2009 fall

Advanced Physical Metallurgy

"Phase Equilibria in Materials"

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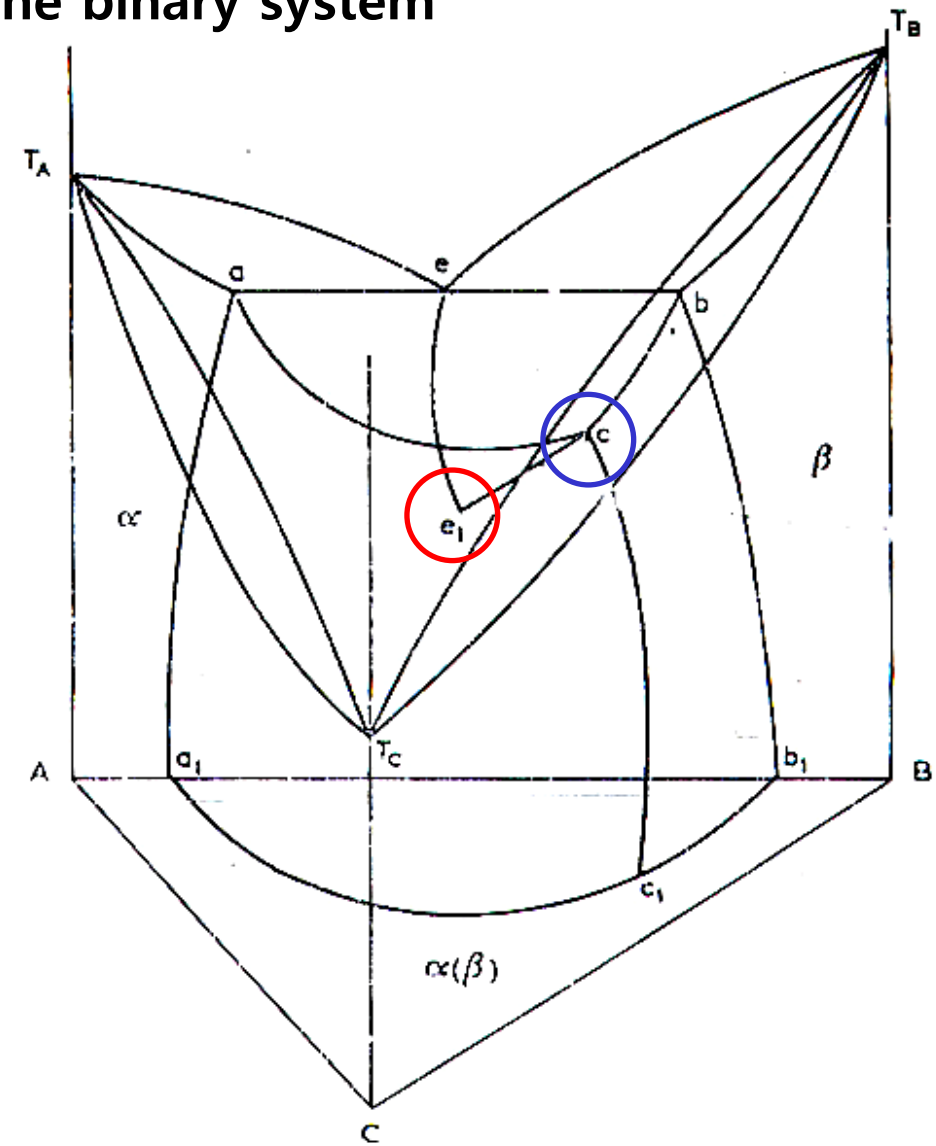
Contents for previous class

9.3. THREE-PHASE EQUILIBRIUM INVOLVING EUTECTIC REACTIONS

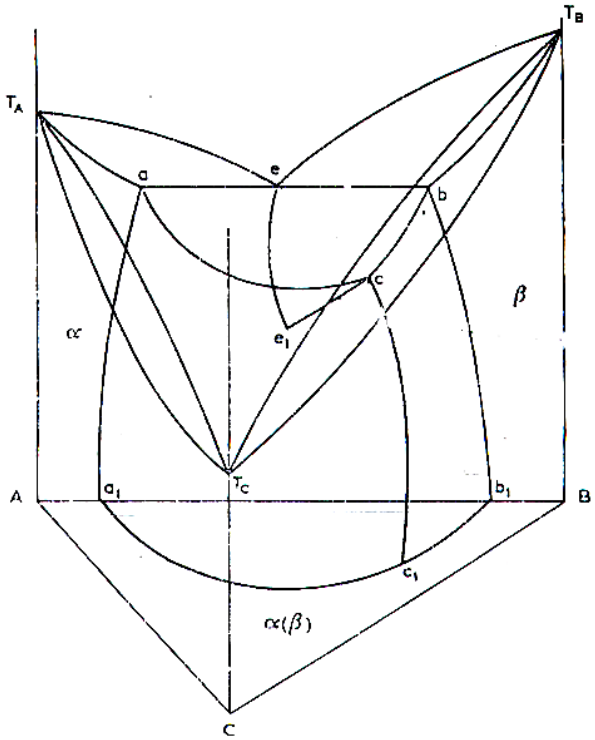
9.3.1. A eutectic solubility gap in one binary system

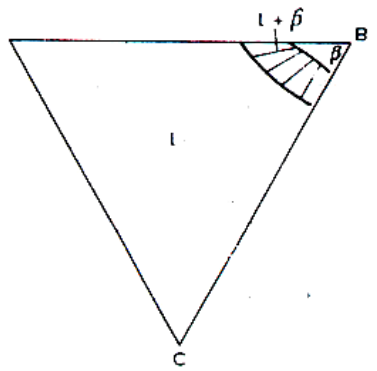
- One binary eutectic : AB
  Complete solid solution : BC, AC



