2017 Fall

"Phase Equilibria *in* Materials"

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Chapter 15. Quaternary Phase Diagrams

* Draw four small equilateral tetrahedron
→ formed with edge lengths of a, b, c, d

a+b+c+d=100

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

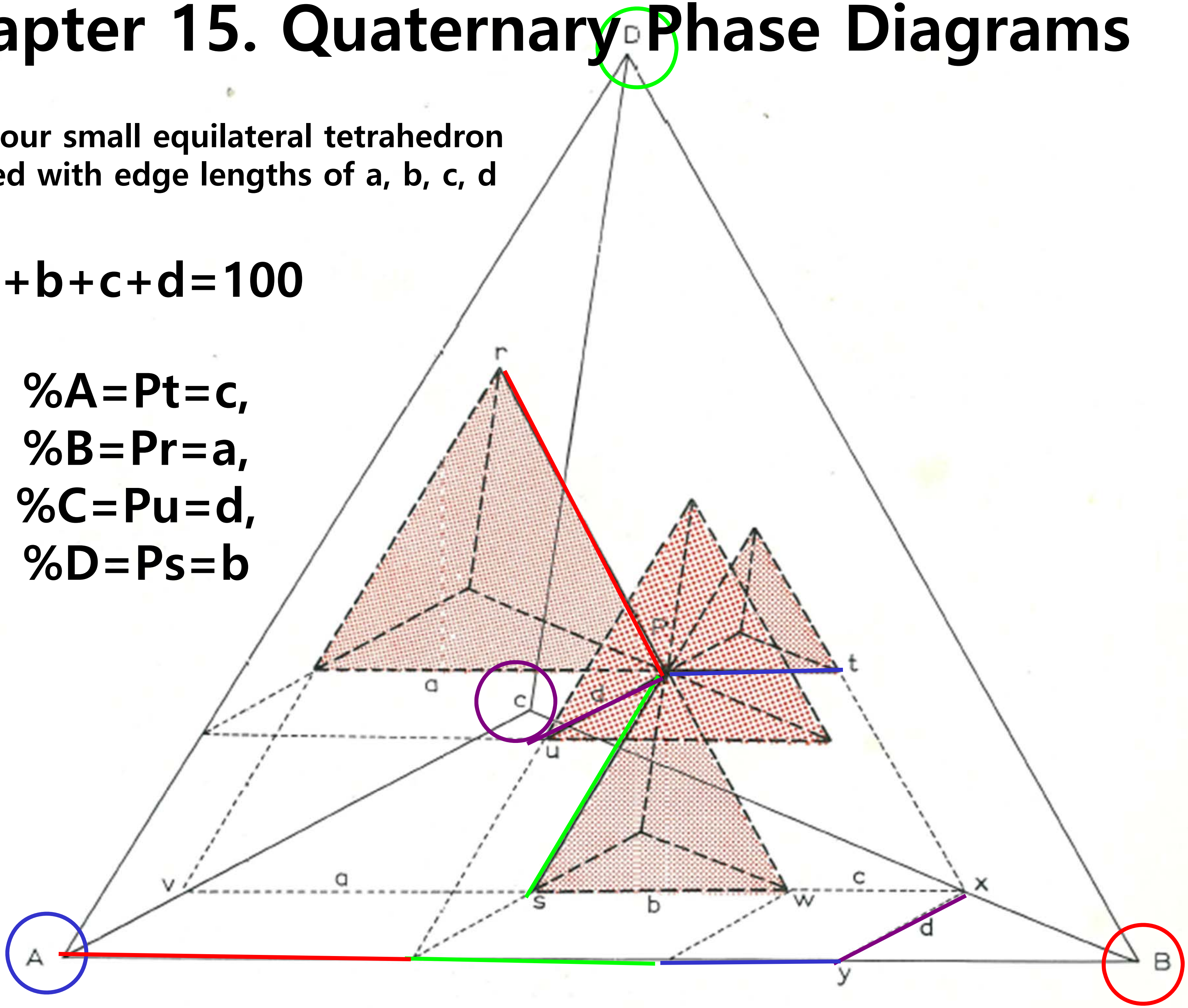
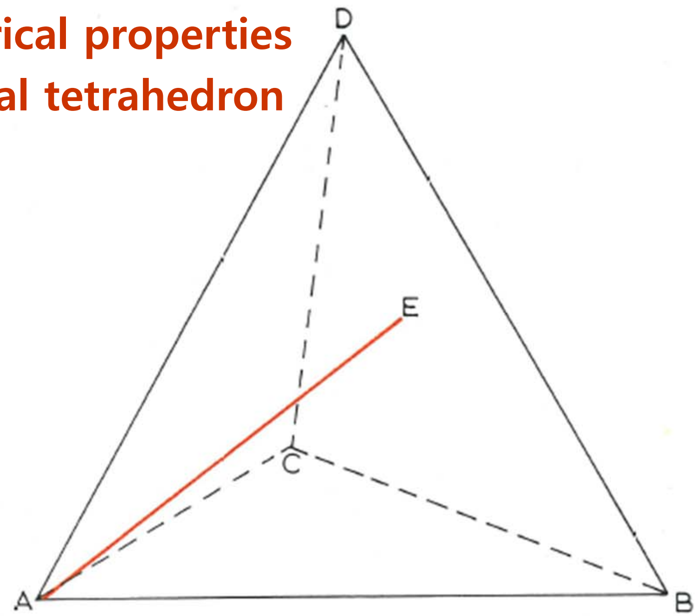
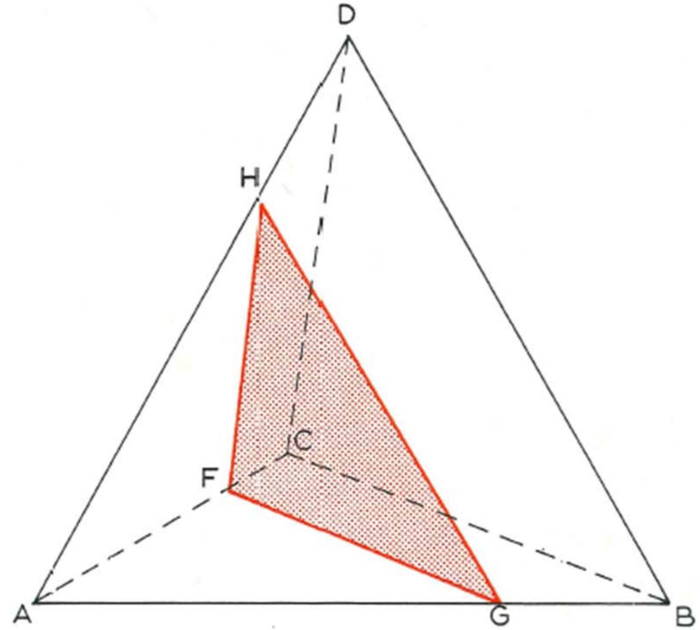


Fig. 247. Representation of a quaternary system by an equilateral tetrahedron.

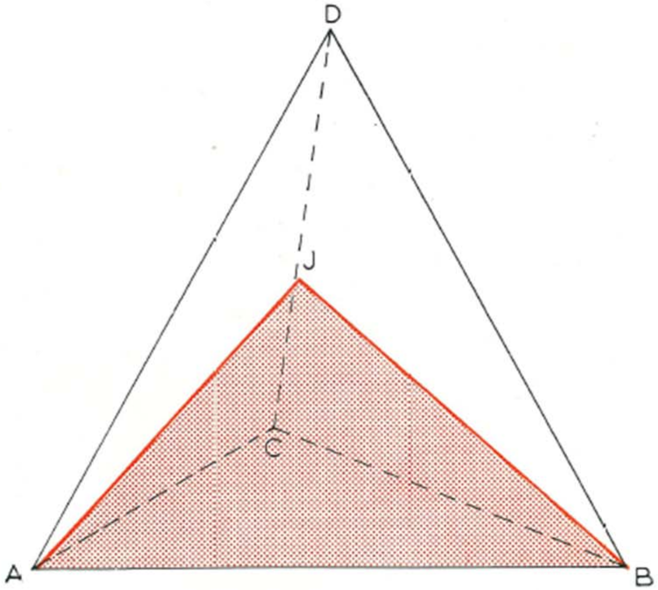
Useful geometrical properties of an equilateral tetrahedron



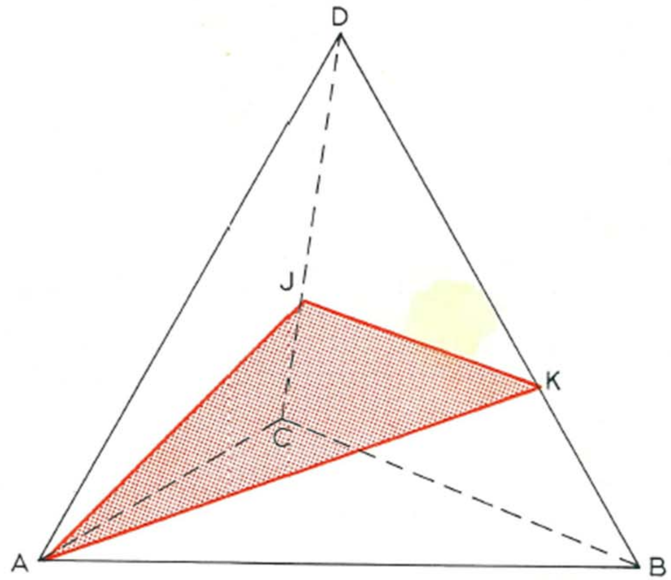
B:C:D constant on line *AE*



A constant on plane *FGH*



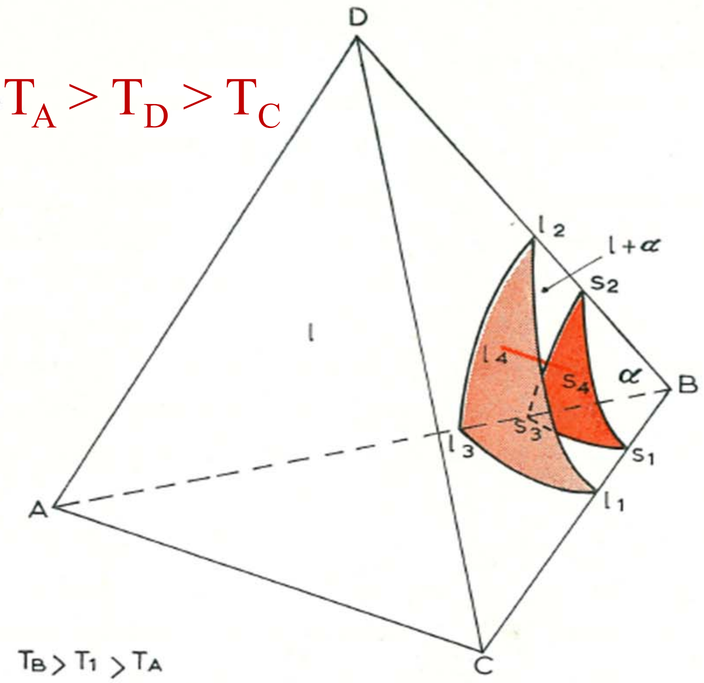
C:D constant on plane *ABJ*

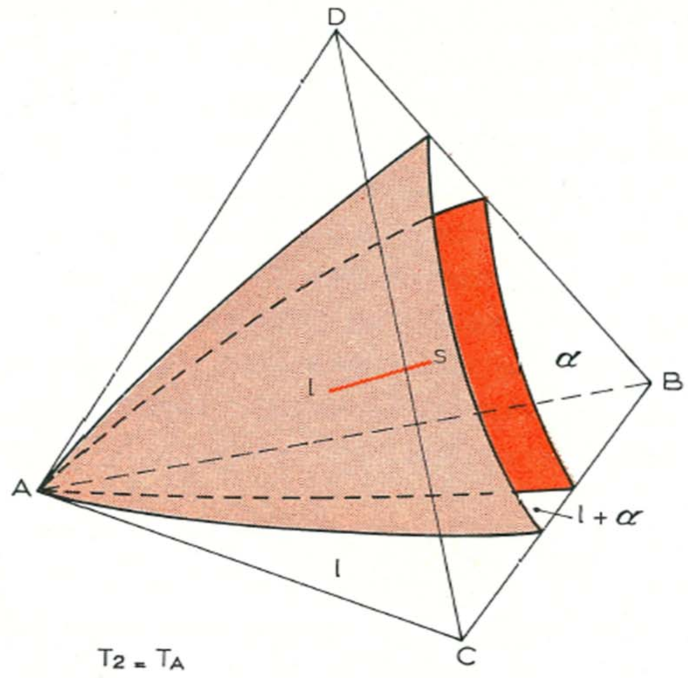


C:D and B:D constant on plane *AJK*

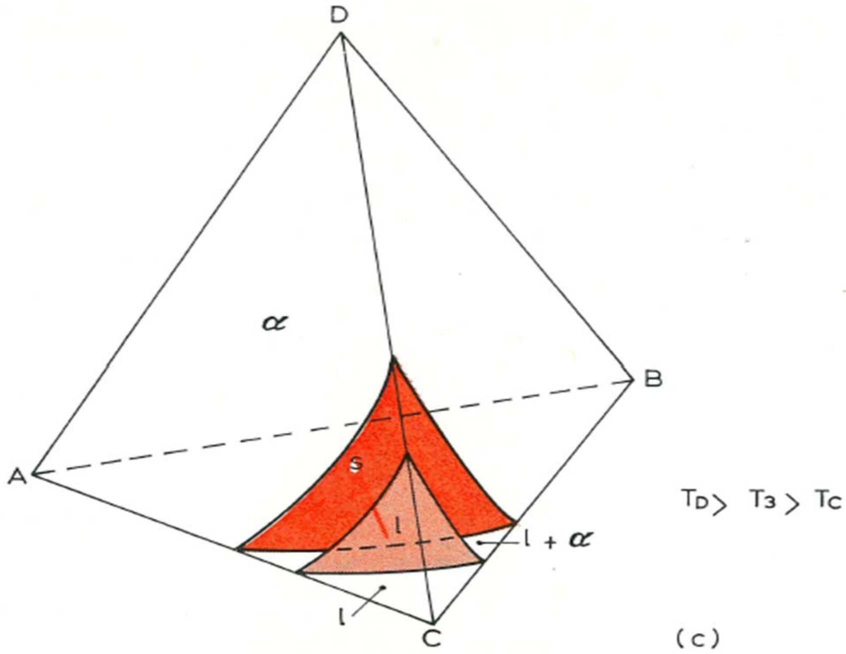
* Isobaric-isothermal sections through a quaternary system involving <u>“two-phase equilibrium”</u>

$T_B > T_A > T_D > T_C$





(b)



(c)

* The quaternary tie lines are going from one isothermal section to another with decreasing temperature the tie lines all change their orientation.

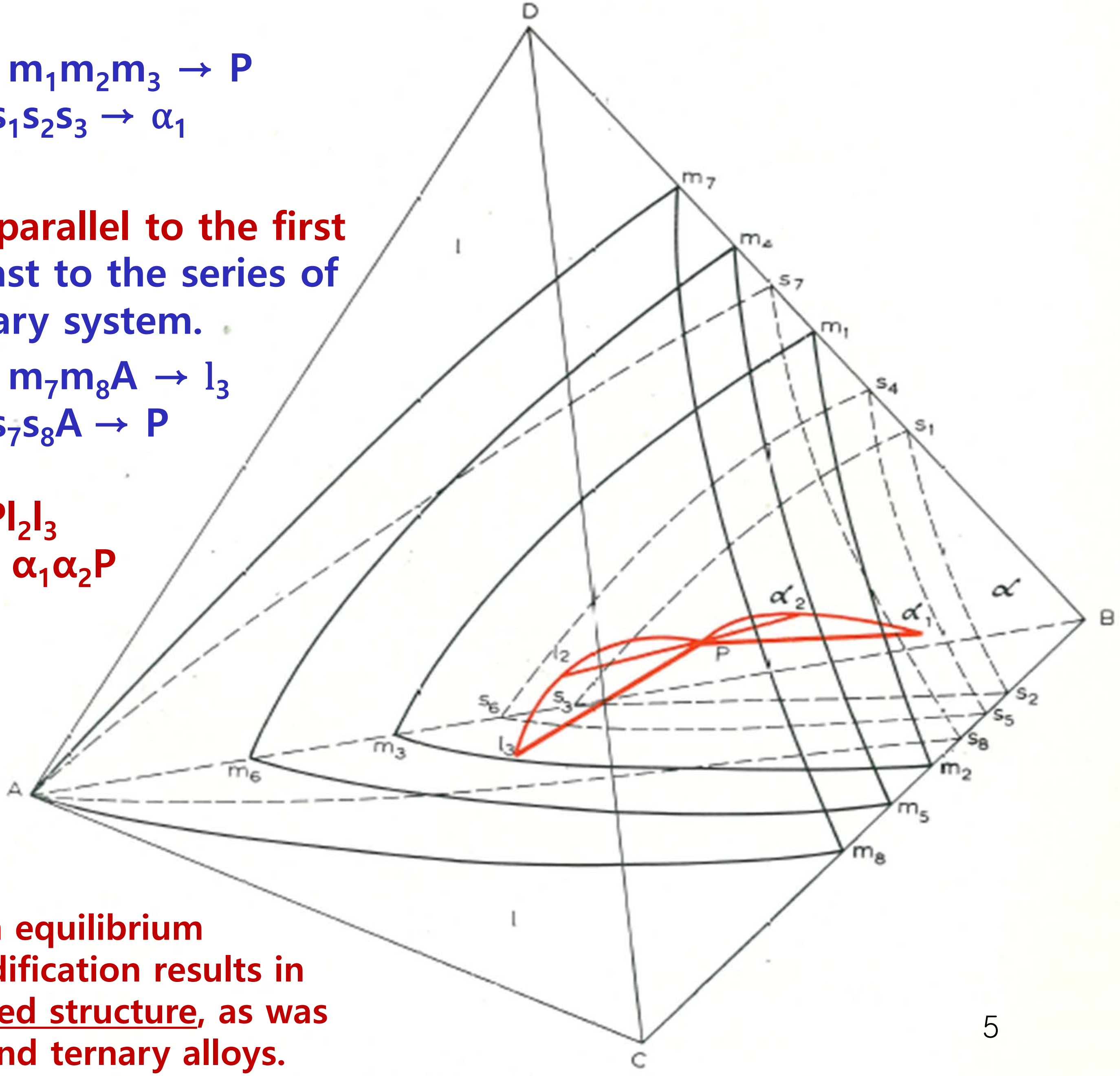
* The quaternary melt is richer in the lower-melting components than the quaternary solid solution it is in equilibrium with <u>Konovalov’s rule</u>.

* The usual lever rule is applicable to tie lines in quaternary systems.

* Course of solidification of quaternary alloy P

* T_1 : liquidus surface $m_1m_2m_3 \rightarrow P$
  Solidus surface $s_1s_2s_3 \rightarrow \alpha_1$
* T_2 : tie line $\alpha_2 l_2$
  → this tie line is not parallel to the first tie line $P\alpha_1$ in contrast to the series of tie lines in the ternary system.
* T_3 : liquidus surface $m_7m_8A \rightarrow l_3$
  Solidus surface $s_7s_8A \rightarrow P$

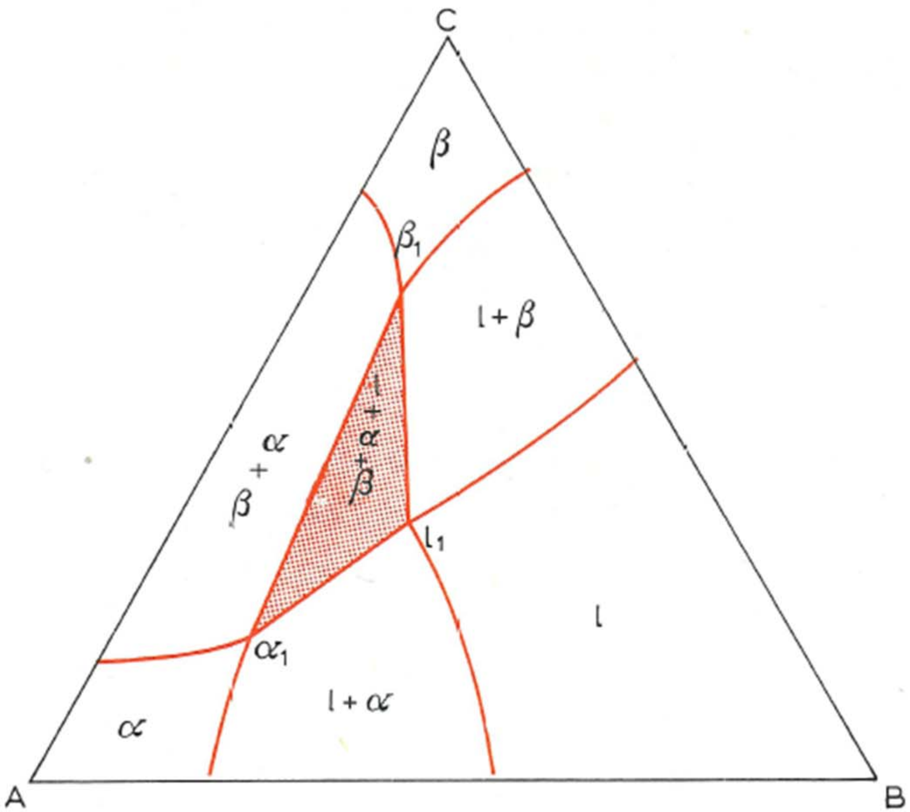
* Liquid trace curve: Pl_2l_3
  α phase trace curve: $\alpha_1\alpha_2P$



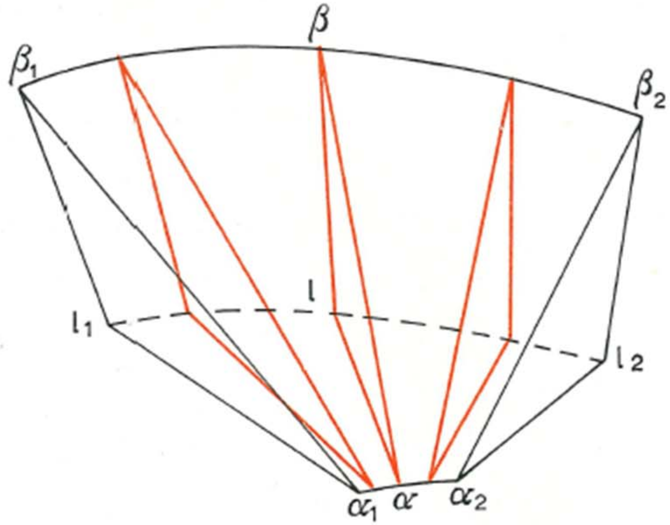
→ Any departure from equilibrium conditions during solidification results in the formation of a cored structure, as was noted for the binary and ternary alloys.

15.3 THREE-PHASE EQUILIBRIUM

* The tie triangles in the quaternary three-phase region do not lie parallel to each other, in contrast to the superficially similar three-phase region in a ternary (isobaric) space model.



(a) Ternary system



(b) quaternary system

Fig. 254. Isobaric-isothermal sections for systems involving three-phase equilibrium.

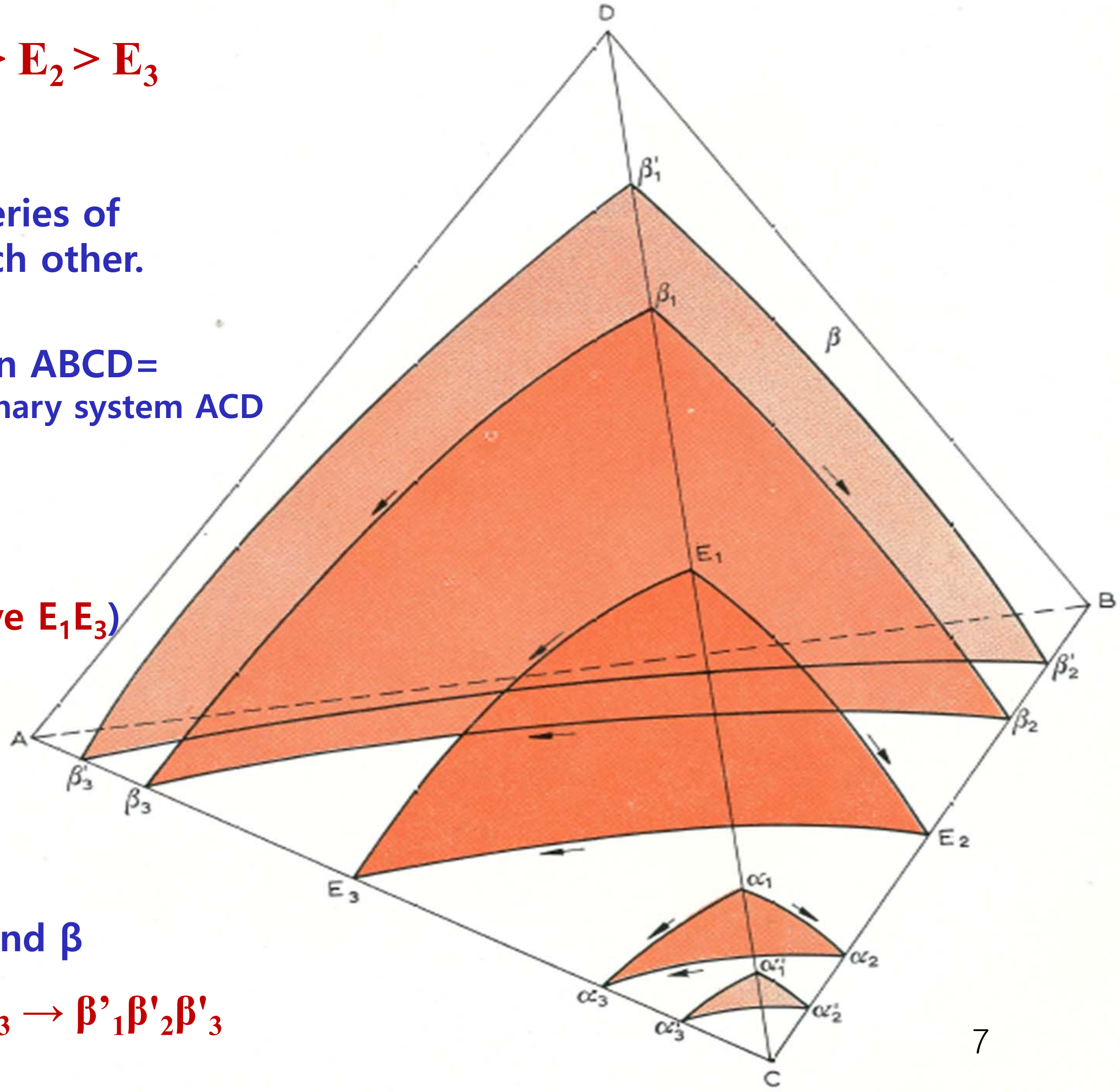
Fig. 255. Polythermal projection of a quaternary system involving three-phase equilibrium of the type l ⇄ α + β

$T_D > T_C > E_1 > T_B > T_A > E_2 > E_3$

* Binary eutectic: CA, CB, CD
& A, B, D form continuous series of binary solid solution with each other.

