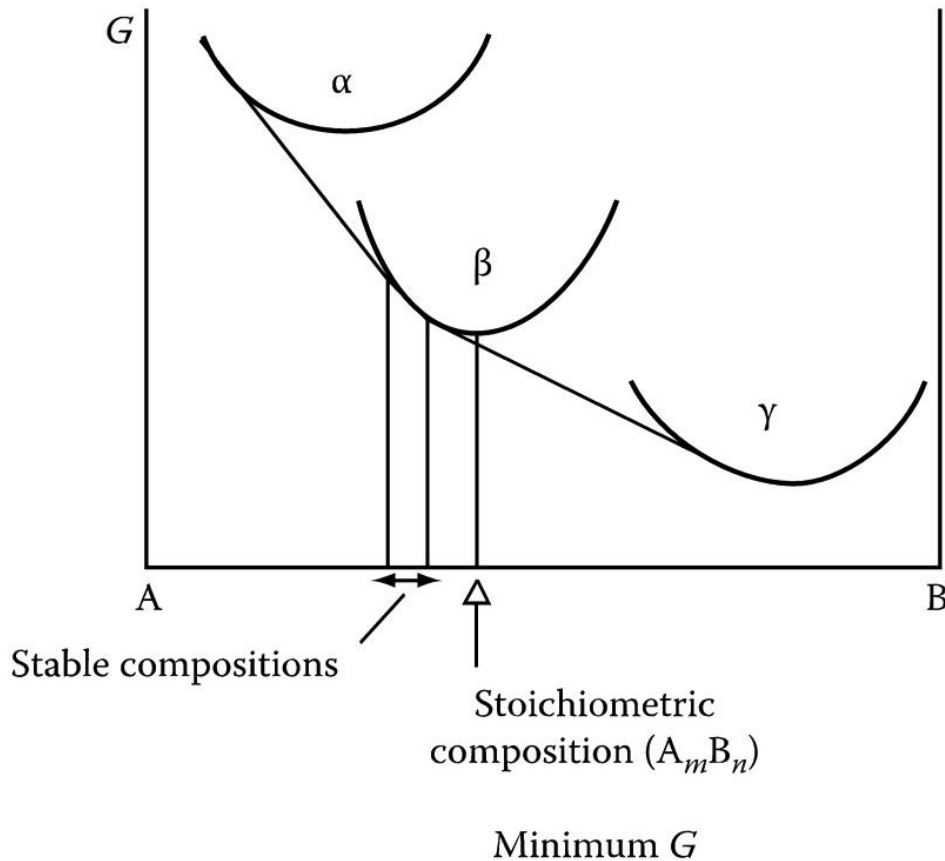
1.5 Binary Phase Diagrams

❖ **The Effect of Temperature on Solid Solubility**

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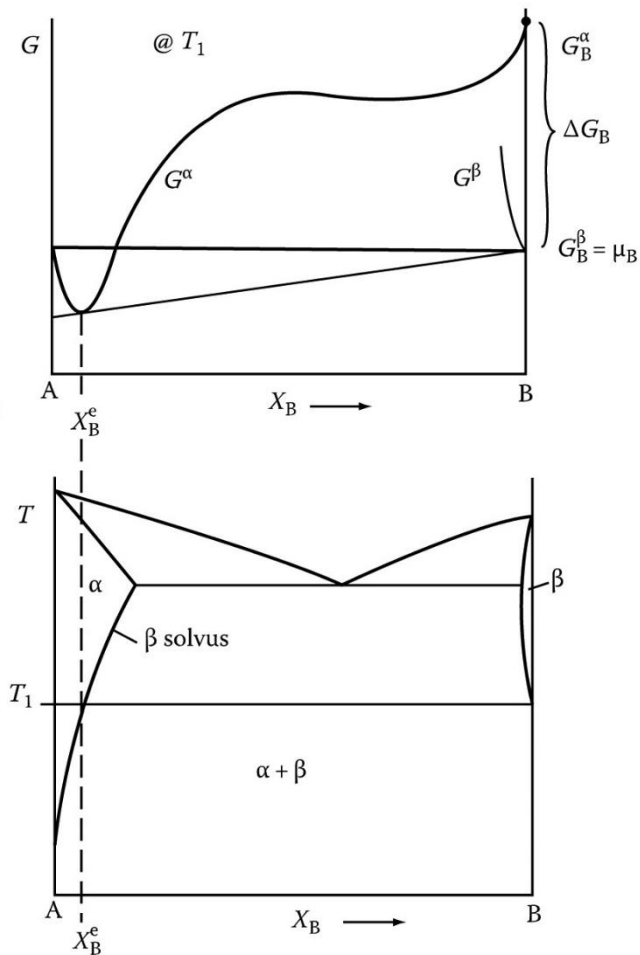
1.5 Binary Phase Diagrams

