2019 Spring

"Phase Equilibria *in* Materials"

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Chapter 11. Ternary phase Diagrams
Intermediate Phases

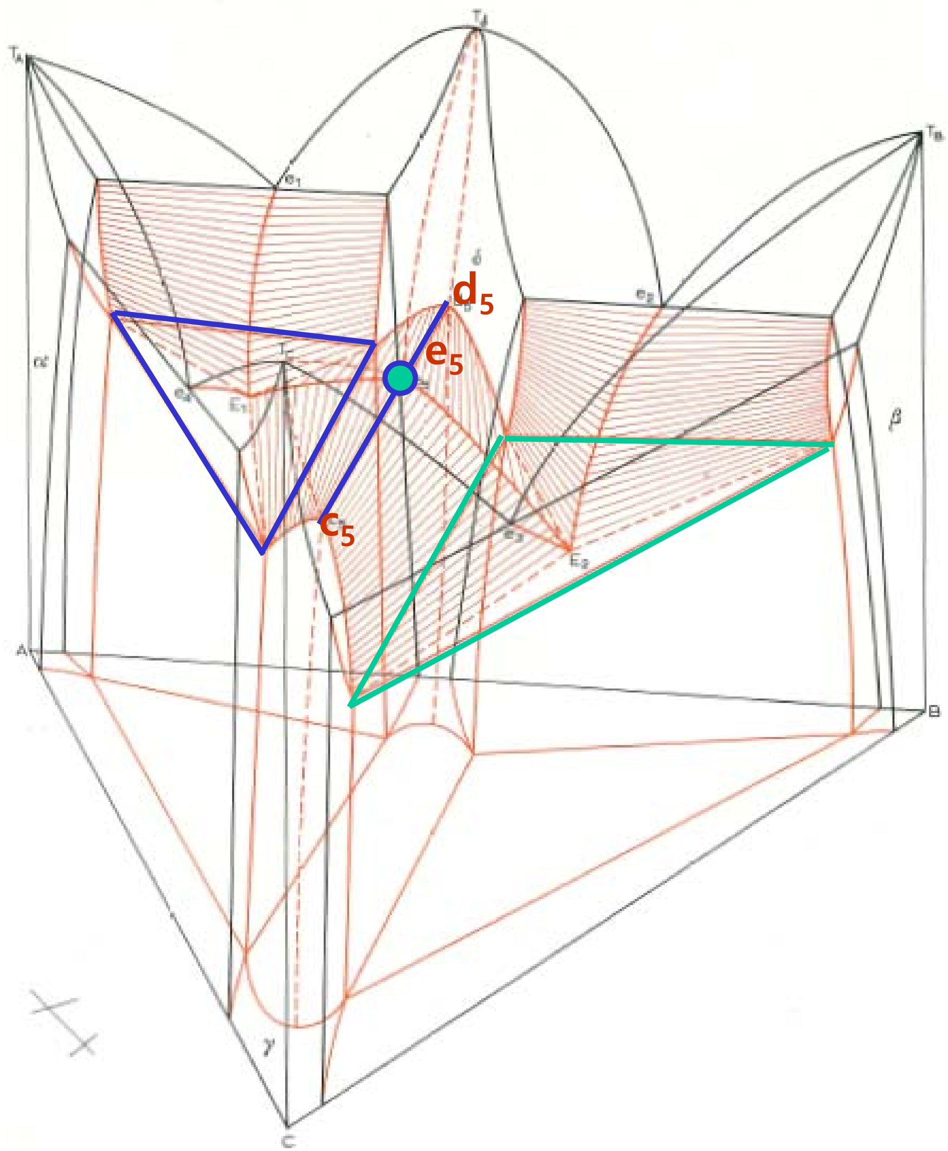
Intermdediate phases may melt congruently or incongruently.

They may occur as either binary or ternary phases.

11.1 Congruently melting intermediate phases

11.1. Binary intermediate phases

1) Two ternary eutectic reactions



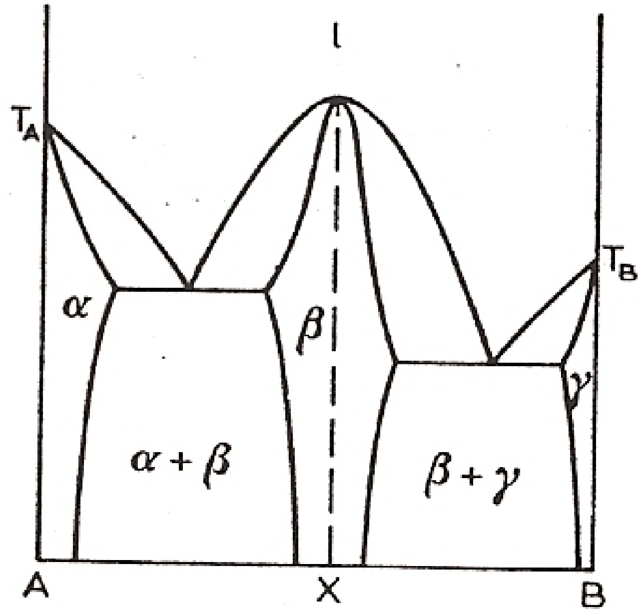


Fig. 78. Phase diagram with a congruent intermediate phase.

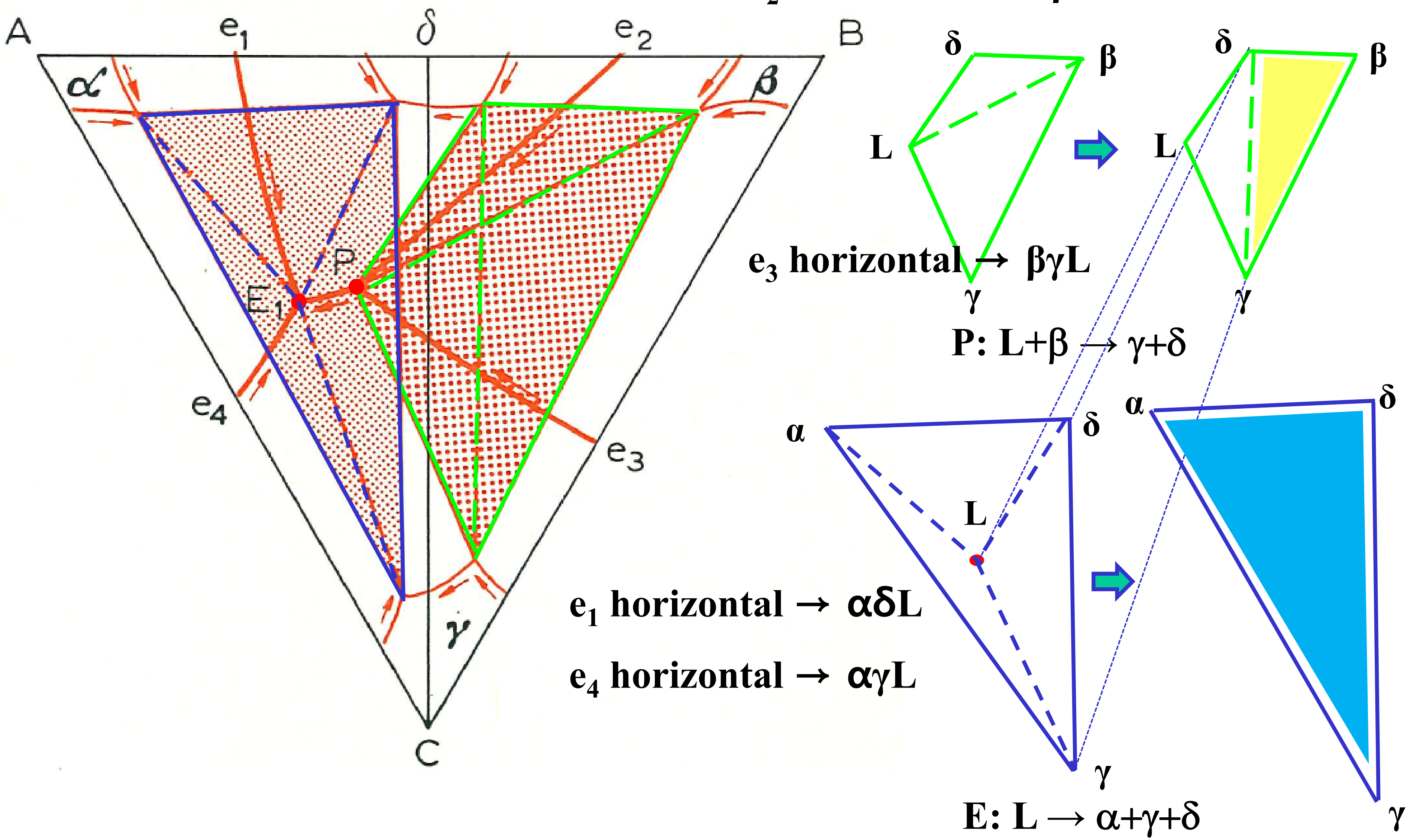
the eutectic point e5 on the quasi-bniary section δC is saddle point.

