2019 Spring

“Phase Equilibria *in* Materials”

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Eun Soo Park

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

Chapter 10. Ternary phase Diagrams

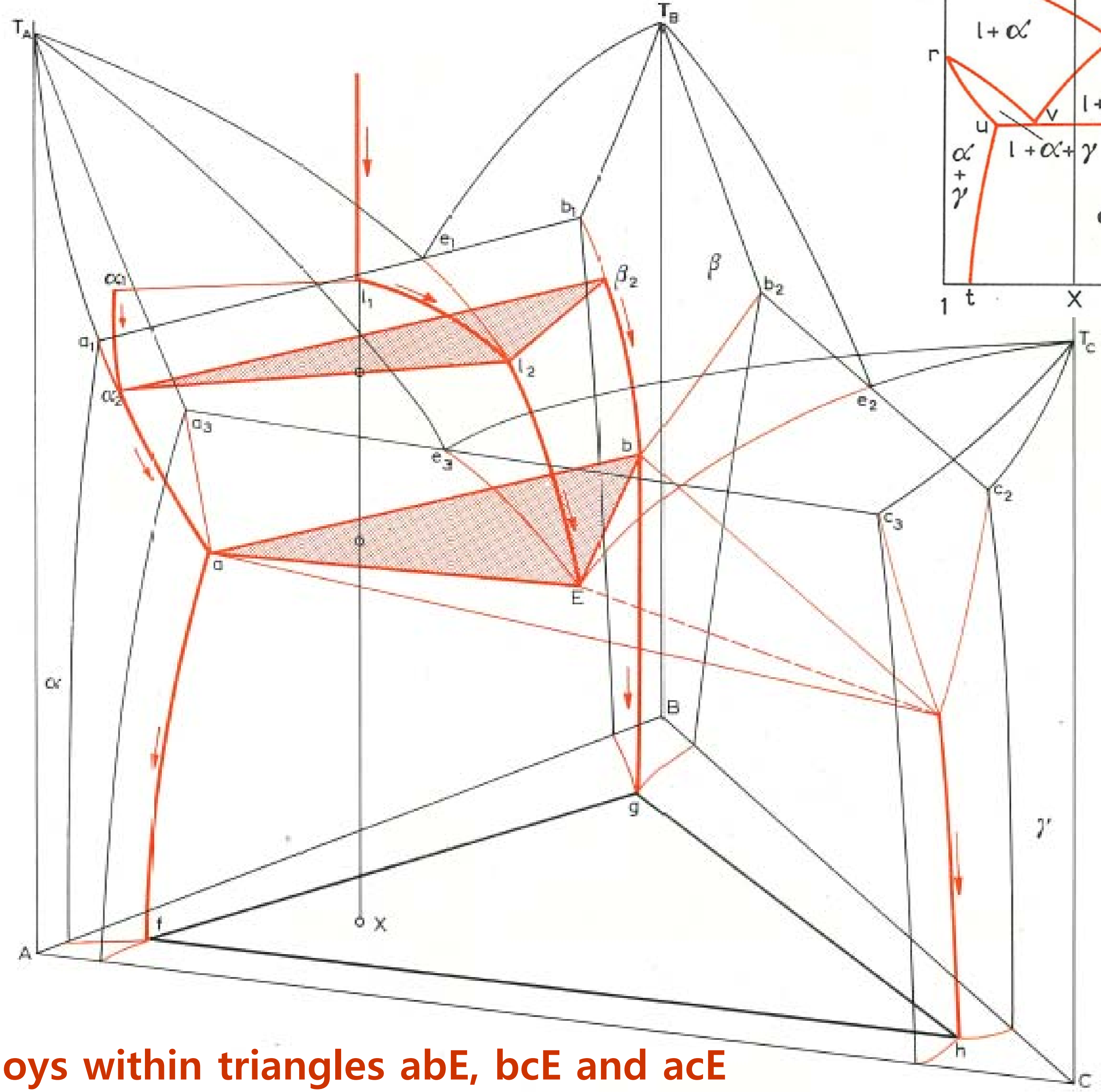
Four-Phase Equilibrium

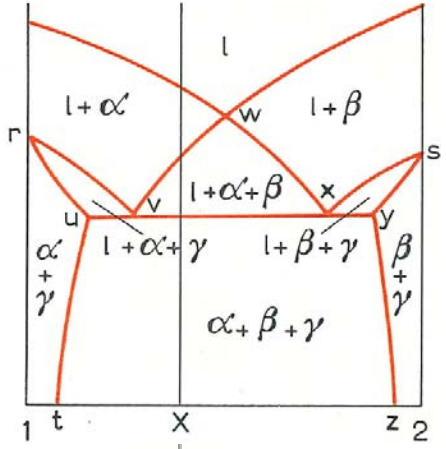
a. THE TERNARY EUTECTIC EQUILIBRIUM ($l = \alpha + \beta + \gamma$)

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

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

Transformation during cooling



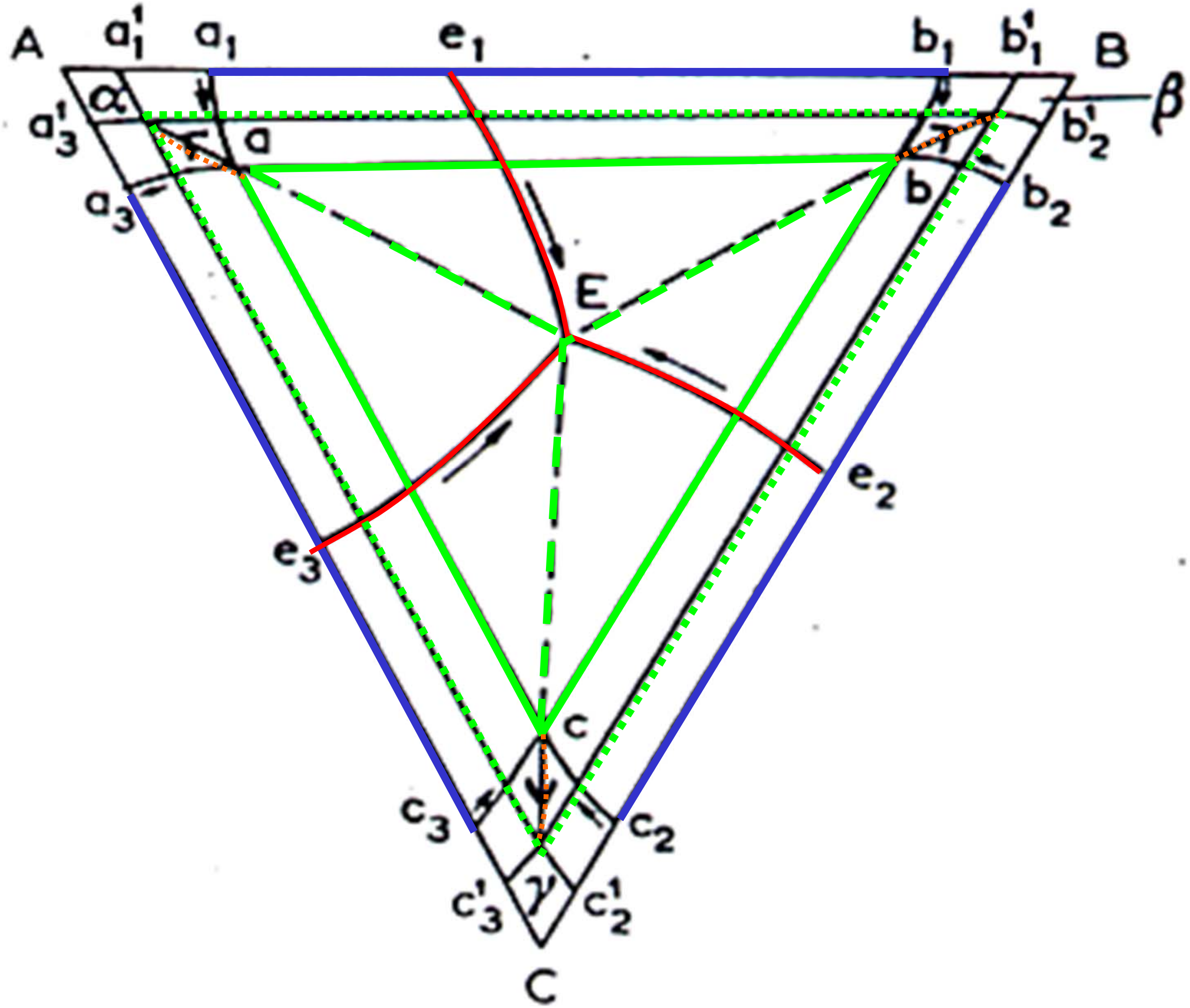


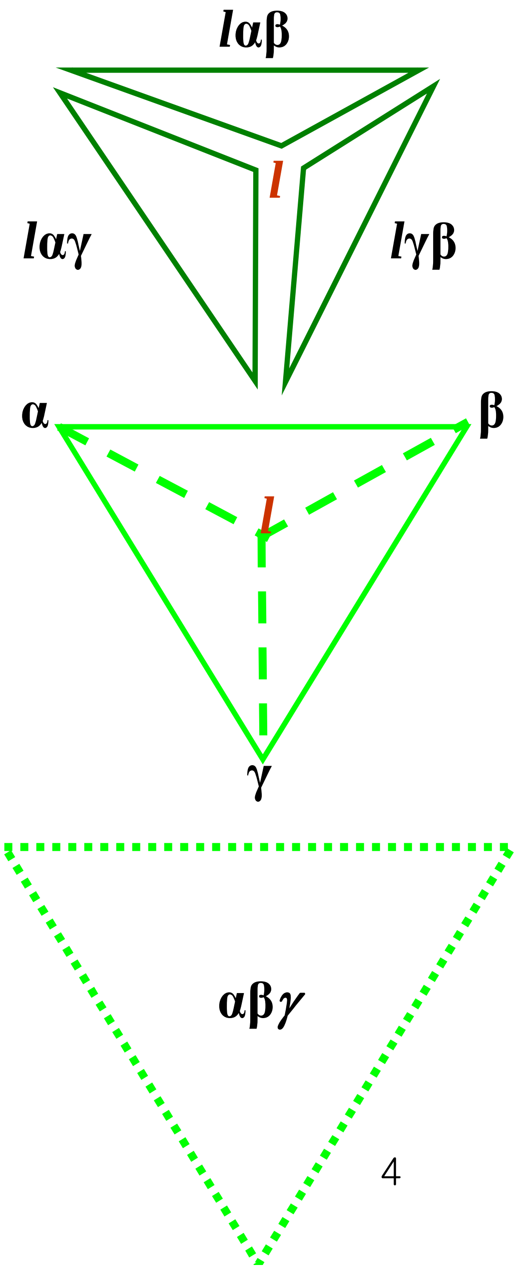
④ Alloys within triangles abE, bcE and acE

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

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

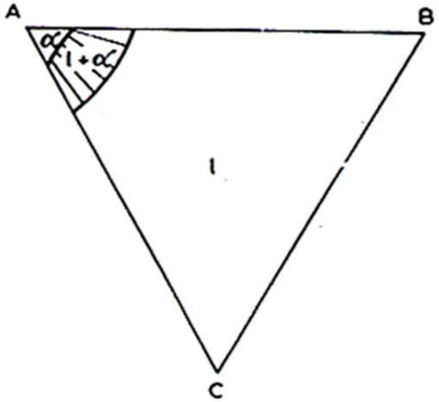
- **Projection** : solid solubility limit surface
  : monovariant liquidus curve



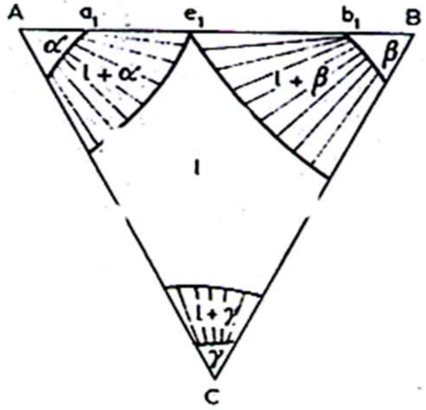


10.1. THE EUTECTIC EQUILIBRIUM ($l = \alpha + \beta + \gamma$)

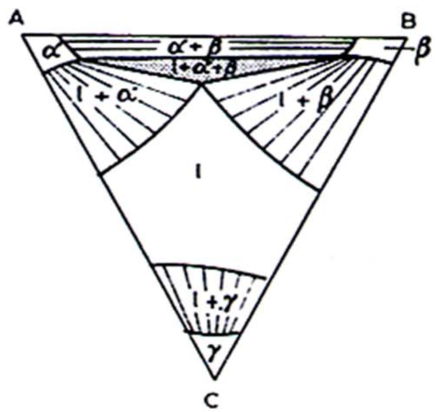
- **Isothermal section** ($T_A > T > T_B$)



