2009 fall

Phase Transformation of Materials

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Contents for previous class

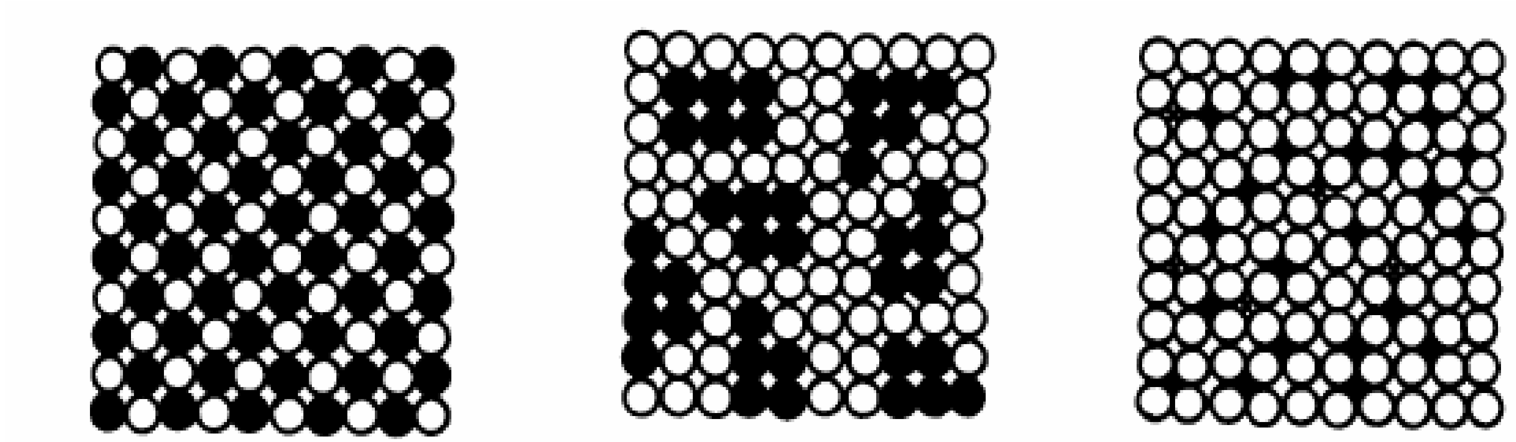
- Binary System   mixture/ solution / compound