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

11.1 Congruently-melting intermediate phases

- Binary intermediate phases

2) Quasi peritectic reaction



11.1 Congruently-melting intermediate phases

- **Binary intermediate phases**

Quasi peritectic reaction

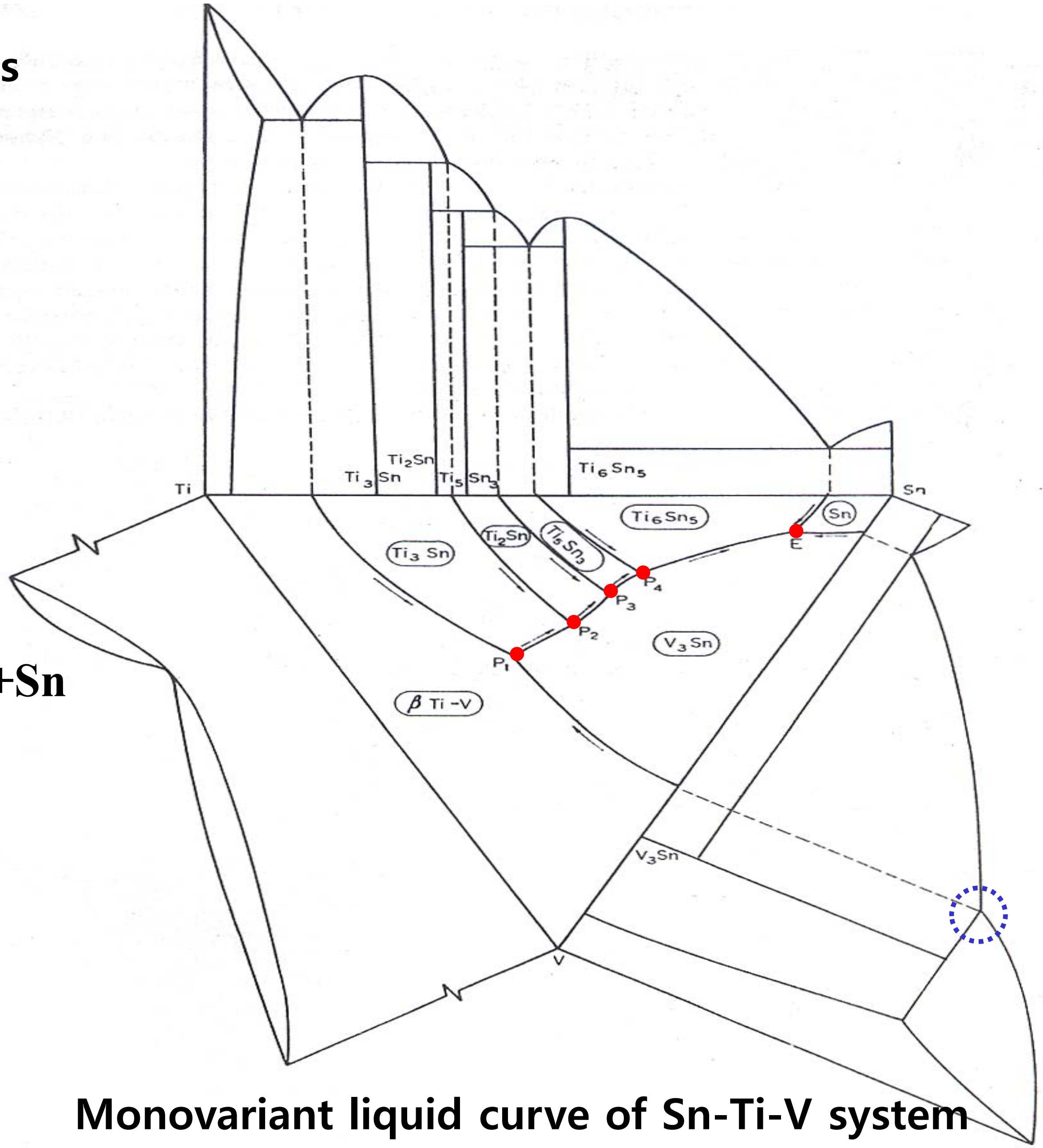
P_1: L+β Ti-V → Ti_3Sn + V_3Sn

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

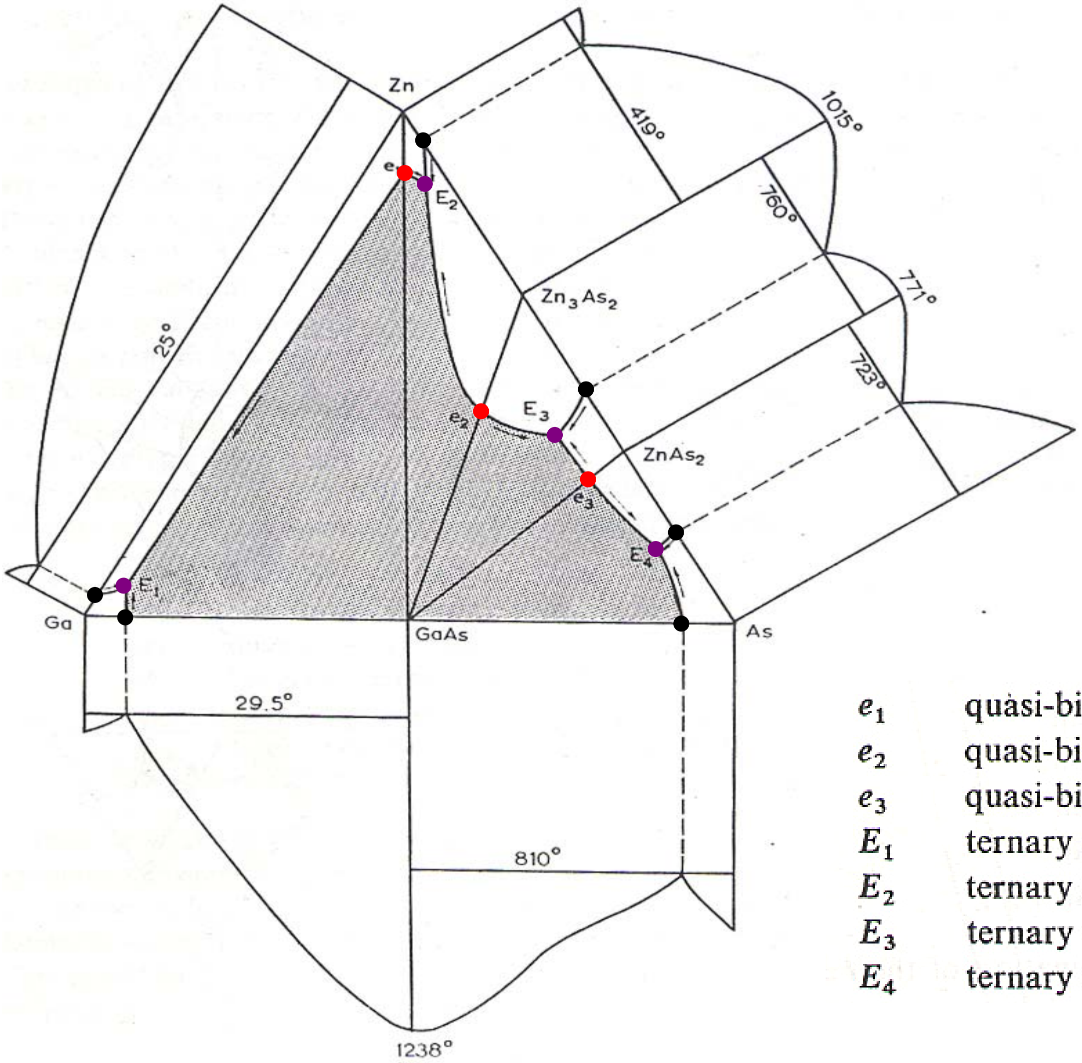


Monovariant liquid curve of Sn-Ti-V system

11.1 Congruently-melting intermediate phases

- **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.

11.1 Congruently-melting intermediate phases

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

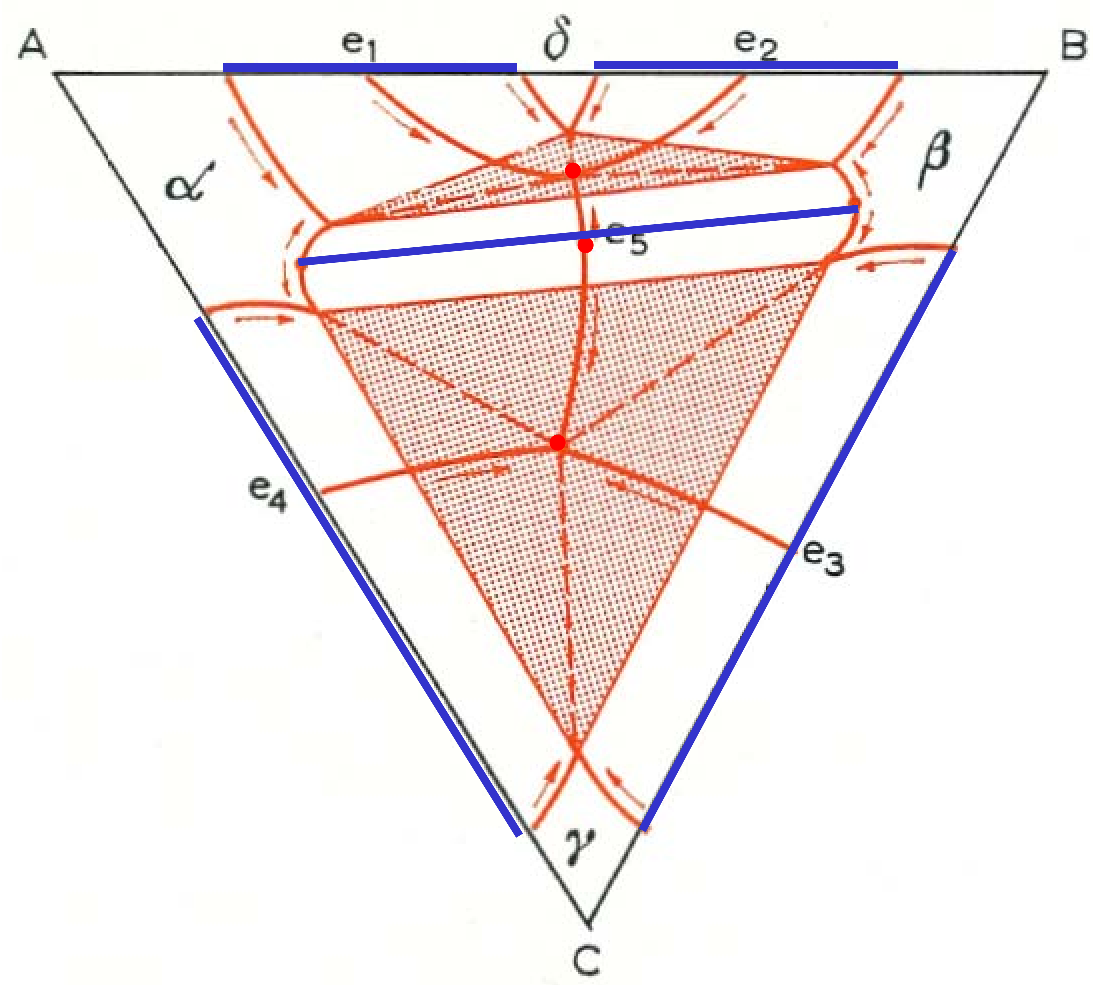
$l \leftrightarrow \alpha + \beta + \delta$

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

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

- **Binary intermediate phases**

3) No quasi binary eutectic : two ternary eutectic



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

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

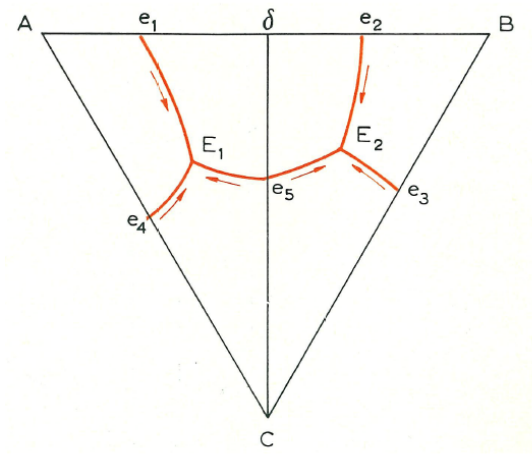
e_5: saddle point

11.1 Congruently-melting intermediate phases

- **Binary intermediate phases: 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

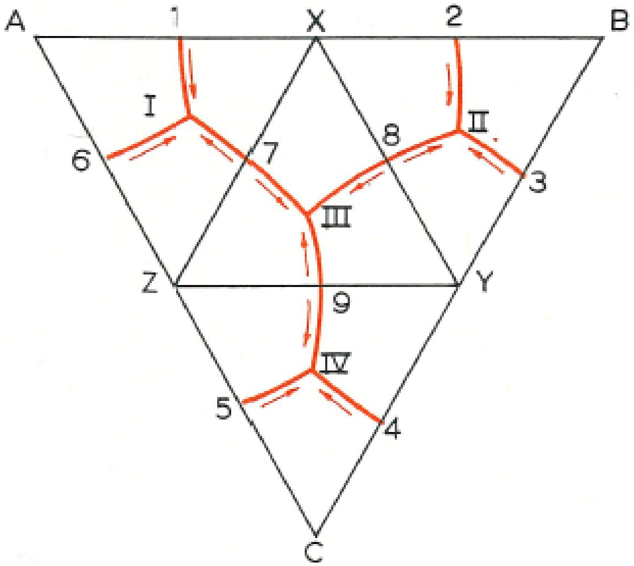
2) Case2: with only ternary congruent intermediate phases

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

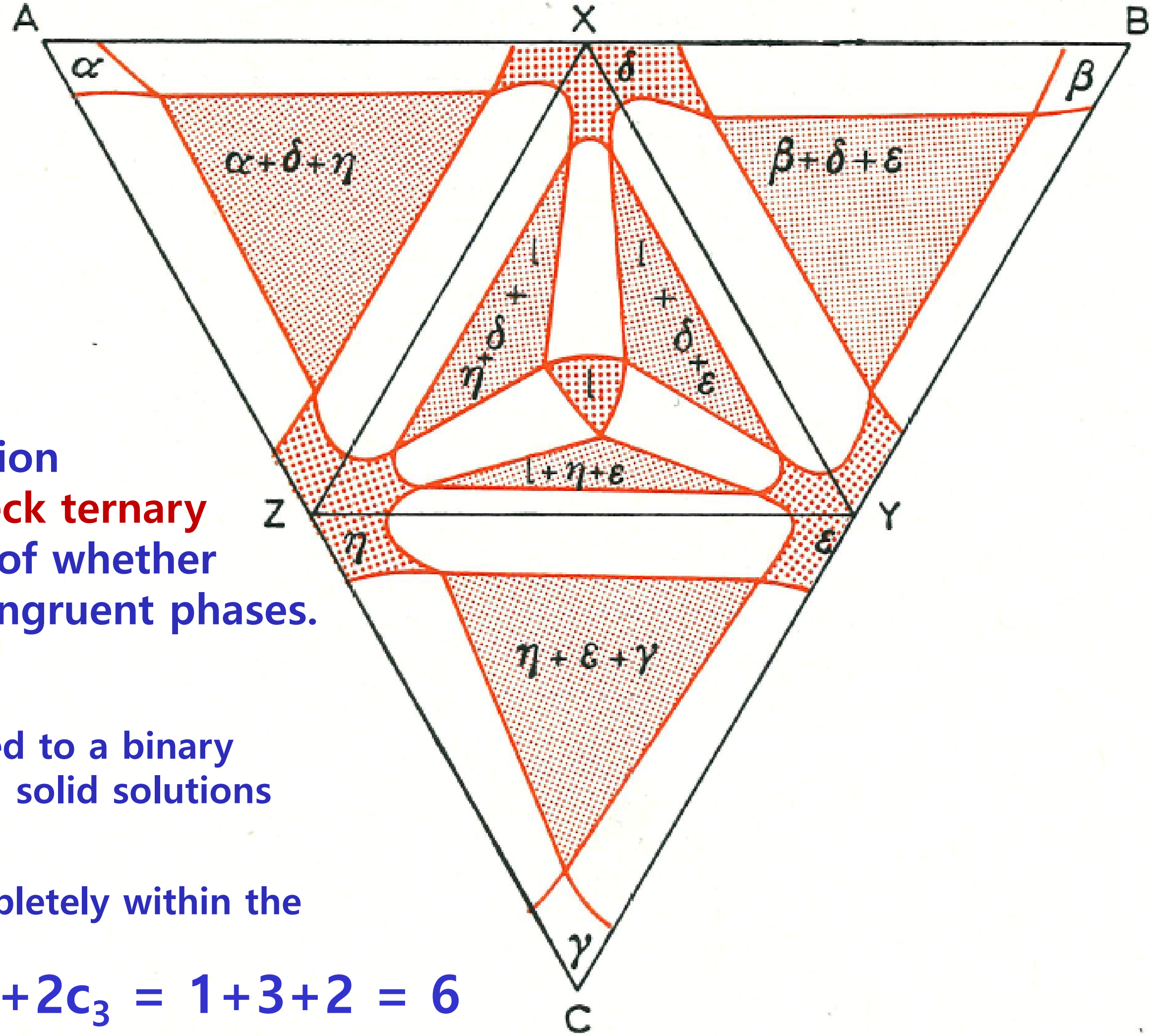
c_3 = ternary congruent intermediate phases

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.

