2009 fall

Phase Transformation of Materials

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Contents for previous class

Chapter 1 Thermondynamics and Phase Diagrams

- **Equilibrium** $dG = 0$

  Lowest possible value of G

  No desire to change ad infinitum

- **Phase Transformation** $\Delta G = G_2 - G_1 < 0$

- **Single component system**

  Gibbs Free Energy as a Function of Temp. and Pressure

  $\left(\frac{\partial G}{\partial T}\right)_P = -S, \quad \left(\frac{\partial G}{\partial P}\right)_T = V$

  $(\frac{dP}{dT})_{eq} = \frac{\Delta H}{T_{eq}\Delta V}$ ***Clausius-Clapeyron Relation*** :

- **Driving force for solidification** $\Delta G = \frac{L\Delta T}{T_m}$

- **Classification of phase transition**

  First order transition: CDD/Second order transition: CCD

Contents for today's class

- Binary System

- Gibbs Free Energy in Binary System

  Ideal solution and Regular solution

- Chemical potential and Activity

1.3 Binary Solutions

* **Single component system** **One element (Al, Fe), One type of molecule (H_2O)**

: 평형 상태 압력과 온도에 의해 결정됨

* **Binary System (two component)** → A, B

: 평형 상태 압력과 온도 이외에도 조성의 변화를 고려

- **Mixture ; A – A, B – B ;** → 각각의 성질 유지, **boundary**는 존재,
  섞이지 않고 기계적 혼합

  A B

- **Solution ; A – A – A ;** → **atomic scale**로 섞여 있다. **Random distribution**

  A – B – A **Solid solution : substitutional or interstitial**

- **compound ; A – B – A – B ;** → **A, B**의 위치가 정해짐, **Ordered state**

  B – A – B – A

