2019 Spring

"Phase Equilibria *in* Materials"

04.29.2019

Eun Soo Park

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

- **How is the reaction in three phase region among liquid, α and β?**

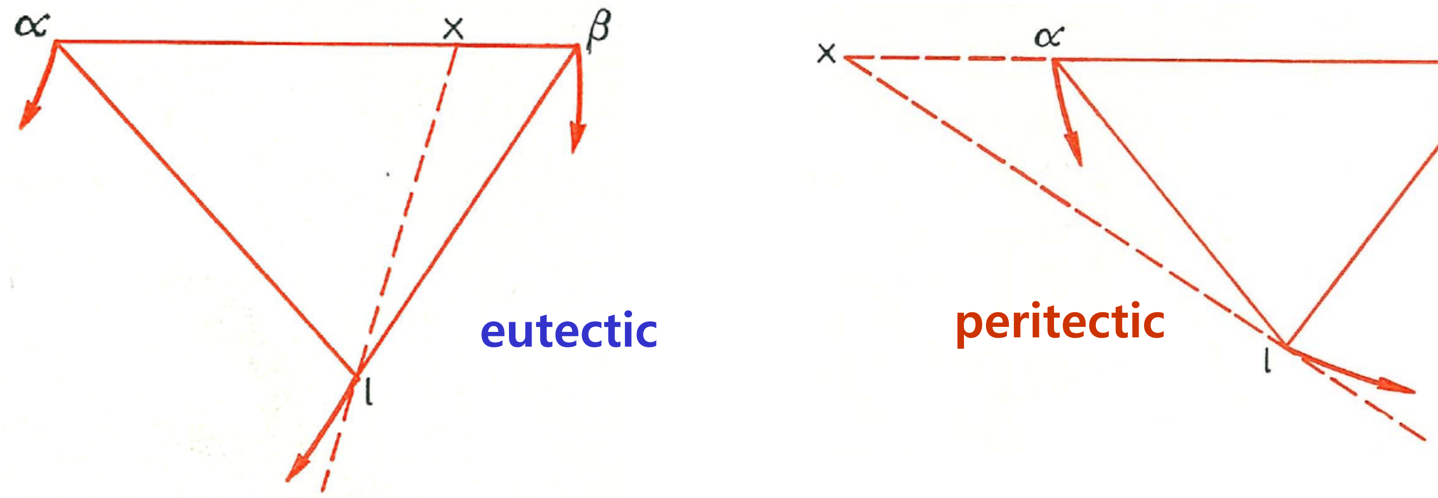


Fig. 149. Criteria for distinguishing eutectic and peritectic reactions in ternary three-phase equilibrium.

The tangent to the liquid curve at a particular temperature is extrapolated to meet the tie line connecting the α and β phases.

1) If the extrapolated line intersected the αβ tie line, the equilibrium was considered to be eutectic

2) If it met the αβ tie line only when the latter was extrapolated, the equilibrium was considered to be peritectic.

Similarly, a eutectoid reaction could be distinguished from a peritectoid and a monotectic from a syntectic.

9.3. THREE-PHASE EQUILIBRIUM INVOLVING EUTECTIC REACTIONS

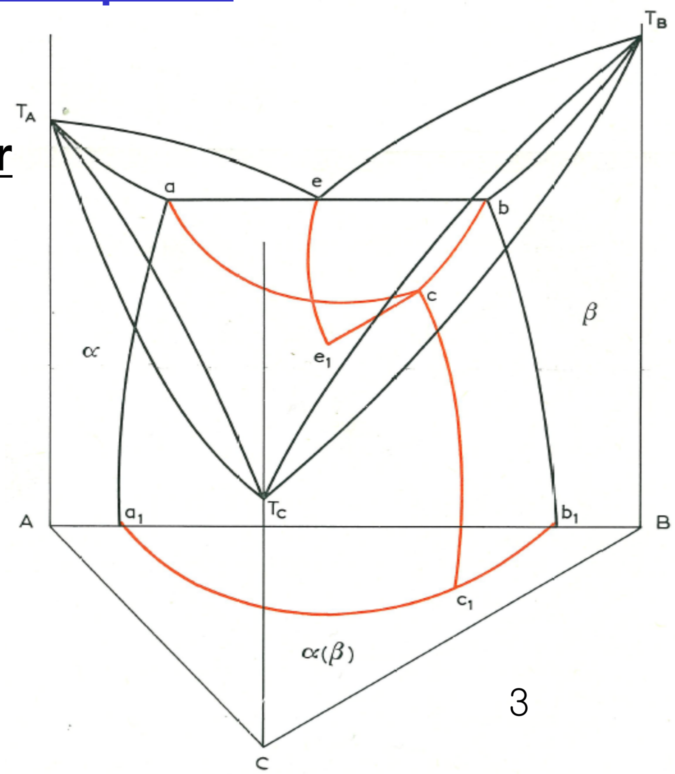
- **How is the reaction in three phase region?**

<Hillert's criterion>

Basically, the reaction we can expect is eutectic reaction

($l \rightarrow \alpha + \beta$). But, in reality, we can have eutectic and peritectic reaction depending on the relative amount of three phase.

The average composition of the alloy then determines for a particular temperature whether the reaction will be eutectic or peritectic.



A small change in temperature, d*T*, causes a small change in the composition and amounts of each phase, but not of the alloy itself,

$$X_A, X_B, X_C = \text{constant}, \Delta X_A = 0, \text{ and } \Delta m_\alpha + \Delta m_\beta + \Delta m_l = 0$$

$$\Delta X_A = m_\alpha \cdot \Delta X_A^\alpha + m_\beta \cdot \Delta X_A^\beta + m_l \cdot \Delta X_A^l + X_A^\alpha \cdot \Delta m_\alpha + X_A^\beta \cdot \Delta m_\beta + X_A^l \cdot \Delta m_l = 0$$

1) Assumption, $X_A^\beta = X_A^l > X_A^\alpha$

(New coordinate system)

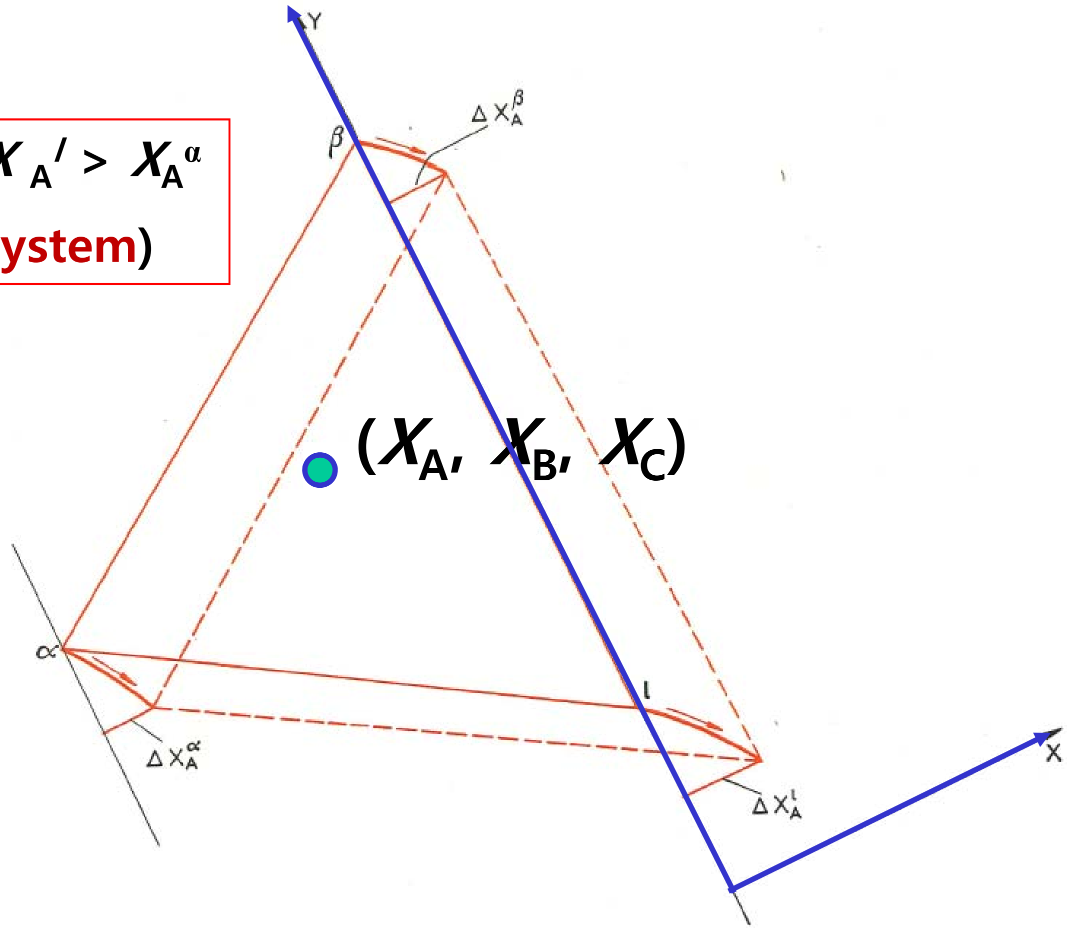


Fig. 150. Illustration of Hillert's criterion for distinguishing eutectic and peritectic reaction in ternary three-phase equilibrium; ———, equilibrium at T; – – – – – –, equilibrium at $T-dT$.

To simplify the calculation,

Assumption, $X_A^\beta = X_A^l > X_A^\alpha$ (New coordinate system) $\Delta m_\beta + \Delta m_l = -\Delta m_\alpha$

$$\Delta X_A = m_\alpha \cdot \Delta X_A^\alpha + m_\beta \cdot \Delta X_A^\beta + m_l \cdot \Delta X_A^l + X_A^\alpha \cdot \Delta m_\alpha + X_A^\beta \cdot \Delta m_\beta + X_A^l \cdot \Delta m_l = 0$$

$$-X_A^\alpha \Delta m_\alpha - X_A^\beta \Delta m_\beta - X_A^l \Delta m_l = m_\alpha \Delta X_A^\alpha + m_\beta \Delta X_A^\beta + m_l \Delta X_A^l$$

$$\Delta m_\alpha (X_A^\beta - X_A^\alpha) = m_\alpha \Delta X_A^\alpha + m_\beta \Delta X_A^\beta + m_l \Delta X_A^l$$

Sign	Assumption	Sign
$\Delta m_\alpha (X_A^\beta - X_A^\alpha)$	$X_A^\beta = X_A^l > X_A^\alpha$	$m_\alpha \Delta X_A^\alpha + m_\beta \Delta X_A^\beta + m_l \Delta X_A^l$
$\Delta m_\beta (X_A^\alpha - X_A^\beta)$	$X_A^\alpha = X_A^l > X_A^\beta$	$m_\alpha \Delta X_A^\alpha + m_\beta \Delta X_A^\beta + m_l \Delta X_A^l$
$\Delta m_l (X_A^\alpha - X_A^l)$	$X_A^\alpha = X_A^\beta > X_A^l$	$m_\alpha \Delta X_A^\alpha + m_\beta \Delta X_A^\beta + m_l \Delta X_A^l$

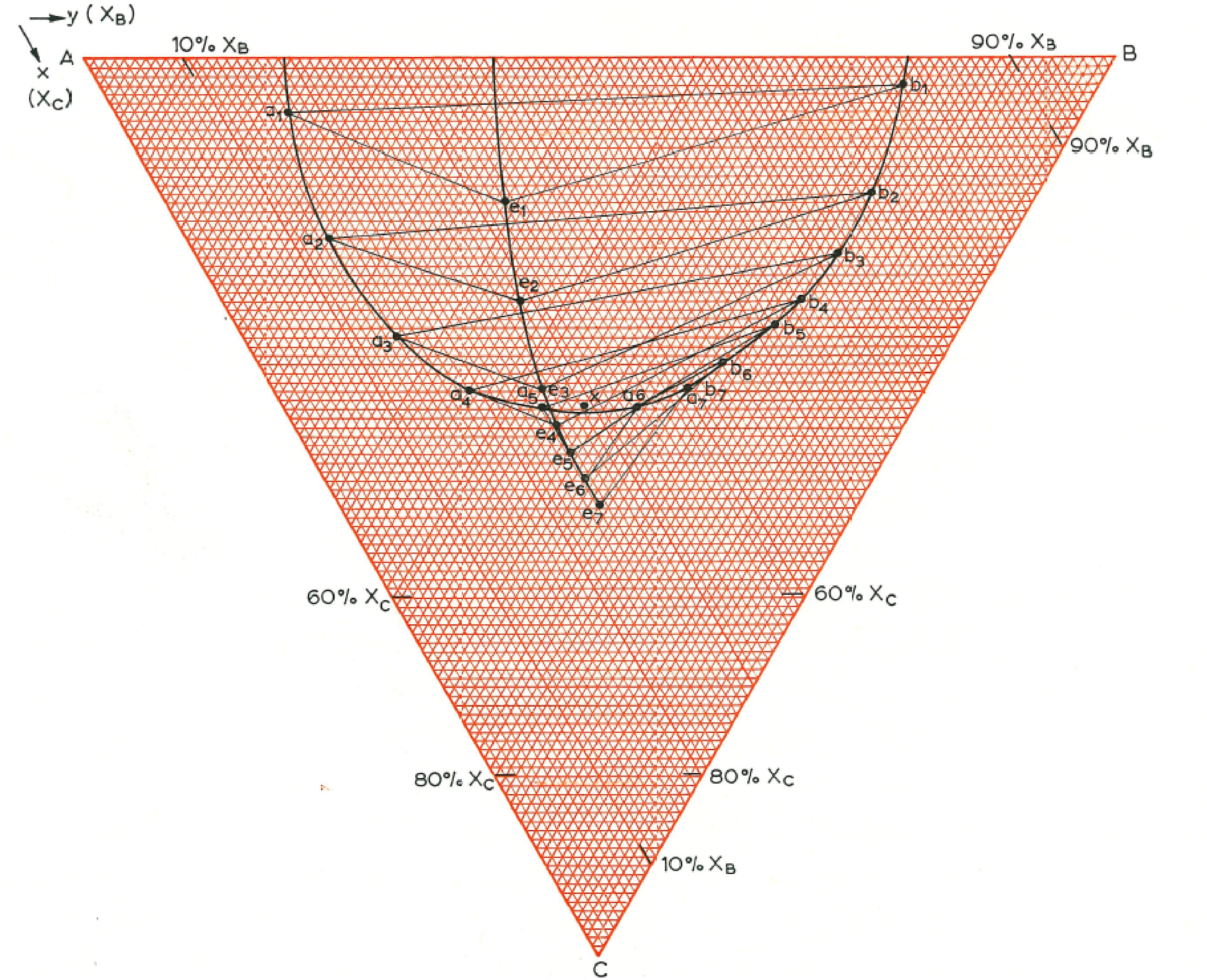
here, Δm_α : change of α phase fraction with ΔT

Δm_α	Δm_β	Δm_l		
+	+	-	$l \rightarrow \alpha + \beta$	eutectic
+	-	-	$l + \beta \rightarrow \alpha$	peritectic
-	+	-	$l + \alpha \rightarrow \beta$	peritectic

Hillert's criterion indicates that the relative amounts of the α, β and liquid phases (the average alloy composition) are of importance in determining the type of reaction.

9.3. THREE-PHASE EQUILIBRIUM INVOLVING EUTECTIC REACTIONS

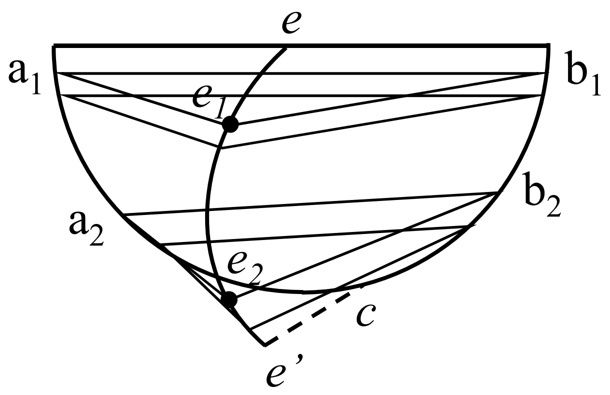
- **three phase regions $a_1e_1b_1$, $a_2e_2b_2$, … , $a_7e_7(b_7)$ projected on the concentration triangle.**



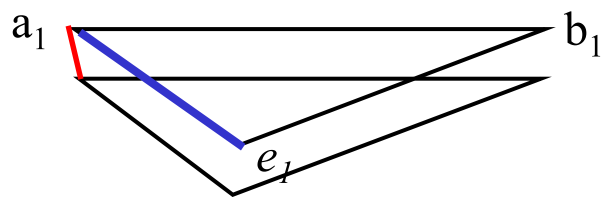
To determine whether the reaction is always a monovariant eutectic type, irrespective of alloy composition within the three-phase region, we apply Hillert's criterion to each pair of isotherms.

9.3. THREE-PHASE EQUILIBRIUM INVOLVING EUTECTIC REACTIONS

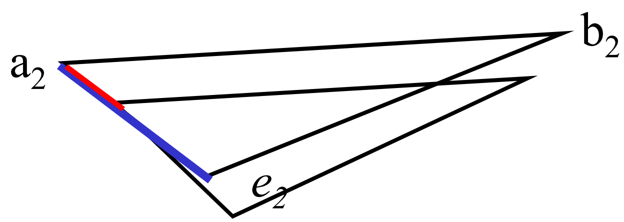
- **Relative position of vertex in tie triangle with ΔT**

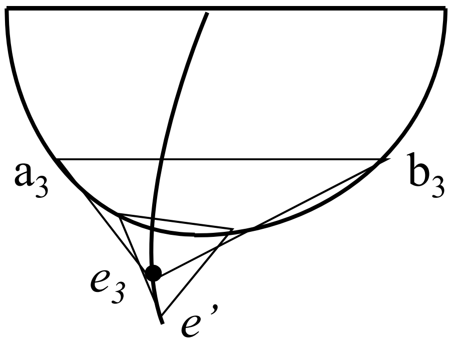


① Slope of tangent line at a_1 > slope of line a_1e_1

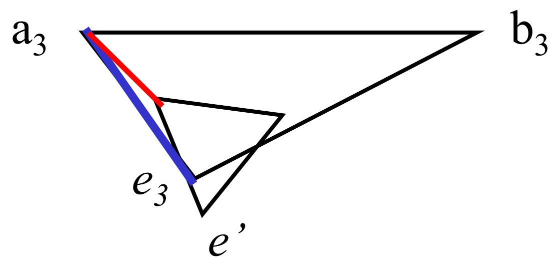


② Slope of tangent line at a_2 = slope of line a_2e_2





③ Slope of tangent line at a_3 < slope of line a_3e_3



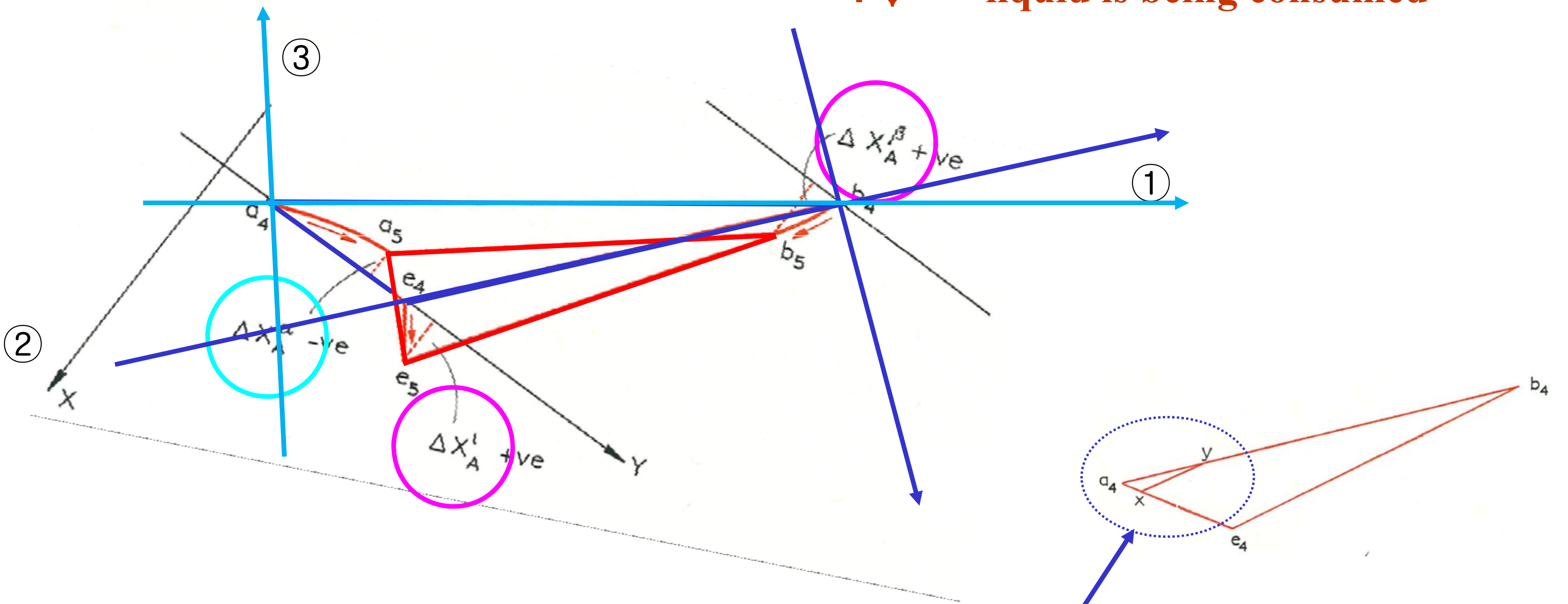
Consider tie triangle $a_4e_4b_4$, and $a_5e_5b_5$

① $X_A^{\beta} = X_A^{l} > X_A^{\alpha}$

$m_\alpha \Delta X_A^{\alpha}(+) + m_\beta \Delta X_A^{\beta}(+) + m_l \Delta X_a^{l}(+) \rightarrow \Delta m_\alpha (+) \ \ \Delta m_l (-) \rightarrow m_\alpha \Delta X_A^{\alpha}(-) + m_\beta \Delta X_A^{\beta}(-) + m_l \Delta X_a^{l}(-)$

③ $X_A^{\alpha} = X_A^{\beta} > X_A^{l}$

T↓ → liquid is being consumed



② $X_A^{\alpha} = X_A^{l} > X_A^{\beta}$ $\quad \Delta m_\beta \rightarrow m_\alpha \Delta X_A^{\alpha}(-) + m_\beta \Delta X_A^{\beta}(+) + m_l \Delta X_a^{l}(+)$

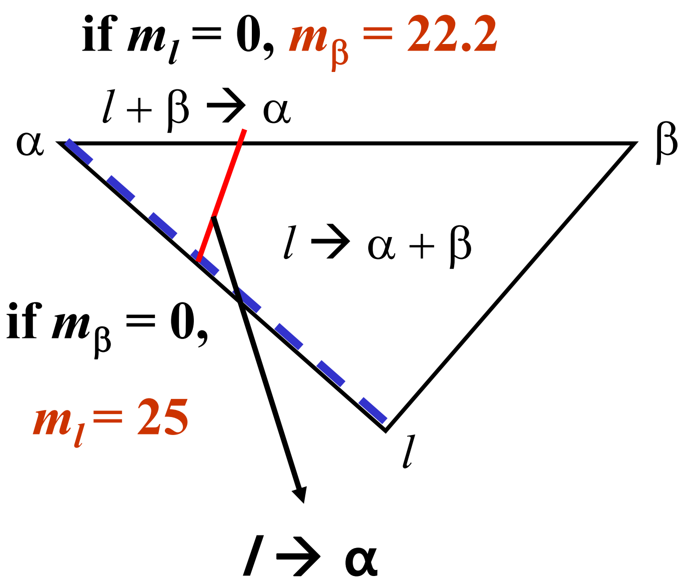
❖ $\Delta m_\alpha(+)$, Δm_l (-); if m_α is very larger than m_β and m_l → Δm_β (-) → (l + β → α)

if m_α is much smaller than m_β *and* m_l → Δm_β (+) → (l → α + β)