* Face *ACD* of the tetrahedron ABCD= polythermal projection of the ternary system ACD

: Continuous transition from the binary eutectic CD to the binary eutectic AC (monovariant liquidus curve E_1E_3)

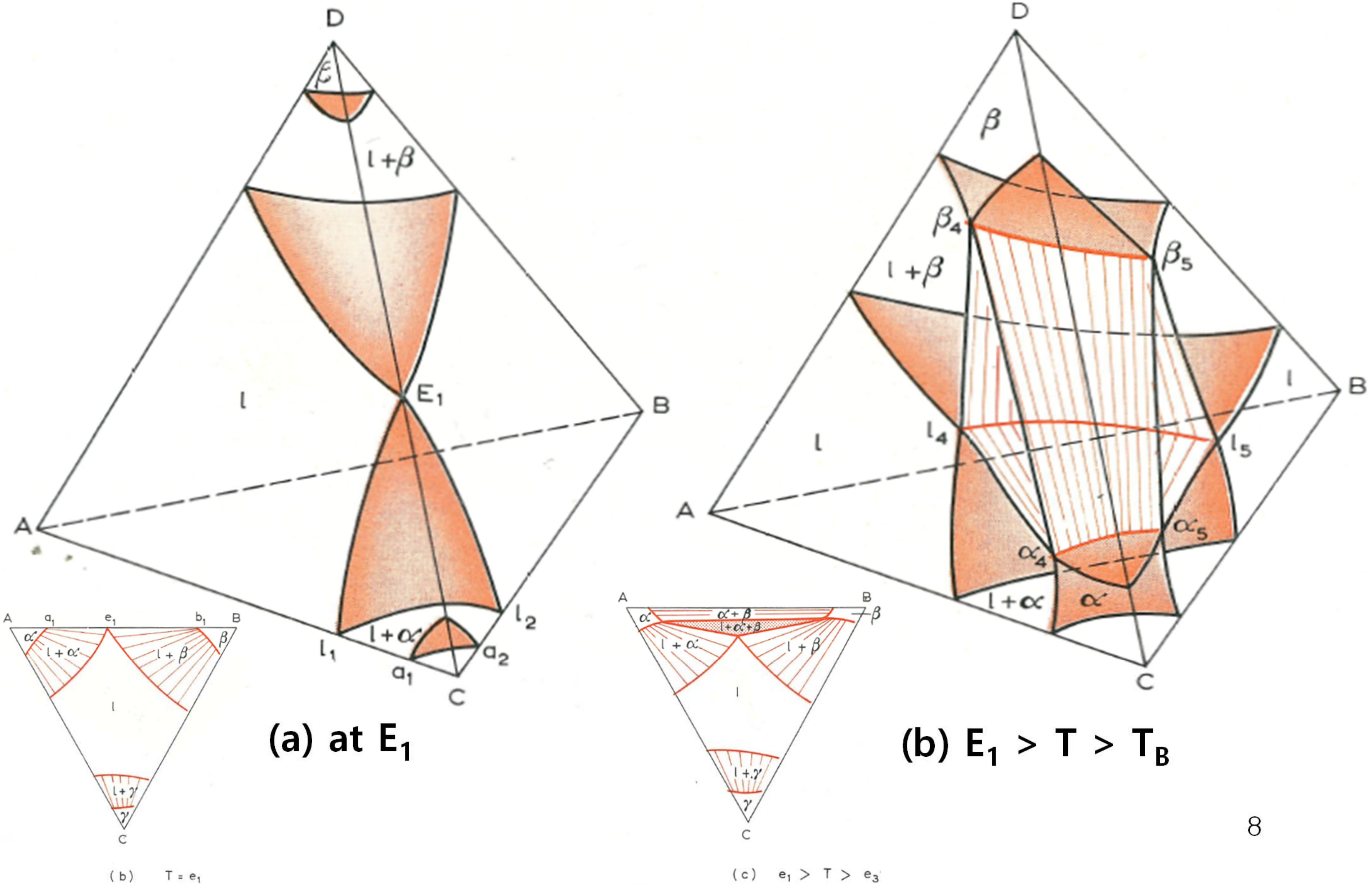


* Change in solubility in α and β

$\alpha_1\alpha_2\alpha_3 \rightarrow \alpha'_1\alpha'_2\alpha'_3$, $\beta_1\beta_2\beta_3 \rightarrow \beta'_1\beta'_2\beta'_3$

$T_D > T_C > E_1 > T_B > T_A > E_2 > E_3$

Fig. 256. Isobaric-isothermal sections through the quaternary system of Fig. 255

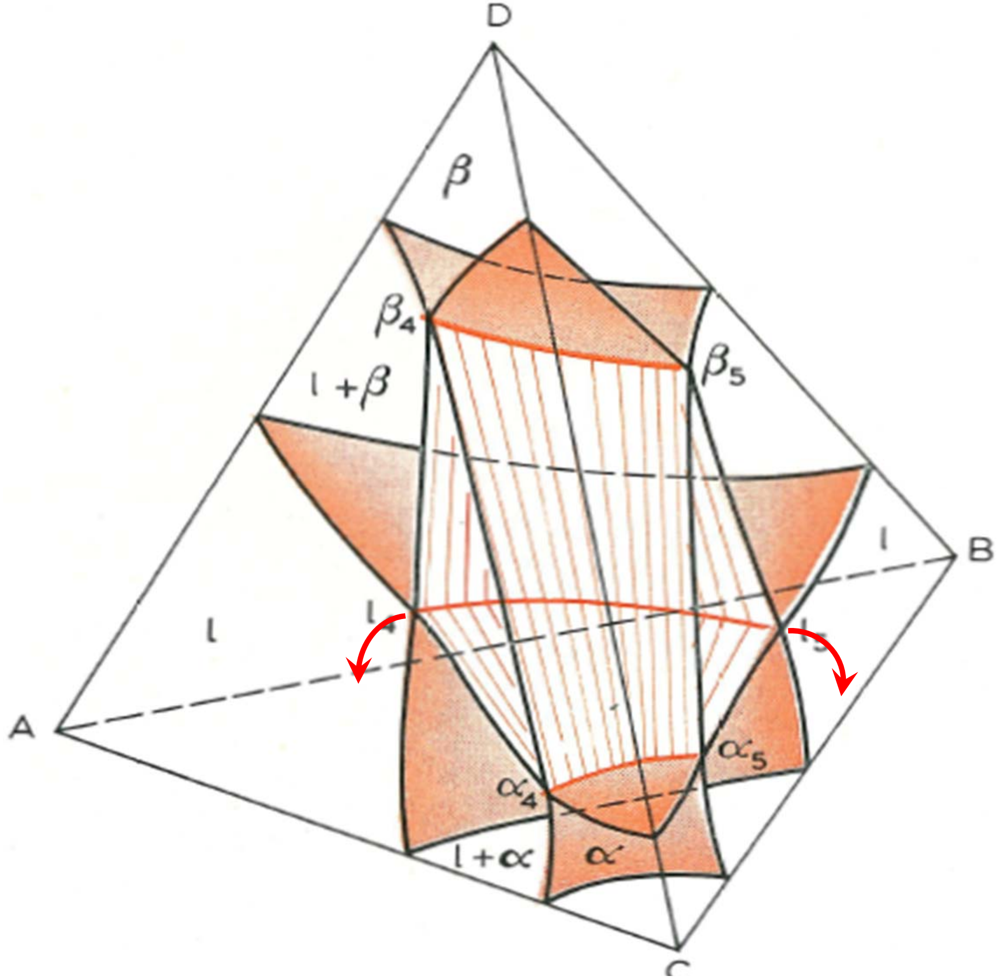


(a) at E_1

(b) $E_1 > T > T_B$

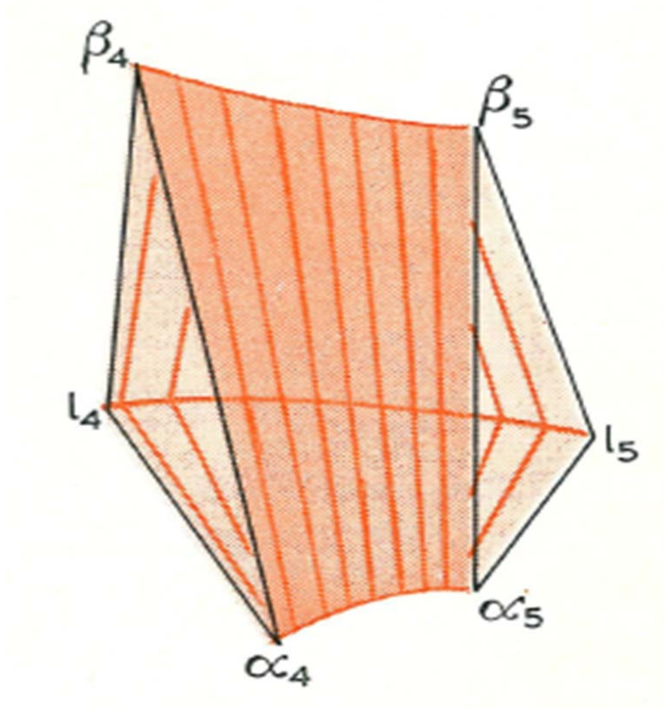
$T_D > T_C > E_1 > T_B > T_A > E_2 > E_3$

Fig. 256. Isobaric-isothermal sections through the quaternary system of Fig. 255



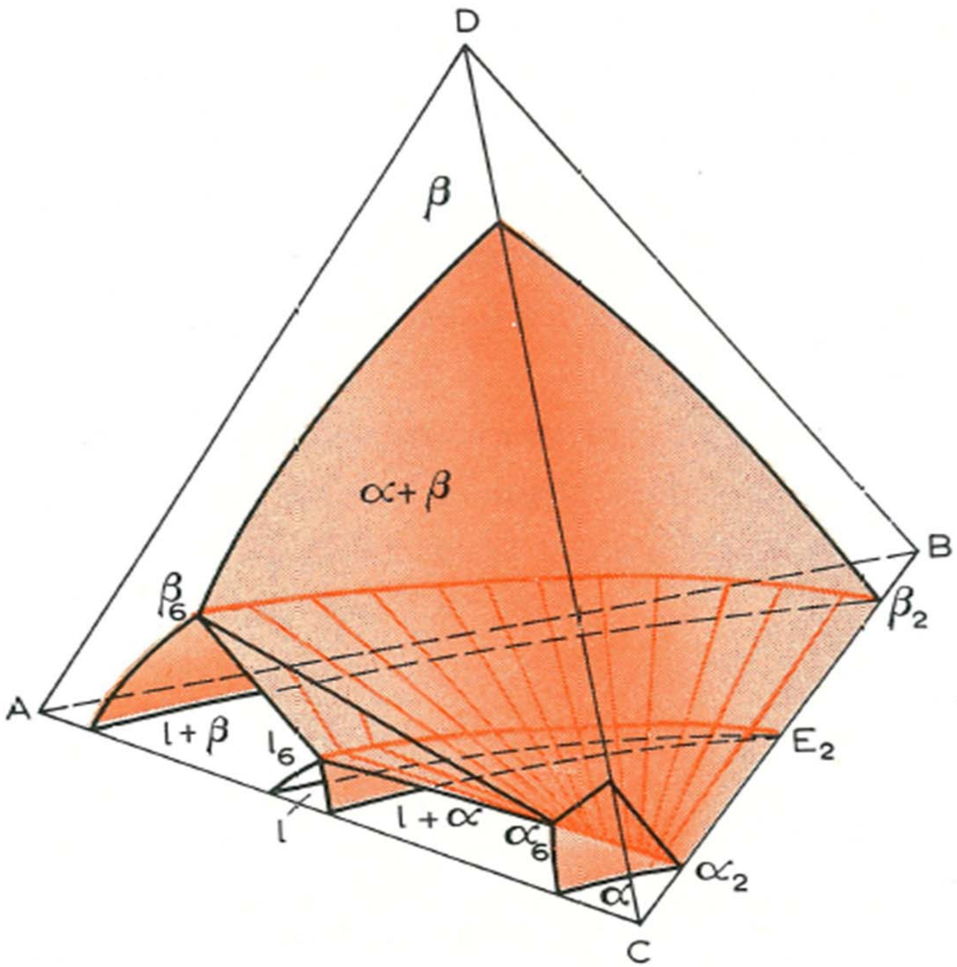
(b) E_1 > T > T_B

*** Quaternary three phase region**

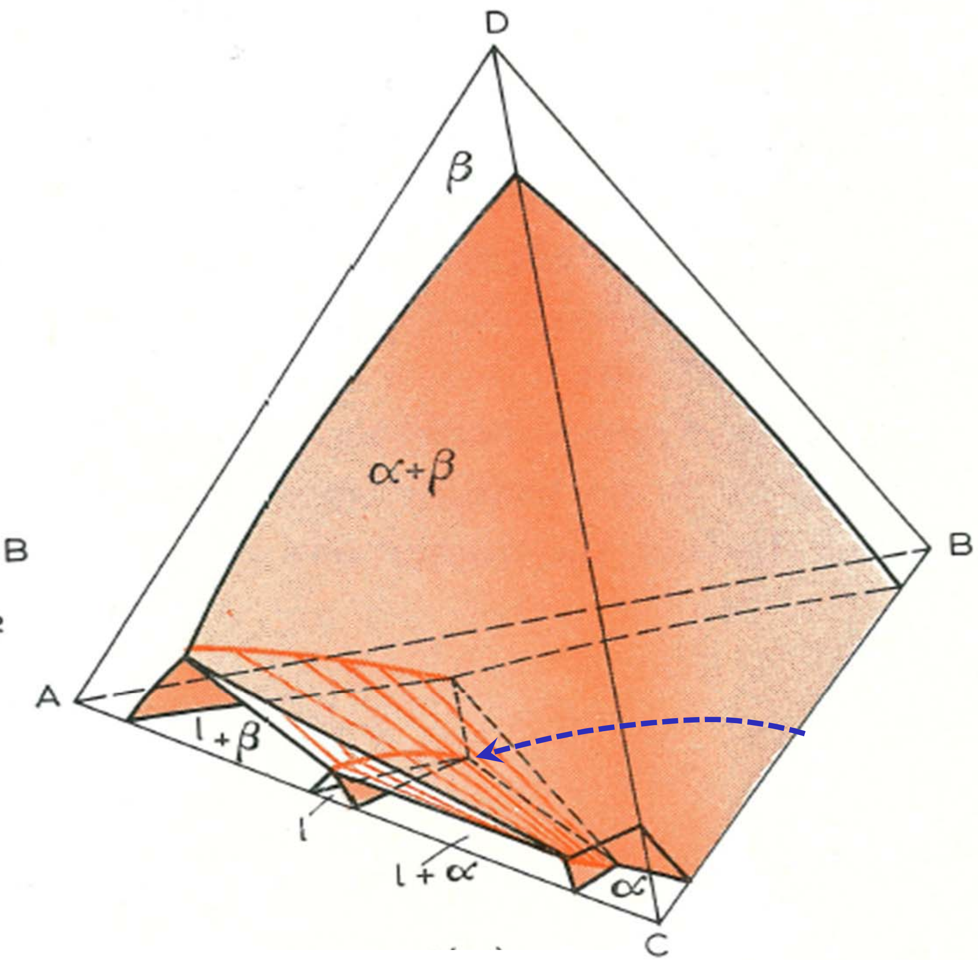


$T_D > T_C > E_1 > T_B > T_A > E_2 > E_3$

Fig. 256. Isobaric-isothermal sections through the quaternary system of Fig. 255



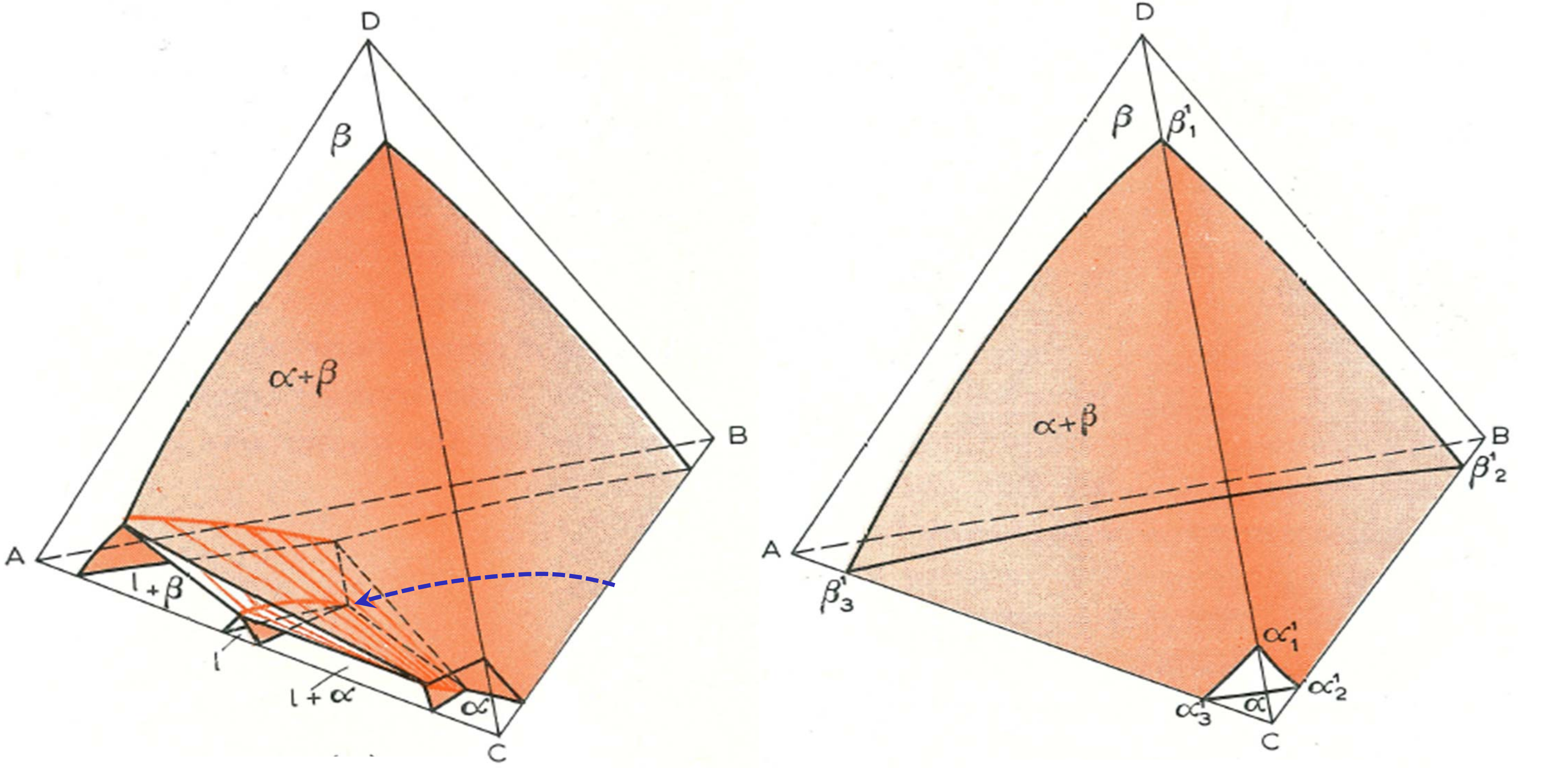
(d) at E_2



(e) $E_2 > T > E_3$

$T_D > T_C > E_1 > T_B > T_A > E_2 > E_3$

Fig. 256. Isobaric-isothermal sections through the quaternary system of Fig. 255



(e) E_2 > T > E_3 **(f) below E_3**

1) At E_3 , the last drop of liquid is consumed and all alloys in the quaternary system are completely solid at temperatures below E_3.

2) Below E_3, change in solubility in α and β ($\alpha_1\alpha_2\alpha_3 \rightarrow \alpha'_1\alpha'_2\alpha'_3$, $\beta_1\beta_2\beta_3 \rightarrow \beta'_1\beta'_2\beta'_3$)

The three-phase regions from Fig. 256.b, d, and e have been superimposed on the polythermal projection in Fig. 257.

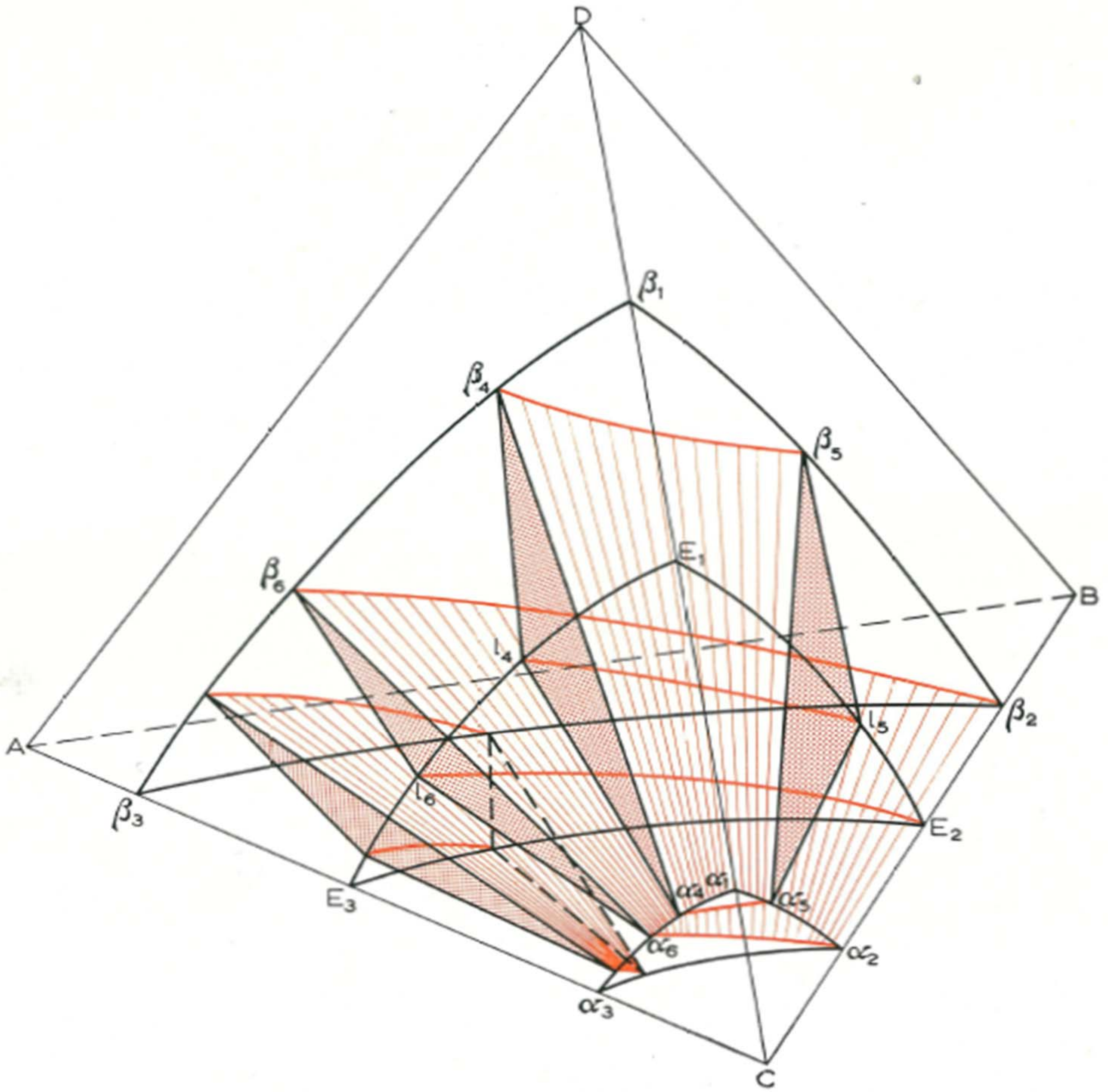


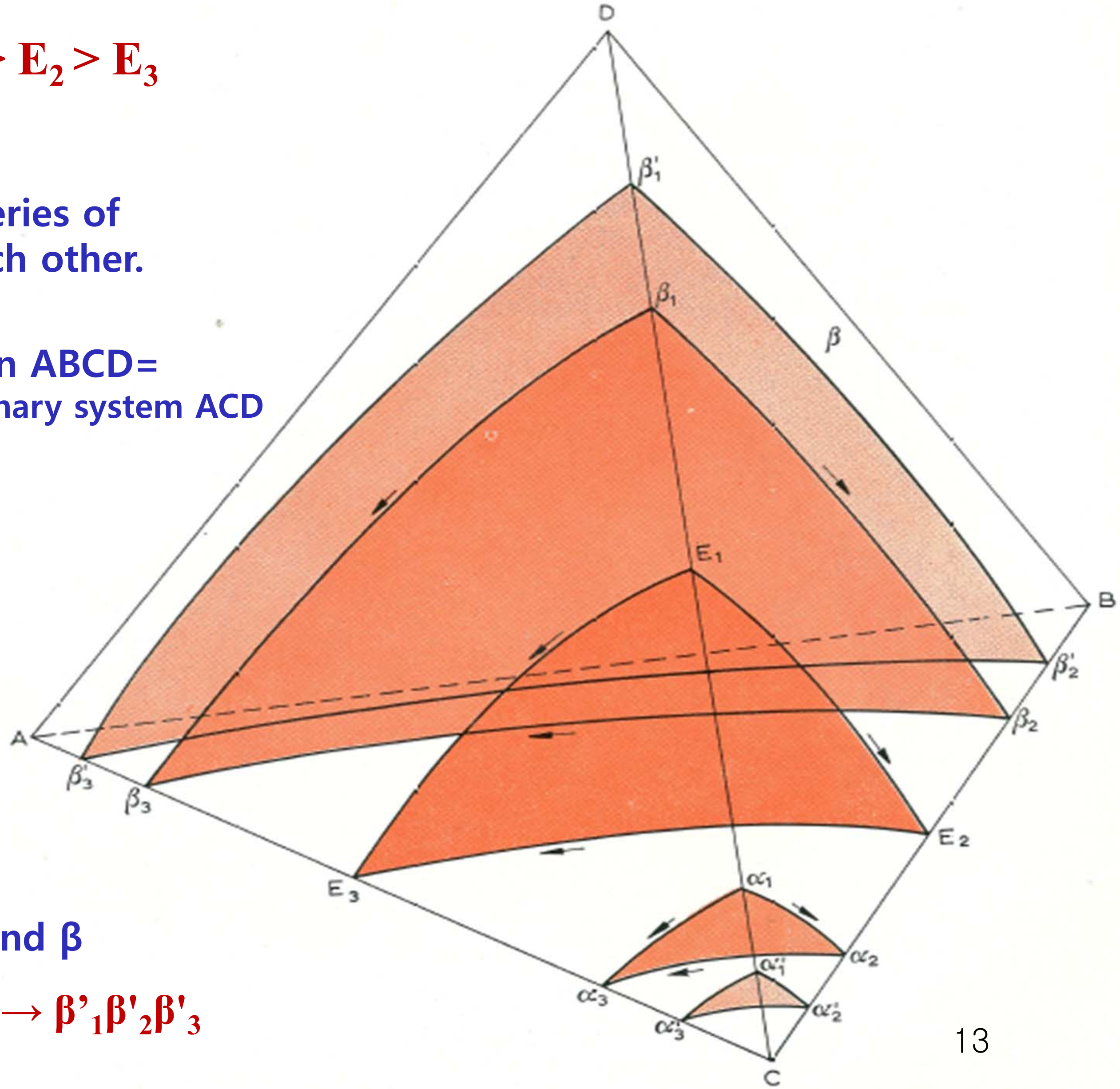
Fig. 255. Polythermal projection of a quaternary system involving three-phase equilibrium of the type $l \rightleftarrows \alpha + \beta$

$T_D > T_C > E_1 > T_B > T_A > E_2 > E_3$

* Binary eutectic: CA, CB, CD
& A, B, D form continuous series of binary solid solution with each other.

