

**2015 Fall**

# **“Phase Equilibria *in* Materials”**

**11.04.2015**

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**Office: 33-313**

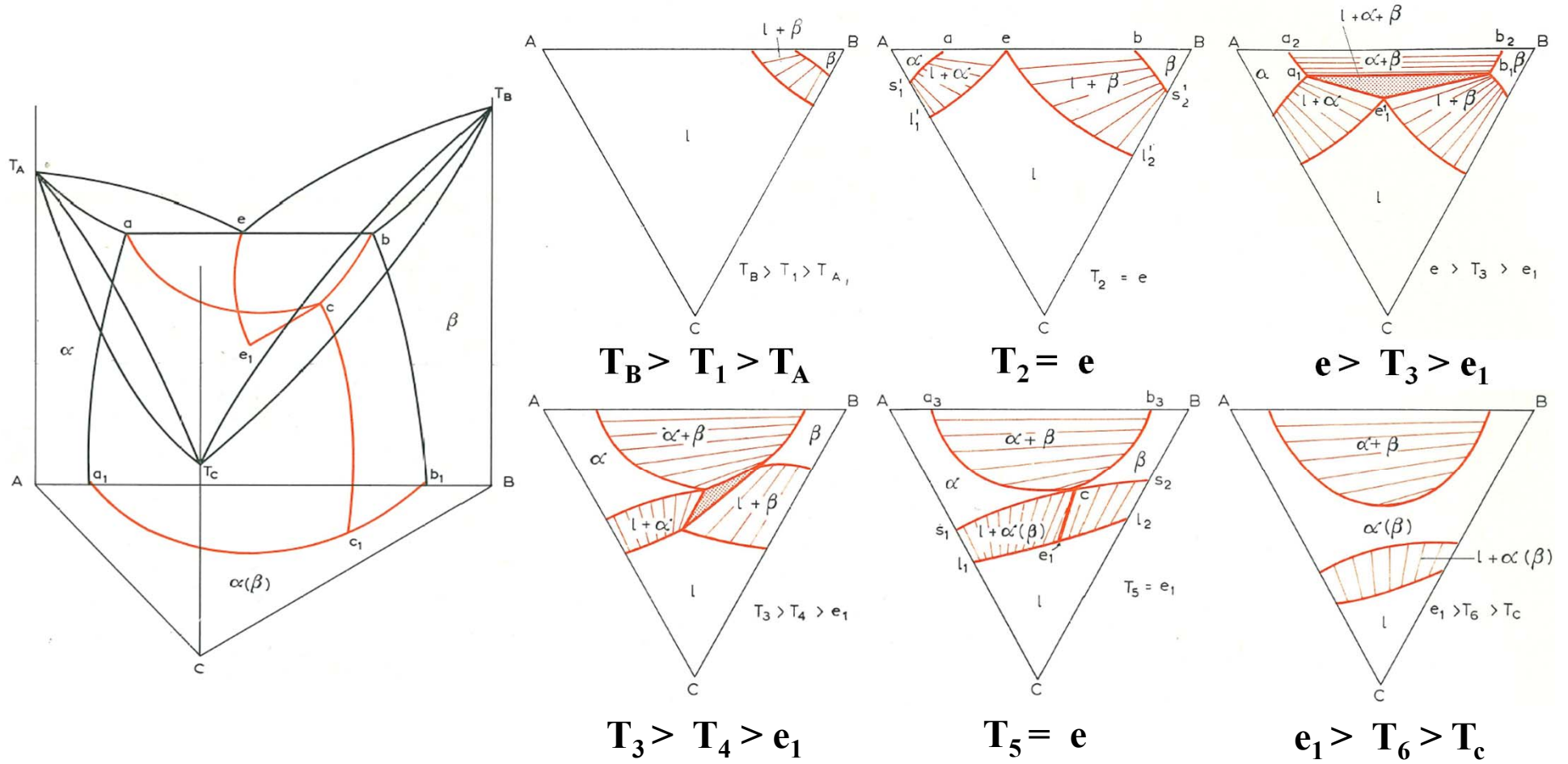
**Telephone: 880-7221**

**Email: [espark@snu.ac.kr](mailto:espark@snu.ac.kr)**

**Office hours: by an appointment**

# 9.3. THREE-PHASE EQUILIBRIUM INVOLVING EUTECTIC REACTIONS

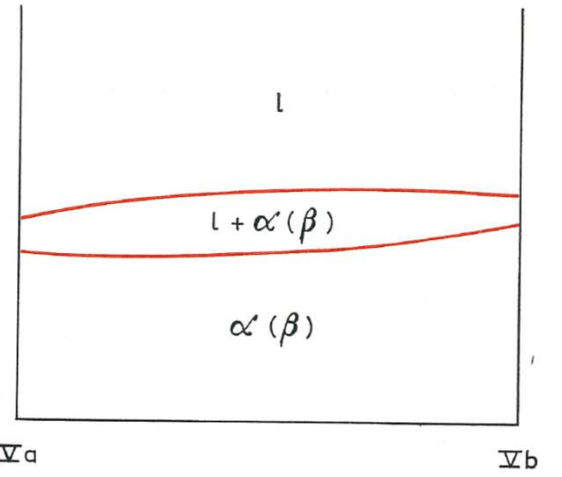
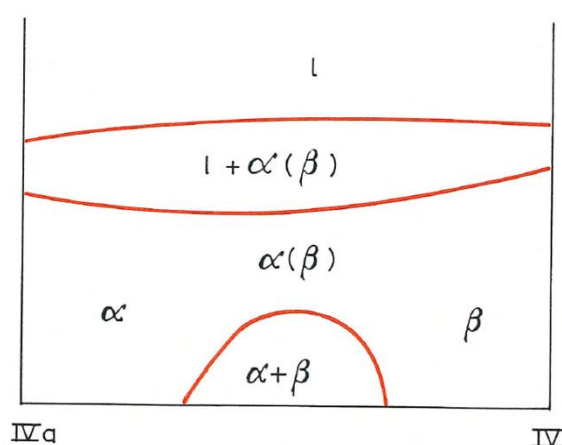
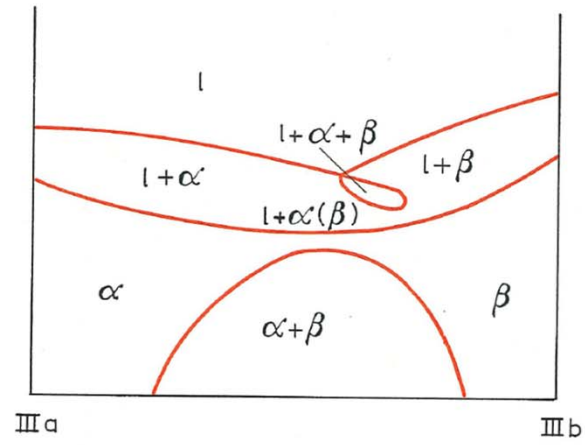
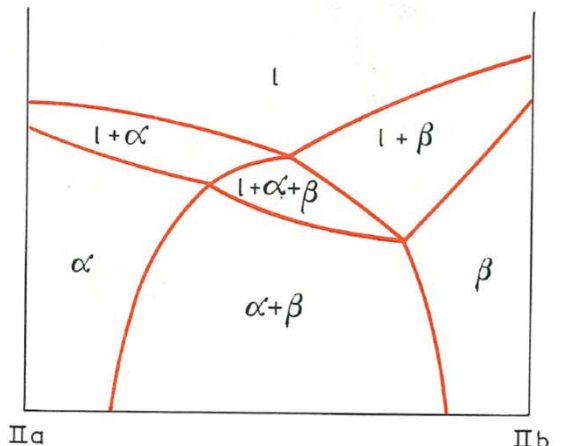
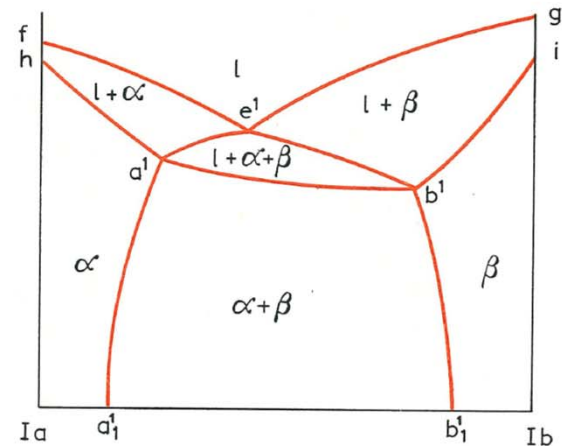
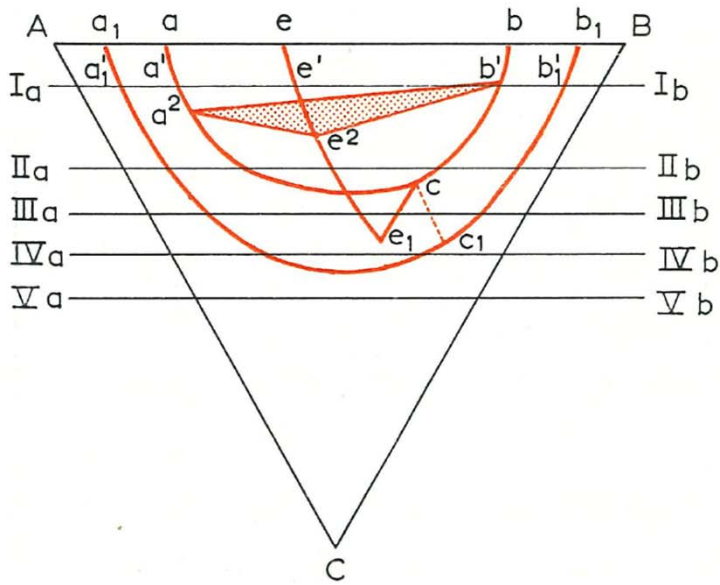
- Isothermal section



cf) Movie

# 9.3. THREE-PHASE EQUILIBRIUM INVOLVING EUTECTIC REACTIONS

## • Vertical section



> Point 1: 4 on the  $\alpha$  solidus surface

> Point 1- Point 2

\* 4→6 on the  $\alpha$  solidus surface

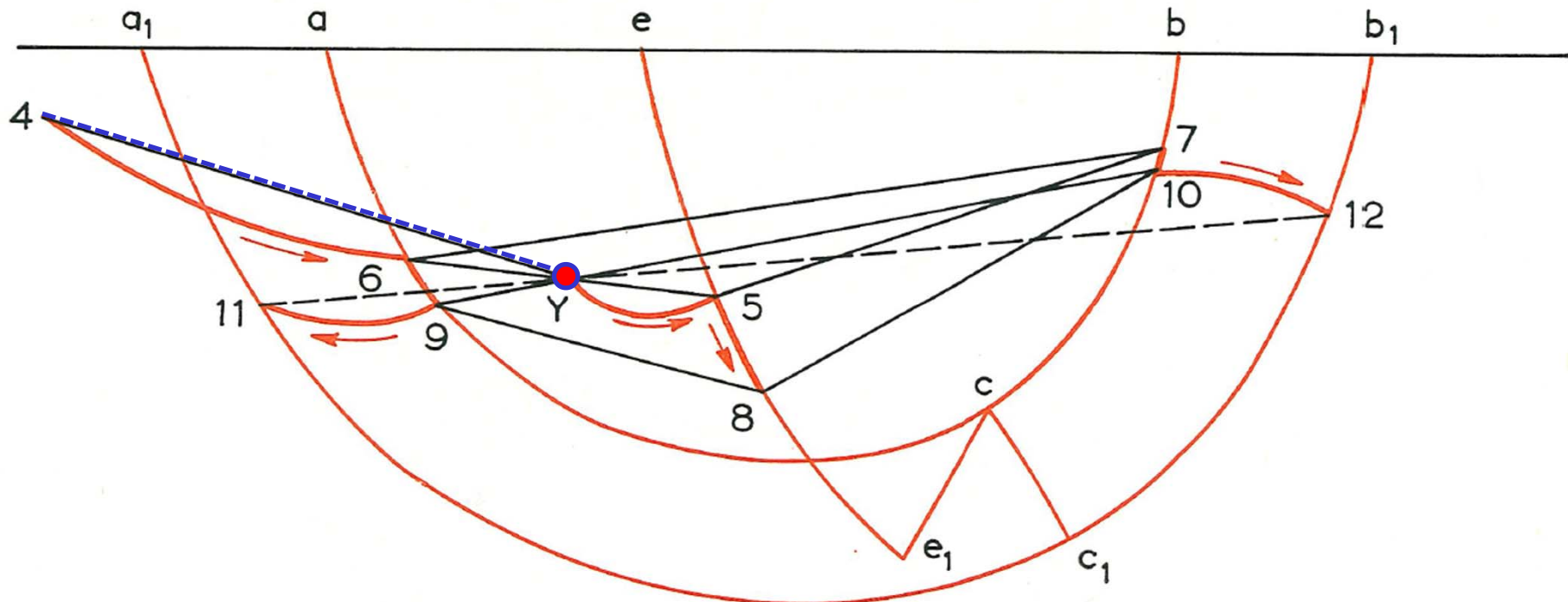
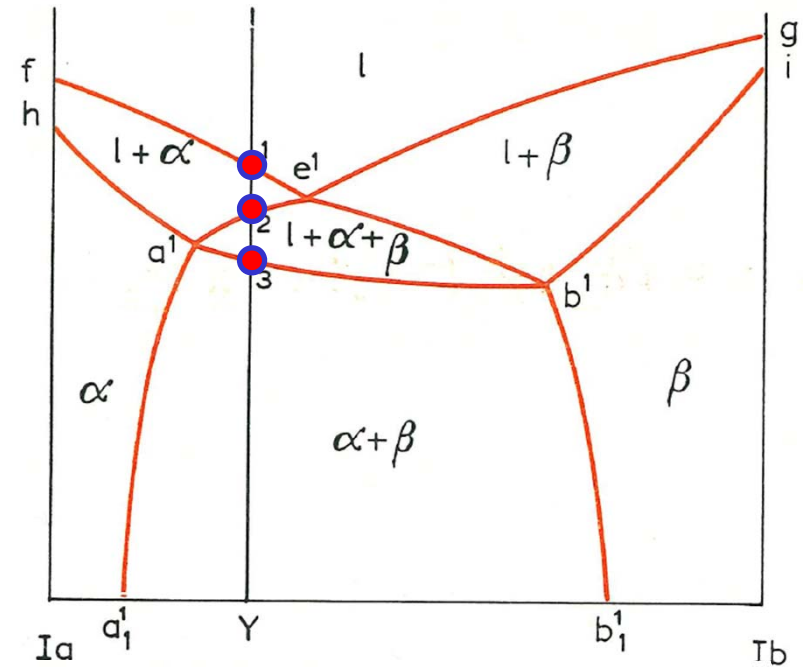
\* 1→5 on the  $\alpha$  liquidus surface

Three phase equilibrium l5,  $\alpha$ 6,  $\beta$ 7

\*  $\alpha$ : 6→9,  $\beta$ : 7→10, l: 5→8

> Point 3: on the tie line 9-10

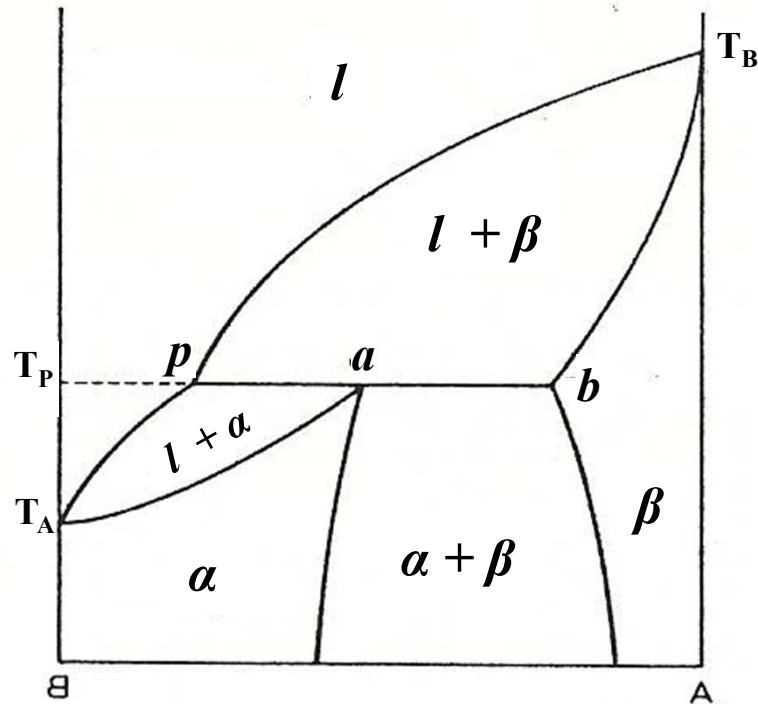
> Point 3-Y:  $\alpha$ : 9→11,  $\beta$ : 10→12



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

## 9.4. THREE-PHASE EQUILIBRIUM INVOLVING PERITECTIC REACTIONS

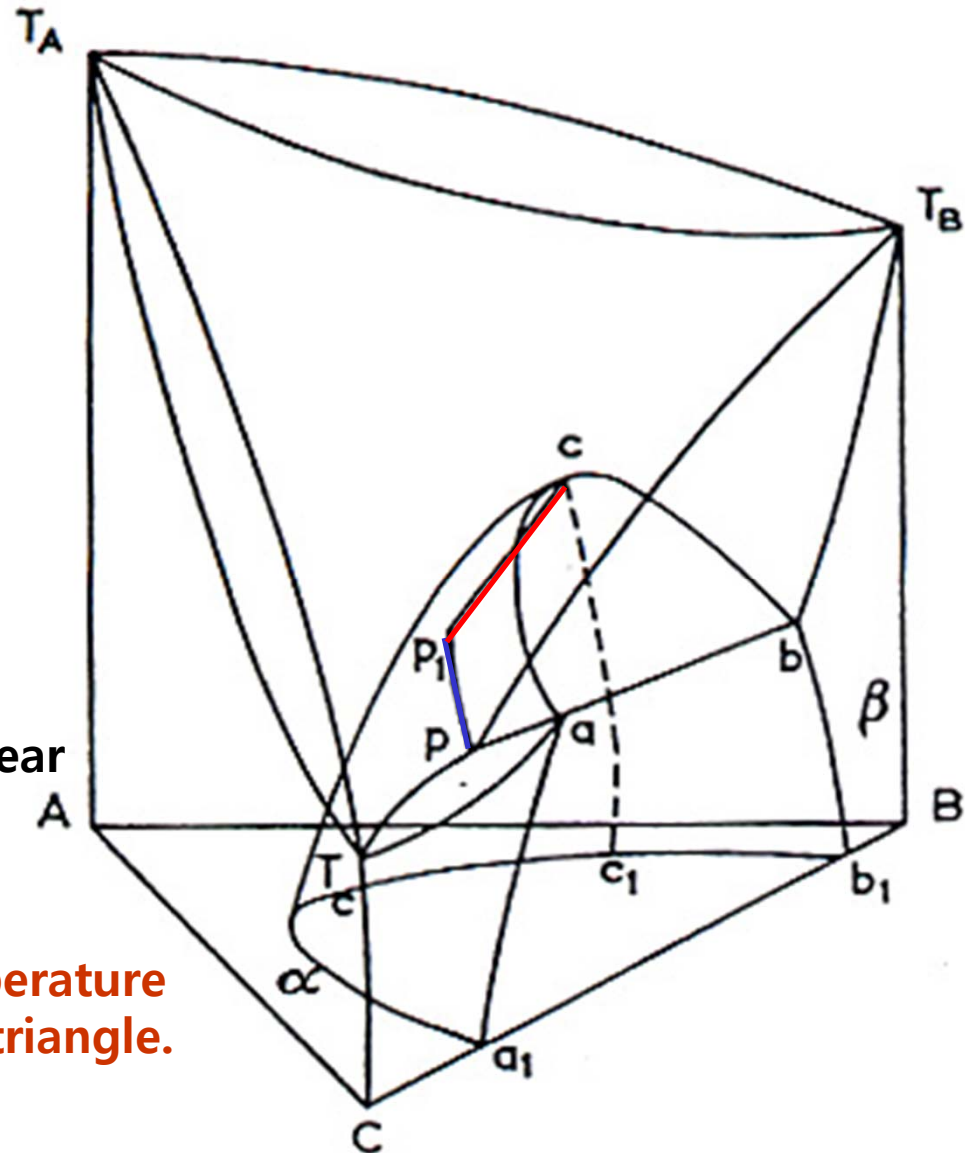
- A peritectic solubility gap in one binary system



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

PP<sub>1</sub>: monovariant curve for liquid

Points P<sub>1</sub> and c lie at the same temperature and the line P<sub>1</sub>c is a degenerate tie triangle.

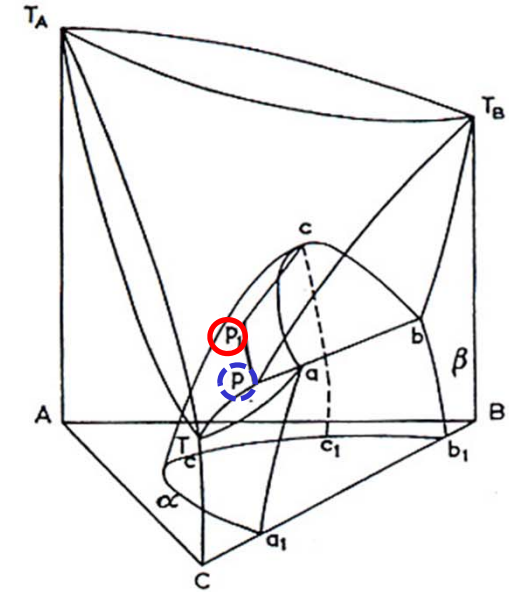


# 9.4. THREE-PHASE EQUILIBRIUM INVOLVING PERITECTIC REACTIONS

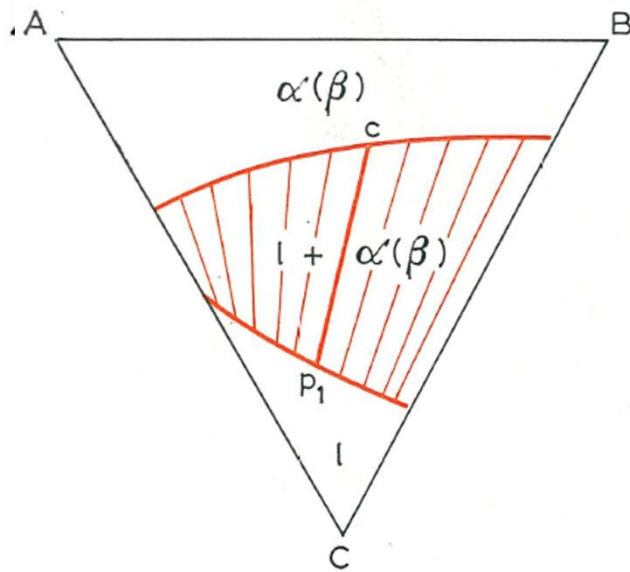
- A peritectic solubility gap in one binary system

$PP_1$ : monovariant curve for liquid

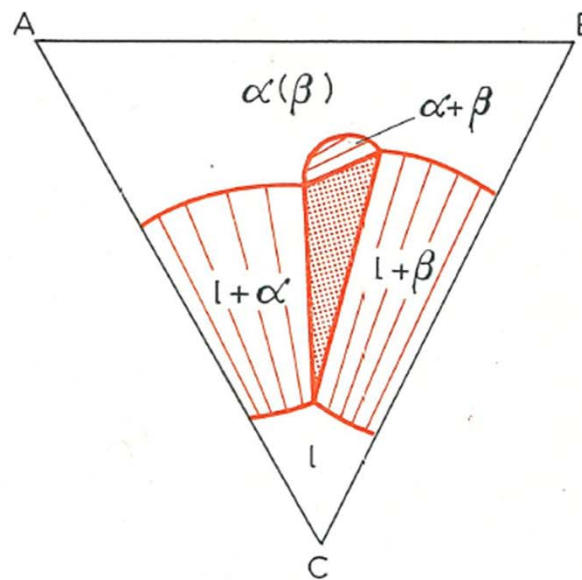
Points  $P_1$  and  $c$  lie at the same temperature and the line  $P_1c$  is a degenerate tie triangle.



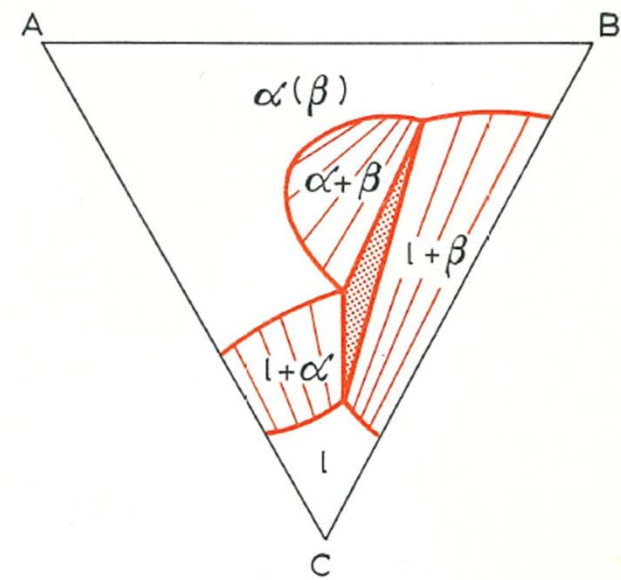
isothermal section



$$T = P_1$$



$$P_1 > T_1 > P$$



$$T_1 > T_2 > P$$



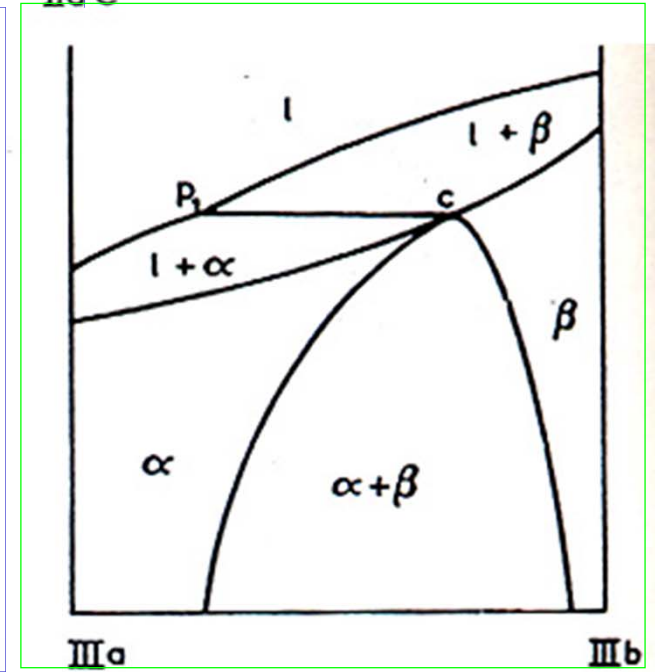
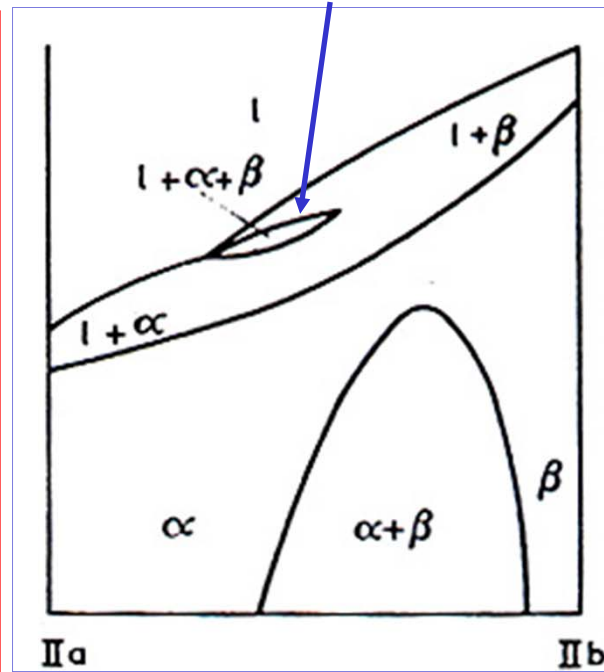
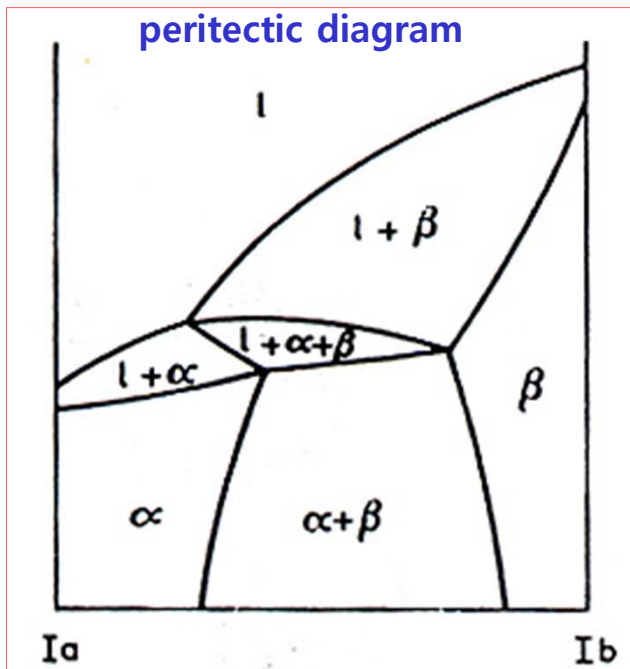
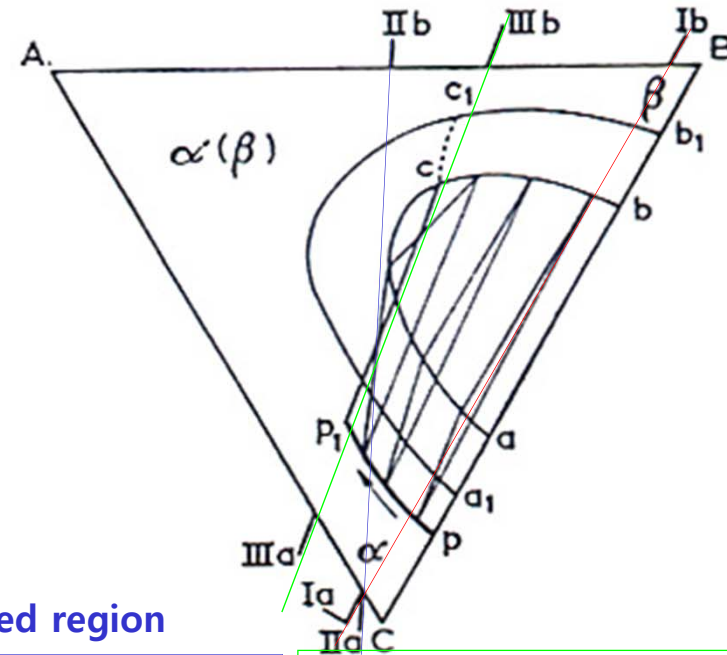
## 9.4. THREE-PHASE EQUILIBRIUM INVOLVING PERITECTIC REACTIONS

- A peritectic solubility gap in one binary system

<vertical section>

Similar to the binary peritectic diagram

loop shaped region



## 9.4. THREE-PHASE EQUILIBRIUM INVOLVING PERITECTIC REACTIONS

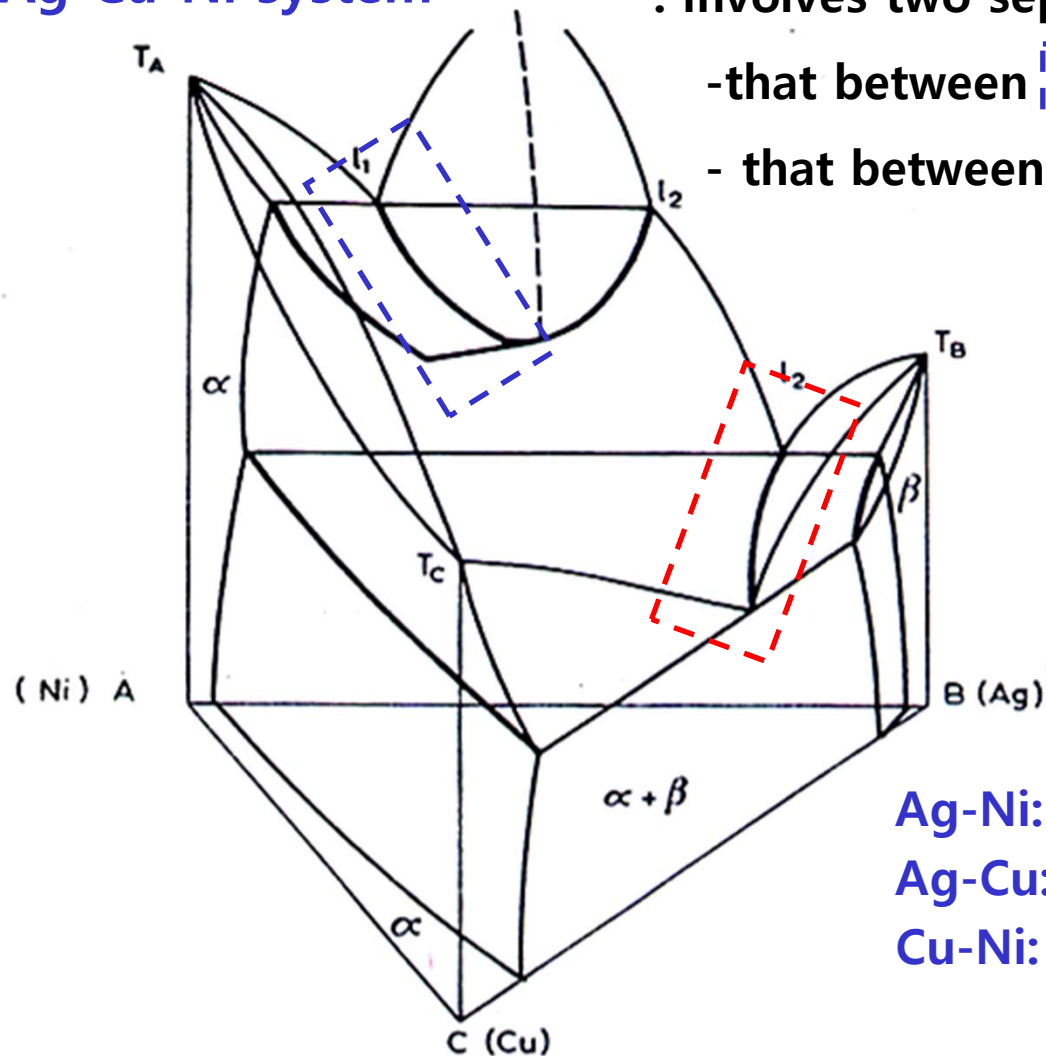
- Binary Monotectic, syntectic and metatectic reactions in combination with each other as well as with binary eutectic and peritectic reactions.