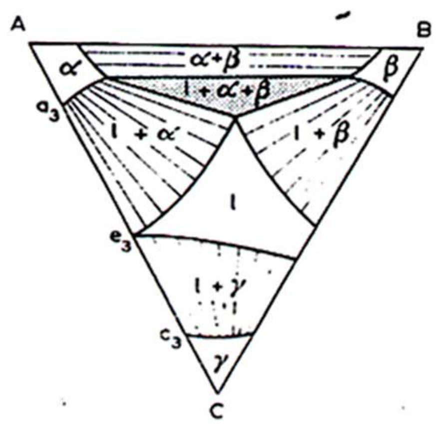
(a) $T_A > T > T_B$



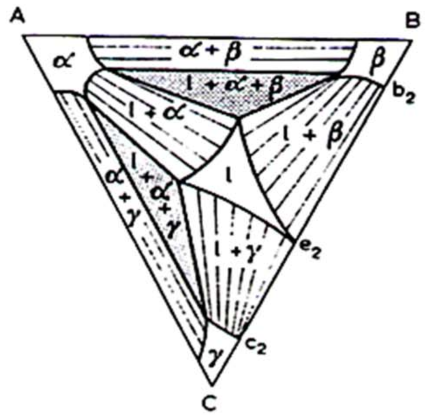
(b) $T = e_1$



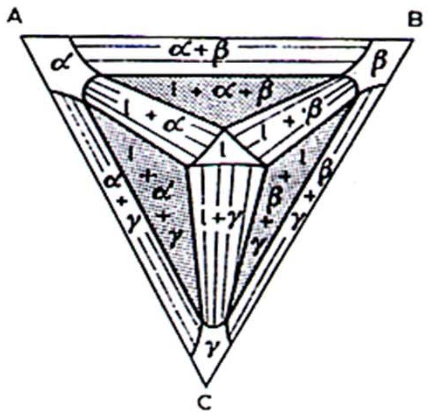
(c) $e_1 > T > e_3$



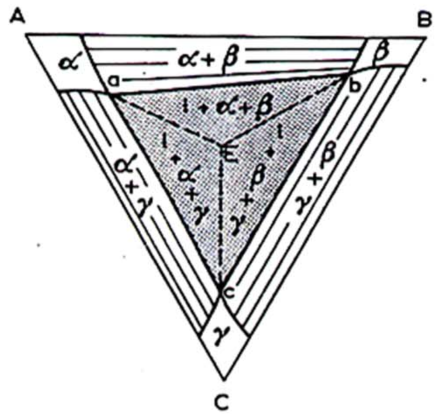
(d) $T = e_3$



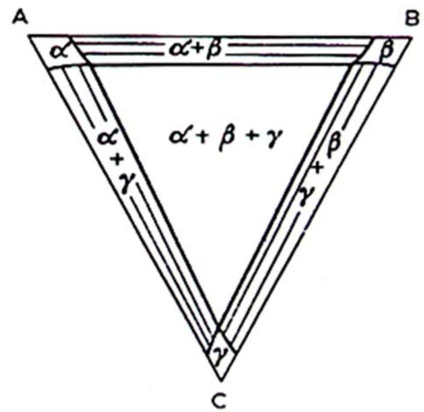
(e) $T = e_2$



(f) $e_2 > T > E$

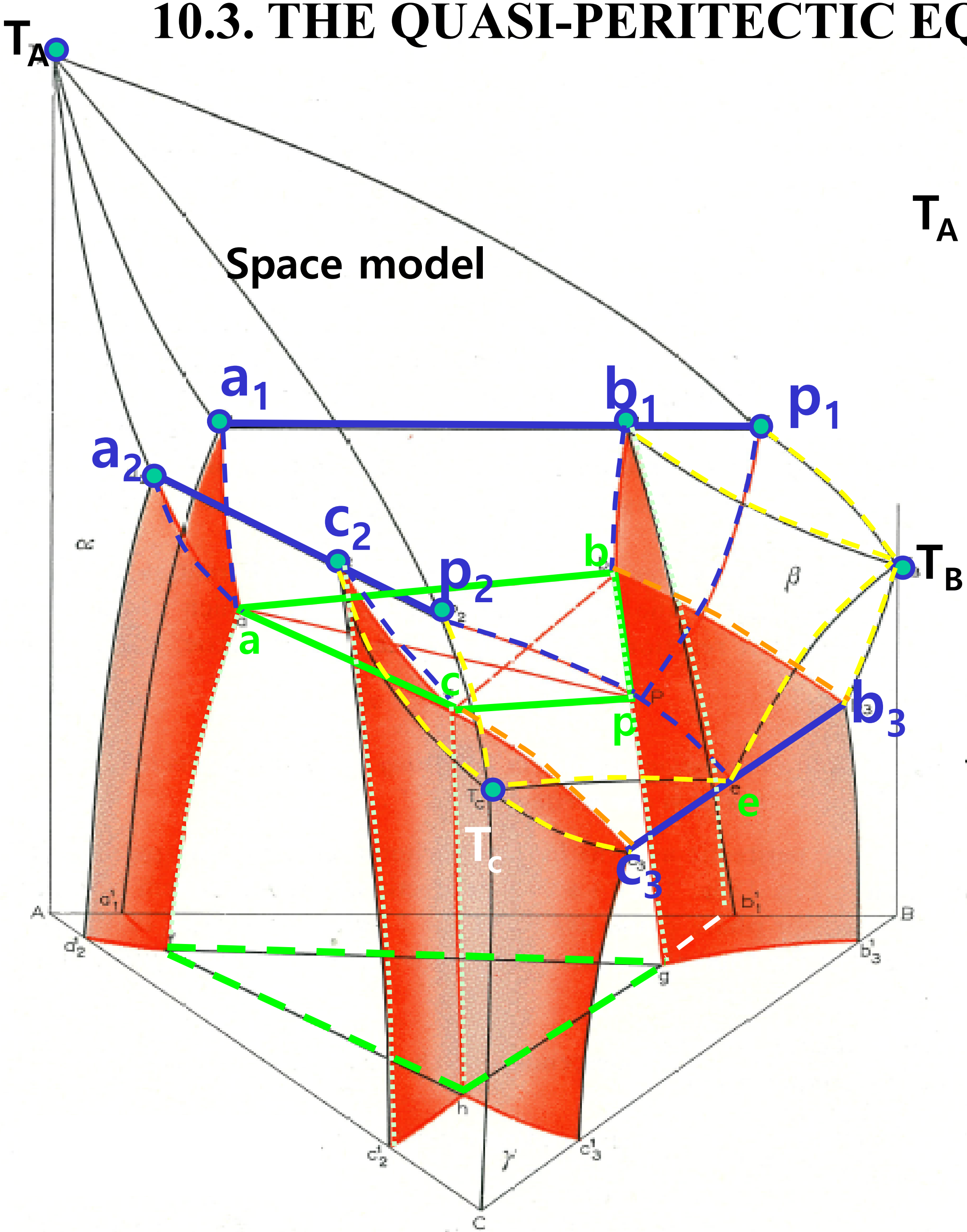


(g) $T_A = E$



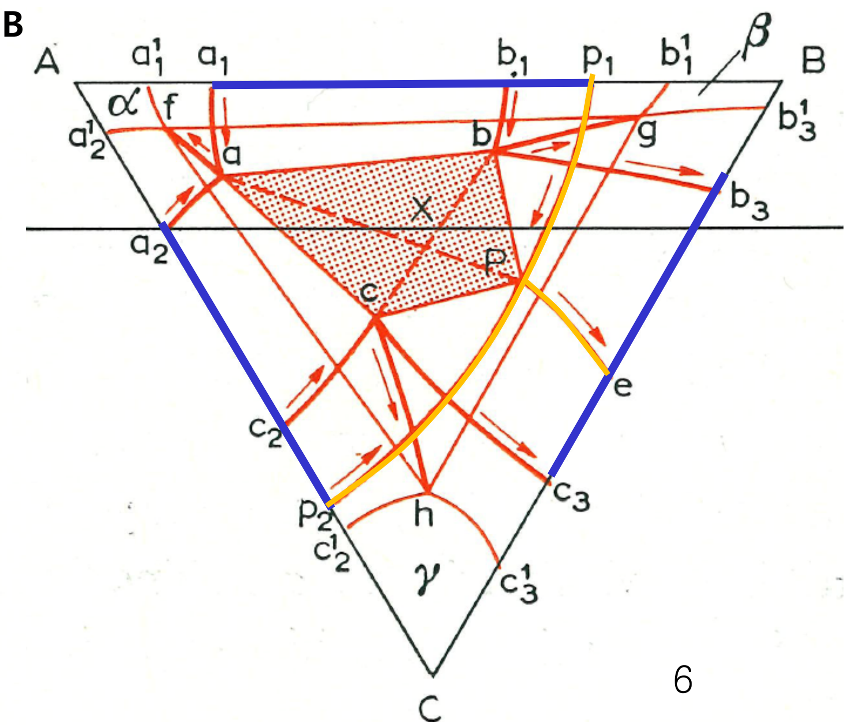
(h) $E = T$

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

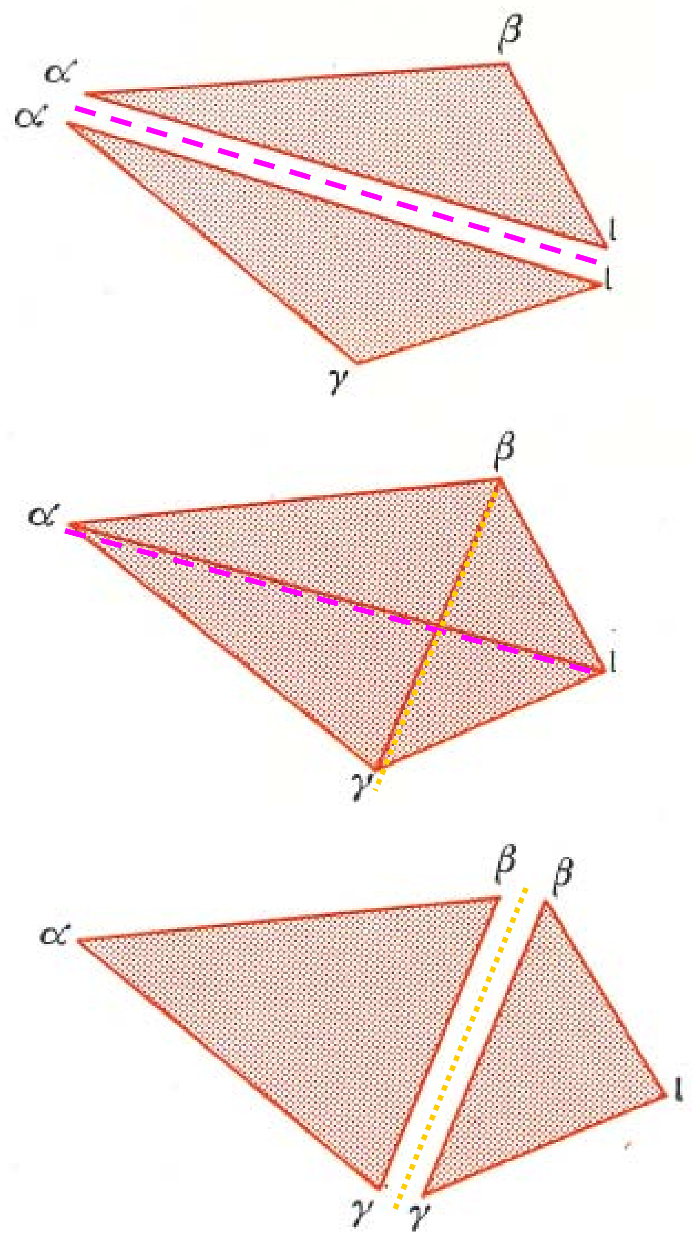


$T_A > P_1 > P_2 > T_B > P > T_C > e$

Projection



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



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

abP peritectic lαβ equilibrium

acP peritectic lαγ equilibrium

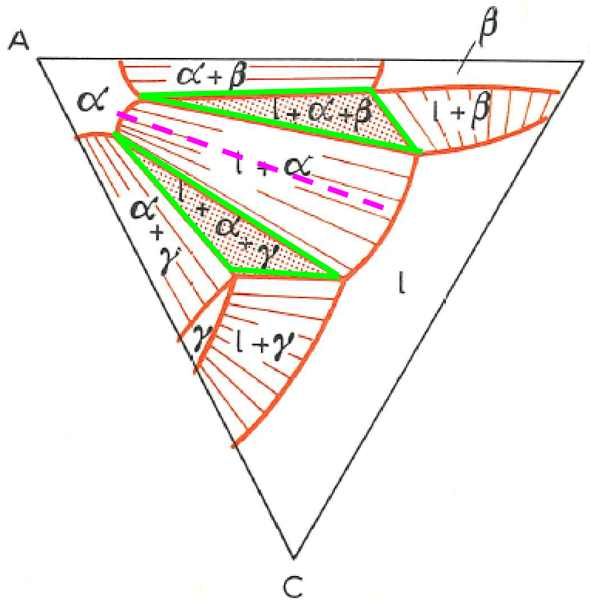
decreasing temperature

bcP eutectic lβγ equilibrium

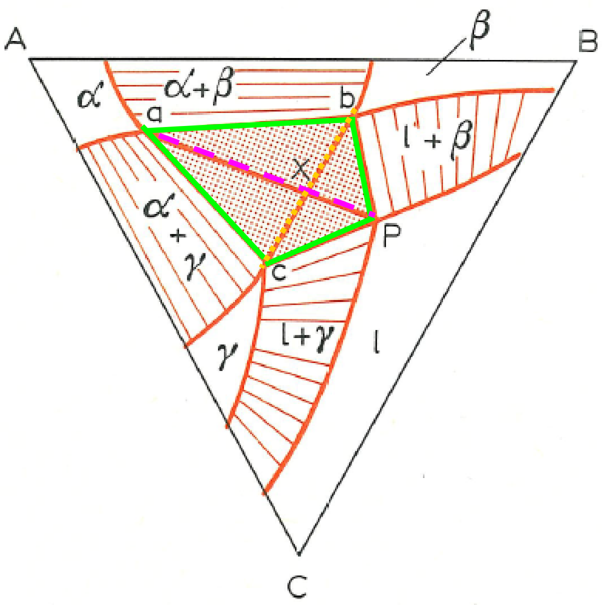
abc peritectic αβγ equilibrium

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

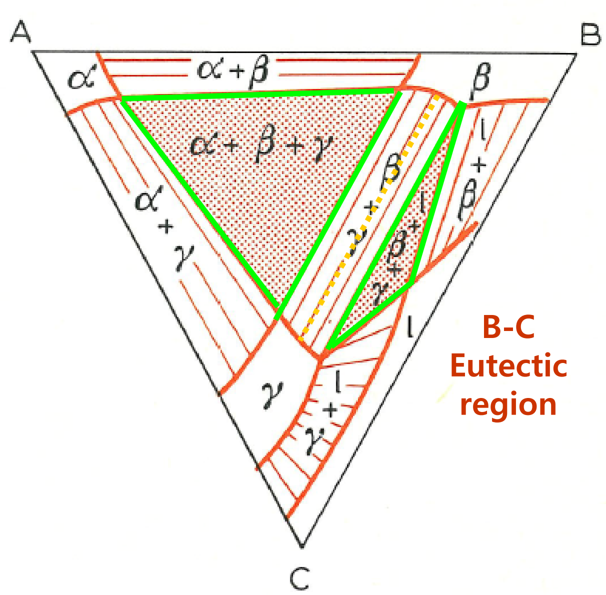
Isothermal section



$T_B > T > P$



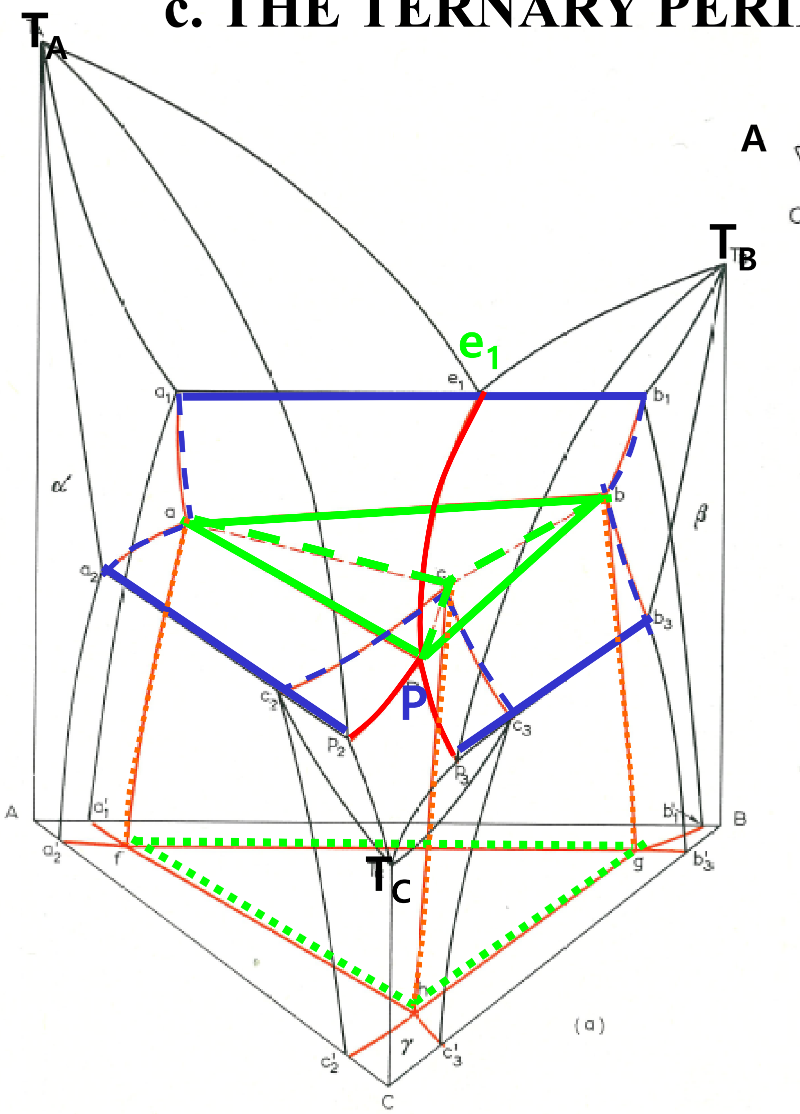
$T = P$

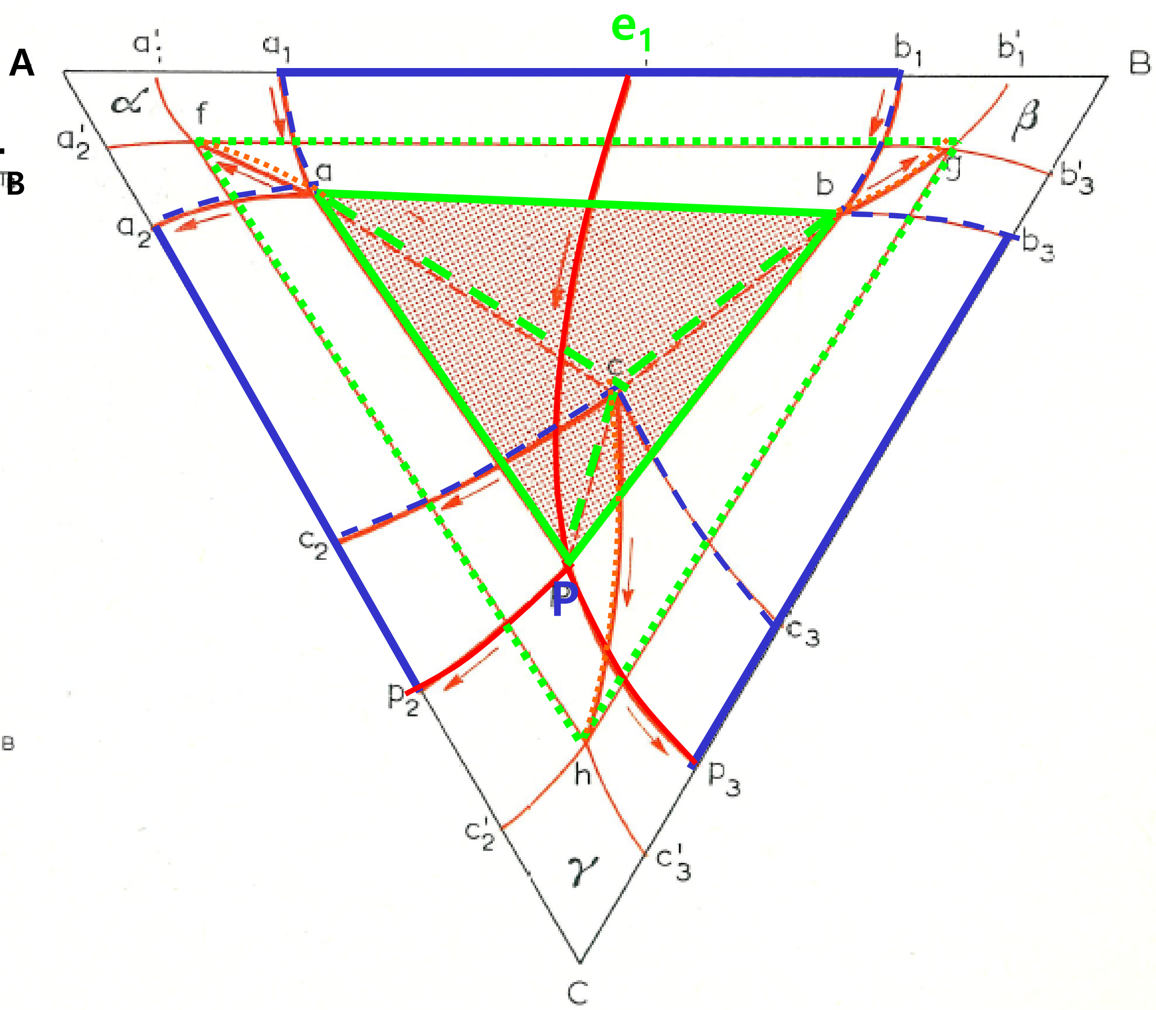


$P > T > T_C$

abP	peritectic $l\alpha\beta$ equilibrium	descending to the four-phase plane;
acP	peritectic $l\alpha\gamma$ equilibrium	
bcP	eutectic $l\beta\gamma$ equilibrium	descending from the four-phase plane.
abc	$\alpha\beta\gamma$ equilibrium	

