PMT-5778 (Diagramas de Fases)
Augusto Camara Neiva

APRESENTAÇÃO 5

Esta apresentação traz inúmeras figuras do livro “Alloy Phase Equilibria”, de Allan Prince. Esta e outras referências são listas e discutidas no texto “Bibliografia e Nomenclatura de Diagramas de Equilíbrio”, inserido no moodle.

Nós já vimos:

Binários com três fases (líquido, alfa e beta)

As duas fases sólidas eram terminais

Binários com quatro fases (líquido, alfa, beta e gama)

uma das fases sólidas não era terminal

Ternários com quatro fases (líquido, alfa, beta e gama)

As três fases sólidas eram terminais

Vamos ver agora:

Ternários com cinco fases (líquido, alfa, beta, gama e delta)

uma delas não será terminal

Antes disso, vamos retomar um pouco os binários, para ver dois diagramas com uma fase não-terminal (uma “fase intermediária”, um “composto intermetálico”).

Um deles nós já vimos: uma fase intermediária formada periteticamente. Diremos que ela é uma fase de “formação incongruente”, pois ela é originada de um líquido com composição diferente da dela.

Este nome surge em contraste com fases de “formação congruente”, que surgem de líquidos com a mesma composição das mesmas. Ou seja, elas se formam sem necessidade de difusão.

figuras do Prince

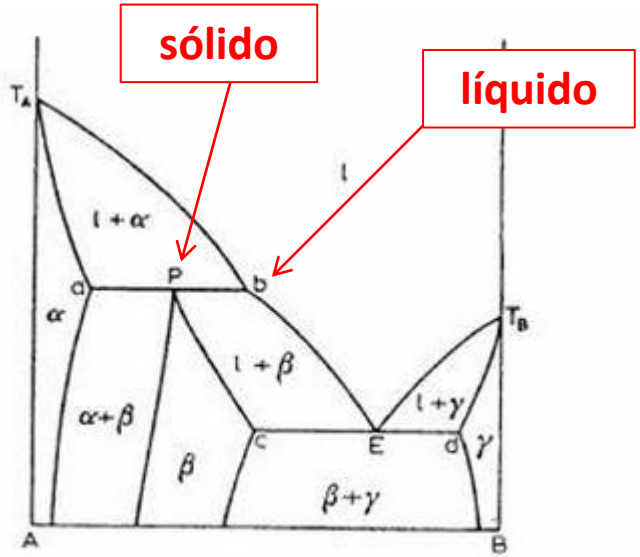


Fig. 68. Formation of an intermediate phase, β, by peritectic reaction.

incongruente

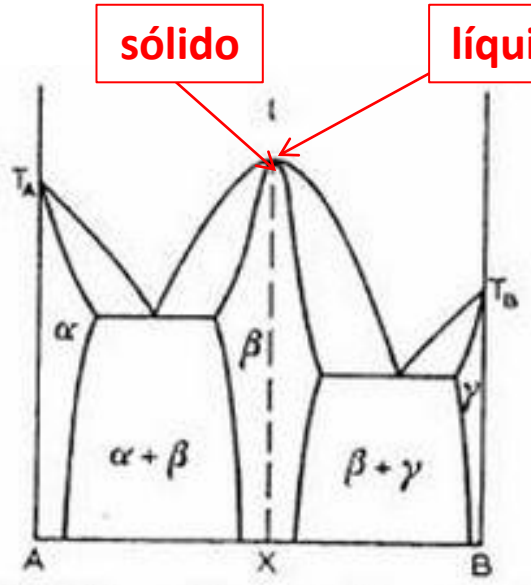


Fig. 78. Phase diagram with a congruent intermediate phase.

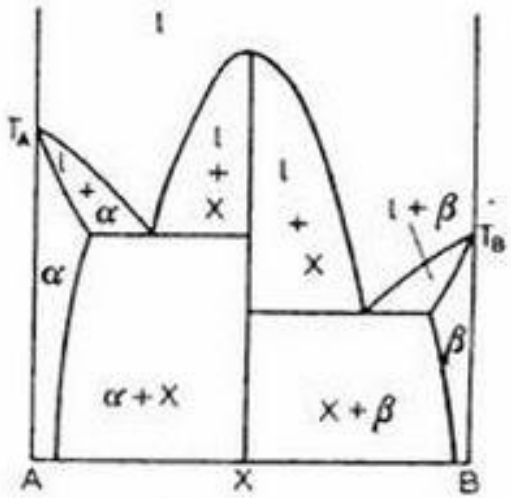


Fig. 79. Limiting case of Fig. 78.

congruente

figuras do Prince

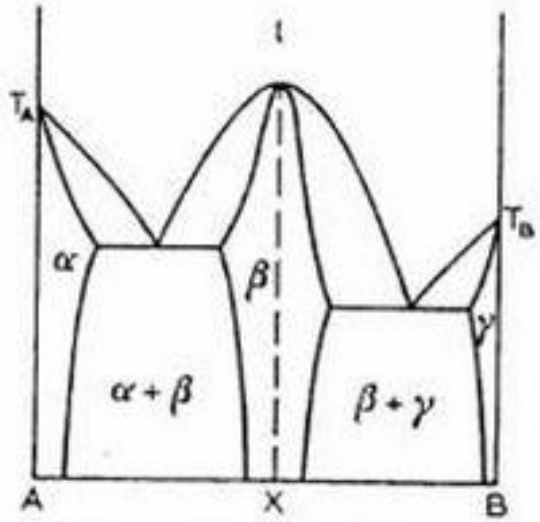


Fig. 78. Phase diagram with a congruent intermediate phase.

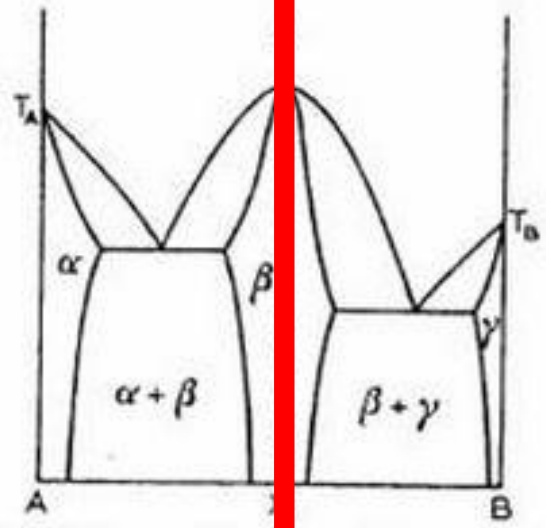


Fig. 78. Phase diagram with a congruent intermediate phase.

Observem: neste caso, o diagrama pode ser dividido em dois diagramas eutéticos (poderiam também ser peritéticos)

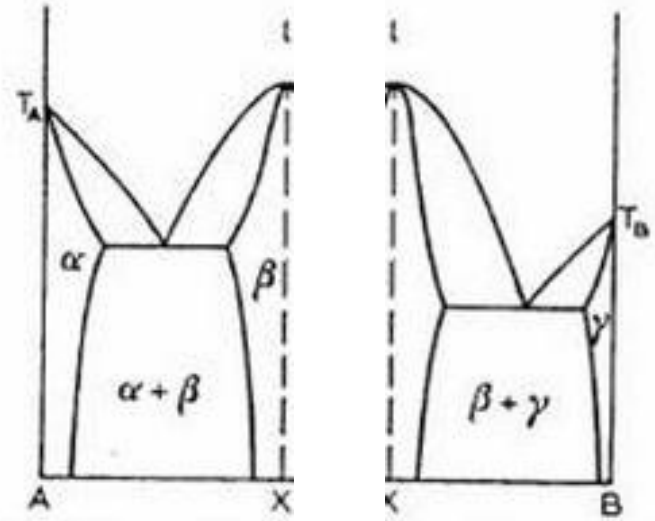
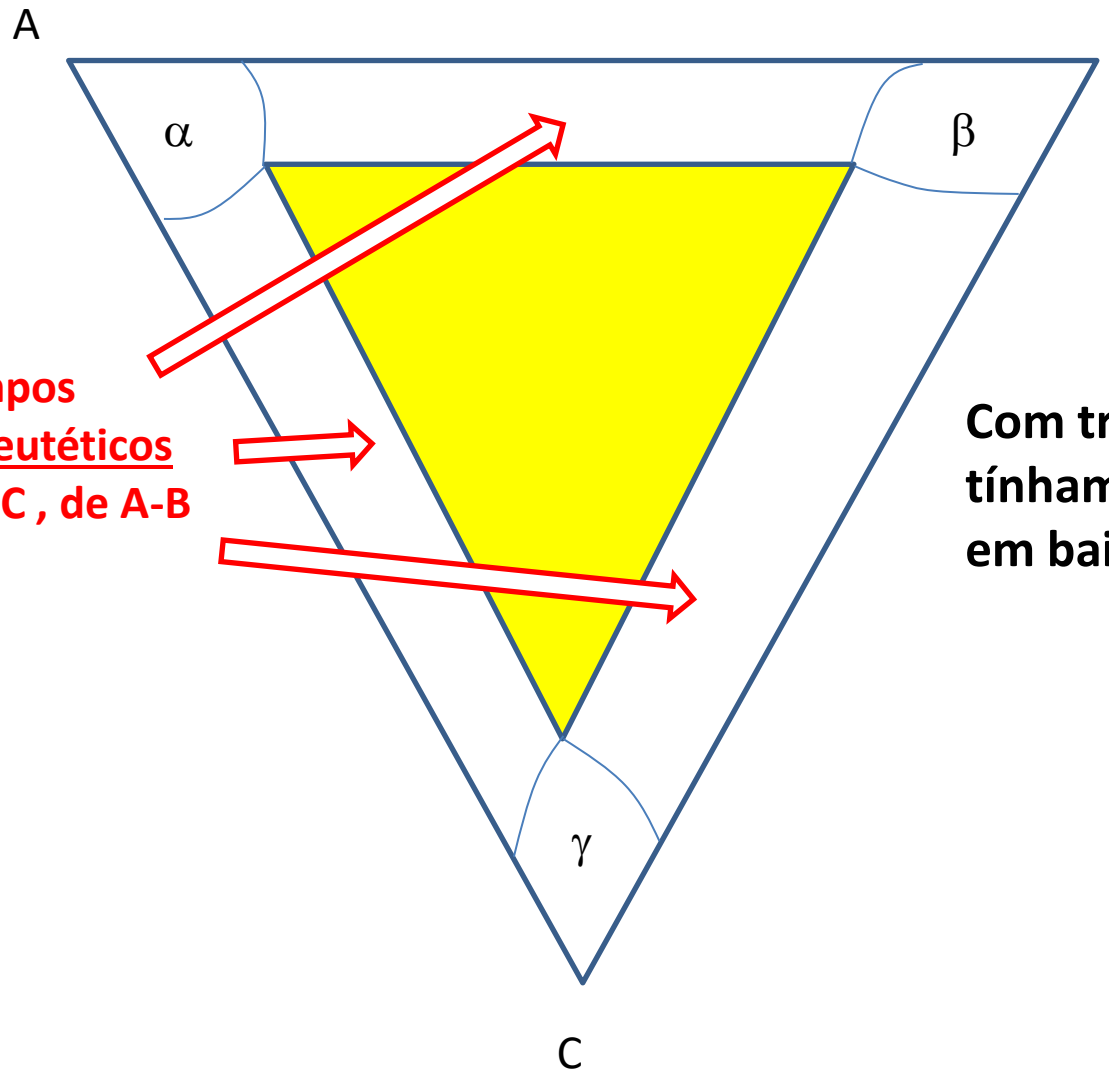


Fig. 78. Phase diagra… …am with a congruent intermediat… …te phase.

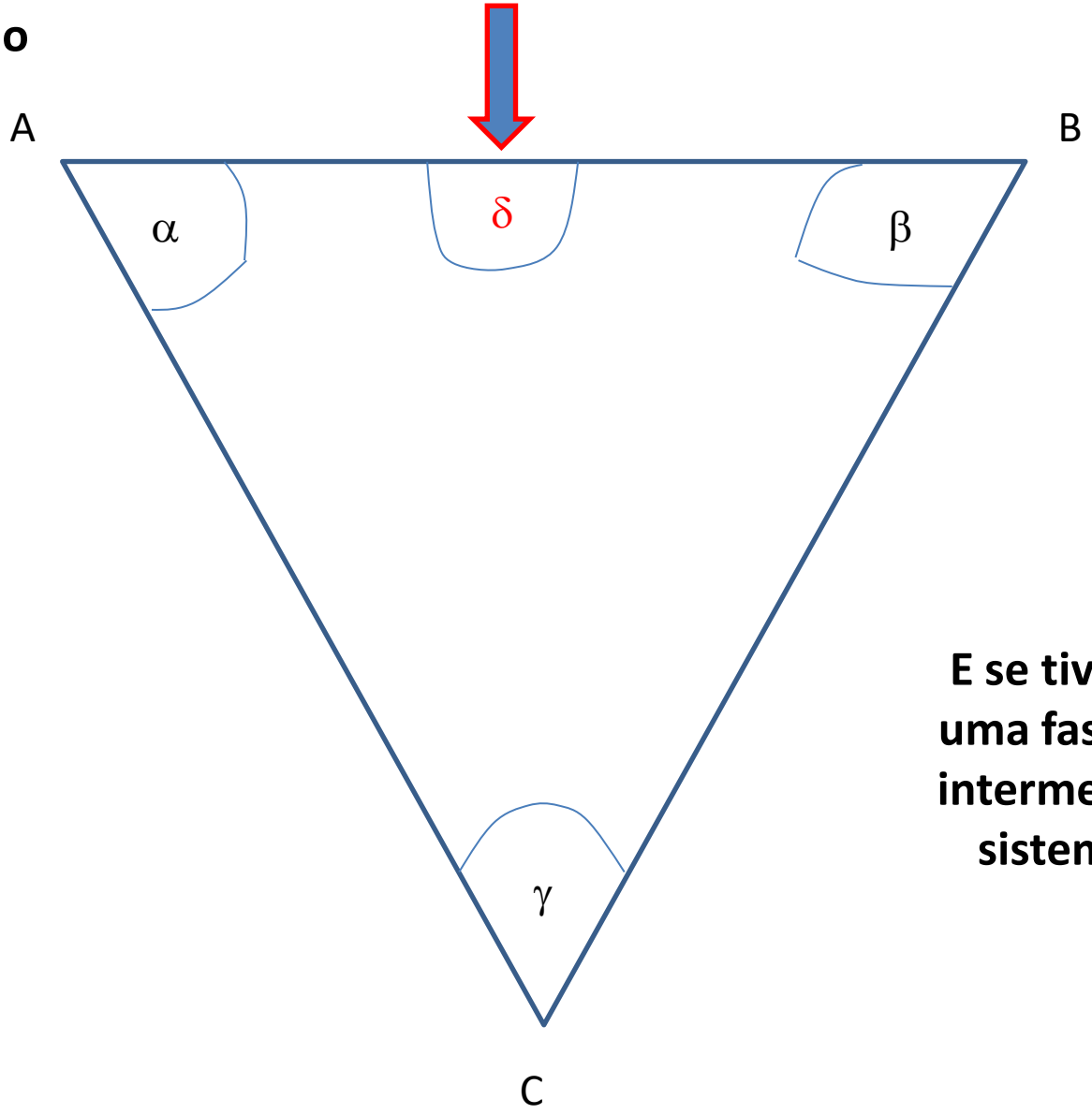
Vamos pensar agora em um sistema ternário



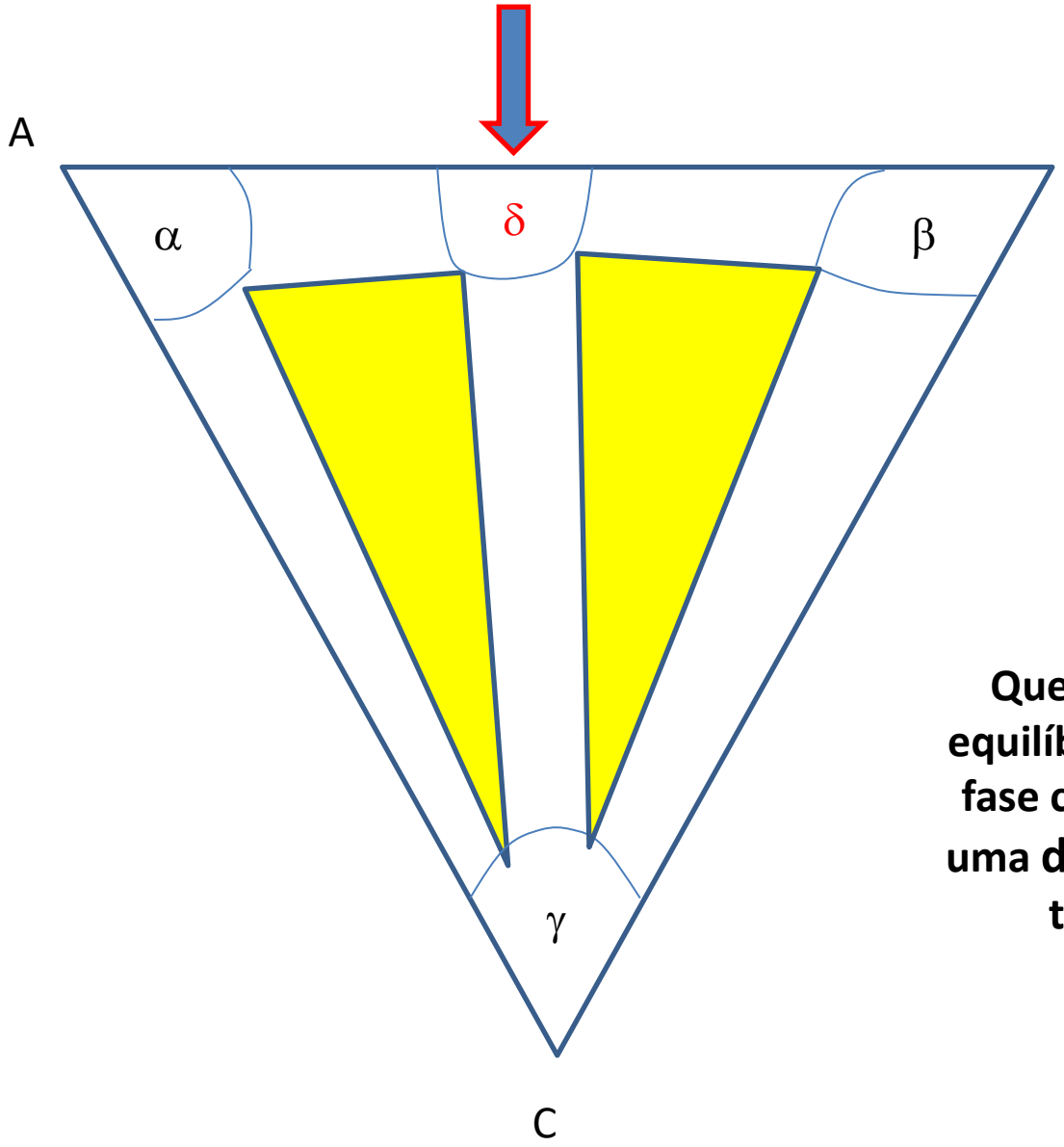
Estes três campos surgiram dos <u>eutéticos binários</u> de A-C , de A-B e de B-C

Com três fases sólidas, tínhamos algo assim em baixas temperaturas

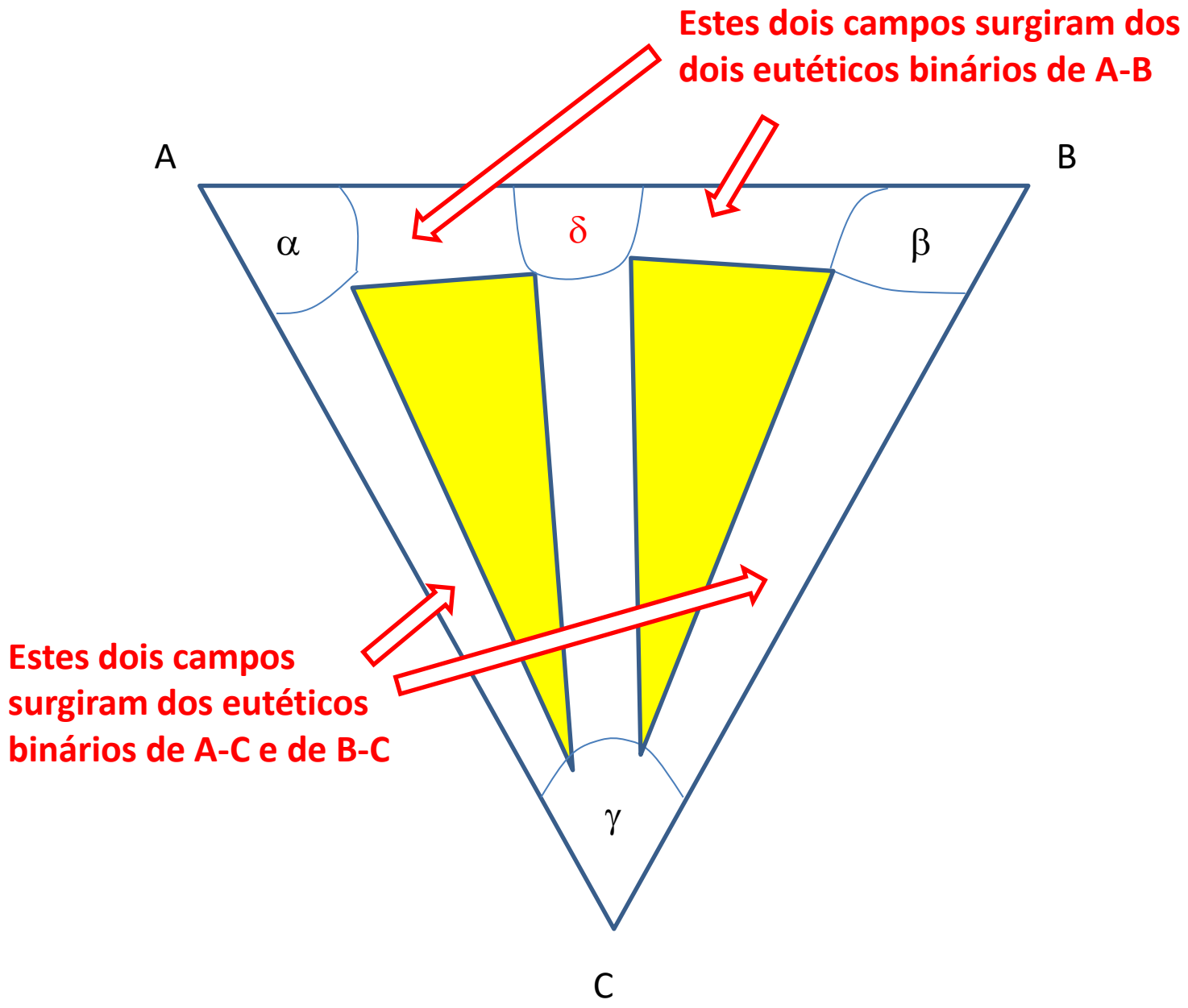
E agora em um <u>outro</u> sistema ternário