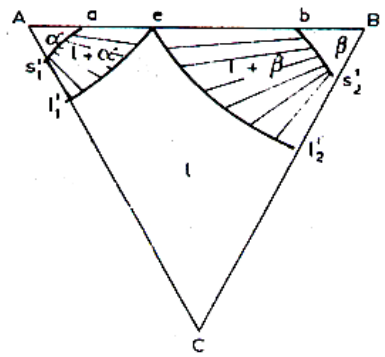
9.3. THREE-PHASE EQUILIBRIUM INVOLVING EUTECTIC REACTIONS

- **Isothermal section**

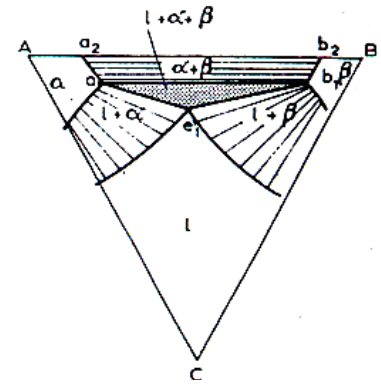




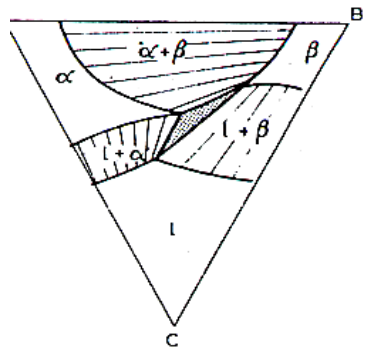
$T_B > T_1 > T_A$



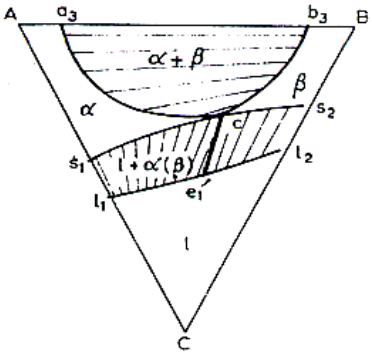
$T_2 = e$



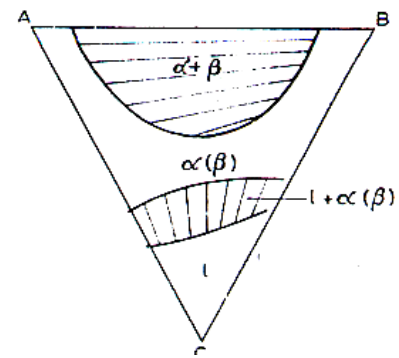
$e > T_3 > e_1$



$T_3 > T_4 > e_1$



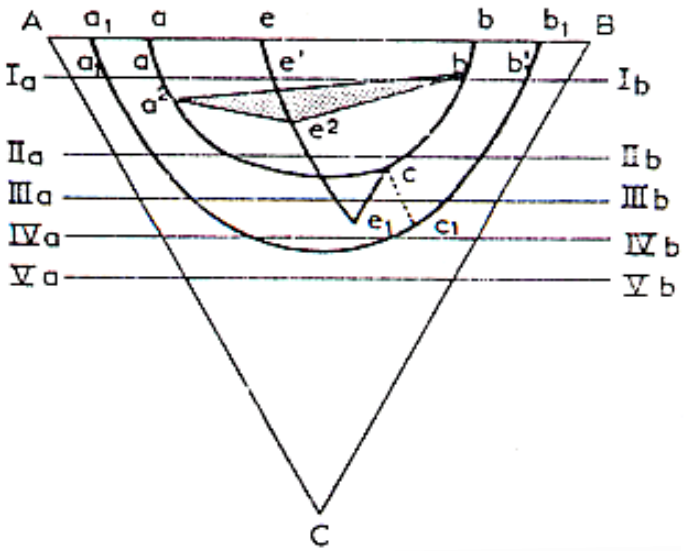
$T_5 = e$

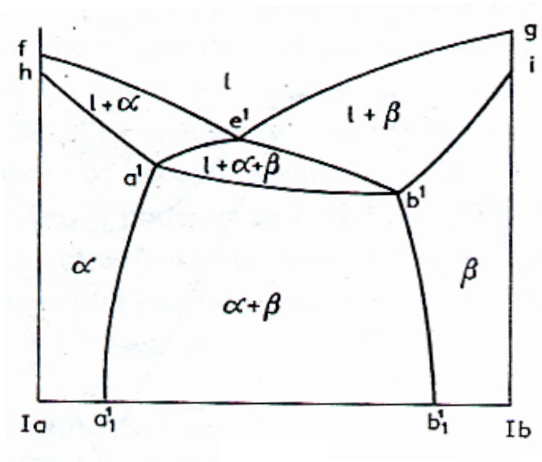


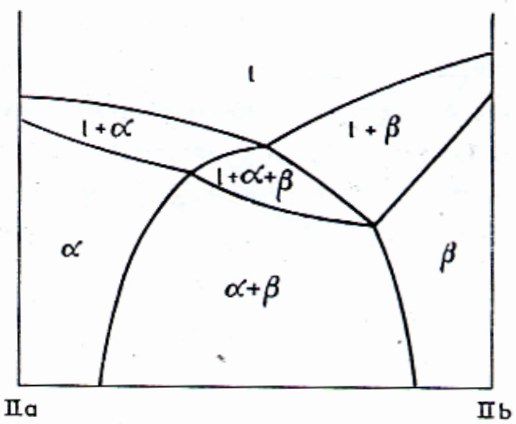
$e_1 > T_6 > T_c$

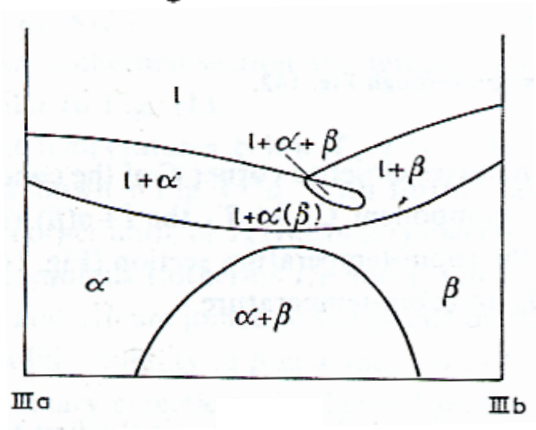
9.3. THREE-PHASE EQUILIBRIUM INVOLVING EUTECTIC REACTIONS

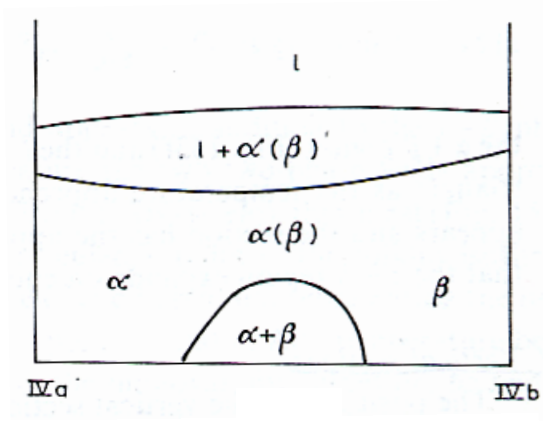
- **Vertical section**

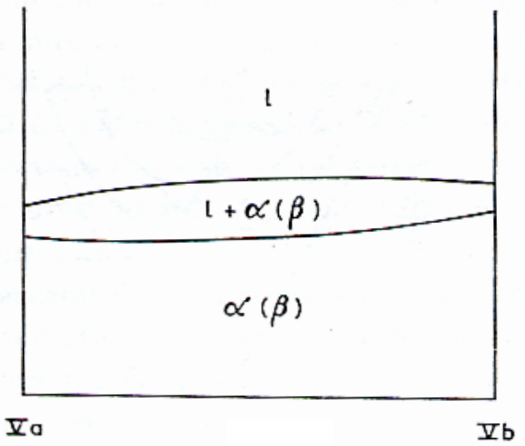












- **How is the reaction in three phase region among liquid, α and β?**

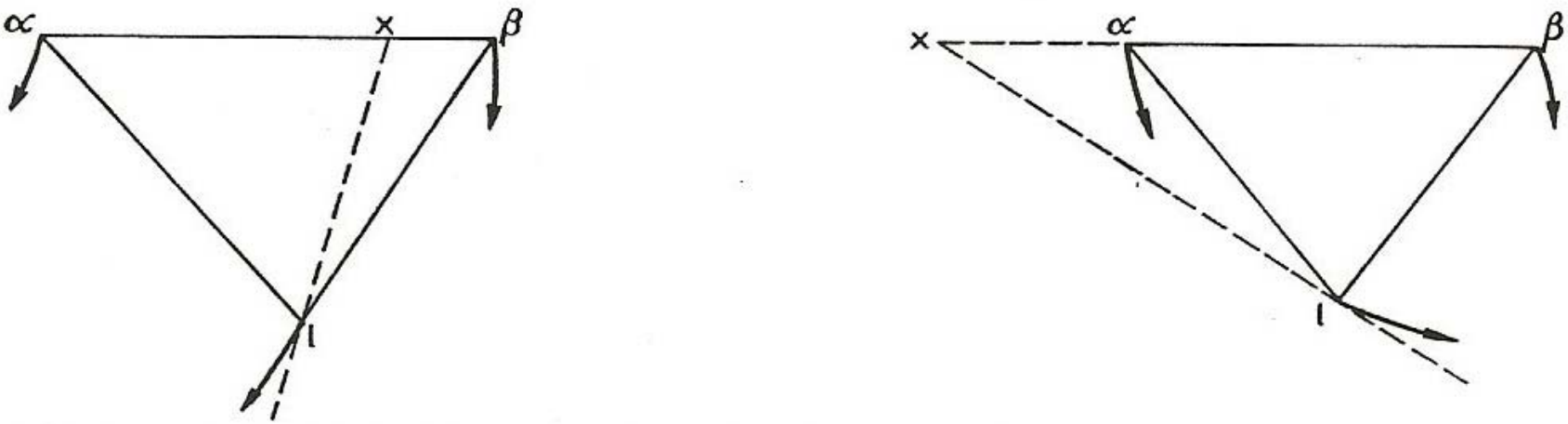


Fig. 149. Criteria for distinguishing eutectic and peritectic reactions in ternary three-phase equilibrium.

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

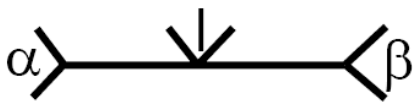
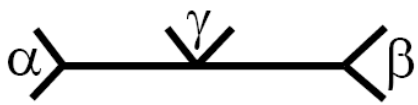
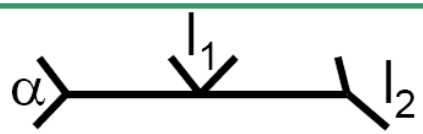
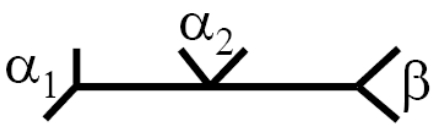
1) If the extrapolated line intersected the αβ tie line, the equilibrium was considered to be eutectic

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

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

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

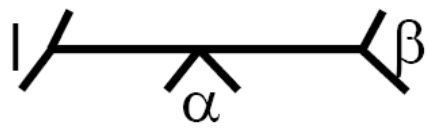
Metatectic reaction: $\beta \leftrightarrow L + \alpha$ **Ex. Co-Os, Co-Re, Co-Ru**

Review of Invariant Binary Reactions

Peritectic Type

Peritectic

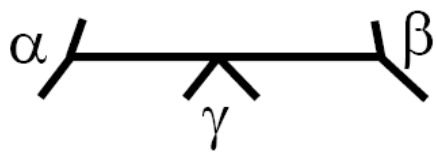
$l + \beta \rightleftarrows \alpha$



Fe-C

Peritectoid

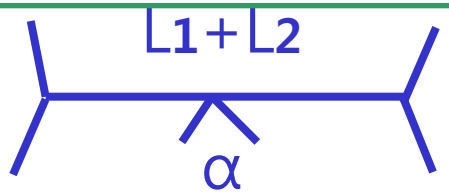
$\alpha + \beta \rightleftarrows \gamma$



Cu-Al

Synthetic reaction

Liquid1+Liquid2 ↔ α



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

On cooling two phases going to one phase

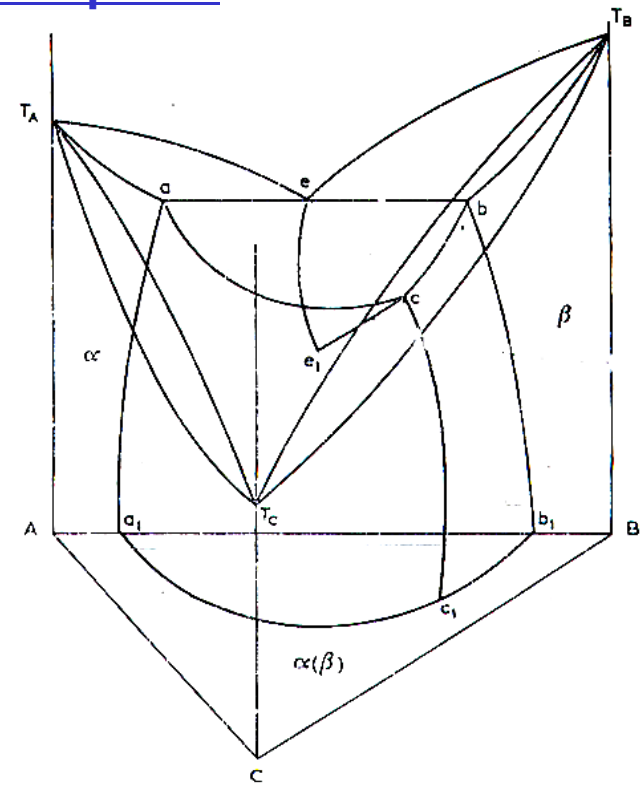
9.3. THREE-PHASE EQUILIBRIUM INVOLVING EUTECTIC REACTIONS

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

<Hillert's criterion>

Basically, the reaction we can expect is eutectic reaction (*l* → a + b). 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.



X_A, X_B, X_C → alloy with in a three-phase triangle

α, β , *l* → m_α, m_β, m_l ($m_\alpha + m_\beta + m_l = 100$)

$$X_A = \frac{m_\alpha \cdot X_A^\alpha + m_\beta \cdot X_A^\beta + m_l \cdot X_A^l}{m_\alpha + m_\beta + m_l} \quad X_B = \frac{m_\alpha \cdot X_B^\alpha + m_\beta \cdot X_B^\beta + m_l \cdot X_B^l}{m_\alpha + m_\beta + m_l} \quad X_A + X_B + X_C = 100$$