9.3. THREE-PHASE EQUILIBRIUM INVOLVING EUTECTIC REACTIONS

- **How to decide the boundary btw eutectic & peritectic?**

Reactions in the tie triangle $a_4e_4b_4$,



along boundary, β plays no role → $l = \alpha$

$$X_A^\alpha = X_A^l > X_A^\beta$$

$$\Delta m_\beta (X_A^\alpha - X_A^\beta) = m_\alpha \Delta X_A^\alpha + m_\beta \Delta X_A^\beta + m_l \Delta X_A^l$$

$(\Delta X_A^\alpha = -1, \Delta X_A^\beta = 3.5, \Delta X_A^l = 3)$ **(next page)**

$-m_\alpha + 3.5 m_\beta + 3 m_l = 0 \quad (m_\alpha + m_\beta + m_l = 100)$

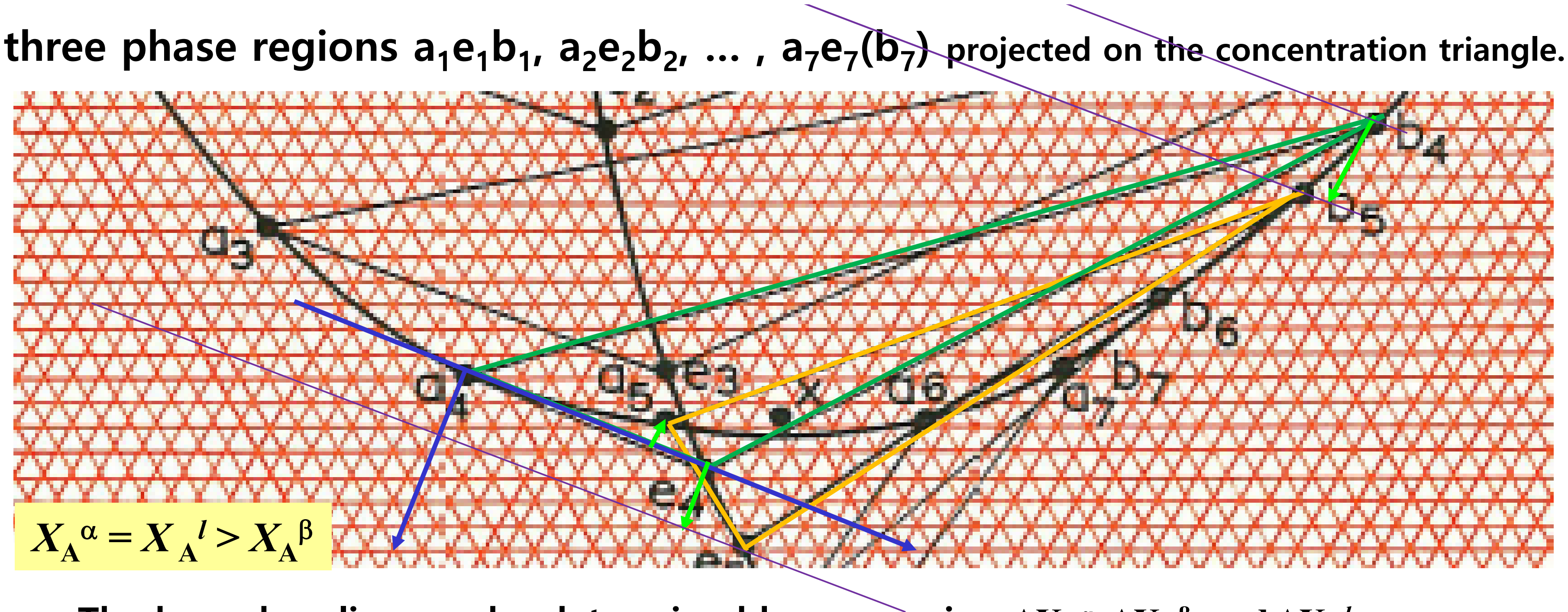
$-100 + 4.5 m_\beta + 4 m_l = 0$

if $m_\beta = 0$, $m_l = 25$

if $m_l = 0$, $m_\beta = 22.2$

Initially, peritectic region confined the α corner.
Consideration of three-phase triangles at lower temperatures will indicate that the peritectic region sweeps round from the α corner towards the β and liquid corners.

• **three phase regions $a_1e_1b_1$, $a_2e_2b_2$, ... , $a_7e_7(b_7)$** projected on the concentration triangle.



The boundary line can be determined by measuring ΔX_A^{α}, ΔX_A^{β}, and ΔX_A^{l}.

In Fig. 151,
ΔX_A^{α}= -1, ΔX_A^{β}= -3.5 and ΔX_A^{l}=3 units.

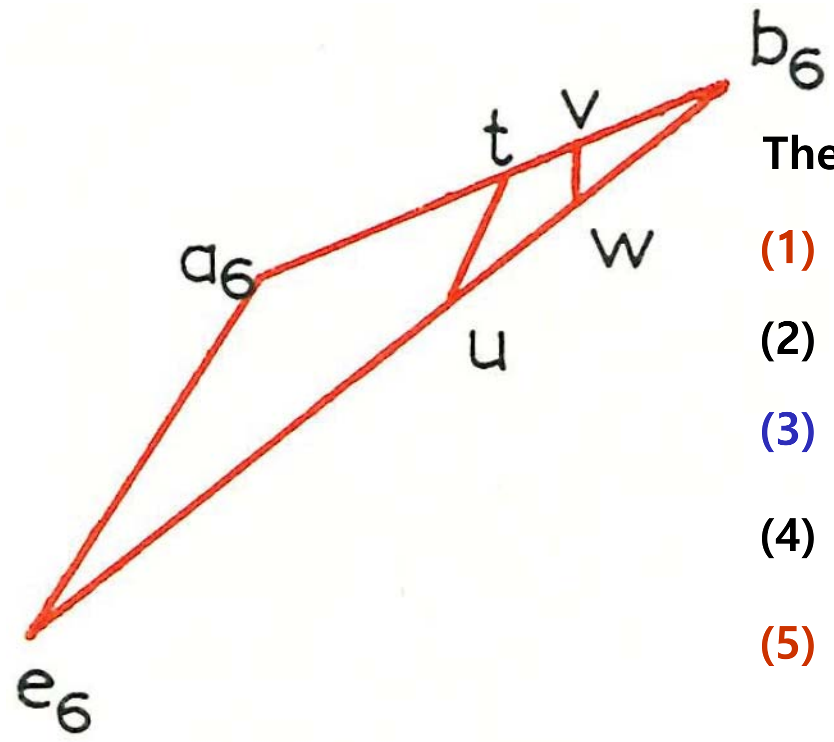
Figure 151

Table 2

	X_B,	X_C		X_B,	X_C		X_B,	X_C
e_1	33,	16	a_1	17,	6	b_1	78,	3
e_2	29,	27	a_2	14,	20	b_2	69,	15
e_3	26,	37	a_3	15,	31	b_3	62,	22
e_4	25.3,	41	a_4	19,	37	b_4	56,	27
e_5	25,	44	a_5	25,	39	b_5	52,	30
e_6	25,	47	a_6	34,	39	b_6	45,	34
e_7	25,	50	$a_7(b_7)$	40,	37			

Monovariant β curve coincides with the lα tie line between isotherms $a_5e_5b_5$ and $a_6e_6b_6$

➡ **Second peritectic reaction area appears at the β corner of the three–phase triangle**



The tie triangle $a_6e_6b_{6,}$, reaction equilibria

(1) Peritectic l + β ↔ α in area $a_6e_6$ut

(2) Two-phase l ↔ α along line tu

(3) eutectic l ↔ α+β in area tuwv

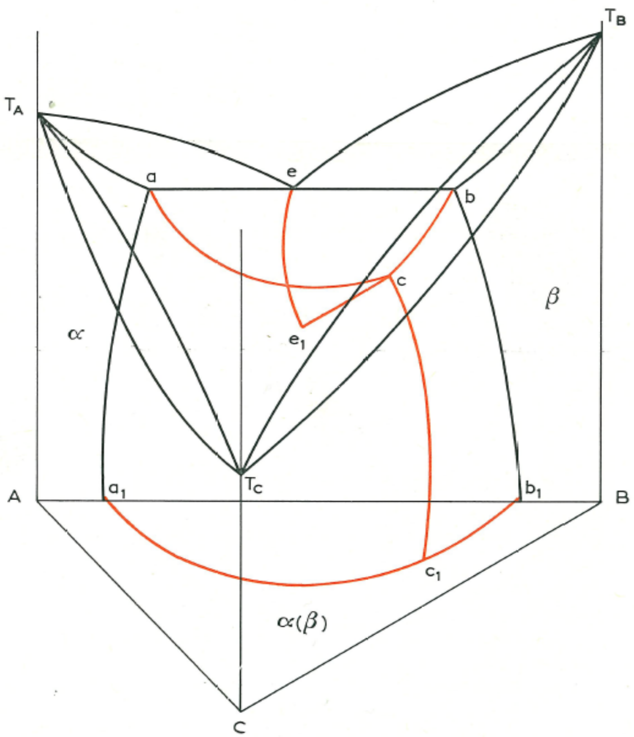
(4) two-phase l ↔ β along line vw

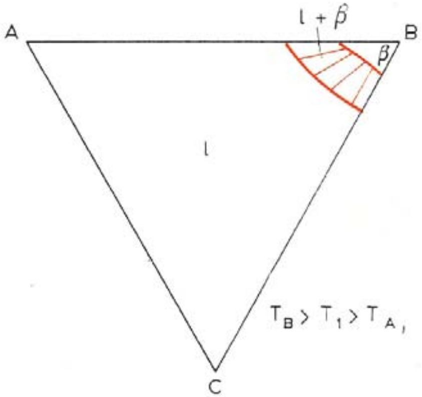
(5) Peritectic l + α ↔ β in area $b_6$vw

To summarise, the three-phase reaction is initially eutectic for all alloys untill the temperature of the three phase triangle $a_4e_4b_{4,}$ is reached.
From that temperature until the end of the three-phase reaction at the tie line $e_7a_7(b_7)$, the reaction type is dependent on the alloy composition within the sequence of the three-phase triangles.