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

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

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

Real solution   **Ordered structure**



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

Ordered alloys

$P_{AB} \uparrow \longrightarrow$ 내부 E $\downarrow$

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

Clustering

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

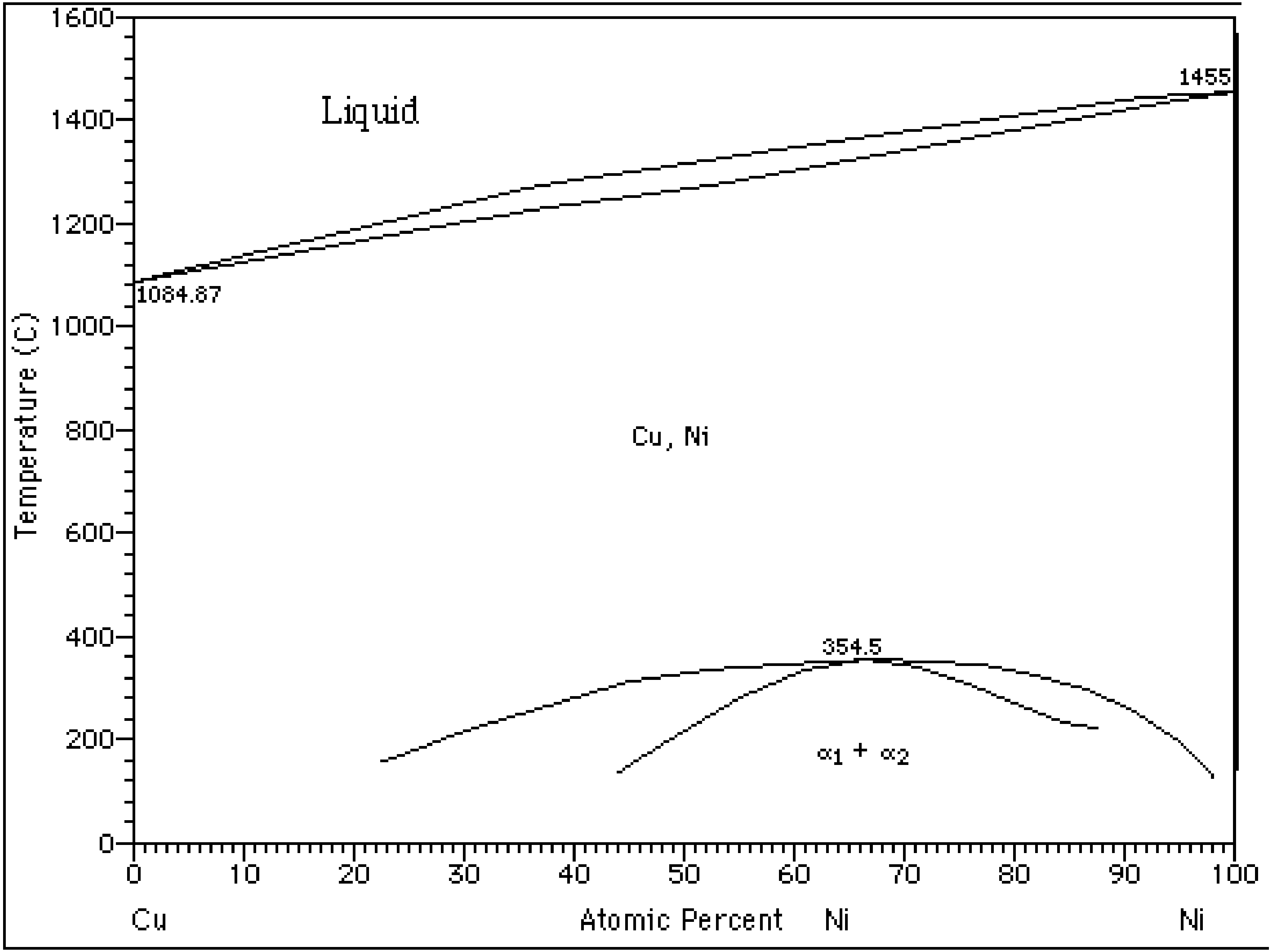
(c) when the size difference is large

strain effect

Interstitial solution

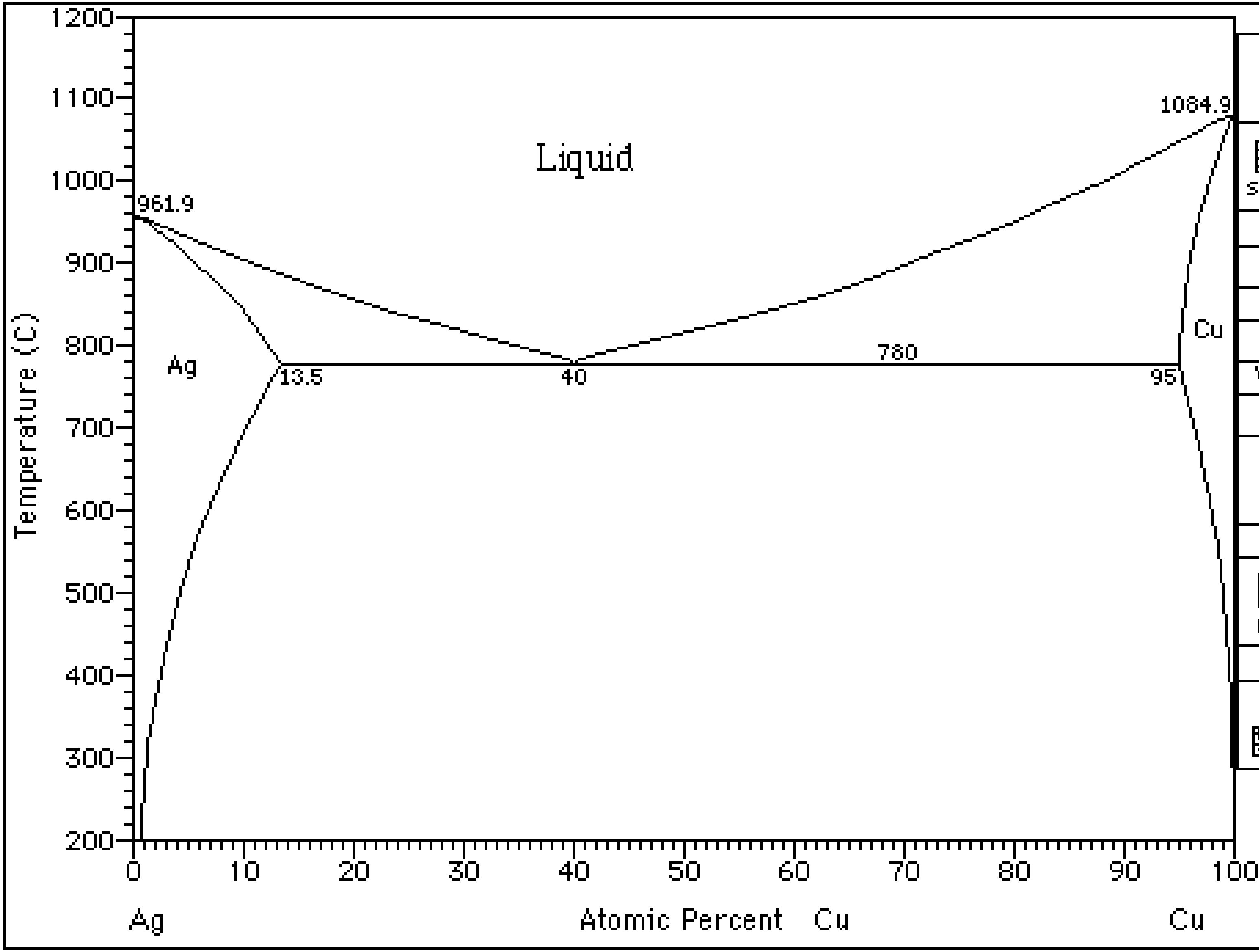
Contents for previous class

$\varepsilon > 0$, $\Delta H_{mix} > 0$ / $\Delta H_{mix} \sim$ +26 kJ/mol



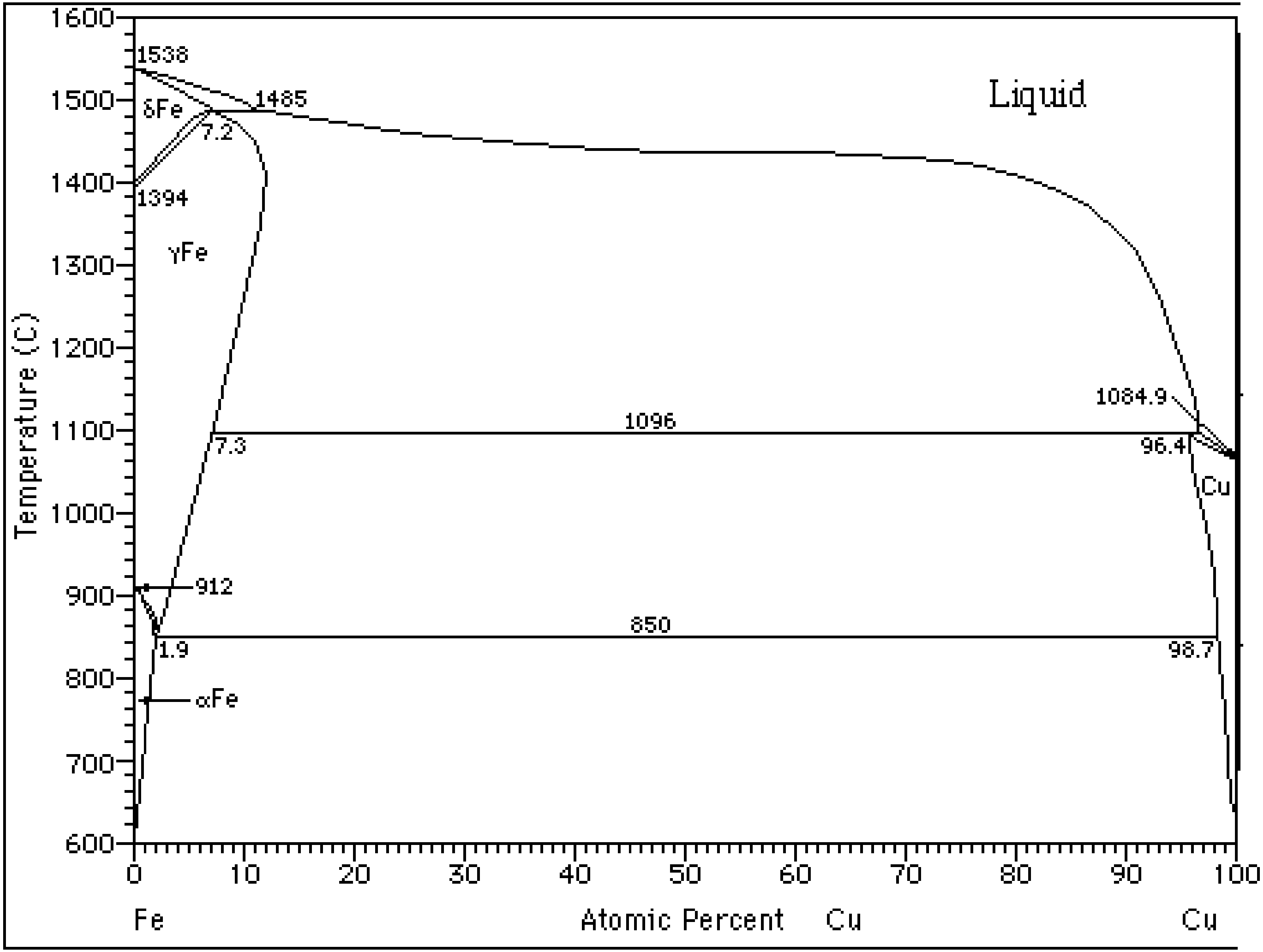
Contents for previous class

$\varepsilon > 0$, $\Delta H_{mix} > 0$ / $\Delta H_{mix} \sim$ +5 kJ/mol