- **Ag-Cu-Ni system**

: involves two separate three phase equilibria

- that between  $\alpha$ ,  $l_1$  and  $l_2$ , and

- that between  $\alpha$ ,  $\beta$  and  $l_2$



Ag-Ni: monotectic

Ag-Cu: eutectic

Cu-Ni: continuous series of solid soln



# Chapter 10. Ternary phase Diagrams

## Four-Phase Equilibrium

**a. THE TERNARY EUTECTIC EQUILIBRIUM ( $l = \alpha + \beta + \gamma$ )**

**b. THE QUASI-PERITECTIC EQUILIBRIUM ( $l + \alpha = \beta + \gamma$ )**

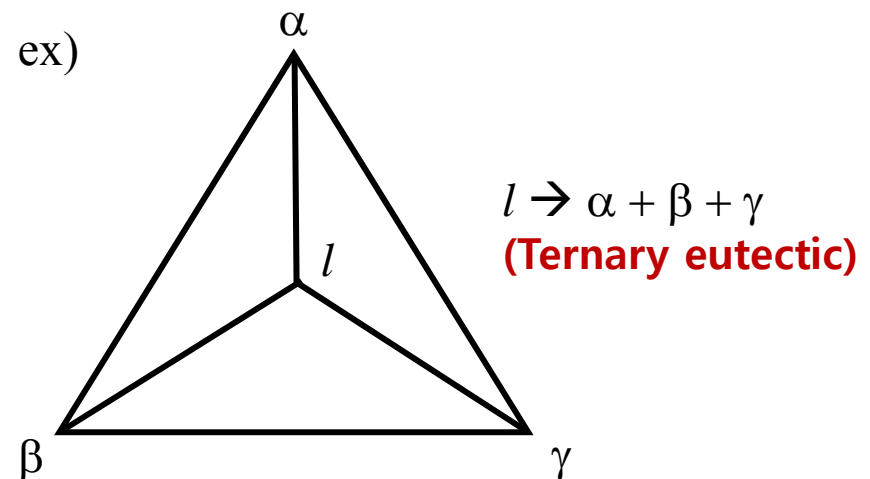
**c. THE TERNARY PERIECTIC EQUILIBRIUM ( $l + \alpha + \beta = \gamma$ )**

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

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

Now we consider of four-phase equilibrium

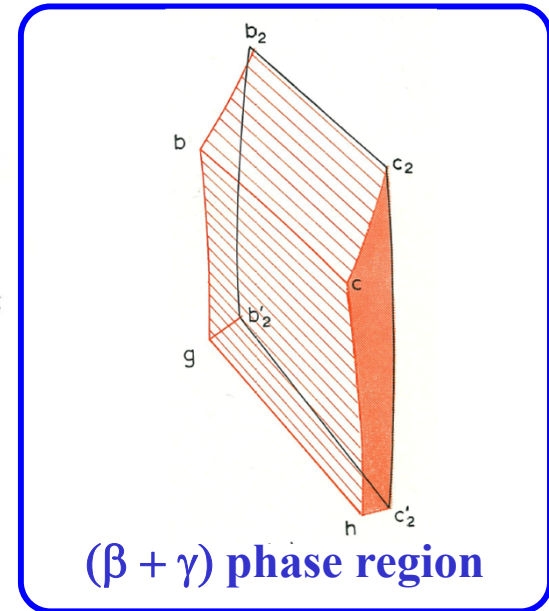
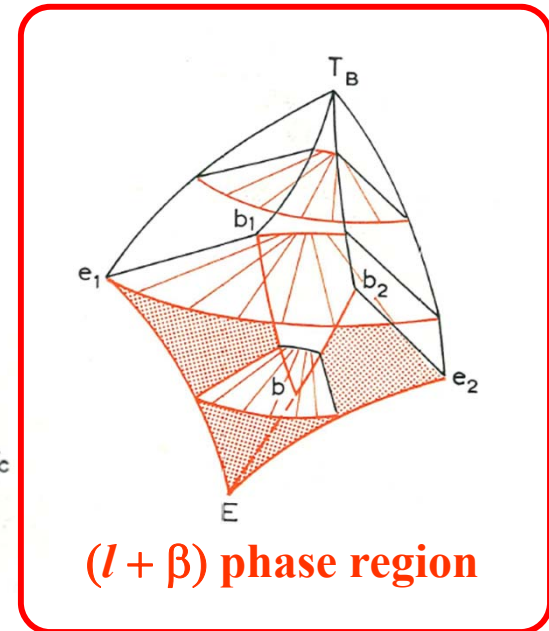
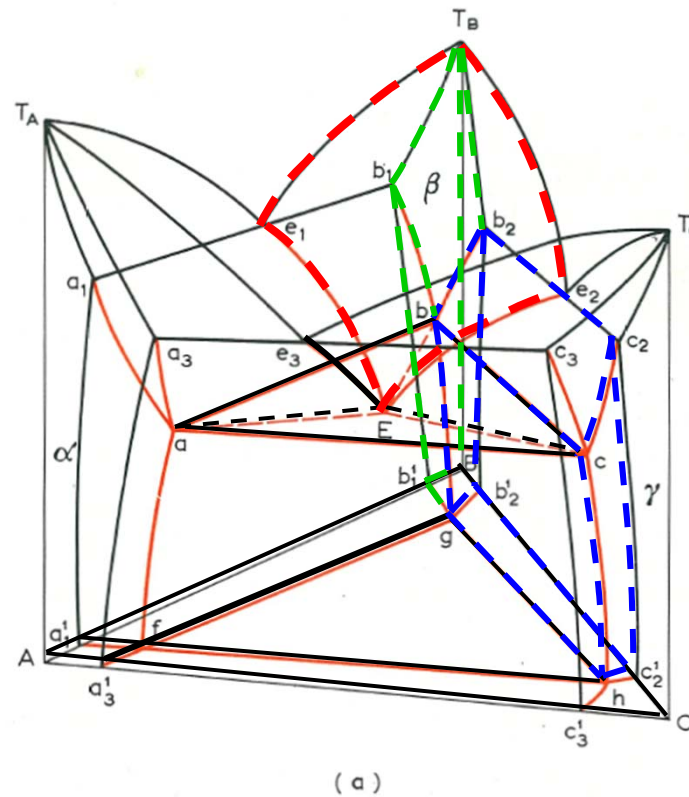
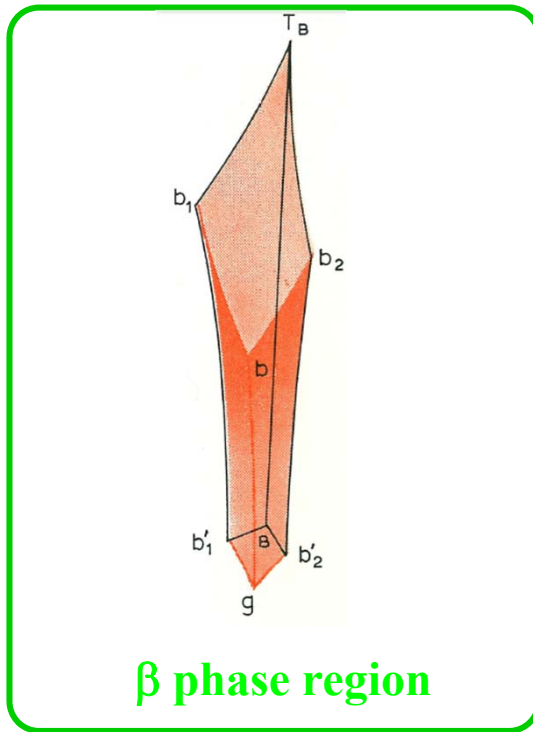
- max  $N$  of phase
- $f = 0$  : composition of four phases at temp.  $\rightarrow$  fixed
- isothermal four phase regions



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

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

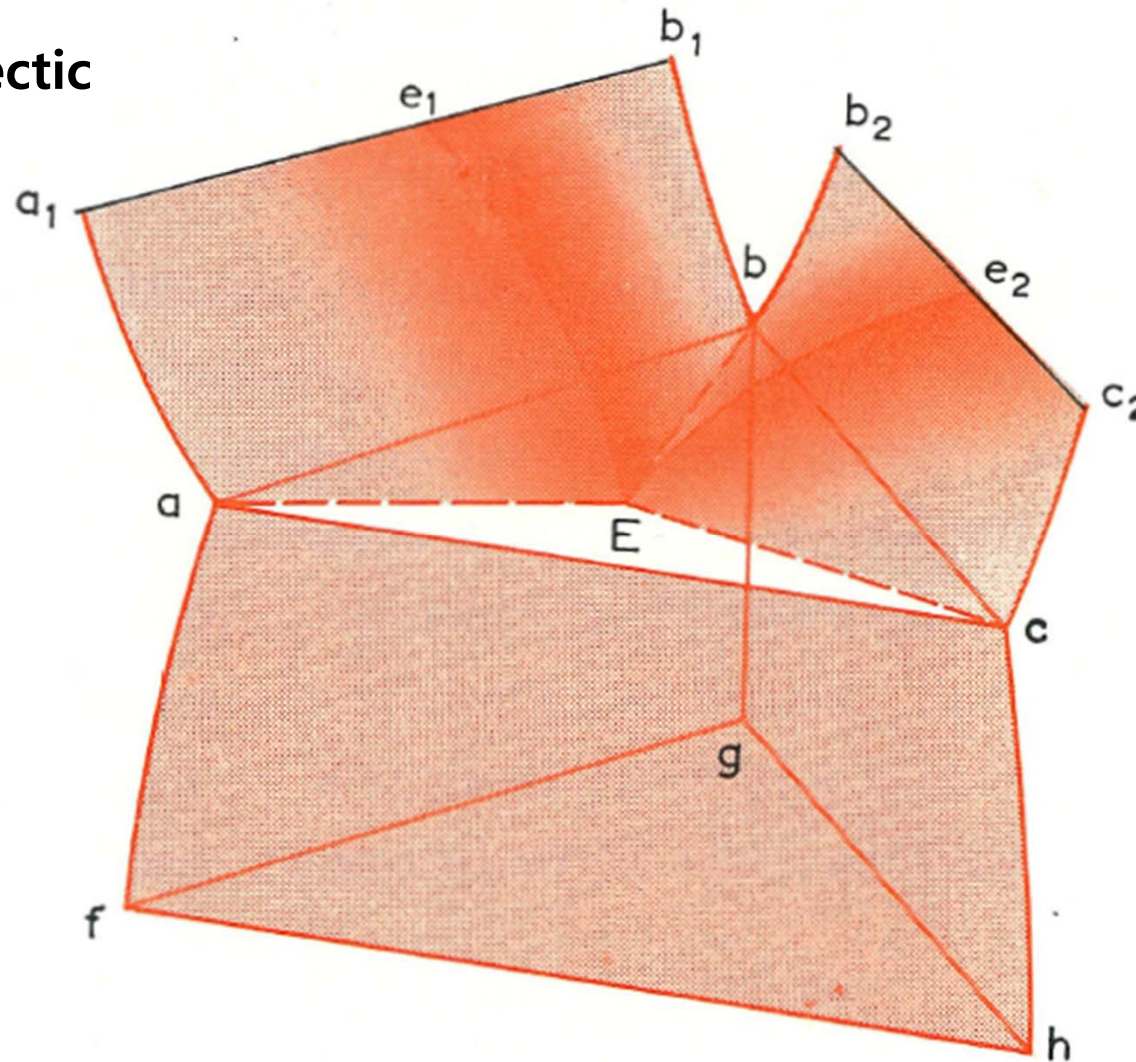
## Ternary eutectic



$$T_A > T_B > T_C > e_1 > e_3 > e_2 > E$$

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

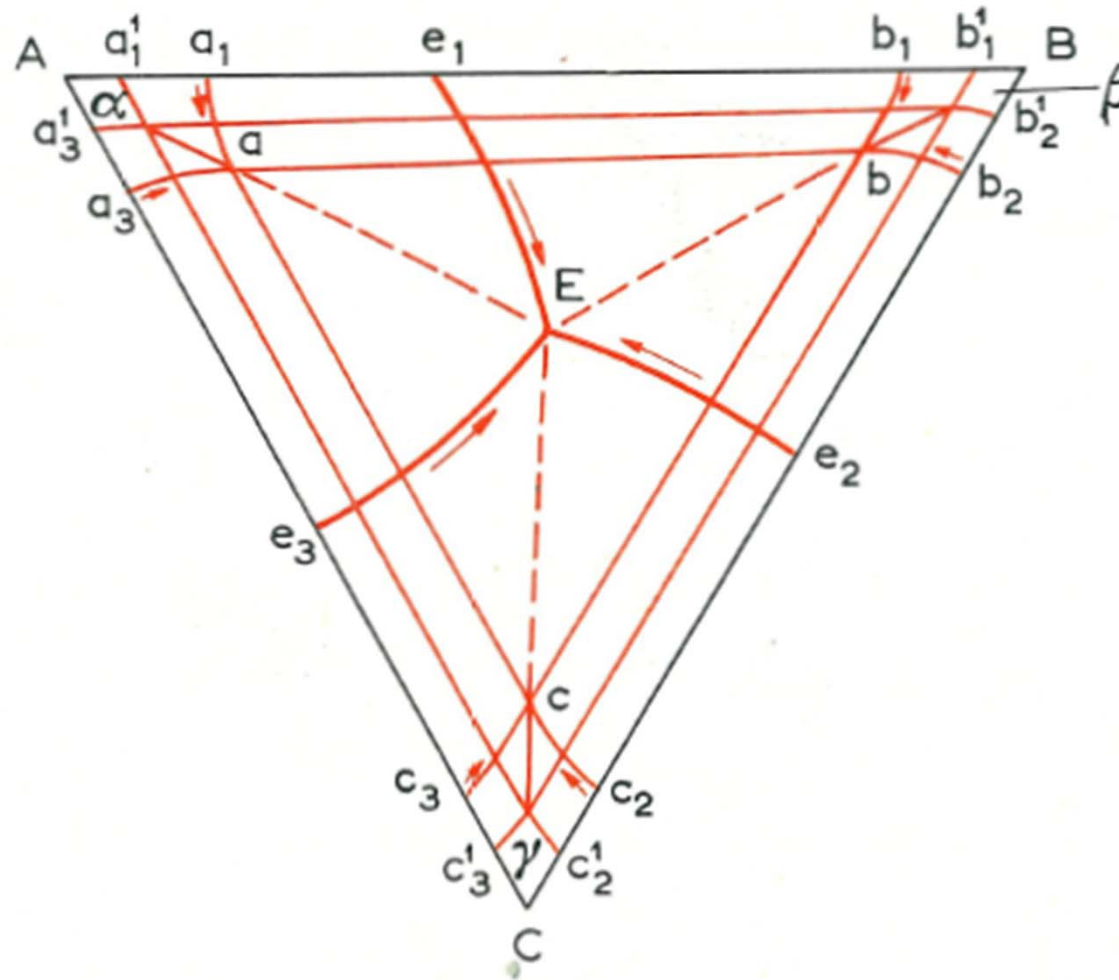
Ternary eutectic



The eutectic four-phase plane as the junction of four tie triangles

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

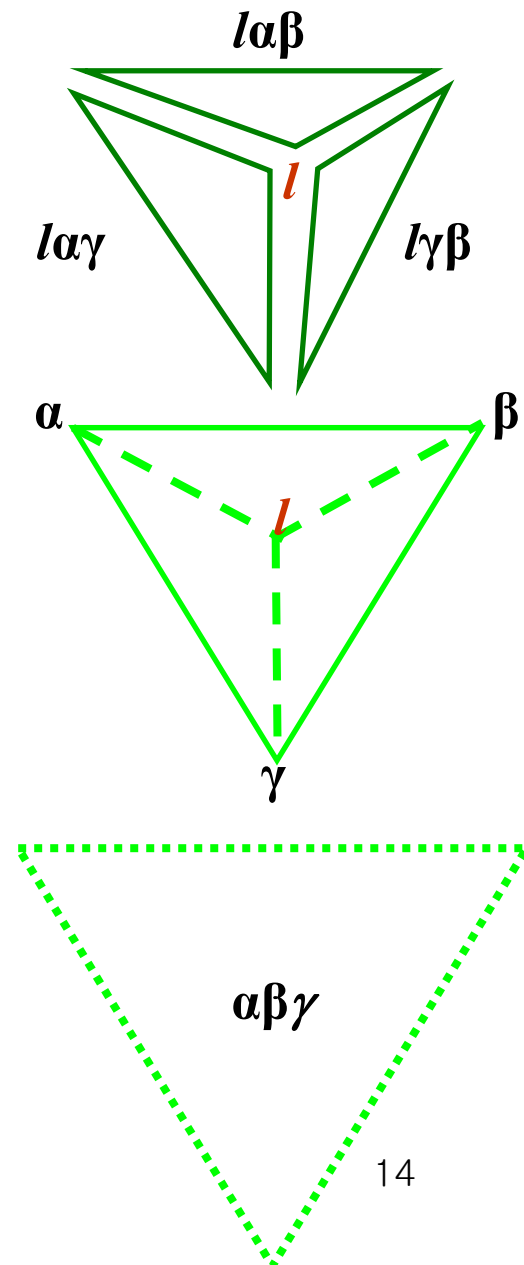
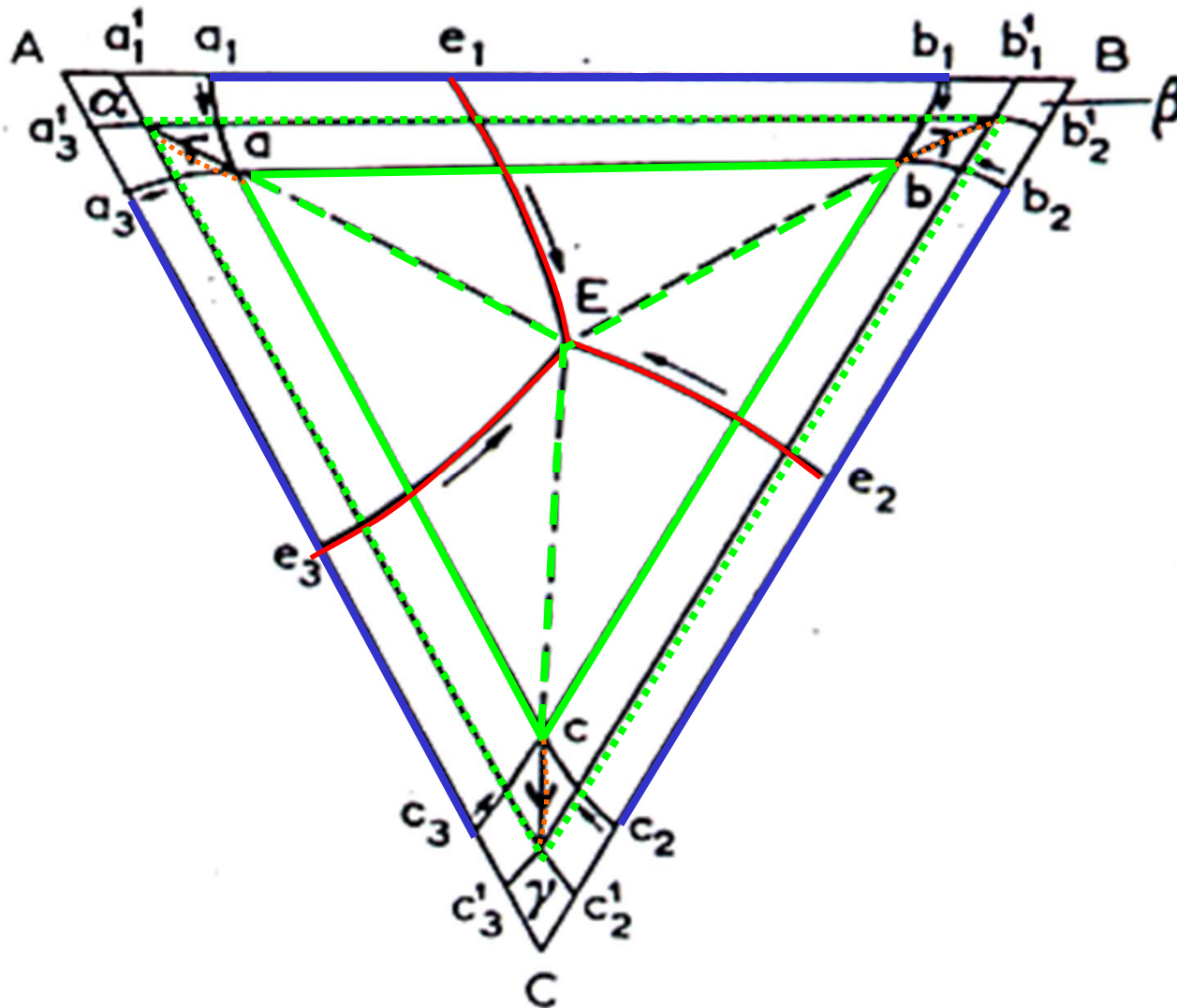
Ternary eutectic • Projection : solid solubility limit surface  
: monovariant liquidus curve



$$T_A > T_B > T_C > e_1 > e_3 > e_2 > E$$

# THE TERNARY EUTECTIC EQUILIBRIUM ( $l = \alpha + \beta + \gamma$ )

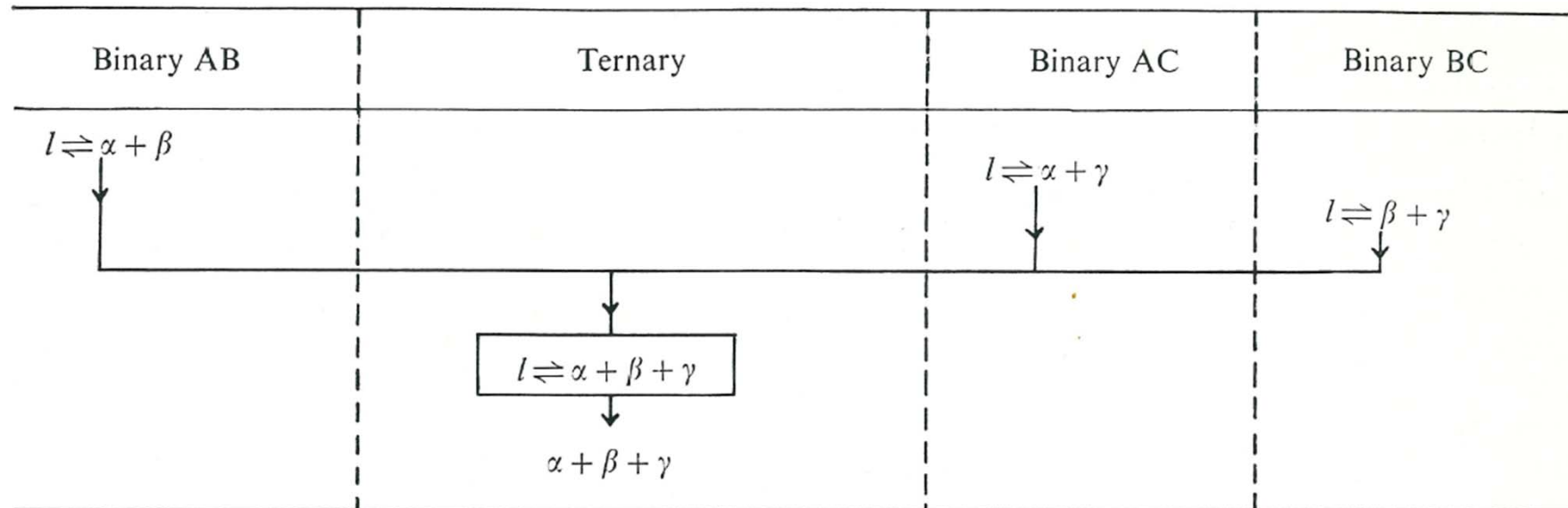
- **Projection** : solid solubility limit surface  
: monovariant liquidus curve



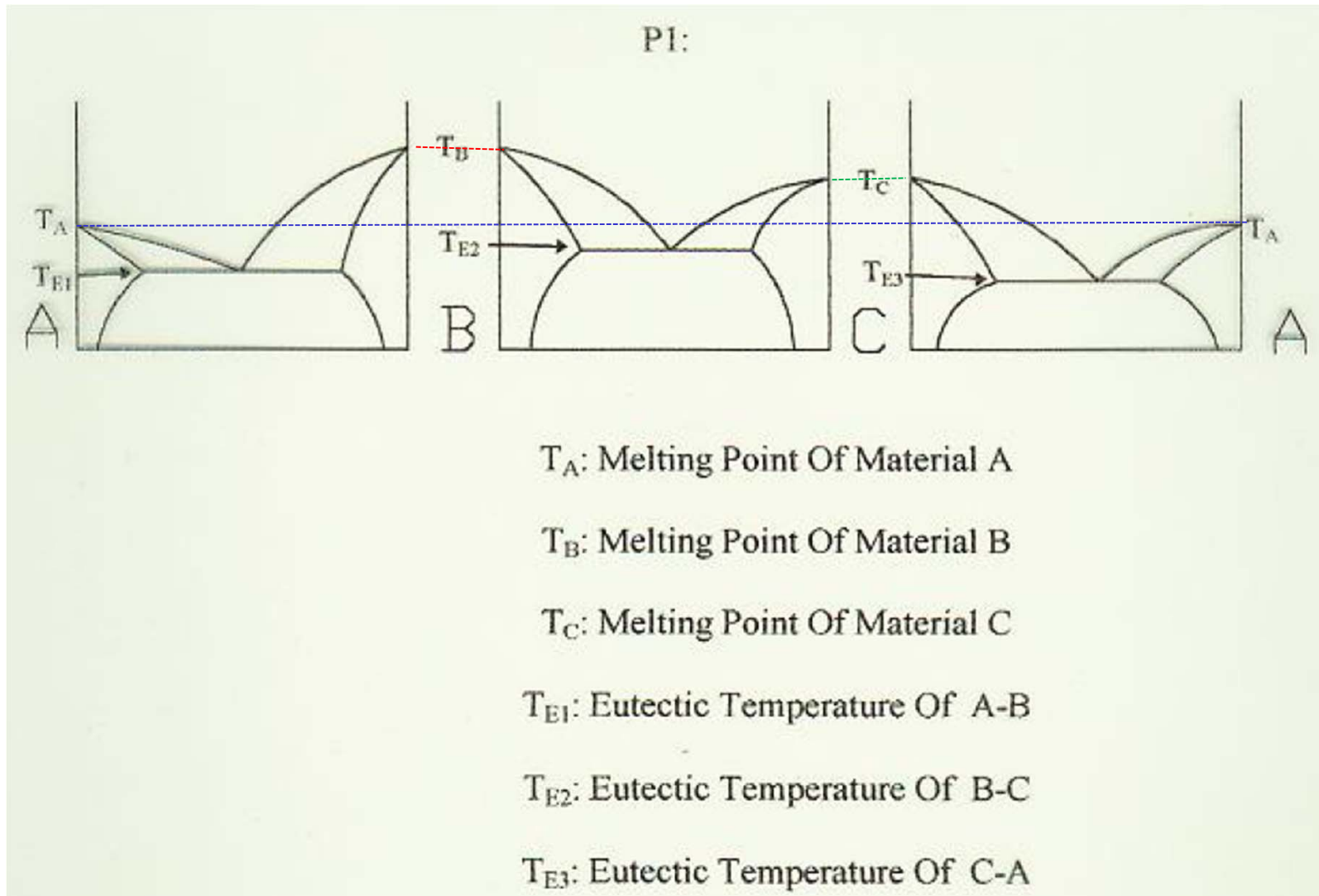


**Tabular representation of ternary equilibria:  
interlinks the binary and ternary reactions in tabular form**

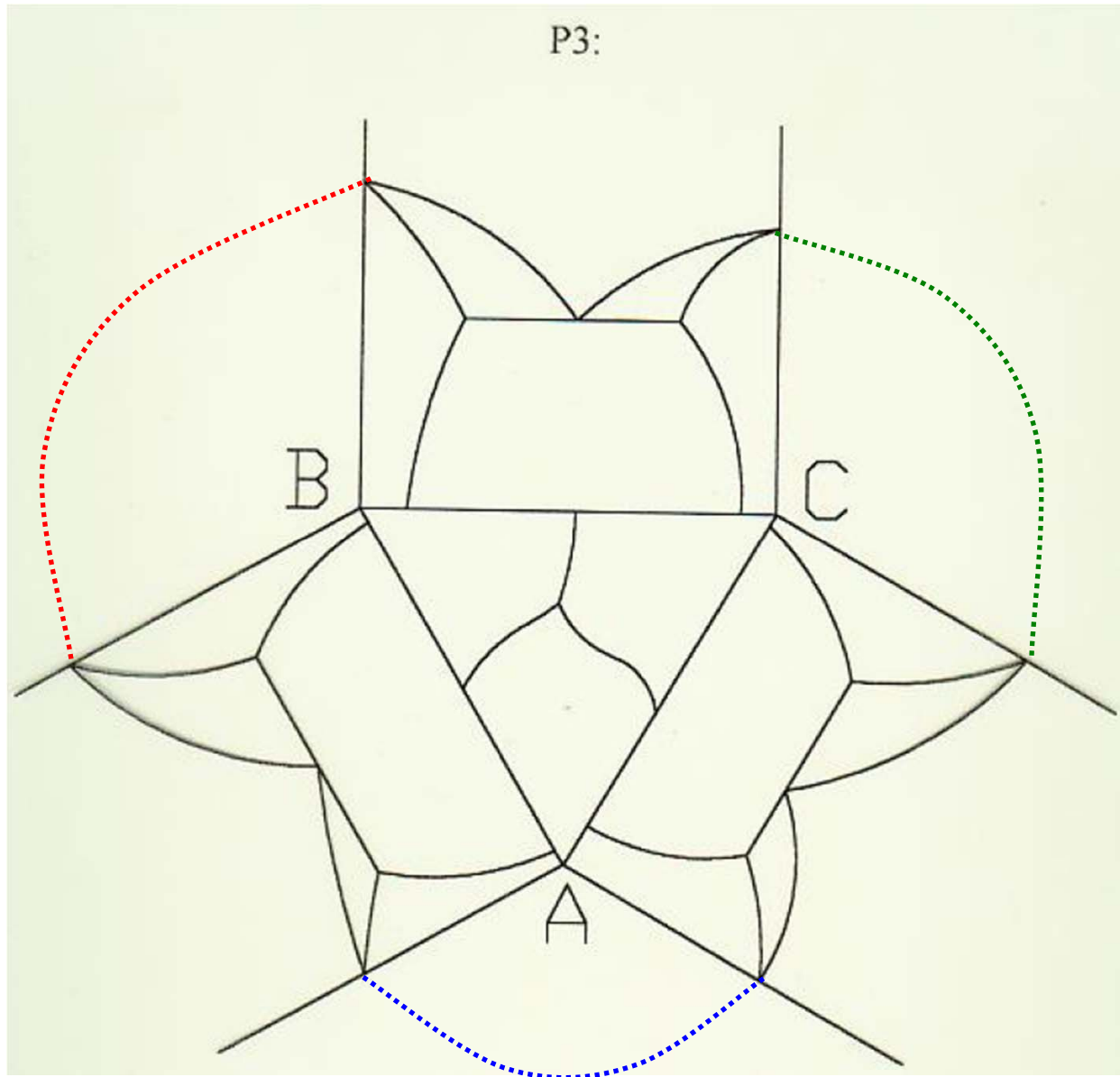
**EUTECTIC EQUILIBRIUM  $l \rightleftharpoons \alpha + \beta + \gamma$**



