2023 Fall

“Phase Transformation *in* Materials”

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- 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

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

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

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

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

μ는 조성에 의해 결정되기 때문에 dn_A가 매우 작아서 조성변화 없어야

- 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**

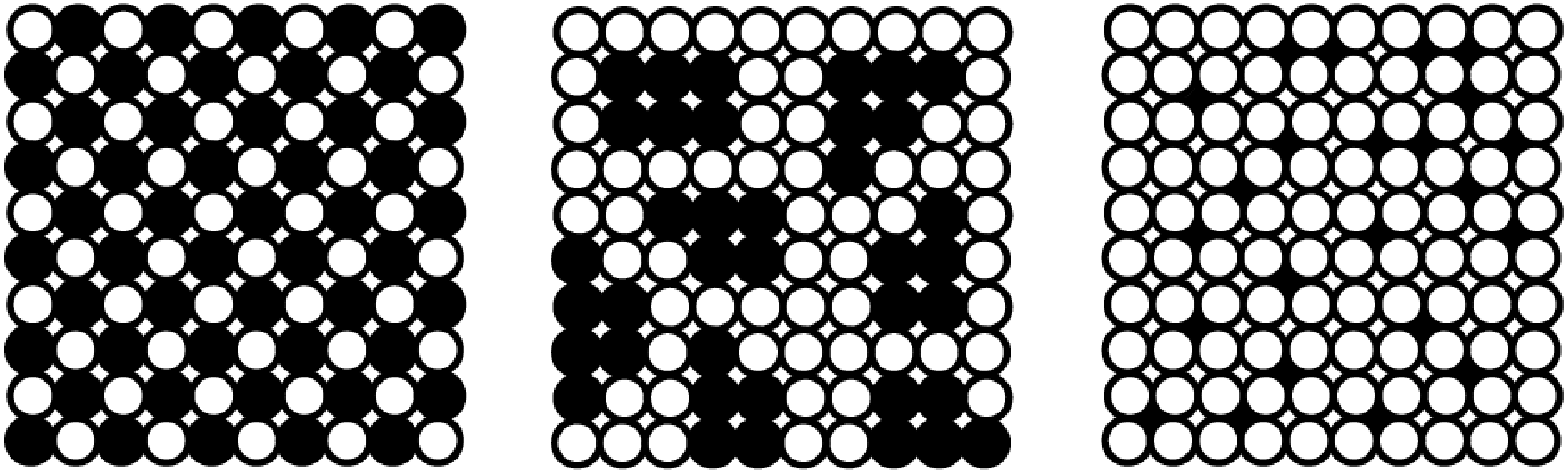


Fig. 1.8 (a) $\varepsilon < 0$, $\Delta H_{mix} < 0$ (b) $\varepsilon > 0$, $\Delta H_{mix} > 0$ (c) when the size difference is large

Ordered alloys

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

Clustering

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

strain effect

Interstitial solution

Q9: Ordered phase II:

“Long range order (LRO)”

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

*** Solid solution → ordered phase**

→ random mixing

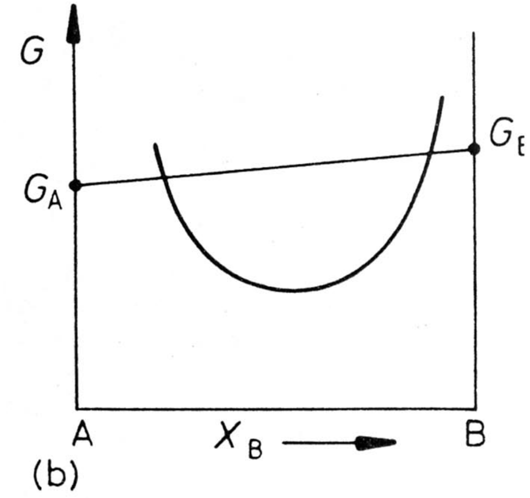
→ entropy ↑

negative enthalpy ↓

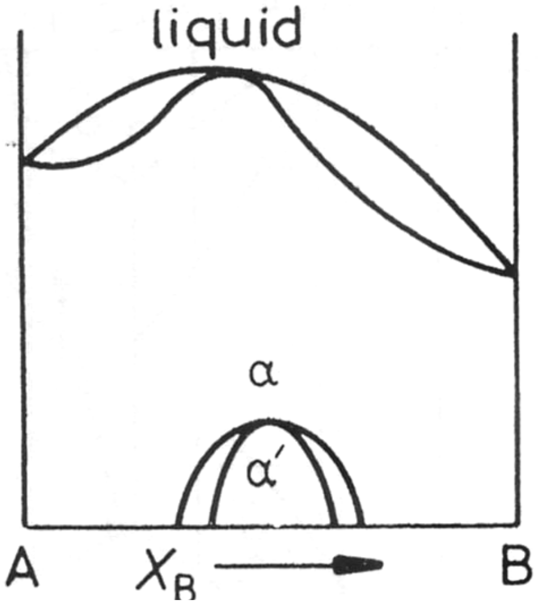
$$\boxed{\Delta H^{S}_{mix} < 0}$$

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 ↓

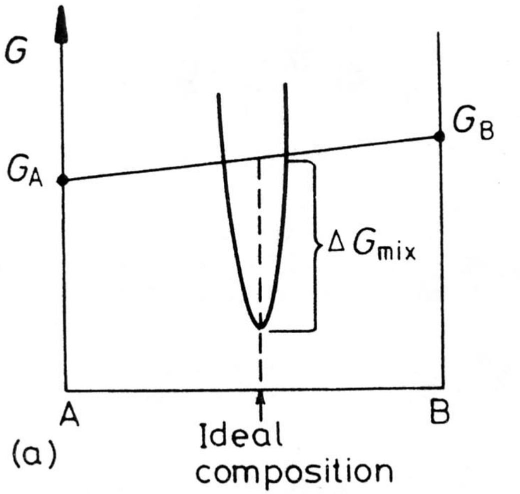
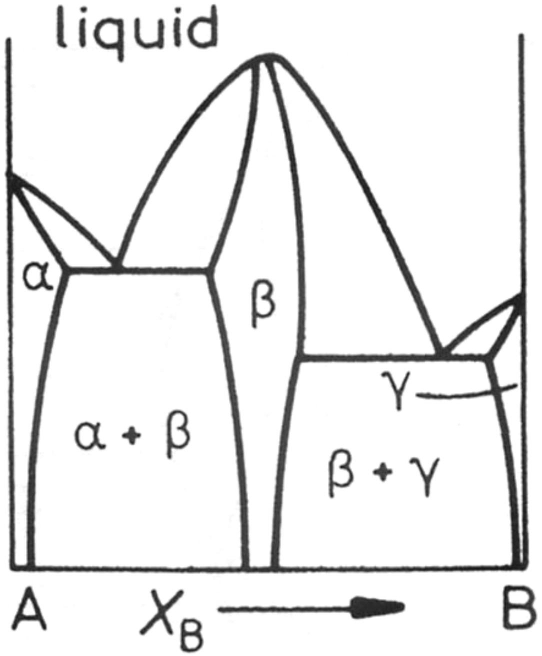


Fig. 1.23 Free energy curves for intermed
pound with a very narrow stability range, (
stability range.

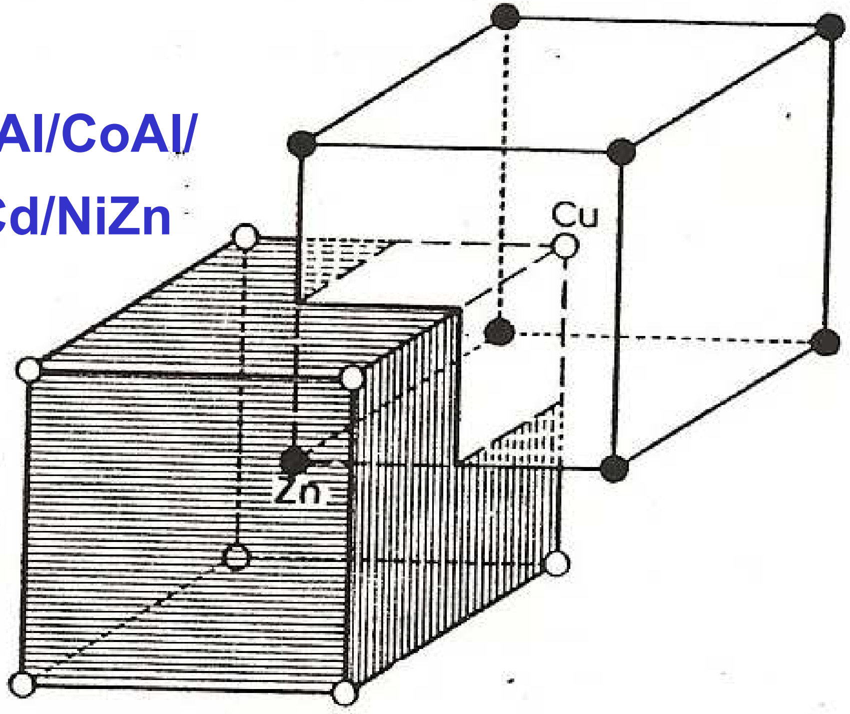


Superlattice formation: order-disorder transformation

- $\varepsilon < 0$, $\Delta H_{mix} < 0$
- between dissimilar atoms than between similar atoms
- Large electrochemical factor: tendency for the solute atoms to avoid each other and to associate with the solvent atoms
- Size factor just within the favorable limit: lead to atomic rearrangement so as to relieve the lattice distortion imposed by the solute atoms

(a)$L2_0$:

CuZn/FeCo/NiAl/CoAl/FeAl/AgMg/AuCd/NiZn



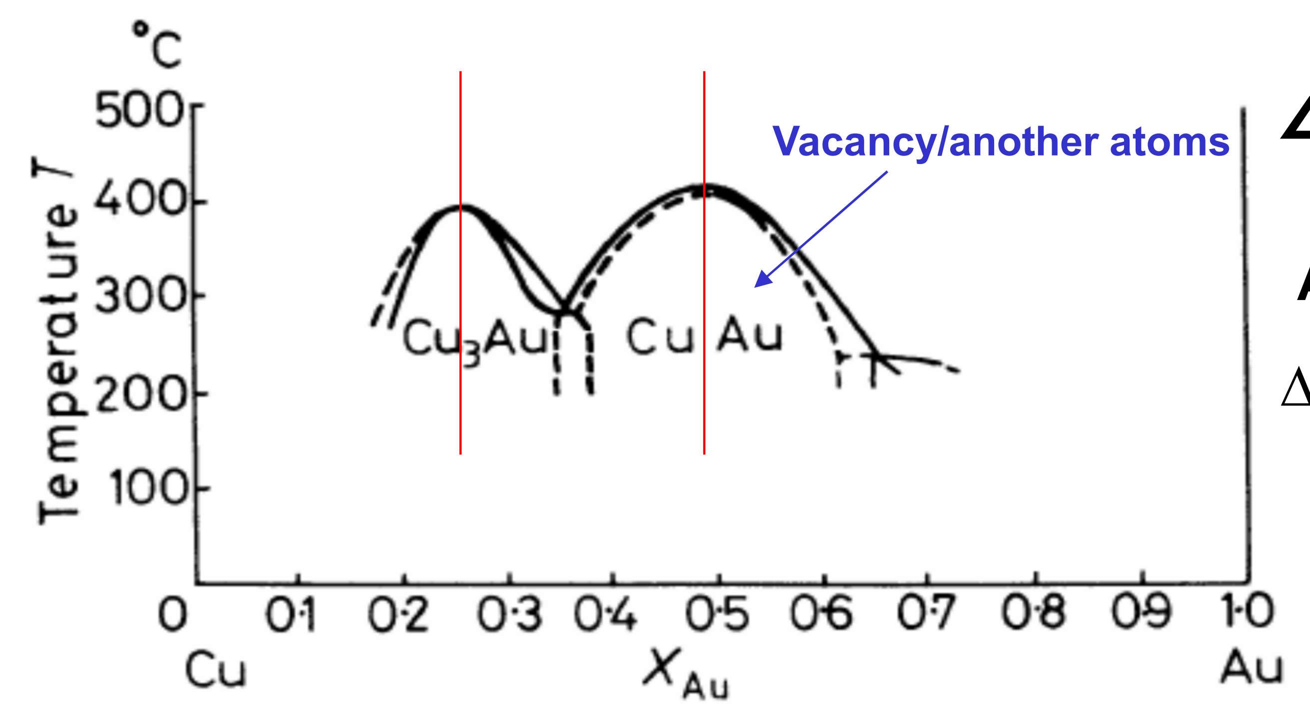
β brass superlattice viewed as two inter-penetrating cubic lattices

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

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.



ΔS_{mix}~small

At high Temp.,

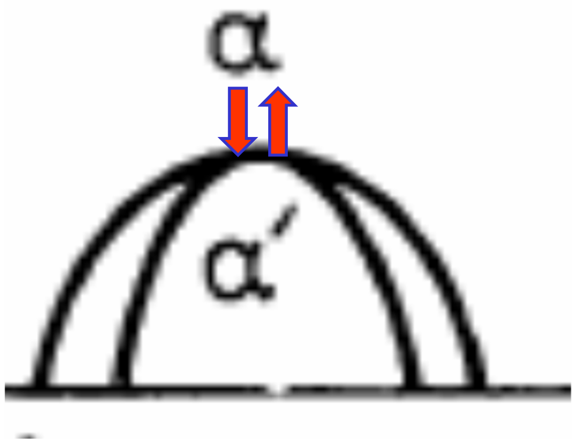
ΔG_{mix}~ large (-)

- 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.

Order-disorder phase transformation

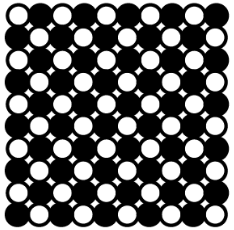
- Not classical phase change=~not depend on diffusion process
- change of temperature allowed a continuous re-arrangement of atoms without changing the phase = “2^{nd} order transition”
- boundary: ordered lattice & disordered lattice/phase rule could not applied

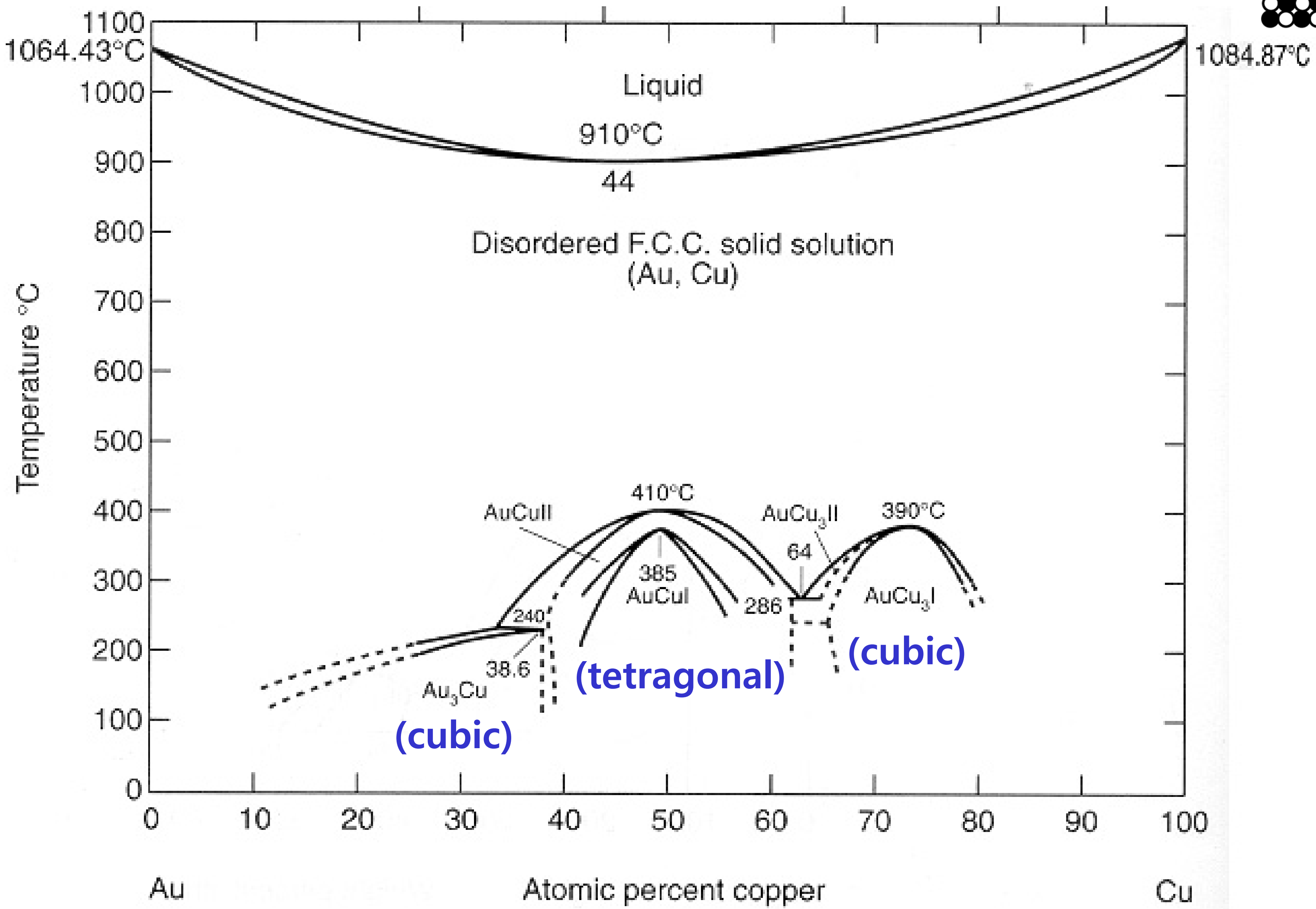
  there are cases in which an ordered phase of one composition exists in equilibrium with a disordered phase of a different composition.
- Simple composition of the type AB or AB_3 can the transformation (i.e. at the temperature maximum) be considered diffusionless.



Ordered Phase

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





(tetragonal)

(cubic)

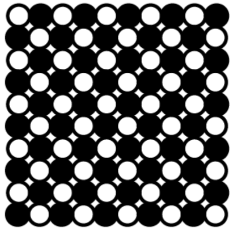
(cubic)

(fcc)

(complete solid solution)

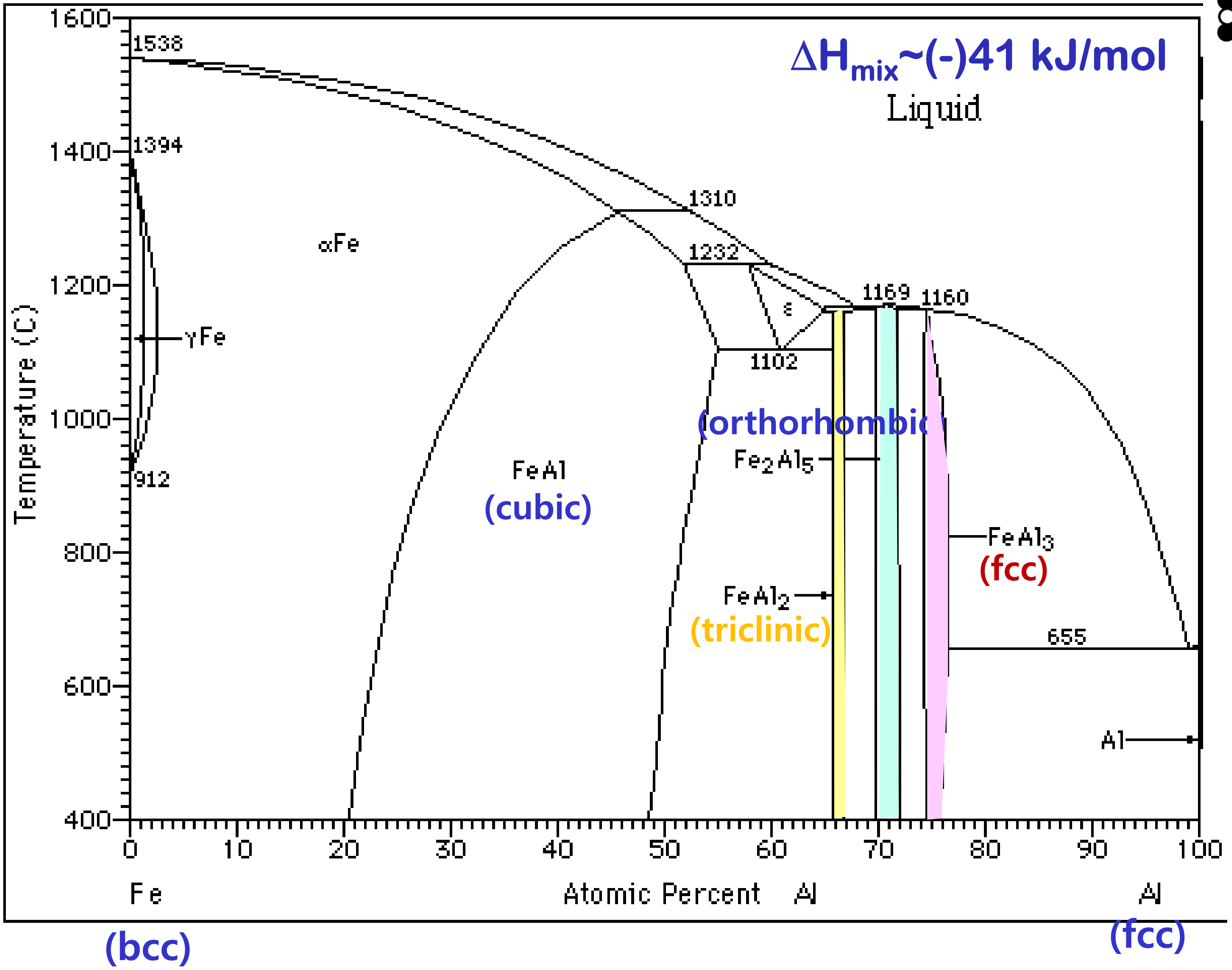
(fcc)

Intermediate Phase



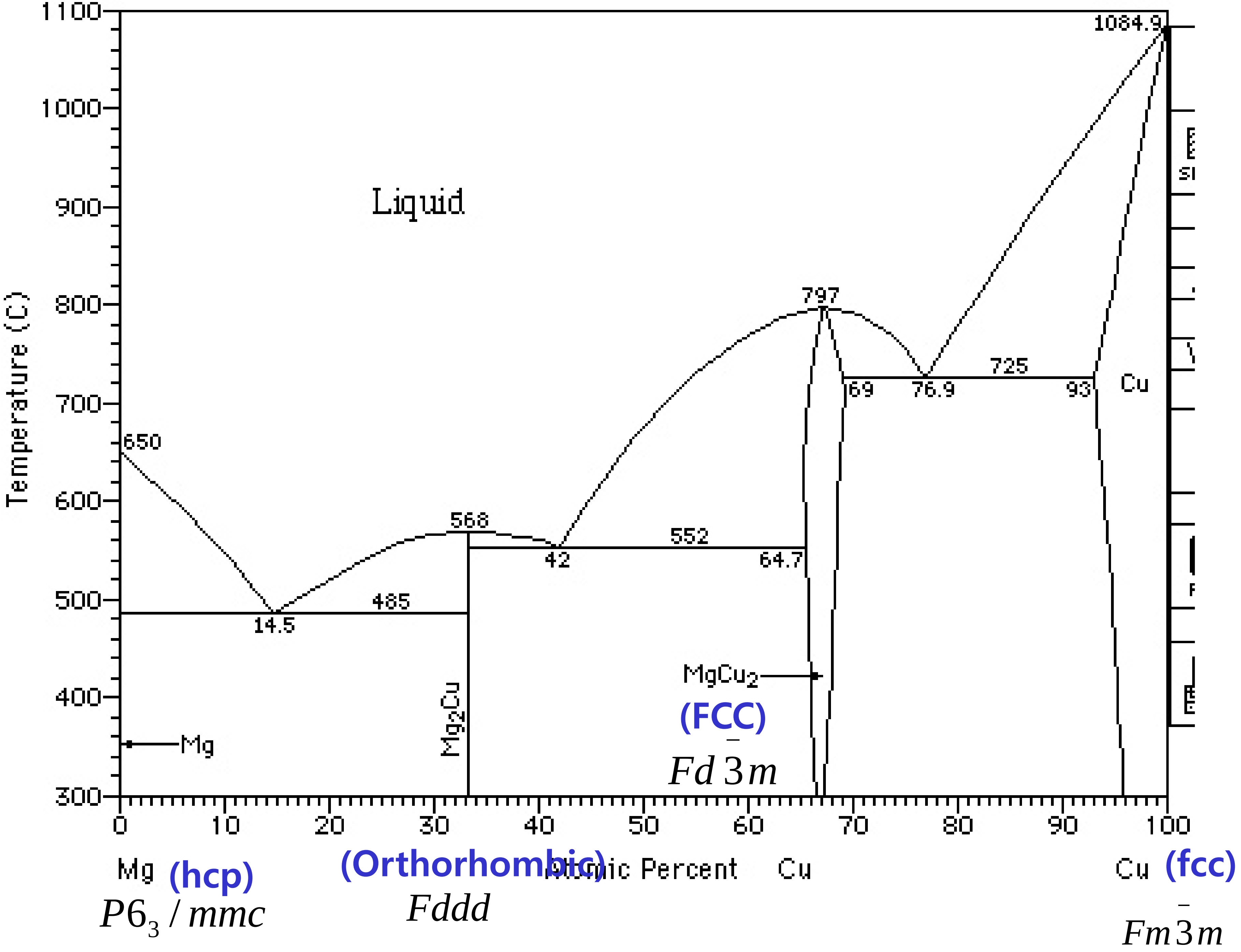
$\varepsilon < 0,\ \Delta H_{mix} < 0$

ΔH_{mix}~(-)41 kJ/mol



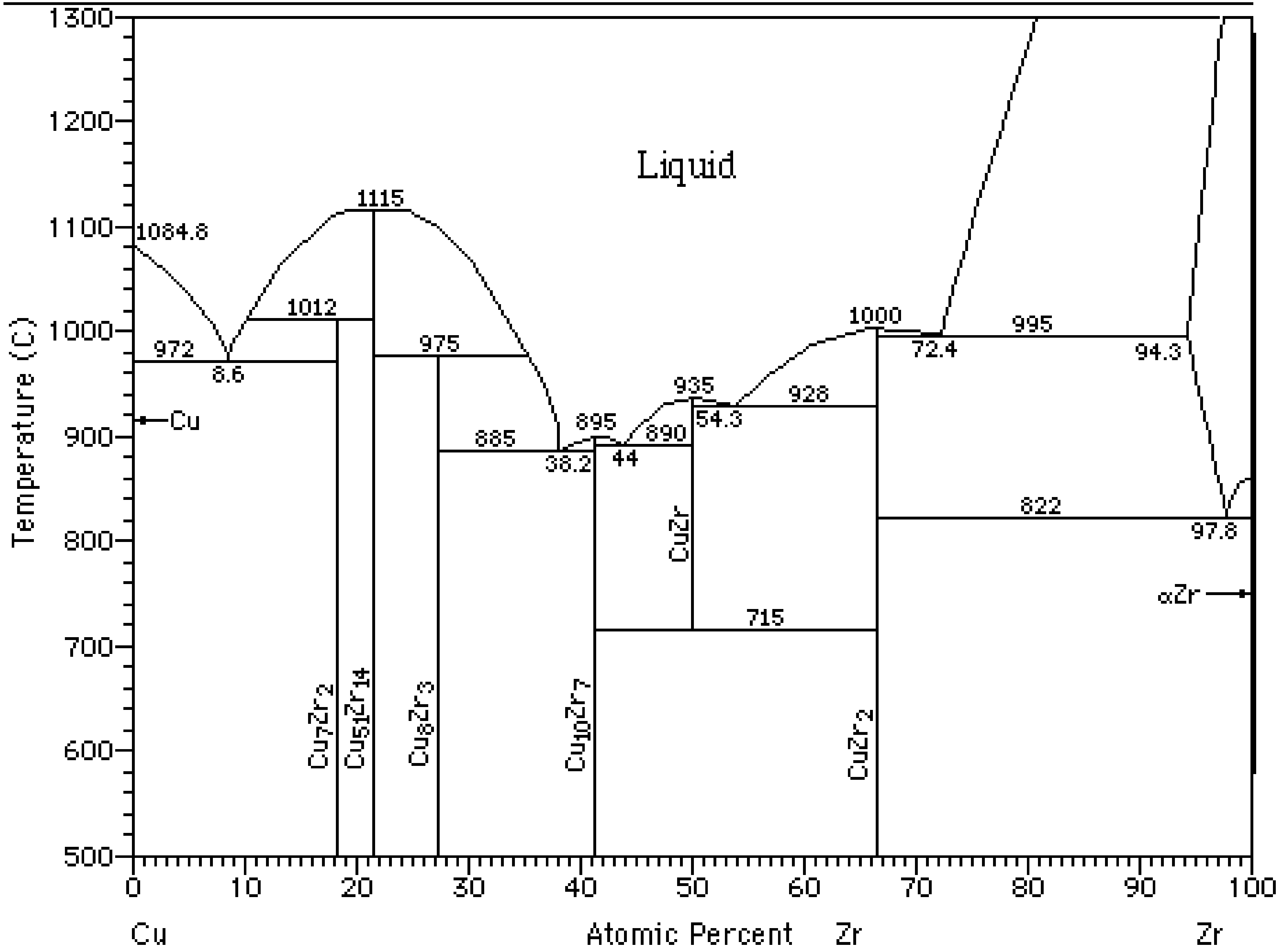
Intermediate Phase

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



Intermediate Phase

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



Intermediate Phase

_"different crystal structure as either of the pure component"

3 main factors

determining the structure of Intermediate phase ?