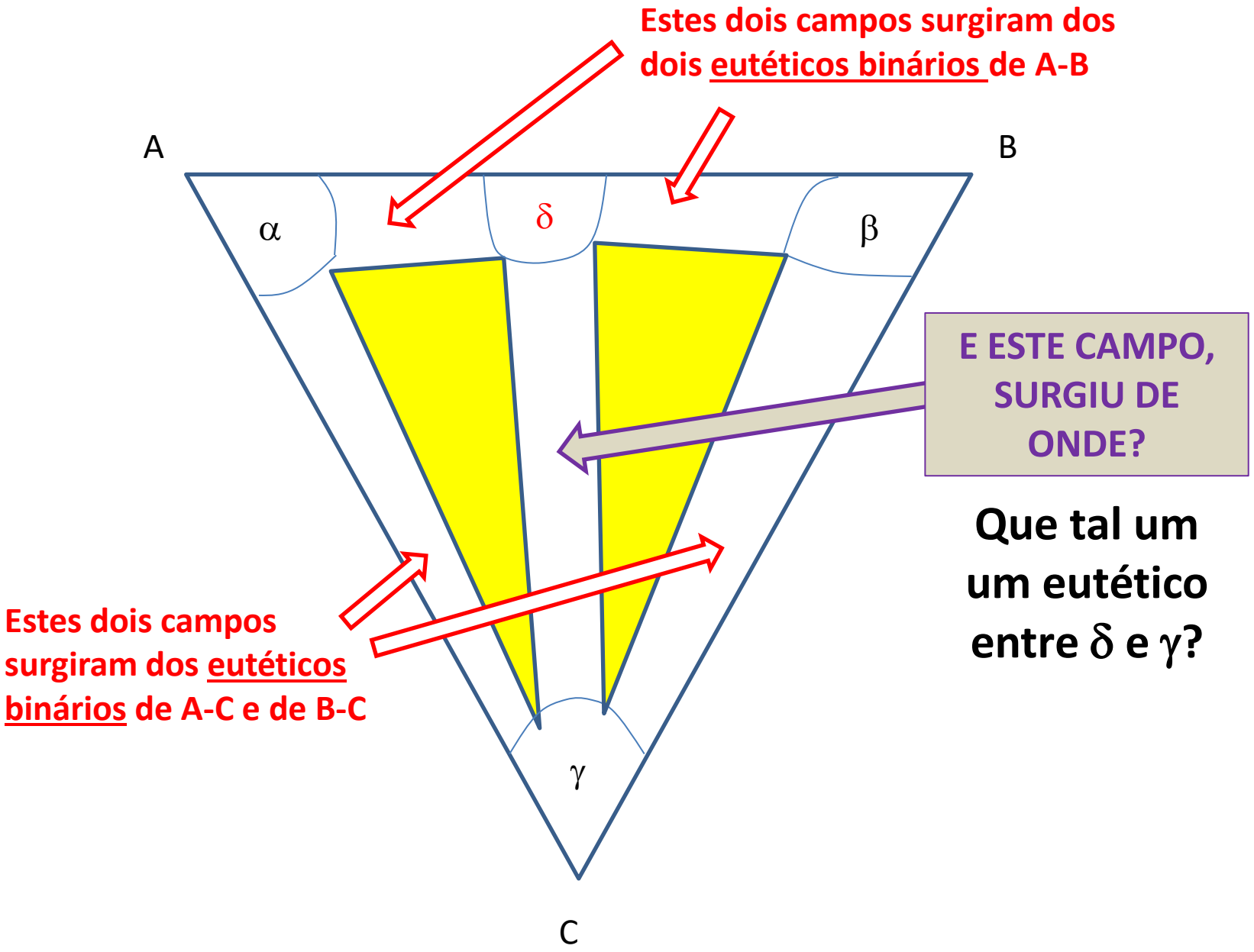


E se tivéssemos uma fase binária intermediária no sistema A-B?

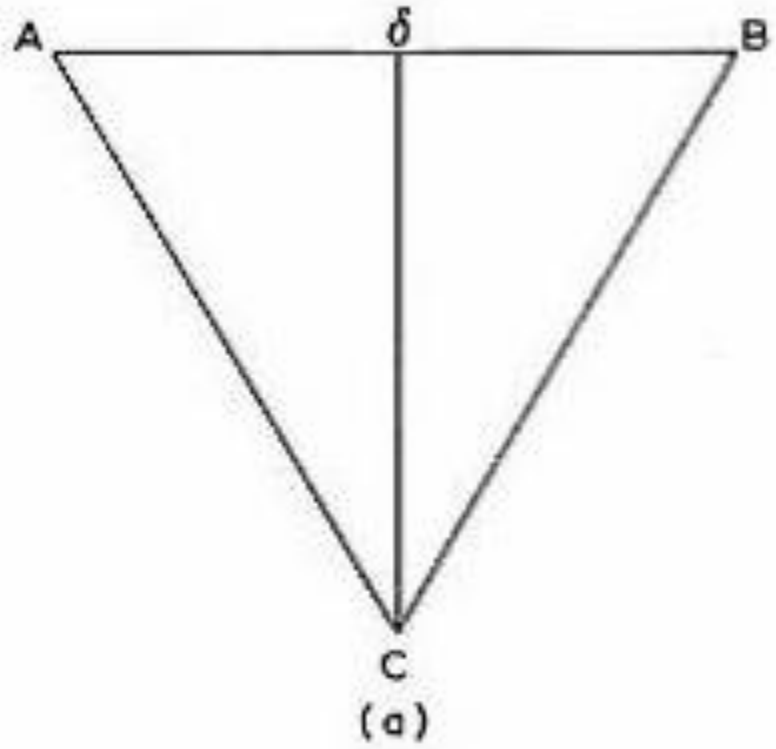


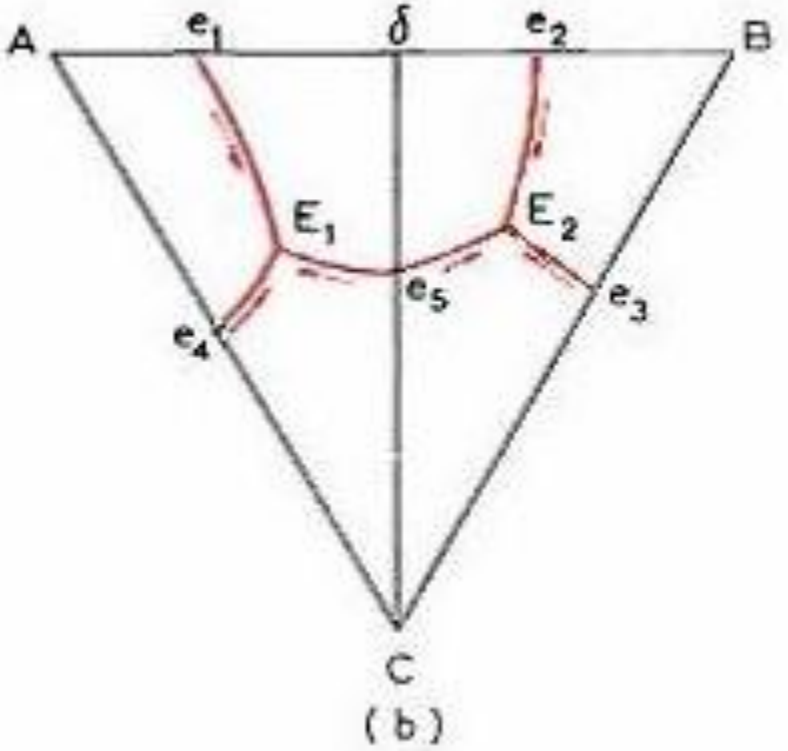
Que tal um equilíbrio desta fase com cada uma das outras três?


Estes dois campos surgiram dos dois eutéticos binários de A-B
A
B
α
δ
β
Estes dois campos surgiram dos eutéticos binários de A-C e de B-C
γ
C

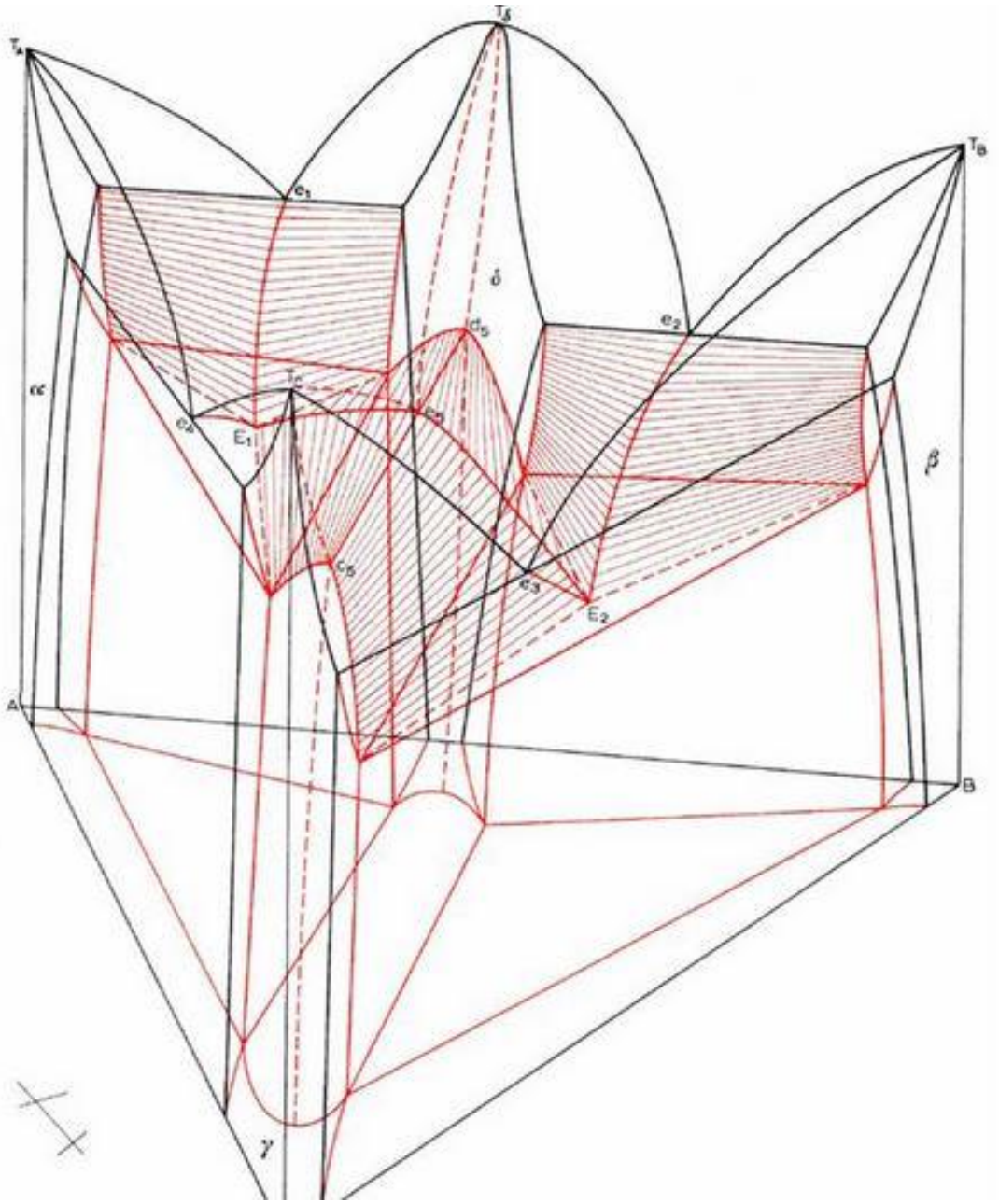

Estes dois campos surgiram dos dois eutéticos binários de A-B
A
B
α
δ
β
E ESTE CAMPO, SURGIU DE ONDE?
Que tal um um eutético entre δ e γ?
Estes dois campos surgiram dos eutéticos binários de A-C e de B-C
γ
C

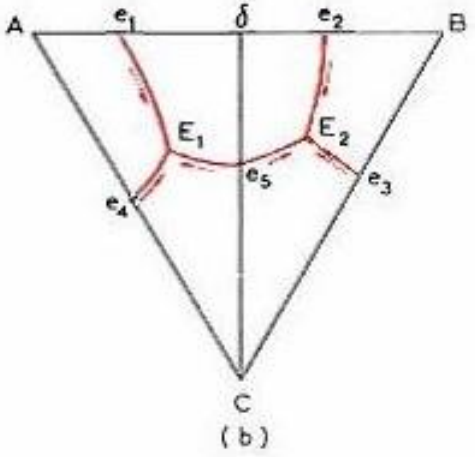
figuras do Prince





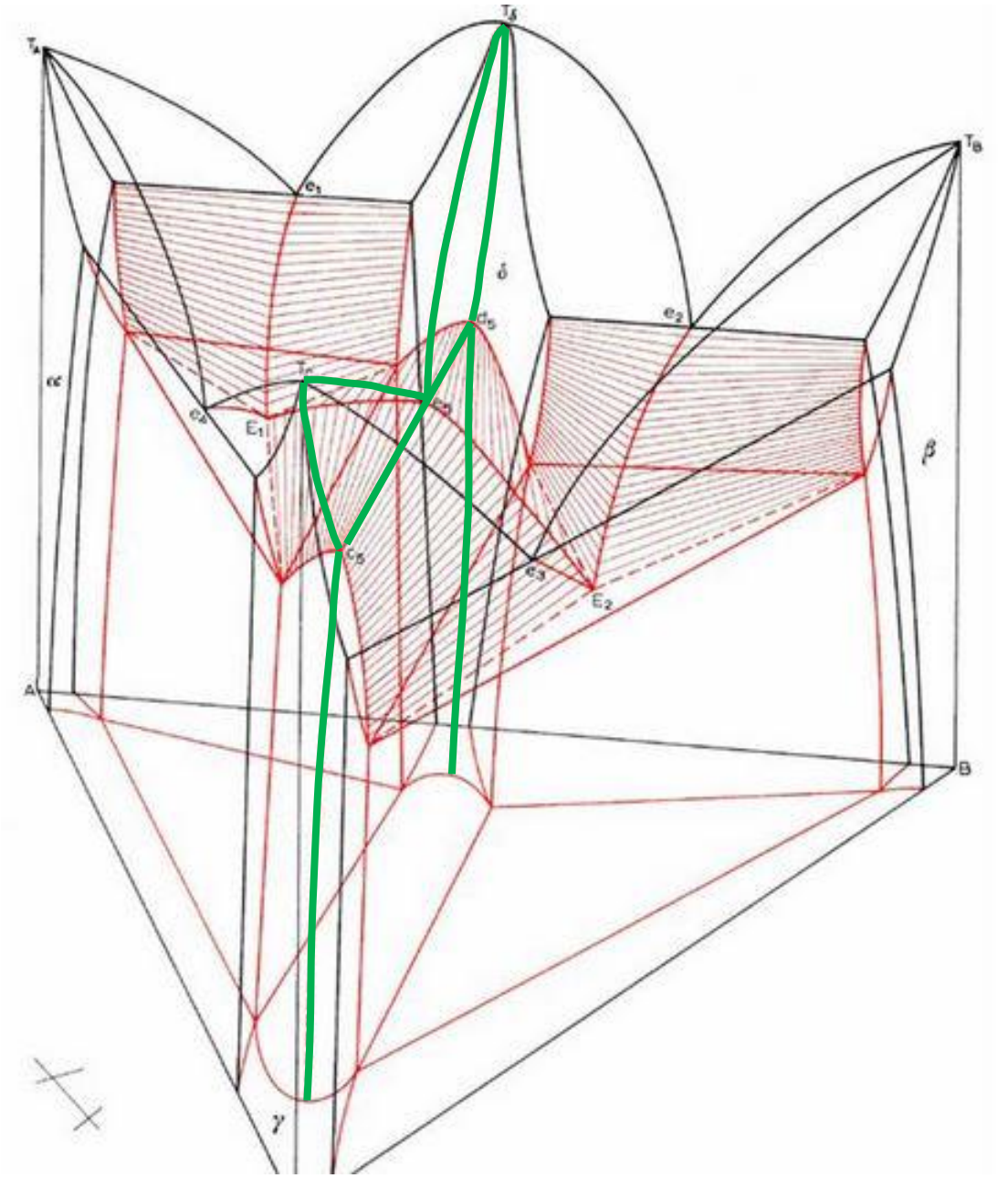
figuras do Prince

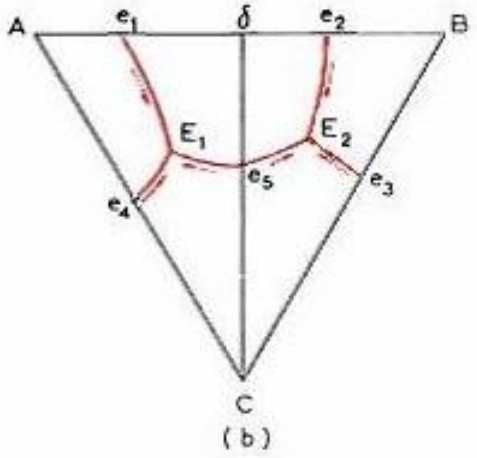




figuras do Prince

em verde, o "quase-binário" (destaque meu)

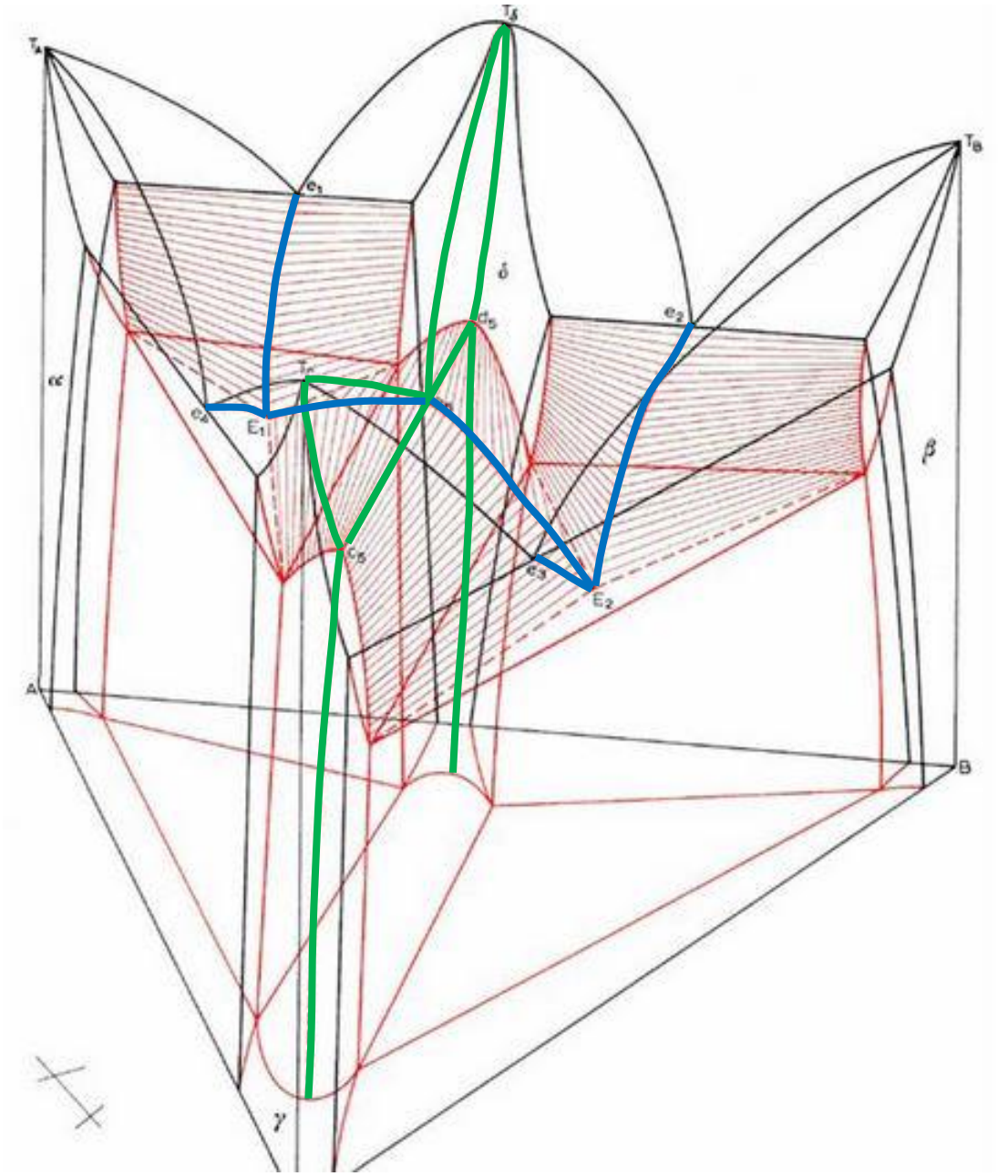


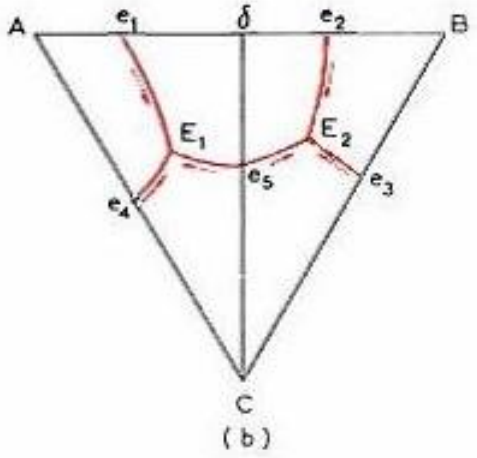


figuras do Prince

em verde, o "quase-binário" (destaque meu)

em azul, as calhas (destaque meu)