* Face *ACD* of the tetrahedron ABCD= polythermal projection of the ternary system ACD

: Continuous transition from the binary eutectic CD to the binary eutectic AC (monovariant liquidus curve E_1E_3)



* Change in solubility in α and β

$\alpha_1\alpha_2\alpha_3 \rightarrow \alpha'_1\alpha'_2\alpha'_3$, $\beta_1\beta_2\beta_3 \rightarrow \beta'_1\beta'_2\beta'_3$

* Equilibrium freezing of alloys

A method proposed by Schrader and Hannemann

: the construction of a three-dimensional temperature-concentration section for a constant amount of one of the components.

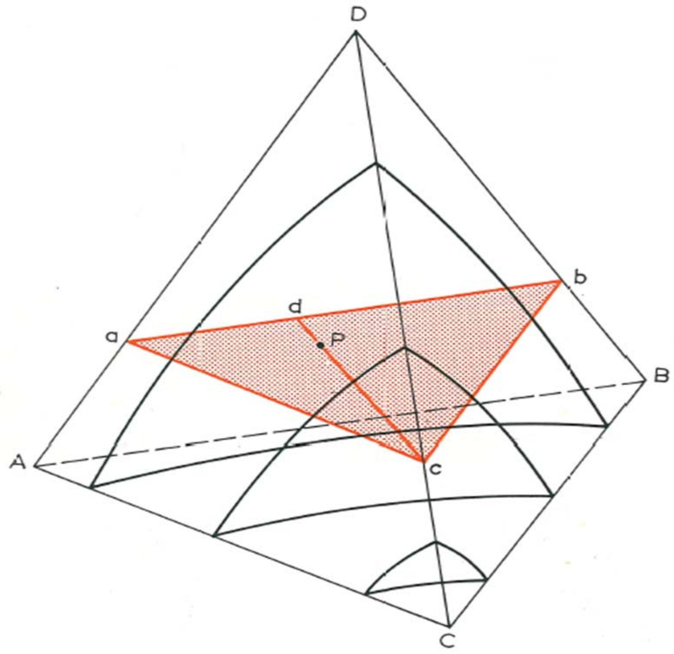
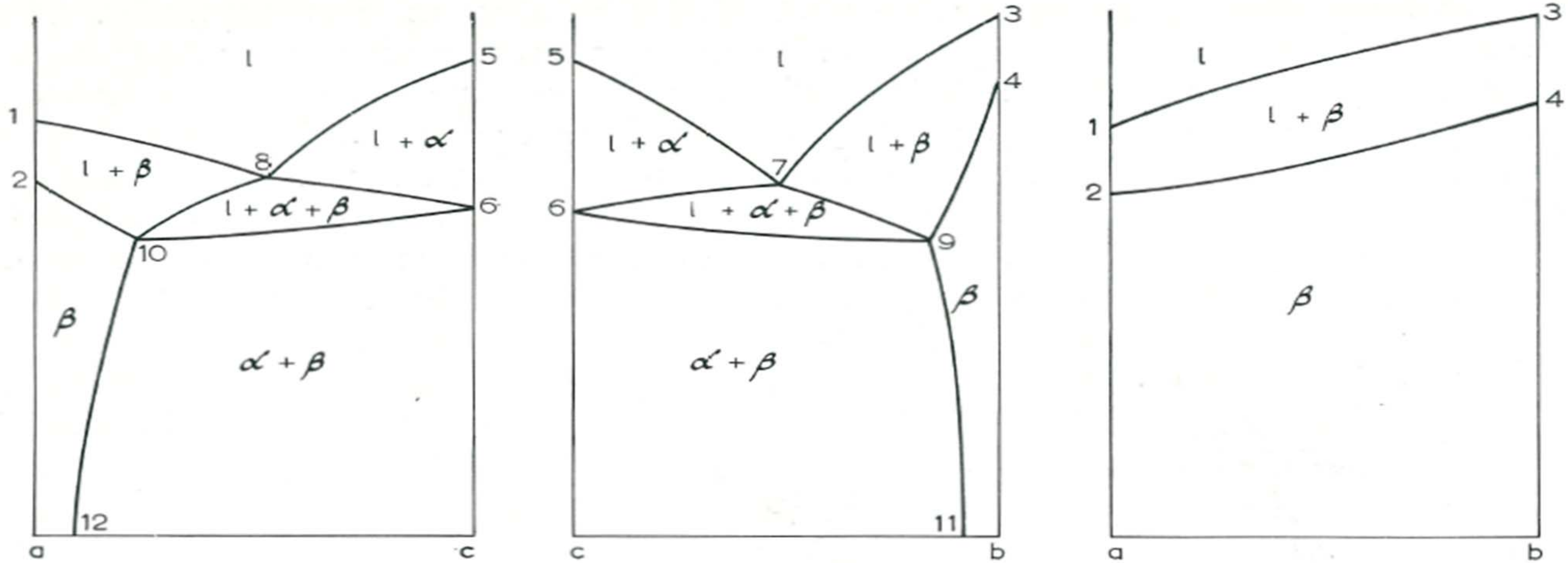
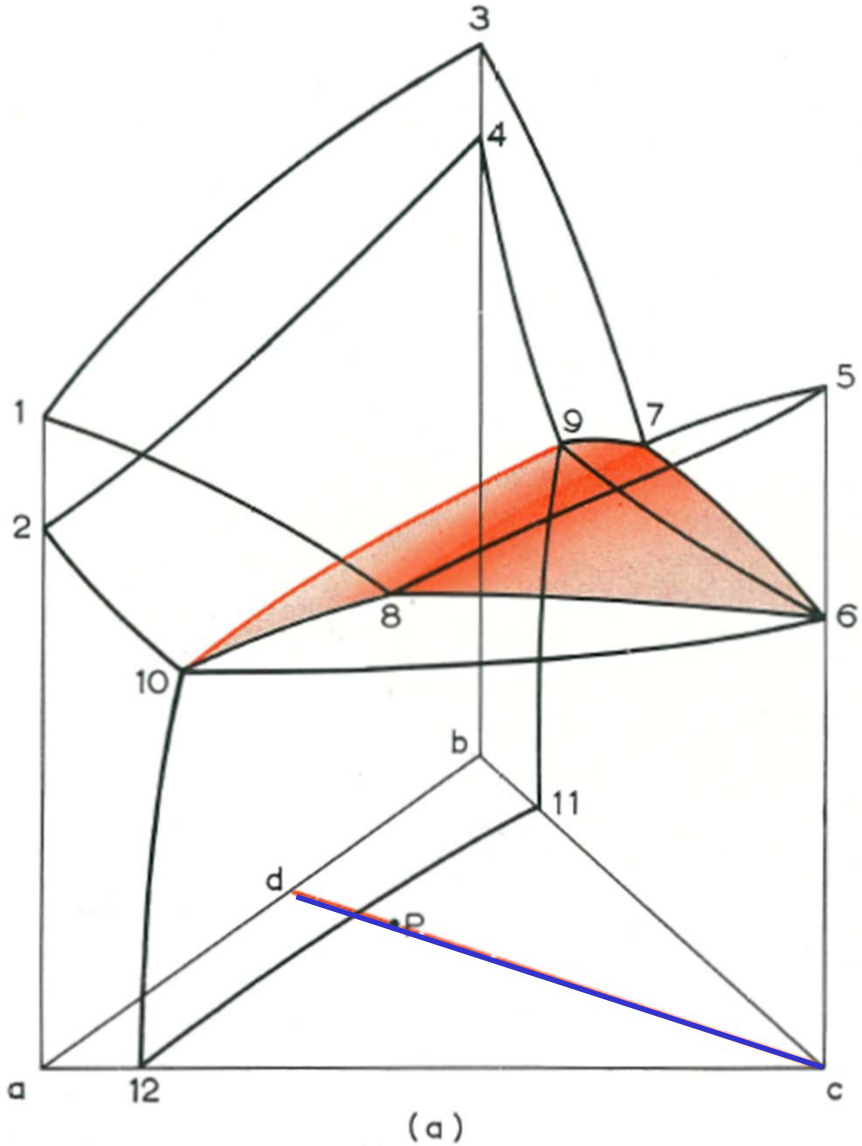


Fig. 258. Position of alloy *P* on plane *abc*.



Vertical sections a-c, c-b, and a-b at the ternary faces ACD, BCD, and ABD

Fig. 260. (a) Three-dimensional temperature-concentration diagram for a quaternary system abc; (b) two-dimensional section throgh Fig. 260 (a).



* Consider the solidification of alloy P on plane abc,

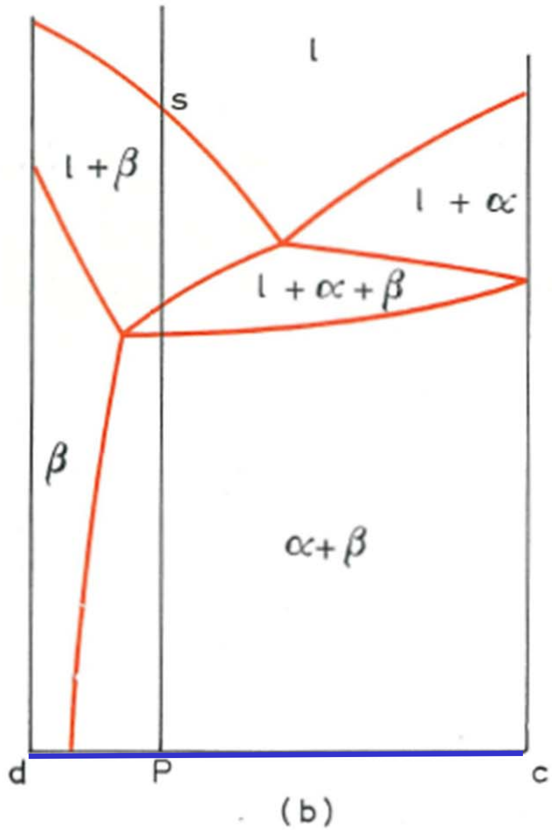
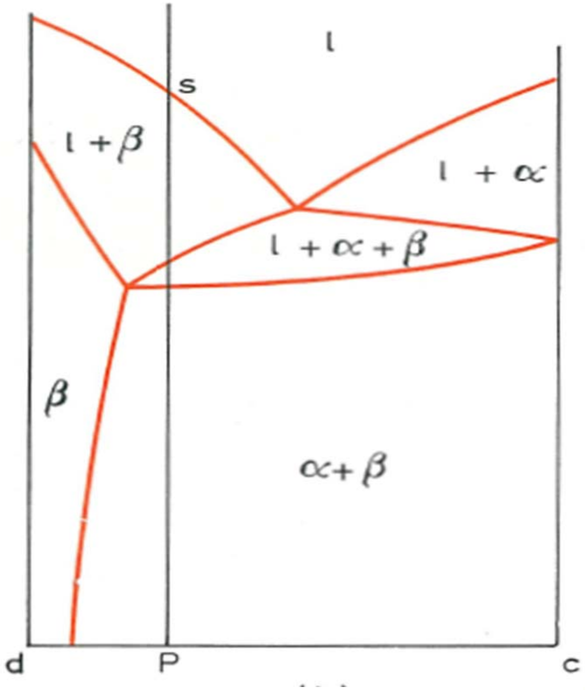


Fig. 261. Freezing of quaternary alloy P illustrated by reference to the polythermal projection of Fig. 255.

* Consider the solidification of alloy P

1) β solid solution precipitation with β_4 composition



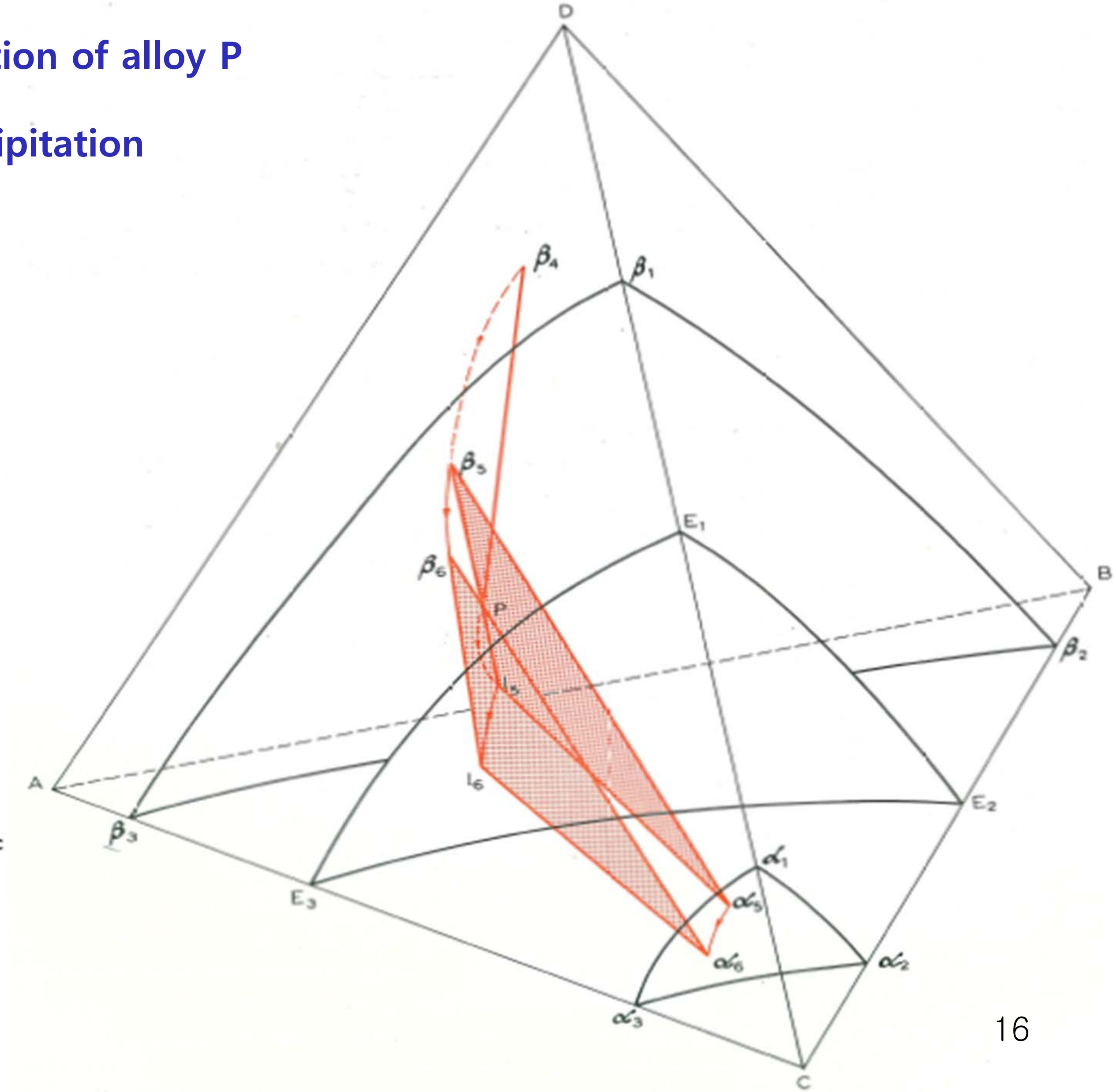


Fig. 261. Freezing of quaternary alloy P illustrated by reference to the polythermal projection of Fig. 255.

* Consider the solidification of alloy P
: primary (1) and secondary crystallization (3)

T ↓

1) β solid solution precipitation with β_4 composition

2) β phases trace paths similar to those shown in Fig. 253. ($\beta_4 \rightarrow \beta_5$)

3) Liquid meet the eutectic surface $E_1E_2E_3$.
→ three phase equilibrium appear.
($l_5\alpha_5\beta_5 \rightarrow l_6\alpha_6\beta_6$)

4) With cooling to room temperature,
$\alpha_1\alpha_2\alpha_3 \rightarrow \alpha'_1\alpha'_2\alpha'_3$, $\beta_1\beta_2\beta_3 \rightarrow \beta'_1\beta'_2\beta'_3$

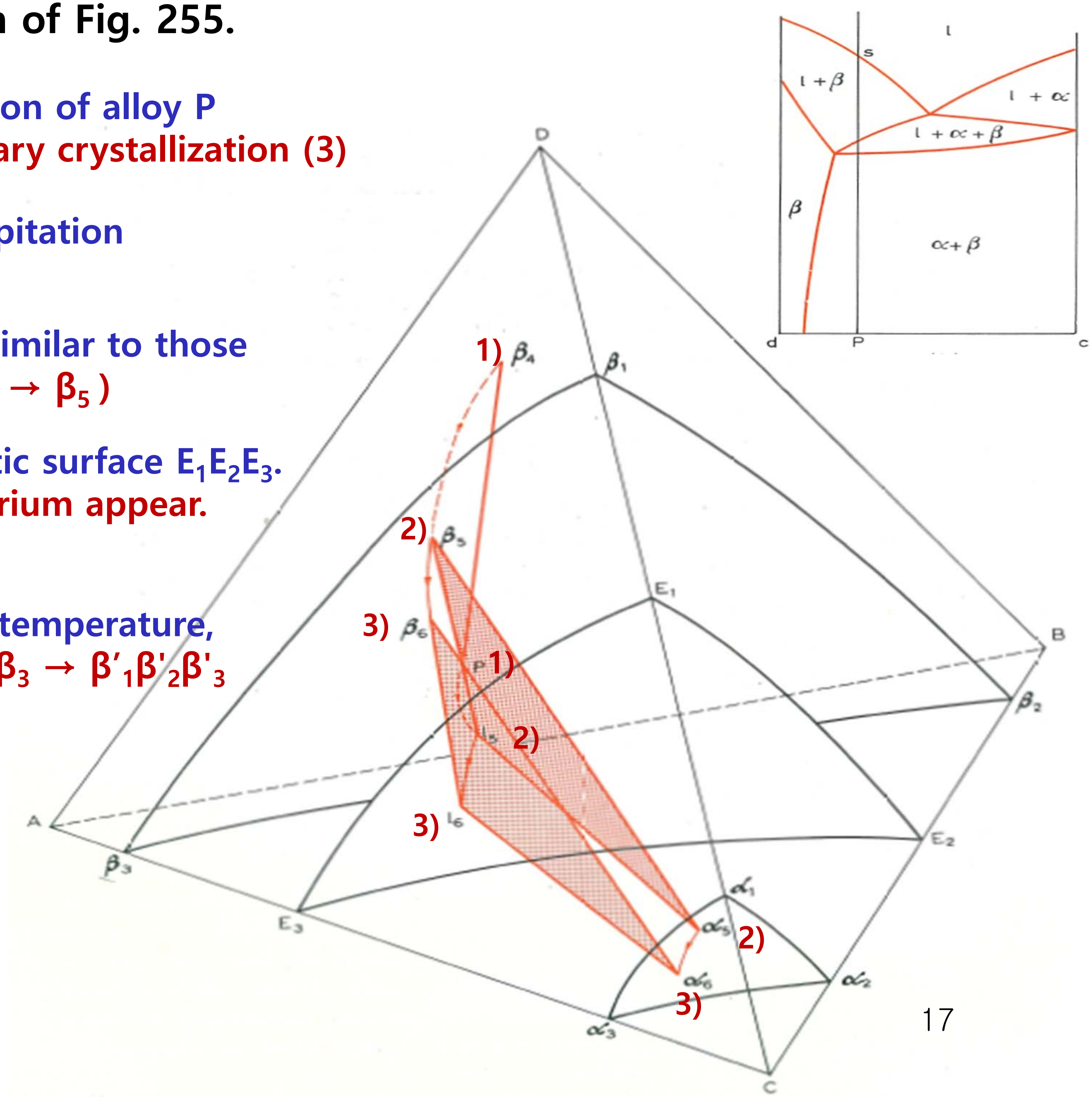


Fig. 261. Freezing of quaternary alloy P illustrated by reference to the polythermal projection of Fig. 255.

* Consider the solidification of alloy P
: primary (1) and secondary crystallization (3)

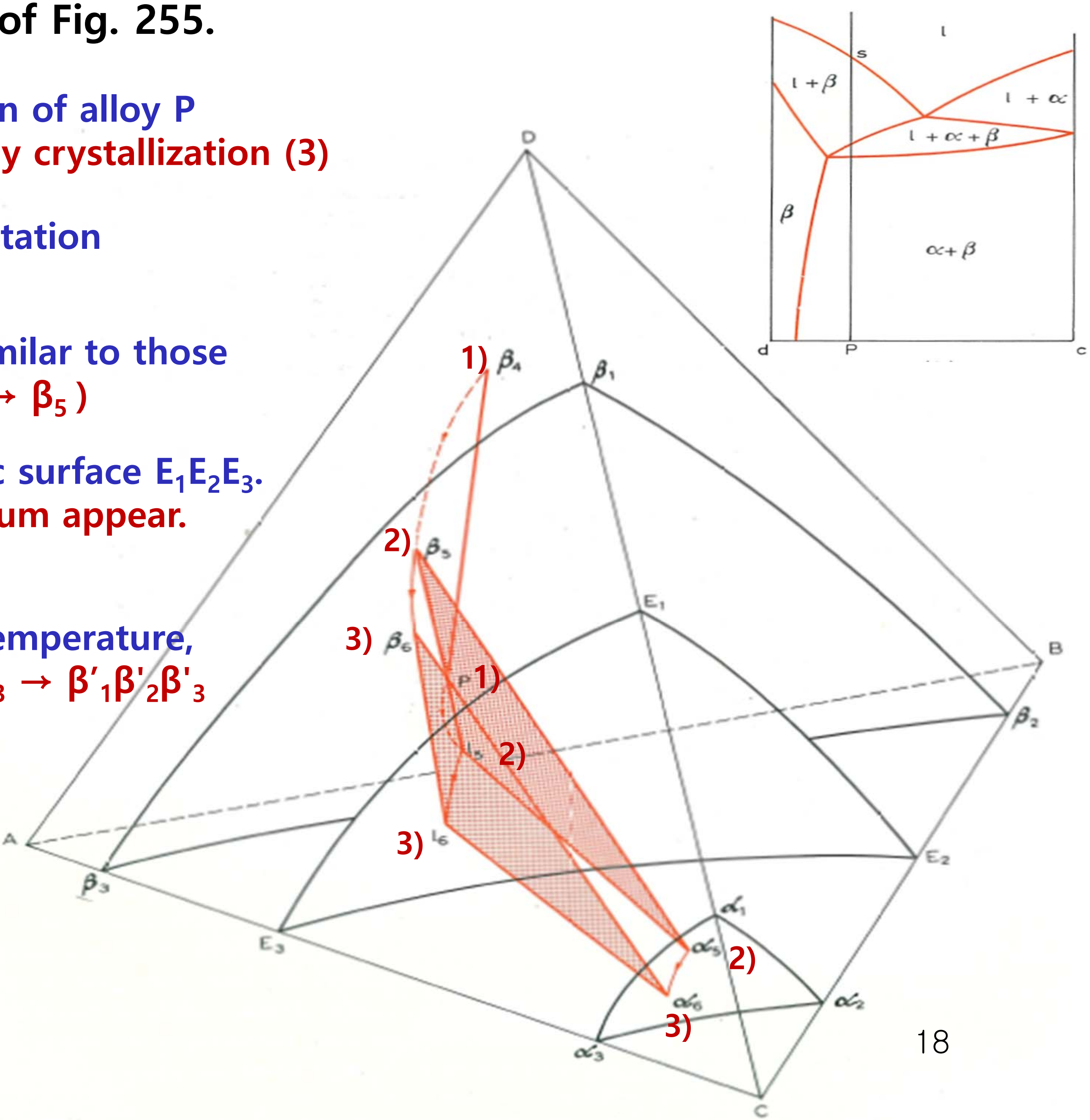
T
↓

1) β solid solution precipitation with β_4 composition

2) β phases trace paths similar to those shown in Fig. 253. ($\beta_4 \rightarrow \beta_5$)

3) Liquid meet the eutectic surface $E_1E_2E_3$.
→ three phase equilibrium appear.
($l_5\alpha_5\beta_5 \rightarrow l_6\alpha_6\beta_6$)

4) With cooling to room temperature,
$\alpha_1\alpha_2\alpha_3 \rightarrow \alpha'_1\alpha'_2\alpha'_3$, $\beta_1\beta_2\beta_3 \rightarrow \beta'_1\beta'_2\beta'_3$



15.4 FOUR-PHASE EQUILIBRIUM

Four phases can only exist at one temperature in a ternary system.

