2015 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

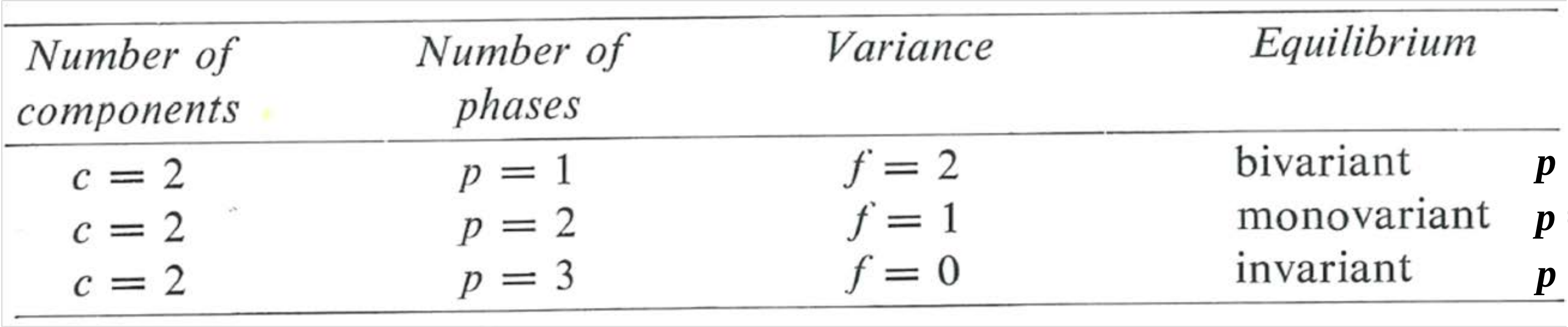
Formation of intermediate phases by peritectic reaction

Non-stoichiometeric compounds

4) Congruent transformations

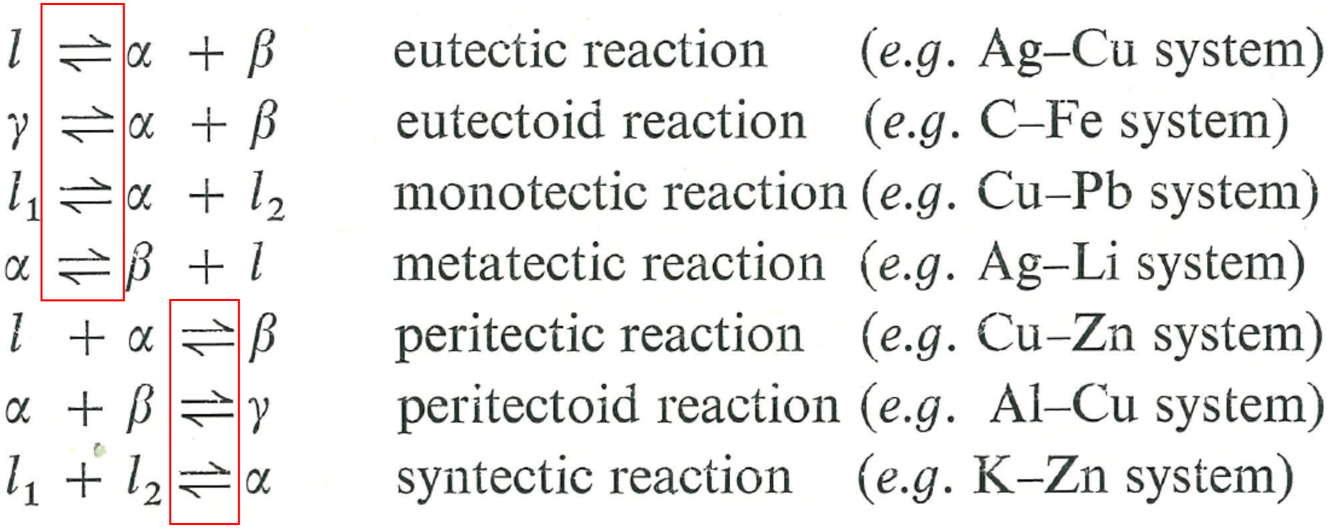
According to the condensed Phase Rule, $f = c - p + 1$

For a binary system the equilibria possible are summarized below.



Number of components	*Number of phases*	*Variance*	*Equilibrium*	
$c = 2$	$p = 1$	$f = 2$	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	(*e.g.* Ag–Cu system)
$\gamma \rightleftharpoons \alpha + \beta$	eutectoid reaction	(*e.g.* C–Fe system)
$l_1 \rightleftharpoons \alpha + l_2$	monotectic reaction	(*e.g.* Cu–Pb system)
$\alpha \rightleftharpoons \beta + l$	metatectic reaction	(*e.g.* Ag–Li system)
$l + \alpha \rightleftharpoons \beta$	peritectic reaction	(*e.g.* Cu–Zn system)
$\alpha + \beta \rightleftharpoons \gamma$	peritectoid reaction	(*e.g.* Al–Cu system)
$l_1 + l_2 \rightleftharpoons \alpha$	syntectic reaction	(*e.g.* 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

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

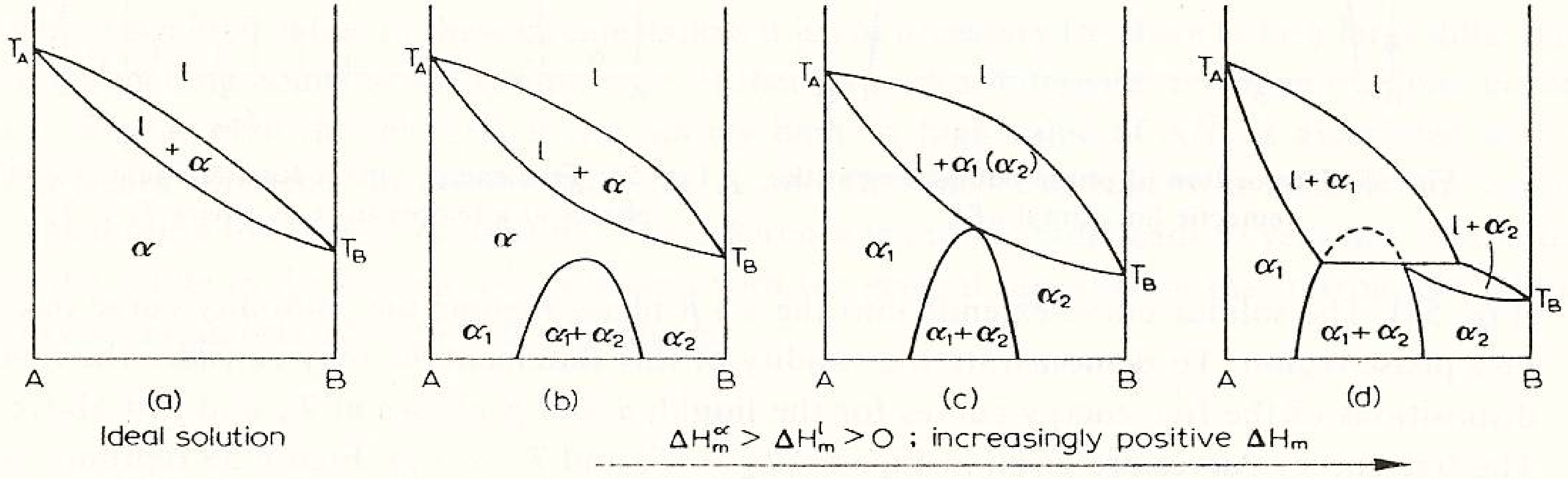


Fig. 61. Effect of increasingly positive departure from ideality in changing the phase diagram from a continuous series of solutions to a peritectic-type.

Eutectic reaction

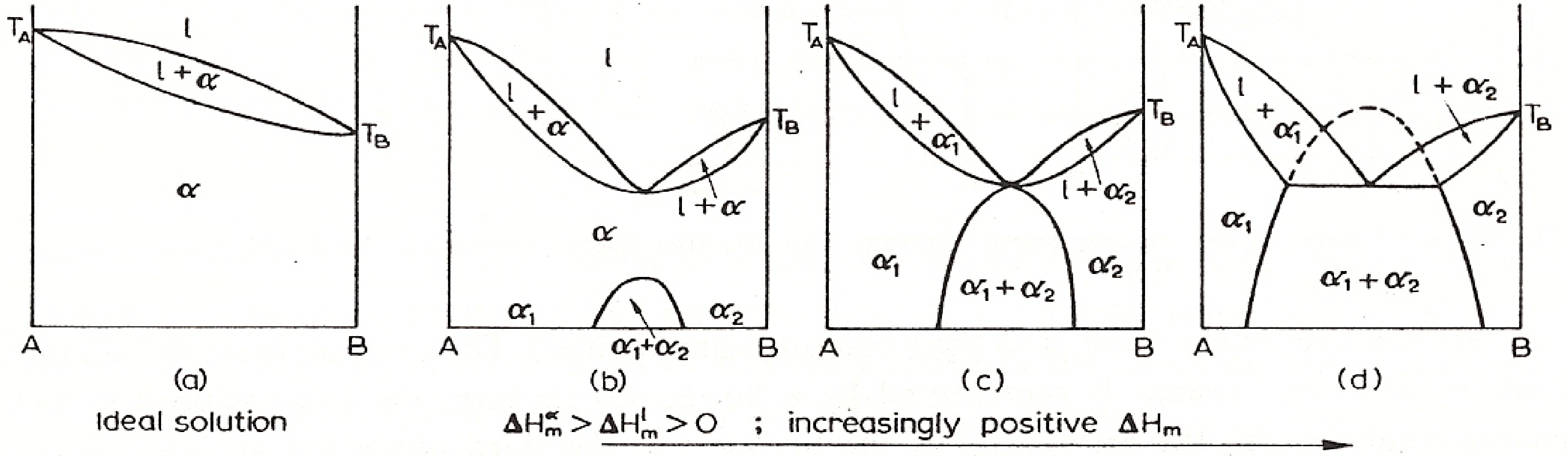


Fig. 43. Effect of increasingly positive departure from ideality in changing the phase diagram for a continuous series of solutions to a eutectic-type.

Peritectic reaction

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

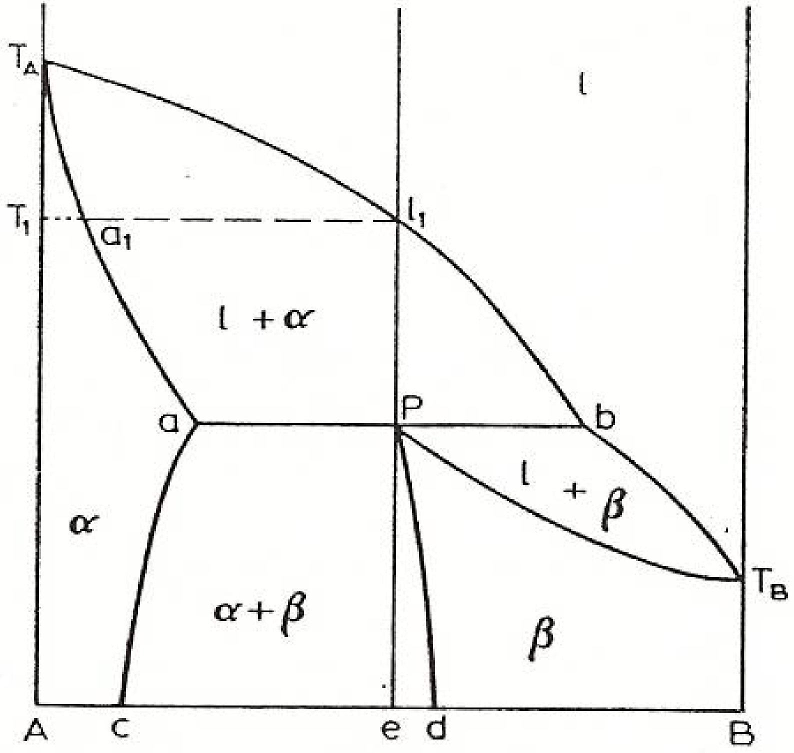


Fig. 65. Freezing of the peritectic alloy *P*.

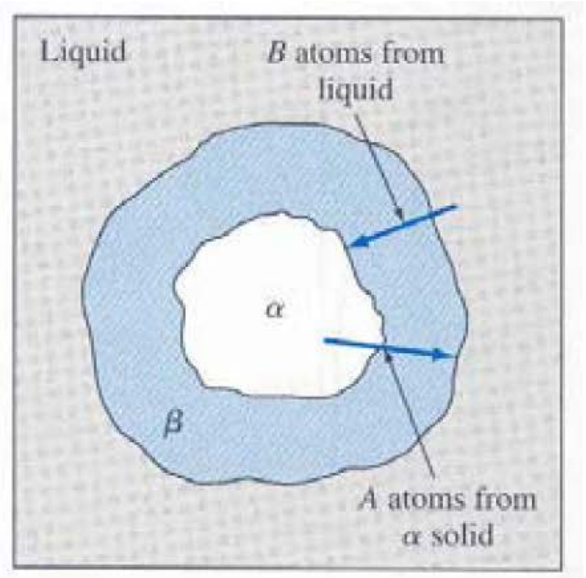


Figure 8.19

4.3.4. Formation of intermediate phases by peritectic reaction

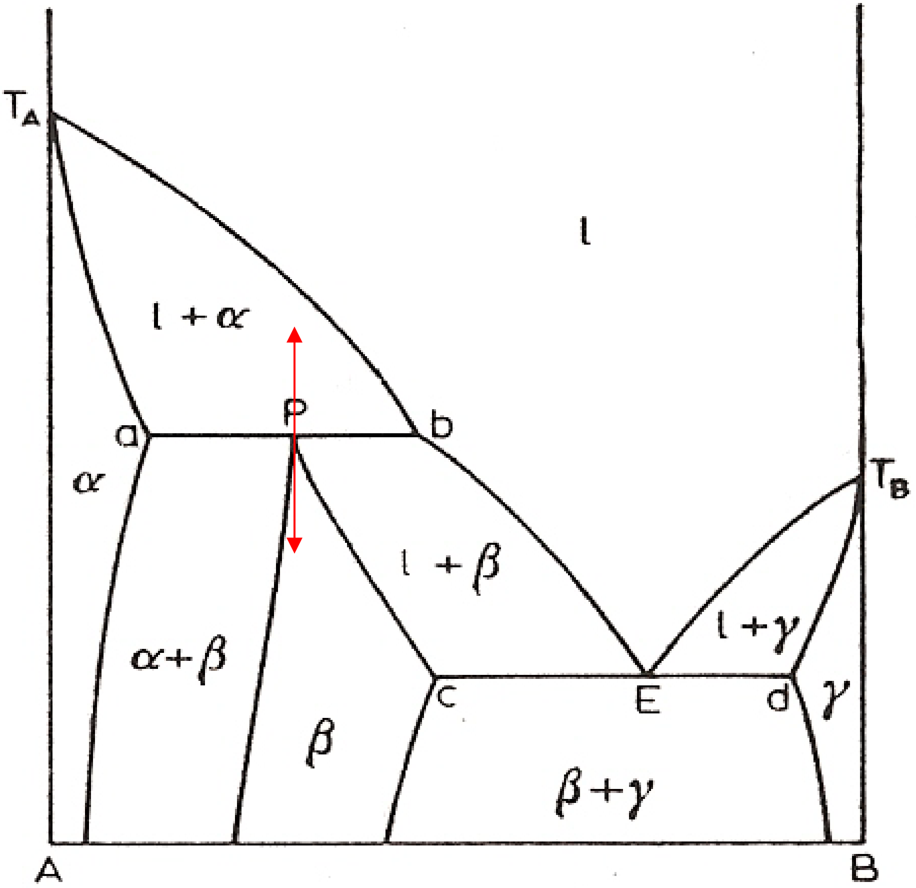


Fig. 68. Formation of an intermediate phase, β, by peritectic reaction.