1.3 Binary Solutions

- **Mixture ; A – A, B – B ;** → 각각의 성질 유지, **boundary**는 존재,
  섞이지 않고 기계적 혼합

A **B**

사금 채취

키질

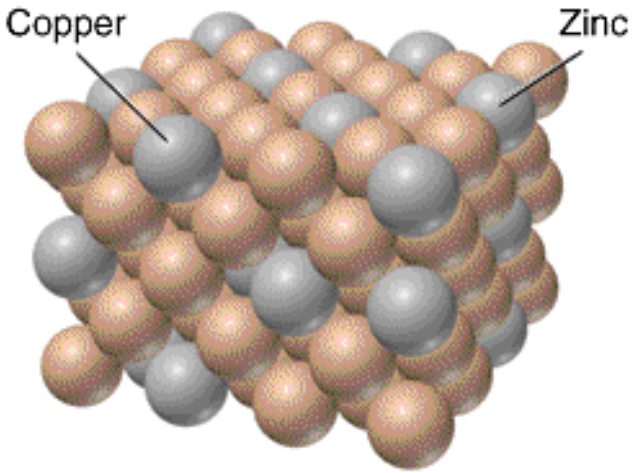
쌀 씻기

달걀 고르기

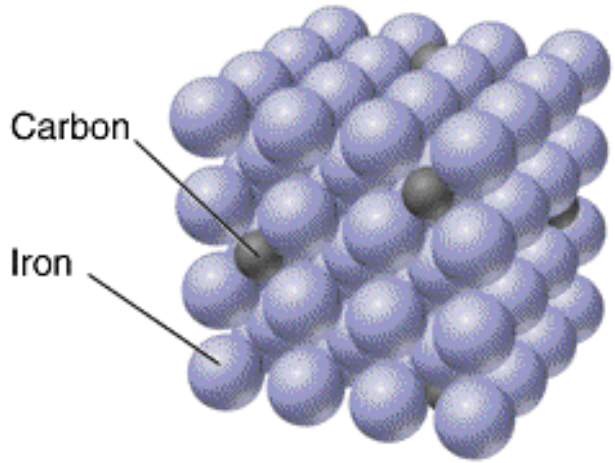
1.3 Binary Solutions

- **Solution ; A – A – A ; → atomic scale로 섞여 있다. Random distribution**

  A – B – A Solid solution : substitutional or interstitial



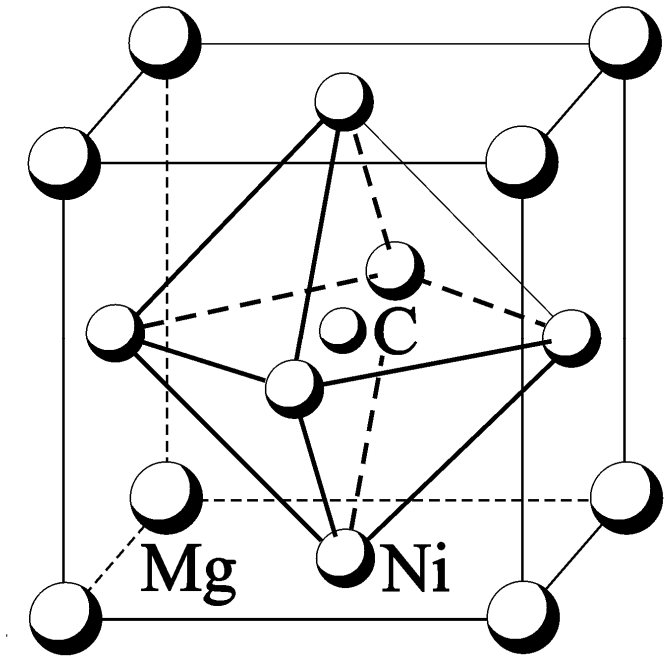
A Brass, a substitutional alloy



B Carbon steel, an interstitial alloy

- **Compound ; A – B – A – B ; → A, B** 의 위치가 정해짐, **Ordered state**

B – A – B – A

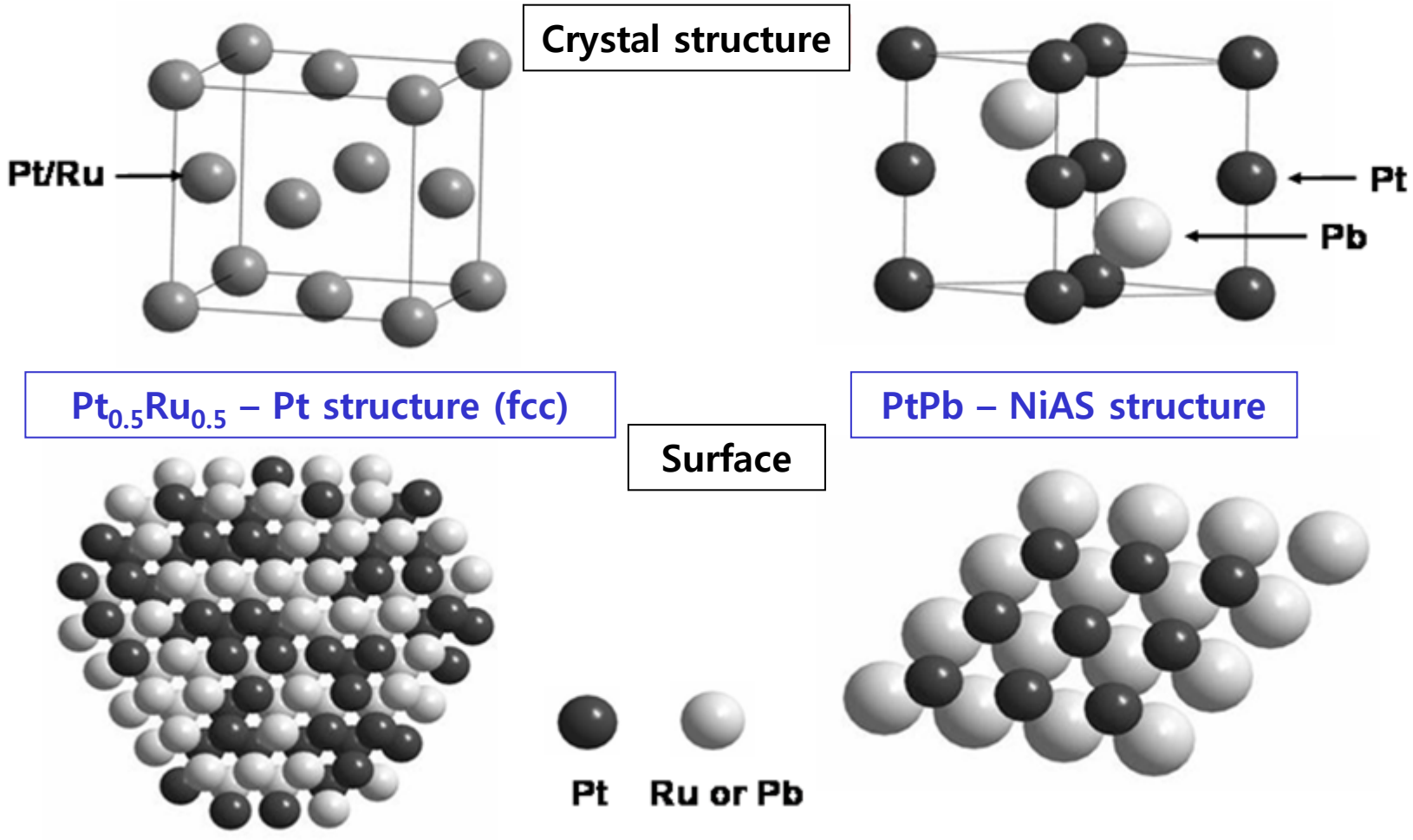


MgCNi3

1.3 Binary Solutions

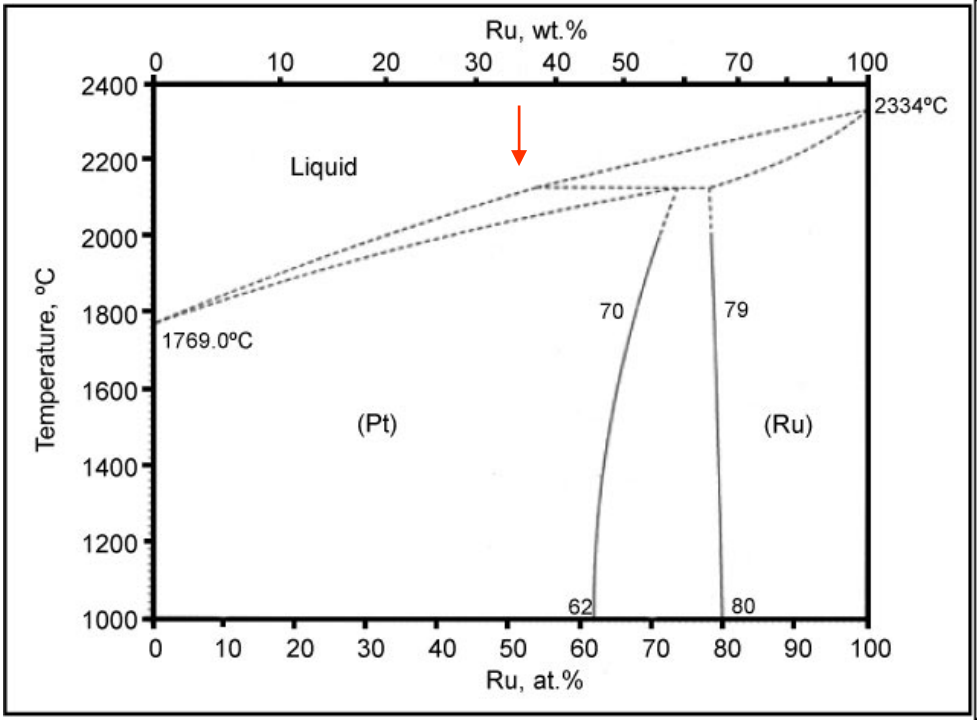
Alloying: atoms mixed on a lattice ➡ partial or complete solid solution

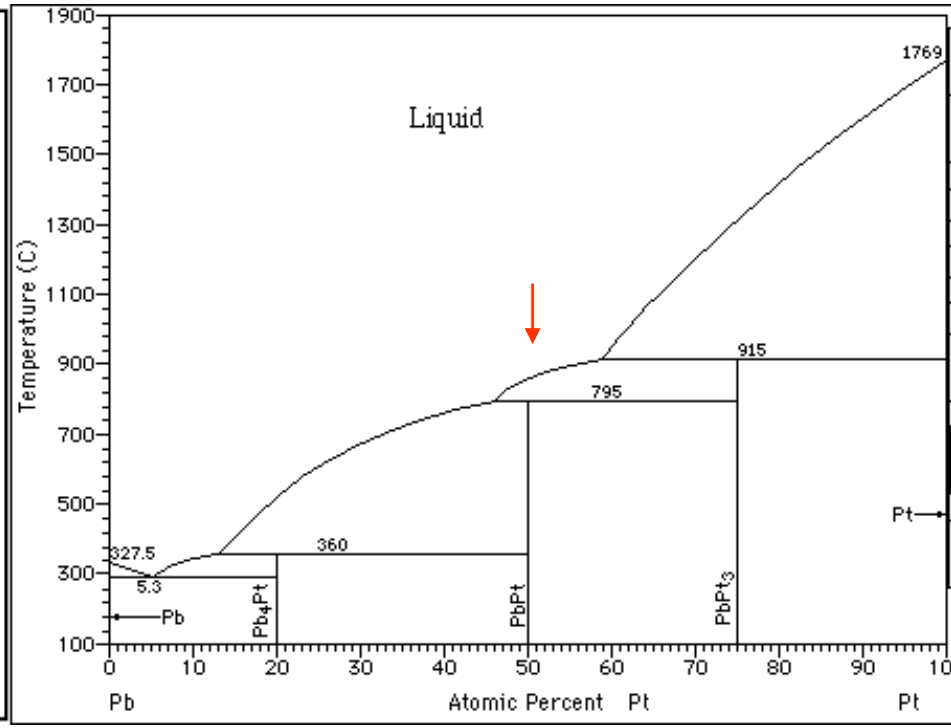
Solid Solution vs. Intermetallic Compounds



ruthenium 루테늄《백금류의 금속 원소;기호 Ru, 번호 44》

Solid Solution vs. Intermetallic Compounds





$Pt_{0.5}Ru_{0.5}$ – Pt structure (fcc)

PbPt – NiAS structure

1.3 Binary Solutions

- ***Solid solution:***
  - Crystalline solid
  - Multicomponent yet homogeneous
  - Impurities are randomly distributed throughout the lattice

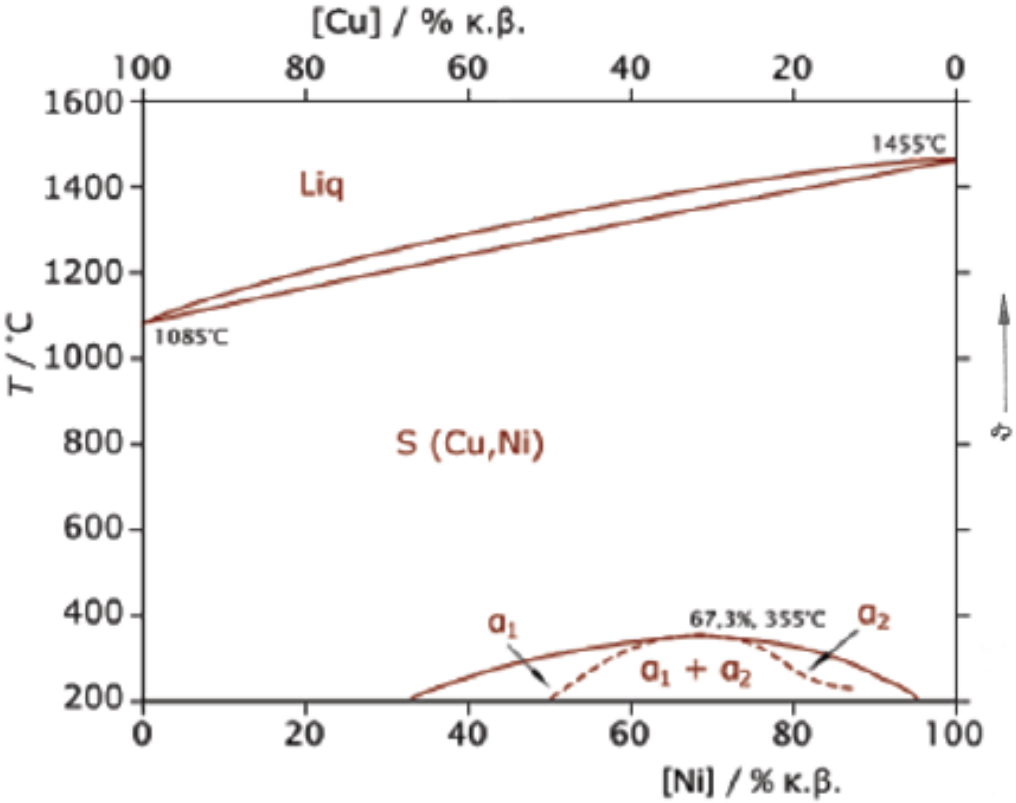
- **Factors favoring solubility of B in A (Hume-Rothery Rules)**
  - ***Similar atomic size:*** $\Delta r/r \leq 15\%$
  - ***Same crystal structure*** for A and B
  - ***Similar electronegativities:*** $|\chi_A - \chi_B| \leq 0.6$ (preferably ≤ 0.4)
  - ***Similar valence***