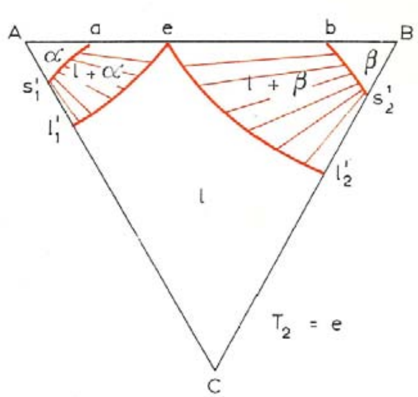
9.3. THREE-PHASE EQUILIBRIUM INVOLVING EUTECTIC REACTIONS

- **Isothermal section**

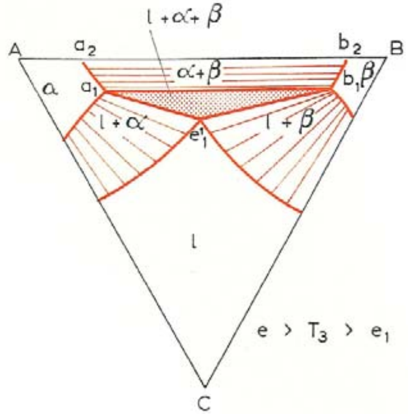




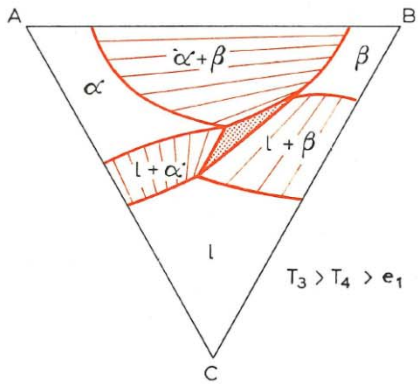
$T_B > T_1 > T_A$



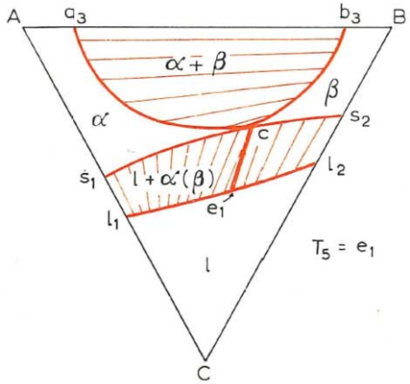
$T_2 = e$



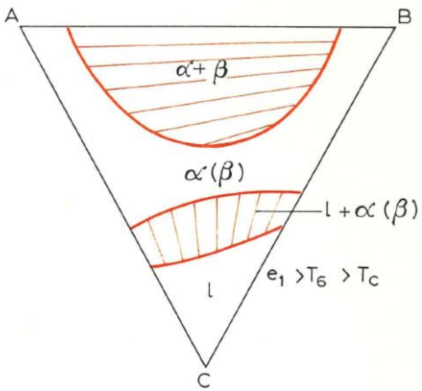
$e > T_3 > e_1$



$T_3 > T_4 > e_1$



$T_5 = e$



$e_1 > T_6 > T_c$

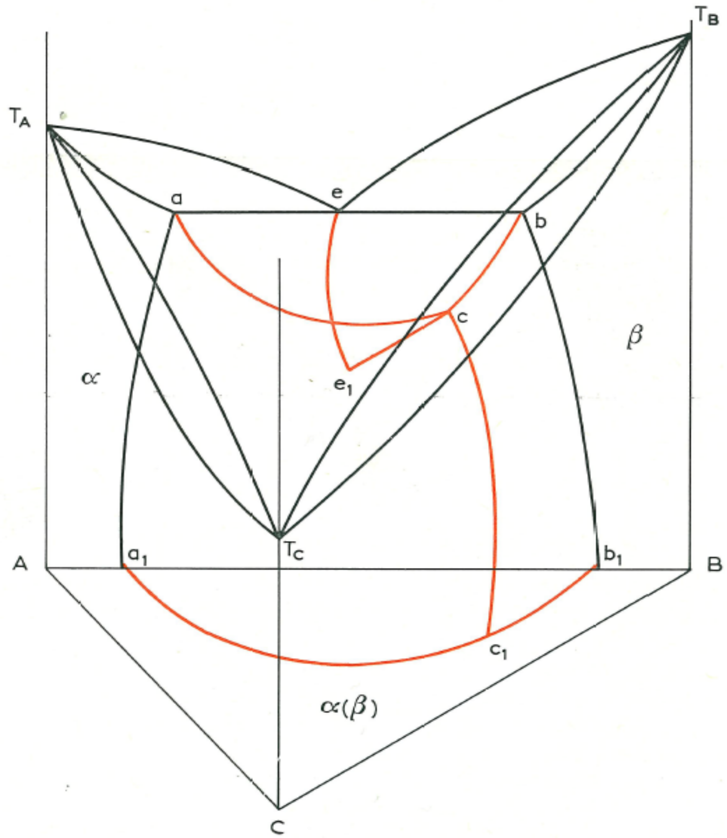
A-B: eutectic

A-C/B-C: continuous series of solid soln

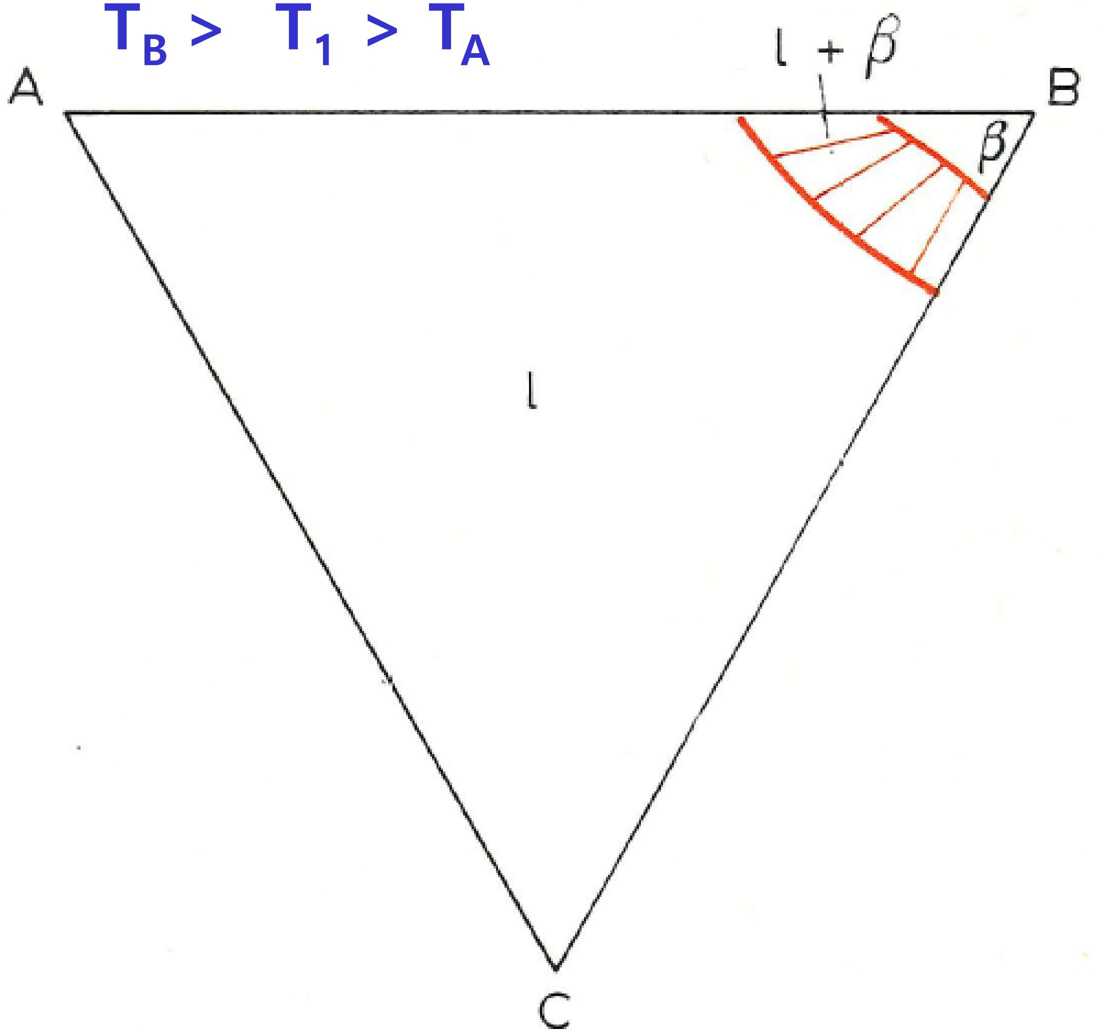
cf) Movie

9.3. THREE-PHASE EQUILIBRIUM INVOLVING EUTECTIC REACTIONS

- **Isothermal section**

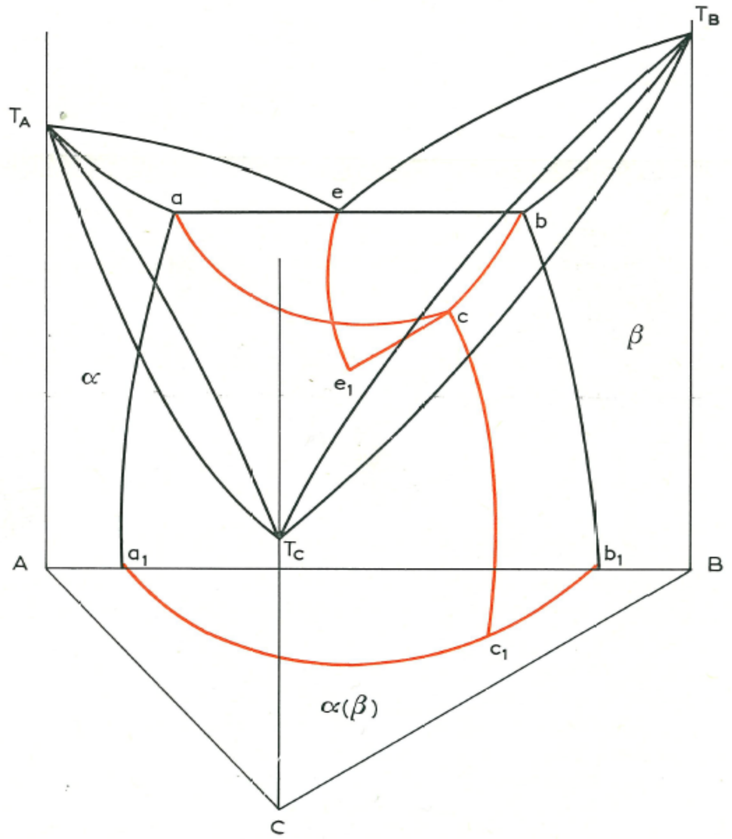


$T_B > T_1 > T_A$

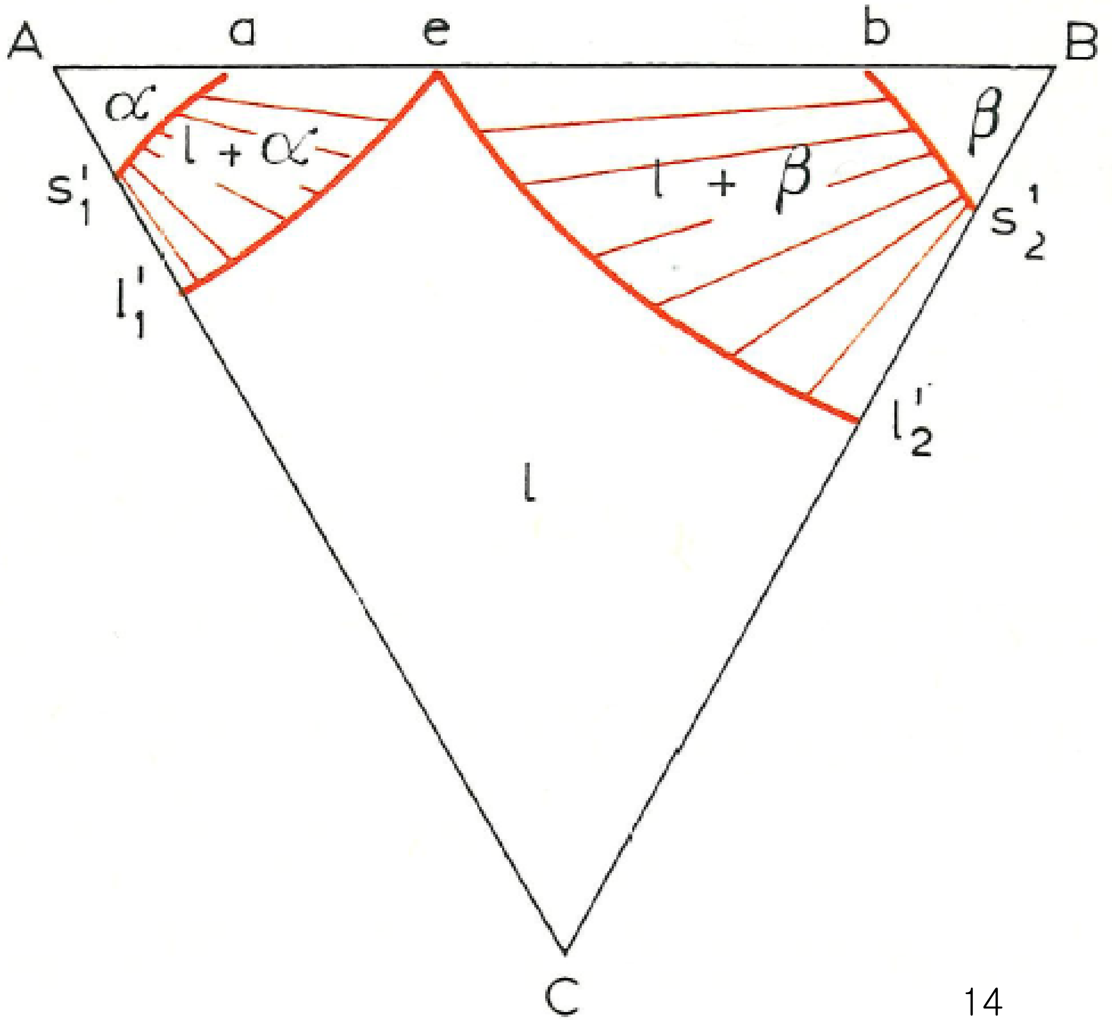


9.3. THREE-PHASE EQUILIBRIUM INVOLVING EUTECTIC REACTIONS

- **Isothermal section**

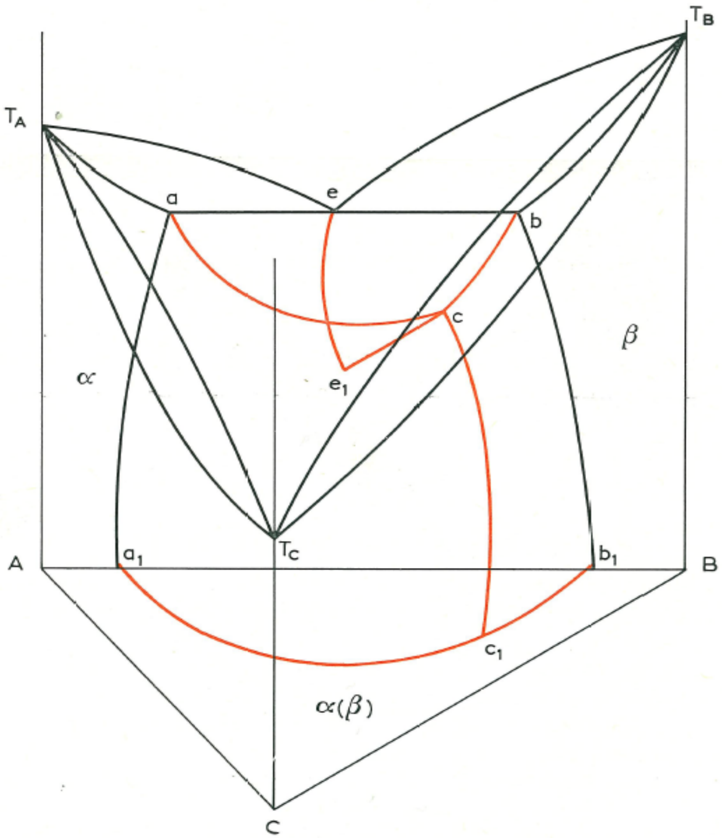


T_2 = e

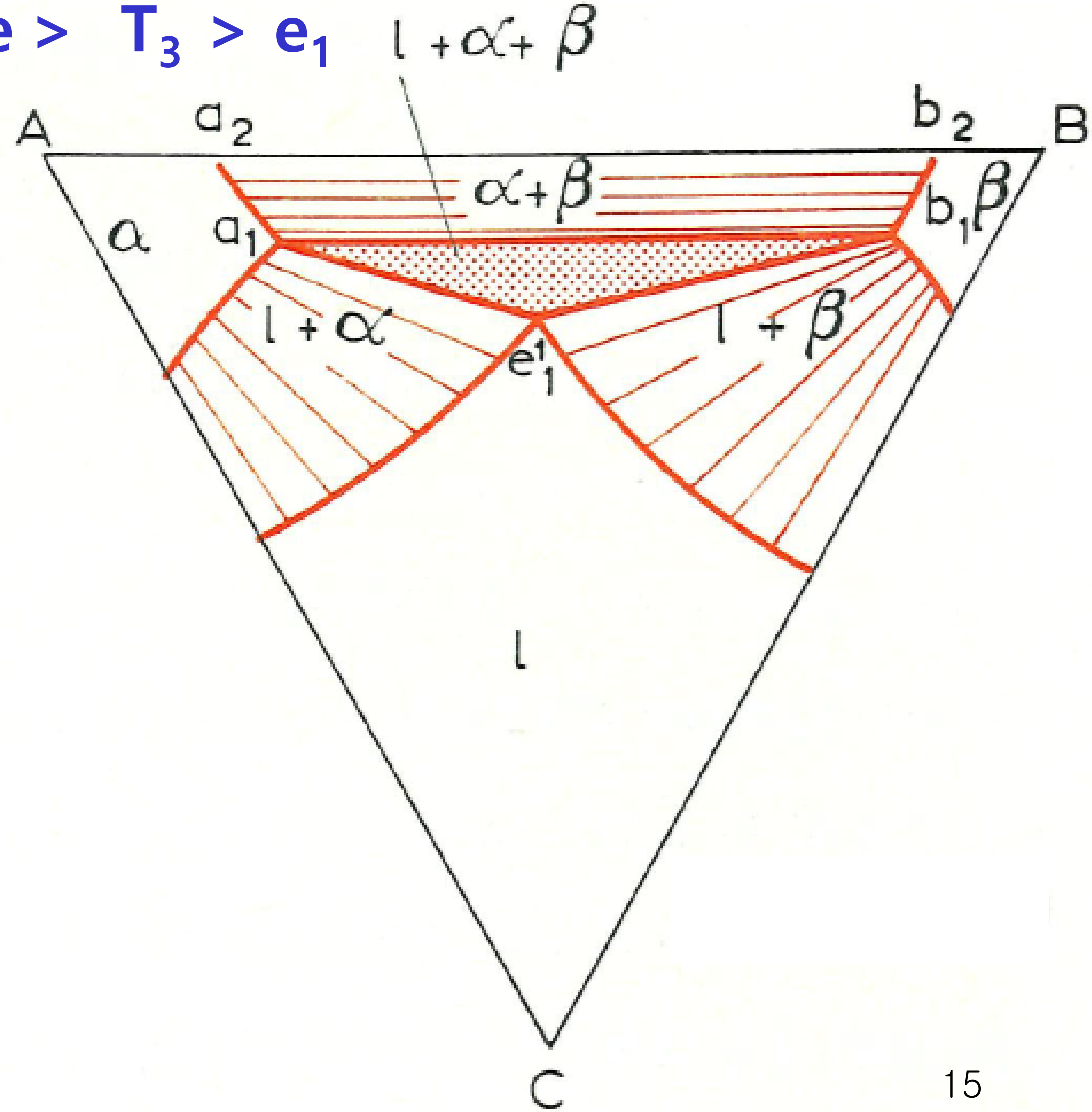


9.3. THREE-PHASE EQUILIBRIUM INVOLVING EUTECTIC REACTIONS

- **Isothermal section**

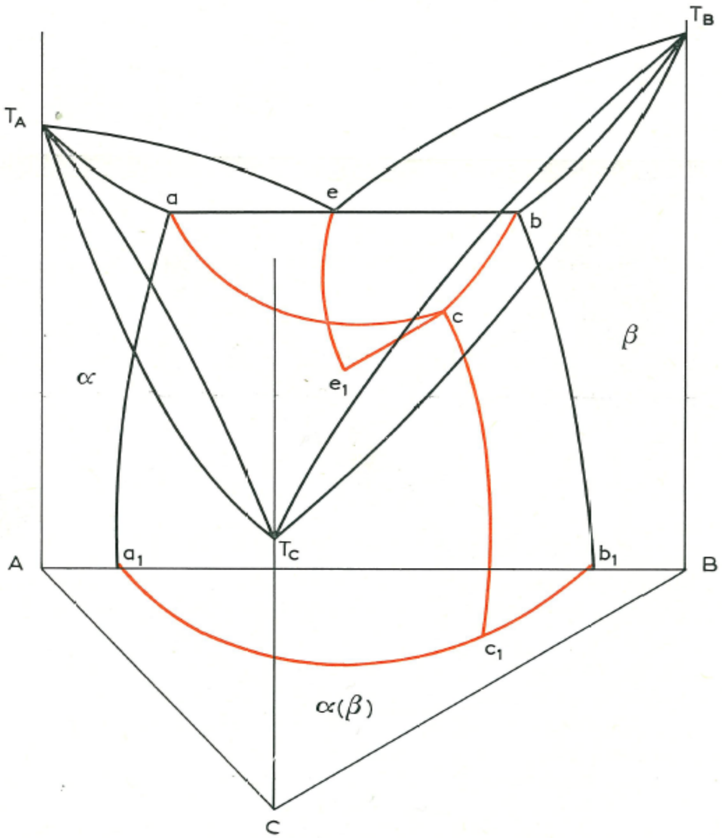


$e > T_3 > e_1$

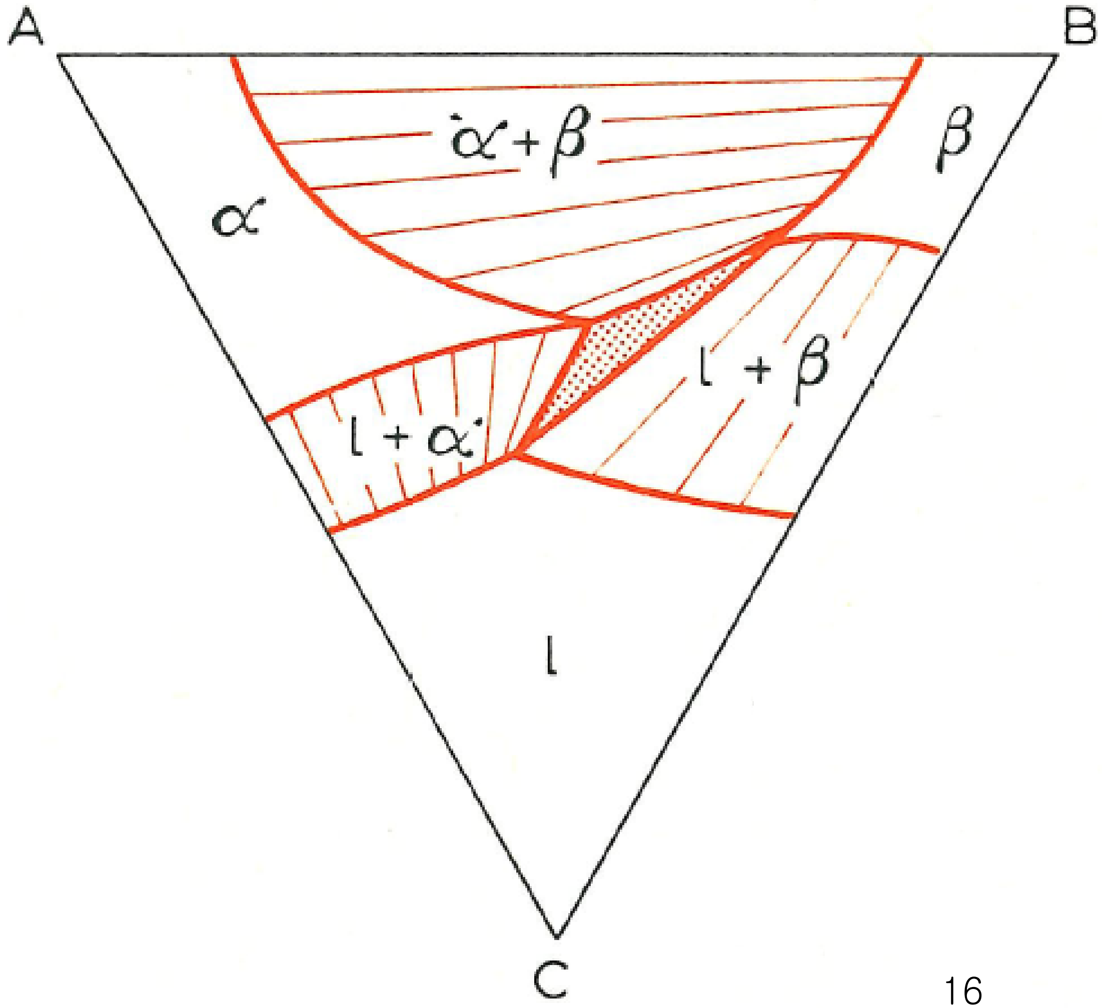


9.3. THREE-PHASE EQUILIBRIUM INVOLVING EUTECTIC REACTIONS

- **Isothermal section**

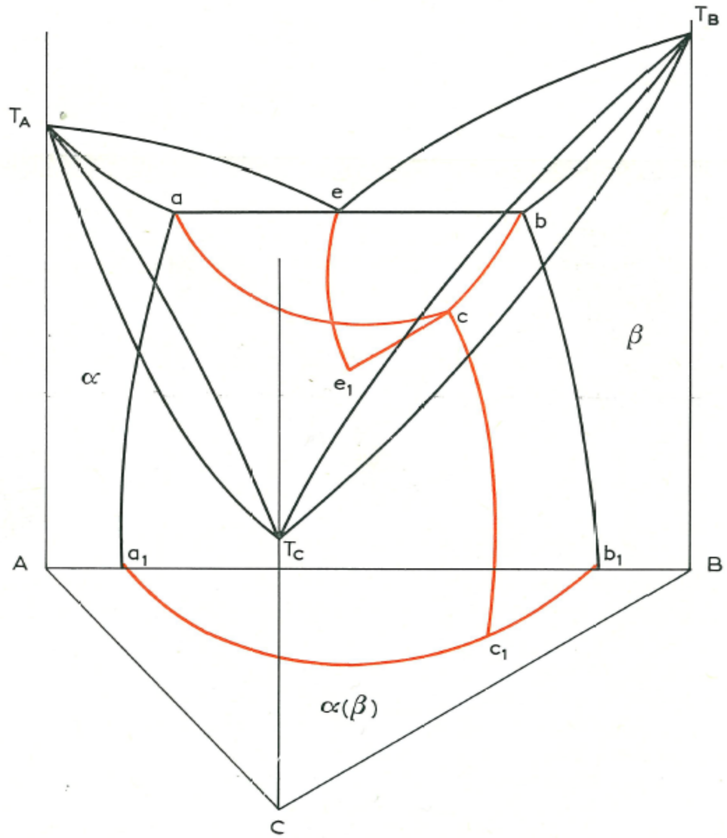


T_3 > T_4 > e_1

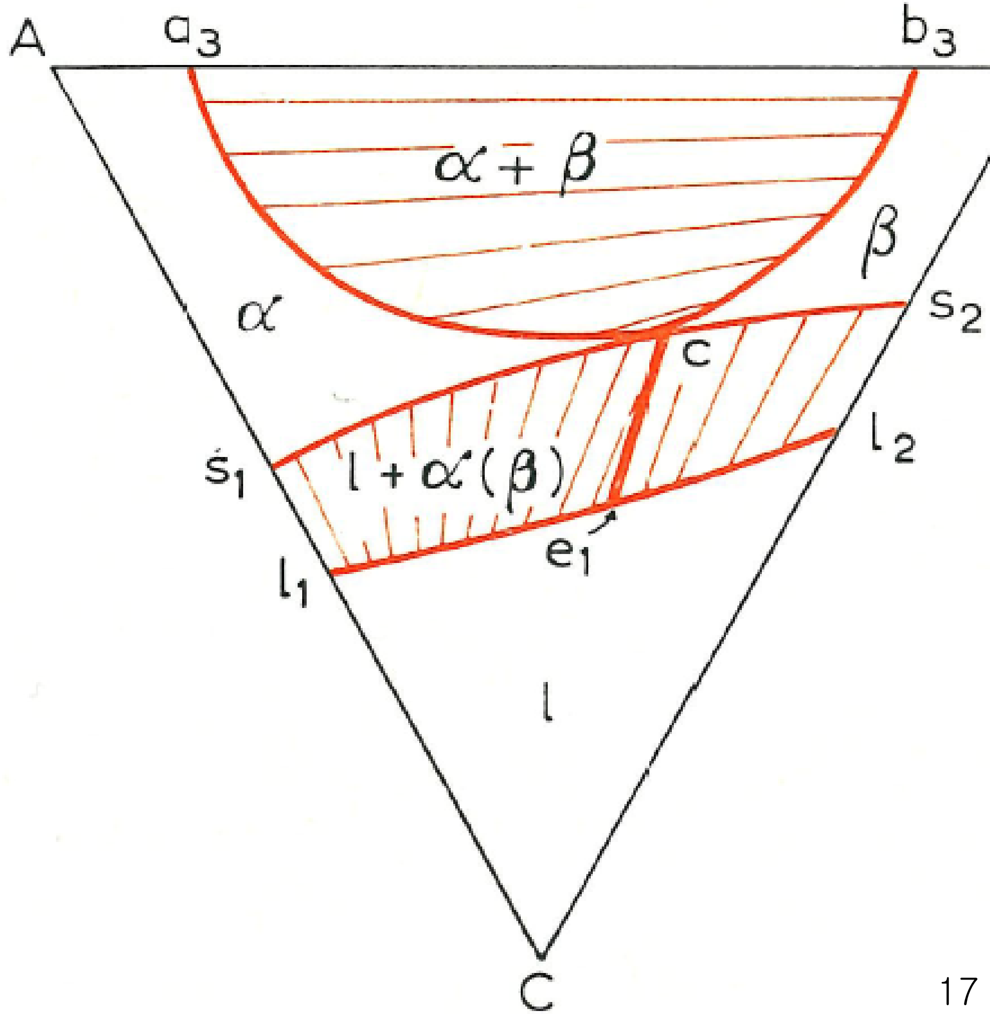


9.3. THREE-PHASE EQUILIBRIUM INVOLVING EUTECTIC REACTIONS

• **Isothermal section**

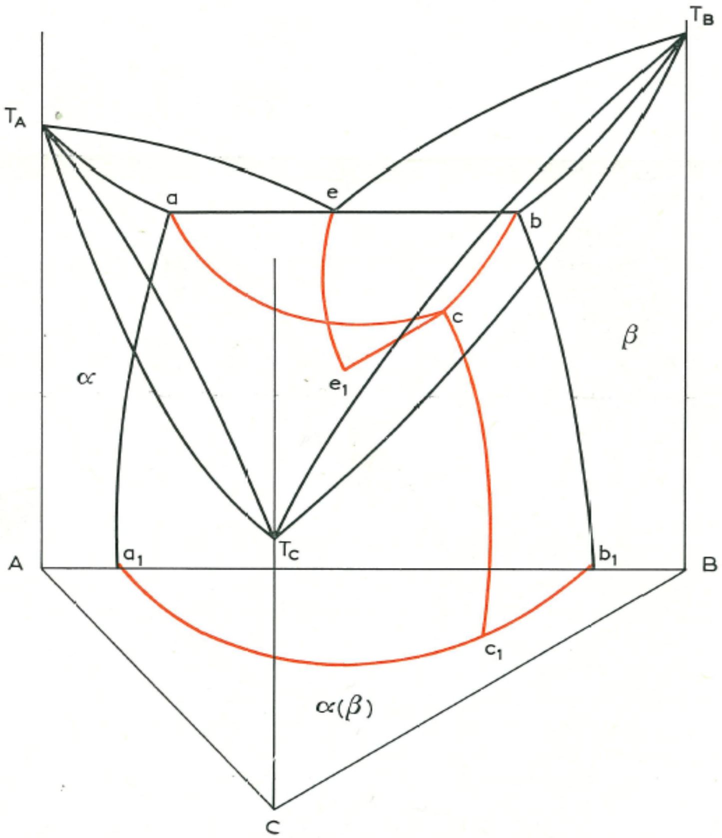


$T_5 =\ \ e$

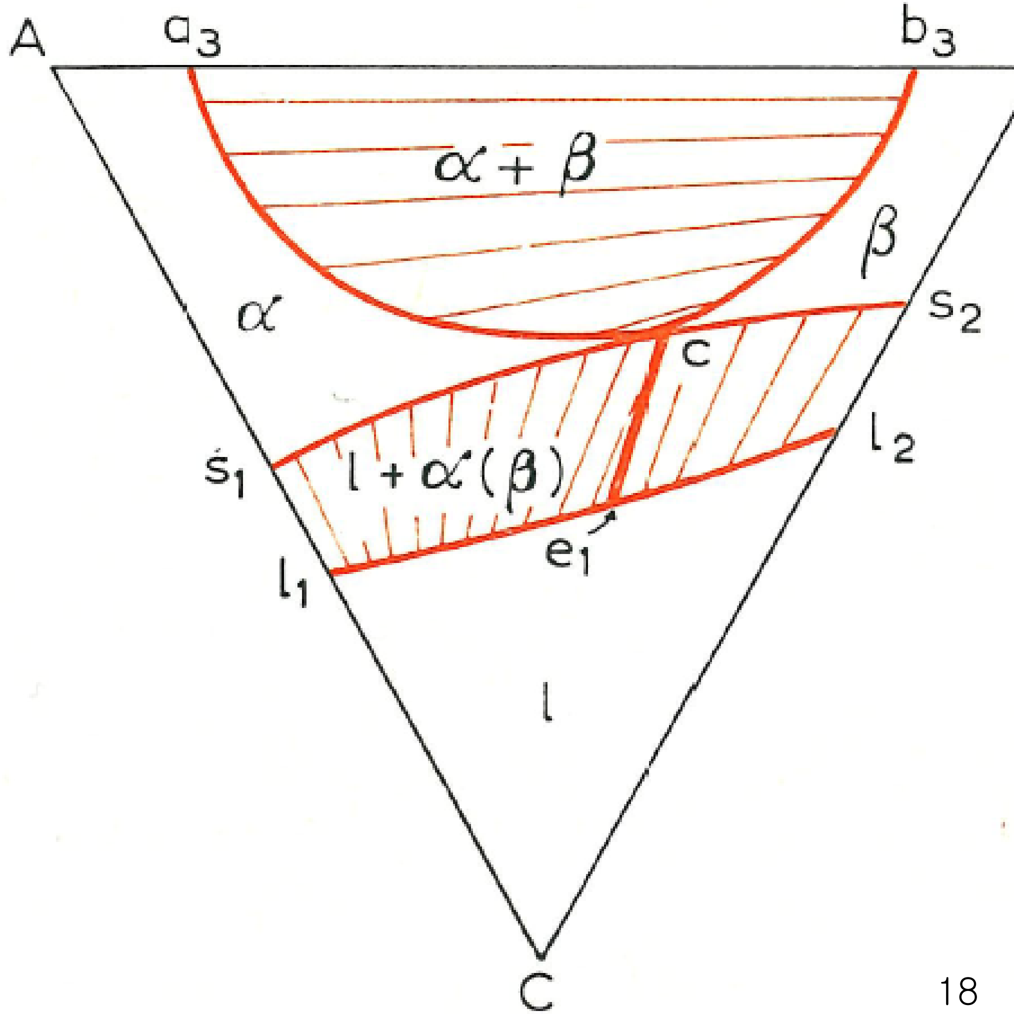


9.3. THREE-PHASE EQUILIBRIUM INVOLVING EUTECTIC REACTIONS

- **Isothermal section**



T_5 = e



9.2. THREE-PHASE EQUILIBRIUM

① Coalescence of miscibility gap and two phase region

- **How we can have 3 phase equil.?**

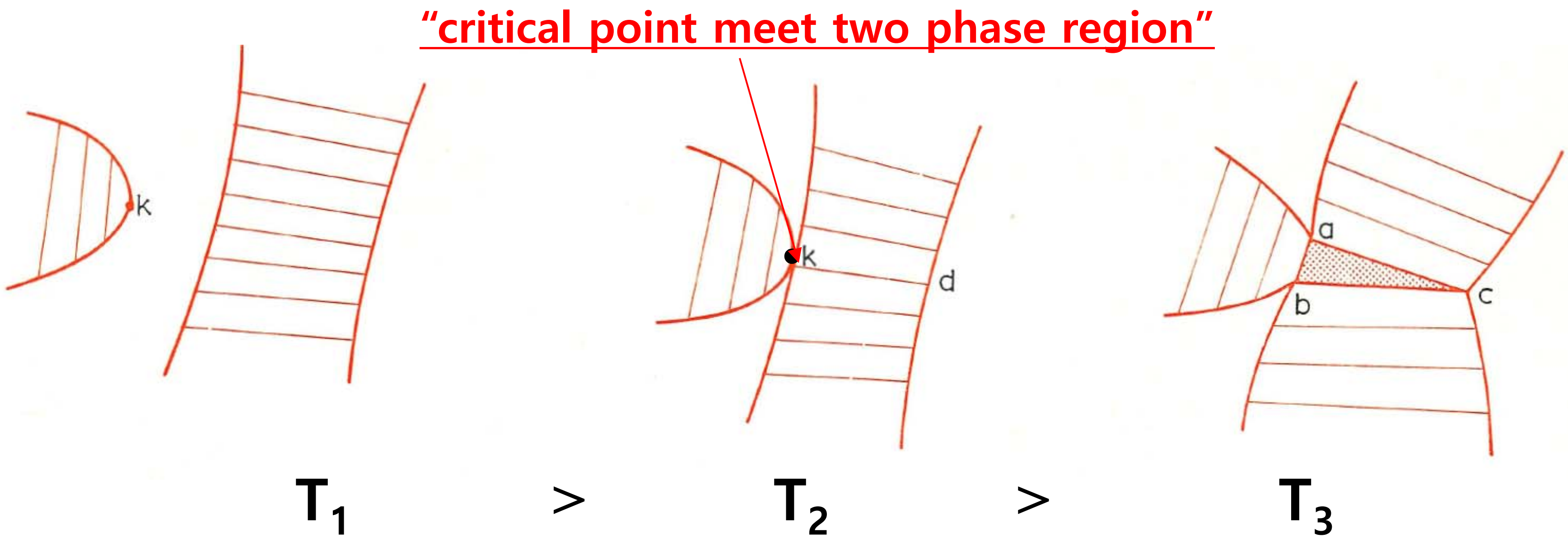
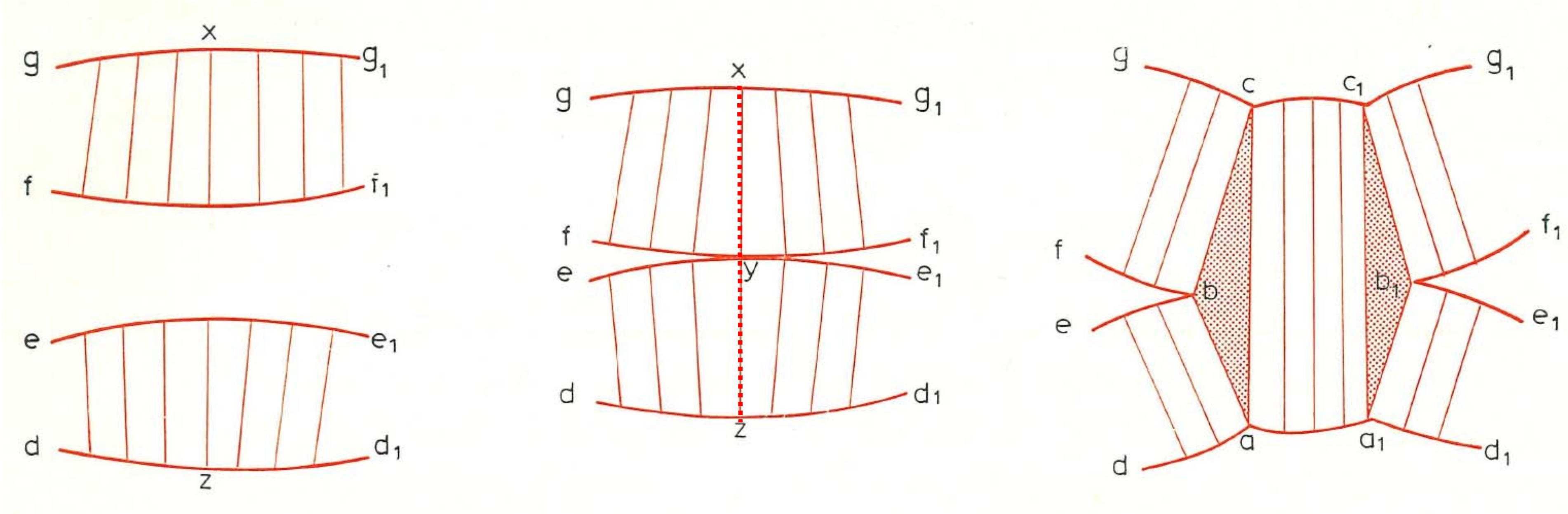


