2015 Fall

"Phase Equilibria *in* Materials"

11.16.2015

Eun Soo Park

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

Chapter 12. Ternary phase Diagrams

Liquid Immiscibility

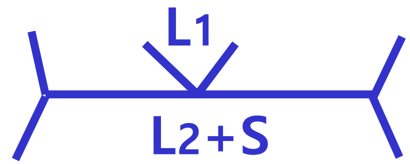
Liquid immiscibility in one or more of the binary systems can lead to either three-phase or four-phase equilibria in the ternary system.

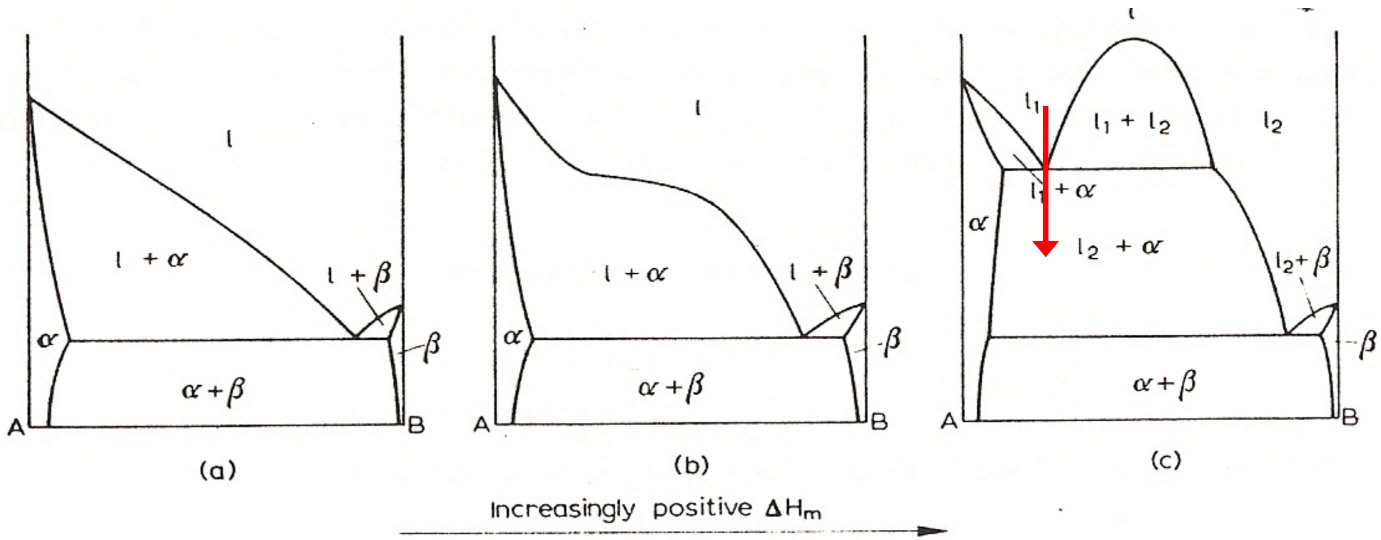
Immiscibility can arise if either monotectic or syntectic reactions occur in the binary system; true ternary immiscibility is also possible.

1) Liquid immiscibility in binary system

* Monotectic reaction:

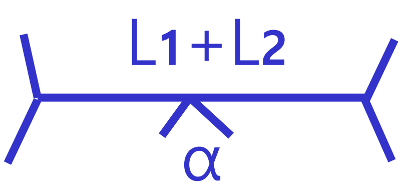
Liquid1 ↔Liquid2+ Solid



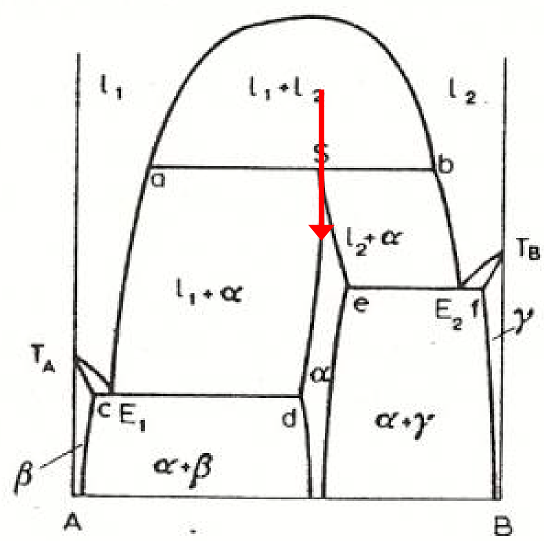


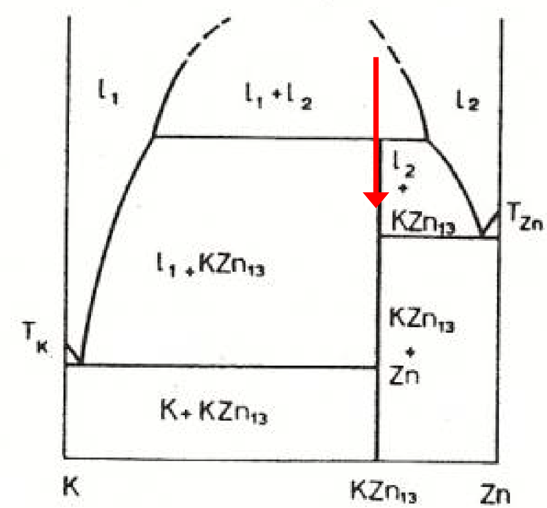
* Syntectic reaction:

Liquid1+Liquid2 ↔ α



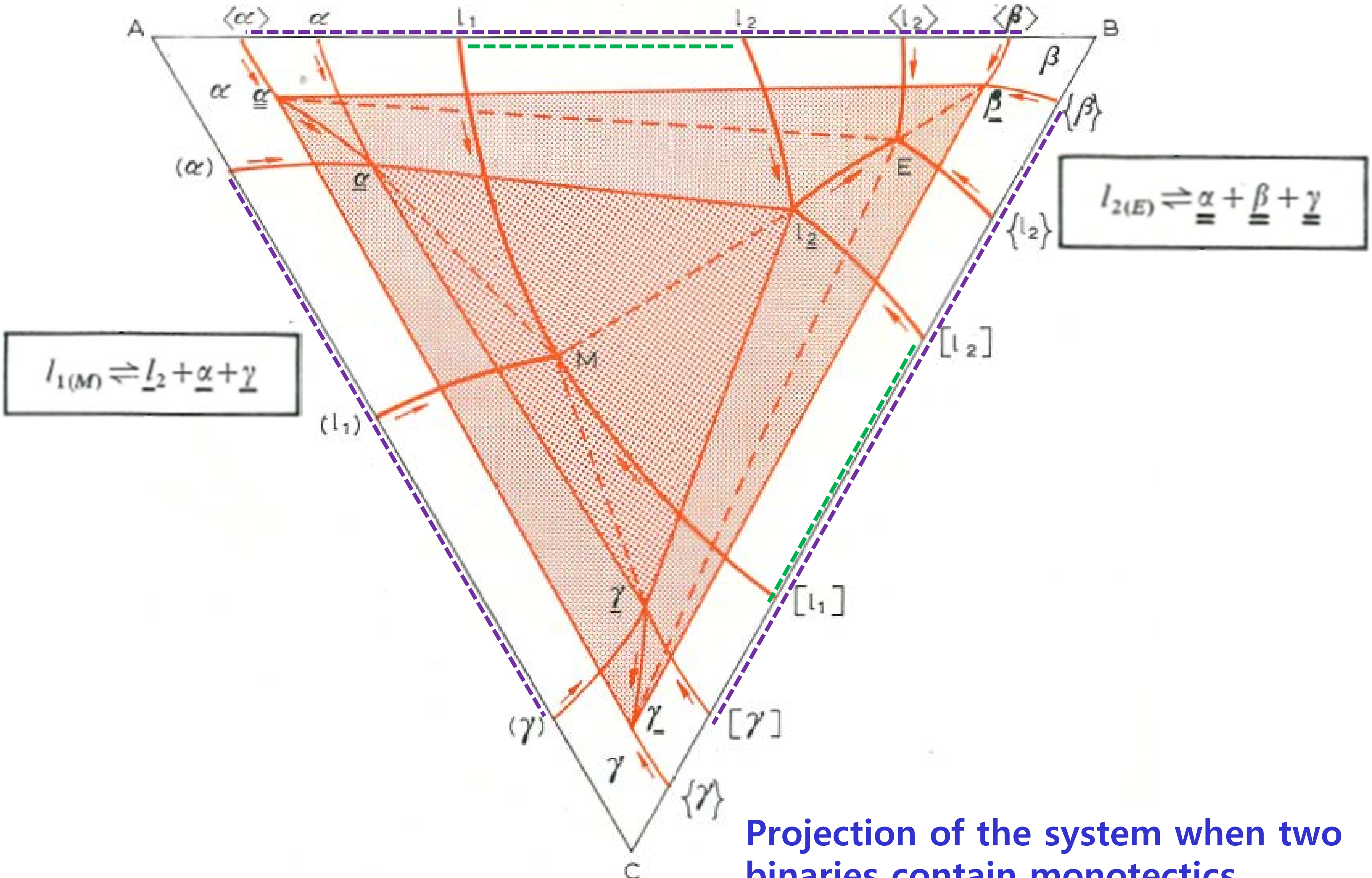
K-Zn, Na-Zn,
K-Pb, Pb-U, Ca-Cd





12.1. Two Binary Systems are Monotectic

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

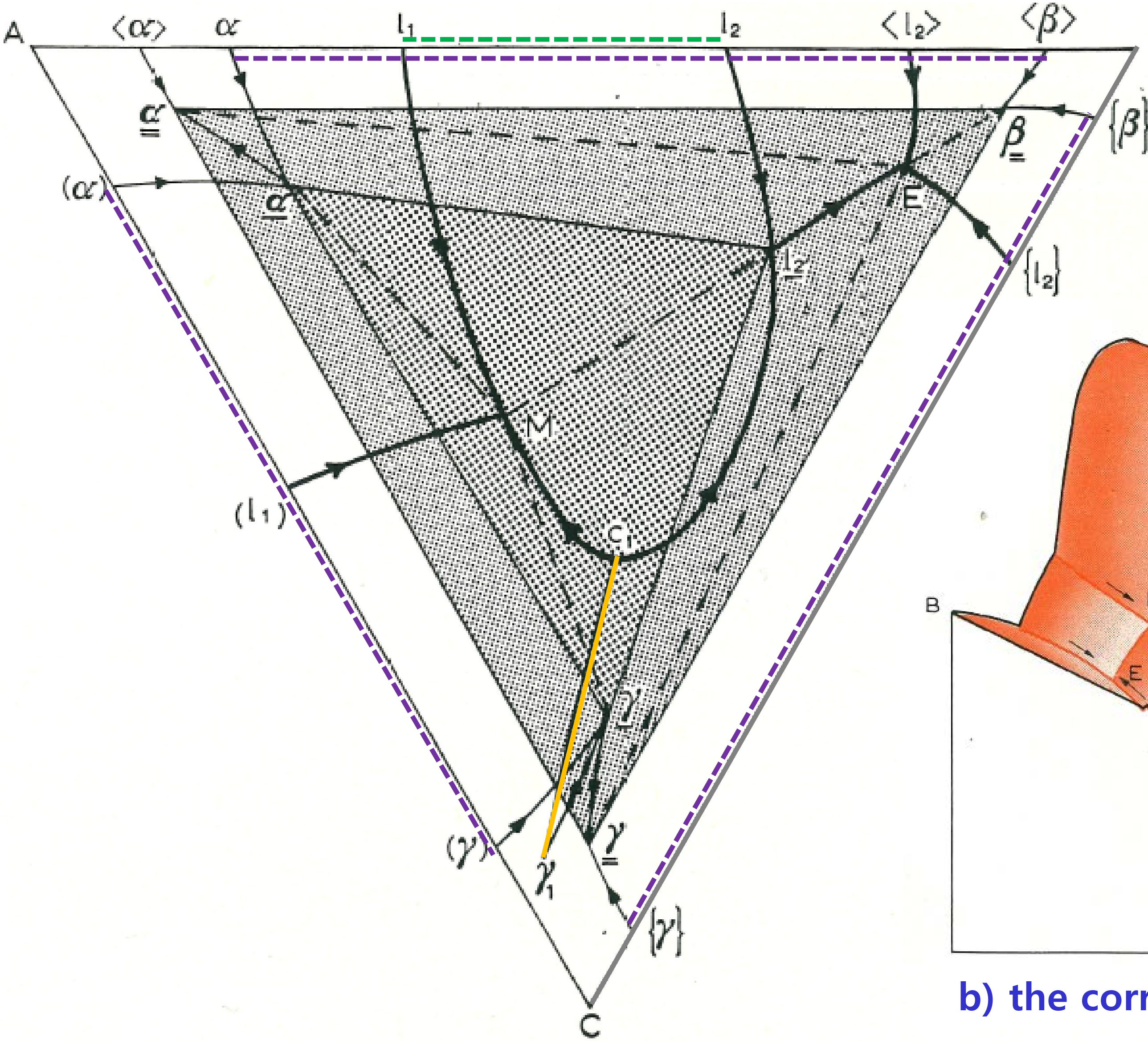


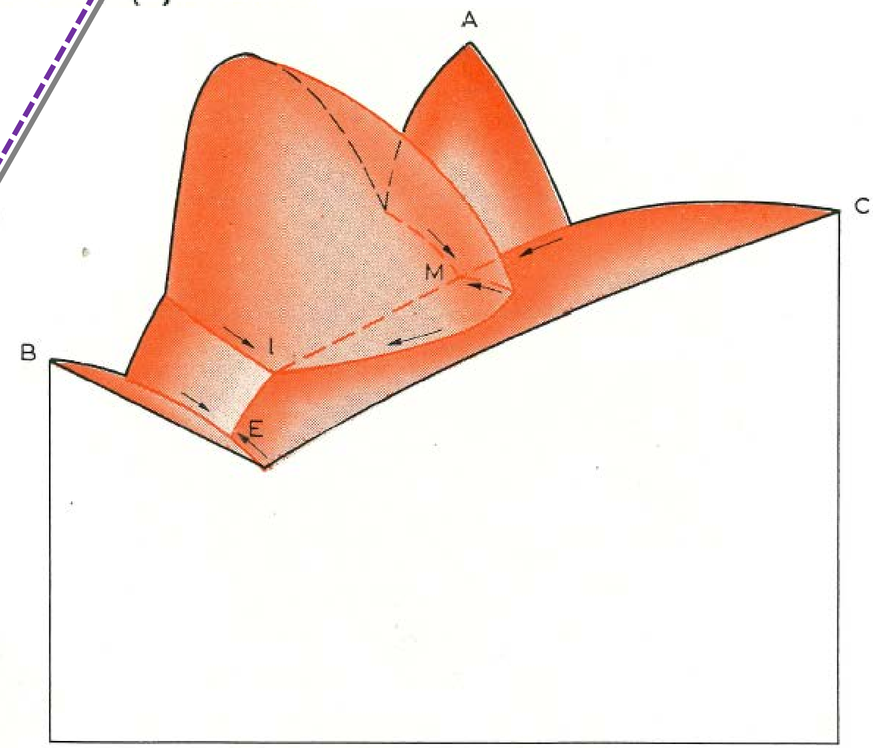
Projection of the system when two binaries contain monotectics

12.2. One Binary System is Monotectic

Liquid immiscibility in ternary system

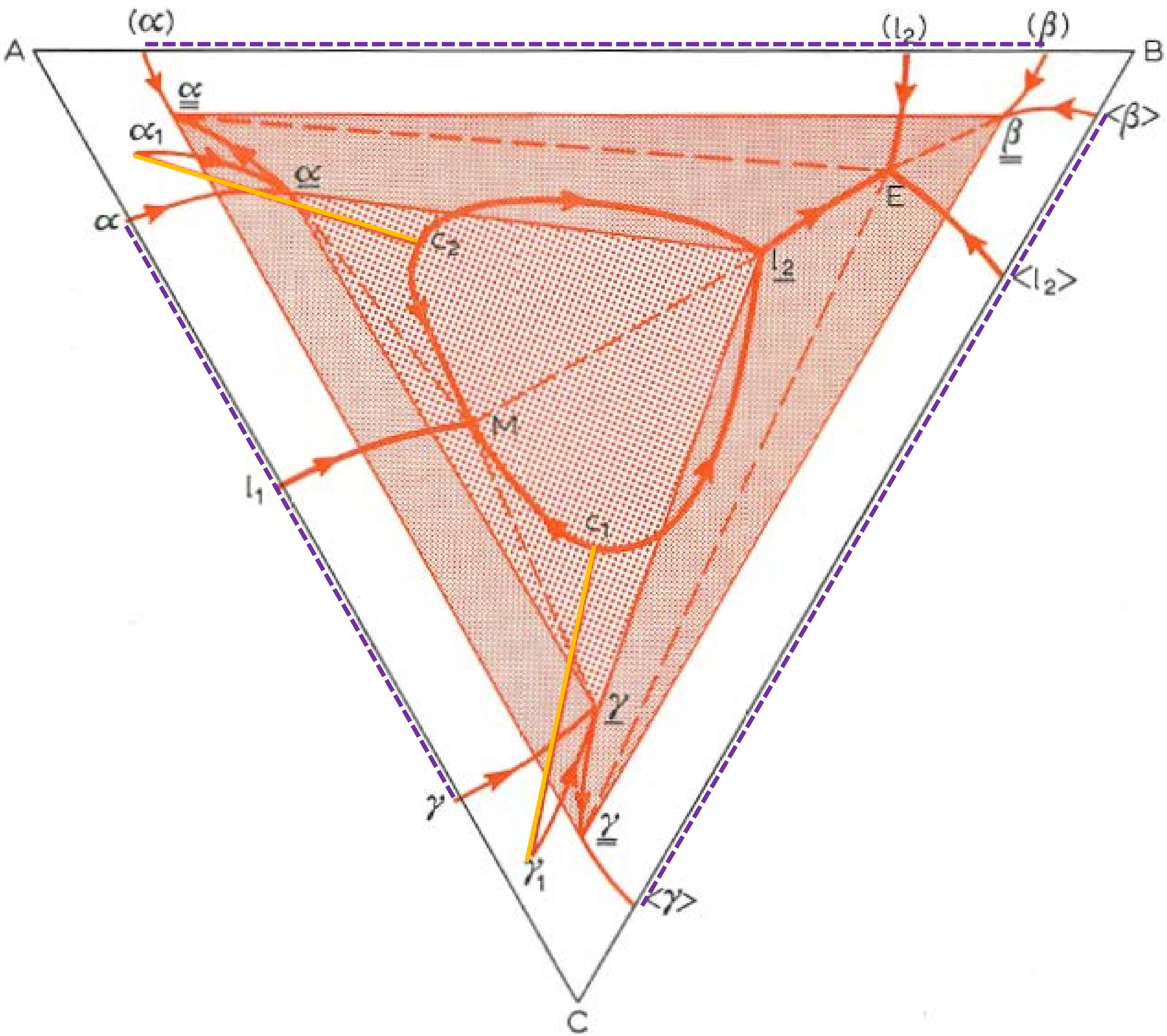
a) Projection of the system when only one binary is monotectic and two binaries are simple eutectic.





b) the corresponding liquidus surface

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



Chapter 13. Ternary phase Diagrams

Four-phase Equilibrium involving Allotropy of one component

In the transition from (b) a binary diagram of the closed γ type to (a) one of the expanded γ type, a four-phase equilibrium will appear.
It is assumed that BC binary shows a complete series of solid solutions

