2009 fall

Advanced Physical Metallurgy

"Phase Equilibria in Materials"

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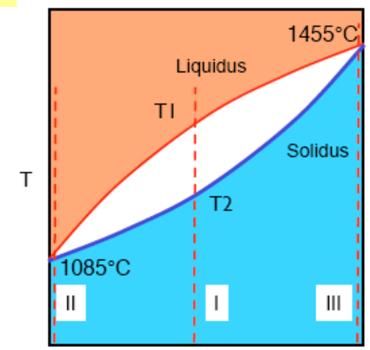
Contents for previous class

- Equilibrium in Heterogeneous Systems

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



- Binary phase diagrams

1) Simple Phase Diagrams

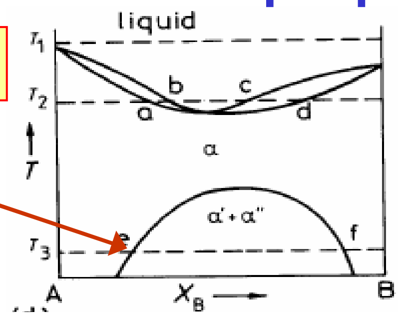
$\Delta H^{L}_{mix} = 0 \ \Delta H^{S}_{mix} = 0$

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

2) Variant of the simple phase diagram

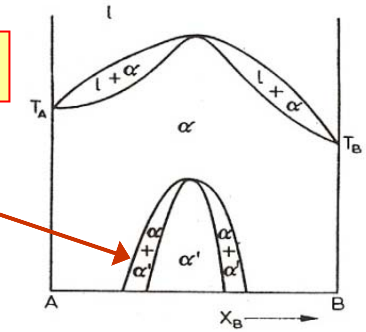
$\Delta H^{\alpha}_{mix} > \Delta H^{l}_{mix} > 0$

miscibility gab

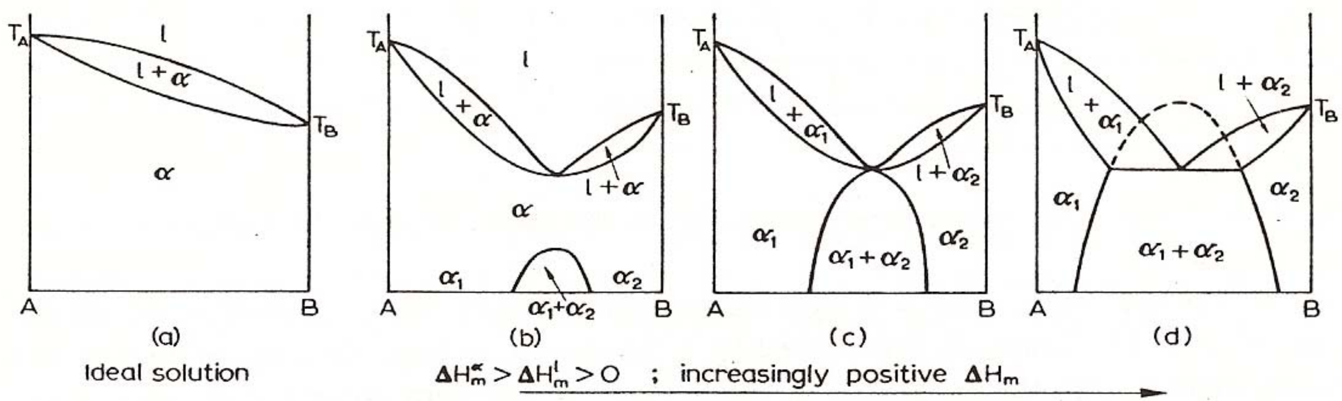


$\Delta H^{\alpha}_{mix} < \Delta H^{l}_{mix} < 0$

Ordered phase



3) Simple Eutectic Systems



Contents for today's class

- Gibbs Phase Rule

- Eutectoid reaction

- Peritectic reaction

  Formation of intermediate phases by peritectic reaction

  Non-stoichiometeric compounds

- Congruent transformations

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 $\quad F = C + N - P$

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

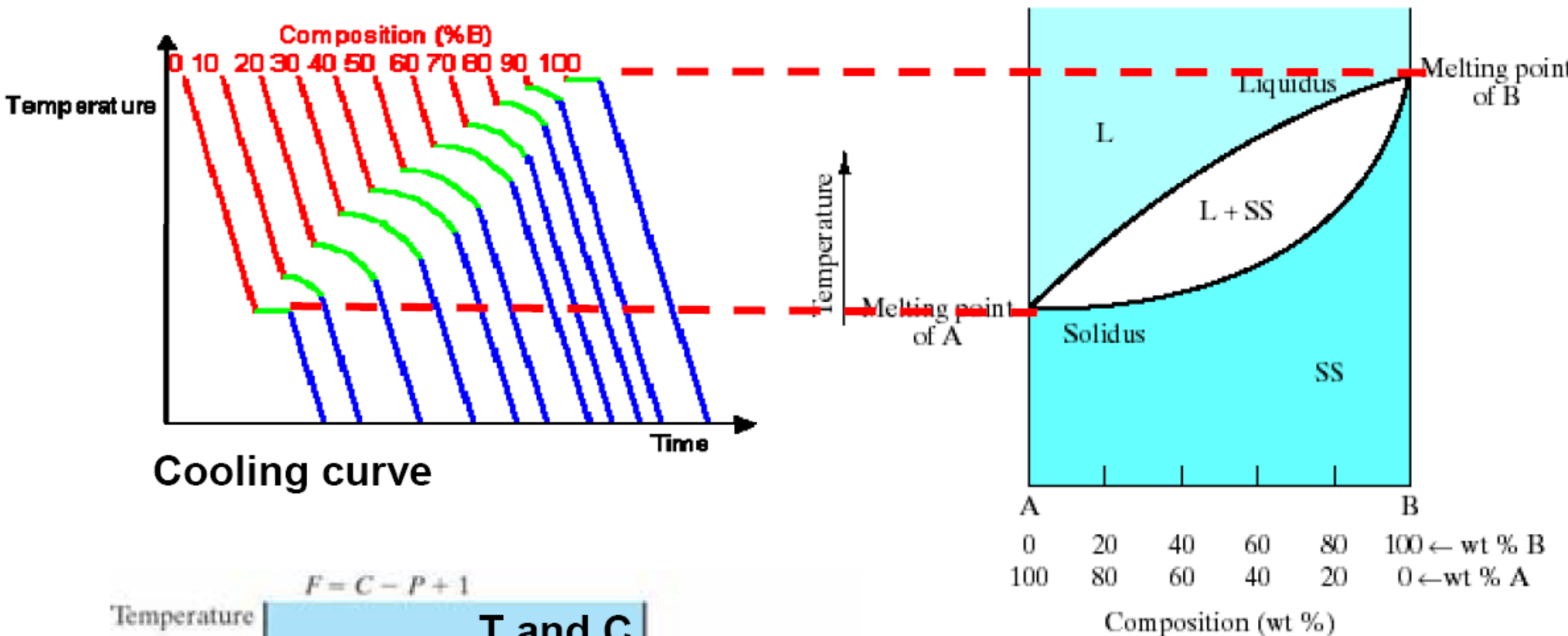
For a binary system the equilibria possible are summarised below.

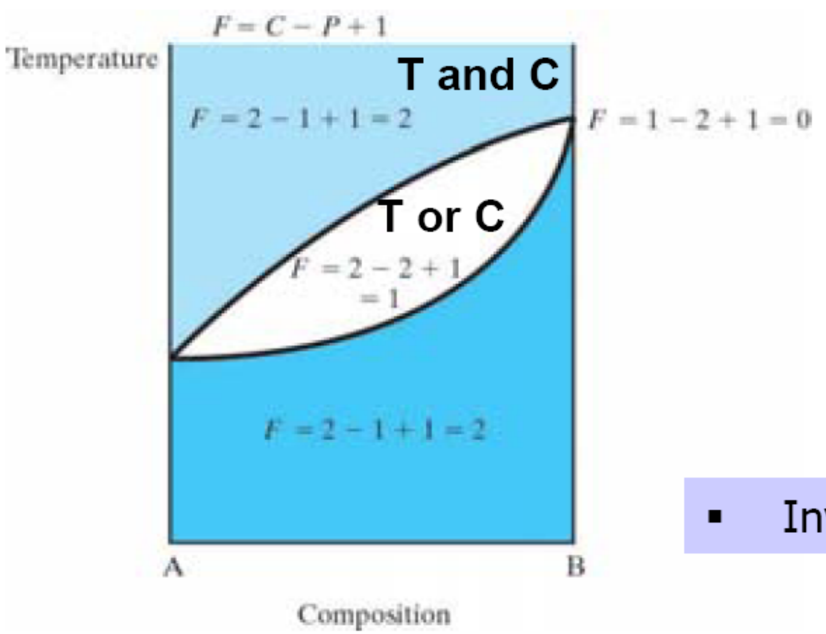
Number of components	Number of phases	Variance	Equilibrium	
$c = 2$	$p = 1$	$f = 2$	bivariant	**P=c-1**
$c = 2$	$p = 2$	$f = 1$	monovariant	**P=c**
$c = 2$	$p = 3$	$f = 0$	invariant	**P=c+1**

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

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

How to Construct a Phase Diagram



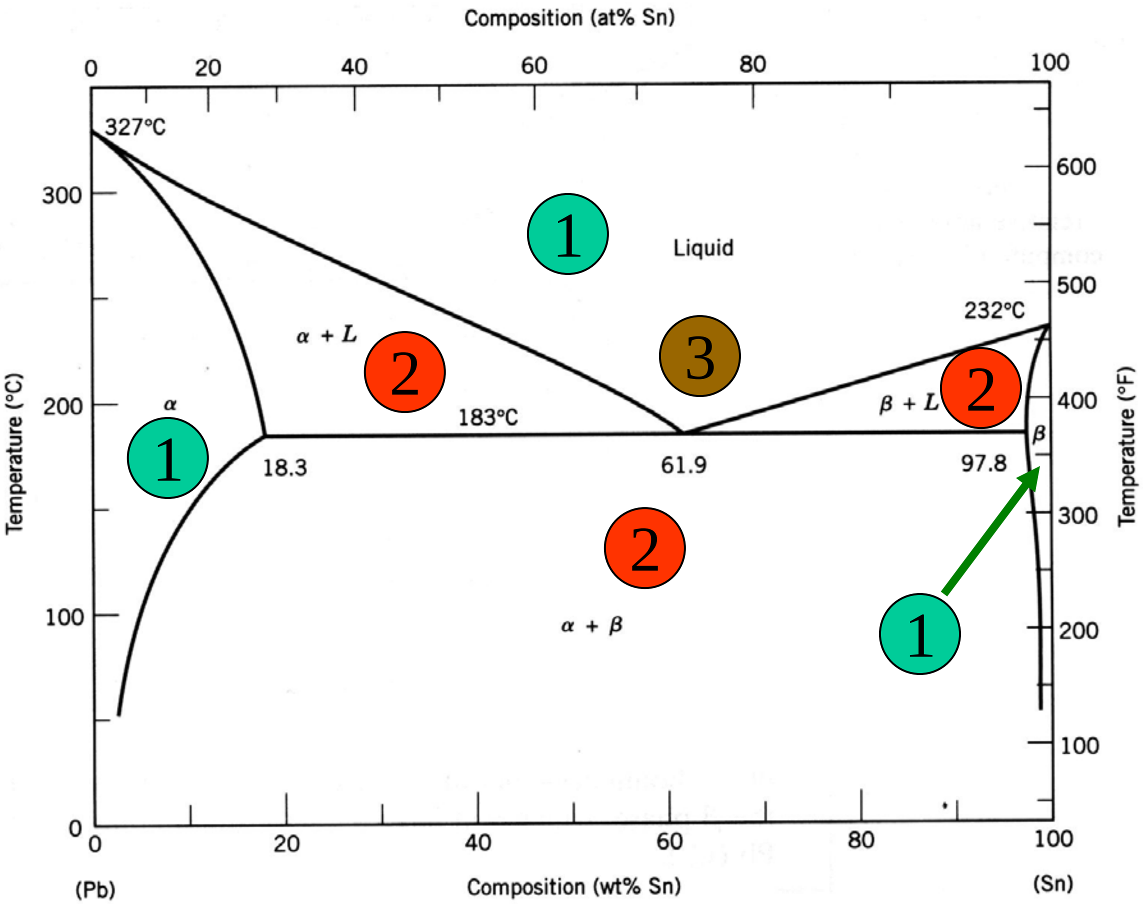


- Invariant point is that at which F = 0.

