

2017 Fall

# **“Phase Transformation *in* Materials”**

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**Office hours: by an appointment**

- **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** ( $\Delta H_{mix}=0$ )  $\Delta G^{mix} = RT(X_A \ln X_A + X_B \ln X_B)$

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

**Regular solution**  $\Delta H_{mix} = P_{AB} \varepsilon$  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**

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

$$\bullet \quad \mu_A = G_A + RT \ln a_A \quad \ln \left( \frac{a_A}{X_A} \right) = \frac{\Omega}{RT} (1 - X_A)^2$$

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

$\mu$ 는 조성에 의해 결정되기 때문에  $dn_A$ 가 매우 작아서 조성변화 없어야

## Contents for previous class

### - Binary System mixture/ solution / compound

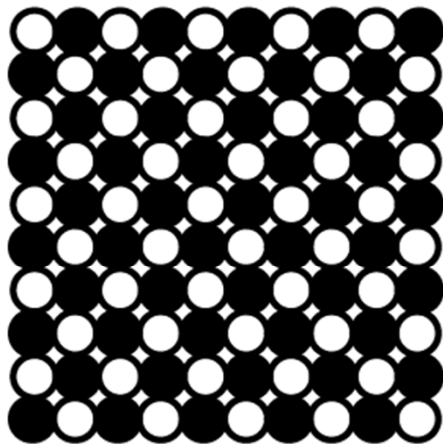
Ideal solution ( $\Delta H_{\text{mix}} = 0$ ) Random distribution

Regular solution  $\Delta H_{\text{mix}} = P_{AB}\epsilon$  where  $\epsilon = \epsilon_{AB} - \frac{1}{2}(\epsilon_{AA} + \epsilon_{BB})$   $\epsilon \approx 0$

$\Delta H_{\text{mix}} > 0$  or  $\Delta H_{\text{mix}} < 0$

Real solution

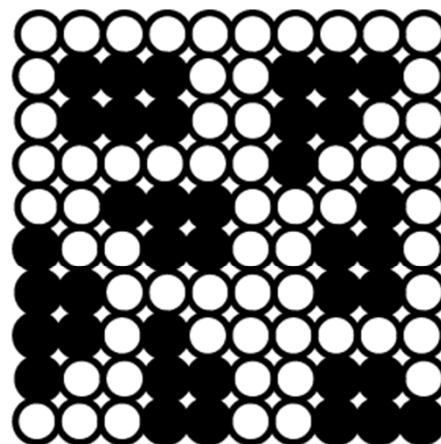
Ordered structure



(a)  $\epsilon < 0$ ,  $\Delta H_{\text{mix}} < 0$

Ordered alloys

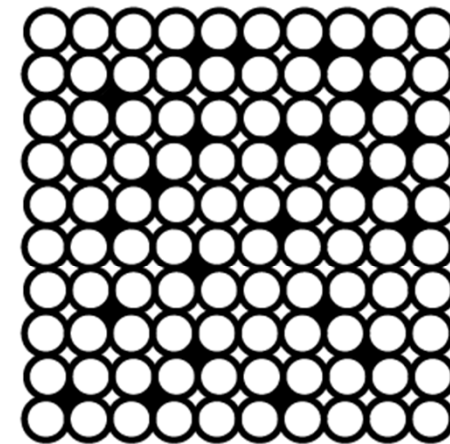
$P_{AB} \uparrow \longrightarrow \text{Internal } E \downarrow$



(b)  $\epsilon > 0$ ,  $\Delta H_{\text{mix}} > 0$

Clustering

$P_{AA}, P_{BB} \uparrow$



(c) when the size difference is large

strain effect

Interstitial solution

## - Equilibrium in Heterogeneous Systems

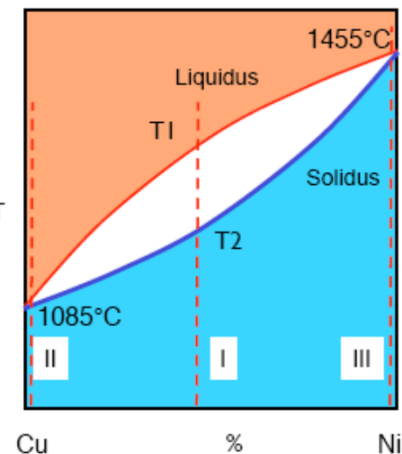
$$G_0^\beta > G_0^\alpha > G_0^{\alpha+\beta} \Rightarrow \alpha + \beta \text{ separation} \Rightarrow \text{unified chemical potential}$$

## - Binary phase diagrams

### 1) Simple Phase Diagrams

$$\Delta H_{mix}^L = 0 \quad \Delta H_{mix}^S = 0$$

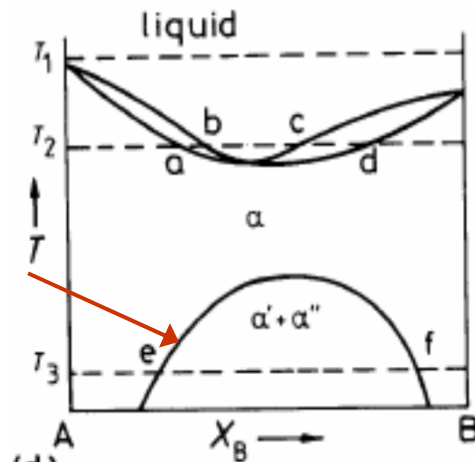
Assume: (1) completely miscible in solid and liquid.  
(2) Both are ideal soln.



### 2) Variant of the simple phase diagram

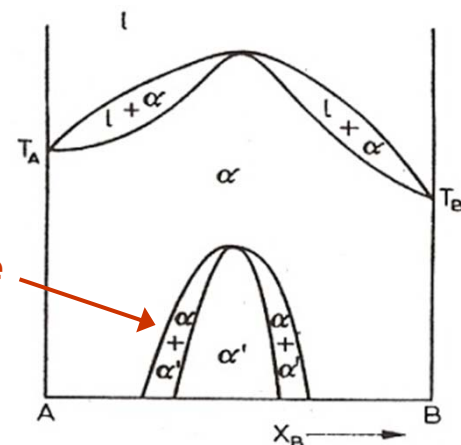
$$\Delta H_{mix}^\alpha > \Delta H_{mix}^l > 0$$

miscibility gap

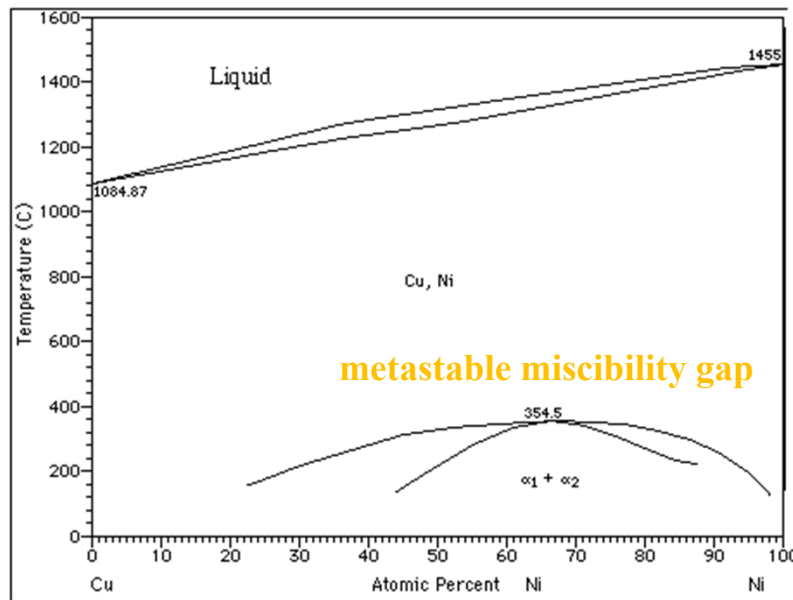


$$\Delta H_{mix}^\alpha < \Delta H_{mix}^l < 0$$

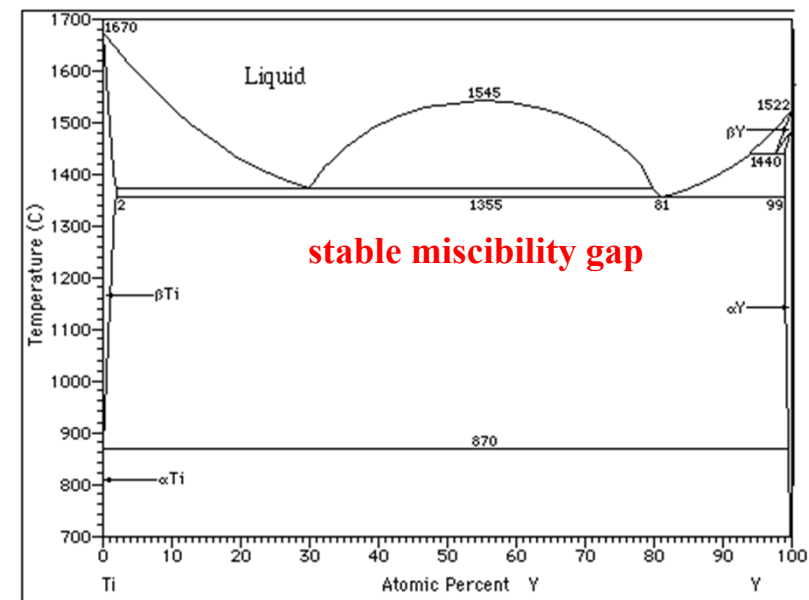
Ordered phase



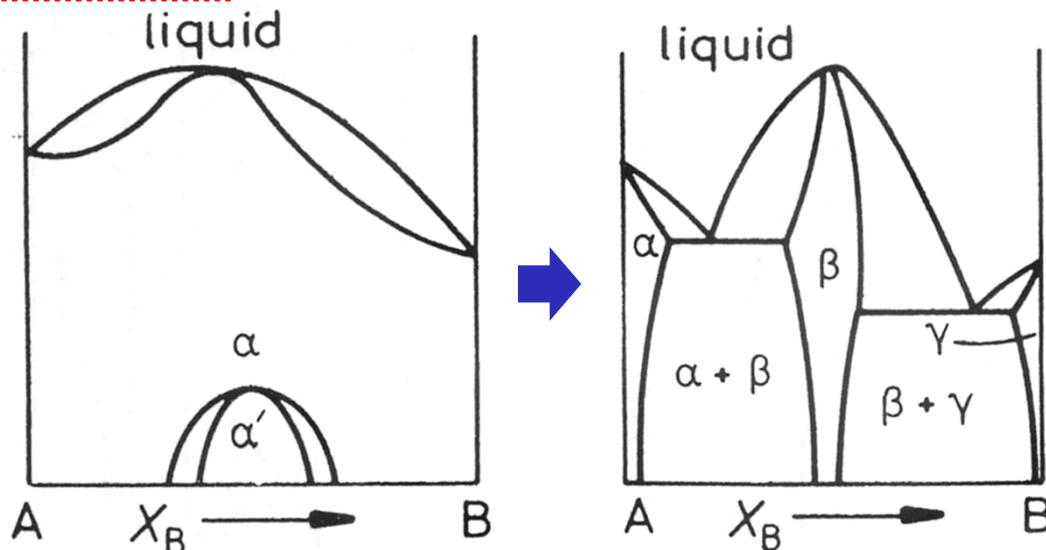
$\Delta H_{mix}^S > 0$  : Solid solution  $\rightarrow$  solid state phase separation (two solid solutions)



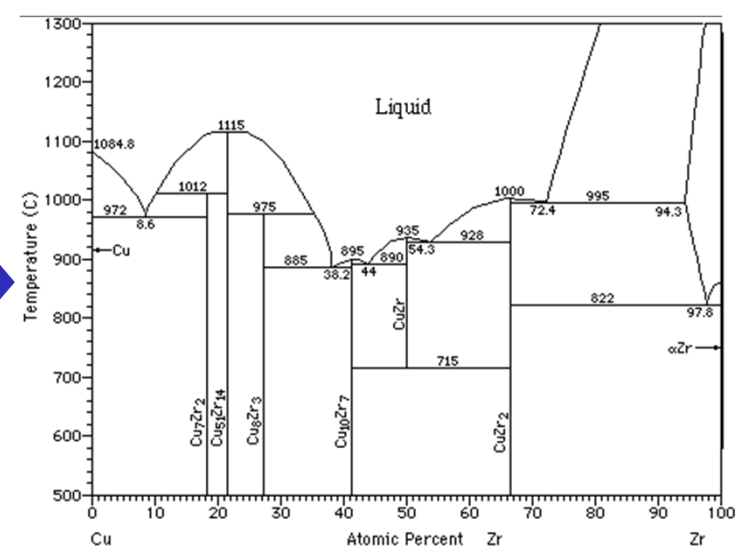
$\Delta H_{mix}^S \gg 0$  : liquid state phase separation (up to two liquid solutions)



$\Delta H_{mix}^S < 0$  : Solid solution  $\rightarrow$  ordered phase



$\Delta H_{mix}^S \ll 0$  : Compound : AB,  $A_2B$ ...



**Q5: How can we define equilibrium  
in heterogeneous systems?**

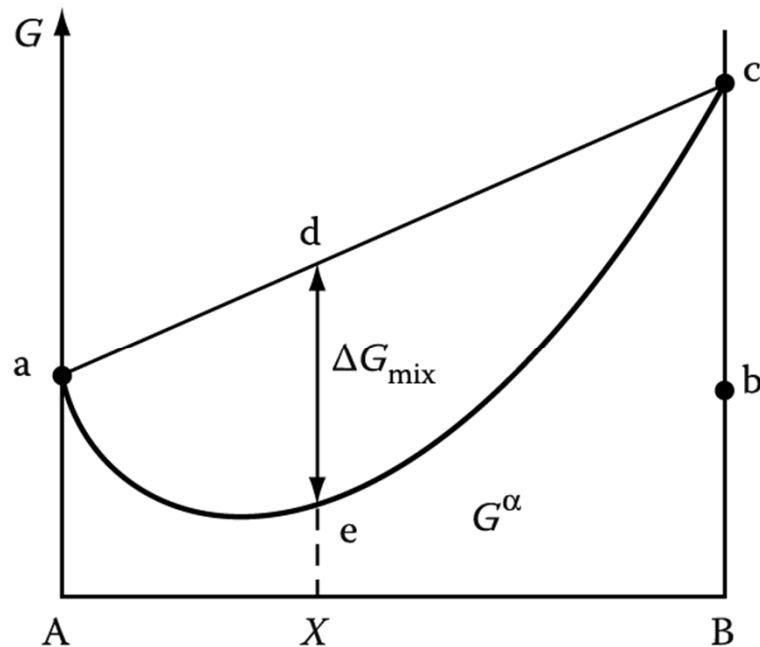
# 1.4

## Equilibrium in Heterogeneous Systems

A, B different crystal structure → two free energy curves must be drawn, one for each structure.

We have dealt with the case where the components A and B have the same crystal structure.

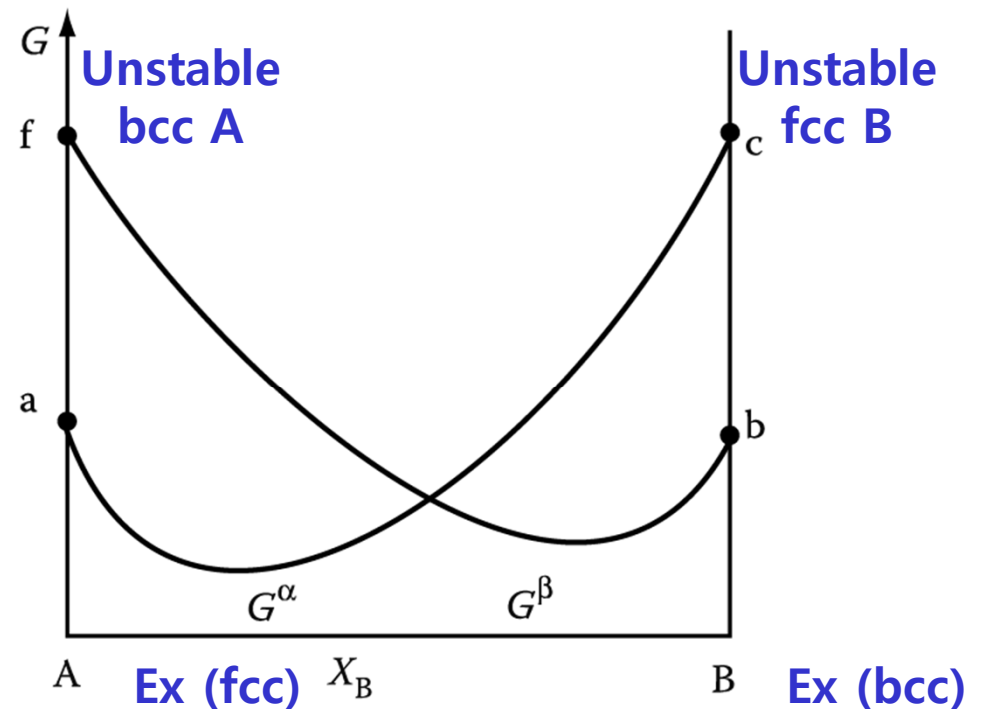
$$G = X_A G_A + X_B G_B + \Omega X_A X_B + RT(X_A \ln X_A + X_B \ln X_B)$$



(a)

What would happen when the components A and B have a different crystal structure?

