

2017 Fall

“Phase Equilibria *in* Materials”

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Contents for previous class

CHAPTER 4

Binary Phase Diagrams

Three-Phase Equilibrium Involving Limited Solubility of the Components in the Solid State but Complete Solubility in the Liquid State

4.3. Three-Phase Equilibrium : Peritectic Reactions

2) Eutectoid reaction

3) Peritectic reaction

Formation of intermediate phases by peritectic reaction

Non-stoichiometric compounds

4) Congruent transformations

According to the condensed Phase Rule, $f = c - p + 1$

For a binary system the equilibria possible are summarized below.

<i>Number of components</i>	<i>Number of phases</i>	<i>Variance</i>	<i>Equilibrium</i>
$c = 2$	$p = 1$	$f = 2$	bivariant $p = c - 1$
$c = 2$	$p = 2$	$f = 1$	monovariant $p = c$
$c = 2$	$p = 3$	$f = 0$	invariant $p = c + 1$

Invariant reactions which have been observed in binary diagrams are listed below, together with the nomenclature given to such reactions.

$l \rightleftharpoons \alpha + \beta$	eutectic reaction	(<i>e.g.</i> Ag–Cu system)
$\gamma \rightleftharpoons \alpha + \beta$	eutectoid reaction	(<i>e.g.</i> C–Fe system)
$l_1 \rightleftharpoons \alpha + l_2$	monotectic reaction	(<i>e.g.</i> Cu–Pb system)
$\alpha \rightleftharpoons \beta + l$	metatectic reaction	(<i>e.g.</i> Ag–Li system)
$l + \alpha \rightleftharpoons \beta$	peritectic reaction	(<i>e.g.</i> Cu–Zn system)
$\alpha + \beta \rightleftharpoons \gamma$	peritectoid reaction	(<i>e.g.</i> Al–Cu system)
$l_1 + l_2 \rightleftharpoons \alpha$	syntectic reaction	(<i>e.g.</i> K–Zn system)

Invariant reactions involving liquid phases have a name ending in *-tectic* while those occurring completely in the solid state end in *-tectoid*.

Peritectic reaction

Considerable difference between the melting points

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

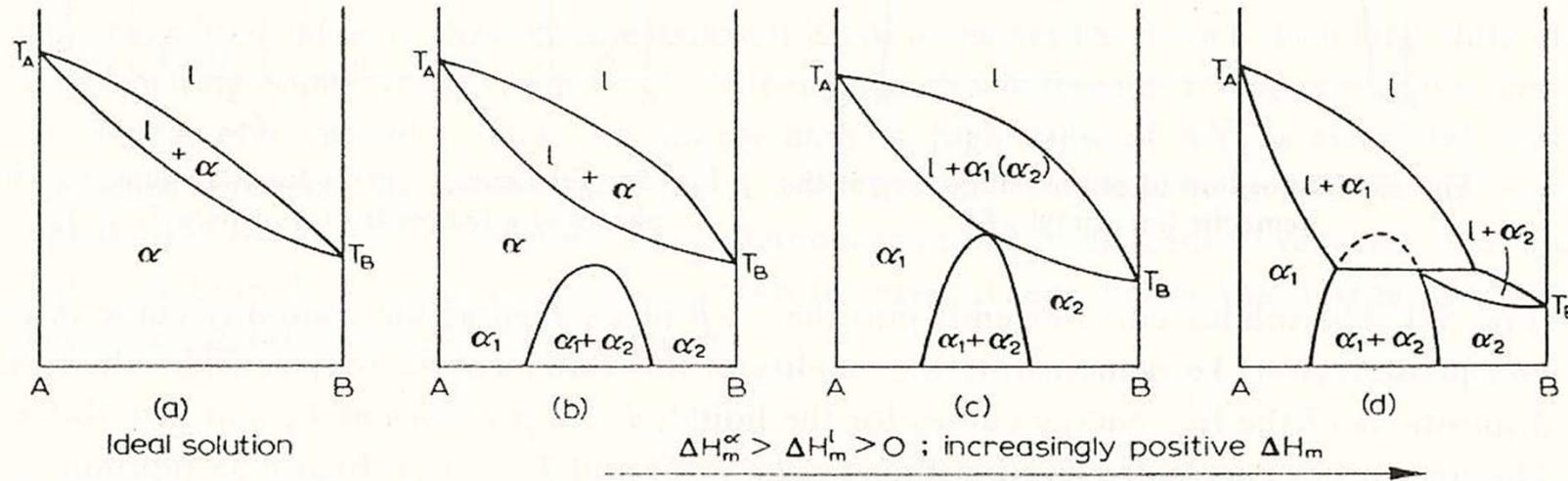


Fig. 61. Effect of increasingly positive departure from ideality in changing the phase diagram from a continuous series of solutions to a peritectic-type.

Eutectic reaction

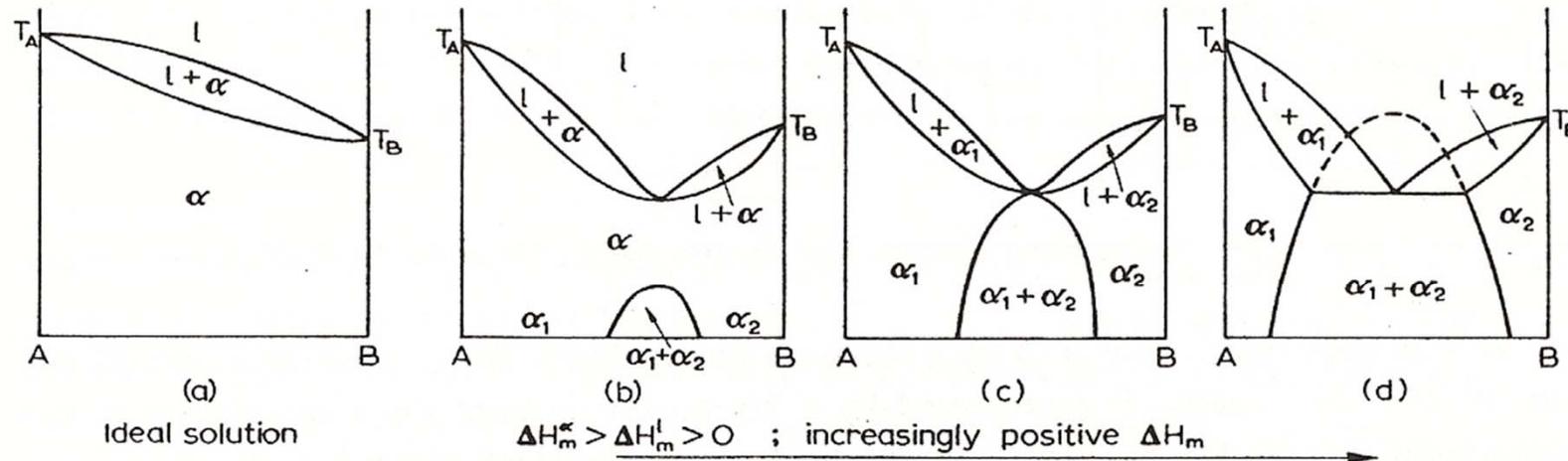


Fig. 43. Effect of increasingly positive departure from ideality in changing the phase diagram for a continuous series of solutions to a eutectic-type.

Peritectic reaction

- **Surrounding or Encasement:** During peritectic reaction, $L + \alpha \rightarrow \beta$, the beta phase created surrounds primary alpha.
- Beta creates **diffusion barrier** resulting in coring.

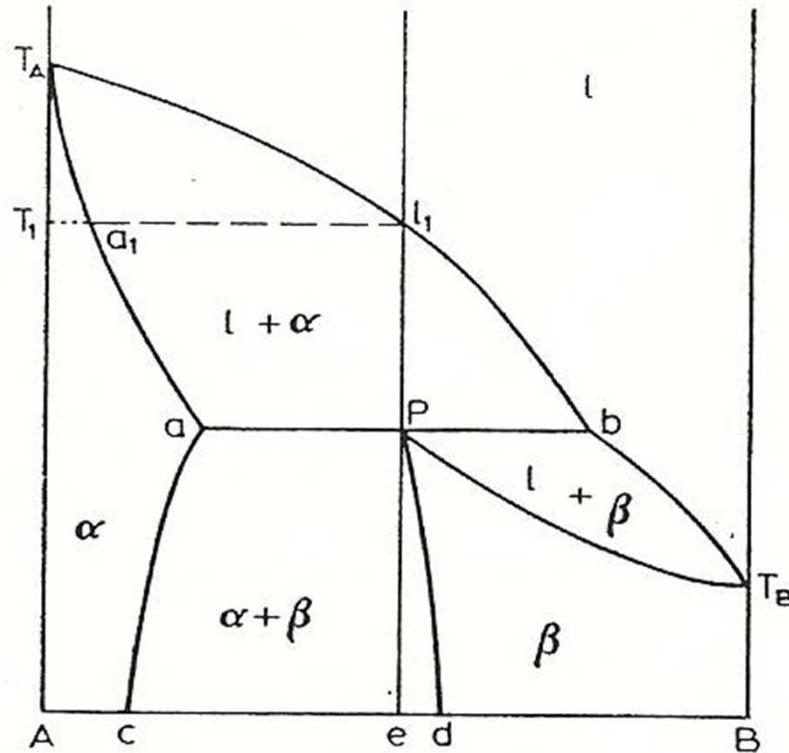


Fig. 65. Freezing of the peritectic alloy P .

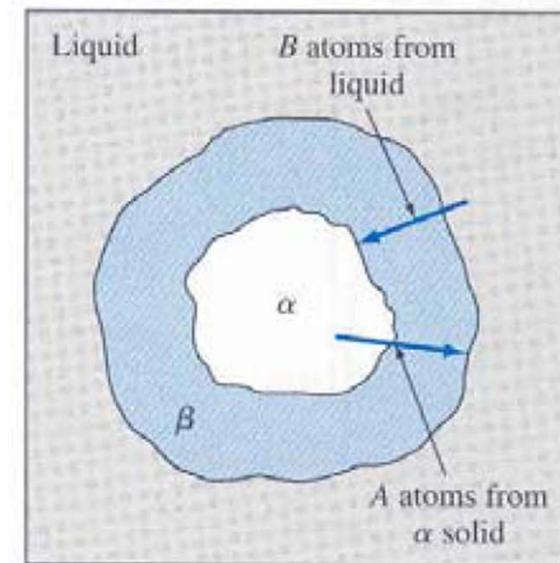


Figure 8.19

4.3.4. Formation of intermediate phases by peritectic reaction

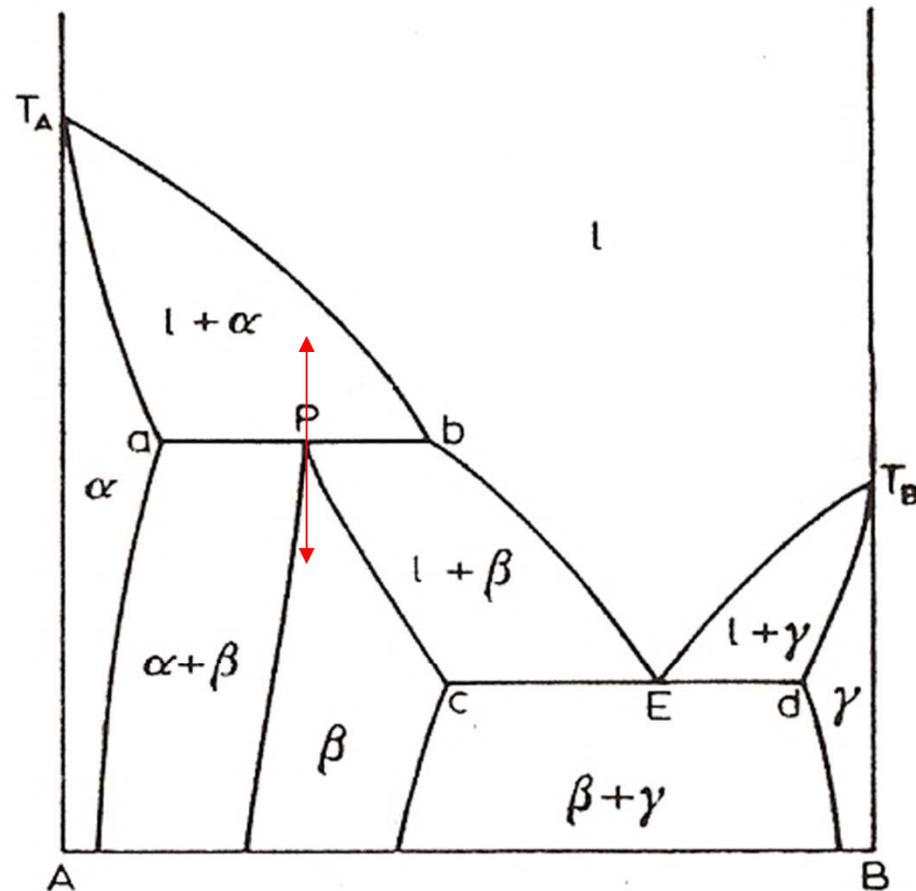


Fig. 68. Formation of an intermediate phase, β , by peritectic reaction.

β : different crystal structure with those of the component

older literature_ intermediate phases ~regarded as a chemical compounds

Thus, **called intermetallic compounds** but, cannot expect from valency

considerations & not fixed composition (different with chemical compounds)

* Intermediate phases

(1) Size-factor compounds ~ relatively large size differences of the constituent atoms

e.g. a) **Laves phases**, which are intermediate phases based on the formula AB_2 , where atom A has the larger atomic diameter.

b) **Interstitial compounds**: metal carbides, nitrides and borides

(2) Electron compounds ~ similar electrochemical properties and a favorable size-factor occurs at one of three valency electron-to-atom ratios.

e.g. a) **3:2 electron compounds** CuZn, Cu₃Ga, and Cu₅Sn
different %Cu, same electron concentration and similar crystal structure (BCC)

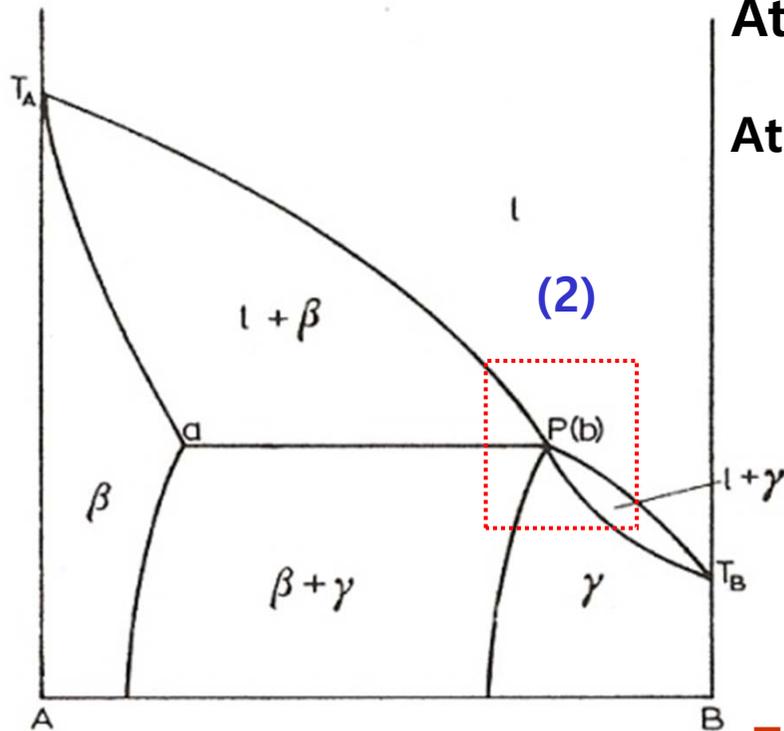
b) **21:13 electron compounds** γ brass (complex cubic lattice with 52 atoms per unit cell)

c) **7:4 electron compounds** close-packed hexagonal structure similar to ϵ brass

(3) Normal valency compounds (partly-ionic compounds) ~ obey the valency rules

e.g. Mg₂Si, Mg₂Sn, Mg₂Pb and Mg₃Sb₂/
much common in ionic compounds such as NaCl and CaF₂

1) Peritectic point virtually coincides with the liquid composition.
 But, thermodynamically, points P and b is not possible to coincide.



