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

* Three-Phase Equilibrium : Eutectic Reactions

a) Structural Factor: Hume-Rothery Rules

Empirical rules for substitutional solid-solution

complete solid solution ↔ **limited solid solution**

Similar atomic radii, the same valency and crystal structure

b) The eutectic reaction

c) Limiting forms of eutectic phase diagrams

d) Retrogade solidus curves

Contents for previous class

- Binary phase diagrams

1) Simple Phase Diagrams

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

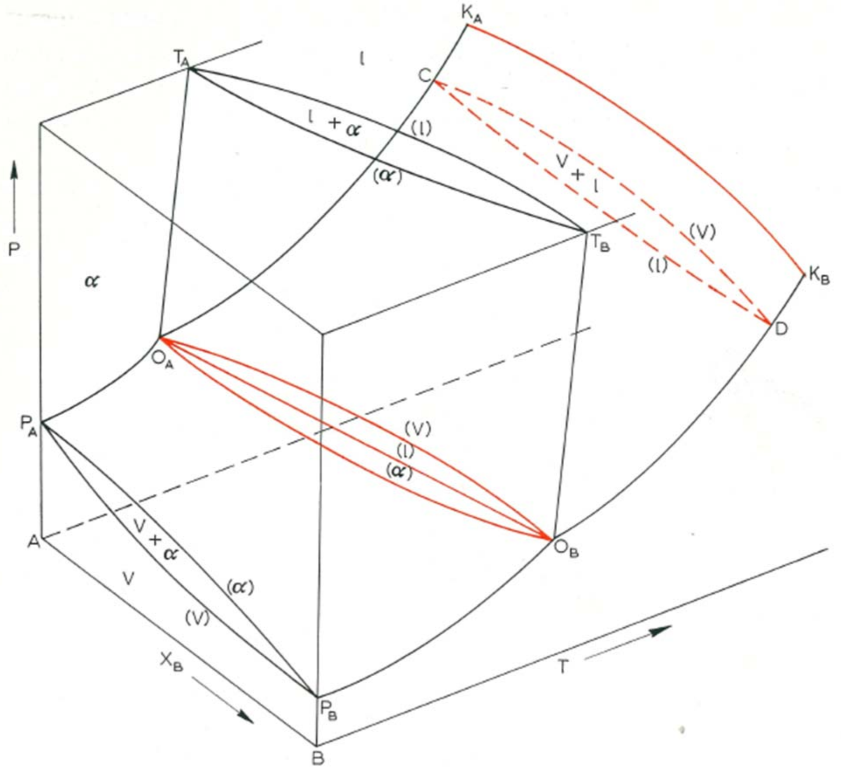
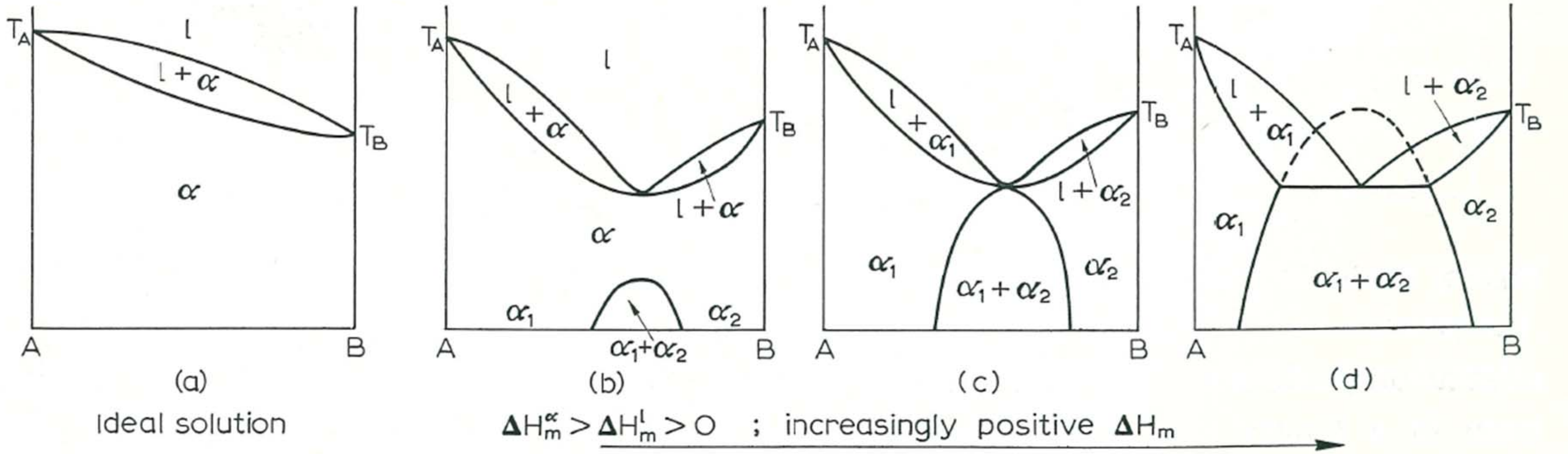


Fig. 35. Pressure–temperature–composition phase diagram for a system with continuous series of solutions

3) Simple Eutectic Systems



(a) Ideal solution (b) (c) (d)

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

By plotting a series of the free energy-composition curves at different temperatures we established the manner in which the phase compositions changes with temperature. In other words, we determined the phase limits or phase boundaries as a function of temperature. A phase diagram is nothing more than a presentation of data on the position of phase boundaries as a function of temperature.

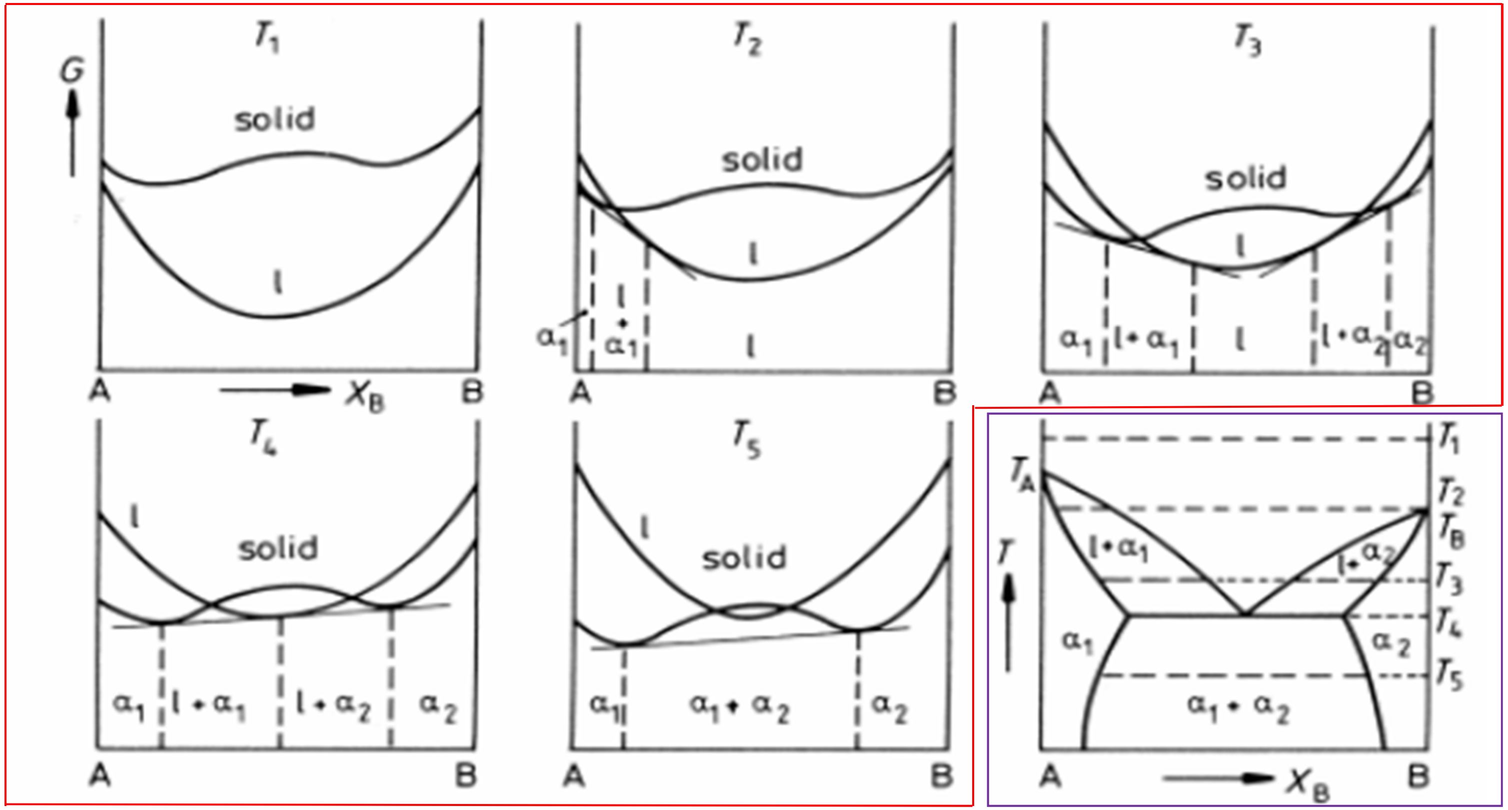
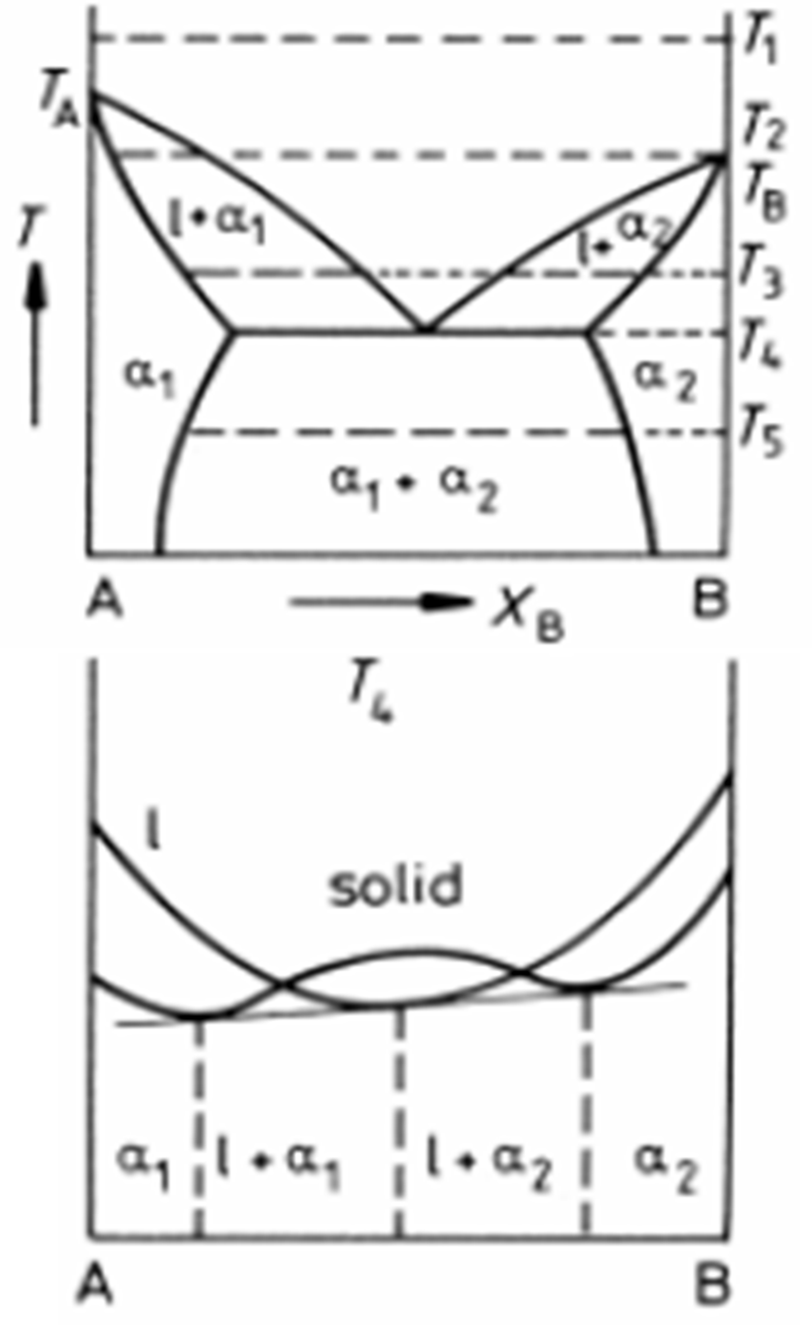
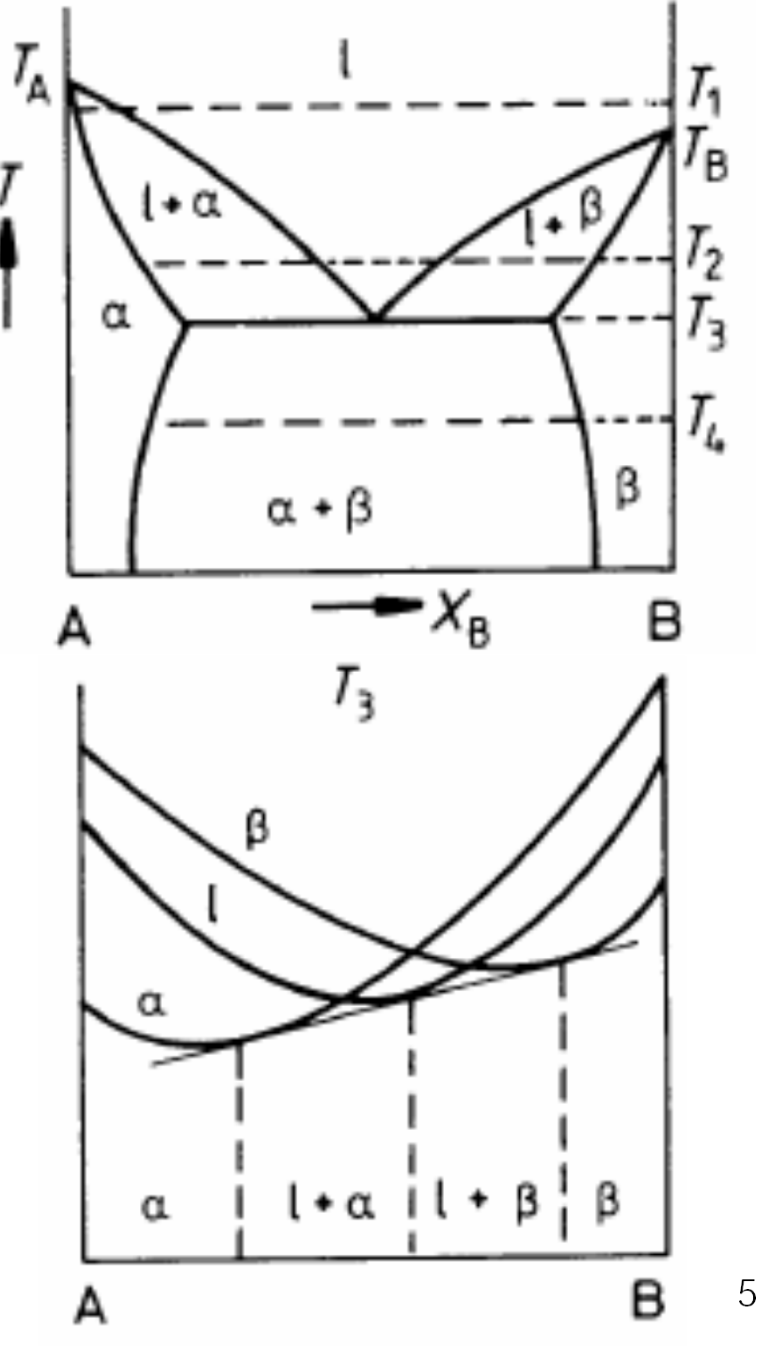


Fig 1.32 The derivation of a eutectic phase diagram where both solid phases have the same crystal structure. (After A.H. Cottrell, *Theoretical Structural Metallurgy*, Edward Arnold, London, 1955,©Sir Alan Cottrell.)

