

2015 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**

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

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

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

μ 는 조성에 의해 결정되기 때문에 dn_A 가 매우 작아서 조성변화 없어야

- **Chemical equilibrium**

Regular Solutions

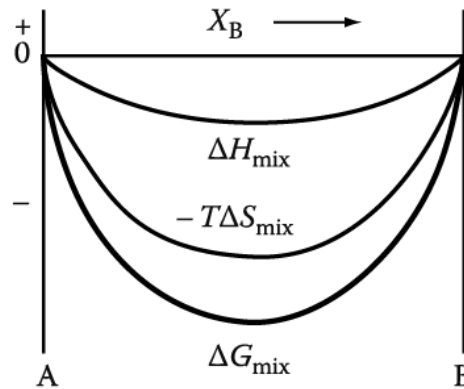
$$G_2 = G_1 + \Delta G_{\text{mix}}$$

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

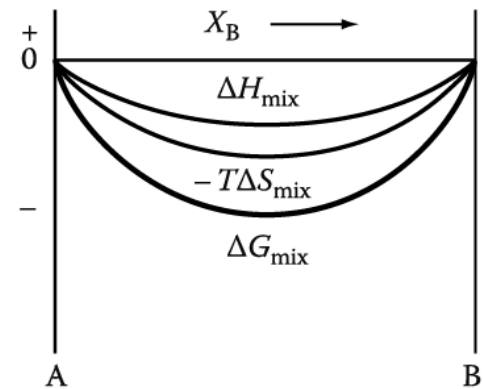
Reference state

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

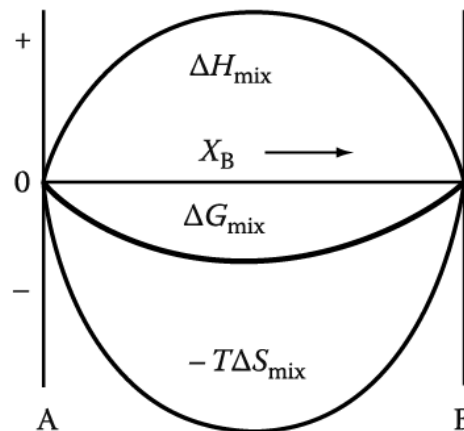
$$\Delta G_{\text{mix}} = \Delta H_{\text{mix}} - T\Delta S_{\text{mix}}$$



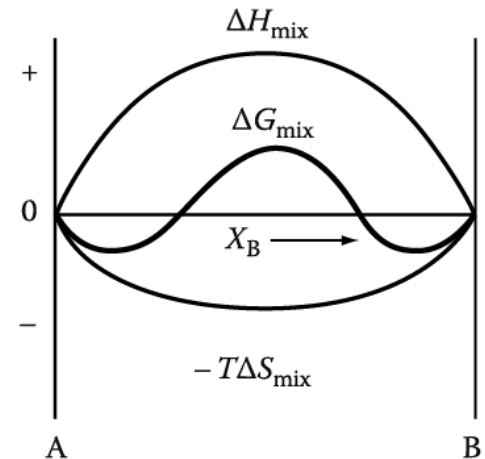
(a) $\Omega < 0$, high T



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



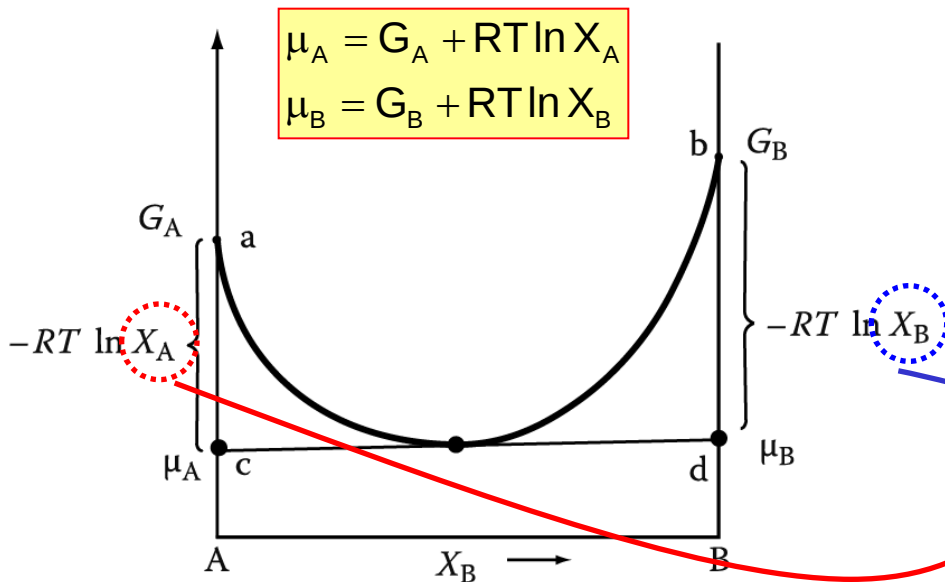
(c) $\Omega > 0$, high T



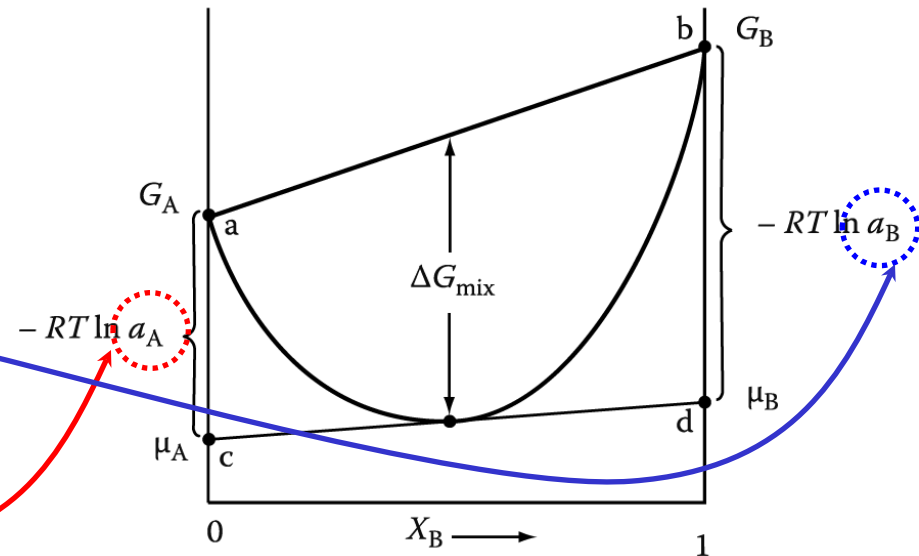
(d) $\Omega > 0$, low T

Activity, a : effective concentration for mass action

ideal solution



regular solution



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

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

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

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

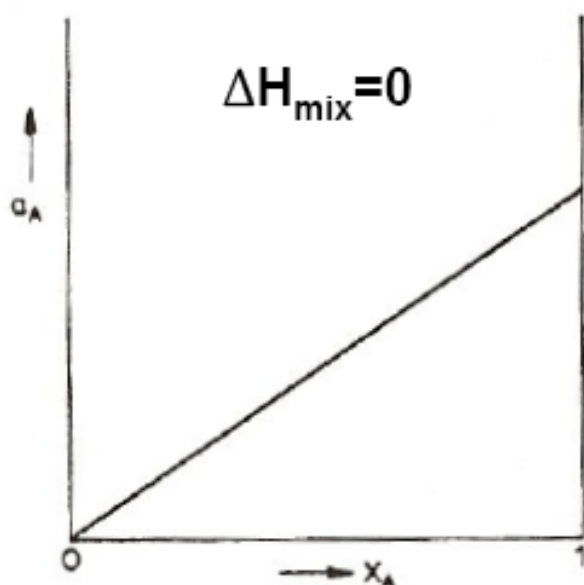
$$\ln \left(\frac{a_A}{X_A} \right) = \frac{\Omega}{RT} (1 - X_A)^2$$

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

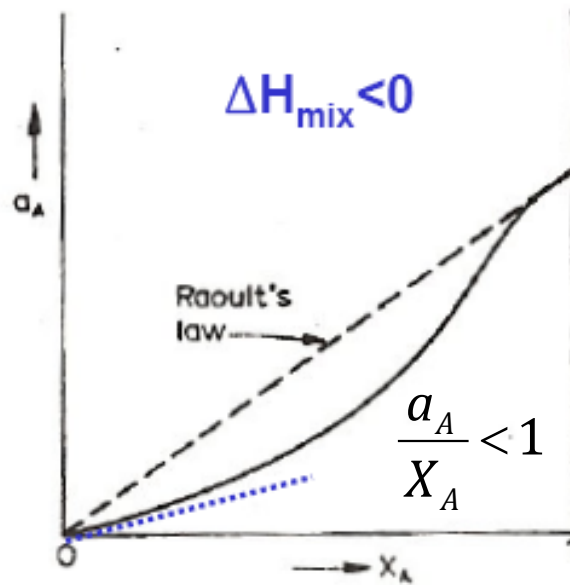
$$\frac{a_A}{X_A} = \gamma_A = \text{activity coefficient}$$

$$\gamma_B = \frac{a_B}{X_B}$$

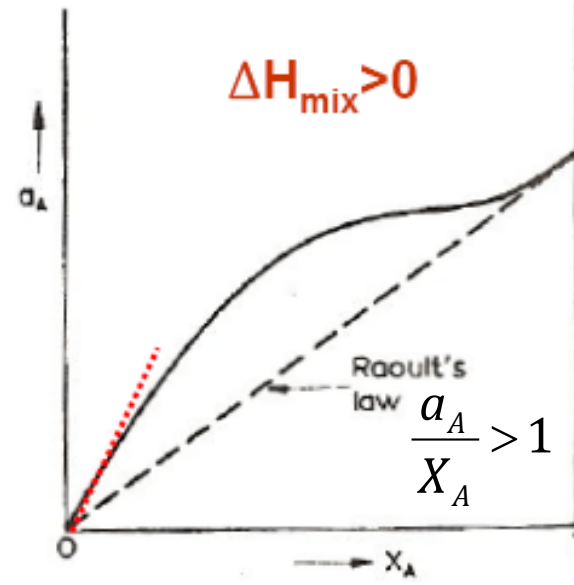
Activity-composition curves for solutions



(a)
Ideal solution
 $A \rightleftharpoons B = \frac{1}{2}(A \rightleftharpoons A + B \rightleftharpoons B)$
e.g. Bi-Sn at 335°C
 $a_A = a_{\text{Sn}}$



(b)
Actual solution
 $A \rightleftharpoons B > \frac{1}{2}(A \rightleftharpoons A + B \rightleftharpoons B)$
e.g. Au-Sn at 600°C
 $a_A = a_{\text{Sn}}$



(c)
Actual solution
 $A \rightleftharpoons B < \frac{1}{2}(A \rightleftharpoons A + B \rightleftharpoons B)$
e.g. Cd-Pb at 500°C
 $a_A = a_{\text{Cd}}$

Degree of non-ideality

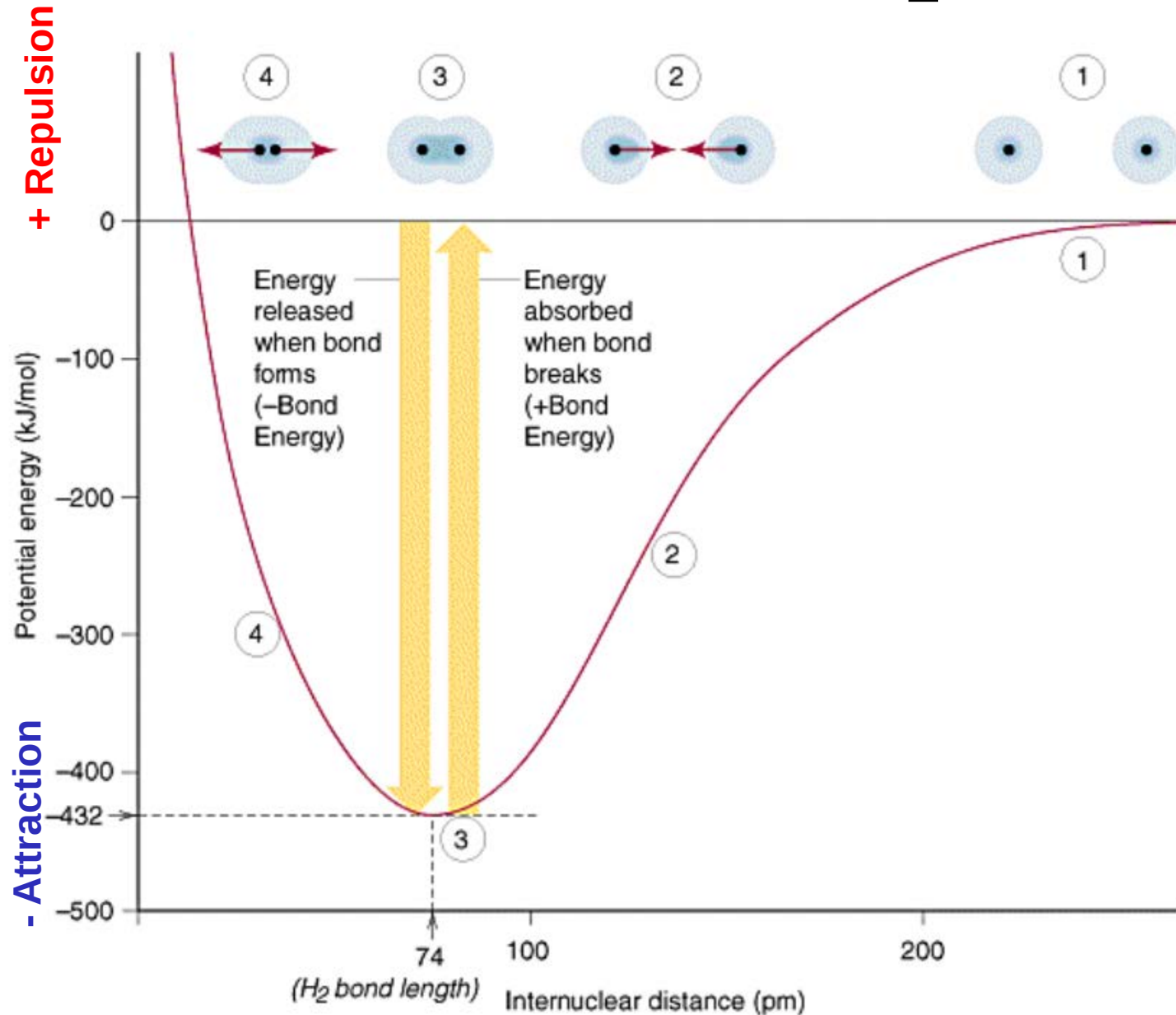
- For a dilute solution of B in A ($X_B \rightarrow 0$)

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

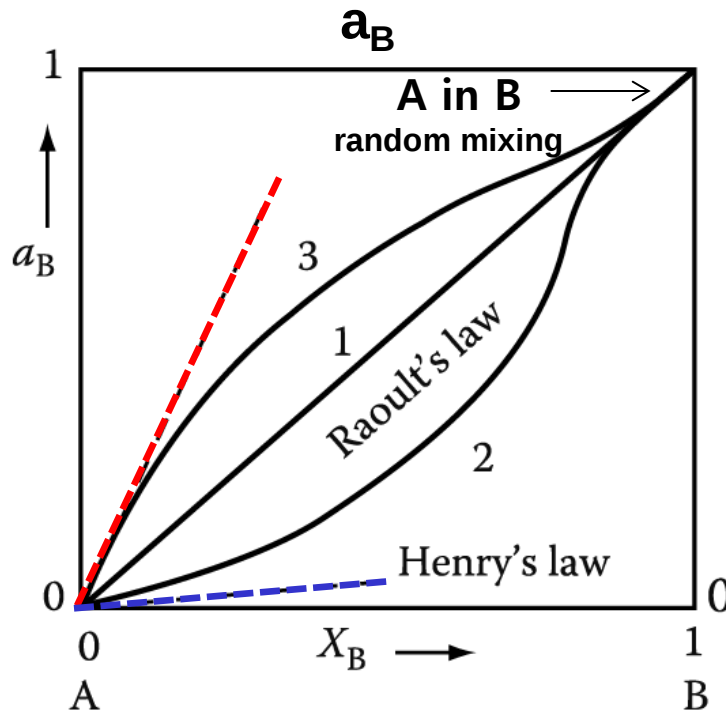
$$\gamma_A = \frac{a_A}{X_A} \cong 1 \quad (\text{Raoult's Law})$$

$$\Delta H_{\text{mix}} = P_{AB} \epsilon$$

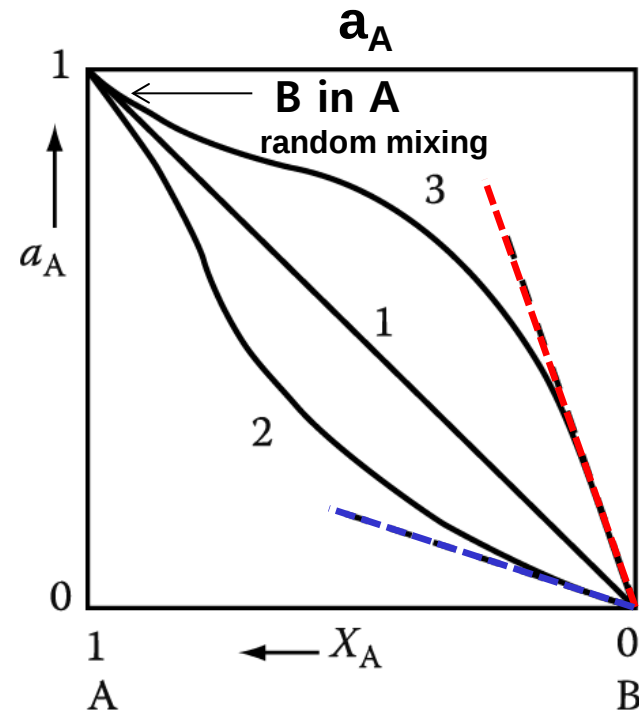
$$\text{where } \epsilon = \epsilon_{AB} - \frac{1}{2}(\epsilon_{AA} + \epsilon_{BB})$$



Variation of activity with composition (a) a_B , (b) a_A



(a)



(b)

Line 1 : (a) $a_B = X_B$, (b) $a_A = X_A$

Line 2 : (a) $a_B < X_B$, (b) $a_A < X_A$

Line 3 : (a) $a_B > X_B$, (b) $a_A > X_A$

ideal solution...Raoult's law

$$\Delta H_{\text{mix}} < 0 \quad \leftarrow \quad \ln\left(\frac{a_A}{X_A}\right) = \frac{\Omega}{RT}(1-X_A)^2$$

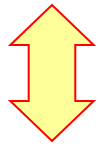
$$\Delta H_{\text{mix}} > 0$$

Contents for previous class

- Binary System mixture/ solution / compound

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

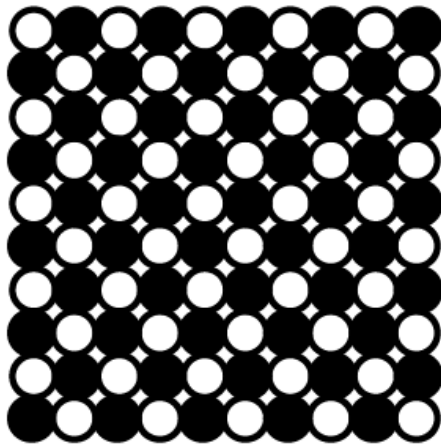
Regular solution $\Delta H_{\text{mix}} = P_{AB}\epsilon$ where $\epsilon = \epsilon_{AB} - \frac{1}{2}(\epsilon_{AA} + \epsilon_{BB})$ $\epsilon \approx 0$



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

Real solution

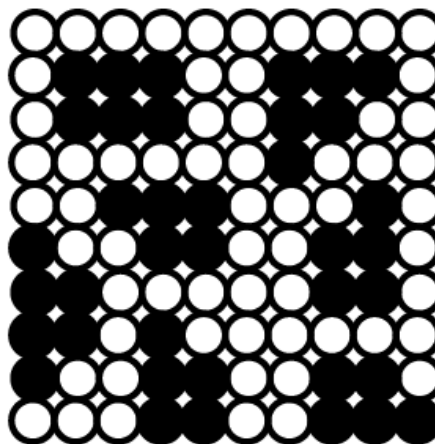
Ordered structure



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

Ordered alloys

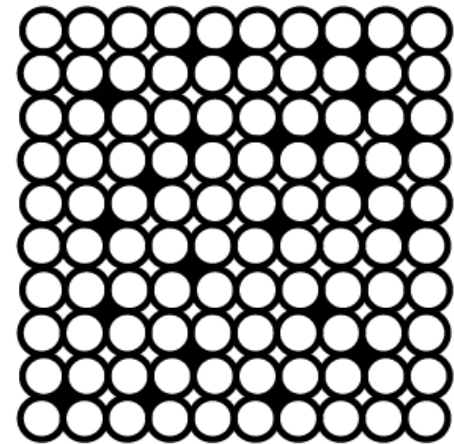
$P_{AB} \uparrow \longrightarrow \text{Internal } E \downarrow$



(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

Ordered phase II: “Long range order (LRO)”

(①superlattice, ②intermediate phase, ③intermetallic compound)

* Solid solution → ordered phase

→ random mixing

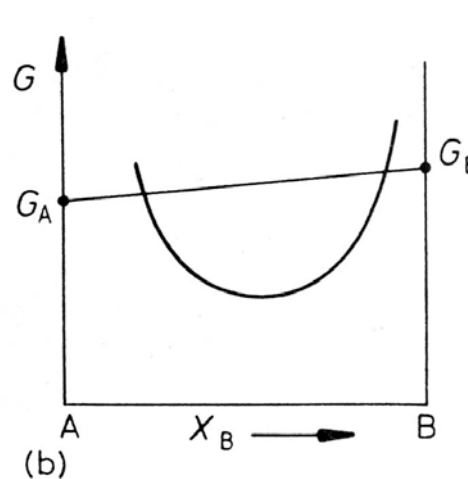
→ entropy ↑

negative enthalpy ↓

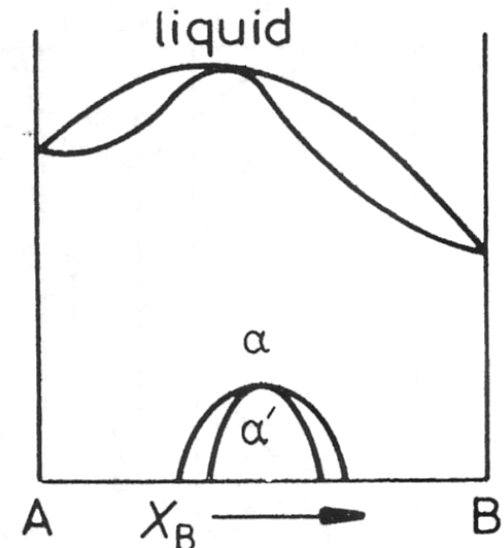
$$\Delta H_{mix}^S < 0$$

Large composition range

→ G ↓



intermediate phases: (a) for an intermetallic compound with a narrow stability range, (b) for an intermediate phase with a wide stability range.



* Compound : AB, A₂B...

→ entropy ↓

→ covalent, ionic contribution.

→ enthalpy more negative ↓

$$\Delta H_{mix}^S \ll 0$$

Small composition range

→ G ↓

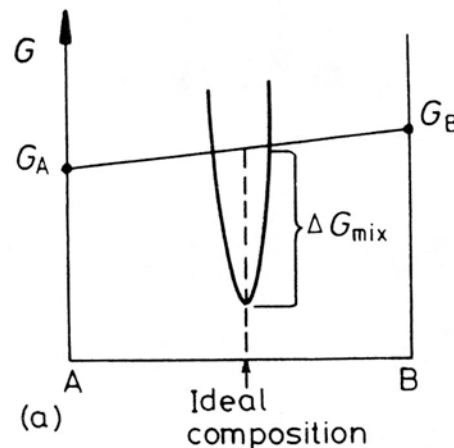
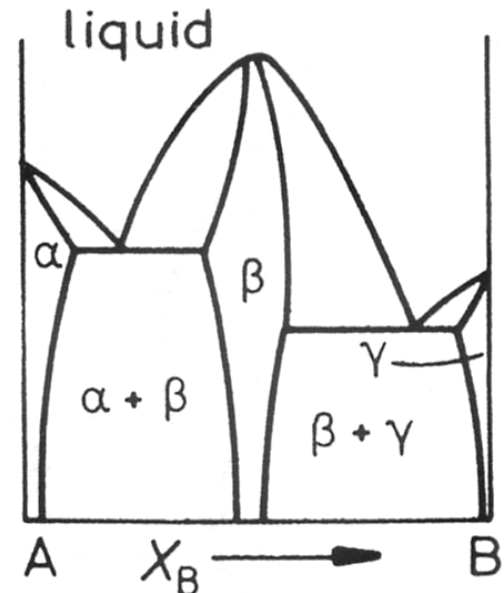


Fig. 1.23 Free energy curves for intermediate phases: (a) for an intermetallic compound with a very narrow stability range, (b) for an intermediate phase with a wide stability range.