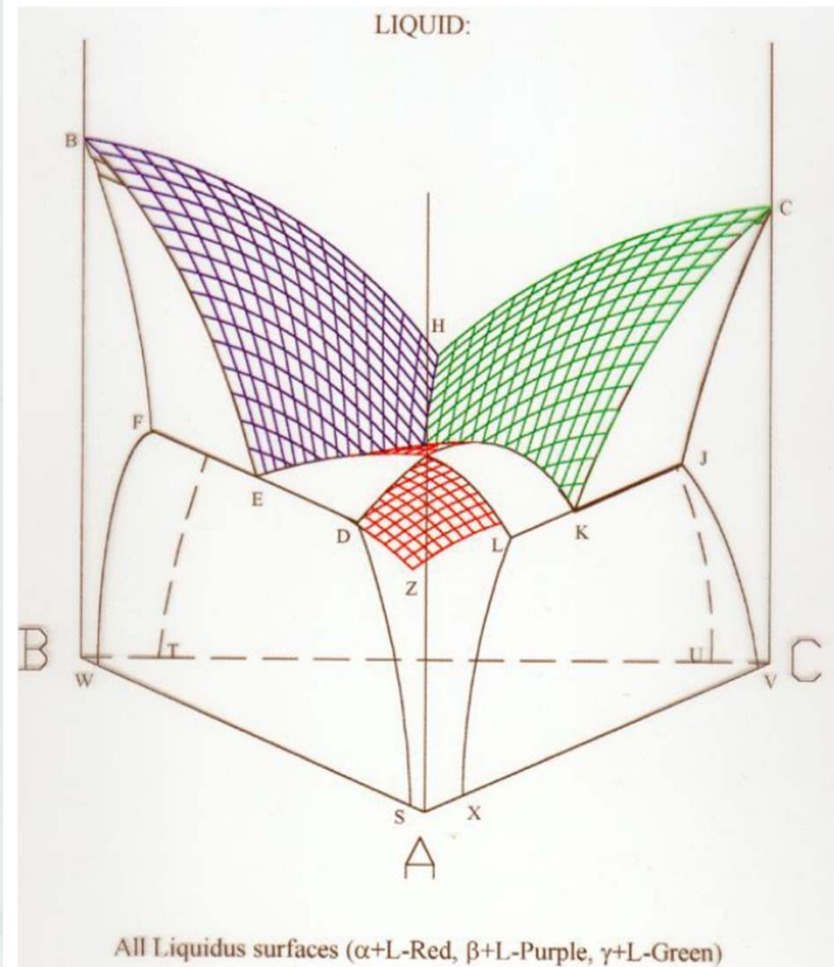
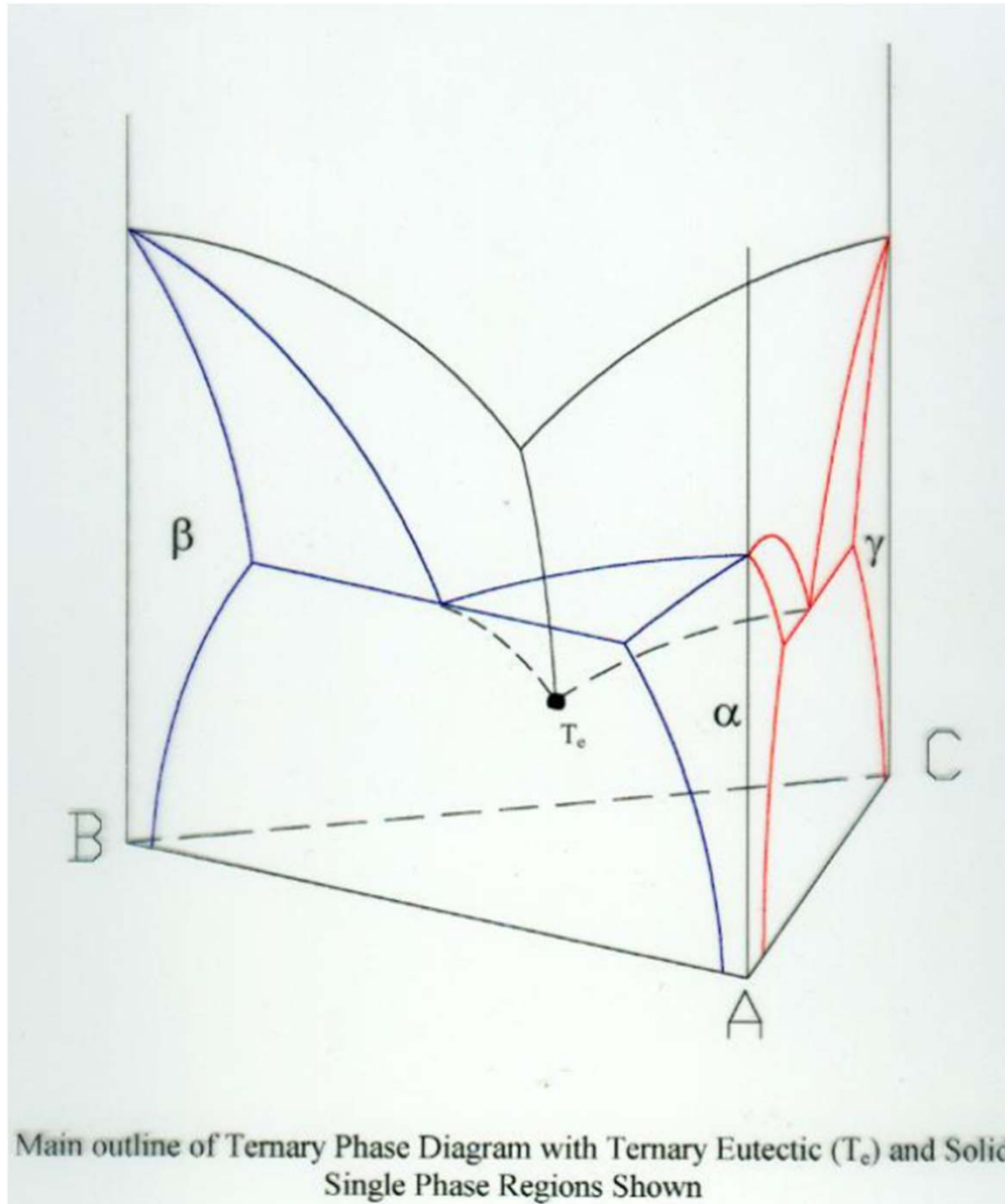
# Ternary Eutectic System (with Solid Solubility)



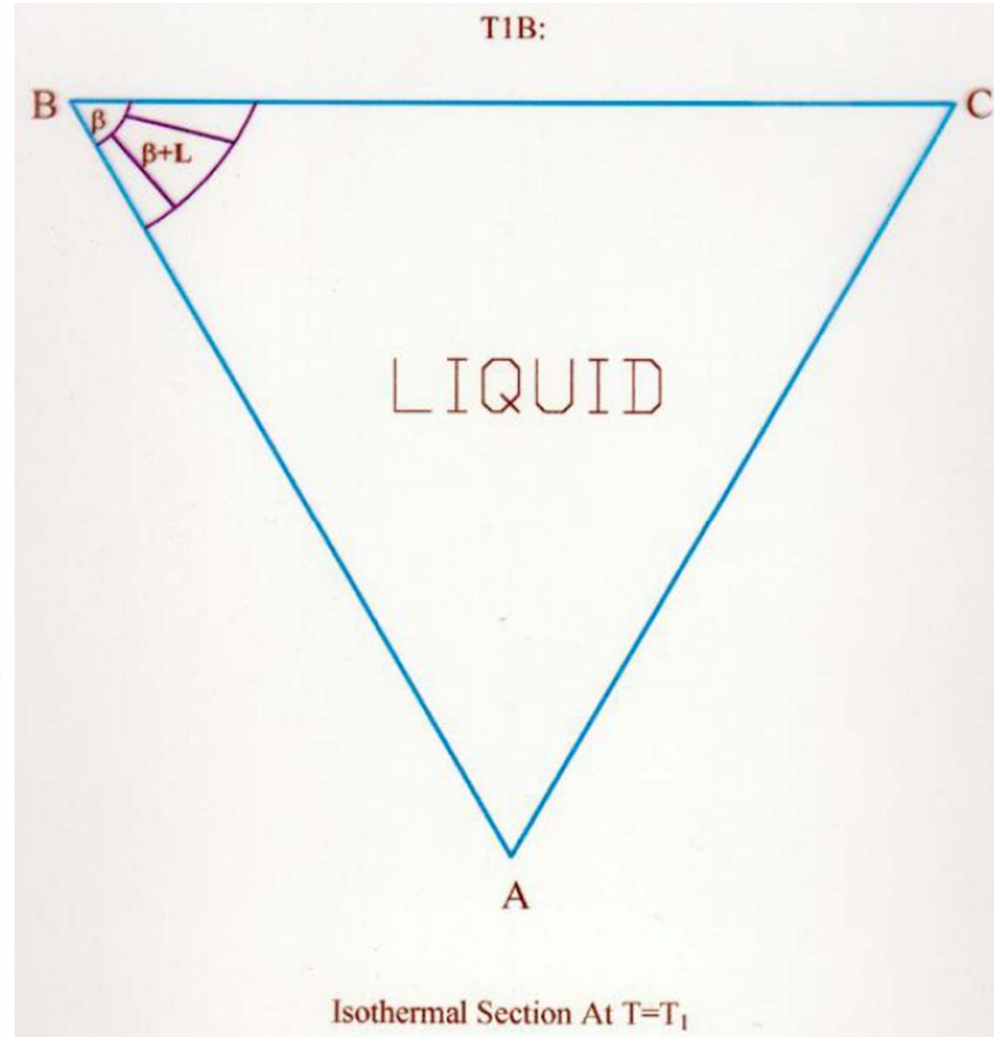
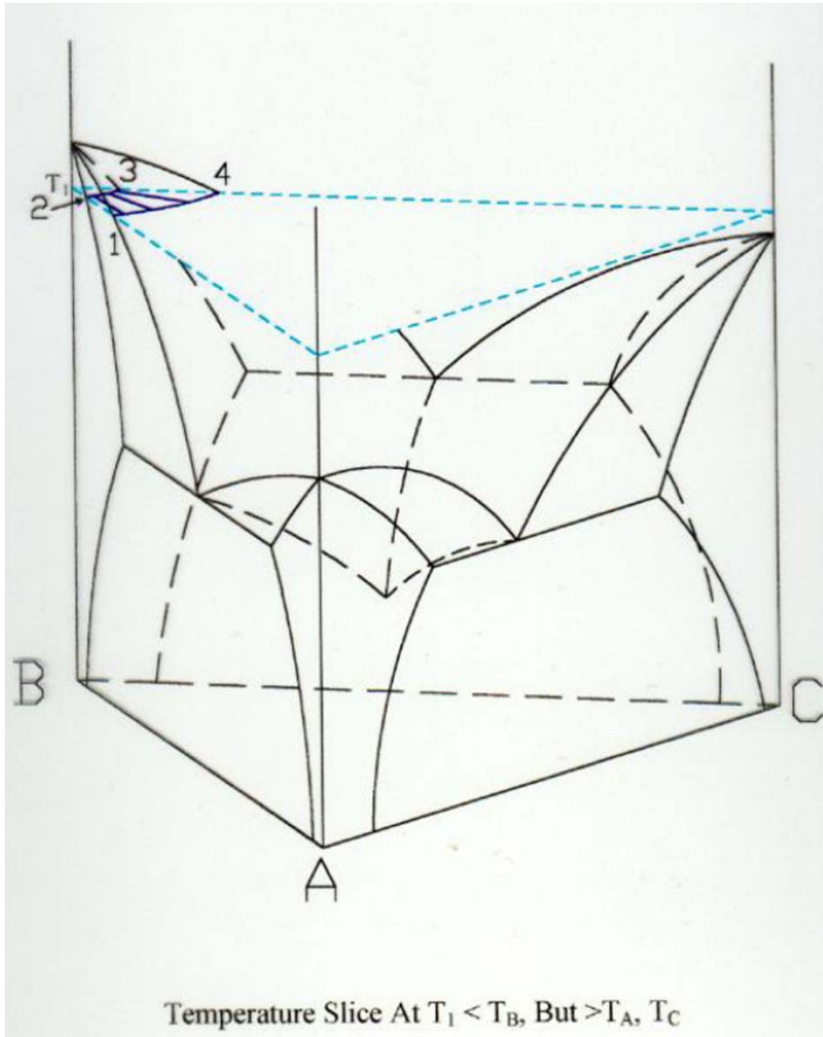
# Ternary Eutectic System (with Solid Solubility)



# Ternary Eutectic System (with Solid Solubility)

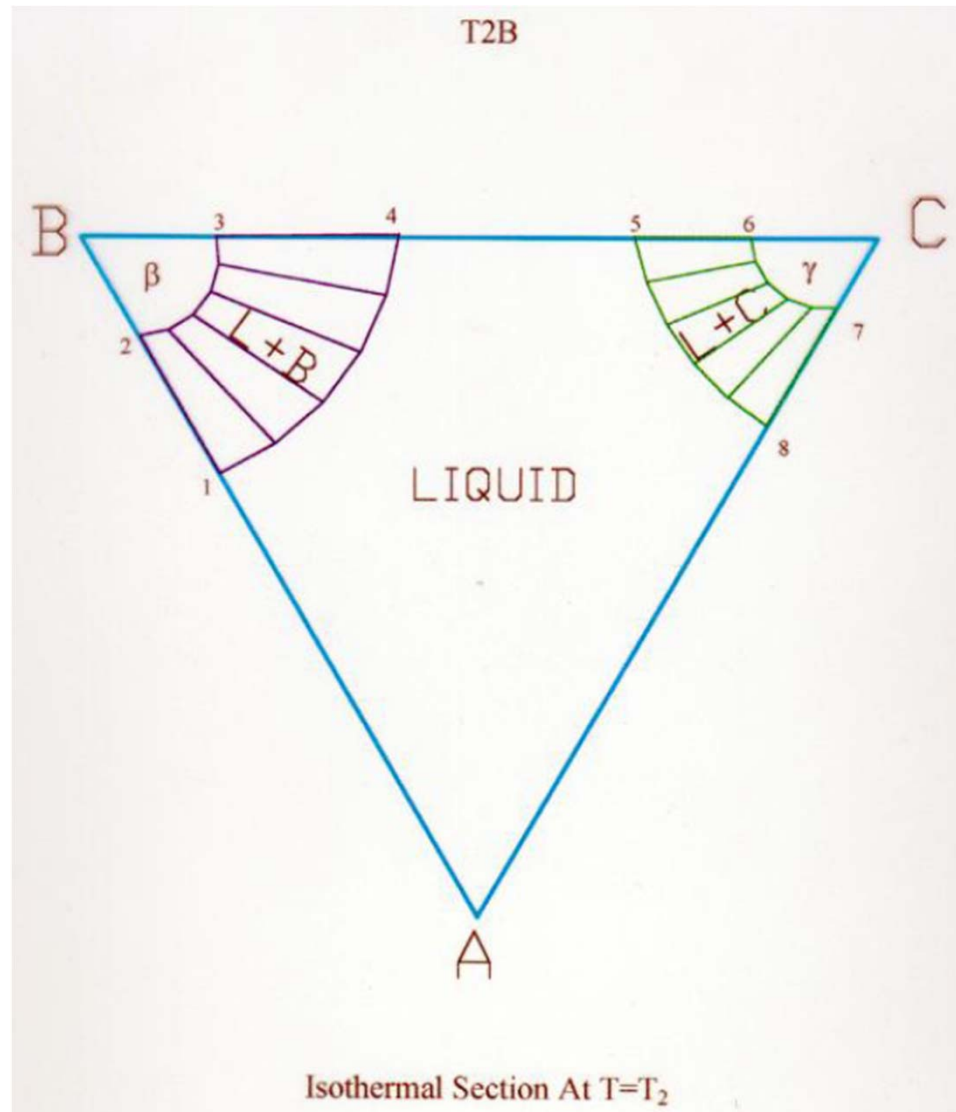
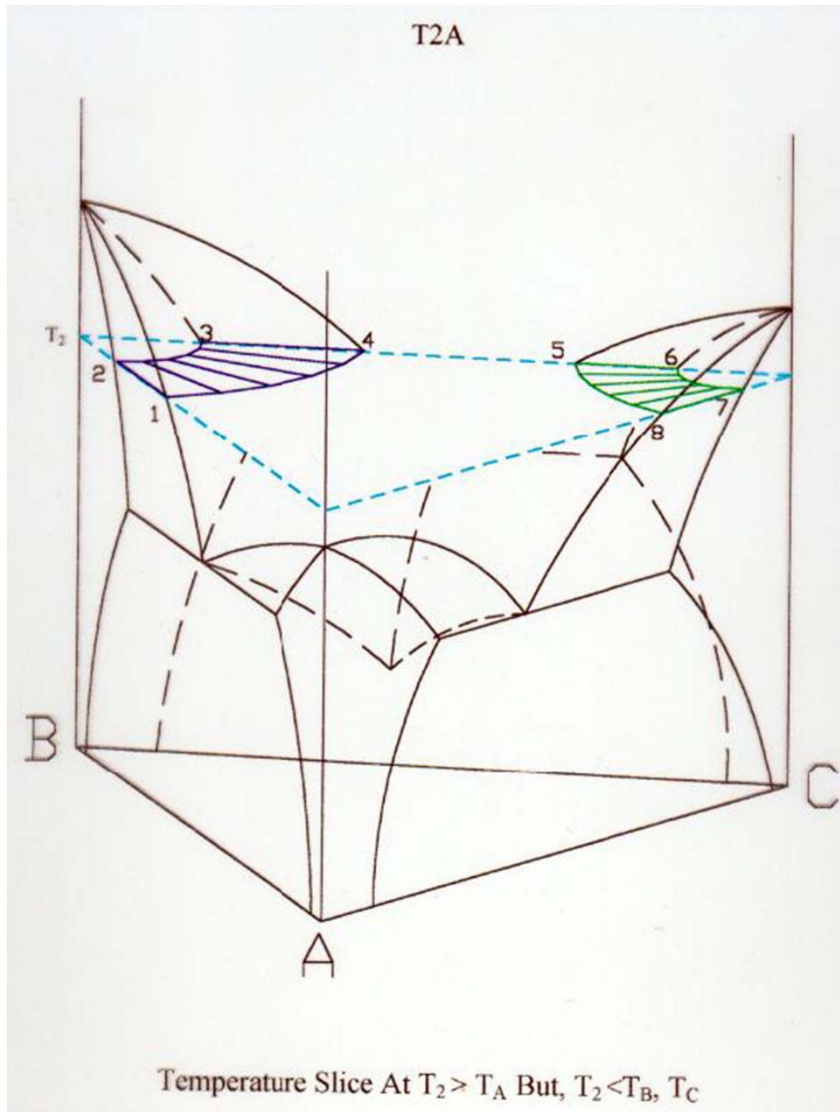


# Ternary Eutectic System (with Solid Solubility)



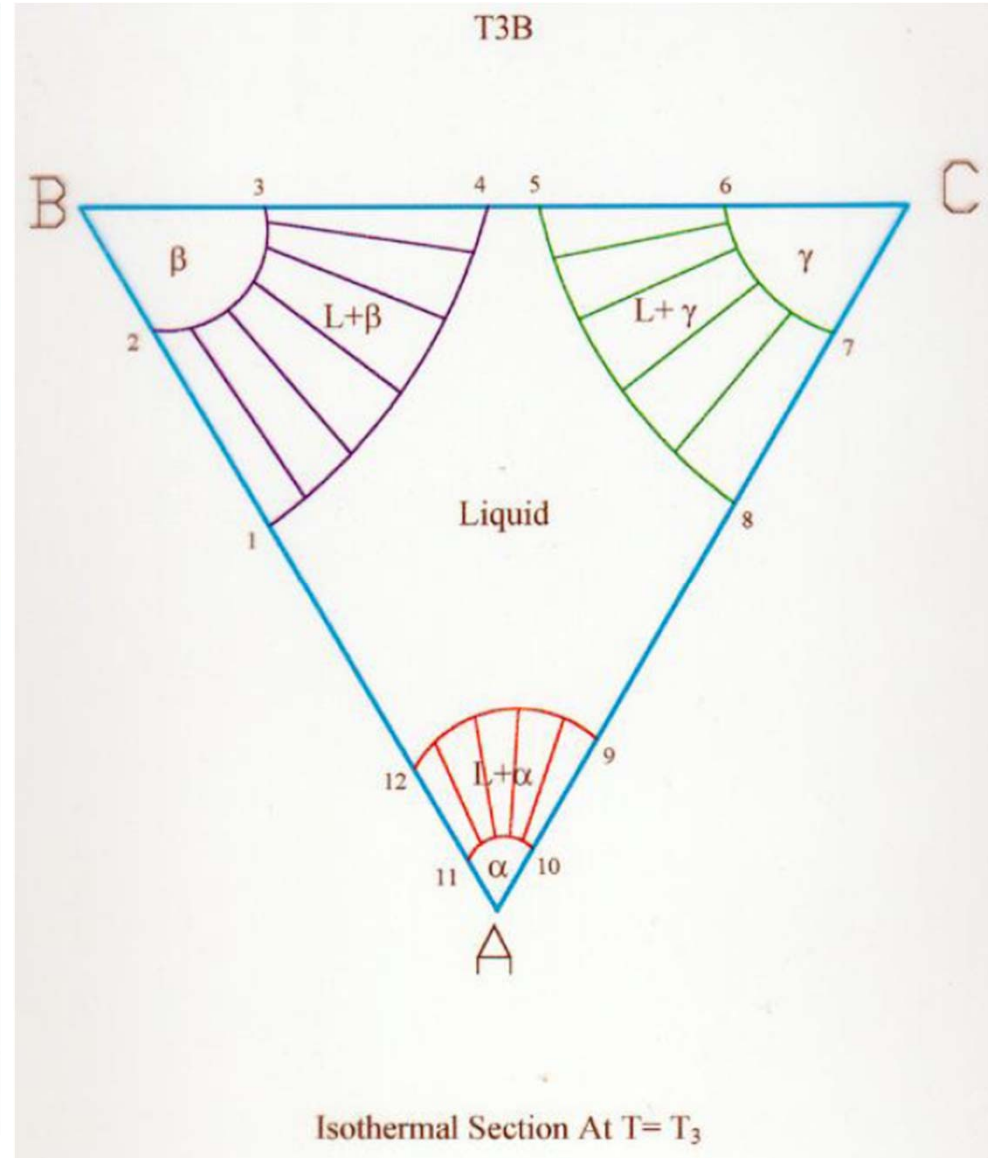
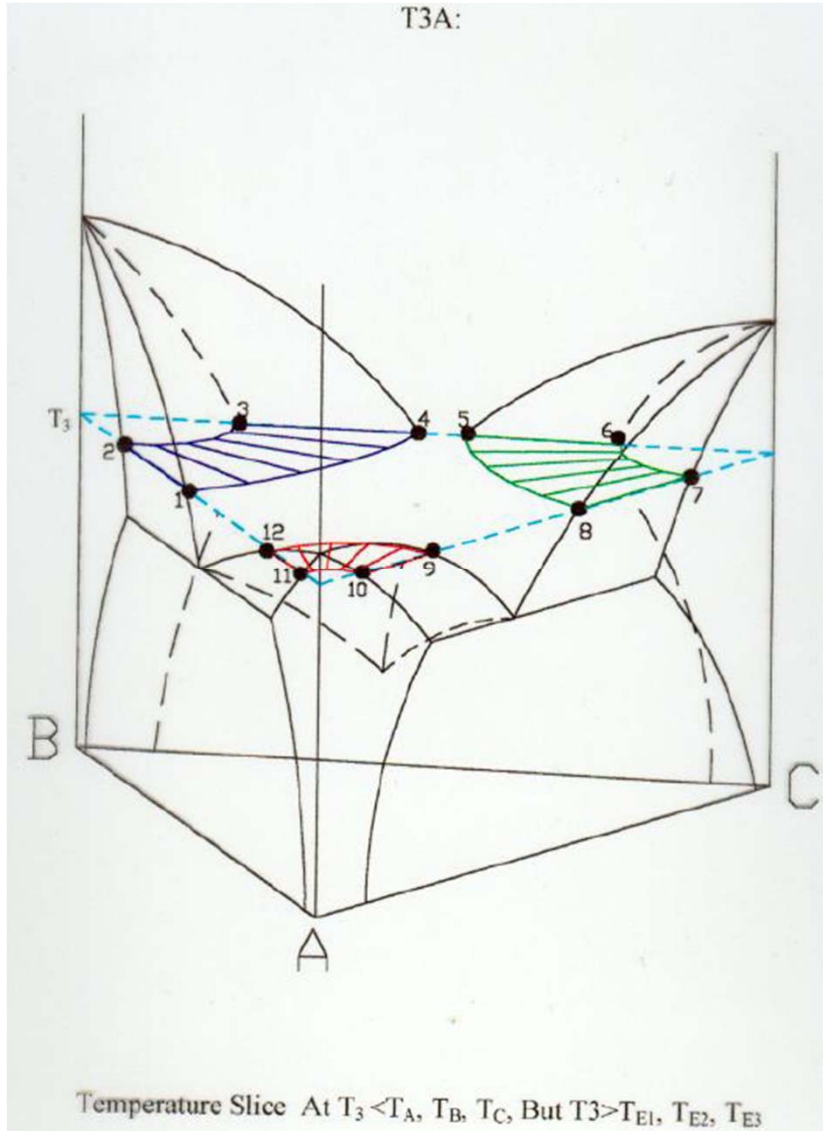


