2021 Spring

"Phase Equilibria in Materials"

05.11.2021

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Chapter 12. Ternary phase Diagrams Liquid Immiscibility

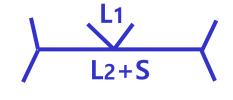
Liquid immiscibility in one or more of the binary systems can lead to either three-phase or four-phase equilibria in the ternary system.

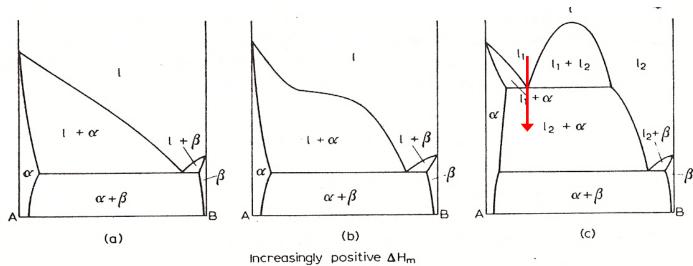
Immiscibility can arise if either <u>monotectic or syntectic reactions</u> occur in the binary system; <u>true ternary immiscibility</u> is also possible.

1) Liquid immiscibility in binary system

* Monotectic reaction:

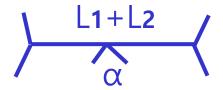
Liquid1 ↔ Liquid2+ Solid



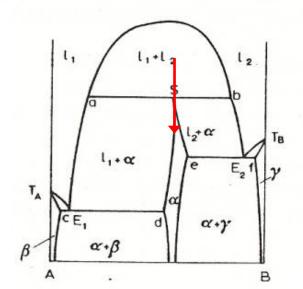


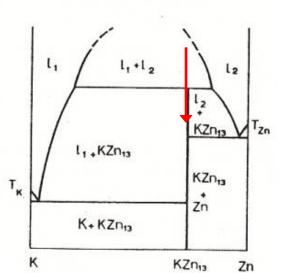
* Syntectic reaction:

Liquid1+Liquid2 $\leftrightarrow \alpha$



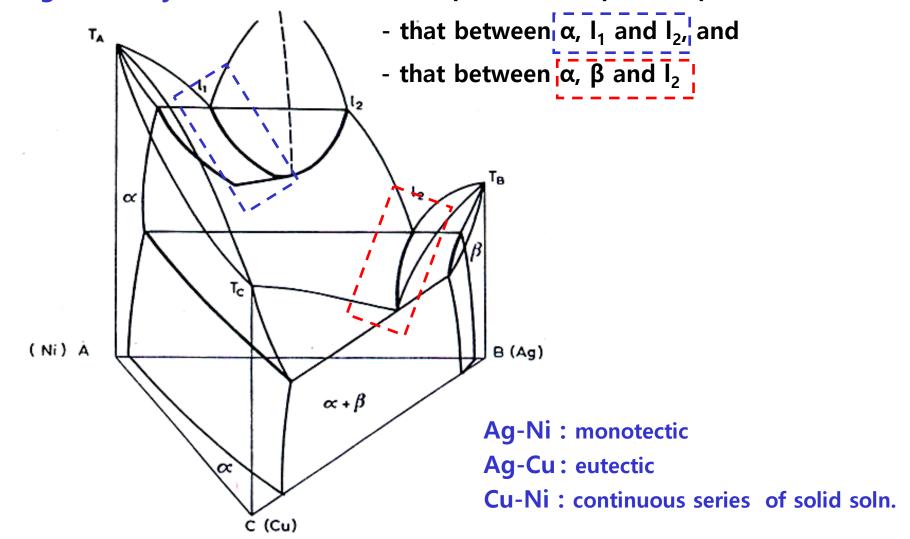
K-Zn, Na-Zn, K-Pb, Pb-U, Ca-Cd





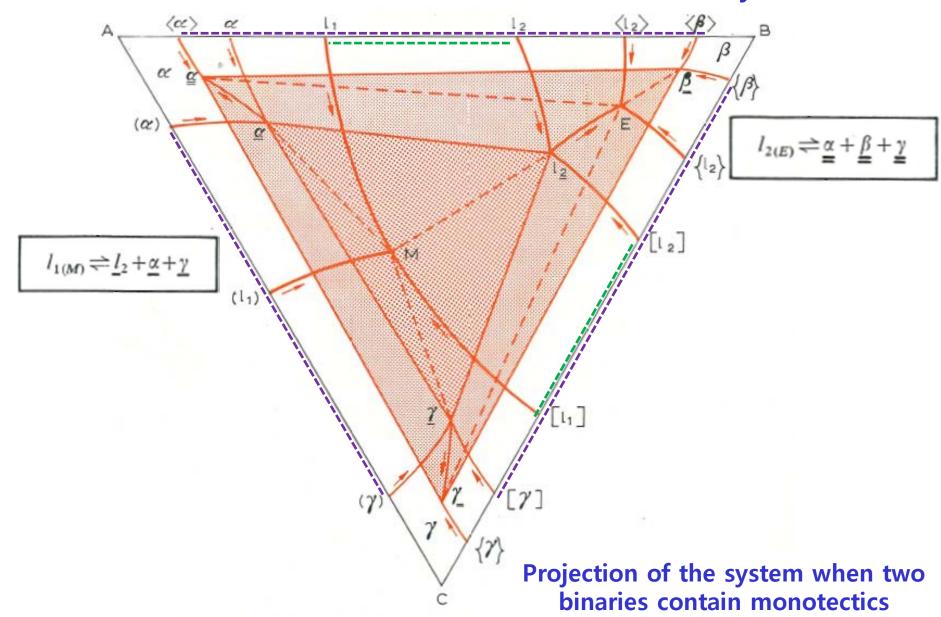
2) One binary liquid miscibilty gap in ternary system

- 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

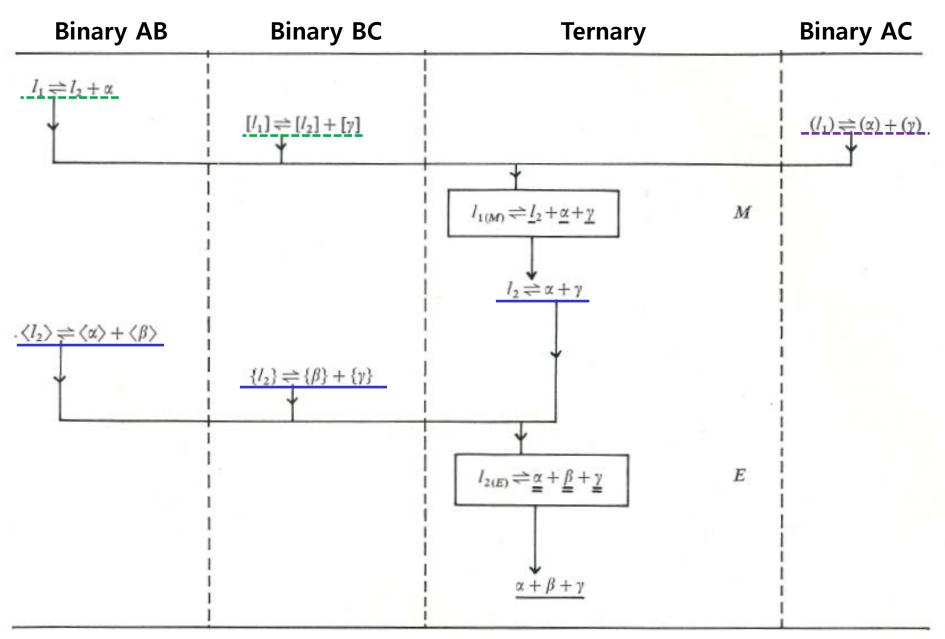


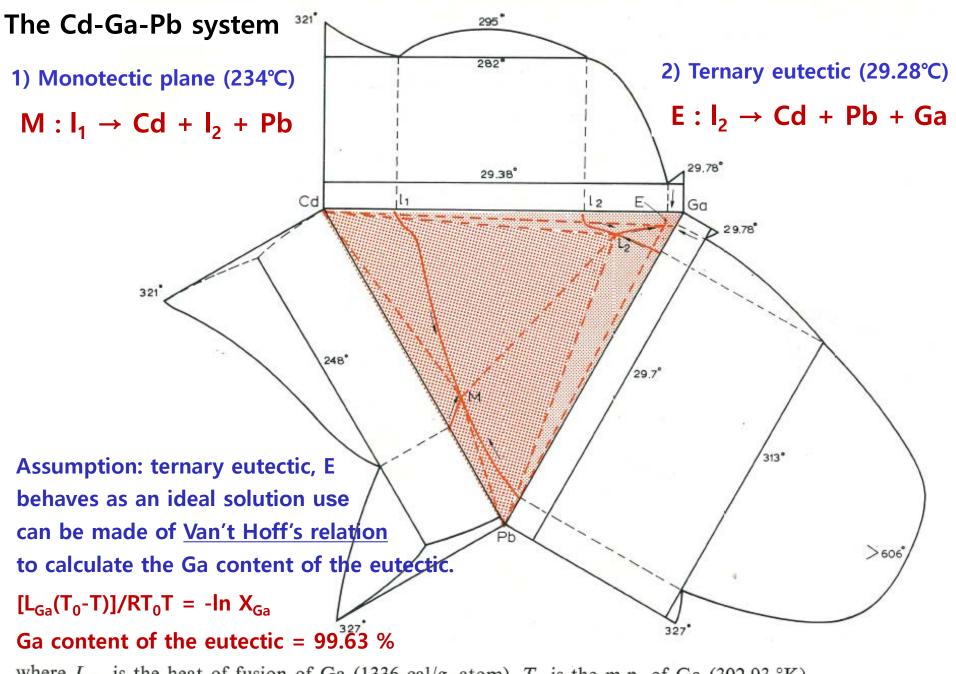
12.1. Two Binary Systems are Monotectic

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



* Tabular foam of the system when two binaries contain monotectics

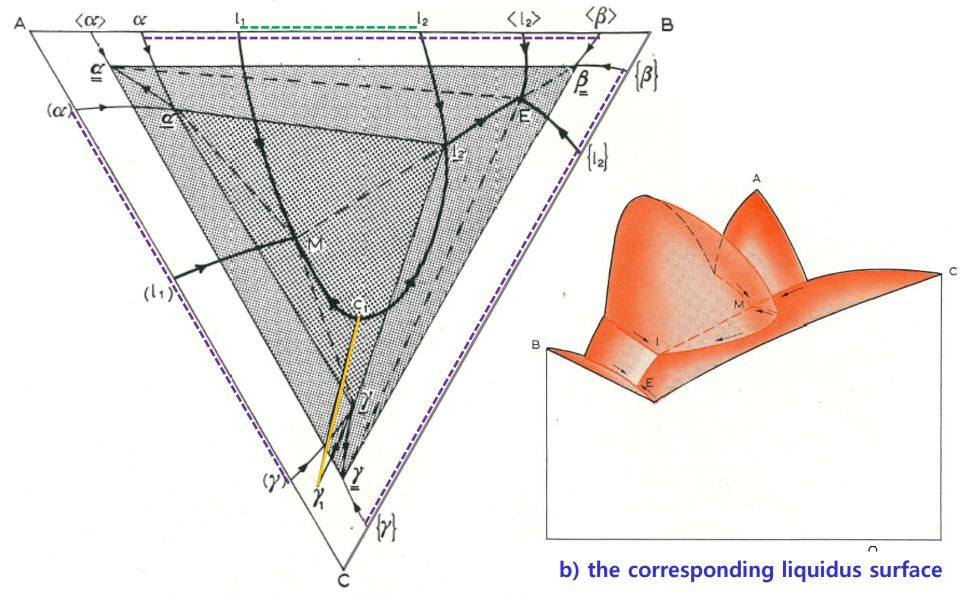




where L_{Ga} is the heat of fusion of Ga (1336 cal/g.-atom), T_0 is the m.p. of Ga (302.93 °K), T is the ternary eutectic temperature, R the gas constant, and X_{Ga} the Ga content of the ternary eutectic E_1

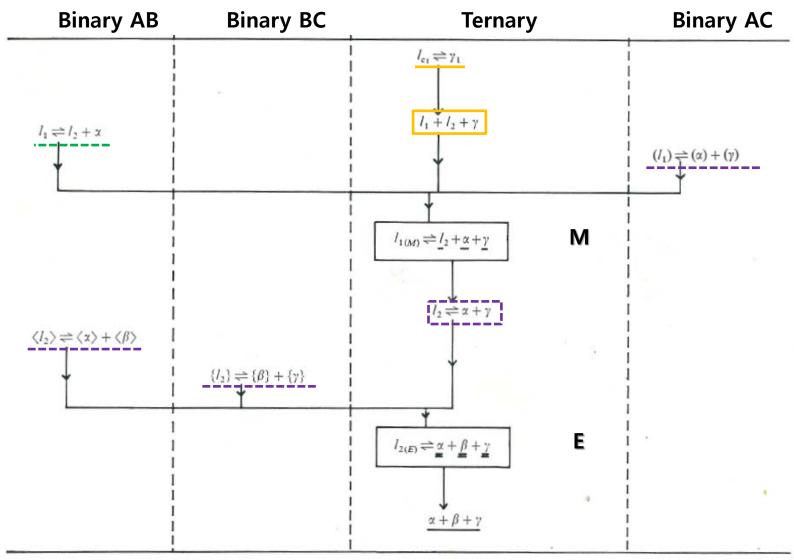
12.2. One Binary System is Monotectic Liquid immiscibility in ternary system