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



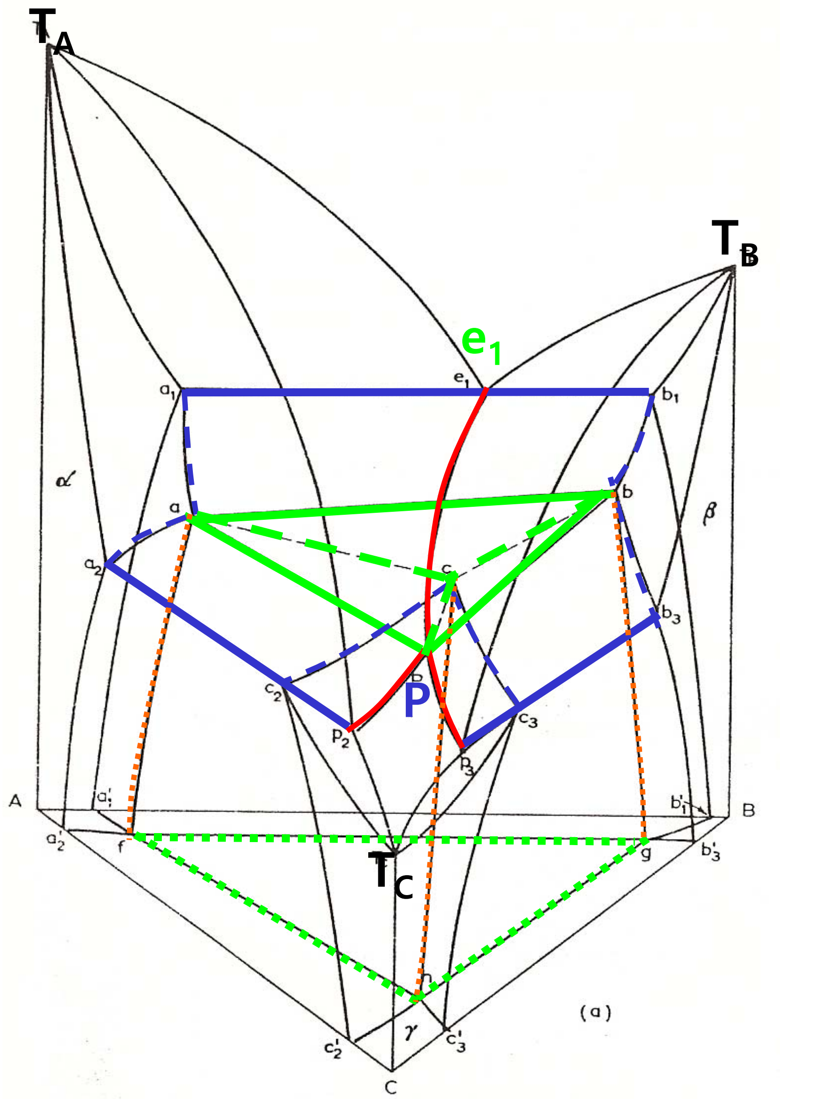


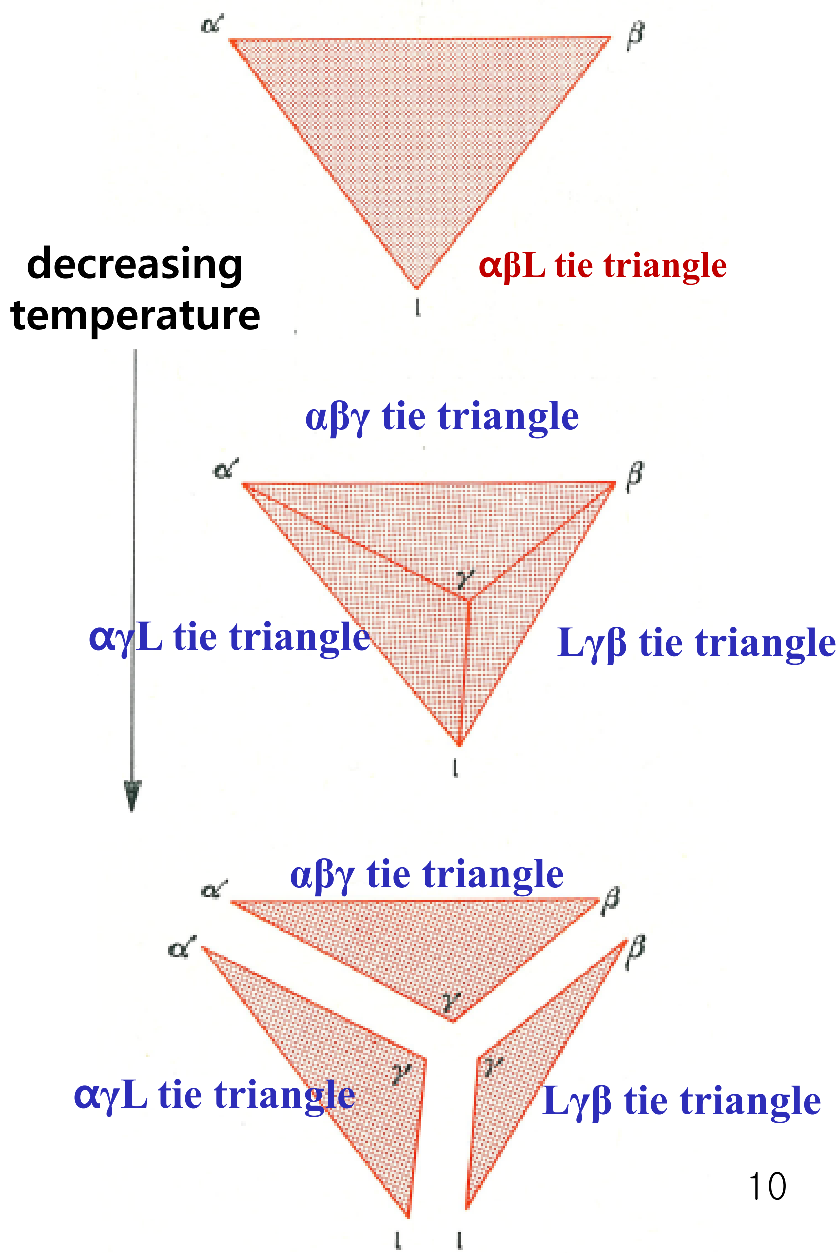
$\underline{a_1 e_1 b_1} \rightarrow$ abP ($\alpha\beta L$)

$T_A > T_B > \underline{e_1 > P > P_2 > P_3} > T_C$

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 ($\alpha\beta\gamma$)

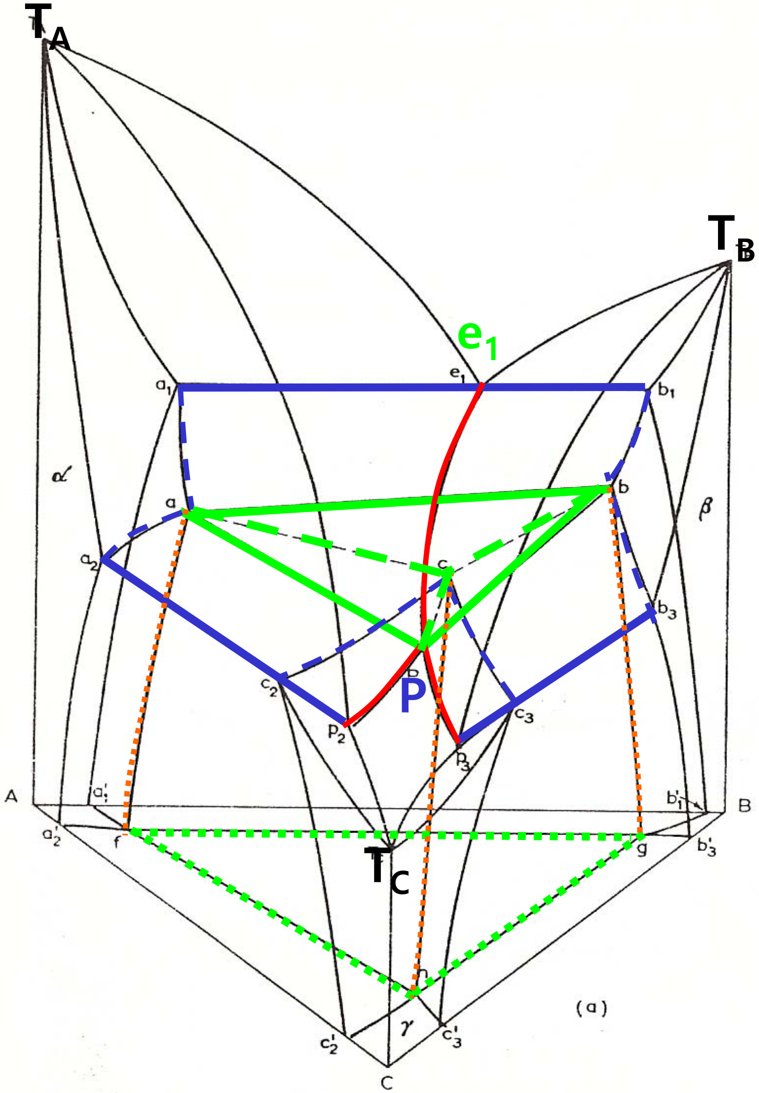
10.4. THE TERNARY PERIECTIC EQUILIBRIUM ($l + \alpha + \beta = \gamma$)