→ heterogeneous system



(b)

## 1.4

# Equilibrium in Heterogeneous Systems

If  $G^\alpha(X_B^\alpha)$  and  $G^\beta(X_B^\beta)$  are given,  
what would be  $G(\alpha + \beta)$  at  $X_B^0 = ?$

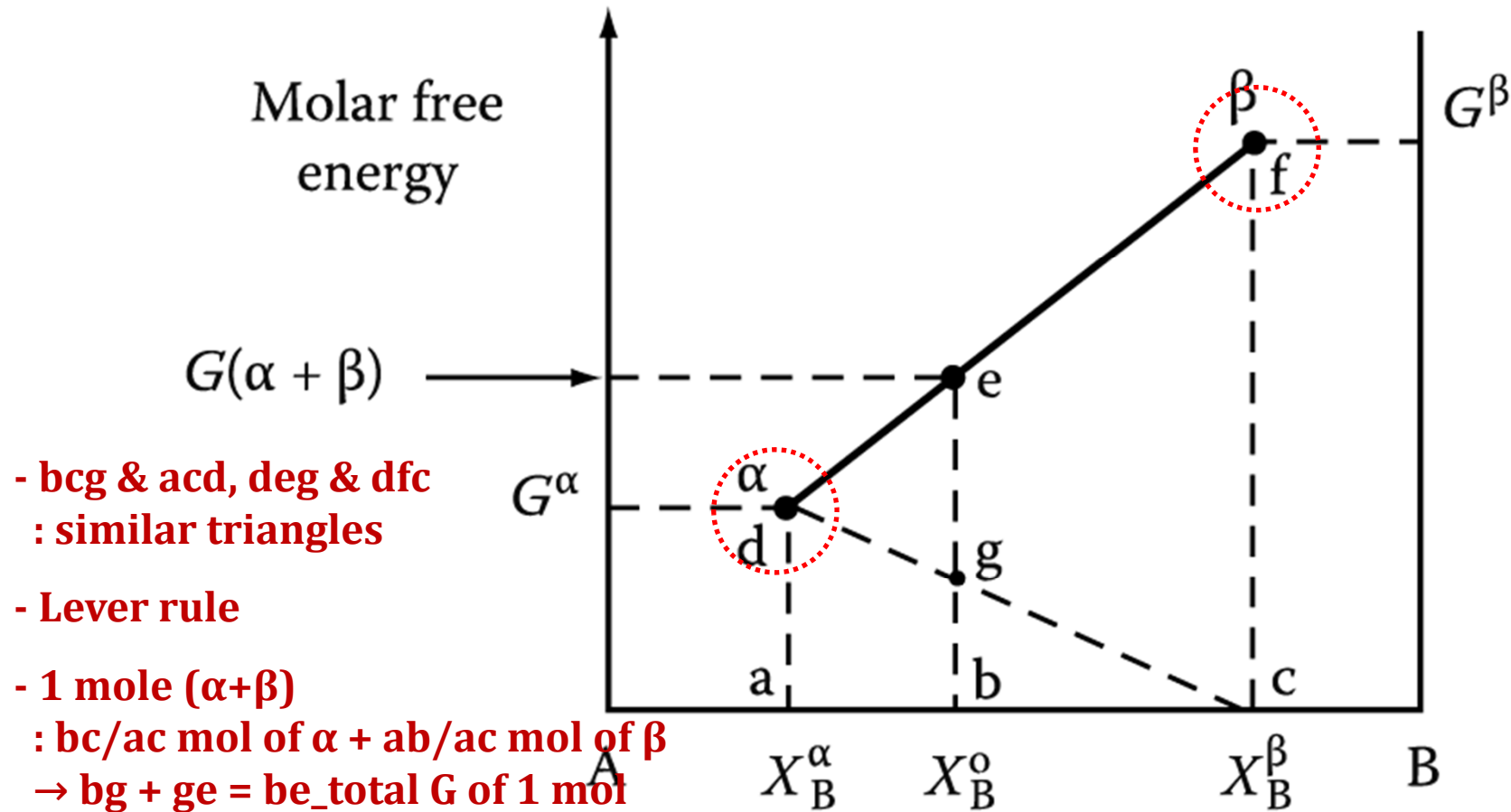
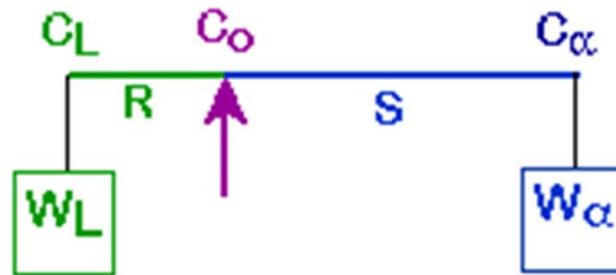


Fig. 1.26 The molar free energy of a two-phase mixture ( $\alpha + \beta$ )



# Lever rule

A geometric interpretation:



moment equilibrium:

$$W_L R = W_\alpha S$$

$\nwarrow$   
 $1 - W_\alpha$

solving gives Lever Rule

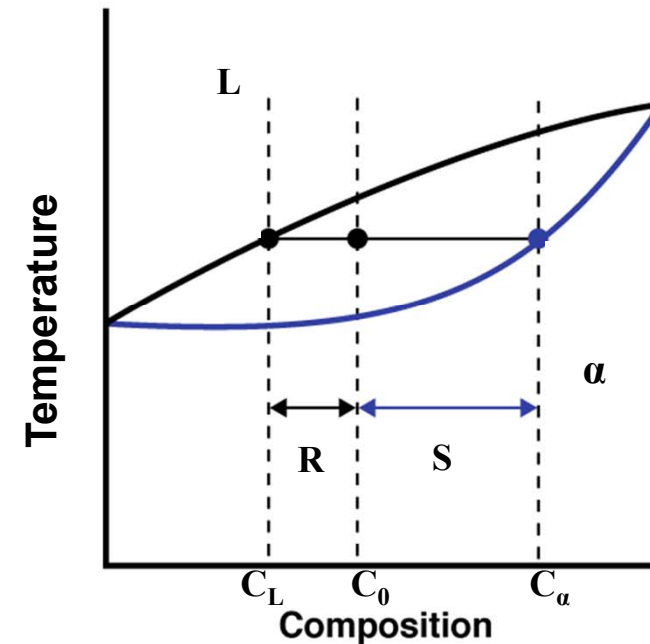
Sum of weight fractions:  $W_L + W_\alpha = 1$

Conservation of mass (Ni):  $C_0 = W_L C_L + W_\alpha C_\alpha$

Combine above equations:

$$W_L = \frac{C_\alpha - C_0}{C_\alpha - C_L} = \frac{S}{R + S}$$

$$W_\alpha = \frac{C_0 - C_L}{C_\alpha - C_L} = \frac{R}{R + S}$$



# 1.4

## Equilibrium in Heterogeneous Systems

In  $X^0$ ,  $G_0^\beta > G_0^\alpha > G_1$

Exchange of A and B atoms

→  $\alpha + \beta$  phase separation

Chemical Equilibrium ( $\mu$ ,  $a$ )

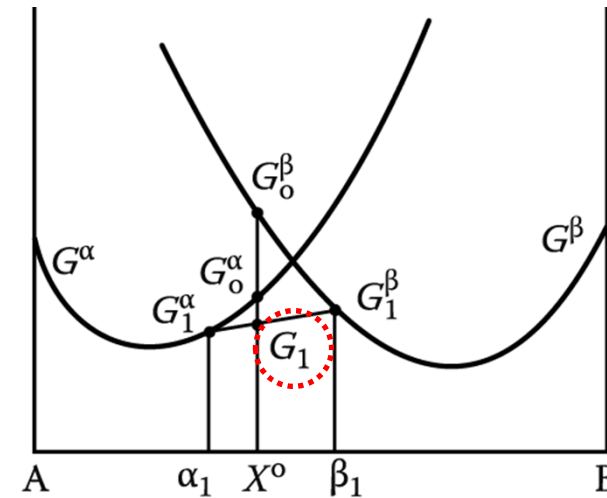
→ multiphase and multicomponent

( $\mu_i^\alpha = \mu_i^\beta = \mu_i^\gamma = \dots$ ), ( $a_i^\alpha = a_i^\beta = a_i^\gamma = \dots$ )

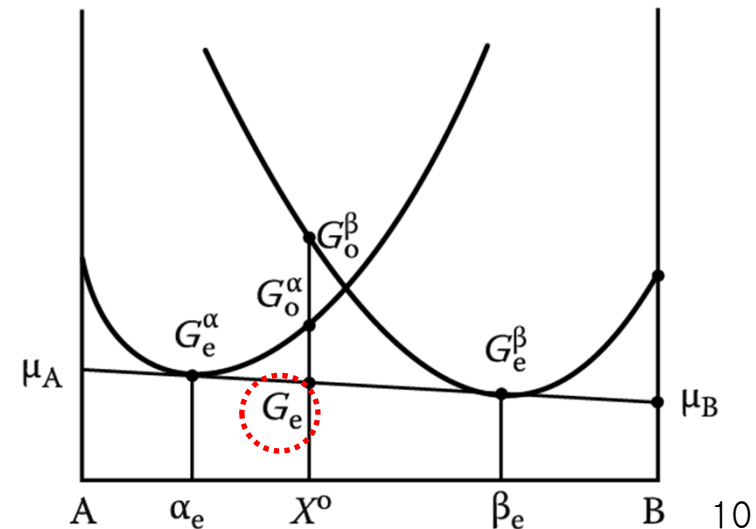
$$\mu_A^\alpha = \mu_A^\beta$$

$$\mu_B^\alpha = \mu_B^\beta$$

Unified Chemical potential of two phases



(a)



(b)

## Variation of activity with composition

The most stable state, with the lowest free energy, is usually defined as the state in which the pure component has unit activity of A in pure  $\alpha$ .

$$\text{when } X_A = 1 \rightarrow a_A^\alpha = 1$$

$$\text{when } X_B = 1 \rightarrow a_B^\beta = 1$$

when  $\alpha$  and  $\beta$  in equil.

$$a_A^\alpha = a_A^\beta$$

$$a_B^\alpha = a_B^\beta$$

**Unified activity of two phase**

Activity,  $a$  : effective concentration for mass action

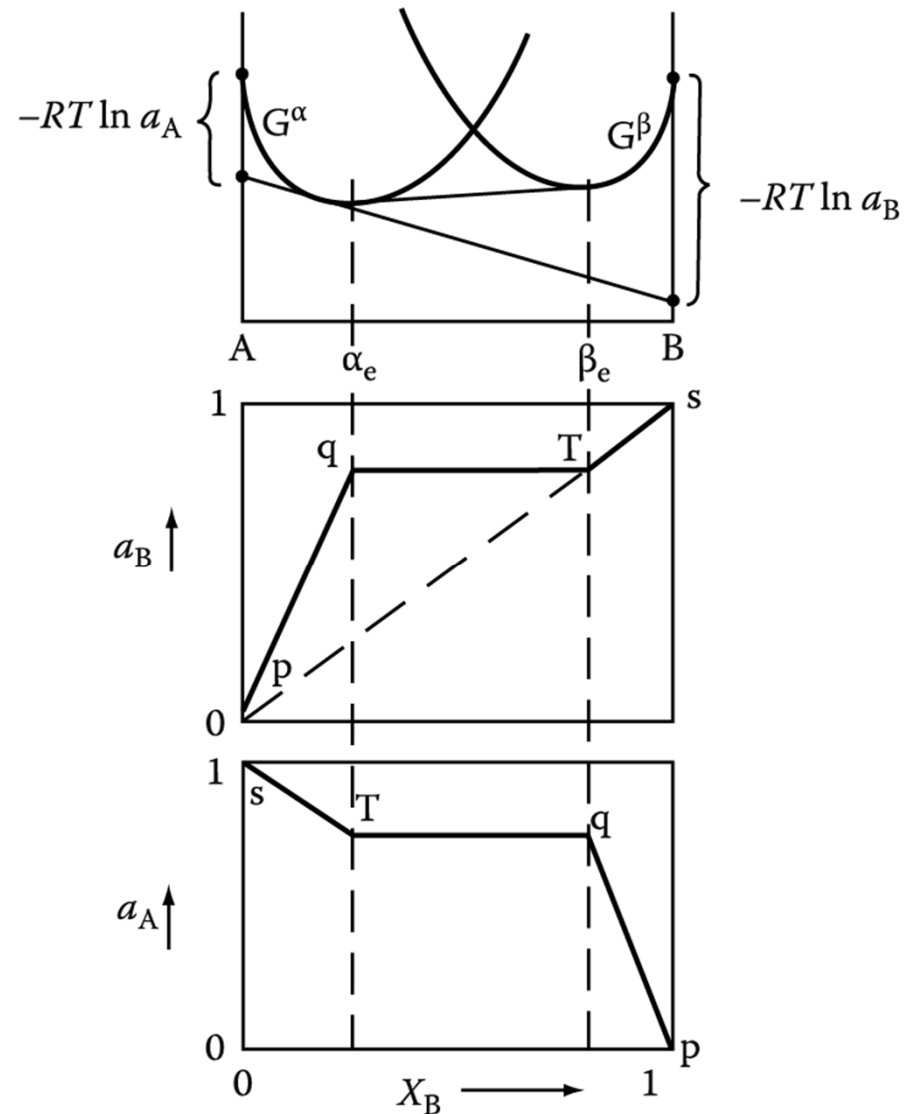
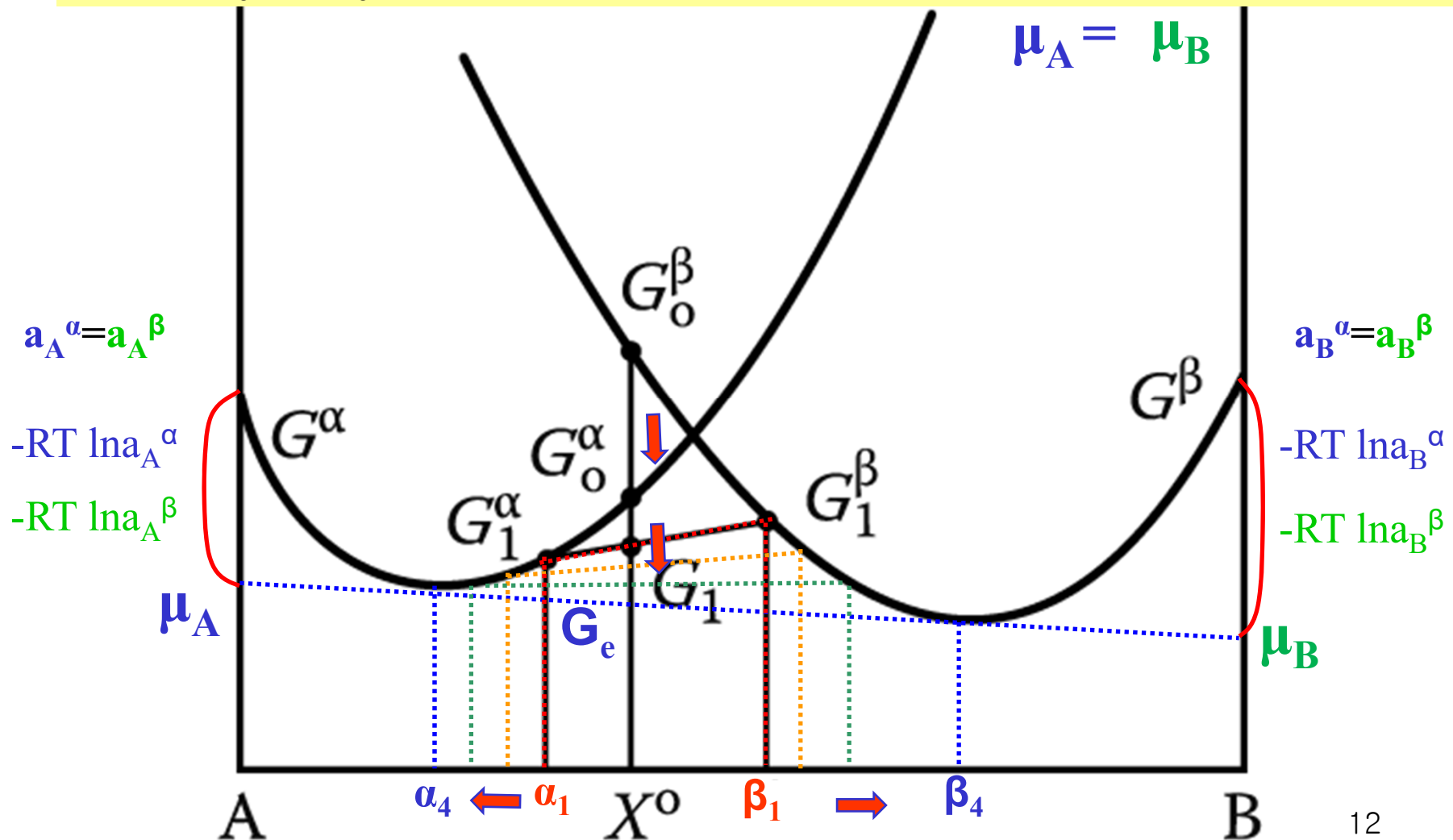