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



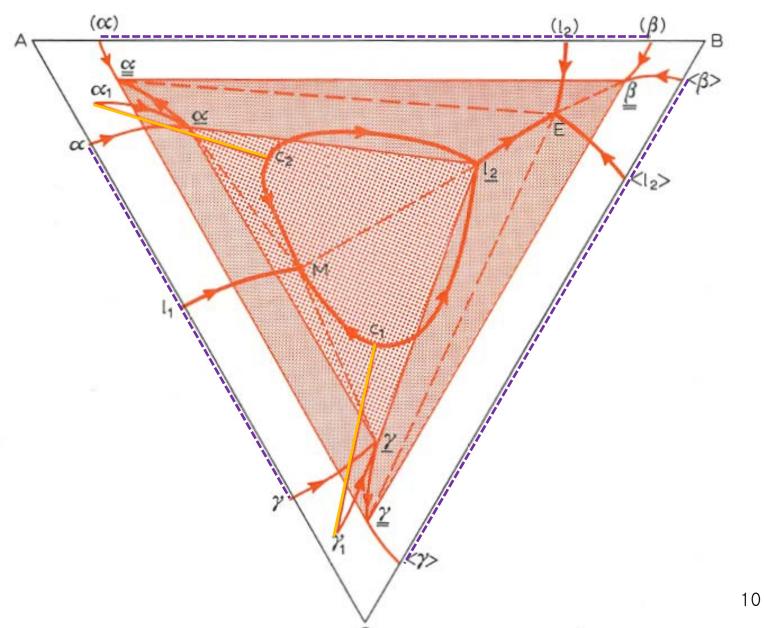
12.2. One Binary System is Monotectic

* Tabular foam of the system when two binaries contain monotectics



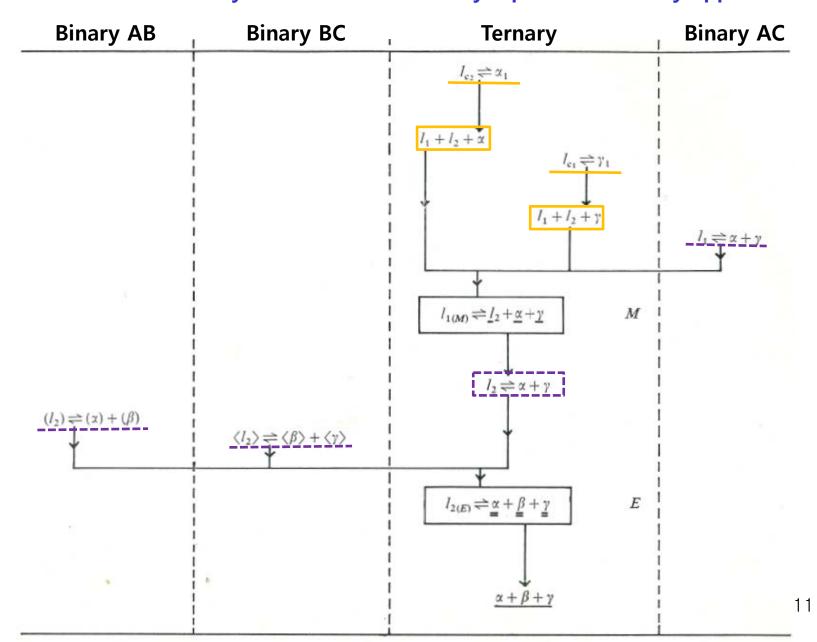
^{*} ex) Fe₃C-FeS-Fe: partial system of C-Fe-S ternary

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



12.3. True Ternary Liquid Immiscibility Appears

* Tabular foam of the system when 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

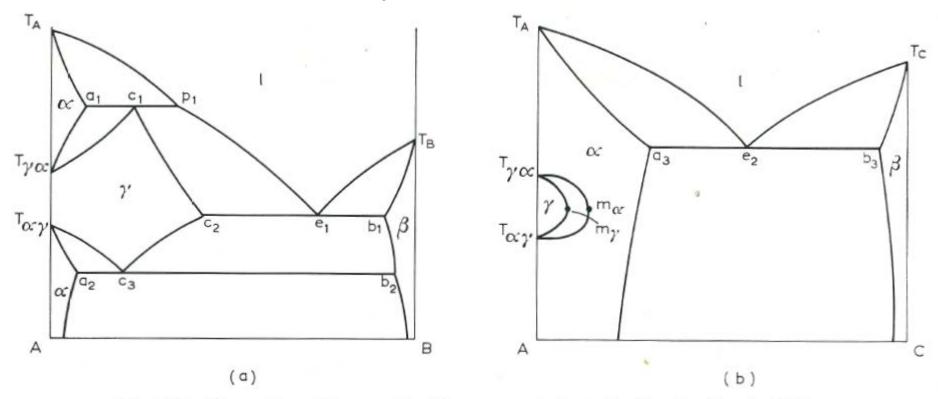


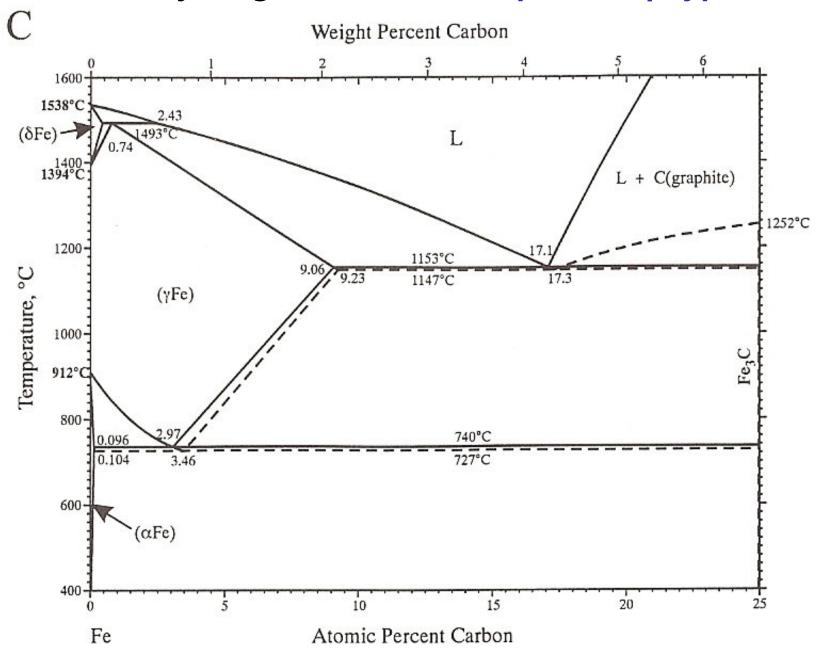
Fig. 220. Binary phase diagram (a) with an expanded γ field, (b) with closed γ field.

Recognisable as the Fe-Fe₃C 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