# Ternary Eutectic System (with Solid Solubility)

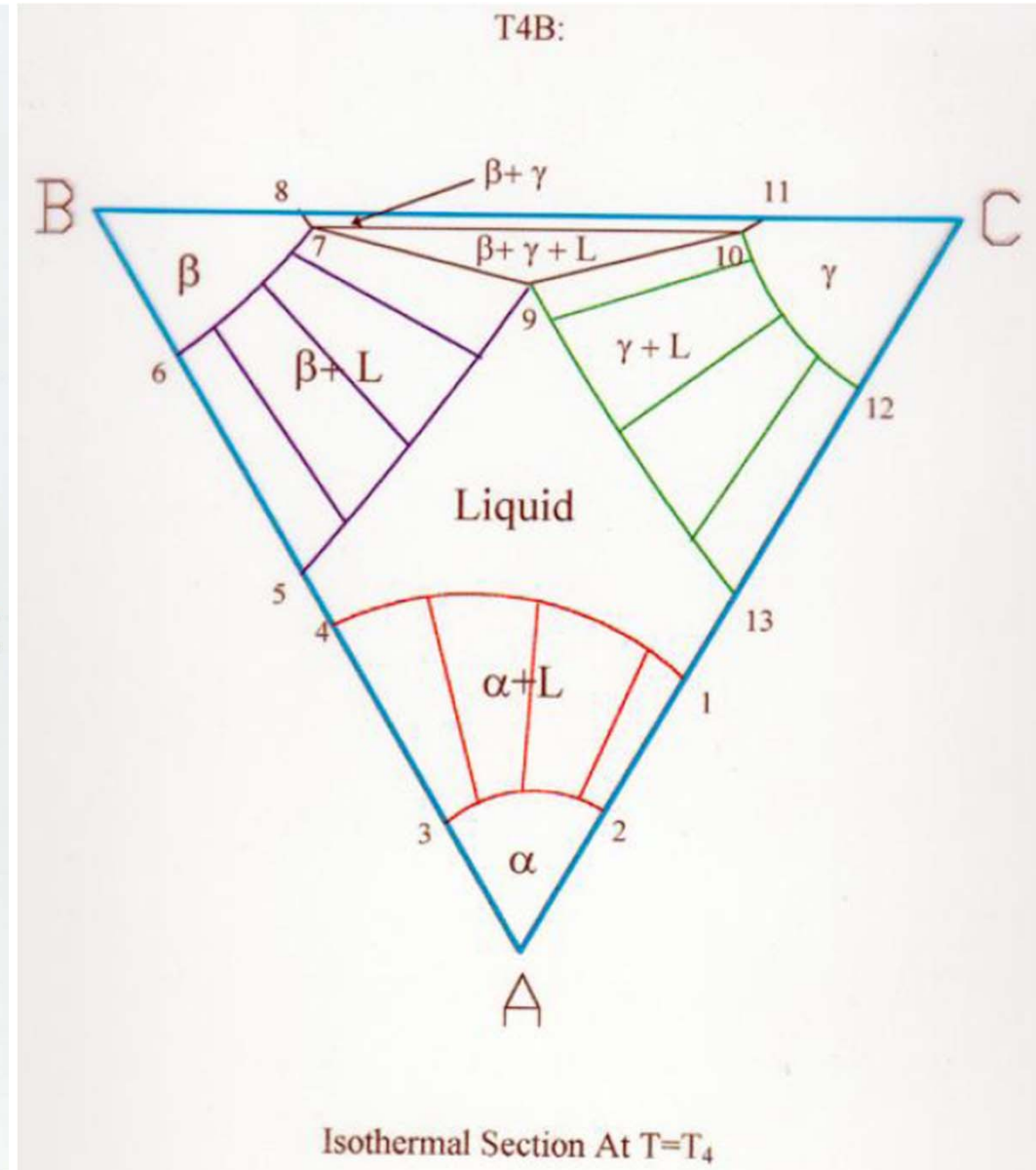
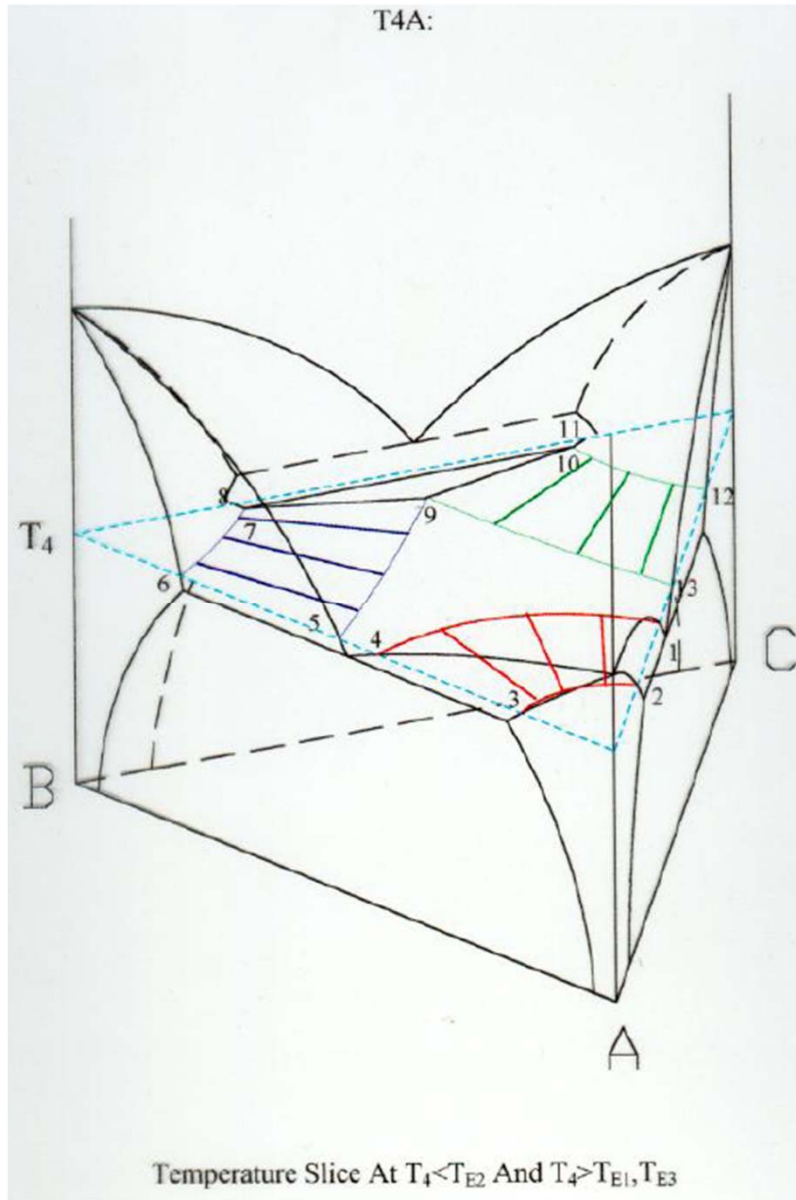




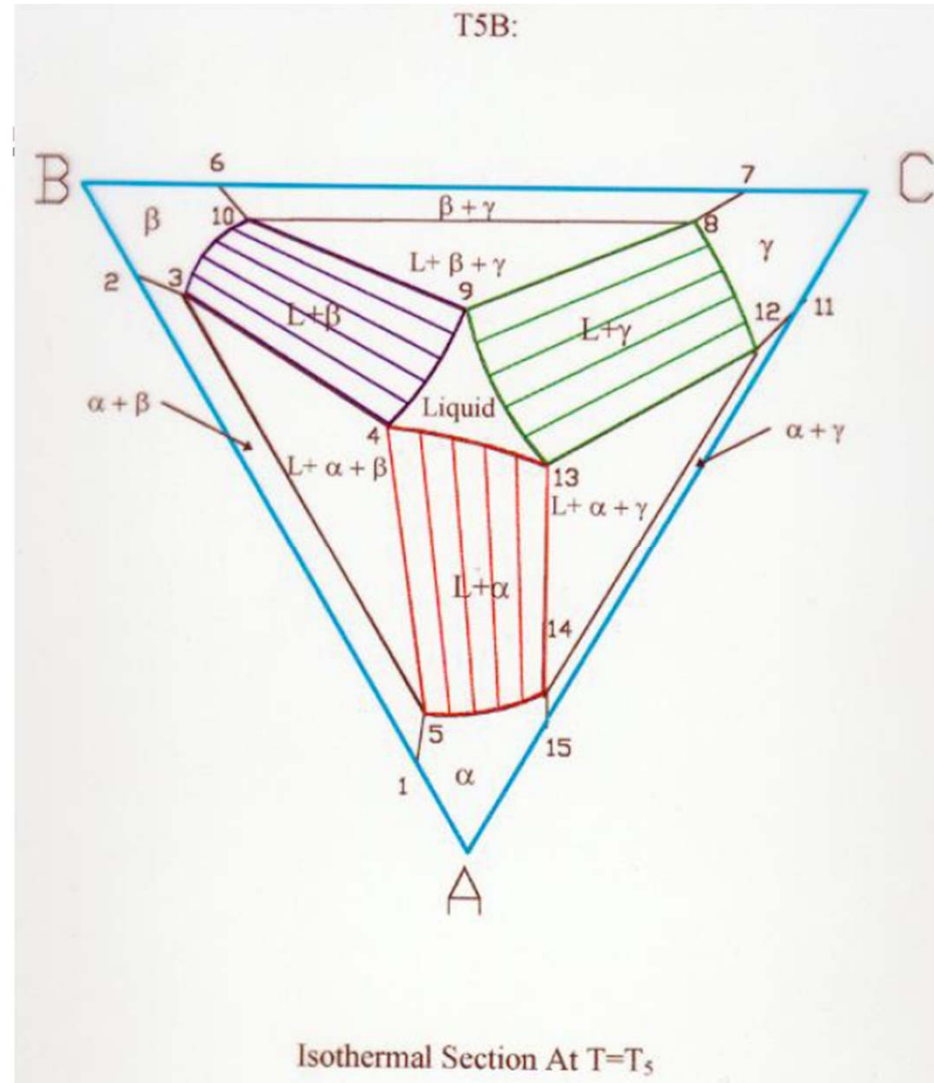
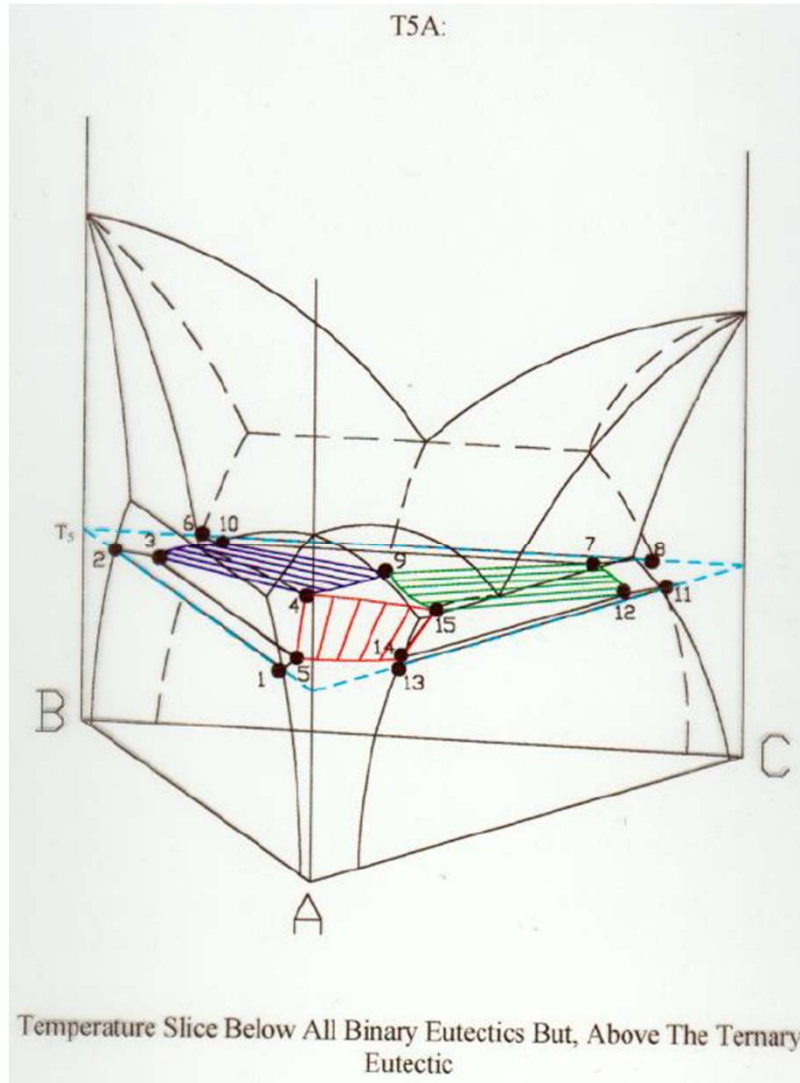
# Ternary Eutectic System (with Solid Solubility)



# Ternary Eutectic System (with Solid Solubility)

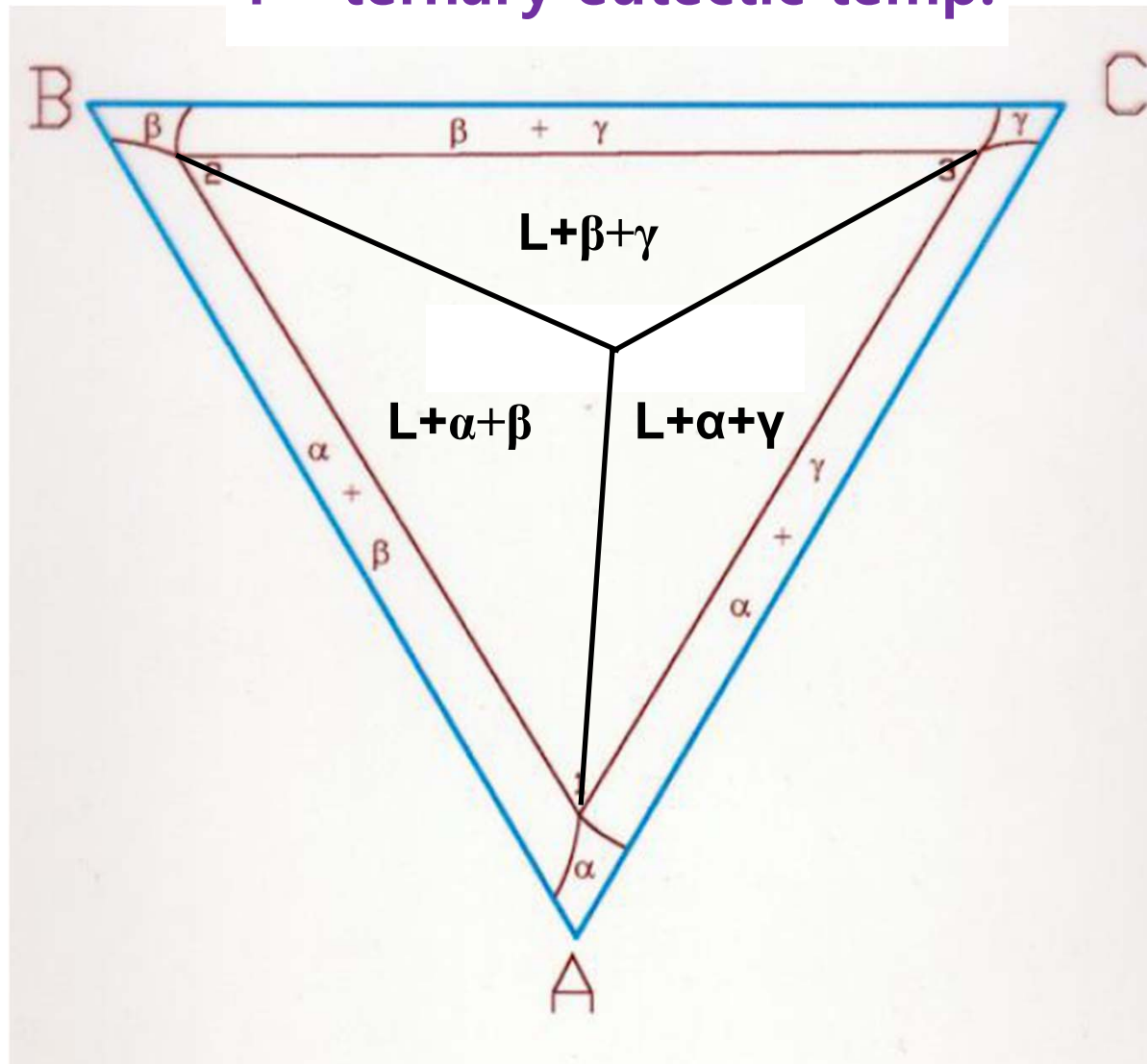


# Ternary Eutectic System (with Solid Solubility)



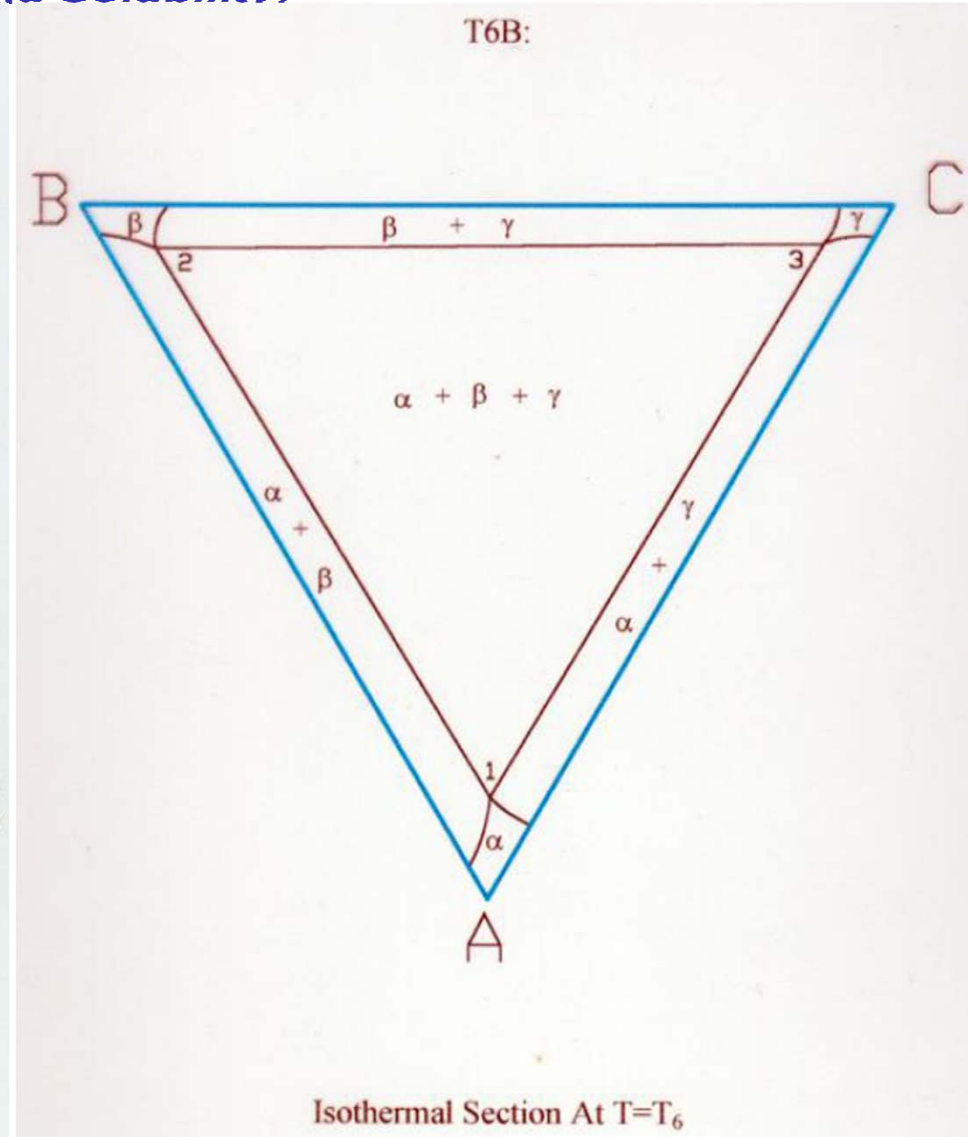
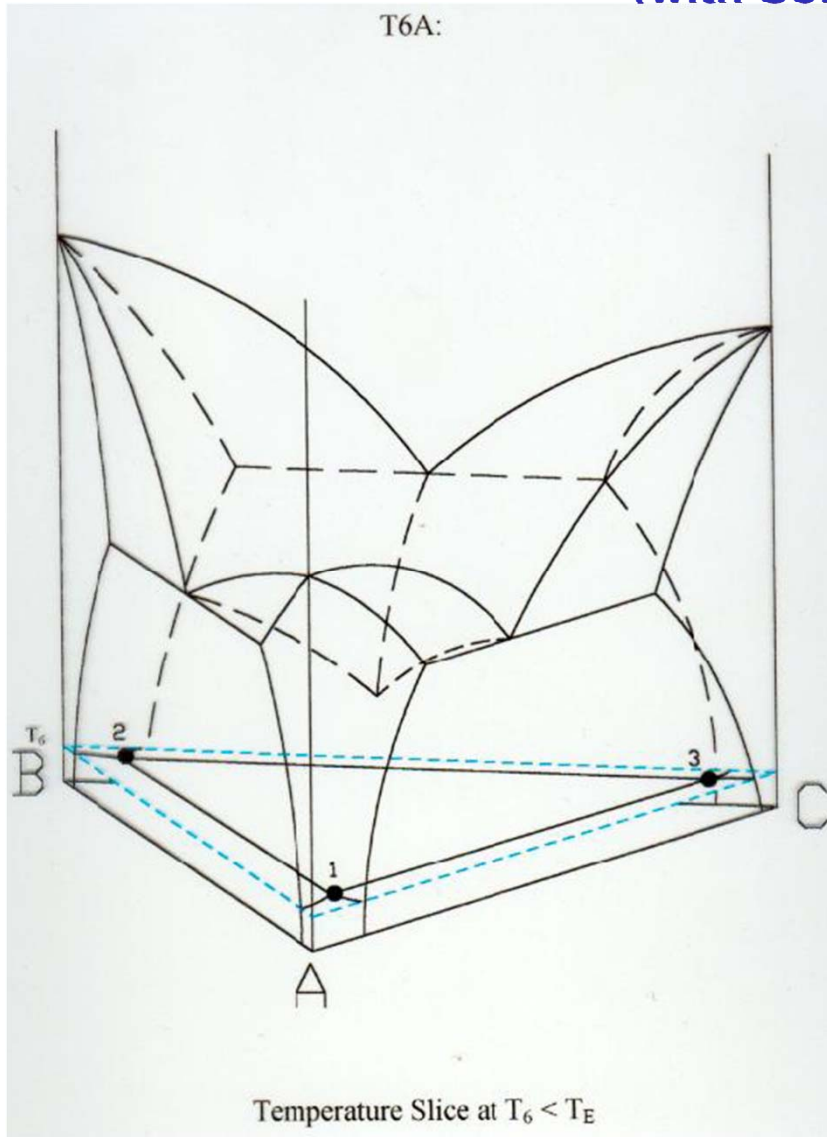
# Ternary Eutectic System (with Solid Solubility)

T = ternary eutectic temp.



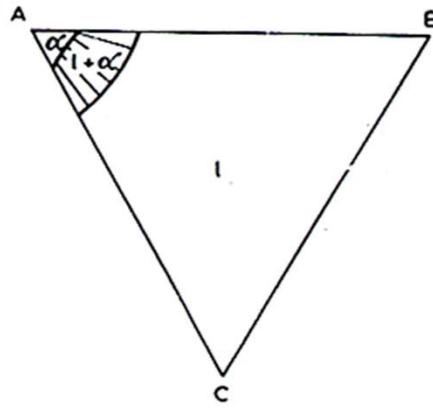


# Ternary Eutectic System (with Solid Solubility)

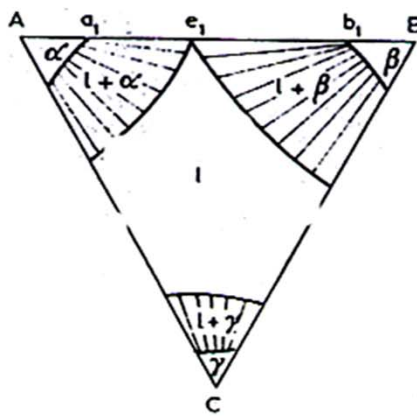


# 10.1. THE EUTECTIC EQUILIBRIUM ( $l = \alpha + \beta + \gamma$ )

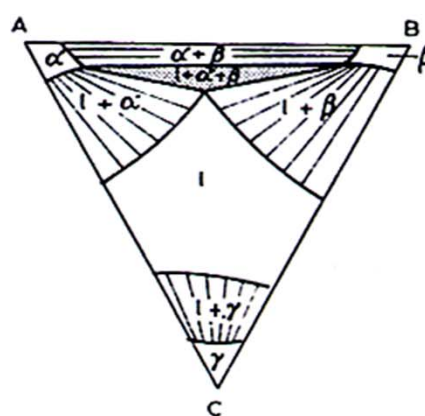
- Isothermal section ( $T_A > T > T_B$ )



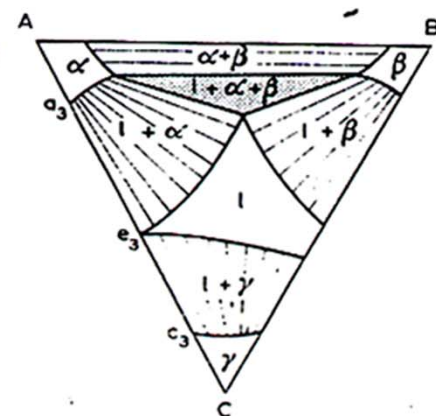
(a)  $T_A > T > T_B$



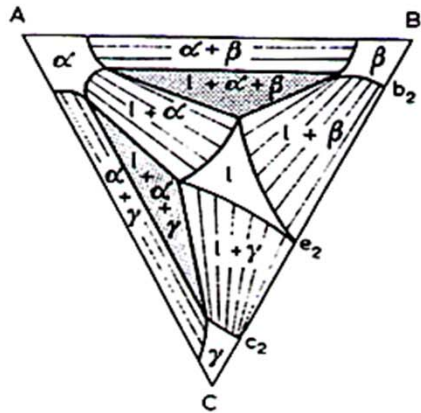
(b)  $T = e_1$



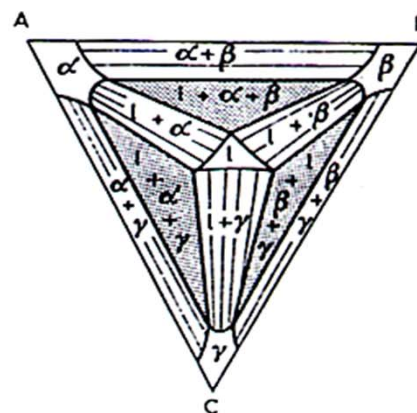
(c)  $e_1 > T > e_3$



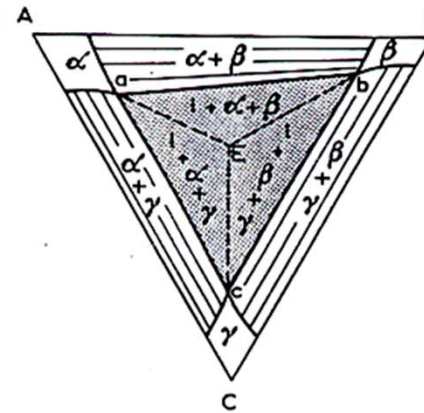
(d)  $T = e_3$



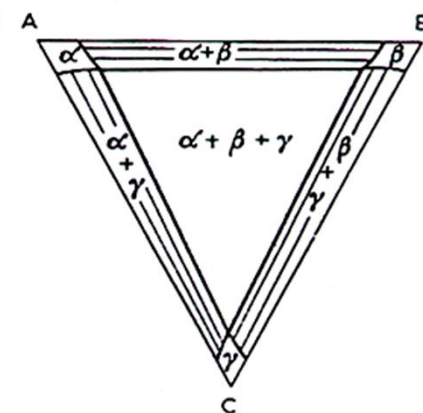
(e)  $T = e_2$



(f)  $e_2 > T > E$



(g)  $T_A = E$



(h)  $E = T$



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

Vertical section

Location of vertical section

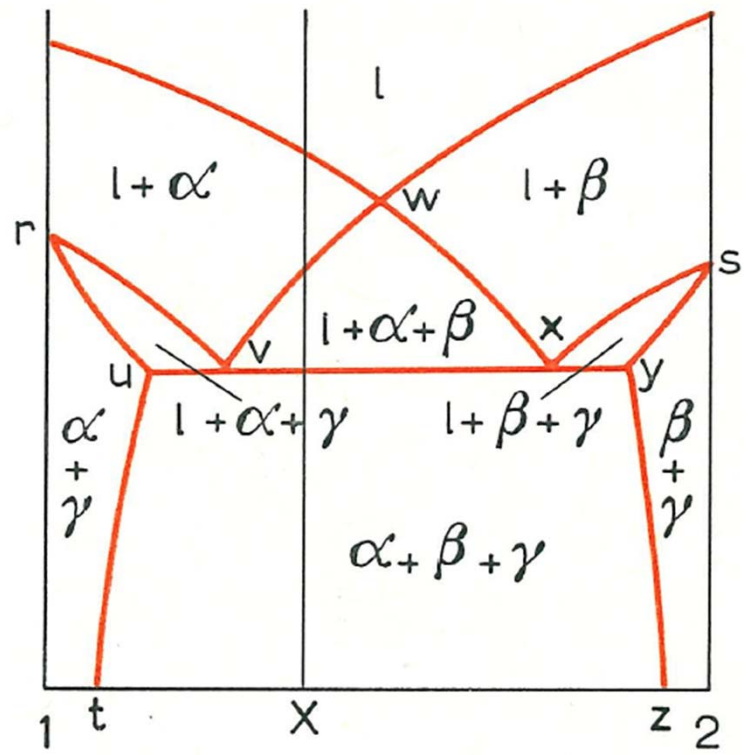
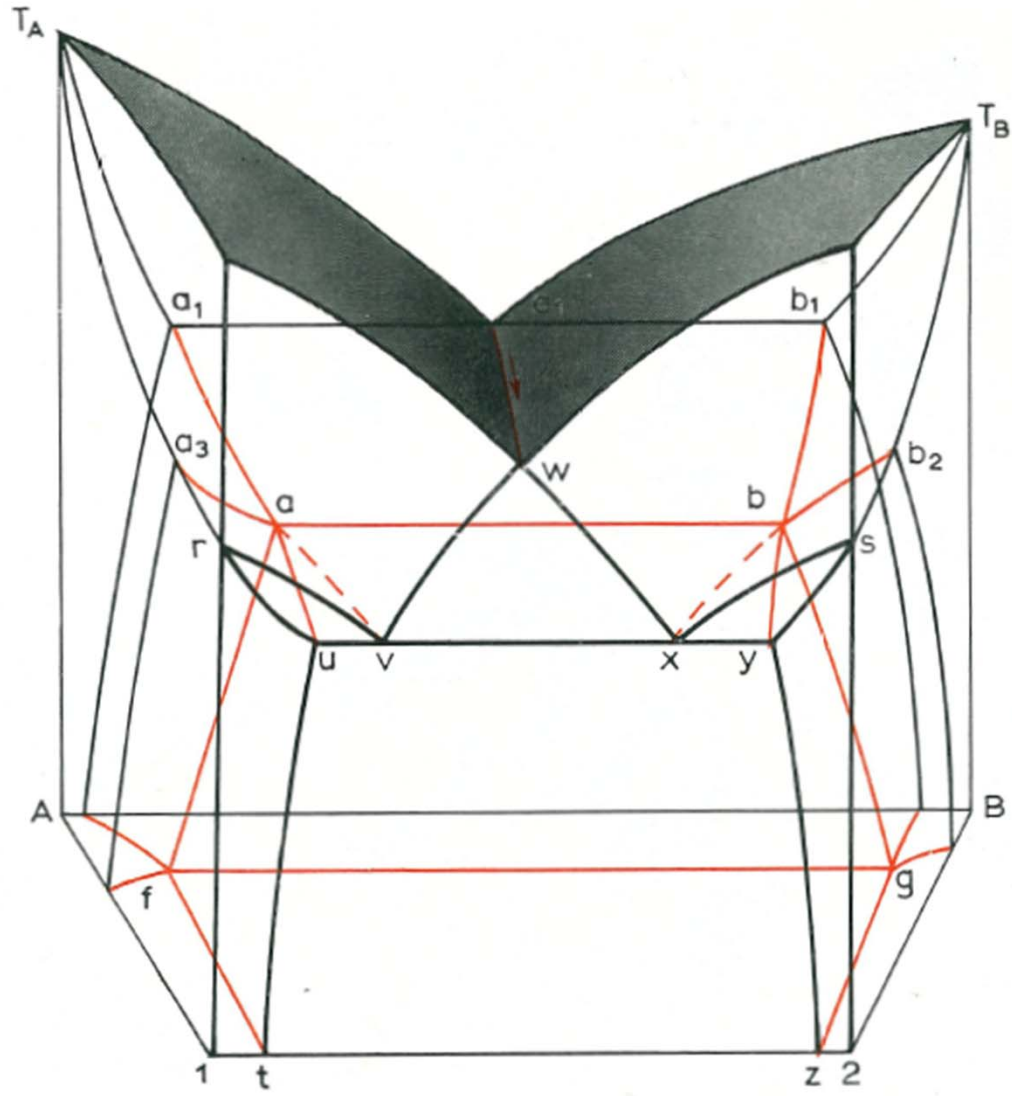


