

2021 Spring

“Phase Equilibria *in* Materials”

05.04.2021

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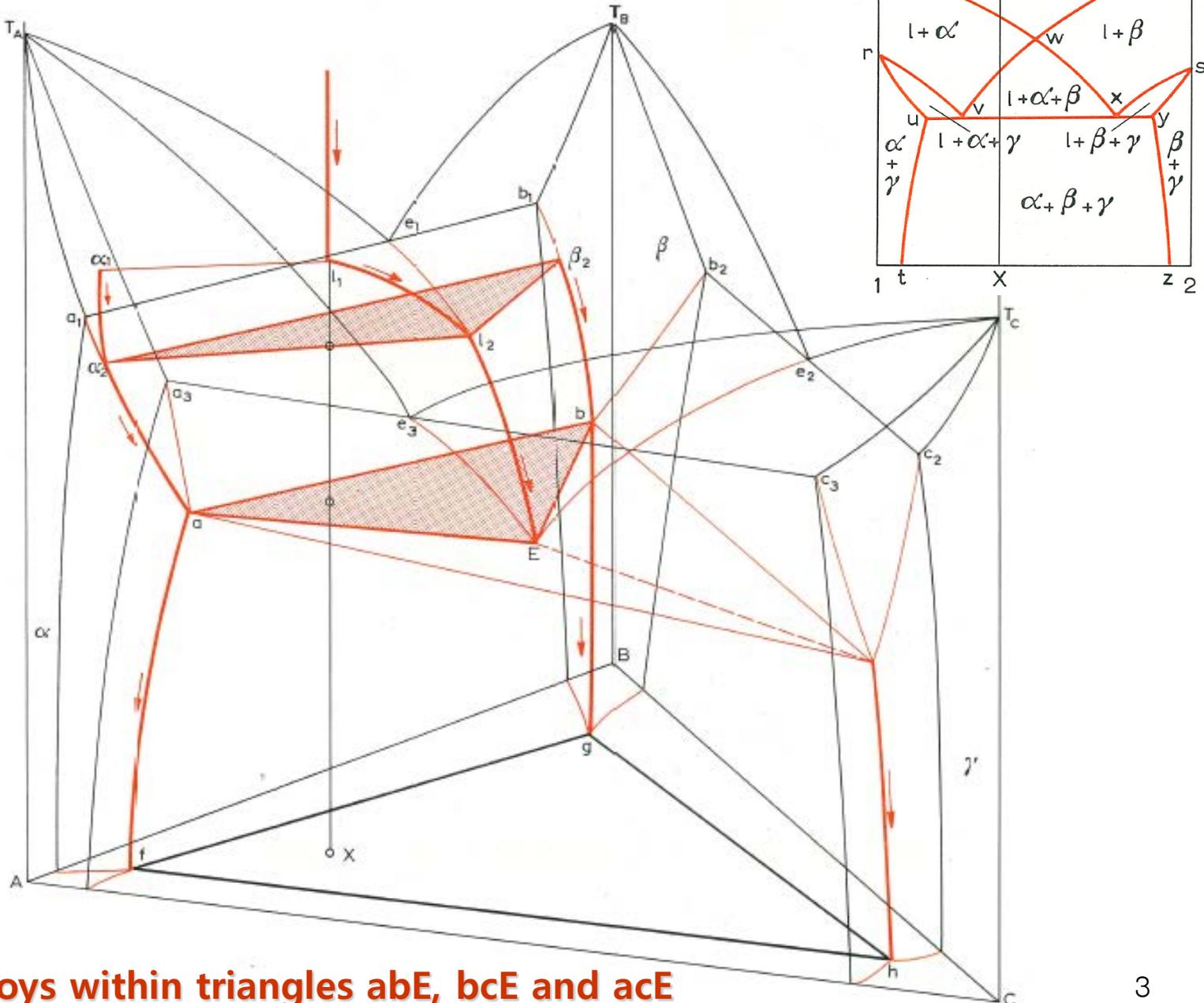
Office hours: by an appointment

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

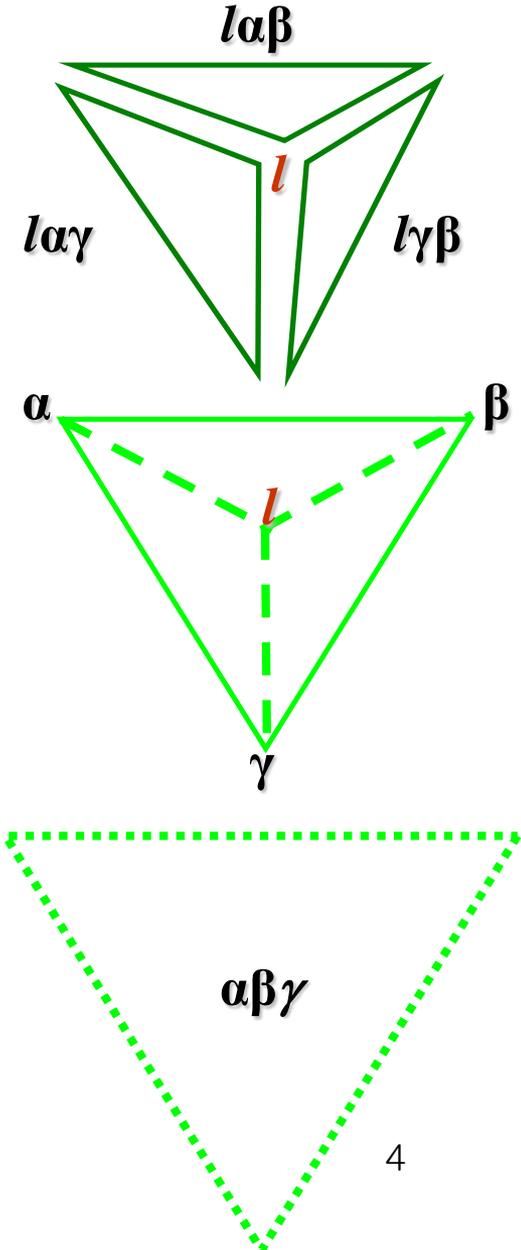
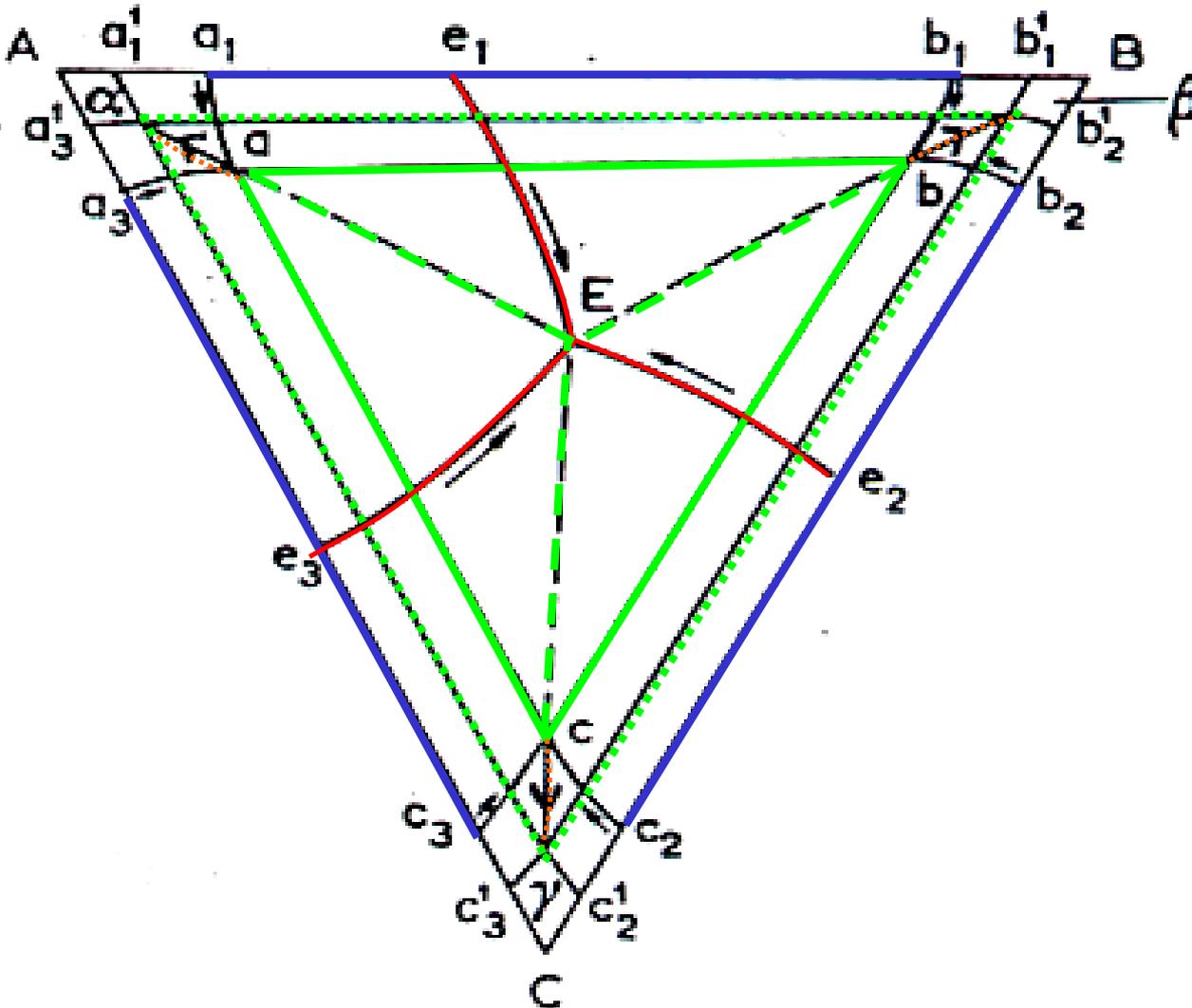
Transformation during cooling



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

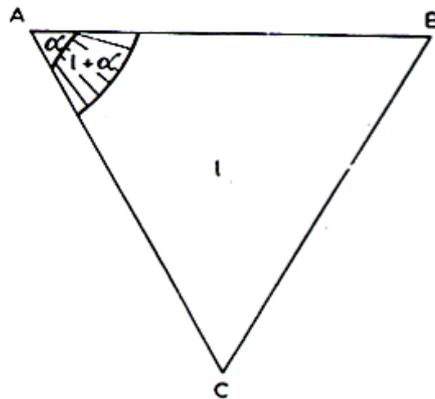
THE TERNARY EUTECTIC EQUILIBRIUM ($l = \alpha + \beta + \gamma$)

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

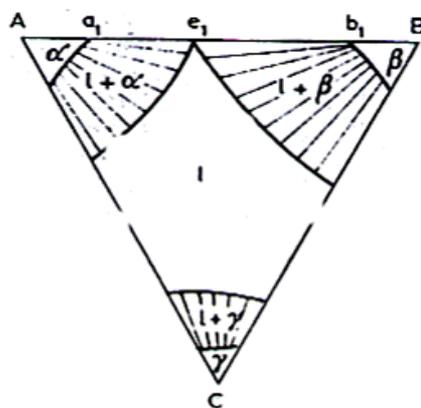


10.1. THE EUTECTIC EQUILIBRIUM ($l = \alpha + \beta + \gamma$)

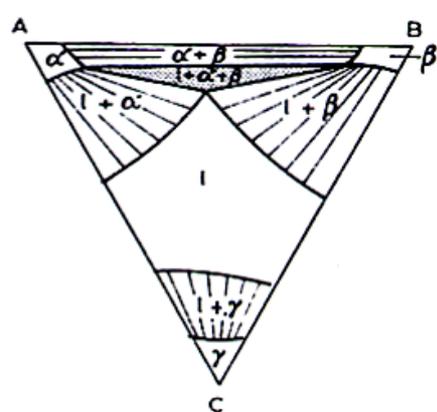
- Isothermal section ($T_A > T > T_B$)



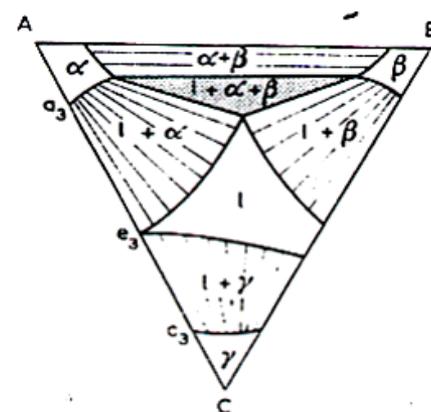
(a) $T_A > T > T_B$



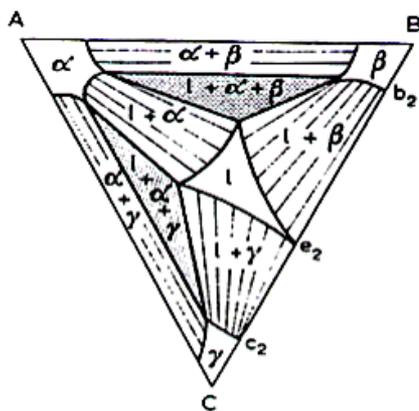
(b) $T = e_1$



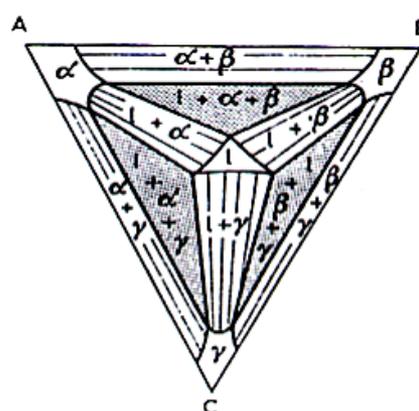
(c) $e_1 > T > e_3$



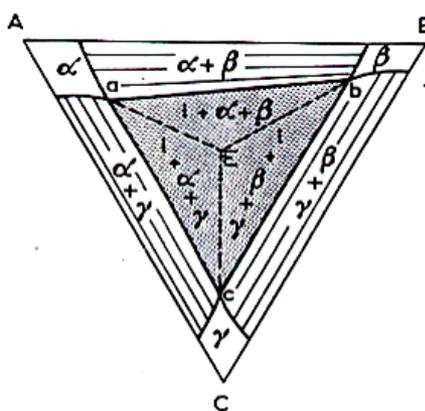
(d) $T = e_3$



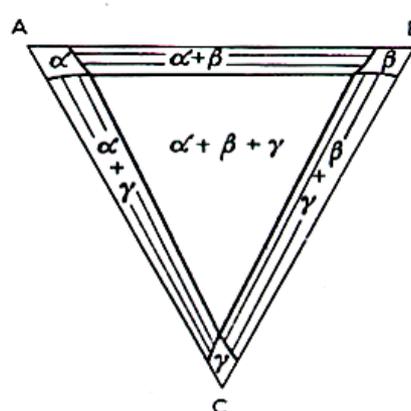
(e) $T = e_2$



(f) $e_2 > T > E$



(g) $T_A = E$

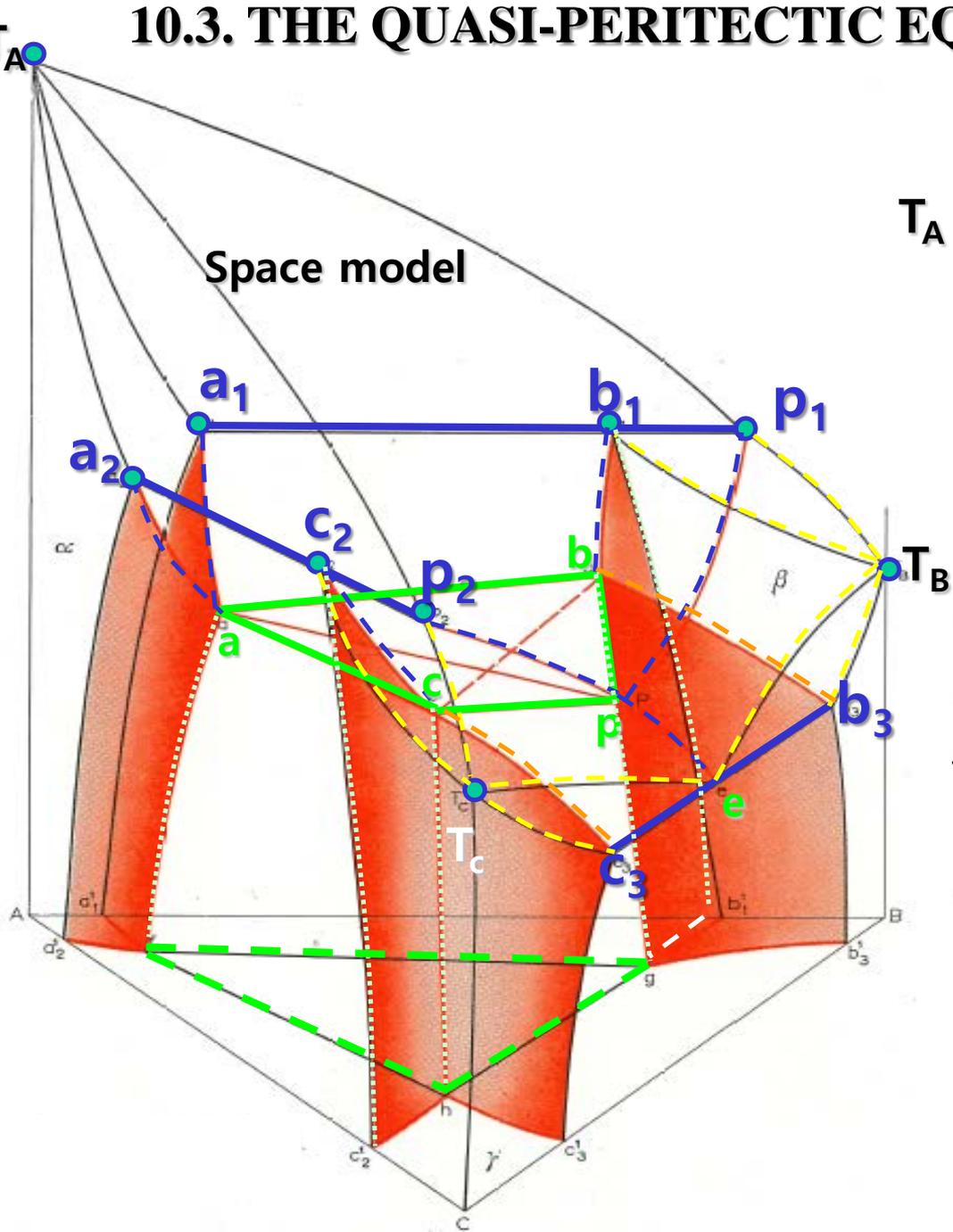


(h) $E = T$

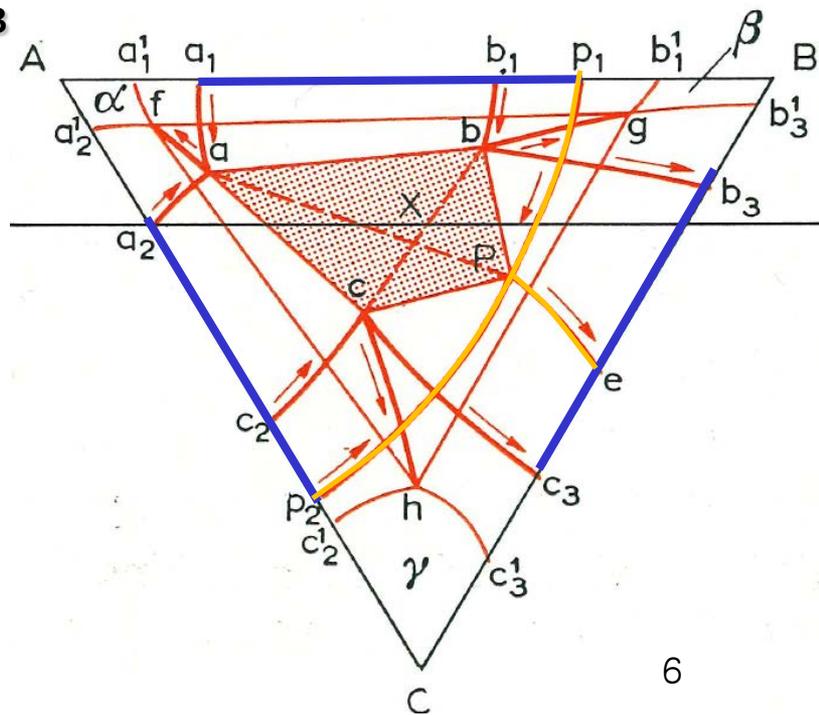
10.3. THE QUASI-PERITECTIC EQUILIBRIUM ($l + \alpha = \beta + \gamma$)