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, Cu_3Ga, and Cu_5Sn
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. Mg_2Si, Mg_2Sn, Mg_2Pb and Mg_3Sb_2/
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.

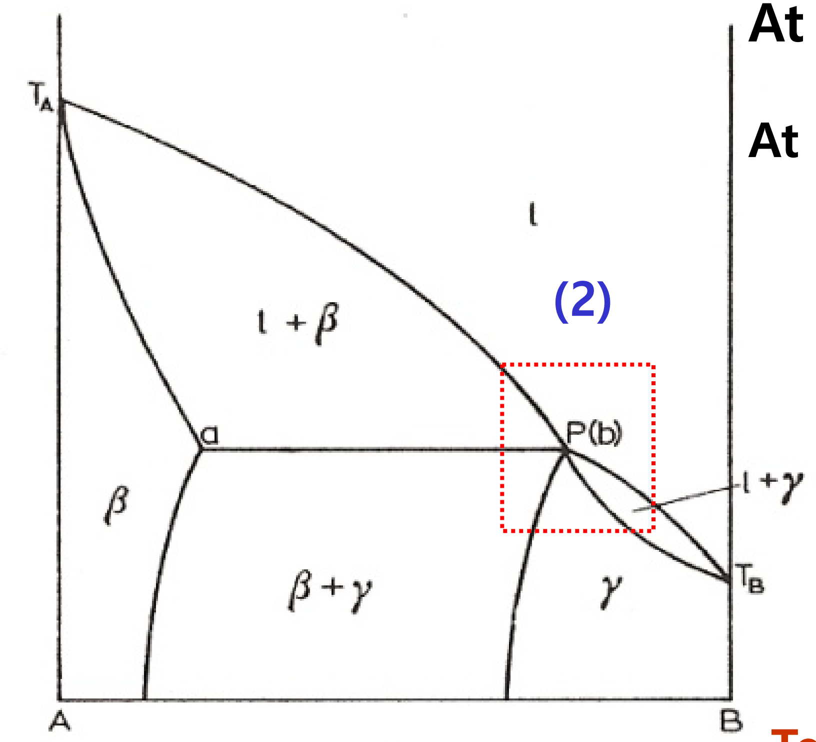


Fig. 72. Limiting case of the peritectic reaction.

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

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

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

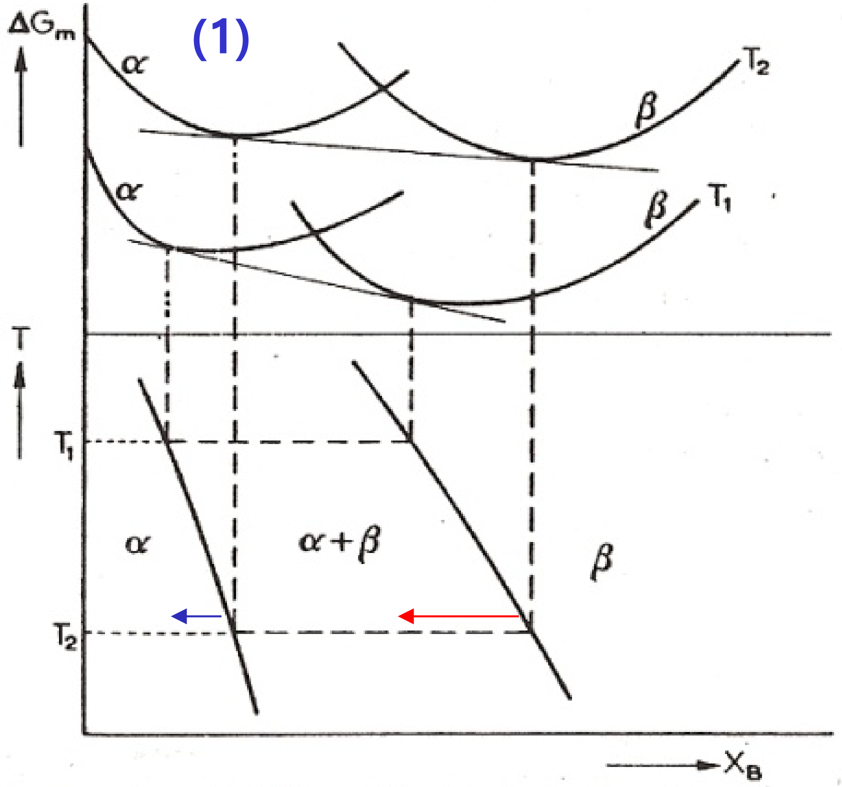
$$S^S \neq S^l, \boxed{dT / dX_A = 0}$$

Temp. maximum or minimum must be present.

(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.

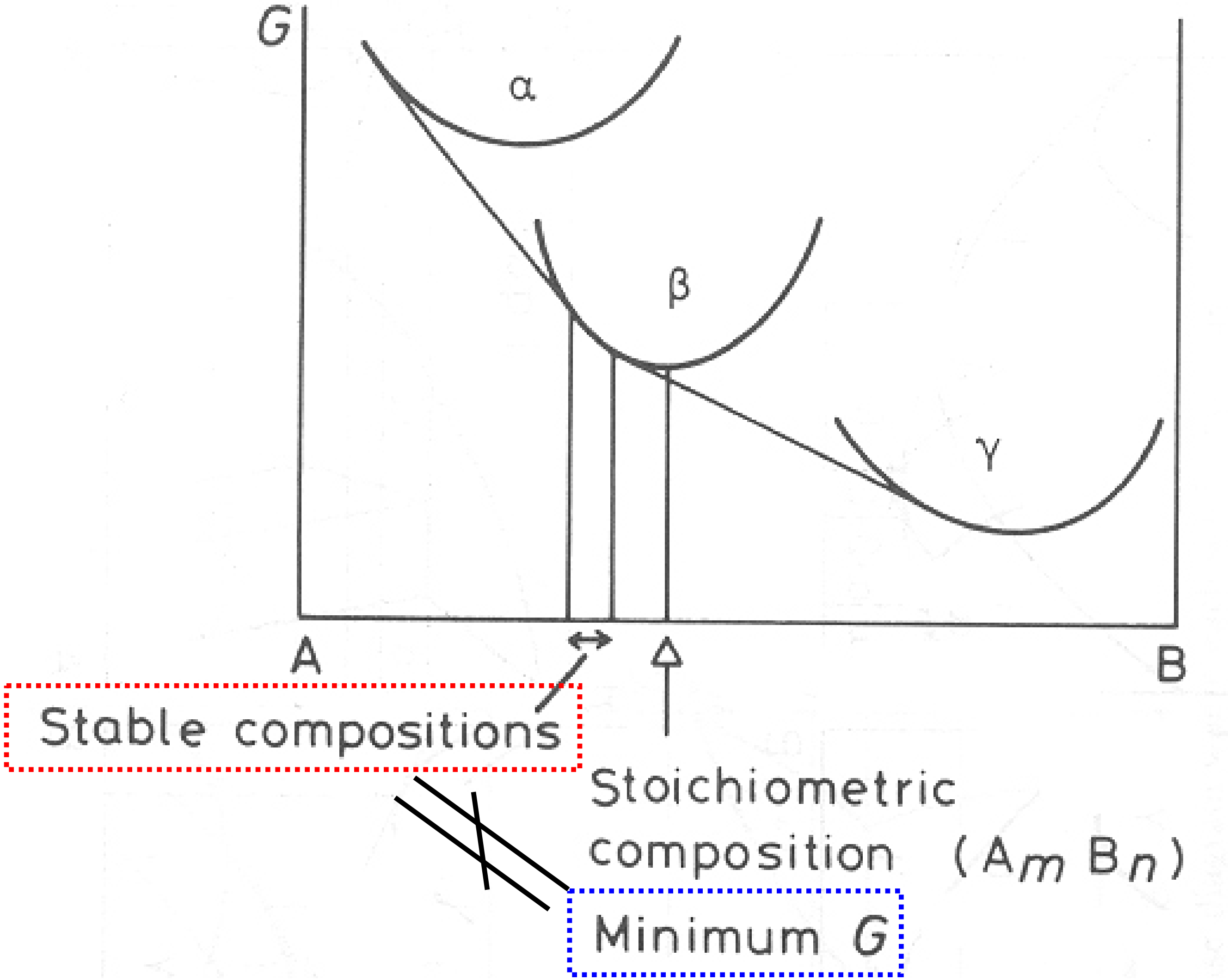
2) Decreasing solubility of Zn in Cu with rise in temperature in contrast to the normal decrease in solubility with fall in temperature



Due to an equilibrium with a disordered intermediate phase (e.g. the β phase above 454 ℃, 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-stoichiometeric compounds

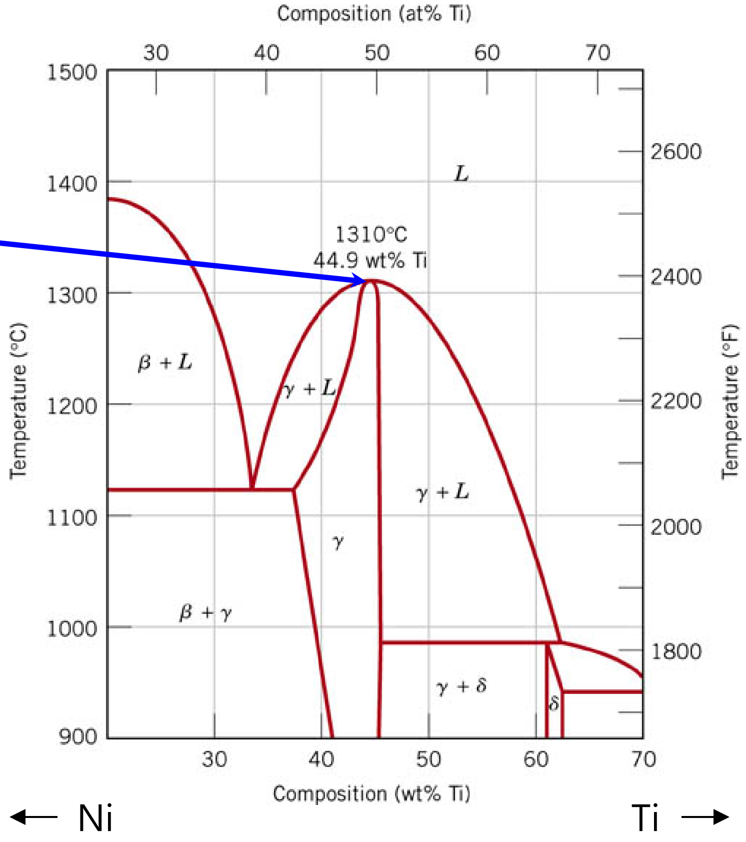


Congruent vs Incongruent

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**
- **Pertectic Reactions**
- **Eutectoid reactions**

4.4. Congruent transformations

Congruent transformation:

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

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

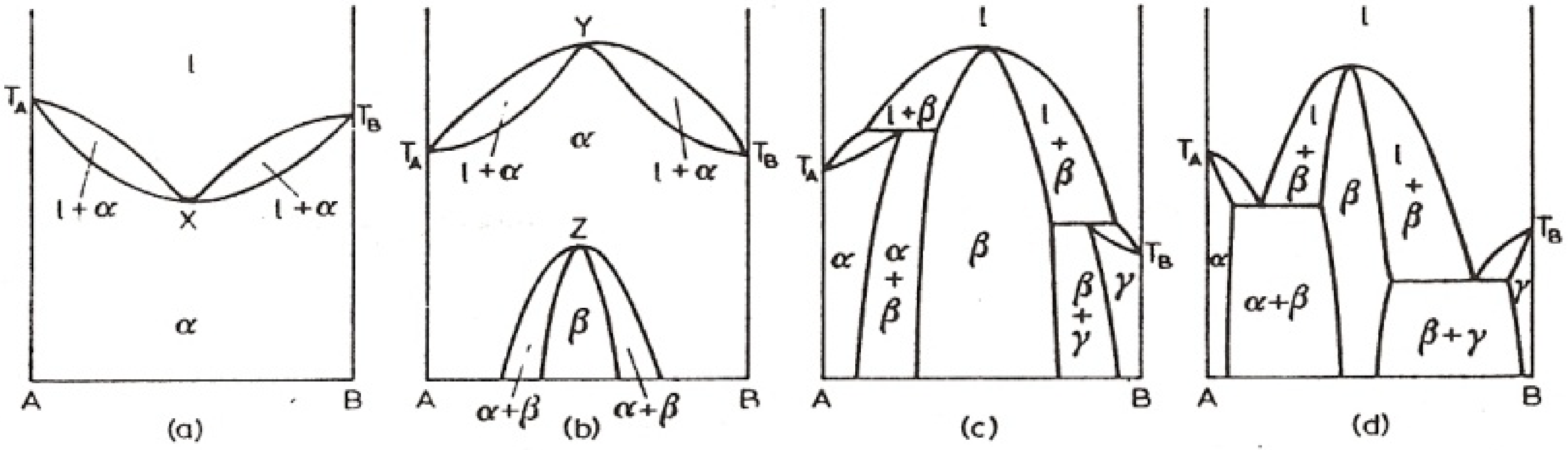


Fig. 76. Examples of congruent transformations.