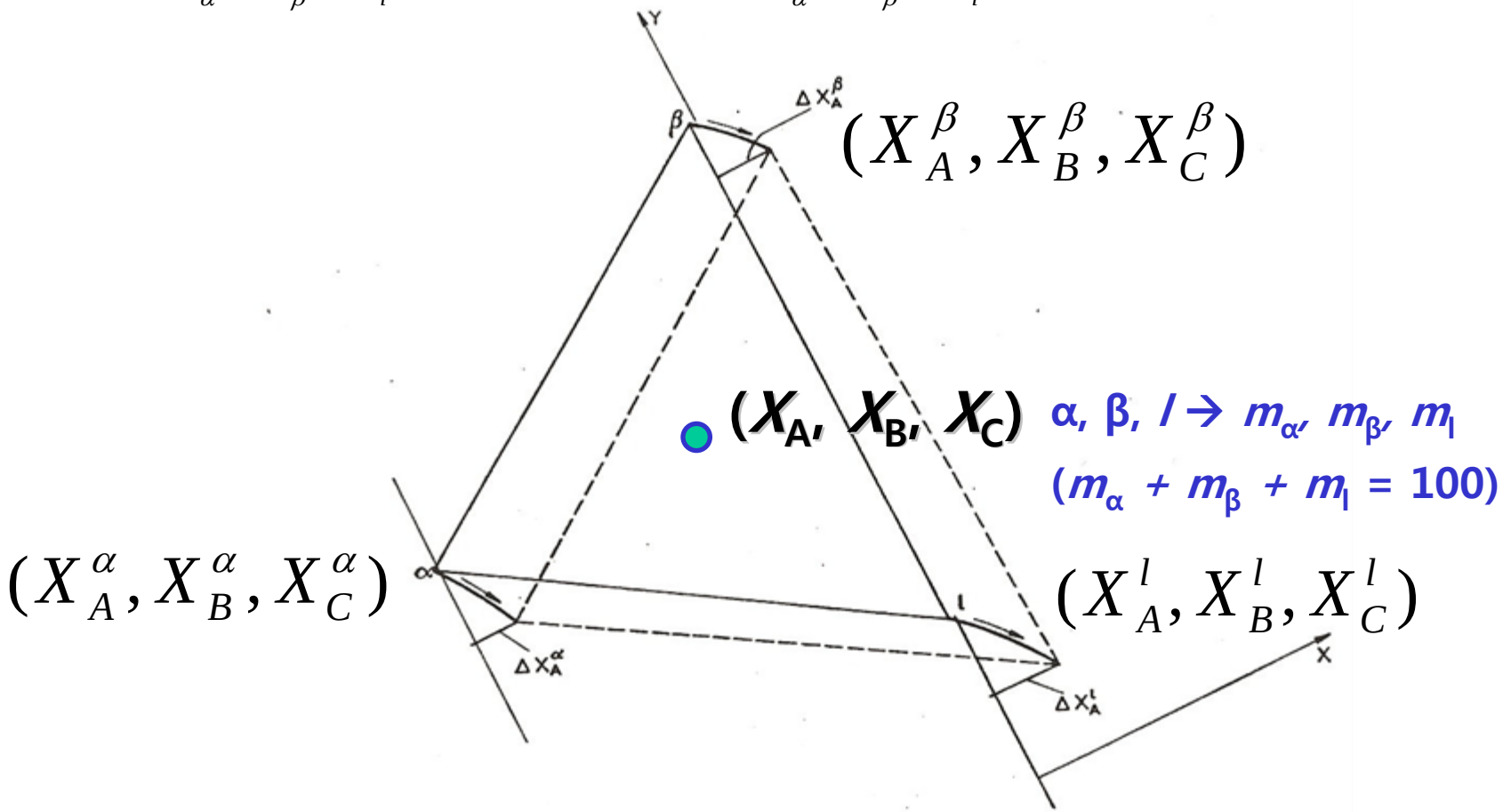


Fig. 150. Illustration of Hillert's criterion for distinguishing eutectic and peritectic reaction in terna phase equilibrium; ———, equilibrium at T; – – – – – –, equilibrium at $T-dT$.

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,

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

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

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

(New coordinate system)

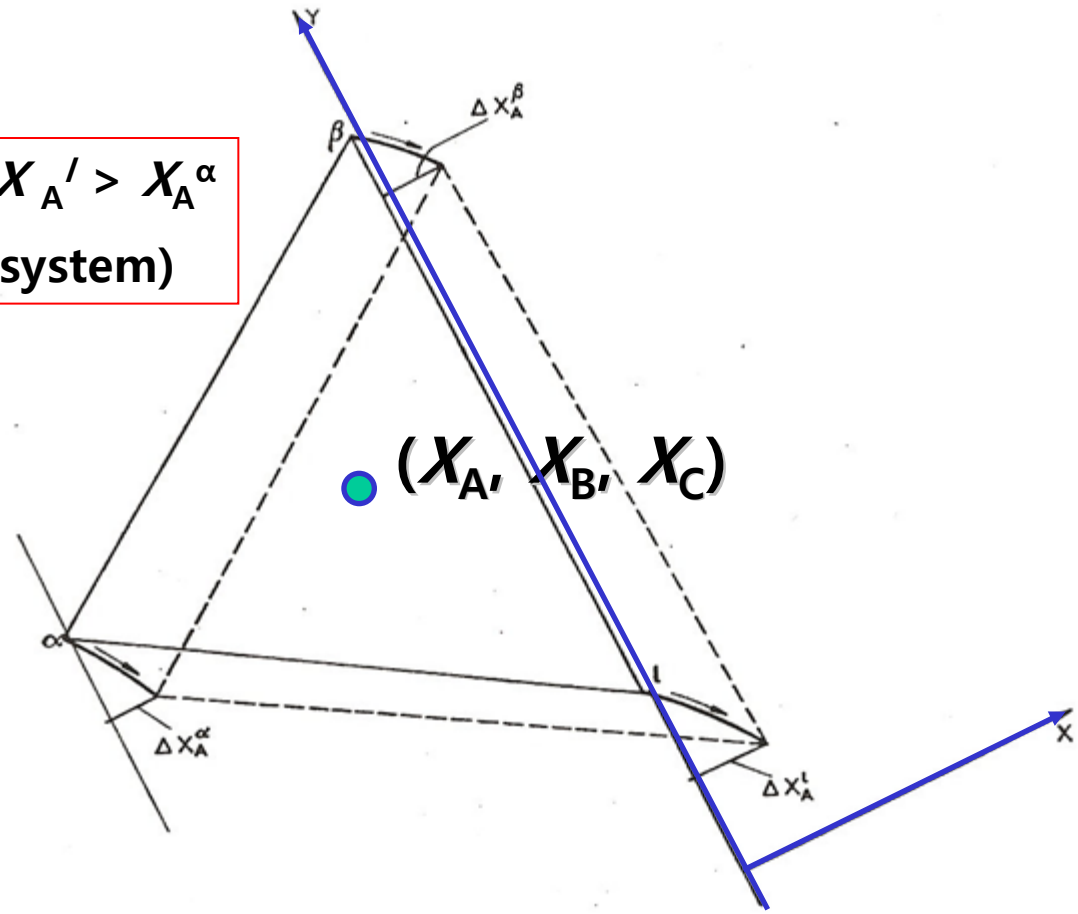


Fig. 150. Illustration of Hillert's criterion for distinguishing eutectic and peritectic reaction in terna phase equilibrium; ———, equilibrium at T; – – – – – –, equilibrium at $T-dT$.

To simplify the calculation,

Assumption, $X_A^{\beta} = X_A^{l} > X_A^{\alpha}$ (New coordinate system)

$\Delta m_\beta + \Delta m_l = -\Delta m_\alpha$

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

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

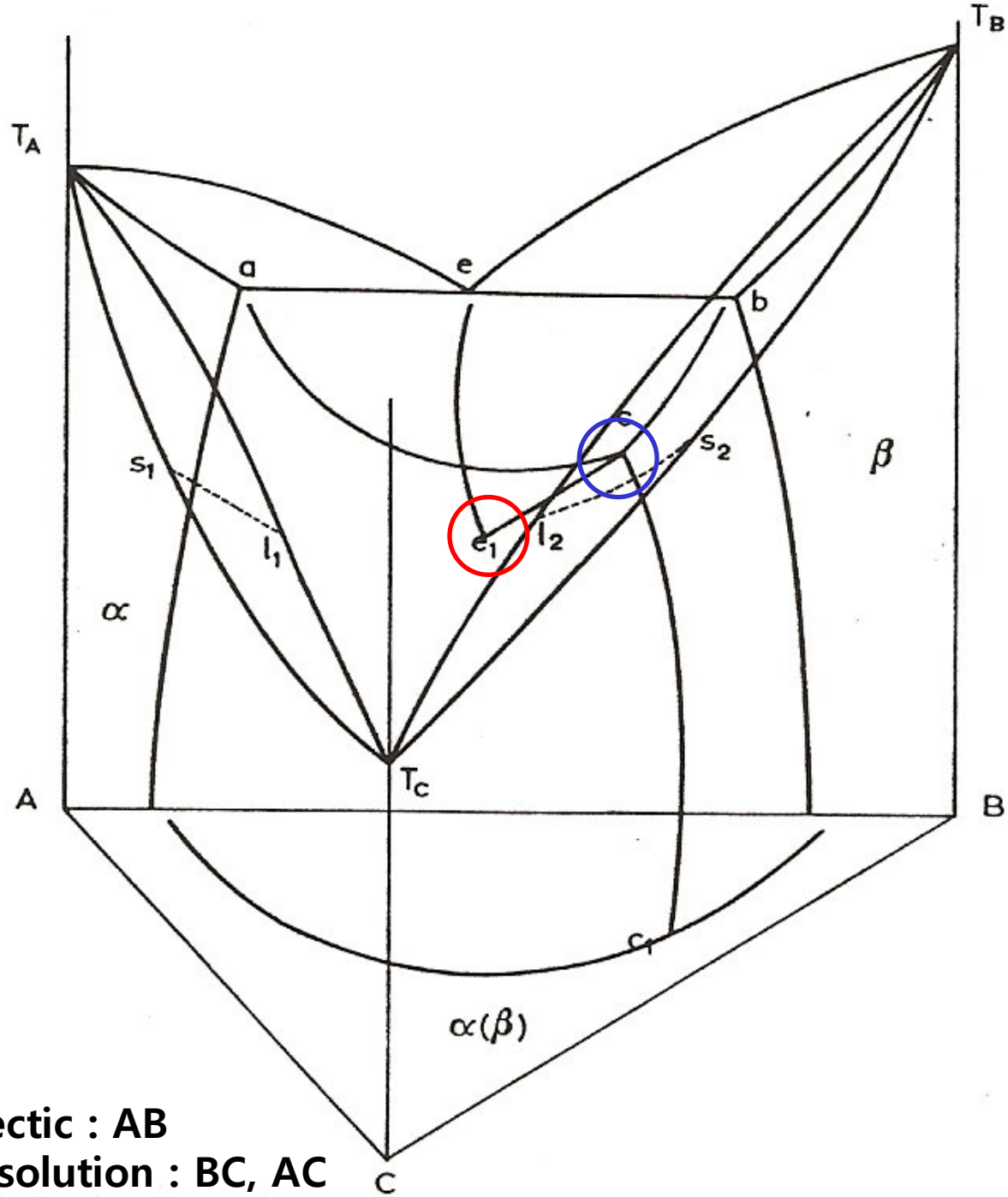
$$\Delta m_\alpha (X_A^\beta - X_A^\alpha) = m_\alpha \Delta X_A^\alpha + m_\beta \Delta X_A^\beta + m_l \Delta X_A^l$$

