2019 Spring

"Phase Equilibria *in* Materials"

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Contents for previous class "Ternary Phase diagram"

Ternary isomorphous system

: "Two-phase equilibrium" between the liquid and a solid solution

How to show in 2-dim. space?

① Projection (liquidus & solidus surface/solid solubility surface)

→ No information on 2 phase region

② Isothermal section → most widely used → F = C - P

Rules for tie line

(i) Slope gradually changes.
(ii) Tie lines cannot intersect.
(iii) Extension of tie line cannot intersect the vertex of triangle.
(iv) Tie lines at T's will rotate continuously.

Konovalov's Rule: $X_A^S > X_A^l$ when addition of A increases the T_m.

③ Vertical section

Solidification sequence: useful for effect of 3rd alloying element

However, it is not possible to draw horizontal tie lines across two-phase regions in vertical sections to indicate the true compositions of the co-existing phases at a given temperature.

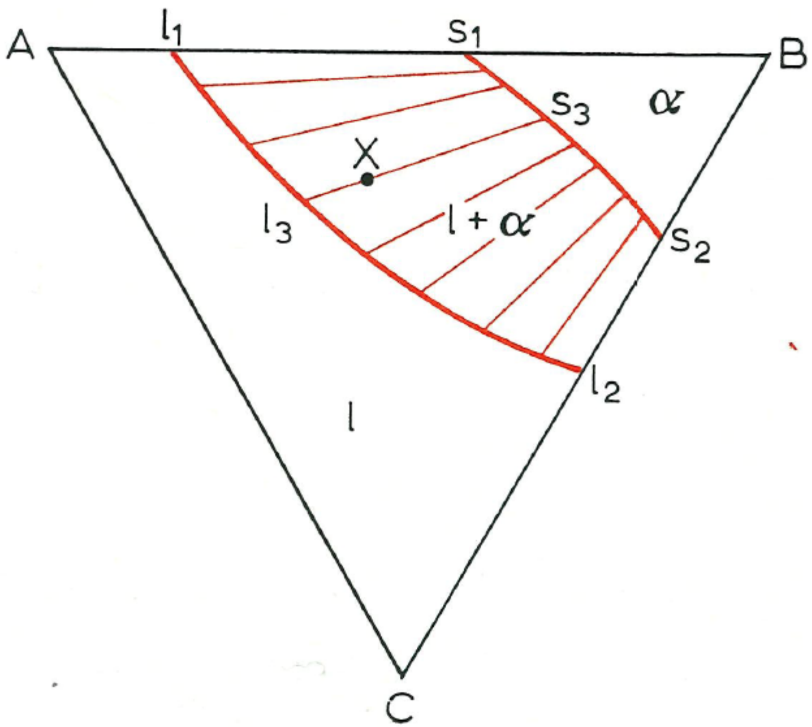
④ Polythermal projection

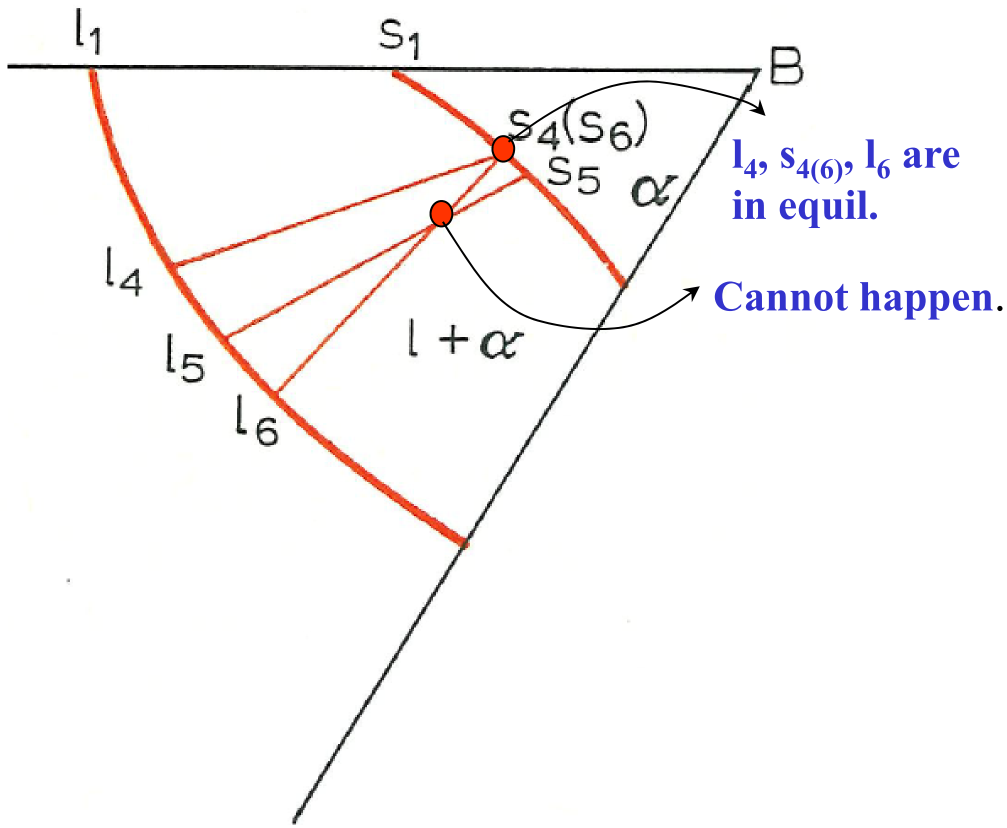
8.4 TWO-PHASE EQUILIBRIUM

8.4.1 Two-phase equilibrium between the liquid and a solid solution

Rules for tie line

(i) Slope gradually changes.　　**(ii) Tie lines cannot intersect** at constant temperature.



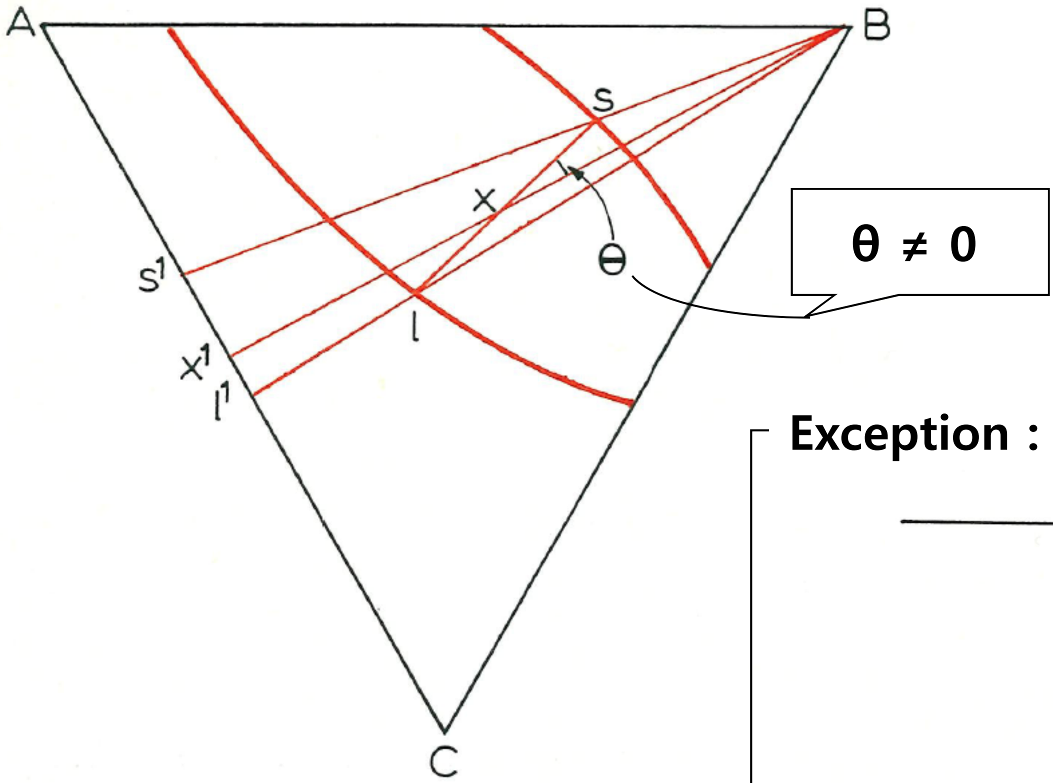


8.4 TWO-PHASE EQUILIBRIUM

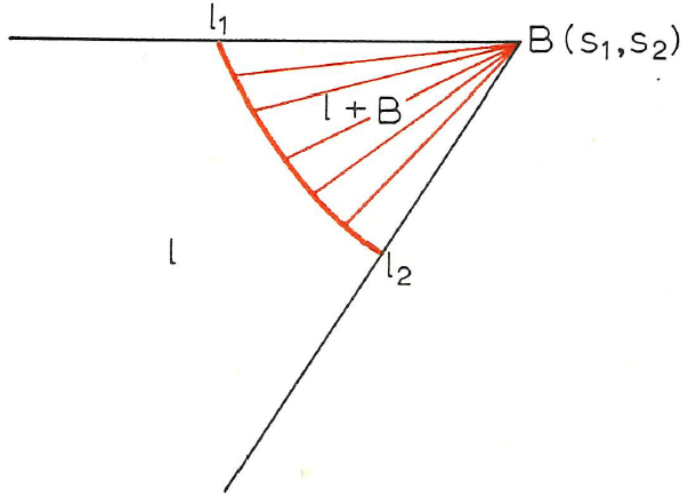
8.4.1 Two-phase equilibrium between the liquid and a solid solution

Rules for tie line

(iii) Extension of tie line cannot intersect the vertex of triangle.



Exception : solubility is infinitely small.



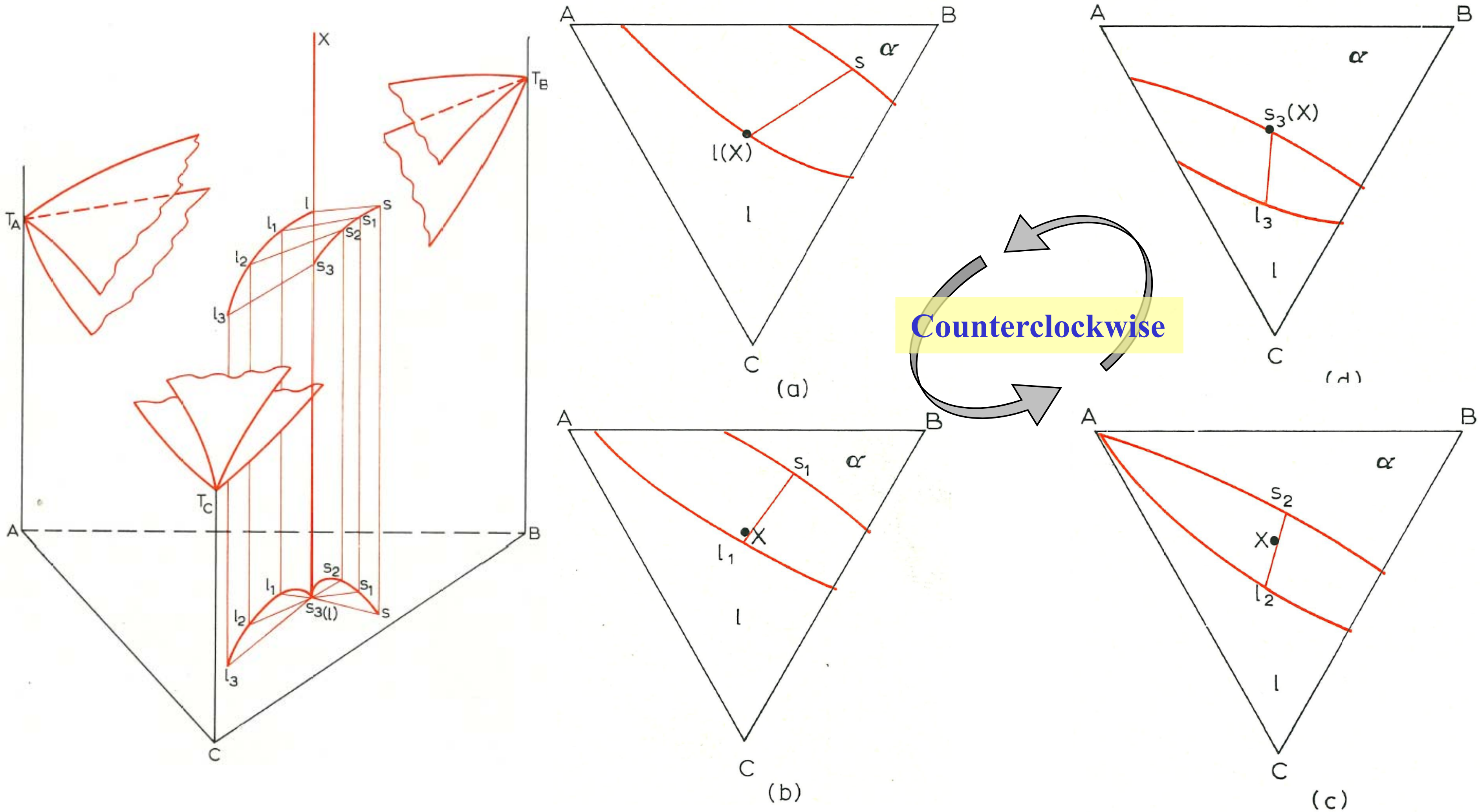
8.4 TWO-PHASE EQUILIBRIUM

8.4.1 Two-phase equilibrium between the liquid and a solid solution

Rules for tie line

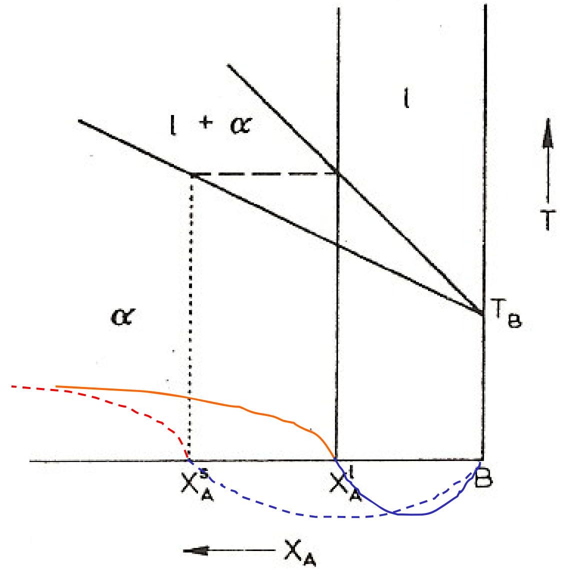
(iv) Tie lines at T's will rotate continuously. (Konovalov's Rule)

: Clockwise or counterclockwise



Konovalov's Rule

: Solid is always richer than the melt with which it is in equilibrium in that component which raises the melting point when added to the system.



$$X_A^S > X_A^l$$

$$X_A^S + X_B^S = X_A^l + X_B^l = 1$$

then

$$\frac{X_A^S}{X_A^S + X_B^S} > \frac{X_A^l}{X_A^l + X_B^l}$$

$$X_A^S > X_A^l$$

and

$$\frac{X_A^S}{X_A^S + X_B^S - X_A^S} > \frac{X_A^l}{X_A^l + X_B^l - X_A^l}$$

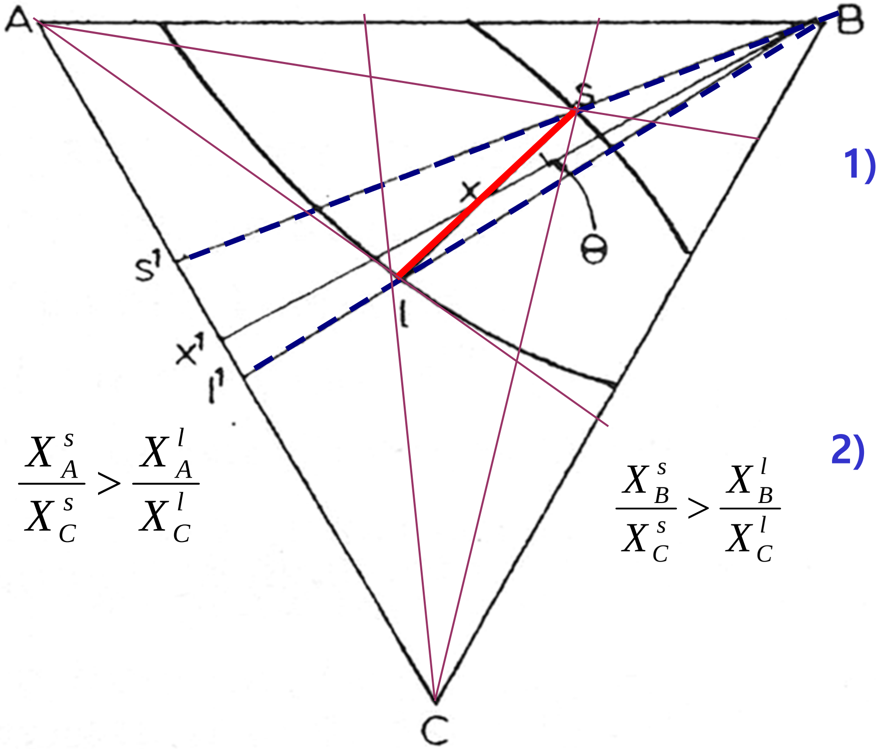
Therefore,

$$\frac{\boxed{X_A^S}}{\boxed{X_B^S}} > \frac{\boxed{X_A^l}}{\boxed{X_B^l}}$$

In this form Konovalov's Rule can be applied to ternary systems to indicate the direction of tie lines.