Fig. 136. Production of a ternary three-phase equilibrium by the coalescence of two two-phase regions

9.2. THREE-PHASE EQUILIBRIUM

② Coalescence of two two-phase region



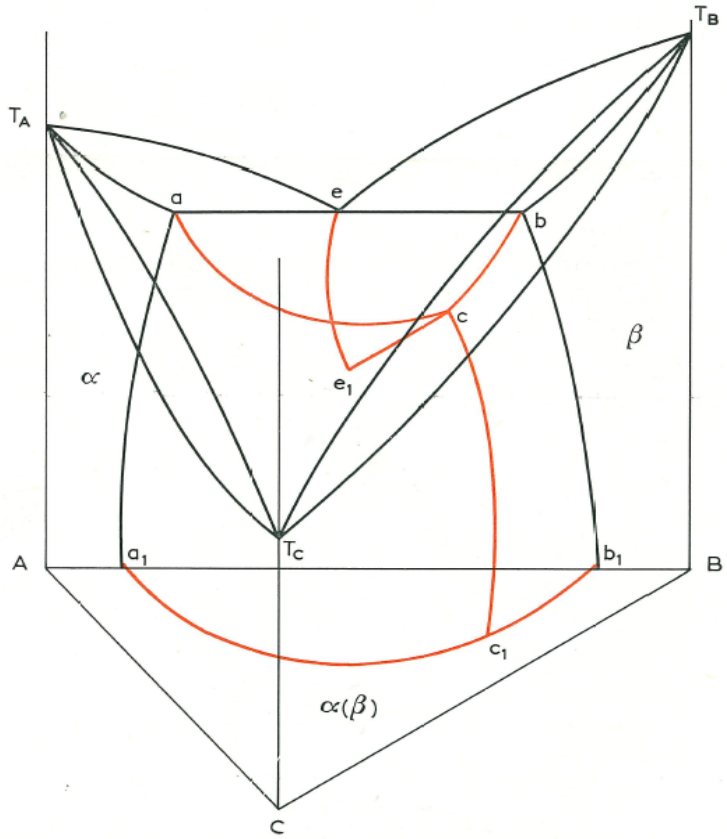
T_1 > T_2 > T_3

Two three-phase tie triangles *abc* and $a_1b_1c_1$

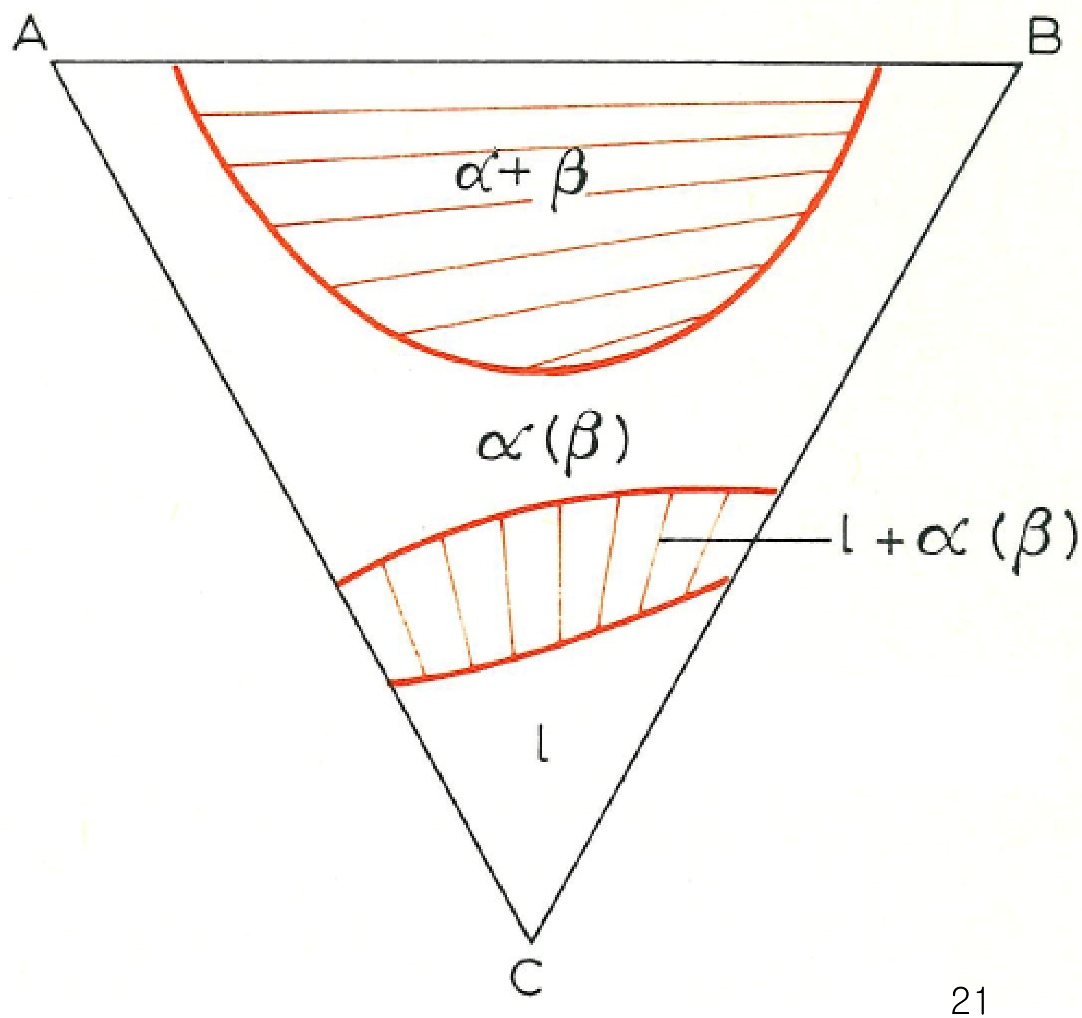
Fig. 138. Alternative method to Fig. 136 for the production of a ternary three-phase equilibrium by the coalescence of two two-phase regions