❖ **Equilibrium Vacancy Concentration**
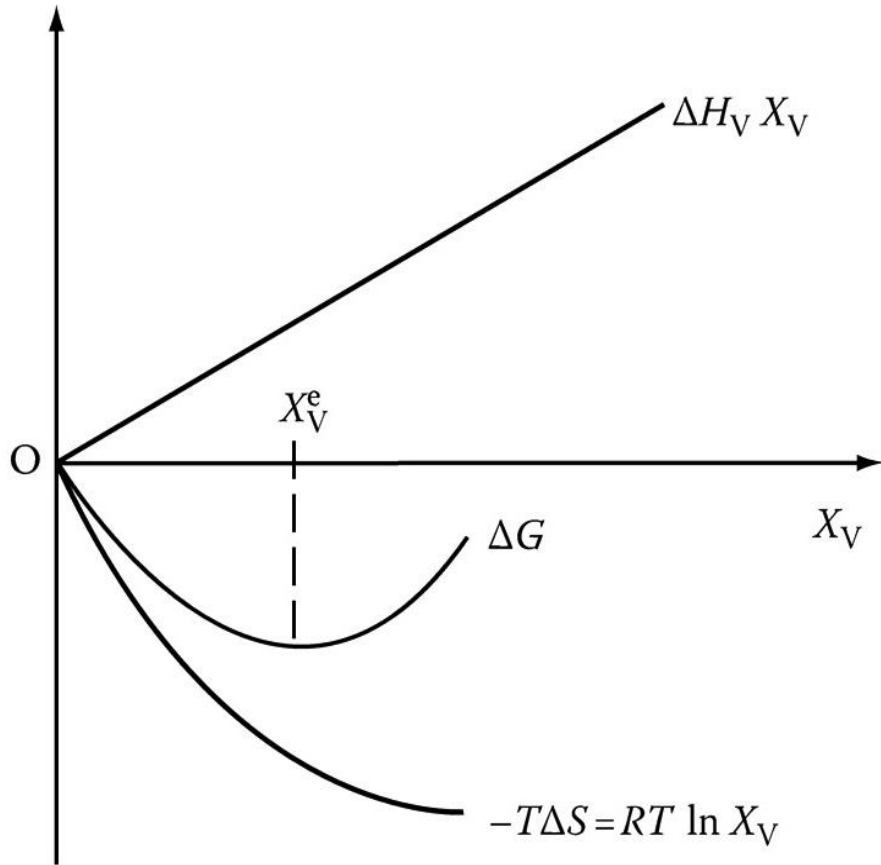
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1.6 The Influence of Interfaces on Equilibrium

❖ **The effect of interfacial energy on the solubility of small particles.**

Phase β in α
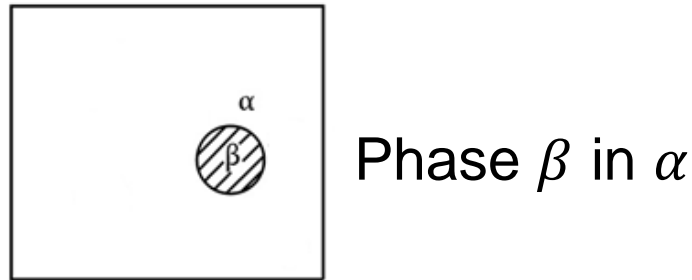
✓ Gibbs – Thompson Effect :

Extra pressure due to the curvature of α/β interface

ΔP

$$\boxed{\Delta P = \frac{2\gamma}{r}}$$

PV term in G increase

$$\Delta G = \Delta P \cdot V$$

Atmospheric pressure
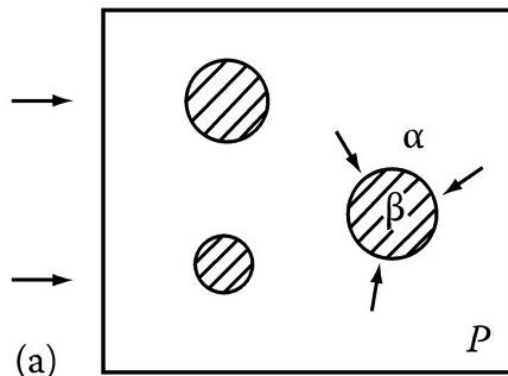
$$\boxed{\Delta G_r = \frac{2\gamma V_m}{r}}$$

