2019 Spring

"Phase Equilibria *in* Materials"

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“Ternary Phase diagram”

“ Two phase equilibrium (*f* = 2)”

1) Two-phase equilibrium between the liquid and a solid solution

2) Ternary two-phase equilibrium with a saddle point

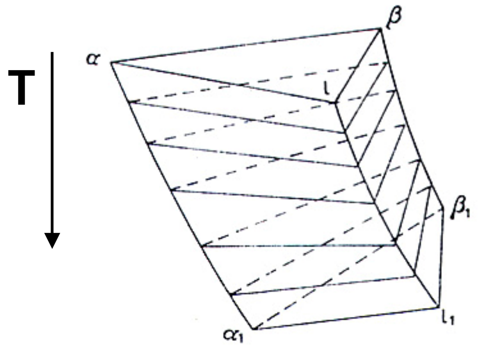
3) Two-phase equilibrium between solid or liquid solutions: $\alpha_1 \rightleftarrows \alpha_2$ or $l_1 \rightleftarrows l_2$

* Tie lines are not parallel to the binary tie line. Miscibility gap

- Addition of C to a heterogeneous mixture of A & B in a ratio corresponding to the distribution of C

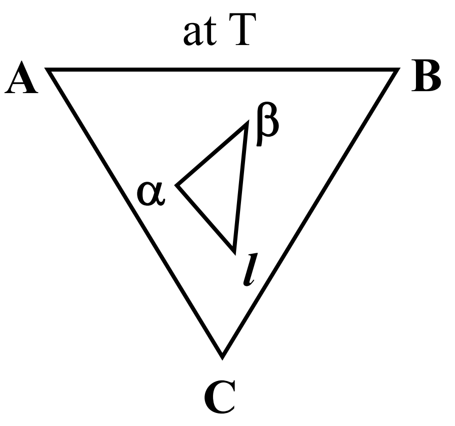
“ Three phase equilibrium (*f* =1)”

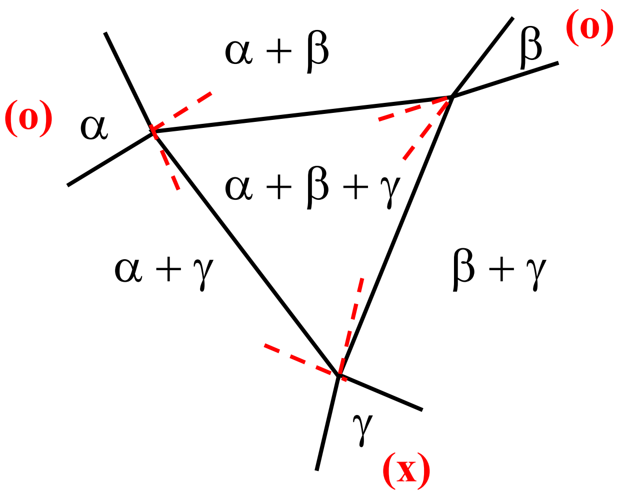
- Tie triangle



vertex of tie triangle

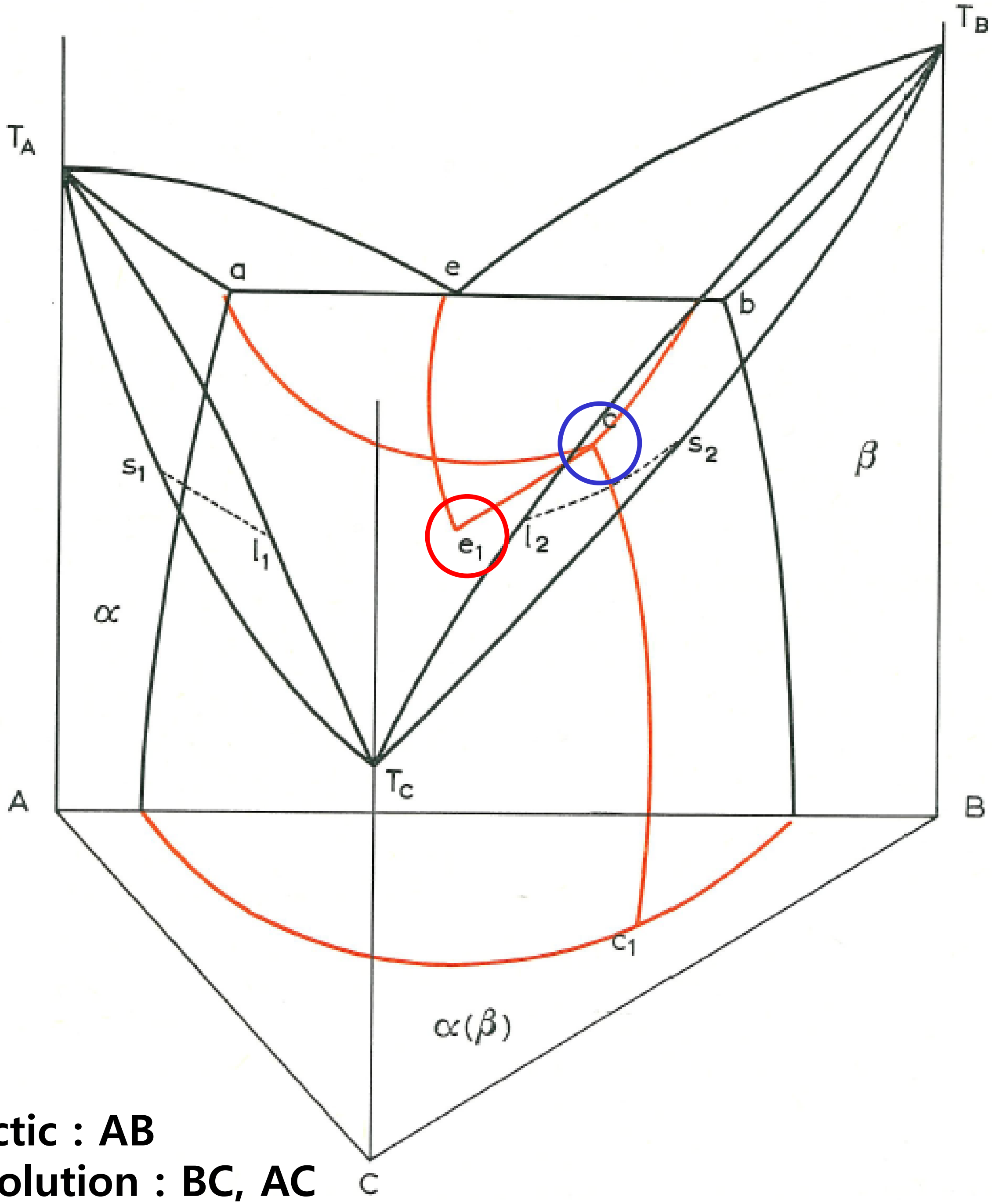
→ composition of three phases





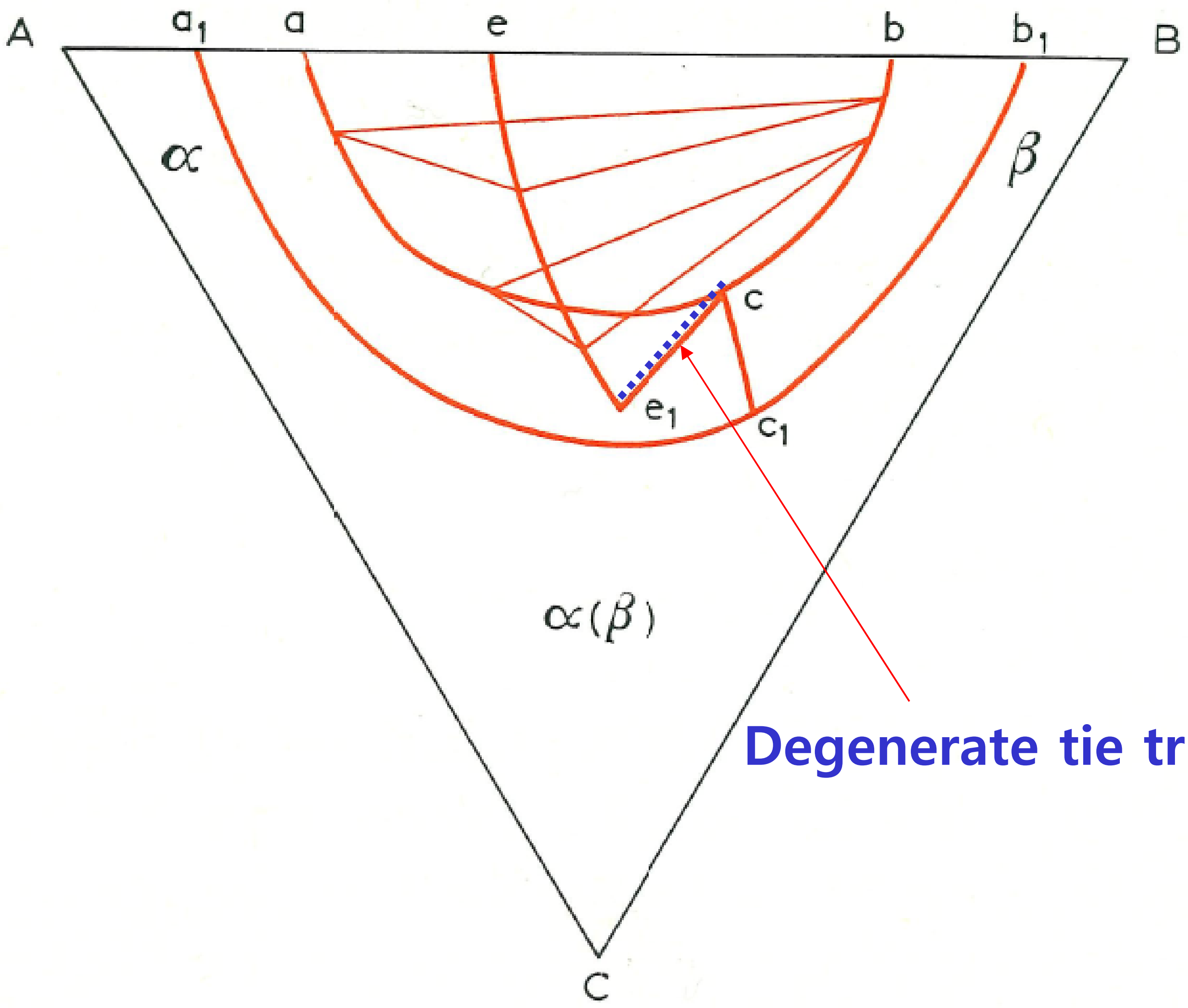
① Coalescence of miscibility gap and two phase region

