2009 fall

Advanced Physical Metallurgy

"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

- 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.

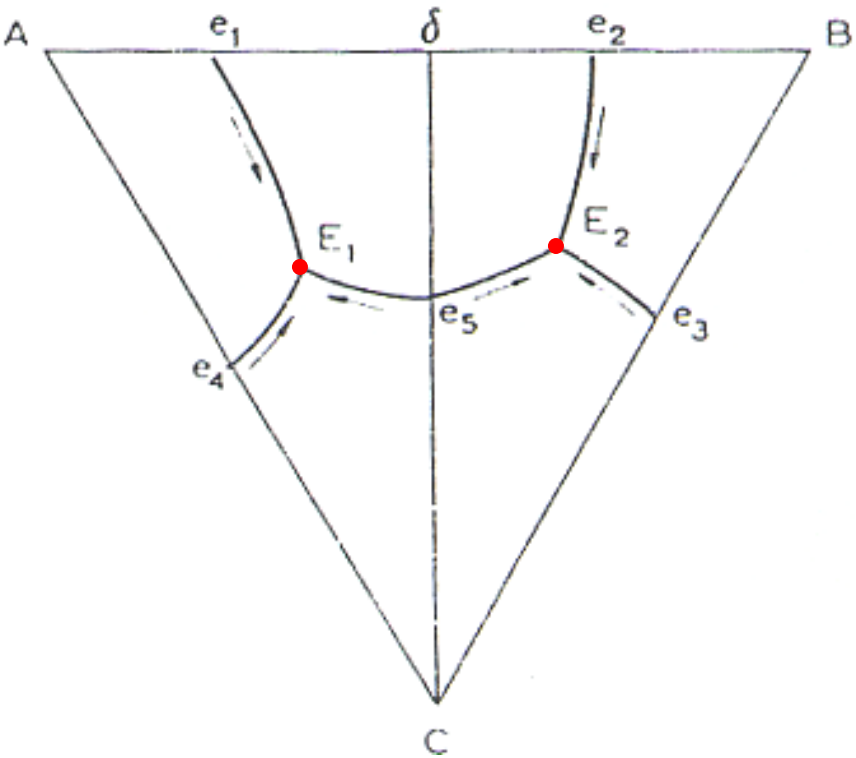
- If there is direct equilibrium between γ and δ, splitting the ternary system into two partial system AδC and BδC. It often happens that the δ phase forms <u>a quasi-binary system</u> with component C.

11.1 Congruently melting intermediate phases

$$l \leftrightarrow \alpha + \beta + \gamma$$
$$l \leftrightarrow \alpha + \beta + \delta$$
$$\boxed{\begin{array}{l} l \leftrightarrow \alpha + \gamma + \delta \\ l \leftrightarrow \beta + \gamma + \delta \end{array}}$$

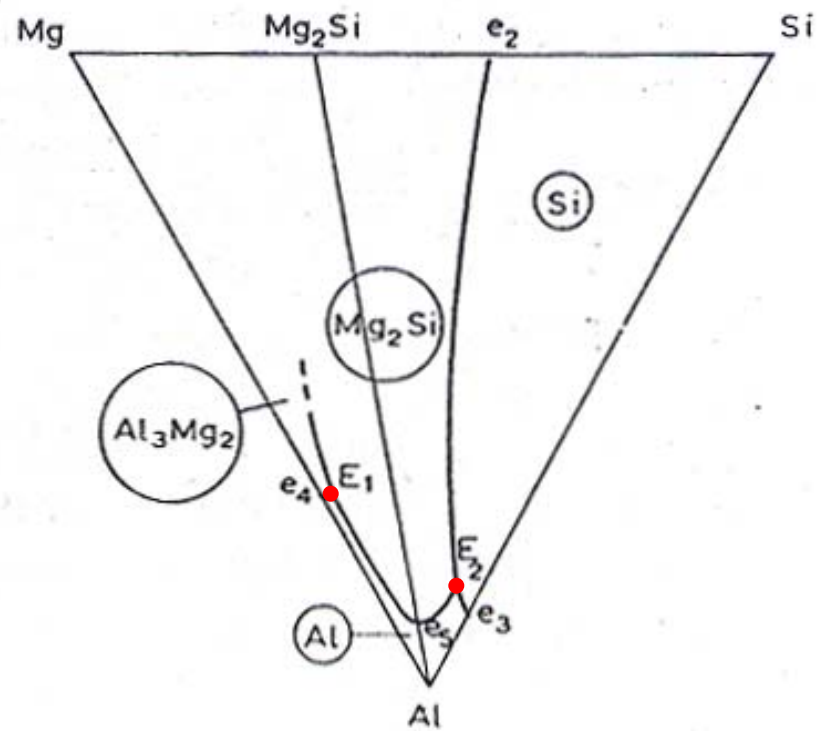
11.1. Binary intermediate phases

1) Quasi binary eutectic



E_1: L→α+γ+δ

E_2: L→β+γ+δ



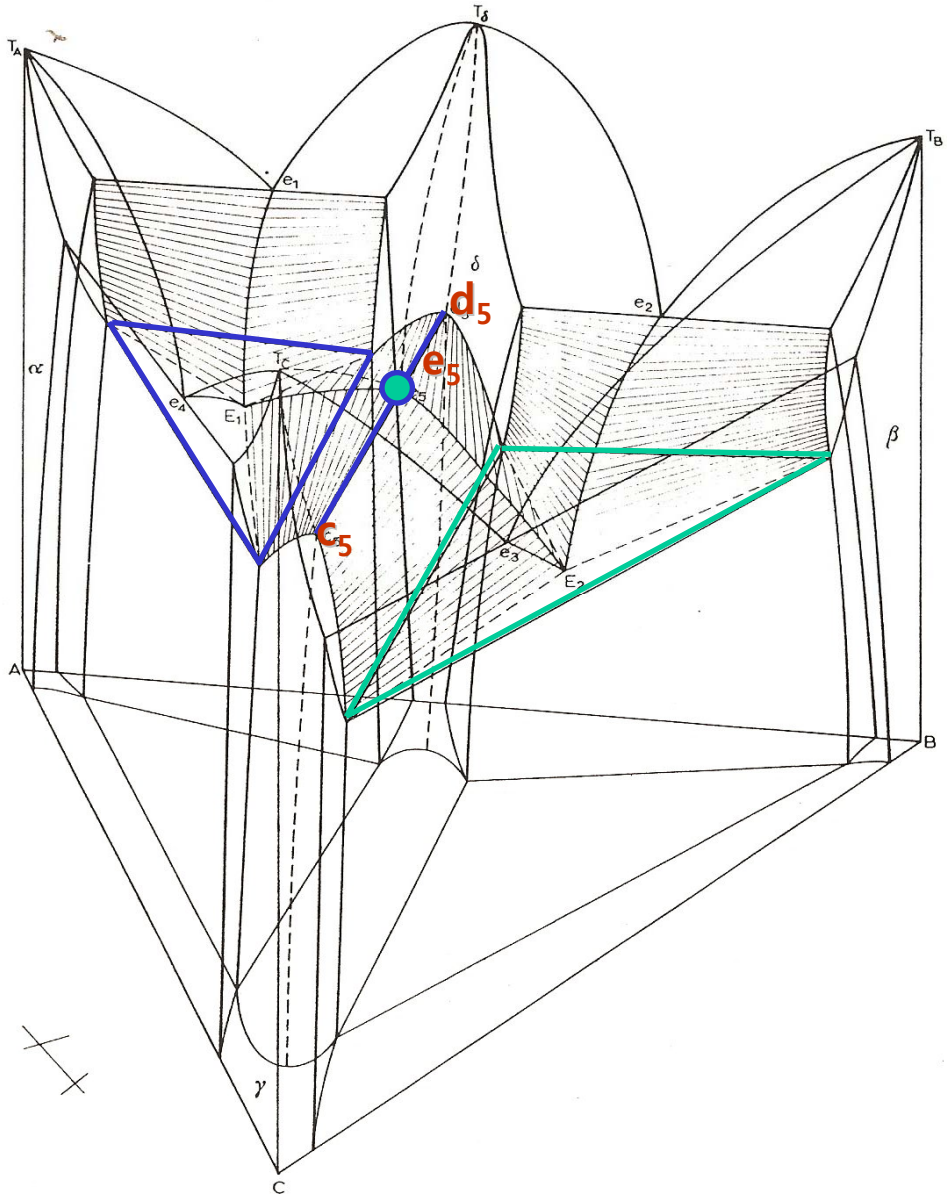
Al-Mg-Si system

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



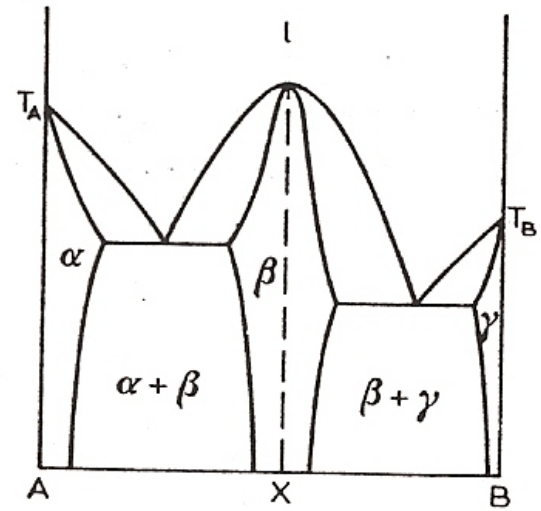


Fig. 78. Phase diagram with a congruent intermediate phase.

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

the straight line in question is the quasi-Binary eutectic horizontal c5e5d5.

11.1. Binary intermediate phases

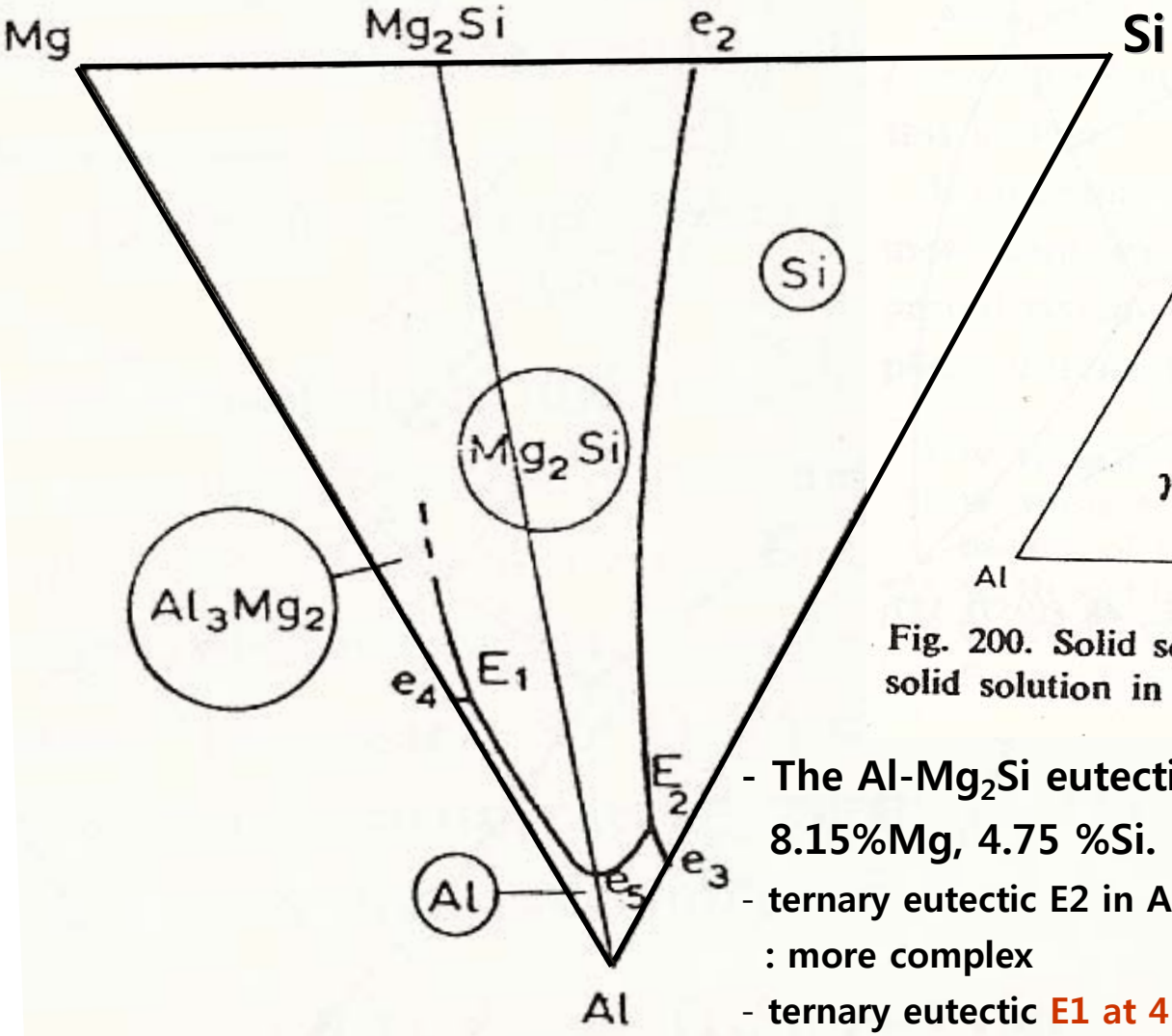


Fig. 199. The Al–Mg–Si system (schematic).