At equilibrium, $dG^s = dG^l, \mu_A^s = \mu_A^l, \mu_B^s = \mu_B^l$

At const P and differentiating with respect to X_A

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

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

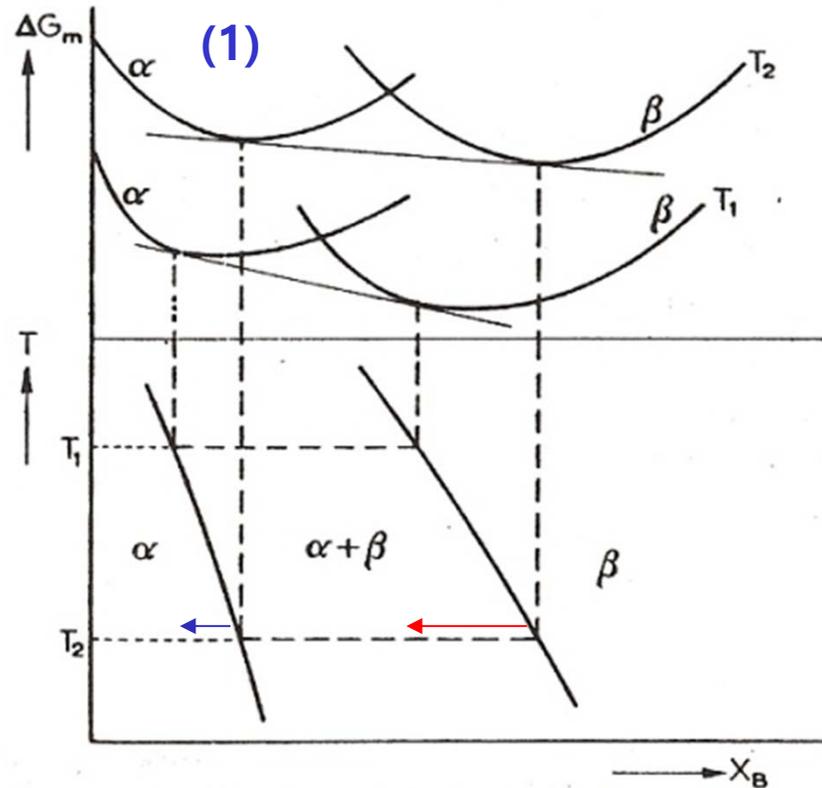
$$S^s \neq S^l, \frac{dT}{dX_A} = 0$$

Temp. maximum or minimum must be present.

Fig. 72. Limiting case of the peritectic reaction. (next page)

Peritectic point and the liquid composition are so close to each other that the experimental techniques used were not able to distinguish them. More refined methods would be expected to produce evidence of a compositional difference these two points.

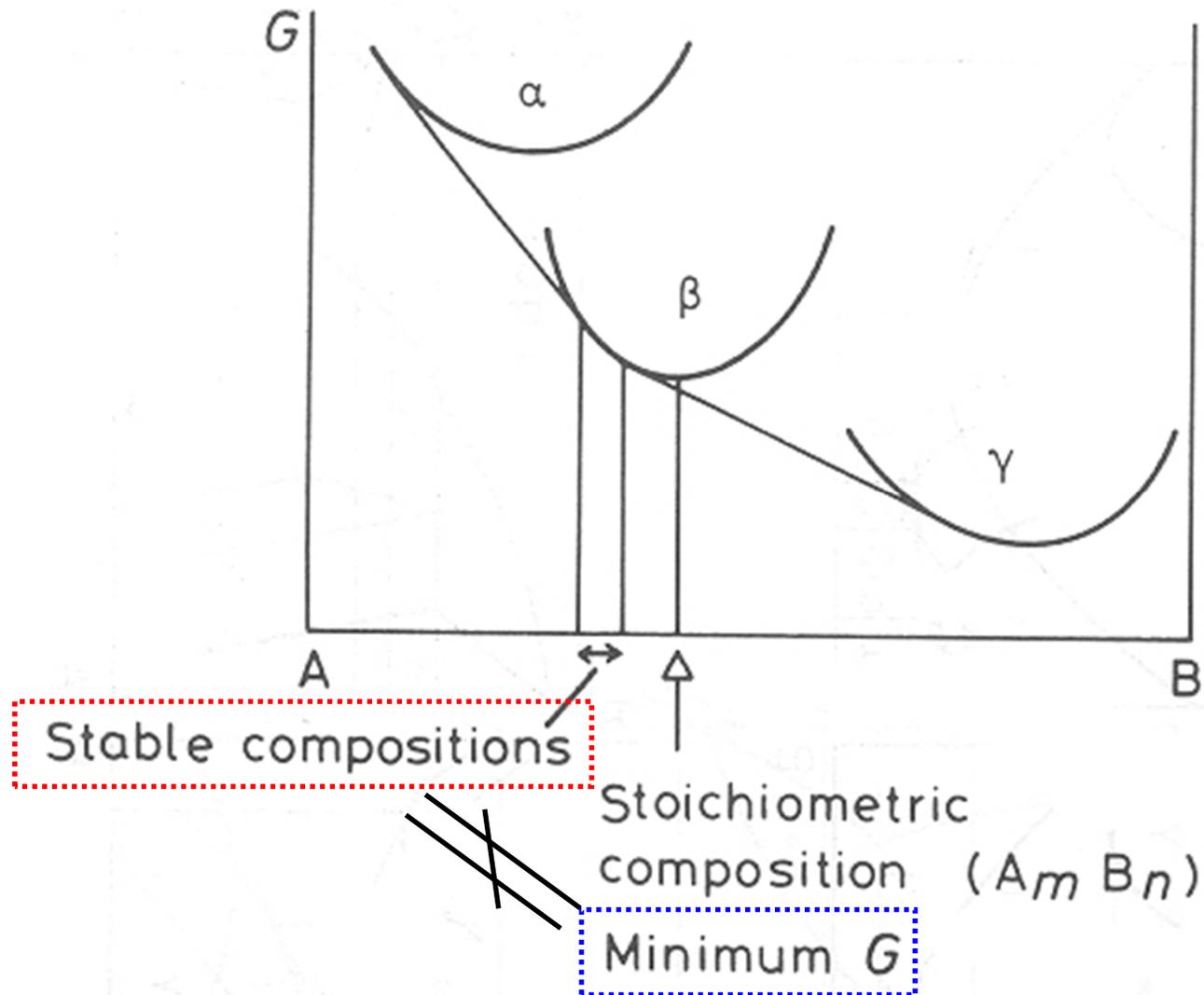
2) Decreasing solubility of Zn in Cu with rise in temperature in contrast to the normal decrease in solubility with fall in temperature



Due to an equilibrium with a disordered intermediate phase (e.g. the β phase above 454 °C, Fig. 71)

This has been explained as being due to a greater relative movement of the free energy curve of the intermediate phase compared with the α solid solution with rise in temperature.

4.3.5. Non-stoichiometric compounds



4.4 Congruent phase transformations

Congruent vs Incongruent

Congruent phase transformations: no compositional change associated with transformation

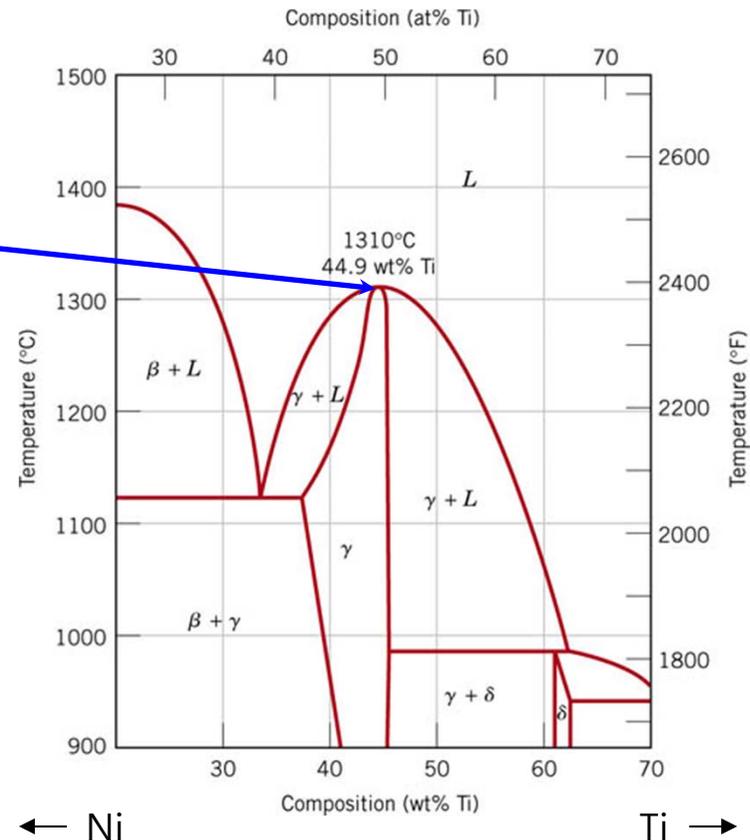
Examples:

- Allotropic phase transformations
- Melting points of pure metals
- **Congruent Melting Point**

Incongruent phase transformation: at least one phase will experience change in composition

Examples:

- Melting in isomorphous alloys
- Eutectic reactions
- Peritectic Reactions
- Eutectoid reactions



4.4. Congruent transformations

Congruent transformation:

(a): a melting point minimum, a melting point maximum, and a critical temperature associated with an order-disorder transformation

(b), (c) and (d): formation of an intermediate phase (next page)

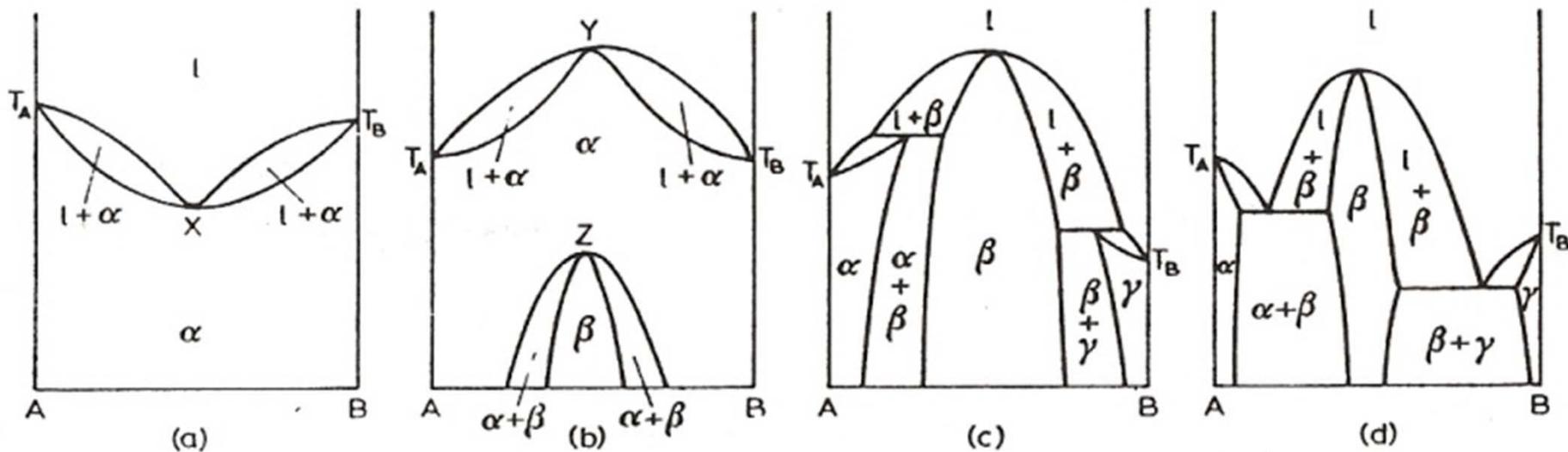


Fig. 76. Examples of congruent transformations.

4.4. Congruent transformations

b. More usual type of congruently-melting intermediate phase

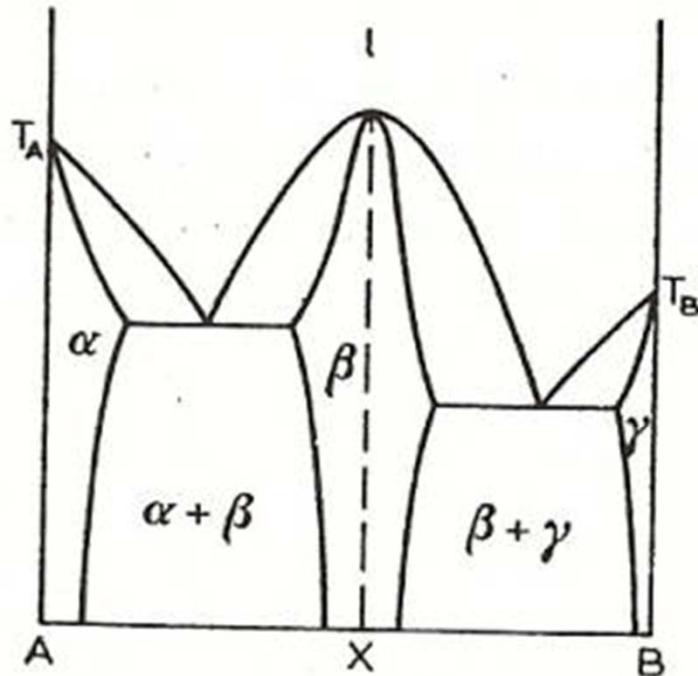
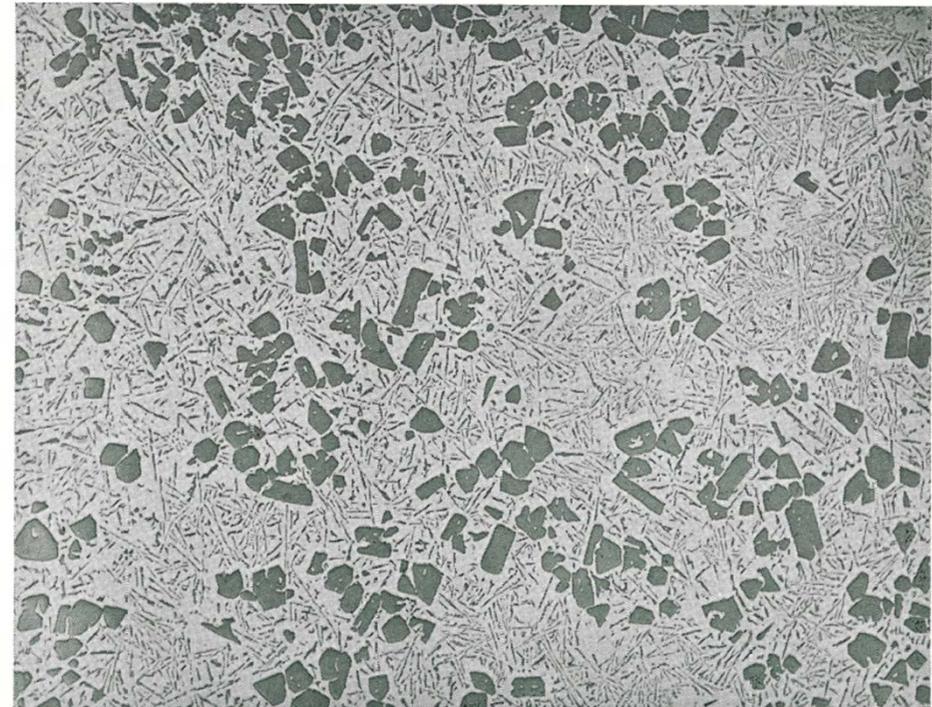


Fig. 78. Phase diagram with a congruent intermediate phase.