* The lines from B through *s* and *l* intersect the side AC of the triangle at points s^1 and l^1 respectively. Then,

$$\frac{X_B^s}{X_A^s} > \frac{X_B^l}{X_A^l}$$



$$\frac{X_A^s}{X_C^s} > \frac{X_A^l}{X_C^l}$$

$$\frac{X_B^s}{X_C^s} > \frac{X_B^l}{X_C^l}$$

$$\frac{X_A^l}{X_C^l} = \frac{l^1C}{l^1A} \quad \textbf{and} \quad \frac{X_A^S}{X_C^S} = \frac{s^1C}{s^1A}$$

1) Melting point of A is higher than that of C.

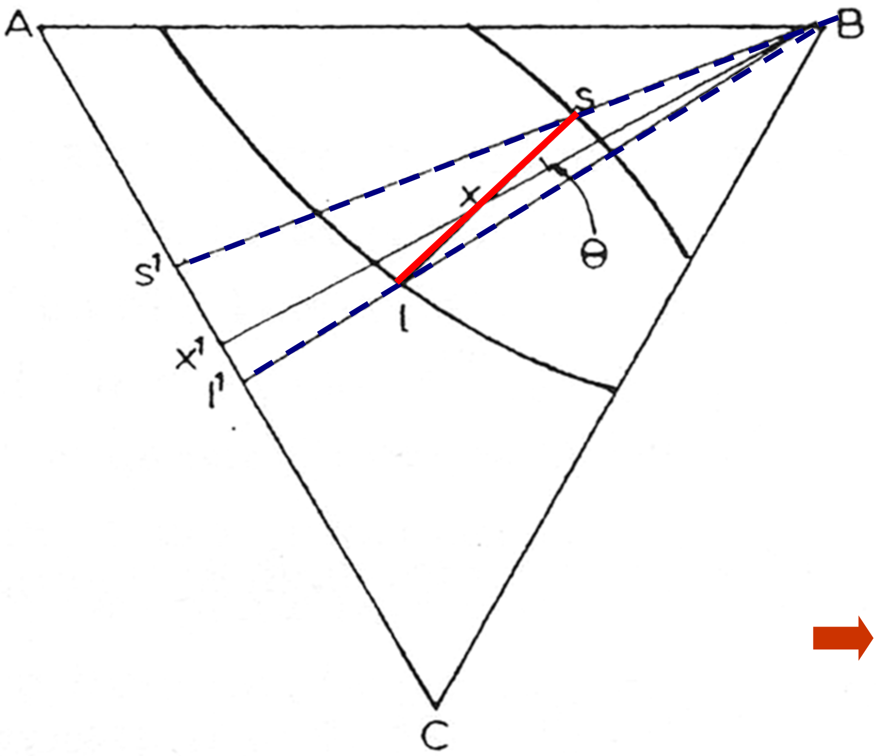
$$\frac{s^1C}{s^1A} > \frac{l^1C}{l^1A} \quad \textbf{and} \quad \frac{X_A^s}{X_C^s} > \frac{X_A^l}{X_C^l}$$

2) The relative positions of points l and s are in agreement with Konovalov's Rule.

$$\frac{X_B^s}{X_C^s} > \frac{X_B^l}{X_C^l} \quad \textbf{and} \quad \frac{X_B^s}{X_A^s} > \frac{X_B^l}{X_A^l}$$

3) Melting point: B > C and B > A
thus, B > A > C

4) Konovalov's Rule applies to each pair of components



The tie line *ls* is rotated anticlockwise by an angle Θ relative to the line Bx¹.

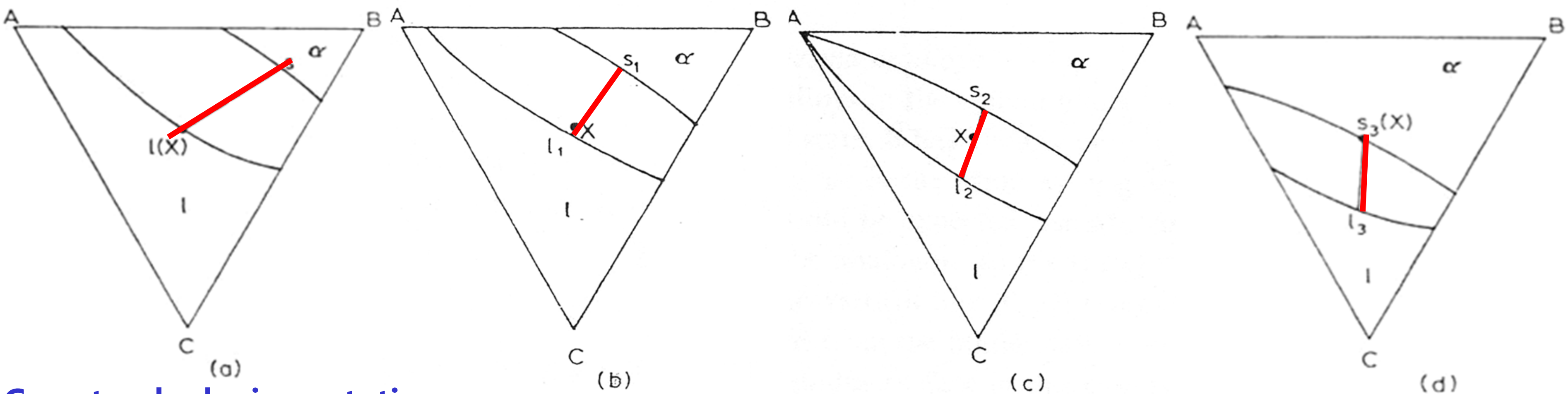
If Θ = 0

then

$$\boxed{X_A^S / X_C^S = X_A^l / X_C^l}$$

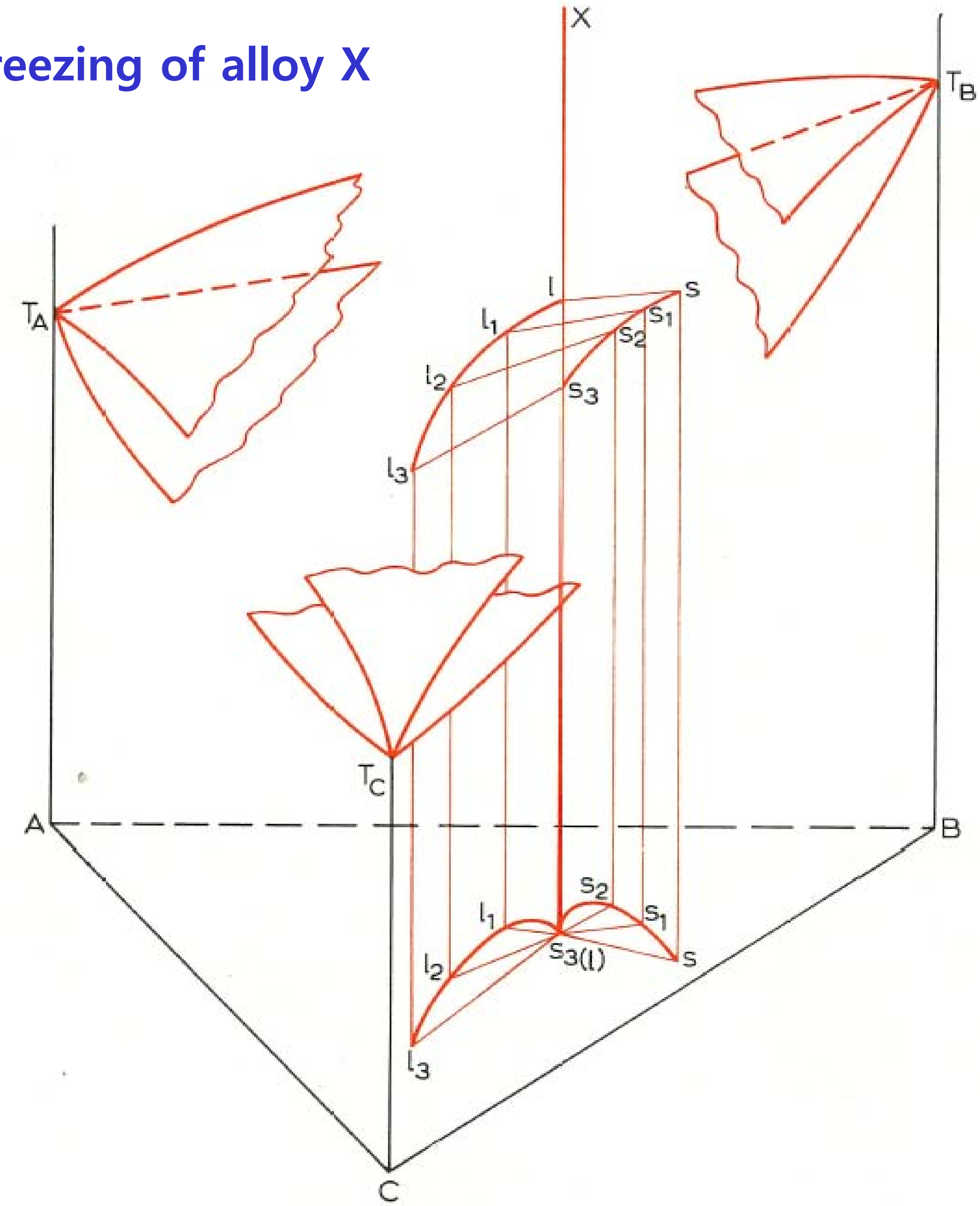
in contradiction to Konovalov's Rule.

➡ **Tie lines when produced do not intersect the corner of the concentration triangle.**



Counterclockwise rotation

Equilibrium freezing of alloy X



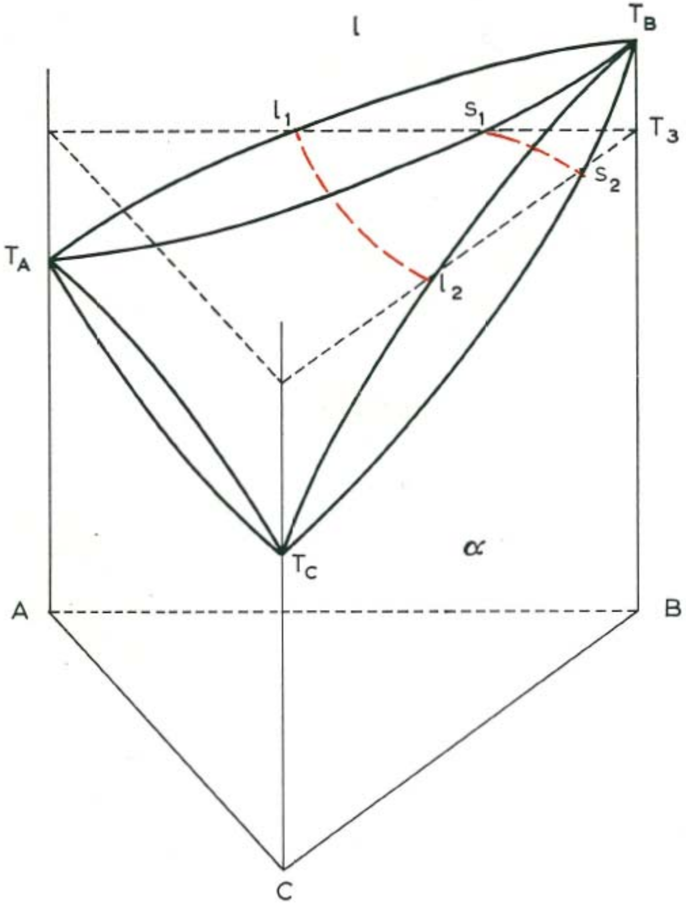
8.4 TWO-PHASE EQUILIBRIUM

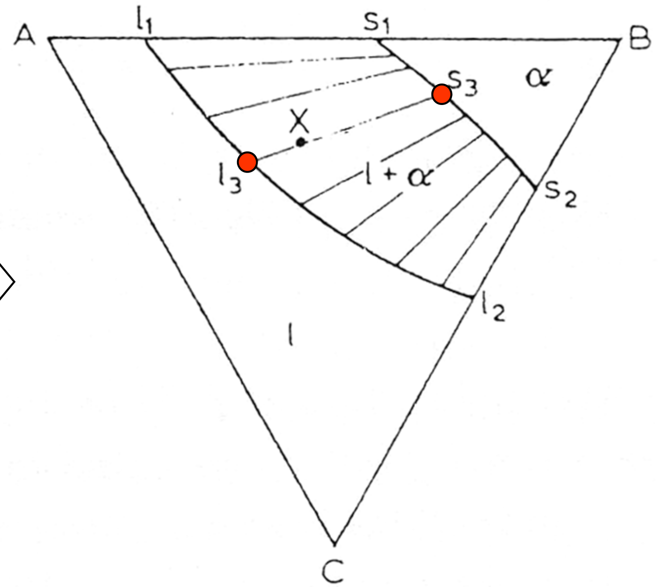
8.4.1 Two-phase equilibrium between the liquid and a solid solution

Two phase equilibrium (f = 2)

→ T, X_A^l, X_B^l (X_C^l), X_A^α, X_B^α (X_C^α)

① If we know T, X_A^l, then others can be decided. → Isothermal section





→ Comp. of liq (X_B^l, X_C^l)