9.3. THREE-PHASE EQUILIBRIUM INVOLVING EUTECTIC REACTIONS

• **Isothermal section**

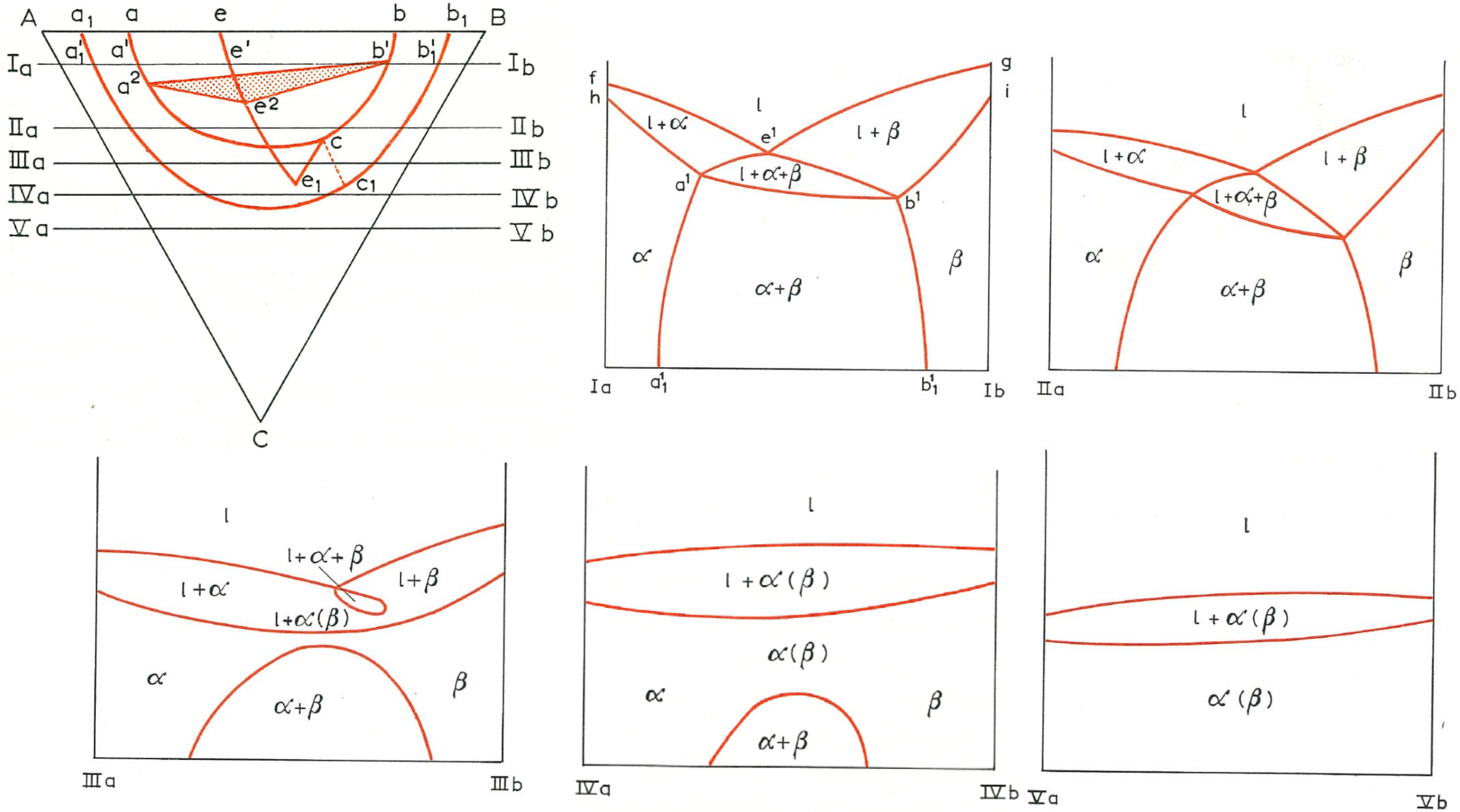


$e_1 > T_6 > T_c$



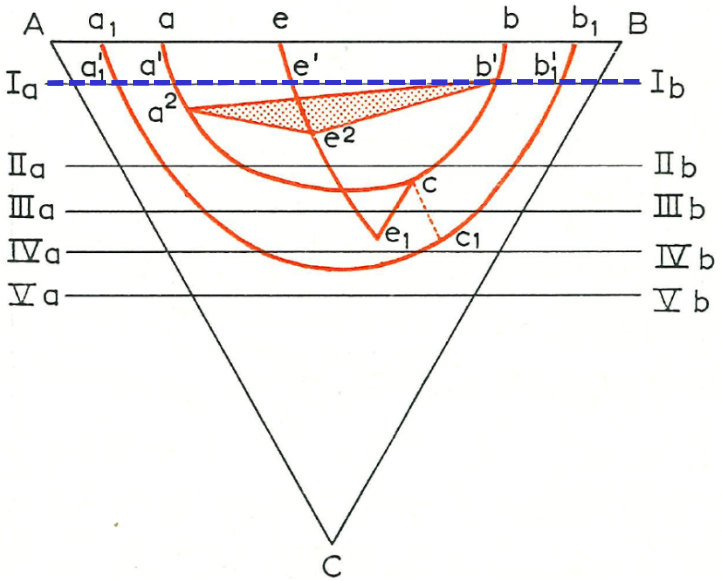
9.3. THREE-PHASE EQUILIBRIUM INVOLVING EUTECTIC REACTIONS

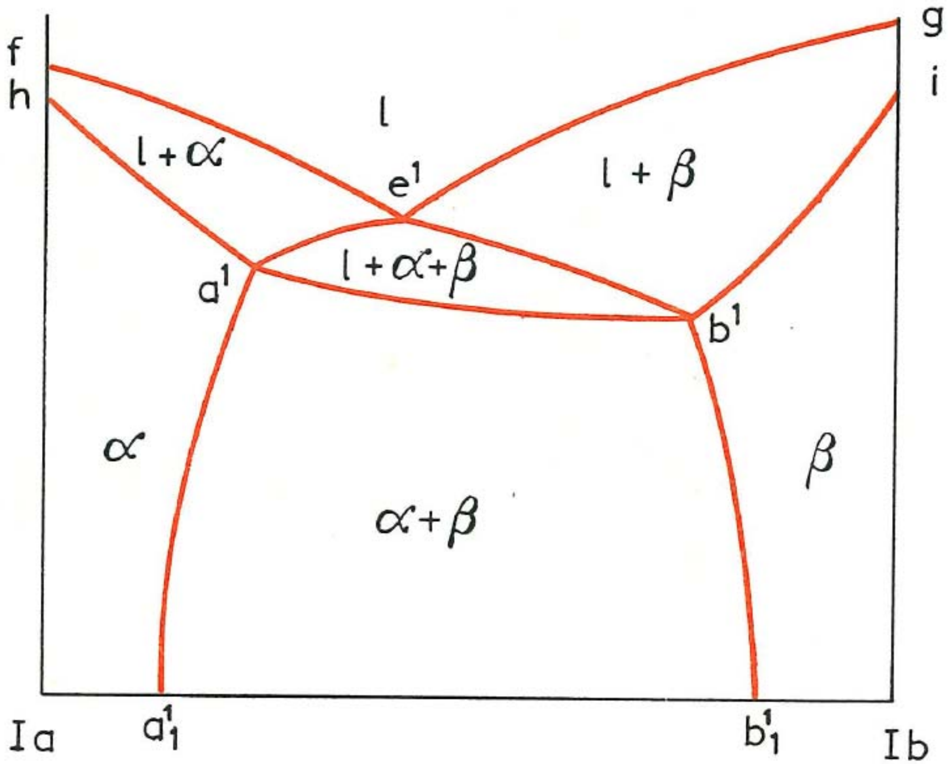
- **Vertical section**



9.3. THREE-PHASE EQUILIBRIUM INVOLVING EUTECTIC REACTIONS

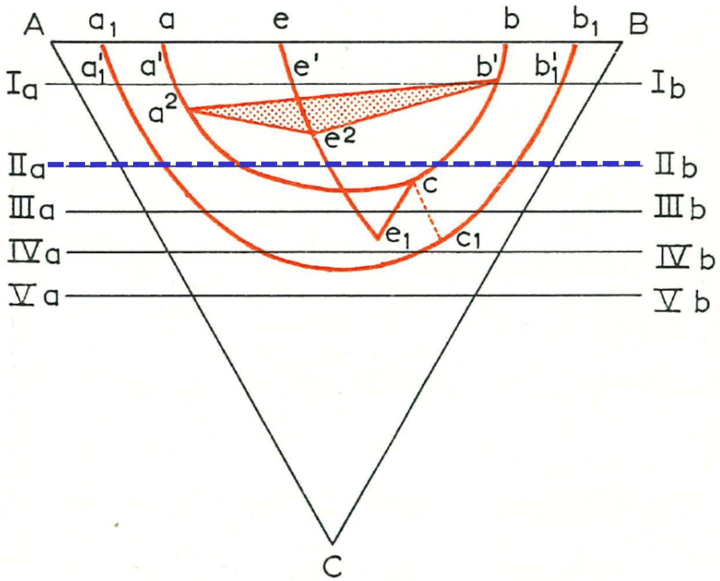
- **Vertical section**

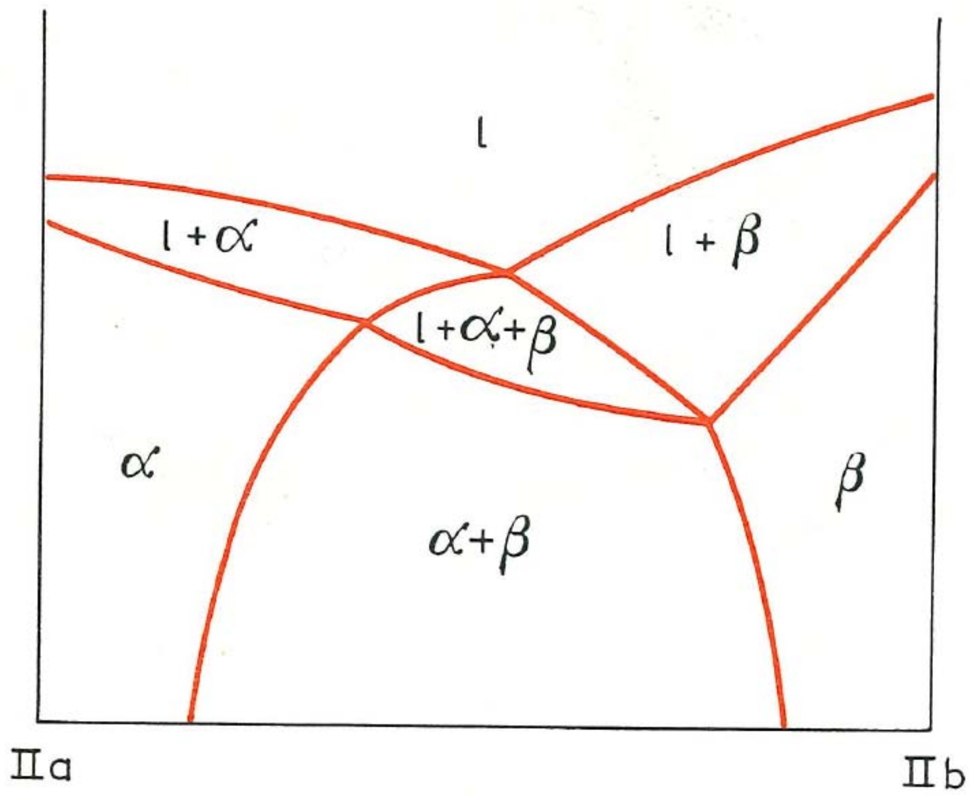




9.3. THREE-PHASE EQUILIBRIUM INVOLVING EUTECTIC REACTIONS

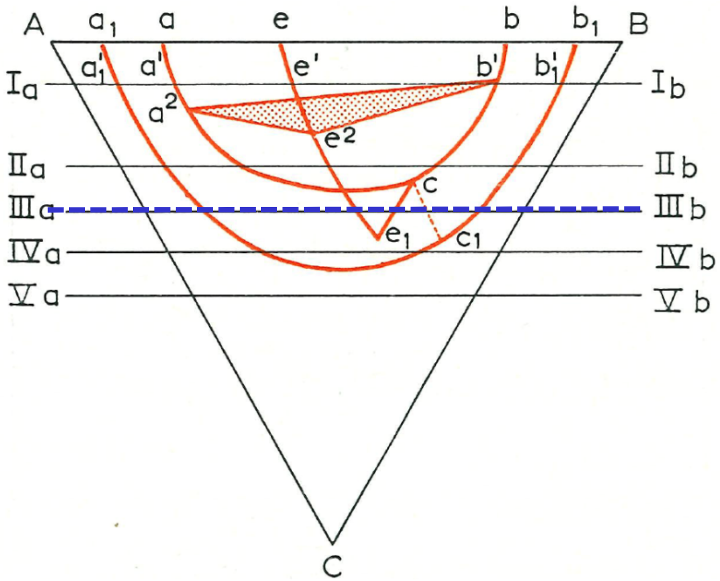
- **Vertical section**

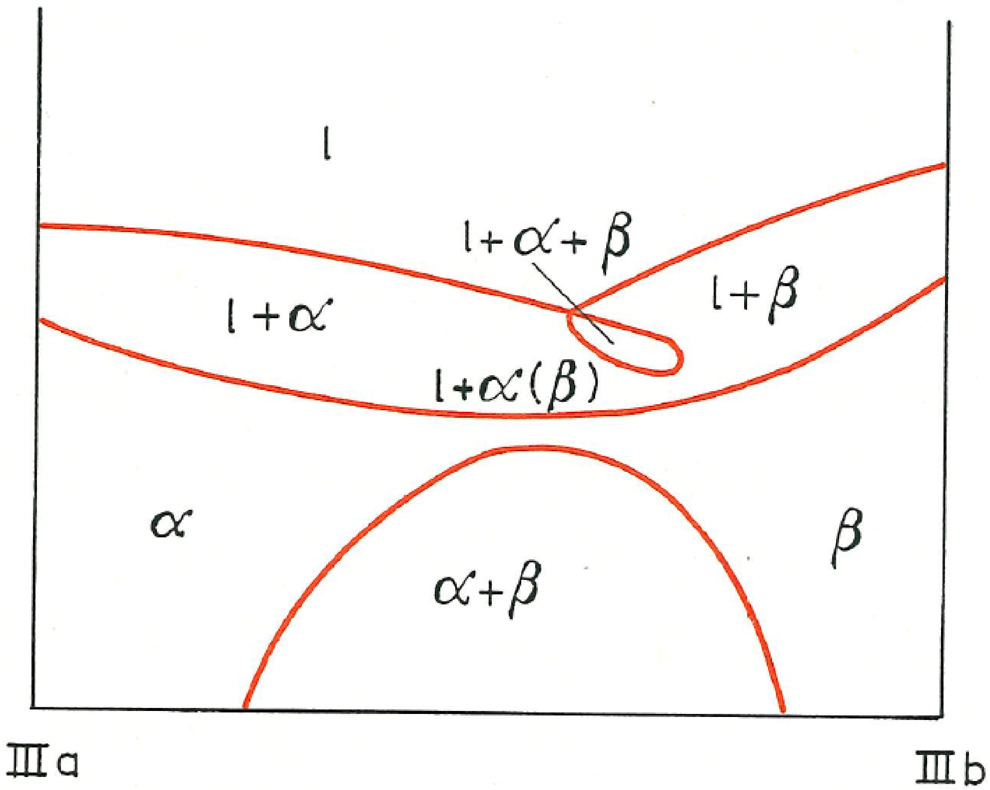




9.3. THREE-PHASE EQUILIBRIUM INVOLVING EUTECTIC REACTIONS

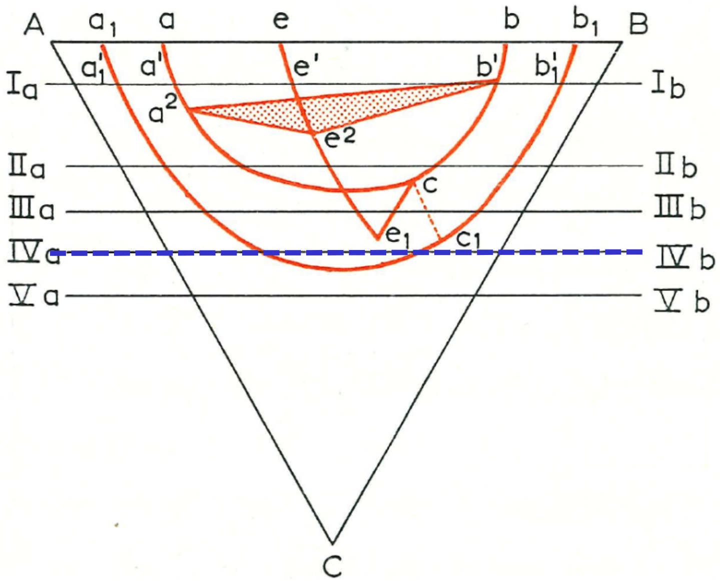
- **Vertical section**

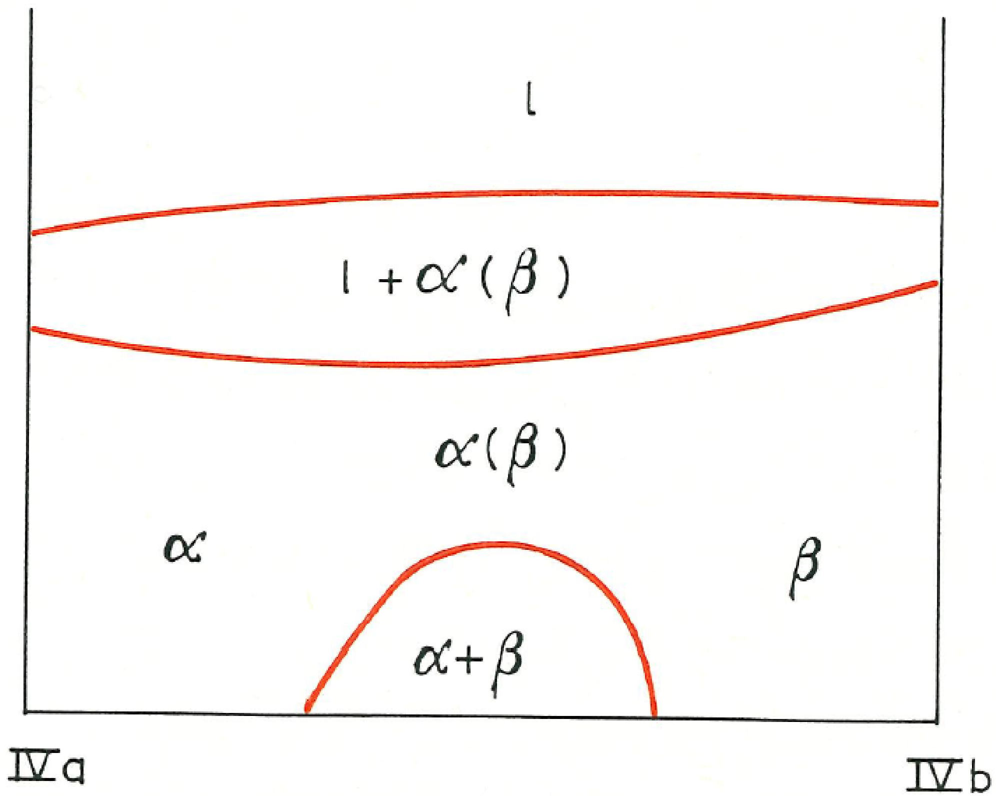




9.3. THREE-PHASE EQUILIBRIUM INVOLVING EUTECTIC REACTIONS

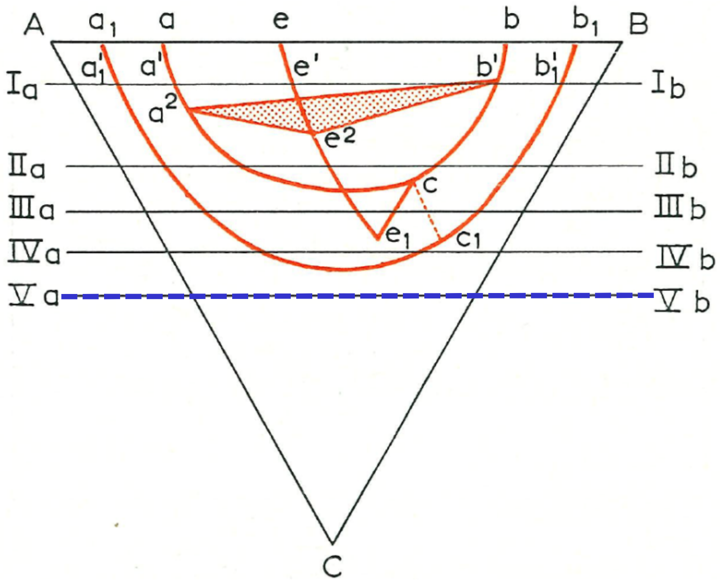
- **Vertical section**

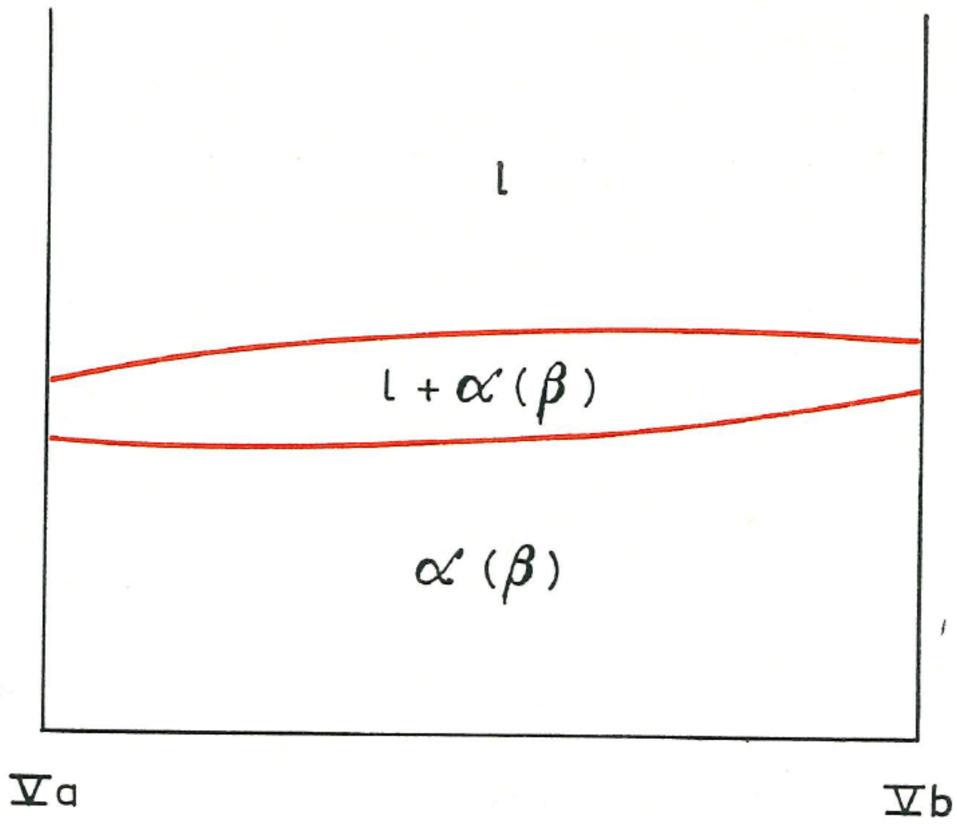




9.3. THREE-PHASE EQUILIBRIUM INVOLVING EUTECTIC REACTIONS

- **Vertical section**



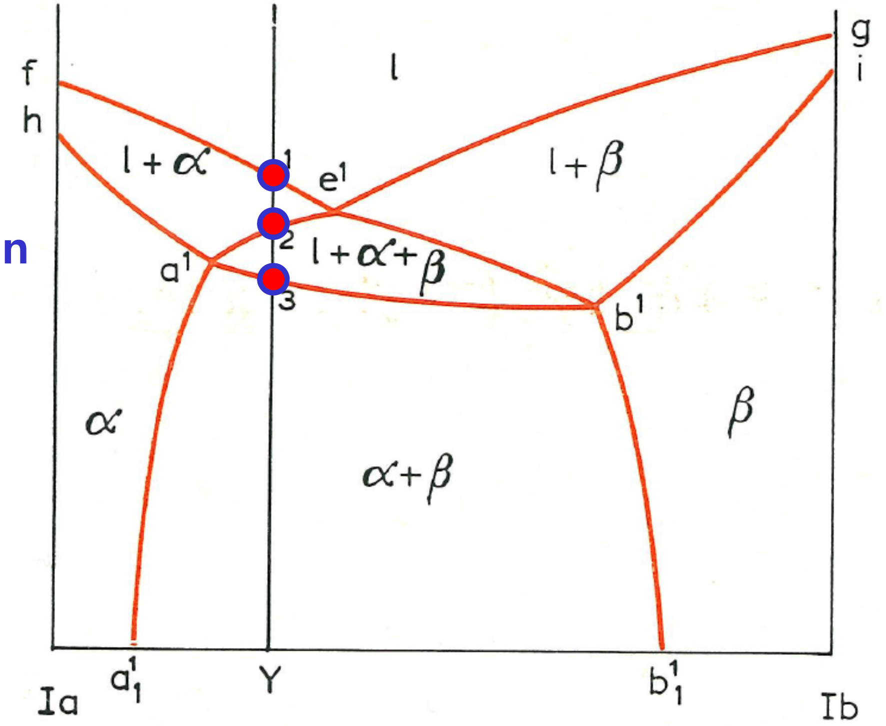


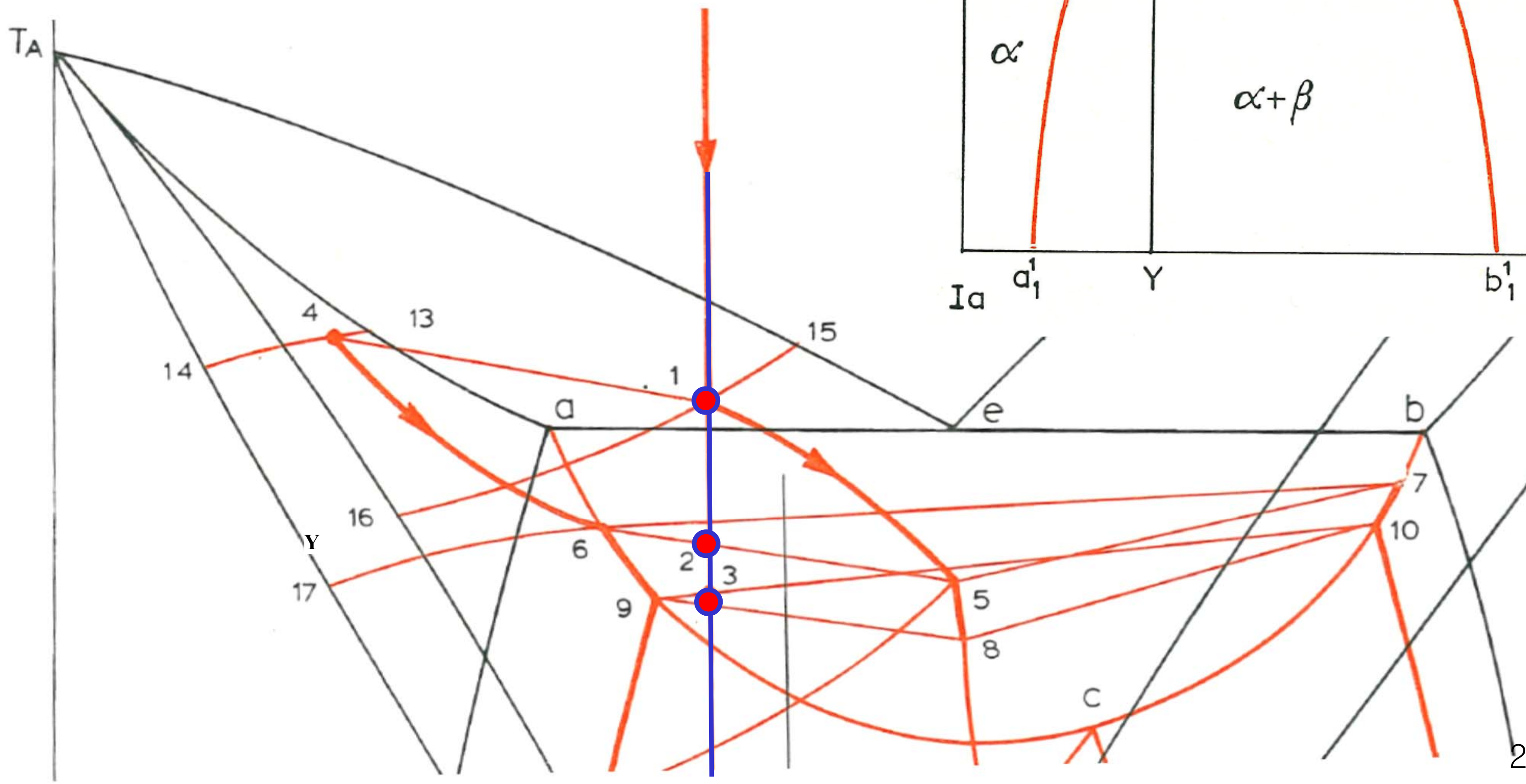
9.3. THREE-PHASE EQUILIBRIUM INVOLVING EUTECTIC REACTIONS

- **Transformation on cooling**

Y alloy : $l \rightarrow l+\alpha \rightarrow l+\alpha+\beta \rightarrow \alpha+\beta$

A clear idea of the sequence of crystallization





> Point 1: 4 on the α solidus surface

> Point 1- Point 2

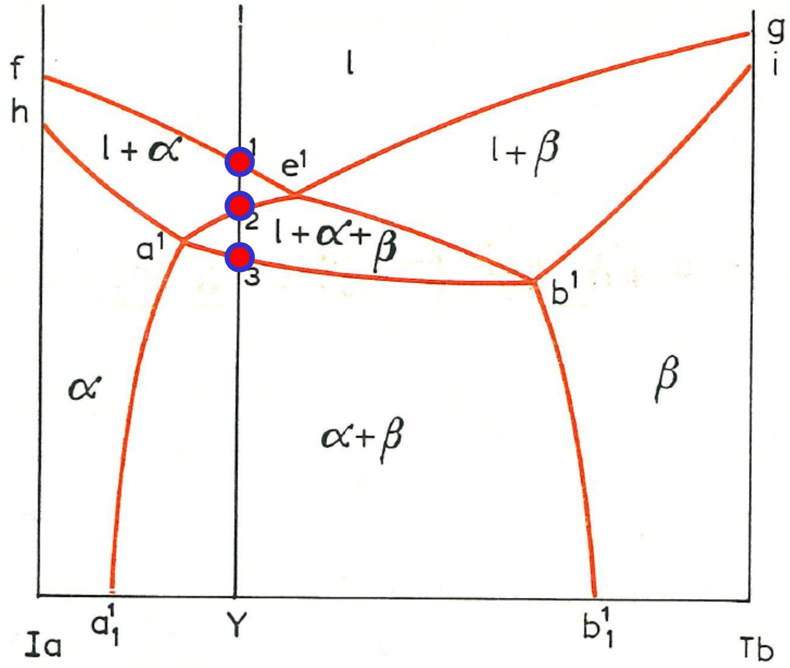
* 4→6 on the α solidus surface
* 1→5 on the α liquidus surface

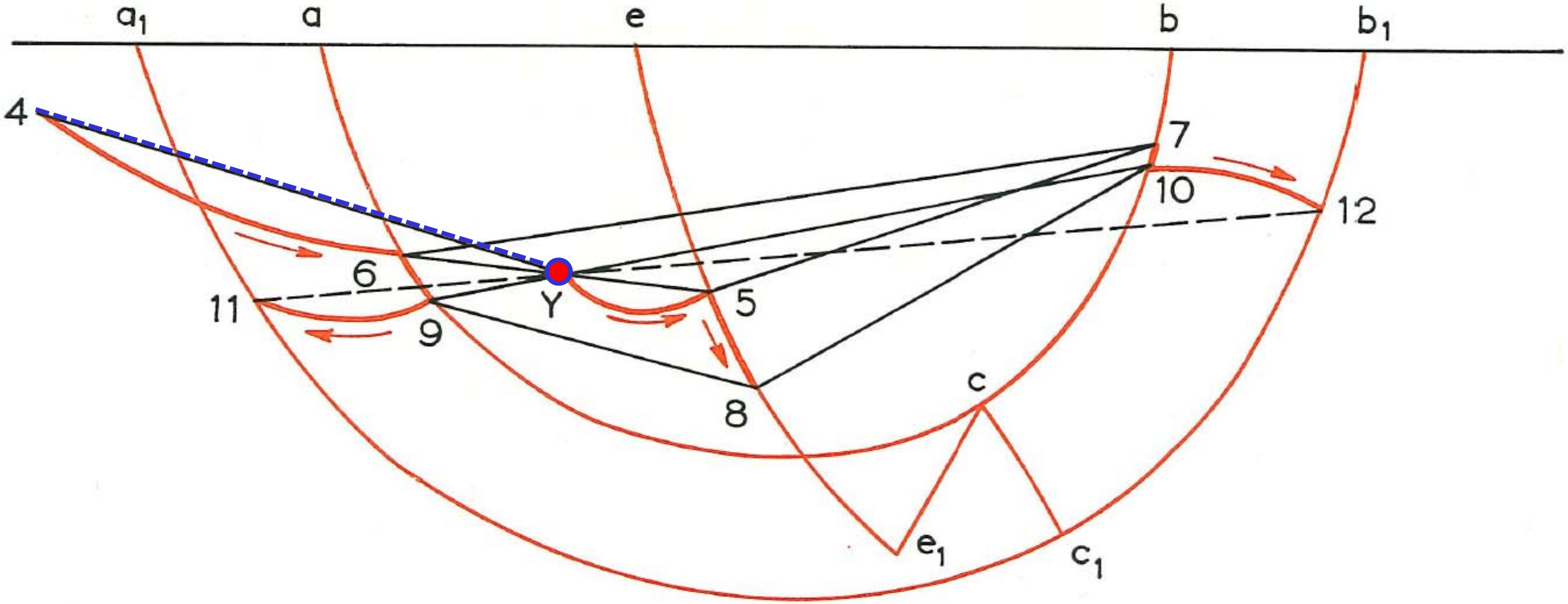
Three phase equilibrium l5, α6, β7

* α: 6→9, β: 7→10, l: 5→8

> Point 3: on the tie line 9-10

> Point 3-Y: α: 9→11, β: 10→12





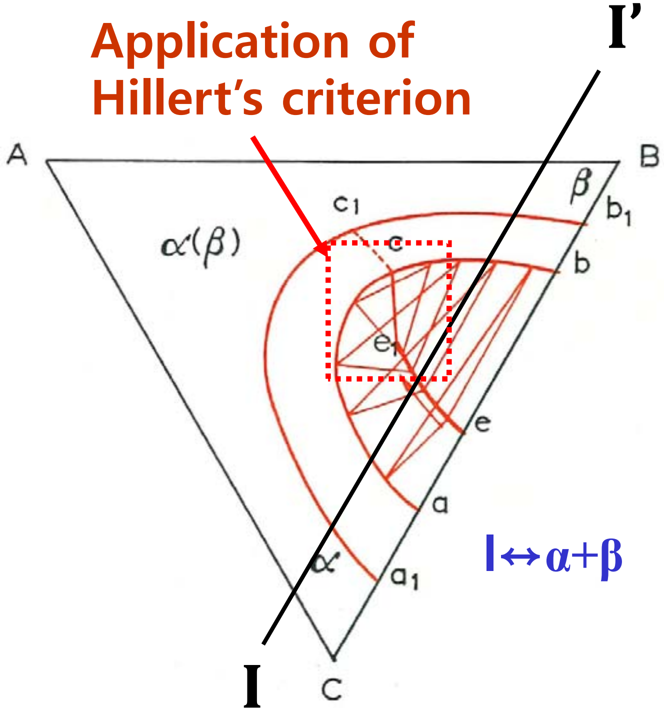
Projection of the solidification sequence for alloy Y on the concentration triangle

9.3. THREE-PHASE EQUILIBRIUM INVOLVING EUTECTIC REACTIONS

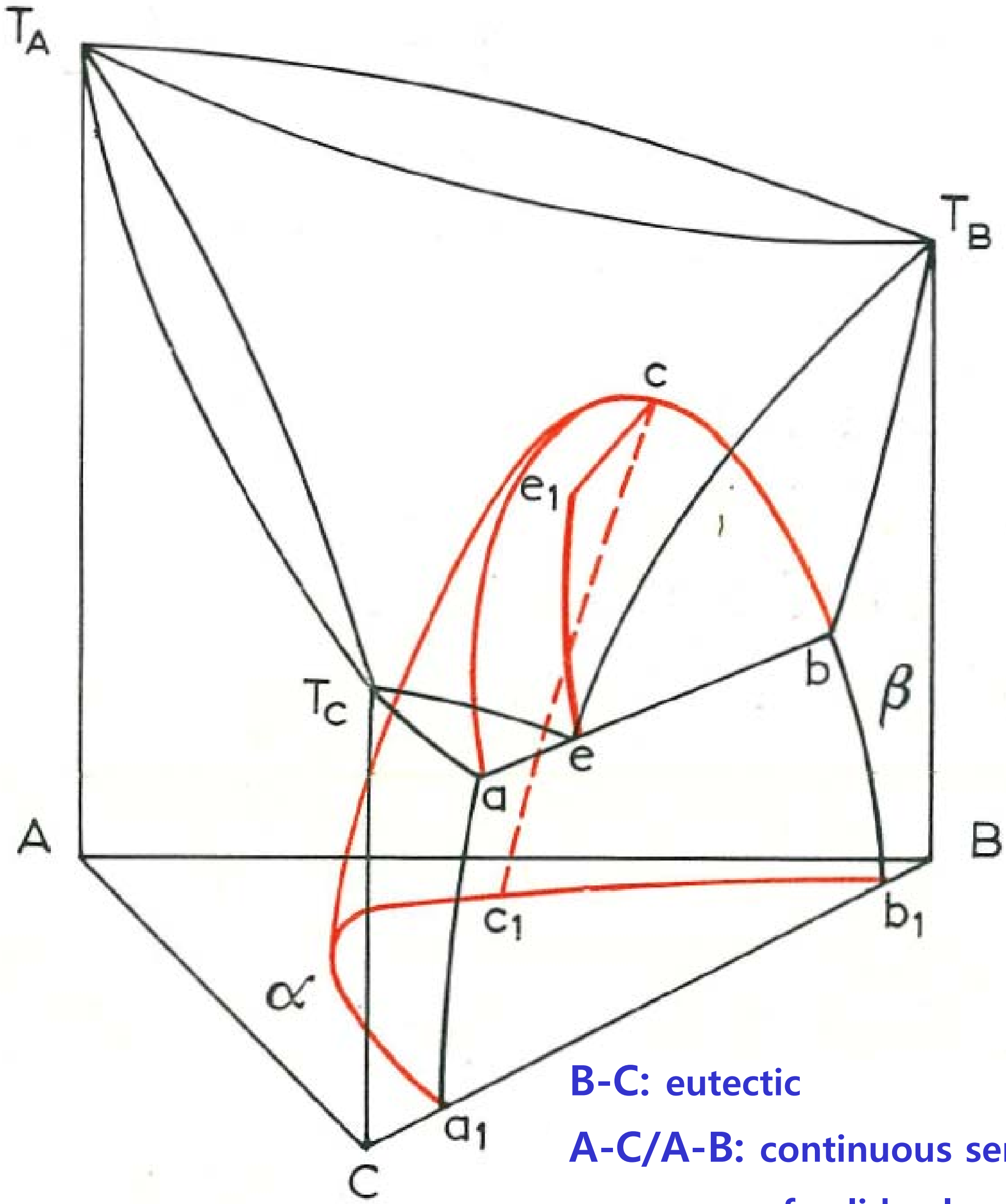
- **A maximum critical point**

Basically, the reaction we can expect is eutectic reaction ($l \rightarrow \alpha + \beta$). But, in reality, we can have eutectic and peritectic reaction depending on the relative amount of three phase.