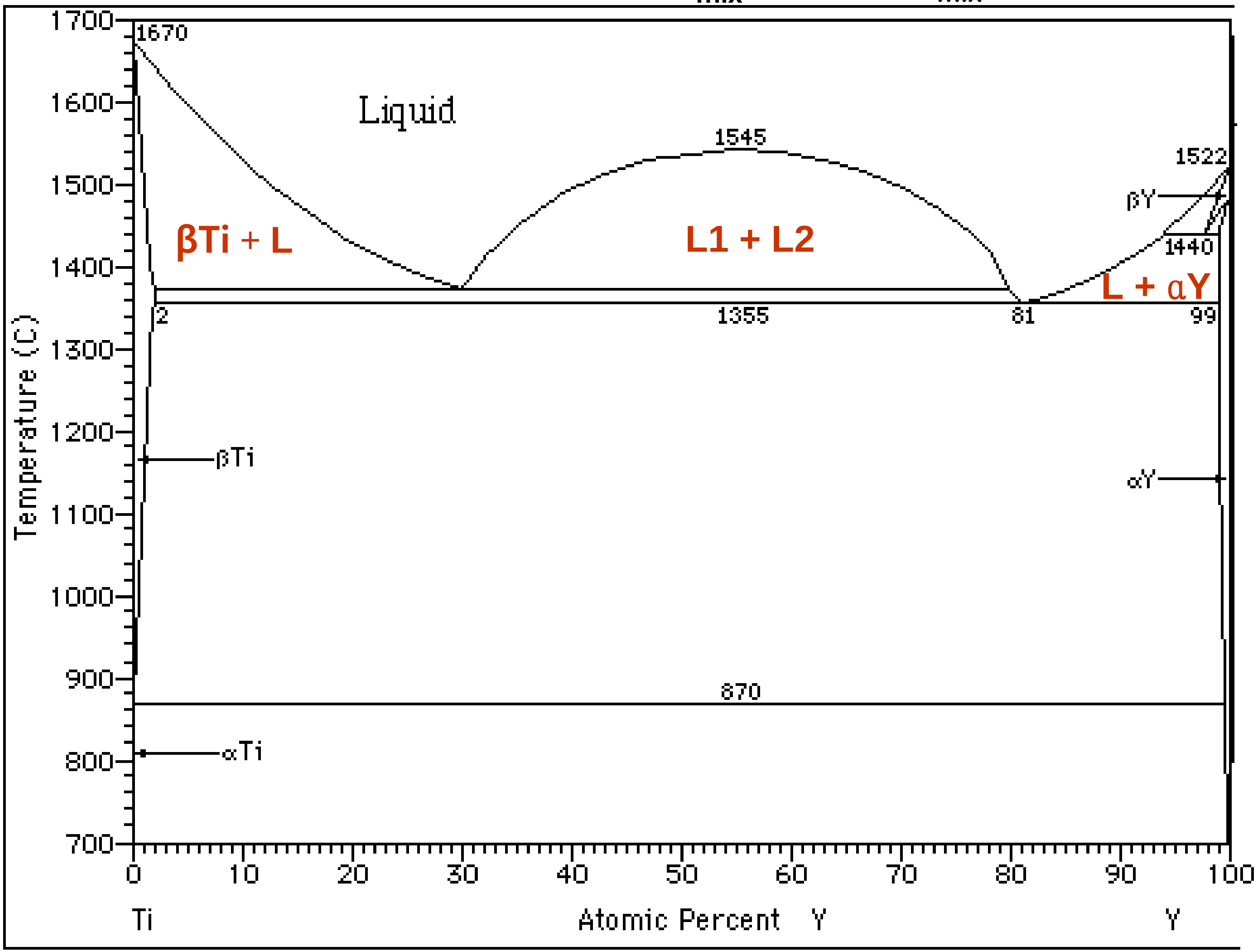
Contents for previous class

$\varepsilon >> 0$, $\Delta H_{mix} >> 0$ / $\Delta H_{mix} \sim$ +60 kJ/mol



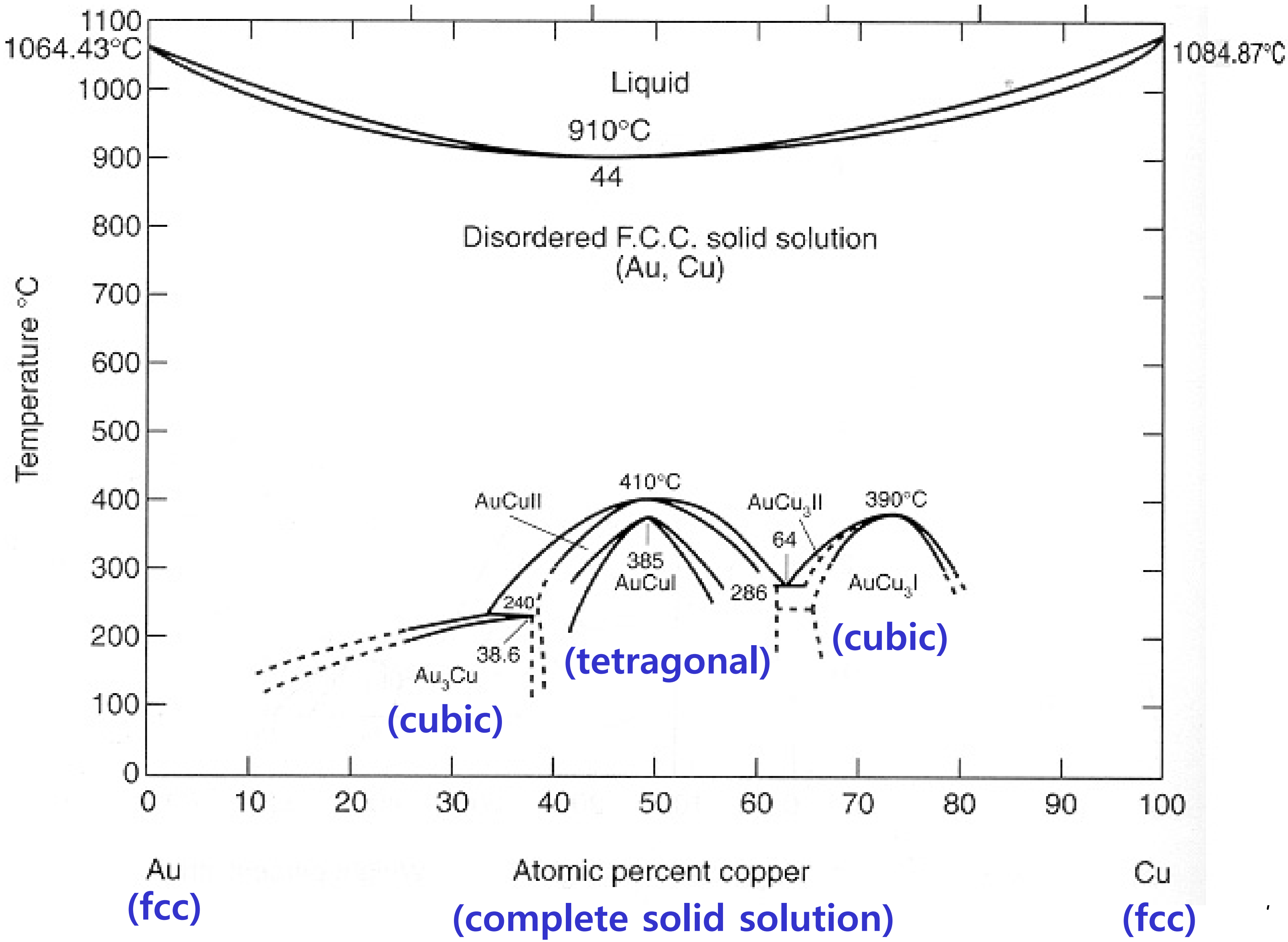
Contents for previous class

$\varepsilon >> 0$, $\Delta H_{mix} >> 0$ / $\Delta H_{mix} \sim$ +58 kJ/mol



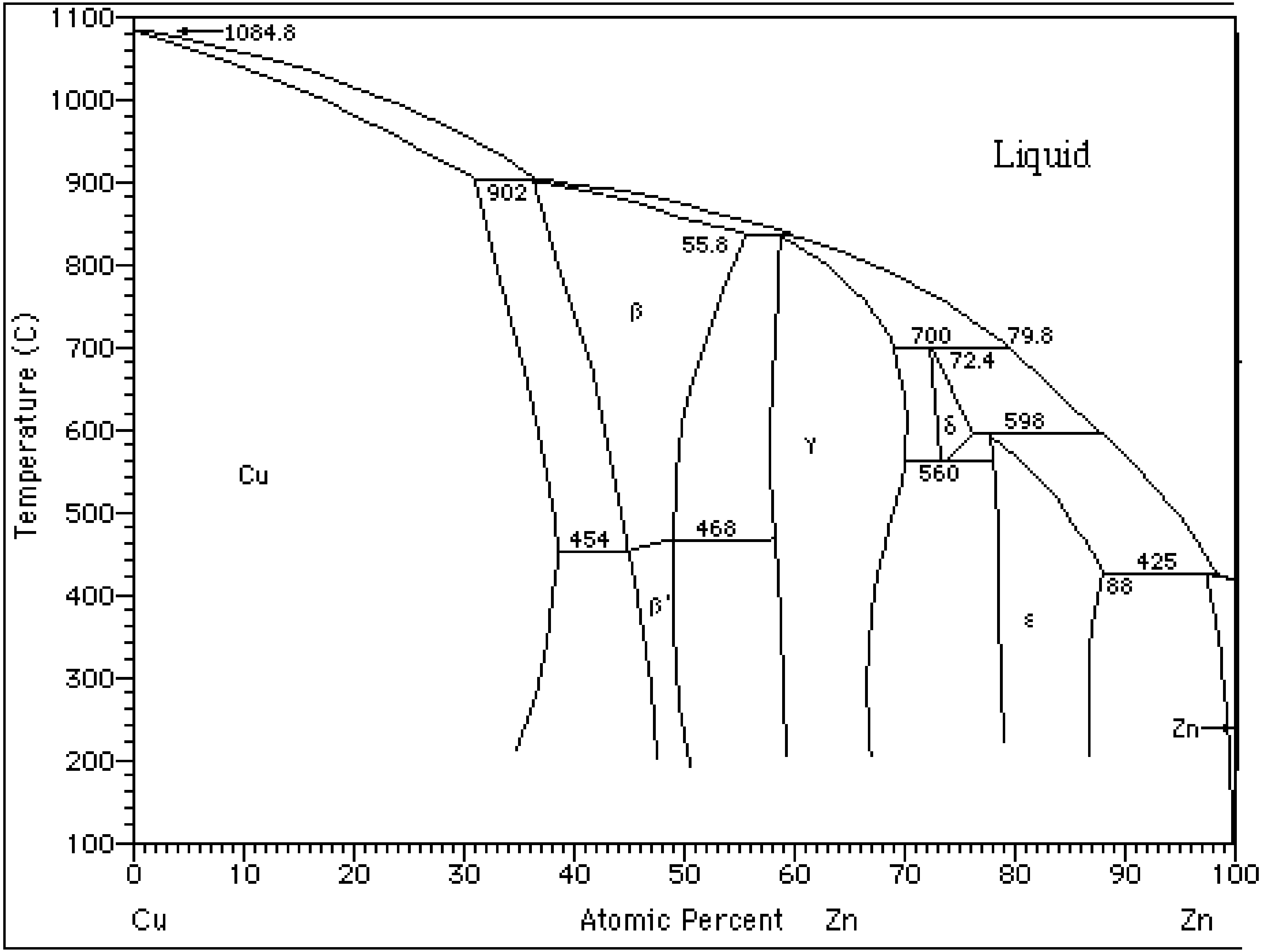
Contents for previous class

$\varepsilon < 0,\ \Delta H_{mix} < 0\ /\ \Delta H_{mix} \sim -20$ kJ/mol



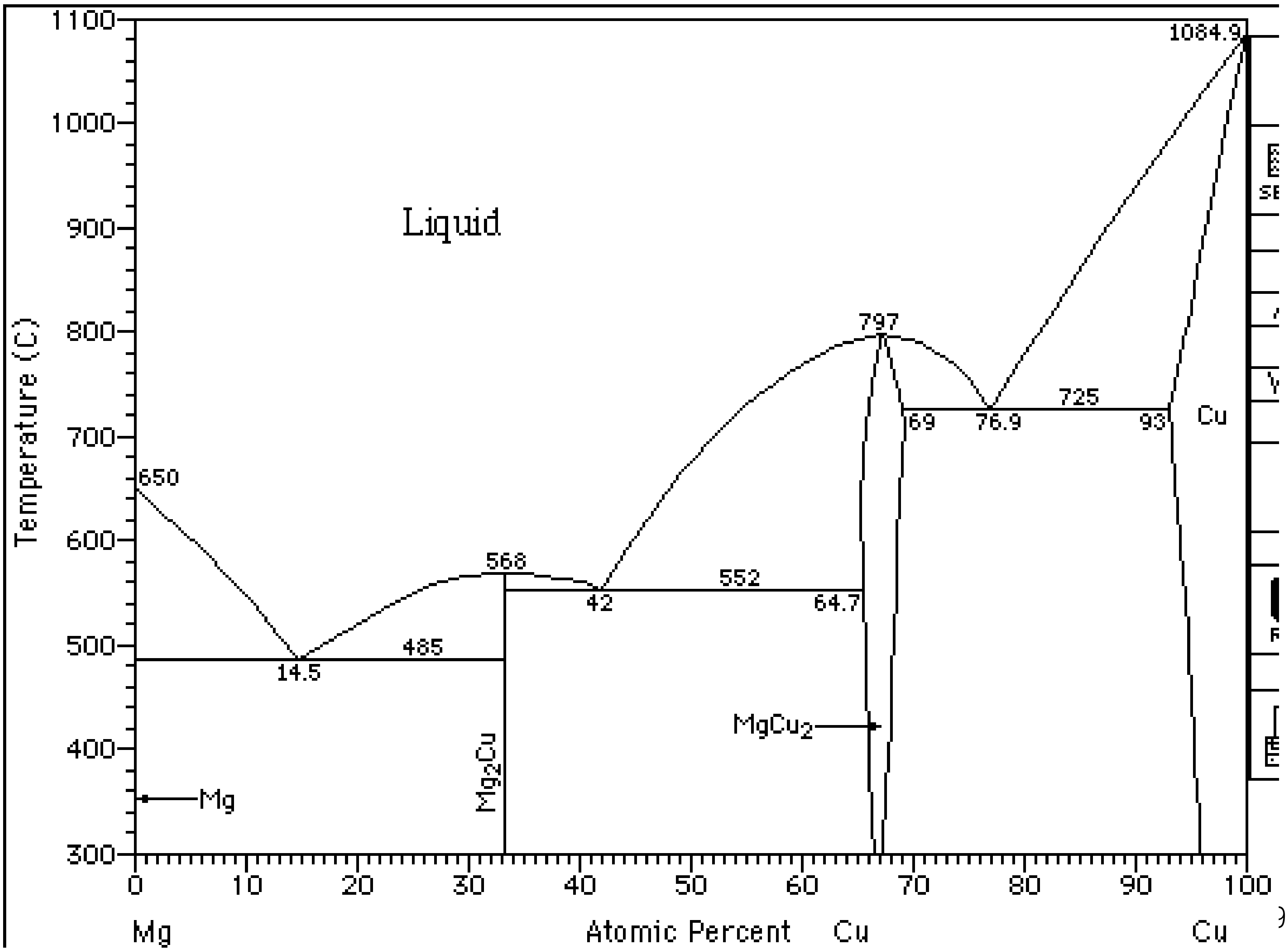
Contents for previous class

$\varepsilon < 0$, $\Delta H_{mix} < 0$ / $\Delta H_{mix} \sim$ -21 kJ/mol



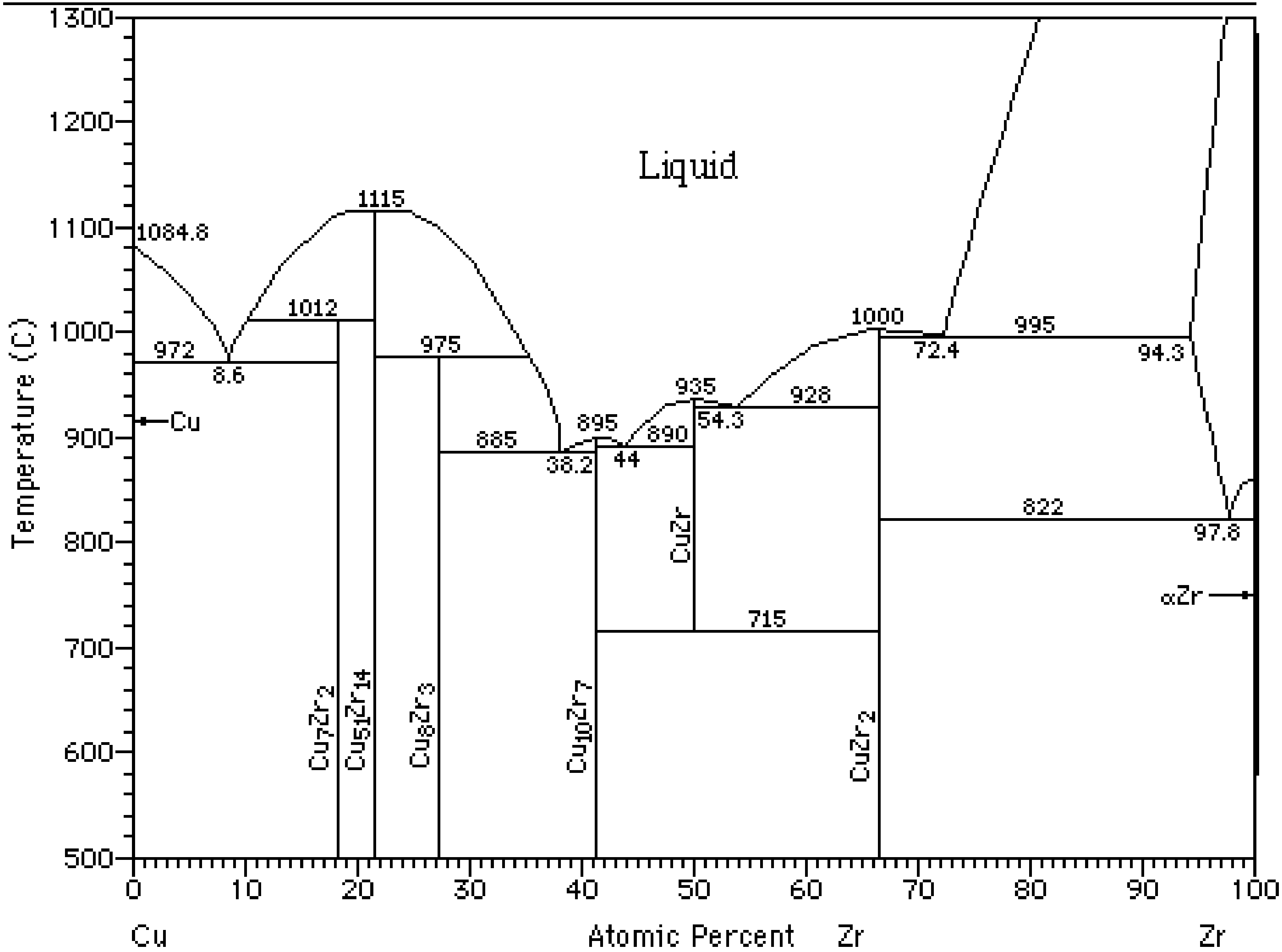
Contents for previous class

$\varepsilon < 0$, $\Delta H_{mix} < 0$ / $\Delta H_{mix} \sim$ -38 kJ/mol



Contents for previous class

$\varepsilon \ll 0$, $\Delta H_{mix} \ll 0$ / $\Delta H_{mix} \sim$ **-142 kJ/mol**