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

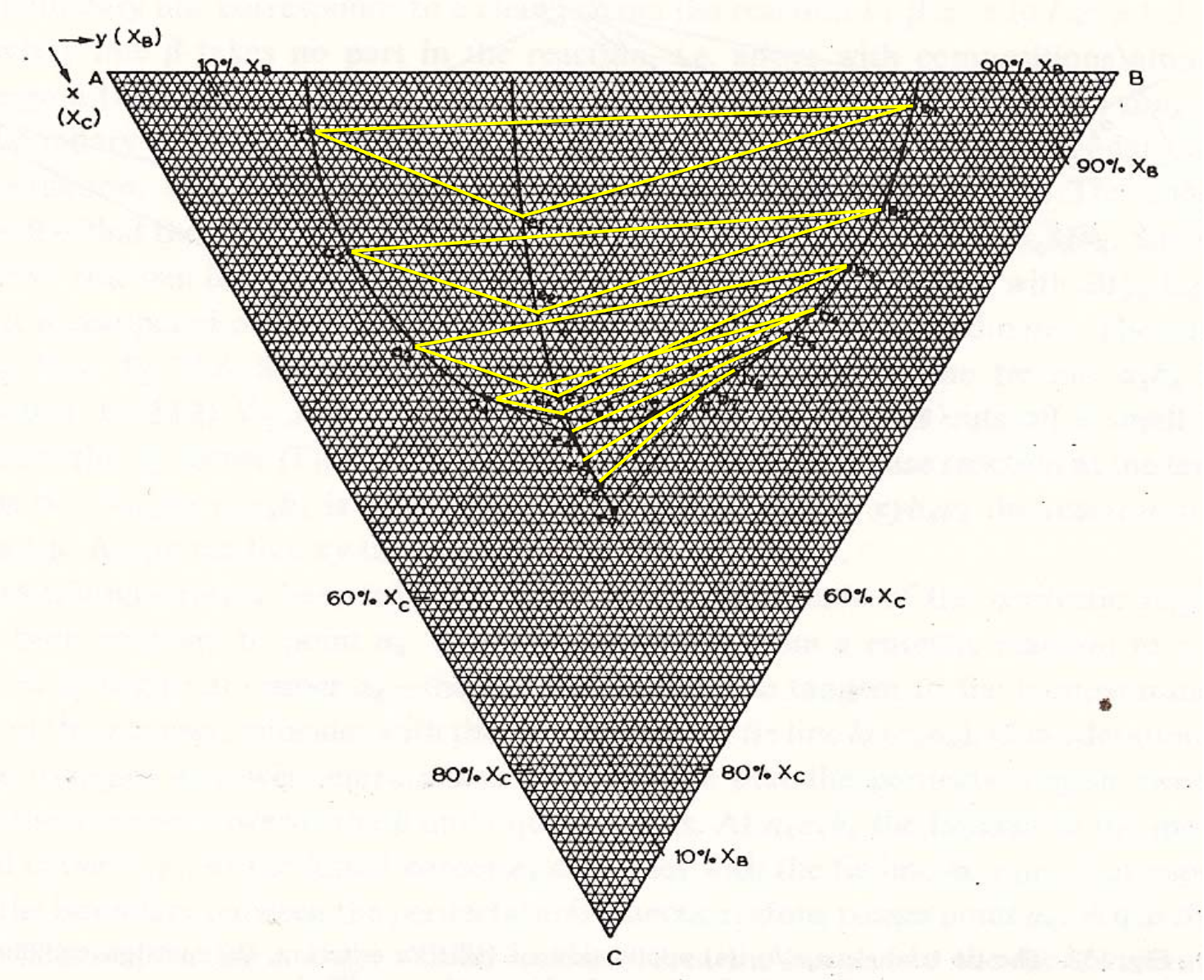
Hillert's criterion indicates that the relative amounts of the α, β and liquid phases (the average alloy composition) are of importance in determining the type of reaction.



- **One binary eutectic : AB**
  Complete solid solution : BC, AC

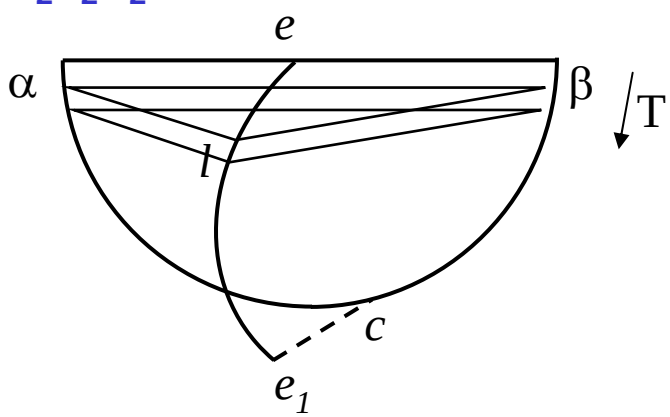
9.3. THREE-PHASE EQUILIBRIUM INVOLVING EUTECTIC REACTIONS

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



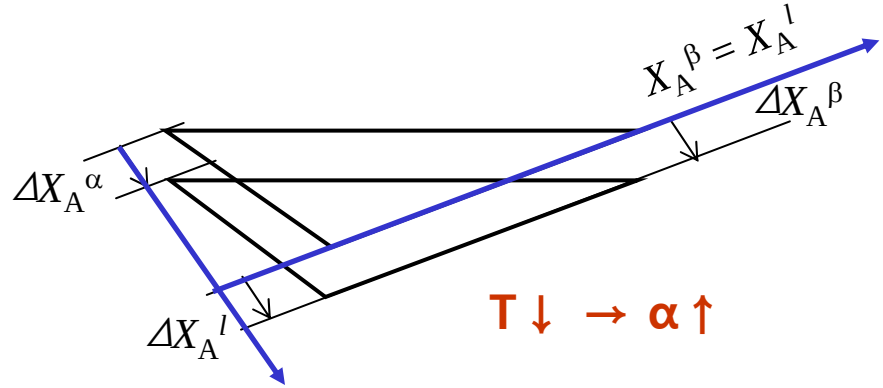
9.3. THREE-PHASE EQUILIBRIUM INVOLVING EUTECTIC REACTIONS

- **Relations between the triangle $a_1e_1b_1$ and $a_2e_2b_2$**



(if $X_A^{\beta} = X_A^{l}, > X_A^{\alpha},$)

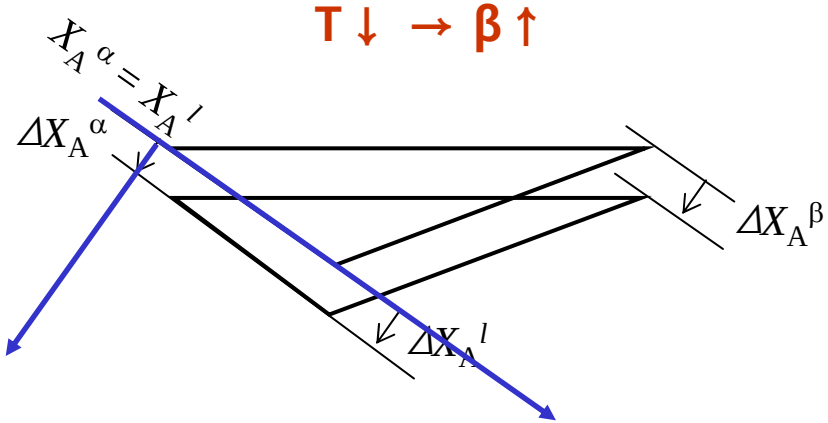
① ΔX_A^{α}, ΔX_A^{β}, ΔX_A^{l} **(+)** → Δm_{α} **(+)**



(if $X_A^{\alpha} = X_A^{l} > X_A^{\beta},$)

② ΔX_A^{α}, ΔX_A^{β}, ΔX_a^{l} **(+)** → Δm_{β} **(+)**

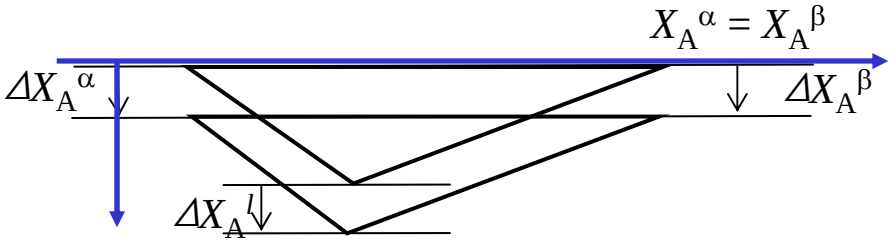
T↓ → β↑



(if $X_A^{a} = X_A^{b} > X_a^{l}$)

③ ΔX_A^{α}, ΔX_A^{β}, ΔX_a^{l} **(-)** → Δm_{l} **(-)**

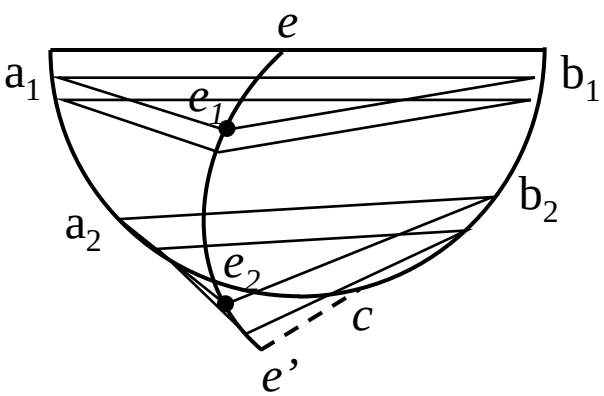
T↓ → liquid is being consumed



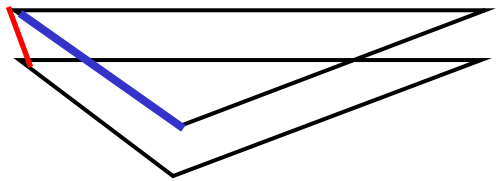
The reaction under gone by any alloy within the triangle $a_1e_1b_1$ is eutectic-type: l↔α+β ex) $a_2e_2b_2$-$a_3e_3b_3$/ $a_3e_3b_3$-$a_4e_4b_4$

9.3. THREE-PHASE EQUILIBRIUM INVOLVING EUTECTIC REACTIONS

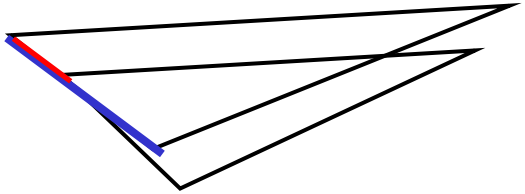
- **Relative position of vertex in tie triangle with ΔT**

