2017 Fall

“Phase Equilibria *in* Materials”

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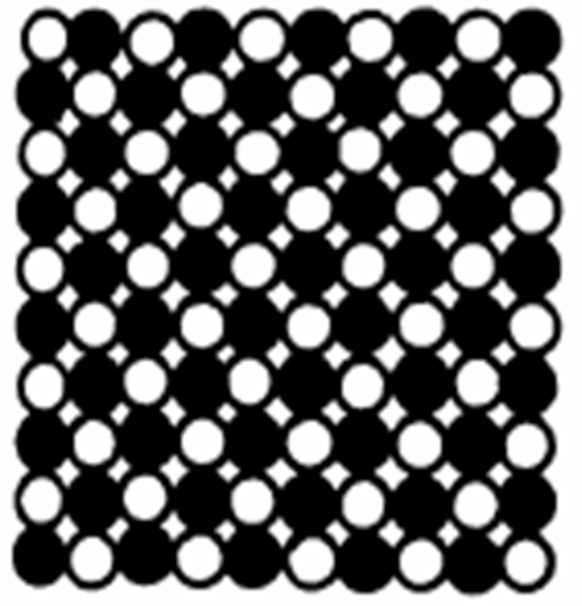
Contents for previous class

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

Ideal or Regular solution : over simplification of reality

Entropy $S = k \ln w$ + $\Delta H_{mix} = \Omega X_A X_B$ where $\Omega = N_a z \varepsilon$ $\varepsilon \approx 0$

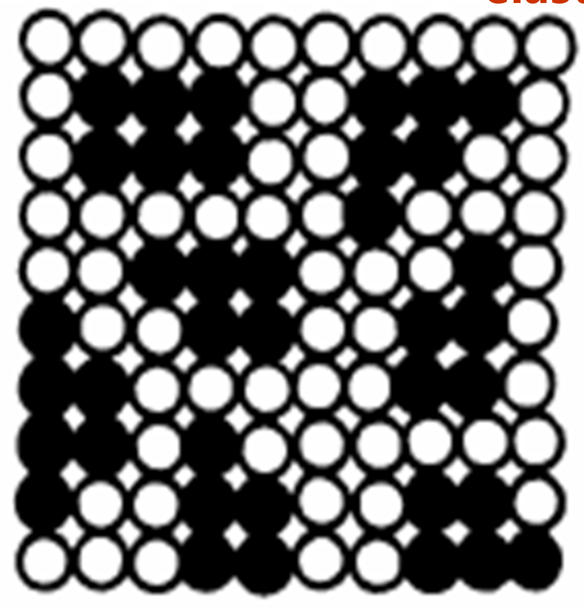
elastic strain



Ordered alloys

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

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

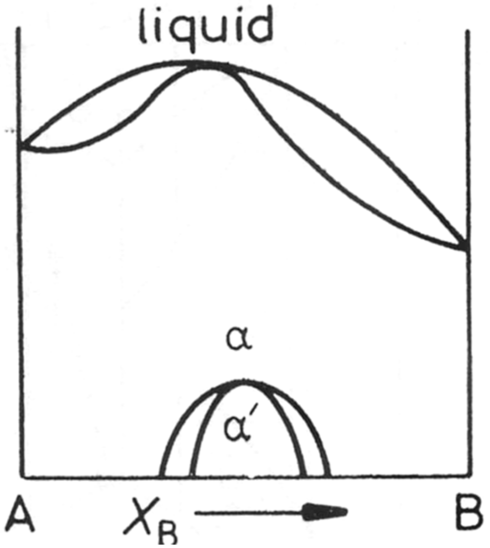


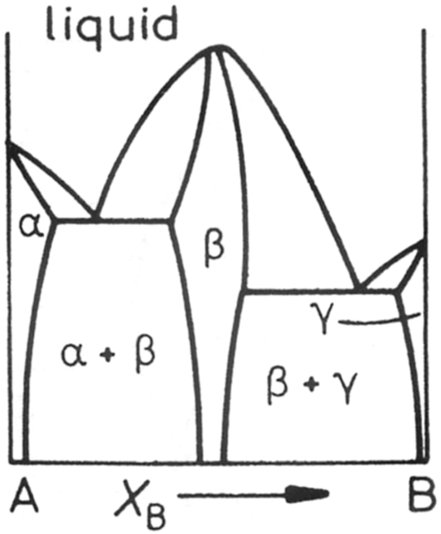
Clustering

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

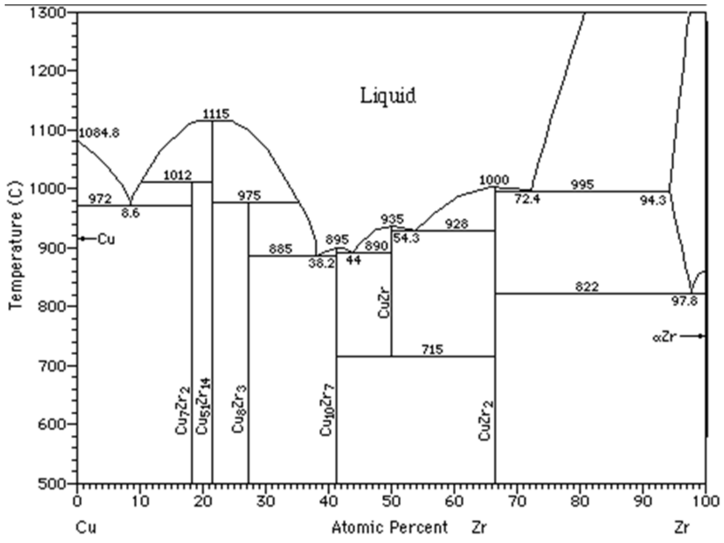
$P_{AA}, P_{BB} \uparrow$

$\Delta H^{S}_{mix} < 0$: Solid solution → ordered phase

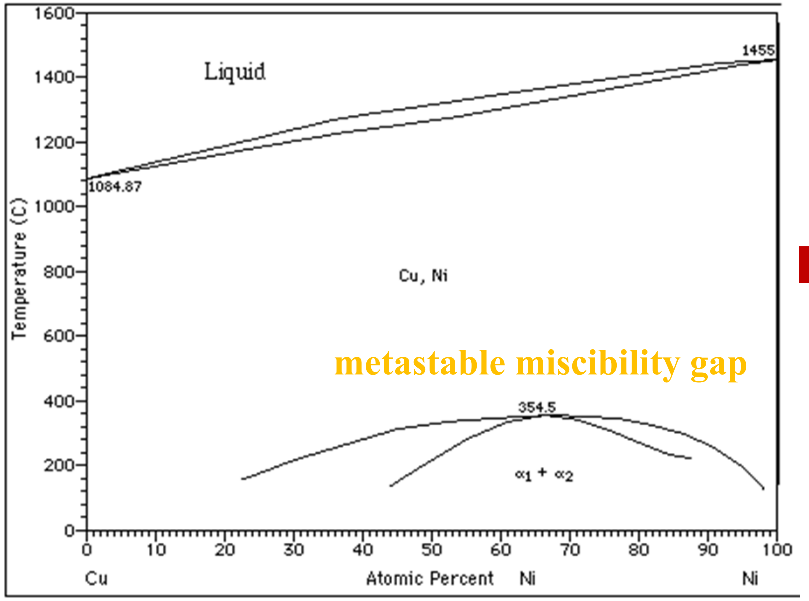




$\Delta H^{S}_{mix} << 0$: Compound : AB, A_2B…

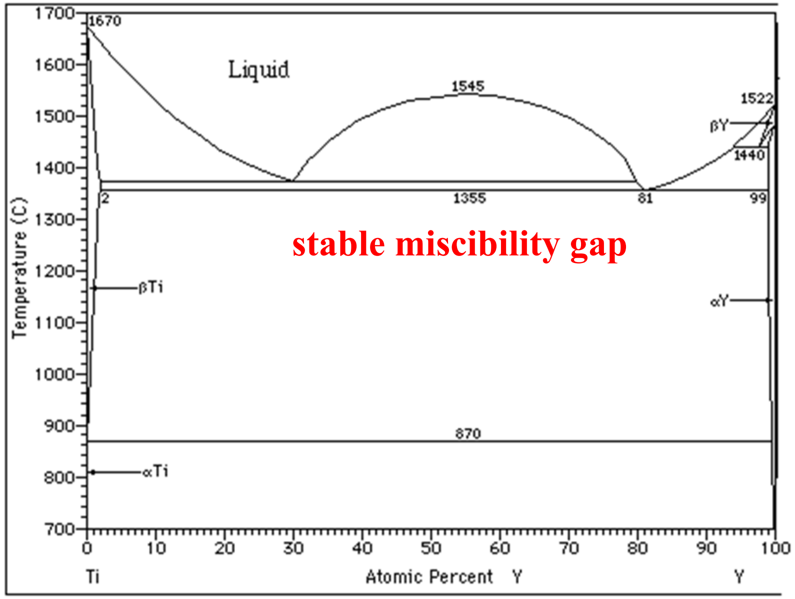


$\Delta H^{S}_{mix} > 0$: Solid solution → solid state phase separation (two solid solutions)



metastable miscibility gap

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



stable miscibility gap

Ordered phase: “Long range order (LRO)”

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

*** Solid solution → ordered phase**

→ random mixing

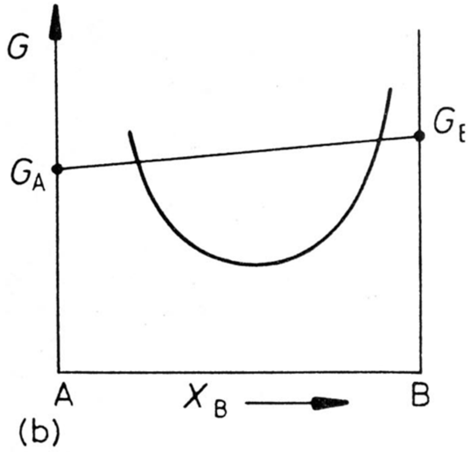
→ entropy ↑

negative enthalpy ↓

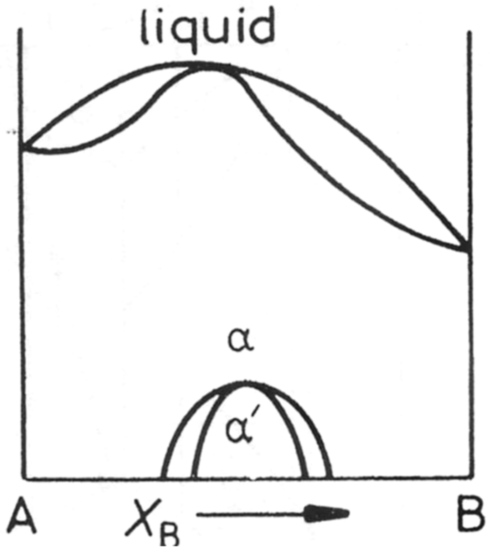
$$\boxed{\Delta H^{S}_{mix} < 0}$$

Large composition range

→ G ↓



diate phases: (a) for an intermetallic com-
(b) for an intermediate phase with a wide



*** Compound : AB, A_2B…**

→ entropy↓

→ covalent, ionic contribution.

→ enthalpy more negative ↓

$$\boxed{\Delta H^{S}_{mix} << 0}$$

Small composition range

→ G ↓

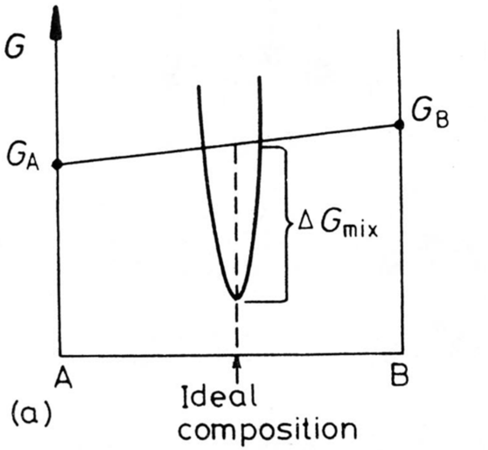
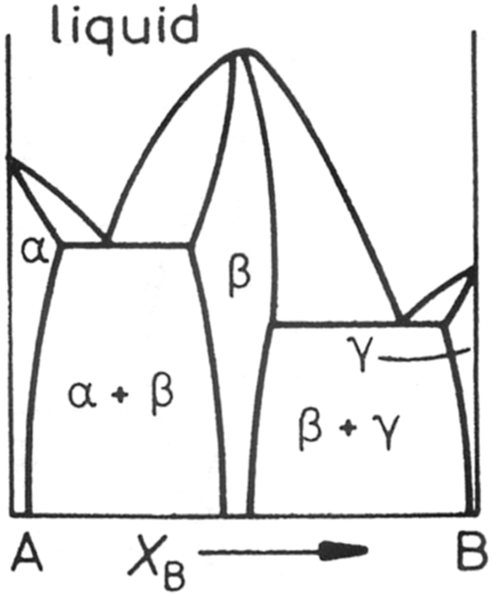
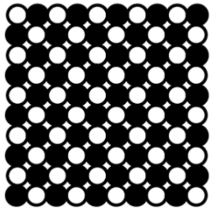


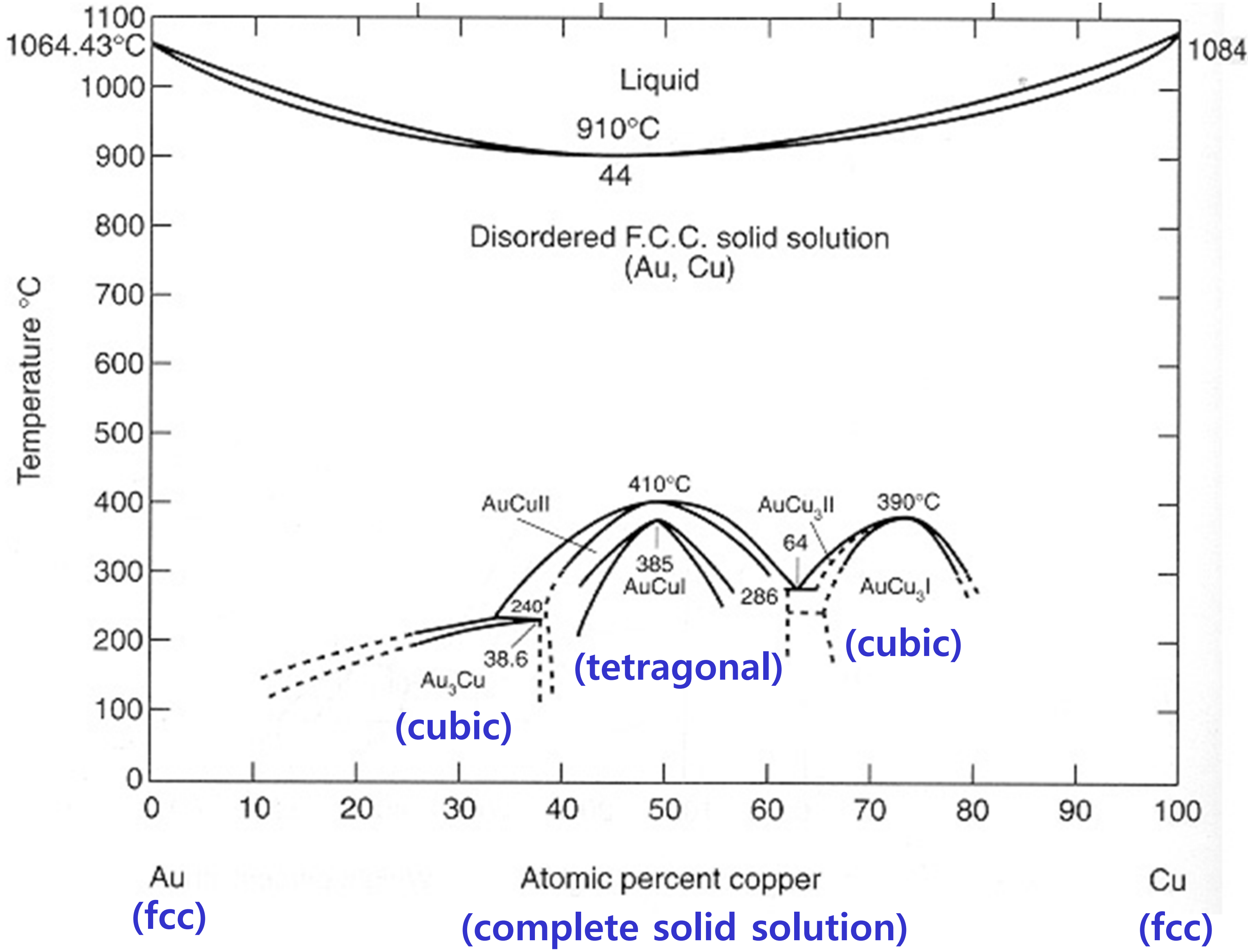
Fig. 1.23 Free energy curves for intermed
pound with a very narrow stability range, (
stability range.