② Coalescence of two two-phase region



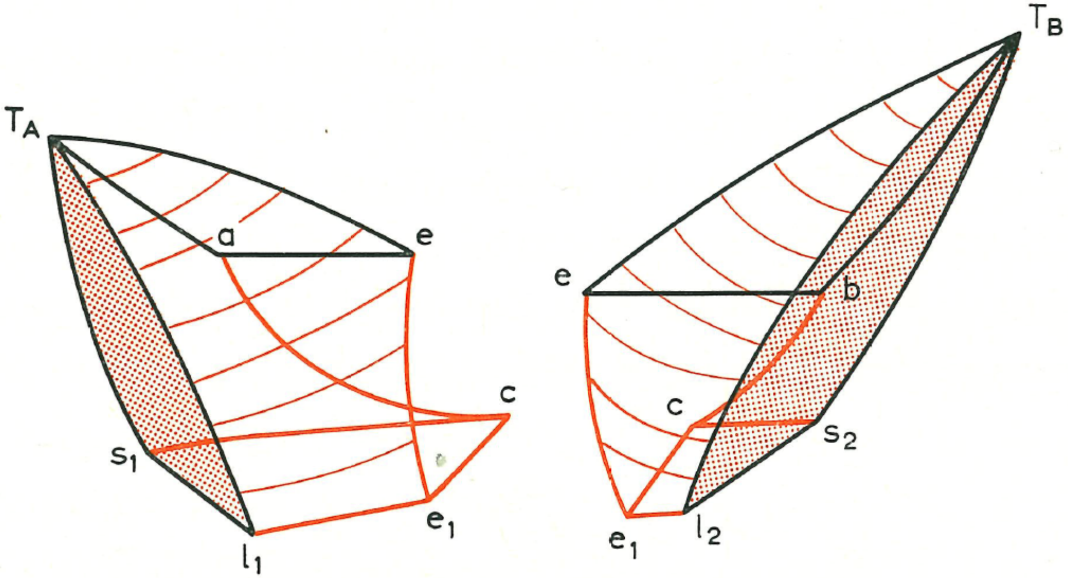
- **One binary eutectic : AB**
  Complete solid solution : BC, AC

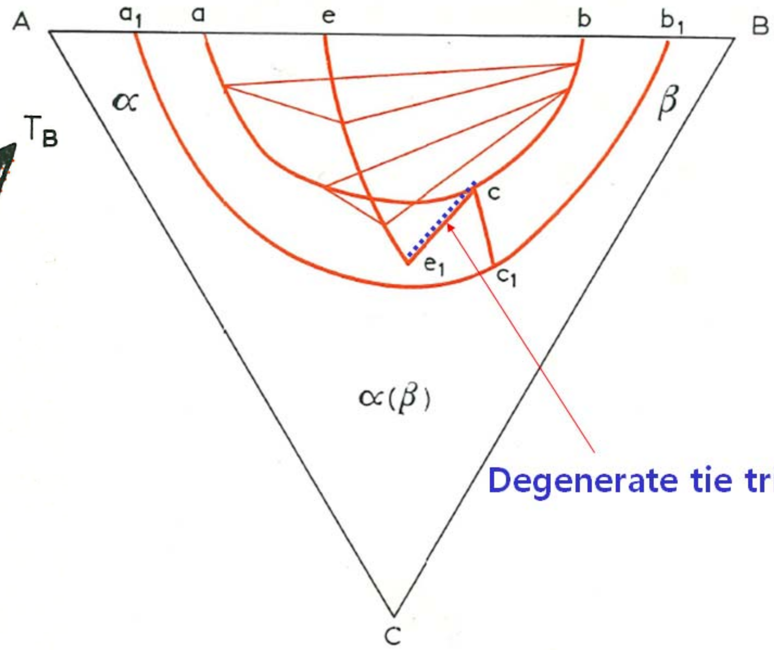
- **Projection on concentration triangle ABC**



Degenerate tie triangle

The three-phase regions





Degenerate tie triangle

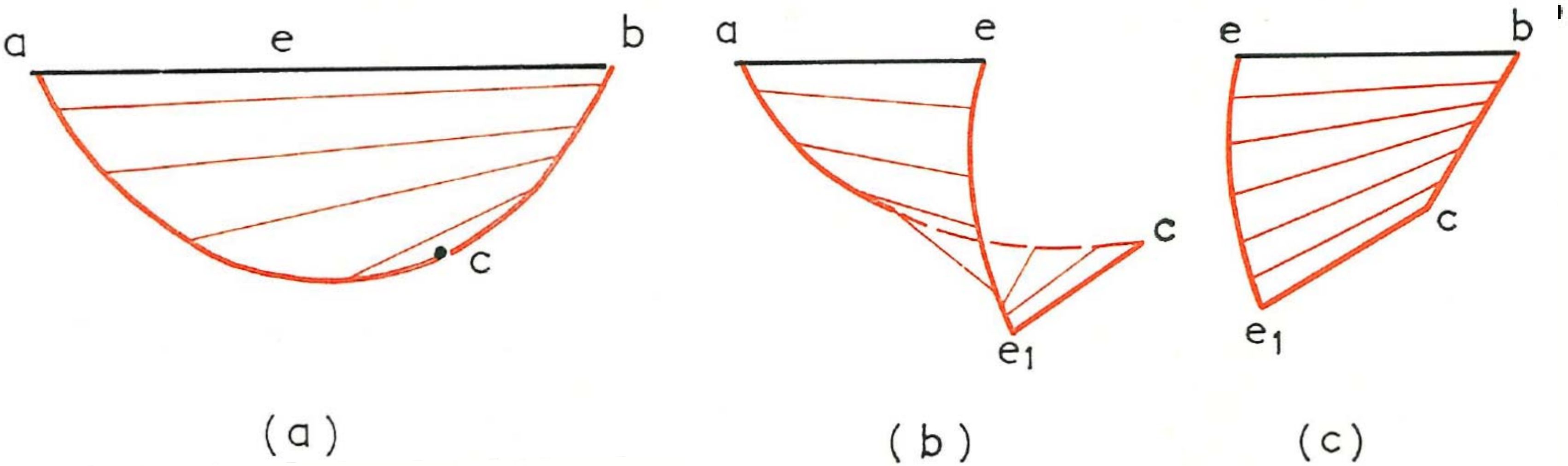


Fig. 147. The ruled surfaces bounding the three-phase ($l+\alpha+\beta$) region in Fig. 142. (a) The $\alpha\beta$ ruled surface; (b) the $l\alpha$ ruled surface; (c) the $l\beta$ ruled surface.

- **How is the reaction in three phase region among liquid, α and β?**

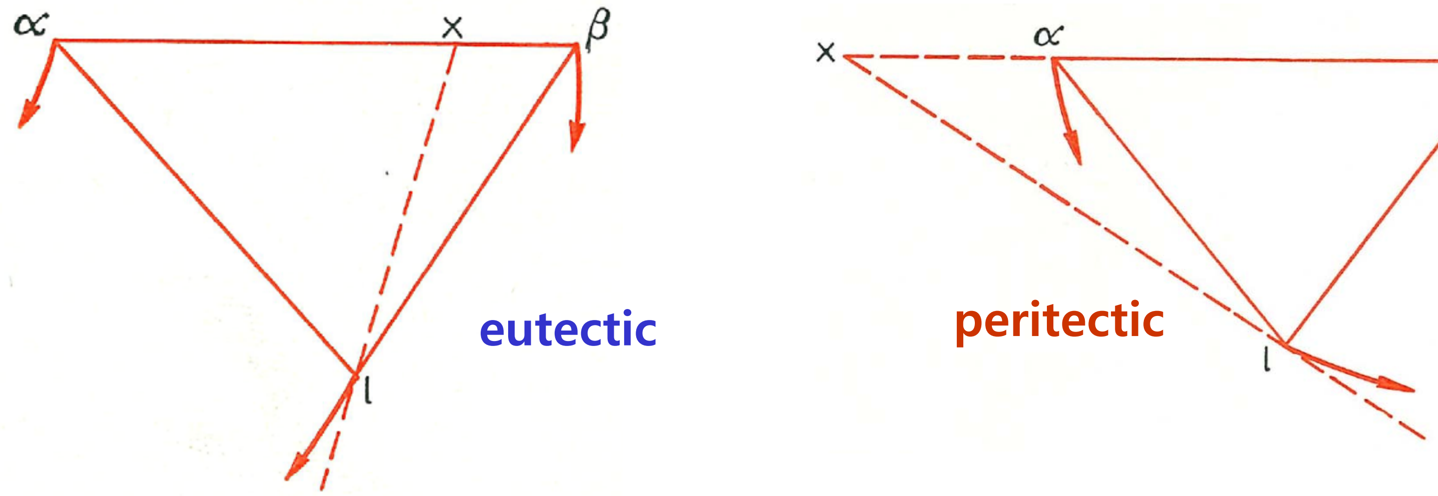


Fig. 149. Criteria for distinguishing eutectic and peritectic reactions in ternary three-phase equilibrium.

The tangent to the liquid curve at a particular temperature is extrapolated to meet the tie line connecting the α and β phases.

1) If the extrapolated line intersected the αβ tie line, the equilibrium was considered to be eutectic

2) If it met the αβ tie line only when the latter was extrapolated, the equilibrium was considered to be peritectic.

Similarly, a eutectoid reaction could be distinguished from a peritectoid and a monotectic from a syntectic.

How is the reaction in three phase region among liquid, α and β?

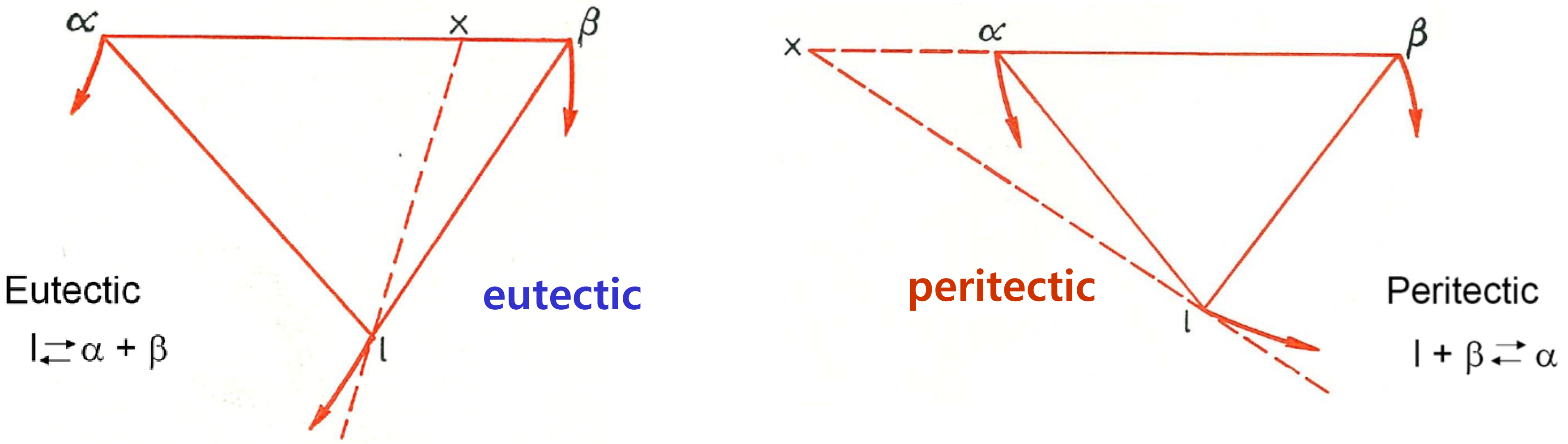


Fig. 149. Criteria for distinguishing eutectic and peritectic reactions in ternary three-phase equilibrium.

The tangent to the liquid curve at a particular temperature is extrapolated to meet the tie line connecting the α and β phases.

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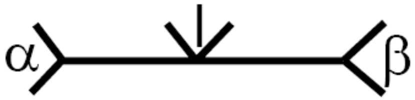
Similarly, a eutectoid reaction could be distinguished from a peritectoid and a monotectic from a syntectic.