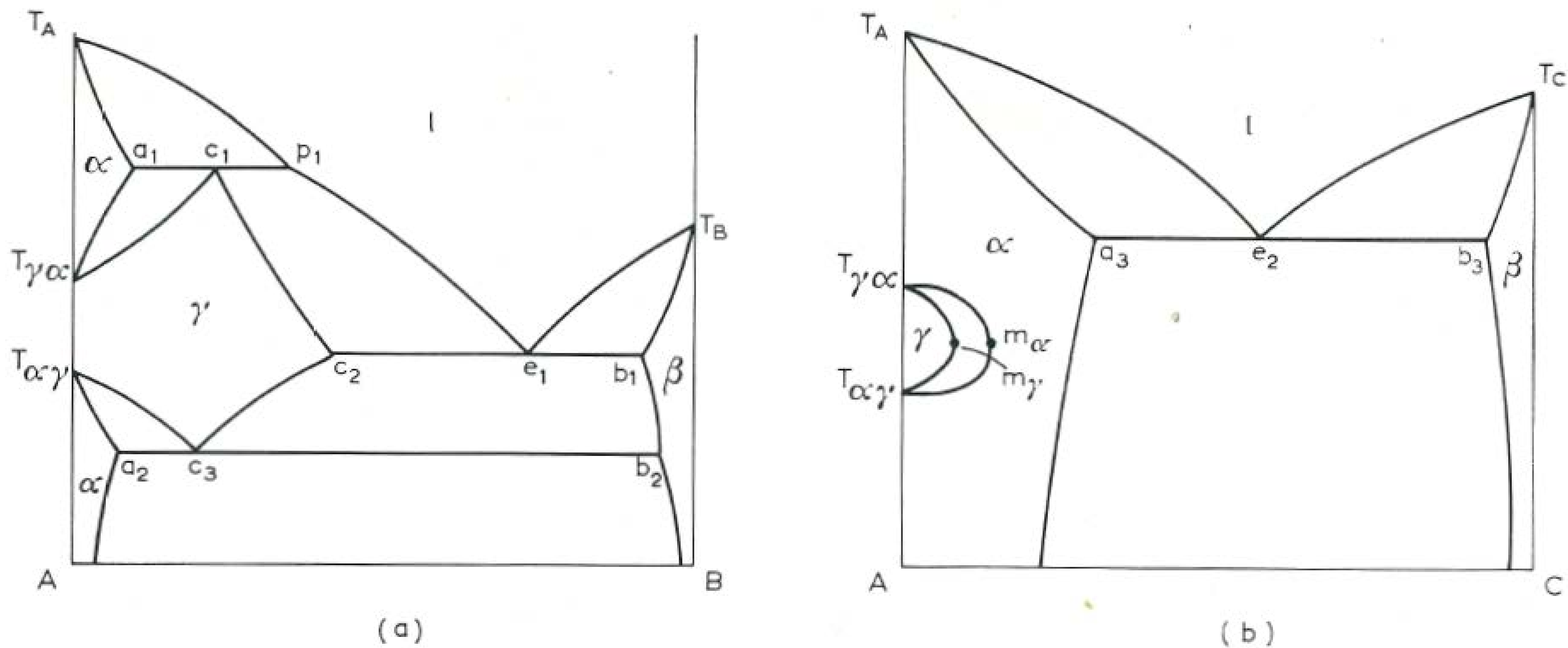


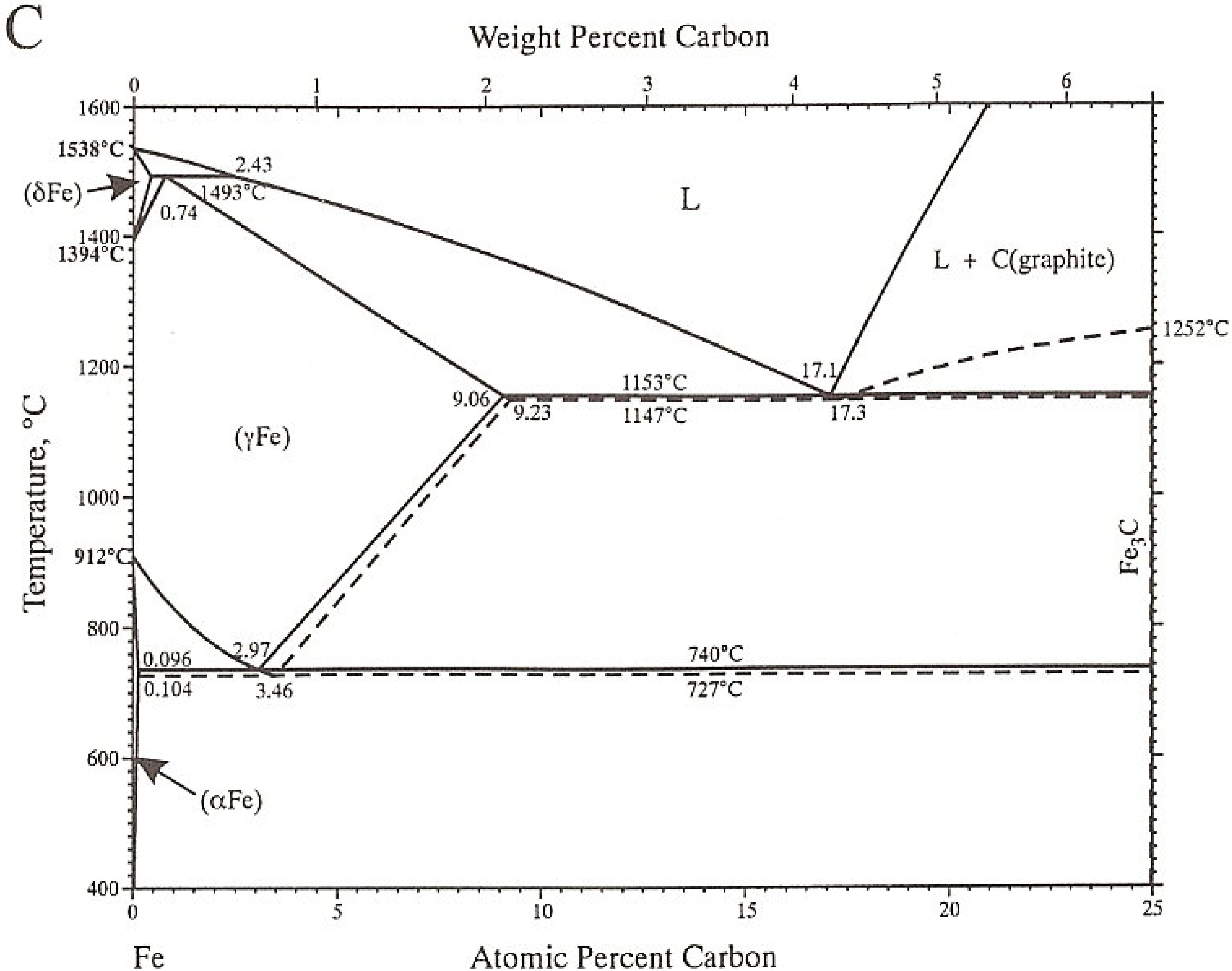
Fig. 220. Binary phase diagram (a) with an expanded γ field, (b) with closed γ field.

Recognisable as the Fe-Fe_3C diagram

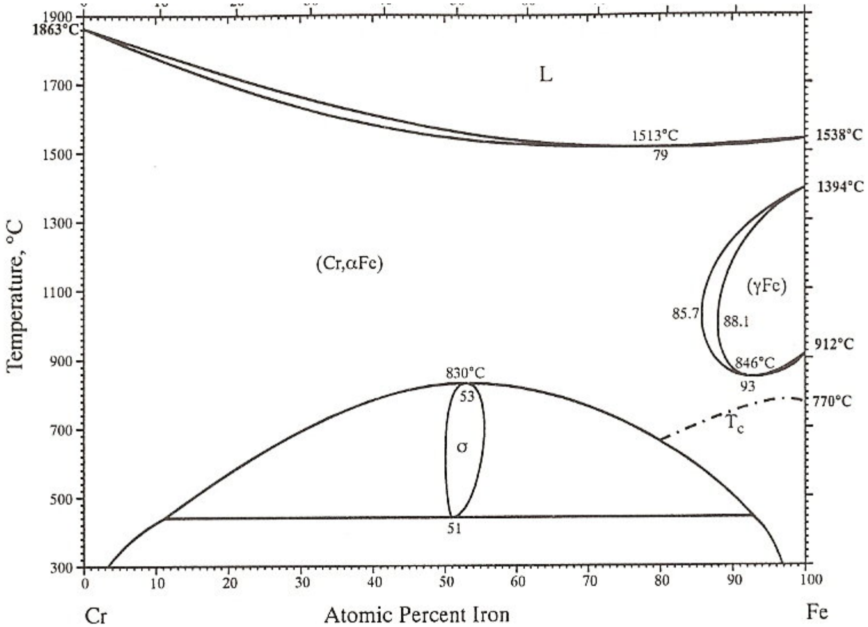
Produce by ferrite forming elements Such as Cr, Mo, Si and W

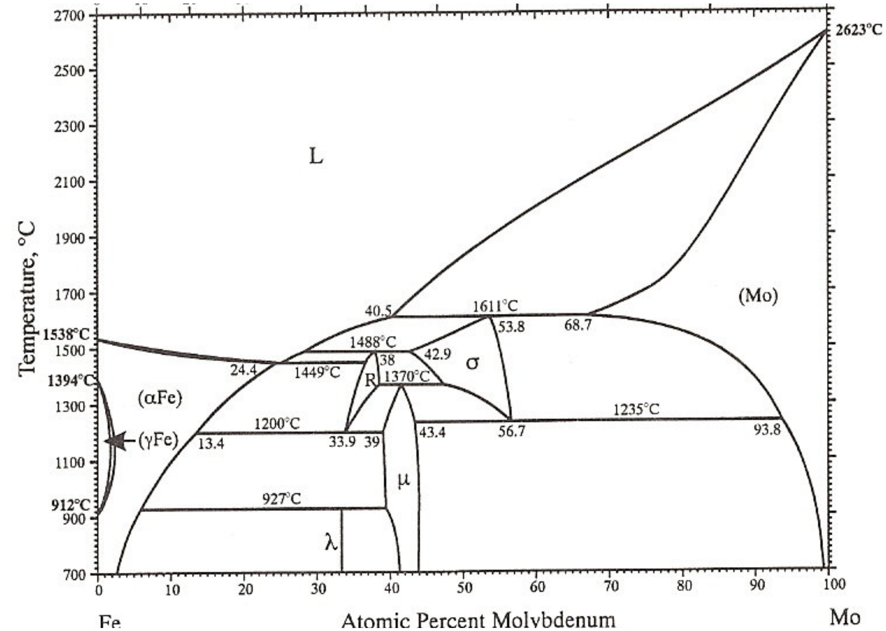
⟹ **This type of ternary is of importance in the metallurgy of low alloy steels.**

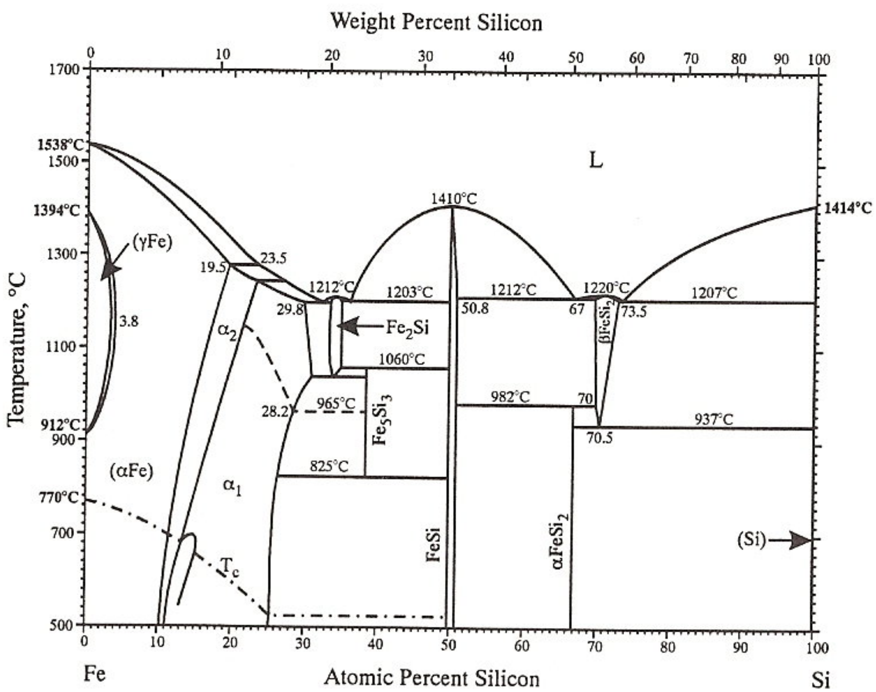
A binary diagram with the expanded γ type

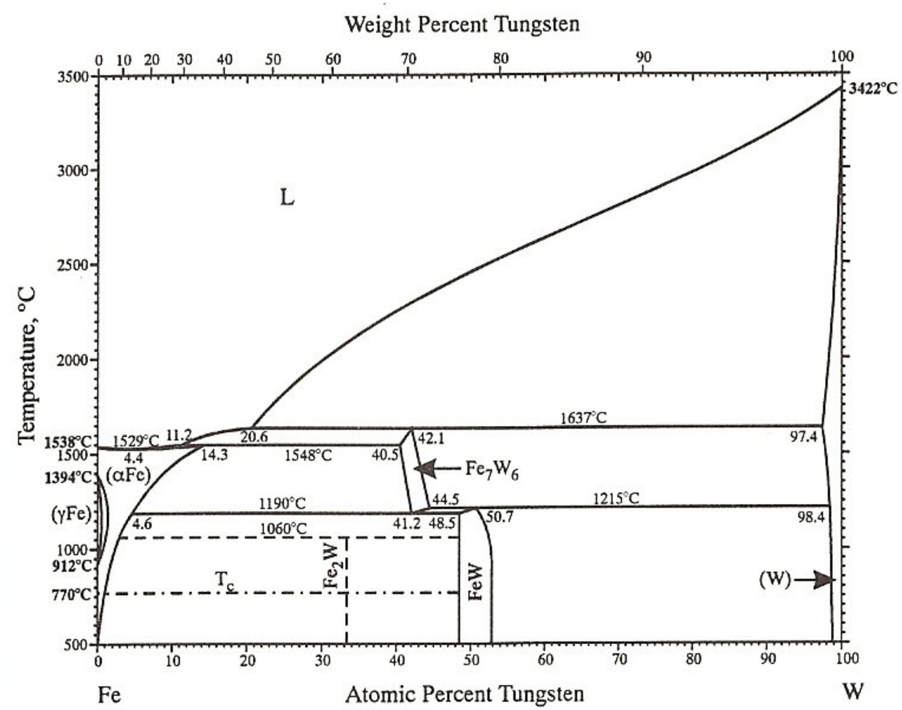


C **binary diagrams with the closed γ type** such as Cr, Mo, Si and W







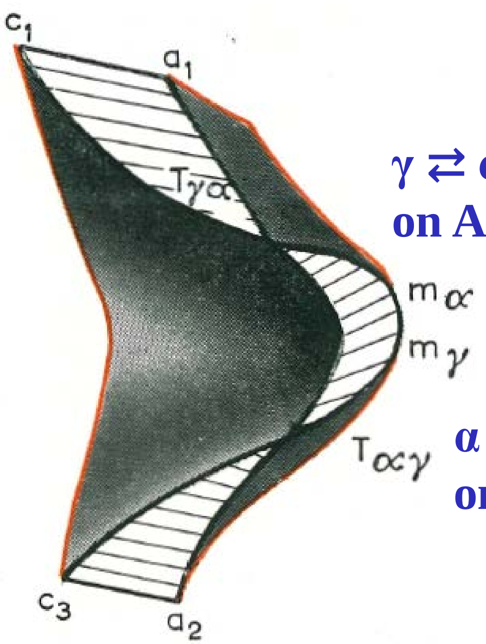


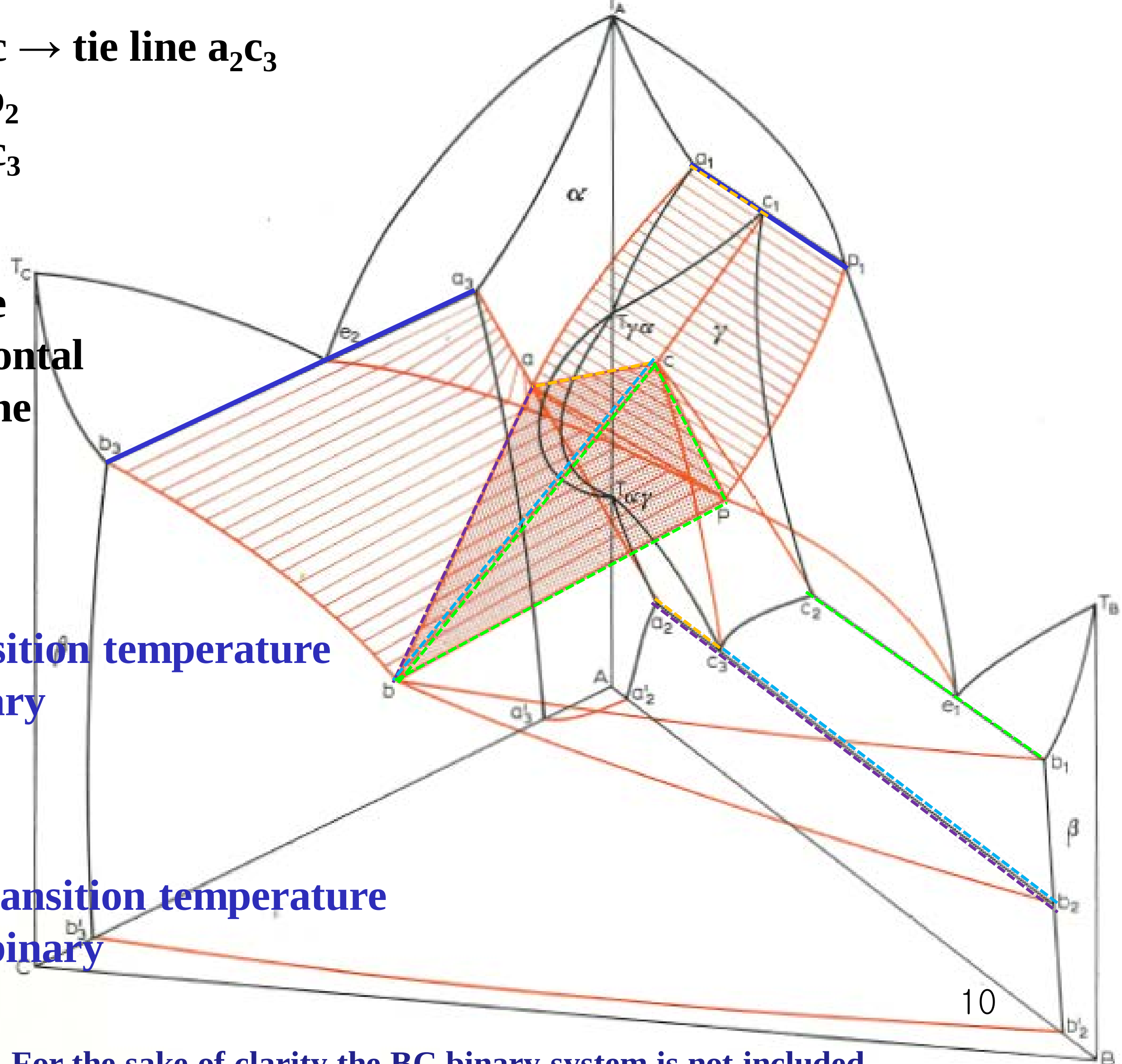
Ternary space model
involving a transition from a closed γ field to an expanded γ field

$\gamma \rightleftarrows \alpha + \beta$ reaction → αβγ phase region

*** αγ ruled surface: tie line ac → tie line a_2c_3**
*** αβ ruled surface: ab → a_2b_2**
*** βγ ruled surface: bc → b_2c_3**

<u>α + γ two phase region</u> :
This region originates at the tie line a_1c_1 on the peritectic horizontal $a_1c_1p_1$ at the time line a_2c_3 on the eutectoid horizontal $a_2c_3b_2$.