→ Partial phase diagram A-X and X-B

: Similar with eutectic alloy system/ primary β phase with well-formed crystal facets (does not form dendrite structure)



Microstructure of a cast Al-22% Si alloy showing polyhedra of primary Si in eutectic matrix

In many cases, X = normal valency compound such as Mg_2Si , Mg_2Sn , Mg_2Pb or Laves phase, particularly stable compounds

b. More usual type of congruently-melting intermediate phase

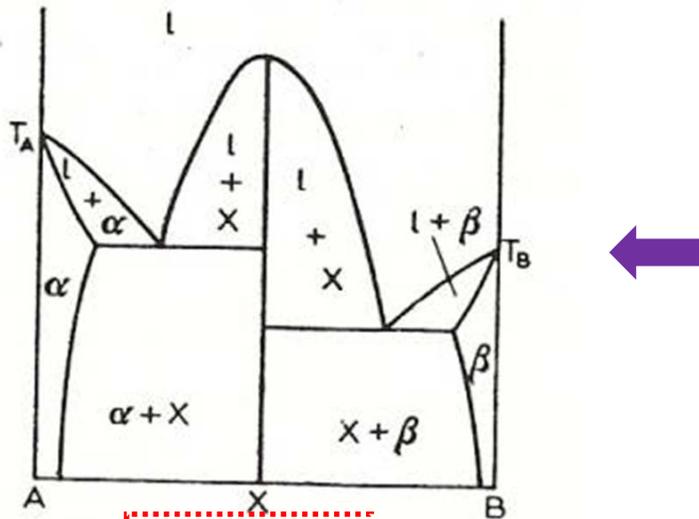
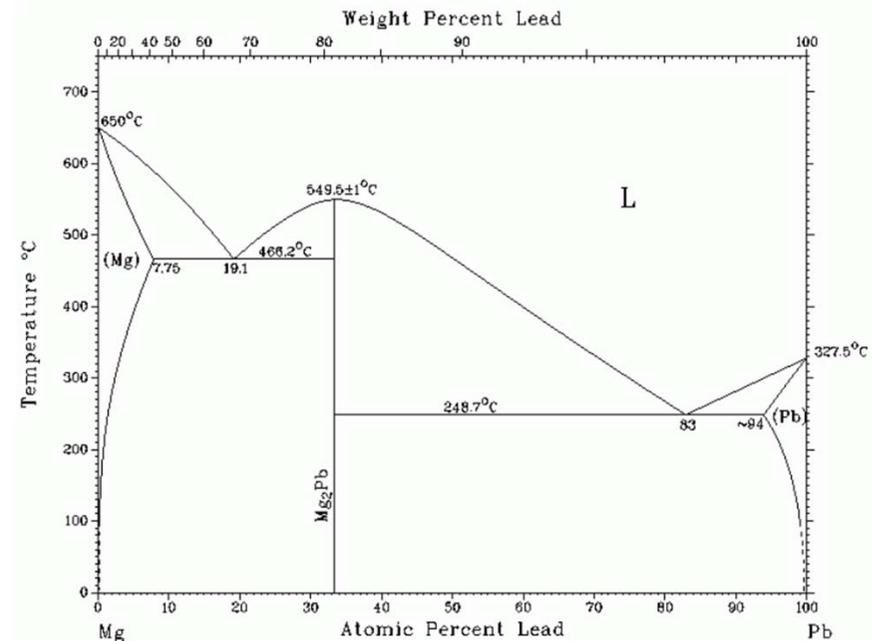
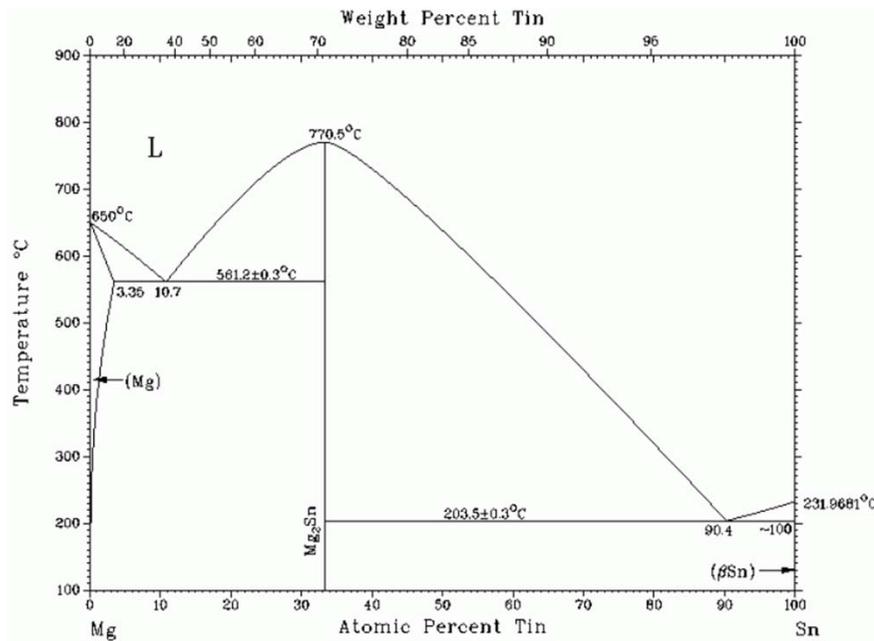
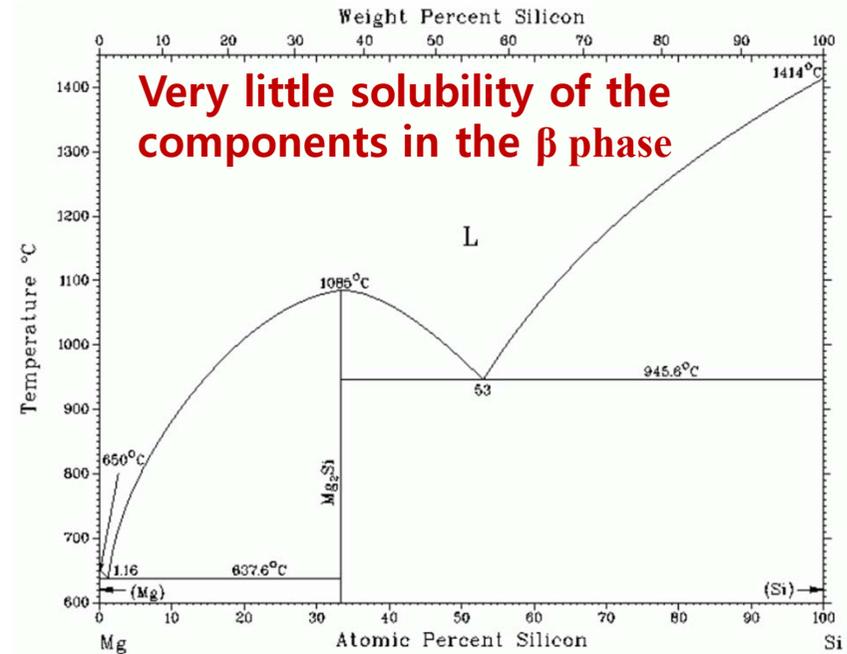


Fig. 79 Limiting case of Fig. 78.



Contents for today's class

CHAPTER 5

Binary Phase Diagrams

Limited Solubility in Both the Liquid and Solid State

1) Limited Solubility in Both the Liquid and Solid State

2) Monotectic reactions

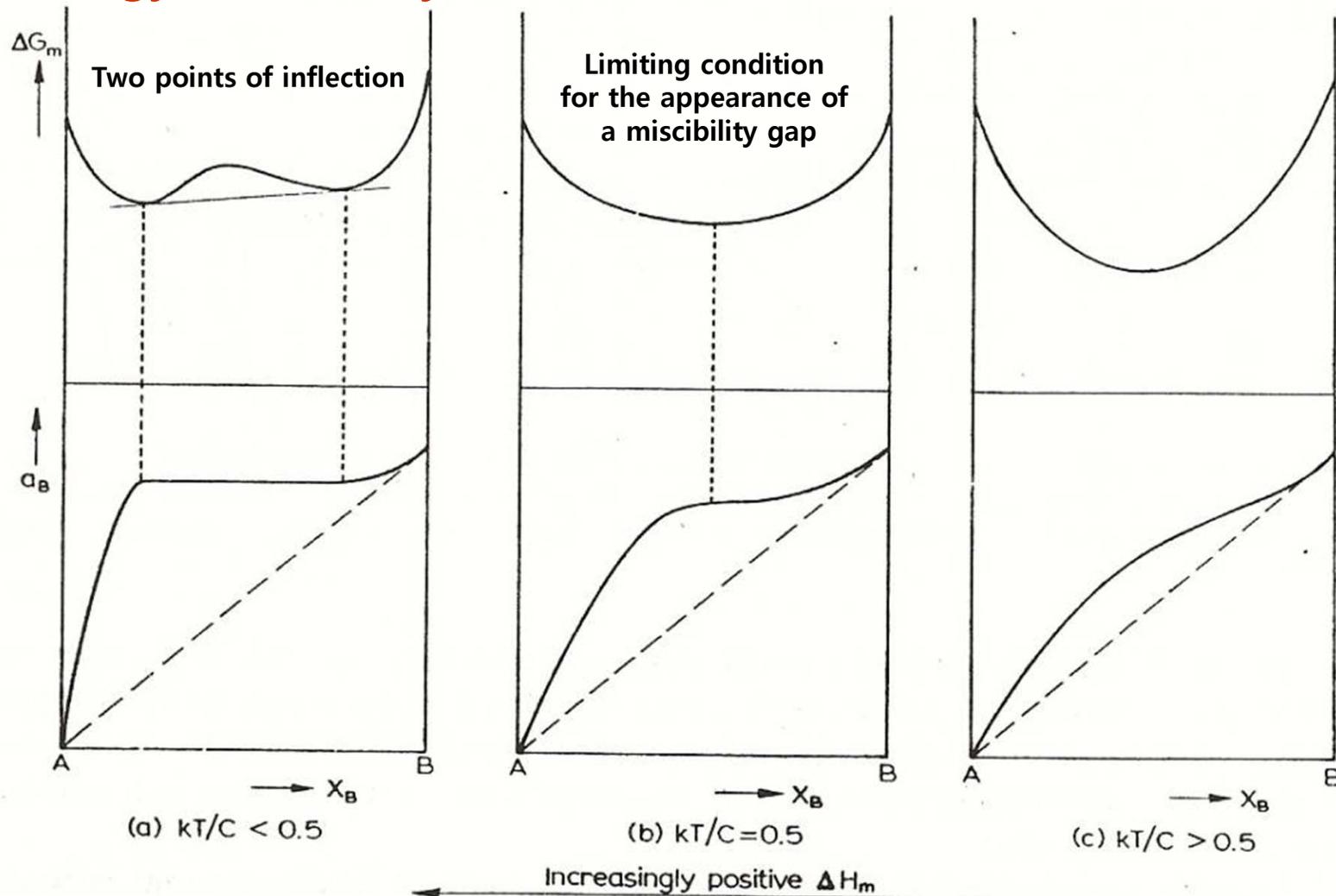
3) Syntectic reactions

1) Limited Solubility in Both the Liquid and Solid State

So far, complete miscibility in the liquid state and limited solid solubility

➡ partial solubility even in the liquid state

Free energy and activity curves for (a) $kT/C < 0.5$, (b) $kT/C = 0.5$ (c) $kT/C > 0.5$