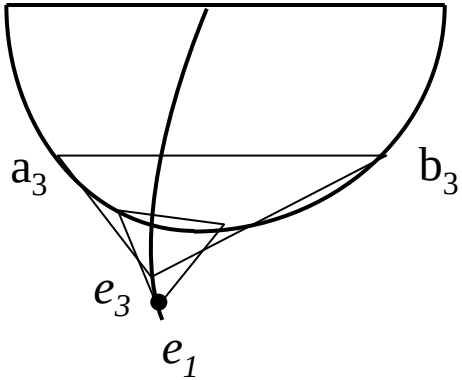


① Slope of tangent line at a_1 > slope of line a_1e_1

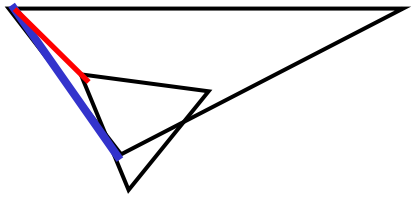


② Slope of tangent line at a_2 ≤ slope of line a_2e_2



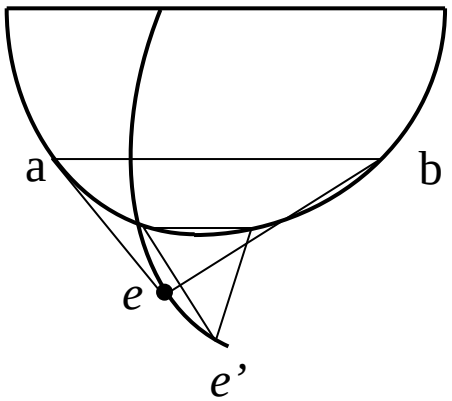


③ Slope of tangent line at a_3 ≤ slope of line a_3e_3



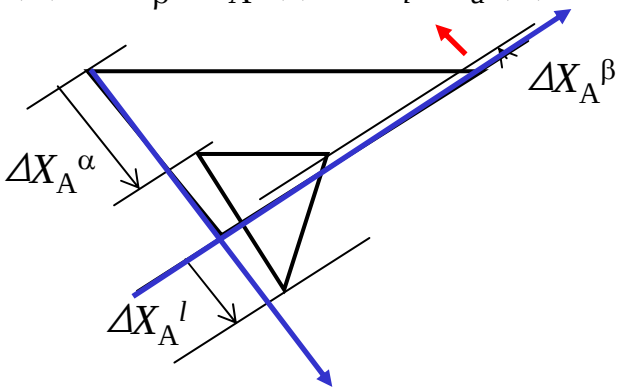
9.3. THREE-PHASE EQUILIBRIUM INVOLVING EUTECTIC REACTIONS

- **Slope of tangent line at *a* = slope of line *ae***



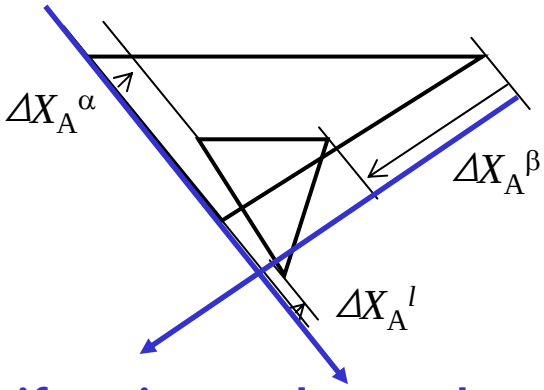
① $X_A^{\beta} = X_A^{l} > X_A^{\alpha}$

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



② $X_A^{\alpha} = X_A^{l} > X_A^{\beta}$

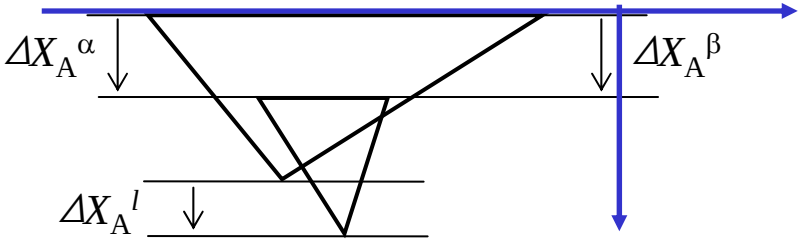
$\Delta m_\beta \rightarrow m_\alpha \Delta X_A^{\alpha}(-) + m_\beta \Delta X_A^{\beta}(+) + m_l \Delta X_a^{l}(-)$



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

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

T ↓ → liquid is being consumed



❖ **Δm_l (-); if m_β is very larger than m_α and m_l → Δm_α(-) and Δm_β (+) → (l + α → β)**

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

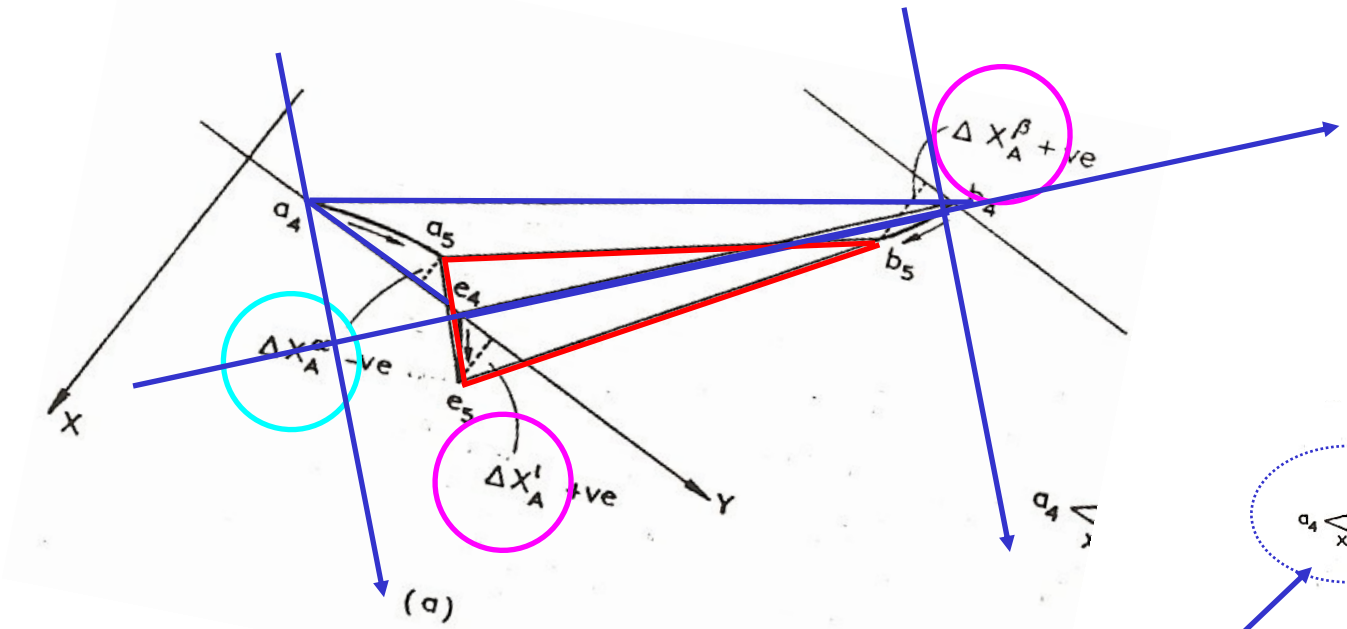
Consider tie triangle $a_4e_4b_4$, and $a_5e_5b_5$

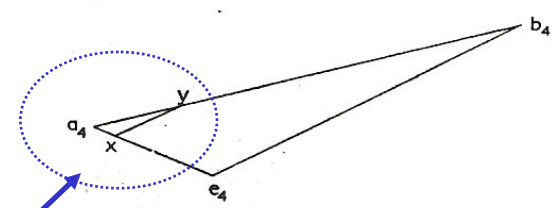
① $X_A^{\beta} = X_A^{l} > X_A^{\alpha}$

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

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

T ↓ → liquid is being consumed



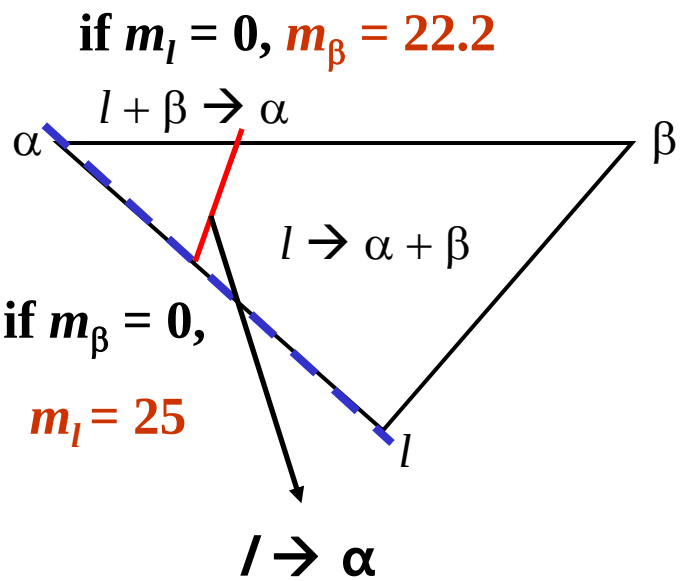


② $X_A^{\alpha} = X_A^{l} > X_A^{\beta}$ $\quad \Delta m_\beta \rightarrow m_\alpha \Delta X_A^{\alpha}(-) + m_\beta \Delta X_A^{\beta}(+) + m_l \Delta X_a^{l}(+)$

❖ $\Delta m_\alpha(+)$, 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)

- **How to decide the boundary?**



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

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

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

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

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

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

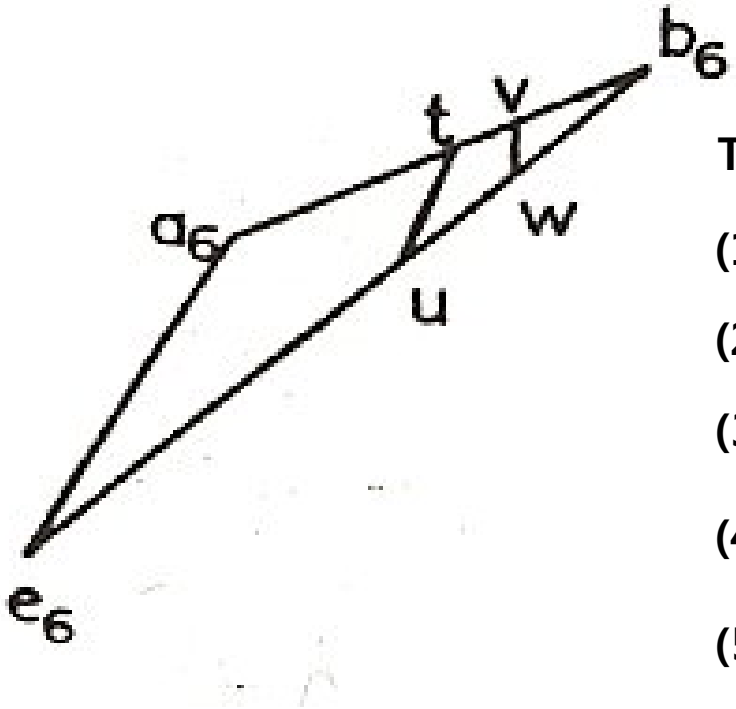
if $m_\beta = 0$, $m_l = 25$

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.