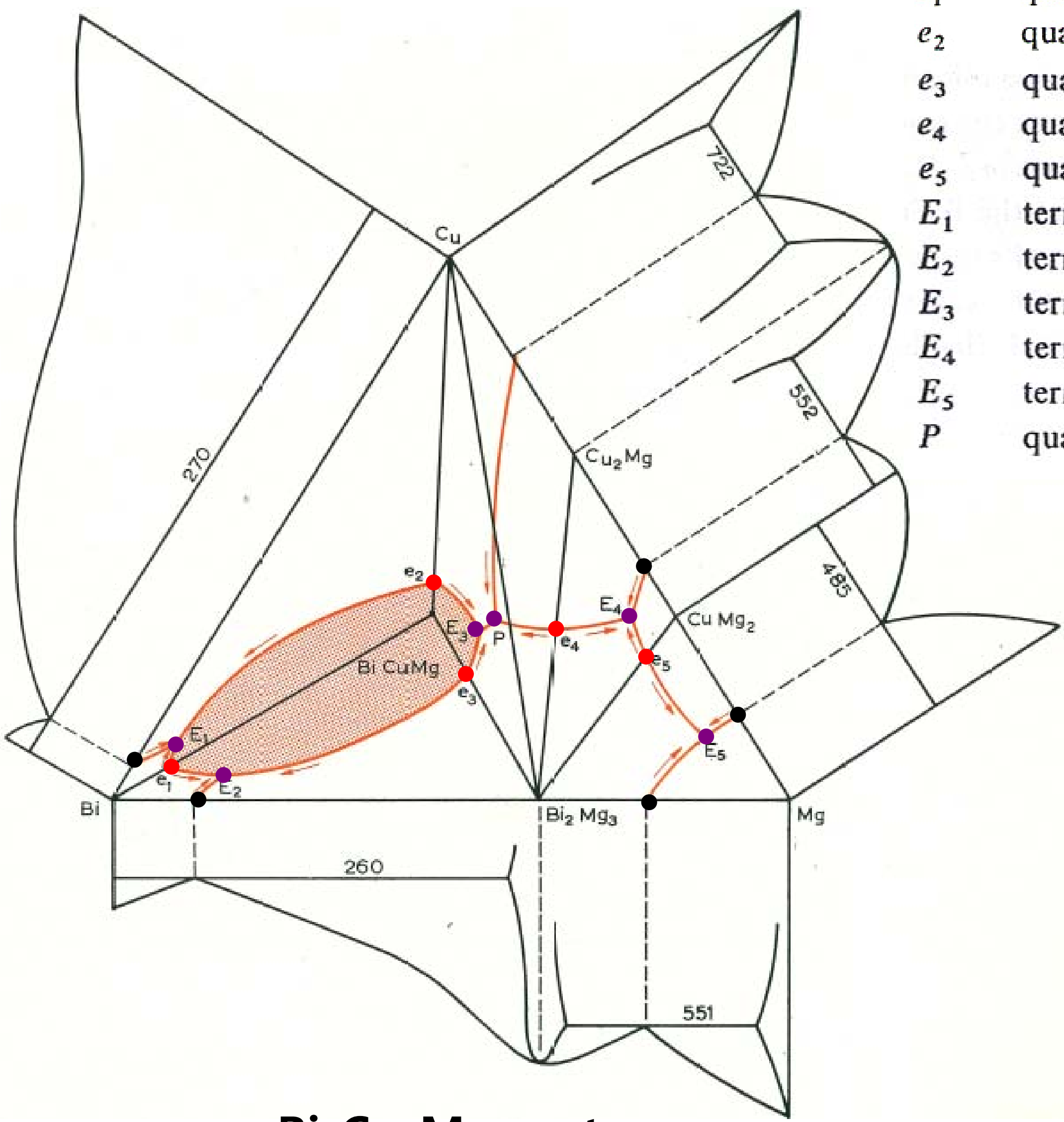
$$K = E = 1+c_2+2c_3 = 1+3+2 = 6$$

- <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>

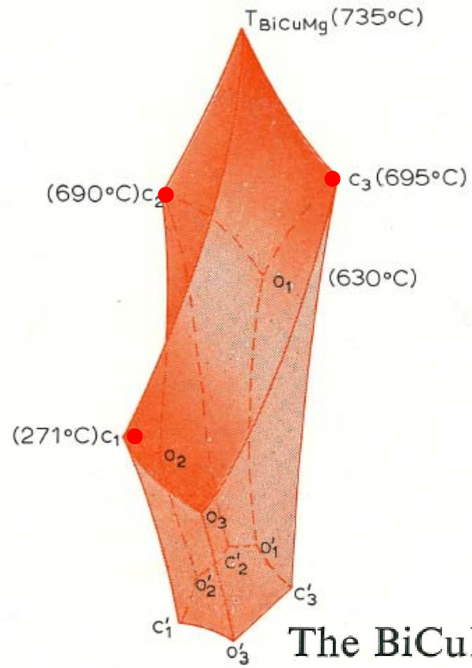
11.1 Congruently-melting intermediate phases

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

e_1	quasi-binary eutectic	$l \rightleftharpoons Bi + BiCuMg$	at	~271 °C
e_2	quasi-binary eutectic	$l \rightleftharpoons Cu + BiCuMg$	at	690 °C
e_3	quasi-binary eutectic	$l \rightleftharpoons Bi_2Mg_3 + BiCuMg$	at	695 °C
e_4	quasi-binary eutectic	$l \rightleftharpoons Bi_2Mg_3 + Cu_2Mg$	at	655 °C
e_5	quasi-binary eutectic	$l \rightleftharpoons Bi_2Mg_3 + CuMg_2$	at	557 °C
E_1	ternary eutectic	$l \rightleftharpoons Bi + Cu + BiCuMg$	at	265 °C
E_2	ternary eutectic	$l \rightleftharpoons Bi + Bi_2Mg_3 + BiCuMg$	at	255 °C
E_3	ternary eutectic	$l \rightleftharpoons Cu + Bi_2Mg_3 + BiCuMg$	at	630 °C
E_4	ternary eutectic	$l \rightleftharpoons Bi_2Mg_3 + Cu_2Mg + CuMg_2$	at	546 °C
E_5	ternary eutectic	$l \rightleftharpoons Mg + Bi_2Mg_3 + CuMg_2$	at	470 °C
P	quasi-peritectic	$l + Cu_2Mg \rightleftharpoons Cu + Bi_2Mg_3$	at	660 °C



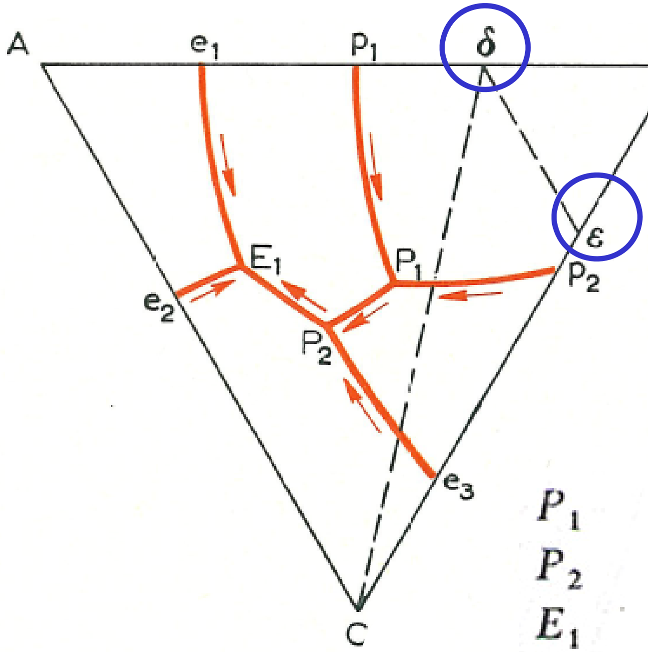
Bi-Cu-Mg system



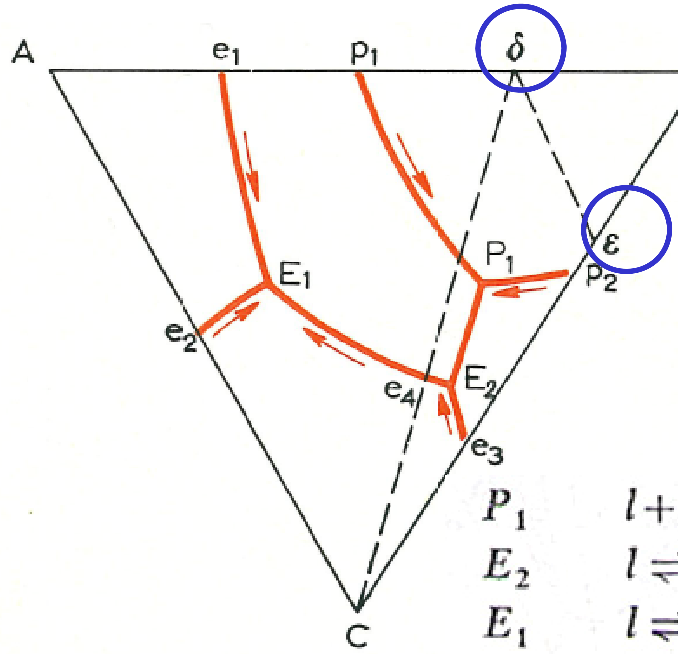
The BiCuMg phase region.

11.2 incongruently-melting intermediate phases

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



P_1	$l+\beta \rightleftharpoons \delta+\varepsilon$
P_2	$l+\varepsilon \rightleftharpoons \delta+\gamma$
E_1	$l \rightleftharpoons \alpha+\delta+\gamma$.

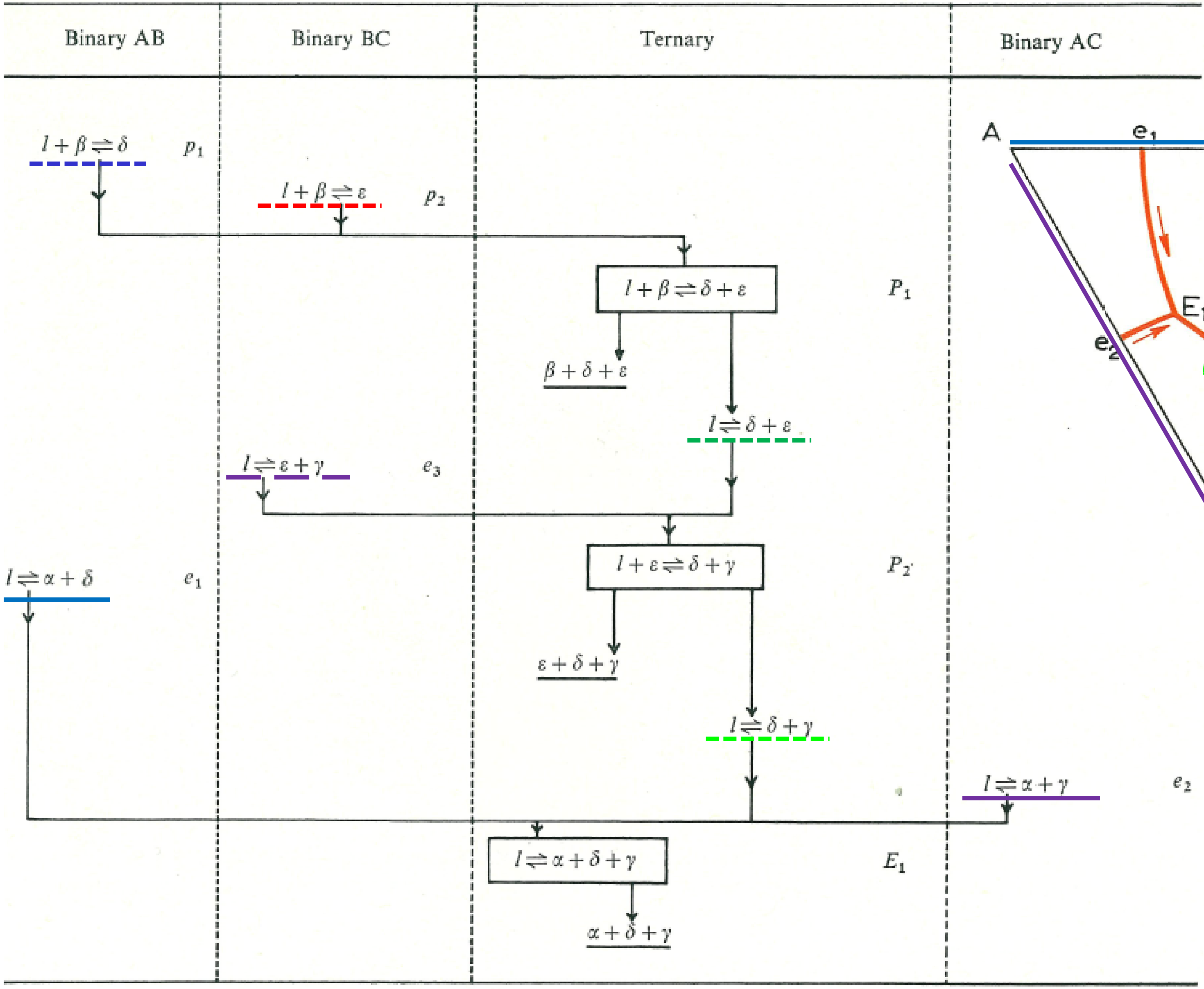


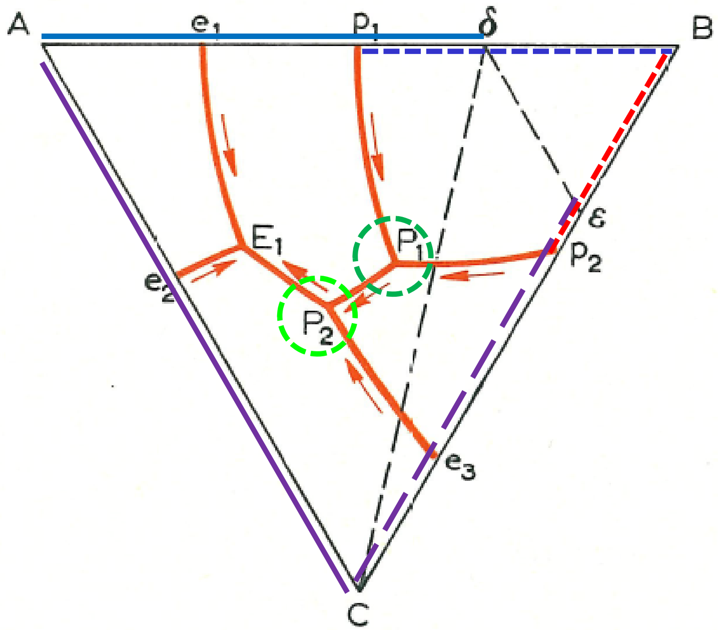
P_1	$l+\beta \rightleftharpoons \delta+\varepsilon$
E_2	$l \rightleftharpoons \delta+\varepsilon+\gamma$
E_1	$l \rightleftharpoons \alpha+\delta+\varepsilon$
e_4	$l \rightleftharpoons \delta+\gamma$.