100

Si

Fe

Fe

Atomic Percent Silicon

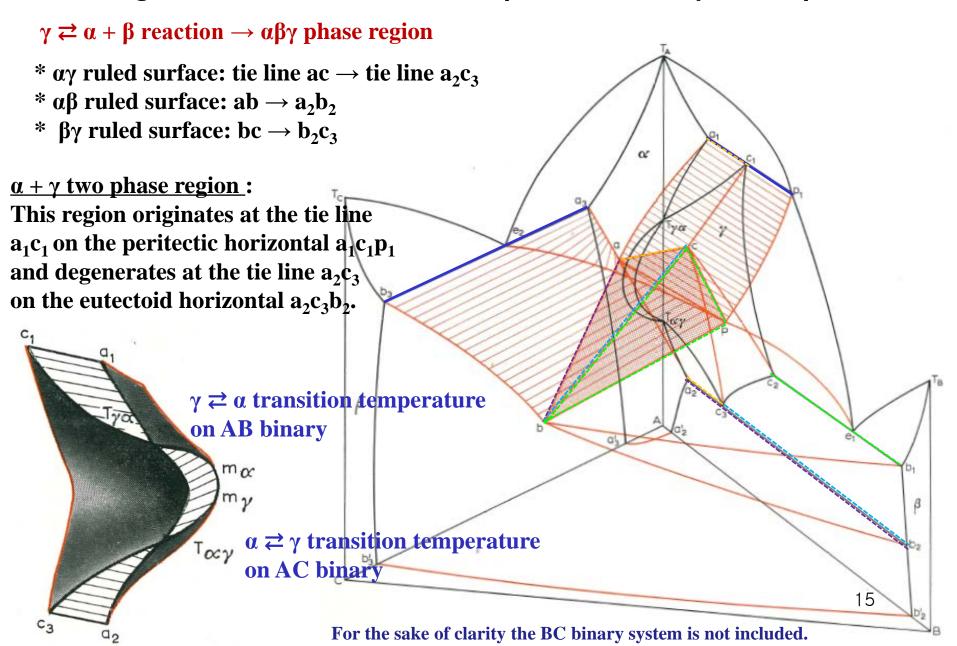
50

Atomic Percent Tungsten

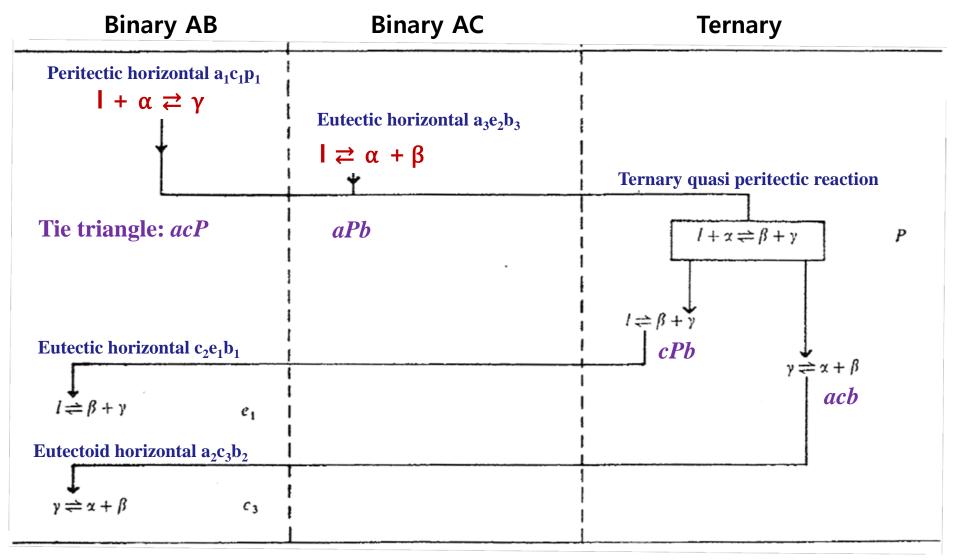
100

W

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

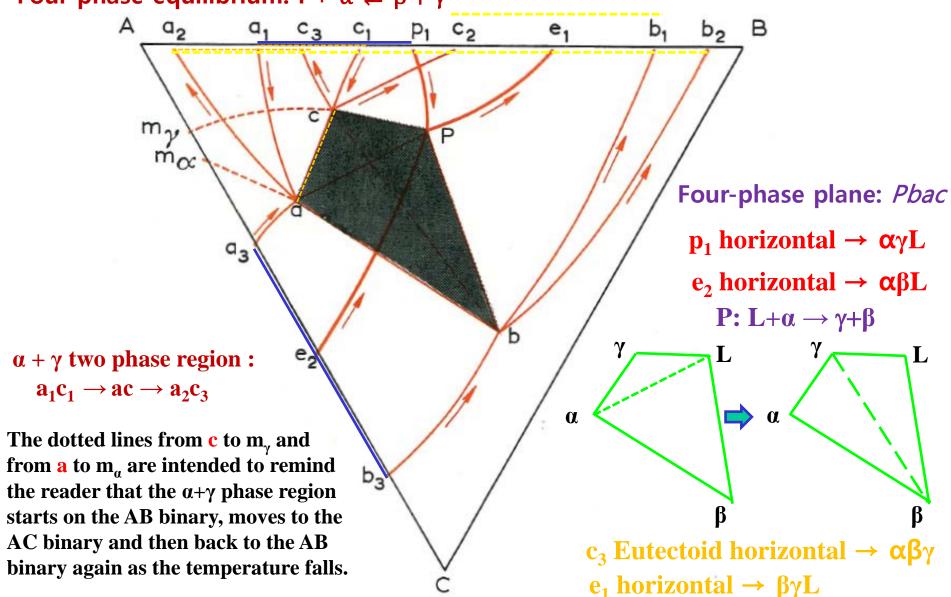


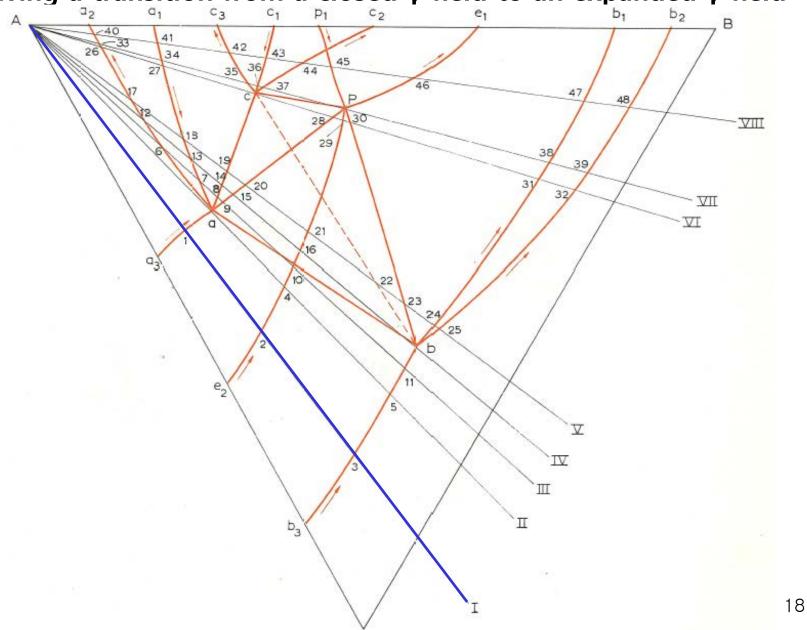
A tabular representation of the ternary

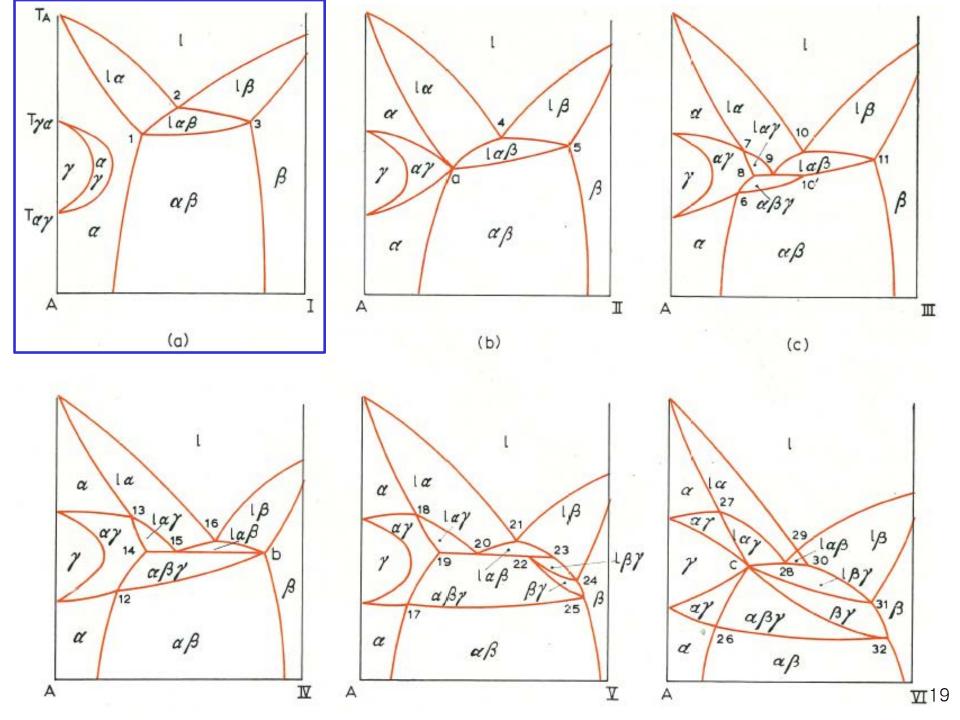


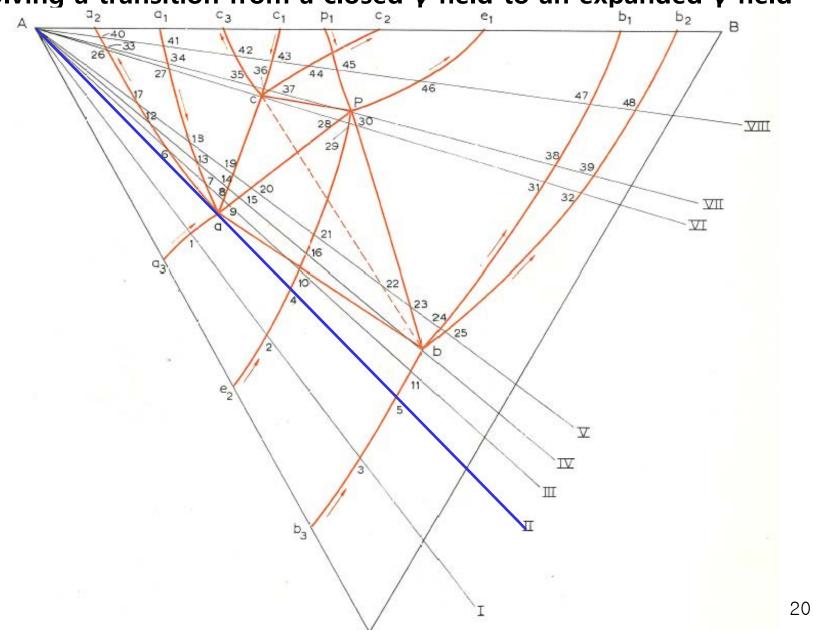
Projection of the ternary system involving a transition from a closed γ field to an expanded γ field

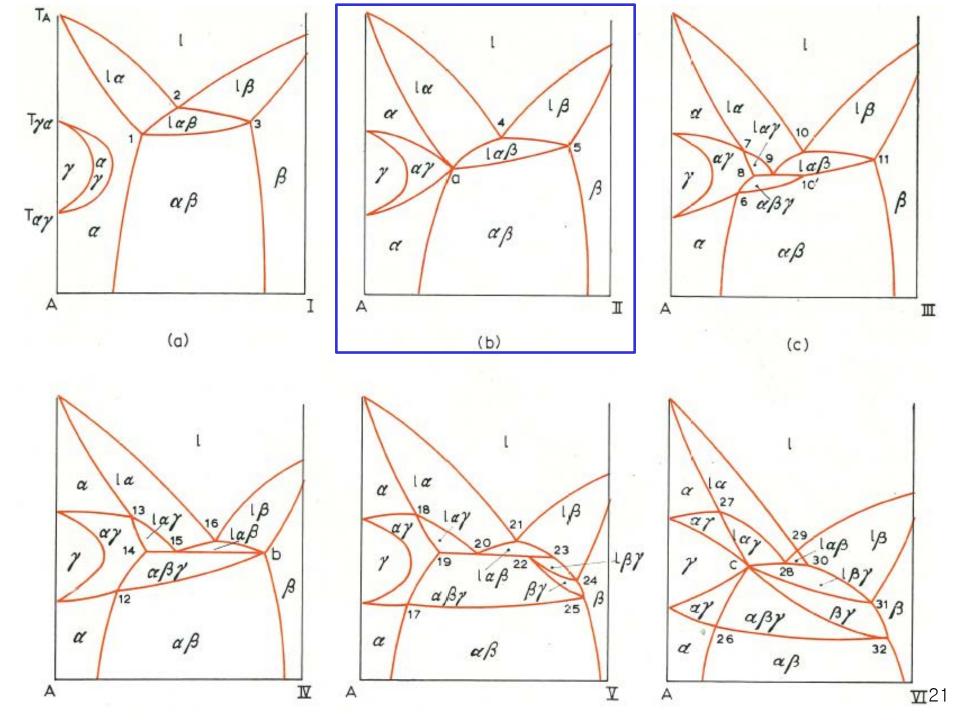
Four-phase equilibrium: $I + \alpha \rightleftharpoons \beta + \gamma$