- If all four criteria are met: ***complete solid solution***

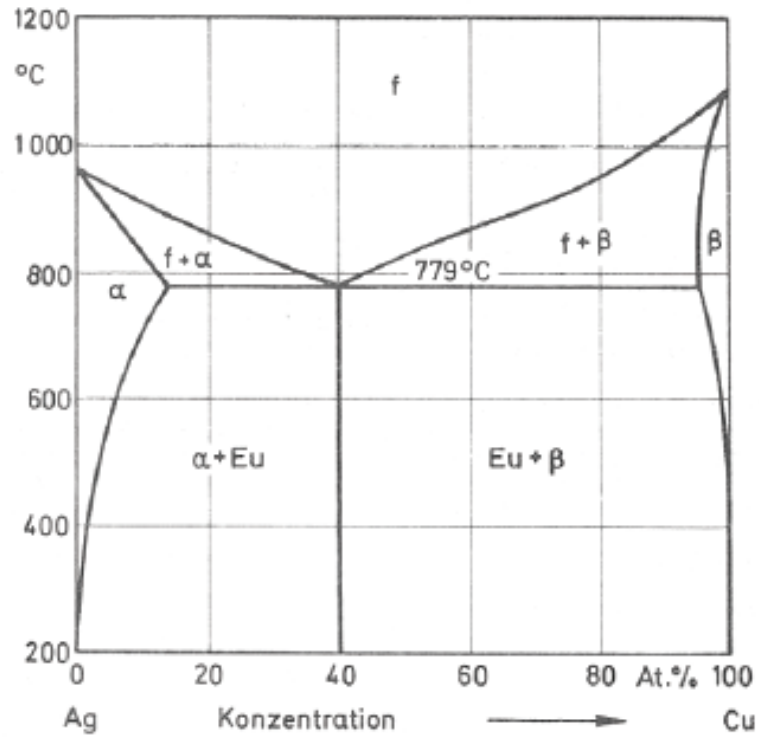
- If any criterion is not met: ***limited solid solution***

1.3 Binary Solutions

Cu-Ni Alloys



Cu-Ag Alloys



complete solid solution

limited solid solution

Binary Solutions

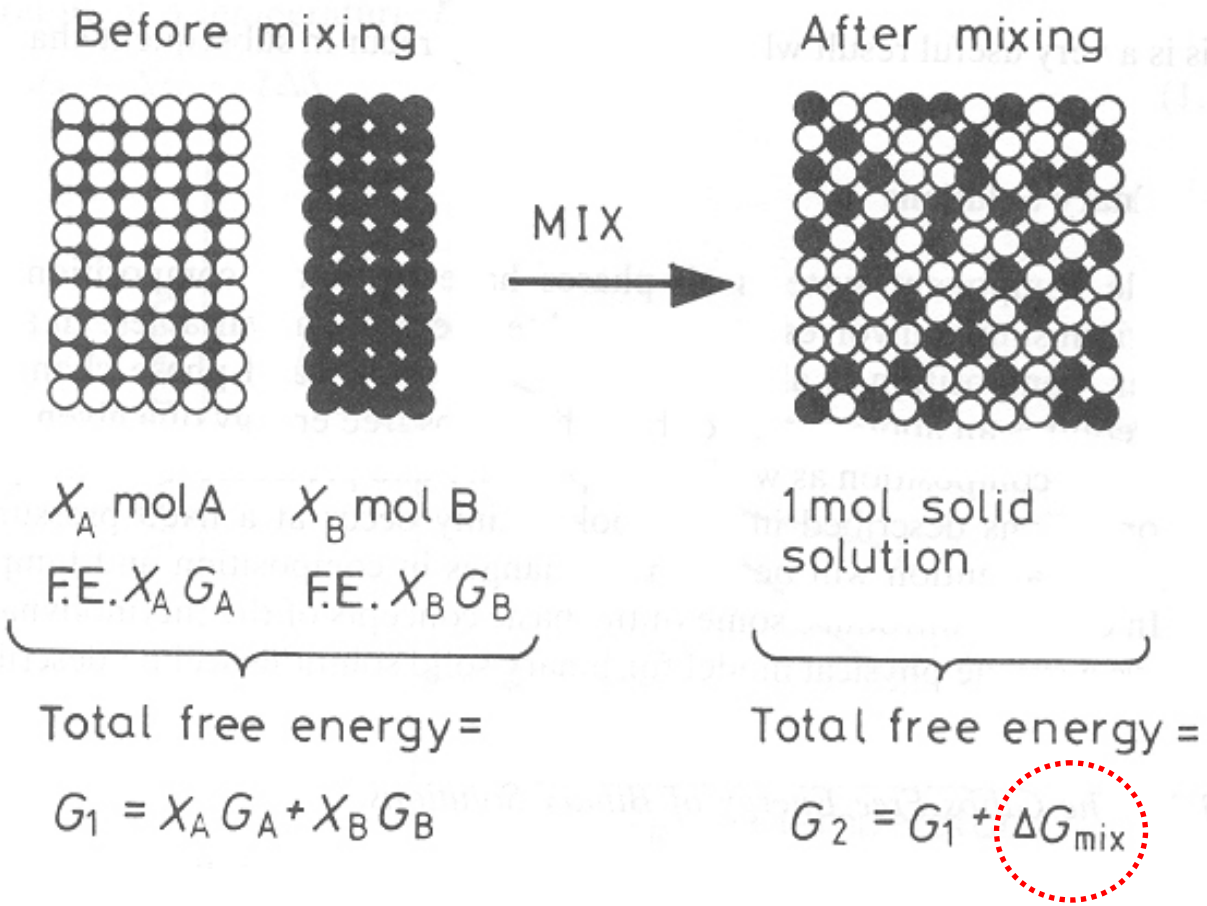
: 합금에 대한 열역학 기본 개념 도입 위해 2원 고용체, 1기압의 고정된 압력 조건 고려

Gibbs Free Energy of Binary Solutions

*** Composition in mole fraction X_A, X_B $X_A + X_B = 1$**

1. bring together X_A mole of pure A and X_B mole of pure B

2. allow the A and B atoms to mix together to make a homogeneous solid solution.



Gibbs Free Energy of The System

In Step 1

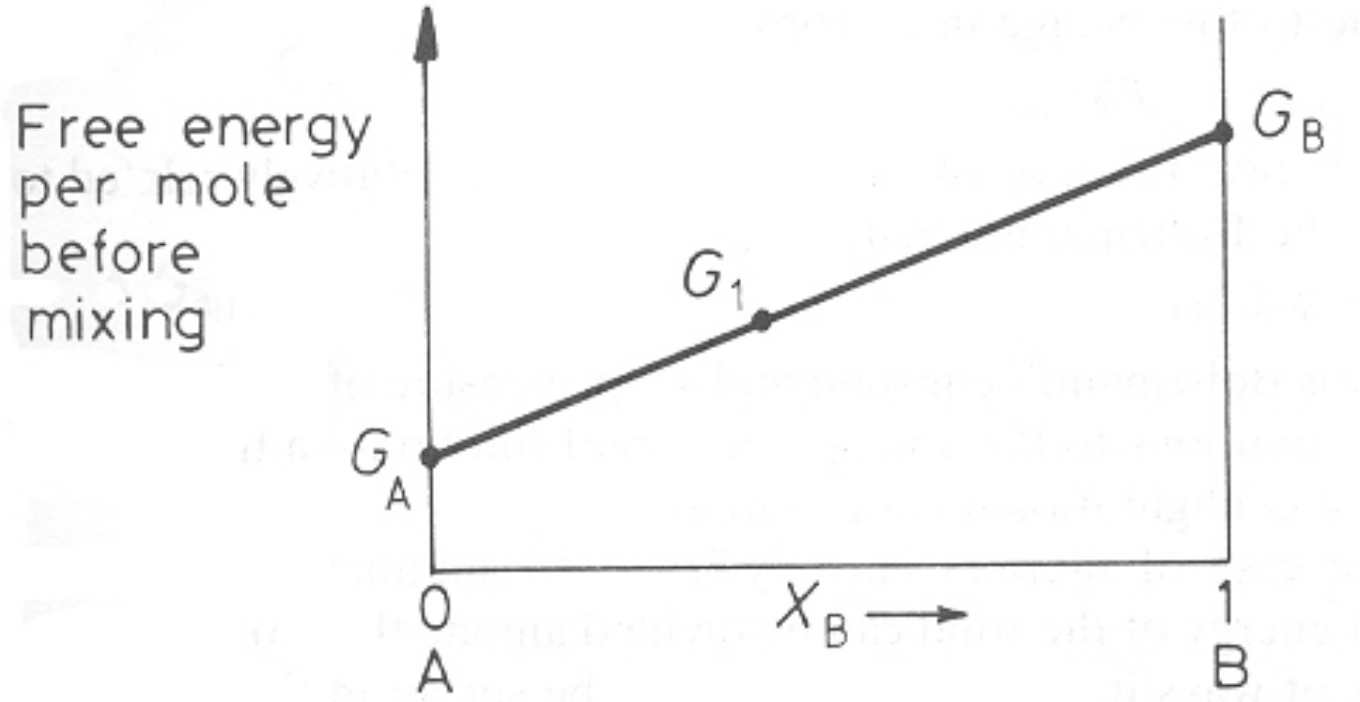
- **The molar free energies of pure A and pure B**

pure A; $G_A(T,P)$

pure B; $G_B(T,P)$

;X_A, X_B (mole fraction)