The Gibbs Phase Rule

For Constant Pressure,

P + F = C + 1



single phase

F = C - P + 1

= 2 - 1 + 1

= 2

can vary T and composition independently

two phase

F = C - P + 1

= 2 - 2 + 1

= 1

can vary T *or* composition

eutectic point

F = C - P + 1

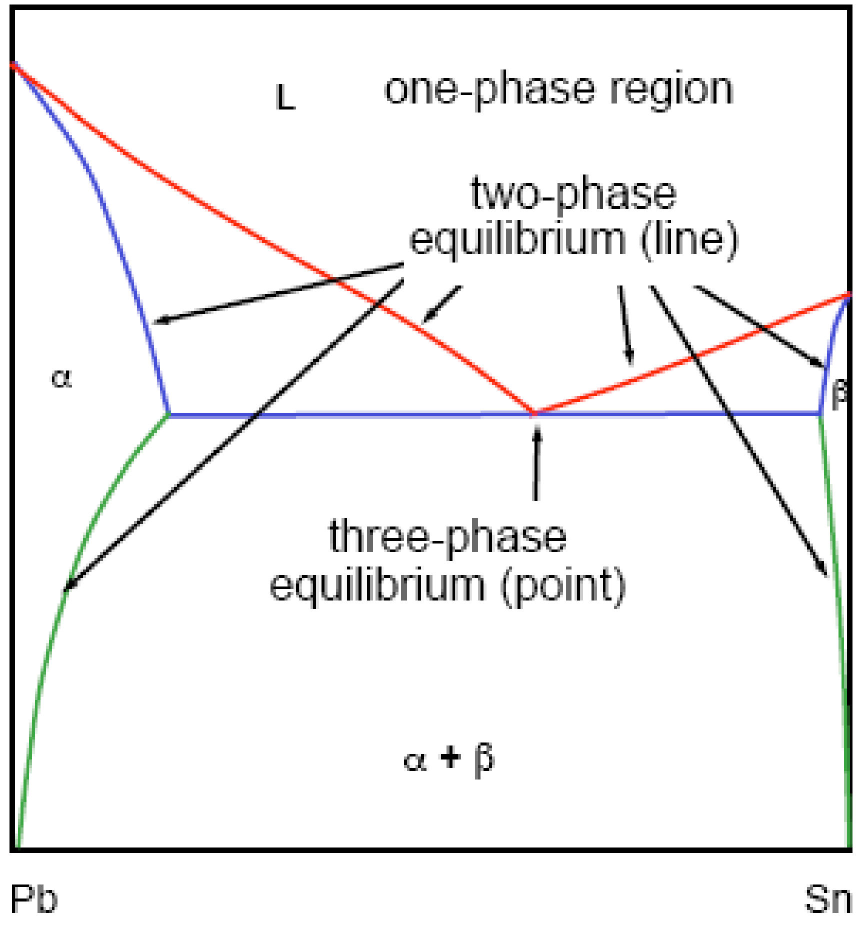
= 2 - 3 + 1

= 0

can't vary T or composition

The Gibbs Phase Rule

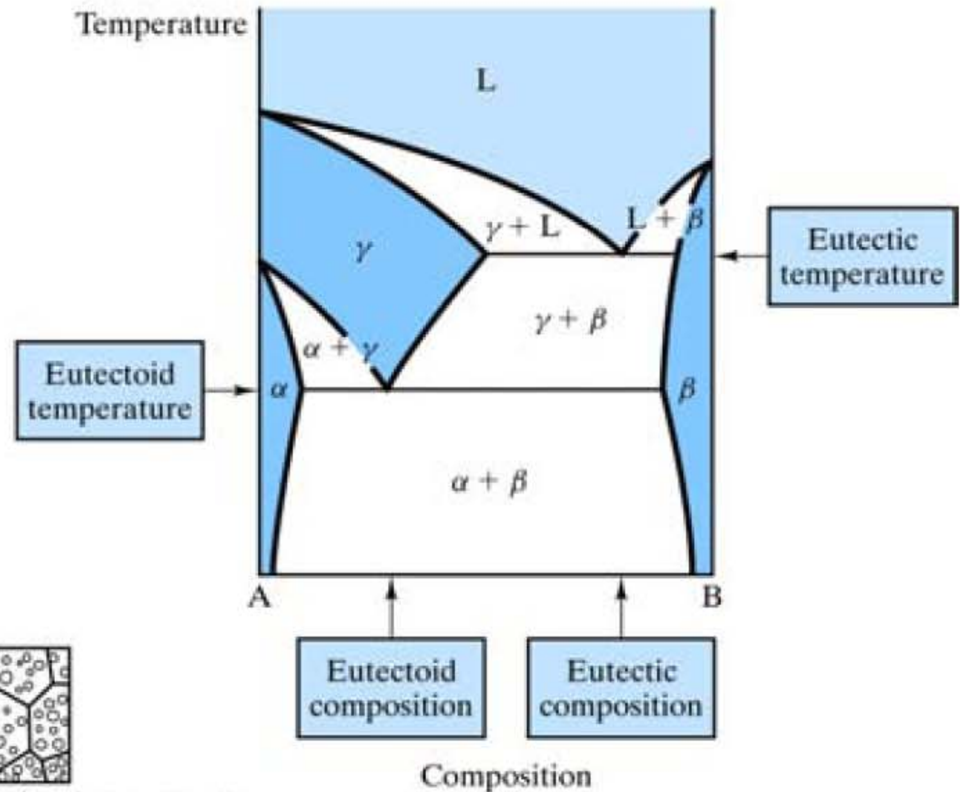
Application of Gibbs phase rule:
For a binary system at ambient pressure:
C=2 (2 elements)
N=1 (temperature, no pressure)
For single phase: F=2: % and T
(a region)
For a 2-phase equilibrium: F=1:
% or T (a line)
For a 3-phase equilibrium: F=0, (invariant point)

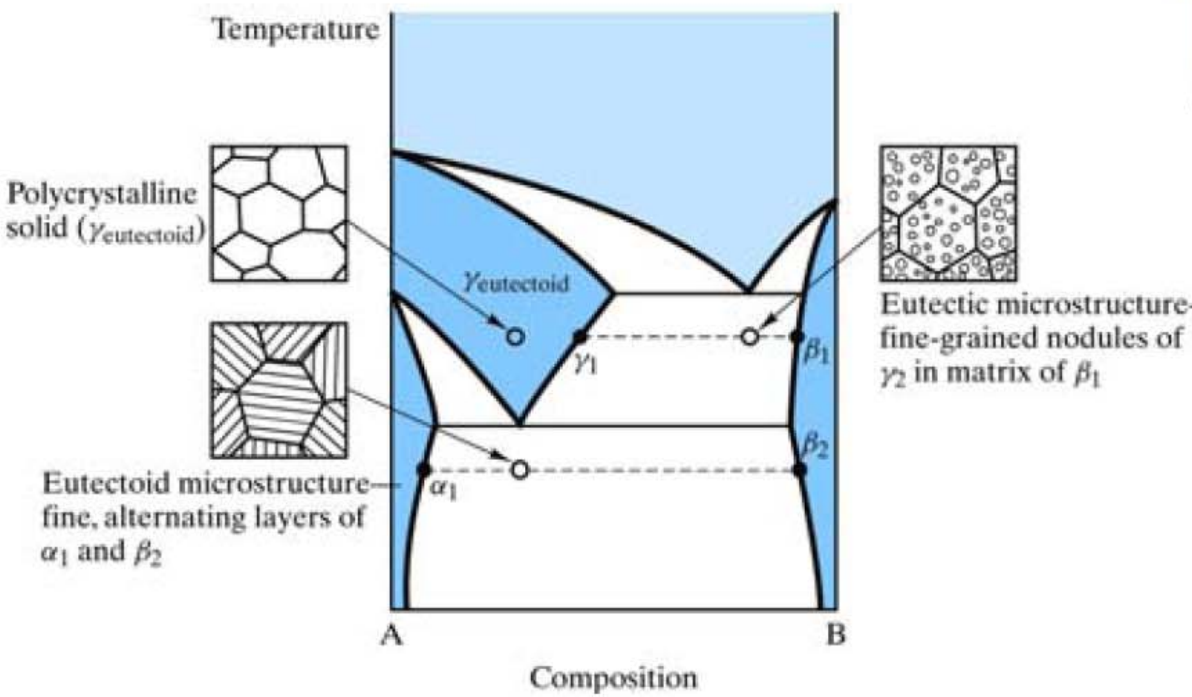


Eutectoid reaction

Eutectoid reaction :