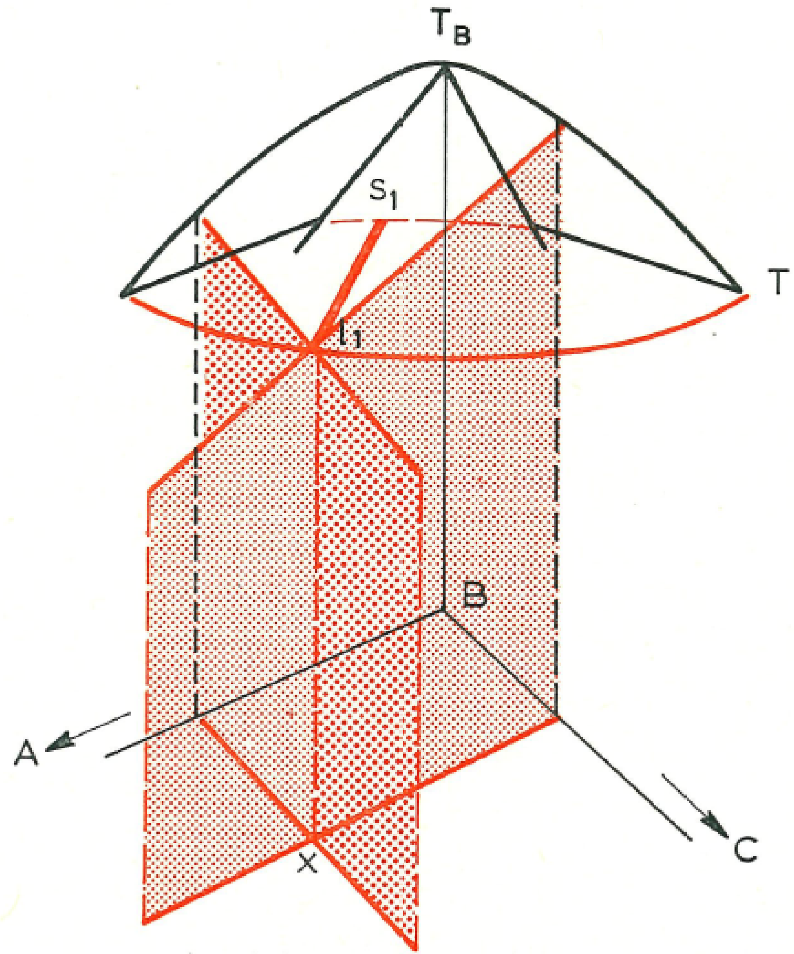
→ Tie line

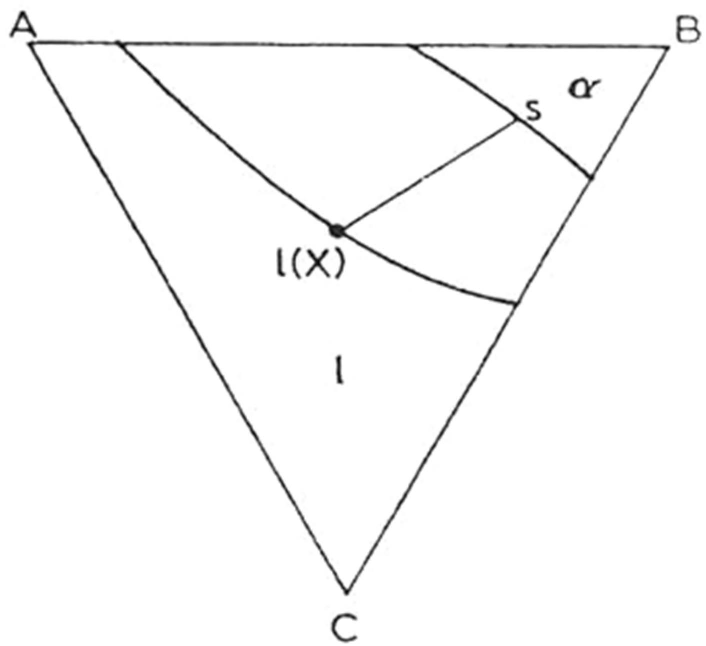
→ Comp. of solid (X_A^α, X_B^α, X_C^α)

8.4 TWO-PHASE EQUILIBRIUM

8.4.1 Two-phase equilibrium between the liquid and a solid solution

② If we know X_A^l, X_C^l, we can know composition of liq.





→ Intersection with liquidus surface

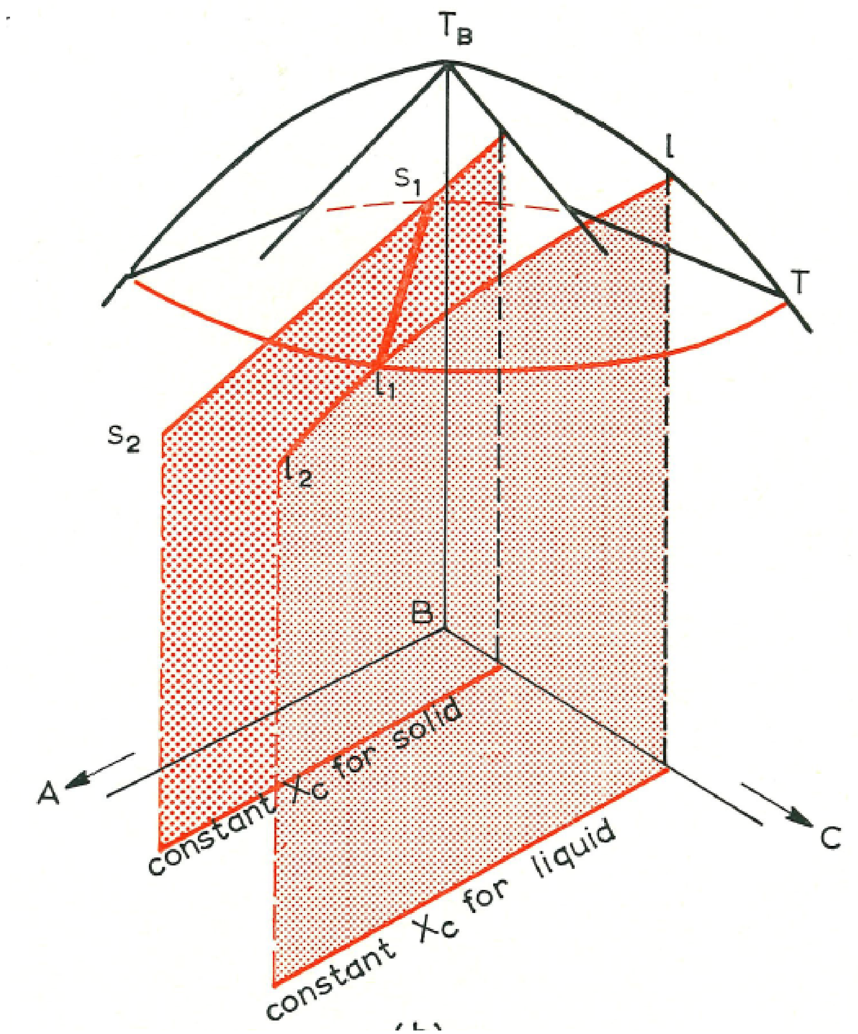
→ Temp. T

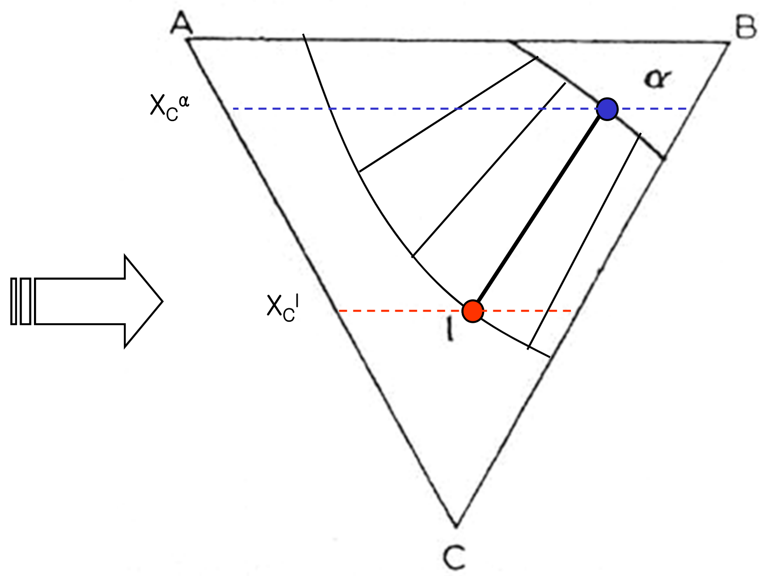
→ Two phase region

8.4 TWO-PHASE EQUILIBRIUM

8.4.1 Two-phase equilibrium between the liquid and a solid solution

③ If we know X_C^l, X_C^α, we can know composition of liq & sol.





→ X_C^α & X_C^l come closer

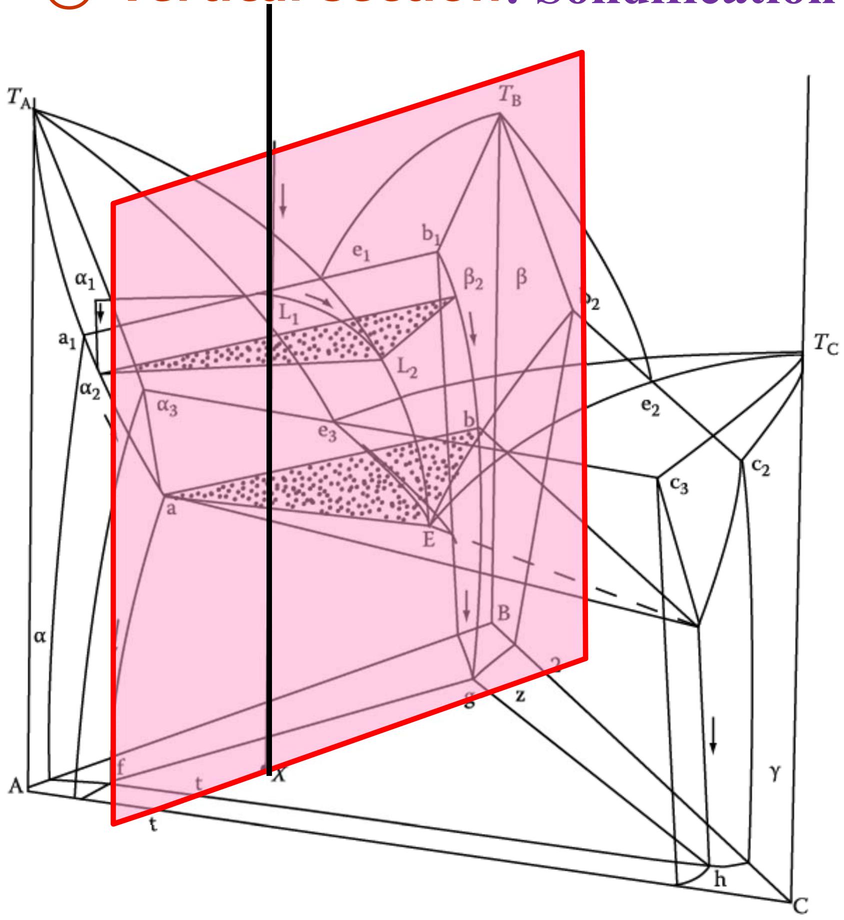
→ <u>will intersect at only one point.</u>

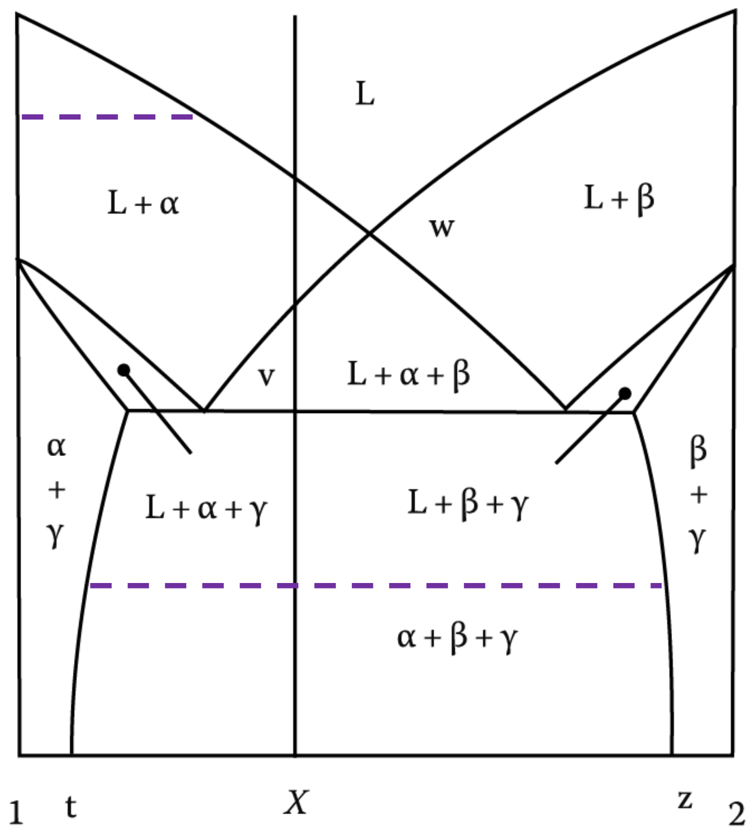
→ Temperature, tie line

→ Composition of liq. & sol.

Ternary Eutectic System

③ Vertical section: Solidification Sequence





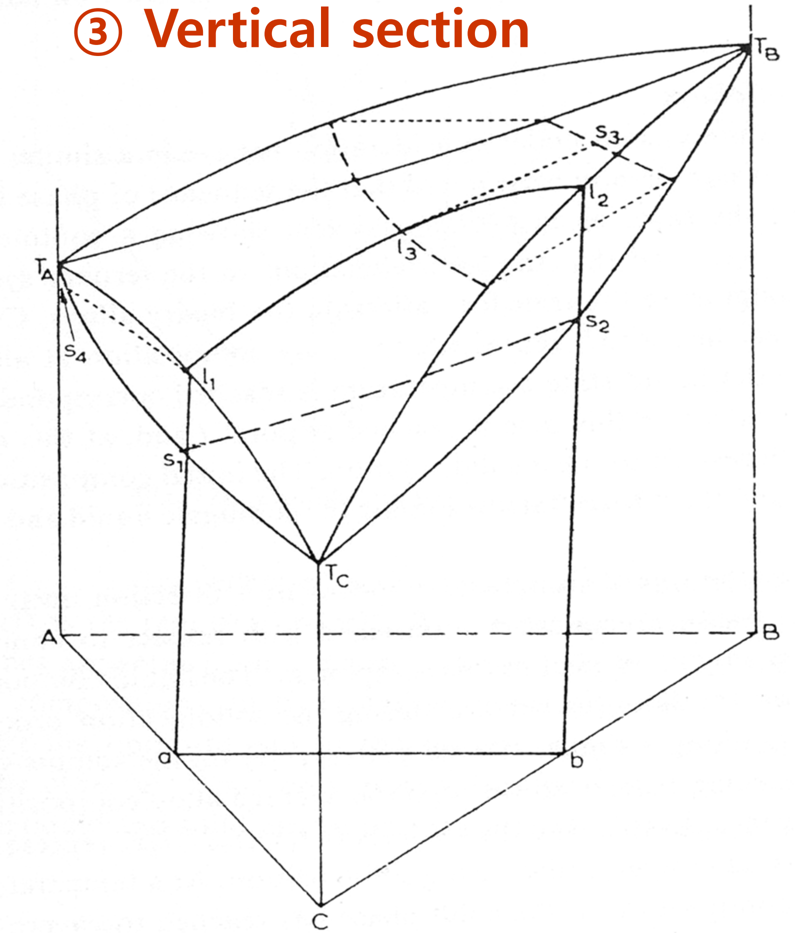
* The horizontal lines are not tie lines.
(no compositional information)

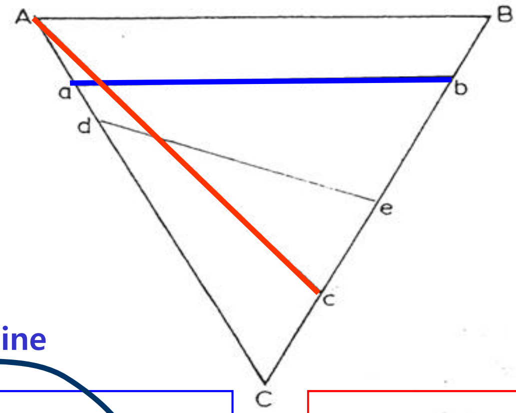
* Information for equilibrium phases at different tempeatures

8.4 TWO-PHASE EQUILIBRIUM

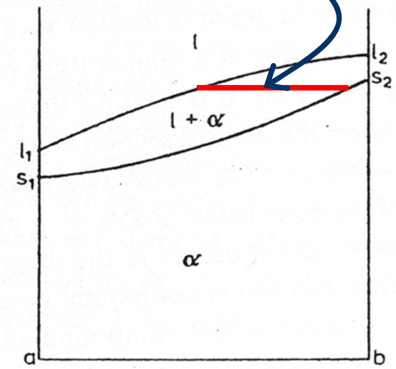
8.4.1 Two-phase equilibrium between the liquid and a solid solution