4.4. Congruent transformations

b. More usual type of congruently-melting intermediate phase

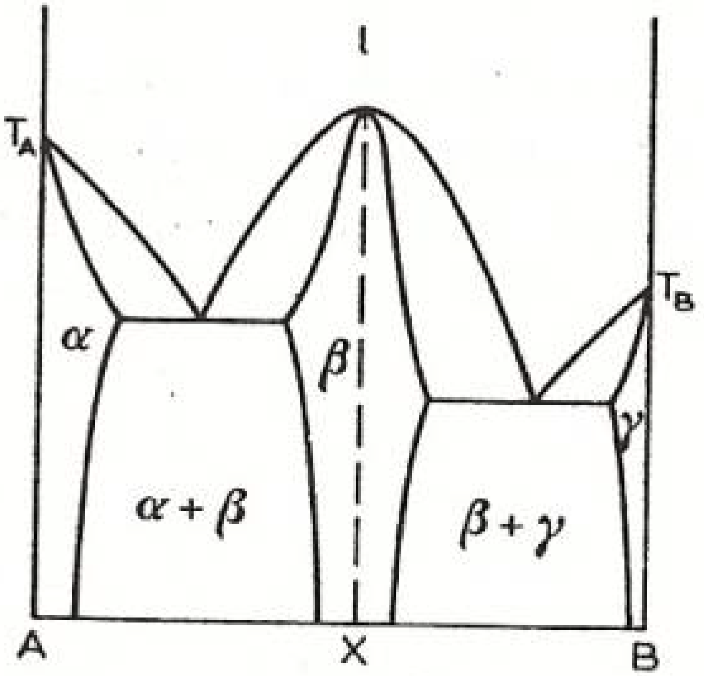
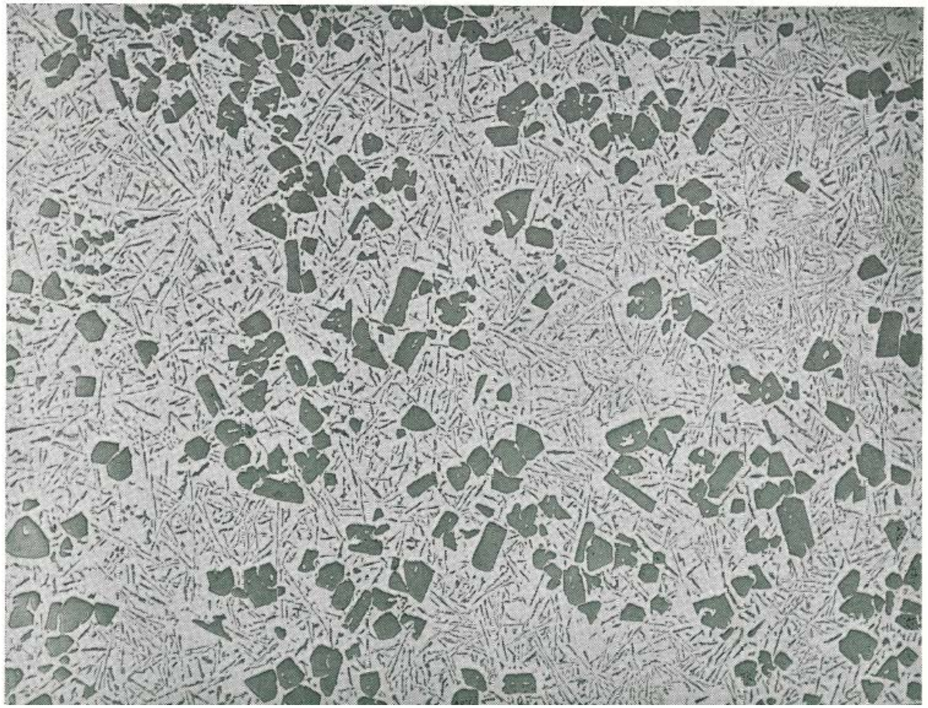


Fig. 78. Phase diagram with a congruent intermediate phase.

→ Partial phase diagram A-X and X-B



Microstructure of a cast Al-22% Si alloy

showing polyhedra of primary Si in eutectic matrix

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

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

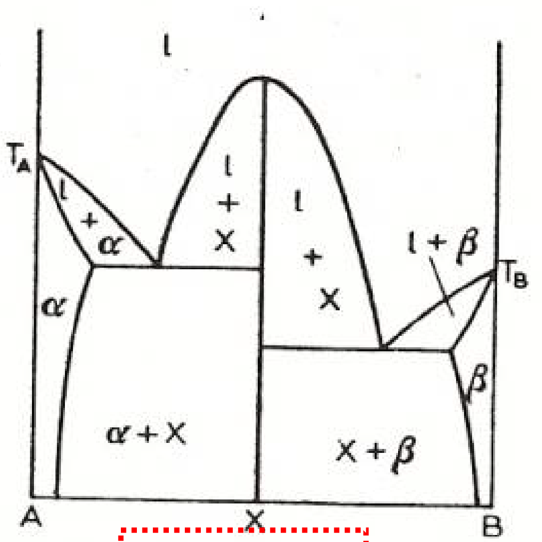
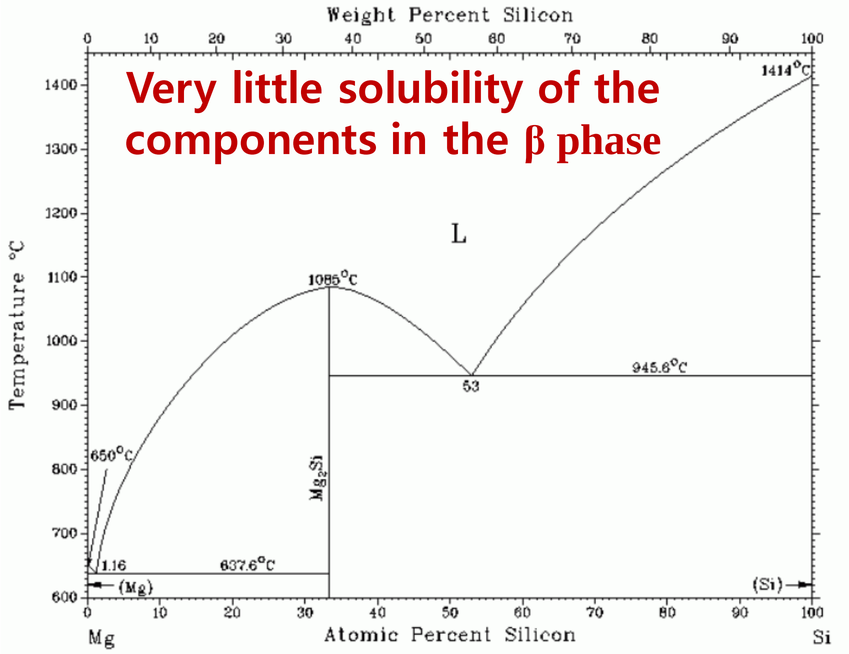
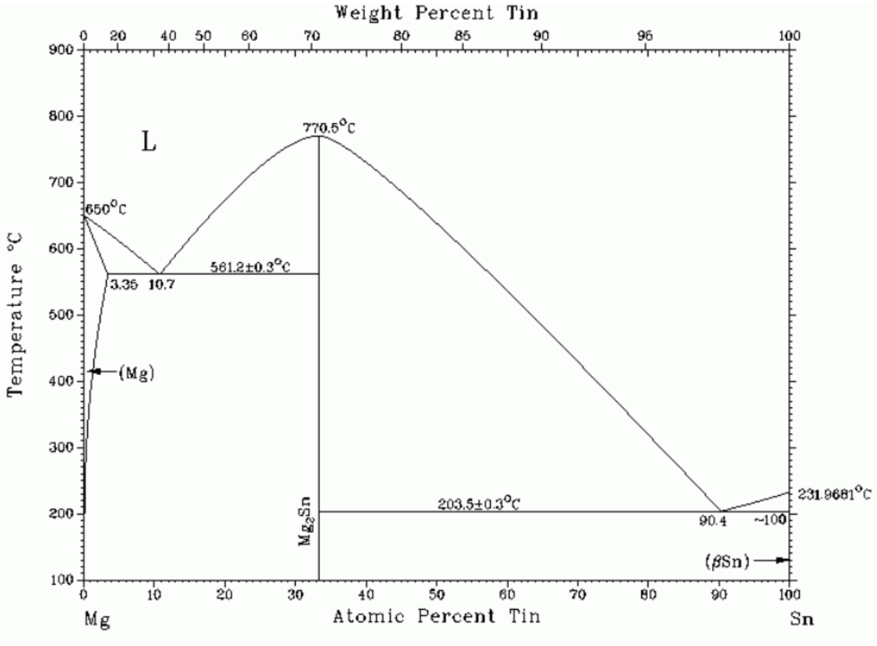
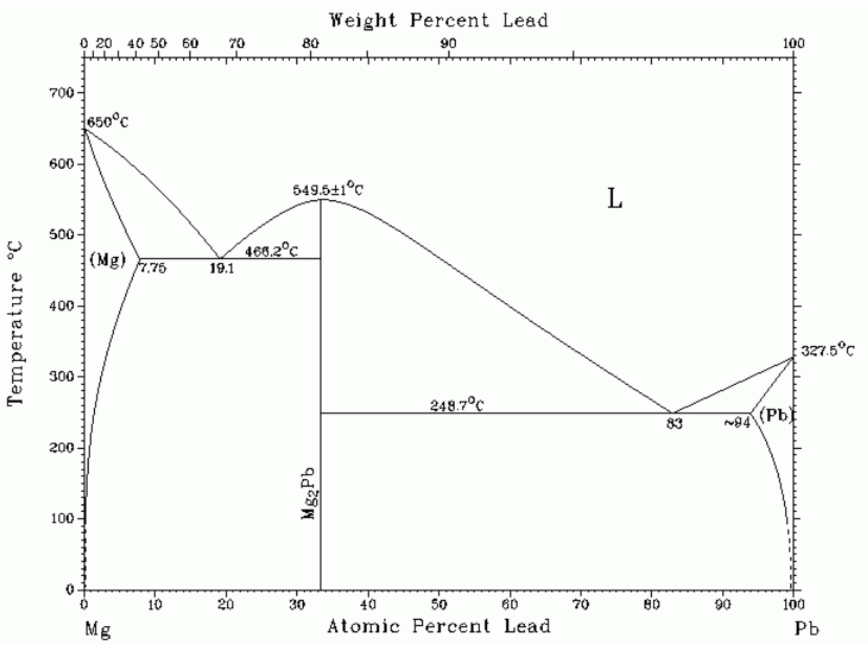


Fig. 79. Limiting case of Fig. 78.