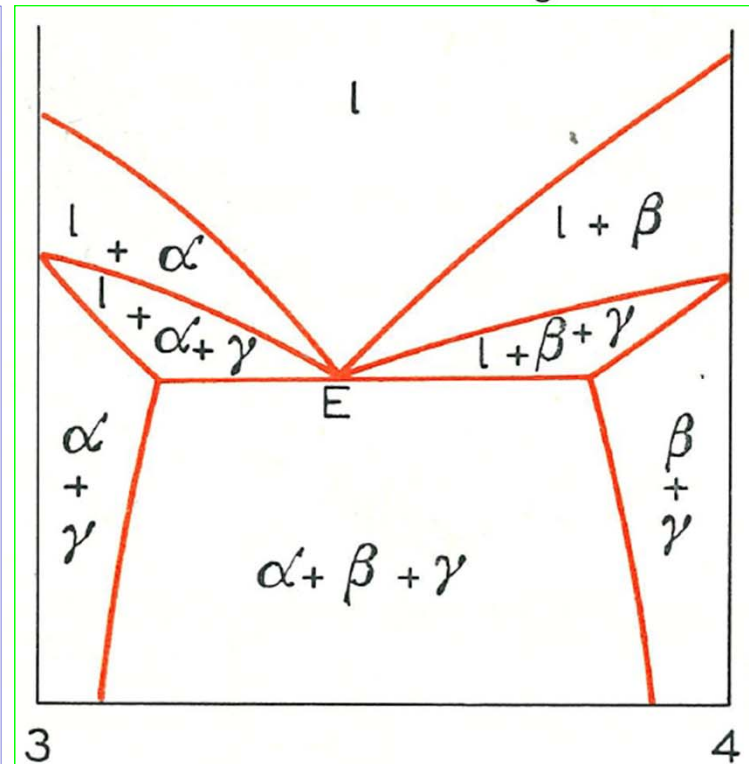
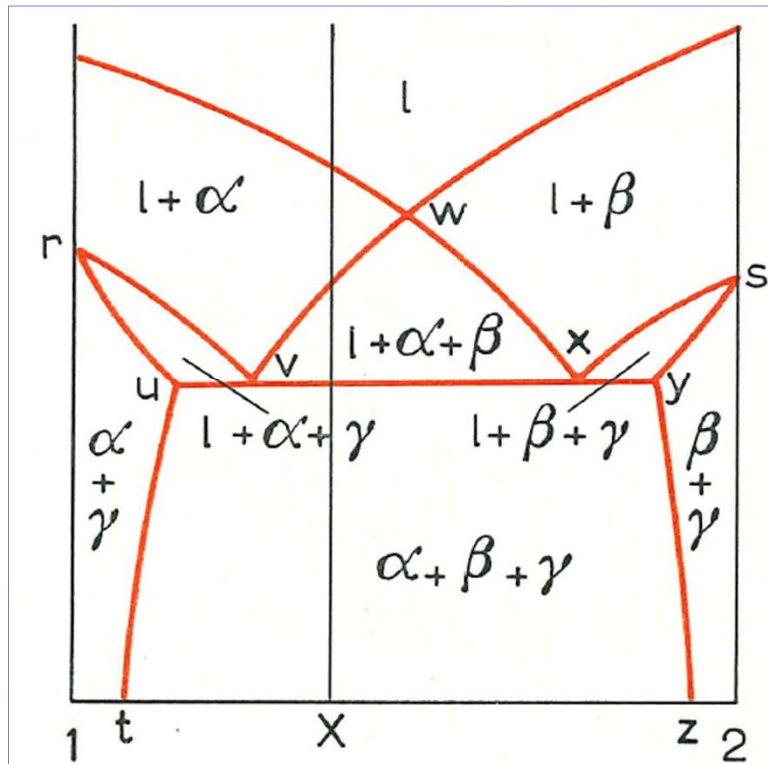
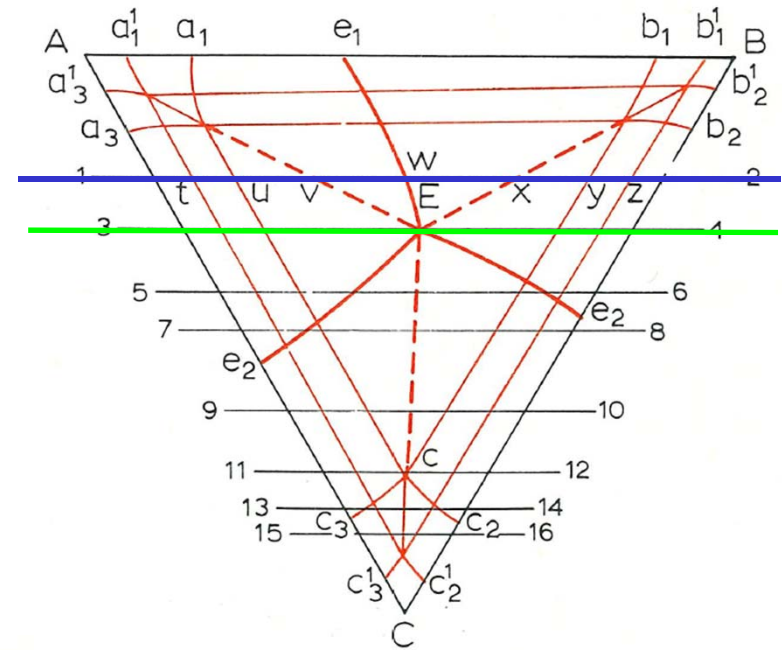
Fig. 179. Construction of vertical section 1-2.

# 10.1. THE EUTECTIC EQUILIBRIUM

$$(l = \alpha + \beta + \gamma)$$

Vertical section

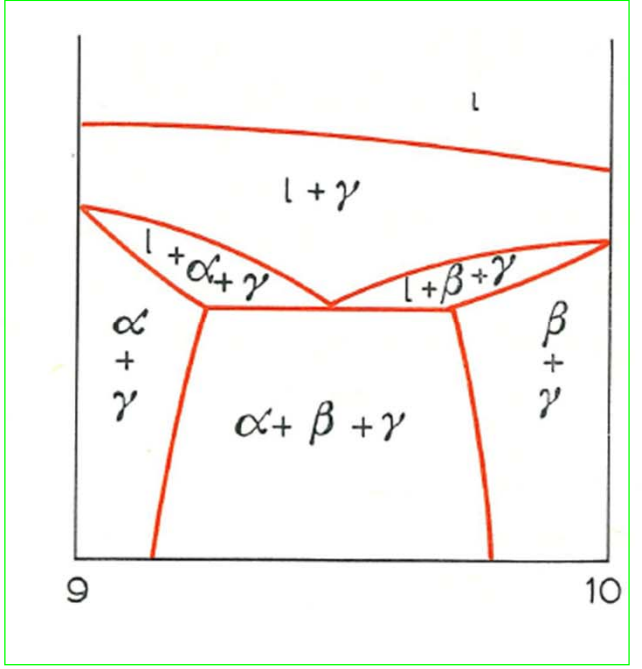
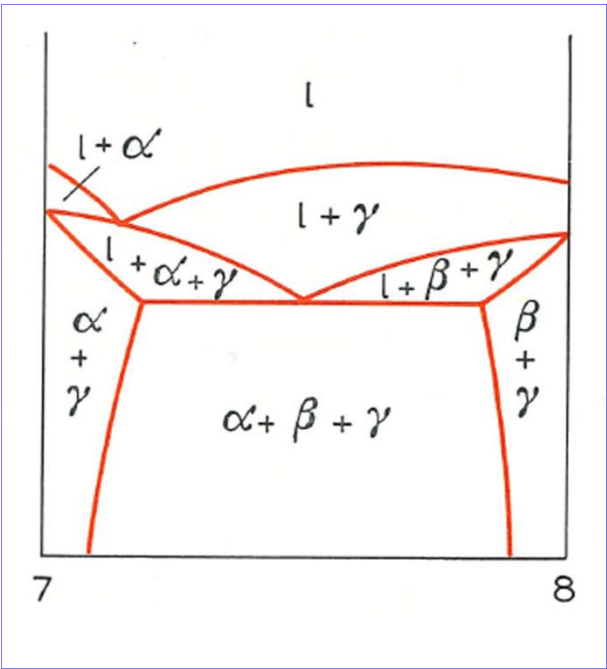
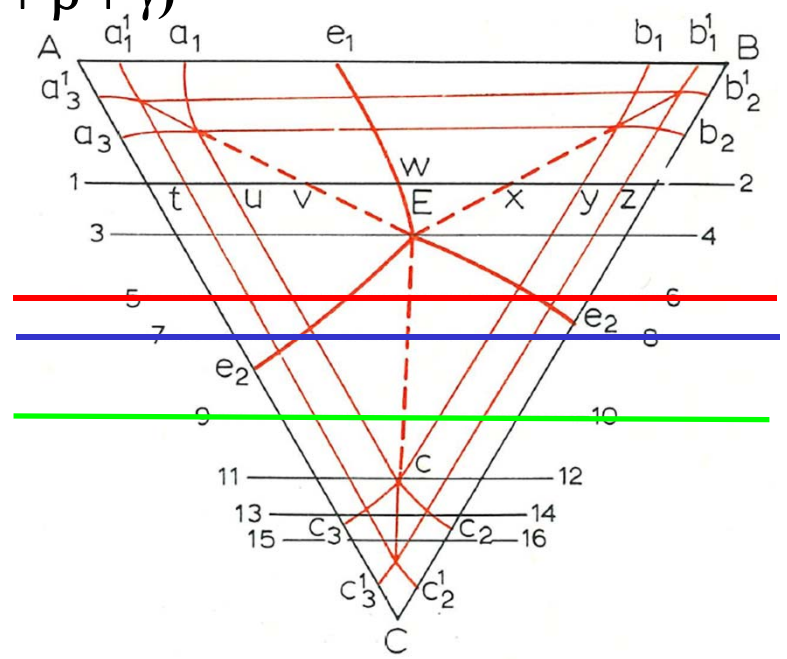
Location of vertical section



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

Vertical section

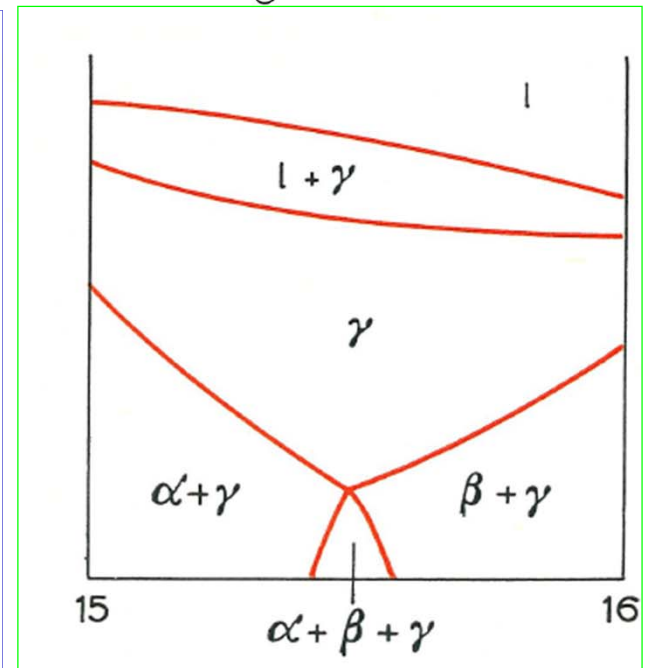
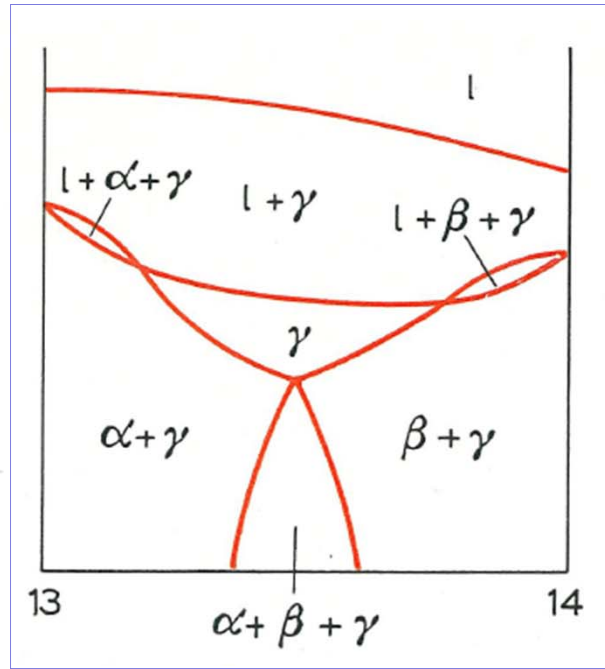
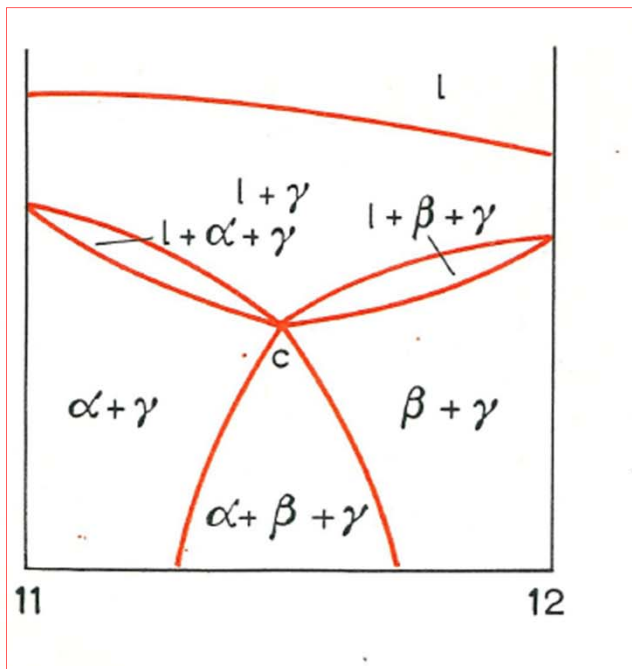
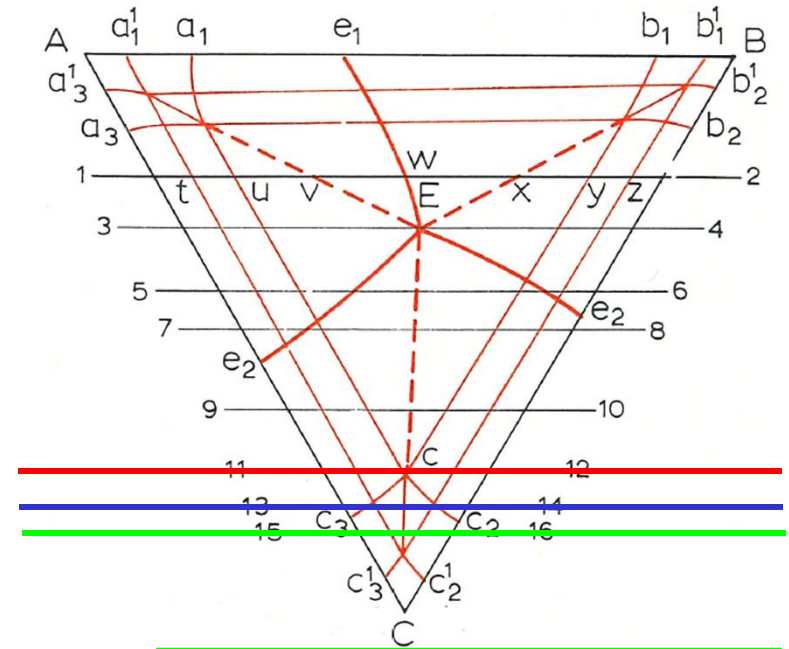
Location of vertical section



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

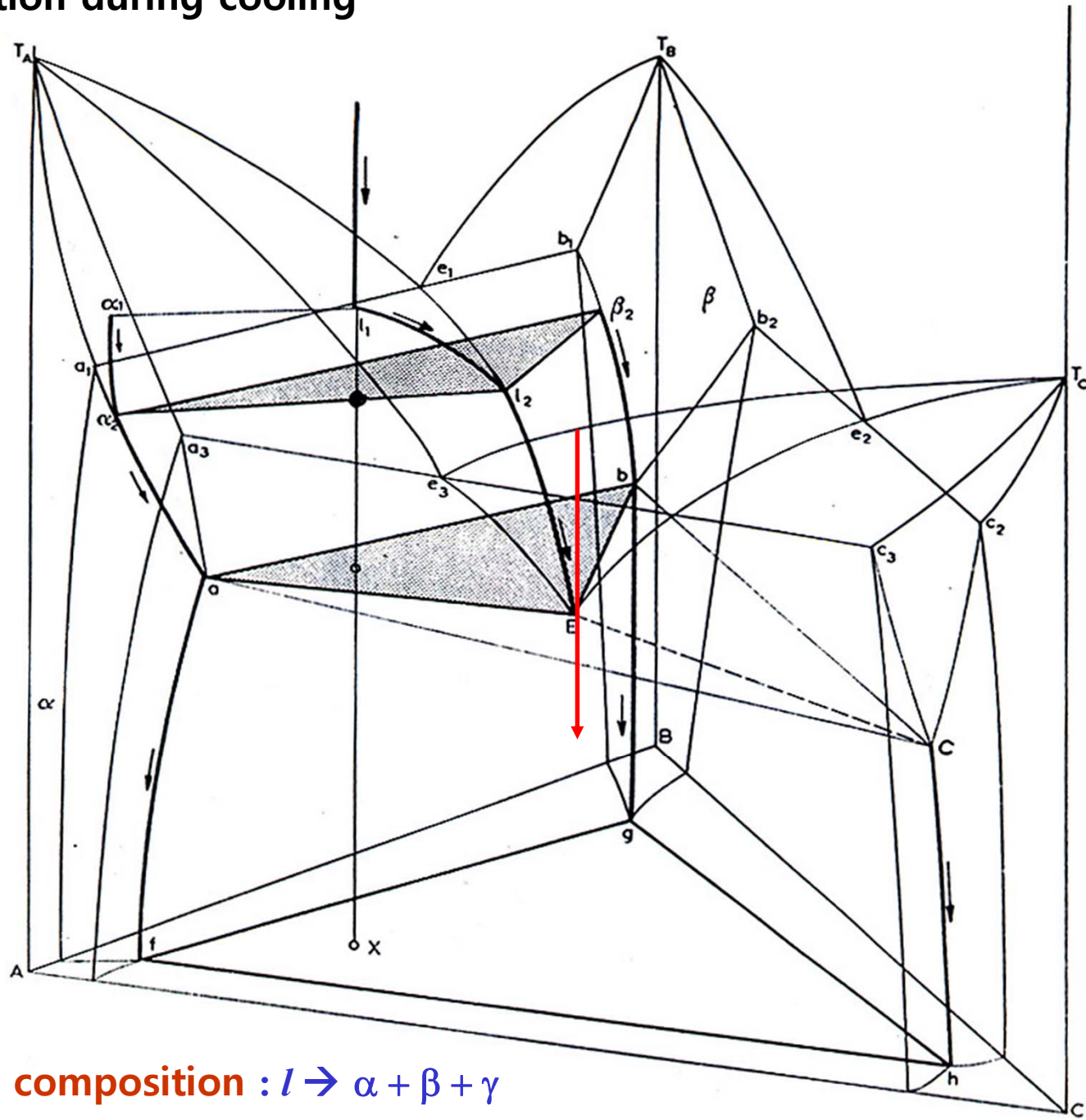
Vertical section

Location of vertical section





# Transformation during cooling



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

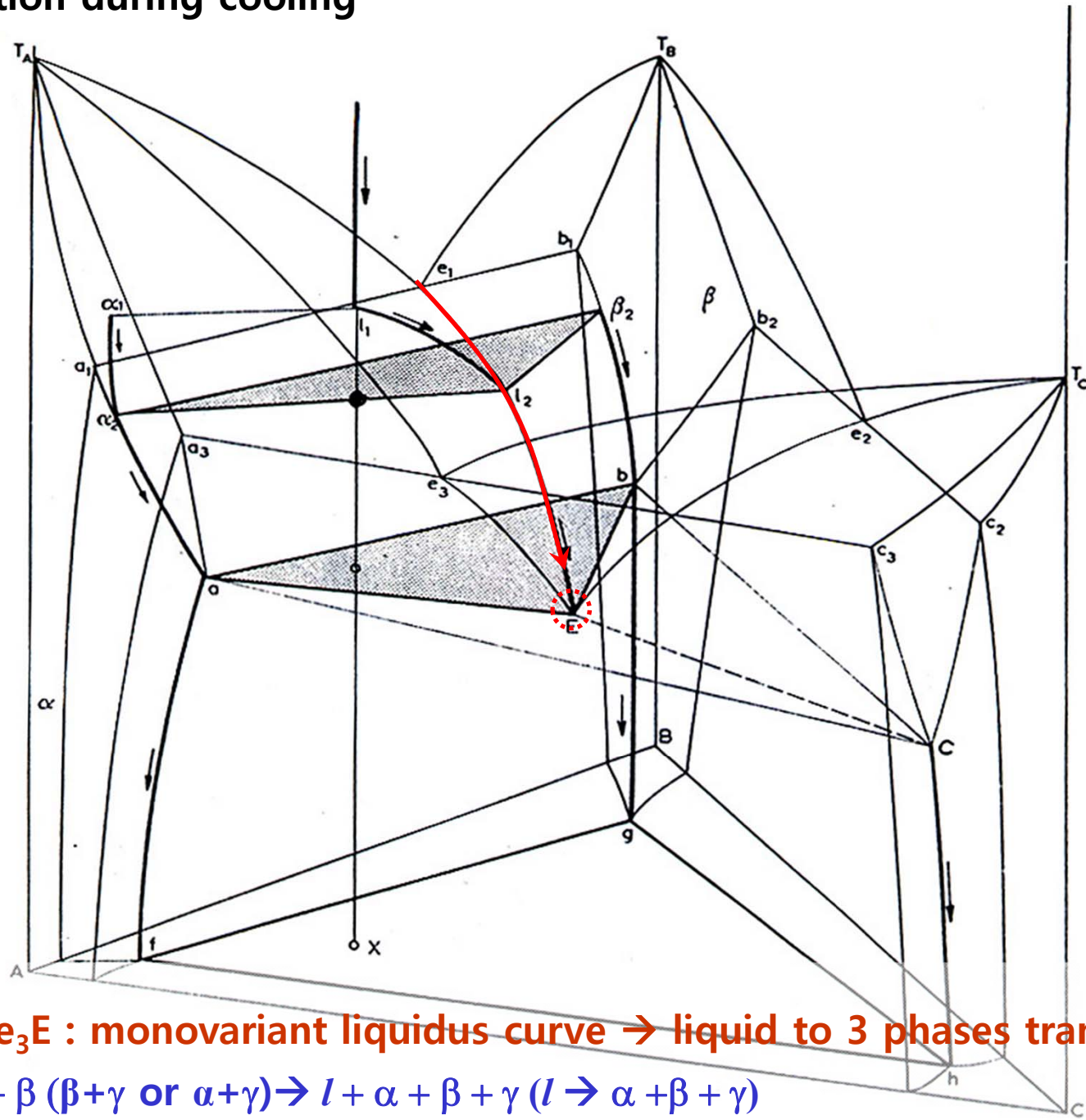
## Ternary Eutectic microstructure



**Microstructure of the ternary eutectic in the Al-Cu-Si system.  $\alpha$  light,  $\theta$  dark, Si grey, (x 900)** 32

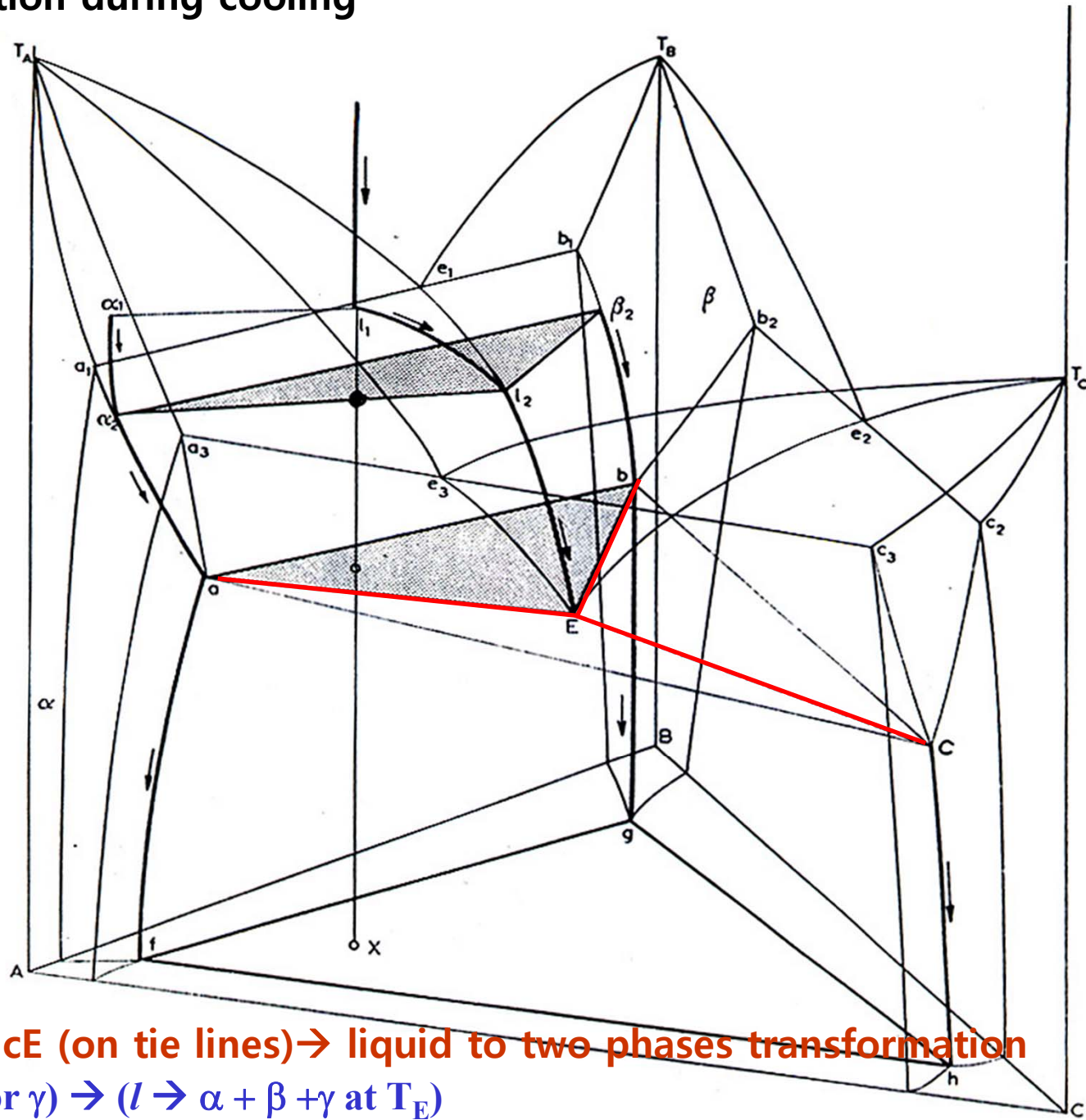


# Transformation during cooling



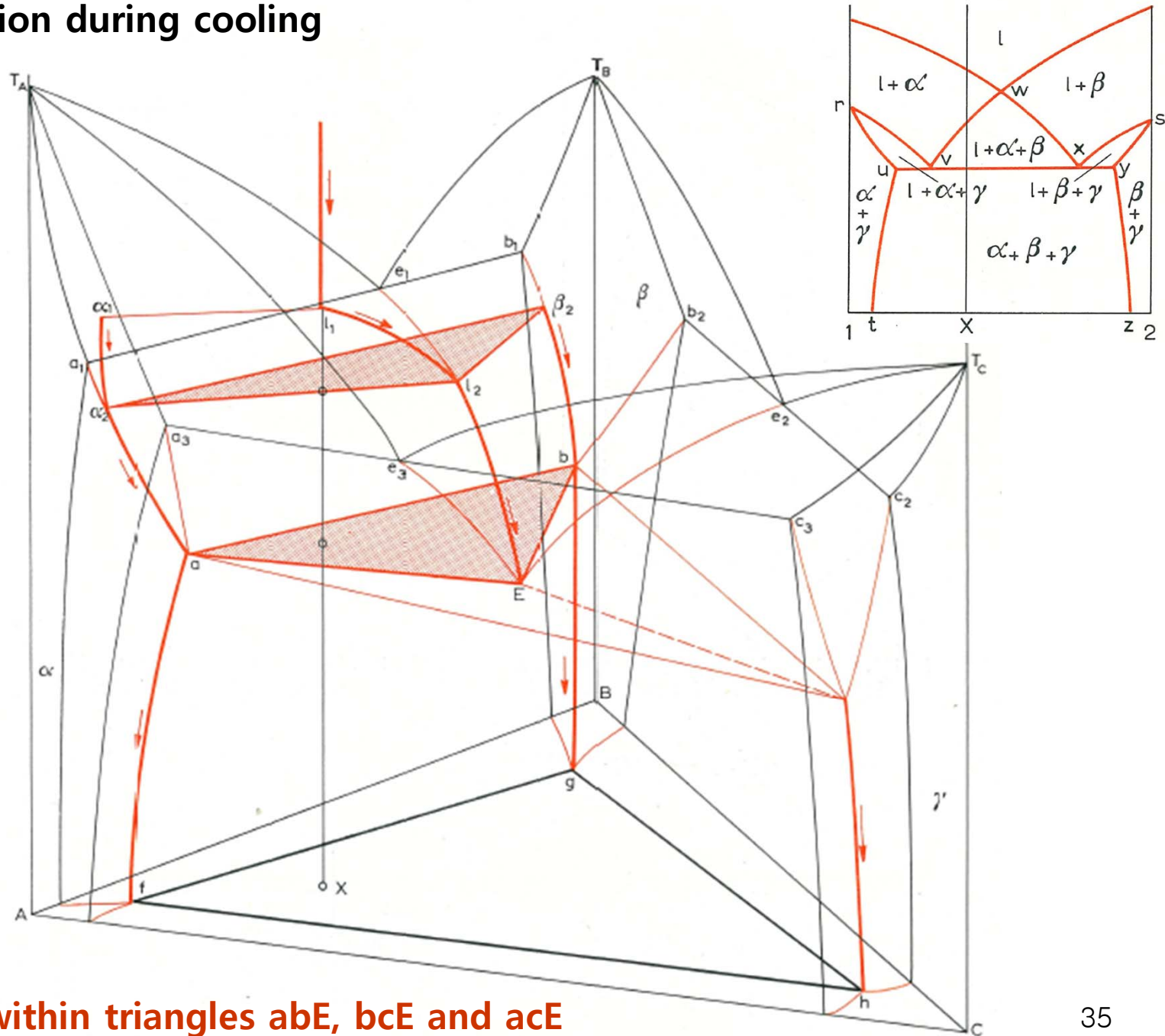
②  $e_1E, e_2E, e_3E$  : monovariant liquidus curve  $\rightarrow$  liquid to 3 phases transformation  
 $: l \rightarrow l + \alpha + \beta$  ( $\beta + \gamma$  or  $\alpha + \gamma$ )  $\rightarrow l + \alpha + \beta + \gamma$  ( $l \rightarrow \alpha + \beta + \gamma$ )

# Transformation during cooling



③ aE, bE, cE (on tie lines)  $\rightarrow$  liquid to two phases transformation  
 :  $l + \alpha$  ( $\beta$  or  $\gamma$ )  $\rightarrow$  ( $l \rightarrow \alpha + \beta + \gamma$  at  $T_E$ )