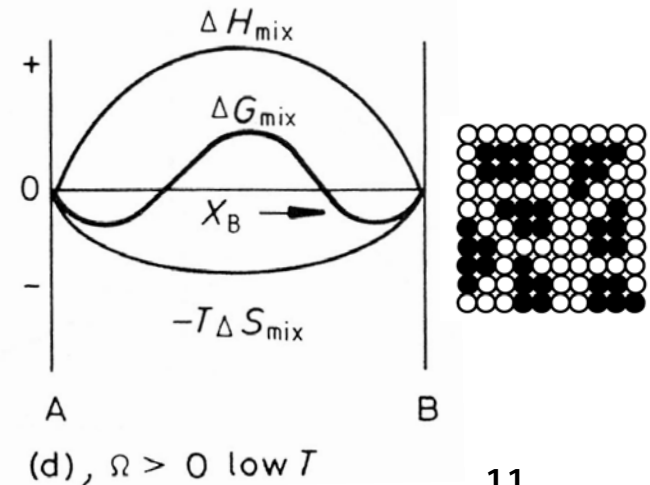
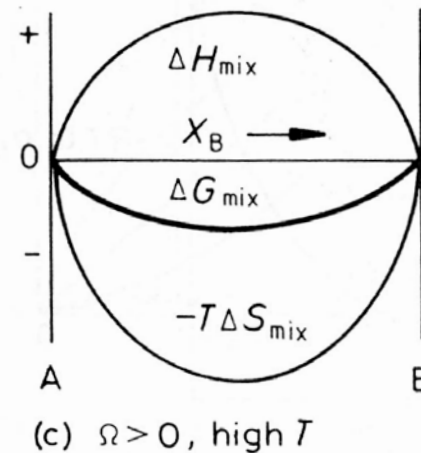
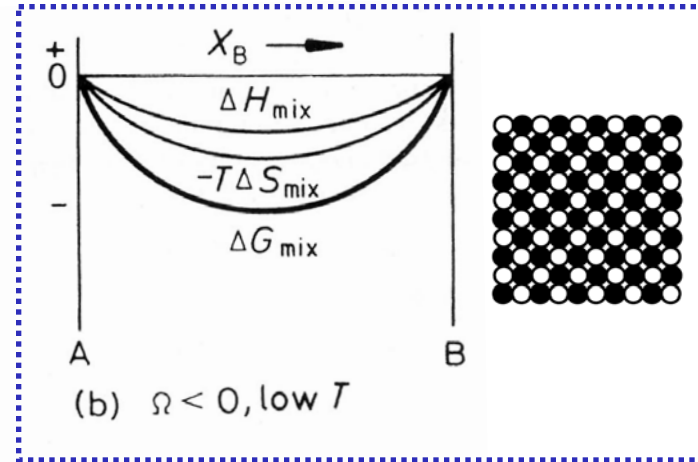
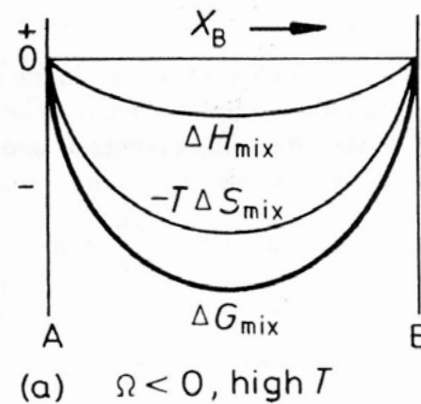


Q1: Superlattice

- * The degree of **ordering or clustering** will **decrease** as temp. **increases** due to the increasing importance of **entropy**.

High temp. $\longrightarrow$ Entropy effect $\uparrow$ $\longrightarrow$ Solution stability $\uparrow$

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



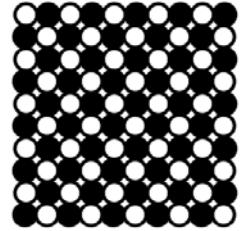
1.3 Binary Solutions

Ordered phase

$$\varepsilon < 0, \Delta H_{\text{mix}} < 0$$

* In solutions with compositions that are close to a simple **ratio of A:B atoms** another type of order can be found.

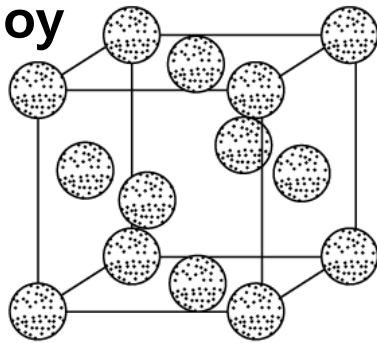
* This is known as **long-range order (LRO)** CuAu, Cu₃Au and many other intermetallics show LRO.



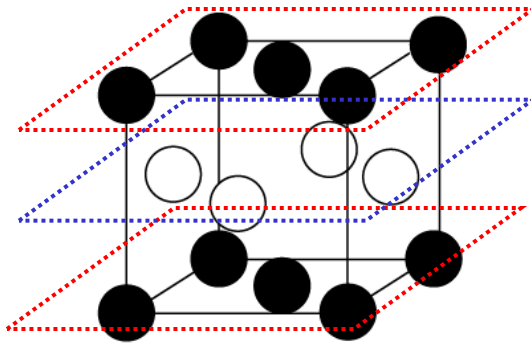
(The atom sites are no longer equivalent but can be labelled as A-sites and B-sites.)

* A **superlattice** forms in materials with LRO

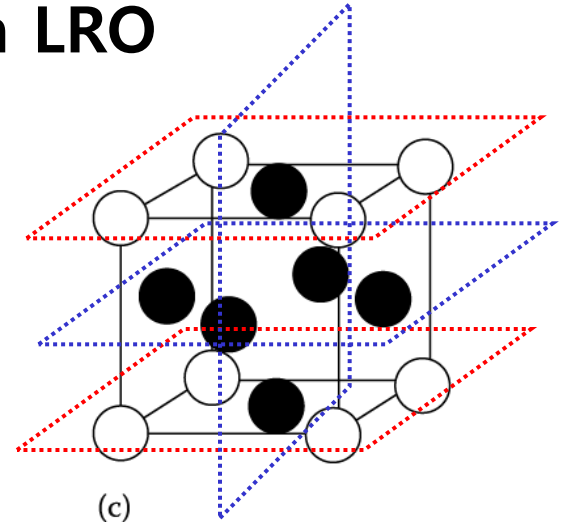
Cu–Au alloy



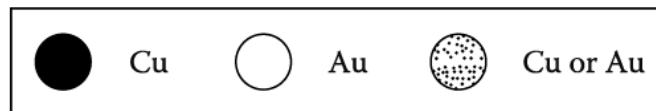
(a)



(b)



(c)



High temp.

Disordered Structure

Low temp.

CuAu superlattice

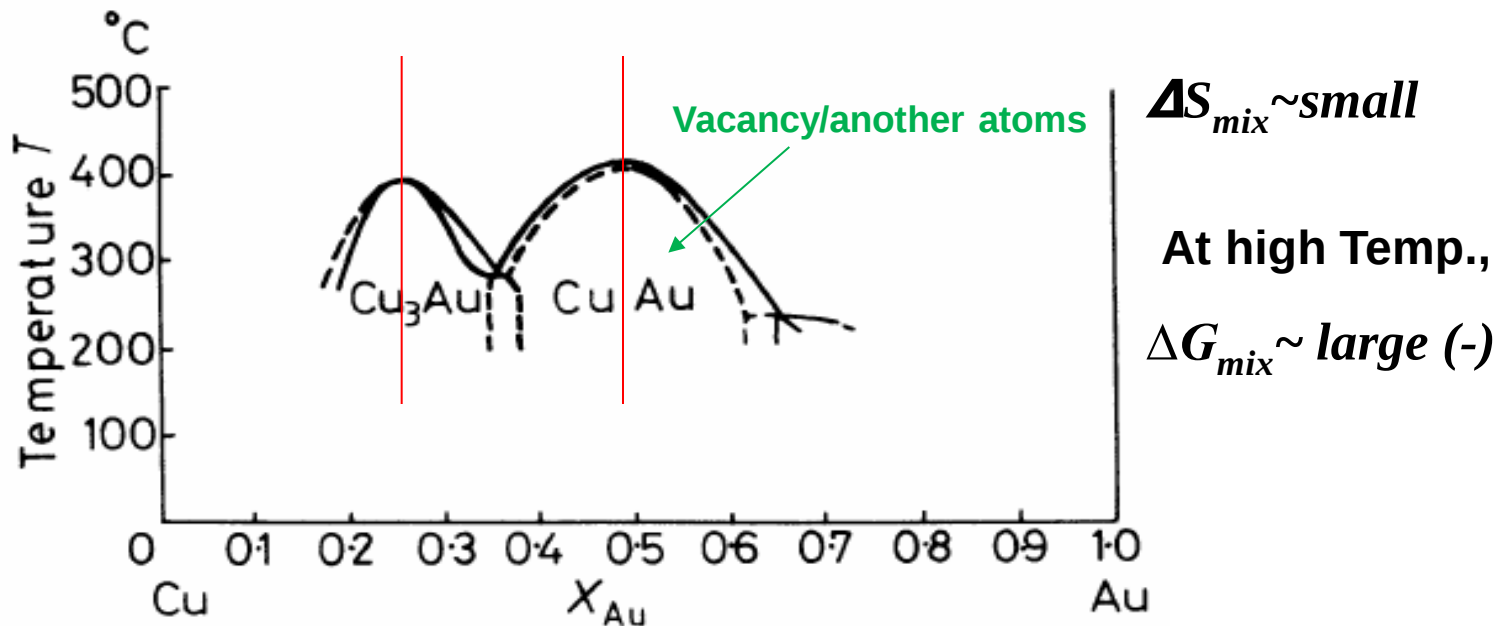
Cu₃Au superlattice

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

Ordered phase

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

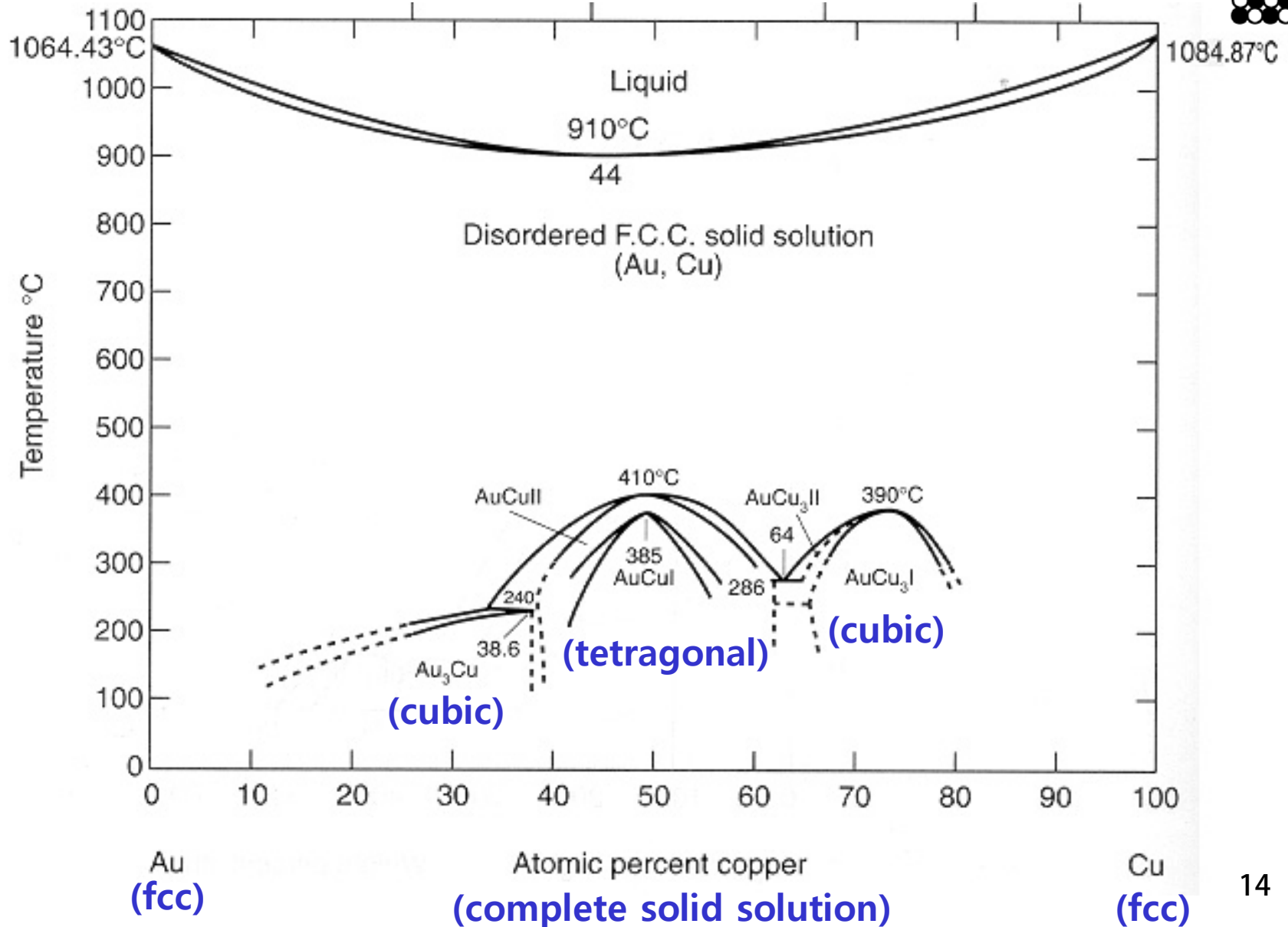
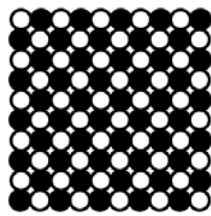
Fig. 1.21. Part of the Cu-Au phase diagram showing the regions where the Cu_3Au and CuAu superlattices are stable.



- The **entropy** of mixing of structure with LRO is **extremely small** and **the degree of order decrease** with **increasing temperature** until above some **critical temperature** there is no LRO at all.
- This temperature is a maximum when the composition is the ideal required for the superlattice.
- The critical temperature for loss of LRO increases with increasing Ω or ΔH_{mix} , and in many systems the ordered phase is stable up to the melting point.

Ordered Phase

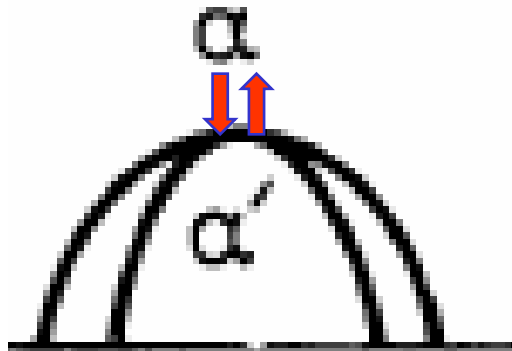
$$\varepsilon < 0, \Delta H_{\text{mix}} < 0 / \Delta H_{\text{mix}} \sim -20 \text{ kJ/mol}$$



Q2: Order-disorder transition

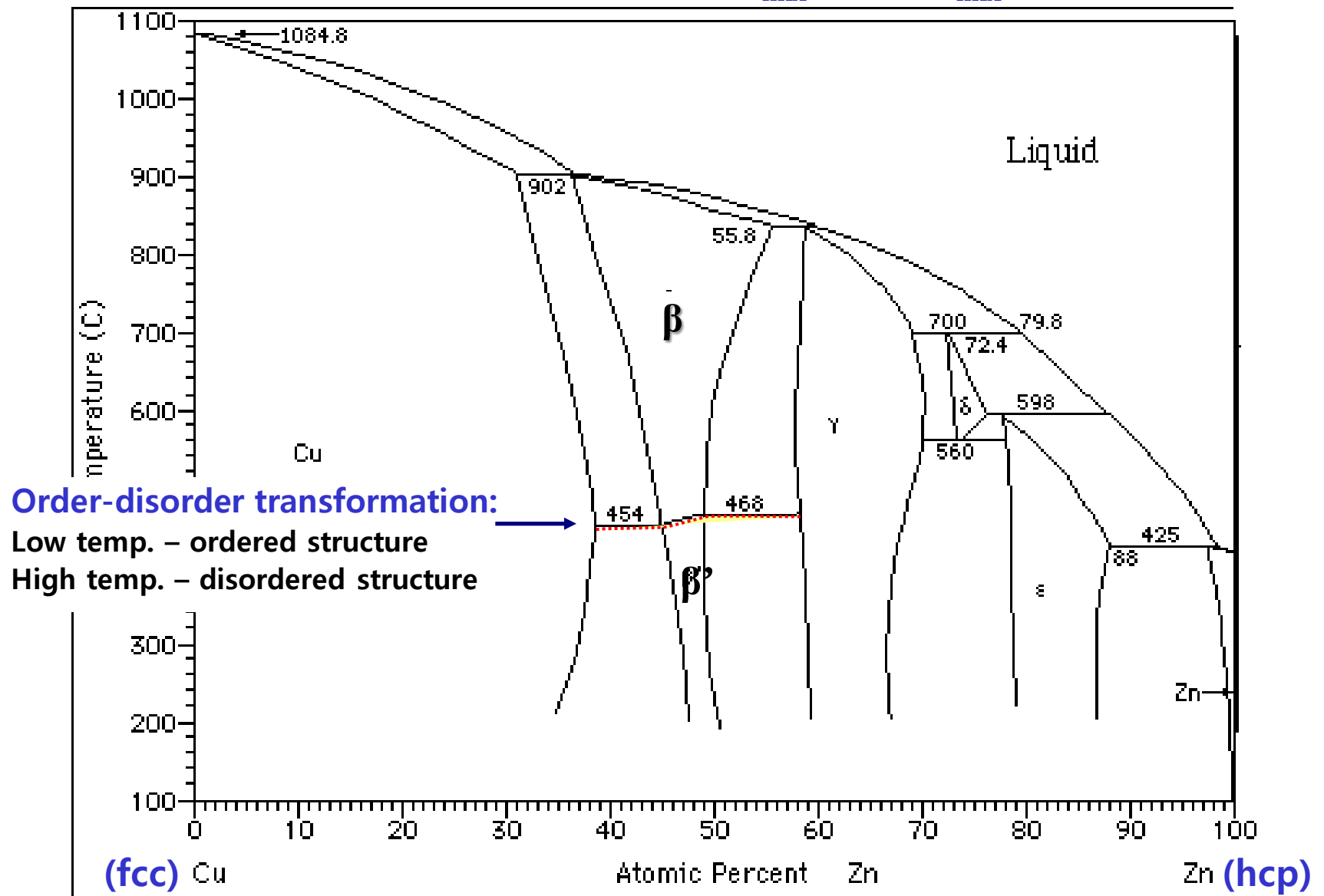
Order-disorder phase transformation

- Not classical phase change = ~not depend on diffusion process
- **change of temperature allowed a continuous re-arrangement of atoms without changing the phase = "2nd order transition"**
- **boundary: ordered lattice & disordered lattice/phase rule could not applied**
there are cases in which an ordered phase of one composition exists in equilibrium with a disordered phase of a different composition.
- Simple composition of the type AB or AB₃ can the transformation (i.e. at the temperature maximum) be considered diffusionless.



Intermediate Phase

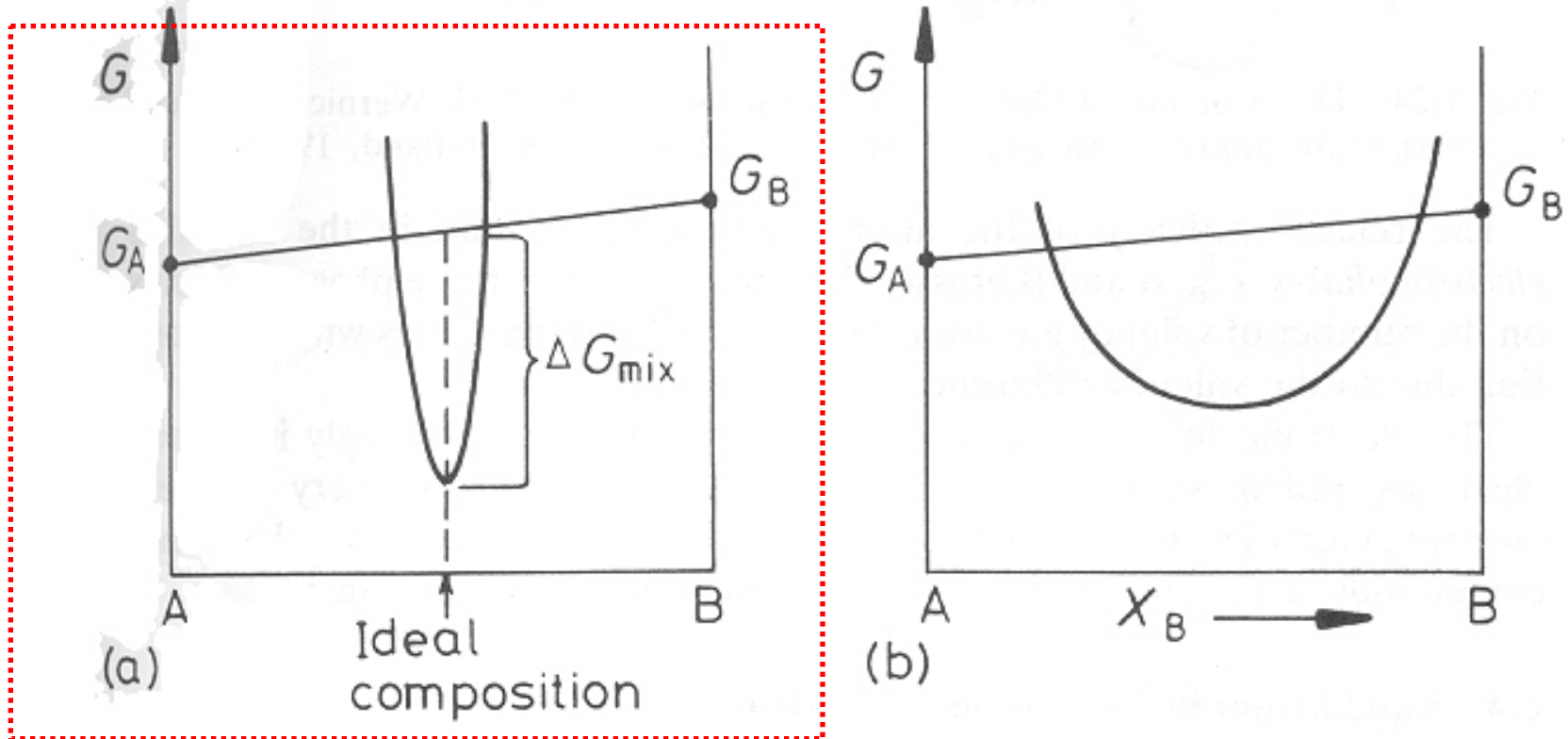
$$\varepsilon < 0, \Delta H_{\text{mix}} < 0 / \Delta H_{\text{mix}} \sim -21 \text{ kJ/mol}$$



- α and η are terminal solid solutions
- β , β' , γ , δ and ε are intermediate solid solutions.

Q3: Intermediate phase vs Intermetallic compound

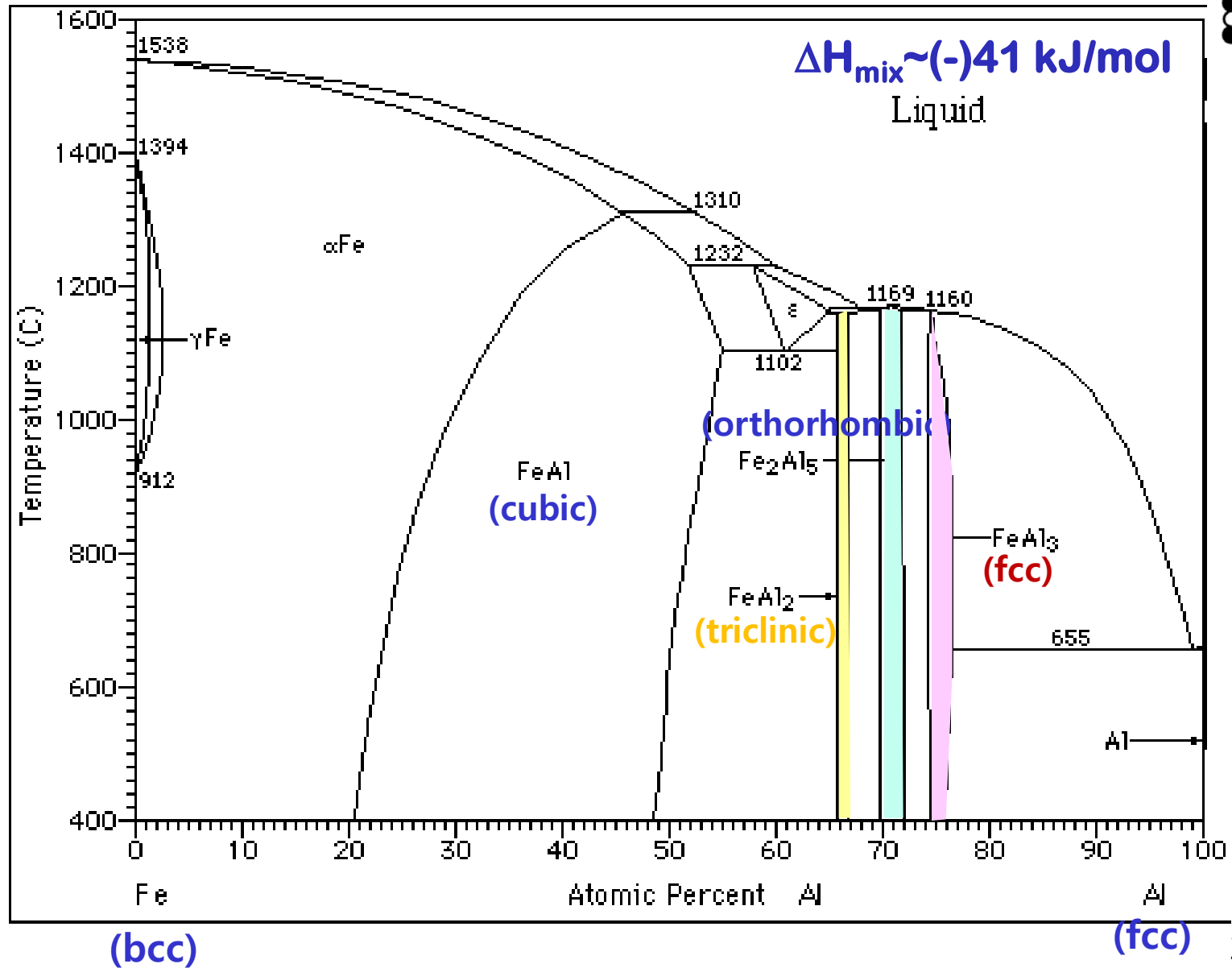
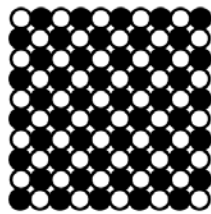
Intermediate Phase



- * **Many intermetallic compounds** have **stoichiometric composition** A_mB_n and a characteristic free energy curve as shown in Fig (a).
- * In other structure, fluctuations in composition can be tolerated by some atoms occupying 'wrong' position or by atom sites being left vacant, and in these cases the curvature of the G curve is much less, Fig (b).