Very little solubility of the components in the β phase





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

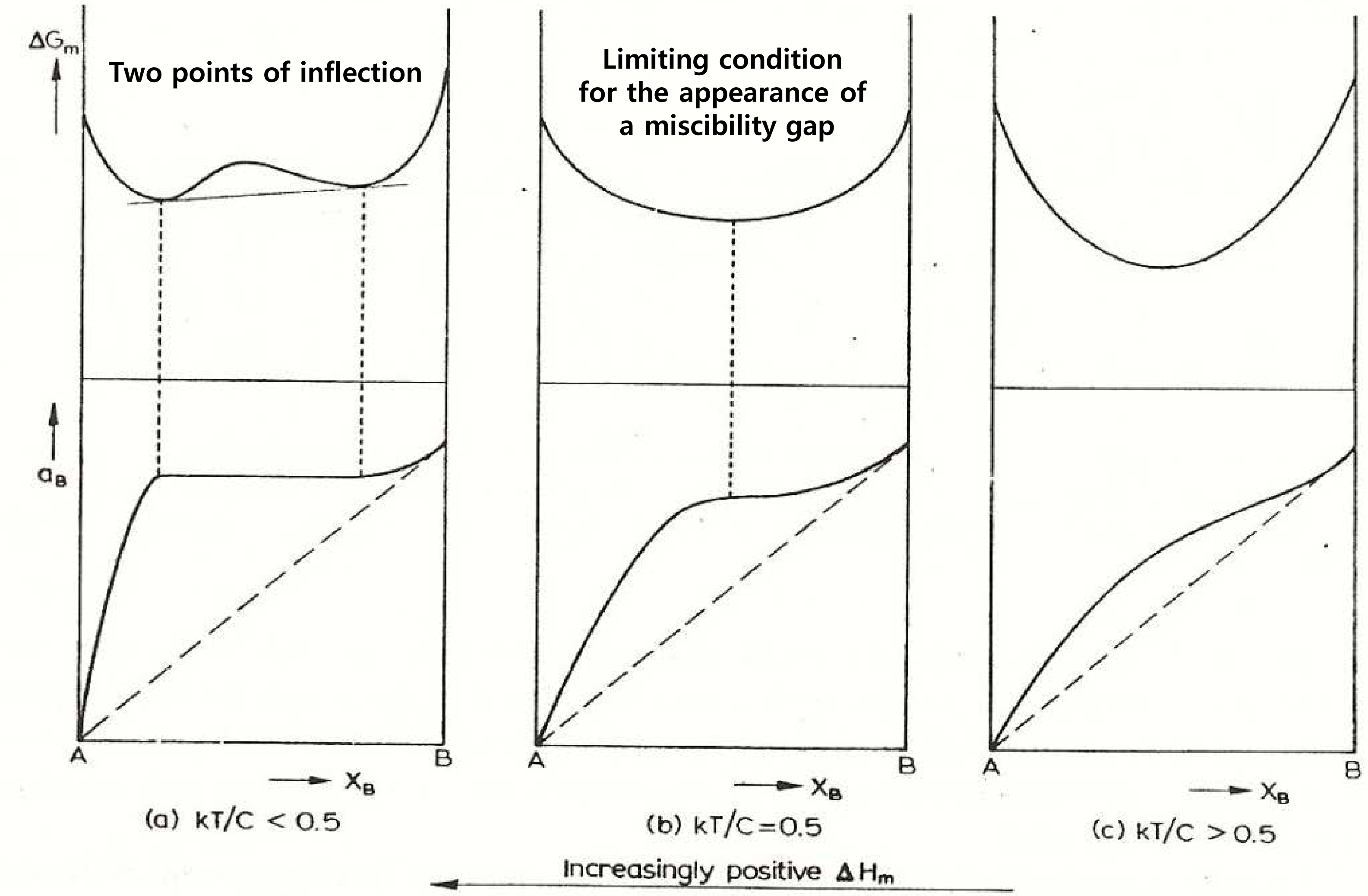
3) Syntectic reactions

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



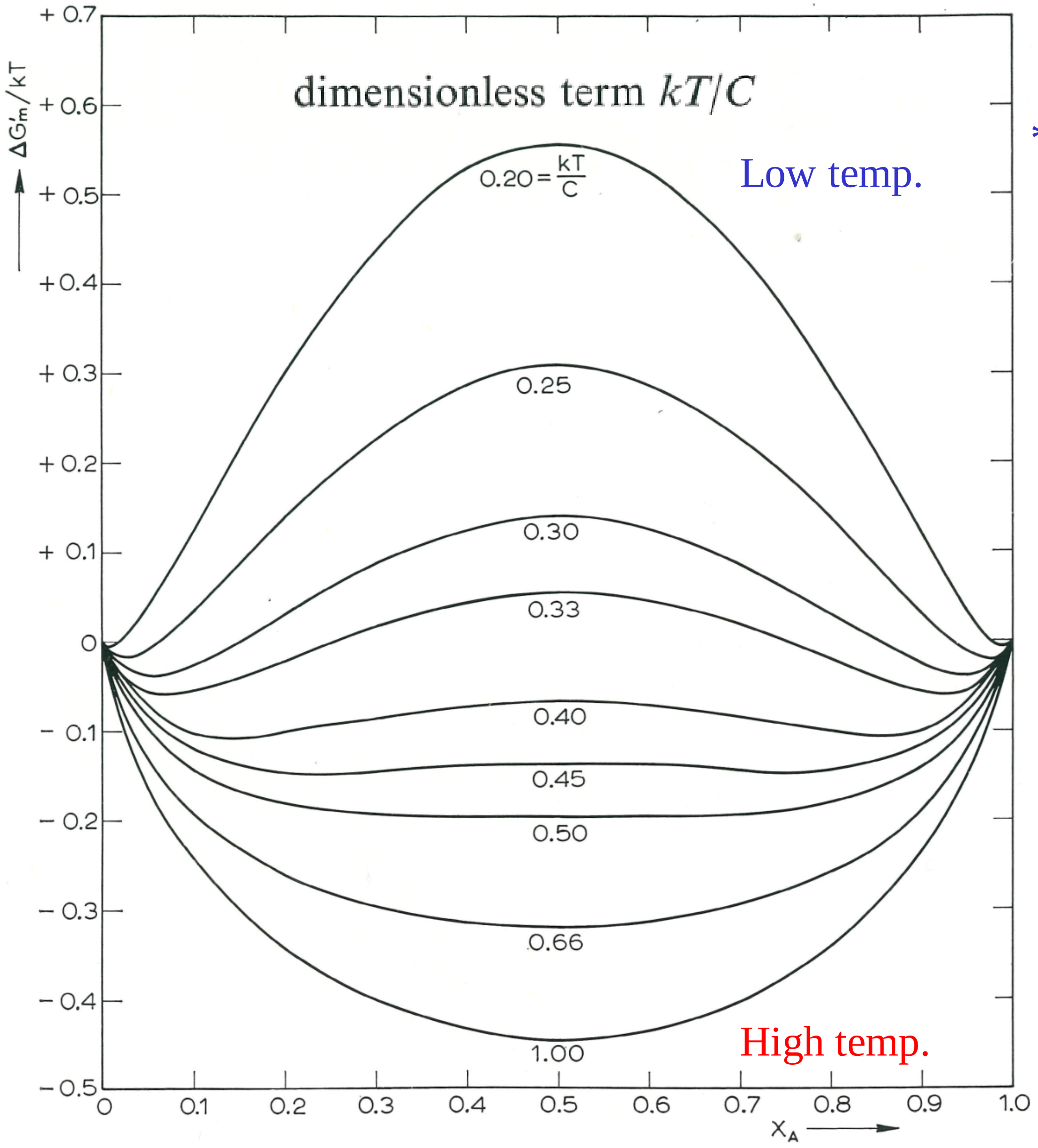
(a) kT/C < 0.5 (b) kT/C=0.5 (c) kT/C > 0.5

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

where,

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

: energy term



dimensionless term kT/C

Low temp.

High temp.

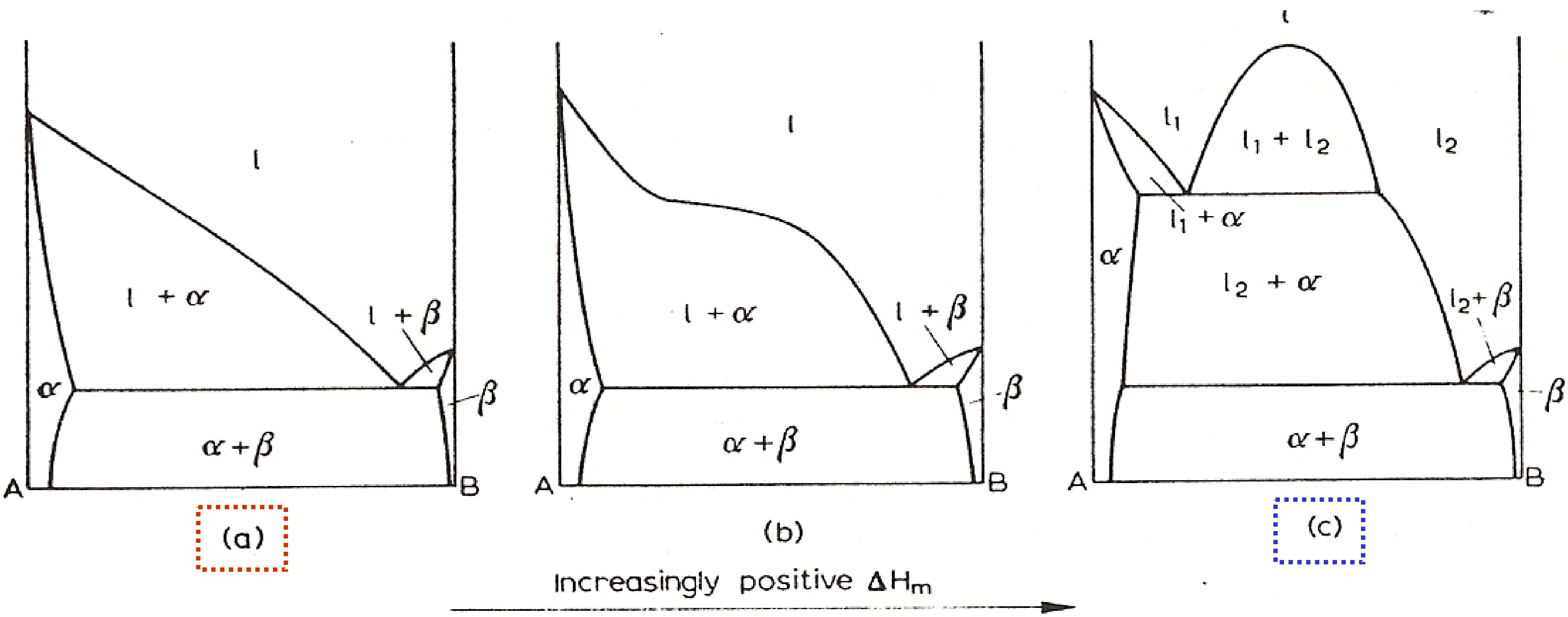
Fig. 14. Variation of free energy with composition for a homogeneous solution with $\Delta H_m > 0$. Free energy–composition curves are given for various values of the parameter kT/C.

- **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.

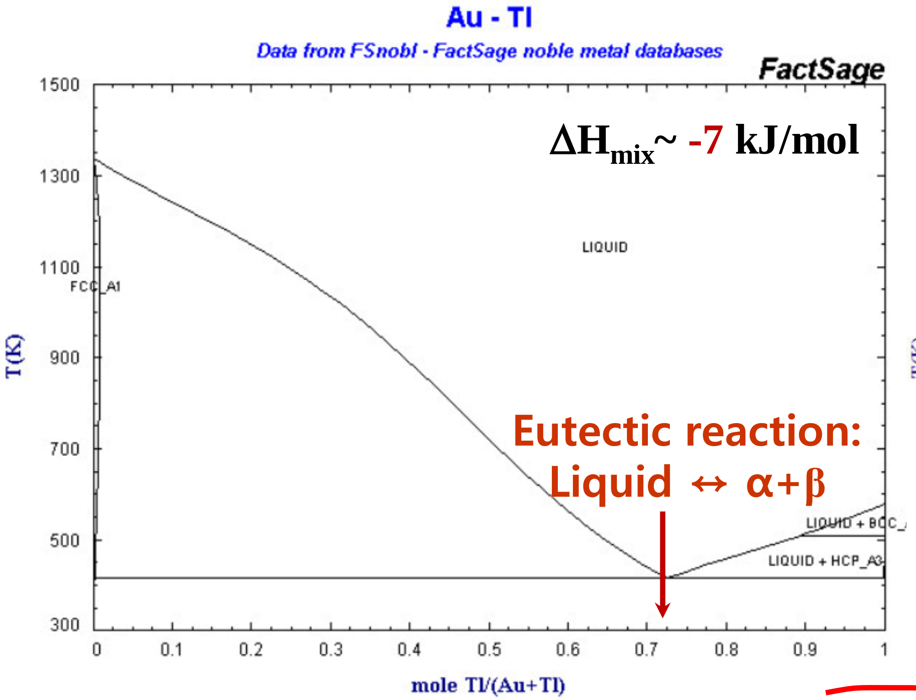
Effect of very large positive deviations from ideality in changing the phase diagram from a eutectic to a monotectic reaction