Fig. 1.28 The variation of  $a_A$  and  $a_B$  with composition for a binary system containing two ideal solutions,  $\alpha$  and  $\beta$

# Equilibrium in Heterogeneous Systems

In  $X^0$ ,  $G_0^\beta > G_0^\alpha > G_1 \Rightarrow \alpha + \beta$  separation  $\Rightarrow$  unified chemical potential



**Q6: How equilibrium is affected by temperature in complete solid solution?**

## 1.5 Binary phase diagrams

### 1) Simple Phase Diagrams

**Assumption: (1) completely miscible in solid and liquid.**

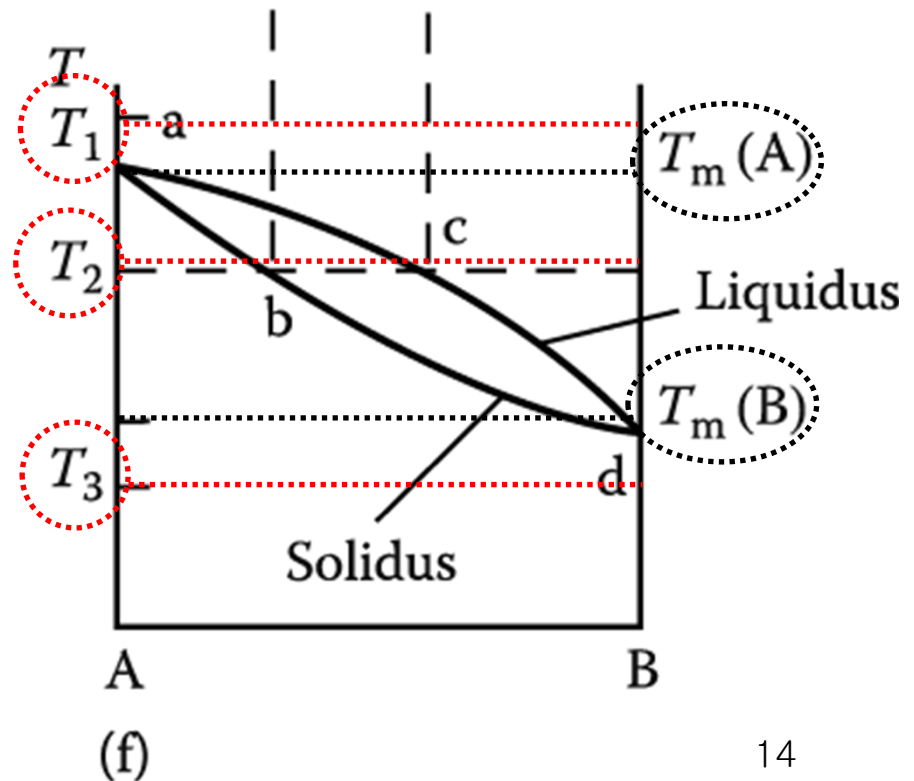
**(2) Both are ideal soln.**

$$\Delta H_{mix}^L = 0 \quad \Delta H_{mix}^S = 0$$

**(3)  $T_m(A) > T_m(B)$**

**(4)  $T_1 > T_m(A) > T_2 > T_m(B) > T_3$**

Draw  $G^L$  and  $G^S$  as a function of composition  $X_B$  at  $T_1$ ,  $T_m(A)$ ,  $T_2$ ,  $T_m(B)$ , and  $T_3$ .



## 1) Simple Phase Diagrams

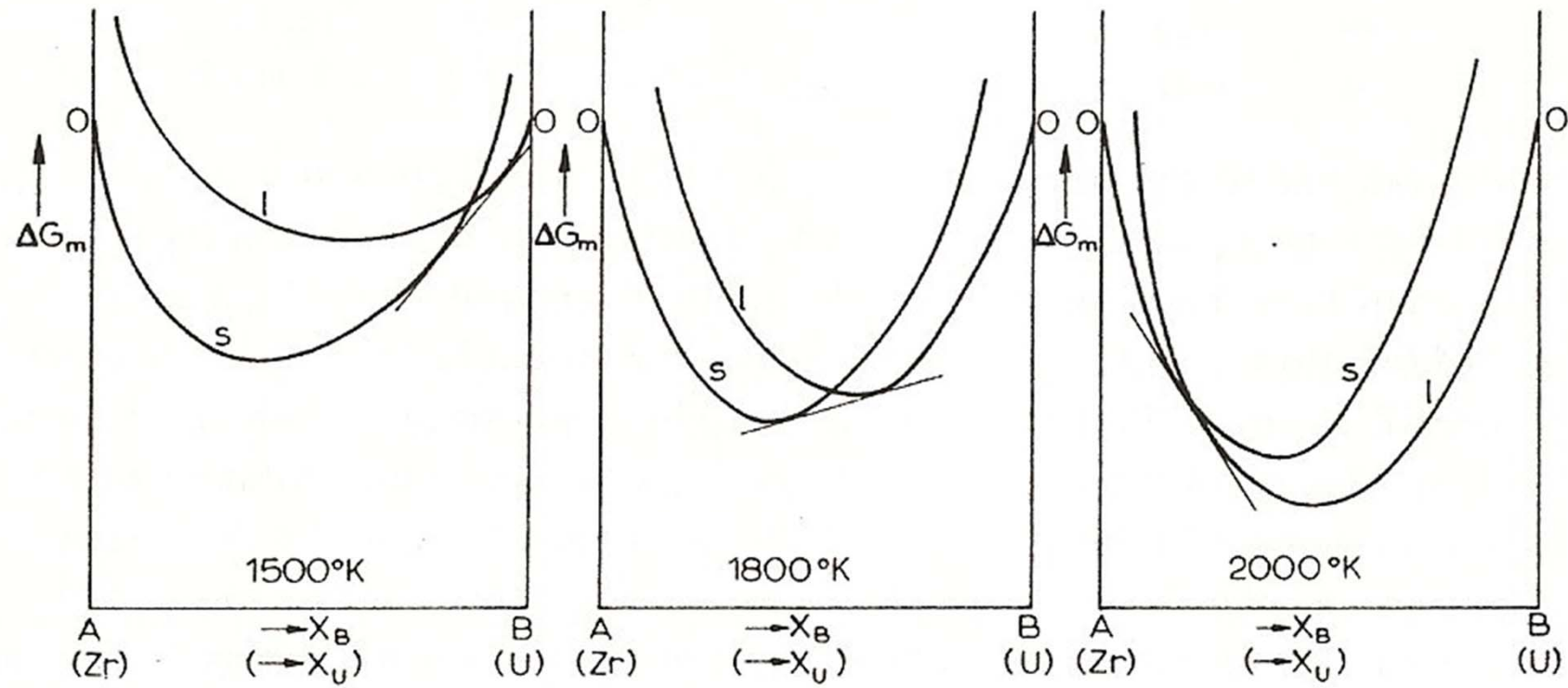


Fig. 26. Free energy curves for liquid and solid phases in the U-Zr system at 1500°, 1800° and 2000 °K.

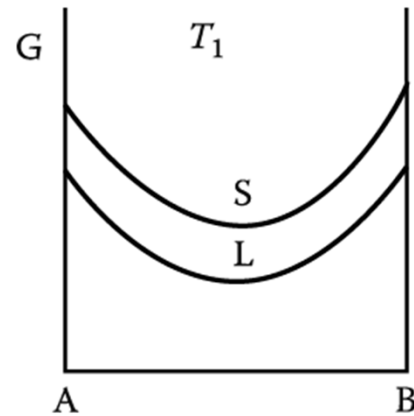
## 1.5 Binary phase diagrams

### 1) Simple Phase Diagrams

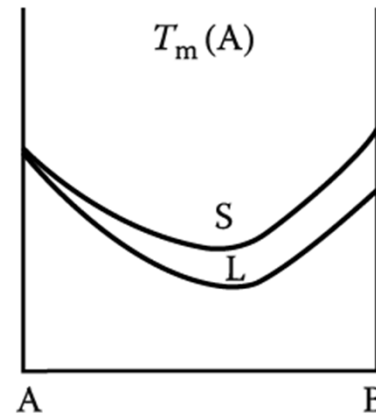
- 1) Variation of temp.:  $G^L > G^S$
- 2) Decrease of curvature of G curve  
( $\because$  decrease of  $-T\Delta S_{\text{mix}}$  effect)

Assumption:

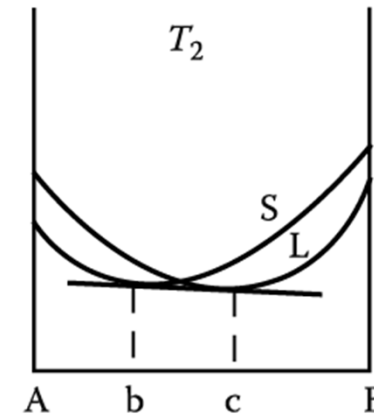
- (1) completely miscible in solid and liquid.
- (2) Both are ideal soln.
- (3)  $T_m(A) > T_m(B)$
- (4)  $T_1 > T_m(A) > T_2 > T_m(B) > T_3$



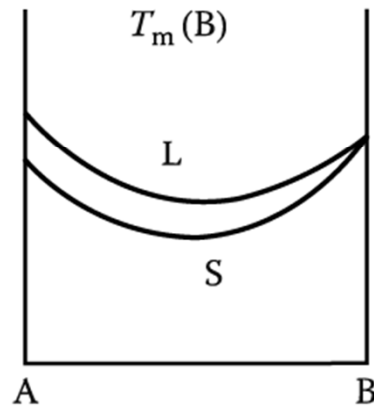
(a)



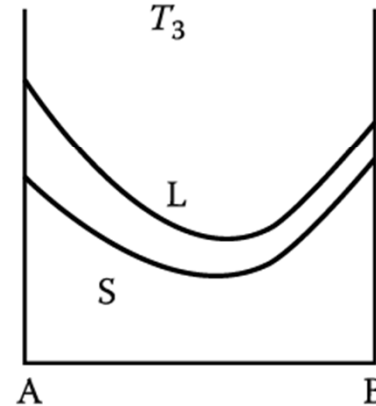
(b)



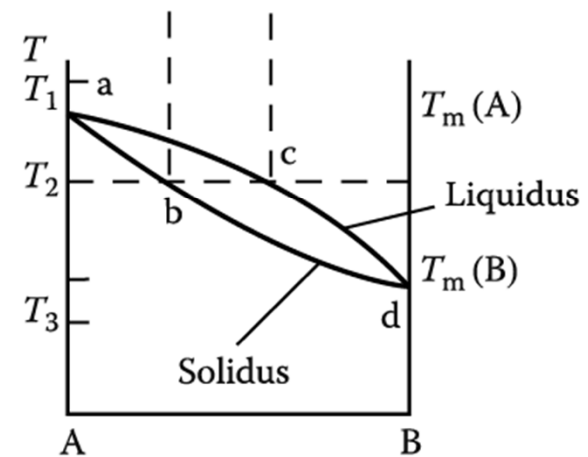
(c)



(d)



(e)



(f)

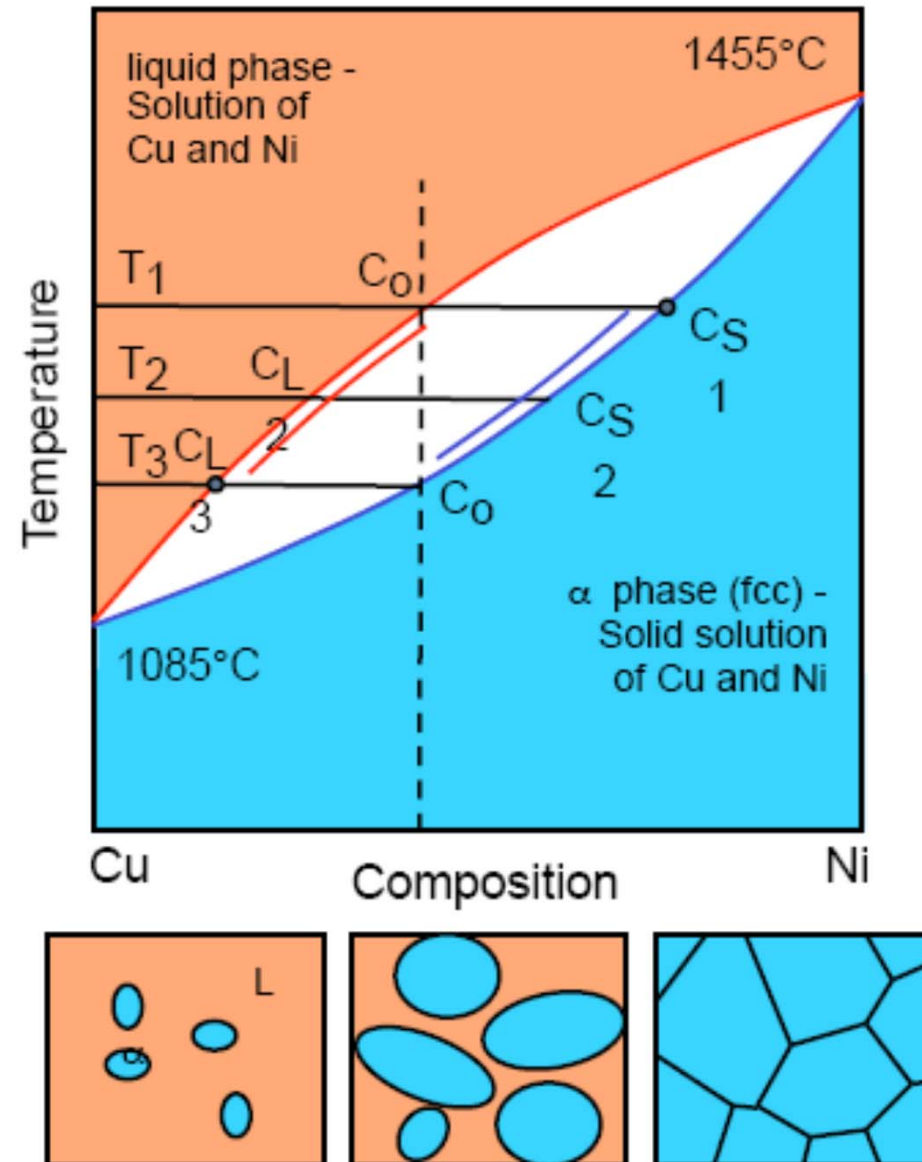


## 1.5 Binary phase diagrams

### 1) Simple Phase Diagrams

The simplest type of binary phase diagrams is the isomorphous system, in which the two constituents form a continuous solid solution over the entire composition range. An example is the Ni-Cu system.

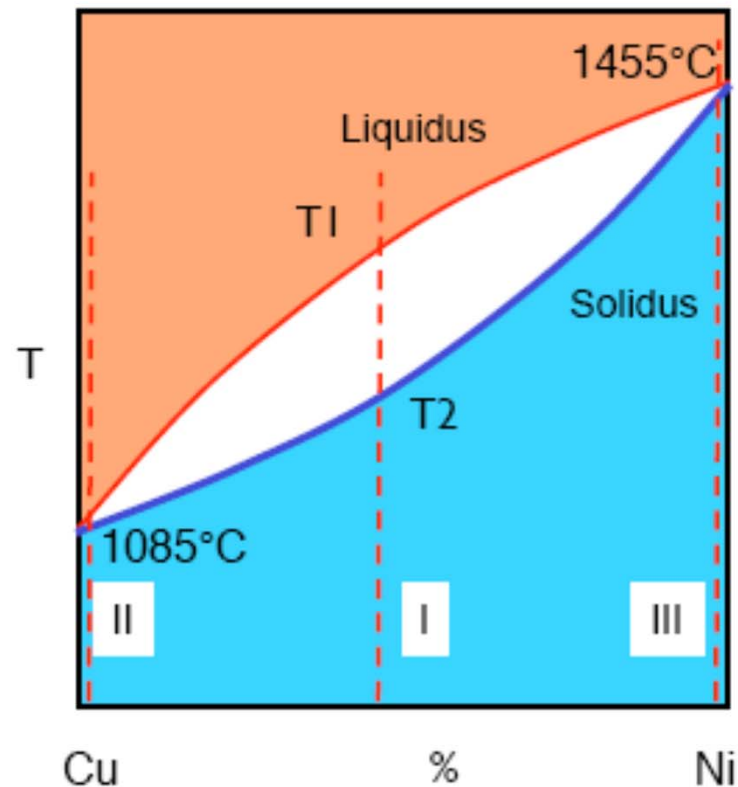
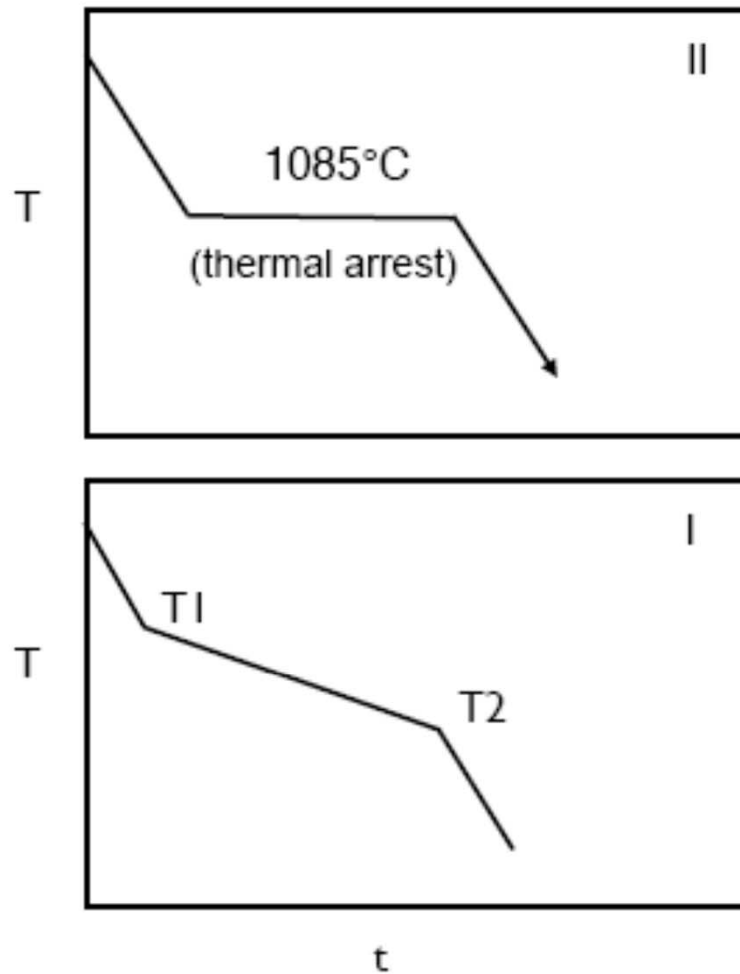
Solidification of alloy  $C_0$  starts on cooling at  $T_1$ . The first solid formed has a composition of  $C_{S1}$  and the liquid  $C_0$ . On further cooling the solid particles grow larger in size and change their composition to  $C_{S2}$  and then  $C_0$ , following the solidus whereas the liquid decrease in volume and changes its composition from  $C_0$  to  $C_{L3}$  following the liquidus. The solidification completes at  $T_3$ .