③ Vertical section

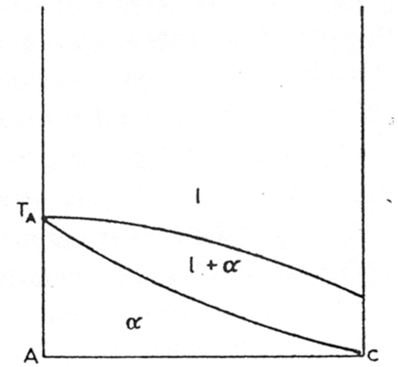




No tie line &
No conjugate line



Paralleled to binary (AB)



Cut through vertex

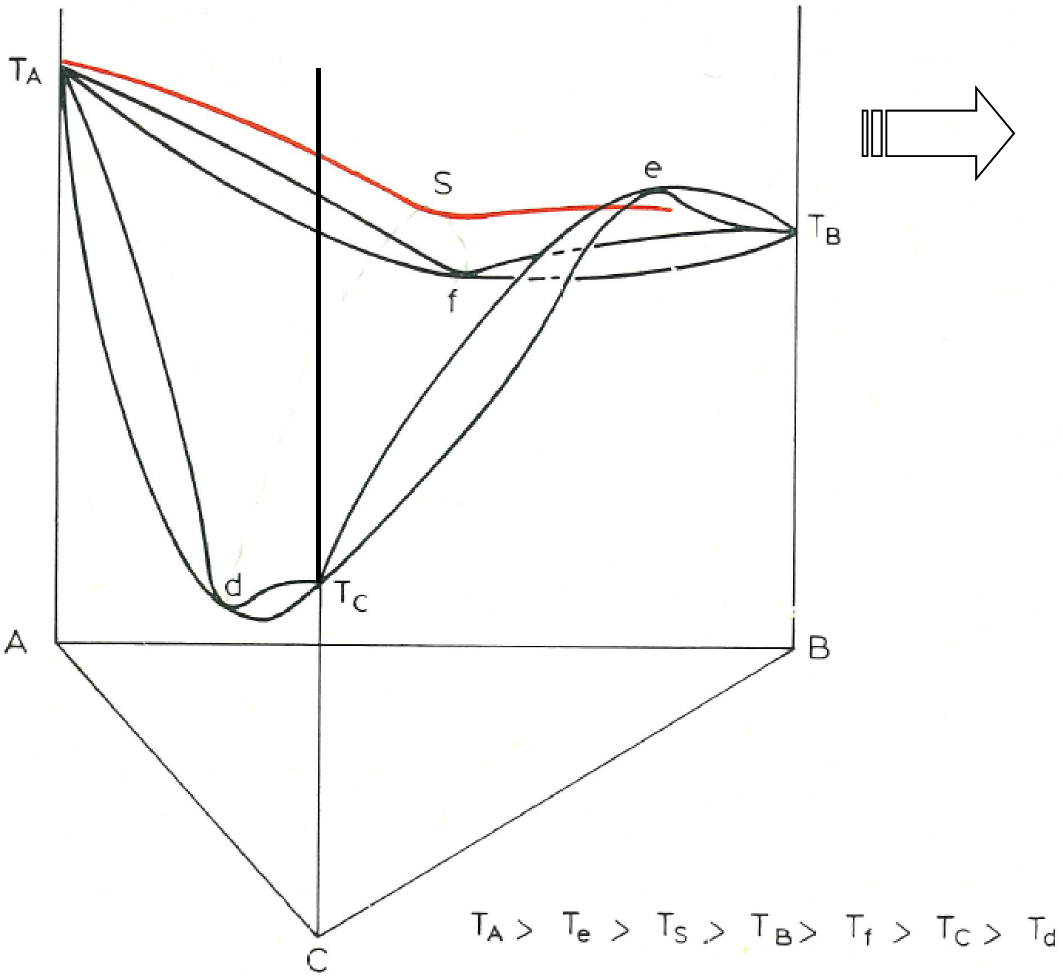
① **Useful for effect of 3rd alloying element**

However, it is not possible to draw horizontal tie lines across two-phase regions in vertical sections to indicate the true compositions of the co-existing phases at a given temperature.

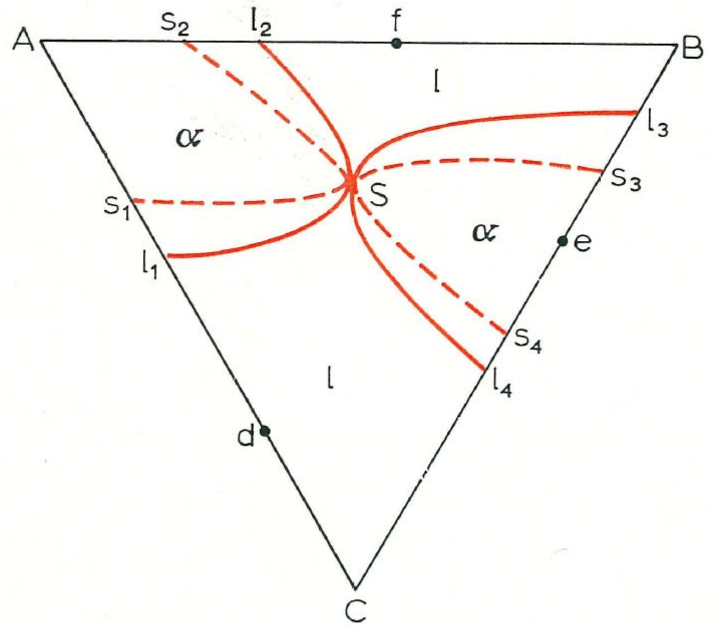
② **Pseudobinary section: the section from the 3rd component to the compound (congruently-melting compound) can then be a binary section**

8.4.2 Variants of the phase diagram
(more complex system)

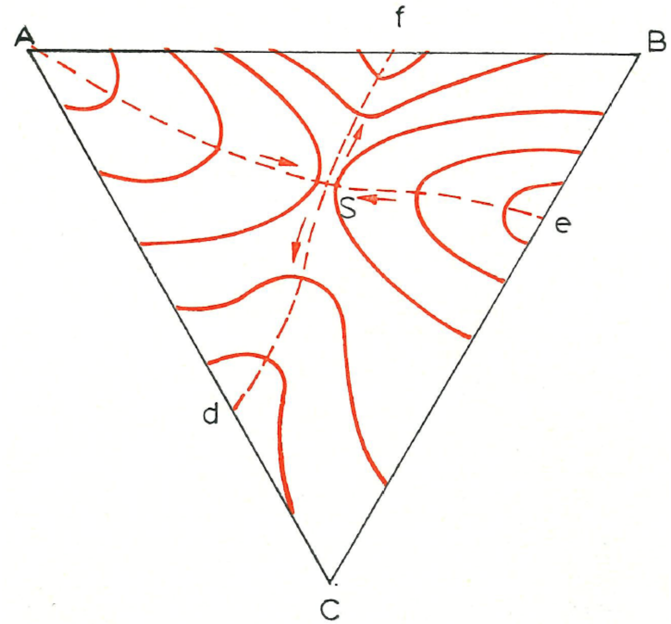
* **Ternary <u>two-phase equilibrium</u> with a saddle point**



Isothermal section ($T=T_s$)



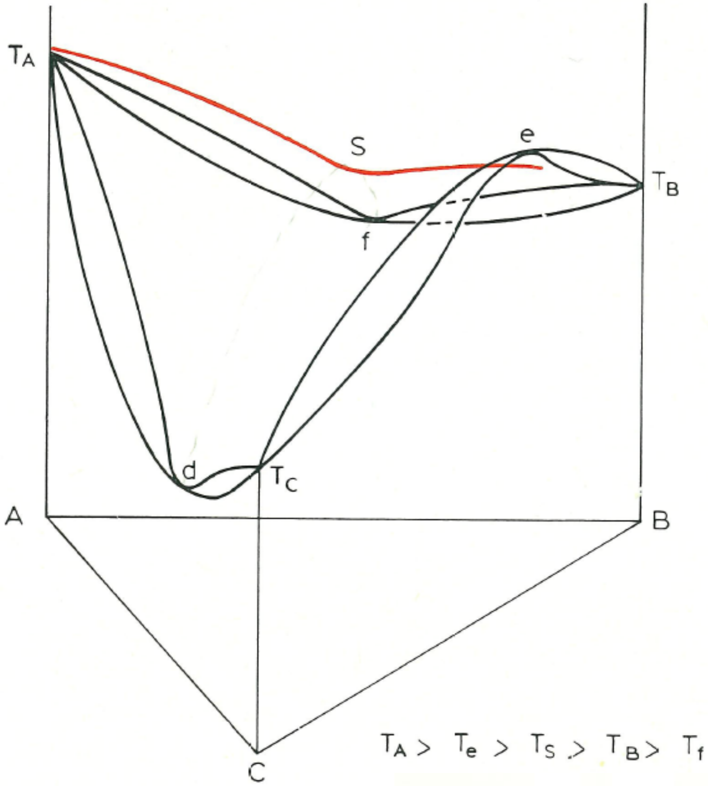
Projection of liquidus isotherms

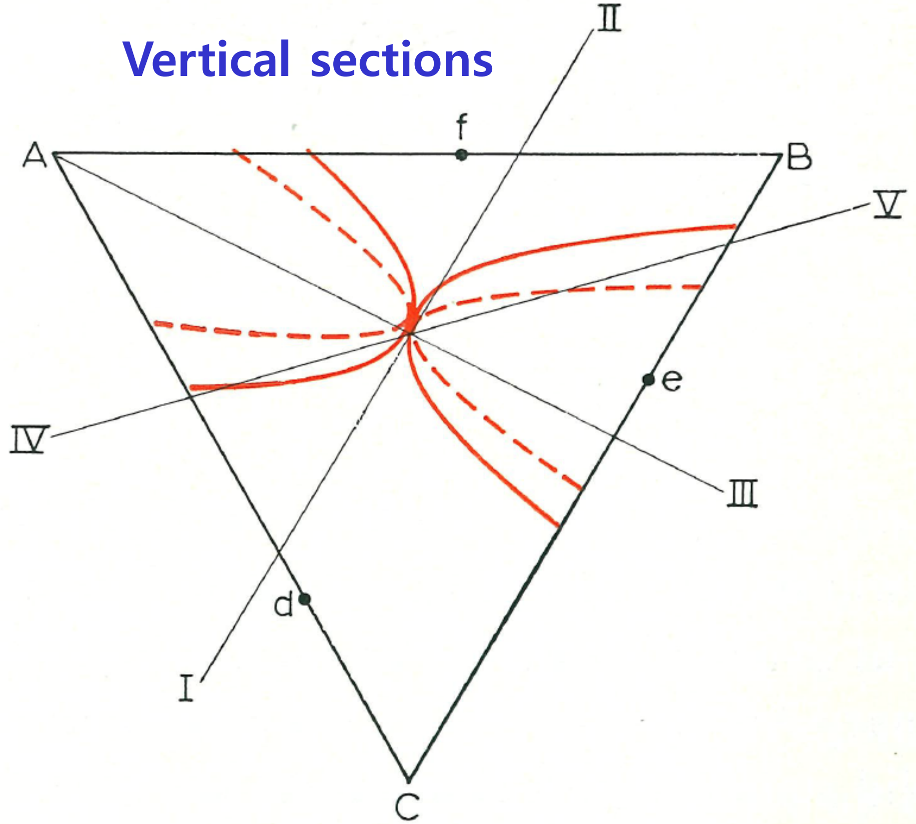


S : <u>saddle pt. where liquidus & solidus surfaces meet</u>

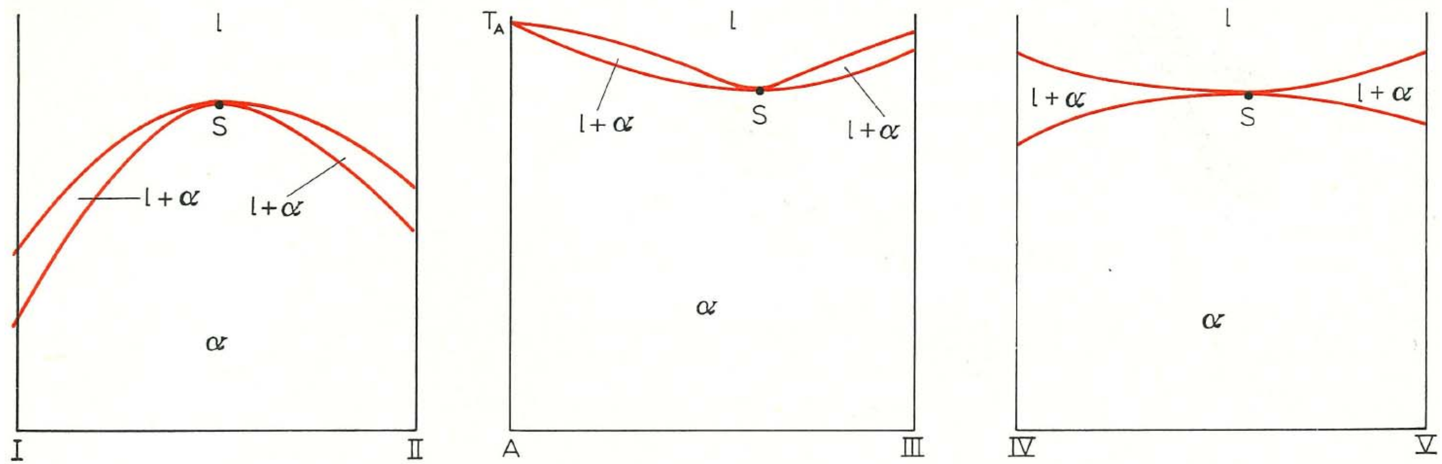
8.4.2 Variants of the phase diagram
(more complex system)