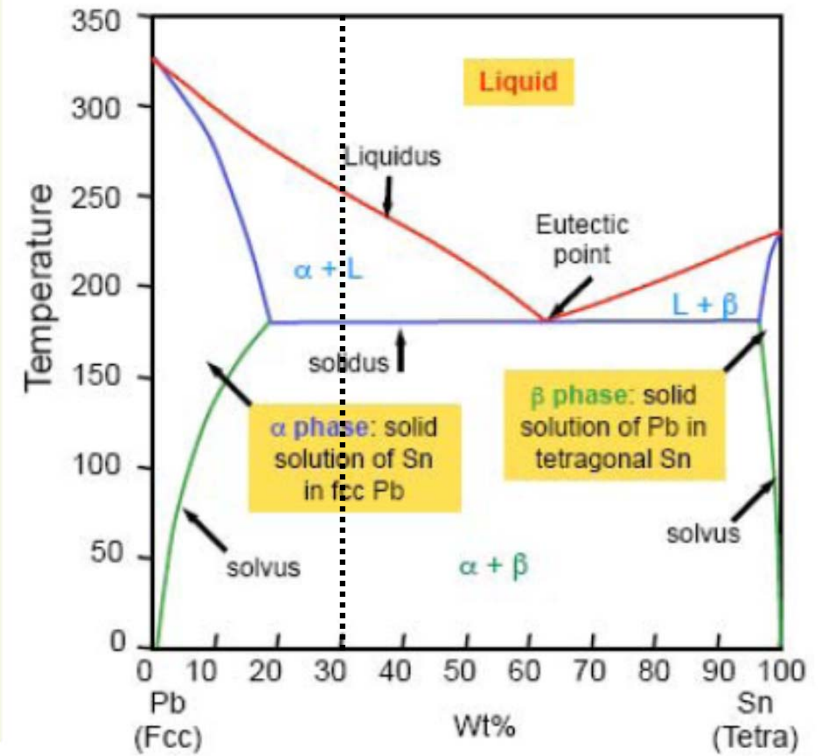
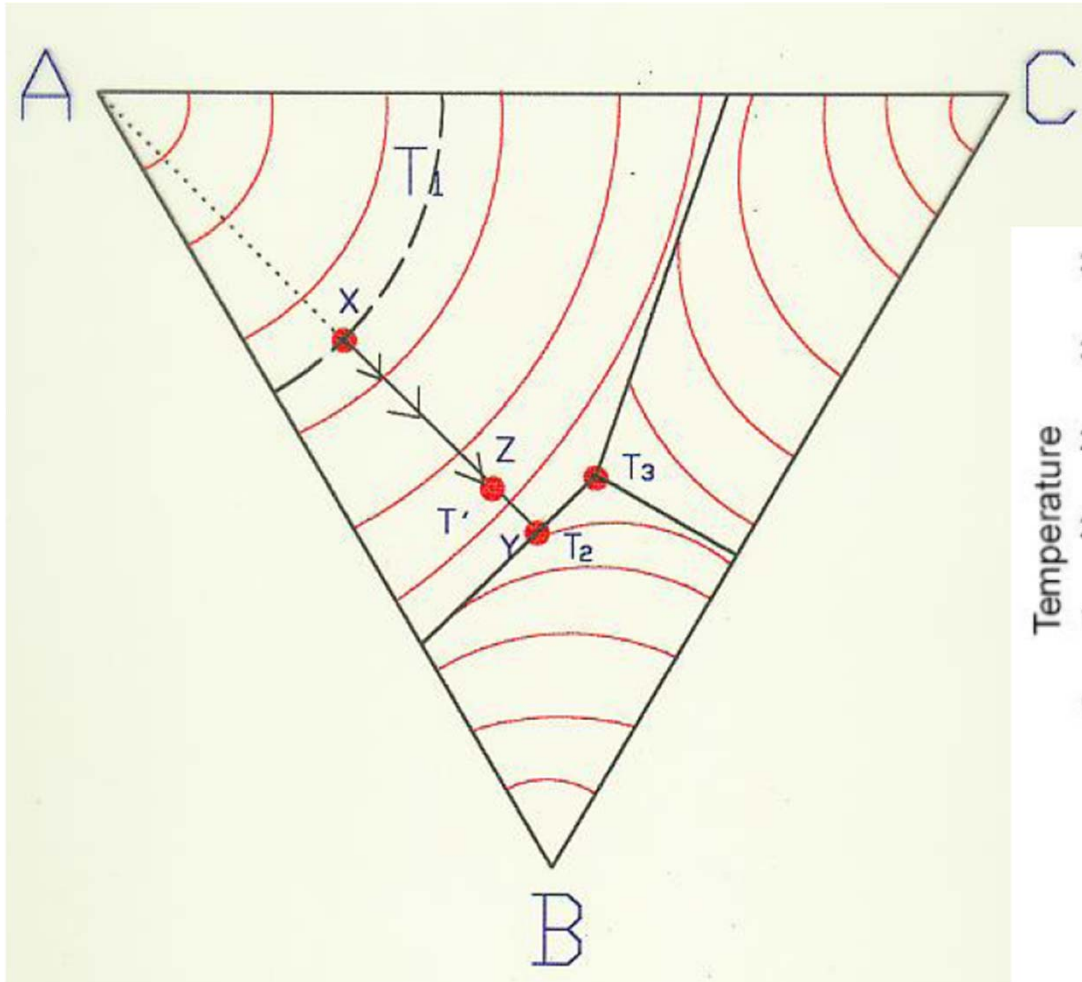
# Transformation during cooling



- ④ Alloys within triangles  $abE$ ,  $bcE$  and  $acE$   
 ex)  $abE$ :  $l + \alpha$  (or  $\beta$ )  $\rightarrow$   $l + \alpha + \beta$   $\rightarrow$  ( $l \rightarrow \alpha + \beta + \gamma$  at  $T_E$ )

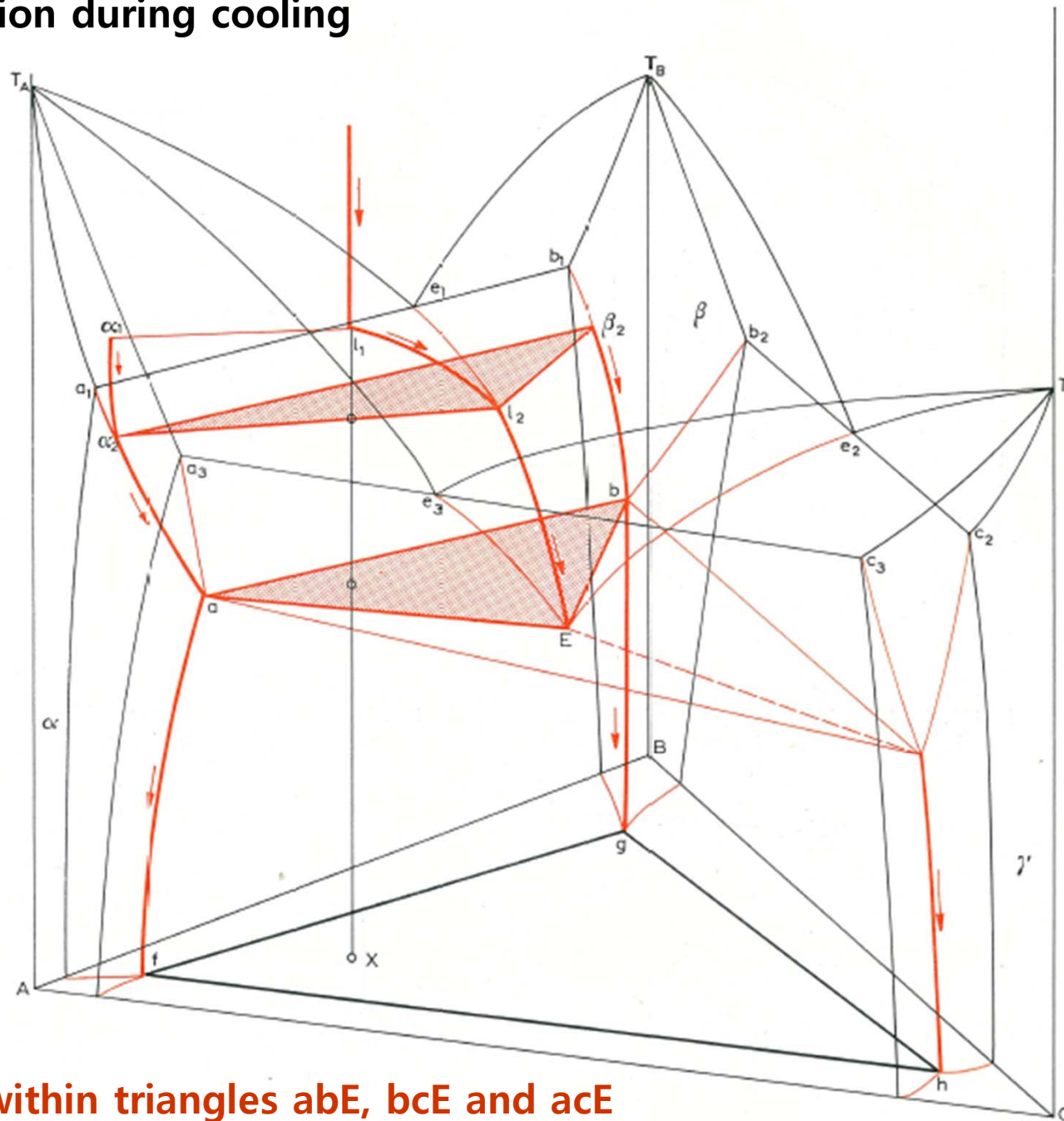
# Ternary Eutectic System

## Solidification Sequence





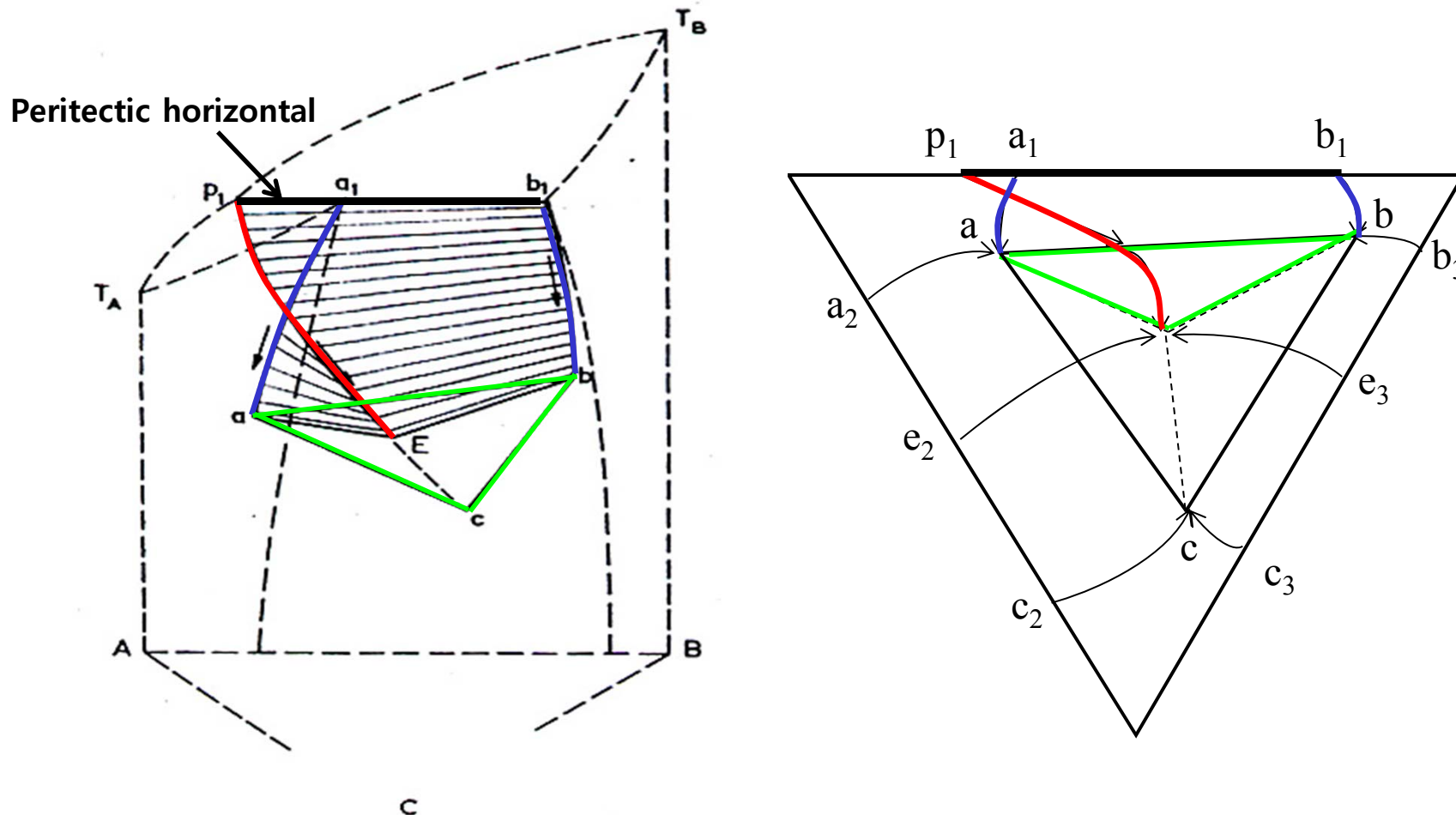
# Transformation during cooling



- ④ Alloys within triangles  $abE$ ,  $bcE$  and  $acE$   
 ex)  $abE$ :  $l + \alpha$  (or  $\beta$ )  $\rightarrow$   $l + \alpha + \beta \rightarrow (l \rightarrow \alpha + \beta + \gamma$  at  $T_E$ )

## 10.2. VARIANTS OF THE TERNARY EUTECTIC DIAGRAM

(a) Variant of the ternary eutectic system in which one binary is a **peritectic**



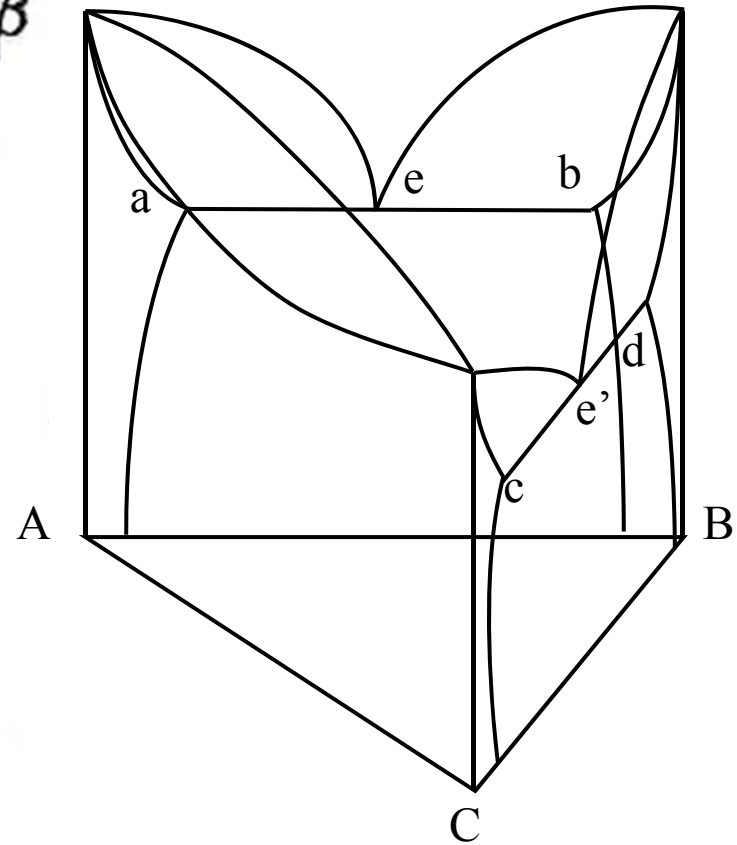
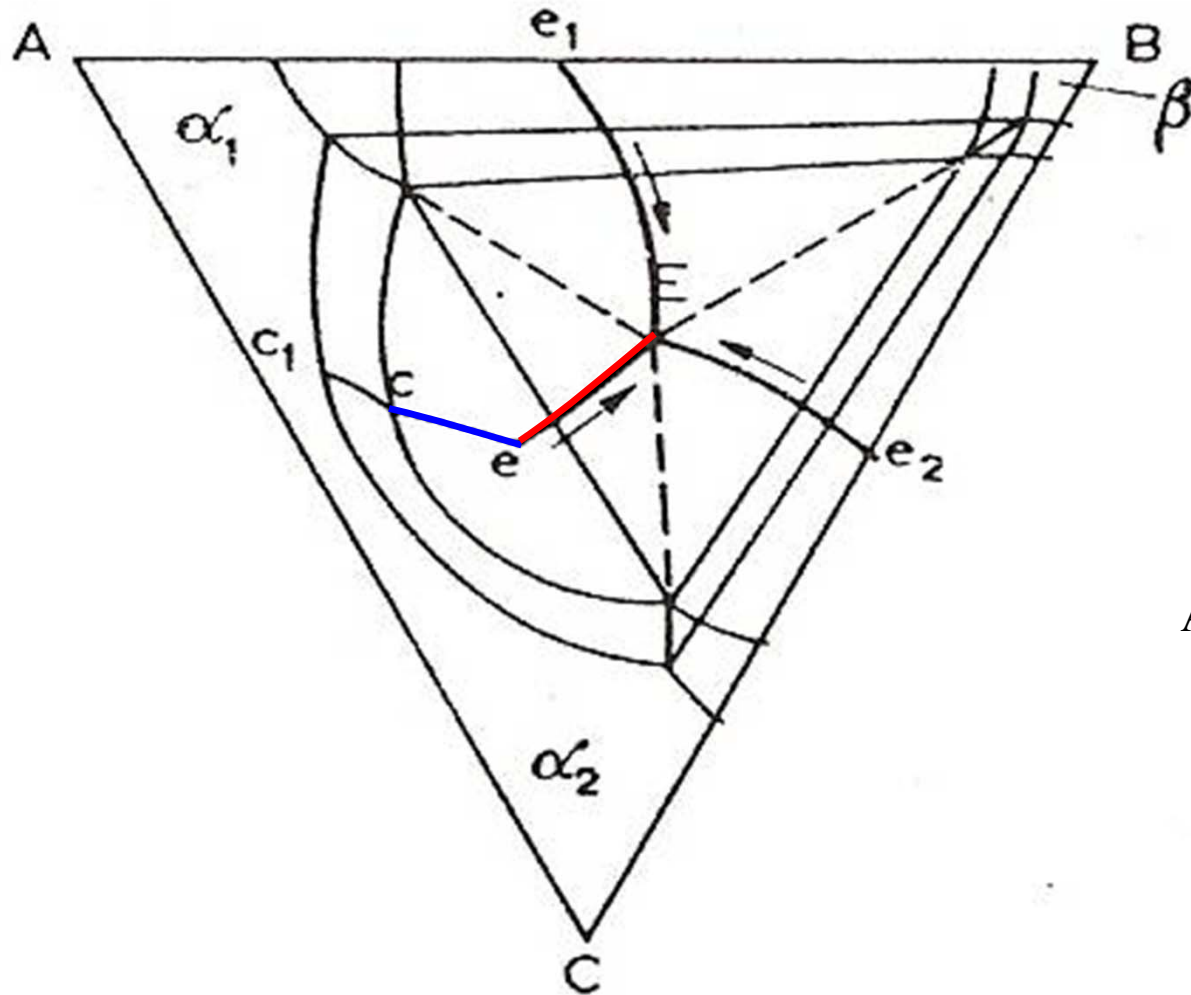
**Monovariant liquidus line ( $P_1E$ )** lies above monovariant solidus line ( $a_1a$ ).

→ A ternary eutectic can be produced with one, two or three binary peritectic systems.



## 10.2. VARIANTS OF THE TERNARY EUTECTIC DIAGRAM

(b) Ternary eutectic system  
 in which **two of the binary eutectics** and **one of ternary miscibility gap** exist.



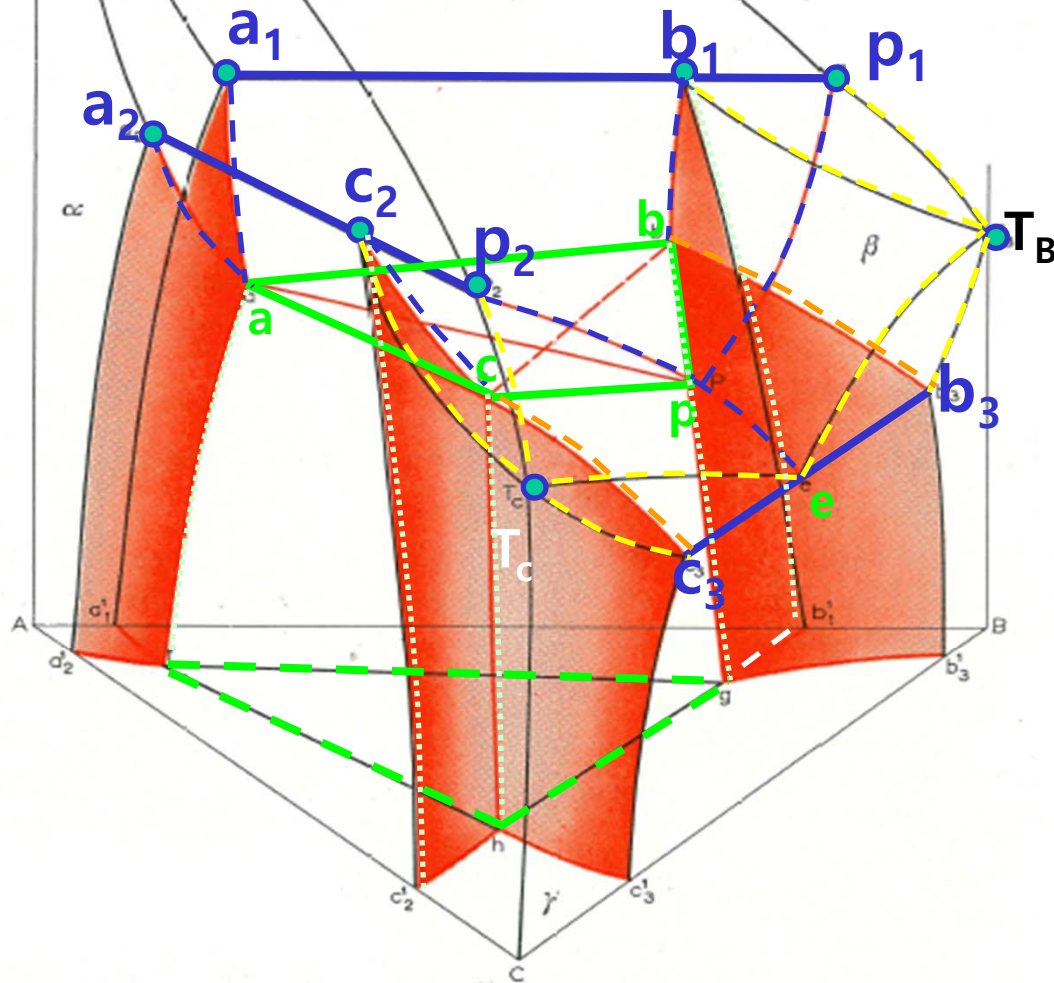
<one complete solid solution + two binary eutectic>

# 10.3. THE QUASI-PERITECTIC EQUILIBRIUM ( $l + \alpha = \beta + \gamma$ )

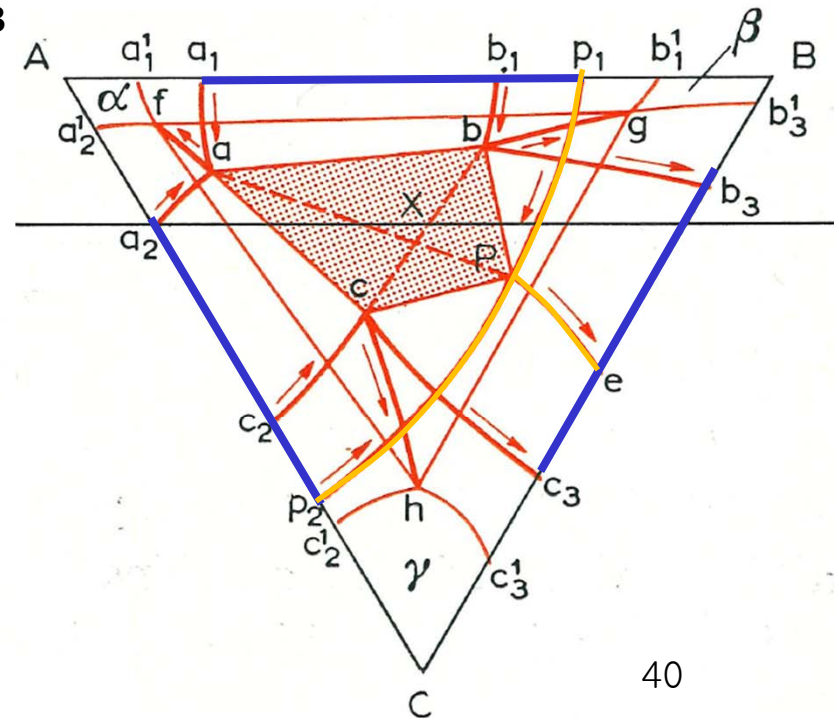
$T_A$

$$T_A > P_1 > P_2 > T_B > P > T_C > e$$

Space model

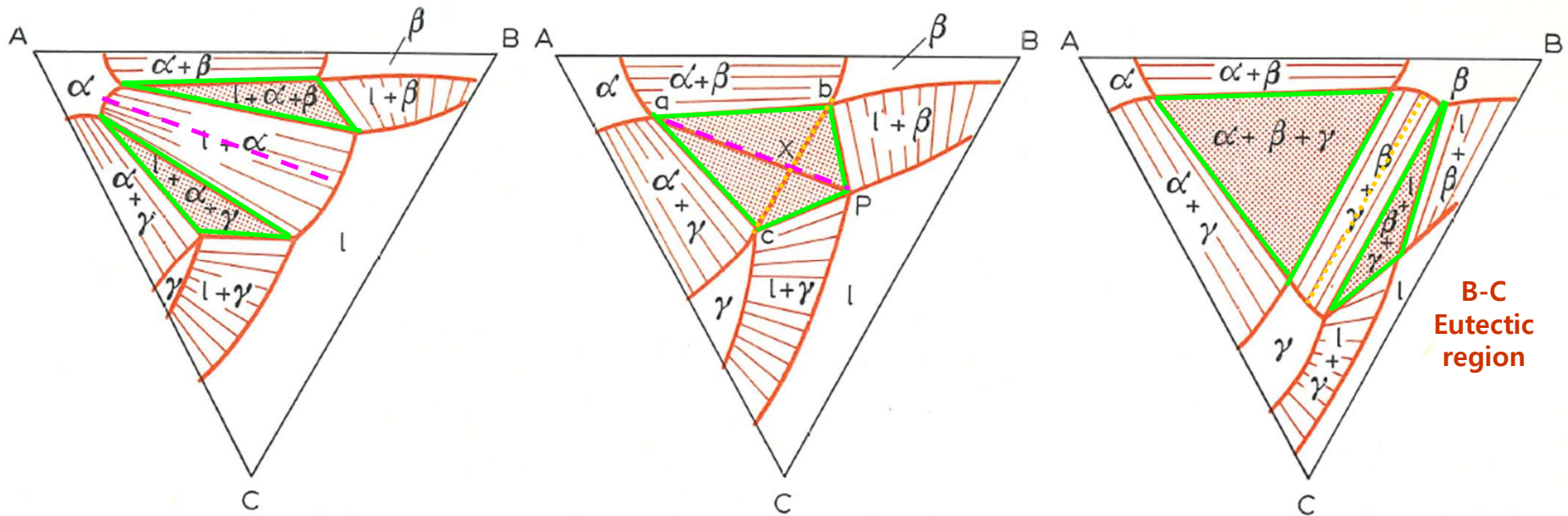


Projection



### 10.3. THE QUASI-PERITECTIC EQUILIBRIUM ( $l + \alpha = \beta + \gamma$ )

#### Isothermal section



$T_B > T > P$

$T = P$

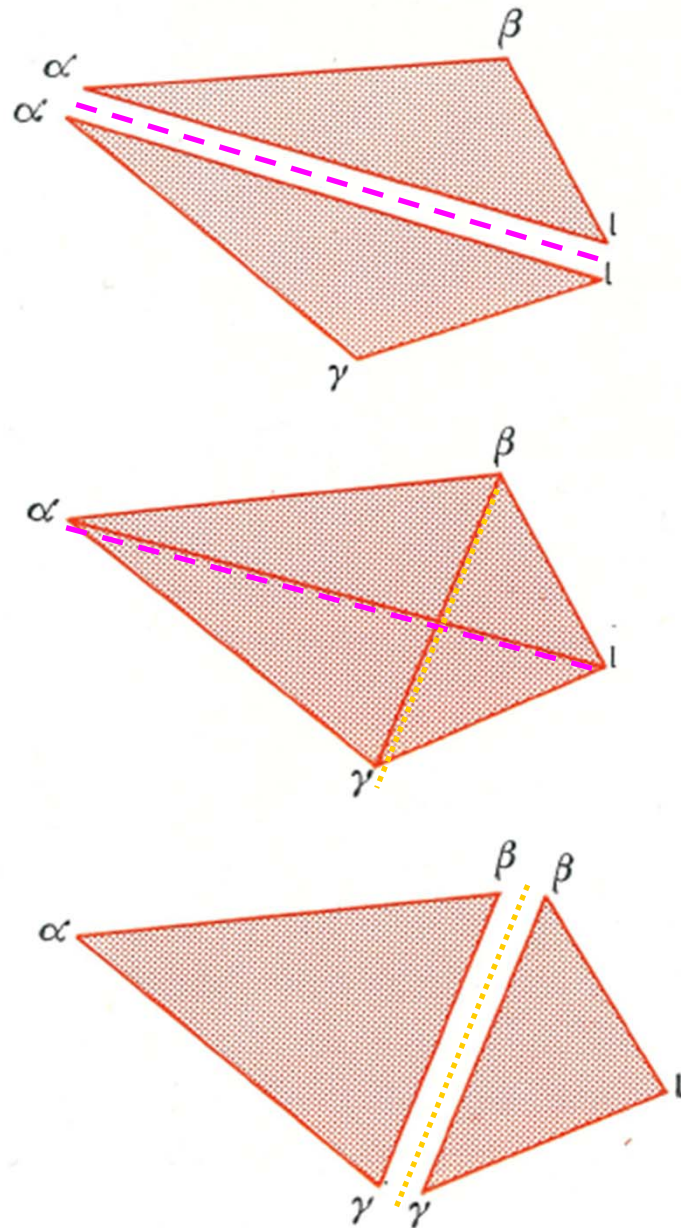
$P > T > T_C$

$abP$	peritectic $l\alpha\beta$ equilibrium	}
$acP$	peritectic $l\alpha\gamma$ equilibrium	
<hr/>		
$bcP$	eutectic $l\beta\gamma$ equilibrium	}
$abc$	$\alpha\beta\gamma$ equilibrium	

descending to the four-phase plane;

descending from the four-phase plane.