Application of Hillert's criterion



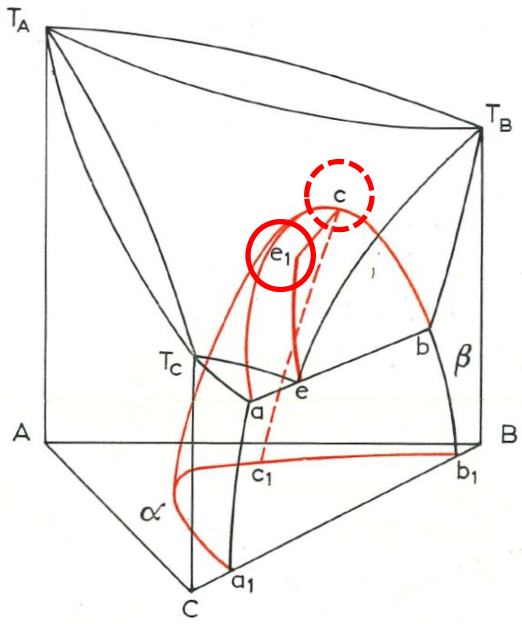
$l \leftrightarrow \alpha+\beta$



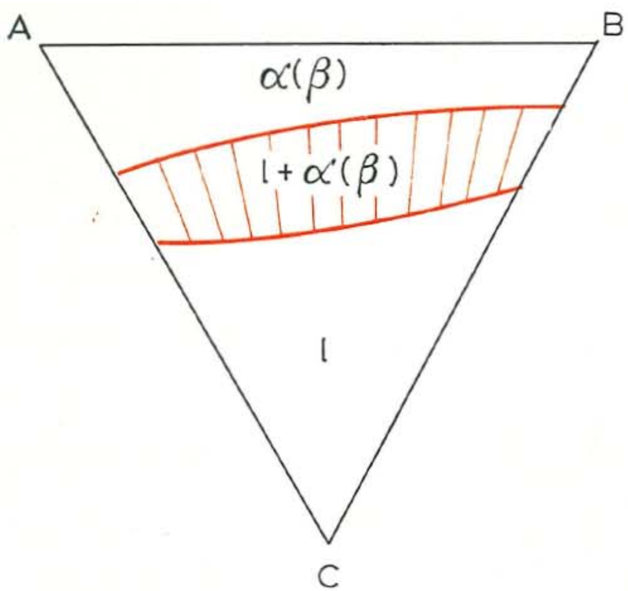
B-C: eutectic

A-C/A-B: continuous series of solid soln

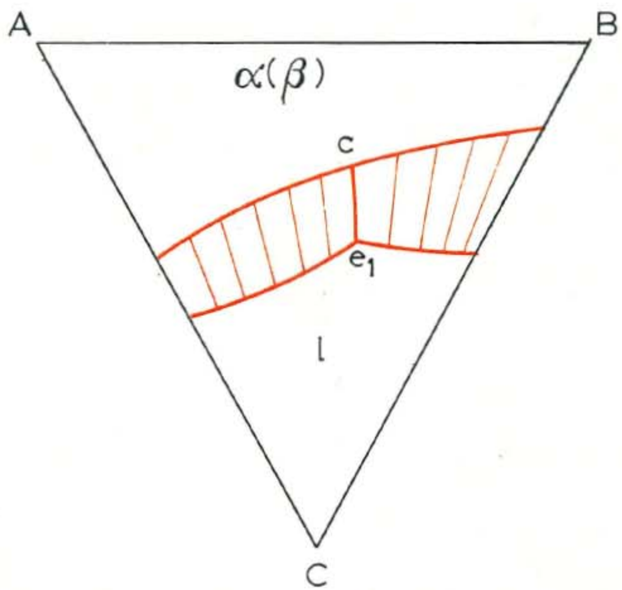
• **A maximum critical point**



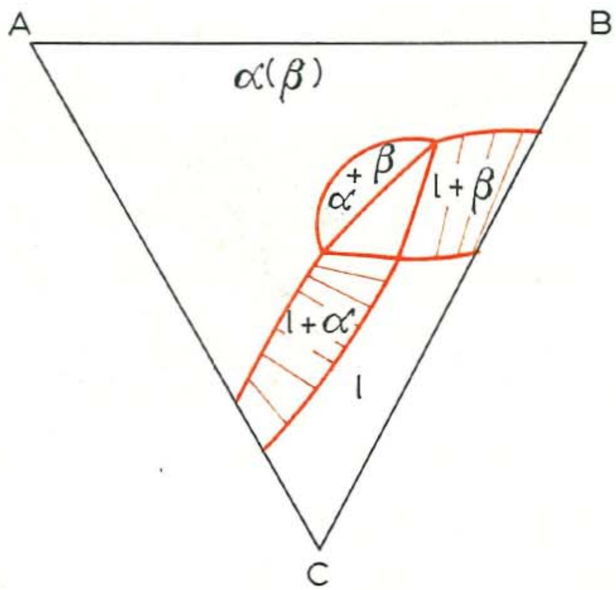
isothermal section



T > e$_1$

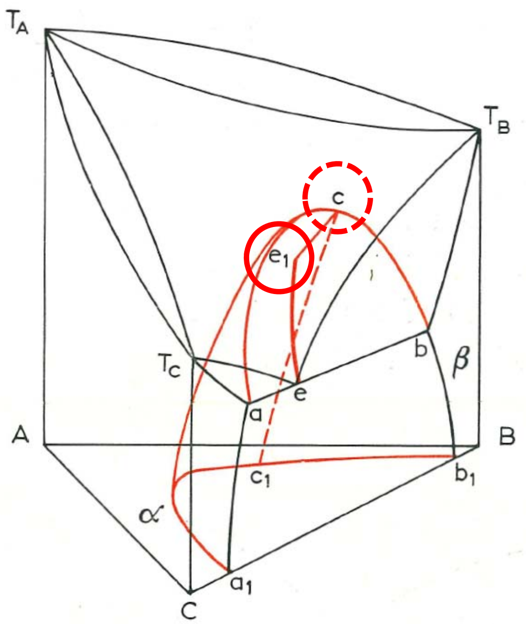


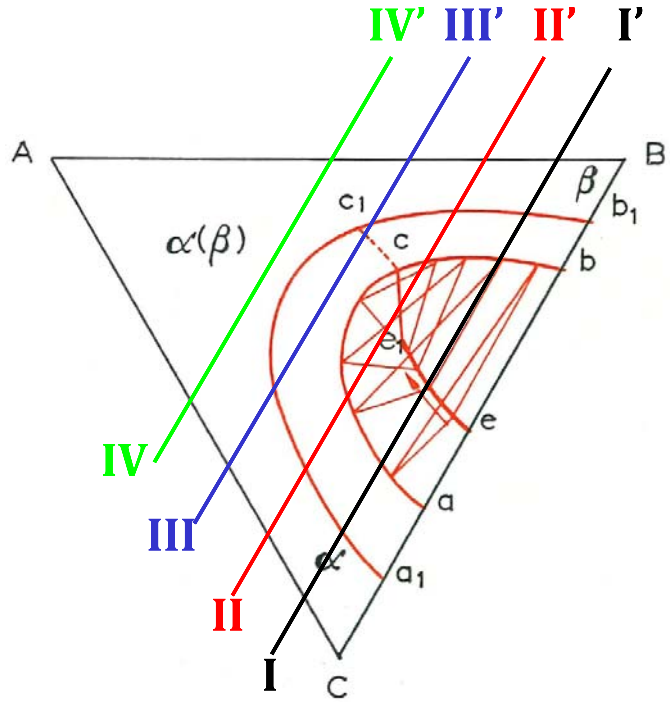
T = e$_1$



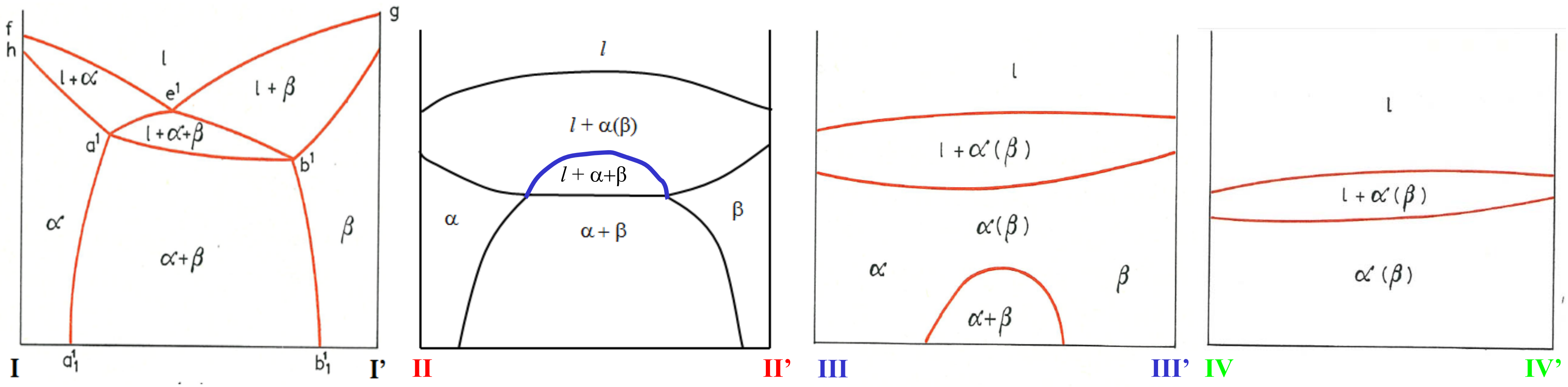
T < e$_1$

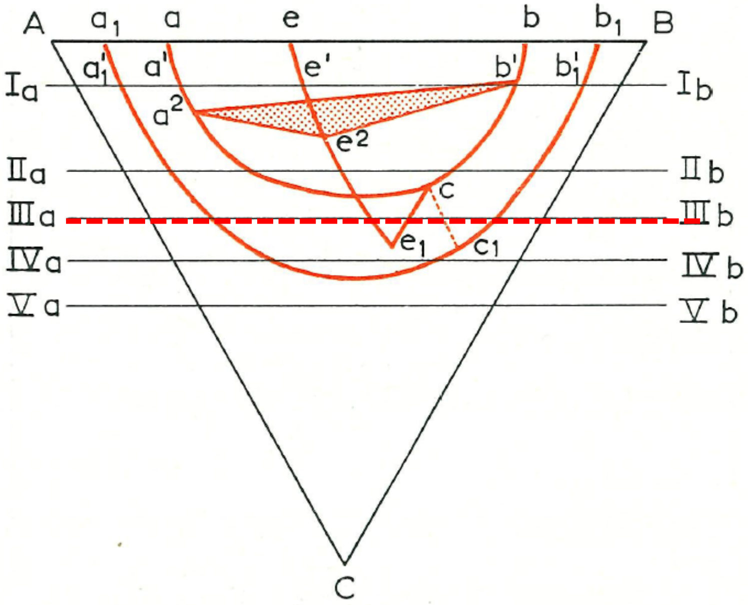
- **A maximum critical point**



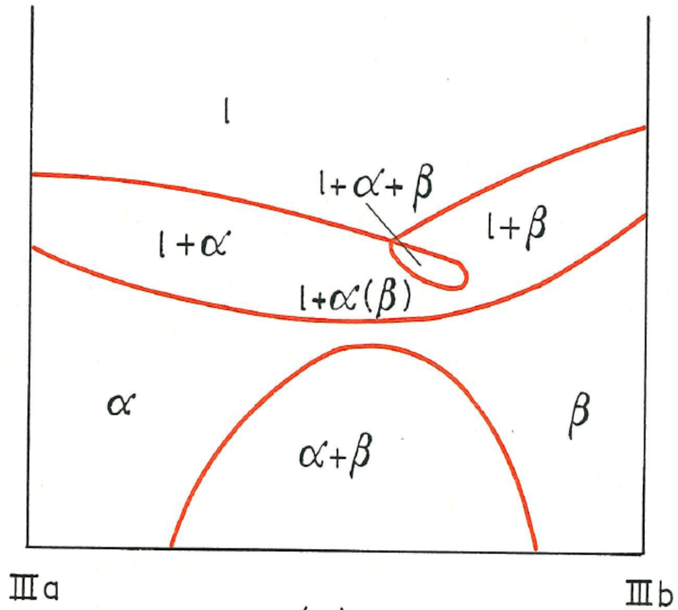


Vertical section

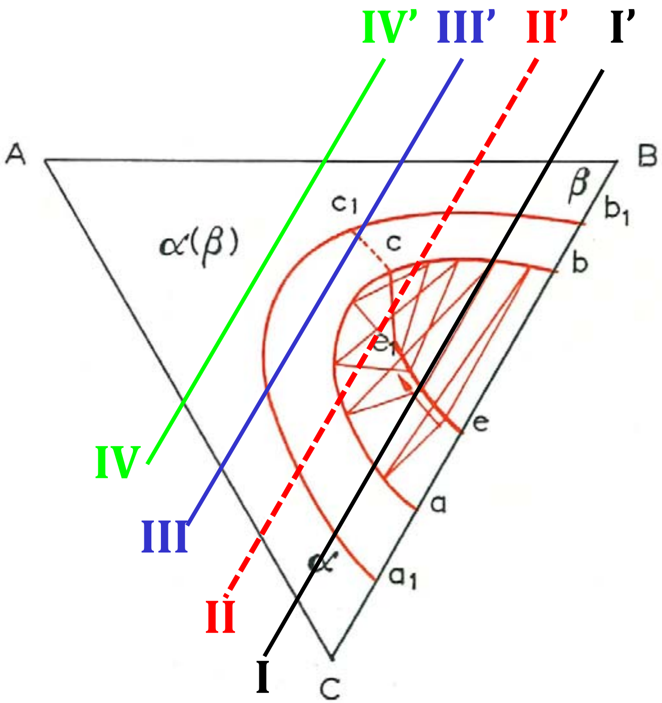


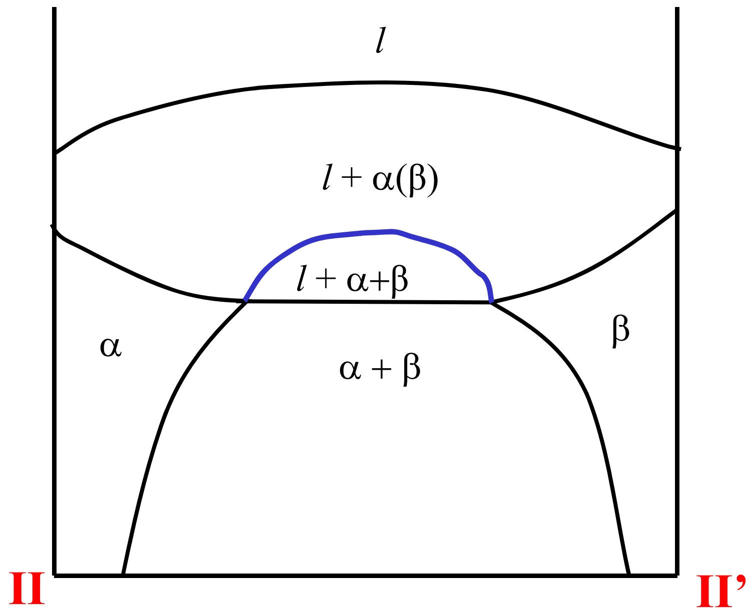


Vertical section



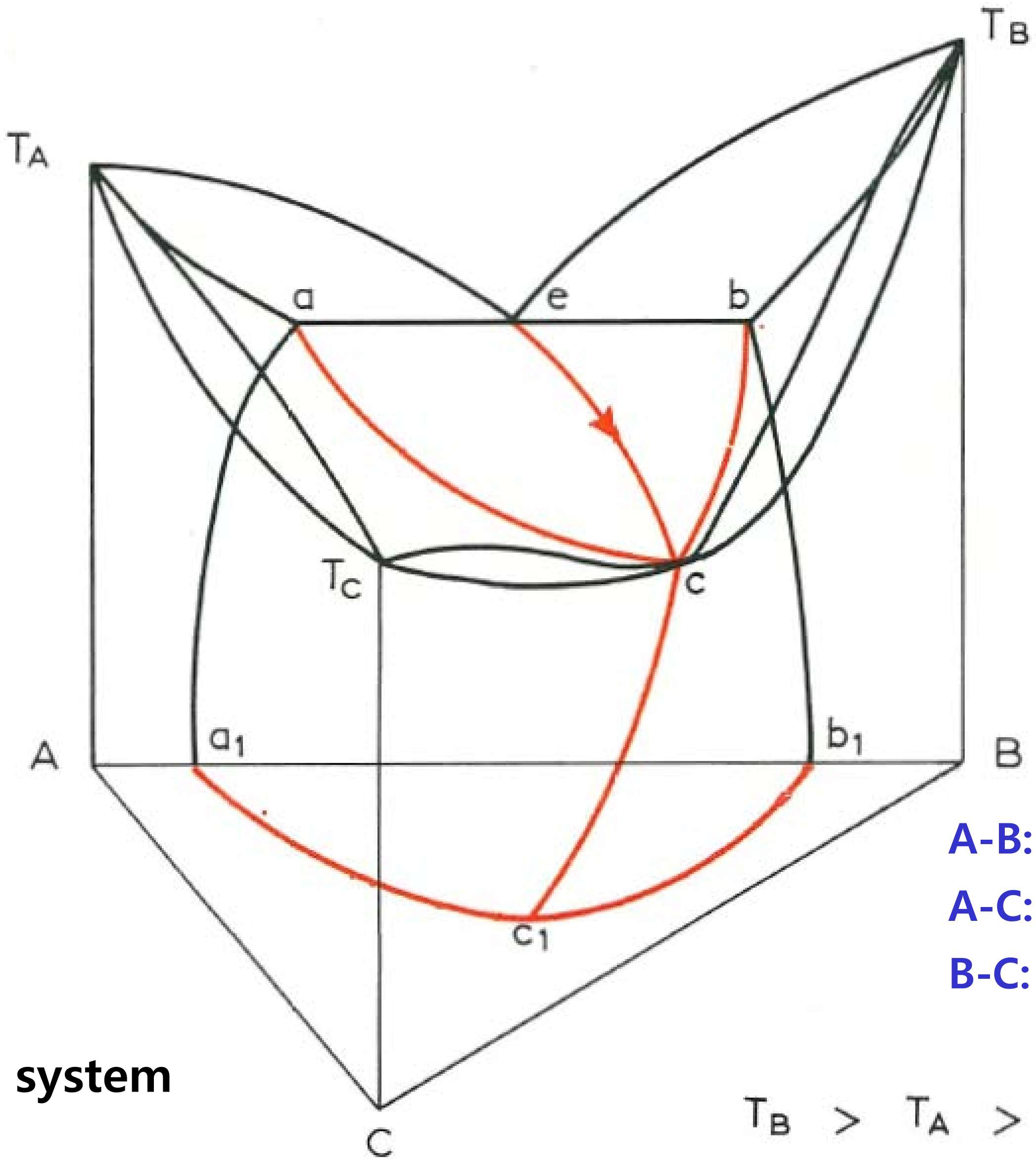
(c)





9.3. THREE-PHASE EQUILIBRIUM INVOLVING EUTECTIC REACTIONS

- A limiting case: solubility gap just reaches one of the binary systems.