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

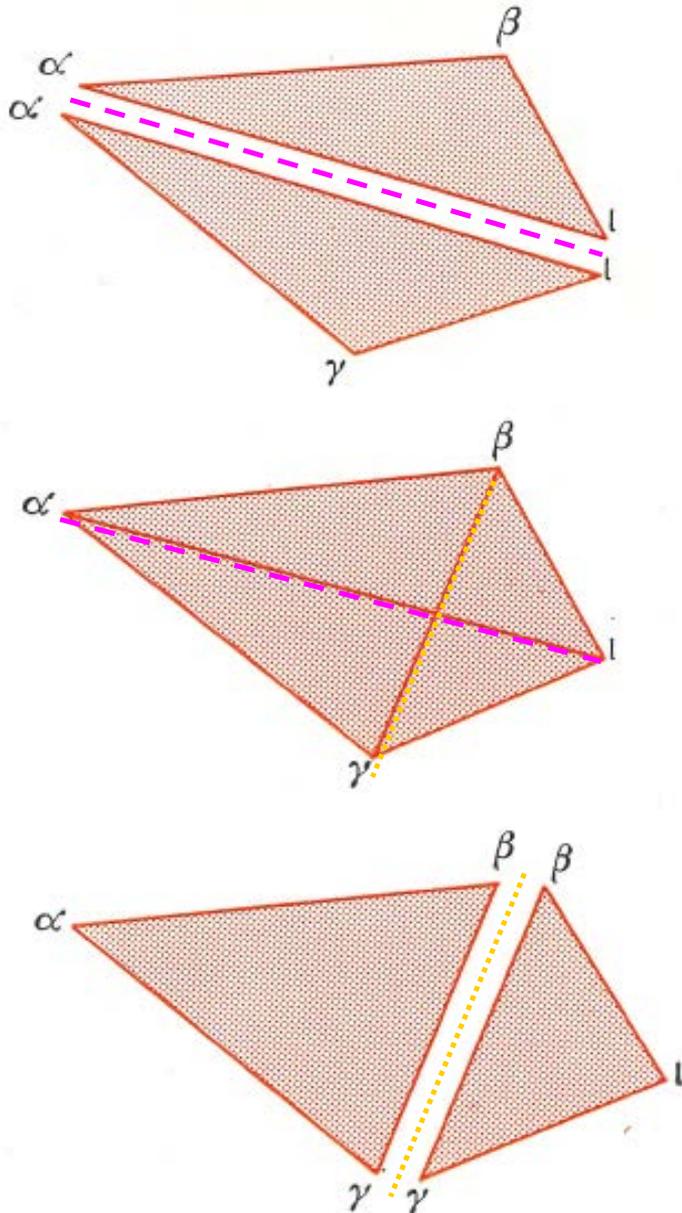
Space model



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 $l\alpha\beta$ equilibrium

acP peritectic $l\alpha\gamma$ equilibrium

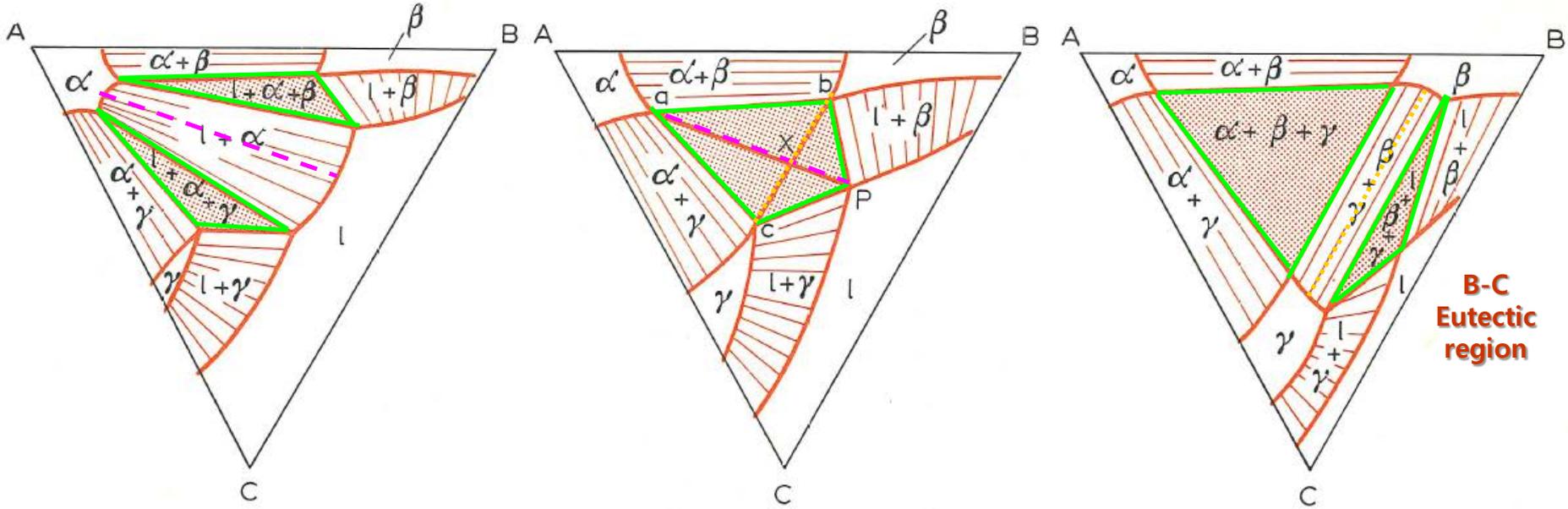
decreasing temperature

bcP eutectic $l\beta\gamma$ equilibrium

abc peritectic $\alpha\beta\gamma$ equilibrium

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

Isothermal section



$T_B > T > P$

$T = P$

$P > T > T_C$

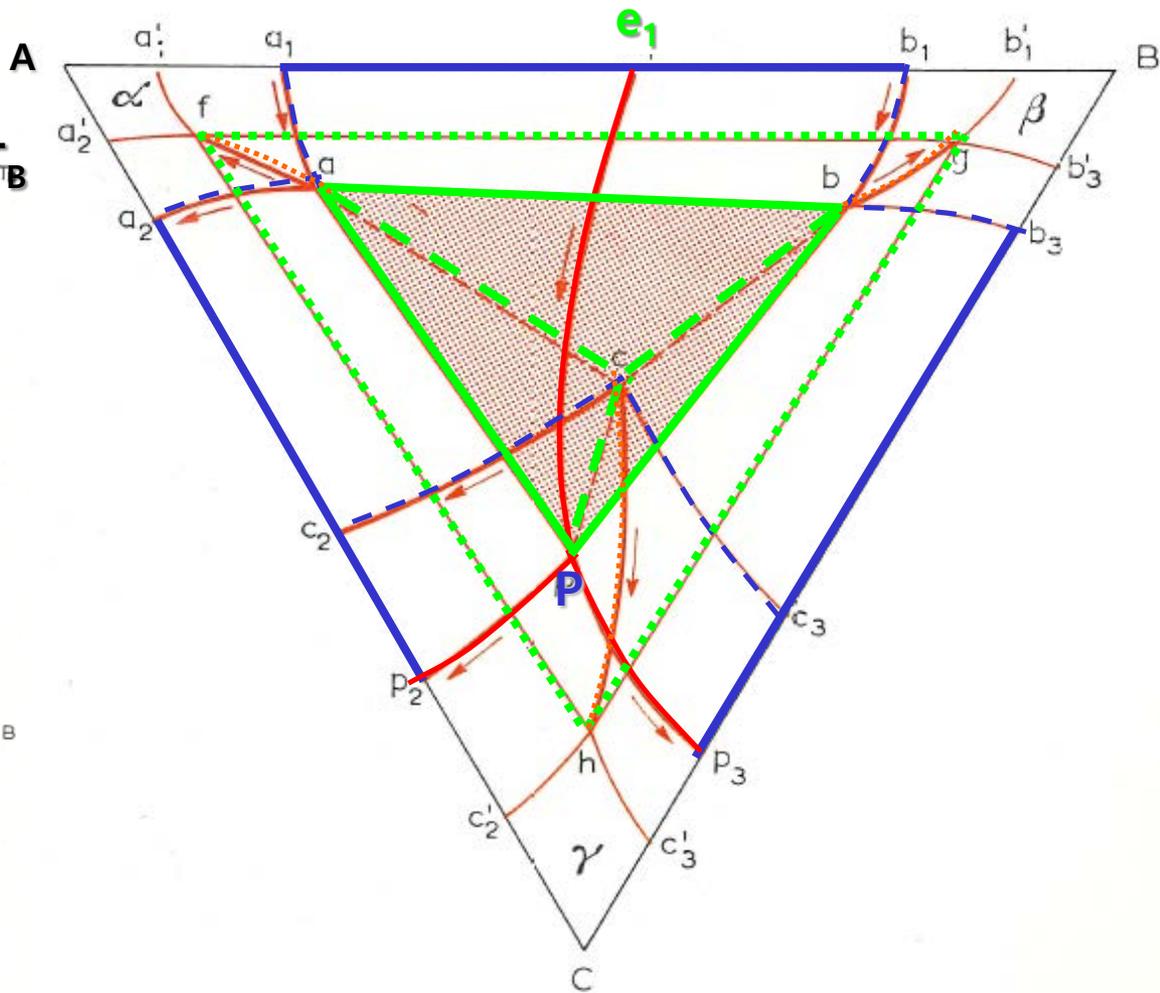
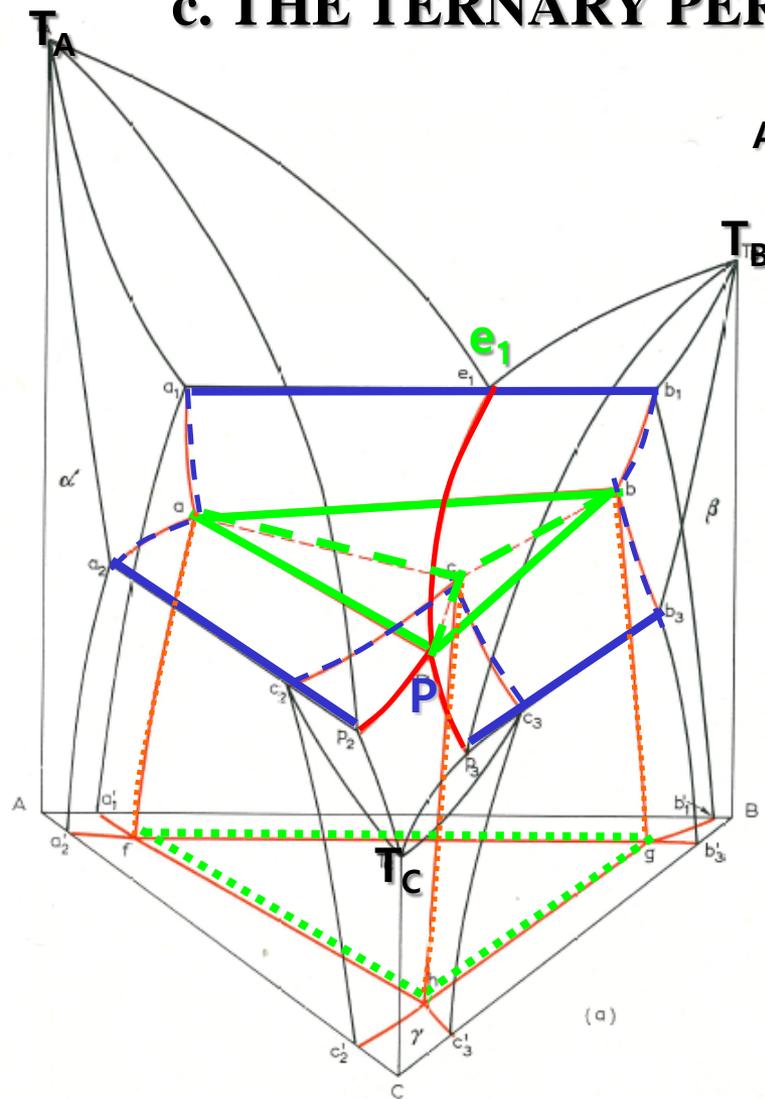
abP peritectic $l\alpha\beta$ equilibrium }
 acP peritectic $l\alpha\gamma$ equilibrium }

bcP eutectic $l\beta\gamma$ equilibrium }
 abc $\alpha\beta\gamma$ equilibrium }

descending to the four-phase plane;

descending from the four-phase plane.

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



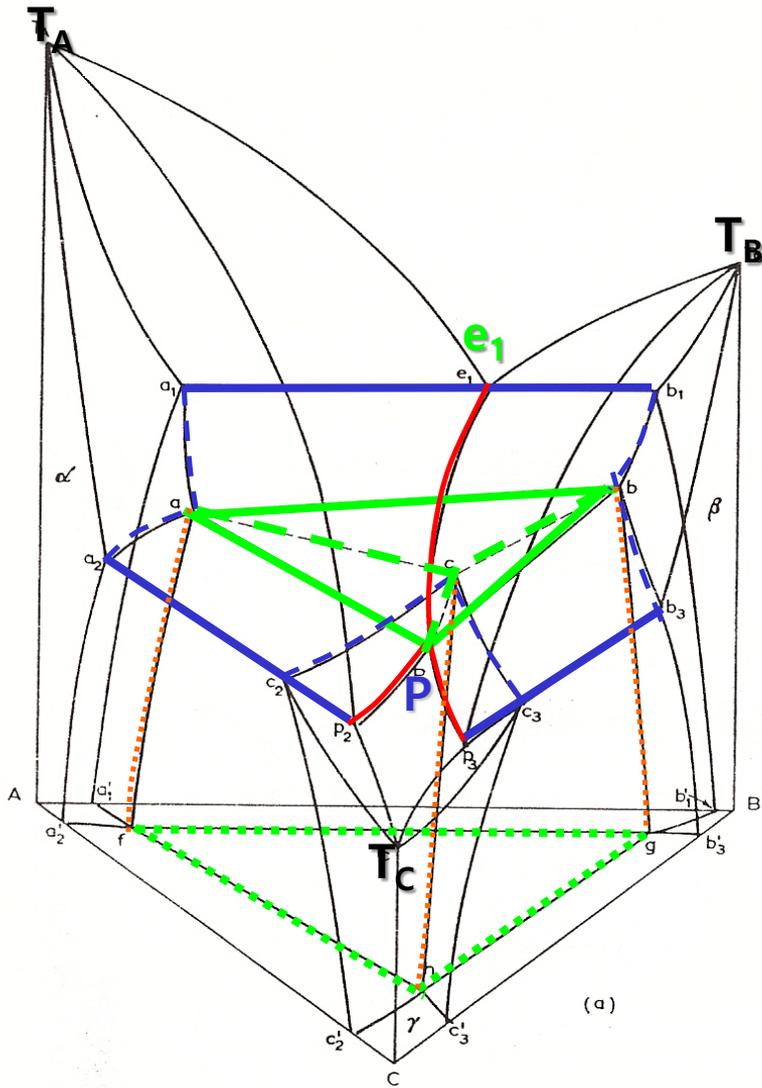
$T_A > T_B > \underline{e_1} > P > P_2 > P_3 > T_C$

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



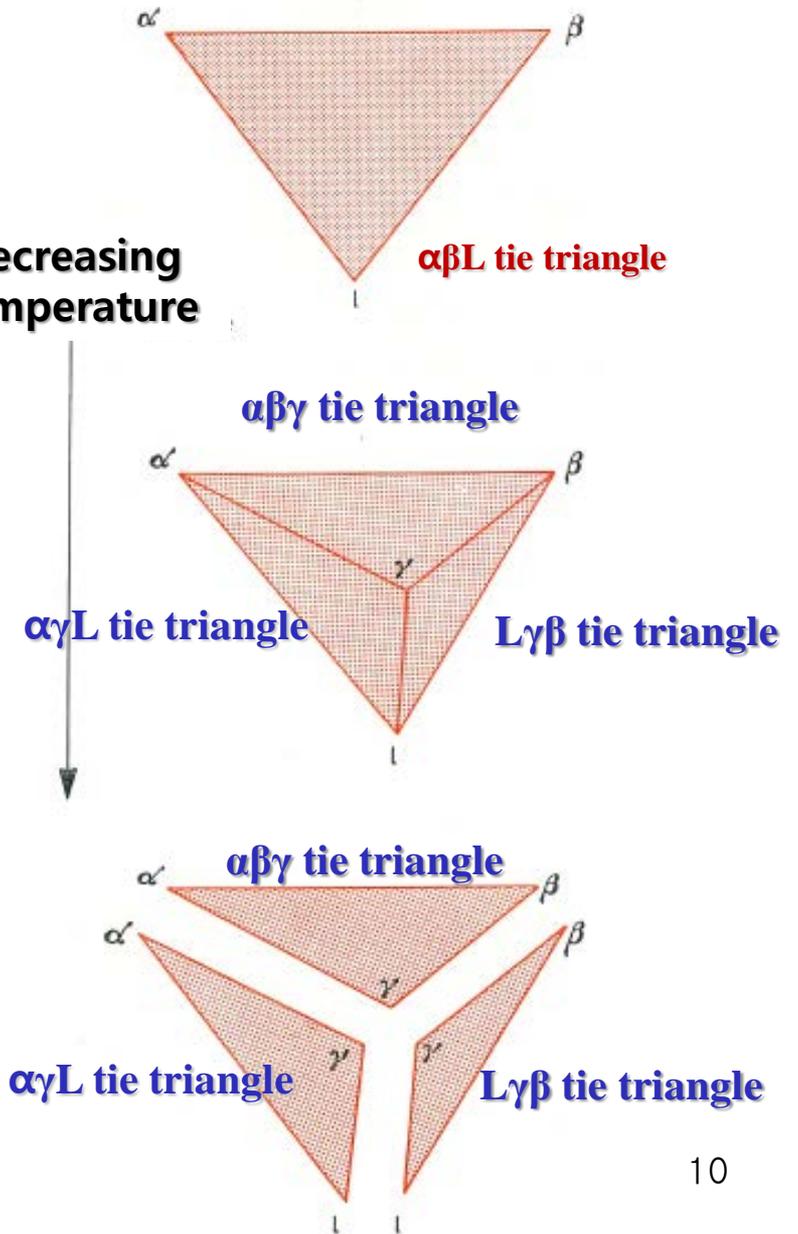
$aPc(\alpha\gamma L) \rightarrow \underline{a_2 c_2 P_2} / Pcb(L\gamma\beta) \rightarrow \underline{P_3 c_3 b_3} / abc(\alpha\beta\gamma) \rightarrow fgh \text{ } (\alpha\beta\gamma)$

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

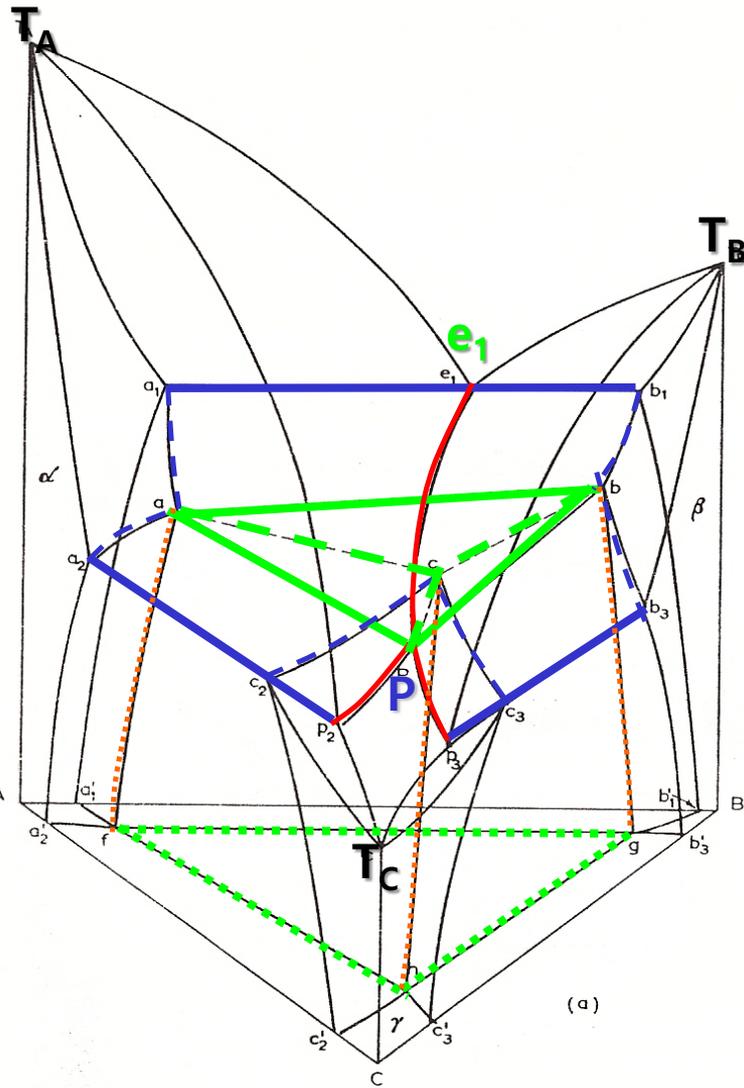


$$T_A > T_B > e_1 > P > P_2 > P_3 > T_C$$

decreasing temperature

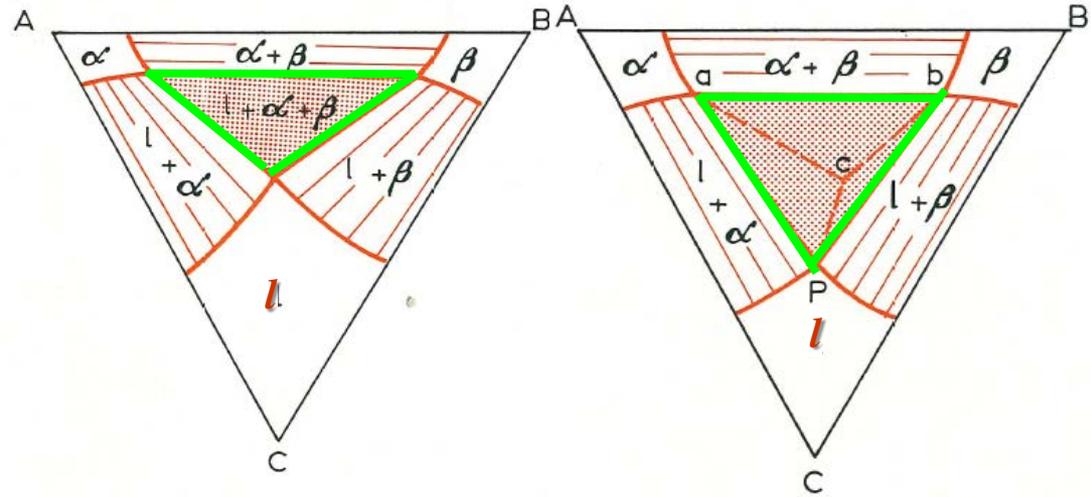


10.4. THE TERNARY PERIECTIC EQUILIBRIUM ($l + \alpha + \beta = \gamma$)



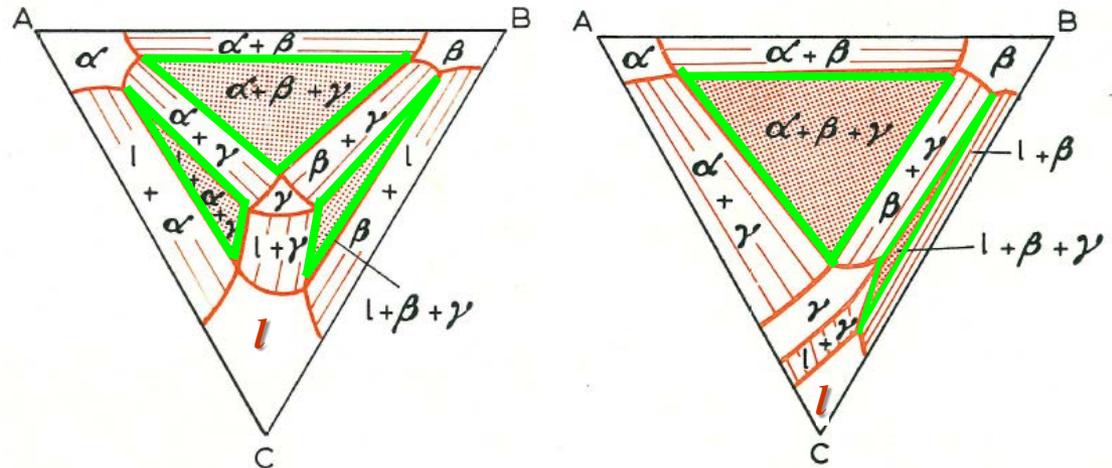
$$T_A > T_B > e_1 > P > P_2 > P_3 > T_C$$

Isothermal section



$$e_1 > T > P$$

$$T = P$$



$$P > T > P_2$$

$$P_2 > T > P_3^1$$

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 δ phase is intermediate phase $AuSb_2$.

$P_1 d_1 b_1 \rightarrow dbp (\delta\beta L) / b_3 e_3 c_3 \rightarrow bpc (\beta L\gamma)$



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



$d^1 \epsilon c^1 (\delta \gamma L) / a_1 e_1 d_2 \rightarrow a^1 \epsilon d^1 (\alpha \delta L) / a_2 e_2 c_2 \rightarrow a^1 \epsilon c^1 (\alpha L \gamma)$



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

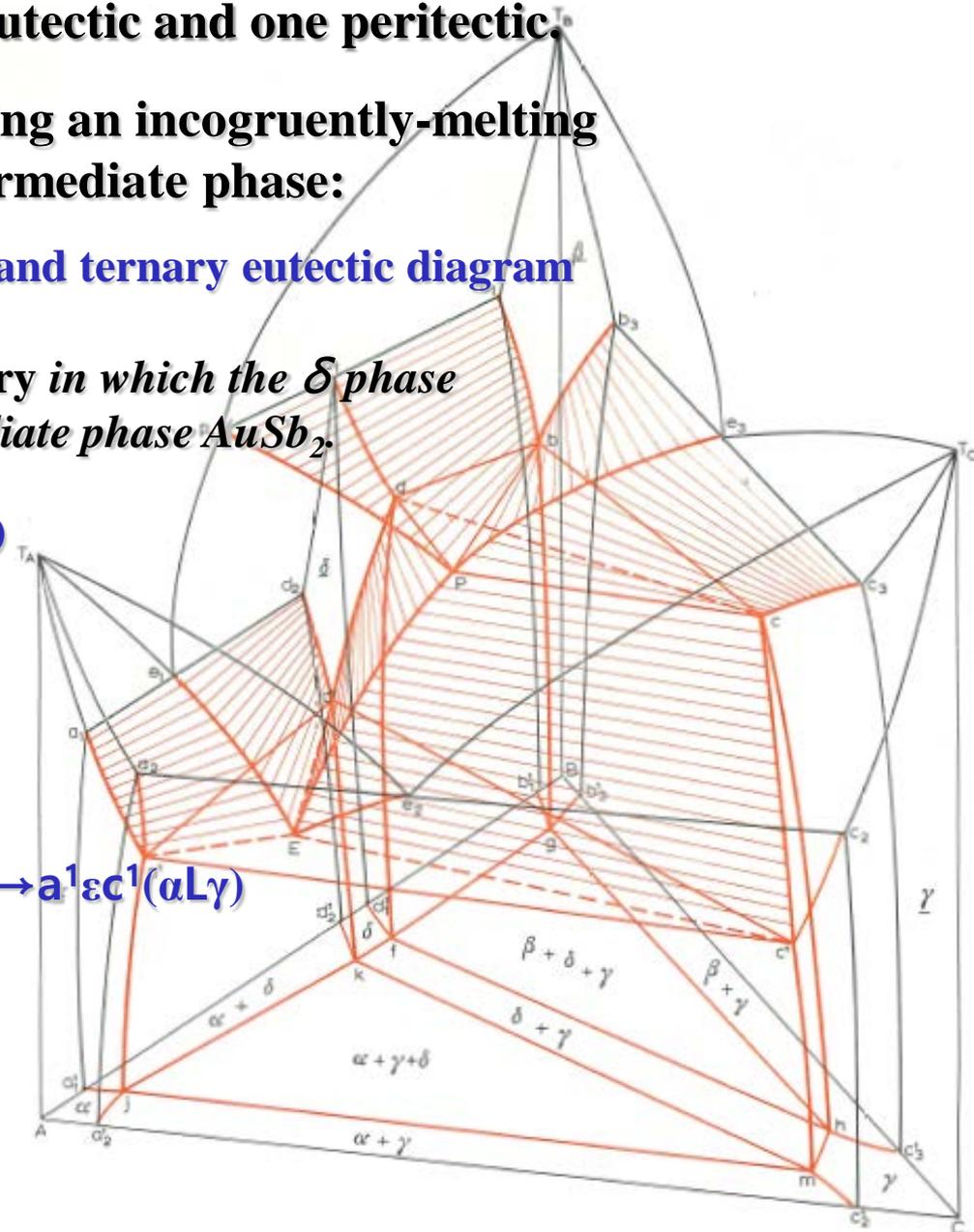
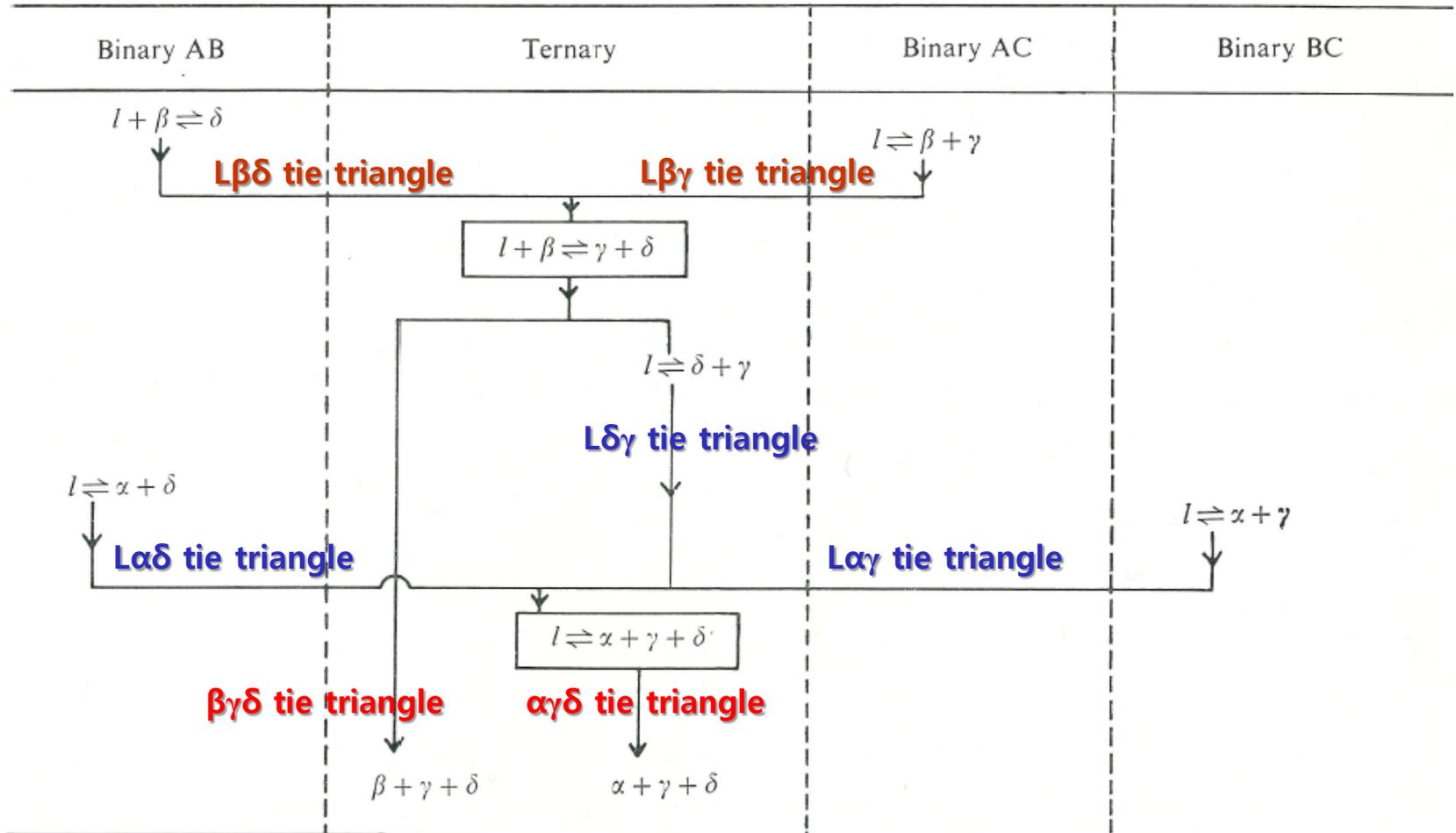


Fig. 189. Ternary system involving an incongruently-melting binary intermediate phase.

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

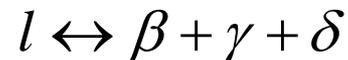
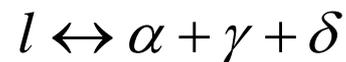
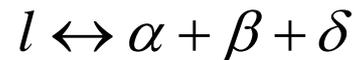
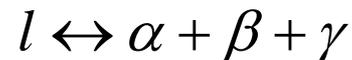
Intermediate Phases

Intermediate phases may **melt congruently** or **incongruently**.
They may occur as **either binary or ternary phases**.

11.1 Congruently melting intermediate phases

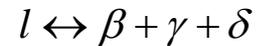
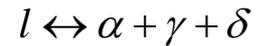
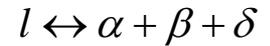
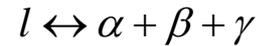
11.1. Binary intermediate phases

- 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.