Contents for today's class

- Equilibrium in Heterogeneous Systems

- Binary phase diagrams

1) Simple Phase Diagrams

2) Systems with miscibility gap

4) Simple Eutectic Systems

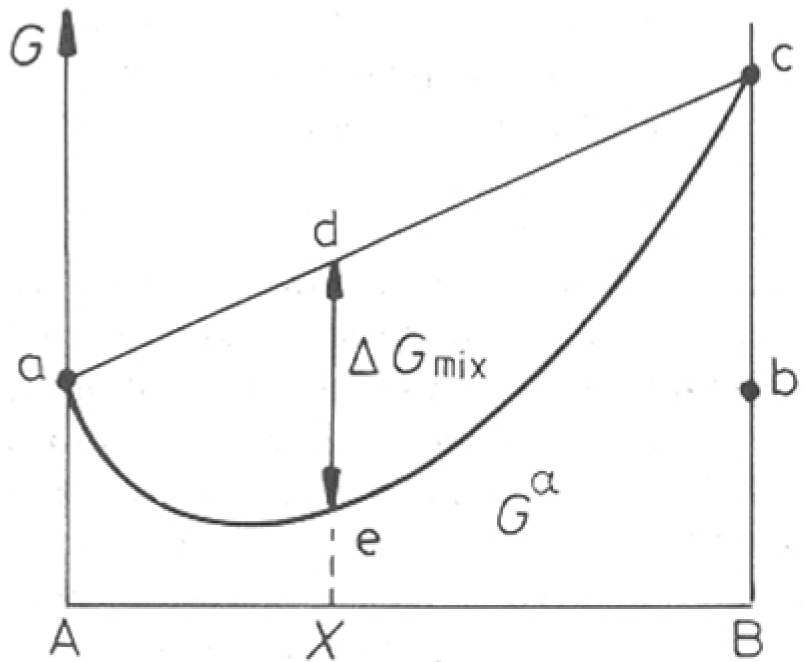
3) Ordered Alloys

5) Phase diagrams containing intermediate phases

Equilibrium in Heterogeneous Systems

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

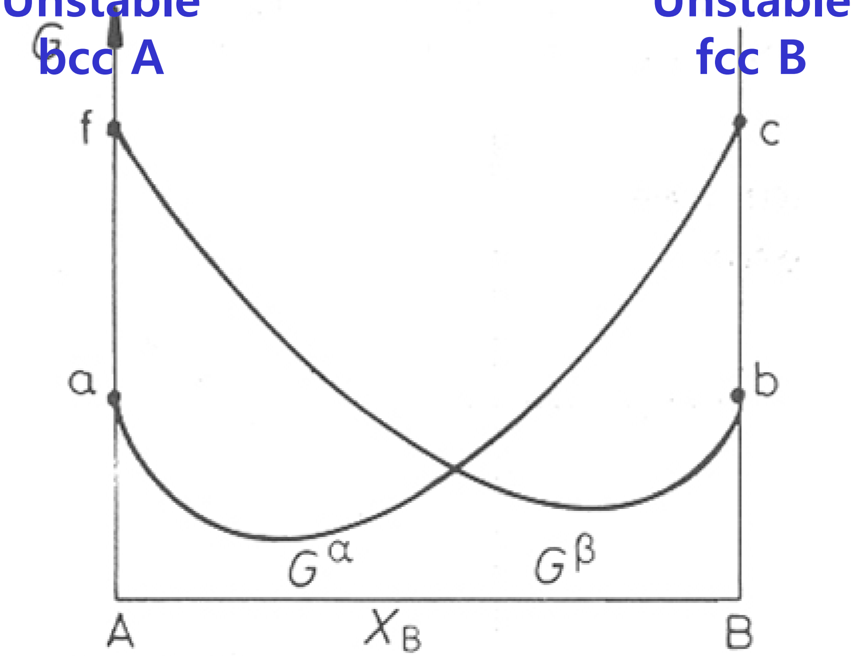
$$G = X_A G_A + X_B G_B + \Omega X_A X_B + RT(X_A \ln X_A + X_B \ln X_B)$$



What would happen when the components A and B have a different crystal structure?
→ **heterogeneous system**

Unstable bcc A

Unstable fcc B



Ex (fcc)

Ex (bcc)

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* $X_B^{o} = ?$

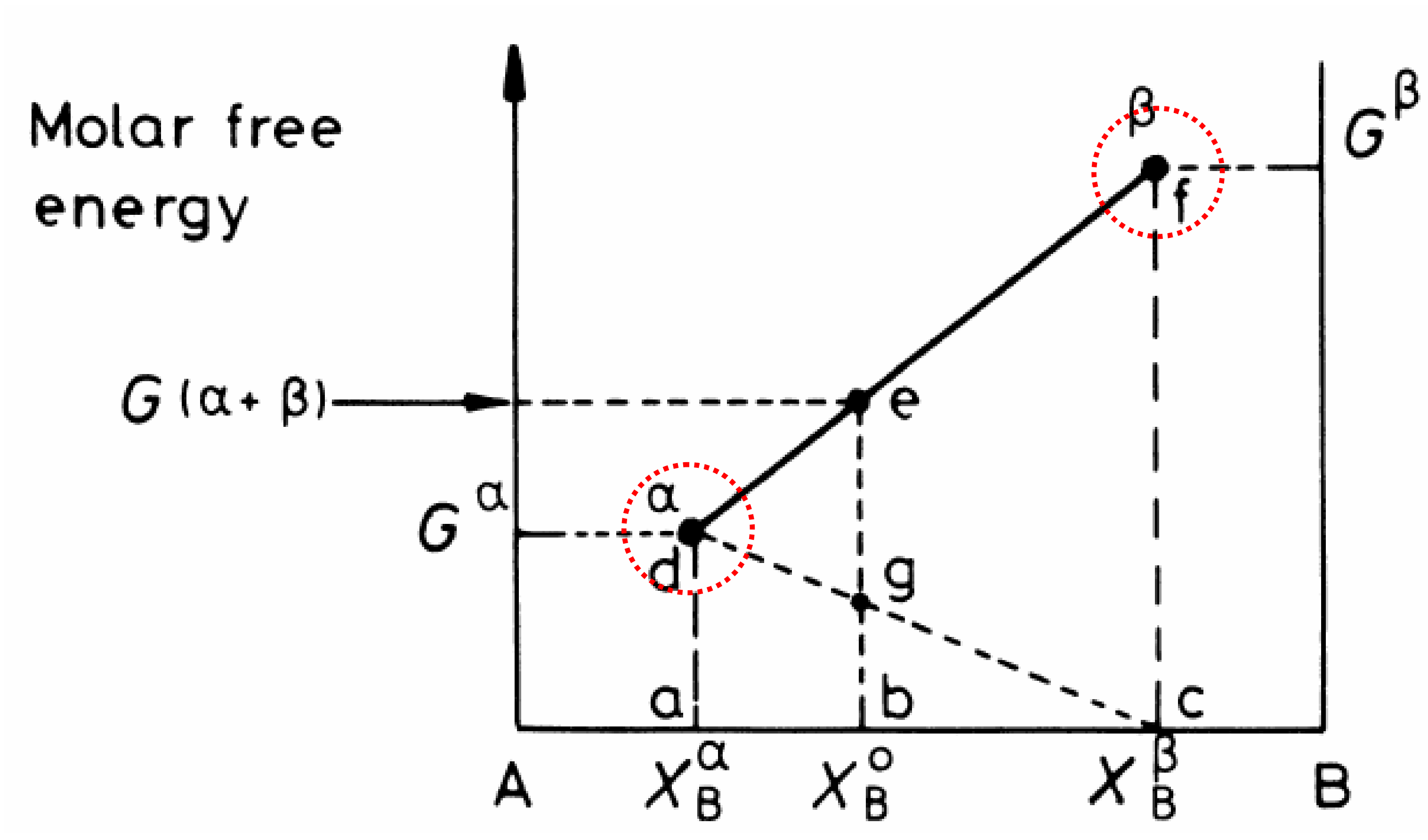
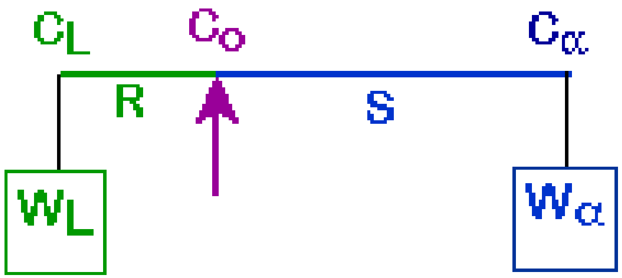