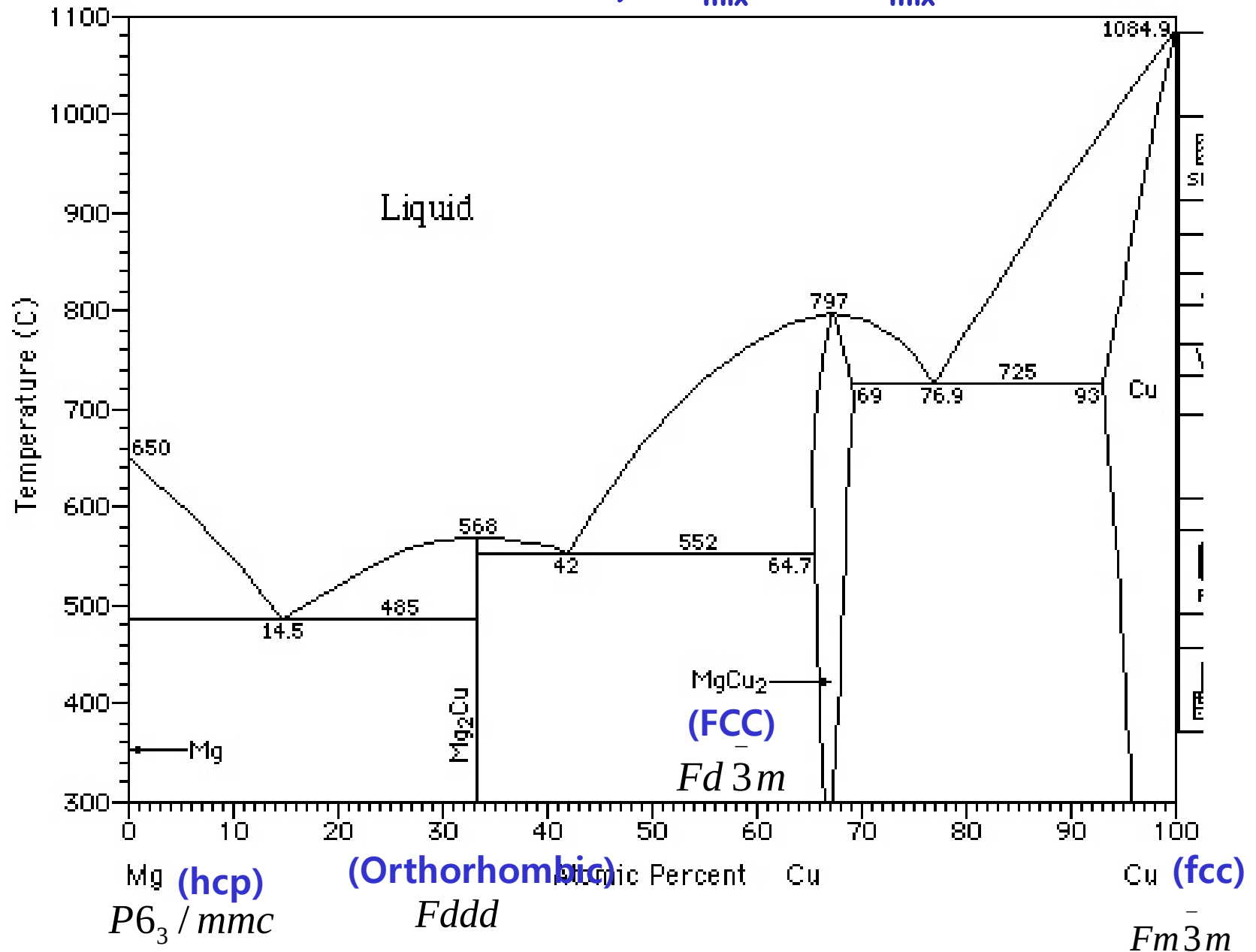
Intermediate Phase

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



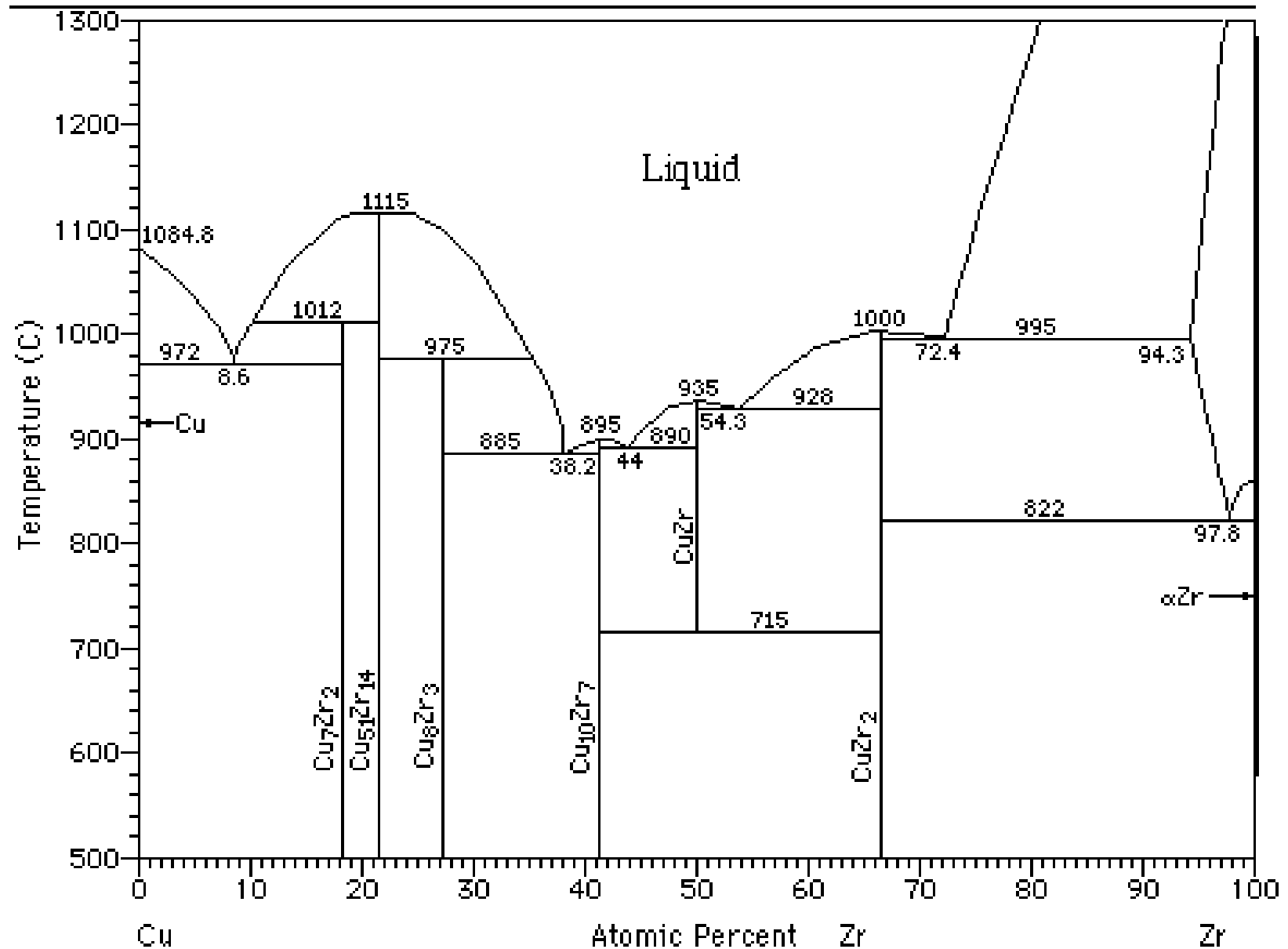
Intermediate Phase

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



Intermediate Phase

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



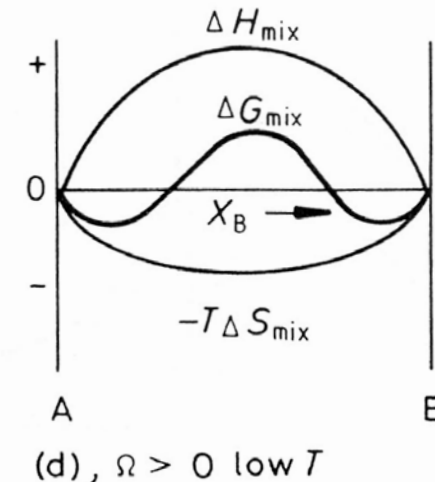
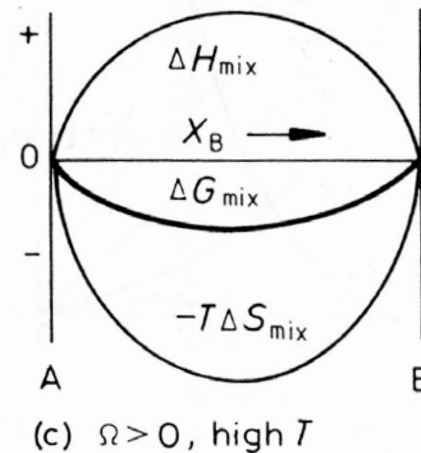
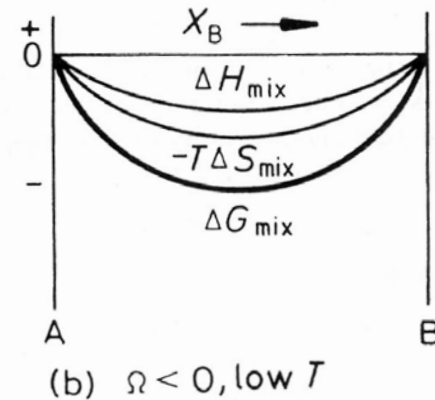
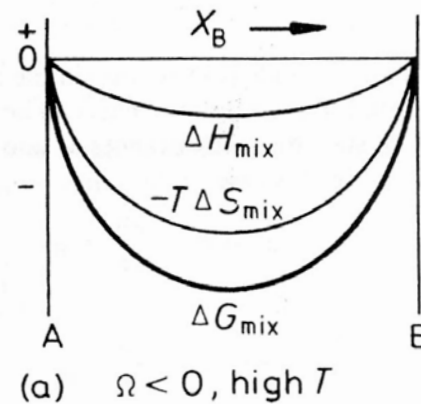
“Clustering”? → Phase separation

Q4: Metastable vs Stable miscibility gap

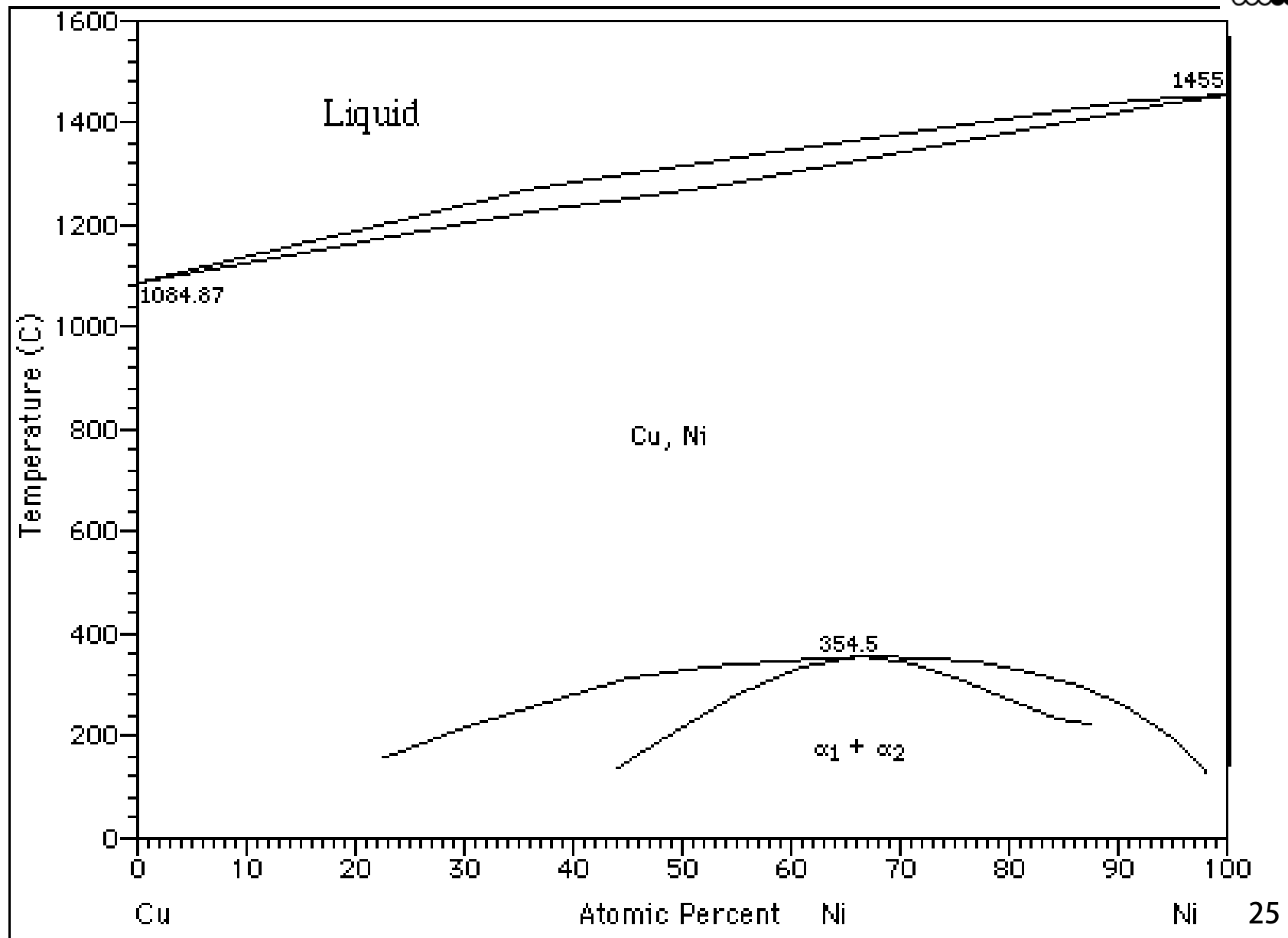
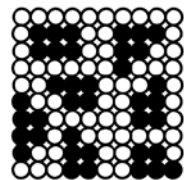
- * The degree of **ordering or clustering** will **decrease** as temp. **increases** due to the increasing importance of **entropy**.

High temp. $\longrightarrow$ Entropy effect $\uparrow$ $\longrightarrow$ Solution stability $\uparrow$

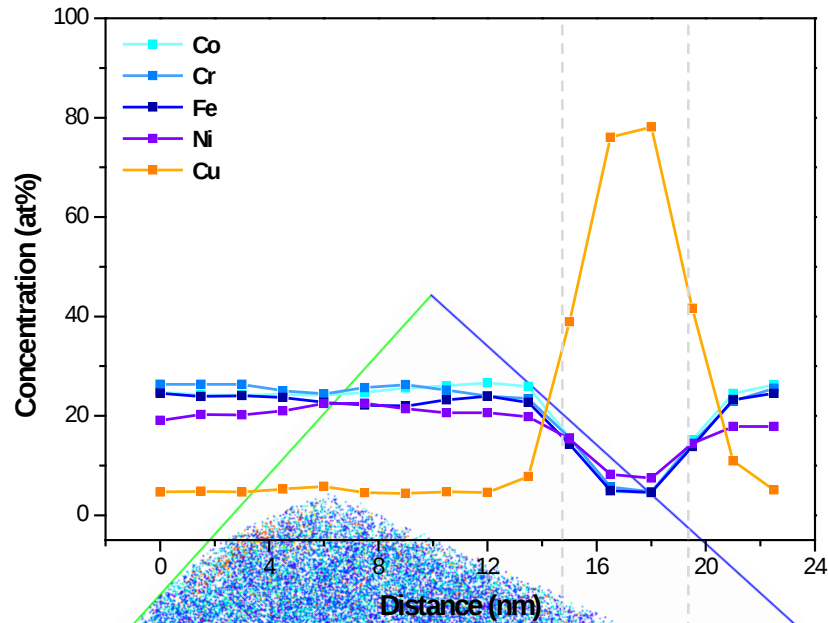
$$\Delta G_{mix} = \Delta H_{mix} - T\Delta S_{mix}$$



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



Compositional analysis of as-cast CoCrFeNi/Cu HEA (dendrite)



ROI 1, 2 : 1.4 nm x 2 nm x 2 nm

ROI 3 : 1.2 nm x 2 nm x 23 nm

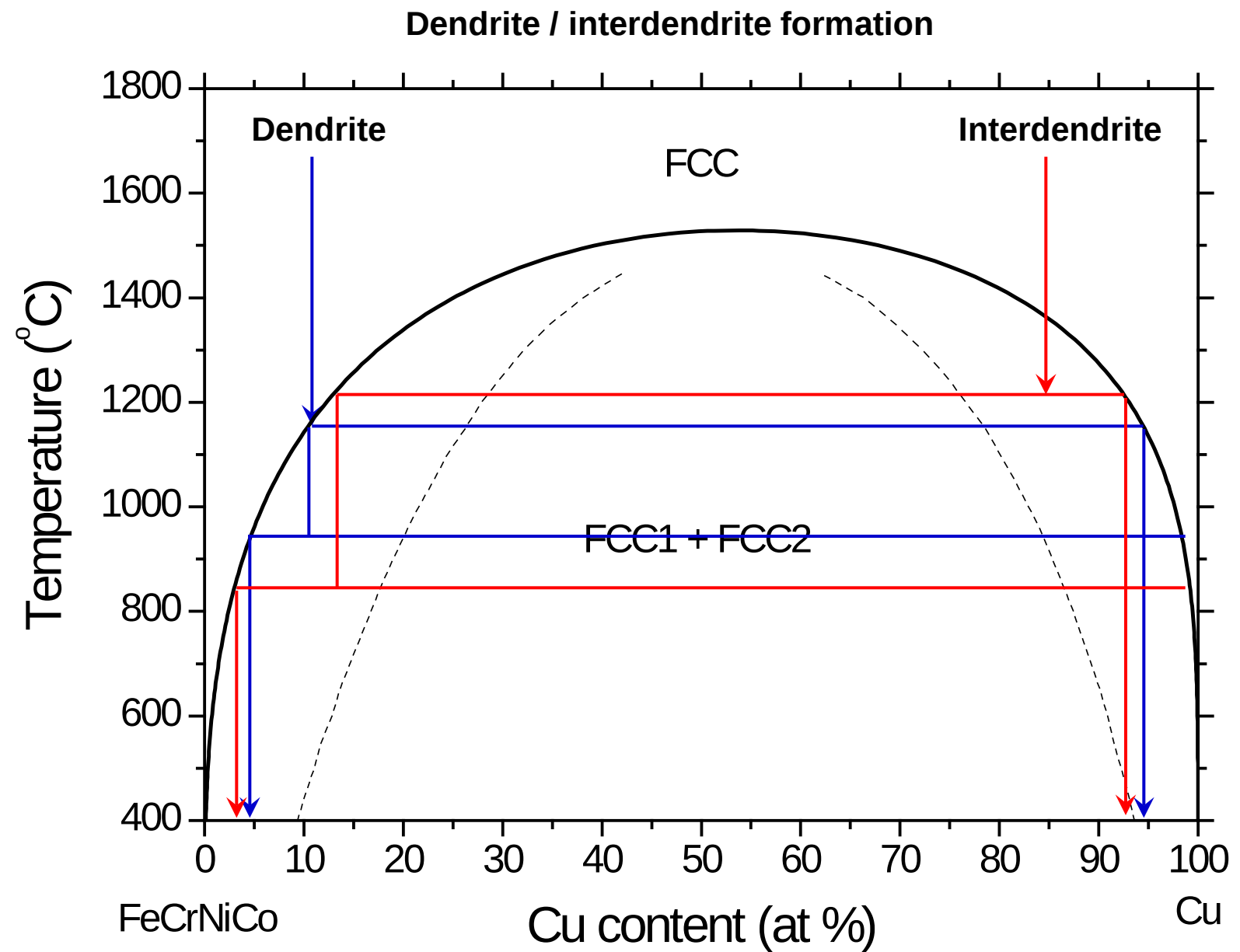
(1D concentration profile)

1	at%	2	at%
Co	26.19	Co	0.33
Cr	24.15	Cr	0.46
Fe	24.59	Fe	0.39
Ni	19.59	Ni	5.00
Cu	4.74	Cu	93.56

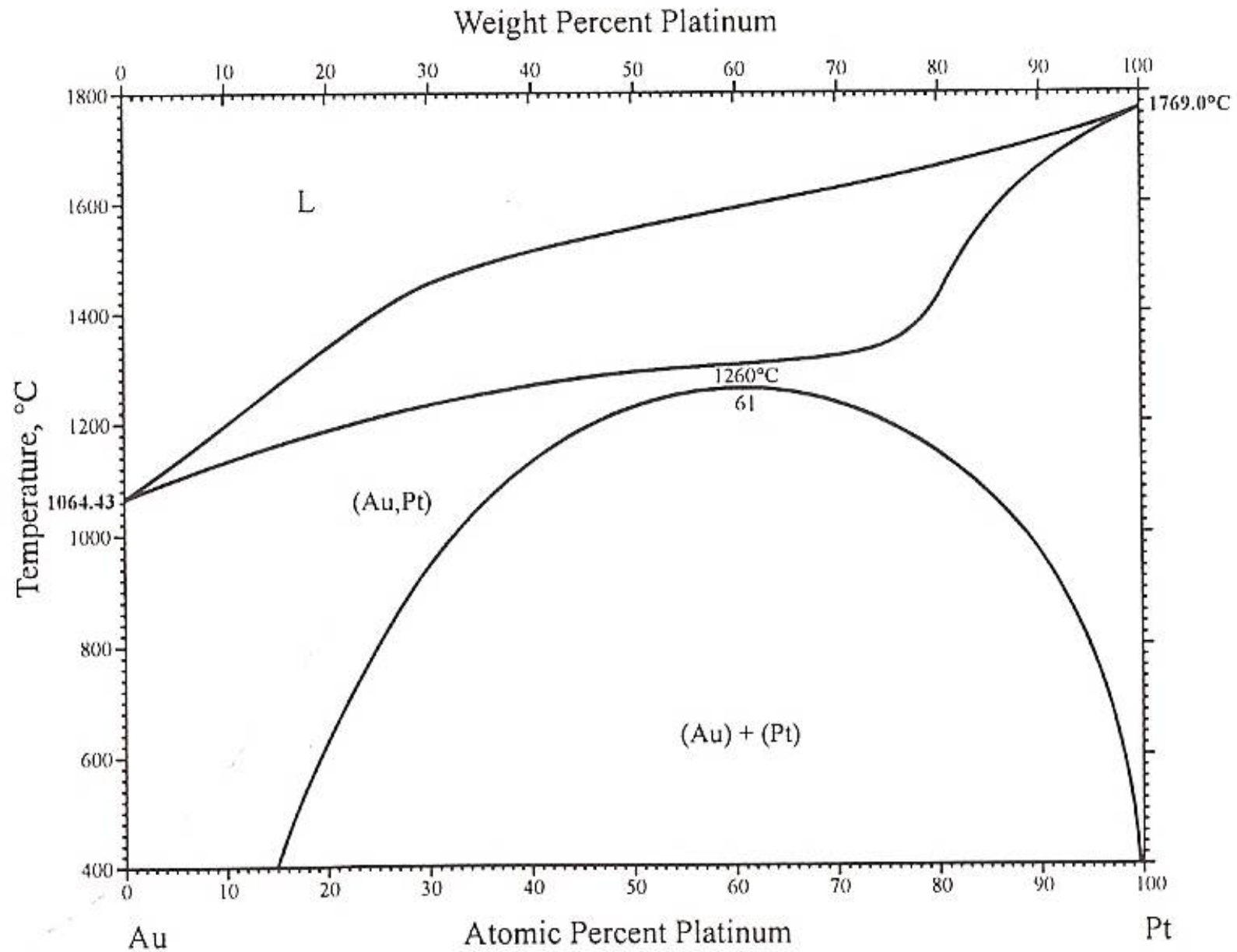
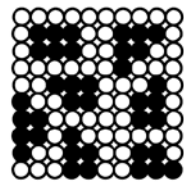
3-1'	at%	3-2'	at%
Co	25.29	Co	2.01
Cr	25.63	Cr	3.35
Fe	23.63	Fe	2.56
Ni	20.66	Ni	6.90
Cu	4.42	Cu	84.92

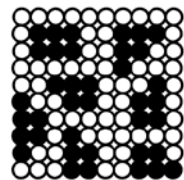
- Dendrite region: matrix (4.74 at%Cu) + 2nd phase (93.56 at%Cu)
- No segregation at the interface between Matrix and 2nd phase