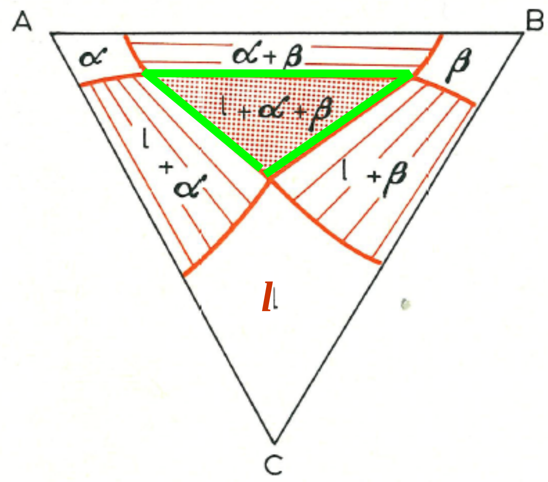
$T_A > T_B > e_1 > P > P_2 > P_3 > T_C$

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

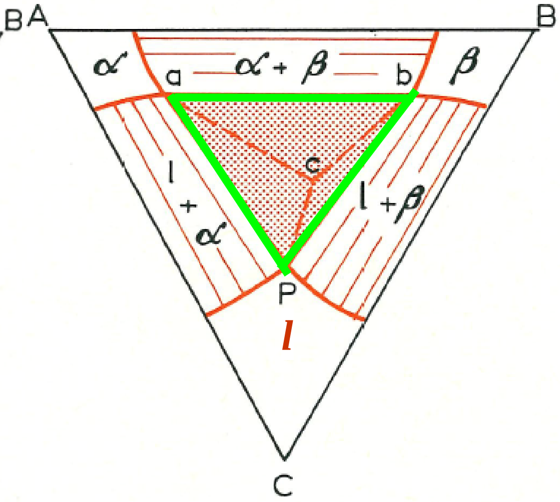


$T_A > T_B > e_1 > P > P_2 > P_3 > T_C$

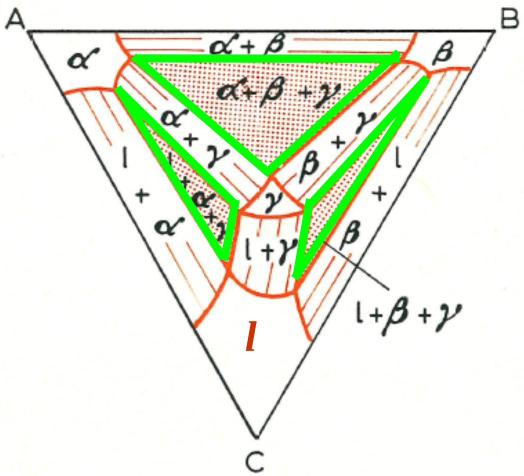
Isothermal section



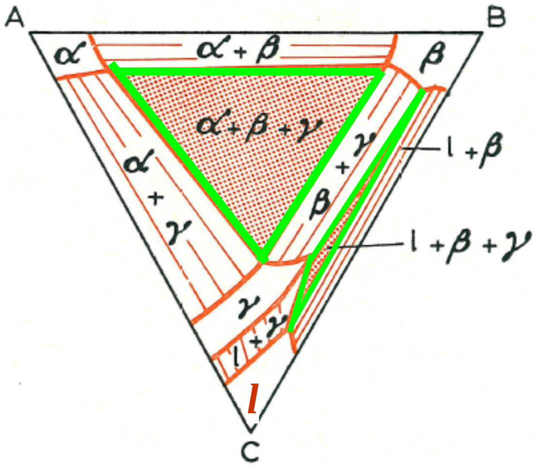
$e_1 > T > P$



$T = P$



$P > T > P_2$



$P_2 > T > P_3$

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

*** Ternary system involving an incogruently-melting binary intermediate phase:**

Quasi-peritectic diagram and ternary eutectic diagram

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

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

⇓

$d^1\varepsilon c(\delta + \gamma + L)$ / $gfn(\beta + \delta + \gamma)$

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

⇓

Jkm $(\alpha + \gamma + \delta)$

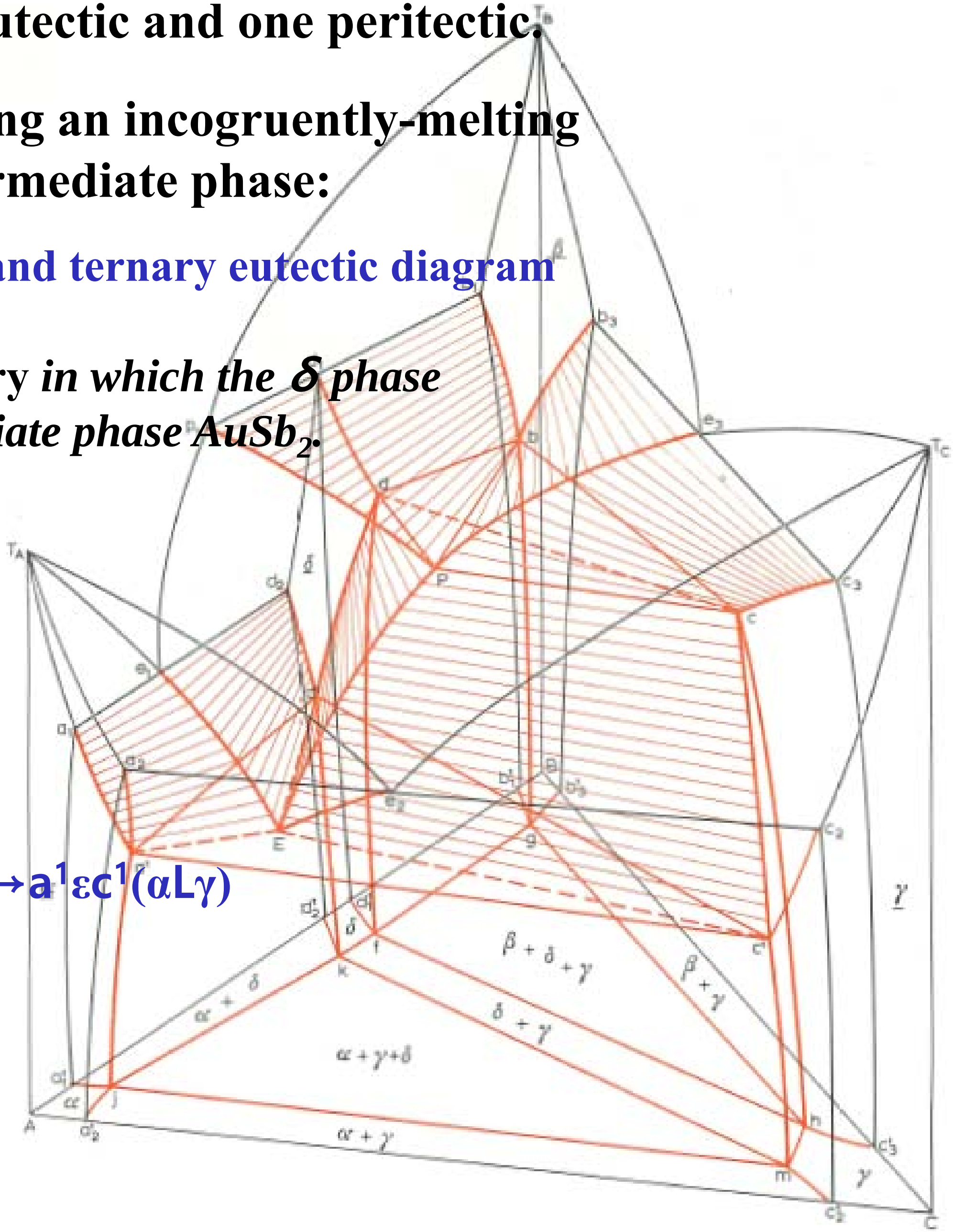
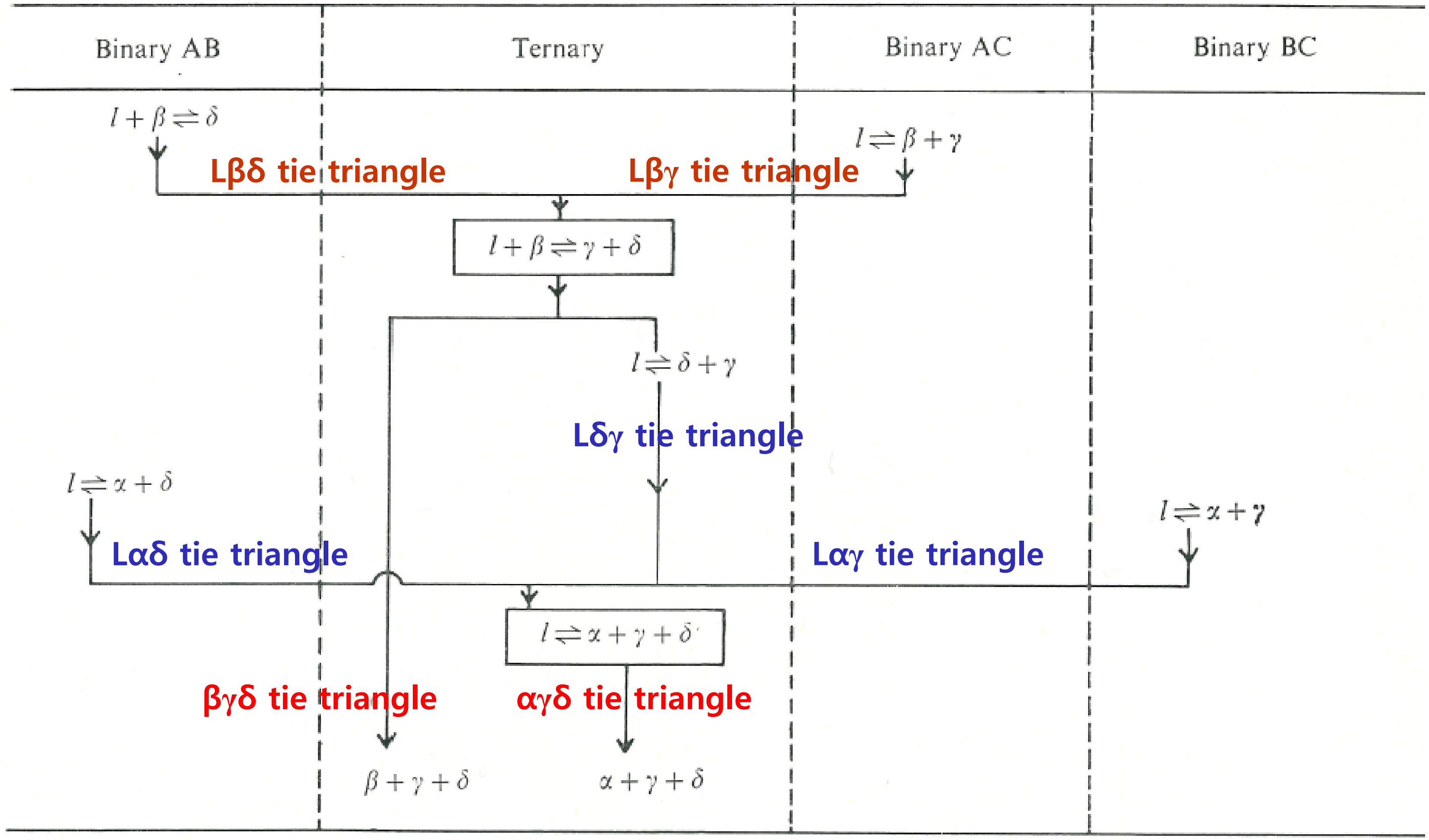


Fig. 189. Ternary system involving an incongruently-melting binary intermediate phase.

Tabular representation of ternary equilibria:

interlinks the binary and ternary reactions in tabular form

Quasi-peritectic diagram and ternary eutectic diagram



Chapter 11. Ternary phase Diagrams

Intermediate Phases

Intermdediate phases may melt congruently or incongruently.

They may occur as either binary or ternary phases.

11.1 Congruently melting intermediate phases

11.1. Binary intermediate phases

- **Assume the AB system contains an intermediate phase δ.**
- **The ternary will contain the five phases α, β, γ, δ and liquid.**
- **Since the maximum number of phases which can coexist is four, there must be more than one four-phase equilibrium in the ternary.**

$$l \leftrightarrow \alpha + \beta + \gamma$$

$$l \leftrightarrow \alpha + \beta + \delta$$

$$l \leftrightarrow \alpha + \gamma + \delta$$

$$l \leftrightarrow \beta + \gamma + \delta$$

- **The more usual combination is of the last two equilibria, implying equilibrium in the solid state between αγδ and βγδ.**

- **This can be envisaged if there is direct equilibrium between γ and δ, splitting the ternary system into two partial system AδC and BδC. It often happens that the δ phase forms 1) a quasi-binary system with component C.**

11.1 Congruently melting intermediate phases

$l \leftrightarrow \alpha + \beta + \gamma$

$l \leftrightarrow \alpha + \beta + \delta$

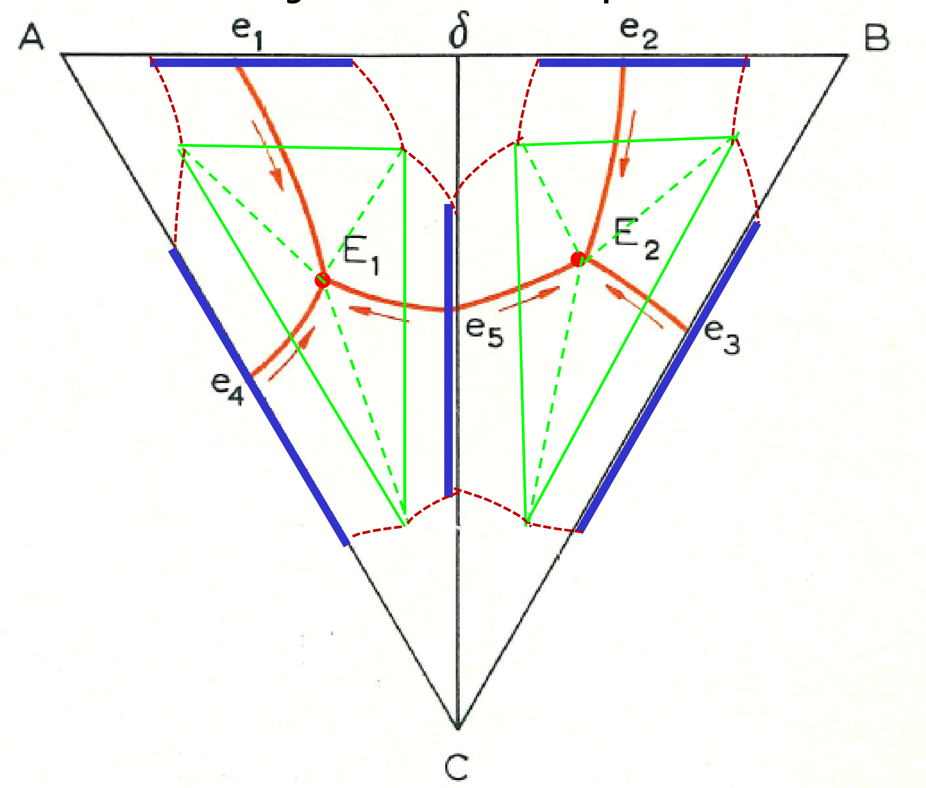
$l \leftrightarrow \alpha + \gamma + \delta$

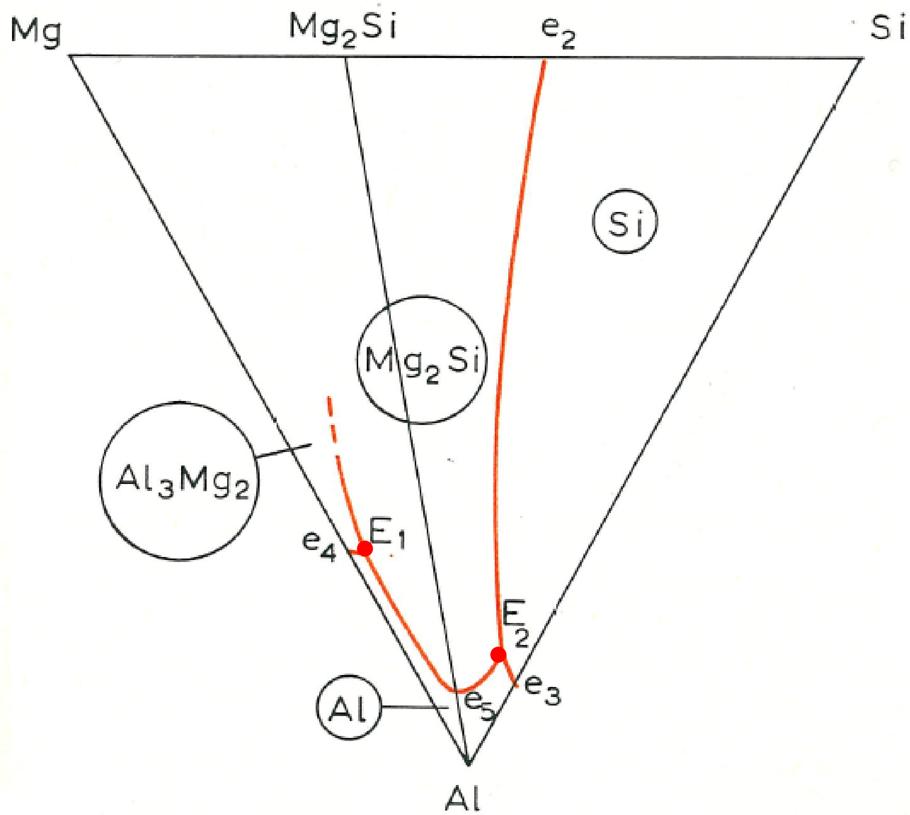
$l \leftrightarrow \beta + \gamma + \delta$

11.1. Binary intermediate phases

1) Quasi binary eutectic δC

Congruent intermediate phase, δ





E_1: L→α+γ+δ , E_2: L→β+γ+δ

Eutectic systems with a saddle point on the quasi-binary section δC

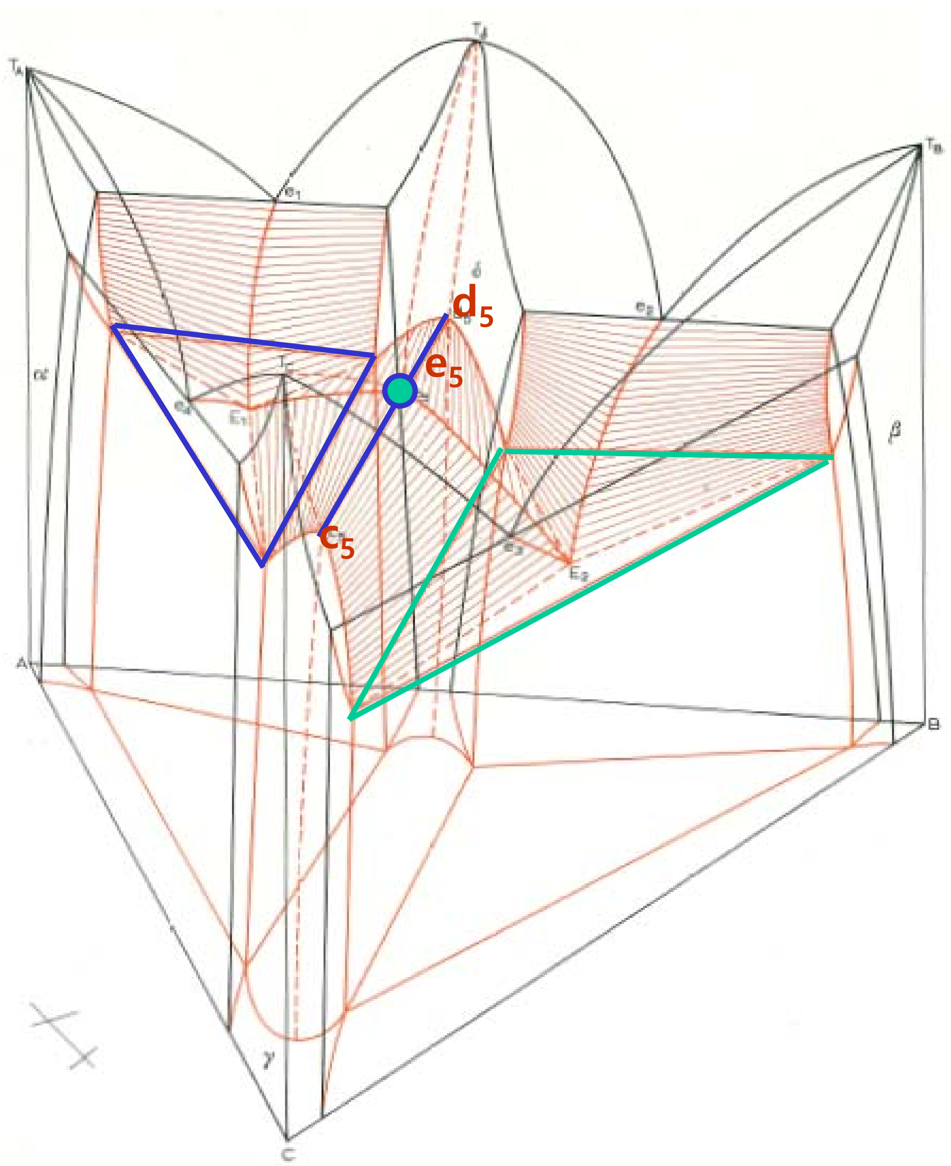
Al-Mg-Si system

E_1: L→α-Al+Si+Mg_2Si

E_2: L→α-Al+Al_3Mg_2+Mg_2Si

11.1 Congruently melting intermediate phases

11.1. Binary intermediate phases



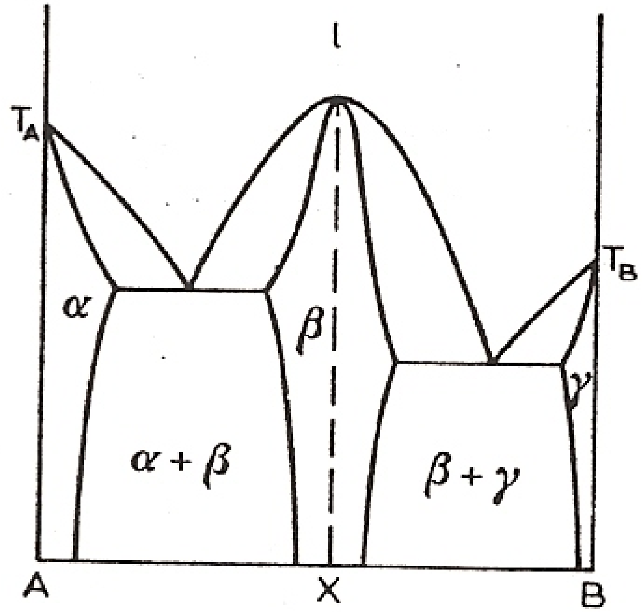


Fig. 78. Phase diagram with a congruent intermediate phase.

the eutectic point e5 on the quasi-bniary section δC is saddle point.

the straight line is the quasi-binary eutectic horizontal c5e5d5.