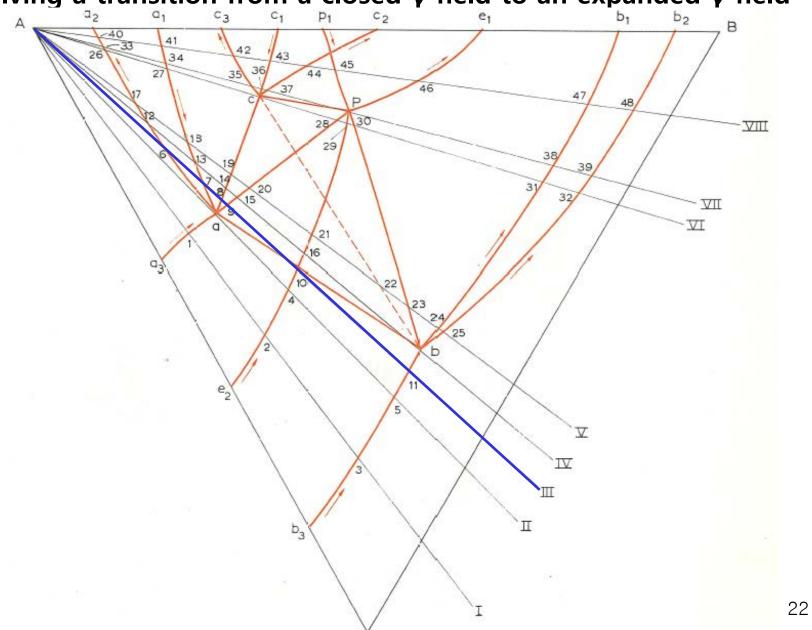


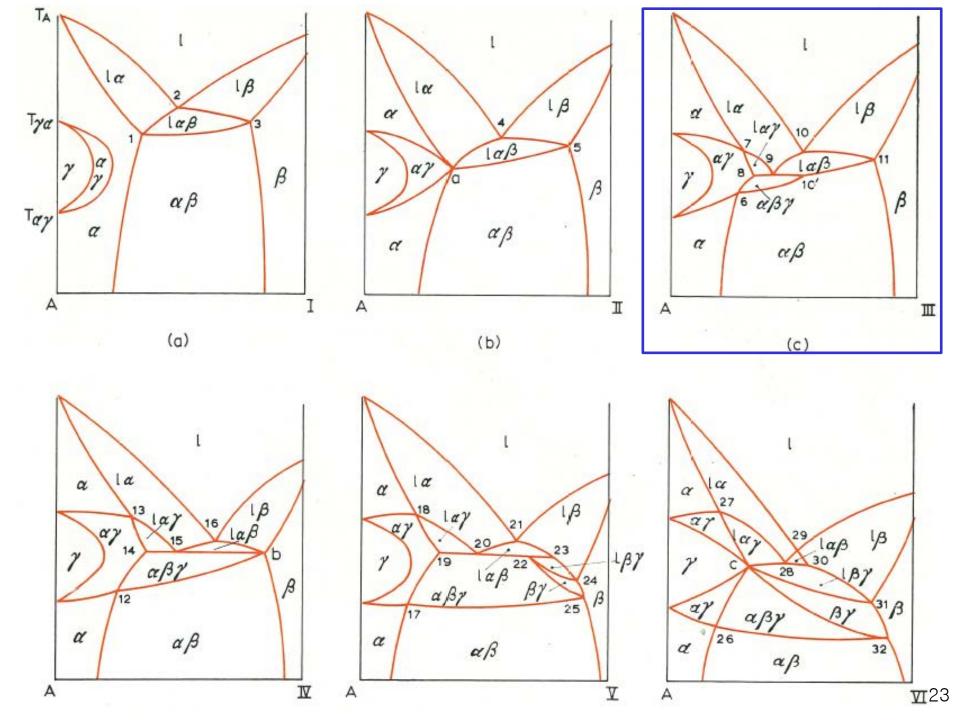


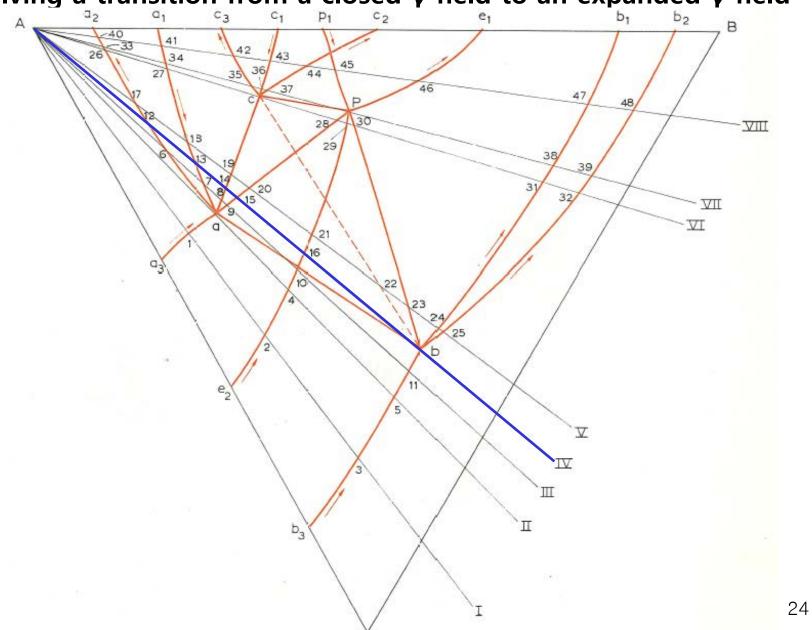


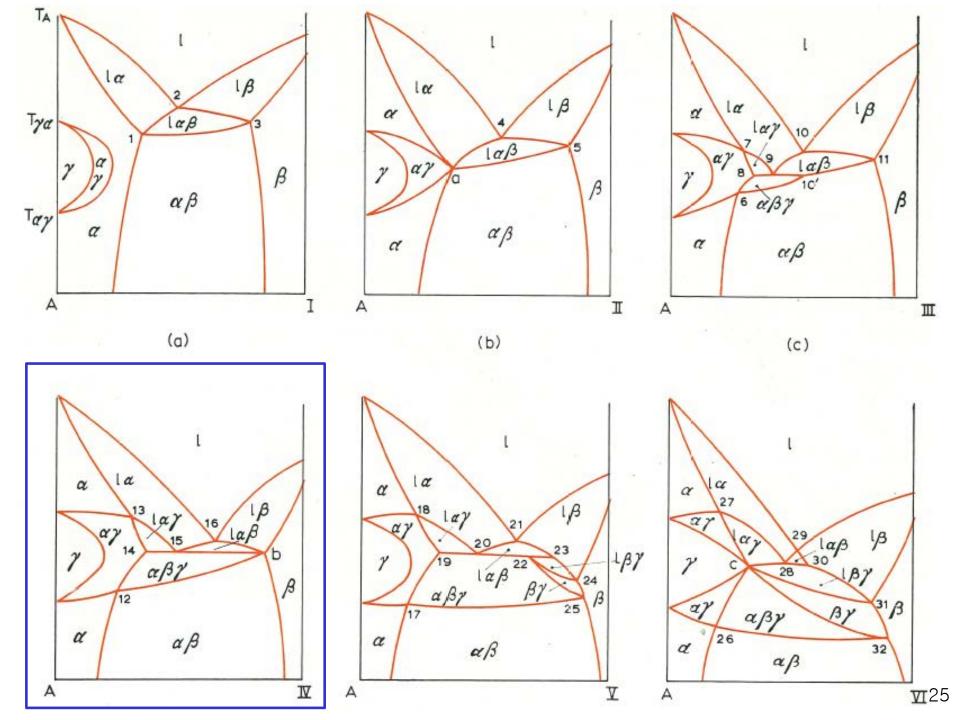


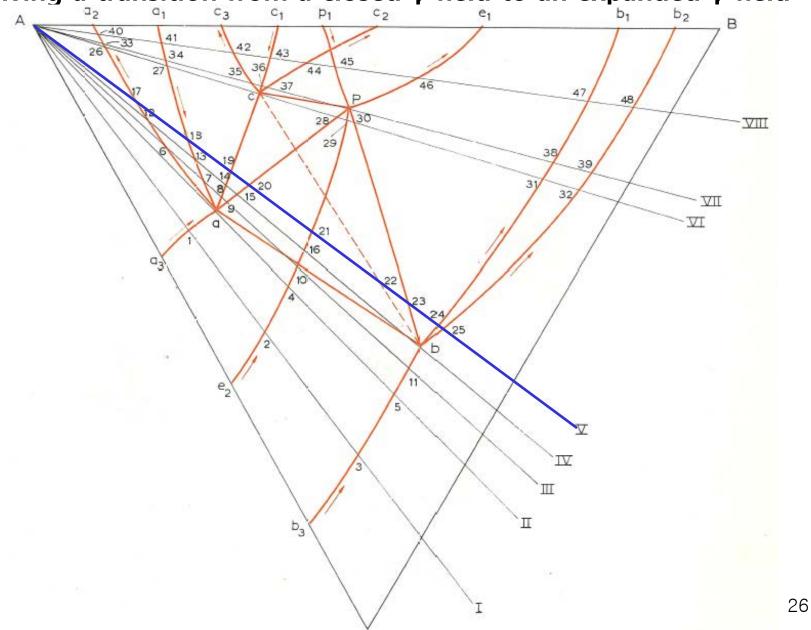


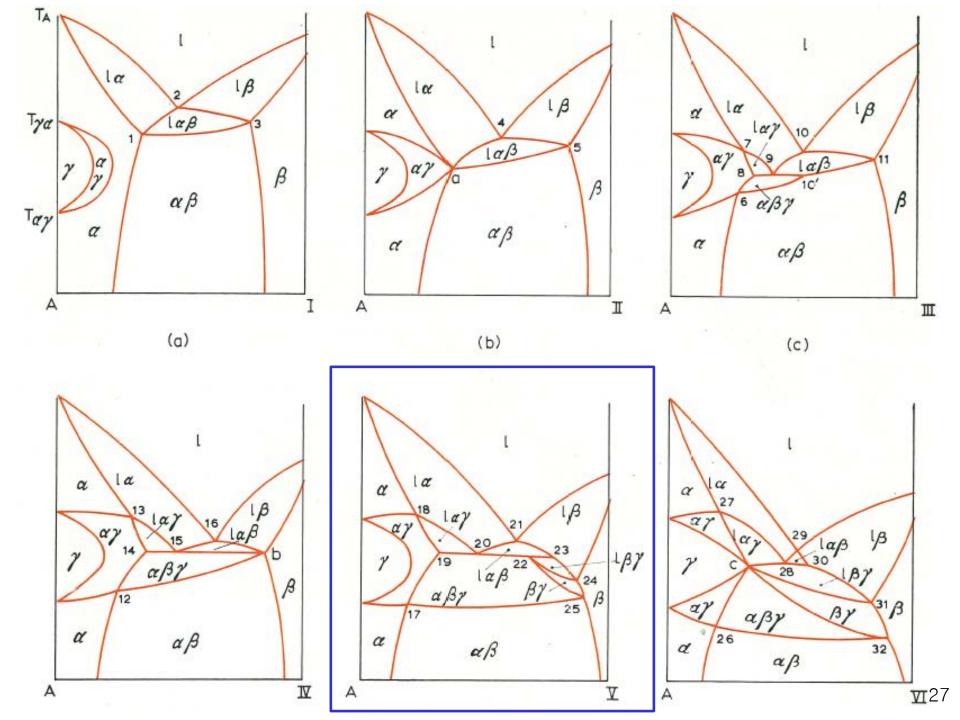


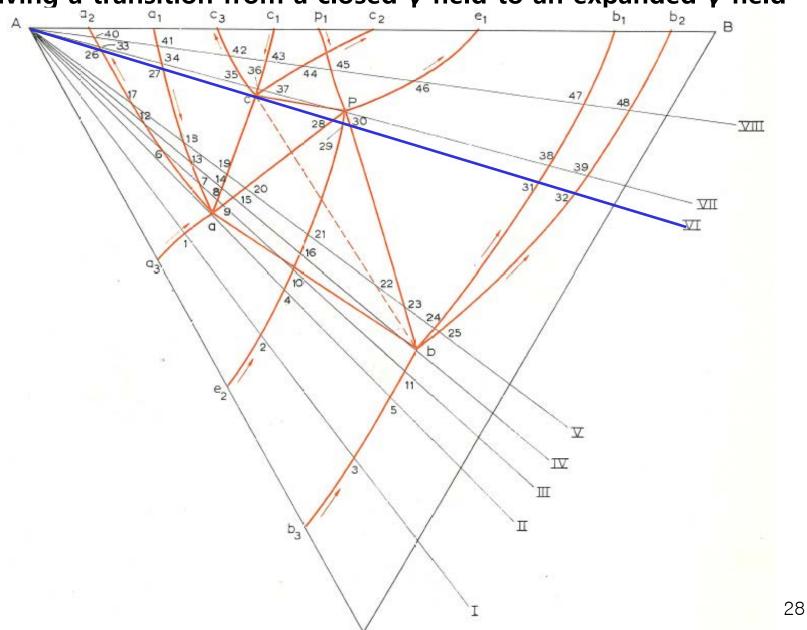


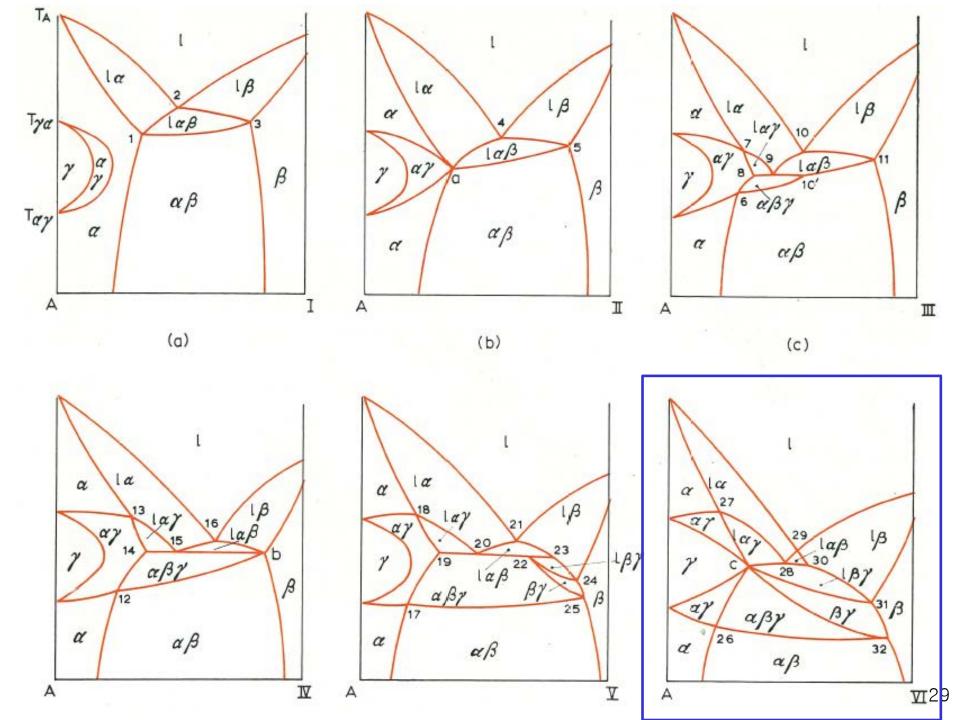


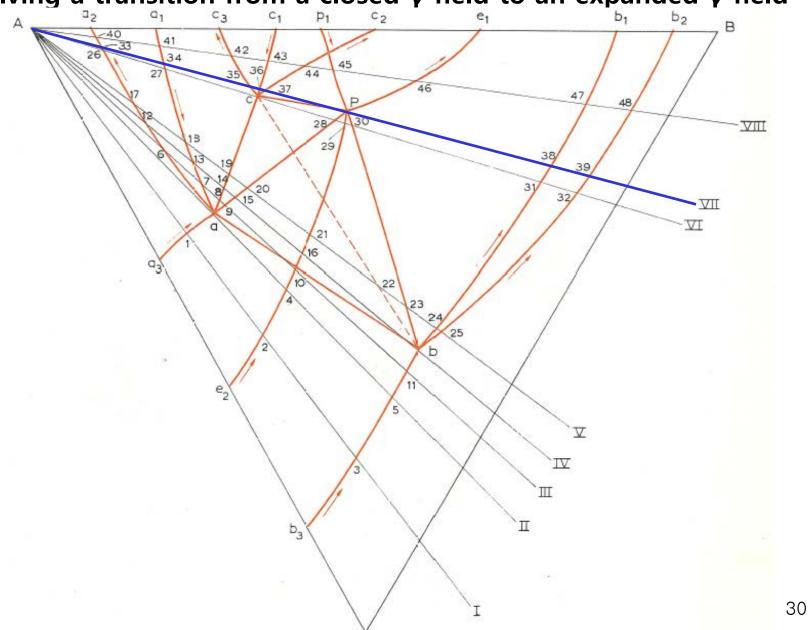


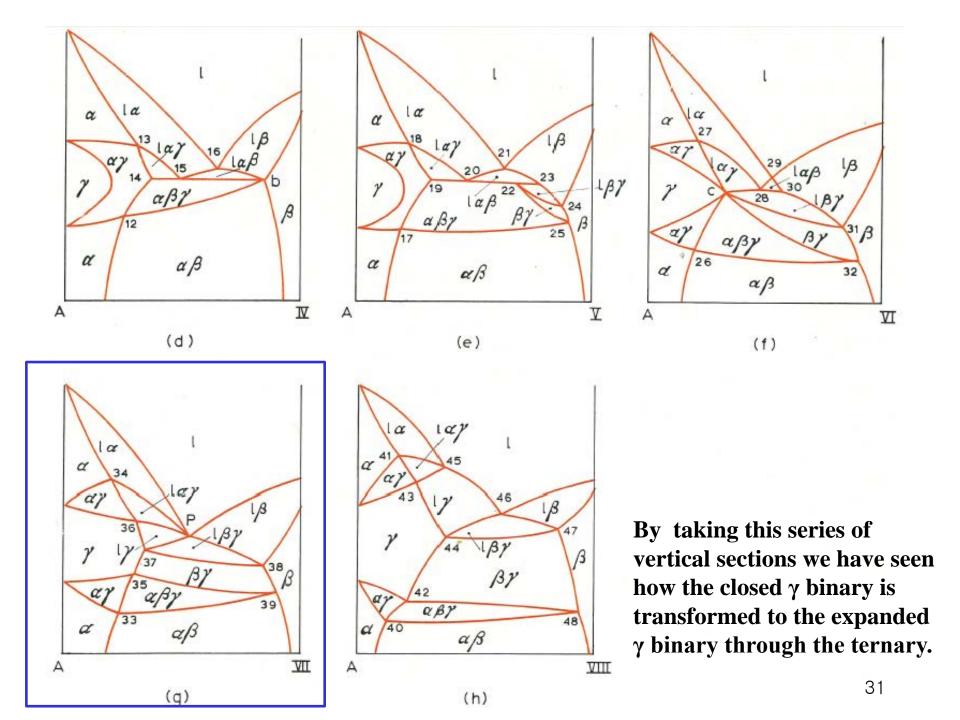