Eutectic reaction: Liquid ↔α+β

Monotectic reaction: Liquid$_1$ ↔Liquid$_2$+ solid

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

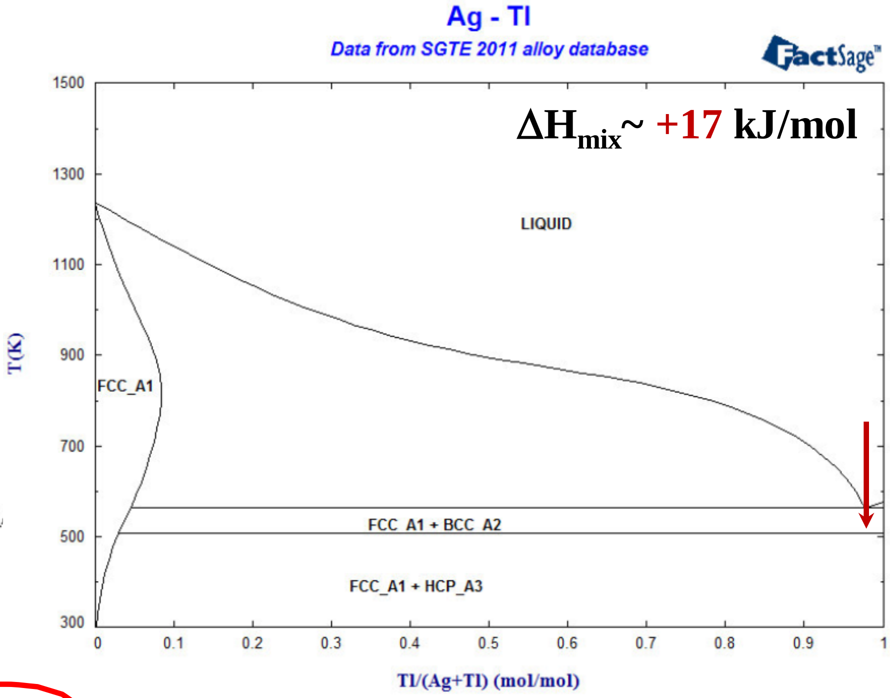


Au - Tl

Data from FSnobl - FactSage noble metal databases

ΔH_{mix}~ -7 kJ/mol

Eutectic reaction:
Liquid ↔ α+β

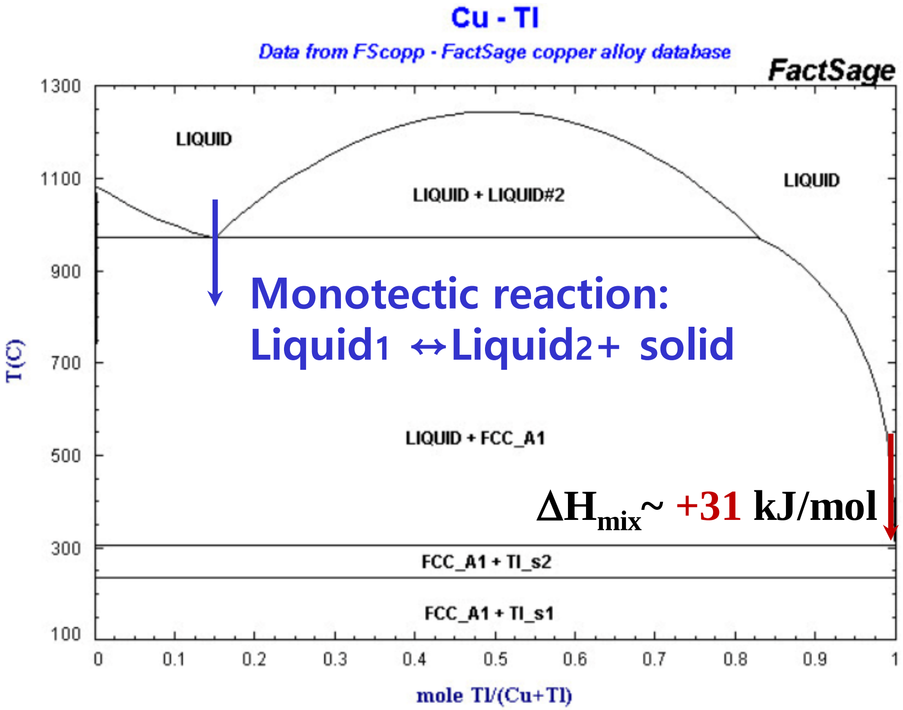


Ag - Tl

Data from SGTE 2011 alloy database

ΔH_{mix}~ +17 kJ/mol

Increasingly positive ΔH_{mix}



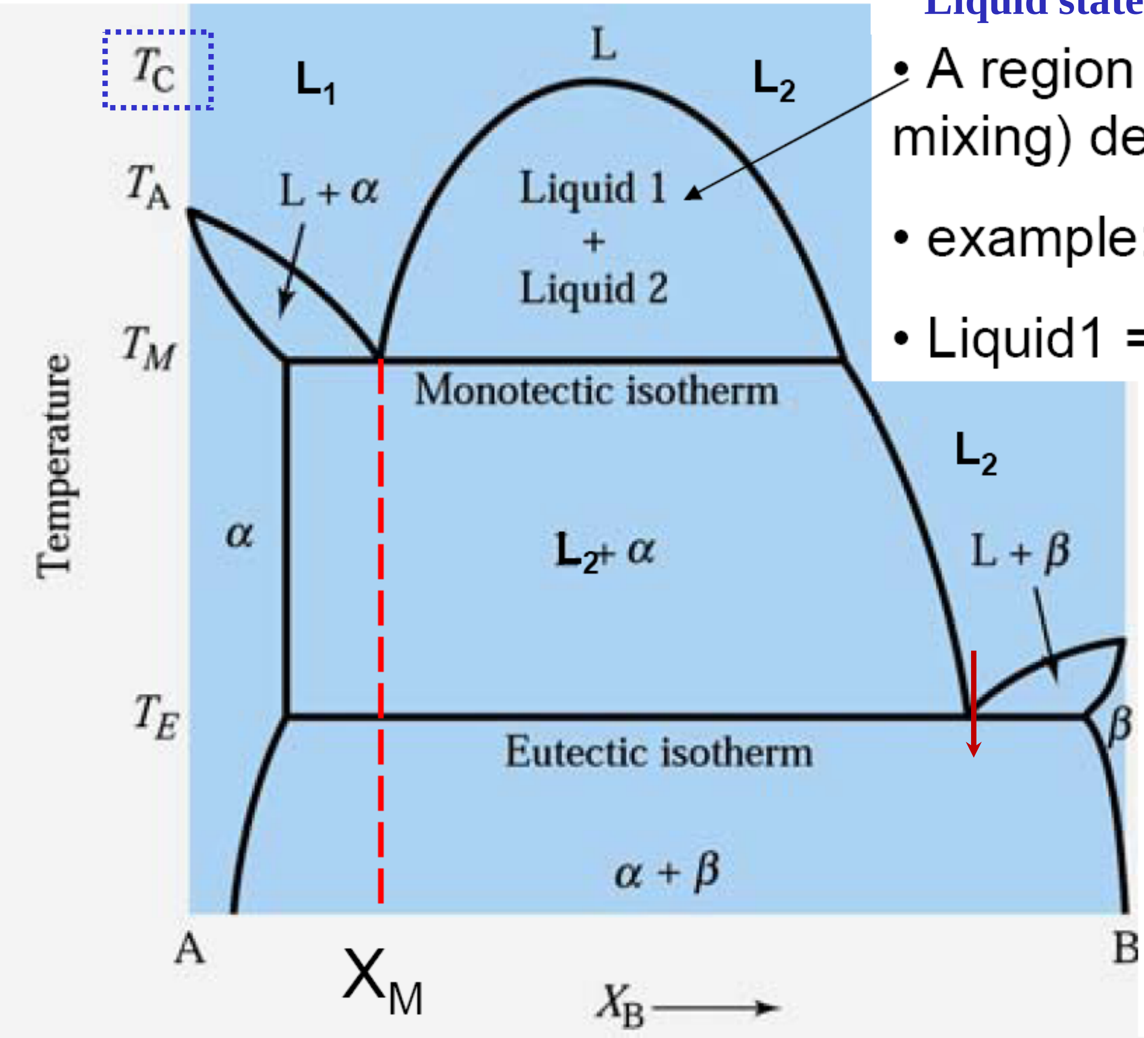
Cu - Tl

Data from FScopp - FactSage copper alloy database

Monotectic reaction:
Liquid1 ↔Liquid2+ solid

ΔH_{mix}~ +31 kJ/mol

2) Monotectic Phase Diagram



Liquid state miscibility gap

- A region of immiscibility (non-mixing) develops in the L phase
- example: oil and water
- Liquid1 = Liquid2 + α (solid)

Eutectic reaction:
Liquid ↔ α+β

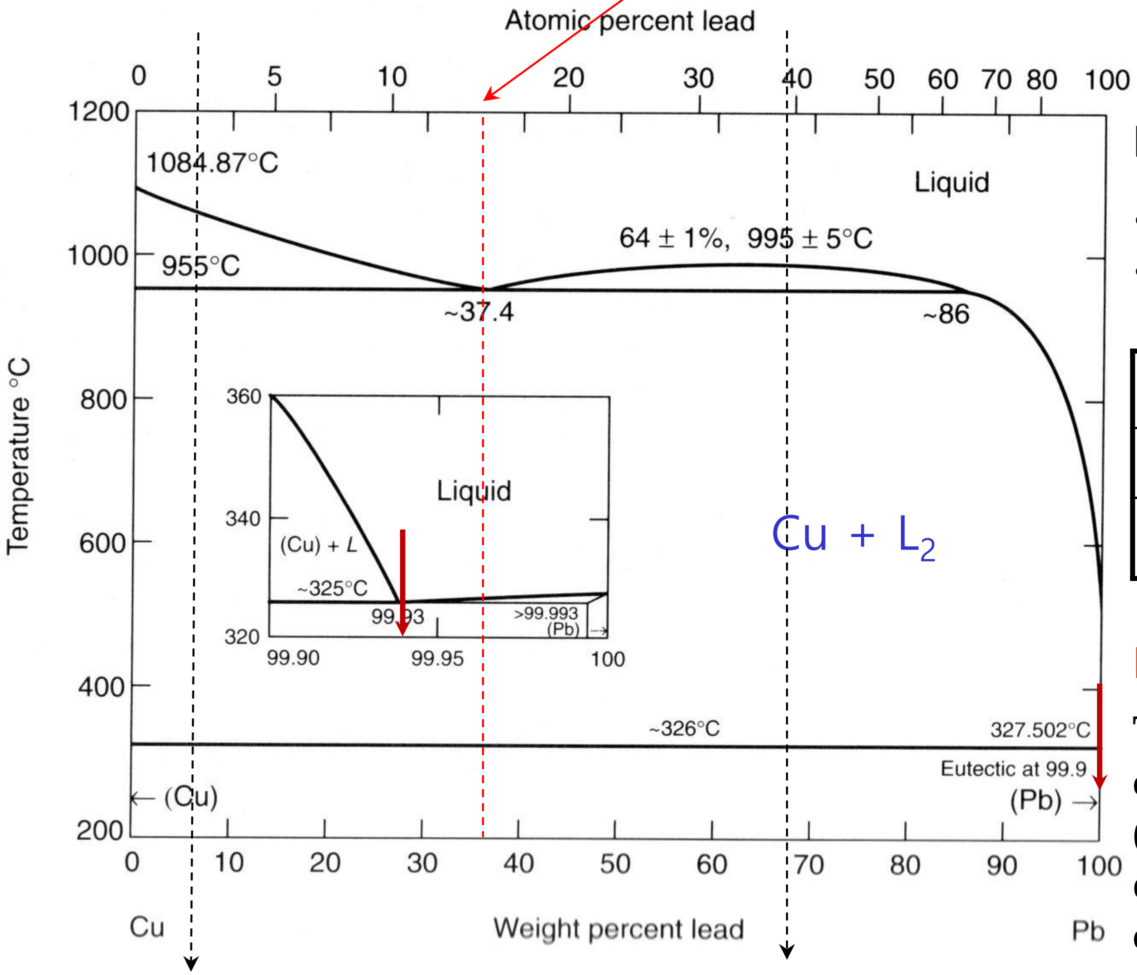
The temperature invariant reaction could be peritectic in nature but this is not usual.

G.A. Chadwick, Brit. J. App. Phys., 16 (1965) 1096

Monotectic

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

Monotectic Reaction: $L \underset{\text{heat}}{\overset{\text{cool}}{\rightleftharpoons}} L_2 + \text{Solid}$



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 cooing: 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

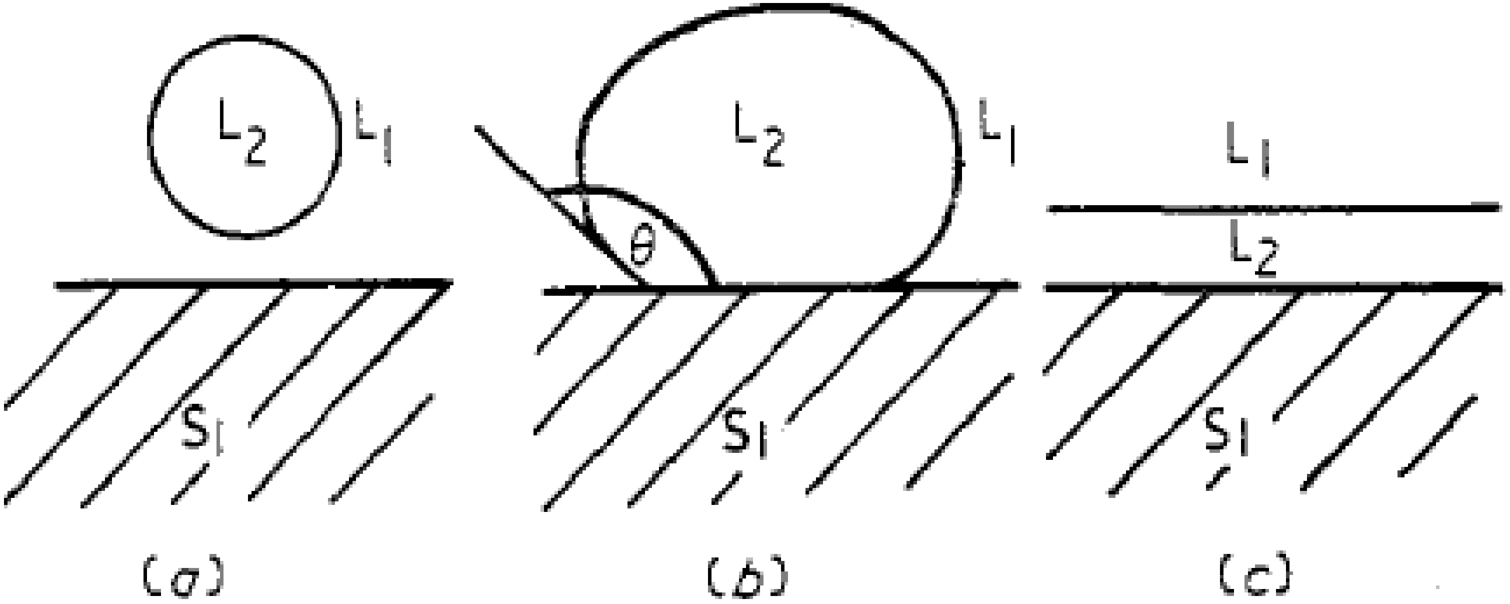
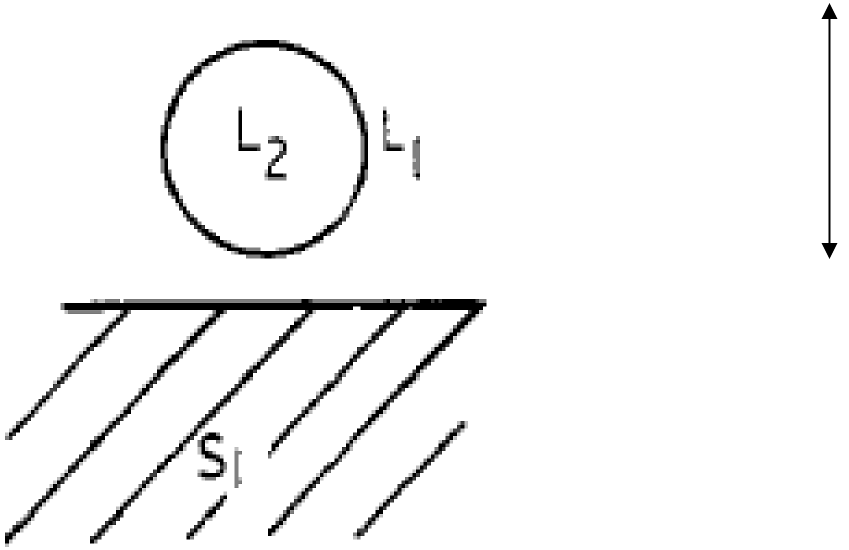


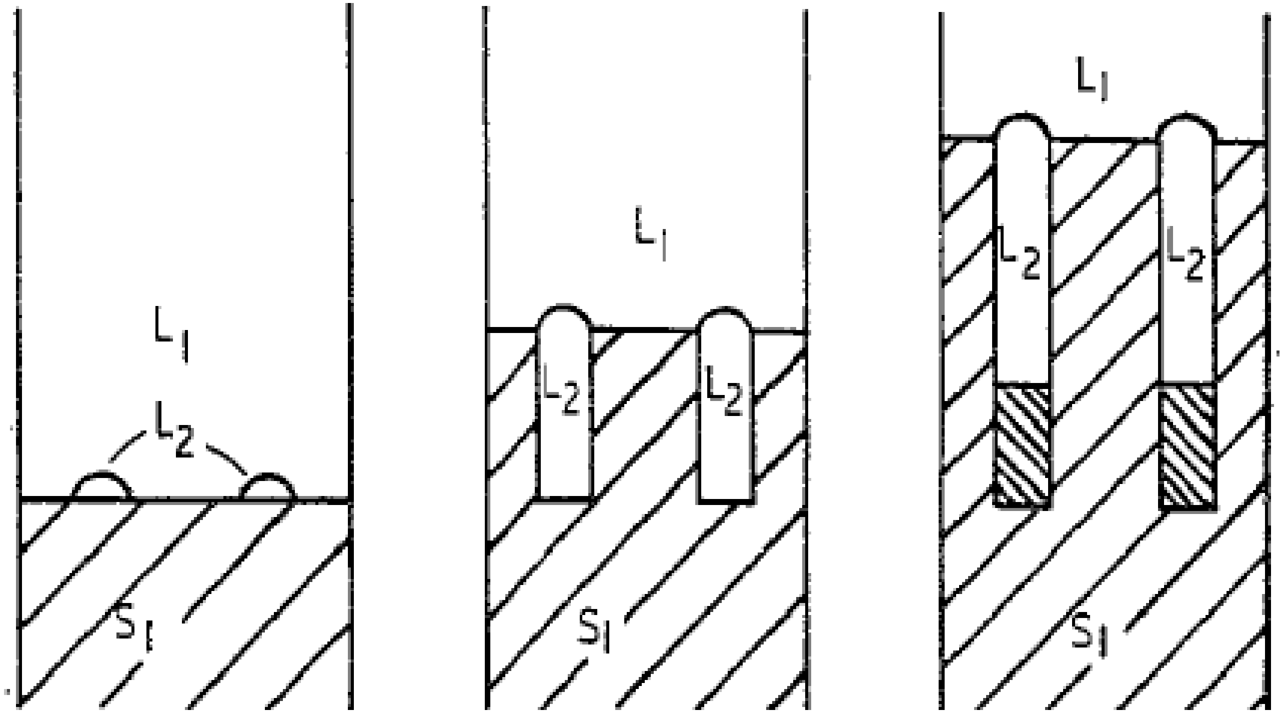
Figure 2. Solid–liquid interface morphology for different interfacial energy conditions: (*a*) $\gamma_{S_1L_2} > \gamma_{S_1L_1} + \gamma_{L_1L_2}$, (*b*) $\gamma_{S_1L_2} = \gamma_{S_1L_1} - \gamma_{L_1L_2} \cos\theta$, (*c*) $\gamma_{S_1L_1} > \gamma_{S_1L_2} + \gamma_{L_1L_2}$.