Fig. 1.26 The molar free energy of a two-phase mixture (α+β)

Lever rule

A geometric interpretation:



moment equilibrium:

$$\boxed{W_L} R = W_\alpha S$$

$$\boxed{1 - W_\alpha}$$

solving gives Lever Rule

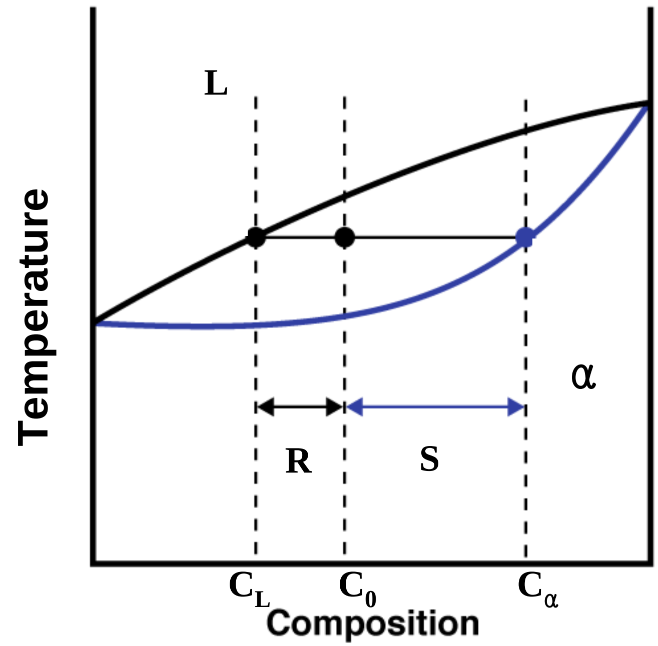
Sum of weight fractions: $W_L + W_\alpha = 1$

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

Combine above equations:

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

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



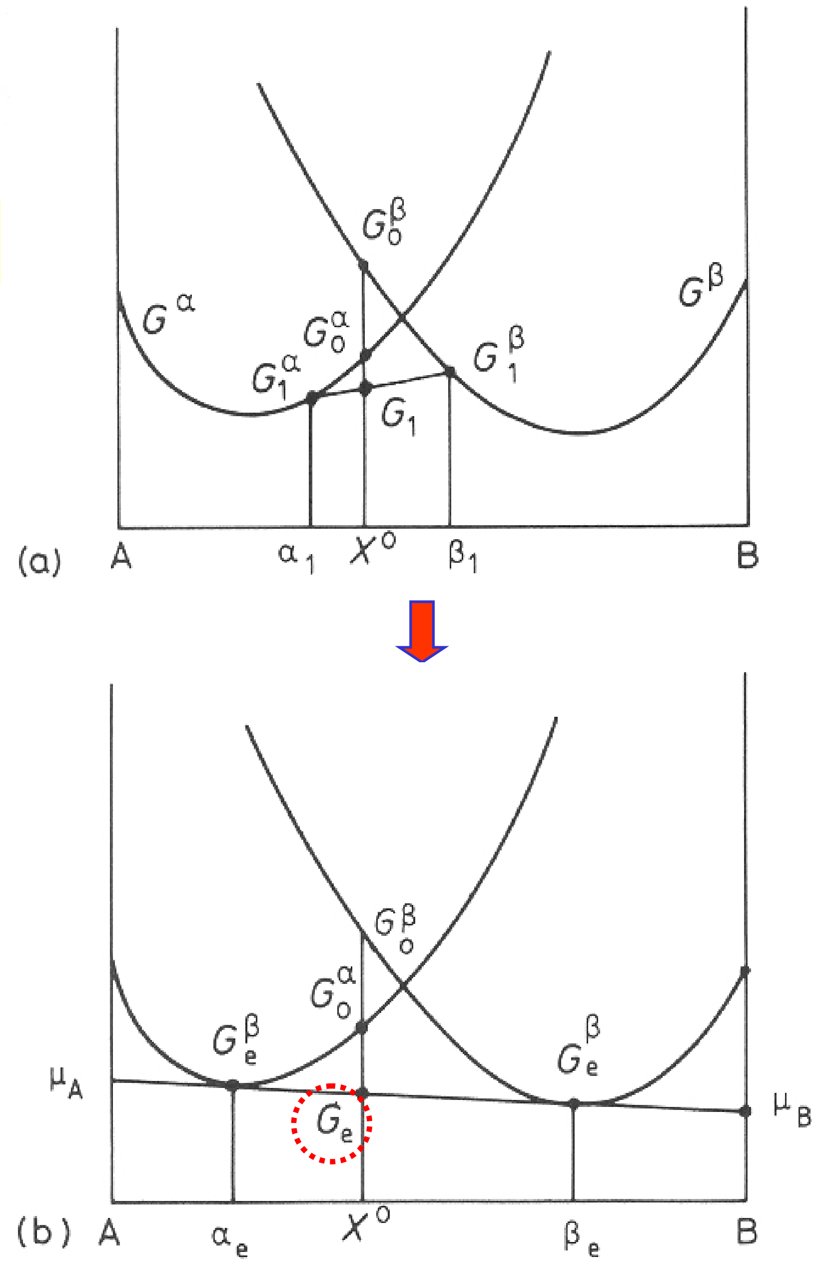
1.4

Equilibrium in Heterogeneous Systems

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

A 및 B 원자 교환

➡ **$\alpha + \beta$ 로 분리**



Chemical Equilibrium (μ, a)
→ multiphase and multicomponent
($\mu_i^{\alpha} = \mu_i^{\beta} = \mu_i^{\gamma} = \ldots$), ($a_i^{\alpha} = a_i^{\beta} = a_i^{\gamma} = \ldots$)

$$\mu_A^{\alpha} = \mu_A^{\beta} \qquad \mu_B^{\alpha} = \mu_B^{\beta}$$

두상의 화학 포텐셜 일치

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 α.

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

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

when α and β in equil.