Cooling process in the miscibility gap

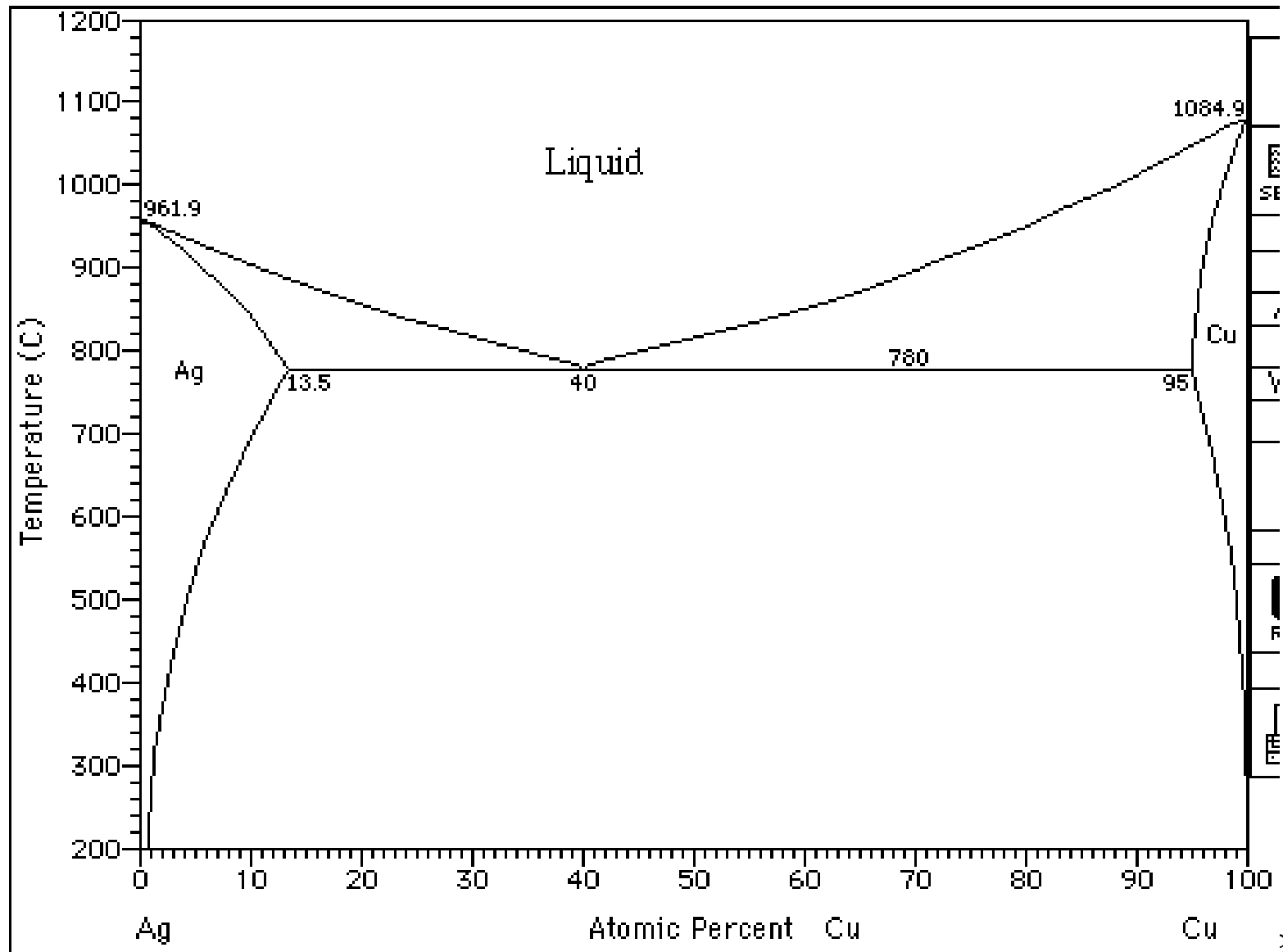


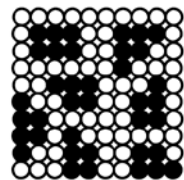
$$\varepsilon > 0, \Delta H_{\text{mix}} > 0 / \Delta H_{\text{mix}} \sim +17 \text{ kJ/mol}$$



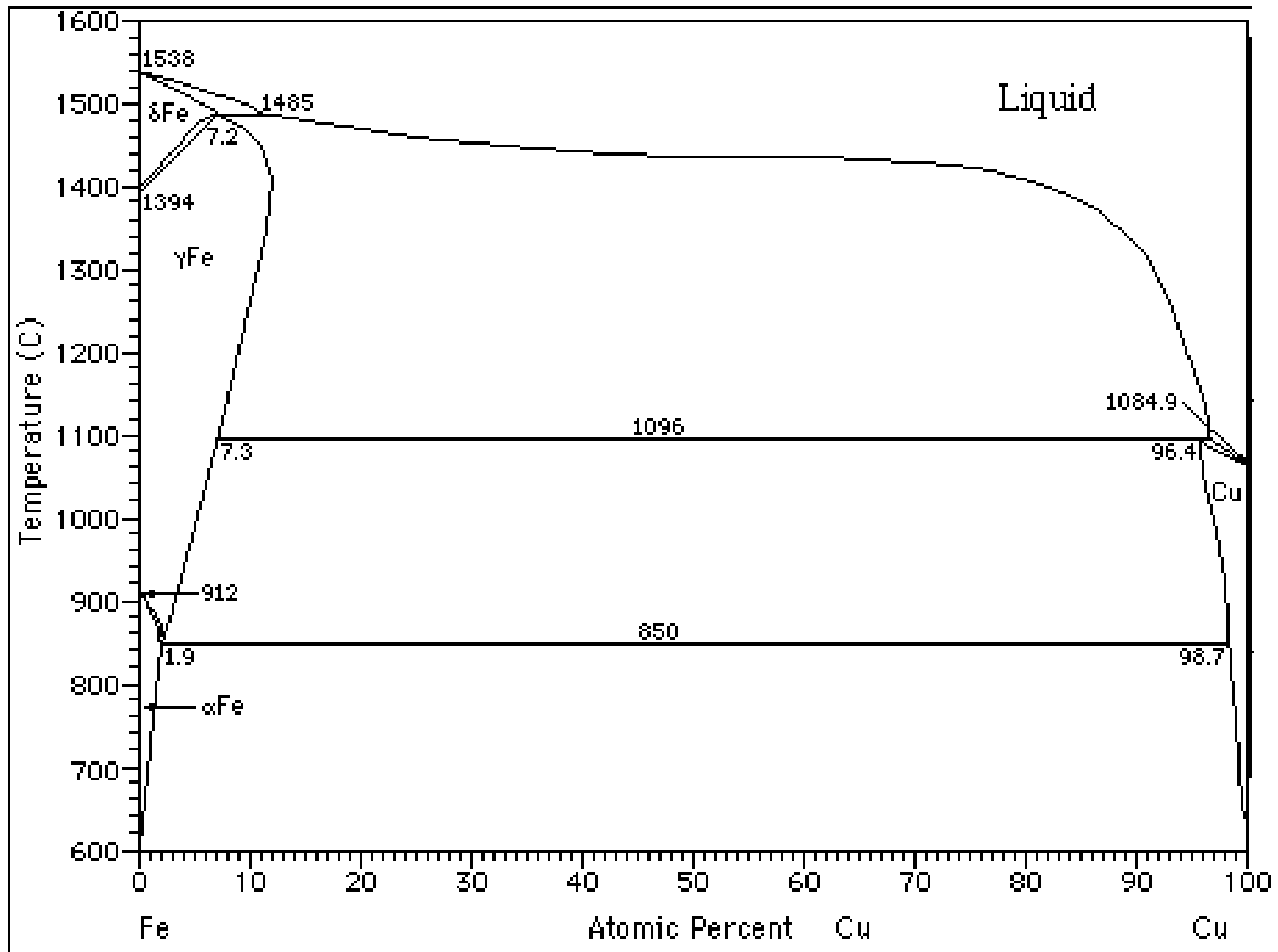


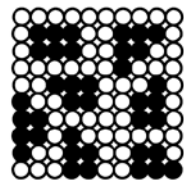
$\varepsilon > 0$, $\Delta H_{\text{mix}} > 0$ / $\Delta H_{\text{mix}} \sim +5 \text{ kJ/mol}$



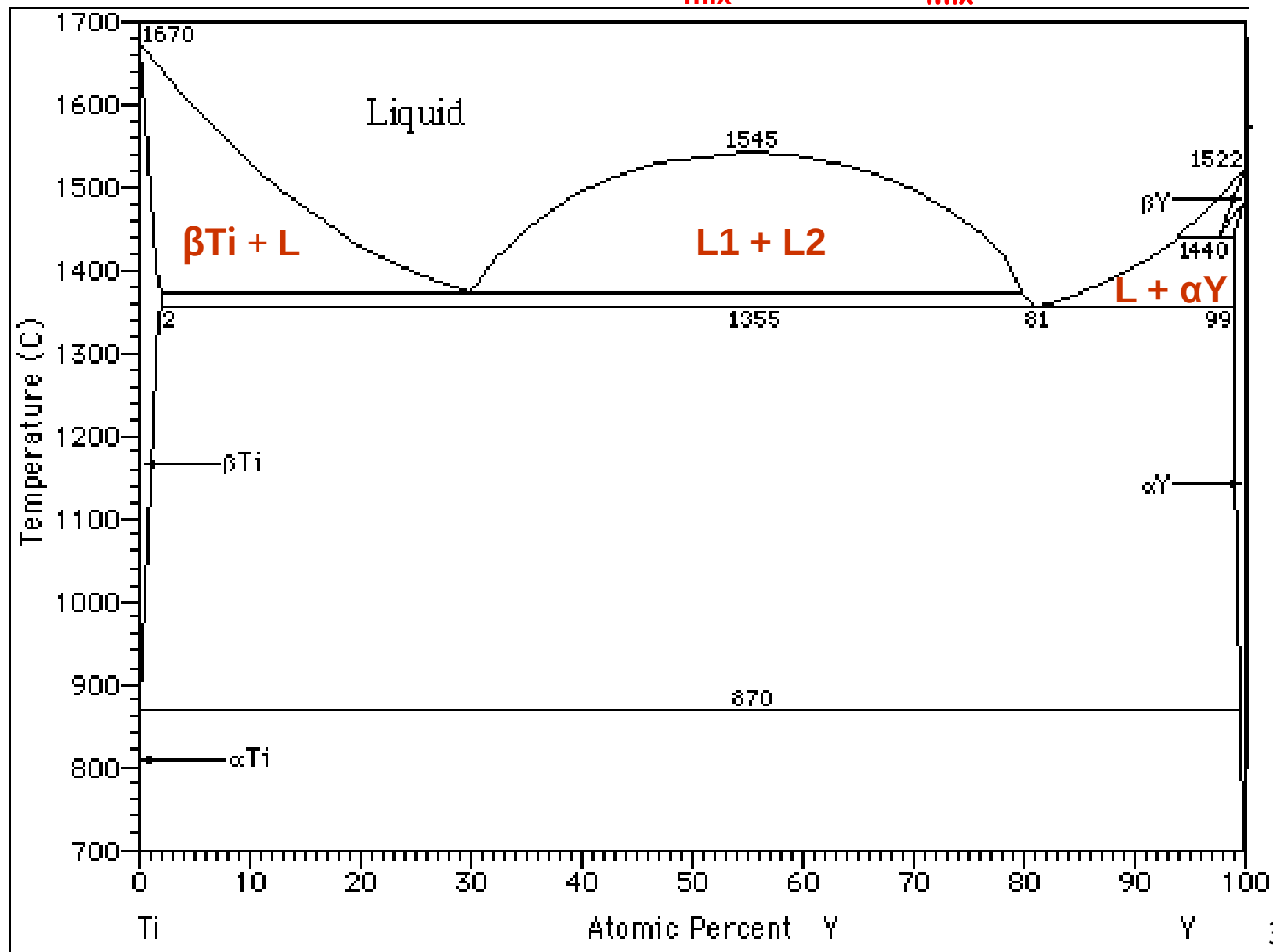


$\epsilon \gg 0$, $\Delta H_{\text{mix}} \gg 0$ / $\Delta H_{\text{mix}} \sim +60 \text{ kJ/mol}$





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



Positive heat of mixing relation among constituent elements

- Alloy design considering heat of mixing relation among constituent elements

$$\Delta H_{\text{mix}} \gg 0 \text{ between A \& B}$$

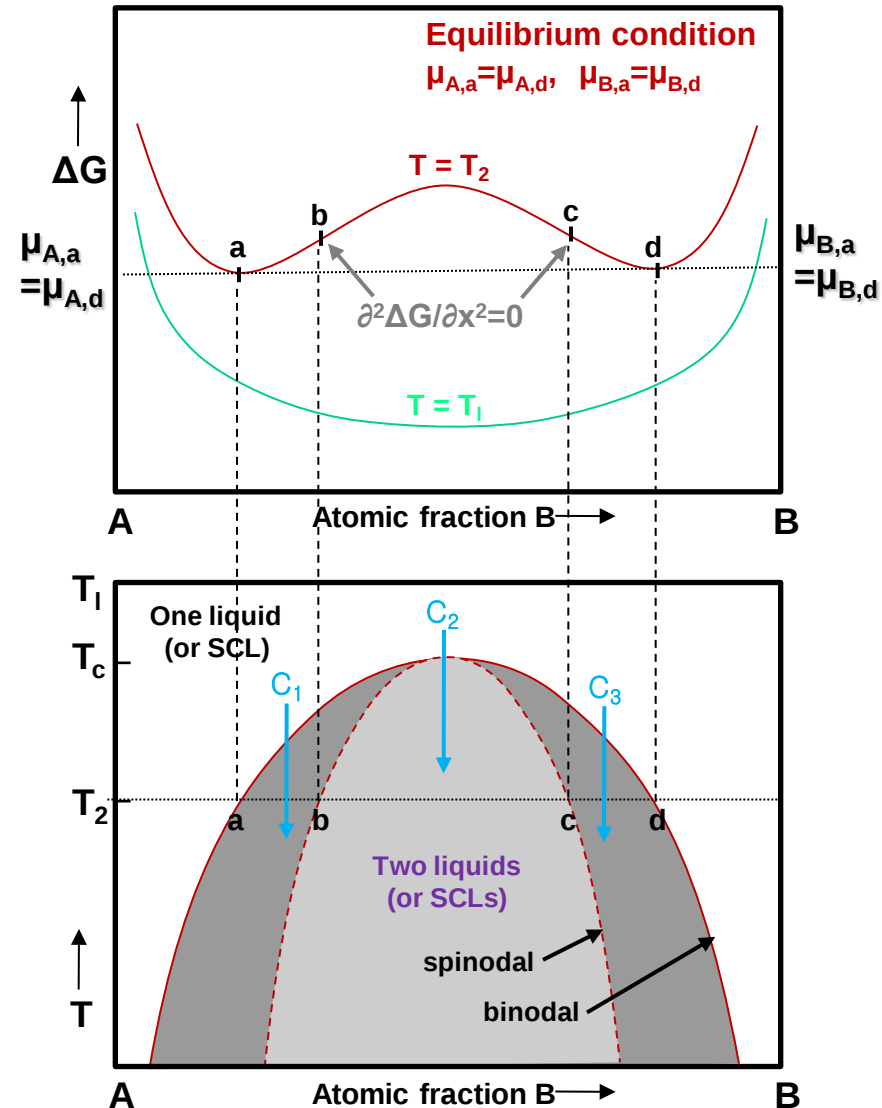
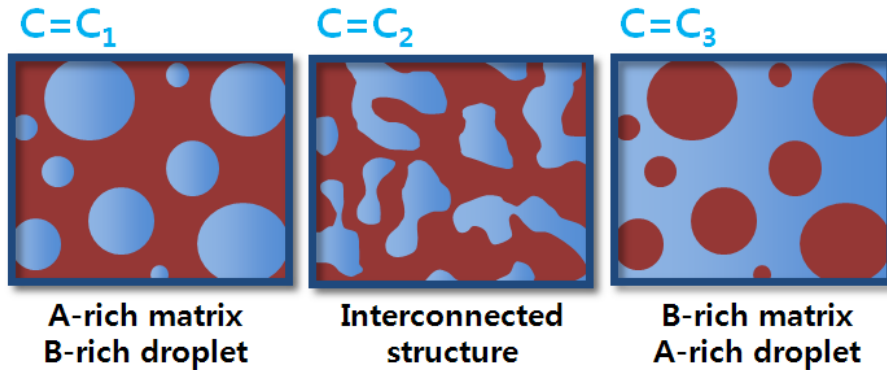


creates (meta)stable miscibility gap
in limited composition range



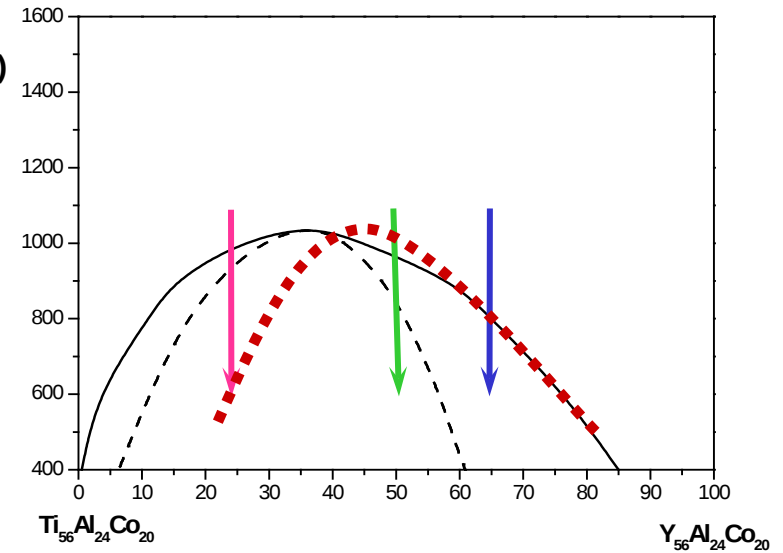
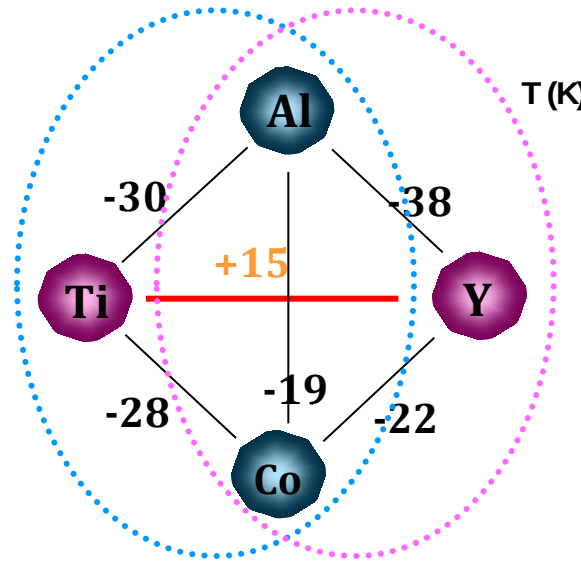
Phase separation to A-rich & B-rich phase

- Different two-phase structure by initial composition before phase separation



Nucleation and growth ↔ Spinodal decomposition without any barrier to the nucleation process

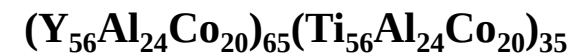
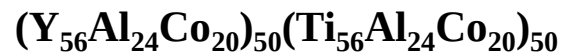
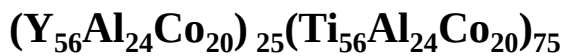
* Ti-Y-Al-Co system



Droplet structure

Interconnected structure

Droplet structure



* La-Zr-Al-Cu-Ni system

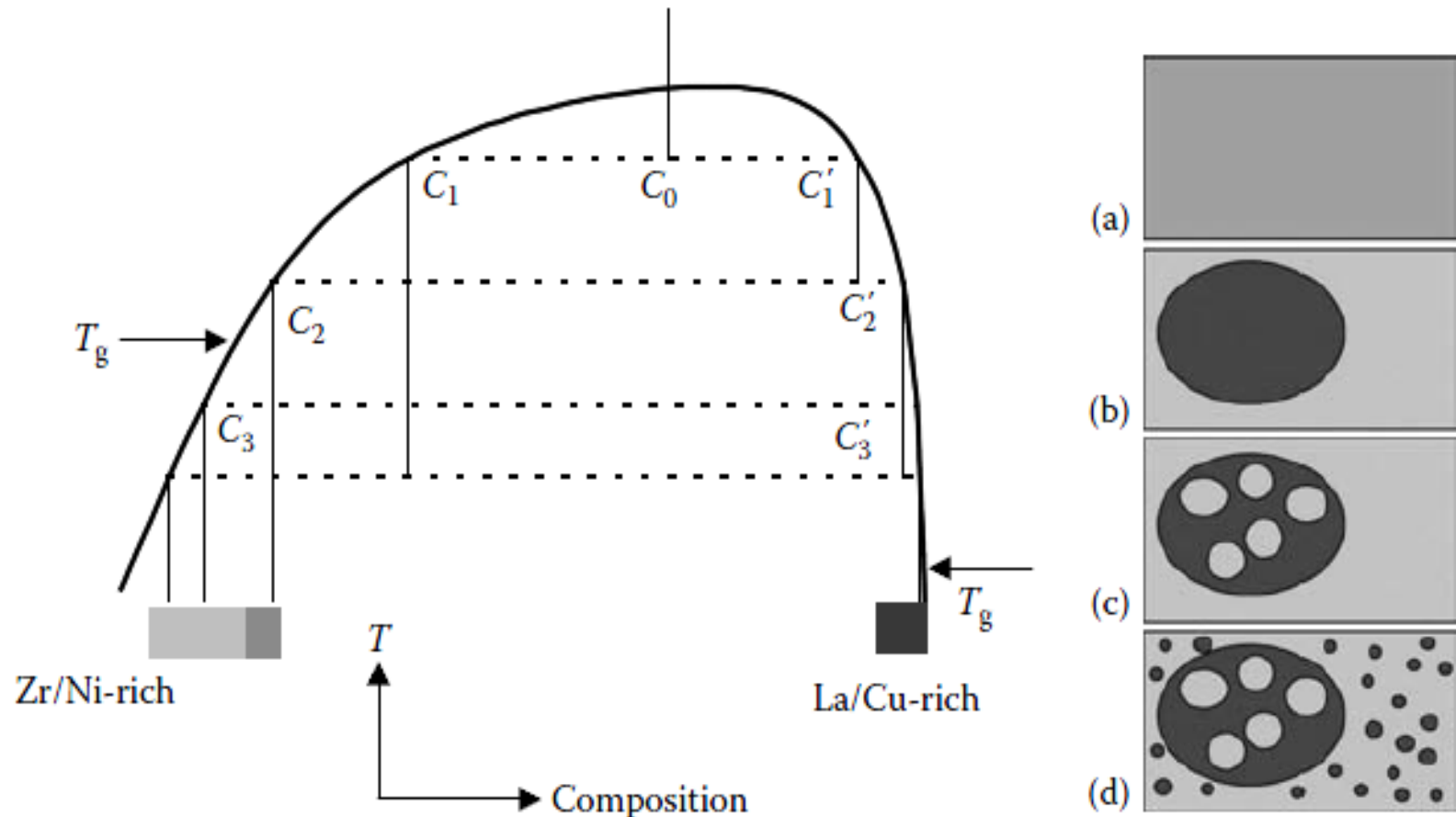
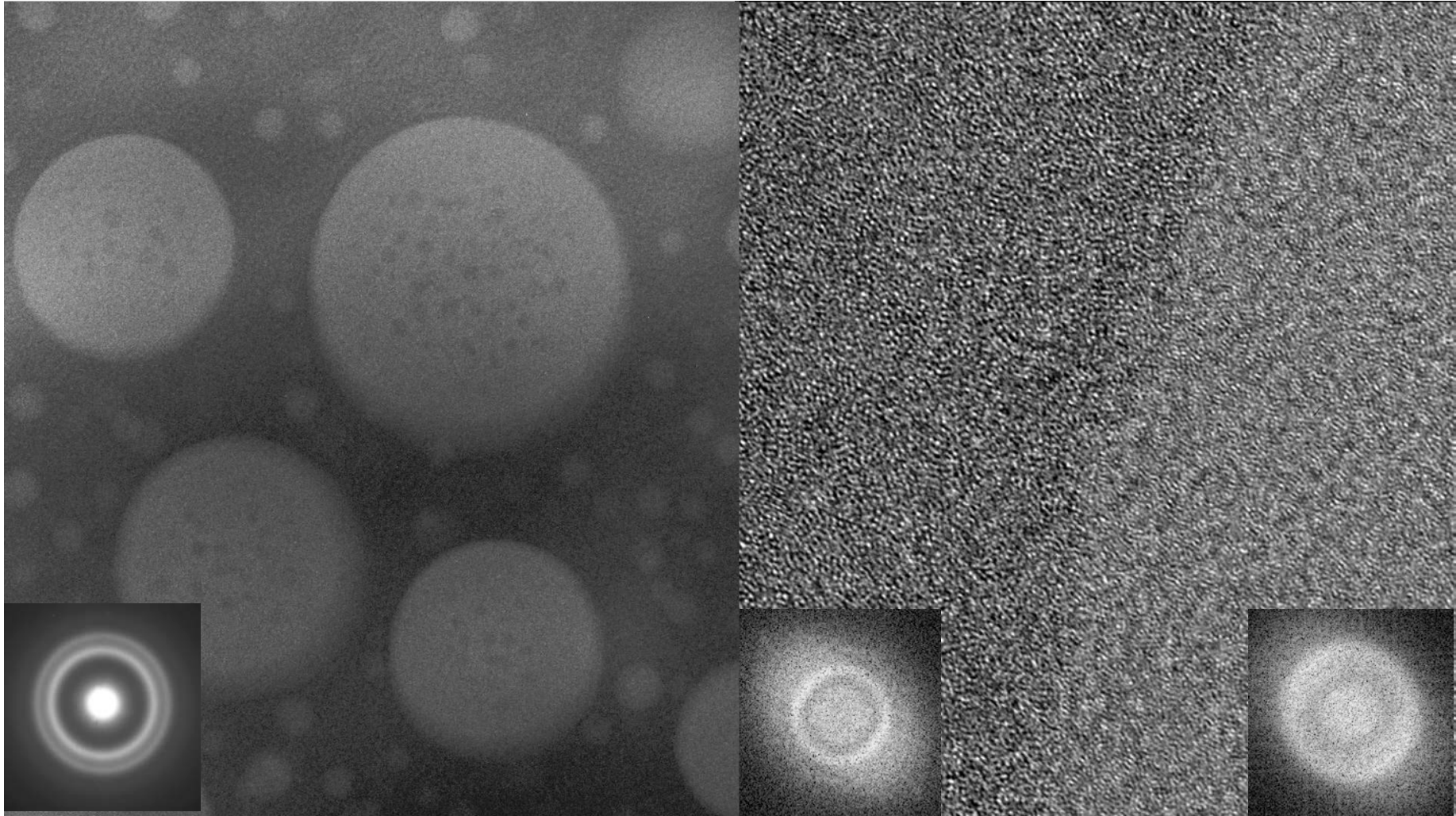
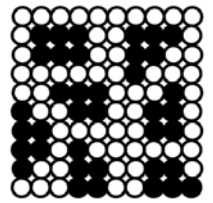


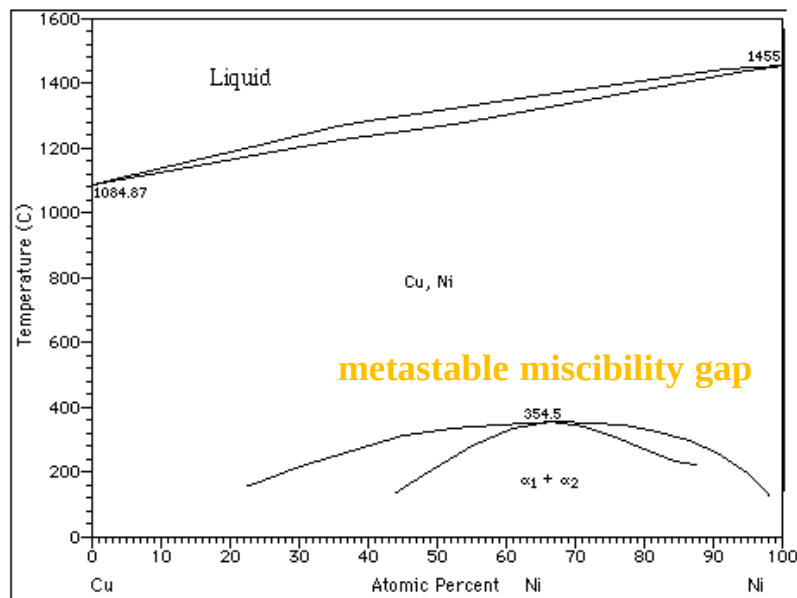
FIGURE 5.17

Schematic of the miscibility gap and the sequence of phase formation during cooling in the La-Zr-Al-Cu-Ni system. The positions of letters (a) to (d) in the diagram on the left correspond to the schematic microstructures (a) to (d) on the right. (Reprinted from Kündig, A.A. et al., *Acta Mater.*, 52, 2441, 2004. With permission.)