### 10.3. THE QUASI-PERITECTIC EQUILIBRIUM ( $l + \alpha = \beta + \gamma$ )



Both three phase monovariant equilibria preceding the quasi-peritectic reaction are peritectic

**abP peritectic  $l\alpha\beta$  equilibrium**

**acP peritectic  $l\alpha\gamma$  equilibrium**

decreasing temperature

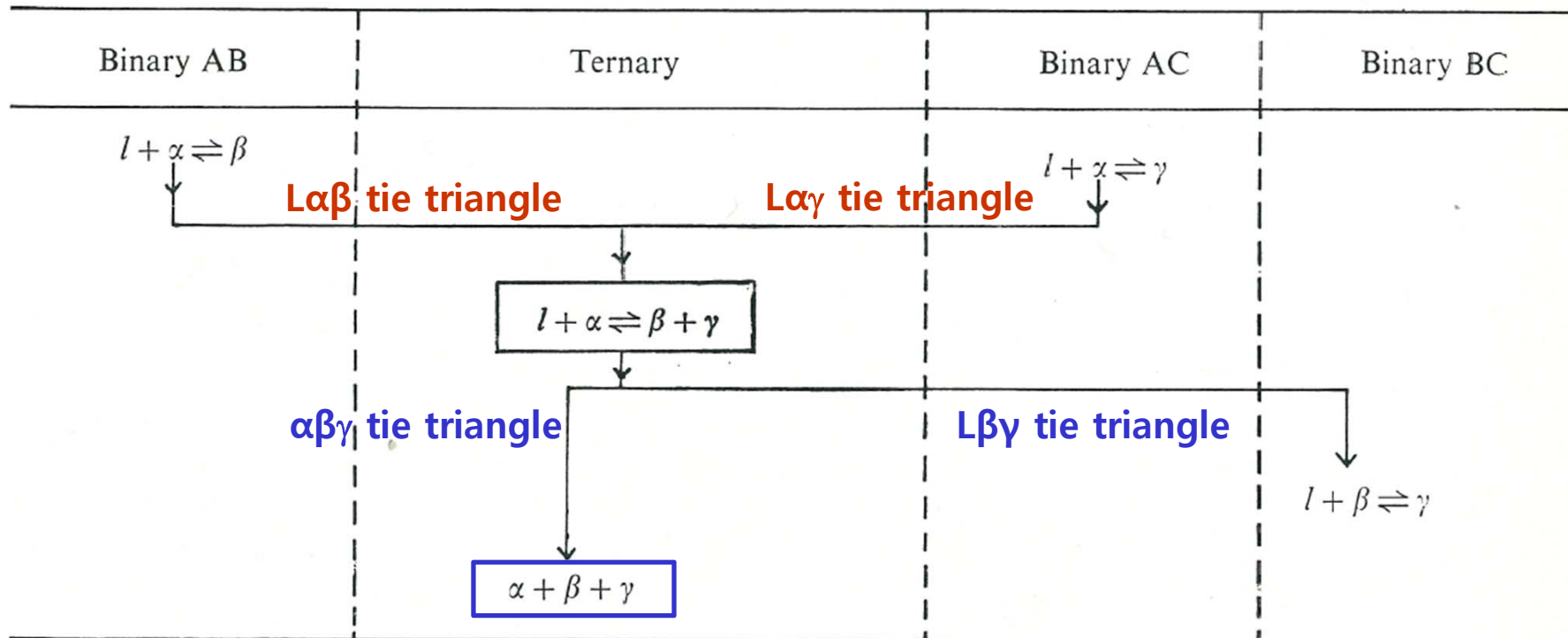
**bcP eutectic  $l\beta\gamma$  equilibrium**

**abc peritectic  $\alpha\beta\gamma$  equilibrium**



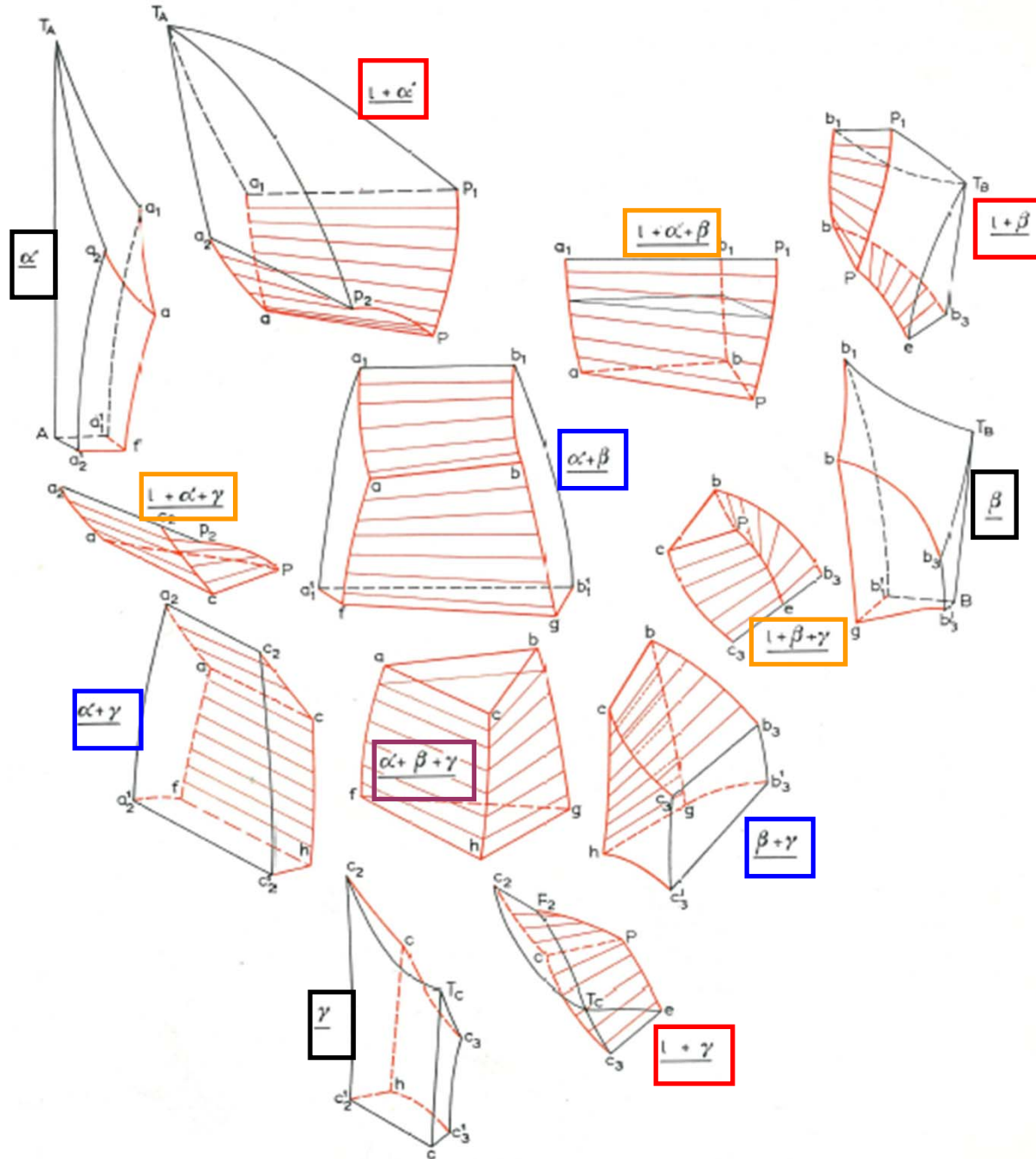
**Tabular representation of ternary equilibria:**  
interlinks the binary and ternary reactions in tabular form

QUASI-PERITECTIC EQUILIBRIUM  $l + \alpha \rightleftharpoons \beta + \gamma$



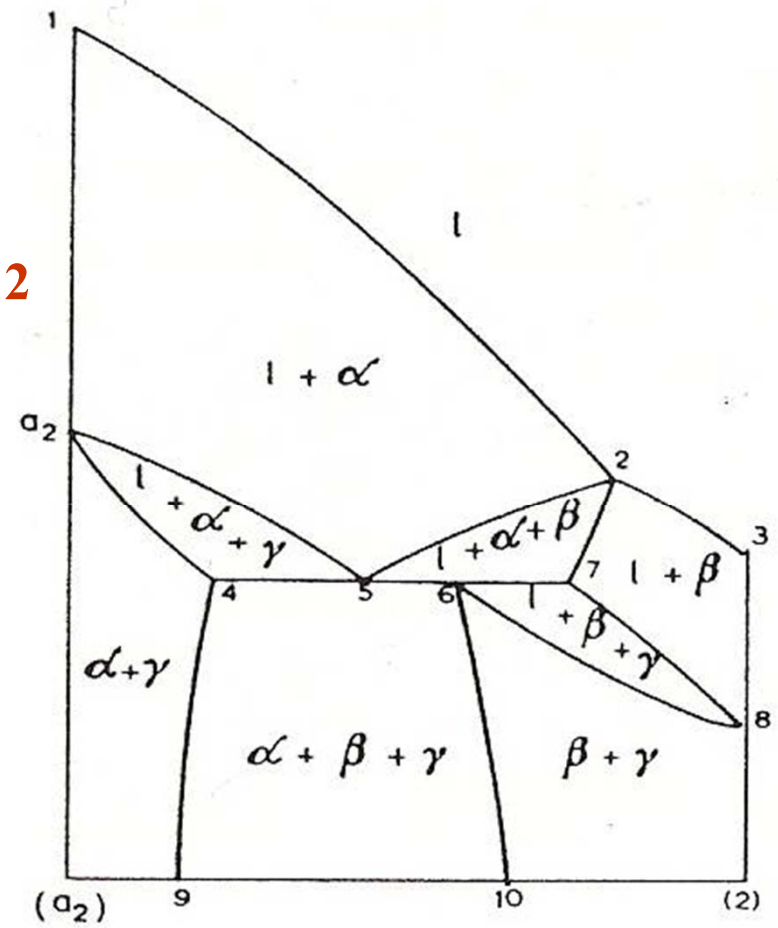
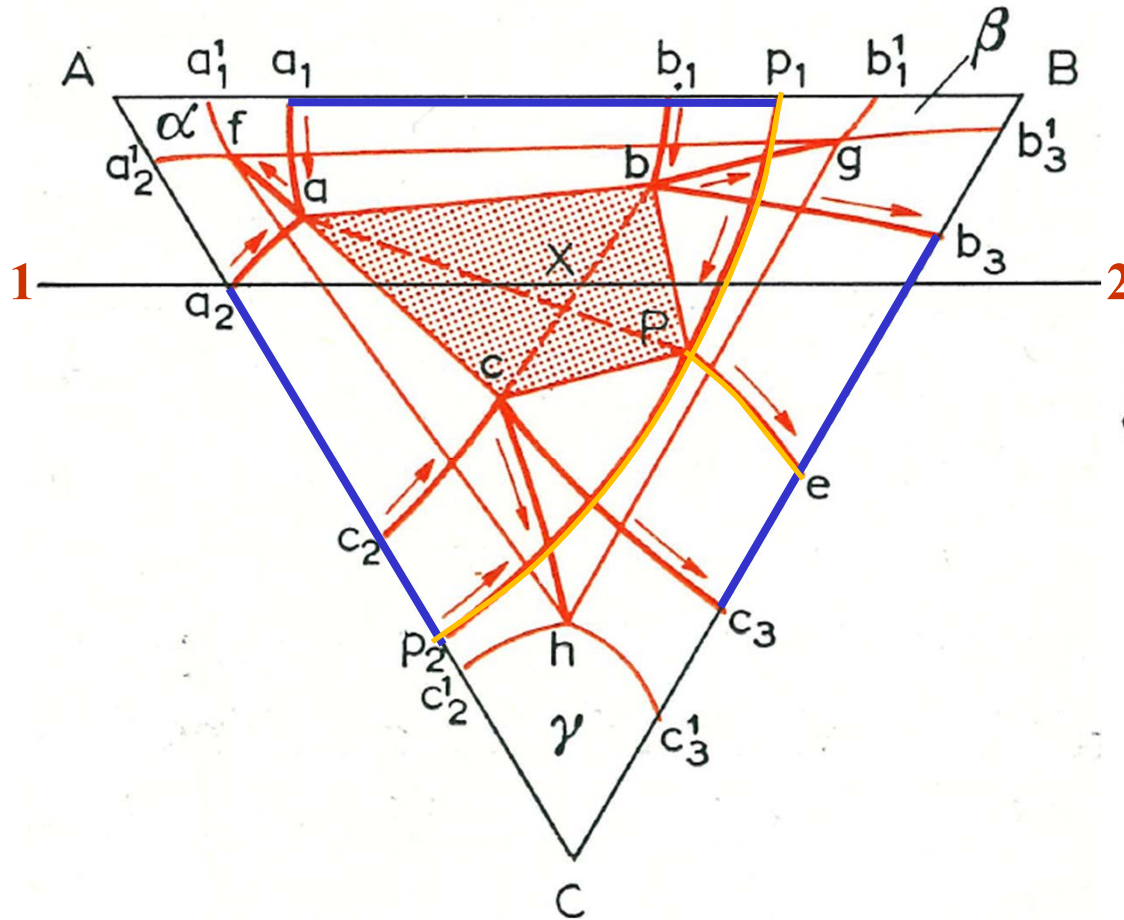


### 10.3. THE QUASI-PERITECTIC EQUILIBRIUM ( $l + \alpha = \beta + \gamma$ )



# 10.3. THE QUASI-PERITECTIC EQUILIBRIUM ( $l + \alpha = \beta + \gamma$ )

## Vertical section



(a)

### 10.3. THE QUASI-PERITECTIC EQUILIBRIUM ( $l + \alpha = \beta + \gamma$ )

#### Vertical section

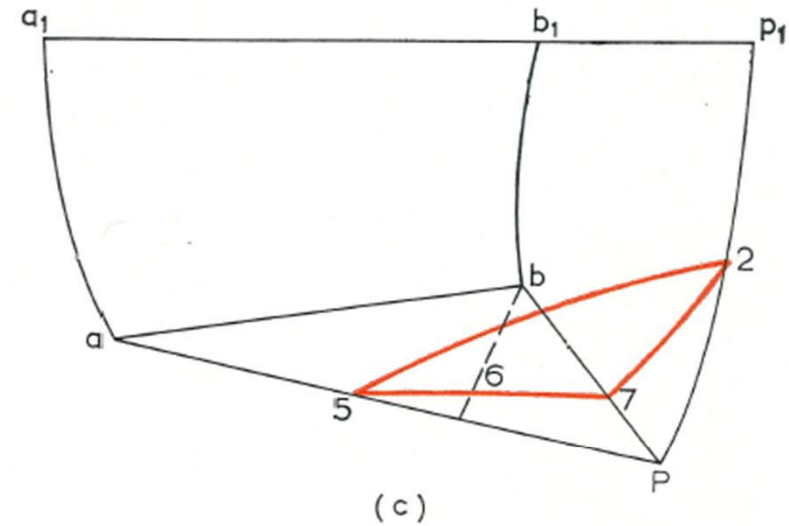
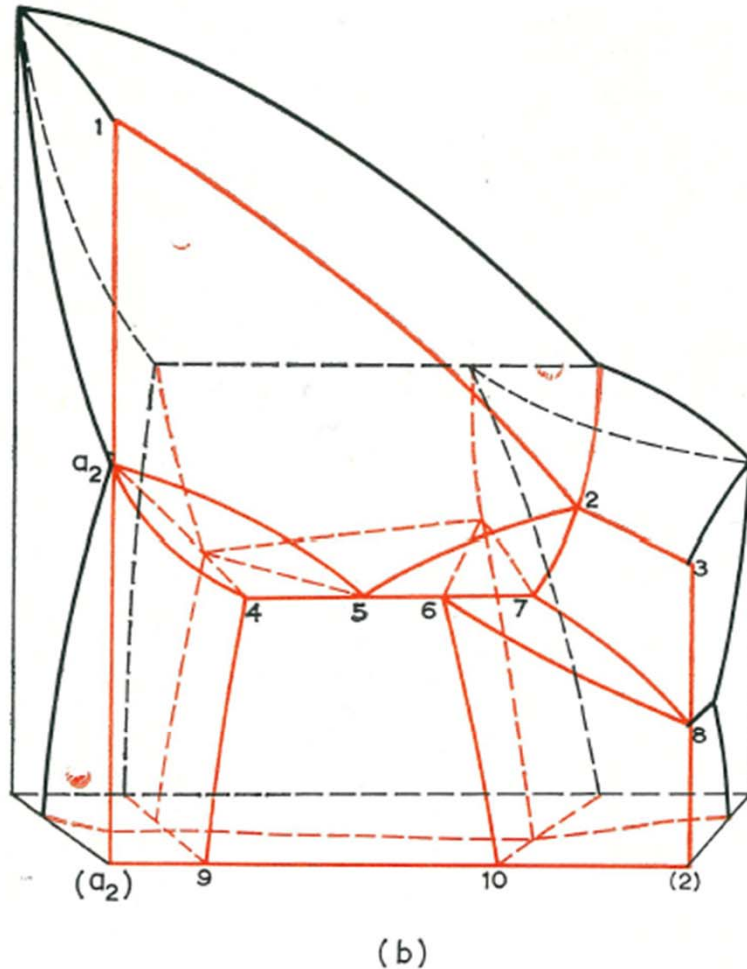


Fig. 188. A vertical section through the space model of Fig. 185a. (a) The vertical section  $a_2-2$ ; (b) construction of the vertical section; (c) intersection of the vertical section with the  $l+\alpha+\beta$  phase region.

10.3.2. one of the three phase monovariant equilibria preceding the quasi-peritectic reaction is eutectic and one peritectic.

\* Ternary system involving an incongruently-melting binary intermediate phase:

Quasi-peritectic diagram and ternary eutectic diagram

e.g. Au-Ge-Sb ternary in which the  $\delta$  phase is intermediate phase  $AuSb_2$ .

$P_1d_1b_1 \rightarrow dbp (\delta\beta L) / b_3e_3c_3 \rightarrow bpc (\beta L\gamma)$



$d^1\epsilon c(\delta + \gamma + L) / \boxed{gfn(\beta + \delta + \gamma)}$



$d^1\epsilon c^1(\delta\gamma L) / a_1e_1d_2 \rightarrow a^1\epsilon d^1(\alpha\delta L) / a_2e_2c_2 \rightarrow a^1\epsilon c^1(\alpha L\gamma)$



$\boxed{Jkm (\alpha + \gamma + \delta)}$

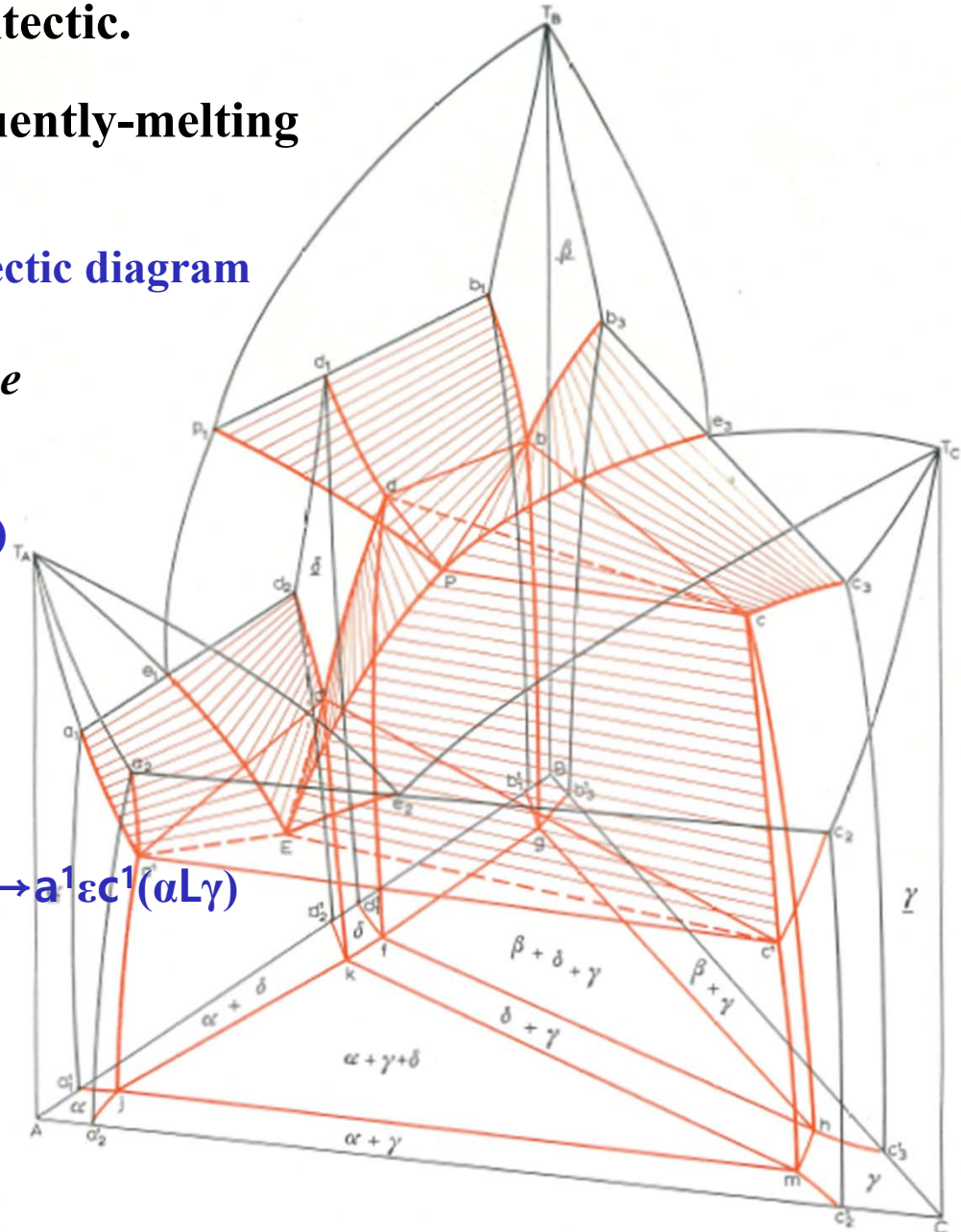
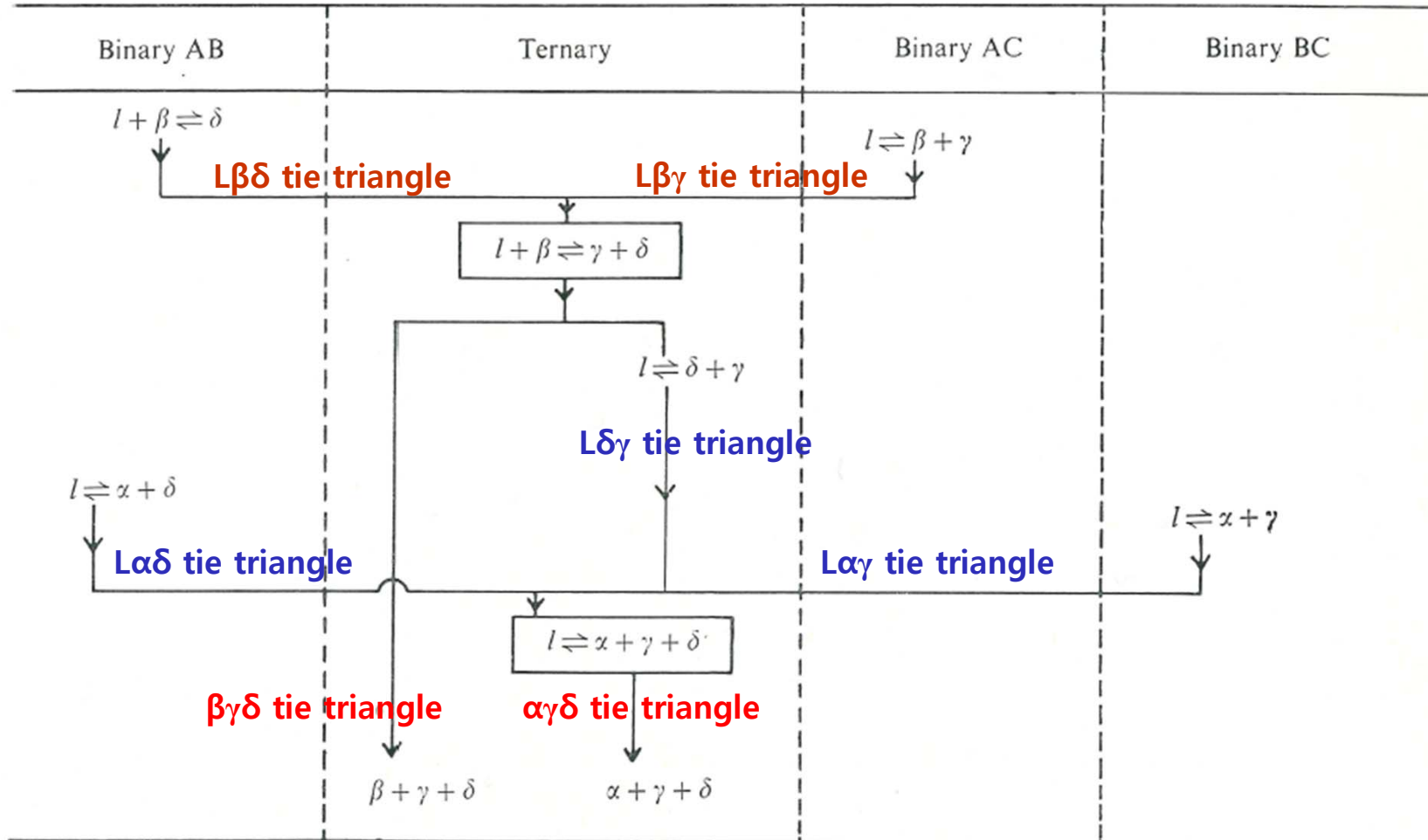


Fig. 189. Ternary system involving an incongruently-melting binary intermediate phase.

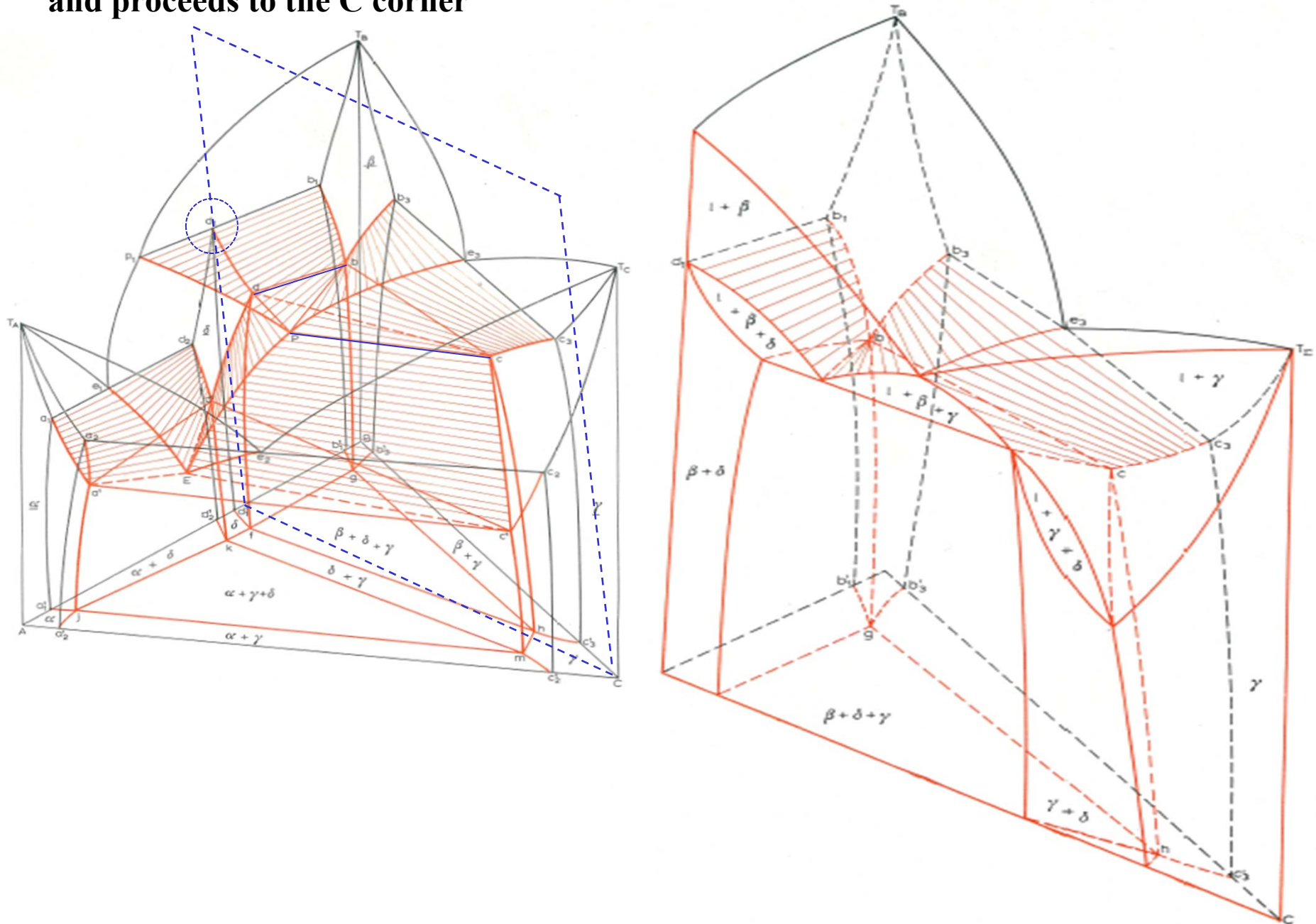
# Tabular representation of ternary equilibria: interlinks the binary and ternary reactions in tabular form