$$a_A^{\alpha} = a_A^{\beta}$$

$$a_B^{\alpha} = a_B^{\beta}$$

두 성분의 activity 일치

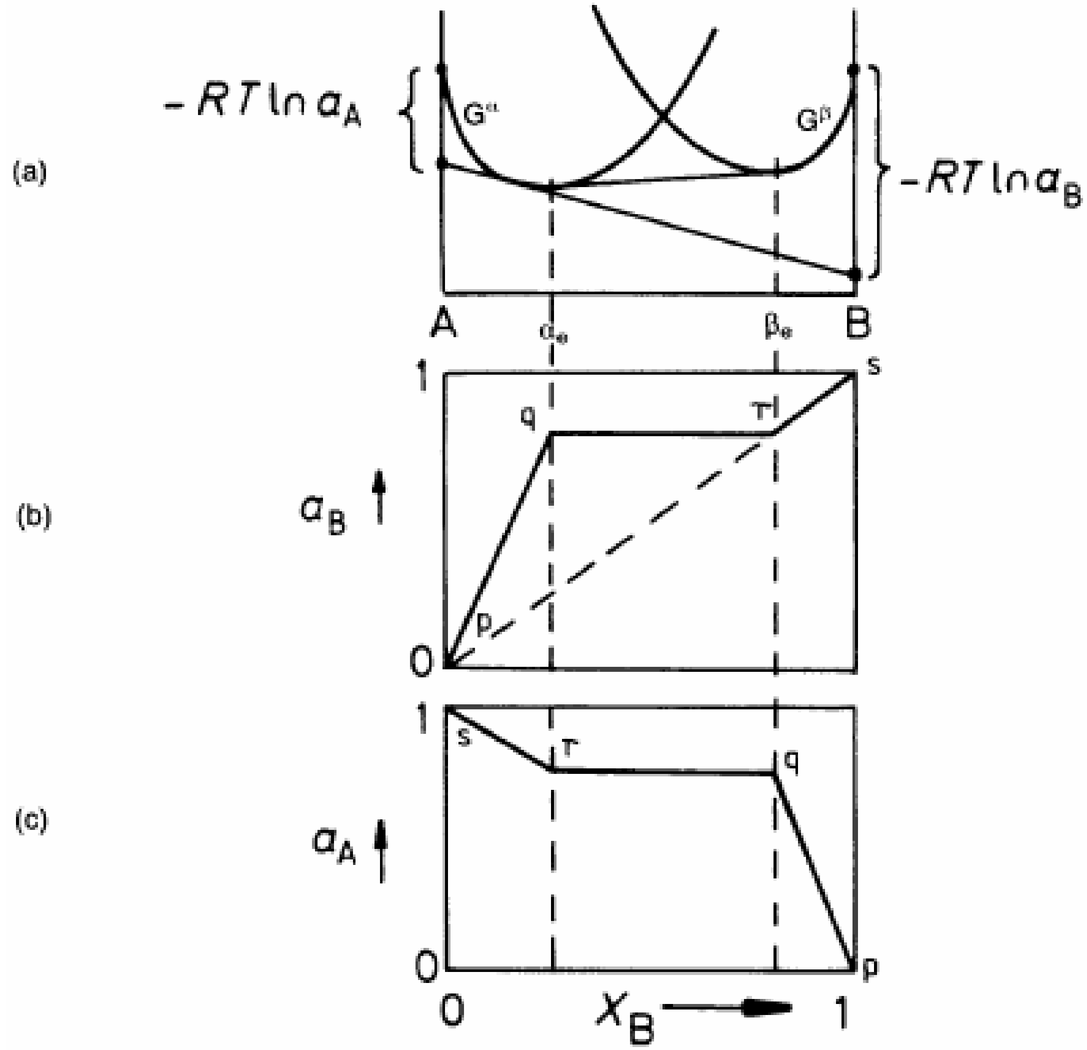
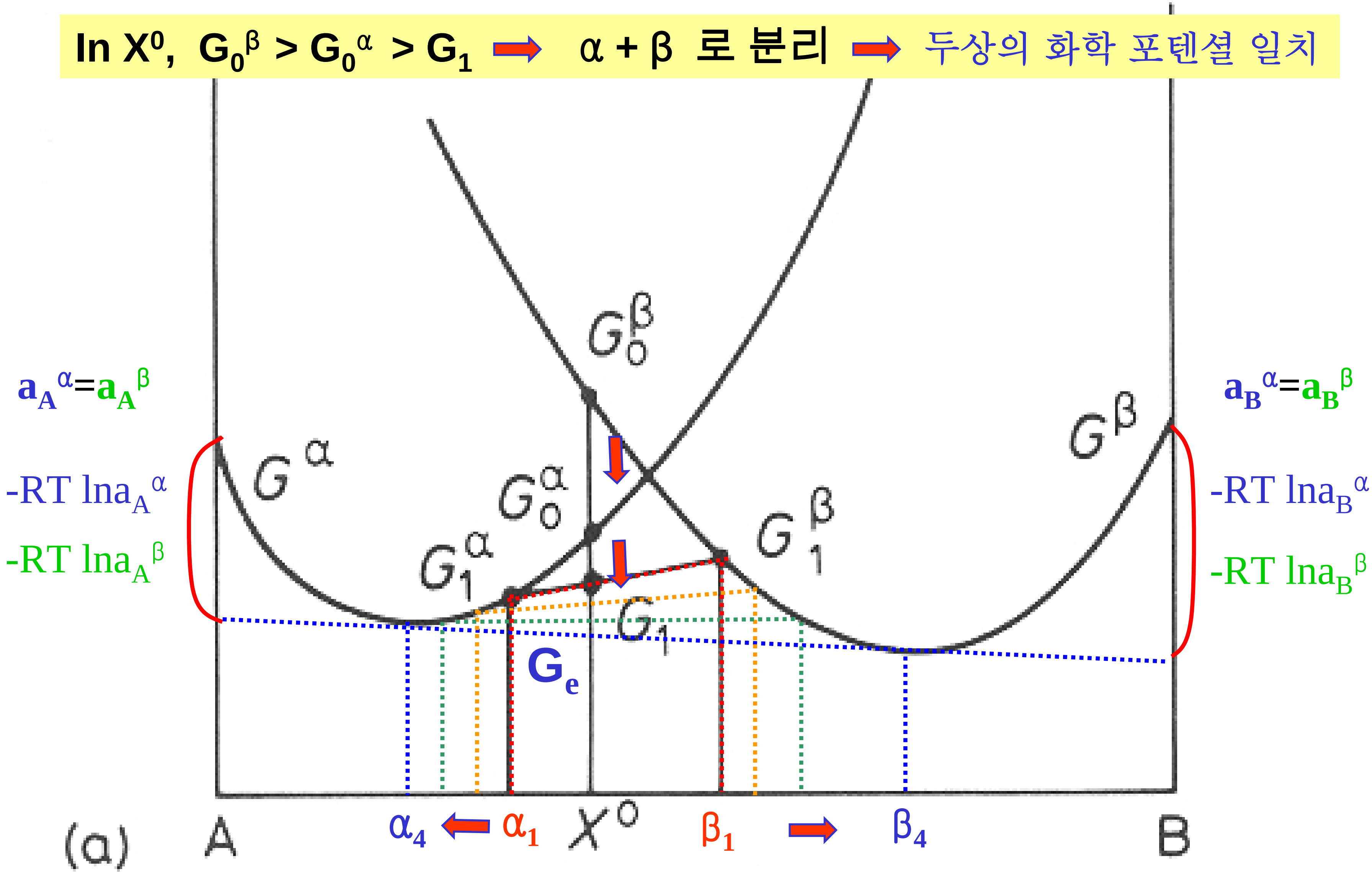


Fig. 1.28 The variation of a_A and a_B with composition for a binary system containing two ideal solutions, α and β

Equilibrium in Heterogeneous Systems

In X^0, $G_0^\beta > G_0^\alpha > G_1$ ➡ **$\alpha + \beta$ 로 분리** ➡ 두상의 화학 포텐셜 일치



1) Simple Phase Diagrams

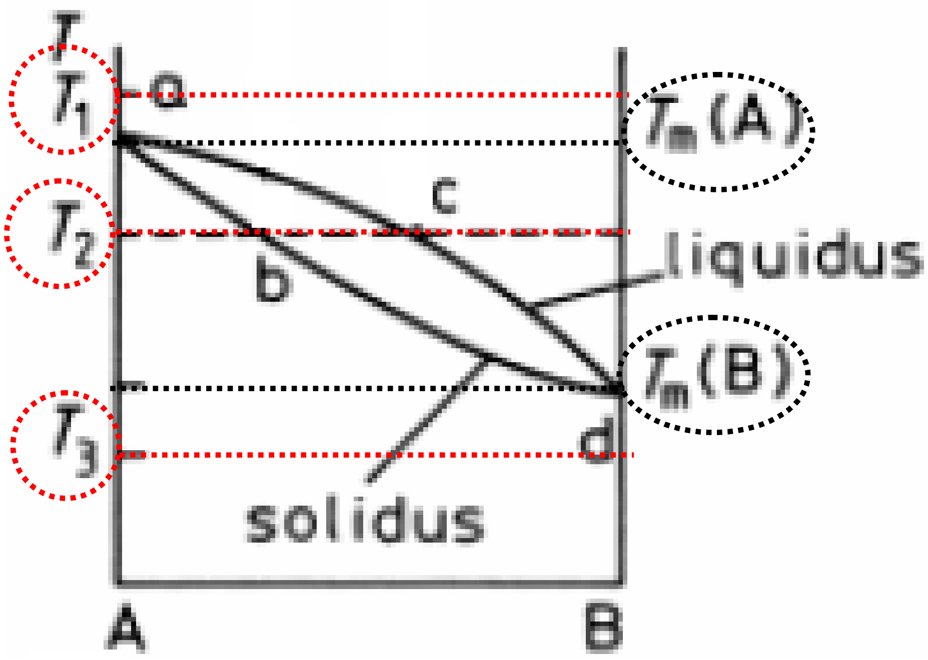
가정: (1) completely miscible in solid and liquid.

(2) Both are ideal soln. $\Delta H^{L}_{mix} = 0 \quad \Delta H^{S}_{mix} = 0$

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

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

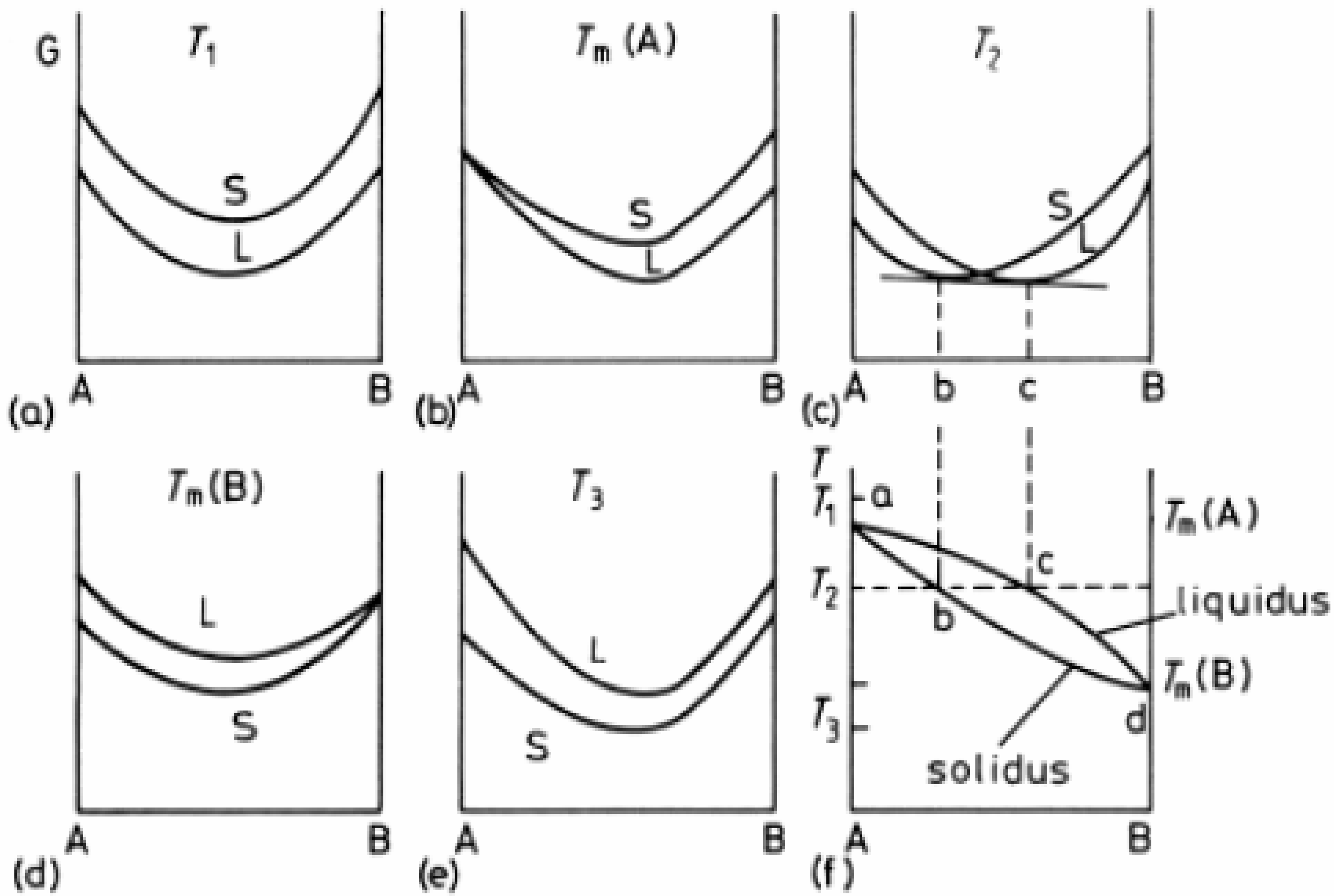
Draw G^L and G^S as a function of composition X_B at T_1, $T_m(A)$, T_2, $T_m(B)$, and T_3.