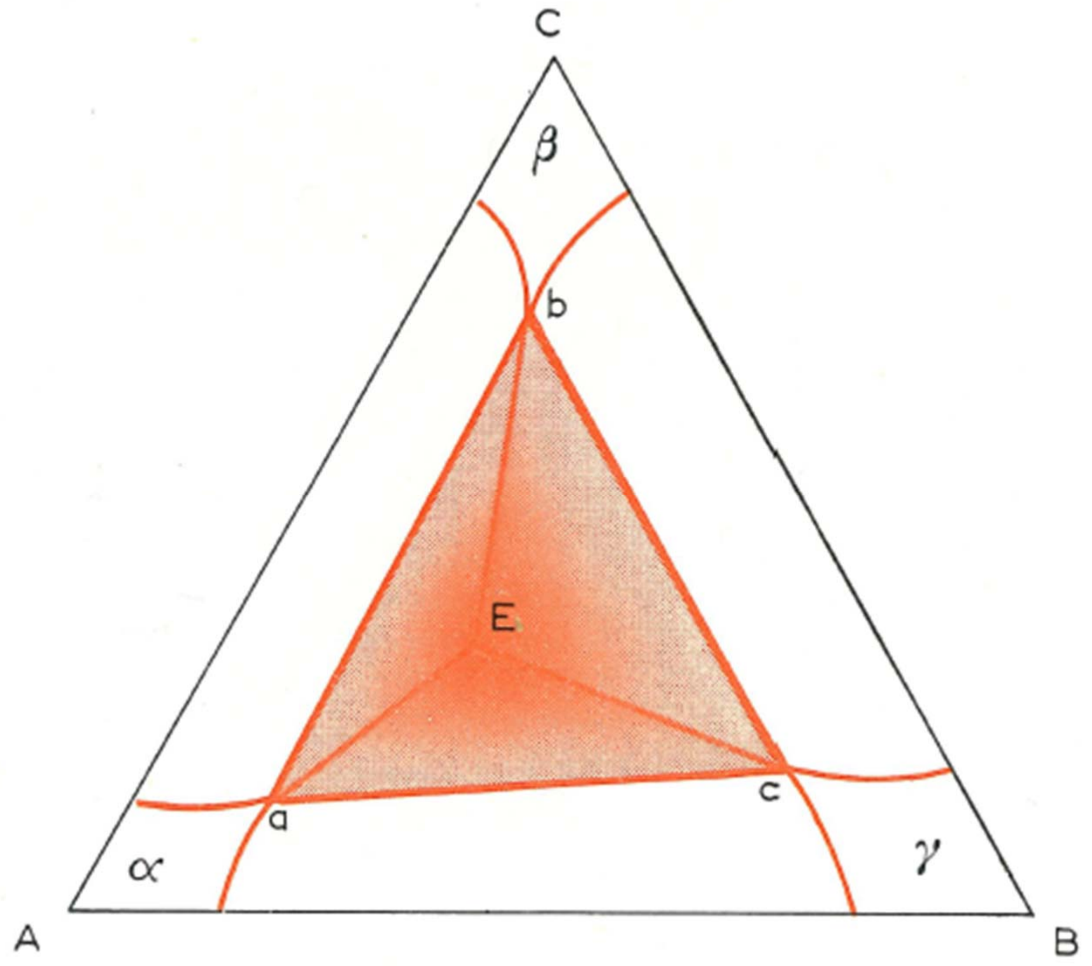
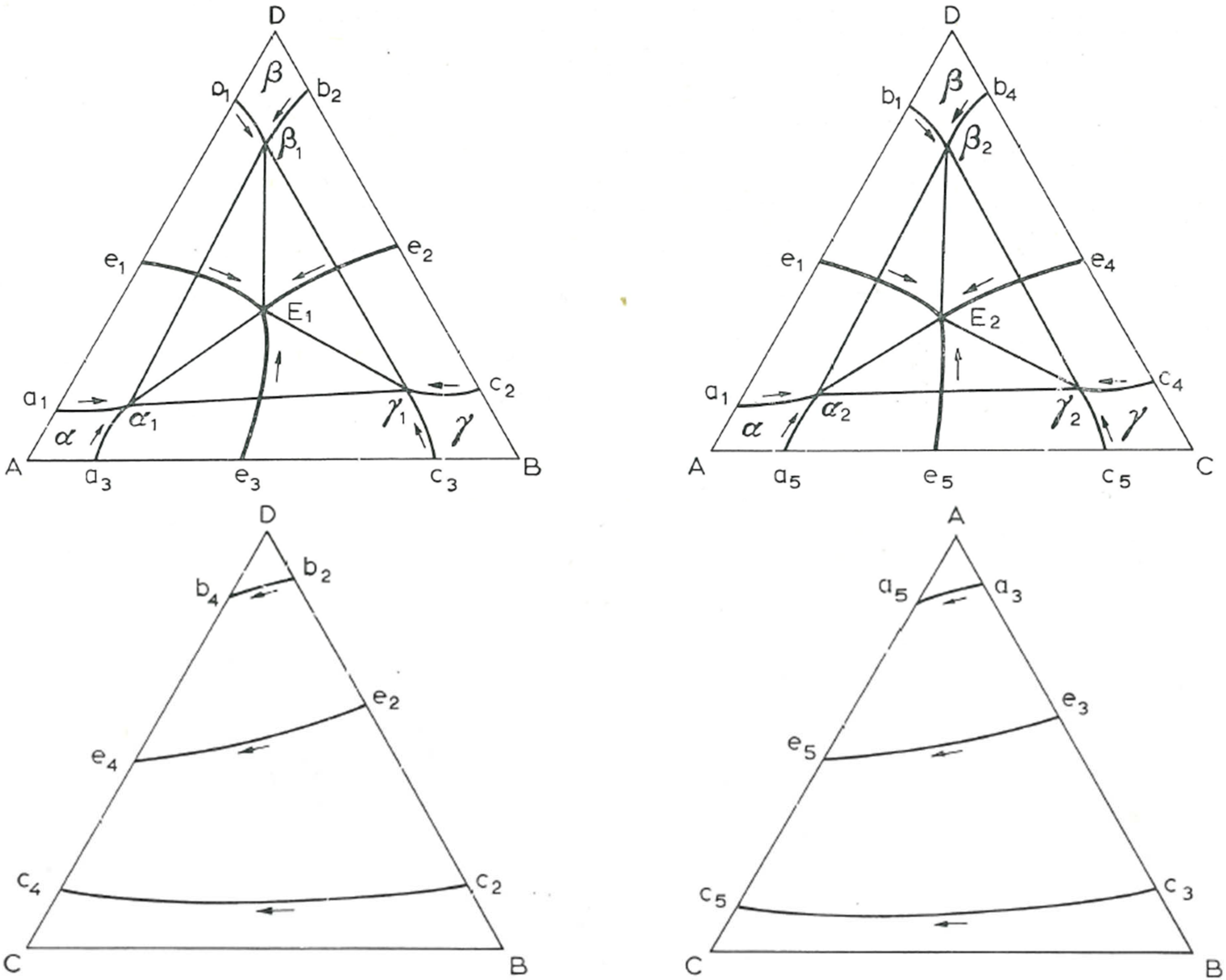


Fig. 262. Isobaric-isothermal section of a ternary system at the ternary eutectic temperature

Fig. 263. Polythermal projection of the ternary systems involved in a quaternary four phase eutectic equilibrium



<Hillert's criterion>

Assumption, $X_A^{\beta} = X_A^{l} > X_A^{\alpha}$ (New coordinate system) $\Delta m_{\beta} + \Delta m_{l} = -\Delta m_{\alpha}$

$$\Delta X_A = m_{\alpha} \cdot \Delta X_A^{\alpha} + m_{\beta} \cdot \Delta X_A^{\beta} + m_l \cdot \Delta X_A^{l} + X_A^{\alpha} \cdot \Delta m_{\alpha} + X_A^{\beta} \cdot \Delta m_{\beta} + X_A^{l} \cdot \Delta m_l = 0$$

$$-X_A^{\alpha}\Delta m_{\alpha} - X_A^{\beta}\Delta m_{\beta} - X_A^{l}\Delta m_l = m_{\alpha}\Delta X_A^{\alpha} + m_{\beta}\Delta X_A^{\beta} + m_l\Delta X_A^{l}$$

$$\Delta m_{\alpha}(X_A^{\beta} - X_A^{\alpha}) = m_{\alpha}\Delta X_A^{\alpha} + m_{\beta}\Delta X_A^{\beta} + m_l\Delta X_A^{l}$$

Sign	Assumption	Sign
$\Delta m_{\alpha}(X_A^{\beta} - X_A^{\alpha})$	$X_A^{\beta} = X_A^{l} > X_A^{\alpha}$	$m_{\alpha}\Delta X_A^{\alpha} + m_{\beta}\Delta X_A^{\beta} + m_l\Delta X_A^{l}$
$\Delta m_{\beta}(X_A^{\alpha} - X_A^{\beta})$	$X_A^{\alpha} = X_A^{l} > X_A^{\beta}$	$m_{\alpha}\Delta X_A^{\alpha} + m_{\beta}\Delta X_A^{\beta} + m_l\Delta X_A^{l}$
$\Delta m_l(X_A^{\alpha} - X_A^{l})$	$X_A^{\alpha} = X_A^{\beta} > X_A^{l}$	$m_{\alpha}\Delta X_A^{\alpha} + m_{\beta}\Delta X_A^{\beta} + m_l\Delta X_A^{l}$

here, Δm_{α} : change of α phase fraction with ΔT

Δm_{α}	Δm_{β}	Δm_l		
+	+	-	$l \rightarrow \alpha + \beta$	eutectic
+	-	-	$l + \beta \rightarrow \alpha$	peritectic
-	+	-	$l + \alpha \rightarrow \beta$	peritectic

Hillert's criterion indicates that the relative amounts of the α, β and liquid phases (the average alloy composition) are of importance in determining the type of reaction.

Hillert's criterion indicates that the relative amounts of the α, β and liquid phases (the average alloy composition) are of importance in determining the type of reaction.

In the case of a quaternary four-phase equilibrium application of the criterion indicates that:

(1) $\Delta m_{\alpha}, \Delta m_{\beta}, \Delta m_{\gamma}$ **are positive and** Δm_{l} **is negative, the quaternary four-phase equilibrium is of the eutectic type: l ⇄ α + β + γ.**

(2) If one the expressions, $\Delta m_{\alpha}, \Delta m_{\beta}, \Delta m_{\gamma}$ **is negative and** Δm_{l} **is negative, the quaternary reaction is a quasi-peritectic type: l + α ⇄ β + γ for negative** Δm_{α}**.**

(3) If two of the expressions $\Delta m_{\alpha}, \Delta m_{\beta}, \Delta m_{\gamma}$ **are negative and** Δm_{l} **is negative, the quaternary reaction is a peritectic type: l + α + β ⇄ γ for negative** Δm_{α} **and** Δm_{β}**.**

* Simplest case of quaternary four-phase equilibrium:

$l \rightleftarrows \alpha + \beta + \gamma$

$T_D > T_A > T_B > e_1 > e_2 > T_C > e_3 > e_4 > e_5 > E_1 > E_2$

1) Five binary eutectic systems
   AB, AC, AD, CD and BD
   & one binary solid solution, BC

2) Ternary eutectic type
   ABD and ACD
   & only ternary three-phase equilibria
   ABC and BCD

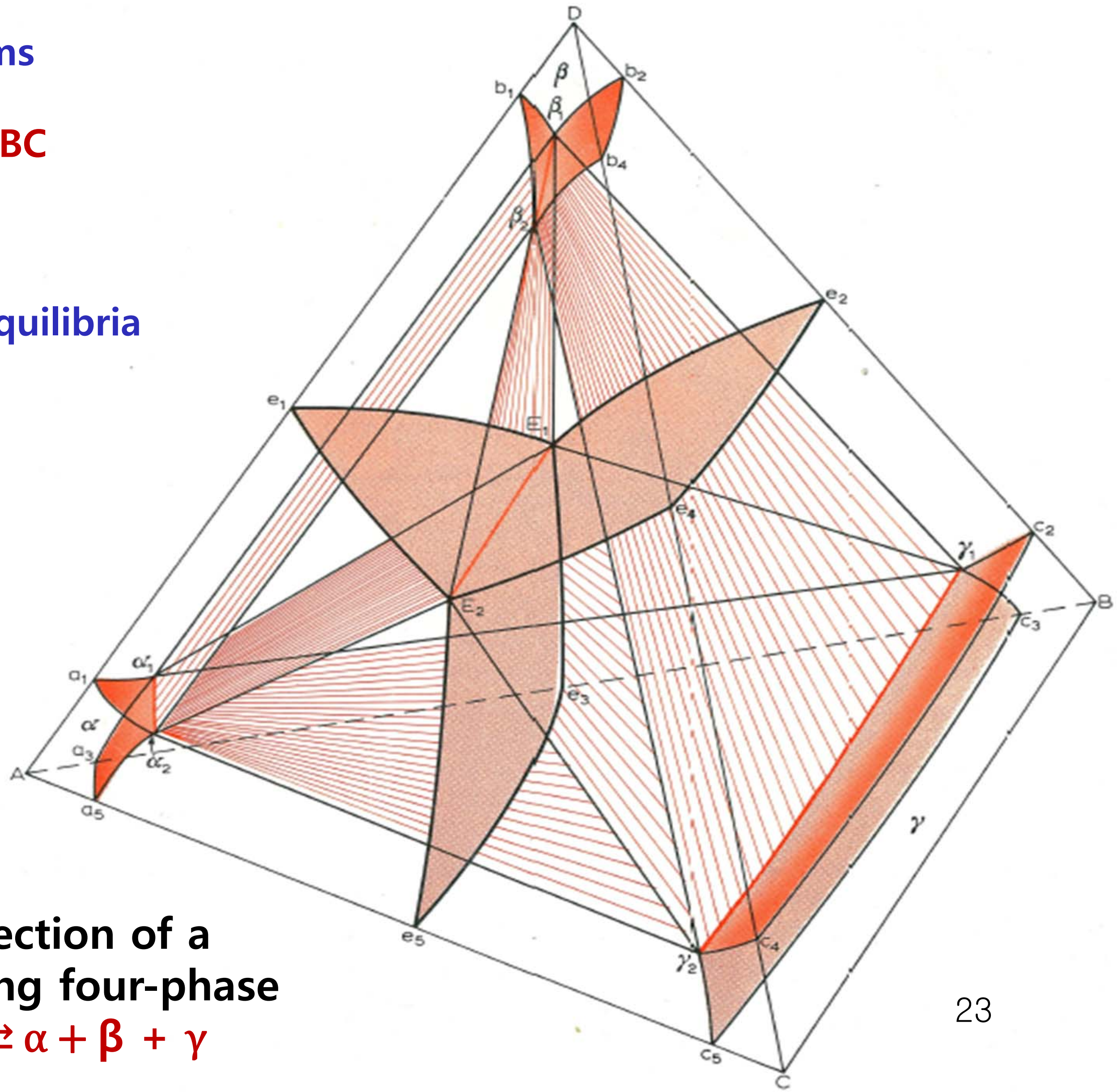


Fig. 264. Polythermal projection of a quaternary system involving four-phase equilibrium of the type $l \rightleftarrows \alpha + \beta + \gamma$

Fig. 264. Polythermal projection of a quaternary system involving four-phase equilibrium of the type l ⇄ α + β + γ

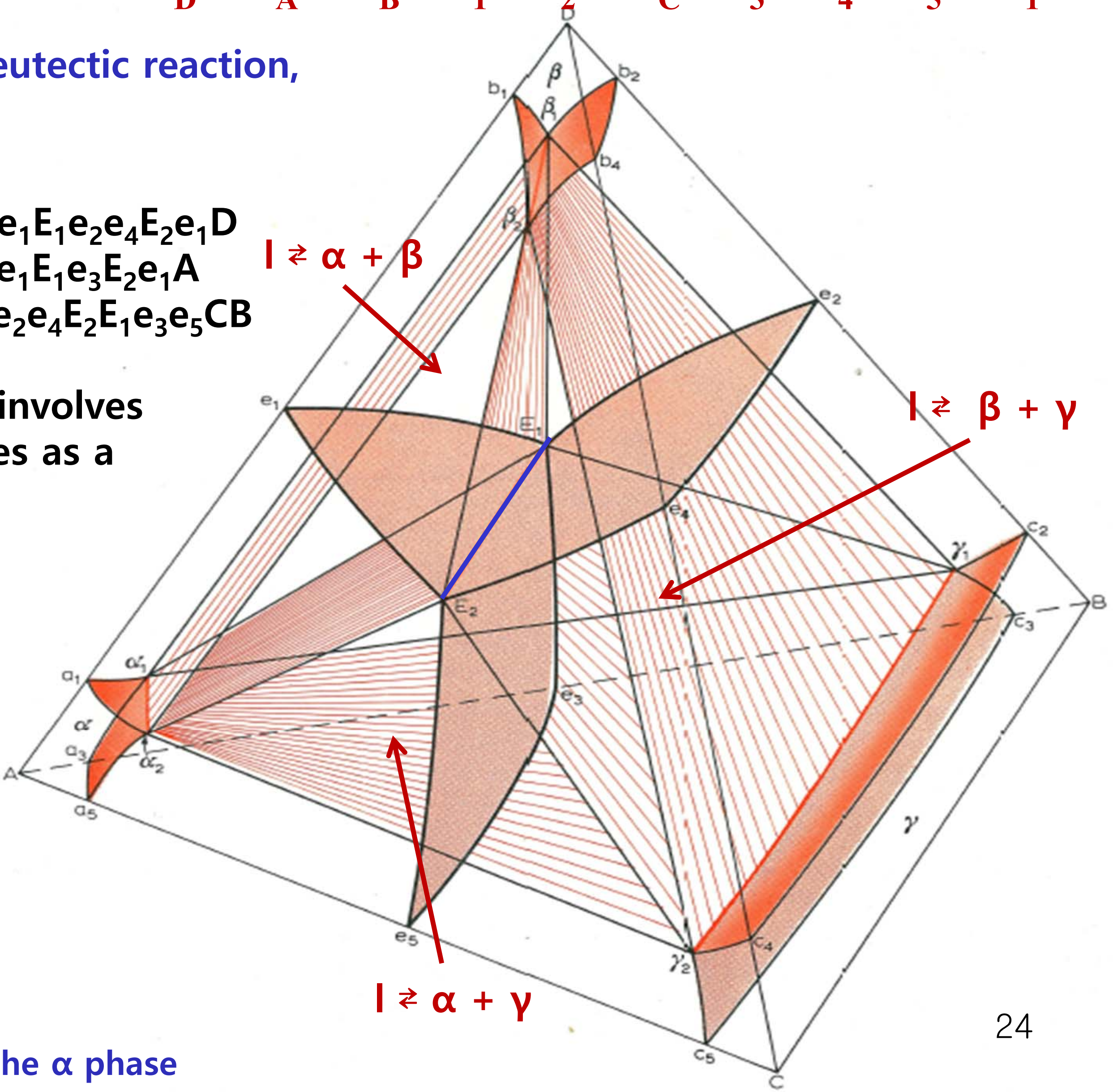
$T_D > T_A > T_B > e_1 > e_2 > T_C > e_3 > e_4 > e_5 > E_1 > E_2$

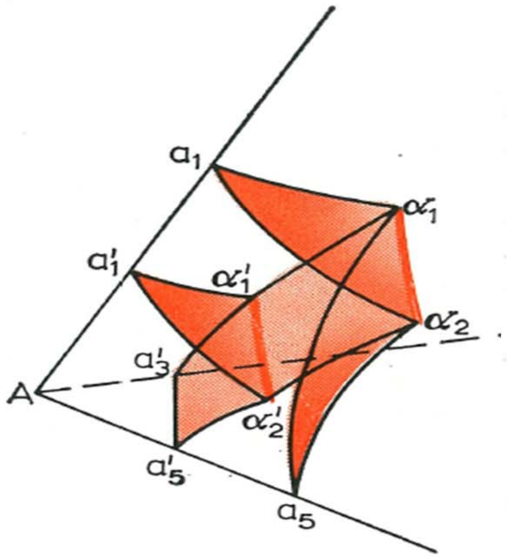
* Monovariant quaternary eutectic reaction,

l ⇄ α + β + γ

* Primary crystallization β: $e_1E_1e_2e_4E_2e_1D$
Primary crystallization α: $e_1E_1e_3E_2e_1A$
Primary crystallization γ: $e_2e_4E_2E_1e_3e_5CB$

* Secondary crystallization involves equilibrium of three phases as a series of tie triangles.

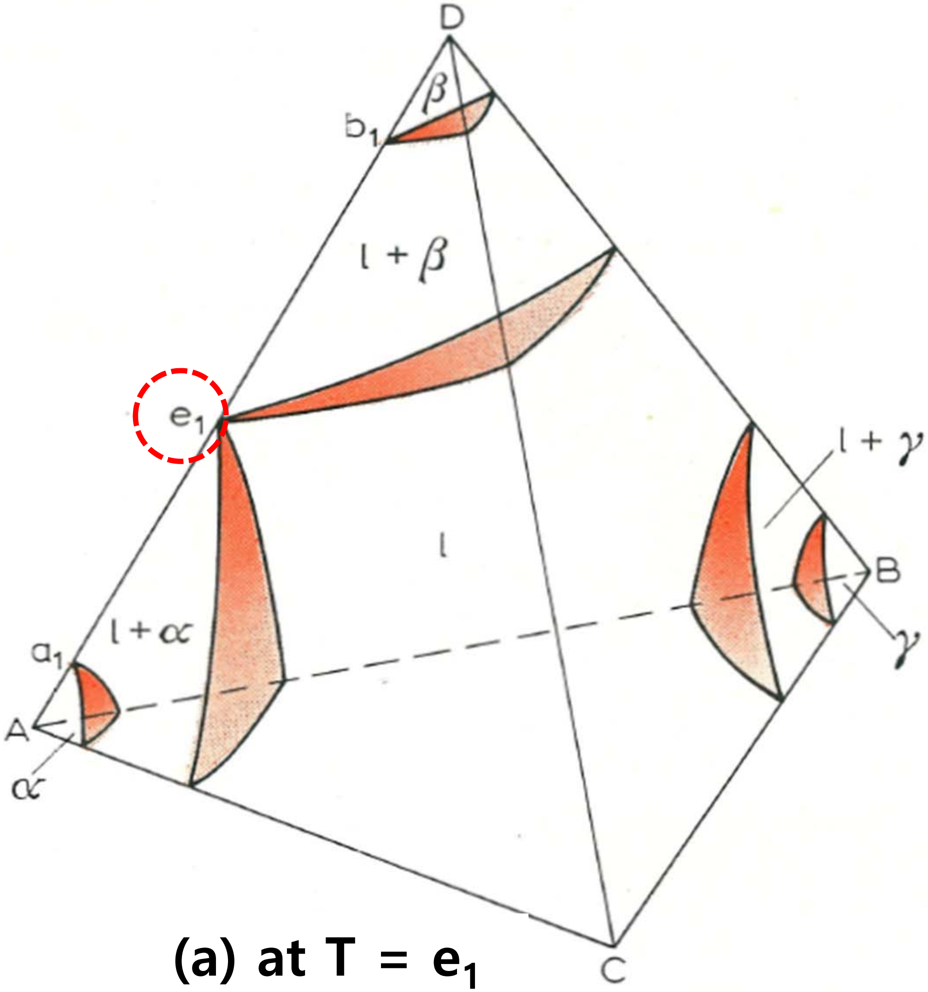




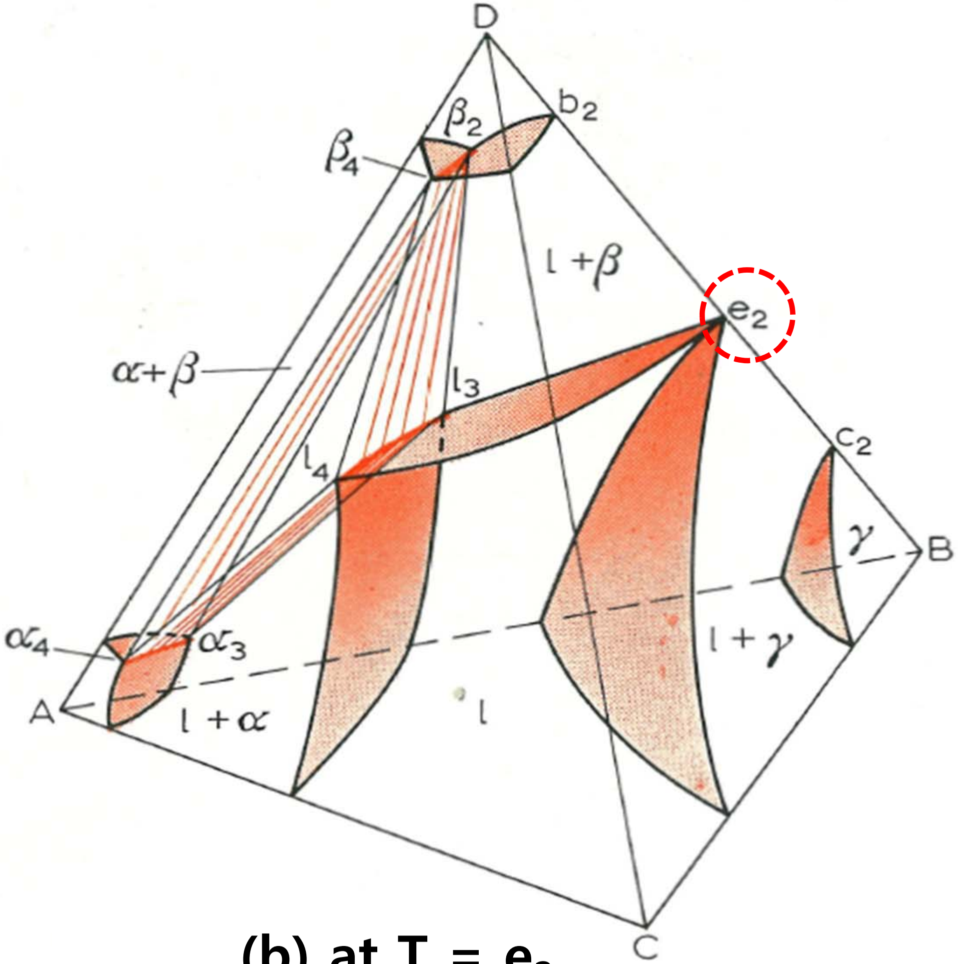
Changes in solid solubility for the α phase

Isobaric-isothermal sections $T_D > T_A > T_B > e_1 > e_2 > T_C > e_3 > e_4 > e_5 > E_1 > E_2$

Through the quaternary system of Fig. 264



(a) at T = e_1



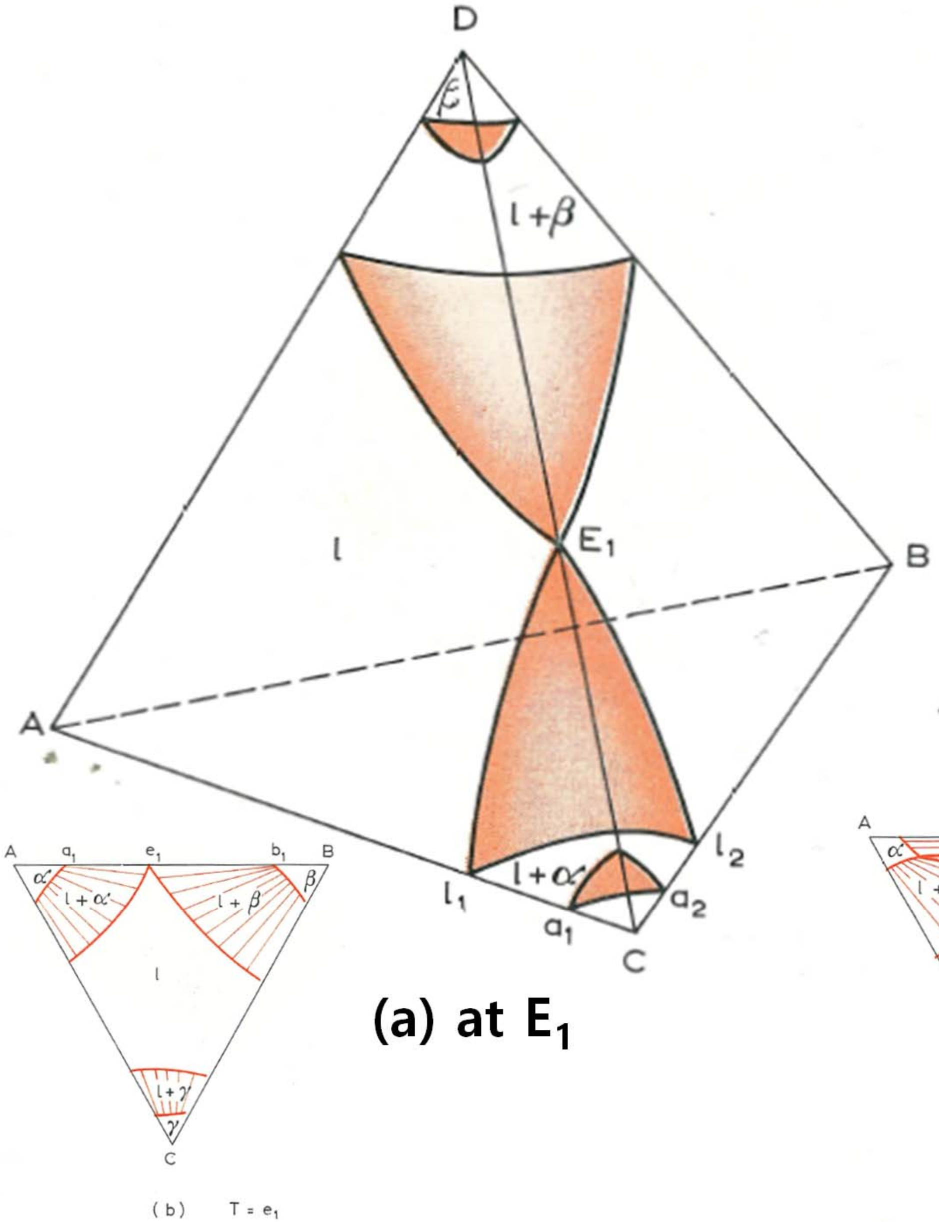
(b) at T = e_2

* Initiation of 1st three phase (l+α+β) region
→ appears in the ternary ACD and ABD