(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) :

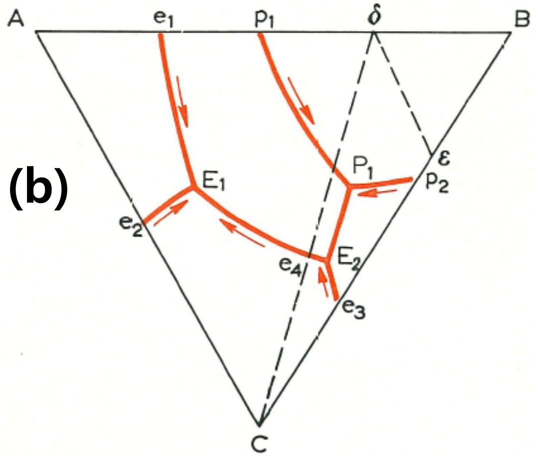


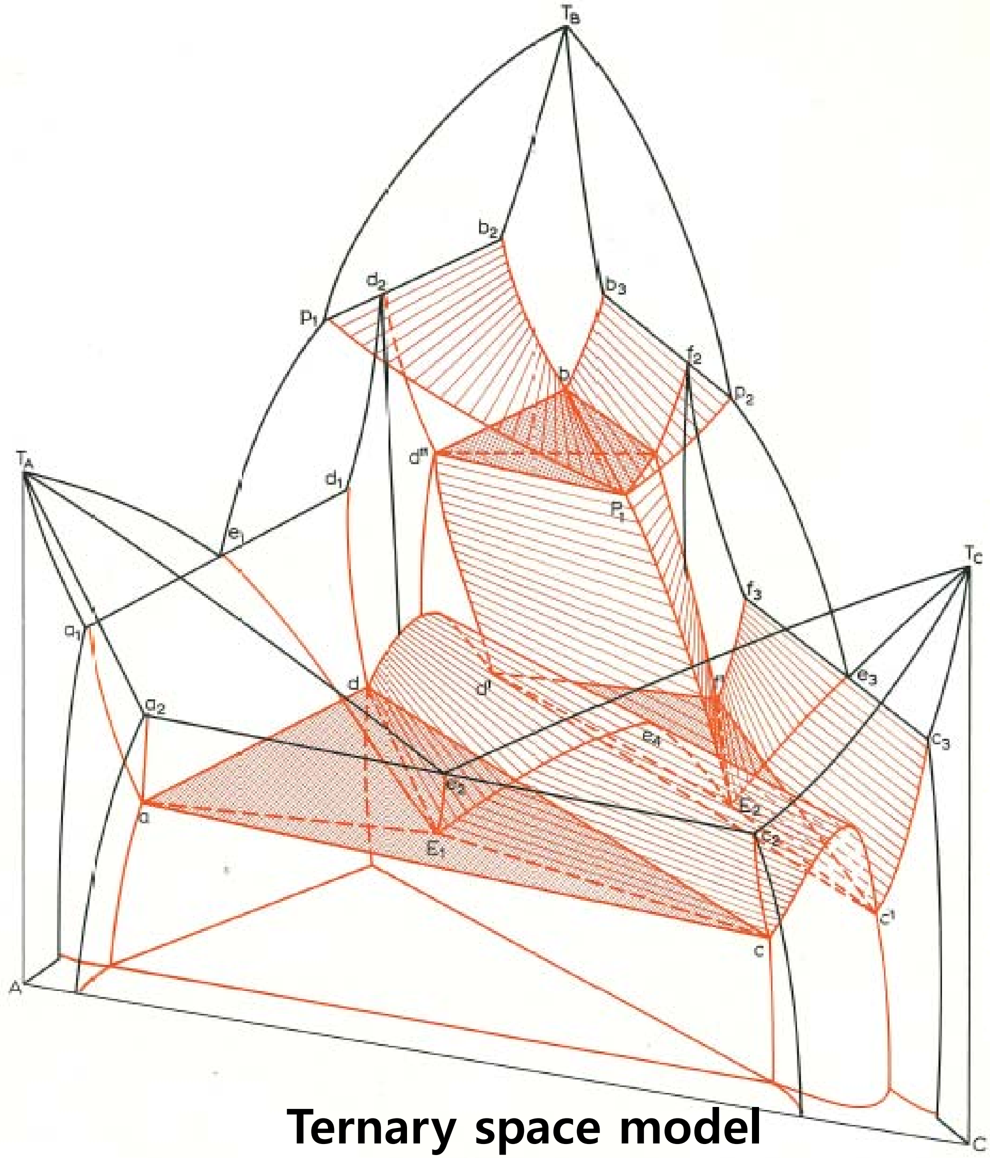


P_1	$l + \beta \rightleftharpoons \delta + \varepsilon$
P_2	$l + \varepsilon \rightleftharpoons \delta + \gamma$
E_1	$l \rightleftharpoons \alpha + \delta + \gamma$.

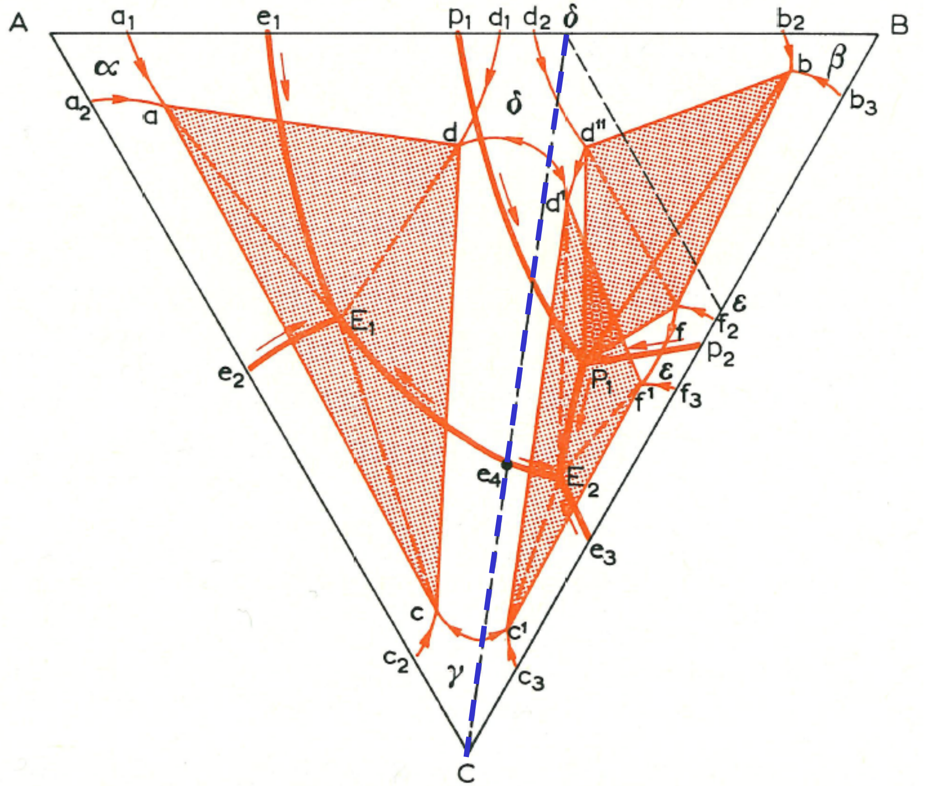
11.2 incongruently-melting intermediate phases

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





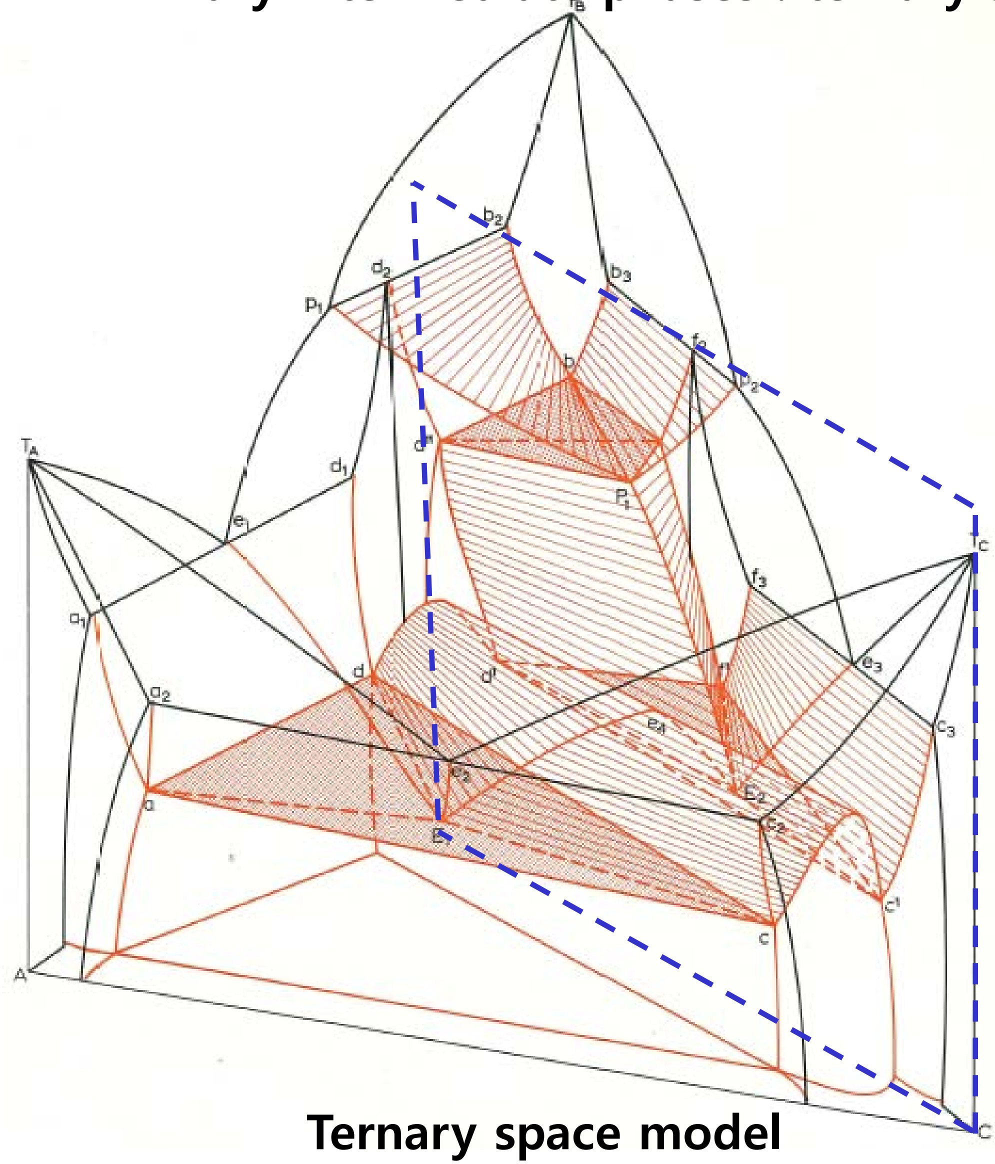
Ternary space model



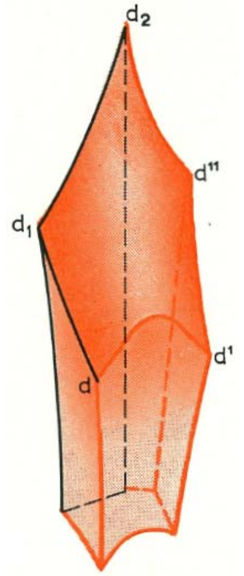
Projection of equilibria

11.2 incongruently-melting intermediate phases

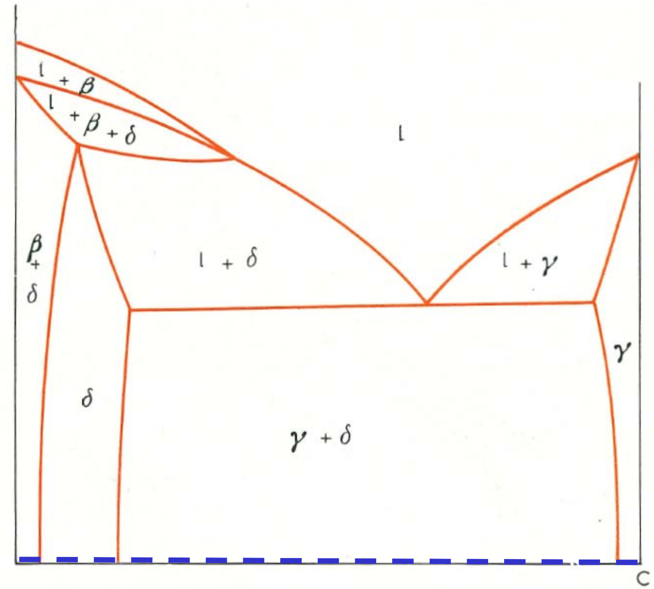
- **Binary intermediate phases : ternary space model of (b)**