Review of Invariant Binary Reactions

Eutectic Type

Eutectic

$l \rightleftarrows \alpha + \beta$



Al-Si, Fe-C

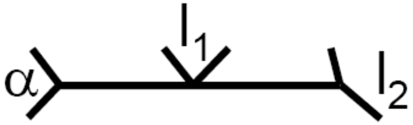
Eutectoid

$\gamma \rightleftarrows \alpha + \beta$

Fe-C

Monotectic

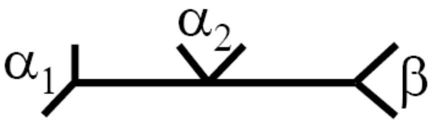
$l_1 \rightleftarrows \alpha + l_2$



Cu-Pb

Monotectoid

$\alpha_2 \rightleftarrows \alpha_1 + \beta$



Al-Zn, Ti-V

On cooling one phase going to two phases

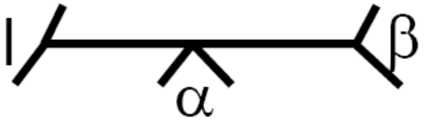
Metatectic reaction: $\beta \leftrightarrow L + \alpha$ **Ex. Co-Os, Co-Re, Co-Ru**

Review of Invariant Binary Reactions

Peritectic Type

Peritectic

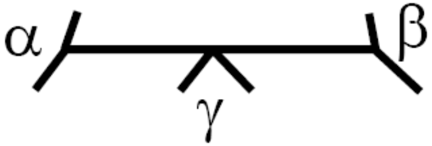
$l + \beta \rightleftarrows \alpha$



Fe-C

Peritectoid

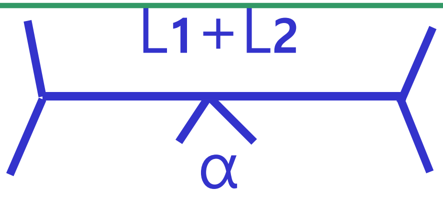
$\alpha + \beta \rightleftarrows \gamma$



Cu-Al

Syntectic reaction

$Liquid_1 + Liquid_2 \leftrightarrow \alpha$

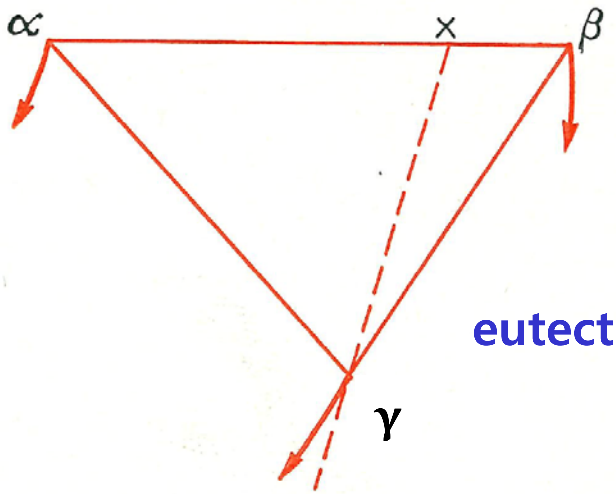


K-Zn, Na-Zn,
K-Pb, Pb-U, Ca-Cd

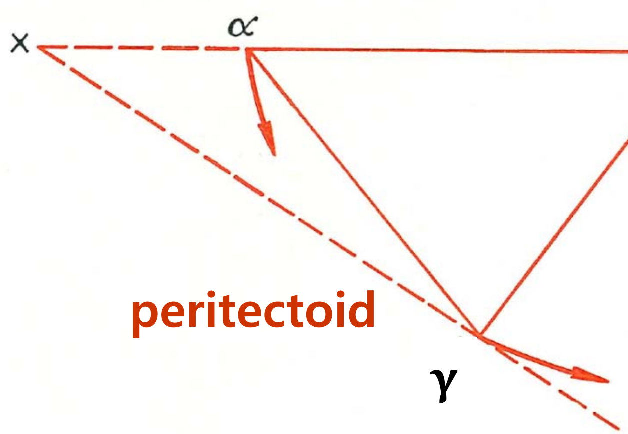
On cooling two phases going to one phase

- **How is the reaction in three phase region among liquid, α and β?**

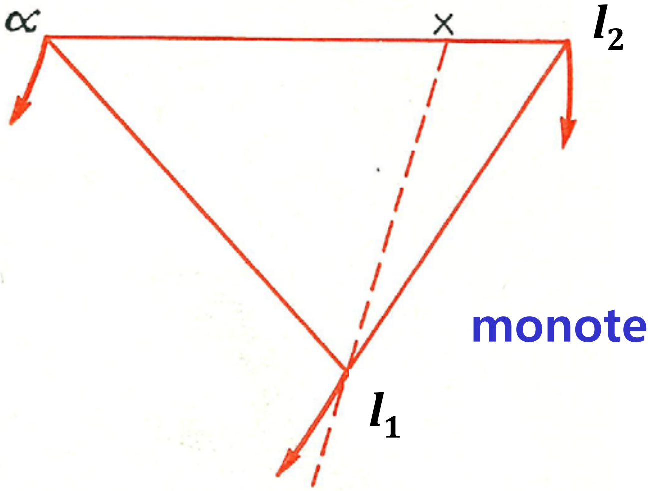
Similarly, a eutectoid reaction could be distinguished from a peritectoid and a monotectic from a syntectic.



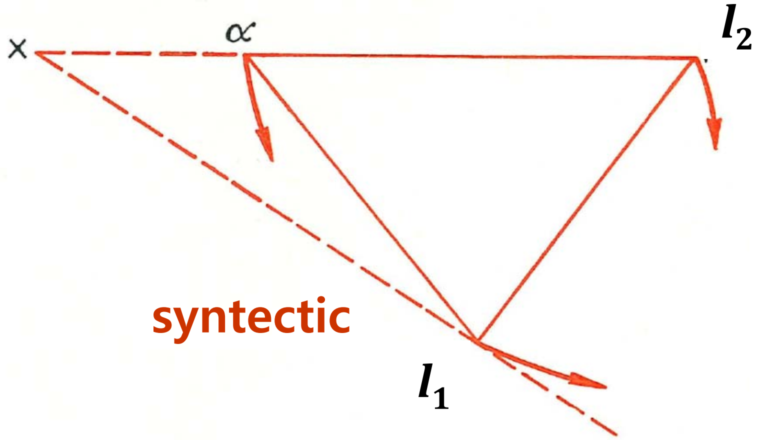
eutectoid



peritectoid



monotectic



syntectic

9.3. THREE-PHASE EQUILIBRIUM INVOLVING EUTECTIC REACTIONS

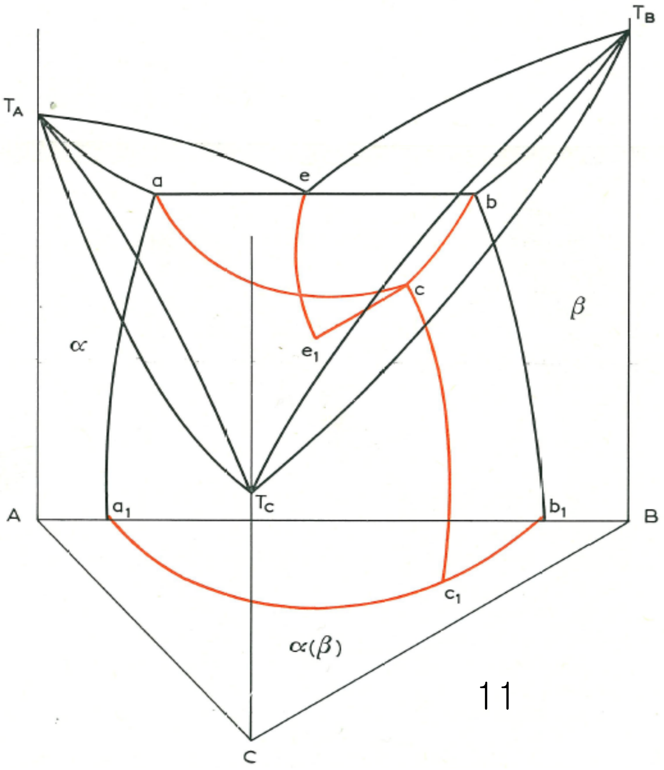
- **How is the reaction in three phase region?**

<Hillert's criterion>

Basically, the reaction we can expect is eutectic reaction

(*l*→ α + β). But, in reality, we can have eutectic and peritectic reaction depending on the relative amount of three phase.

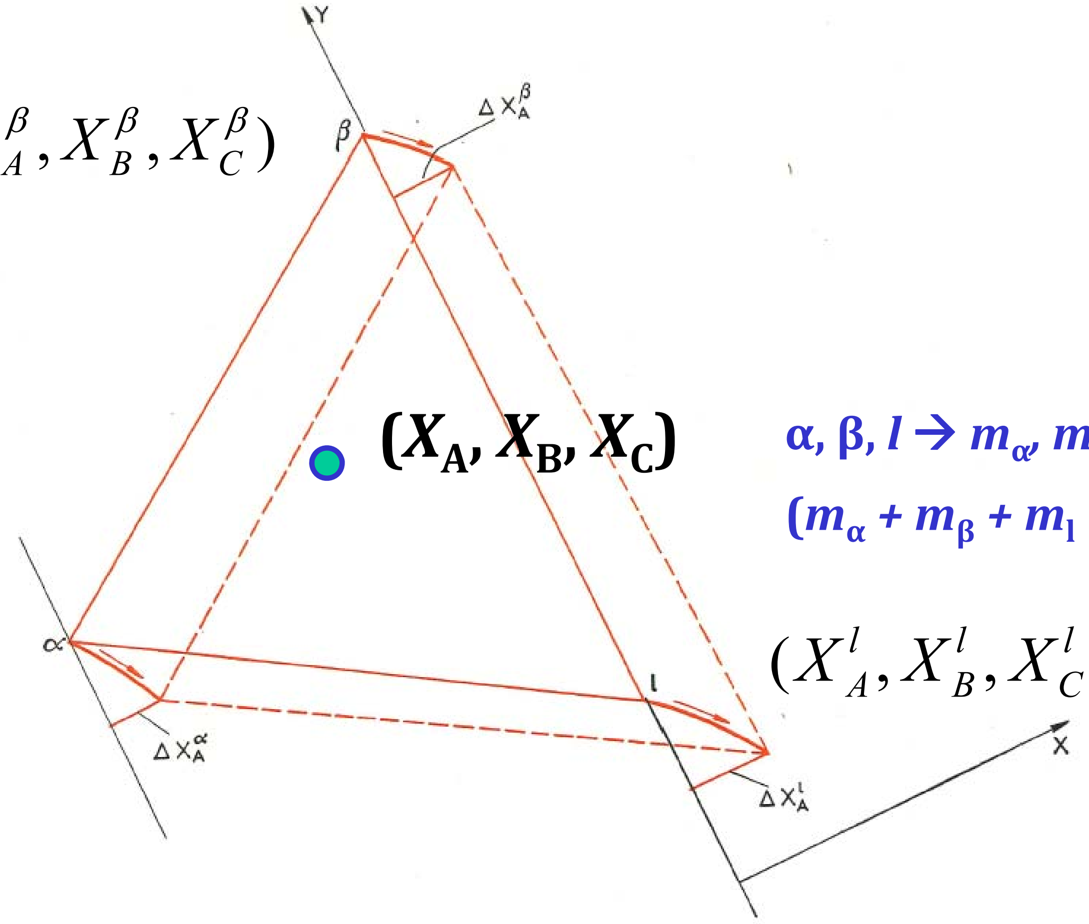
The average composition of the alloy then determines for a particular temperature whether the reaction will be eutectic or peritectic.