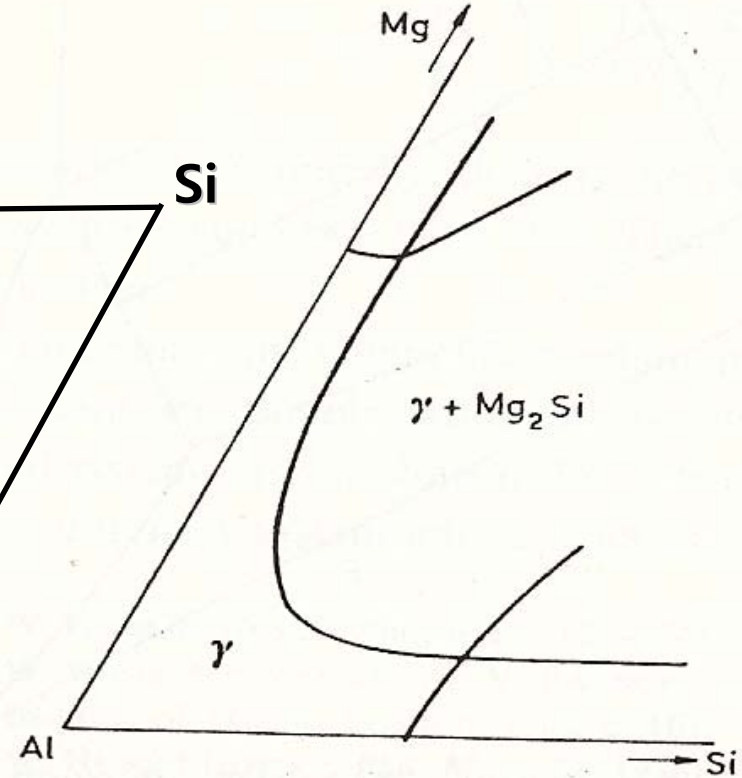


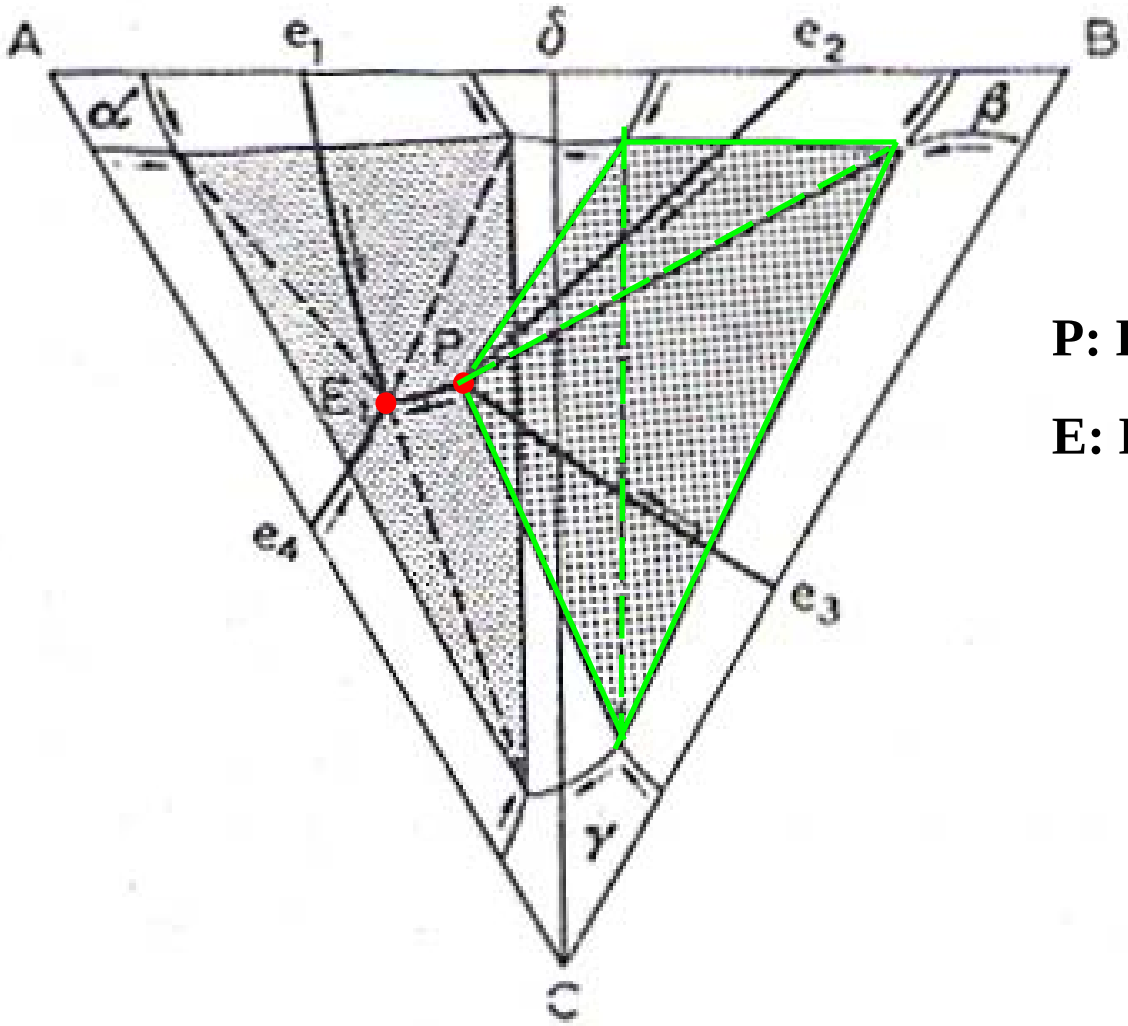
Fig. 200. Solid solubility isotherm for the Al-based solid solution in the Al–Mg–Si system (schematic).

- 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 Congruently-melting intermediate phases

- **Binary intermediate phases**

2) Quasi peritectic reaction



P: L+β → γ+δ

E: L → α+γ+δ

11.1 Congruently-melting intermediate phases

- **Binary intermediate phases**

Quasi peritectic reaction

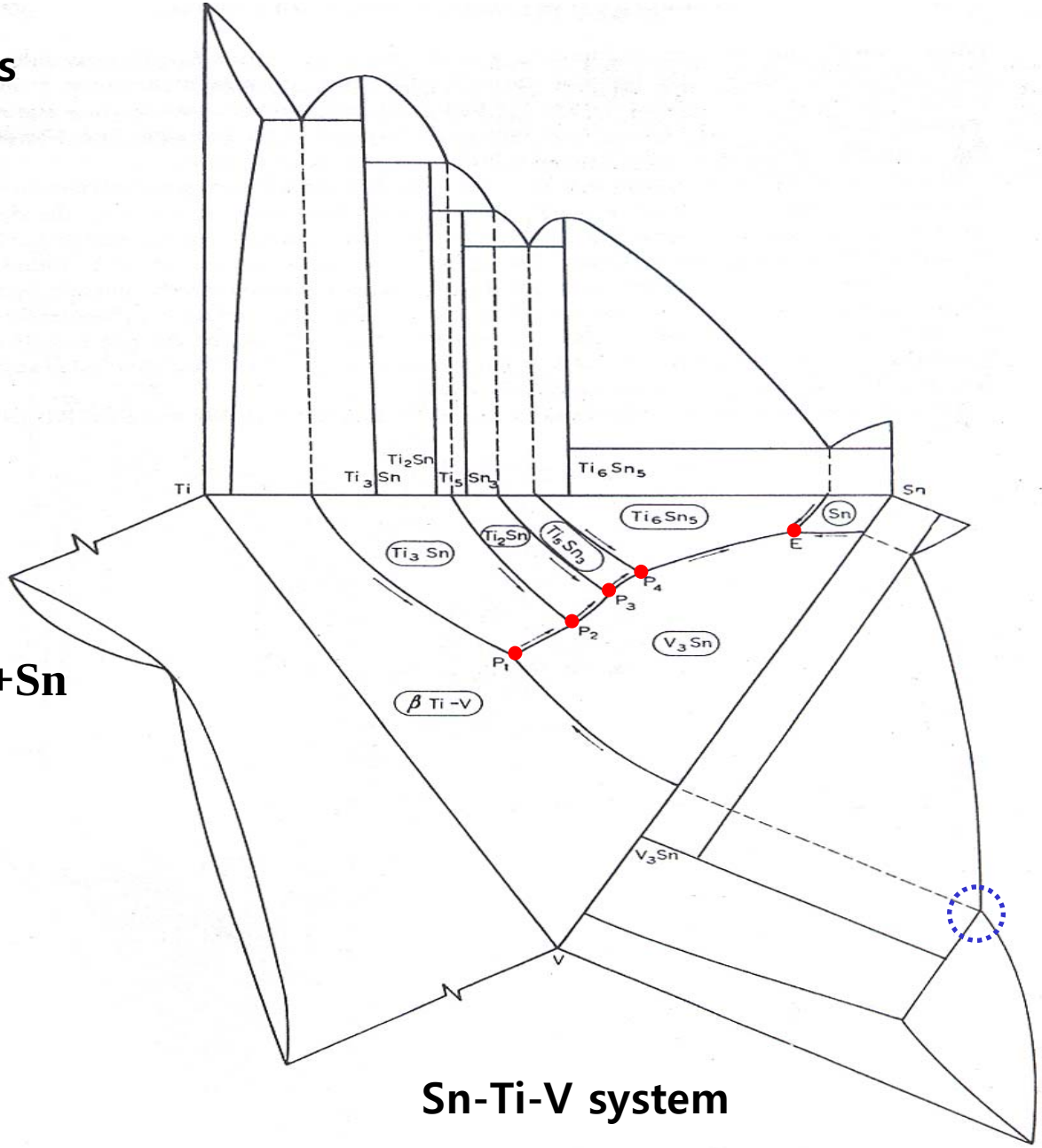
P_1: L+β Ti-V→Ti_3Sn +V_3Sn

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



Sn-Ti-V system

11.1 Congruently-melting intermediate phases

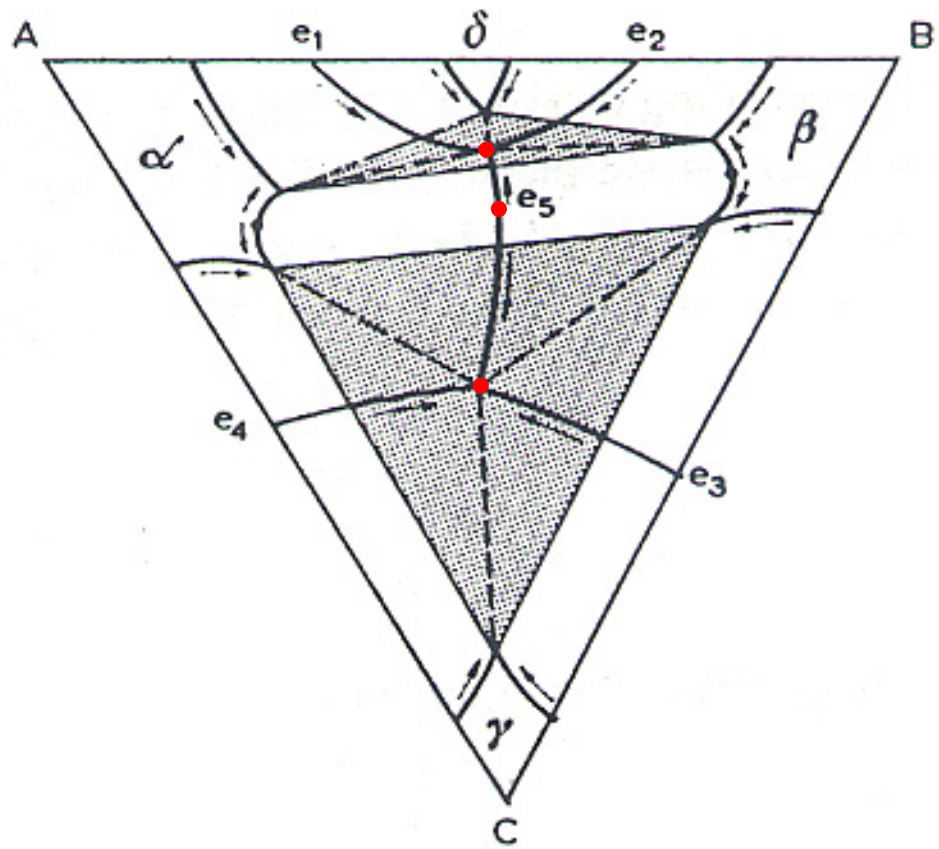
$$\boxed{\begin{array}{l} l \leftrightarrow \alpha + \beta + \gamma \\ l \leftrightarrow \alpha + \beta + \delta \end{array}}$$