## 1.5 Binary phase diagrams

# Cooling Curves

## determination of Phase diagrams

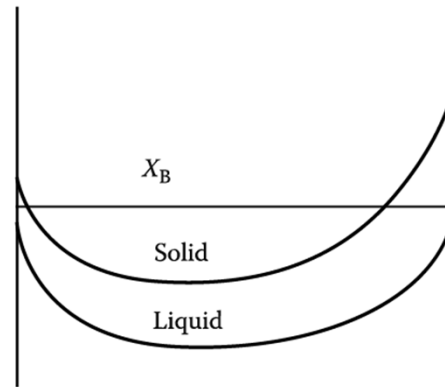


**Q8: How equilibrium is affected by temperature  
in systems with miscibility gap?**

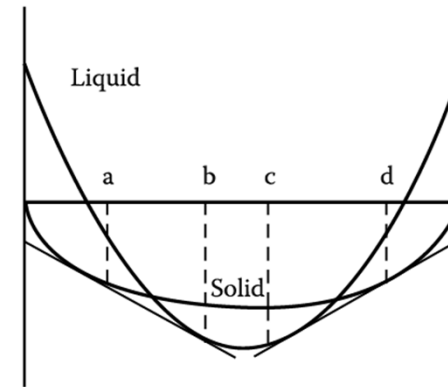
## 1.5 Binary phase diagrams

### 2) Systems with miscibility gap

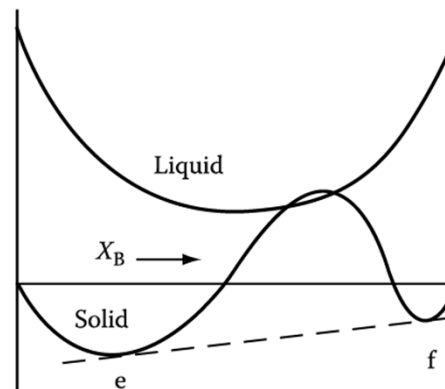
$$\Delta H_{mix}^L = 0 \quad \Delta H_{mix}^S > 0$$



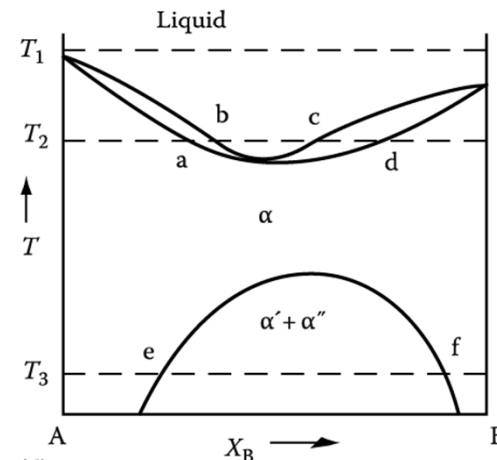
(a)



(b)



(c)



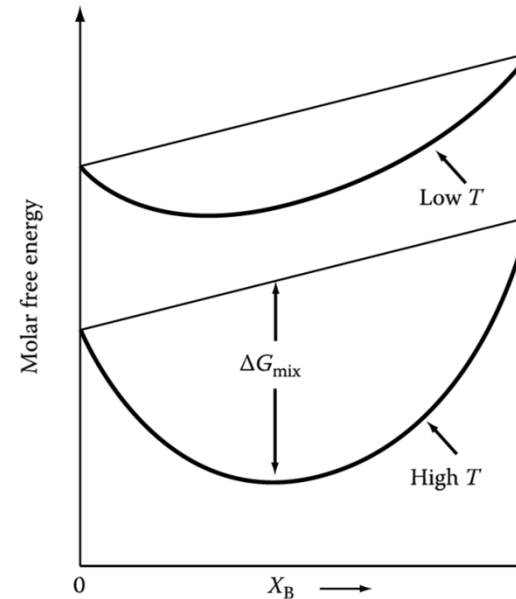
(d)

**congruent minima**

How to characterize  $G^s$  mathematically  
in the region of miscibility gap between e and f ?

# Ideal Solutions

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

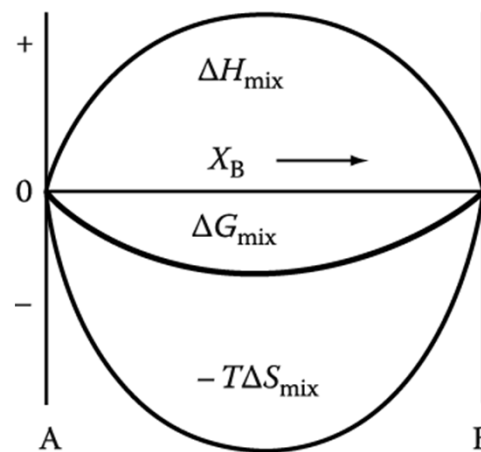


# Regular Solutions

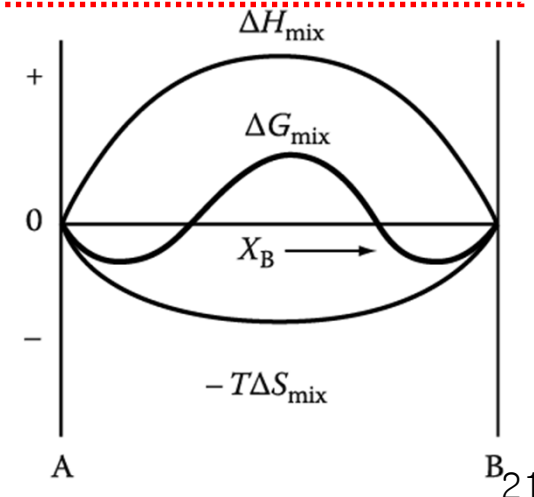
$$G = X_A G_A + X_B G_B + \boxed{\Omega X_A X_B} + \boxed{-T\Delta S_{mix}}$$

Reference state

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



$$\Delta G_{mix} = \Delta H_{mix} - T\Delta S_{mix} \quad (c) \quad \Omega > 0, \text{ high } T$$



$$(d) \quad \Omega > 0, \text{ low } T$$

## 1.5 Binary phase diagrams

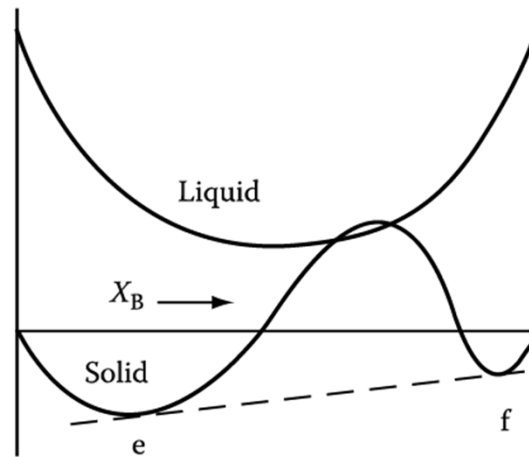
### 2) Systems with miscibility gap

$$\Delta H_{mix}^L = 0 \quad \Delta H_{mix}^S > 0$$

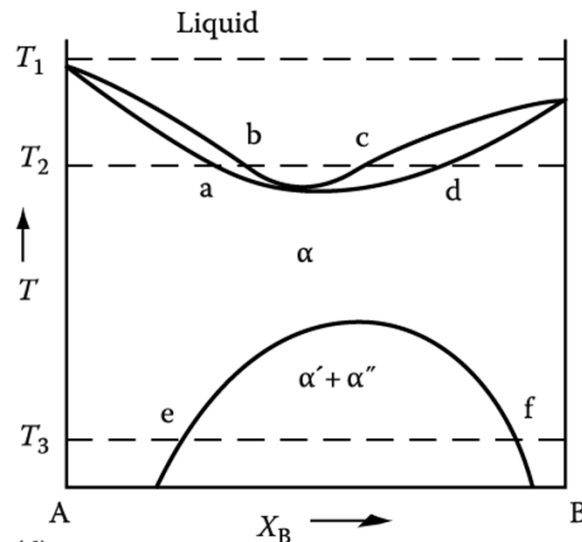
- When A and B atoms dislike each other,  $\Delta H_{mix} > 0$
- In this case, the free energy curve at low temperature has a region of negative curvature,

$$\frac{d^2G}{dX_B^2} < 0$$

- This results in a ‘**miscibility gap**’ of  $\alpha'$  and  $\alpha''$  in the phase diagram



(c)



(d)

**congruent minima**

## 2) Variant of the simple phase diagram

$$\Delta H_{mix} > 0 \quad \Delta H_{mix}^{\alpha} > \Delta H_{mix}^l$$

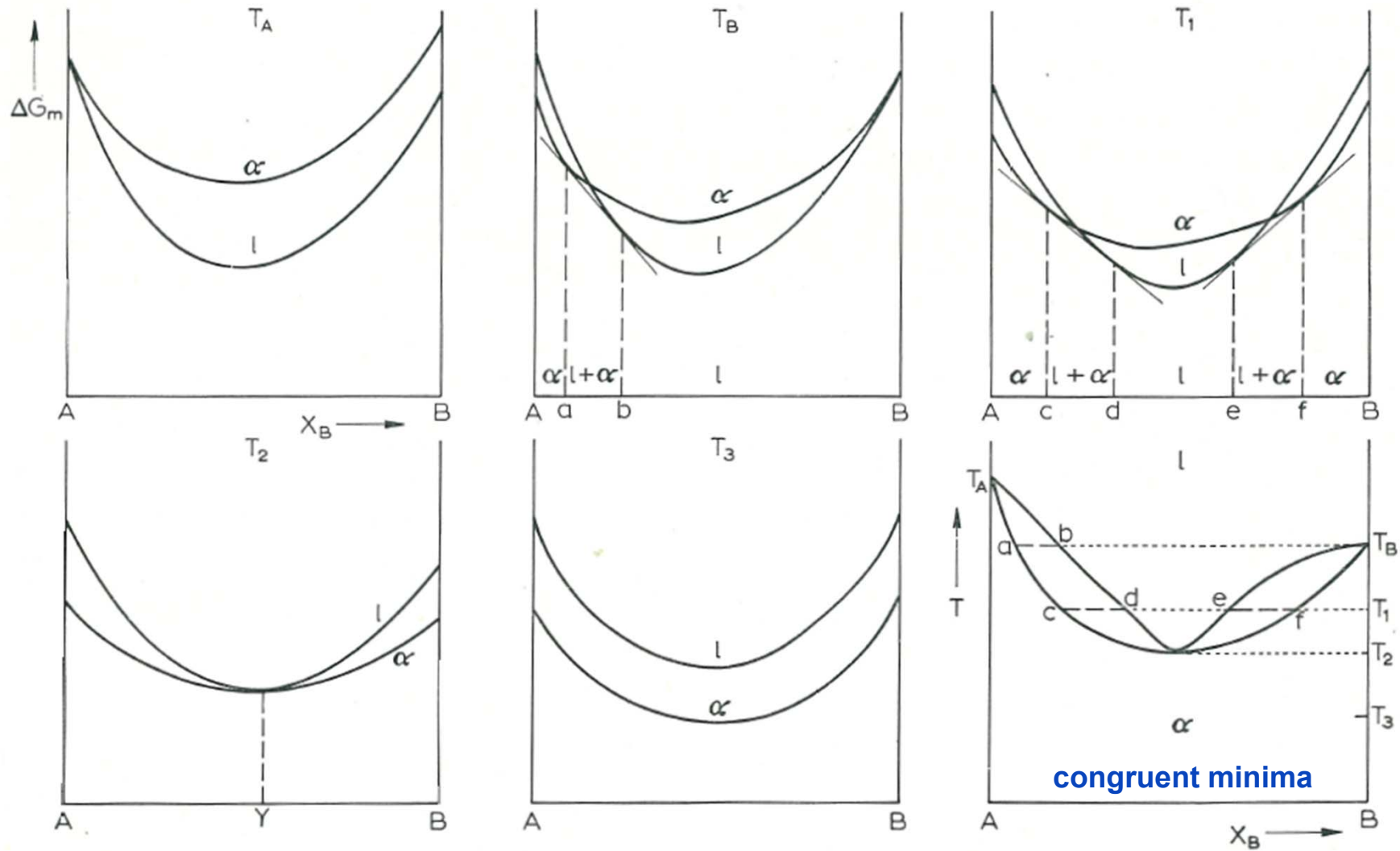


Fig. 30. Derivation of the phase diagram (Fig. 29b) from free energy curves for the liquid and solid phases.

$$T_A > T_B > T_1 > T_2 > T_3.$$

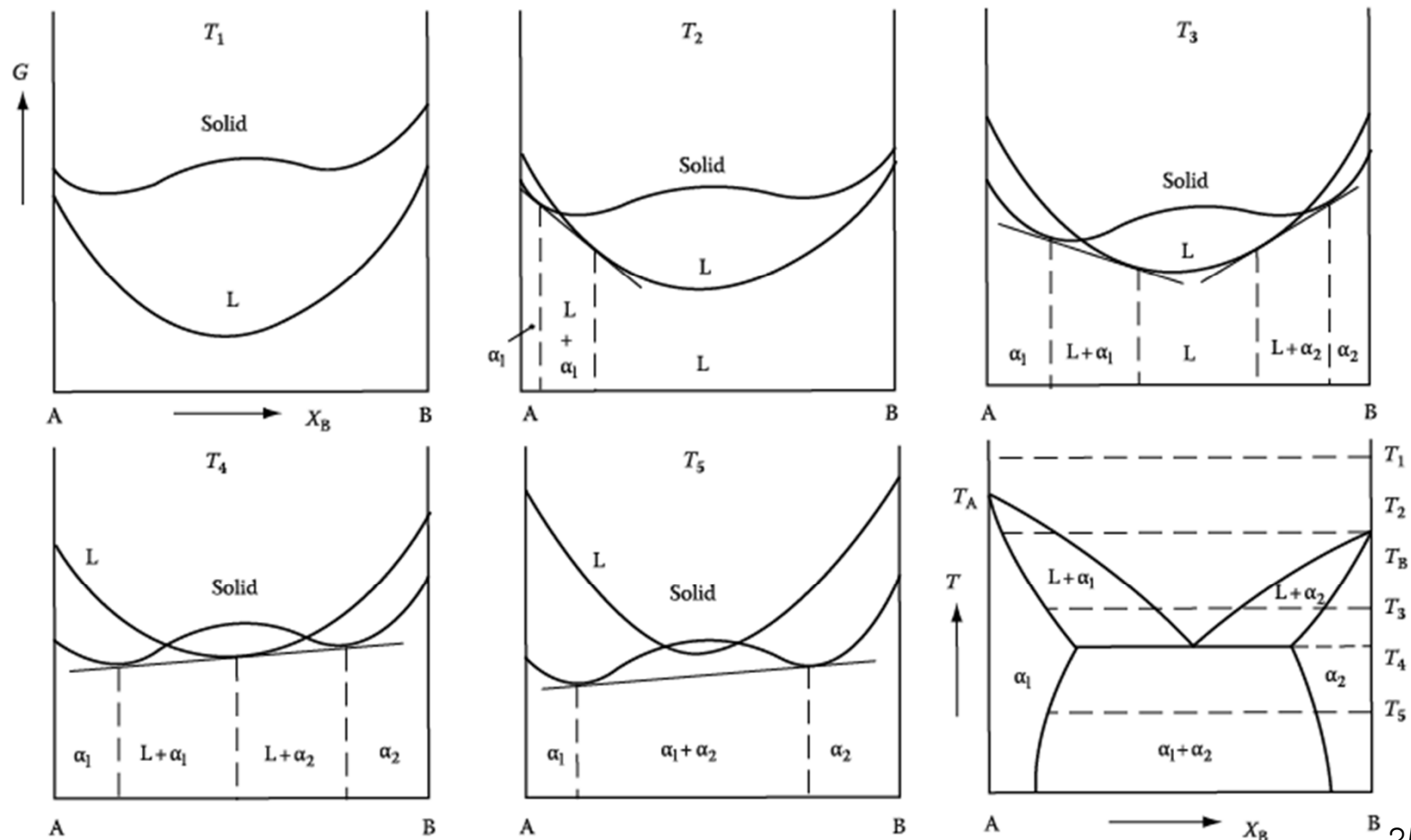
**Q9: How equilibrium is affected by temperature  
in simple eutectic systems?**



## 1.5 Binary phase diagrams

### 4) Simple Eutectic Systems $\Delta H_{mix}^L = 0$ $\Delta H_{mix}^S \gg 0$

- $\Delta H_m > 0$  and the miscibility gap extends to the melting temperature.  
(when both solids have the same structure.)