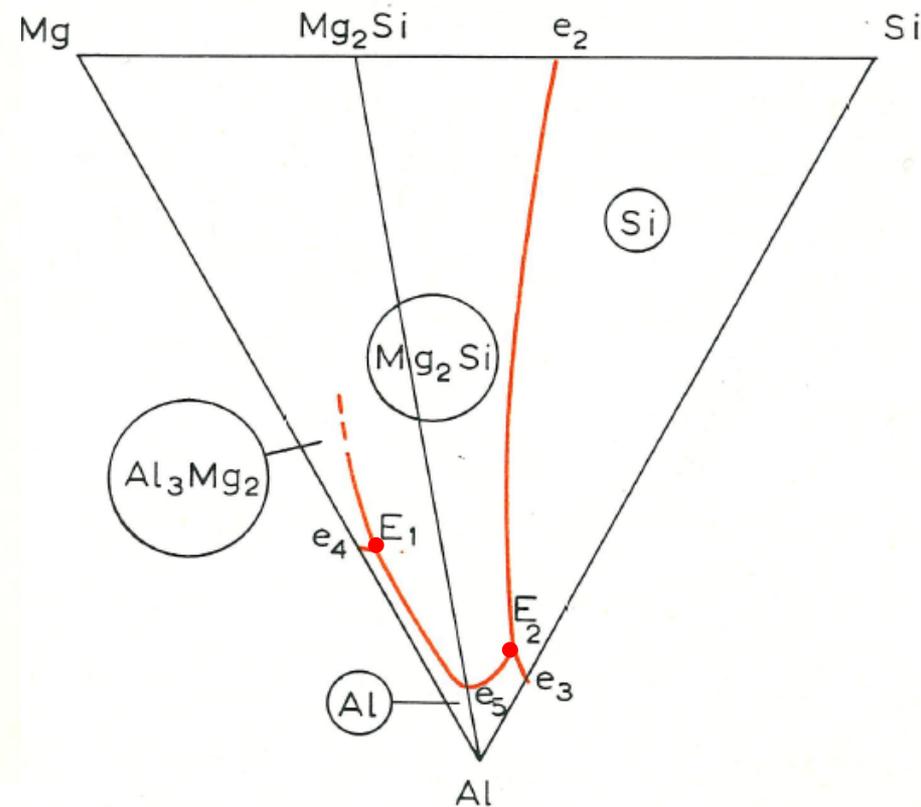
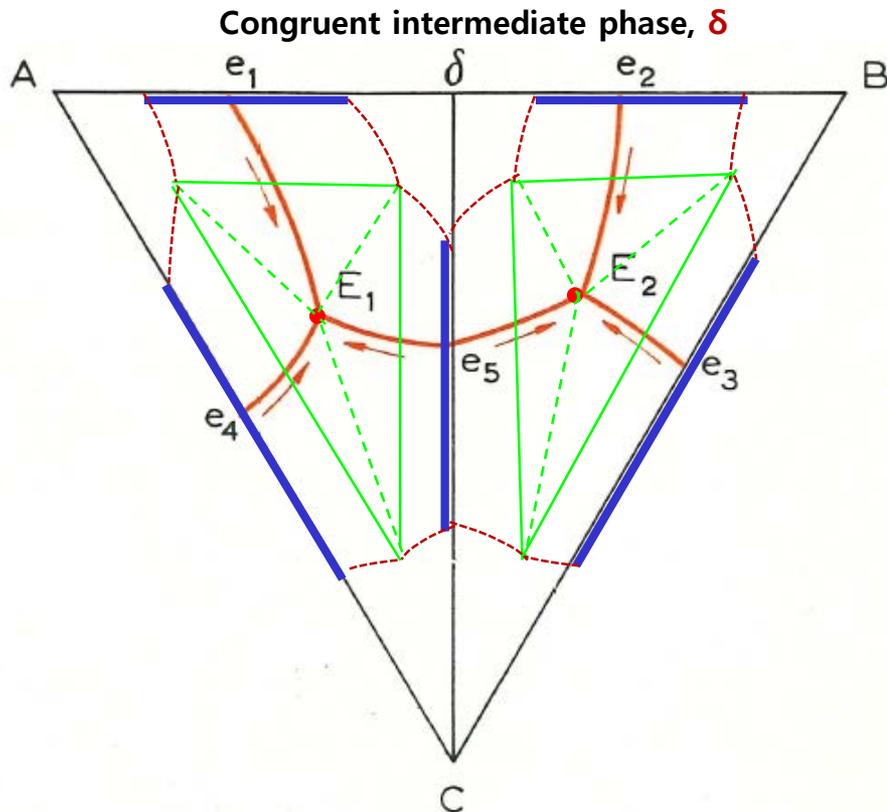
- The more usual combination is of the last two equilibria, implying **equilibrium in the solid state between $\alpha\gamma\delta$ and $\beta\gamma\delta$** .
- This can be envisaged if there is direct equilibrium between γ and δ , splitting the ternary system into **two partial system $A\delta C$ and $B\delta C$** . **It often happens that the δ phase forms 1) a quasi-binary system with component C.**

11.1 Congruently melting intermediate phases



11.1. Binary intermediate phases

1) Quasi binary eutectic δC



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

Al-Mg-Si system



11.1 Congruently melting intermediate phases

11.1. Binary intermediate phases

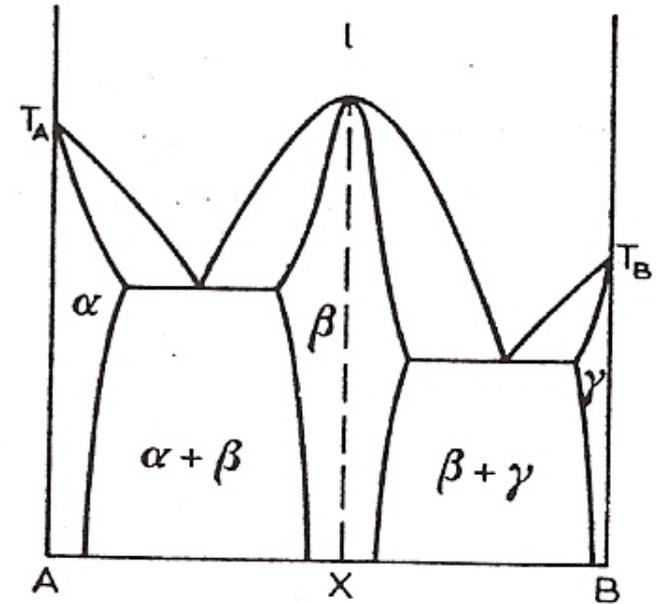
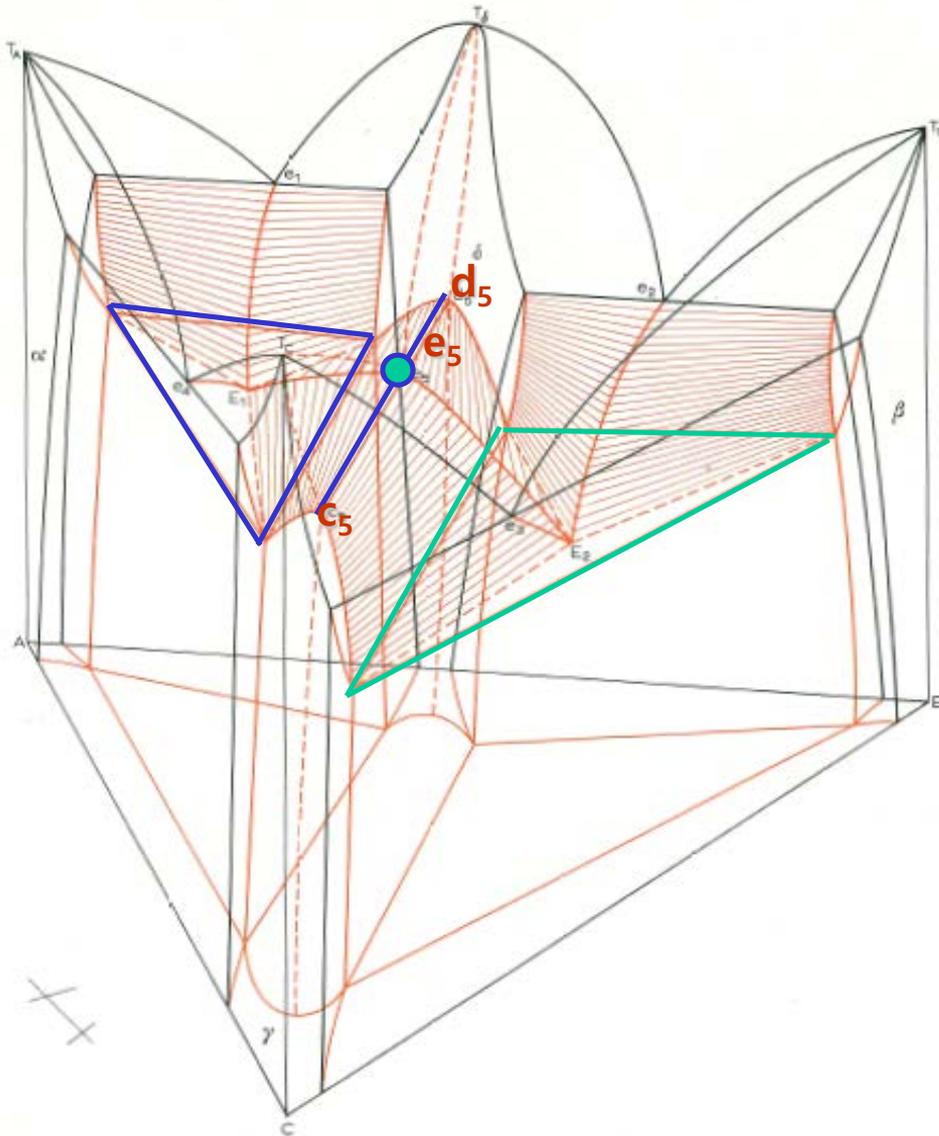


Fig. 78. Phase diagram with a congruent intermediate phase.

the **eutectic point e_5** on the quasi-binary section δC is **saddle point**.

the straight line is the quasi-binary eutectic horizontal **$c_5e_5d_5$** .

11.1. Binary intermediate phases

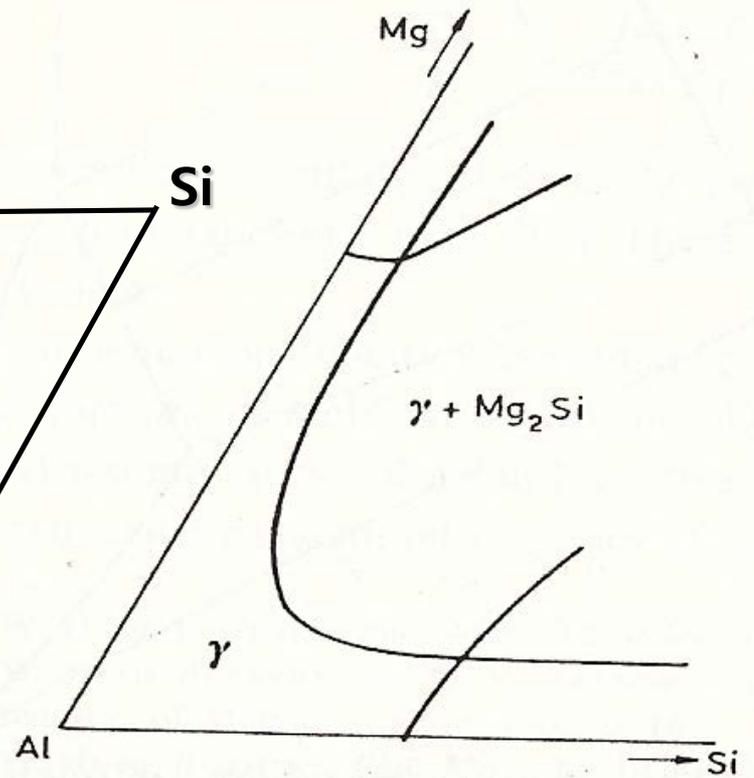
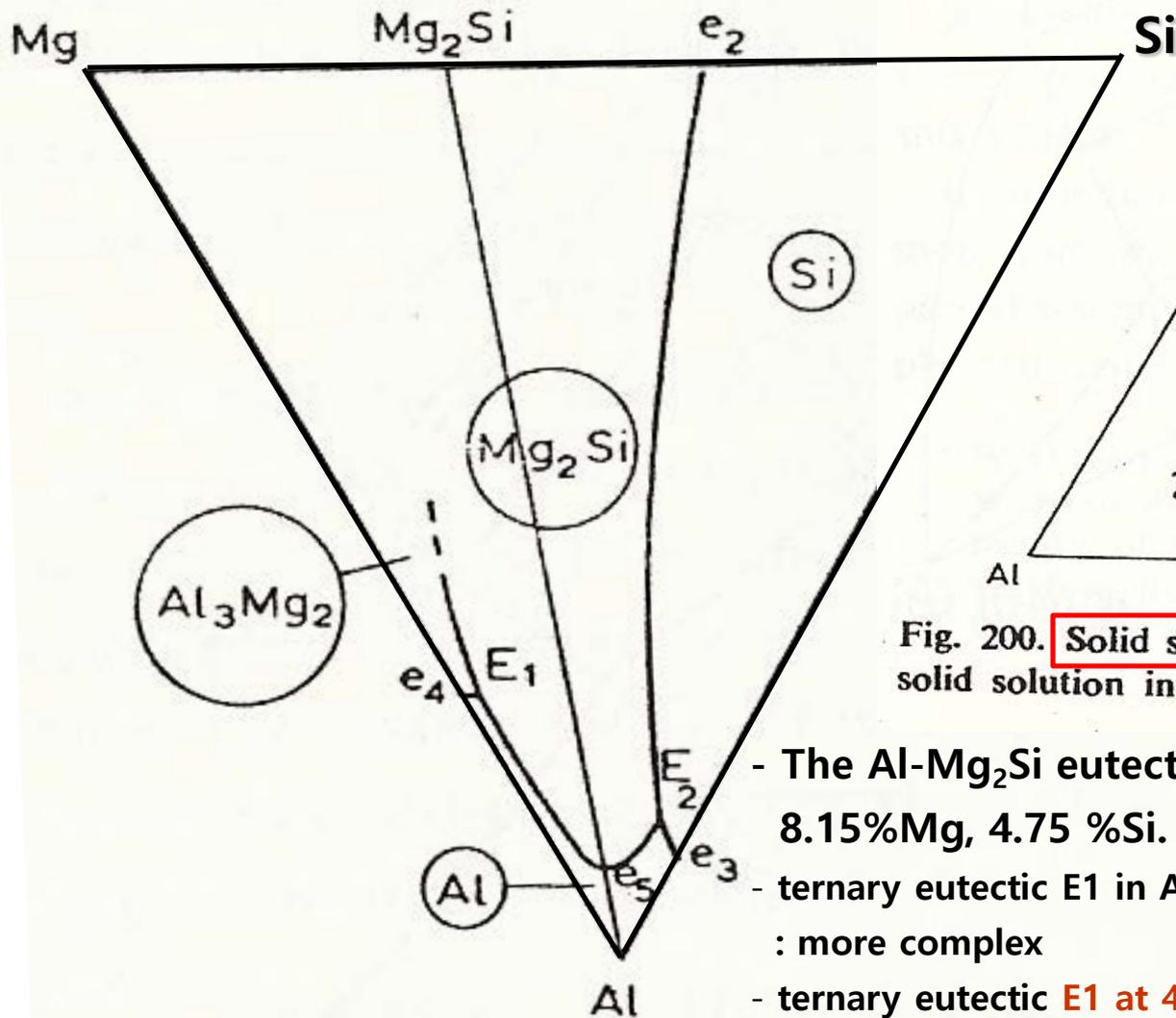
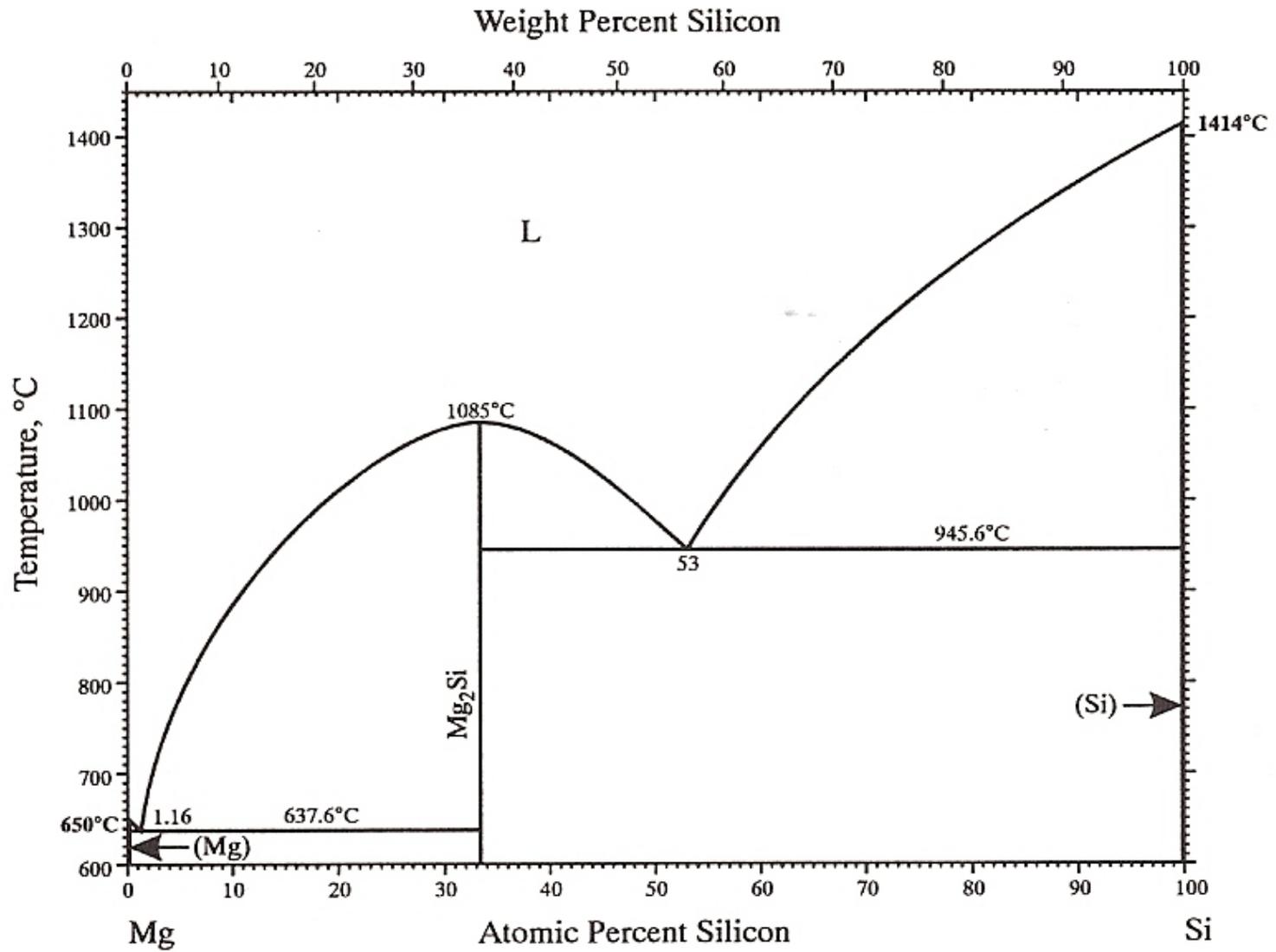


Fig. 200. **Solid solubility isotherm** for the Al-based solid solution in the Al-Mg-Si system (schematic).

- The Al-Mg₂Si eutectic (**e5**) occurs at **595°C** and **8.15%Mg, 4.75 %Si**.
- ternary eutectic E1 in Al-Mg-Mg₂Si partial system : more complex
- ternary eutectic **E1** at **451°C** between Al, Mg₂Si and Al₃Mg₂ contains **33.2 %Mg** and **0.37 %Si**.

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

11.1. Binary intermediate phases

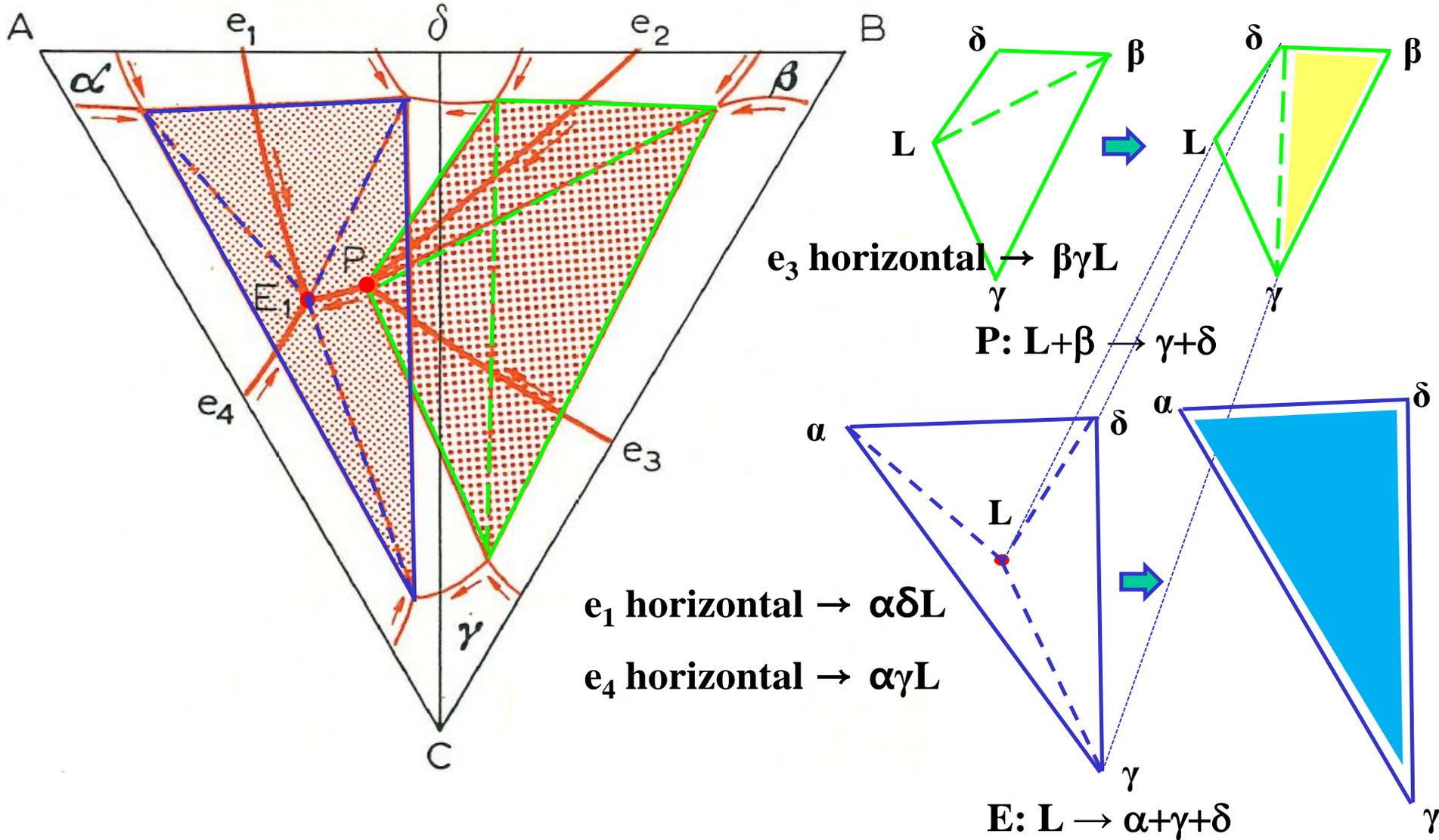


Mg-Si binary phase diagram

11.1 Congruently-melting intermediate phases

- Binary intermediate phases

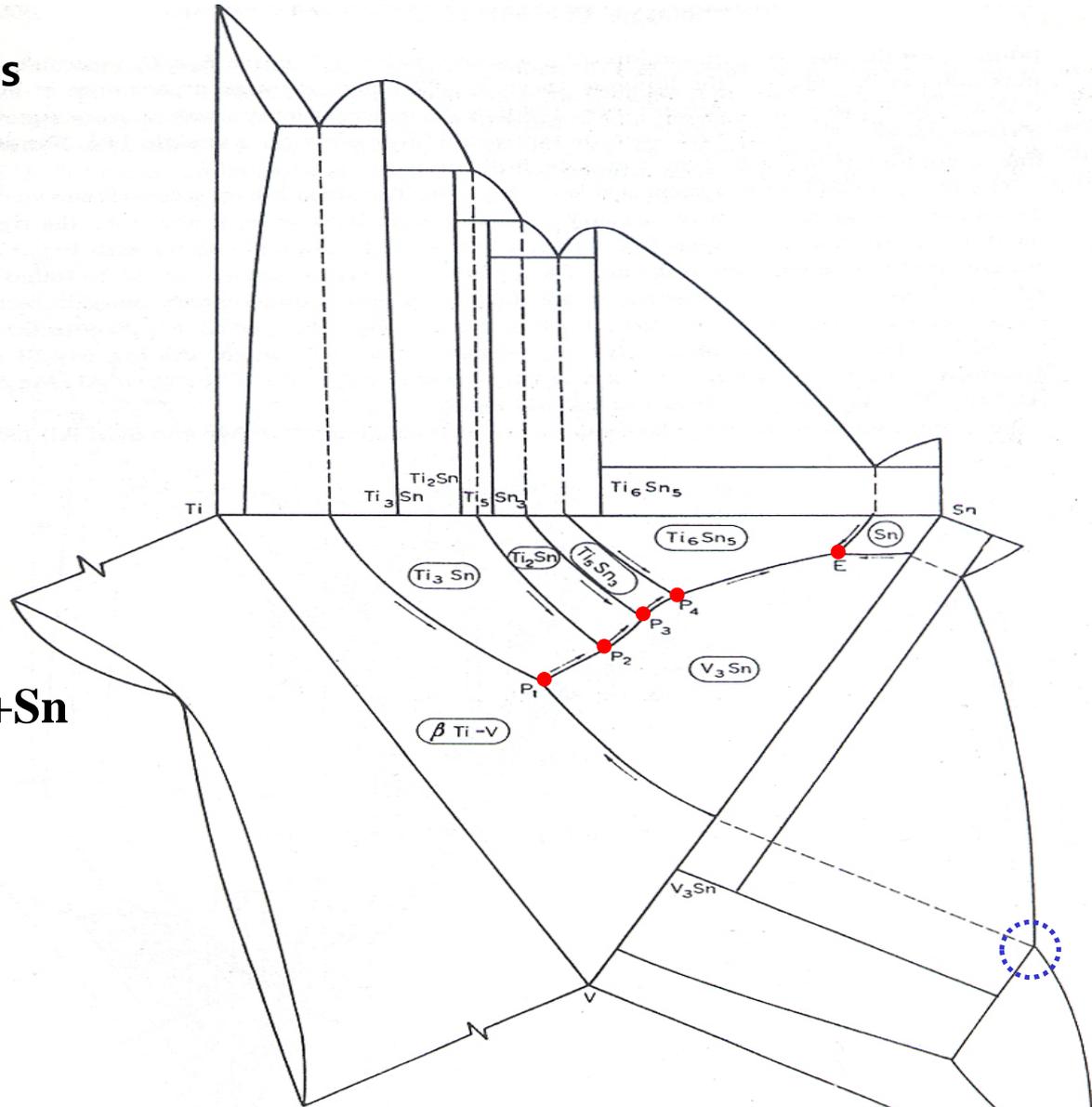
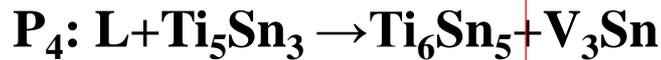
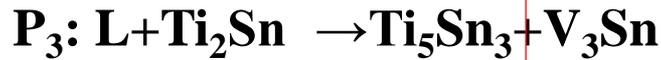
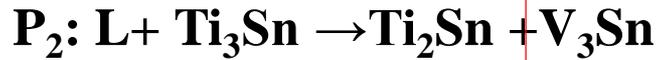
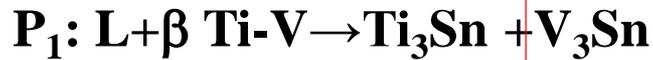
2) Quasi peritectic reaction