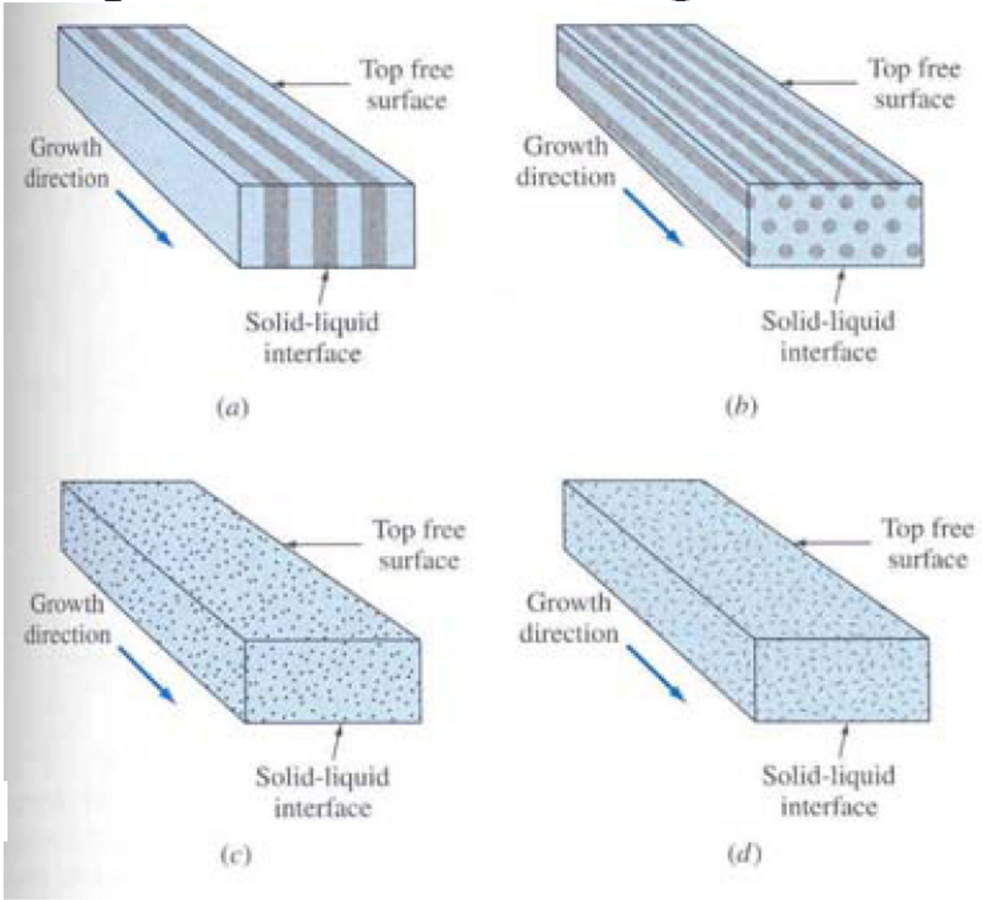
$$\gamma_{\text{eutectoid}} \underset{T_{eu.}}{\overset{\textit{cooling}}{\rightleftarrows}} \alpha + \beta$$





Various Eutectic Structures

- **Structure depends on factors like minimization of free energy at α / β interface.**
- **Manner in which two phases nucleate and grow also affects structures.**



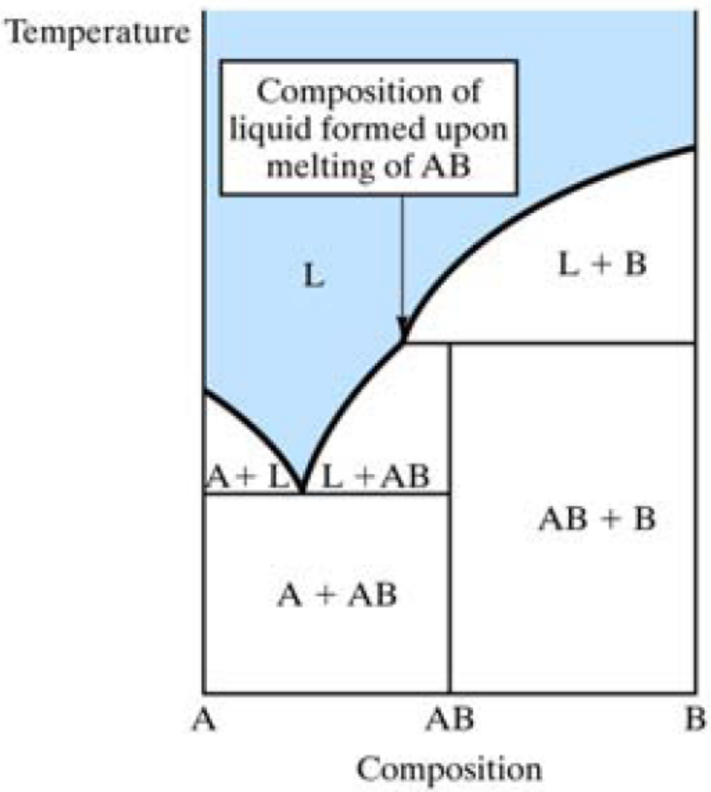
Peritectic reaction

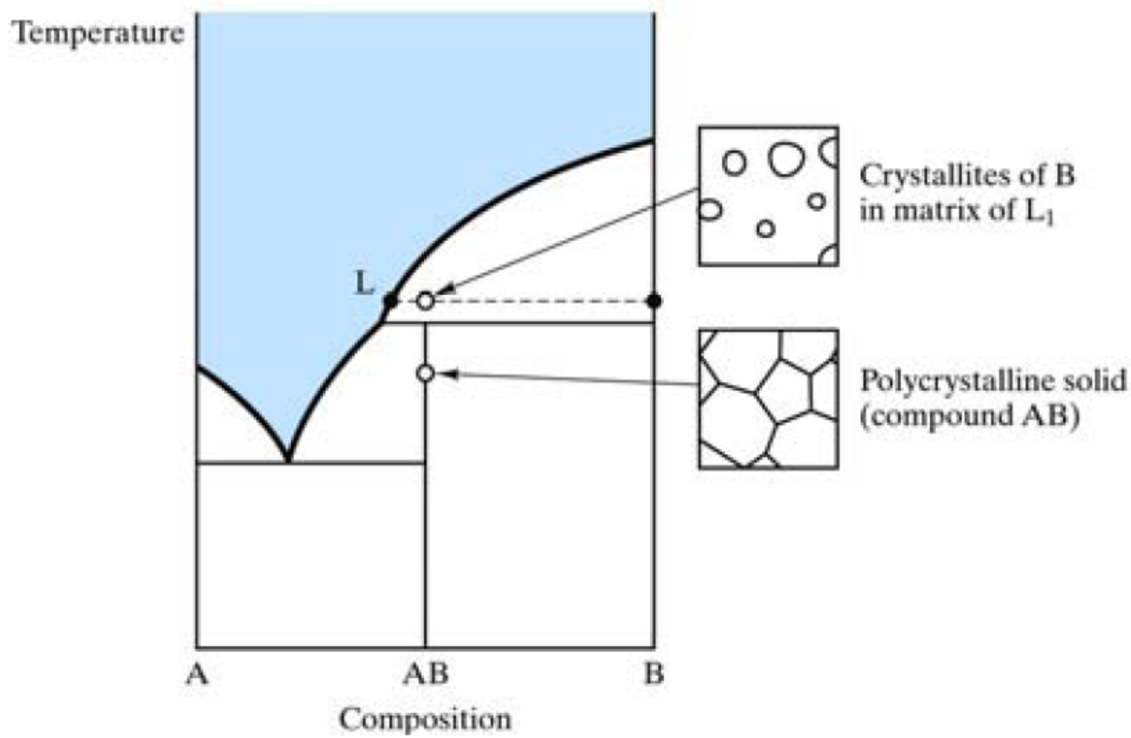
Peritectic reaction : AB $\underset{}{\overset{heating}{\rightleftarrows}}$ L + B

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

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

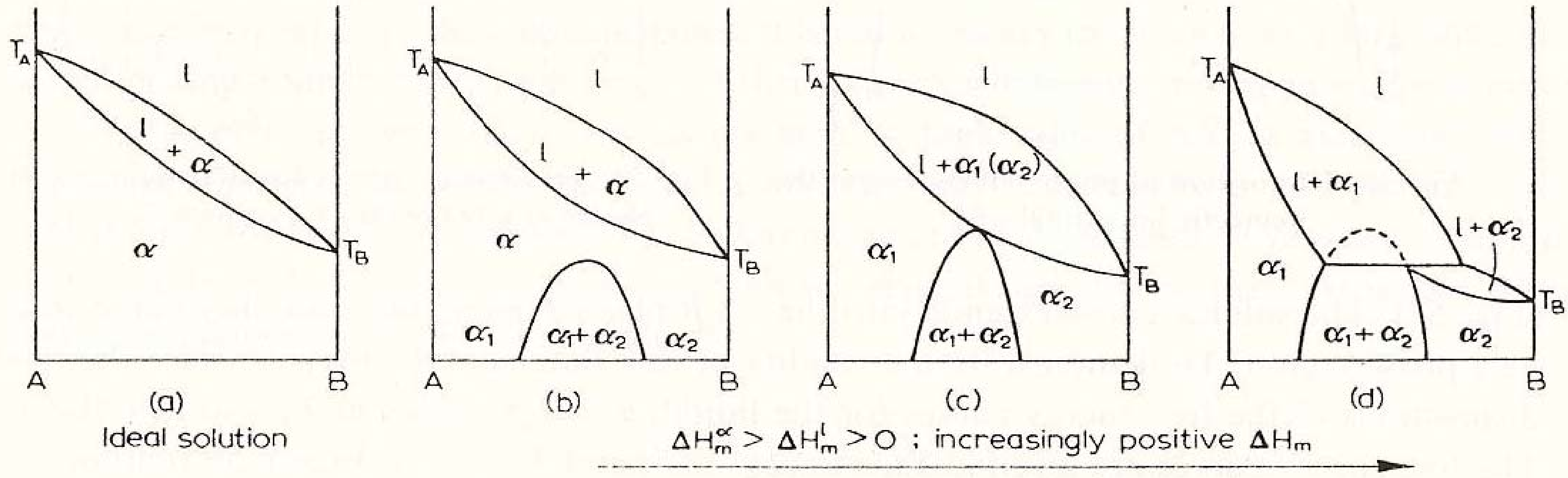


Fig. 61. Effect of increasingly positive departure from ideality in changing the phase diagram from a continuous series of solutions to a peritectic-type.

Eutectic reaction

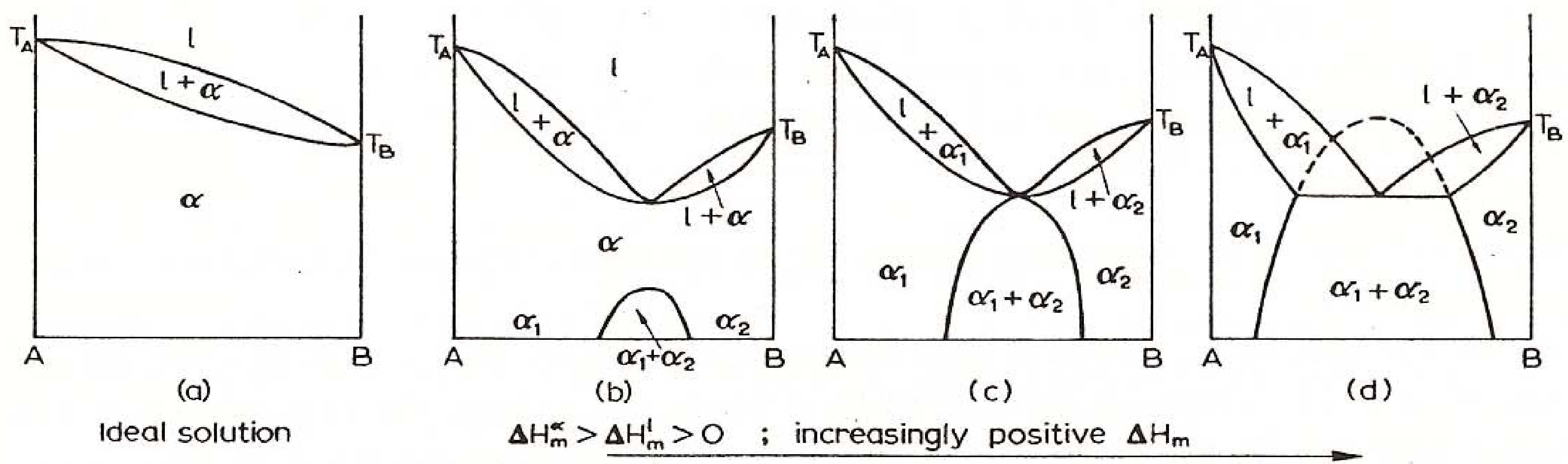


Fig. 43. Effect of increasingly positive departure from ideality in changing the phase diagram for a continuous series of solutions to a eutectic-type.