Vertical sections





$T_A > T_e > T_S > T_B > T_f > T_C > T_d$

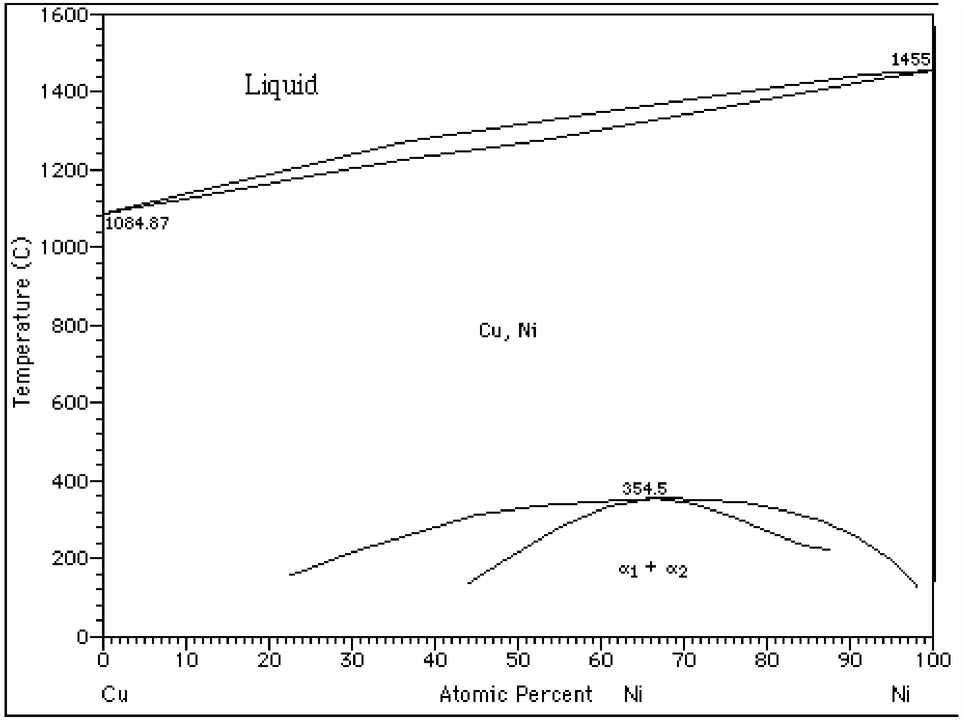


8.4 TWO-PHASE EQUILIBRIUM

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

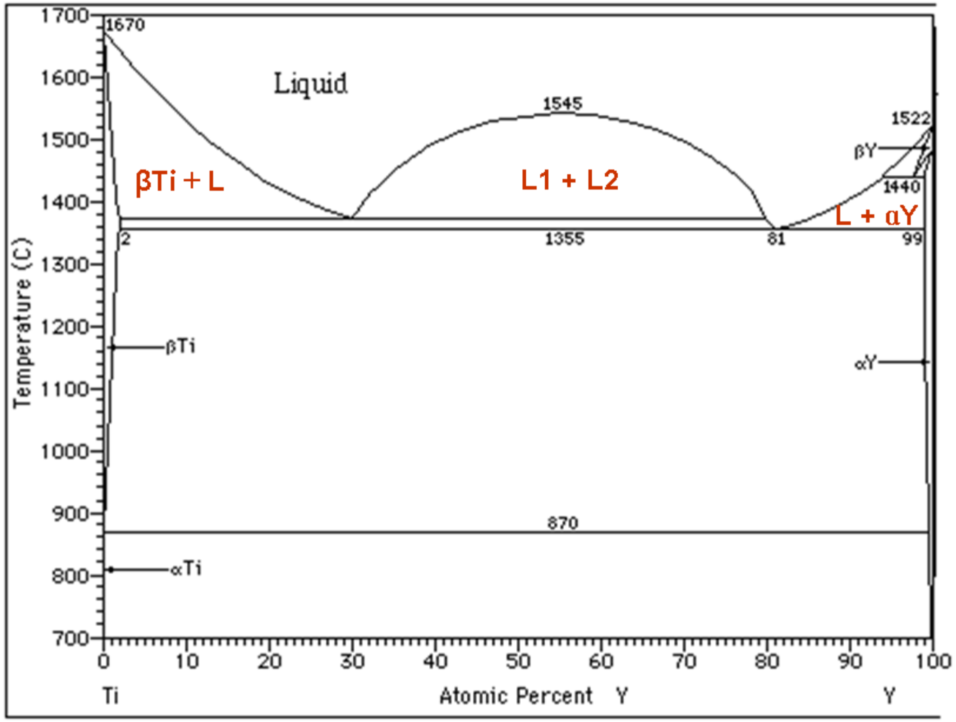
Miscibility gap

$\varepsilon > 0,\ \Delta H_{mix} > 0$



$\Delta H_{mix} \sim +26$ kJ/mol

$\varepsilon >> 0,\ \Delta H_{mix} >> 0$



$\Delta H_{mix} \sim +58$ kJ/mol

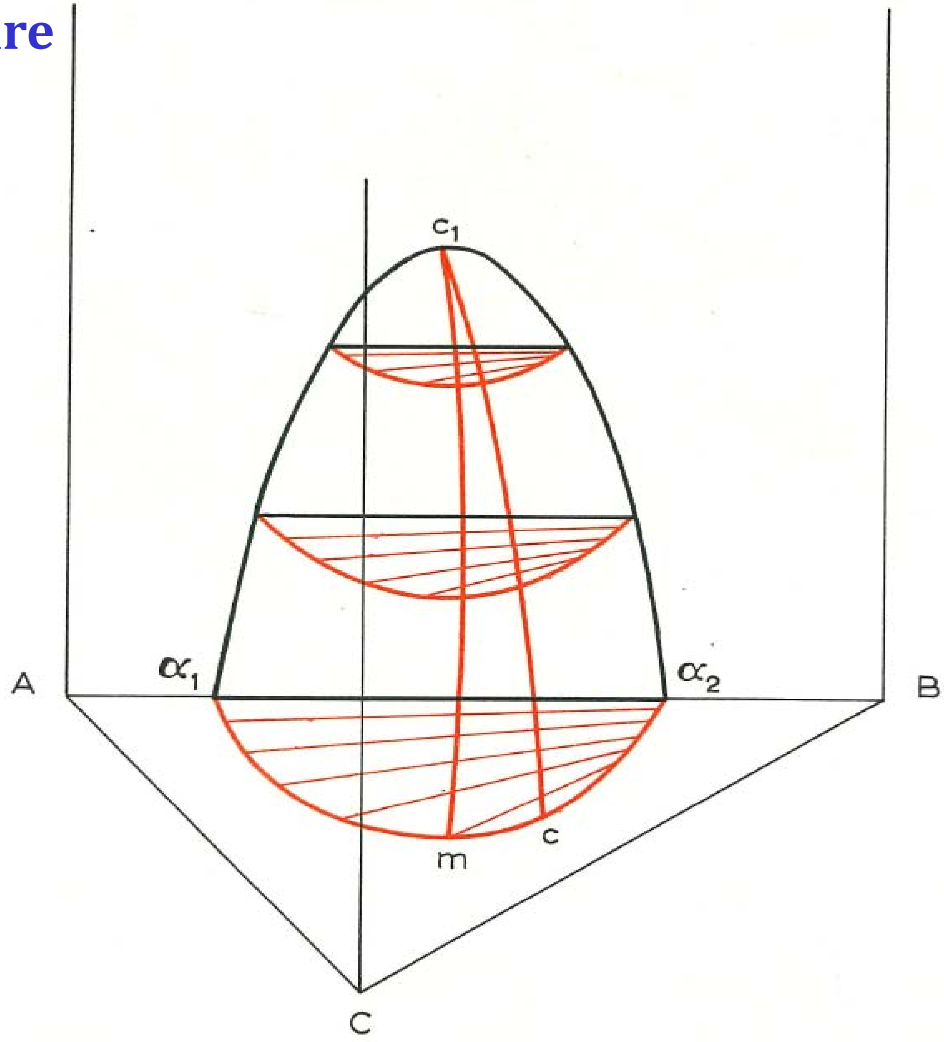
8.4 TWO-PHASE EQUILIBRIUM

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

Miscibility gap

a. Ternary system with a closed miscibility gap associated with a binary critical point c_1

- effect of temperature



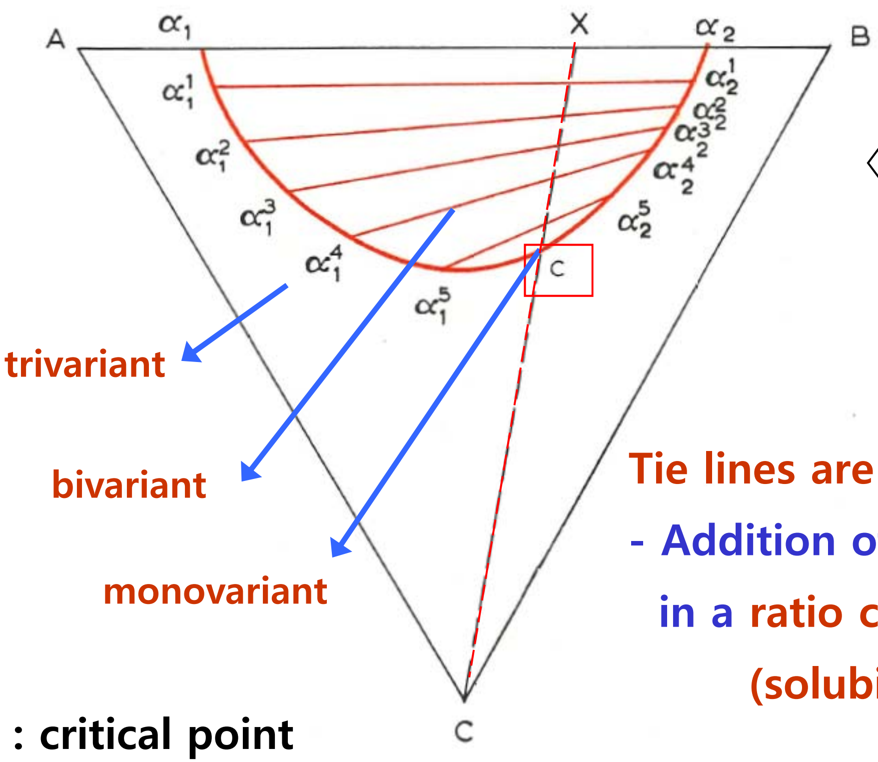
8.4 TWO-PHASE EQUILIBRIUM

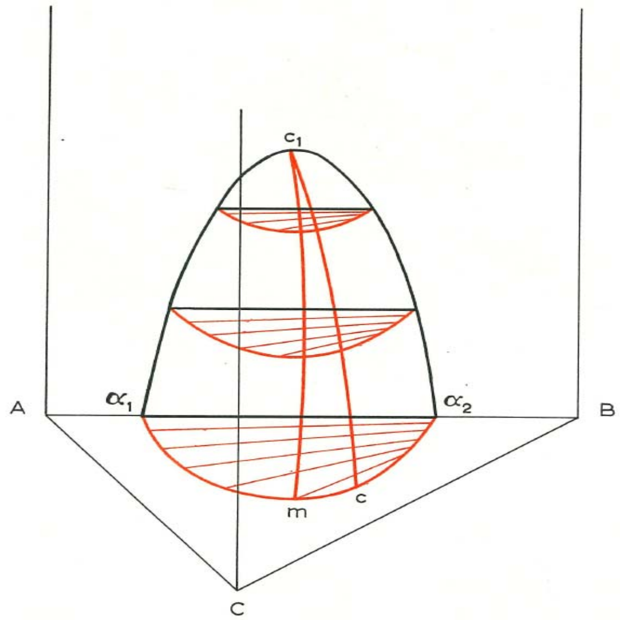
8.4.3. Two-phase equilibrium between solid or liquid solutions: $\alpha_1 \rightleftarrows \alpha_2$ or $l_1 \rightleftarrows l_2$

Miscibility gap

a. Ternary system with only a binary critical point

- Isothermal section at room temp.





Tie lines are not parallel to the binary tie line.

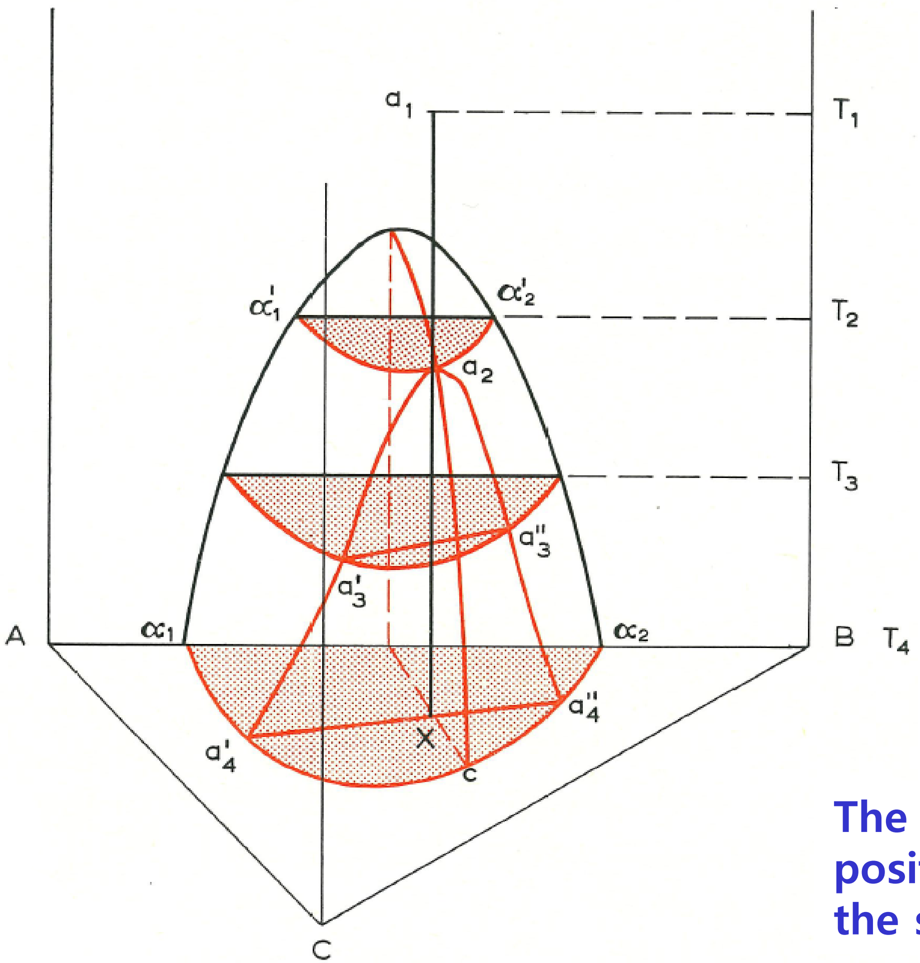
- Addition of C to a heterogeneous mixture of A & B in a ratio corresponding to the distribution of C (solubility)

C : critical point

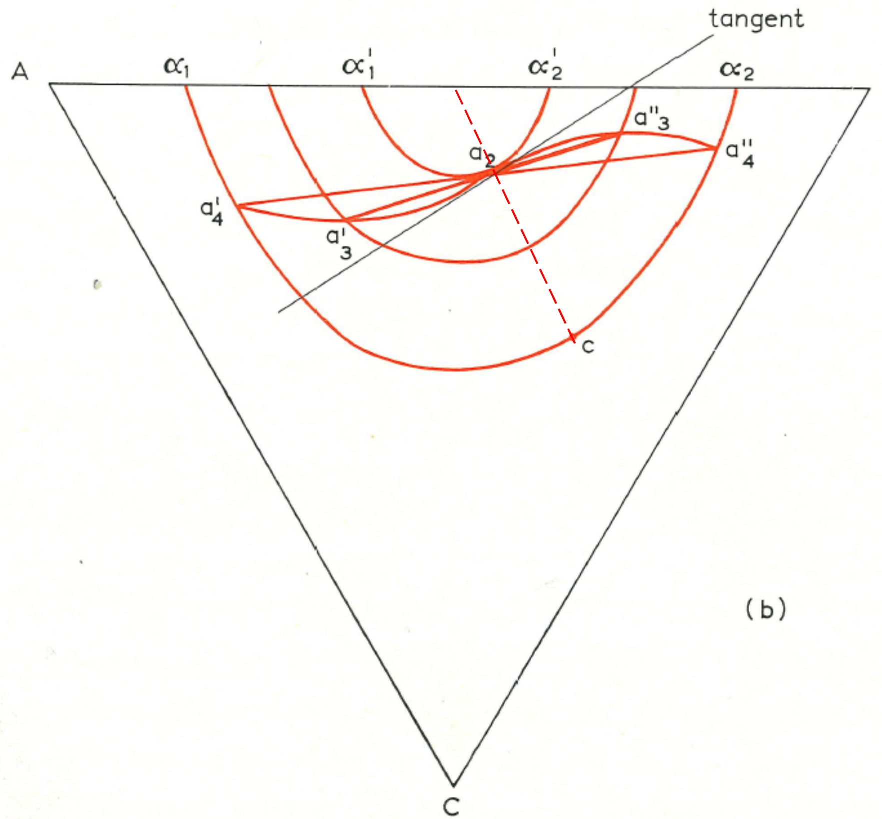
(Max. point, m ≠ critical point, c in most cases)