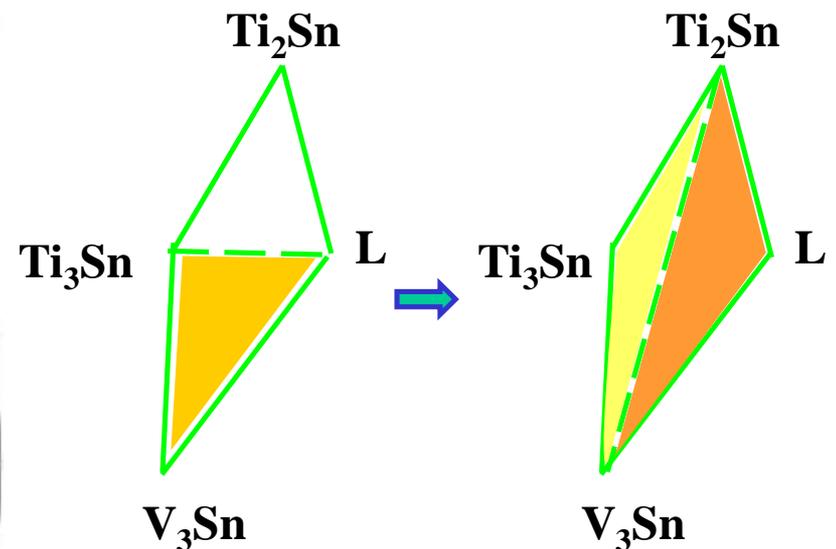
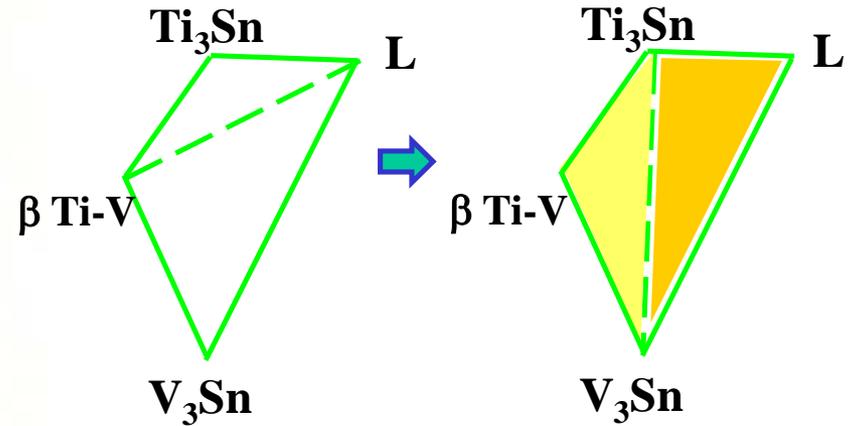
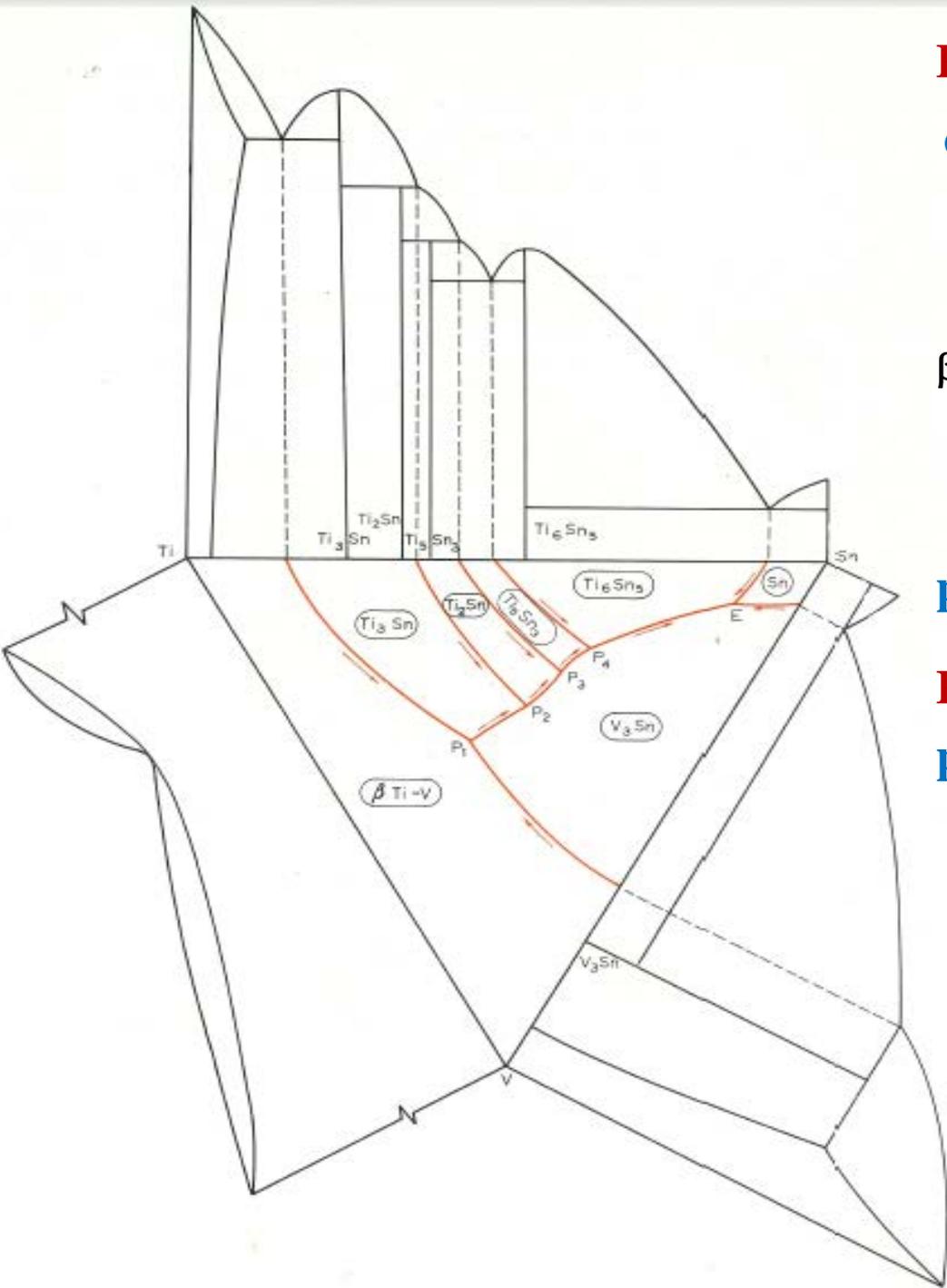
11.1 Congruently-melting intermediate phases

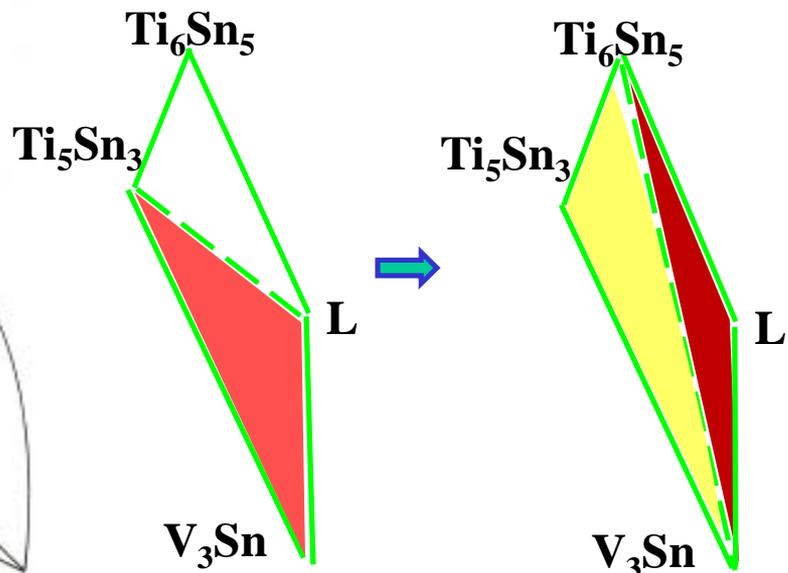
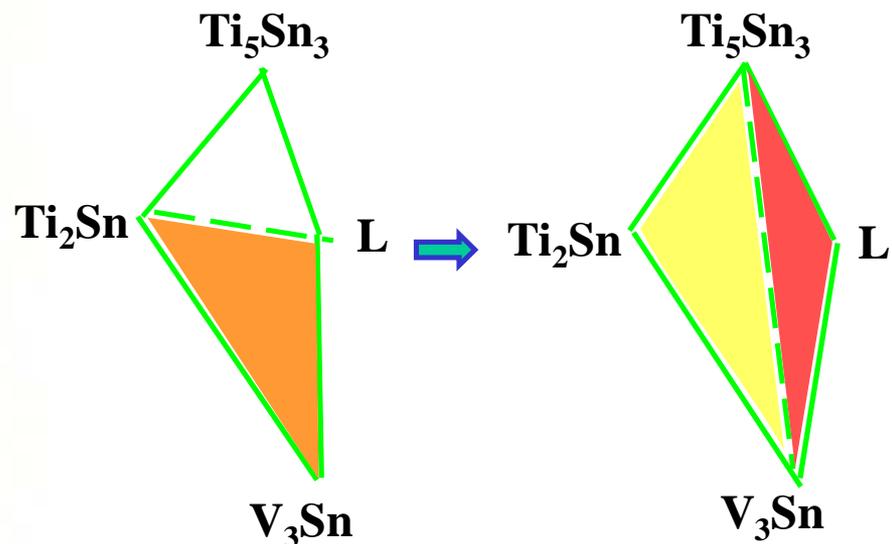
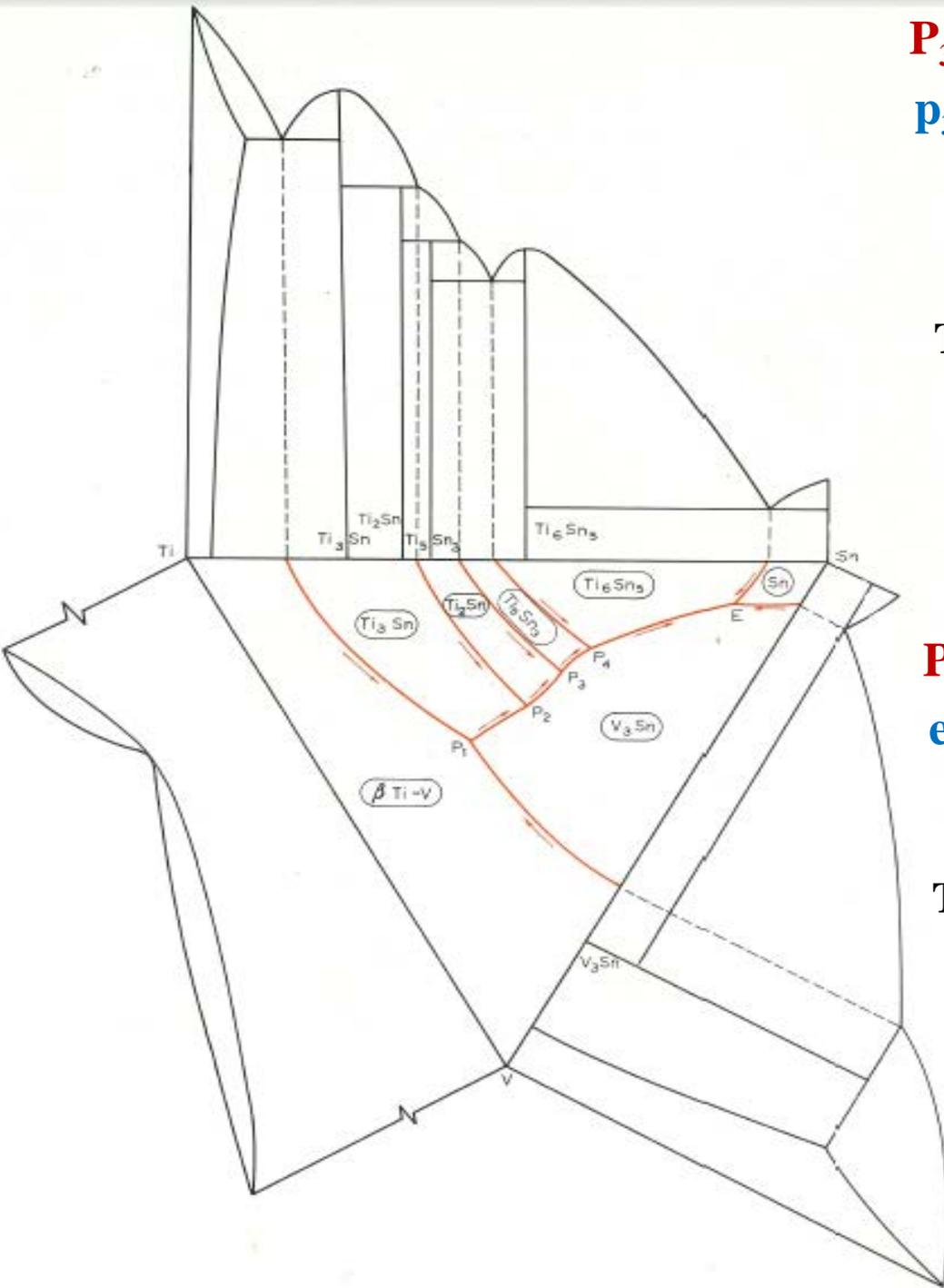
- Binary intermediate phases

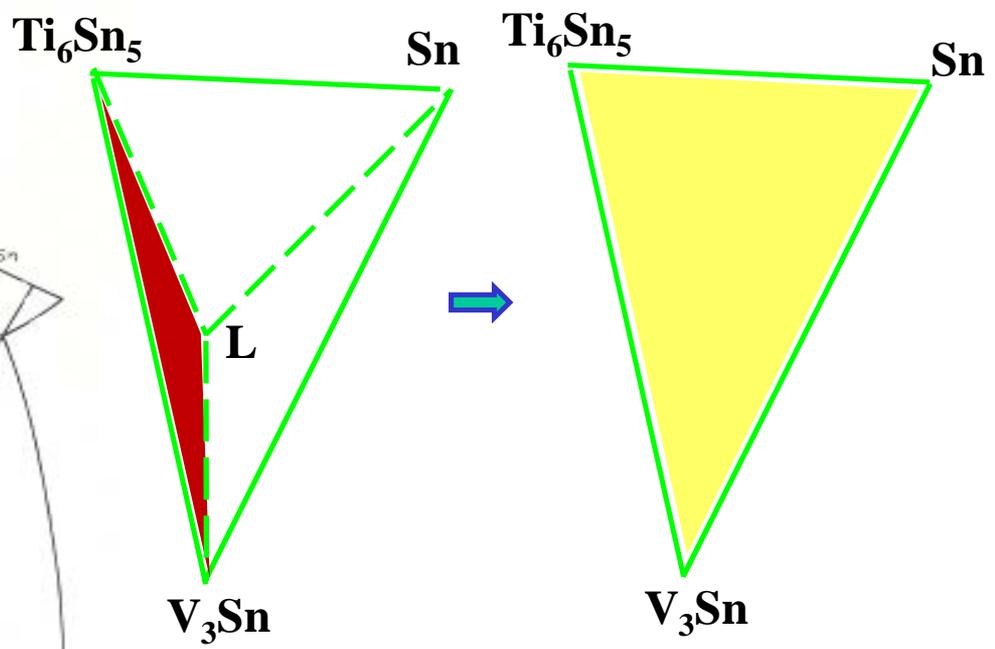
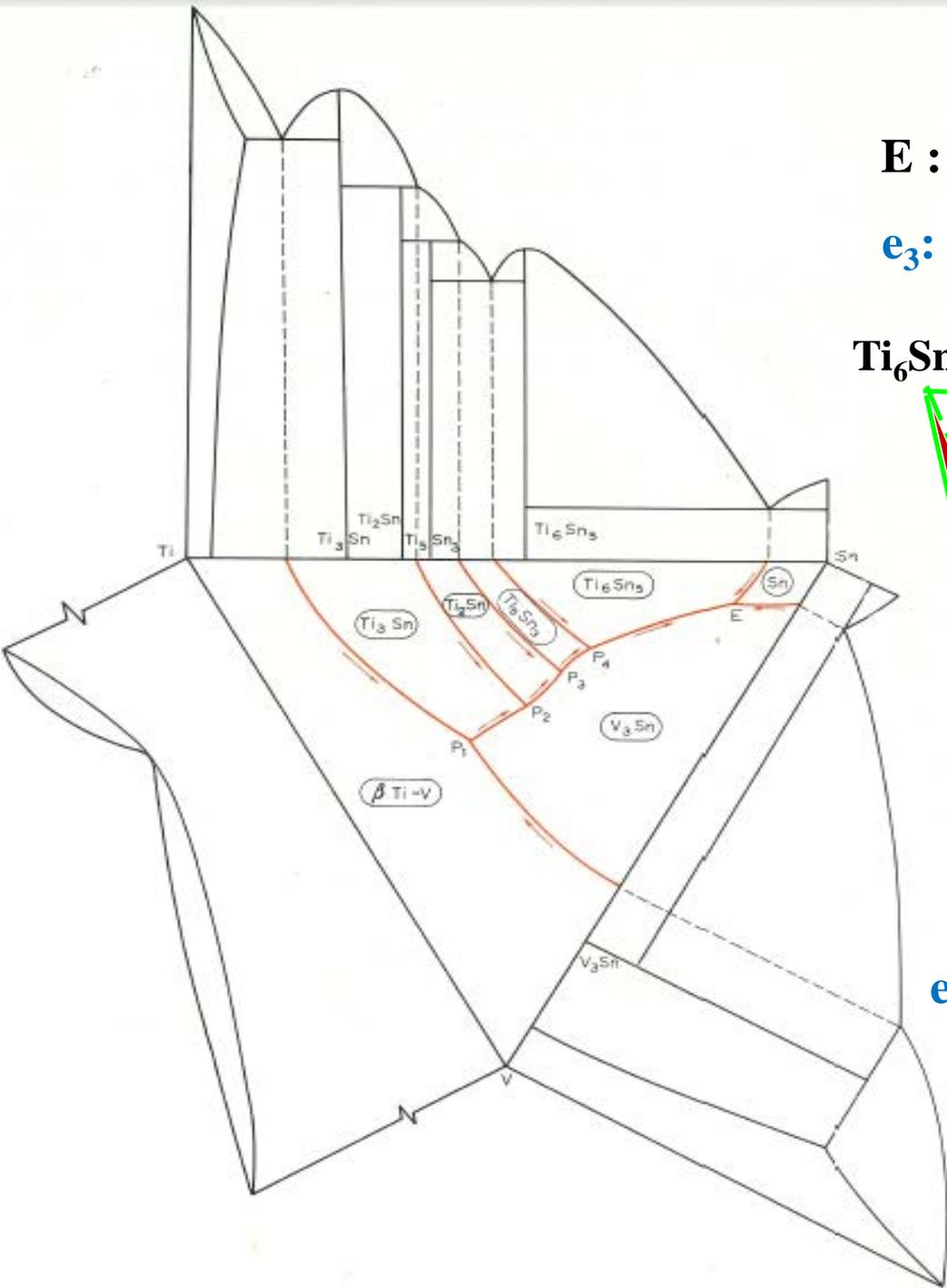
Quasi peritectic reaction



Monovariant liquid curve of Sn-Ti-V system



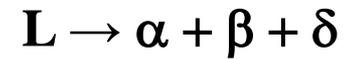
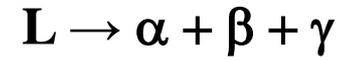
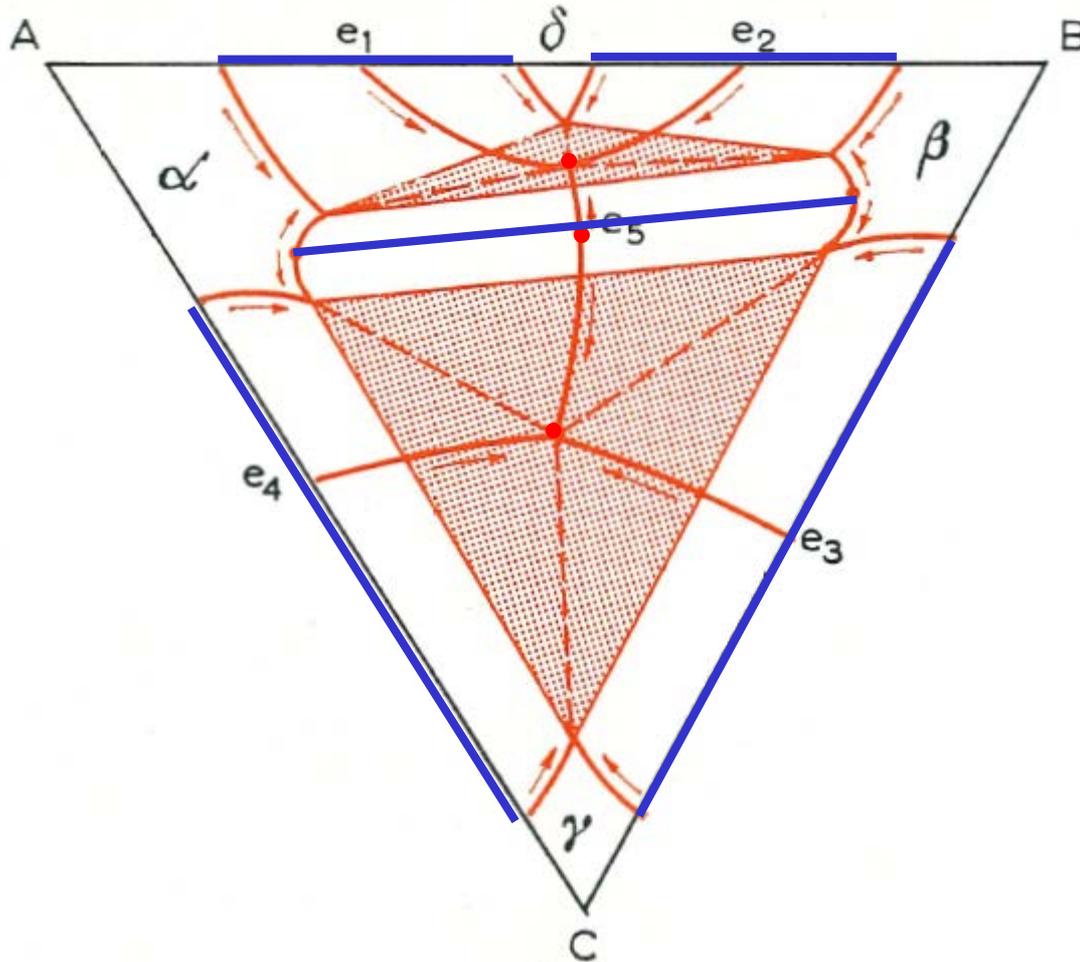
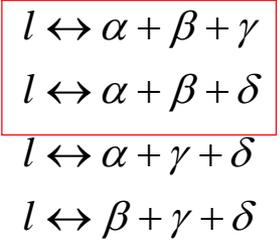




11.1 Congruently-melting intermediate phases

- Binary intermediate phases

3) No quasi binary eutectic : **two ternary eutectic**



e_5 : saddle point

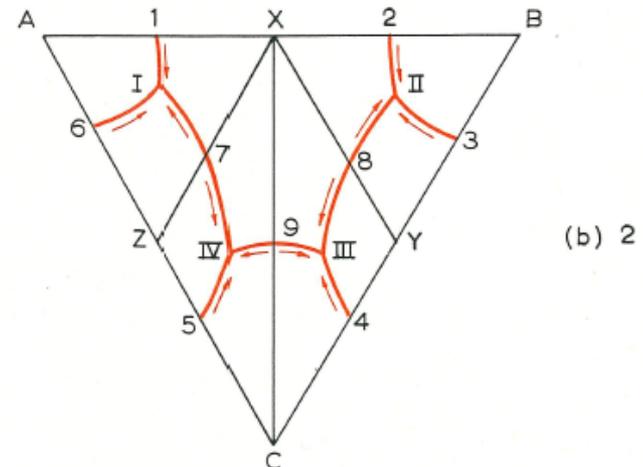
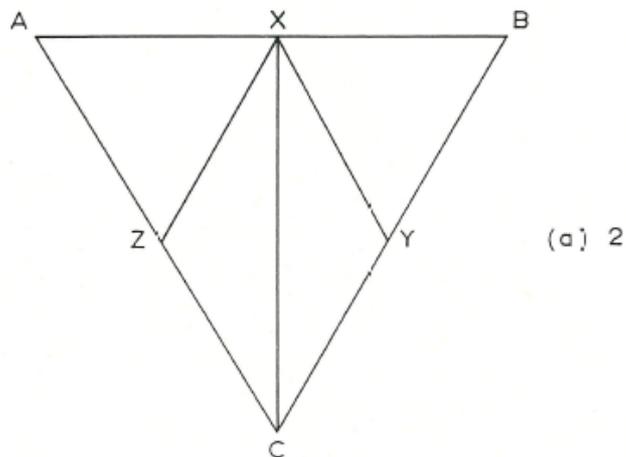
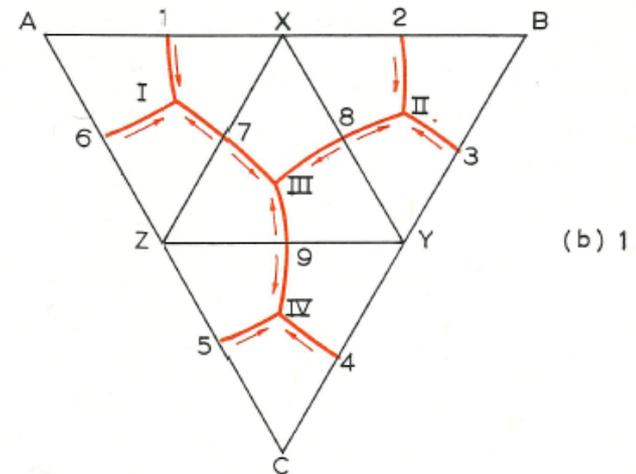
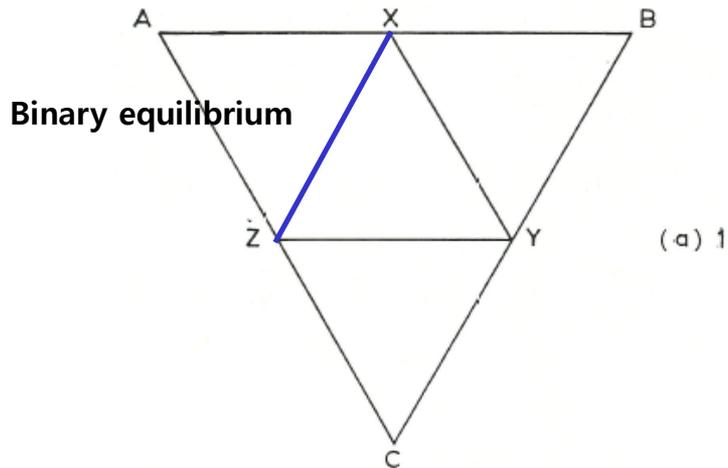
11.1 Congruently-melting intermediate phases

- 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



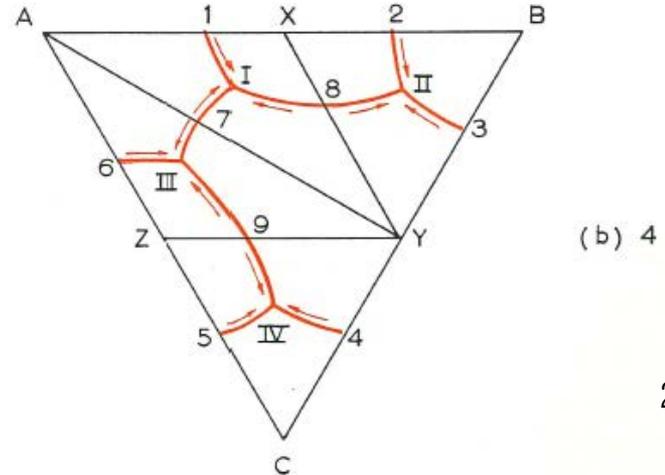
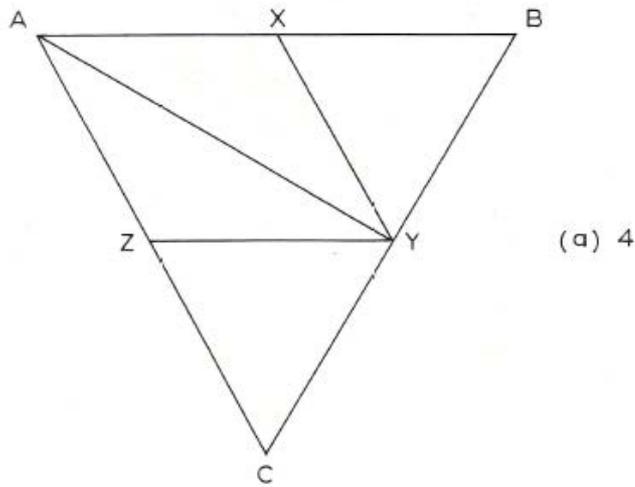
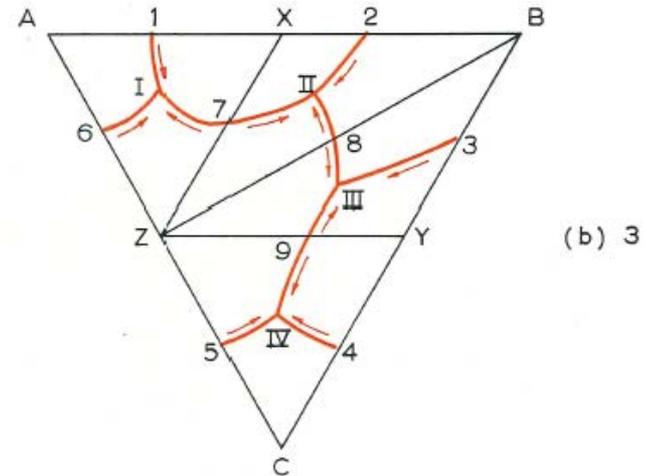
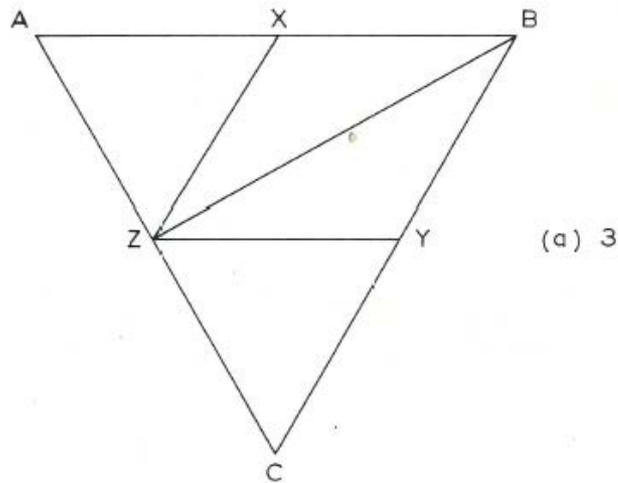
11.1 Congruently-melting intermediate phases