1) Relative atomic size

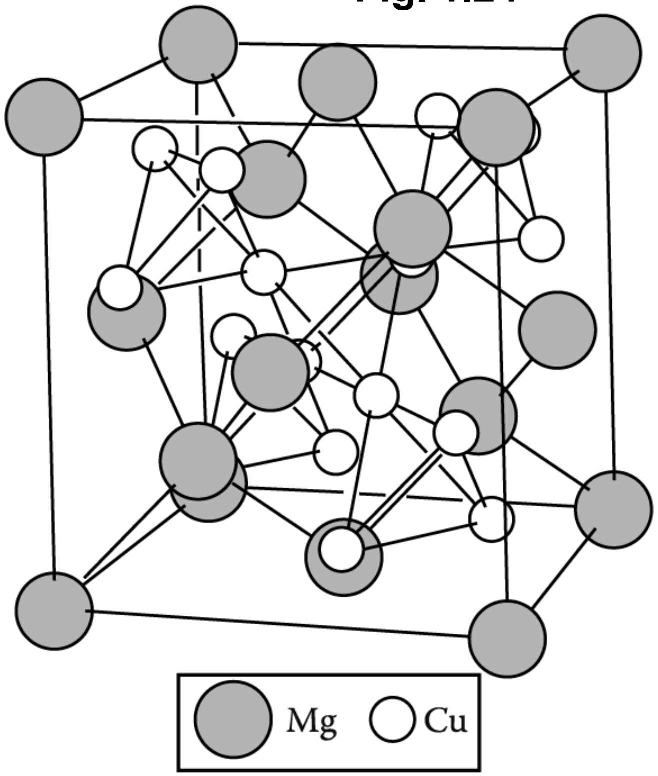
- **Laves phase** (size difference: 1.1~1.6 ex: $MgCu_2$)

  fill space most efficiently ~ stable

- **Interstitial compound**: MX, M_2X, MX_2, M_6X

  M= Cubic or HCP ex: Zr, Ti, V, Cr, etc, X= H, B, C, and N

Fig. 1.24



$MgCu_2$ (A Laves phase)

2) Relative valency electron

- **electron phases** ex_α & β brass

  # of valency electrons per unit cell

  → depending on compositional change

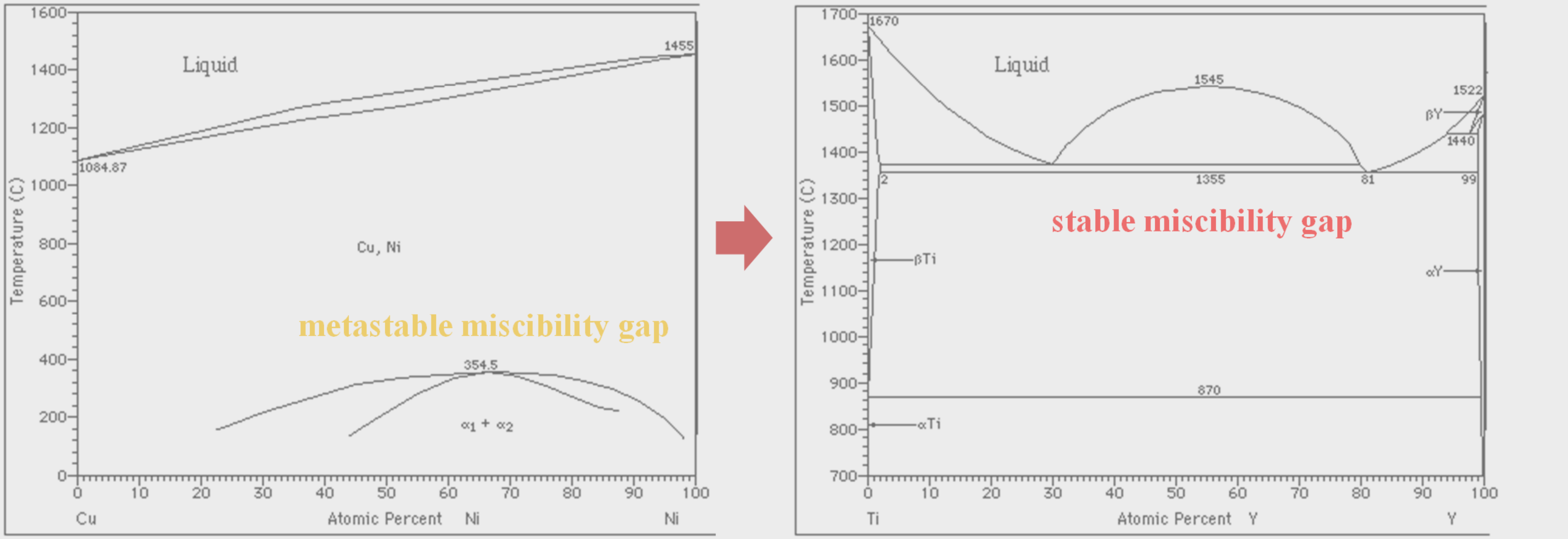
3) Electronegativity

- very different electronegativites → ionic bond_normal valency compounds

  ex Mg_2Sn

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

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



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

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

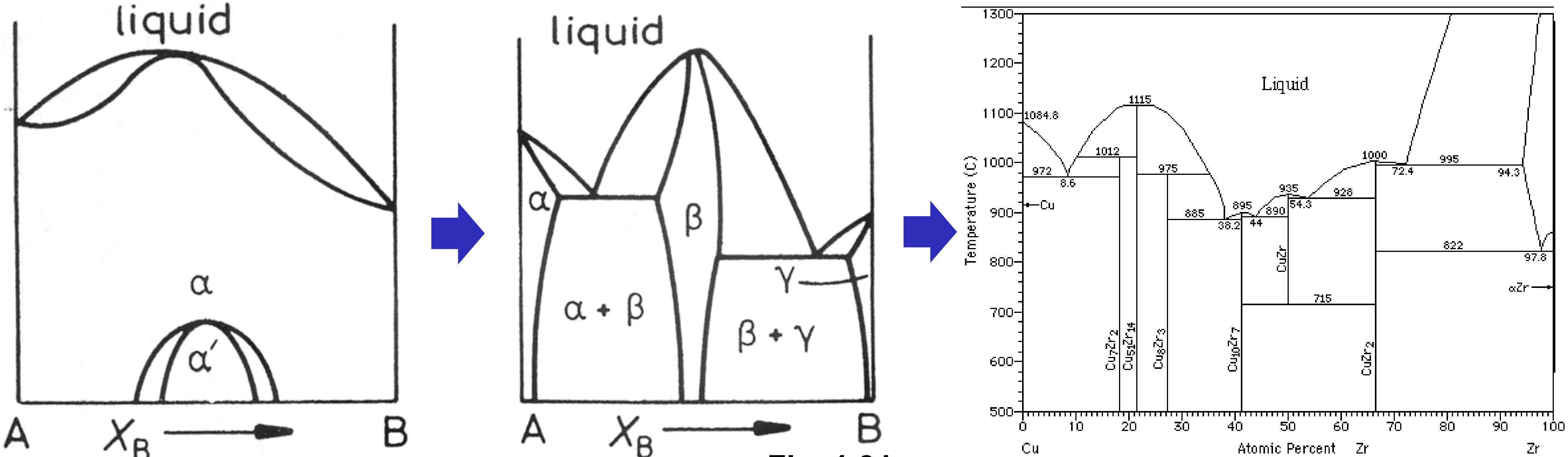


Fig. 1.31

Q1: “Clustering”? → Phase separation

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. → Entropy effect ↑ → Solution stability ↑

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

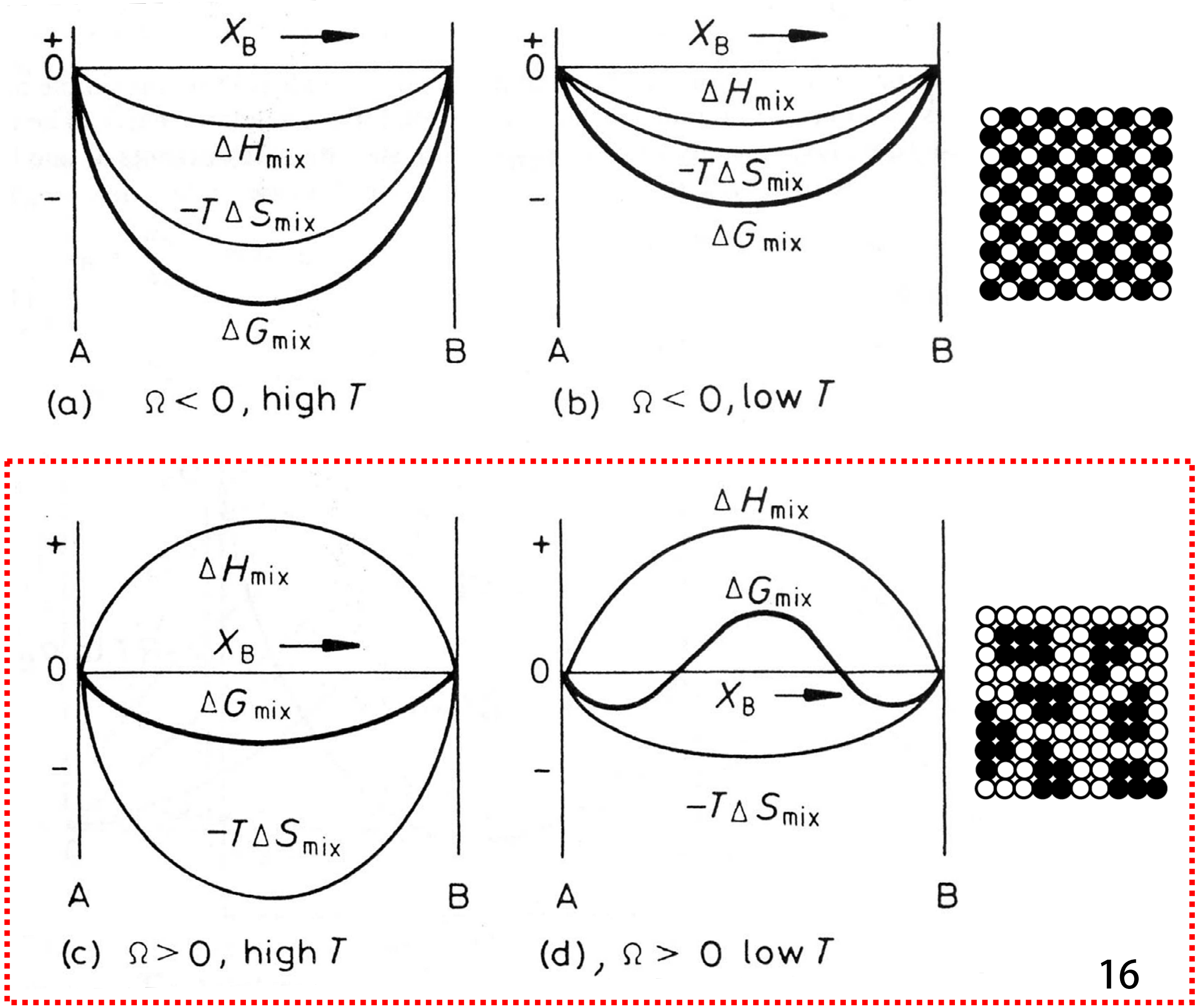
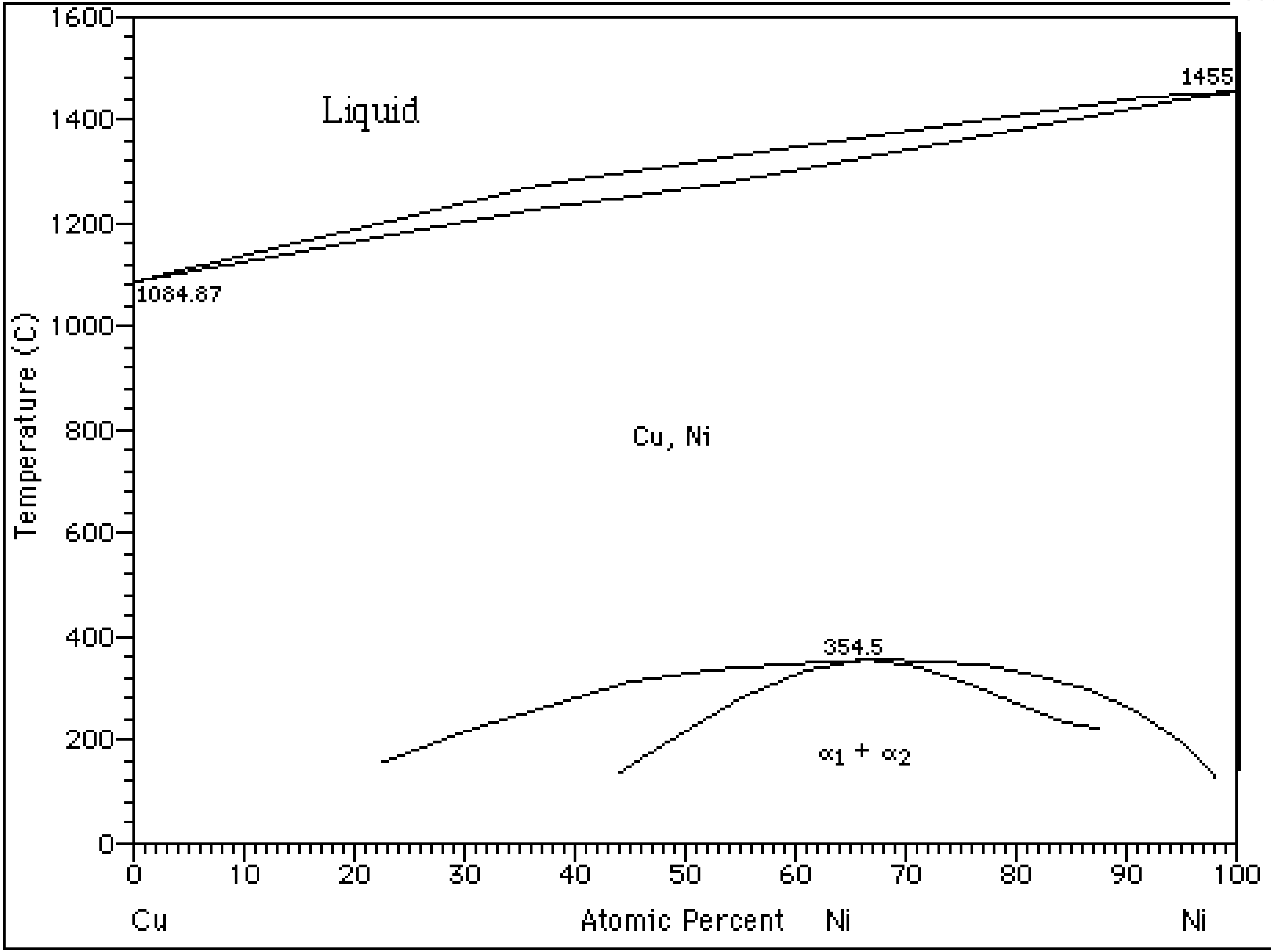
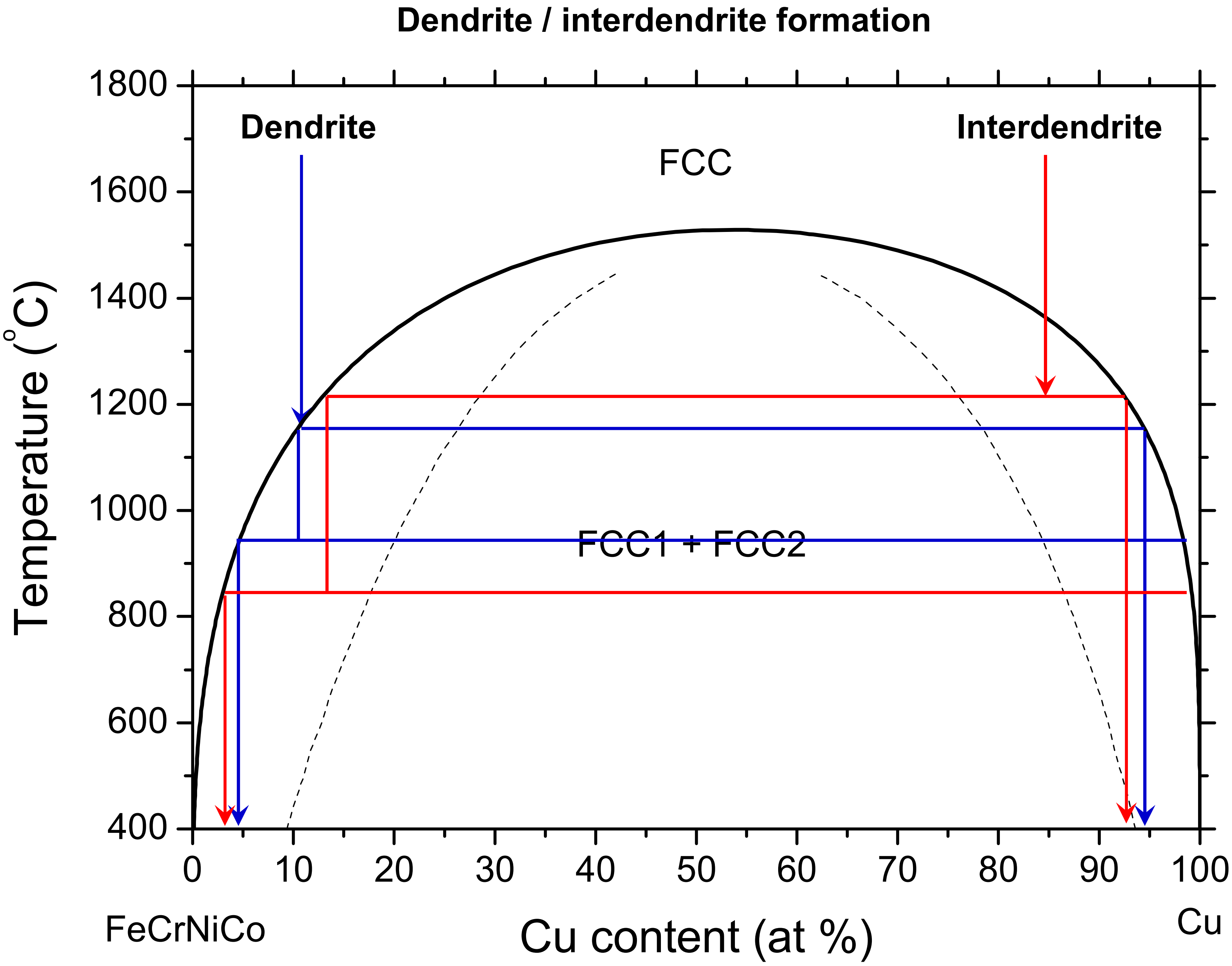


Fig. 1.15

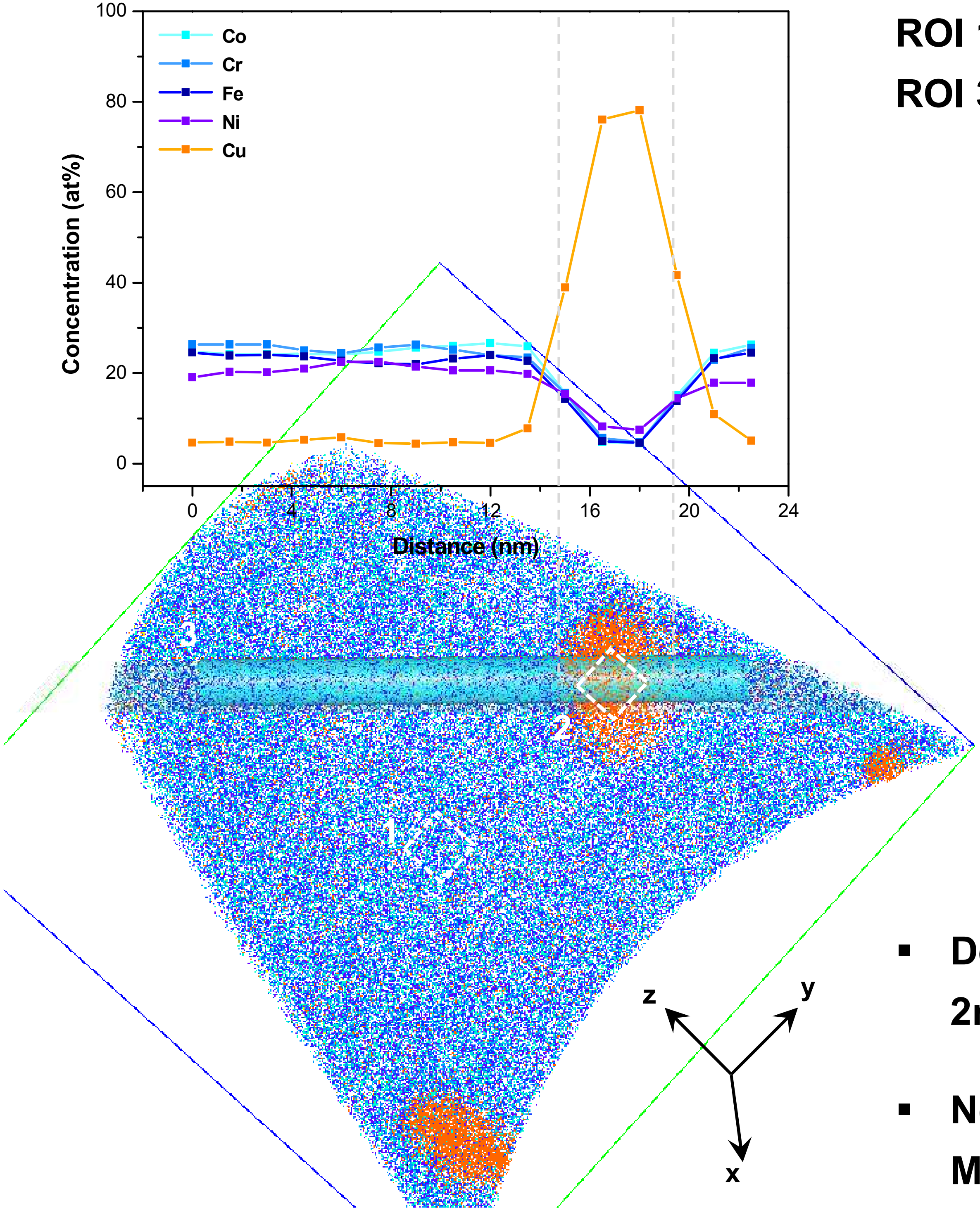
$\varepsilon > 0$, $\Delta H_{mix} > 0$ / $\Delta H_{mix} \sim +26$ kJ/mol



Cooling process in the miscibility gap



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%
Co	26.19
Cr	24.15
Fe	24.59
Ni	19.59
Cu	4.74

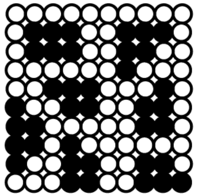
2	at%
Co	0.33
Cr	0.46
Fe	0.39
Ni	5.00
Cu	93.56

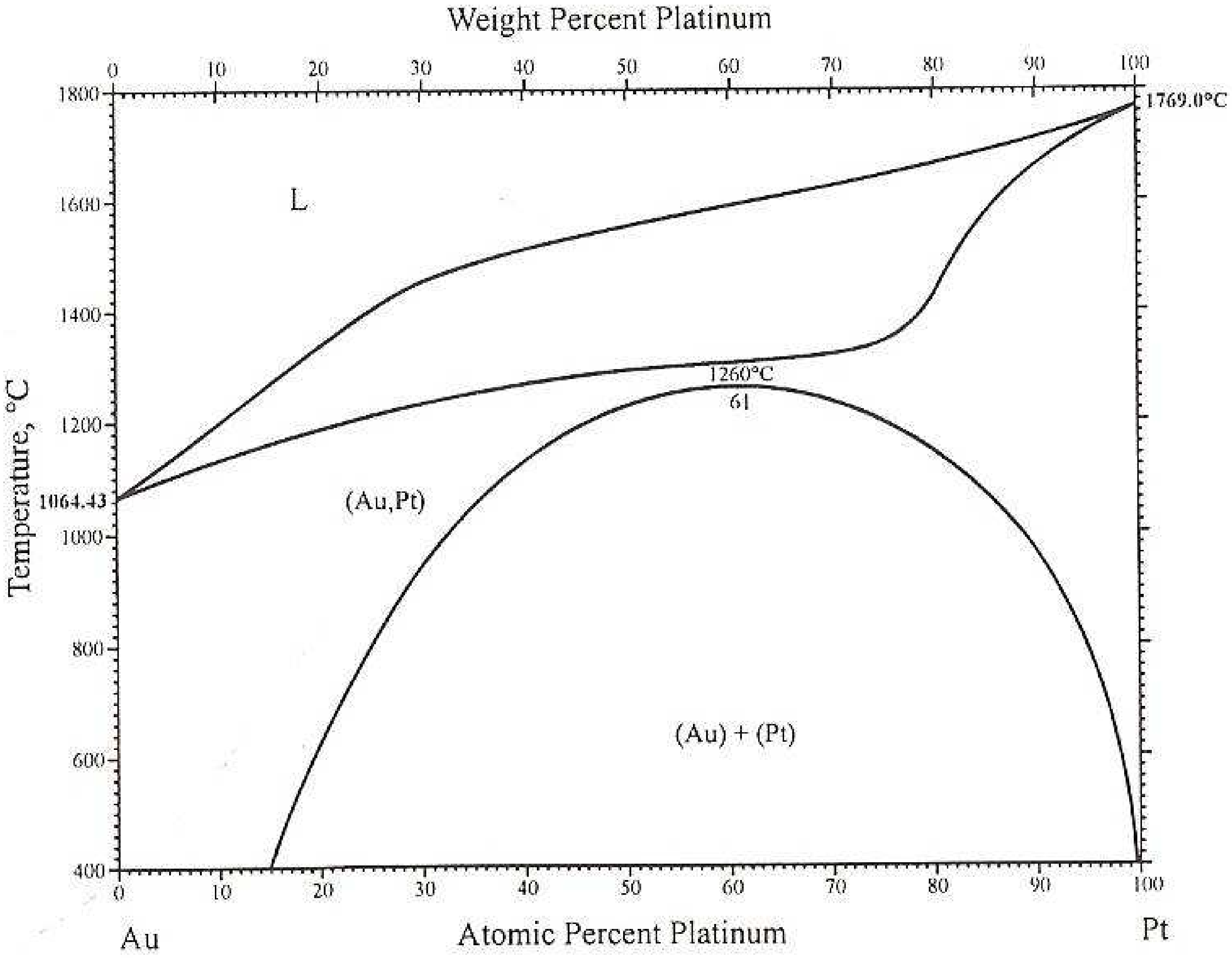
3-1’	at%
Co	25.29
Cr	25.63
Fe	23.63
Ni	20.66
Cu	4.42

3-2’	at%
Co	2.01
Cr	3.35
Fe	2.56
Ni	6.90
Cu	84.92

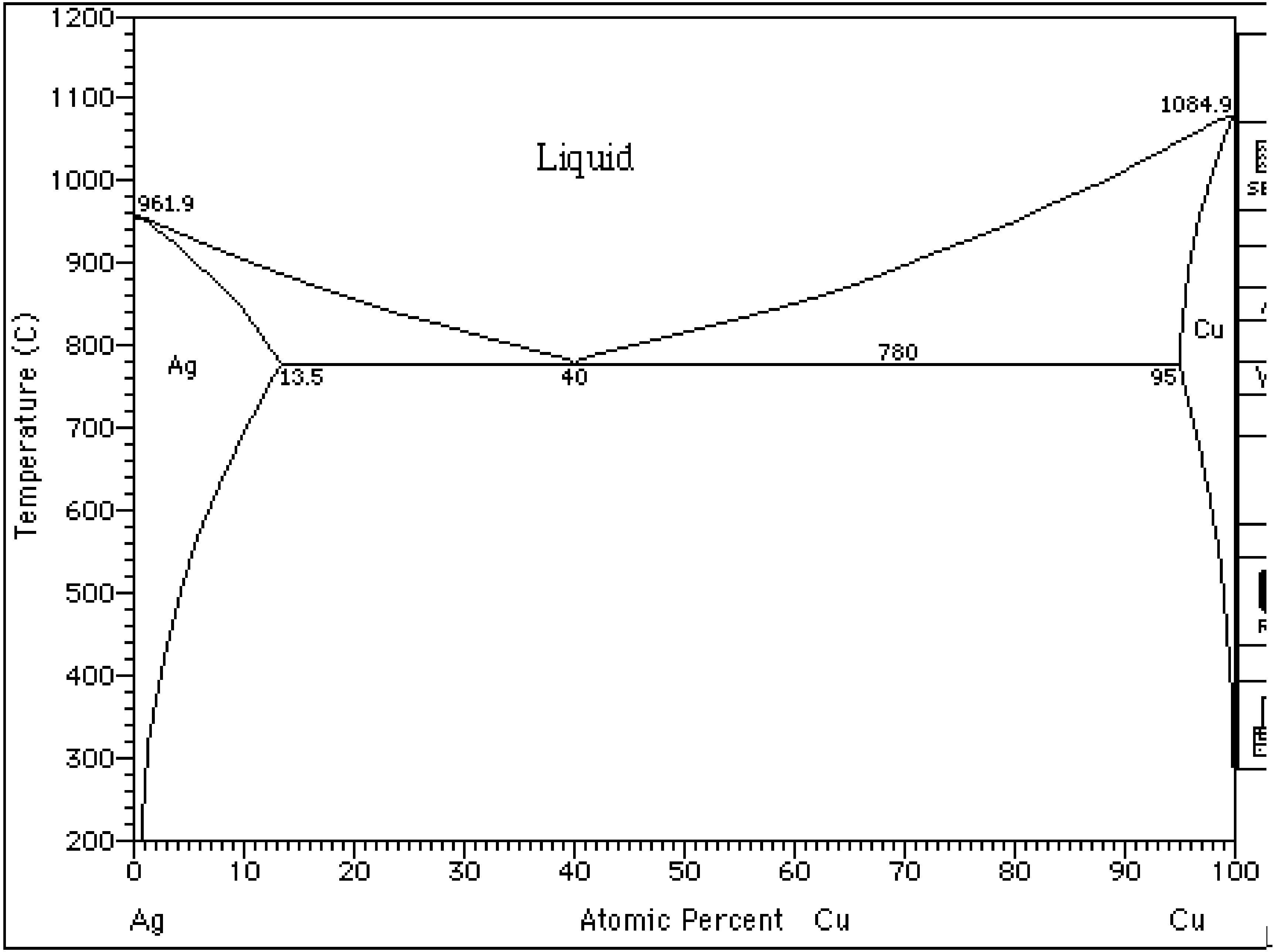
- **Dendrite region: matrix (4.74 at%Cu) + 2nd phase (93.56 at%Cu)**
- **No segregation at the interface between Matrix and 2nd phase**

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

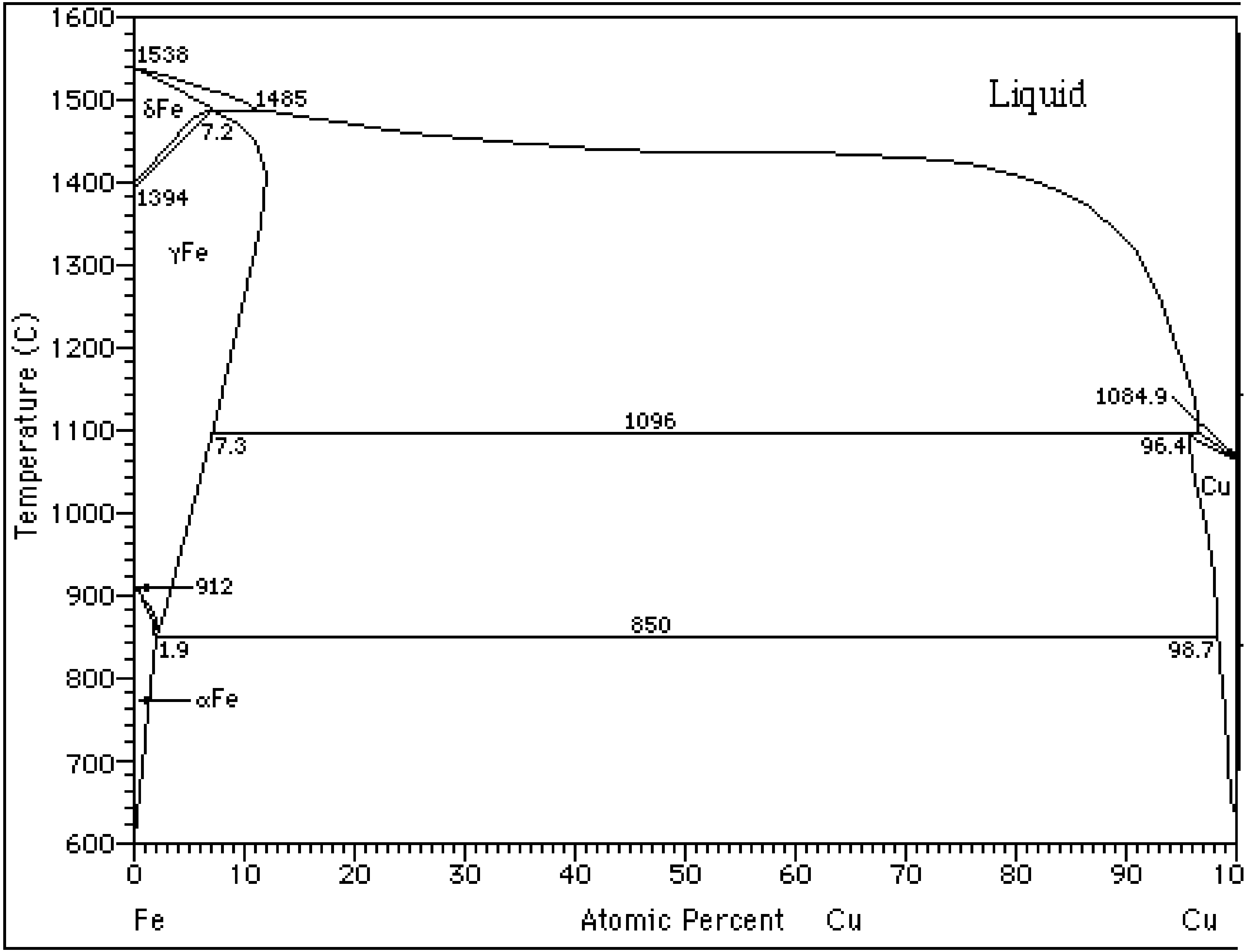




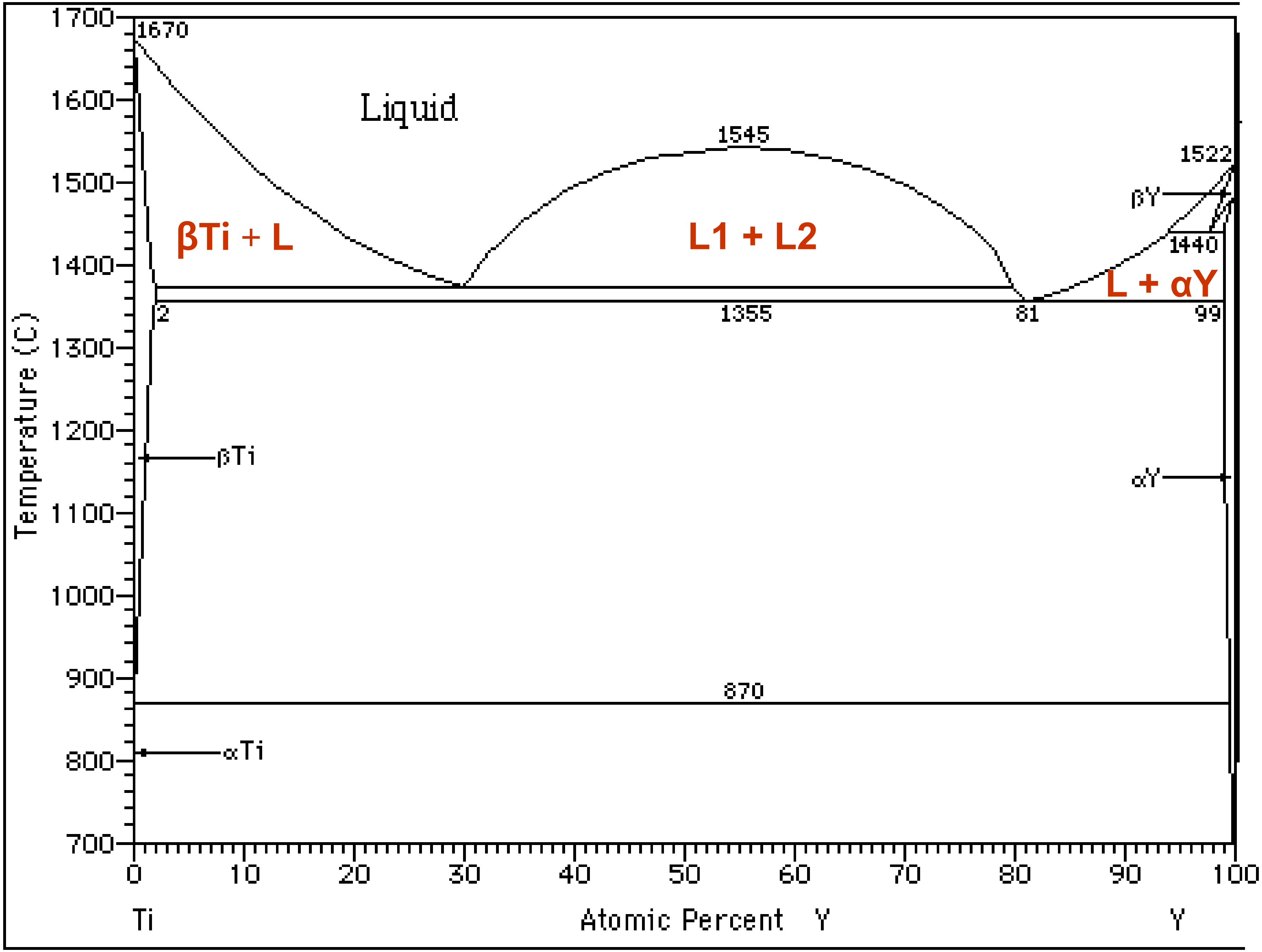
$\varepsilon > 0, \Delta H_{mix} > 0 / \Delta H_{mix} \sim +5$ kJ/mol