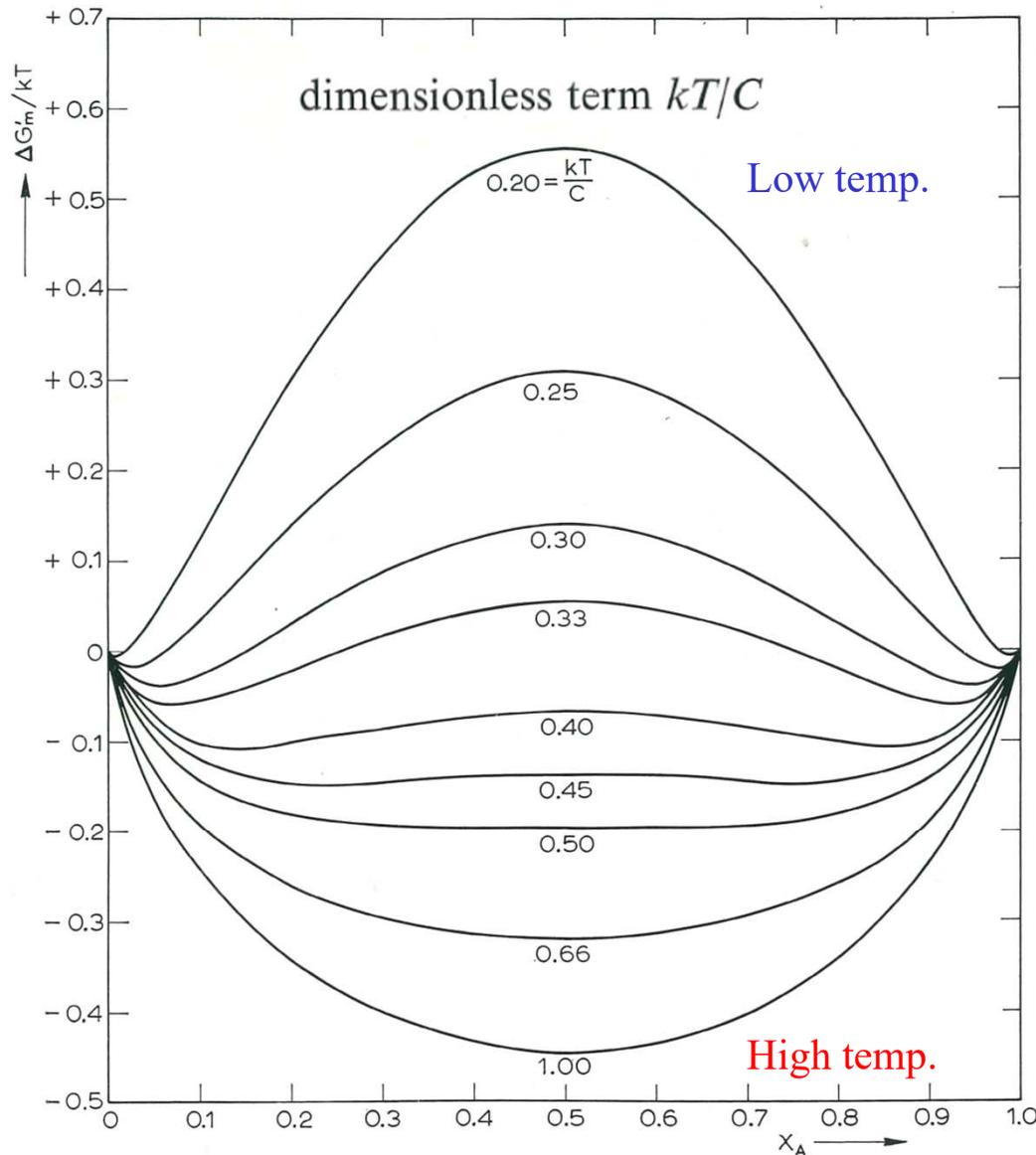


$$\Delta G_m = NCX_A(1-X_A) + NkT[X_A \ln X_A + (1-X_A) \ln (1-X_A)]$$

where,

$$C = z \left[H_{AB} - \frac{H_{AA} + H_{BB}}{2} \right]$$

: energy term



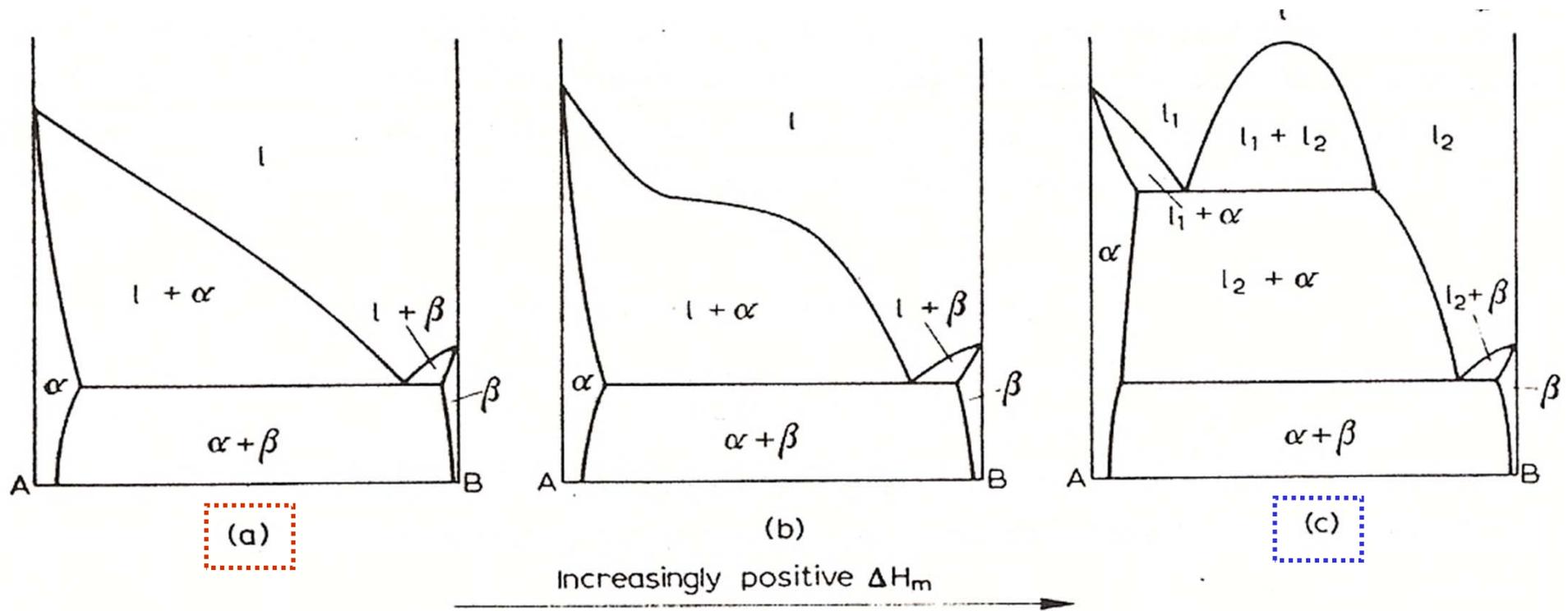
* The curves with $kT/C < 0.5$ show **two minima**, which approach each other as the temperature rise.

* With $kT/C \geq 0.5$ there is a continuous fall in free energy from $X_A=0$ to $X_A=0.5$ and $X_A=1.0$ to $X_A=0.5$. The free energy curve thus assumes the characteristic from one associates with the formation of **homogeneous solutions**.

➡ Exactly the same treatment could have been applied to liquid solutions.

Fig. 14. Variation of free energy with composition for a homogeneous solution with $\Delta H_m > 0$. Free energy-composition curves are given for various values of the parameter kT/C .

Effect of very large positive deviations from ideality in changing the phase diagram from a eutectic to a monotectic reaction



Eutectic reaction: Liquid $\leftrightarrow \alpha + \beta$

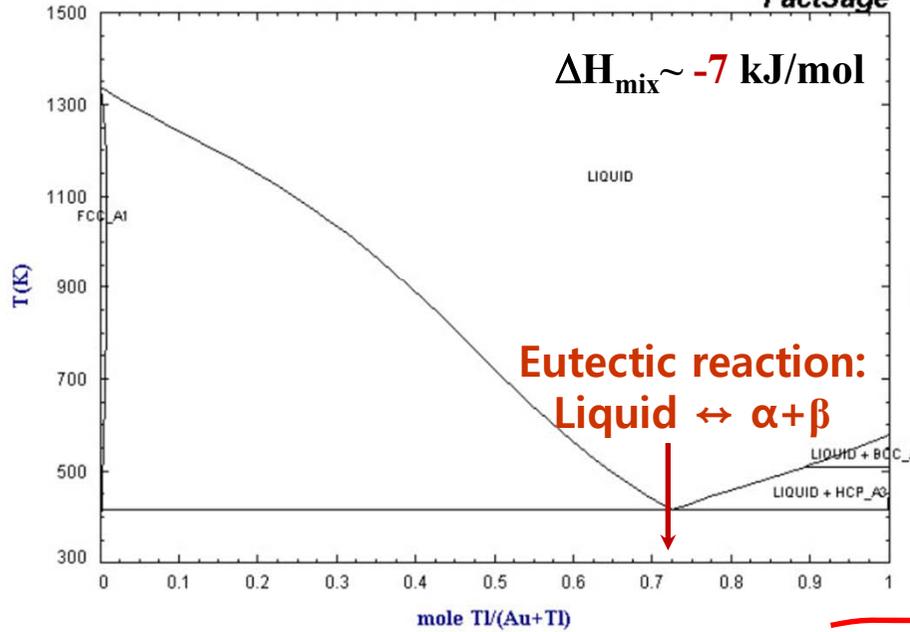
Monotectic reaction: Liquid1 \leftrightarrow Liquid2 + solid

The reversible transition, on cooling, of a liquid to a mixture of a second liquid and a solid

Au - Ti

Data from FSnobl - FactSage noble metal databases

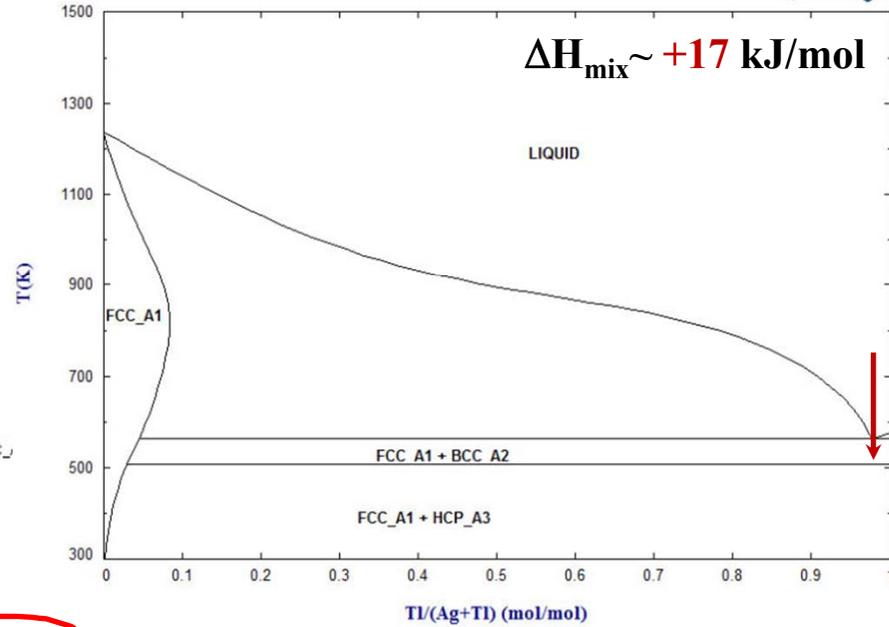
FactSage



Ag - Ti

Data from SGTE 2011 alloy database

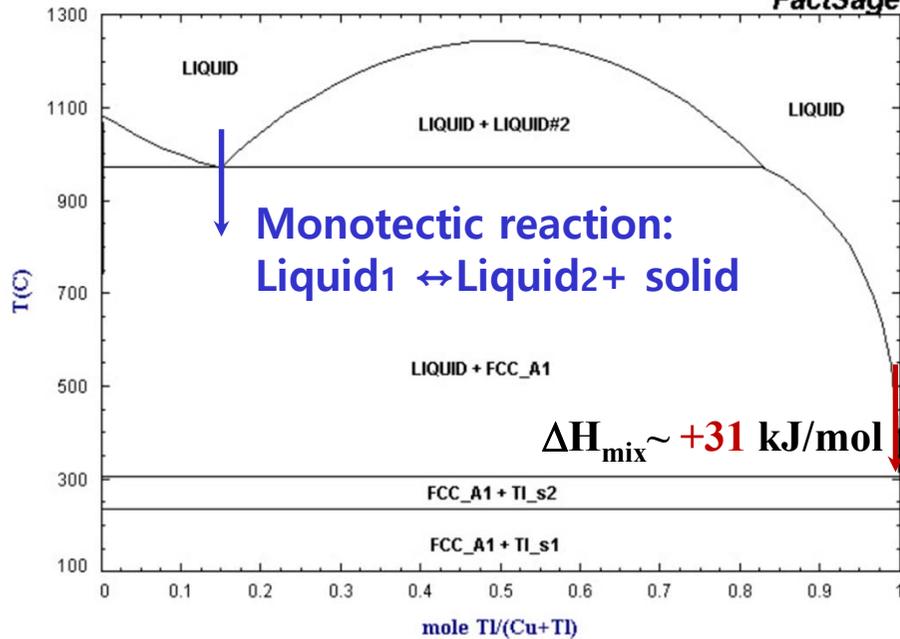
FactSage



Cu - Ti

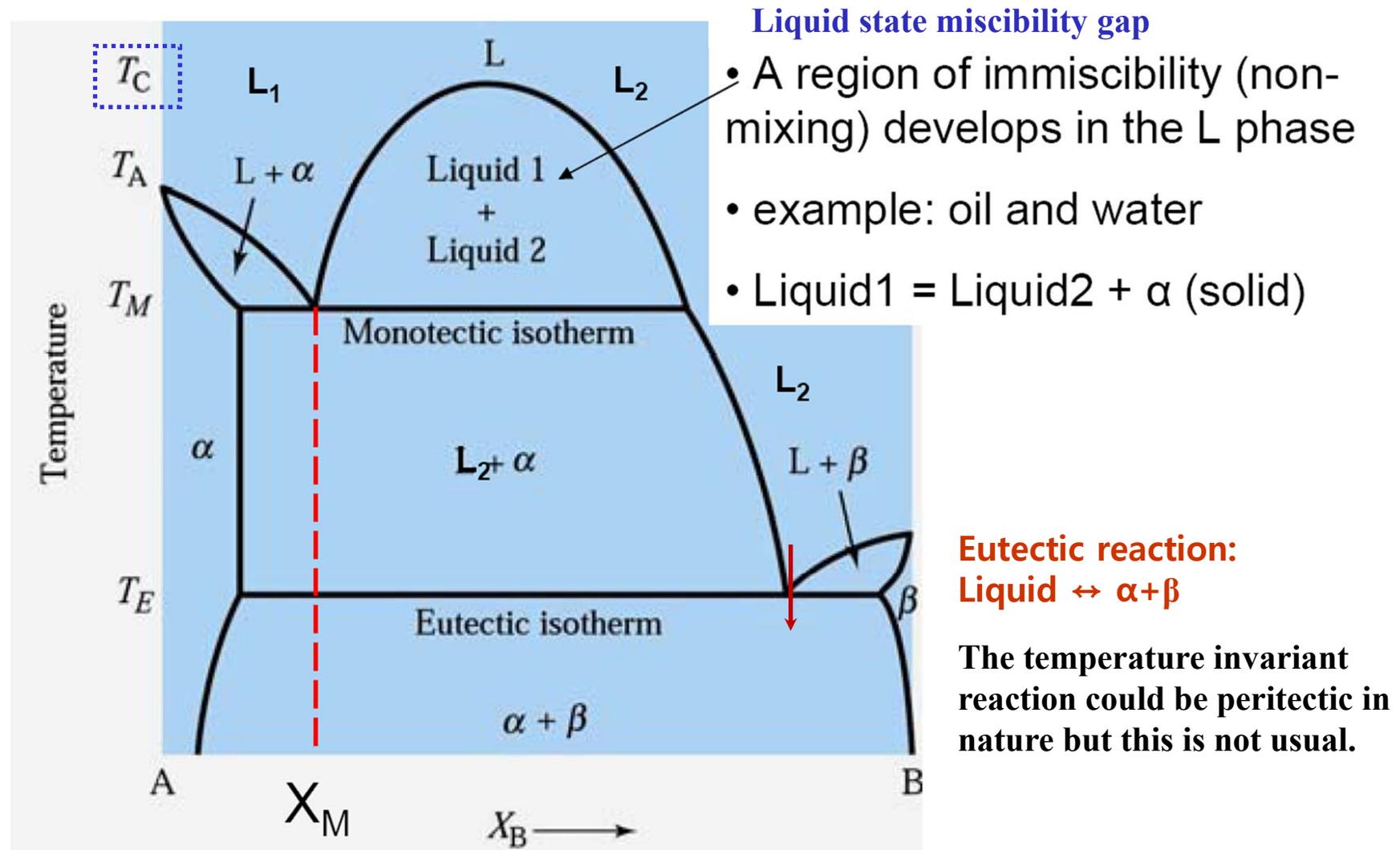
Data from FSscop - FactSage copper alloy database