same crystal structure



different crystal structure



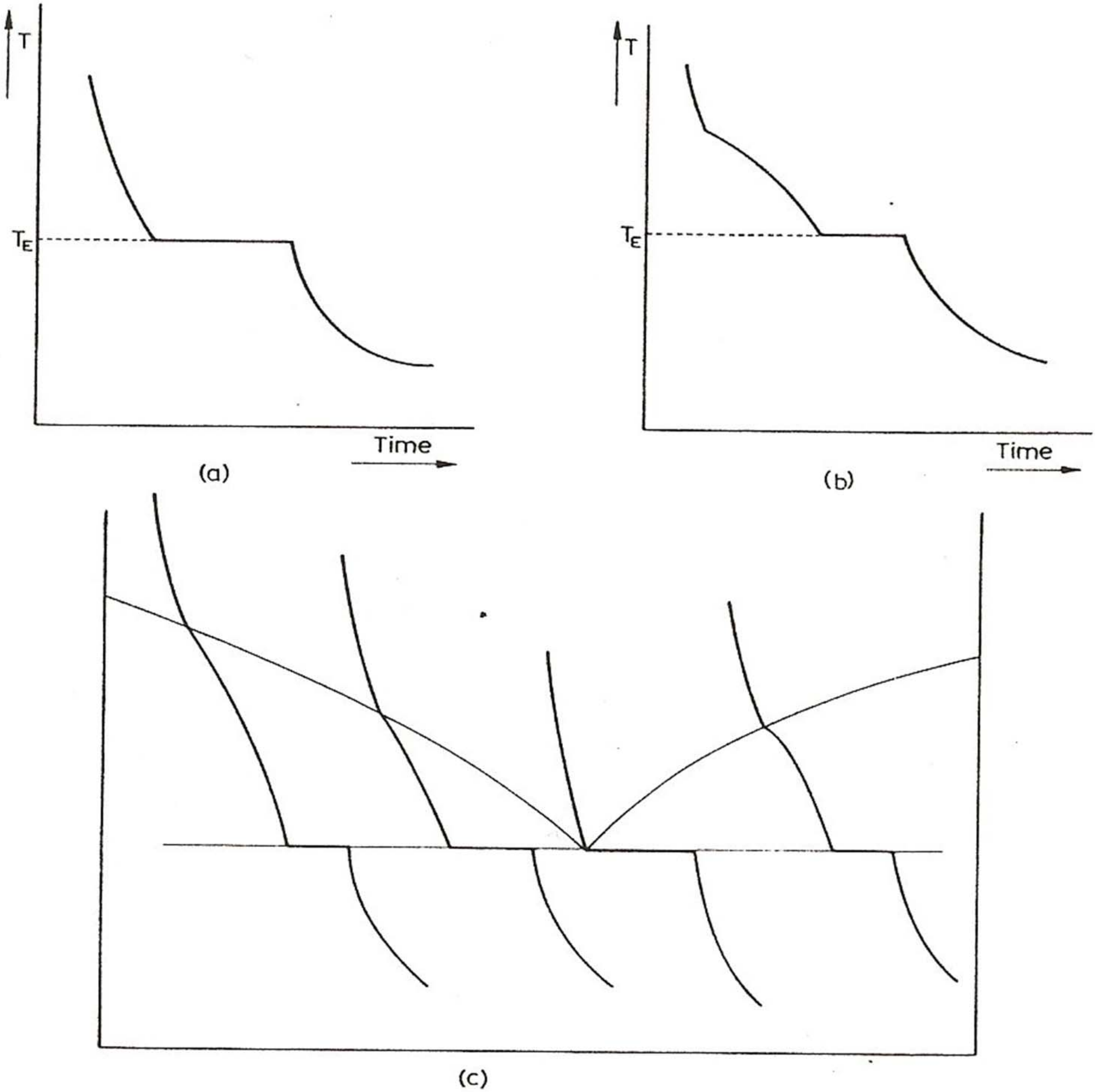


Fig. 48. Cooling curve for (a) the eutectic alloy, (b) hypo-eutectic alloy *N*, and (c) a series of alloys, allowing the determination of the liquidus and eutectic horizontal.

4.2.3. Limiting forms of eutectic phase diagram

1) Complete immiscibility of two metals does not exist.

: **The solubility of one metal in another may be so low** (e.g. Cu in Ge <10^{-7} at%.) **that it is difficult to detect experimentally, but there will always be a measure of solubility.**

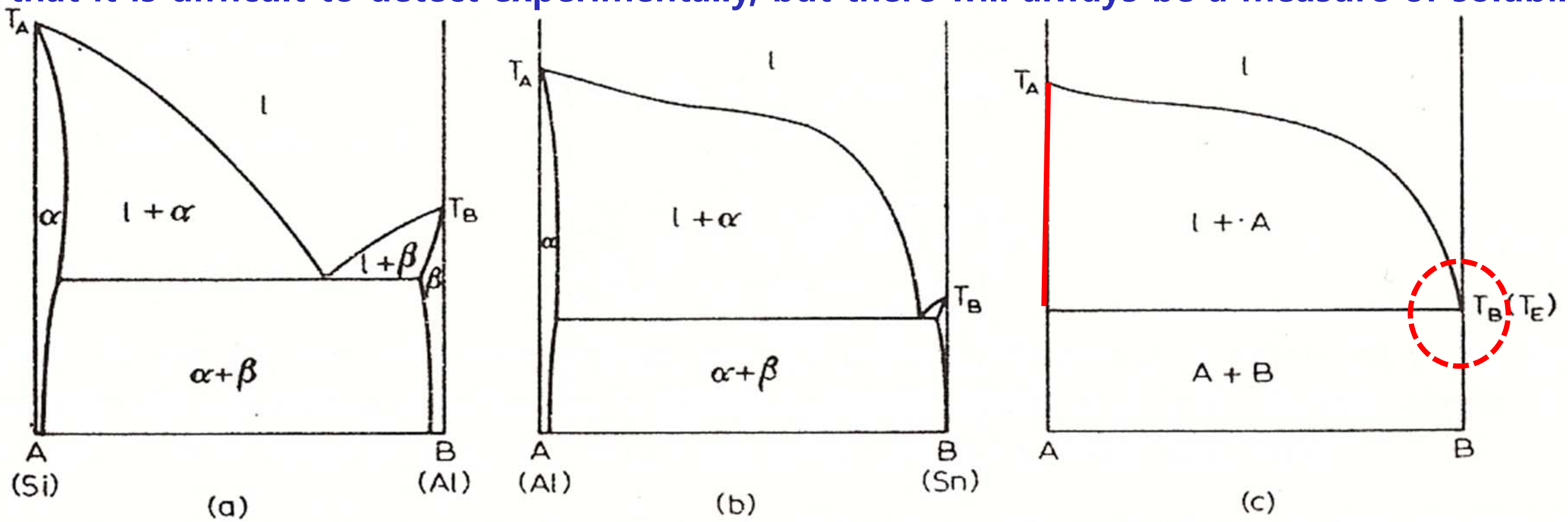


Fig. 53. Evolution of the limiting form of a binary eutectic phase diagram.

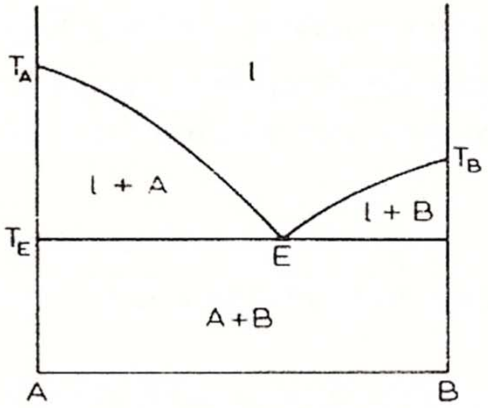


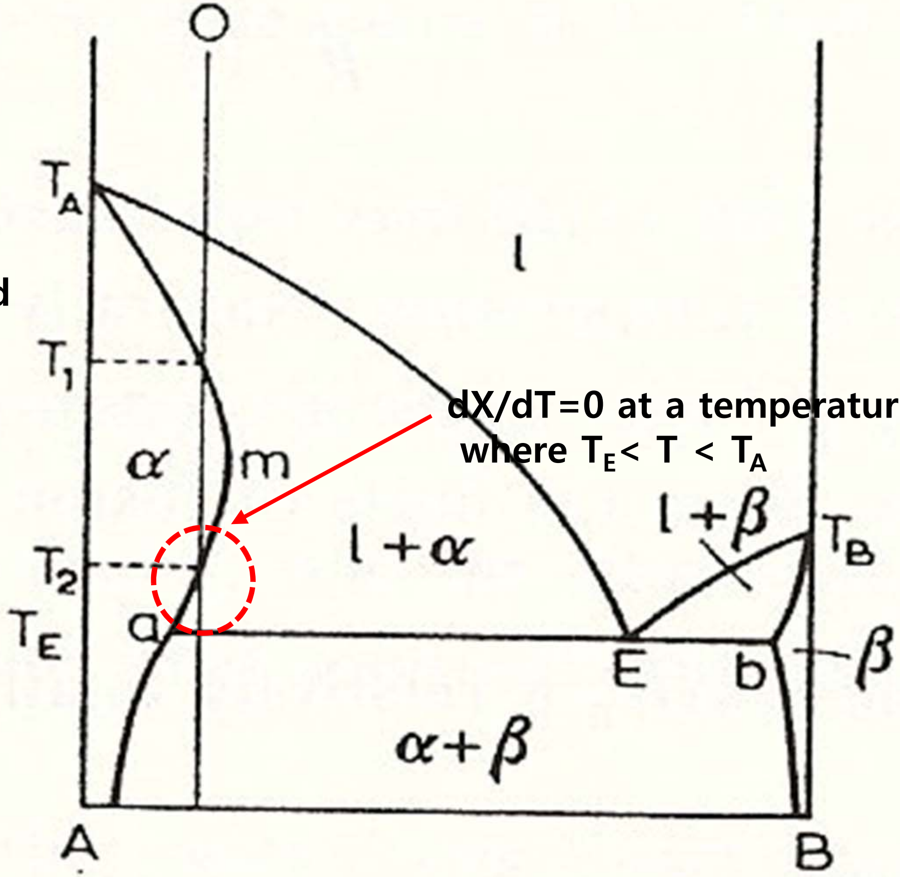
Fig. 54. Impossible form of a binary eutectic phase diagram.

4.2.5. 2) Retrograde solidus curves

: A maximum solubility of the solute at a temperature between the melting point of the solvent and an invariant reaction isothermal

Solidus curve in the systems with low solubility
Ex) semiconductor research using Ge and Si as solvent metals

A high value of ΔH_B^S (or a large difference in the melting points of the components) is associate with a significant difference in atomic radii for A and B, which can lead to a large strain energy contribution to the heat of solutions.



dX/dT=0 at a temperature T, where $T_E < T < T_A$

Fig. 57. Partial re-melting associated with retrograde solubility.

Intensive Homework 2: Understanding of retrograde solidus curves from a thermodynamic standpoint

4.2.5. Disposition of phase boundaries at the eutectic horizontal

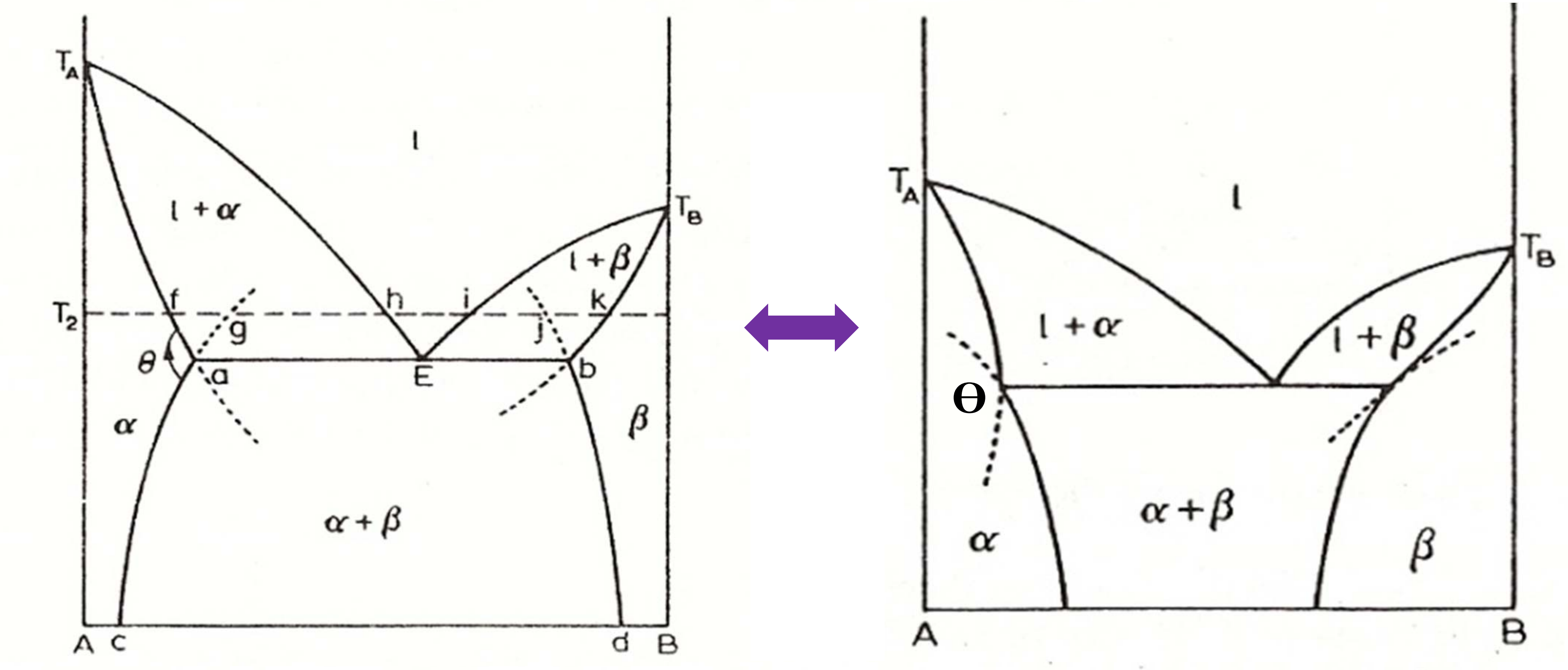


Fig. 60. Impossible dispositions of phase boundaries at a eutectic horizontal.

3) Θ between solidus and solubility curves must be less than 180°.

This is a general rule applicable to all curves which meet at an invariant reaction horizontal in a binary diagram, whether they be eutectic, peritectics, eutectoid, etc., horizontals.

Contents for today's 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

- Gibbs Phase Rule

4.3. Three-Phase Equilibrium : Peritectic Reactions

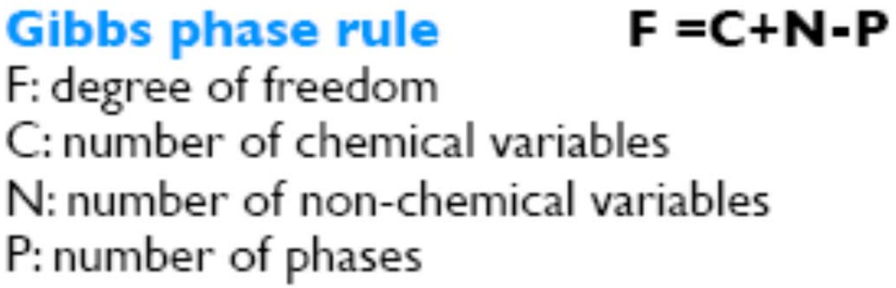
- Eutectoid reaction

- Peritectic reaction
  - Formation of intermediate phases by peritectic reaction
  - Non-stoichiometeric compounds
- Congruent transformations

Equilibria in alloy systems: Phase Rule & Free E-composition curves

The Gibbs Phase Rule: quantitative data

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

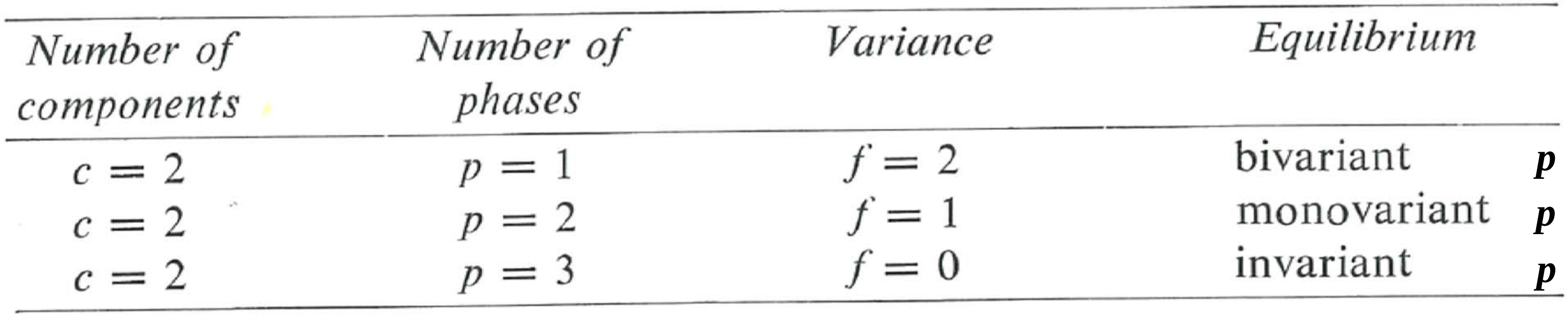
In general, Gibbs' rule then follows, as:

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

From Wikipedia, the free encyclopedia

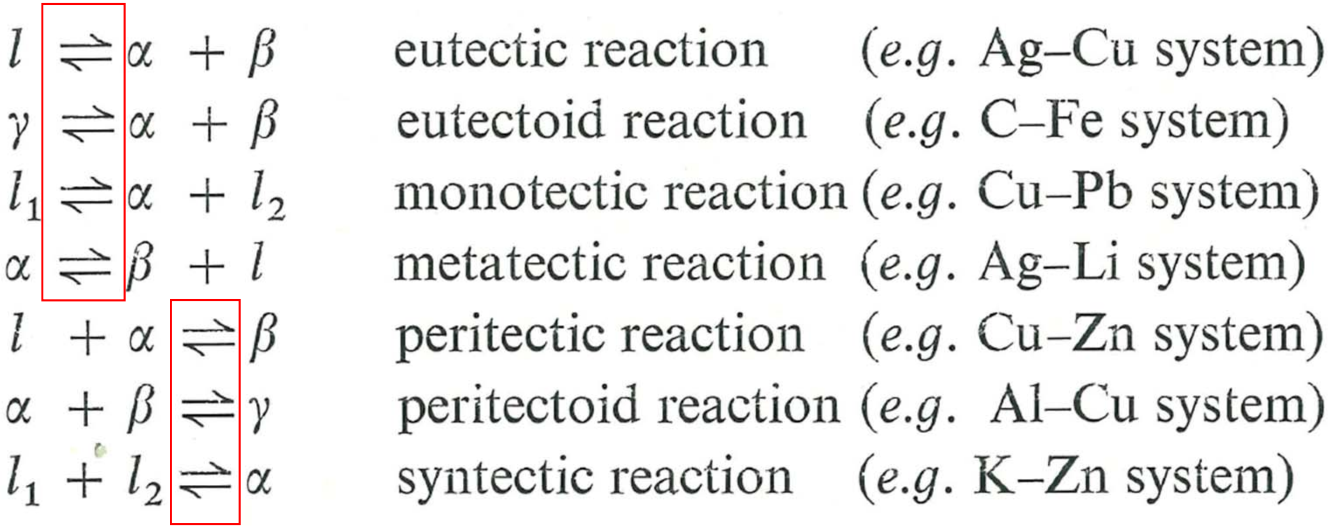
According to the condensed Phase Rule, $f = c - p + 1$

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.