Eutectic: $L \rightarrow \alpha + \beta$ **Peritectic: $L + \alpha \rightarrow \beta$**

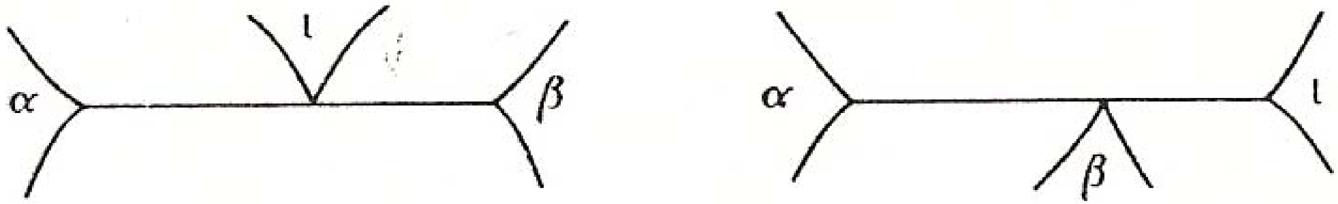


Fig. 63. Relationship between eutectic and peritectic reactions.

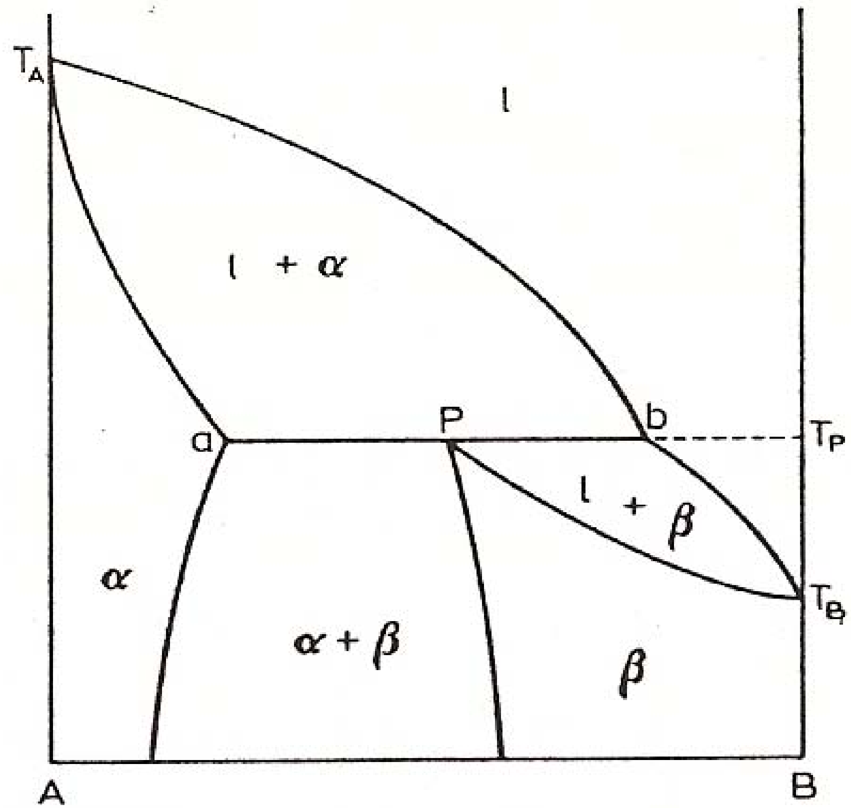


Fig. 64. Binary peritectic phase diagram.

Peritectic reaction

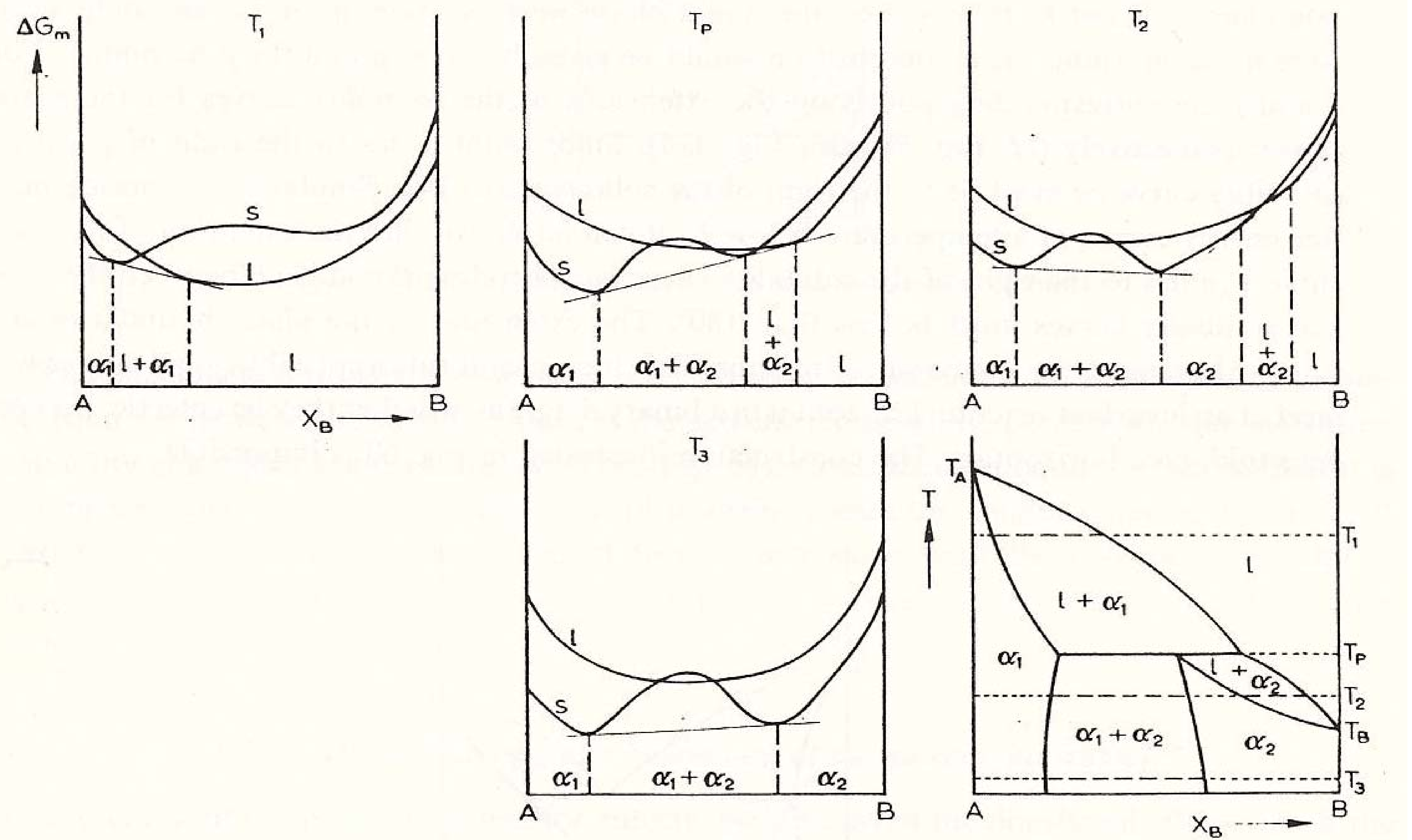


Fig. 62. Derivation of the peritectic phase diagram from the free energy curves for the liquid and solid phases.

Peritectic reaction

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

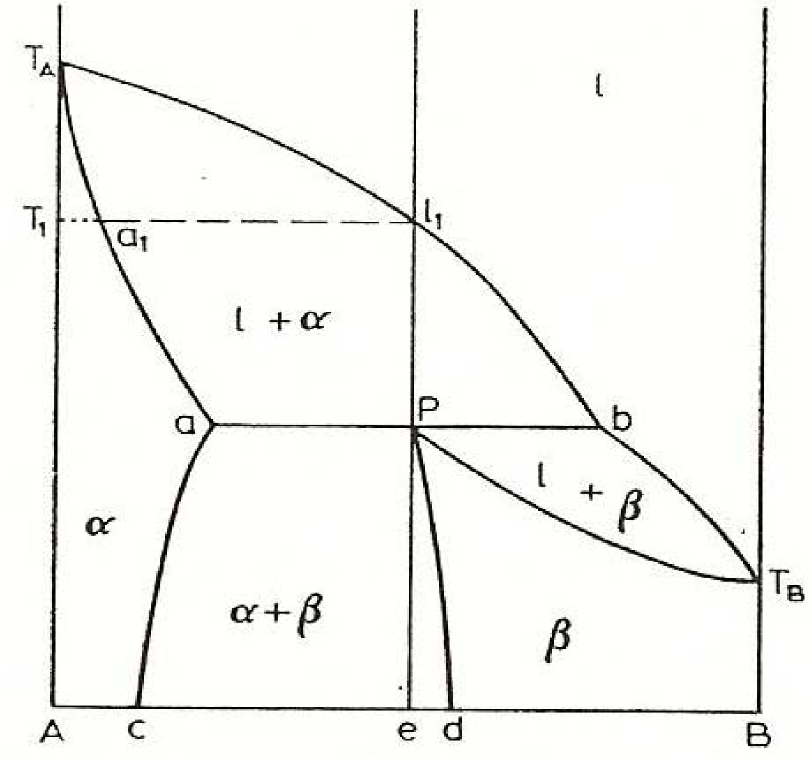


Fig. 65. Freezing of the peritectic alloy *P*.