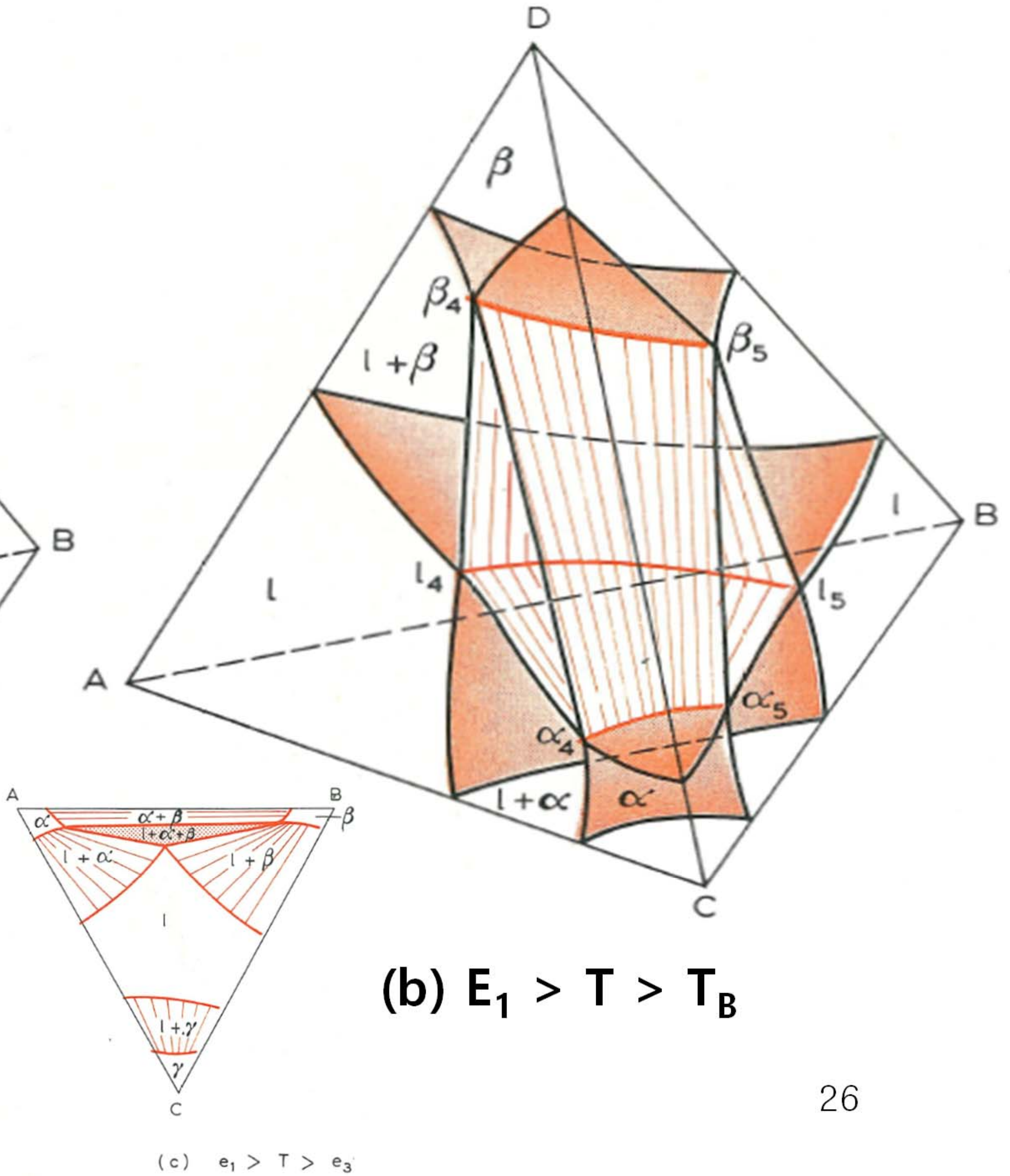
* Initiation of 2nd three phase (l+β+γ) region
→ appears in the ternary ABD and BCD

$T_D > T_C > E_1 > T_B > T_A > E_2 > E_3$

Fig. 256. Isobaric-isothermal sections through the quaternary system of Fig. 255



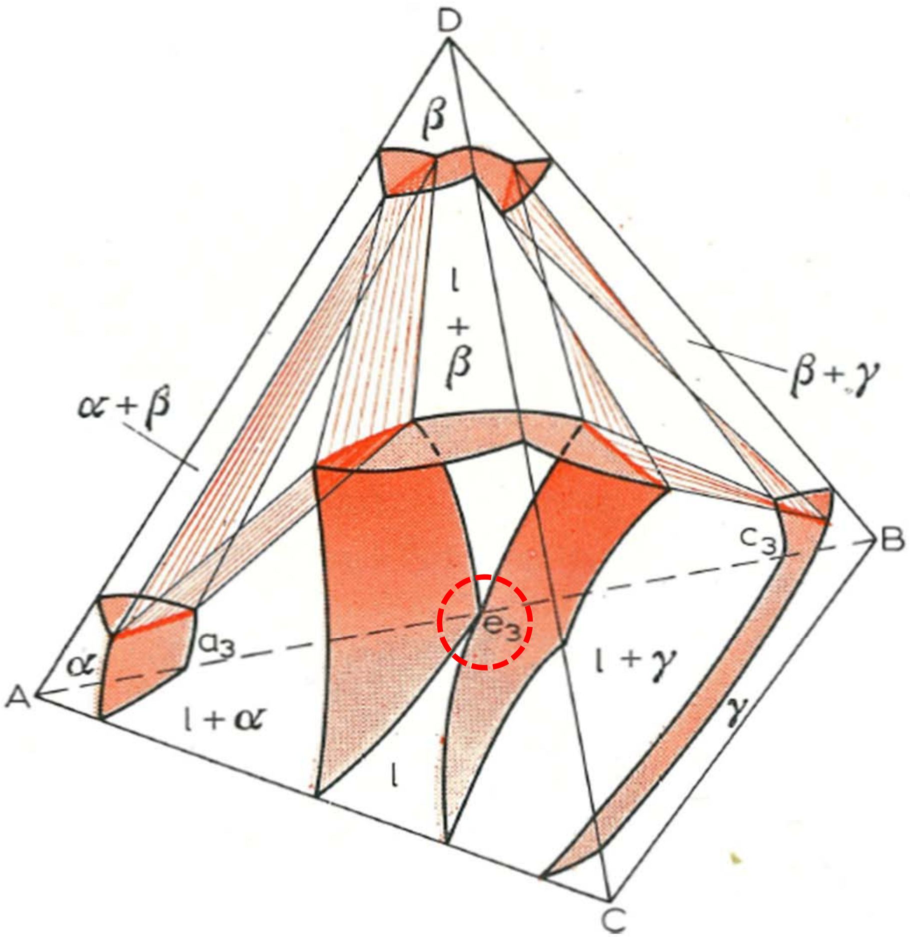
(a) at E_1



(b) $E_1 > T > T_B$

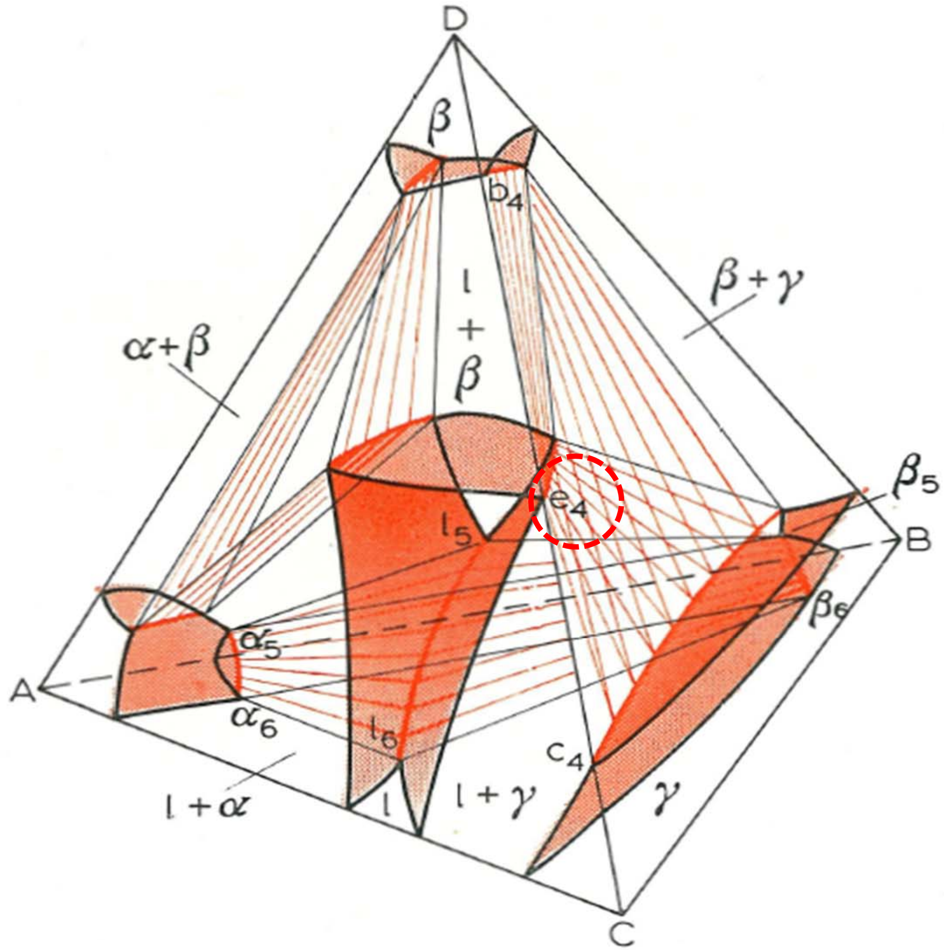
Isobaric-isothermal sections $T_D > T_A > T_B > e_1 > e_2 > T_C > e_3 > e_4 > e_5 > E_1 > E_2$

Through the quaternary system of Fig. 264



(c) at T = e_3

* Initiation of 3rd three phase (l+α+γ) region
→ appears in the ternary ABD and ABC



(d) at T = e_4

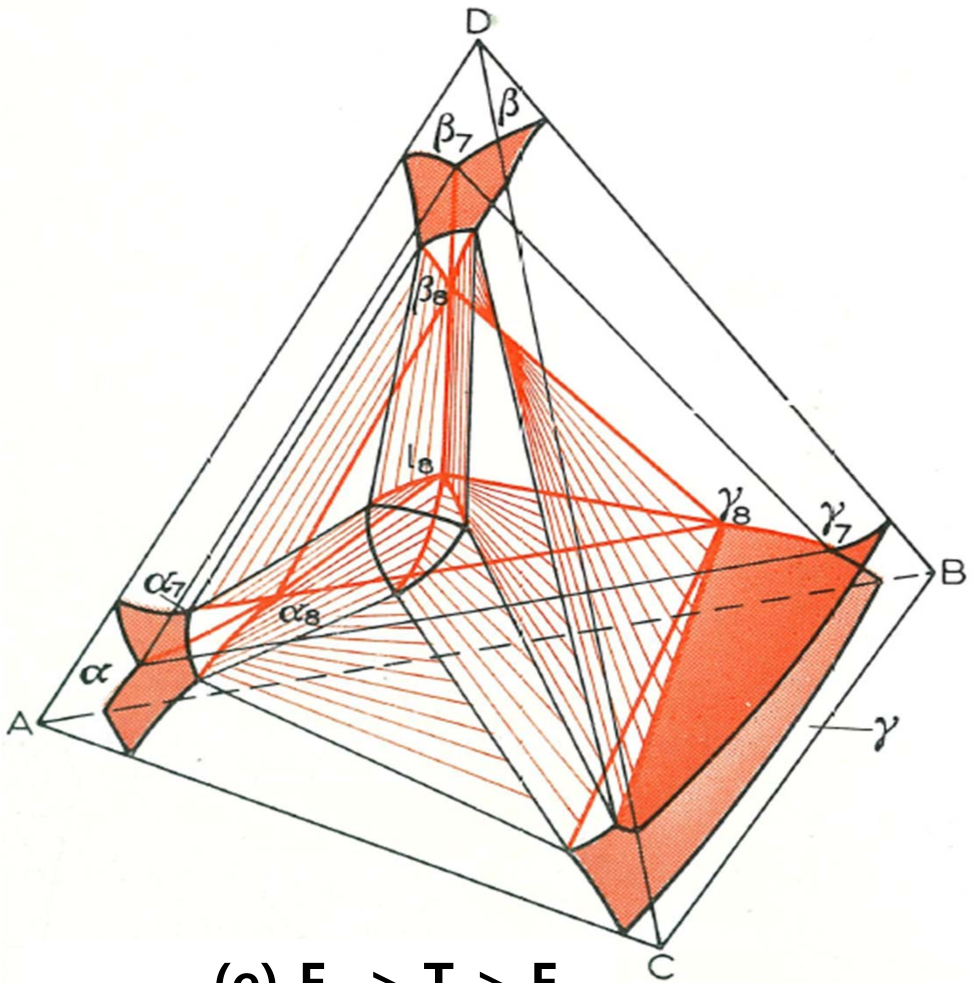
* The liquid phase is restricted to a space which funnels from a triangular region within the ABD face to the rectangular region on the ACD face with a small triangular region on the ABC face.

Isobaric-isothermal sections $T_D > T_A > T_B > e_1 > e_2 > T_C > e_3 > e_4 > e_5 > E_1 > E_2$

Through the quaternary system of Fig. 264

* at T = e_5, three phase ($l+\alpha+\gamma$) region will degenerate into the tie line $a_5e_5c_5$ on edge AC.

* Below e_5, three phase ($l+\alpha+\gamma$) region will make its first appearance on face ACD.



(e) $E_1 > T > E_2$

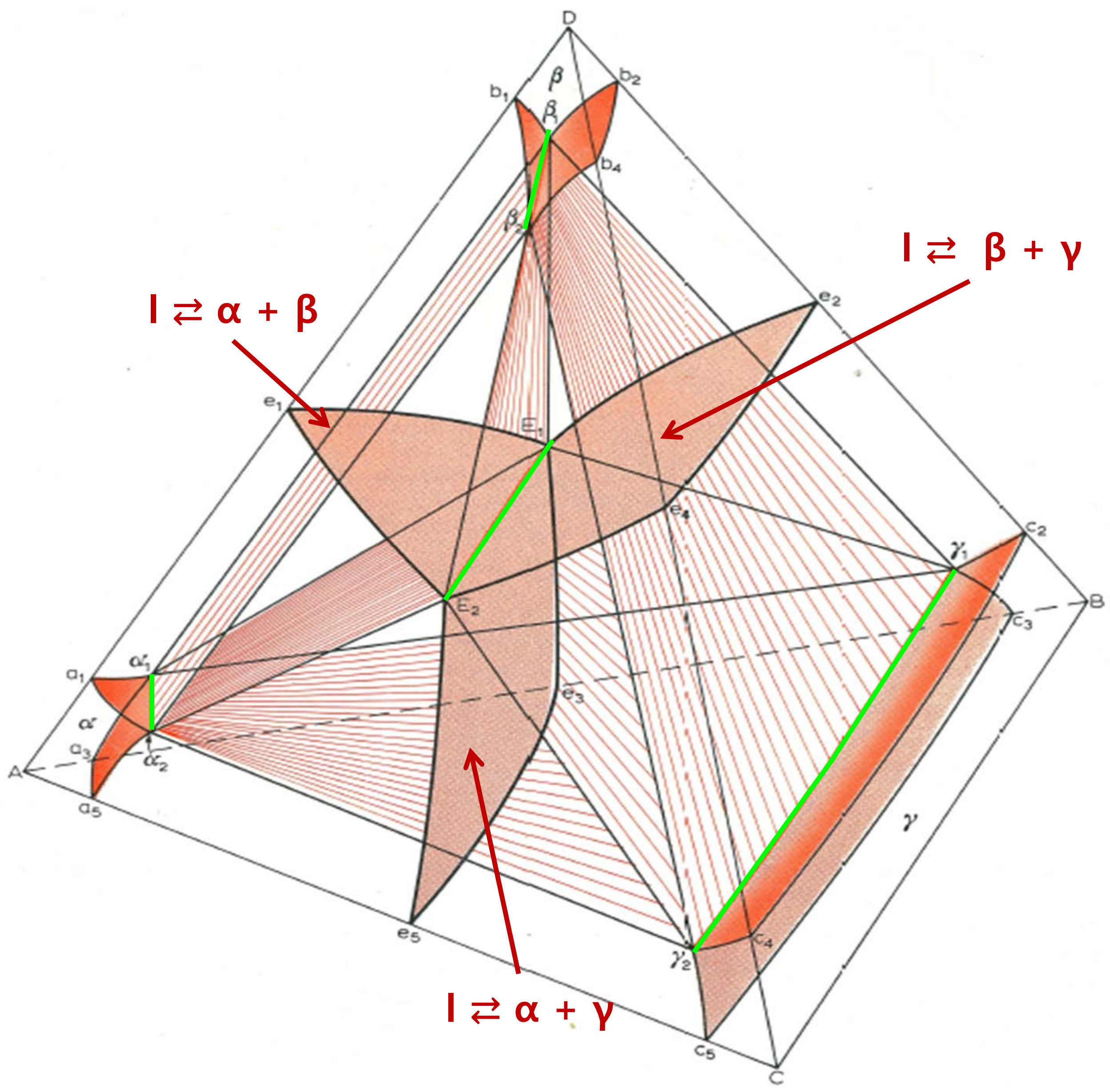
* Below E_1 on face ABD
: ($\alpha+\beta+\gamma$) region will appear on face ABD.
→ $\alpha\beta\gamma$ surface extend from tie triangle $\alpha_7\beta_7\gamma_7$ to $\alpha\beta\gamma$ surface $\alpha_8\beta_8\gamma_8$.

* surface $\alpha_8\beta_8\gamma_8$ is one surface of the tie tetrahedron which represents equilibrium between l, α, β and γ.

* Points l_8, α_8, β_8 and γ_8 lie on curve E_1E_2, $\alpha_1\alpha_2$, $\beta_1\beta_2$, and $\gamma_1\gamma_2$ (Fig. 264,NEXT page).

Fig. 264. Polythermal projection of a quaternary system involving four-phase equilibrium of the type l ⇄ α + β + γ

$T_D > T_A > T_B > e_1 > e_2 > T_C > e_3 > e_4 > e_5 > E_1 > E_2$

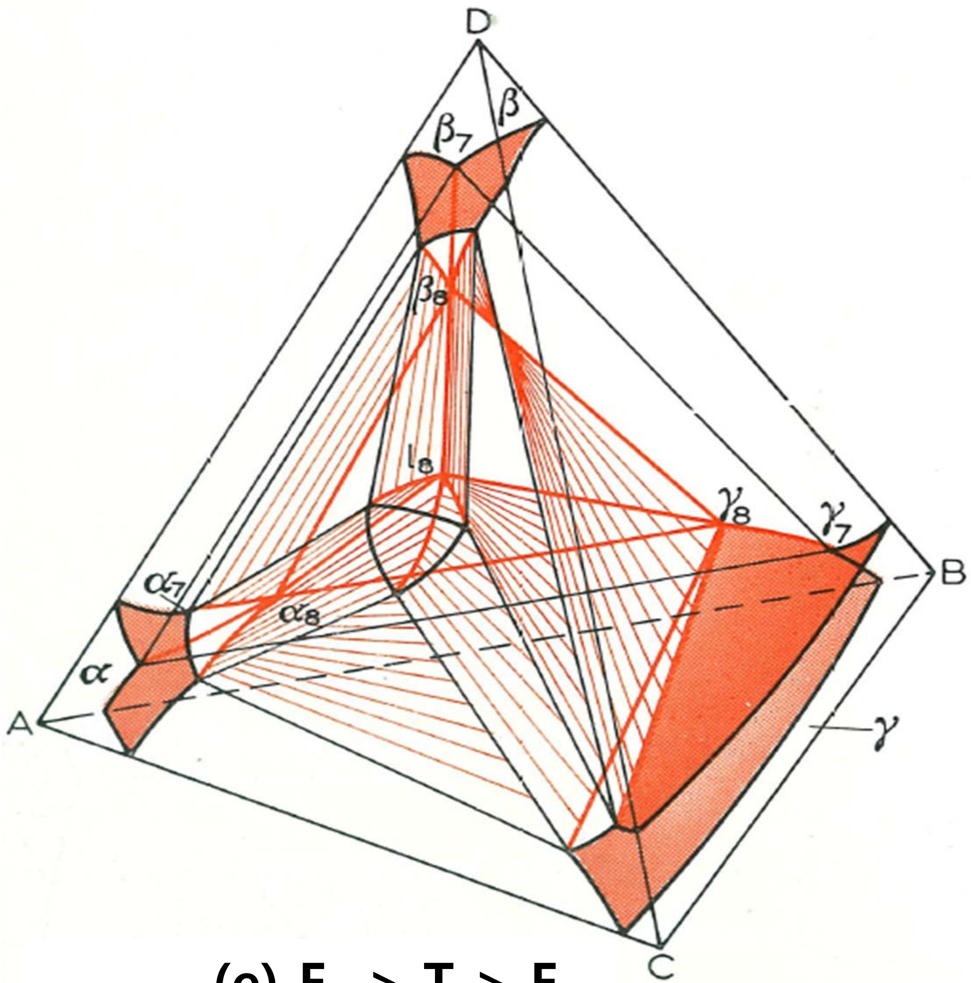


Isobaric-isothermal sections $T_D > T_A > T_B > e_1 > e_2 > T_C > e_3 > e_4 > e_5 > E_1 > E_2$

Through the quaternary system of Fig. 264

* **at T = e_5**, three phase ($l+\alpha+\gamma$) region will degenerate into the tie line $a_5e_5c_5$ on edge AC.

* **Below e_5**, three phase ($l+\alpha+\gamma$) region will make its first appearance on face ACD.



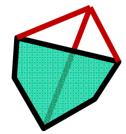
(e) $E_1 > T > E_2$

* Below E_1 on face ABD
  : ($\alpha+\beta+\gamma$) region will appear on face ABD.
  → $\alpha\beta\gamma$ surface extend from tie triangle $\alpha_7\beta_7\gamma_7$ to $\alpha\beta\gamma$ surface $\alpha_8\beta_8\gamma_8$.

* surface $\alpha_8\beta_8\gamma_8$ is one surface of the tie tetrahedron which represents equilibrium between l, α, β and γ.

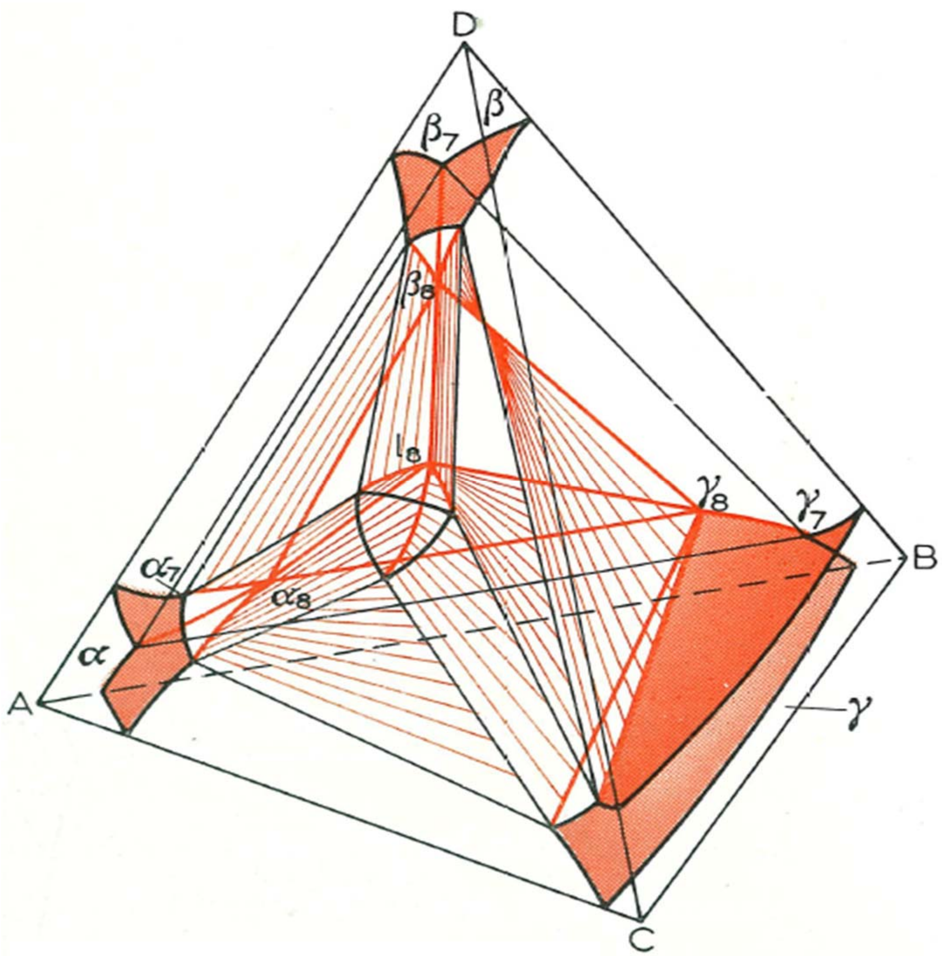
* Points l_8, α_8, β_8 and γ_8 lie on curve E_1E_2, $\alpha_1\alpha_2$, $\beta_1\beta_2$, and $\gamma_1\gamma_2$ (Fig. 264).

* The liquid region is now a curved tetrahedron based on the ternary face ACD.