- Binary intermediate phases

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

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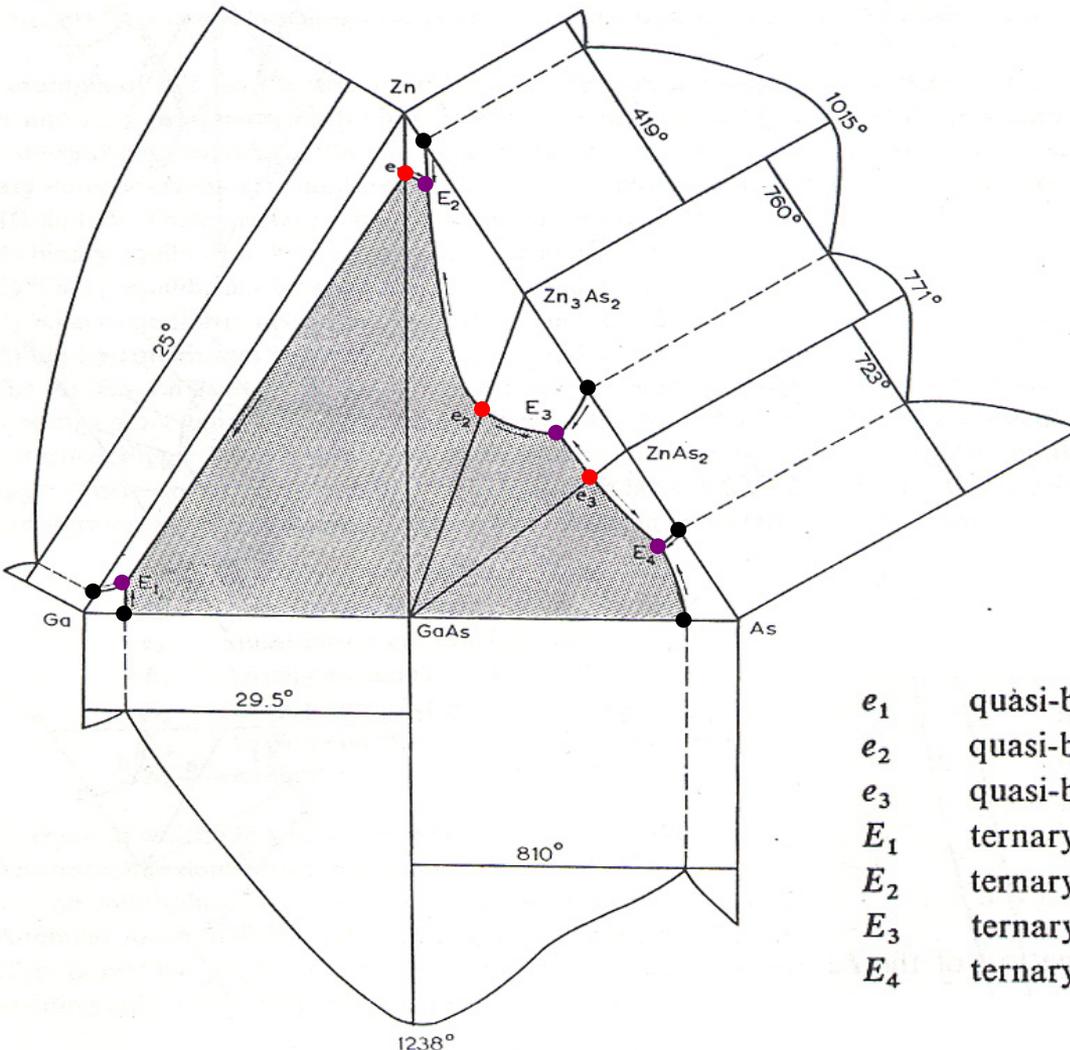
binary eutectic points: 1, 2, 3, ... , 9/ternary eutectic points: I, II, III, IV



11.1 Congruently-melting intermediate phases

a) Binary intermediate phases

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

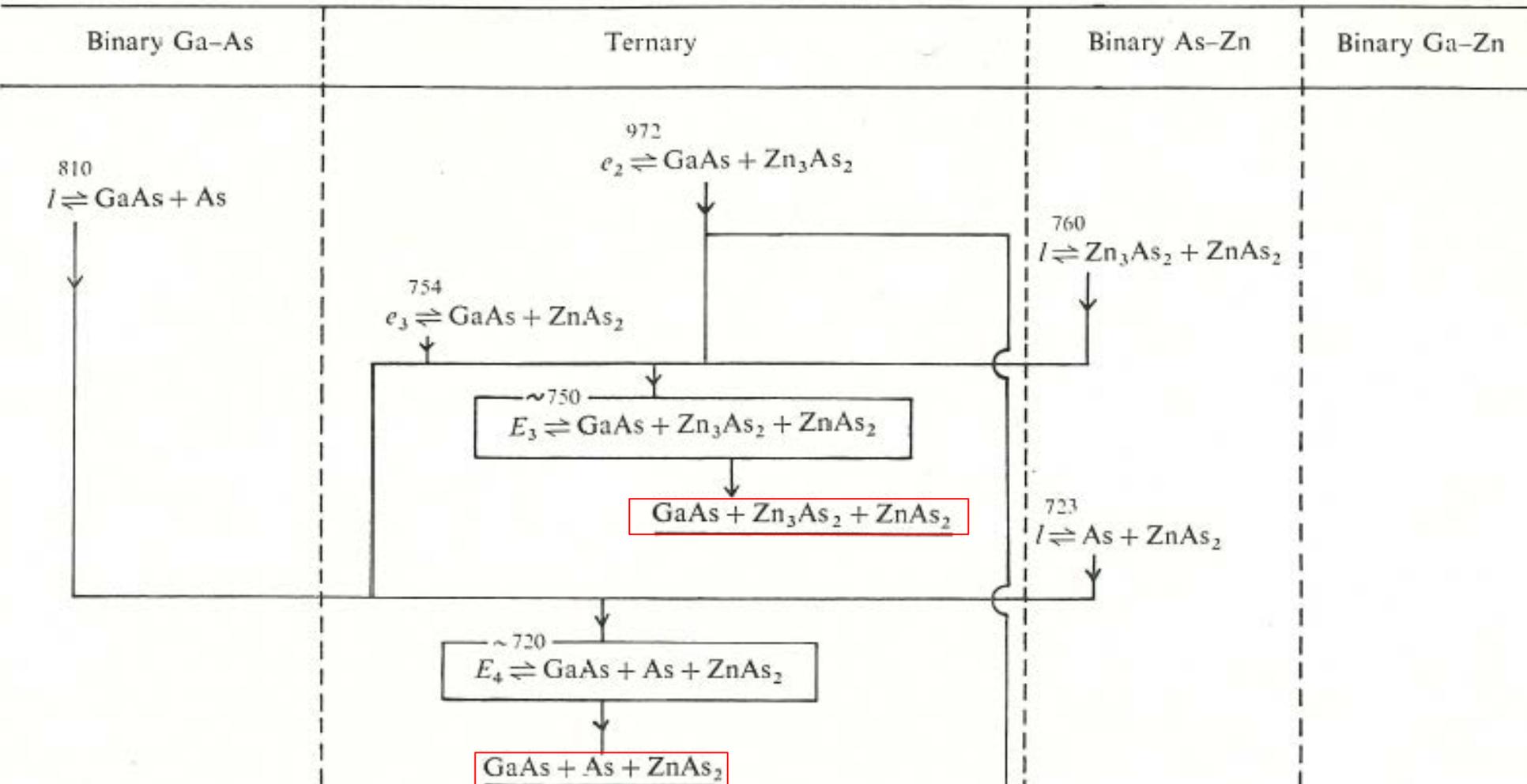


- The region in which GaAs is the primary phase to crystallize from the liquid is lightly shaded.
- It illustrates the dominating behavior of the **high melting phase GaAs** in this system
- For clarity, **no solid solubility** between any of the phases has been indicated.

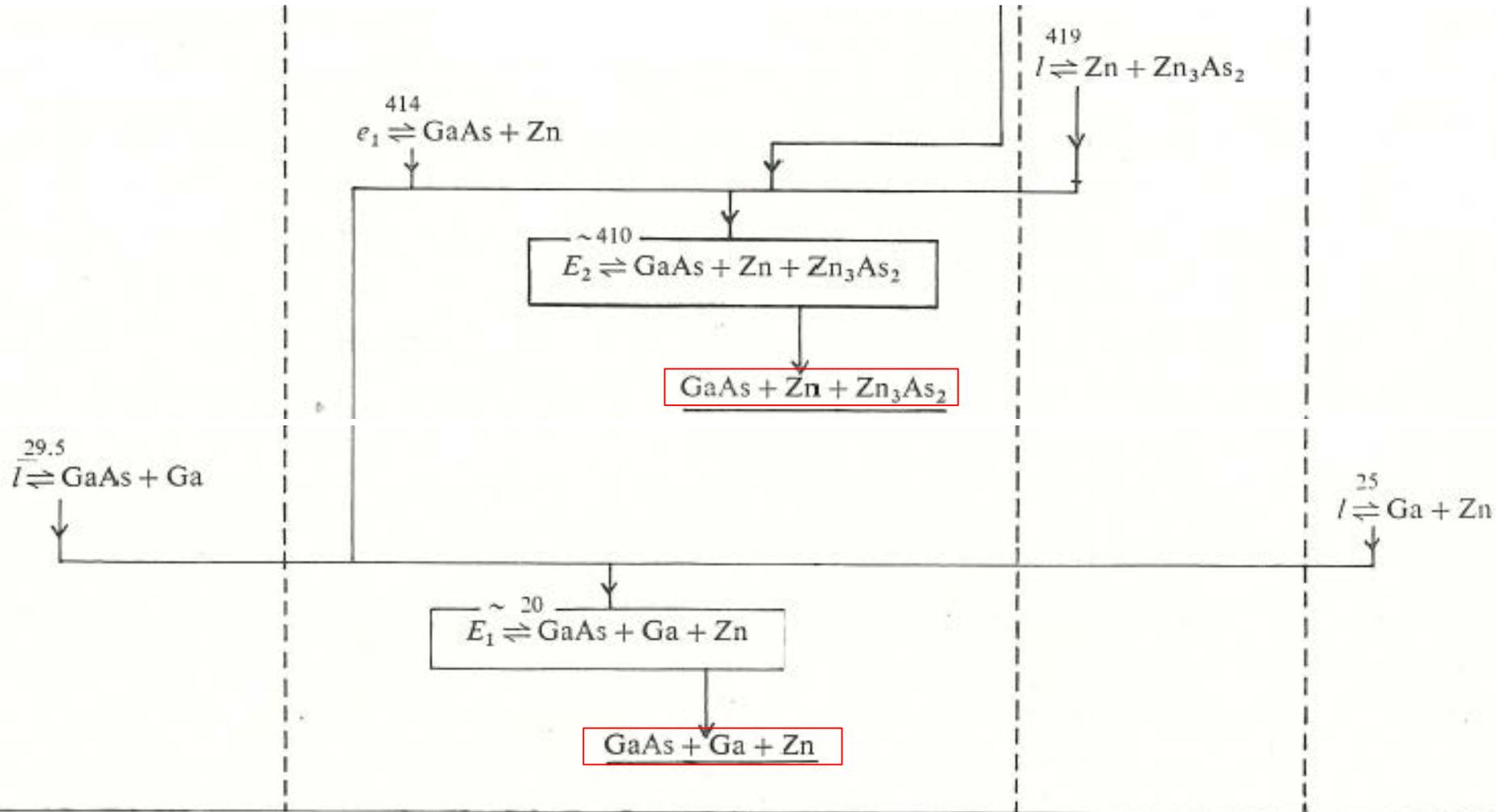
e_1	quasi-binary eutectic $l \rightleftharpoons \text{GaAs} + \text{Zn}$	at	414 °C,
e_2	quasi-binary eutectic $l \rightleftharpoons \text{GaAs} + \text{Zn}_3\text{As}_2$	at	972 °C,
e_3	quasi-binary eutectic $l \rightleftharpoons \text{GaAs} + \text{ZnAs}_2$	at	754 °C,
E_1	ternary eutectic $l \rightleftharpoons \text{GaAs} + \text{Zn} + \text{Ga}$	at	~ 20 °C,
E_2	ternary eutectic $l \rightleftharpoons \text{GaAs} + \text{Zn} + \text{Zn}_3\text{As}_2$	at	~410 °C,
E_3	ternary eutectic $l \rightleftharpoons \text{GaAs} + \text{Zn}_3\text{As}_2 + \text{ZnAs}_2$	at	~750 °C,
E_4	ternary eutectic $l \rightleftharpoons \text{GaAs} + \text{ZnAs}_2 + \text{As}$	at	~720 °C.

As-Ga-Zn system

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

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

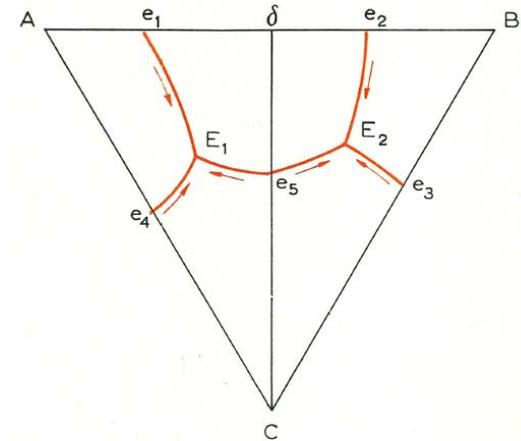
K = # of secondary triangles

E = # of ternary eutectic points

c_2 = binary congruent intermediate phases

q = quasi binary reaction

m = saddle point



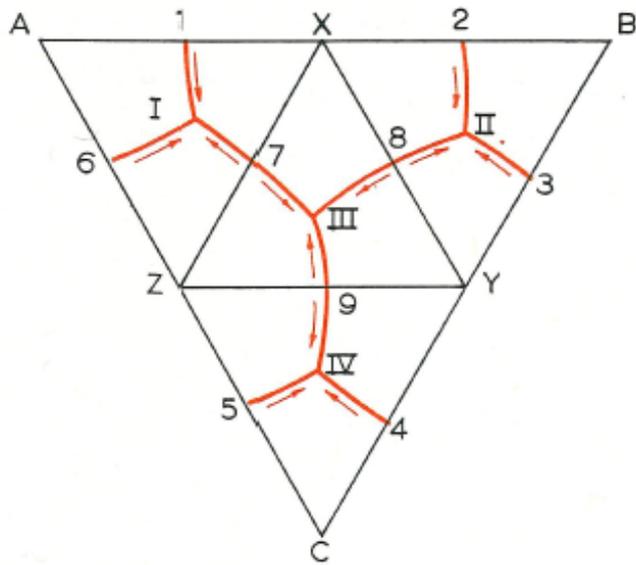
2) Case2: with only ternary congruent intermediate phases

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

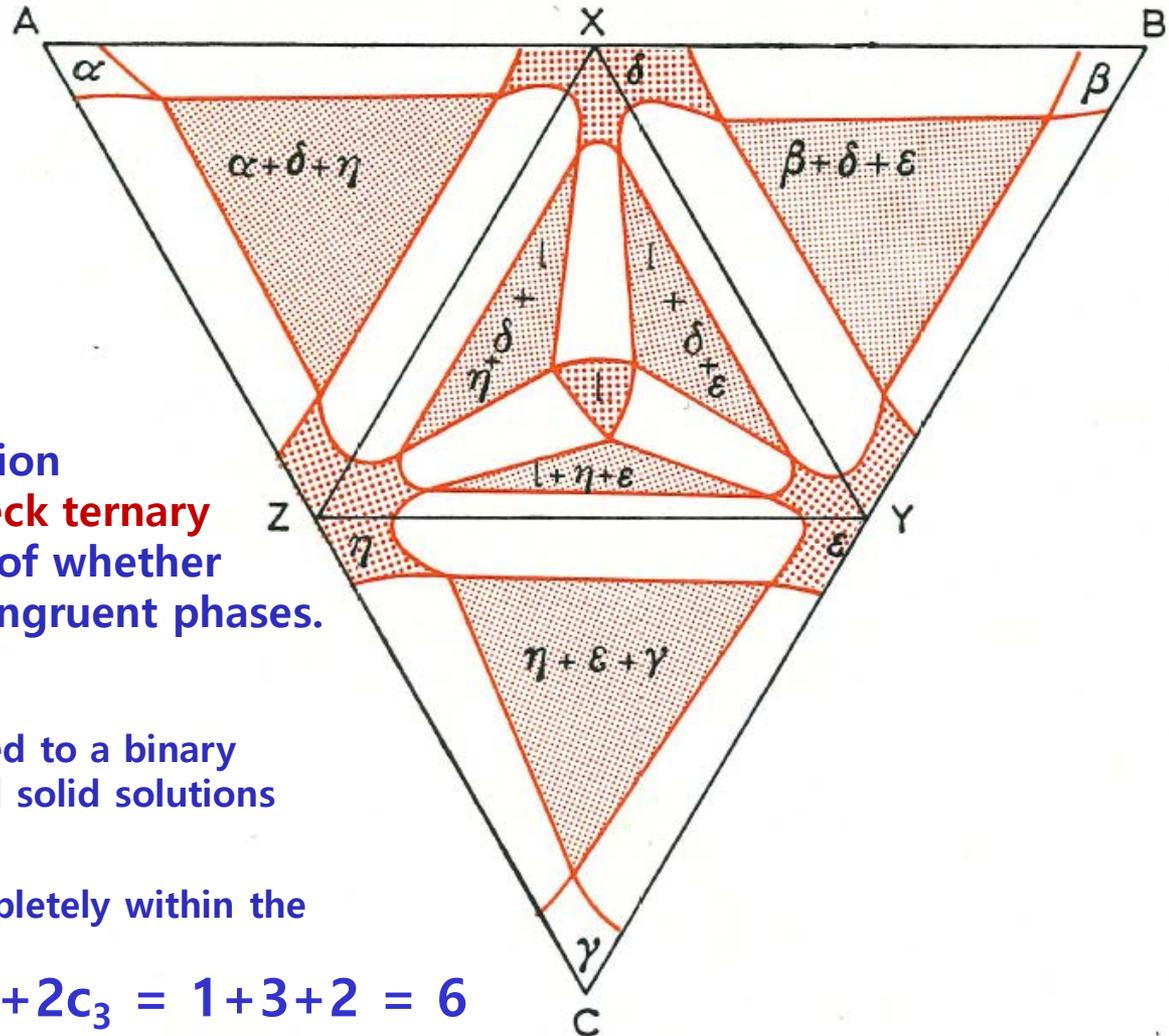
c_3 = ternary congruent intermediate phases

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.

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

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

2021 Spring

“Phase Equilibria *in* Materials”

05.06.2021

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Chapter 11. Ternary phase Diagrams

Intermediate Phases

Intermediate 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

1) Two ternary eutectic reactions

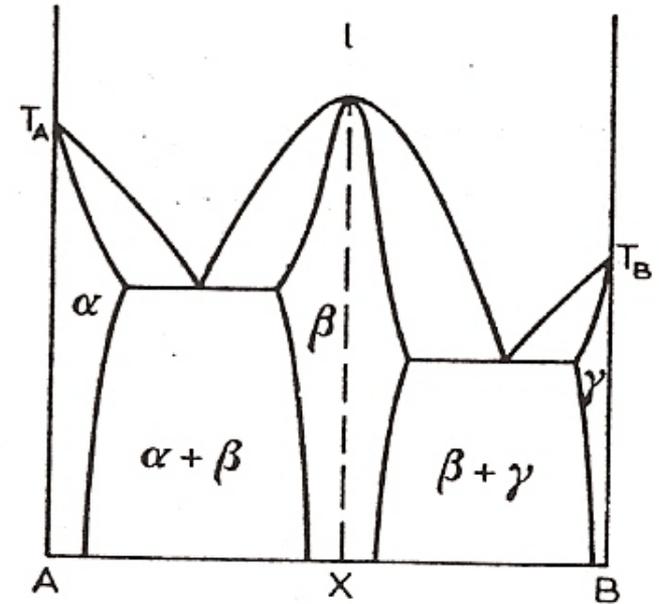
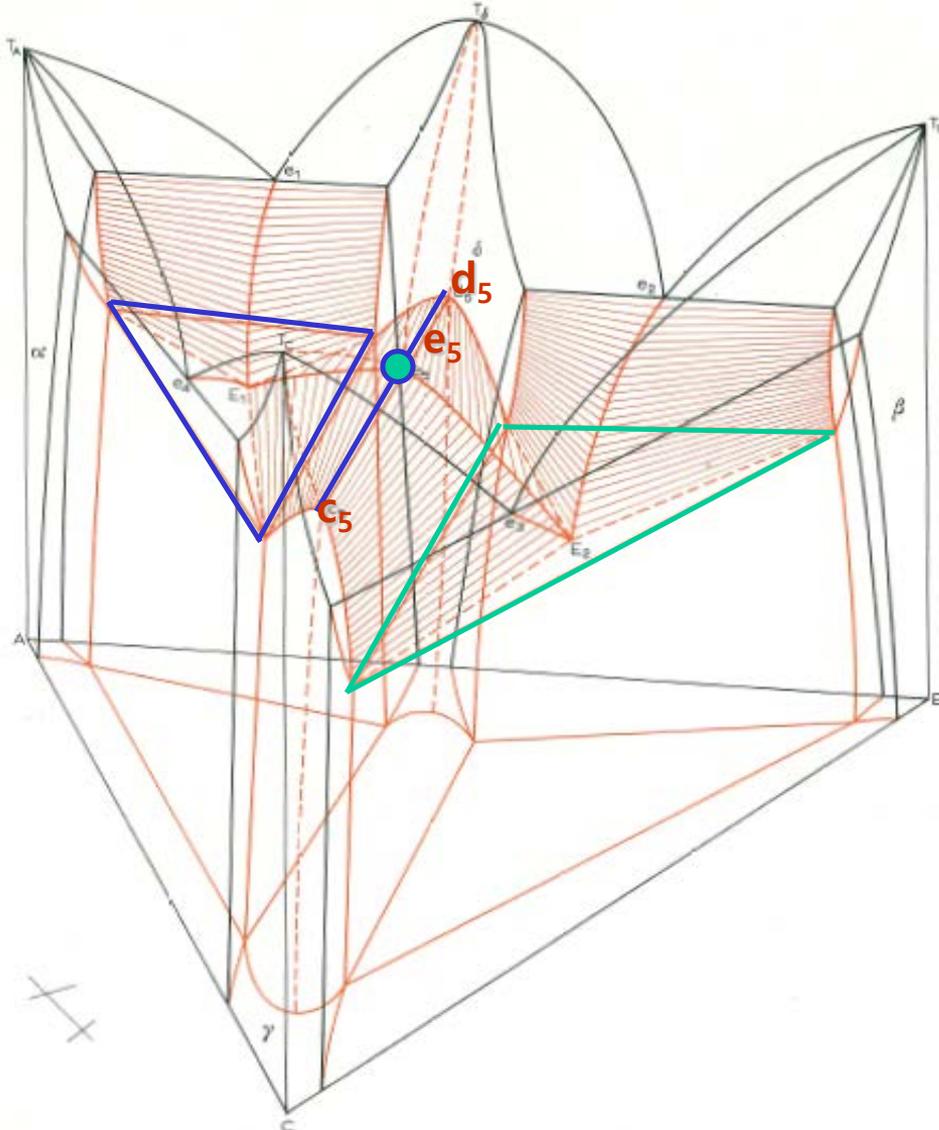


Fig. 78. Phase diagram with a congruent intermediate phase.

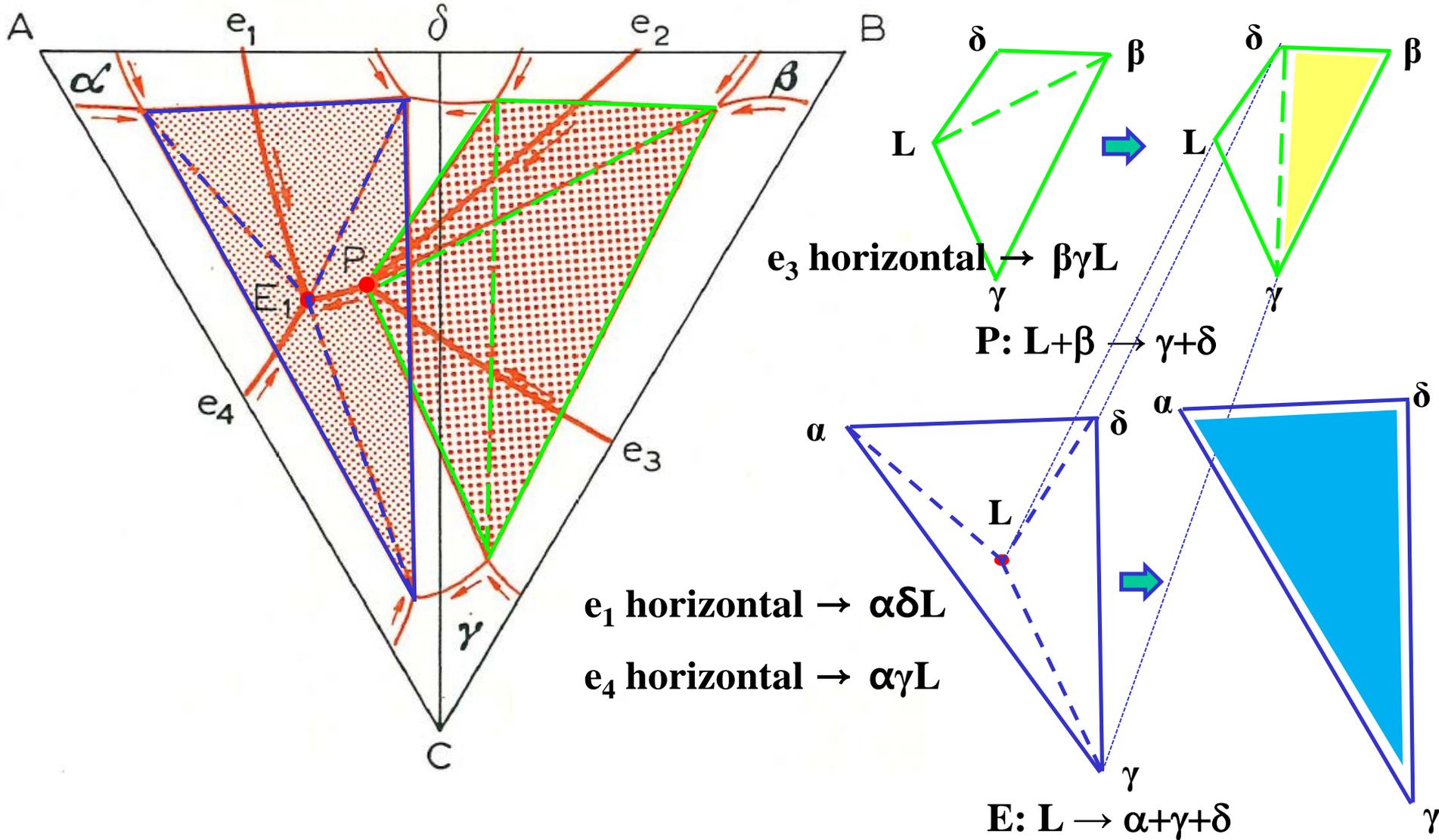
the **eutectic point e_5** on the quasi-binary section δC is **saddle point**.

the straight line is the quasi-binary eutectic horizontal **$c_5e_5d_5$** .