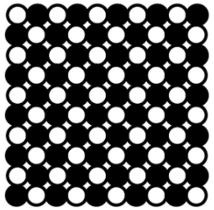
Ordered Phase



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

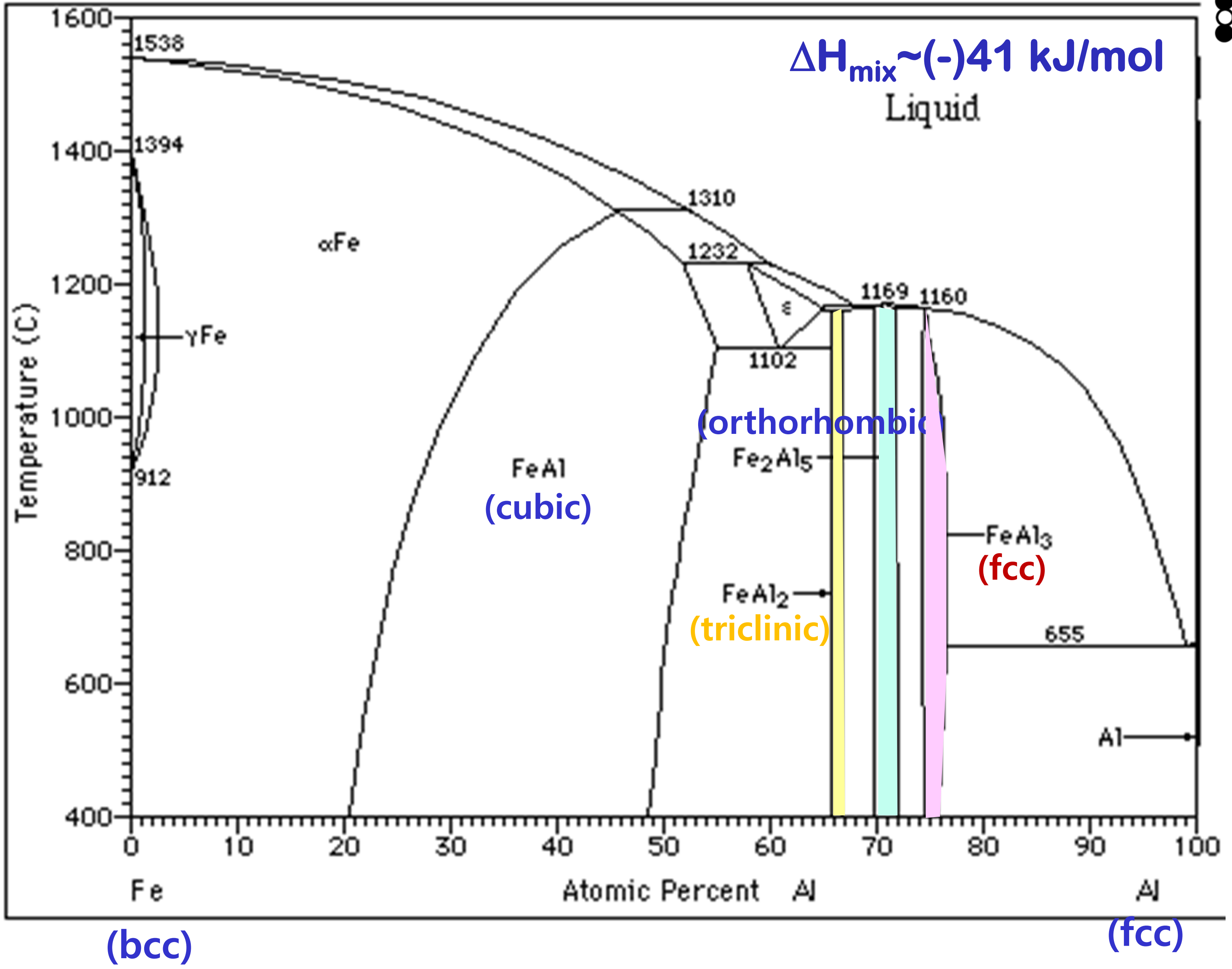


Intermediate Phase



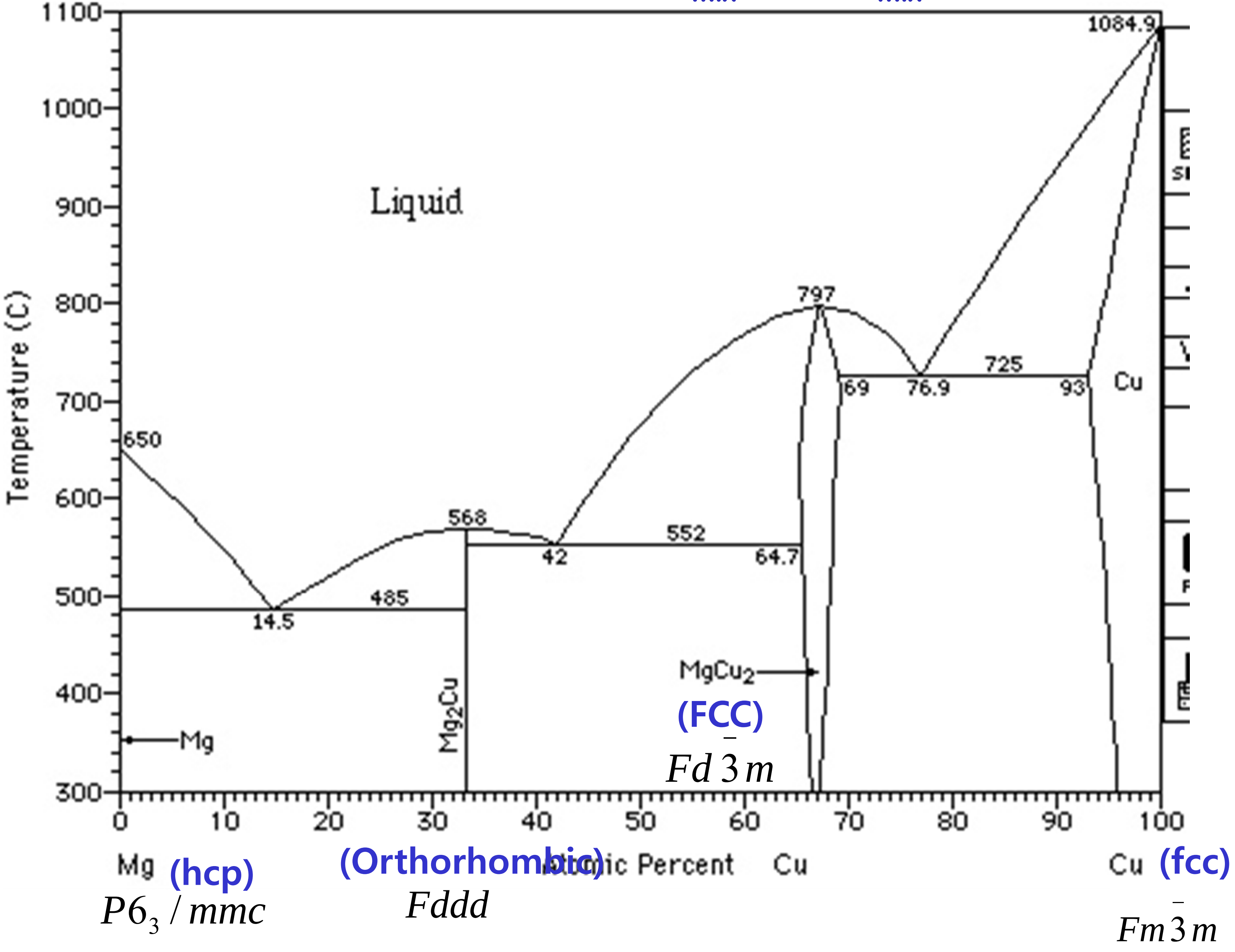
$\varepsilon < 0$, $\Delta H_{mix} < 0$

$\Delta H_{mix} \sim (-)41$ kJ/mol



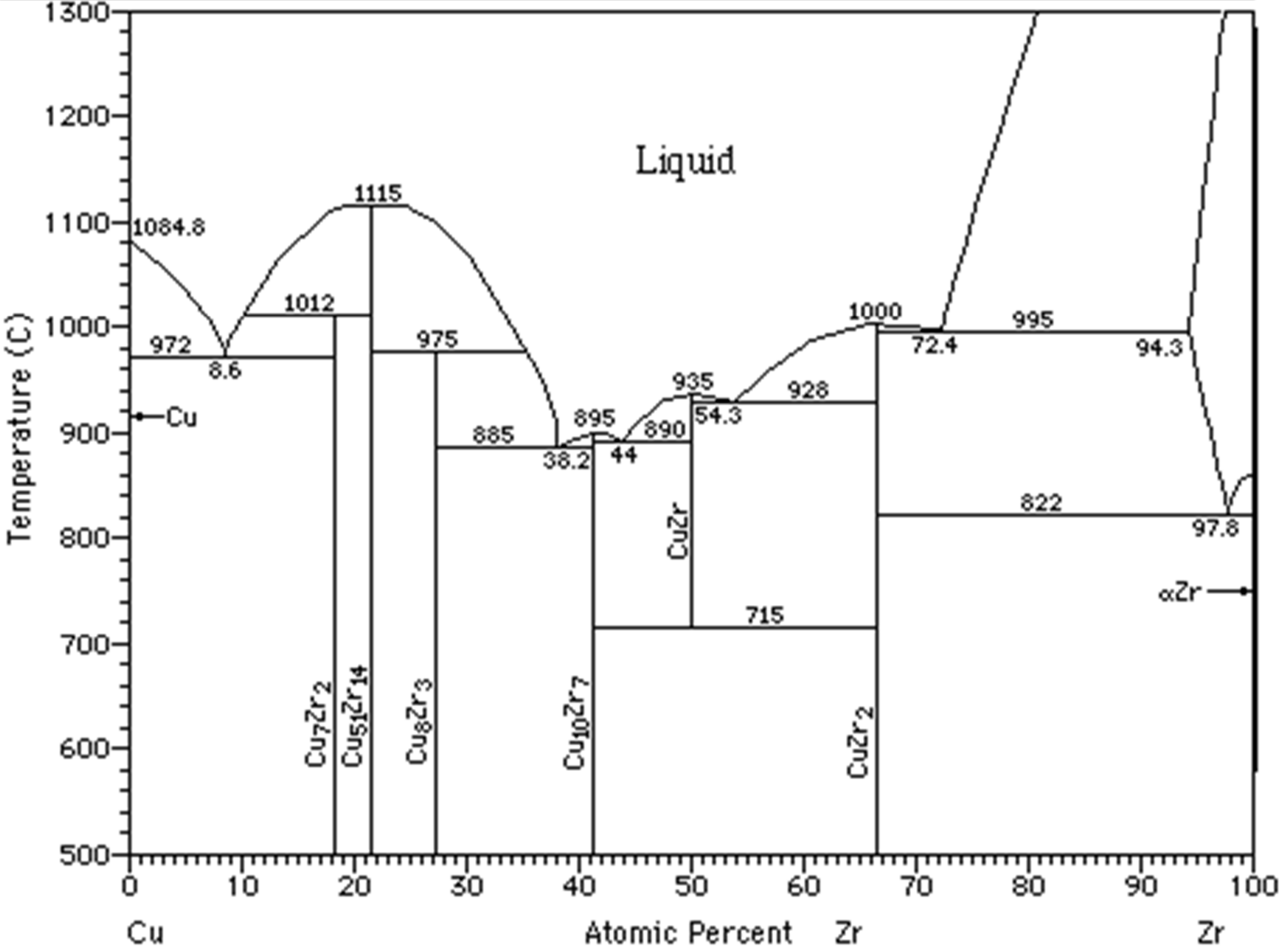
Intermediate Phase

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



Intermetallic compound

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

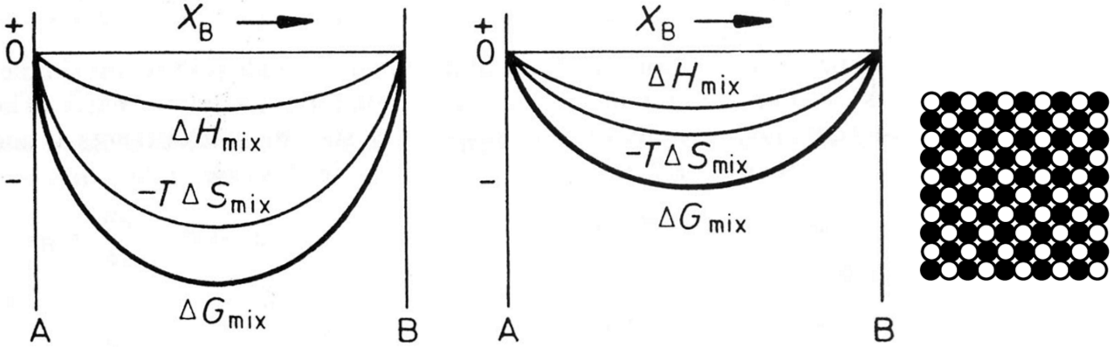


Clustering → "Phase separation"

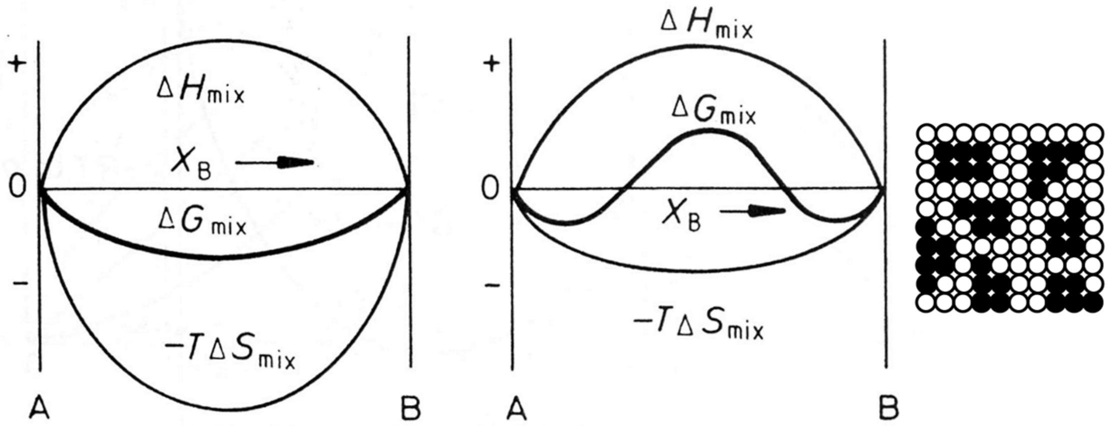
* The degree of **ordering or clustering** will **decrease as temp. increases** due to the increasing importance of **entropy**.

High temp. → Entropy effect ↑ → Solution stability ↑

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

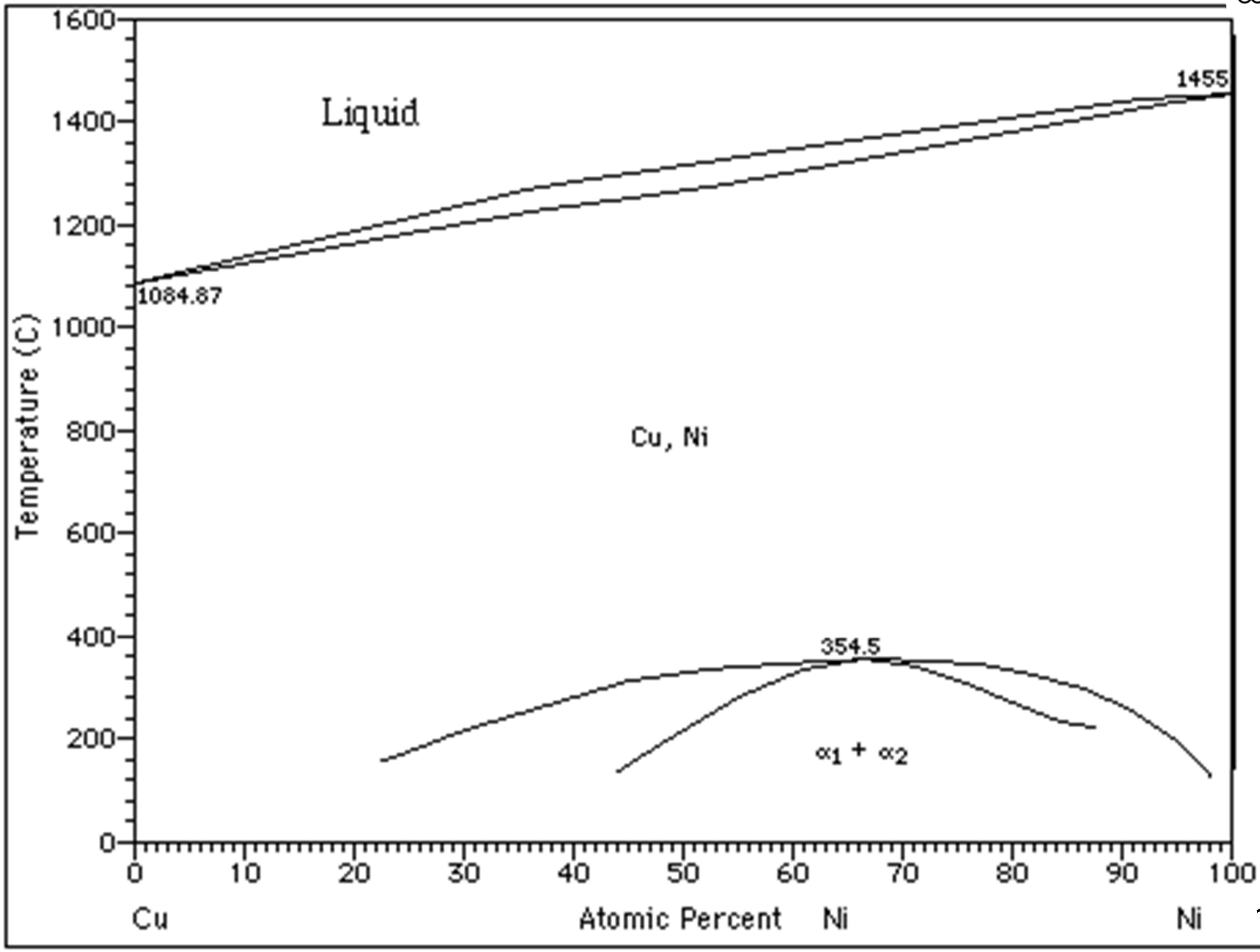


(a) $\Omega < 0$, high T (b) $\Omega < 0$, low T

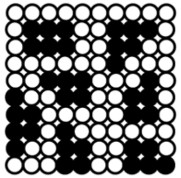


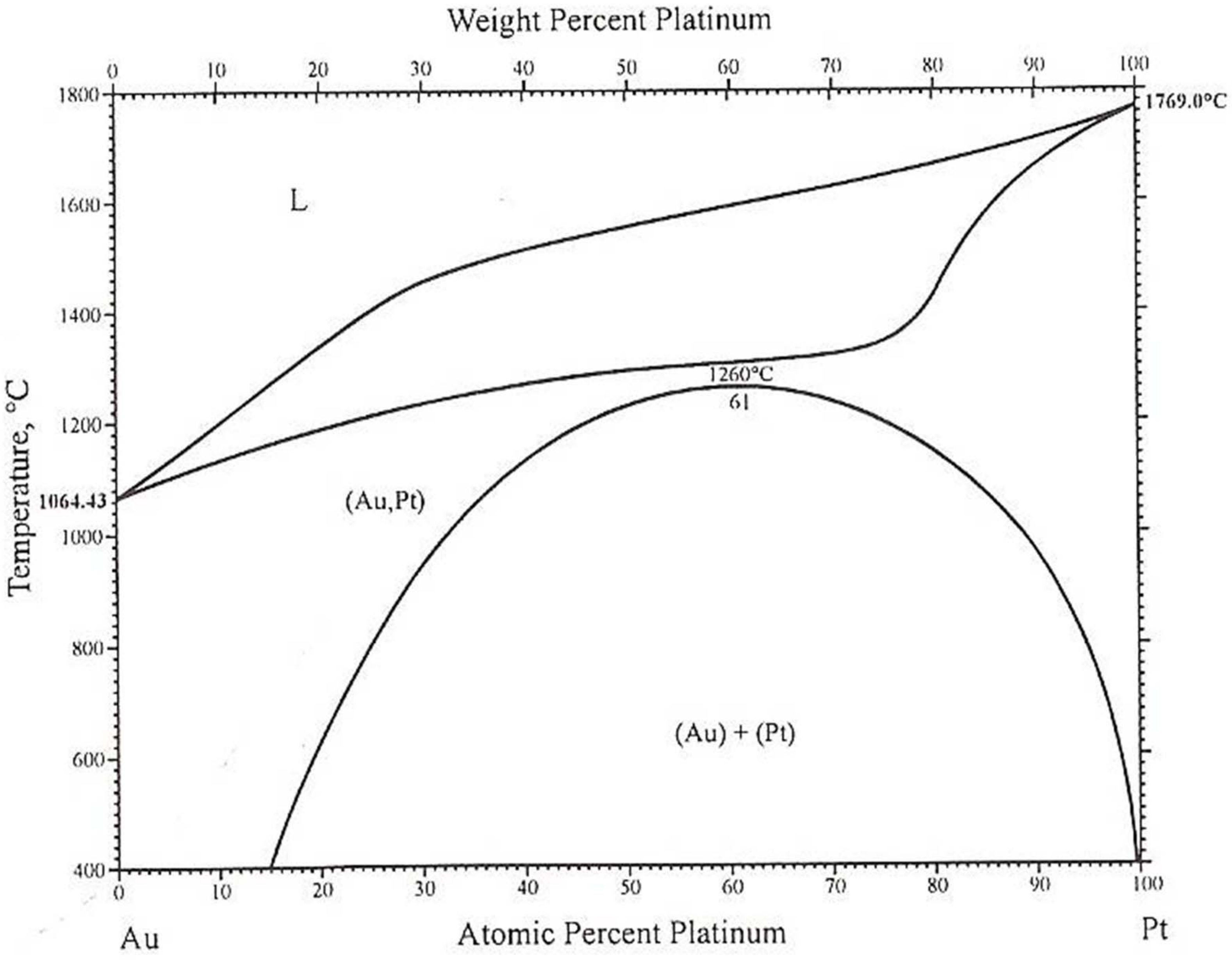
(c) $\Omega > 0$, high T (d), $\Omega > 0$ low T