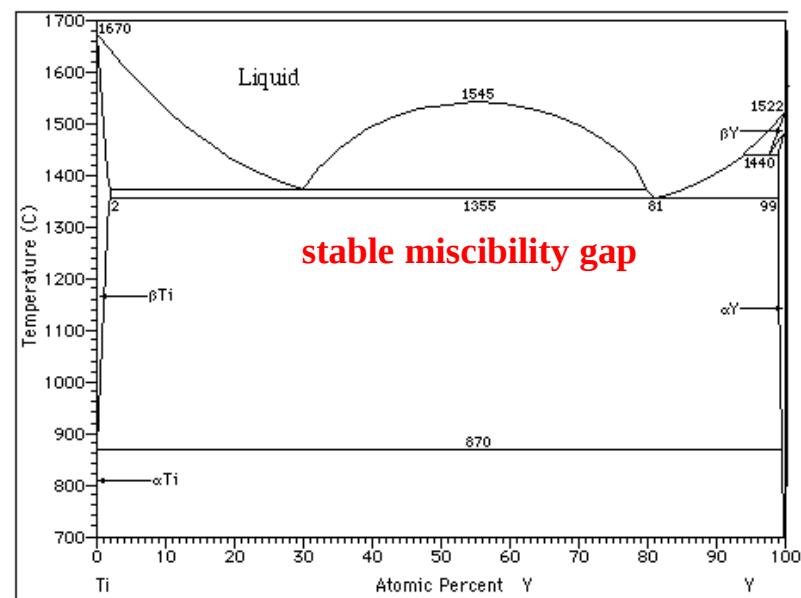
Phase separation in metallic glasses



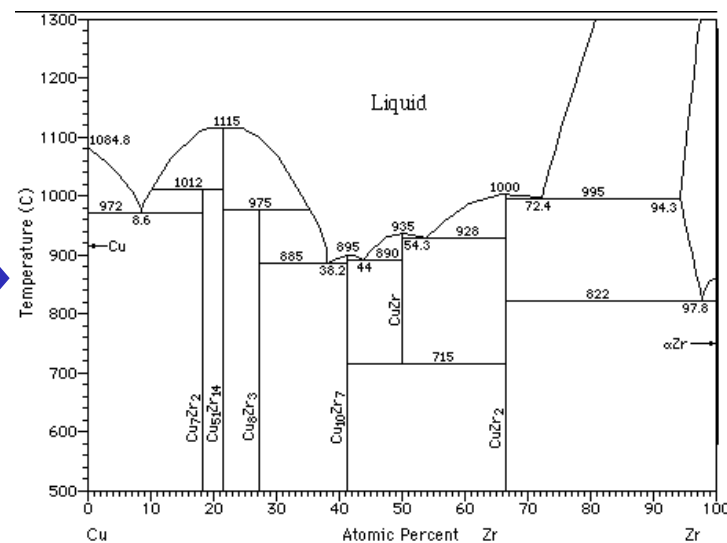
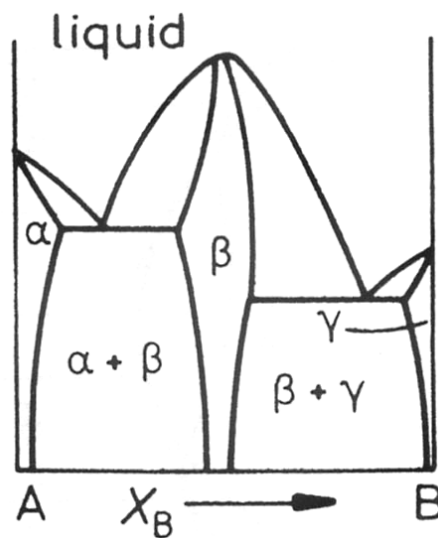
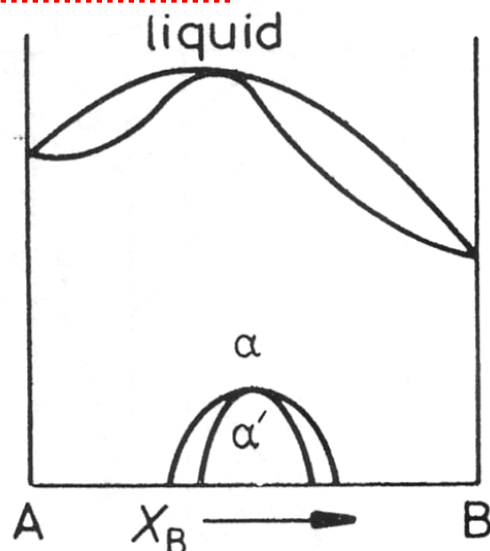
$\Delta H_{mix}^S > 0$: Solid solution $\rightarrow$ solid state phase separation (two solid solutions)



$\Delta H_{mix}^S \gg 0$: 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, A₂B...

Contents for today's class

- **Equilibrium in Heterogeneous Systems**
- **Binary phase diagrams**

How the **equilibrium state of an alloy** can be obtained from the **free energy curves at a given temperature**

→ **How equilibrium is affected by temperature**

a) **Variation of temp.: $G^L > G^S$**

b) **At low temp. ($\therefore$ decrease of $-T\Delta S_{\text{mix}}$ effect): Decrease of curvature of G curve**

1) Simple Phase Diagrams

2) Systems with miscibility gap

4) Simple Eutectic Systems

3) Ordered Alloys

5) Phase diagrams containing intermediate phases

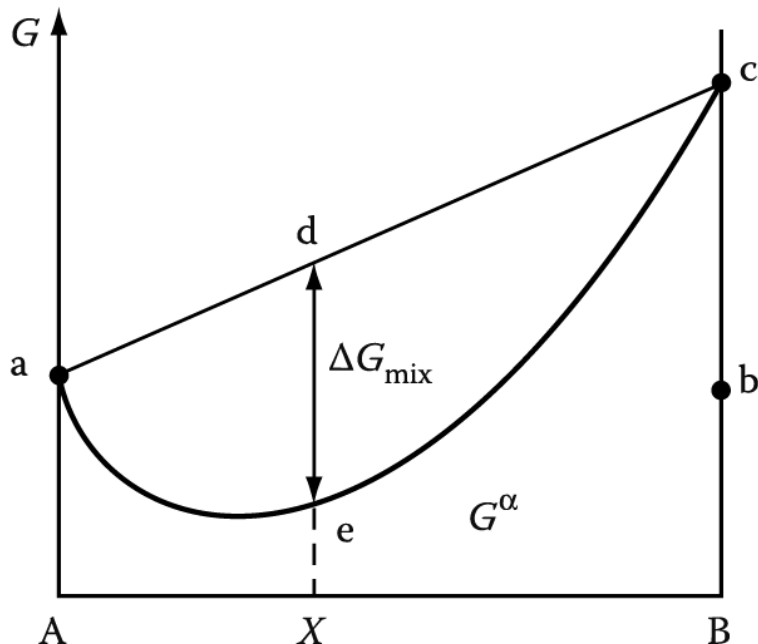
**Q5: How can we define equilibrium
in heterogeneous systems?**

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.

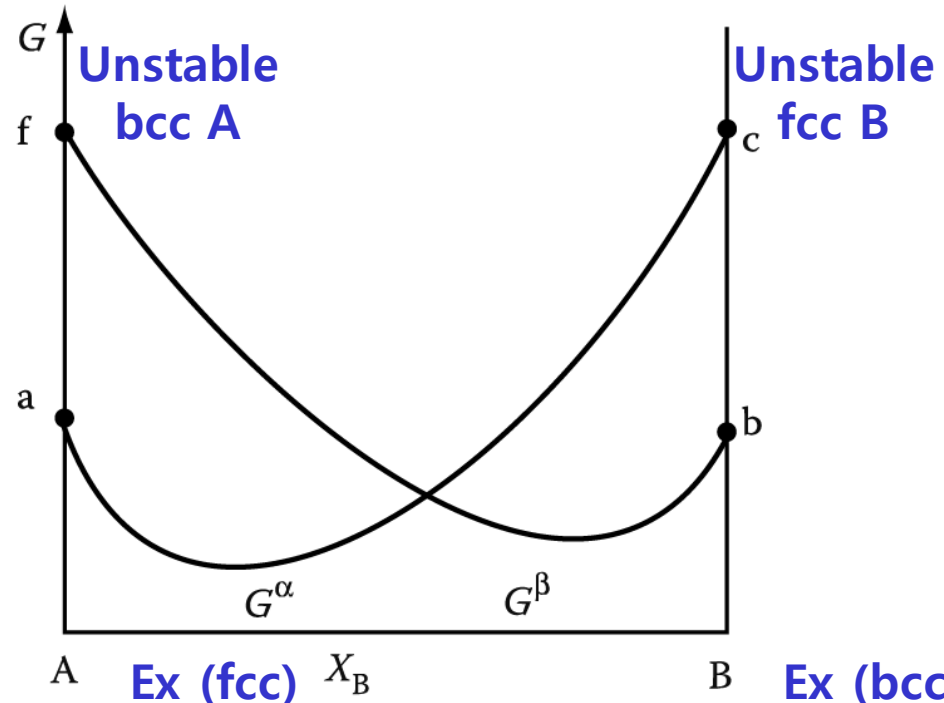
$$G = X_A G_A + X_B G_B + \Omega X_A X_B + RT(X_A \ln X_A + X_B \ln X_B)$$



(a)

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

→ **heterogeneous system**



(b)

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 $X_B^0 = ?$*

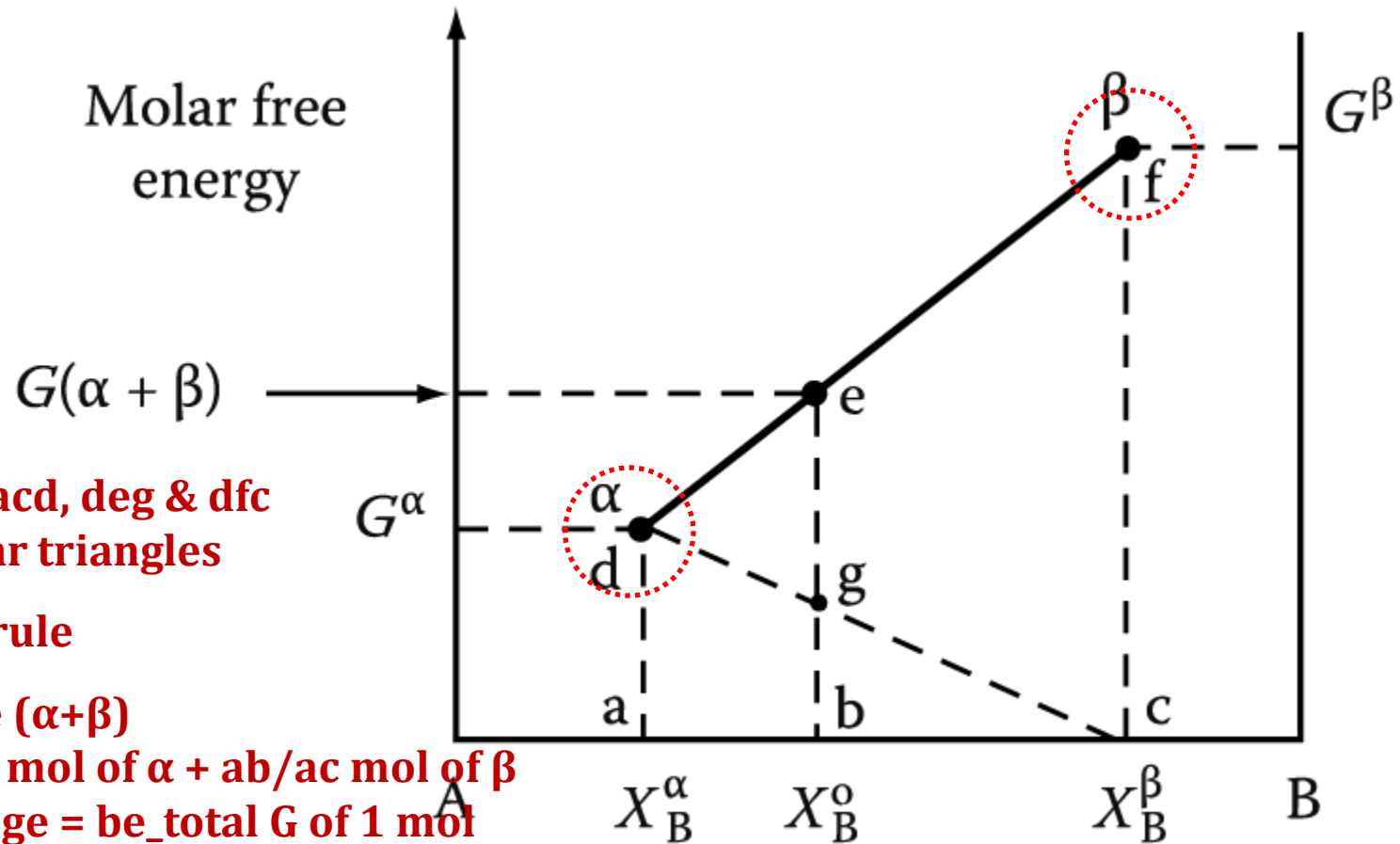
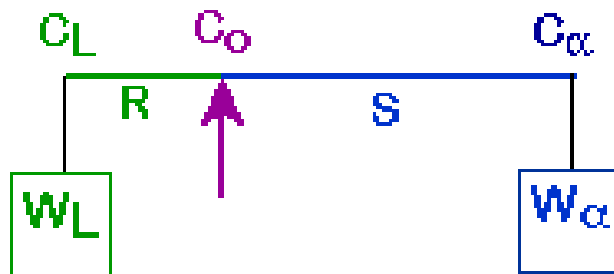


Fig. 1.26 The molar free energy of a two-phase mixture ($\alpha + \beta$)

Lever rule

A geometric interpretation:



moment equilibrium:

$$W_L R = W_\alpha S$$

$$1 - W_\alpha$$

solving gives Lever Rule

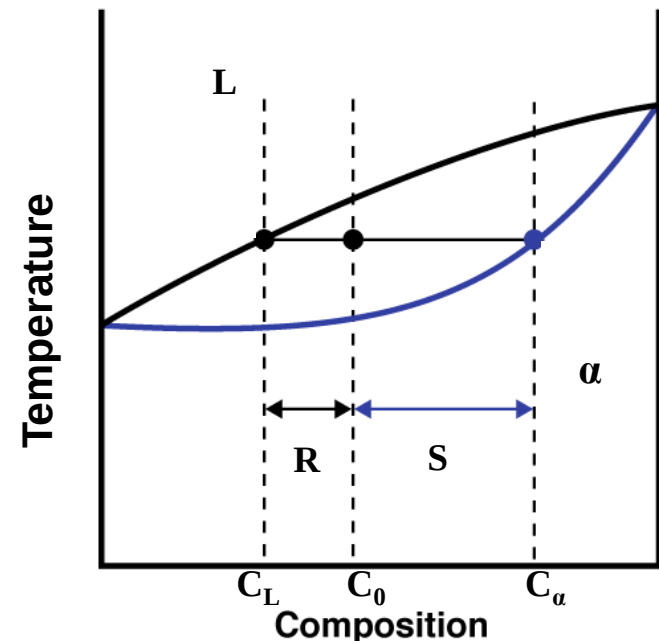
Sum of weight fractions: $W_L + W_\alpha = 1$

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

Combine above equations:

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

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

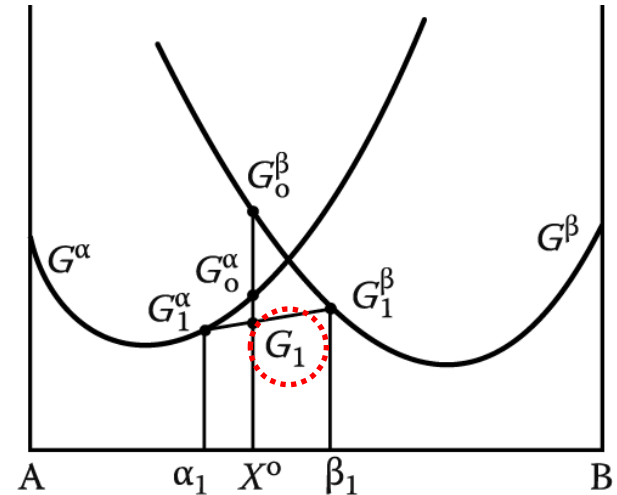


Equilibrium in Heterogeneous Systems

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

Exchange of A and B atoms

→ $\alpha + \beta$ phase separation



(a)

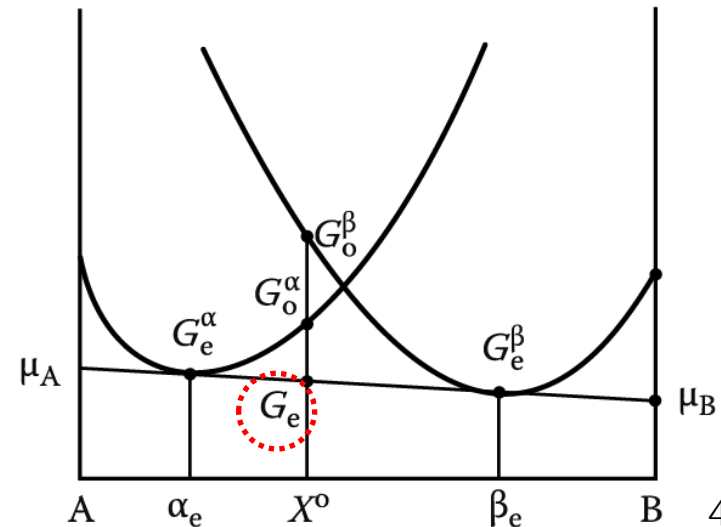


Chemical Equilibrium (μ , a)
 → multiphase and multicomponent
 ($\mu_i^\alpha = \mu_i^\beta = \mu_i^\gamma = \dots$), ($a_i^\alpha = a_i^\beta = a_i^\gamma = \dots$)

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

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

Unified Chemical potential of two phases



(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 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.

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

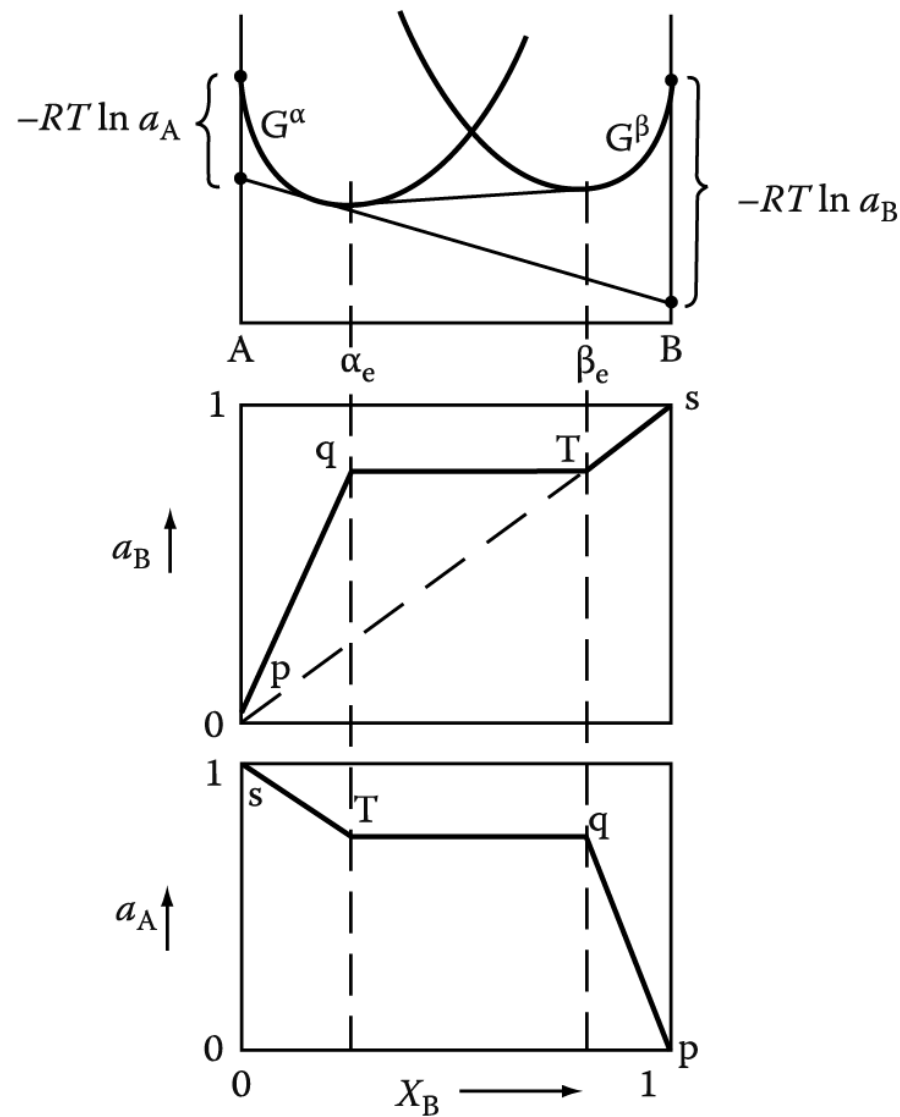
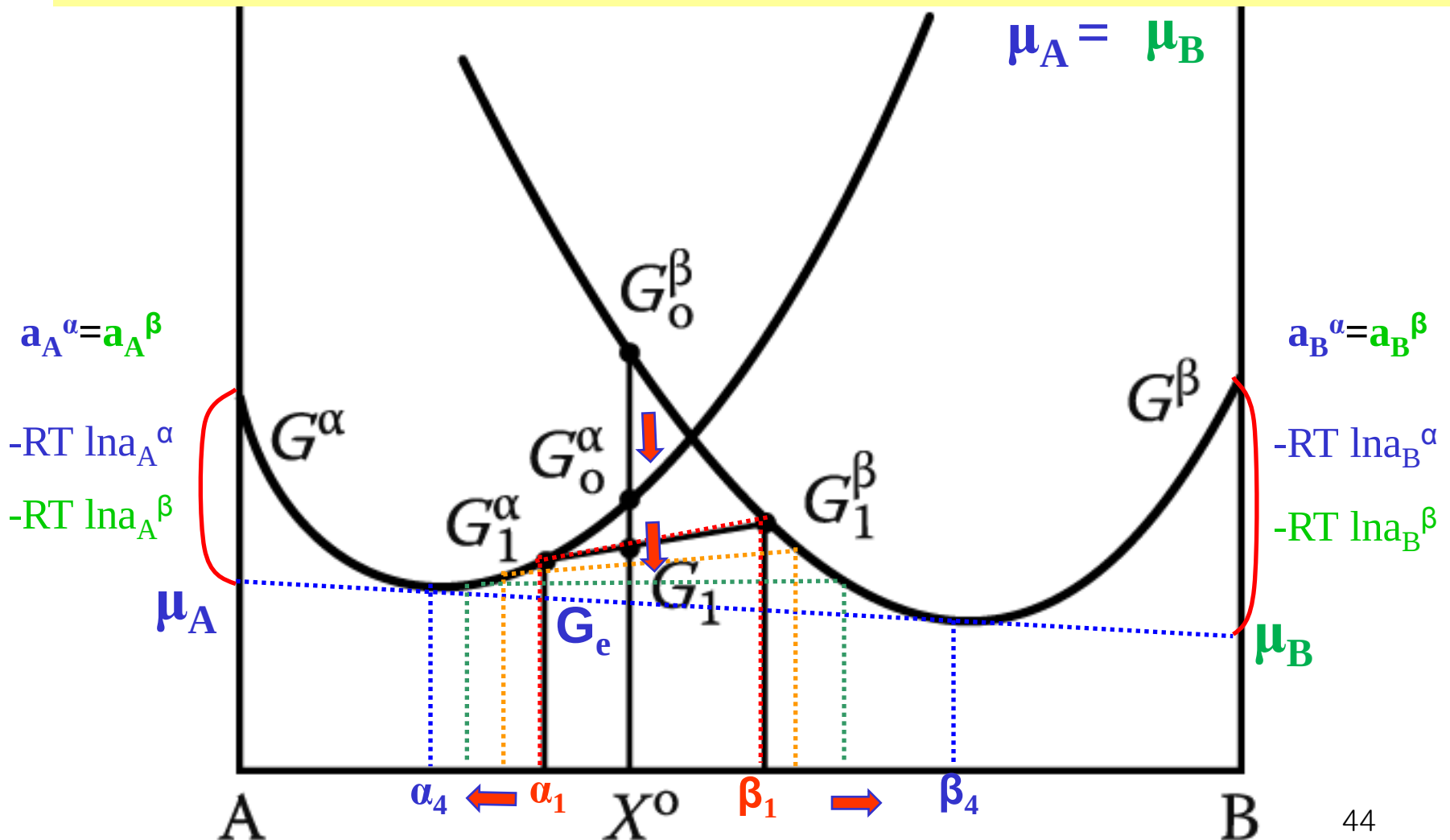


Fig. 1.28 The variation of a_A and a_B with composition for a binary system containing two ideal solutions, α and β

Unified activity of two phase

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.

