2009 fall

Advanced Physical Metallurgy

"Phase Equilibria in Materials"

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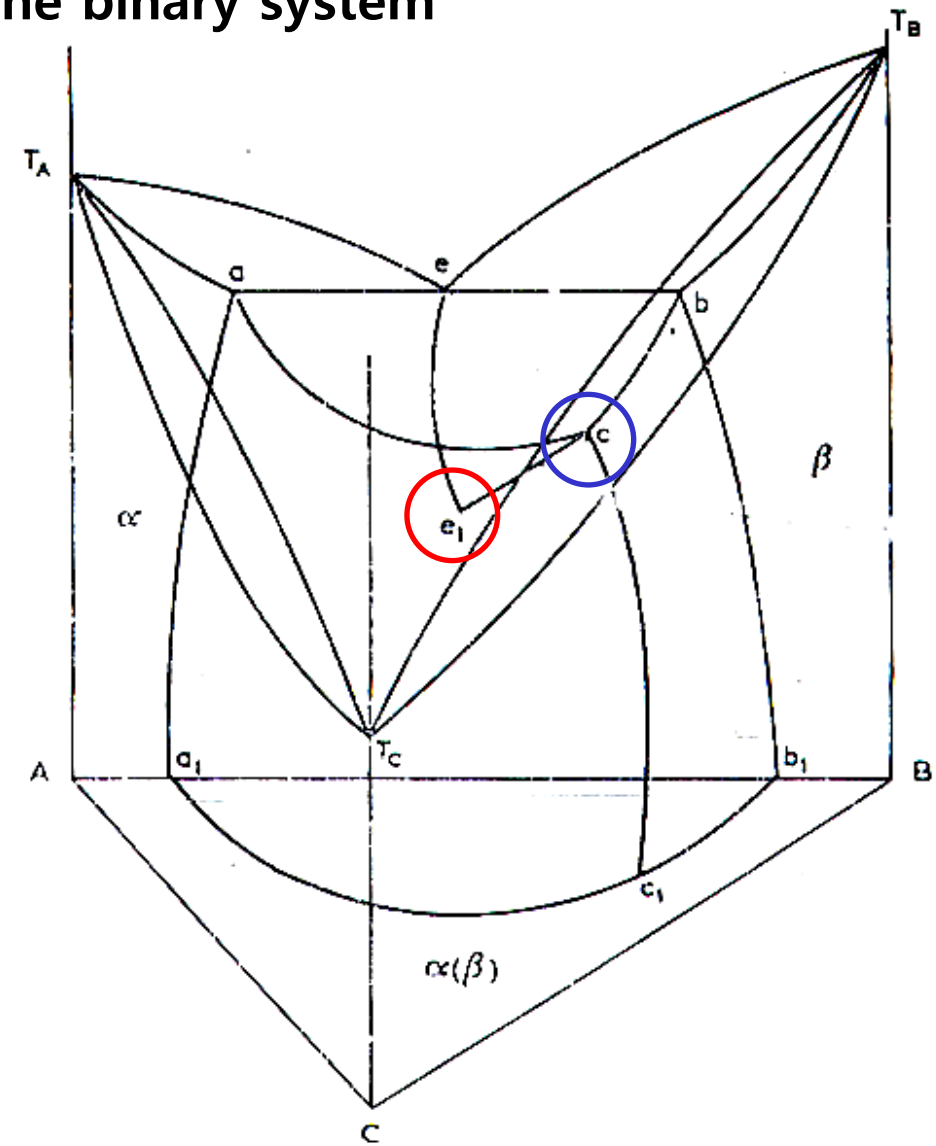
Contents for previous class

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



Contents for previous class

9.3. THREE-PHASE EQUILIBRIUM INVOLVING EUTECTIC REACTIONS

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,

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

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.

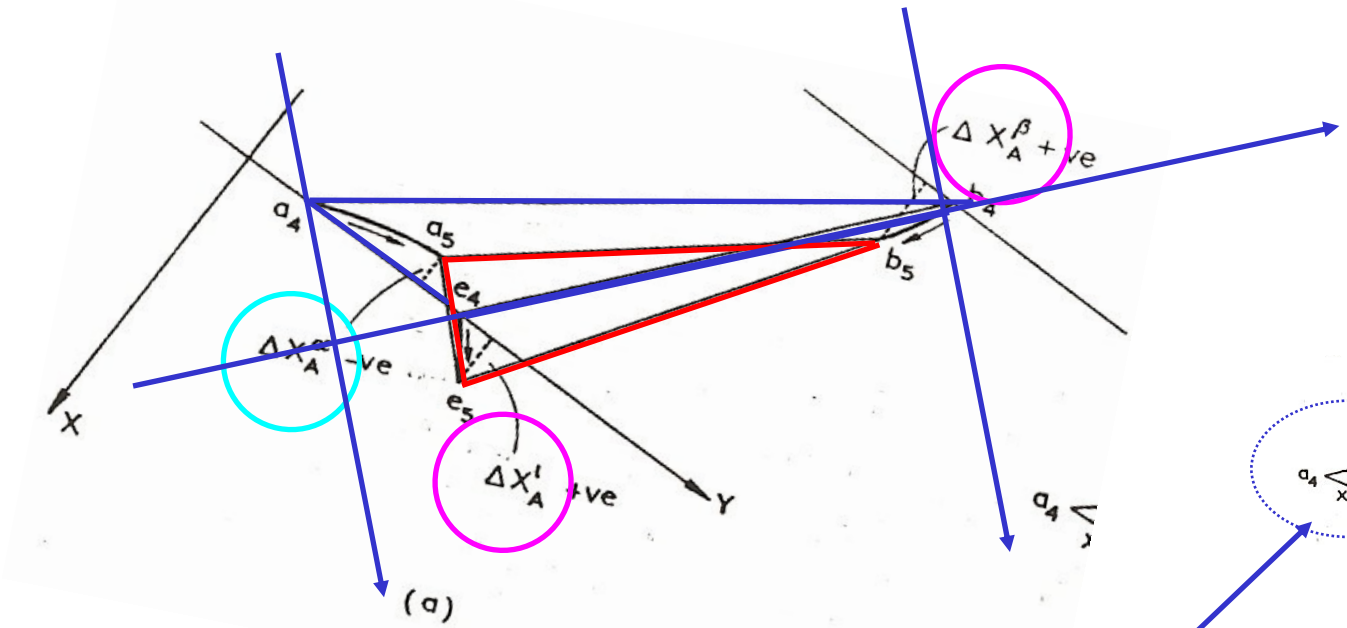
Consider tie triangle $a_4e_4b_4$, and $a_5e_5b_5$

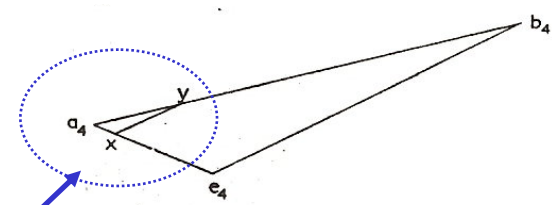
① $X_A^{\beta} = X_A^{l} > X_A^{\alpha}$

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

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

T↓ → liquid is being consumed



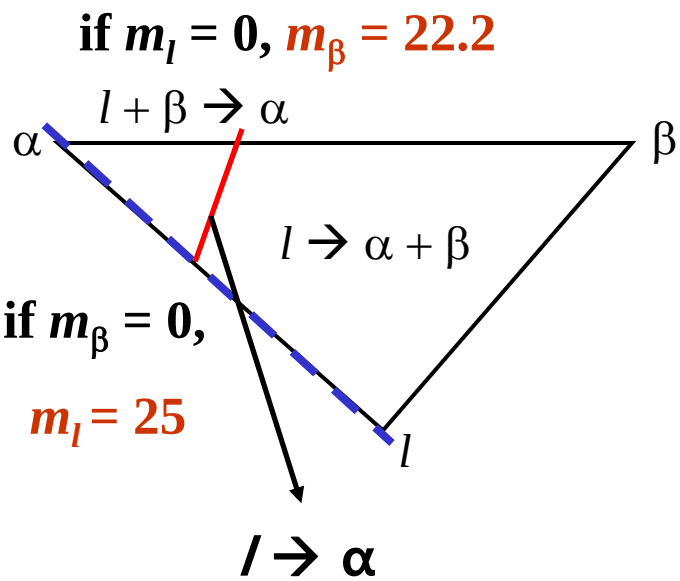


② $X_A^{\alpha} = X_A^{l} > X_A^{\beta}$ $\quad \Delta m_\beta \rightarrow m_\alpha \Delta X_A^{\alpha}(-) + m_\beta \Delta X_A^{\beta}(+) + m_l \Delta X_a^{l}(+)$

❖ $\Delta m_\alpha(+)$, Δm_l (-); <u>if m_α is very larger than m_β and m_l</u> → 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 → $l = \alpha$

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

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

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

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

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

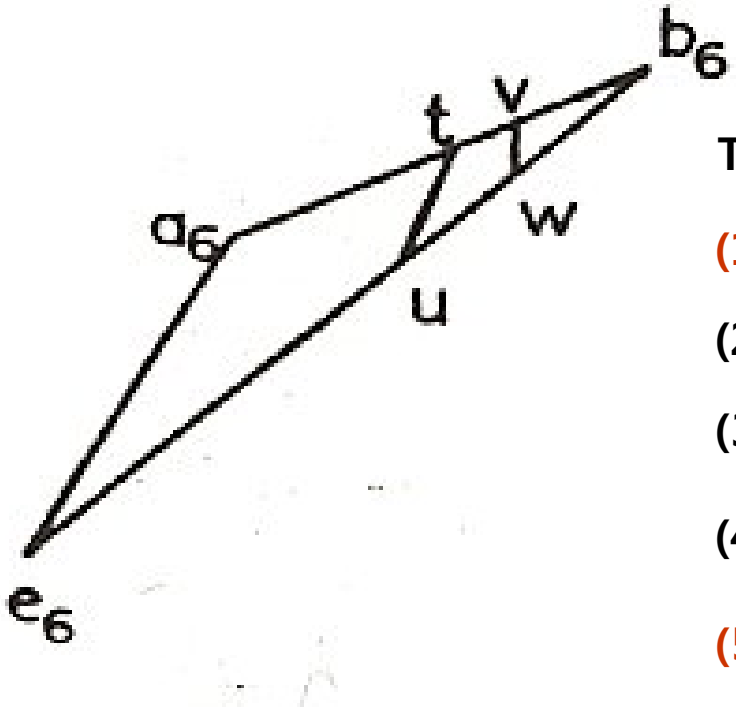
if $m_\beta = 0$, $m_l = 25$

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

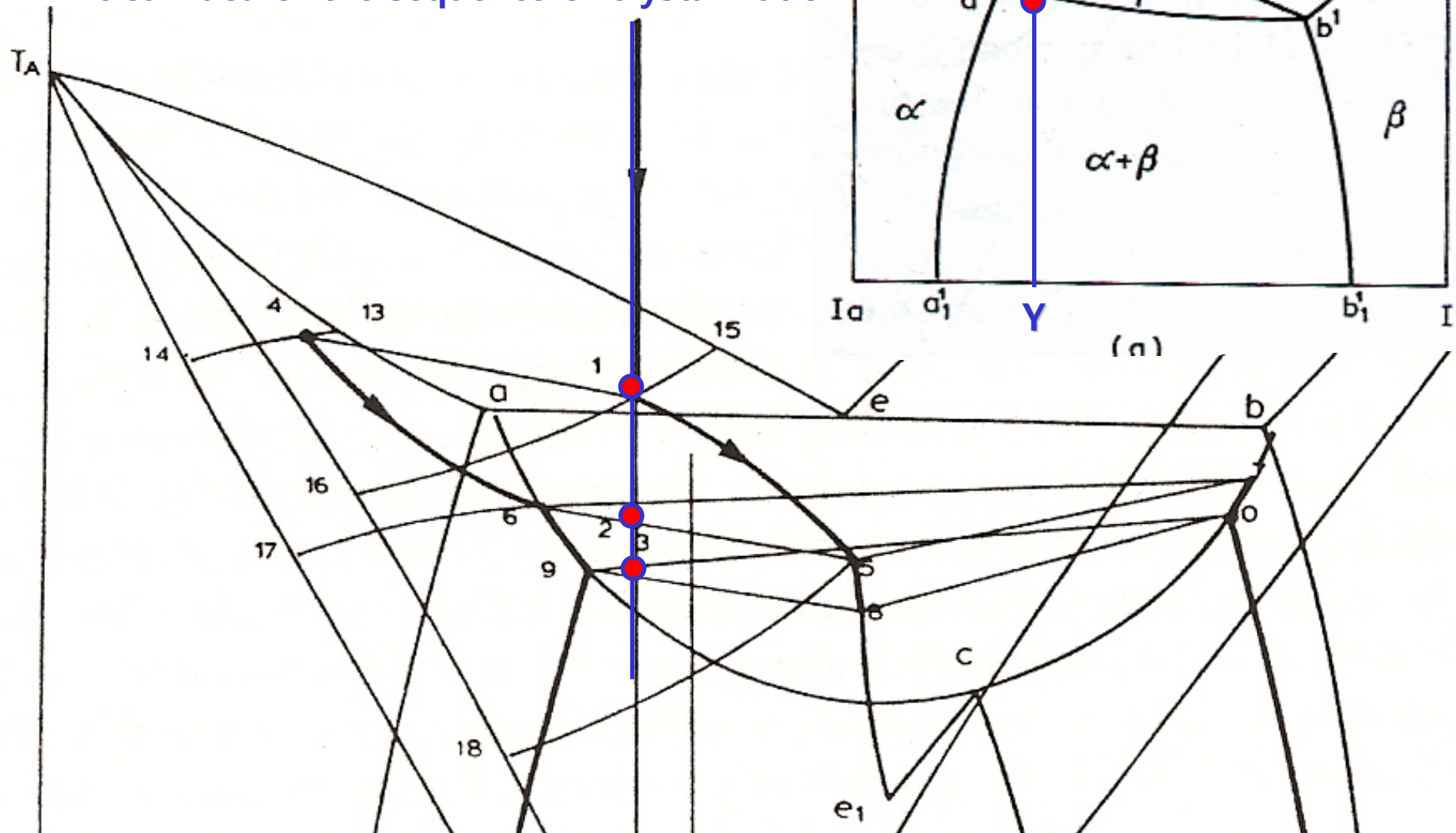
To summarise, the three-phase reaction is initially eutectic for all alloys untill the temperature of the three phase triangle $a_4e_4b_4$, is reached.
From that temperature until the end of the three-phase reaction at the tie line $e_7a_7(b_7)$ the reaction type is dependent on the alloy composition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

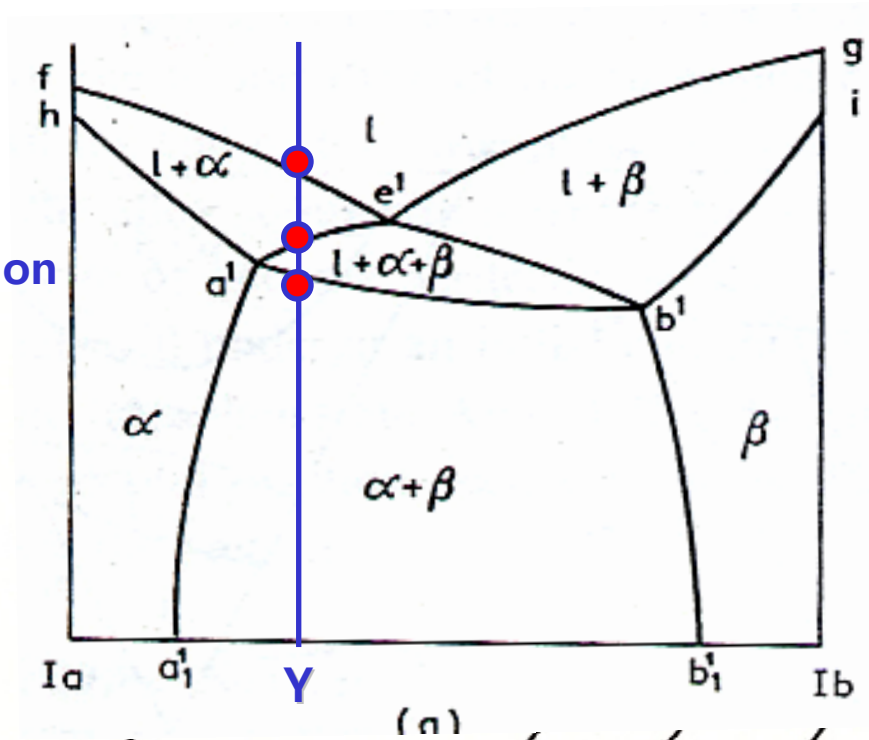
9.3. THREE-PHASE EQUILIBRIUM INVOLVING EUTECTIC REACTIONS

- **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

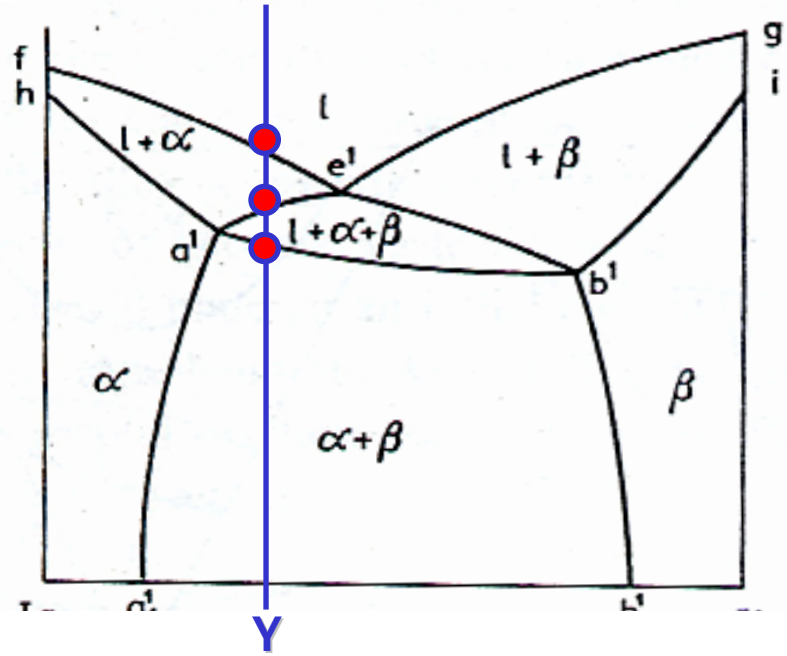
* 4→6 on the α solidus surface
* 1→5 on the α liquidus surface