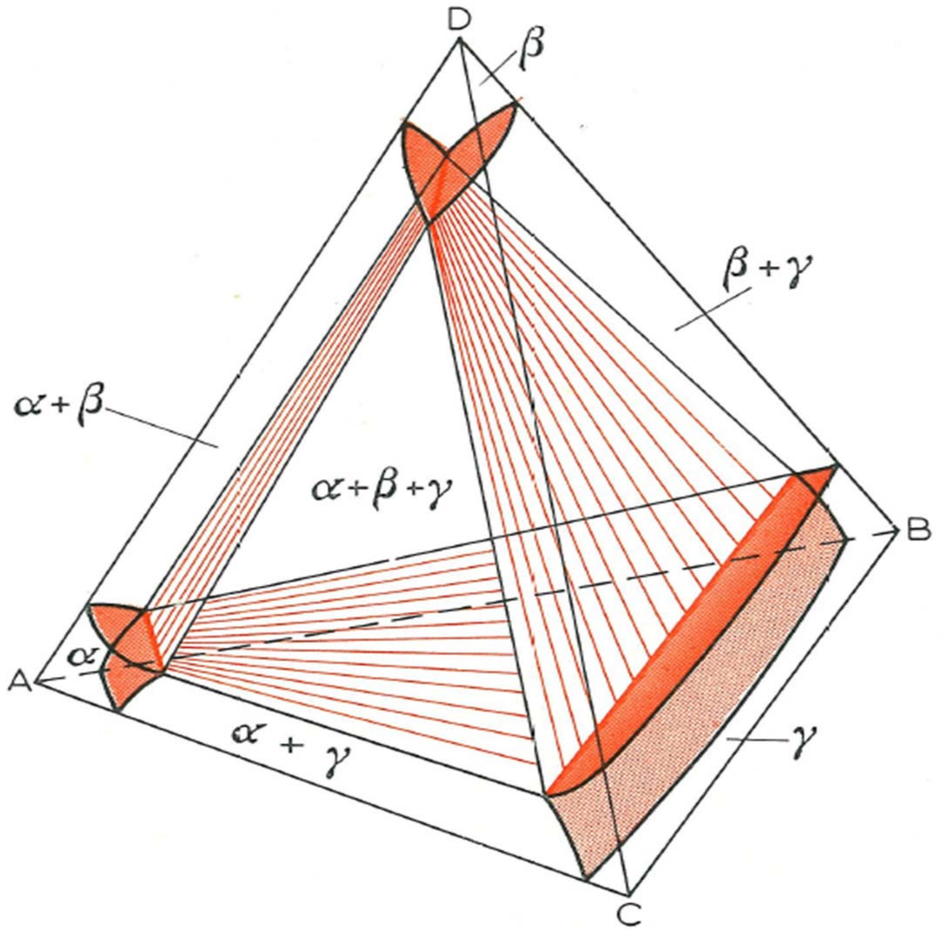


Isobaric-isothermal sections $T_D > T_A > T_B > e_1 > e_2 > T_C > e_3 > e_4 > e_5 > E_1 > E_2$

Through the quaternary system of Fig. 264

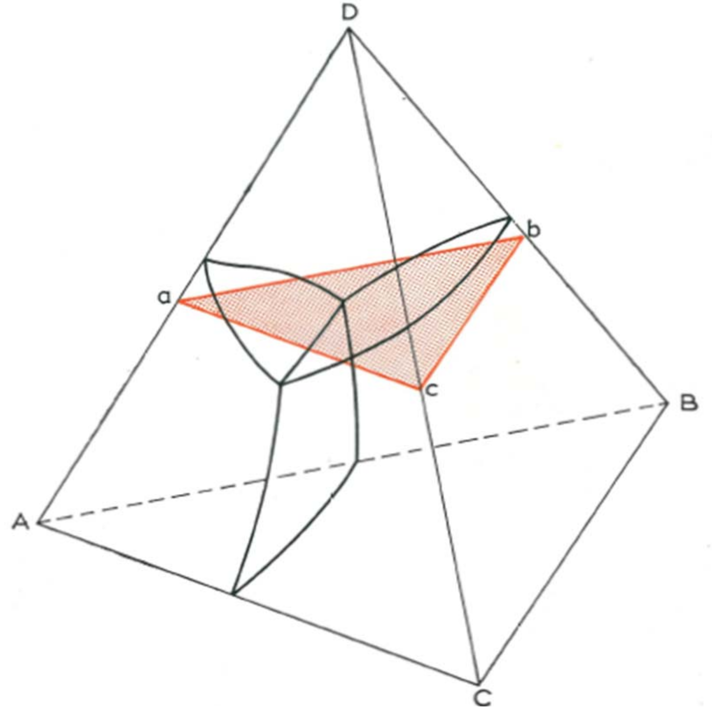


(e) $E_1 > T > E_2$

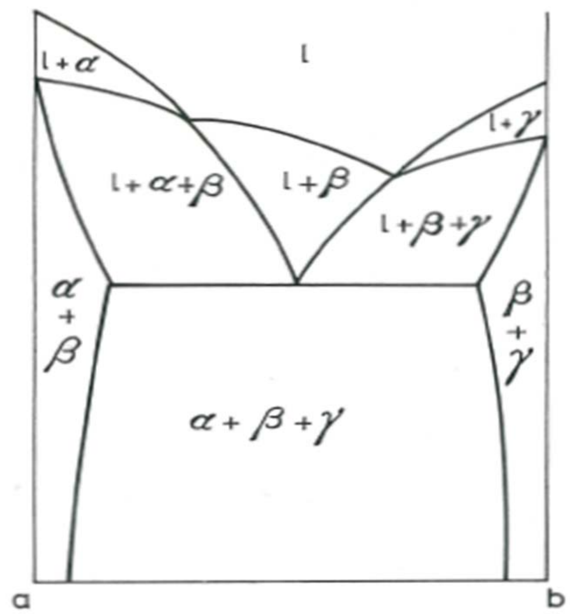


(f) $E_2 > T$

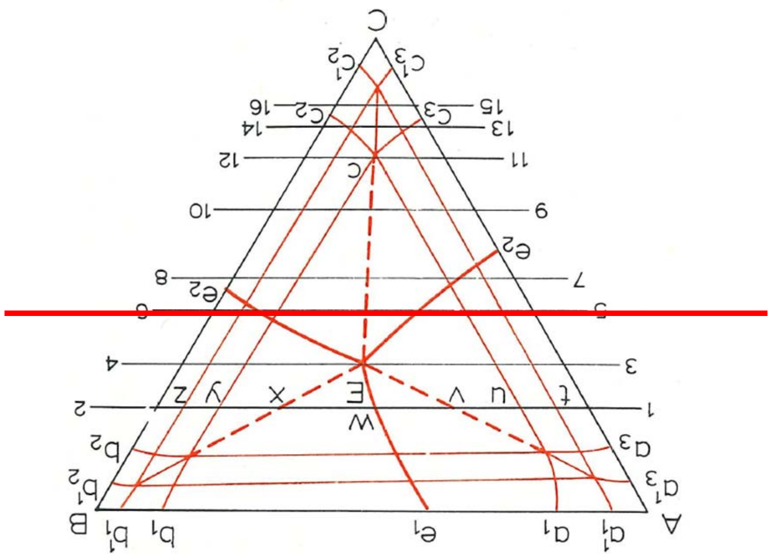
Vertical sections on constant %D



(a) Location of alloys under consideration



(b) Vertical sections of the ternary system



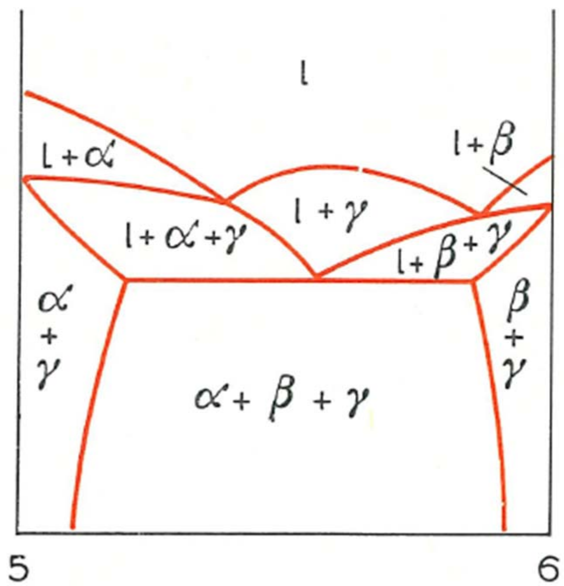


Fig. 264. Polythermal projection of a quaternary system involving four-phase equilibrium of the type l ⇄ α + β + γ

$T_D > T_A > T_B > e_1 > e_2 > T_C > e_3 > e_4 > e_5 > E_1 > E_2$

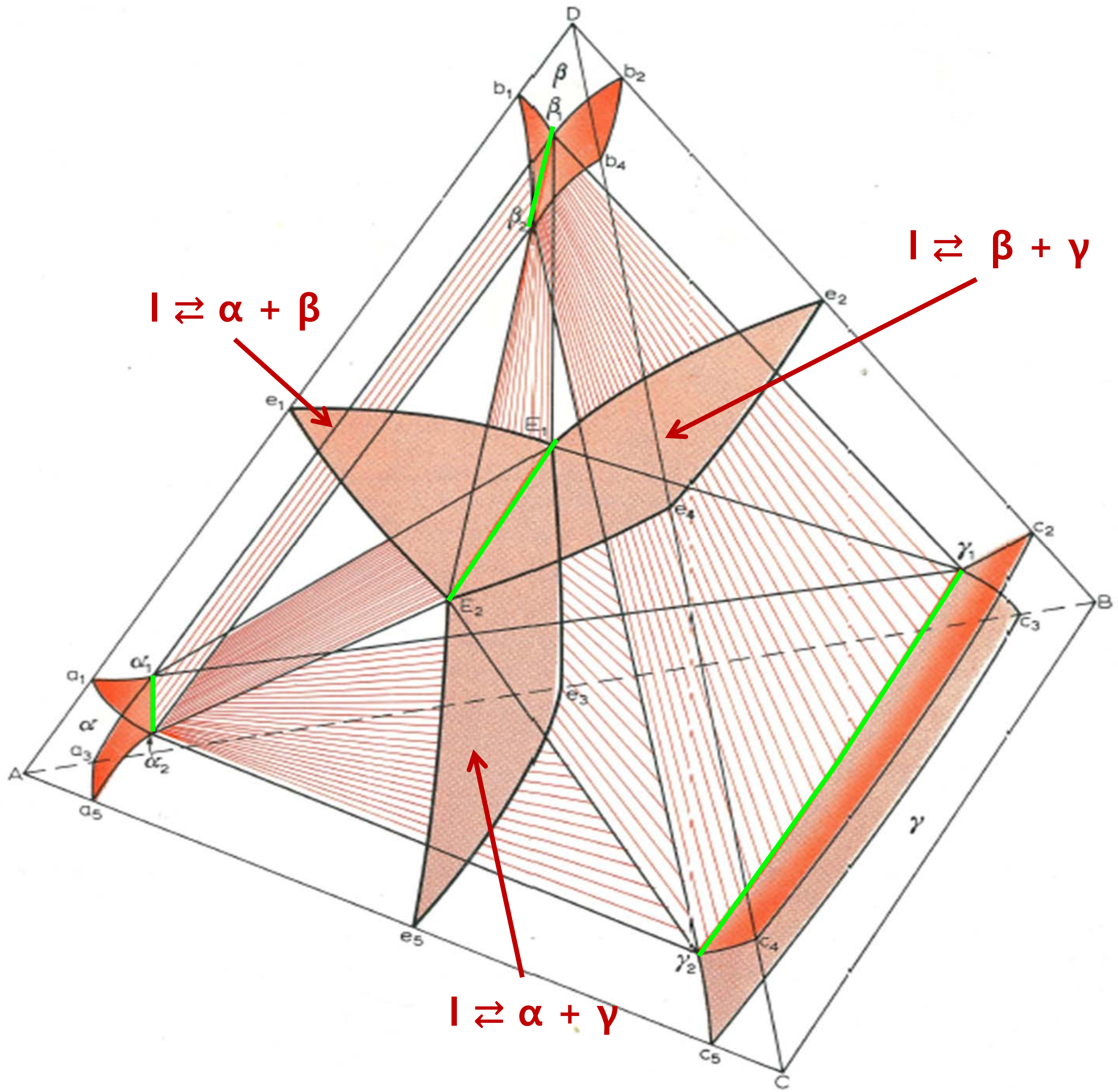
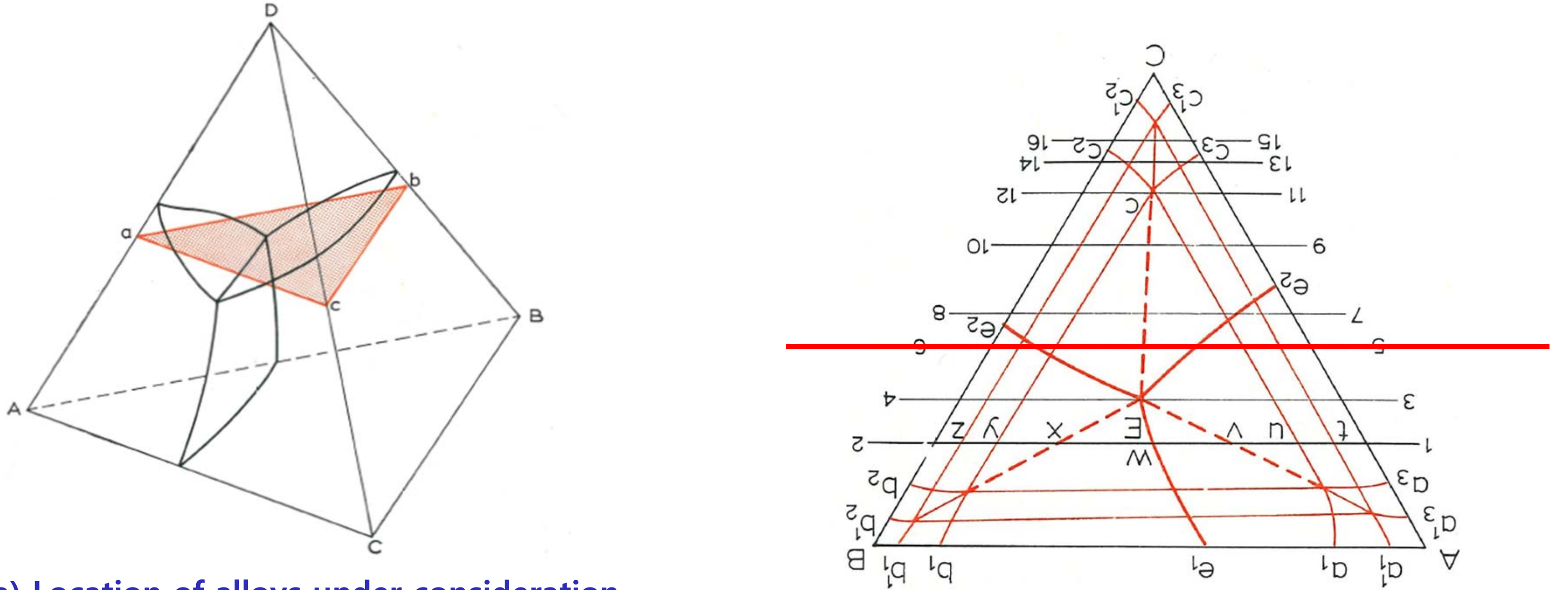
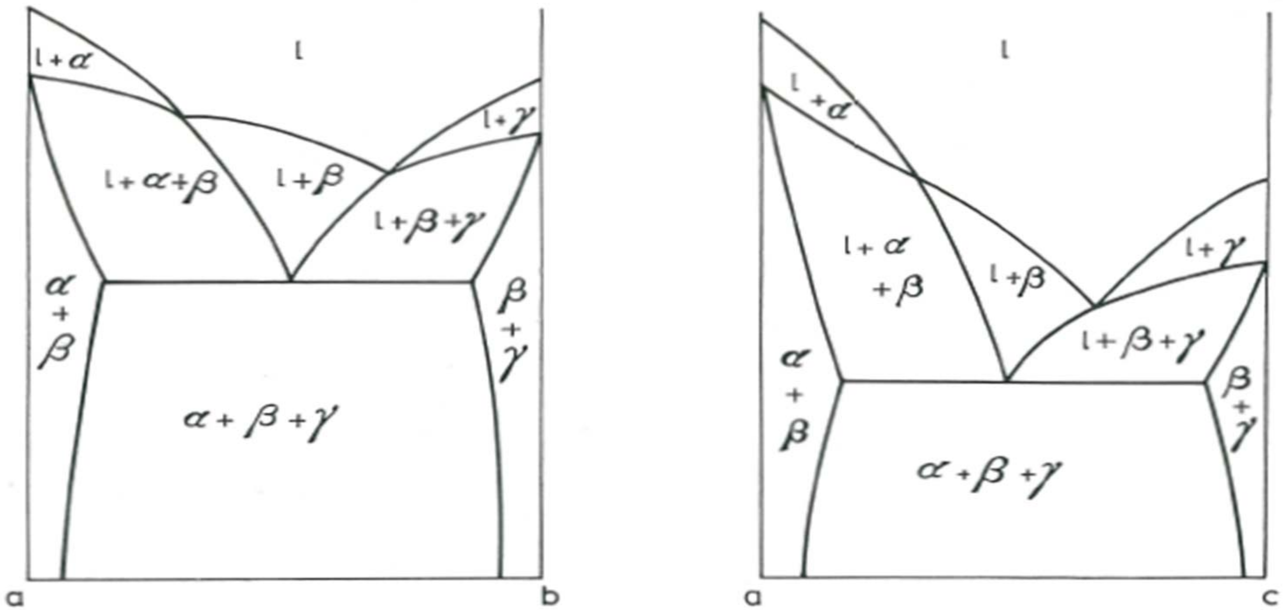


Fig. 267 Vertical sections on constant %D

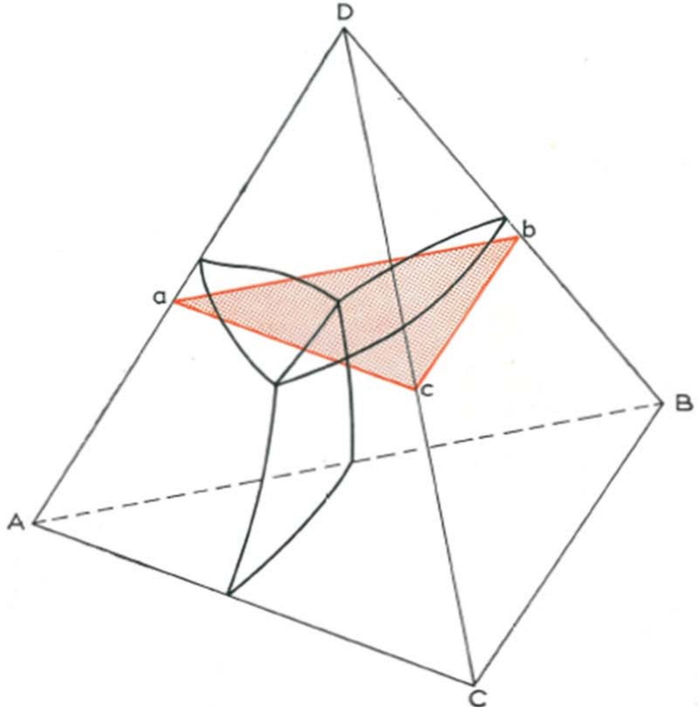


(a) Location of alloys under consideration

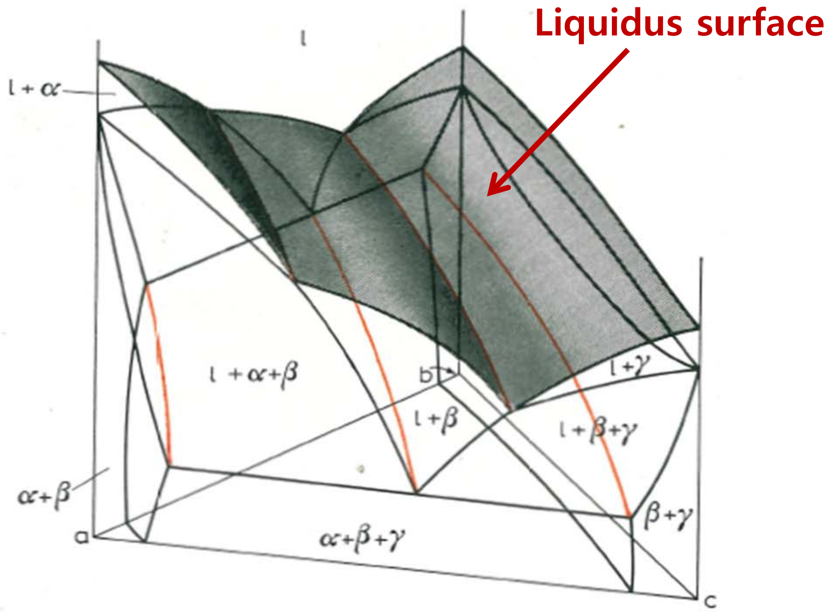


(b) Vertical sections of the ternary system

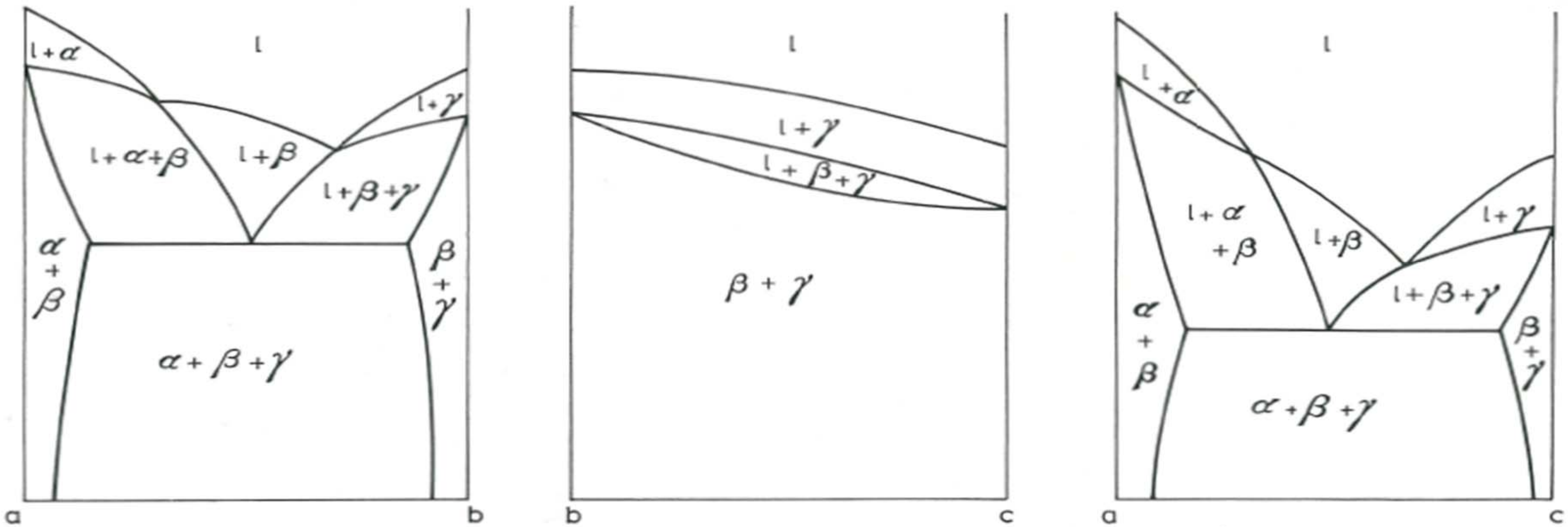
Fig. 267 Vertical sections on constant %D



(a) Location of alloys under consideration

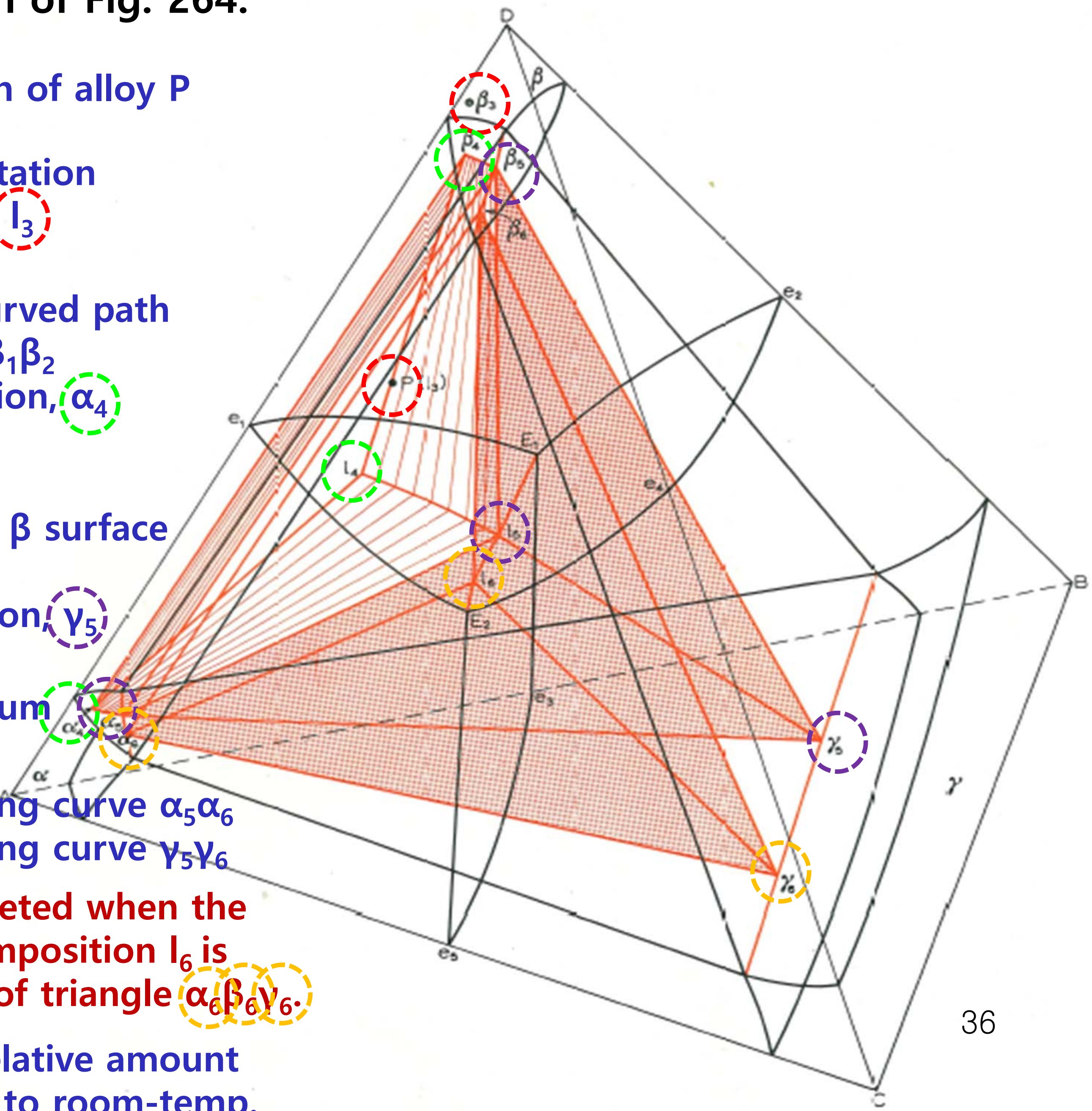


(c) Quaternary temp.-concentration section



(b) Vertical sections of the ternary system

Fig. 268. Freezing of quaternary alloy P illustrated by reference to the polythermal projection of Fig. 264.



* Consider the solidification of alloy P

1) β solid solution precipitation with β_3 composition ⇔ l_3

2) $l_3 \rightarrow l_4$ on $e_1E_1E_2e_1$: a curved path
   $\beta_3 \rightarrow \beta_4$ on β surface $b_1\beta_1\beta_2$
   Initiation of α precipitation, α_4

3) Move over tracing path
   l_4l_5 on $e_1E_1E_2e_1$/ $\beta_4\beta_5$ on β surface
   $\alpha_4\alpha_5$ on α surface
   Initiation of γ precipitation, γ_5
   → $l_5\alpha_5\beta_5\gamma_5$ tetrahedron :
   now four phase equilibrium

4) Liquid moves l_5E_2/ α along curve $\alpha_5\alpha_6$
   β along curve $\beta_5\beta_6$/γ along curve $\gamma_5\gamma_6$
   → solidification is completed when the last drop of liquid of composition l_6 is consumed on the plane of triangle $\alpha_6\beta_6\gamma_6$.

5) Further change in the relative amount α, β, γ with fall in temp. to room-temp.

15.5 FIVE-PHASE EQUILIBRIUM

In an isobaric section of a quaternary system, five phases can only exist in equilibrium at one temperature (invariant reaction).

* invariant reaction (1) l ⇄ α + β + γ + δ quaternary eutectic
(2) l + α ⇄ β + γ + δ 2-3 quaternary quasi-peritectic
(3) l + α + β ⇄ γ + δ 3-2 quaternary quasi-peritectic
(4) l + α + β + γ ⇄ δ quaternary peritectic.