25

Fig. 1.32 The derivation of a eutectic phase diagram where both solid phases have the same crystal structure.

(when each solid has the **different crystal structure.**)

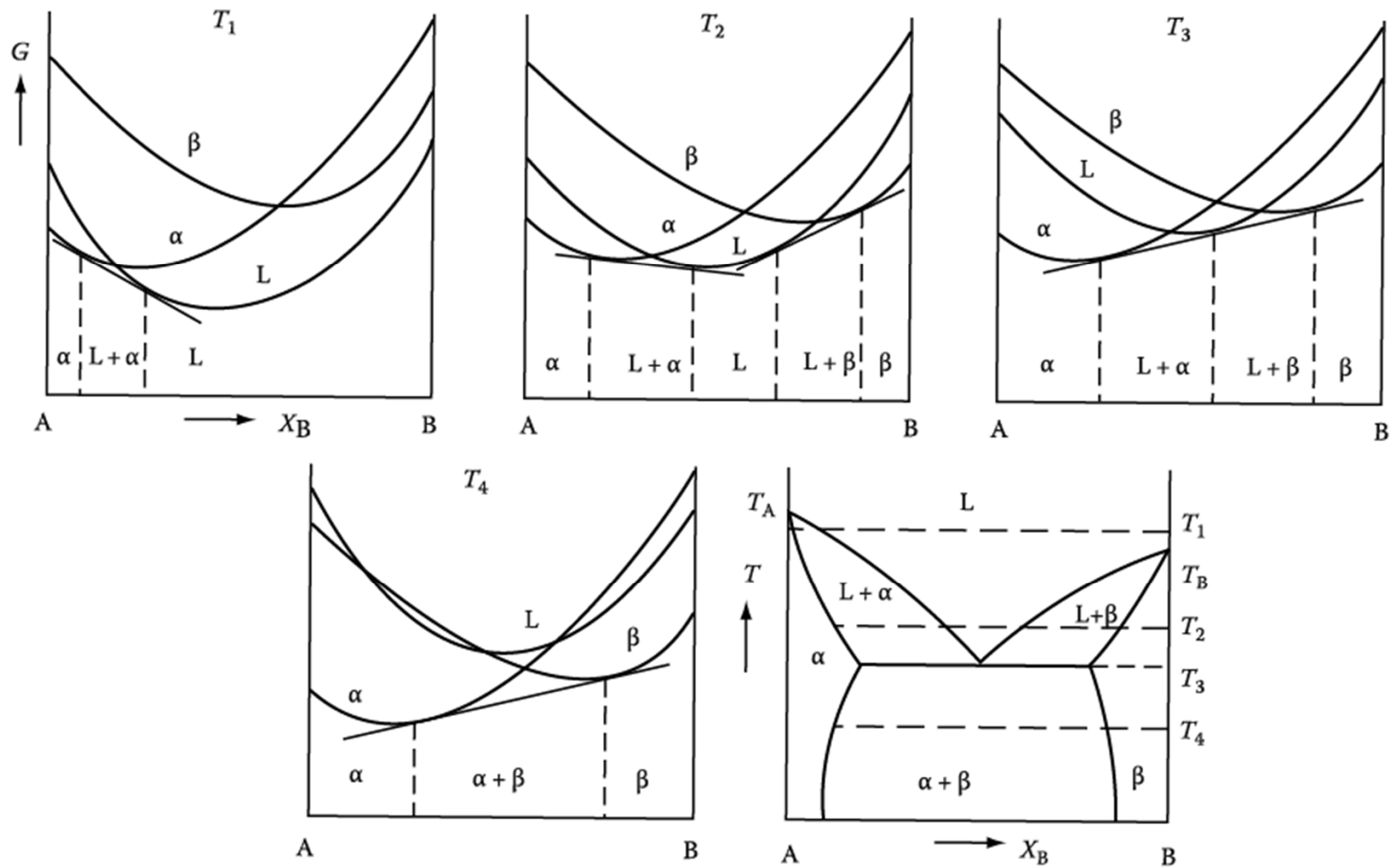
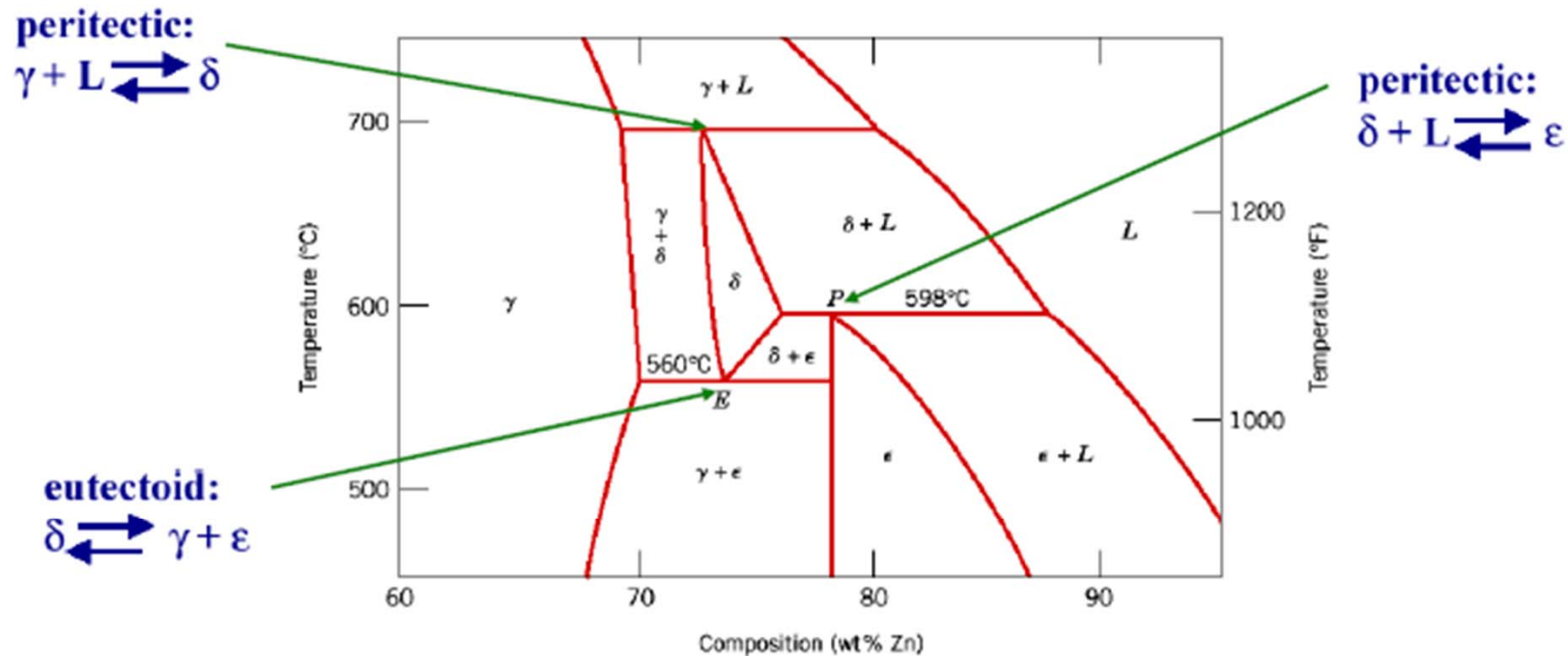


Fig. 1.32 The derivation of a eutectic phase diagram where each solid phases has a different crystal structure.

# Cu-Zn Phase Diagram

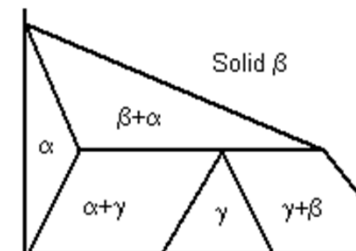
## Eutectoid and Peritectic Reactions



**Eutectoid:** one solid phase transforms into two other solid phases upon cooling

**Peritectic:** one solid and one liquid phase transform into another solid phase upon cooling

**Peritectoid:** two other solid phases transform into another solid phase upon cooling



## 2) Variant of the simple phase diagram

$$\Delta H_{mix} < 0$$

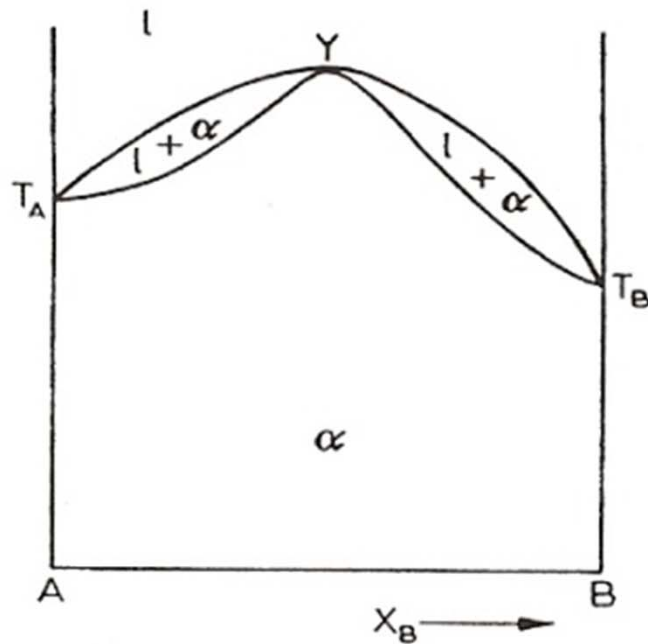


Fig. 32. Phase diagram with a maximum in the liquidus.

**congruent maxima**

$$\Delta H_{mix}^{\alpha} < \Delta H_{mix}^l < 0$$

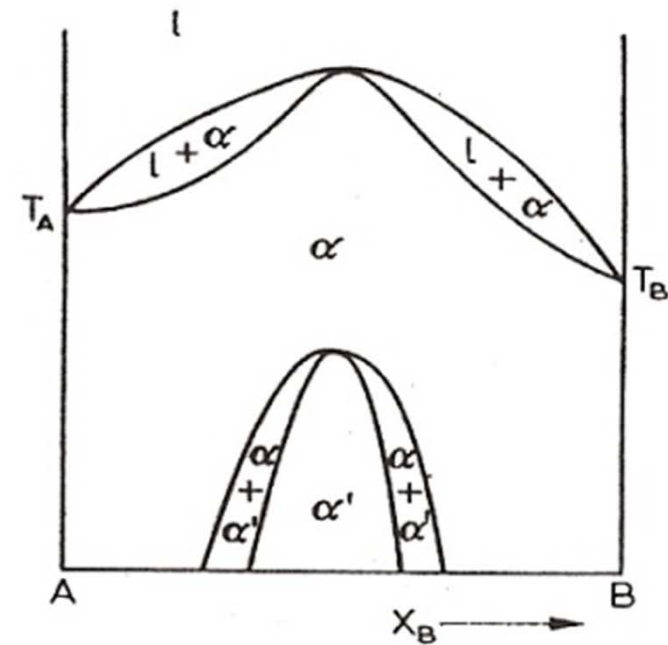
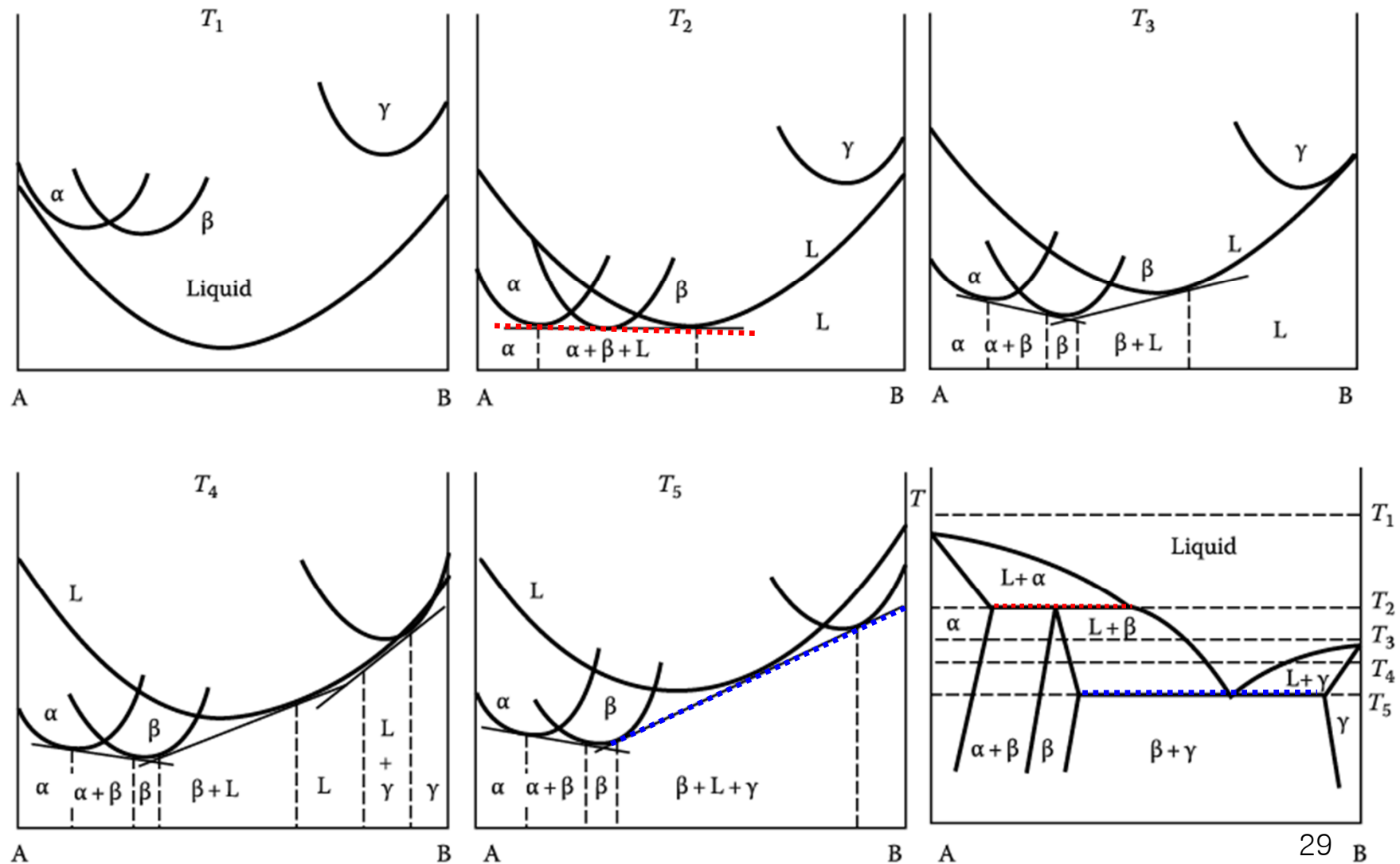


Fig. 33. Appearance of an ordered  $\alpha'$  phase at low temperatures.