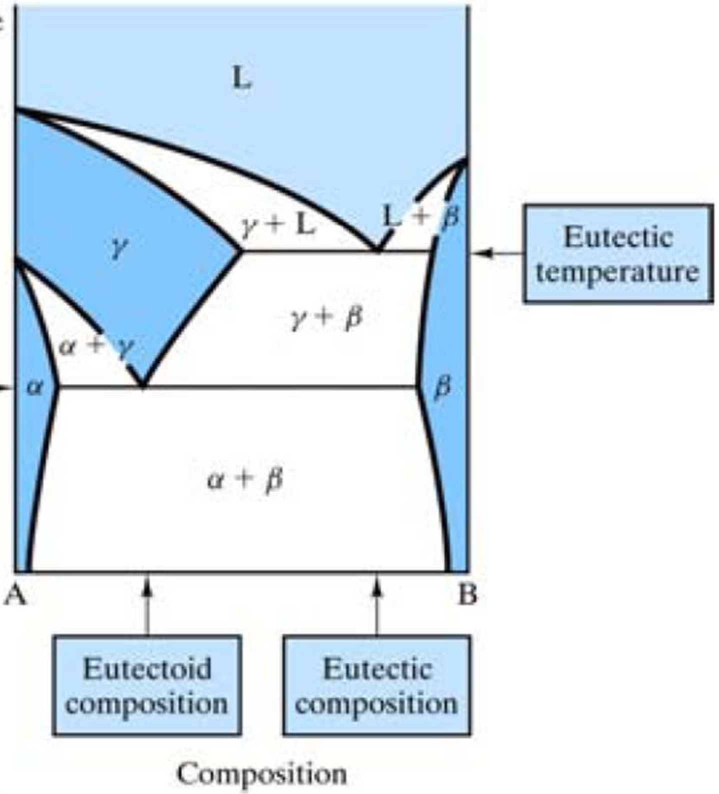
$l \rightleftharpoons \alpha + \beta$	eutectic reaction	(*e.g.* Ag–Cu system)
$\gamma \rightleftharpoons \alpha + \beta$	eutectoid reaction	(*e.g.* C–Fe system)
$l_1 \rightleftharpoons \alpha + l_2$	monotectic reaction	(*e.g.* Cu–Pb system)
$\alpha \rightleftharpoons \beta + l$	metatectic reaction	(*e.g.* 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)

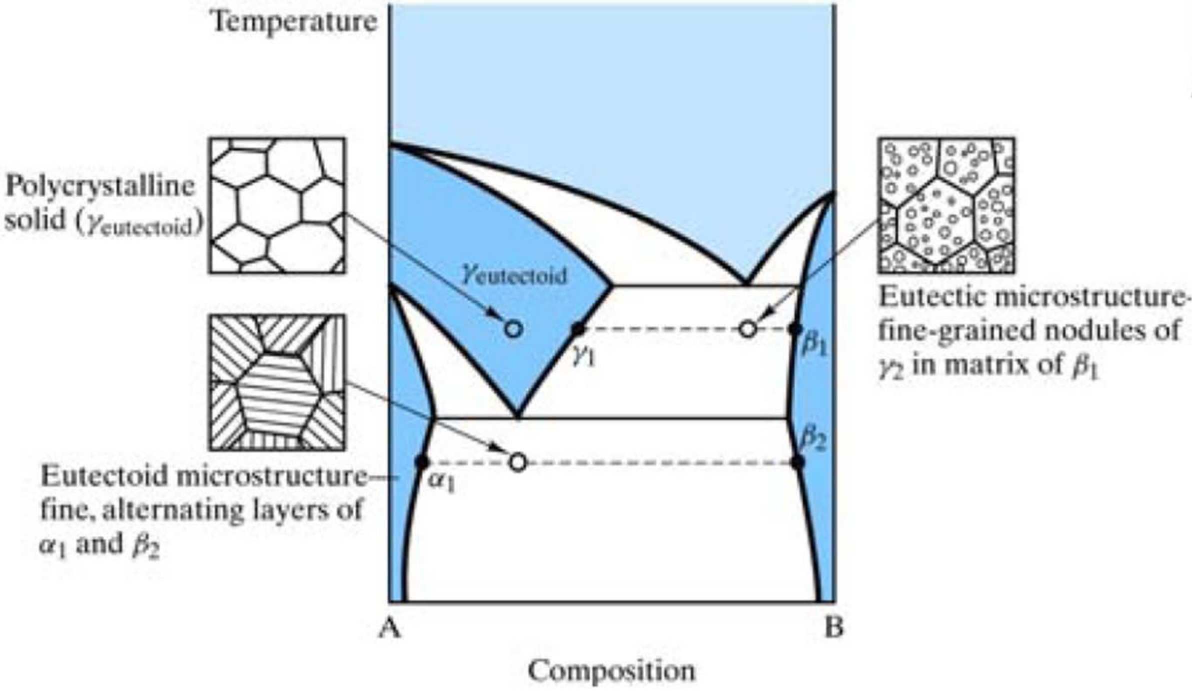
Invariant reactions involving liquid phases have a name ending in *–tectic* whilst those occurring completely in the solid state end in *–tectoid*.

Eutectoid reaction

Eutectoid reaction :

$$\gamma_{\text{eutectoid}} \underset{T_{eu.}}{\overset{\textit{cooling}}{\rightleftarrows}} \alpha + \beta$$





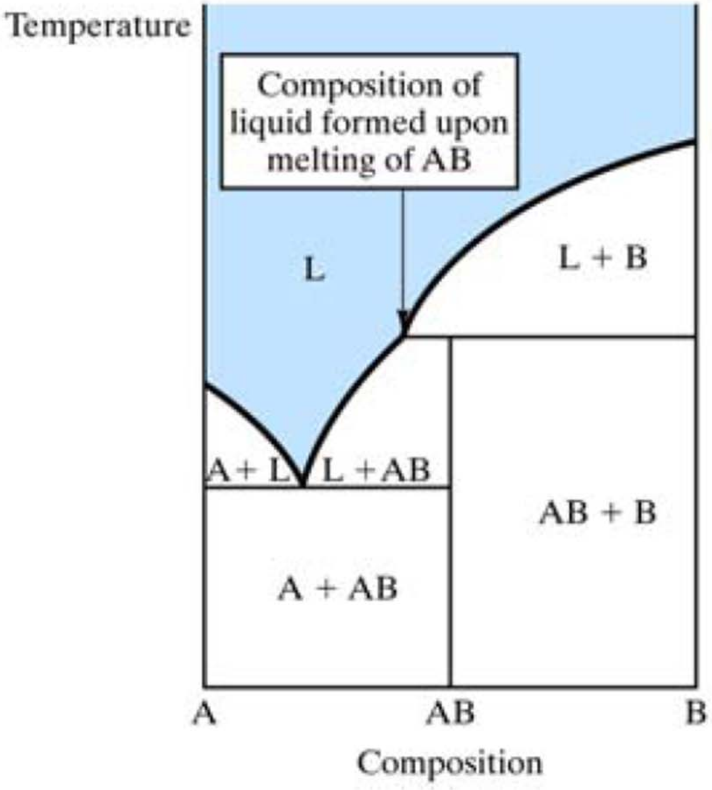
Peritectic reaction

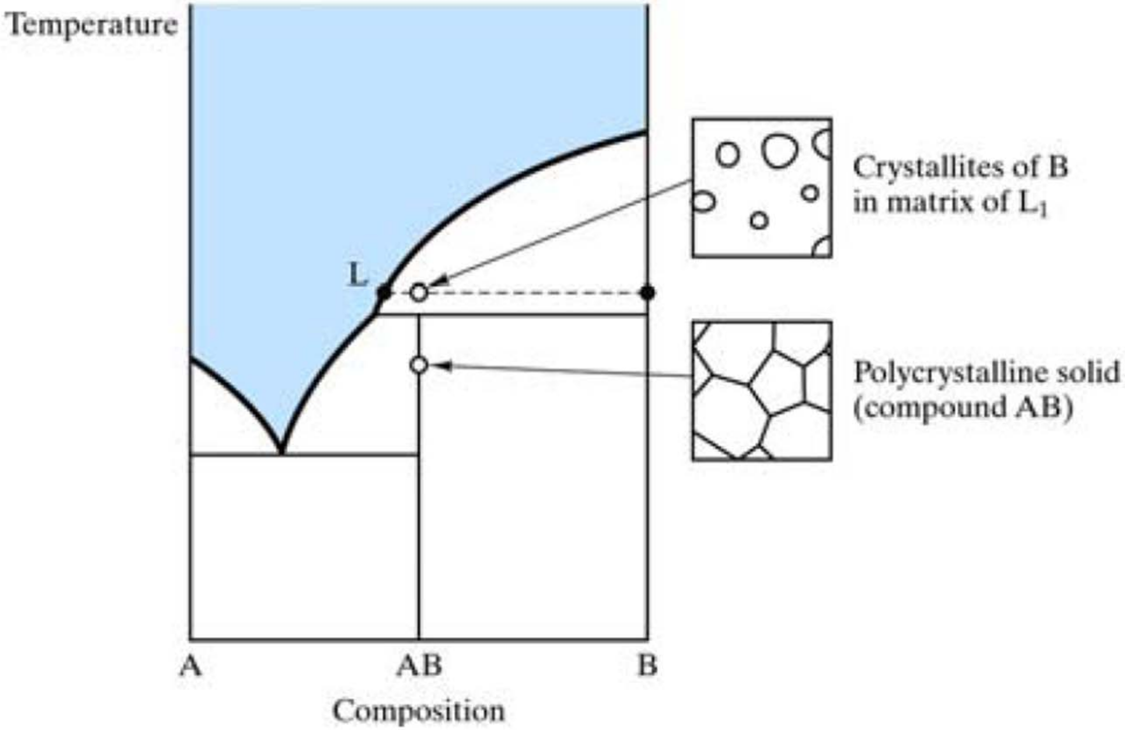
Peritectic reaction : AB $\underset{}{\overset{heating}{\rightleftarrows}}$ L + B

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

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

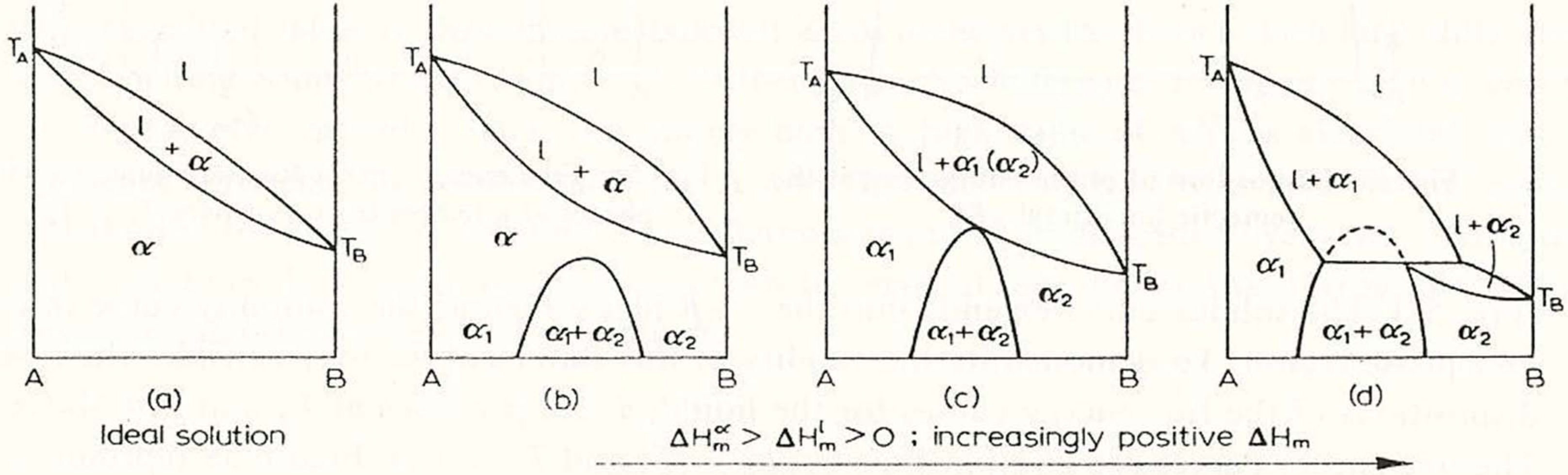


Fig. 61. Effect of increasingly positive departure from ideality in changing the phase diagram from a continuous series of solutions to a peritectic-type.

Eutectic reaction

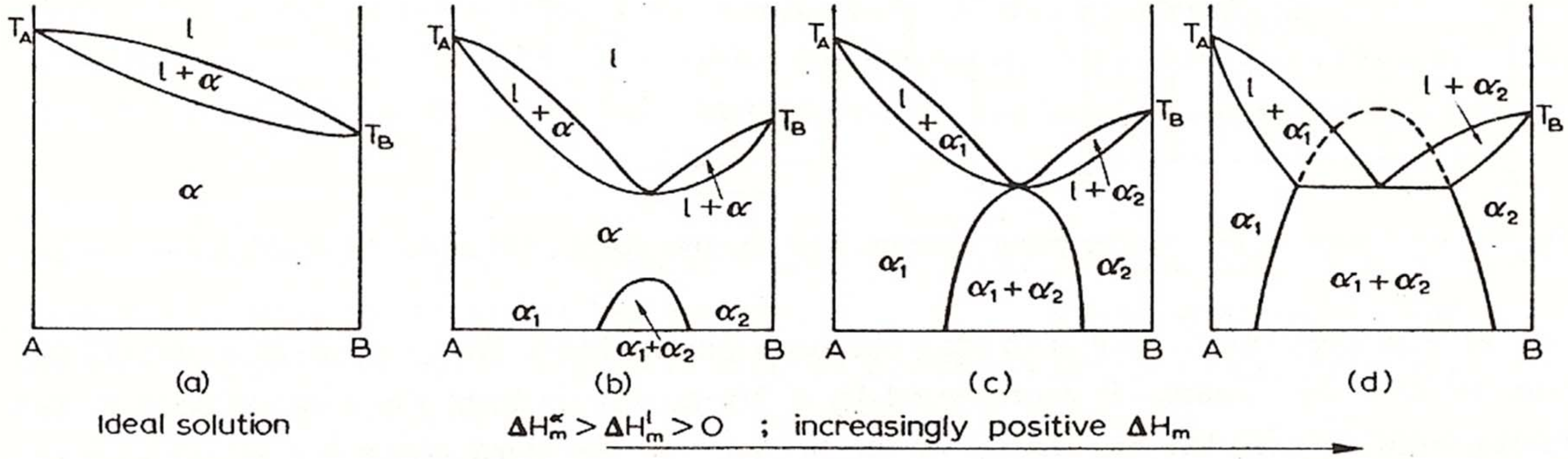


Fig. 43. Effect of increasingly positive departure from ideality in changing the phase diagram for a continuous series of solutions to a eutectic-type.

Eutectic: L→α+β **Peritectic: L+α → β**

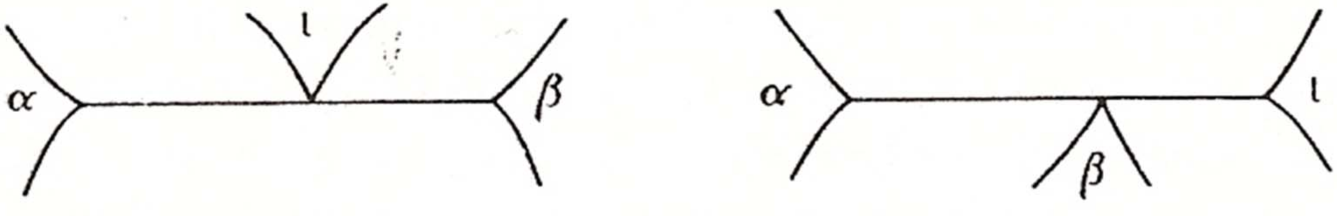


Fig. 63. Relationship between eutectic and peritectic reactions.