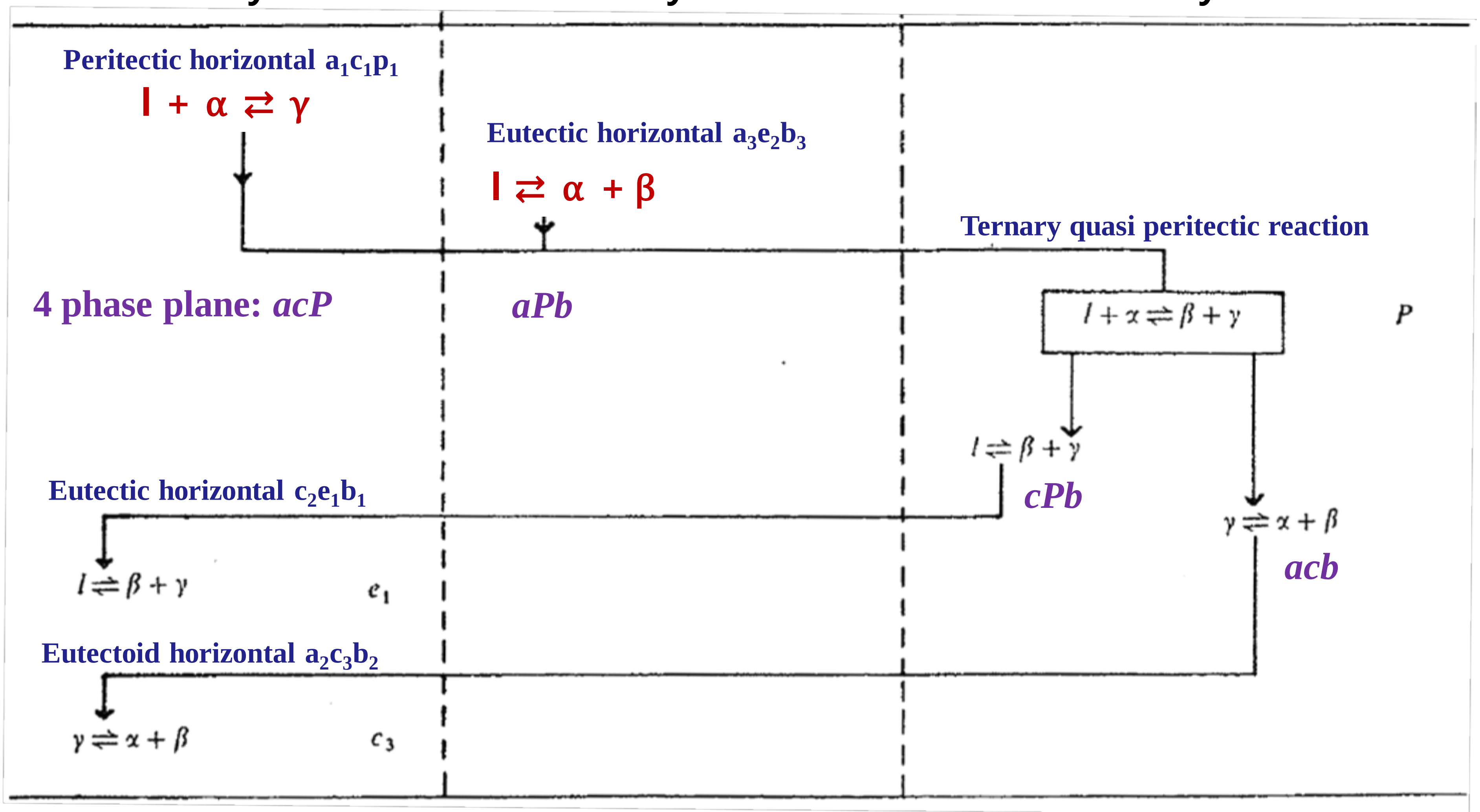
$\gamma \rightleftarrows \alpha$ transition temperature on AB binary

$\alpha \rightleftarrows \gamma$ transition temperature on AC binary

For the sake of clarity the BC binary system is not included.

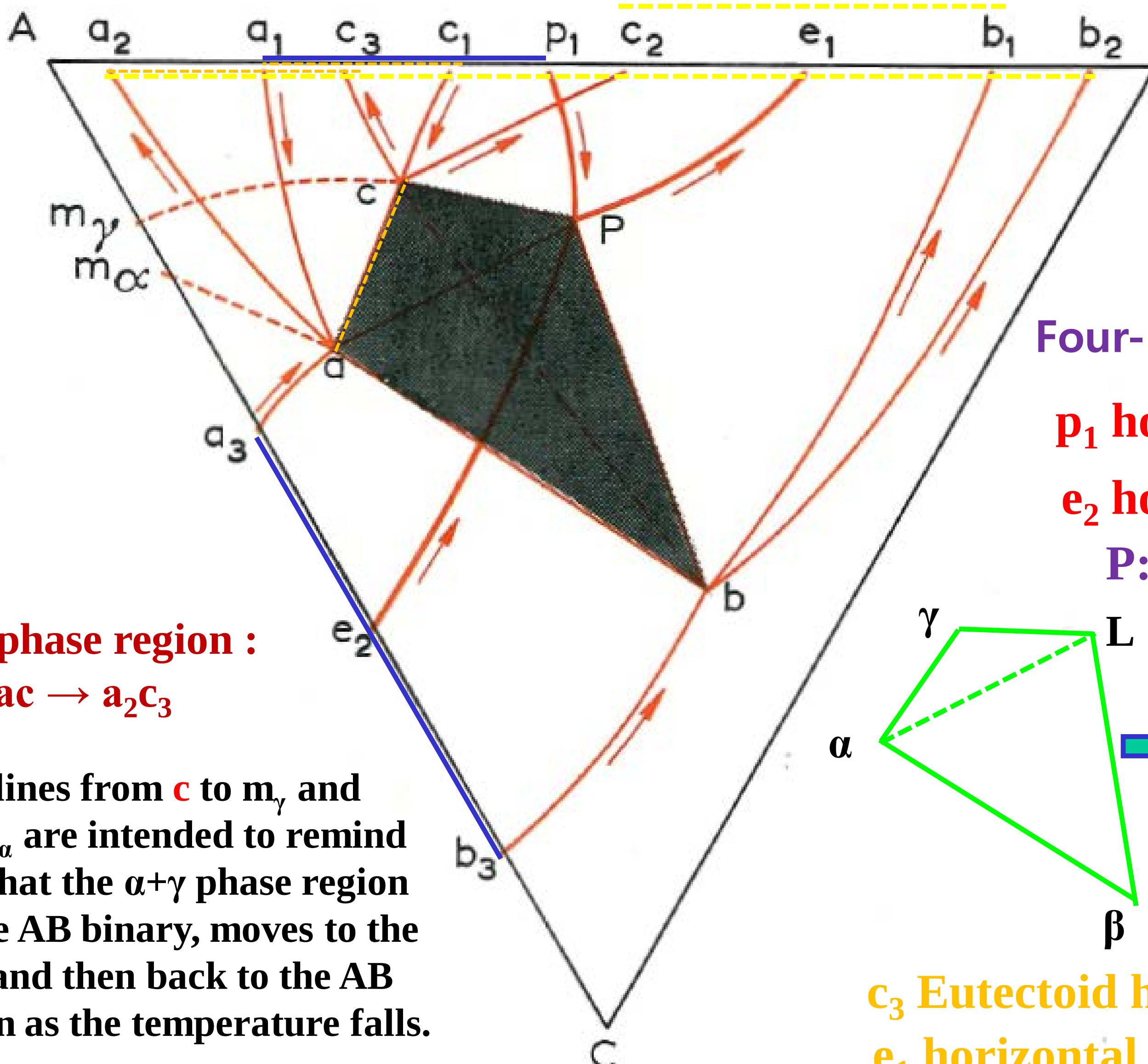
A tabular representation of the ternary

Binary AB | **Binary AC** | **Ternary**



Projection of the ternary system
involving a transition from a closed γ field to an expanded γ field

Four-phase equilibrium: l + α ⇄ β + γ



Four-phase plane: ***Pbac***

p_1 horizontal → αγL

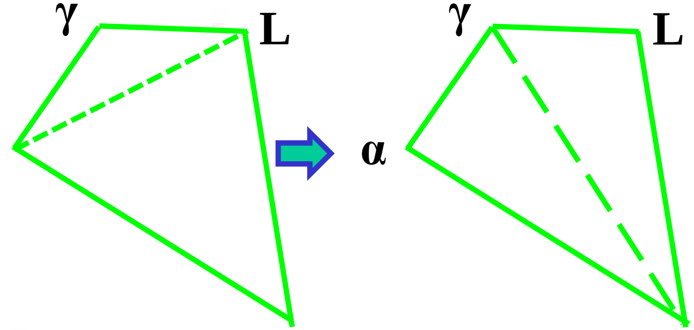
e_2 horizontal → αβL

P: L+α → γ+β

α + γ two phase region :

$a_1c_1 \rightarrow ac \rightarrow a_2c_3$

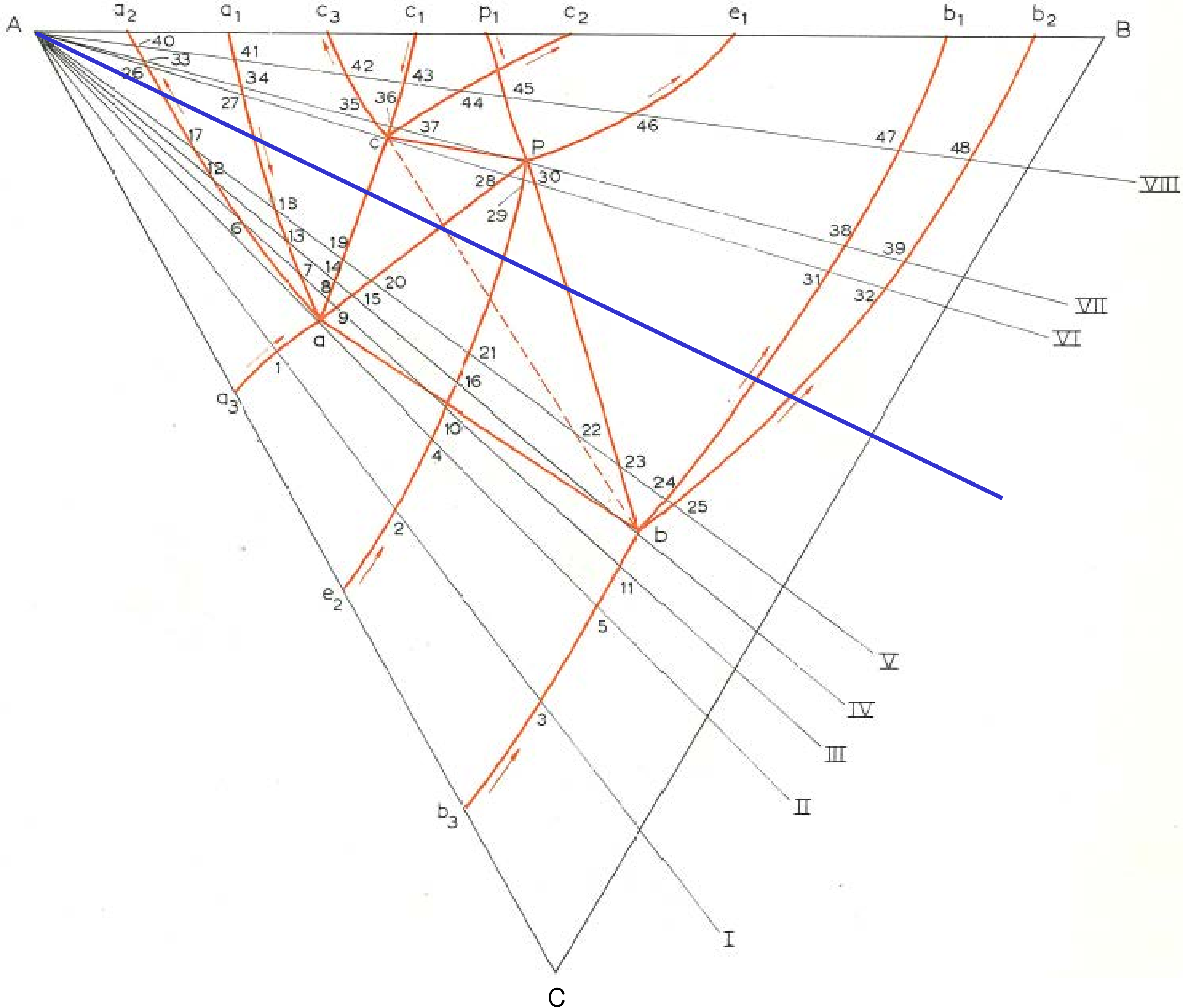
The dotted lines from c to m_γ and from a to m_α are intended to remind the reader that the α+γ phase region starts on the AB binary, moves to the AC binary and then back to the AB binary again as the temperature falls.