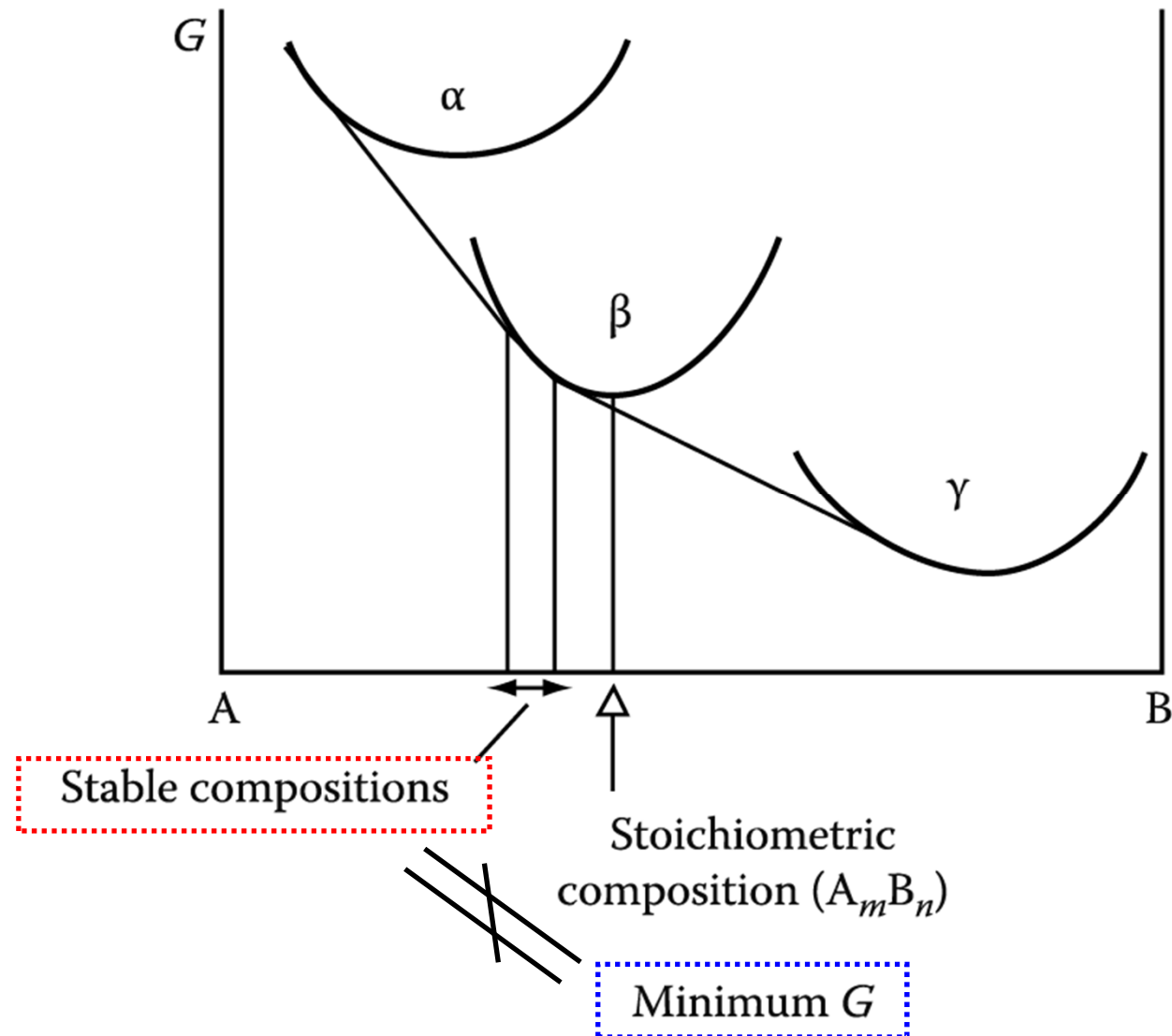
## 1.5 Binary phase diagrams

### 5) Phase diagrams containing intermediate phases

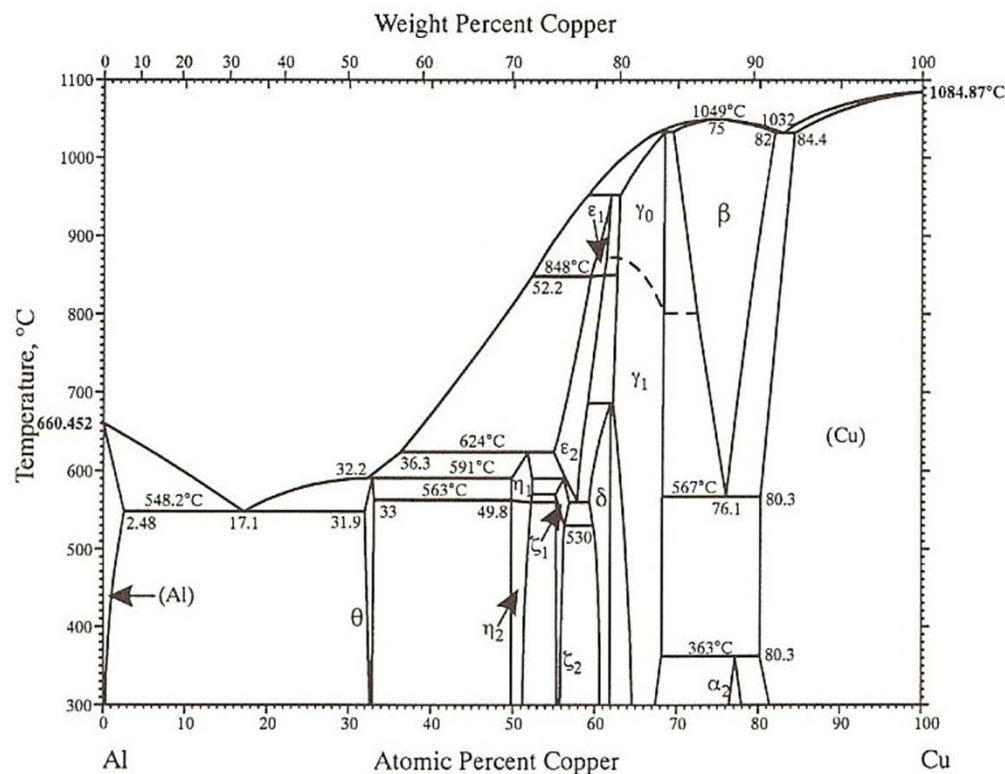


## 1.5 Binary phase diagrams

### 5) Phase diagrams containing intermediate phases



$\theta$  phase in the Cu-Al system is usually denoted as  $\text{CuAl}_2$  although the composition  $X_{\text{Cu}}=1/3$ ,  $X_{\text{Al}}=2/3$  is not covered by the  $\theta$  field on the phase diagram.



Al-Cu

Phase	Composition, at.% Cu	Pearson symbol	Space group	Strukturbericht designation	Prototype
(Al)	0 to 2.48	<i>cF4</i>	<i>Fm</i> $\bar{3}m$	A1	Cu
$\theta$	31.9 to 33.0	<i>tI12</i>	<i>I4/mcm</i>	C16	$\text{Al}_2\text{Cu}$
$\eta_1$	49.8 to 52.4	<i>oP16</i> or <i>oC16</i>	<i>P6</i> $\bar{3}m$ or <i>Cmmm</i>	...	...
$\eta_2$	49.8 to 52.3	<i>mC20</i>	<i>Cm</i> /2	...	...
$\zeta_1$	55.2 to 56.8	<i>hP42</i>	<i>P6</i> $\bar{3}m$	...	...
$\zeta_2$	55.2 to 56.3	<i>m</i> **	...	...	...
$\epsilon_1$	59.4 to 62.1	<i>c</i> **	...	...	...
$\epsilon_2$	55.0 to 61.1	<i>hP4</i>	<i>P6</i> $\bar{3}/mmc$	B8 <sub>1</sub>	NiAs
$\delta$	59.3 to 61.9	<i>hR</i> *	<i>R</i> $\bar{3}m$	...	...
$\gamma_0$	63 to 68.5	<i>cI52</i>	<i>I</i> $\bar{4}3m$	D8 <sub>2</sub>	$\text{Cu}_5\text{Zn}_8$
$\gamma_1$	62.5 to 68.5	<i>cP52</i>	<i>P</i> $\bar{4}3m$	D8 <sub>3</sub>	$\text{Al}_4\text{Cu}_9$
$\beta$	69.5 to 82	<i>cI2</i>	<i>Im</i> $\bar{3}m$	A2	W
$\alpha_2$	76.5 to 78	...	...	...	...
(Cu)	80.3 to 100	<i>cF4</i>	<i>Fm</i> $\bar{3}m$	A1	Cu

J.L. Murray, *Phase Diagrams of Binary Copper Alloys*, P.R. Subramanian, D.J. Chakrabarti, and D.E. Laughlin, ed., ASM International, Materials Park, OH, 18-42 (1994)

X.L. Liu, I. Ohnuma, R. Kainuma, and K. Ishida, *J. Alloys Compds*, 264, 201-208 (1998)

# Summary I: Binary phase diagrams

## 1) Simple Phase Diagrams

Both are ideal soln. → 1) Variation of temp.:  $G^L > G^S$  2) Decrease of curvature of G curve  
( $\therefore$  decrease of  $-T\Delta S_{\text{mix}}$  effect)

## 2) Systems with miscibility gap $\Delta H_{\text{mix}}^L = 0 \quad \Delta H_{\text{mix}}^S > 0$

1) Variation of temp.:  $G^L > G^S$  2) Decrease of curvature of G curve + Shape change of G curve by H

## 4) Simple Eutectic Systems $\Delta H_{\text{mix}}^L = 0 \quad \Delta H_{\text{mix}}^S \gg 0$

→ miscibility gap extends to the melting temperature.

## 3) Ordered Alloys $\Delta H_{\text{mix}}^L = 0 \quad \Delta H_{\text{mix}}^S < 0$

$\Delta H_{\text{mix}} < 0 \rightarrow$  A atoms and B atoms like each other.  $\rightarrow$  Ordered alloy at low T

$\Delta H_{\text{mix}} \ll 0 \rightarrow$  The ordered state can extend to the melting temperature.

## 5) Phase diagrams containing intermediate phases

Stable composition  $\neq$  Minimum G with stoichiometric composition



# The Gibbs Phase Rule

**Degree of freedom** (number of variables that can be varied independently)

**= the number of variables – the number of constraints**

- Number of phases :  $p$ , number of components :  $c$ ,
- # of controllable variable : composition  $(c-1)p$ , temperature :  $p$ , pressure :  $p$
- # of restrictions :

$$(p-1)c \text{ from chemical equilibrium} \quad \mu_i^a = \mu_i^b = \mu_i^c = \dots = \mu_i^p$$

$$p-1 \text{ from thermal equilibrium} \quad T^a = T^b = T^c = \dots = T^p$$

$$p-1 \text{ from mechanical equilibrium} \quad P^a = P^b = P^c = \dots = P^p$$

- Number of variable can be controlled with maintaining equilibrium

$$f = (c-1)p + p + p - (p-1)c - (p-1) - (p-1) = c - p + 2$$

$$f = c - p + 2$$

- If pressure is constant :  $f = (c-1)p + p - (p-1)c - (p-1) = c - p + 1$

## 1.5 Binary phase diagrams

### The Gibbs Phase Rule

In chemistry, Gibbs' phase rule describes the possible number of degrees of freedom (F) in a closed system at equilibrium, in terms of the number of separate phases (P) and the number of chemical components (C) in the system. It was deduced from thermodynamic principles by Josiah Willard Gibbs in the 1870s.

#### Gibbs phase rule

$$F = C + N - P$$

F: degree of freedom

C: number of chemical variables

N: number of non-chemical variables

P: number of phases

In general, Gibbs' rule then follows, as:

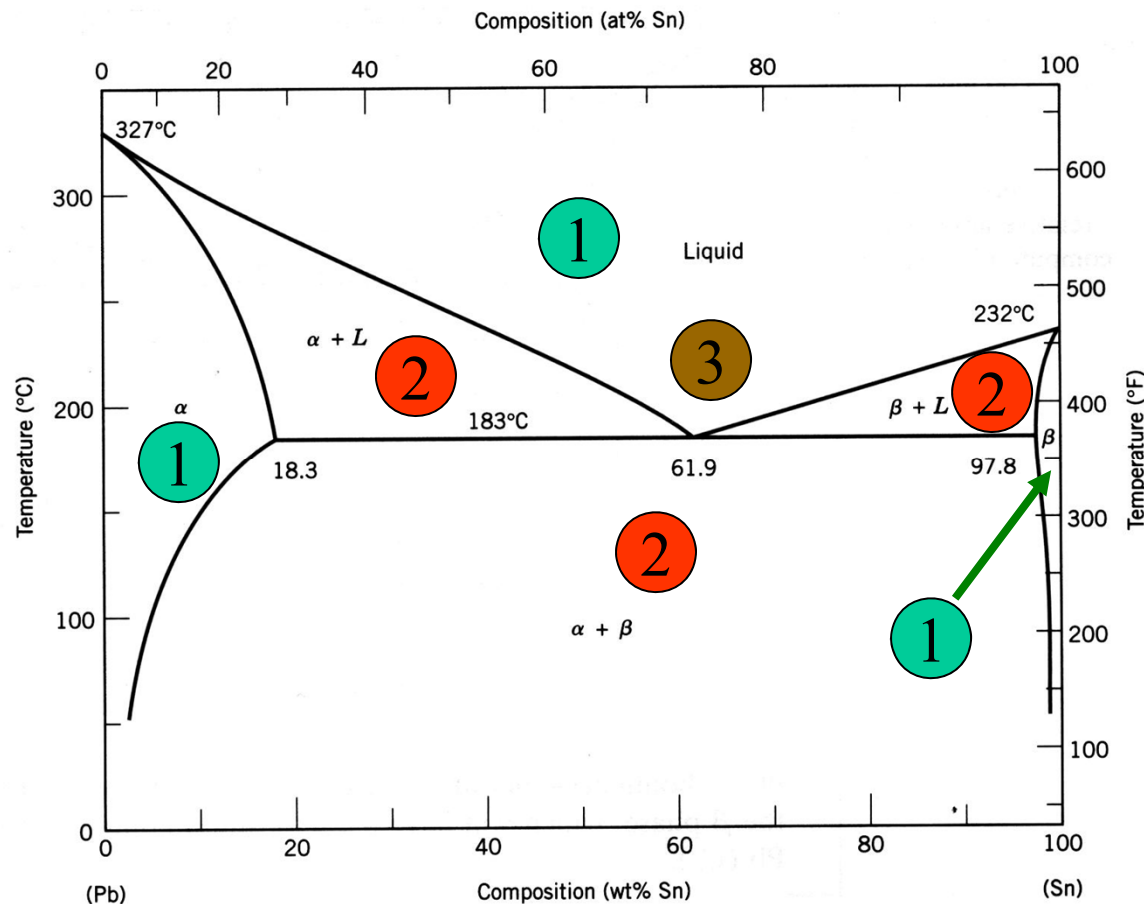
$$F = C - P + 2 \quad (\text{from } T, P).$$