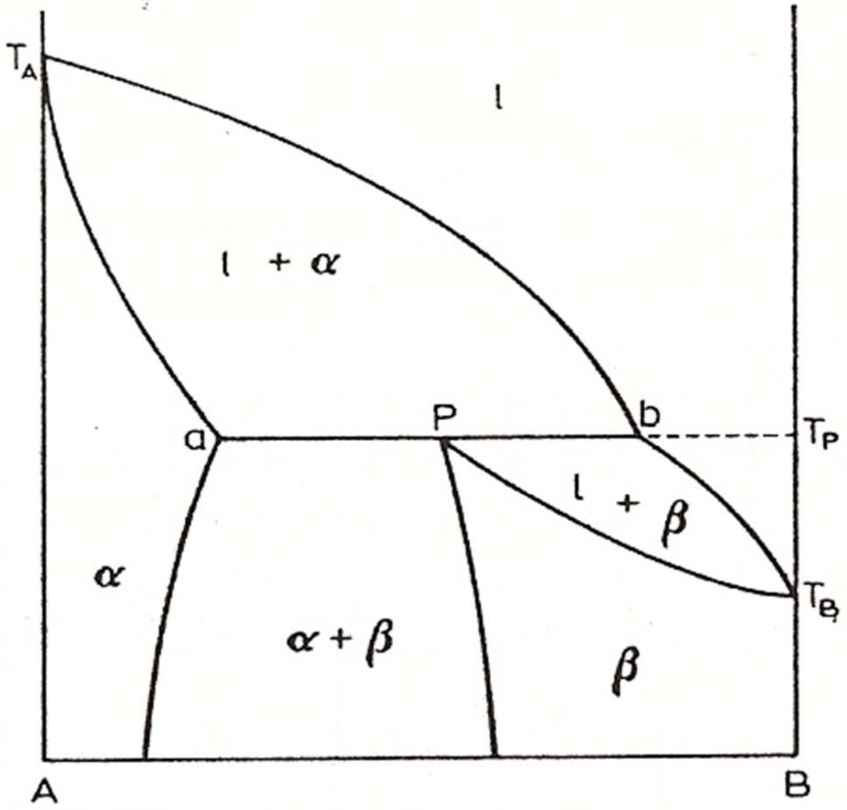


Fig. 64. Binary peritectic phase diagram.

Peritectic reaction

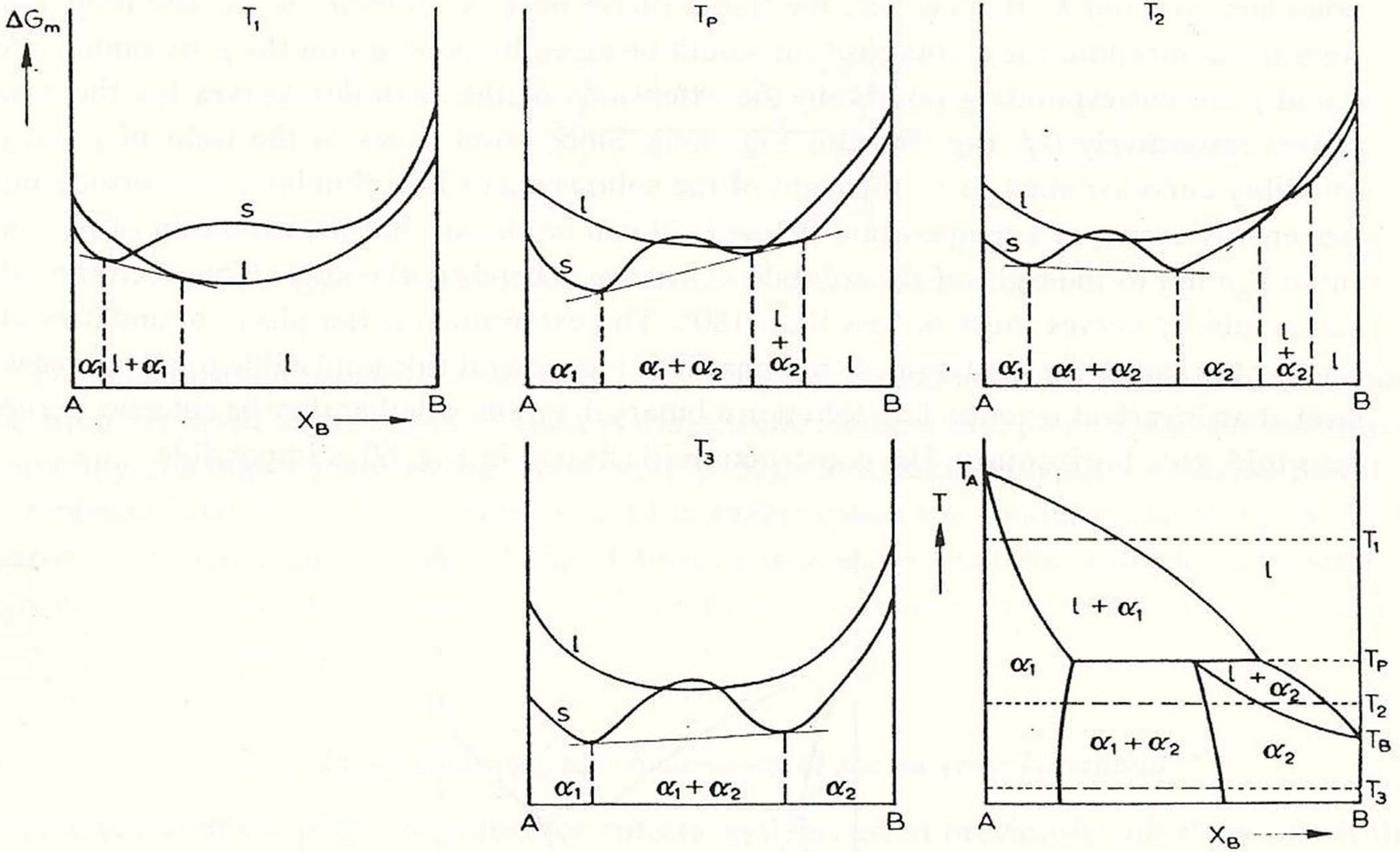


Fig. 62. Derivation of the peritectic phase diagram from the free energy curves for the liquid and solid phases.

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.**

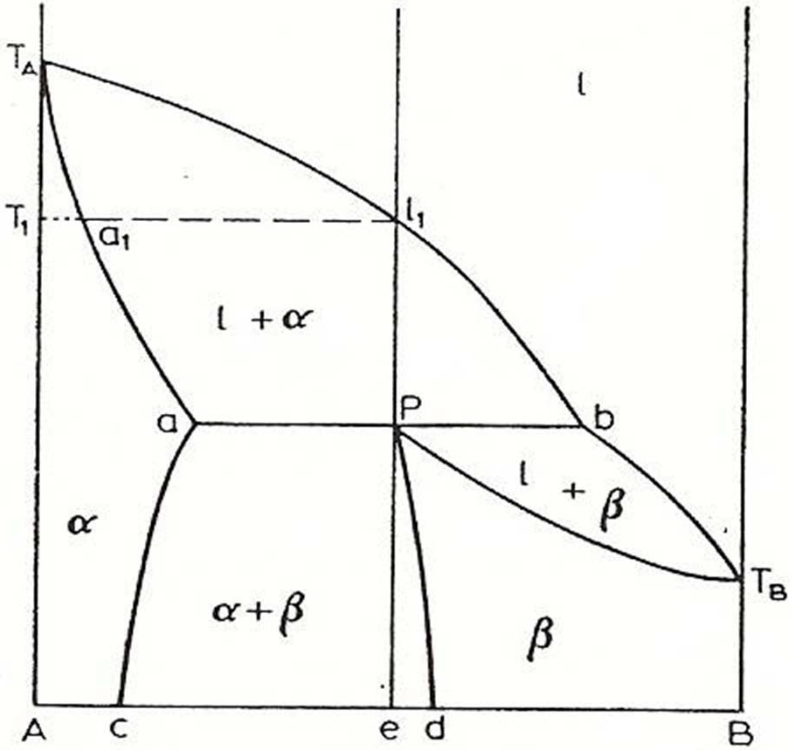


Fig. 65. Freezing of the peritectic alloy *P*.

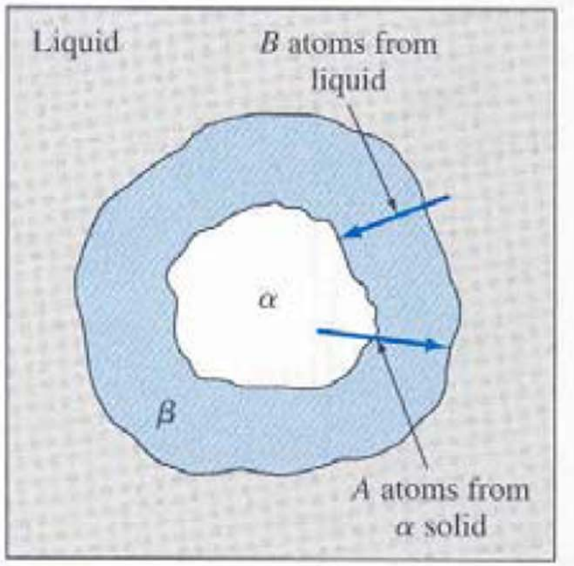


Figure 8.19

Peritectic solidification

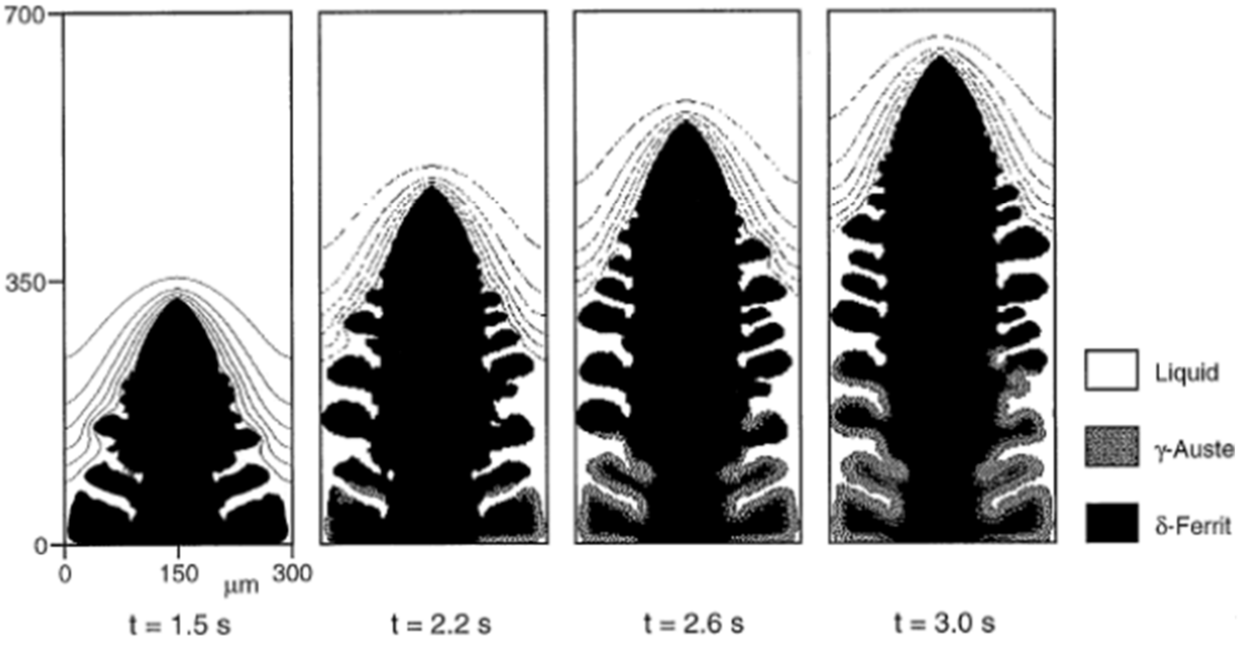
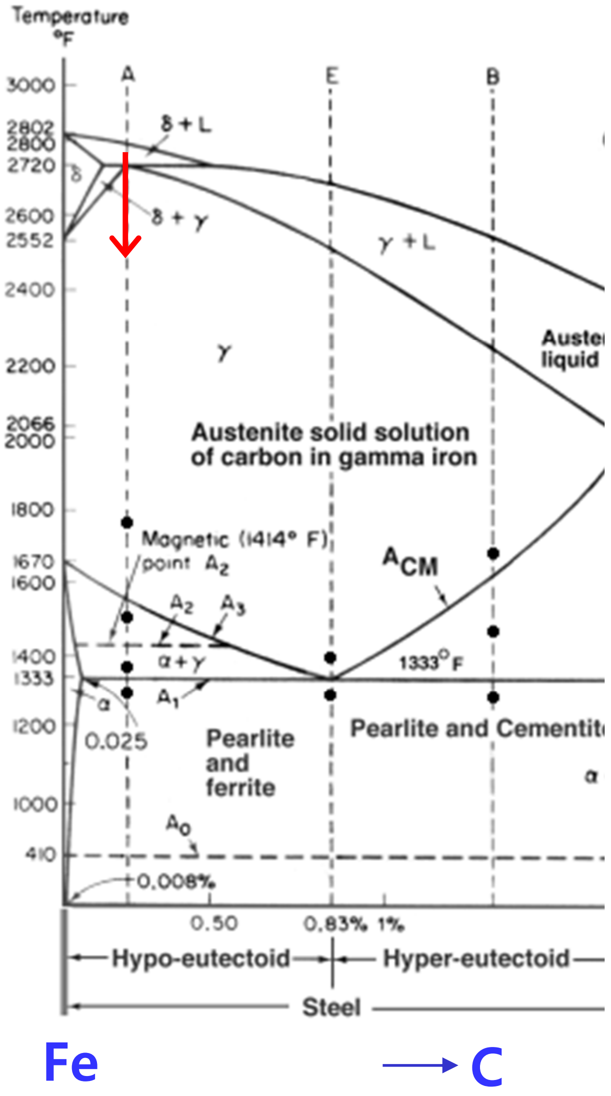


Figure 7. Phase-field simulation of peritectic reaction [3].



Peritectic solidification

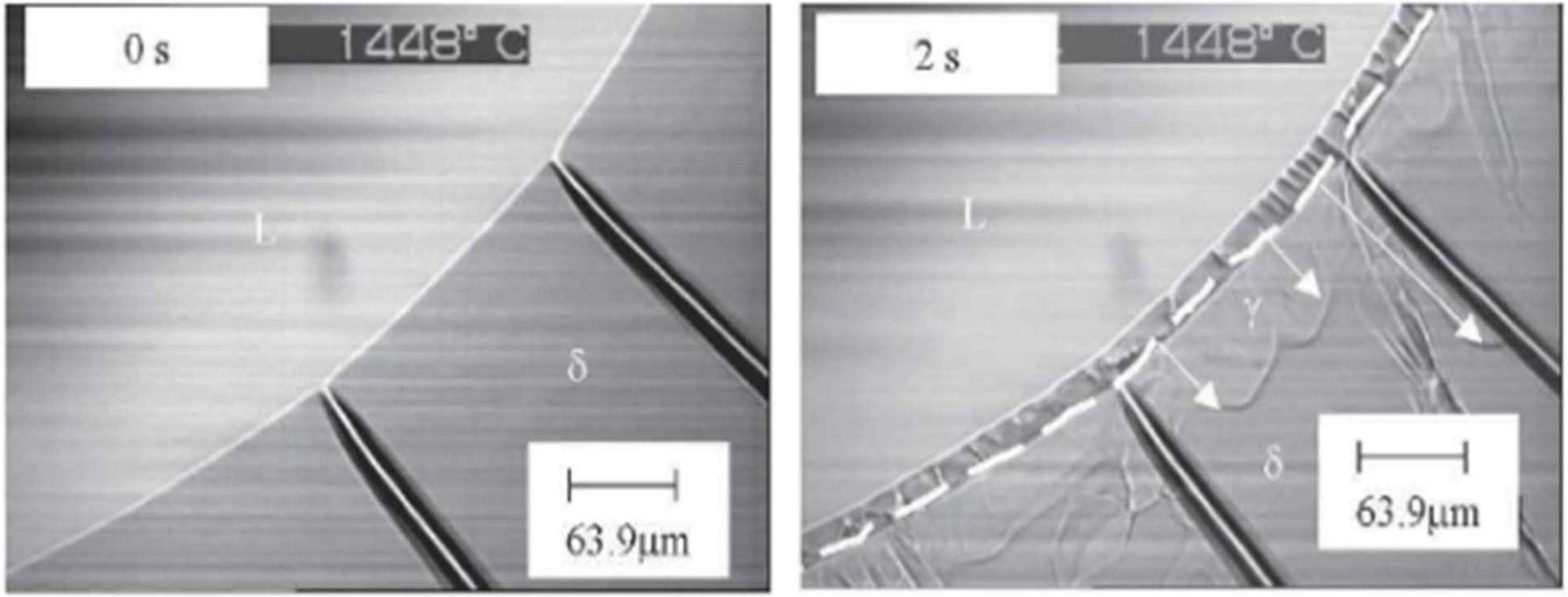
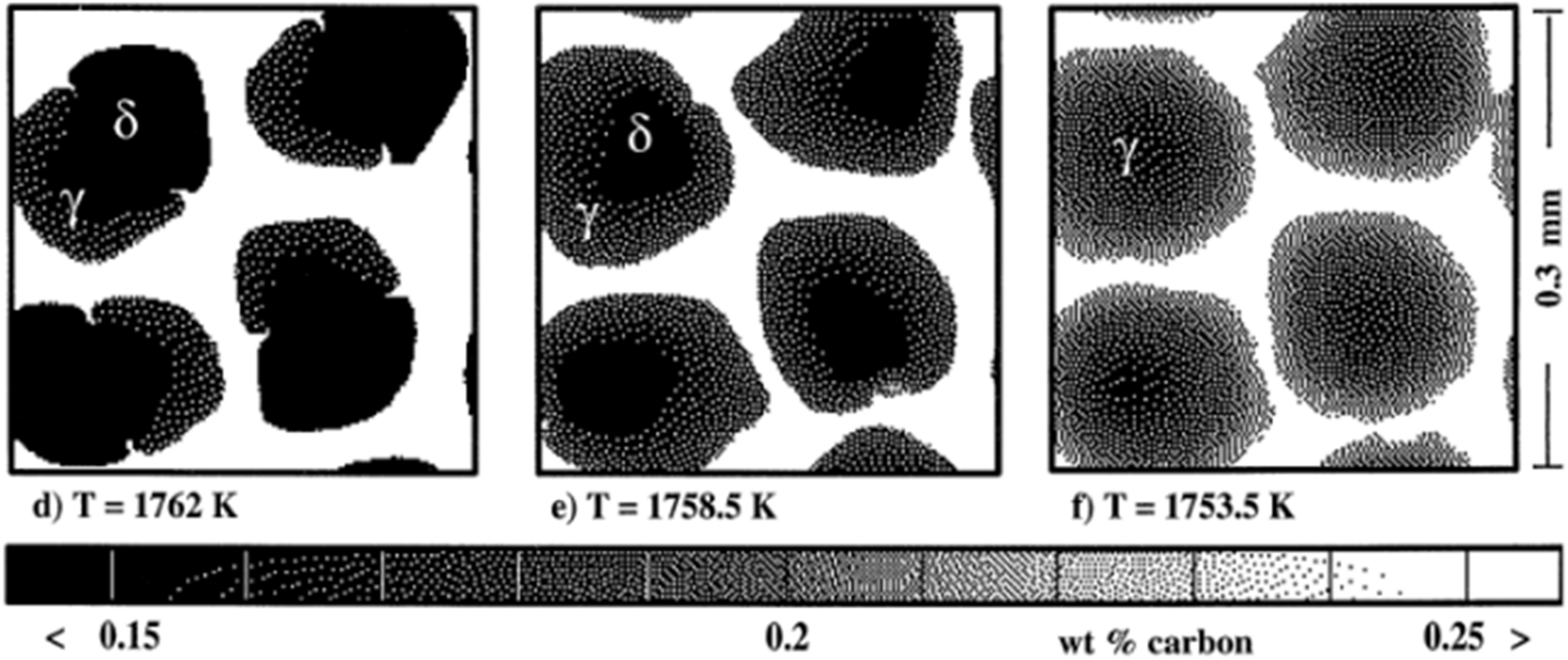


Figure 5. Peritectic reaction in Fe-0.18 pct C alloy: cooling rate =10 K/min [2].