11.1 Congruently-melting intermediate phases

- Binary intermediate phases

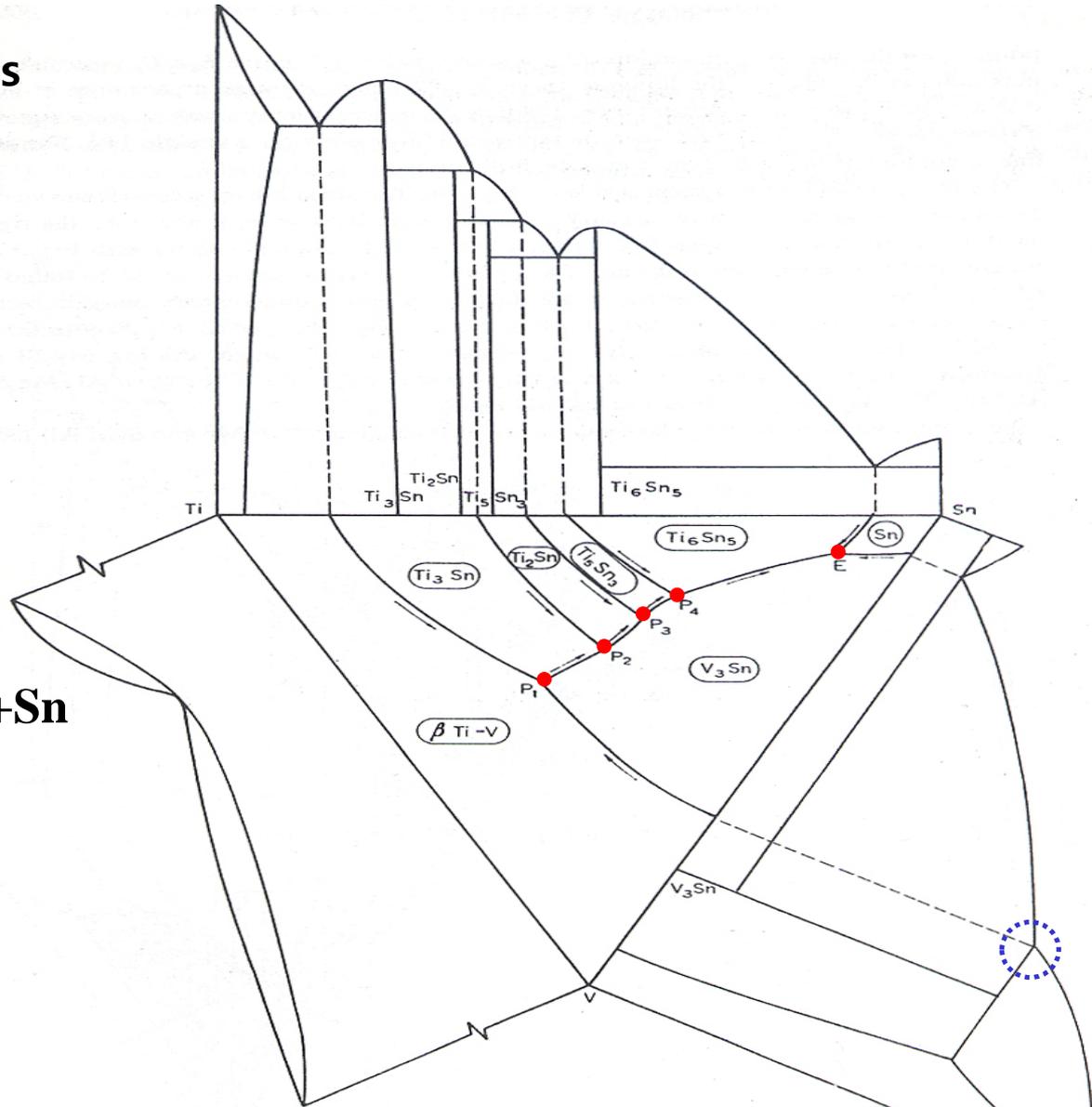
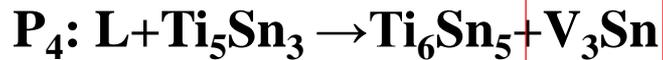
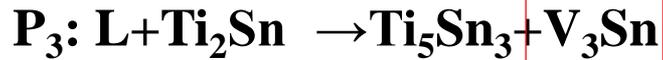
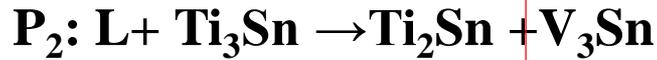
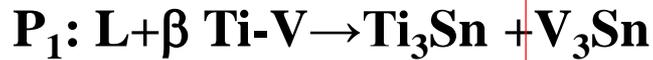
2) Quasi peritectic reaction



11.1 Congruently-melting intermediate phases

- Binary intermediate phases

Quasi peritectic reaction

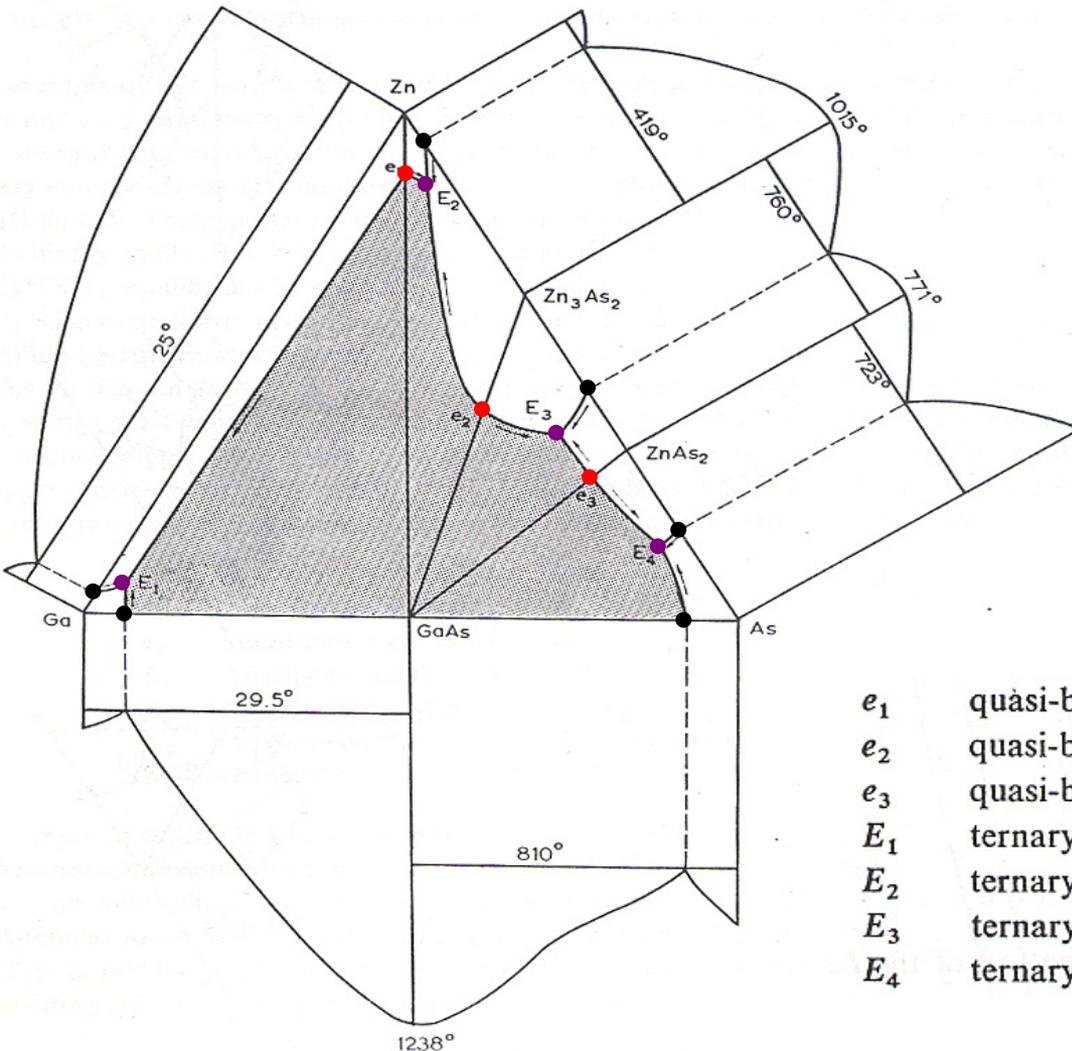


Monovariant liquid curve of Sn-Ti-V system

11.1 Congruently-melting intermediate phases

- Binary intermediate phases

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



- 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.

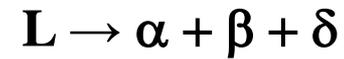
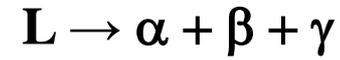
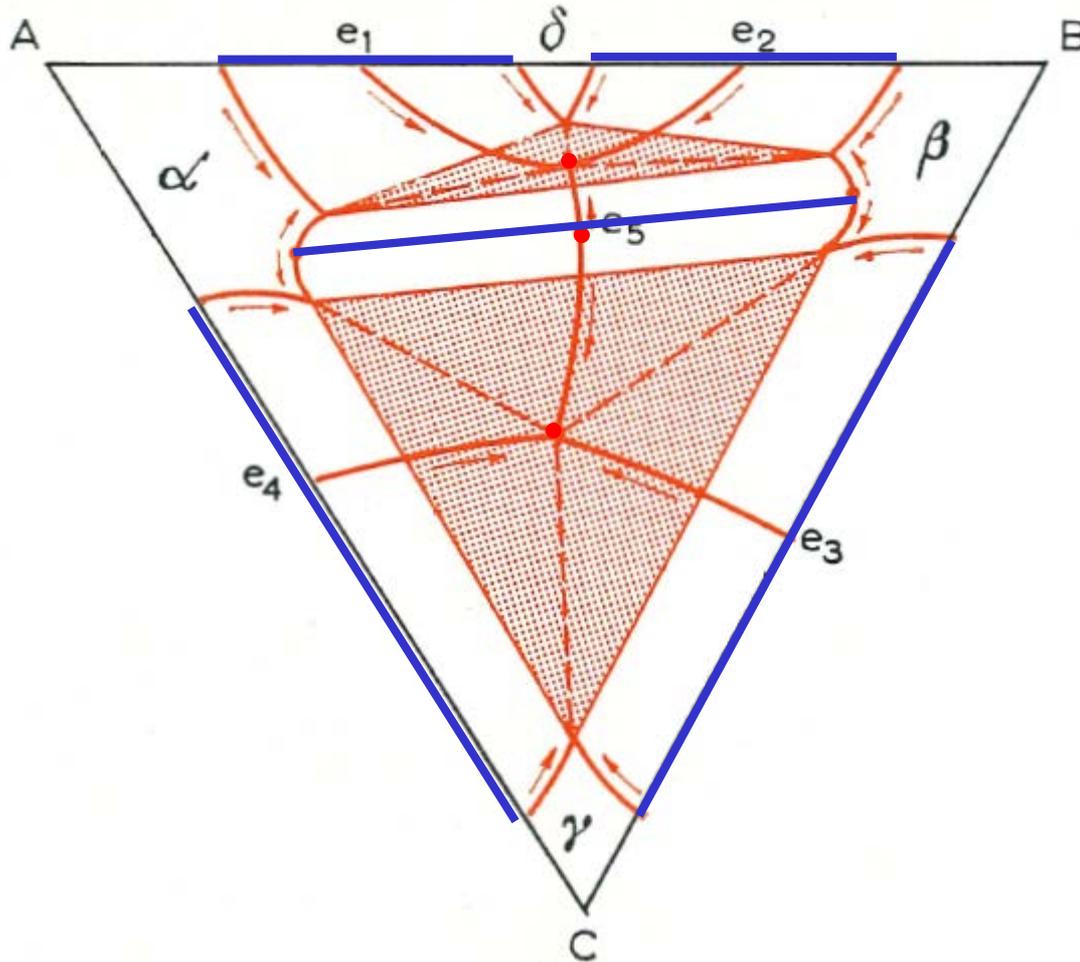
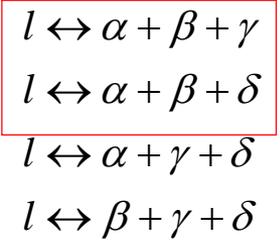
e_1	quasi-binary eutectic $l \rightleftharpoons \text{GaAs} + \text{Zn}$	at	414 °C,
e_2	quasi-binary eutectic $l \rightleftharpoons \text{GaAs} + \text{Zn}_3\text{As}_2$	at	972 °C,
e_3	quasi-binary eutectic $l \rightleftharpoons \text{GaAs} + \text{ZnAs}_2$	at	754 °C,
E_1	ternary eutectic $l \rightleftharpoons \text{GaAs} + \text{Zn} + \text{Ga}$	at	~ 20 °C,
E_2	ternary eutectic $l \rightleftharpoons \text{GaAs} + \text{Zn} + \text{Zn}_3\text{As}_2$	at	~ 410 °C,
E_3	ternary eutectic $l \rightleftharpoons \text{GaAs} + \text{Zn}_3\text{As}_2 + \text{ZnAs}_2$	at	~ 750 °C,
E_4	ternary eutectic $l \rightleftharpoons \text{GaAs} + \text{ZnAs}_2 + \text{As}$	at	~ 720 °C.

As-Ga-Zn system

11.1 Congruently-melting intermediate phases

- Binary intermediate phases

3) No quasi binary eutectic : **two ternary eutectic**



e_5 : saddle point

11.1 Congruently-melting intermediate phases

- Binary intermediate phases: **Kurnakov rule**

1) Case1: with only binary congruent intermediate phases

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

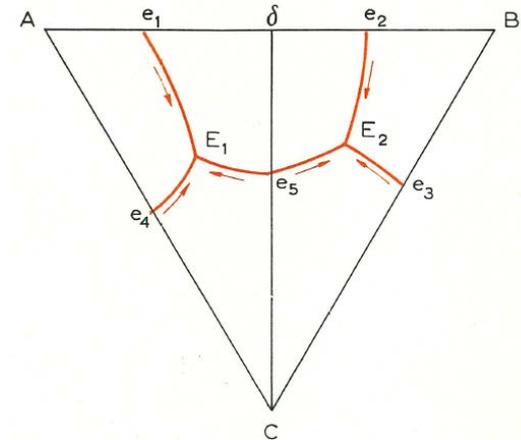
K = # of secondary triangles

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

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

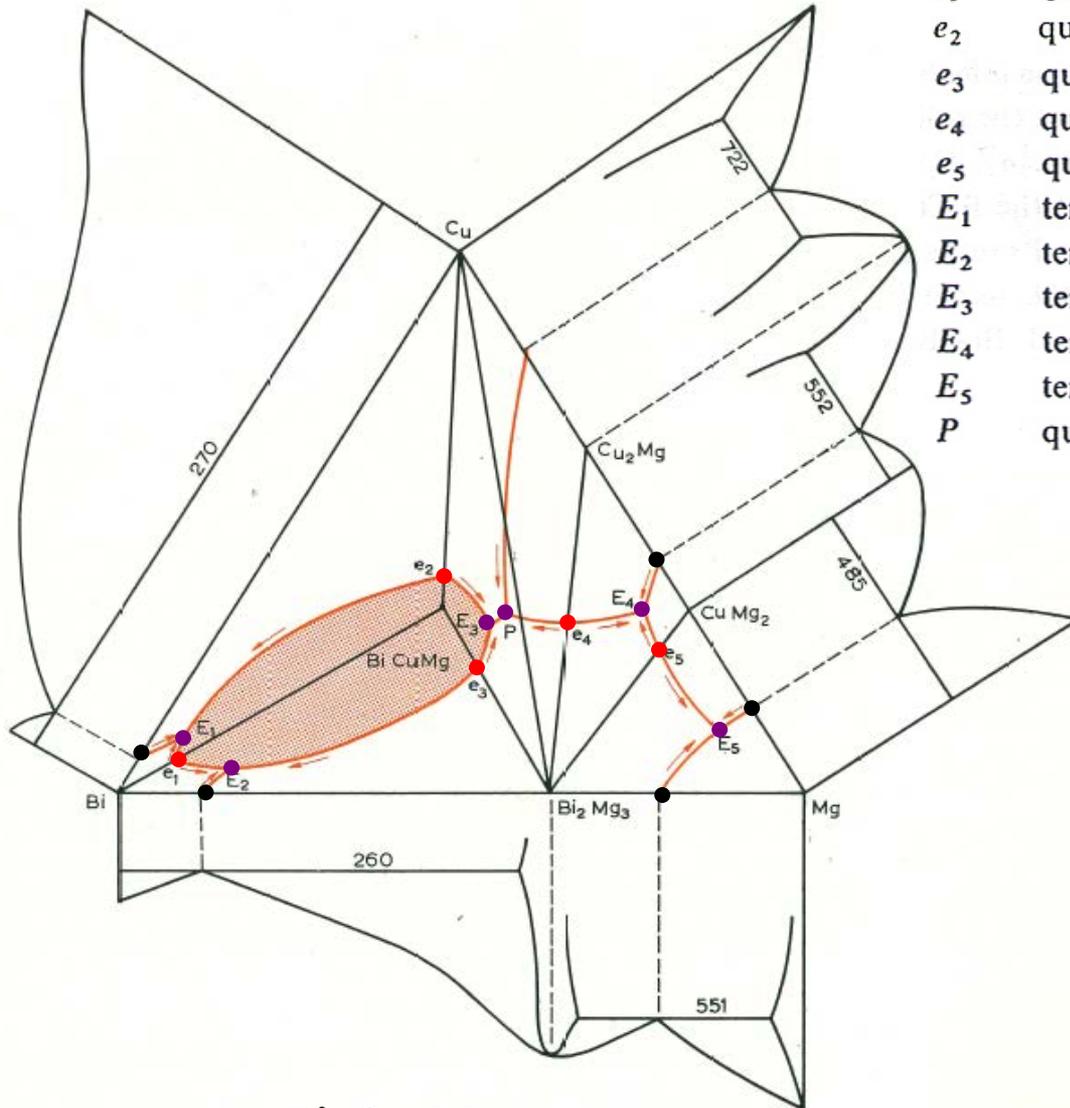
c_3 = ternary congruent intermediate phases

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

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

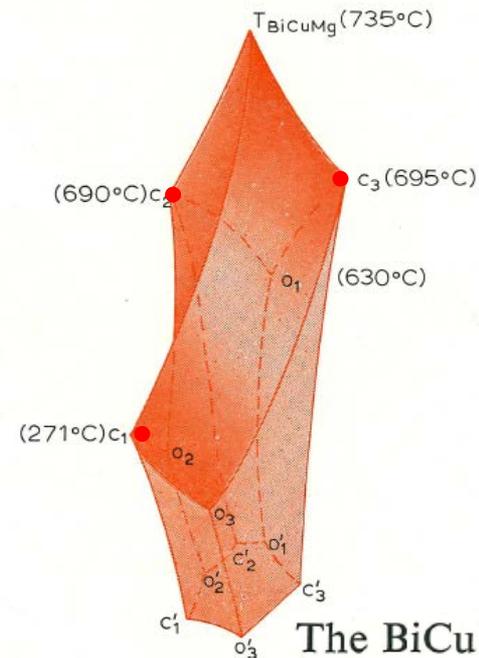
11.1 Congruently-melting intermediate phases

b) Ternary intermediate phase: behaves as a pure metal in that it freezes isothermally and its appearance is associated with a maximum on the liquidus/solidus surfaces



Bi-Cu-Mg system

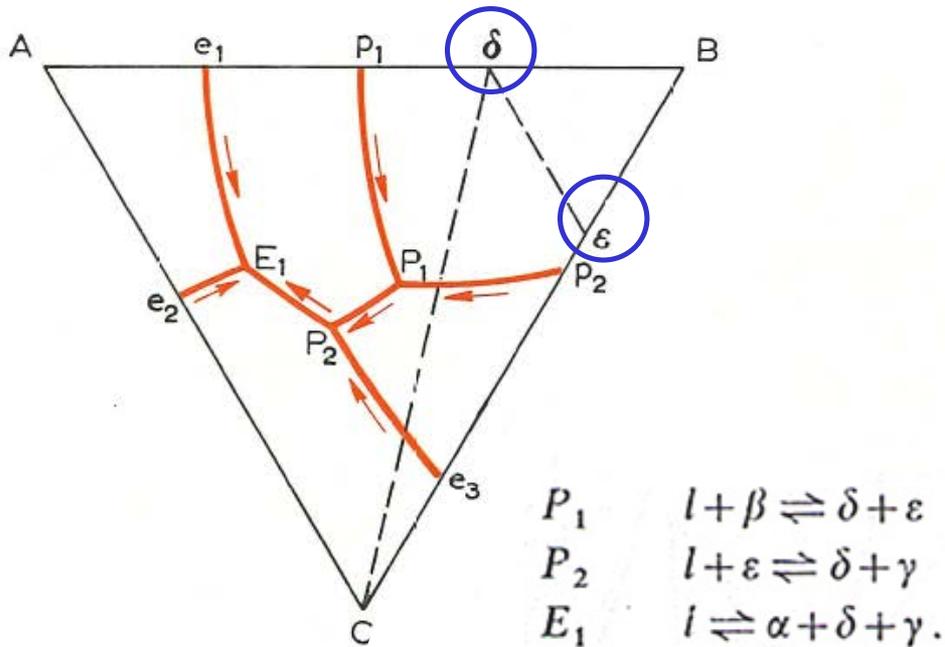
- | | | |
|-------|---|-----------------------------|
| e_1 | quasi-binary eutectic $l \rightleftharpoons \text{Bi} + \text{BiCuMg}$ | at $\sim 271^\circ\text{C}$ |
| e_2 | quasi-binary eutectic $l \rightleftharpoons \text{Cu} + \text{BiCuMg}$ | at 690°C |
| e_3 | quasi-binary eutectic $l \rightleftharpoons \text{Bi}_2\text{Mg}_3 + \text{BiCuMg}$ | at 695°C |
| e_4 | quasi-binary eutectic $l \rightleftharpoons \text{Bi}_2\text{Mg}_3 + \text{Cu}_2\text{Mg}$ | at 655°C |
| e_5 | quasi-binary eutectic $l \rightleftharpoons \text{Bi}_2\text{Mg}_3 + \text{CuMg}_2$ | at 557°C |
| E_1 | ternary eutectic $l \rightleftharpoons \text{Bi} + \text{Cu} + \text{BiCuMg}$ | at 265°C |
| E_2 | ternary eutectic $l \rightleftharpoons \text{Bi} + \text{Bi}_2\text{Mg}_3 + \text{BiCuMg}$ | at 255°C |
| E_3 | ternary eutectic $l \rightleftharpoons \text{Cu} + \text{Bi}_2\text{Mg}_3 + \text{BiCuMg}$ | at 630°C |
| E_4 | ternary eutectic $l \rightleftharpoons \text{Bi}_2\text{Mg}_3 + \text{Cu}_2\text{Mg} + \text{CuMg}_2$ | at 546°C |
| E_5 | ternary eutectic $l \rightleftharpoons \text{Mg} + \text{Bi}_2\text{Mg}_3 + \text{CuMg}_2$ | at 470°C |
| P | quasi-peritectic $l + \text{Cu}_2\text{Mg} \rightleftharpoons \text{Cu} + \text{Bi}_2\text{Mg}_3$ | at 660°C |



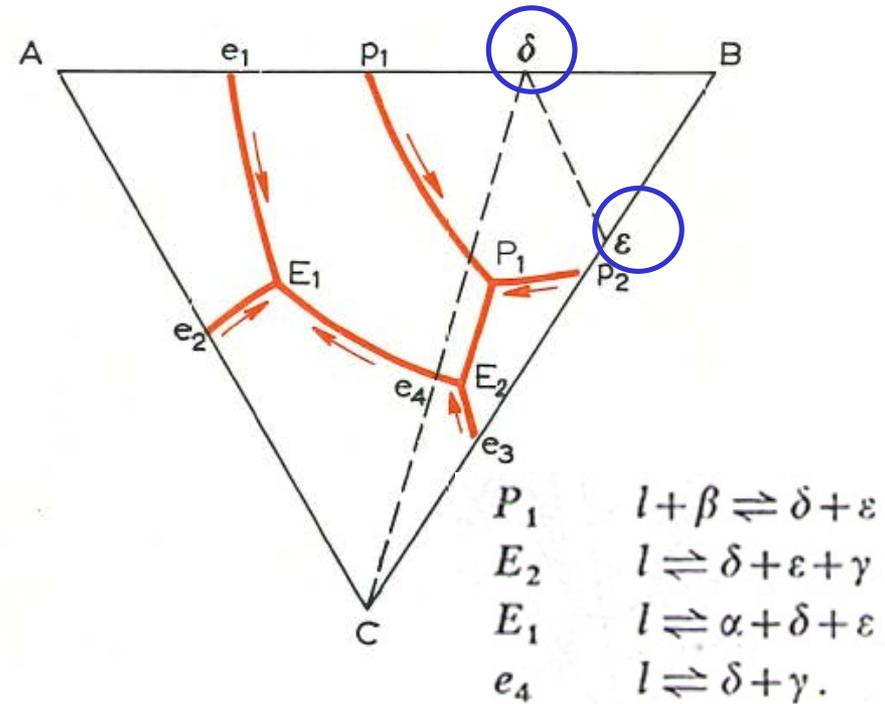
The BiCuMg phase region.