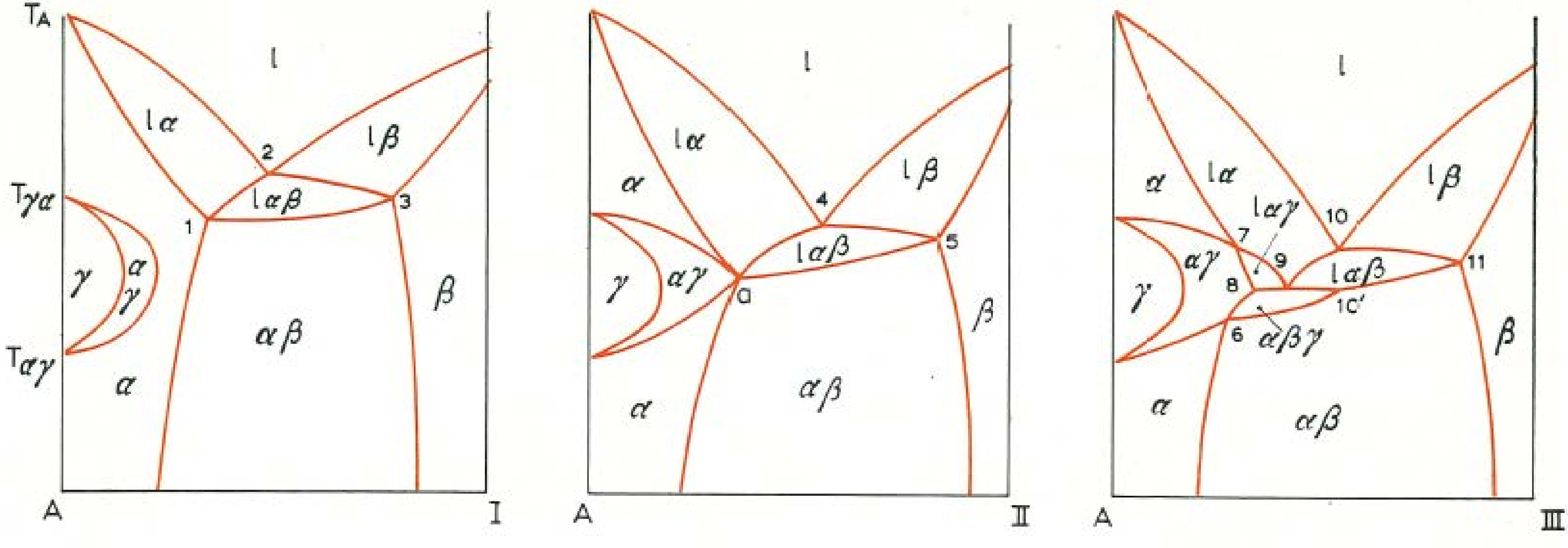


c_3 Eutectoid horizontal → αβγ

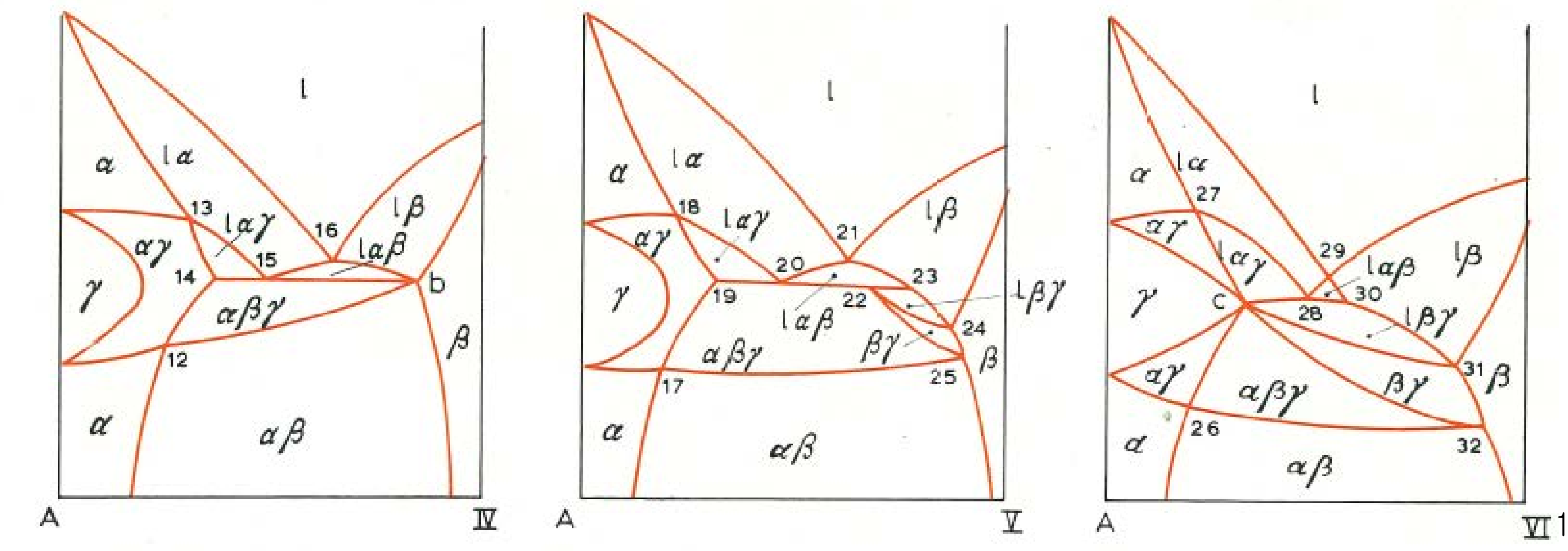
e_1 horizontal → βγL

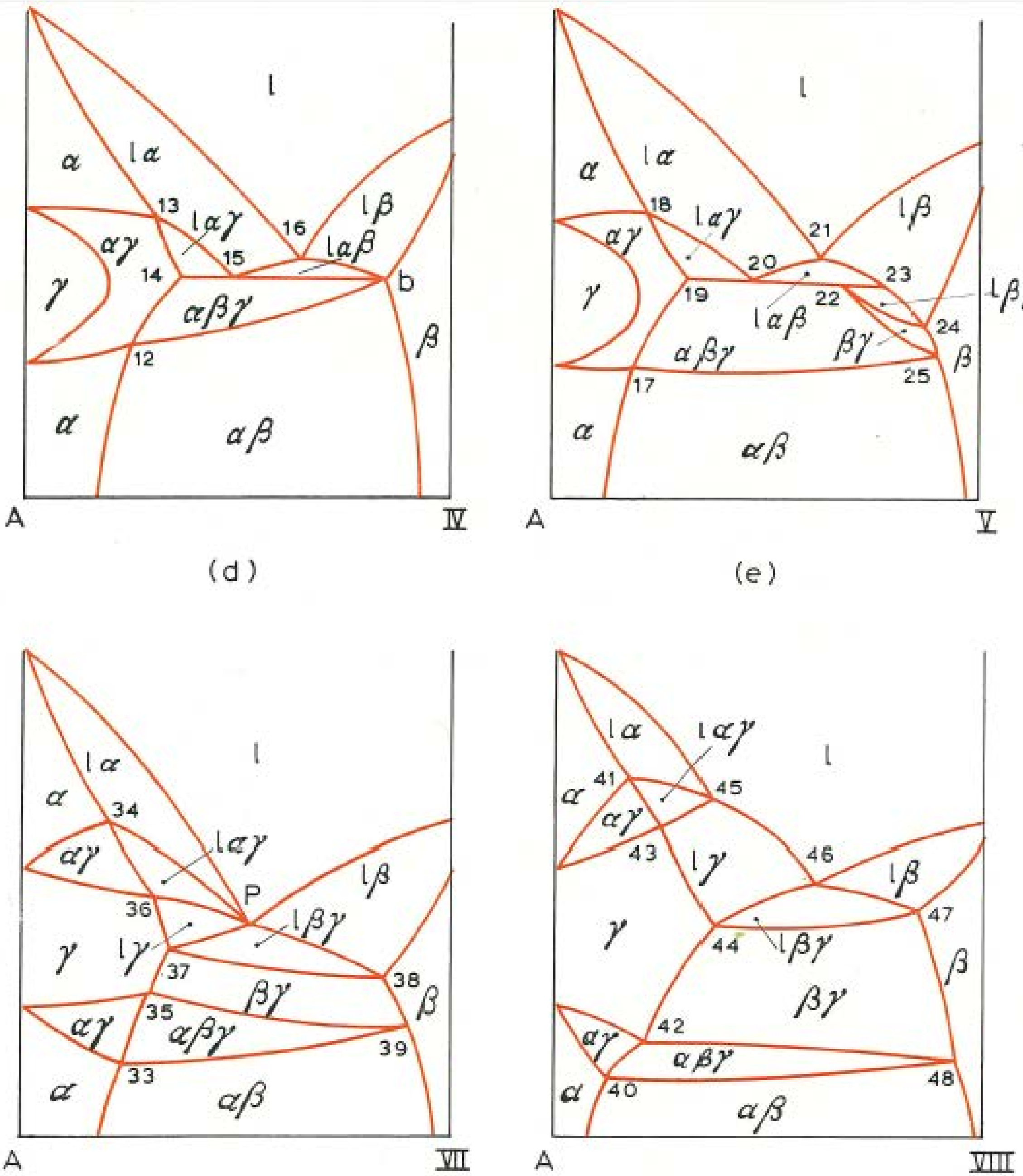
Location of vertical sections through projection involving a transition from a closed γ field to an expanded γ field




TA
Tγα
Tαγ
l
lα
lβ
lαβ
α
γ
β
αβ
1
2
3
4
5
a
6
7
8
9
10
10'
11
lαγ
αγ
αβγ
A
I
II
III

(a) (b) (c)


l
lα
lβ
lαγ
lαβ
lβγ
α
γ
β
αγ
αβ
αβγ
βγ
12
13
14
15
16
b
17
18
19
20
21
22
23
24
25
26
27
28
29
30
31
32
c
A
IV
V
VI



By taking this series of vertical sections we have seen how the closed γ binary is transformed to the expanded γ binary through the ternary.

Chapter 14. The Association of Phase Regions

14.1. Law of adjoining phase regions

* Construction of phase diagram:

Phase rule ~ restrictions on the disposition of the phase regions

e.g. no two single phase regions adjoin each other through a line.

* Rules for adjoining phase regions in ternary systems

1) **Masing, "a state space can ordinarily be bounded by another state space only if <u>the number of phases in the second space is one less or one greater than that in the first space considered</u>."**

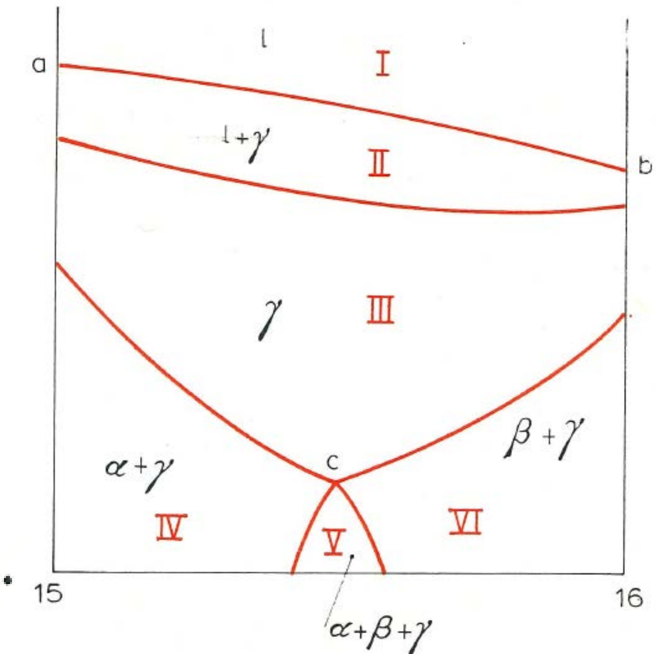


Fig. 226. Application of the law of adjoining phase regions to the vertical section of Fig. 178h.

14.1. Law of adjoining phase regions

* Construction of phase diagram:

Phase rule ~ restrictions on the disposition of the phase regions

e.g. no two single phase regions adjoin each other through a line.

* Rules for adjoining phase regions in ternary systems

1) Masing, "a state space can ordinarily be bounded by another state space only if the number of phases in the second space is one less or one greater than that in the first space considered."

2) **Law of Adjoining Phase Regions: "most useful rule"**

$$R_1 = R - D^- - D^+ \geq 0$$

R_1 : Dimension of the boundary between neighboring phase regions

R : Dimension of the phase diagram or section of the diagram (vertical or isothermal)

D^- : the number of phases that disappear in the transition from one phase region to the other

D^+ : the number of phases that appear in the transition from one phase region to the other

Example 1 $R_1 = R - D^- - D^+ \geq 0$

1) Vertical section is two-dimensional and so R = 2.

2) I → II : D^- = 0/ D^+ = 1 → R_1 = 1 &
II → I : D^- = 1/ D^+ = 0 → R_1 = 1

⇨ boundary ~ one dimension, line ab

3) III → V : D^- = 0/ D^+ = 2 → R_1 = 0 &
V → III : D^- = 2/ D^+ = 0 → R_1 = 0

⇨ boundary ~ zero dimension, point c

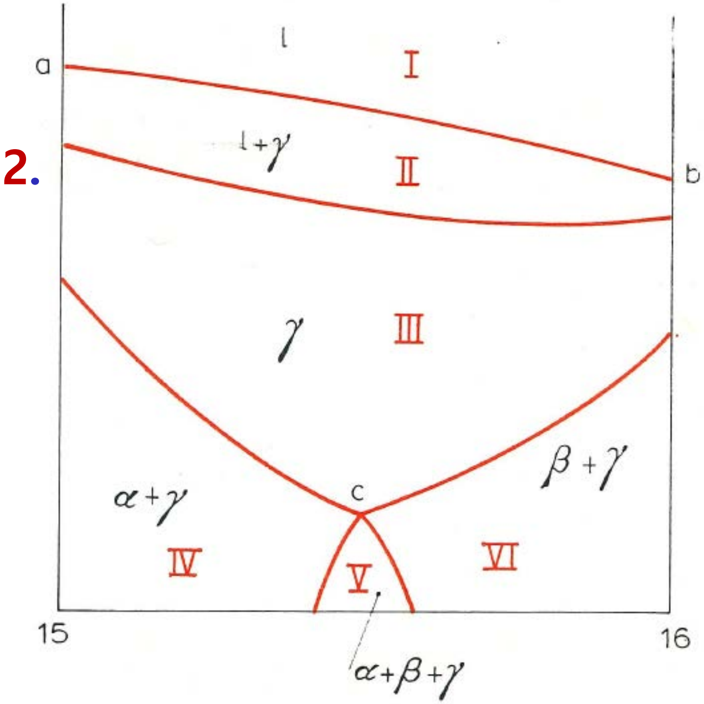
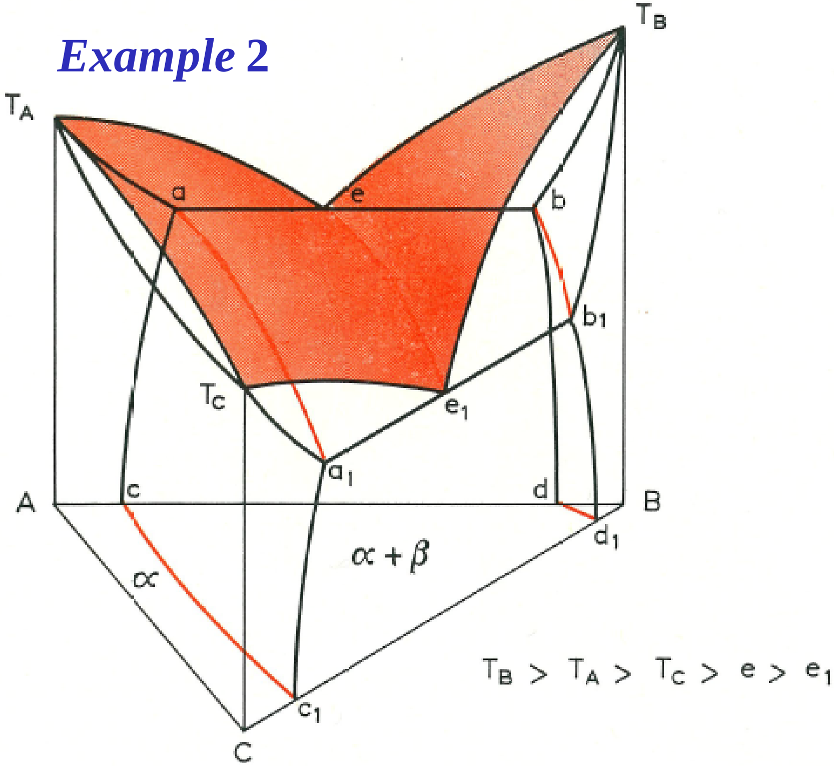


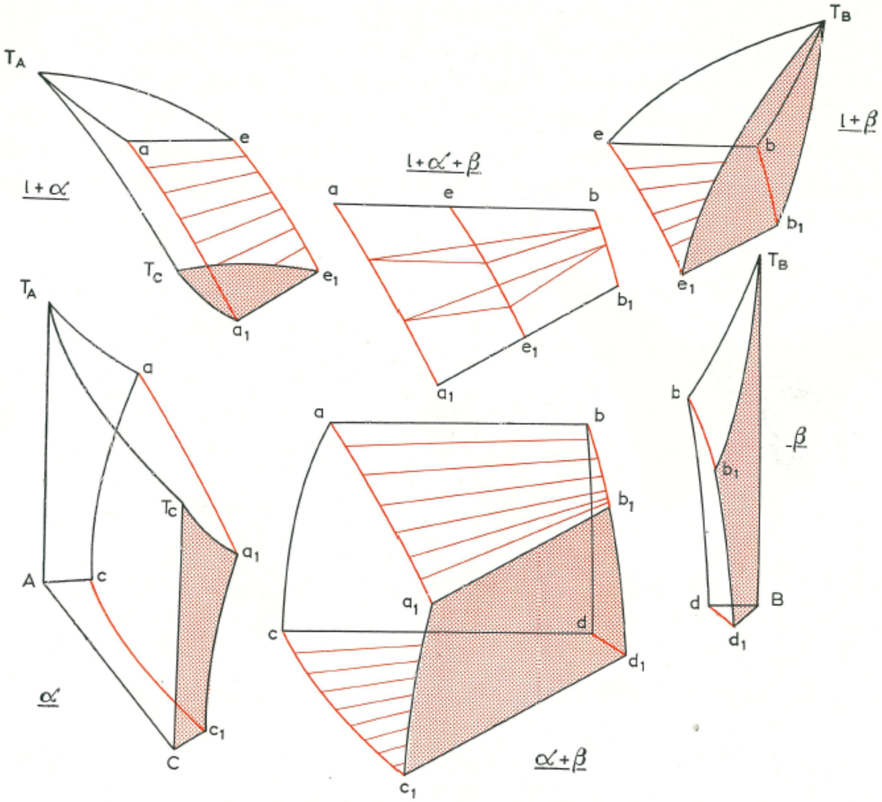
Fig. 226. Application of the law of adjoining phase regions to the vertical section of Fig. 178h.

TABLE 14

Transition from:	I → II	II → I	II → III	III → II	III → IV	IV → III	III → VI	IV → III	III → V	V → III	IV → V	V → IV	VI → V	V → VI
R	2	2	2	2	2	2	2	2	2	2	2	2	2	2
D^-	0	1	1	0	0	1	0	1	0	2	0	1	0	1
D^+	1	0	0	1	1	0	1	0	2	0	1	0	1	0
R_1	1	1	1	1	1	1	1	1	0	0	1	1	1	1
Corresponding geometrical element	line		line		line		line		point		line		line	

Example 2





$$R_1 = R - D^- - D^+ \geq 0$$

TABLE 15

Transition from:	β			l+β				l+α+β					
	l+β	l+α+β	α+β	l	β	α+β	l+α+β	l	α	β	l+α	l+β	α+β
R	3	3	3	3	3	3	3	3	3	3	3	3	3
D^-	0	0	0	1	1	1	0	2	2	2	1	1	1
D^+	1	2	1	0	0	1	1	0	0	0	0	0	0
R_1	2	1	2	2	2	1	2	1	1	1	2	2	2
Corresponding geometrical element	a	b	c	d	e	f	g	h	i	j	k	l	m

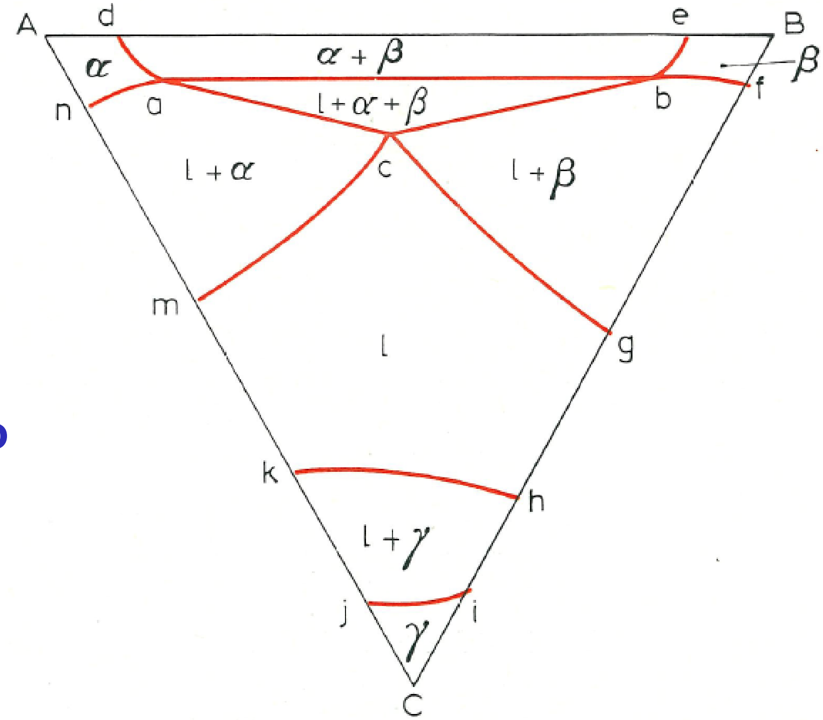
a – surface ($T_Bbb_1T_B$), b – line (bb_1), c – surface (bb_1d_1db), d – surface ($T_Bee_1T_B$), e – surface ($T_Bbb_1T_B$), f – line (bb_1), g – surface (bb_1e_1eb), h – line (ee_1), i – line (aa_1), j – line (bb_1), k – surface (aee_1a_1a), l – surface (bb_1e_1eb), m – surface (abb_1a_1a).

Example 3 $R_1 = R - D^- - D^+ \geq 0$

1) **Isothermal sections are two-dimensional and so R = 2.**

2) **Transitions from a single phase region to its neighbors ➡ line or point**

3) **Other transitions, e.g. l+α+β → α+β or l+α or l+β ➡ line ab/ ac/ bc**



227. Application of the law of adjoining phase regions to the isothermal section of Fig. 176c.

TABLE 16

Transition from:	α			β			l				γ
	α+β	l+α	l+α+β	α+β	l+β	l+α+β	l+α	l+β	l+γ	l+α+β	l+γ
R	2	2	2	2	2	2	2	2	2	2	2
D^-	0	0	0	0	0	0	0	0	0	0	0
D^+	1	1	2	1	1	2	1	1	1	2	1
R_1	1	1	0	1	1	0	1	1	1	0	1
Corresponding geometrical element	line		point	line		point		line		point	line
	(da)	(na)	(a)	(eb)	(bf)	(b)	(mc)	(gc)	(kh)	(c)	(ji)

14.2. Degenerate phase regions

* Law of adjoining phase region ~ applicable to space model and their vertical and isothermal sections, but <u>no invariant reaction isotherm or four-phase plane was included.</u>

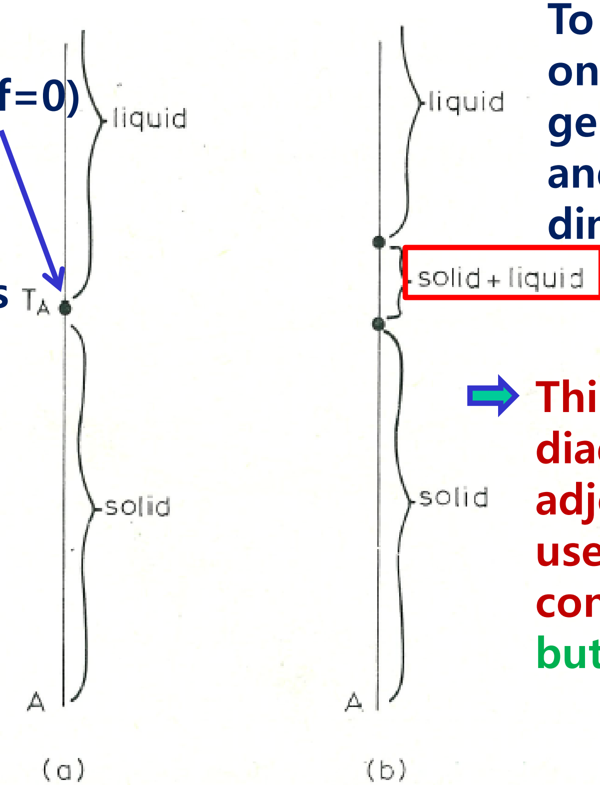
* In considering phase diagrams or section containing degenerate phase regions, it is necessary to replace the missing dimensions before applying the law of adjoining phase regions.