Peritectic solidification


d) T = 1762 K

e) T = 1758.5 K

f) T = 1753.5 K

Figure 6. Phase-field simulation of peritectic reaction [3].

Peritectic Alloy System

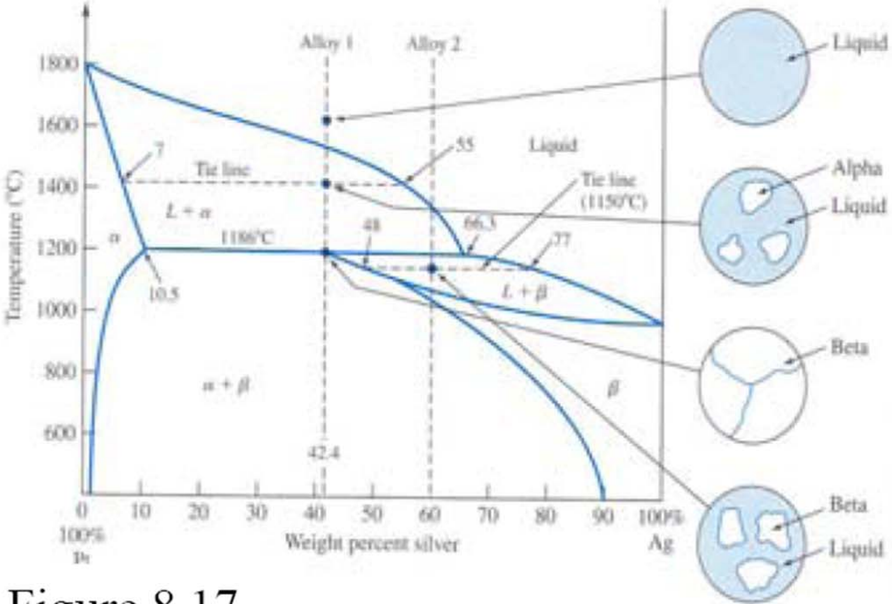


Figure 8.17

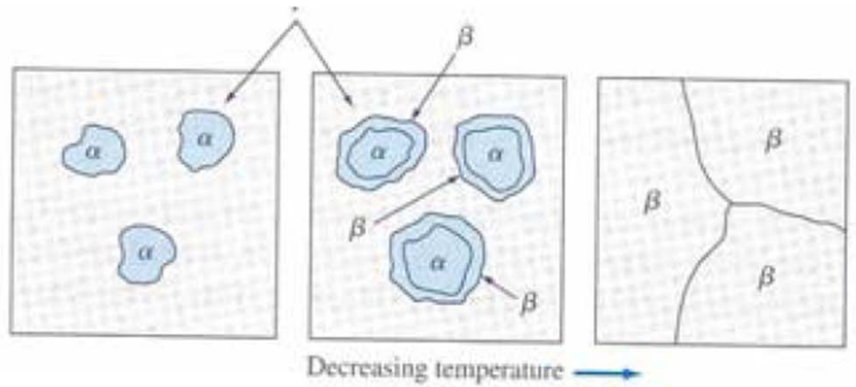


Figure 8.18

- **At 42.4 % Ag & 1400^{0}C**

Phases present	**Liquid**	**Alpha**
Composition	**55% Ag**	**7%Ag**
Amount of Phases	$\frac{42.4-7}{55-7}$ **= 74%**	$\frac{55-42.4}{55-7}$ **= 26%**

- **At 42.4% Ag and 1186^{0}C + ΔT**

Phases present	**Liquid**	**Alpha**
Composition	**66.3% Ag**	**10.5%Ag**
Amount of Phases	$\frac{42.4-10.5}{66.3-10.5}$ **= 57%**	$\frac{66.3-42.4}{66.3-10.5}$ **=43%**
Phases present	**Liquid**	**Alpha**

- **At 42.4% Ag and 1186^{0}C – ΔT**

Phase Present	**Beta only**
Composition	**42.4% Ag**
Amount of Phase	**100%**

4.3.4. Formation of intermediate phases by peritectic reaction

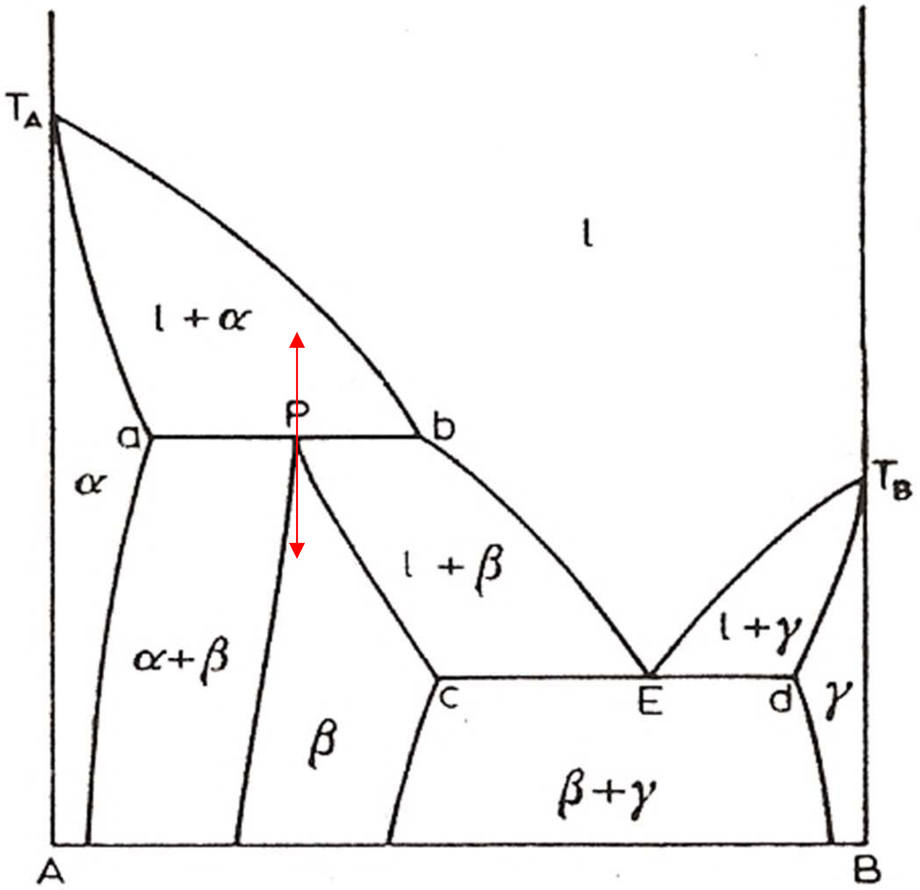


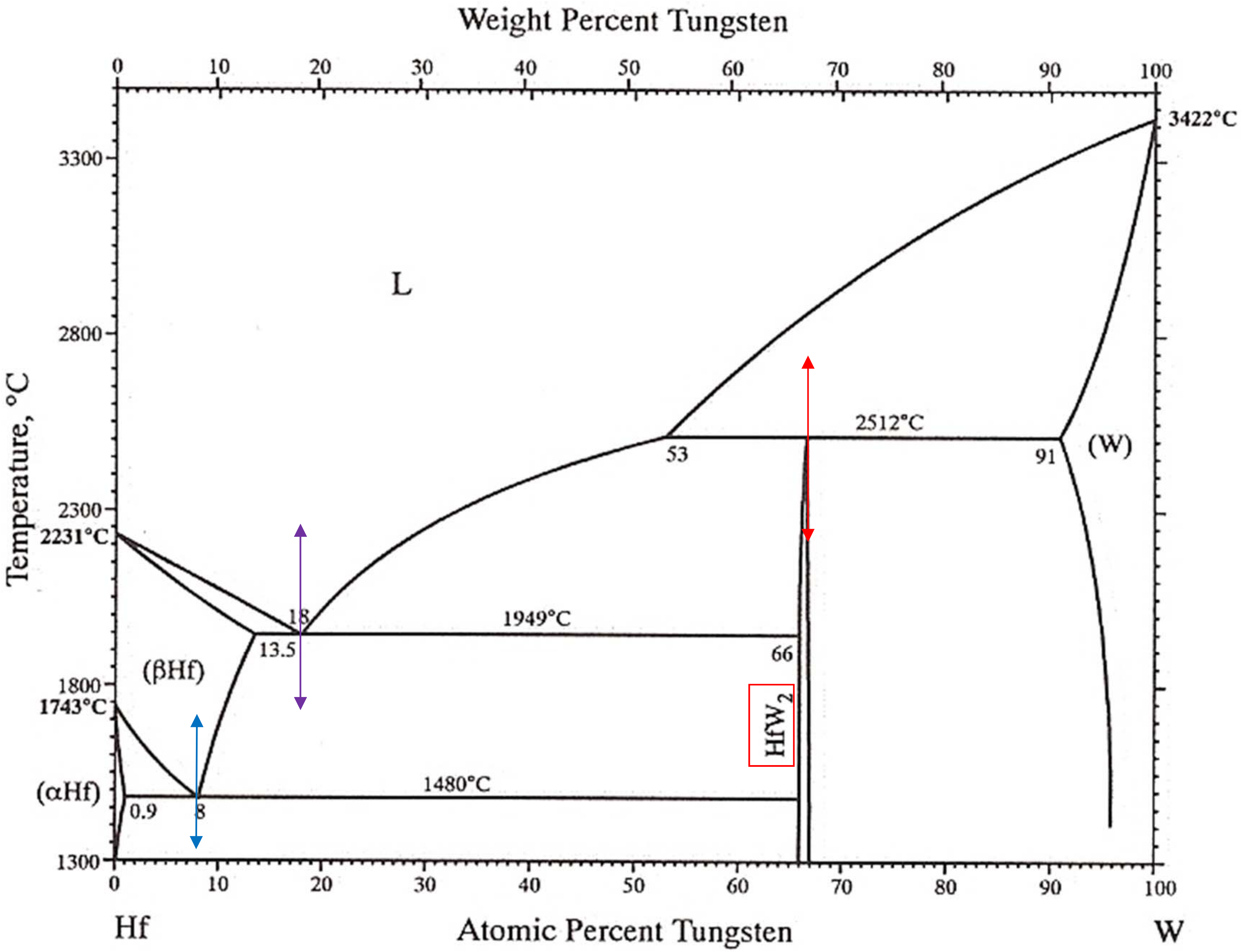
Fig. 68. Formation of an intermediate phase, β, by peritectic reaction.

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)

e.g. In the Hf-W system,

the formation of an intermediate phase, HfW_2 by peritectic reaction



1.3 Binary Solutions

Intermediate Phase_"different crystal structure as either of the pure component"

3 main factors

determining the structure of Intermediate phase ?

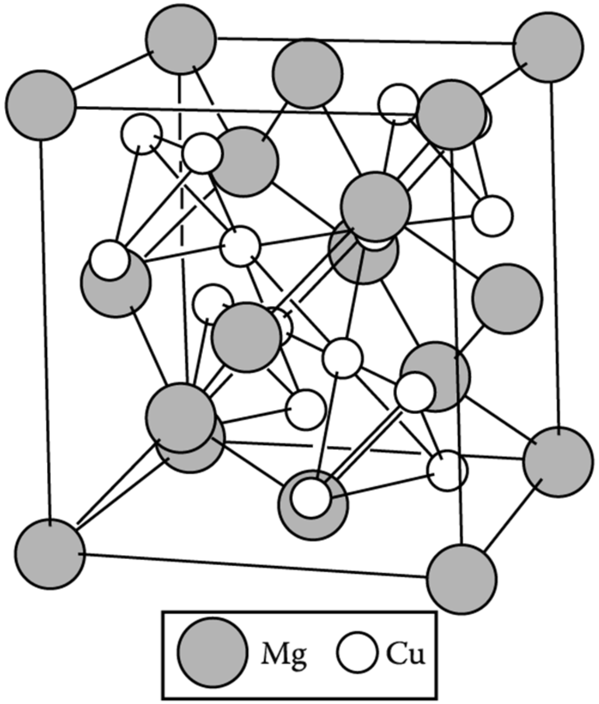
1) Relative atomic size

- **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



$MgCu_2$ (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

* Intermediate phases

(1) 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

(2) 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

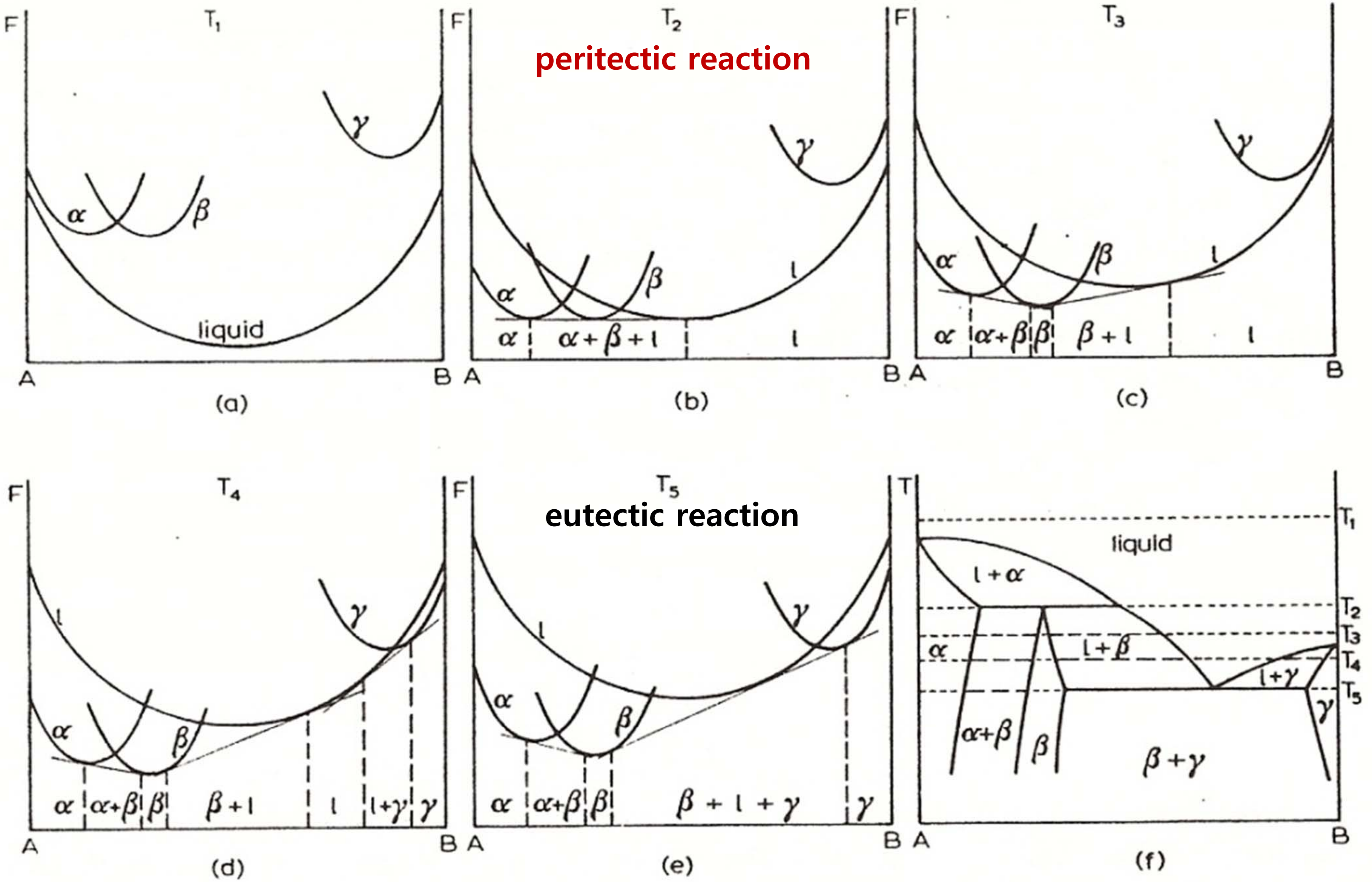
(3) Electron compounds ~ similar electrochemical properties and a favorable size-factor occurs at one of three valency electron-to –atom ratios.