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

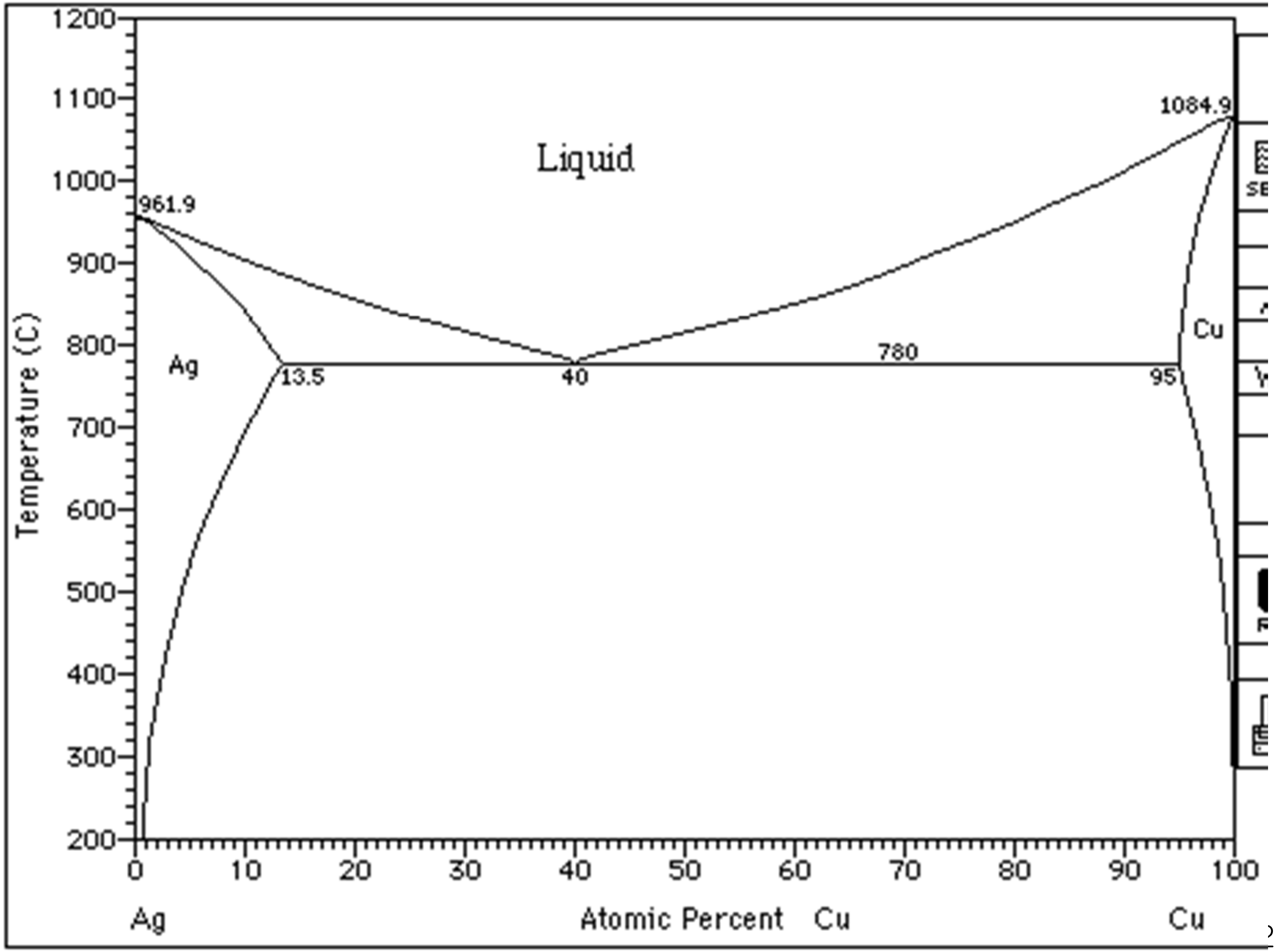


$\varepsilon > 0$, $\Delta H_{mix} > 0$ / $\Delta H_{mix} \sim +17$ kJ/mol

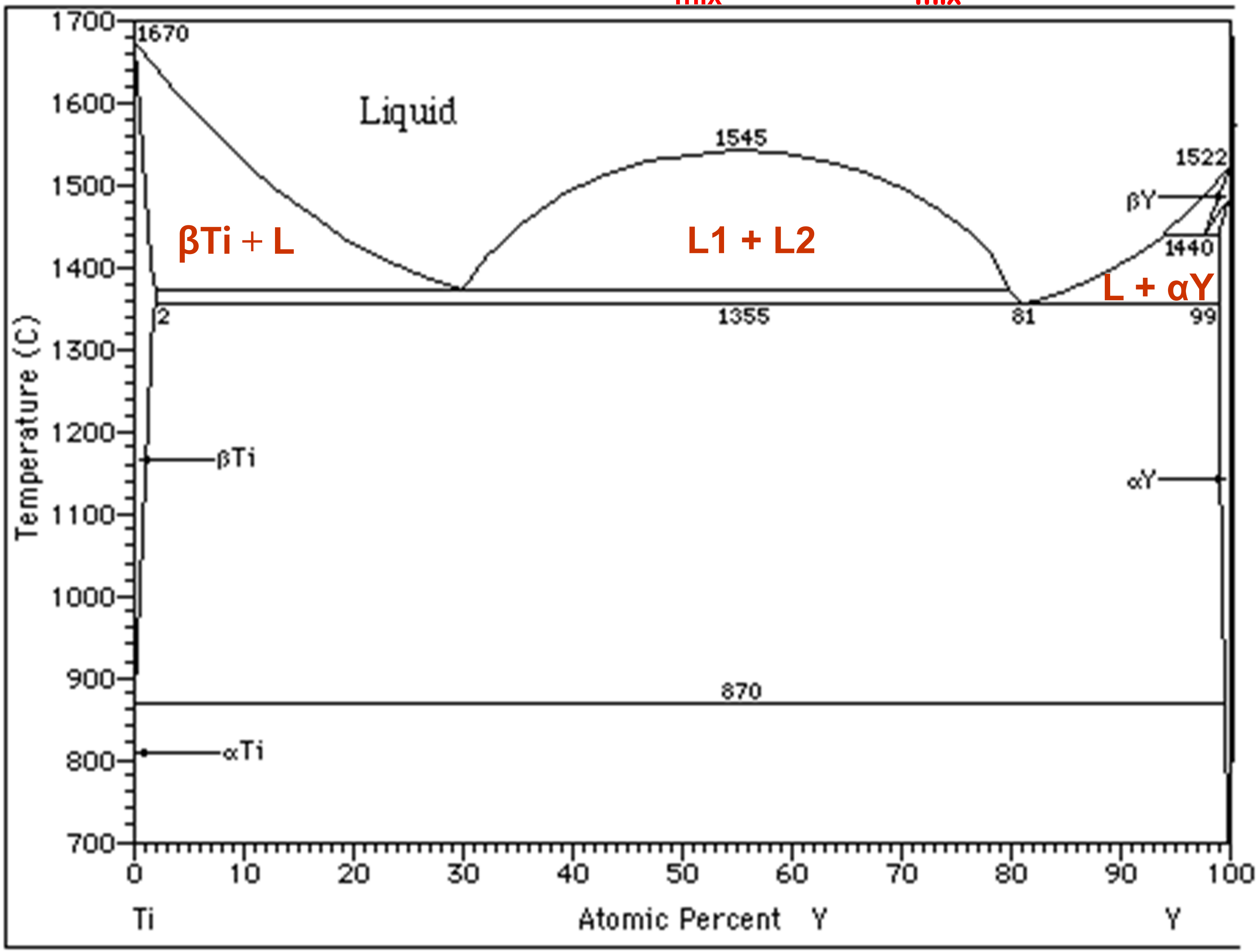




$\varepsilon > 0$, $\Delta H_{mix} > 0$ / $\Delta H_{mix} \sim +5$ kJ/mol



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



5.5.5 Spinodal Decomposition

Spinodal mode of transformation has no barrier to nucleation

: describing the transformation of a system of two or more components in a metastable phase into two stable phases

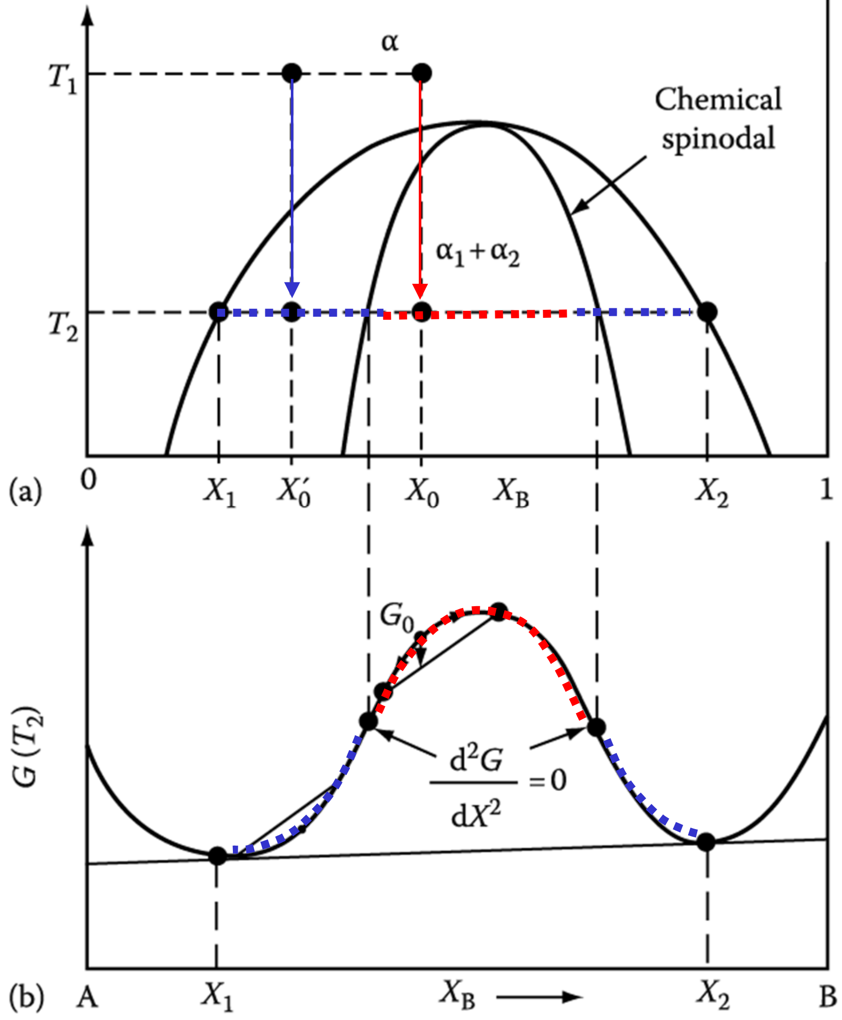


Fig. 5.38 Alloys between the spinodal points are unstable and can decompose into two coherent phasees α_1 and α_2 without overcoming an activation energy barrier. Alloys between the coherent miscibility gaps and the spinodal are metastable and can decompose only after nucleation of the other phase.

How does it differ between inside and outside the inflection point of Gibbs free energy curve?

1) Within the spinodal $\frac{d^2G}{dX^2}<0$

: phase separation by small fluctuations in composition/ "up-hill diffusion"

2) If the alloy lies outside the spinodal, small variation in composition leads to an increase in free energy and the alloy is therefore metastable.

The free energy can only be decreased if nuclei are formed with a composition very different from the matrix.
→ nucleation and growth

: "down-hill diffusion"

Positive heat of mixing relation among constituent elements

- **Alloy design considering heat of mixing relation among constituent elements**

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

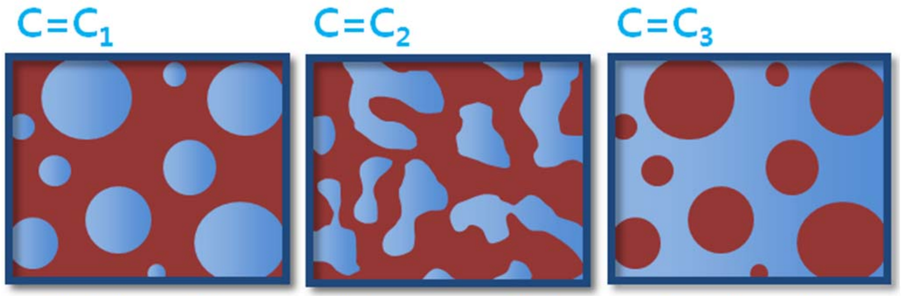
⬇

creates (meta)stable miscibility gap
in limited composition range

⬇

Phase separation to A-rich & B-rich phase

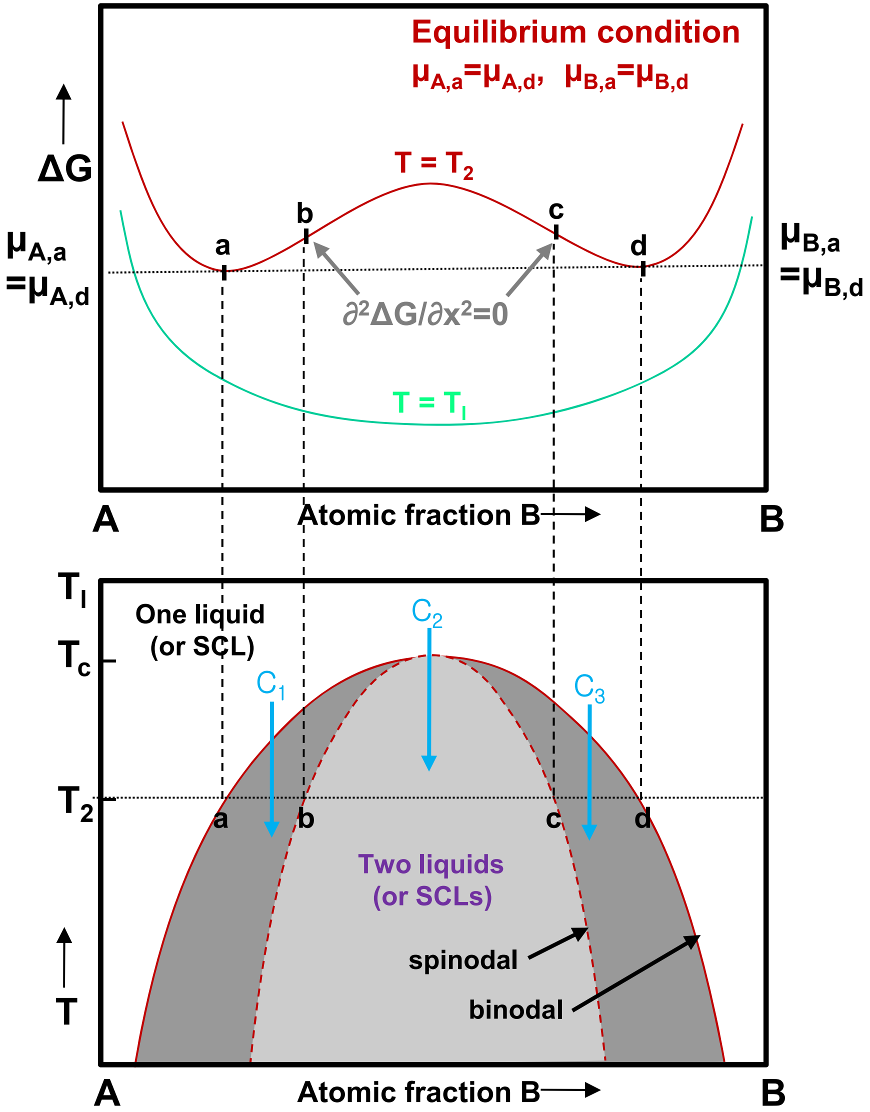
- **Different two-phase structure by initial composition before phase separation**



A-rich matrix
B-rich droplet

Interconnected
structure

B-rich matrix
A-rich droplet



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

* La-Zr-Al-Cu-Ni system

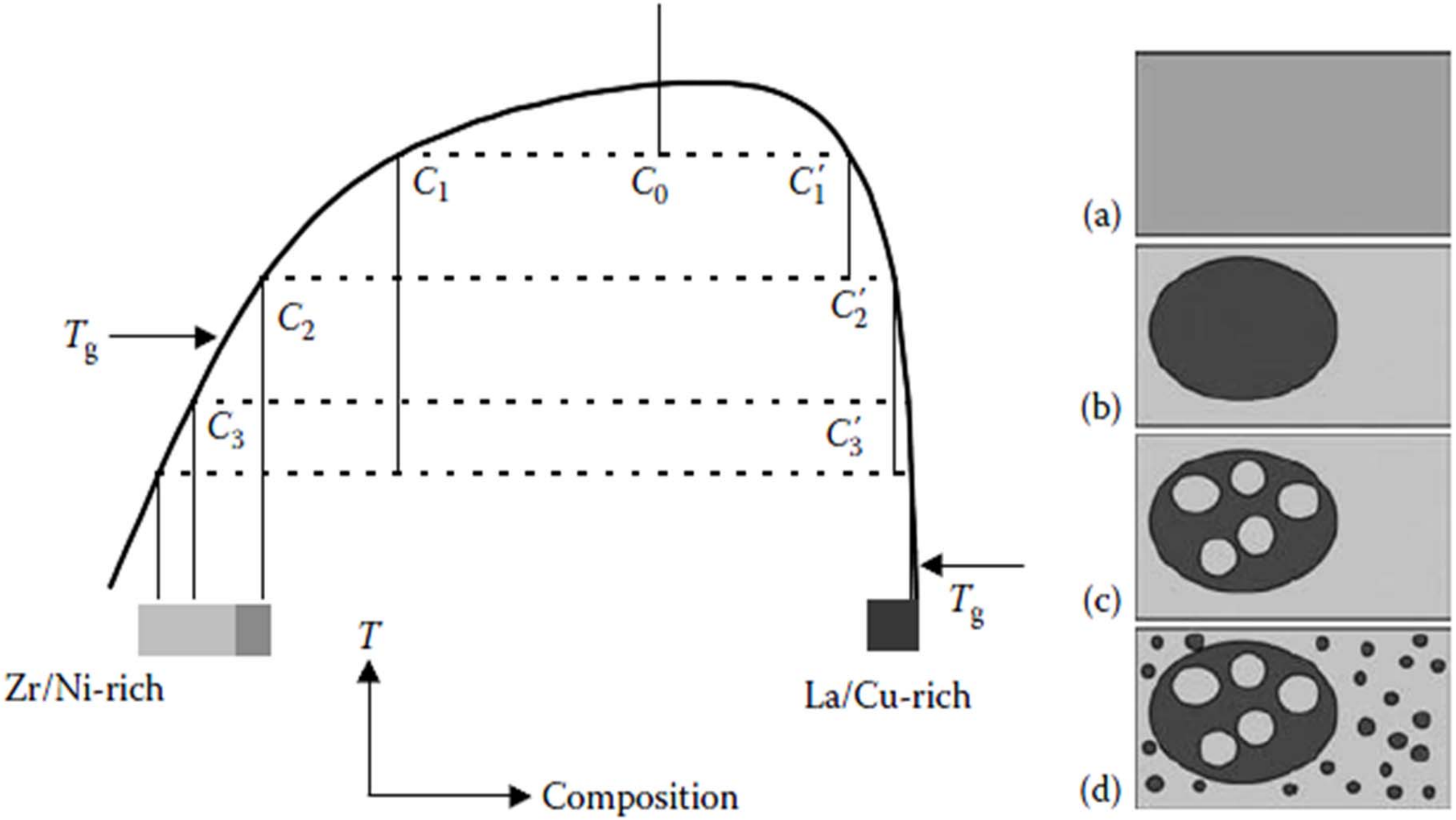


FIGURE 5.17
Schematic of the miscibility gap and the sequence of phase formation during cooling in the La–Zr–Al–Cu–Ni system. The positions of letters (a) to (d) in the diagram on the left correspond to the schematic microstructures (a) to (d) on the right. (Reprinted from Kündig, A.A. et al., *Acta Mater.*, 52, 2441, 2004. With permission.)