11.1. Binary intermediate phases

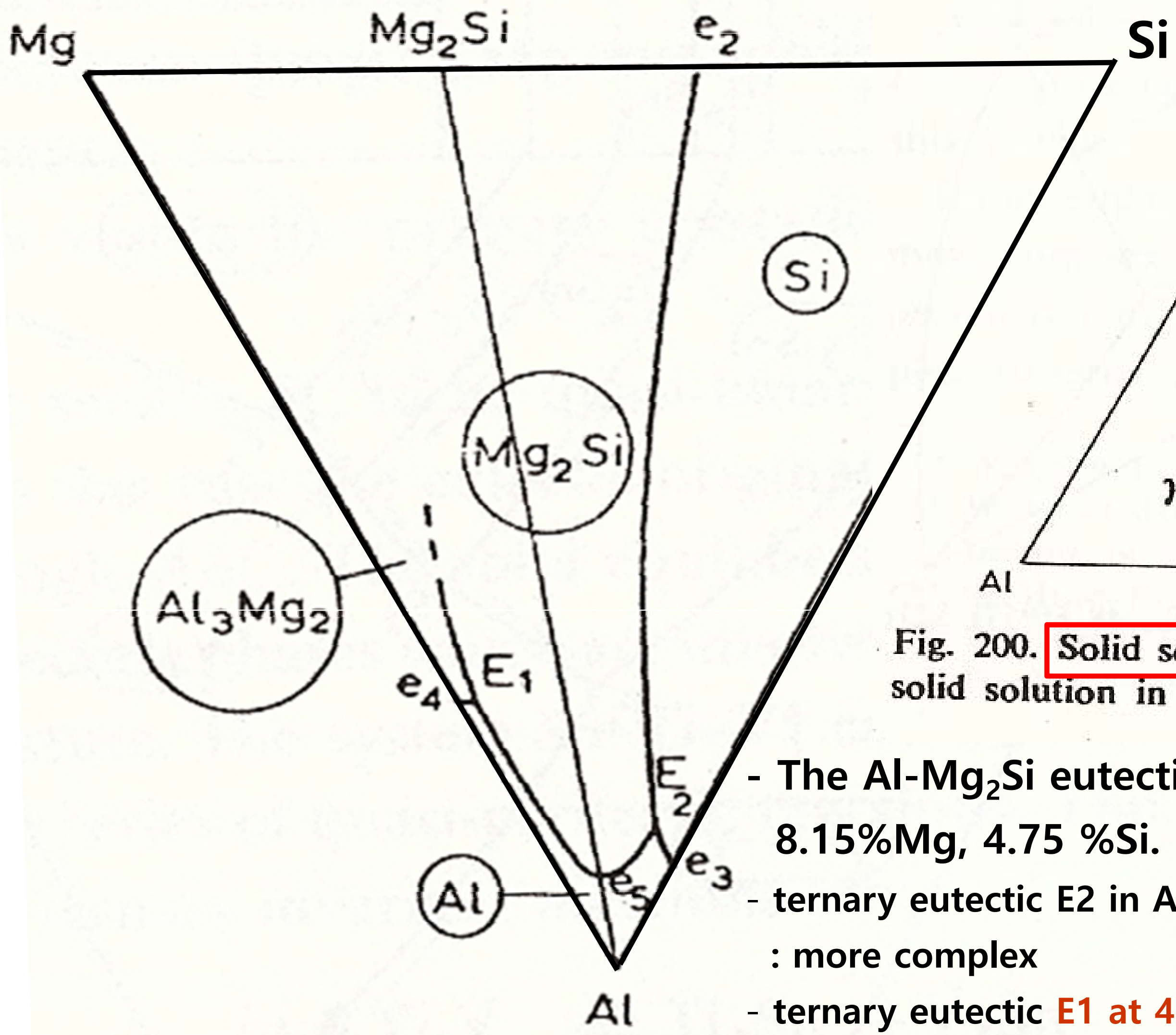


Fig. 199. The Al–Mg–Si system (schematic).

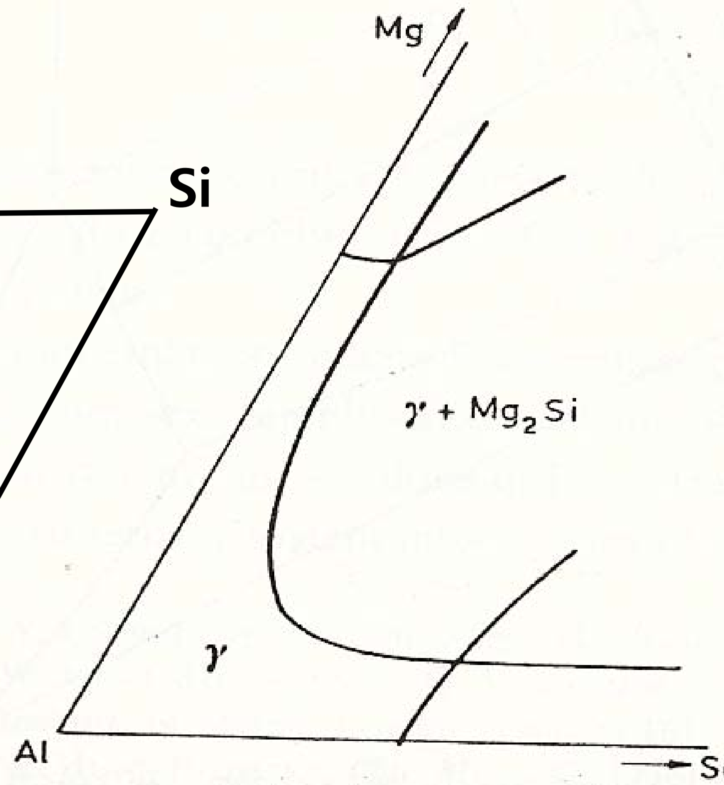
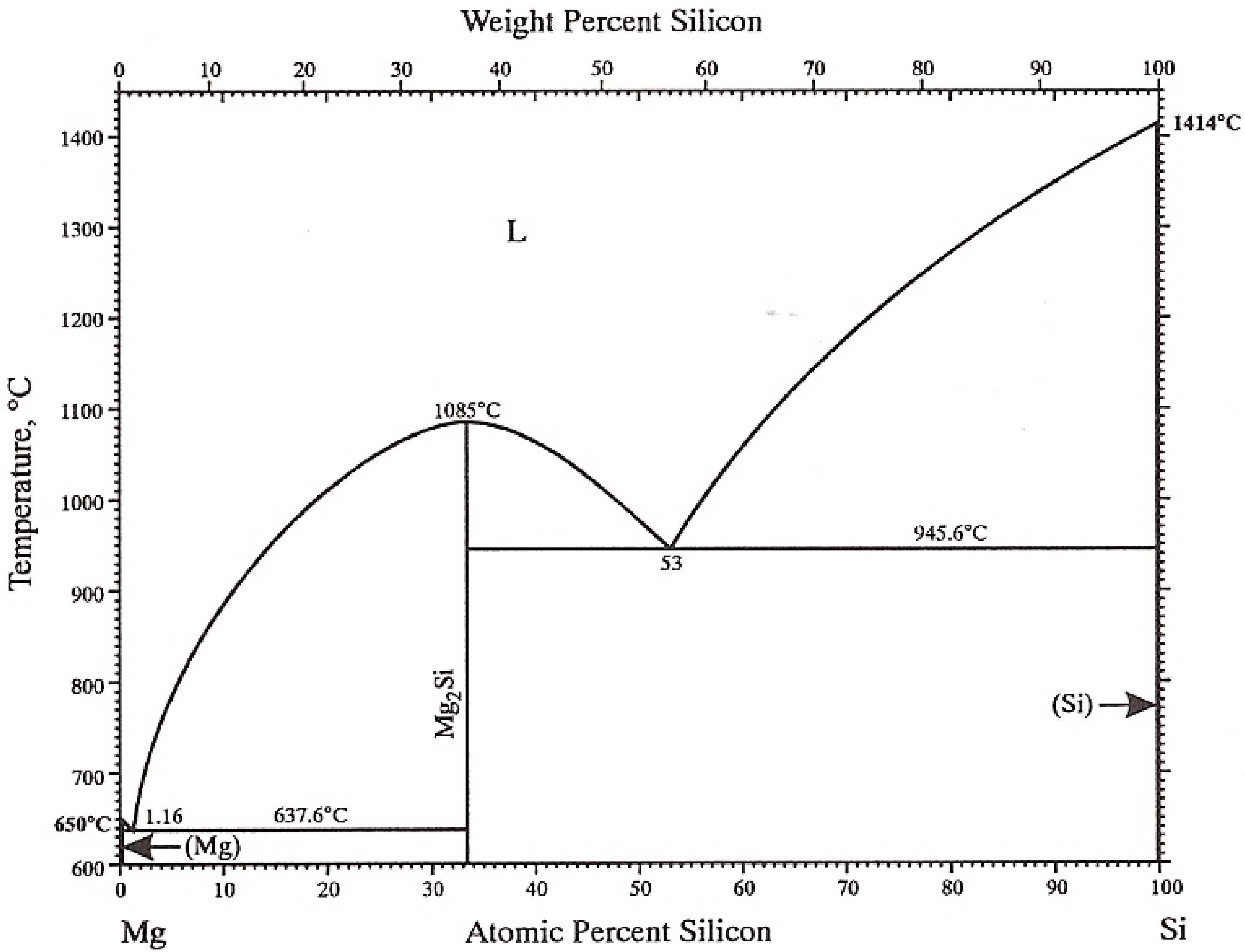


Fig. 200. Solid solubility isotherm for the Al-based solid solution in the Al–Mg–Si system (schematic).

- The Al-Mg_2Si eutectic (e5) occurs at 595℃ and 8.15%Mg, 4.75 %Si.
- ternary eutectic E2 in Al-Mg-Mg_2Si partial system : more complex
- ternary eutectic E1 at 451℃ between Al, Mg_2Si and Al_3Mg_2 contains 33.2 %Mg and 0.37 %Si.