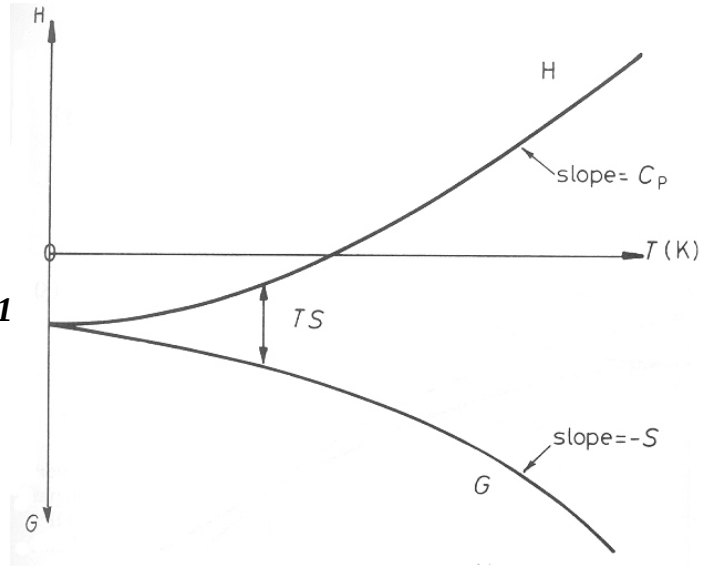
$$G_1 = X_A G_A + X_B G_B \quad J/mol$$



➡ **Free energy of mixture**

Gibbs Free Energy of The System

In Step 2 $G_2 = G_1 + \Delta G_{mix}$ *J/mol*



Since $G_1 = H_1 - TS_1$ and $G_2 = H_2 - TS_2$

And putting $\Delta H_{mix} = H_2 - H_1$ $\Delta S_{mix} = S_2 - S_1$

$$\Delta G_{mix} = \Delta H_{mix} - T\Delta S_{mix}$$

ΔH_{mix} : ***Heat of Solution*** i.e. heat absorbed or evolved during step 2

ΔS_{mix} : ***difference in entropy*** between the mixed and unmixed state.

➡ ***How can you estimate ΔH_{mix} and ΔS_{mix} ?***

Mixing free energy ΔG_{mix}

- Ideal solution

가정1 ; $\Delta H_{mix}=0$:

; A와 B가 complete solid solution

(A,B ; same crystal structure)

; no volume change

$$\Delta G_{mix} = \Delta H_{mix} - T\Delta S_{mix}$$

$$\Delta G_{mix} = -T\Delta S_{mix}\ J/mol$$

Entropy can be computed from randomness

by Boltzmann equation, i.e.,

$$S = k \ln w$$

w : degree of randomness, k: Boltzman constant

→ **thermal**; vibration (no volume change)

→ **Configuration**; atom 의 배열 방법 수 (distinguishable)

$$S = S_{th} + S_{config}$$

Excess mixing Entropy

If there is no volume change or heat change,

$$w_{config} = 1 \quad \rightarrow before\_solution\_(pureA\_pureB)$$

$$w_{config} = \frac{(N_A + N_B)!}{N_A! N_B!} \rightarrow after\_solution\_(N_A, N_B)$$

Number of distinguishable way of atomic arrangement

$$\Delta S^{mix} = S^{after} - S^{before} = k \ln \frac{(N_A + N_B)!}{N_A! N_B!} - k \ln 1$$

$$\rightarrow N_A = X_A N_0 \,,\ N_B = X_B N_0, N_A + N_B = N_0 \quad \text{이므로}$$

using Stirling's approximation $\ln N! \approx N \ln N - N$

and $R = kN_0$

$$= k[(N_o \ln N_o - N_o) - (X_A N_o \ln X_A N_o - X_A N_o) - (X_B N_o \ln X_B N_o - X_B N_o)]$$

Excess mixing Entropy

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

$\Delta G_{mix} = -T\Delta S_{mix}$ ➡ $\Delta G^{mix} = RT(X_A \ln X_A + X_B \ln X_B)$

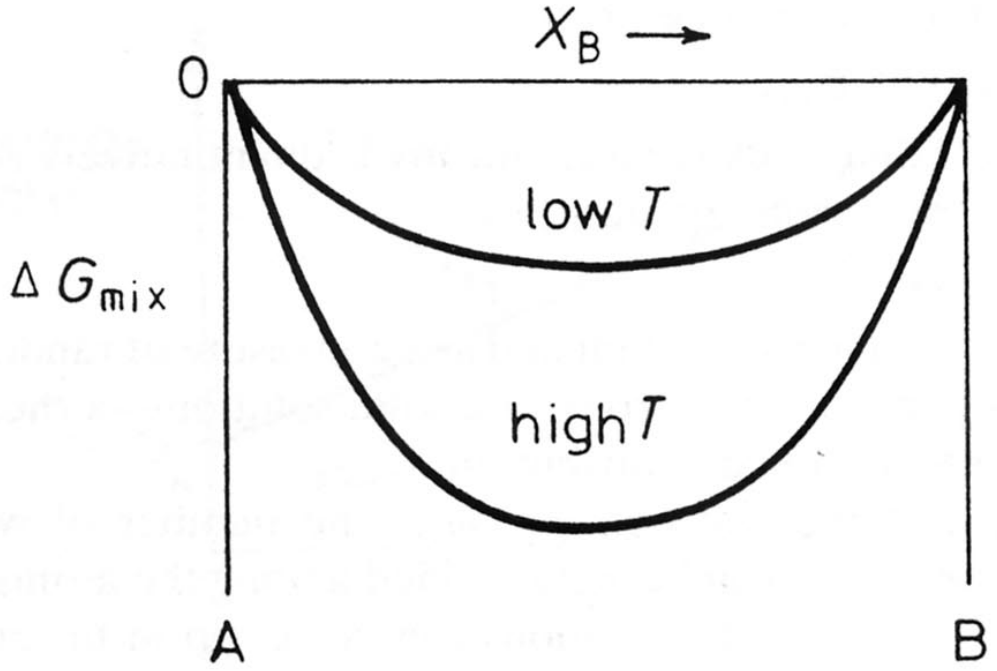


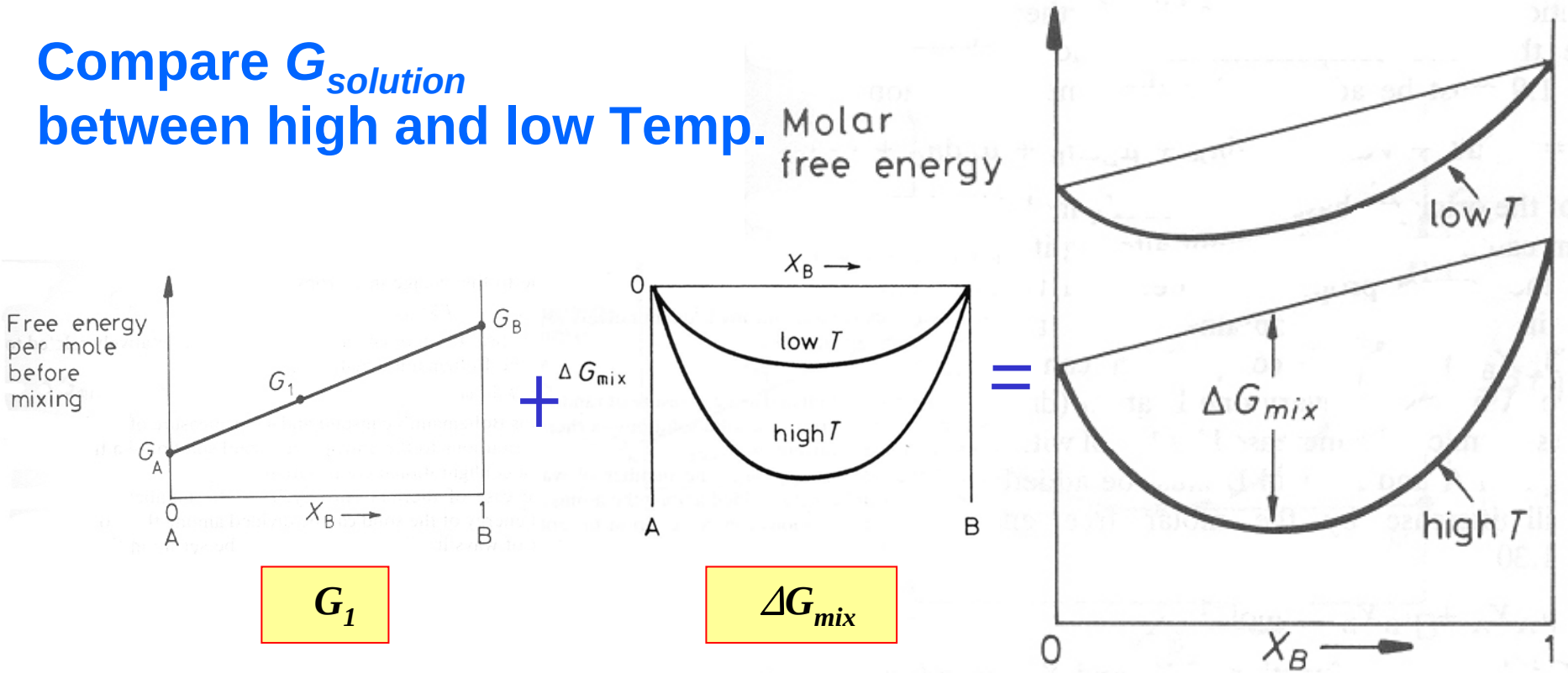
Fig. 1.9 Free energy of mixing for an ideal solution.