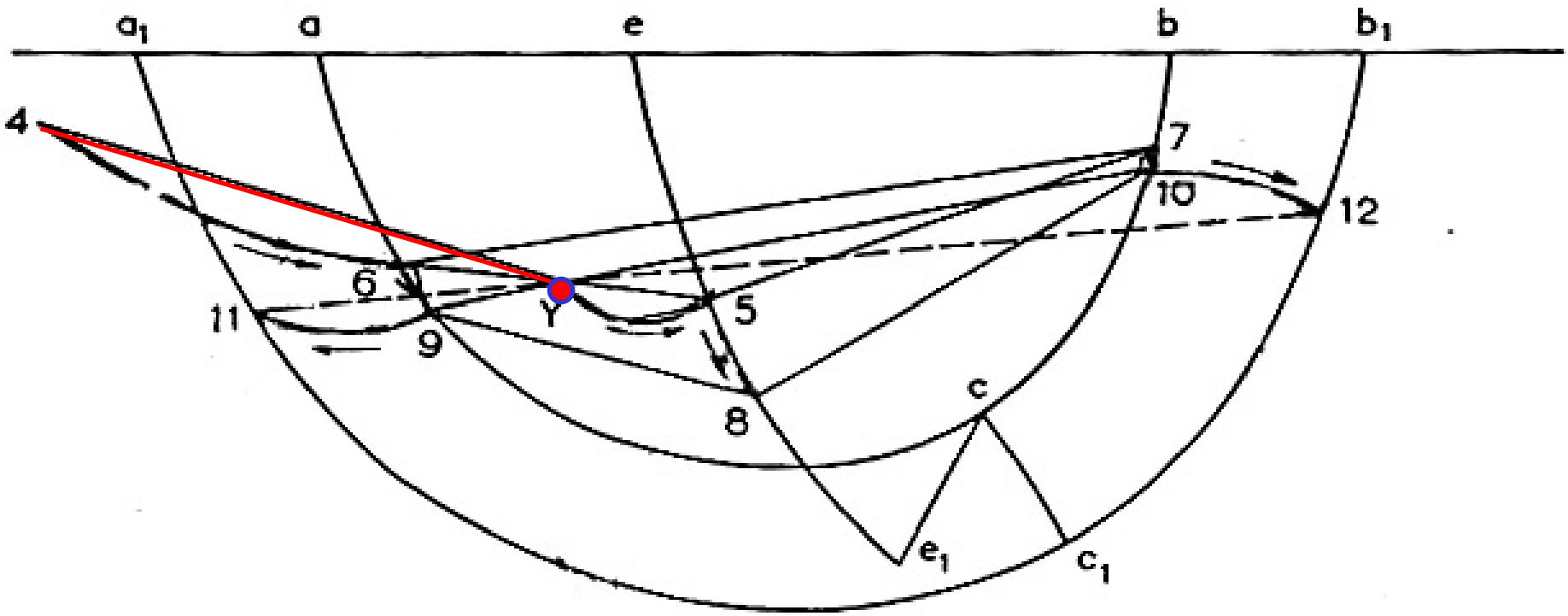
Three phase equilibrium l5, α 6, β7

* 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

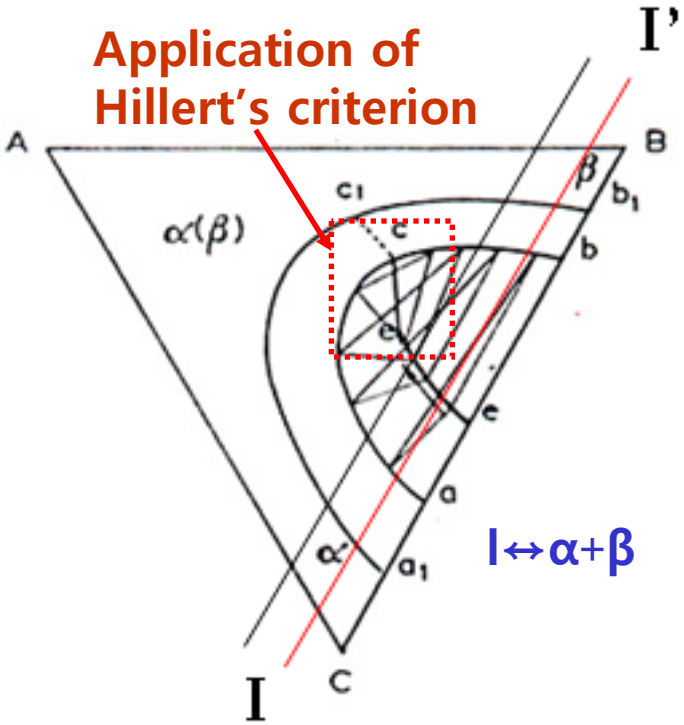


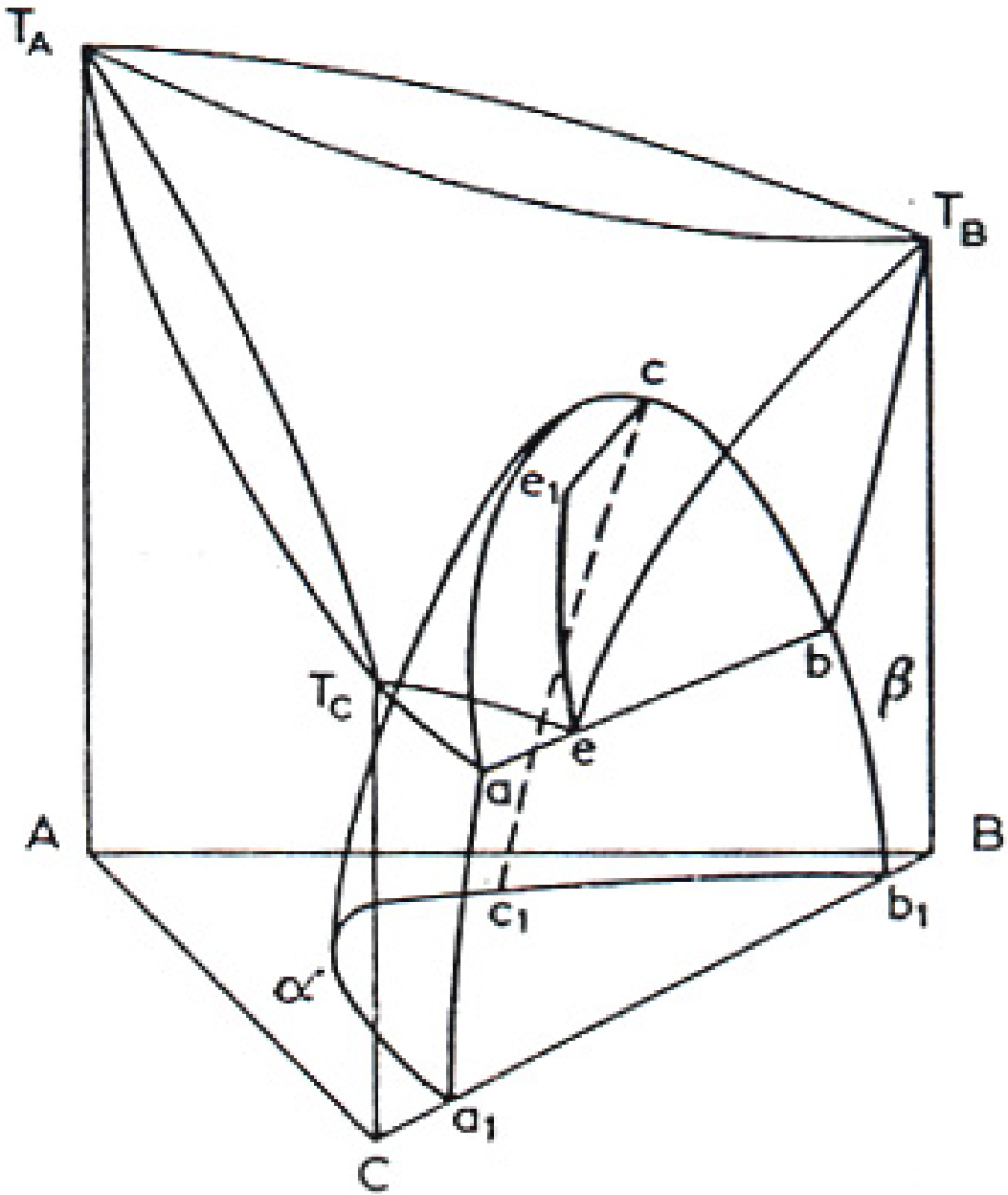


Projection of the solidification sequence for alloy Y on the concentration triangle

9.3. THREE-PHASE EQUILIBRIUM INVOLVING EUTECTIC REACTIONS

- A maximum critical point

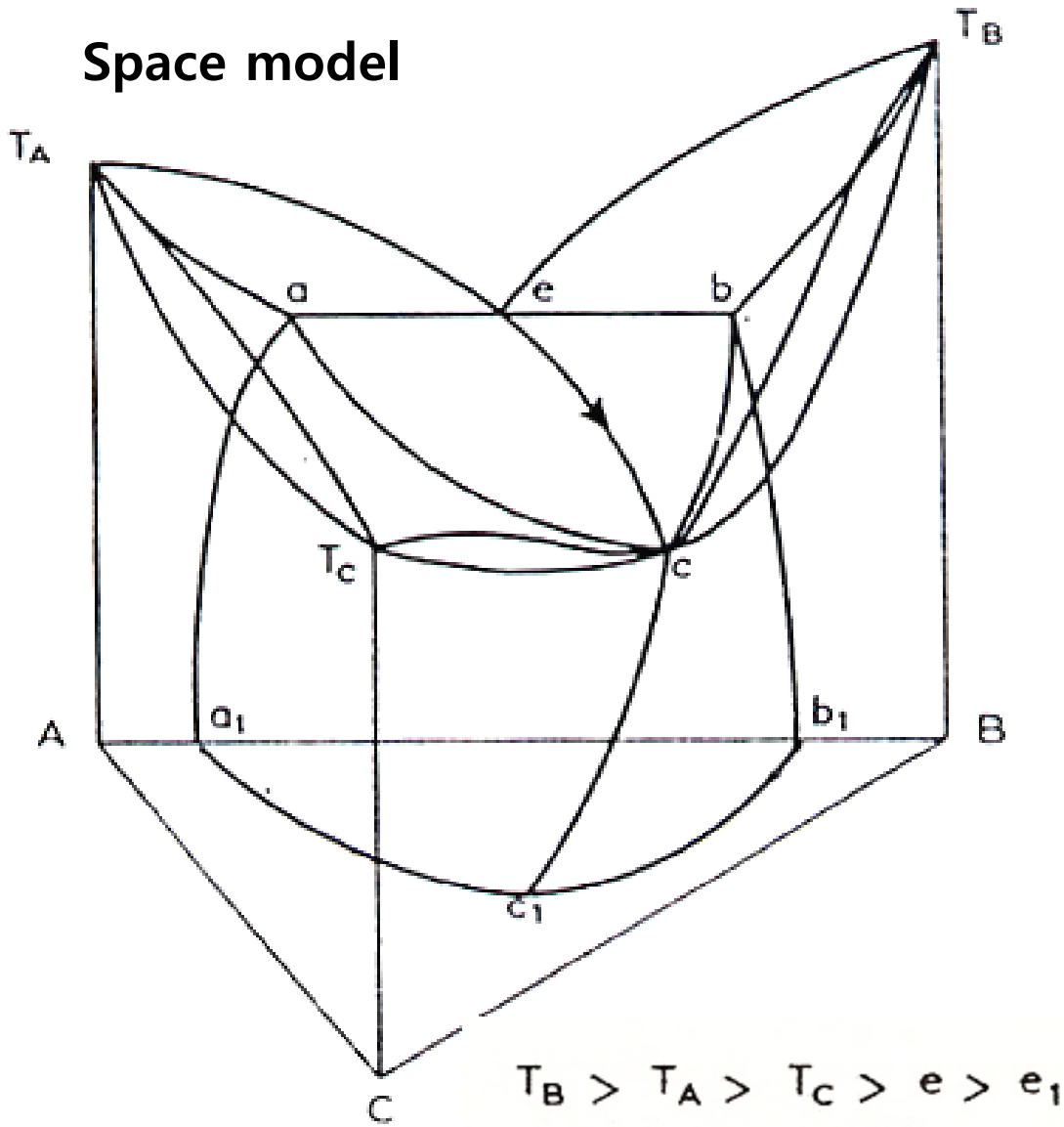




9.3. THREE-PHASE EQUILIBRIUM INVOLVING EUTECTIC REACTIONS

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

Space model

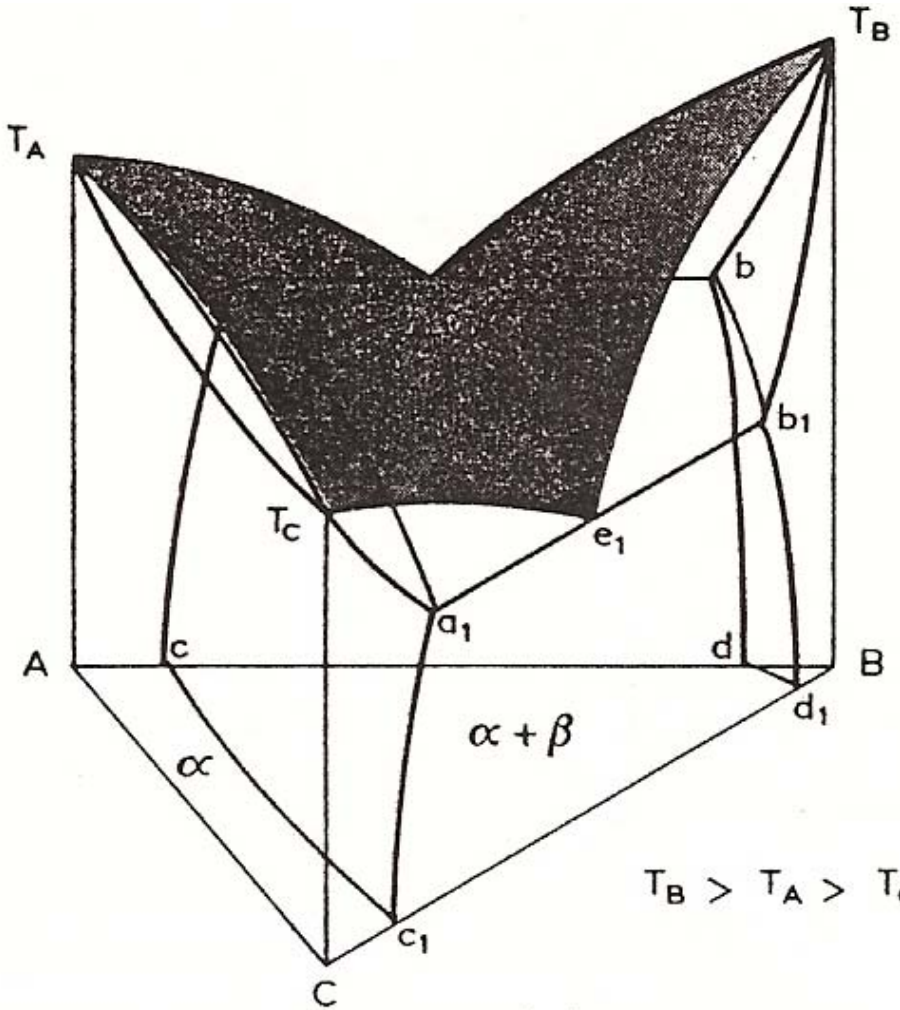


$T_B > T_A > T_C > e > e_1$

9.3. THREE-PHASE EQUILIBRIUM INVOLVING EUTECTIC REACTIONS

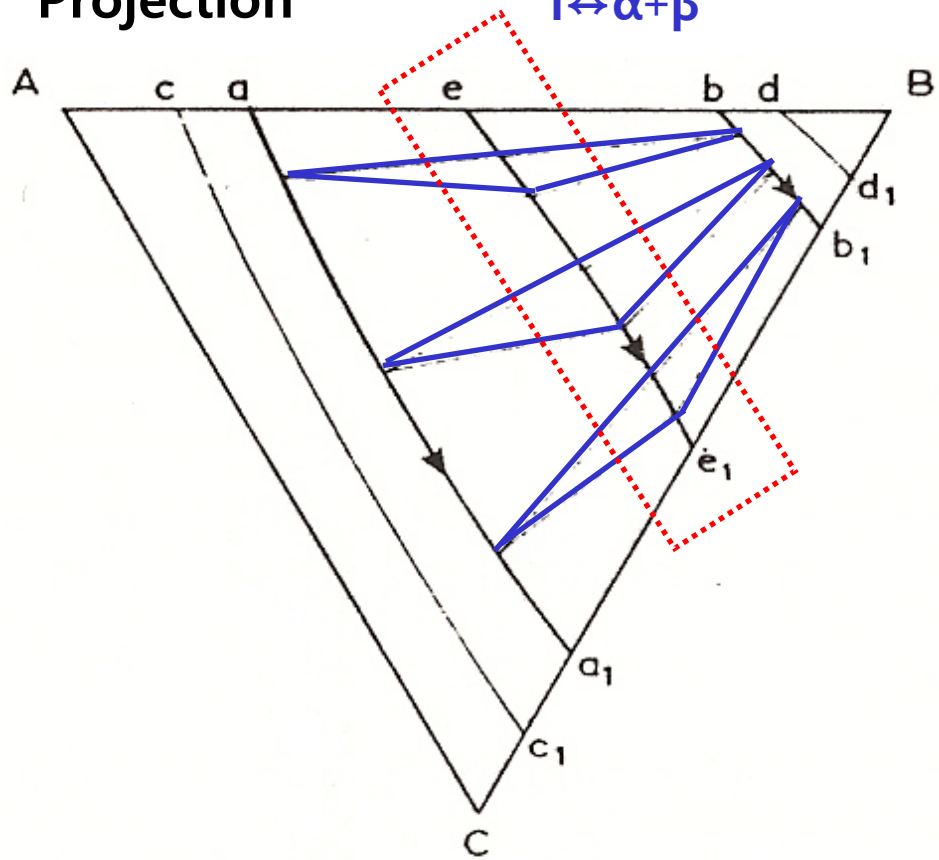
- **A limiting case**

Space model



Projection

l↔α+β



$T_B > T_A > T_C > e > e_1$

9.3. THREE-PHASE EQUILIBRIUM INVOLVING EUTECTIC REACTIONS

- **A limiting case**

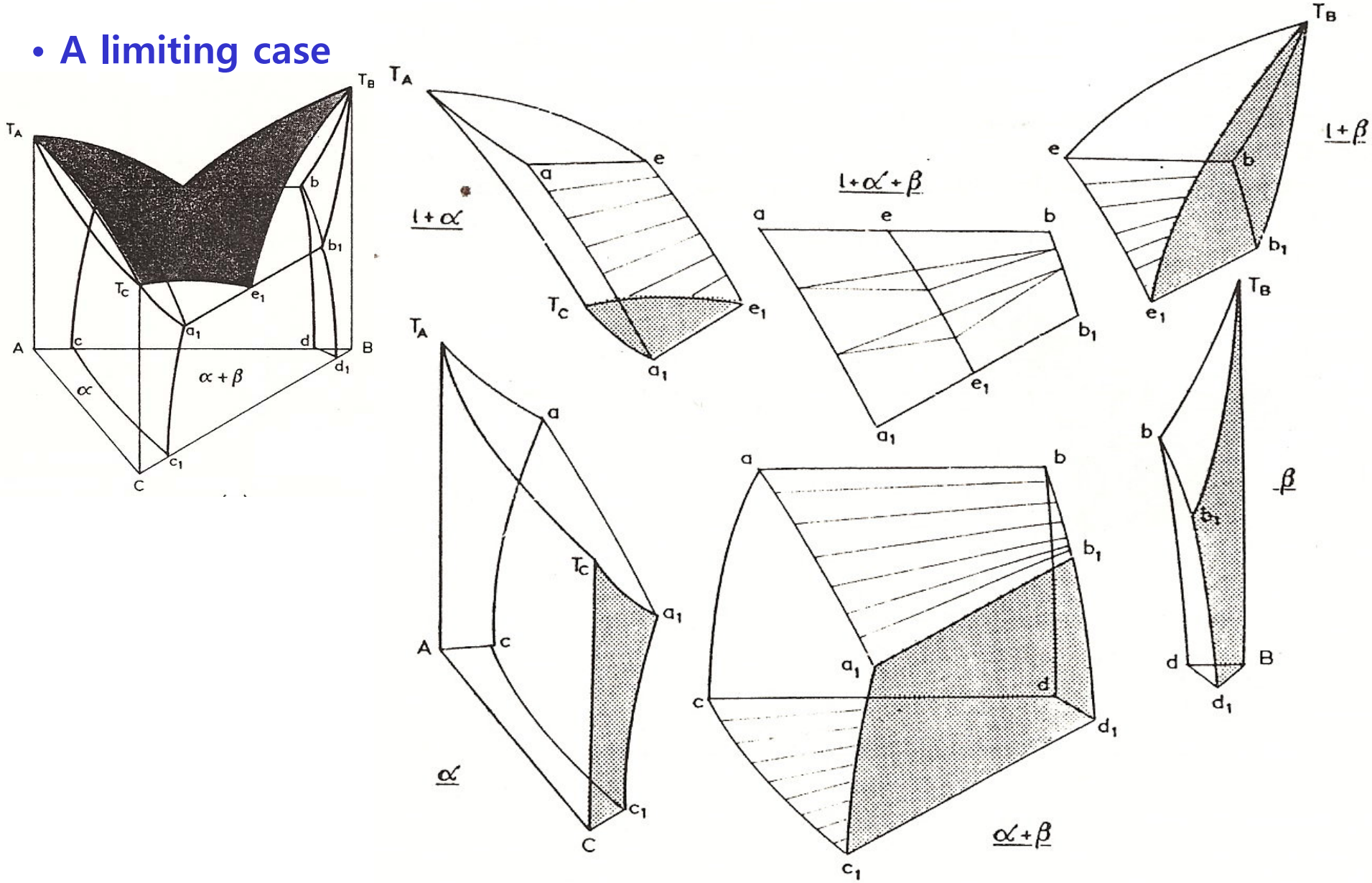
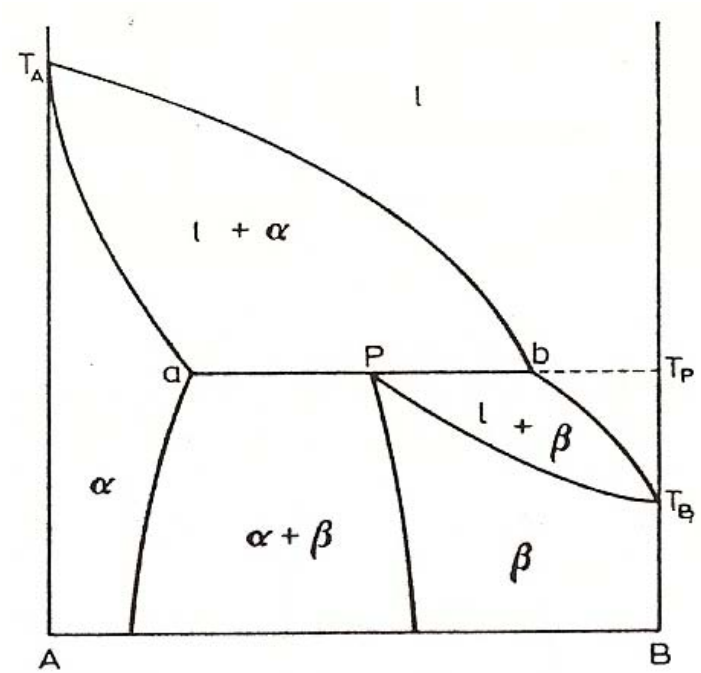
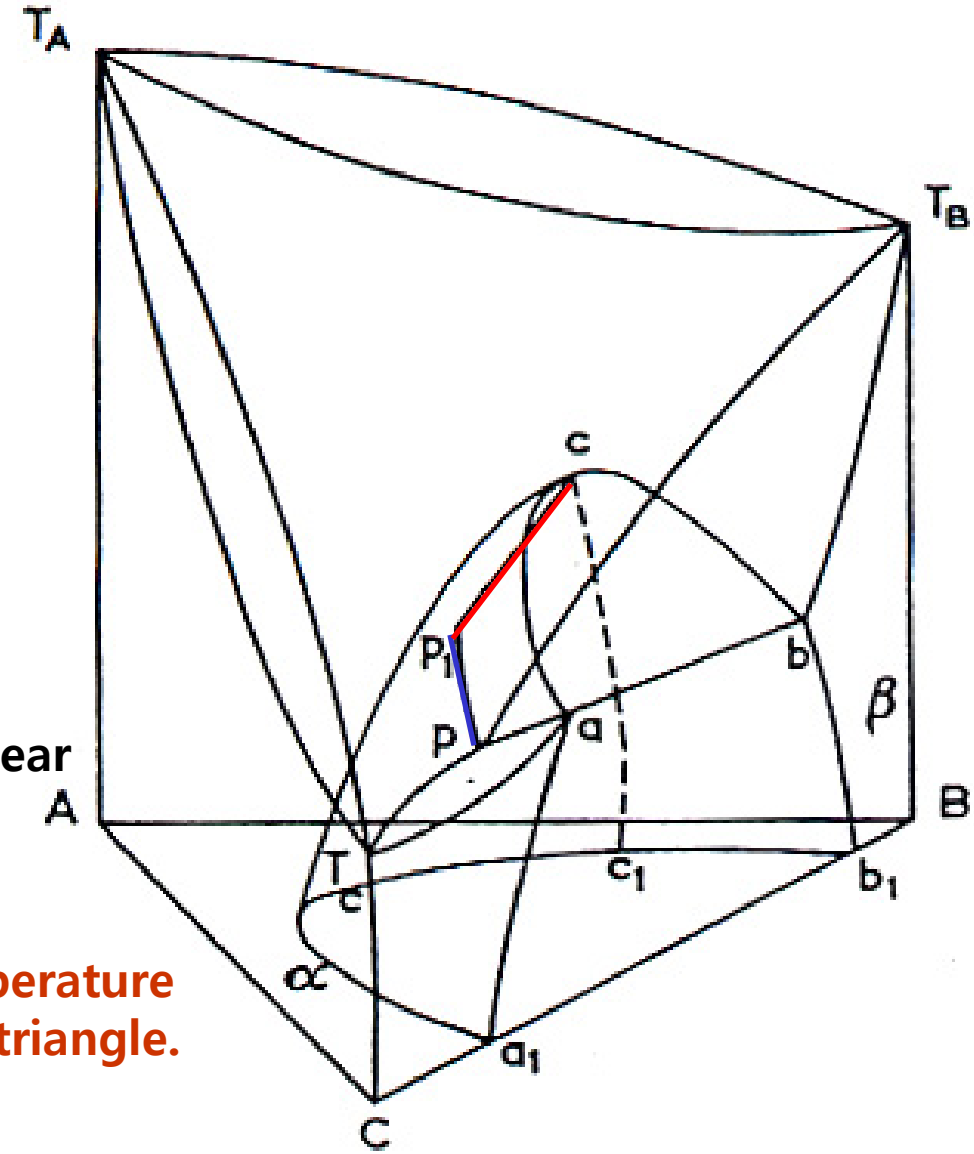


Fig. 165. The phase regions in Fig. 164a.