Q: Microstructure determining parameters of phase separation in metallic glasses

(a) Composition

(b) Critical temperature, T_c

(c) Asymmetry of the spinodal curve/decomposition range

(d) Glass-forming ability of the separated liquid

Contents for today's class

CHAPTER 3
Binary Phase Diagrams_Two-Phase Equilibrium

- Equilibrium in Heterogeneous Systems

- Binary phase diagrams

1) Simple Phase Diagrams

2) Variant of the simple phase diagram

a. $\Delta H_{mix} > 0$ $\Delta H^{\alpha}_{mix} > \Delta H^{l}_{mix}$ **Systems with miscibility gab**

b. $\Delta H_{mix} < 0$ $\Delta H^{\alpha}_{mix} < \Delta H^{l}_{mix} < 0$

c. **Pressure-Temperature-Composition phase diagram for a system with continuous series of solutions**

Q1: How can we define equilibrium in heterogeneous systems?

1.4

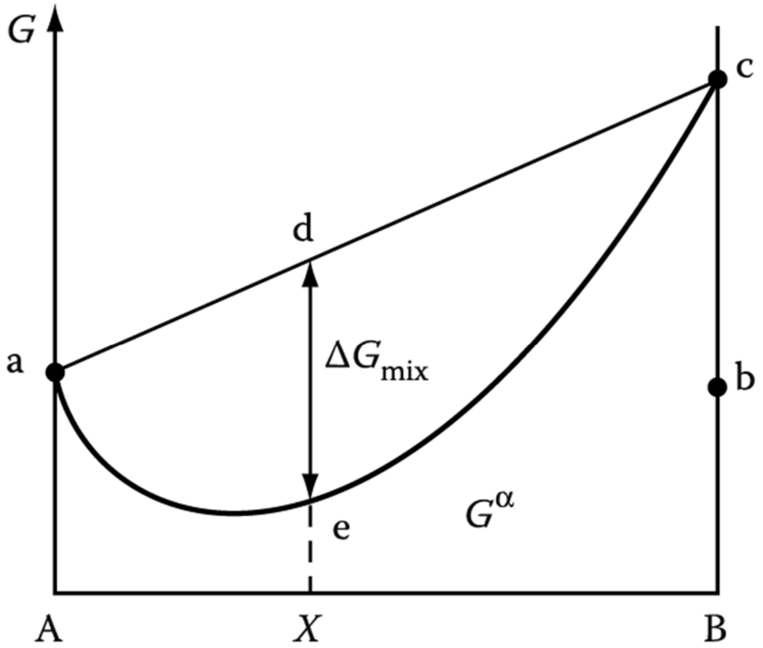
Equilibrium in Heterogeneous Systems

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

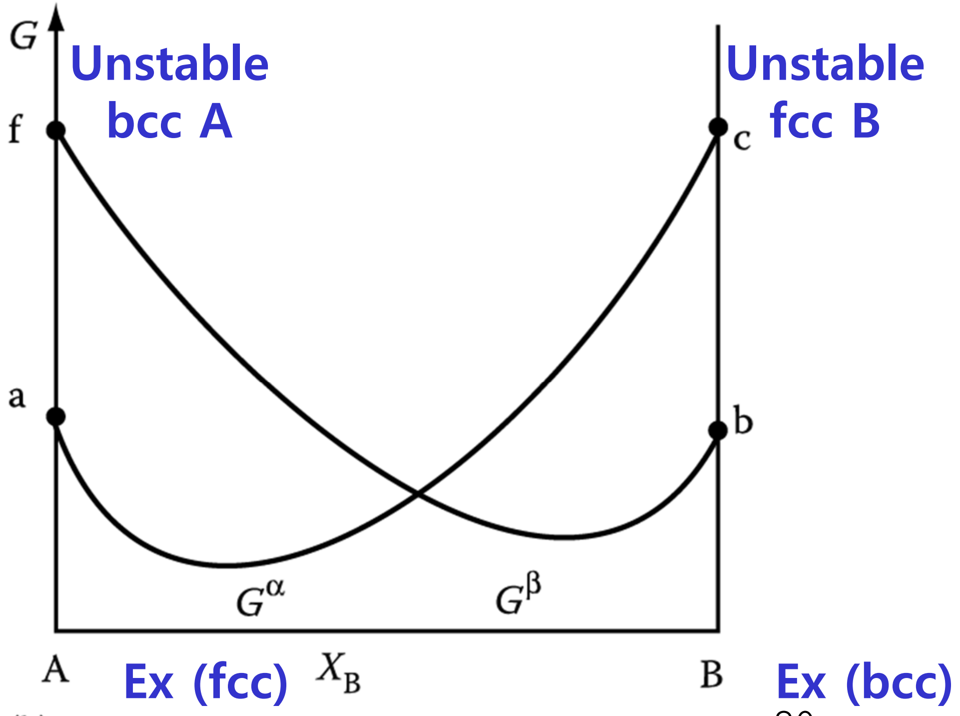
We have dealt with the case where the components A and B have the same crystal structure.

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

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



(a)



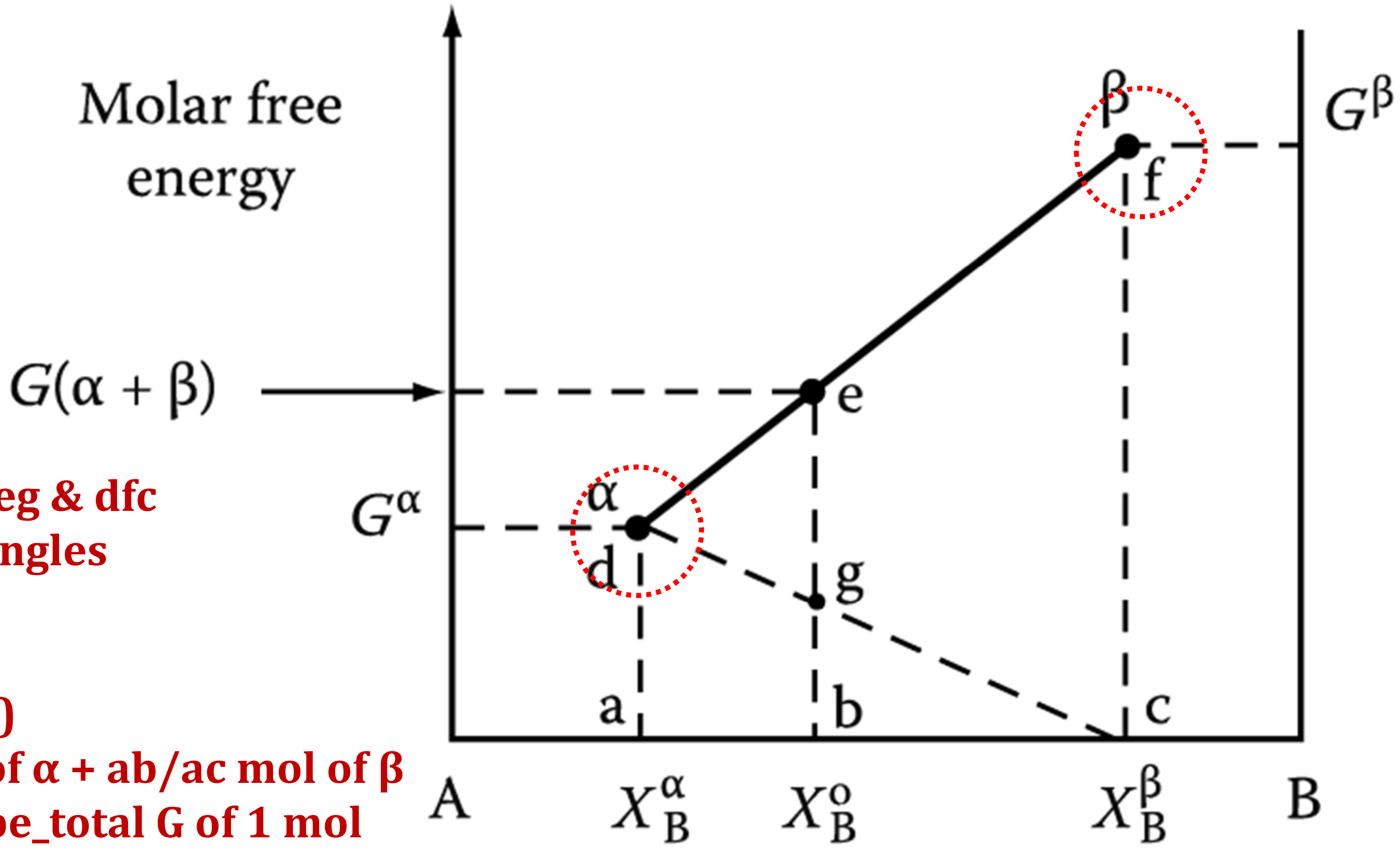
(b)

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* $X_B^{o} = ?$

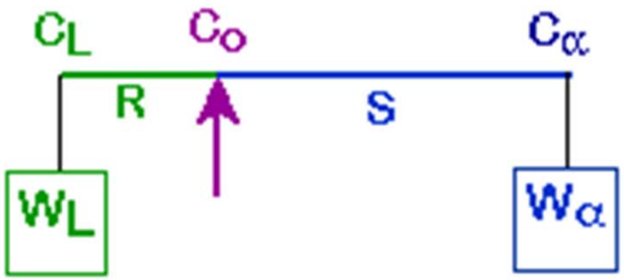


- **bcg & acd, deg & dfc**
  : similar triangles
- **Lever rule**
- **1 mole (α+β)**
  : bc/ac mol of α + ab/ac mol of β
  → bg + ge = be_total G of 1 mol

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

Lever rule

A geometric interpretation:



moment equilibrium:

$$\underbrace{\boxed{W_L}}_{\boxed{1-W_\alpha}} R = W_\alpha S$$

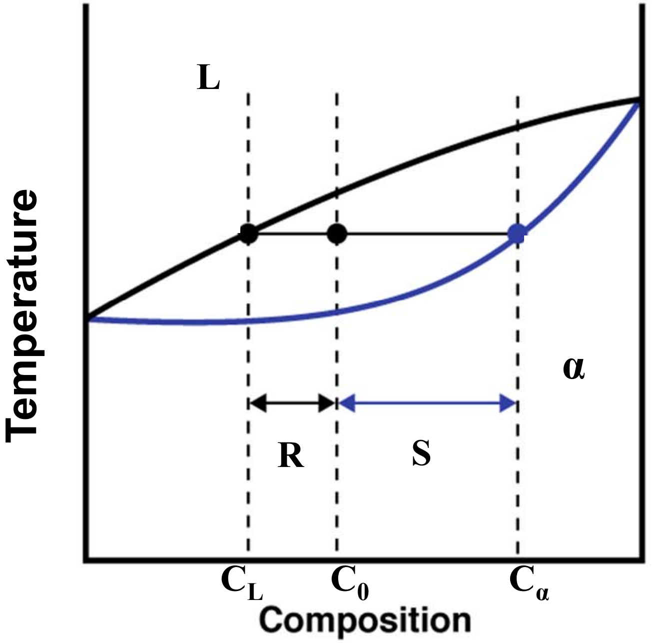
solving gives Lever Rule

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:

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



1.4

Equilibrium in Heterogeneous Systems

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

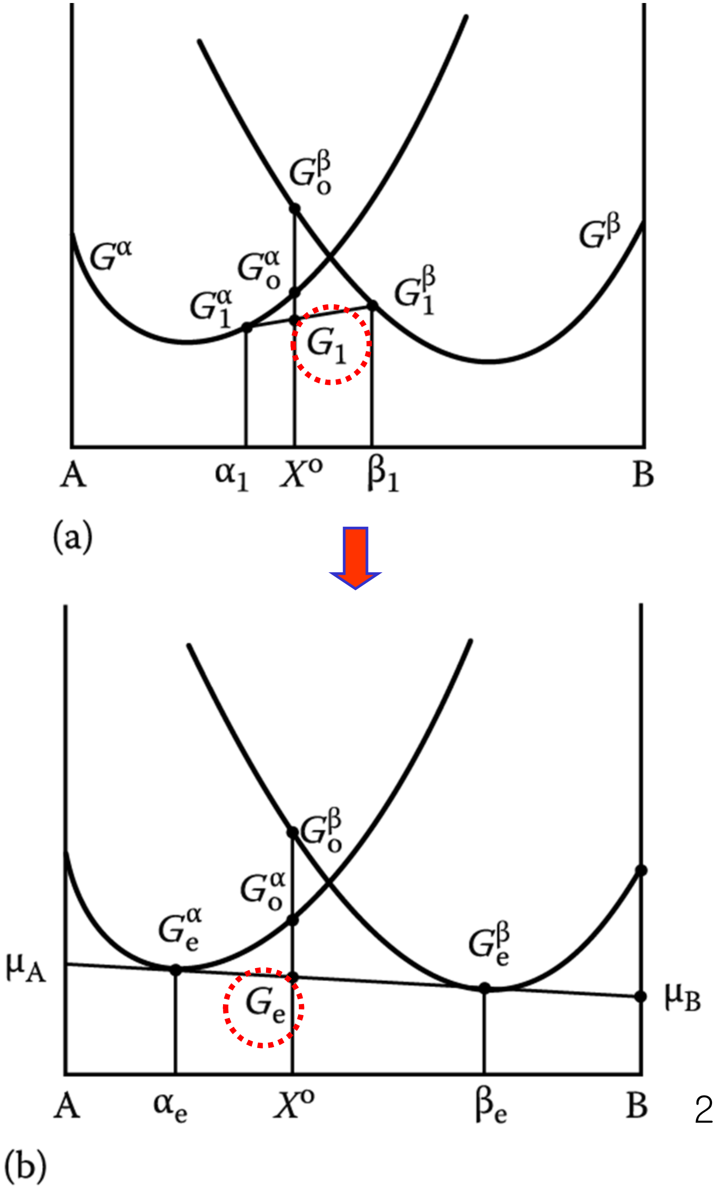
Exchange of A and B atoms

→ **α + β phase separation**

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

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

Unified Chemical potential of two phases



Variation of activity with composition

Activity, a : effective concentration for mass action

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.