FactSage



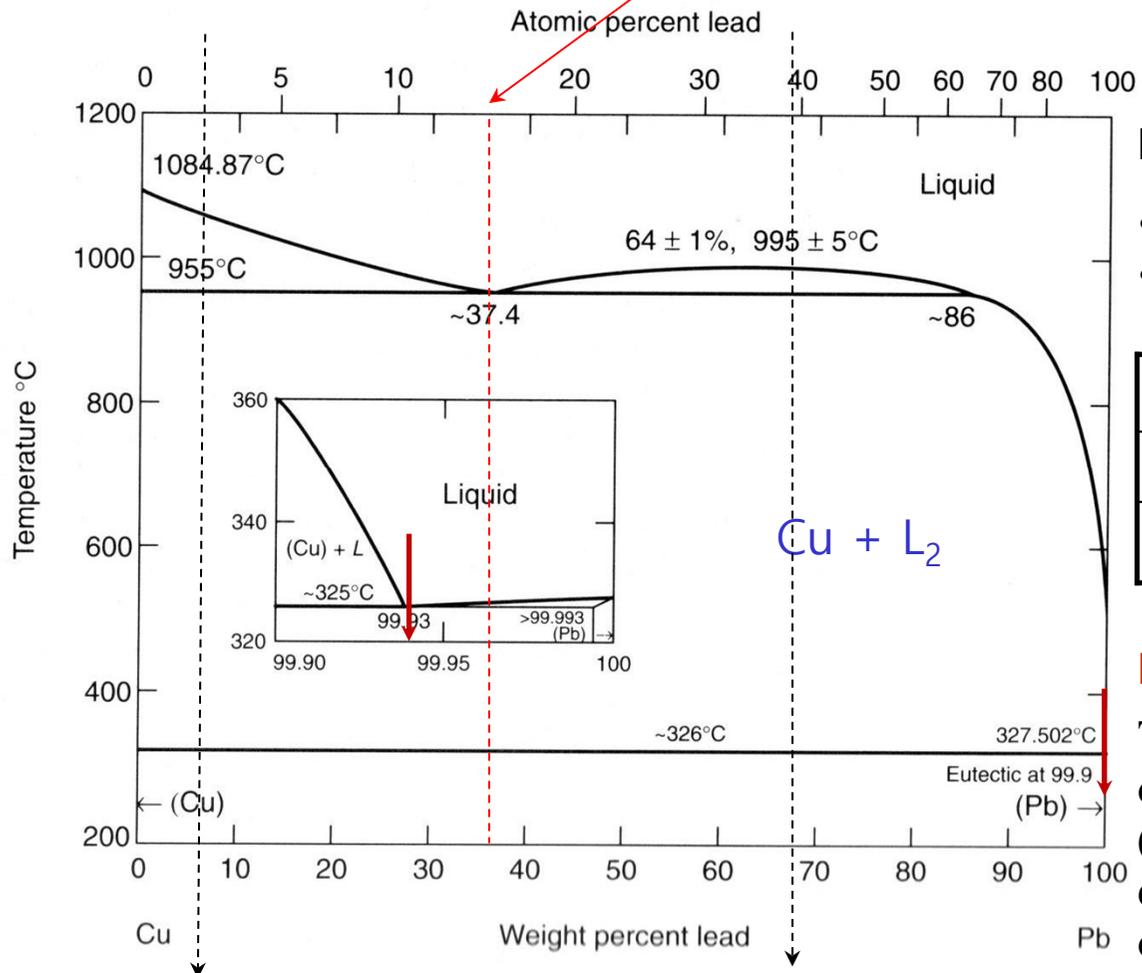
Increasingly positive ΔH_{mix}

2) Monotectic Phase Diagram



Monotectic

Source: Reed-Hill, Abbaschian, **Physical Metallurgy Principles, 3rd Edition**, PWS Publishing Company, 1994.



Pb and Cu do not mix in solid state:

- RT: Cu in Pb < 0.007%
- RT: Pb in Cu ~ 0.002 – 0.005%

	Crystal Structure	Electro negativity	r (nm)
Pb	FCC	1.8	0.175
Cu	FCC	1.9	0.128

26.8%

Eutectic reaction (divorced eutectic):

The eutectic composition is usually very close to the low-melting point component (B) and therefore the eutectic liquid deposits an overwhelming amount of β compared with α.

Hypo-monotectic:

Interdendritic divorced eutectic between an α dendritic matrix

Slow cooling: Two layers ~ Cu-rich liquid L1 top layer / Pb-rich liquid L2 bottom layer (Rapid quenching: droplet structure) →
At T_M , L1 – monotectic reaction/ L2 – α precipitates →
At T_E , top: α + pools of divorced eutectic/ bottom: small particles of α in a divorced eutectic matrix

Morphology in monotectic solidification

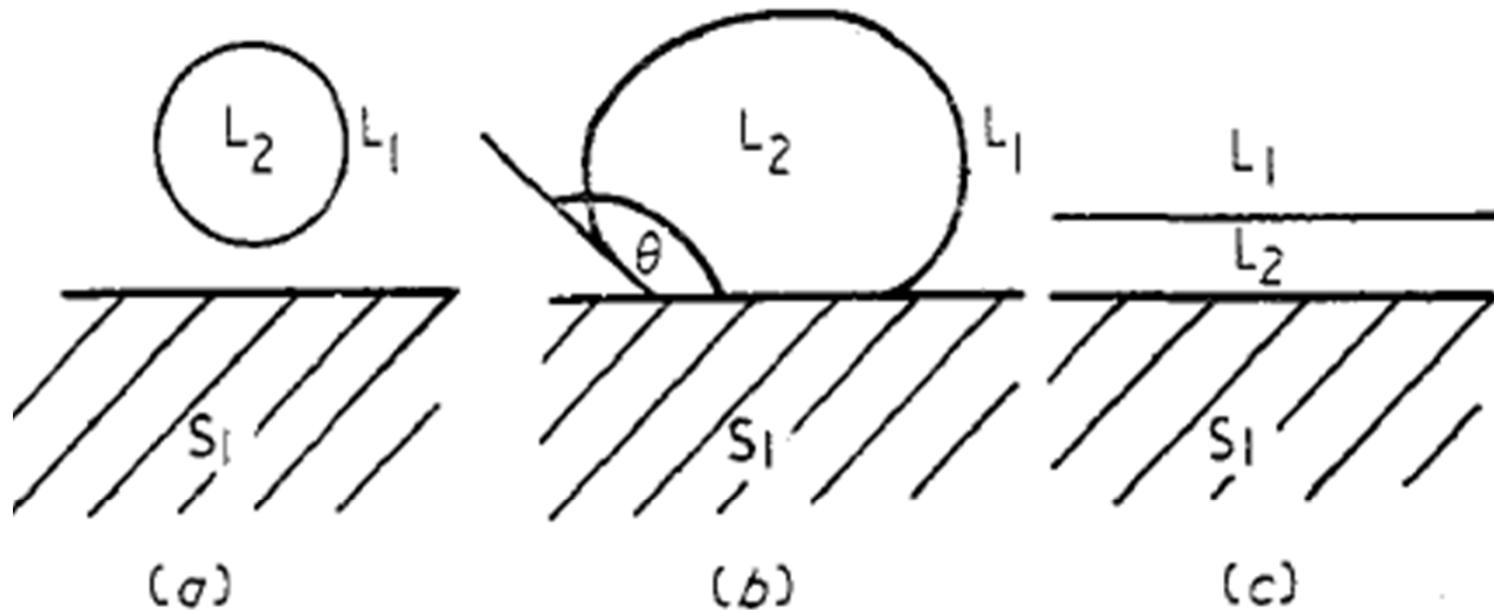
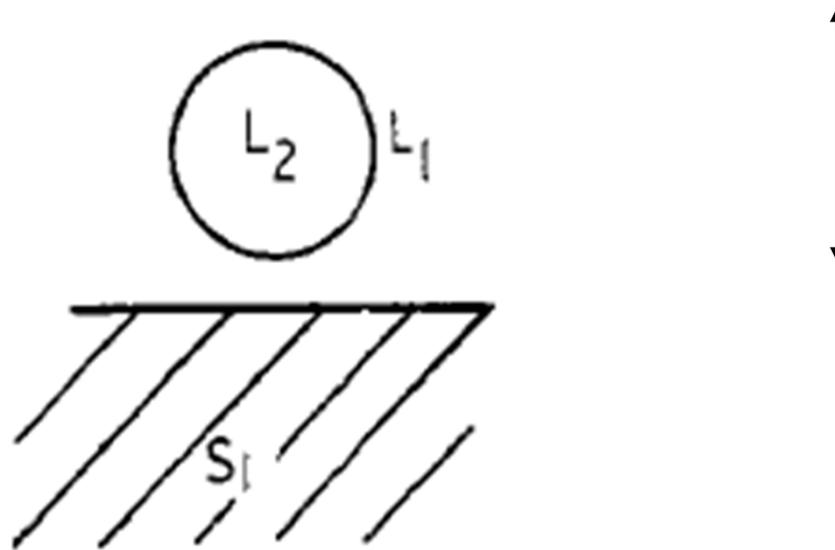


Figure 2. Solid-liquid interface morphology for different interfacial energy conditions:
 (a) $\gamma_{S_1L_2} > \gamma_{S_1L_1} + \gamma_{L_1L_2}$, (b) $\gamma_{S_1L_2} = \gamma_{S_1L_1} - \gamma_{L_1L_2} \cos \theta$, (c) $\gamma_{S_1L_1} > \gamma_{S_1L_2} + \gamma_{L_1L_2}$.

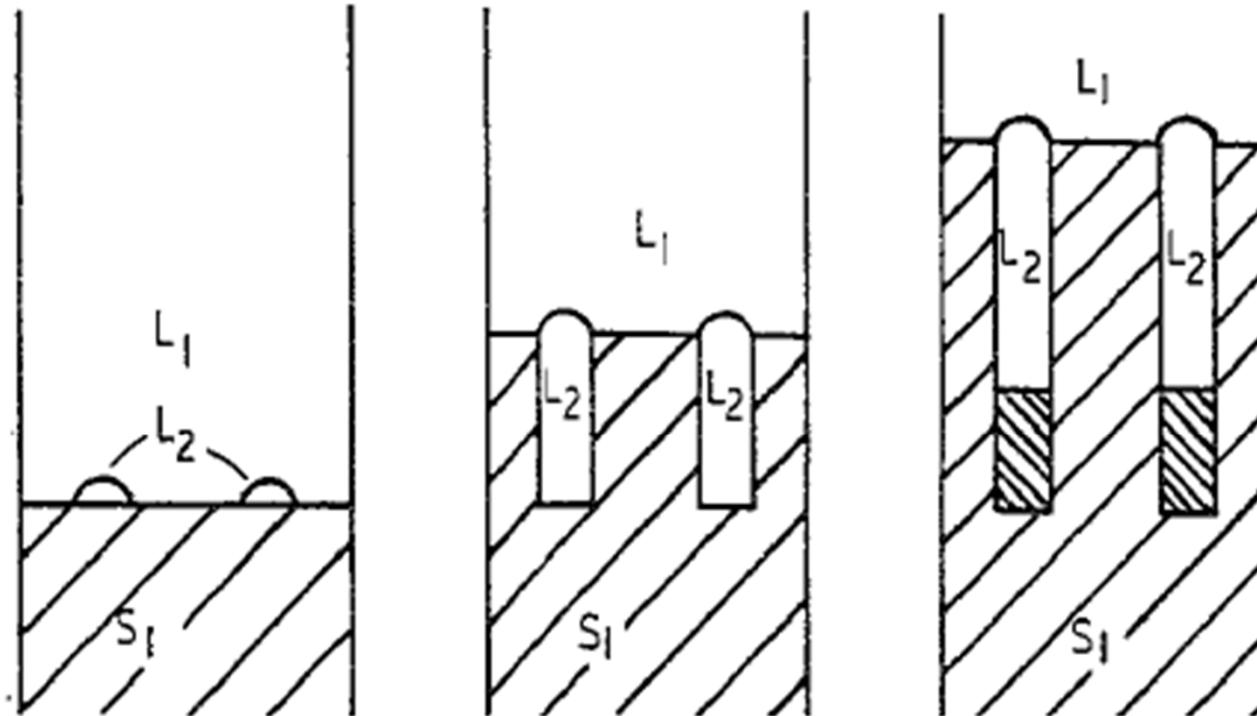
Case 1:

$$\gamma_{\alpha l_1} + \gamma_{l_1 l_2} < \gamma_{\alpha l_2}$$



Hg-Te single crystal

Case 2: $\gamma_{\alpha l_2} = \gamma_{\alpha l_1} - \gamma_{l_1 l_2} \cos \theta$

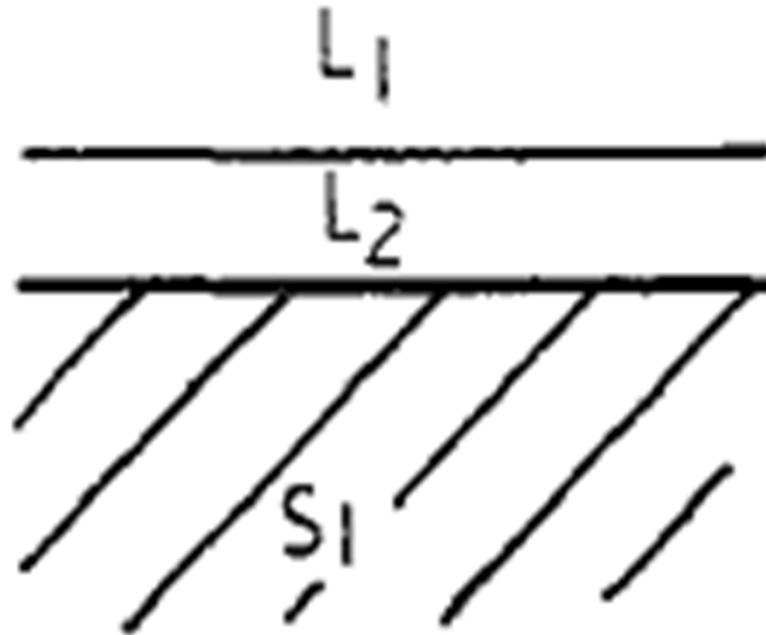


Growth mechanism of alloy of monotectic composition to produce a fibrous structure

$$\lambda \propto V^{-0.5}$$

Case 3:

$$\gamma_{\alpha l_1} > \gamma_{\alpha l_2} + \gamma_{l_1 l_2}$$



4.1.3. Heterogeneous nucleation

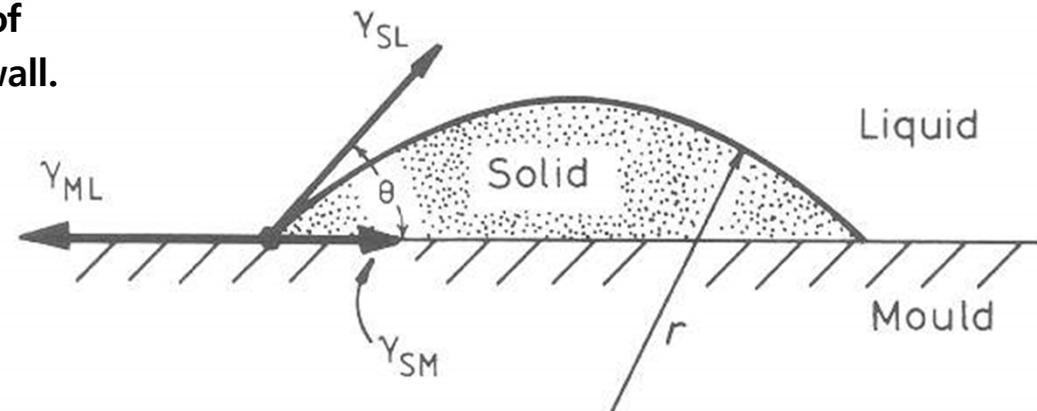
From
$$\Delta G^* = \left(\frac{16\pi\gamma_{SL}^3 T_m^2}{3L_V^2} \right) \frac{1}{(\Delta T)^2}$$

Nucleation becomes easy if $\gamma_{SL} \downarrow$ by forming nucleus from mould wall.