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

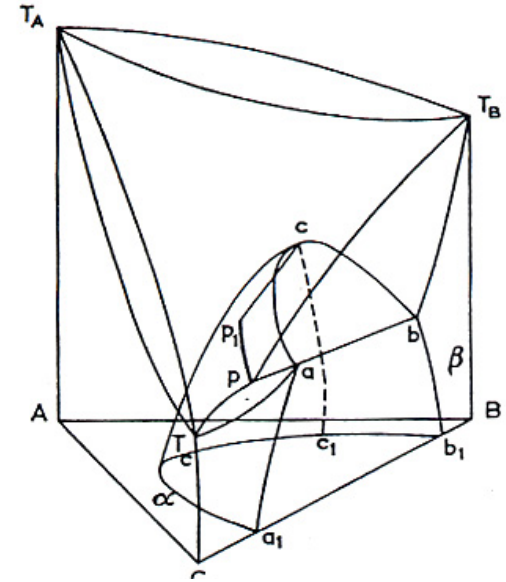
Points P_1 and c lie at the same temperature and the line P_1c is a degenerate tie triangle.

9.4. THREE-PHASE EQUILIBRIUM INVOLVING PERITECTIC REACTIONS

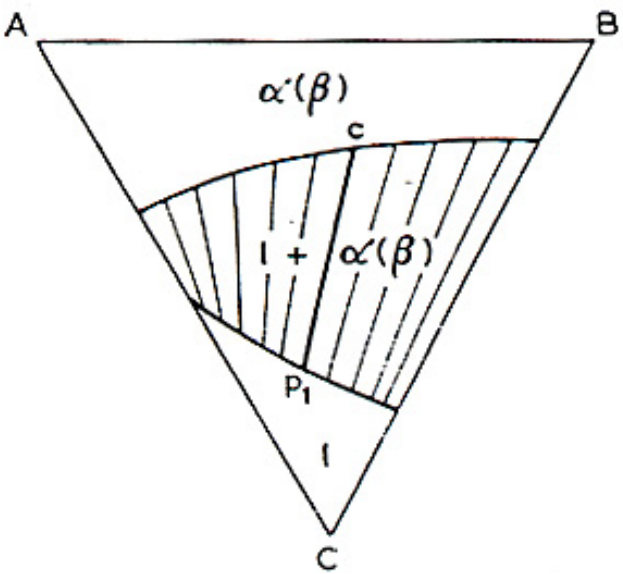
- **A peritectic solubility gap in one binary system**

PP_1: monovariant curve for liquid

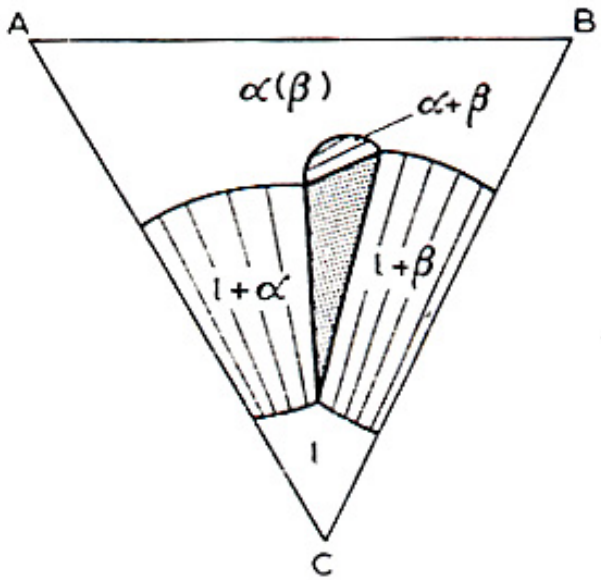
Points P_1 and c lie at the same temperature and the line P_1c is a degenerate tie triangle.



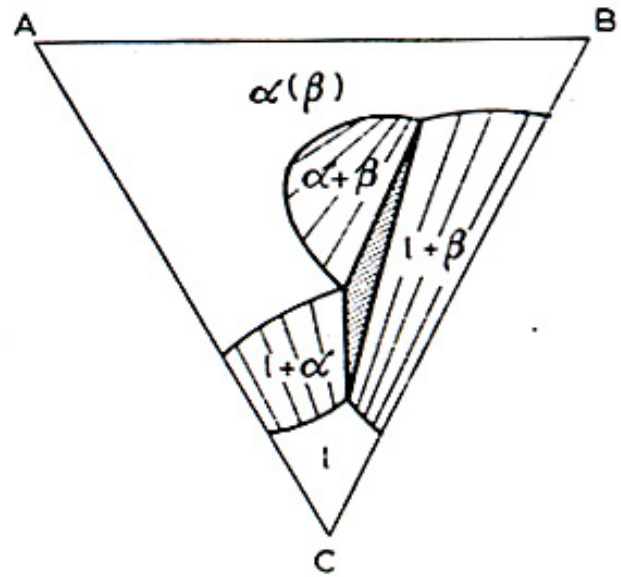
isothermal section



$T = P_1$



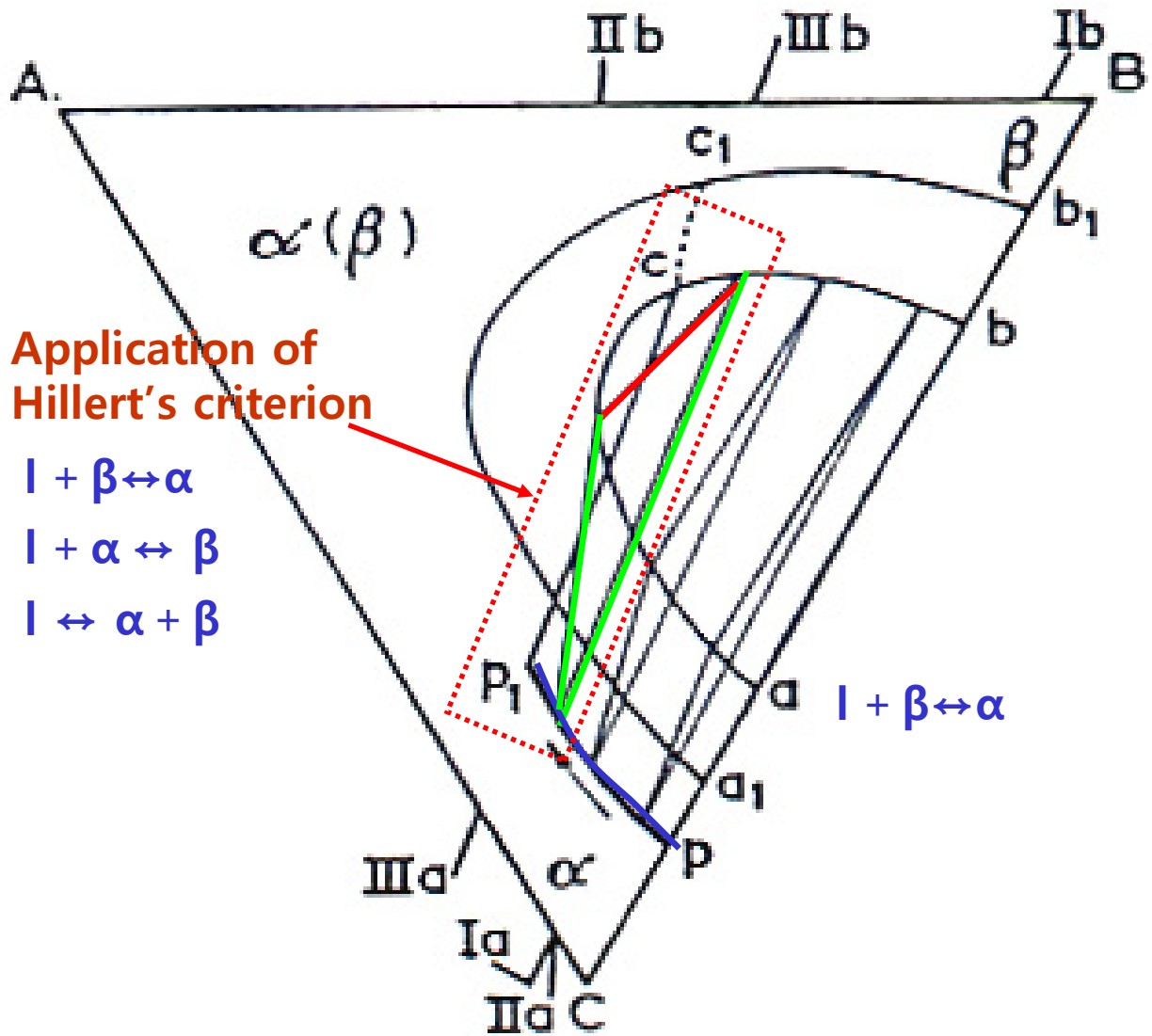
$P_1 > T_1 > P$



$T_1 > T_2 > P$

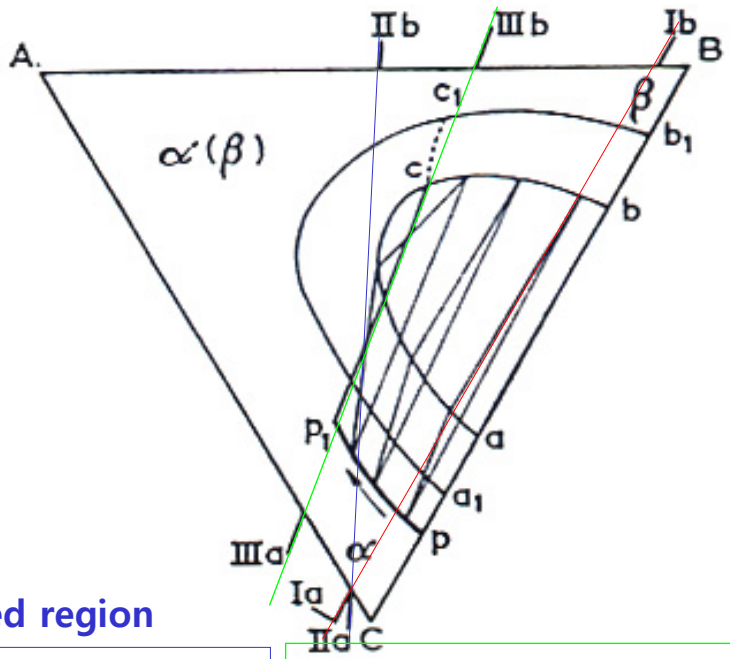
9.4. THREE-PHASE EQUILIBRIUM INVOLVING PERITECTIC REACTIONS

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



9.4. THREE-PHASE EQUILIBRIUM INVOLVING PERITECTIC REACTIONS

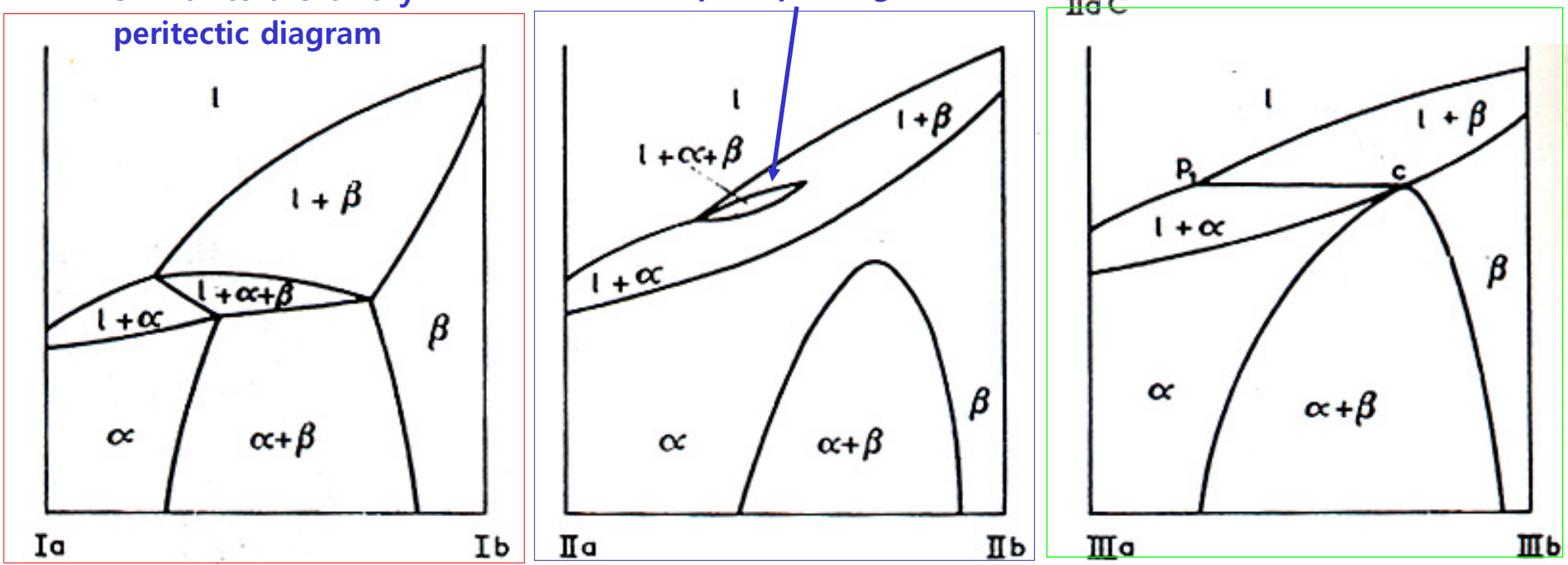
- **A peritectic solubility gap in one binary system**



<vertical section>

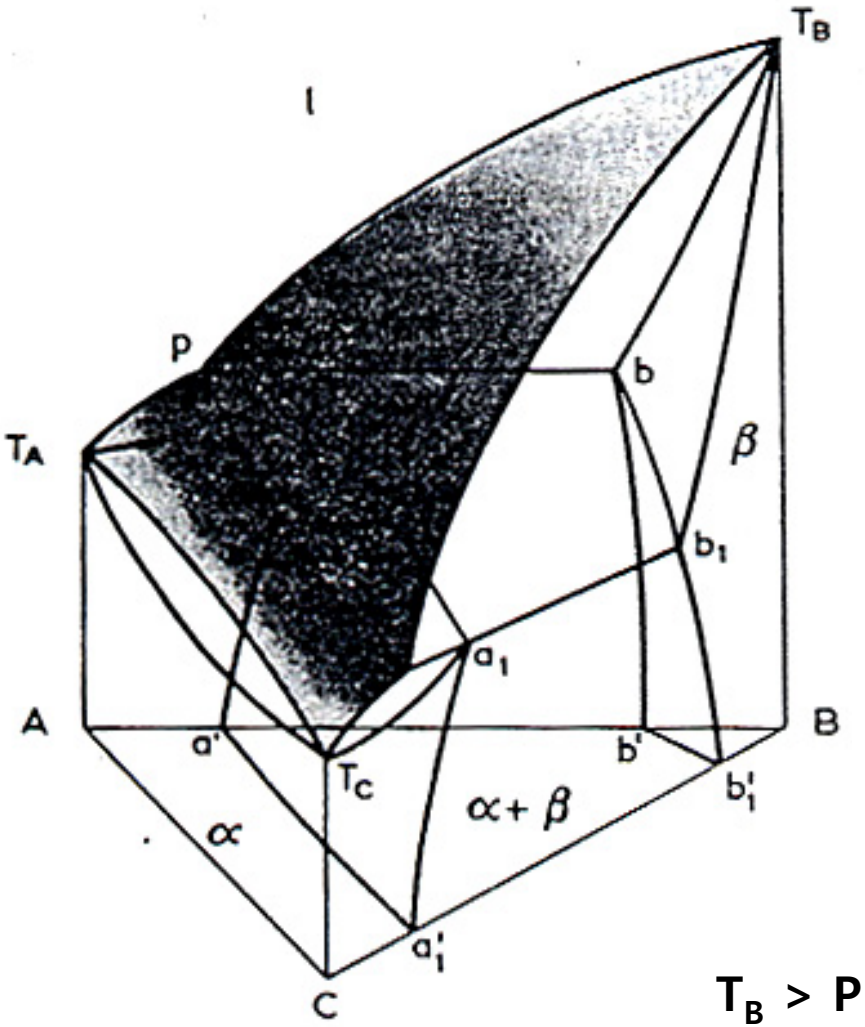
Similar to the binary peritectic diagram