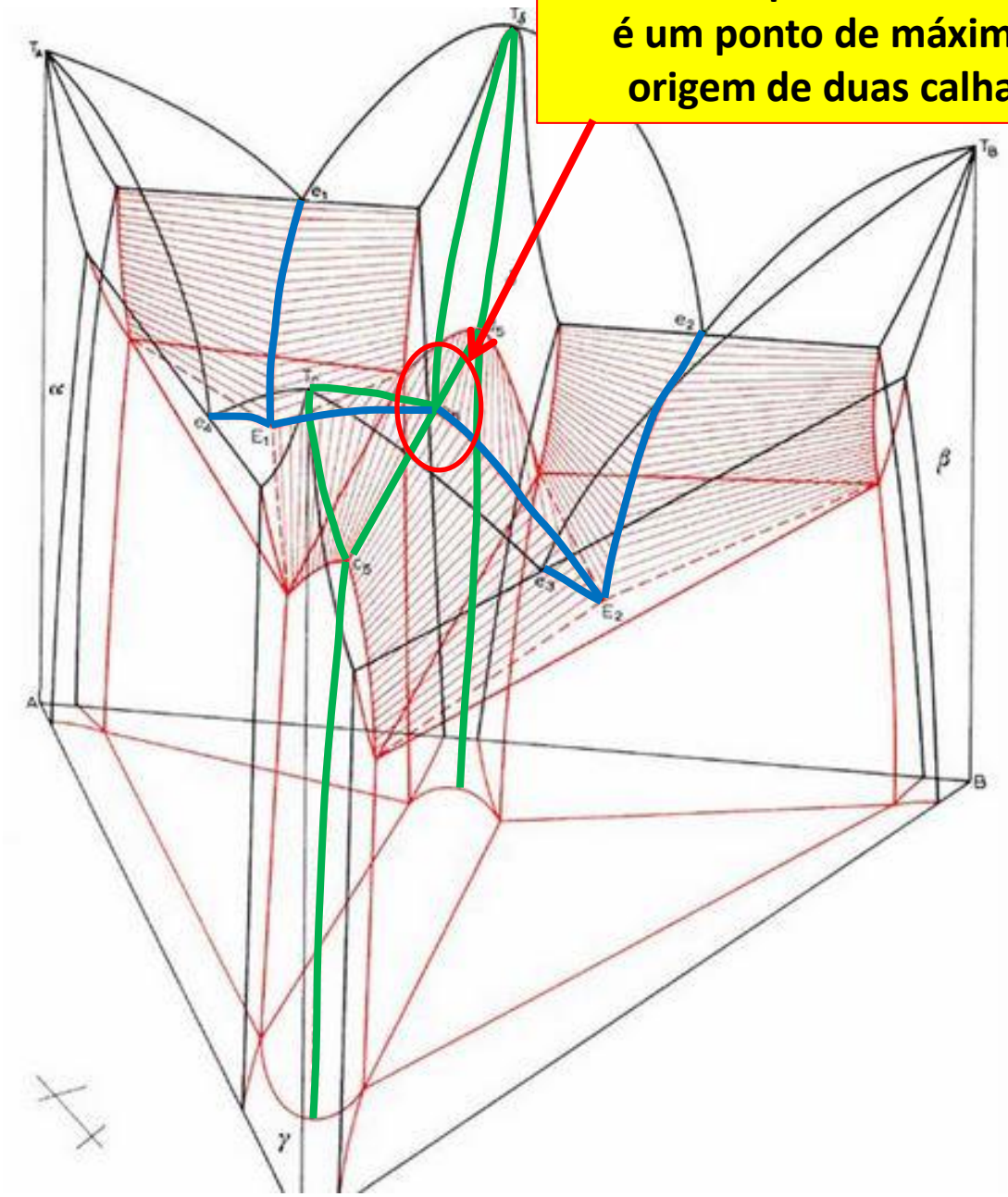


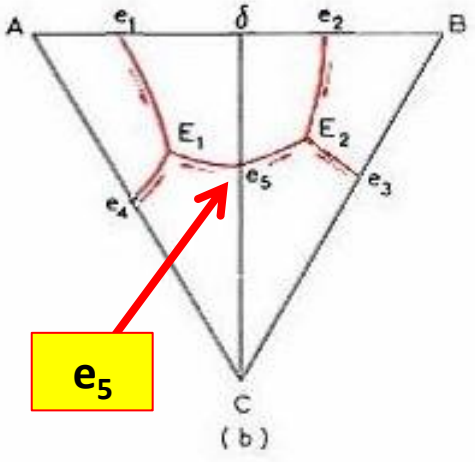
O eutético pseudo-binário e_5 é um ponto de máximo, origem de duas calhas

ras do Prince

em verde, o "quase-binário" (destaque meu)

em azul, as calhas (destaque meu)





e_5

figura do Prince

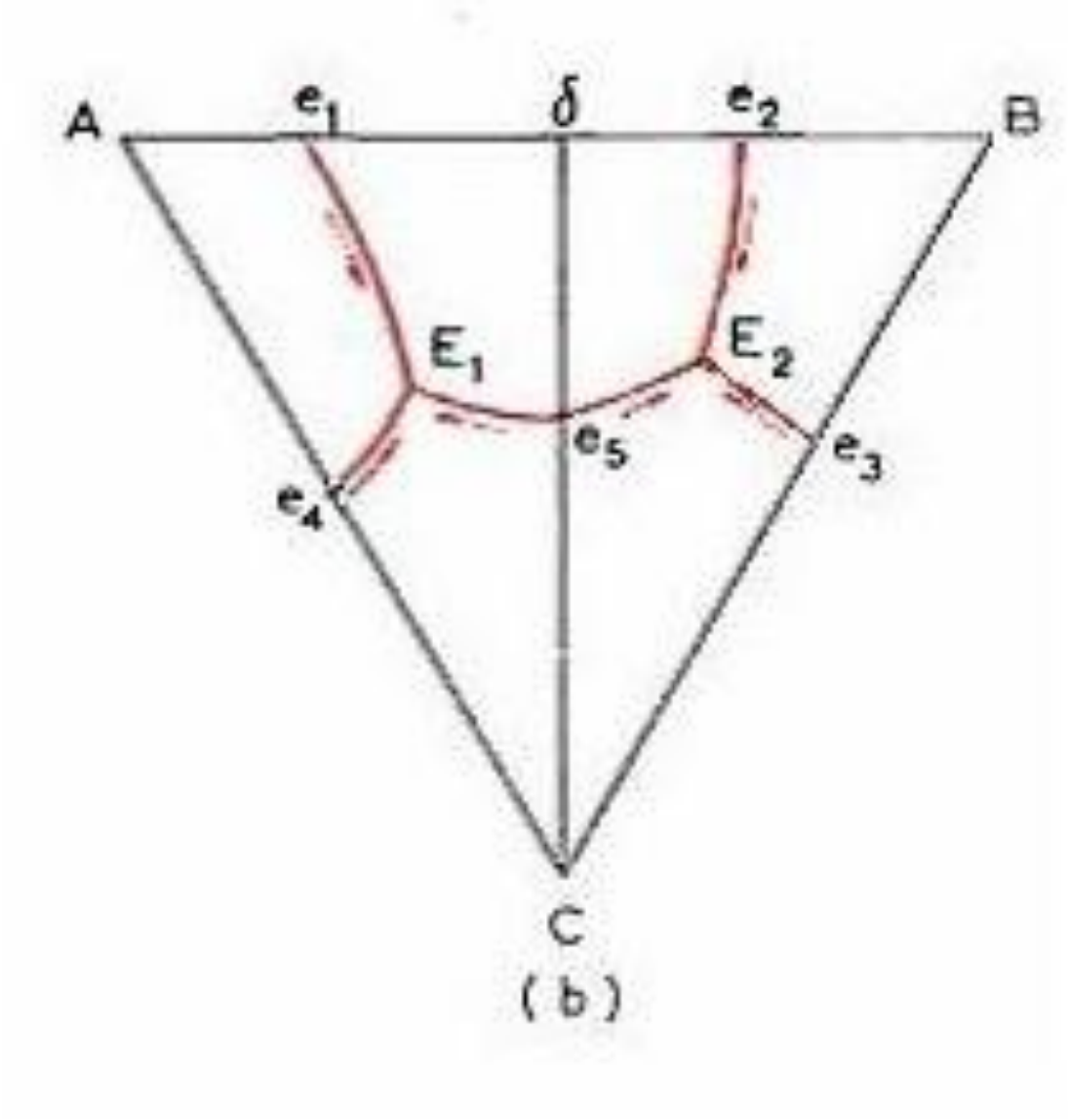


figura do Prince

EXEMPLO: As-Ga-Zn

(três fases congruentes)

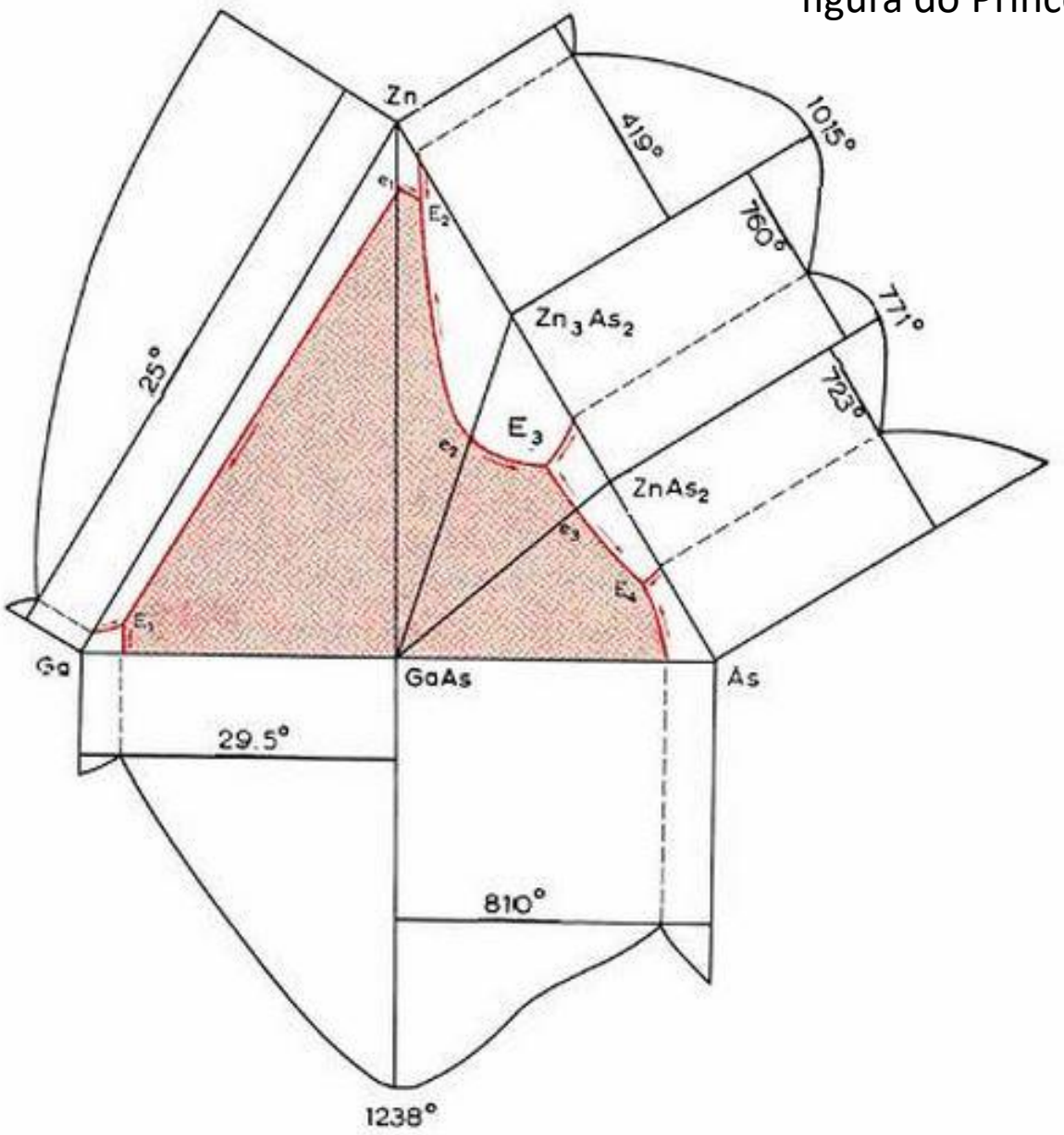


Fig. 205. The As–Ga–Zn system (schematic). (After W. KÖSTER AND W. ULRICH, *Z. Metallk.*, 49 (1958) 361; courtesy Dr. Riederer-Verlag GmbH.)

EXEMPLO: As-Ga-Zn

(três fases congruentes)

figura do Prince

(destaques meus)

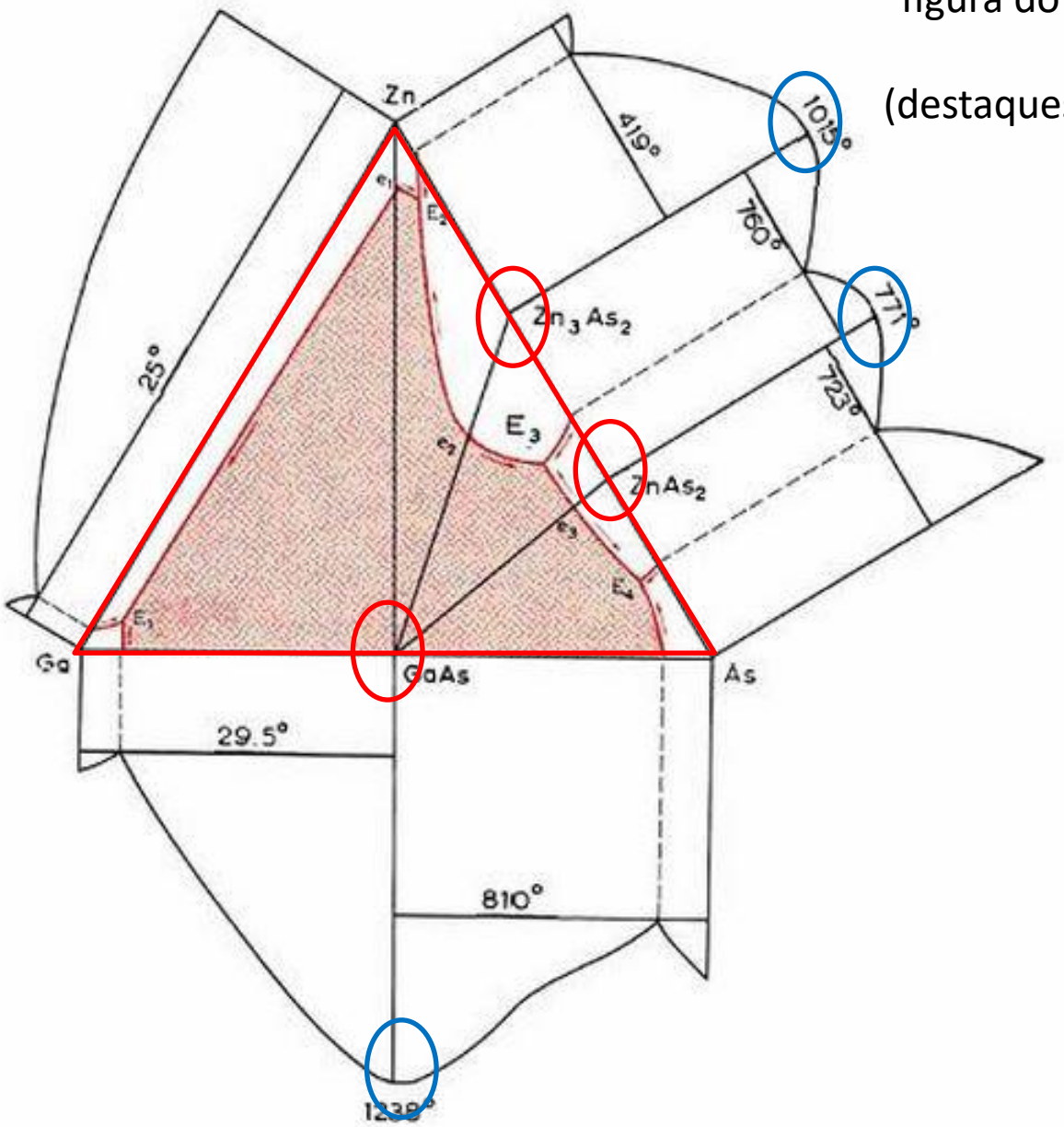


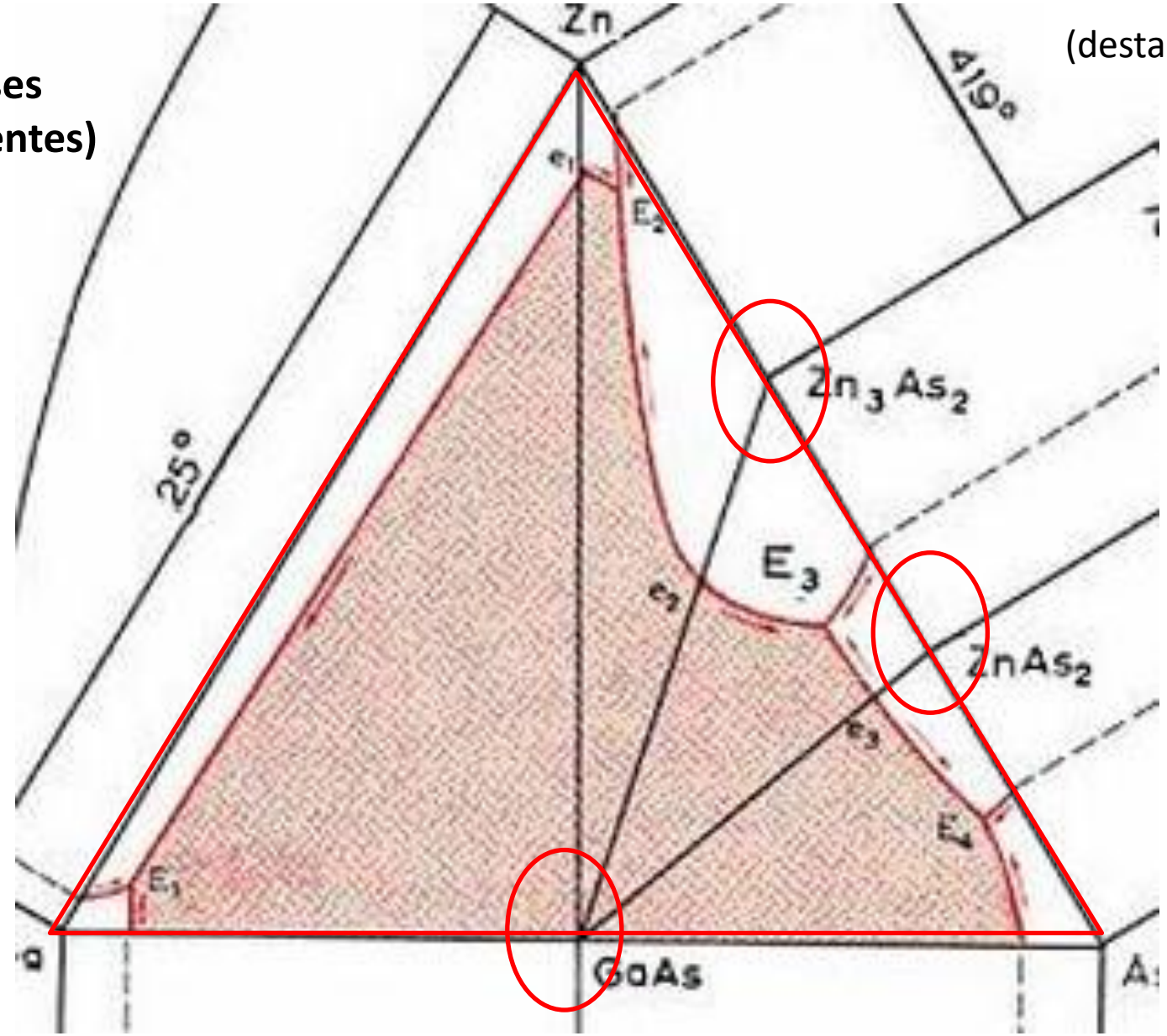
Fig. 205. The As–Ga–Zn system (schematic). (After W. KÖSTER AND W. ULRICH, *Z. Metallk.*, 49 (1958) 361; courtesy Dr. Riederer-Verlag GmbH.)

figura do Prince

(destaques meus)

EXEMPLO: As-Ga-Zn

(três fases congruentes)



EQUILÍBRIOS INVARIANTES

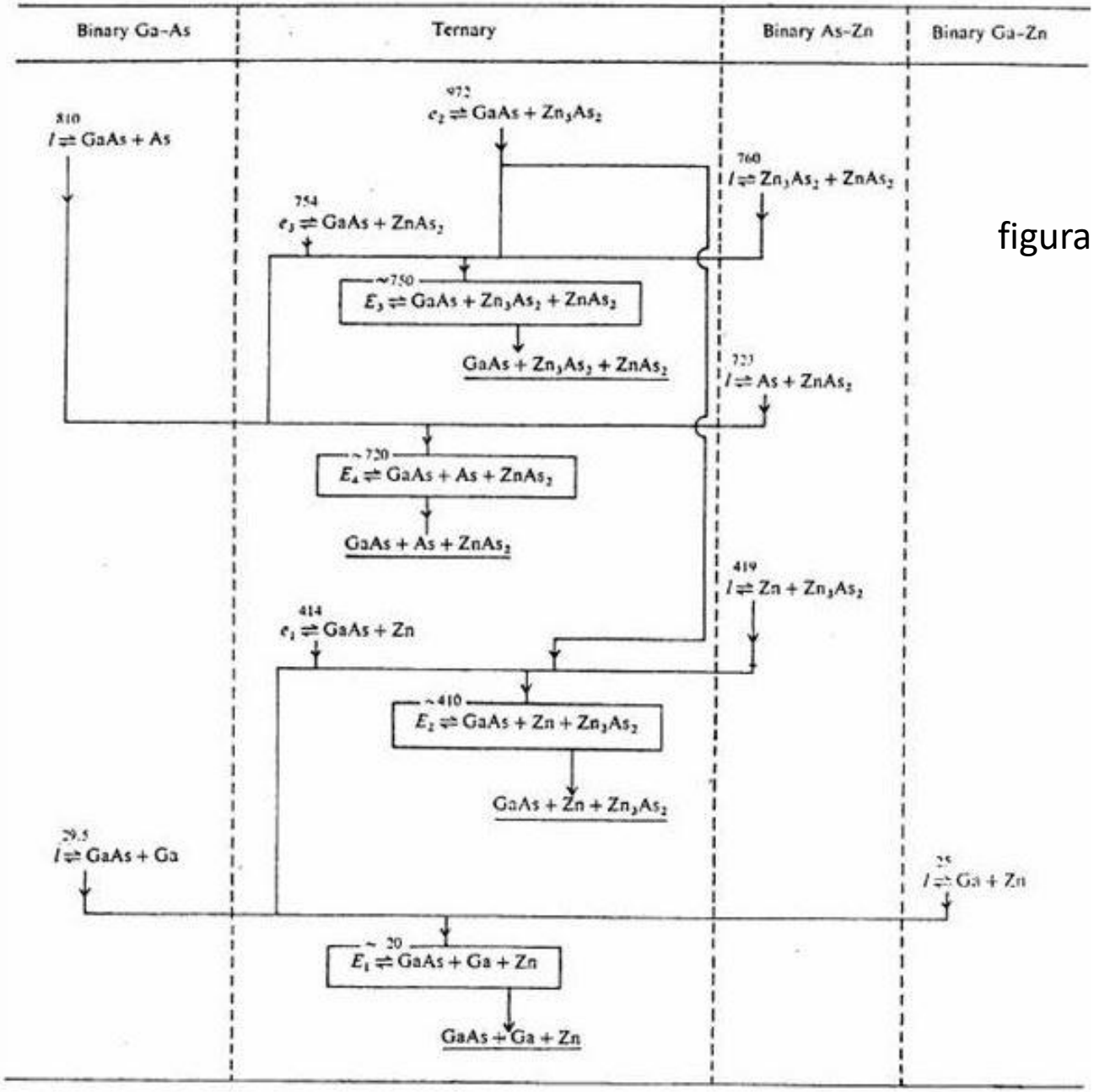
Embora envolvam apenas três fases, são equilíbrios invariantes, pois há uma restrição de composição (as três composições estão na mesma reta)