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

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

- **Binary intermediate phases**

  3) No quasi binary eutectic : two ternary eutectic



L→α+β+γ

L→α+β+δ

e5: saddle point

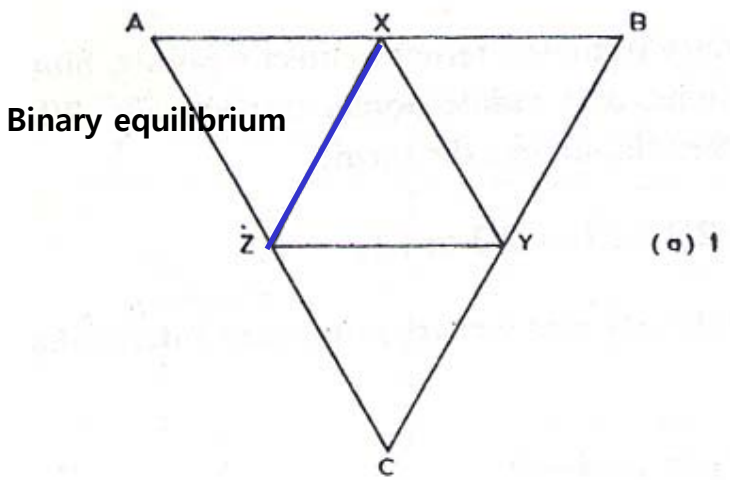
11.1 Congruently-melting intermediate phases

- **Binary intermediate phases**

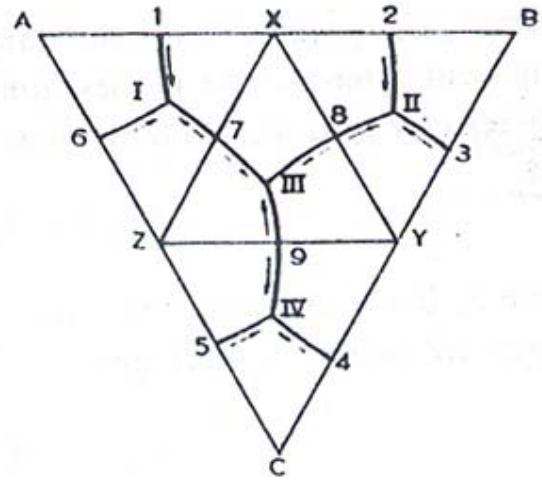
4) (a) containing congruent intermediate phases on each binary system

(b) corresponding equilibria for eutectic reaction

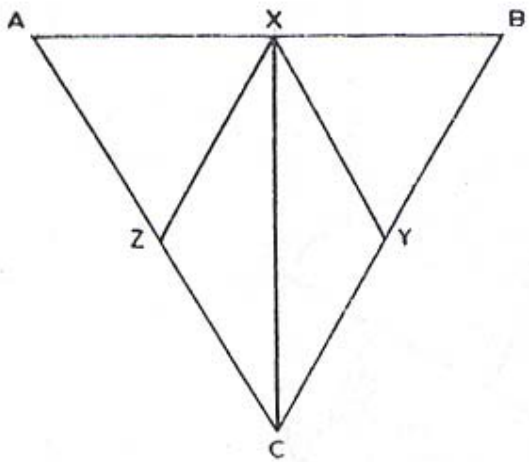
binary eutectic points: 1, 2, 3, … , 9/ternary eutectic points: I, II, III, IV



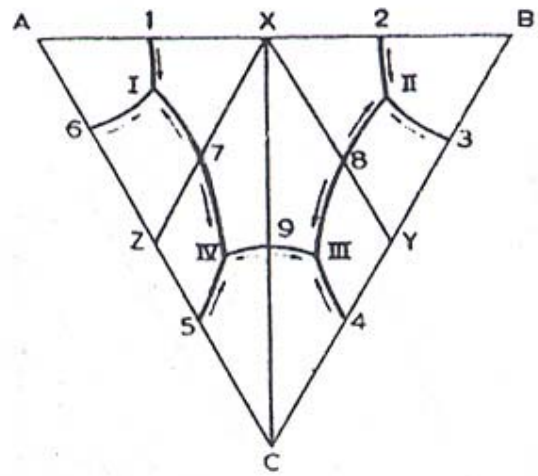
(a) 1



(b) 1



(a) 2



(b) 2

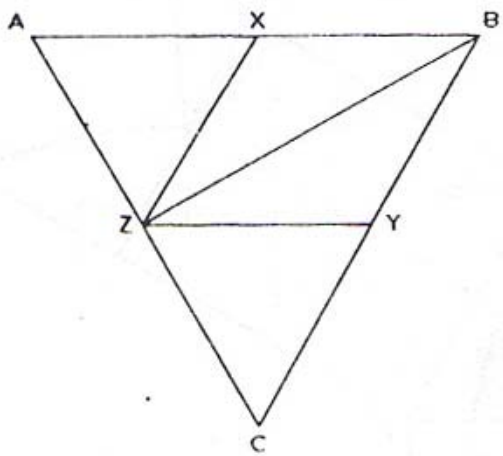
11.1 Congruently-melting intermediate phases

- **Binary intermediate phases**

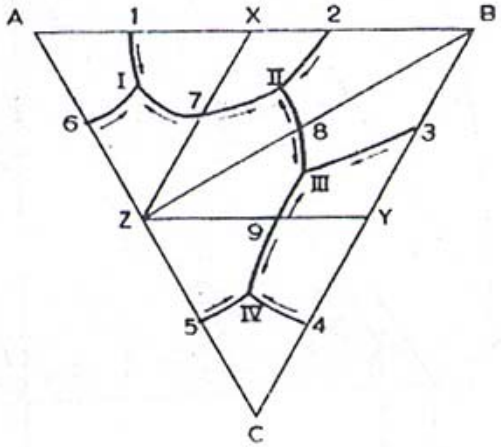
4) (a) containing congruent intermediate phases on each binary system

(b) corresponding equilibria for eutectic reaction

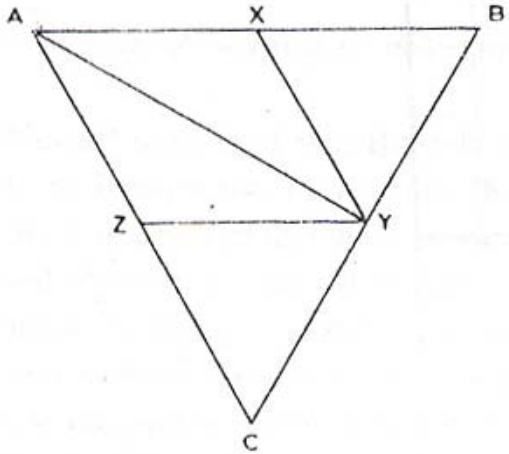
binary eutectic points: 1, 2, 3, … , 9/ternary eutectic points: I, II, III, IV



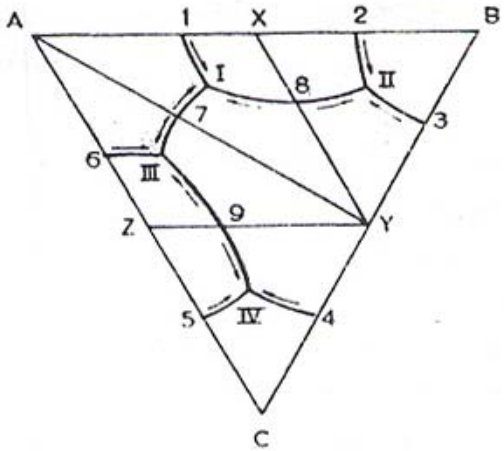
(a) 3



(b) 3



(a) 4

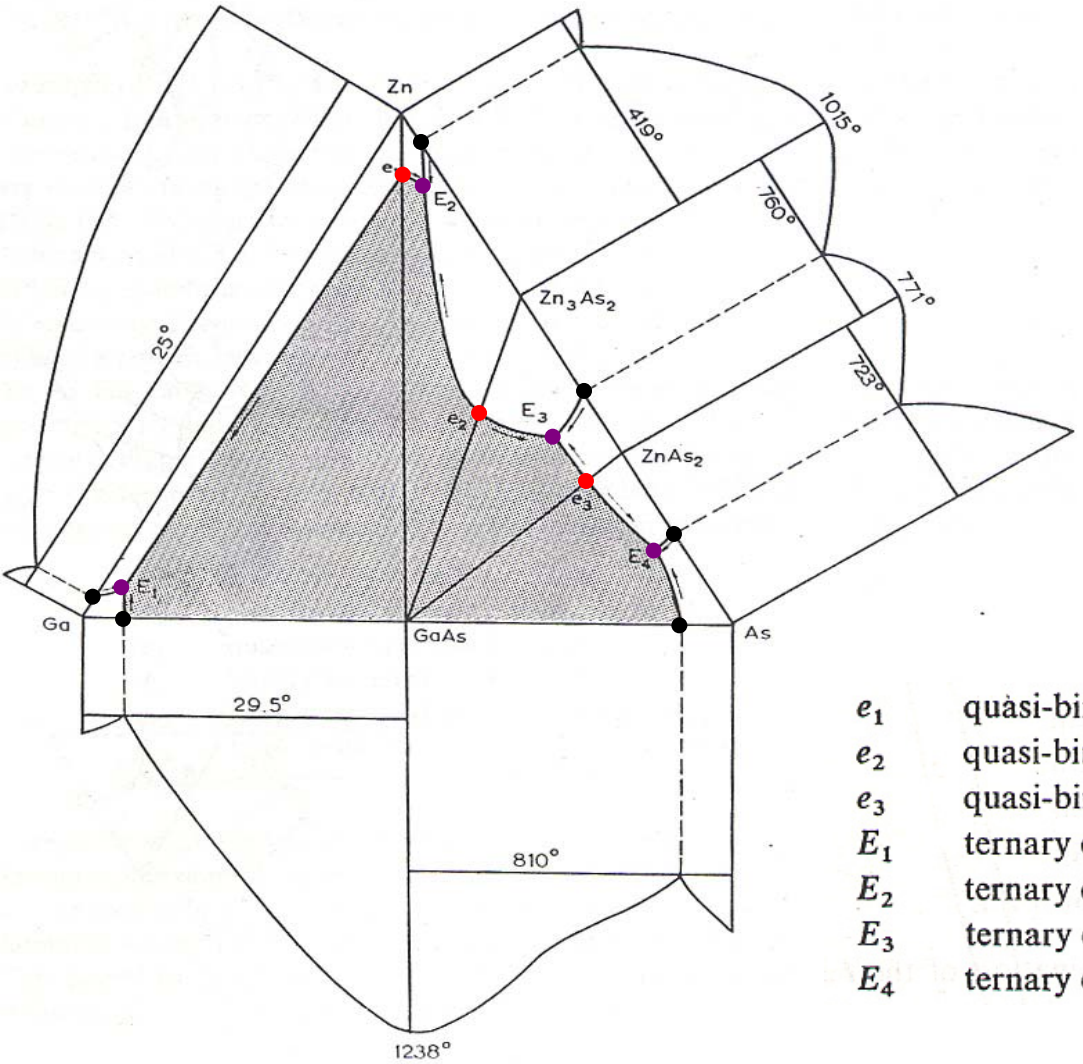


(b) 4

11.1 Congruently-melting intermediate phases

- **Binary intermediate phases**

Quasi binary eutectic rxn. between Ga, As and Zn



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.