11.2 incongruently-melting intermediate phases

a) ternary system formed when two of the Binaries contain incongruent intermediate phases

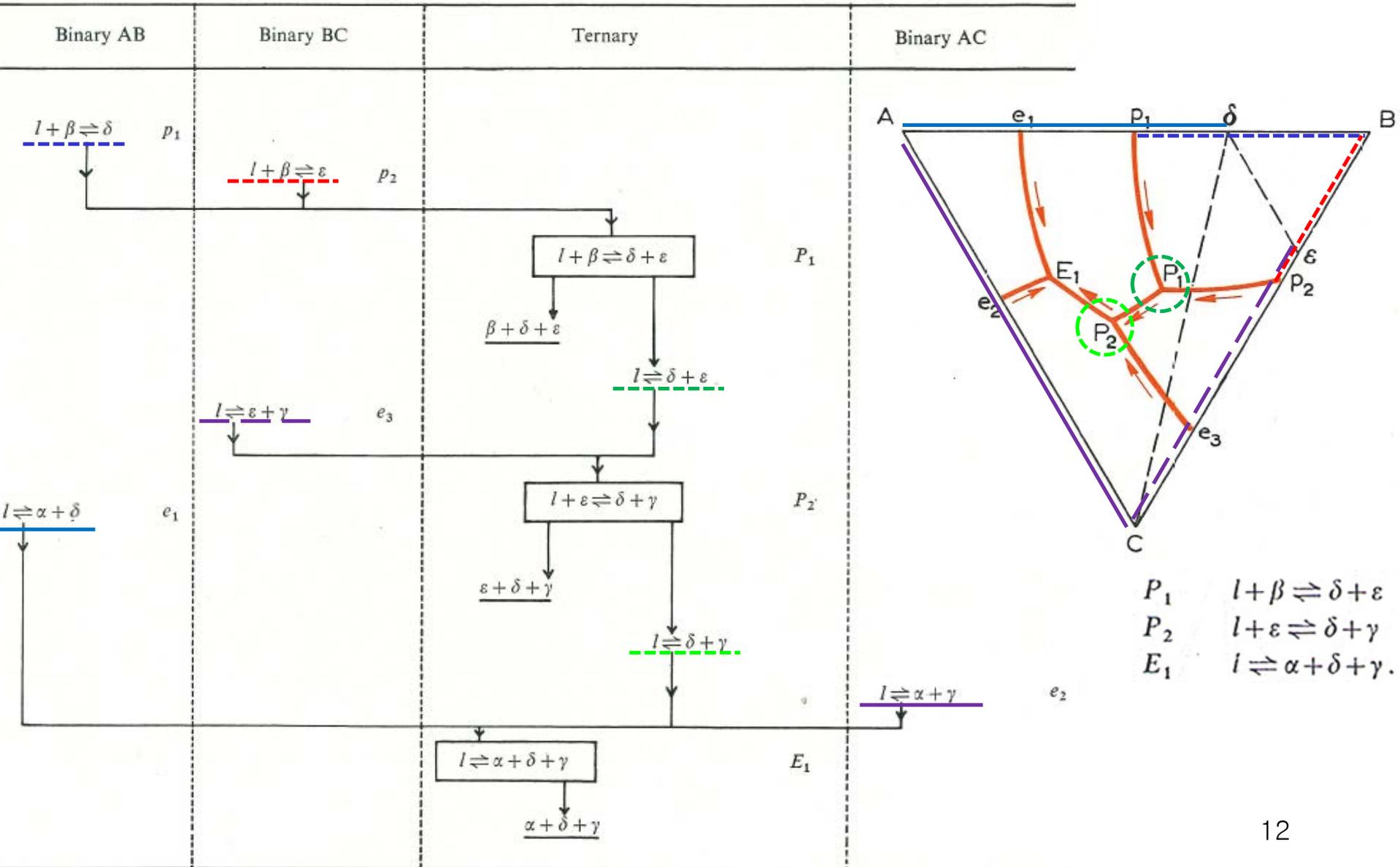


(a) Equilibria when the quasi-peritectic point P is located in the partial system AδC



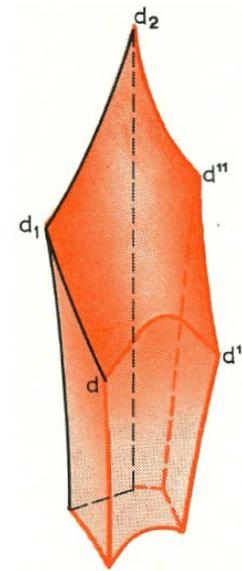
(b) Equilibria when the quasi-peritectic point P is located in the partial system Cδε

Tabular representation of the ternary space model (a) :

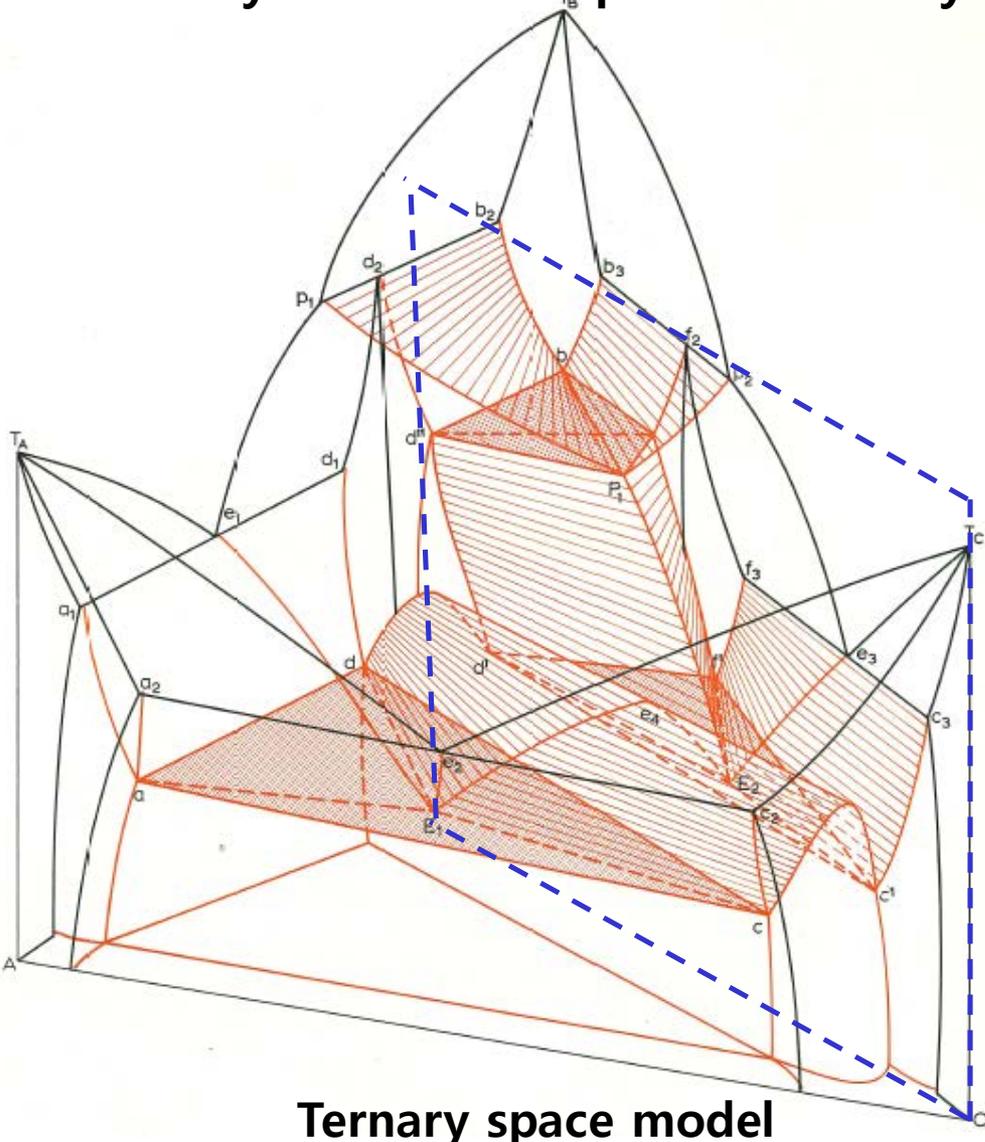


11.2 incongruently-melting intermediate phases

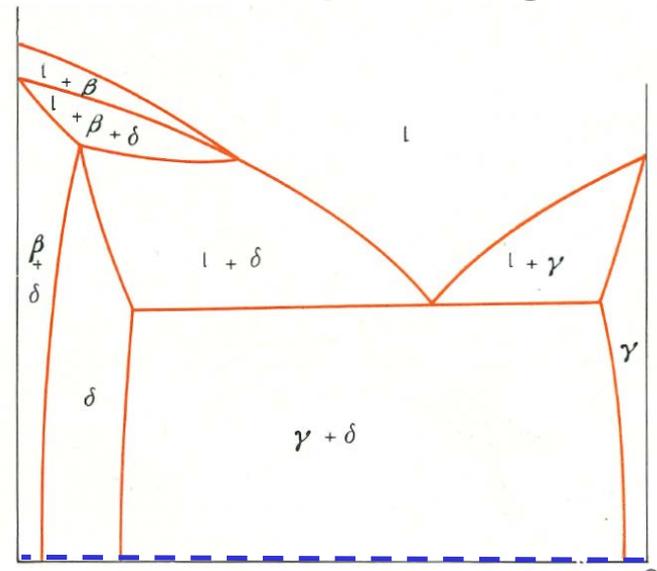
- Binary intermediate phases : ternary space model of (b)



δ phase region



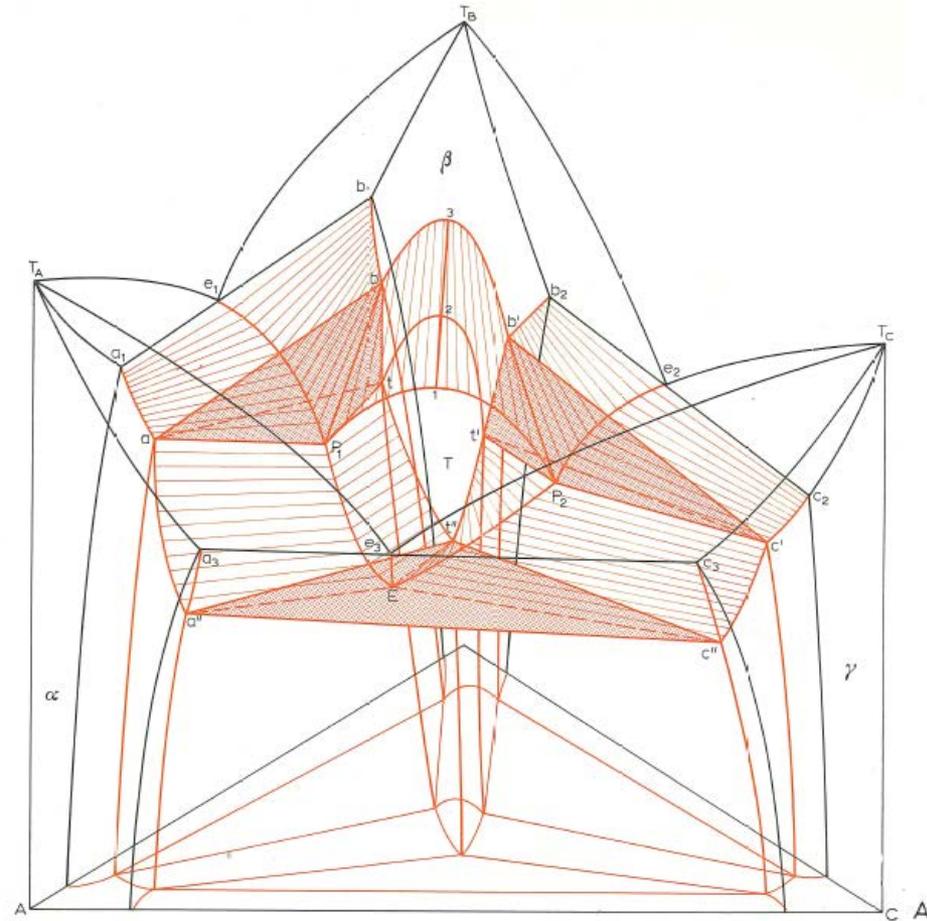
Ternary space model



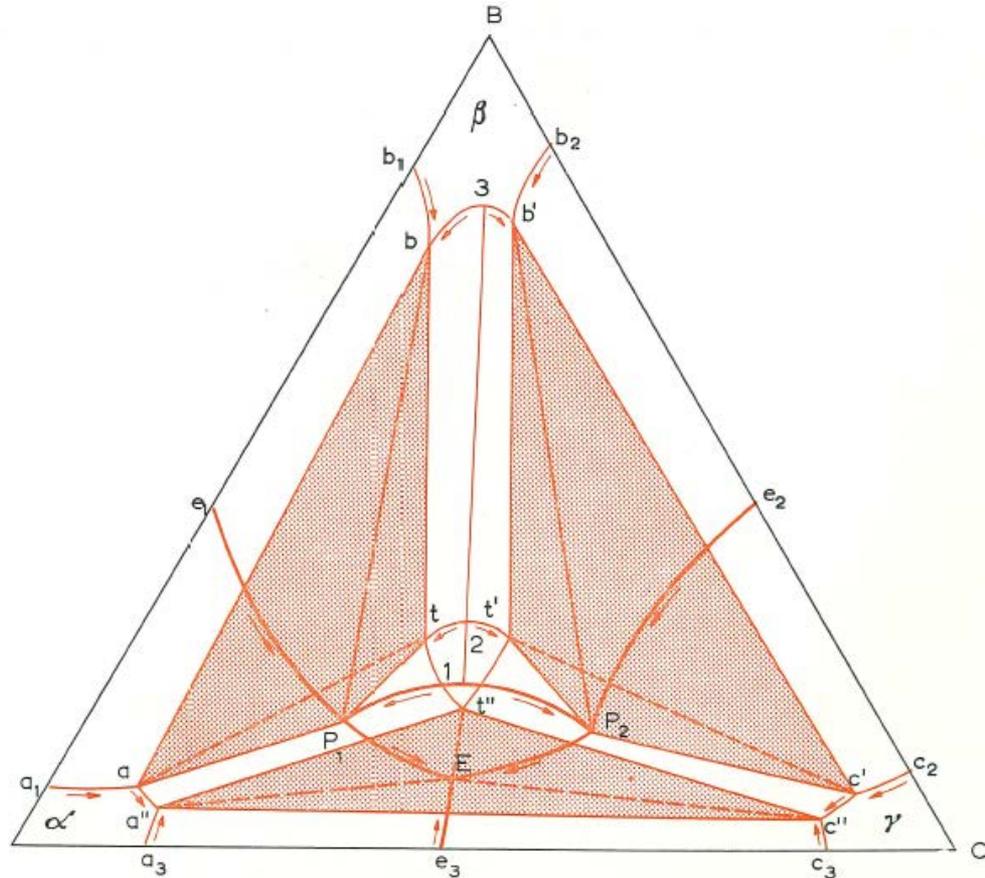
Vertical section from C to δ
 : near quasi-binary nature
 ~ not quasi-binary

11.2 incongruently-melting intermediate phases

b) **one ternary intermediate phase** and all three binary eutectic

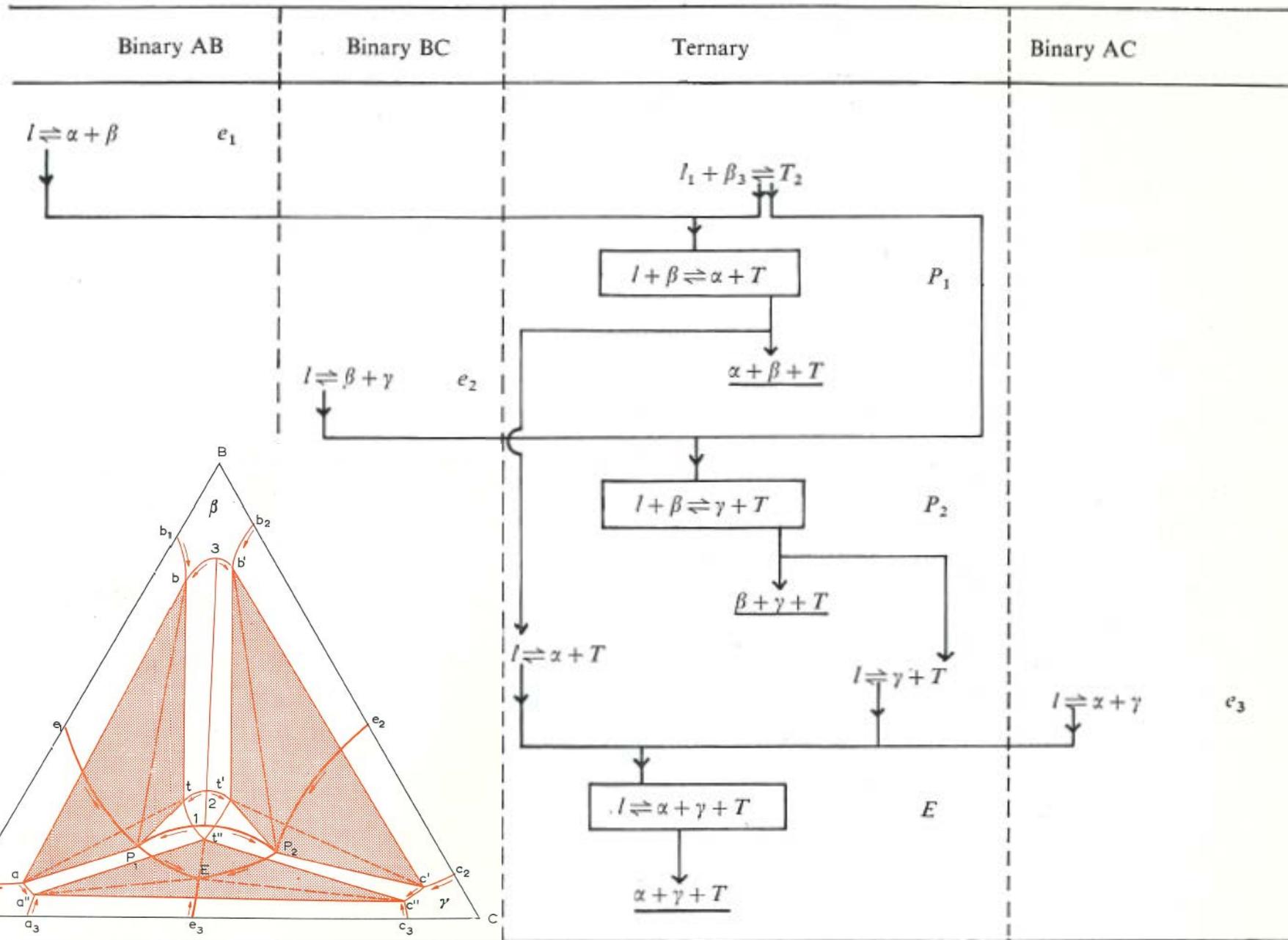


Ternary space model



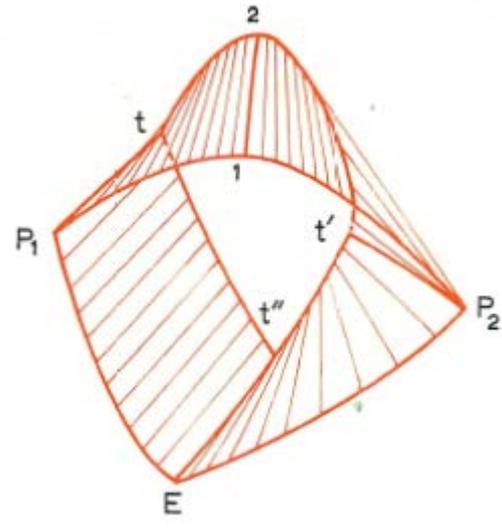
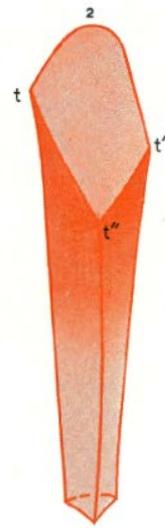
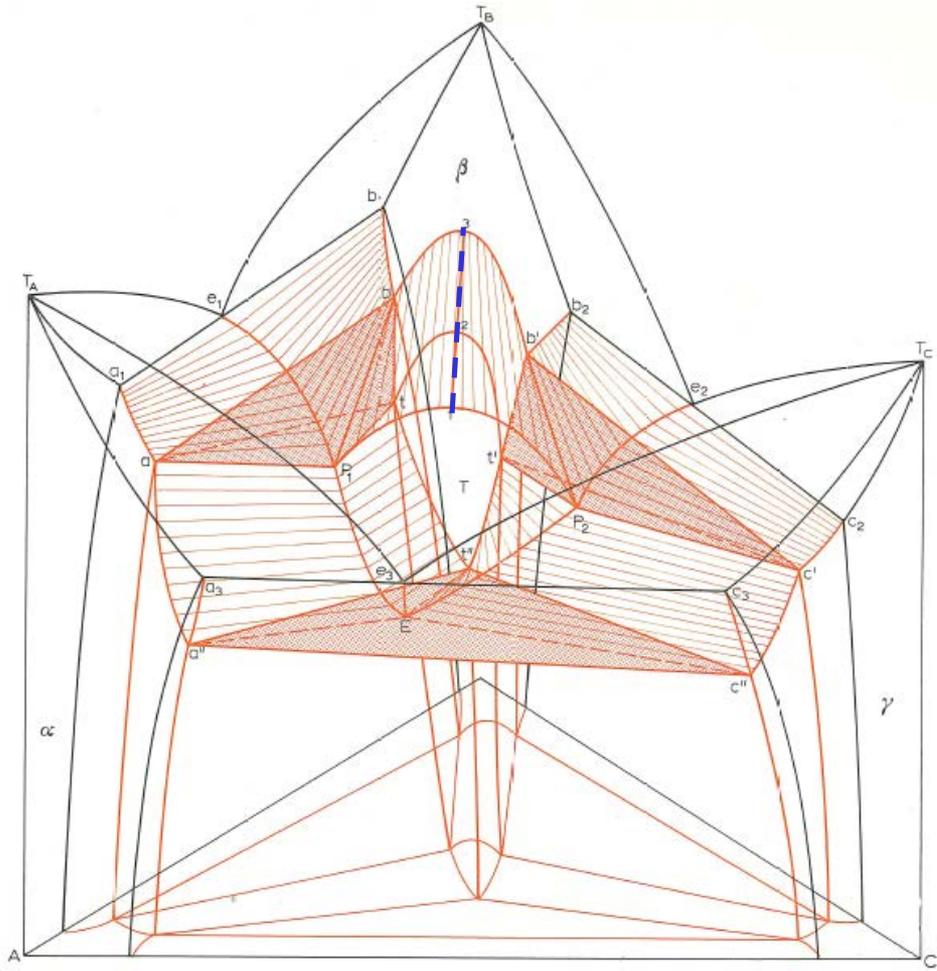
Projection on the concentration triangle

Tabular representation of the ternary equilibria, e.g. Al-Mg-Zn system



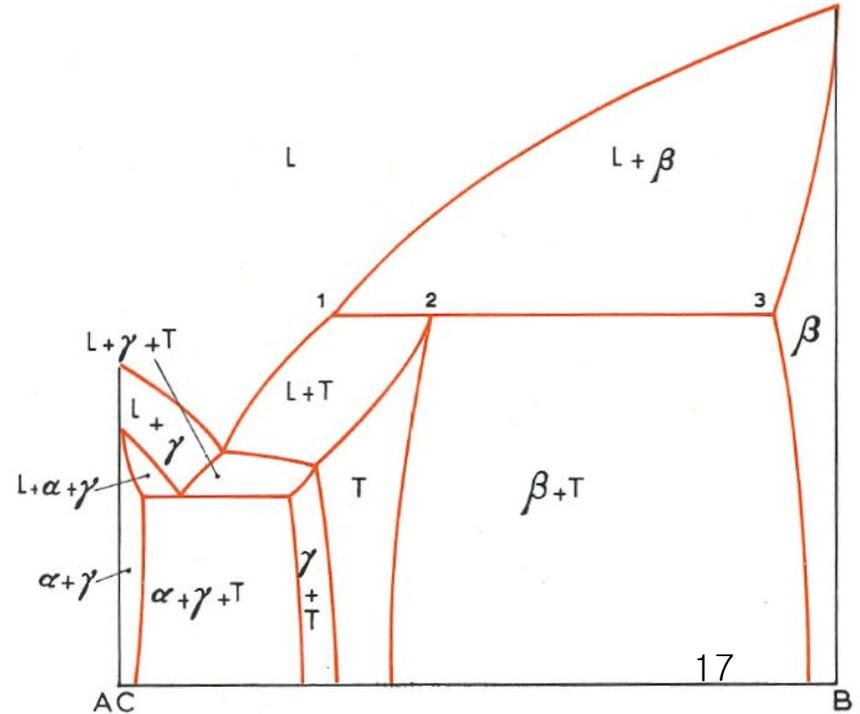
11.2 incongruently-melting intermediate phases

- Ternary intermediate phases

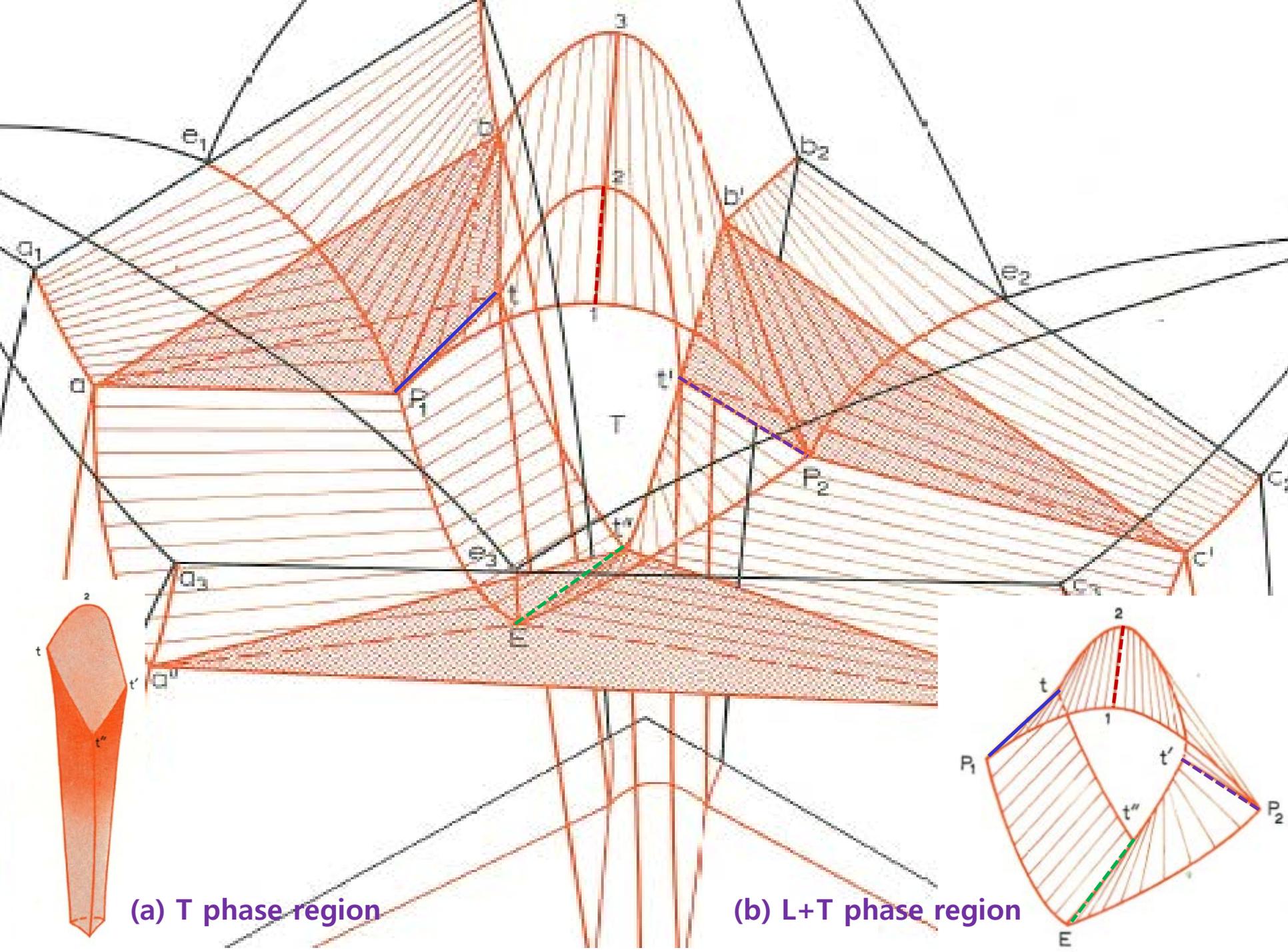


(a) T phase region

(b) L+T phase region



Vertical section along tie line 1-2-3



(a) T phase region

(b) L+T phase region

Chapter 12. Ternary phase Diagrams

Liquid Immiscibility

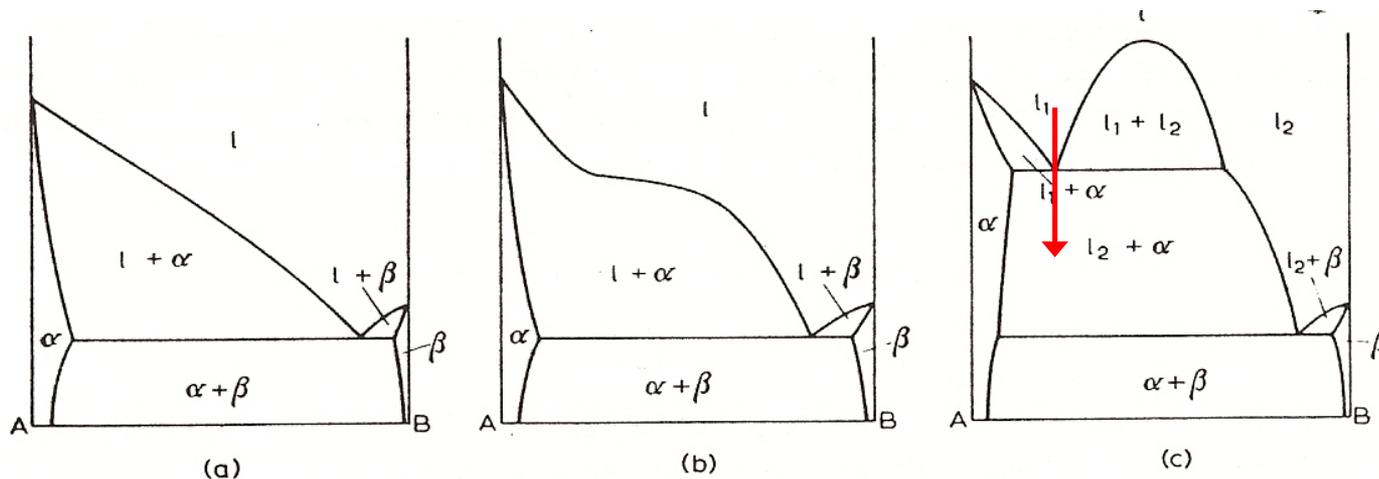
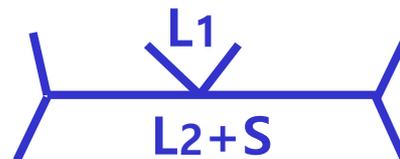
Liquid immiscibility in one or more of the binary systems can lead to either three-phase or four-phase equilibria in the ternary system.