Case 1: $\gamma_{\alpha l_1} + \gamma_{l_1 l_2} < \gamma_{\alpha l_2}$



Hg-Te single crystal

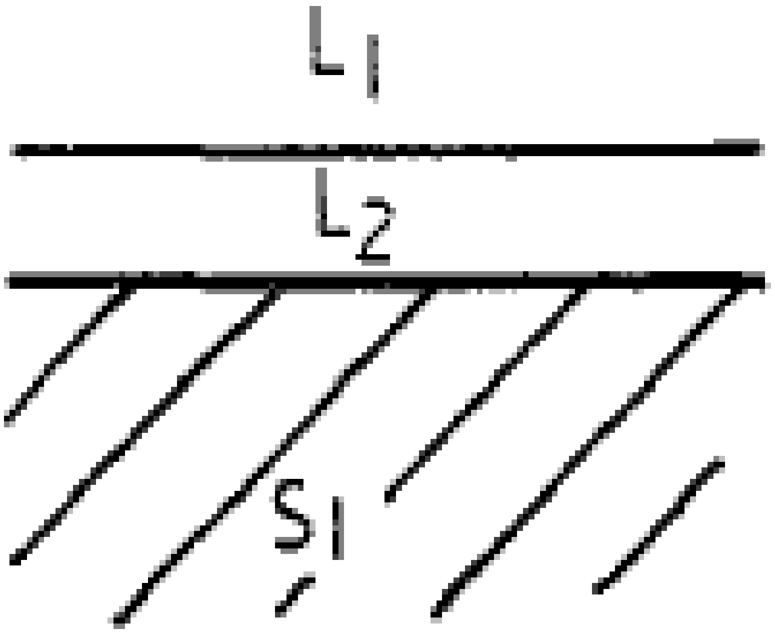
Case 2: $\gamma_{\alpha l_2} = \gamma_{\alpha l_1} - \gamma_{l_1 l_2} \cos\theta$



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

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

Case 3: $\gamma_{\alpha l_1} > \gamma_{\alpha l_2} + \gamma_{l_1 l_2}$

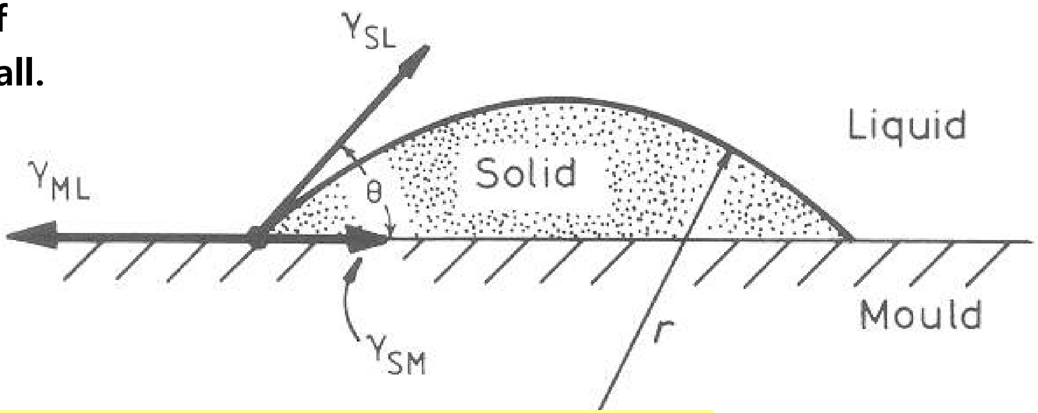


4.1.3. Heterogeneous nucleation

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)**

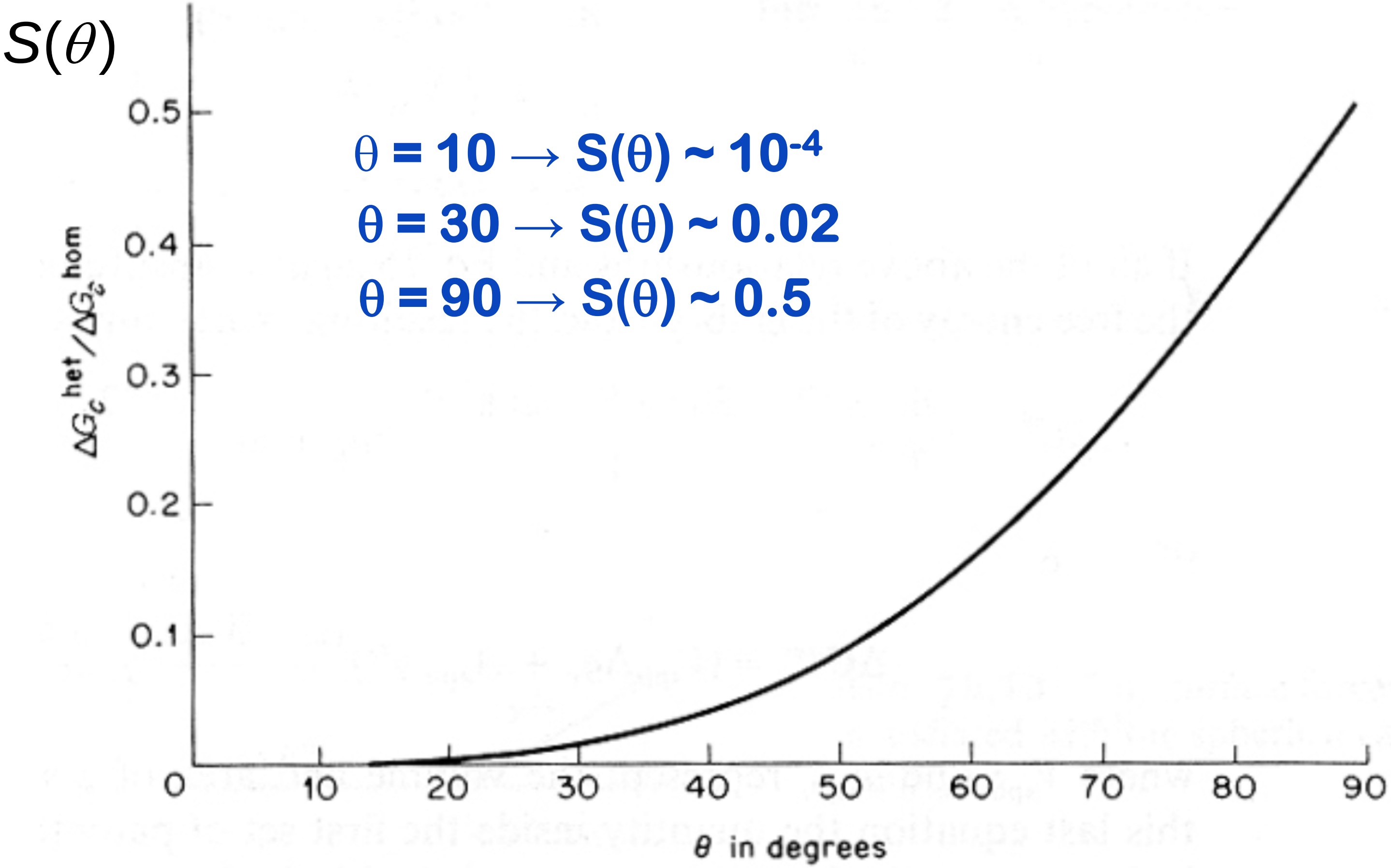
Incentive H4

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

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

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

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



$\theta = 10 \rightarrow S(\theta) \sim 10^{-4}$

$\theta = 30 \rightarrow S(\theta) \sim 0.02$

$\theta = 90 \rightarrow S(\theta) \sim 0.5$

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

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

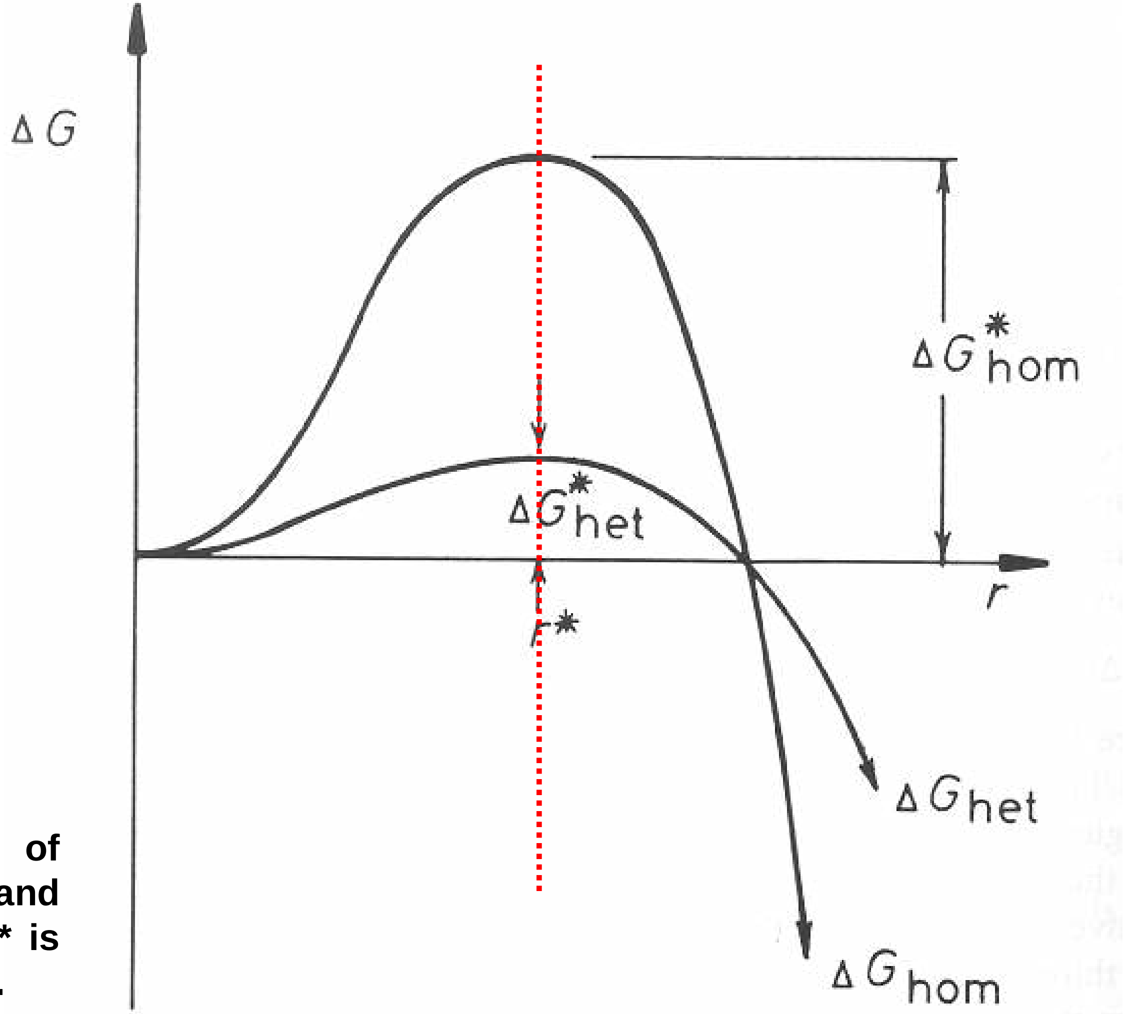
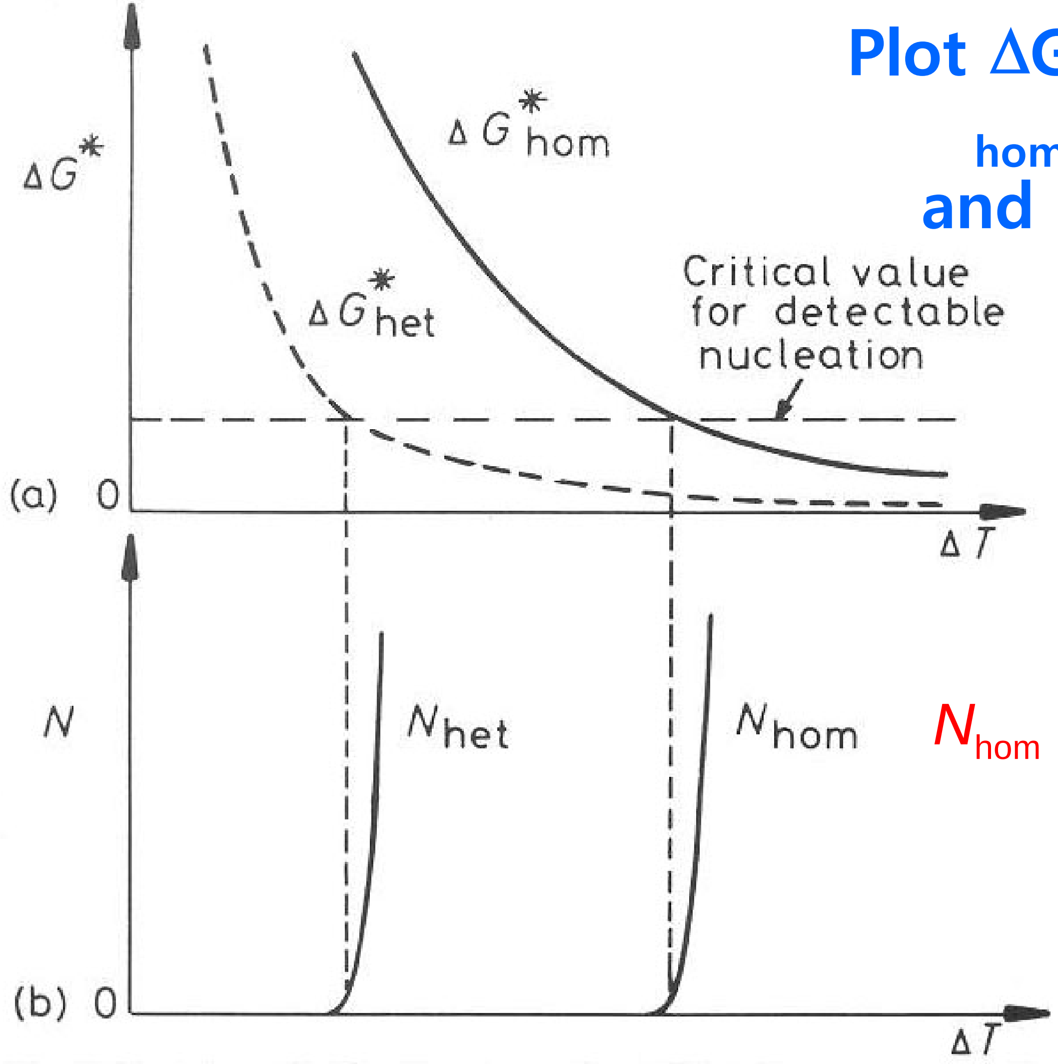


Fig. 4.8 The excess free energy of solid clusters for homogeneous and heterogeneous nucleation. Note r* is independent of the nucleation site.

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

Plot ΔG^*_{het} & ΔG^*_{hom} vs ΔT and N vs ΔT.