As-Ga-Zn system

11.1 Congruently-melting intermediate phases

- **Binary intermediate phases**

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

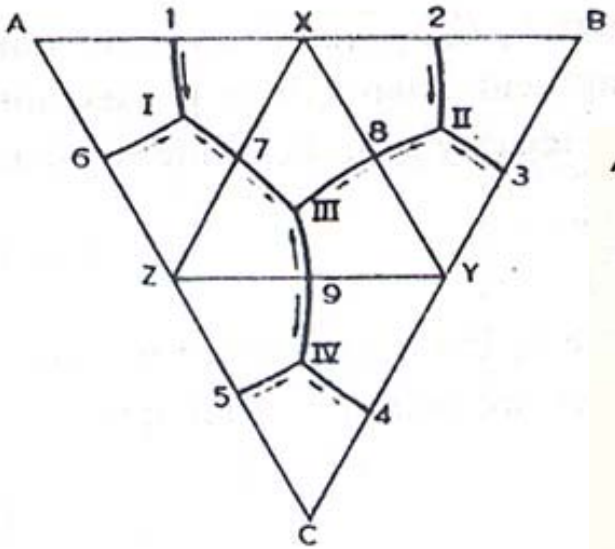
2) Case2 with only ternary congruent intermediate phases

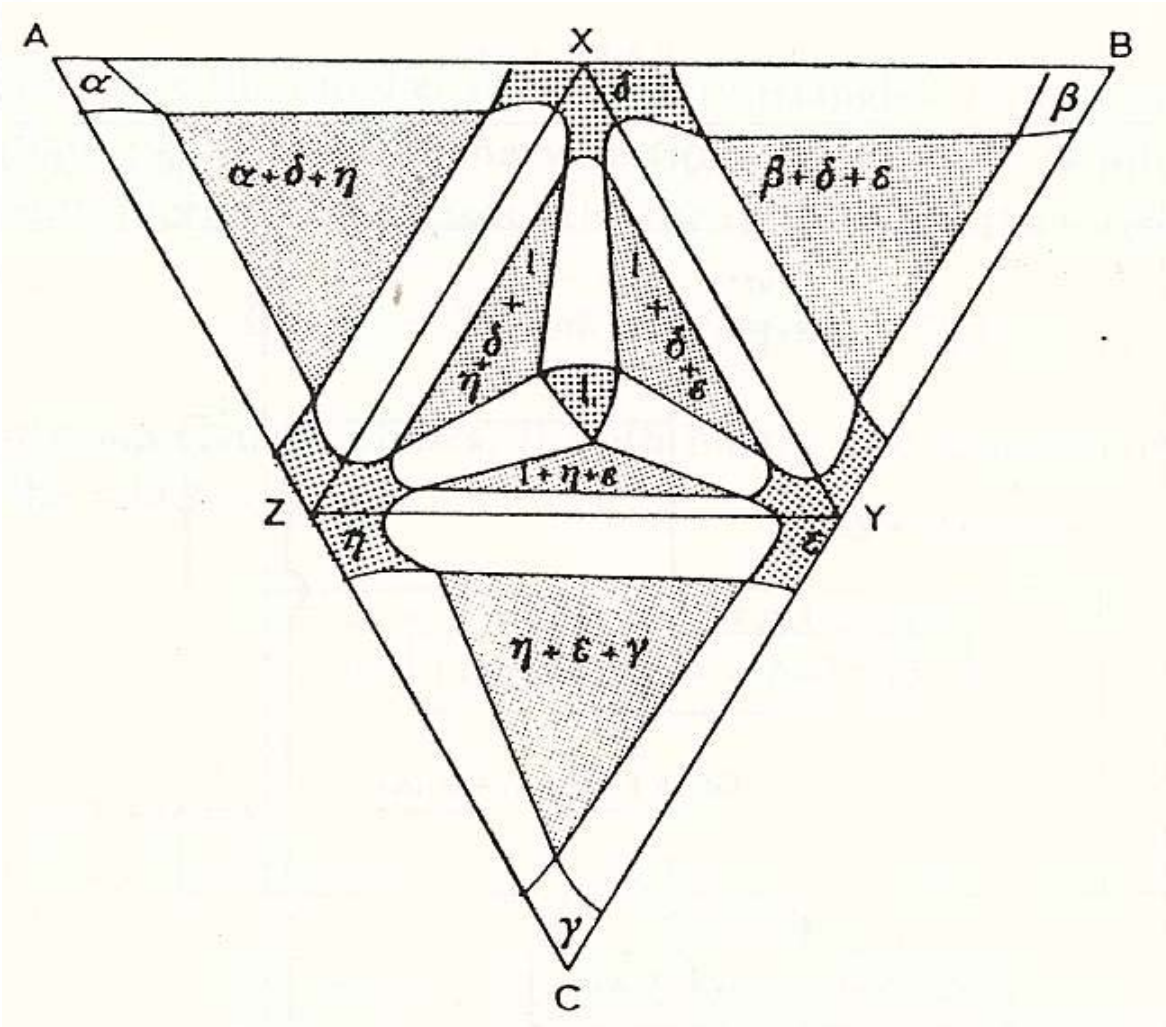
$$K = E = 2c_3+1 = 2/3q+1 = 2/3m+1$$

c_3 = ternary congruent intermediate phases

3) Case3 with both binary and ternary congruent intermediate phases

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





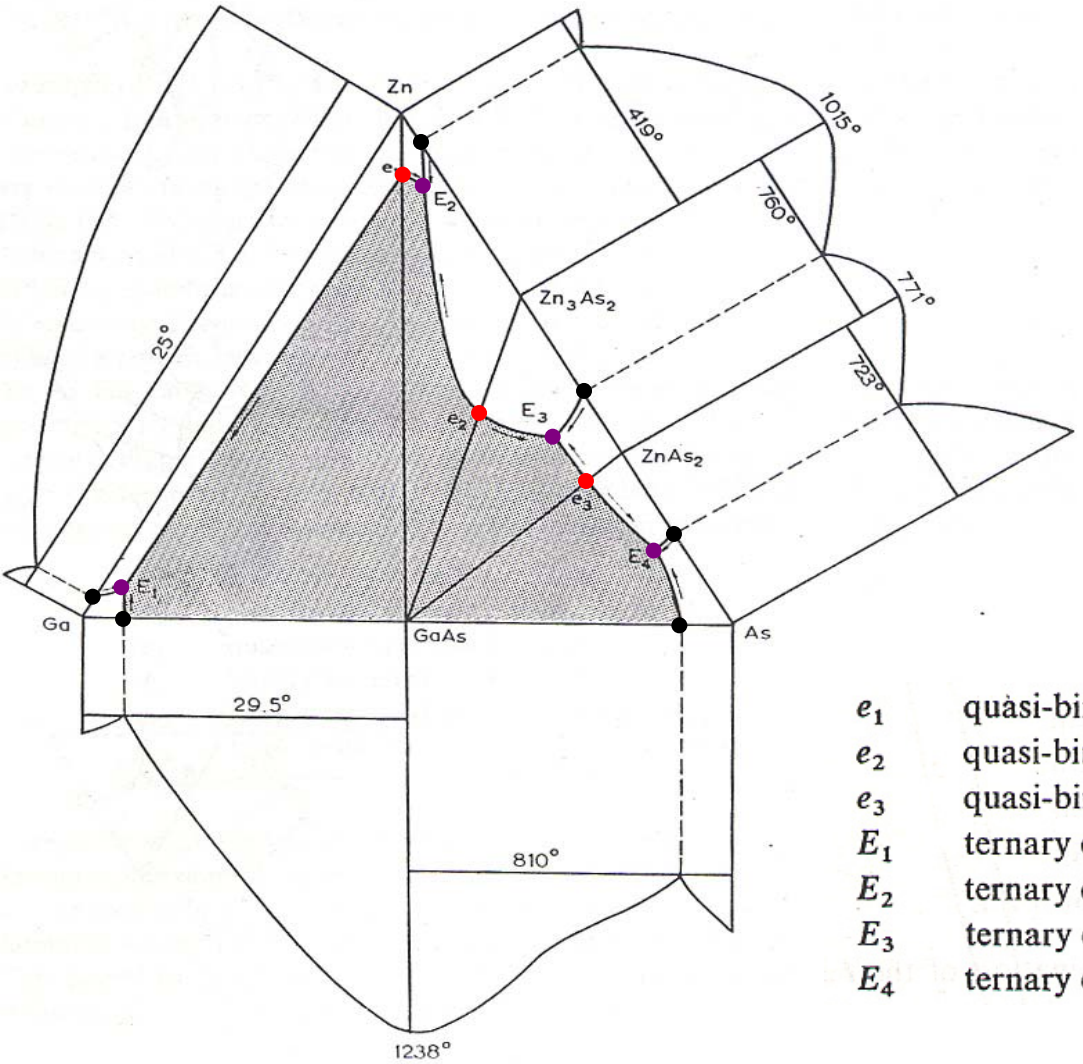
$$K = E = 1 + c_2 + 2c_3 = q + 1 - c_3 = m + 1 - c_3$$

$$= 1 + 3 + 2 = 6$$

11.1 Congruently-melting intermediate phases

- **Binary intermediate phases**

Quasi binary eutectic rxn. between Ga, As and Zn

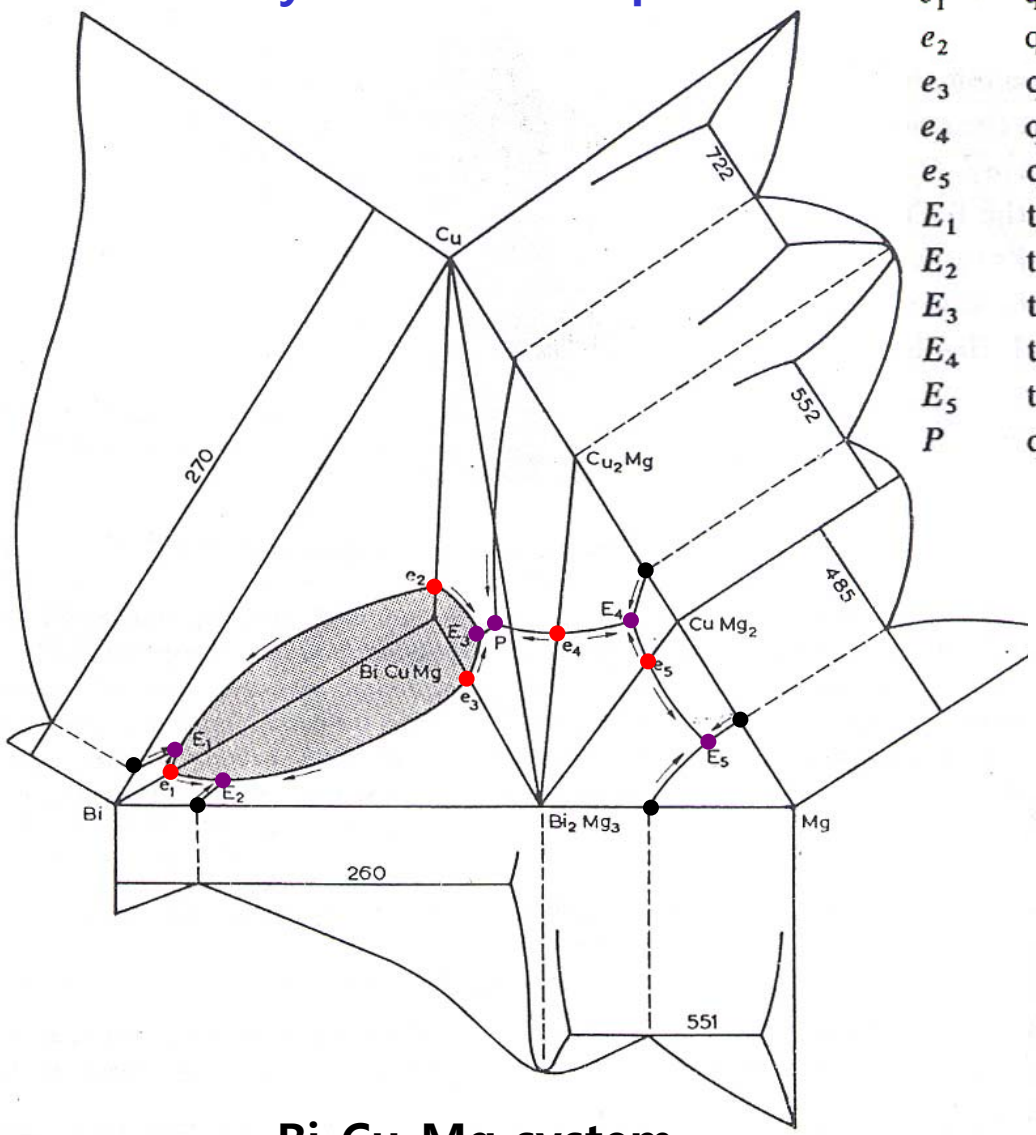


e_1	quasi-binary eutectic $l \rightleftharpoons GaAs + Zn$	at	414 °C,
e_2	quasi-binary eutectic $l \rightleftharpoons GaAs + Zn_3As_2$	at	972 °C,
e_3	quasi-binary eutectic $l \rightleftharpoons GaAs + ZnAs_2$	at	754 °C,
E_1	ternary eutectic $l \rightleftharpoons GaAs + Zn + Ga$	at	~ 20 °C,
E_2	ternary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