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

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

Unified activity of two phase

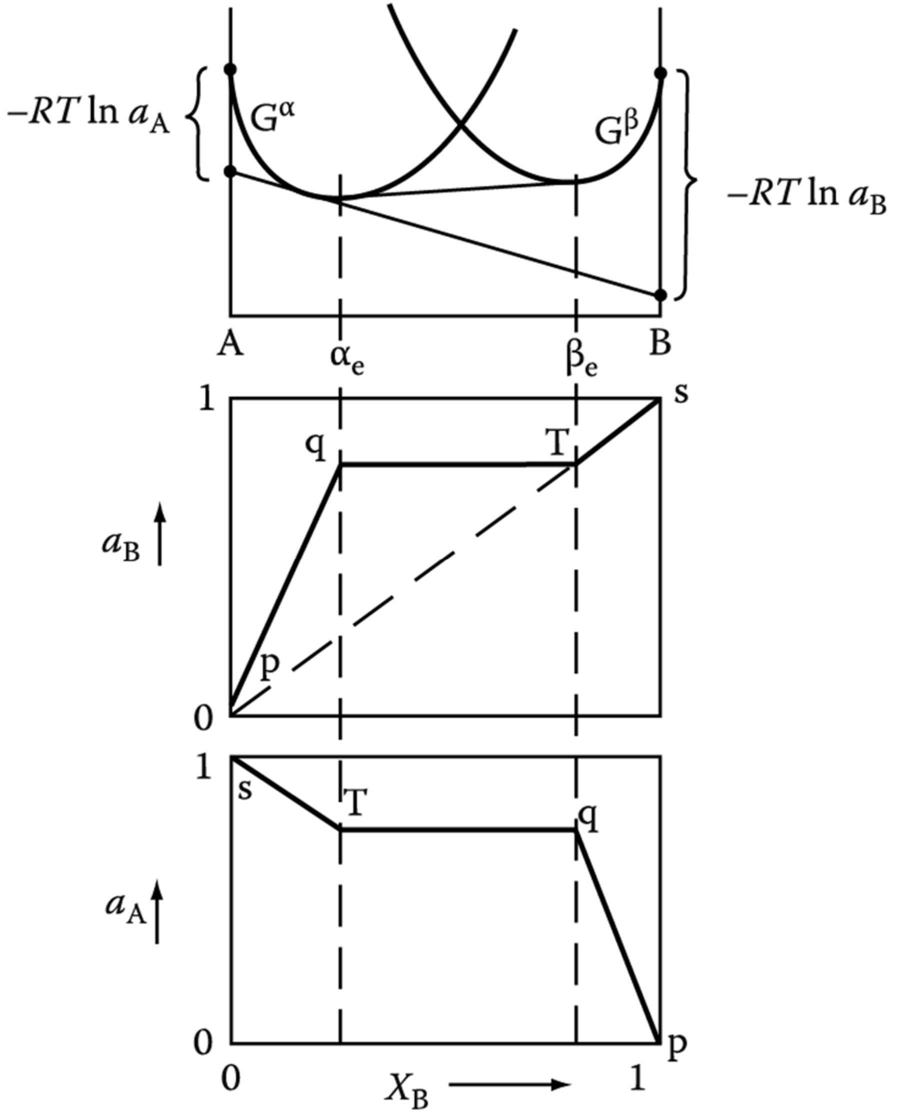
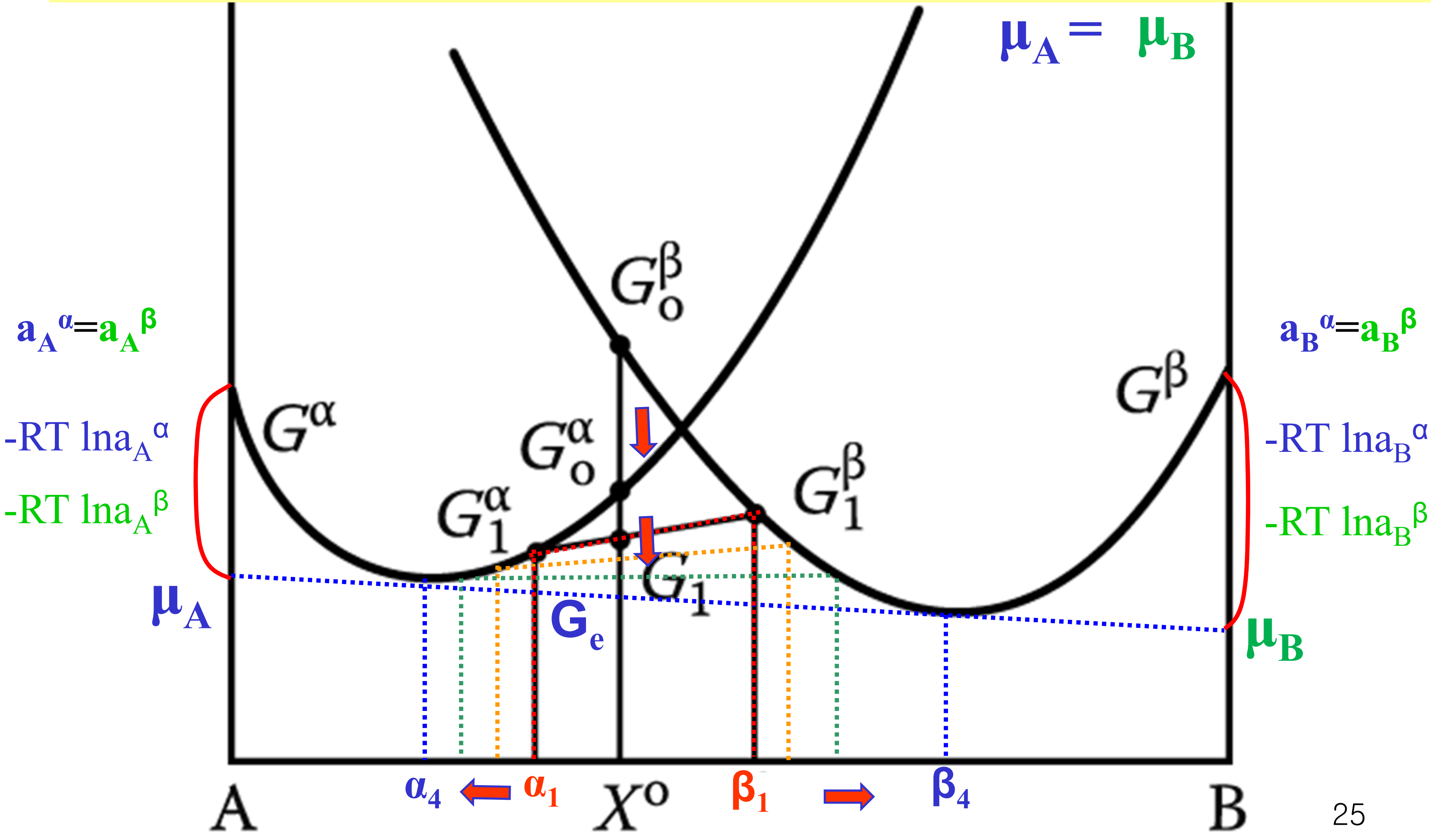


Fig. 1.28 The variation of a_A and a_B with composition for a binary system containing two ideal solutions, α and β

Equilibrium in Heterogeneous Systems

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



Q2: How equilibrium is affected by temperature in complete solid solution?

- Two-Phase Equilibrium

1) Simple Phase Diagrams

Assumption: (1) completely miscible in solid and liquid.
(2) Both are ideal soln.
(3) $T_m(A) > T_m(B)$

$$\boxed{\Delta H^{L}_{mix} = 0 \quad \Delta H^{S}_{mix} = 0}$$

$$dG^s = V^s dP - S^s dT + \mu_A^s\, dX_A^s + \mu_B^s\, dX_B^s$$
$$dG^l = V^l dP - S^l dT + \mu_A^l\, dX_A^l + \mu_B^l\, dX_B^l.$$

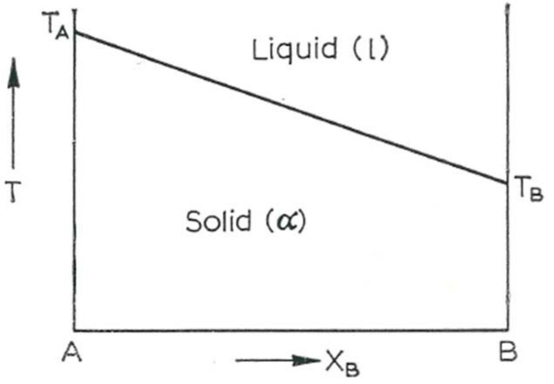


Fig. 22.

At equilibrium

$$dG^s = dG^l, \quad \mu_A^s = \mu_A^l \quad \text{and} \quad \mu_B^s = \mu_B^l.$$

At constant P

$$-(S^s - S^l)\, dT = (\mu_A - \mu_B)(dX_A^l - dX_A^s).$$

Differentiating with respect to X_A,

$$(S^s - S^l)\frac{dT}{dX_A} = (\mu_A - \mu_B)\left(\frac{dX_A^s}{dX_A} - \frac{dX_A^l}{dX_A}\right). \tag{102}$$

If the boundary between liquid and solid were as shown in Fig. 22, then $X_A^s = X_A^l$ (the liquid and solid would have the same composition when in equilibrium at a point on the line $T_A T_B$).

From eqn. (102)

$$(S^s - S^l)\frac{dT}{dX_A} = 0.$$

From eqn. (102)

$$(S^s - S^l)\,\frac{\mathrm{d}T}{\mathrm{d}X_\mathrm{A}} = 0.$$

Since $S^s \neq S^l$, then $\mathrm{d}T/\mathrm{d}X_\mathrm{A} = 0$. Thus the condition $X_\mathrm{A}^s = X_\mathrm{A}^l$ is only associated with $\mathrm{d}T/\mathrm{d}X_\mathrm{A} = 0$, *i.e.* with a minimum or a maximum in the line $T_\mathrm{A}T_\mathrm{B}$ of Fig. 22. Except for this particular case therefore $X_\mathrm{A}^s \neq X_\mathrm{A}^l$. There is a difference between the composition of the liquid and solid phase in the general case.

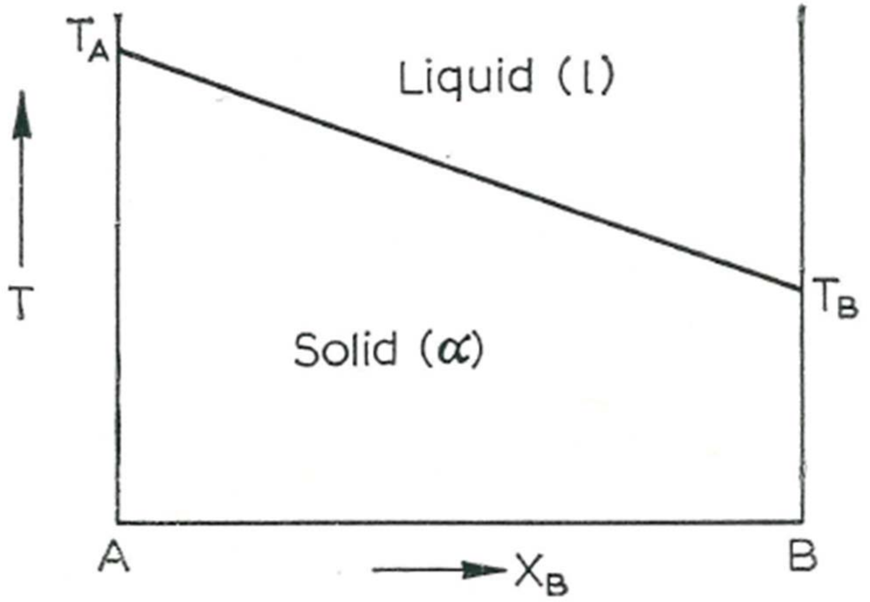
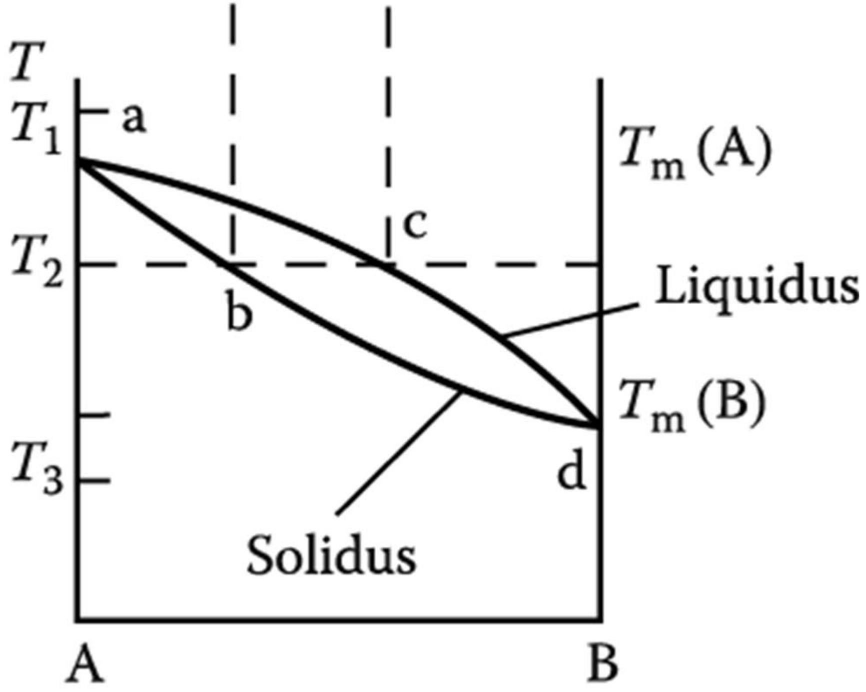


Fig. 22.



(f)

*** Consider the free energy curves for liquid and α phase at a temperature T, where $T_A > T > T_B$. The standard states are pure *solid* A and pure *liquid* B at temperature T. → Derive the free energy curves for the liquid and α phases.**

1) Free energy curve for the liquid phase

For an ideal solution with a reaction

$$X_A \text{ moles of liquid A} + X_B \text{ moles of liquid B} = 1 \text{ mole liquid solution}$$

$$\boxed{\Delta G_m = RT(X_A^l \ln X_A^l + X_B^l \ln X_B^l)} \qquad (61)$$

But the standard state for A is pure solid A. To obtain the free energy change, ΔG_m^l, for the formation of the liquid solution, we must allow for the conversion of X_A moles of solid A into X_A moles of liquid A, *i.e.*

$$X_A \text{ moles solid A} = X_A \text{ moles liquid A}$$

$$\boxed{\Delta G = X_A^l \Delta G_A}$$

where ΔG_A is the difference in free energy between liquid and solid A (the free energy of fusion of A).

Hence for the reaction

$$X_A \text{ moles of solid A} + X_B \text{ moles of liquid B} = 1 \text{ mole liquid solution}$$

$$\boxed{\Delta G_m^l = X_A^l \Delta G_A + RT(X_A^l \ln X_A^l + X_B^l \ln X_B^l).}$$

2) Free energy curve for α phase

For an ideal solid solution formed according to the equation

X_A moles of solid A + X_B moles of solid B = 1 mole α solid solution

$$\boxed{\Delta G_m = RT(X_A^s \ln X_A^s + X_B^s \ln X_B^s).}$$

Since the standard state for B is pure *liquid* B, allowance must be made for the free energy change on transforming X_B moles of liquid B to X_B moles of solid B, *i.e.*

$$\boxed{\Delta G = -X_B^s \Delta G_B}$$

where ΔG_B is the difference in free energy between liquid and solid B. It is a negative quantity since the liquid phase is the more stable at temperature T.

For the reaction

X_A moles of solid A + X_B moles of liquid B = 1 mole α solid solution

$$\boxed{\Delta G_m^s = -X_B^s \Delta G_B + RT(X_A^s \ln X_A^s + X_B^s \ln X_B^s).}$$

At temperature T the chemical potential of component B is identical in the α and liquid phases. Therefore

$$\boxed{\frac{\partial \Delta G_m^s}{\partial X_B} = \frac{\partial \Delta G_m^l}{\partial X_B}}$$

$$\frac{\partial \Delta G_m^s}{\partial X_B} = -\Delta G_B + RT \ln \frac{X_B^s}{X_A^s} \quad \text{and} \quad \frac{\partial \Delta G_m^l}{\partial X_B} = -\Delta G_A + RT \ln \frac{X_B^l}{X_A^l}.$$

Therefore

$$\Delta G_A - \Delta G_B = RT \left(\ln \frac{X_B^l}{X_A^l} - \ln \frac{X_B^s}{X_A^s} \right)$$

or,

$$\Delta G_A - \Delta G_B = RT \left(\ln \frac{X_A^s}{X_A^l} - \ln \frac{X_B^s}{X_B^l} \right).$$

We can relate ΔG_A and ΔG_B to ΔH_A and ΔH_B, T_A and T_B, *i.e.* to the respective molar heats of fusion of pure A and B, and their melting points. For example, for component B at T_B:

$$\Delta G_B = \Delta H_B - T_B \Delta S_B = 0$$

or,

$$\boxed{\Delta S_B = \frac{\Delta H_B}{T_B}.}$$

At a temperature T,

$$\Delta G_B = \Delta H_B - T \Delta S_B \neq 0.$$

Therefore

$$\Delta G_{\mathrm{B}} = \Delta H_{\mathrm{B}} - T\,\frac{\Delta H_{\mathrm{B}}}{T_{\mathrm{B}}}$$

$$\boxed{= \Delta H_{\mathrm{B}}\left(1 - \frac{T}{T_{\mathrm{B}}}\right).}$$

$$\Delta G_{\mathrm{A}} - \Delta G_{\mathrm{B}} = RT\left(\ln\frac{X_{\mathrm{A}}^{s}}{X_{\mathrm{A}}^{l}} - \ln\frac{X_{\mathrm{B}}^{s}}{X_{\mathrm{B}}^{l}}\right).$$

Substituting,

$$\Delta H_{\mathrm{A}}\left(1 - \frac{T}{T_{\mathrm{A}}}\right) - \Delta H_{\mathrm{B}}\left(1 - \frac{T}{T_{\mathrm{B}}}\right) = RT\left(\ln\frac{X_{\mathrm{A}}^{s}}{X_{\mathrm{A}}^{l}} - \ln\frac{X_{\mathrm{B}}^{s}}{X_{\mathrm{B}}^{l}}\right)$$

or,

$$\ln\frac{X_{\mathrm{A}}^{s}}{X_{\mathrm{A}}^{l}} - \ln\frac{X_{\mathrm{B}}^{s}}{X_{\mathrm{B}}^{l}} = \frac{\Delta H_{\mathrm{A}}}{R}\left(\frac{1}{T} - \frac{1}{T_{\mathrm{A}}}\right) - \frac{\Delta H_{\mathrm{B}}}{R}\left(\frac{1}{T} - \frac{1}{T_{\mathrm{B}}}\right).$$

As the temperature approaches T_{A} the quantities X_{A}^{s} and X_{A}^{l} will approach unity, and $1/T$ will approach $1/T_{\mathrm{A}}$.

Hence near T_{A}:

$$\boxed{\ln\frac{X_{\mathrm{B}}^{s}}{X_{\mathrm{B}}^{l}} = \frac{\Delta H_{\mathrm{B}}}{R}\left(\frac{1}{T} - \frac{1}{T_{\mathrm{B}}}\right).} \tag{103}$$

Similarly, if the temperature approaches T_{B}, $X_{\mathrm{B}}^{s} \simeq X_{\mathrm{B}}^{l} \to 1$ and $1/T \to 1/T_{\mathrm{B}}$. Near T_{B}:

$$\boxed{\ln\frac{X_{\mathrm{A}}^{s}}{X_{\mathrm{A}}^{l}} = \frac{\Delta H_{\mathrm{A}}}{R}\left(\frac{1}{T} - \frac{1}{T_{\mathrm{A}}}\right).} \tag{104}$$

Knowing ΔH_{A}, ΔH_{B}, T_{A} and T_{B}, the above two equations can be used to determine the compositions of co-existing phases at a series of temperatures, T, between T_{A} and T_{B}. → **Fig. 23*f***

1) Simple Phase Diagrams

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

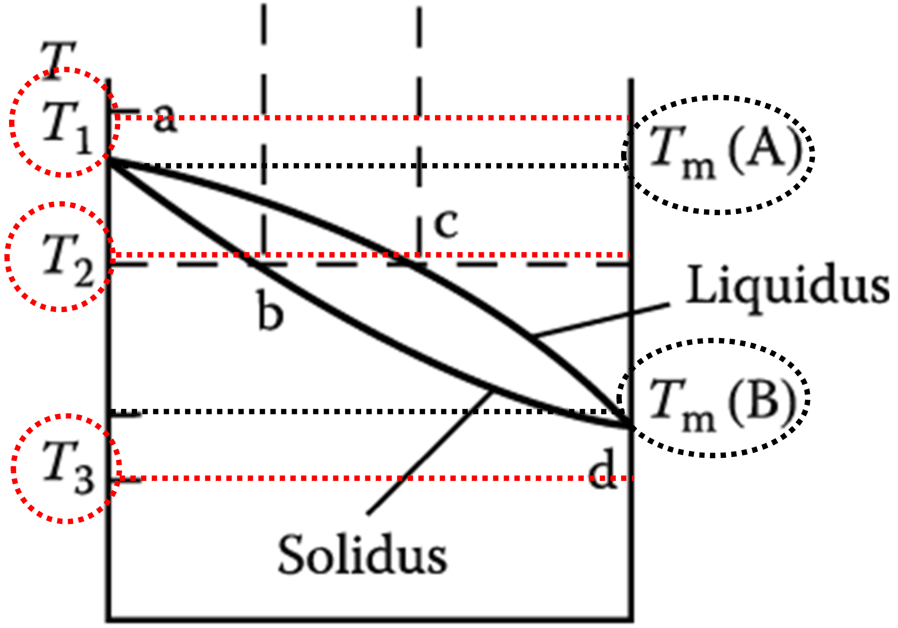
(2) Both are ideal soln.