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_6ut

(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_6vw

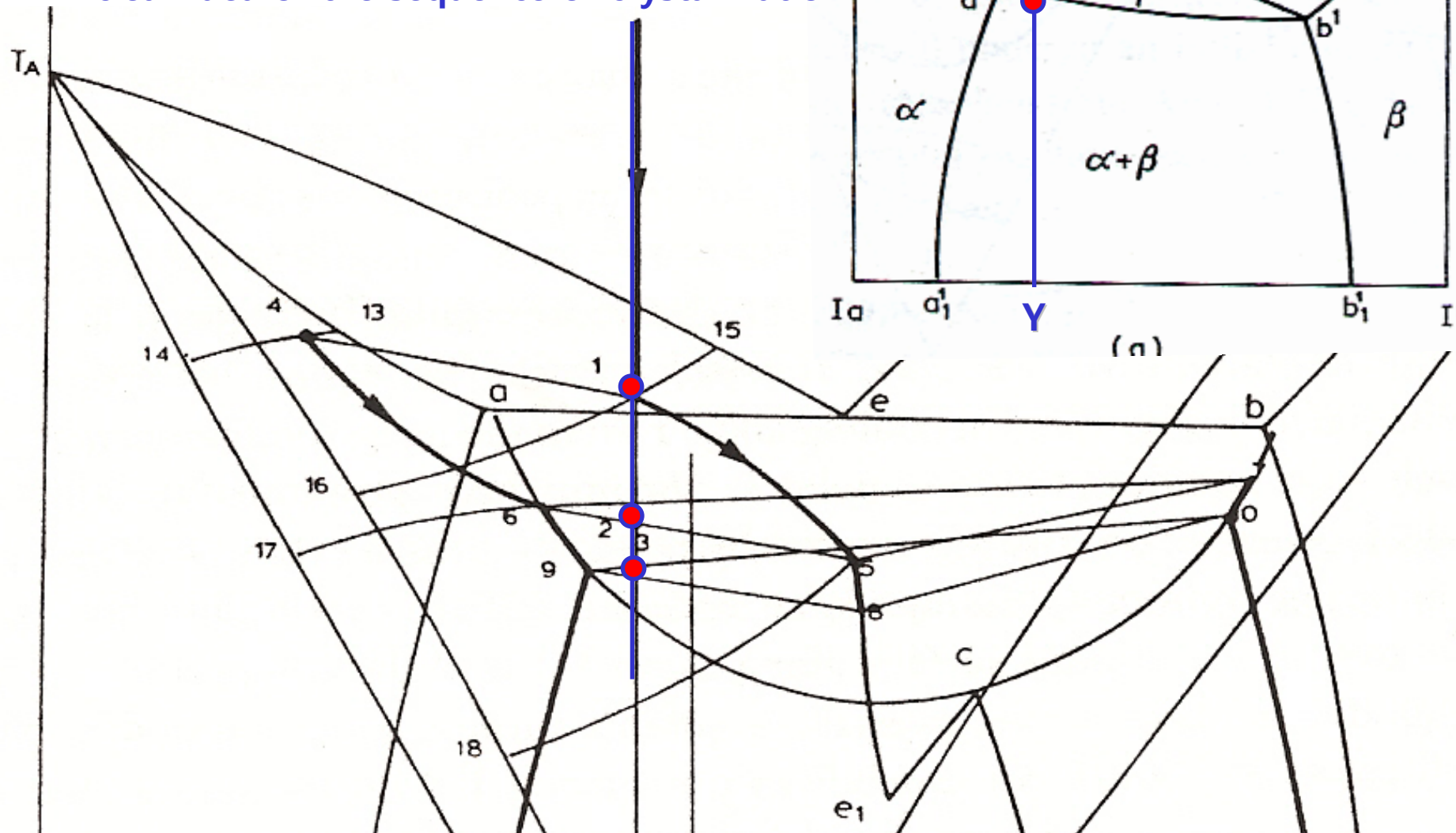
To summarise, the three-phase reaction is initially eutetic for all alloys untill the temperature of the three phase triangle $a_4e_4b_4$, is reached. From that temperature until the end of the three-phase reaction at the tie line $e_7a_7(b_7)$ the reaction type is dependent on the alloy composition within the sequence of the three-phase triangles.

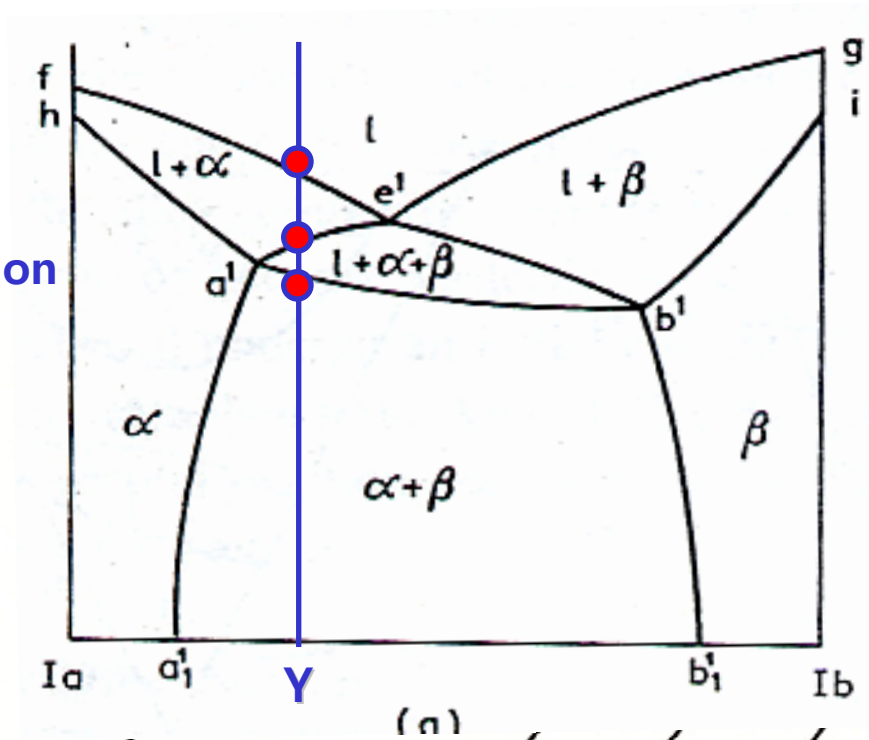
9.3. THREE-PHASE EQUILIBRIUM INVOLVING EUTECTIC REACTIONS

- **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

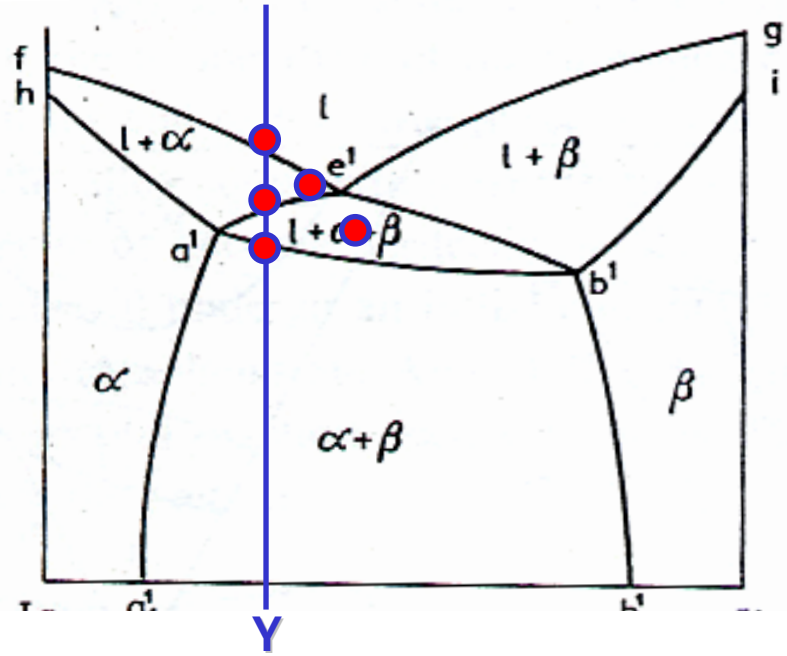
* 4→6 on the α solidus surface
* 1→5 on the α liquidus surface