V_m: molar volume of β phase

(a)

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1.6 The Influence of Interfaces on Equilibrium

❖ **Transfer of dn mol of β from large to small particle.**
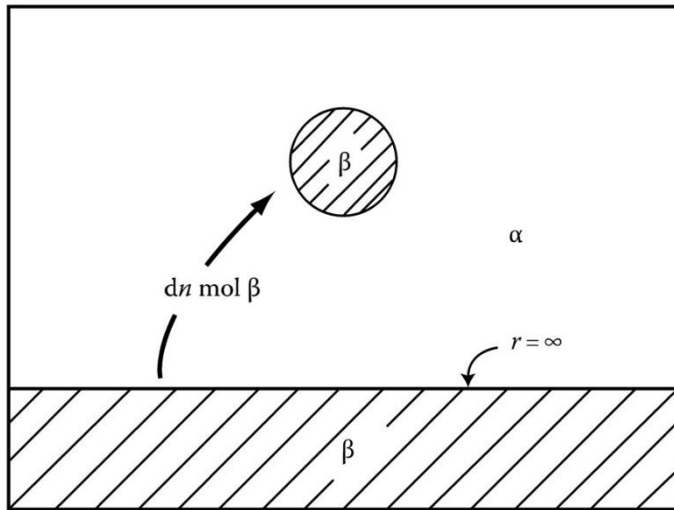
$dG = \Delta G_r \cdot dn$

(ΔG_r: molar free energy difference

between two particles)

$dG = \gamma dA$

($\because$ Large particle $\rightarrow$ unchanged, small $\rightarrow$ changed)

dn mol β

$r = \infty$

$\gamma dA = \Delta G_r \cdot dn$

$\Delta G_r = \gamma \dfrac{dA}{dn}$

$n = \dfrac{4\pi r^2}{3V_m}, \ A = 4\pi r^2, \ \dfrac{dA}{dn} = \dfrac{dA/dr}{dn/dr} = \dfrac{2V_m}{r}$

$\therefore \ \Delta G_r = \dfrac{2\gamma V_m}{r}$

Phase Transformation in Materials

**Nano & Flexible
Device Materials Lab.**

1.6 The influence of interfaces on Equilibrium

❖ **The effect of interfacial energy on the solubility of small particles**

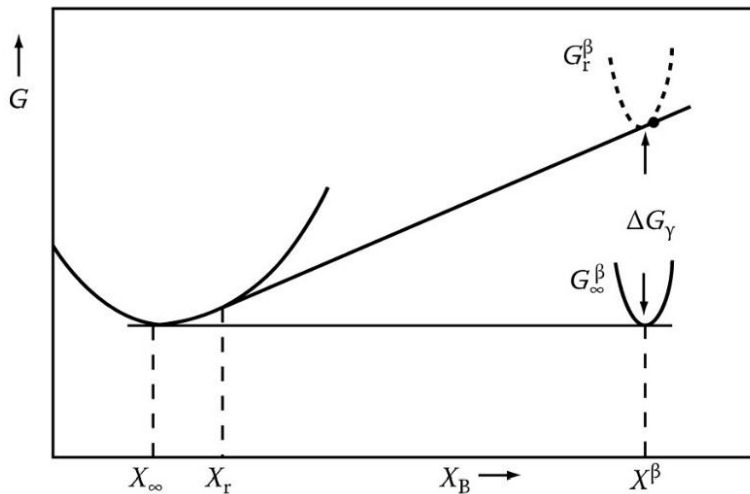$$X_\infty = exp\left(-\frac{\Delta G_B + \Omega}{RT}\right)$$

$$X_r = exp\left(-\frac{\Delta G_B + \Omega - {2\gamma V_m}/{r}}{RT}\right)$$

$$X_r = X_\infty \cdot exp\left(\frac{2\gamma V_m}{RT \cdot r}\right)$$

$$\approx X_\infty \left(1 + \frac{2\gamma V_m}{RT \cdot r}\right)$$

Typical value : $\gamma = 200\ mJ/m^2$, $V_m = 10^{-5}\ m^3$

$$\frac{X_r}{X_\infty} \approx 1 + \frac{1}{r\ (nm)}\ (10\ \text{nm} \rightarrow \frac{X_r}{X_\infty} = 1.1\ (10\ \%\ \text{diff}))$$

Phase Transformation in Materials

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