Since $\Delta H = 0$ for ideal solution,

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

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

Compare $G_{solution}$ between high and low Temp.

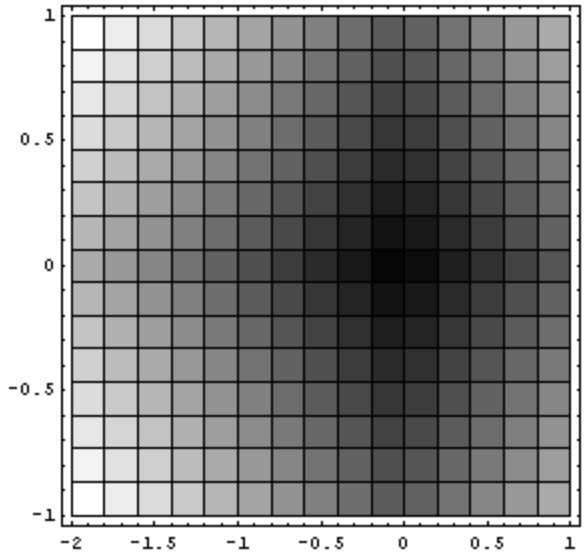


G_1 ΔG_{mix}

Fig. 1.10 The molar free energy (free energy per mole of solution) for an ideal solid solution. A combination of Figs. 1.8 and 1.9.

$G = H-TS = E+PV-TS$

Chemical potential



The increase of the total free energy of the system by the increase of very small quantity of A, dn_A, will be proportional to dn_A.

➡ 소량 첨가에 의한 내부 에너지 변화 계산

$$dG' = \mu_A \, dn_A \qquad (T, P, n_B: \text{constant})$$

μ_A : **partial molar free energy of A or chemical potential of A**

$$\mu_A = \left(\frac{\partial G'}{\partial n_A}\right)_{T,P,n_B} \qquad \mu_B = \left(\frac{\partial G'}{\partial n_B}\right)_{T,P,n_A}$$

For A-B binary solution, $dG' = \mu_A dn_A + \mu_B dn_B$

For variable T and P

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

Chemical potential 과 Free E와의 관계

1) Ideal solution

For 1 mole of the solution (T, P: constant)

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

$$dG = \mu_A dX_A + \mu_B dX_B \qquad \frac{dG}{dX_B} = \mu_B - \mu_A$$

$$\mu_A = \mu_B - \frac{dG}{dX_B}$$

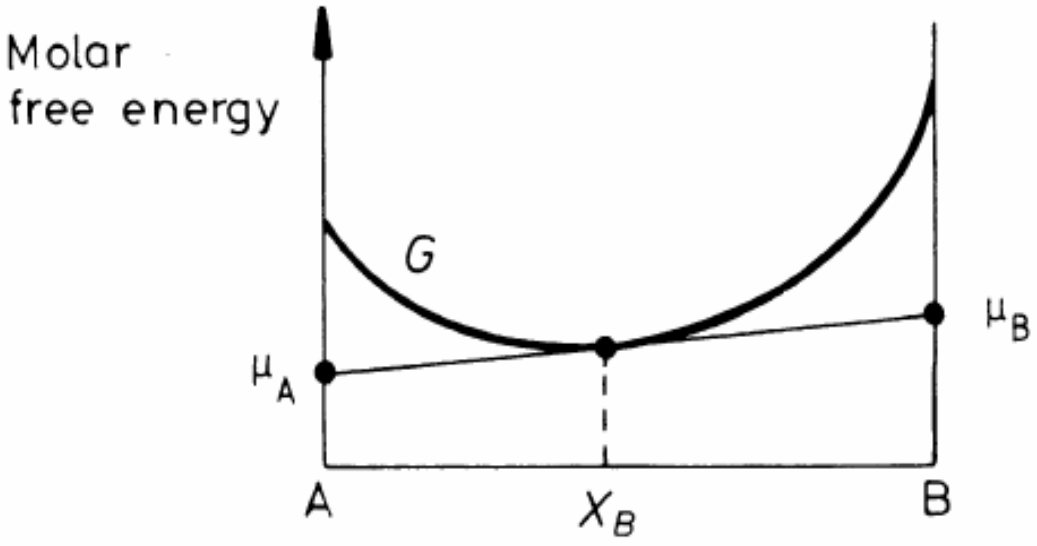


Fig. 1.11 The relationship between the free energy curve for a solution and the chemical potentials of the components.

$$G = \left(\mu_B - \frac{dG}{dX_B}\right) X_A + \mu_B X_B$$

$$= \mu_B X_A - \frac{dG}{dX_B} X_A + \mu_B X_B$$

$$= \mu_B - \frac{dG}{dX_B} X_A$$

$$= \mu_B - \frac{dG}{dX_B}(1 - X_B)$$

$$\mu_B = G + \frac{dG}{dX_B} X_A$$

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

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

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

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

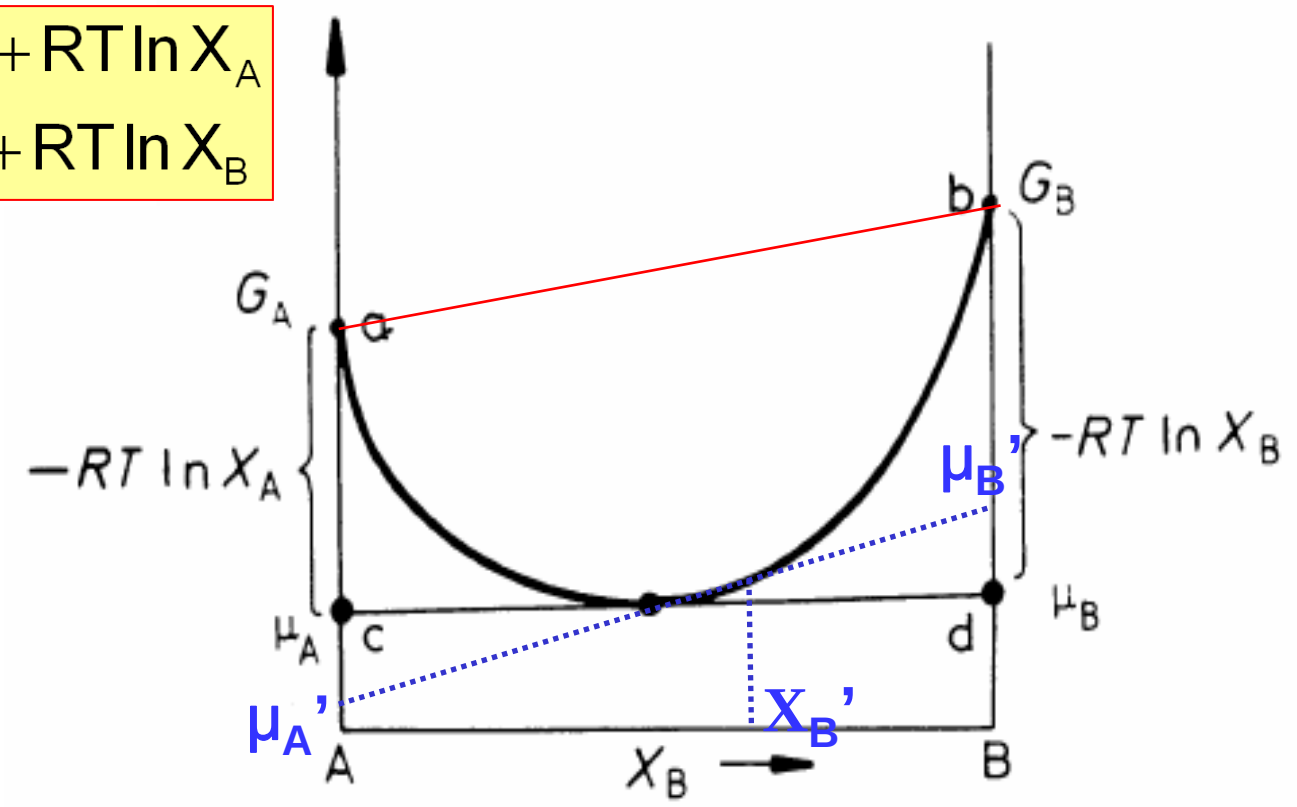


Fig. 1.12 The relationship between the free energy curve and chemical potentials for an ideal solution.