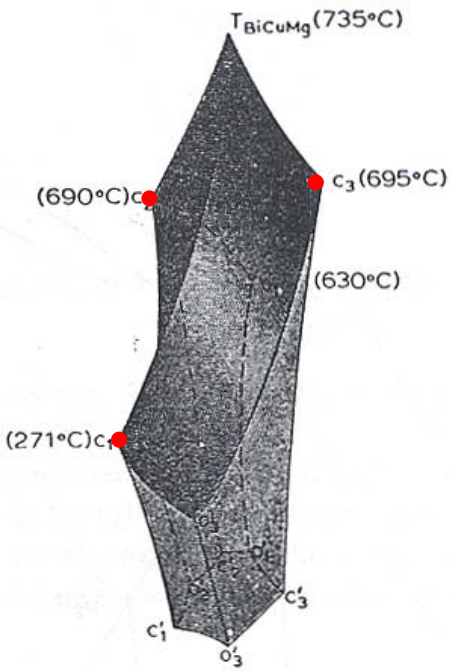
As-Ga-Zn system

11.1 Congruently-melting intermediate phases

- **Ternary intermediate phases**



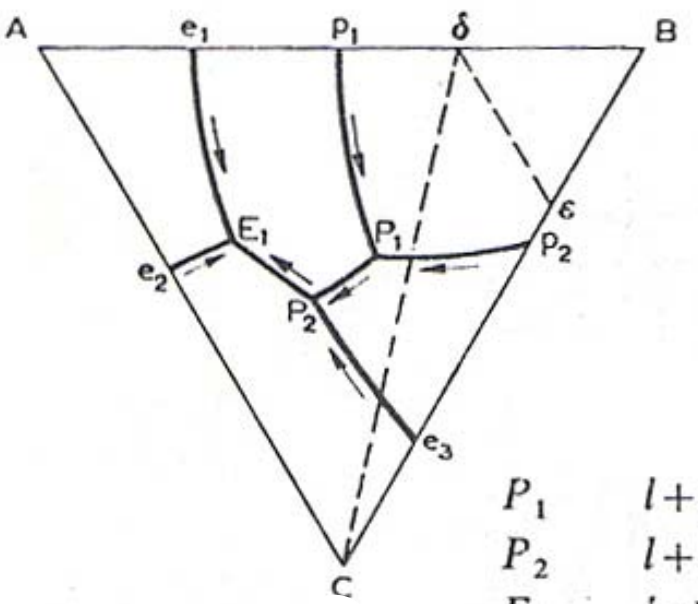
e_1	quasi-binary eutectic $l \rightleftharpoons Bi + BiCuMg$	at	~271 °C
e_2	quasi-binary eutectic $l \rightleftharpoons Cu + BiCuMg$	at	690 °C
e_3	quasi-binary eutectic $l \rightleftharpoons Bi_2Mg_3 + BiCuMg$	at	695 °C
e_4	quasi-binary eutectic $l \rightleftharpoons Bi_2Mg_3 + Cu_2Mg$	at	655 °C
e_5	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

11.2 incongruently-melting intermediate phases

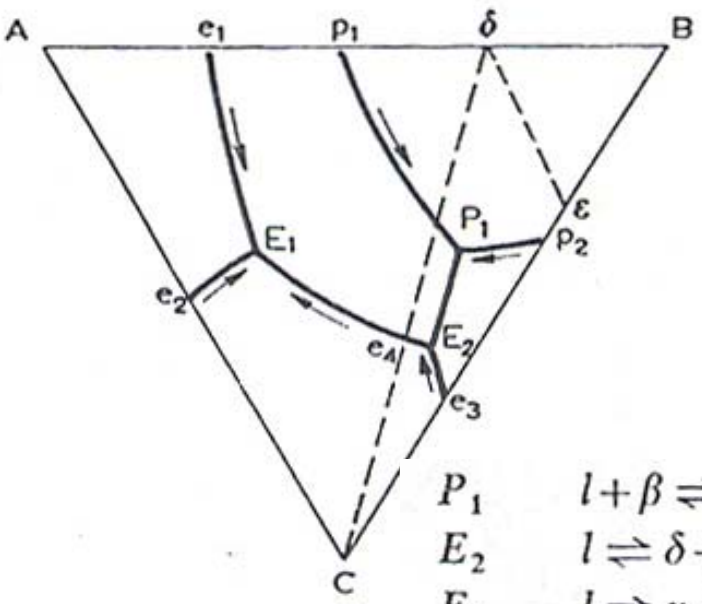
- **Binary intermediate phases**



$P_1 \quad l+\beta \rightleftharpoons \delta+\varepsilon$

$P_2 \quad l+\varepsilon \rightleftharpoons \delta+\gamma$

$E_1 \quad l \rightleftharpoons \alpha+\delta+\gamma.$



$P_1 \quad l+\beta \rightleftharpoons \delta+\varepsilon$

$E_2 \quad l \rightleftharpoons \delta+\varepsilon+\gamma$

$E_1 \quad l \rightleftharpoons \alpha+\delta+\varepsilon$

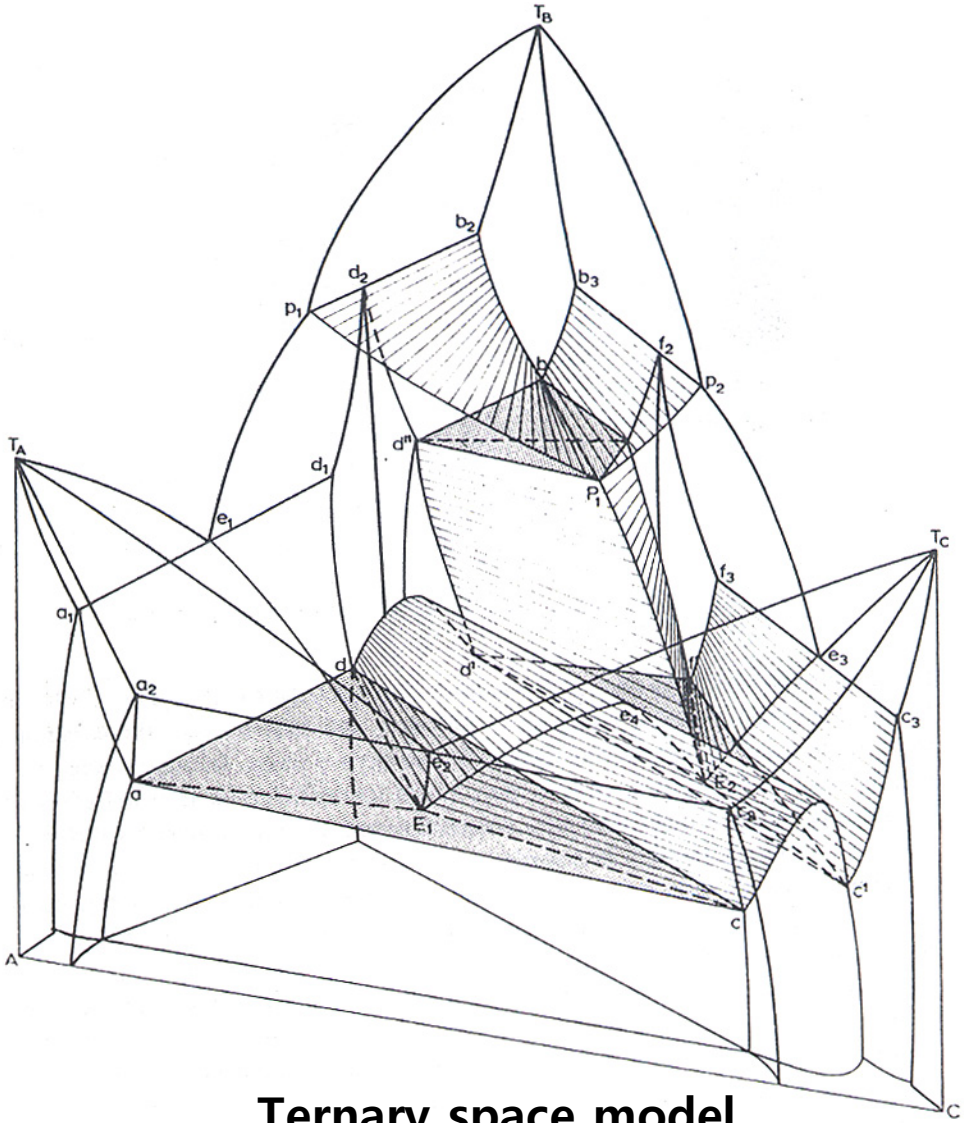
$e_4 \quad l \rightleftharpoons \delta+\gamma.$

- **Binary intermediate phases Equilibria when the quasi-peritectic point P is located in the partial system AδC**

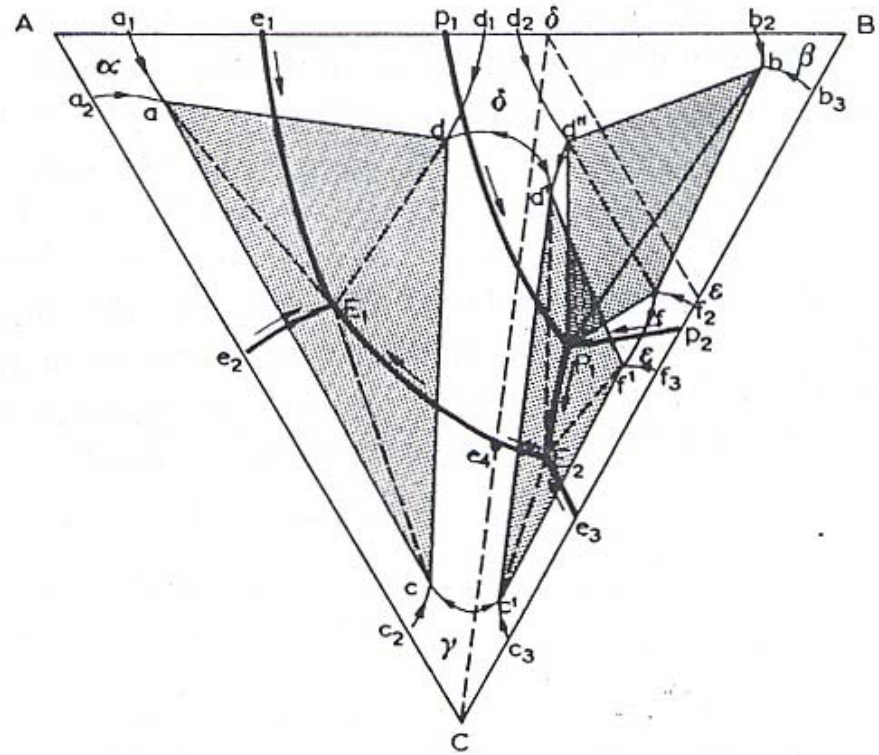
- **Binary intermediate phases Equilibria when the quasi-peritectic point P is located in the partial system Cδe**