Immiscibility can arise if either monotectic or syntectic reactions occur in the binary system; true ternary immiscibility is also possible.

1) Liquid immiscibility in binary system

* **Monotectic reaction:**

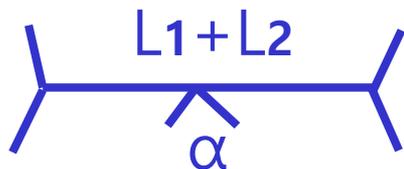
Liquid1 \leftrightarrow Liquid2 + Solid



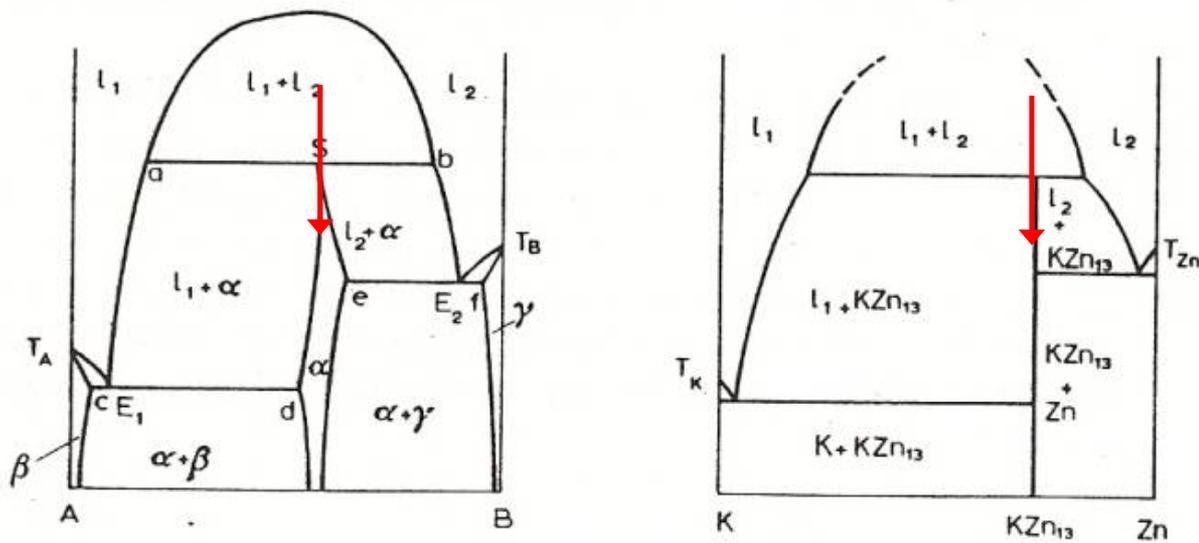
Increasingly positive ΔH_m

* **Syntectic reaction:**

Liquid1 + Liquid2 \leftrightarrow α



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



2) One binary liquid miscibility gap in ternary system

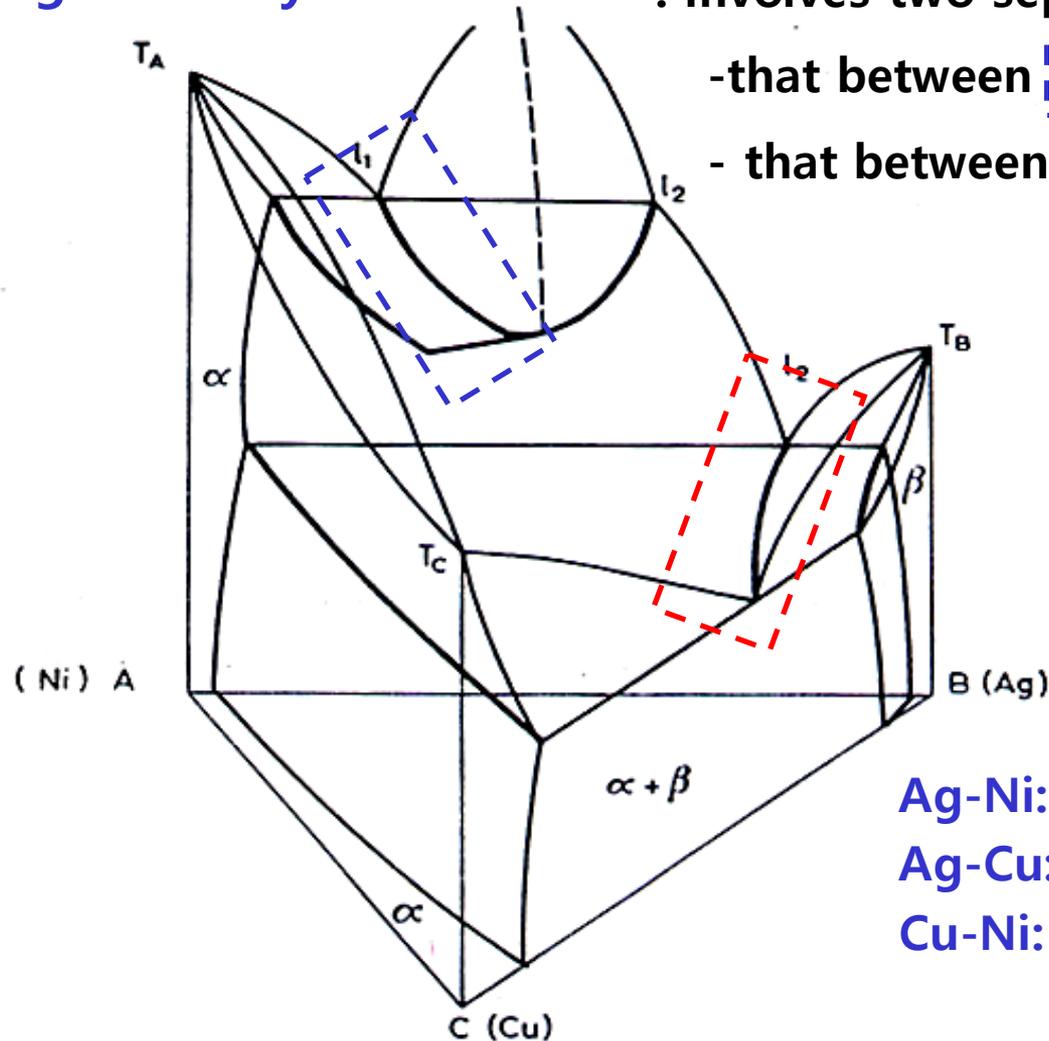
- Binary Monotectic, syntectic and metatectic reactions in combination with each other as well as with binary eutectic and peritectic reactions.

- **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



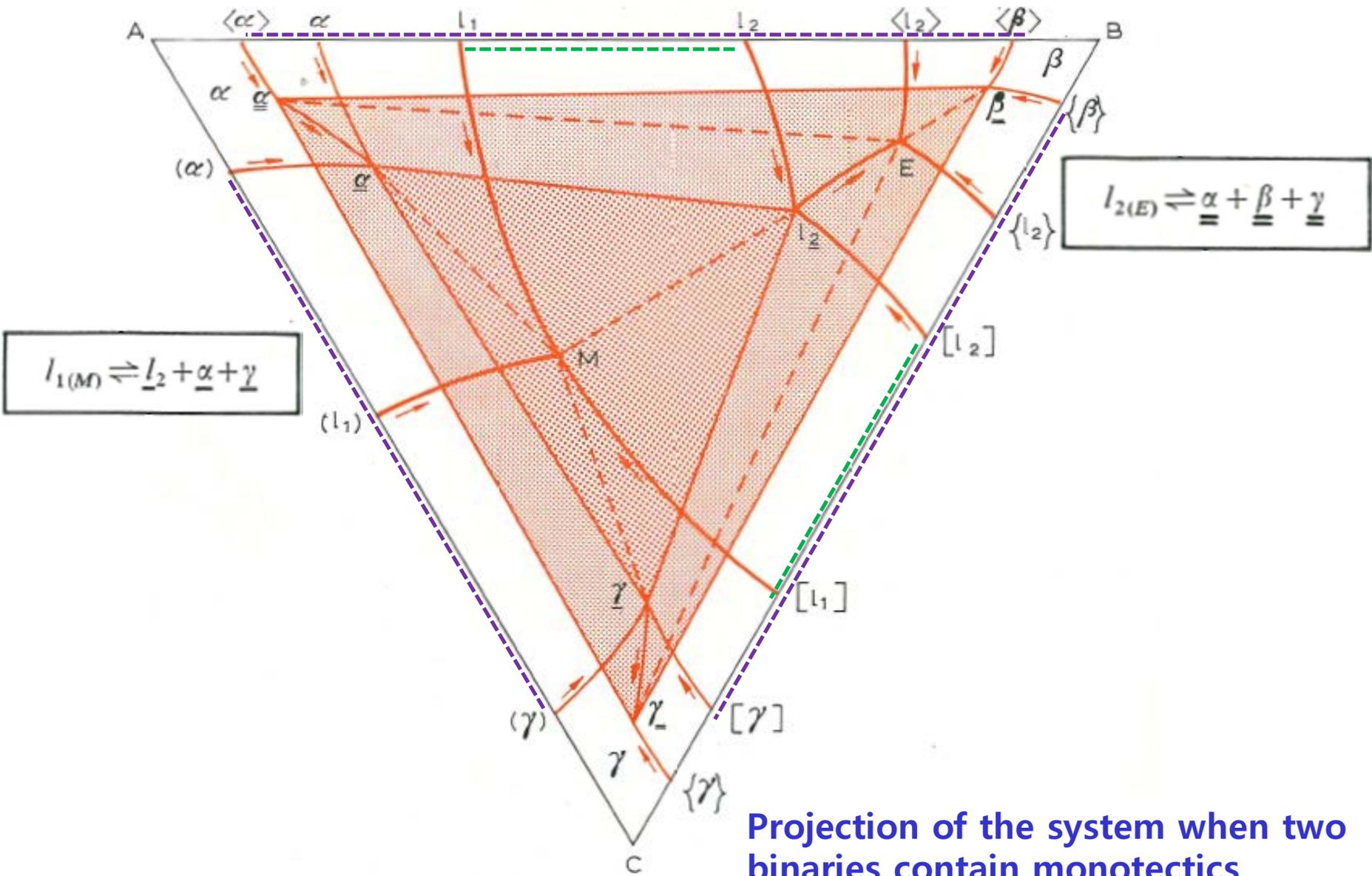
Ag-Ni: monotectic

Ag-Cu: eutectic

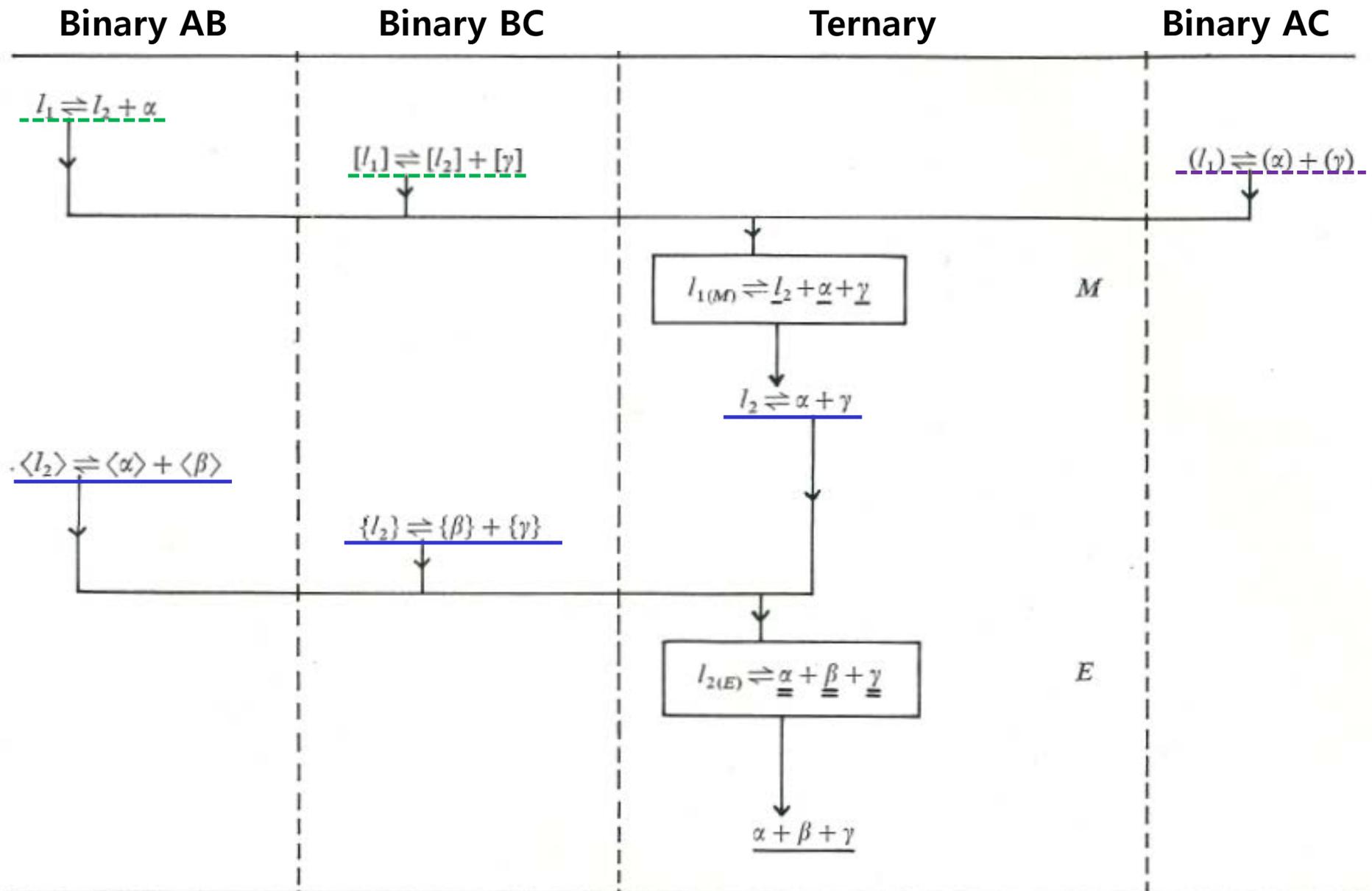
Cu-Ni: continuous series of solid soln

12.1. Two Binary Systems are Monotectic

- The AB and BC binaries are monotectic, the AC binary is eutectic.



* Tabular foam of the system when two binaries contain monotectics

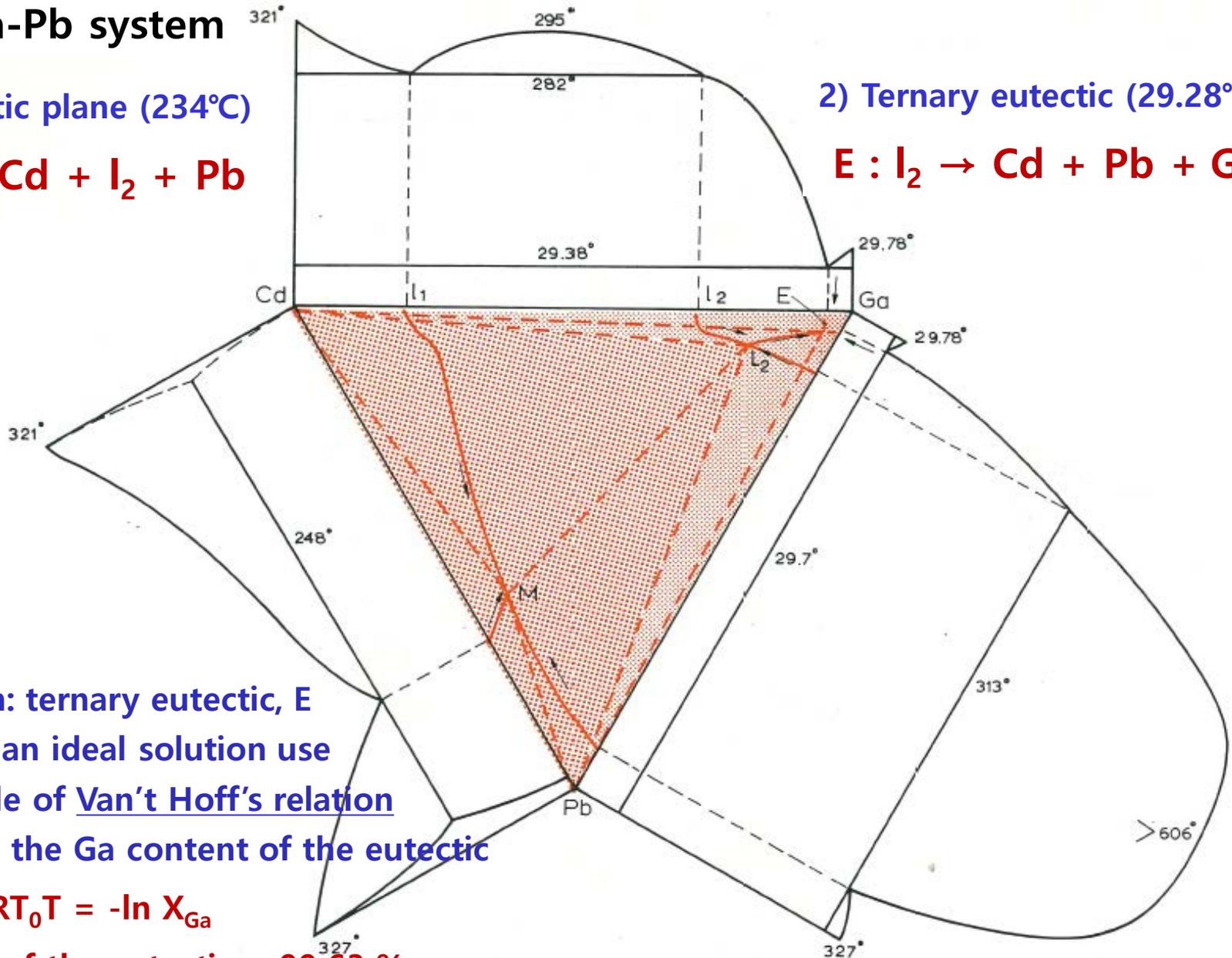


The Cd-Ga-Pb system

1) Monotectic plane (234°C)



2) Ternary eutectic (29.28°C)



Assumption: ternary eutectic, E behaves as an ideal solution use can be made of Van't Hoff's relation to calculate the Ga content of the eutectic

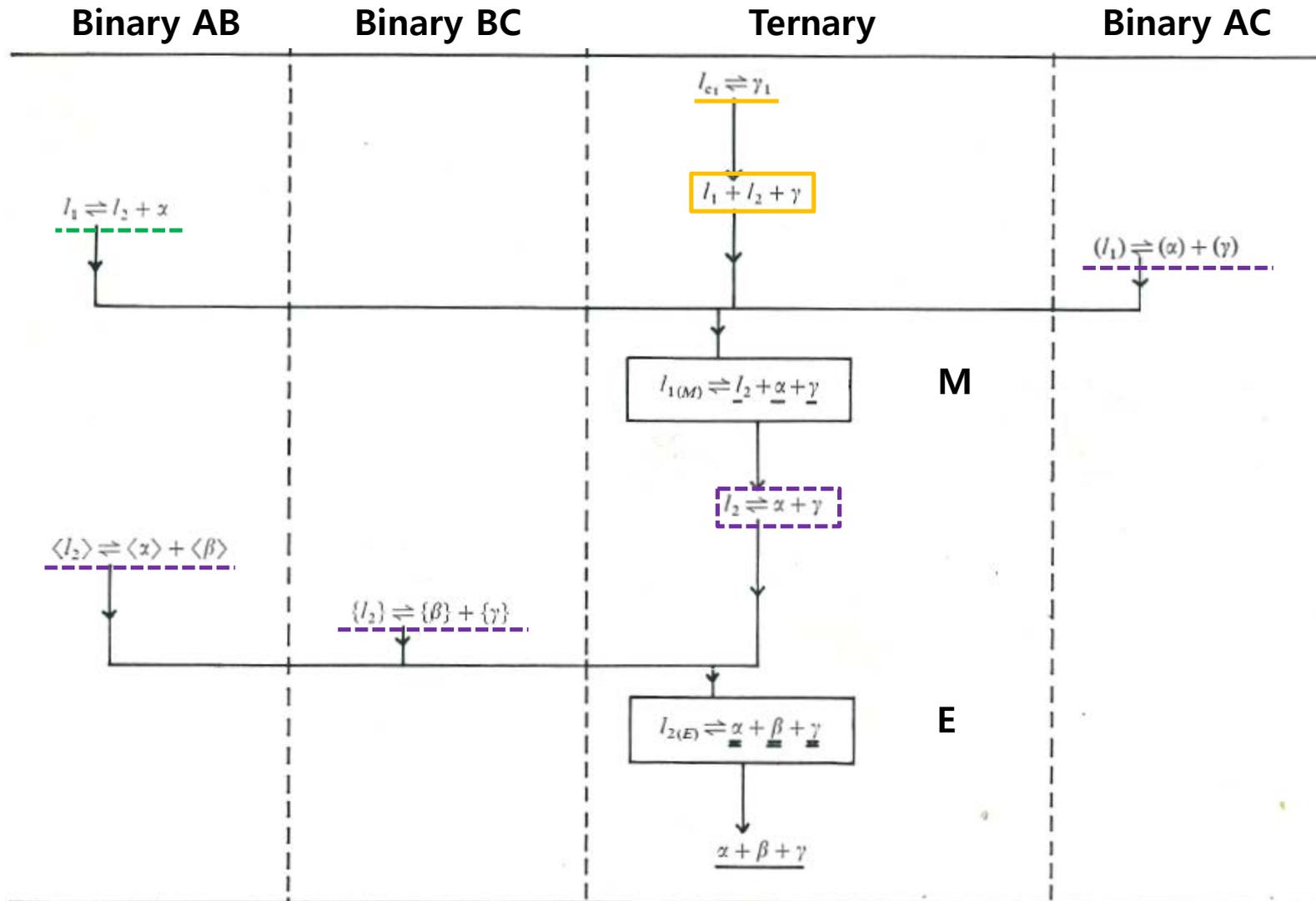
$$[L_{Ga}(T_0 - T)]/RT_0T = -\ln X_{Ga}$$

Ga content of the eutectic = 99.63 %

where L_{Ga} is the heat of fusion of Ga (1336 cal/g.-atom), T_0 is the m.p. of Ga (302.93 °K), T is the ternary eutectic temperature, R the gas constant, and X_{Ga} the Ga content of the ternary eutectic E .

12.2. One Binary System is Monotectic

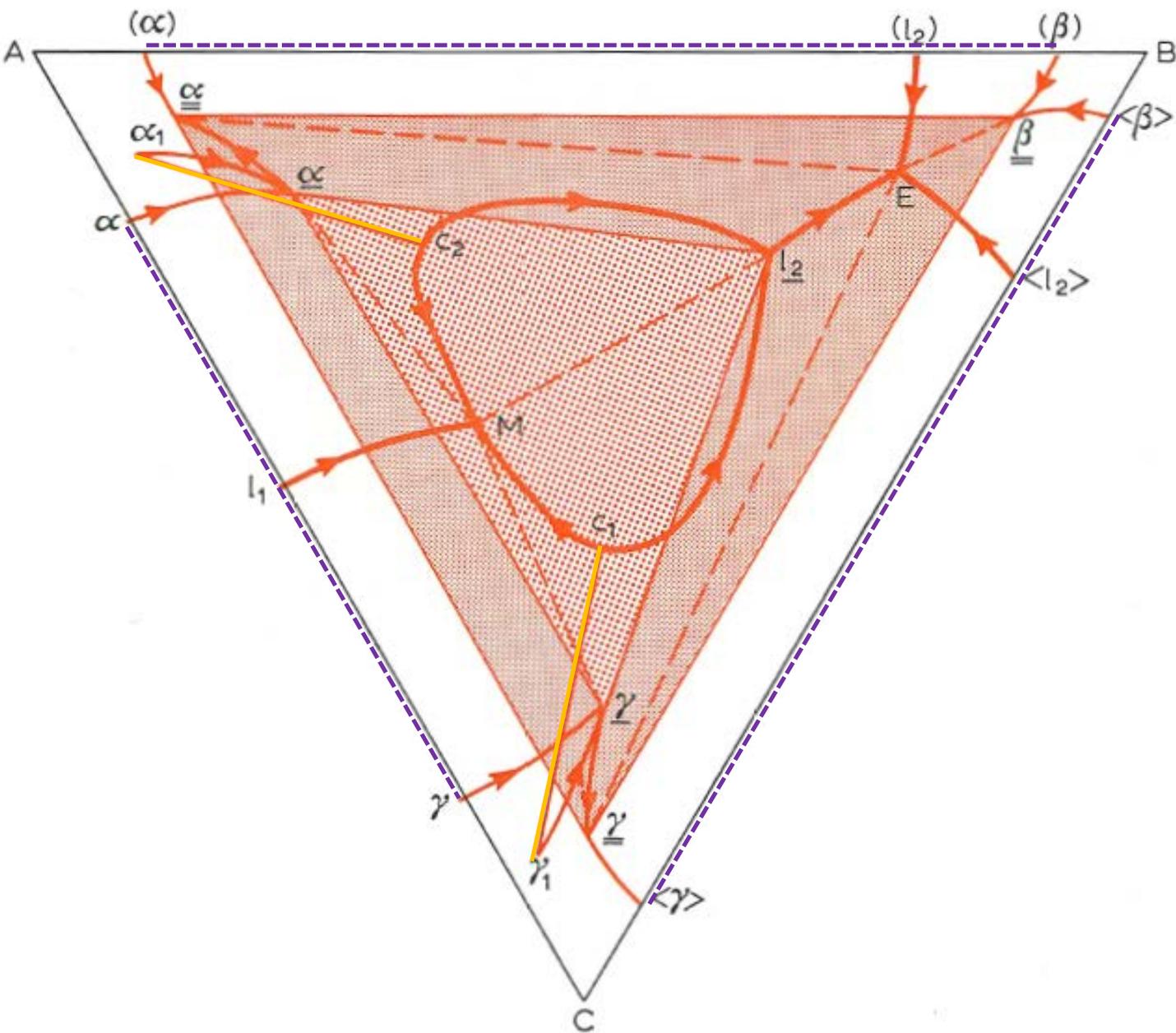
* Tabular foam of the system when two binaries contain monotectics



* ex) Fe_3C -FeS-Fe: partial system of C-Fe-S ternary

quasi-binary system Fe-Fe₃C: monotectic/ Fe-Fe₃C & Fe-FeS: simple eutectic

12.3. None of the Binaries contain liquid miscibility gaps but True Ternary Liquid Immiscibility Appears



12.3. True Ternary Liquid Immiscibility Appears

* Tabular foam of the system when true ternary liquid immiscibility appears