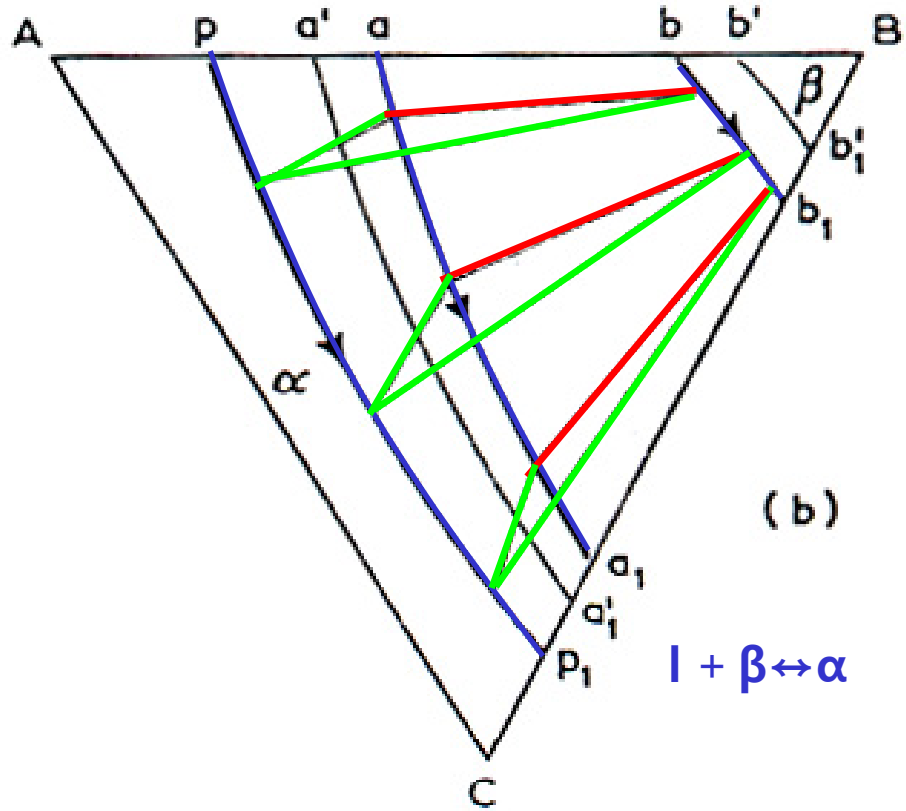
loop shaped region



9.4. THREE-PHASE EQUILIBRIUM INVOLVING PERITECTIC REACTIONS

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

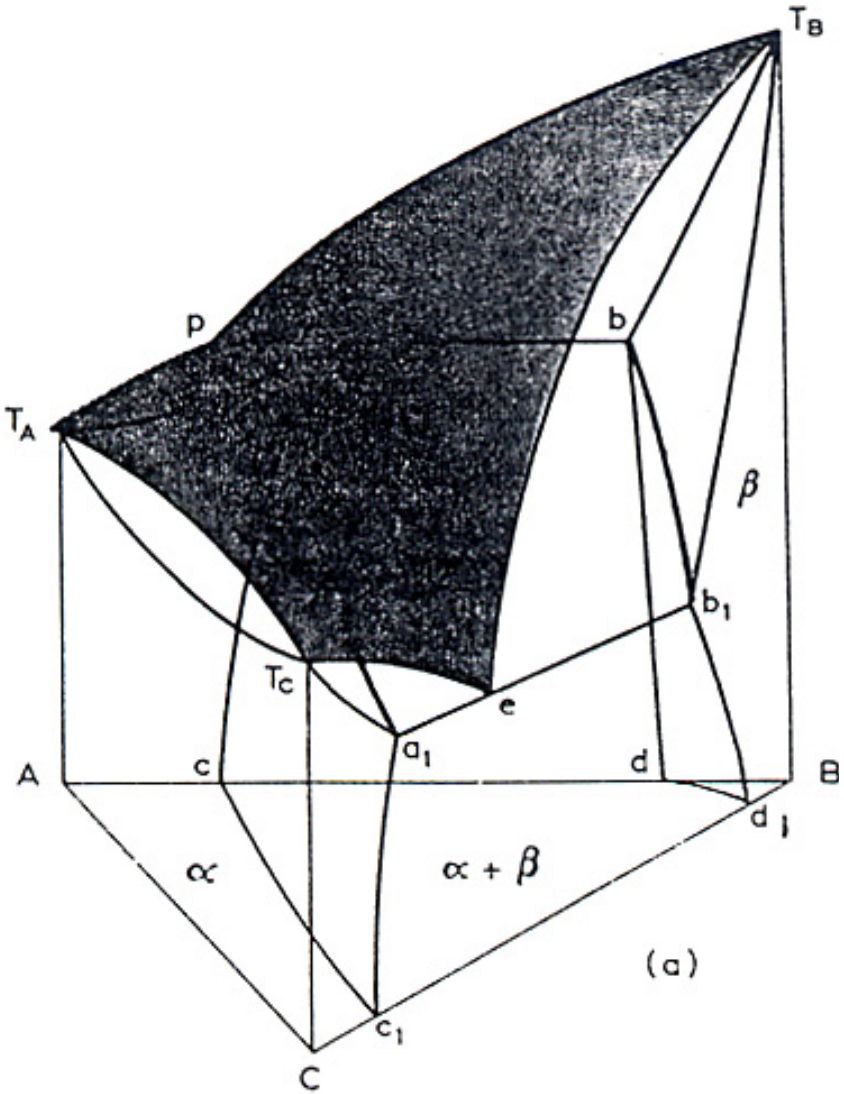


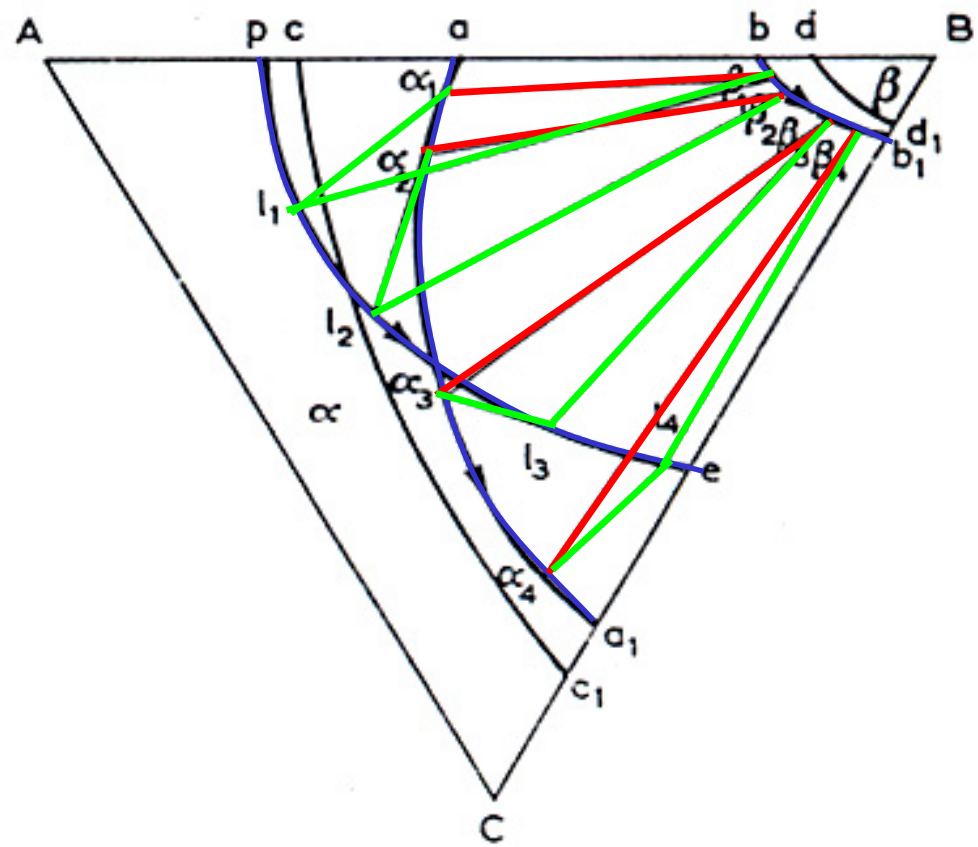


$T_B > P > T_A > P_1 > T_C$

9.4. THREE-PHASE EQUILIBRIUM INVOLVING PERITECTIC REACTIONS

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



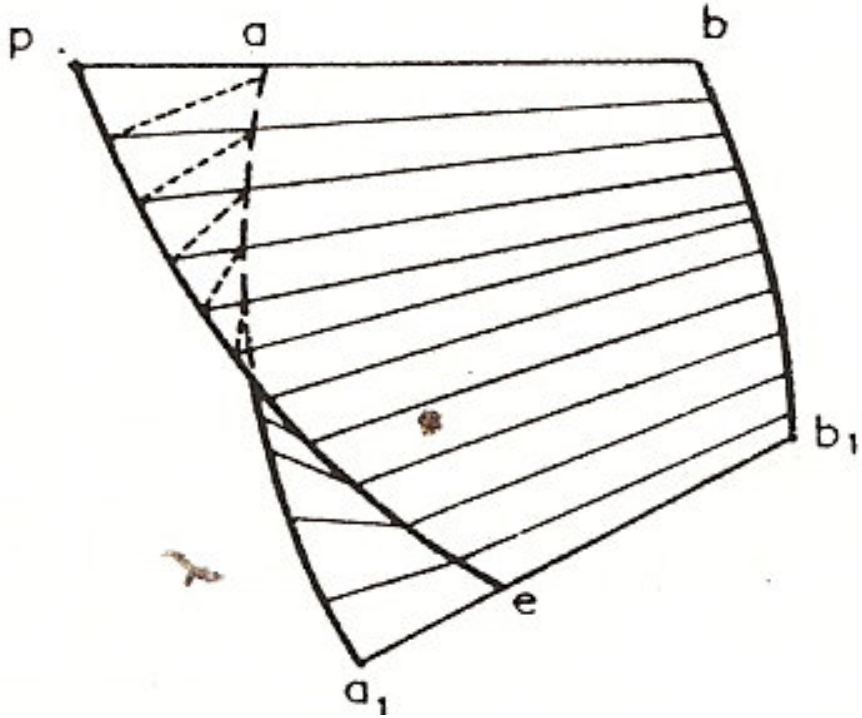


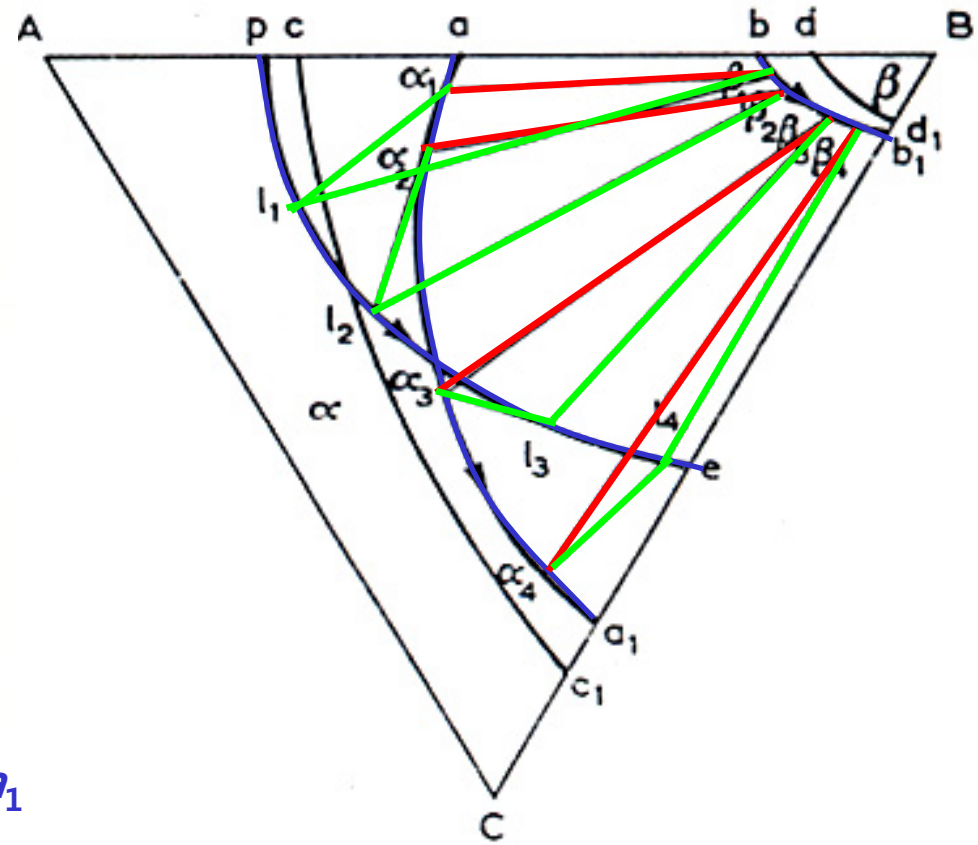
$T_B > P > T_A > T_c > e$

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 the transition form a peritectic to a eutectic reaction does not occur at a unique temperature.**

9.4. THREE-PHASE EQUILIBRIUM INVOLVING PERITECTIC REACTIONS

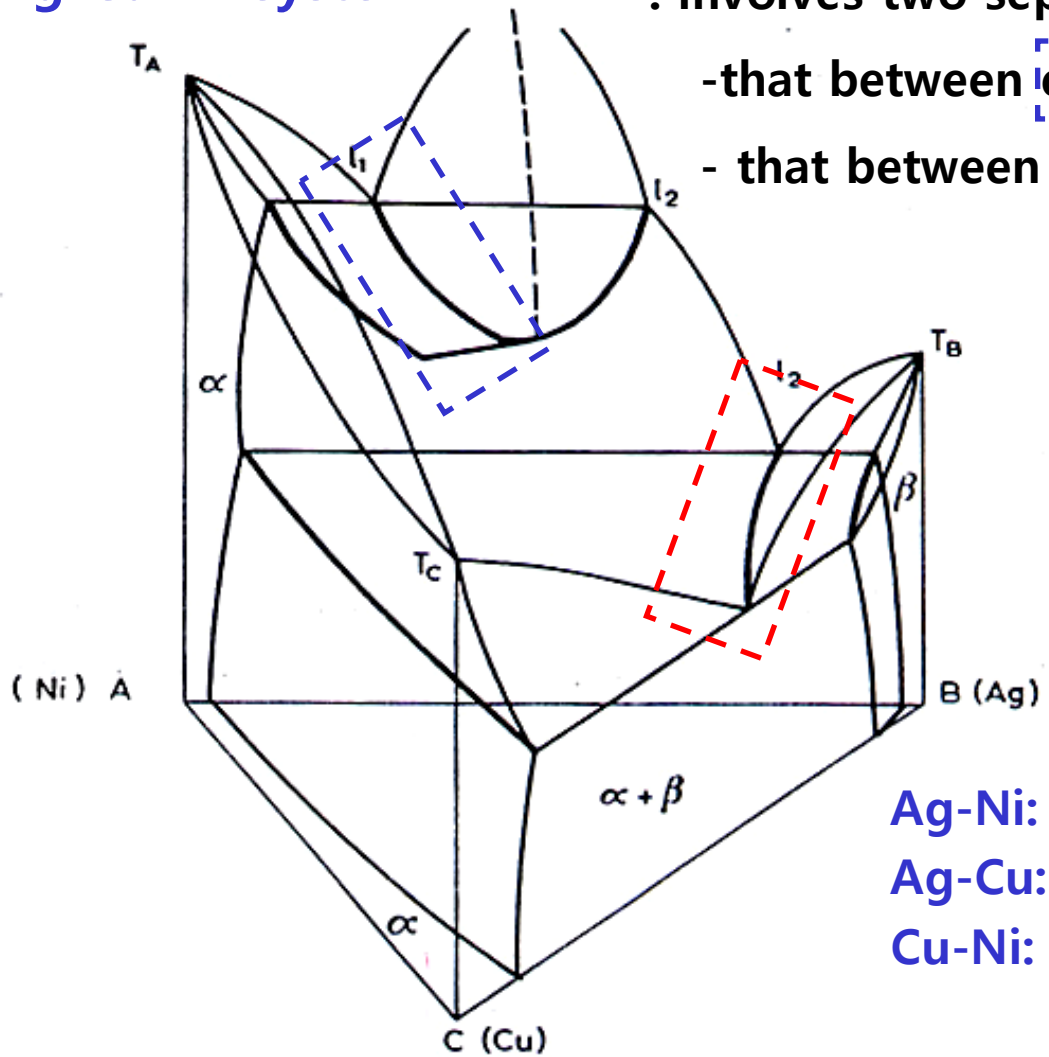
- Binary Monotectic, syntectic and metatectic reactions in combination with each other as well as with binary eutectic and peritectic reactions.

- 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: continuous series of solid soln

Chapter 10. Ternary phase Diagrams

Four-Phase Equilibrium

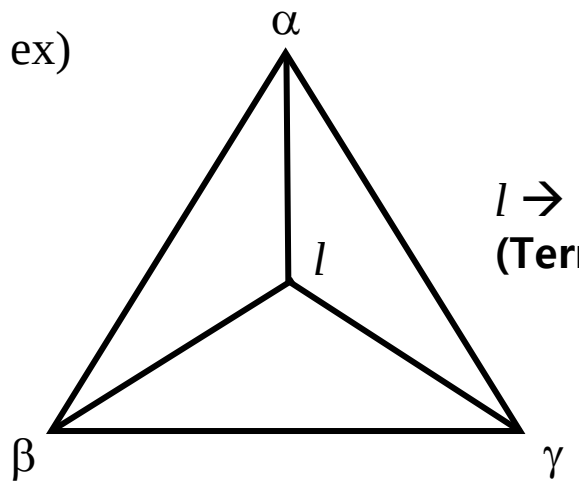
10.1. THE EUTECTIC EQUILIBRIUM ($l = \alpha + \beta + \gamma$)

Three phase equil. (f = 1) - eutectic, peritectic

Now we consider of four equilibrium

- **max N of phase**
- **f = 0** : composition of four phases at temp.→ fixed
- **isothermal four phase regions**

ex)

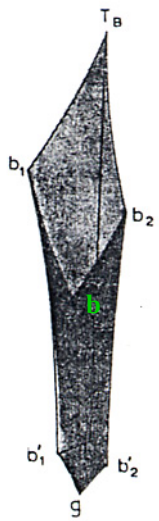


$l \rightarrow \alpha + \beta + \gamma$
(Ternary eutectic)

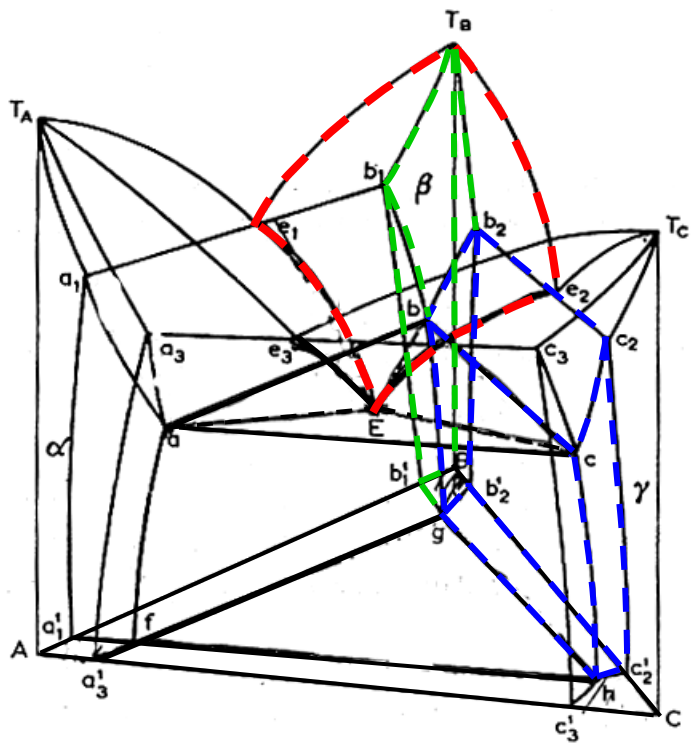
cf) $l + \alpha \rightarrow \beta + \gamma$: **ternary quasi-peritectic**
$l + \alpha + \beta \rightarrow \gamma$: **ternary peritectic**

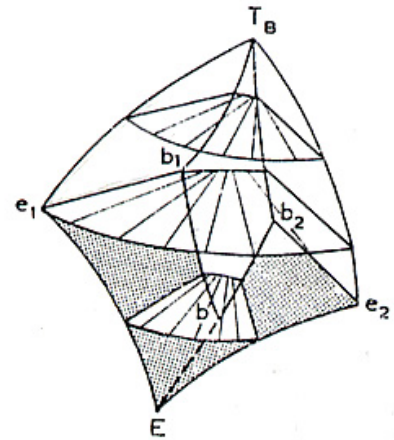
10.1. THE EUTECTIC EQUILIBRIUM ($l = \alpha + \beta + \gamma$)

Ternary eutectic

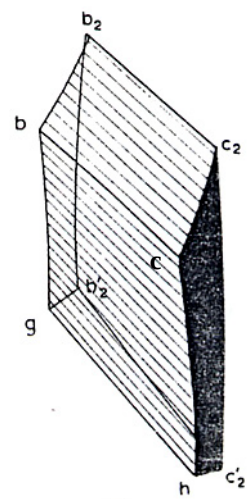


β phase region





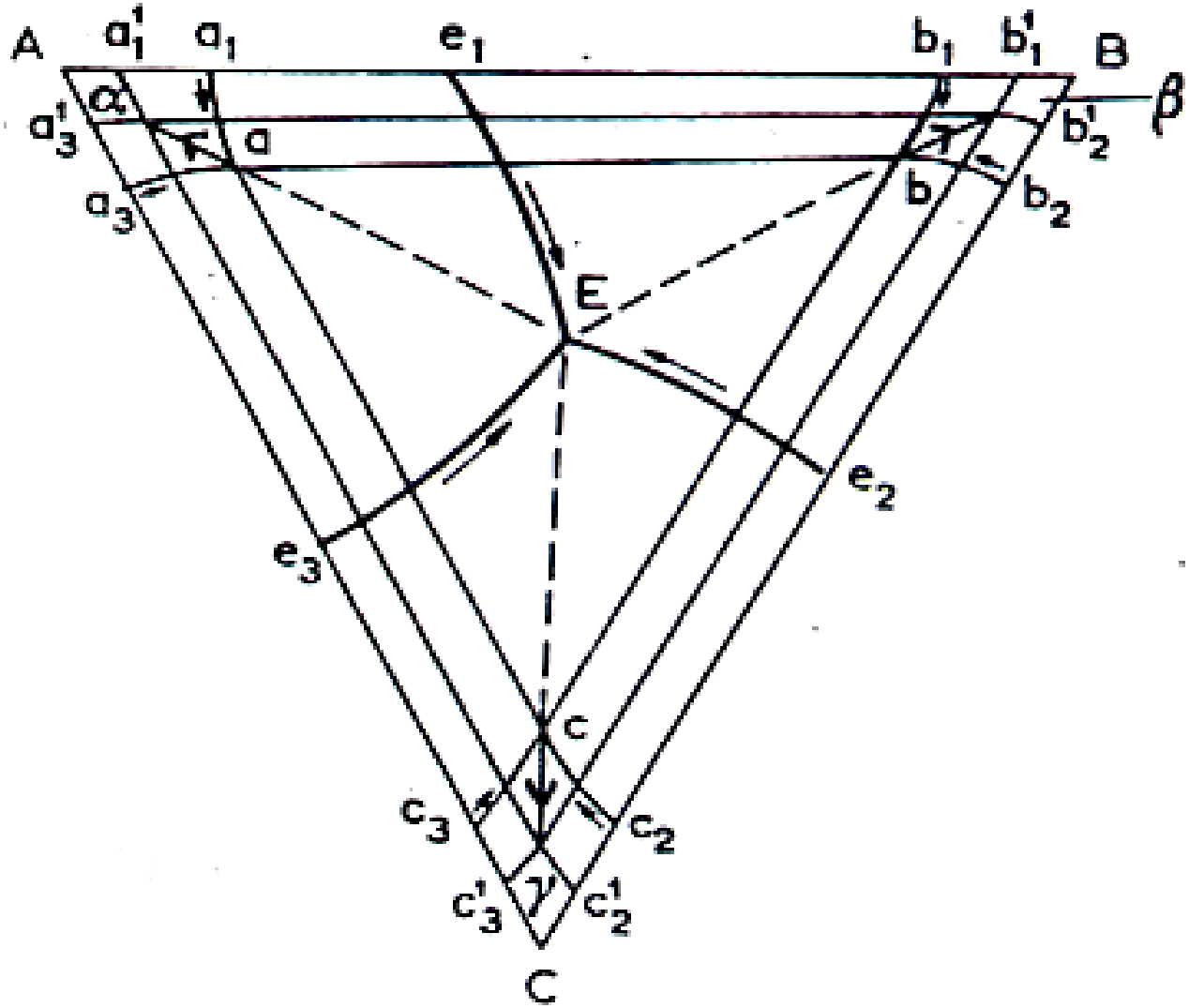
(l + β) phase region



(β + γ) phase region

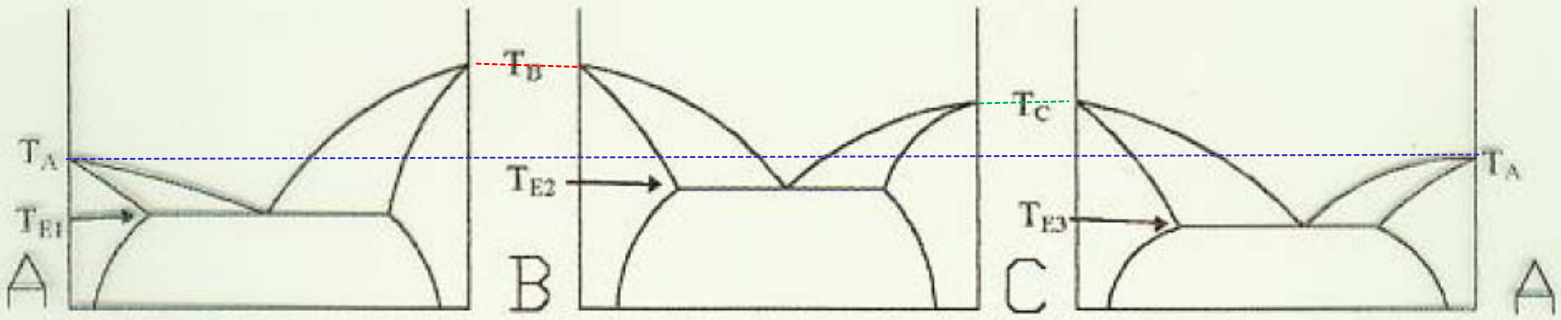
10.1. THE EUTECTIC EQUILIBRIUM ($l = \alpha + \beta + \gamma$)

Ternary eutectic • **Projection : solid solubility limit surface**
: monovariant liquidus curve



Ternary Eutectic System
(with Solid Solubility)

P1:



T_A: Melting Point Of Material A

T_B: Melting Point Of Material B

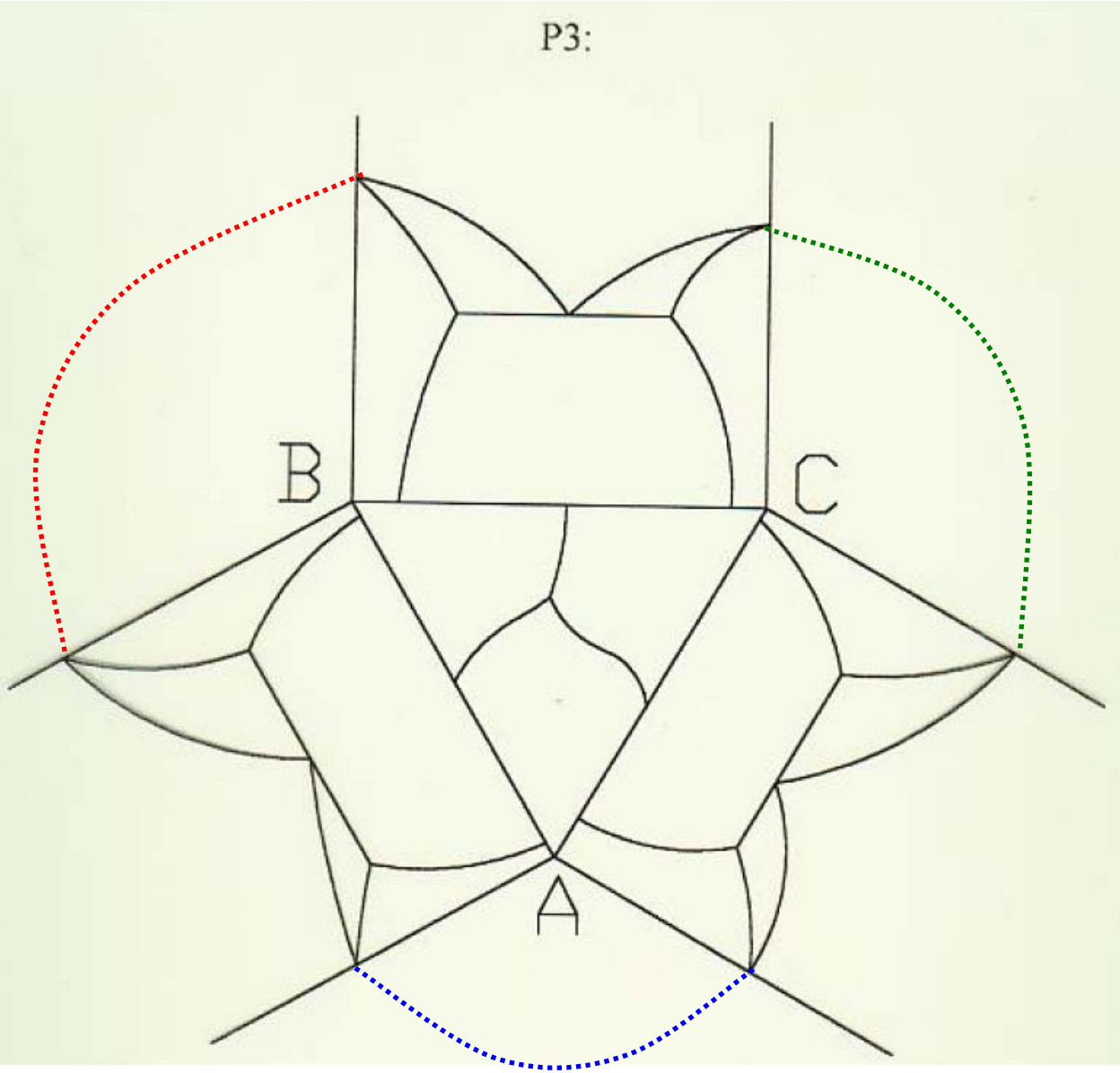
T_C: Melting Point Of Material C

T_{E1}: Eutectic Temperature Of A-B

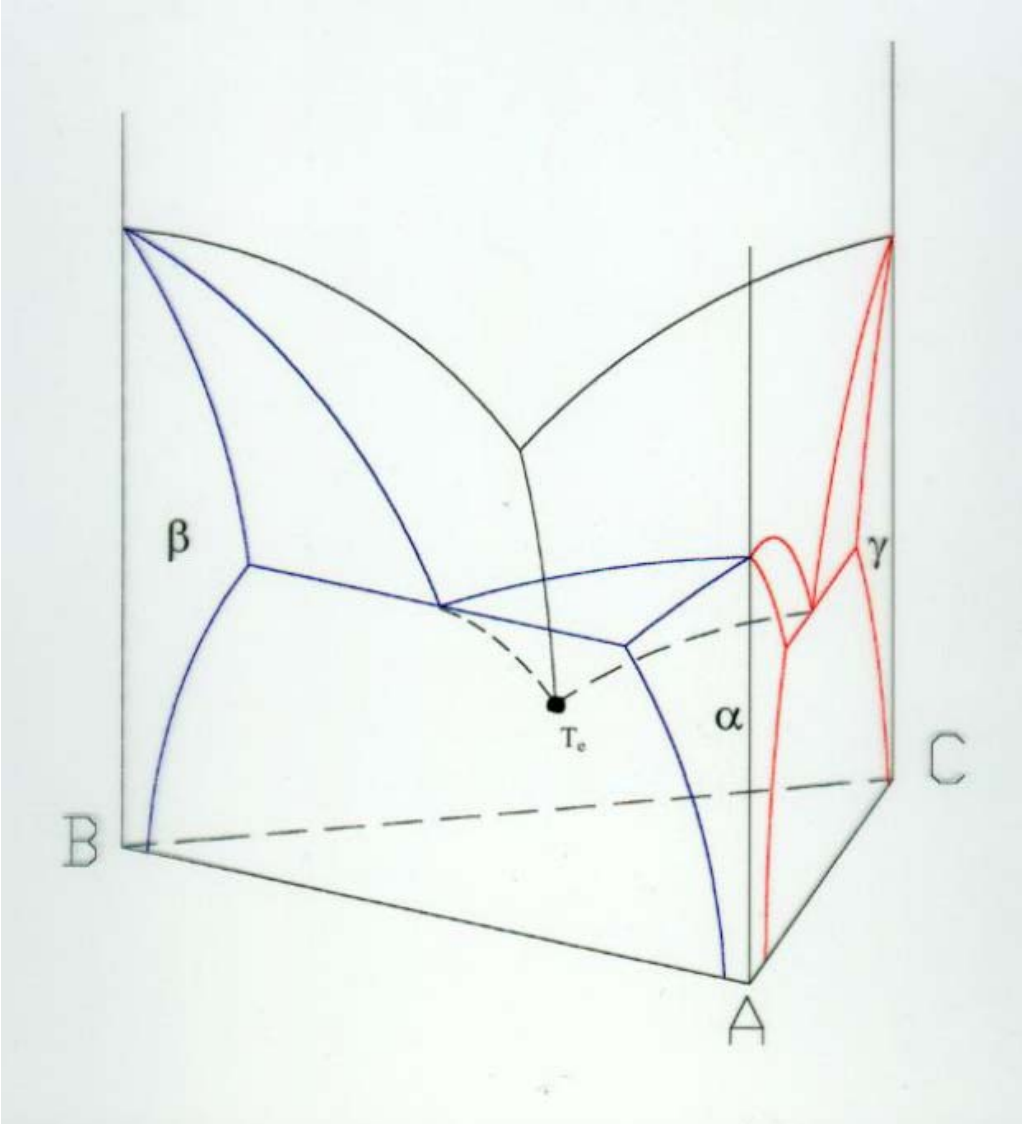
T_{E2}: Eutectic Temperature Of B-C

T_{E3}: Eutectic Temperature Of C-A

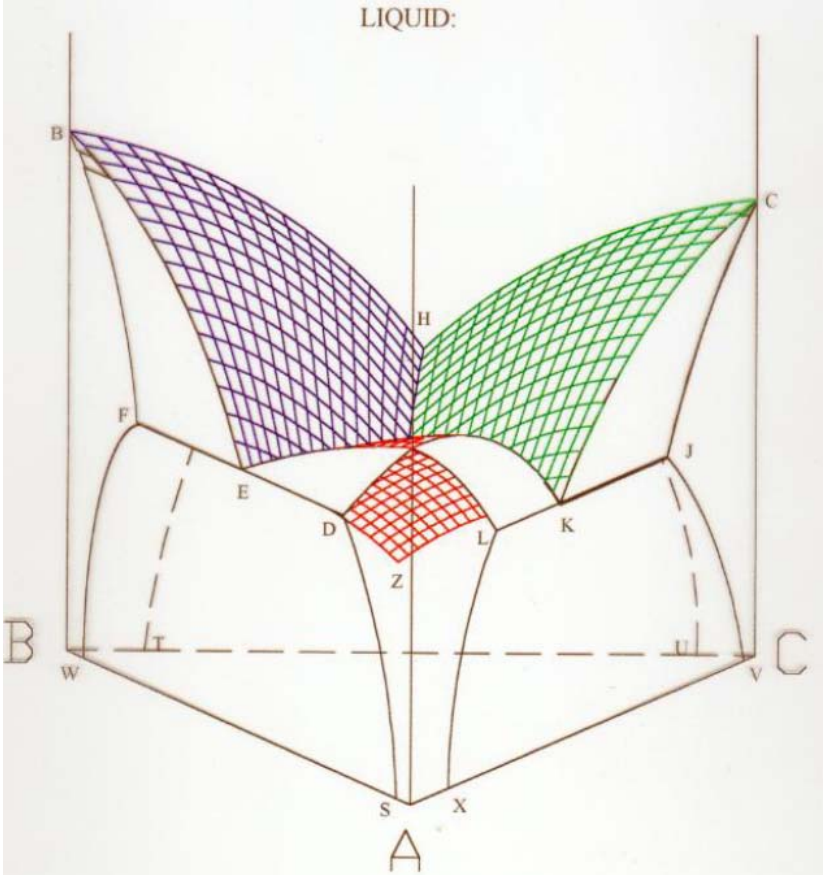
Ternary Eutectic System
(with Solid Solubility)



Ternary Eutectic System
(with Solid Solubility)

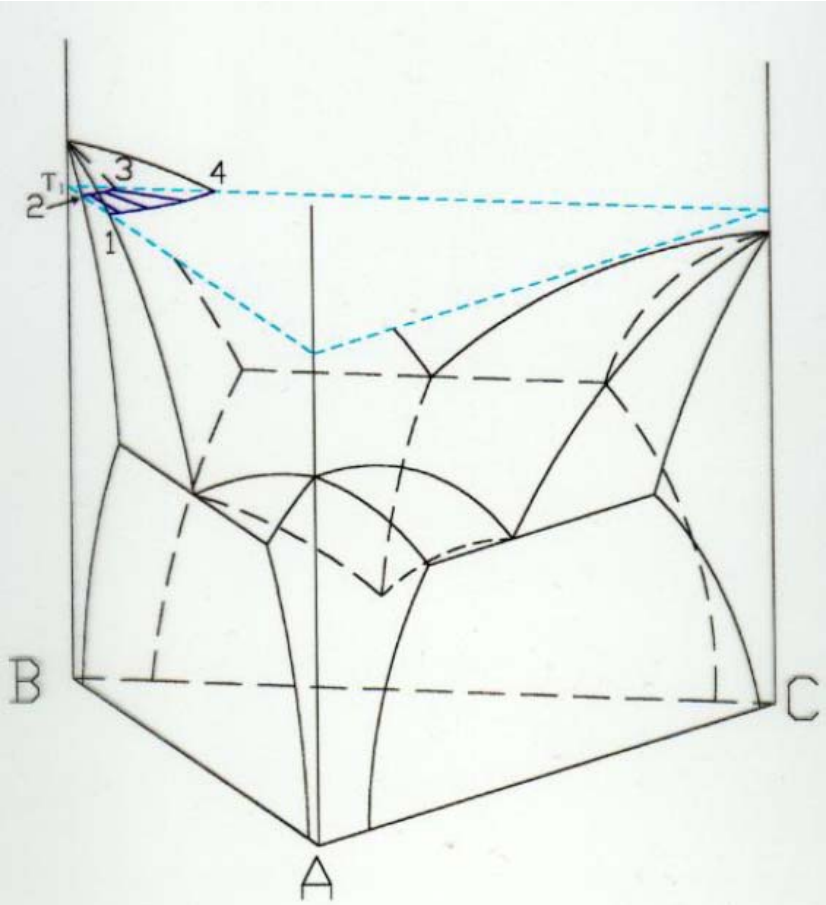


Main outline of Ternary Phase Diagram with Ternary Eutectic (T_e) and Solid Single Phase Regions Shown

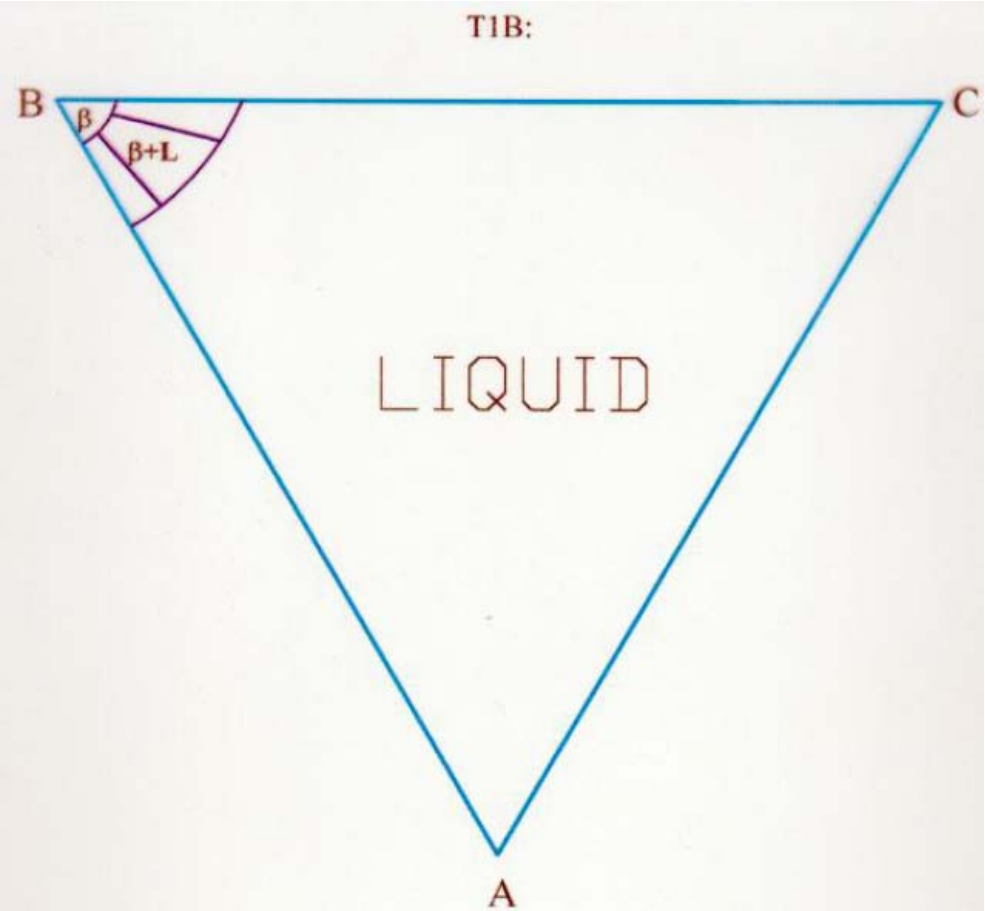


All Liquidus surfaces (α+L-Red, β+L-Purple, γ+L-Green)

Ternary Eutectic System
(with Solid Solubility)

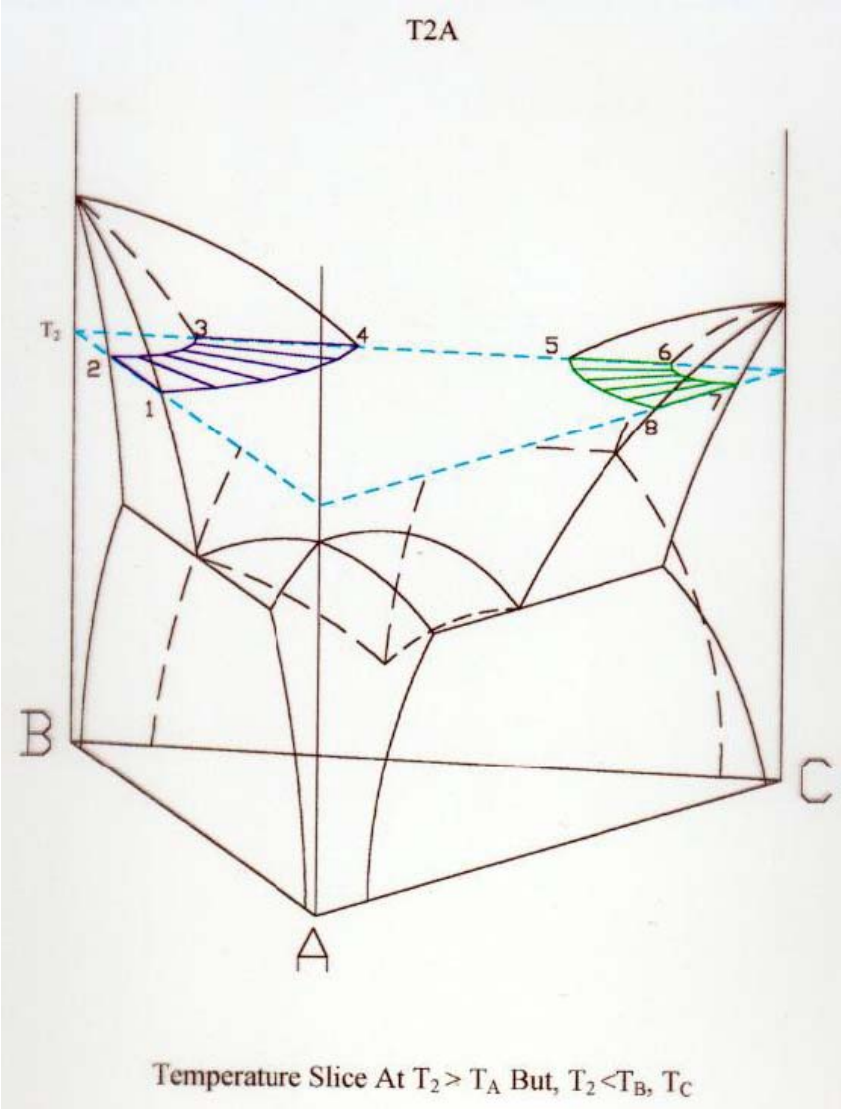


Temperature Slice At $T_1 < T_B$, But $>T_A$, T_C

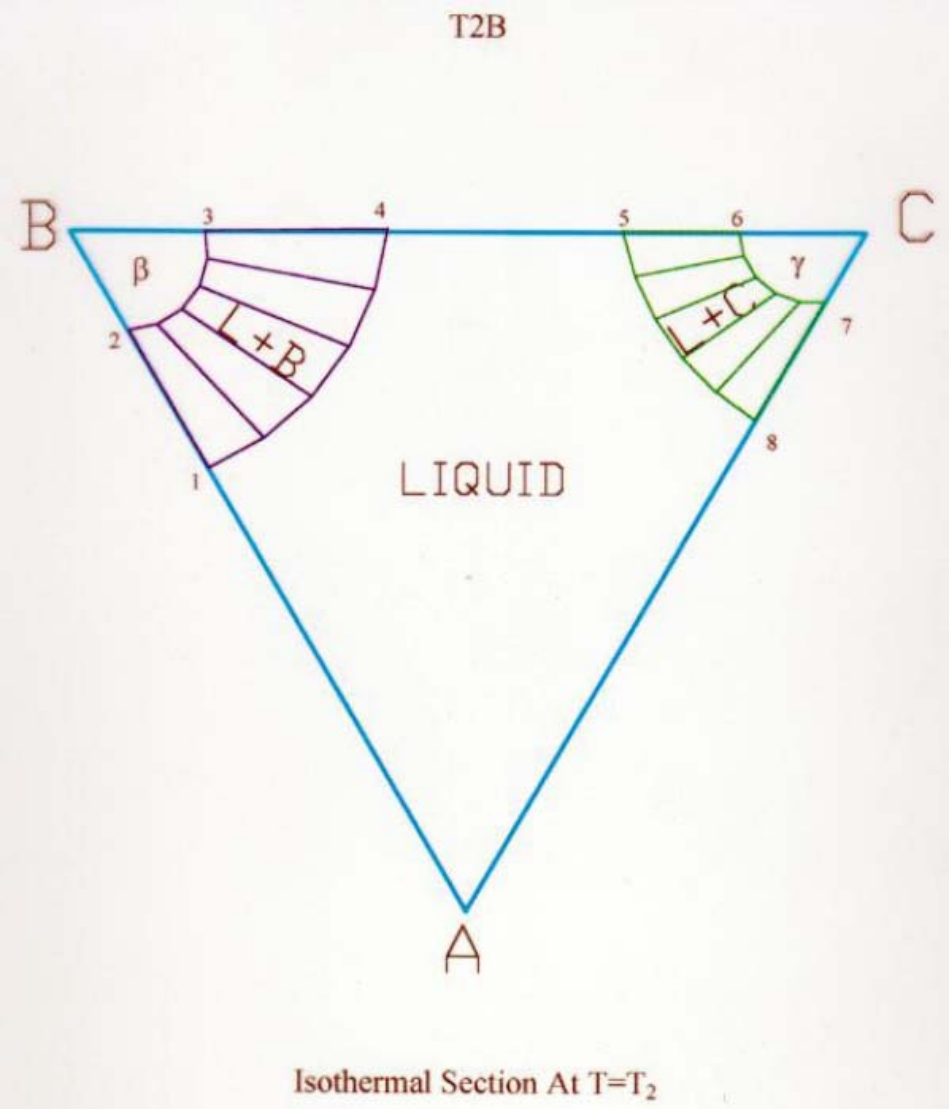


Isothermal Section At $T=T_1$

Ternary Eutectic System
(with Solid Solubility)