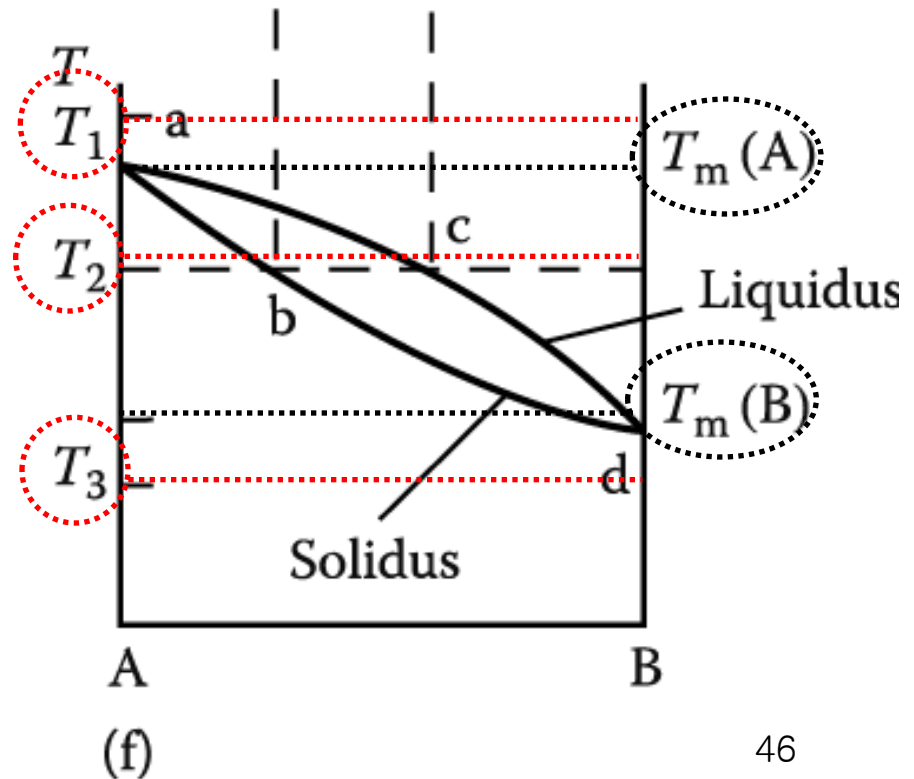
(2) **Both are ideal soln.**

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

(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

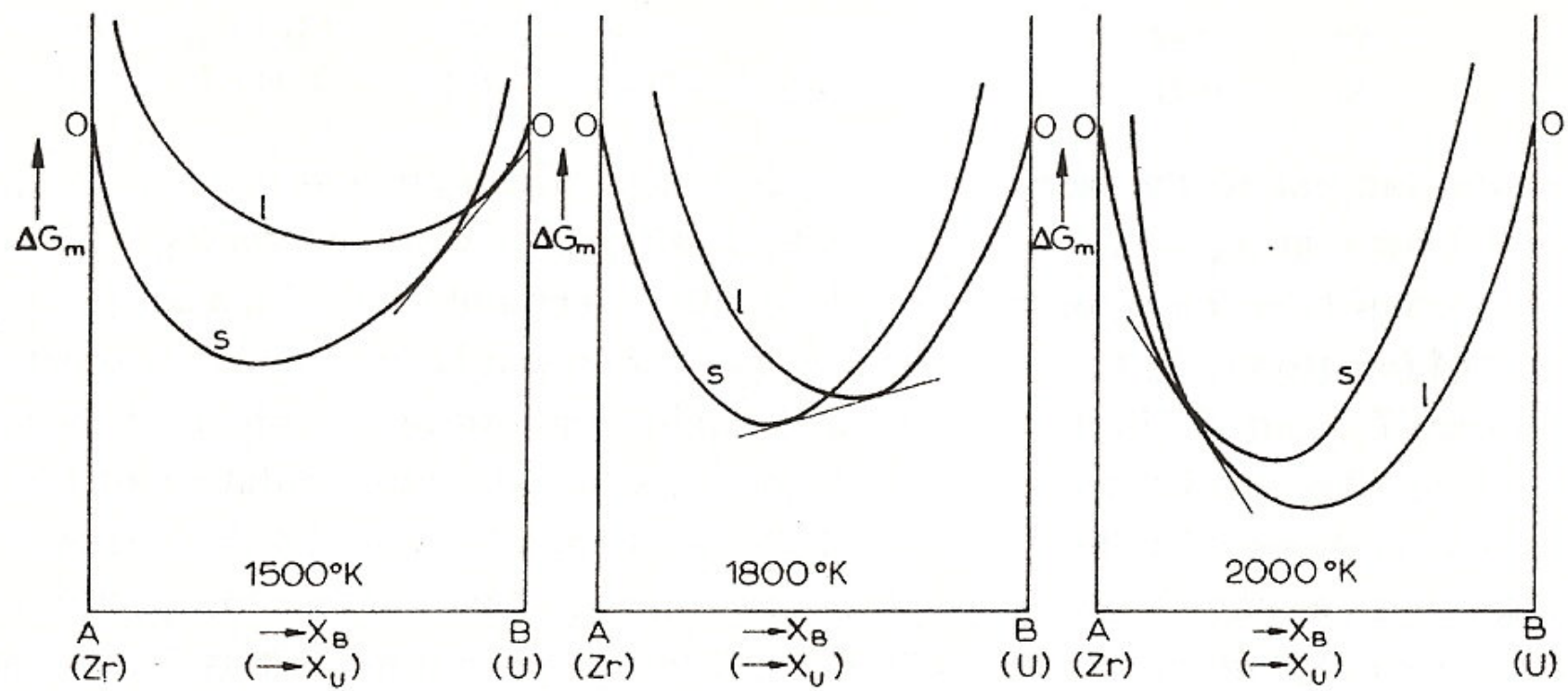


Fig. 26. Free energy curves for liquid and solid phases in the U-Zr system at 1500°, 1800° and 2000 °K.

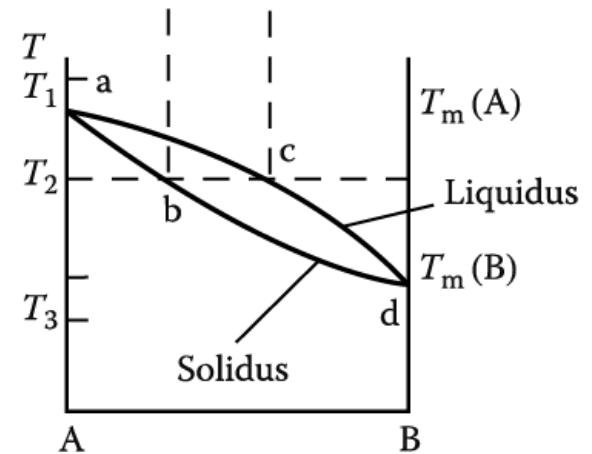
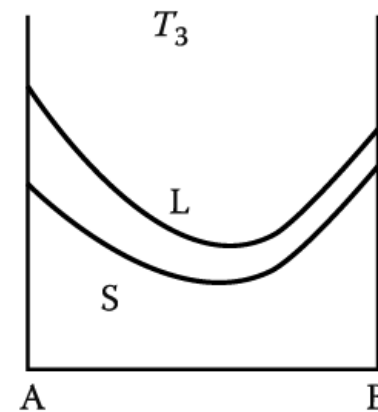
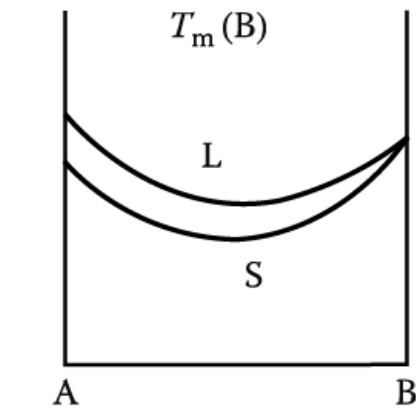
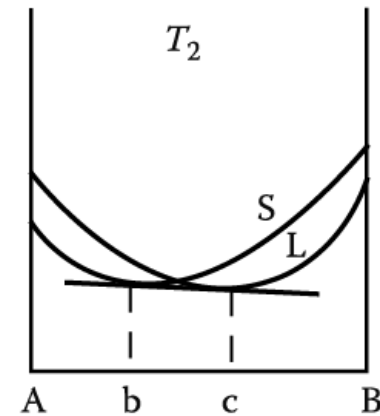
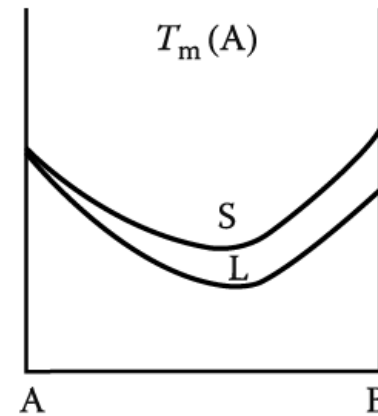
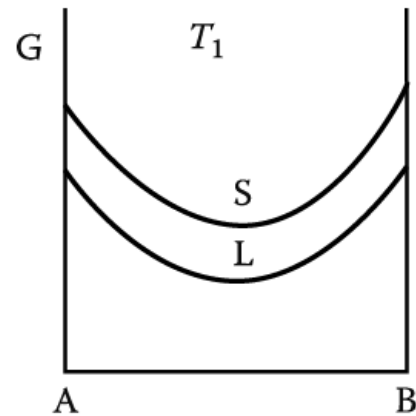
1.5 Binary phase diagrams

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

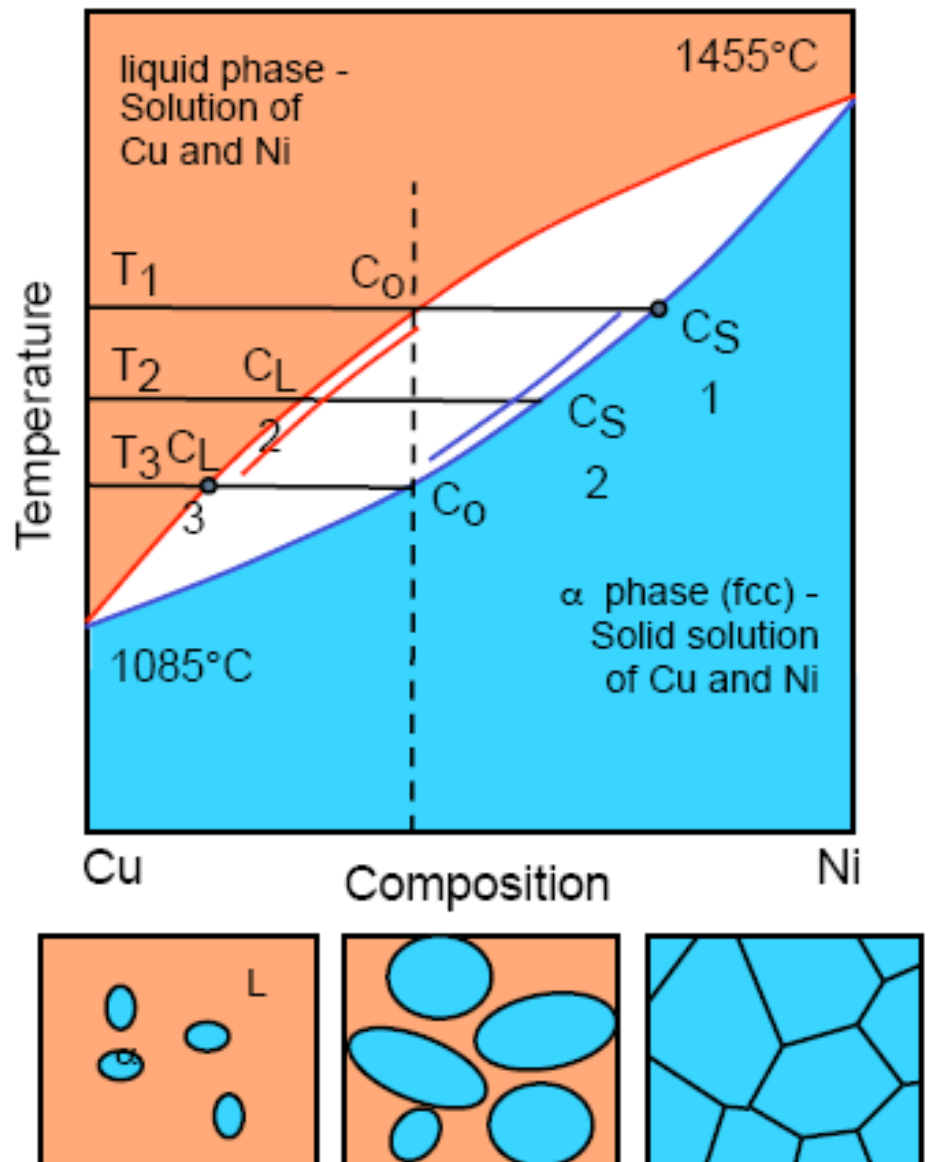


1.5 Binary phase diagrams

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.

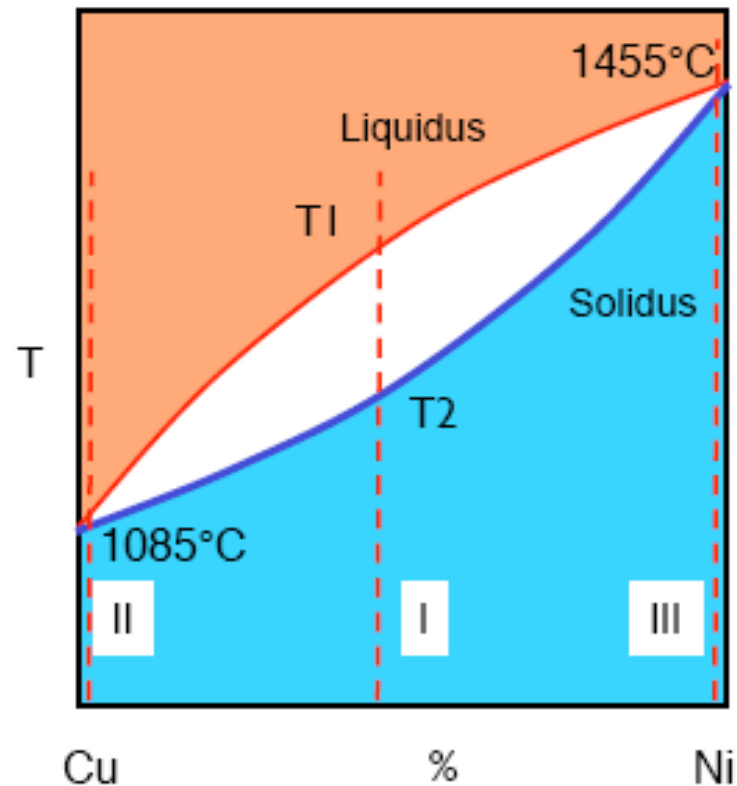
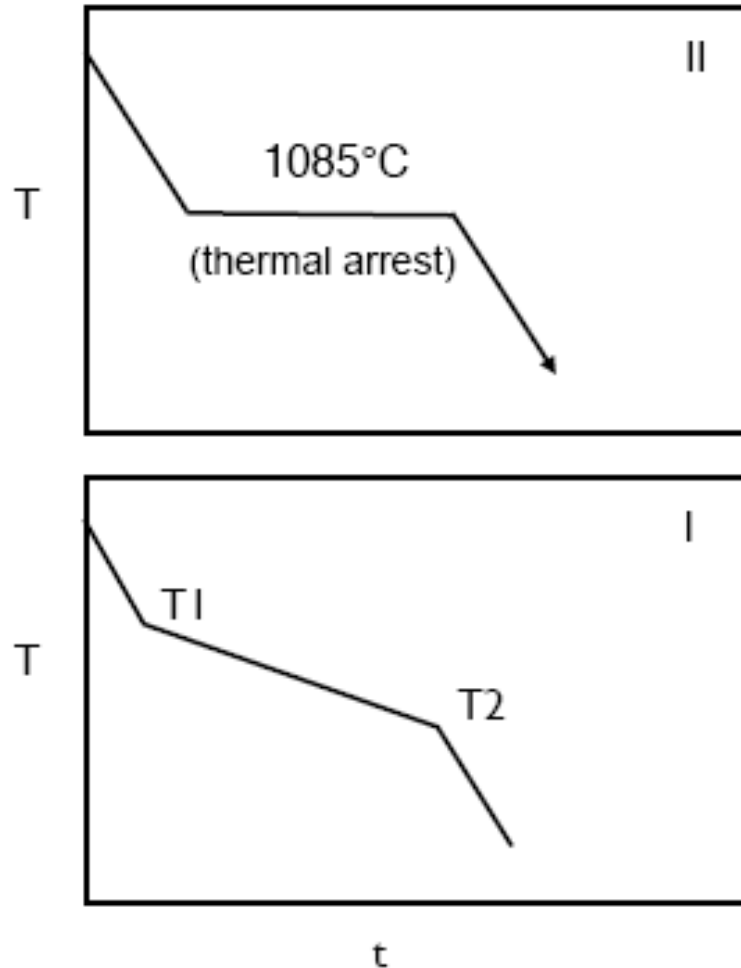
Solidification of alloy C_0 starts on cooling at T_1 . The first solid formed has a composition of C_{S1} and the liquid C_0 . On further cooling the solid particles grow larger in size and change their composition to C_{S2} and then C_0 , following the solidus whereas the liquid decrease in volume and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



Q7: How can we draw cooling curve depending on compositions in complete solid solution?

1.5 Binary phase diagrams

Cooling Curves determination of Phase diagrams



1.5 Binary phase diagrams

Example

At temperature T_1 , alloy C_0 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

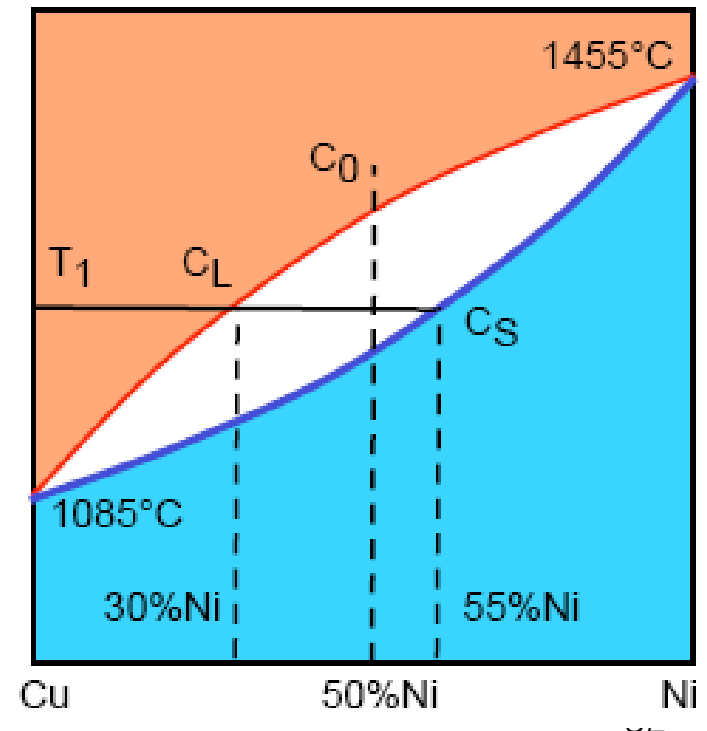
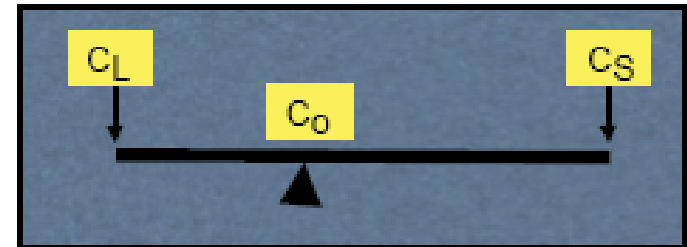
α -phase: Cu-55%Ni

$$W_L = \frac{C_s - C_0}{C_s - C_L} = \frac{55 - 50}{55 - 30} = 0.2 = 20\%$$

$$W_\alpha = \frac{C_0 - C_L}{C_s - C_L} = \frac{50 - 30}{55 - 30} = 0.8 = 80\%$$

or

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

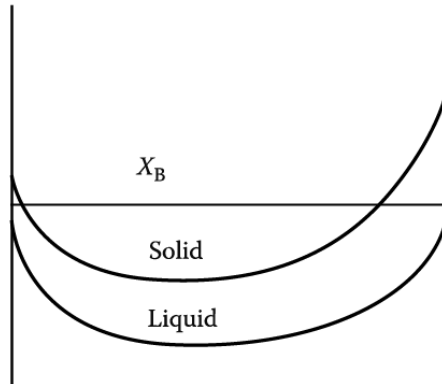


Q8: How equilibrium is affected by temperature in systems with miscibility gap?