Phase rule: invariant reaction (f=0)

$(p+f = c+1;\ 2+f = 1+1)$

Law of adjoining phase regions

-1 ($R = 1,\ D^- = 1,\ D^+ = 1$; therefore $R_l = -1$)



To overcome this situation, one regards the point T_A as a degenerate (liquid+solid) phase region and one replaces the missing dimension to give the diagram.

➡ This is now a topologically correct diagram which obeys the law of adjoining phase regions (a very useful method for checking the construction of phase diagrams) but lead to violation of phase rule.

Fig. 228. Illustration of a degenerate phase region. (a) The melting of pure A; (b) the melting of pure A when point T_A is regarded as a degenerate phase region and replaced by a "solid+liquid" phase region.

*** Degenerate phase regions in space models of phase diagrams and in their sections can be dealt with in a similar manner by replacing the missing dimensions.**

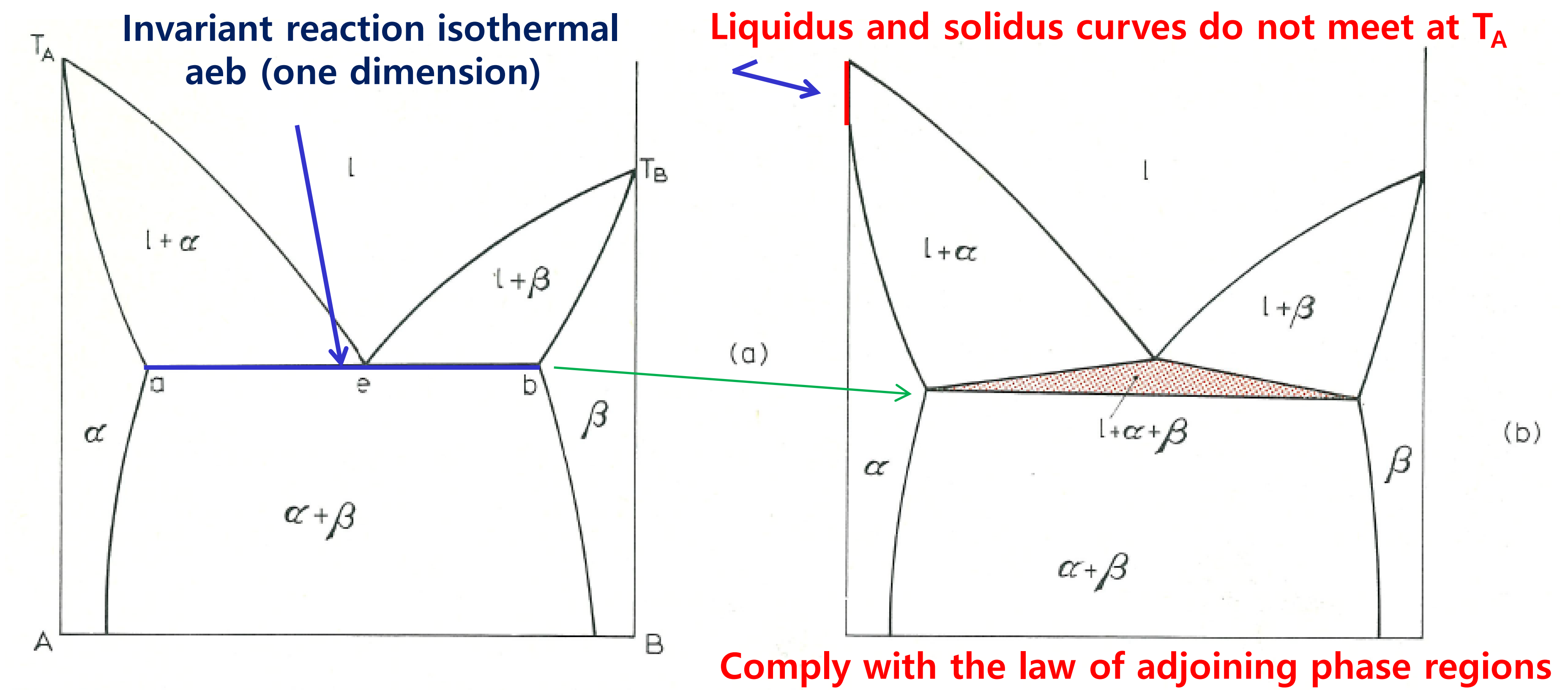
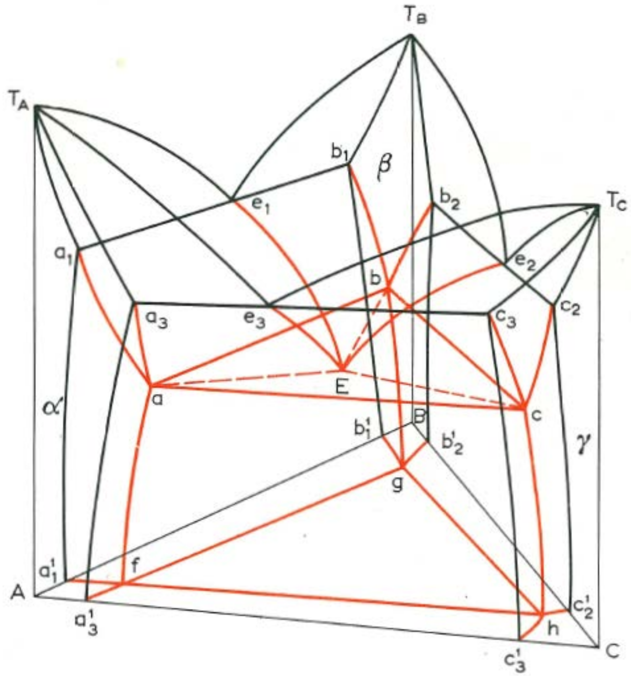


Fig. 229. Illustration of degenerate phase regions. (a) The eutectic phase diagram; (b) corresponding diagram allowing for degeneration of the phase regions.

* Sections through invariant four-phase planes in ternary systems



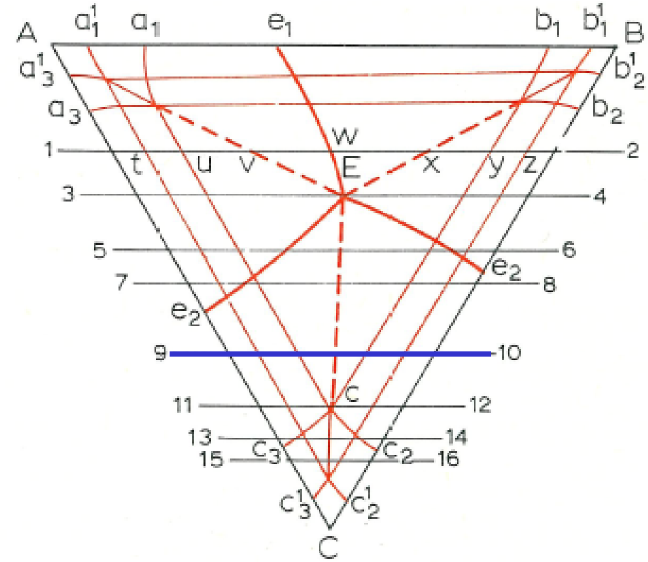


Fig. 177. Location of vertical section through Fig. 173a.

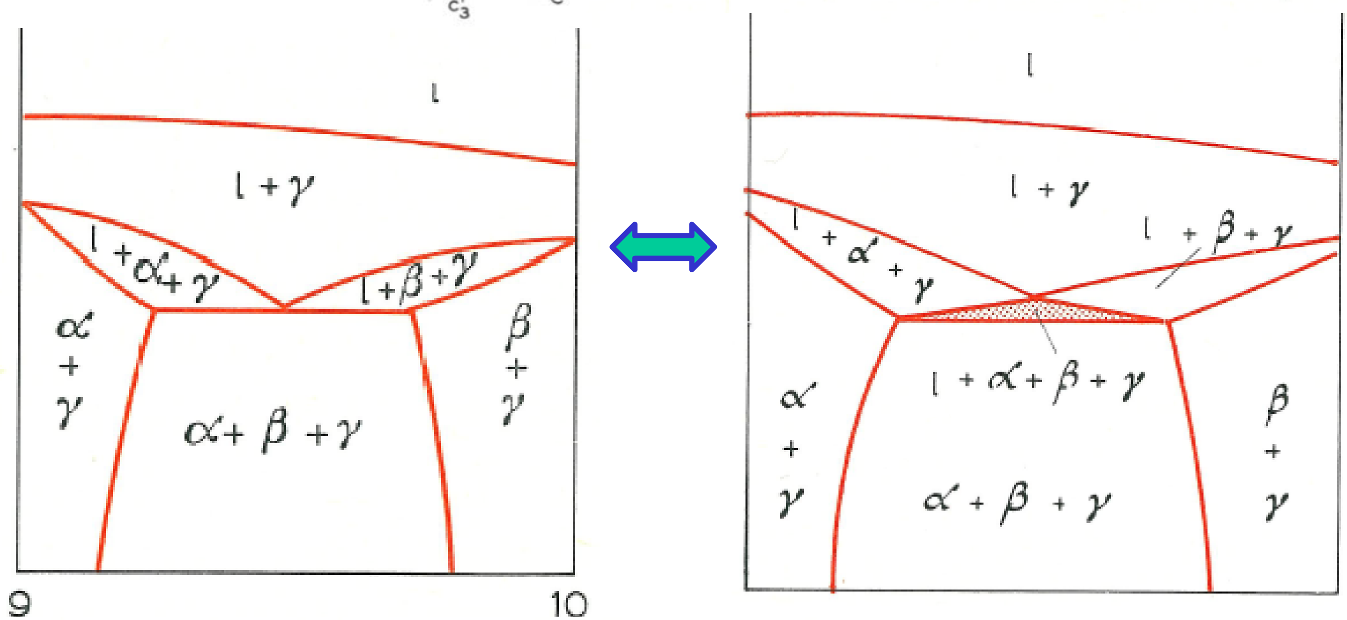
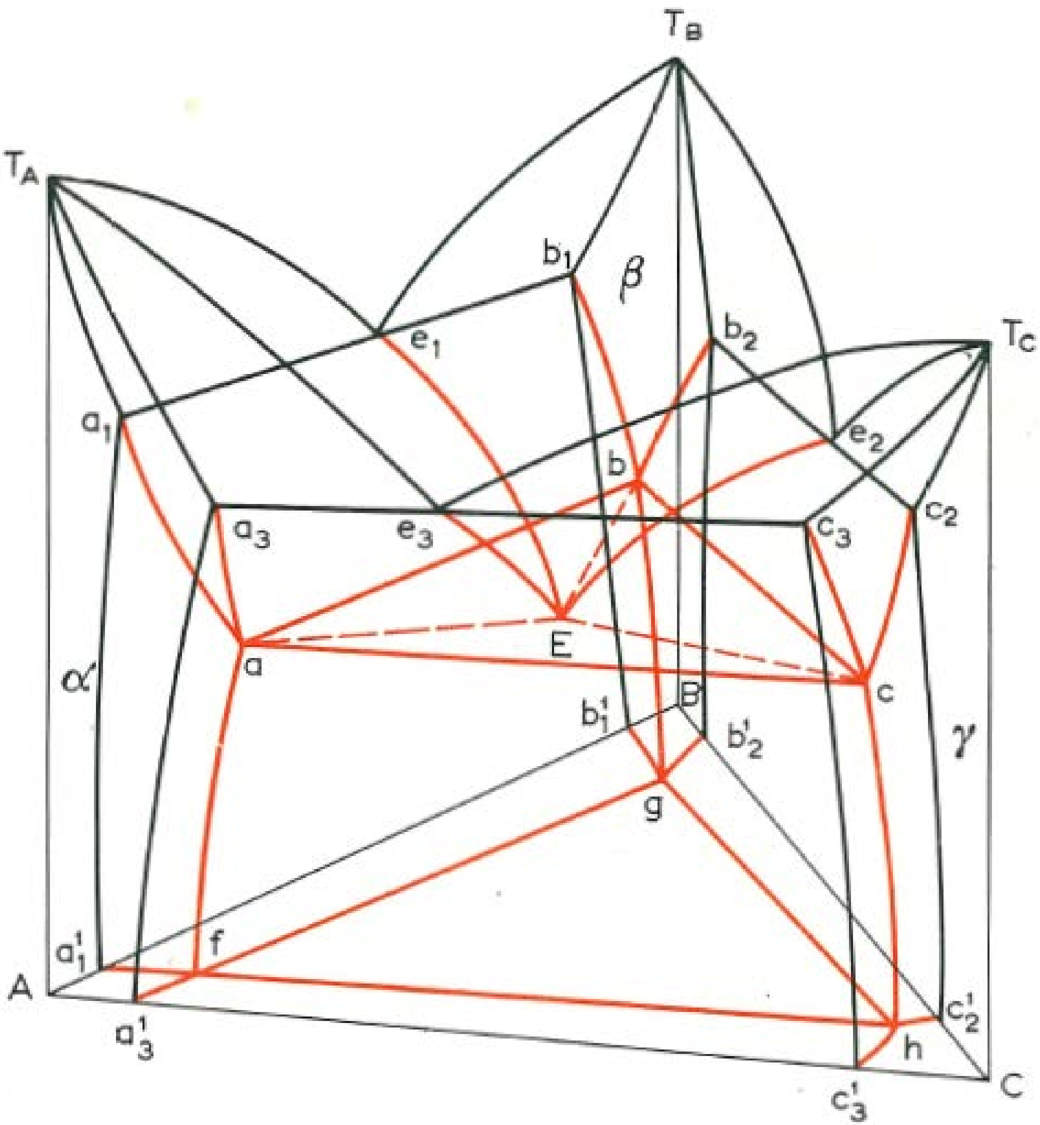


Fig. 230. Degeneration phase regions in vertical sections through ternary space models (Fig. 178e).

*** In three dimensional representations of ternary systems the junction of various phase regions can be summarized as follows:**



(1) A single phase region with a two phase region over a surface,

(2) A single phase region with a three phase region along a line (non-isothermal)

(3) A single phase region with a four-phase region at a points,

(4) a two phase region with a three phase region over a ruled surface,

(5) a two phase region with a four phase region along a tie line,

(6) a three phase region with a four phase region over a tie triangle,

(7) a surface separated two neighboring phase regions,

(8) four neighboring phase regions meet along a common line,

(9) six neighboring phase regions meet at a common points.

14.3. Two-dimensional sections of phase diagrams

*** The boundary between adjoining phase regions in a two-dimensional phase diagram or a two-dimensional section of a phase diagram can be either a line or a point. ($R_1 \leqslant R-1$)**

(a) R =2; R_1 = 1 _a line separates phase regions containing λ and λ+1 phases

(α from α+β, Fig. 220a; α+γ from α+β+γ, Fig. 178e; and l+α+γ from l+α+β+γ, Fig. 230). As stressed previously, the missing dimensions have to be added to degenerate phase regions to allow application of the law.

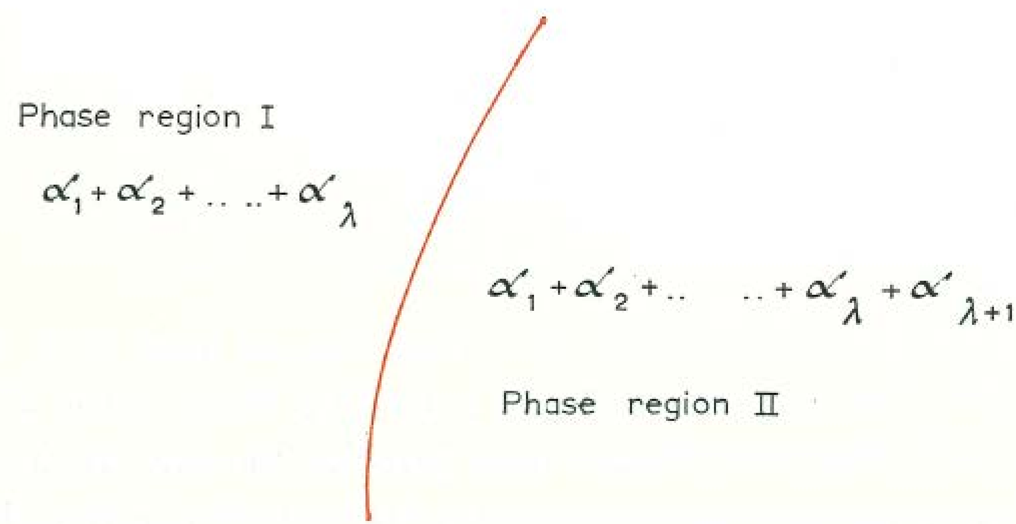


Fig. 231. Phase distribution in a two-dimensional diagram when the boundary between adjoining phase regions is one-dimensional.

14.3. Two-dimensional sections of phase diagrams

*** The boundary between adjoining phase regions in a two-dimensional phase diagram or a two-dimensional section of a phase diagram can be either a line or a point. ($R_1 \leqslant R-1$)**

(b) R =2; R_1 = 0_three boundary lines to meet at a point in a two dimensional diagram (Impossible)

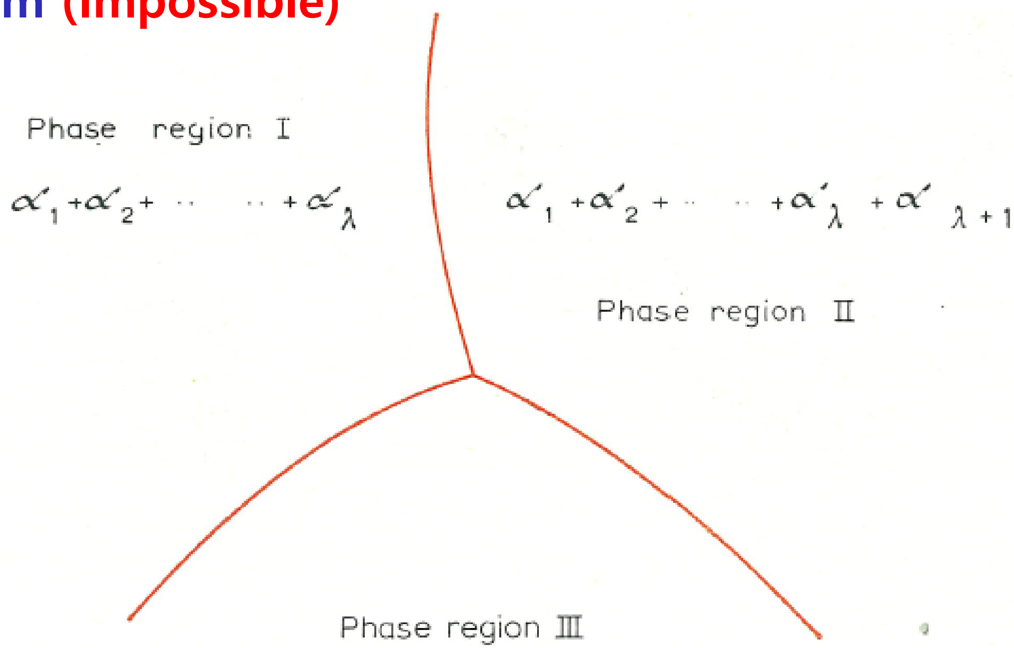


Fig. 232. Impossibility of three boundary lines meeting at a point in a two-dimensional diagram.