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

(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.



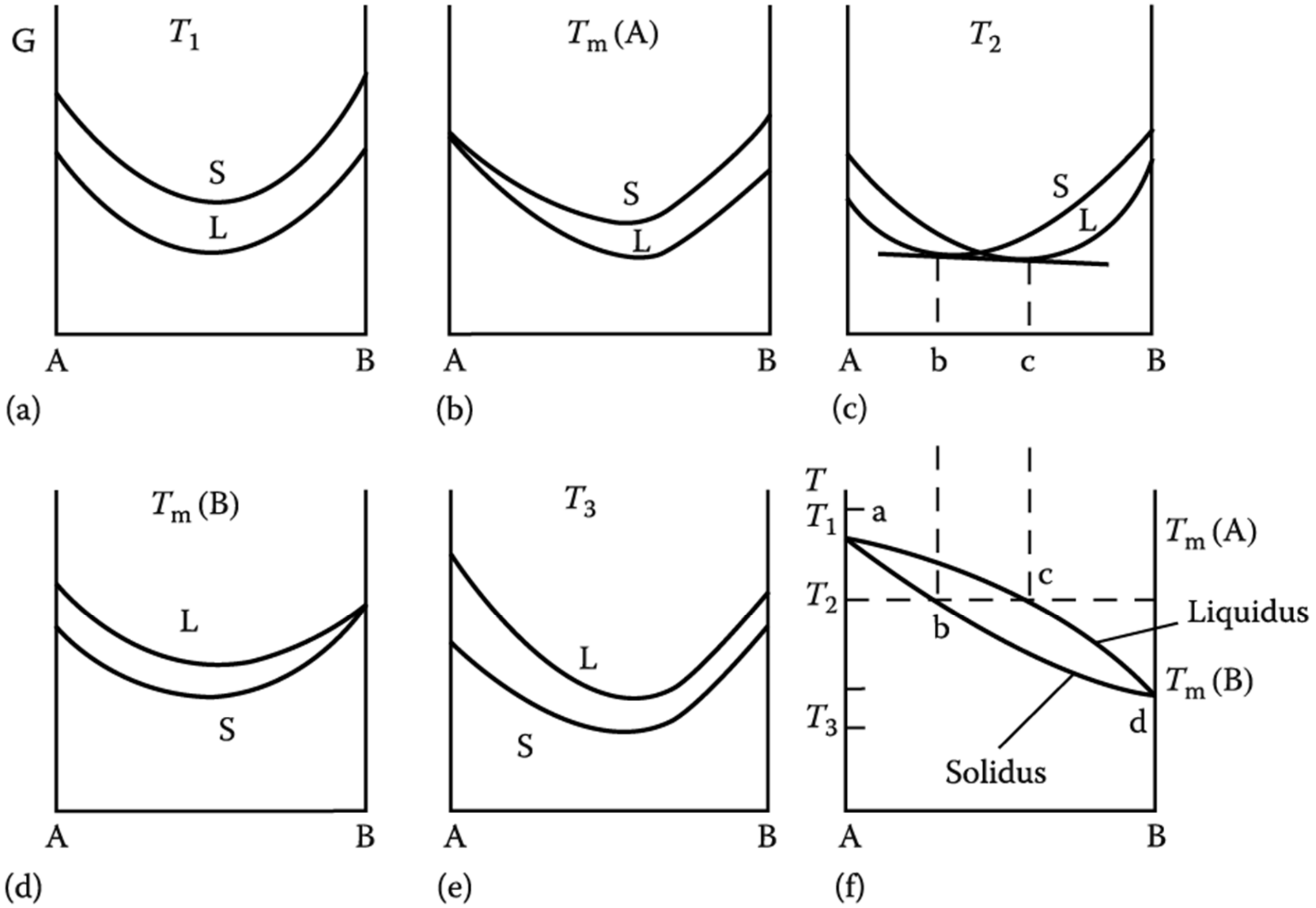
(f)

1.5 Binary phase diagrams

1) Simple Phase Diagrams

Assumption:

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



*** Consider actual** (or so-called regular) **solutions**

in which $\Delta H_m \neq 0$, but $\Delta S_m = \Delta S_{m,\text{ideal}}$.

$$\Delta G_m^l = \Delta H_m^l + X_A^l \Delta G_A + RT(X_A^l \ln X_A^l + X_B^l \ln X_B^l).$$

Since

$$\Delta G_A = \Delta H_A - T\Delta S_A$$

then,

$$\Delta G_m^l = \Delta H_m^l + X_A^l \Delta H_A - X_A^l T\Delta S_A + RT(X_A^l \ln X_A^l + X_B^l \ln X_B^l).$$

The free energy curve for the solid phase is:

$$\Delta G_m^s = \Delta H_m^s - X_B^s \Delta G_B + RT(X_A^s \ln X_A^s + X_B^s \ln X_B^s)$$

or,

$$\Delta G_m^s = \Delta H_m^s - X_B^s \Delta H_B + X_B^s T\Delta S_B + RT(X_A^s \ln X_A^s + X_B^s \ln X_B^s).$$

1) Simple Phase Diagrams

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

b) T ↓ → Decrease of curvature of G curve

(∵ decrease of $-T\Delta S_{mix}$ effect)

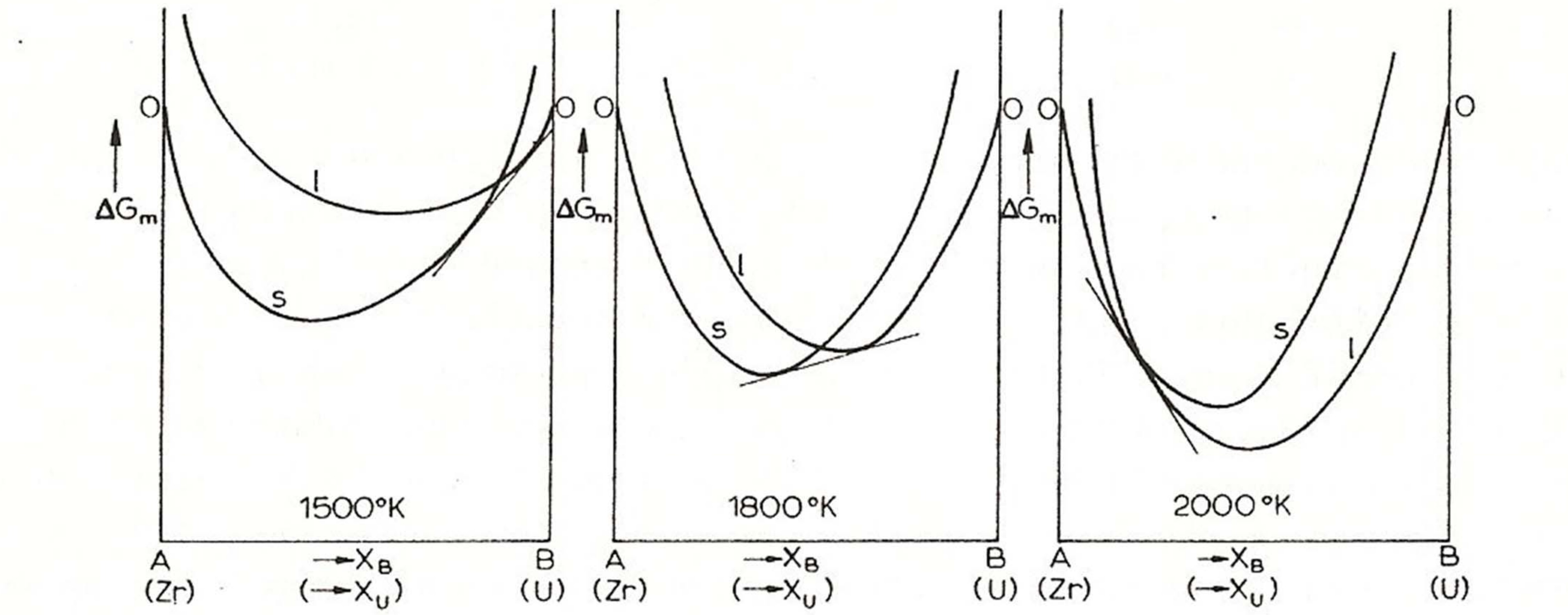


Fig. 26. Free energy curves for liquid and solid phases in the U–Zr system at 1500°, 1800° and 2000 °K.

It was assumed that $\Delta H_m^l = \Delta H_m^s$

1.5 Binary phase diagrams

1) Simple Phase Diagrams

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

b) T ↓ → Decrease of curvature of G curve

(∵ decrease of $-T\Delta S_{mix}$ effect)

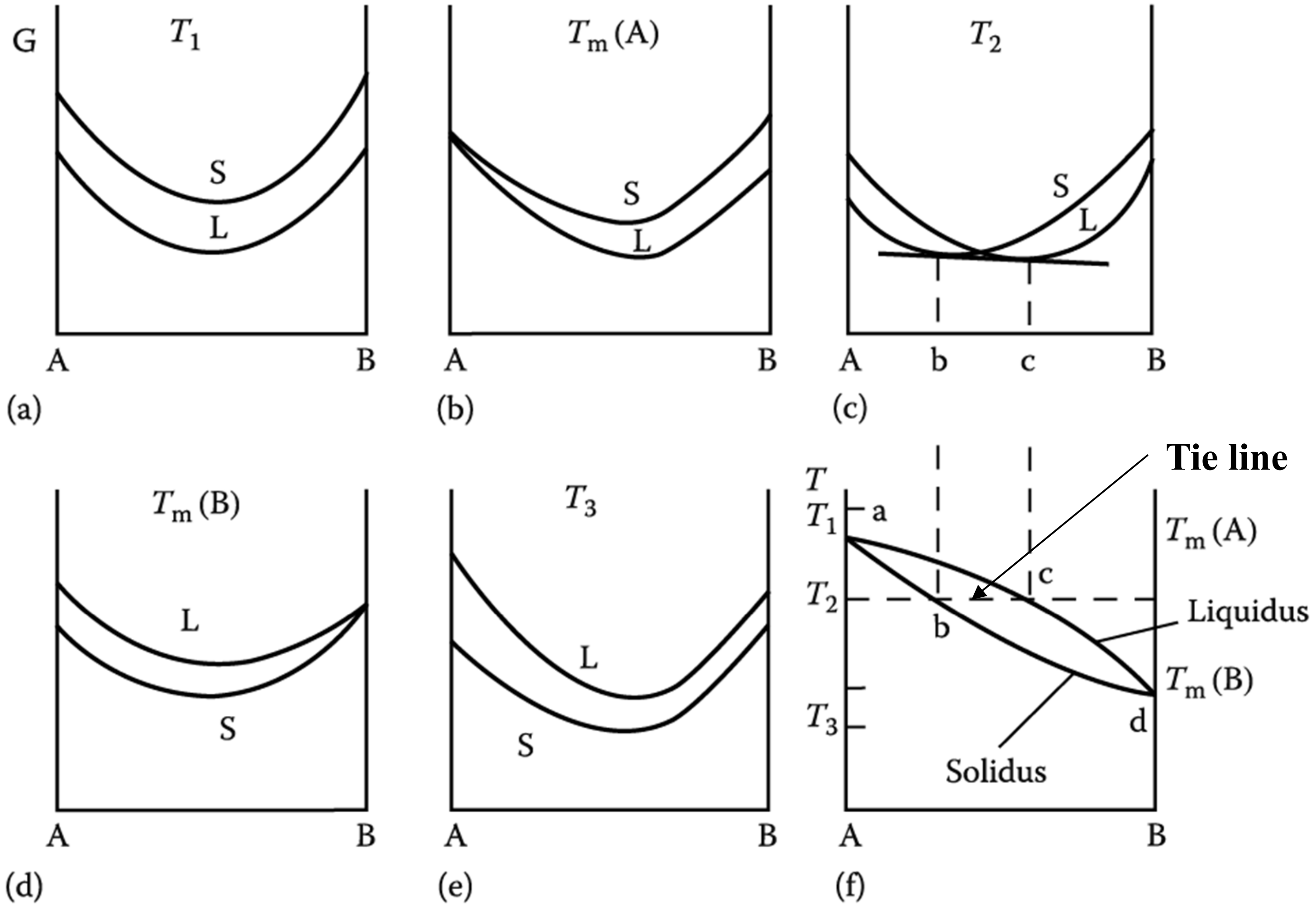
Assumption:

(1) completely miscible in solid and liquid.

(2) Both are ideal soln.

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

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



Referring to Fig. 23f, if A is regarded as the solvent, for very dilute solutions of B in A we can write

$$X_{\mathrm{A}} \rightarrow 1 \quad \text{and} \quad -\ln X_{\mathrm{A}} \simeq X_{\mathrm{B}}.$$

In terms of eqn. (104):

$$X_{\mathrm{A}}^{l} - X_{\mathrm{A}}^{s} = \frac{\Delta H_{\mathrm{A}}}{R}\left(\frac{T_{\mathrm{A}}-T}{T T_{\mathrm{A}}}\right).$$

Since $X_{\mathrm{A}}^{l} = 1 - X_{\mathrm{B}}^{l}$ and $X_{\mathrm{A}}^{s} = 1 - X_{\mathrm{B}}^{s}$

$$X_{\mathrm{B}}^{s} - X_{\mathrm{B}}^{l} = \frac{\Delta H_{\mathrm{A}}}{R}\left(\frac{T_{\mathrm{A}}-T}{T T_{\mathrm{A}}}\right). \tag{105}$$

As T approaches T_{A} (in dilute solutions of B in solvent A), the denominator on the right-hand side of eqn. (105) can be written RT_{A}^{2}. Therefore

$$X_{\mathrm{B}}^{s} - X_{\mathrm{B}}^{l} = \frac{\Delta H_{\mathrm{A}}}{RT_{\mathrm{A}}^{2}}(T_{\mathrm{A}} - T) \tag{106}$$

or,

$$\left(\frac{\mathrm{d}X_{\mathrm{B}}^{s}}{\mathrm{d}T} - \frac{\mathrm{d}X_{\mathrm{B}}^{l}}{\mathrm{d}T}\right)_{T=T_{\mathrm{A}}} = \frac{\Delta H_{\mathrm{A}}}{RT_{\mathrm{A}}^{2}}. \tag{107}$$

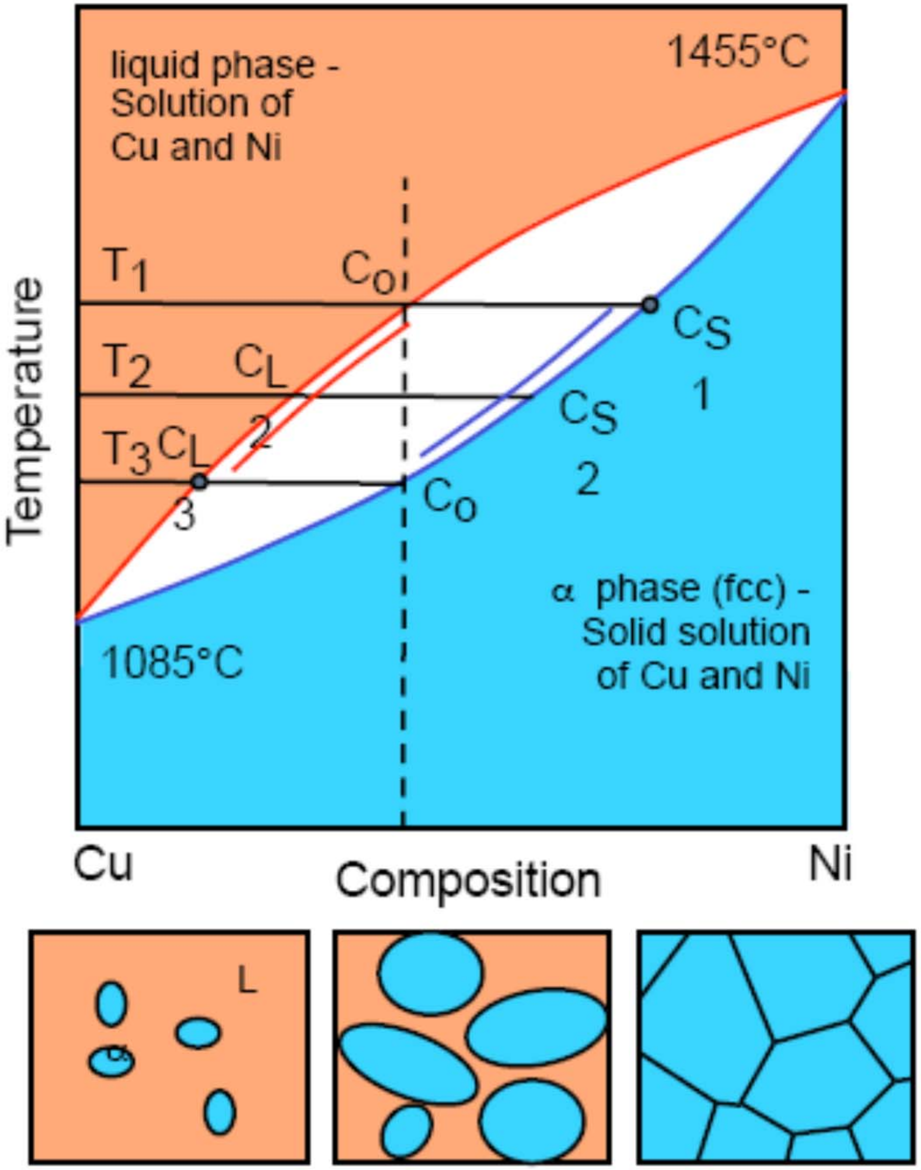
Equations (106) and (107) are referred to as the Van't Hoff relation. They give the depression of the freezing point for a liquid solution in equilibrium with a solid solution. The difference in initial slopes of the solidus and liquidus curves, the slopes at $T = T_{\mathrm{A}}$ and $X_{\mathrm{A}} = 1$, are dependent on the latent heat of fusion of pure A (ΔH_{A}) but independent of the nature of the solute.