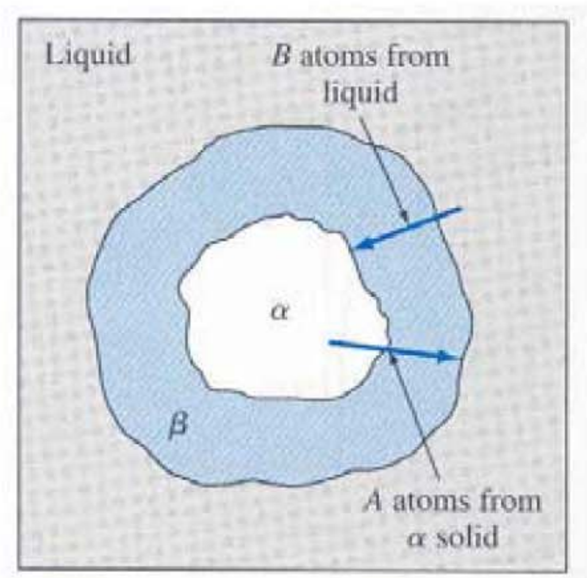


Figure 8.19

Peritectic Alloy System

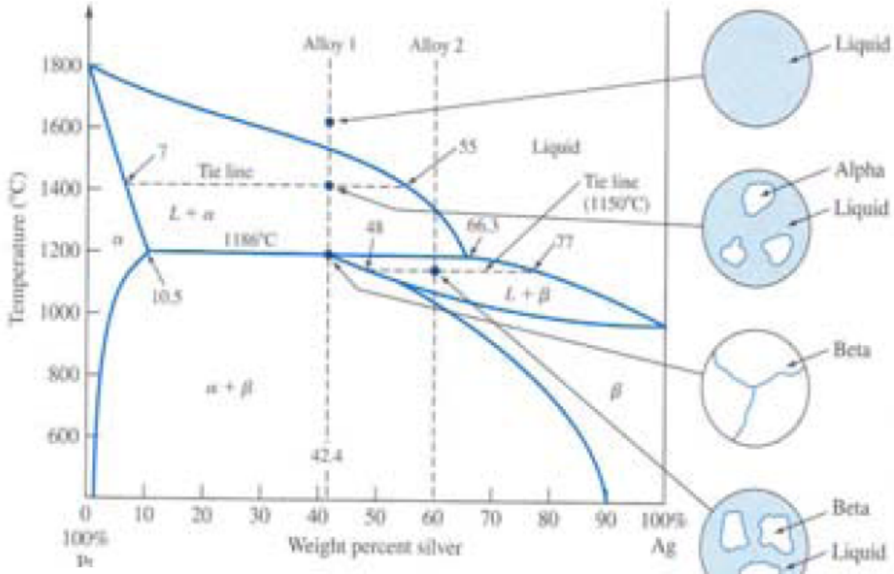


Figure 8.17

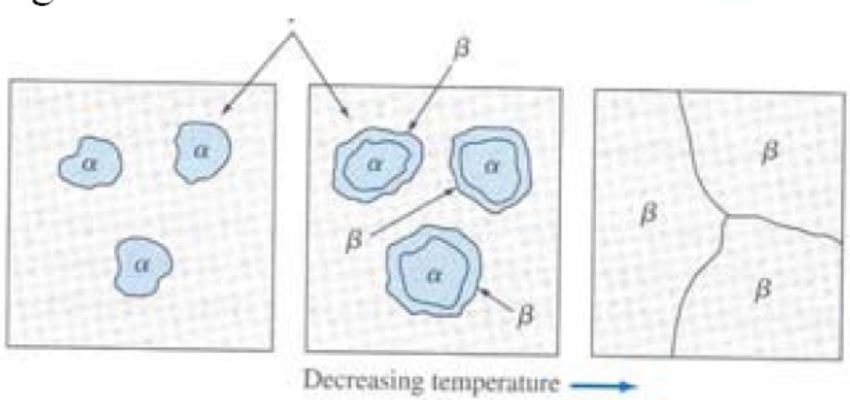


Figure 8.18

- **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**

Phase Present **Beta only**

Composition **42.4% Ag**

Amount of Phase **100%**

- **At 42.4% Ag and 1186^{0}C + ΔT**

Phases present **Liquid** **Alpha**

Composition **66.3% Ag** **10.5%Ag**

Amount of Phases $\frac{42.4-10.5}{66.3-10.5} = 57\%$ $\frac{66.3-42.4}{66.3-10.5} = 43\%$

4.3.4. Formation of intermediate phases by peritectic reaction

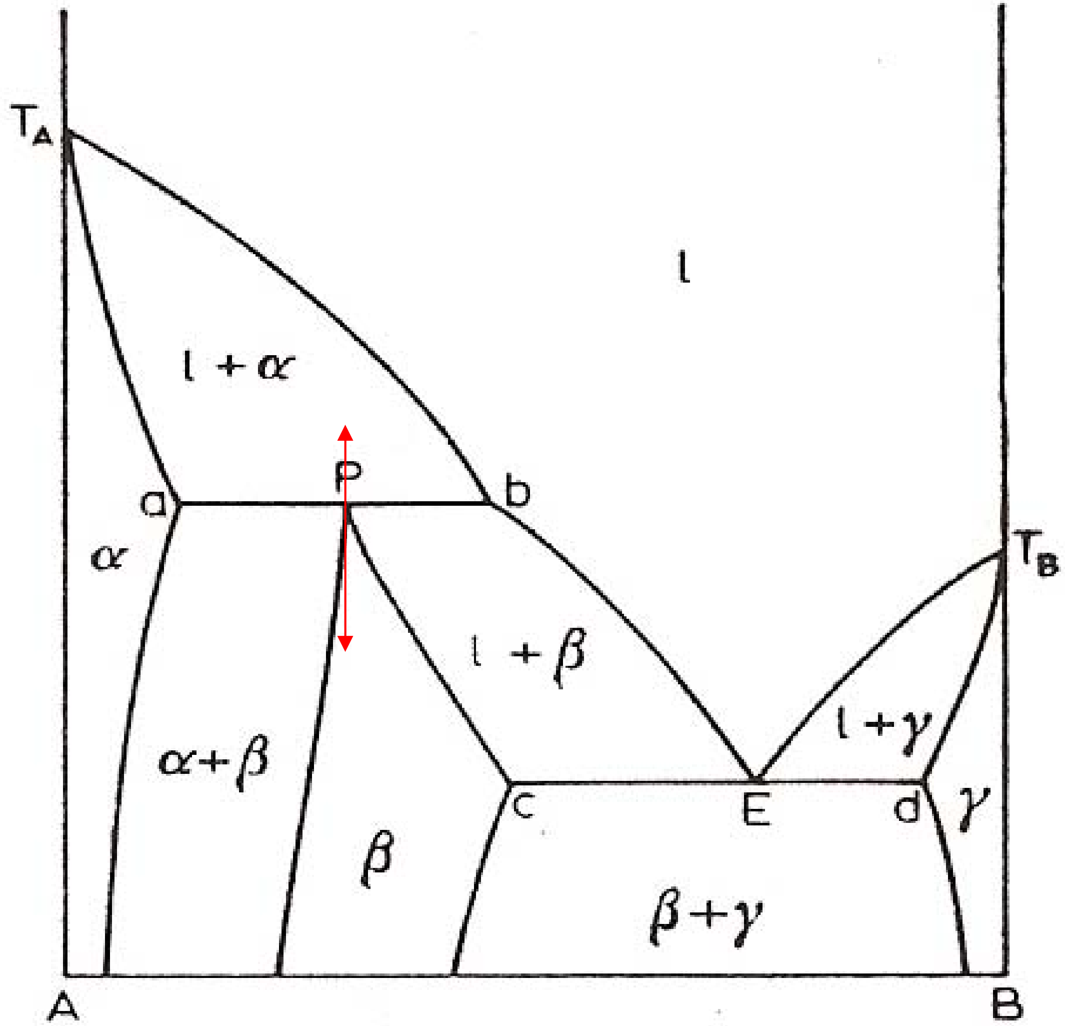


Fig. 68. Formation of an intermediate phase, β, by peritectic reaction.

4.3.4. Formation of intermediate phases by peritectic reaction

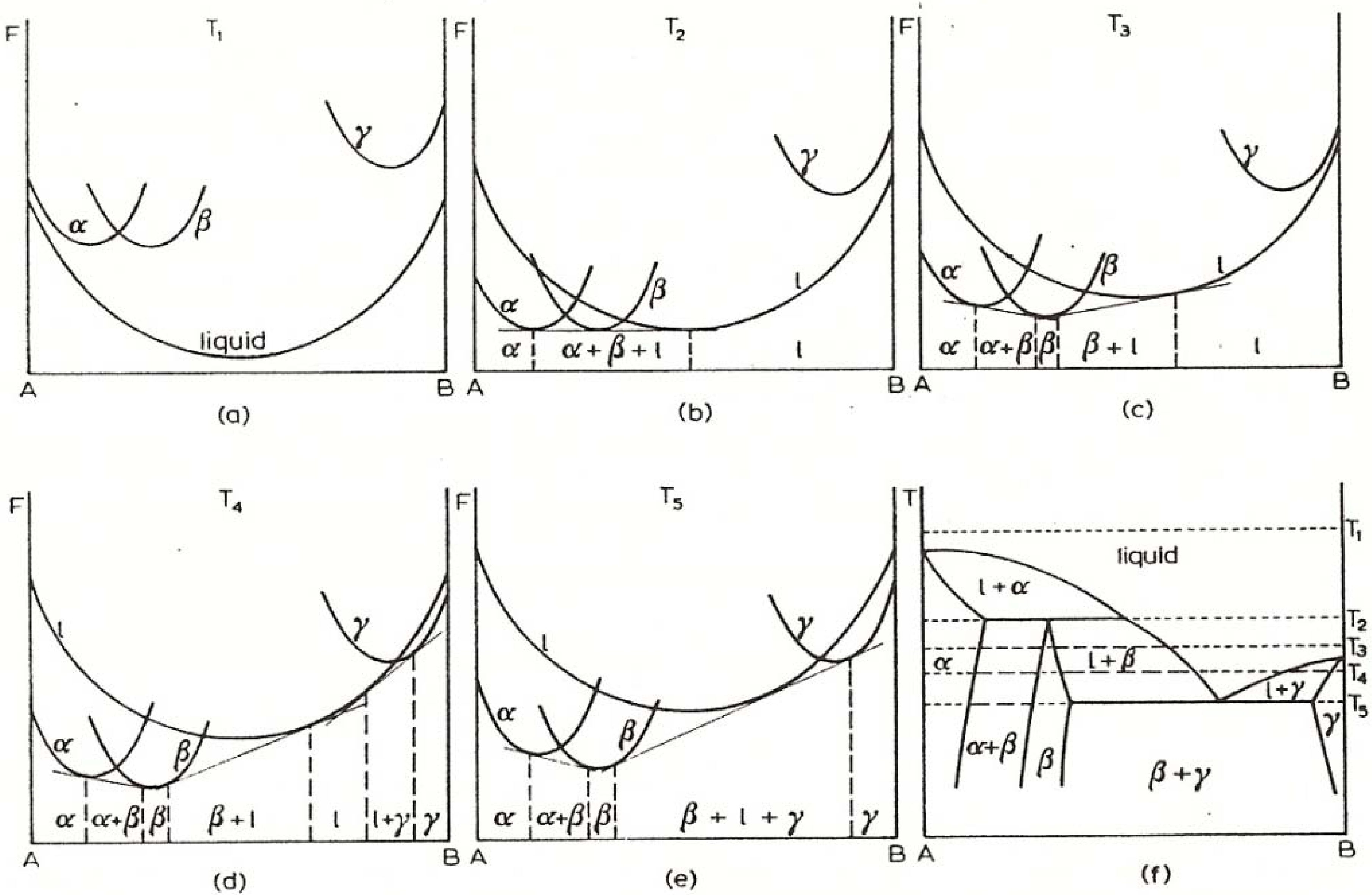


Fig. 69. Derivation of the phase diagram (Fig. 68) from the free energy curves of the liquid, α, β and γ phases. (After A. H. COTTRELL; courtesy Edward Arnold.)