11.2 incongruently-melting intermediate phases

- **Binary intermediate phases : ternary space model**



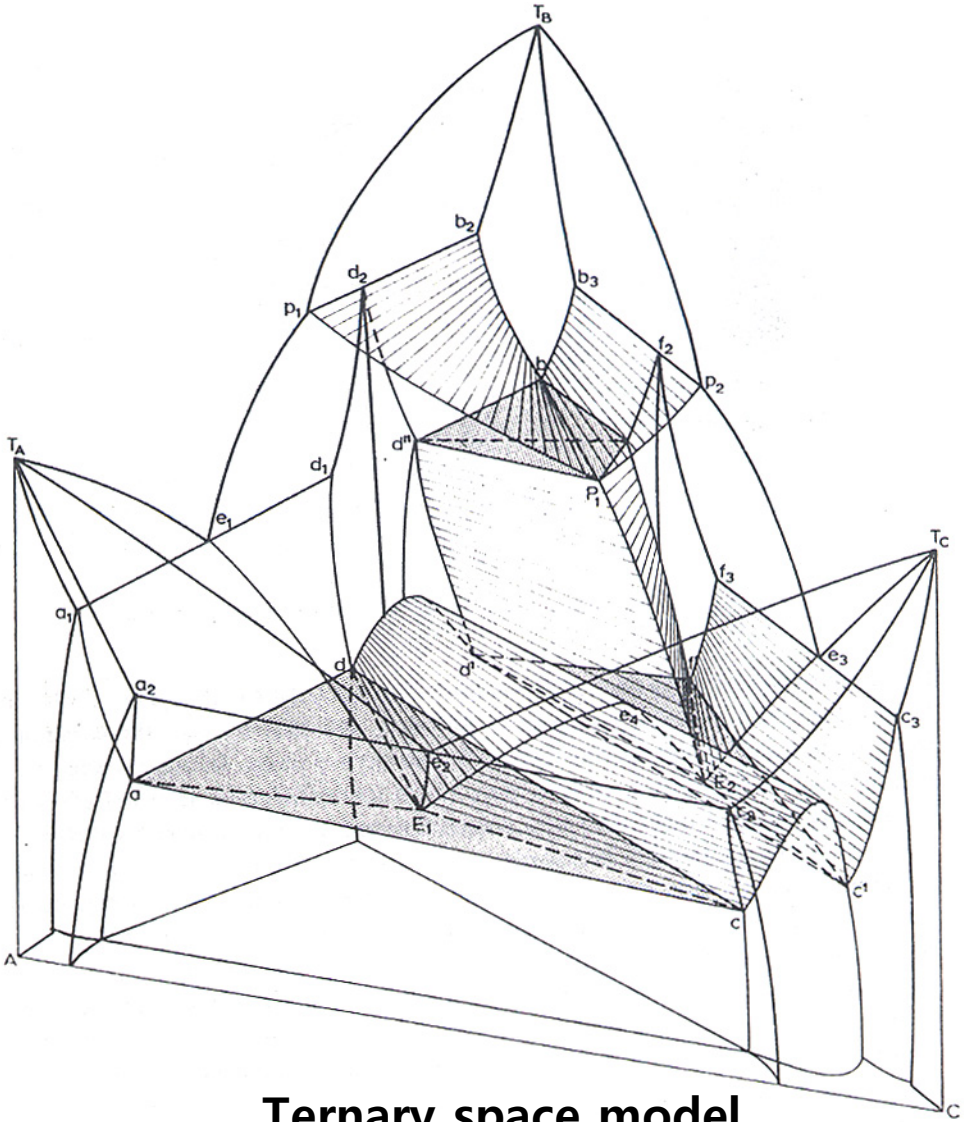
Ternary space model



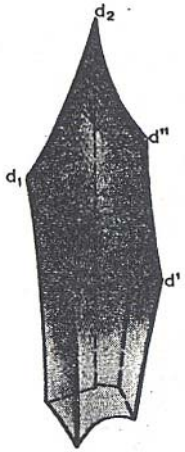
Projection of equilibria

11.2 incongruently-melting intermediate phases

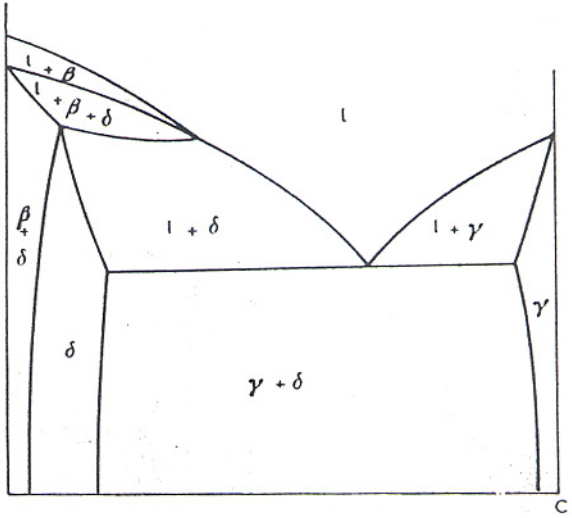
- **Binary intermediate phases : ternary space model**