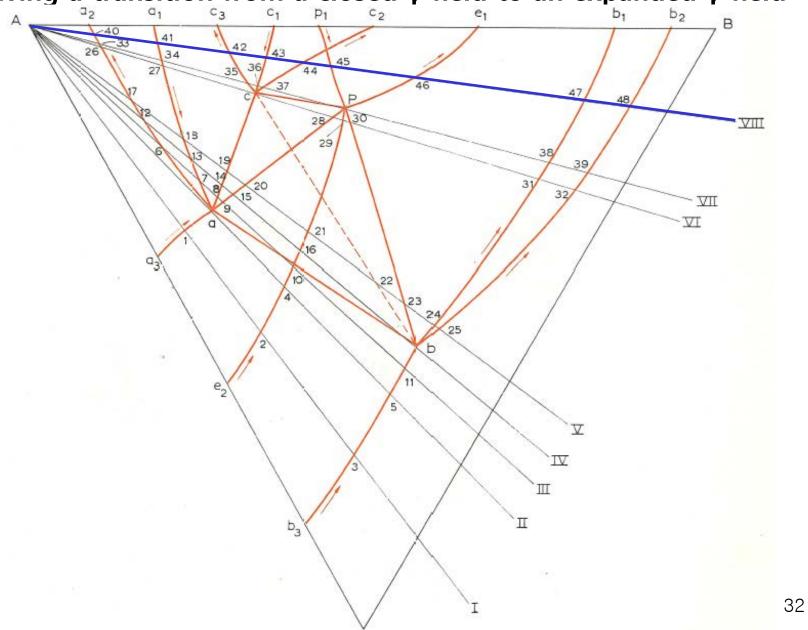


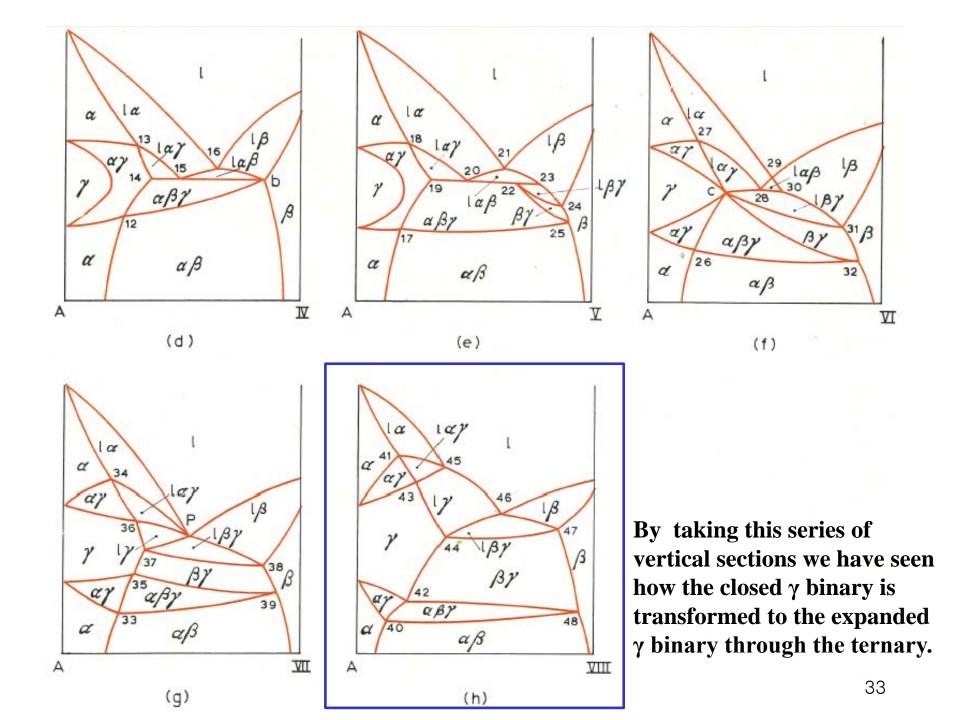












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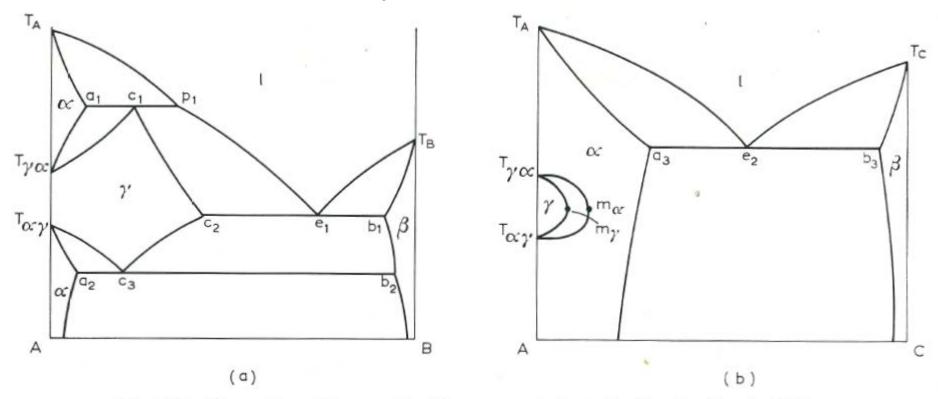


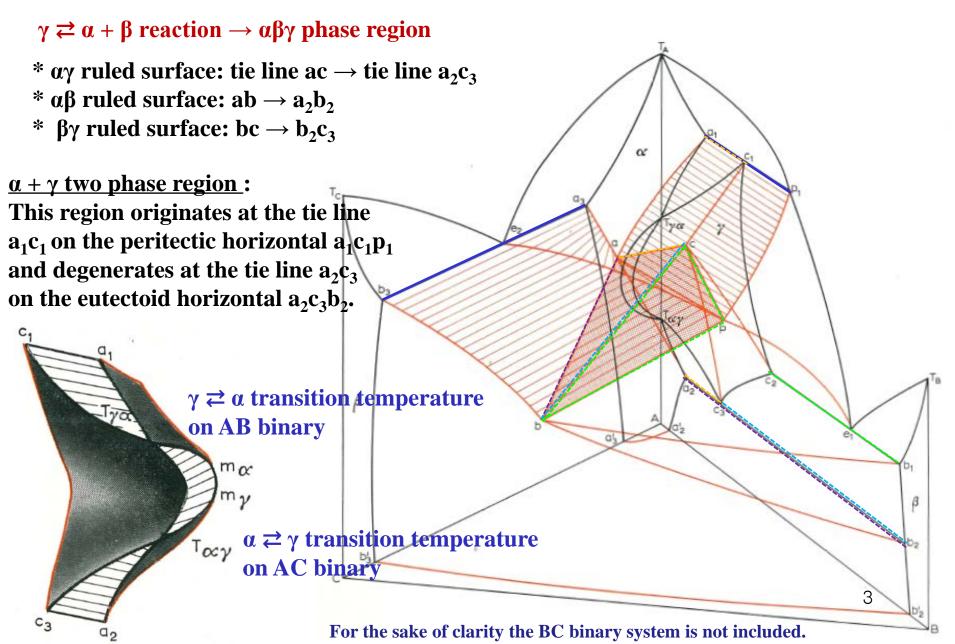
Fig. 220. Binary phase diagram (a) with an expanded γ field, (b) with closed γ field.

Recognisable as the Fe-Fe₃C diagram

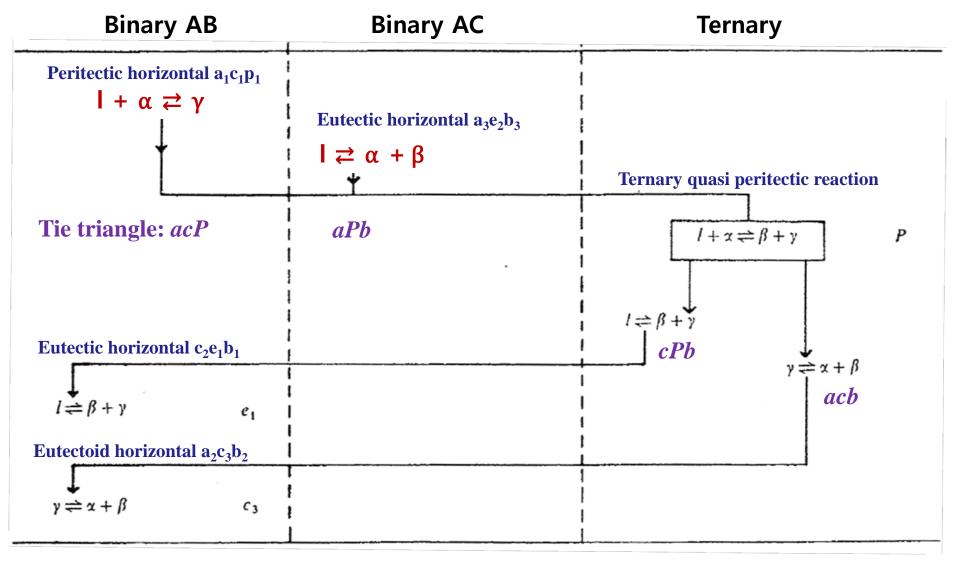
Produce by ferrite forming elements Such as Cr, Mo, Si and W