Fig. 4.7 Heterogeneous nucleation of spherical cap on a flat mould wall.

$$\gamma_{ML} = \gamma_{SL} \cos \theta + \gamma_{SM}$$

$$\cos \theta = (\gamma_{ML} - \gamma_{SM}) / \gamma_{SL}$$



$$\Delta G_{het} = -V_S \Delta G_V + A_{SL} \gamma_{SL} + A_{SM} \gamma_{SM} - A_{SM} \gamma_{ML}$$

In terms of the wetting angle (θ) and the cap radius (r)

(Exercies 4.6)

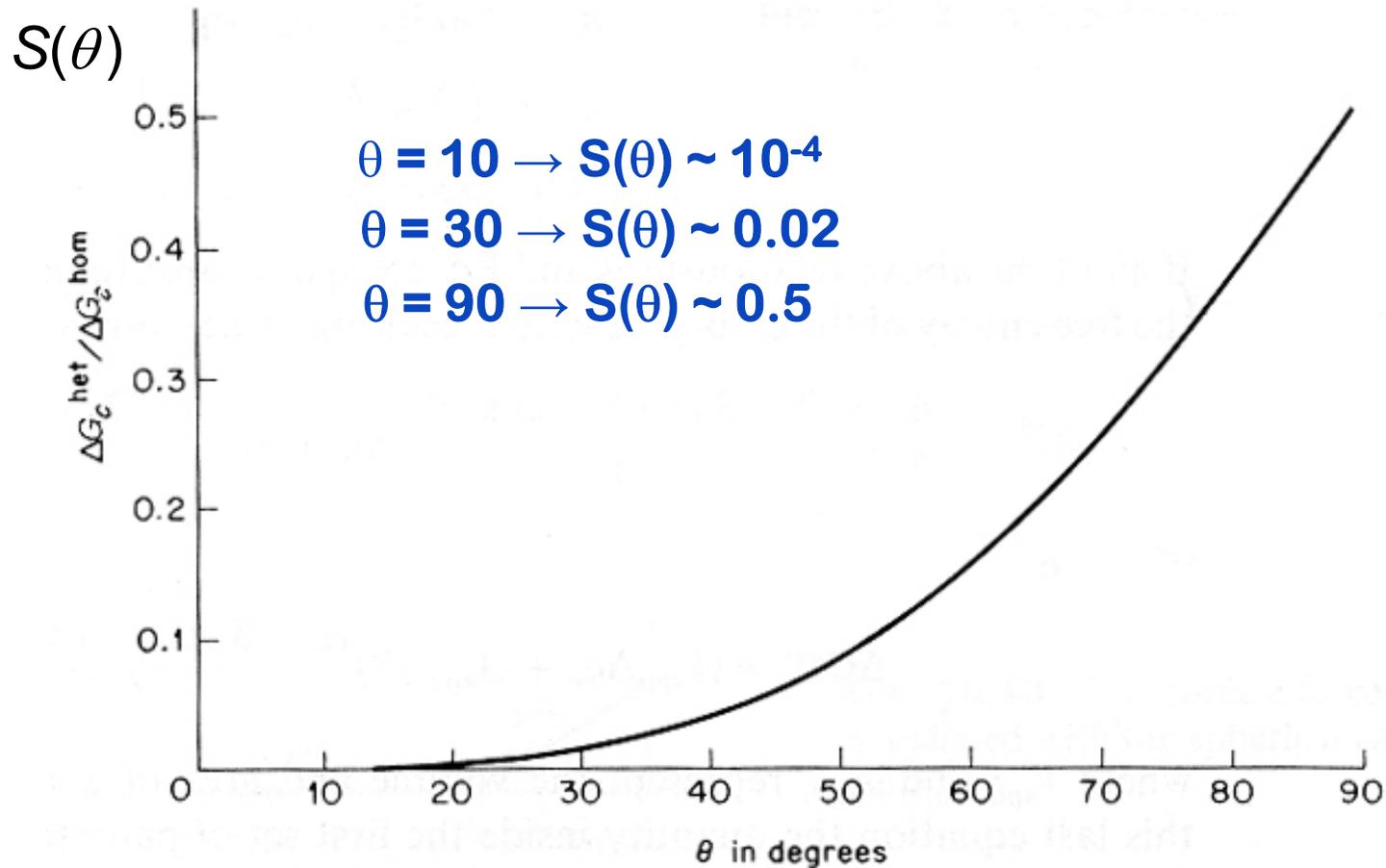
$$\Delta G_{het} = \left\{ -\frac{4}{3} \pi r^3 \Delta G_V + 4\pi r^2 \gamma_{SL} \right\} S(\theta)$$

Incentive H4

where $S(\theta) = (2 + \cos \theta)(1 - \cos \theta)^2 / 4$

$S(\theta)$ has a numerical value ≤ 1 dependent only on θ (the shape of the nucleus)

$$\Delta G_{het}^* = S(\theta) \Delta G_{hom}^* \quad \Rightarrow \quad r^* = \frac{2 \gamma_{SL}}{\Delta G_V} \quad \text{and} \quad \Delta G^* = \frac{16 \pi \gamma_{SL}^3}{3 \Delta G_V^2} \cdot S(\theta)$$



$S(\theta)$ has a numerical value ≤ 1 dependent only on θ (the shape of the nucleus)

$$\Delta G_{het}^* = S(\theta)\Delta G_{hom}^* \quad \Rightarrow \quad r^* = \frac{2\gamma_{SL}}{\Delta G_V} \quad \text{and} \quad \Delta G^* = \frac{16\pi\gamma_{SL}^3}{3\Delta G_V^2} \cdot S(\theta)$$

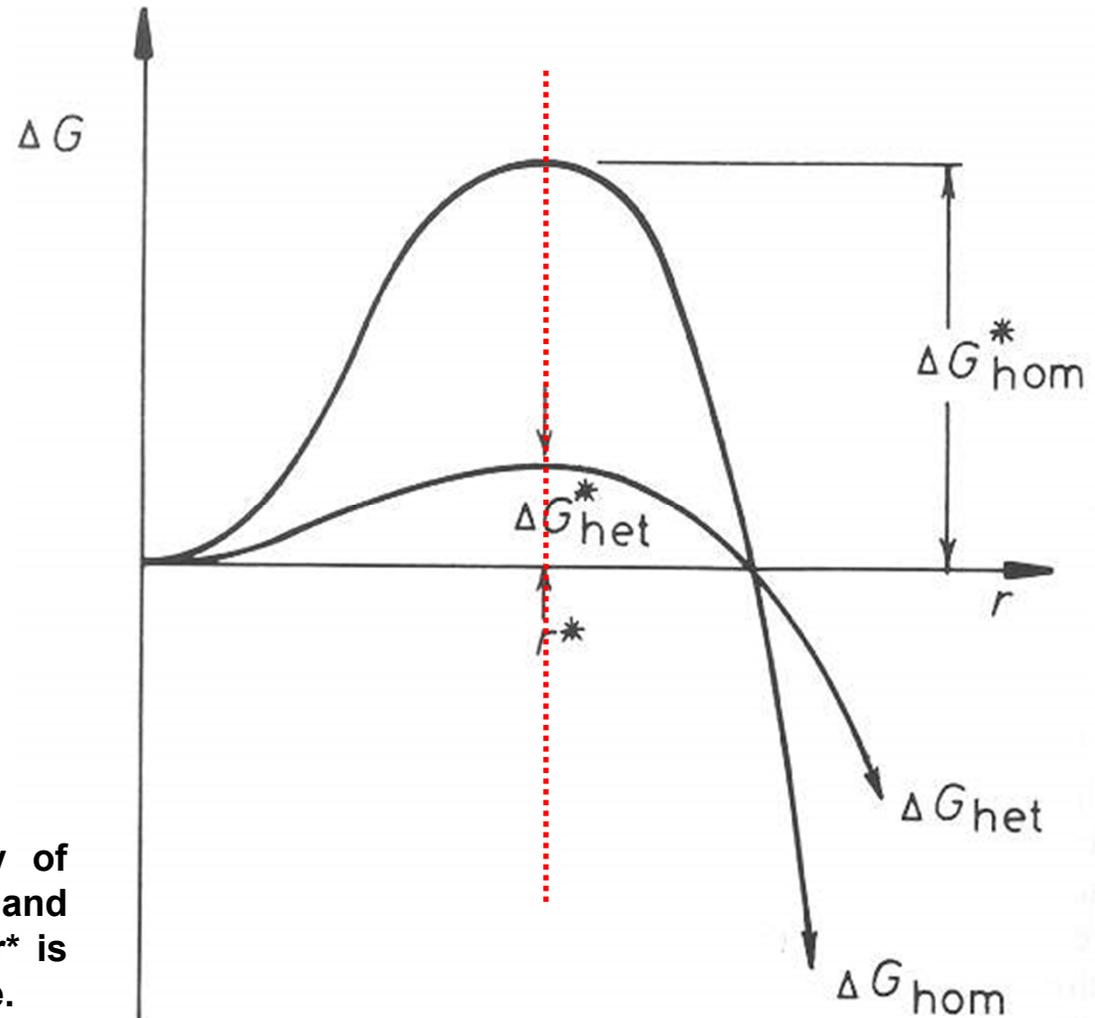


Fig. 4.8 The excess free energy of solid clusters for homogeneous and heterogeneous nucleation. Note r^* is independent of the nucleation site.

The Effect of ΔT on ΔG^*_{het} & ΔG^*_{hom} ?

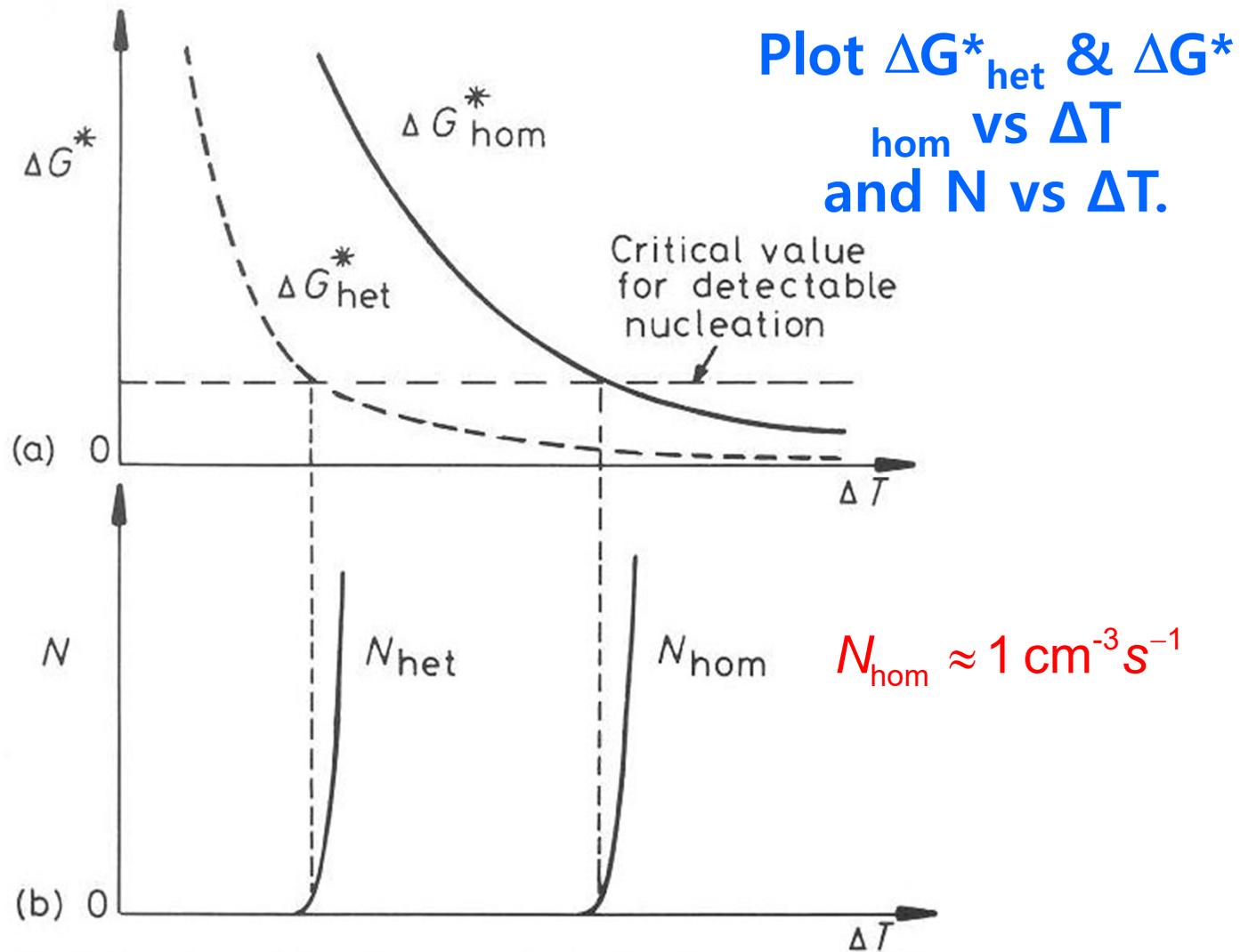
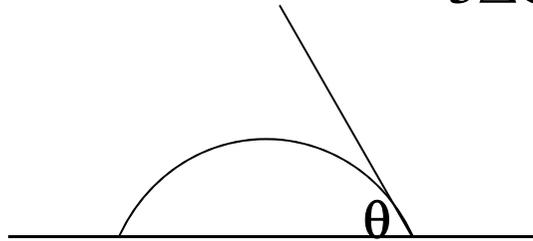


Fig. 4.9 (a) Variation of ΔG^* with undercooling (ΔT) for homogeneous and heterogeneous nucleation.