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

4.3.4. Formation of intermediate phases by peritectic reaction



peritectic reaction

eutectic reaction

Fig. 69. Derivation of the phase diagram (Fig. 68) from the free energy curves of the liquid, α, β and γ phases. (After A. H. COTTRELL; courtesy Edward Arnold.)

4.3.4. Formation of intermediate phases by peritectic reaction

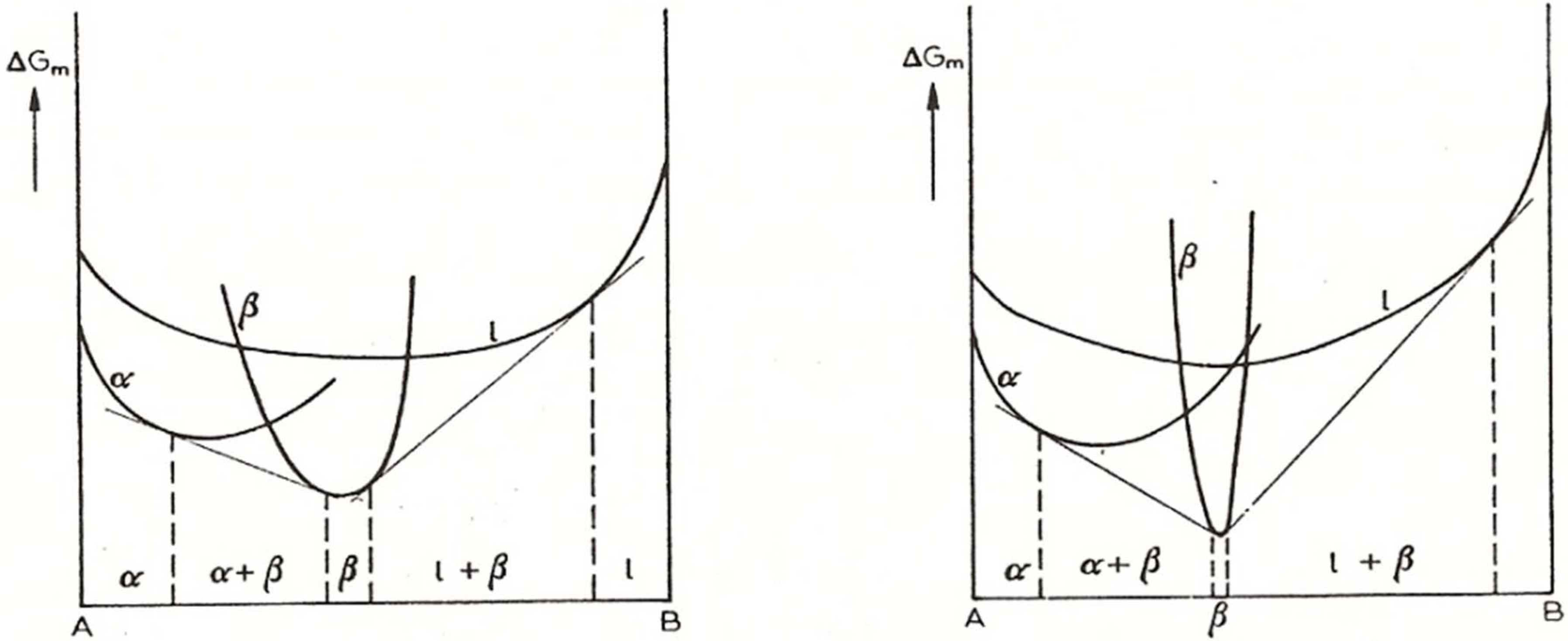


Fig. 70. Decreasing range of stability of an intermediate phase with its increasing stability relative to the termina solid solutions.

4.3.4. Formation of intermediate phases by peritectic reaction

Five successive peritectic reaction

(1) $l+\alpha \rightleftharpoons \beta$

(2) $l+\beta \rightleftharpoons \gamma$

(3) $l+\gamma \leftrightharpoons \delta$

(4) $l+\delta \rightleftharpoons \varepsilon$

(5) $l+\varepsilon \rightleftharpoons \eta$

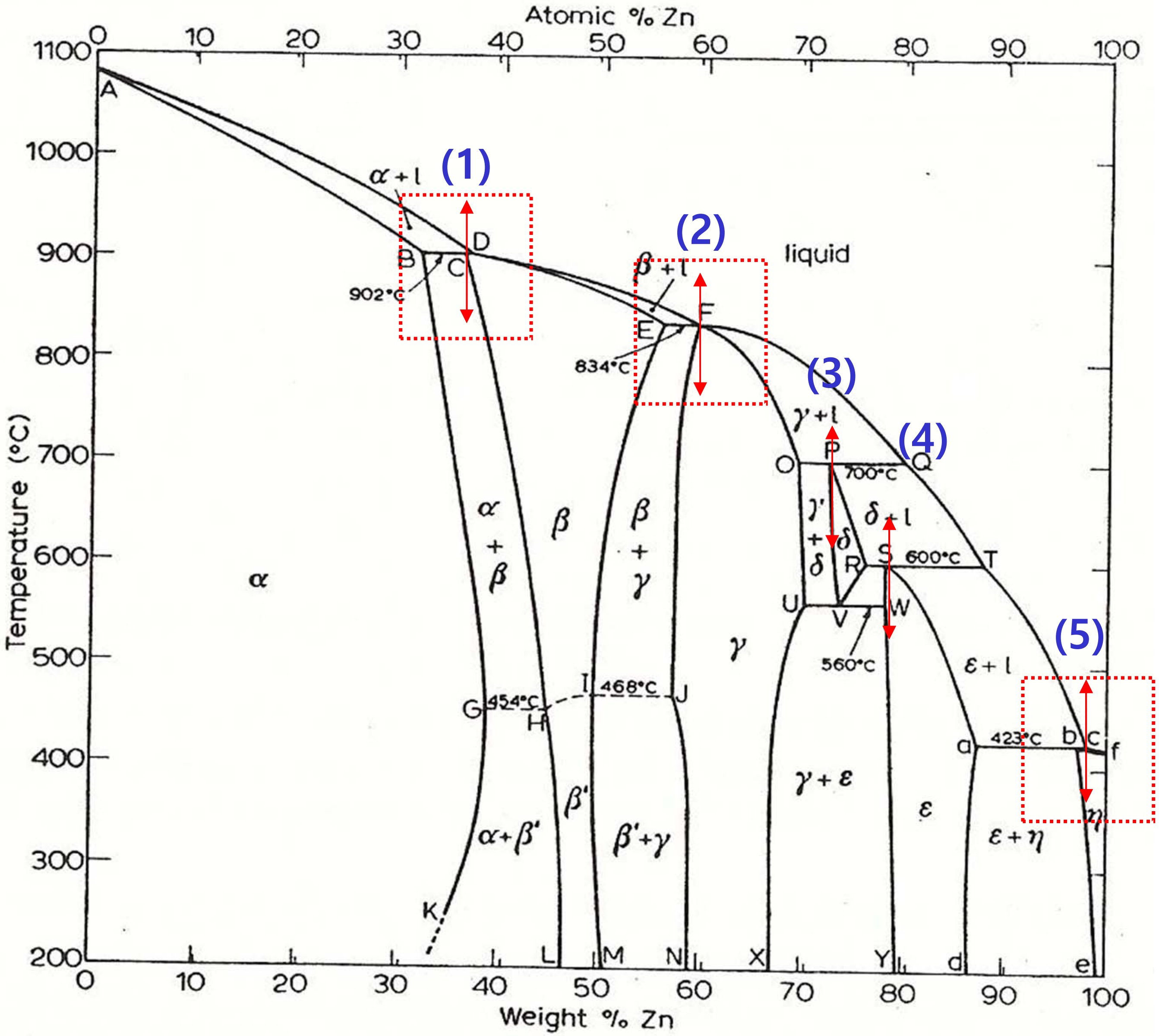


Fig. 71. The Cu–Zn phase diagram. (After G. V. RAYNOR; courtesy Institute of Metals.)

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

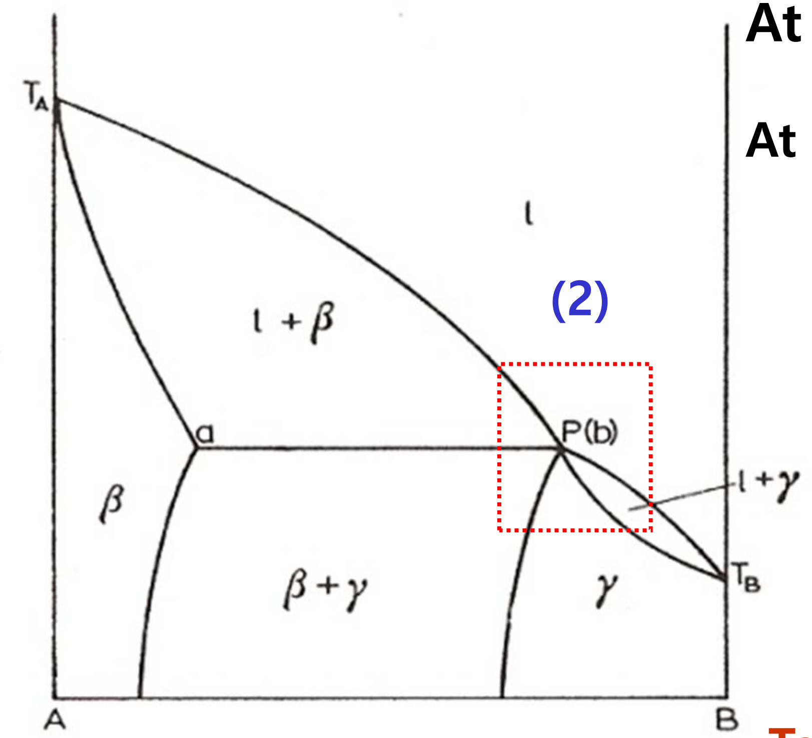


Fig. 72. Limiting case of the peritectic reaction.

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 <u>compositional difference these two points</u>.

The condition for a liquid and a solid phase to have identical compositions is that a temperature maximum or minimum must be present.

From eqn. (102)

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

Since $S^s \neq S^l$, then $dT/dX_A = 0$. Thus the condition $X_A^s = X_A^l$ is only associated with $dT/dX_A = 0$, *i.e.* with a minimum or a maximum in the line $T_A T_B$ of Fig. 22. Except for this particular case therefore $X_A^s \neq X_A^l$. There is a difference between the composition of the liquid and solid phase in the general case.

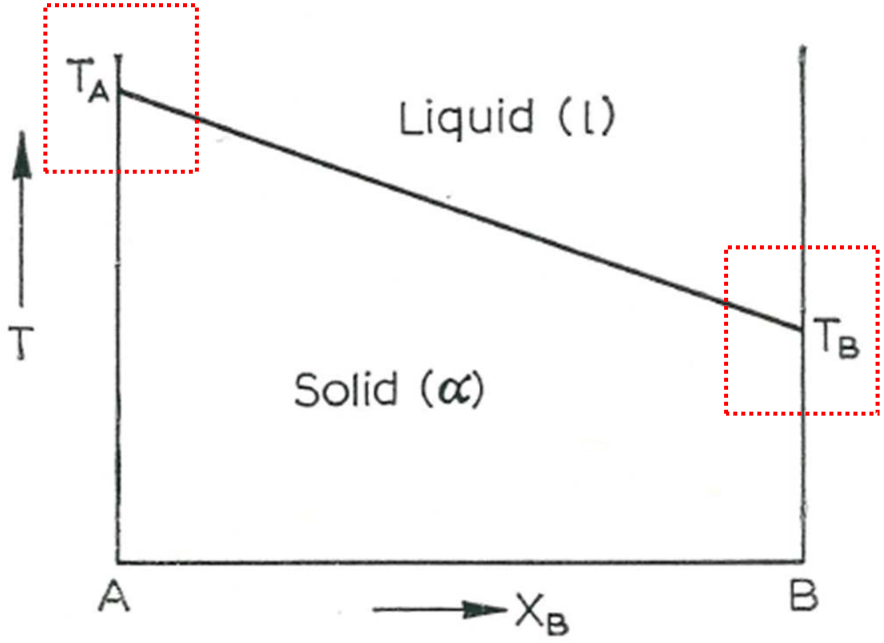
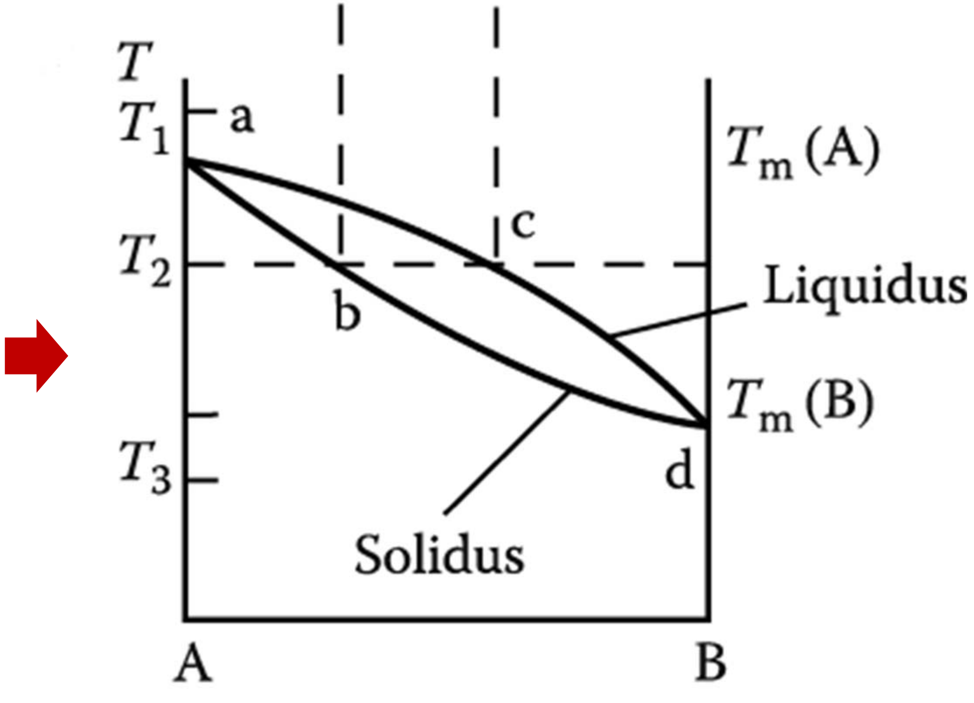
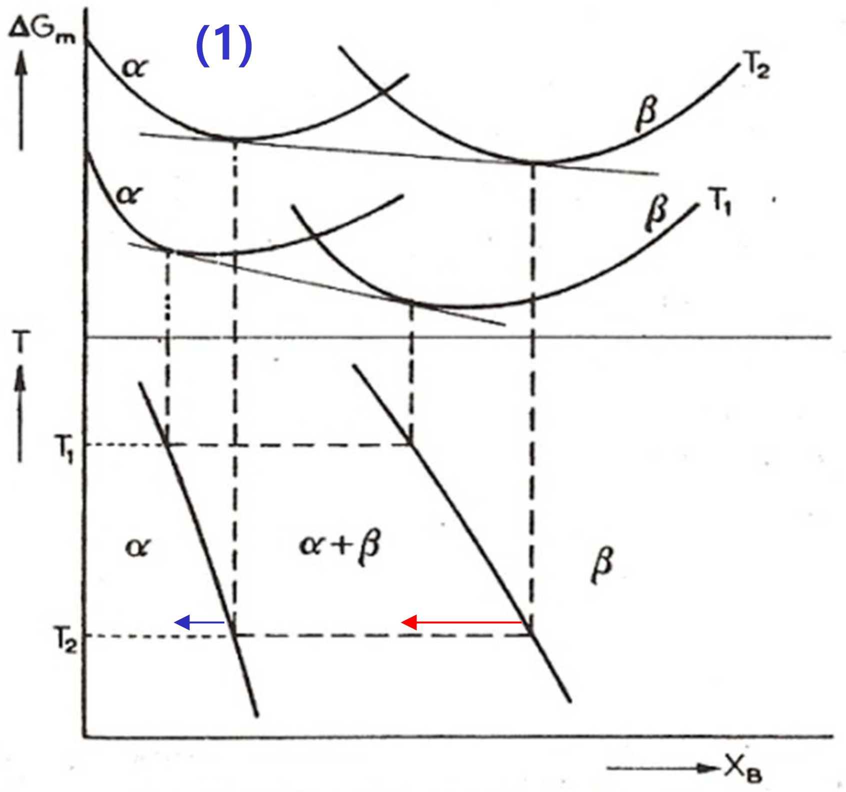


Fig. 22.