11.1. Binary intermediate phases

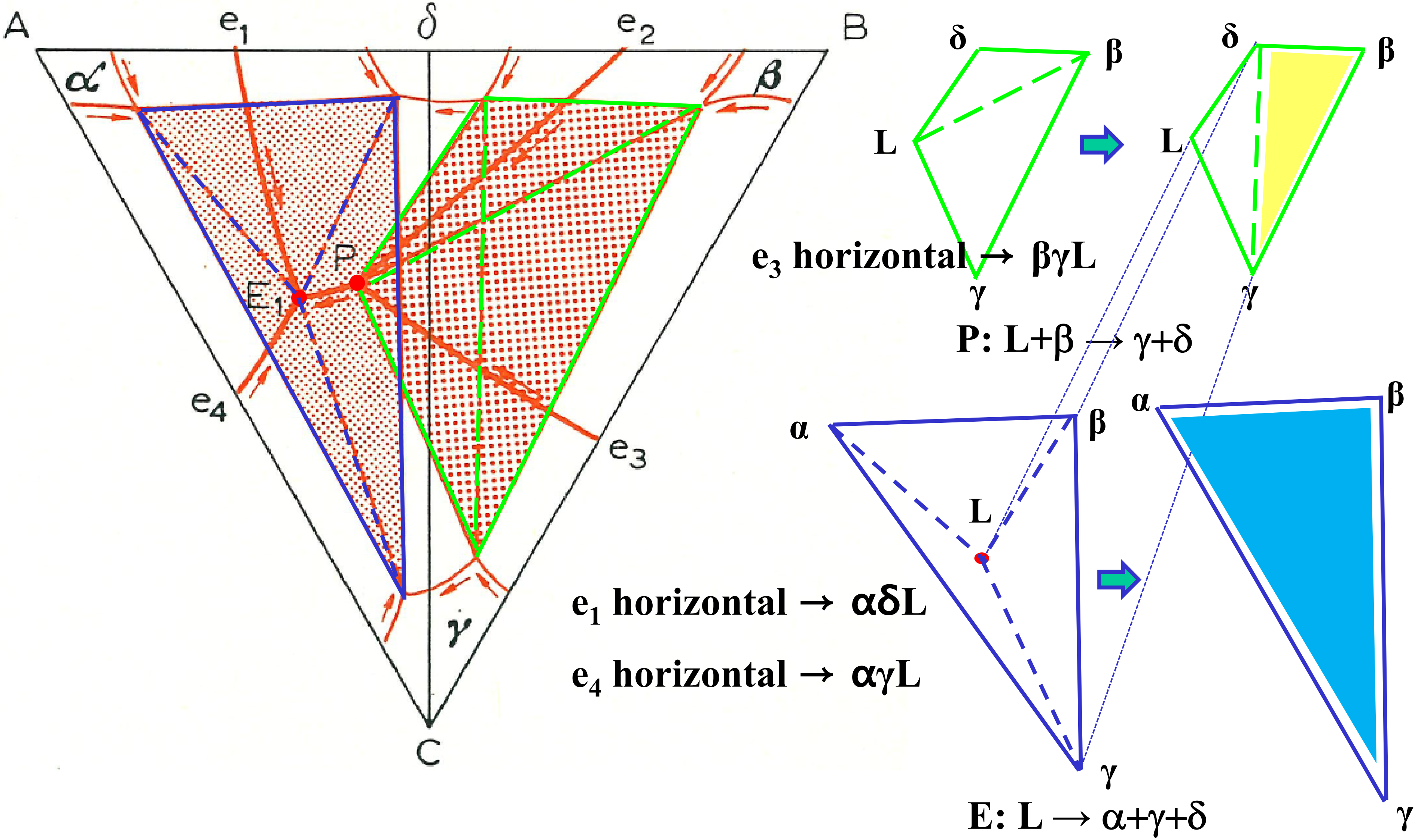


Mg-Si binary phase diagram

11.1 Congruently-melting intermediate phases

- **Binary intermediate phases**

2) Quasi peritectic reaction



11.1 Congruently-melting intermediate phases

- **Binary intermediate phases**

Quasi peritectic reaction

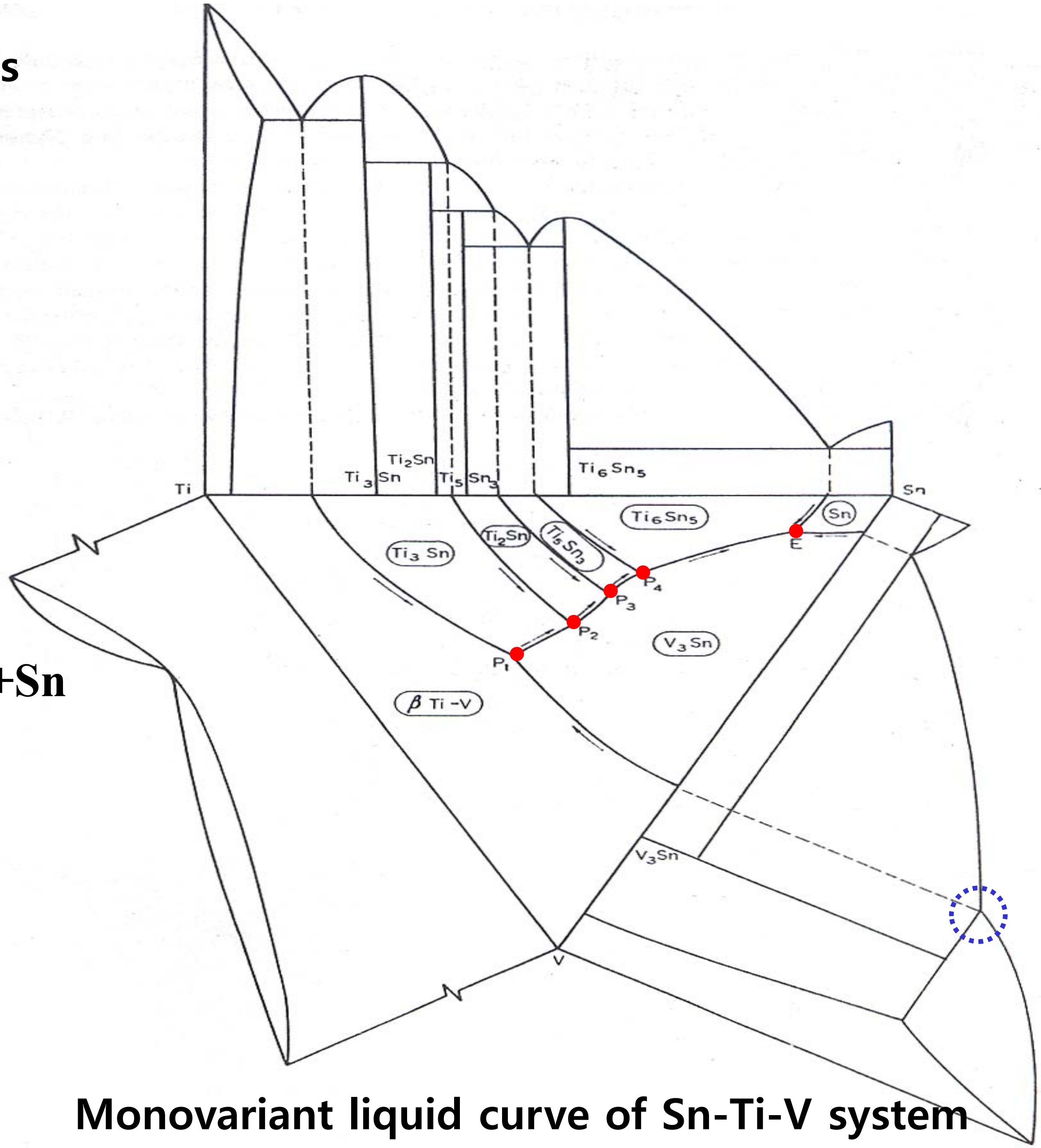
P_1: L+β Ti-V→Ti_3Sn +V_3Sn

P_2: L+ Ti_3Sn →Ti_2Sn +V_3Sn

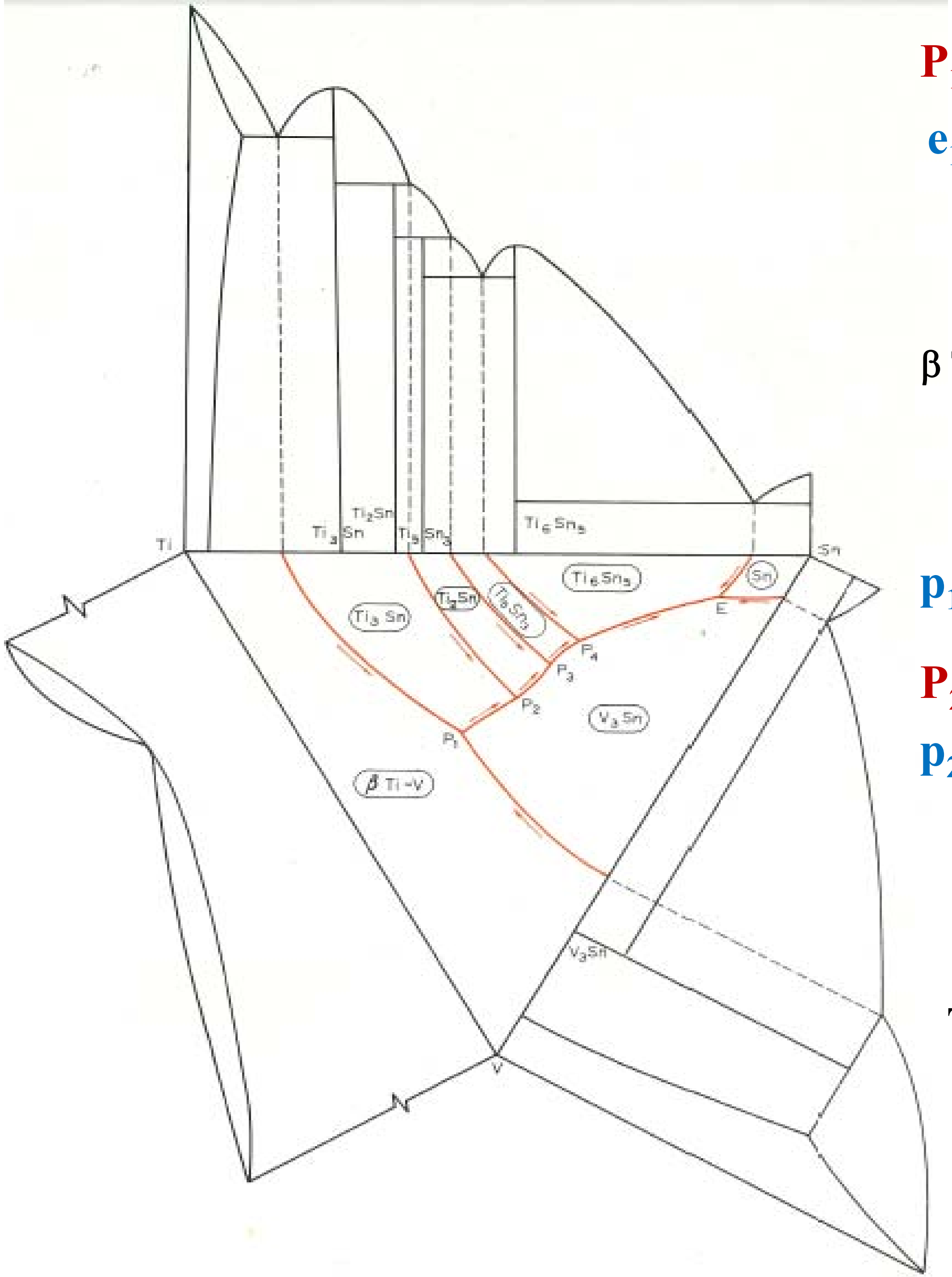
P_3: L+Ti_2Sn →Ti_5Sn_3+V_3Sn

P_4: L+Ti_5Sn_3 →Ti_6Sn_5+V_3Sn

E : L →Ti_6Sn_5+V_3Sn+Sn

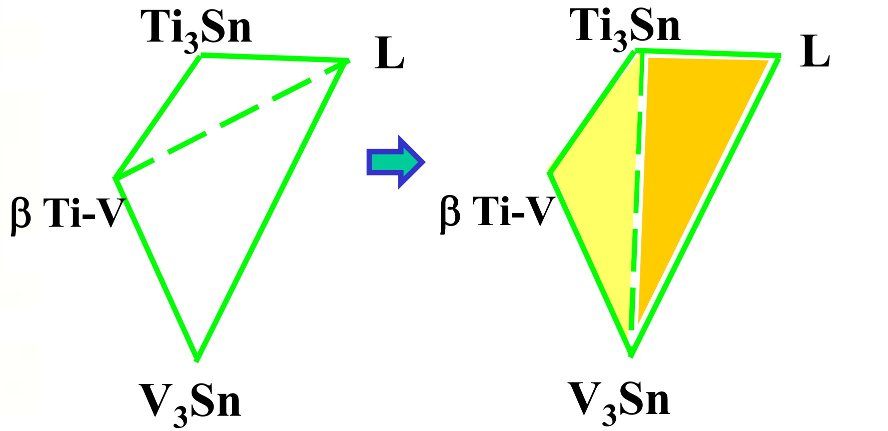


Monovariant liquid curve of Sn-Ti-V system



P_1: L+β Ti-V → Ti_3Sn +V_3Sn

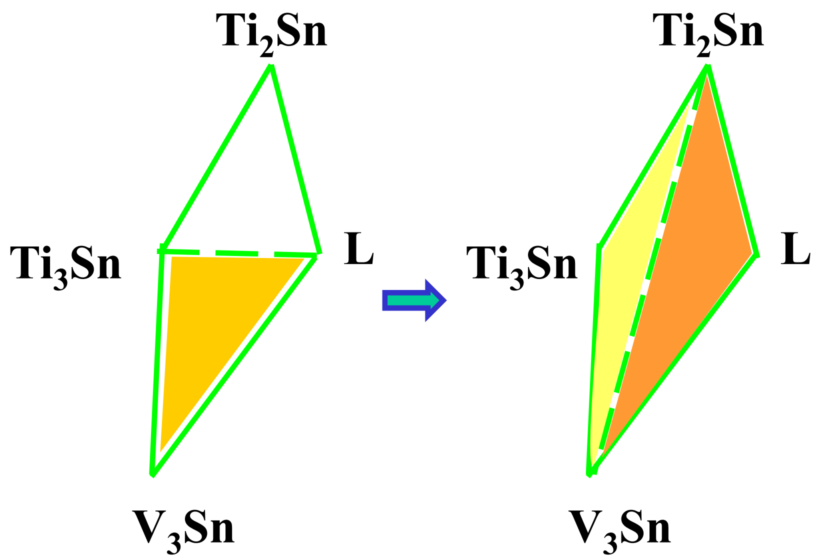
e_1: L→β Ti-V+Ti_3Sn L/β Ti-V/Ti_3Sn

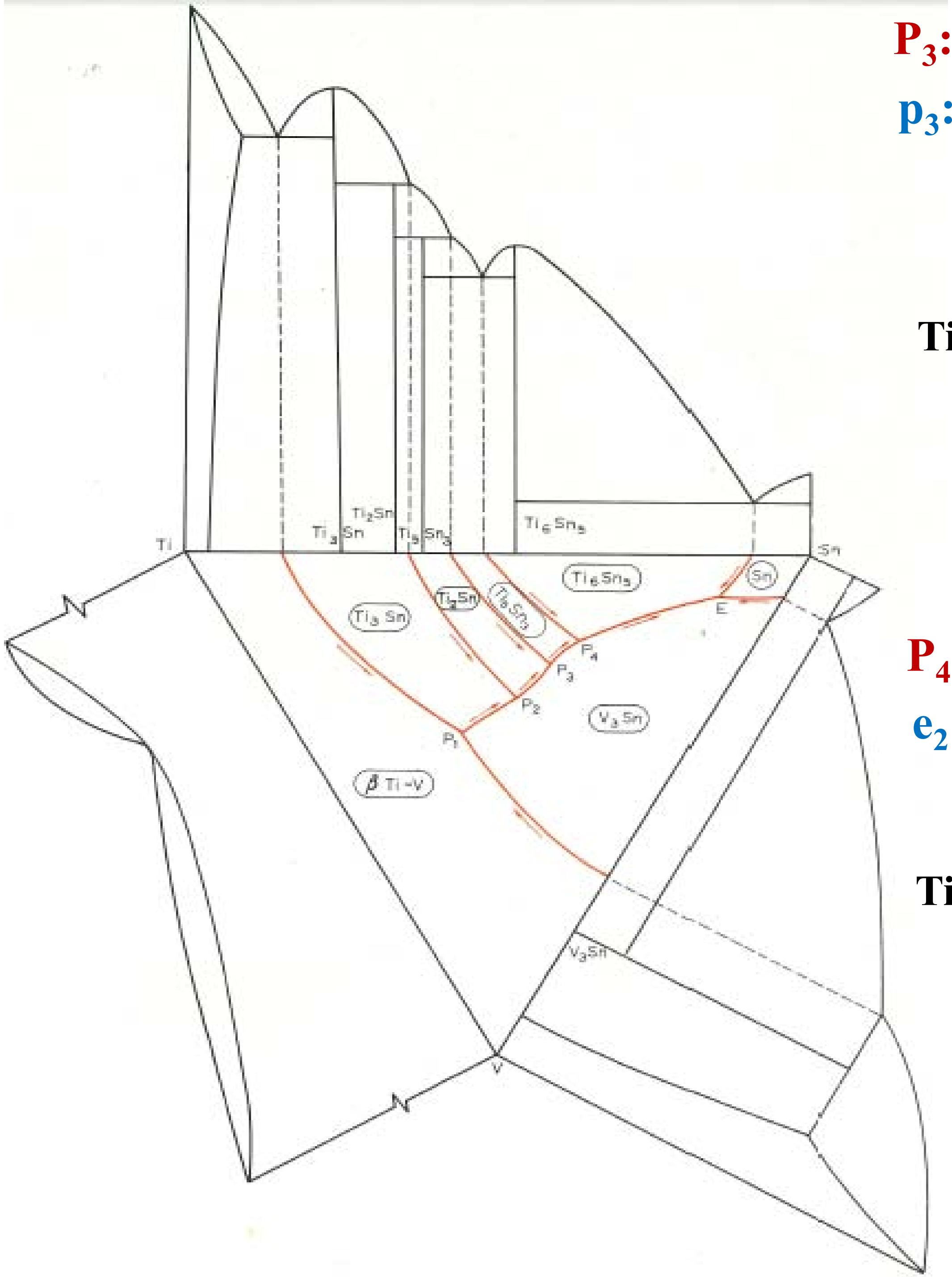


p_1: L+β Ti-V→V_3Sn L/β Ti-V/ V_3Sn

P_2: L+ Ti_3Sn → Ti_2Sn +V_3Sn

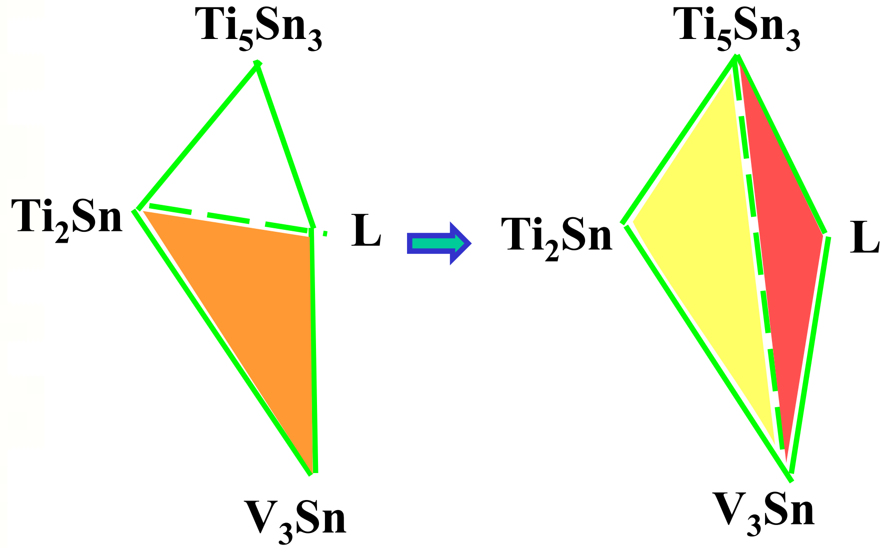
p_2: L+Ti_3Sn→Ti_2Sn L/Ti_3Sn/ Ti_2Sn





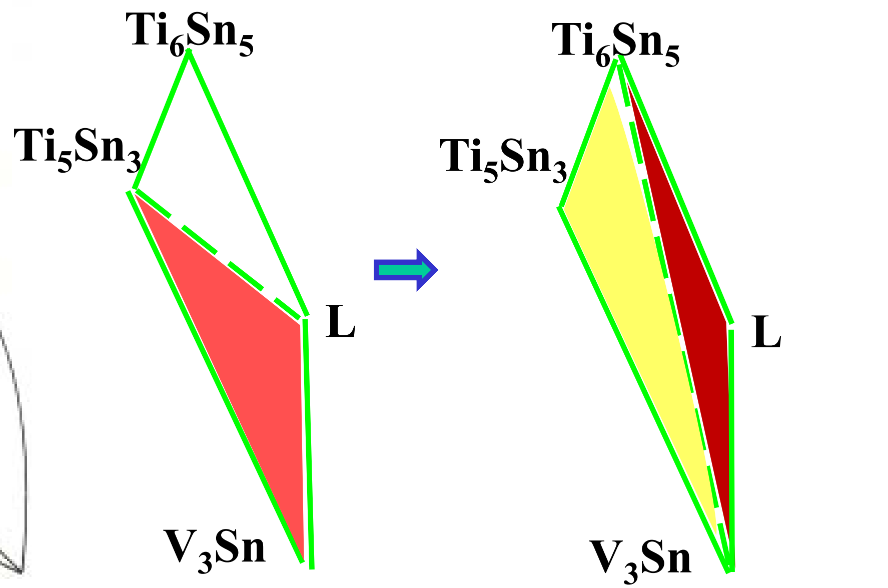
P_3: $L + Ti_2Sn \rightarrow Ti_5Sn_3 + V_3Sn$

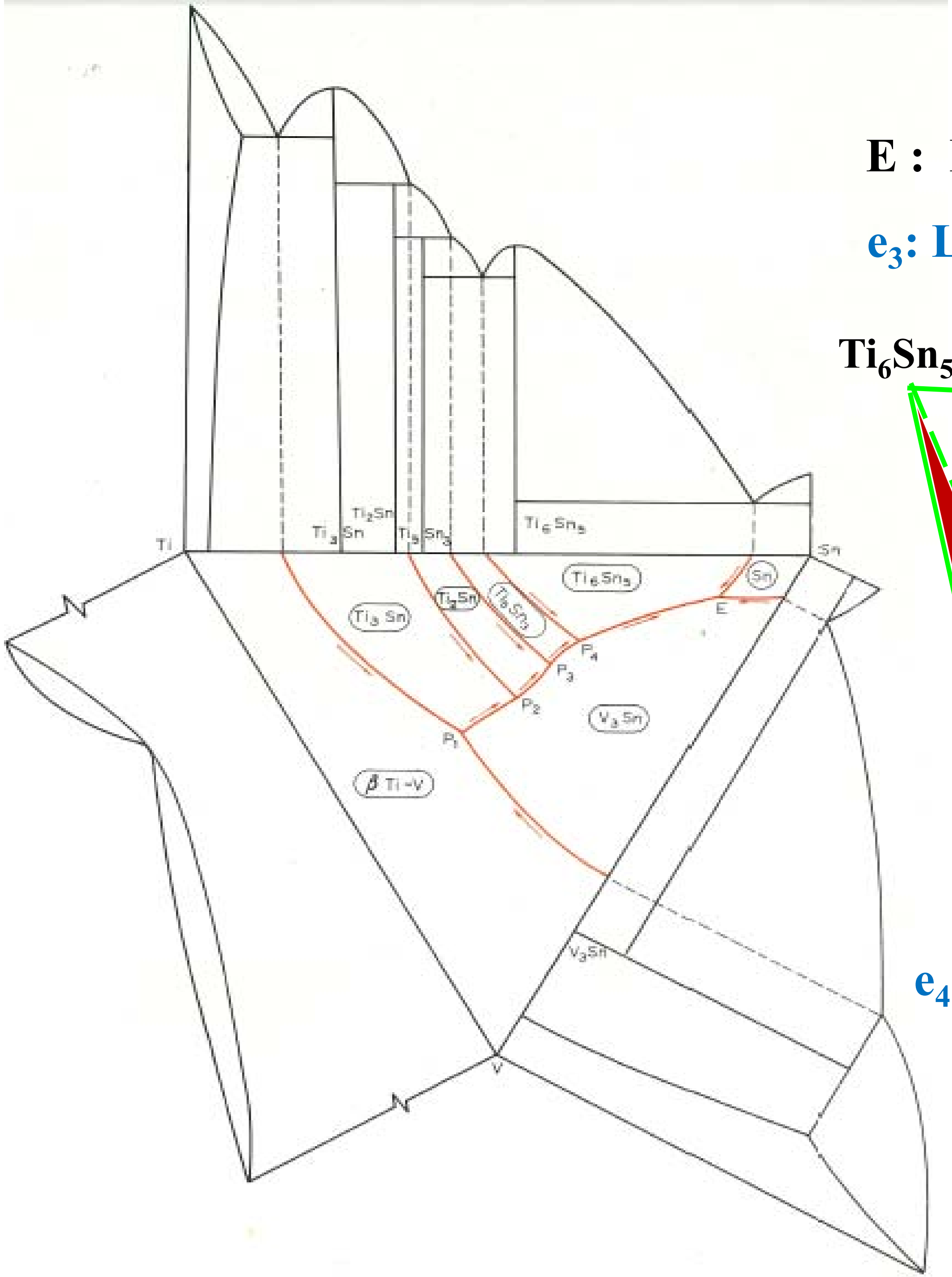
p_3: $L + Ti_2Sn \rightarrow Ti_5Sn_3$ $L/Ti_2Sn/Ti_5Sn_3$