1.5 Binary phase diagrams

1) Simple Phase Diagrams

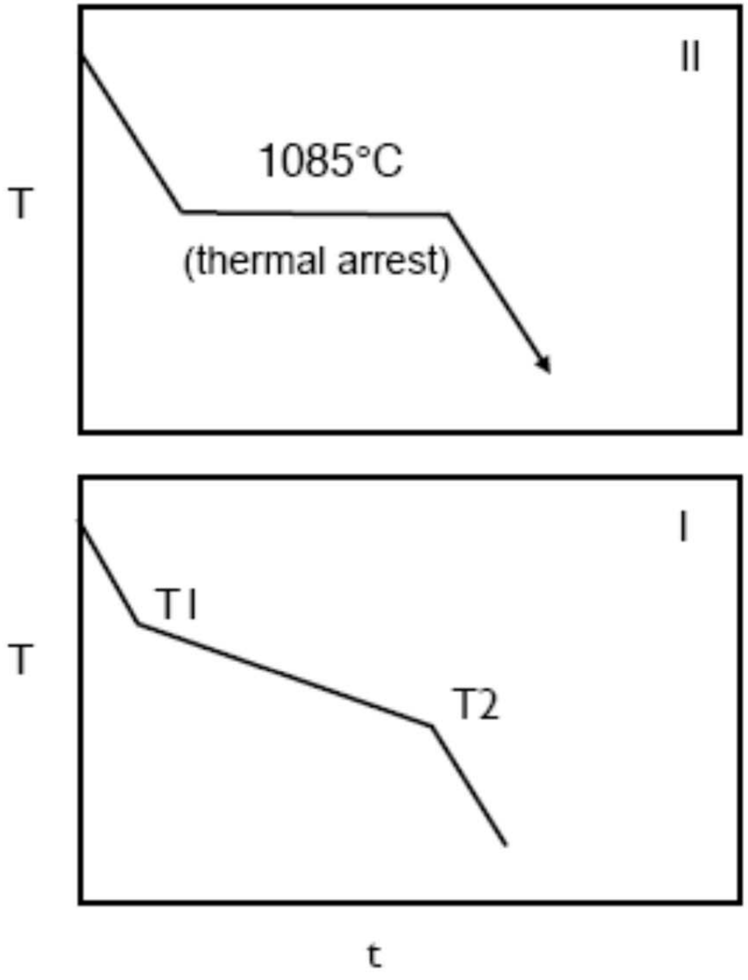
The simplest type of binary phase diagrams is the isomorphous system, in which the two constituents form a continuous solid solution over the entire composition range. An example is the Ni-Cu system.

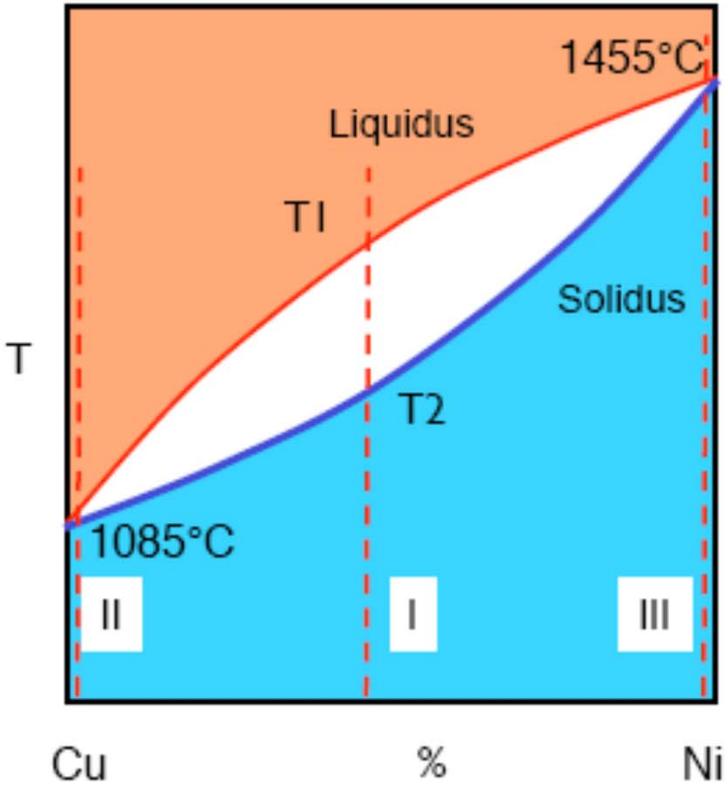
Solidification of alloy C_o starts on cooing at T_1. The first solid formed has a composition of C_{s1} and the liquid C_o. On further cooling the solid particles grow larger in size and change their composition to C_{s2} and then C_o, following the solidus whereas the liquid decrease in volume and changes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



Cooling Curves

determination of Phase diagrams



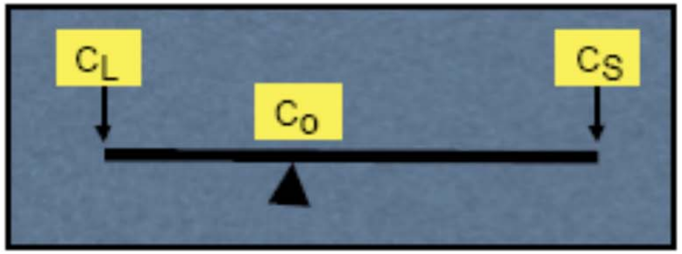


1.5 Binary phase diagrams

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



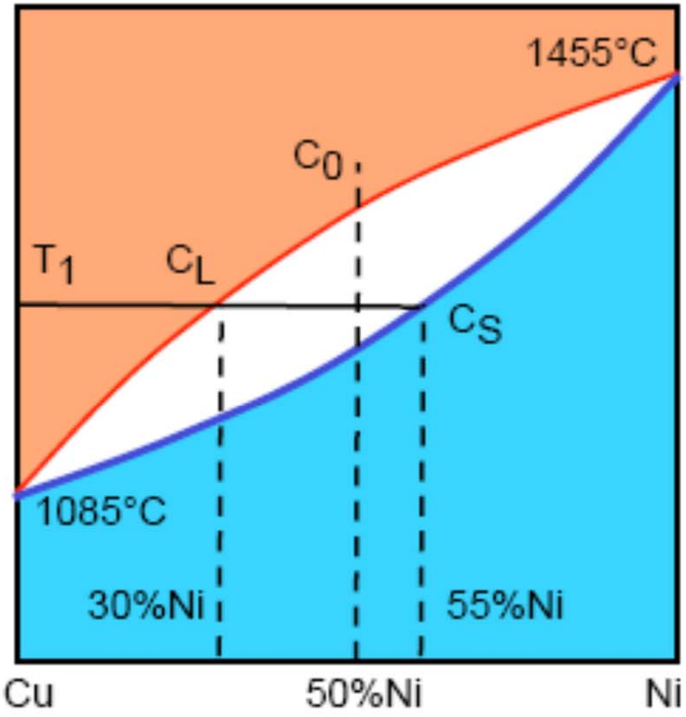
Read from the tie line:
Liquid phase: Cu-30%Ni
α-phase: Cu-55%Ni

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

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

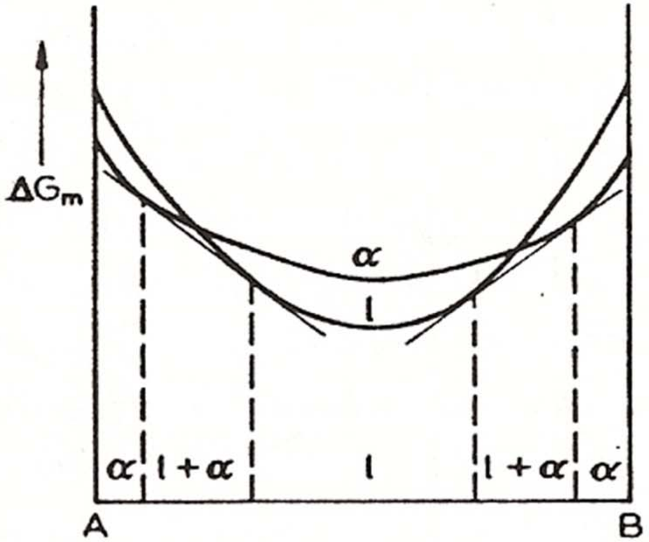
or

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

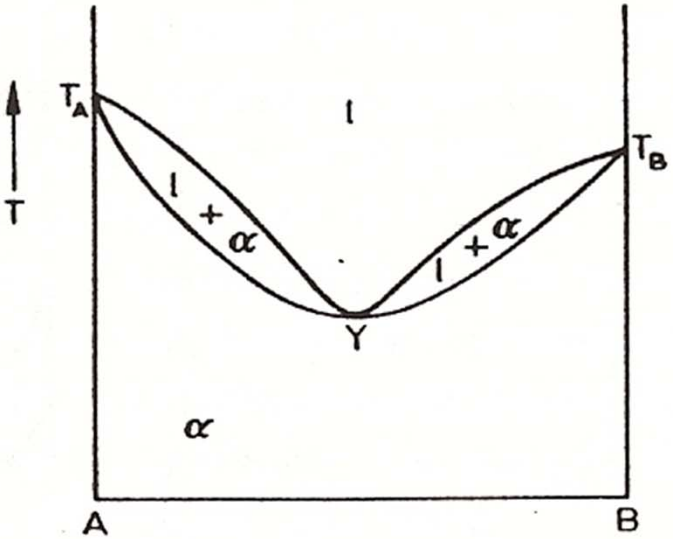


2) Variant of the simple phase diagram

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



(a)



(b)

2) Variant of the simple phase diagram

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

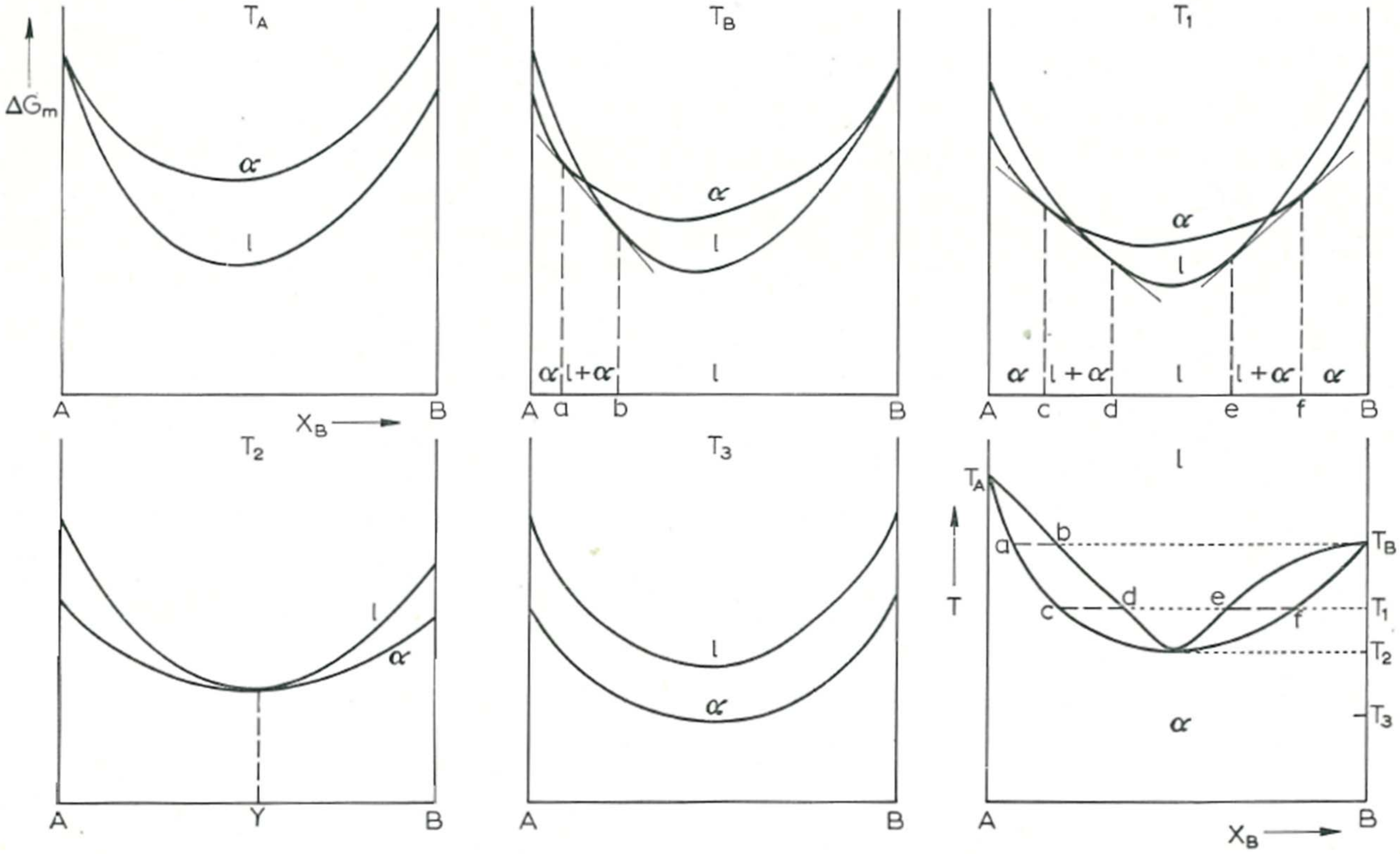
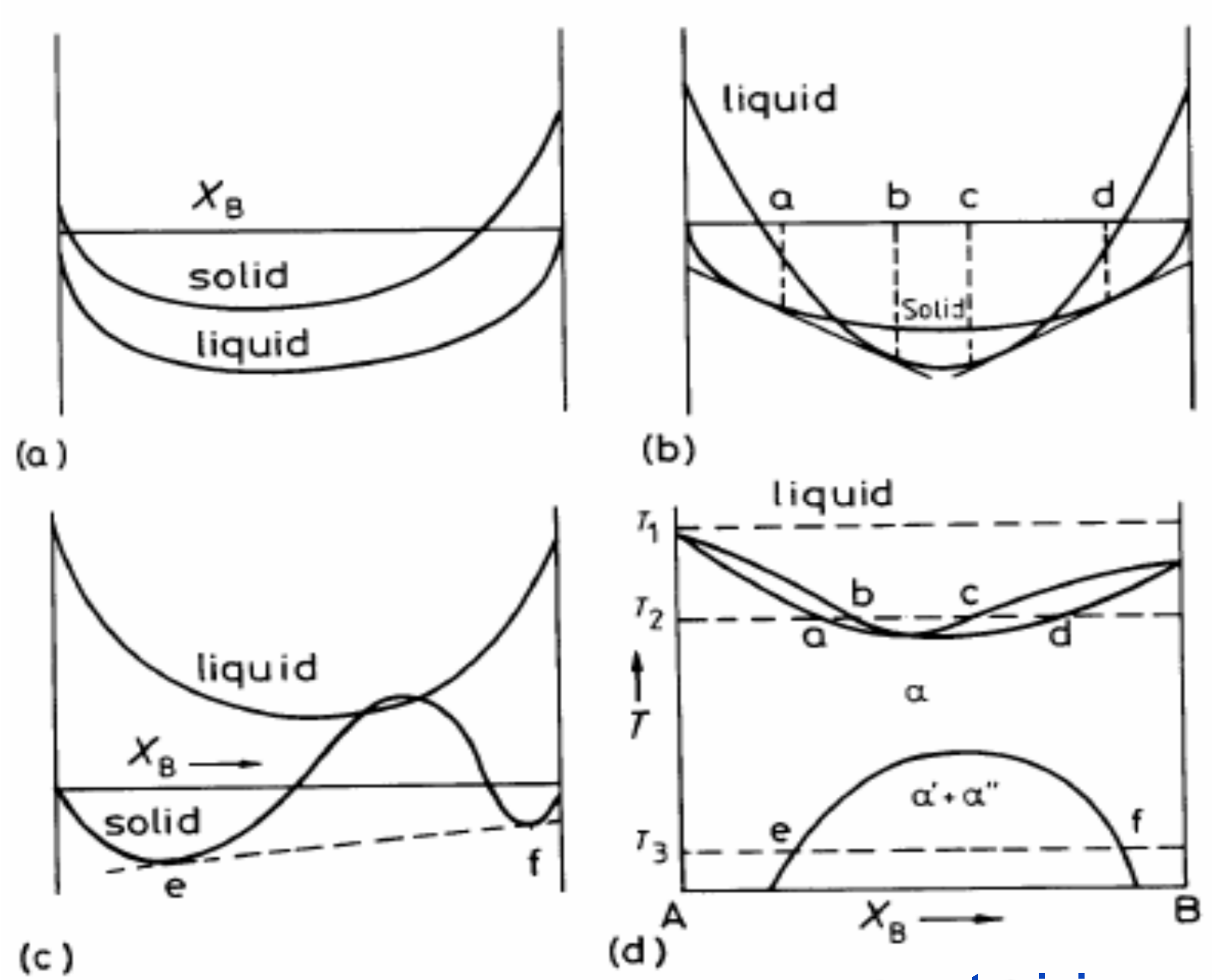


Fig. 30. Derivation of the phase diagram (Fig. 29b) from free energy curves for the liquid and solid phases. $T_A > T_B > T_1 > T_2 > T_3$.

2) Variant of the simple phase diagram

Systems with miscibility gab $\Delta H_{mix} > 0 \quad \Delta H^{\alpha}_{mix} > \Delta H^{l}_{mix}$



congruent minima

2) Variant of the simple phase diagram

$\Delta H_{mix} < 0$

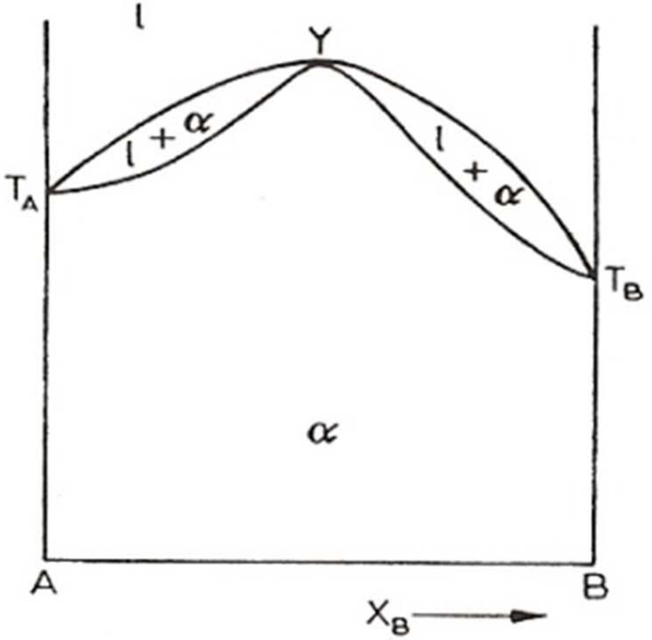


Fig. 32. Phase diagram with a maximum in the liquidus.

$\Delta H^{\alpha}_{mix} < \Delta H^{l}_{mix} < 0$

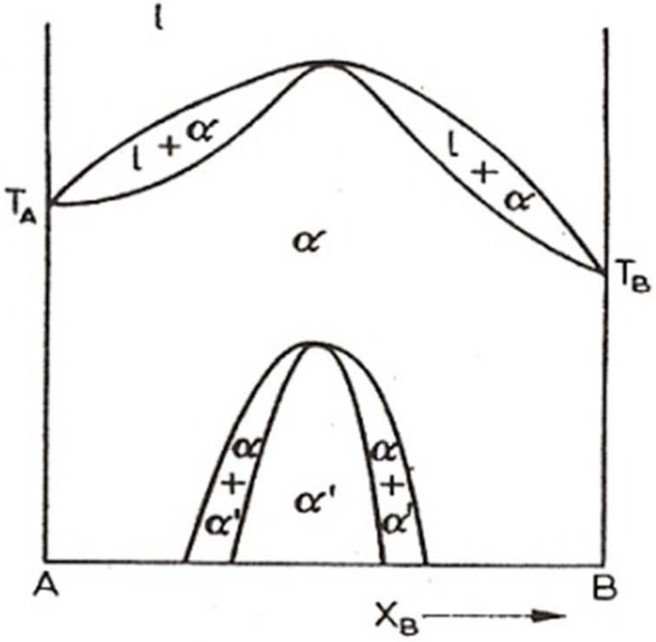


Fig. 33. Appearance of an ordered α′ phase at low temperatures.