X_A, X_B, X_C → alloy with in a three-phase triangle

α, β , l → m_α, m_β, m_l ($m_\alpha + m_\beta + m_l = 100$)

$$X_A = \frac{m_\alpha \cdot X_A^\alpha + m_\beta \cdot X_A^\beta + m_l \cdot X_A^l}{m_\alpha + m_\beta + m_l} \quad X_B = \frac{m_\alpha \cdot X_B^\alpha + m_\beta \cdot X_B^\beta + m_l \cdot X_B^l}{m_\alpha + m_\beta + m_l} \quad X_A + X_B + X_C = 100$$



$(X_A^\beta, X_B^\beta, X_C^\beta)$

(X_A, X_B, X_C)

$(X_A^\alpha, X_B^\alpha, X_C^\alpha)$

(X_A^l, X_B^l, X_C^l)

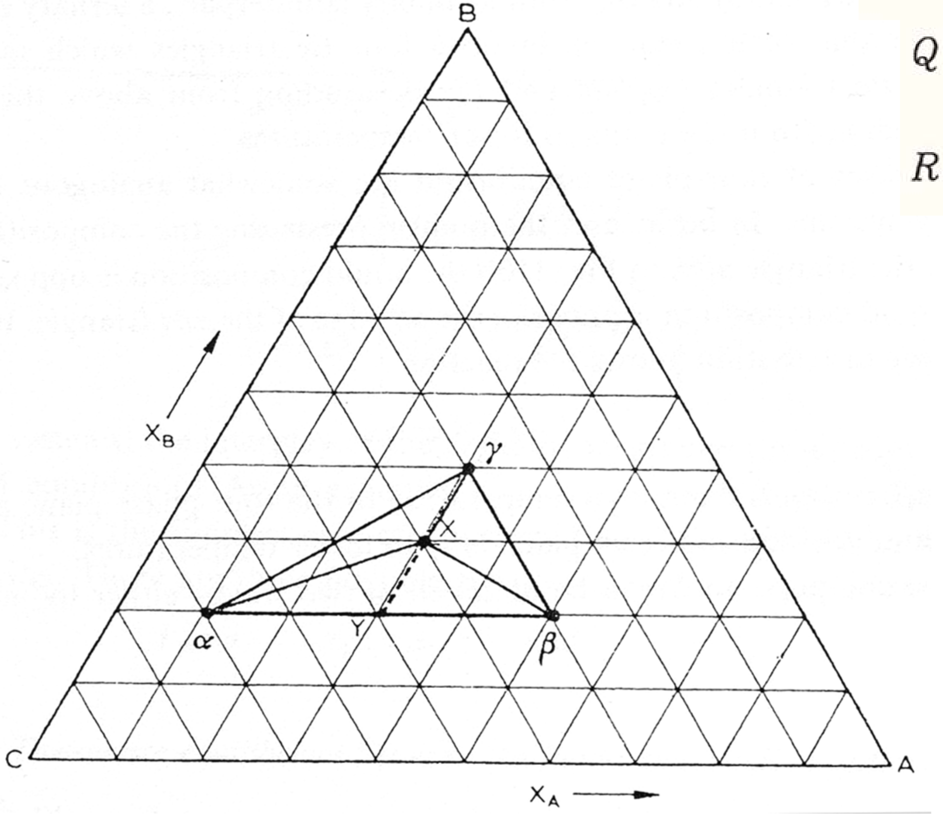
α, β, l → m_α, m_β, m_l

($m_\alpha + m_\beta + m_l = 100$)

Fig. 150. Illustration of Hillert's criterion for distinguishing eutectic and peritectic reaction in ternary three-phase equilibrium; ————, equilibrium at T; – – – – – –, equilibrium at $T-\mathrm{d}T$.

8.3 TIE LINES AND TIE TRIANGLES

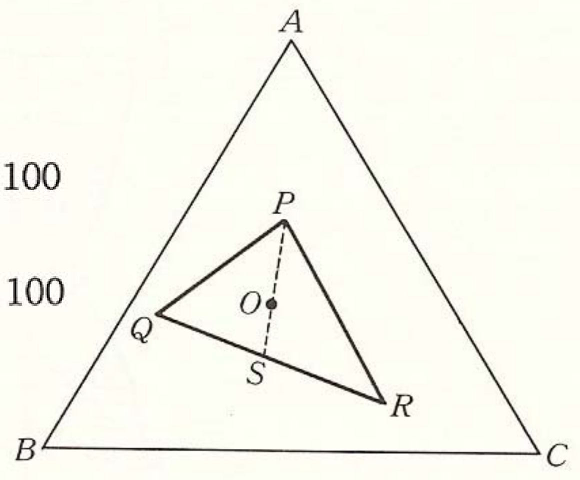
P=3 Tie triangle : 3 phase equil.



$$P\,\% = \frac{OS}{PS} \times 100$$

$$Q\,\% = \frac{RS}{QR}\,\frac{PO}{PS} \times 100$$

$$R\,\% = \frac{QS}{QR}\,\frac{PO}{PS} \times 100$$



α : A(10%), B(20%), C(70%)
β : A(50%), B(20%), C(30%)
γ : A(30%), B(40%), C(30%)

$m_\alpha : m_\beta : m_\gamma$ = 1: 1: 2

Comp. of X ;

A : 0.25 x 10%+0.25 x 50%+0.5 x 30%

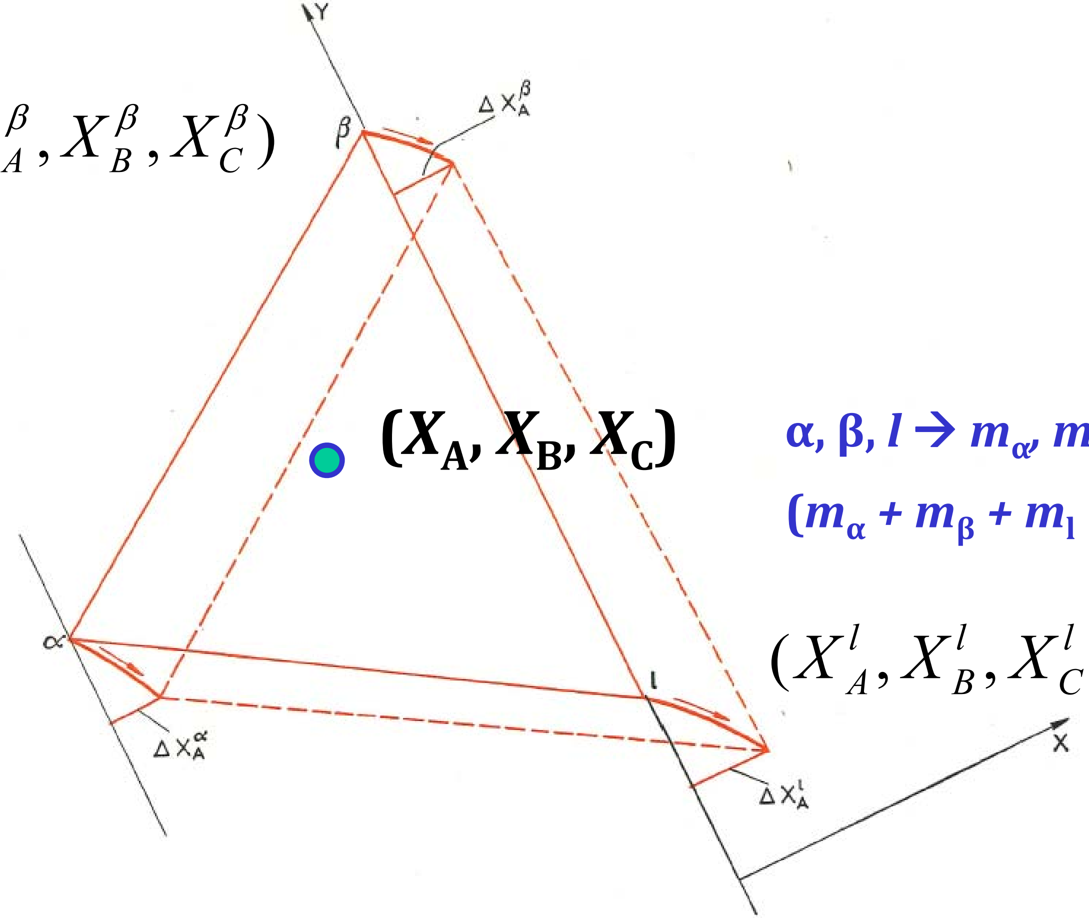
B : 0.25 x 20%+0.25 x 20%+0.5 x 40%

C : 0.25 x 70%+0.25 x 30%+0.5 x 30%

X_A, X_B, X_C → alloy with in a three-phase triangle

α, β , l → m_α, m_β, m_l ($m_\alpha + m_\beta + m_l = 100$)

$$X_A = \frac{m_\alpha \cdot X_A^\alpha + m_\beta \cdot X_A^\beta + m_l \cdot X_A^l}{m_\alpha + m_\beta + m_l} \quad X_B = \frac{m_\alpha \cdot X_B^\alpha + m_\beta \cdot X_B^\beta + m_l \cdot X_B^l}{m_\alpha + m_\beta + m_l} \quad X_A + X_B + X_C = 100$$



$(X_A^\beta, X_B^\beta, X_C^\beta)$

$(X_A^\alpha, X_B^\alpha, X_C^\alpha)$

(X_A, X_B, X_C)

(X_A^l, X_B^l, X_C^l)

α, β, l → m_α, m_β, m_l

($m_\alpha + m_\beta + m_l = 100$)

Fig. 150. Illustration of Hillert's criterion for distinguishing eutectic and peritectic reaction in ternary three-phase equilibrium; ———, equilibrium at T; – – – – – –, equilibrium at $T-\mathrm{d}T$.

A small change in temperature, d*T*, causes a small change in the composition and amounts of each phase, but not of the alloy itself,

$$X_A, X_B, X_C = \text{constant}, \Delta X_A = 0, \text{ and } \Delta m_\alpha + \Delta m_\beta + \Delta m_l = 0$$

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

1) Assumption, $X_A^\beta = X_A^l > X_A^\alpha$

(New coordinate system)