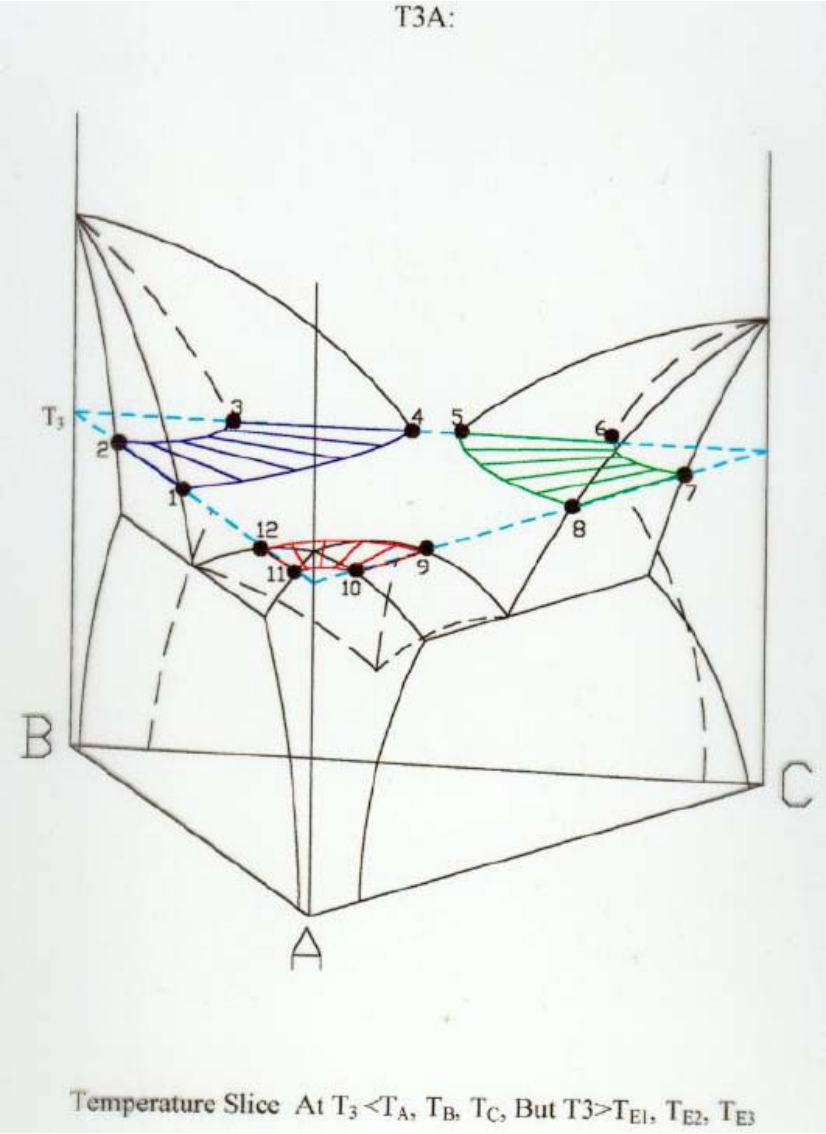


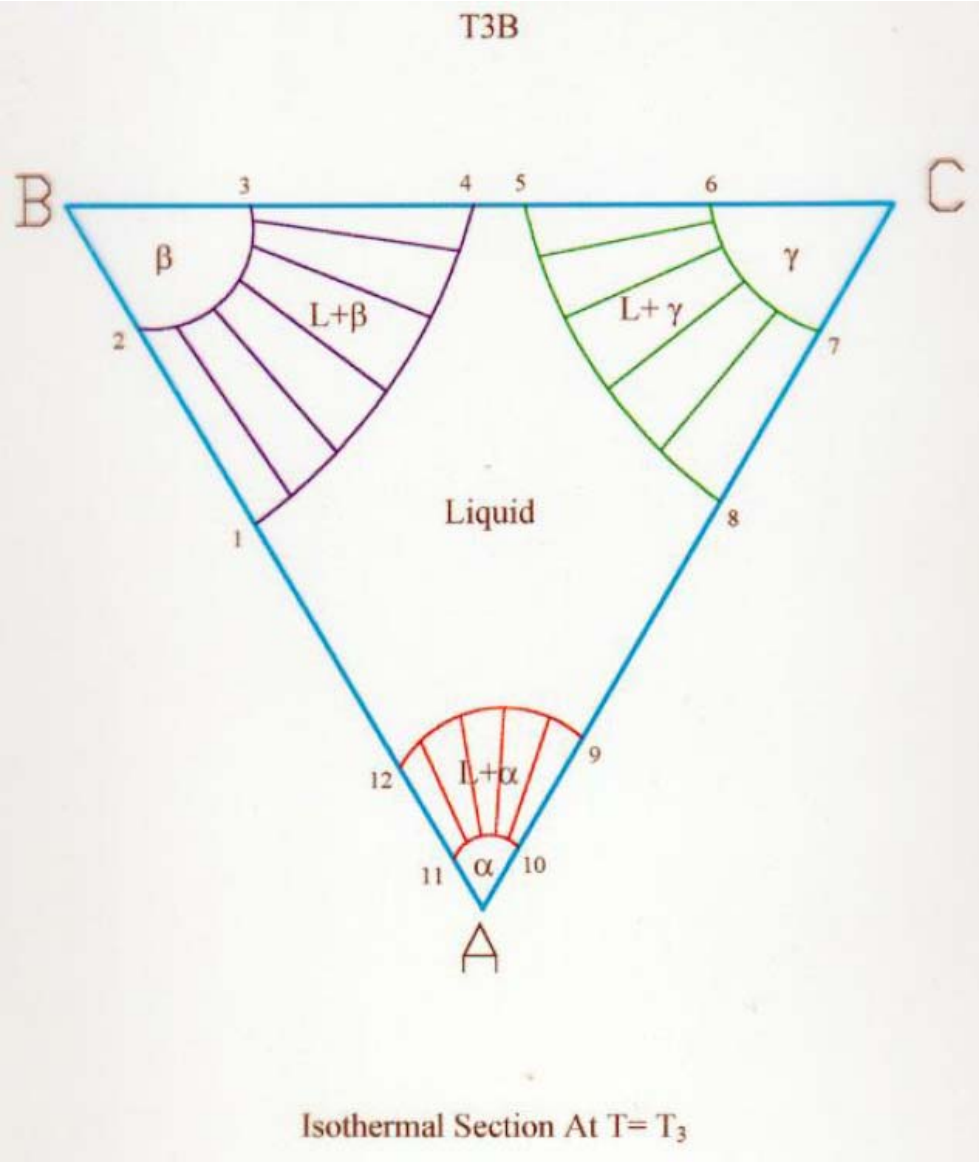
Temperature Slice At $T_2 > T_A$ But, $T_2 < T_B$, T_C



Isothermal Section At $T=T_2$

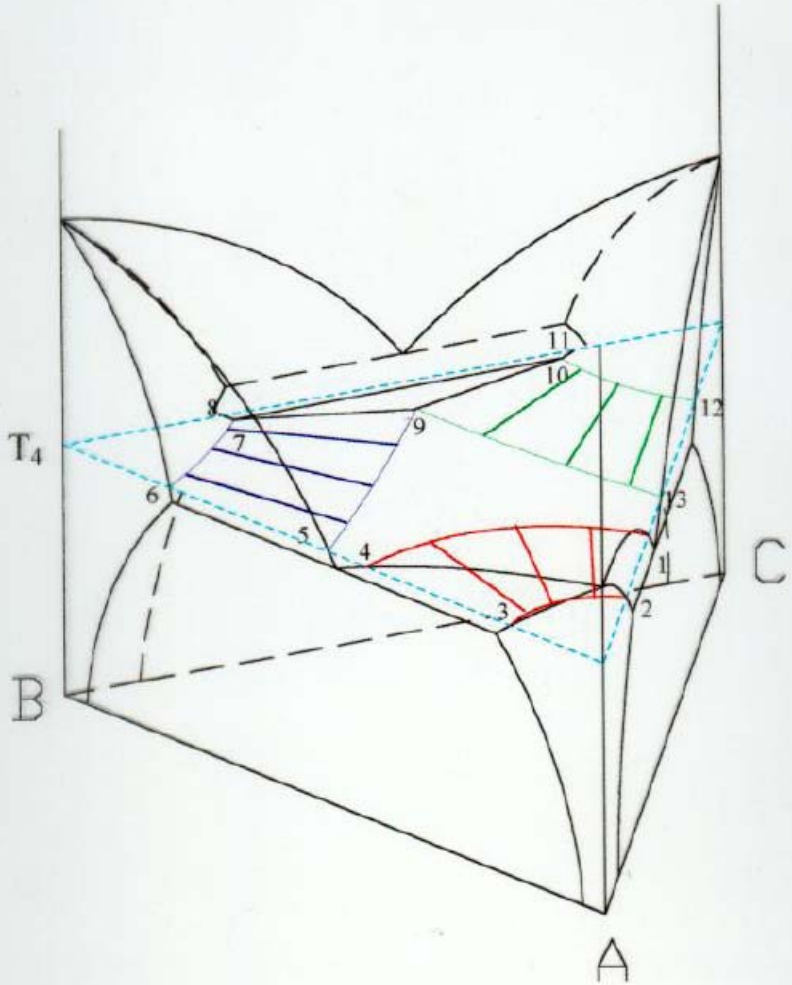
Ternary Eutectic System
(with Solid Solubility)





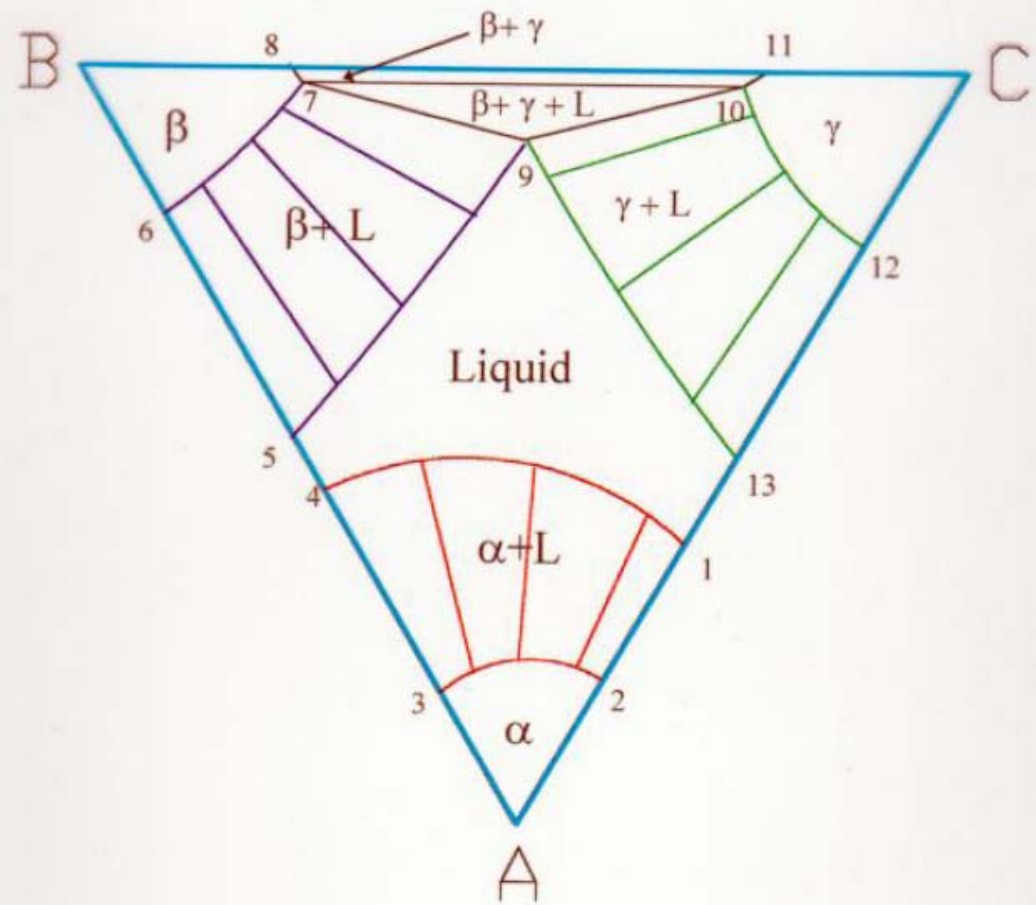
Ternary Eutectic System
(with Solid Solubility)

T4A:



Temperature Slice At $T_4 < T_{E2}$ And $T_4 > T_{E1}, T_{E3}$

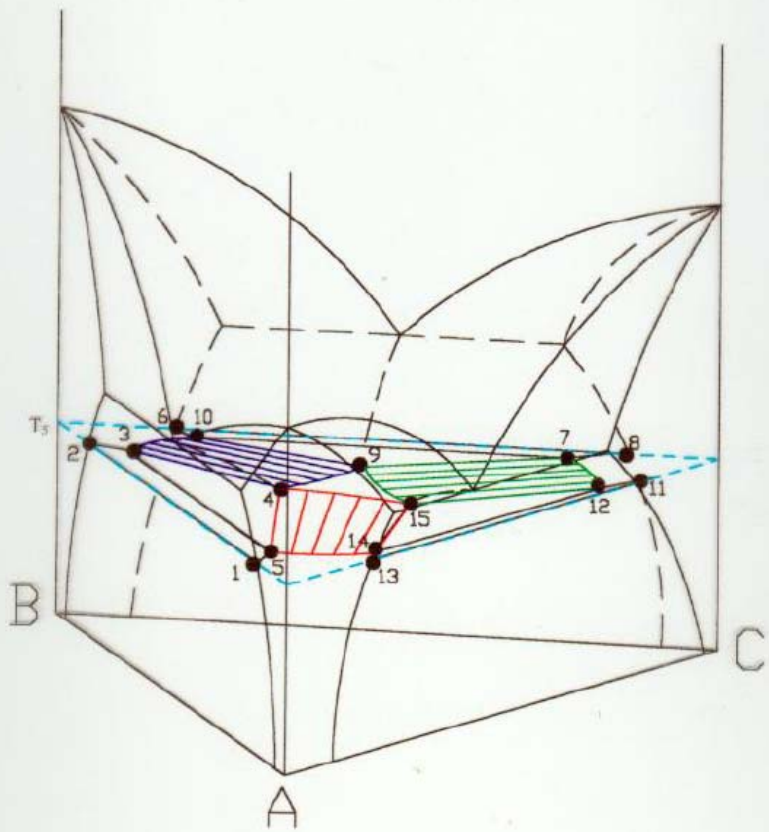
T4B:



Isothermal Section At $T=T_4$

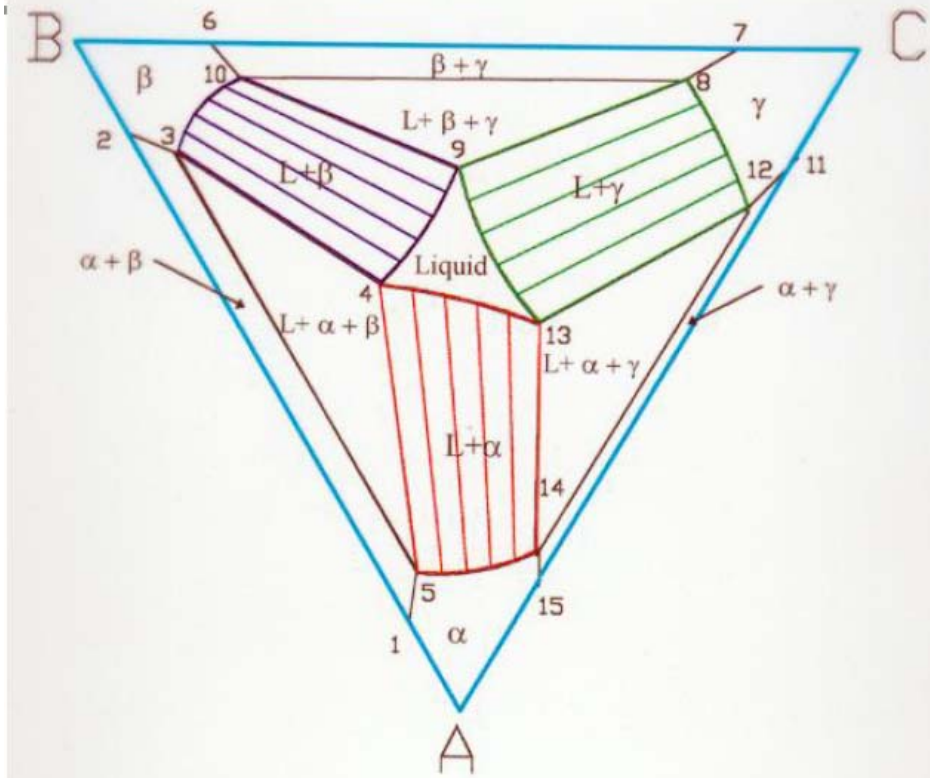
Ternary Eutectic System
(with Solid Solubility)

T5A:



Temperature Slice Below All Binary Eutectics But, Above The Ternary Eutectic

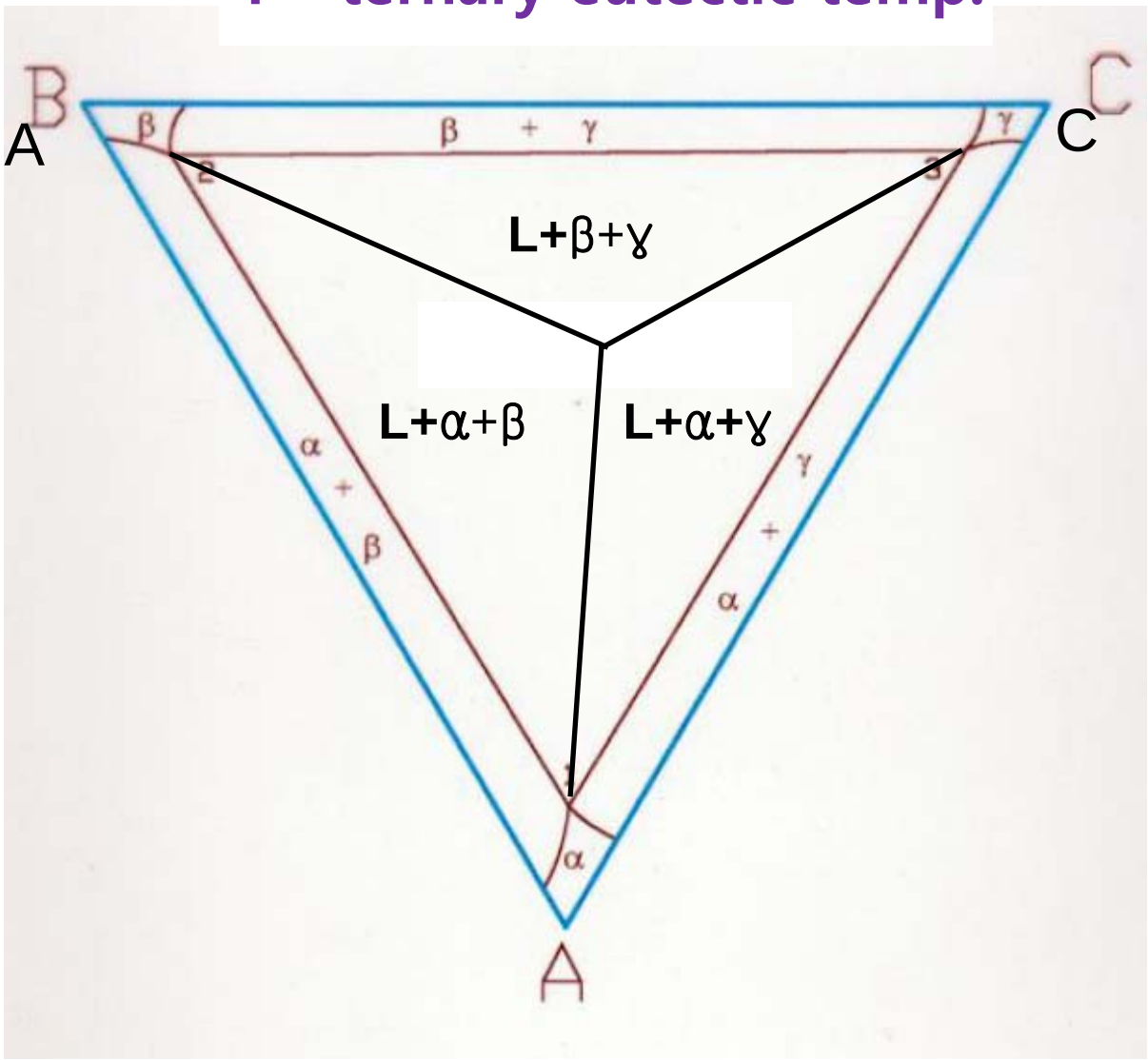
T5B:



Isothermal Section At $T=T_5$

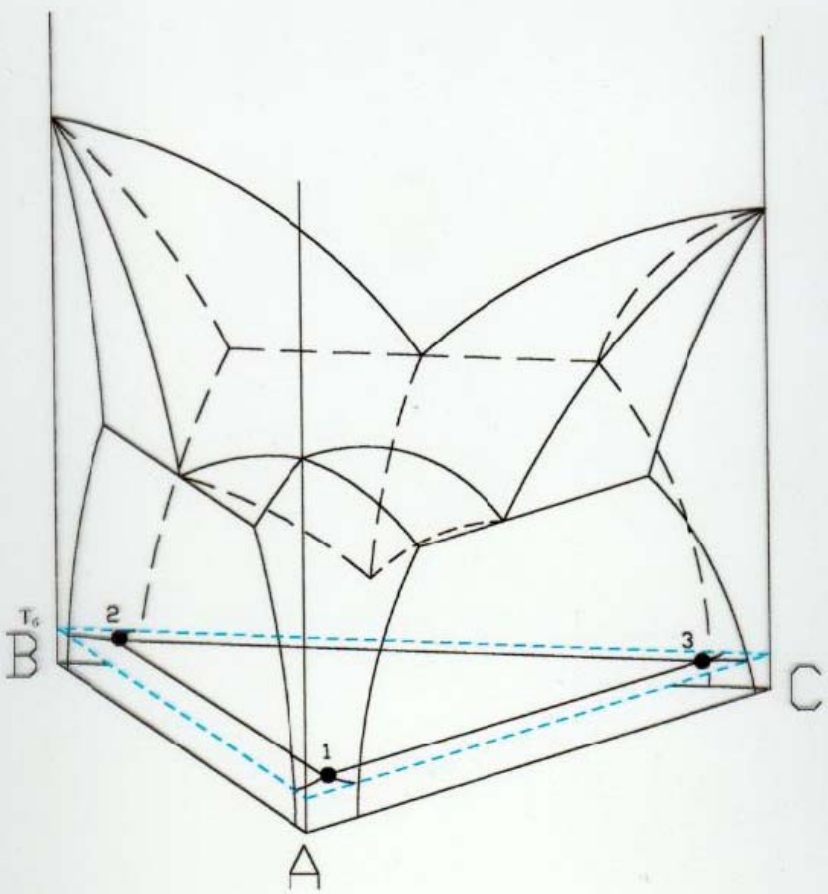
Ternary Eutectic System
(with Solid Solubility)

T= ternary eutectic temp.