ε >> 0, ΔH_{mix} >> 0 / ΔH_{mix} ~ +60 kJ/mol



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



Positive heat of mixing relation among constituent elements

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

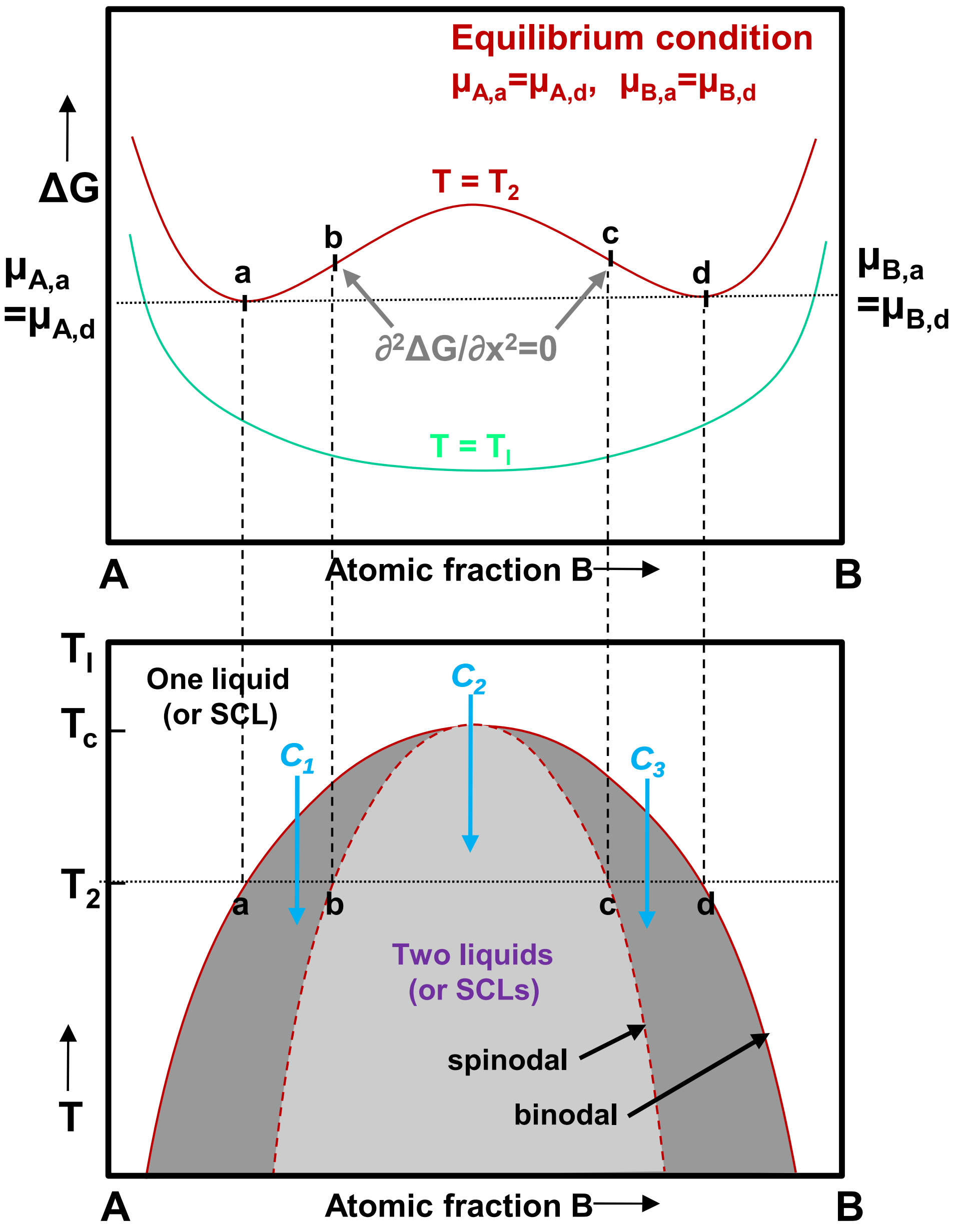
$\Delta H_{mix} \gg 0$ between A & B

⬇

creates (meta)stable miscibility gap
in limited composition range

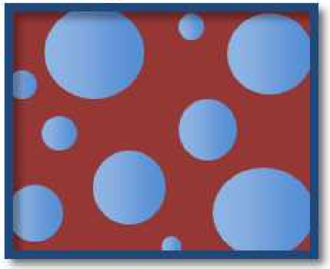
⬇

Phase separation to A-rich & B-rich phase



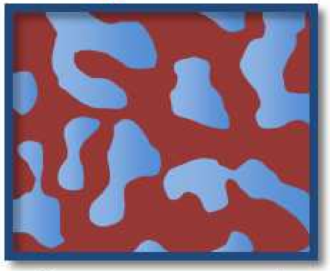
- **Different two-phase structure by initial composition before phase separation**

$C=C_1$



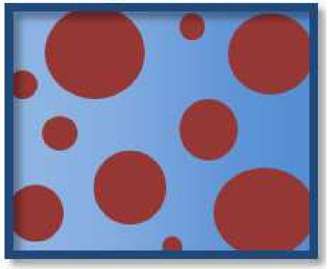
A-rich matrix
B-rich droplet

$C=C_2$



Interconnected
structure

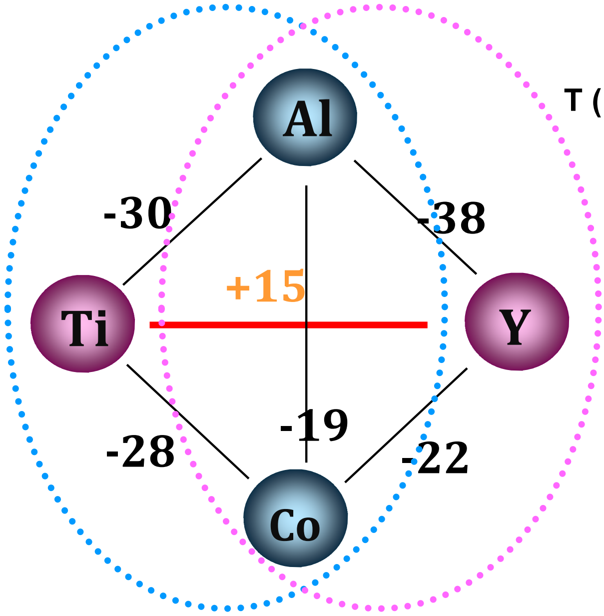
$C=C_3$

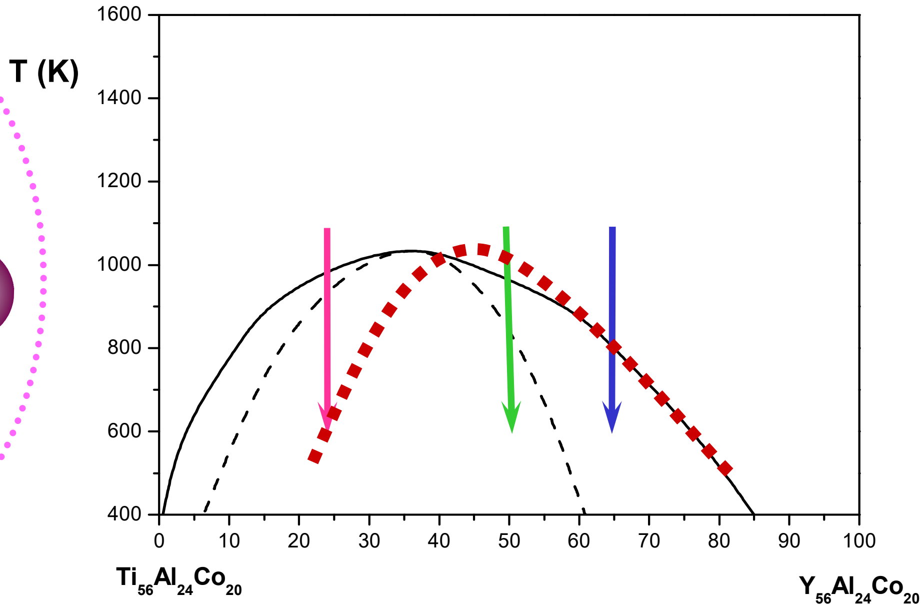


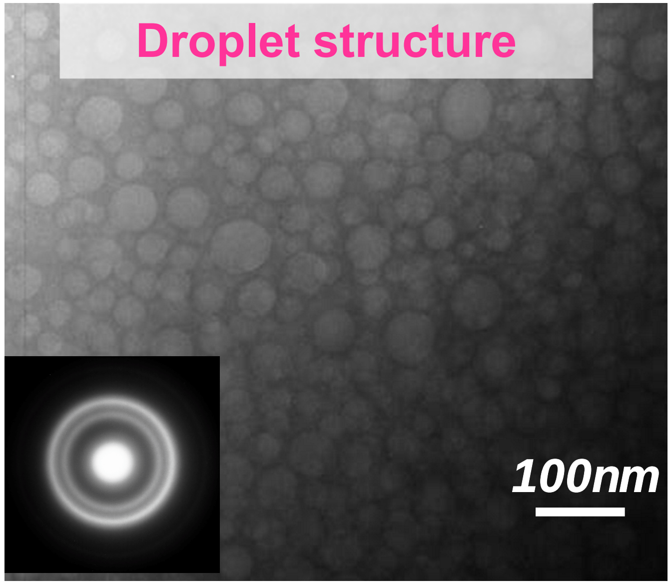
B-rich matrix
A-rich droplet

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

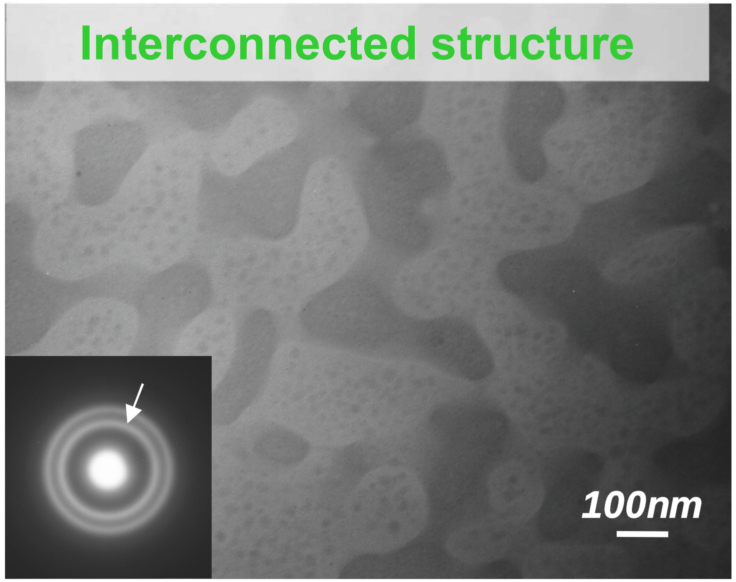
* Ti-Y-Al-Co system



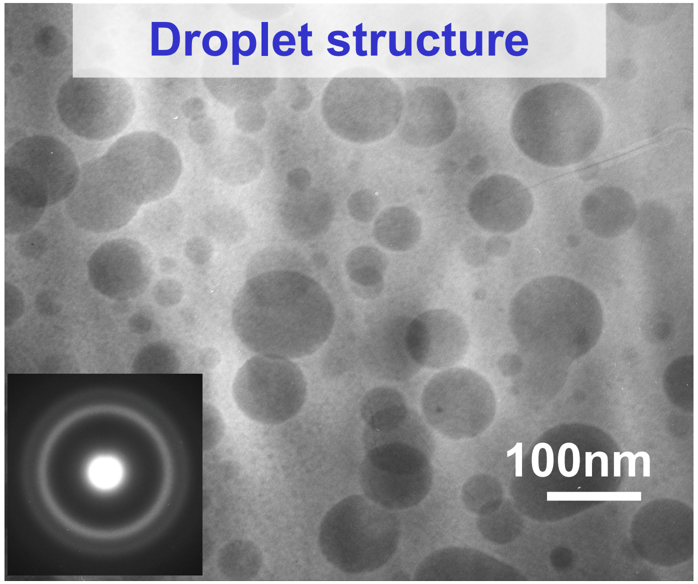




$(Y_{56}Al_{24}Co_{20})_{25}(Ti_{56}Al_{24}Co_{20})_{75}$



$(Y_{56}Al_{24}Co_{20})_{50}(Ti_{56}Al_{24}Co_{20})_{50}$



$(Y_{56}Al_{24}Co_{20})_{65}(Ti_{56}Al_{24}Co_{20})_{35}$

* La-Zr-Al-Cu-Ni system

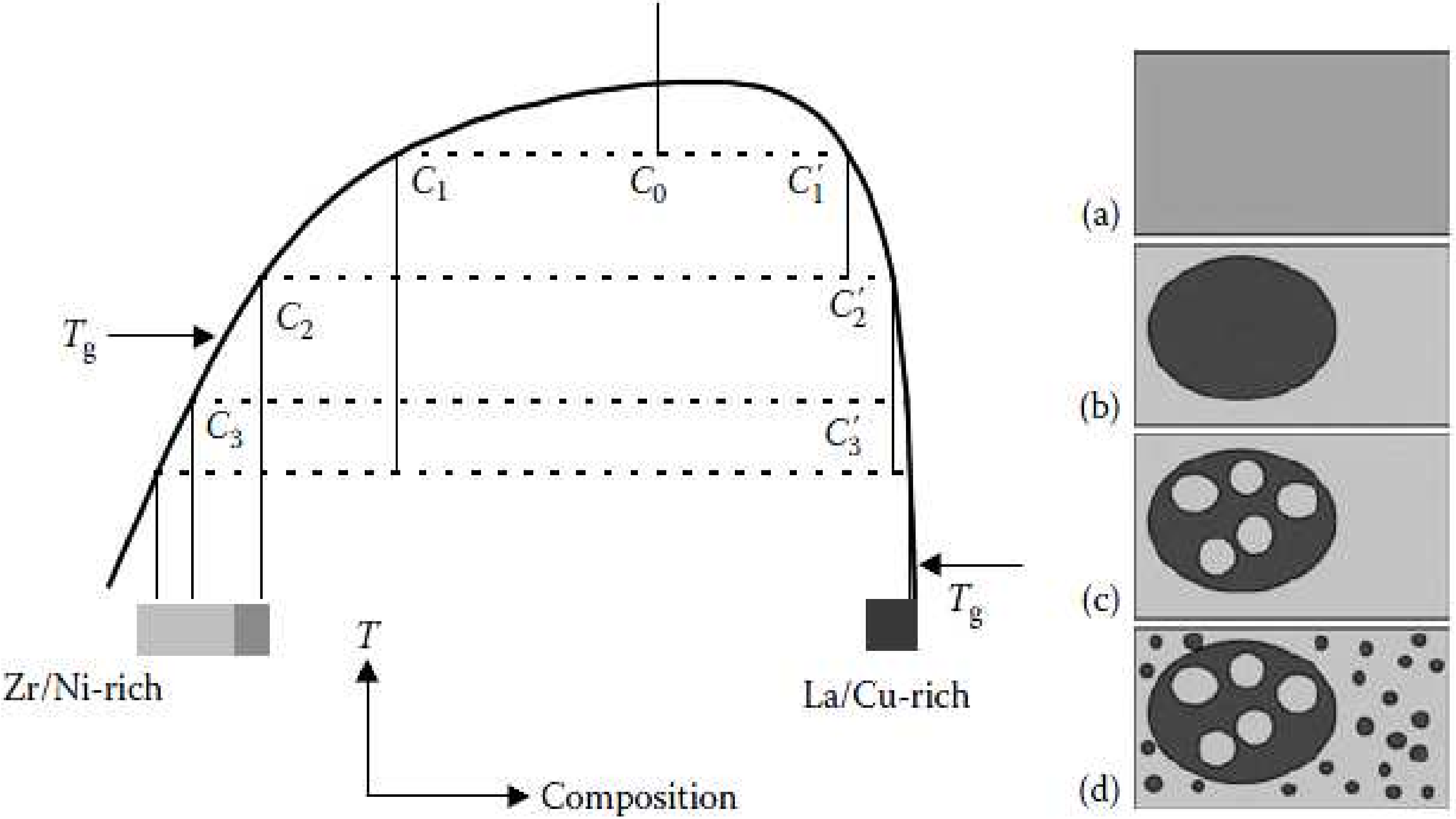
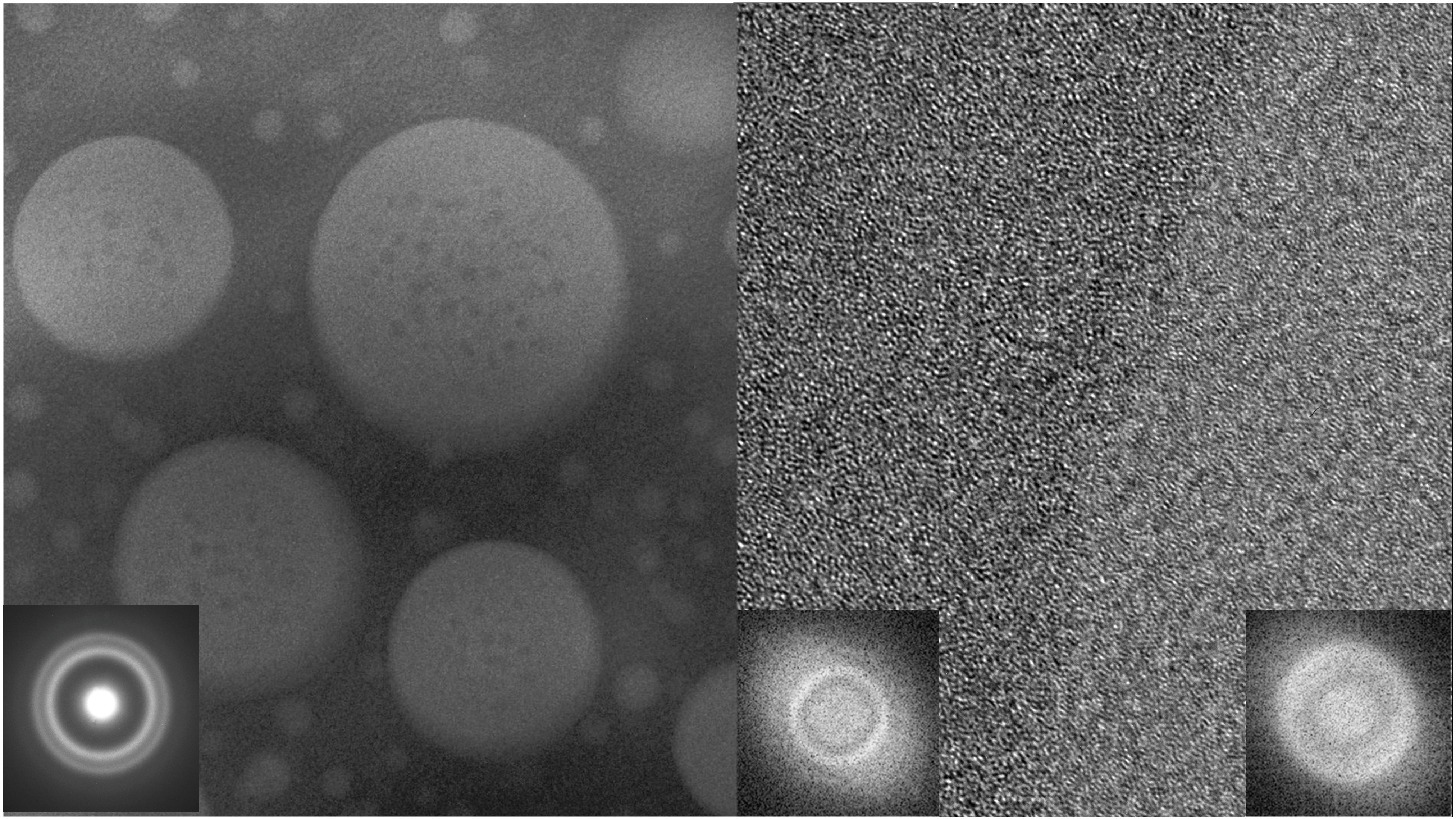


FIGURE 5.17
Schematic of the miscibility gap and the sequence of phase formation during cooling in the La–Zr–Al–Cu–Ni system. The positions of letters (a) to (d) in the diagram on the left correspond to the schematic microstructures (a) to (d) on the right. (Reprinted from Kündig, A.A. et al., *Acta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

Phase separation in metallic glasses



- 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**

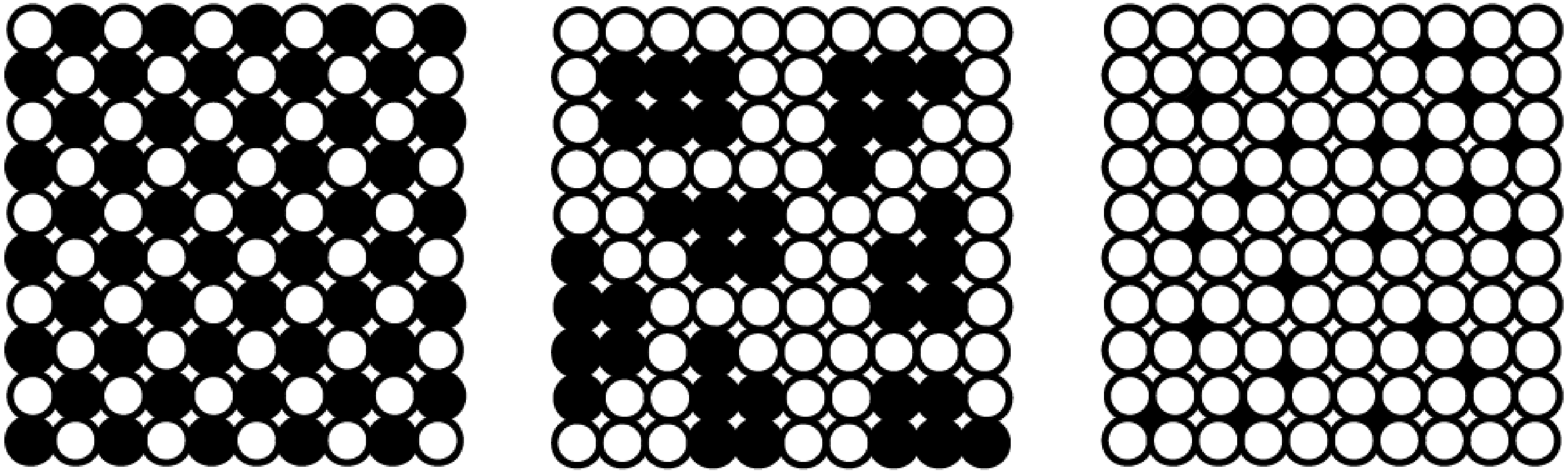


Fig. 1.8 (a) $\varepsilon < 0$, $\Delta H_{mix} < 0$ (b) $\varepsilon > 0$, $\Delta H_{mix} > 0$ (c) when the size difference is large

Ordered alloys

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

Clustering

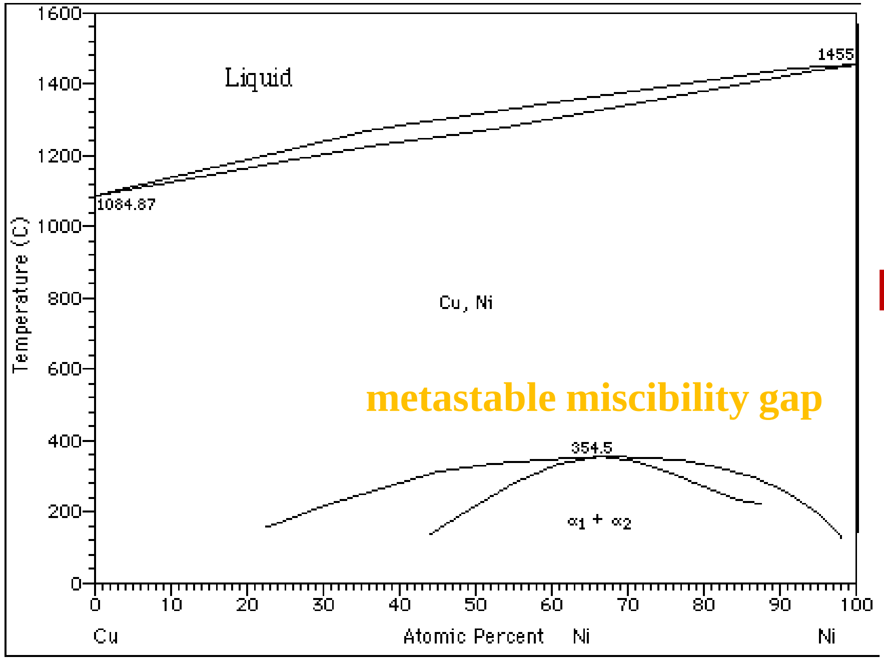
P_{AA}, P_{BB} $\uparrow$

strain effect

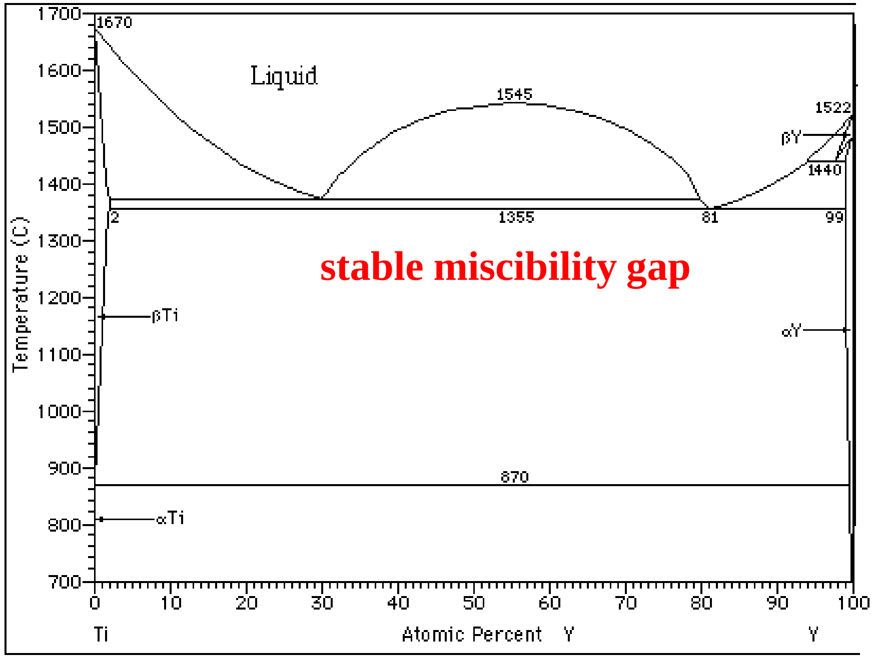
Interstitial solution

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

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



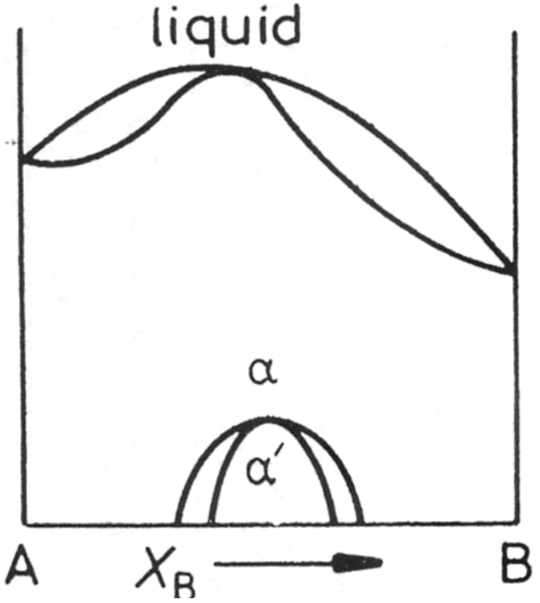
metastable miscibility gap

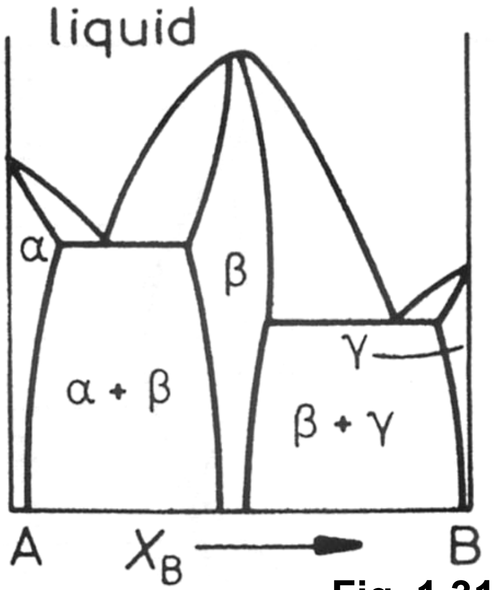


stable miscibility gap

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

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





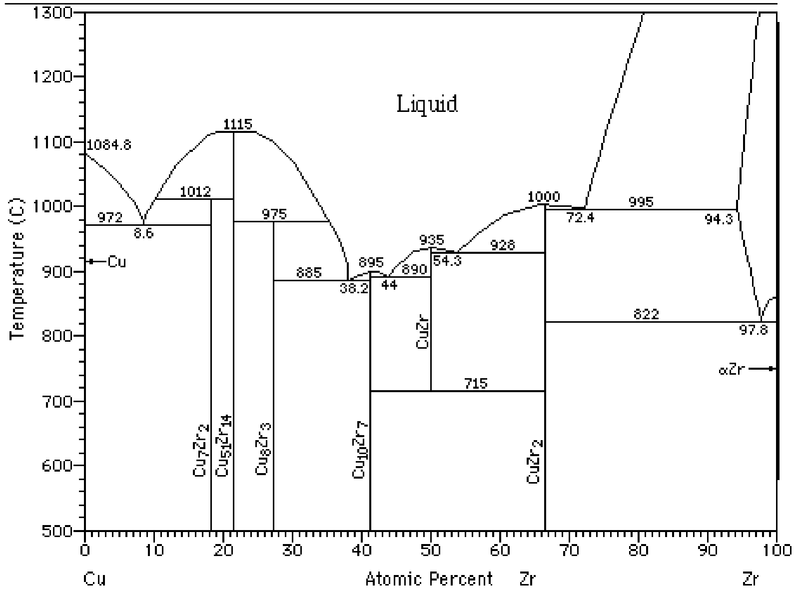


Fig. 1.31

Q2: How can we define equilibrium in heterogeneous systems?