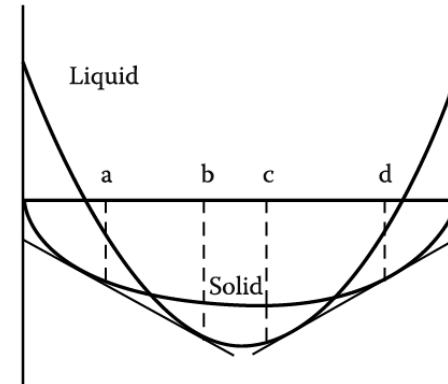
1.5 Binary phase diagrams

2) Systems with miscibility gap

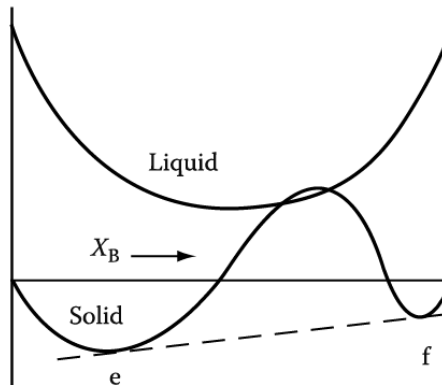
$$\Delta H_{mix}^L = 0 \quad \Delta H_{mix}^S > 0$$



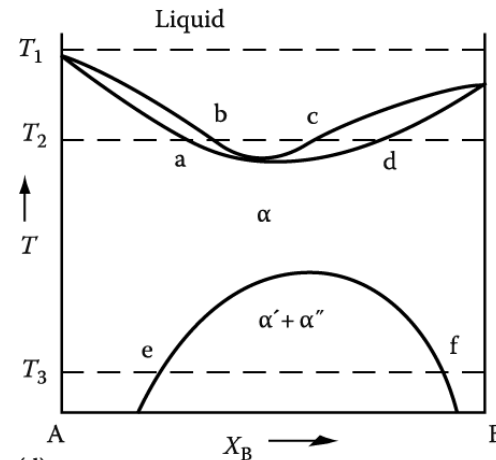
(a)



(b)



(c)

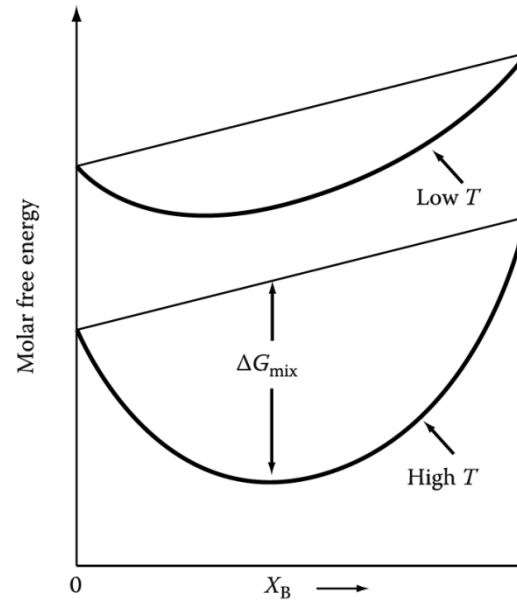


(d) congruent minima

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

Ideal Solutions

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

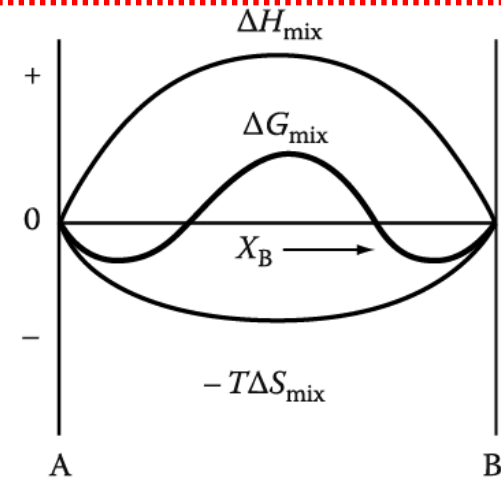
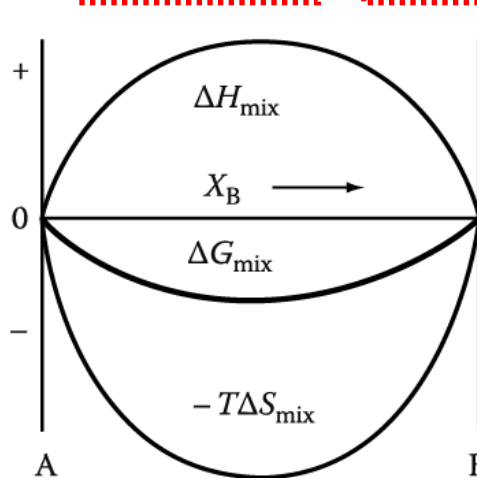


Regular Solutions

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

Reference state

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



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

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

1.5 Binary phase diagrams

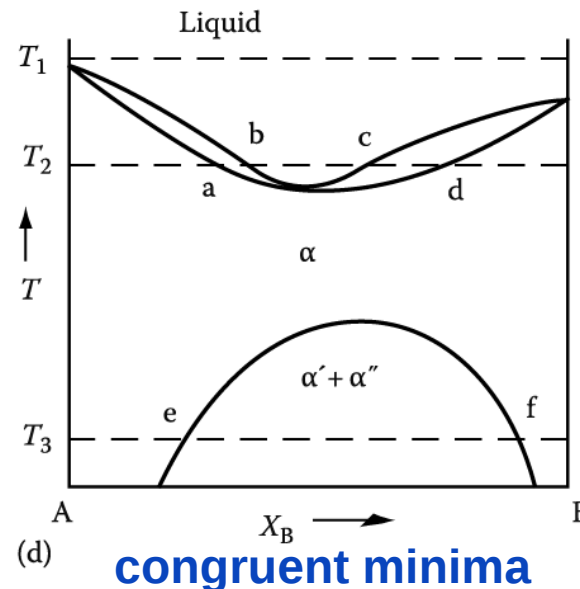
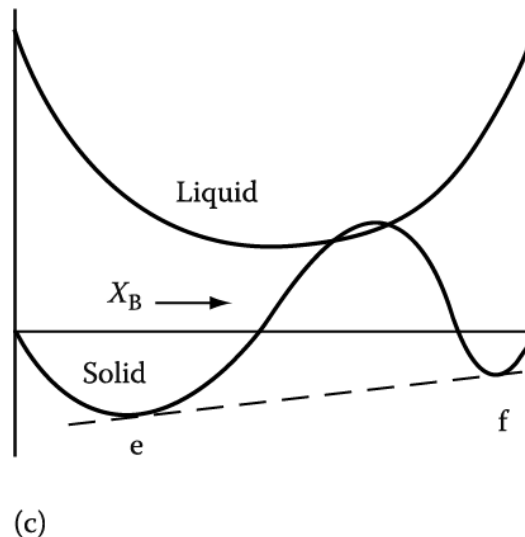
2) Systems with miscibility gap

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

- 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 α' and α'' in the phase diagram



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

1.5 Binary phase diagrams

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

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

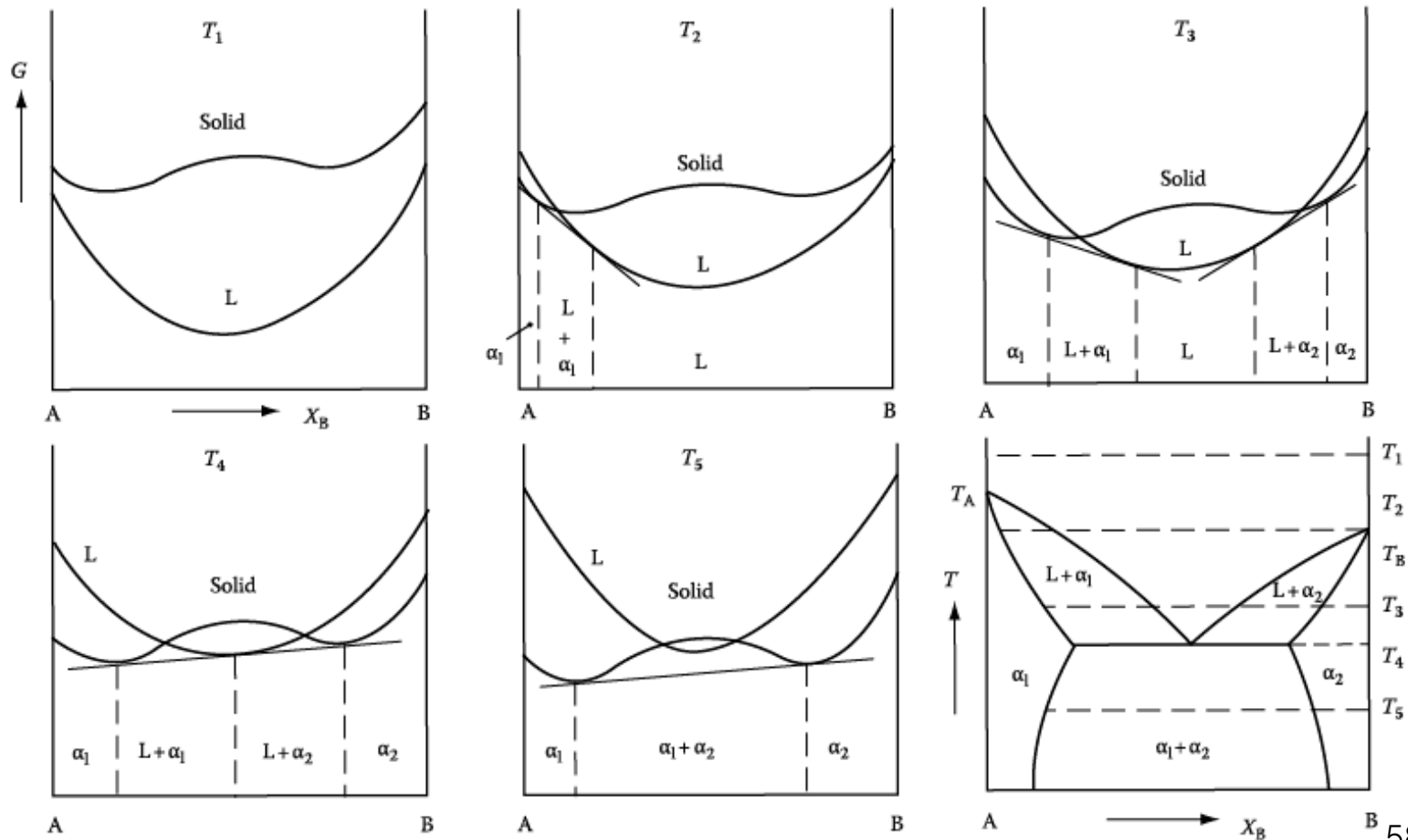
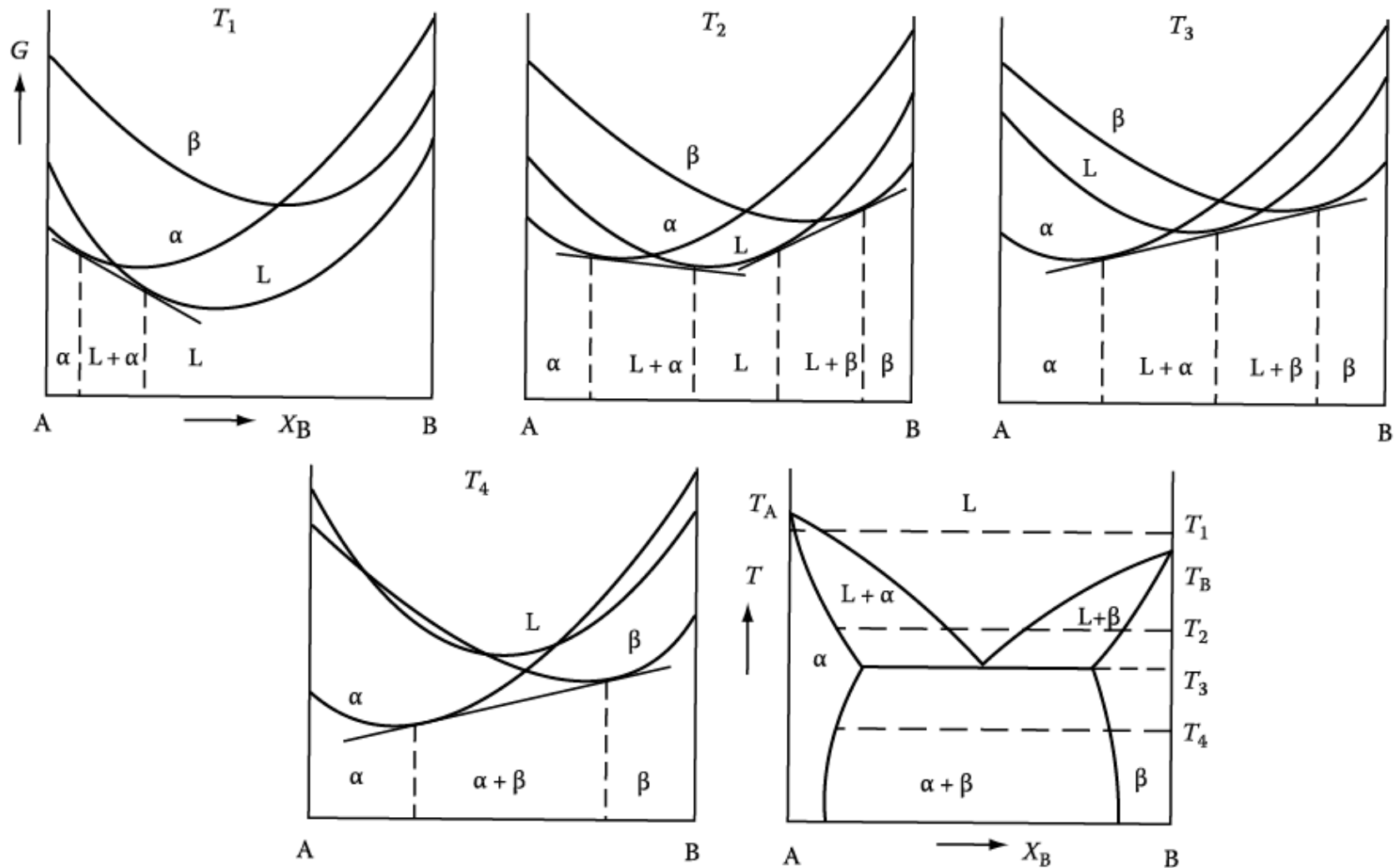


Fig. 1.32 The derivation of a eutectic phase diagram where both solid phases have the same crystal structure.

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



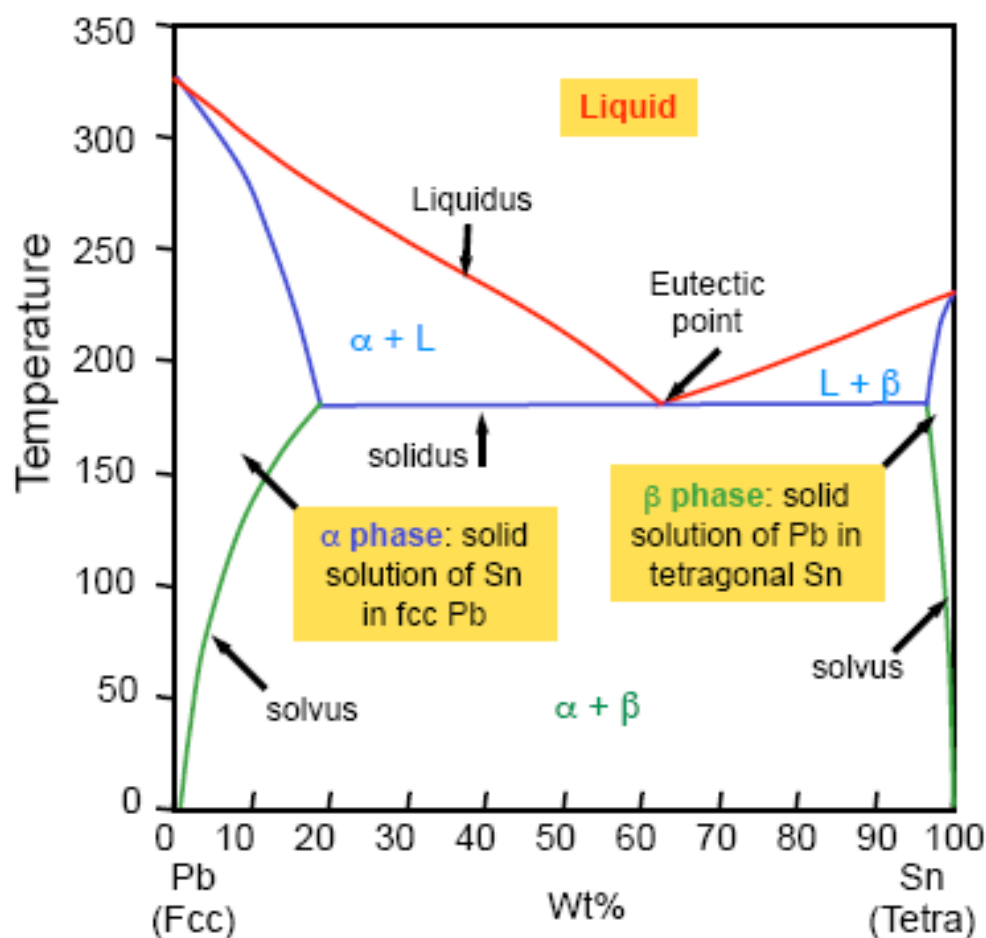
1.5 Binary phase diagrams

Eutectic Systems

Pb-Sn phase diagram

The Pb-Sn system is characteristic of a valley in the middle. Such system is known as the **Eutectic** system. The central point is the Eutectic point and the transformation though this point is called Eutectic reaction: $L \rightleftharpoons \alpha + \beta$

Pb has a fcc structure and Sn has a tetragonal structure. The system has three phases: L, α and β .



1.5 Binary phase diagrams

Solidification of Eutectic Systems

Alloy II:

At point I: Liquid

Solidification starts at eutectic point (where liquidus and solidus join)

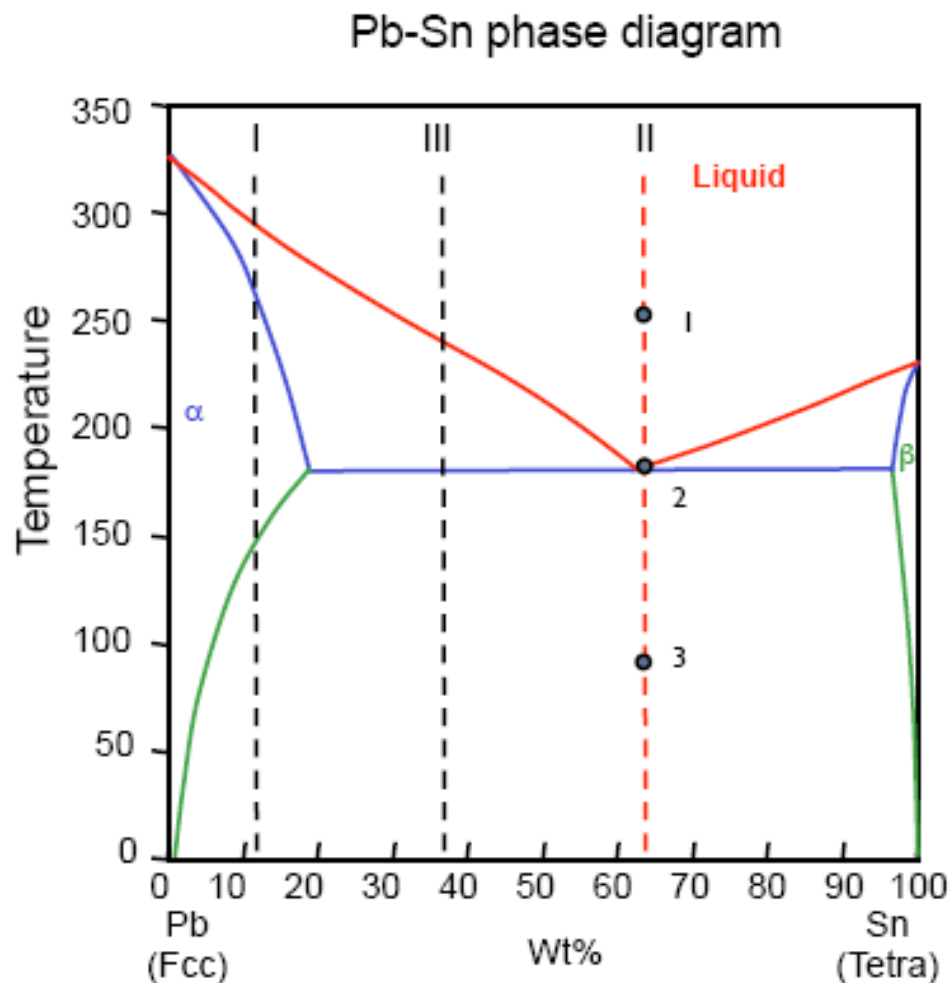
At point 2: $L \rightarrow (\alpha + \beta)$ (eutectic reaction)

The amounts of α and β increase in proportion with time.

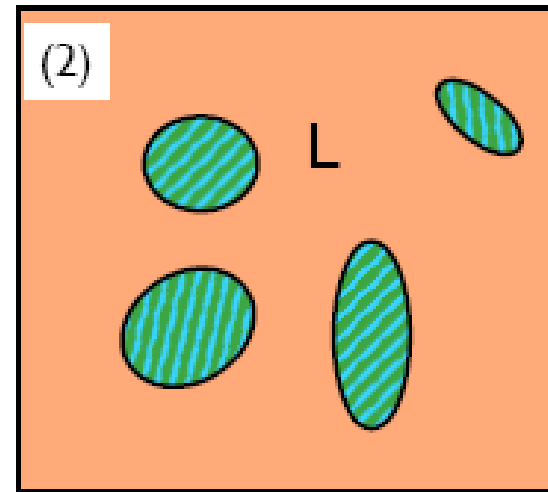
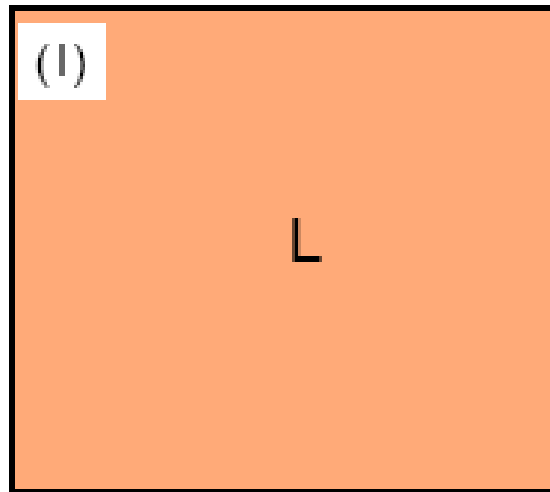
Solidification finishes at the same temperature.

At point 3: $\alpha + \beta$

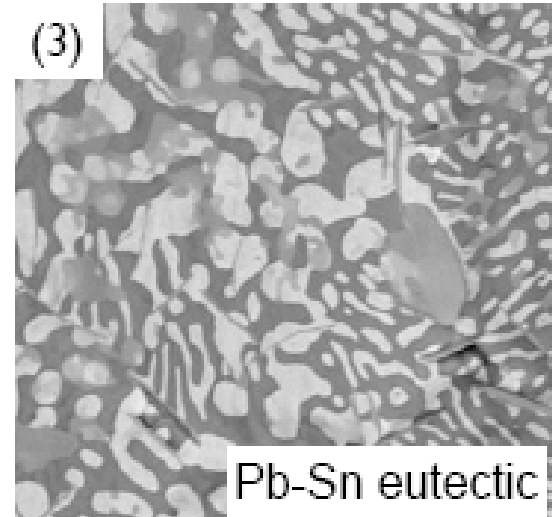
Further cooling leads to the depletion of Sn in α and the depletion of Pb in β .



1.5 Binary phase diagrams



Nucleation of colonies
of α and β laminates



Eutectic structure of
intimate mix of α and β to
minimise diffusion path

1.5 Binary phase diagrams

Solidification of Eutectic Systems

Alloy I:

At point 1: Liquid

Solidification starts at liquidus

At point 2: L+ α

The amount α $\uparrow$ with $\downarrow$ T

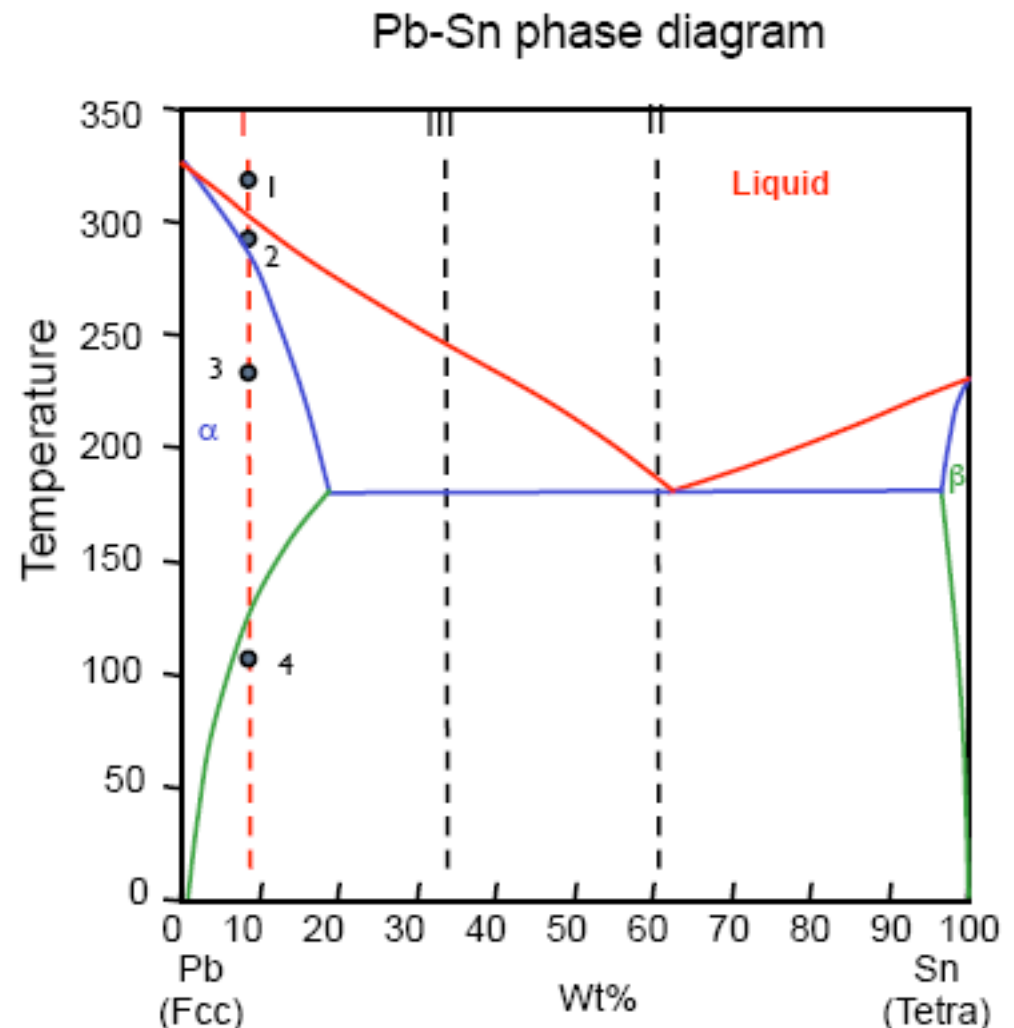
Solidification finishes at solidus

At point 3: α

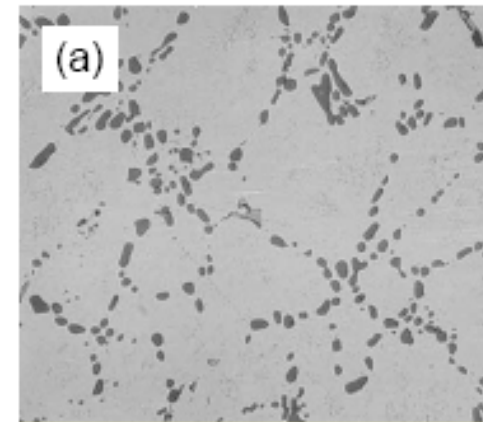
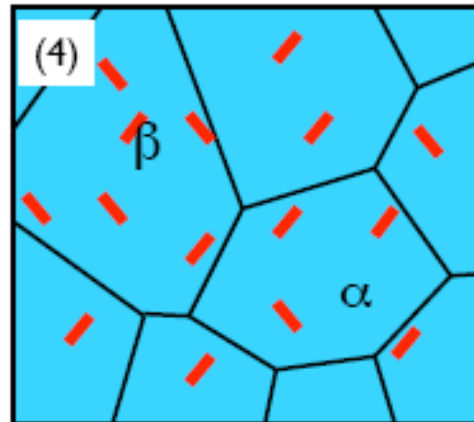
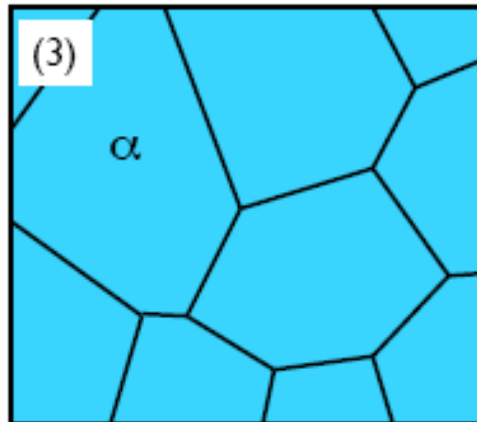
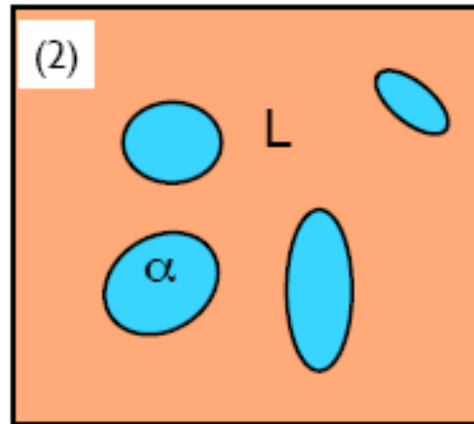
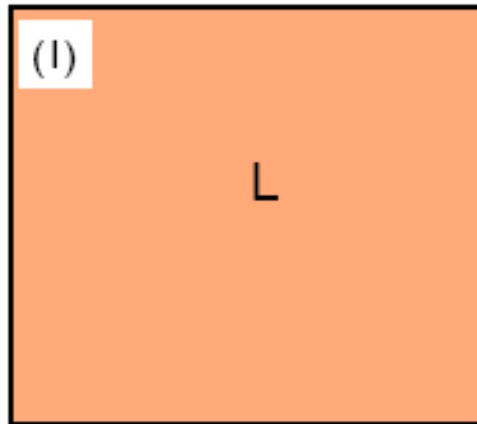
Precipitation starts at solvus

At point 4: $\alpha + \beta$

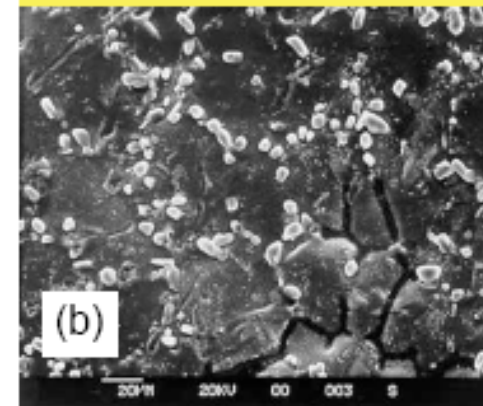
Further cooling leads to formation and growth of more β precipitates whereas Sn% in α decreases following the solvus.