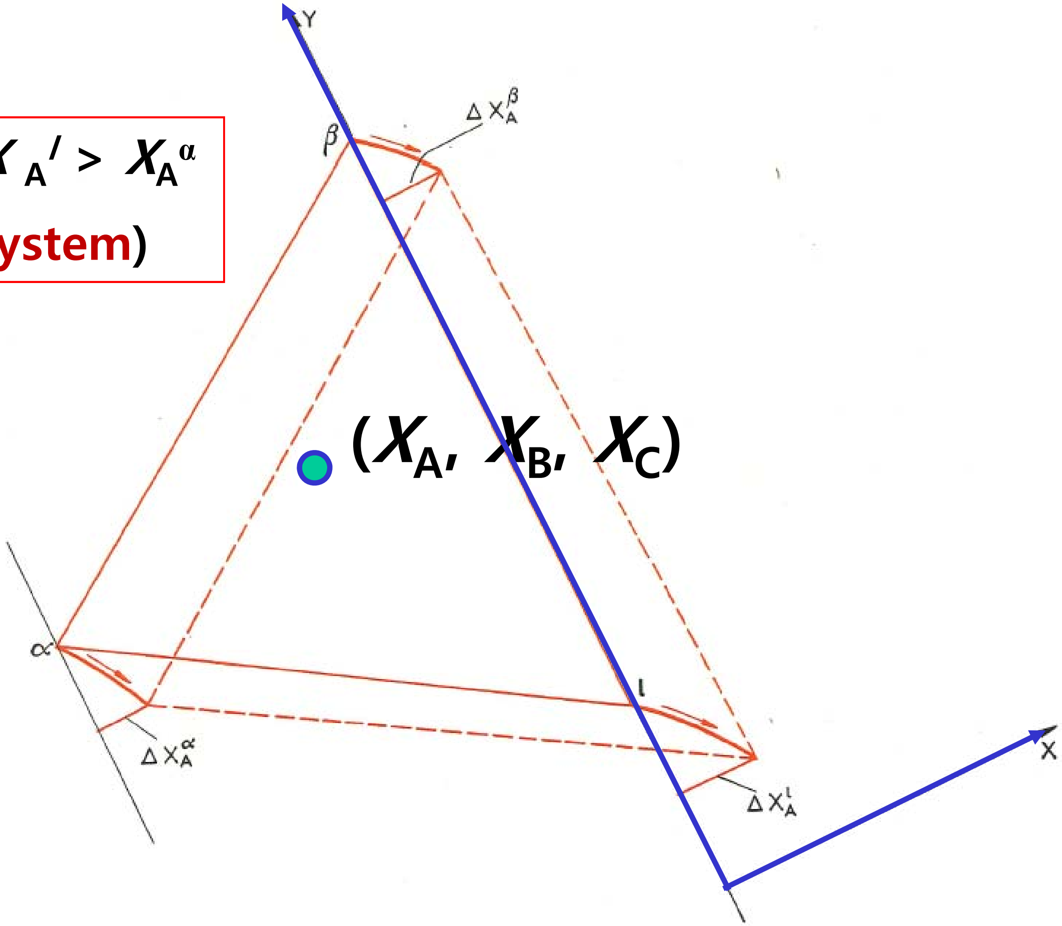
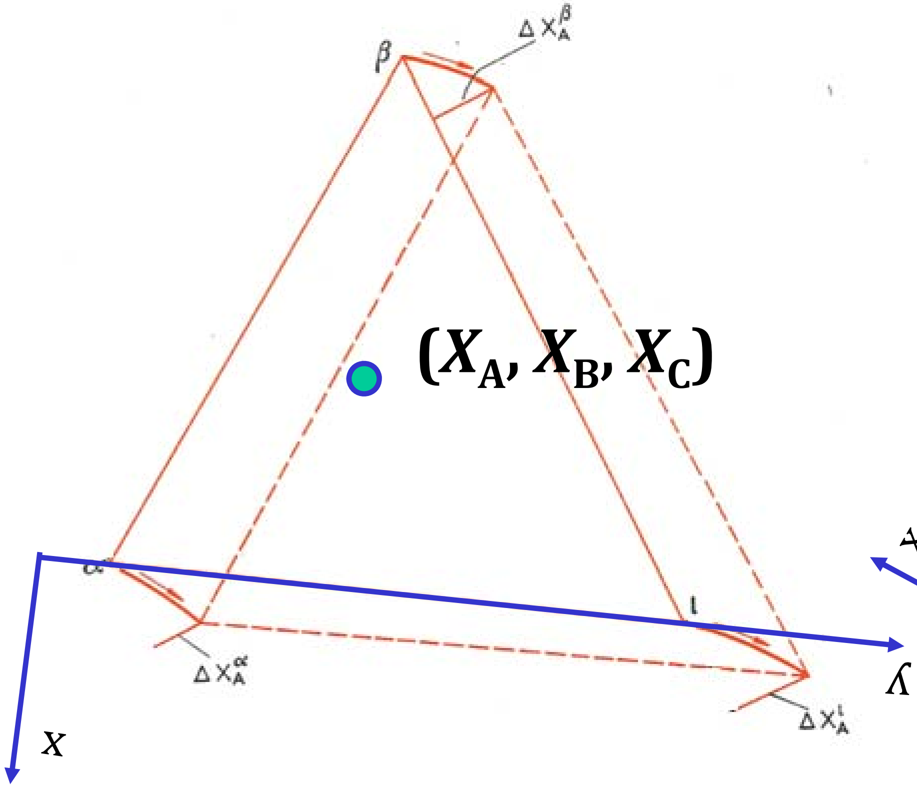


Fig. 150. Illustration of Hillert's criterion for distinguishing eutectic and peritectic reaction in ternary three-phase equilibrium; ———, equilibrium at *T*; – – – – – –, equilibrium at *T*—d*T*.

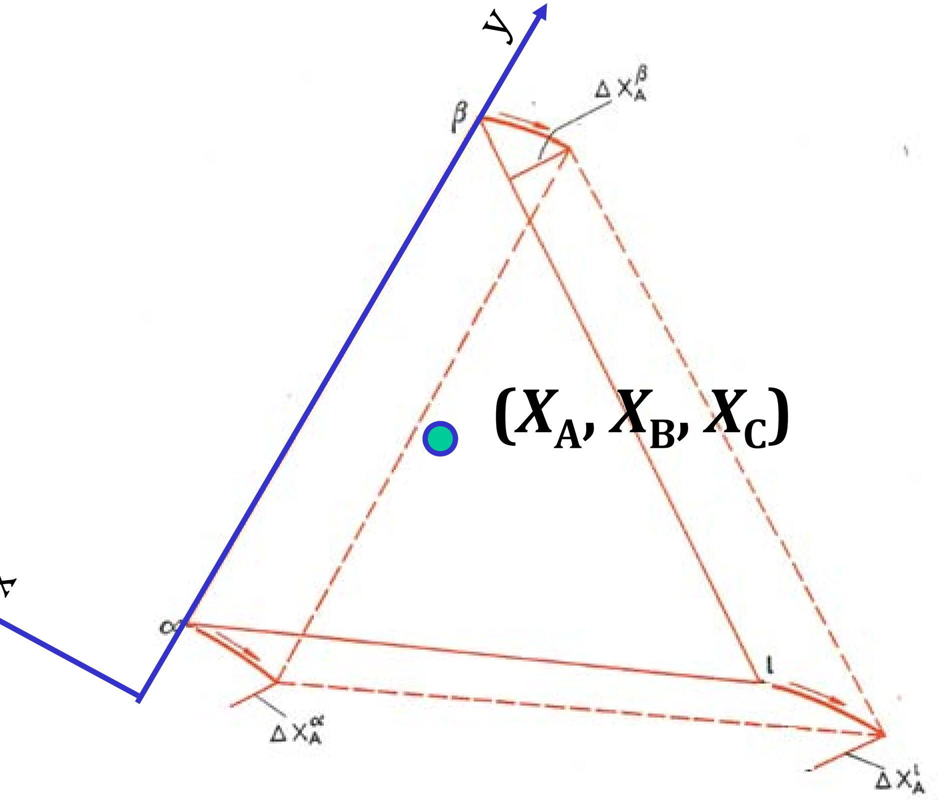
2) Assumption, $X_A^{\alpha} = X_A^{l} > X_A^{\beta}$

(New coordinate system)



3) Assumption, $X_A^{\alpha} = X_A^{\beta} > X_A^{l}$

(New coordinate system)



To simplify the calculation,

Assumption, $X_A^\beta = X_A^l > X_A^\alpha$ (New coordinate system)

$\Delta m_\beta + \Delta m_l = - \Delta m_\alpha$

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

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

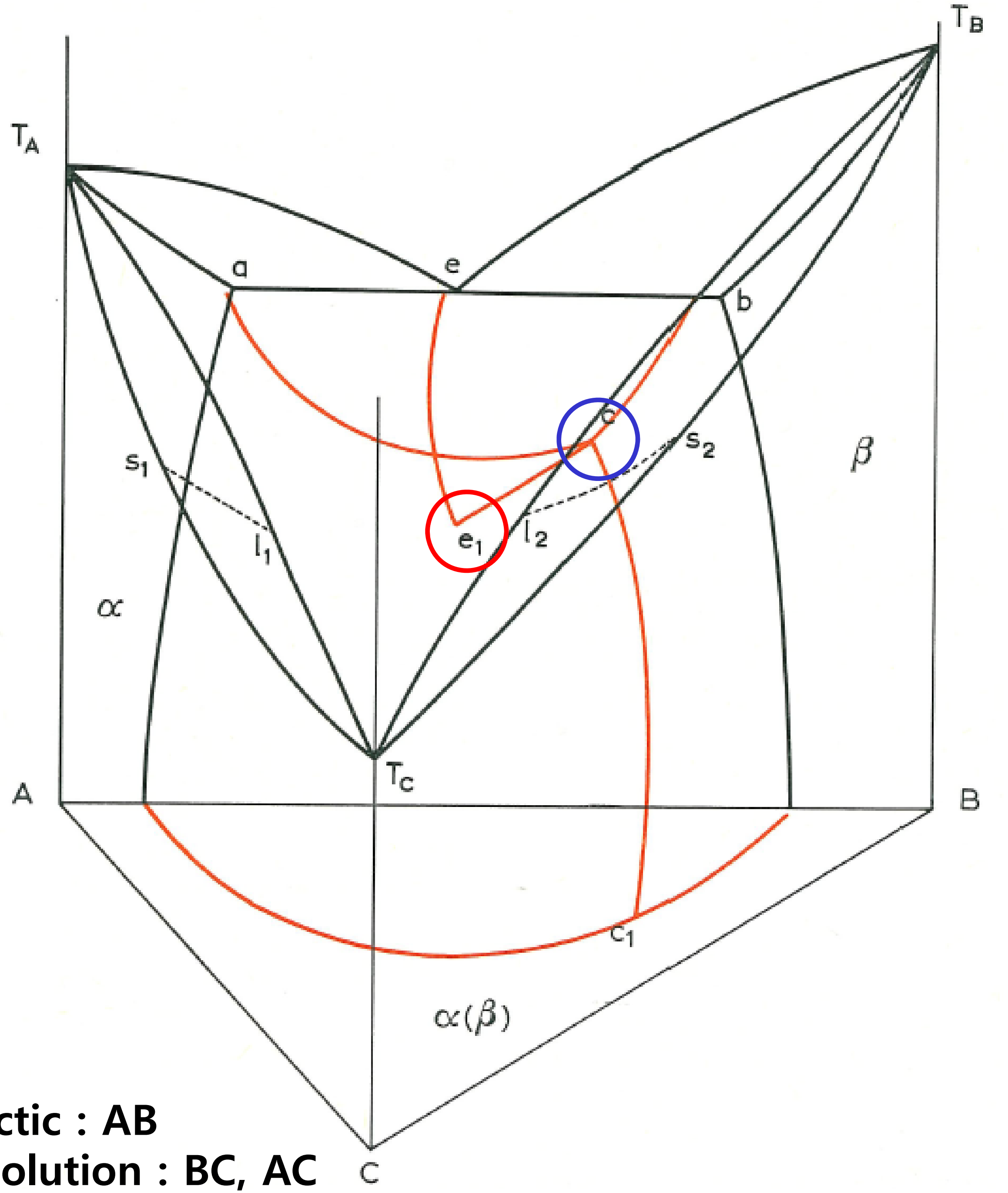
$$\Delta m_\alpha (X_A^\beta - X_A^\alpha) = m_\alpha \Delta X_A^\alpha + m_\beta \Delta X_A^\beta + m_l \Delta X_A^l$$