1.4

Equilibrium in Heterogeneous Systems

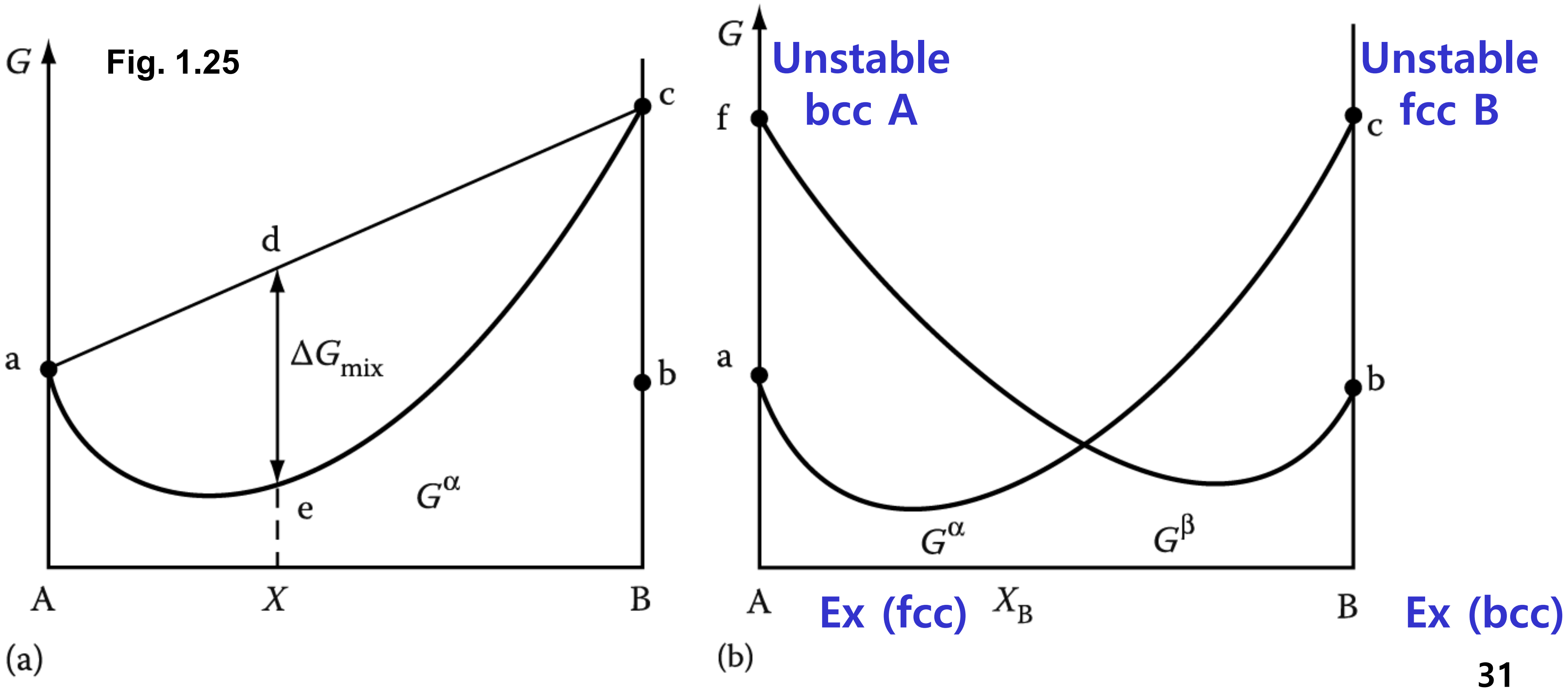
A, B different crystal structure → two free energy curves must be drawn, one for each structure.

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

Fig. 1.25



Unstable bcc A

Unstable fcc B

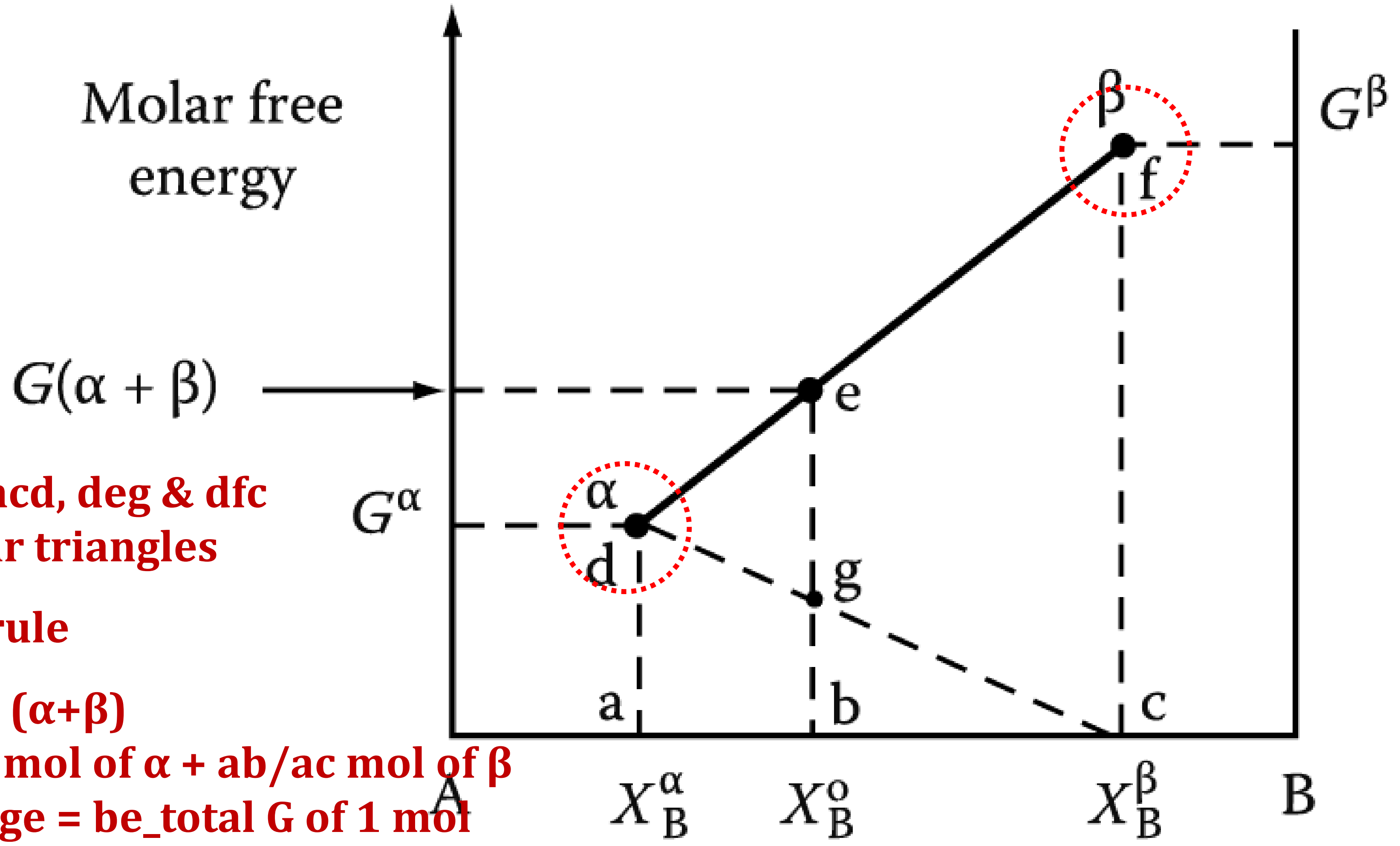
Ex (fcc)

Ex (bcc)

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

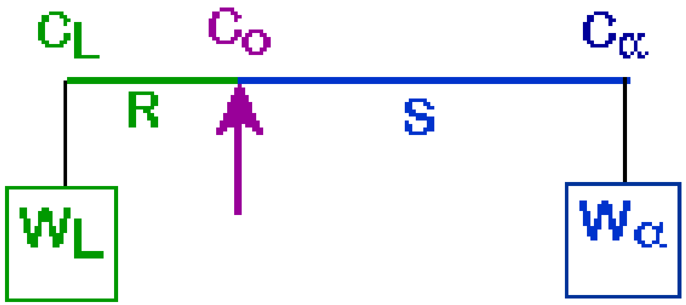
- Lever rule

- 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

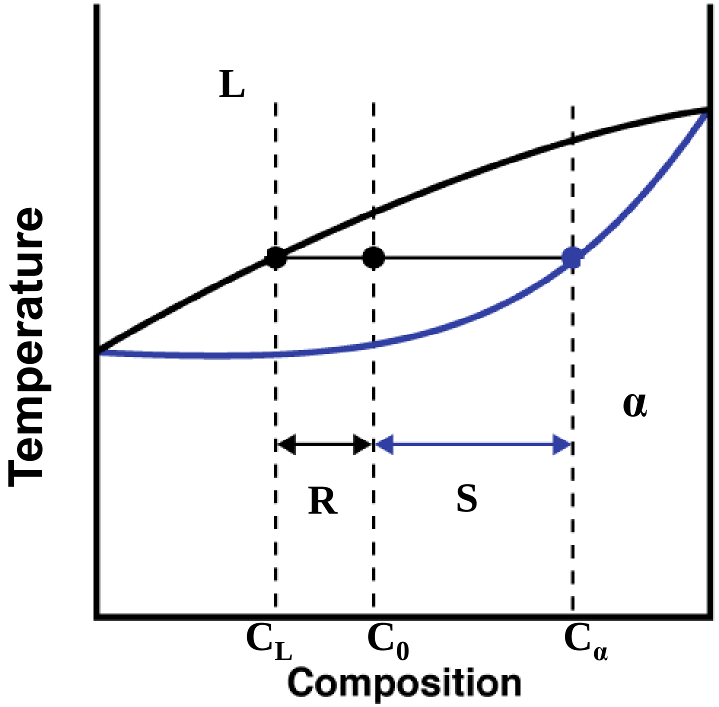
A geometric interpretation:



moment equilibrium:

$$\underset{\underset{\boxed{1-W_\alpha}}{\uparrow}}{\boxed{W_L}} R = W_\alpha S$$

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:

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

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

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

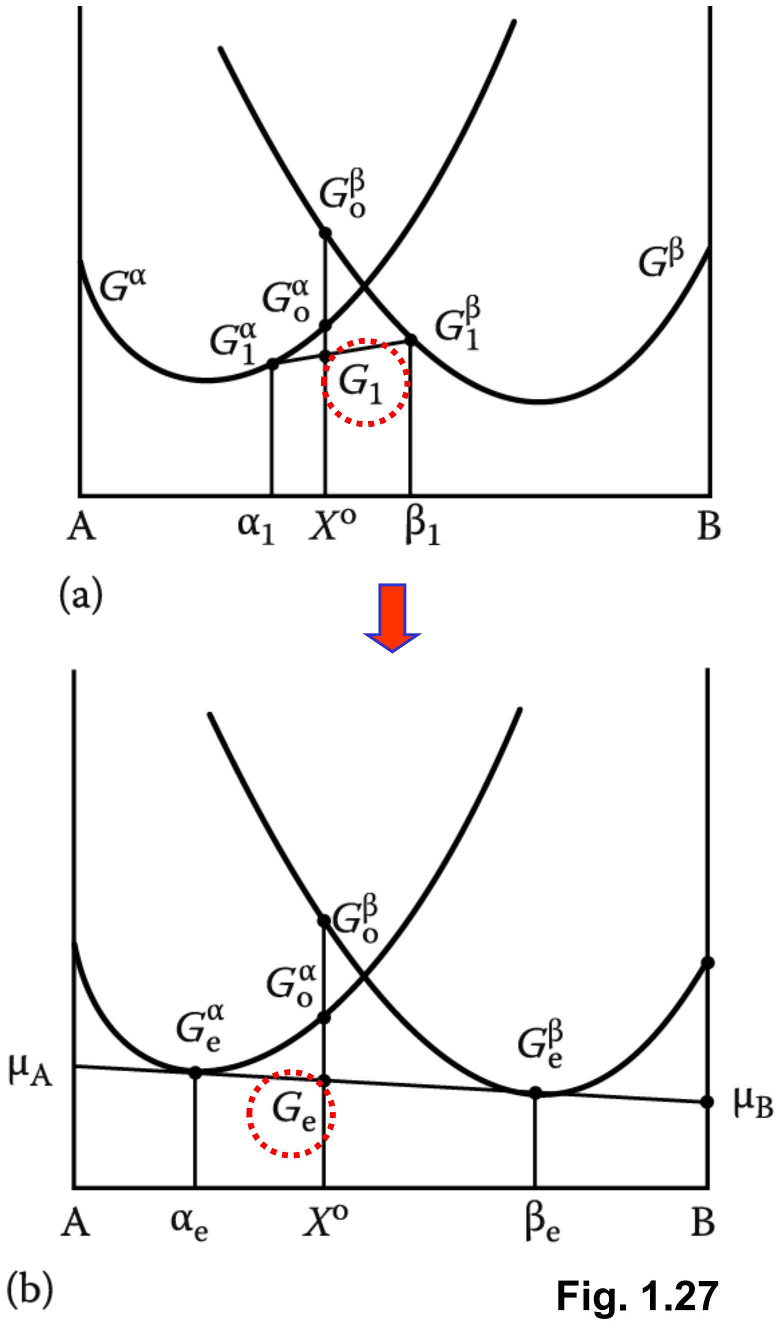


Fig. 1.27

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

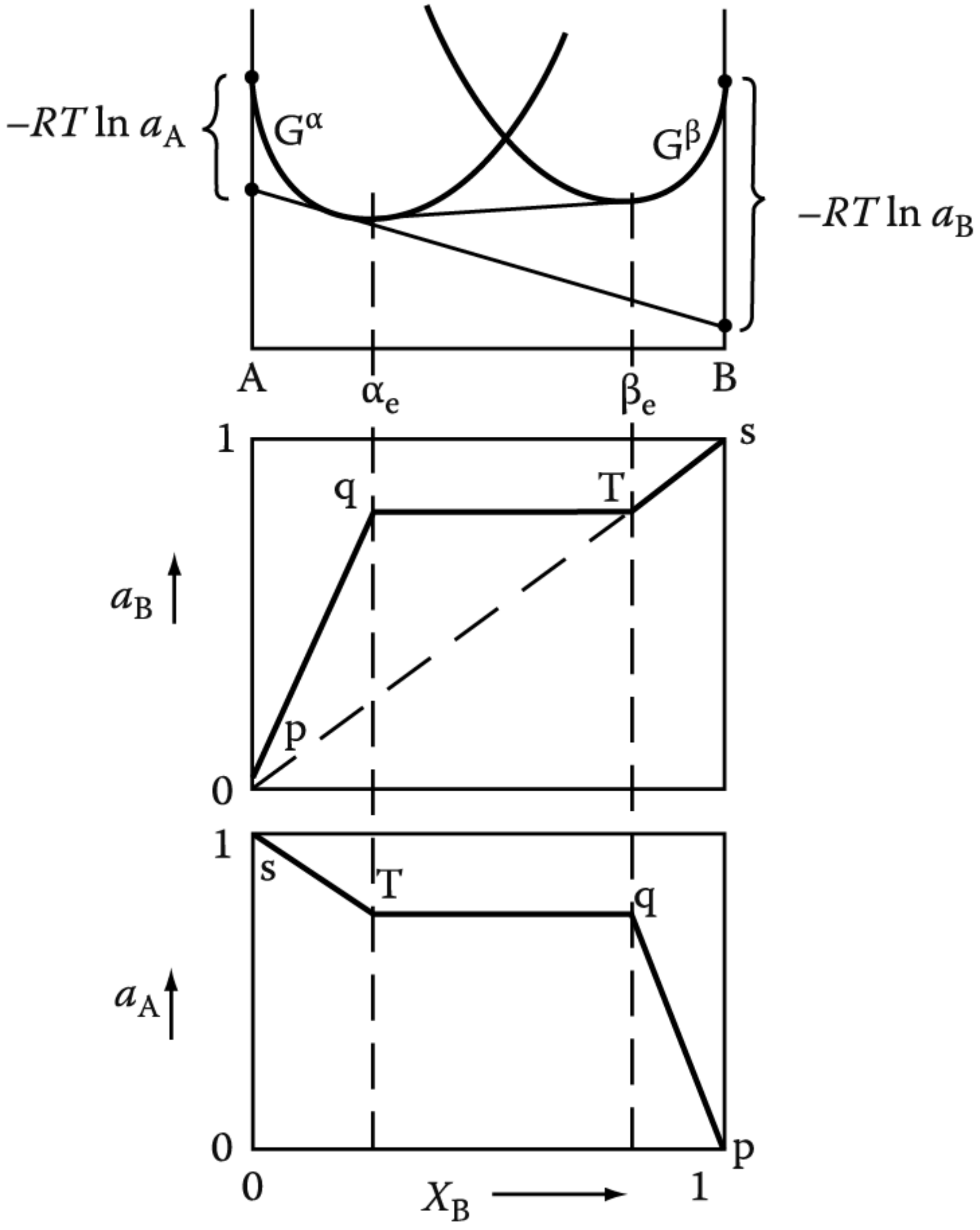
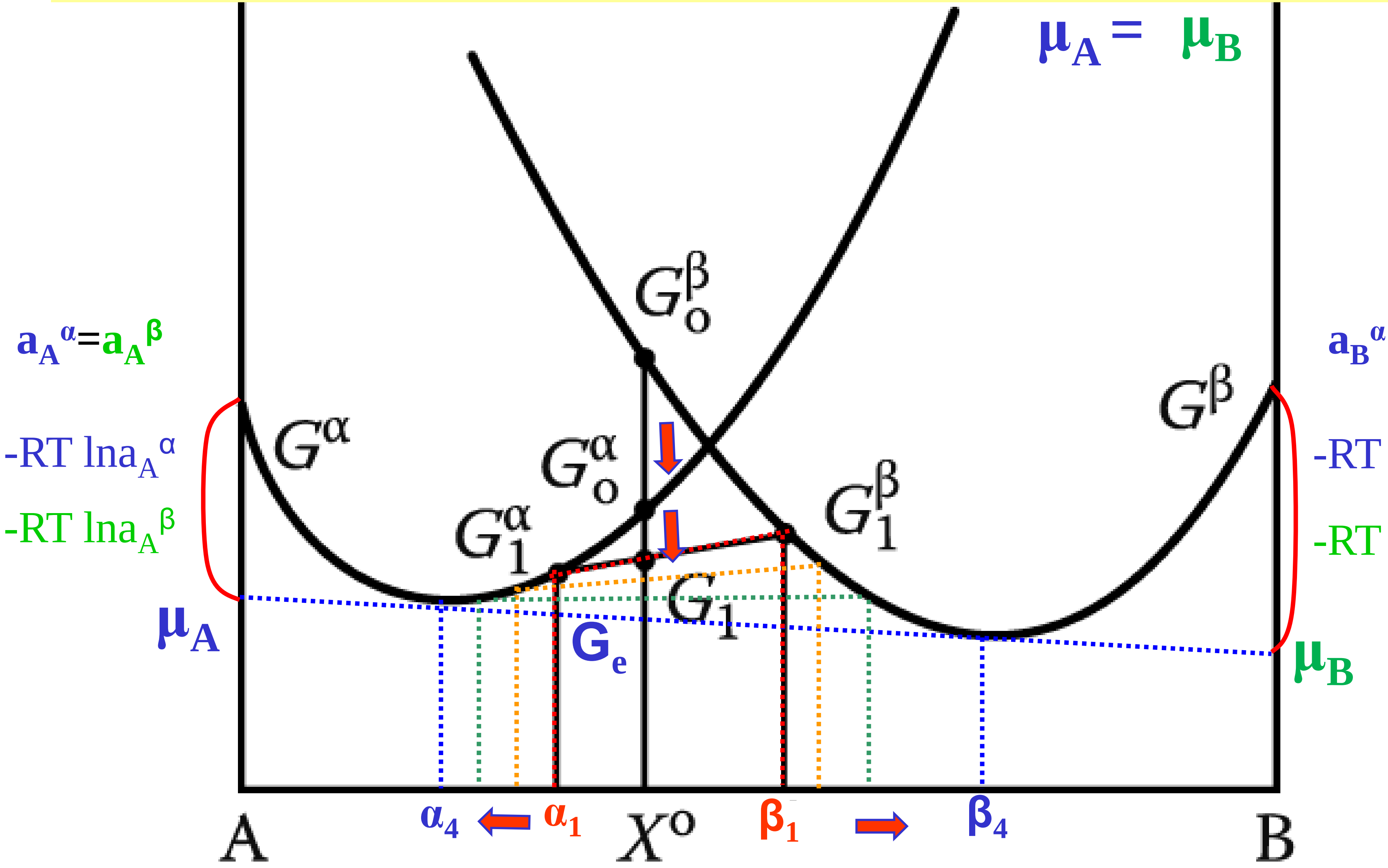


Fig. 1.28 The variation of a_A and a_B with composition for a binary system containing two ideal solutions, α and β

Equilibrium in Heterogeneous Systems

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



2023 Fall

“Phase Transformation *in* Materials”

09. 20. 2023

Eun Soo Park

Office: 33-313
Telephone: 880-7221
Email: espark@snu.ac.kr
Office hours: by an appointment

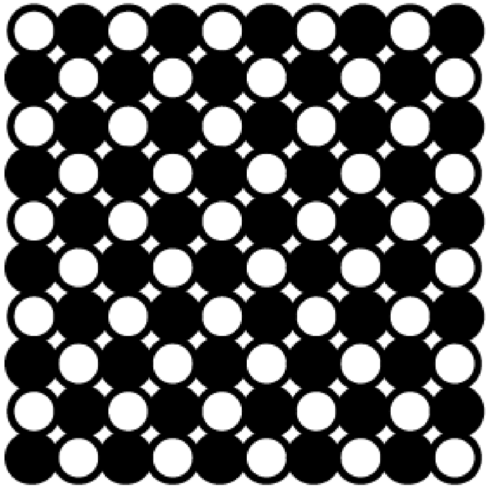
- Binary System mixture/ solution / compound

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 $\Delta H_{mix} < 0$

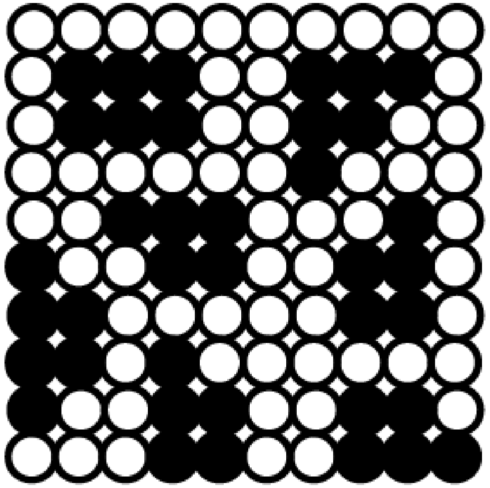
Real solution **Ordered structure**



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

Ordered alloys

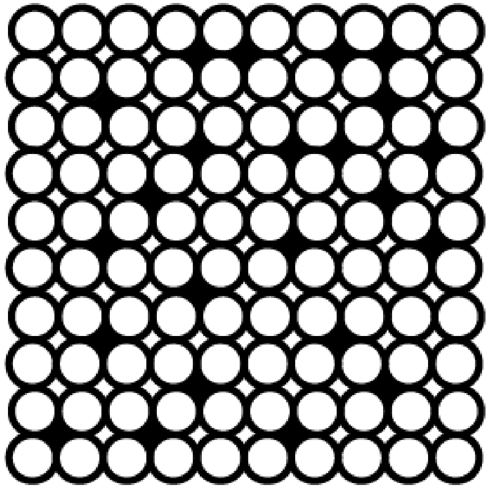
$P_{AB} \uparrow \longrightarrow$ Internal E $\downarrow$



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

Clustering

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

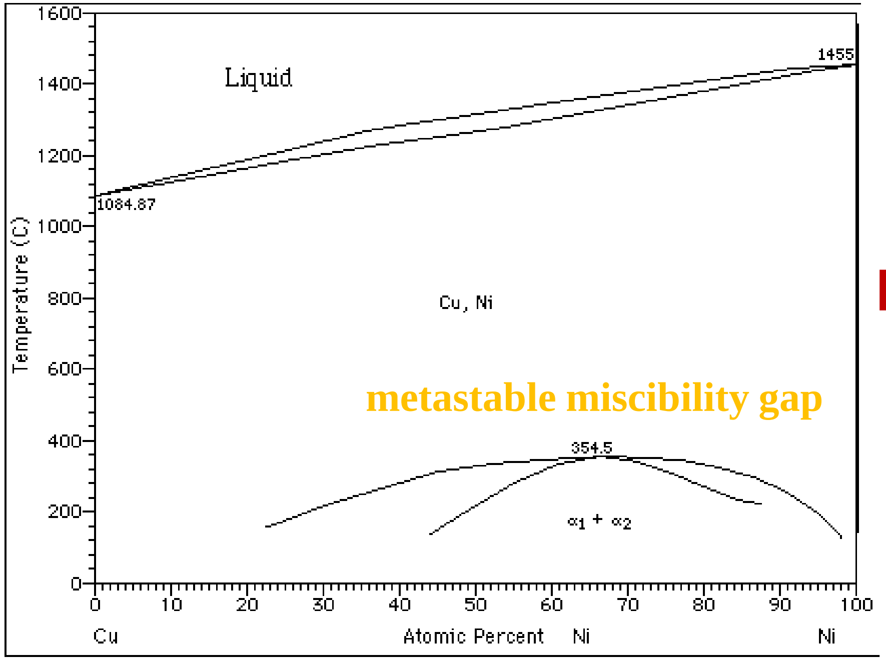


(c) when the size difference is large

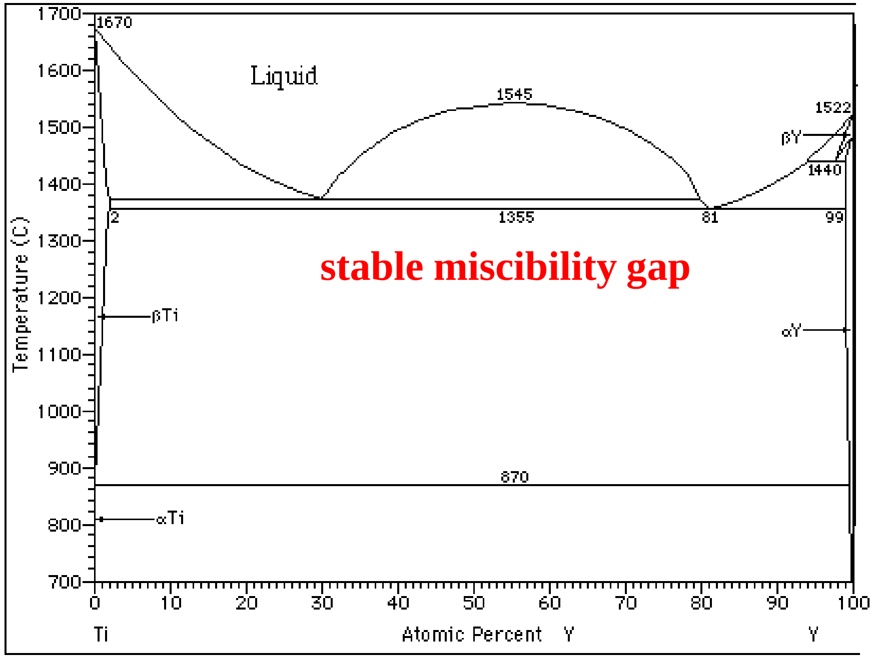
strain effect

Interstitial solution

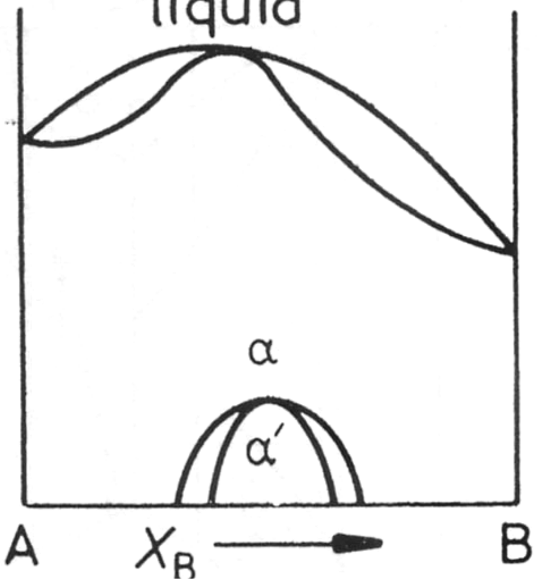
$\Delta H^{S}_{mix} > 0$: Solid solution → solid state phase separation (two solid solutions)

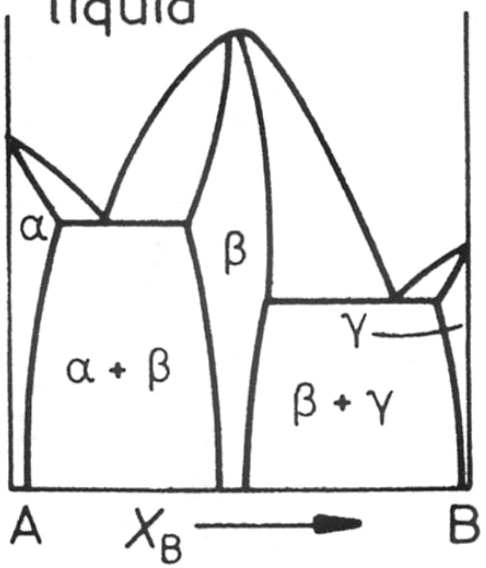


$\Delta H^{S}_{mix} >> 0$: liquid state phase separation (up to two liquid solutions)

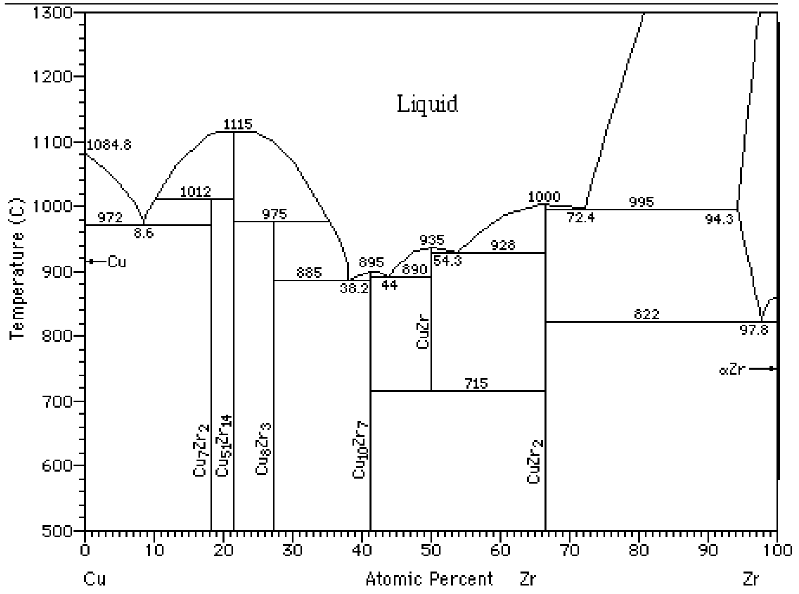


$\Delta H^{S}_{mix} < 0$: Solid solution → ordered phase



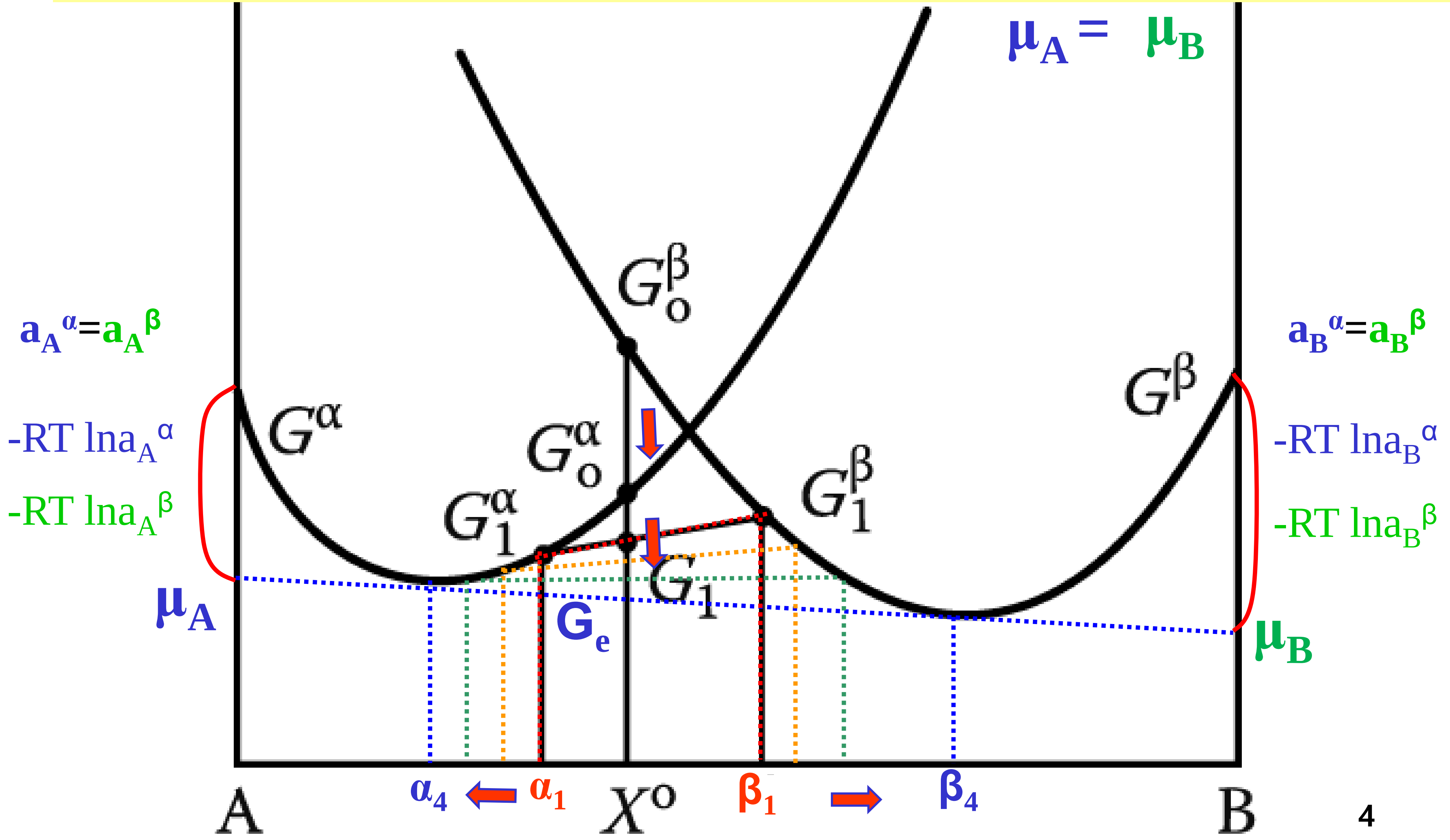


$\Delta H^{S}_{mix} << 0$: Compound : AB, A_2B…



Equilibrium in Heterogeneous Systems

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



Contents for today's class

1.5 Binary phase diagrams_Variation of the simple phase diagram

complete solid solution → eutectic/peritectic system

1.5.6

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

1.5.7

- **Effect of Temperature on Solid Solubility**

1.5.8

- **Equilibrium Vacancy Concentration**

1.6 Influence of Interfaces on Equilibrium

1.8 Additional thermodynamic relationships for binary solutions

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

Q1: How equilibrium is affected by temperature in complete solid solution?