4.3.4. Formation of intermediate phases by peritectic reaction

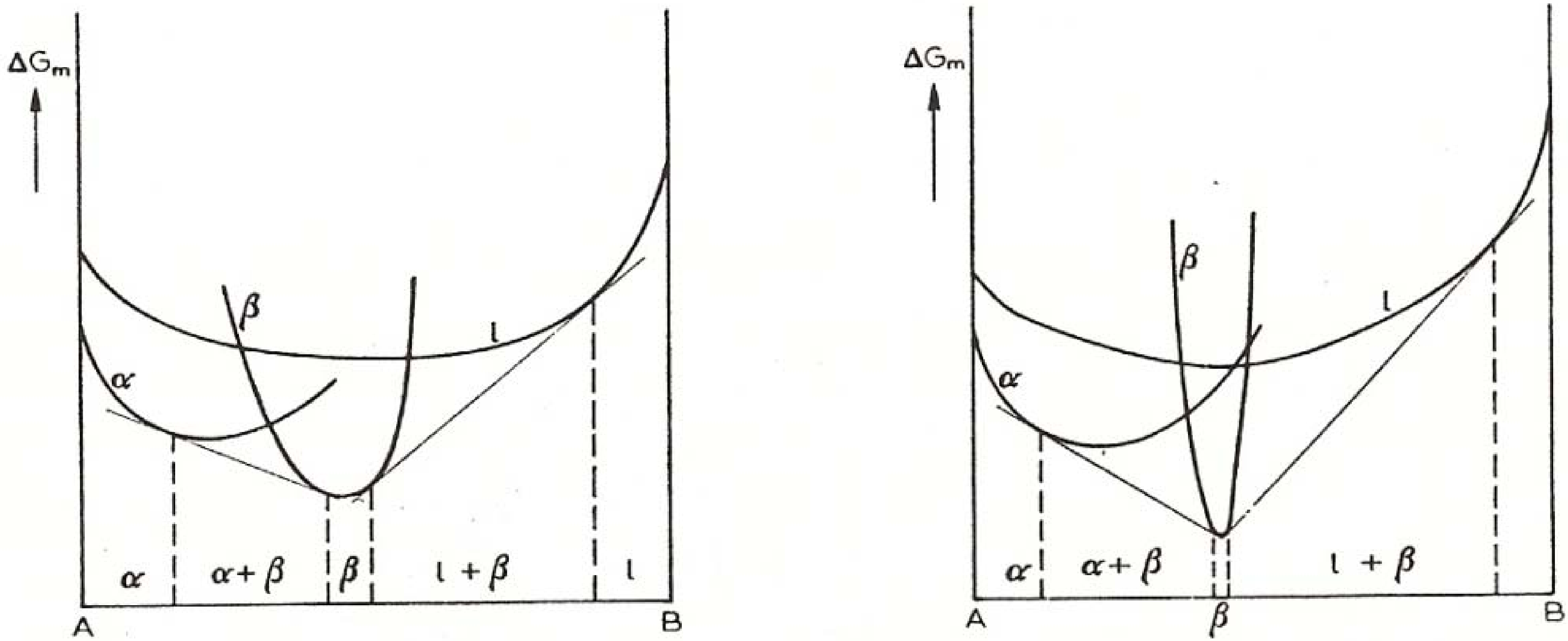


Fig. 70. Decreasing range of stability of an intermediate phase with its increasing stability relative to the termina solid solutions.

4.3.4. Formation of intermediate phases by peritectic reaction

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

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

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

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

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

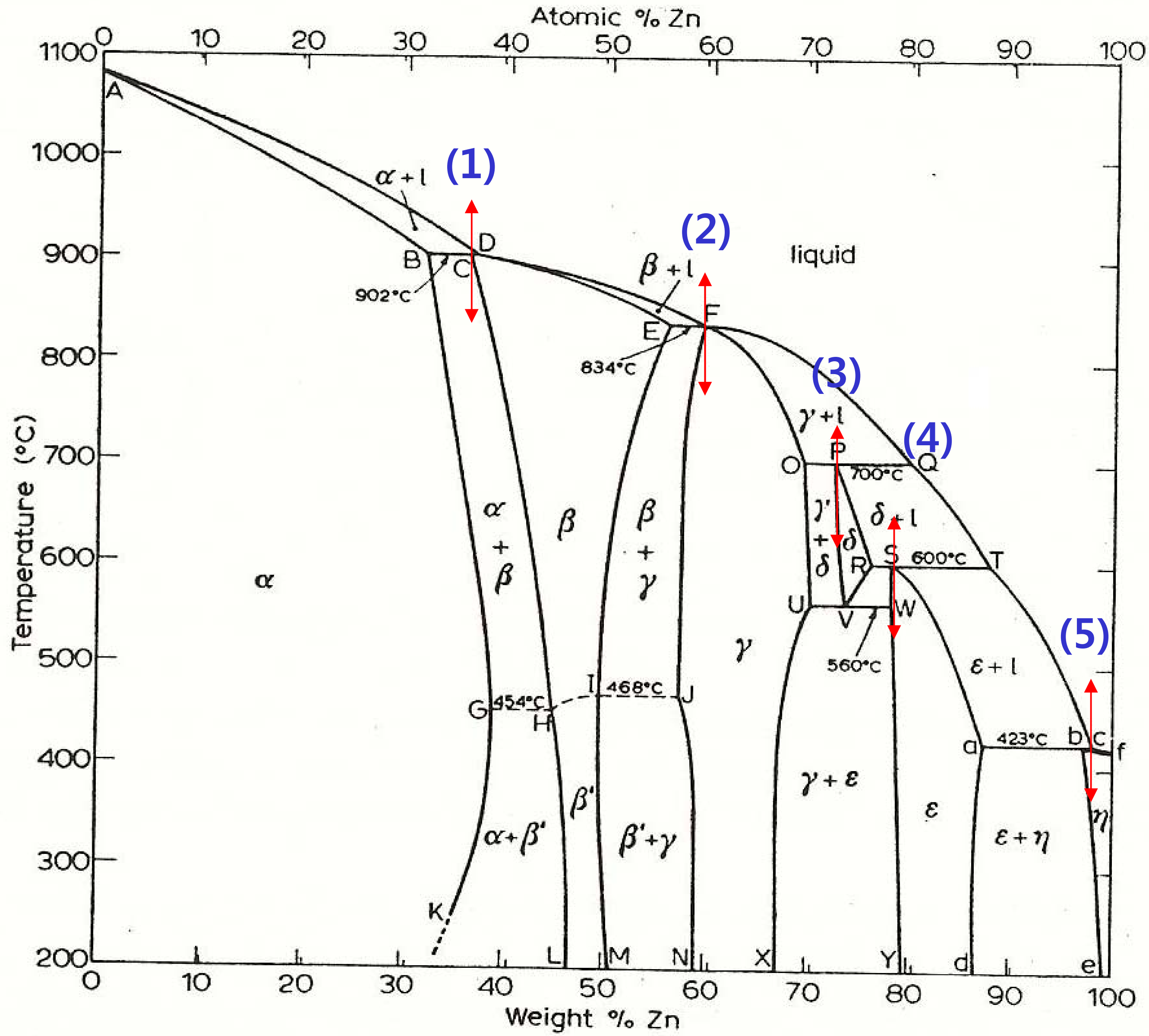


Fig. 71. The Cu–Zn phase diagram. (After G. V. RAYNOR; courtesy Institute of Metals.)

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

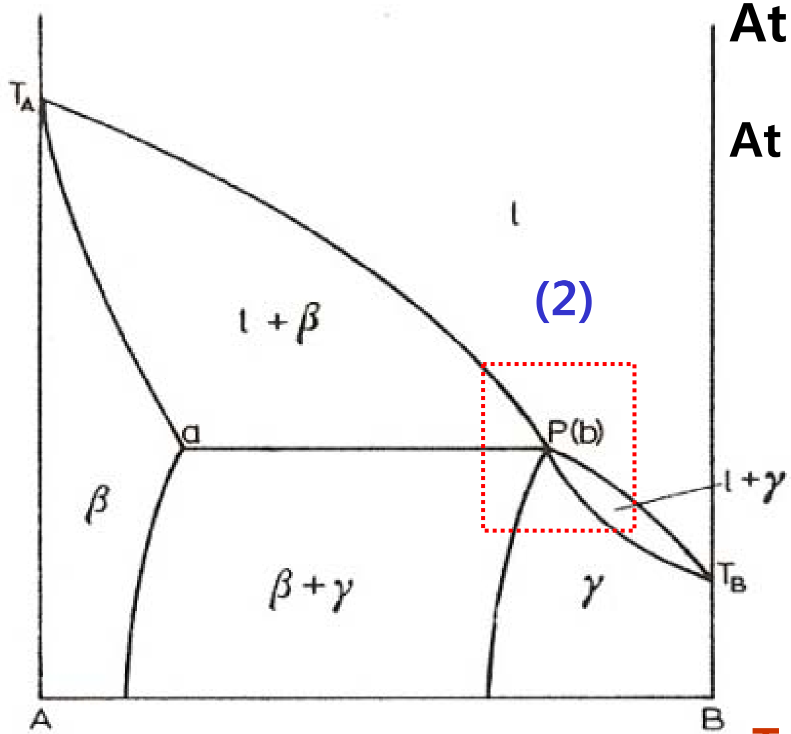


Fig. 72. Limiting case of the peritectic reaction.