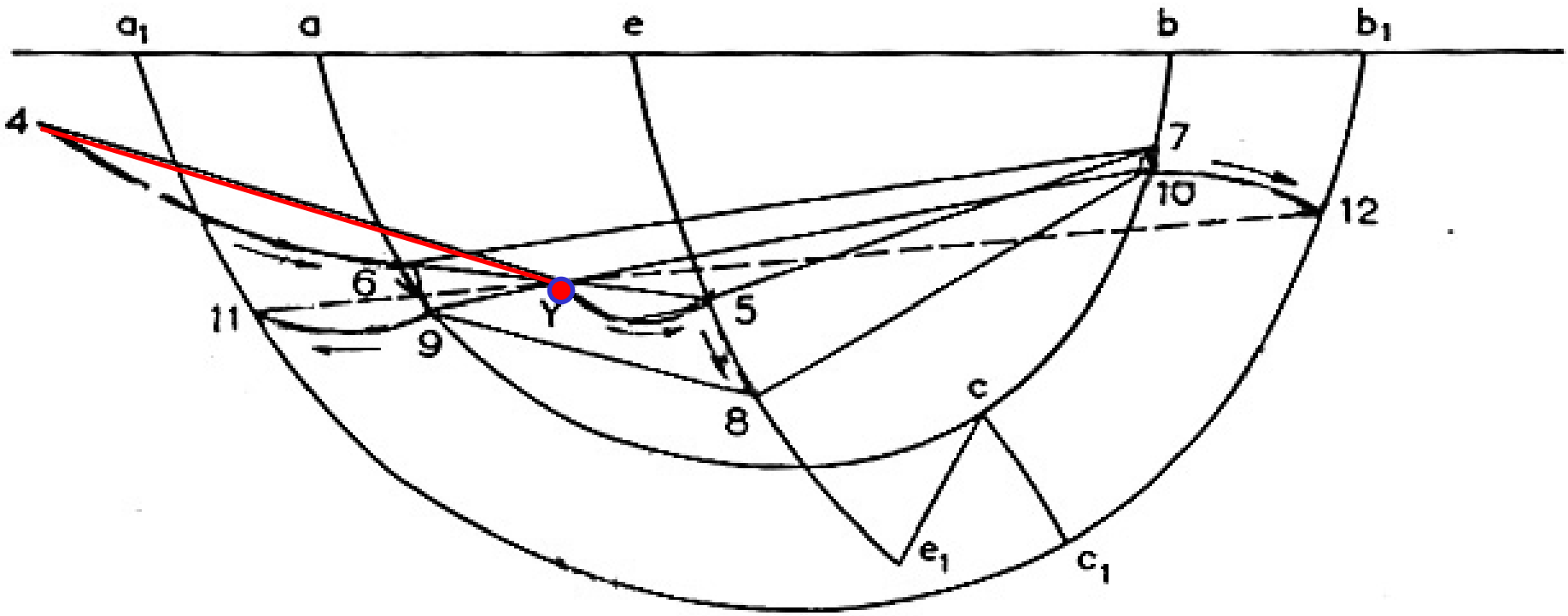
Three phase equilibrium l5, α 6, β7

* 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



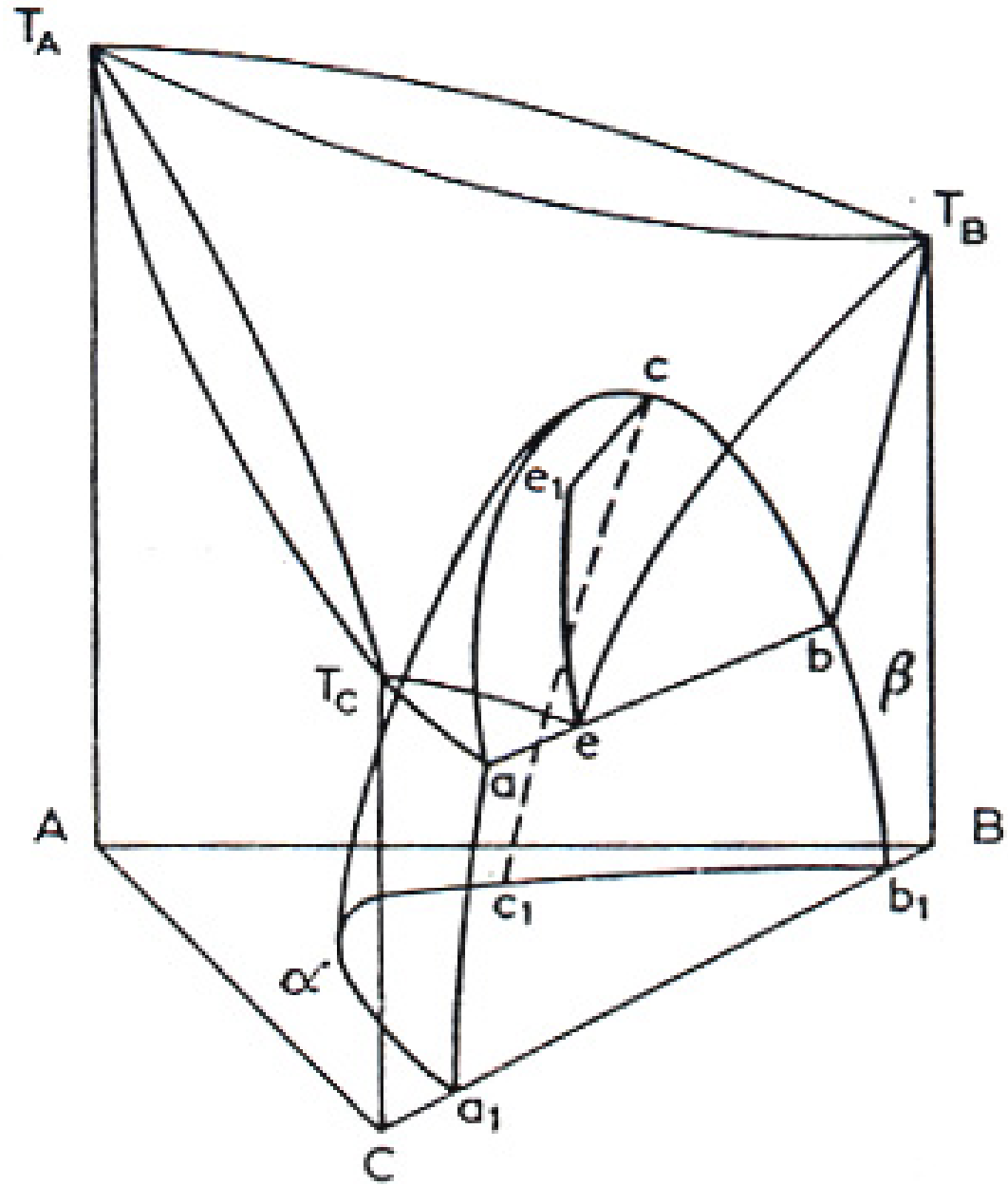


Projection of the solidification sequence for alloy Y on the concentration triangle

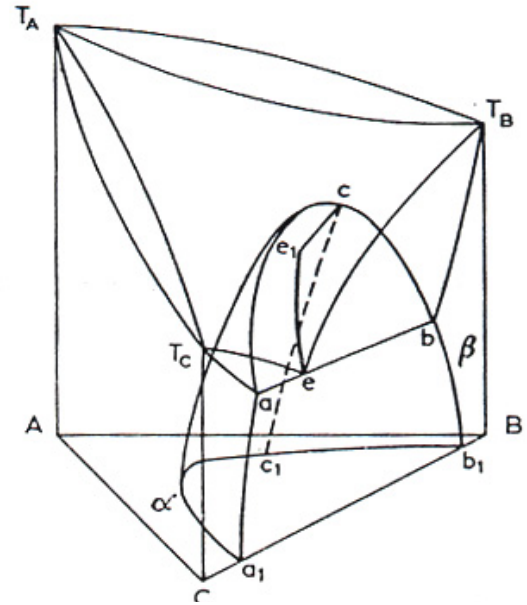
9.3. THREE-PHASE EQUILIBRIUM INVOLVING EUTECTIC REACTIONS

- **A maximum critical point**

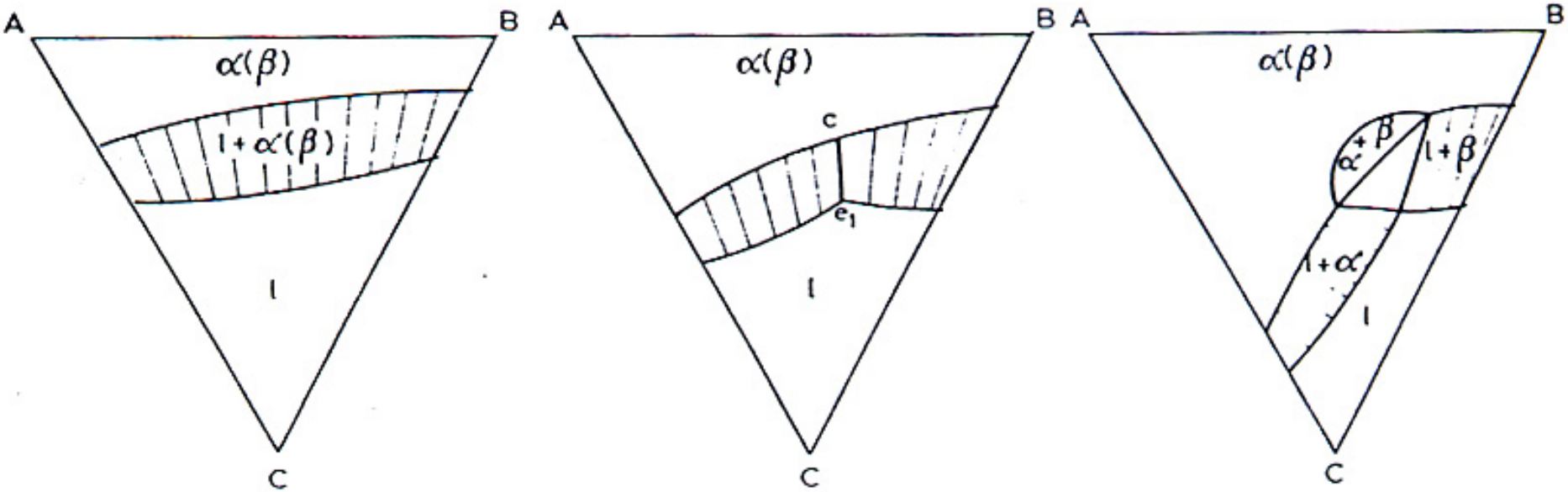
I’