Ternary space model



δ phase region



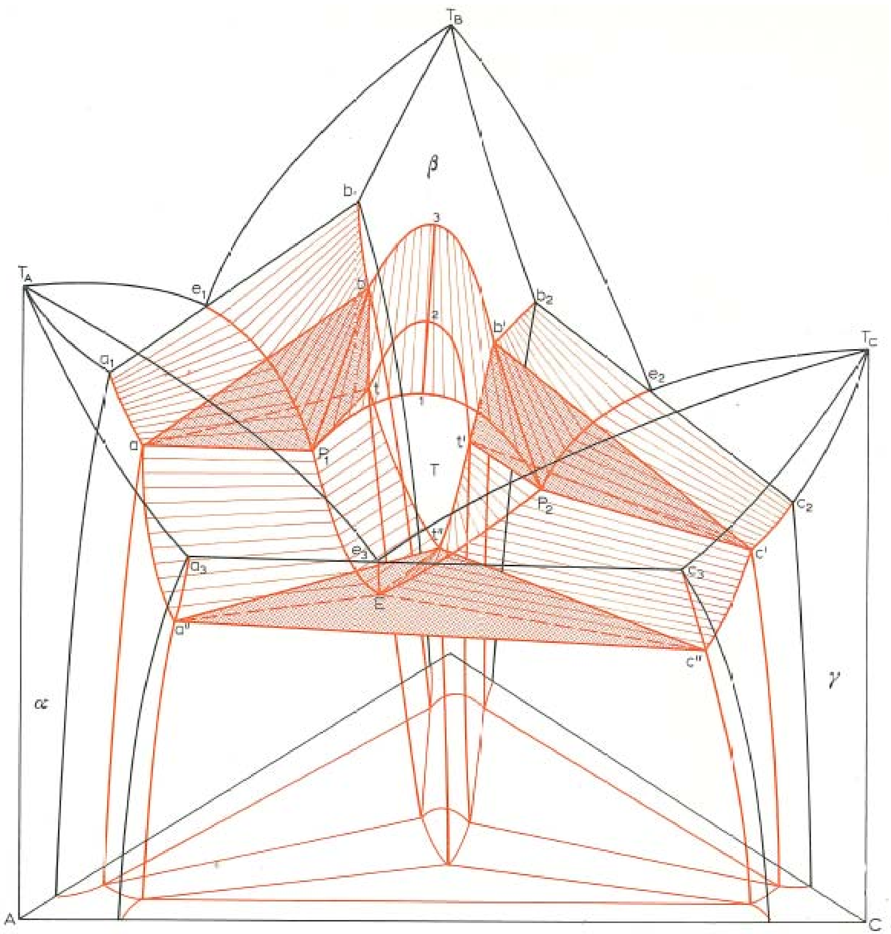
Vertical section from C to δ

: near quasi-binary nature

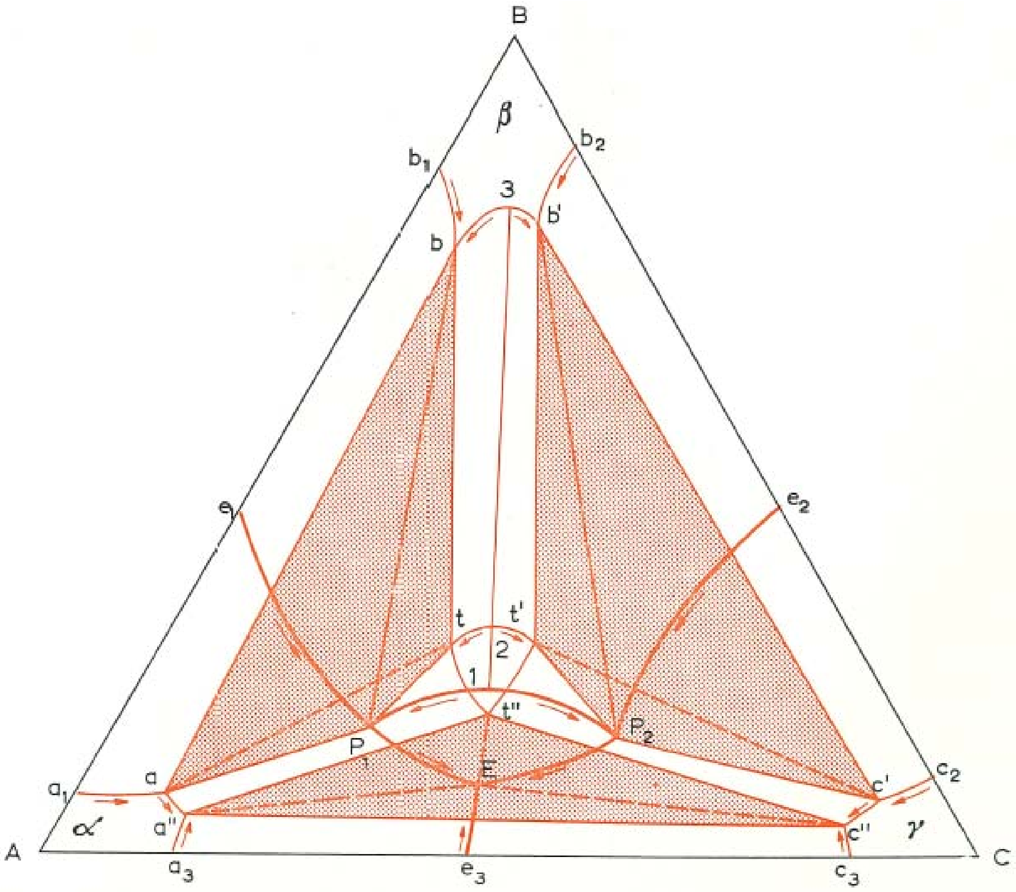
~ not quasi-binary

11.2 incongruently-melting intermediate phases

b) one ternary intermediate phase and all three binary eutectic

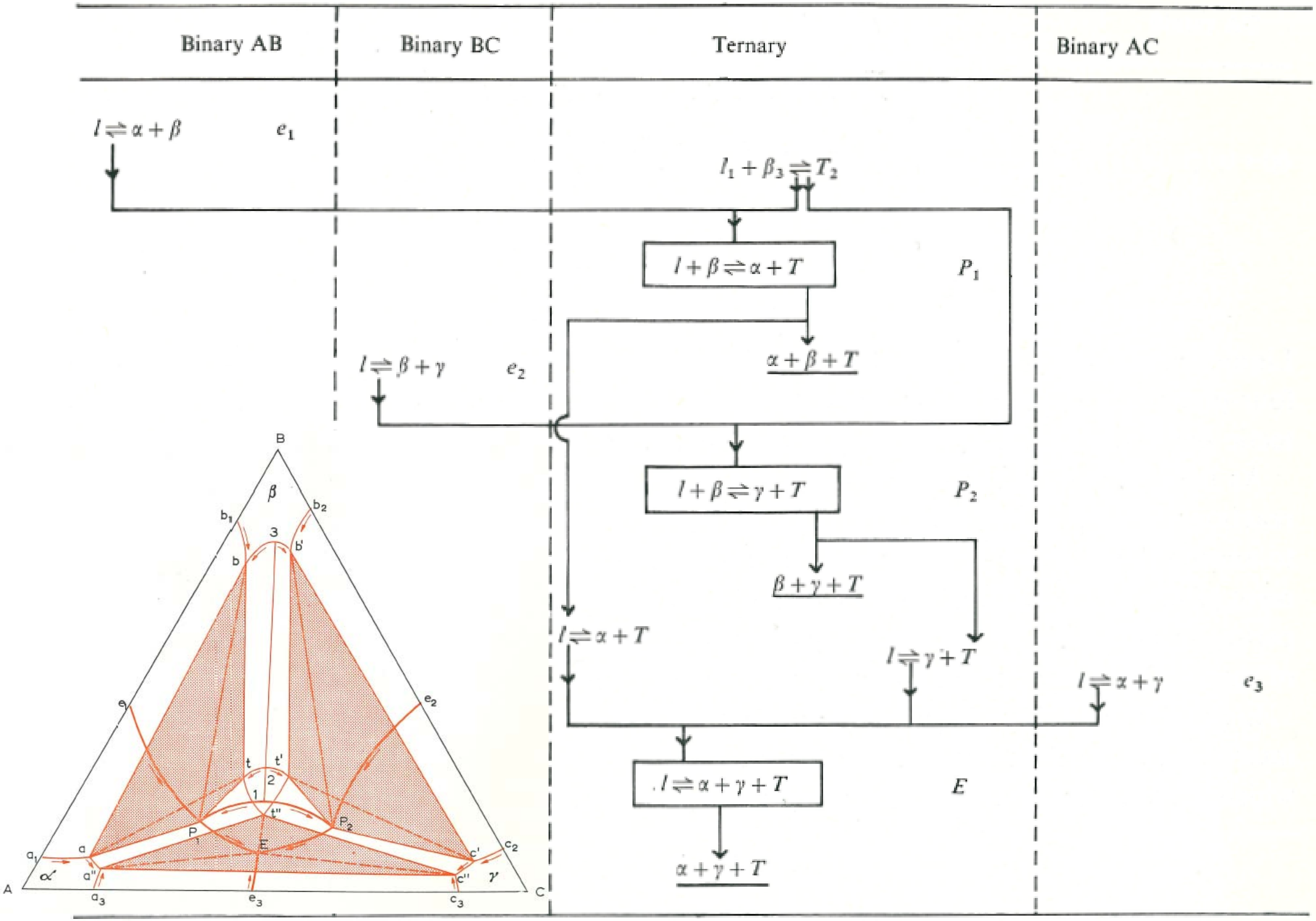


Ternary space model



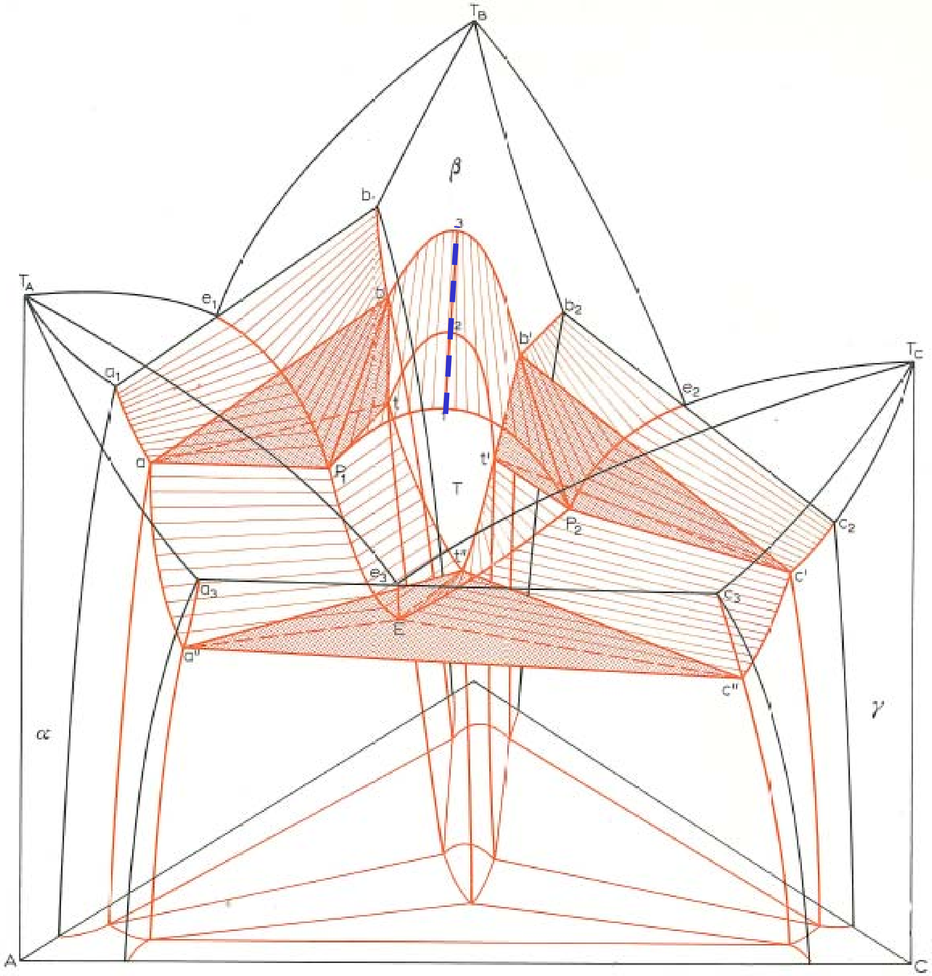
Projection on the concentration triangle