(f)

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 <u>disordered intermediate phase</u> (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

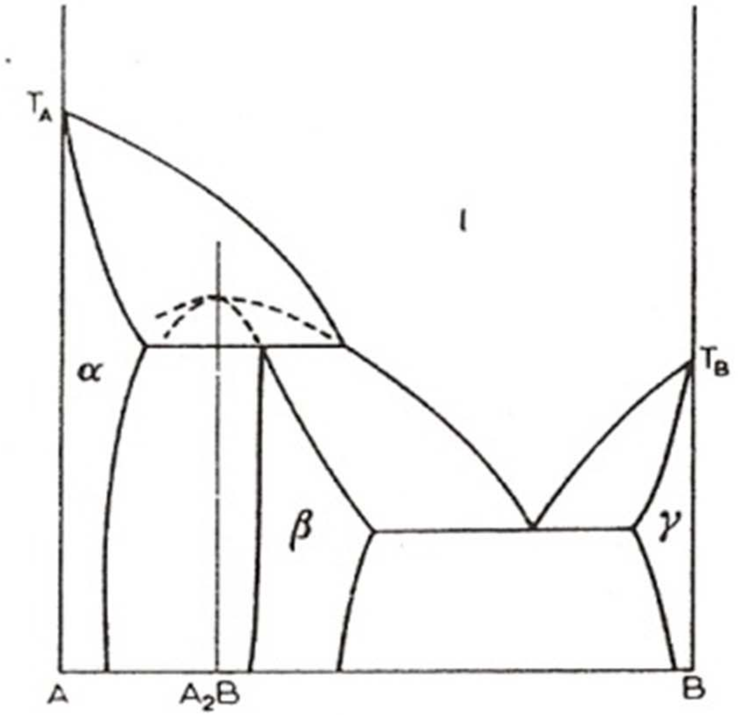


Fig. 74. A non-stoichiometric β phase based on the intermediate phase A_2B.

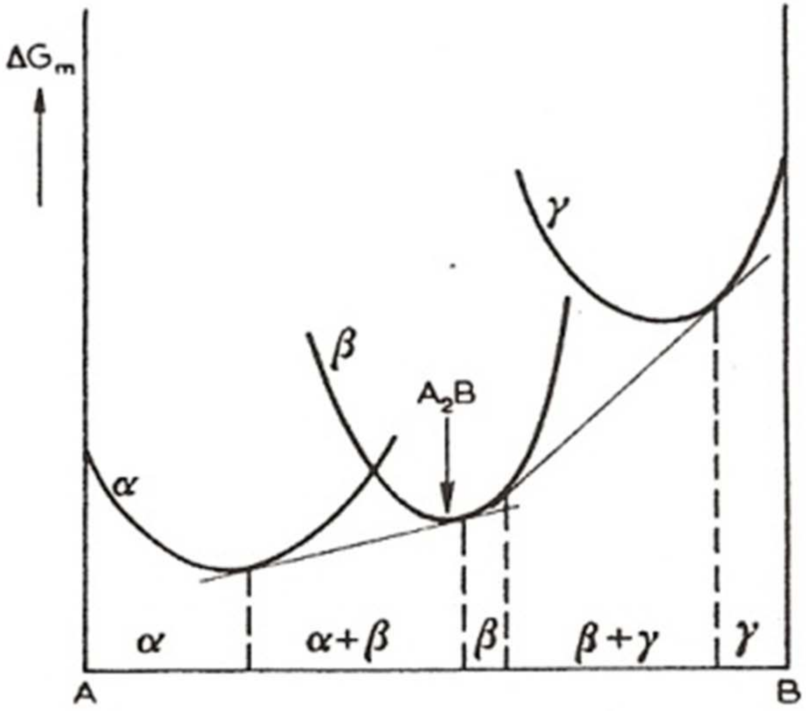
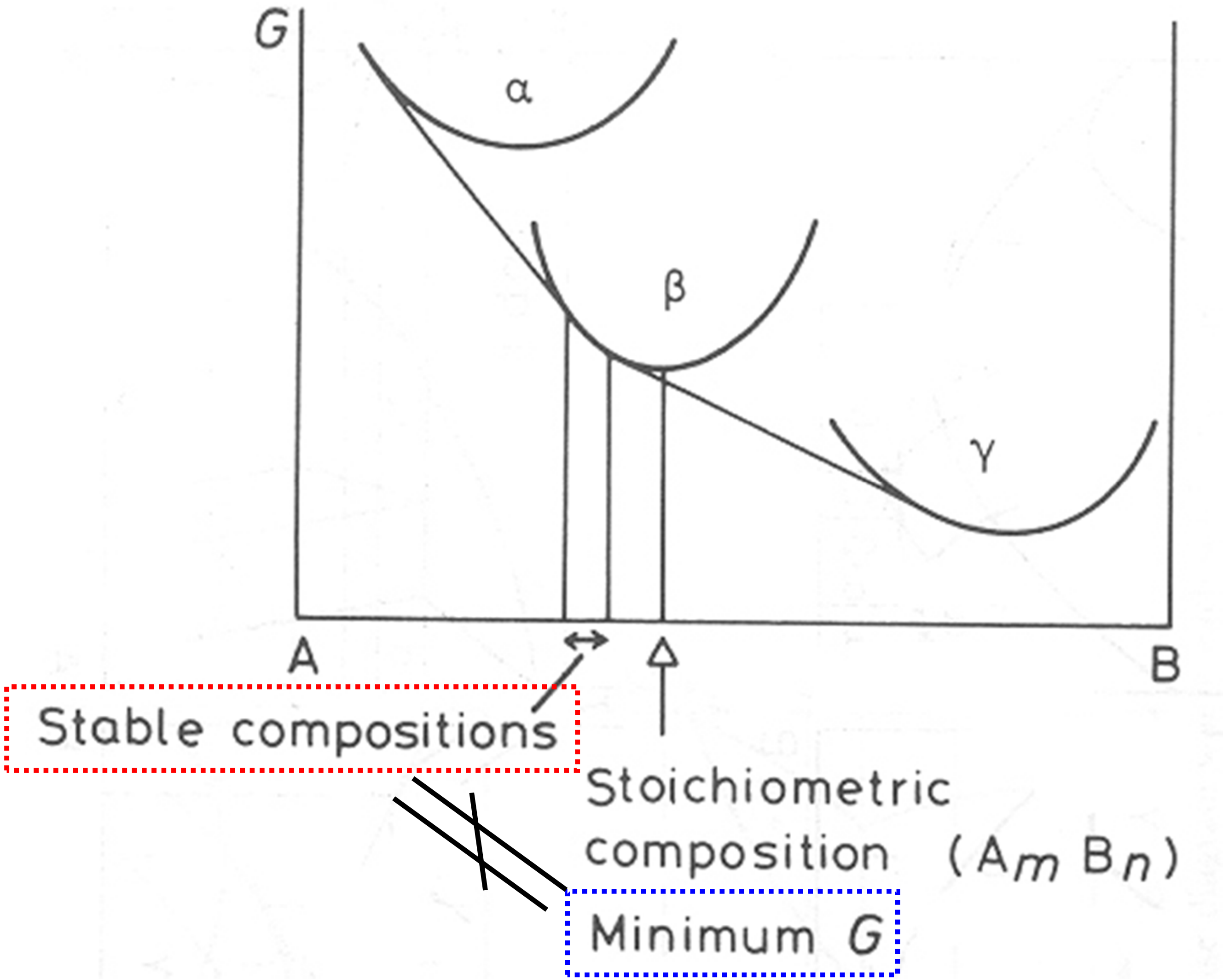


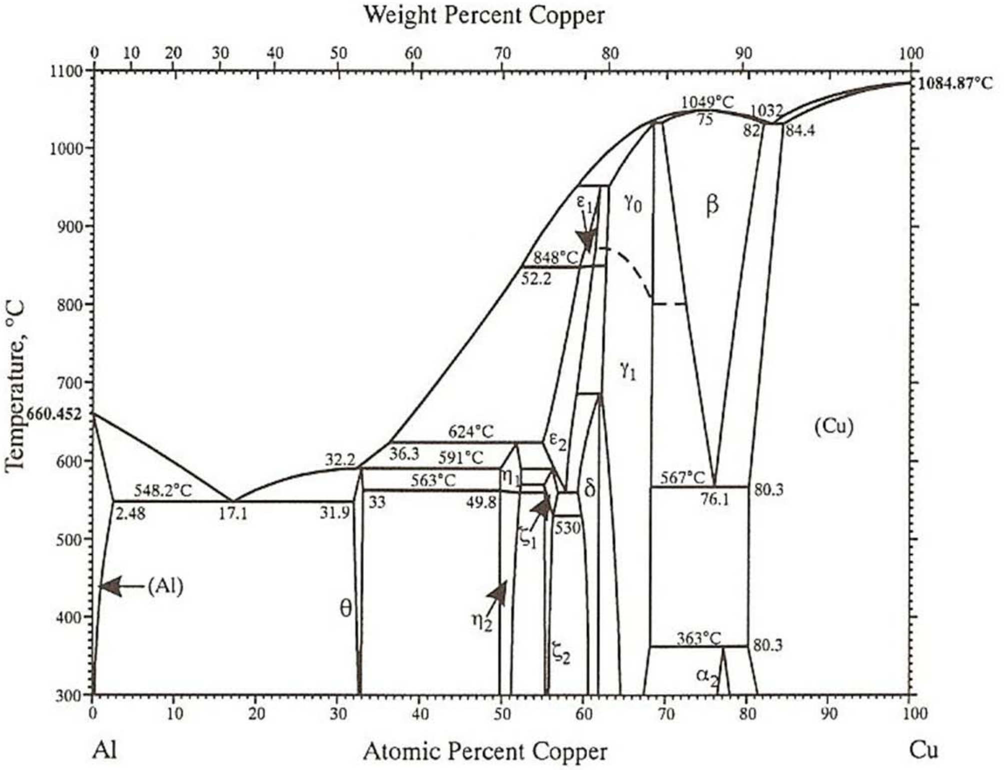
Fig. 75. Use of free energy curves to illustrate the occurrence of non-stoichiometric phases.

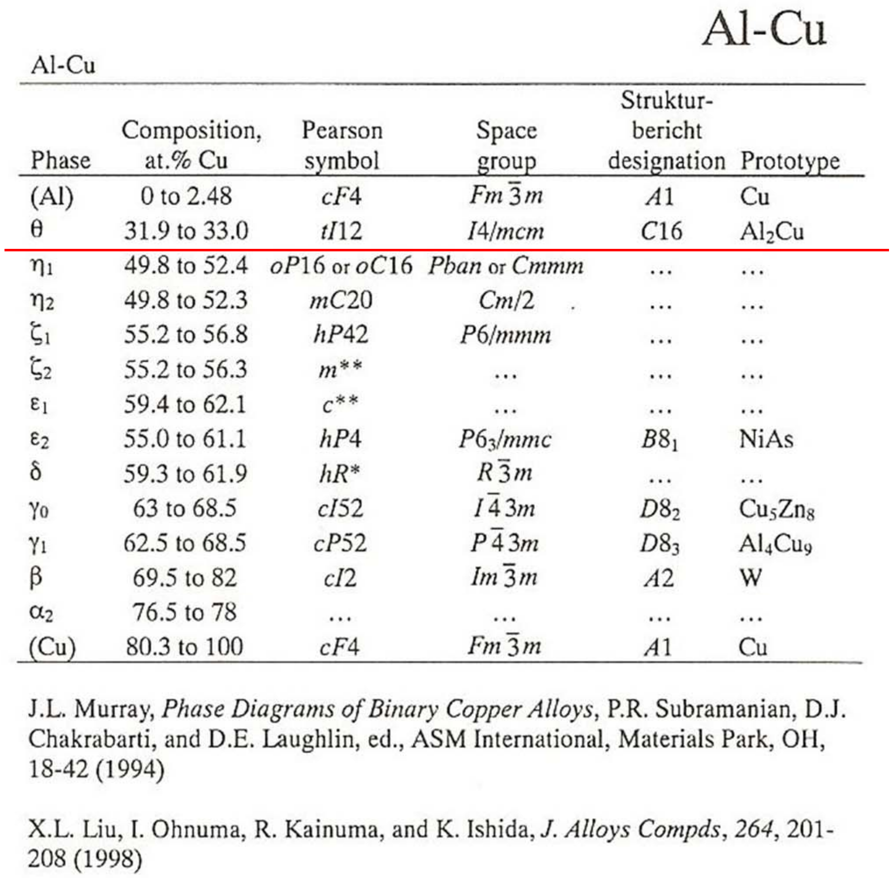
4.3.5. Non-stoichiometeric compounds



4.3.5. Non-stoichiometeric compounds

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	cF4	$Fm\bar{3}m$	A1	Cu
θ	31.9 to 33.0	tI12	I4/mcm	C16	Al_2Cu
η_1	49.8 to 52.4	oP16 or oC16	Pban or Cmmm	…	…
η_2	49.8 to 52.3	mC20	Cm/2	…	…
ζ_1	55.2 to 56.8	hP42	P6/mmm	…	…
ζ_2	55.2 to 56.3	m**	…	…	…
ε_1	59.4 to 62.1	c**	…	…	…
ε_2	55.0 to 61.1	hP4	$P6_3/mmc$	$B8_1$	NiAs
δ	59.3 to 61.9	hR*	$R\bar{3}m$	…	…
γ_0	63 to 68.5	cI52	$I\bar{4}3m$	$D8_2$	Cu_5Zn_8
γ_1	62.5 to 68.5	cP52	$P\bar{4}3m$	$D8_3$	Al_4Cu_9
β	69.5 to 82	cI2	$Im\bar{3}m$	A2	W
α_2	76.5 to 78	…	…	…	…
(Cu)	80.3 to 100	cF4	$Fm\bar{3}m$	A1	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)

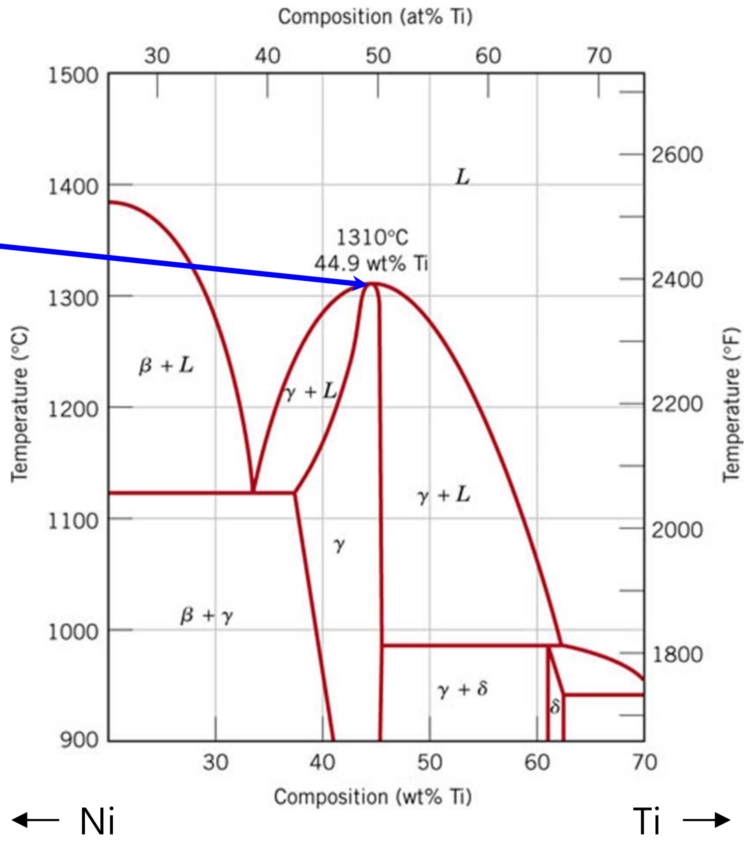
4.4 Congruent phase transformations

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

4.4. Congruent transformations

Congruent transformation:

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

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

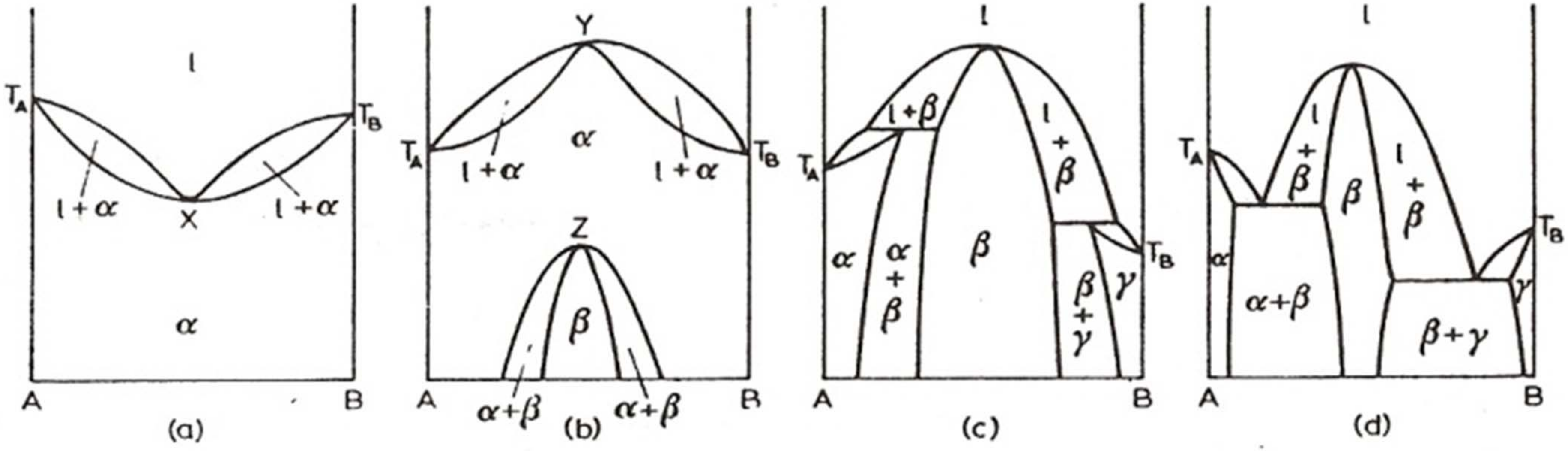


Fig. 76. Examples of congruent transformations.