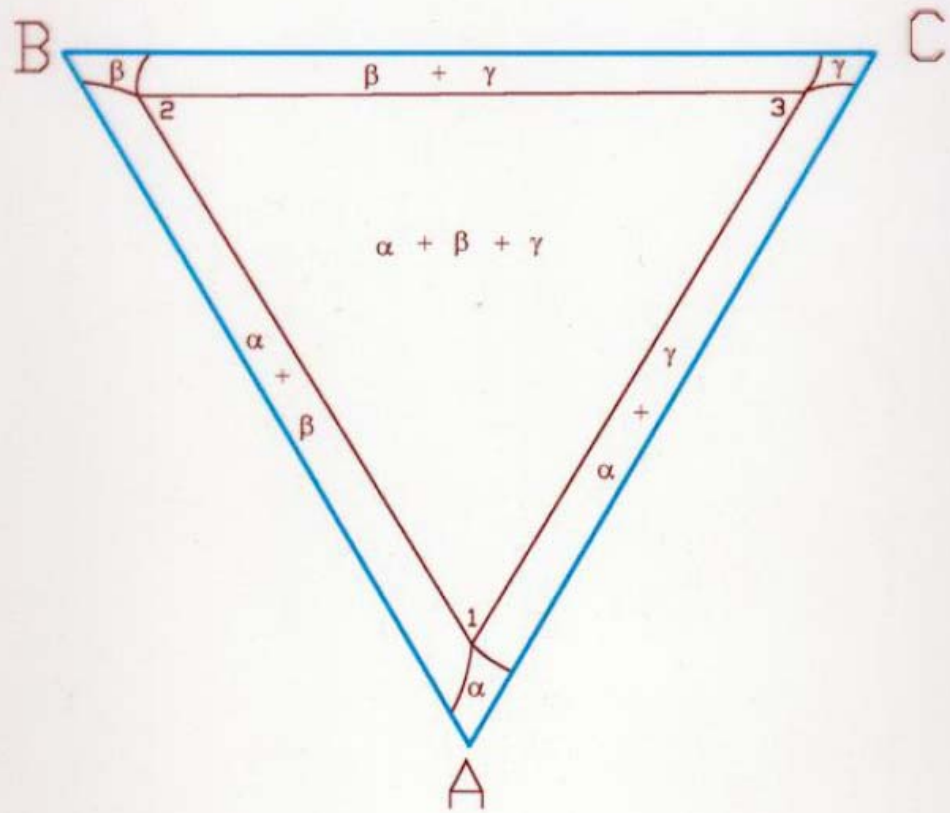
Ternary Eutectic System
(with Solid Solubility)

T6A:



Temperature Slice at $T_6 < T_E$

T6B:



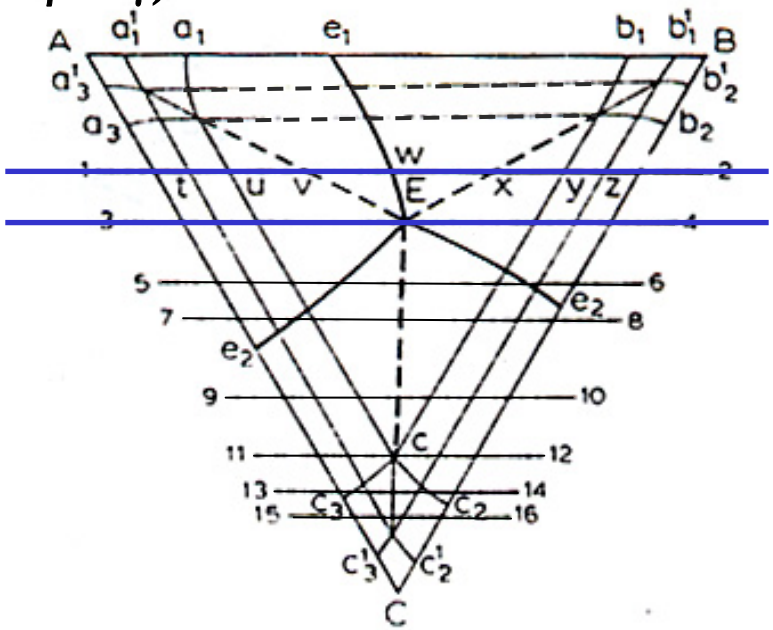
Isothermal Section At $T=T_6$

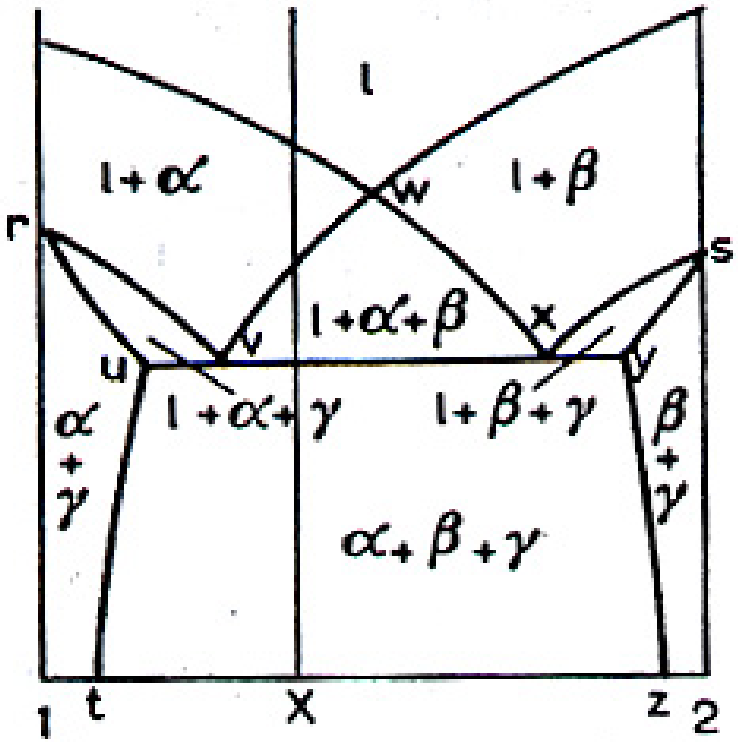
http://www.youtube.com/watch?v=yzhVomAdetM

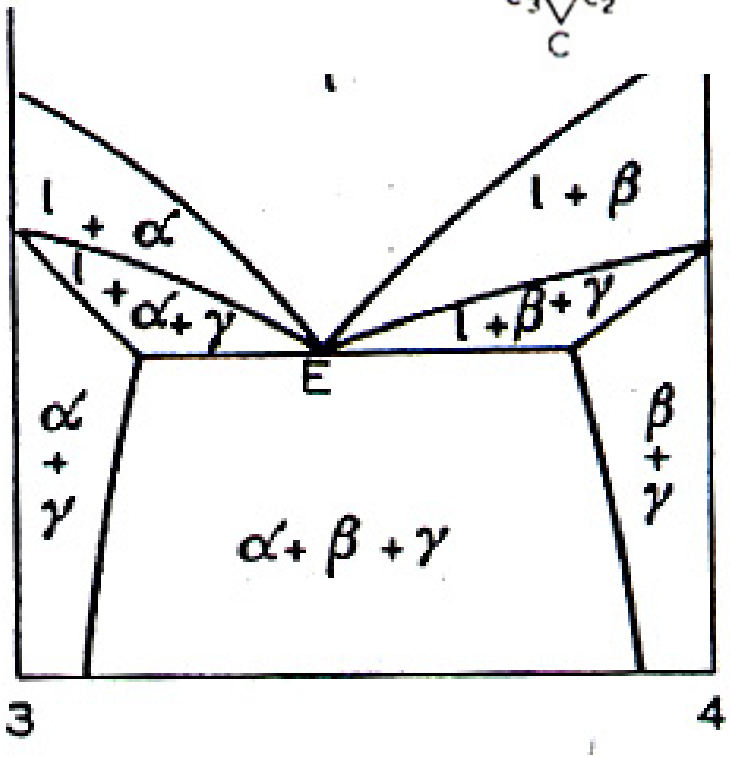
10.1. THE EUTECTIC EQUILIBRIUM ($l = \alpha + \beta + \gamma$)

Vertical section

Location of vertical section

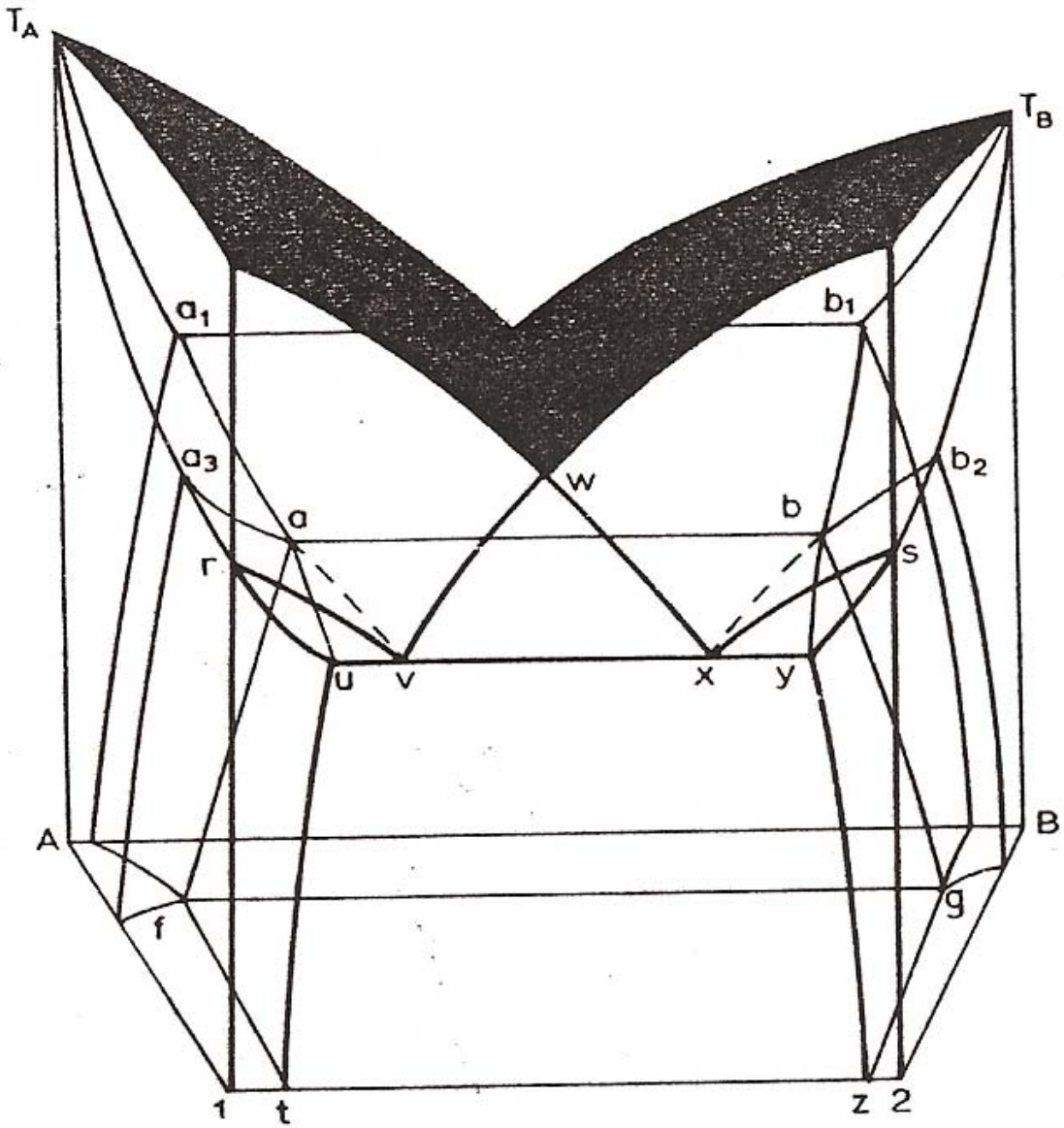




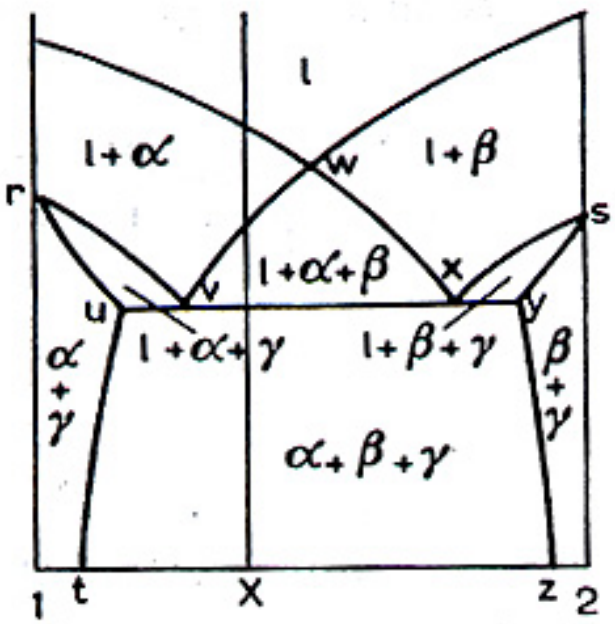


10.1. THE EUTECTIC EQUILIBRIUM ($l = \alpha + \beta + \gamma$)

Vertical section



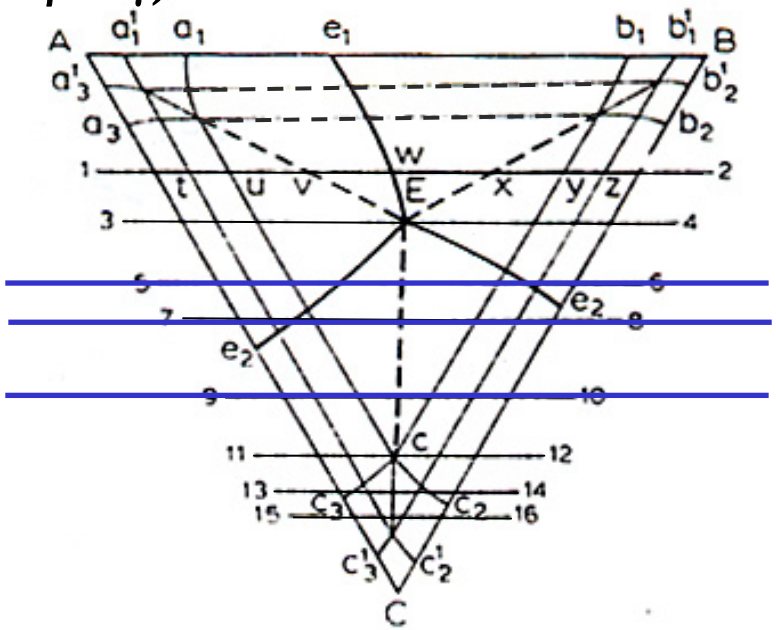
Location of vertical section

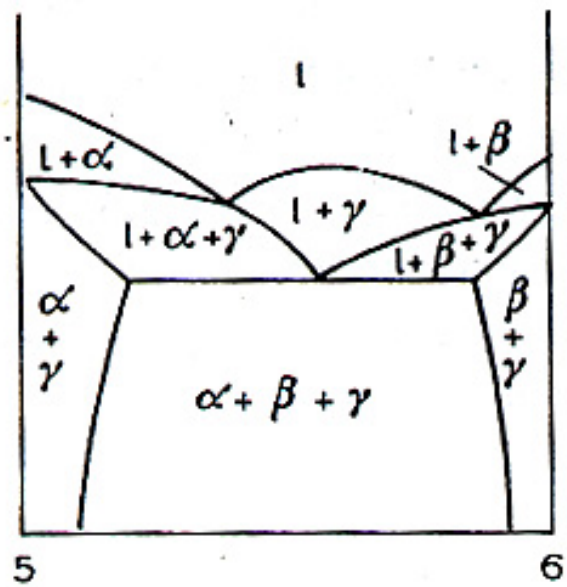


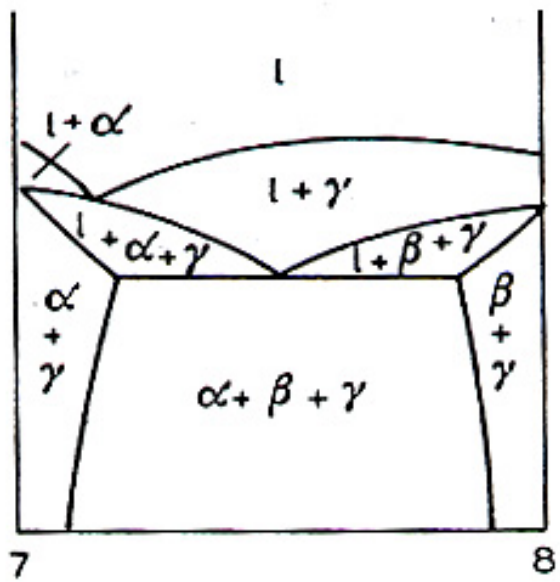
10.1. THE EUTECTIC EQUILIBRIUM ($l = \alpha + \beta + \gamma$)