## Quasi-peritectic diagram and ternary eutectic diagram



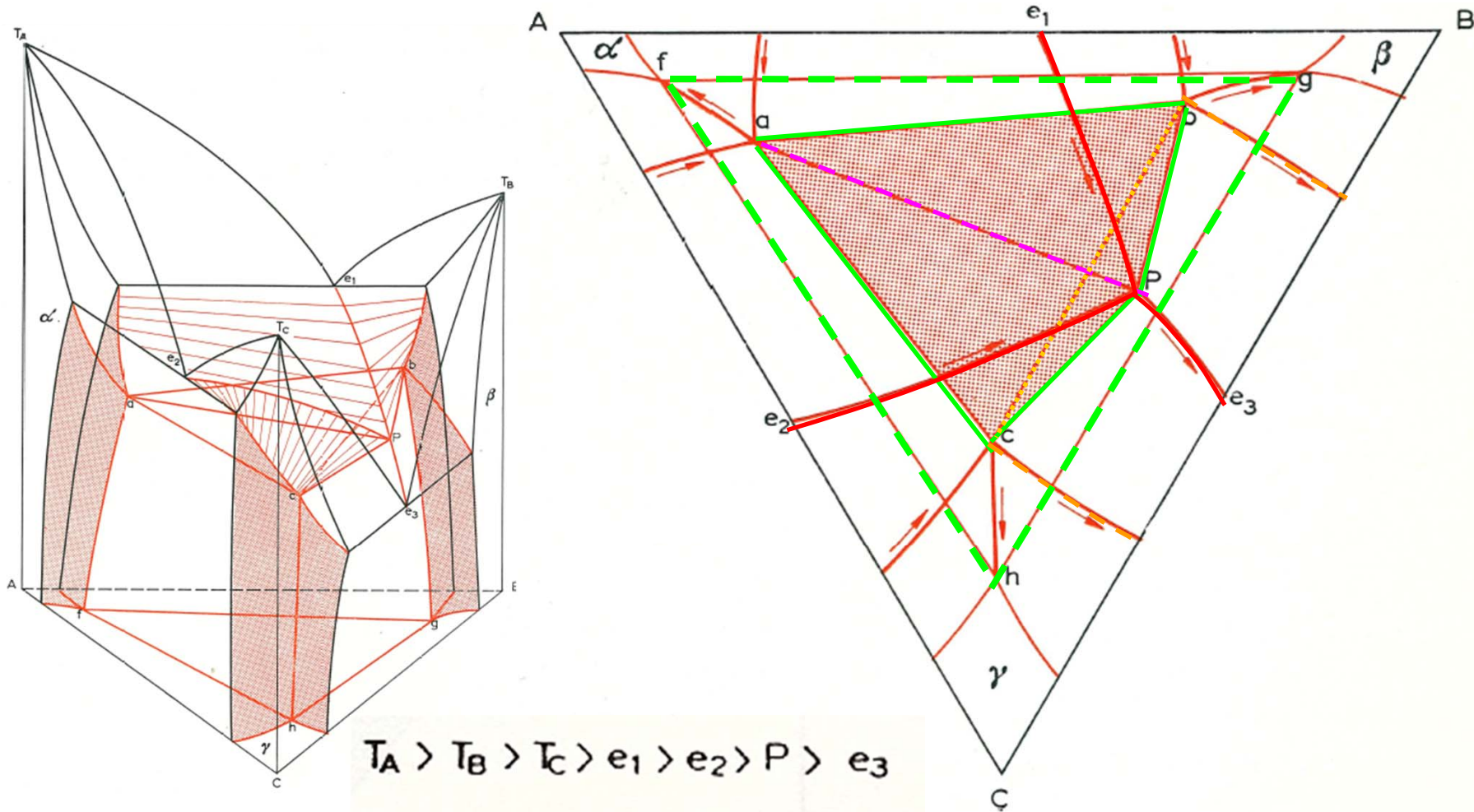


**Vertical section** which intersects point  $d_1$  on the AB binary, the tie lines  $db$  and  $Pc$ , and proceeds to the C corner

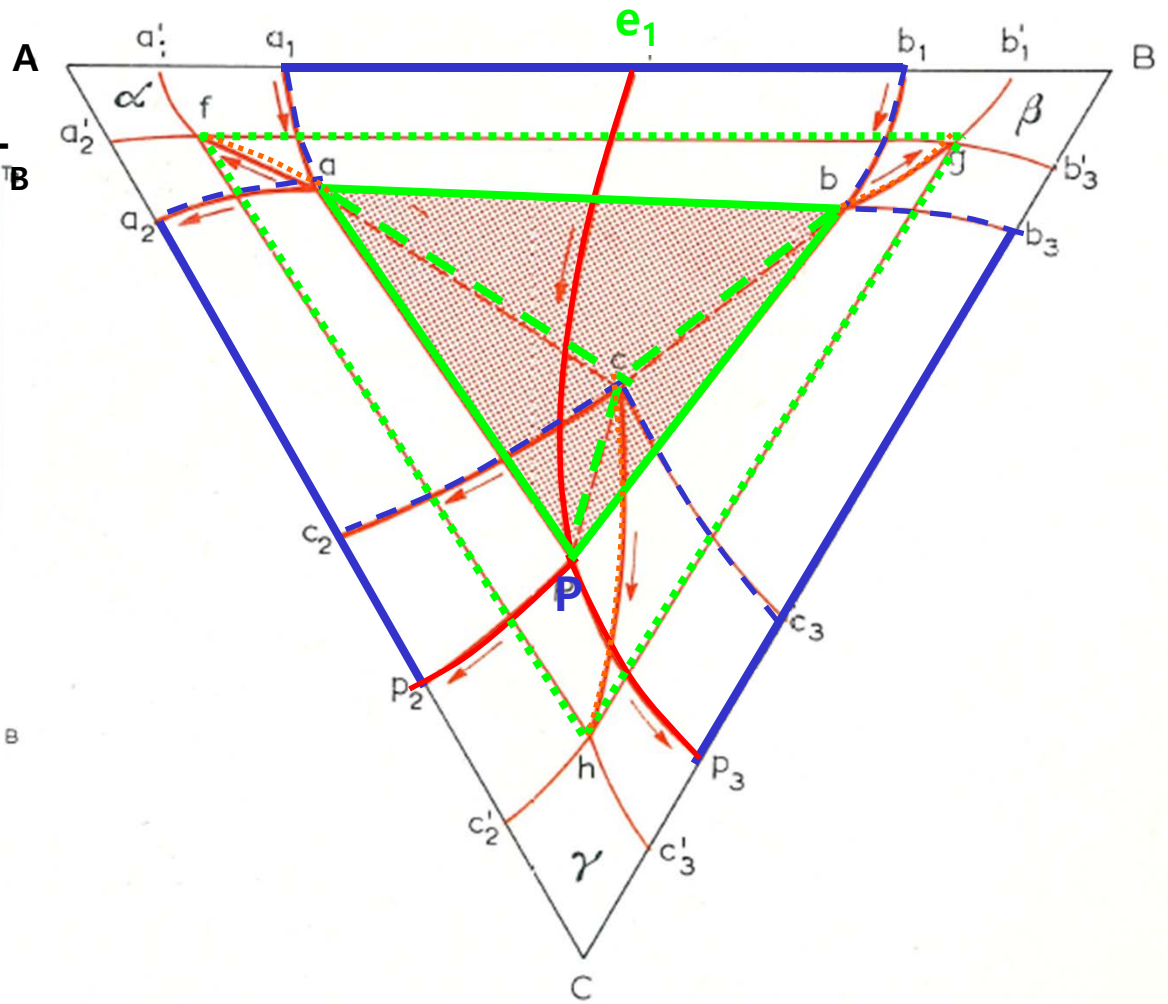
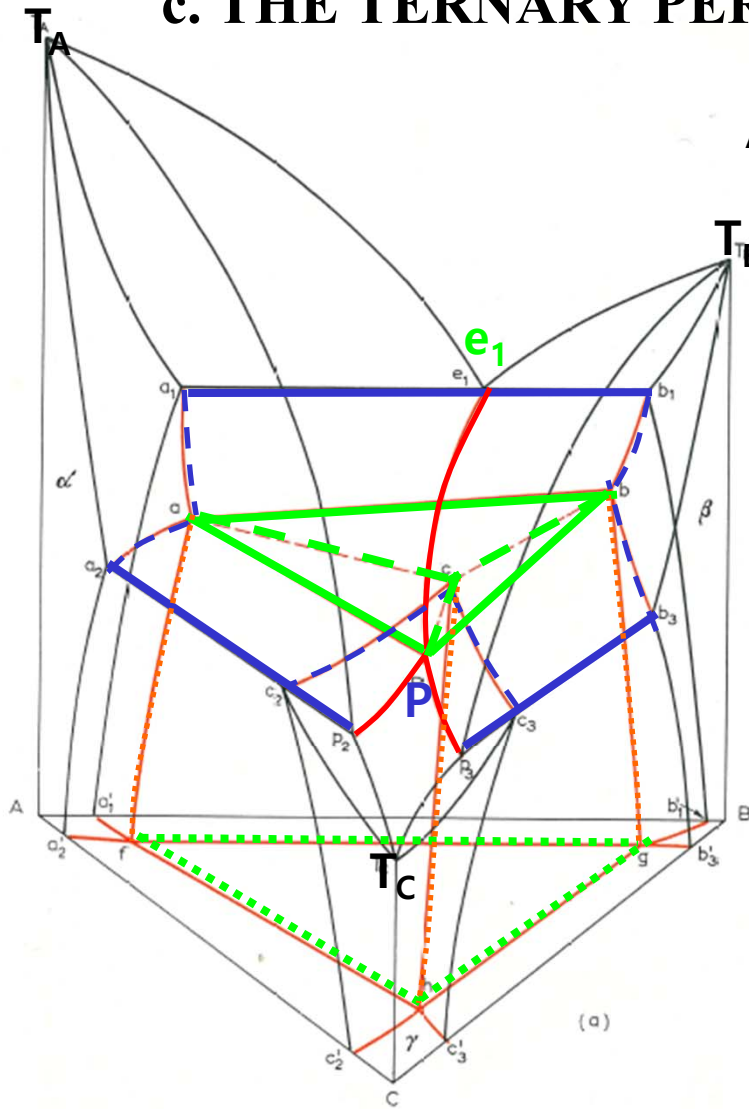


### 10.3. THE QUASI-PERITECTIC EQUILIBRIUM ( $l + \alpha = \beta + \gamma$ )

Fig. 191. The ternary quasi-peritectic system formed when all three binaries are eutectics.  
 (a) Space model; (b) projection on the concentration triangle.



### c. THE TERNARY PERIECTIC EQUILIBRIUM ( $l + \alpha + \beta = \gamma$ )



$T_A > T_B > e_1 > P > P_2 > P_3 > T_C$

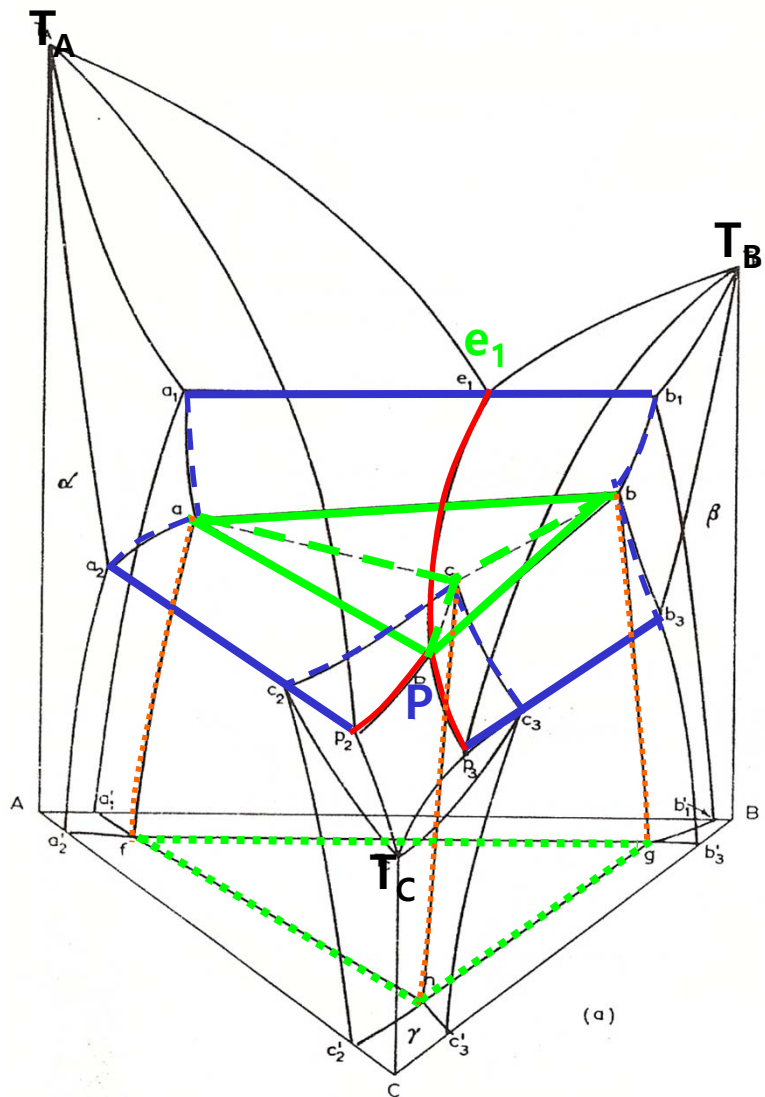
$\underline{a_1 e_1 b_1} \rightarrow abP \ (\alpha\beta L)$



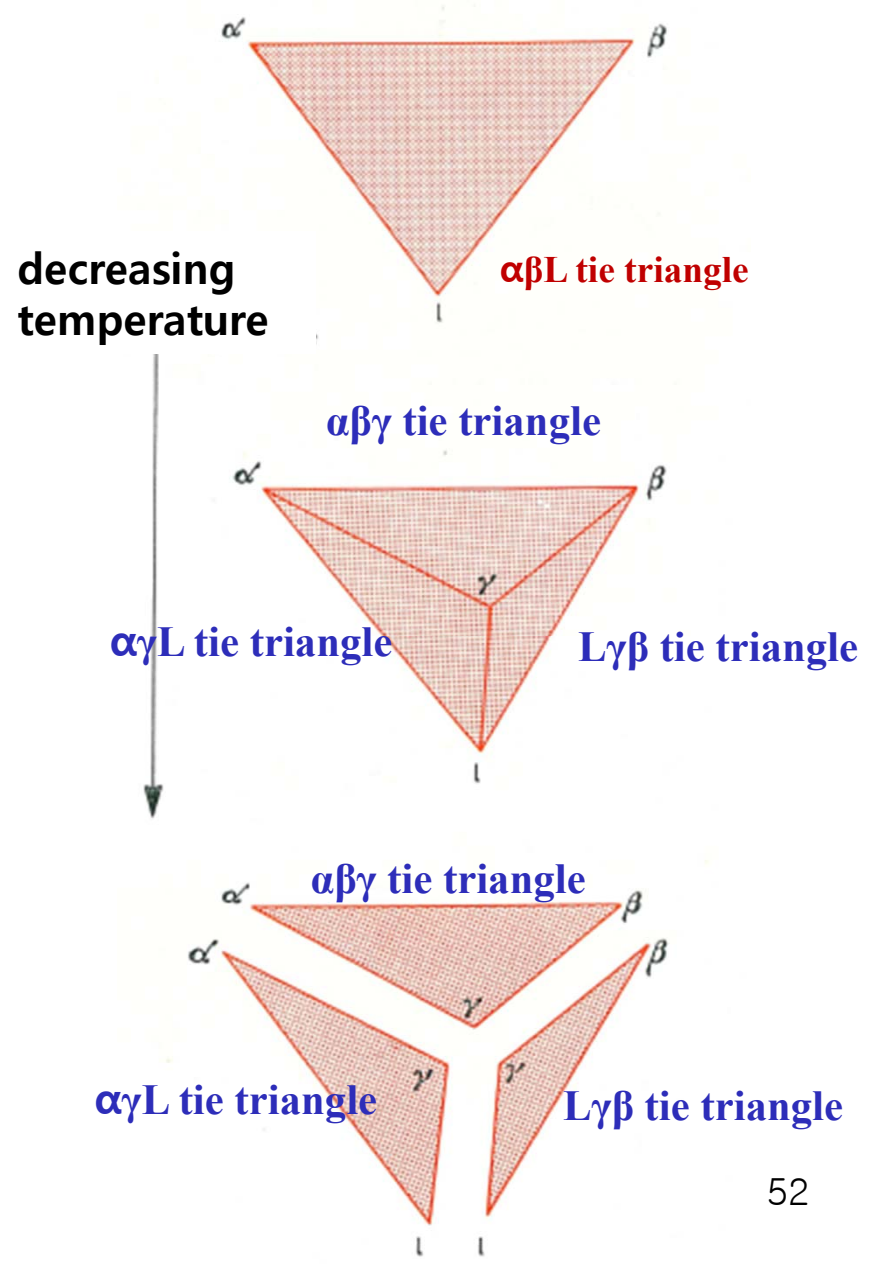
$aPc(\alpha\gamma L) \rightarrow \underline{a_2 c_2 P_2} / Pcb(L\gamma\beta) \rightarrow \underline{P_3 c_3 b_3} / abc(\alpha\beta\gamma) \rightarrow fgh \ (\alpha\beta\gamma)$



# 10.4. THE TERNARY PERIECTIC EQUILIBRIUM ( $l + \alpha + \beta = \gamma$ )

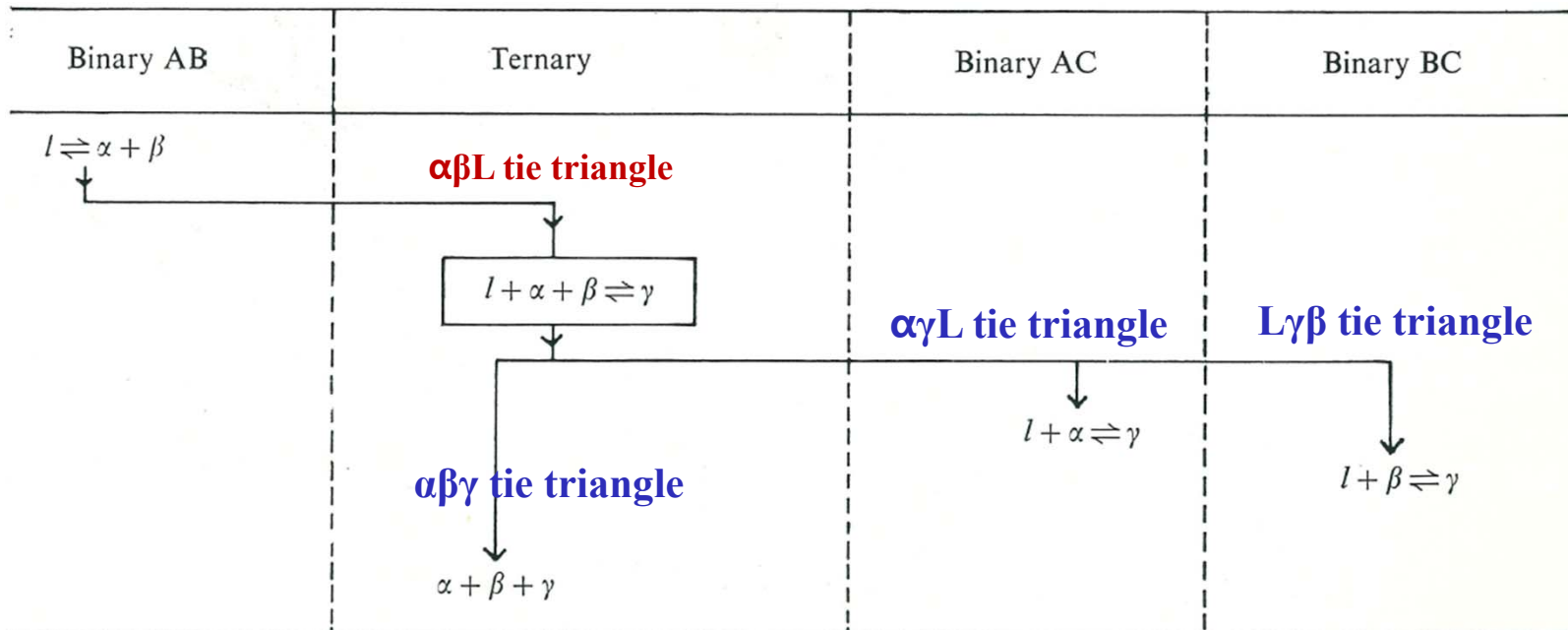


$$T_A > T_B > e_1 > P > P_2 > P_3 > T_C$$



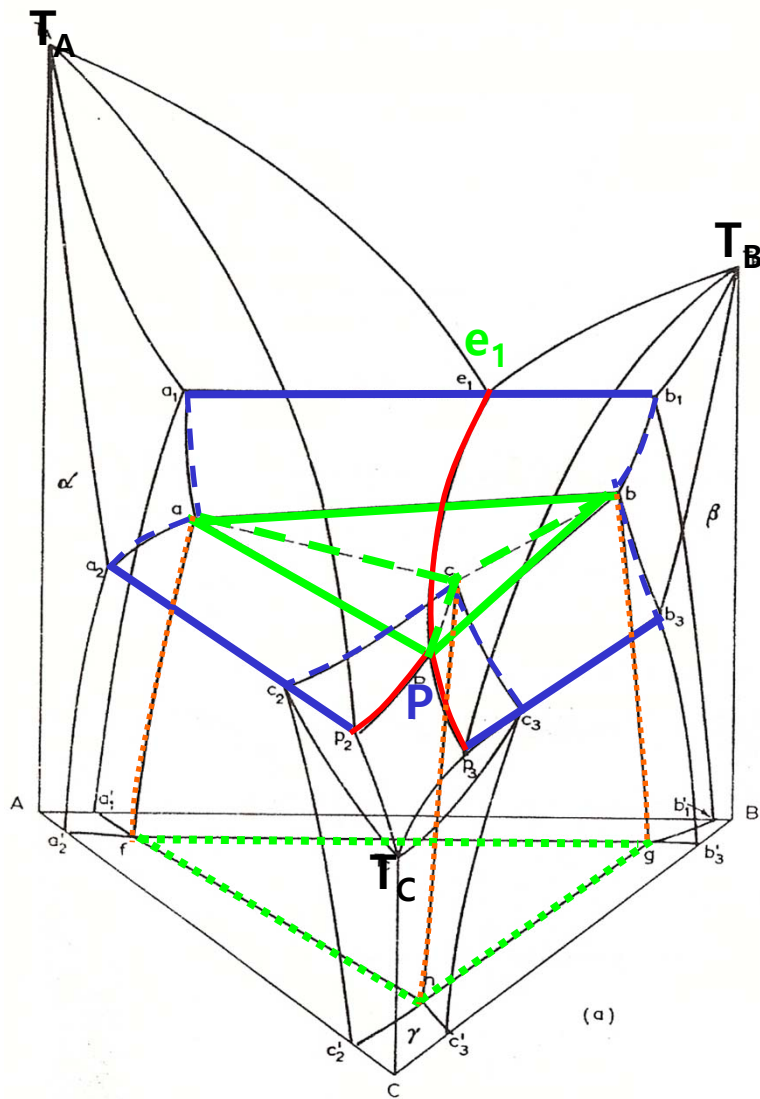
**Tabular representation of ternary equilibria:  
interlinks the binary and ternary reactions in tabular form**

TERNARY PERITECTIC EQUILIBRIUM  $l + \alpha + \beta \rightleftharpoons \gamma$



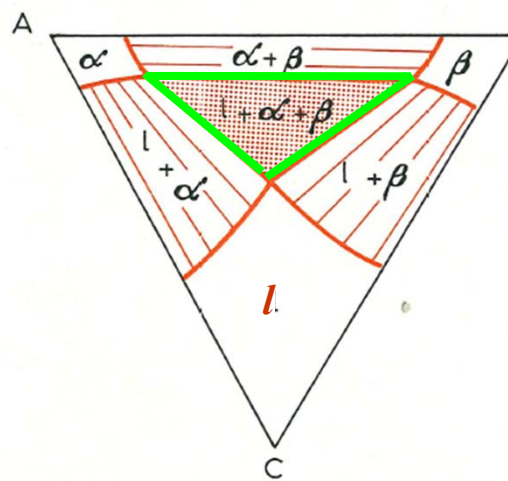


# 10.4. THE TERNARY PERIECTIC EQUILIBRIUM ( $l + \alpha + \beta = \gamma$ )

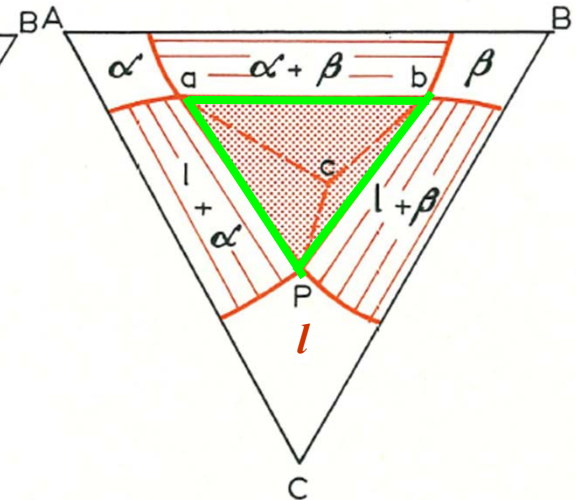


$$T_A > T_B > e_1 > P > P_2 > P_3 > T_C$$

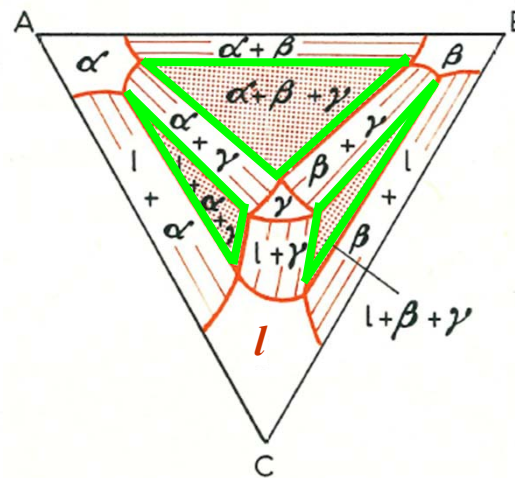
Isothermal section



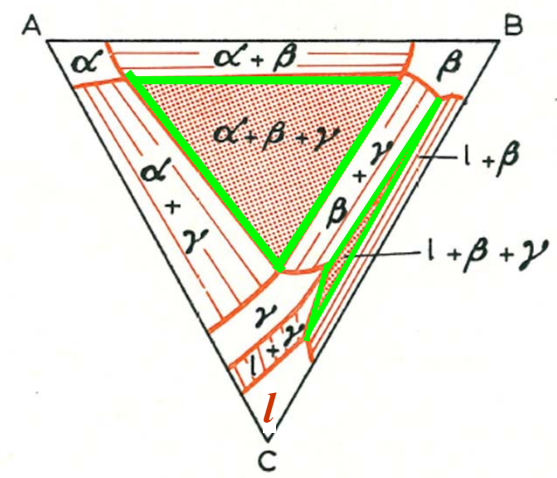
$$e_1 > T > P$$



$$T = P$$

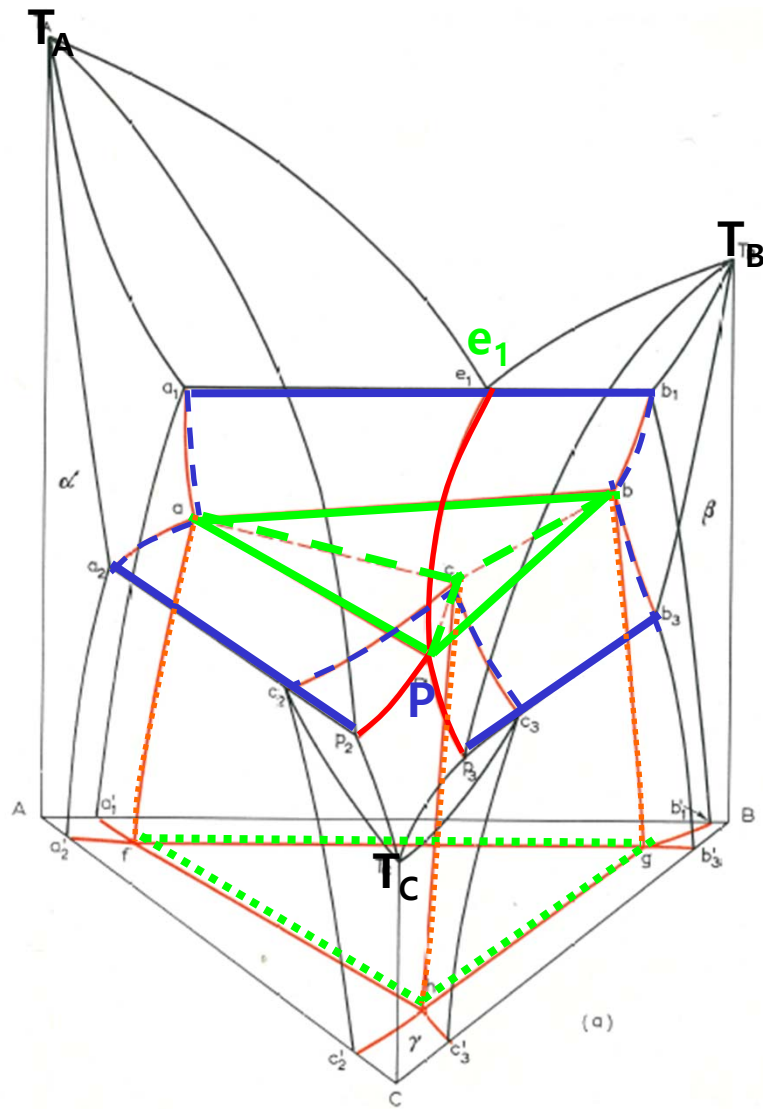


$$P > T > P_2$$

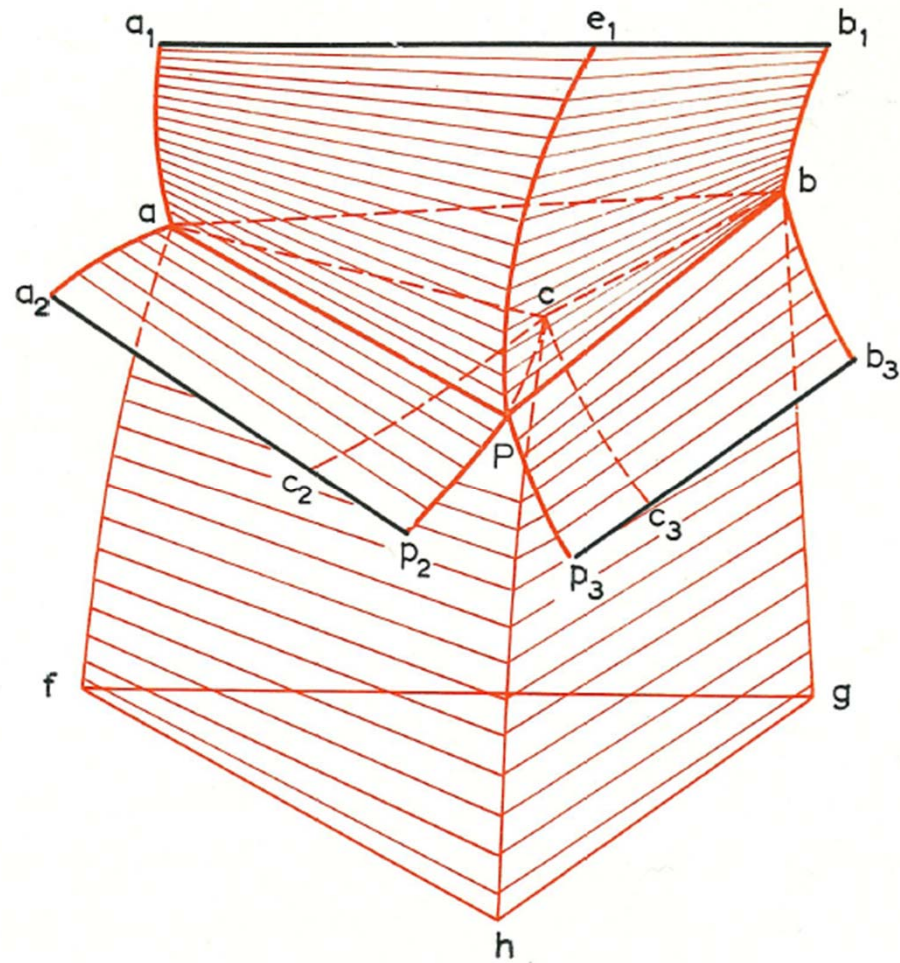


$$P_2 > T > P_3$$

## 10.4. THE TERNARY PERIECTIC EQUILIBRIUM ( $l + \alpha + \beta = \gamma$ )



$$T_A > T_B > e_1 > P > P_2 > P_3 > T_C$$



The ternary peritectic four-phase plane  
as the junction of four tie triangles

# 10.4. THE TERNARY PERIECTIC EQUILIBRIUM ( $l + \alpha + \beta = \gamma$ )