1.5 Binary phase diagrams



Precipitates in a Al-Si alloy;
(a) optical microscopy,
(b) scanning electron
microscopy of fracture surface



1.5 Binary phase diagrams

Solidification of Eutectic Systems

Alloy III:

At point 1: Liquid

Solidification starts at liquidus

At point 2: $L \rightarrow L + \alpha$ (pre-eutectic α)

The amount $\alpha \uparrow$ with $\downarrow T$

At point 3: $L \rightarrow (\alpha + \beta)$ (eutectic reaction)

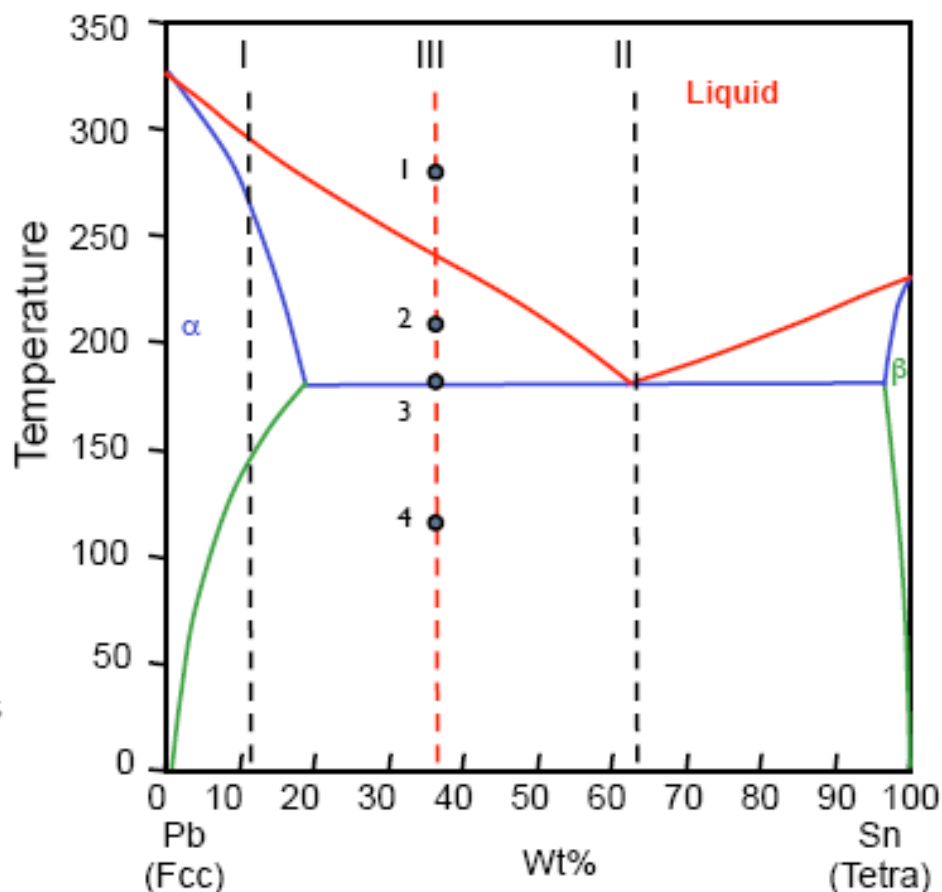
Solidification finishes at the eutectic temperature

At point 4: $\alpha + \beta$ (pre-eutectic α + $(\alpha + \beta)$ eutectic mixture)

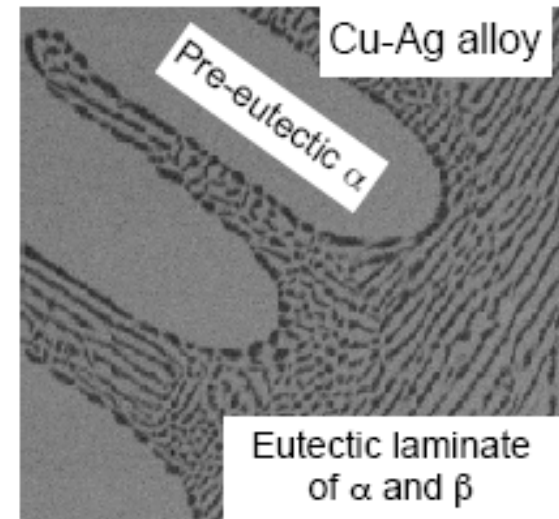
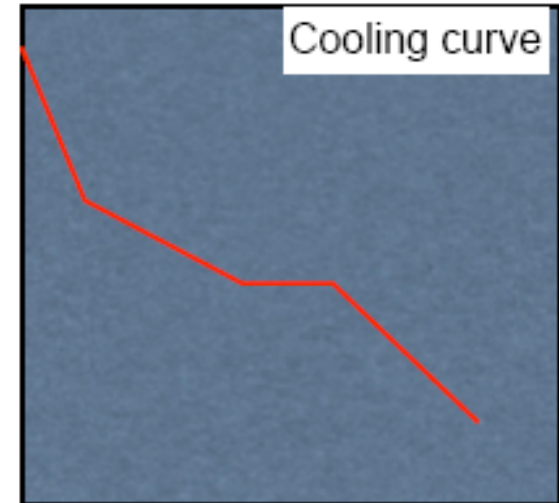
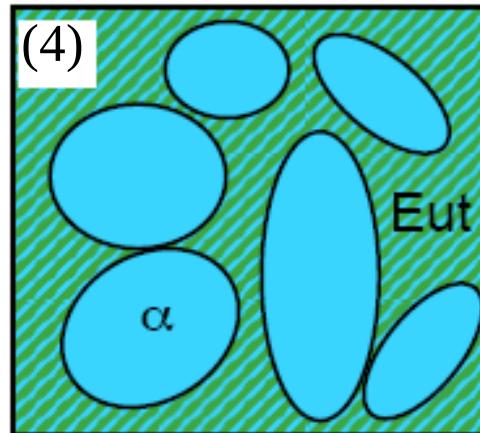
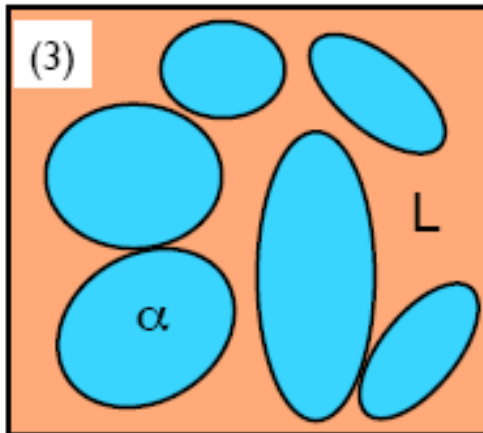
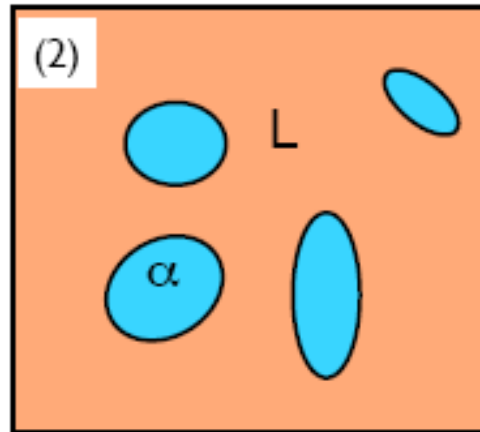
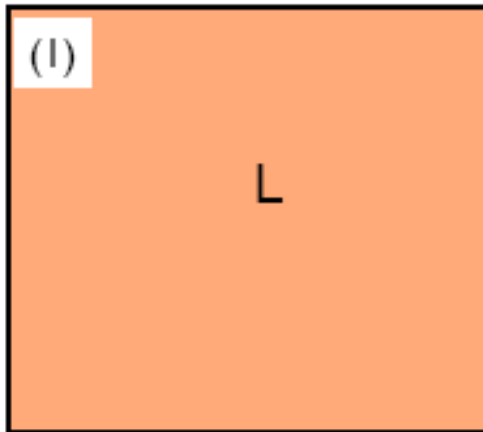
Further cooling leads to the depletion of Sn in α and the depletion of Pb in β .

The cooling curve of this alloy is a combination of the two cooling curves shown in slide 9.

Pb-Sn phase diagram



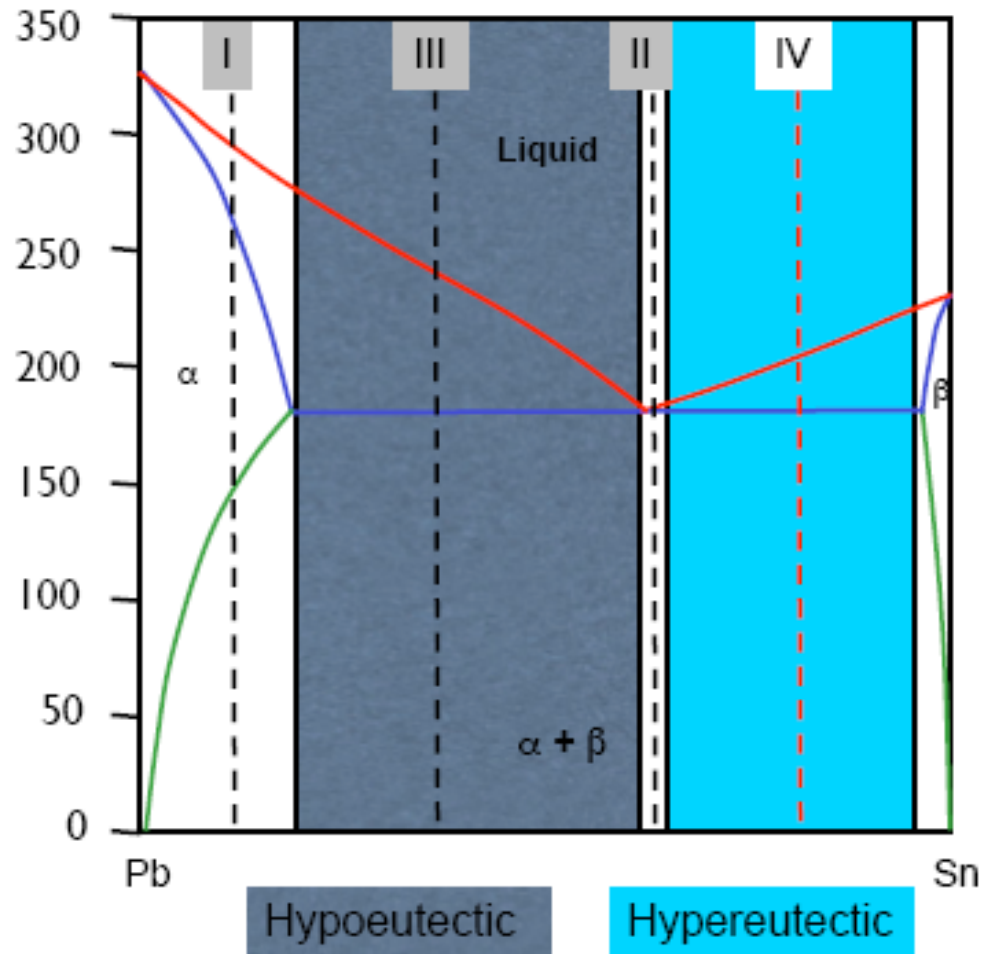
1.5 Binary phase diagrams: Hypoeutectic



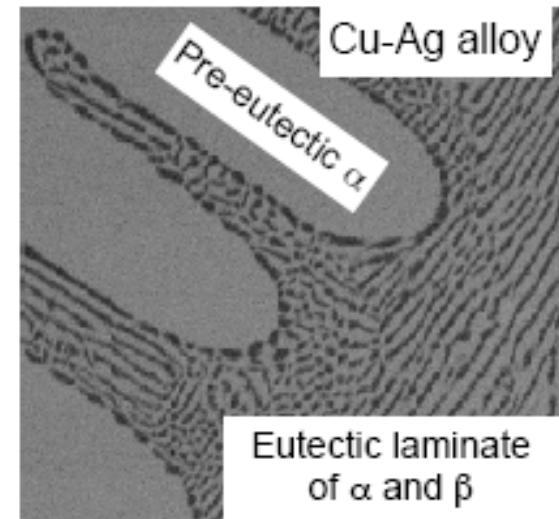
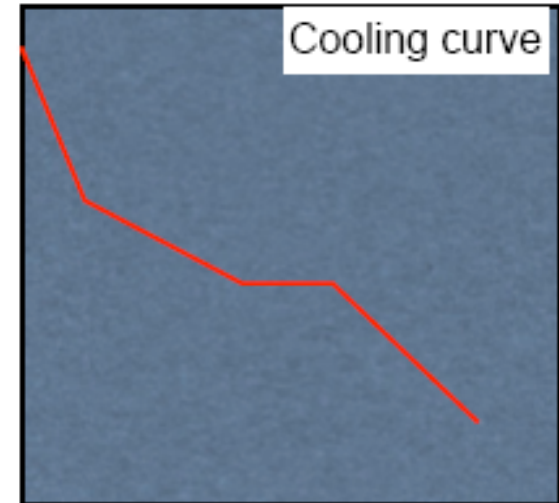
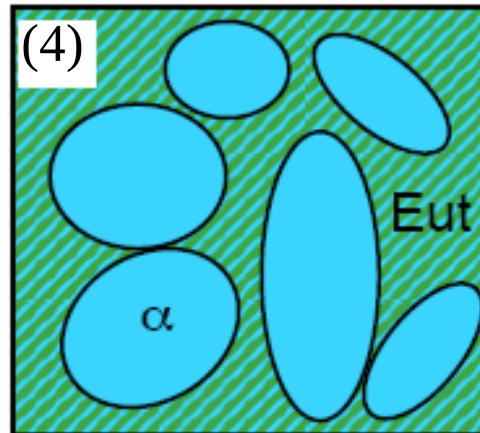
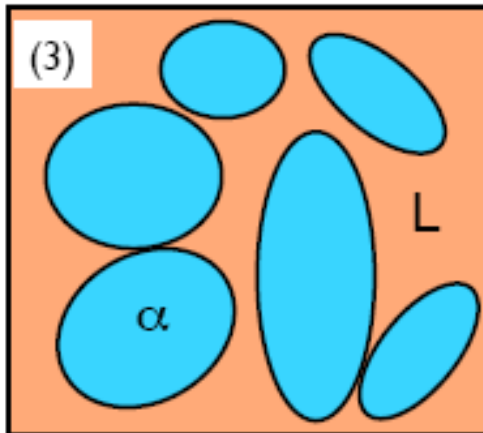
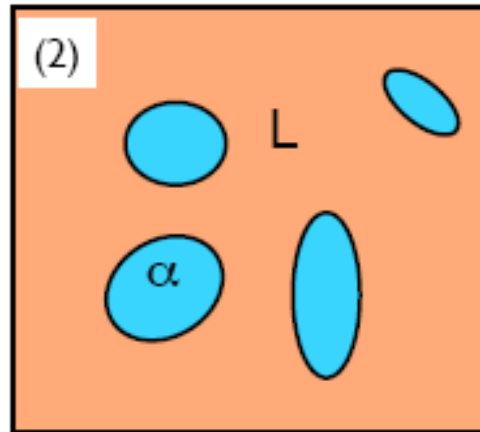
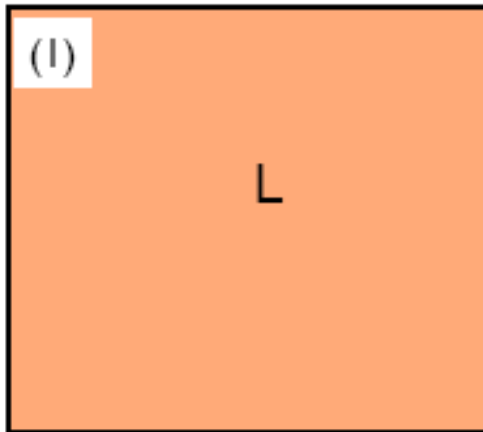
1.5 Binary phase diagrams

Solidification of Eutectic Systems

Can you describe the solidification process of alloy IV, including microstructure evolution, morphology of phases and cooling curve?

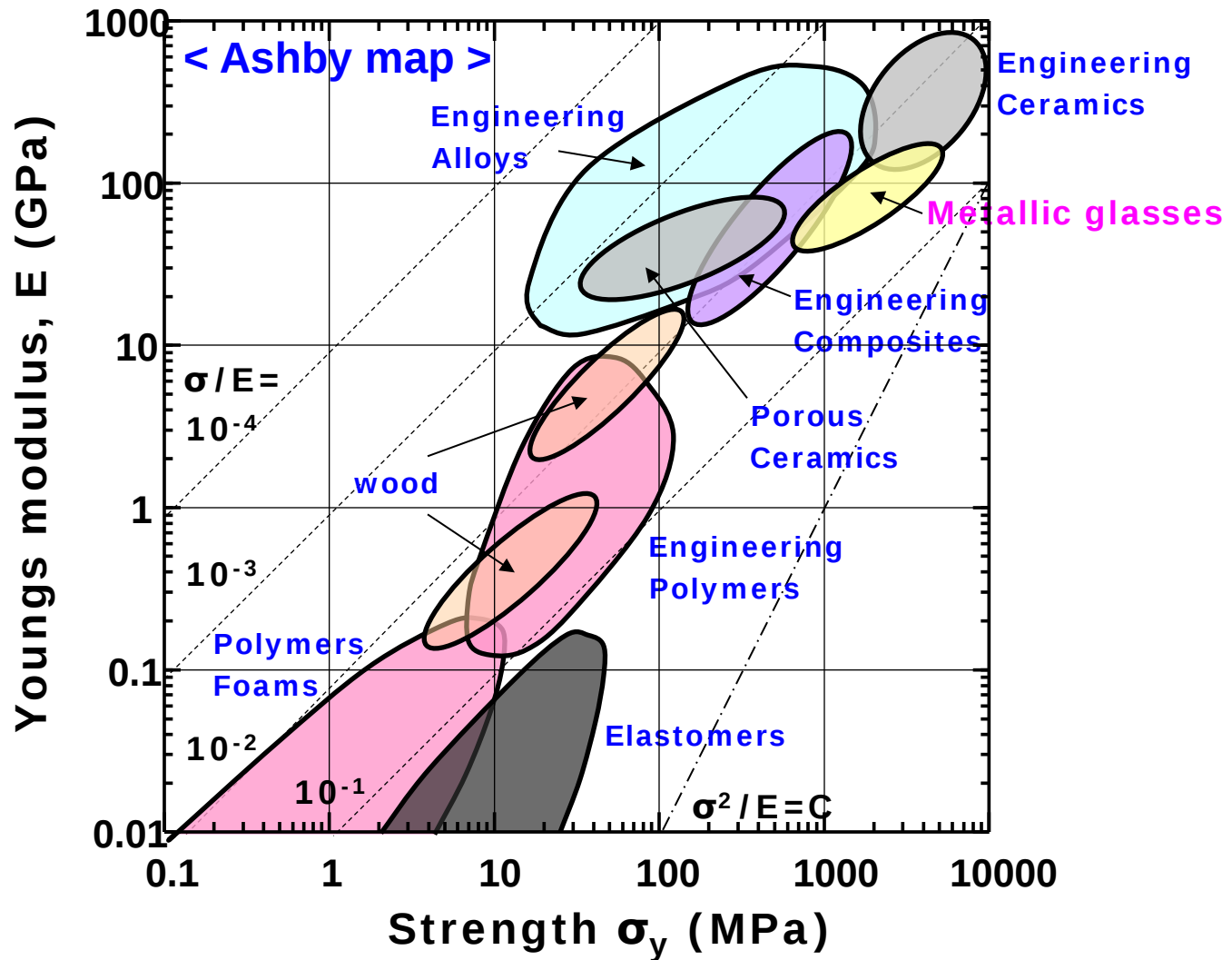


1.5 Binary phase diagrams : Hypereutectic



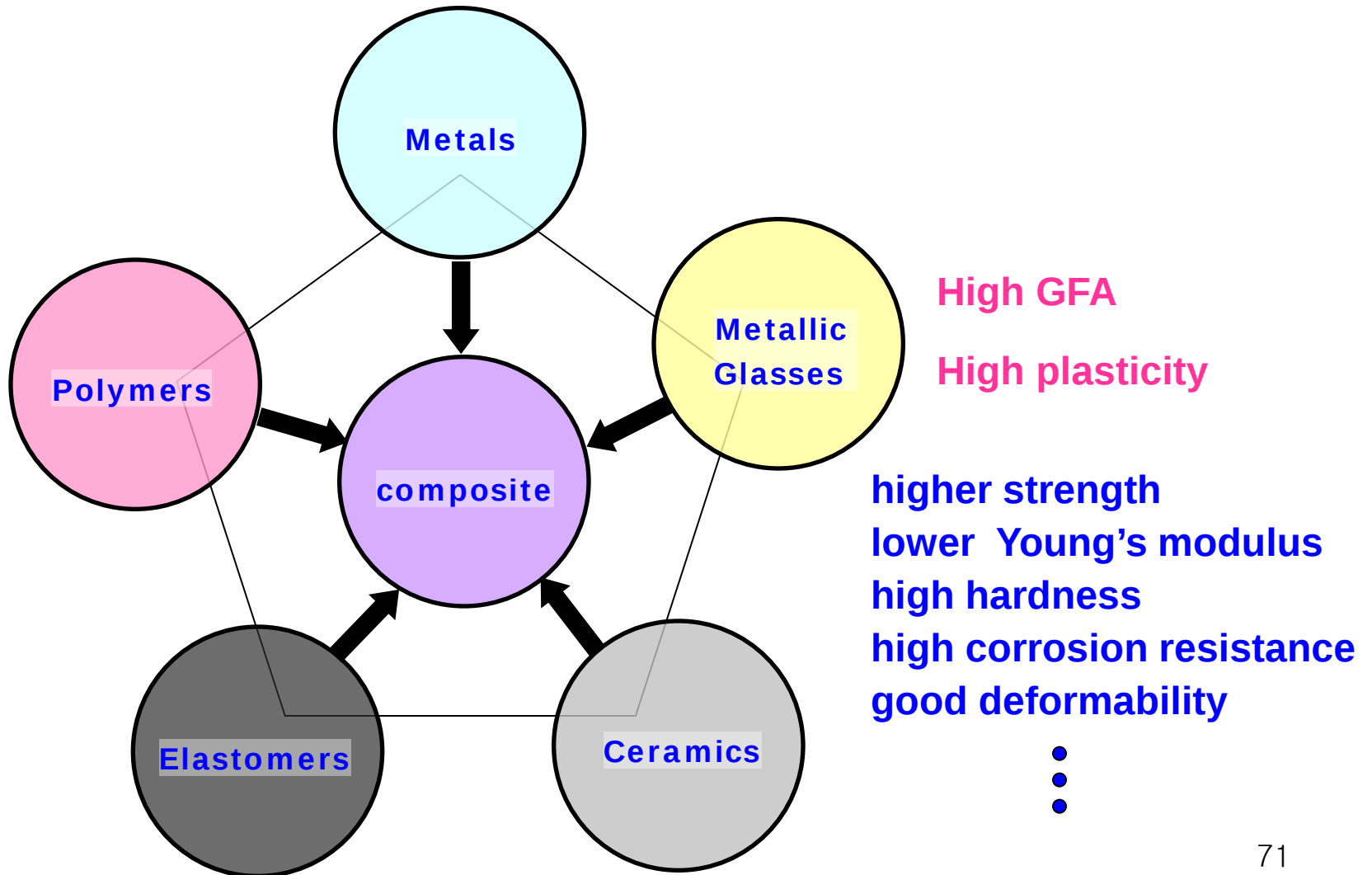
Q10: Materials design
Proposal for final presentation?

Materials Design



Materials Design

Menu of engineering materials



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 23rd on eTL.

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