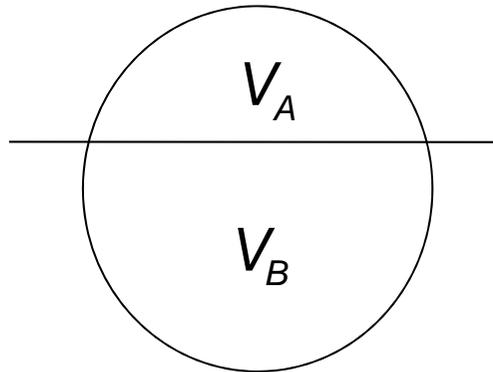
(b) The corresponding nucleation rates assuming the same critical value of ΔG^*

Barrier of Heterogeneous Nucleation

$$\Delta G^* = \frac{16\pi\gamma_{SL}^3}{3\Delta G_V^2} \cdot S(\theta) = \frac{16\pi\gamma_{SL}^3}{3\Delta G_V^2} \cdot \frac{(2 - 3\cos\theta + \cos^3\theta)}{4}$$



$$\Delta G_{het}^* = S(\theta)\Delta G_{hom}^*$$



$$\Delta G_{sub}^* = \Delta G_{homo}^* \left(\frac{2 - 3\cos\theta + \cos^3\theta}{4} \right)$$

$$\frac{V_A}{V_A + V_B} = \frac{2 - 3\cos\theta + \cos^3\theta}{4} = S(\theta)$$

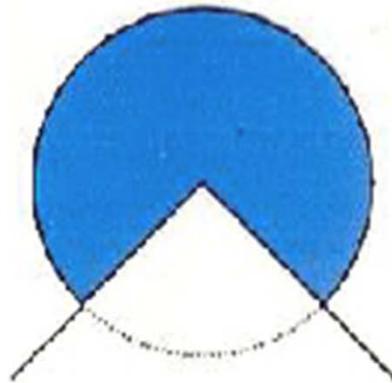
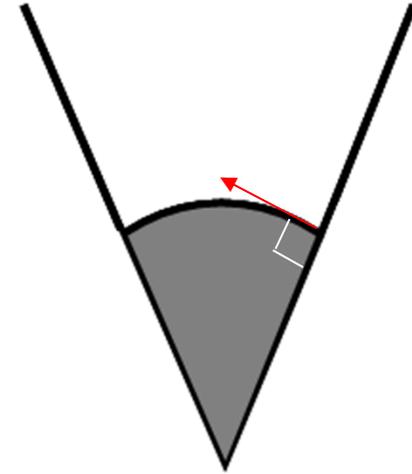
How about the nucleation at the crevice or at the edge?

Nucleation Barrier at the crevice

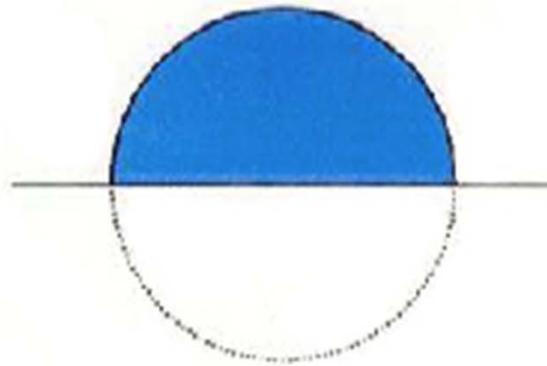
What would be the shape of nucleus and the nucleation barrier for the following conditions?

contact angle = 90
groove angle = 60

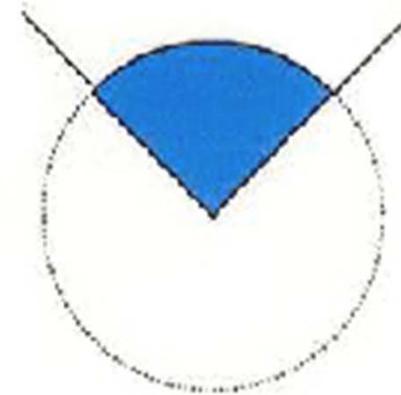
$$\frac{1}{6} \Delta G_{\text{homo}}^*$$



$$\frac{3}{4} \Delta G_{\text{homo}}^*$$

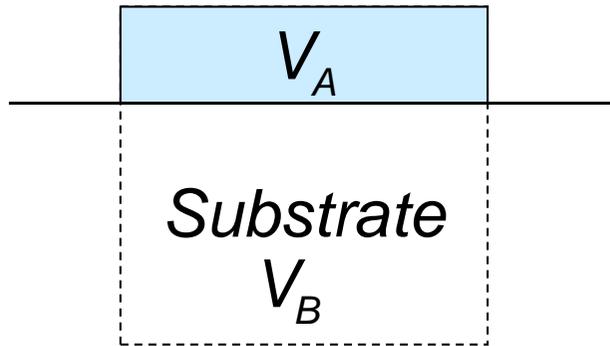


$$\frac{1}{2} \Delta G_{\text{homo}}^*$$

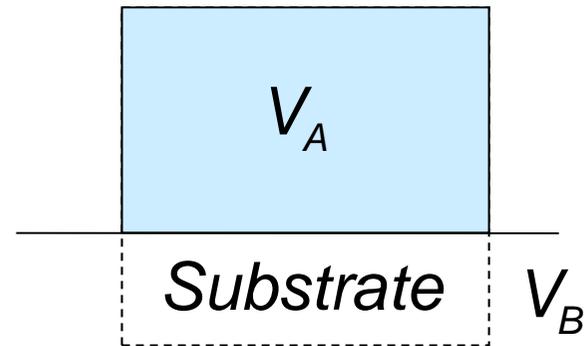


$$\frac{1}{4} \Delta G_{\text{homo}}^*$$

How do we treat the non-spherical shape?



Good Wetting



Bad Wetting

$$\Delta G_{sub}^* = \Delta G_{homo}^* \left(\frac{V_A}{V_A + V_B} \right)$$

Effect of good and bad wetting on substrate

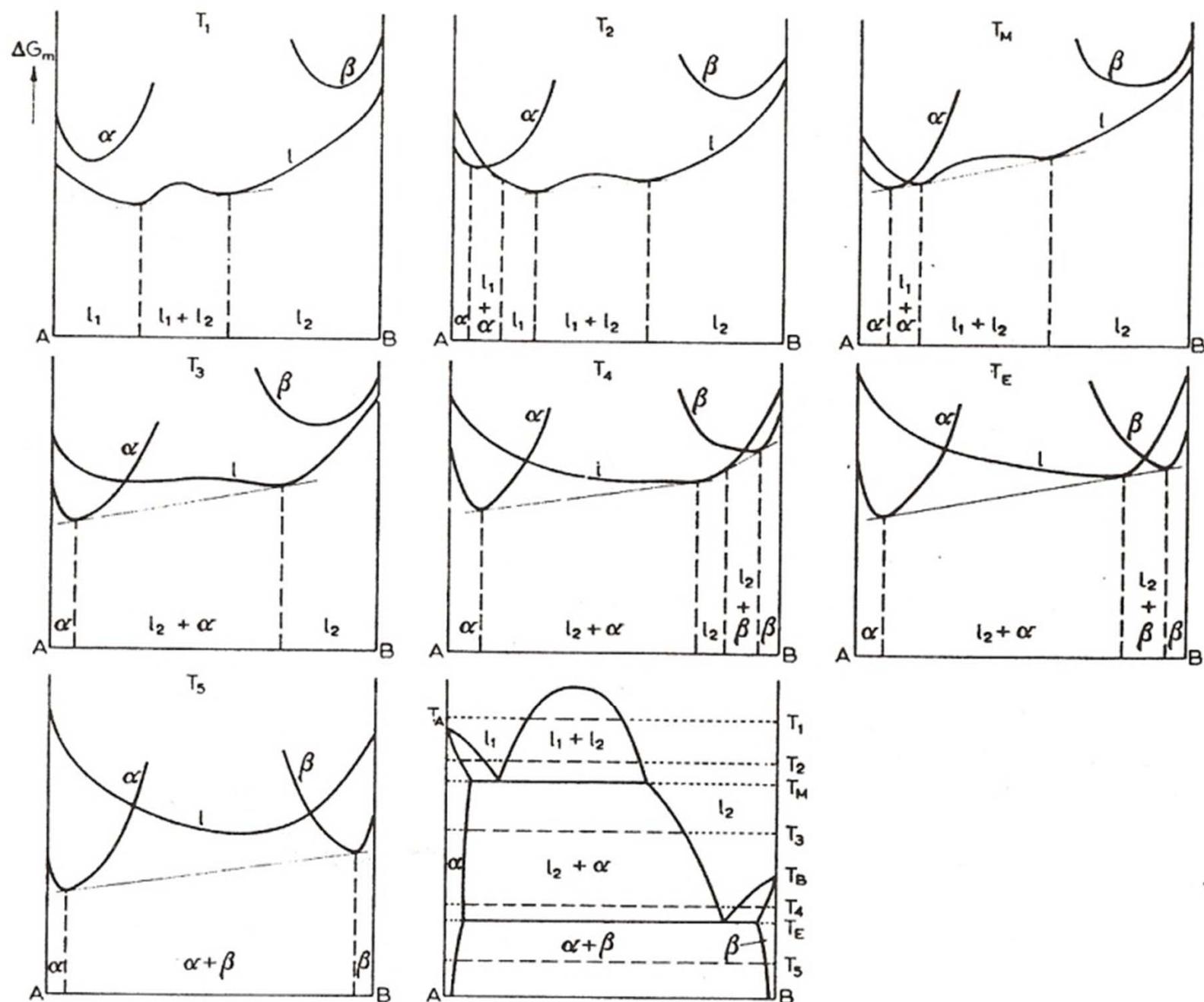


Fig. 85. Derivation of the monotectic phase diagram from the free energy curves for the liquid, α and β phases.

* Limiting forms of monotectic phase diagram

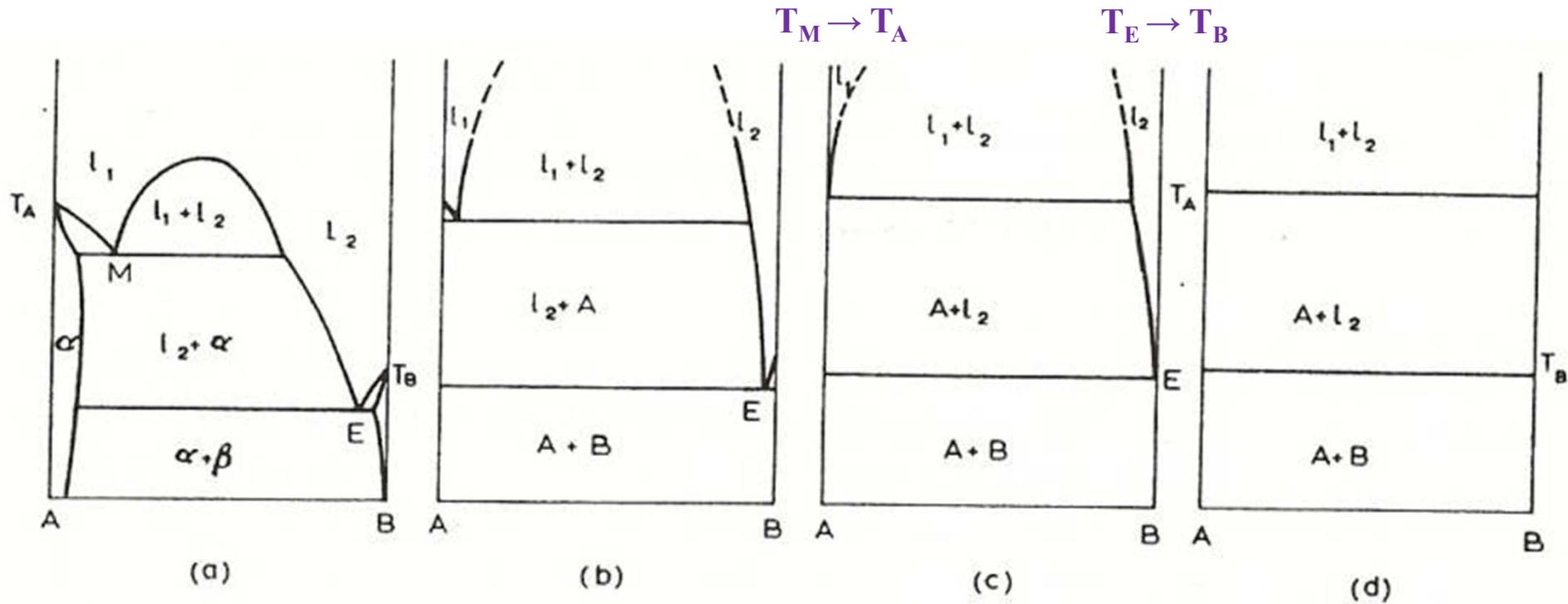
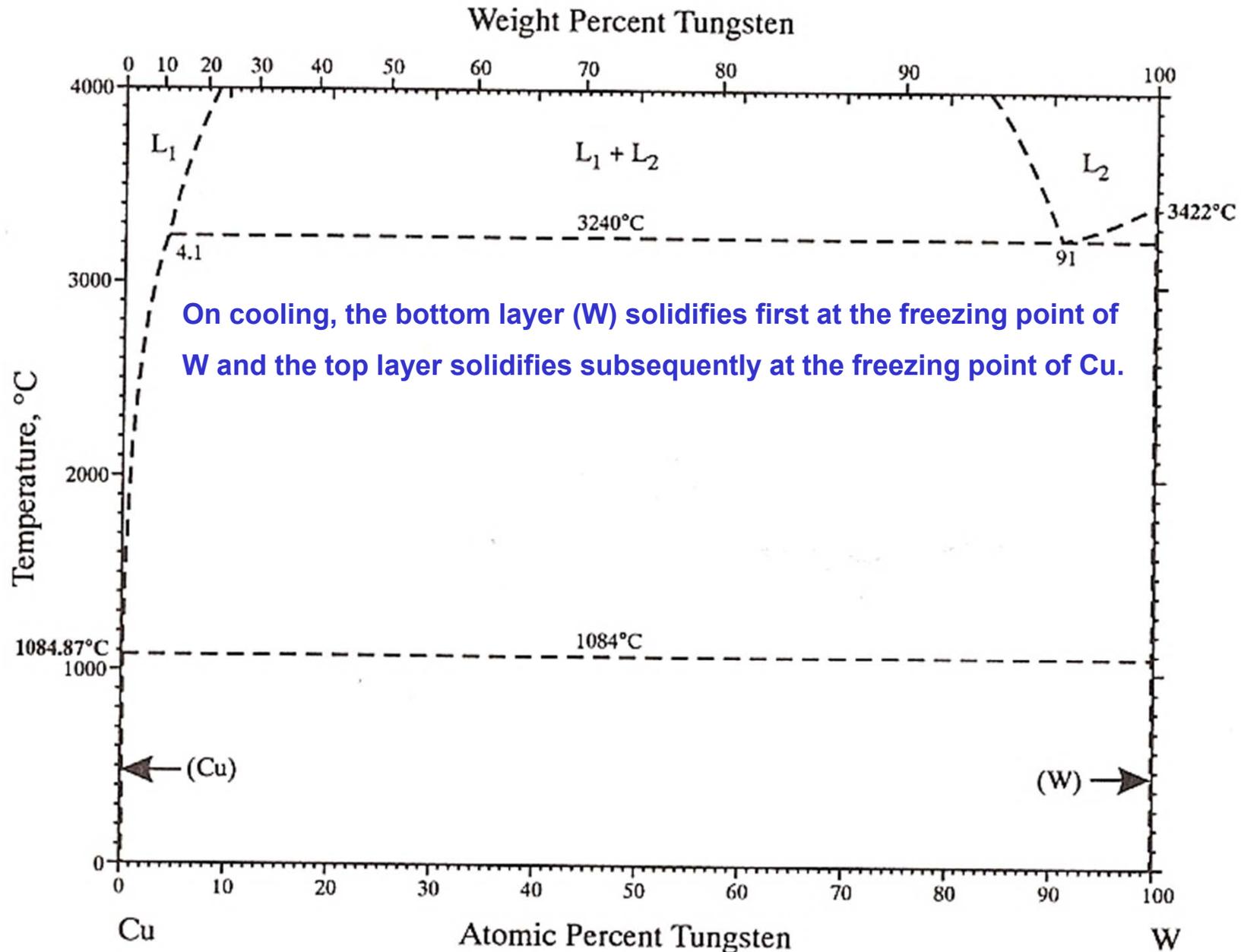


Fig. 86. Limiting form of the monotectic phase diagram.