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

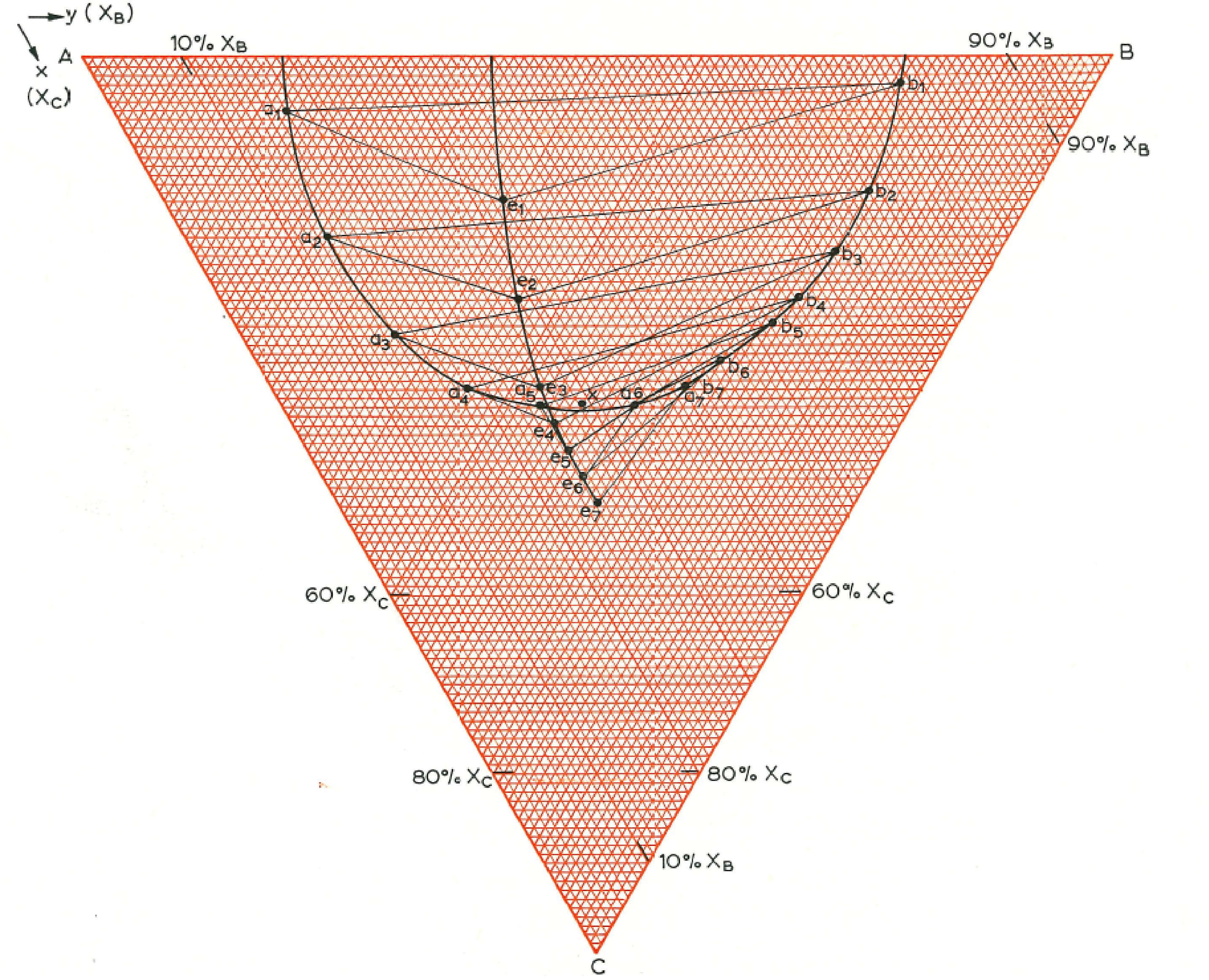
Hillert's criterion indicates that the relative amounts of the α, β and liquid phases (the average alloy composition) are of importance in determining the type of reaction.



- **One binary eutectic : AB**
  Complete solid solution : BC, AC

9.3. THREE-PHASE EQUILIBRIUM INVOLVING EUTECTIC REACTIONS

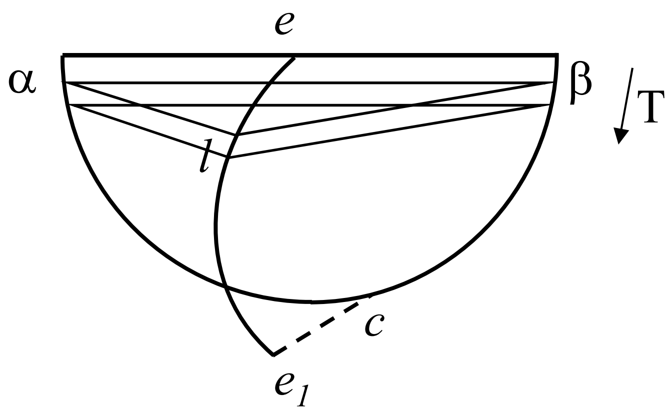
- **three phase regions $a_1e_1b_1$, $a_2e_2b_2$, … , $a_7e_7(b_7)$ projected on the concentration triangle.**



To determine whether the reaction is always a monovariant eutectic type, irrespective of alloy composition within the three-phase region, we apply Hillert's criterion to each pair of isotherms.

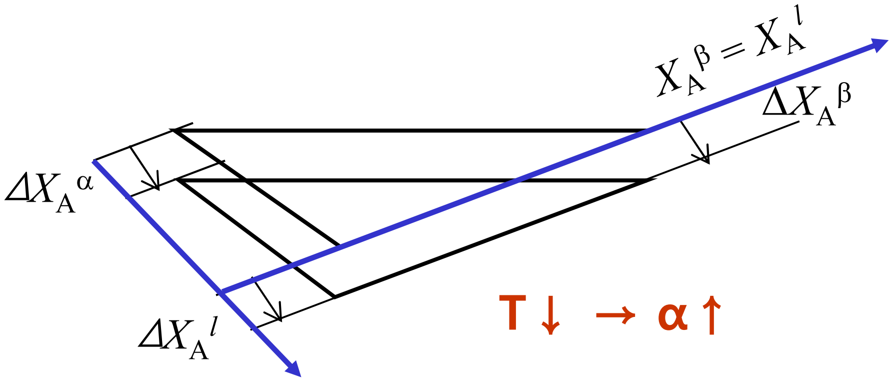
9.3. THREE-PHASE EQUILIBRIUM INVOLVING EUTECTIC REACTIONS

- **Relations between the triangle $a_1e_1b_1$ and $a_2e_2b_2$**



(if $X_A^{\beta} = X_A^{l,} > X_A^{\alpha},$)

① $\Delta X_A^{\alpha}, \Delta X_A^{\beta}, \Delta X_A^{l}$ (+) → Δm_{α} (+)

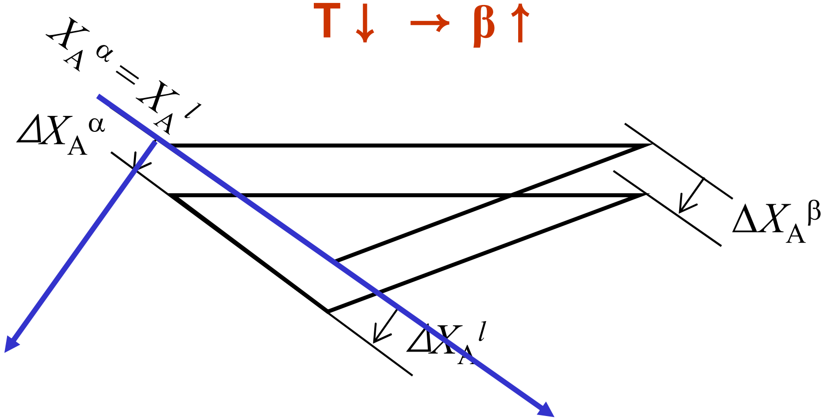


T↓ → α↑

(if $X_A^{\alpha} = X_A^{l} > X_A^{\beta},$)

② $\Delta X_A^{\alpha}, \Delta X_A^{\beta}, \Delta X_a^{l}$ (+) → Δm_{β} (+)

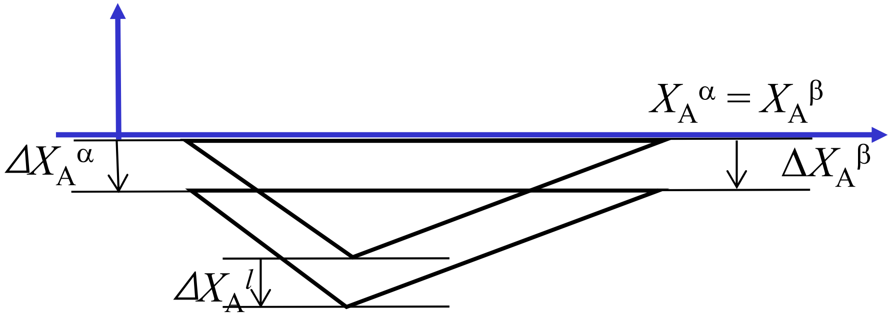
T↓ → β↑



(if $X_A^{a} = X_A^{b} > X_A^{l}$)

③ $\Delta X_A^{\alpha}, \Delta X_A^{\beta}, \Delta X_a^{l}$ (-) → Δm_{l} (-)

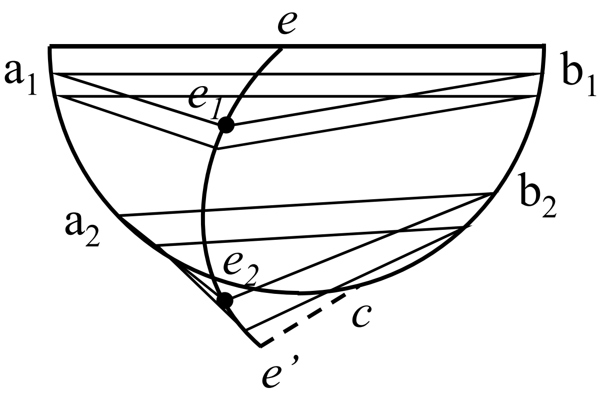
T↓ → liquid is being consumed



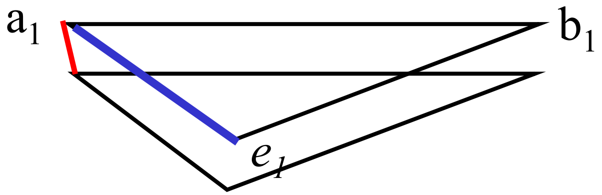
The reaction under gone by any alloy within the triangle $a_1e_1b_1$ is eutectic-type: l↔α+β ex) $a_2e_2b_2$-$a_3e_3b_3$/ $a_3e_3b_3$-$a_4e_4b_4$

9.3. THREE-PHASE EQUILIBRIUM INVOLVING EUTECTIC REACTIONS

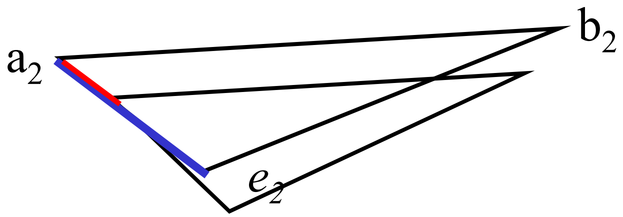
- **Relative position of vertex in tie triangle with ΔT**