P_4: $L + Ti_5Sn_3 \rightarrow Ti_6Sn_5 + V_3Sn$

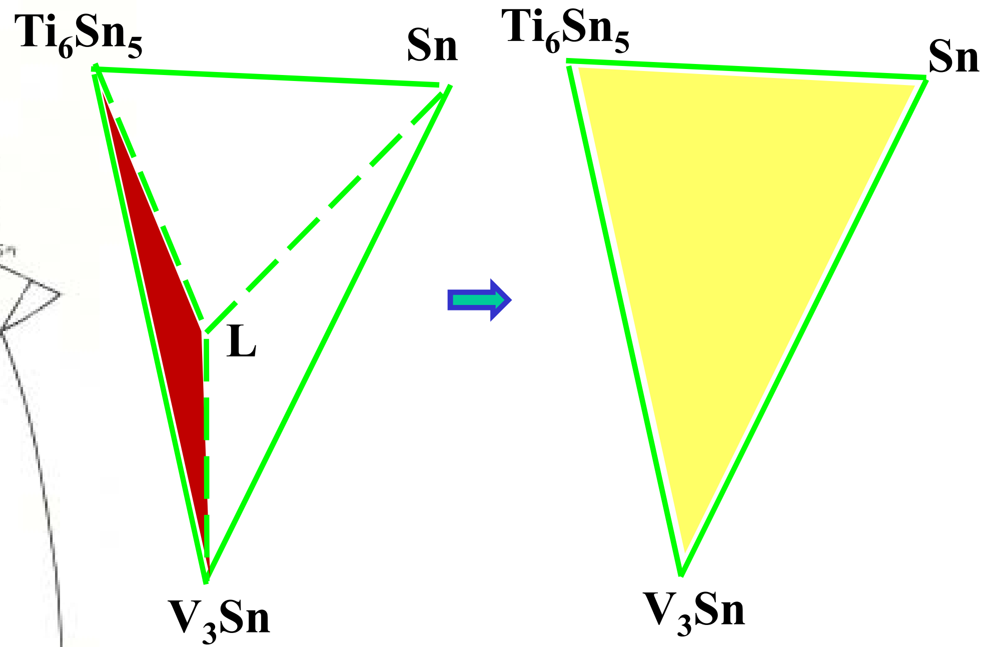
e_2: $L \rightarrow Ti_5Sn_3 + Ti_6Sn_5$ $L/Ti_5Sn_3/Ti_6Sn_5$





E : $L \rightarrow Ti_6Sn_5 + V_3Sn + Sn$

e_3: $L \rightarrow Ti_6Sn_5 + Sn$ L/ Ti_6Sn_5/ Sn



e_4: $L \rightarrow V_3Sn + Sn$ L/ V_3Sn/ Sn

$l \leftrightarrow \alpha + \beta + \gamma$

$l \leftrightarrow \alpha + \beta + \delta$

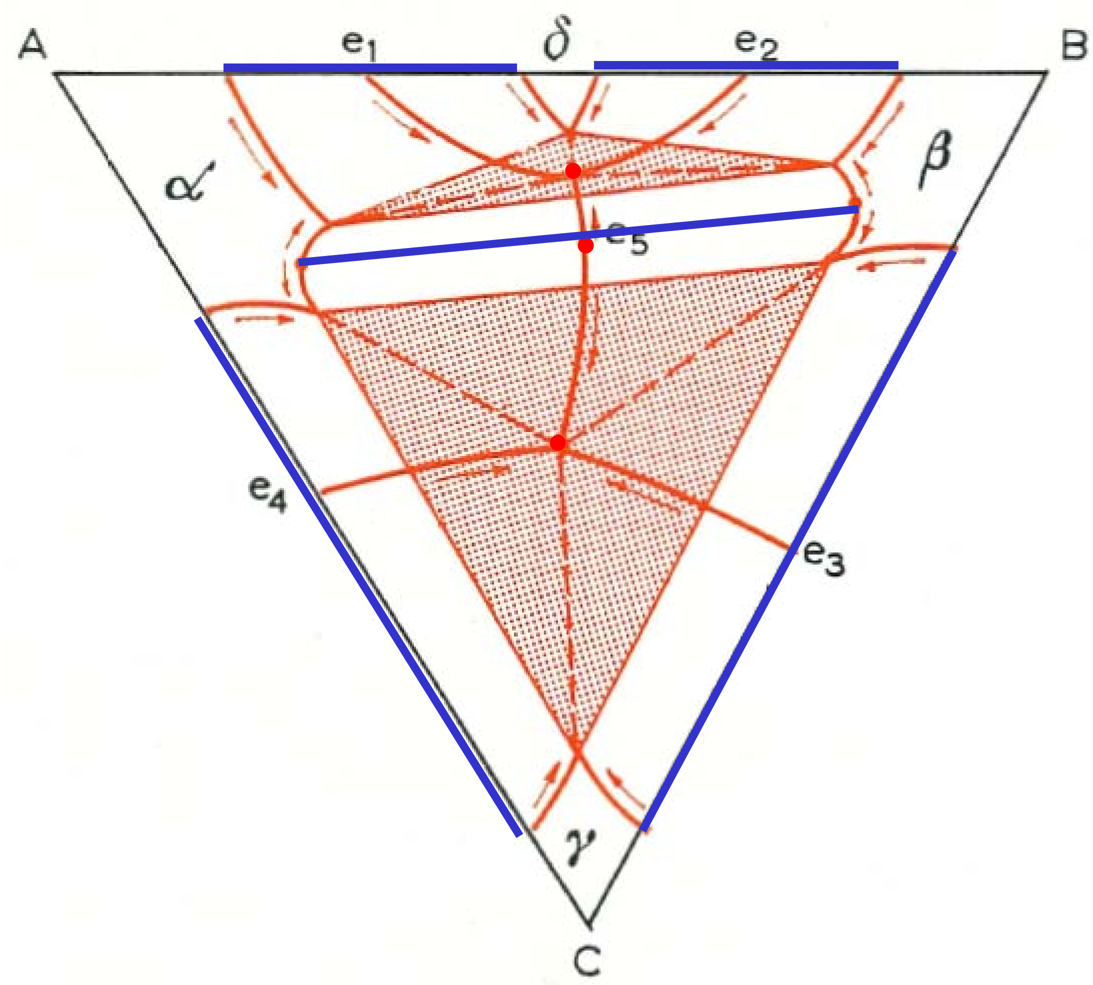
$l \leftrightarrow \alpha + \gamma + \delta$

$l \leftrightarrow \beta + \gamma + \delta$

11.1 Congruently-melting intermediate phases

- **Binary intermediate phases**

3) No quasi binary eutectic : two ternary eutectic



$L \rightarrow \alpha + \beta + \gamma$

$L \rightarrow \alpha + \beta + \delta$

e_5: saddle point

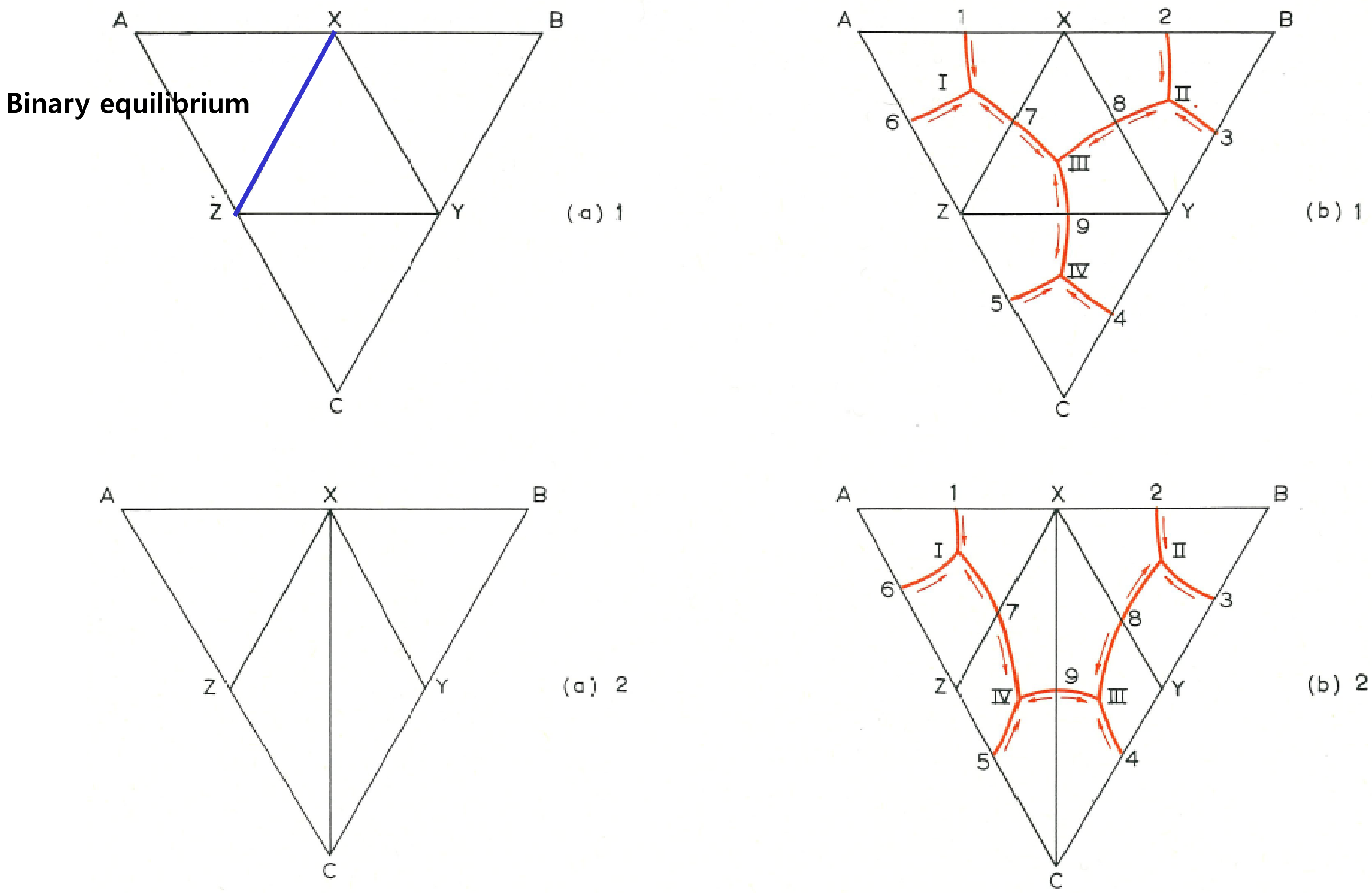
11.1 Congruently-melting intermediate phases

- **Binary intermediate phases**

4) (a) containing congruent intermediate phases on each binary system

(b) corresponding equilibria for eutectic reaction

binary eutectic points: 1, 2, 3, … , 9/ternary eutectic points: I, II, III, IV



11.1 Congruently-melting intermediate phases

- **Binary intermediate phases**

4) (a) containing congruent intermediate phases on each binary system

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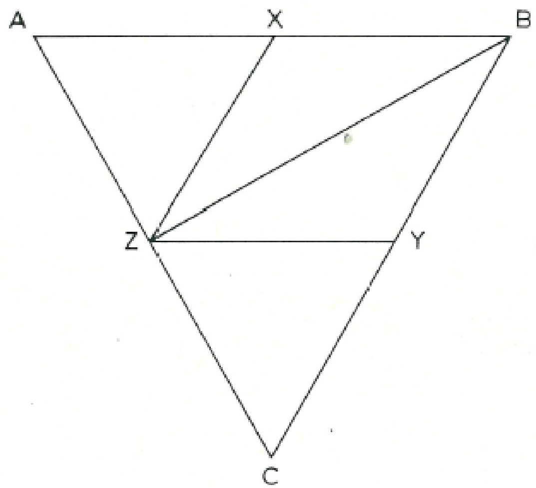
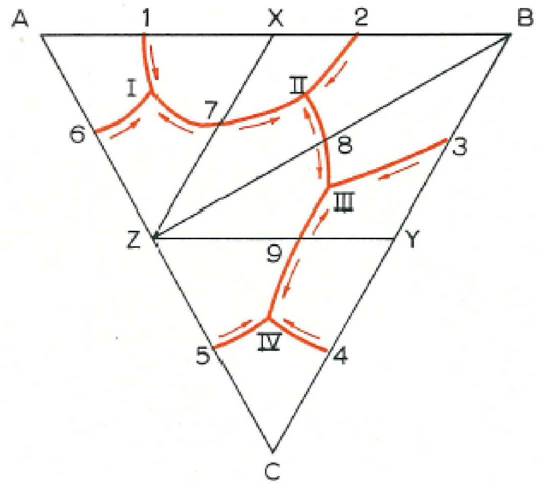
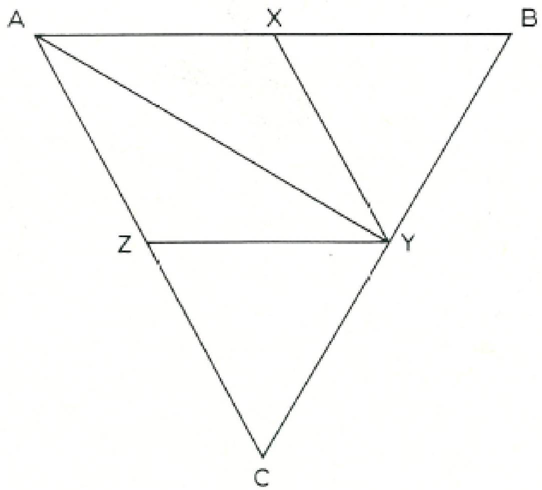