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.

dados do Prince

(destaques meus)

TABLE 7



The four three-phase equilibria underlined are stable down to room-temperature.

figura do Prince

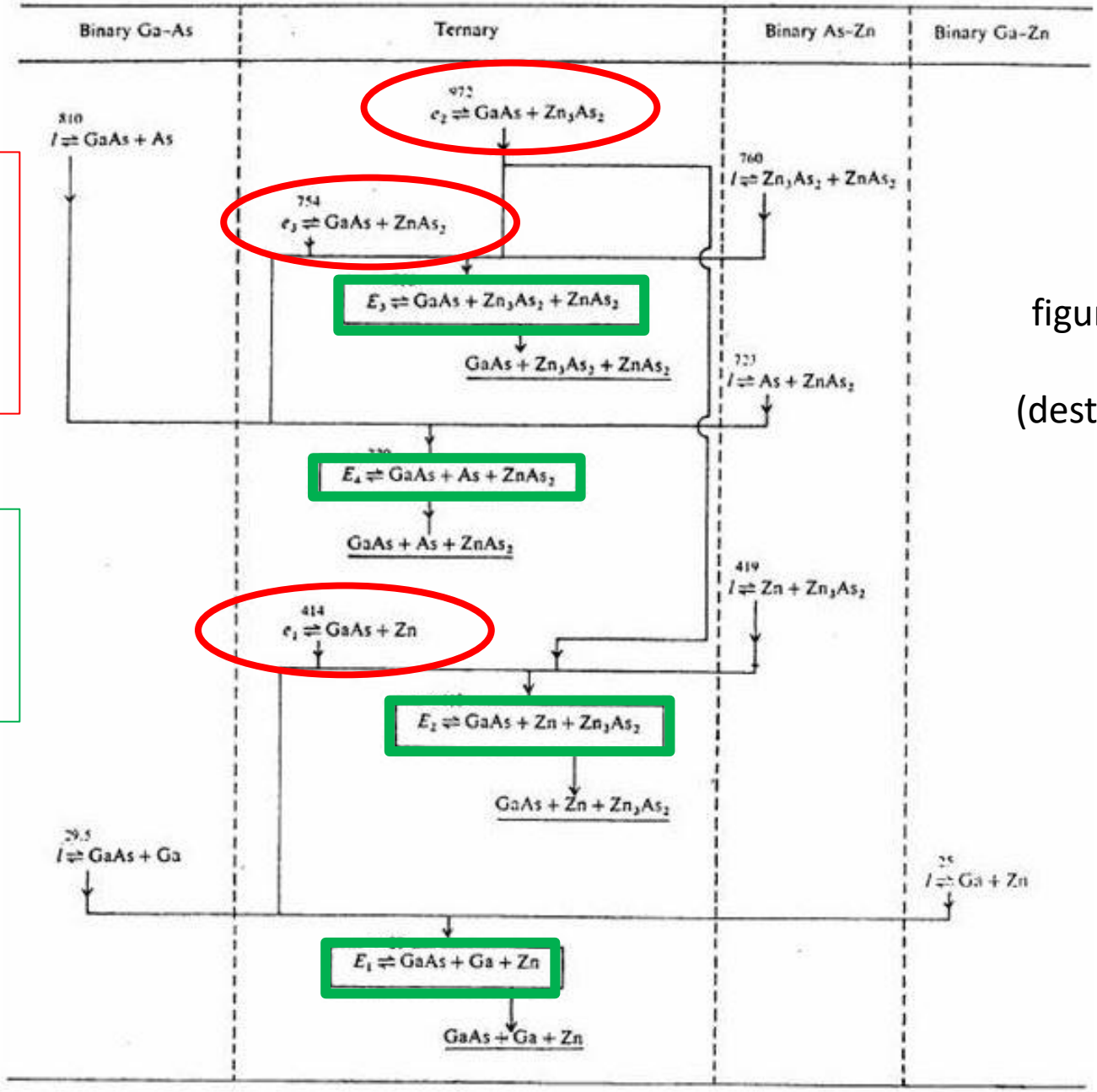
Destaque: os três máximos eutéticos quase-binários

Destaque: os quatro eutéticos ternários

figura do Prince

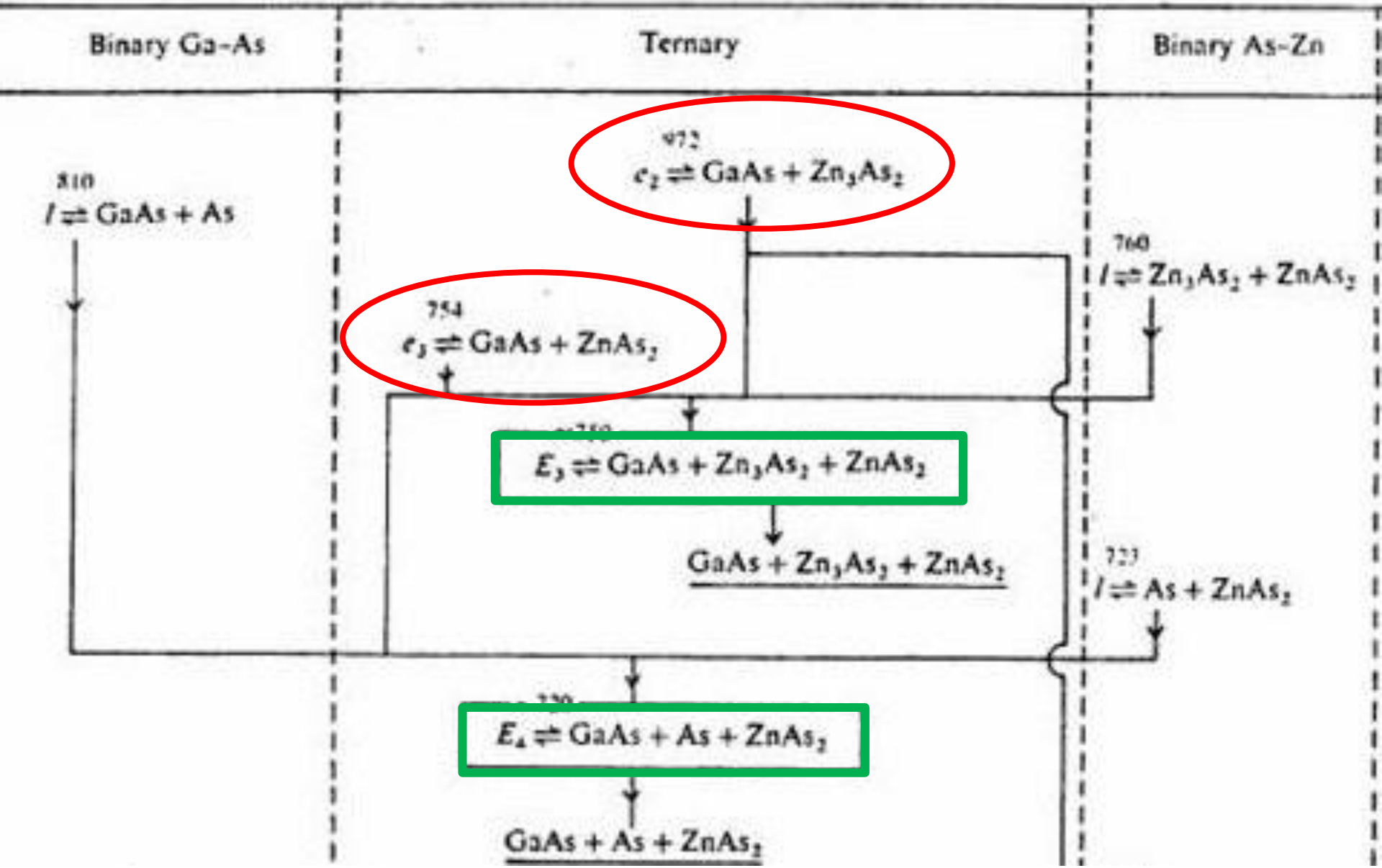
(destaques meus)

TABLE 7



The four three-phase equilibria underlined are stable down to room-temperature.

TABLE 7


Binary Ga-As
Ternary
Binary As-Zn
810
$l \rightleftharpoons GaAs + As$
772
$e_2 \rightleftharpoons GaAs + Zn_3As_2$
760
$l \rightleftharpoons Zn_3As_2 + ZnAs_2$
754
$e_3 \rightleftharpoons GaAs + ZnAs_2$
$E_3 \rightleftharpoons GaAs + Zn_3As_2 + ZnAs_2$
$GaAs + Zn_3As_2 + ZnAs_2$
723
$l \rightleftharpoons As + ZnAs_2$
$E_4 \rightleftharpoons GaAs + As + ZnAs_2$
$GaAs + As + ZnAs_2$

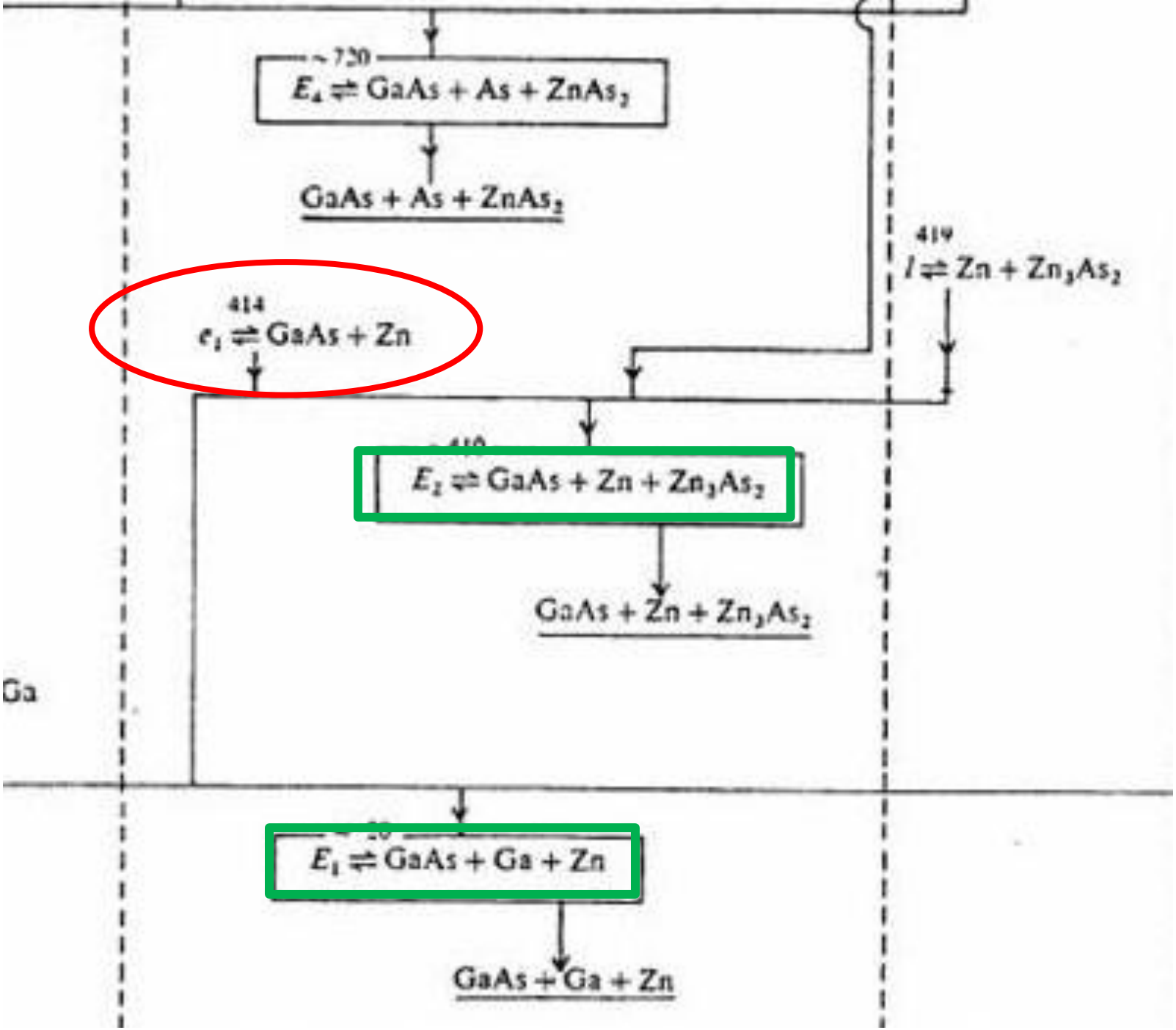
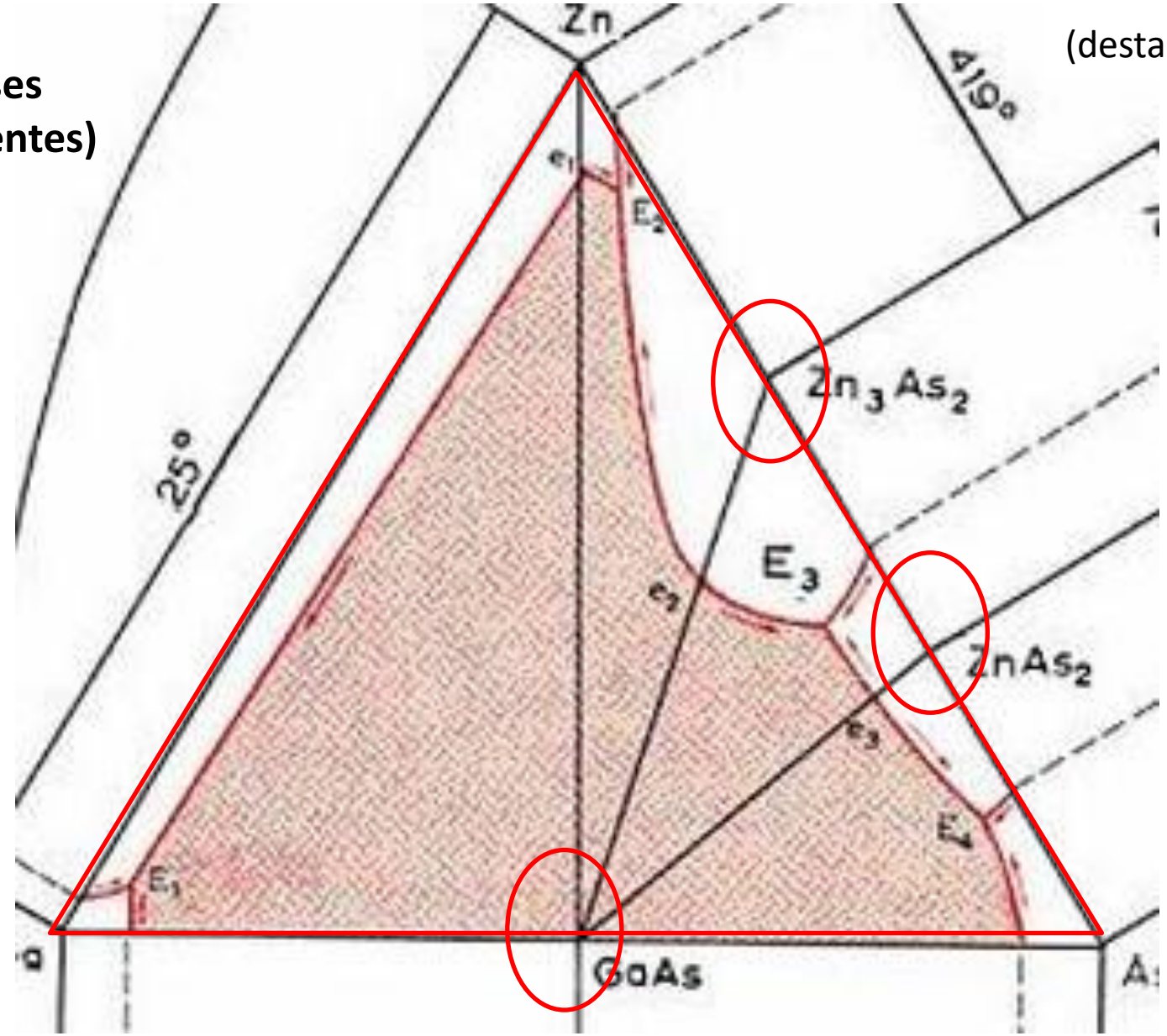

~720
$E_4 \rightleftharpoons GaAs + As + ZnAs_2$
$GaAs + As + ZnAs_2$
419
$I \rightleftharpoons Zn + Zn_3As_2$
414
$e_1 \rightleftharpoons GaAs + Zn$
$E_2 \rightleftharpoons GaAs + Zn + Zn_3As_2$
$GaAs + Zn + Zn_3As_2$
Ga
$E_1 \rightleftharpoons GaAs + Ga + Zn$
$GaAs + Ga + Zn$

figura do Prince

(destaques meus)

EXEMPLO: As-Ga-Zn

(três fases congruentes)



POSSIBILIDADES PARA SISTEMA COM UMA FASE CONGRUENTE EM CADA BINÁRIO

figura do Prince

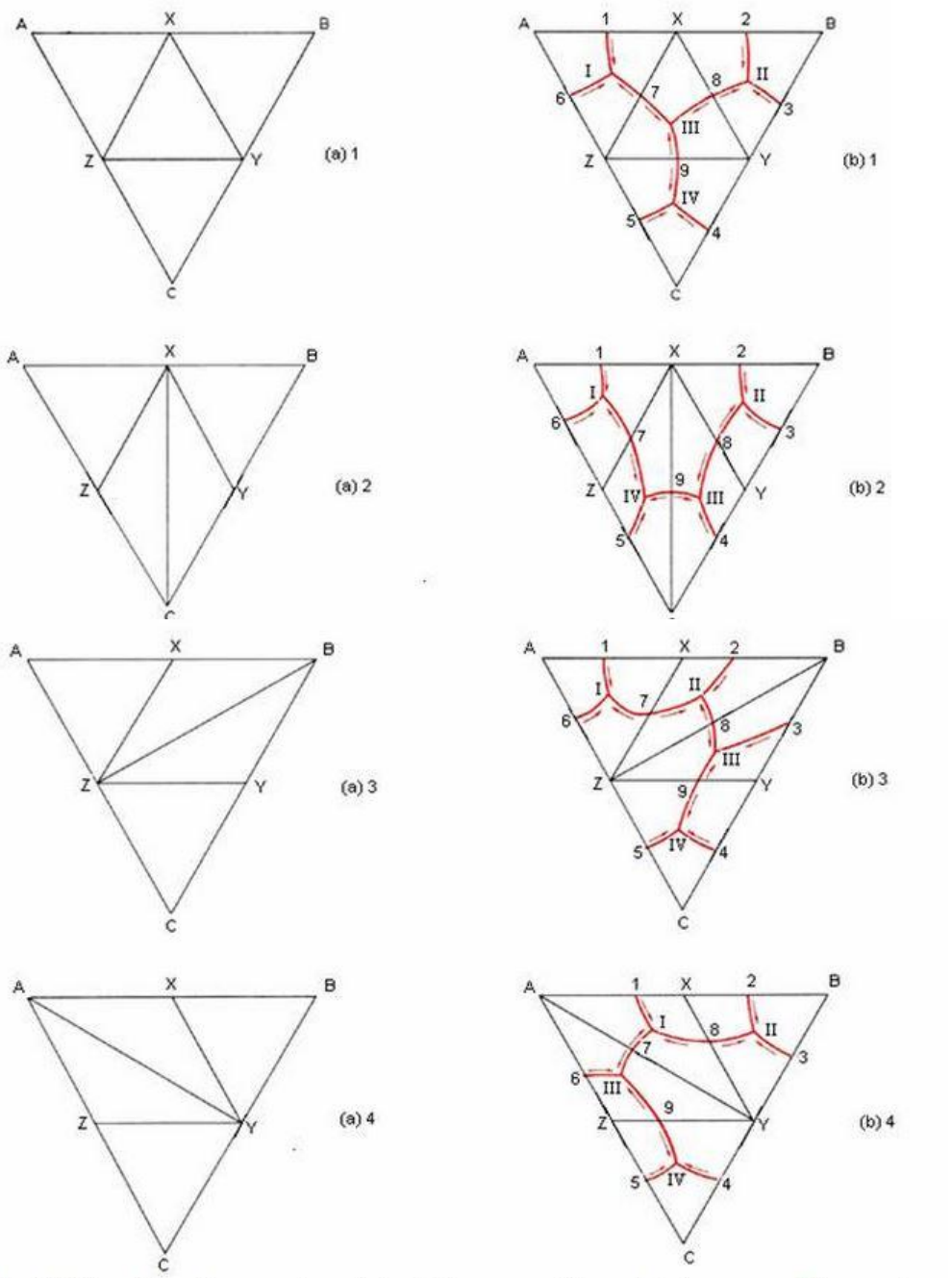


Fig. 204. Triangulation of ternary systems ; (a) containing congruent intermediate phases on each binary system, (b) the corresponding equilibria for eutectic reactions.