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

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

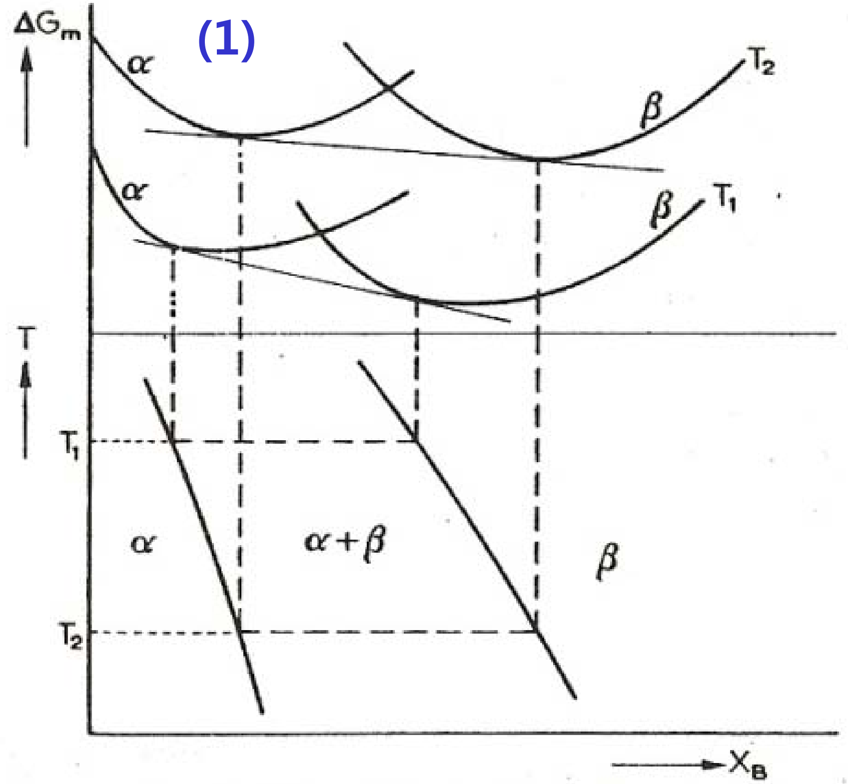
$$\boxed{X_A^S = X_A^l} \Rightarrow (S^S - S^l)\frac{dT}{dX_A} = 0$$

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

Temp. maximum or minimum must be present.

Peritectic point and the liquid composition are so close to each other that the experimental techniquies used were not able to distinguish them.

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

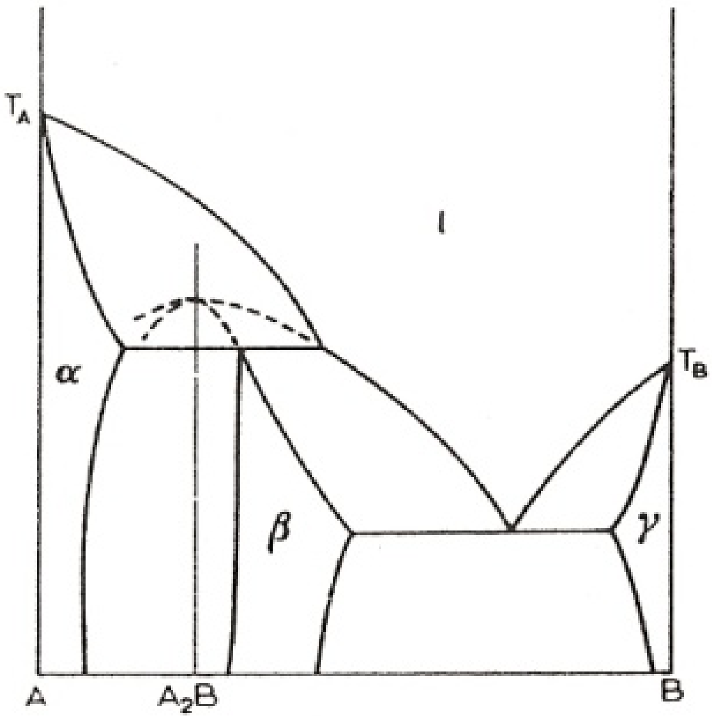


Fig. 74. A non-stoichiometric β phase based on the intermediate phase A_2B.

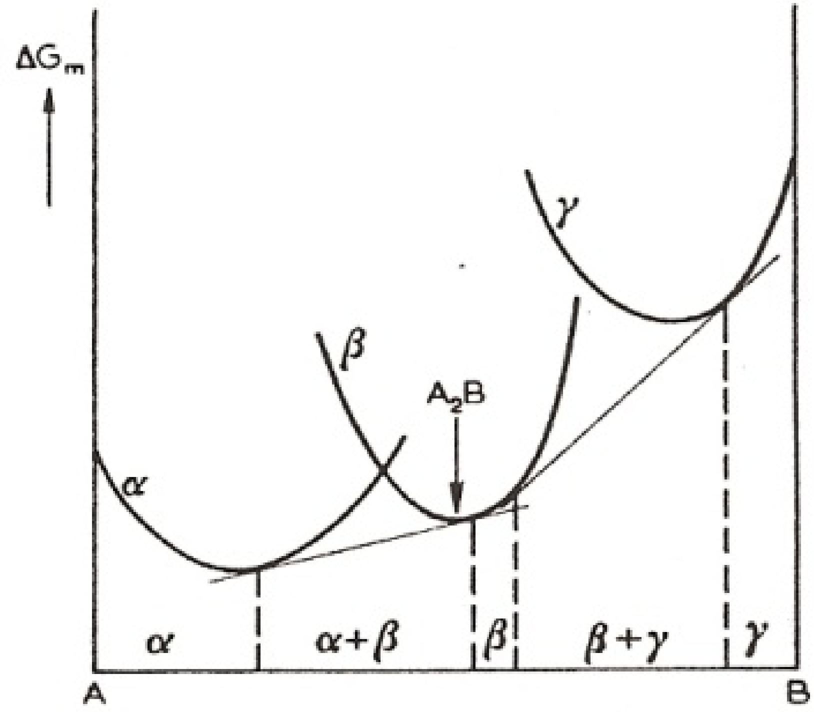
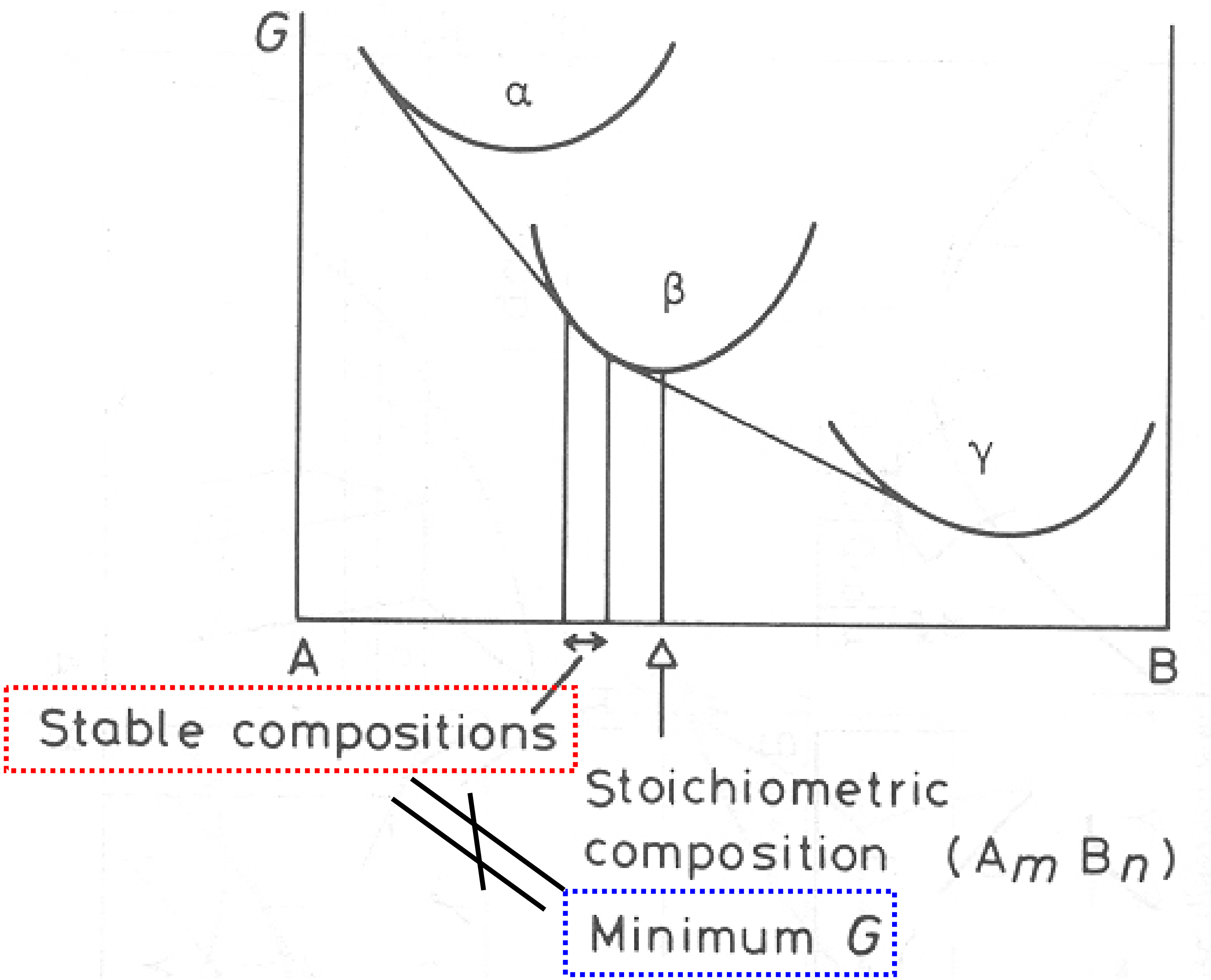


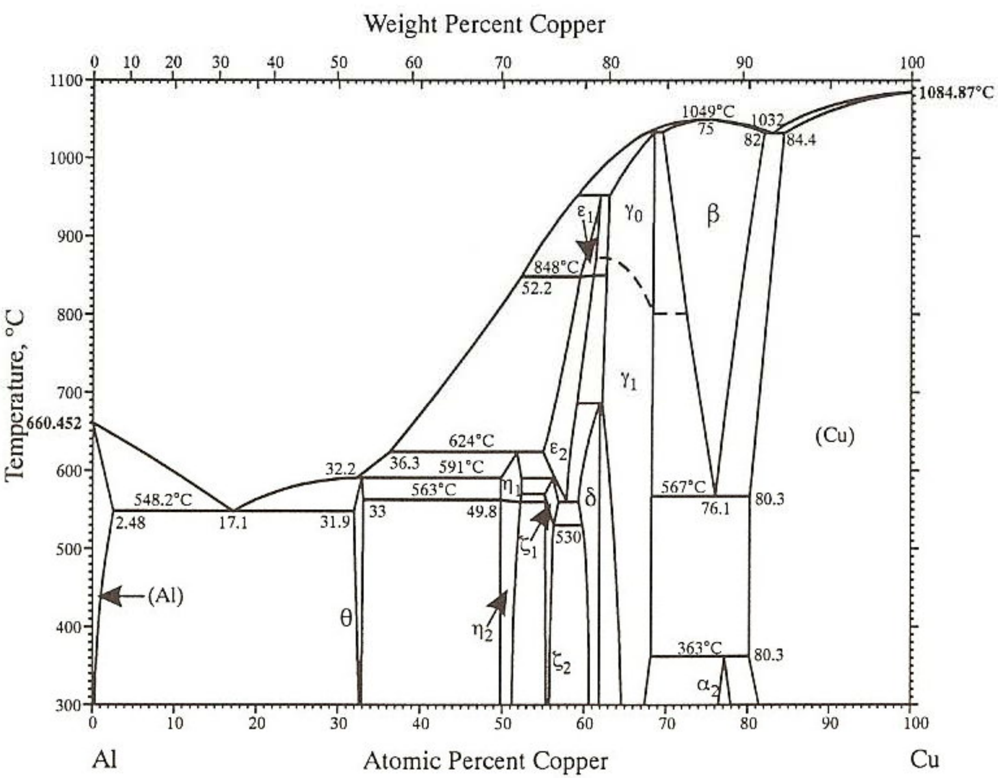
Fig. 75. Use of free energy curves to illustrate the occurrence of non-stoichiometric phases.