- **A maximum critical point**

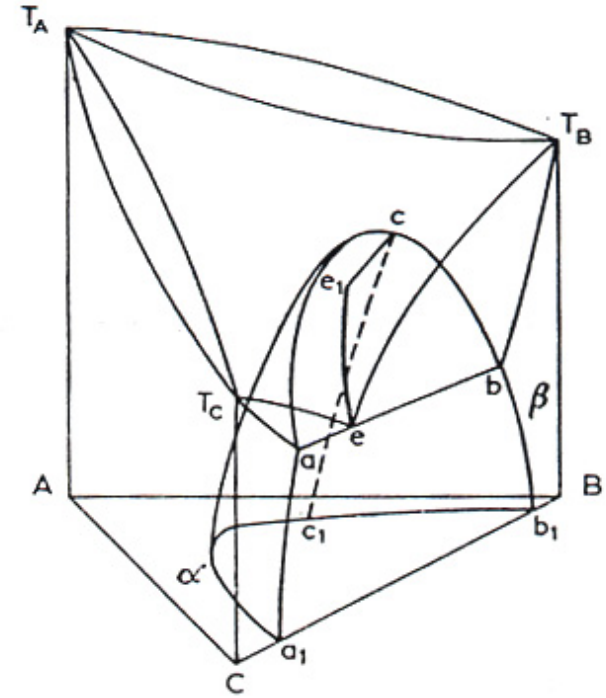


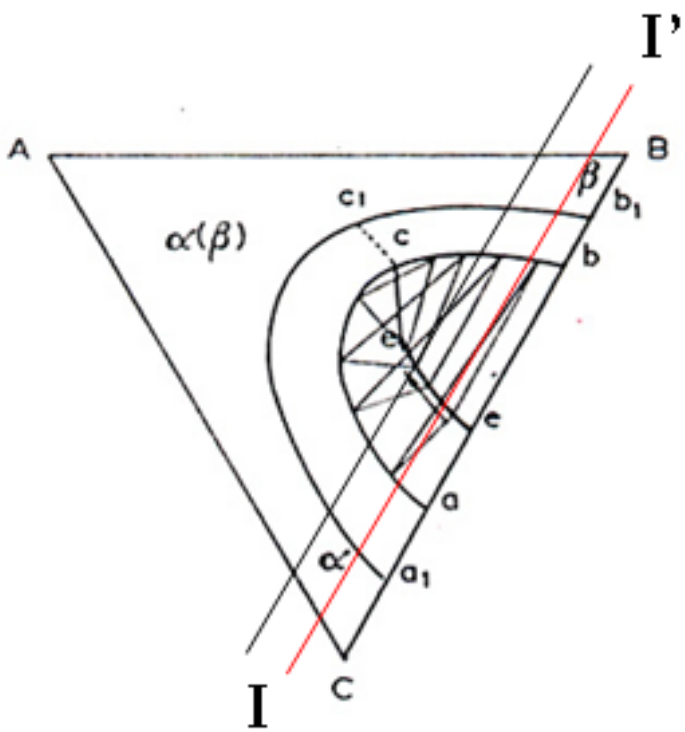
isothermal section



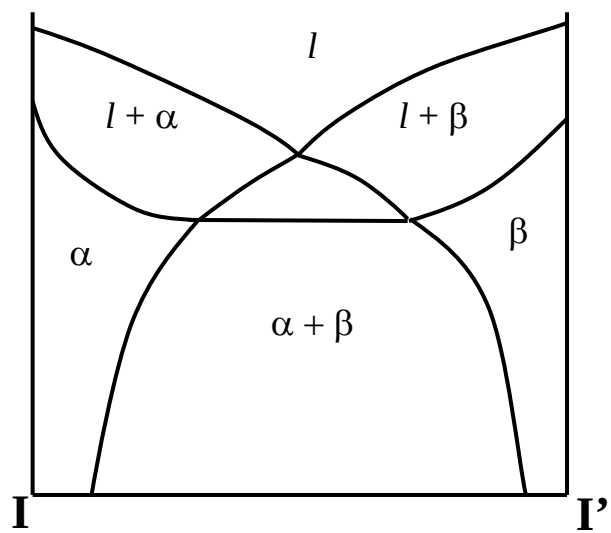
$T > e_1$ **$T = e_1$** **$T < e_1$**

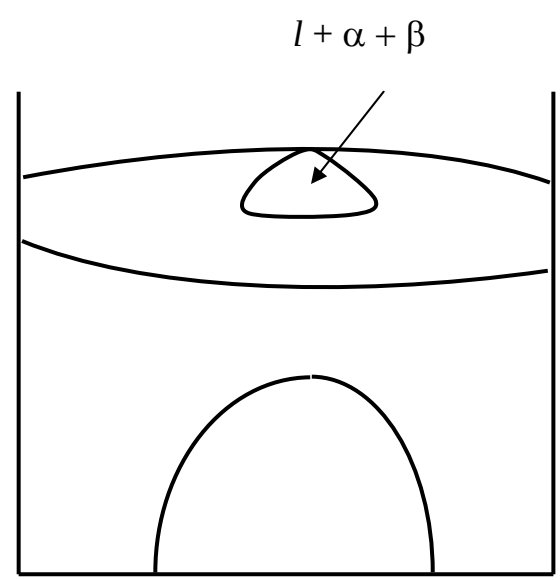
- **A maximum critical point**





vertical section

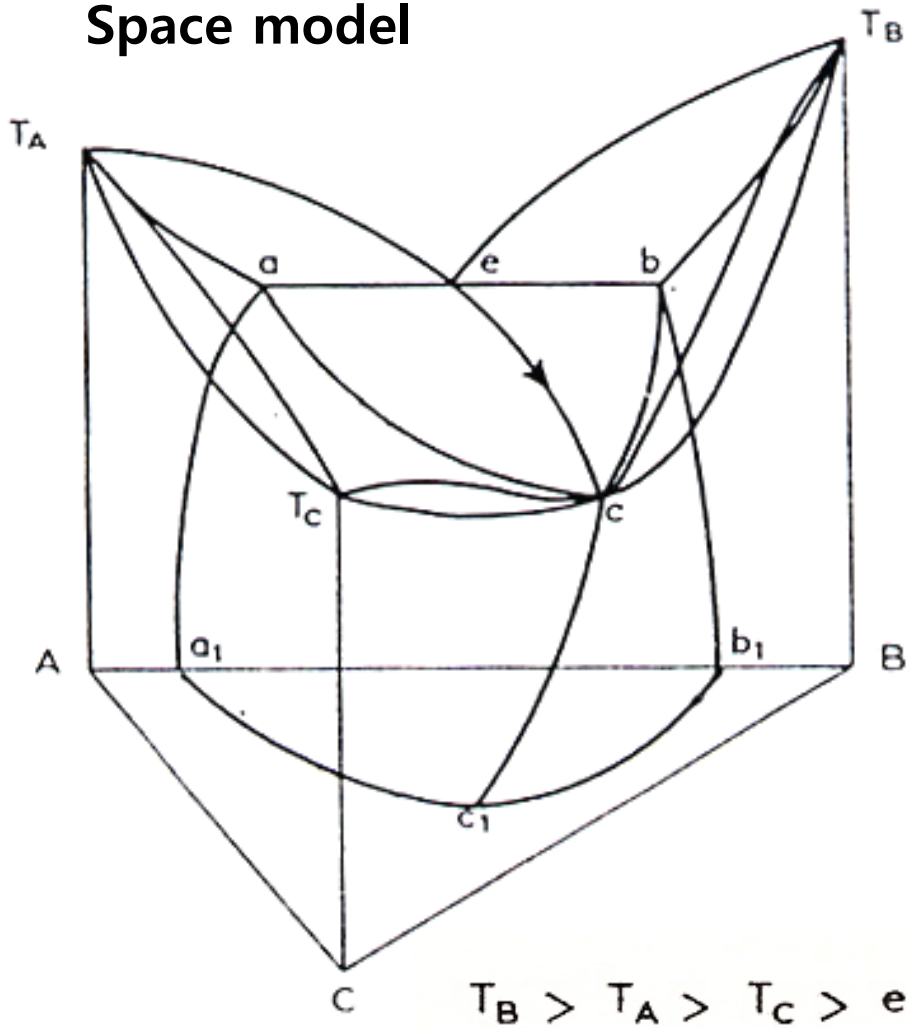




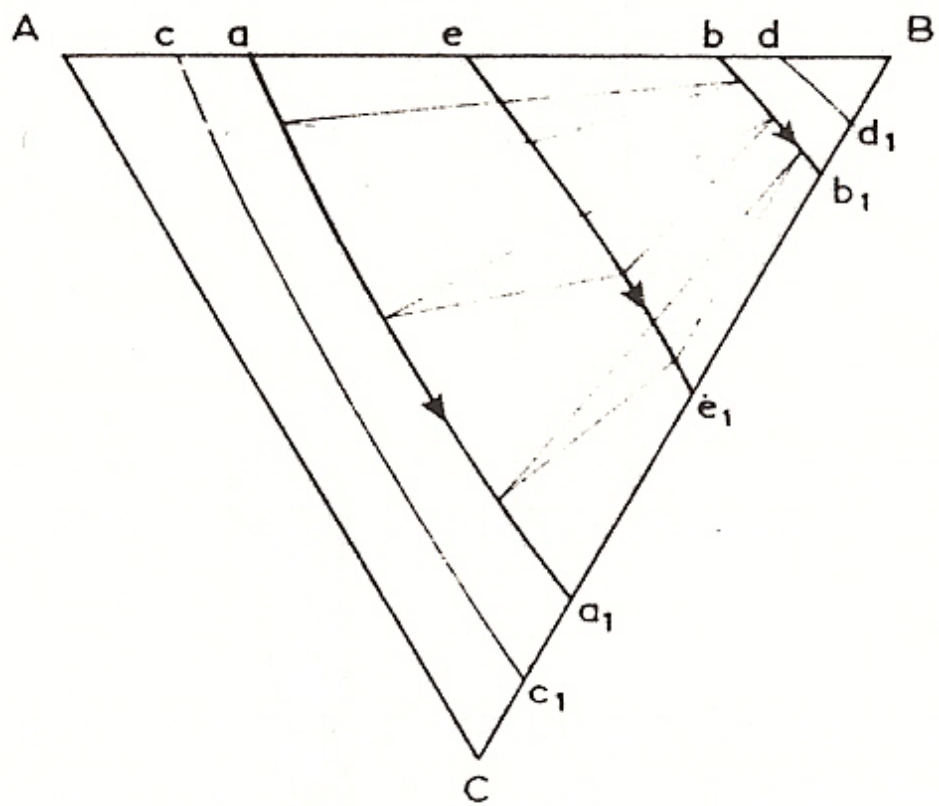
9.3. THREE-PHASE EQUILIBRIUM INVOLVING EUTECTIC REACTIONS

- **A limiting case**

Space model



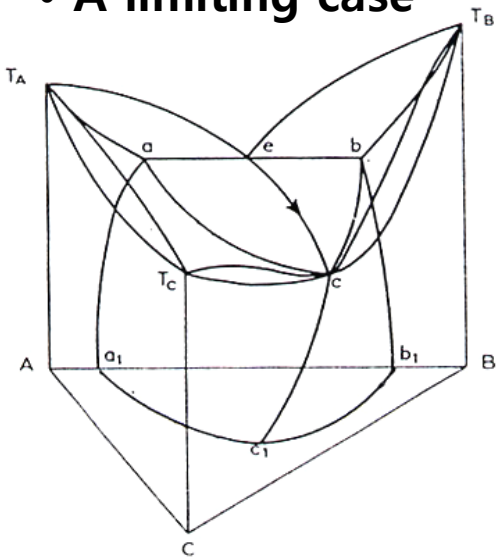
Projection



$T_B > T_A > T_C > e > e_1$

9.3. THREE-PHASE EQUILIBRIUM INVOLVING EUTECTIC REACTIONS

- **A limiting case**



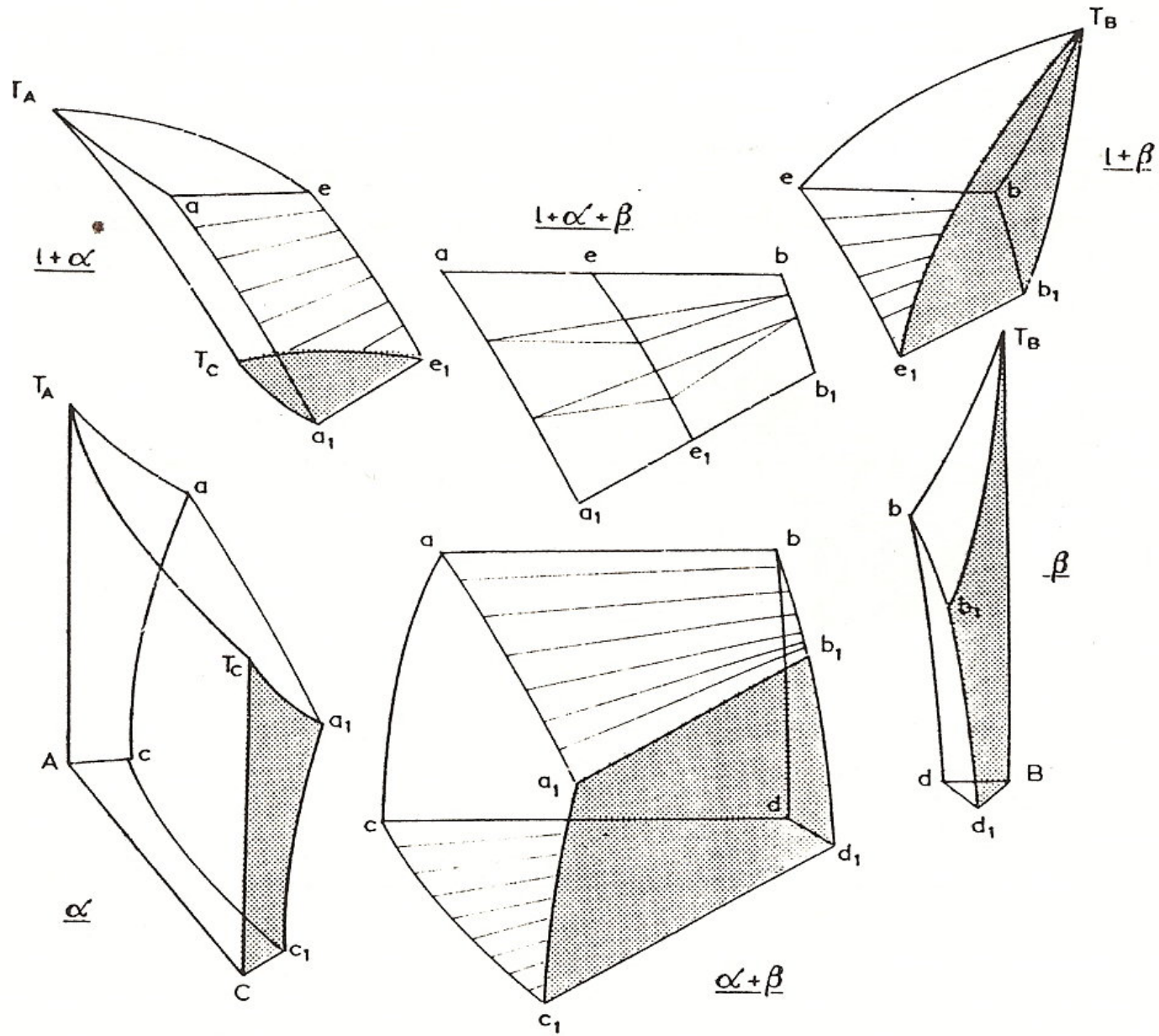


Fig. 165. The phase regions in Fig. 164a.