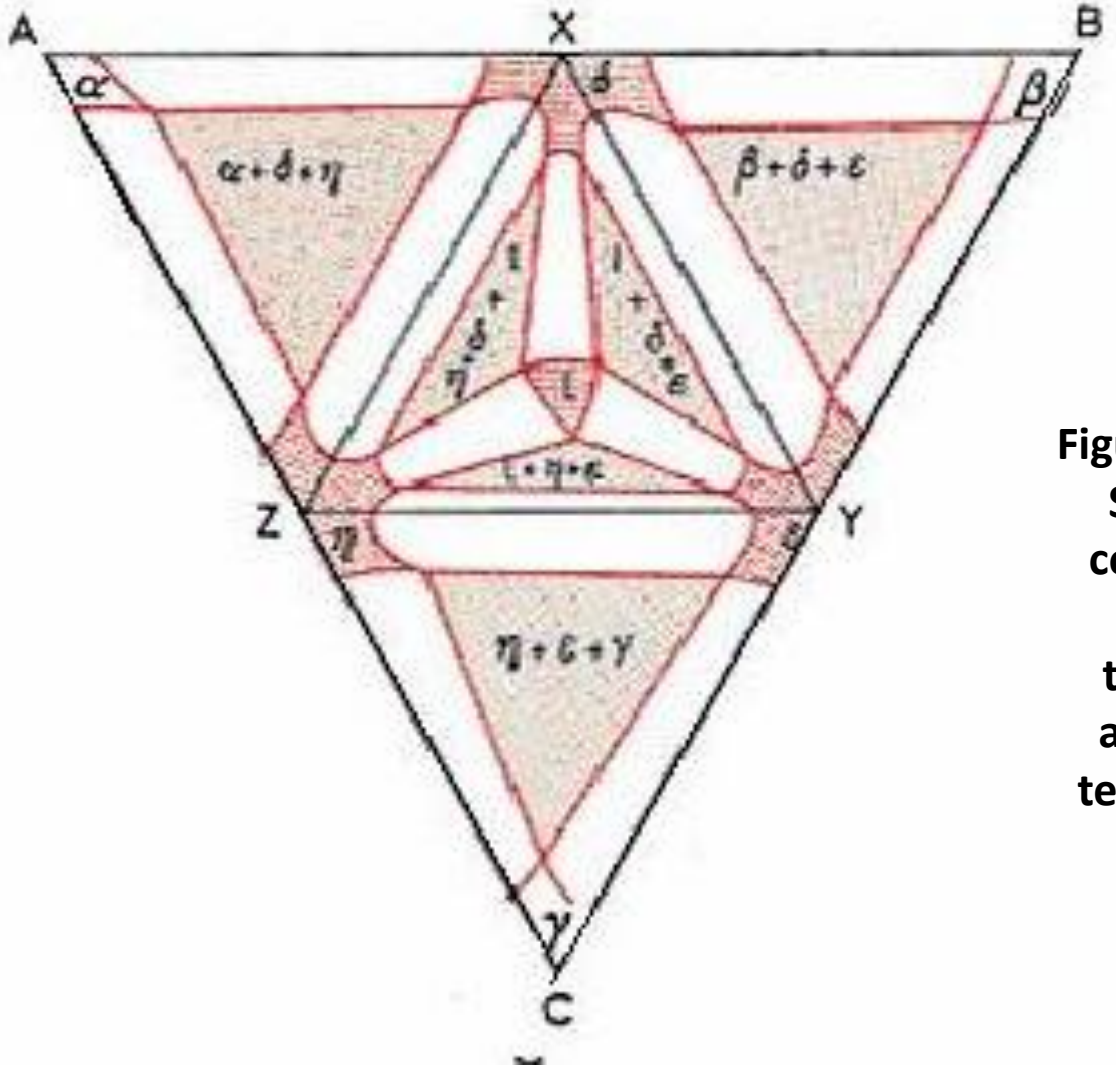
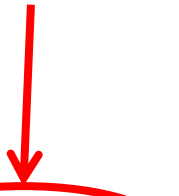


Figura 206 do Prince – Seção isotérmica correspondente ao caso 1, em temperatura logo acima do eutético ternário mais baixo.

EXEMPLO COM FASE CONGRUENTE <u>TERNÁRIA</u>



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

dados do Prince

figura do Prince

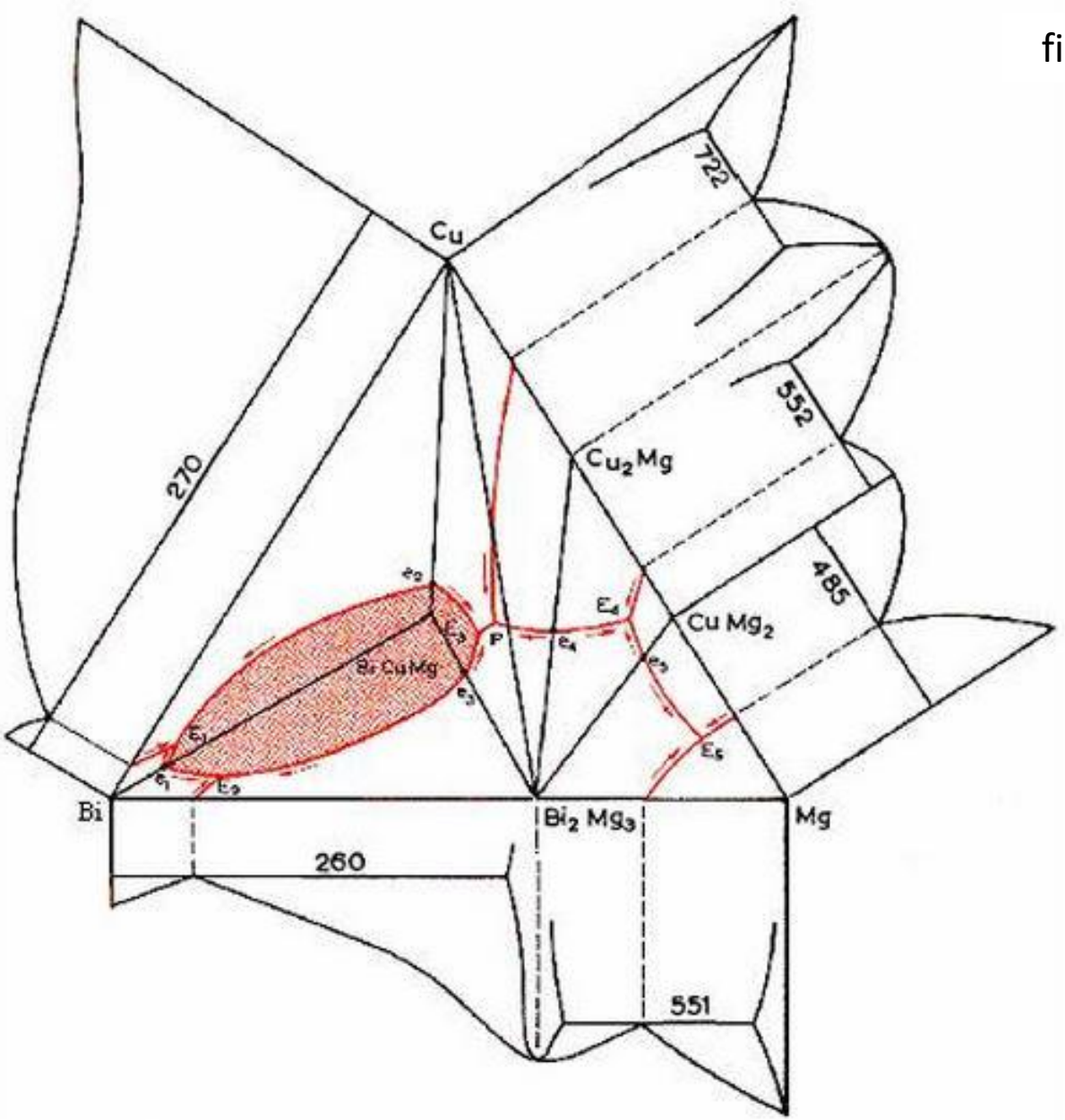


Fig. 207. The Bi–Cu–Mg system (schematic). (After R. DOBBENER, *Z. Metallk.*, **48** (1957) 413; courtesy Dr. Riederer-Verlag GmbH.)

figura do Prince

(destaques meus)

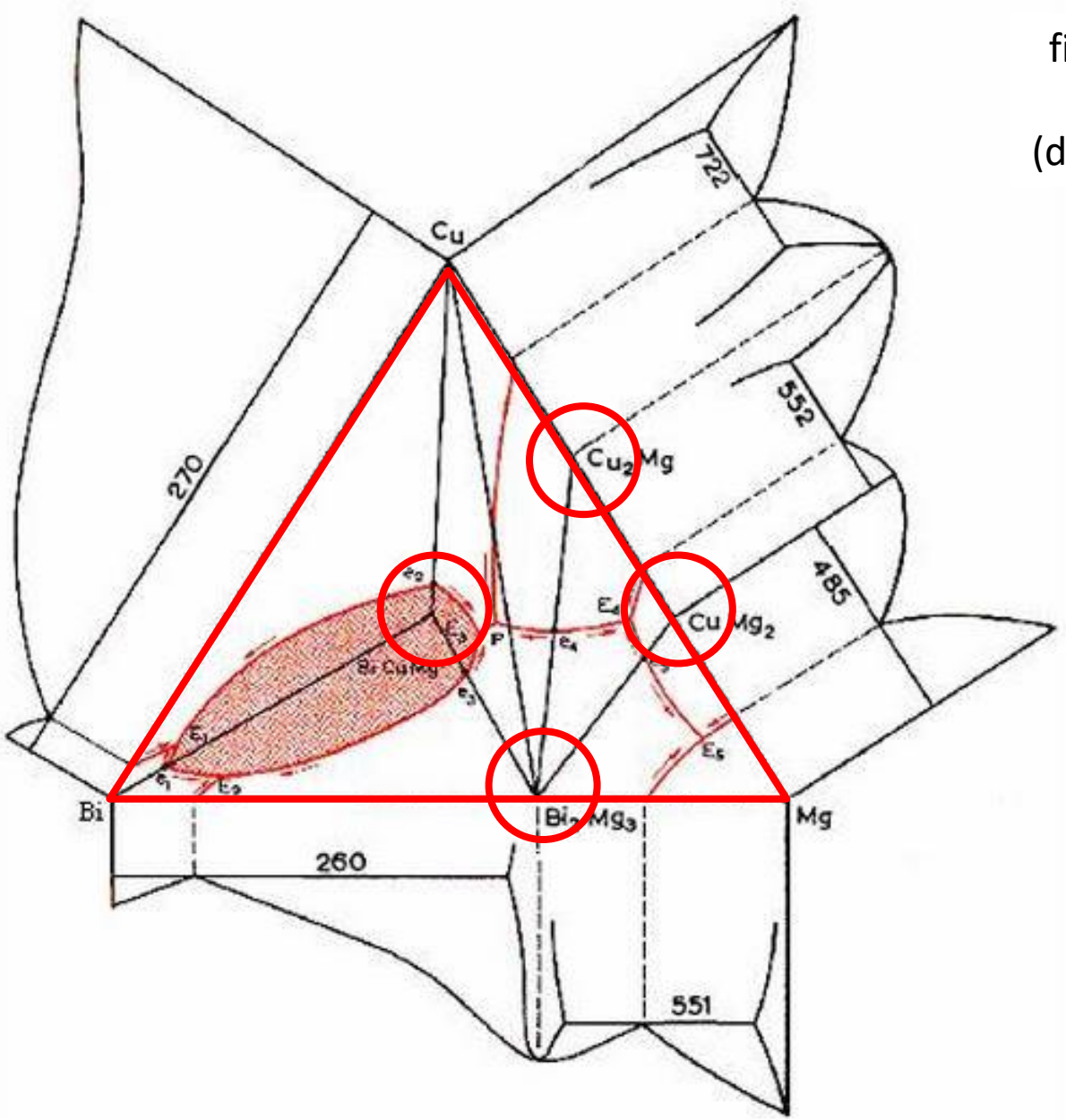
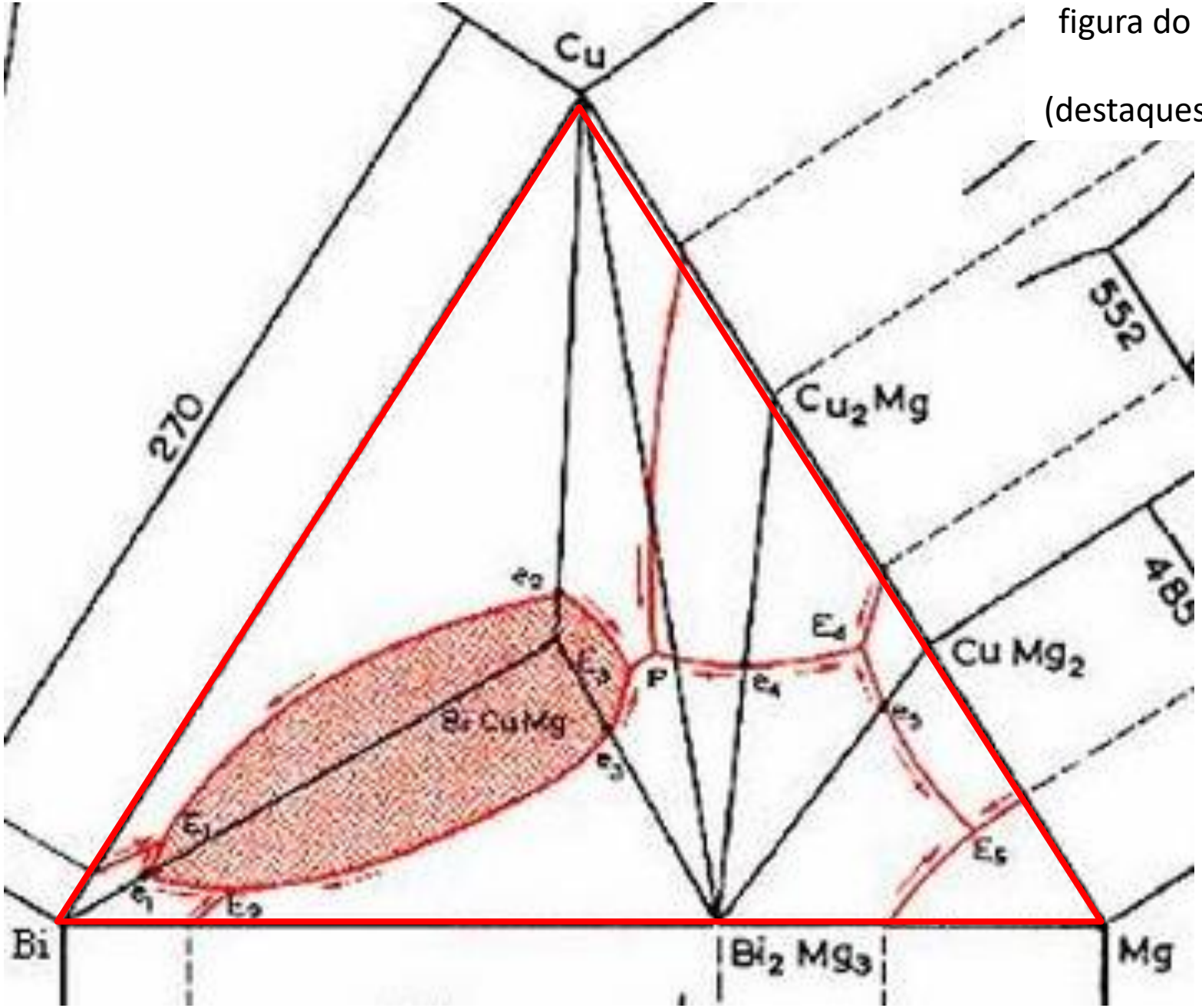


Fig. 207. The Bi–Cu–Mg system (schematic). (After R. Dobbener, *Z. Metallk.*, **48** (1957) 413; courtesy Dr. Riederer-Verlag GmbH.)

figura do Prince

(destaques meus)



Reparem:
A composição "P" está fora do triângulo Cu-BiCuMg-Bi_2Mg_3.
É uma reação de transição (ou "quasi-peritetic", na nomenclatura do Prince)

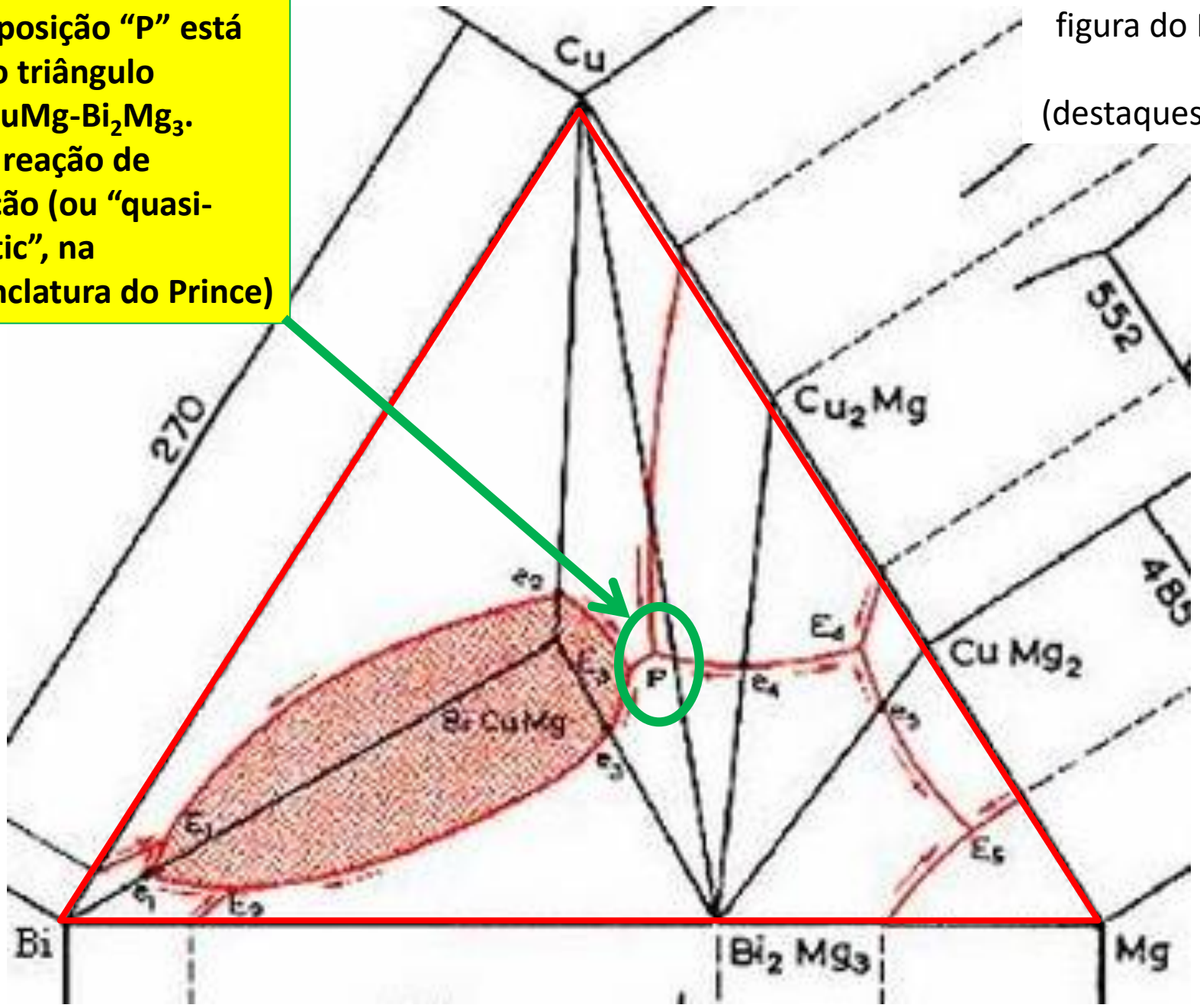


figura do Prince

(destaques meus)

EXEMPLO COM FASE CONGRUENTE TERNÁRIA

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

dados do Prince

Reparem:
A composição "P" está fora do triângulo Cu-BiCuMg-Bi_2Mg_3.
É uma reação de transição (ou "quasi-peritetic", na nomenclatura do Prince)

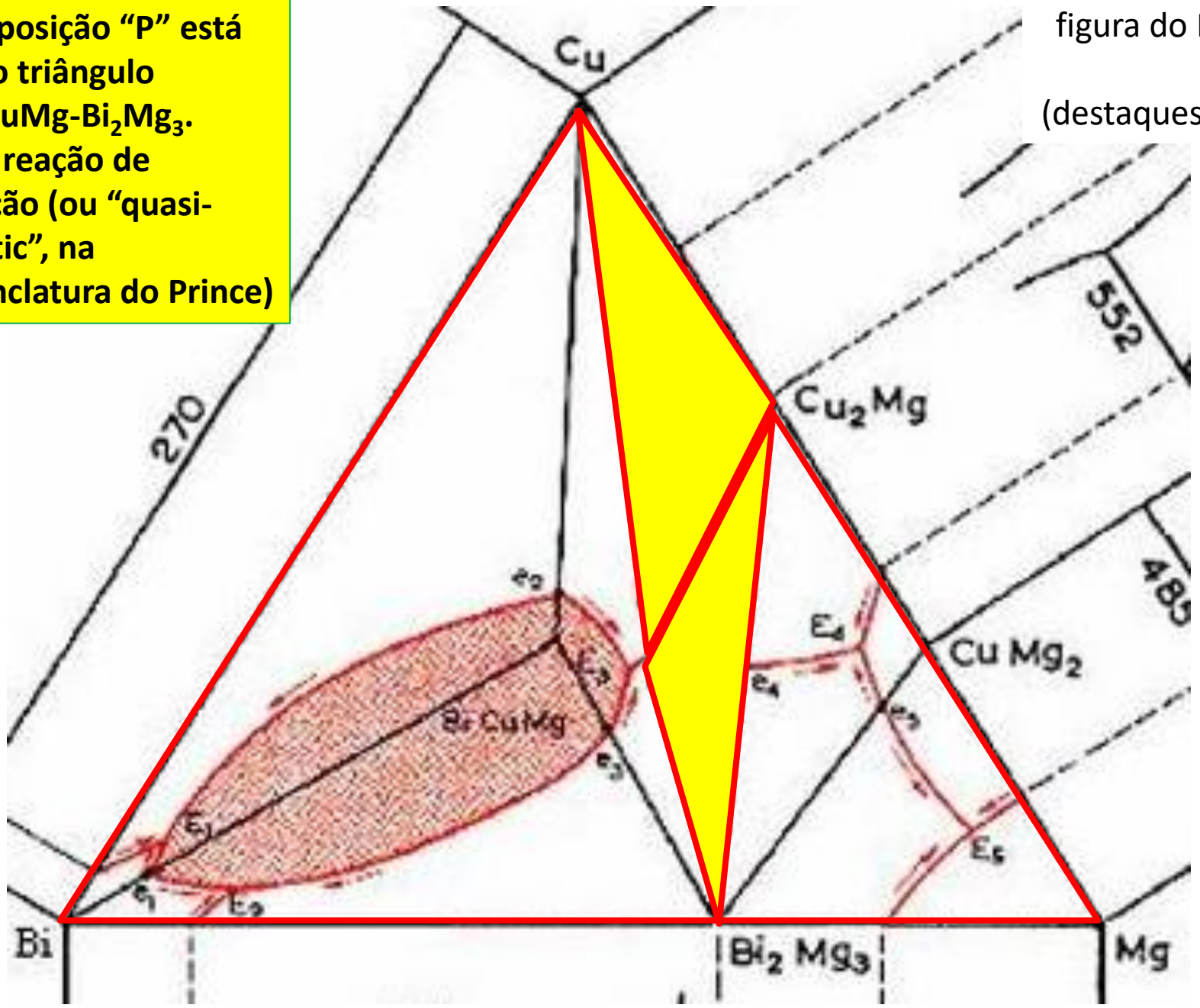


figura do Prince

(destaques meus)

Reparem:
A composição "P" está fora do triângulo Cu-BiCuMg-Bi_2Mg_3.
É uma reação de transição (ou "quasi-peritetic", na nomenclatura do Prince)