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

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

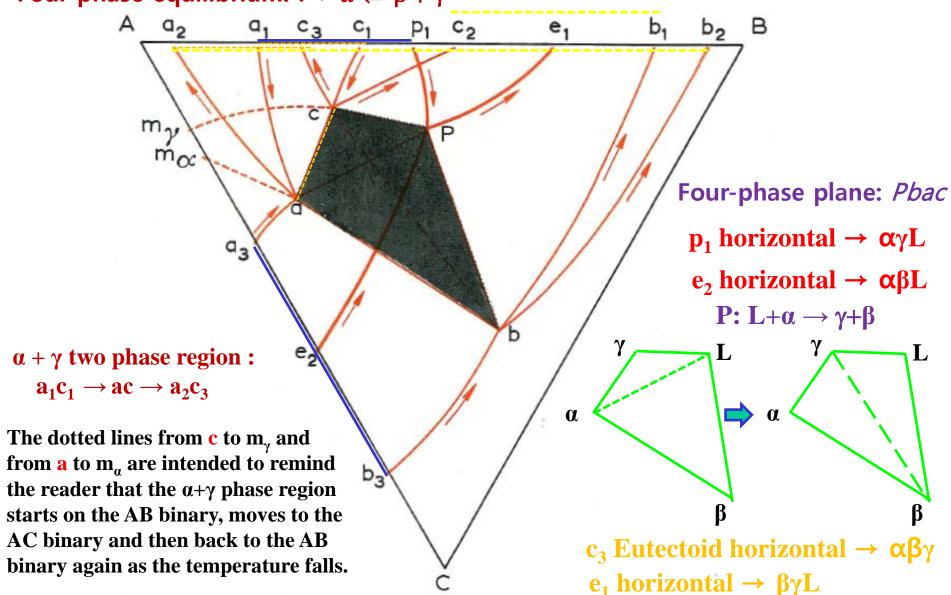


A tabular representation of the ternary

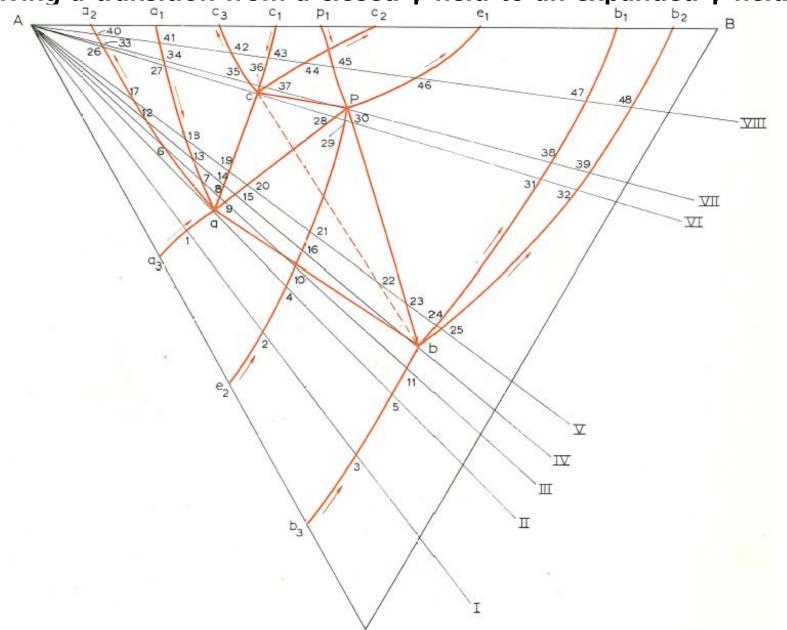


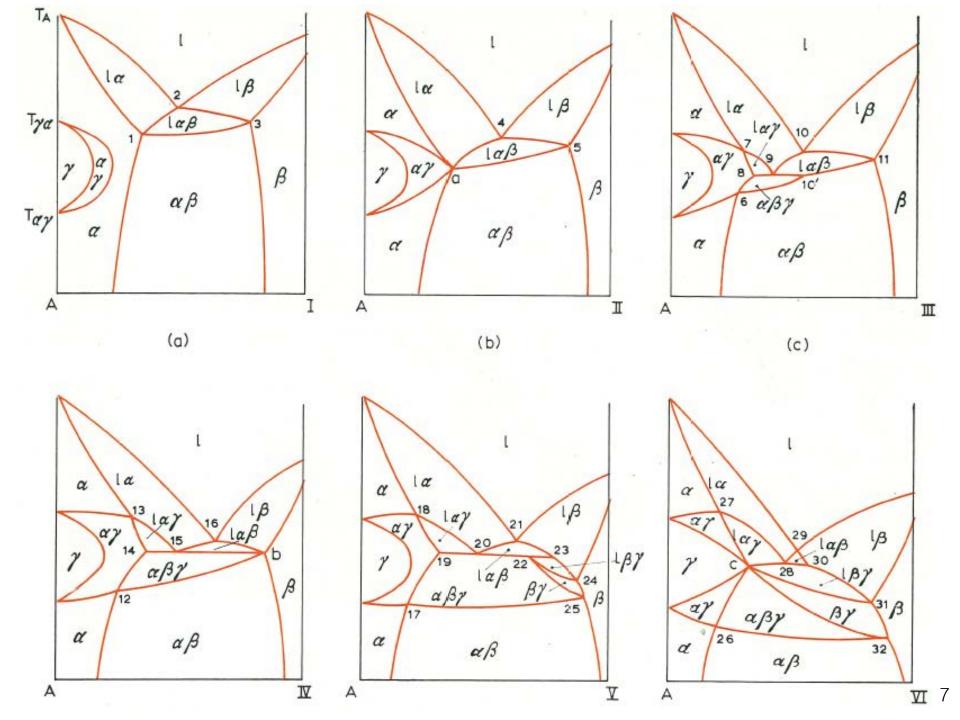
Projection of the ternary system involving a transition from a closed γ field to an expanded γ field

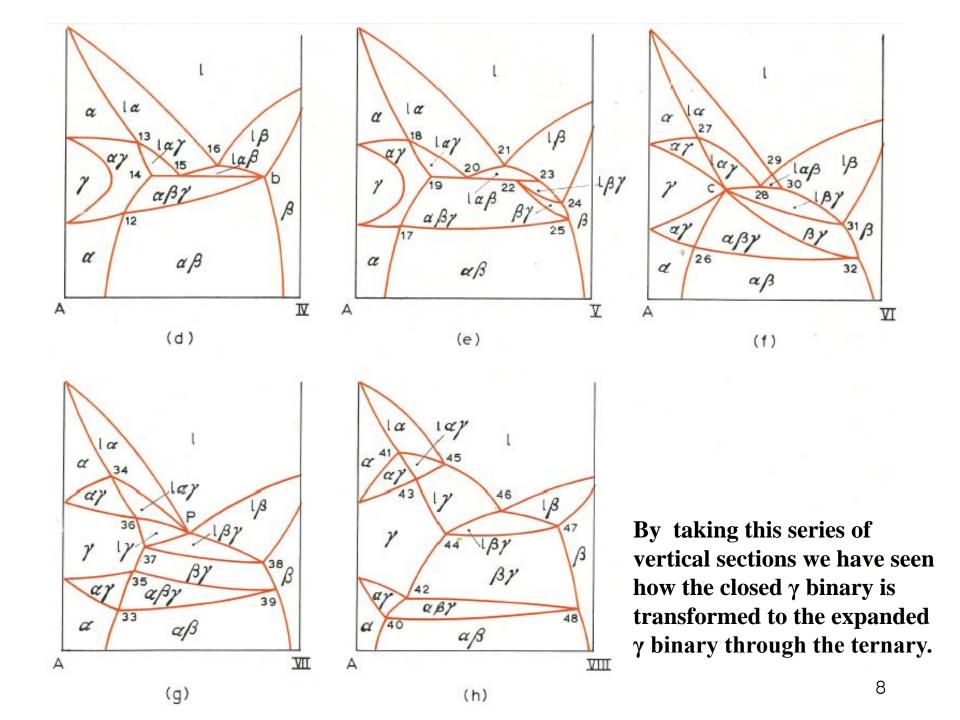
Four-phase equilibrium: $I + \alpha \rightleftharpoons \beta + \gamma$



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







Chapter 14. The Association of Phase Regions

14.1. Law of adjoining phase regions

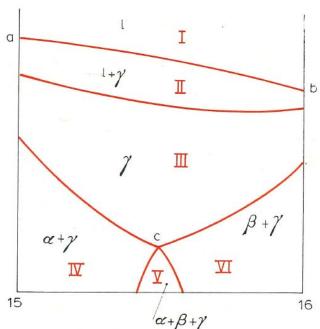
* Construction of phase diagram:

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 the number of phases in the second space is one less or one greater than that in the first space considered."

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"

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

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

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

2)
$$I \rightarrow II : D^{-} = 0/D^{+} = 1 \rightarrow R_{1} = 1 \& II \rightarrow I : D^{-} = 1/D^{+} = 0 \rightarrow R_{1} = 1$$

boundary ~ one dimension, line ab

3) III
$$\rightarrow$$
 V : D⁻ = 0/ D⁺= 2 \rightarrow R₁ = 0 & V \rightarrow III : D⁻ = 2/ D⁺= 0 \rightarrow R₁ = 0

⇒ boundary ~ zero dimension, point c

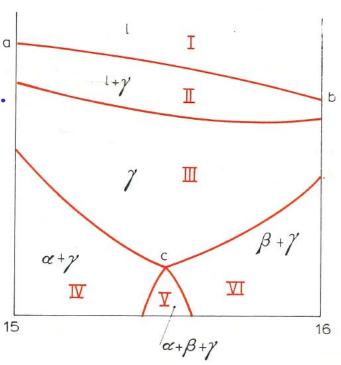
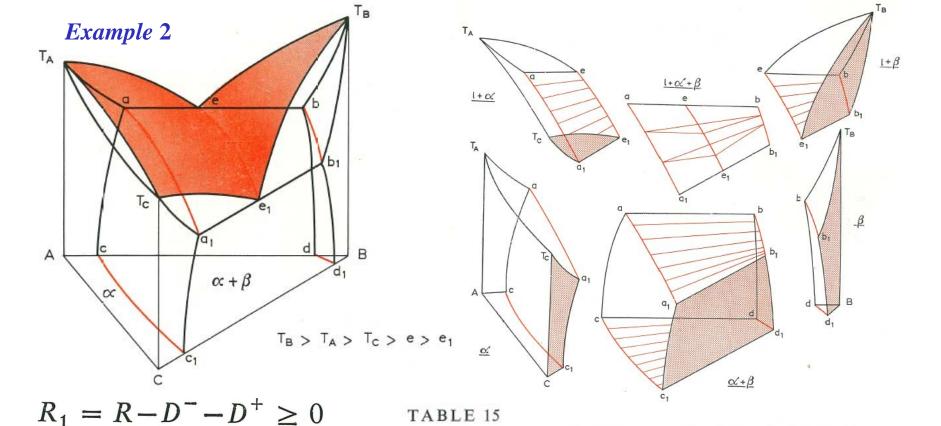


Fig. 226. Application of the law of adjoining phase regions to the vertical section of Fig. 178h.

Transition	I ↓	ii	II	III	III ↓	IV ↓	III	IV ↓	III ↓ V	V ↓	IV ↓ V	V ↓ IV	VI ↓ V	V ↓
from:	II		III	II	IV	III	VI	III	v	III	v	1 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		ine	1	ine	1:	ine	1	ine	po	oint	1	ine	1i	ne
geometrical elen	nent												12	



Transition				$l+\beta$	$I+\alpha+\beta$								
from:	$l+\beta$	$l+\alpha+\beta$	$\alpha + \beta$	l	β	$\alpha + \beta$	$l+\alpha+\beta$	1	α	β	$l+\alpha$	$l+\beta$	$\alpha+\beta$
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													

d e f

geometrical

element

b

a

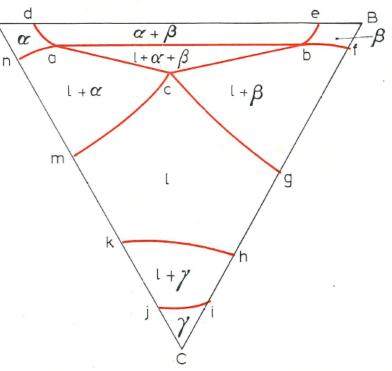
g h

k

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

- 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. $I+\alpha+\beta \rightarrow \alpha+\beta$ or $I+\alpha$ or $I+\beta \implies$ 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			Y			
	$\alpha + \beta$	$l+\alpha$	$l+\alpha+\beta$		$\alpha + \beta$	$l+\beta$	$l+\alpha+\beta$	$l+\infty$	$l+\beta$	$l+\gamma$	$l+\alpha+\beta$	$l+\gamma$
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 Corresponding	1	1	0		1	1	0	1	1	1	0	1
geometrical	line		point		1ii	ne point		line			point	line
element	(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</u> <u>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.

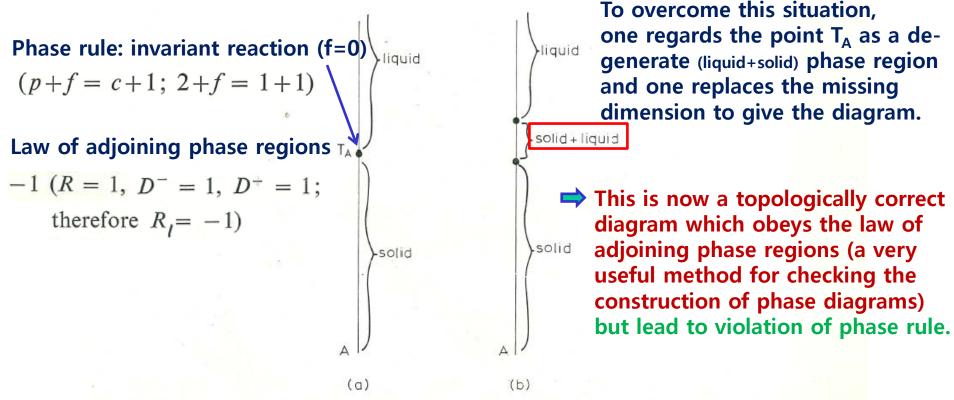


Fig. 228. Illustration of a degenerate phase region. (a) The melting of pure A; (b) the melting of pure A when point T_A is regarded as a degenerate phase region and replaced by a "solid+liquid" phase region.

* 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.