A-B: eutectic

A-C: complete solid soln

B-C: complete solid soln
with congruent minima

Au-Co-Pd system

$T_B > T_A > T_C > e > c$

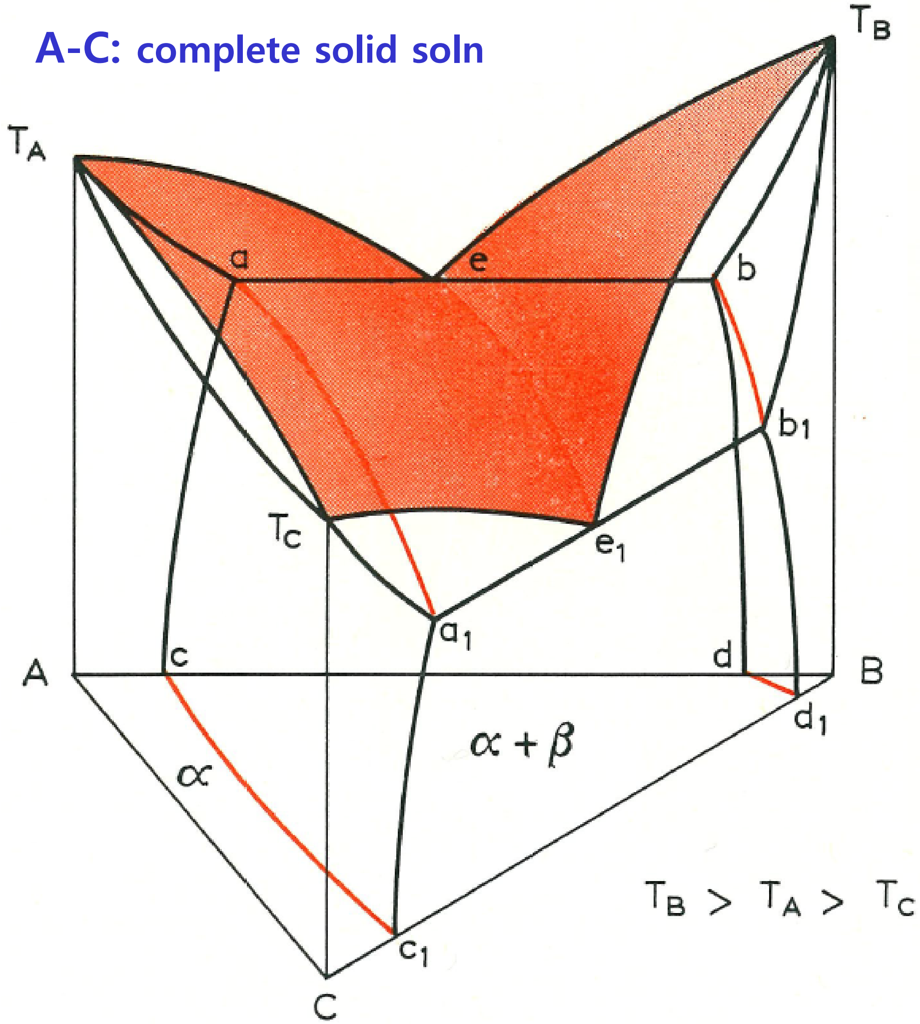
9.3. THREE-PHASE EQUILIBRIUM INVOLVING EUTECTIC REACTIONS

- **A limiting case**

Space model

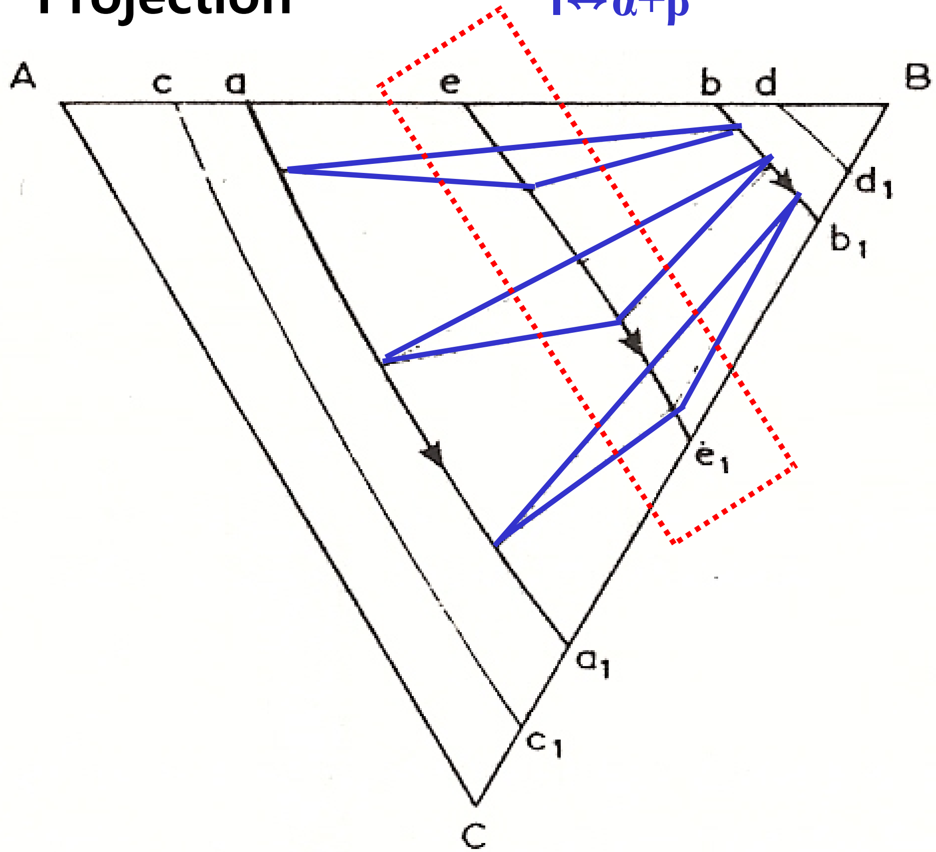
A-B/B-C: eutectic

A-C: complete solid soln



Projection

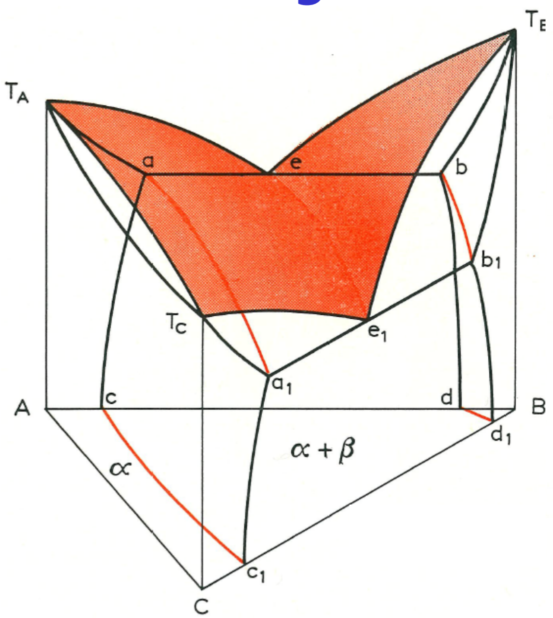
$l \leftrightarrow \alpha+\beta$



$T_B > T_A > T_C > e > e_1$

9.3. THREE-PHASE EQUILIBRIUM INVOLVING EUTECTIC REACTIONS

- **A limiting case**



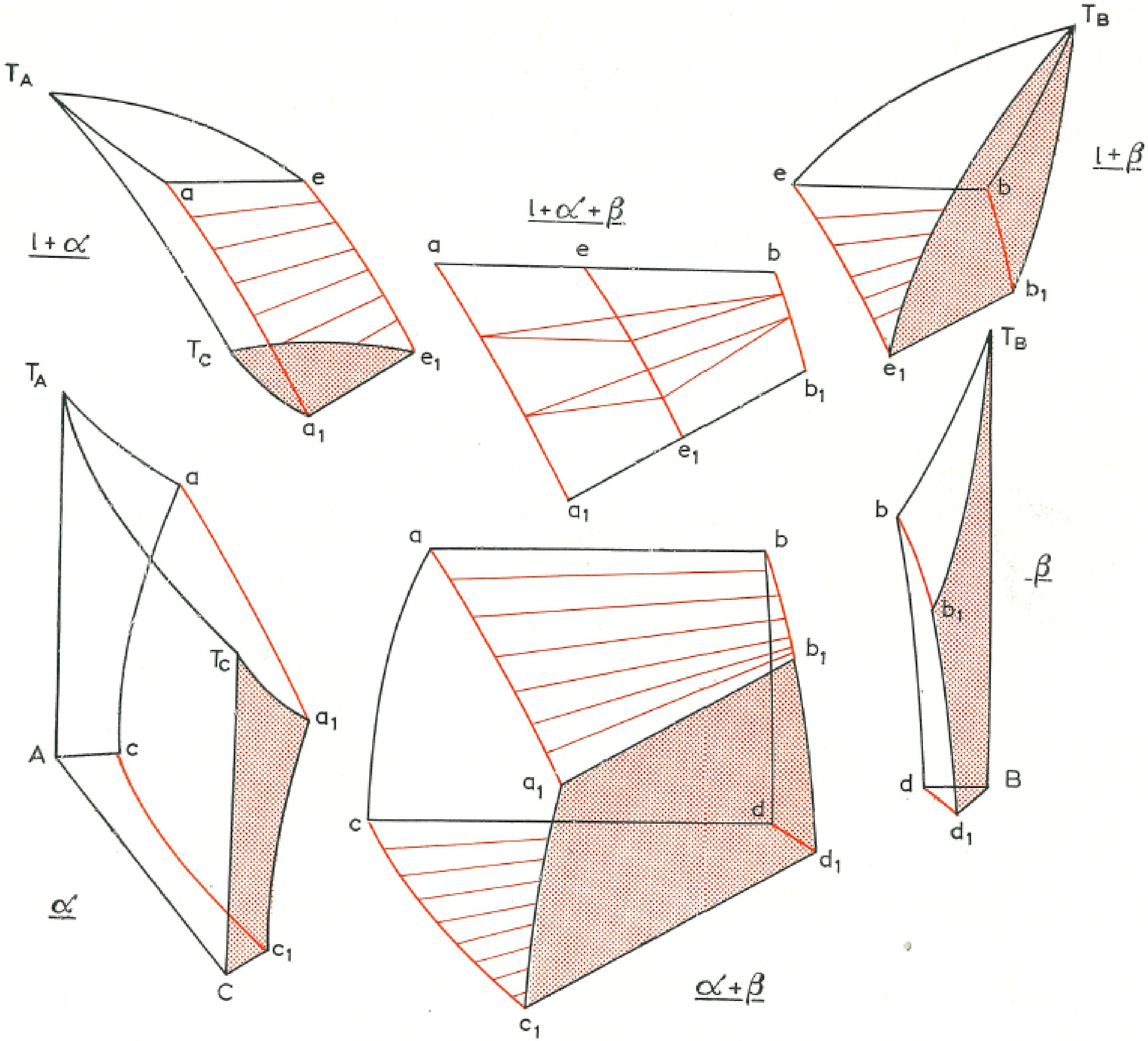
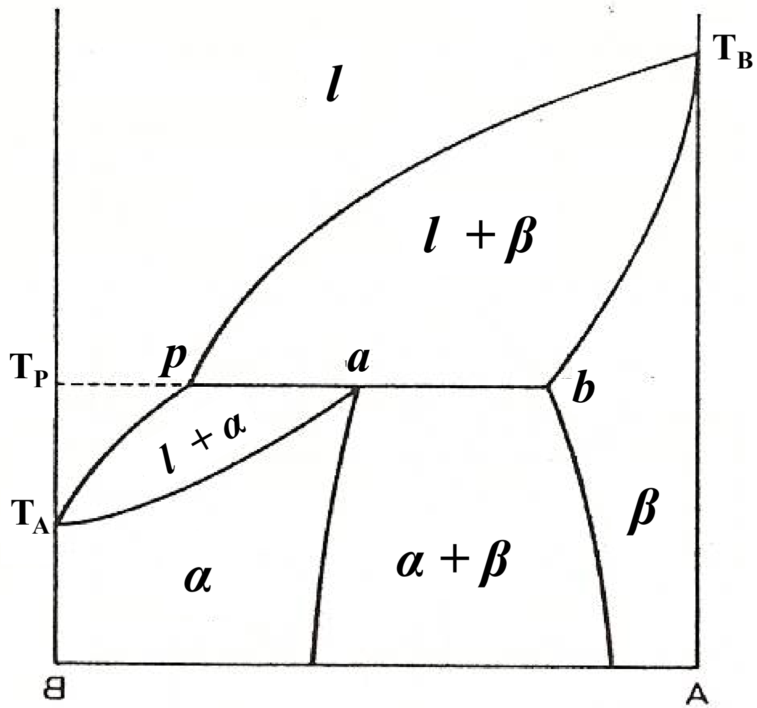


Fig. 165. The phase regions in Fig. 164a.

9.4. THREE-PHASE EQUILIBRIUM INVOLVING PERITECTIC REACTIONS

- A peritectic solubility gap in one binary system



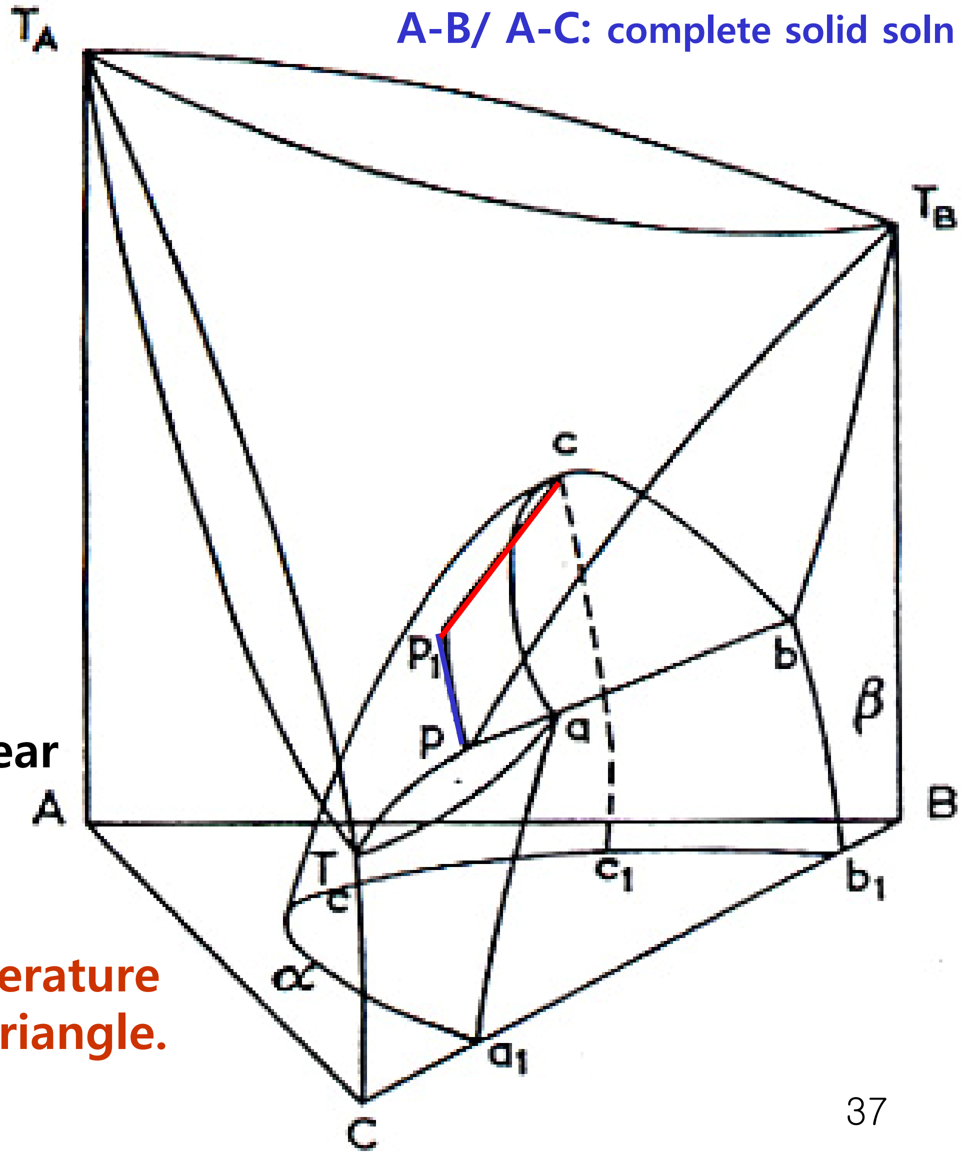
: A minimum or a maximum may appear in the monovariant liquid curve.

PP$_1$: monovariant curve for liquid

Points P$_1$ and c lie at the same temperature and the line P$_1$c is a degenerate tie triangle.

B-C: peritectic

A-B/ A-C: complete solid soln

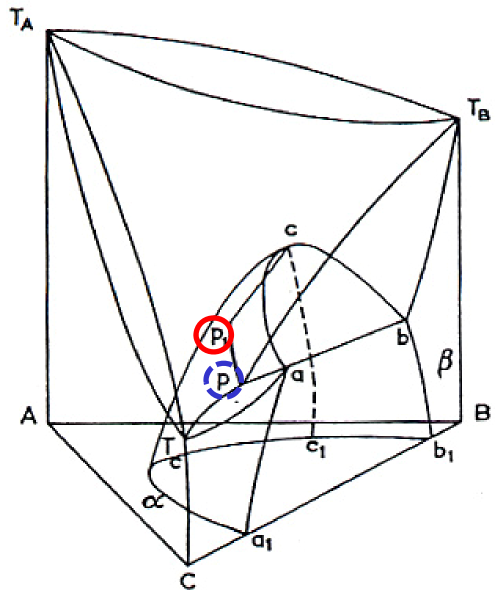


9.4. THREE-PHASE EQUILIBRIUM INVOLVING PERITECTIC REACTIONS

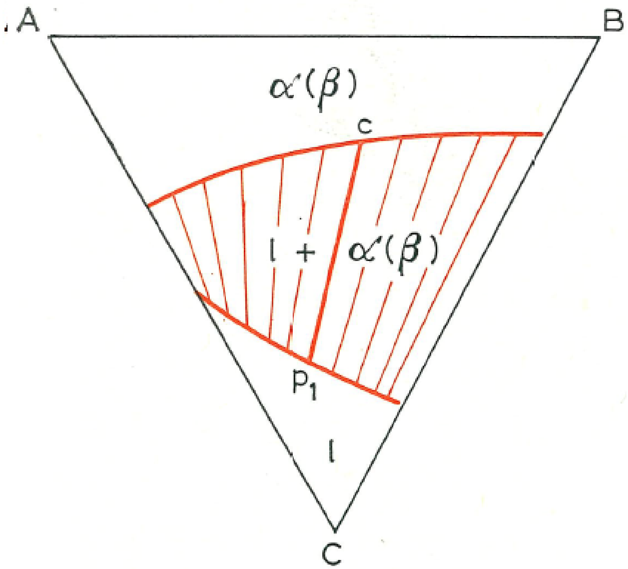
- **A peritectic solubility gap in one binary system**

PP_1: monovariant curve for liquid

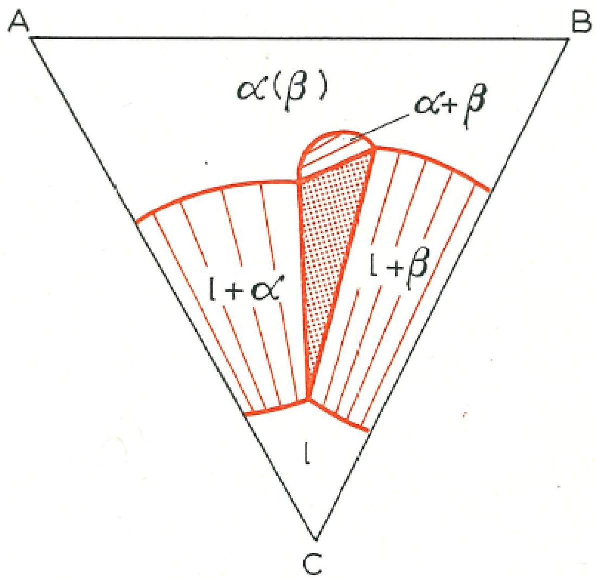
Points P_1 and c lie at the same temperature and the line P_1c is a degenerate tie triangle.



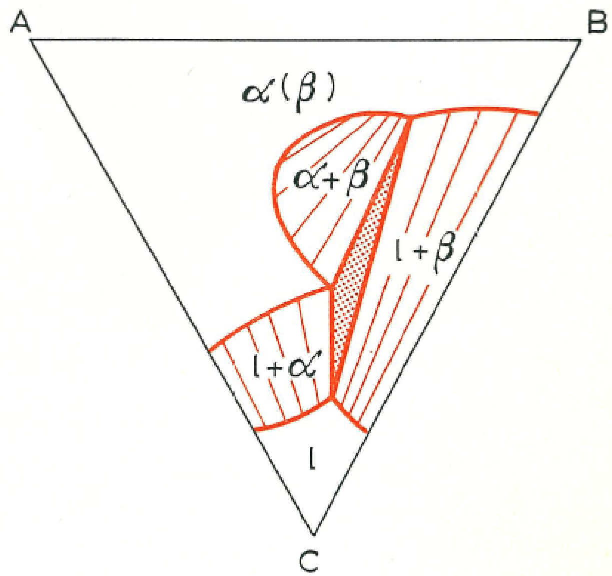
isothermal section



$T = P_1$



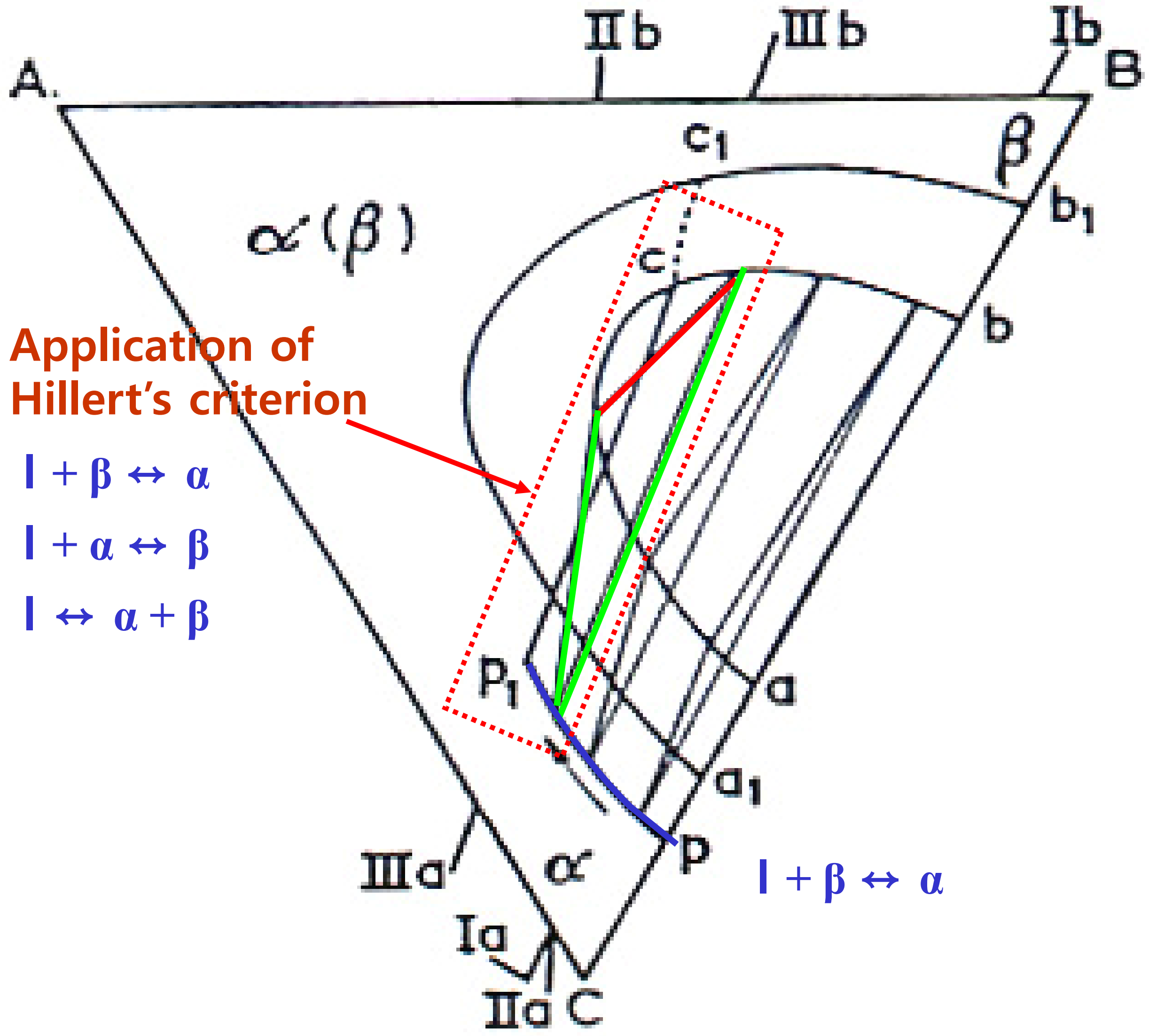
$P_1 > T_1 > P$



$T_1 > T_2 > P$

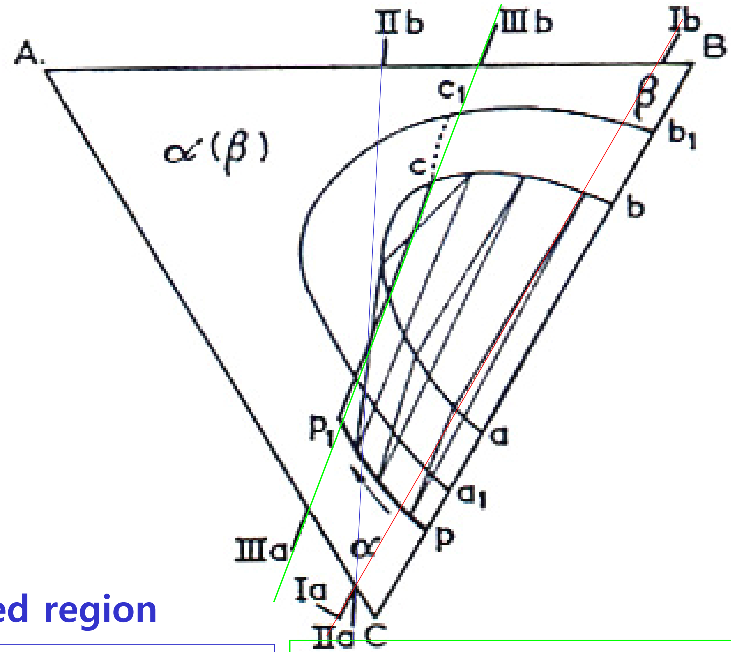
9.4. THREE-PHASE EQUILIBRIUM INVOLVING PERITECTIC REACTIONS

- A peritectic solubility gap in one binary system



9.4. THREE-PHASE EQUILIBRIUM INVOLVING PERITECTIC REACTIONS

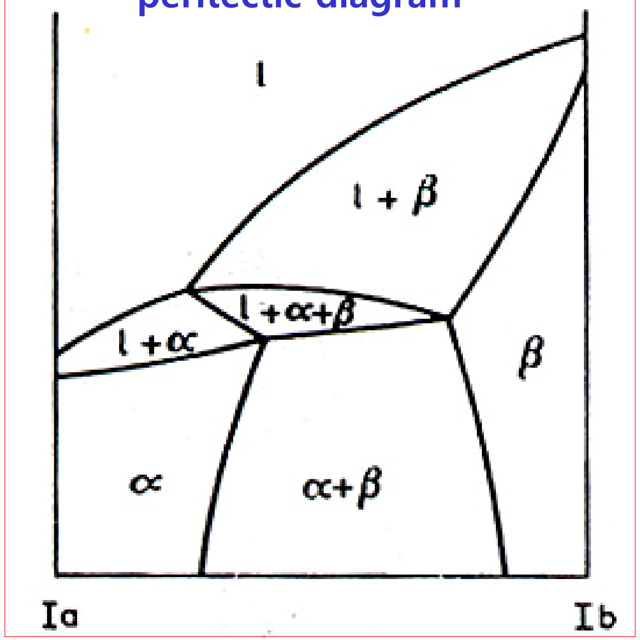
- **A peritectic solubility gap in one binary system**