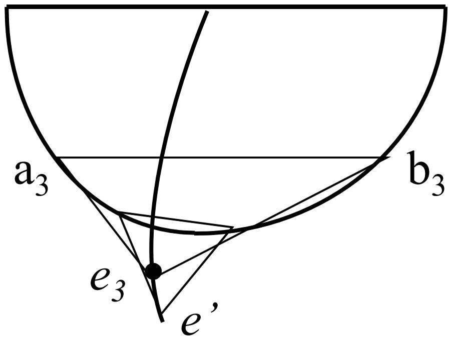


① Slope of tangent line at a_1 > slope of line a_1e_1

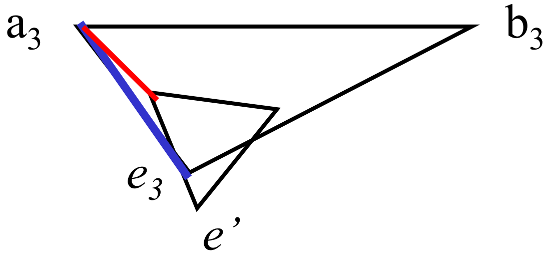


② Slope of tangent line at a_2 = slope of line a_2e_2



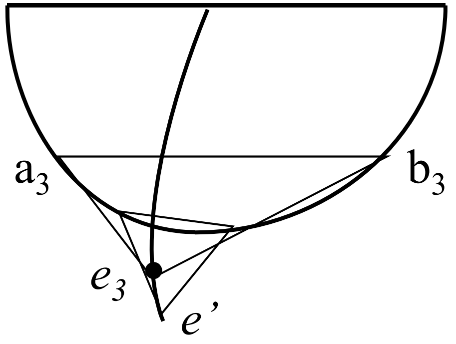


③ Slope of tangent line at a_3 < slope of line a_3e_3



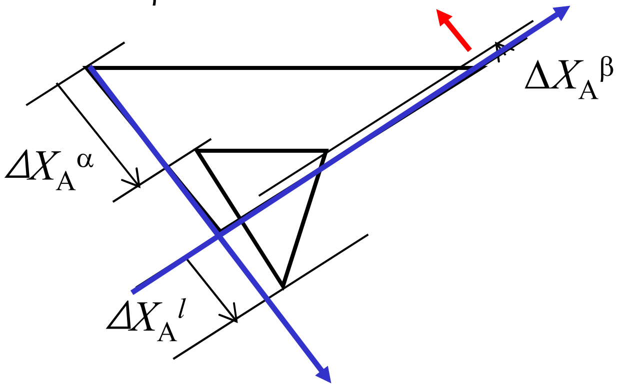
9.3. THREE-PHASE EQUILIBRIUM INVOLVING EUTECTIC REACTIONS

③ Slope of tangent line at $a_3 \leq$ slope of line a_3e_3



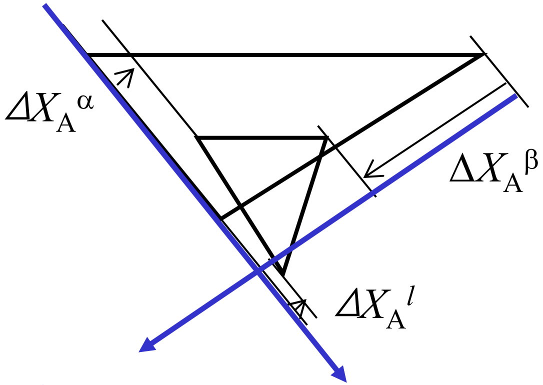
① $X_A^\beta = X_A^l > X_A^\alpha$

$m_\alpha \Delta X_A^\alpha(+) + m_\beta \Delta X_A^\beta(-) + m_l \Delta X_a^l(+) \rightarrow \Delta m_\alpha$



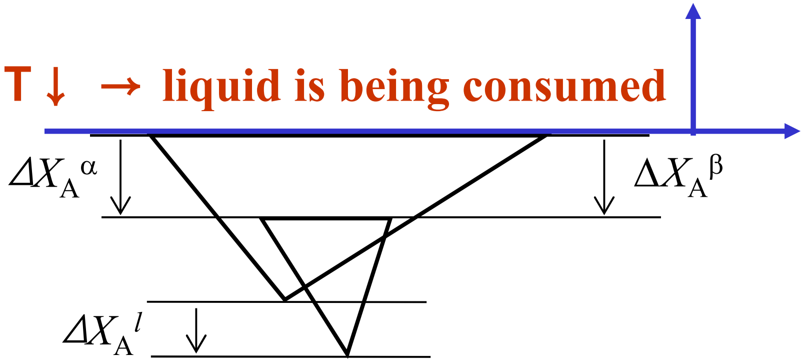
② $X_A^\alpha = X_A^l > X_A^\beta$

$\Delta m_\beta \rightarrow m_\alpha \Delta X_A^\alpha(-) + m_\beta \Delta X_A^\beta(+) + m_l \Delta X_a^l(-)$



③ $X_A^\alpha = X_A^\beta > X_A^l$

$\Delta m_l (-) \rightarrow m_\alpha \Delta X_A^\alpha (-) + m_\beta \Delta X_A^\beta (-) + m_l \Delta X_a^l (-)$

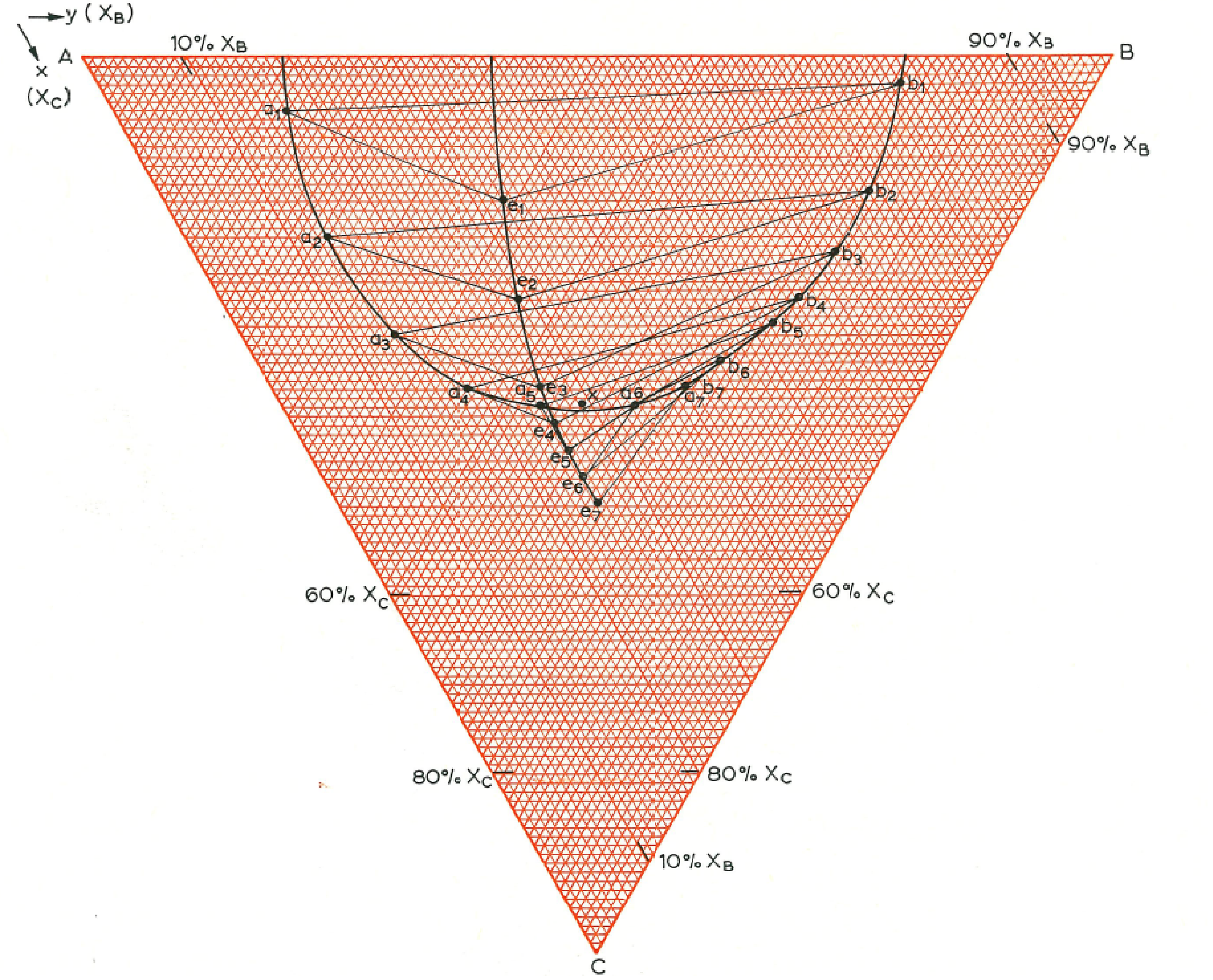

T ↓ → liquid is being consumed

❖Δm_l (-); if m_β is very larger than m_α and m_l → Δm_α(-) and Δm_β (+) → (l + α → β)

if m_β is much smaller than m_α *and* m_l → Δm_α(+) and Δm_β (-) → (l + β → α)

9.3. THREE-PHASE EQUILIBRIUM INVOLVING EUTECTIC REACTIONS

- **three phase regions $a_1e_1b_1$, $a_2e_2b_2$, … , $a_7e_7(b_7)$ projected on the concentration triangle.**



To determine whether the reaction is always a monovariant eutectic type, irrespective of alloy composition within the three-phase region, we apply Hillert's criterion to each pair of isotherms.

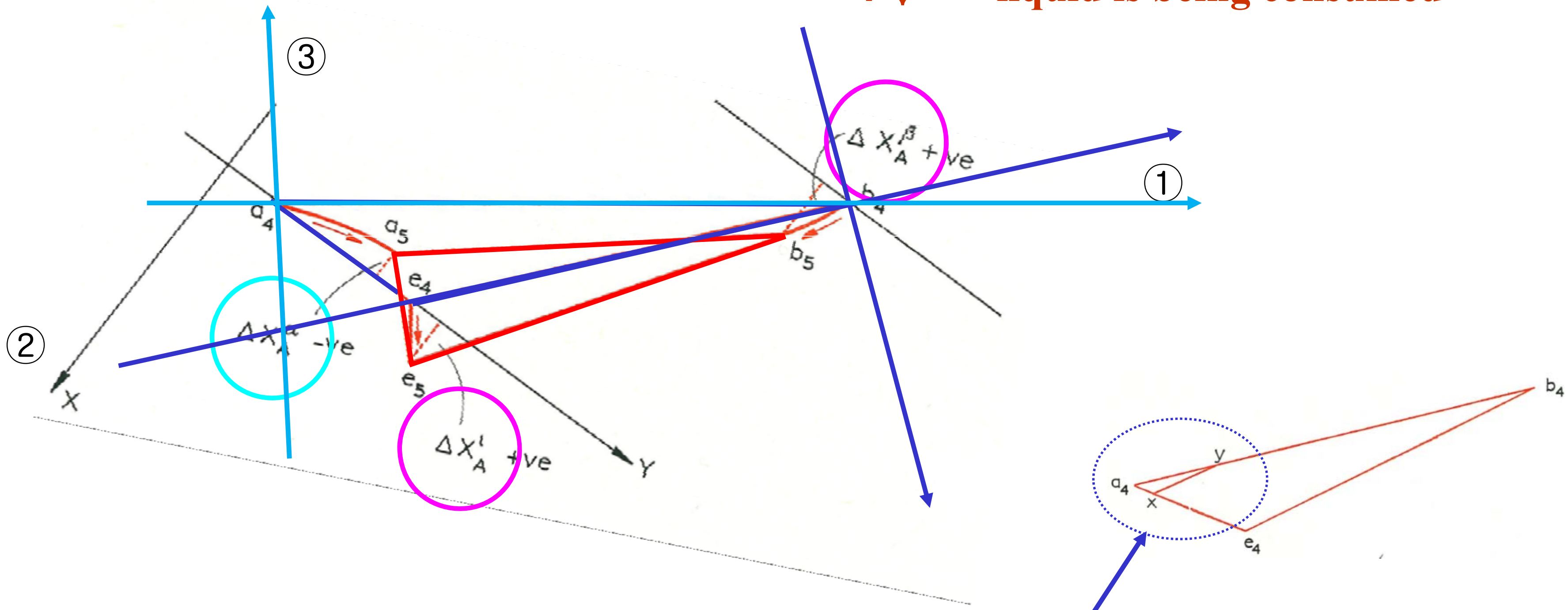
Consider tie triangle $a_4e_4b_4$, and $a_5e_5b_5$