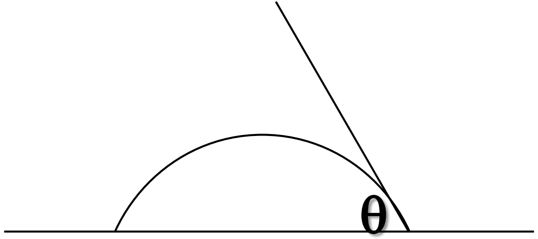


$N_{hom} \approx 1\ \mathrm{cm^{-3}s^{-1}}$

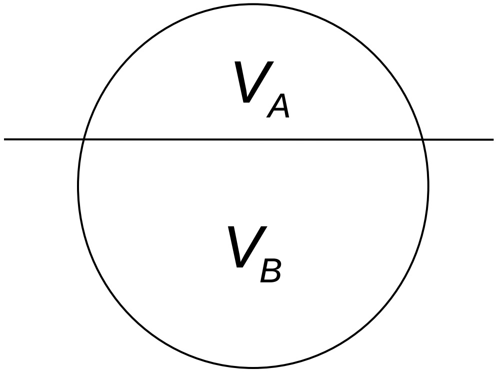
Fig. 4.9 (a) Variation of ΔG* with undercooling (ΔT) for homogeneous and heterogeneous nucleation. (b) The corresponding nucleation rates assuming the same critical value of ΔG*

Barrier of Heterogeneous Nucleation

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



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



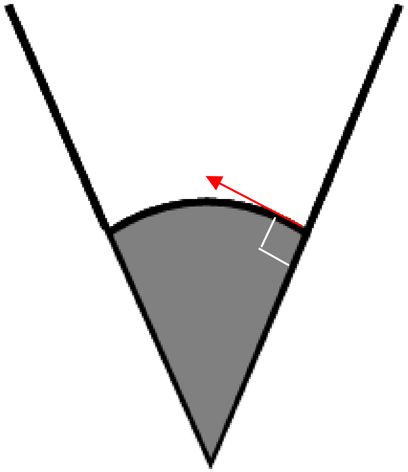
$$\Delta G_{sub}^* = \Delta G_{homo}^* \left(\frac{2-3\cos\theta+\cos^3\theta}{4} \right)$$

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

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

Nucleation Barrier at the crevice

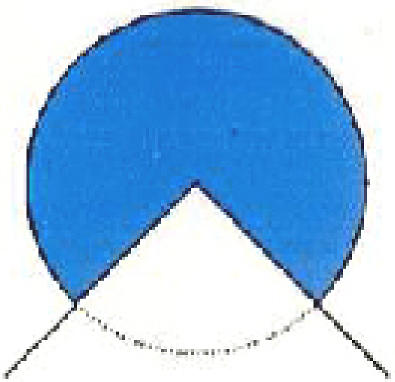
What would be the shape of nucleus and the nucleation barrier for the following conditions?



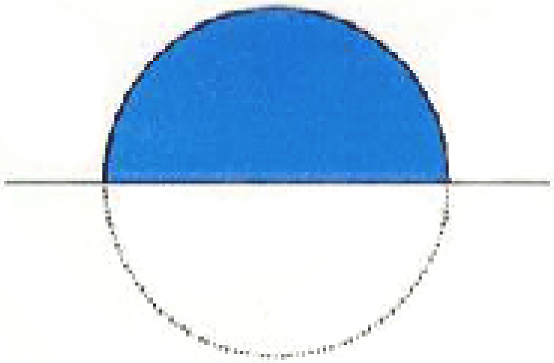
contact angle = 90

groove angle = 60

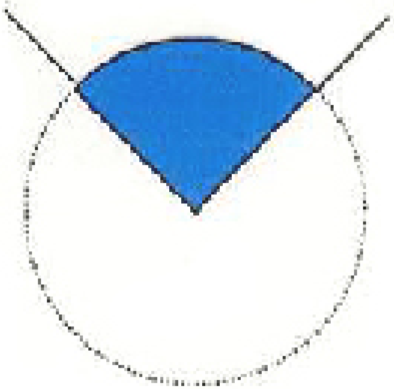
$$\frac{1}{6}\Delta G^{*}_{\text{homo}}$$



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

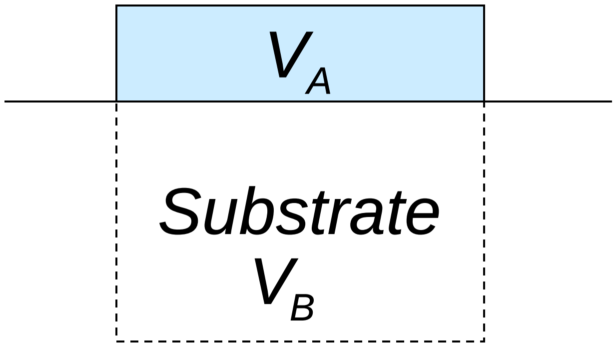


$$\frac{1}{2}\Delta G^{*}_{\text{homo}}$$

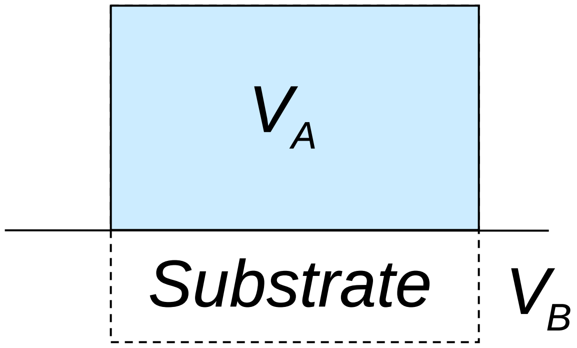


$$\frac{1}{4}\Delta G^{*}_{\text{homo}}$$

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

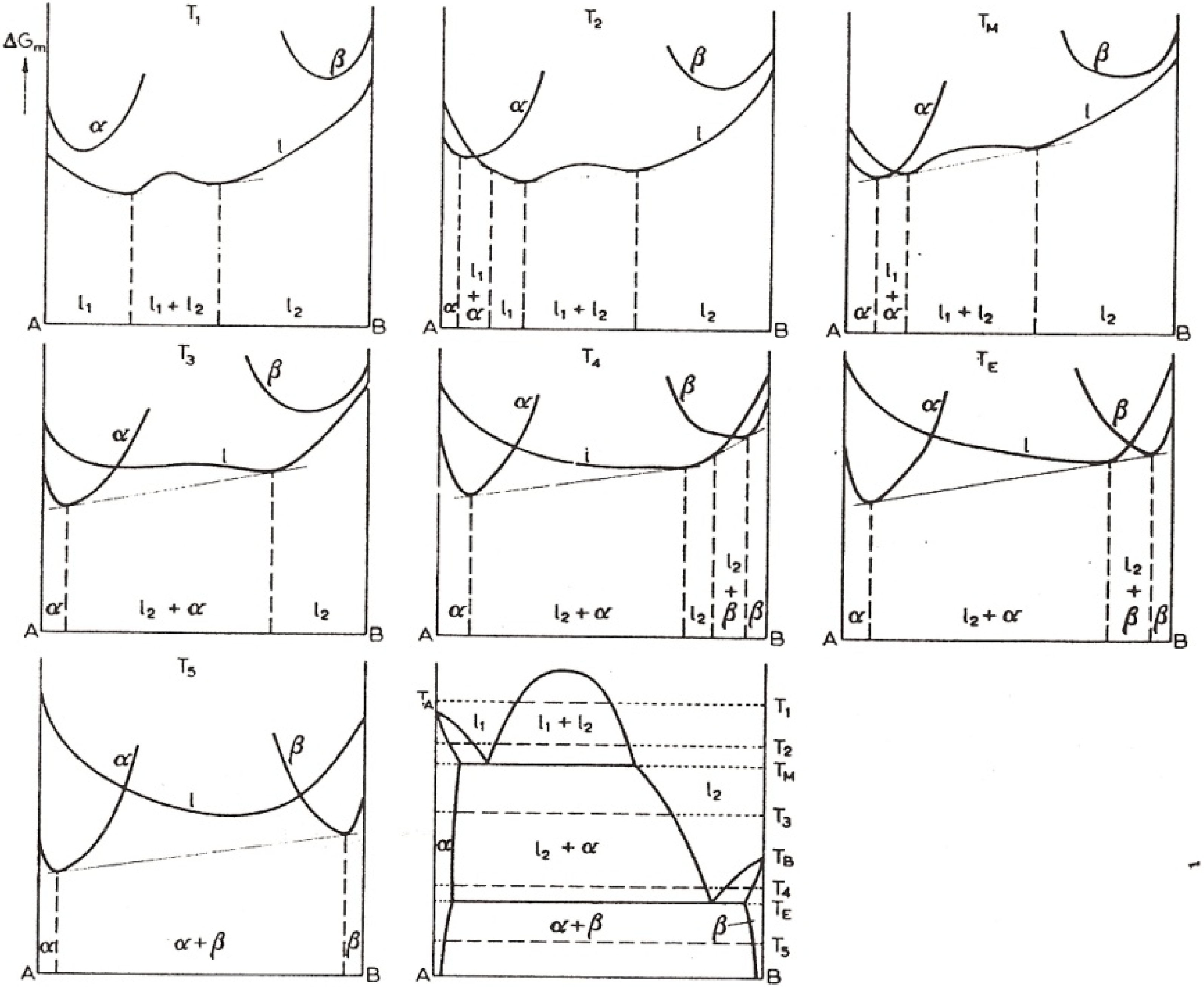


Fig. 85. Derivation of the monotectic phase diagram from the free energy curves for the liquid, α and β phases.

* Limiting forms of monotectic phase diagram

$T_M \rightarrow T_A$ $T_E \rightarrow T_B$

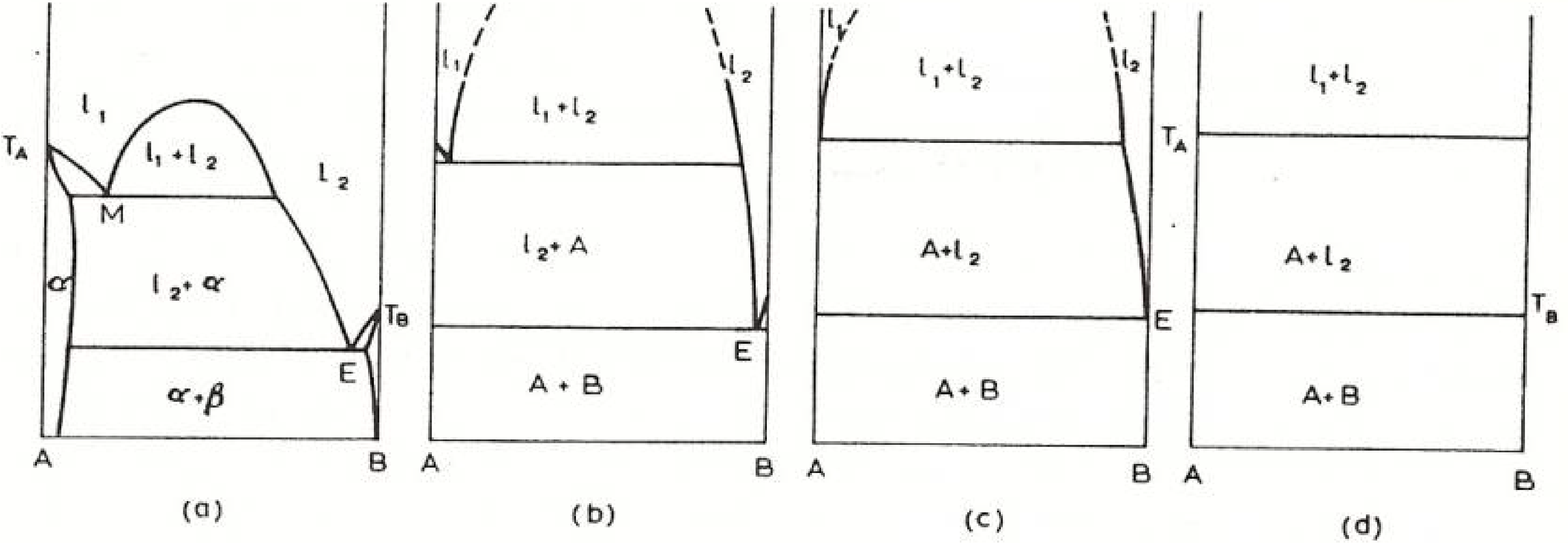
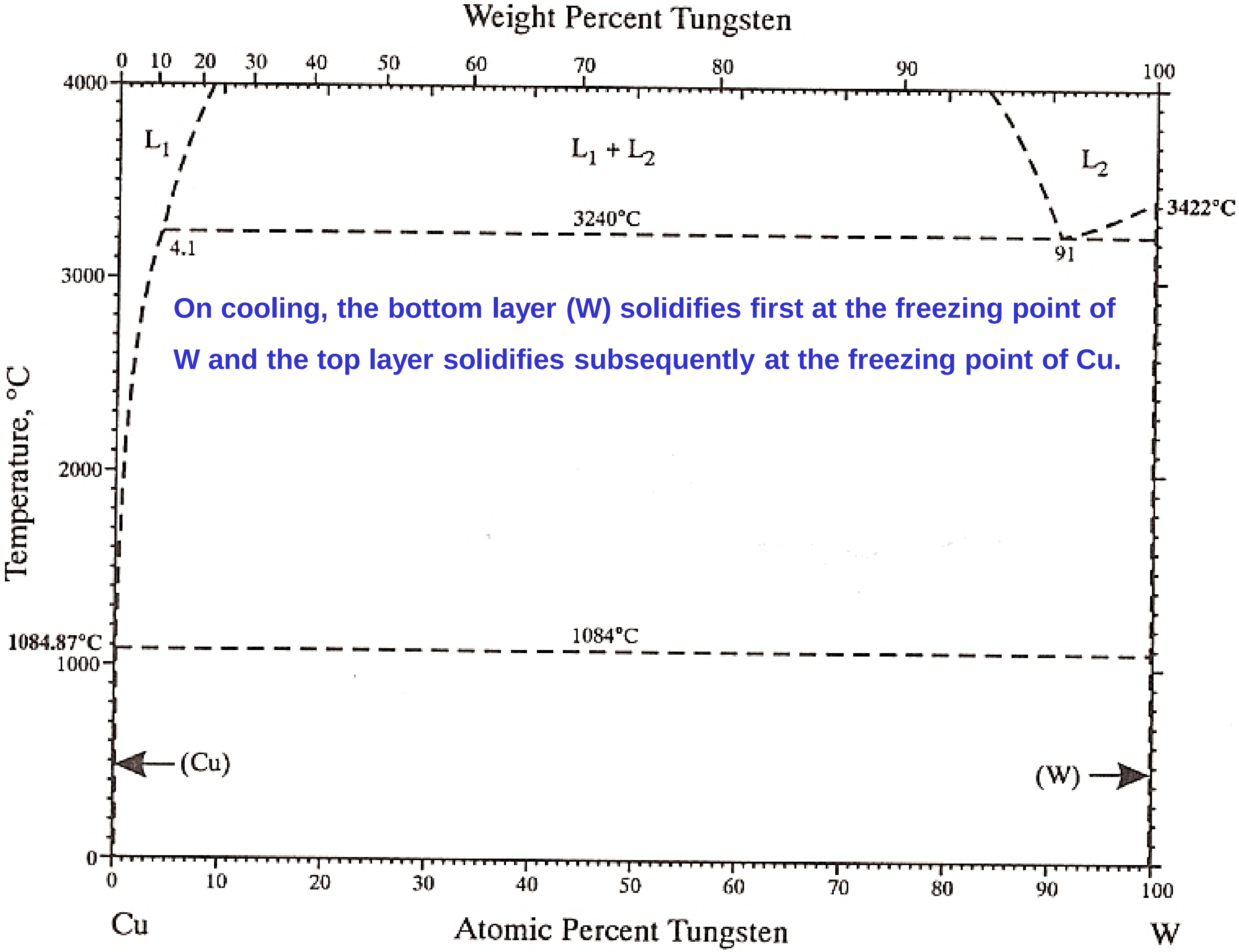


Fig. 86. Limiting form of the monotectic phase diagram.