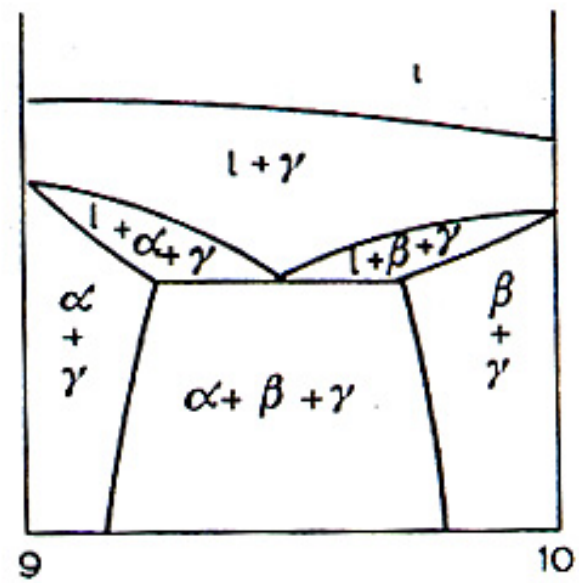
Vertical section

Location of vertical section



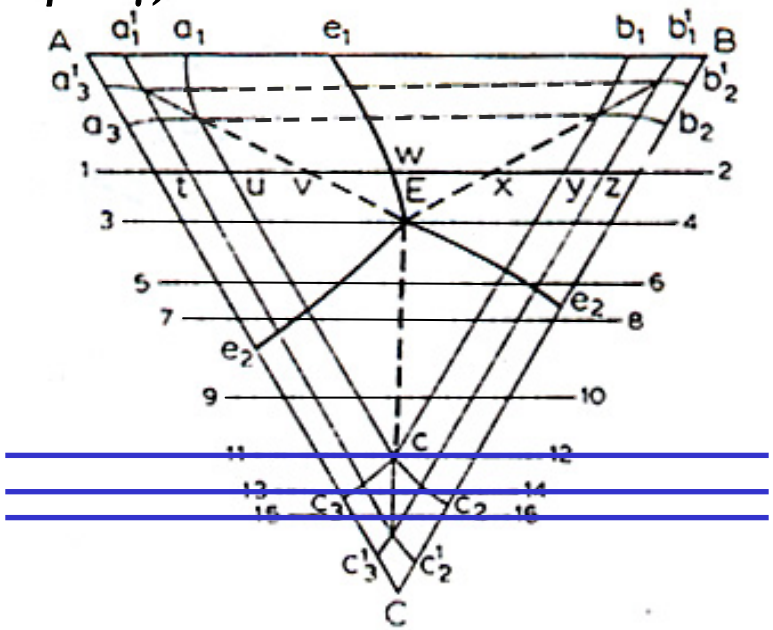


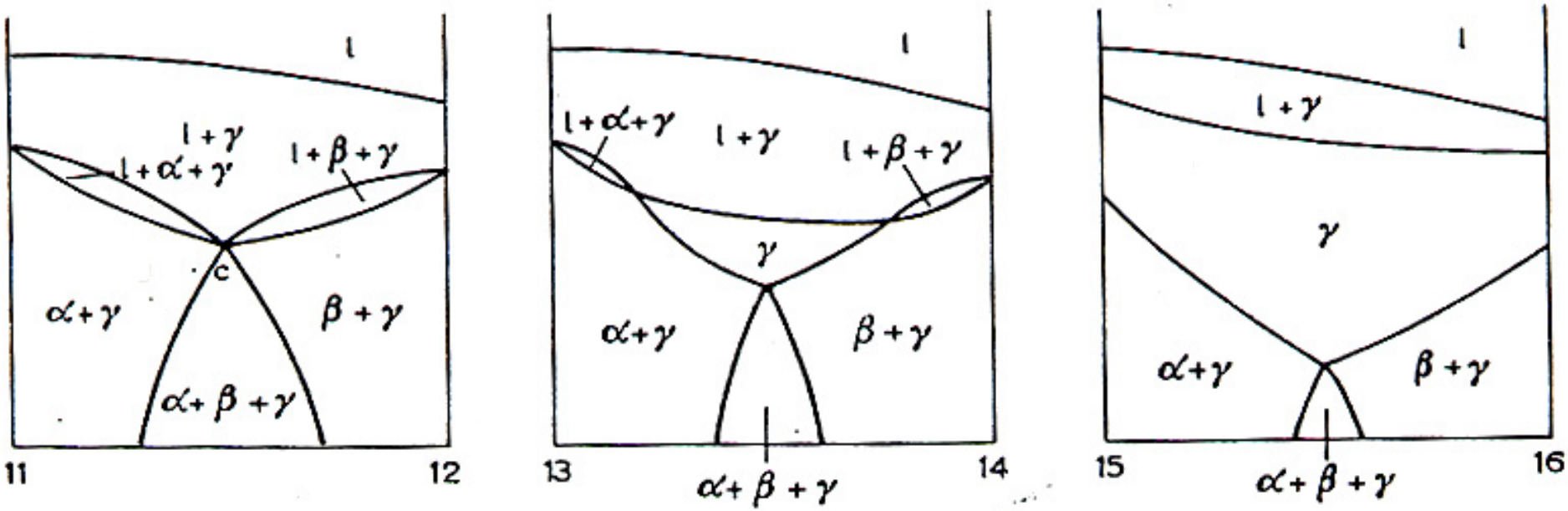




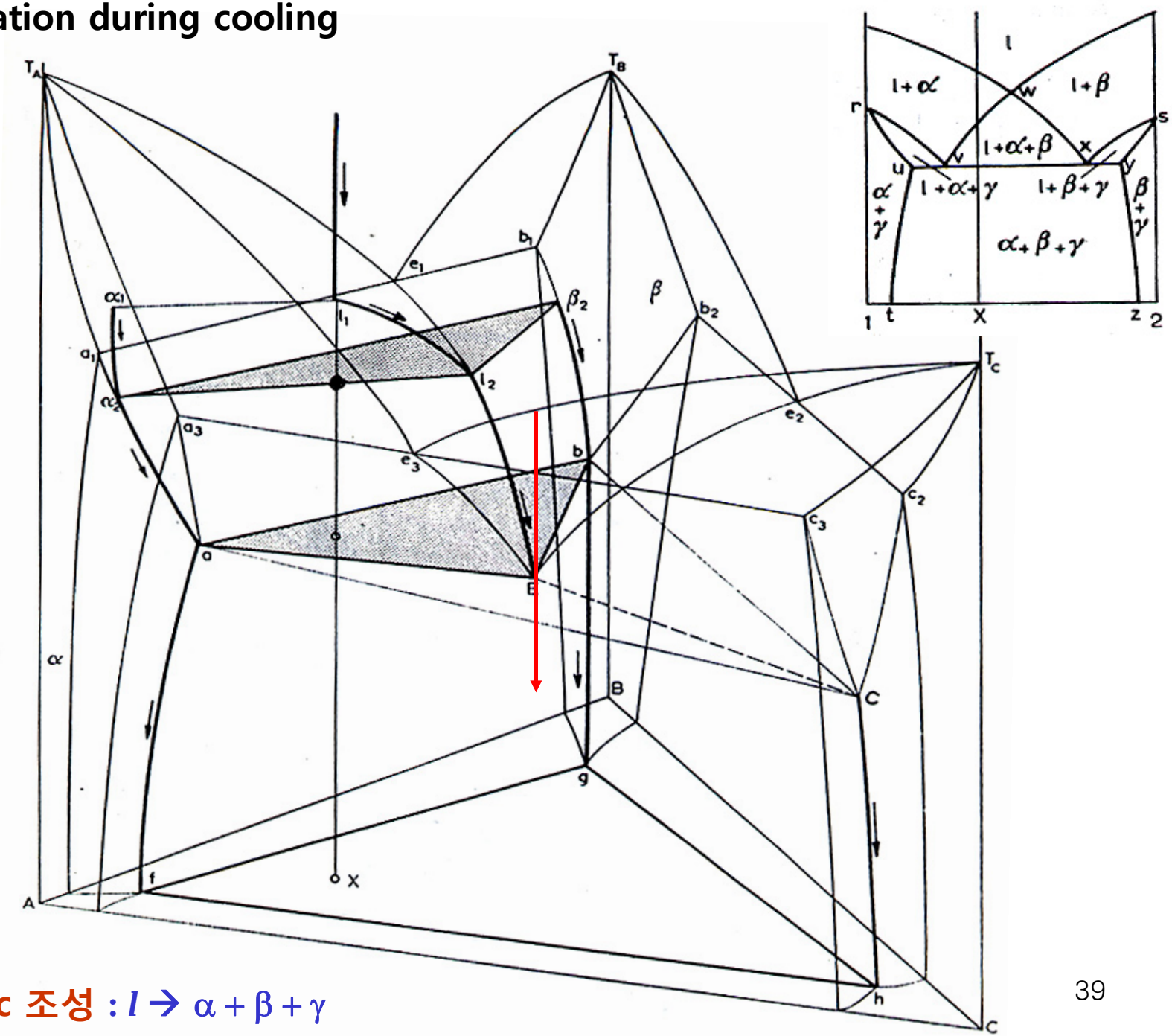
10.1. THE EUTECTIC EQUILIBRIUM ($l = \alpha + \beta + \gamma$)

Vertical section **Location of vertical section**



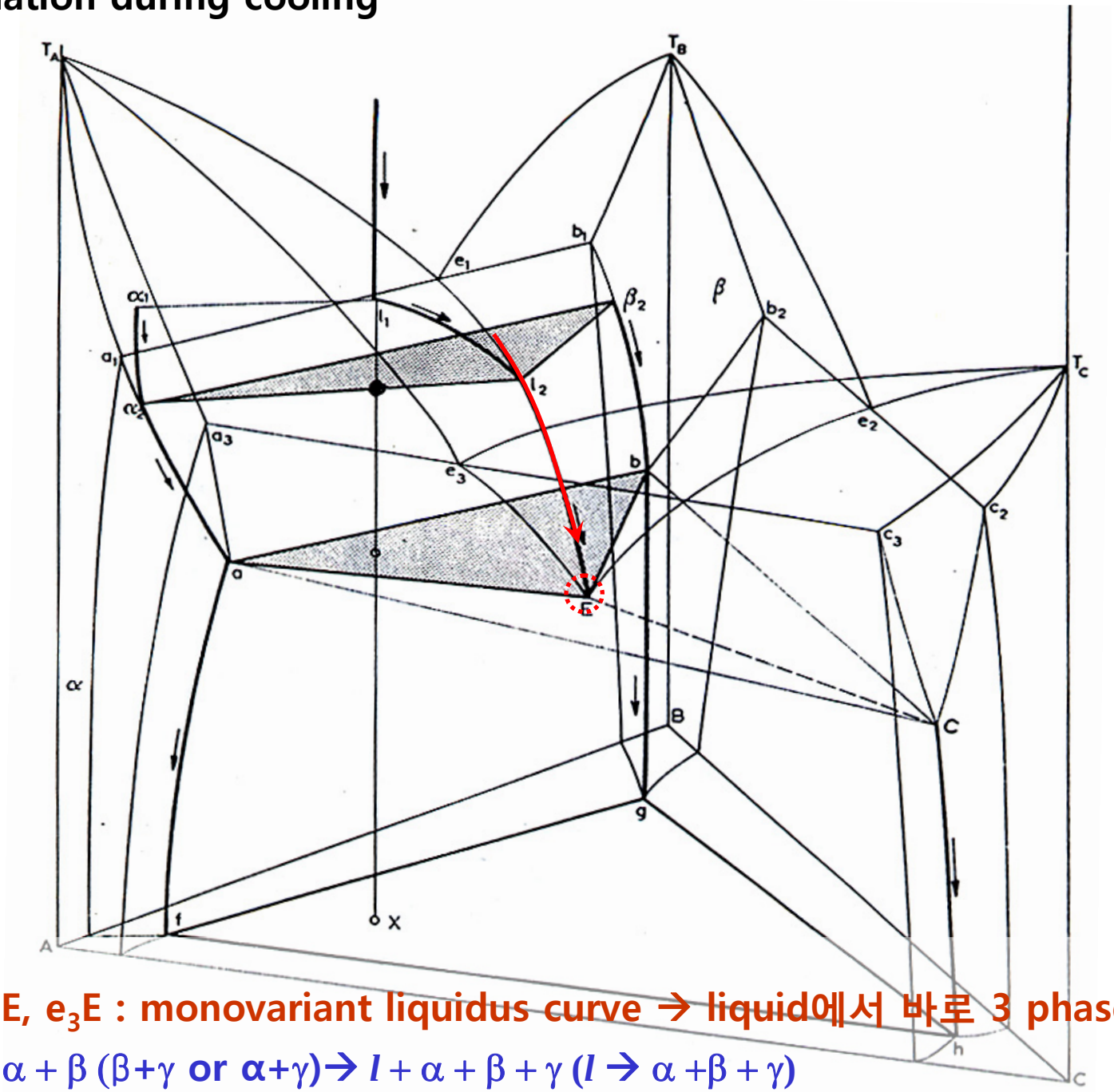


Transformation during cooling



① Eutectic 조성 : $l \rightarrow \alpha + \beta + \gamma$

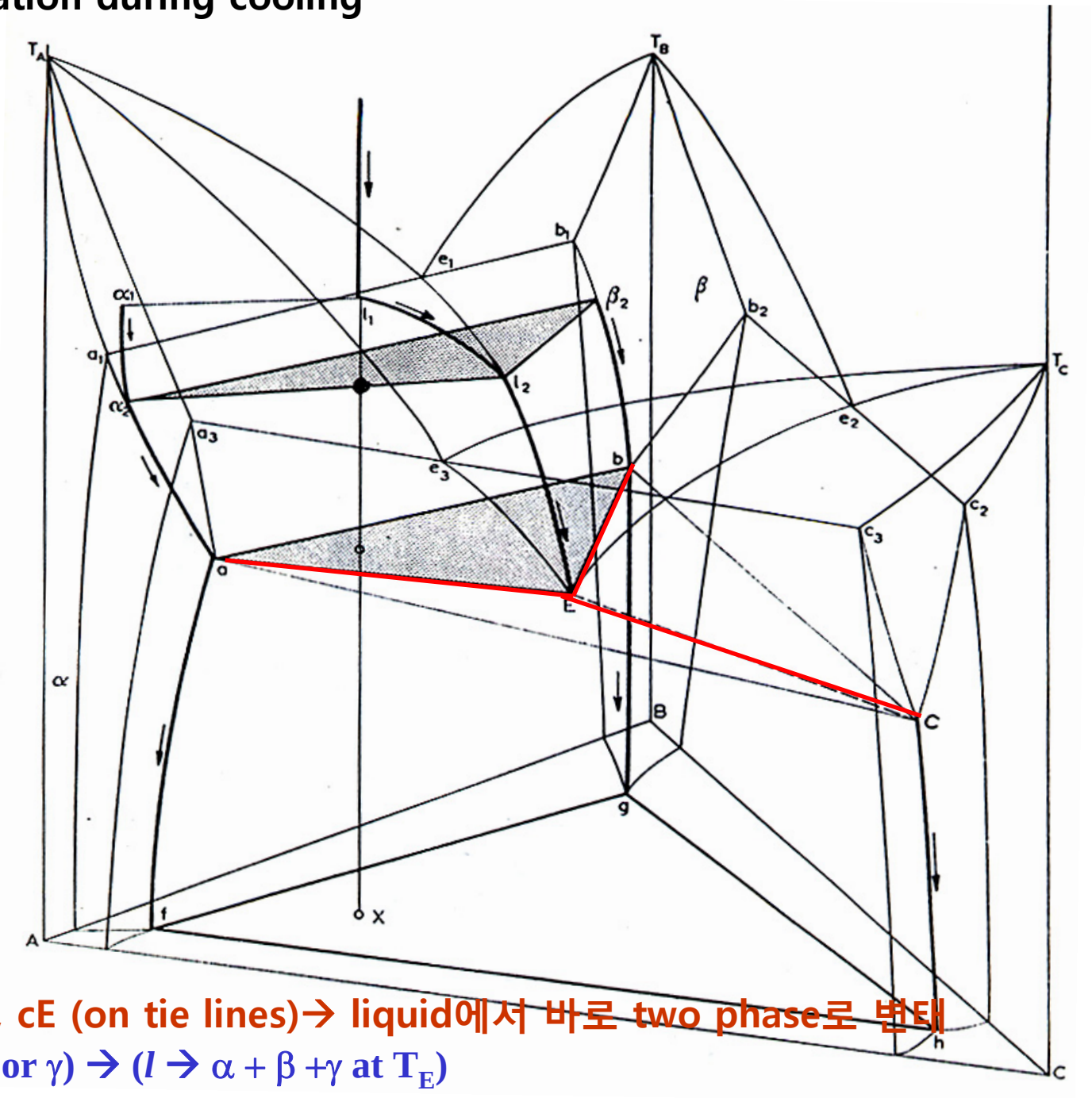
Transformation during cooling



② e_1E, e_2E, e_3E : monovariant liquidus curve → liquid에서 바로 3 phases로 변태

: $l \rightarrow l + \alpha + \beta$ ($\beta+\gamma$ or $\alpha+\gamma$) $\rightarrow l + \alpha + \beta + \gamma$ ($l \rightarrow \alpha + \beta + \gamma$)

Transformation during cooling

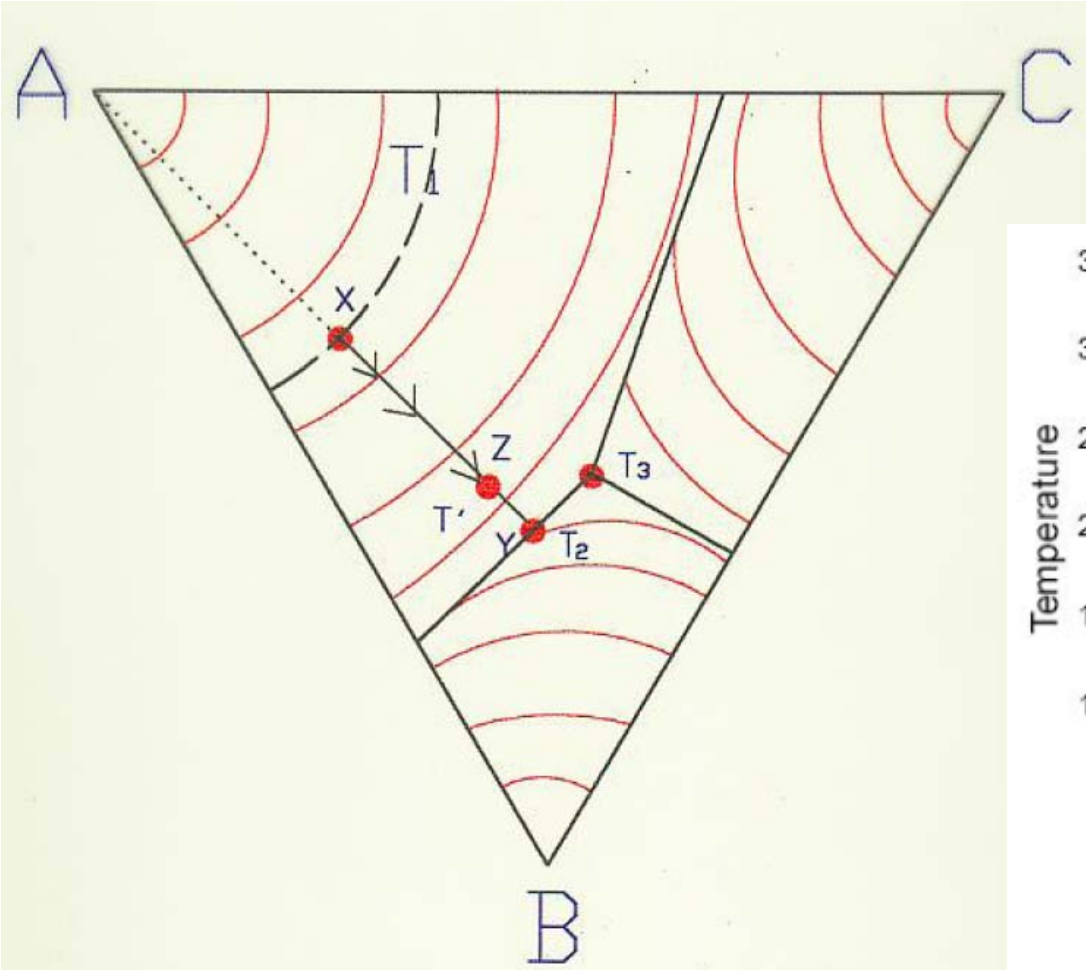


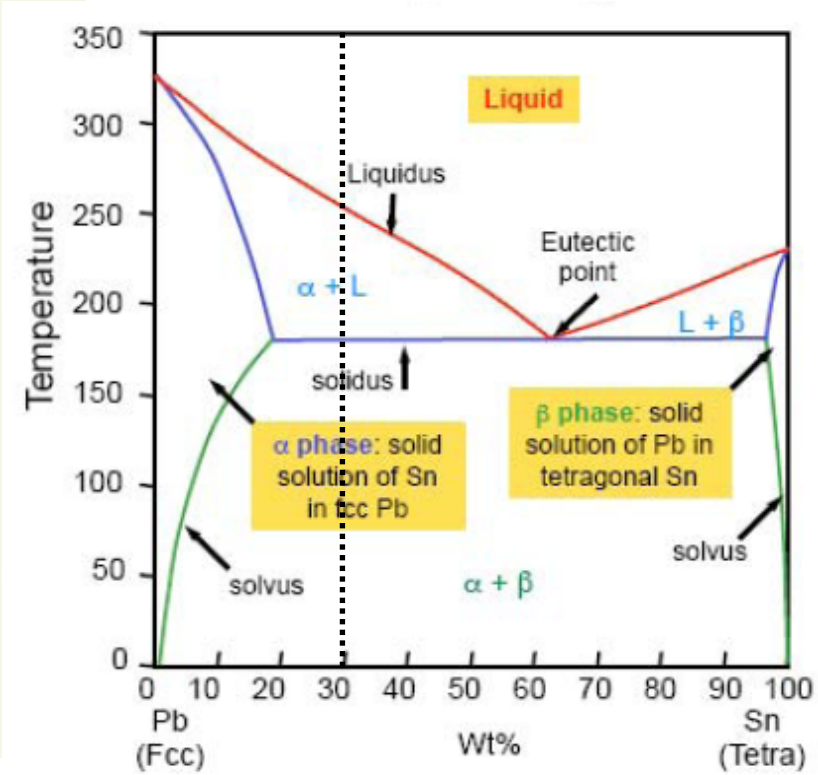
③ aE, bE, cE (on tie lines)→ liquid에서 바로 two phase로 변태

: $l + \alpha$ (β or γ) → (l → $\alpha + \beta + \gamma$ at T_E)

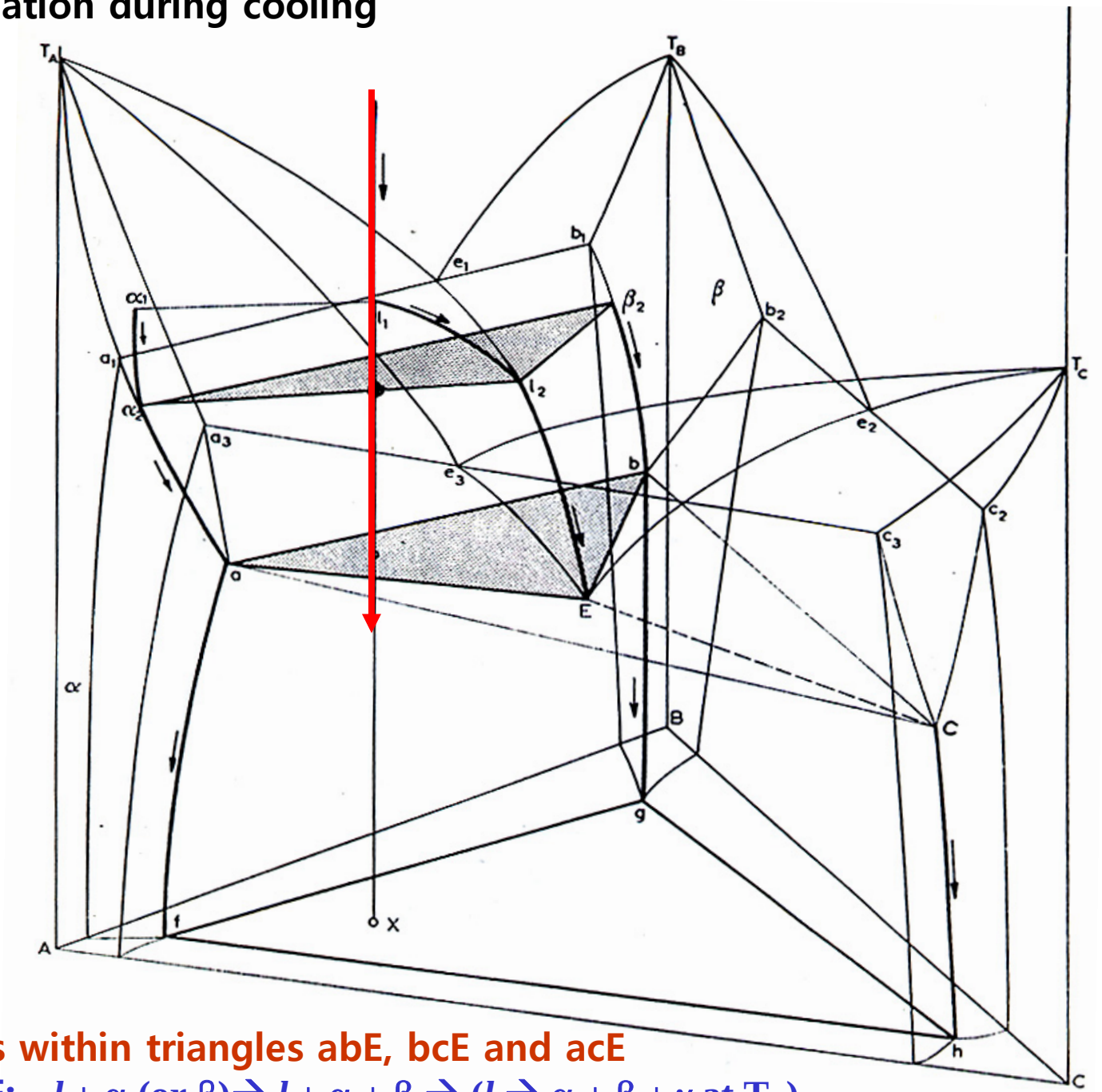
Ternary Eutectic System

Solidification Sequence





Transformation during cooling



④ Alloys within triangles abE, bcE and acE

ex) abE: $l + \alpha$ (or β) → $l + \alpha + \beta$ → (l → $\alpha + \beta + \gamma$ at T_E)