4.4. Congruent transformations

a. Formation of congruently-melting intermediate phase

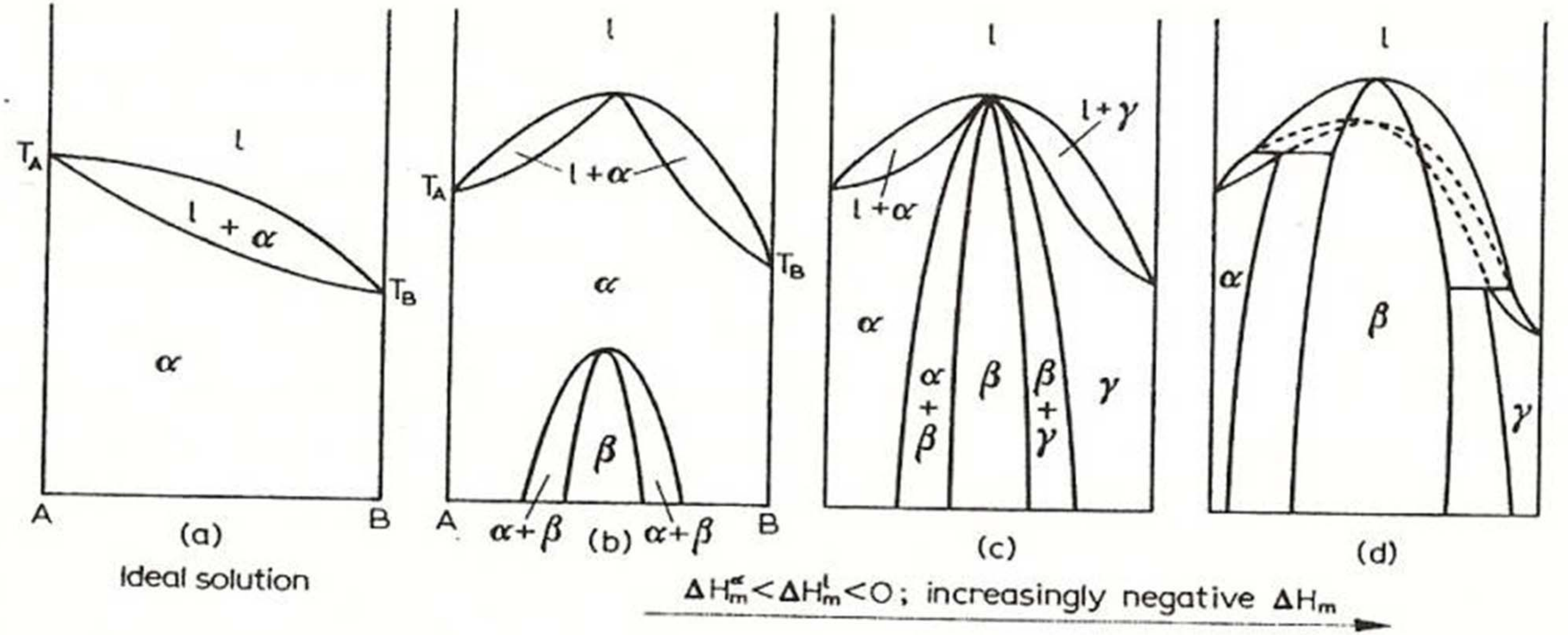


Fig. 77. Effect of increasingly negative departure from ideality in changing the phase diagram from a continuous series of solutions to one containing a congruent intermediate phase.

4.4. Congruent transformations

b. More usual type of congruently-melting intermediate phase

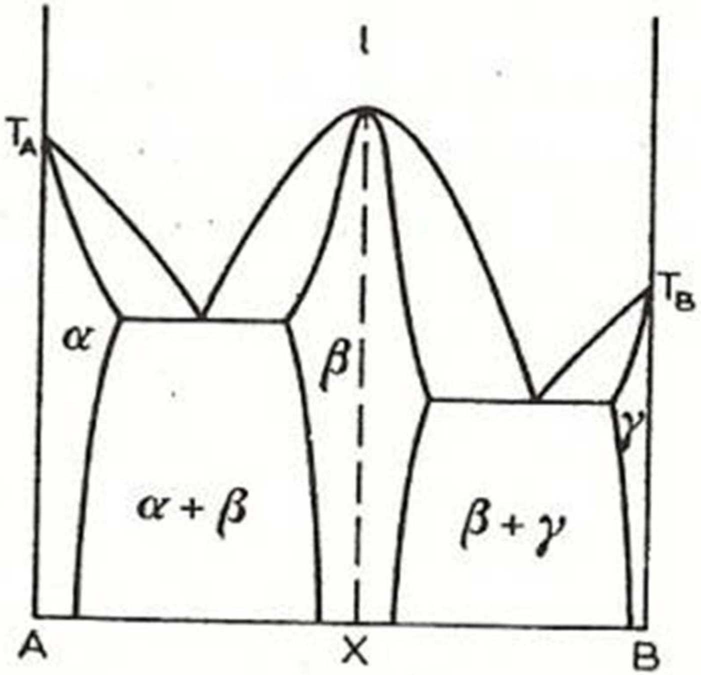
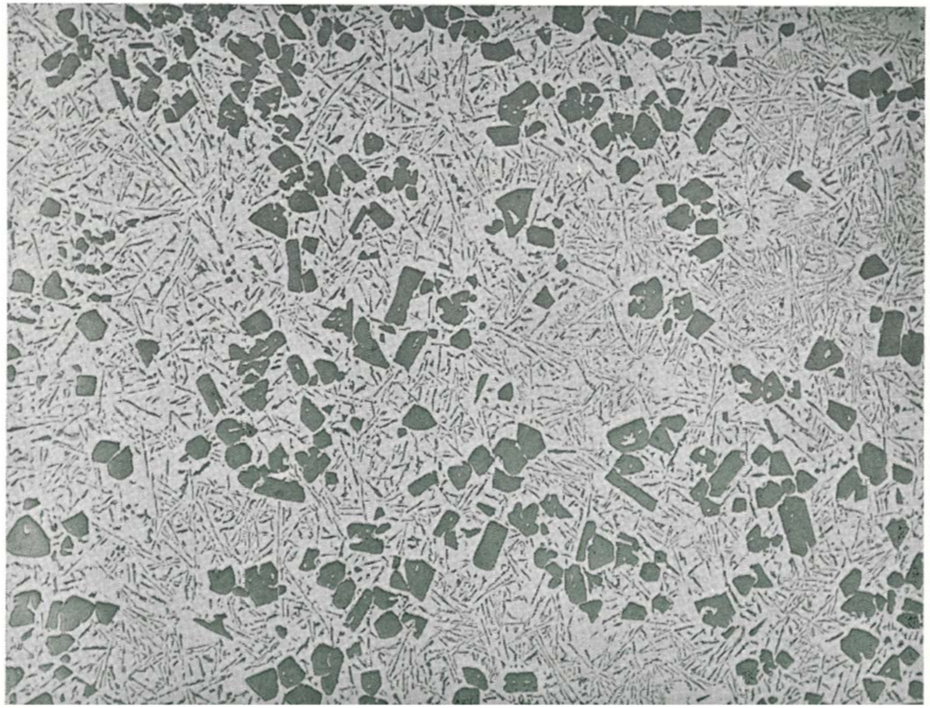


Fig. 78. Phase diagram with a congruent intermediate phase.

→ 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

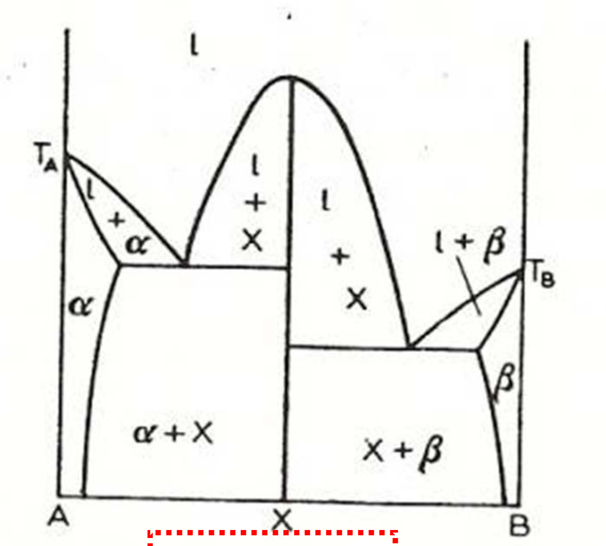
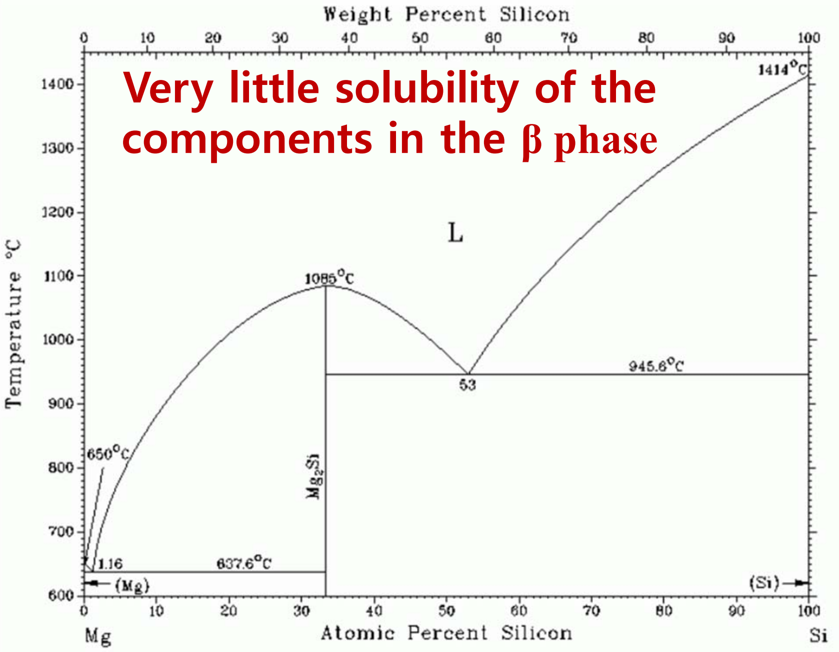
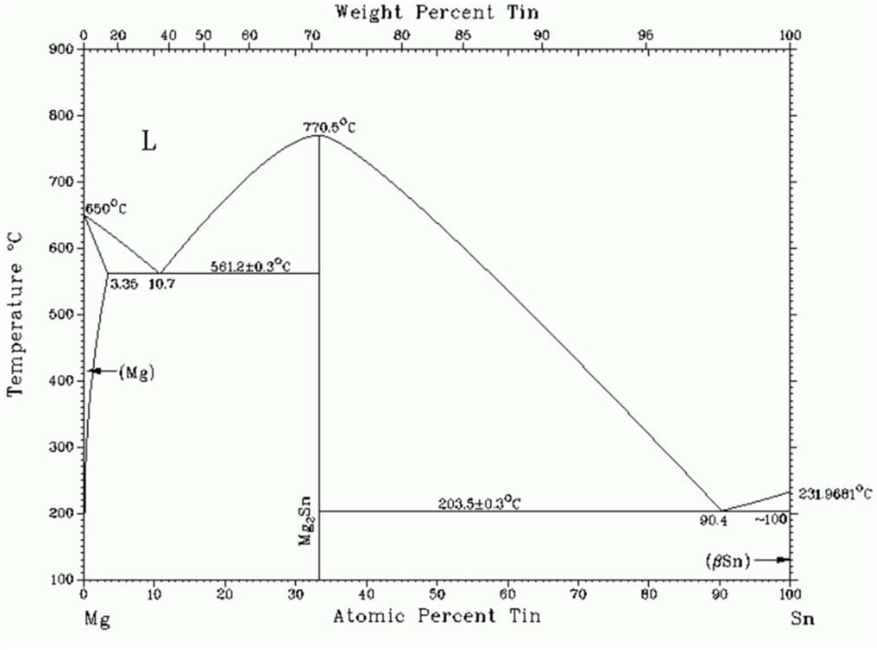
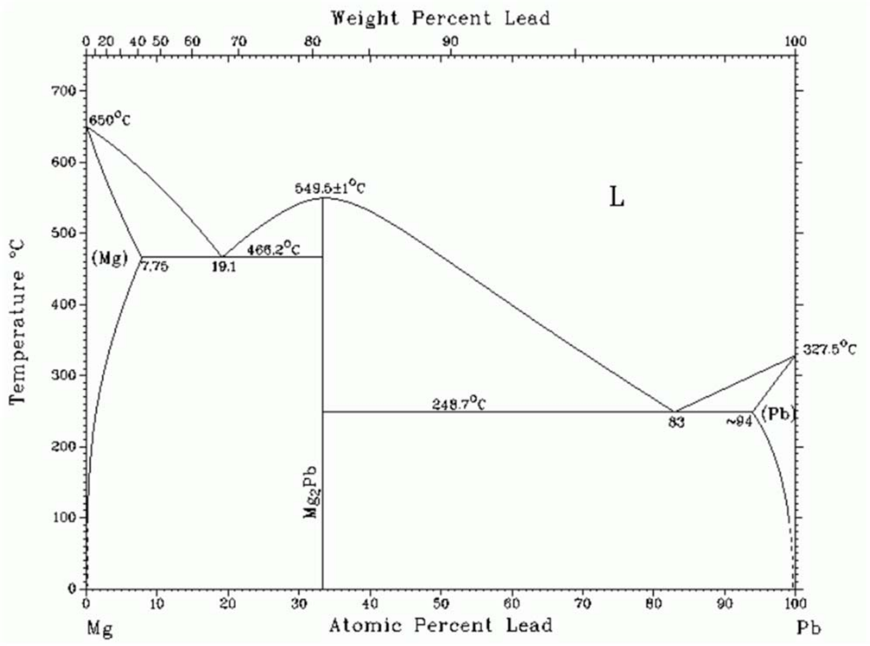


Fig. 79. Limiting case of Fig. 78.

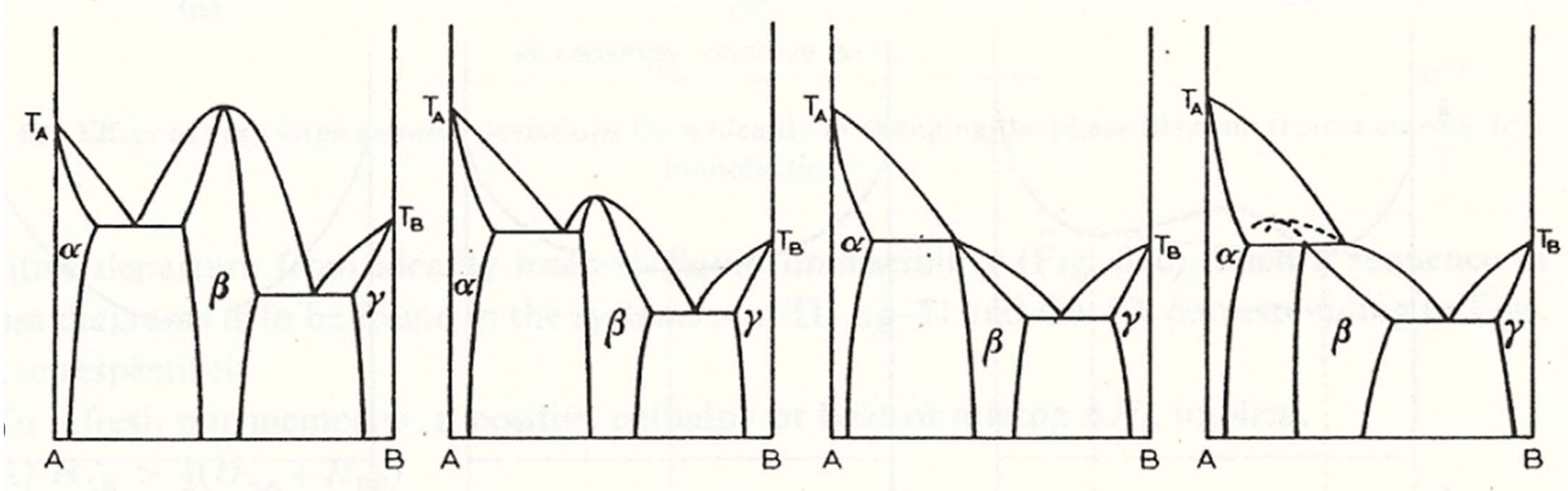

Very little solubility of the components in the β phase





4.4. Congruent transformations

c. Relationship between phase diagrams containing congruent and incongruent intermediate phases



MIDTERM: ?

Scopes: Text ~ page 117/ Teaching note ~10

QUIZs and Homeworks