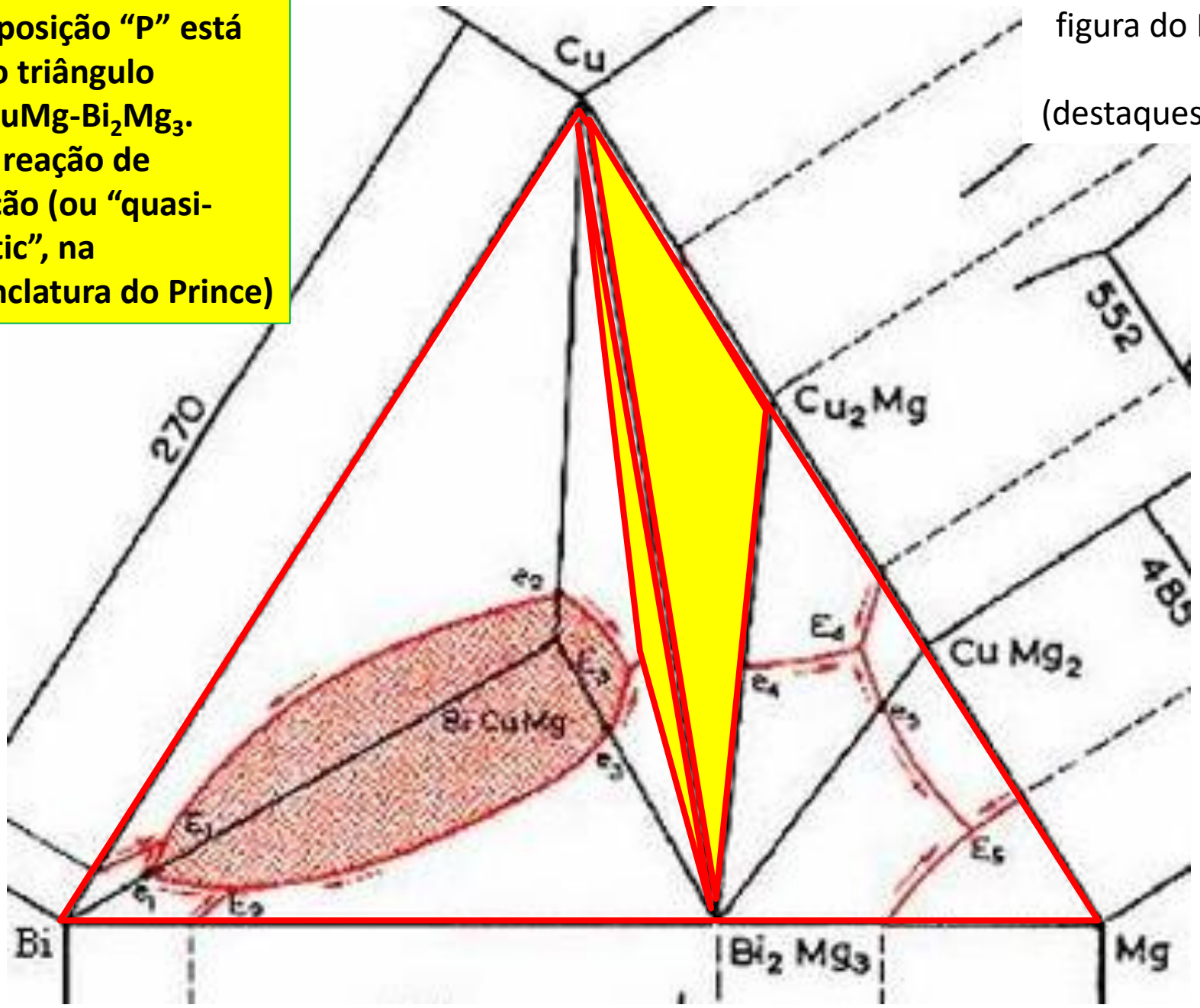


figura do Prince

(destaques meus)

Reparem:
A composição "P" está fora do triângulo Cu-BiCuMg-Bi_2Mg_3.
É uma reação de transição (ou "quasi-peritetic", na nomenclatura do Prince)

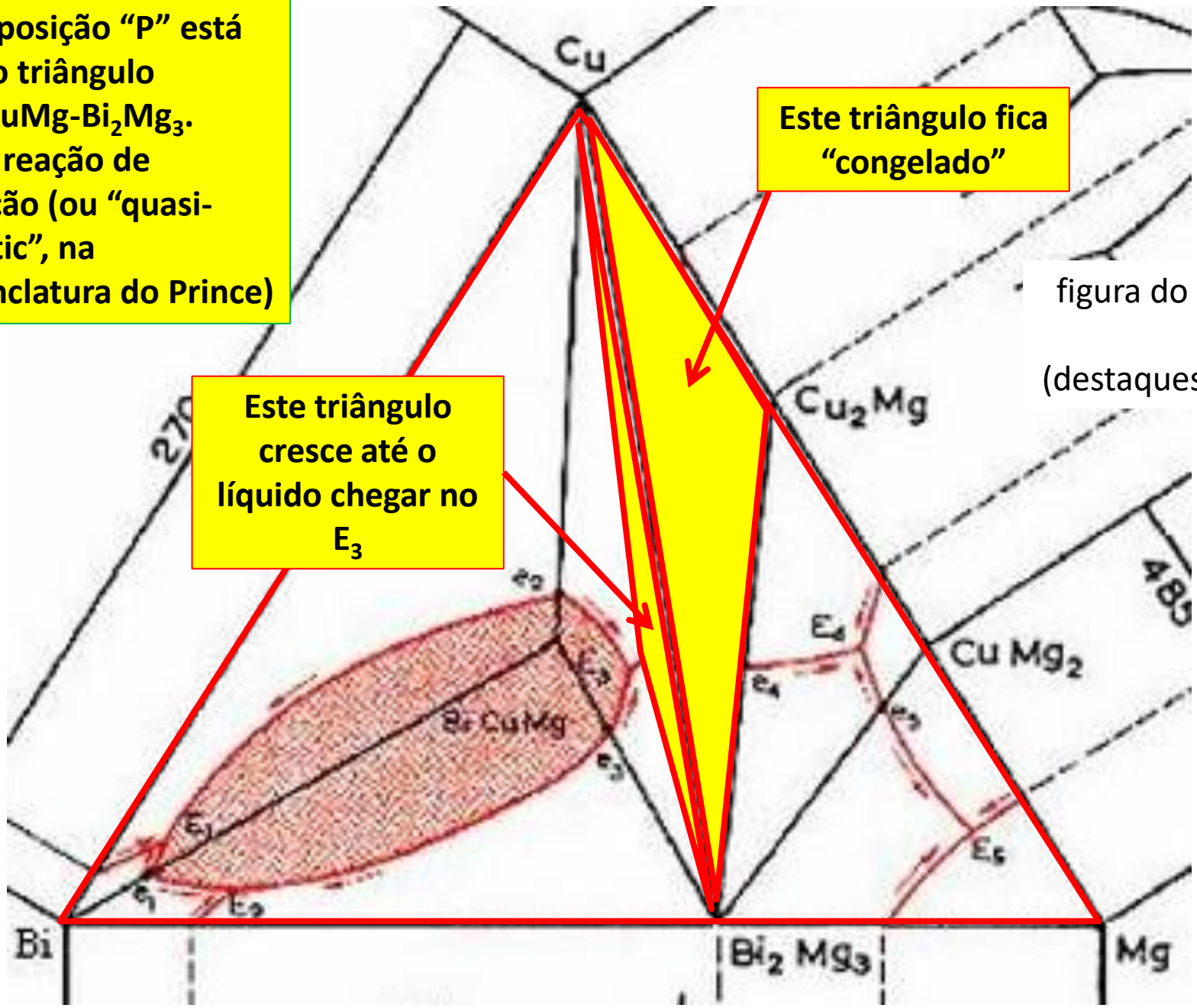


figura do Prince

(destaques meus)

figura do Prince

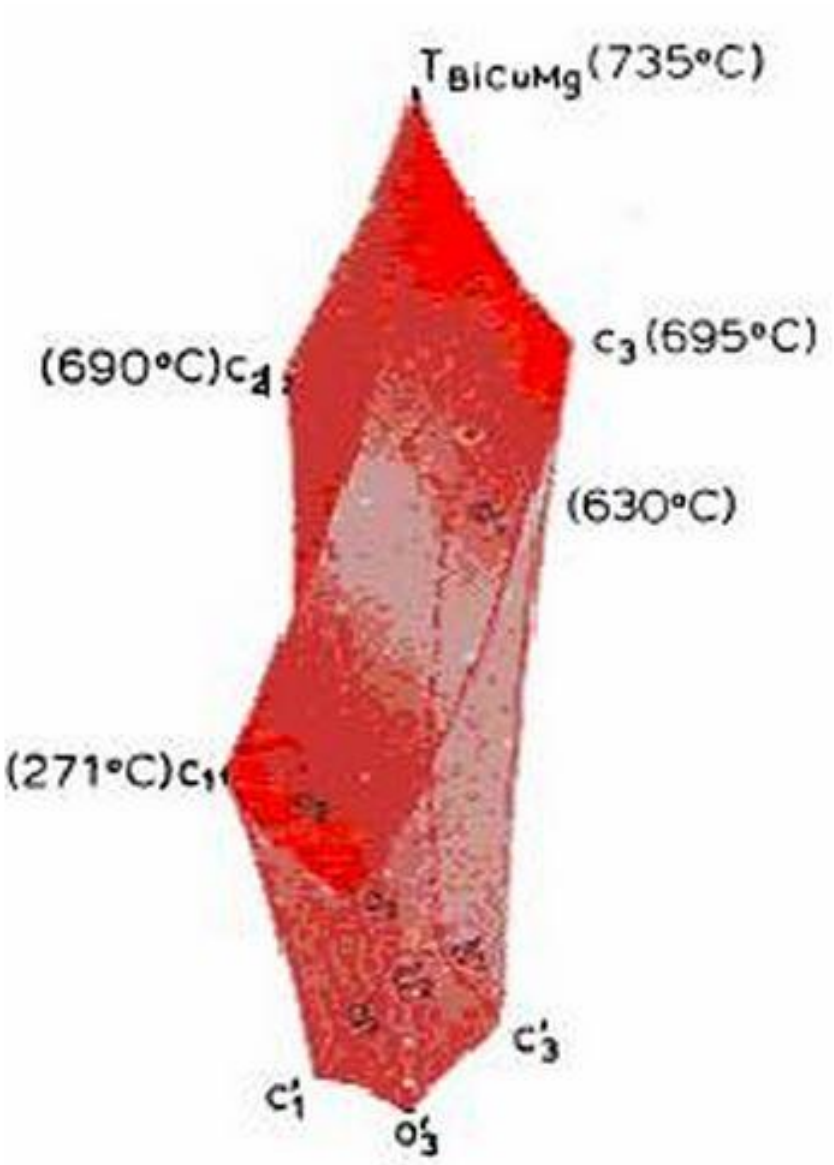


Fig. 208. The BiCuMg phase region.

FASES INTERMEDIÁRIAS INCONGRUENTES

Caso A1 -
FASES BINÁRIAS, SEM REAÇÕES INVARIANTES DE TRÊS FASES

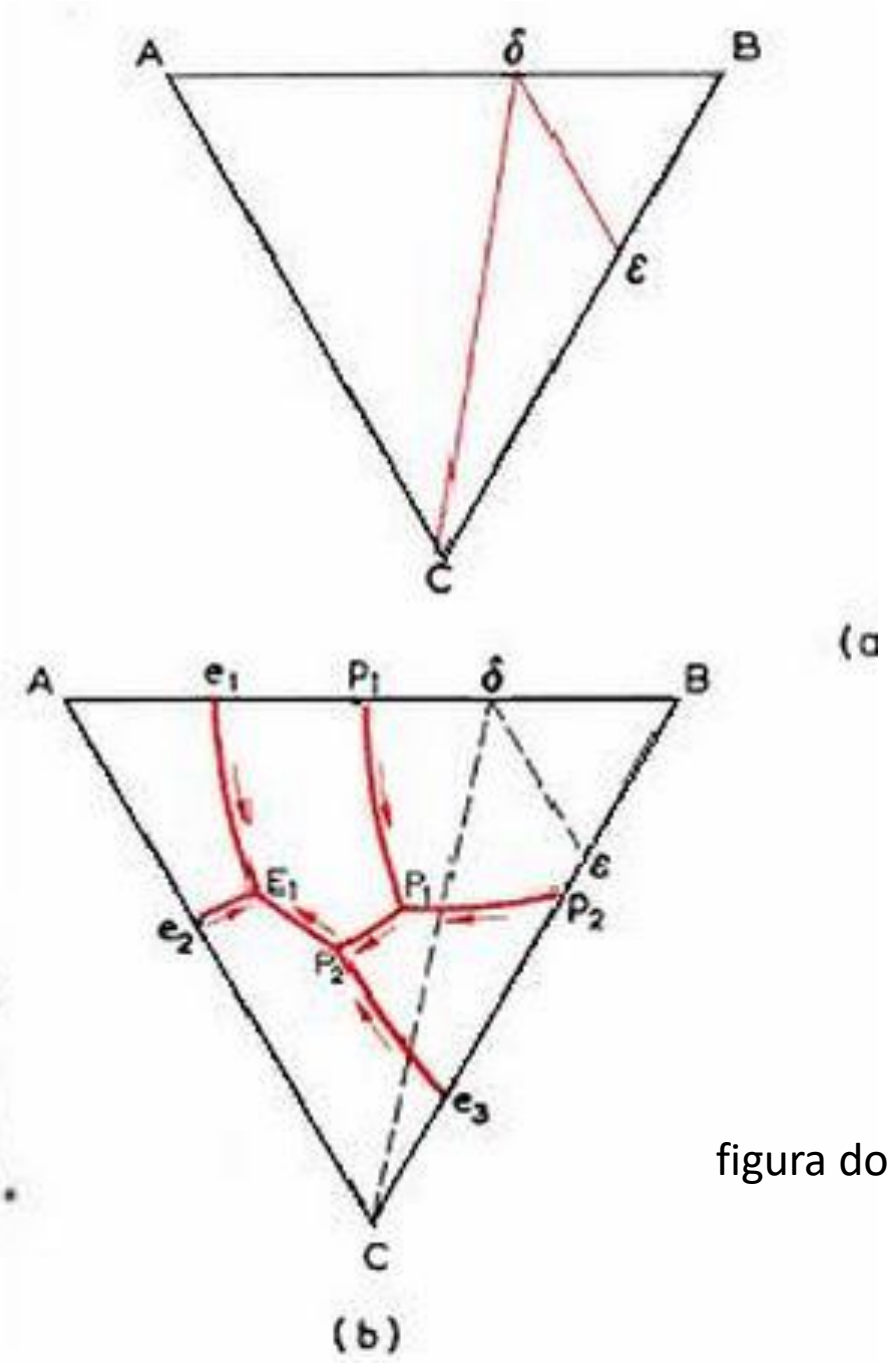
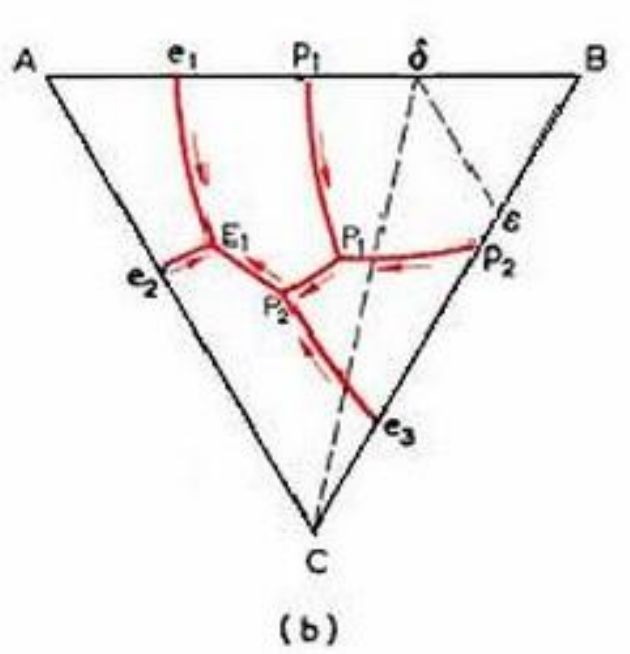


figura do Prince

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

TABLE 8

Binary AB	Binary BC	Ternary	Binary AC
$l+\beta \rightleftharpoons \delta$ p_1			
	$l+\beta \rightleftharpoons \varepsilon$ p_2		
		$l+\beta \rightleftharpoons \delta+\varepsilon$ P_1	
		$\beta+\delta+\varepsilon$	
		$l \rightleftharpoons \delta+\varepsilon$	
	$l \rightleftharpoons \varepsilon+\gamma$ e_3		
		$l+\varepsilon \rightleftharpoons \delta+\gamma$ P_2	
$l \rightleftharpoons \alpha+\gamma$ e_1			
		$\varepsilon+\delta+\gamma$	
		$l \rightleftharpoons \delta+\gamma$	
			$l \rightleftharpoons \alpha+\gamma$ e_2
		$l \rightleftharpoons \alpha+\delta+\gamma$ E_1	
		$\alpha+\delta+\gamma$	



figuras do Prince

FASES INTERMEDIÁRIAS INCONGRUENTES

Caso A2 -
FASES BINÁRIAS, COM UM MÁXIMO EUTÉTICO

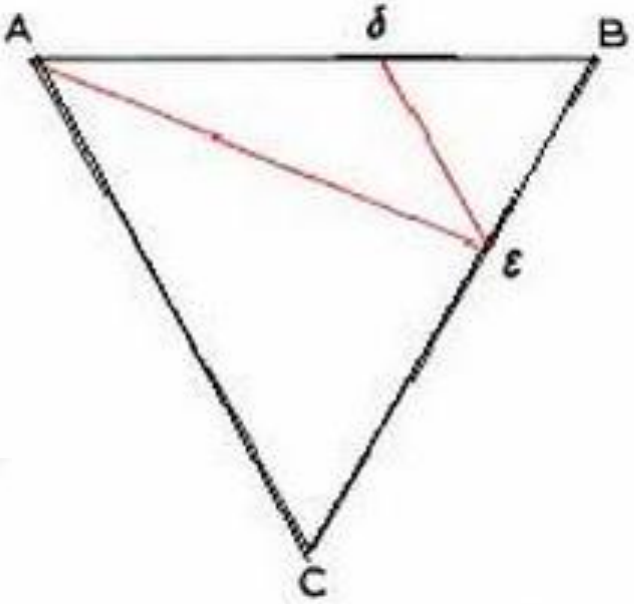


figura do Prince

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

Surgiu um equilíbrio invariante quase-binário. E é um máximo.