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

(a) Transformation in alloy X on cooling from the $\alpha_{1(2)}$ phase region

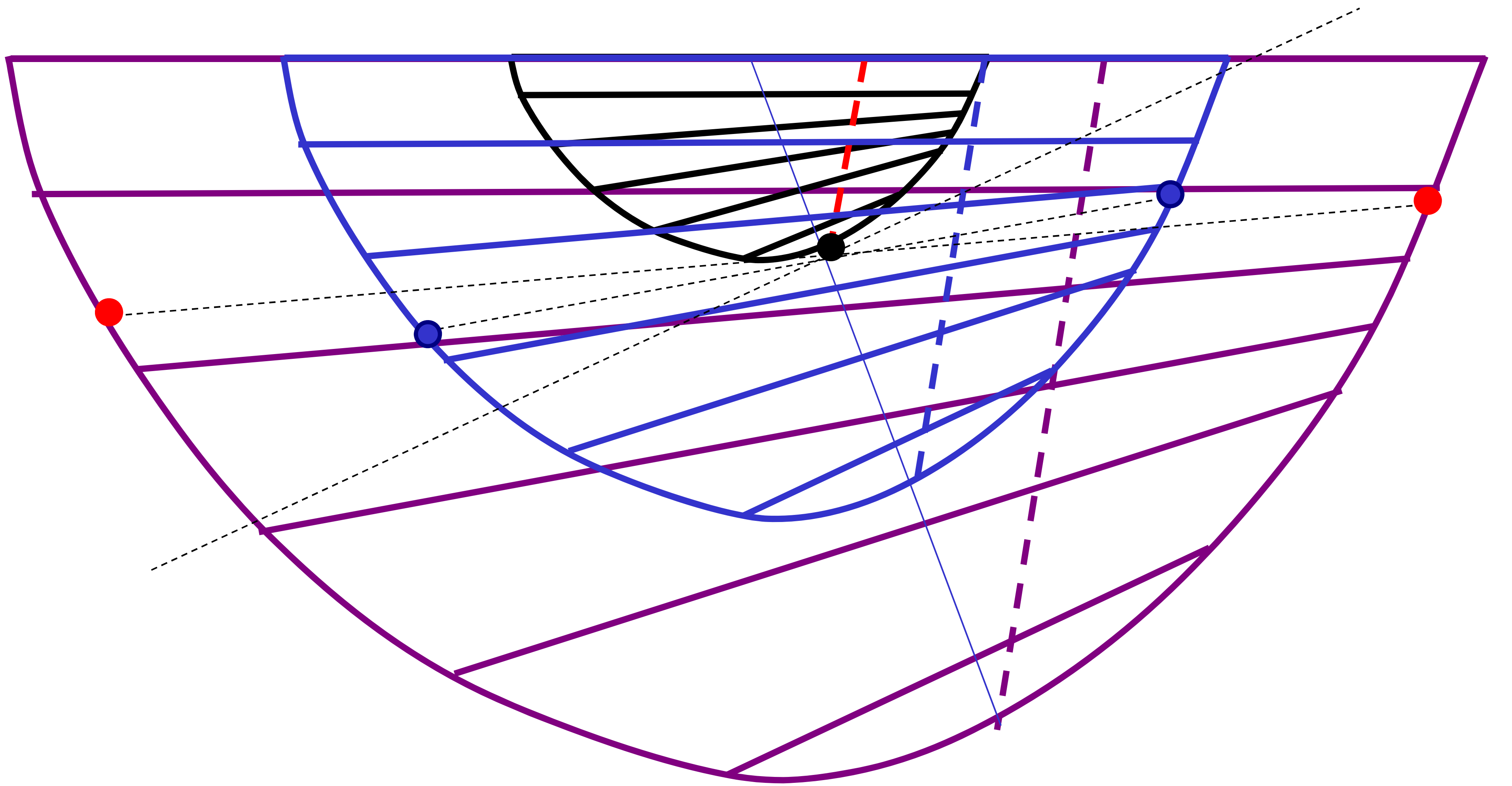


(b) Changes in composition of the co-exisitng α_1 and α_2 phases

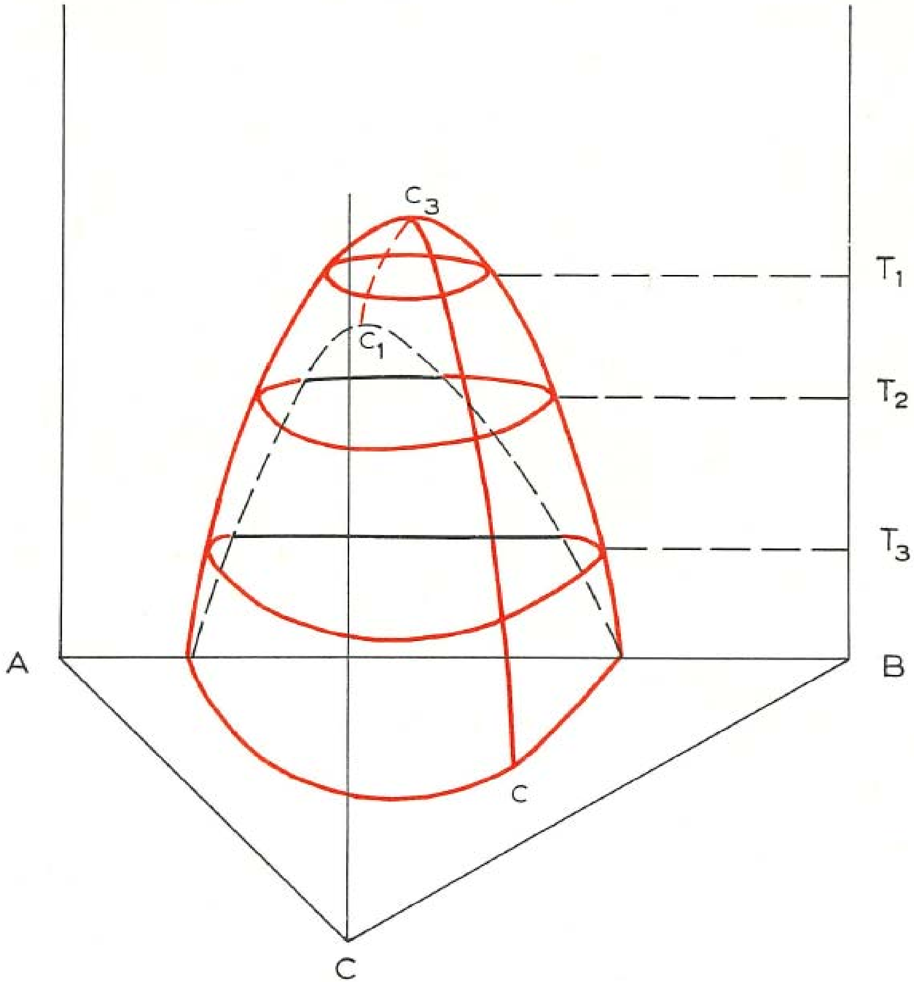


The course of the curves is defined by the relative position of the tie lines which skew round towards the side AB as the temperature decreases.

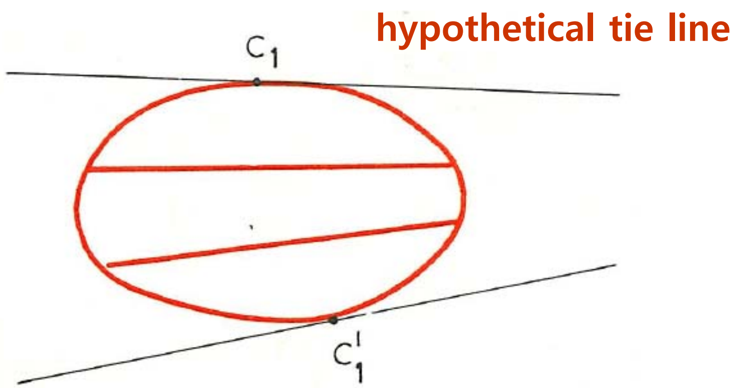
➡ Curves changes along a line which is tangential to the solubility curve



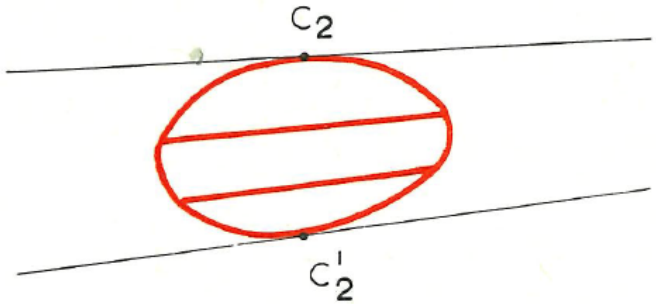
b. A ternary system with a binary and a ternary critical point



Isotherms



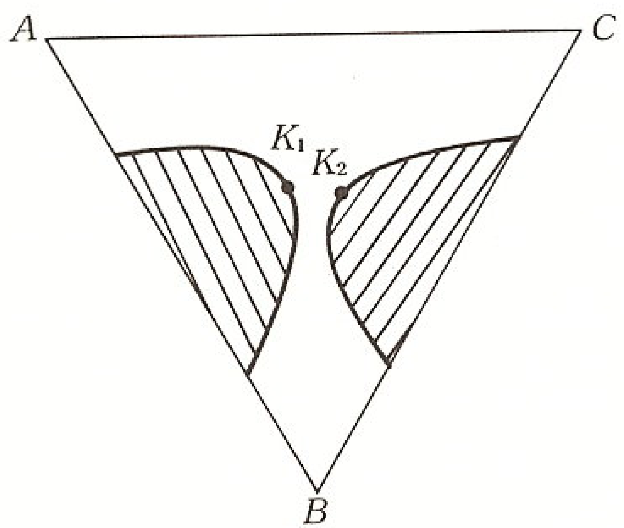
(a) The binary critical point temperature

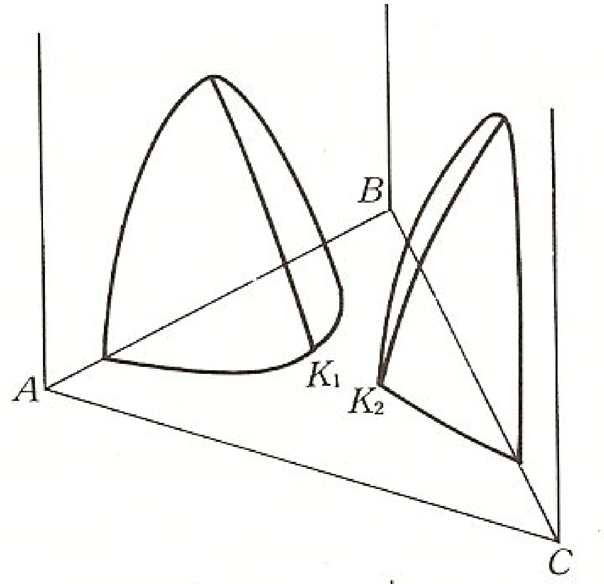


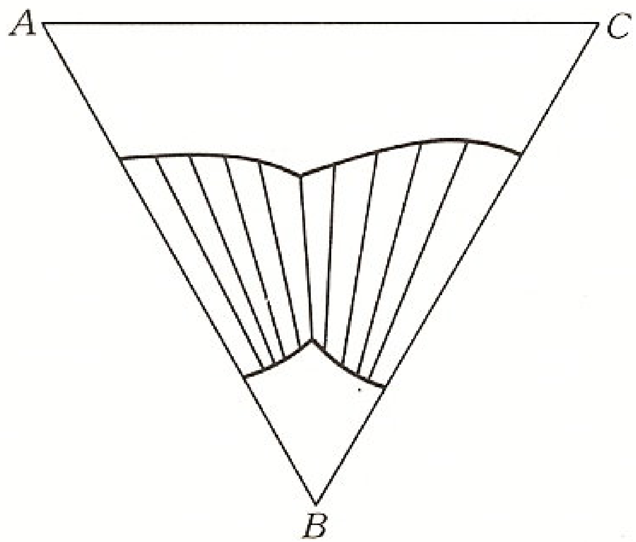
(b) A temperature between c_1 and c_3

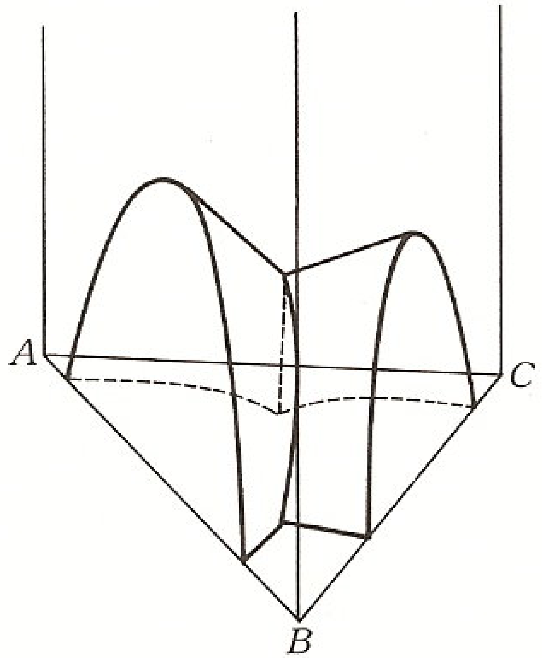
(c) The ternary critical point temperature

c. ternary system with two miscibility gaps

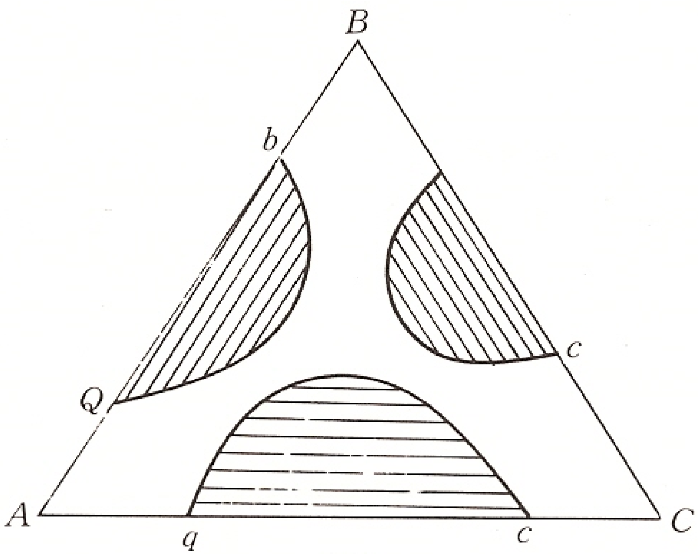




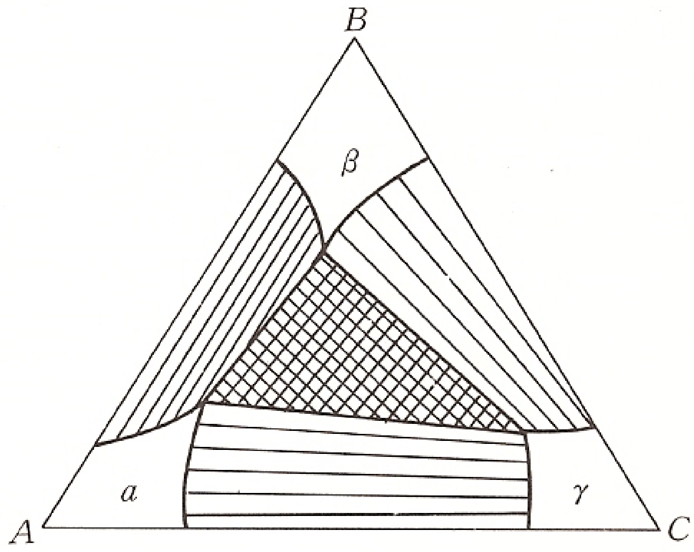




c. Ternary system with three miscibility gaps

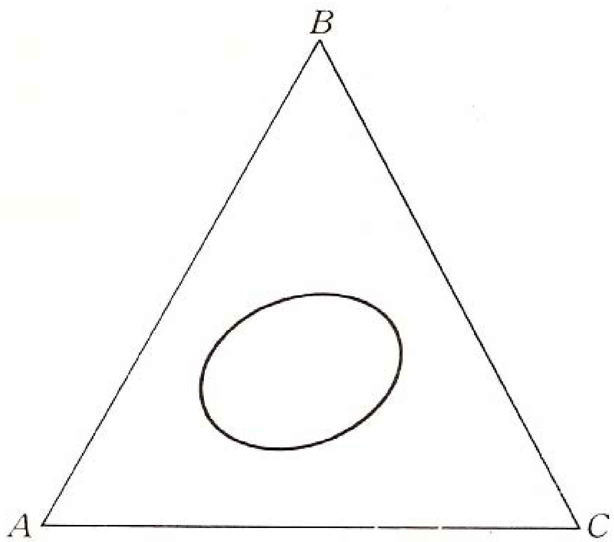


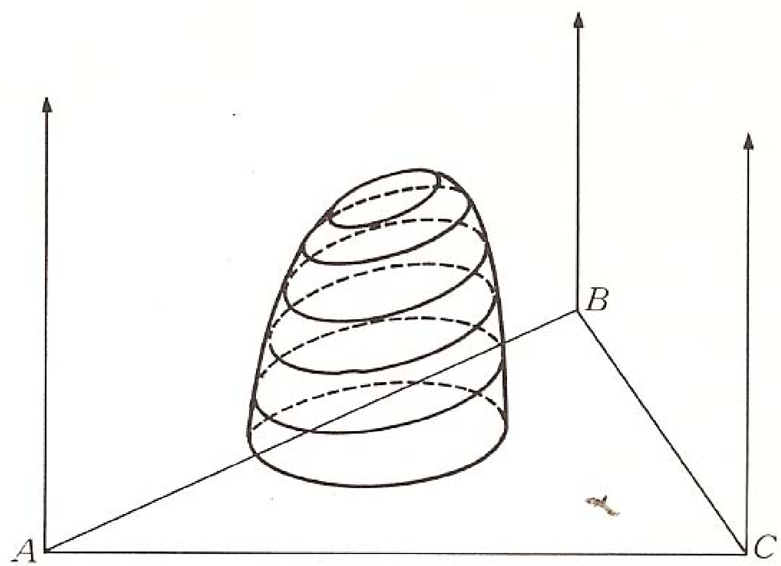
(a)