1) A Simple Phase Diagram

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

(2) Both are ideal soln.

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

(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.

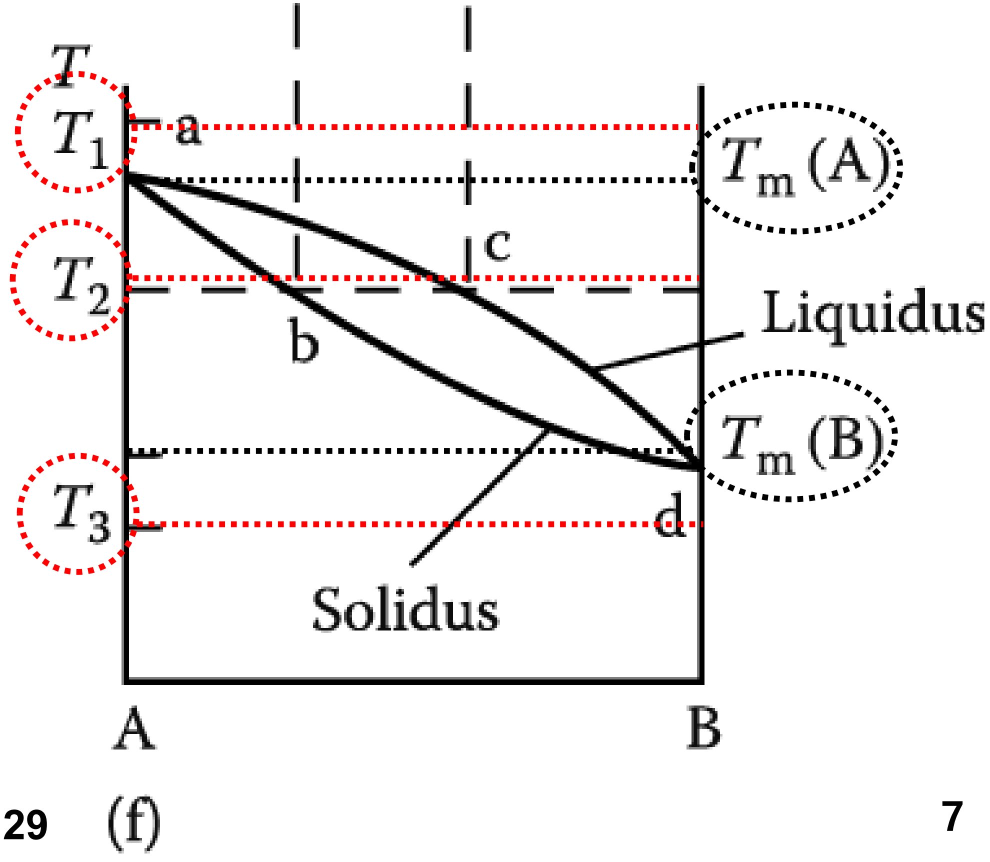


Fig. 1.29

1) A Simple Phase Diagram

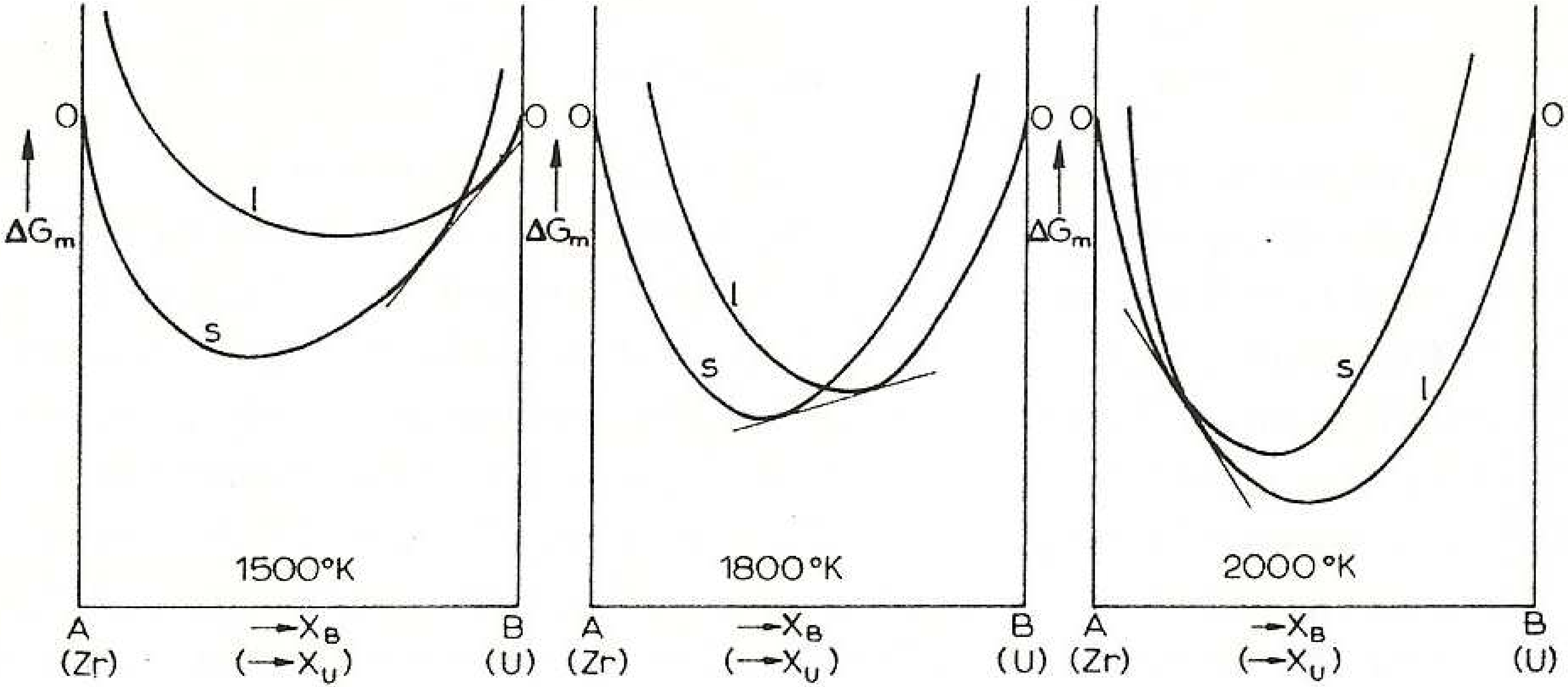


Fig. Free energy curves for liquid and solid phases in the U–Zr system at 1500°, 1800° and 2000 °K.

1.5 Binary phase diagrams

1) A Simple Phase Diagram

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

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

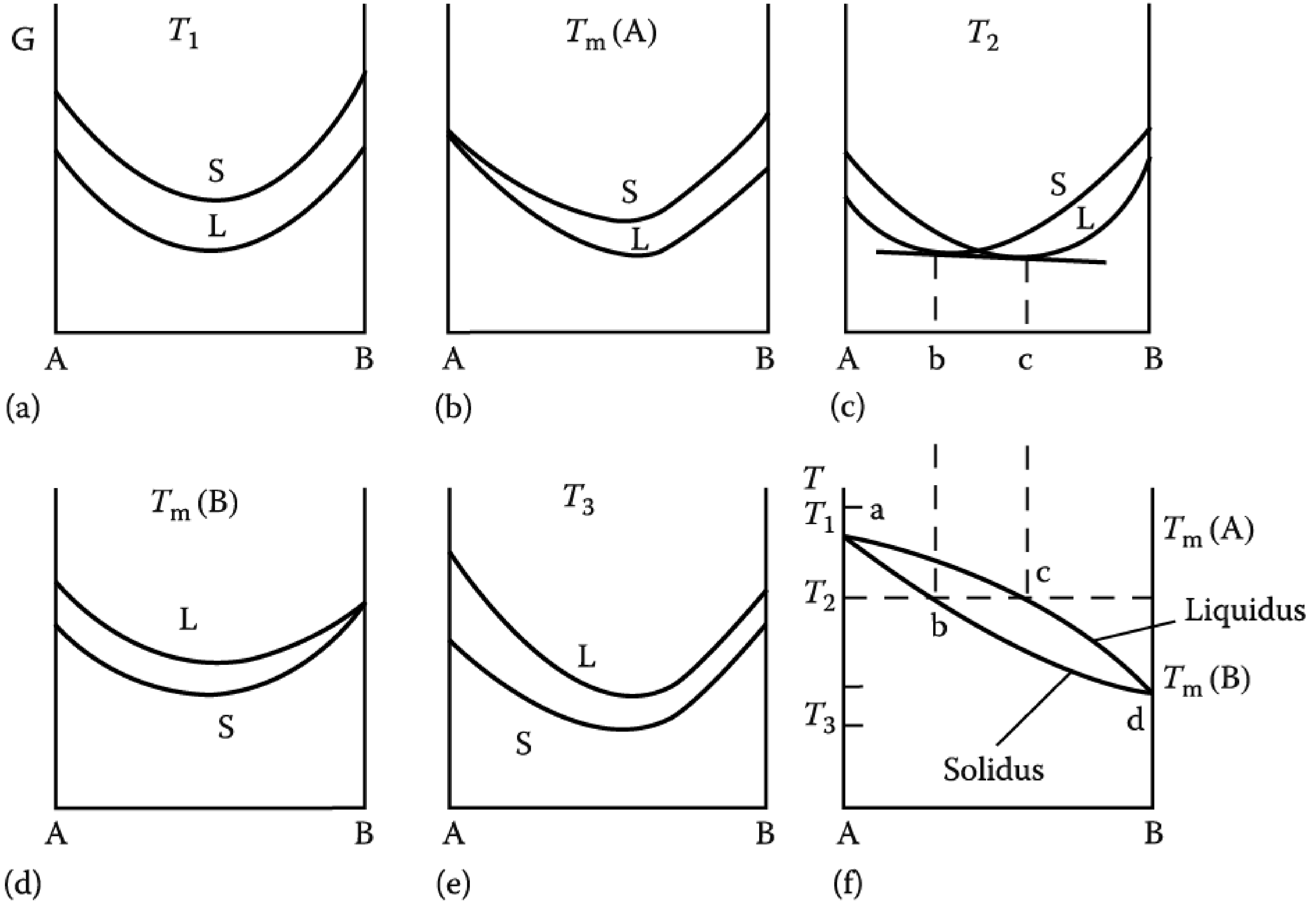


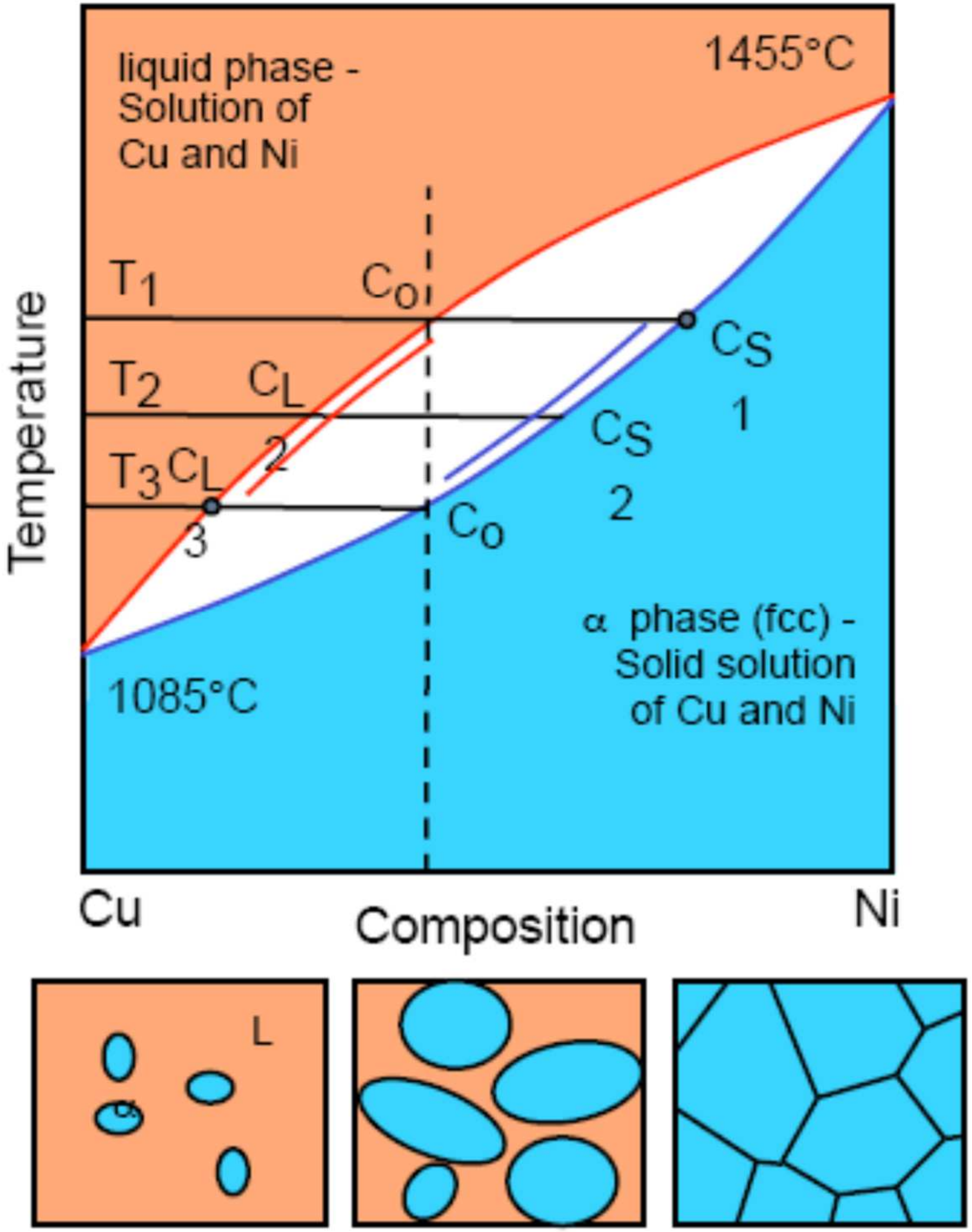
Fig. 1.29

1.5 Binary phase diagrams

1) A Simple Phase Diagram

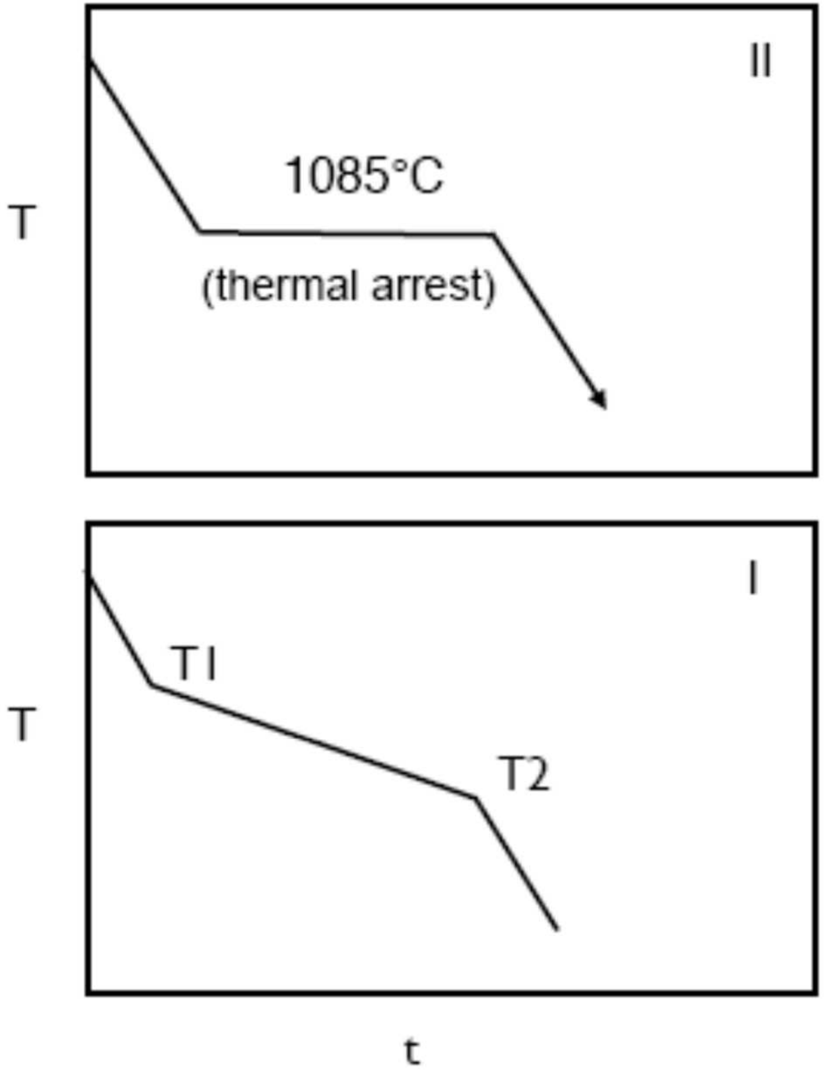
The simplest type of binary phase diagrams is the isomorphous system, in which the two constituents form a continuous solid solution over the entire composition range. An example is the Ni-Cu system.

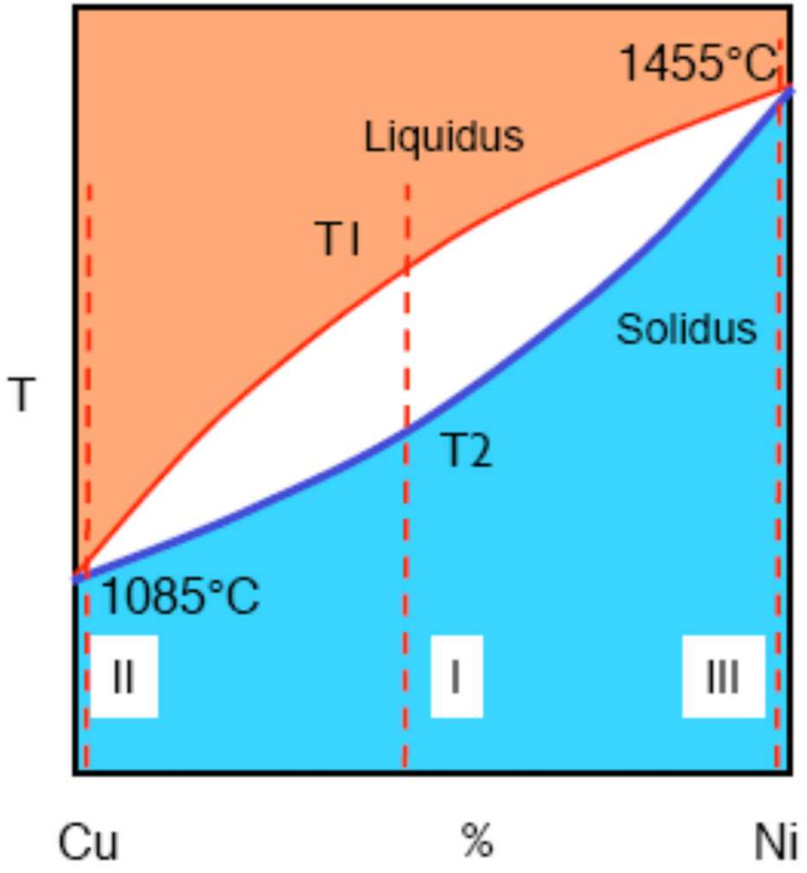
Solidification of alloy C_o starts on cooing at T_1. The first solid formed has a composition of C_{s1} and the liquid C_o. On further cooling the solid particles grow larger in size and change their composition to C_{s2} and then C_o, following the solidus whereas the liquid decrease in volume and changes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



Cooling Curves

determination of Phase diagrams





Q4: How equilibrium is affected by temperature in systems with miscibility gap?

2) Systems with miscibility gab

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

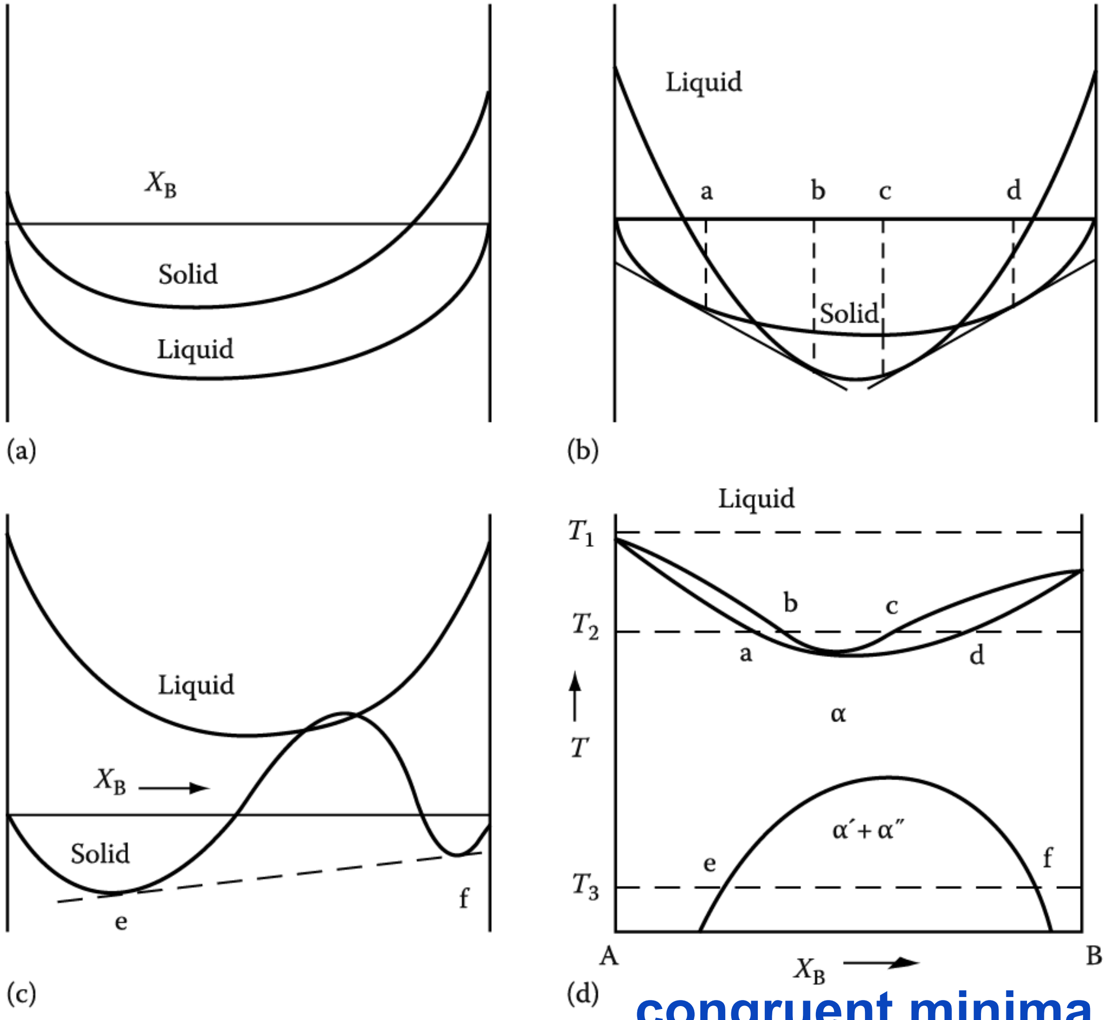


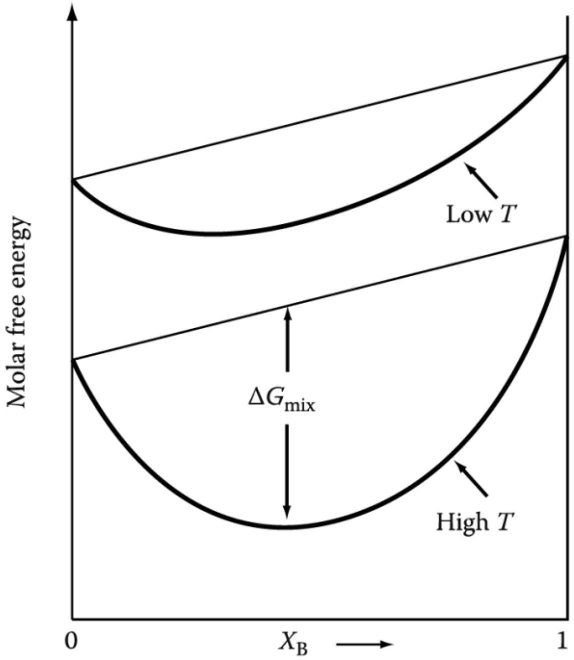
Fig. 1.30

congruent minima

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

Ideal Solutions

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



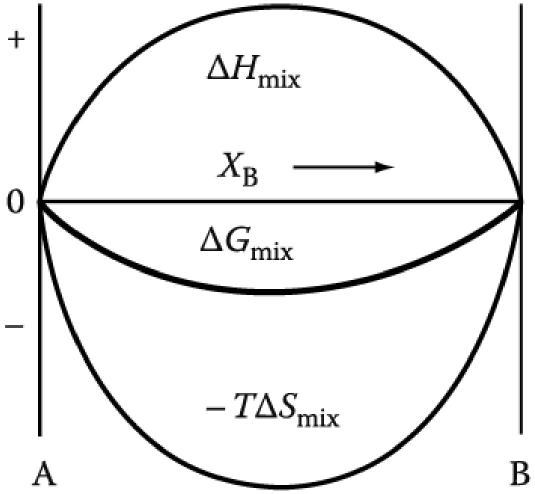
Regular Solutions

$$G = X_A G_A + X_B G_B + \overset{\Delta H_{mix}}{\boxed{\Omega \; X_A X_B}} + \overset{-T\Delta S_{mix}}{\boxed{RT\,(X_A \ln X_A + X_B \ln X_B)}}$$

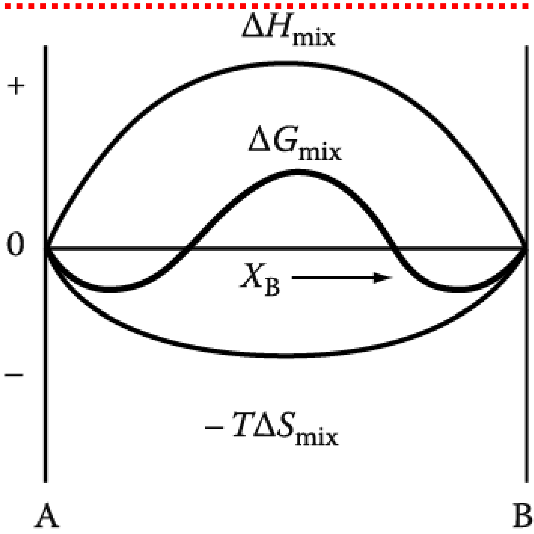
Reference state

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

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



(c) Ω > O, high T



(d) Ω > O, low T

1.5 Binary phase diagrams

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,** $\dfrac{d^2G}{dX_B^2} < 0$
- **This results in a 'miscibility gap' of α′ and α″ in the phase diagram**

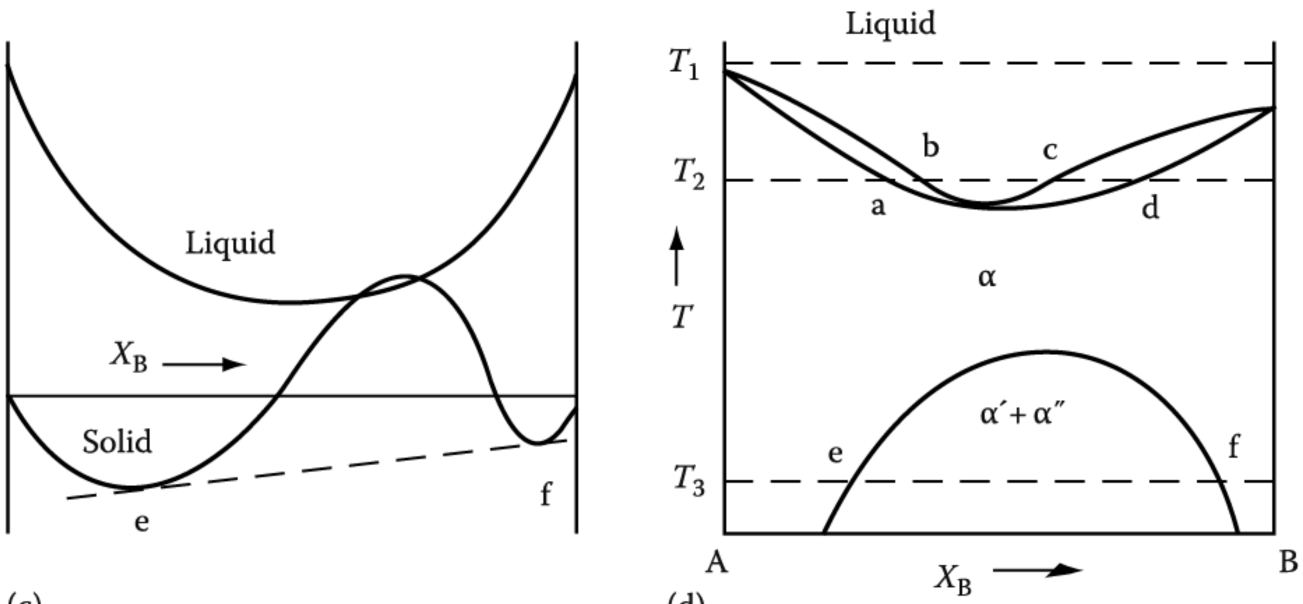
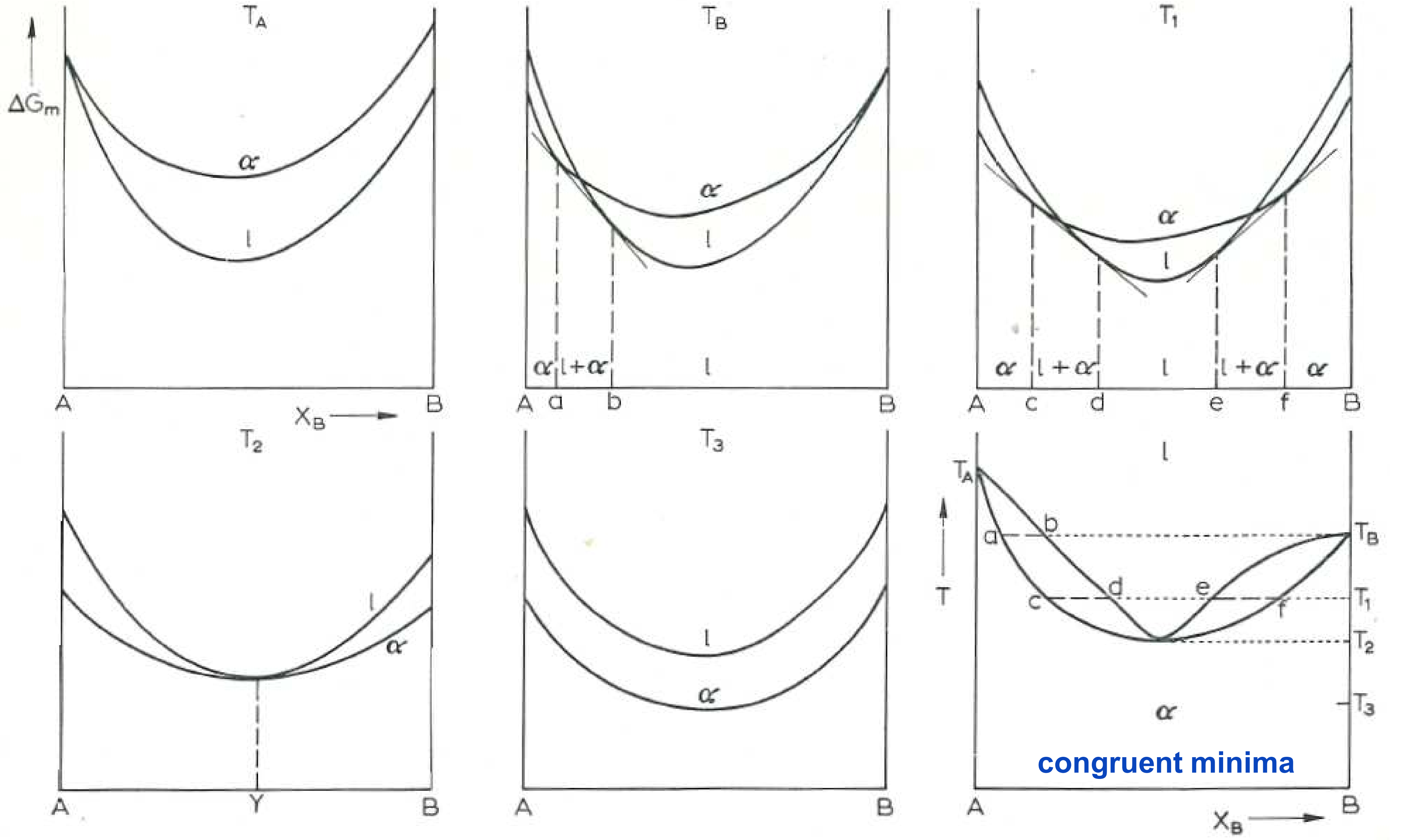


Fig. 1.30 (c) (d)

congruent minima

* Variant of the simple phase diagram

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



congruent minima

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

3) Ordered alloys_Variation of the simple phase diagram

$\Delta H_{mix} < 0$

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

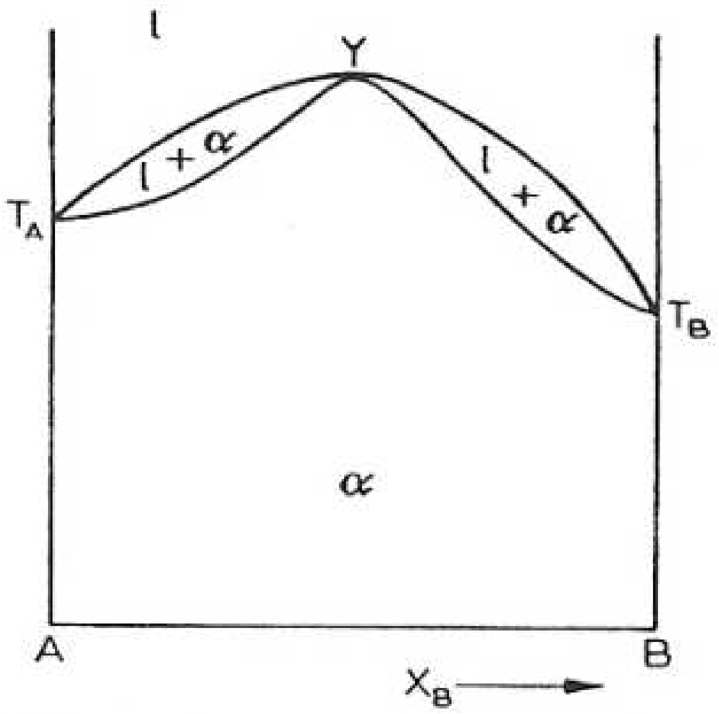


Fig. Phase diagram with a maximum in the liquidus.