Ternary space model



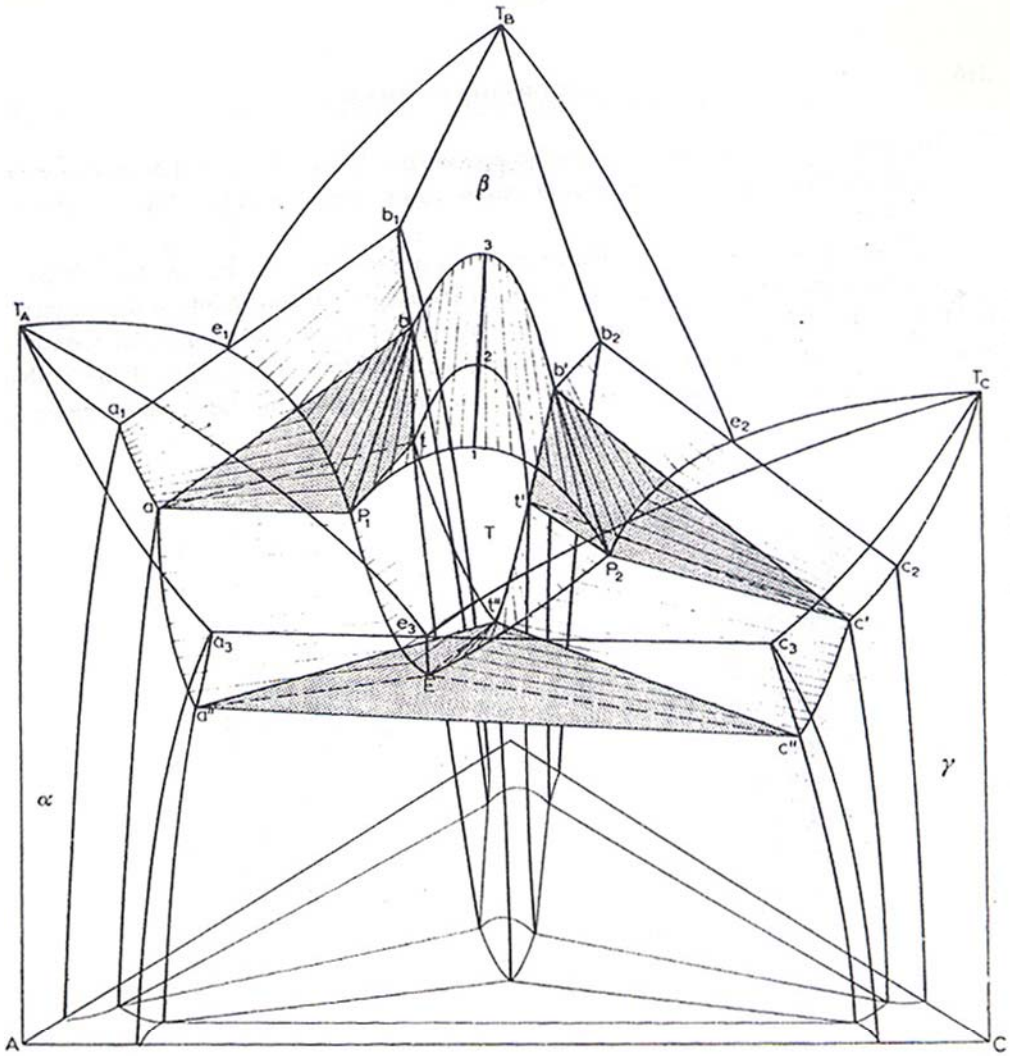
δ phase region

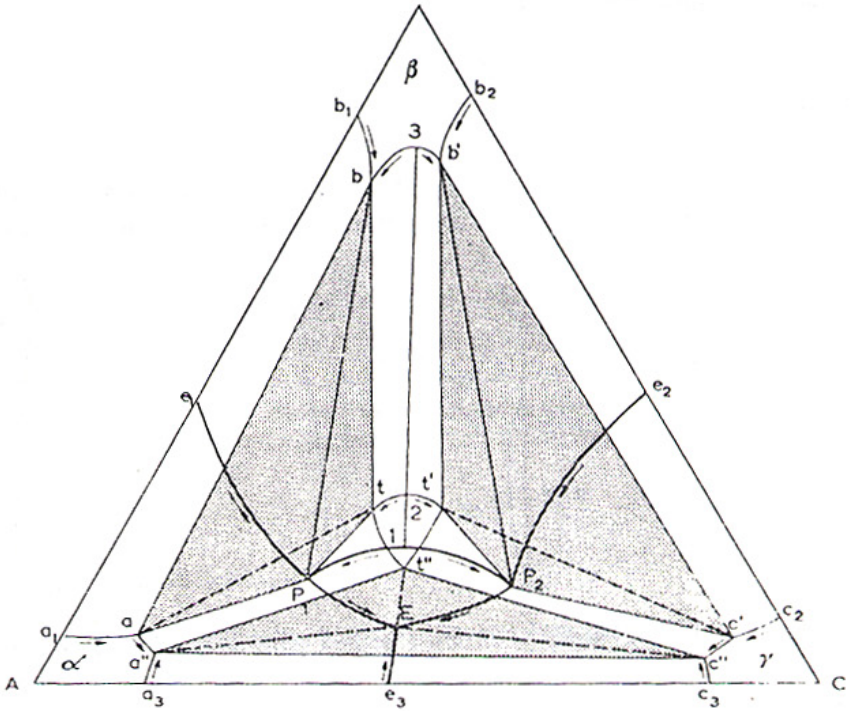


Vertical section from C to δ

11.2 incongruently-melting intermediate phases

- **Ternary intermediate phases**

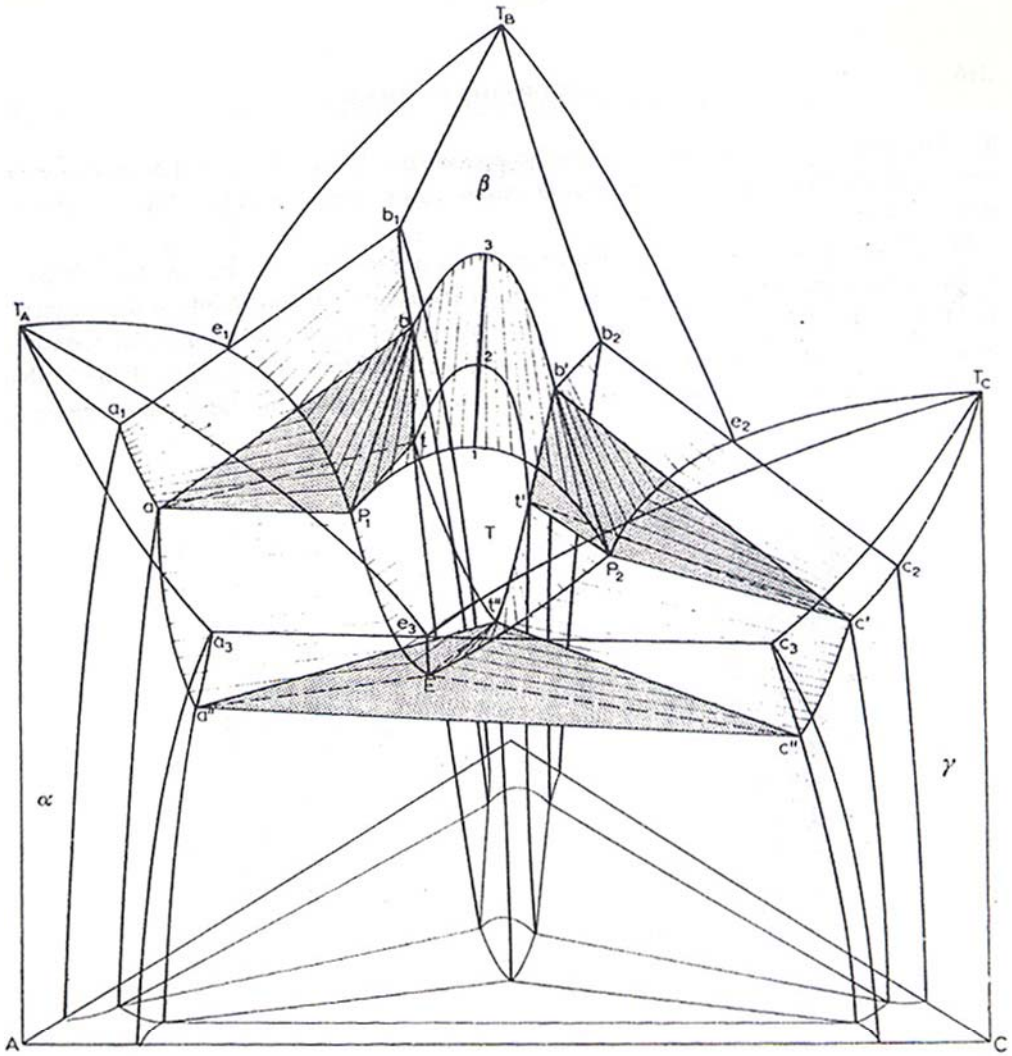


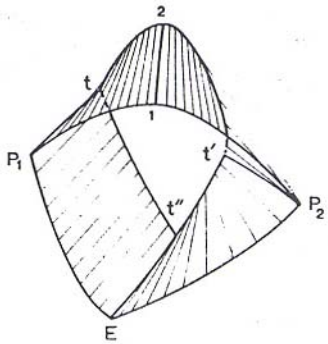


Projection on the concentration triangle

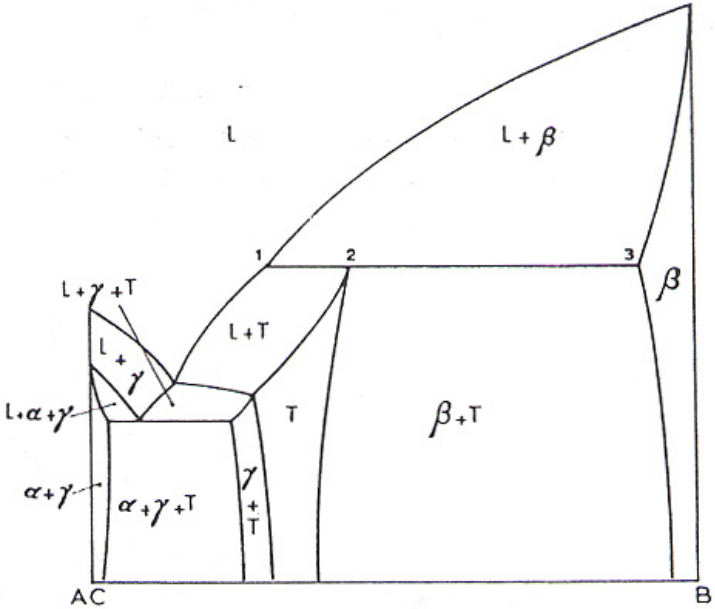
11.2 incongruently-melting intermediate phases

- **Ternary intermediate phases**



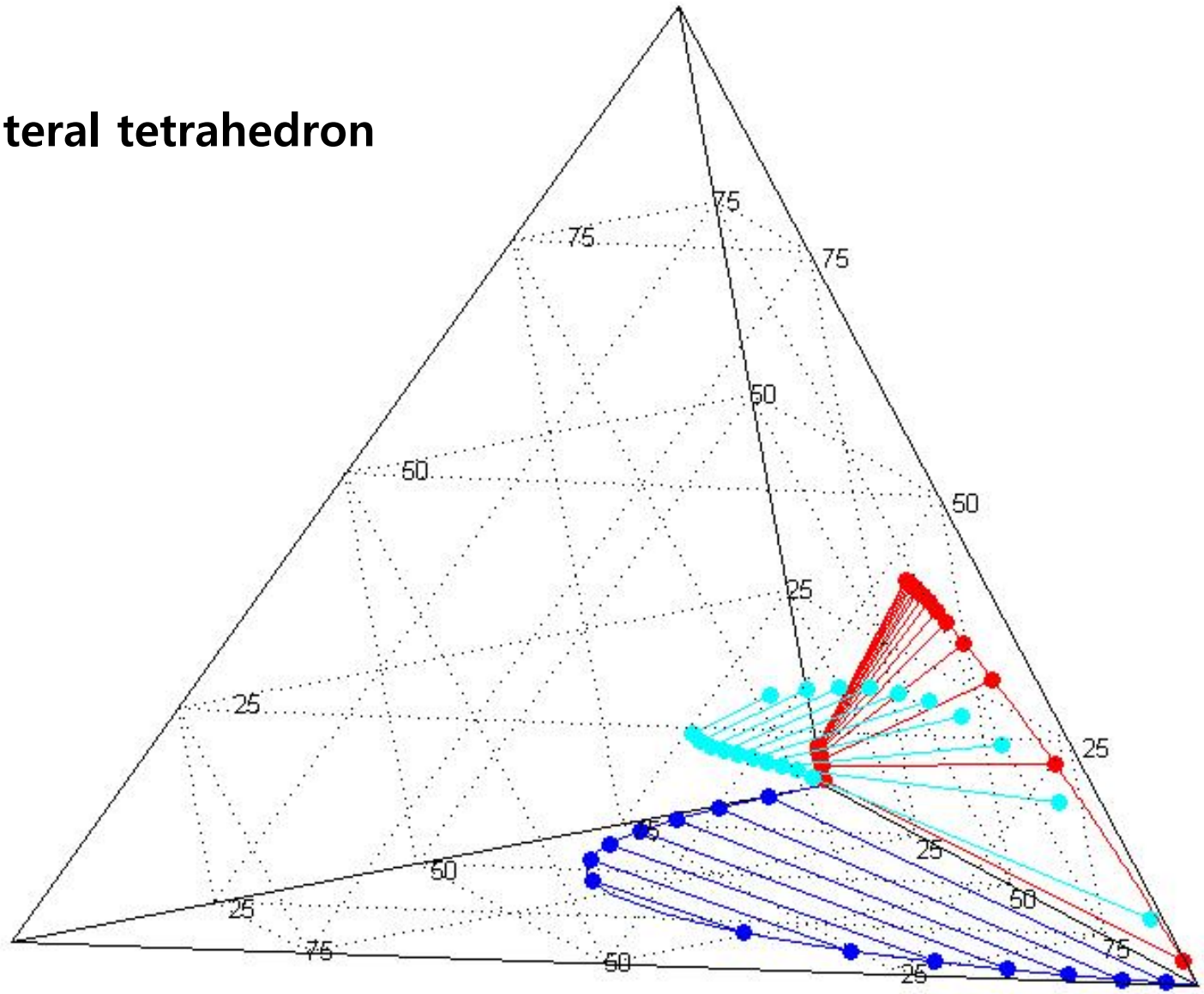


(b)



Chapter 15. Quaternary phase Diagrams

Equilateral tetrahedron



a+b+c+d=100

%A=Pt=c,
%B=Pr=a,
%C=Pu=d,
%D=Ps=b

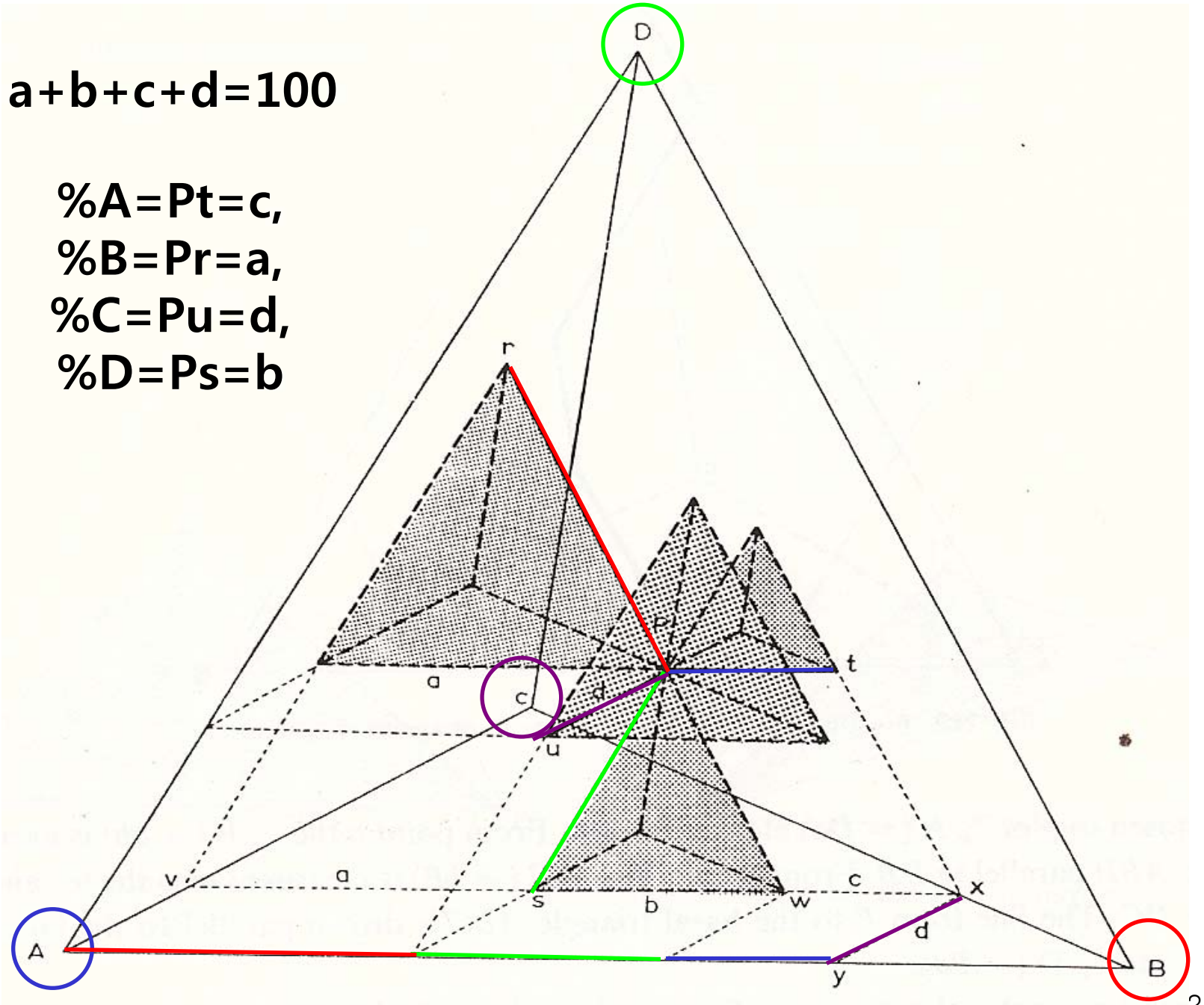
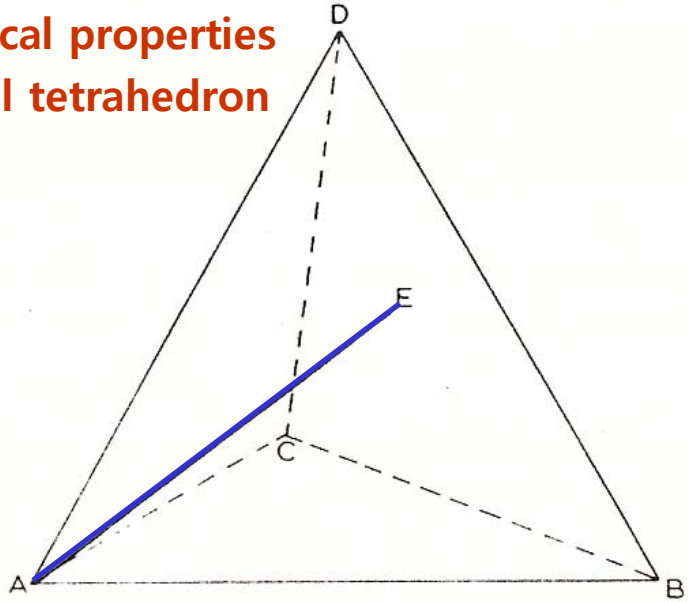
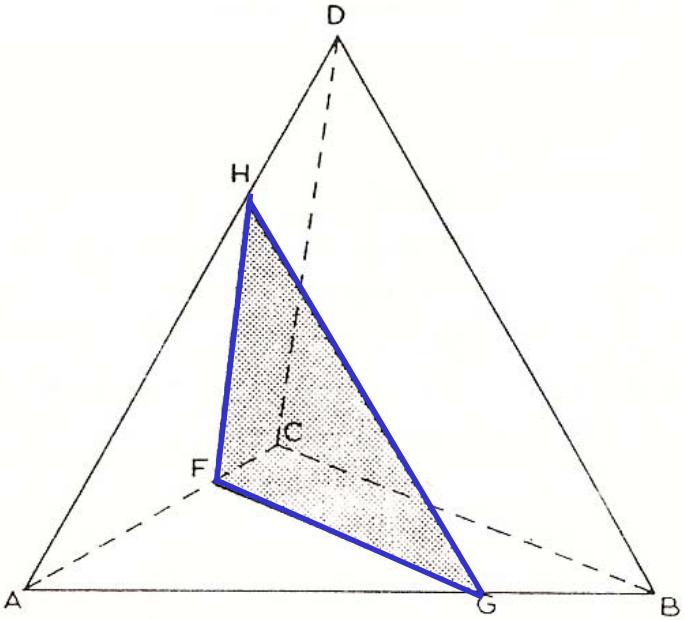


Fig. 247. Representation of a quaternary system by an equilateral tetrahedron.