(b)

d. Ternary system with miscibility gap in three component region





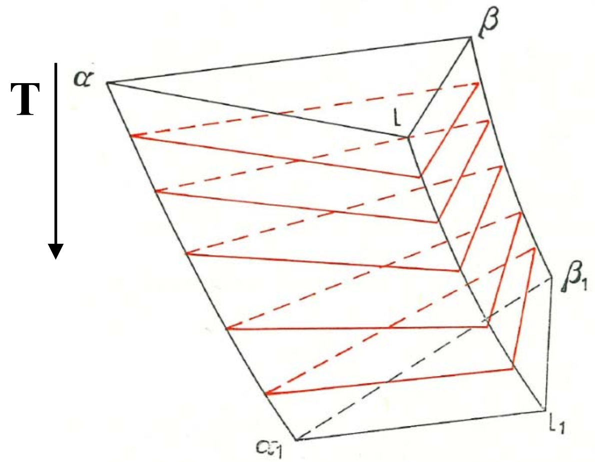
Chapter 9. Ternary phase Diagrams

Three-Phase Equilibrium

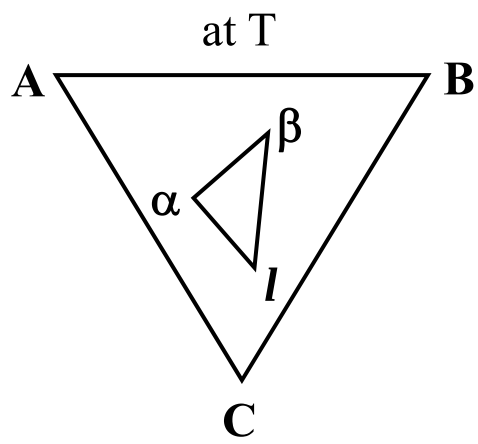
9.1. PROPERTIES OF THREE-PHASE TIE TRIANGLES

Two phase equil. (f = 2)
- ideal system
- liquidus max. (or min.)
- miscibility gap

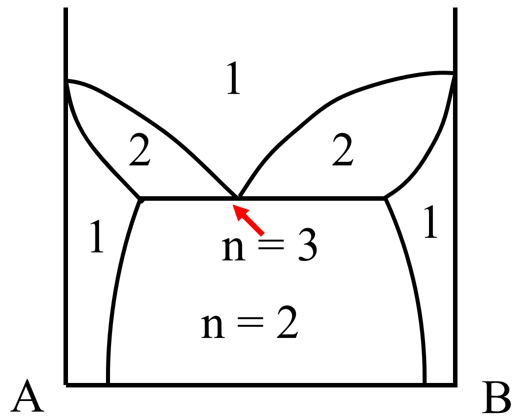
Three phase equil. (f = 1)
- **Tie triangle**



① vertex of tie triangle
→ composition of three phases

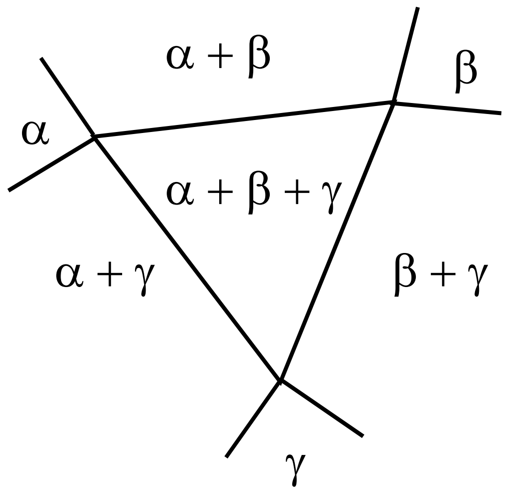


cf) *n* phase region is surrounded by $n \pm 1$ phase region



9.1. PROPERTIES OF THREE-PHASE TIE TRIANGLES

② tie triangle will be surrounded by 2 phase region

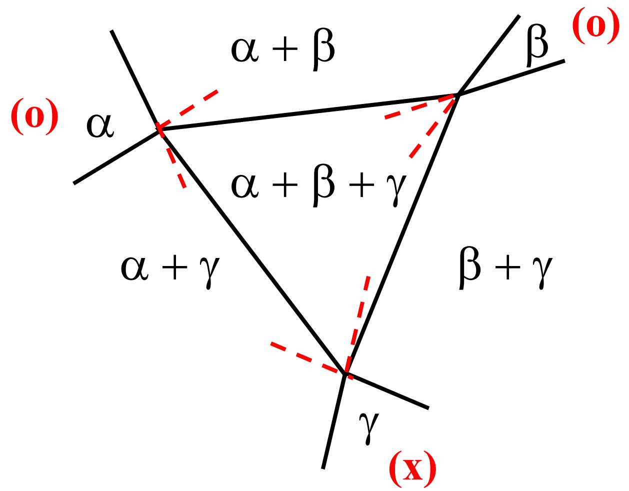


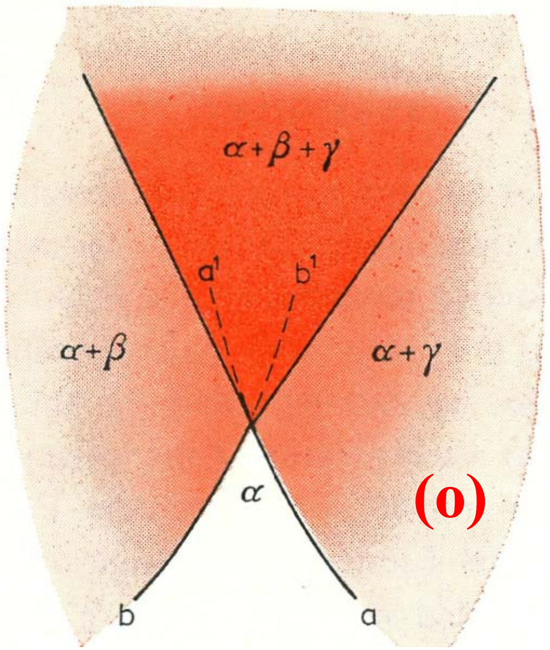
③ at vertex, single phase region will exist.

④ rule for phase boundary between single and two phase regions

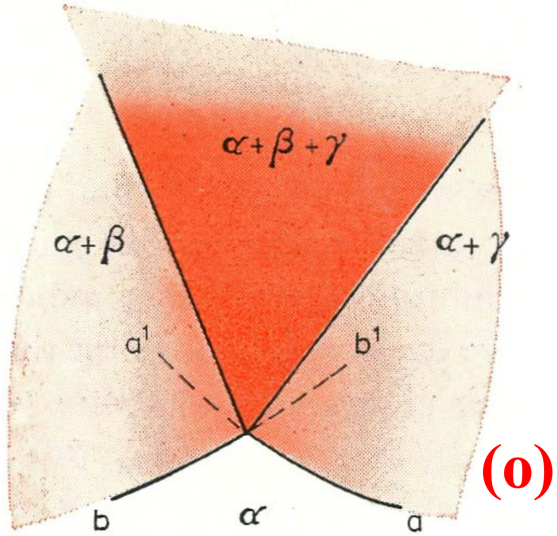
- extension of boundary (two)

→ **both should toward outside the triangle or inside the triangle**

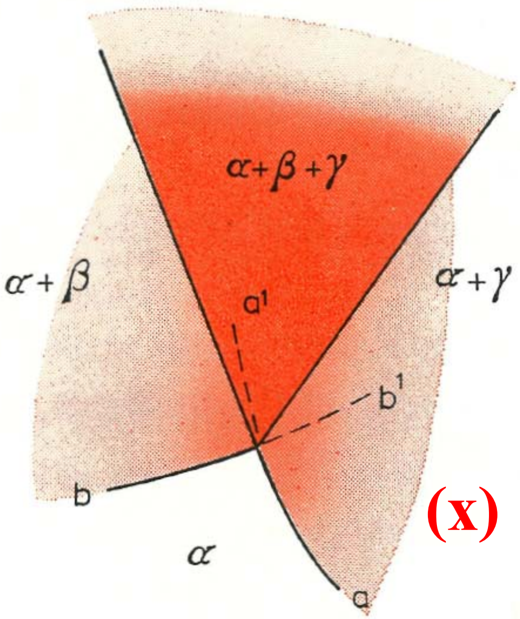




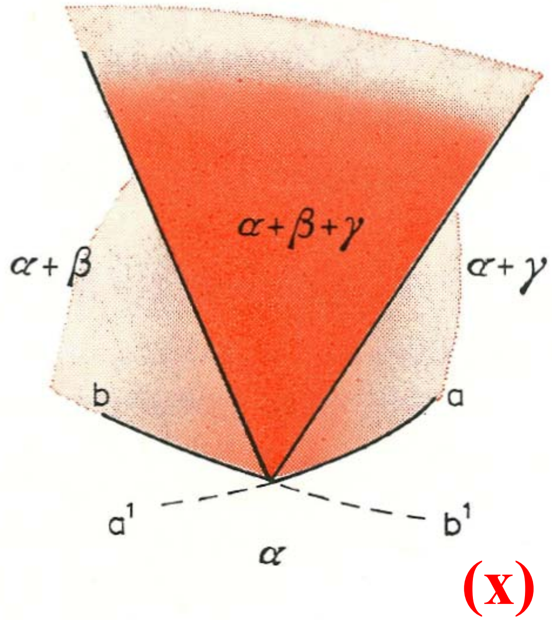
$\alpha+\beta+\gamma$
a^1
b^1
$\alpha+\beta$
$\alpha+\gamma$
α
(o)
b
a



$\alpha+\beta+\gamma$
$\alpha+\beta$
$\alpha+\gamma$
a^1
b^1
(o)
b
α
a



$\alpha+\beta+\gamma$
$\alpha+\beta$
$\alpha+\gamma$
a^1
b^1
b
(x)
α
a



$\alpha+\beta+\gamma$
$\alpha+\beta$
$\alpha+\gamma$
b
a
a^1
b^1
α
(x)

9.2. THREE-PHASE EQUILIBRIUM

① **Coalescence of <u>miscibility gap</u> and <u>two phase region</u>**

- **How we can have 3 phase equil.?**

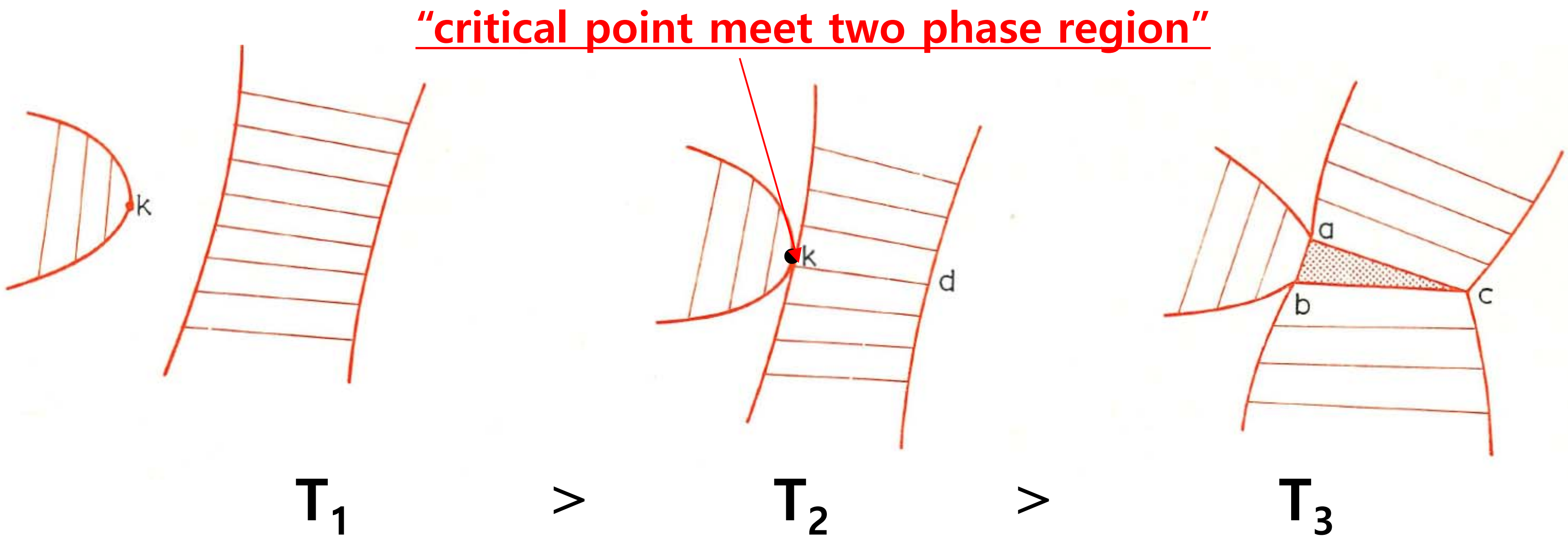
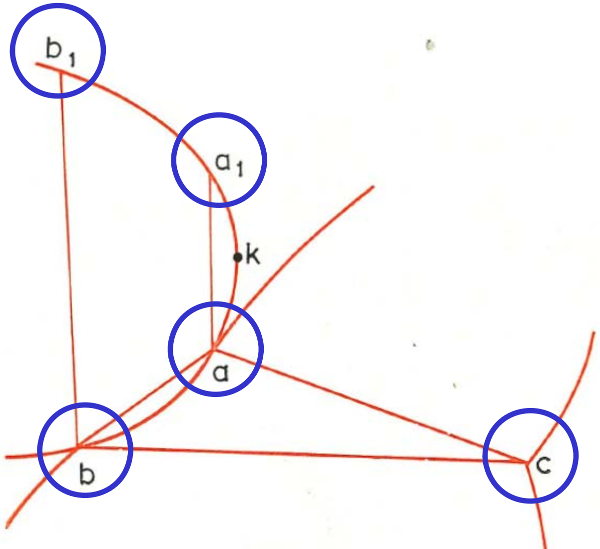


Fig. 136. Production of a ternary three-phase equilibrium by the coalescence of two two-phase regions

9.2. THREE-PHASE EQUILIBRIUM

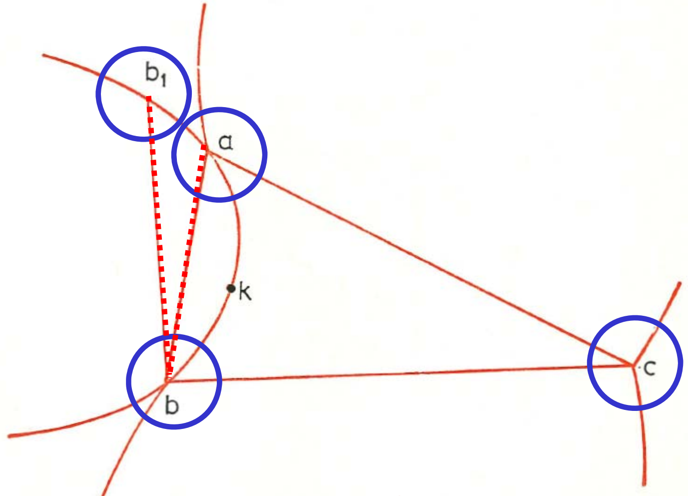
① Coalescence of miscibility gap and two phase region