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	Strukturbericht 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)

4.4. Congruent transformations

Congruent transformation:

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

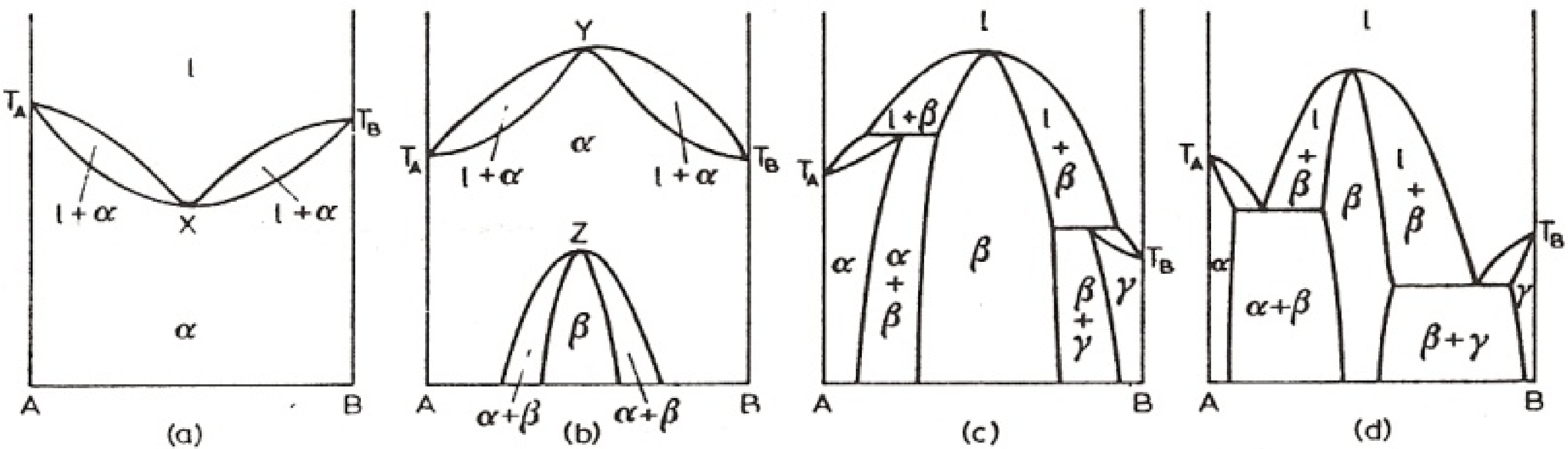


Fig. 76. Examples of congruent transformations.

4.4. Congruent transformations

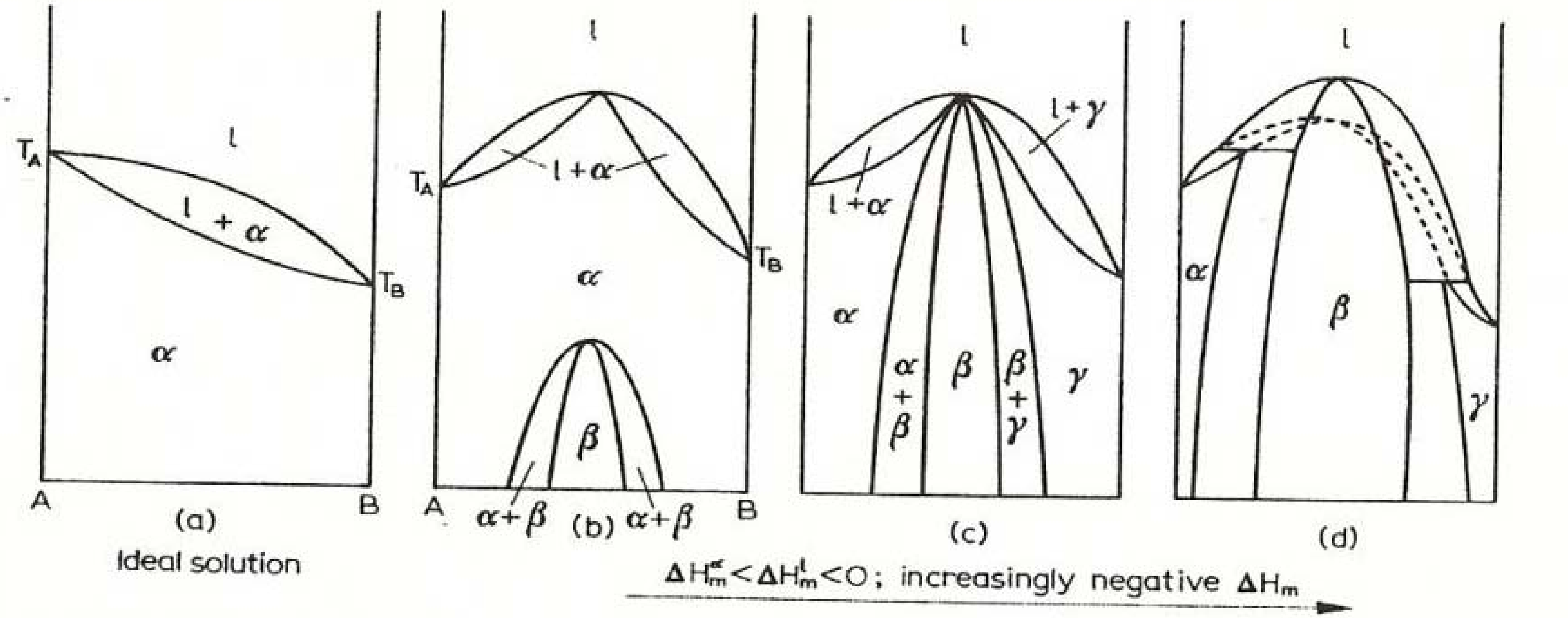


Fig. 77. Effect of increasingly negative departure from ideality in changing the phase diagram from a continuous series of solutions to one containing a congruent intermediate phase.

4.4. Congruent transformations

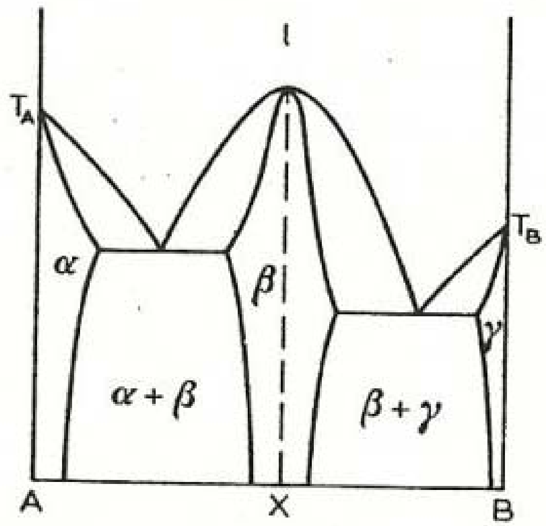


Fig. 78. Phase diagram with a congruent intermediate phase.

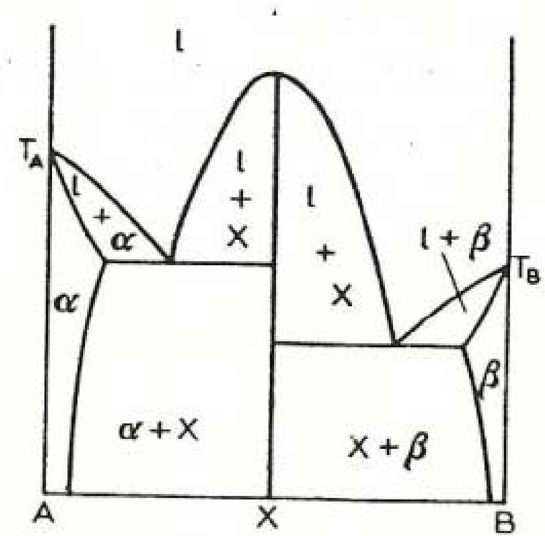
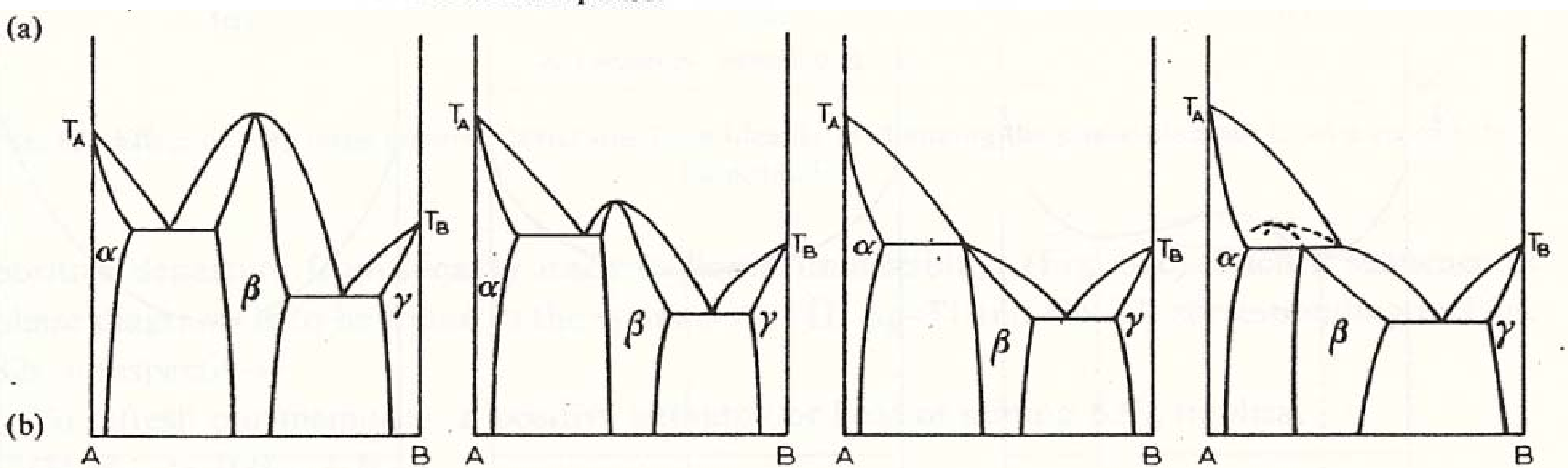


Fig. 79. Limiting case of Fig. 78.



Relationship between phase diagrams containing congruent and incongruent intermediate phases