From Wikipedia, the free encyclopedia

# The Gibbs Phase Rule

For Constant Pressure,

$$P + F = C + 1$$



1 single phase

$$F = C - P + 1$$

$$= 2 - 1 + 1$$

$$= 2$$

can vary T and composition independently

2 two phase

$$F = C - P + 1$$

$$= 2 - 2 + 1$$

$$= 1$$

can vary T *or* composition

3 eutectic point

$$F = C - P + 1$$

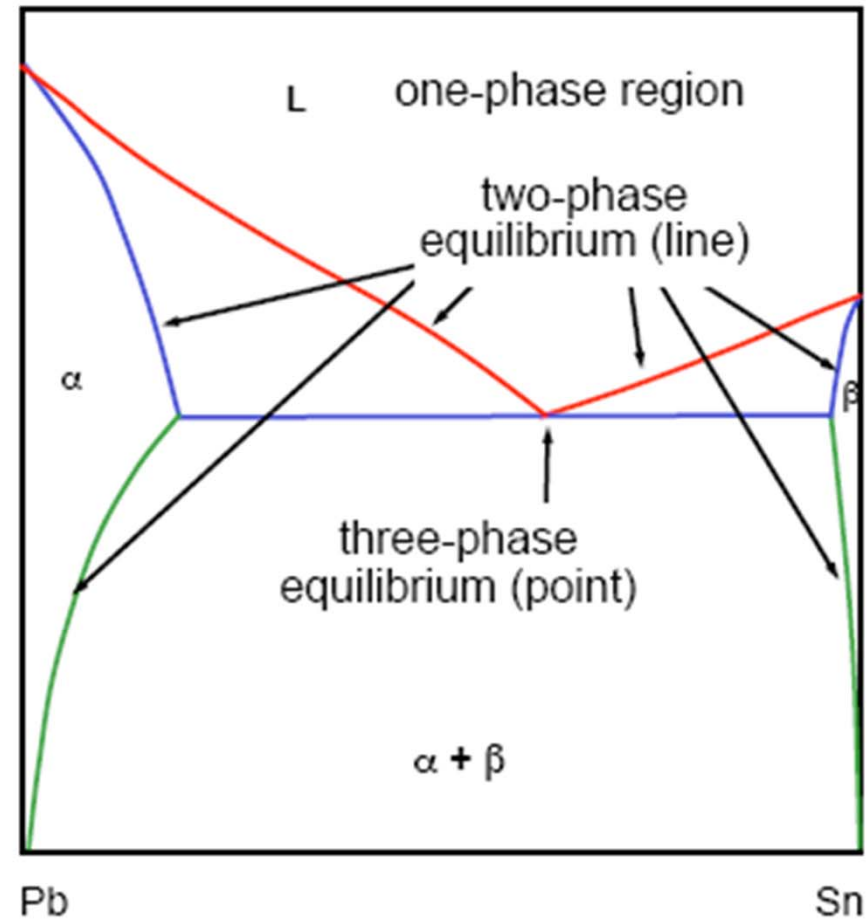
$$= 2 - 3 + 1$$

$$= 0$$

can't vary T or composition

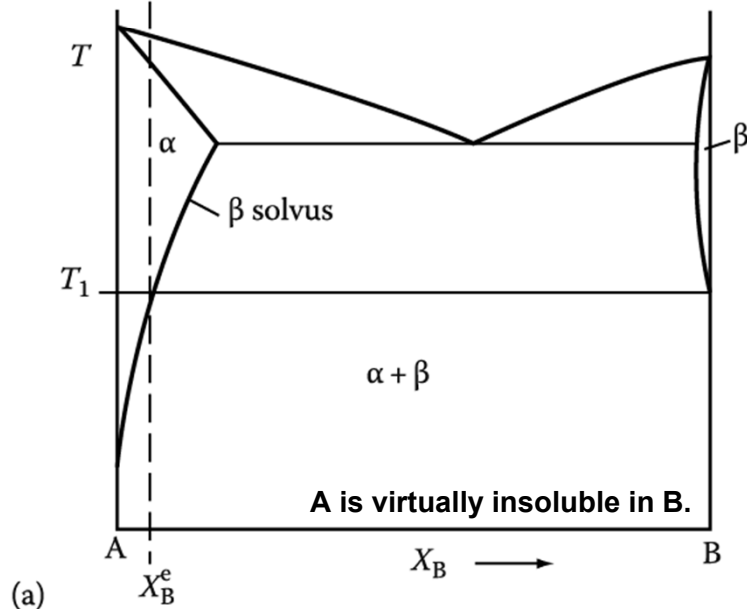
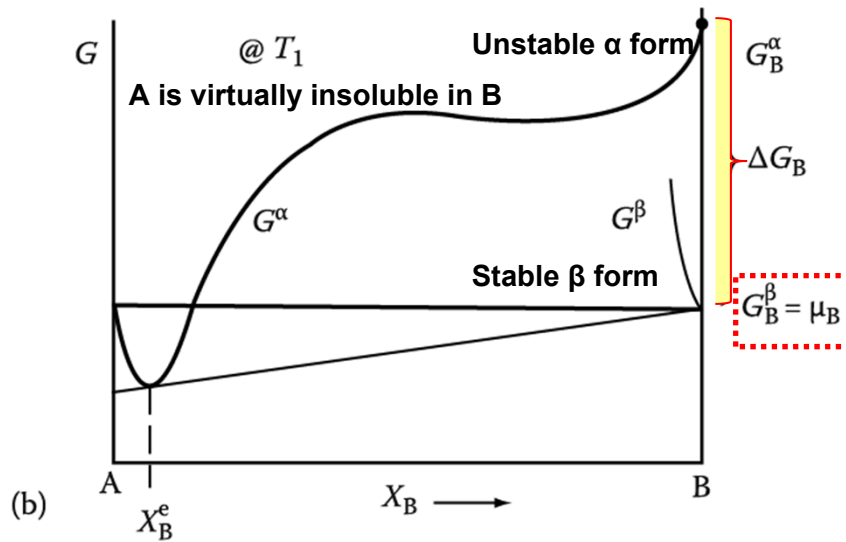
# The Gibbs Phase Rule

Application of Gibbs phase rule:  
For a binary system at ambient pressure:  
 $C=2$  (2 elements)  
 $N=1$  (temperature, no pressure)  
For single phase:  $F=2$ : % and  $T$   
(a region)  
For a 2-phase equilibrium:  $F=1$ :  
% or  $T$  (a line)  
For a 3-phase equilibrium:  $F=0$ , (invariant  
point)



## 1.5.7 Effect of T on solid solubility

$$T \uparrow \Rightarrow X_B^e \uparrow$$



$$\mu_B^\alpha = {}^oG_B^\alpha + \Omega(1 - X_B)^2 + RT \ln X_B = \mu_B^\beta \approx {}^oG_B^\beta$$

$$\Delta G_B^{\beta \rightarrow \alpha} = {}^oG_B^\alpha - {}^oG_B^\beta = {}^oG_B^\alpha - \mu_B^\beta = {}^oG_B^\alpha - \mu_B^\alpha$$

$${}^oG_B^\alpha - \mu_B^\alpha = -\Omega(1 - X_B)^2 - RT \ln X_B$$

$$\Delta G_B^{\beta \rightarrow \alpha} = -\Omega(1 - X_B)^2 - RT \ln X_B$$

$$RT \ln X_B = -\Delta G_B^{\beta \rightarrow \alpha} - \Omega(1 - X_B)^2$$

(here,  $X_B^e \ll 1$ )

$$RT \ln X_B^e = -\Delta G_B^{\beta \rightarrow \alpha} - \Omega$$

$$\gg X_B^e = \exp\left(-\frac{\Delta G_B^{\beta \rightarrow \alpha} + \Omega}{RT}\right)$$

$$\Delta G_B^{\beta \rightarrow \alpha} = \Delta H_B^{\beta \rightarrow \alpha} - T\Delta S_B^{\beta \rightarrow \alpha} \quad \text{이므로}$$

$$X_B^e = \exp\left(\frac{\Delta S_B^{\beta \rightarrow \alpha}}{R}\right) \exp\left(-\frac{\Delta H_B^{\beta \rightarrow \alpha} + \Omega}{RT}\right)$$

$$X_B^e = A \exp\left\{-\frac{Q}{RT}\right\}$$

$$T \uparrow \Rightarrow X_B^e \uparrow$$

**Q** : heat absorbed (enthalpy) when 1 mole of  $\beta$  dissolves in A rich  $\alpha$  as a dilute solution.

\* Limiting forms of eutectic phase diagram

The solubility of one metal in another may be so low.

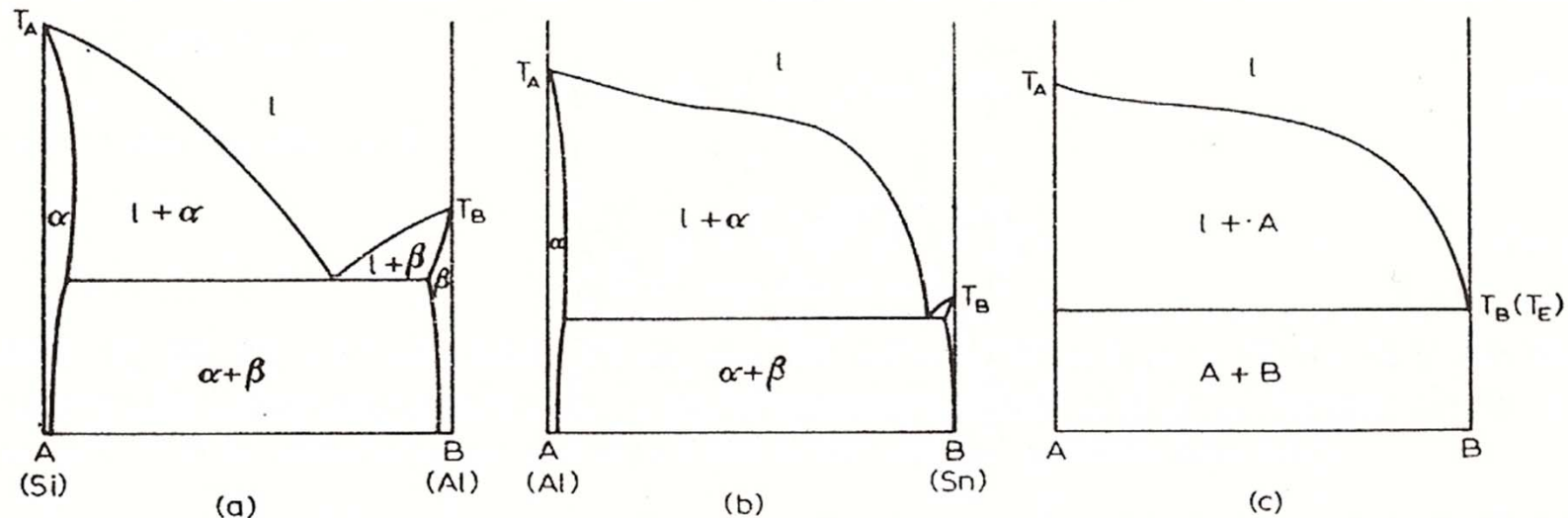


Fig. 53. Evolution of the limiting form of a binary eutectic phase diagram.

$$X_B^e = A \exp\left\{-\frac{Q}{RT}\right\}$$

a)

$$T \uparrow \Rightarrow X_B^e \uparrow$$

b) It is interesting to note that, **except at absolute zero,  $X_B^e$  can never be equal to zero**, that is, no two components are ever completely insoluble in each other.

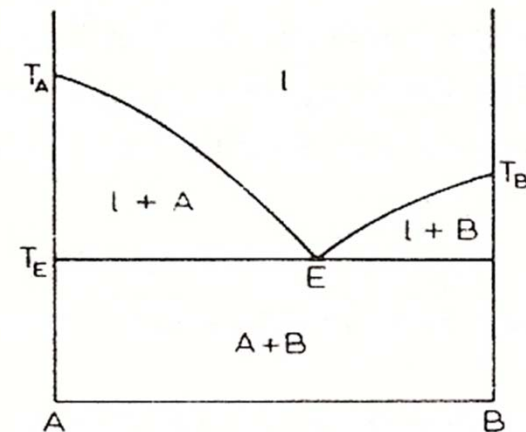
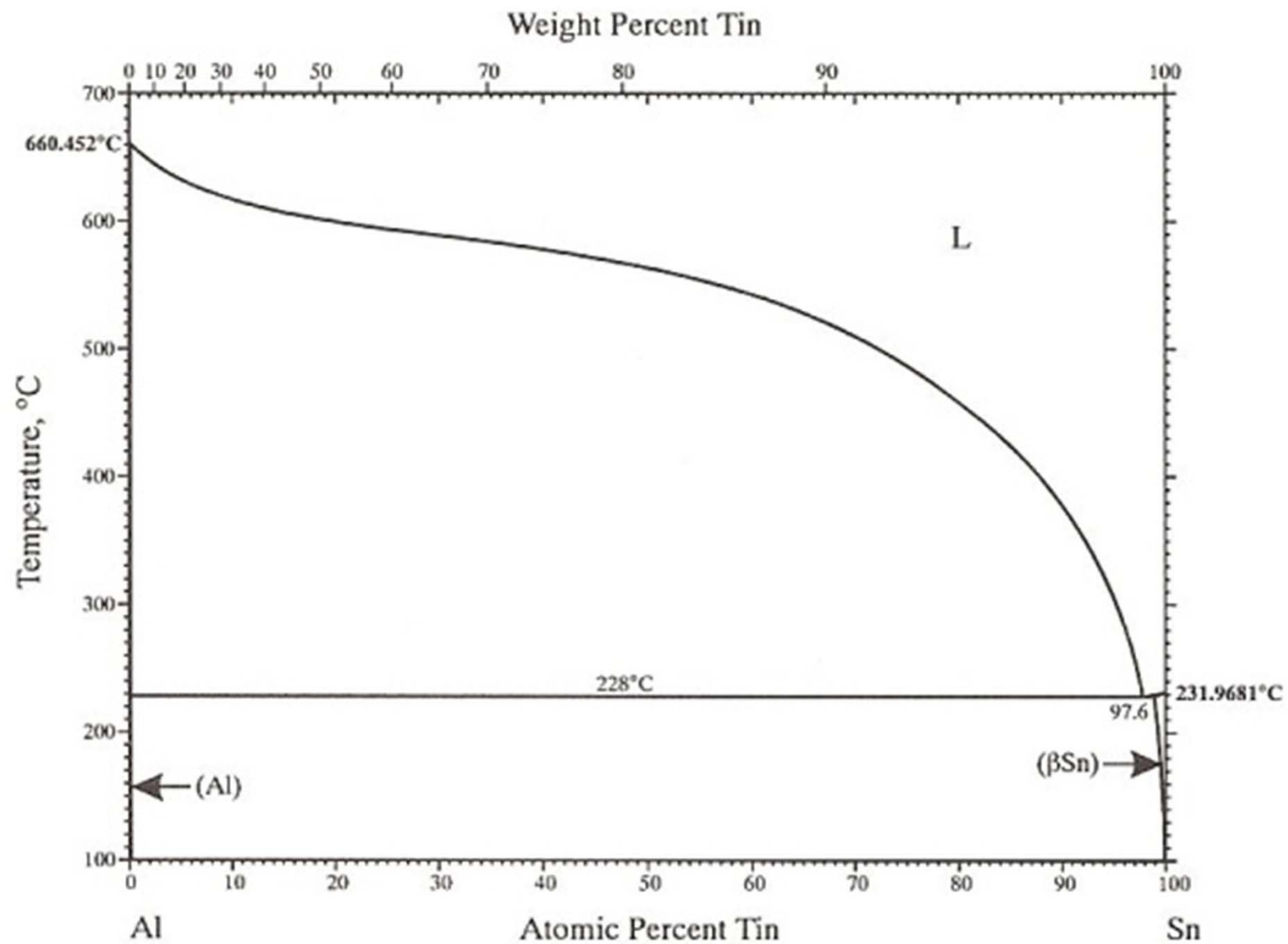


Fig. 54. Impossible form of a binary eutectic phase diagram.



a) 평형에 미치는 공공의 영향

### 1.5.8. Equilibrium Vacancy Concentration $\Delta G = \Delta H - T\Delta S$

G of the alloy will depend on the concentration of vacancies and  $X_V^e$  will be that which gives the minimum free energy.

- 1) **Vacancies increase the internal energy of crystalline metal due to broken bonds formation.** (Here, vacancy-vacancy interactions are ignored.)

$$\Delta H \cong \Delta H_V X_V$$

- 2) **Vacancies increase entropy** because they change the **thermal vibration frequency** and also the **configurational entropy**.
- Small change due to changes in the vibrational frequencies      "Largest contribution"

- Total entropy change is thus

$$\Delta S = \Delta S_V X_V - R\{X_V \ln X_V + (1 - X_V) \ln(1 - X_V)\}$$

The molar free energy of the crystal containing  $X_V$  mol of vacancies

$$G = G_A + \Delta G = G_A + \Delta H_V X_V - T\Delta S_V X_V + RT\{X_V \ln X_V + (1 - X_V) \ln(1 - X_V)\}$$

➡ **With this information,  
estimate the equilibrium vacancy concentration.**



Equilibrium concentration  $X_V^e$  will be that which gives the minimum free energy.

at equilibrium  $\left( \frac{dG}{dX_V} \right)_{X_V = X_V^e} = 0$

$$\Delta H_V - T\Delta S_V + RT \ln X_V^e = 0$$

A constant ~3, independent of T

Rapidly increases with increasing T

$$X_V^e = \exp \frac{\Delta S_V}{R} \cdot \exp \frac{-\Delta H_V}{RT}$$

putting  $\Delta G_V = \Delta H_V - T\Delta S_V$

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

- In practice,  $\Delta H_V$  is of the order of 1 eV per atom and  $X_V^e$  reaches a value of about  $10^{-4} \sim 10^{-3}$  at the melting point of the solid

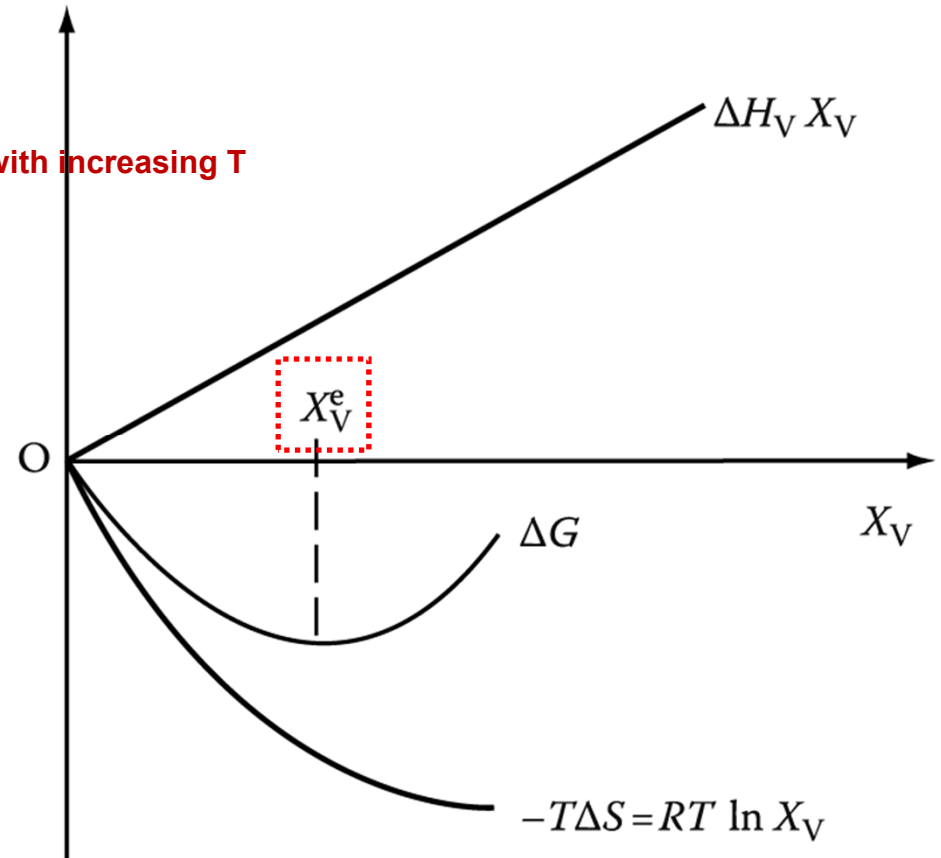


Fig. 1.37 Equilibrium vacancy concentration.