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

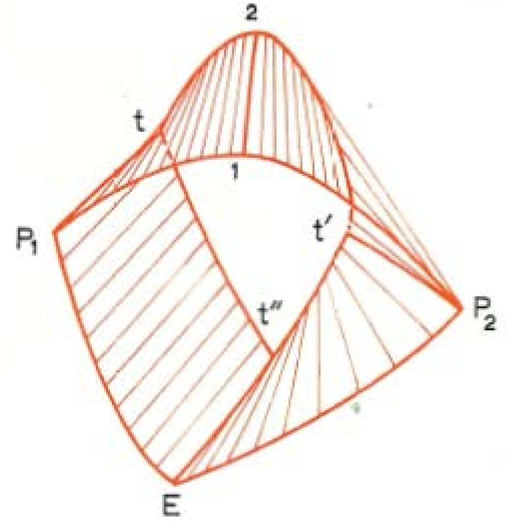


11.2 incongruently-melting intermediate phases

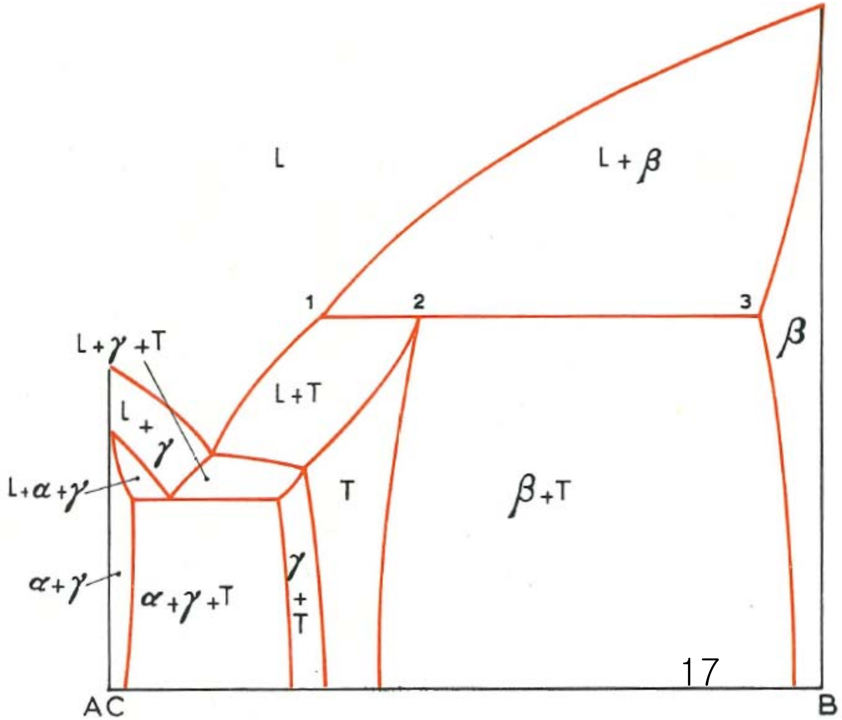
- **Ternary intermediate phases**



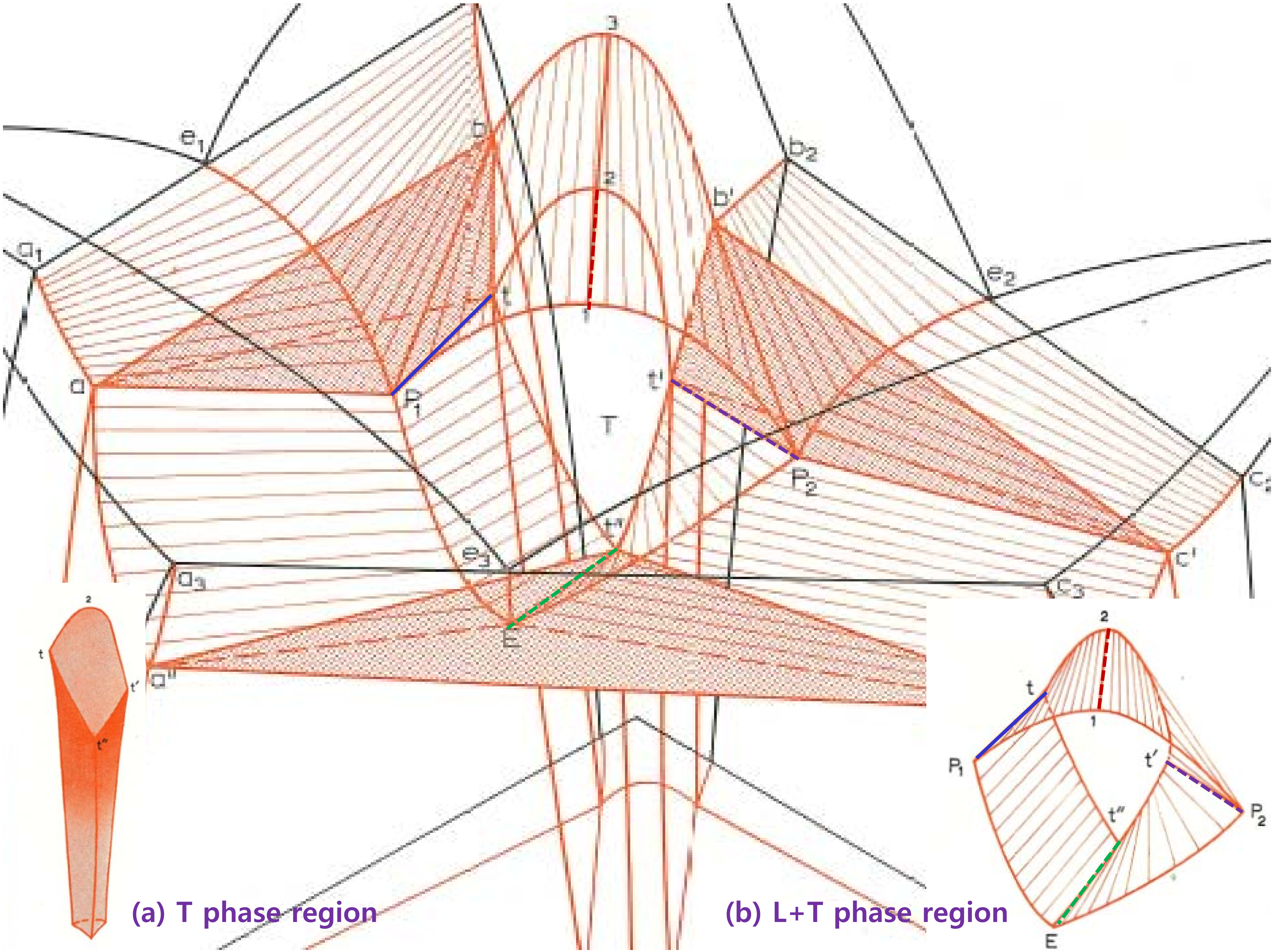
(a) T phase region



(b) L+T phase region



Vertical section along tiel line 1-2-3



(a) T phase region

(b) L+T phase region

Chapter 12. Ternary phase Diagrams

Liquid Immiscibility

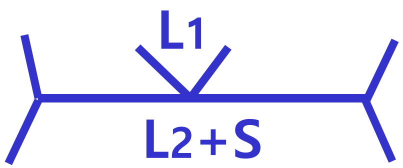
Liquid immiscibility in one or more of the binary systems can lead to either three-phase or four-phase equilibria in the ternary system.

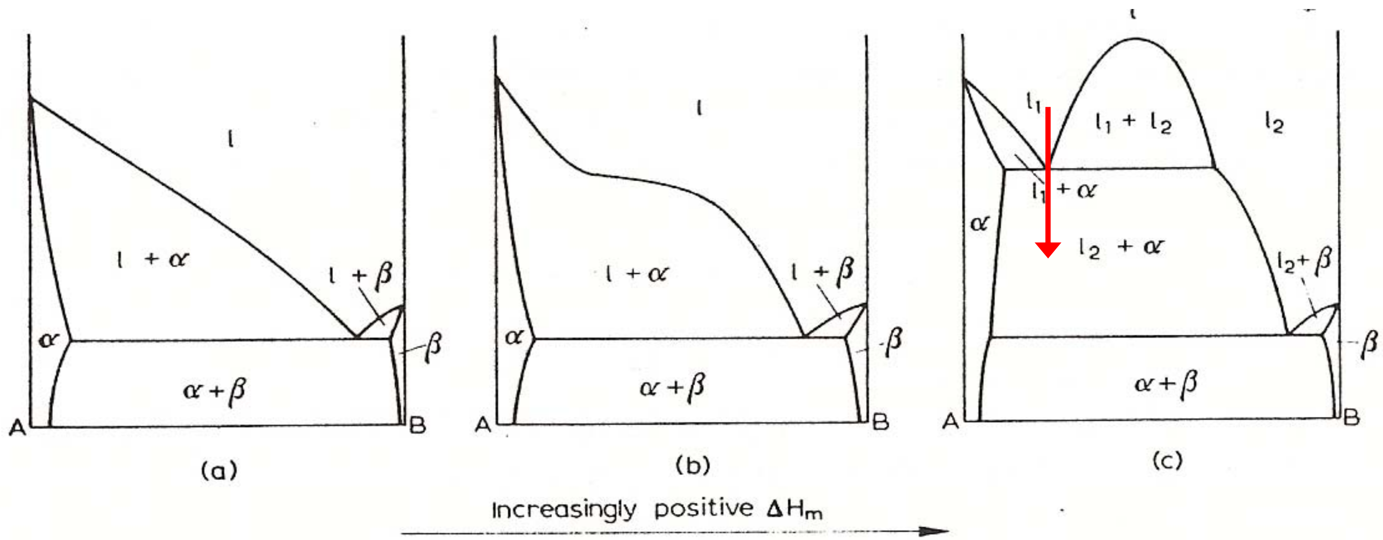
Immiscibility can arise if either monotectic or syntectic reactions occur in the binary system; true ternary immiscibility is also possible.

1) Liquid immiscibility in binary system

* Monotectic reaction:

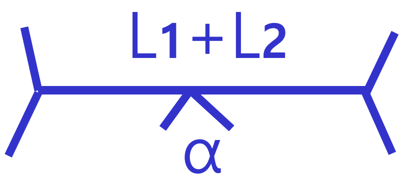
Liquid1 ↔Liquid2+ Solid



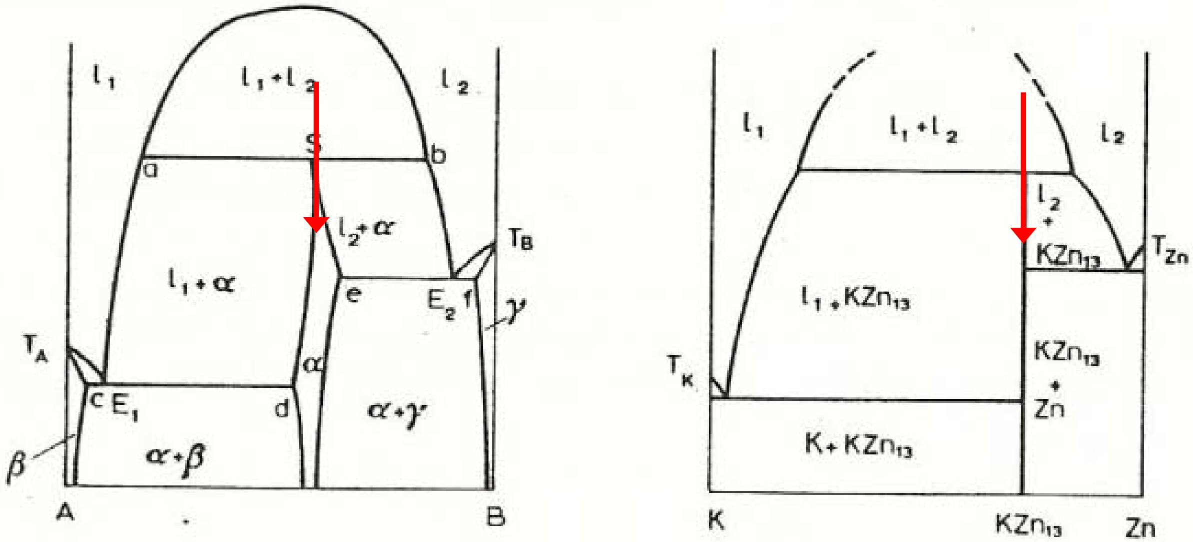


* Syntectic reaction:

Liquid1+Liquid2 ↔ α



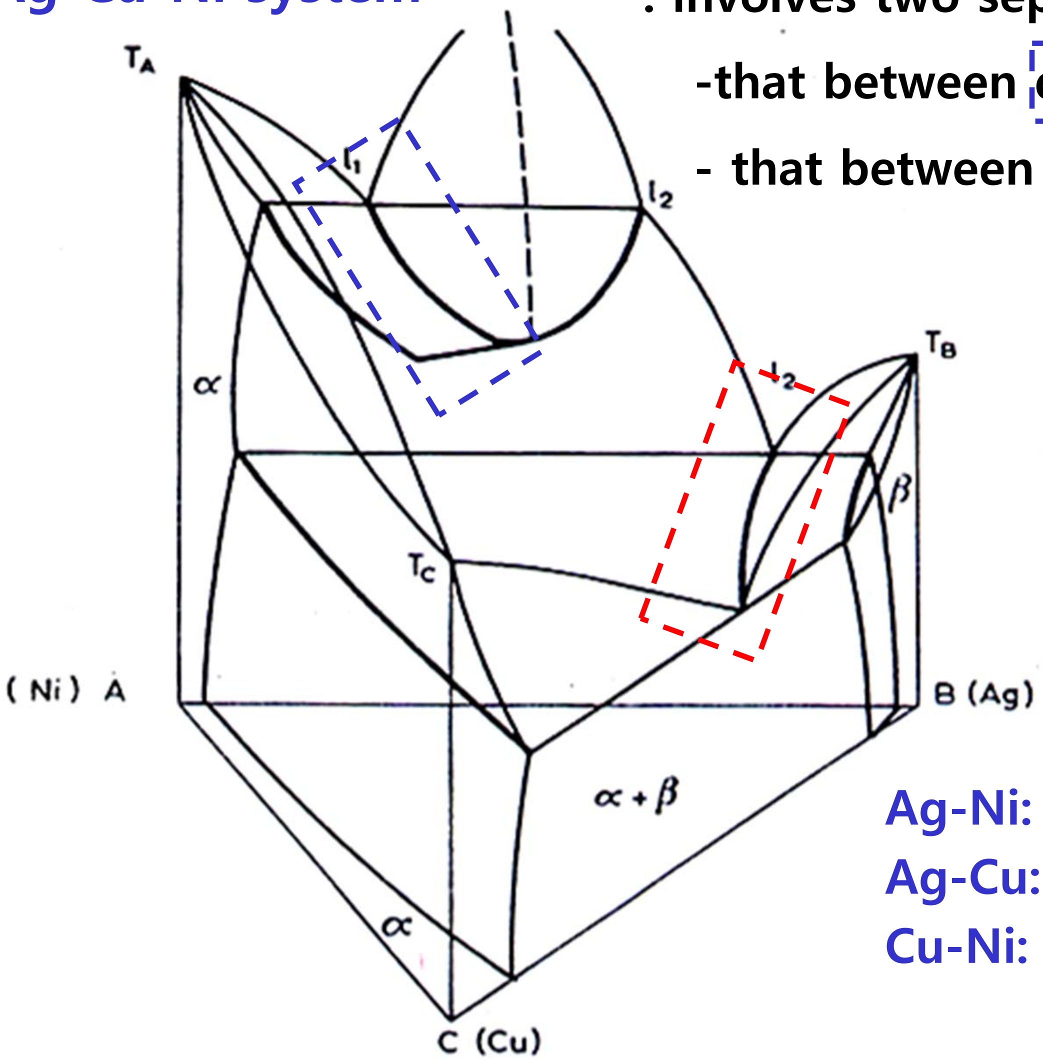
K-Zn, Na-Zn,
K-Pb, Pb-U, Ca-Cd



2) One binary liquid miscibilty 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