(1) Quaternary eutectic l ⇄ α + β + γ + δ

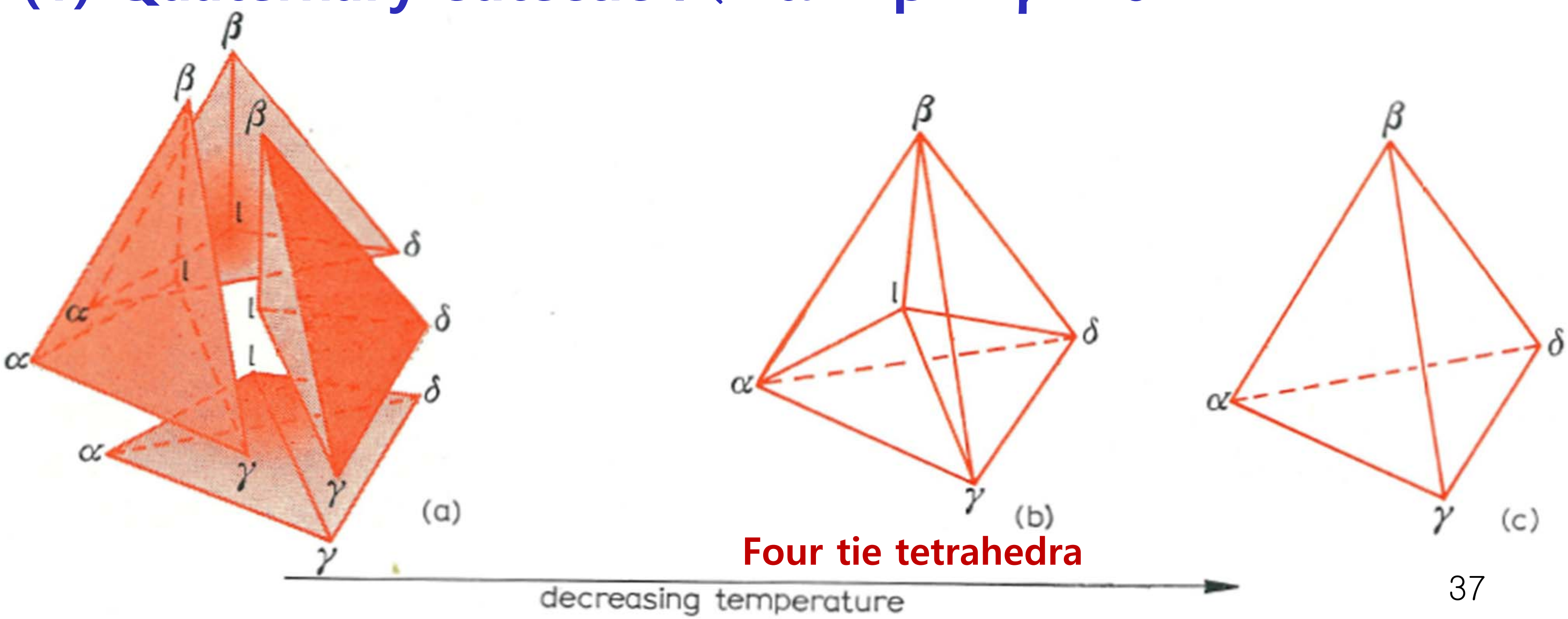


Fig. 269. Sequence of tie-tetrahedron on cooling through the quaternary eutectic temperature

15.5 FIVE-PHASE EQUILIBRIUM

(2) 2-3 Qaternary quasi-peritectic l + α ⇄ β + γ + δ

$$
\begin{array}{l}
l + \alpha \rightleftarrows X \\
X \rightleftarrows \beta + \gamma + \delta \\
\hline
l + \alpha \rightleftarrows \beta + \gamma + \delta
\end{array}
$$

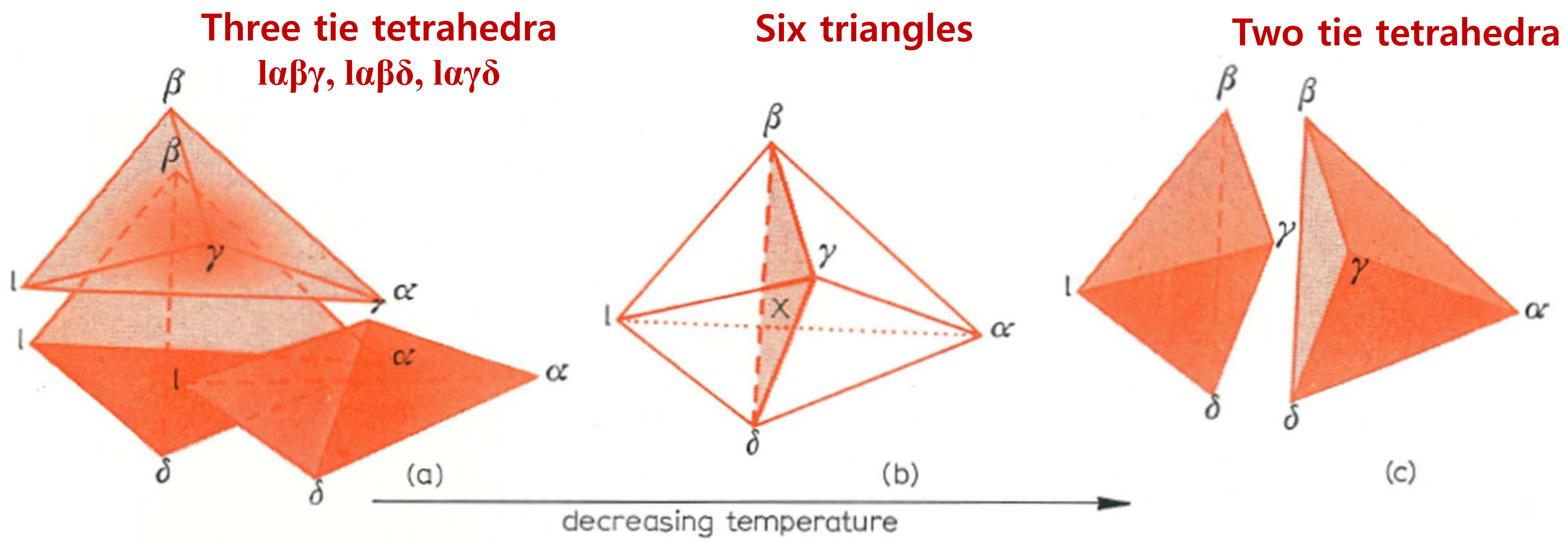


Fig. 270. Sequence of tie-tetrahedra on cooling through the quaternary 2-3 quasi-peritectic temperature

15.5 FIVE-PHASE EQUILIBRIUM

(3) 3-2 Qaternary quasi-peritectic l + α + β ⇄ γ + δ

l + α + β ⇄ Υ

Υ ⇄ γ + δ

---

l + α + β ⇄ γ + δ

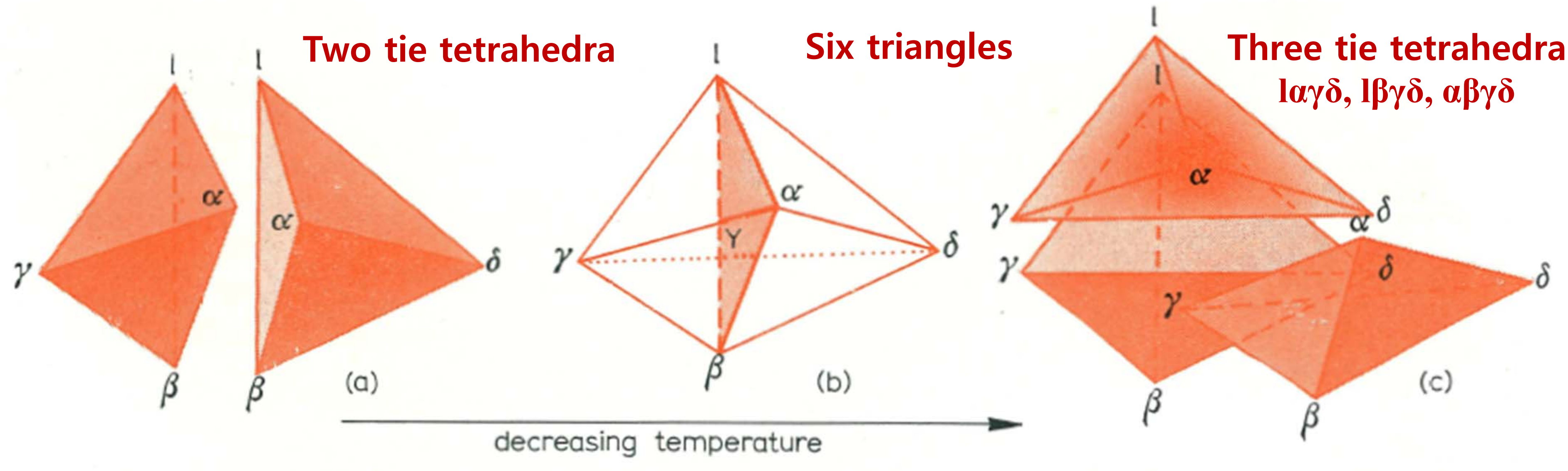
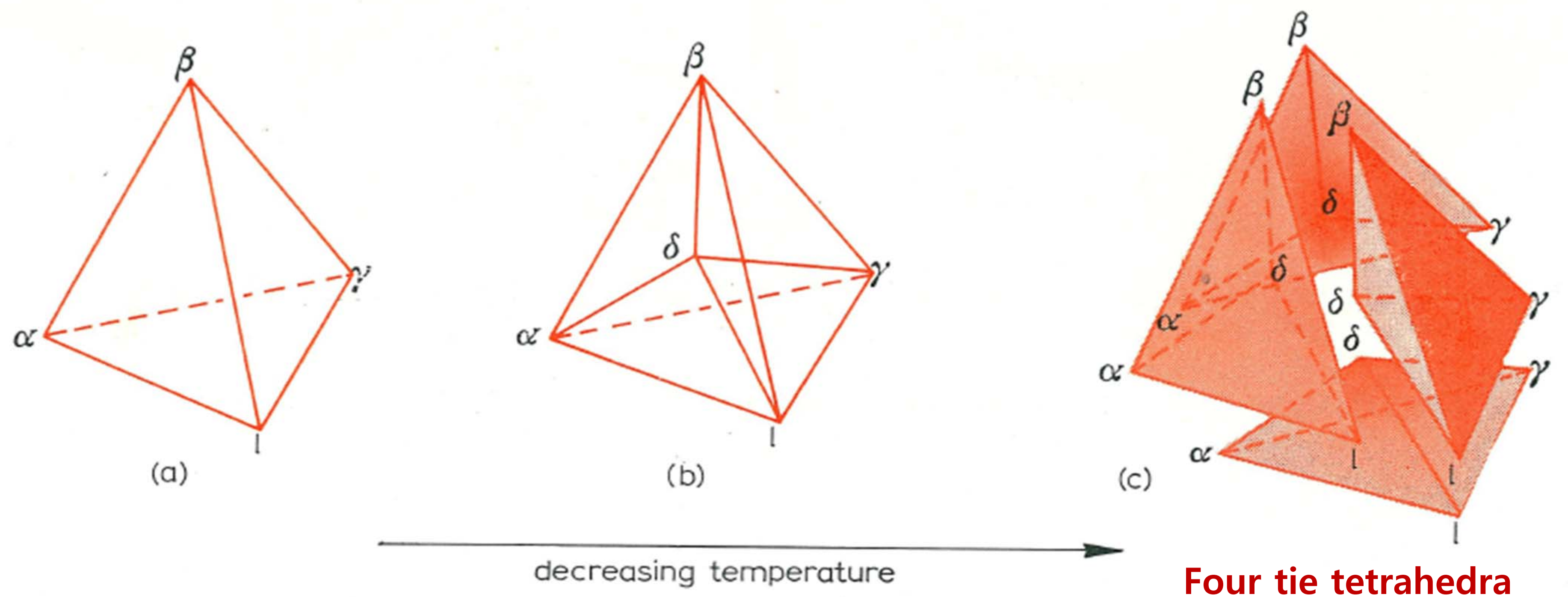


Fig. 271. Sequence of tie-tetrahedra on cooling through the quaternary 3-2 quasi-peritectic temperature

15.5 FIVE-PHASE EQUILIBRIUM

(4) Qaternary quasi-peritectic l + α + β + γ ⇄ δ



Four tie tetrahedra
lαβδ, lαγδ, lβγδ, αβγδ

Fig. 272. Sequence of tie-tetrahedra on cooling through the quaternary peritectic temperature

Fig. 273. Polythermal projectin of a quaternary system involving five-phase equilibrium of the type l ⇄ α + β + γ + δ (schematic representation of the Bi-Cd-Pb-Sn quaternary eutectic system).

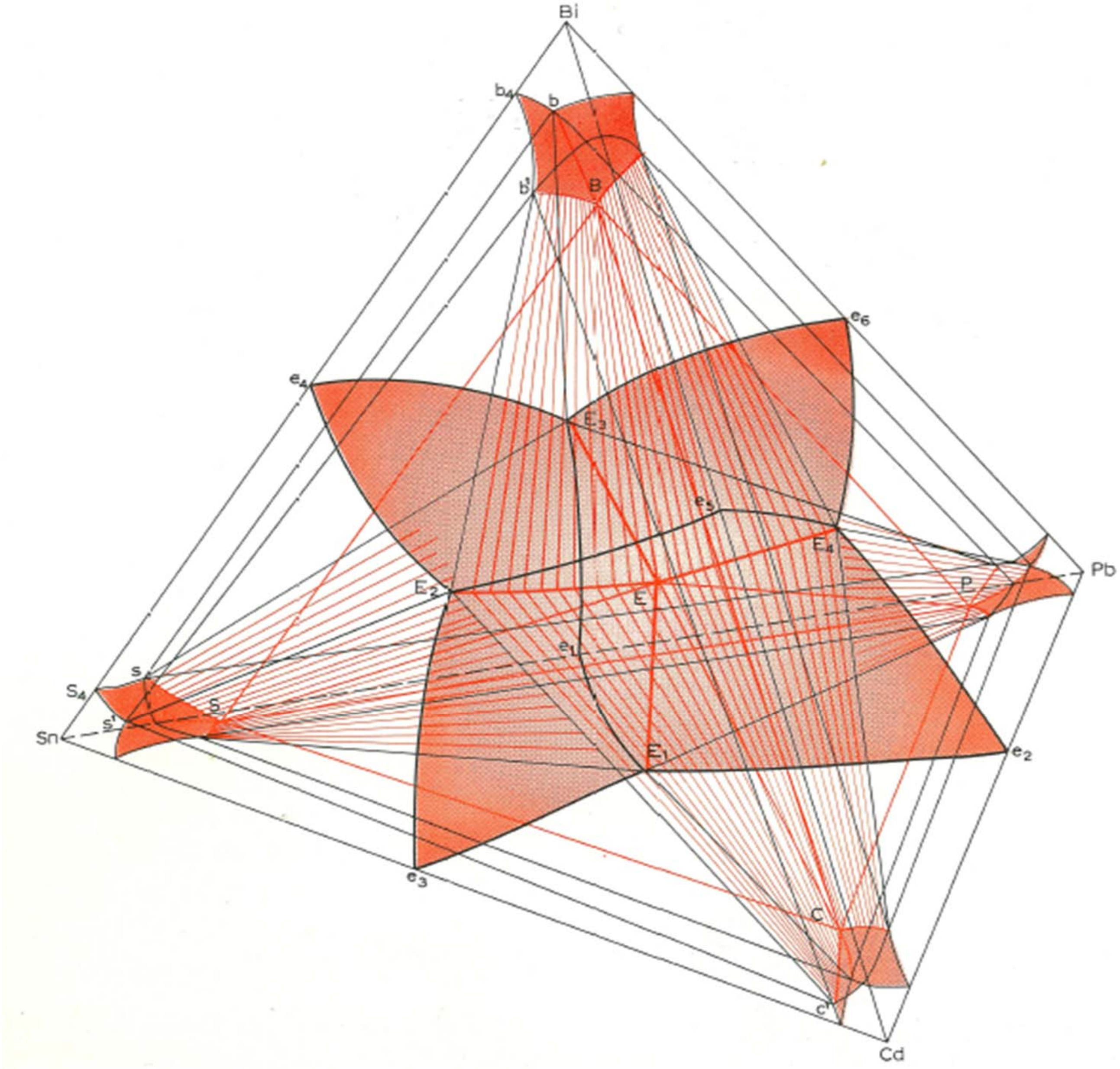


Fig. 274. Regions of primary crystallization in the Bi-Cd-Pb-Sn system

*** Primary crystallization**

Bi region/ Pb region/
Cd region/ Sn region/

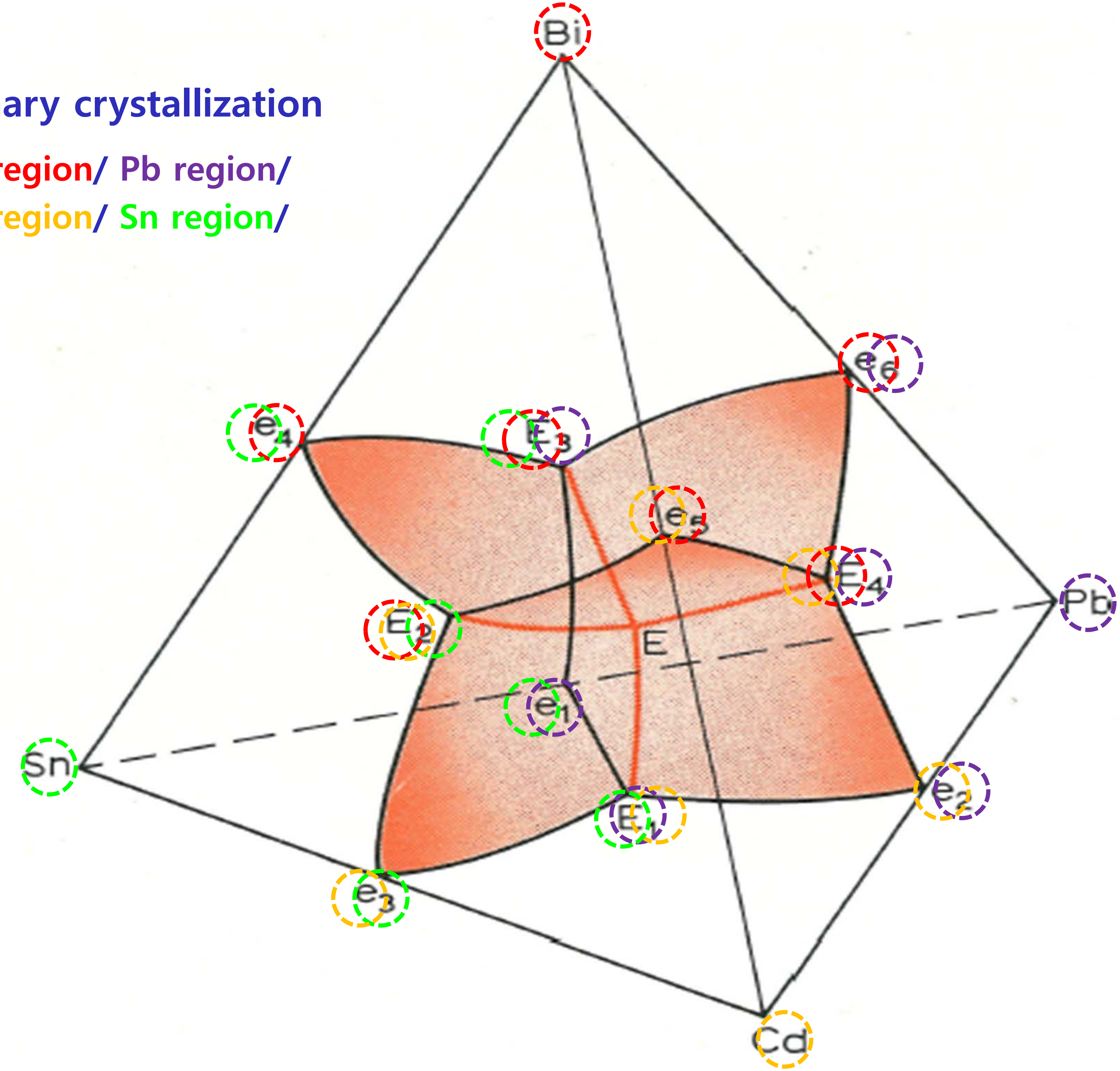


Fig. 275. Regions of secondary crystallization in the Bi-Cd-Pb-Sn system, (a) assuming complete insolubility of the metals in the solid state

* **Secondary crystallization** in which the liquid phase is precipitating two solid phases simultaneously

$l \rightleftharpoons Bi + Sn$ region $(Bi)(Sn)E_2EE_3$

$l \rightleftharpoons Bi + Pb$ region $(Bi)(Pb)E_3EE_4$

$l \rightleftharpoons Bi + Cd$ region $(Bi)(Cd)E_2EE_4$

$l \rightleftharpoons Pb + Sn$ region $(Pb)(Sn)E_1EE_3$

$l \rightleftharpoons Pb + Cd$ region $(Pb)(Cd)E_1EE_4$

$l \rightleftharpoons Cd + Sn$ region $(Cd)(Sn)E_2EE_1$

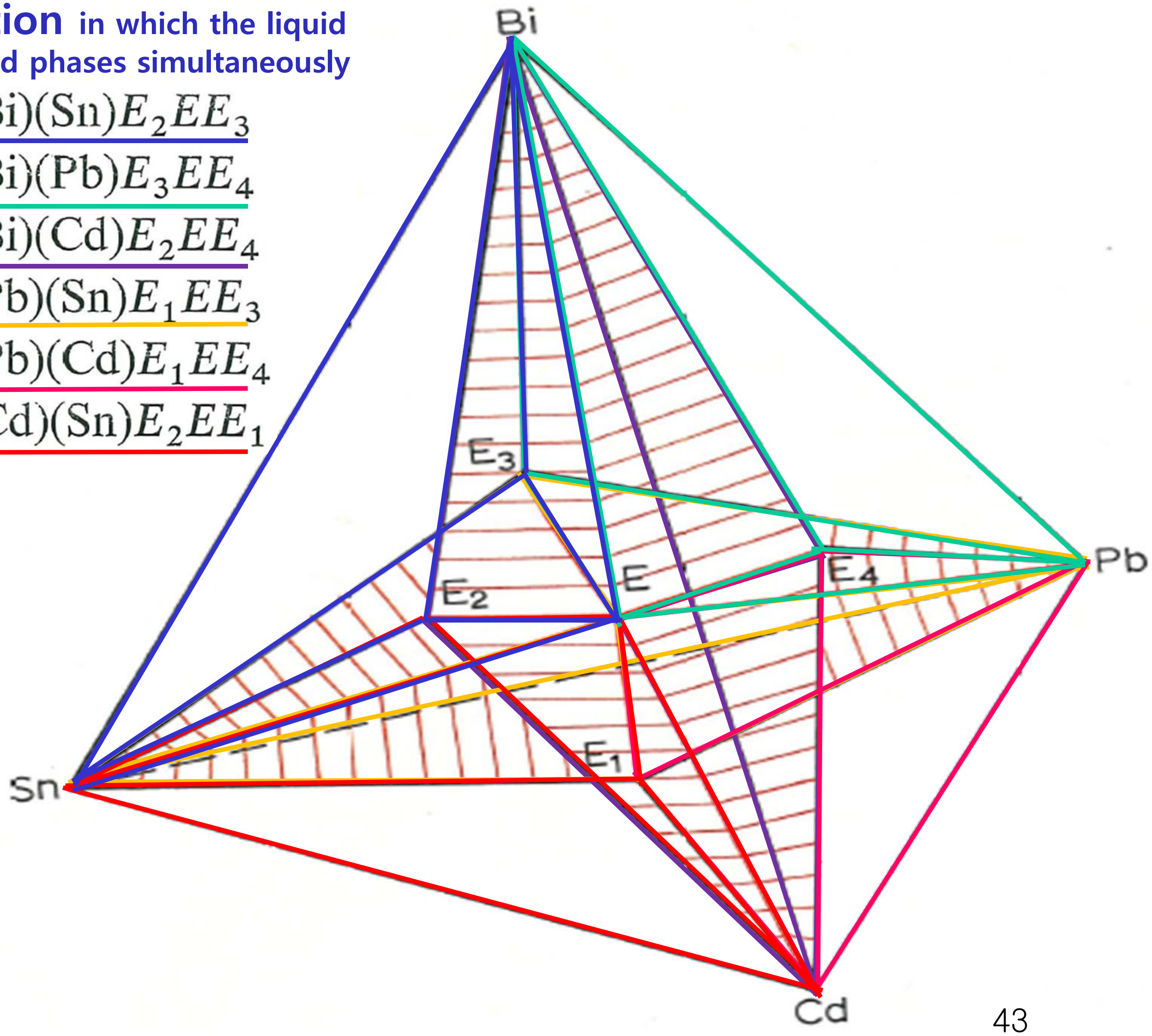


Fig. 275. Regions of secondary crystallization in the Bi-Cd-Pb-Sn system,
(b) with solid solubility

* Secondary crystallization

$l \rightleftharpoons \text{Bi} + \text{Sn}$ region $(\text{Bi})(\text{Sn})E_2EE_3$

$l \rightleftharpoons \text{Bi} + \text{Pb}$ region $(\text{Bi})(\text{Pb})E_3EE_4$

$l \rightleftharpoons \text{Bi} + \text{Cd}$ region $(\text{Bi})(\text{Cd})E_2EE_4$

$l \rightleftharpoons \text{Pb} + \text{Sn}$ region $(\text{Pb})(\text{Sn})E_1EE_3$

$l \rightleftharpoons \text{Pb} + \text{Cd}$ region $(\text{Pb})(\text{Cd})E_1EE_4$

$l \rightleftharpoons \text{Cd} + \text{Sn}$ region $(\text{Cd})(\text{Sn})E_2EE_1$