If we now consider the transition from region III to region II it is evident that none of the three possible phase compositions for region III satisfy the law of adjoining phase regions. At least four lines must meet at a point in a two-dimensional diagram. In general, only four lines meet at a point in a two-dimension diagram.

(b) R=2; R_1=0_only four lines may meet at a point in two-dimensional diagrams

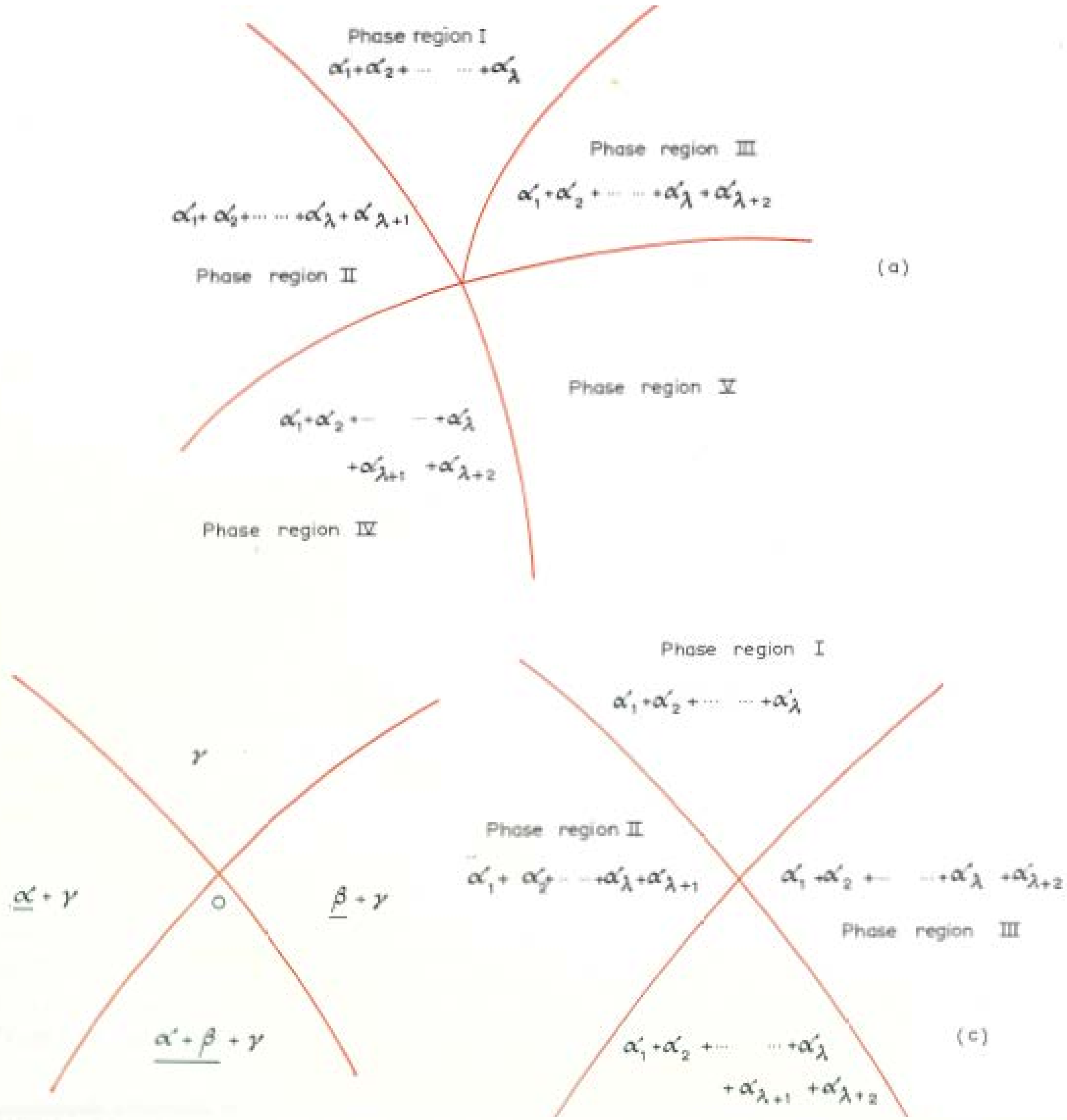


Fig. 233. Boundary lines meeting at a point in a two-dimensional diagram. (a) Impossibility of five lines meeting at a point; (b) distribution of phase regions when four lines meet at a point; (c) only four lines may meet at a point.

That there are exceptions to the rule that four lines meet at a point in a two-dimensional diagram is evident from an examination of Fig. 178b and f. In each case six lines meet at a central point. It will be noted, however, that in both cases the section passes through an invariant point—*E* and *c* respectively. Palatnik and Landau call such sections nodal or non-regular sections. Only regular sections obey the law of adjoining phase regions completely.

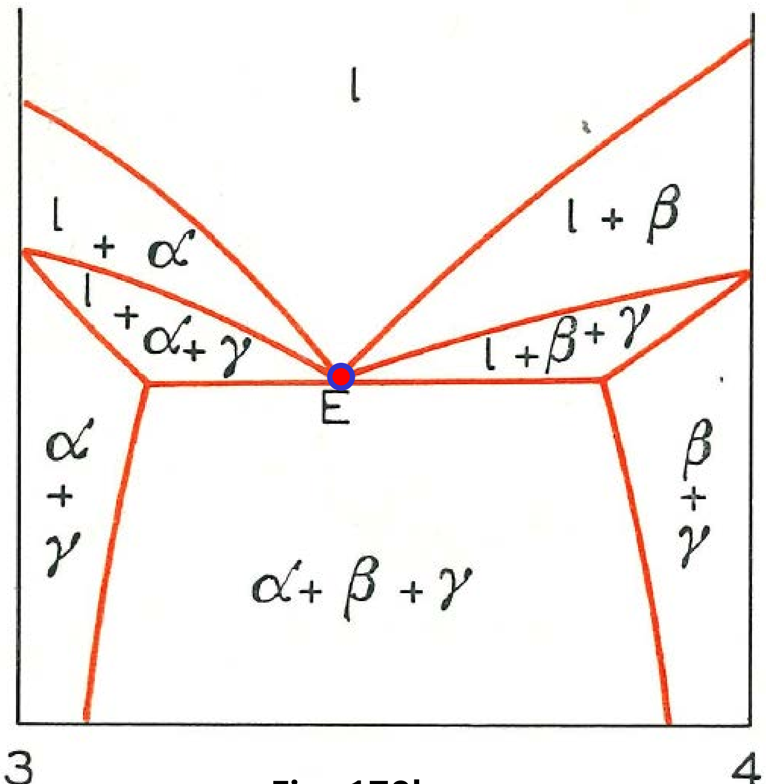


Fig. 178b

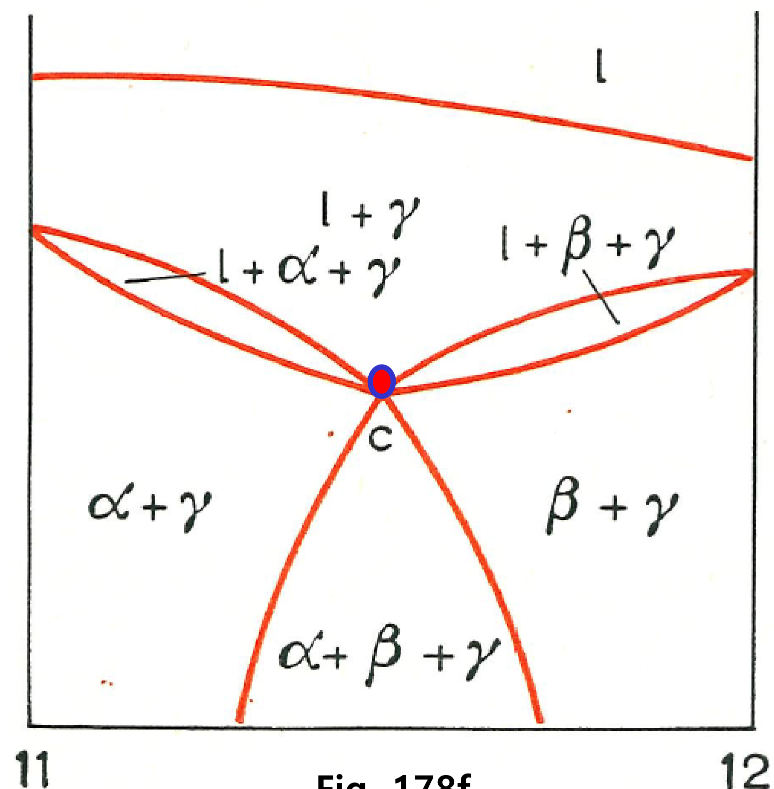


Fig. 178f

14.4. The Cross Rule: useful in checking the phases present in phase regions adjoining a point in two-dimensional diagrams

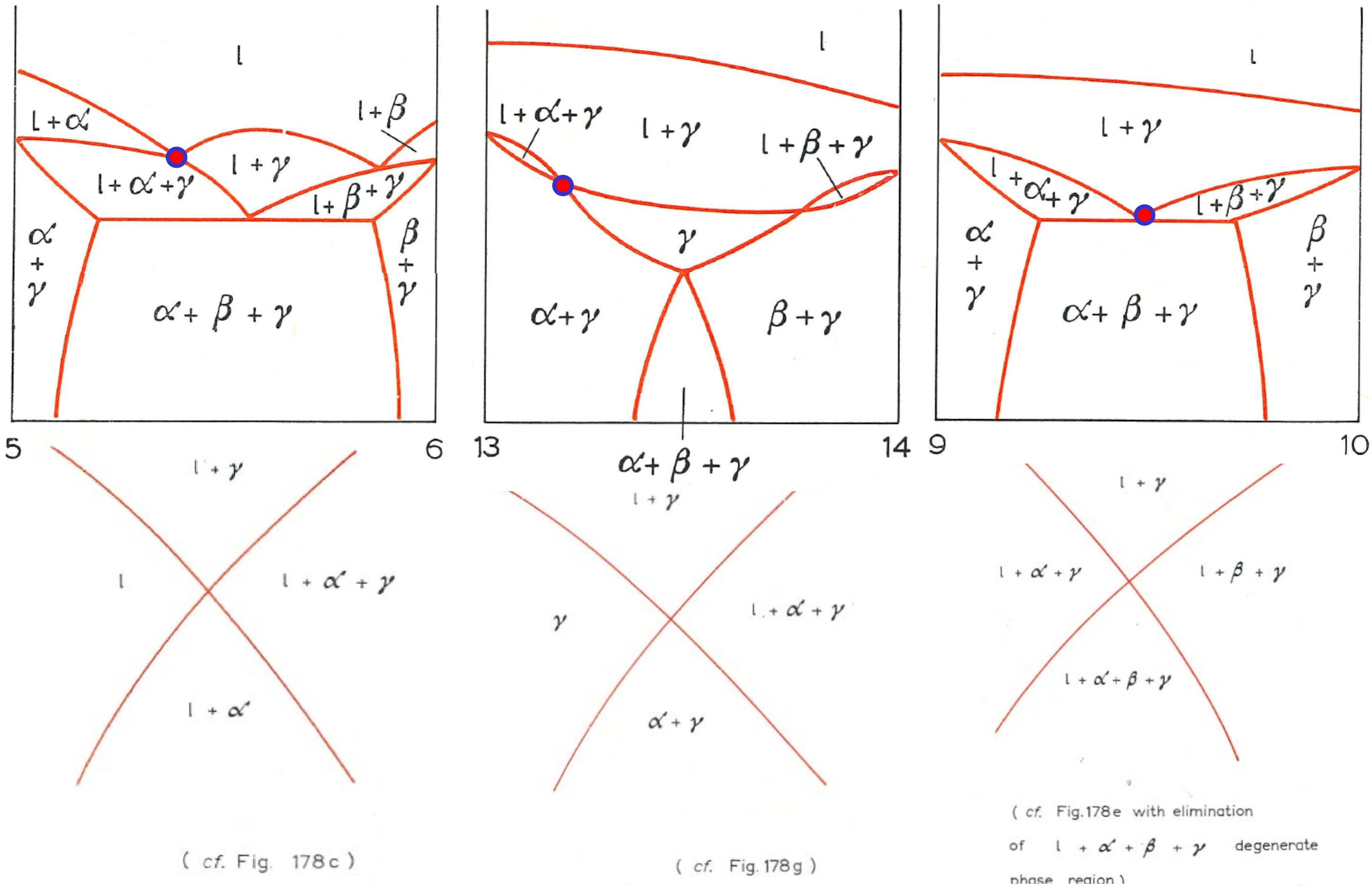
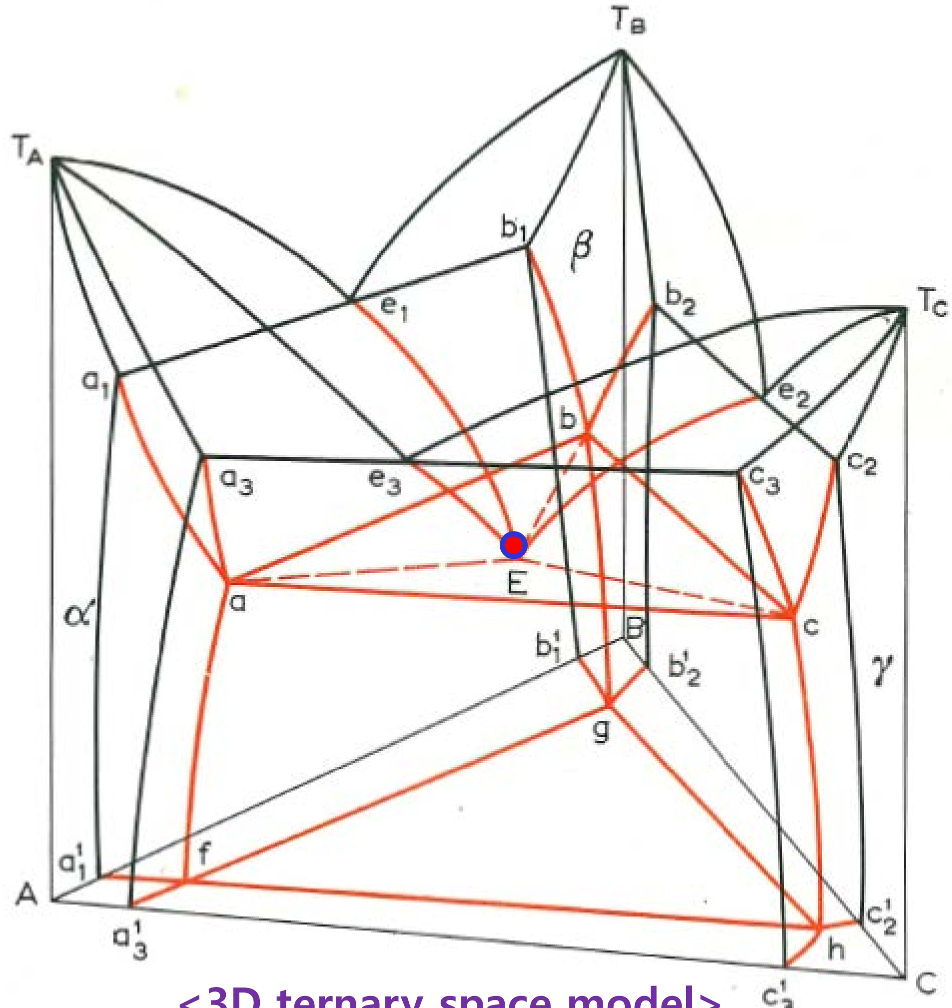


Fig. 234. The cross rule, (a) disposition of phase regions when one region is $l+\gamma$, (b) alternative disposition of phase regions.

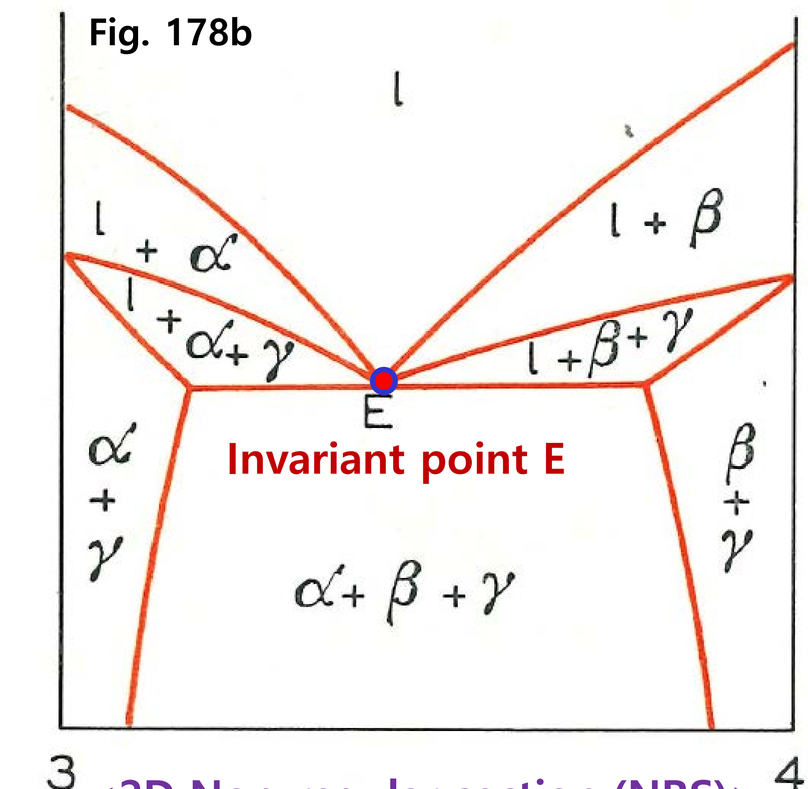
14.5. Non-regular two-dimensional sections

Non-regular sections behave erratically and the dimensions of the phase region boundaries in such sections are reduced irregularly compared to those in the phase diagram.



<3D ternary space model>

exceptions to the rule that four lines meet at a point in a two-dimensional



<2D Non-regular section (NRS)>

This boundary exists as a point in both the space model and the non-regular section. The point E and the associated boundaries (NRS) is a nodal plexus. Note that the degenerate phase region l + α + β + γ is not shown in (NRS).