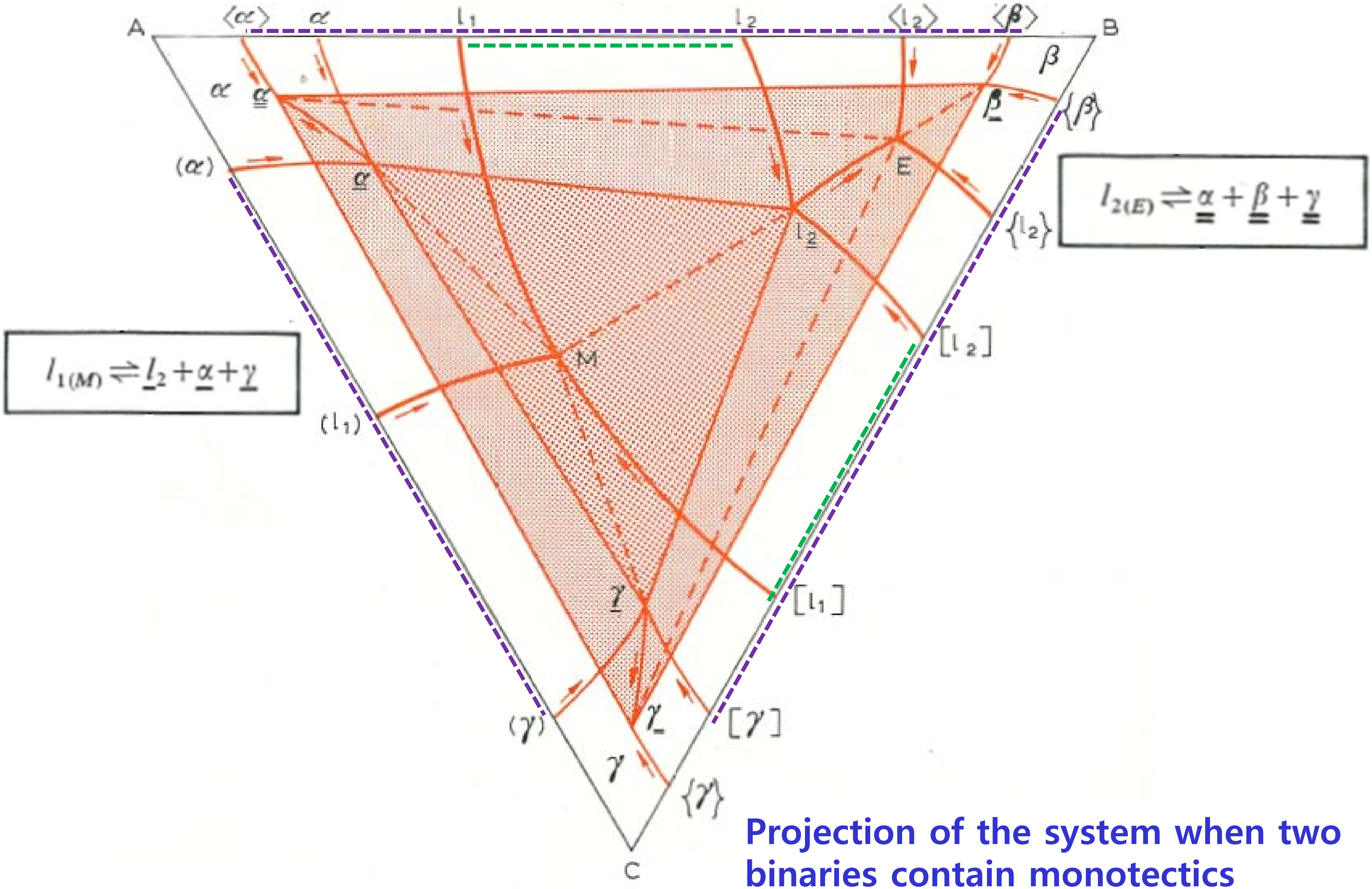
Ag-Ni: monotectic

Ag-Cu: eutectic

Cu-Ni: continuous series of solid soln

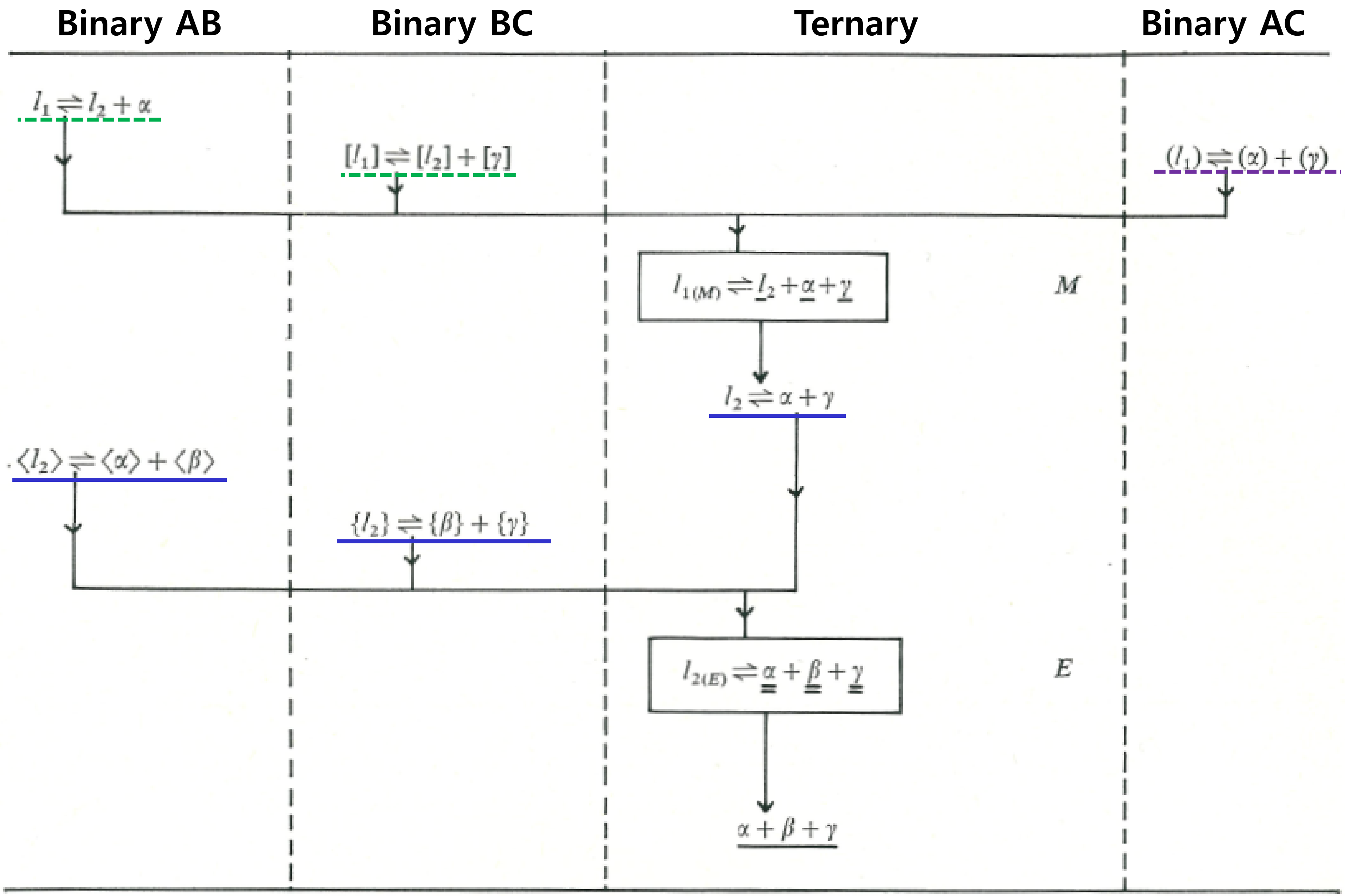
12.1. Two Binary Systems are Monotectic

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



Projection of the system when two binaries contain monotectics

* Tabular foam of the system when two binaries contain monotectics



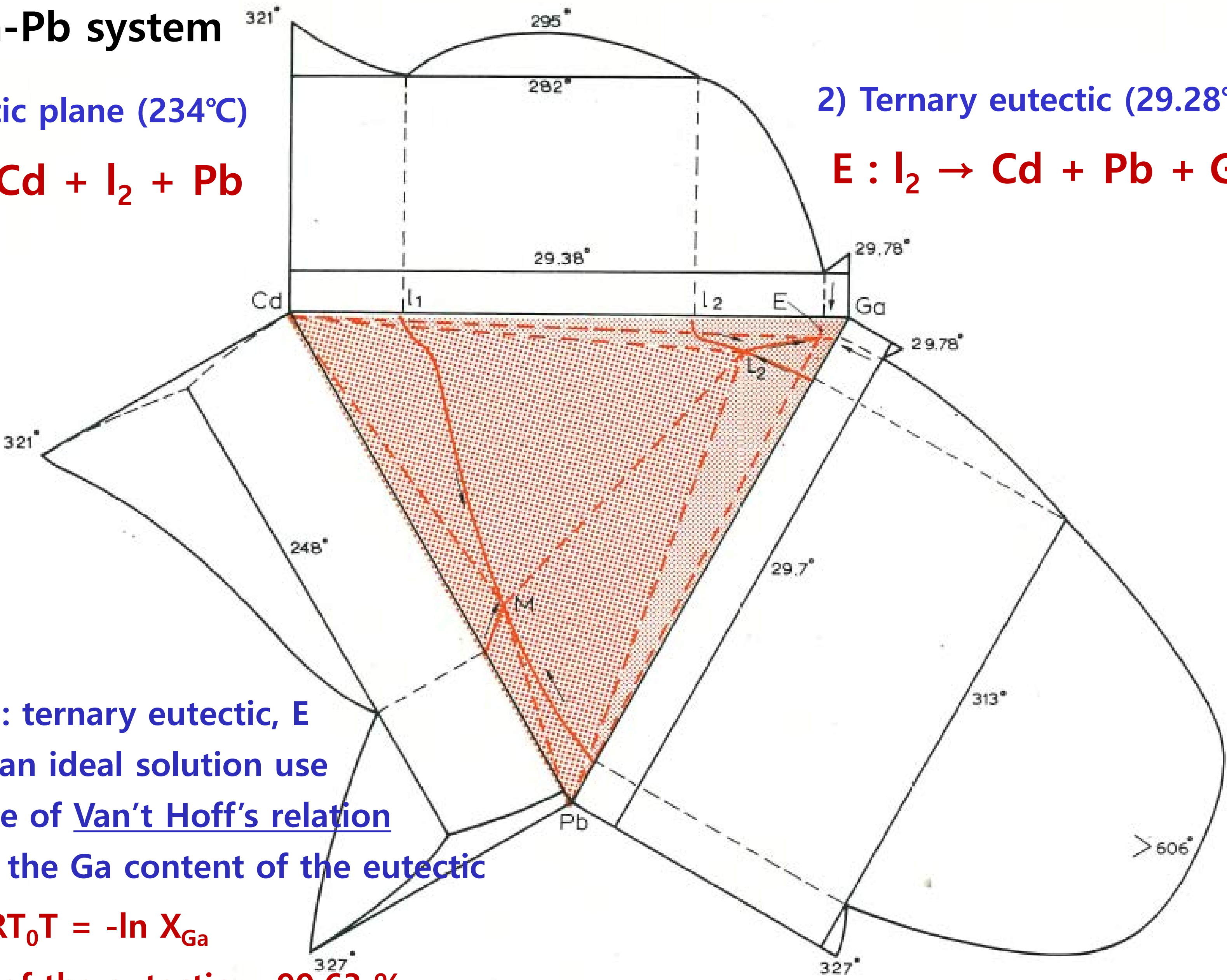
The Cd-Ga-Pb system

1) Monotectic plane (234℃)

M : $l_1 \rightarrow Cd + l_2 + Pb$

2) Ternary eutectic (29.28℃)