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

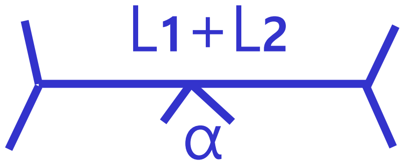
* Limiting forms of monotectic phase diagram



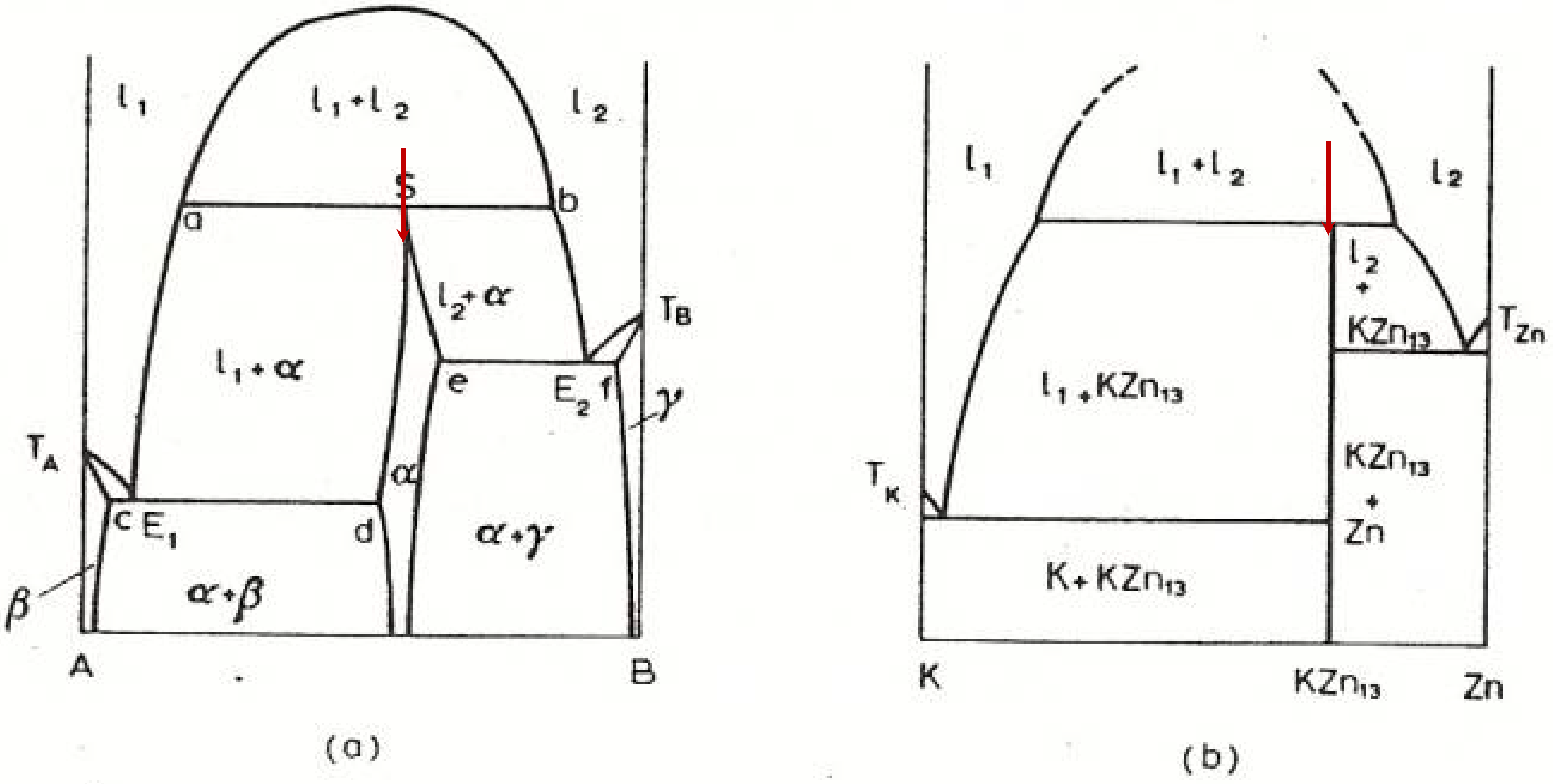
On cooling, the bottom layer (W) solidifies first at the freezing point of W and the top layer solidifies subsequently at the freezing point of Cu.

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



(a) (b)

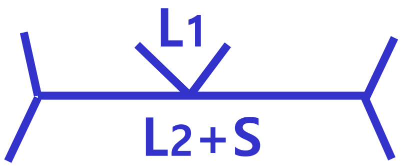
Fig. 87. Syntectic phase diagrams. (a) Schematic; (b) the K–Zn system.

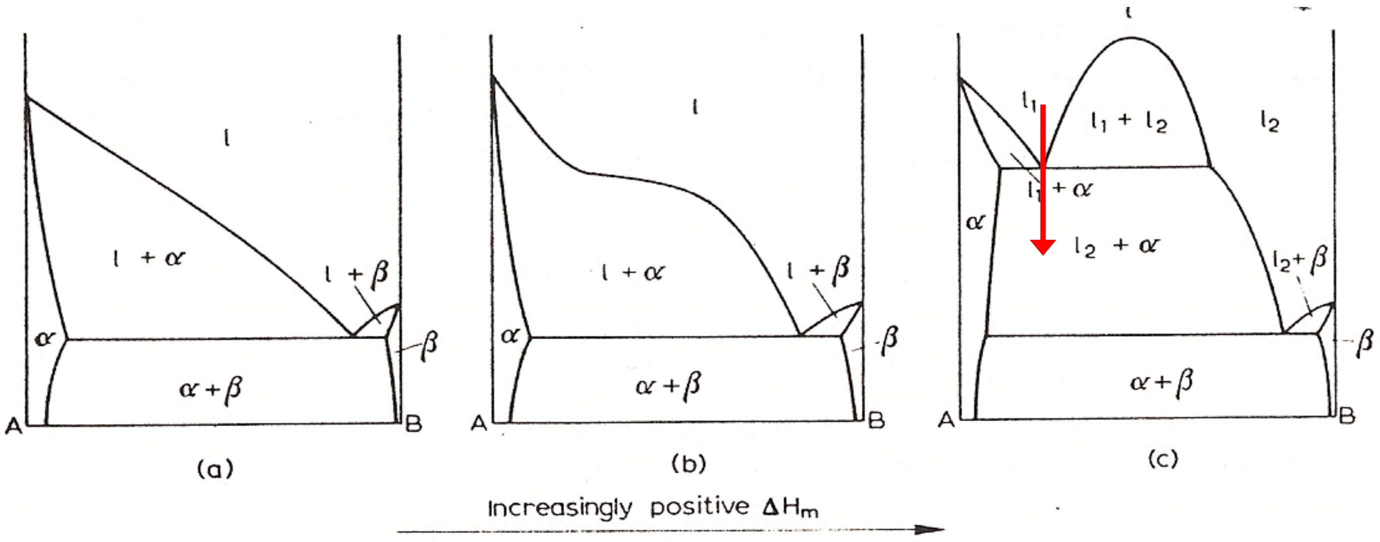
e.g. K-Zn, Na-Zn, K-Pb, Pb-U and Ca-Cd

Contents for today's class

* Monotectic reaction:

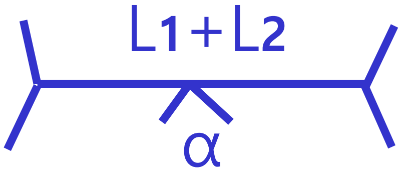
Liquid1 ↔Liquid2+ Solid



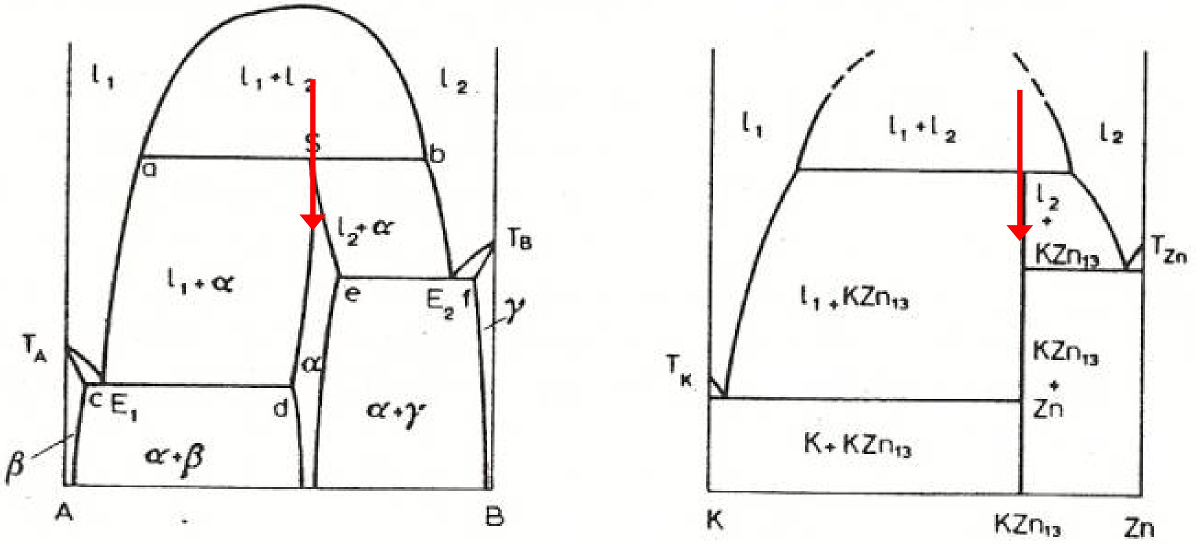


* Syntectic reaction:

Liquid1+Liquid2 ↔ α



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



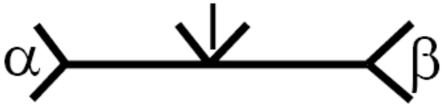
Contents for previous class

Review of Invariant Binary Reactions

Positive ΔH_m

Eutectic

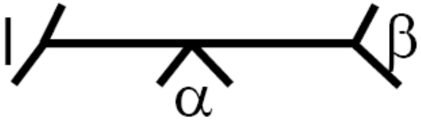
$l \rightleftarrows \alpha + \beta$



Al-Si, Fe-C

Peritectic

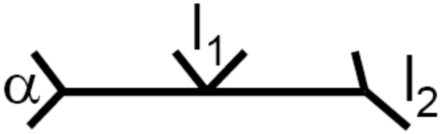
$l + \beta \rightleftarrows \alpha$



Fe-C

Monotectic

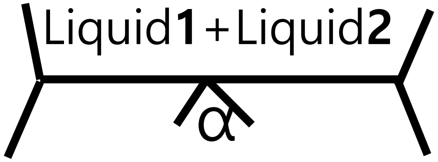
$l_1 \rightleftarrows \alpha + l_2$



Cu-Pb

Synthetic reaction

Liquid**1**+Liquid**2** ↔ α



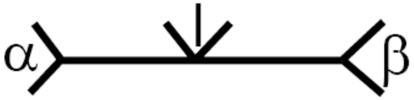
K-Zn, Na-Zn,
K-Pb, Pb-U, Ca-Cd

Review of Invariant Binary Reactions

Eutectic Type

Eutectic

$l \rightleftarrows \alpha + \beta$



Al-Si, Fe-C

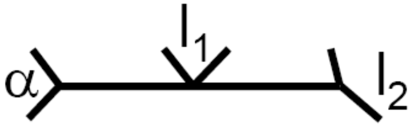
Eutectoid

$\gamma \rightleftarrows \alpha + \beta$

Fe-C

Monotectic

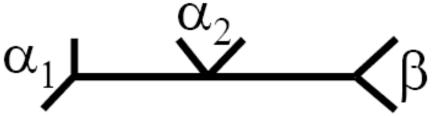
$l_1 \rightleftarrows \alpha + l_2$



Cu-Pb

Monotectoid

$\alpha_2 \rightleftarrows \alpha_1 + \beta$



Al-Zn, Ti-V

On cooling one phase going to two phases

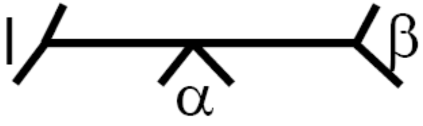
Metatectic reaction: $\beta \leftrightarrow L + \alpha$ **Ex. Co-Os, Co-Re, Co-Ru**

Review of Invariant Binary Reactions

Peritectic Type

Peritectic

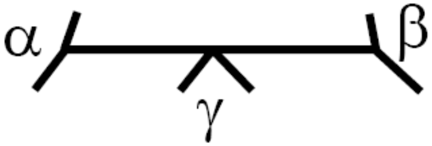
$l + \beta \rightleftarrows \alpha$



Fe-C

Peritectoid

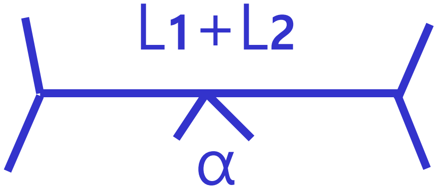
$\alpha + \beta \rightleftarrows \gamma$



Cu-Al

Synthetic reaction

$\text{Liquid}_1 + \text{Liquid}_2 \leftrightarrow \alpha$



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

On cooling two phases going to one phase