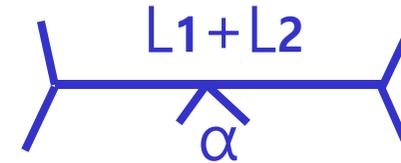
→
 The solubility is so small as to be undetected experimentally to date.

*** Limiting forms of monotectic phase diagram**



The solubility is so small as to be undetected experimentally to date.

Syntectic reaction: Liquid₁+Liquid₂ ↔ α



This reaction will proceed at the interface between the two liquid layers.
 ~ difficult to maintain equilibrium conditions in a syntectic system

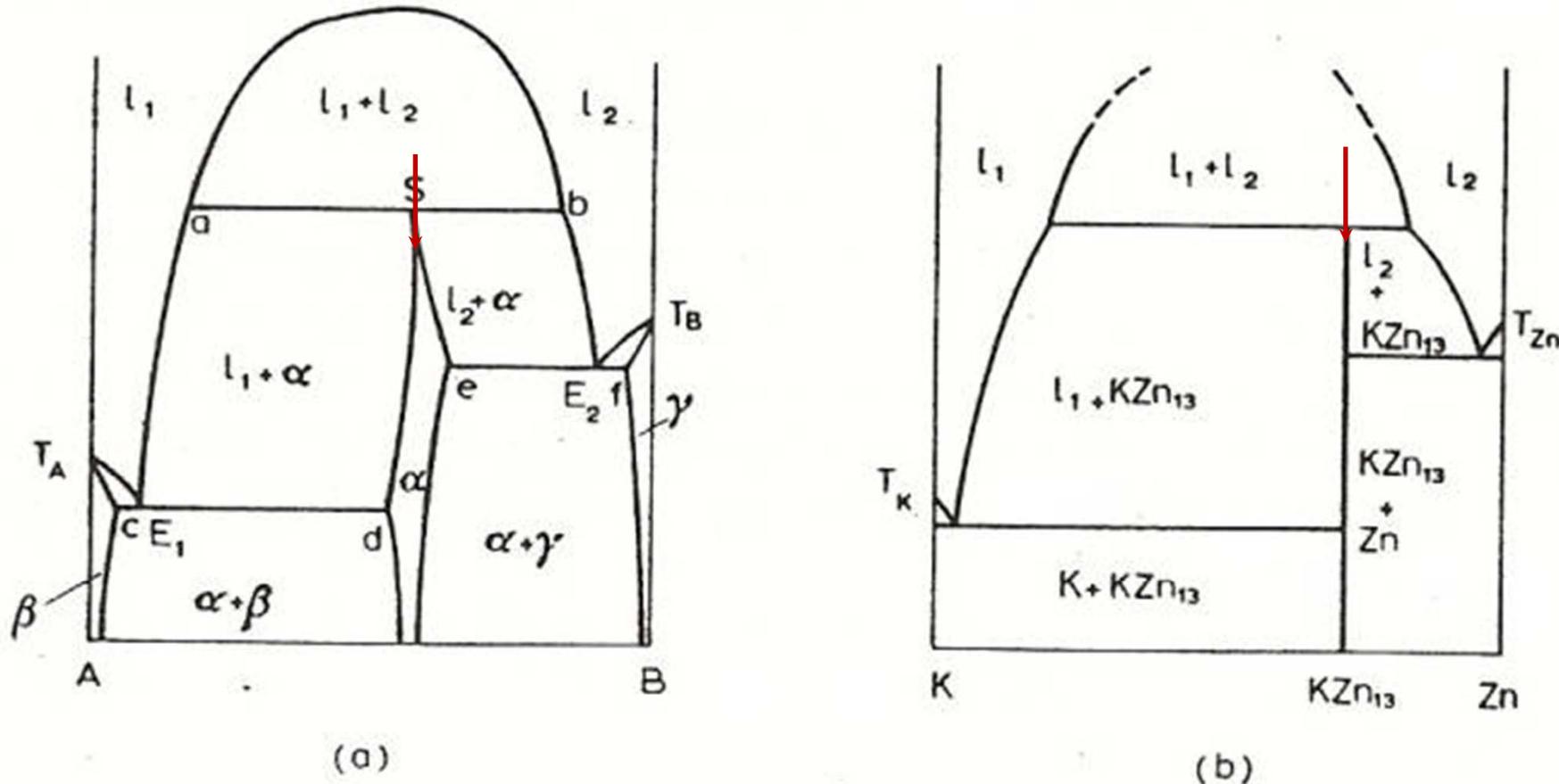
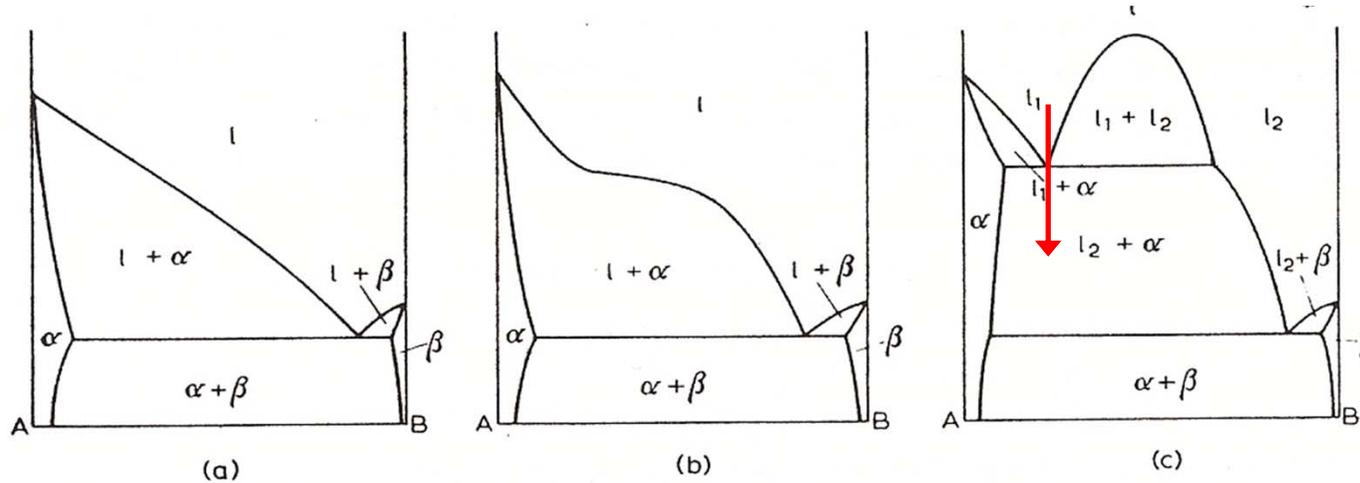
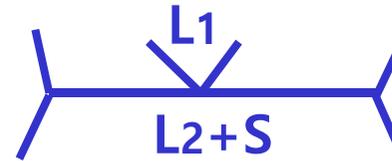


Fig. 87. Syntectic phase diagrams. (a) Schematic: (b) the K–Zn system.

e.g. K-Zn, Na-Zn, K-Pb, Pb-U and Ca-Cd

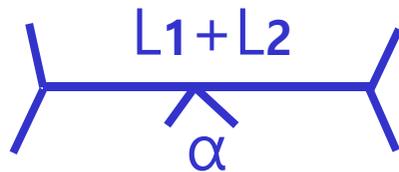
Contents for today's class

* Monotectic reaction:

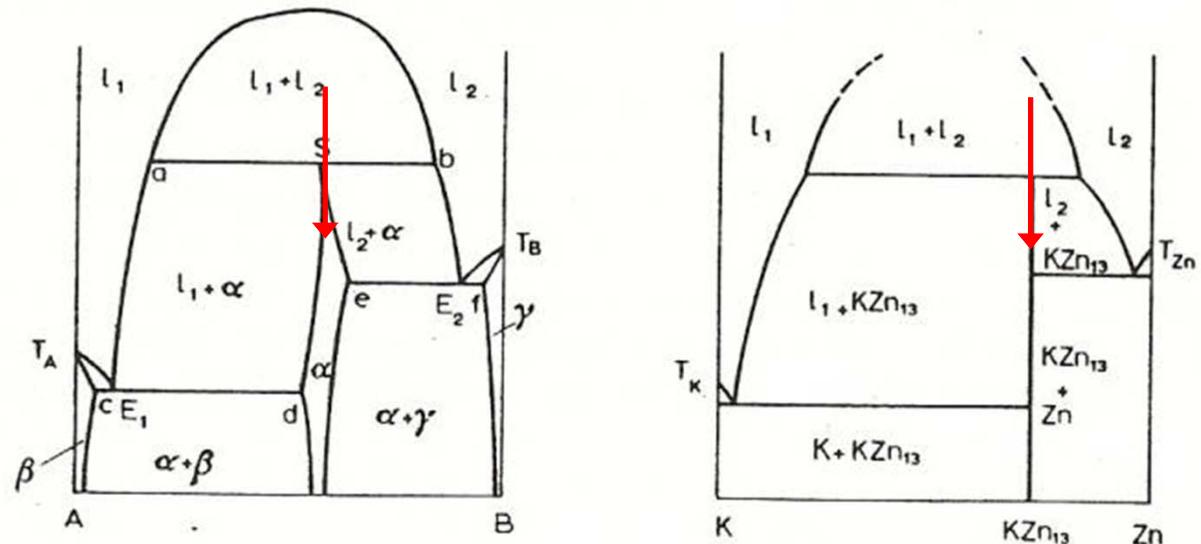


Increasingly positive ΔH_m \rightarrow

* Syntectic reaction:



K-Zn, Na-Zn,
K-Pb, Pb-U, Ca-Cd

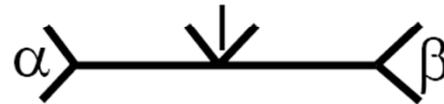
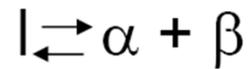


Contents for previous class

Review of Invariant Binary Reactions

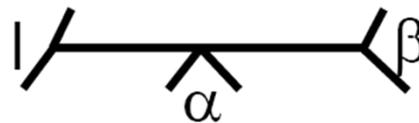
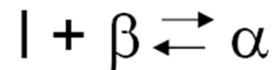
Positive ΔH_m

Eutectic



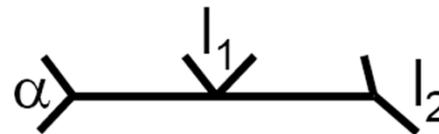
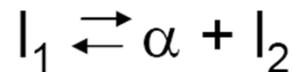
Al-Si, Fe-C

Peritectic



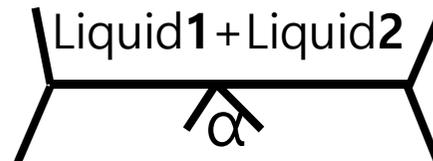
Fe-C

Monotectic



Cu-Pb

Synthetic reaction

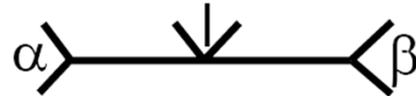
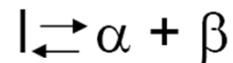


**K-Zn, Na-Zn,
K-Pb, Pb-U, Ca-Cd**

Review of Invariant Binary Reactions

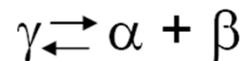
Eutectic Type

Eutectic



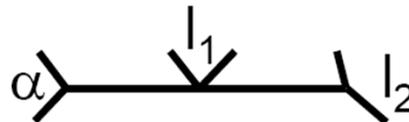
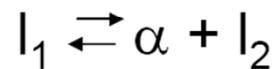
Al-Si, Fe-C

Eutectoid



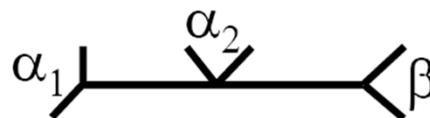
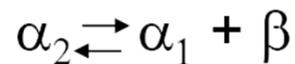
Fe-C

Monotectic



Cu-Pb

Monotectoid



Al-Zn, Ti-V

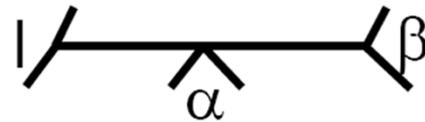
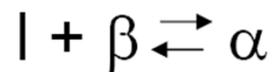
On cooling one phase going to two phases

Metatectic reaction: $\beta \leftrightarrow L + \alpha$ **Ex. Co-Os, Co-Re, Co-Ru**

Review of Invariant Binary Reactions

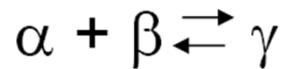
Peritectic Type

Peritectic



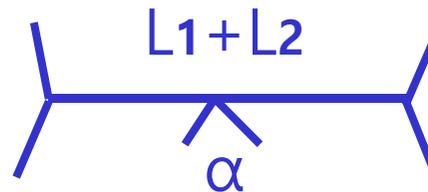
Fe-C

Peritectoid



Cu-Al

Synthetic reaction



K-Zn, Na-Zn,
K-Pb, Pb-U, Ca-Cd

On cooling two phases going to one phase