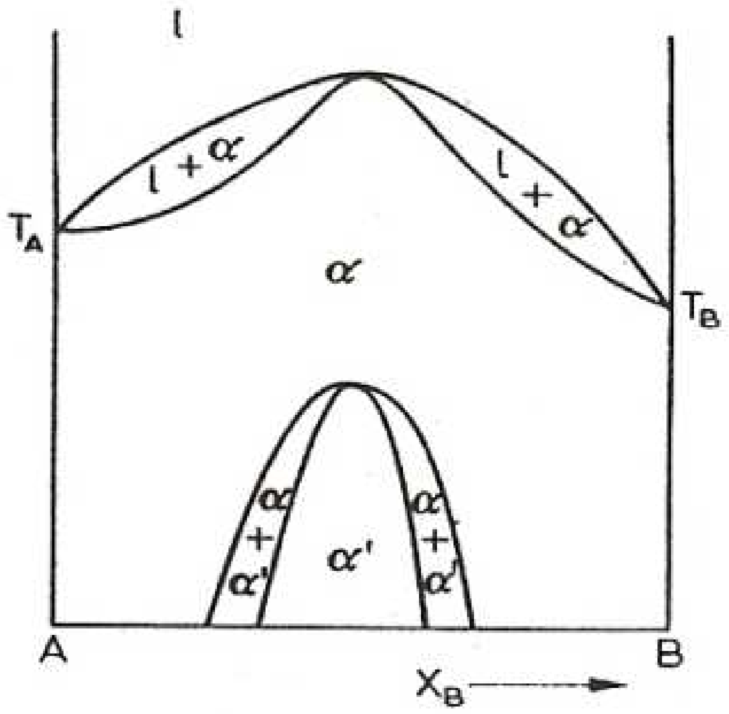


Fig. Appearance of an ordered α' phase at low temperatures.

congruent maxima

Q2: How equilibrium is affected by temperature in simple eutectic/peritectic systems?

1.5 Binary phase diagrams

4) a. Simple Eutectic Systems $\Delta H^{L}_{mix} = 0 \quad \Delta H^{S}_{mix} >> 0$

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

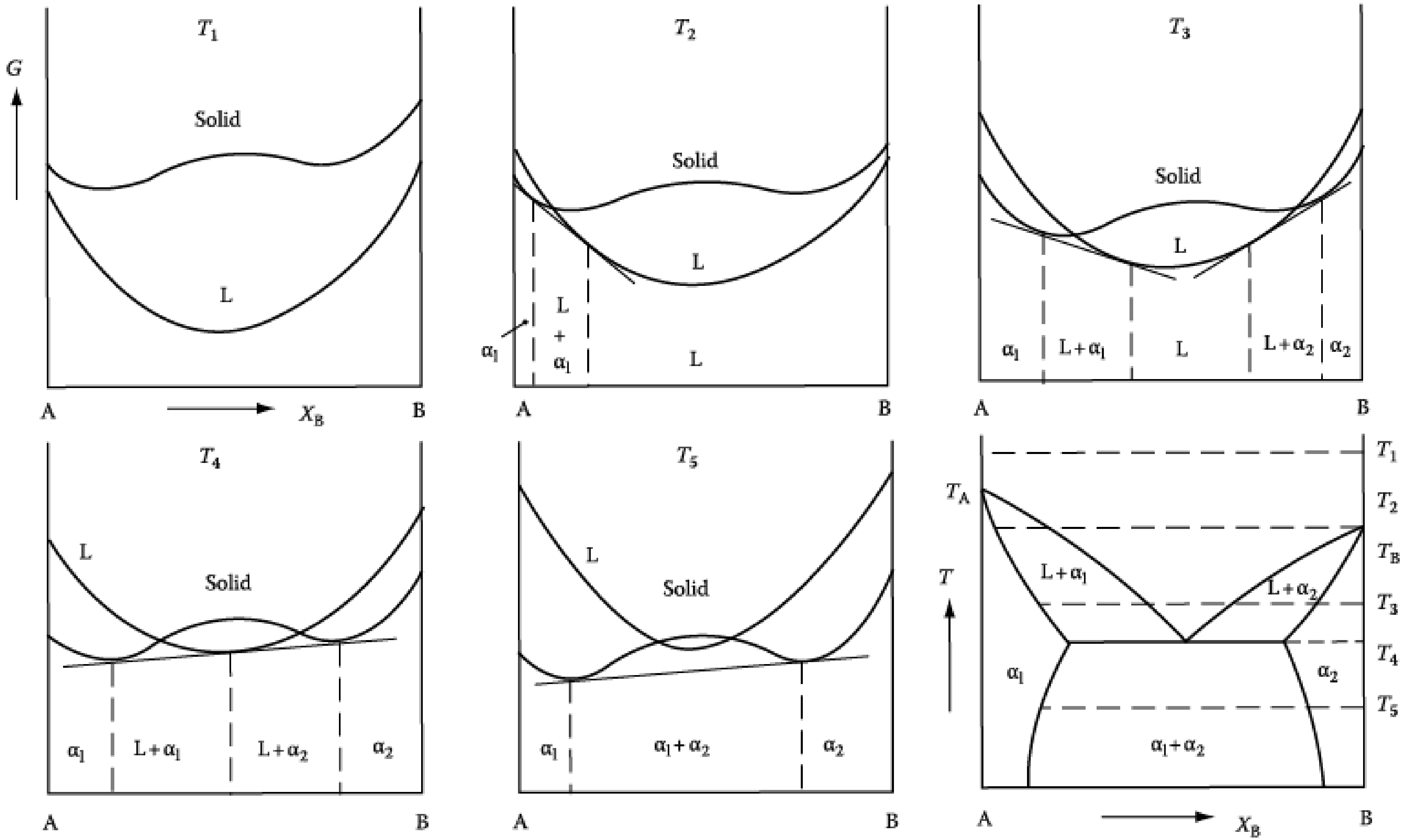


Fig. 1.32 The derivation of a eutectic phase diagram where both solid phases have the same crystal structure.

(when each solid has the different crystal structure.)

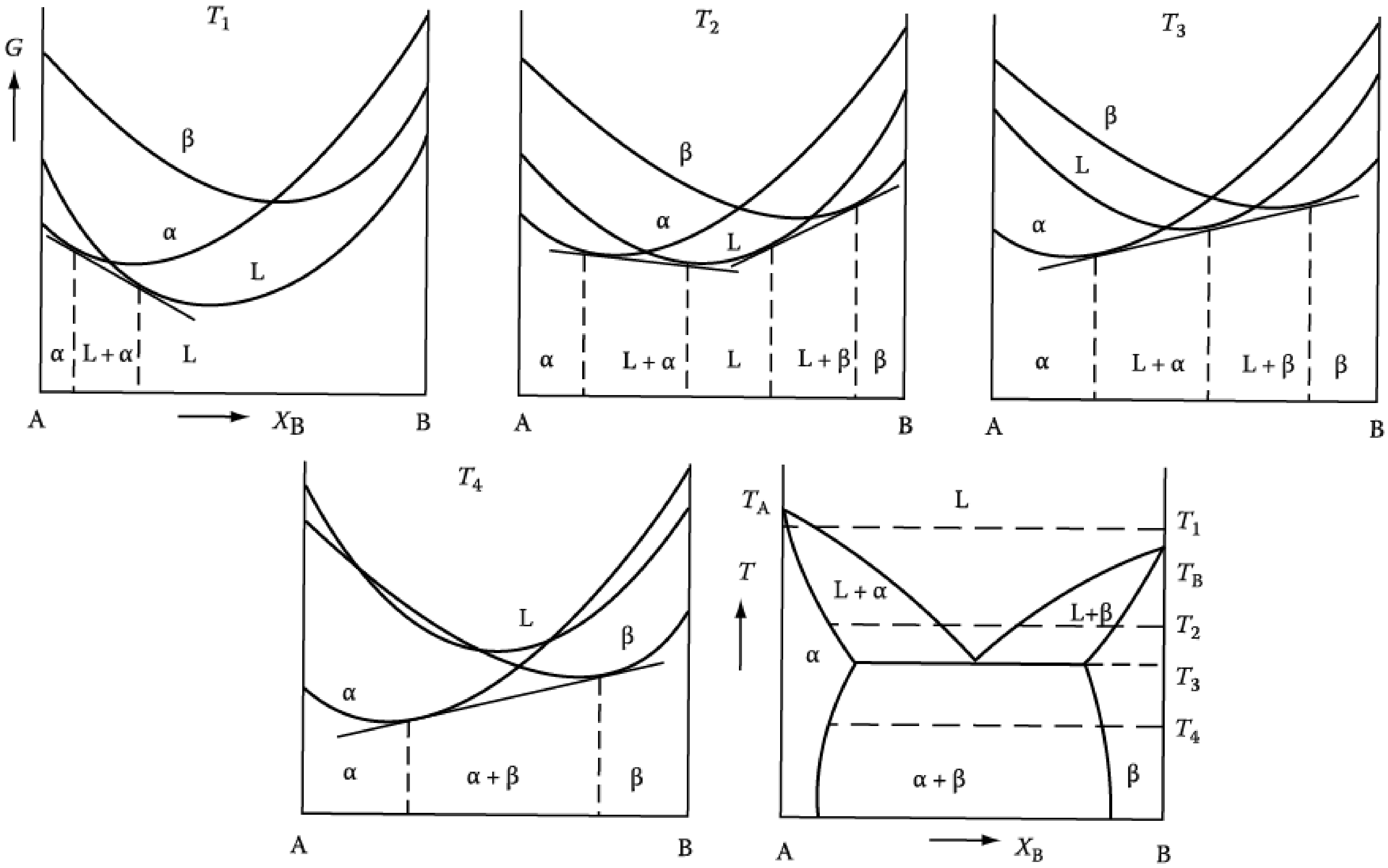


Fig. 1.32 The derivation of a eutectic phase diagram where each solid phases has a different crystal structure.

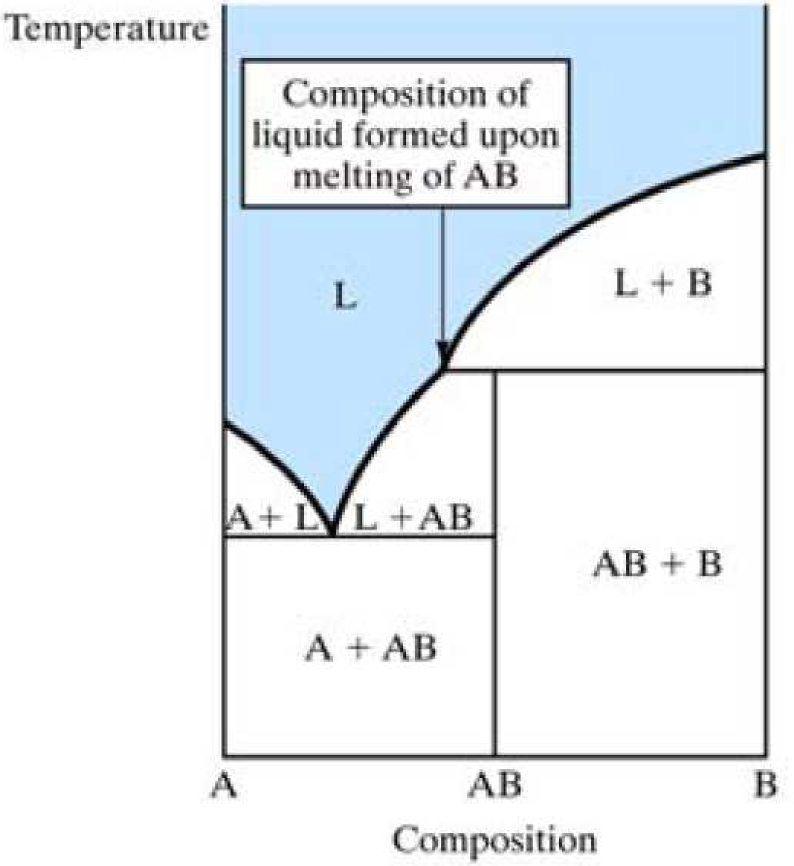
4) b. Simple Peritectic Systems

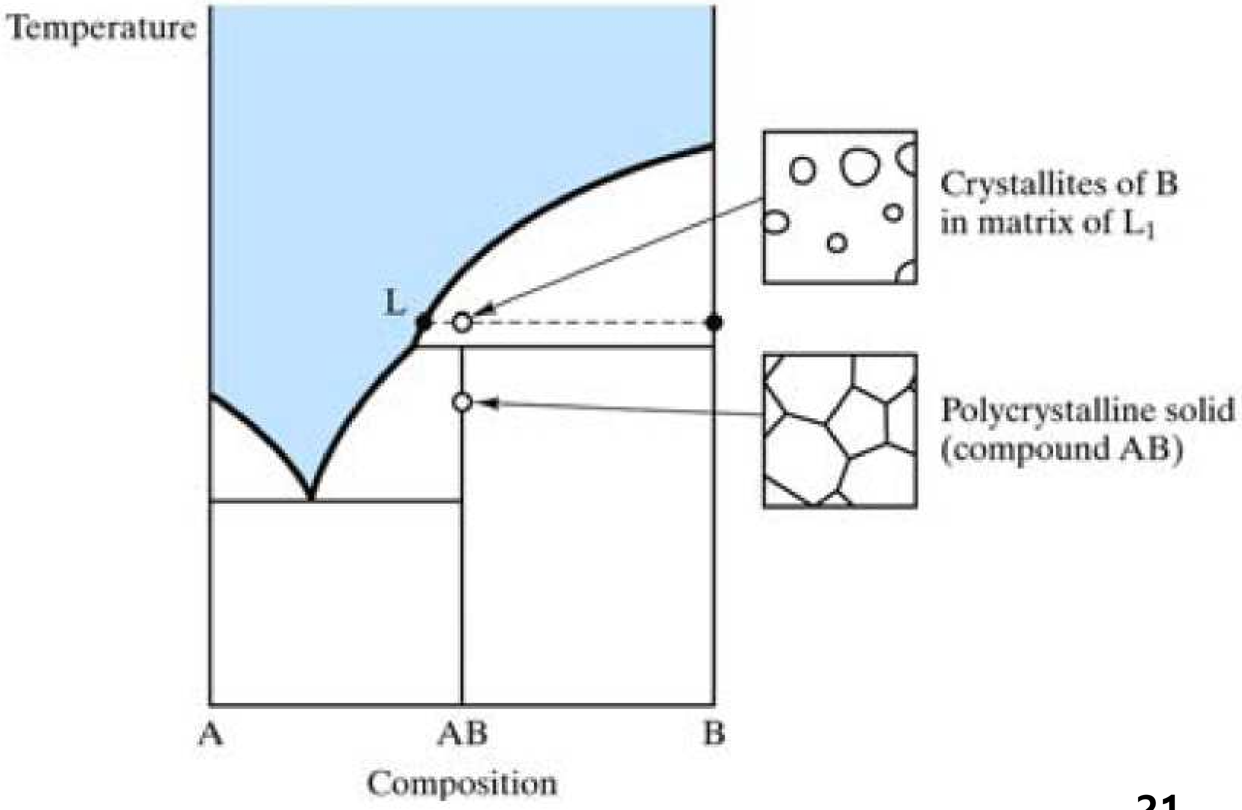
Peritectic reaction : $AB \overset{heating}{\rightleftarrows} L + B$

Congruent melting : $S_{x1} \xrightarrow{melting} L_{x1}$

Incongruent melting : $S_{x1} \xrightarrow{melting} L_{x2}$

Which one here??





Peritectic reaction

Considerable difference between the melting points

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

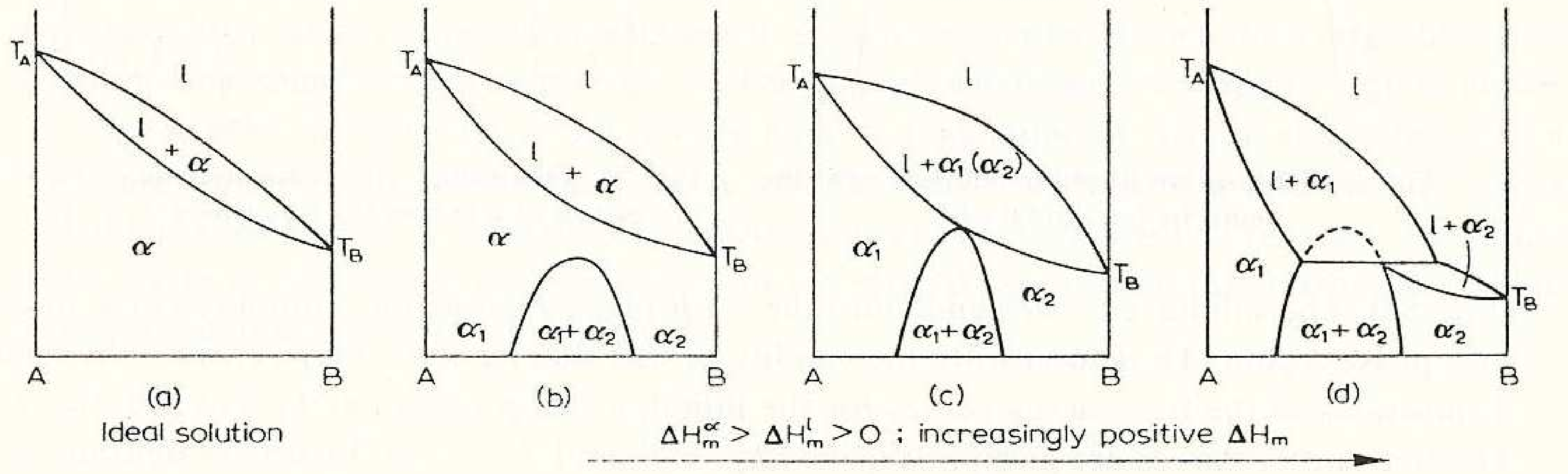


Fig. 61. Effect of increasingly positive departure from ideality in changing the phase diagram from a continuous series of solutions to a peritectic-type.

Eutectic reaction

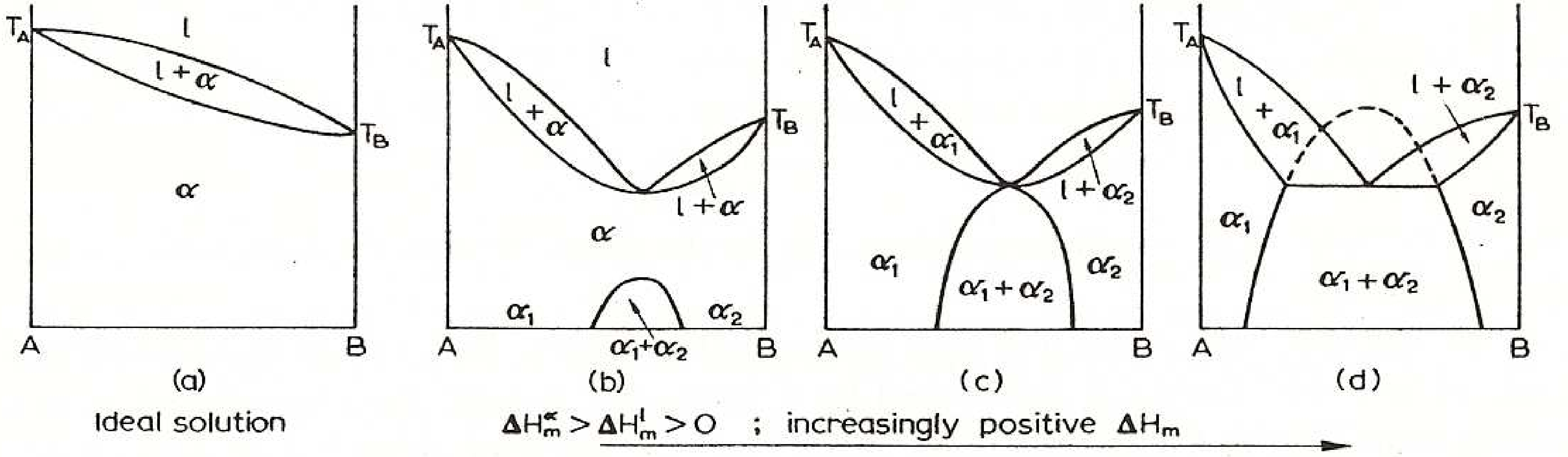


Fig. 43. Effect of increasingly positive departure from ideality in changing the phase diagram for a continuous series of solutions to a eutectic-type.

Peritectic reaction (when both solids have the same crystal structure.)

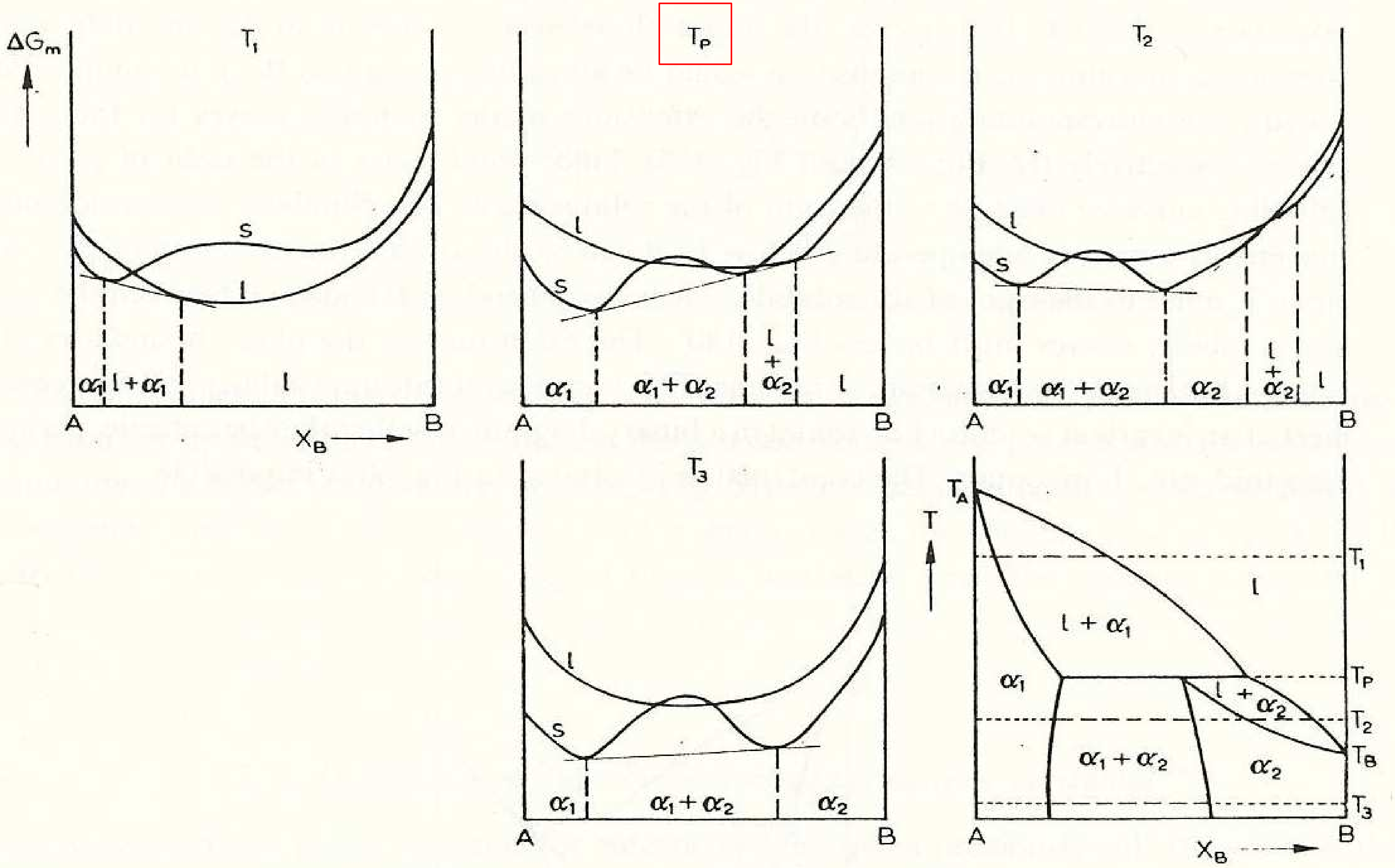


Fig. 62. Derivation of the peritectic phase diagram from the free energy curves for the liquid and solid phases.

Peritectic reaction (when both solids have the different crystal structure.)

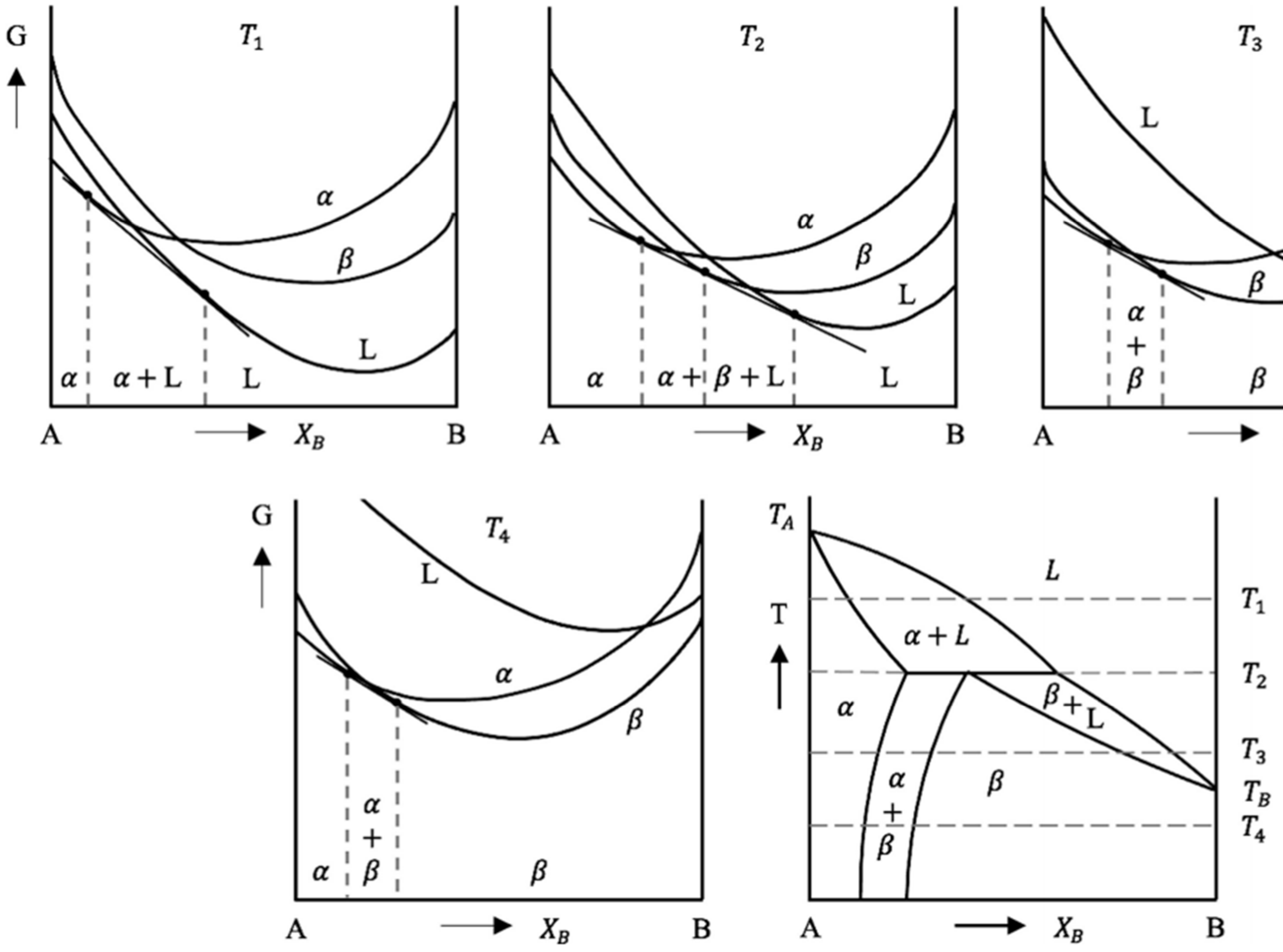
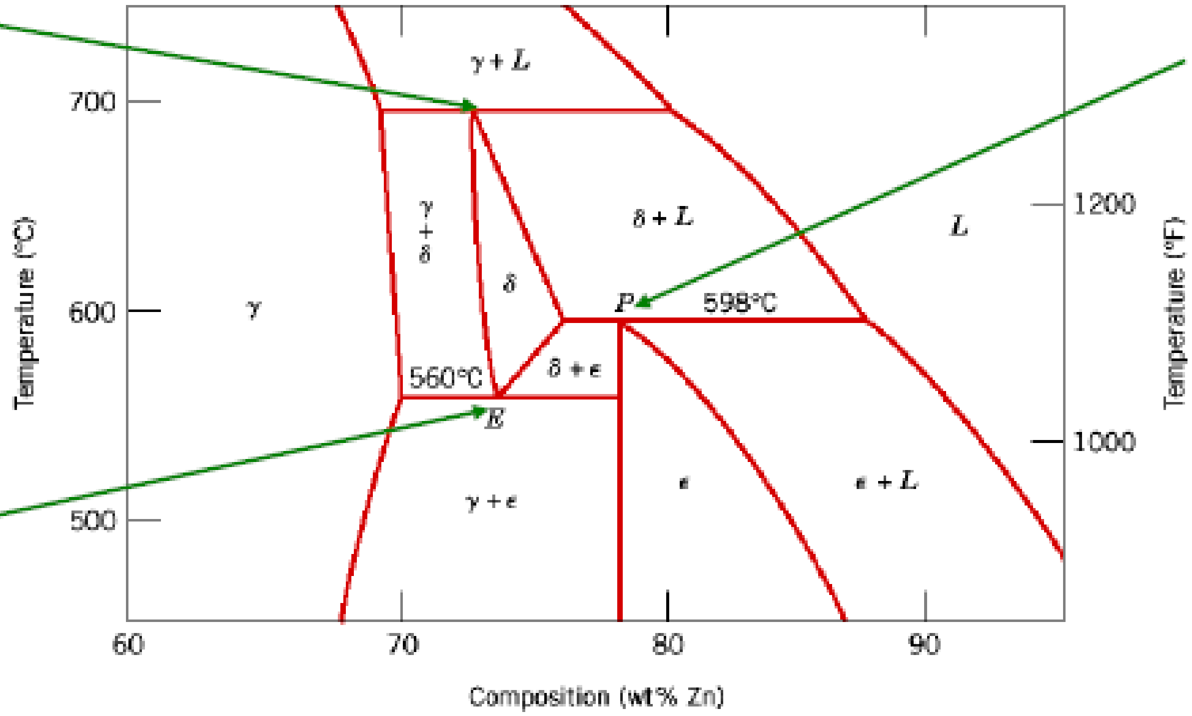


Fig. 1.33 Free energy curves resulting in a peritectic phase diagram. T2 is the peritectic temperature.