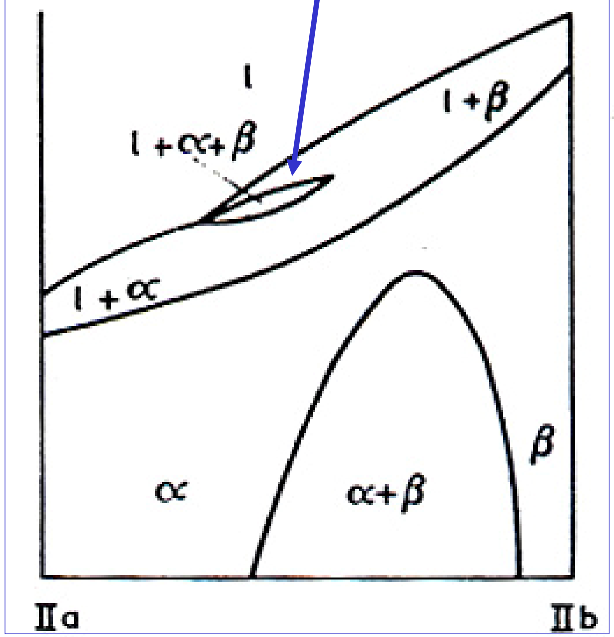


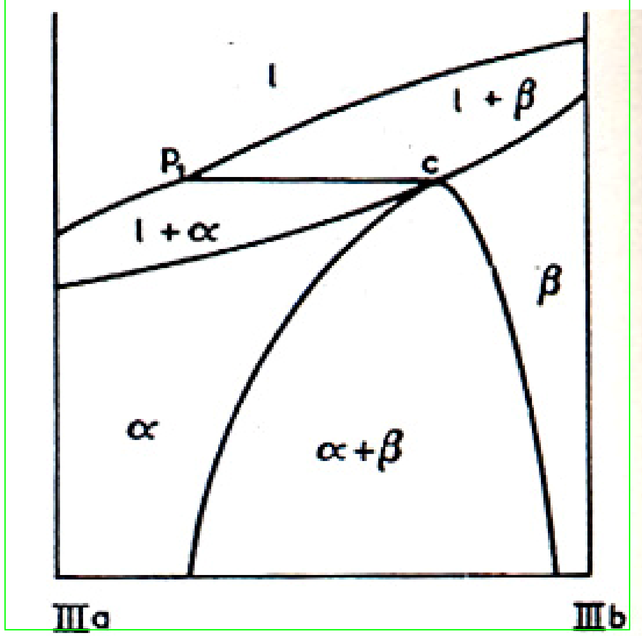
<vertical section>

Similar to the binary peritectic diagram

loop shaped region

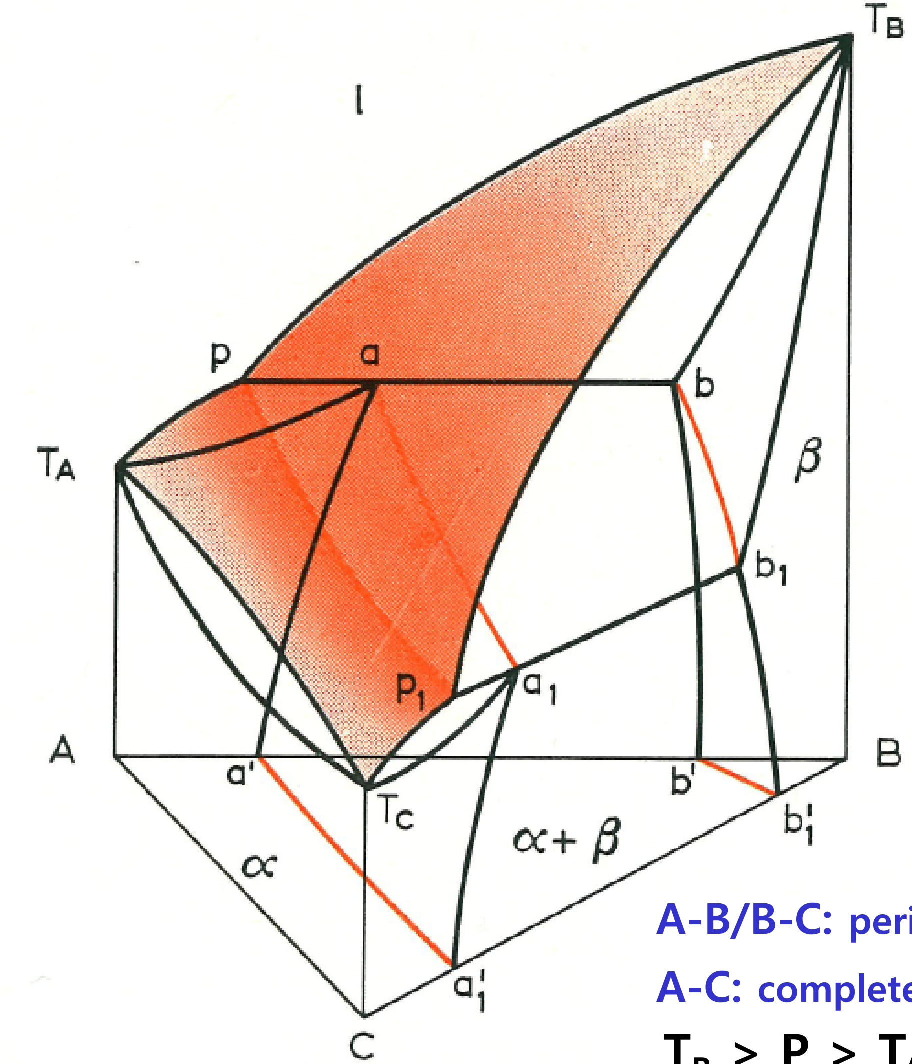


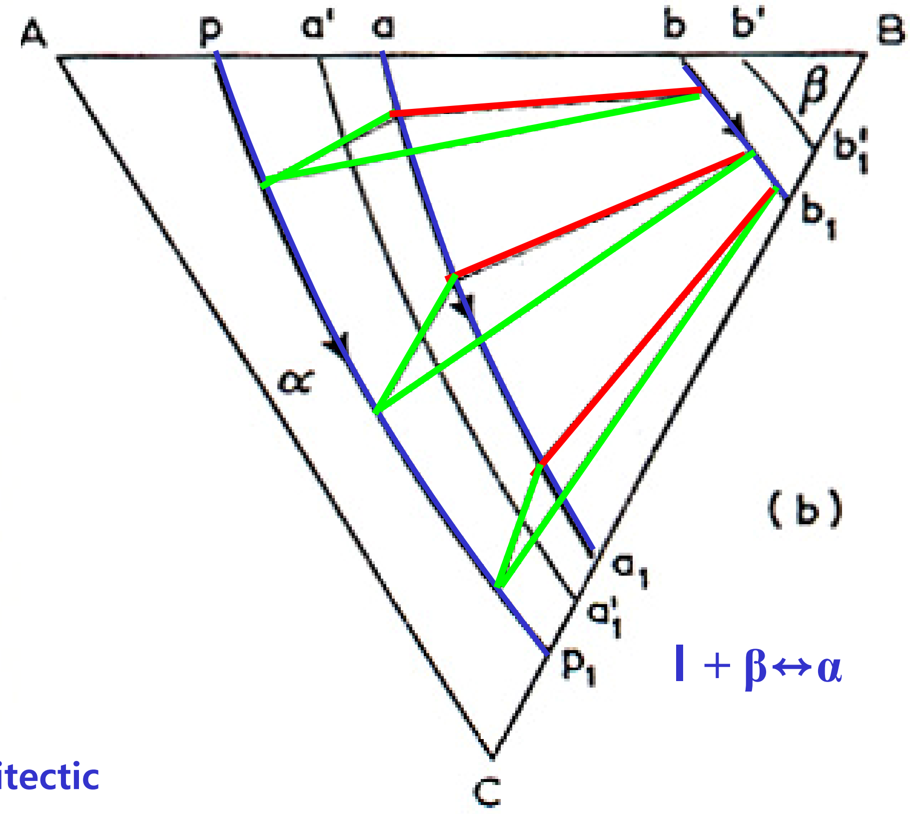




9.4. THREE-PHASE EQUILIBRIUM INVOLVING PERITECTIC REACTIONS

- **A peritectic solubility gap in two binary system**





A-B/B-C: peritectic

A-C: complete solid soln

$T_B > P > T_A > P_1 > T_C$

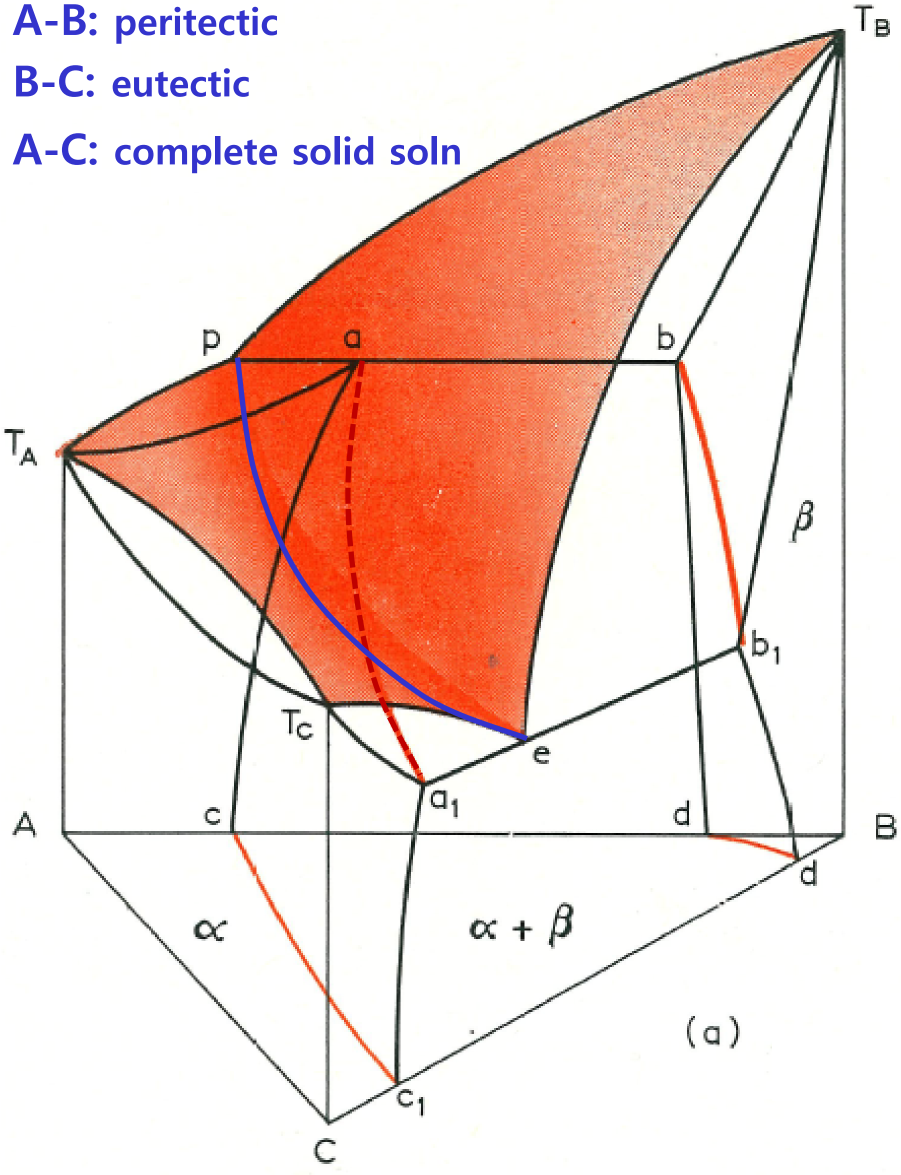
9.4. THREE-PHASE EQUILIBRIUM INVOLVING PERITECTIC REACTIONS

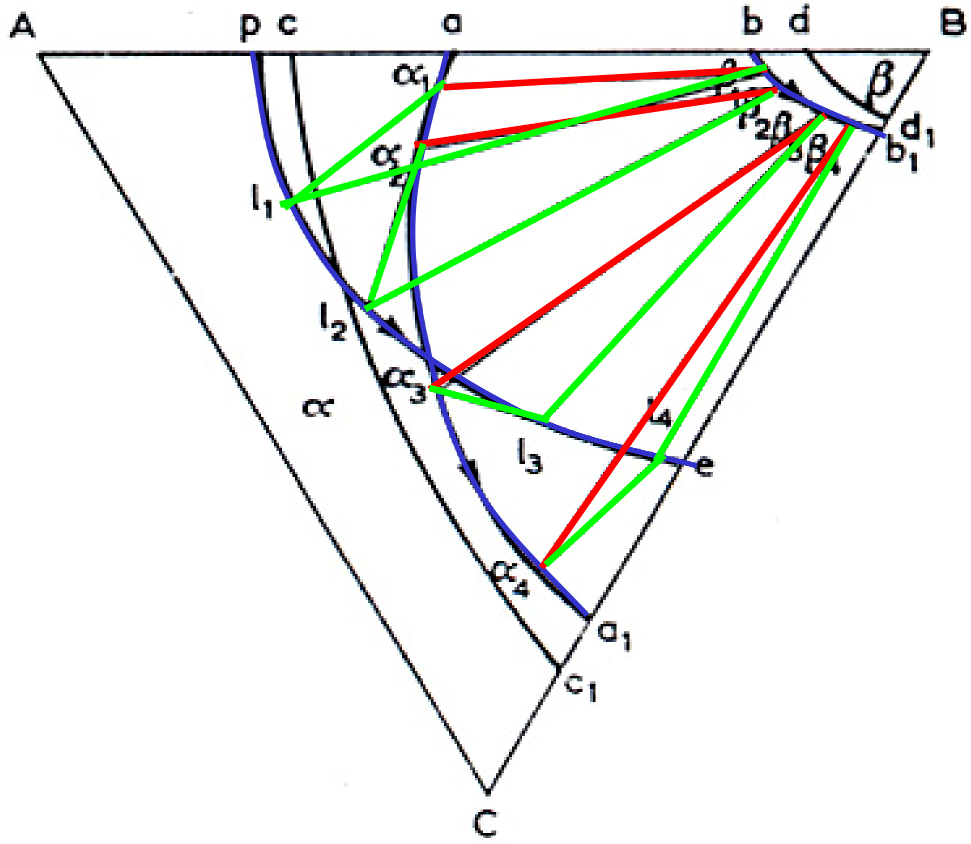
- **A transition from a binary eutectic to a binary peritectic reaction**

A-B: peritectic

B-C: eutectic

A-C: complete solid soln



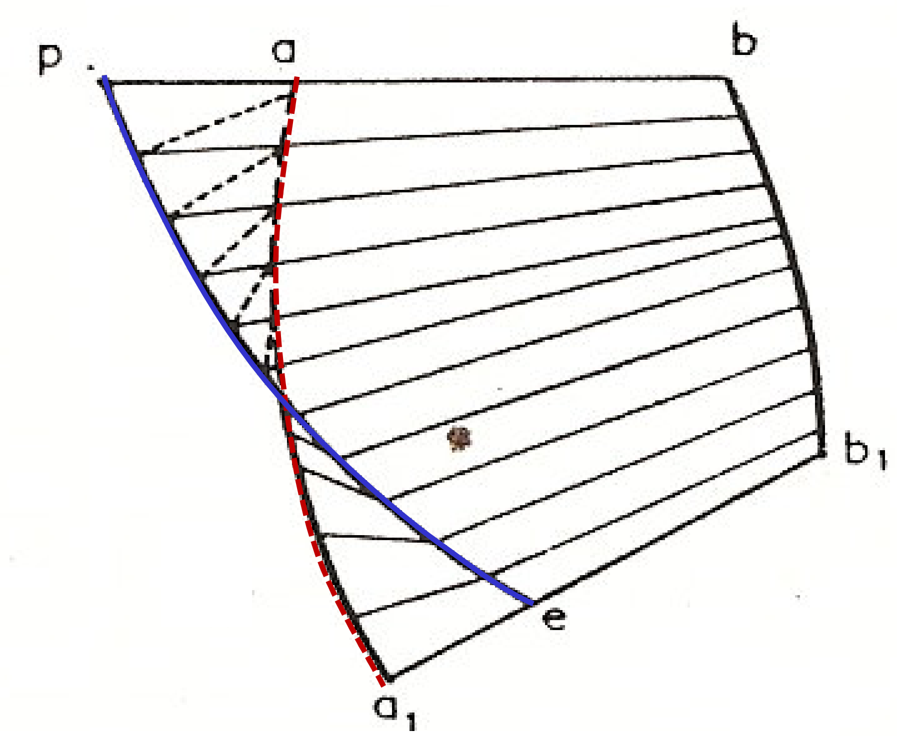


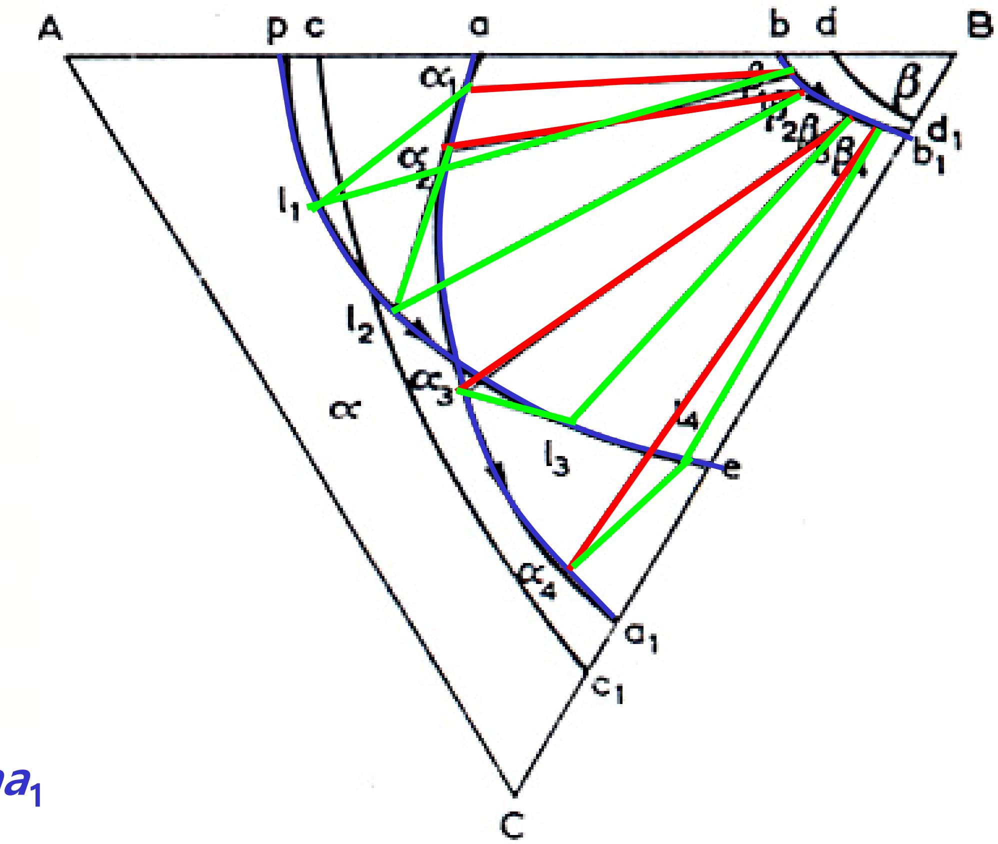
$T_B > P > T_A > T_c > e$

9.4. THREE-PHASE EQUILIBRIUM INVOLVING PERITECTIC REACTIONS

- **A transition from a binary eutectic to a binary peritectic reaction**

$T_B > P > T_A > T_c > e$





- **curve *pe* always lies above curve *aa*$_1$**
- **Tie lines are drawn on the lβ and lα surfaces only.**
- **By Hillert to show that <u>the transition form a peritectic to a eutectic reaction does not occur at a unique temperature.</u>**

9.4. THREE-PHASE EQUILIBRIUM INVOLVING PERITECTIC REACTIONS

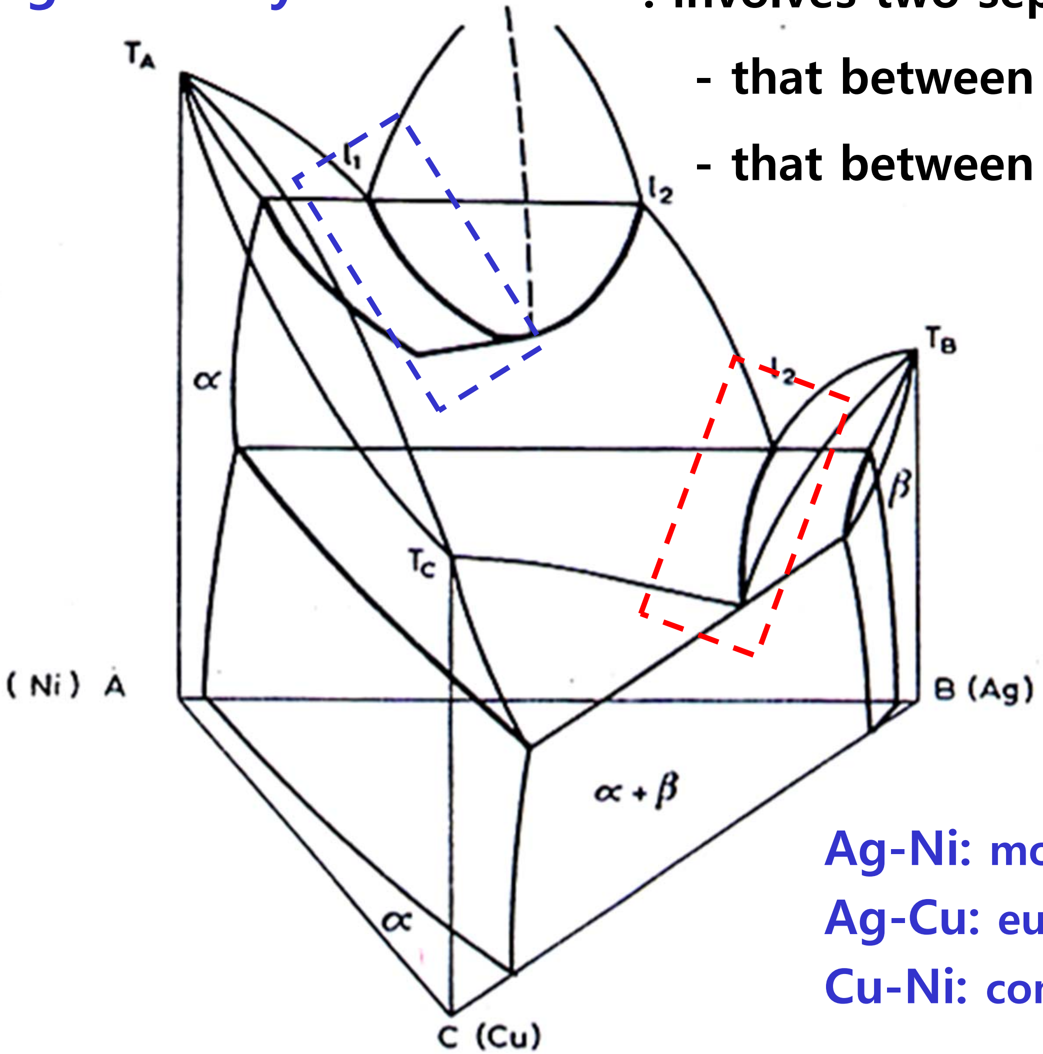
- **Binary Monotectic, syntectic and metatectic reactions in combination with each other as well as with binary eutectic and peritectic reactions.**

- **Ag-Cu-Ni system**

: involves two separate three phase equilibria

- that between α, l_1 and l_2, and

- that between α, β and l_2



Ag-Ni: monotectic

Ag-Cu: eutectic

Cu-Ni: complete solid soln