E : $l_2 \rightarrow Cd + Pb + Ga$



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

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

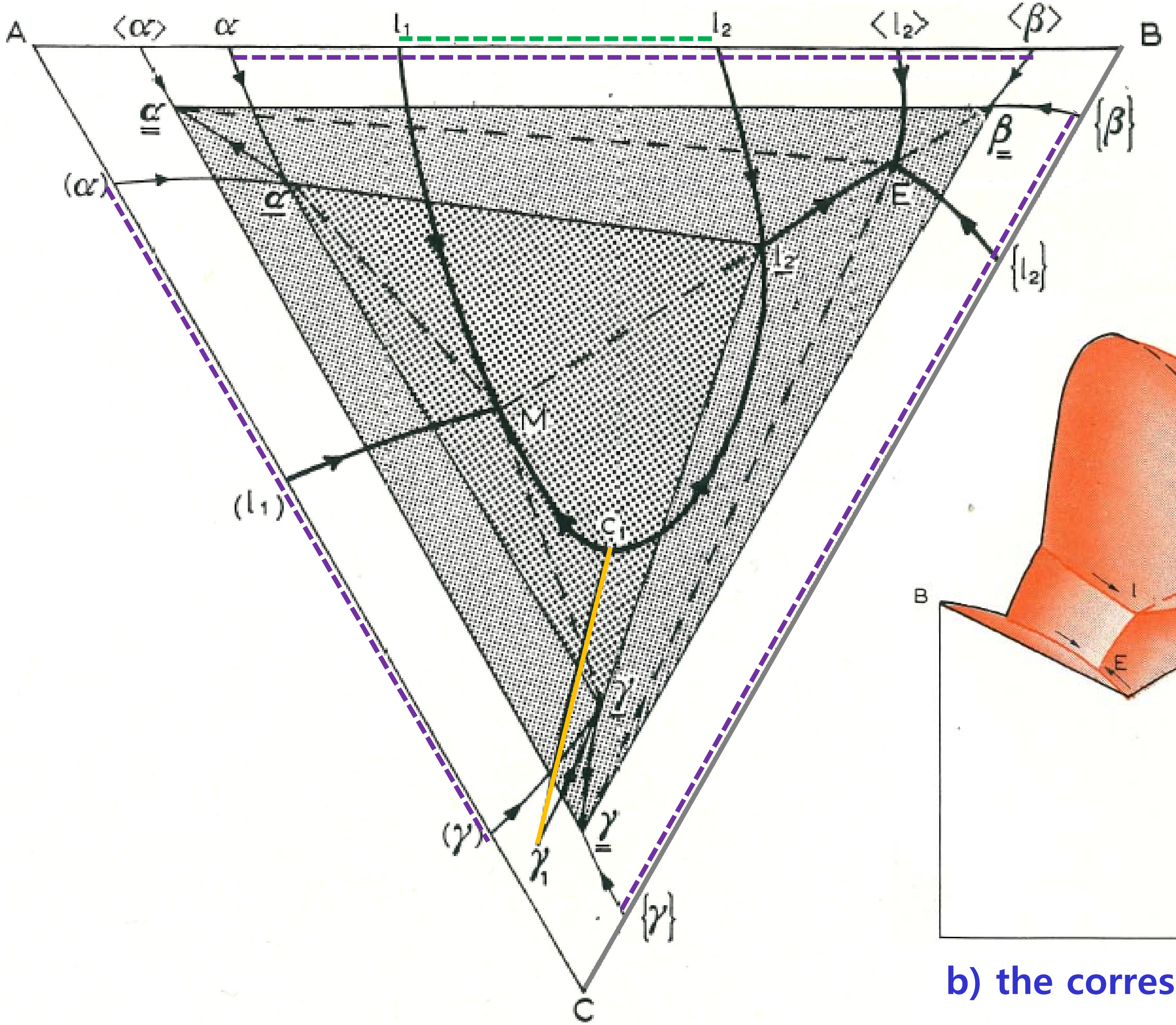
Ga content of the eutectic = 99.63 %

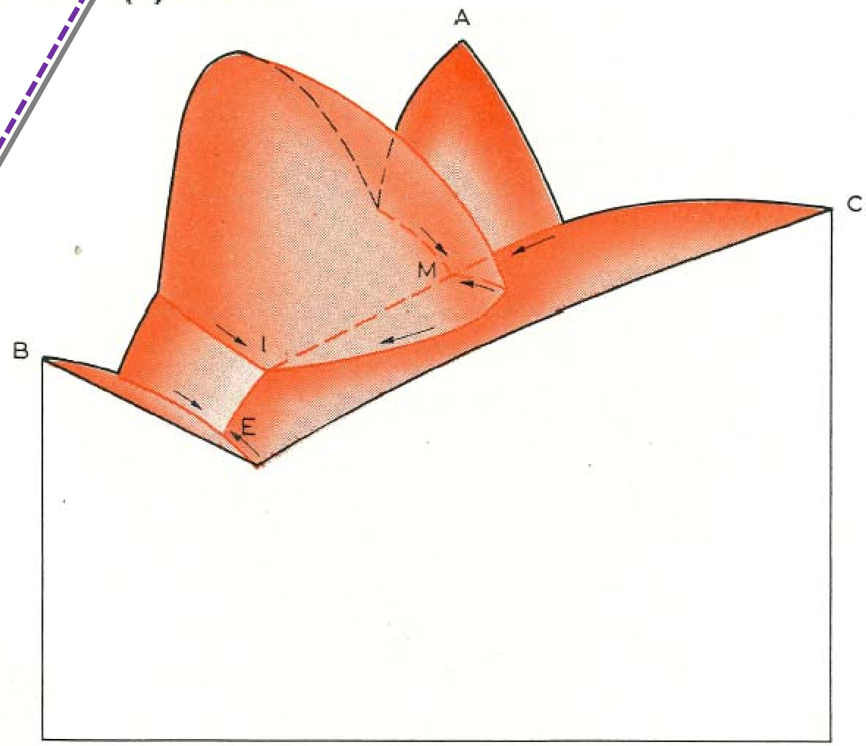
where L_{Ga} is the heat of fusion of Ga (1336 cal/g.-atom), T_0 is the m.p. of Ga (302.93 °K), T is the ternary eutectic temperature, R the gas constant, and X_{Ga} the Ga content of the ternary eutectic E.

12.2. One Binary System is Monotectic

Liquid immiscibility in ternary system

a) Projection of the system when only one binary is monotectic and two binaries are simple eutectic.

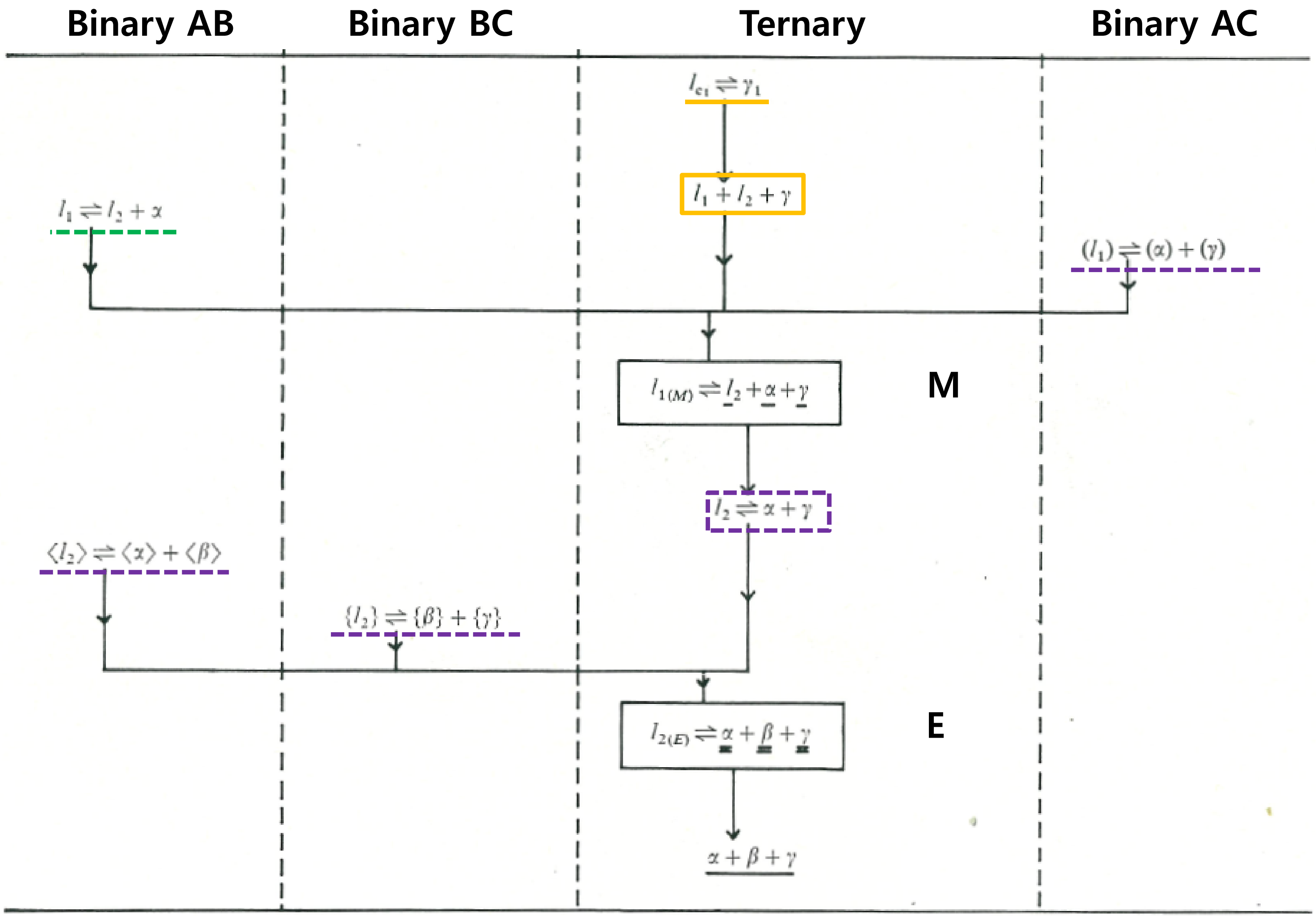




b) the corresponding liquidus surface

12.2. One Binary System is Monotectic

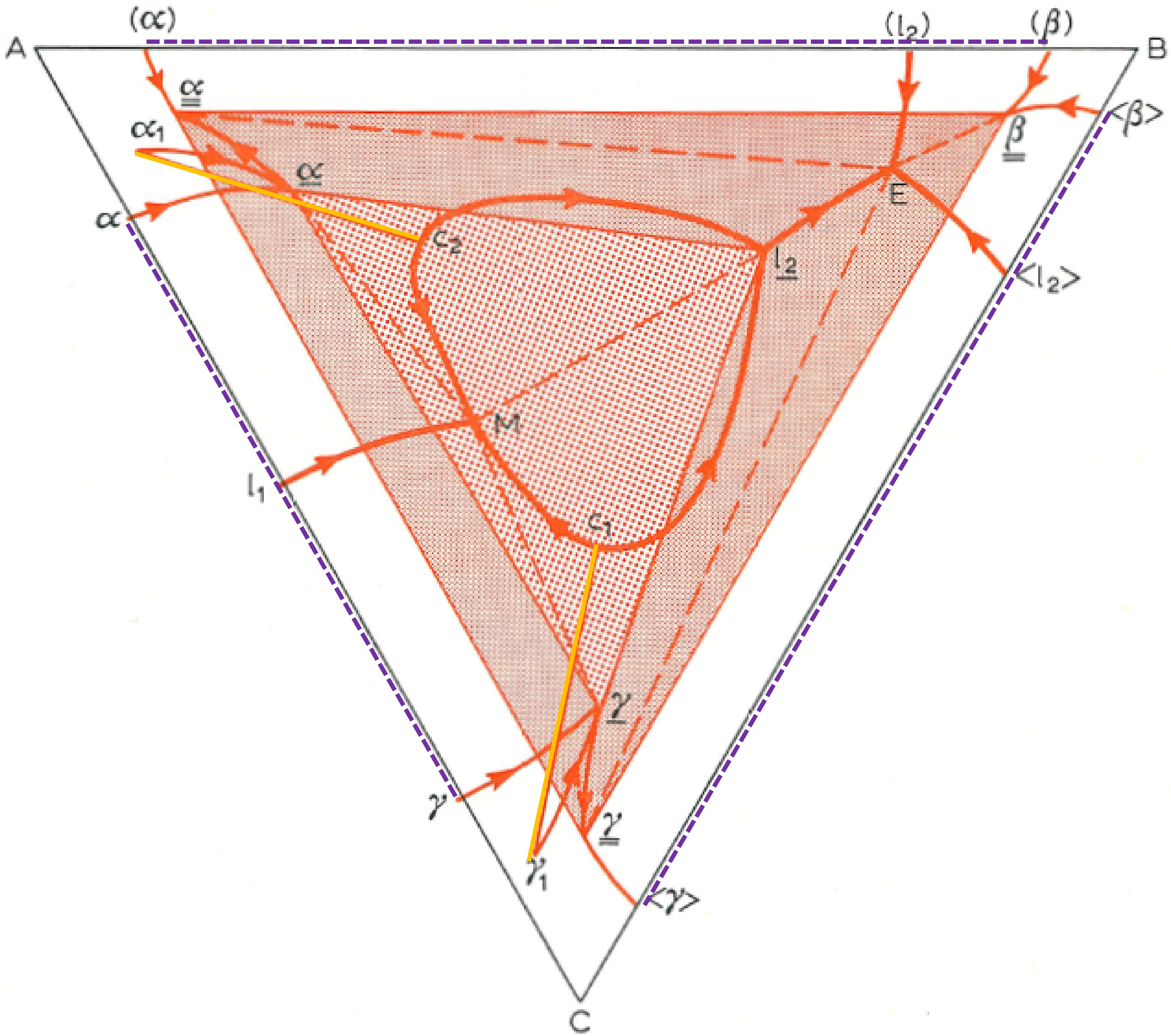
* Tabular foam of the system when two binaries contain monotectics



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

quasi-binary system Fe-Fe_3C: monotectic/ Fe-Fe_3C & 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