1.5 Binary phase diagrams

1) Simple Phase Diagrams

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

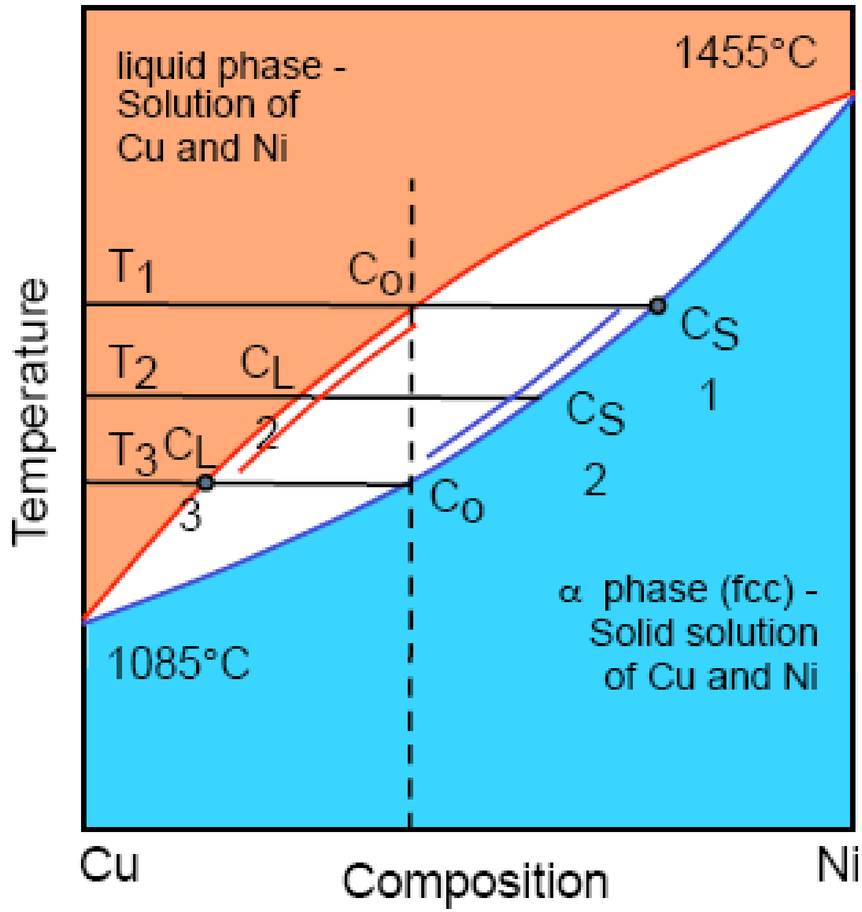


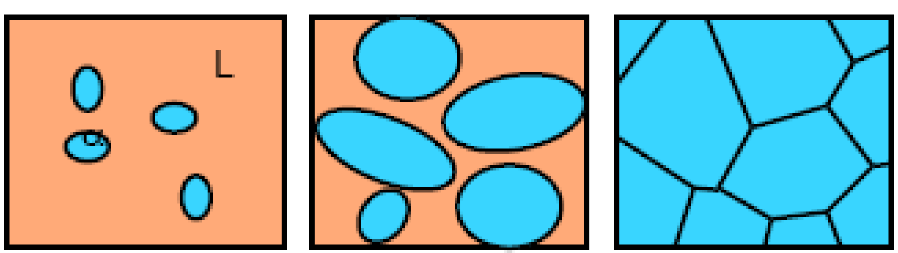
1.5 Binary phase diagrams

1) Simple Phase Diagrams

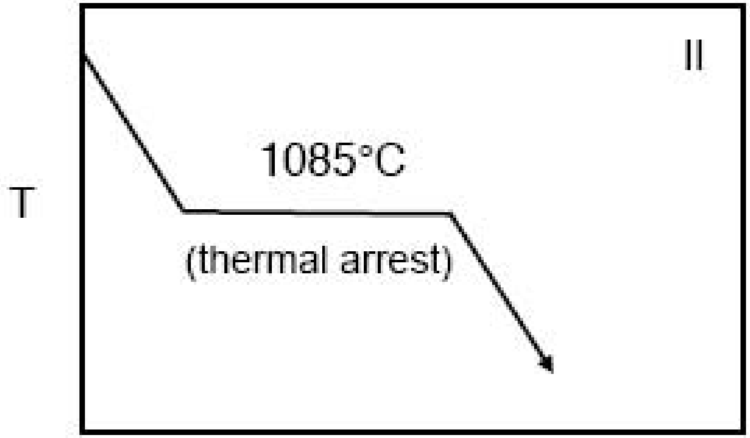
The simplest type of binary phase diagrams is the isomorphous system, in which the two constituents form a continuous solid solution over the entire composition range. An example is the Ni-Cu system.

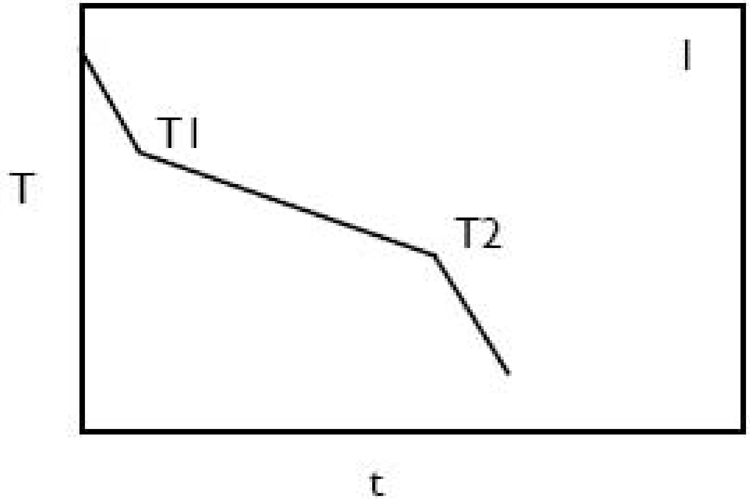
Solidification of alloy C_o starts on cooing at T_1. The first solid formed has a composition of C_{s1} and the liquid C_o. On further cooling the solid particles grow larger in size and change their composition to C_{s2} and then C_o, following the solidus whereas the liquid decrease in volume and changes its composition from C_o to C_{L3} following the liquidus. The solidification completes at T_3.

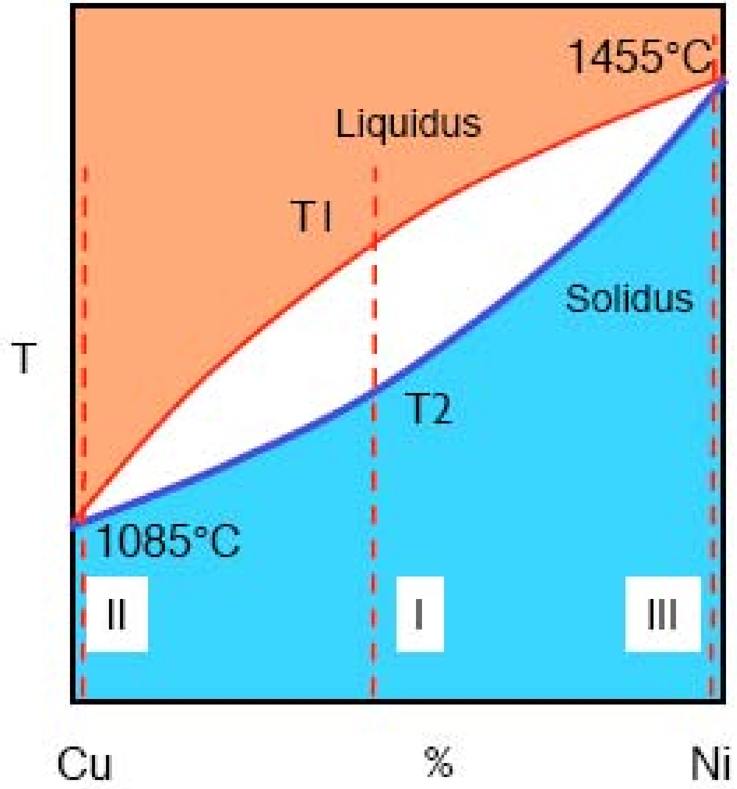




Cooling Curves
determination of Phase diagrams



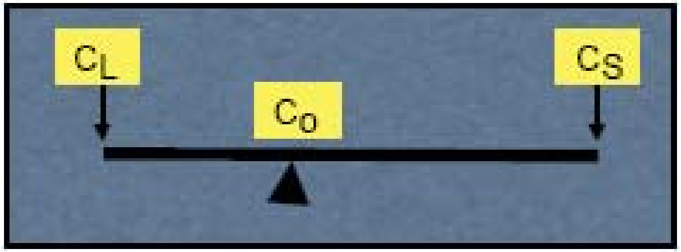




Example

At temperature T_1, alloy C_o is in the dual phase region, comprising the liquid phase and the α-phase.