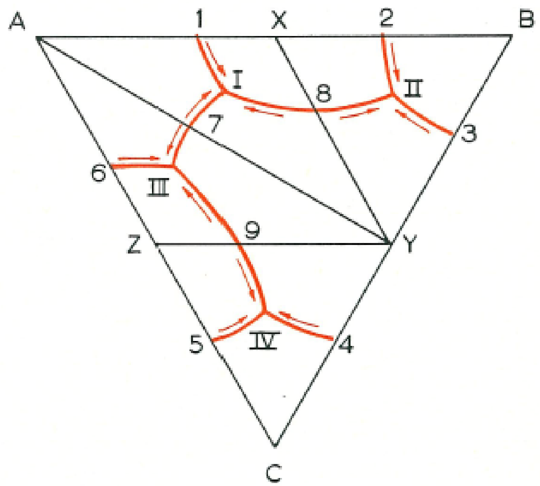
(a) 3



(b) 3



(a) 4

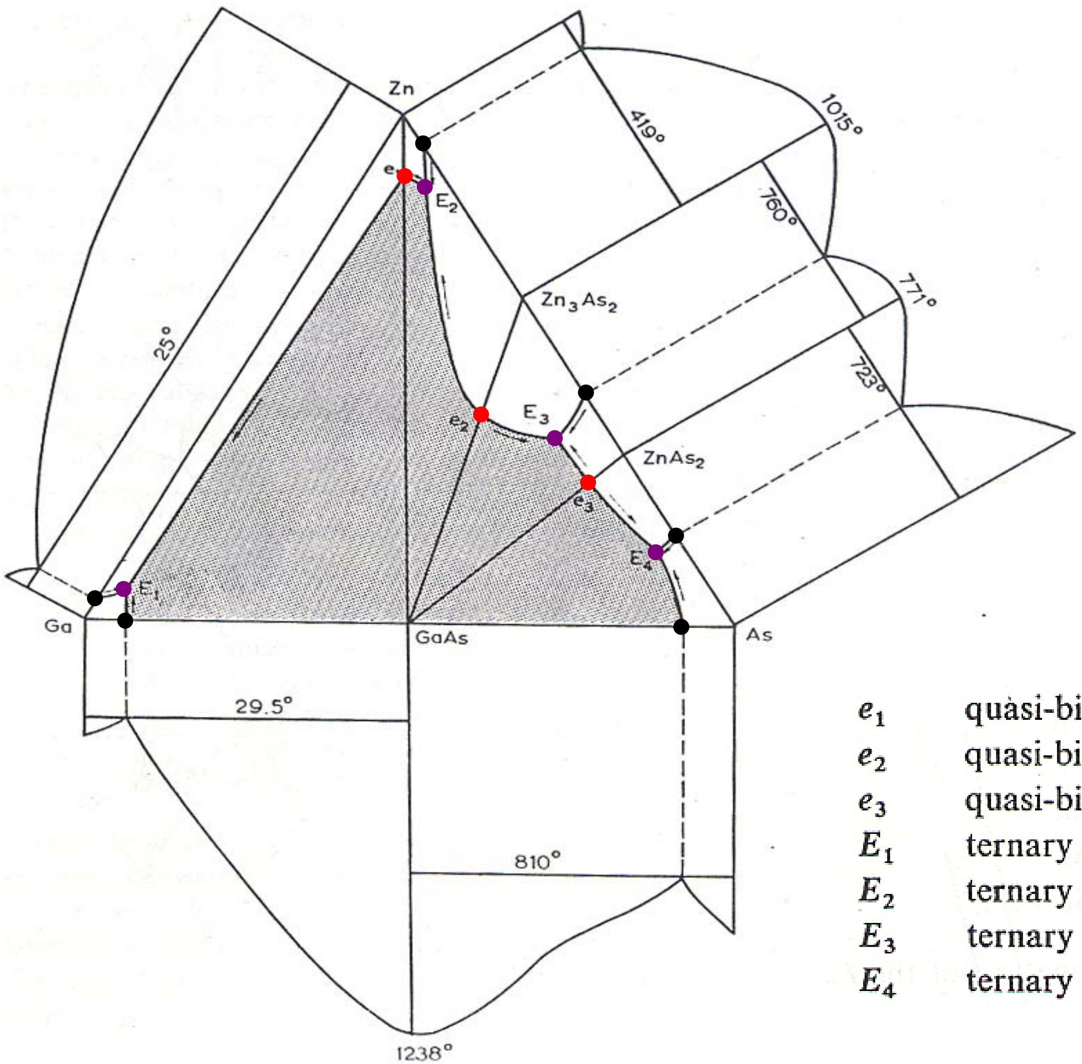


(b) 4

11.1 Congruently-melting intermediate phases

a) Binary intermediate phases

: Quasi binary eutectic rxn. between Ga, As and Zn

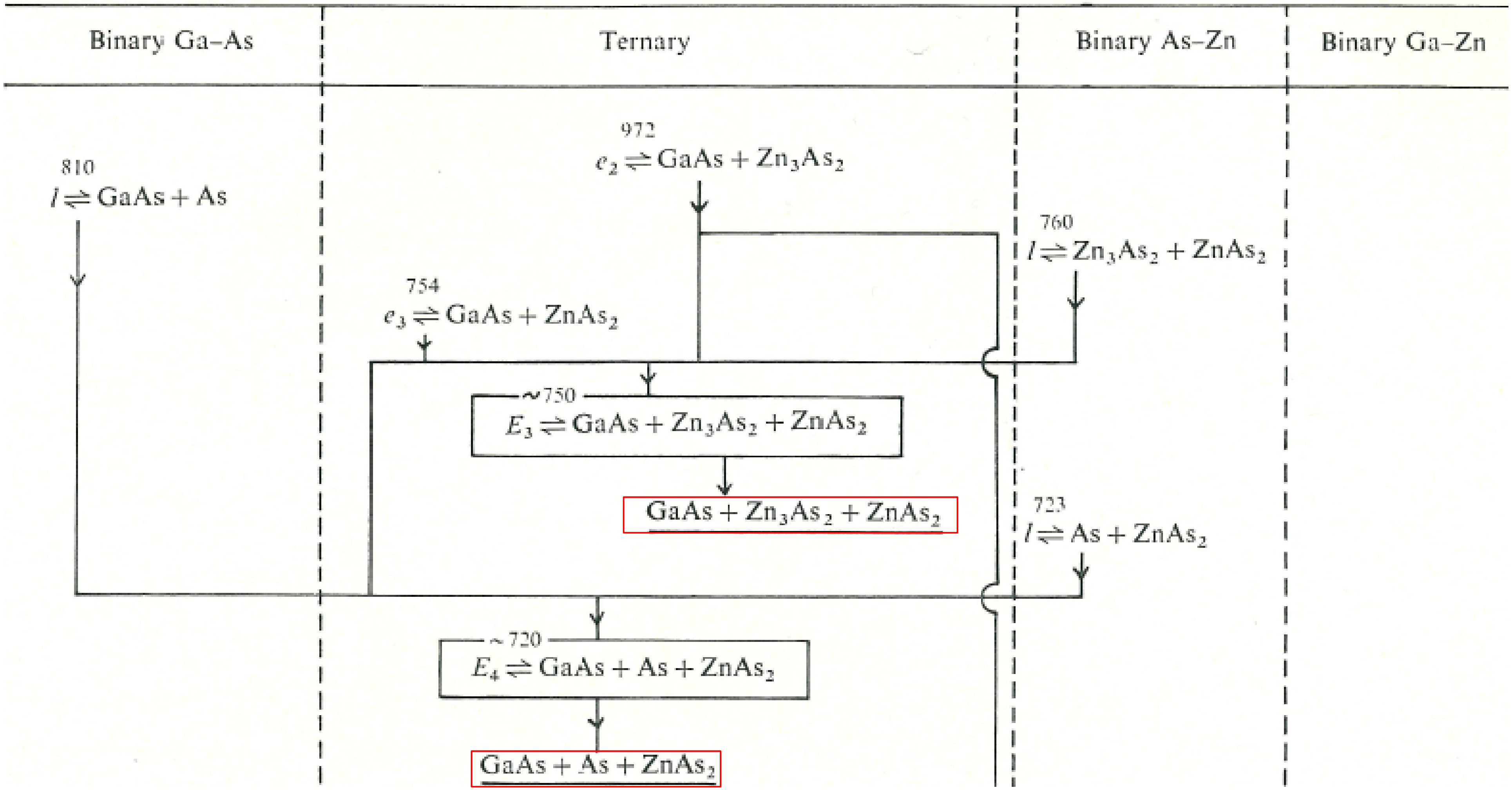


As-Ga-Zn system

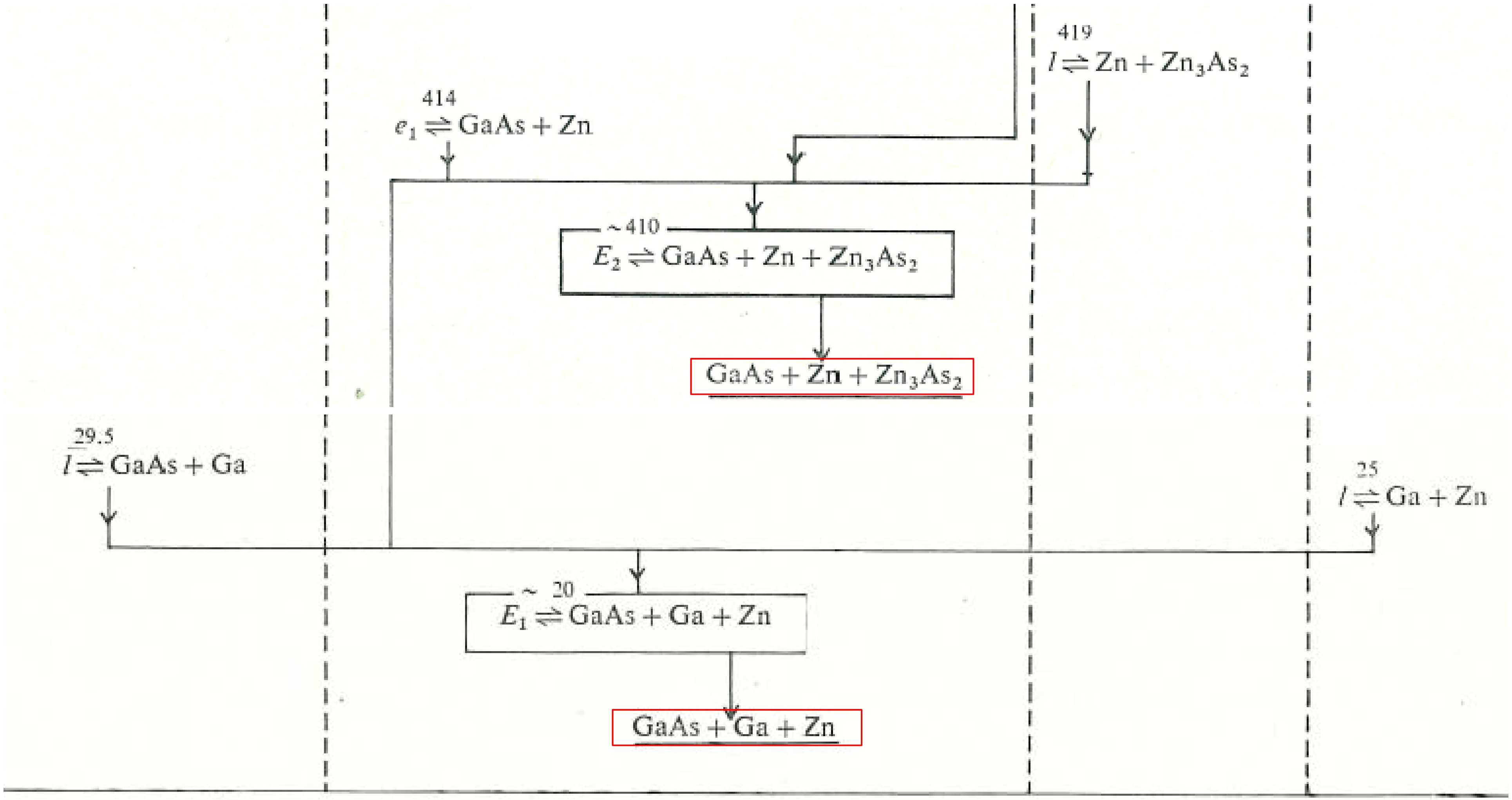
- **The region in which GaAs is the primary phase to crystallize from the liquid is lightly shaded.**
- **It illustrates the dominating behavior of the high melting phase GaAs in this system**
- **For clarity, no solid solubility between any of the phases has been indicated.**

e_1	quasi-binary eutectic $l \rightleftharpoons GaAs+Zn$	at	414 °C,
e_2	quasi-binary eutectic $l \rightleftharpoons GaAs+Zn_3As_2$	at	972 °C,
e_3	quasi-binary eutectic $l \rightleftharpoons GaAs+ZnAs_2$	at	754 °C,
E_1	ternary eutectic $l \rightleftharpoons GaAs+Zn+Ga$	at	~ 20 °C,
E_2	ternary eutectic $l \rightleftharpoons GaAs+Zn+Zn_3As_2$	at	~410 °C,
E_3	ternary eutectic $l \rightleftharpoons GaAs+Zn_3As_2+ZnAs_2$	at	~750 °C,
E_4	ternary eutectic $l \rightleftharpoons GaAs+ZnAs_2+As$	at	~720 °C.

Tabular representation of the ternary equilibria in the As-Ga-Zn system:



Tabular representation of the ternary equilibria in the As-Ga-Zn system:



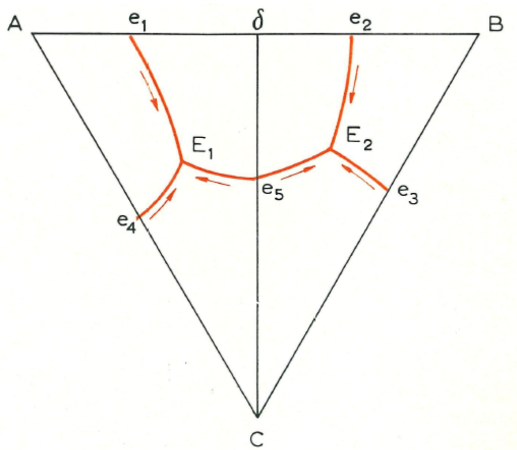
The four three-phase equilibria underlined are stable down to room-temperature.

11.1 Congruently-melting intermediate phases

- **Binary intermediate phases: Kurnakov rule**

1) Case1: with only binary congruent intermediate phases

$$K = E = c_2 + 1 = q + 1 = m + 1$$



K = # of secondary triangles
E = # of ternary eutectic points
c_2 = binary congruent intermediate phases
q = quasi binary reaction
m = saddle point

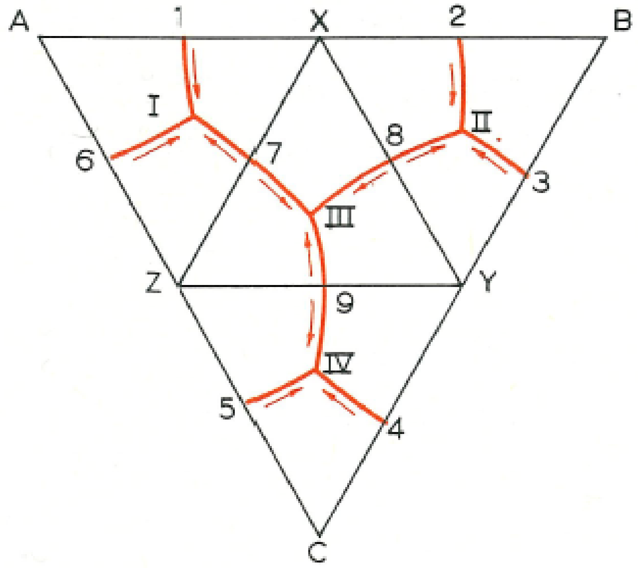
2) Case2: with only ternary congruent intermediate phases

$$K = E = 2c_3 + 1 = 2/3q + 1 = 2/3m + 1$$

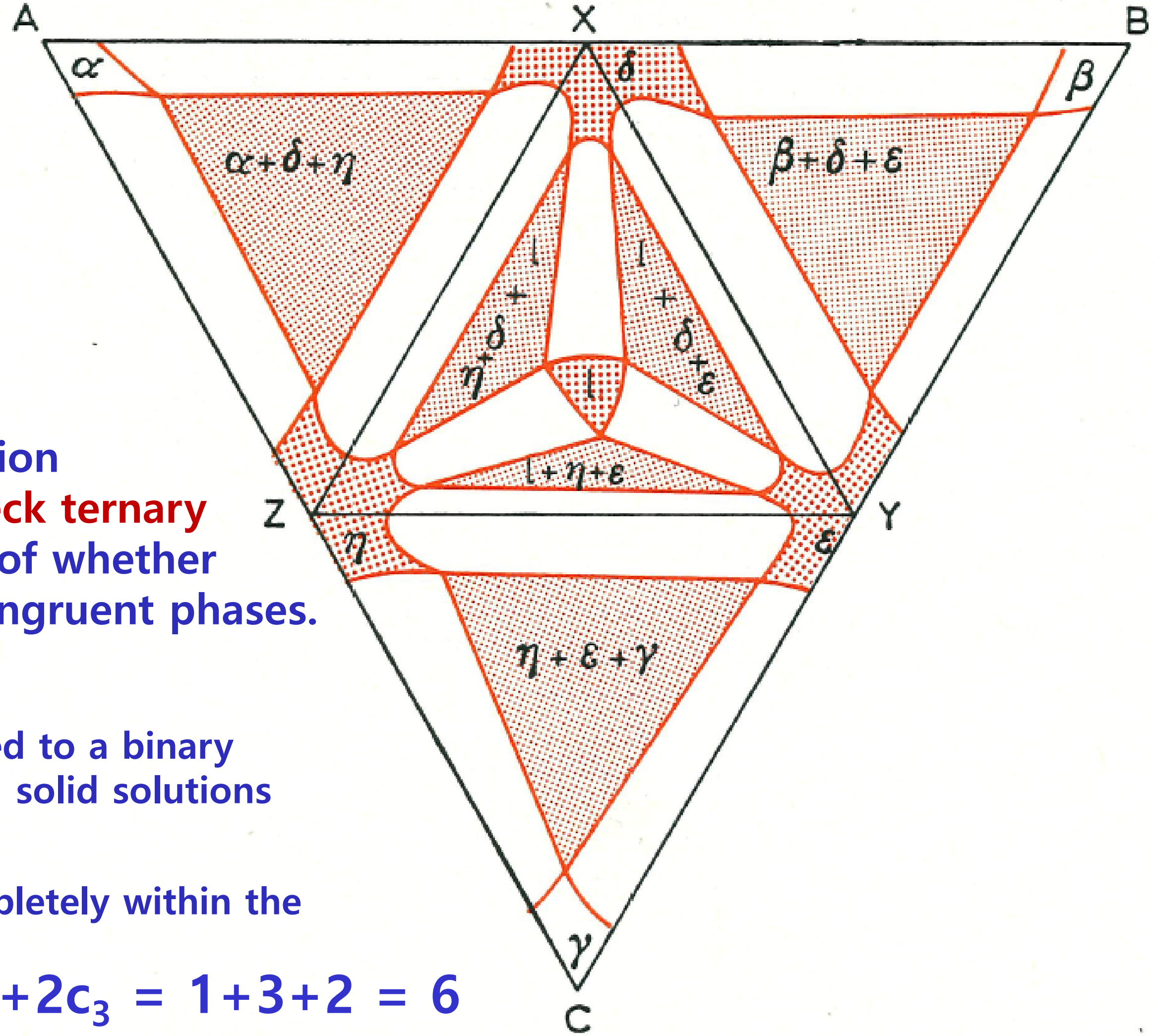
c_3 = ternary congruent intermediate phases

3) Case3: with both binary and ternary congruent intermediate phases

$$K = E = 1 + c_2 + 2c_3 = q + 1 - c_3 = m + 1 - c_3$$



- Isothermal section at a temperature just above the lowest melting ternary eutectic (III)



- **Rhines** has noted that the relation $k=1+c_2+2c_3$ can be used to **check ternary isothermal section** irrespective of whether they contain congruent or incongruent phases.
  - K: # of 3 phase tie triangles,
- - C_2: # of single phase regions joined to a binary edge (excluding the α, β, γ terminal solid solutions based on components A, B and C),
- - C_3: # of single phase regions completely within the ternary system.

$$K = E = 1+c_2+2c_3 = 1+3+2 = 6$$

- <u>**The Kurnakove and Rhines' rules are useful in checking the construction of ternary systems and their isothermal sections when intermediate phases are involved.**</u>