Regular Solutions

Ideal solution : $\Delta H_{mix} = 0$

$$\Delta G_{mix} = \Delta H_{mix} - T\Delta S_{mix}$$

Quasi-chemical model assumes that heat of mixing, ΔH_{mix}, is only due to the bond energies between adjacent atoms.

Structure model of a binary solution

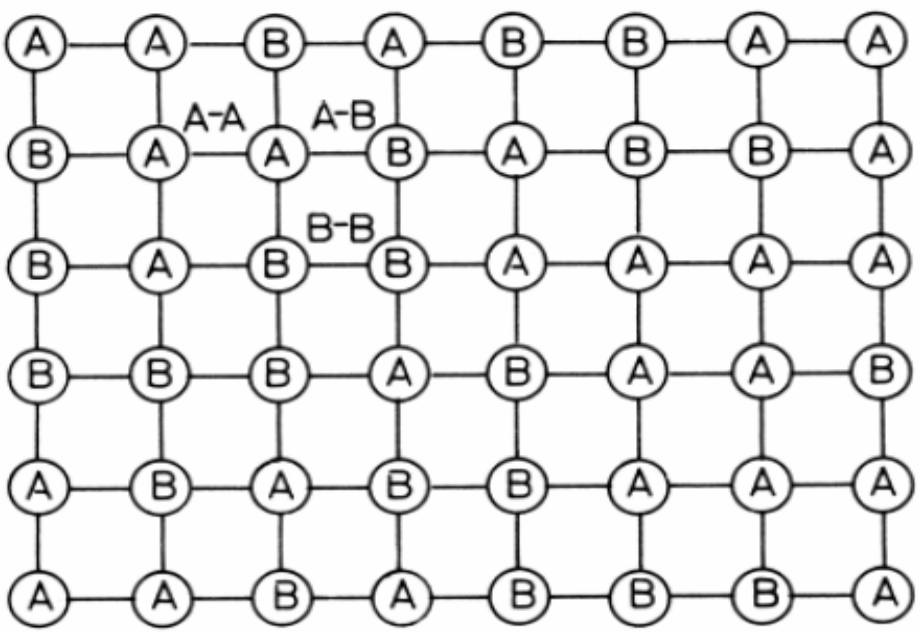


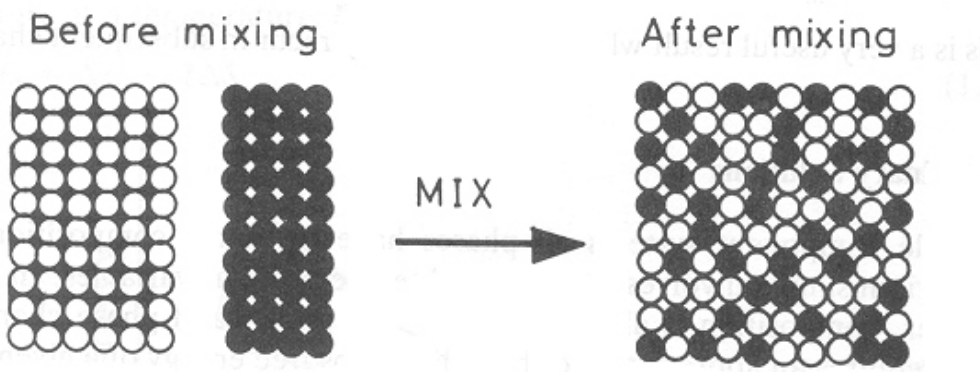
Fig. 1.13 The different types of interatomic bond in a solid solution.

Regular Solutions

	Bond energy	Number of bond
A-A	ε_{AA}	P_{AA}
B-B	ε_{BB}	P_{BB}
A-B	ε_{AB}	P_{AB}

Internal energy of the solution

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



$$\Delta H_{mix} = P_{AB}\varepsilon \quad \text{where } \varepsilon = \varepsilon_{AB} - \frac{1}{2}(\varepsilon_{AA} + \varepsilon_{BB})$$

Regular Solutions

Completely random arrangement

$$\varepsilon = 0 \quad \Rightarrow \quad \varepsilon_{AB} = \frac{1}{2}(\varepsilon_{AA} + \varepsilon_{BB})$$

$\Delta H_{mix} = 0$ ideal solution

$P_{AB} = N_a z X_A X_B$ bonds per mole

N_a : Avogadro's number

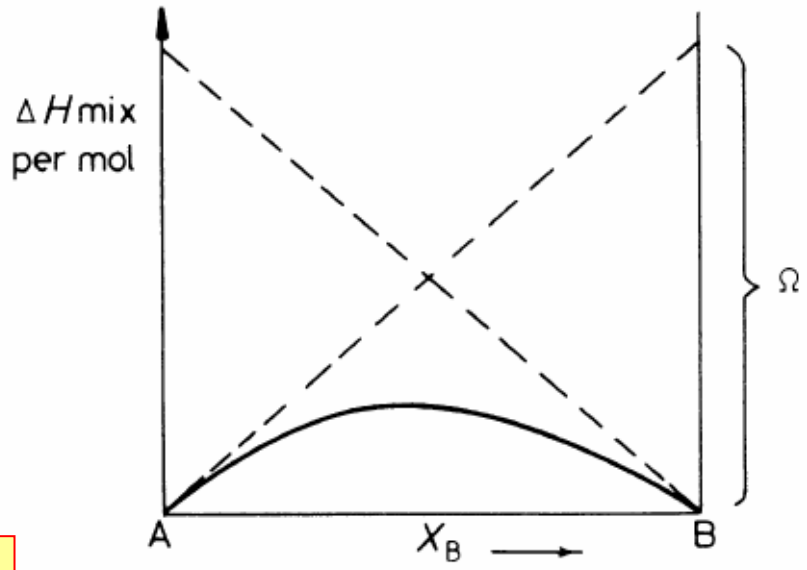
z : number of bonds per atom

$\varepsilon < 0 \rightarrow P_{AB} \uparrow$ $\varepsilon > 0 \rightarrow P_{AB} \downarrow$

$\varepsilon \approx 0 \quad \Rightarrow \quad \Delta H_{mix} = P_{AB}\varepsilon$

$\Delta H_{mix} = \Omega X_A X_B$ where $\Omega = N_a z \varepsilon$

Regular solution



Ω >0 인 경우

Fig. 1.14 The variation of ΔH_{mix} with composition for a regular solution.