Cu-Zn Phase Diagram

Eutectoid and Peritectic Reactions



peritectic:
$\gamma + L \rightleftarrows \delta$

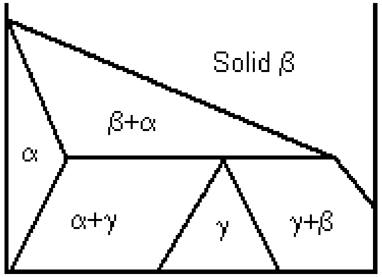
peritectic:
$\delta + L \rightleftarrows \varepsilon$

eutectoid:
$\delta \rightleftarrows \gamma + \varepsilon$

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



5) Phase diagrams containing intermediate phases

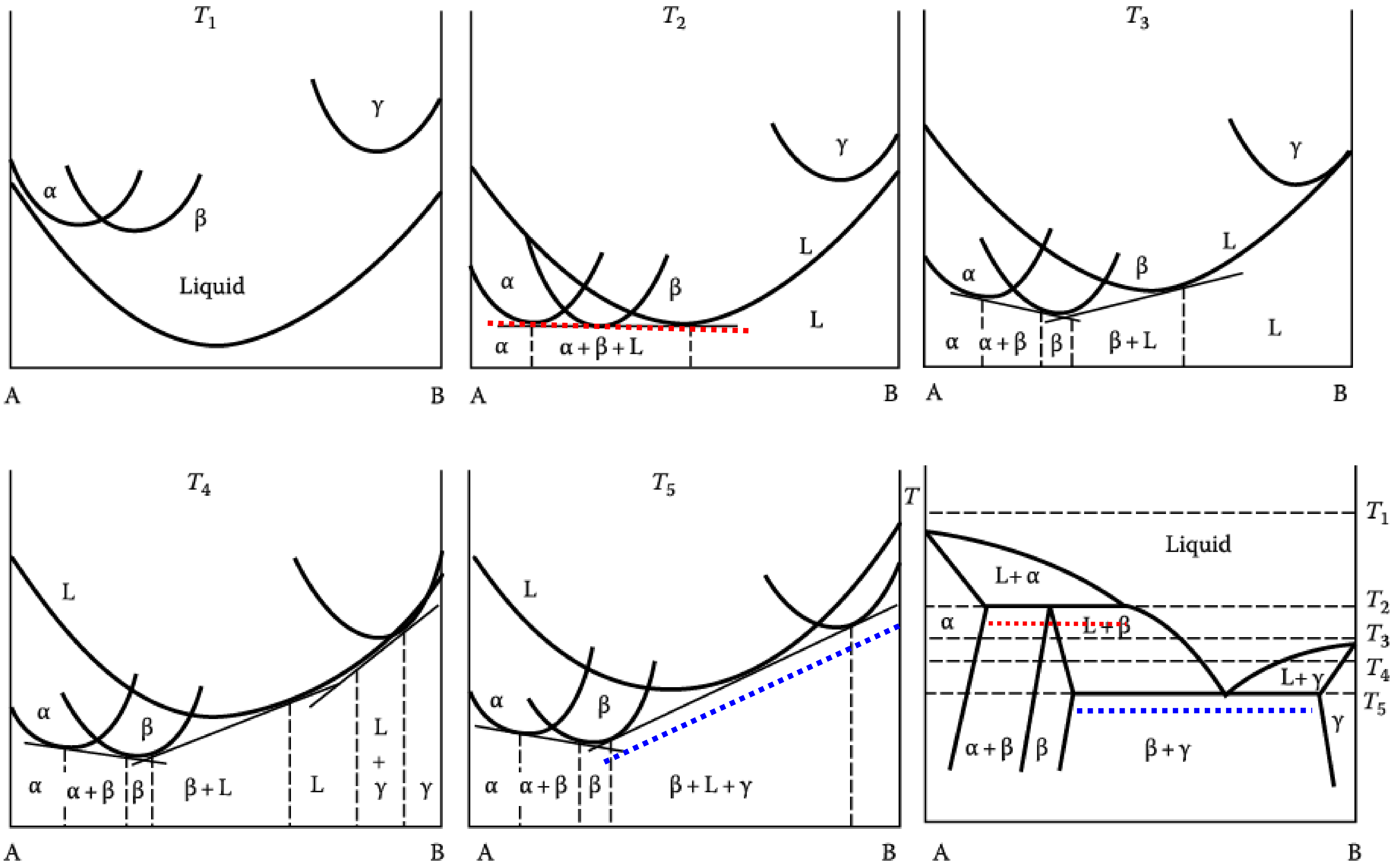


Fig. 1.34 The derivation of a complex phase diagram.

1.5 Binary phase diagrams

5) Phase diagrams containing intermediate phases

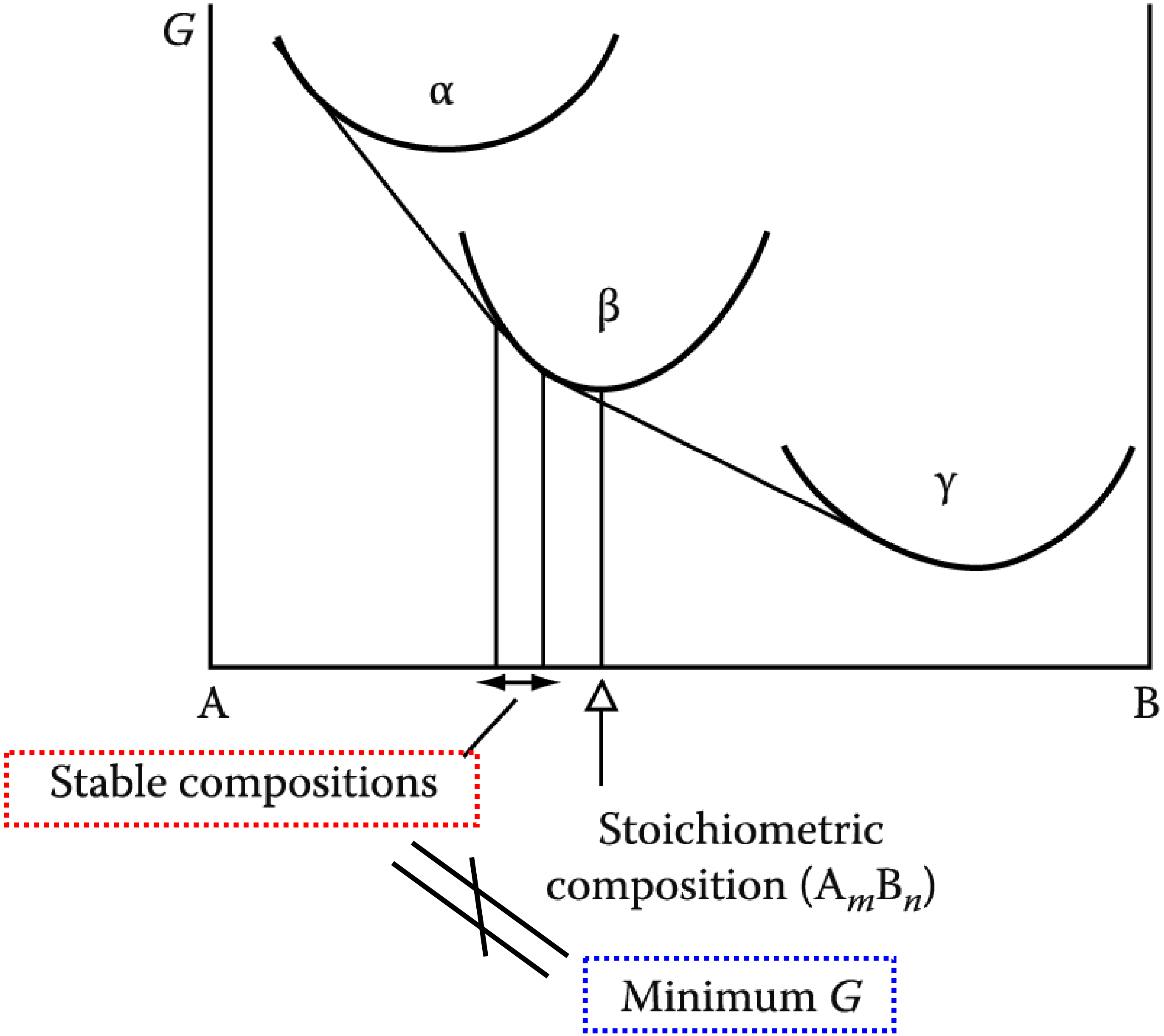
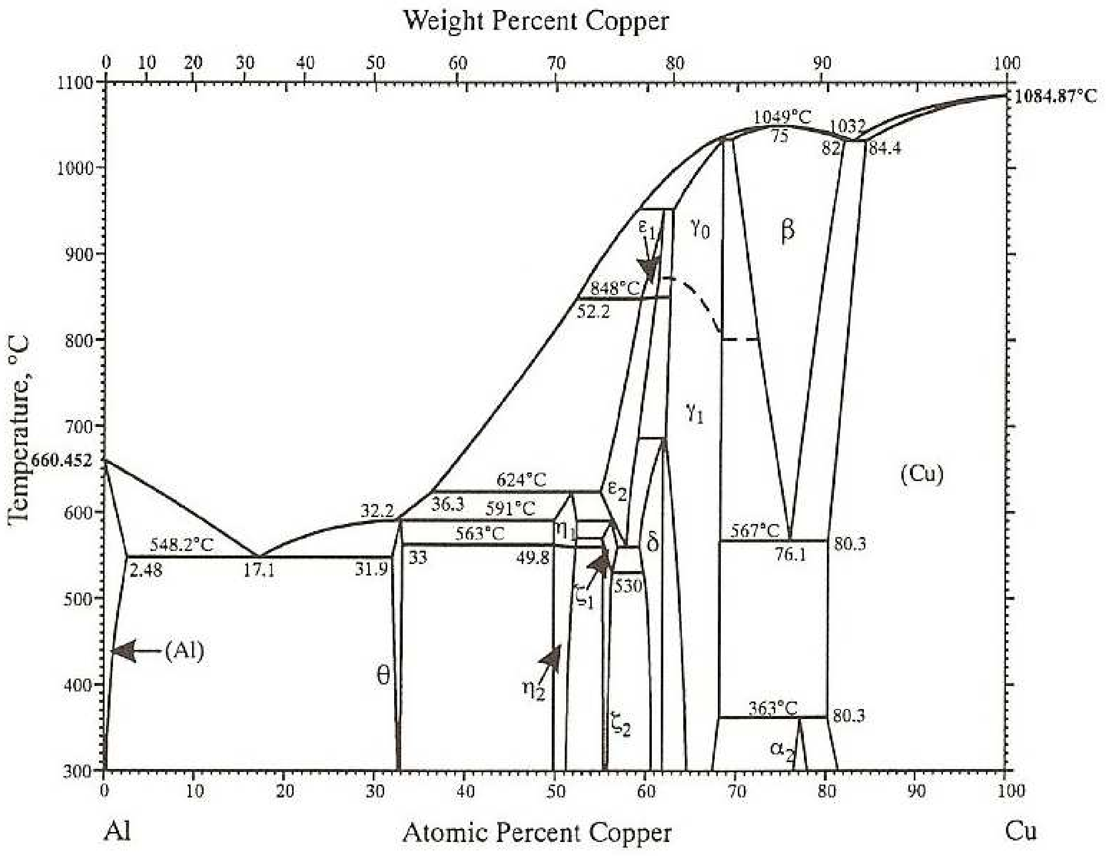


Fig. 1.35 Free energy diagram to illustrate that the range of compositions over which a phase is stable depends on the free energies of the other phases in equilibrium.

θ phase in the Cu-Al system is usually denoted as $CuAl_2$ although the composition X_{Cu}=1/3, X_{Al}=2/3 is not covered by the θ field on the phase diagram.



Al-Cu

Al-Cu

Phase	Composition, at.% Cu	Pearson symbol	Space group	Struktur-bericht designation	Prototype
(Al)	0 to 2.48	*cF*4	$Fm\bar{3}m$	*A*1	Cu
θ	31.9 to 33.0	*tI*12	*I*4/*mcm*	*C*16	Al_2Cu
η_1	49.8 to 52.4	*oP*16 or *oC*16	*Pban* or *Cmmm*	...	...
η_2	49.8 to 52.3	*mC*20	*Cm*/2	...	...
ζ_1	55.2 to 56.8	*hP*42	*P*6/*mmm*	...	...
ζ_2	55.2 to 56.3	*m***	...	...	...
ε_1	59.4 to 62.1	*c***	...	...	...
ε_2	55.0 to 61.1	*hP*4	$P6_3/mmc$	$B8_1$	NiAs
δ	59.3 to 61.9	*hR**	$R\bar{3}m$	...	...
γ_0	63 to 68.5	*cI*52	$I\bar{4}3m$	$D8_2$	Cu_5Zn_8
γ_1	62.5 to 68.5	*cP*52	$P\bar{4}3m$	$D8_3$	Al_4Cu_9
β	69.5 to 82	*cI*2	$Im\bar{3}m$	*A*2	W
α_2	76.5 to 78	...	...	...	...
(Cu)	80.3 to 100	*cF*4	$Fm\bar{3}m$	*A*1	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 (∵ decrease of $-T\Delta S_{mix}$ effect)

2) Systems with miscibility gap

$\Delta H^L_{mix} = 0 \quad \Delta H^S_{mix} > 0$

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

3) Ordered Alloys

$\Delta H^L_{mix} = 0 \quad \Delta H^S_{mix} < 0$

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

$\Delta H_{mix} << 0$ → The ordered state can extend to the melting temperature.

4) a. Simple Eutectic Systems

$\Delta H^L_{mix} = 0 \quad \Delta H^S_{mix} >> 0$

→ miscibility gap extends to the melting temperature.

Simple Peritectic Systems

→ Considerable difference between the melting points

5) Phase diagrams containing intermediate phases

Stable composition $\neq$ Minimum G with stoichiometric composition

Summary I: Binary phase diagrams

- Equilibrium in Heterogeneous Systems

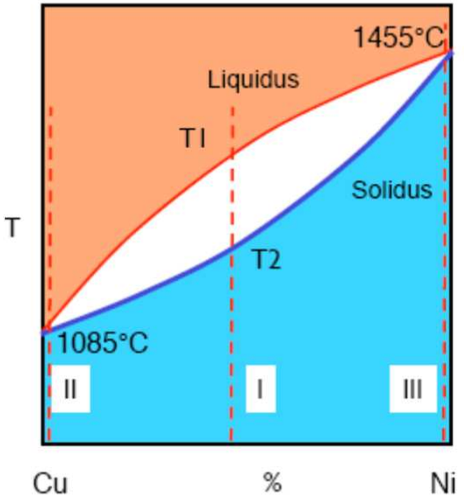
$G_0^{\beta} > G_0^{\alpha} > G_0^{\alpha+\beta}$ ➡ α + β separation ➡ unified chemical potential

- Binary phase diagrams

1) Simple Phase Diagrams

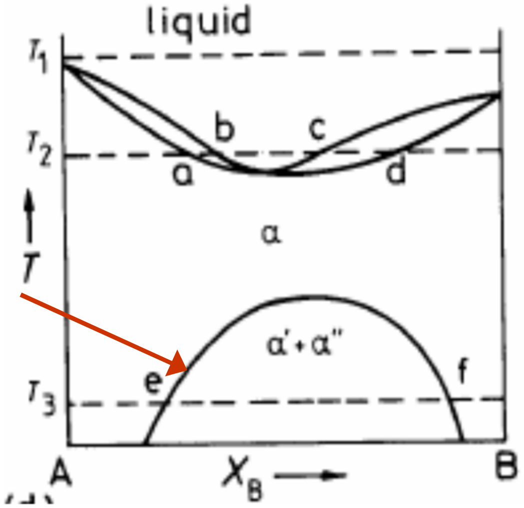
$$\Delta H_{mix}^{L} = 0 \ \Delta H_{mix}^{S} = 0$$

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



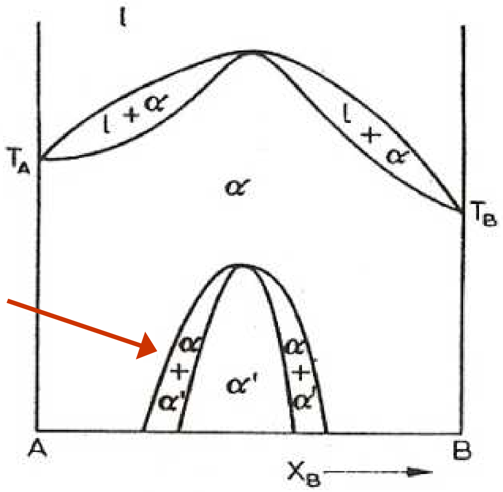
2) Variant of the simple phase diagram

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



miscibility gab

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



Ordered phase

Eutectic reaction

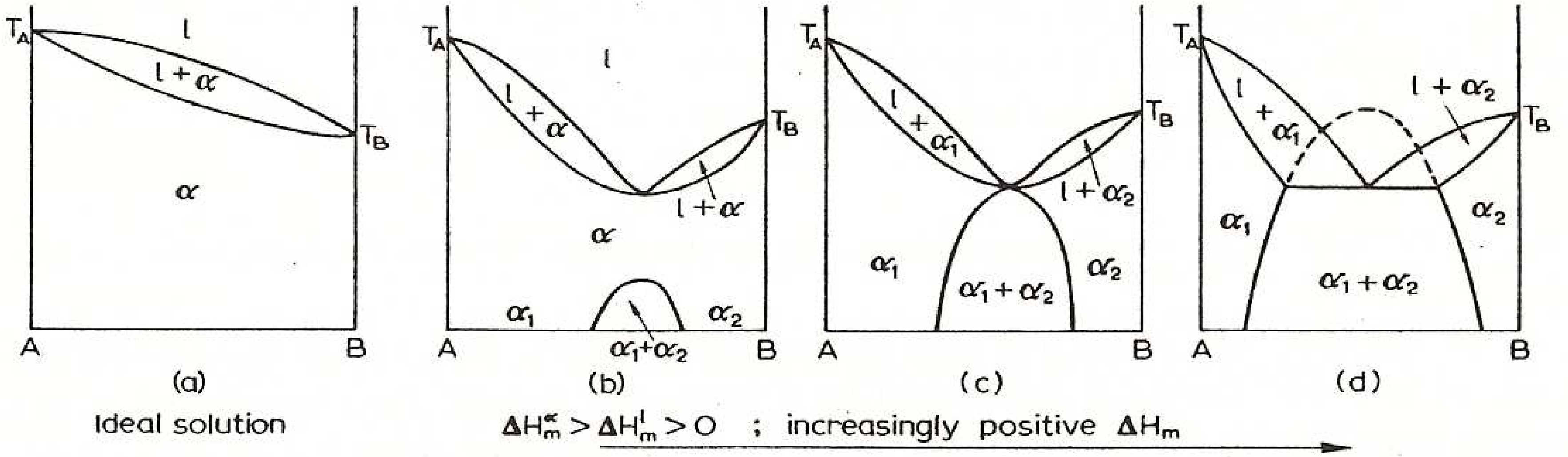


Fig. 43. Effect of increasingly positive departure from ideality in changing the phase diagram for a continuous series of solutions to a eutectic-type.

Peritectic reaction

<u>Considerable difference between the melting points</u>

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

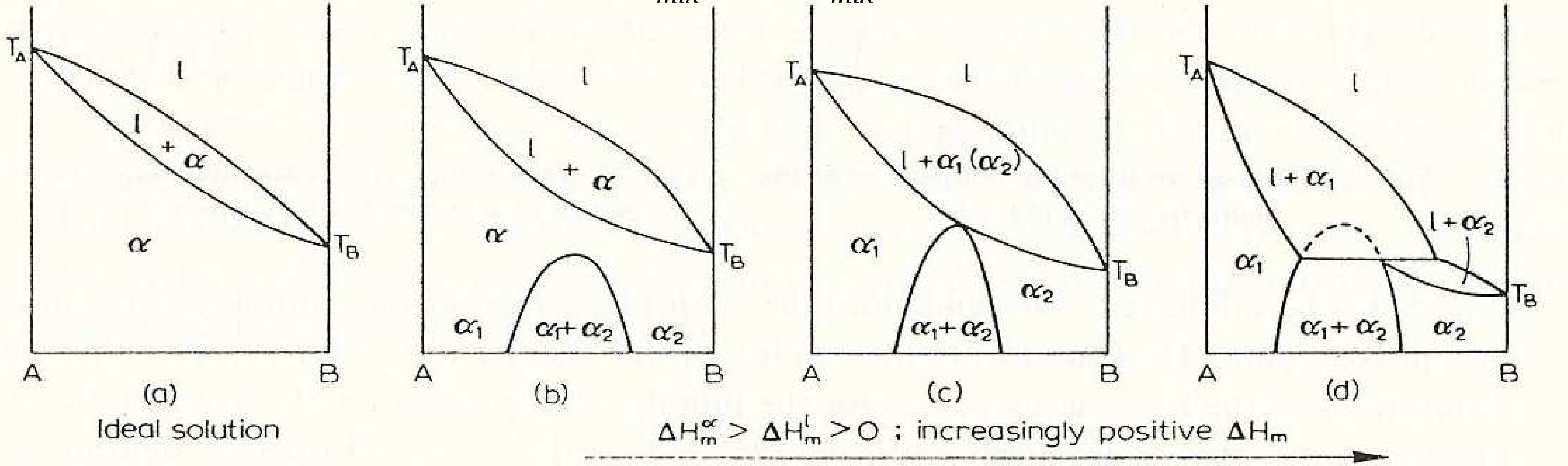


Fig. 61. Effect of increasingly positive departure from ideality in changing the phase diagram from a continuous series of solutions to a peritectic-type.

Q3: "Gibbs Phase Rule"?

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

$$F = C - P + 1$$ **(constant pressure)**

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 from chemical equilibrium $\mu_i^\alpha = \mu_i^\beta = \mu_i^\gamma = \cdots = \mu_i^p$

p-1 from thermal equilibrium $T^\alpha = T^\beta = T^\gamma = \cdots = T^p$

p-1 from mechanical equilibrium $P^\alpha = P^\beta = P^\gamma = \cdots = P^p$

- Number of variable can be controlled with maintaining equilibrium

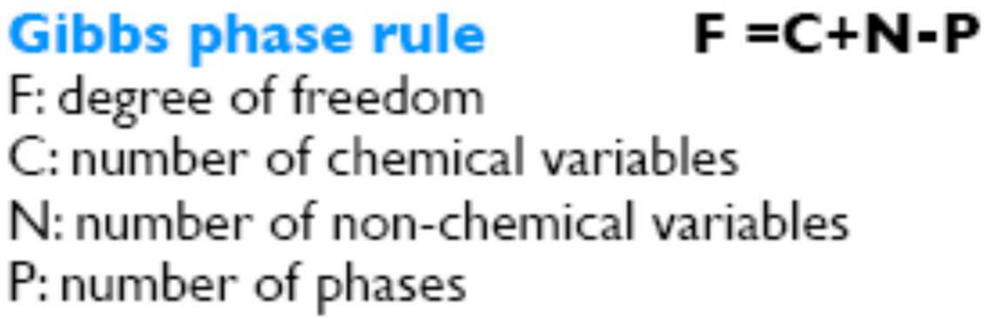
$$f = \boxed{(c-1)p + p + p}\boxed{-(p-1)c-(p-1)-(p-1)} = c - p + 2$$

$$\boxed{f = c - p + 2} \quad \textbf{(1.49)}$$

- If pressure is constant : $f = (c-1)p + p - (p-1)c - (p-1) = \boxed{c - p + 1}$ **(1.50)**

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:

$$F = C - P + 2 \quad \text{(from T, P).} \qquad (1.49)$$

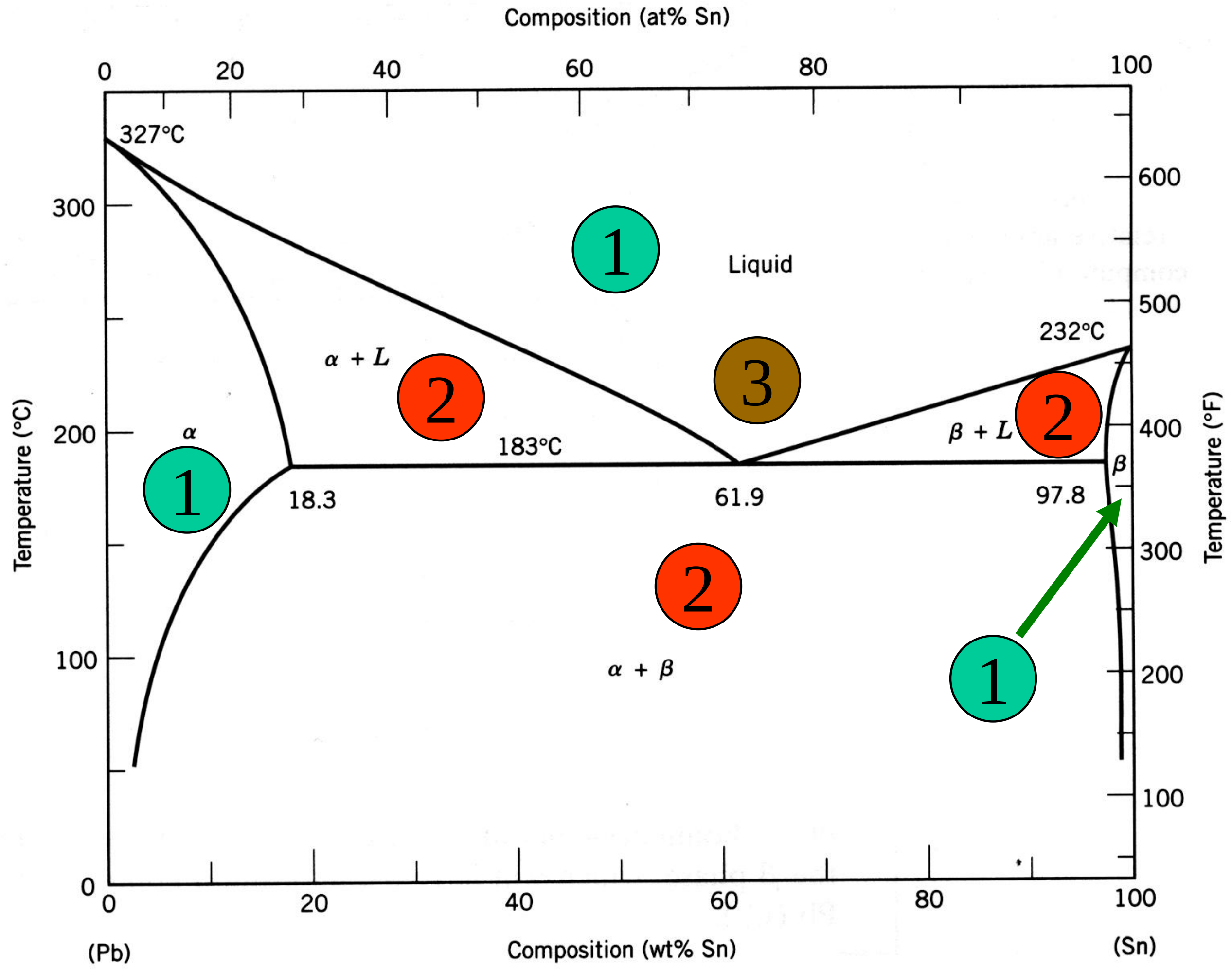
From Wikipedia, the free encyclopedia

The Gibbs Phase Rule

For Constant Pressure,

(1.50) **$P + F = C + 1$**

When C=2, $P+F = 3$



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**

$F = C - P + 1$

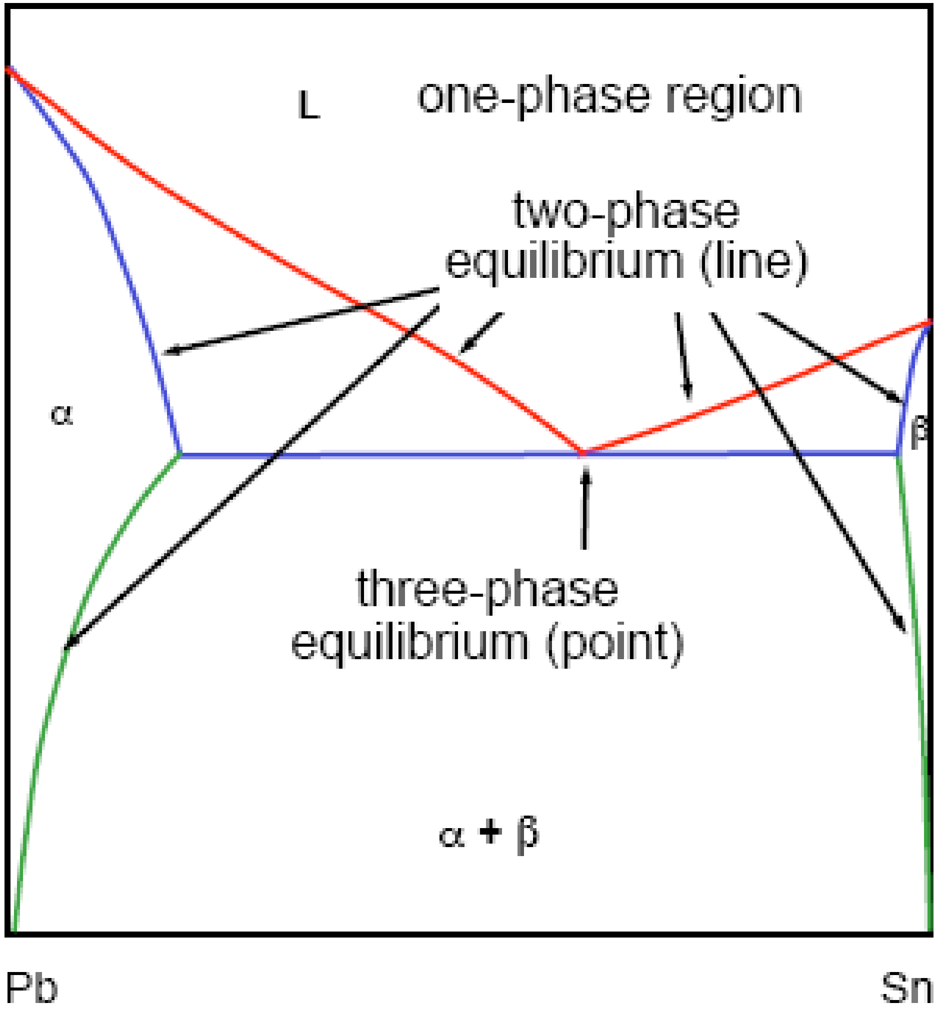
$= 2 - 3 + 1$

$= 0$

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)



Q4: “Effect of Temperature on Solid Solubility”?

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

a) $\boxed{T\uparrow \Rightarrow X_B^e\uparrow}$

b) X_B^e can never be equal to zero.