14.5. Non-regular two-dimensional sections

Nodal plexi can be classified into four types according to the manner of their formation:

Type 1 The nodal plexus is formed without degeneration of any geometrical element of the two-dimensional regular section to elements of a lower dimension

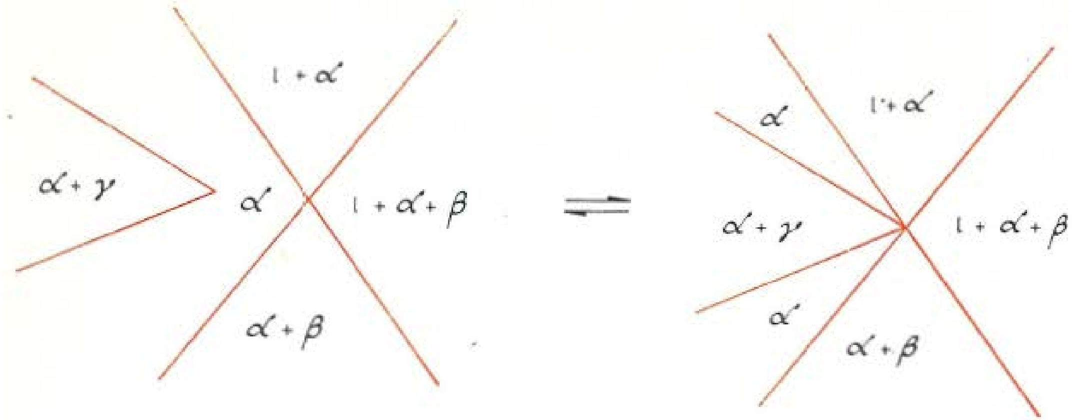


Fig. 235. Type 1 nodal plexus.

Type 2 The number of lines degenerate to a point but there is no degeneration of two dimensional phase regions. In the formation of a type 2 nodal plexus the line O_1O_2 in the regular section degenerates into point O of the nodal plexus associated with the non-regular section.

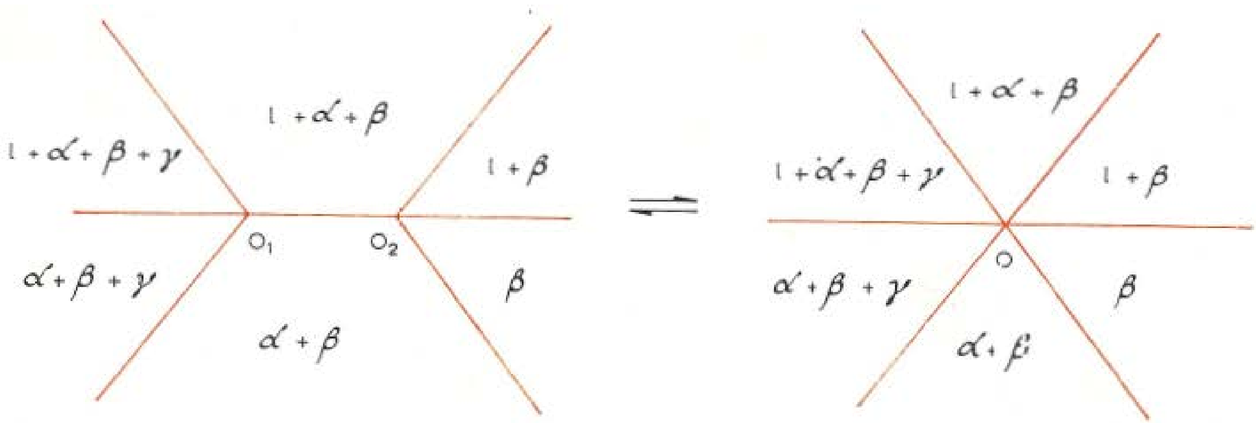


Fig. 236. Type 2 nodal plexus.

14.5. Non-regular two-dimensional sections

Nodal plexi can be classified into four types according to the manner of their formation:

***Type* 3** **A number of two dimensional phase regions degenerate into a point.** **In this case the phase region l + α + β disappears with the transition from a regular to a non-regular two dimensional section.**

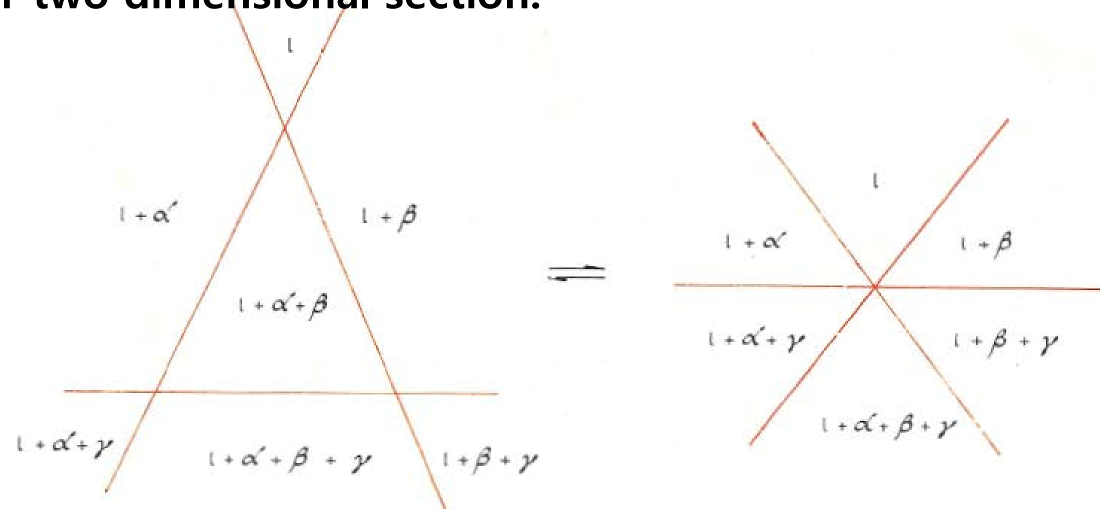


Fig. 237. Type 3 nodal plexus.

***Type* 4** **A number of two dimensional phase regions degenerate to a line.** **In the formation of the nodal plexus the phase region l + β + γ and β + γ have degenerated into the line O_1O_2.**

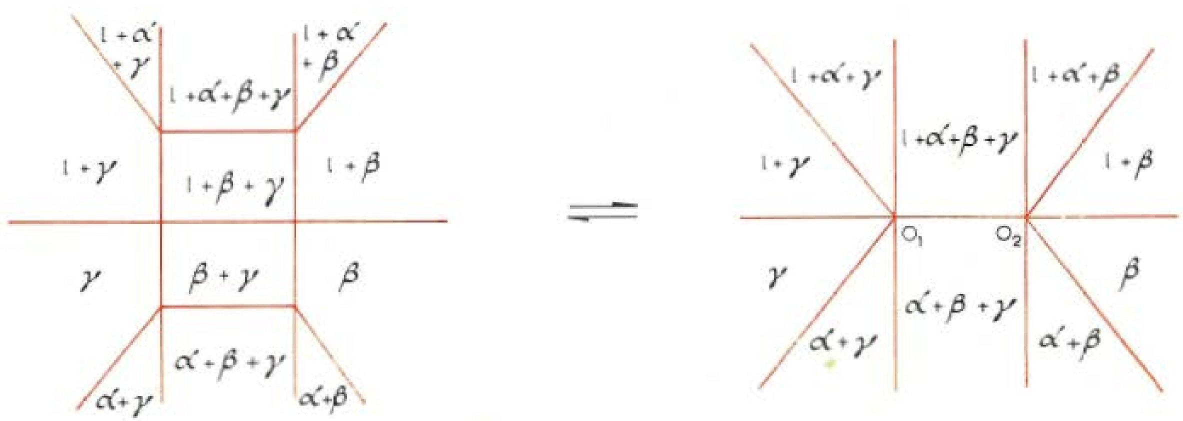


Fig. 238. Type 4 nodal plexus.

14.5. Non-regular two-dimensional sections

Nodal plexi can be classified into four types according to the manner of their formation:

Nodal plexi of mixed types may also be formed. A type 2/3 one is shown in Fig. 239. In the formation of the nodal plexus the two dimensional l + γ region degenerates to a point – triangle $O_2O_3O_4$ degenerates to point O – and the line O_1O_2 degenerates to the same point O. The former process corresponds to the formation of a type 3 nodal plexus and the latter to the formation of a type 2 nodal plexus.

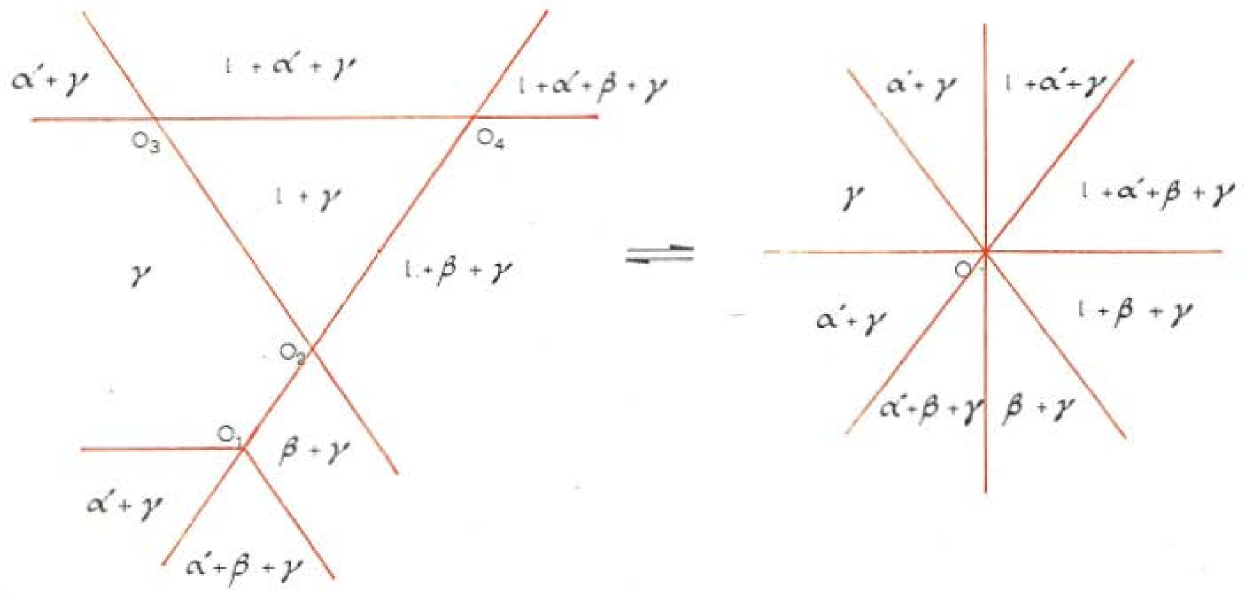


Fig. 239. Mixed type 2/3 nodal plexus.

1) **Formation of nodal plexi:**
   Transition from a regular section to a non-regular section of a ternary system

2) **Opening of nodal plexi:**
   Subsequent transition from the non-regular section back to a regular section

Fig. 240. Formation and opening of nodal plexi

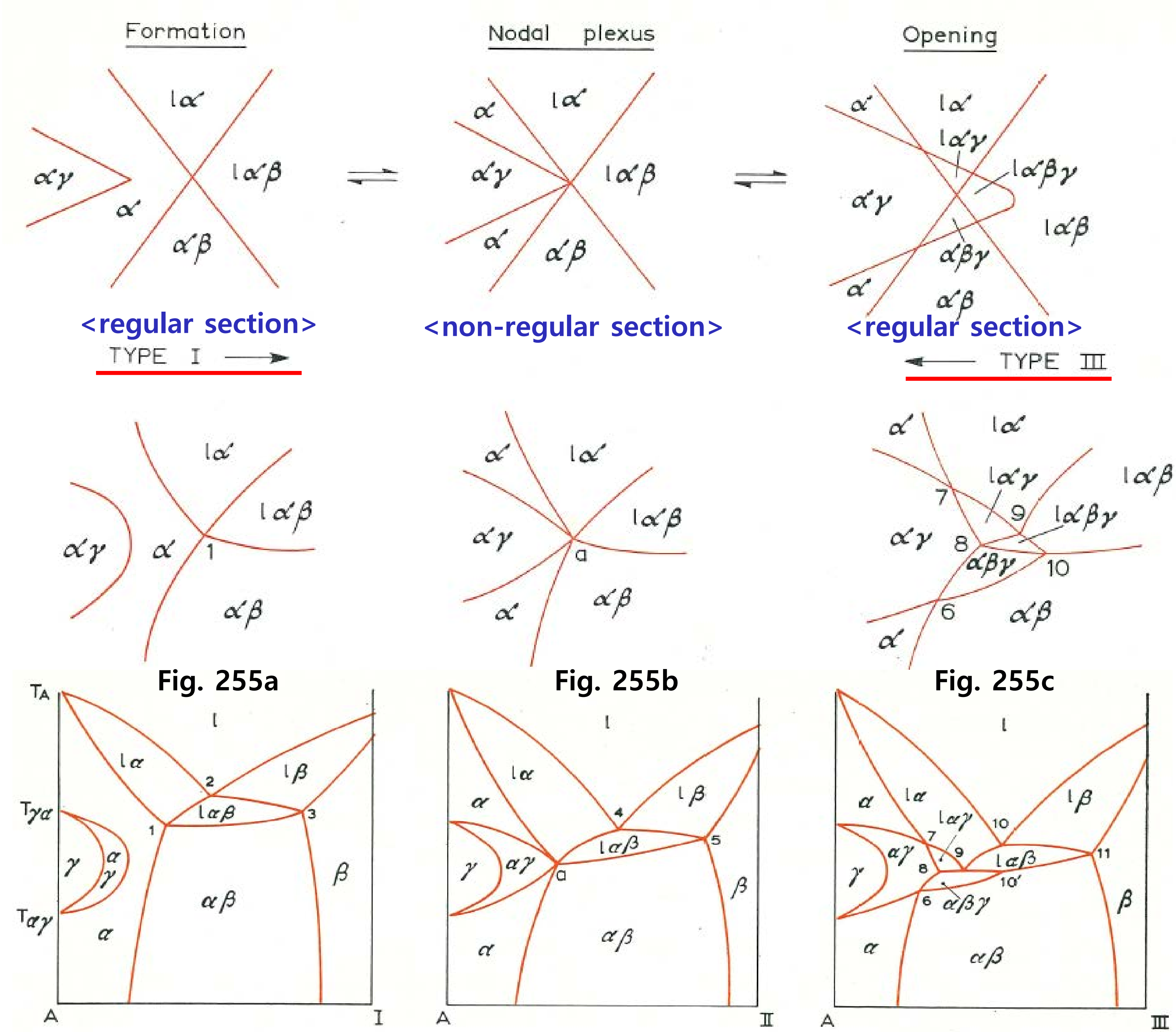
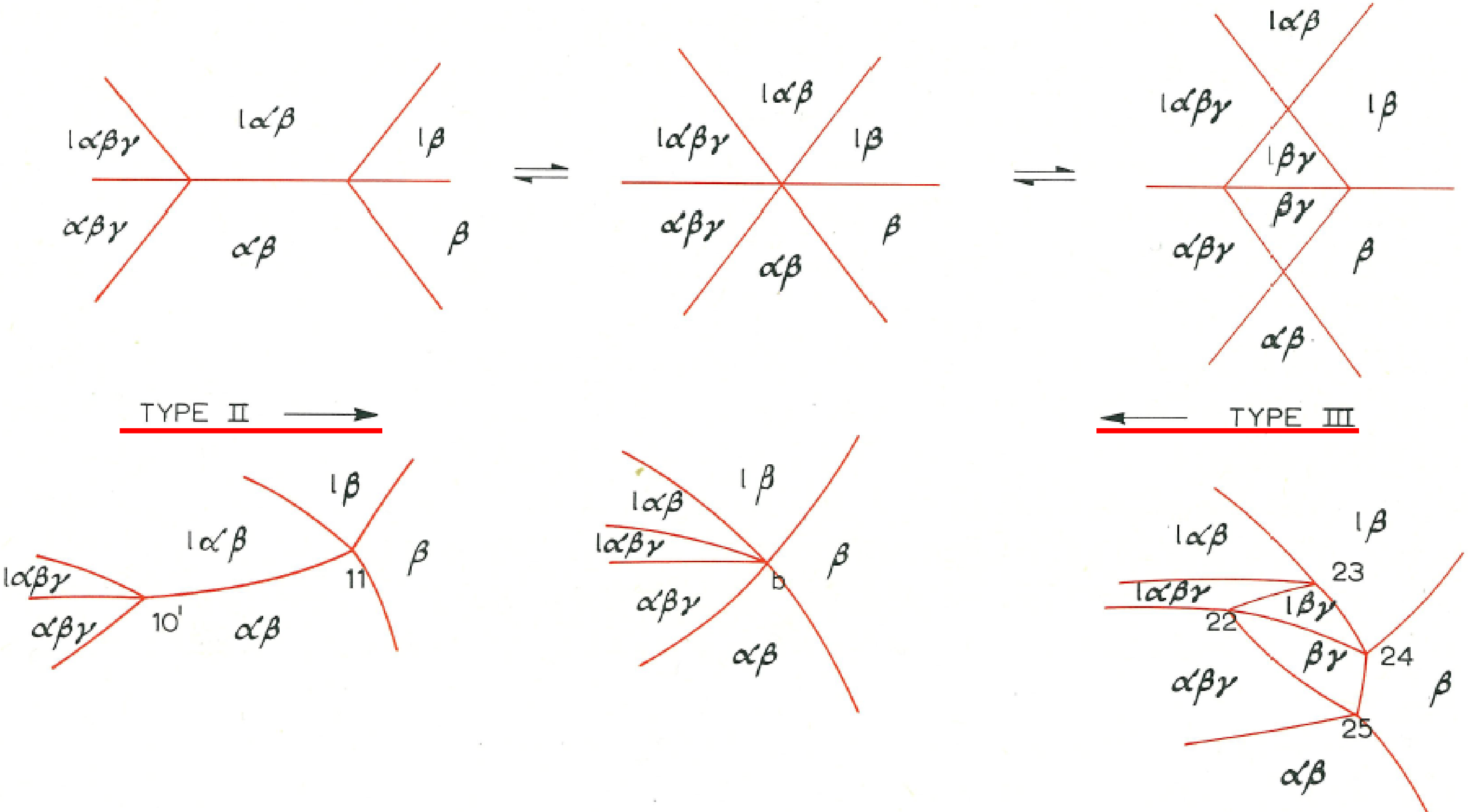