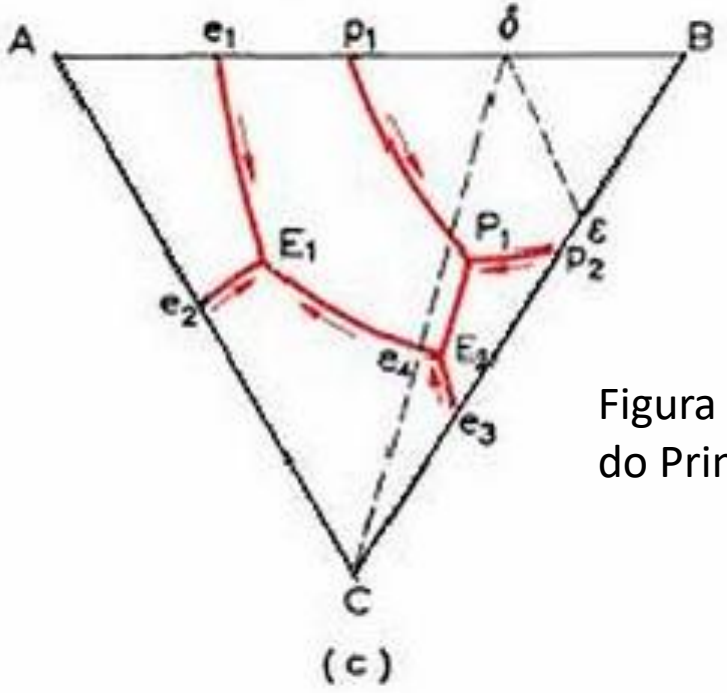


Figura 209c do Prince

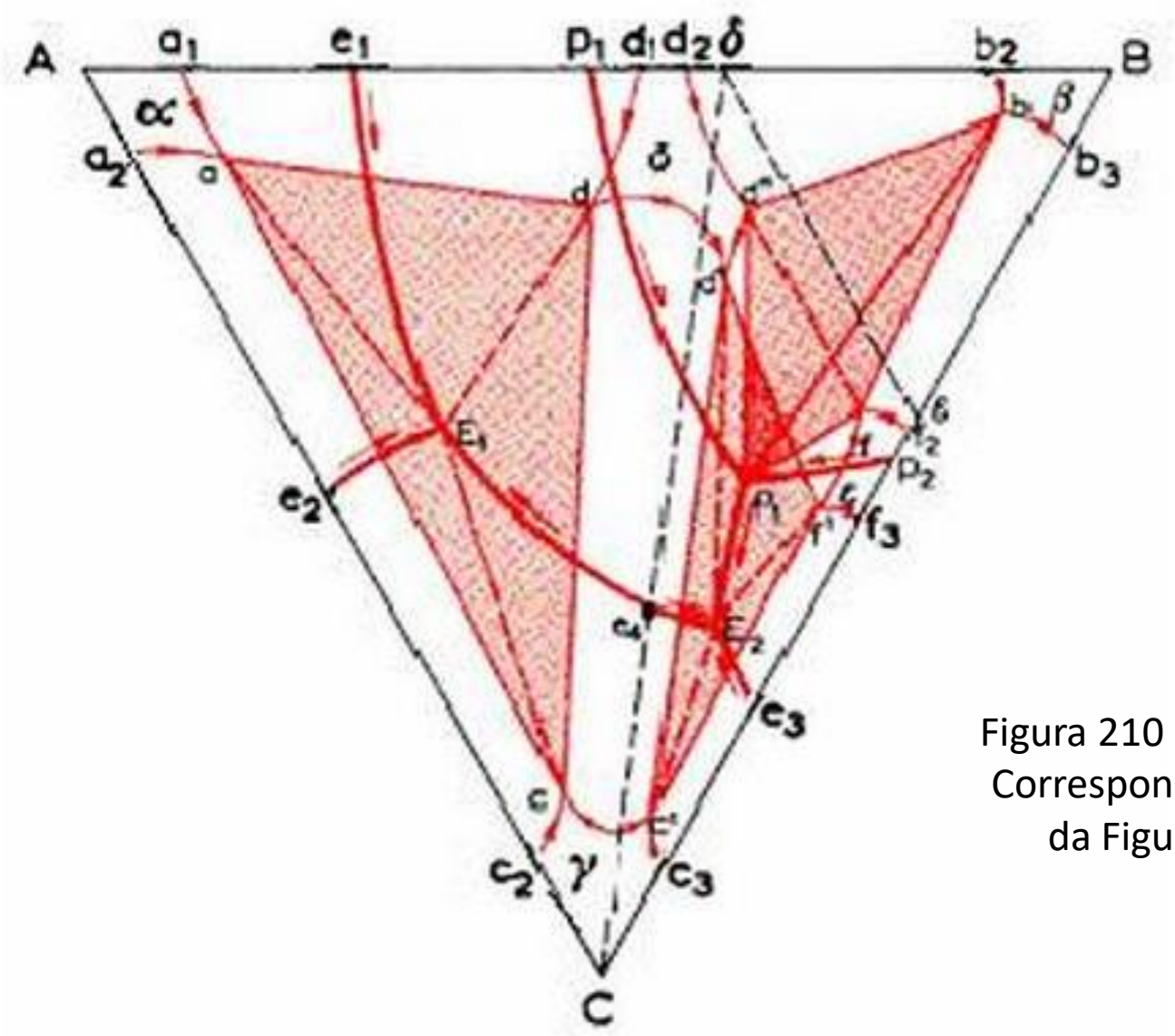
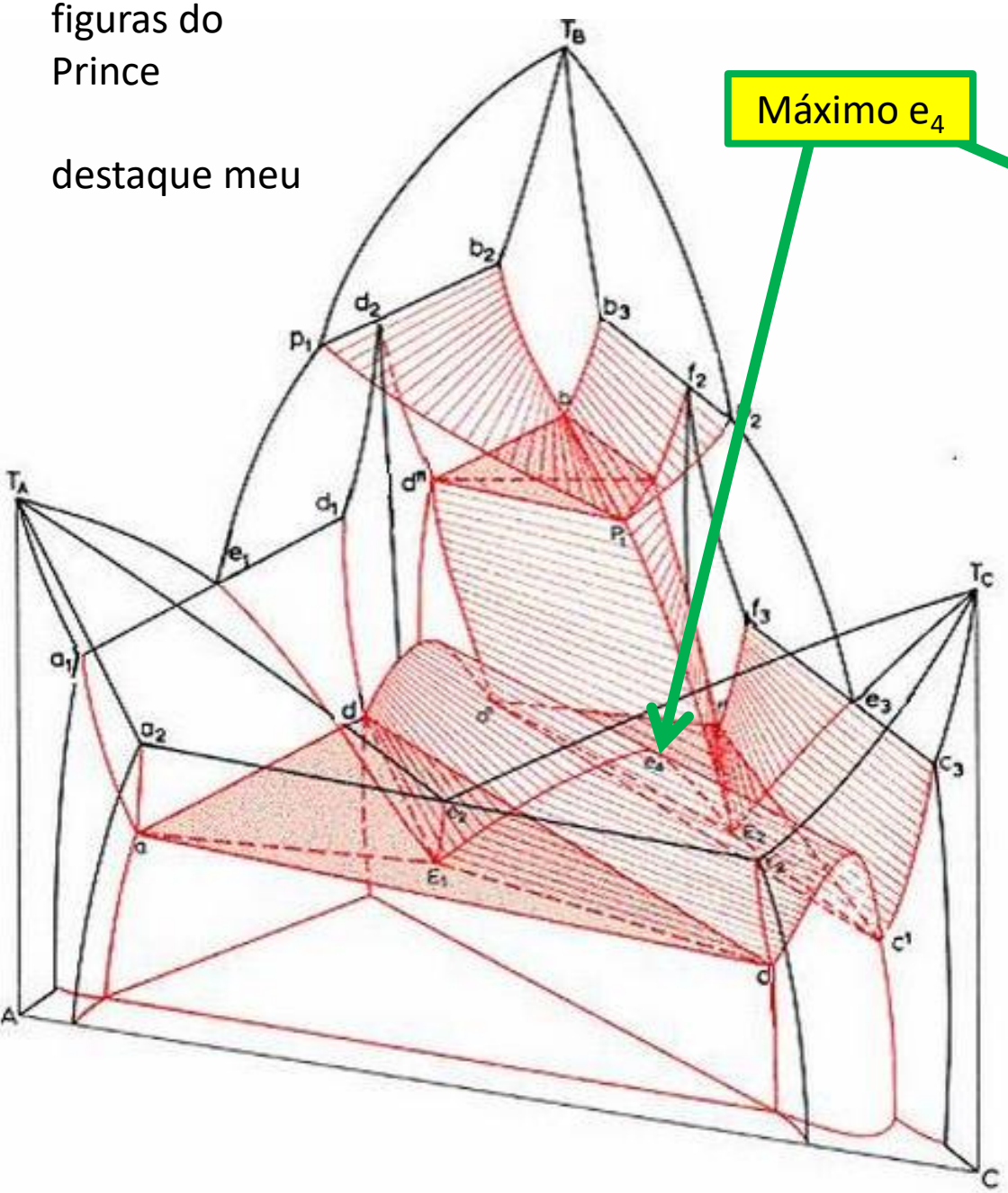


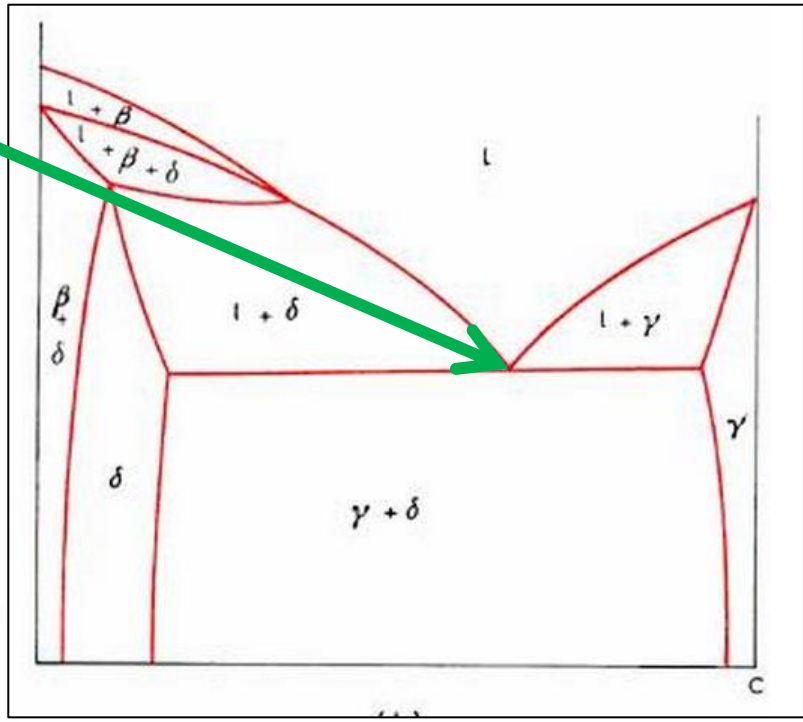
Figura 210 do Prince – Corresponde ao caso da Figura 209c

figuras do Prince

destaque meu

Máximo e_4





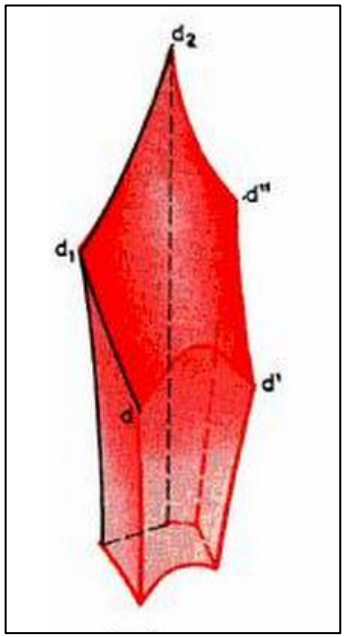


Fig. 211. Ternary space model corresponding to Fig. 210 (simplified).

Por exemplo, se fizermos uma liga com composição que pertença a este quase-binário entre os pontos 2 e 3, irão se formar simplesmente gama + delta (ou só gama), como se fosse um binário. Se a composição estiver entre 1 e 2, a solidificação seguirá caminhos estranhos (formando-se beta, que depois desaparecerá) mas também chegará em gama + delta (ou só delta)

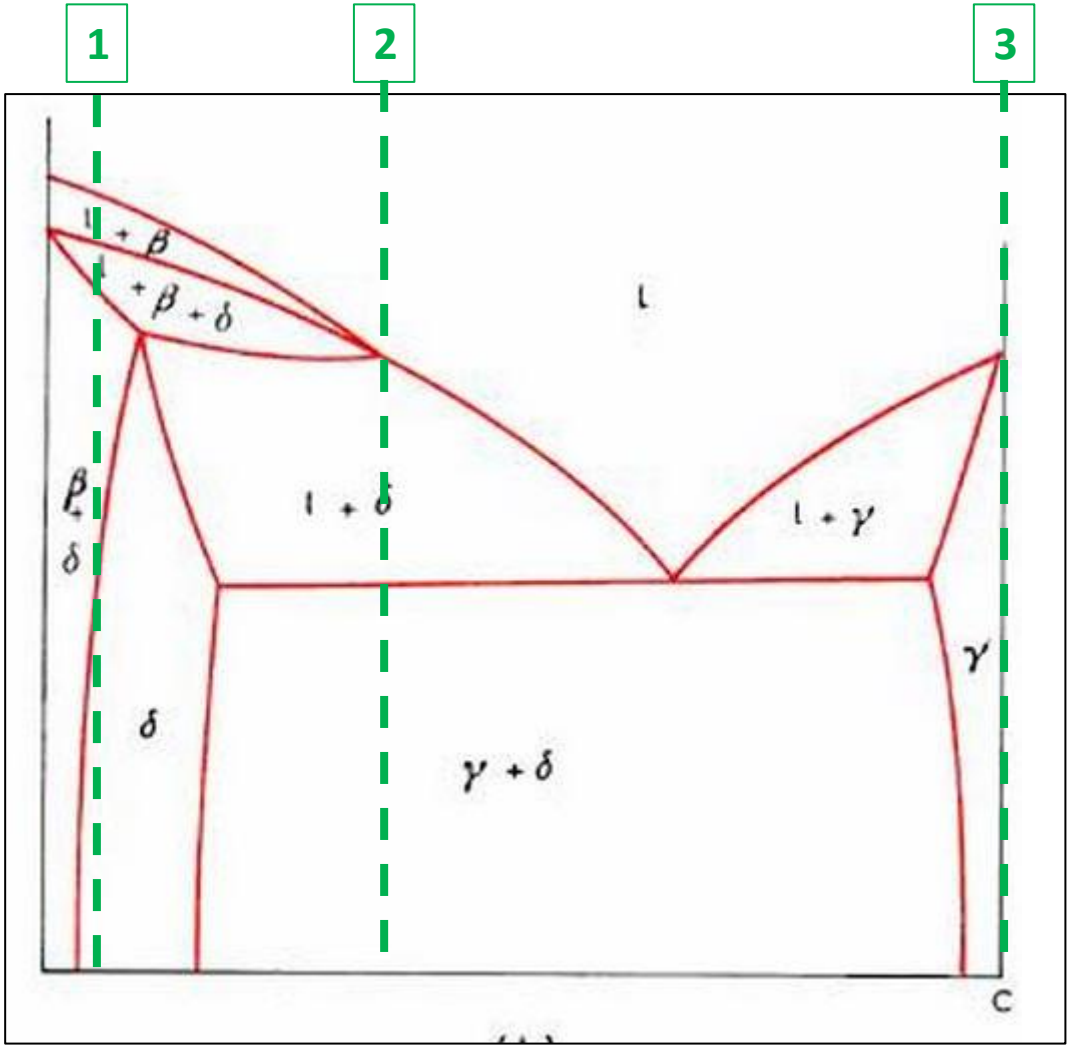


figura do Prince

acréscimo meu

Pode ser muito difícil acompanhar uma solidificação no desenho tridimensional. Talvez o mais simples seja desenhar a evolução dos triângulos ao longo das temperaturas (supondo campos de solubilidade nula para as fases sólidas)

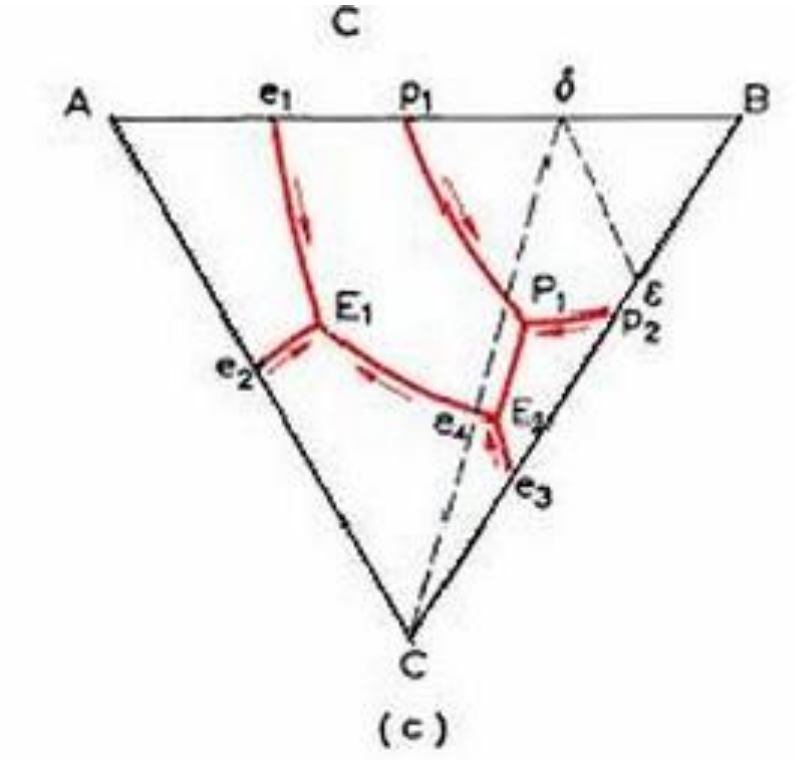


figura do Prince

Por exemplo, um pouco abaixo da temperatura do peritético p_1, teríamos:

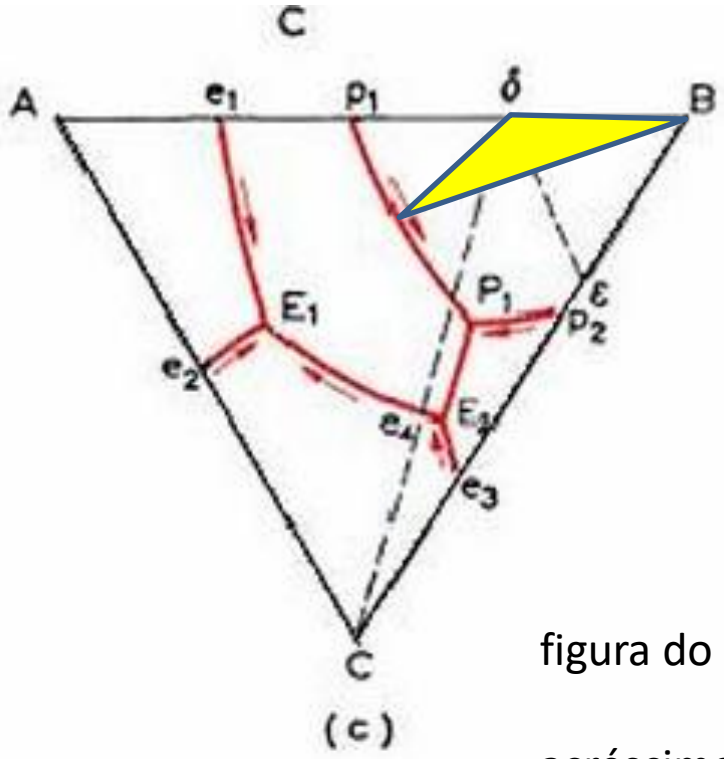


figura do Prince

acréscimo meu

figura do Prince

acréscimos meus

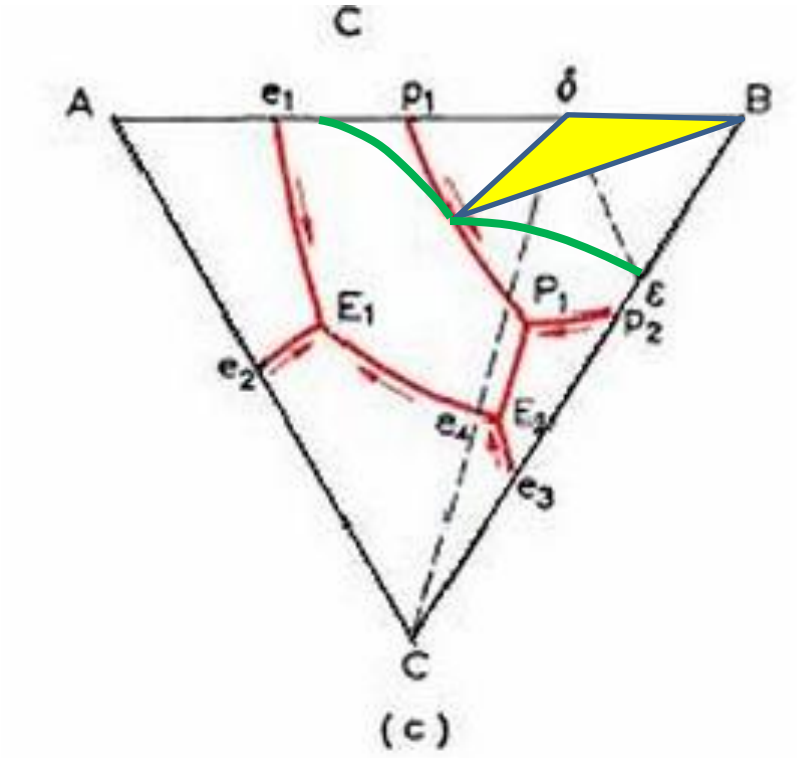
E o campo do líquido?

Precisamos da superfície liquidus.

Não temos?

Então chutemos...

Por exemplo, um pouco abaixo da temperatura do peritético p_1, teríamos:



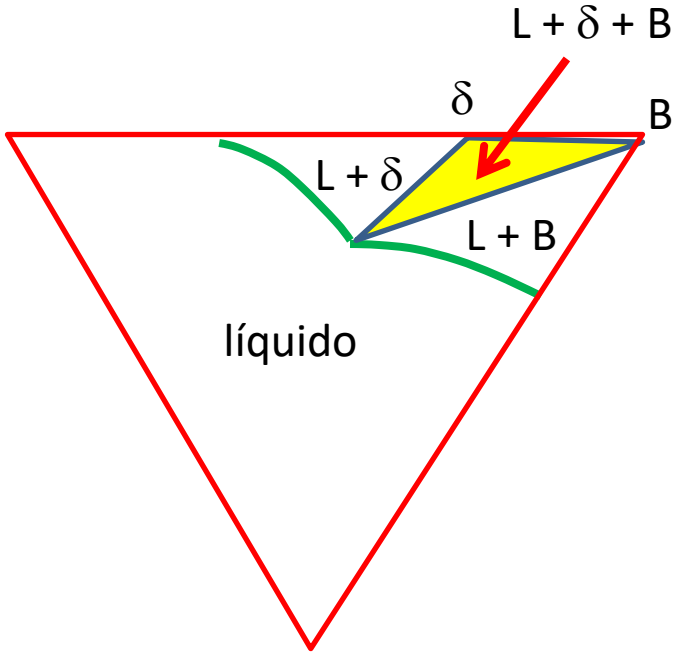
E o campo do líquido?

Precisamos da superfície liquidus.

Não temos?

Então chutemos...

Por exemplo, um pouco abaixo da temperatura do peritético p_1, teríamos:



FASES INTERMEDIÁRIAS INCONGRUENTES

Caso B - FASES TERNÁRIAS

If only one ternary intermediate phase is formed and all three binaries are eutectic, there are four cases to be distinguished. These can be classified according to whether one, two, three, or none of the sections from the ternary phase to the components are quasi-binary sections. The first case only will be considered. The space model and its projection are given in Fig. 213a–b. There are three invariant four-phase planes, corresponding to the equilibria:

$$\begin{array}{ll} P_1 & l_{P_1} + \beta_b \rightleftharpoons \alpha_a + T_t \\ P_2 & l_{P_2} + \beta_{b'} \rightleftharpoons \gamma_{c'} + T_{t'} \\ E & l_E \rightleftharpoons \alpha_{a''} + \gamma_{c''} + T_{t''} \end{array}$$

where T is a solid solution based on the ternary intermediate phase T. A quasi-binary section is assumed between T and β. This section is a peritectic type involving the reaction of liquid with β to form T:

$$l_1 + \beta_3 \rightleftharpoons T_2 .$$

texto do Prince

figura do Prince

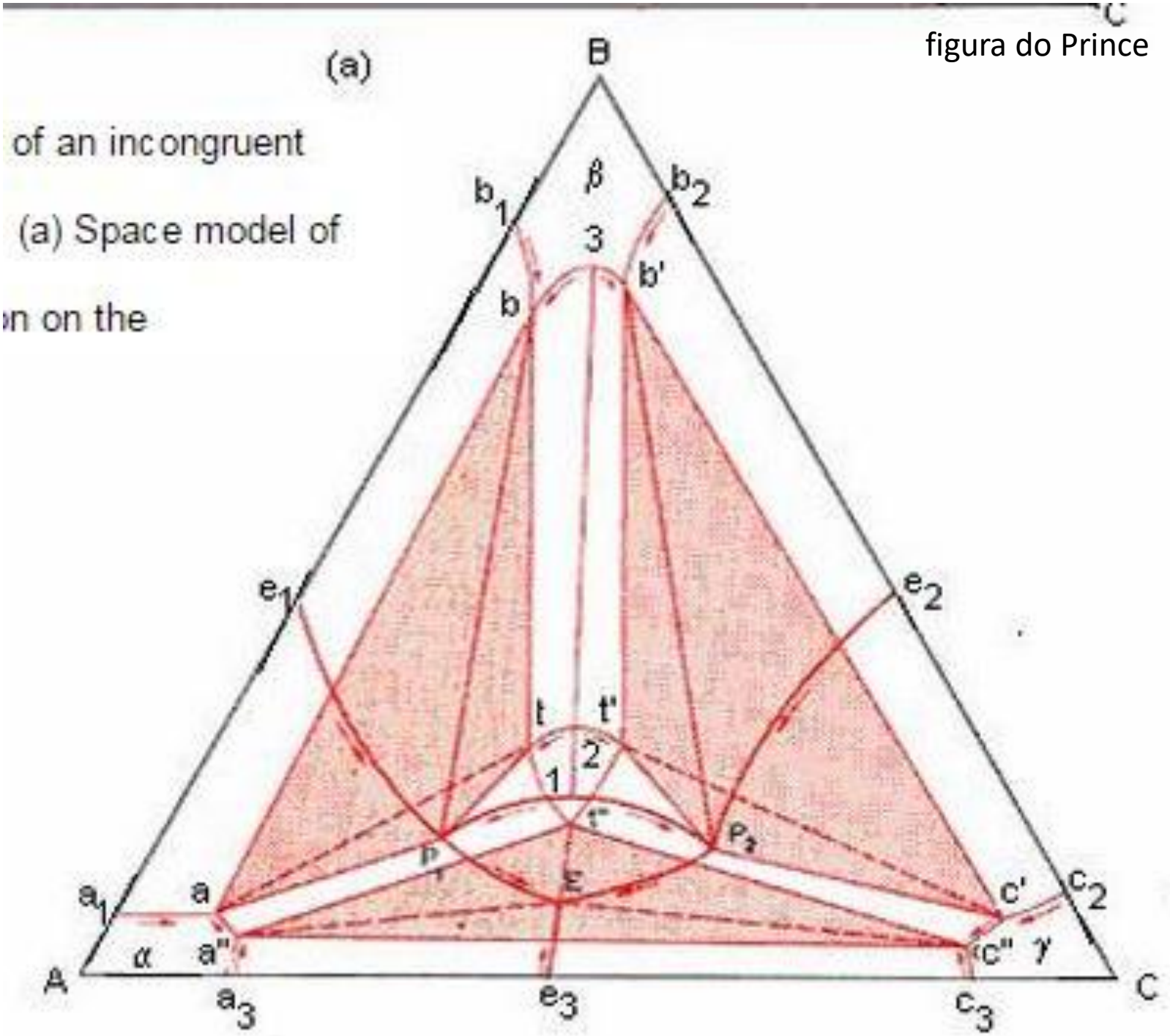


figura do Prince

destaques meus

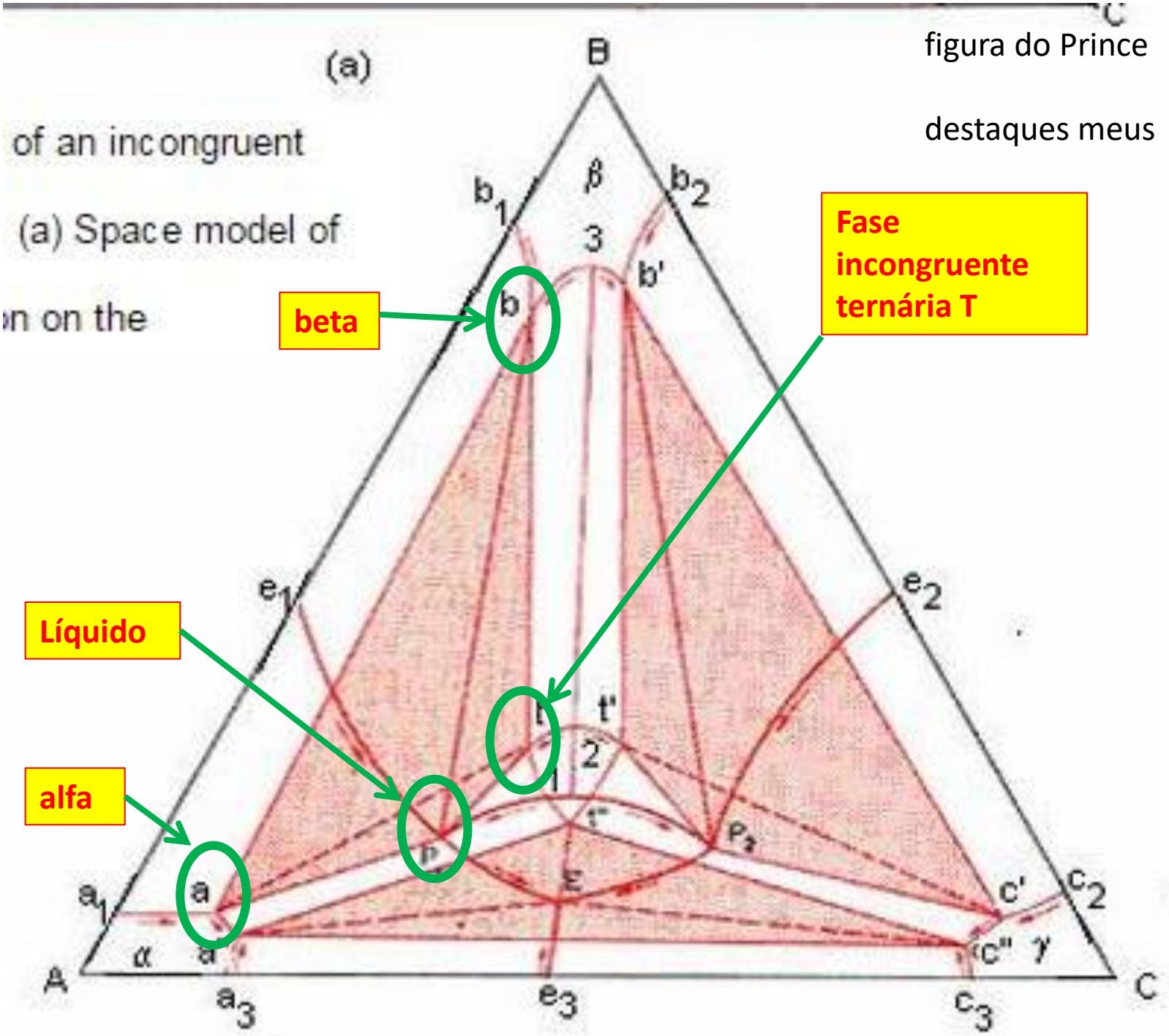


figura do Prince

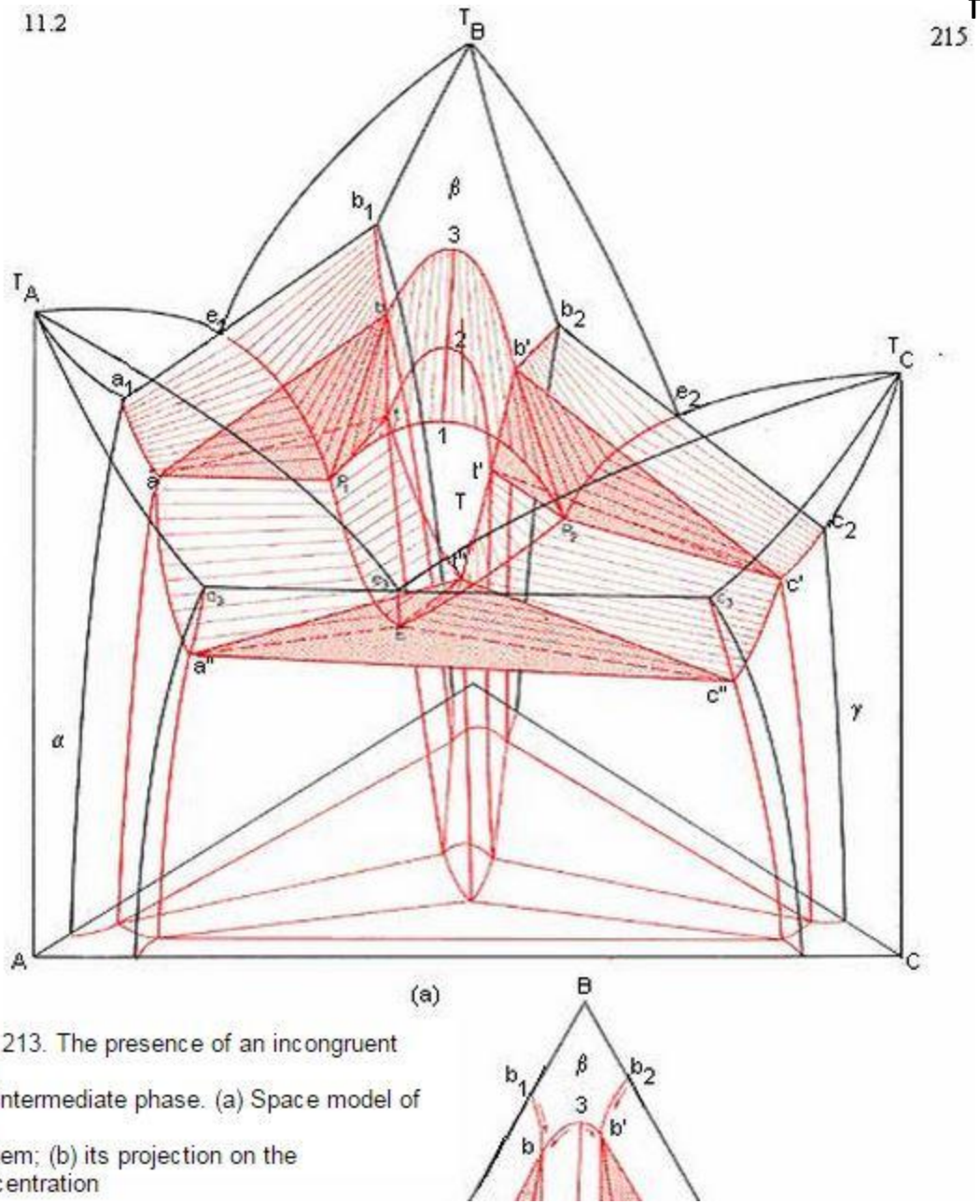


Fig. 213. The presence of an incongruent ter-
nar intermediate phase. (a) Space model of the
system; (b) its projection on the concentration

figura do Prince

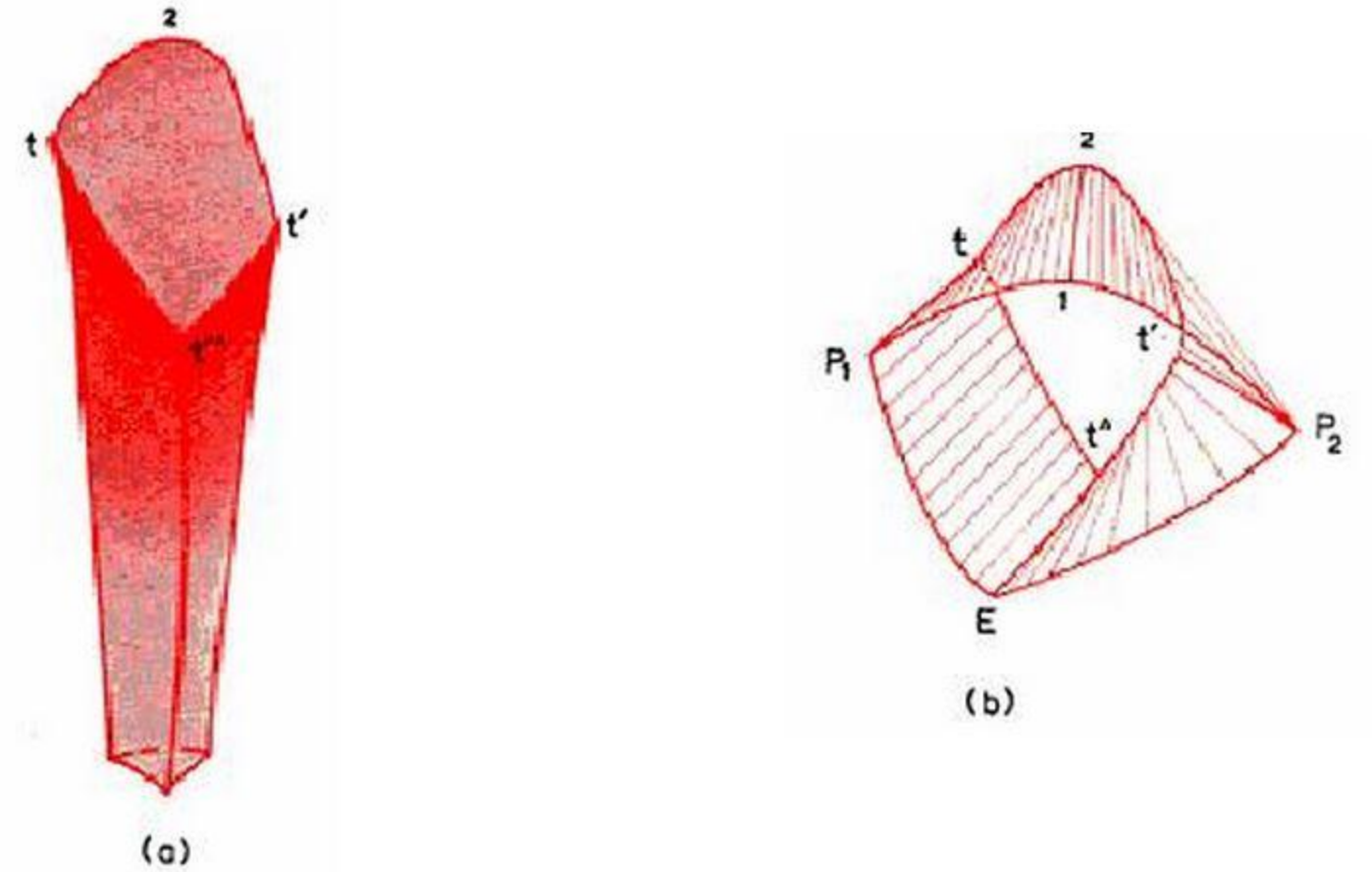


Fig. 214. Phase regions in the ternary system of Fig. 213a. (a) The T phase region; (b) the $l+T$ phase region.

figura do Prince

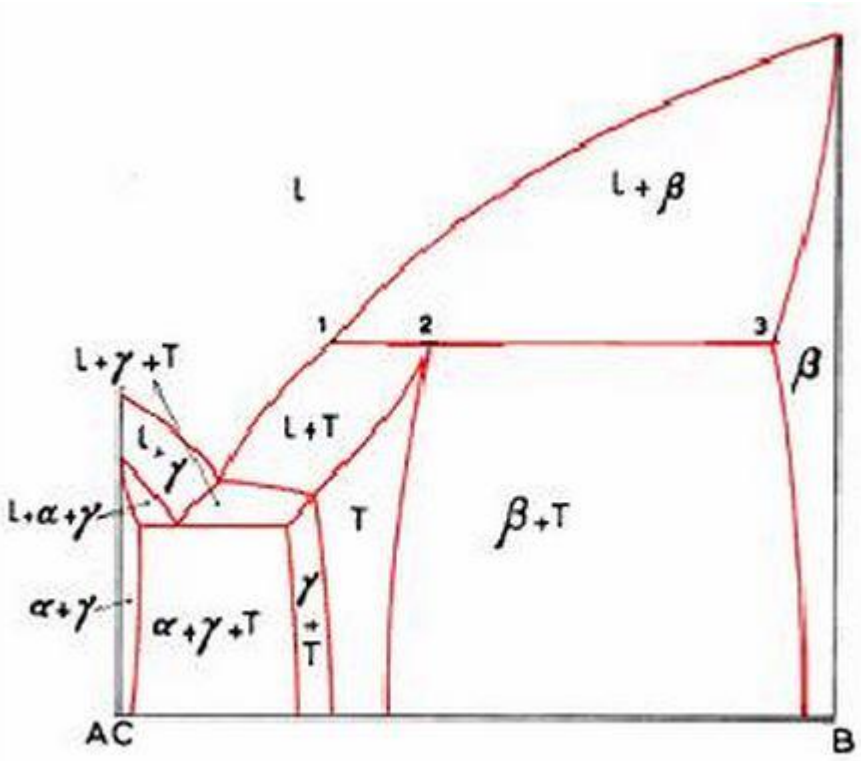
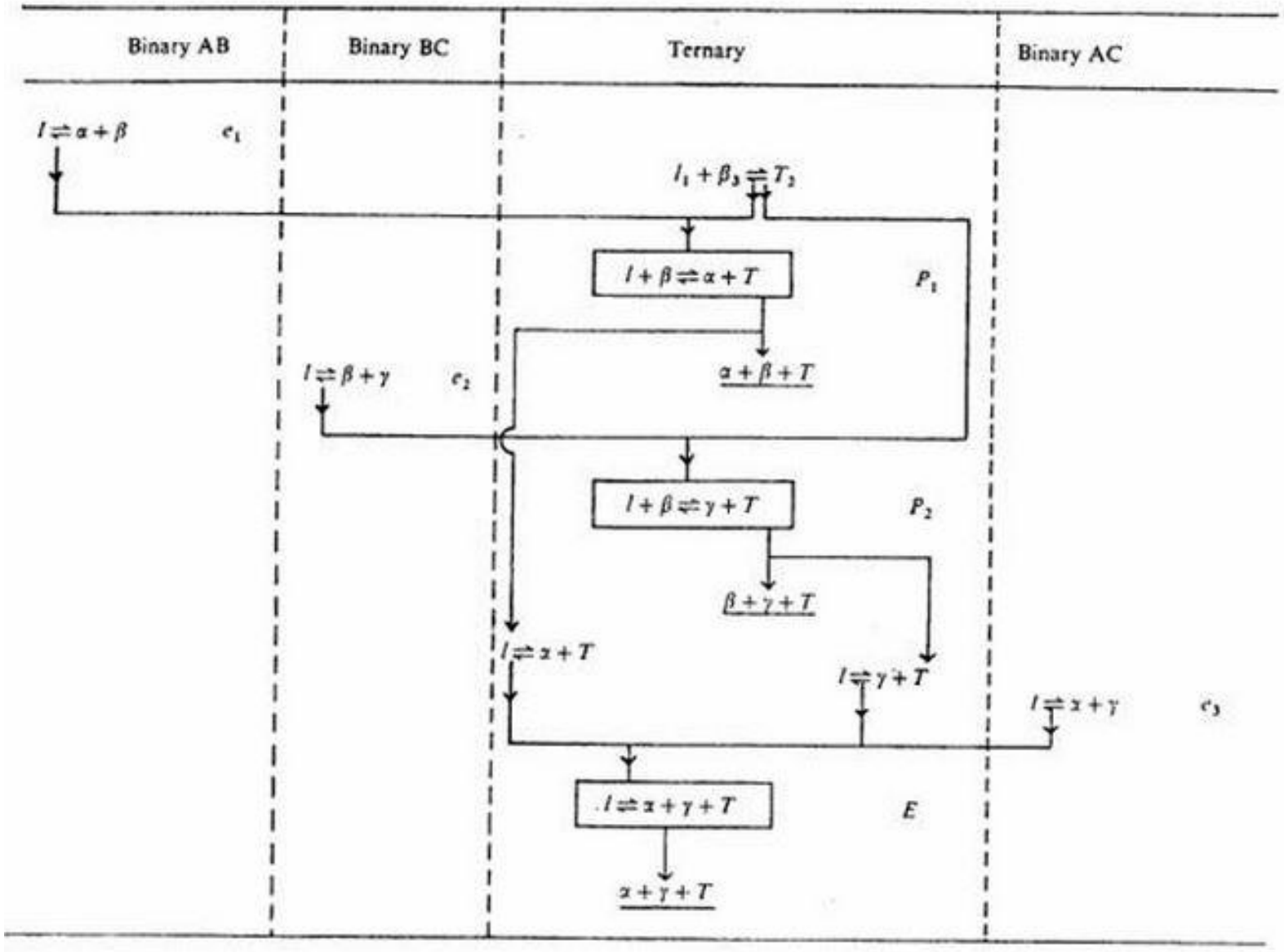


Fig. 215. The vertical section along tie line 1–2–3 of Fig. 213a.

figura do Prince

TABLE 9



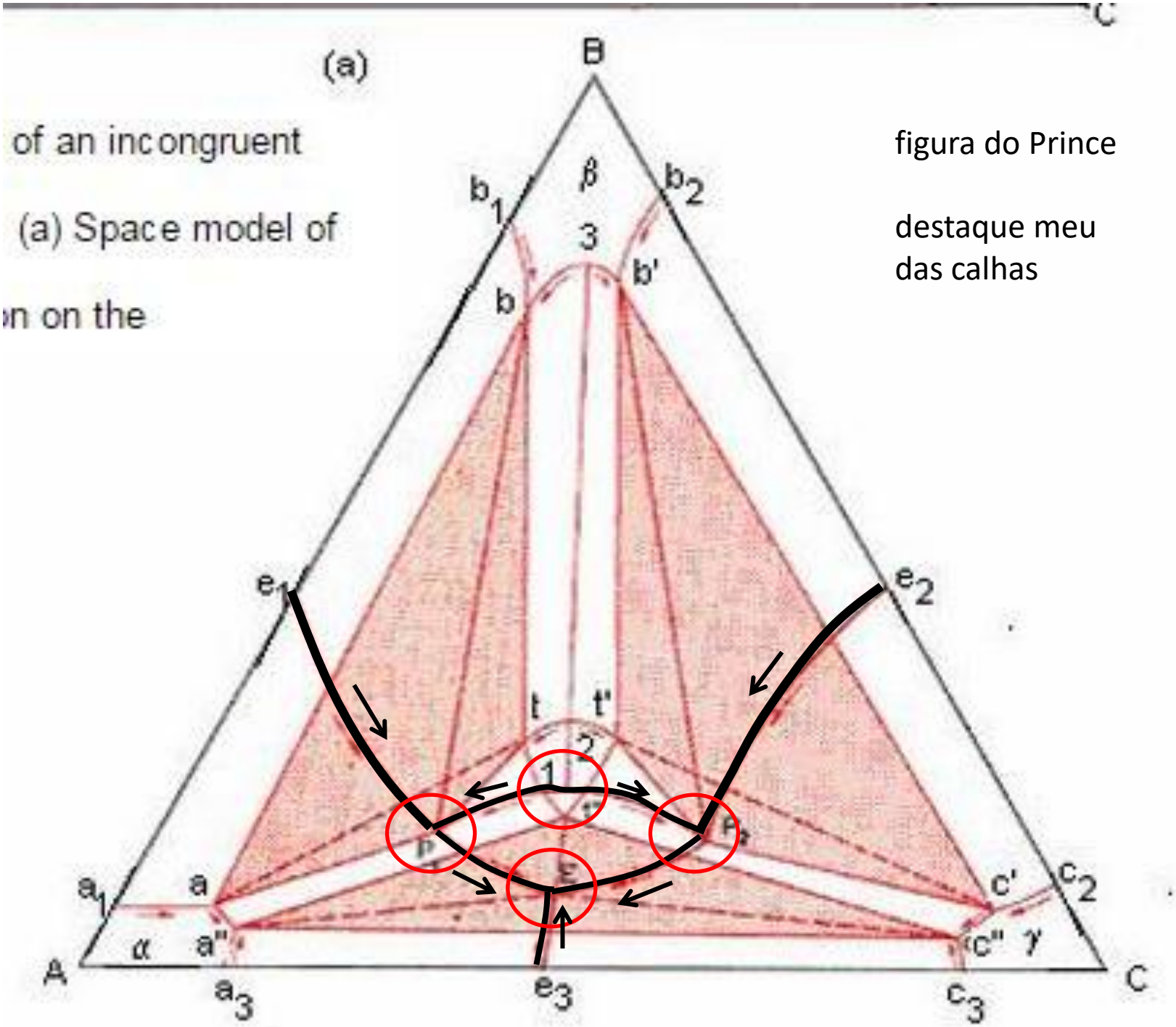


figura do Prince

destaque meu das calhas