3.2.6 Pressure-Temperature-Composition phase diagram for a system with continuous series of solutions

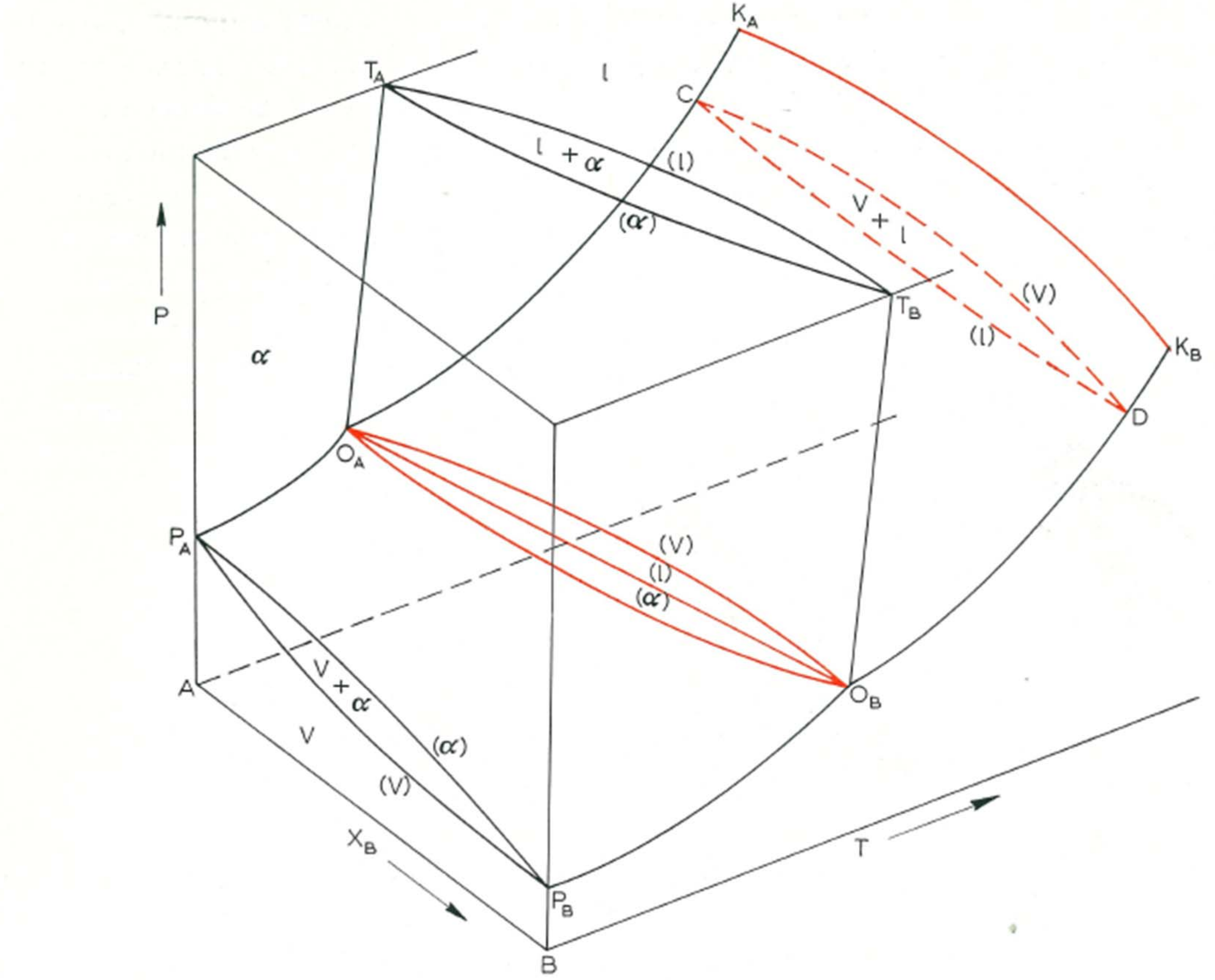


Fig. 35. Pressure–temperature–composition phase diagram for a system with continuous series of solutions

3.2.6 Pressure-Temperature-Composition phase diagram for a system with continuous series of solutions

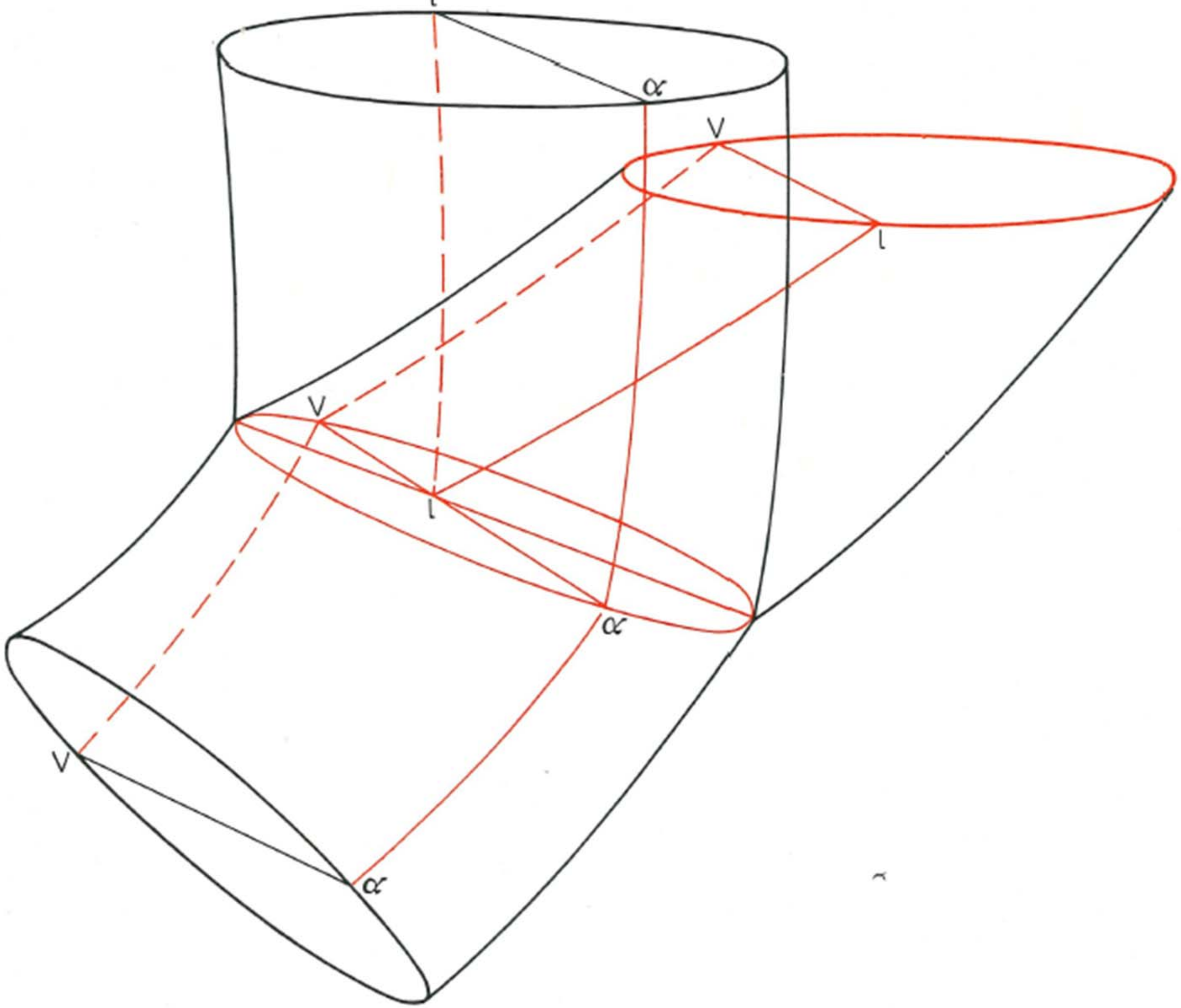


Fig. 36. Formation of a three-phase tie line $Vl\alpha$.

3.2.6 Pressure-Temperature-Composition phase diagram for a system with continuous series of solutions

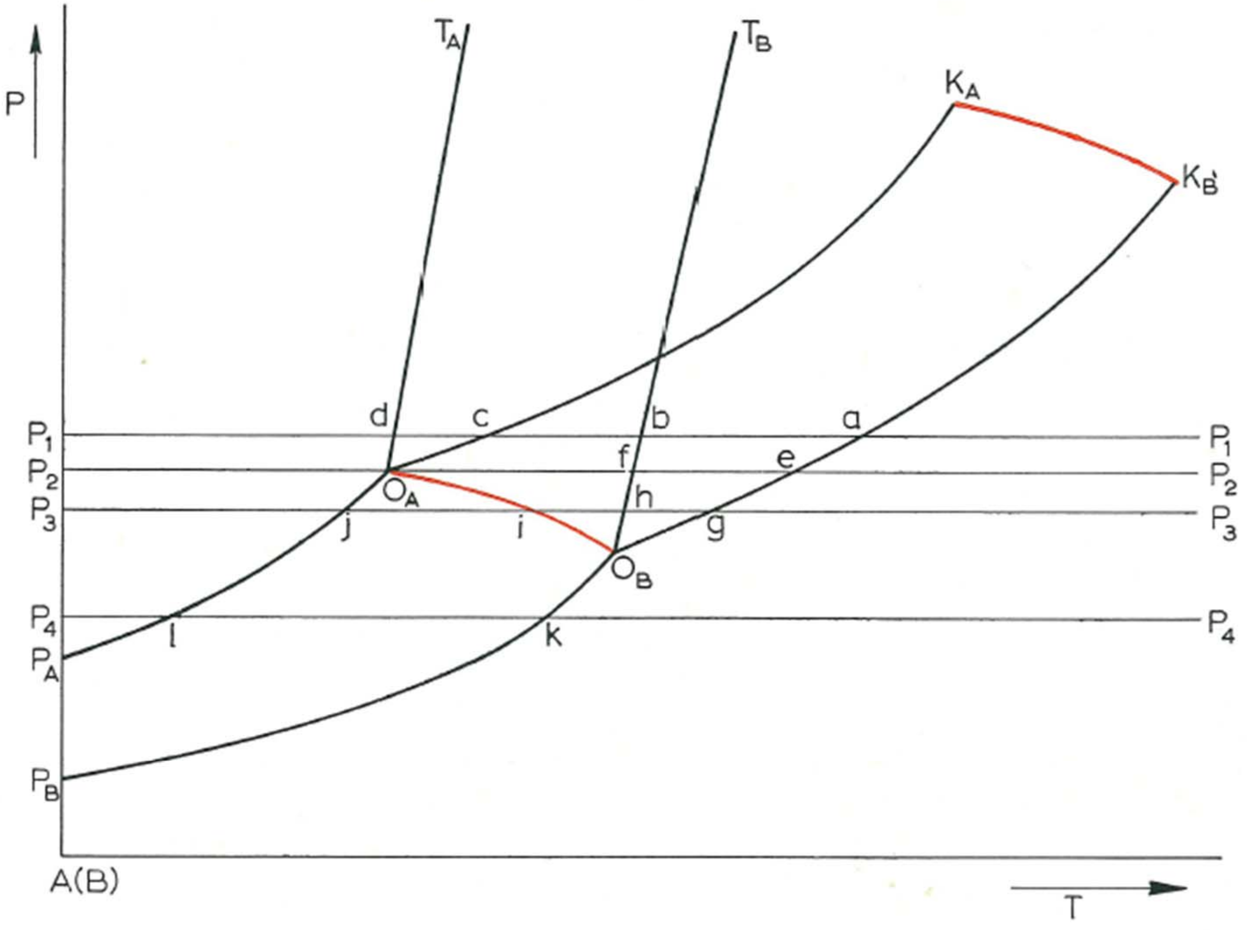


Fig. 37. Two-dimensional projection of Fig. 35 on the P–T plane for component A. P_AO_A — equilibrium between V_A and α_A; P_BO_B — V_B and α_B; O_AT_A — l_A and α_A; O_BT_B — l_B and α_B; O_AK_A — V_A and l_A; O_BK_B — V_B and l_B; O_AO_B — V_{AB}, l_{AB} and α_{AB}; O_A — V_A, l_A and α_A; O_B — V_B, l_B and α_B; K_AK_B — $V_{AB} = l_{AB}$.

3.2.6 Pressure-Temperature-Composition phase diagram for a system with continuous series of solutions

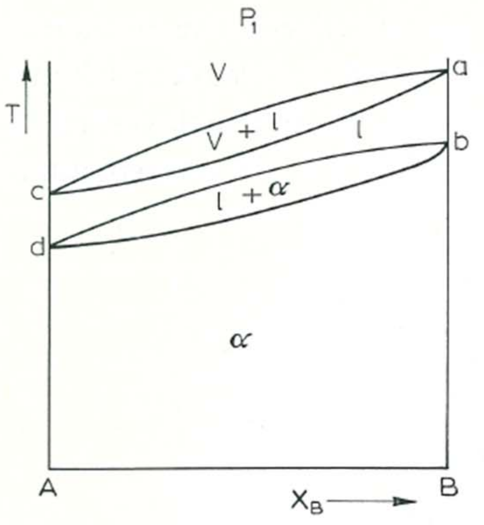


Fig. 38. T–X section through Fig. 35 at a pressure P_1 where $K_B > P_1 > O_A$.

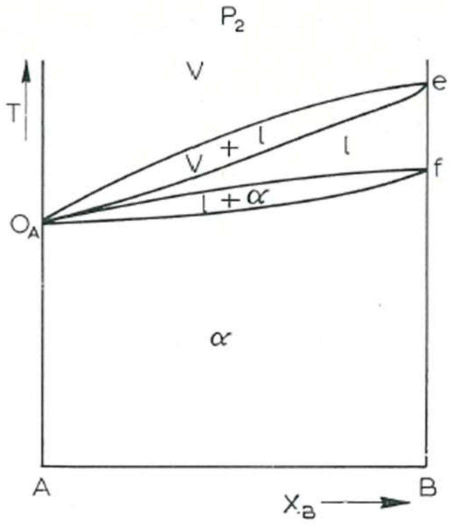


Fig. 39. T–X section through Fig. 35 at a pressure P_2 where $P_2 = O_A$

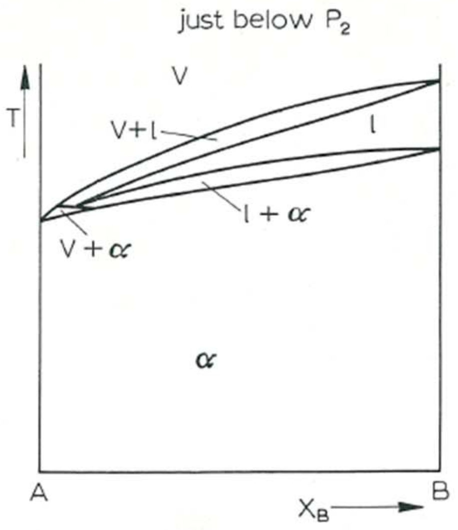


Fig. 40. T–X section through Fig. 35 at a pressure just below P_2.

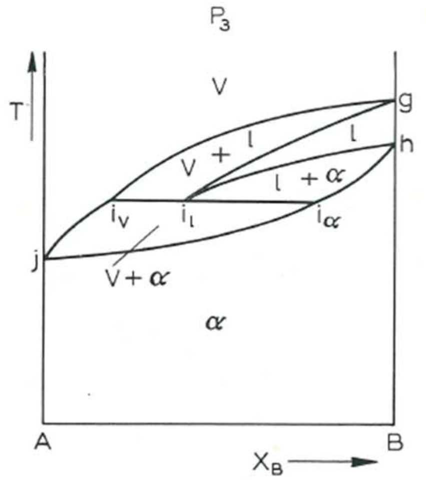


Fig. 41. T–X section through Fig. 35 at a pressure P_3 where $O_A > P_3 > O_B$.

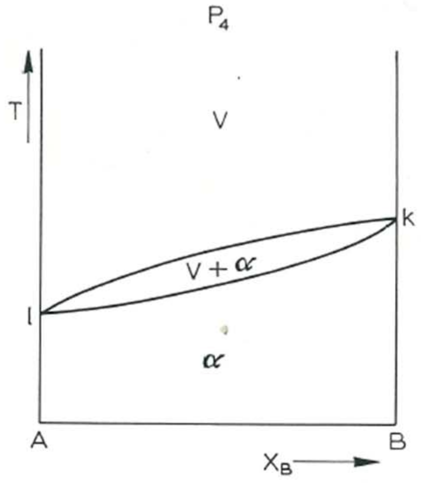


Fig. 42. T–X section through Fig. 35 at a pressure P_4 where $O_B > P_4 > P_B$.

Contents for today's class

- Equilibrium in Heterogeneous Systems

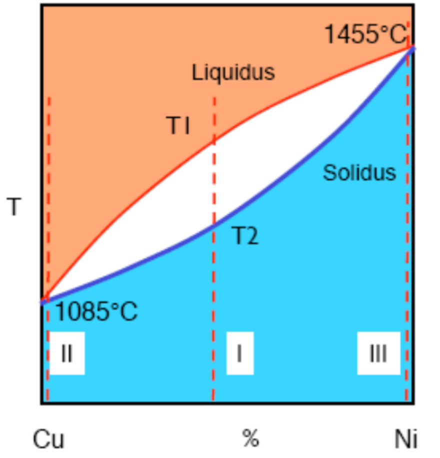
$G_0^{\beta} > G_0^{\alpha} > G_0^{\alpha+\beta}$ ➡ α + β separation ➡ unified chemical potential

- Binary phase diagrams

1) Simple Phase Diagrams

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

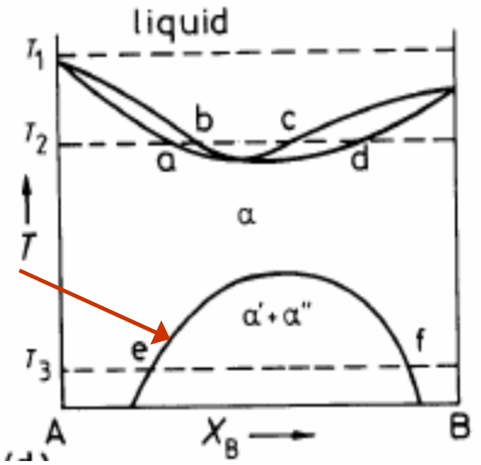
Assume: (1) completely miscible in solid and liquid.
(2) Both are ideal soln.



2) Variant of the simple phase diagram

$\Delta H^{\alpha}_{mix} > \Delta H^{l}_{mix} > 0$

miscibility gab



$\Delta H^{\alpha}_{mix} < \Delta H^{l}_{mix} < 0$

Ordered phase