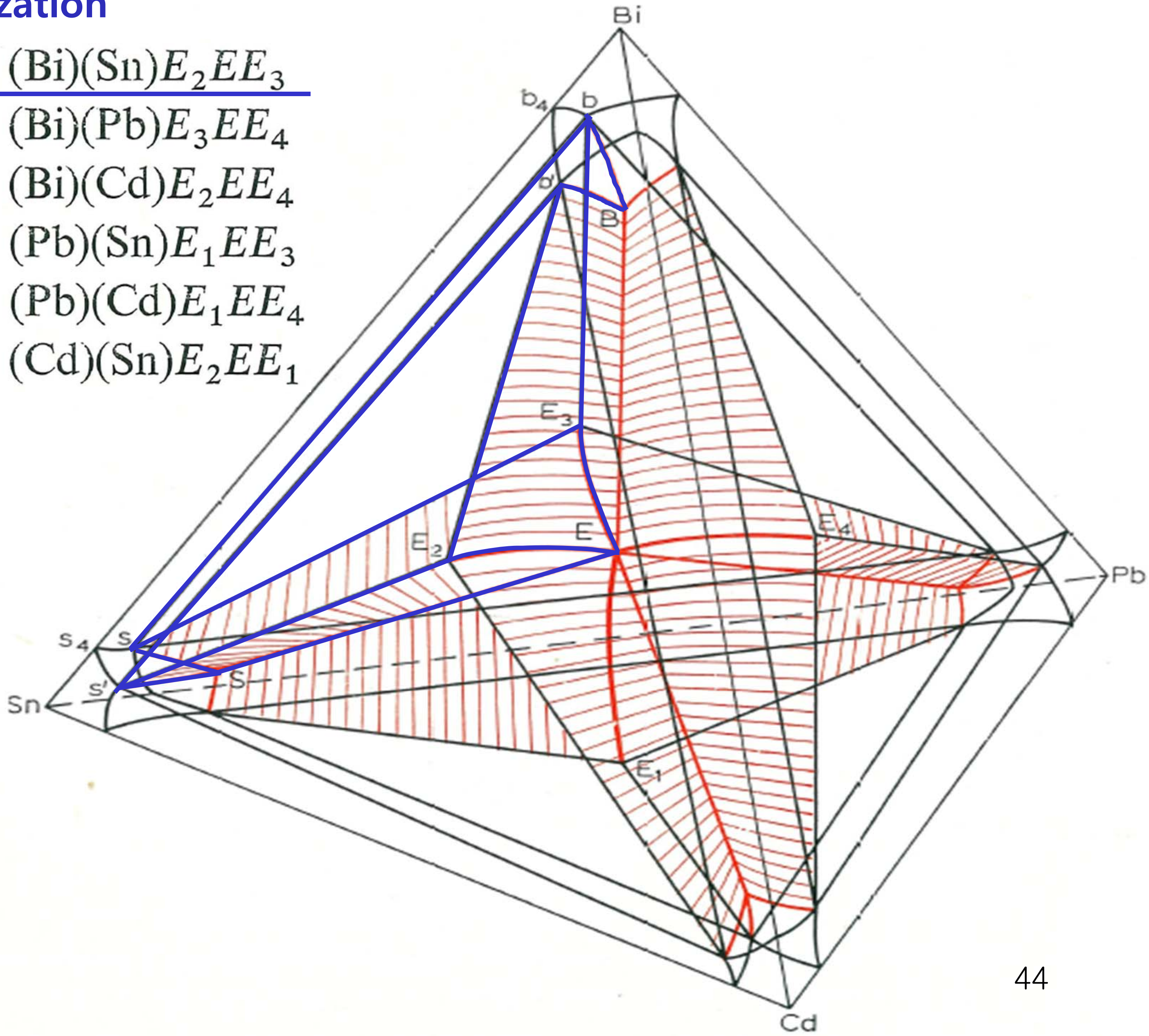
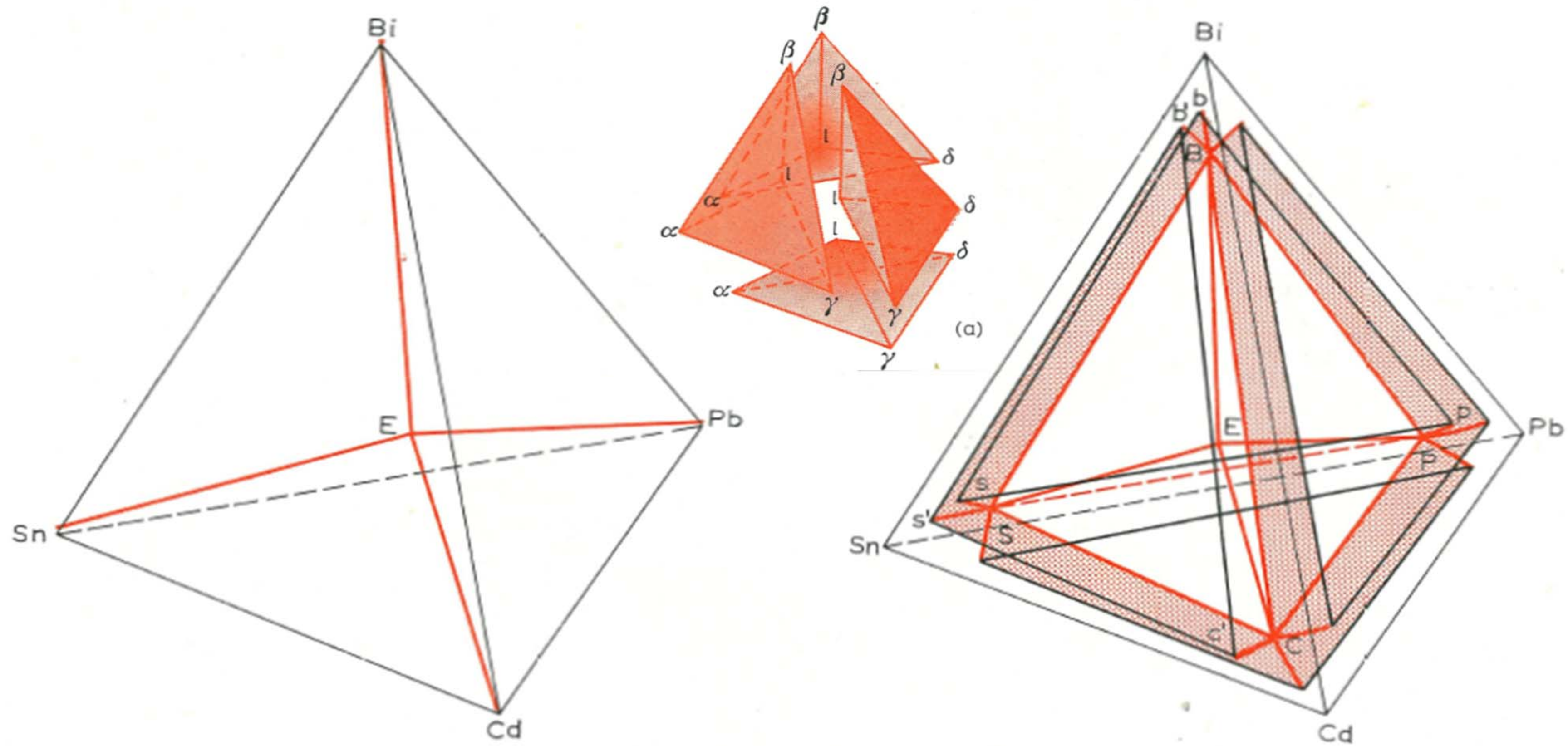


Fig. 276. **Regions of tertiary crystallization** **in the Bi-Cd-Pb-Sn system,**

(a) assuming complete insolubility of the metals in the solid state

(b) with solid solubility

$l \rightleftharpoons Bi + Sn + Pb$	region (Bi)(Sn)(Pb)*E*
$l \rightleftharpoons Bi + Cd + Pb$	region (Bi)(Cd)(Pb)*E*
$l \rightleftharpoons Bi + Cd + Sn$	region (Bi)(Cd)(Sn)*E*
$l \rightleftharpoons Cd + Pb + Sn$	region (Cd)(Pb)(Sn)*E*

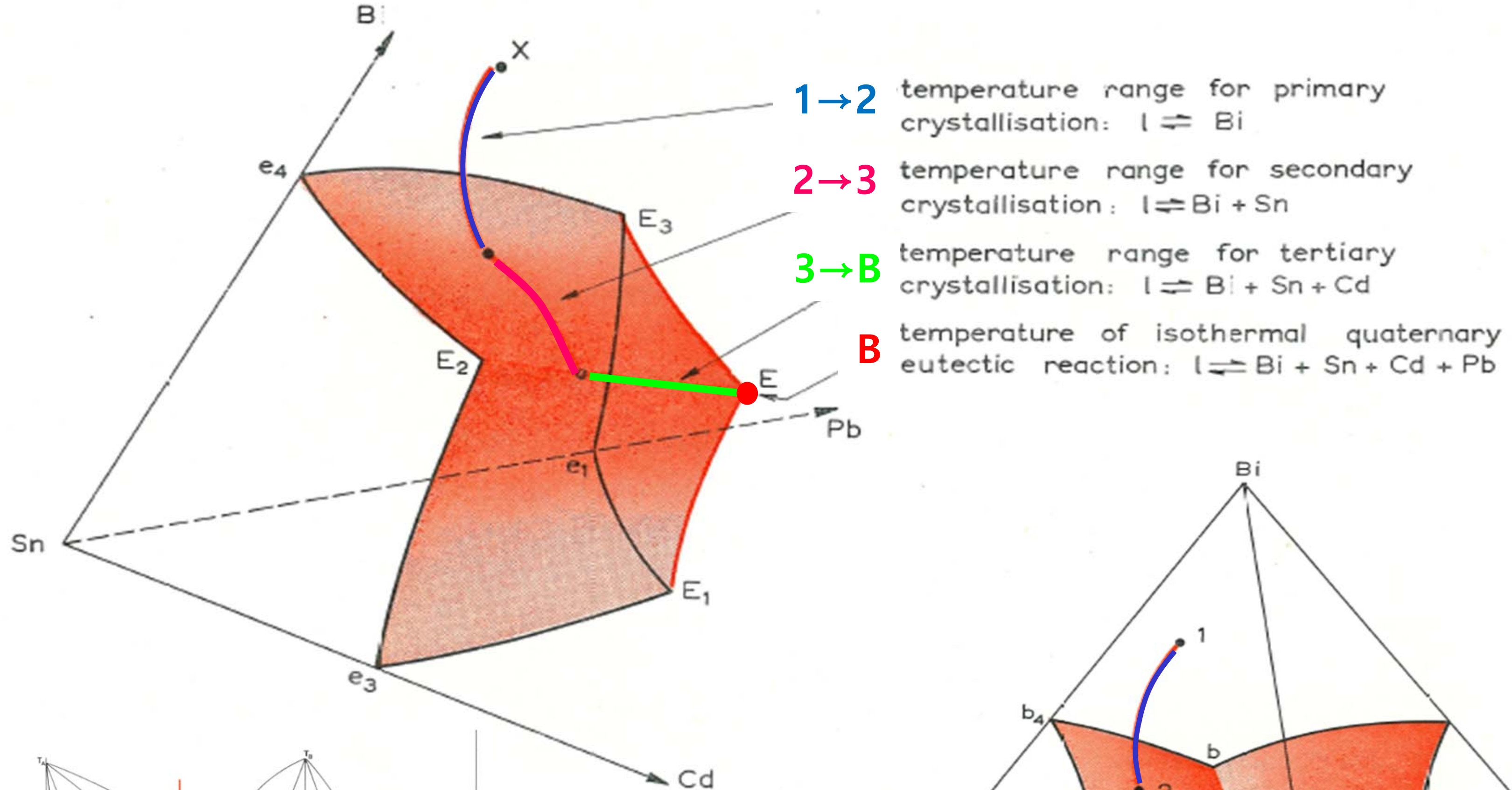


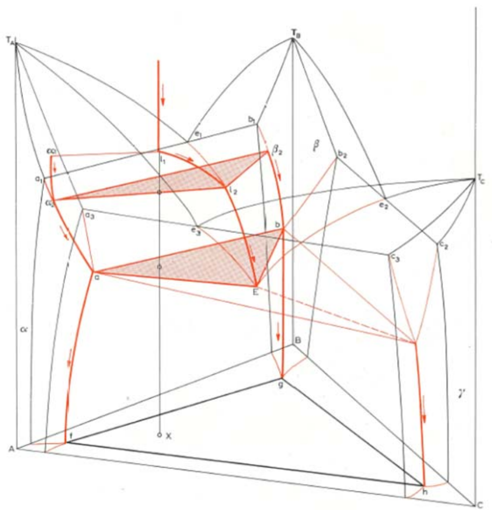
One region of quaternary crystallization **in the Bi-Cd-Pb-Sn system:**

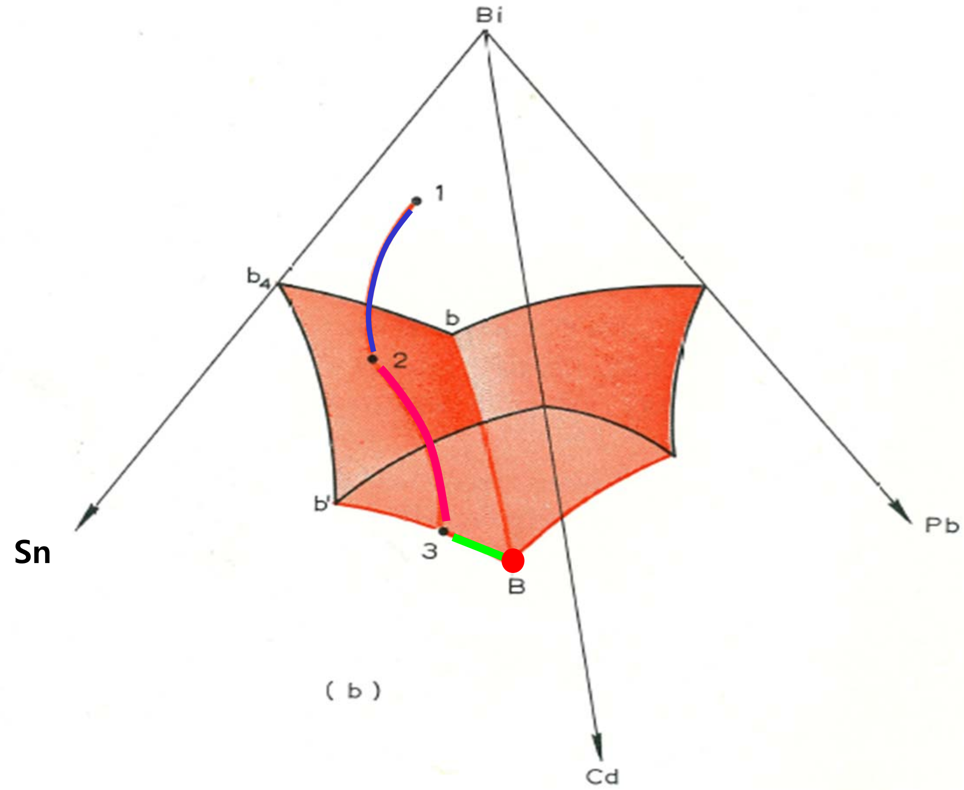
invariant quaternary eutectic reaction, E

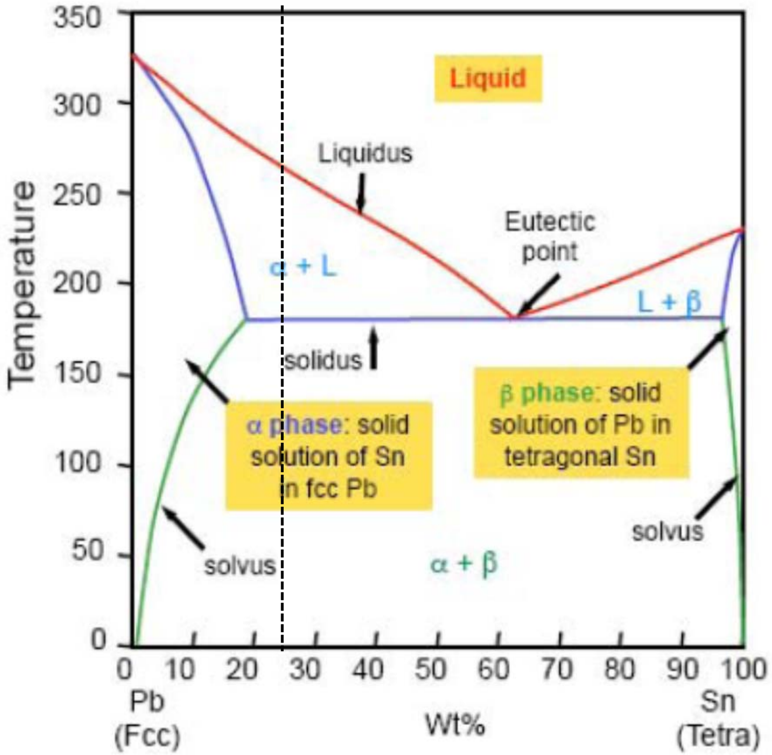
(isothermal separation from the remaining melt)

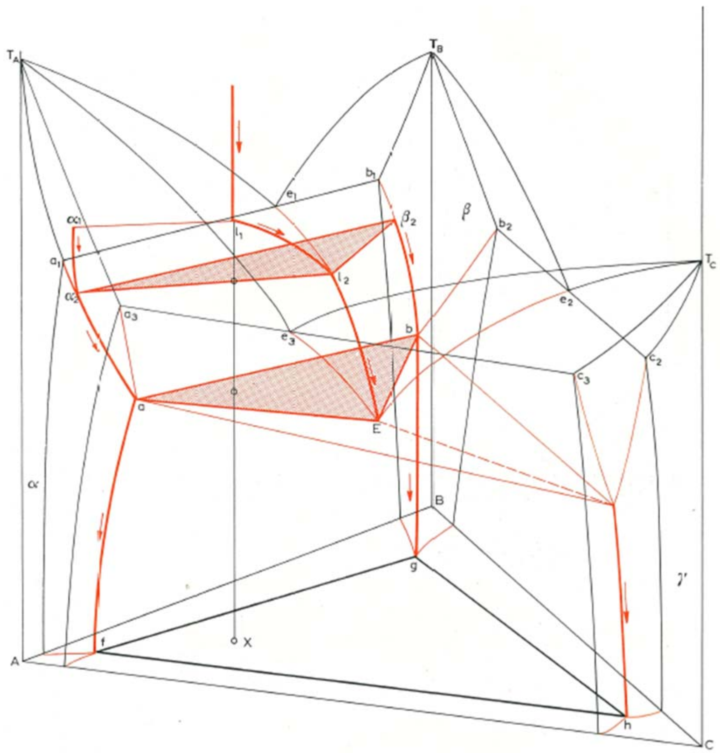
Fig. 277. (a) Change in liquid composition during freezing of an alloy whose composition lies in the primary Bi phase region, (b) corresponding change in composition of the Bi solid solution

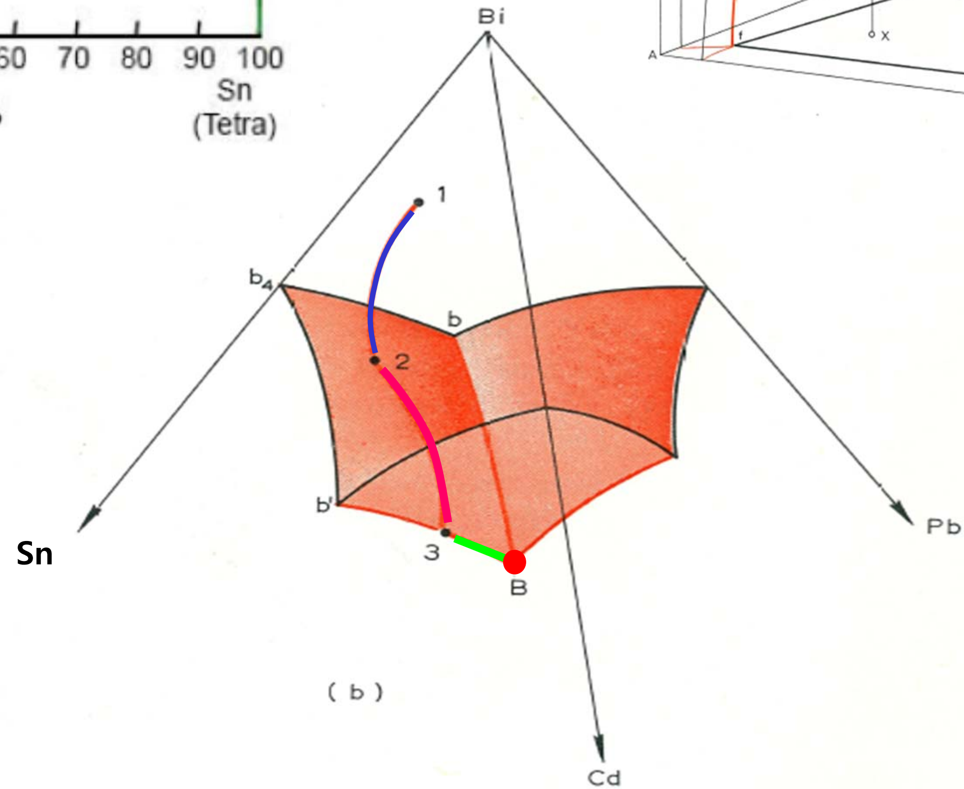







Temperature
350
300
250
200
150
100
50
0
Liquid
Liquidus
Eutectic
point
α + L
L + β
solidus
β phase: solid
solution of Pb in
tetragonal Sn
α phase: solid
solution of Sn
in fcc Pb
solvus
solvus
α + β
0 10 20 30 40 50 60 70 80 90 100
Pb
(Fcc)
Wt%
Sn
(Tetra)


A
B
C
X
E
β
γ'


Bi
1
2
3
b
b'
B
Sn
Pb
Cd
(b)

A. PRINCE, "Alloy Phase Equilibria", Thermodynamics

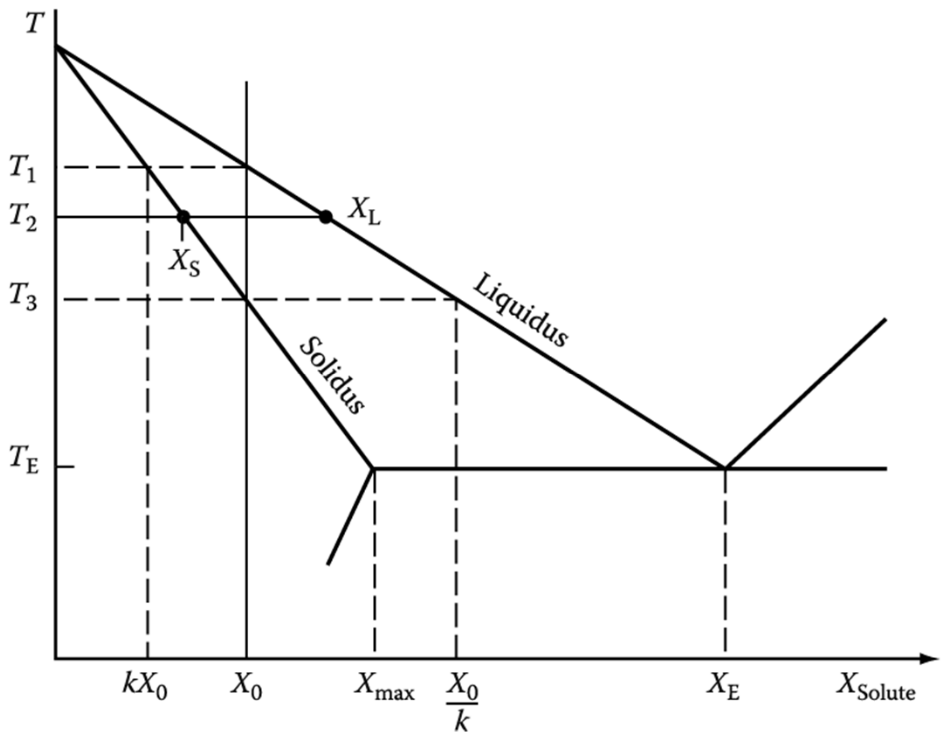
Elsevier publishing company (1966)_an out-of-printed book

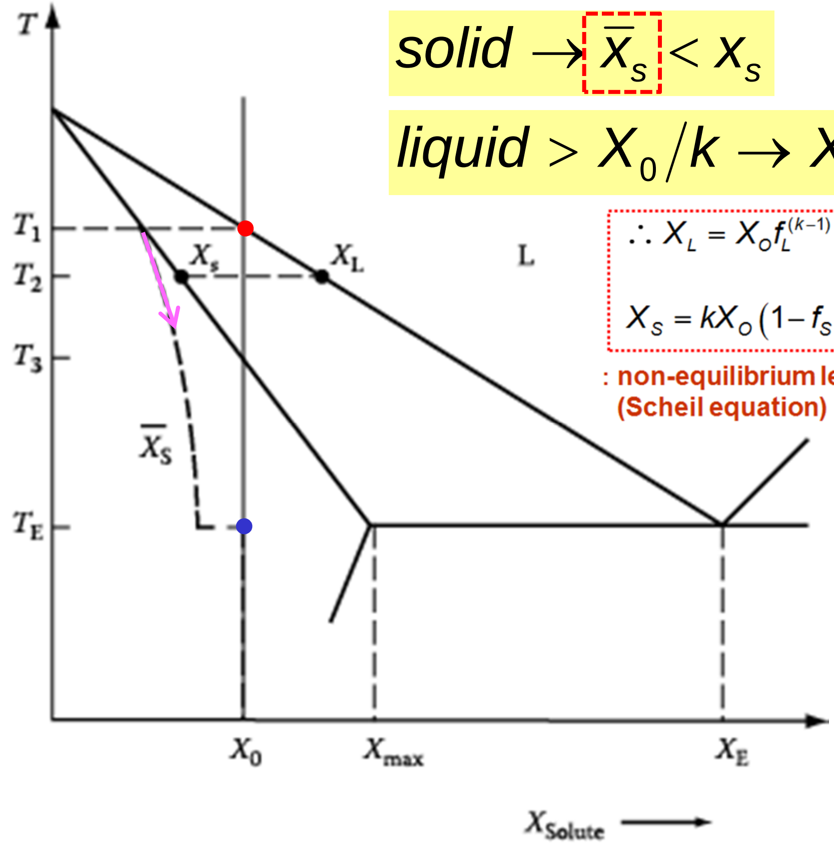
week 1 Introductory Thermodynamics
week 2 Thermodynamics of Solutions
week 3 Binary Phase Diagrams: Two-phase Equilibrium
week 4 Binary Phase Diagrams: Three-phase Equilibrium
week 5 Binary Phase Diagrams: Limited Solubility in Both the Liquid and Solid State
week 6 Binary Phase Diagrams: Reactions in the Solid State
week 7 Binary Phase Diagrams: Allotropy of the Components
week 8 Ternary Phase Diagrams: Two-phase Equilibrium
week 9 Ternary Phase Diagrams: Three-phase Equilibrium
week 10 Ternary Phase Diagrams: Four-phase Equilibrium
week 11 Ternary Phase Diagrams: Intermediate Phases
week 12 Ternary Phase Diagrams: Liquid Immiscibility
week 13 Ternary Phase Diagrams: Four-phase Equilibrium Involving Allotropy of One Component
week 14 The Association of Phase Regions
week 15 Quaternary Phase Diagrams I
week 16 Quaternary Phase Diagrams II

Equilibrium Solidification
: perfect mixing in solid and liquid

vs

Non-equilibrium Solidification
: No Diffusion in Solid, Perfect Mixing in Liquid





$$solid \rightarrow \bar{X}_s < X_s$$

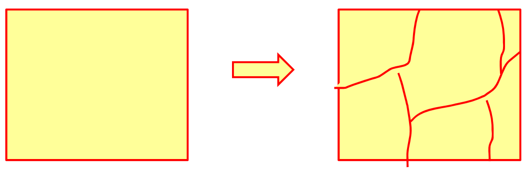
$$liquid > X_0/k \rightarrow X_E$$

$$\therefore X_L = X_O f_L^{(k-1)}$$

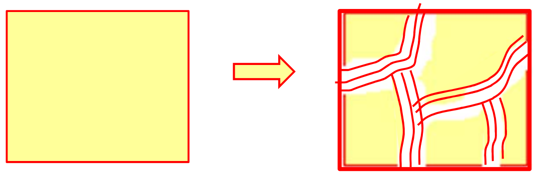
$X_s = kX_L$

$$X_S = kX_O(1-f_S)^{(k-1)}$$

: non-equilibrium lever rule (Scheil equation)



Liquid α



Liquid Primary α + Eutectic (coring)

Phase Transformation = Thermodynamics + Kinetics

Crystallization vs **Amorphization**

: slower cooling rate — : faster cooling rate