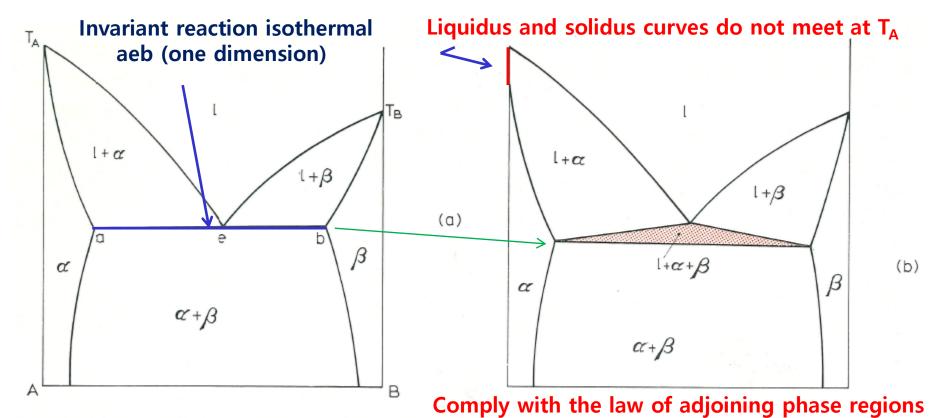


Fig. 229. Illustration of degenerate phase regions. (a) The eutectic phase diagram; (b) corresponding diagram allowing for degeneration of the phase regions.

* Sections through invariant four-phase planes in ternary systems

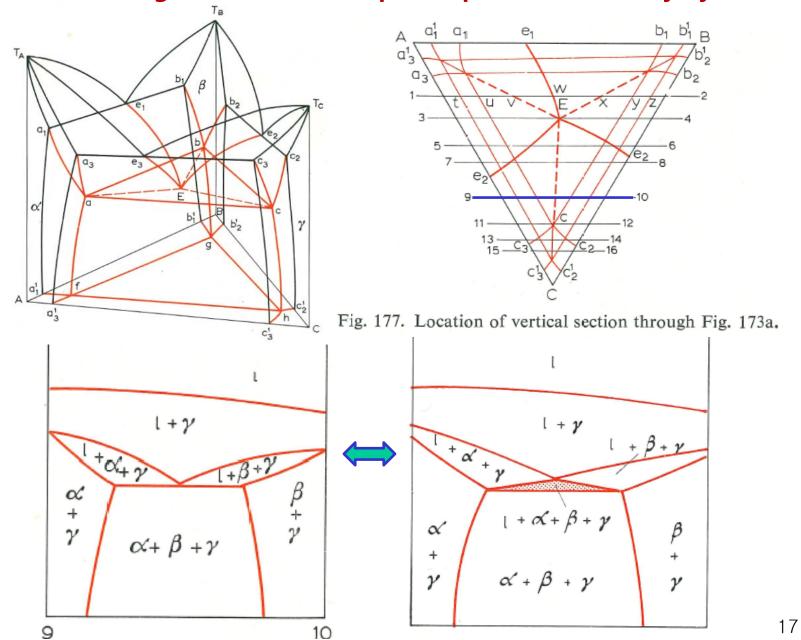
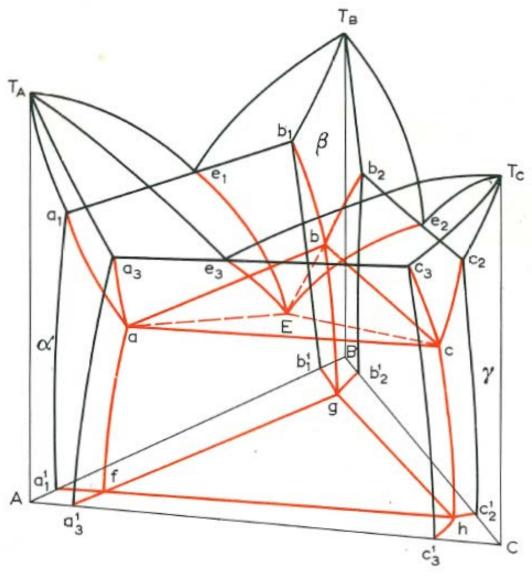


Fig. 230. Degeneration phase regions in vertical sections through ternary space models (Fig. 178e).

* 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)
- T_c (3) A single phase region with a fourphase 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. ($R_1 \leq R-1$)

(a) R = 2; R₁ = 1 _a line separates phase regions containing λ and $\lambda+1$ phases

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

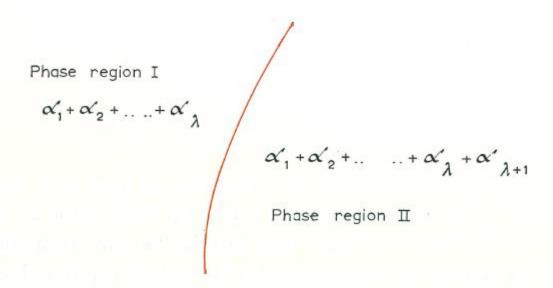


Fig. 231. Phase distribution in a two-dimensional diagram when the boundary between adjoining phase regions is one-dimensional.

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. $(R_1 \leq R-1 \rightarrow R_1 \leq 1)$

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

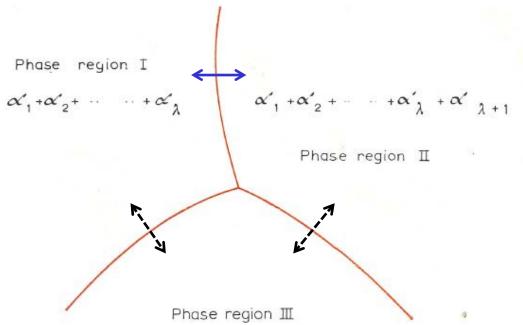


Fig. 232. Impossibility of three boundary lines meeting at a point in a two-dimensional diagram.

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

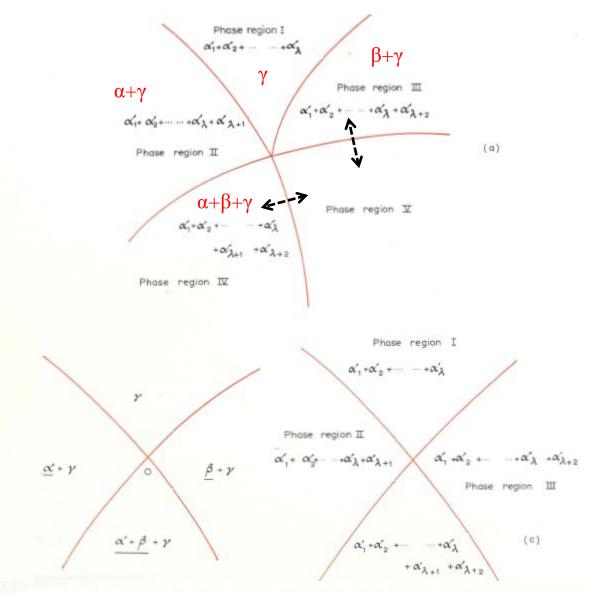
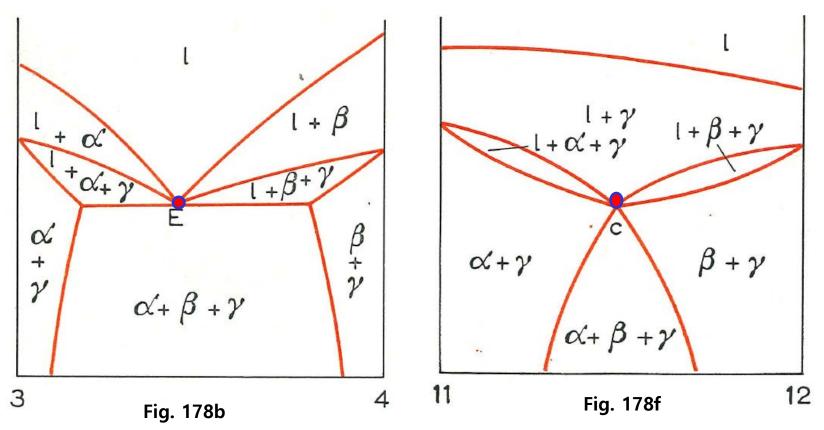


Fig. 233. Boundary lines meeting at a point in a two-dimensional diagram. (a) Impossibility of five lines meeting at a point; (b) distribution of phase regions when four lines meet at a point; (c) only four lines may meet at a point.

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.



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

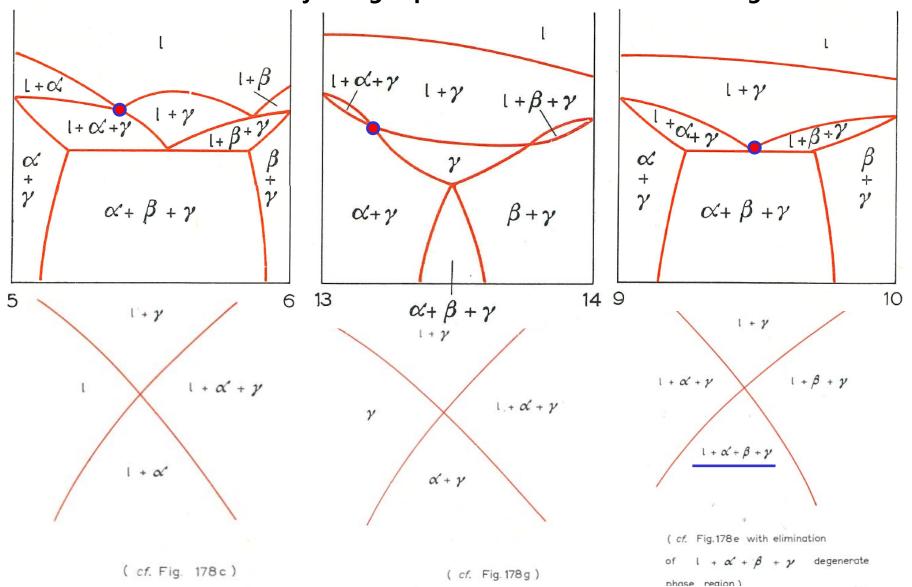
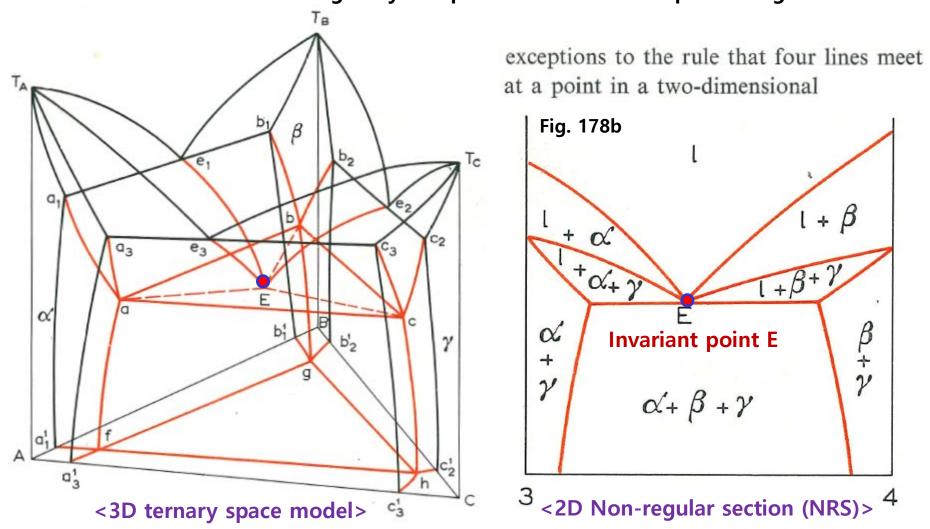


Fig. 234. The cross rule, (a) disposition of phase regions when one region is $l+\gamma$, (b) alternative disposition of phase regions.

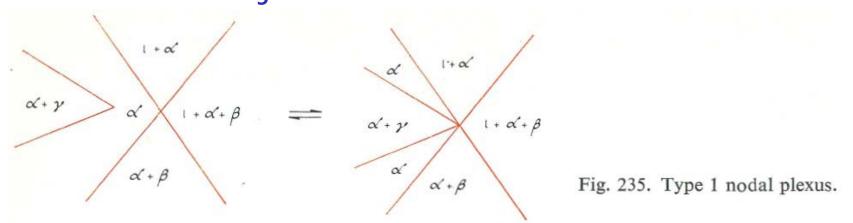
Non-regular sections behave erratically and the dimensions of the phase region boundaries in such sections are reduced irregularly compared to those in the phase diagram.



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 <u>nodal plexus</u>. Note that the degenerate phase region $I + \alpha + \beta + \gamma$ is not shown in (NRS).

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



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.