Regular Solutions

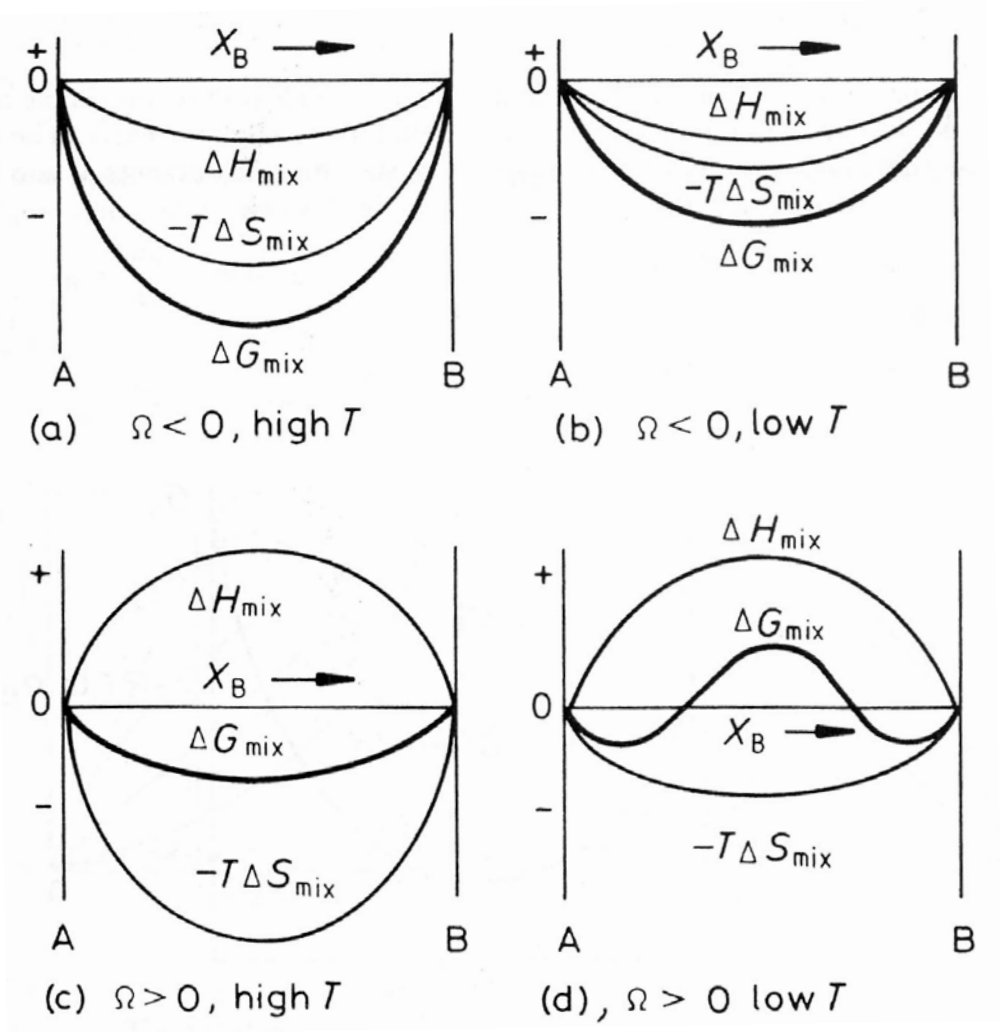
$$G_2 = G_1 + \Delta G_{mix}$$

$$G = X_A G_A + X_B G_B + \underbrace{\Omega X_A X_B}_{\Delta H_{mix}} + \underbrace{RT(X_A \ln X_A + X_B \ln X_B)}_{-T\Delta S_{mix}}$$

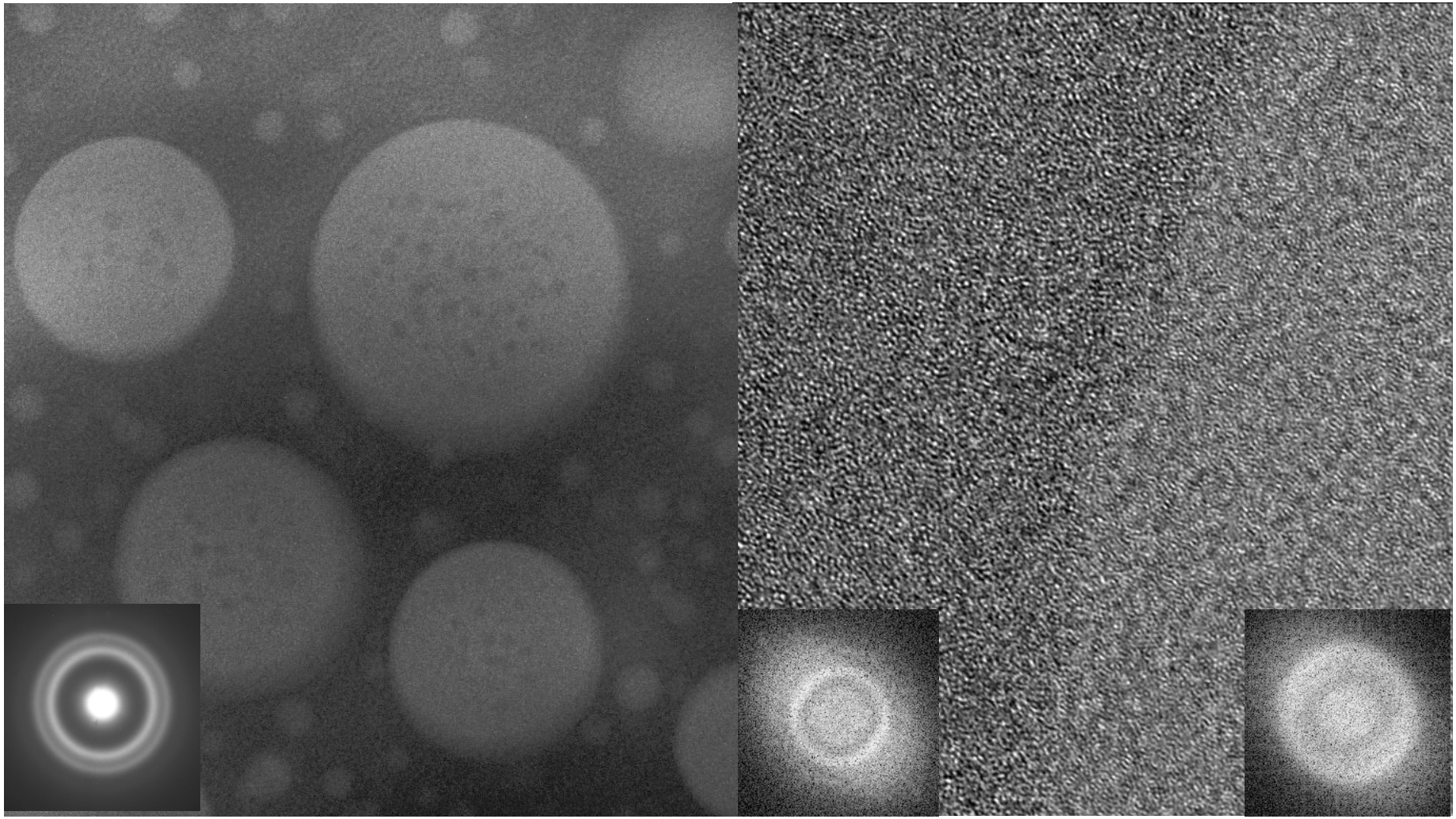
Reference state

Pure metal $G_A^0 = G_B^0 = 0$

$$\Delta G_{mix} = \Delta H_{mix} - T\Delta S_{mix}$$



Phase separation in metallic glasses



Chemical potential 과 Free E와의 관계

For 1 mole of the solution **(T, P: constant)**

G = E+PV-TS $G = \mu_A X_A + \mu_B X_B \quad \text{Jmol}^{-1}$

G = H-TS $G = X_A G_A + X_B G_B + \Omega X_A X_B + RT(X_A \ln X_A + X_B \ln X_B)$

$\longrightarrow \quad X_A X_B = X_A^2 X_B + X_B^2 X_A$

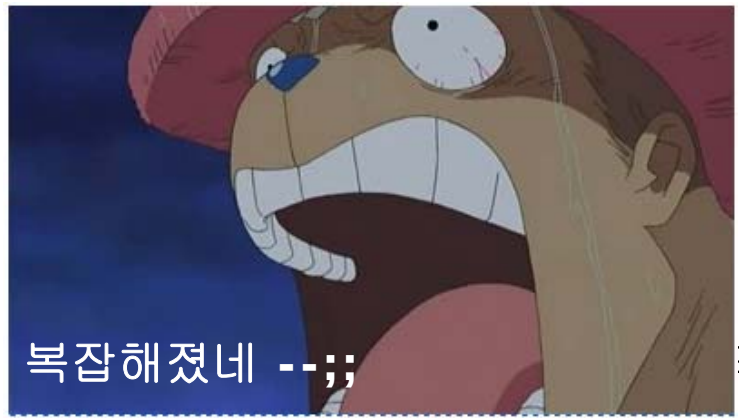
$= \mu_A(G_A + \Omega(1-X_A)^2 + RT \ln X_A) + \mu_B(G_B + \Omega(1-X_B)^2 + RT \ln X_B)$

Regular solution

$$\mu_A = G_A + \Omega (1-X_A)^2 + RT \ln X_A$$
$$\mu_B = G_B + \Omega (1-X_B)^2 + RT \ln X_B$$