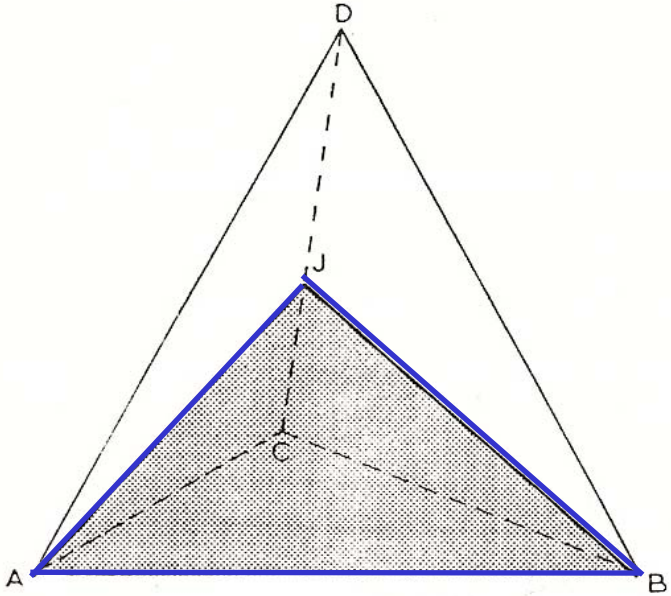
Useful geometrical properties of an equilateral tetrahedron



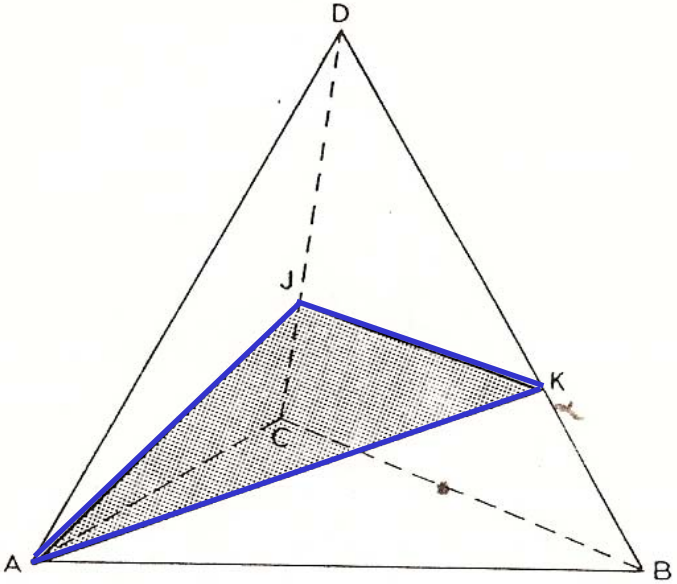
B:C:D constant on line *AE*



A constant on plane *FGH*



C:D constant on plane *ABJ*



C:D and B:D constant on plane *AJK*

The three-dimensional equilateral tetrahedron can be used to study quarternary equilibria in the following ways.

1) Isobaric-isothermal section

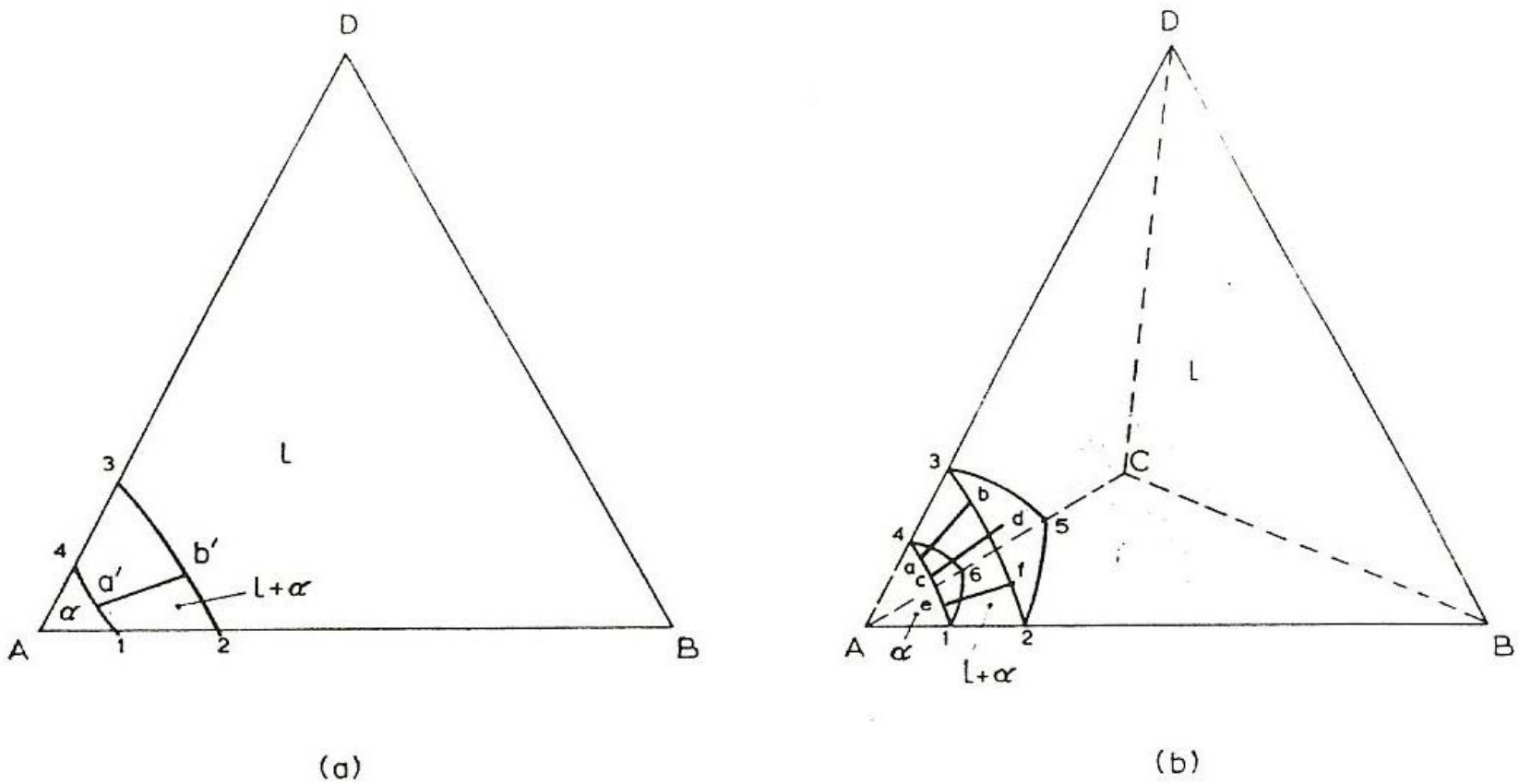


Fig. 251. Isobaric–isothermal sections for systems involving two-phase equilibrium. (a) Ternary system; (b) quaternary system.

2) Polythermal sections

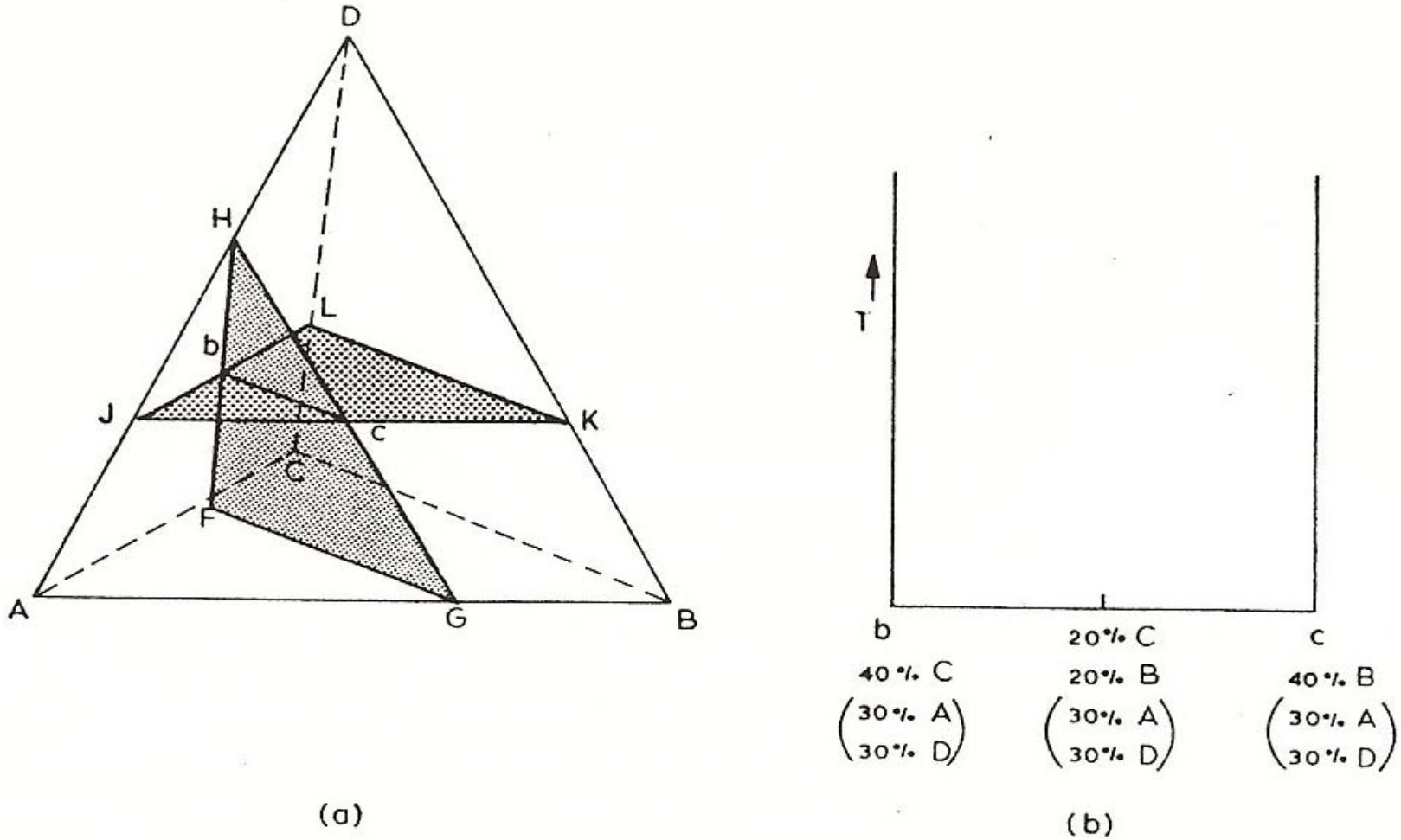


Fig. 250. Production of a two-dimensional section through a quaternary system. (a) Alloys on line *bc* contain constant content of A and D; (b) erection of temperature axis on line *bc* to give the two-dimensional section.