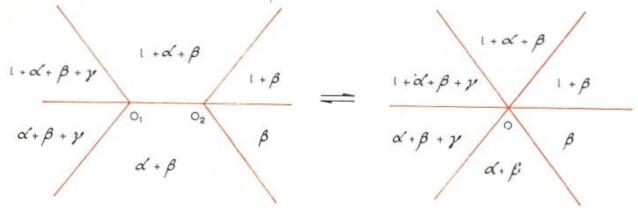
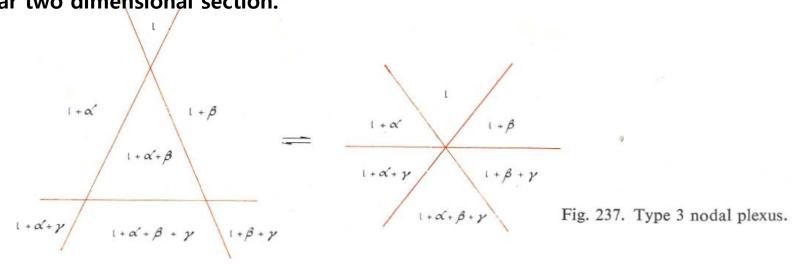


Fig. 236. Type 2 nodal plexus.

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 $I + \alpha + \beta$ disappears with the transition from a regular to a non-regular two dimensional section.



Type 4 A number of two dimensional phase regions degenerate to a line. In the formation of the nodal plexus the phase region $I + \beta + \gamma$ and $\beta + \gamma$ have degenerated into the line O_1O_2 .

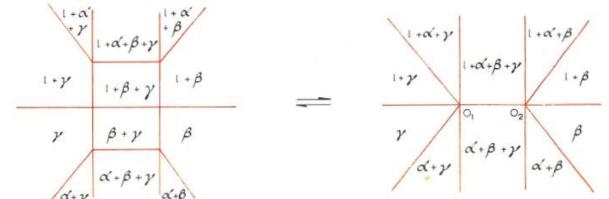


Fig. 238. Type 4 nodal plexus

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 $I + \gamma$ 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.

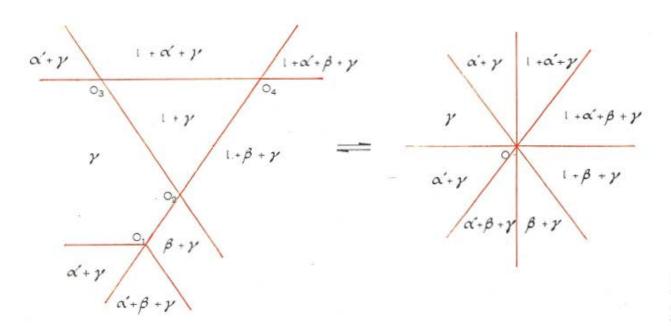
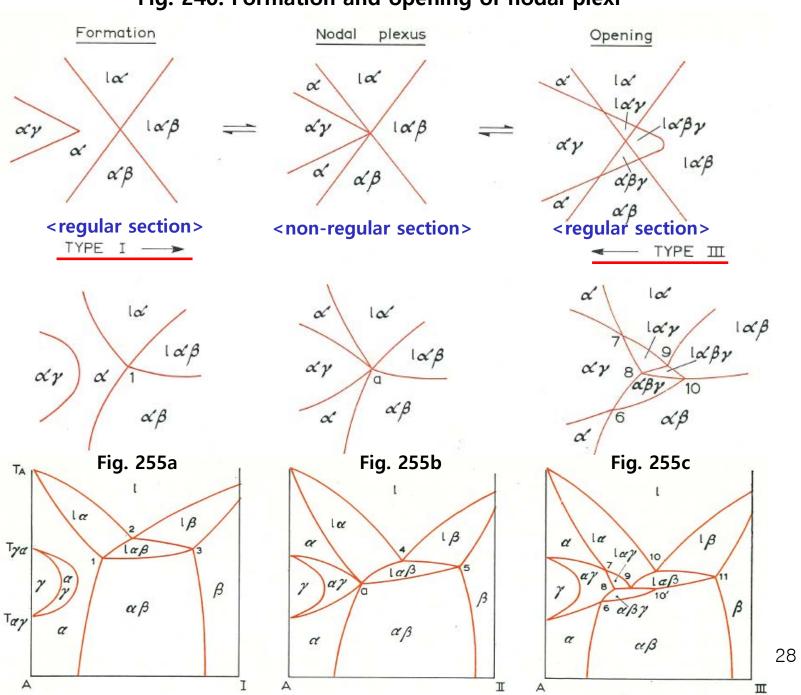


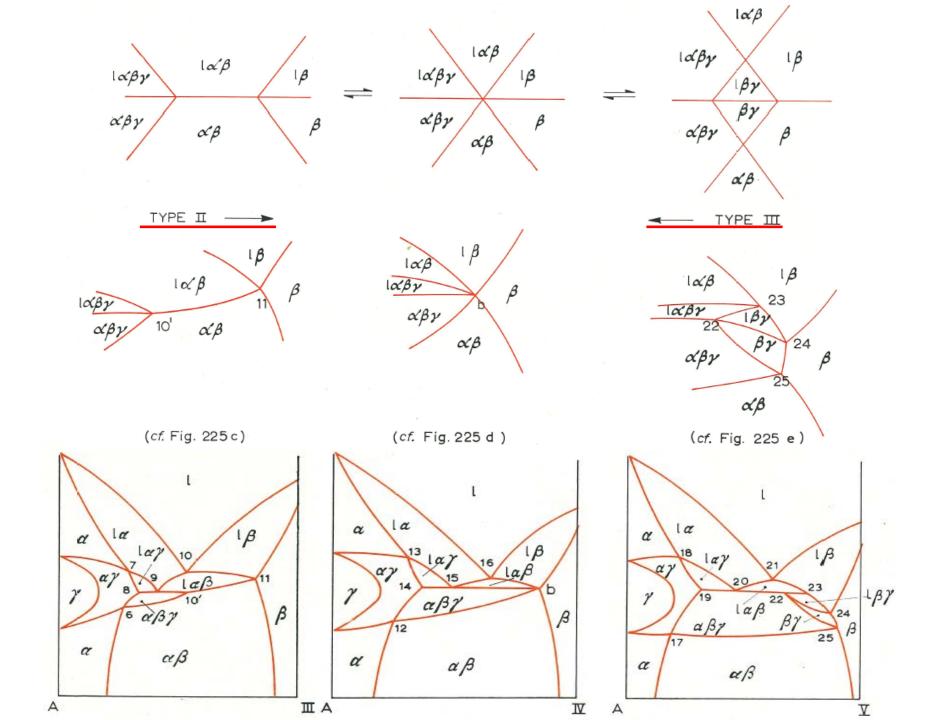
Fig. 239. Mixed type 2/3 nodal plexus.

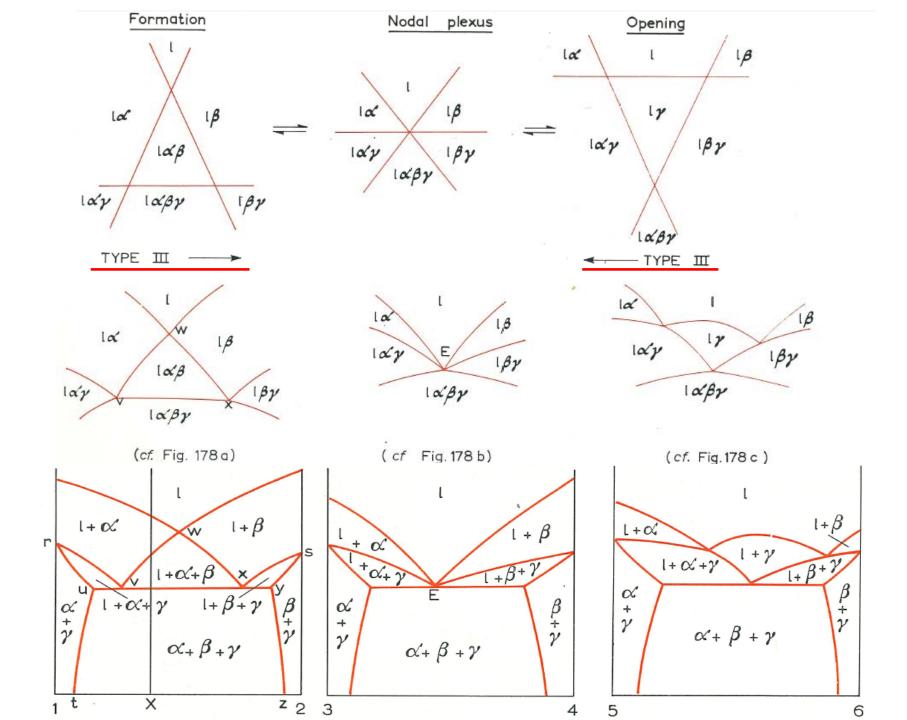
- 1) Formation of nodal plexi:

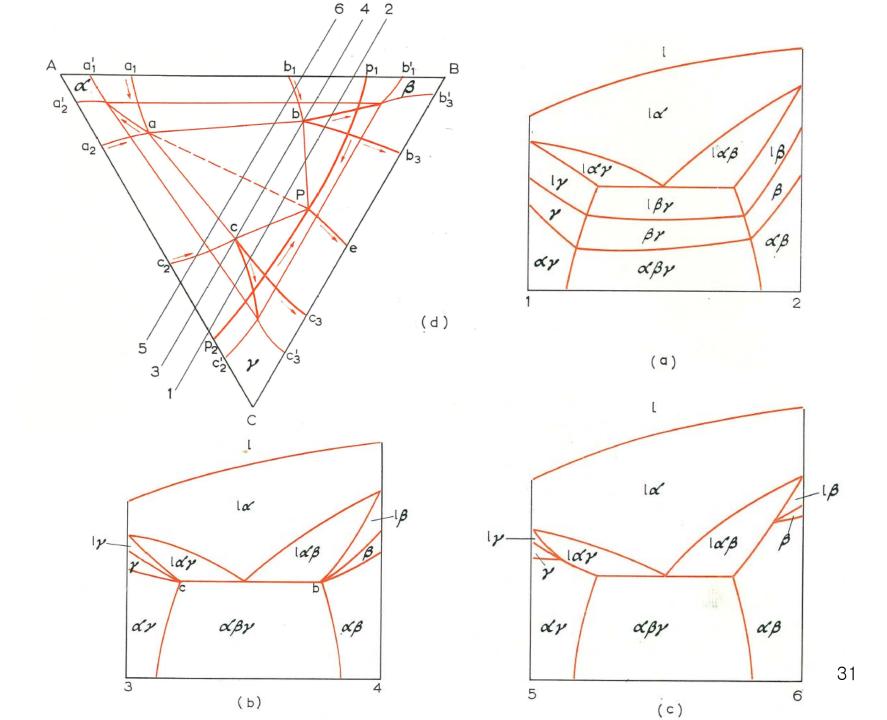
 Transition from a regular section to a non-regular section of a ternary system
- 2) Opening of nodal plexi:
 Subsequent transition from the non-regular section back to a regular section

Fig. 240. Formation and opening of nodal plexi









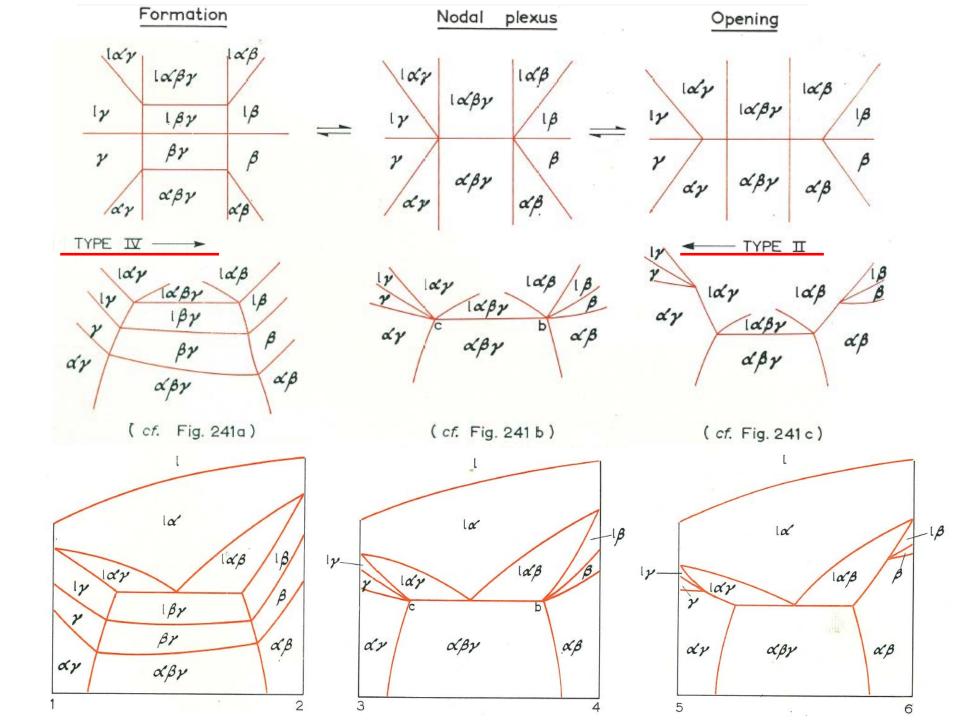


Fig. 240. Formation and opening of nodal plexi