1.5.7 Effect of T on solid solubility

$$\boxed{T\uparrow \;\Rightarrow\; X_B^e \uparrow}$$

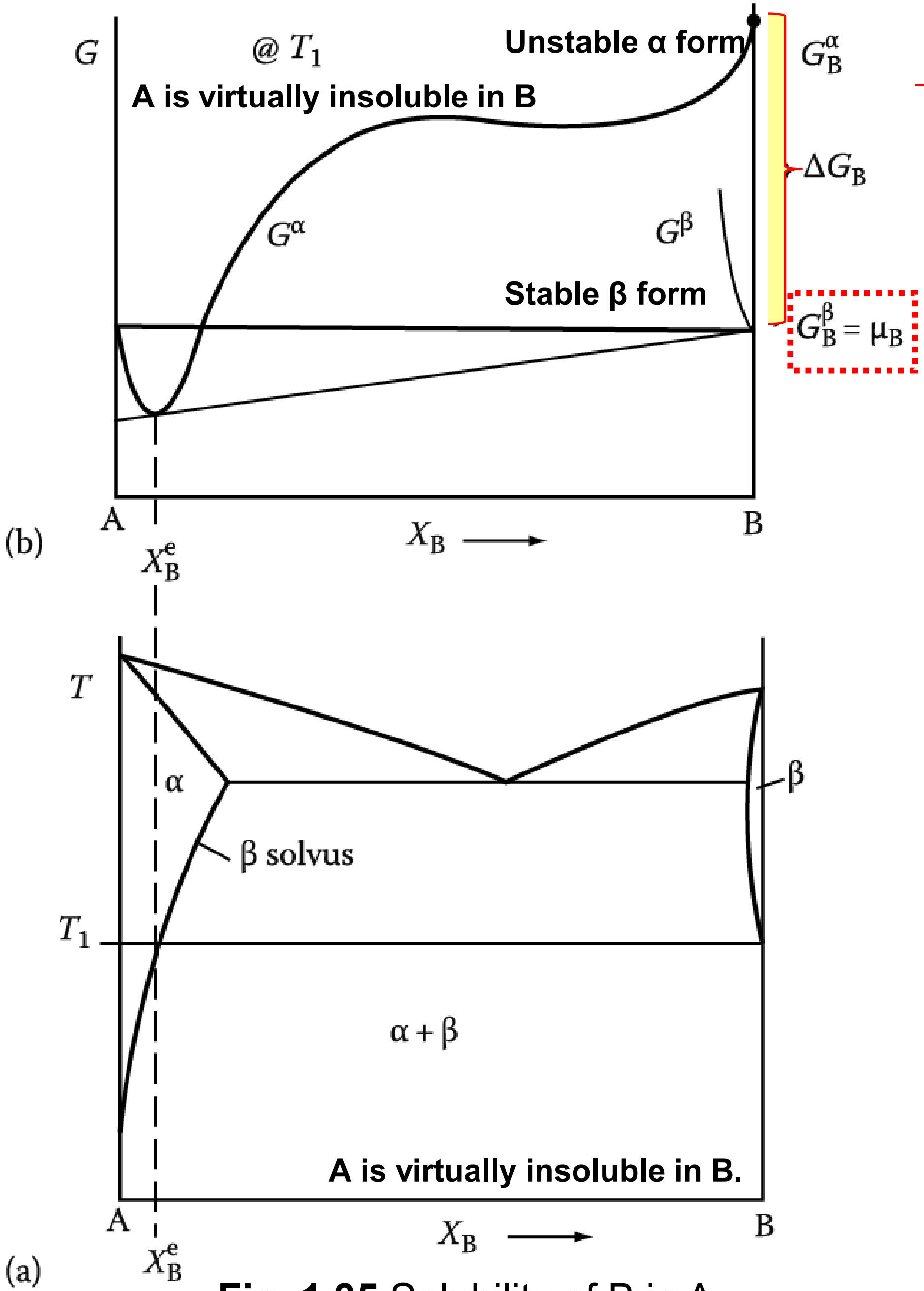


Fig. 1.35 Solubility of B in A.

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

$$\Delta G_B^{\beta\to\alpha} = {}^0G_B^\alpha - {}^oG_B^\beta = {}^oG_B^\alpha - \mu_B^\beta = {}^oG_B^\alpha - \mu_B^\alpha$$

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

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

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

$$(here, X_B^e << 1)$$

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

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

$\Delta G_B^{\beta\to\alpha} = \Delta H_B^{\beta\to\alpha} - T\Delta S_B^{\beta\to\alpha}$ 이므로

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

$$\boxed{X_B^e = A\exp\left\{-\frac{Q}{RT}\right\}} \qquad \boxed{T\uparrow \;\Rightarrow\; X_B^e \uparrow}$$

Q : heat absorbed (enthalpy) when 1 mole of β dissolves in A rich α as a dilute solution.

* Limiting forms of eutectic phase diagram

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

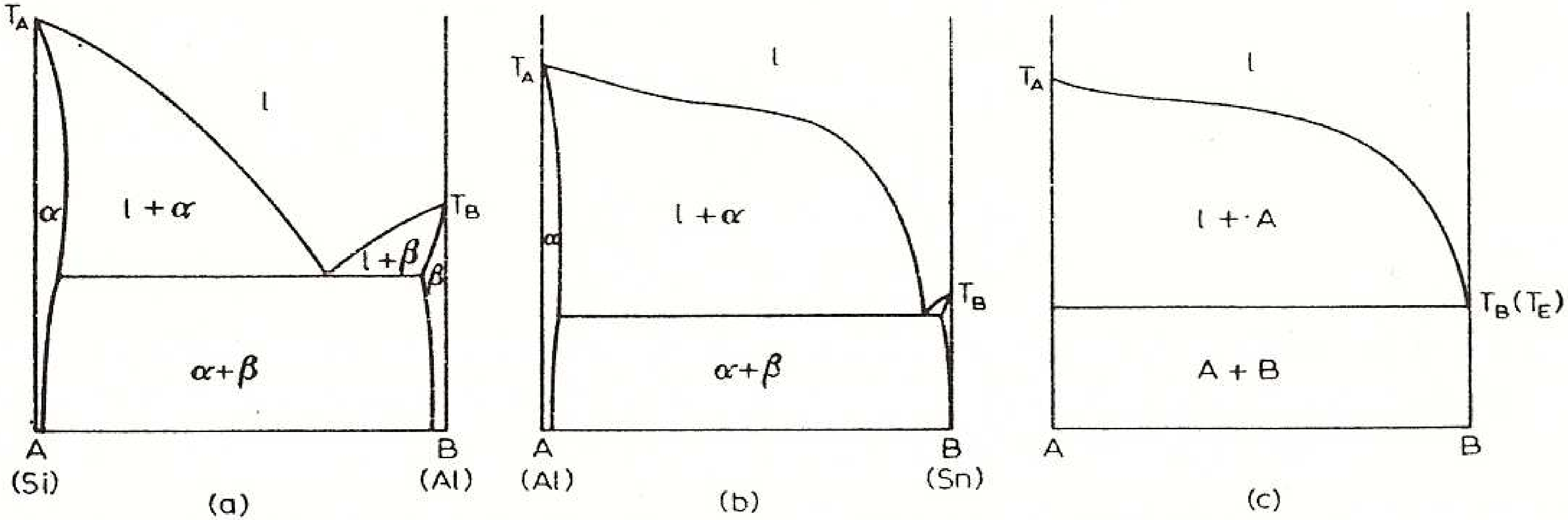
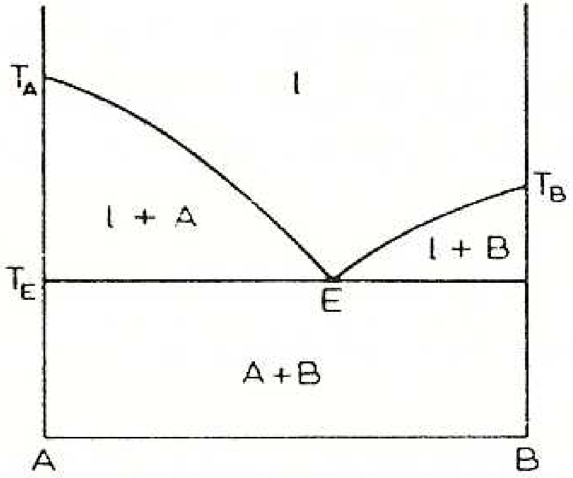


Fig. 53. Evolution of the limiting form of a binary eutectic phase diagram.

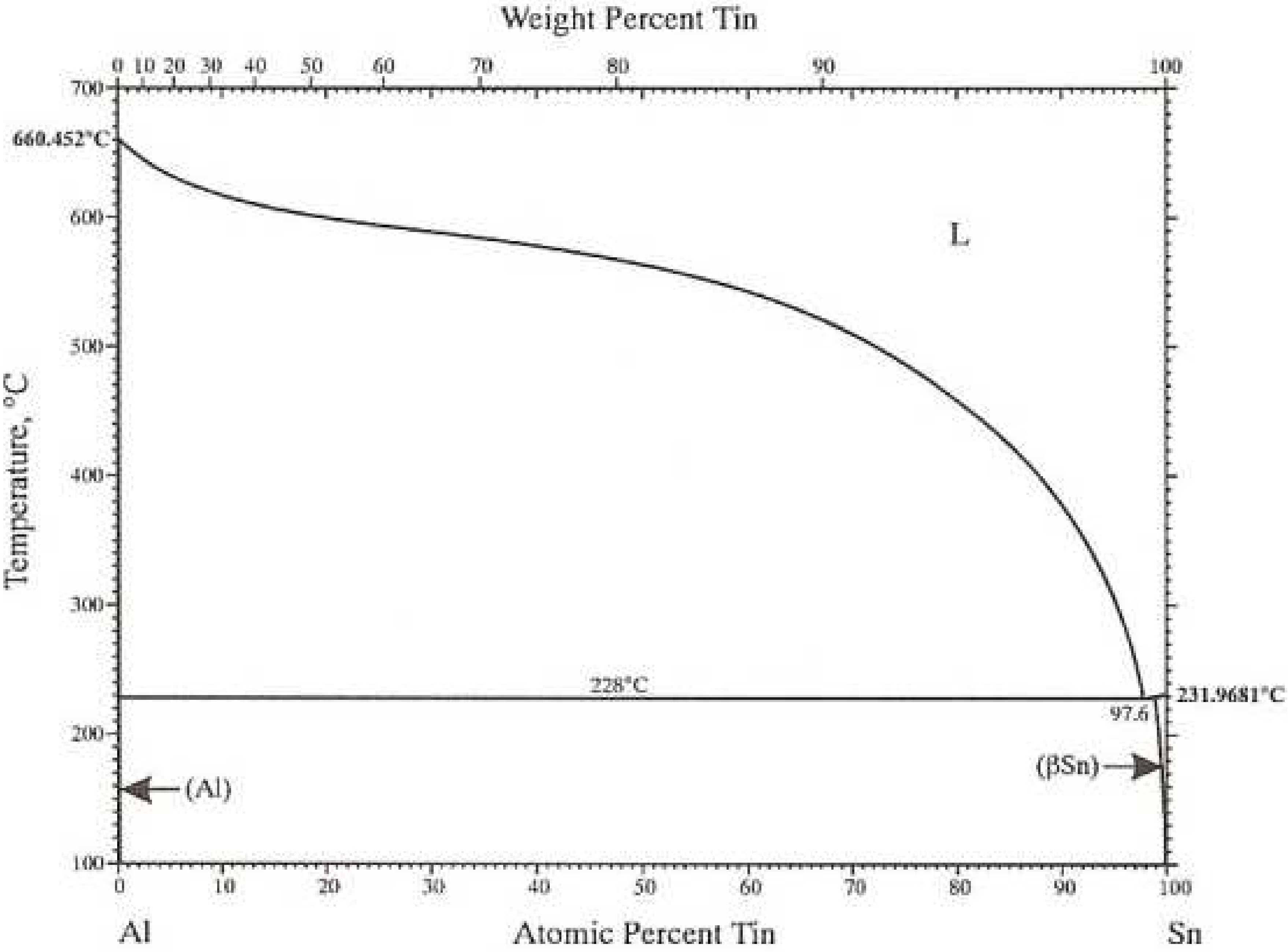
$$X_B^e = A\exp\left\{-\frac{Q}{RT}\right\}$$

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.


Weight Percent Tin
0 10 20 30 40 50 60 70 80 90 100
700
660.452°C
600
500
400
300
200
100
Temperature, °C
L
228°C
231.9681°C
97.6
(βSn)
(Al)
0 10 20 30 40 50 60 70 80 90 100
Al
Atomic Percent Tin
Sn

Q5: “Equilibrium Vacancy Concentration”?

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

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**

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

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

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

- **In practice, ΔH_V is of the order of 1 eV per atom and X_V^e reaches a value of about 10^{-4}~10^{-3} at the melting point of the solid**

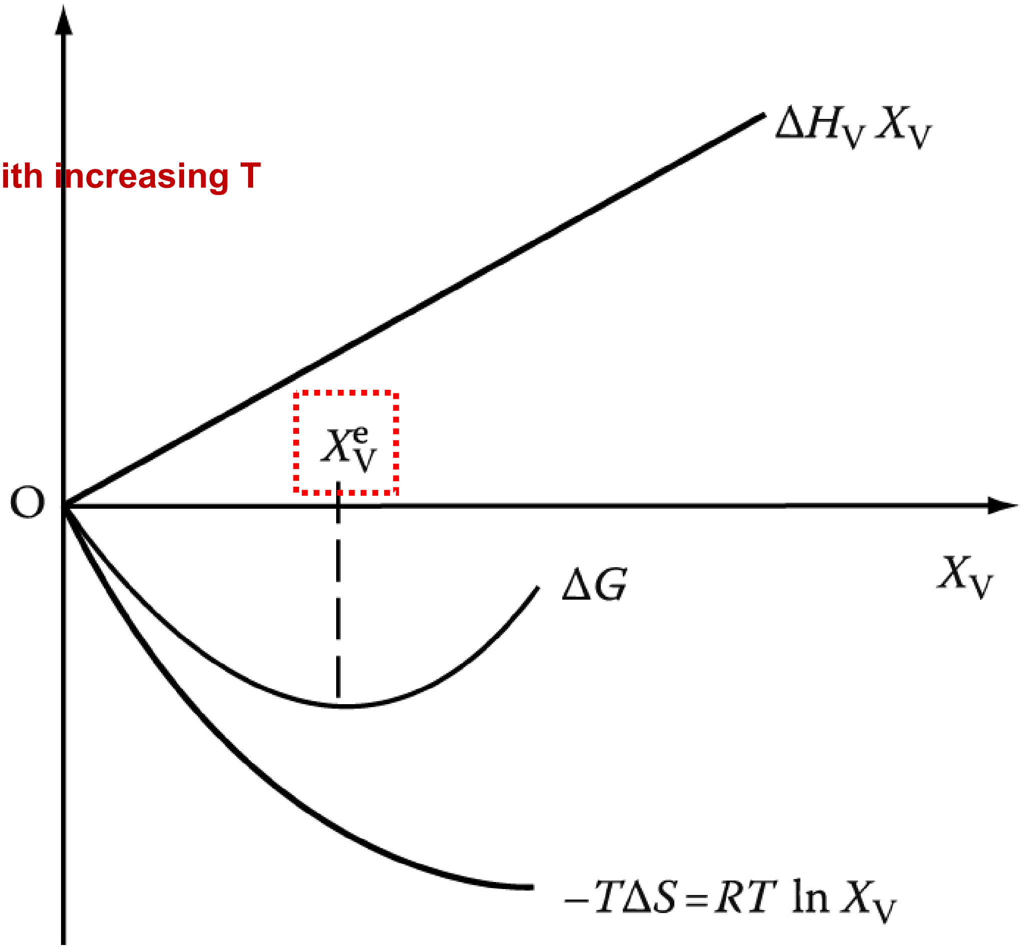


Fig. 1.37 Equilibrium vacancy concentration.

: adjust so as to reduce G to a minimum

Q6: “Influence of Interfaces on Equilibrium”?

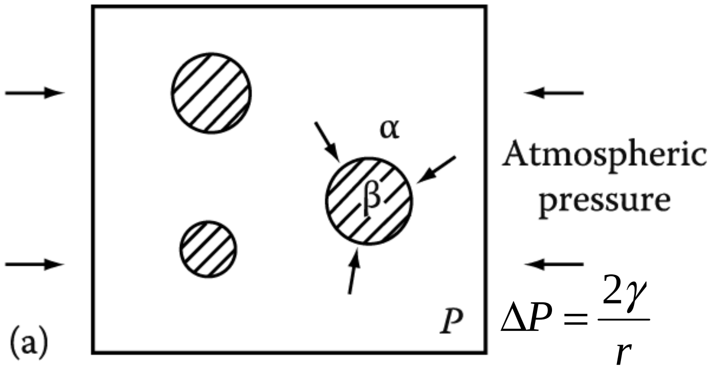
$$\Delta G = \frac{2\gamma V_m}{r}$$ **Gibbs-Thomson effect**

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 ΔP due to curvature of the **α/β**



$$\Delta P = \frac{2\gamma}{r}$$

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

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

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

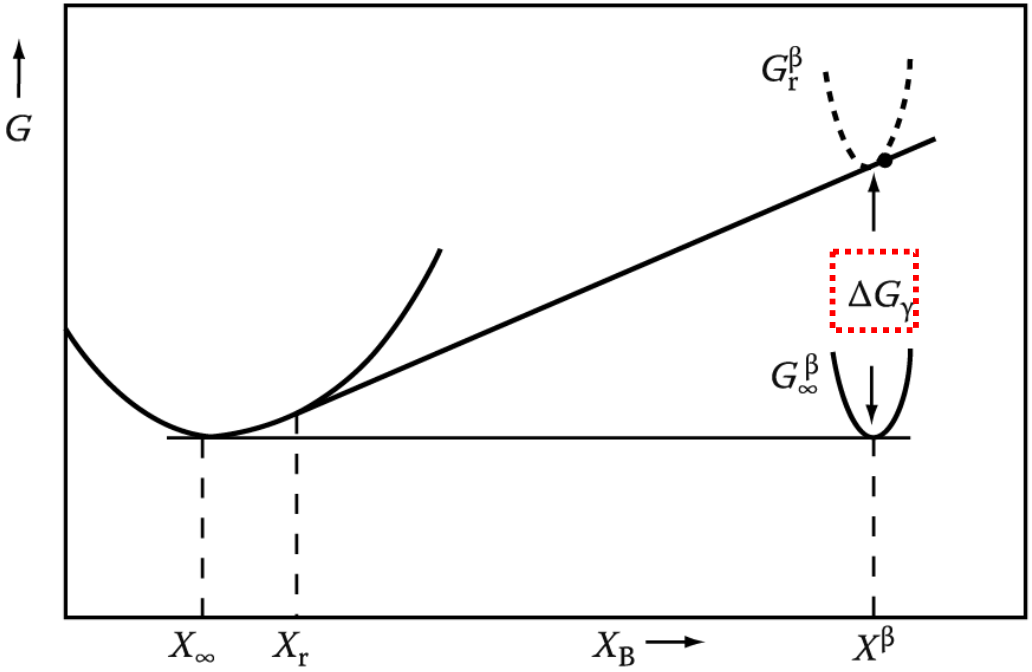


Fig. 1.38 The effect of interfacial E on the solubility of small particle

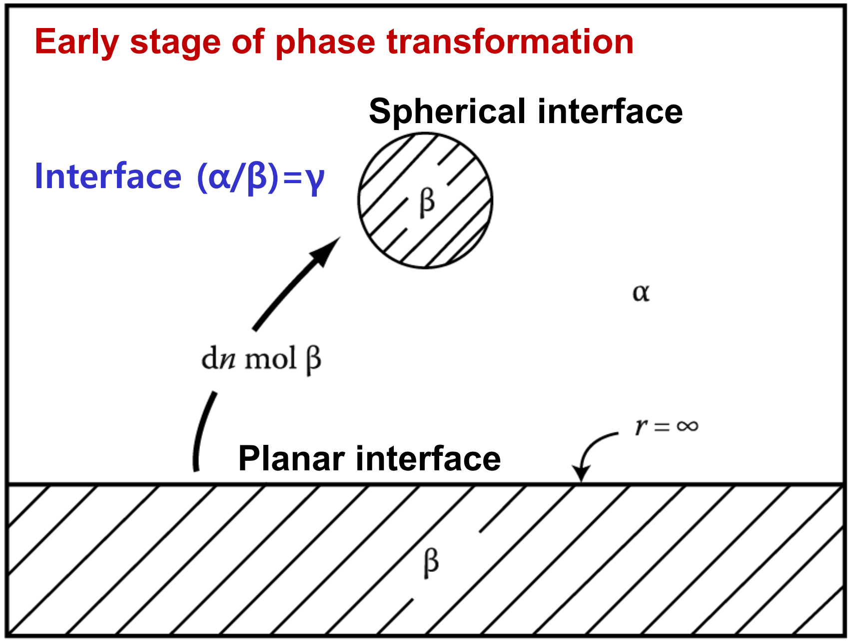


Fig. 1.39 Transfer of dn mol of β from large to a small particle.

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

Gibbs-Thomson effect (capillarity effect):

Free energy increase due to interfacial energy

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

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

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

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

Quite large solubility differences can arise for particles in the range r=1-100 nm. However, for particles visible in the light microscope (r>1um) capillarity effects are very small.

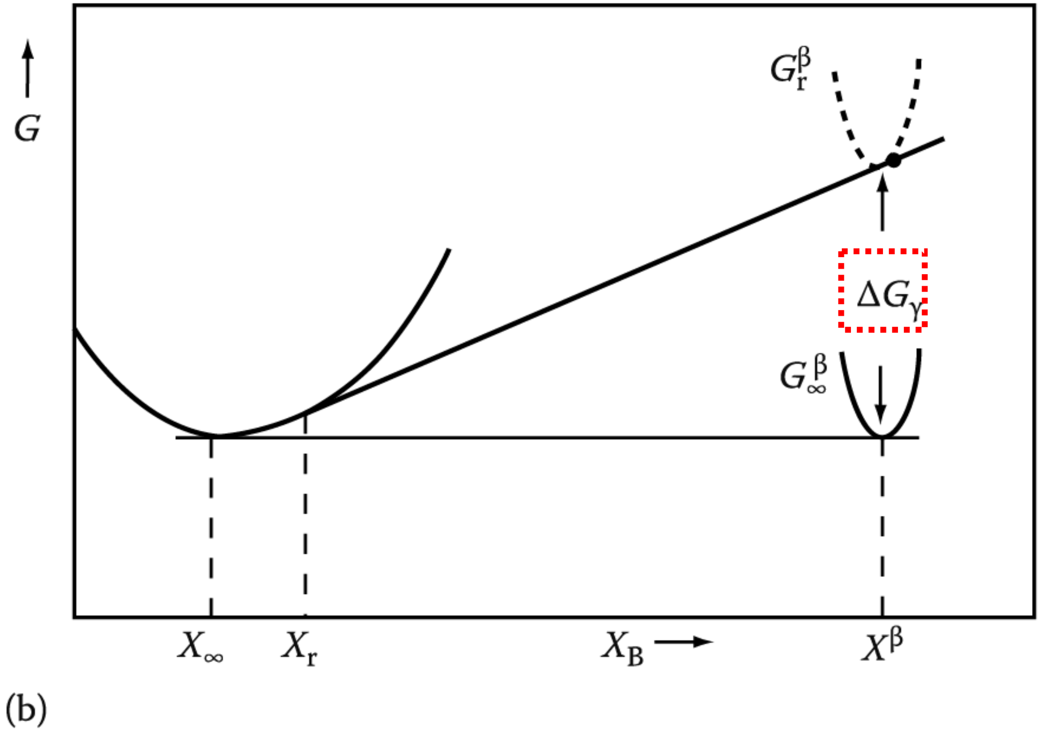


Fig. 1.38 The effect of interfacial energy on the solubility of small particles.

For small values of the exponent,

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

Ex) **γ=200mJ/m^2, V$_m$=10^{-5} m^3,T=500K**

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

For r=10 nm, solubility~10% increase

Total Free Energy Decrease per Mole of Nuclei $\Delta G_0 = -V\Delta G_V + A\gamma + V\Delta G_s$

Chapter 5.1

: 변태를 위한 전체 구동력, 핵생성을 위한 구동력은 아님

Driving Force for Precipitate Nucleation $\boxed{\alpha \rightarrow \alpha + \beta}$ ΔG_V

$$\Delta G_1 = \mu_A^{\alpha} X_A^{\beta} + \mu_B^{\alpha} X_B^{\beta}$$

: Decrease of total free E of system by removing a small amount of material with the nucleus composition (X_B^{β}) (P point)

$$\Delta G_2 = \mu_A^{\beta} X_A^{\beta} + \mu_B^{\beta} X_B^{\beta}$$

: Increase of total free E of system by forming β phase with composition X_B^{β} (Q point)

$$\boxed{\Delta G_n = \Delta G_2 - \Delta G_1}$$ (length PQ)

$$\boxed{\Delta G_V} = \frac{\Delta G_n}{V_m} \quad \text{per unit volume of } \beta$$

: driving force for β precipitation

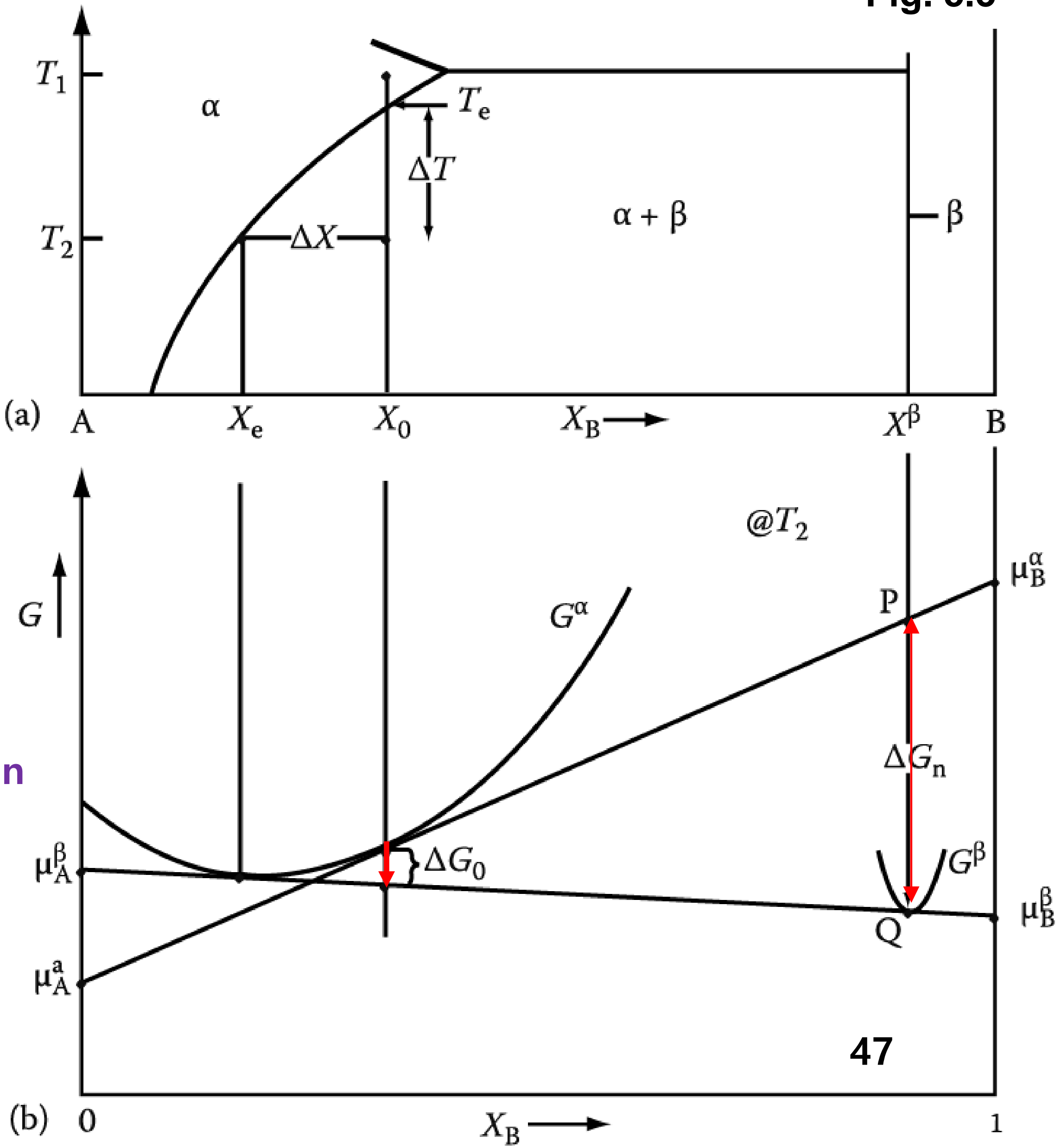
For dilute solutions,

$$\Delta G_V \propto \Delta X \quad \text{where } \Delta X = X_0 - X_e$$

$$\boxed{\Delta G_V \propto \Delta X \propto \Delta T}$$

∝ undercooling below T_e

Fig. 5.3



Q7: “Gibbs-Duhem Equation”?

: Be able to calculate the change in chemical potential that result from a change in alloy composition.

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

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

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

1.8 Additional Thermodynamic Relationships for Binary Solutions

➡ **Gibbs-Duhem equation:** Calculate the change in (dμ) that results from a change in (dX)

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

(T, P: constant)

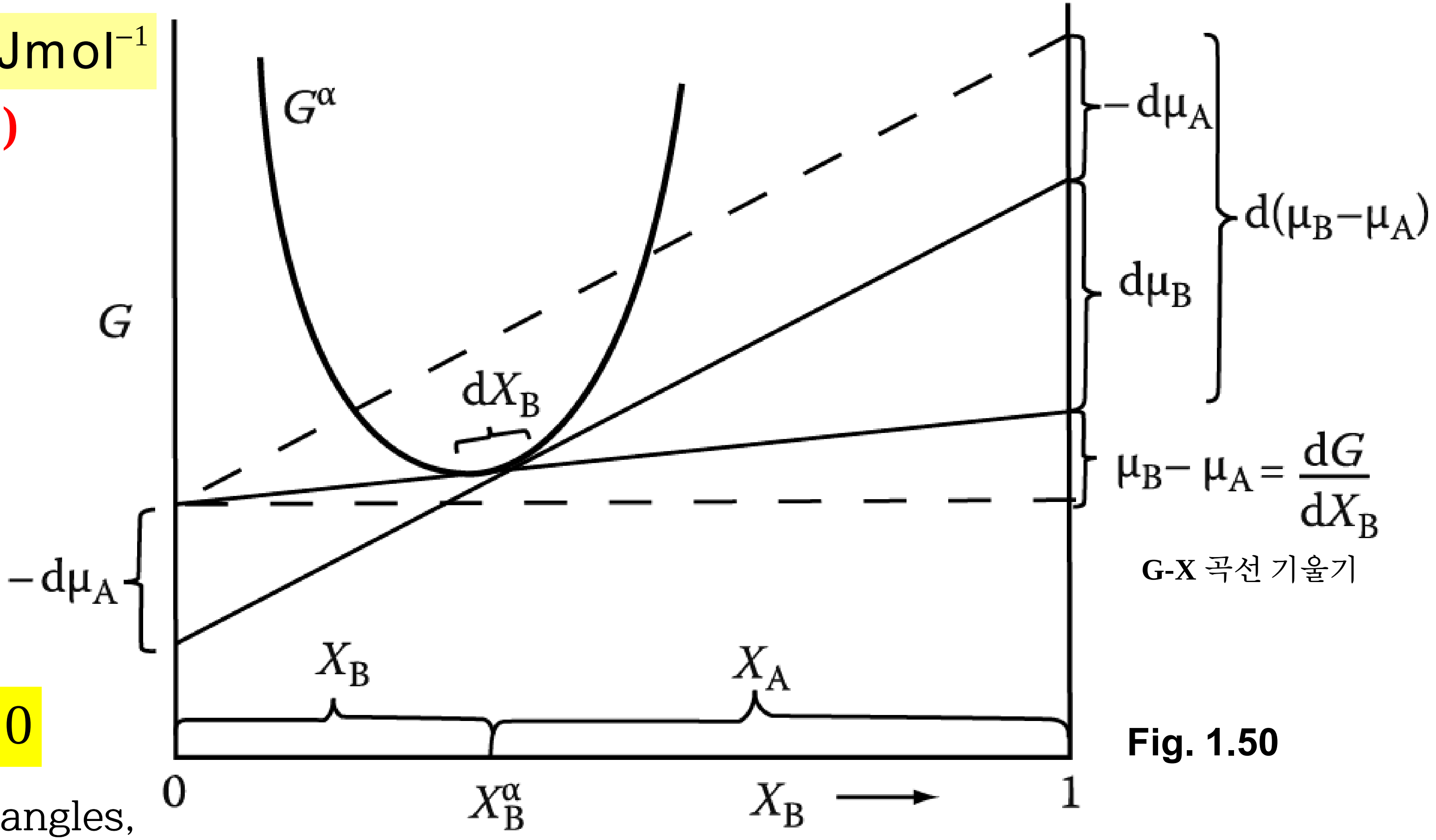


Fig. 1.50

Gibbs-Duhem Equation

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

Comparing two similar triangles,

$$-\frac{d\mu_A}{X_B} = \frac{d\mu_B}{X_A} = \frac{d(\mu_B - \mu_A)}{1} \quad ⇦ \quad \frac{dG}{dX_B} = \frac{\mu_B - \mu_A}{1},$$

d^2G/dX^2

$(\because d^2G/dX_B^2 = d^2G/dX_A^2)$

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. 1.75

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,

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

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

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

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

② Different form Eq. 1.75

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

$$\xrightarrow{\gamma_B = a_B/X_B}$$

Differentiating With respect to X_B,

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

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

Eq. 1.79

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

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

Eq. 1.80

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

Eq. 1.81

The Gibbs-Duhem Equation $X_A d\mu_A + X_B d\mu_B = 0$

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

be able to calculate the change in chemical potential (dμ) 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**

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

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

b) X_B^e can never be equal to zero.

- **Equilibrium Vacancy Concentration**

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

- **Influence of Interfaces on Equilibrium**

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

- **Gibbs-Duhem Equation:** $X_A d\mu_A + X_B d\mu_B = 0$

: Be able to calculate the change in chemical potential that result from a change in alloy composition.

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

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