$\mu_A = G_A + RT \ln X_A$
$\mu_B = G_B + RT \ln X_B$

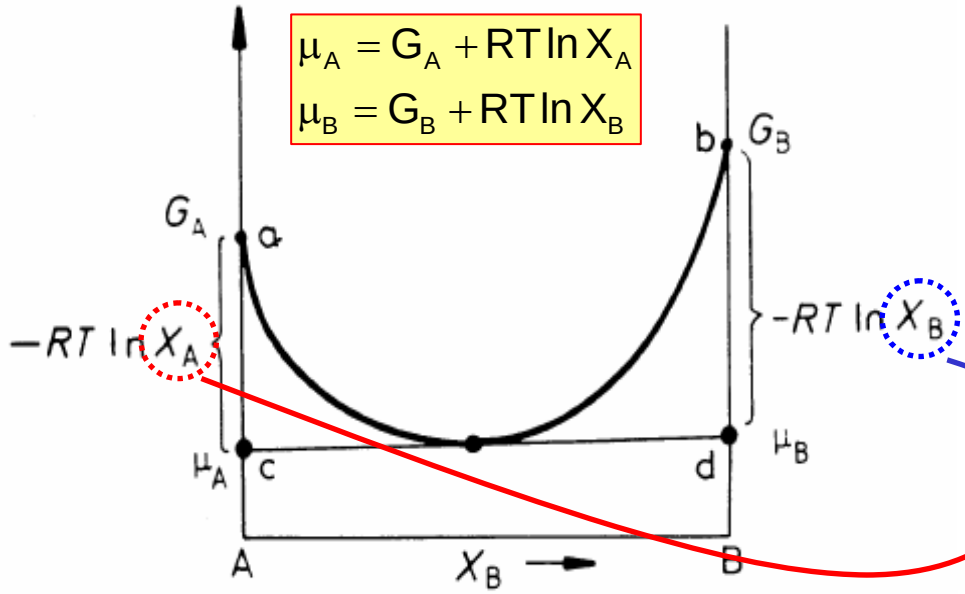
Ideal solution



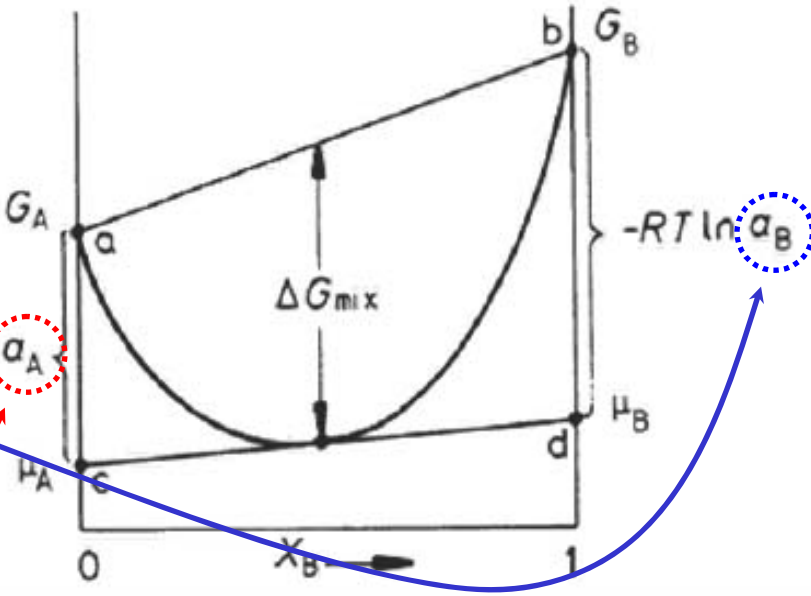
Activity, a : mass action을 위해 effective concentration

ideal solution

$$\mu_A = G_A + RT\ln X_A$$
$$\mu_B = G_B + RT\ln X_B$$



regular solution



$$\mu_A = G_A + RT\ln a_A \qquad \mu_B = G_B + RT\ln a_B$$

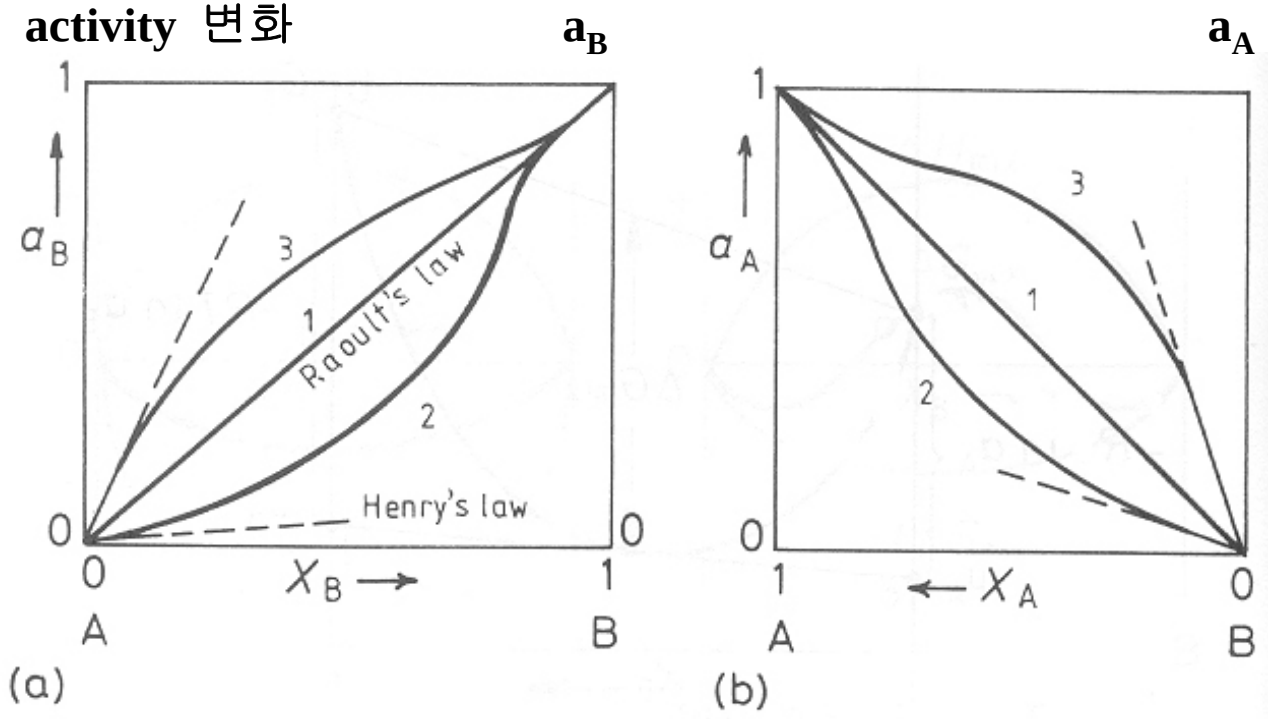
$$\mu_A = G_A + \Omega(1-X_A)^2 + RT\ln X_A \qquad \mu_B = G_B + \Omega(1-X_B)^2 + RT\ln X_B$$

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

$$\frac{a_A}{X_A} = \gamma_A = \text{activity coefficient} \qquad \gamma_B = \frac{a_B}{X_B}$$

Solution에서 a와 X와의 관계

조성 따른 **activity** 변화



Line 1 : (a) $a_B=X_B$, (b) $a_A=X_A$ **ideal solution…Rault's law**

Line 2 : (a) $a_B<X_B$, (b) $a_A<X_A$ **$\Delta H_{mix}<0$** ⇐ $\ln\left(\frac{a_A}{X_A}\right)=\frac{\Omega}{RT}(1-X_A)^2$

Line 3 : (a) $a_B>X_B$, (b) $a_A>X_A$ **$\Delta H_{mix}>0$**

- **For a dilute solution of B in A ($X_B \rightarrow 0$)**

$$\gamma_B = \frac{a_B}{X_B} \cong \text{constant} \quad \text{(Henry's Law)}$$

$$\gamma_A = \frac{a_A}{X_A} \cong 1 \quad \text{(Rault's Law)}$$

degree of non-ideality ? $\rightarrow \frac{a_A}{X_A}$

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

γ_A : activity coefficient

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

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

Activity는 **solution**의 상태를 나타내는
조성 과 **Chemical potential** 과 상관관계 가짐.

Chemical Equilibrium (μ, a) → multiphase and multicomponent

$$(\mu_i^{\alpha} = \mu_i^{\beta} = \mu_i^{\gamma} = \ldots), (a_i^{\alpha} = a_i^{\beta} = a_i^{\gamma} = \ldots)$$

Contents for today's class

- **Binary System** mixture/ solution / compound
- **Gibbs Free Energy in Binary System**

$$G_1 = X_A G_A + X_B G_B \quad J/mol$$

$$G_2 = G_1 + \Delta G_{mix} \quad J/mol$$

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

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

Regular solution

$$\Delta H_{mix} = P_{AB}\varepsilon$$

$$\Delta G^{mix} = RT(X_A \ln X_A + X_B \ln X_B)$$

where $\varepsilon = \varepsilon_{AB} - \frac{1}{2}(\varepsilon_{AA} + \varepsilon_{BB})$

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

- **Chemical potential** and **Activity**

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

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

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

$$\frac{a_A}{X_A} = \gamma_A = \text{activity coefficient}$$