(i) Determine the compositions of the two phases;
(ii) Determine the weight fractions of the two phases



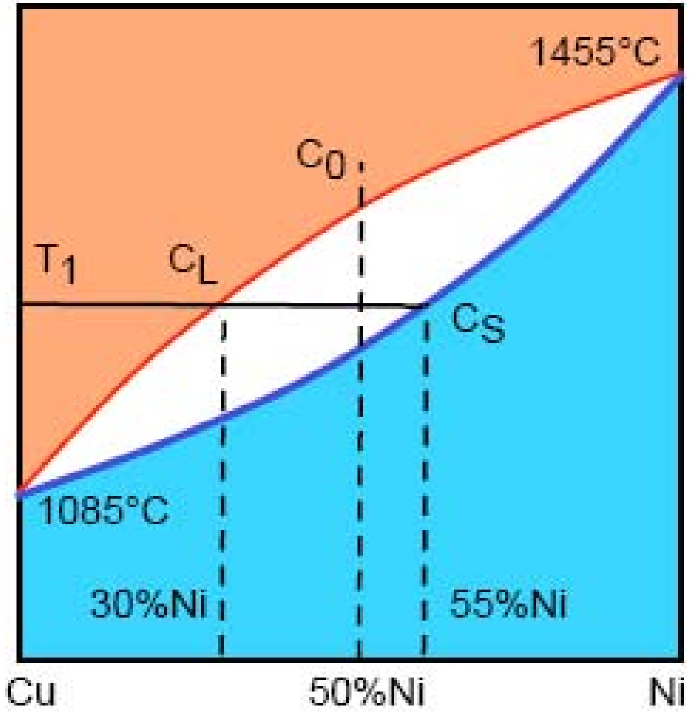
Read from the tie line:
Liquid phase: Cu-30%Ni
α-phase: Cu-55%Ni

$$W_L = \frac{C_s - C_o}{C_s - C_L} = \frac{55-50}{55-30} = 0.2 = 20\%$$

$$W_\alpha = \frac{C_o - C_L}{C_s - C_L} = \frac{50-30}{55-30} = 0.8 = 80\%$$

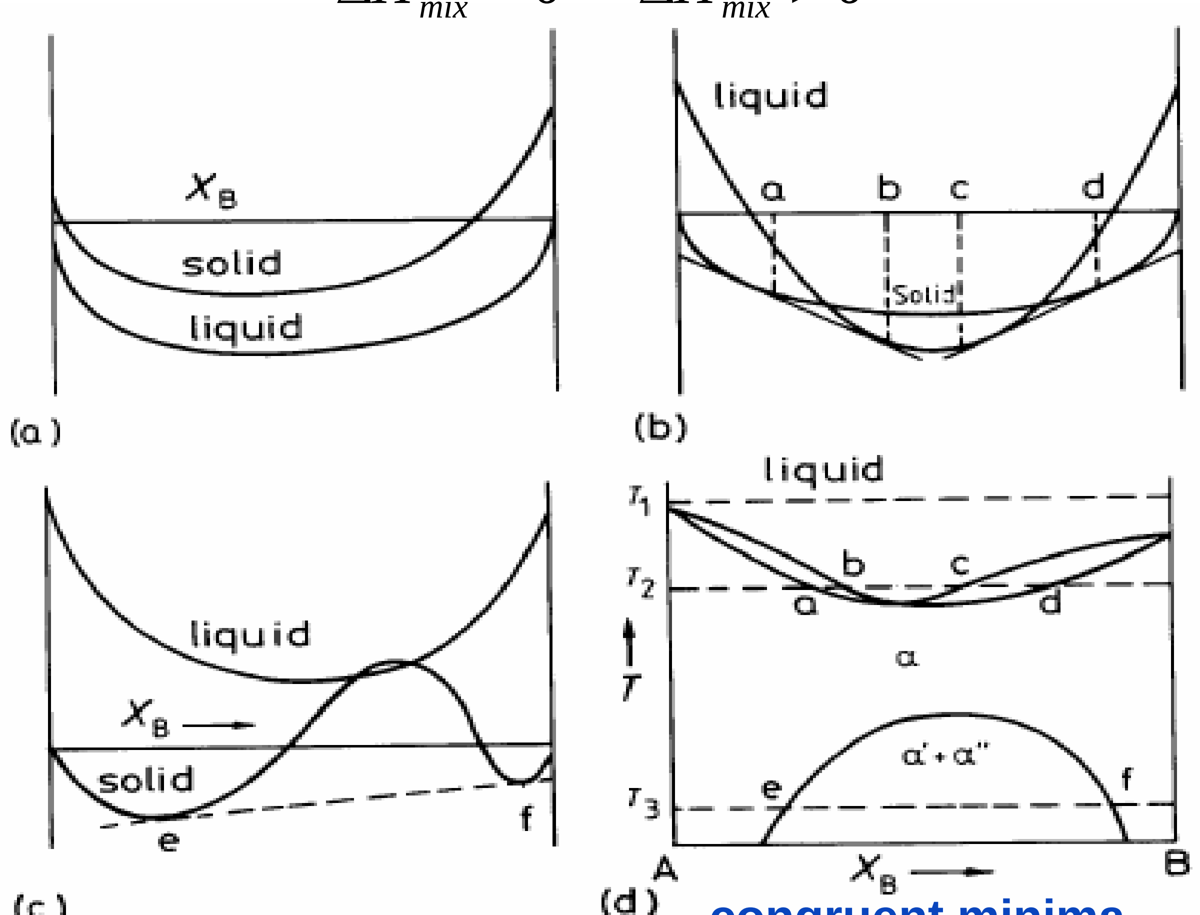
or

$$W_\alpha = 1 - W_L = 1 - 0.2 = 0.8 = 80\%$$



2) Systems with miscibility gab

$$\Delta H^{L}_{mix} = 0 \qquad \Delta H^{S}_{mix} > 0$$

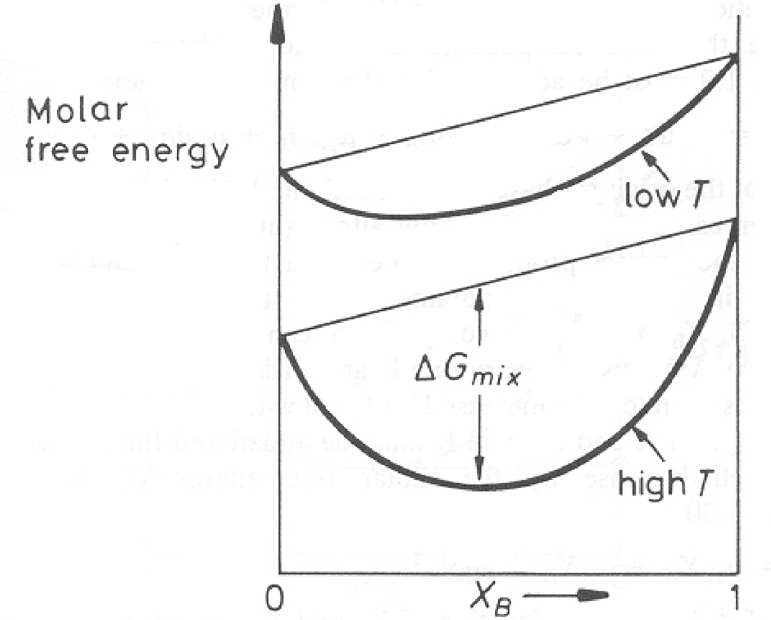


congruent minima

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

Ideal Solutions

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



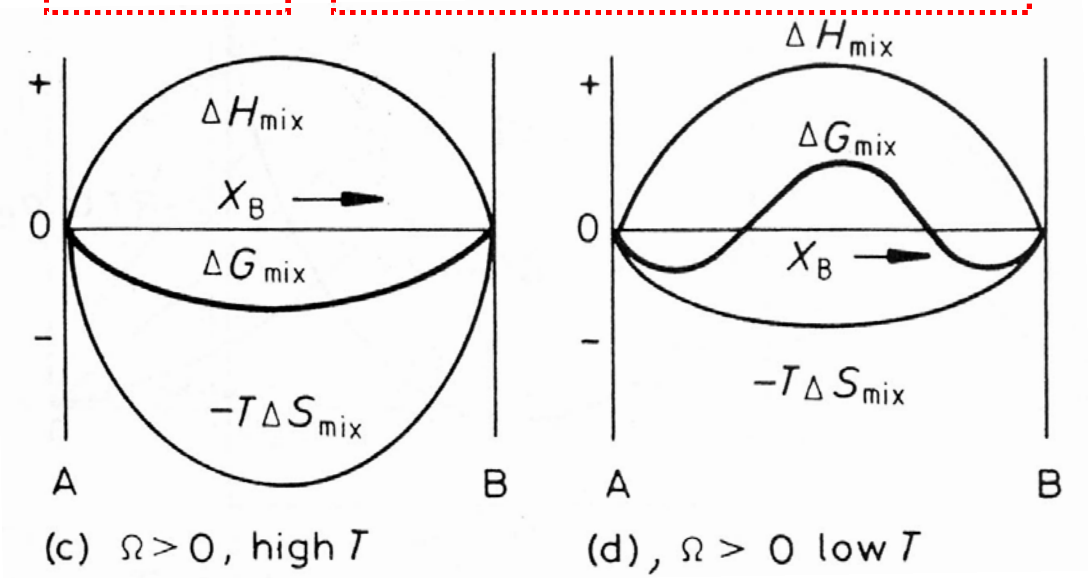
Regular Solutions

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

Reference state

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

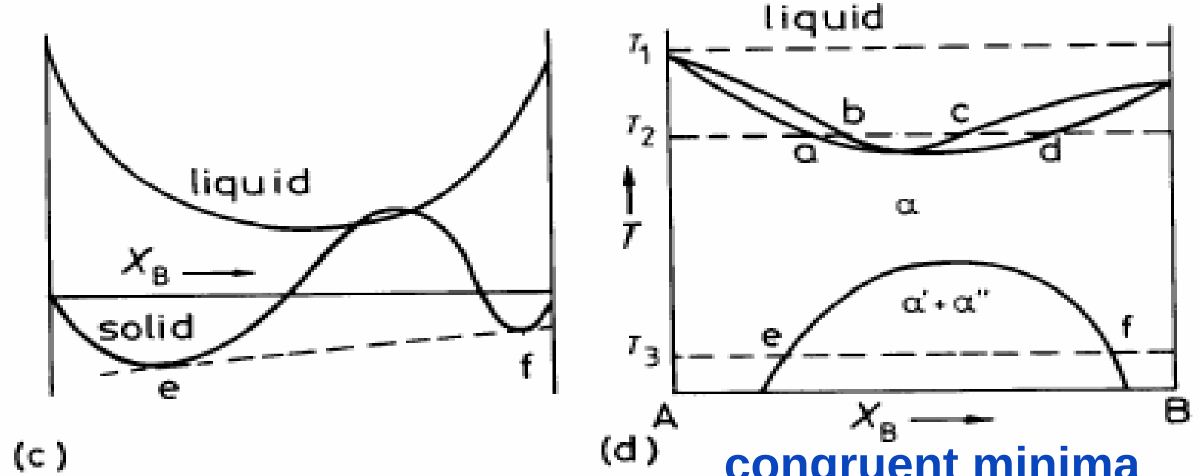
$$\Delta G_{mix} = \Delta H_{mix} - T\Delta S_{mix}$$



2) Systems with miscibility gab

$$\Delta H^{L}_{mix} = 0 \qquad \Delta H^{S}_{mix} > 0$$

- **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 α´ and α˝ in the phase diagram**



congruent minima