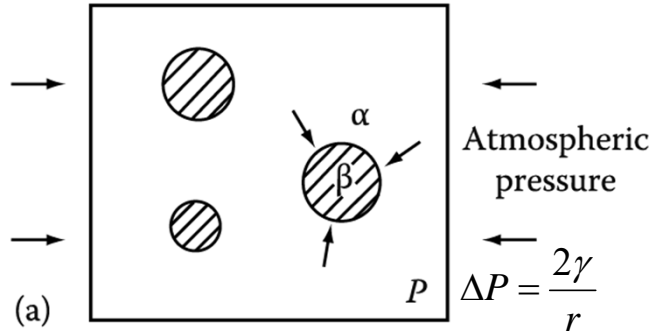
: adjust so as to reduce G to a minimum

The G curves so far have been based on the molar Gs of infinitely large amounts of material of a perfect single crystal. Surfaces, GBs and interphase interfaces have been ignored.

## 1.6 Influence of Interfaces on Equilibrium - b) 평형에 미치는 계면의 영향

$$\Delta G = \Delta P \cdot V \Rightarrow \Delta G = \frac{2\gamma V_m}{r}$$

Extra pressure  $\Delta P$  due to curvature of the  $\alpha/\beta$



The concept of a pressure difference is very useful for spherical liquid particles, but it is less convenient in solids (often nonspherical shape).

$$dG = \Delta G_\gamma dn = \gamma dA \quad \Delta G_\gamma = \gamma dA/dn$$

Since  $n = 4\pi r^3/3V_m$  and  $A = 4\pi r^2$   $\Delta G = \frac{2\gamma V_m}{r}$

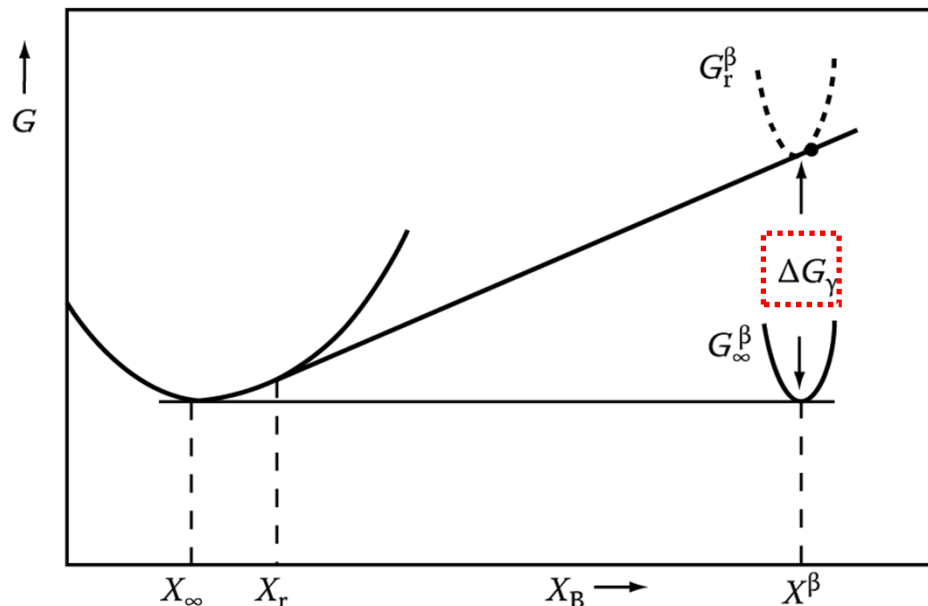


Fig. 1.38 The effect of interfacial E on the solubility of small particle

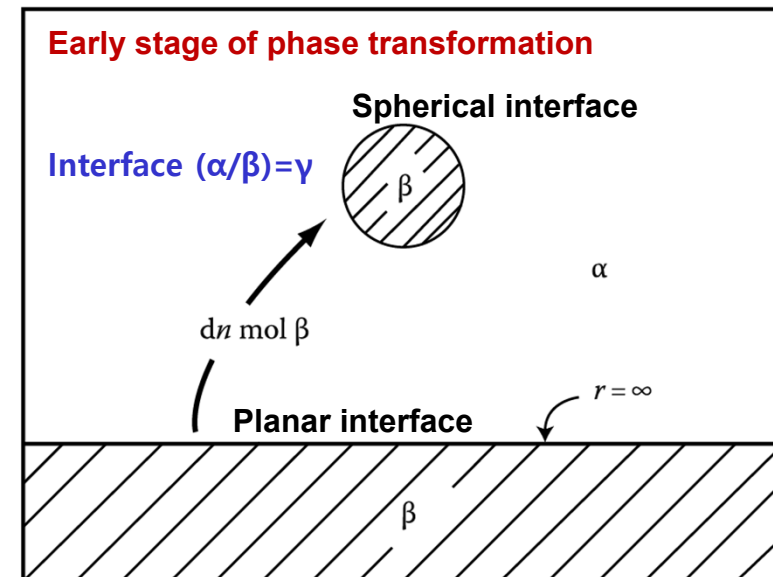
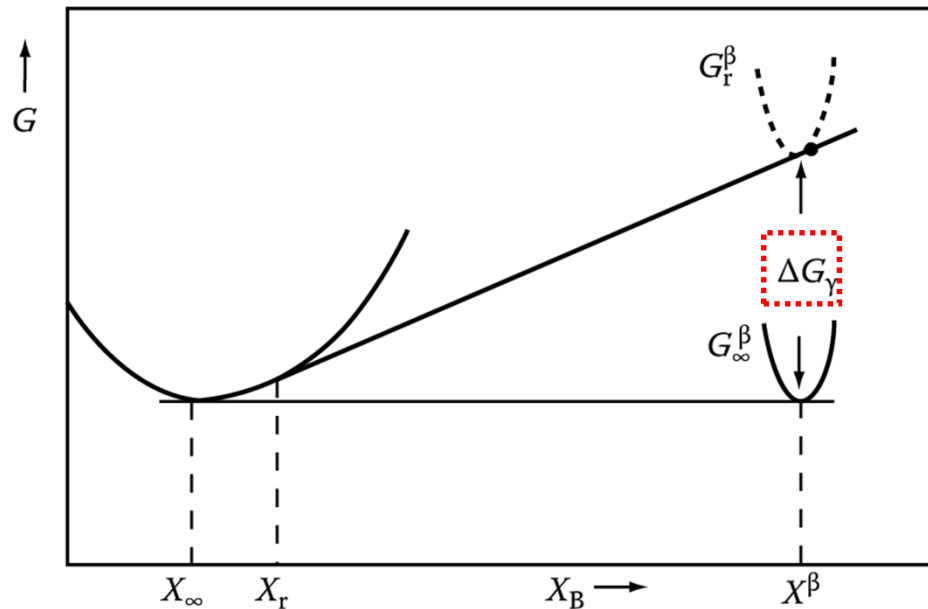


Fig. 1.39 Transfer of  $dn$  mol of  $\beta$  from large to a small particle.

## Gibbs-Thomson effect (capillarity effect):

Free energy increase due to interfacial energy

Quite large solubility differences can arise for particles in the range  $r=1-100$  nm. However, for particles visible in the light microscope ( $r>1\mu\text{m}$ ) capillarity effects are very small.



(b)

Fig. 1.38 The effect of interfacial energy on the solubility of small particles.

$$X_B^e = A \exp\left\{-\frac{Q}{RT}\right\}$$

$$X_B^e = \exp\left(-\frac{\Delta G_B + \Omega}{RT}\right)$$

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

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

$$= X_B^{r=\infty} \exp\left(\frac{2\gamma V_m}{RT r}\right)$$

For small values of the exponent,

$$\frac{X_B^{r=r}}{X_B^{r=\infty}} = \exp\left(\frac{2\gamma V_m}{RT r}\right) \approx 1 + \frac{2\gamma V_m}{RT r}$$

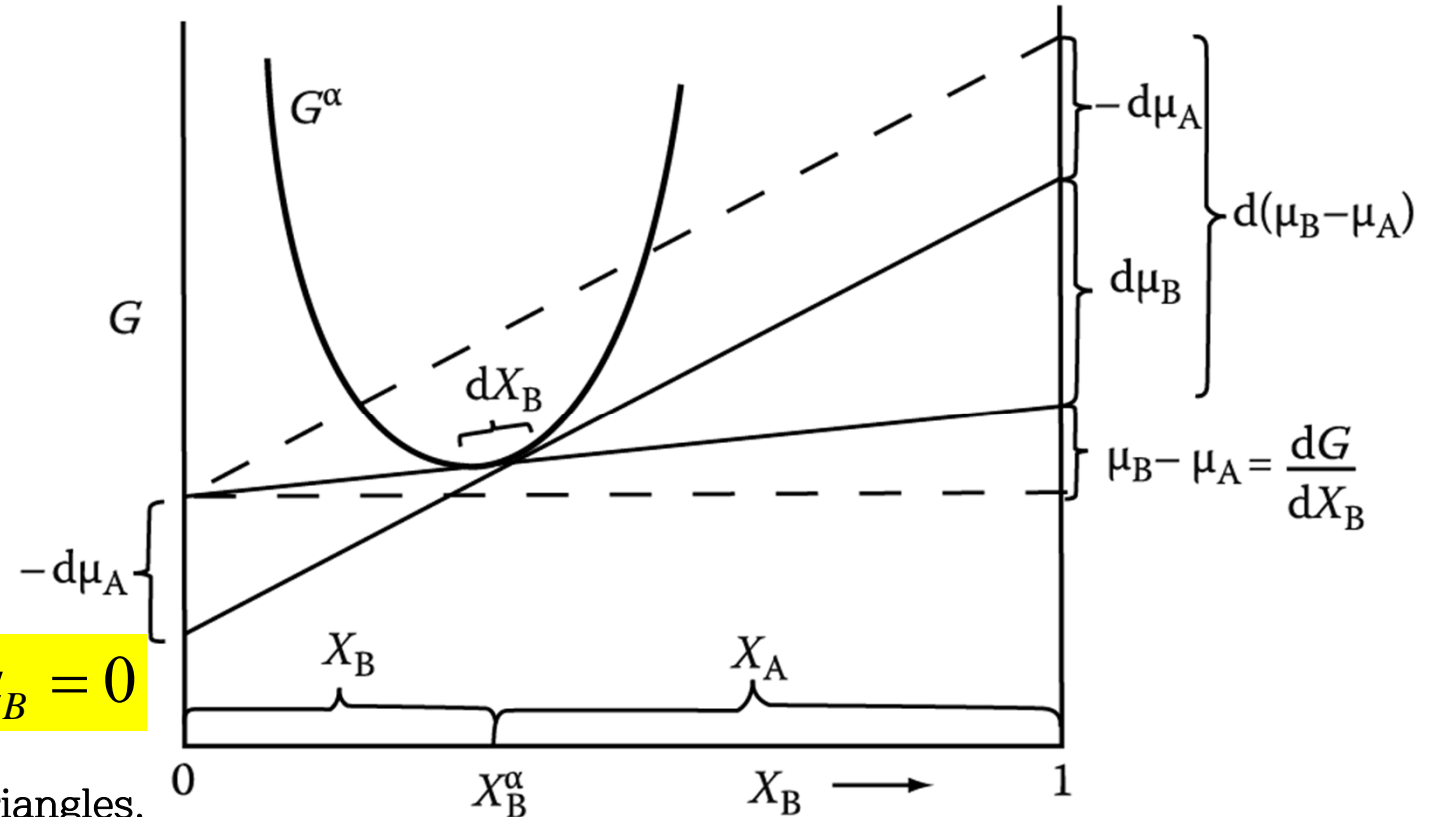
Ex)  $\gamma = 200 \text{ mJ/m}^2$ ,  $V_m = 10^{-5} \text{ m}^3$ ,  $T = 500 \text{ K}$

$$\frac{X_r}{X_\infty} = 1 + \frac{1}{r(\text{nm})}$$

For  $r = 10$  nm, solubility  $\sim 10\%$  increase

## 1.8 Additional Thermodynamic Relationships for Binary Solutions

➡ **Gibbs-Duhem equation:** Calculate the change in ( $d\mu$ ) that results from a change in ( $dX$ )



$$X_A d\mu_A + X_B d\mu_B = 0$$

Comparing two similar triangles,

$$-\frac{d\mu_A}{X_B} = \frac{d\mu_B}{X_A} = \frac{d(\mu_B - \mu_A)}{1} \quad \leftarrow \quad \frac{dG}{dX_B} = \frac{\mu_B - \mu_A}{1}, \quad \frac{d^2G/dX^2}{d^2G/dX_B^2} = d^2G/dX_A^2$$

Substituting right side Eq.  
& Multiply  $X_A X_B$

$$-X_A d\mu_A = X_B d\mu_B = X_A X_B \frac{d^2G}{dX^2} dX_B$$

**Eq. 1.65**

# Additional Thermodynamic Relationships for Binary Solutions

**The Gibbs-Duhem Equation** 합금조성의 미소변화 (dX)로 인한 화학퍼텐셜의 미소변화(dμ)를 계산  
be able to calculate the change in chemical potential (dμ) that result from a change in alloy composition (dX).

① For a regular solution,

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

$$\frac{d^2 G}{dX^2} = \frac{RT}{X_A X_B} - 2\Omega$$

For an ideal solution,  $\Omega = 0$ ,

$$\frac{d^2 G}{dX^2} = \frac{RT}{X_A X_B}$$

② Different form  
Eq. 1.65

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

$$\gamma_B = a_B / X_B \rightarrow$$

Differentiating  
With respect to  $X_B$ ,

$$\frac{d\mu_B}{dX_B} = \frac{RT}{X_B} \left\{ 1 + \frac{X_B}{\gamma_B} \frac{d\gamma_B}{dX_B} \right\} = \frac{RT}{X_B} \left\{ 1 + \frac{d \ln \gamma_B}{d \ln X_B} \right\}$$

$$\boxed{\frac{d\mu_B}{dX_B}} = \frac{RT}{X_B} \left\{ 1 + \frac{X_B}{\gamma_B} \frac{d\gamma_B}{dX_B} \right\} = \frac{RT}{X_B} \left\{ 1 + \frac{d \ln \gamma_B}{d \ln X_B} \right\} \quad \text{Eq. 1.69}$$

a similar relationship can be derived for  $d\mu_A/dX_B$

$$\left. \begin{aligned} -X_A d\mu_A &= X_B d\mu_B = RT \left\{ 1 + \frac{d \ln \gamma_A}{d \ln X_A} \right\} dX_B = RT \left\{ 1 + \frac{d \ln \gamma_B}{d \ln X_B} \right\} dX_B \end{aligned} \right\} \quad \text{Eq. 1.70}$$

$$\left. \begin{aligned} -X_A d\mu_A &= X_B d\mu_B = X_A X_B \frac{d^2 G}{dX^2} dX_B \end{aligned} \right\} \quad \text{Eq. 1.65}$$

**The Gibbs-Duhem Equation**

$$X_A X_B \frac{d^2 G}{dX^2} = RT \left\{ 1 + \frac{d \ln \gamma_A}{d \ln X_A} \right\} = RT \left\{ 1 + \frac{d \ln \gamma_B}{d \ln X_B} \right\}$$

be able to calculate the change in chemical potential ( $d\mu$ ) that result from a change in alloy composition ( $dX$ ).



## Summary II: Binary phase diagrams

### - Gibbs Phase Rule $F = C - P + 1$ (constant pressure)

Gibbs' Phase Rule allows us to construct phase diagram to represent and interpret phase equilibria in heterogeneous geologic systems.

### • Effect of Temperature on Solid Solubility

$$X_B^e = A \exp\left\{-\frac{Q}{RT}\right\} \quad \text{a) } T \uparrow \Rightarrow X_B^e \uparrow \quad \text{b) } X_B^e \text{ can never be equal to zero.}$$

### • Equilibrium Vacancy Concentration

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

### • Influence of Interfaces on Equilibrium

$$\Delta G = \frac{2\gamma V_m}{r} \quad \text{Gibbs-Thomson effect}$$

### • Gibbs-Duhem Equation: Be able to calculate the change in chemical potential that result from a change in alloy composition.

$$X_A X_B \frac{d^2 G}{dX^2} = RT \left\{ 1 + \frac{d \ln \gamma_A}{d \ln X_A} \right\} = RT \left\{ 1 + \frac{d \ln \gamma_B}{d \ln X_B} \right\}$$

합금조성의 미소변화 (dX)로 인한 화학퍼텐셜의 미소변화(dμ)를 계산



## Topic proposal for materials design

Please submit 3 materials that you want to explore for materials design and do final presentations on in this semester. Please make sure to thoroughly discuss why you chose those materials (up to 1 page on each topic). The proposal is due by September 25 on eTL.

Ex) stainless steel/ graphene/ OLED/  
Bio-material/ Shape memory alloy  
Bulk metallic glass, etc.