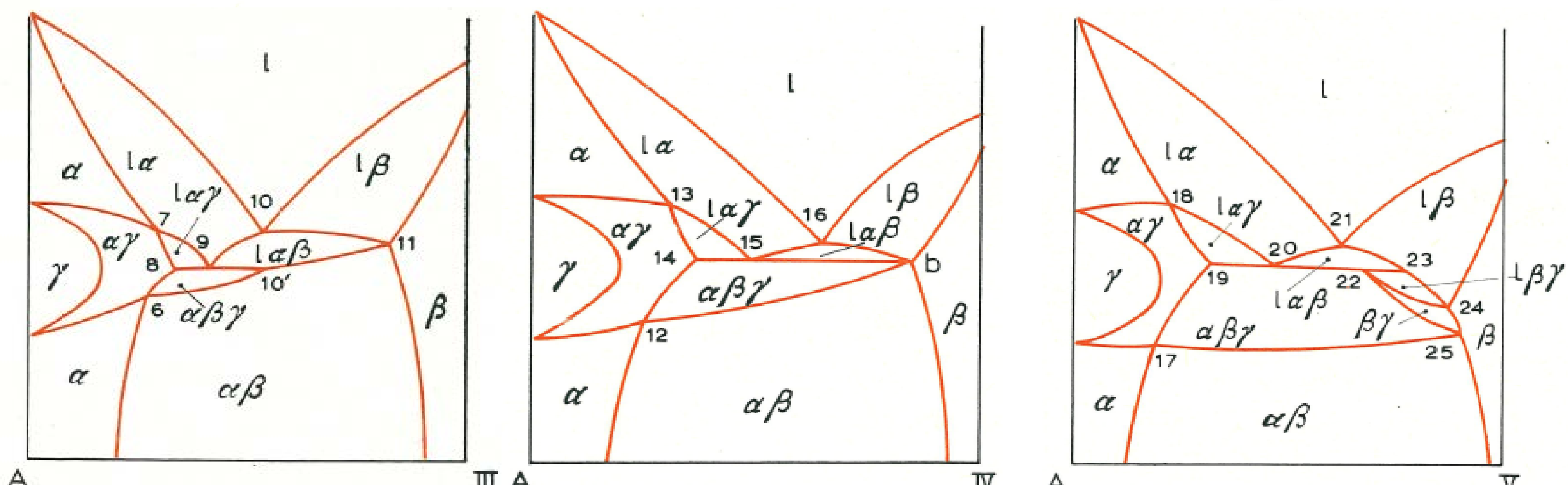
Fig. 255a

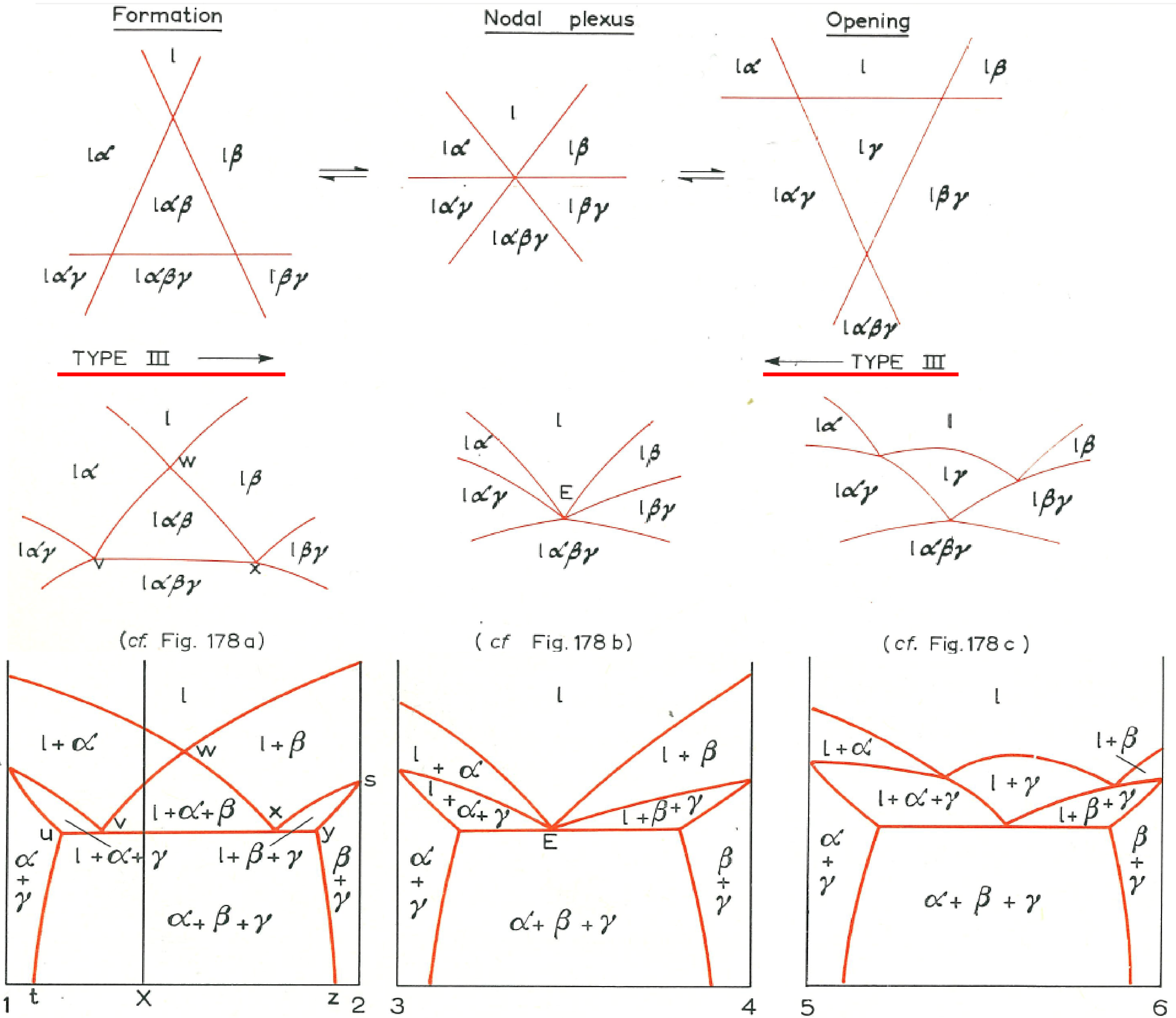
Fig. 255b

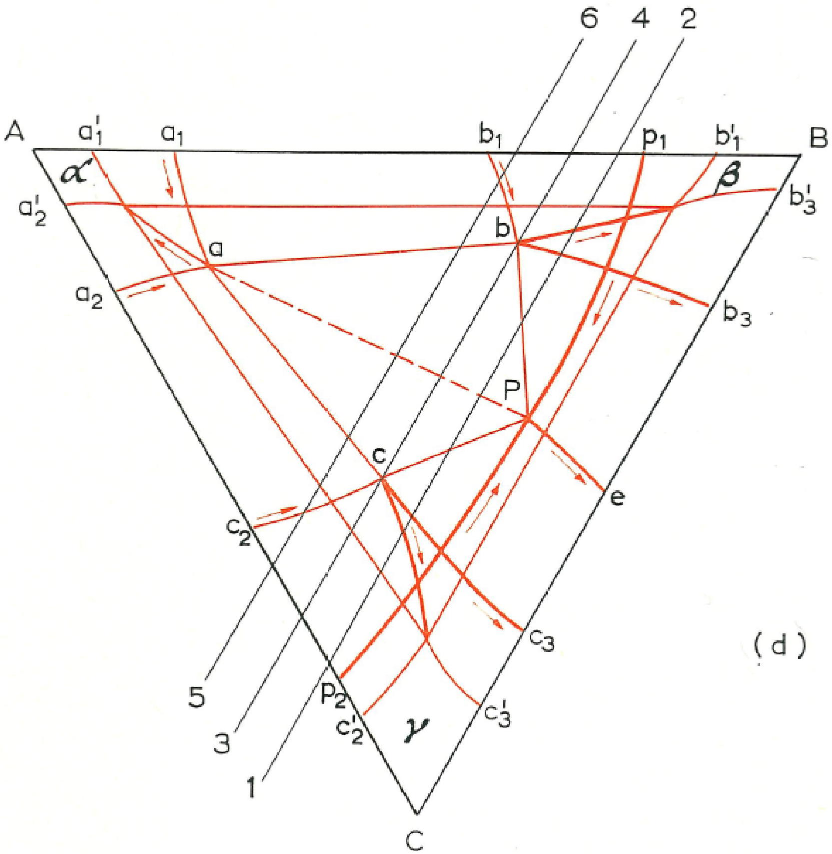
Fig. 255c

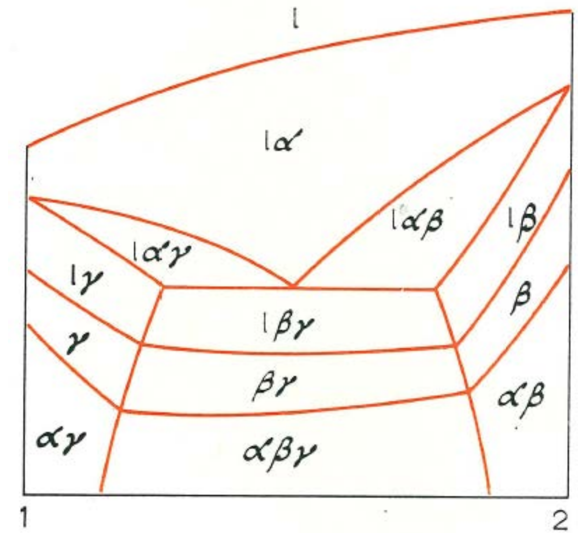


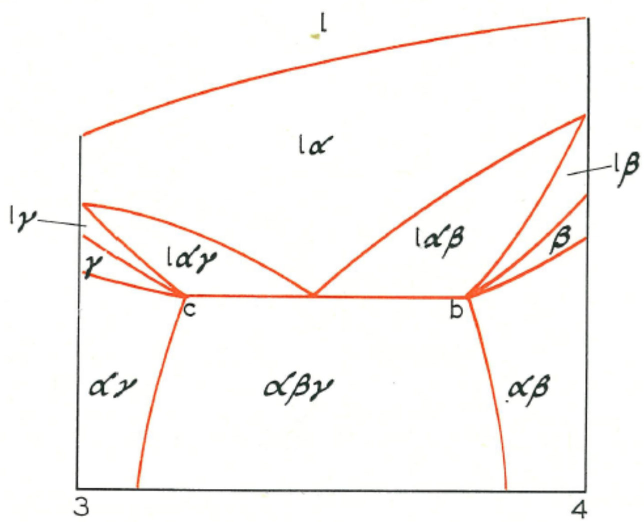
(cf. Fig. 225 c) (cf. Fig. 225 d) (cf. Fig. 225 e)

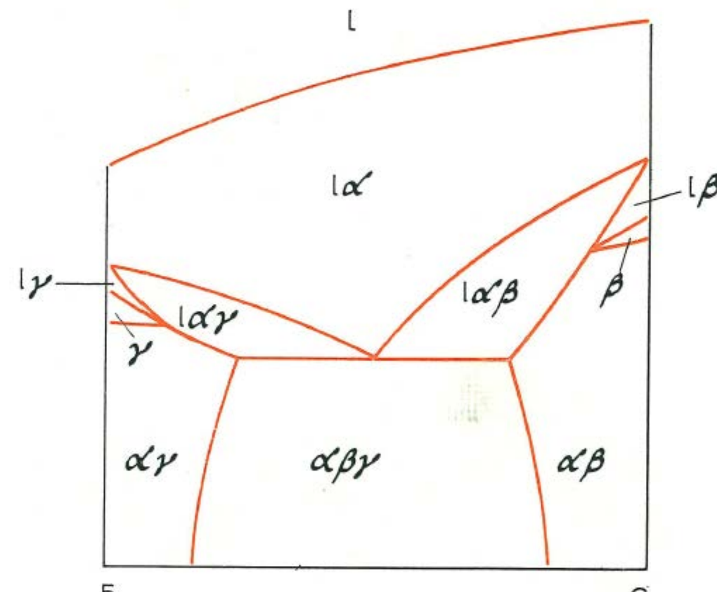



Formation
Nodal plexus
Opening
l
lα
lβ
lαβ
lαγ
lαβγ
lβγ
lγ
TYPE III
TYPE III
w
v
x
E
(cf. Fig. 178 a)
(cf Fig. 178 b)
(cf. Fig. 178 c)
l + α
l + β
l + α + β
l + α + γ
l + β + γ
l + γ
α + γ
β + γ
α + β + γ
r
s
u
y
t
X
z
1
2
3
4
5
6


A
B
C
α
β
γ
a'1
a1
b1
p1
b'1
a'2
b'3
a
b
a2
b3
P
c
e
c2
c3
p2
c'2
c'3
1
2
3
4
5
6
(d)


l
lα
lαβ
lβ
lαγ
lγ
β
lβγ
γ
βγ
αβ
αγ
αβγ
1
2
(a)


l
lα
lβ
lγ
lαβ
γ
lαγ
β
c
b
αγ
αβγ
αβ
3
4
(b)


l
lα
lβ
lγ
lαβ
lαγ
β
γ
αγ
αβγ
αβ
5
6
(c)

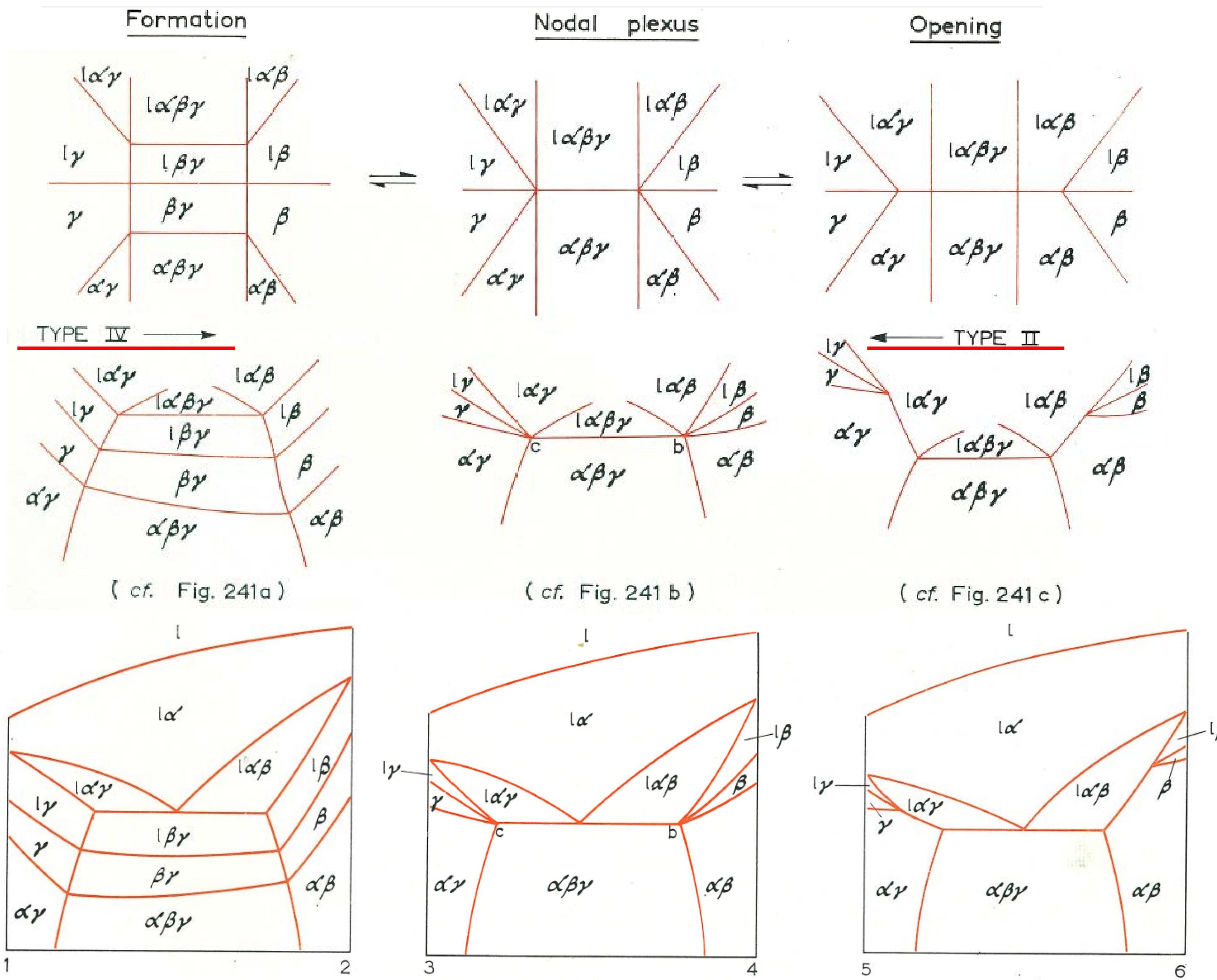

Formation
Nodal plexus
Opening
TYPE IV
TYPE II
(cf. Fig. 241a)
(cf. Fig. 241 b)
(cf. Fig. 241 c)
l
lα
lγ
lβ
lαγ
lαβ
lβγ
γ
β
βγ
αγ
αβ
αβγ
lαβγ
c
b
1
2
3
4
5
6

Fig. 240. Formation and opening of nodal plexi

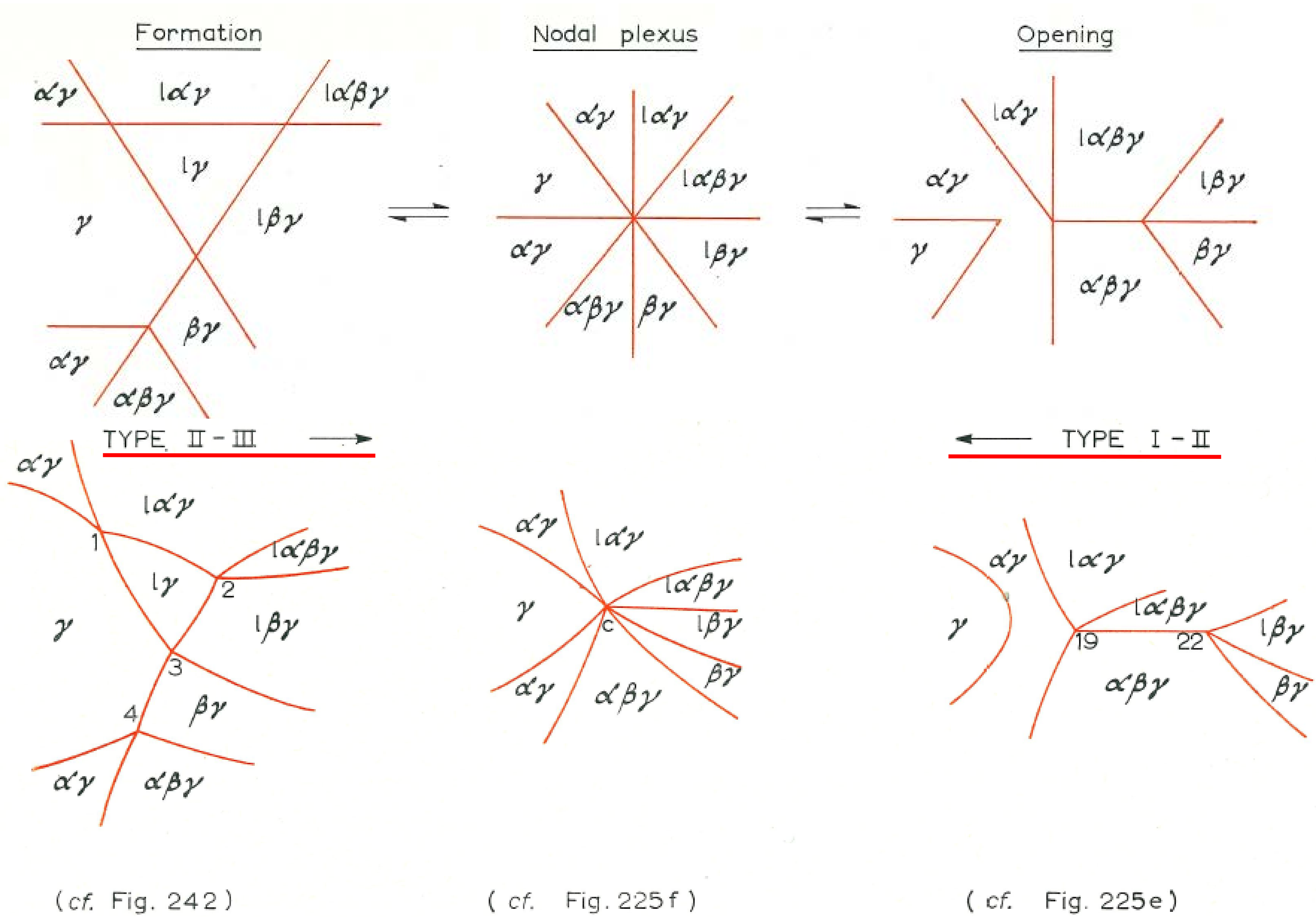


Fig. 240 (e).