① $X_A^{\beta} = X_A^{l} > X_A^{\alpha}$

③ $X_A^{\alpha} = X_A^{\beta} > X_A^{l}$

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

T ↓ → liquid is being consumed



② $X_A^{\alpha} = X_A^{l} > X_A^{\beta}$ $\quad\quad \Delta m_\beta \rightarrow m_\alpha \Delta X_A^{\alpha}(-) + m_\beta \Delta X_A^{\beta}(+) + m_l \Delta X_a^{l}(+)$

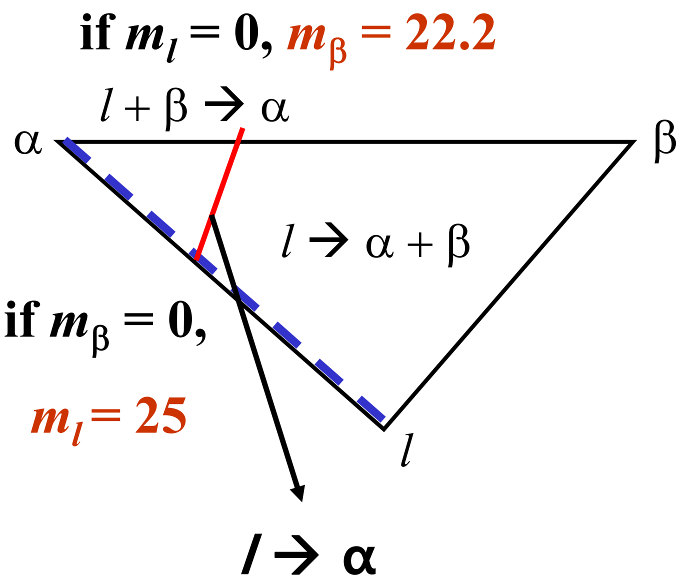
❖ $\Delta m_\alpha(+)$, Δm_l (-); **if m_α is very larger than m_β and m_l** $\rightarrow \Delta m_\beta$ (-) $\rightarrow$ ($l + \beta \rightarrow \alpha$)

if m_α is much smaller than m_β *and* m_l $\rightarrow \Delta m_\beta$ (+) $\rightarrow$ ($l \rightarrow \alpha + \beta$)

9.3. THREE-PHASE EQUILIBRIUM INVOLVING EUTECTIC REACTIONS

- **How to decide the boundary btw eutectic & peritectic?**

Reactions in the tie triangle $a_4e_4b_4$,



if $m_l = 0$, $m_\beta = 22.2$

if $m_\beta = 0$,

$m_l = 25$

along boundary, β plays no role → $l = \alpha$

$$X_A^\alpha = X_A^l > X_A^\beta$$

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

$(\Delta X_A^\alpha = -1,\ \Delta X_A^\beta = 3.5,\ \Delta X_A^l = 3)$ (next page)

$-m_\alpha + 3.5 m_\beta + 3 m_l = 0$ $(m_\alpha + m_\beta + m_l = 100)$

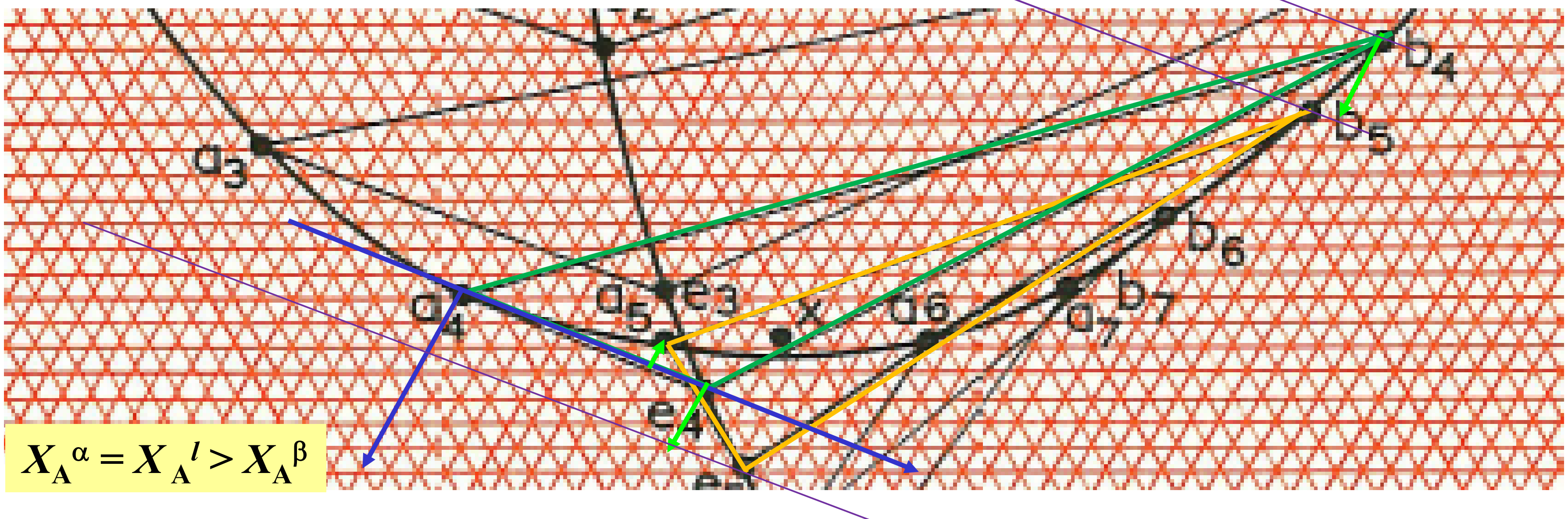
$-100 + 4.5 m_\beta + 4 m_l = 0$

if $m_\beta = 0$, $m_l = 25$

if $m_l = 0$, $m_\beta = 22.2$

Initially, peritectic region confined the α corner.
Consideration of three-phase triangles at lower temperatures will indicate that the peritectic region sweeps round from the α corner towards the β and liquid corners.

- **three phase regions $a_1e_1b_1$, $a_2e_2b_2$, … , $a_7e_7(b_7)$ projected on the concentration triangle.**



$X_A^\alpha = X_A^l > X_A^\beta$

The boundary line can be determined by measuring ΔX_A^α, ΔX_A^β, and ΔX_A^l.

In Fig. 151,
ΔX_A^α= -1, ΔX_A^β= -3.5 and ΔX_A^l=3 units.

Figure 151

Table 2

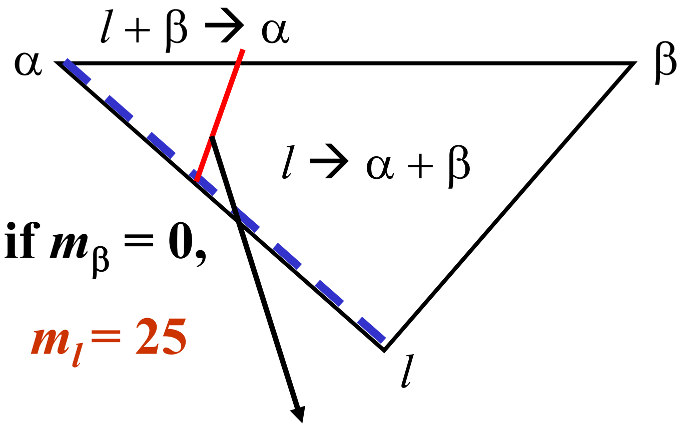
	X_B,	X_C		X_B,	X_C		X_B,	X_C
e_1	33,	16	a_1	17,	6	b_1	78,	3
e_2	29,	27	a_2	14,	20	b_2	69,	15
e_3	26,	37	a_3	15,	31	b_3	62,	22
e_4	25.3,	41	a_4	19,	37	b_4	56,	27
e_5	25,	44	a_5	25,	39	b_5	52,	30
e_6	25,	47	a_6	34,	39	b_6	45,	34
e_7	25,	50	$a_7(b_7)$	40,	37			

9.3. THREE-PHASE EQUILIBRIUM INVOLVING EUTECTIC REACTIONS

- How to decide the boundary btw eutectic & peritectic?

Reactions in the tie triangle $a_4e_4b_4$,

if $m_l = 0$, $m_\beta = 22.2$



if $m_\beta = 0$,

$m_l = 25$

$l \rightarrow \alpha$

along boundary, β plays no role → $l = \alpha$

$$X_A^\alpha = X_A^l > X_A^\beta$$

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

$$(\Delta X_A^\alpha = -1,\ \Delta X_A^\beta = 3.5,\ \Delta X_A^l = 3)$$

$$-m_\alpha + 3.5m_\beta + 3m_l = 0 \quad (m_\alpha + m_\beta + m_l = 100)$$

$$-100 + 4.5m_\beta + 4m_l = 0$$

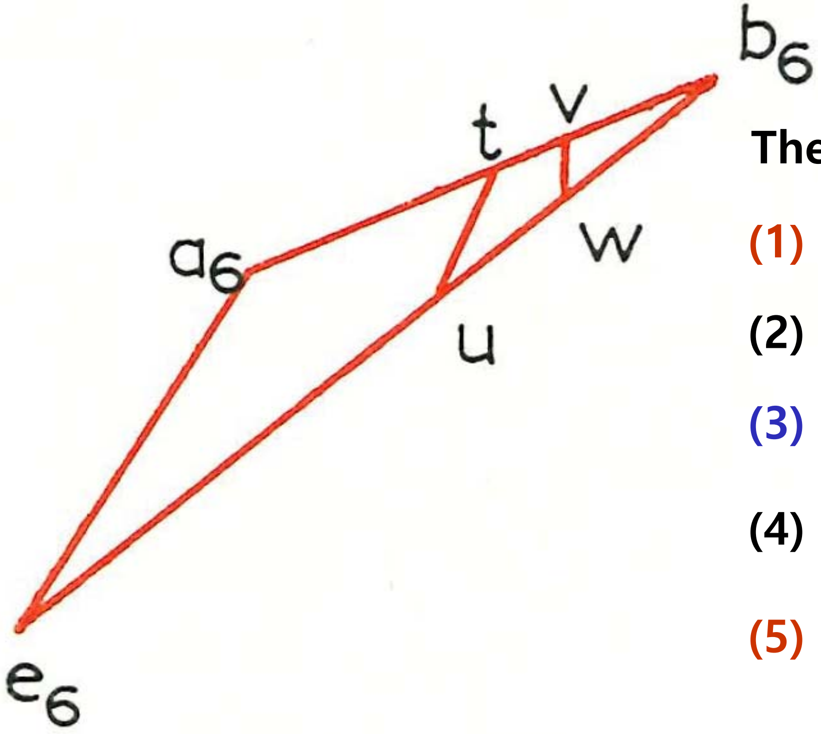
if $m_\beta = 0$, $m_l = 25$

if $m_l = 0$, $m_\beta = 22.2$

Initially, peritectic region confined the α corner.
Consideration of three-phase triangles at lower temperatures will indicate that the peritectic region sweeps round from the α corner towards the β and liquid corners.

Monovariant β curve coincides with the lα tie line between isotherms $a_5e_5b_5$ and $a_6e_6b_6$

⇨ **Second peritectic reaction area appears at the β corner of the three–phase triangle**



The tie triangle $a_6e_6b_{6,}$, reaction equilibria

(1) Peritectic l + β ↔ α in area $a_6e_6$ut

(2) Two-phase l ↔ α along line tu

(3) eutectic l ↔ α+β in area tuwv

(4) two-phase l ↔ β along line vw

(5) Peritectic l + α ↔ β in area $b_6$vw

To summarise, the three-phase reaction is initially eutectic for all alloys untill the temperature of the three phase triangle $a_4e_4b_{4,}$ is reached. From that temperature until the end of the three-phase reaction at the tie line $e_7a_7(b_7)$, the reaction type is dependent on the alloy composition within the sequence of the three-phase triangles.