- **When does not meet at critical point ?**



<u>Five phase equilibrium: this is impossible.</u>

- **When two phase region does not overlapped onto same tie line in miscibility gap region?**



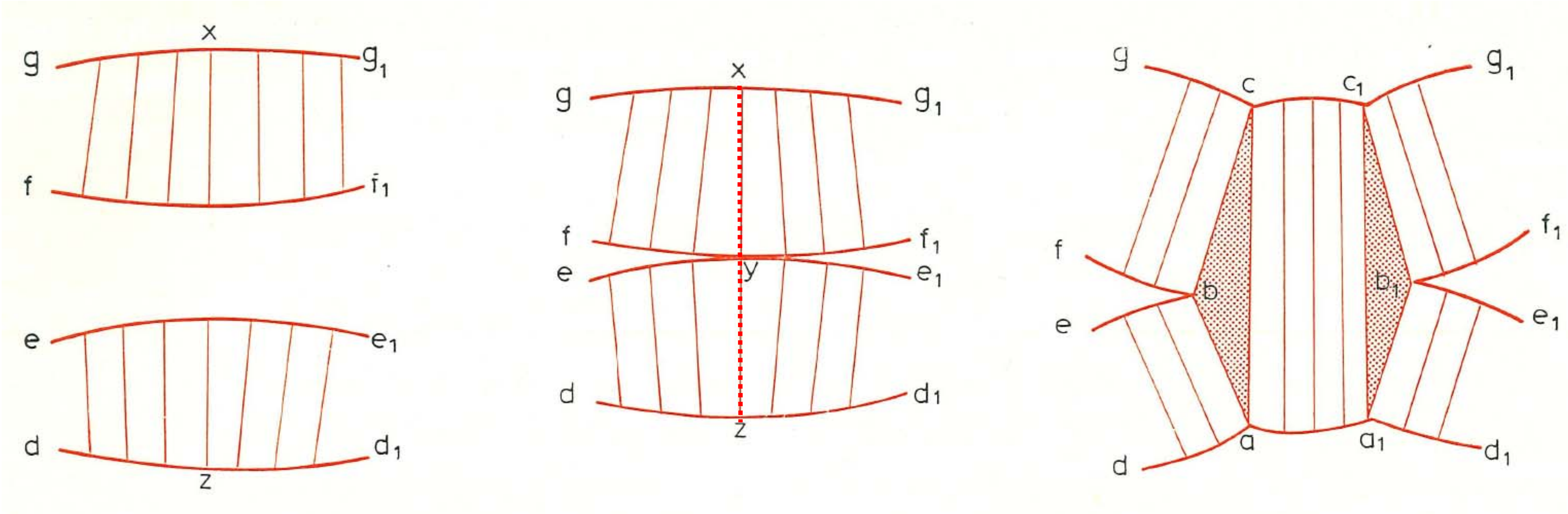
<u>impossible condition of two tie lines: ab and bb_1</u>

Fig. 137. Conditions for the coalescence of two two-phase regions.
(a) Initial contact of the phase regions with point *k* outside curve *ab*
(b) initial contact with point k on curve *ab*.

⇨ **<u>Phase a and b lie on the same tie line</u> and with fall in temperature these phases approach <u>point k, which is the first point of contact with the second two-phase region</u>.**

9.2. THREE-PHASE EQUILIBRIUM

② Coalescence of two two-phase region



T_1 > T_2 > T_3

Two three-phase tie triangles *abc* and *$a_1b_1c_1$*

Fig. 138. Alternative method to Fig. 136 for the production of a ternary three-phase equilibrium by the coalescence of two two-phase regions

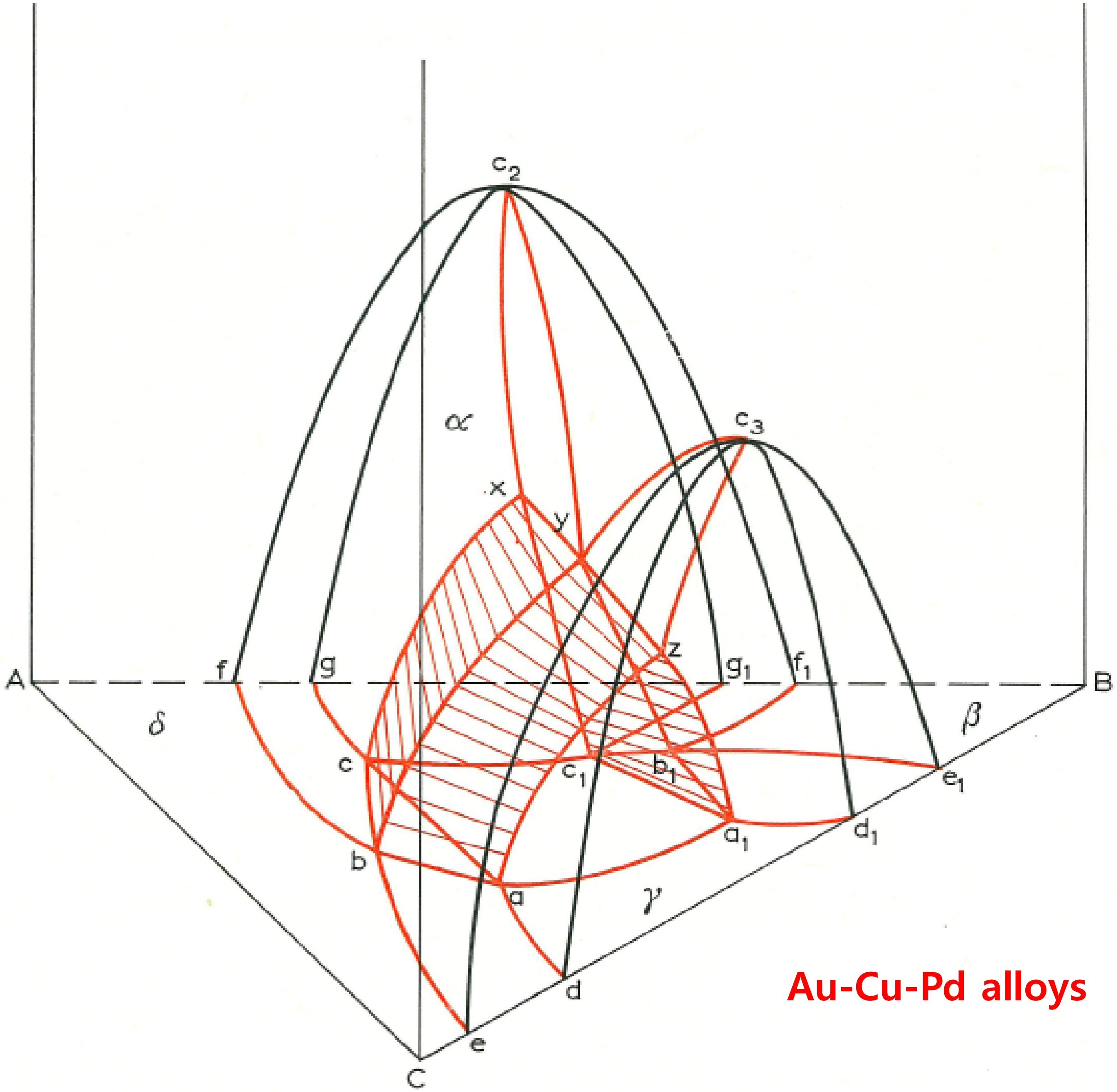
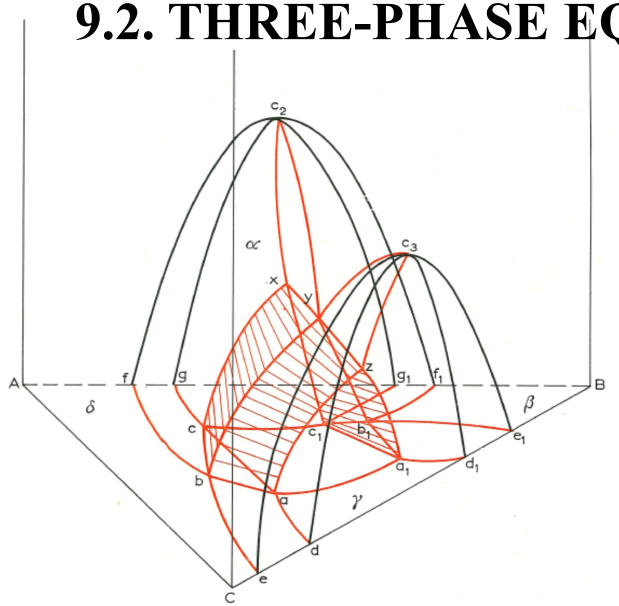
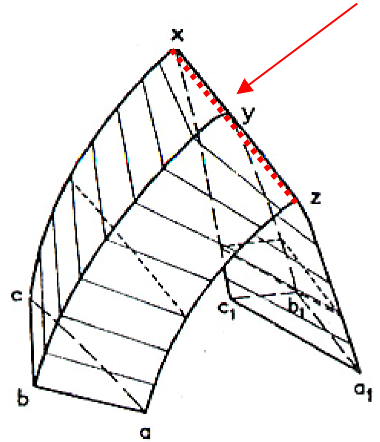


Fig. 139. Space model of a ternary system corresponding to Fig. 138

9.2. THREE-PHASE EQUILIBRIUM



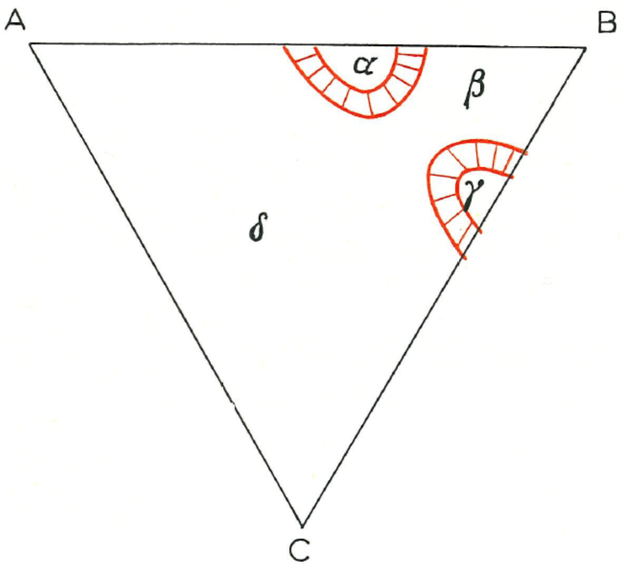
Degenerate tie triangle



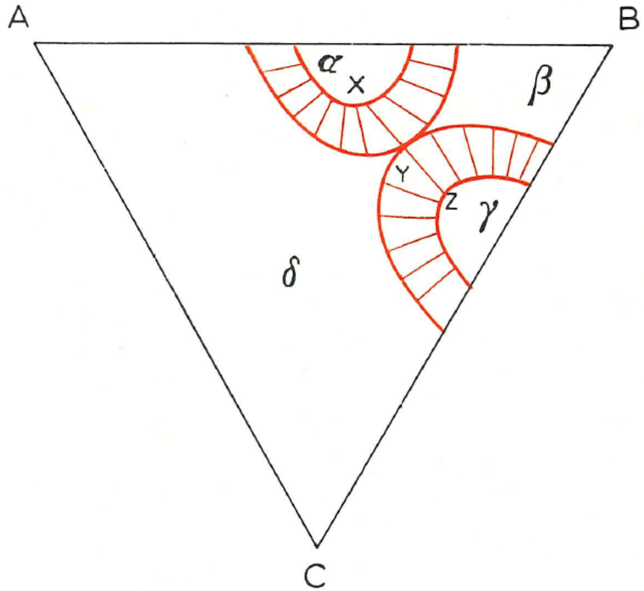
→ *n* component system, reaction between *n* phases occur then the temperature is max or min

→ ternary system, 3 phases are in a straight line as three points.

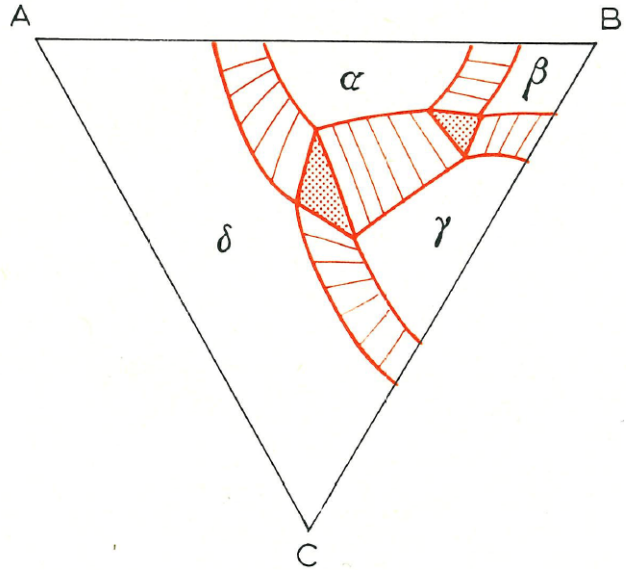
Three isothermal sections



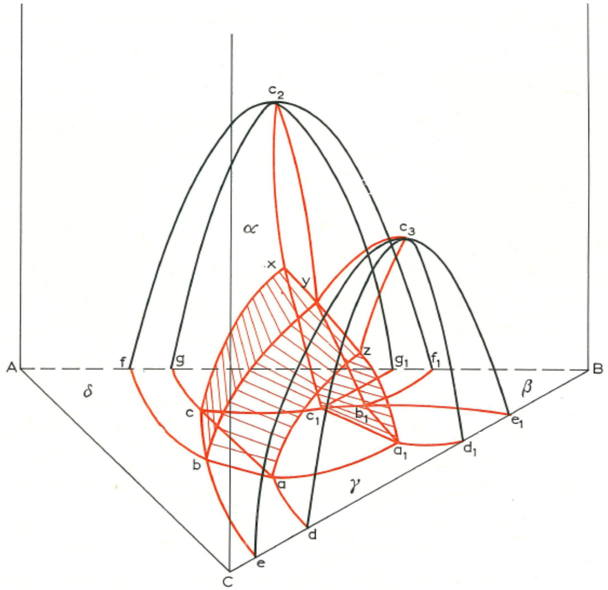
$T_1 > T_{xyz}$ (T_2)

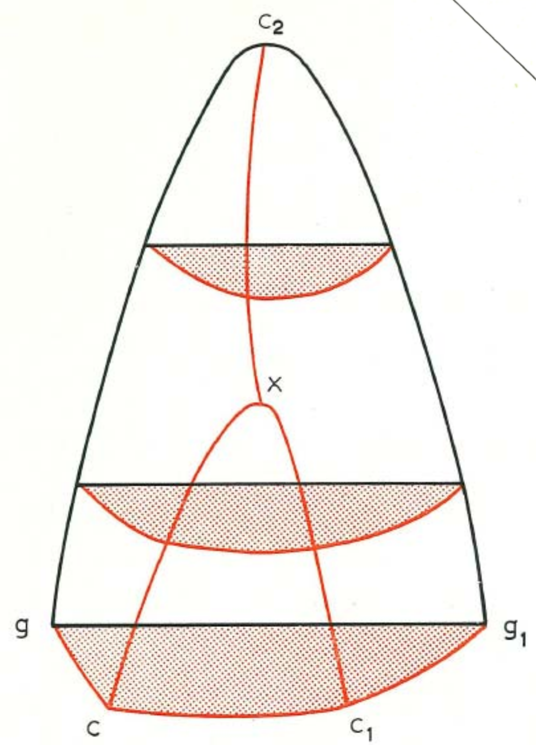


$T_2 = T_{xyz}$

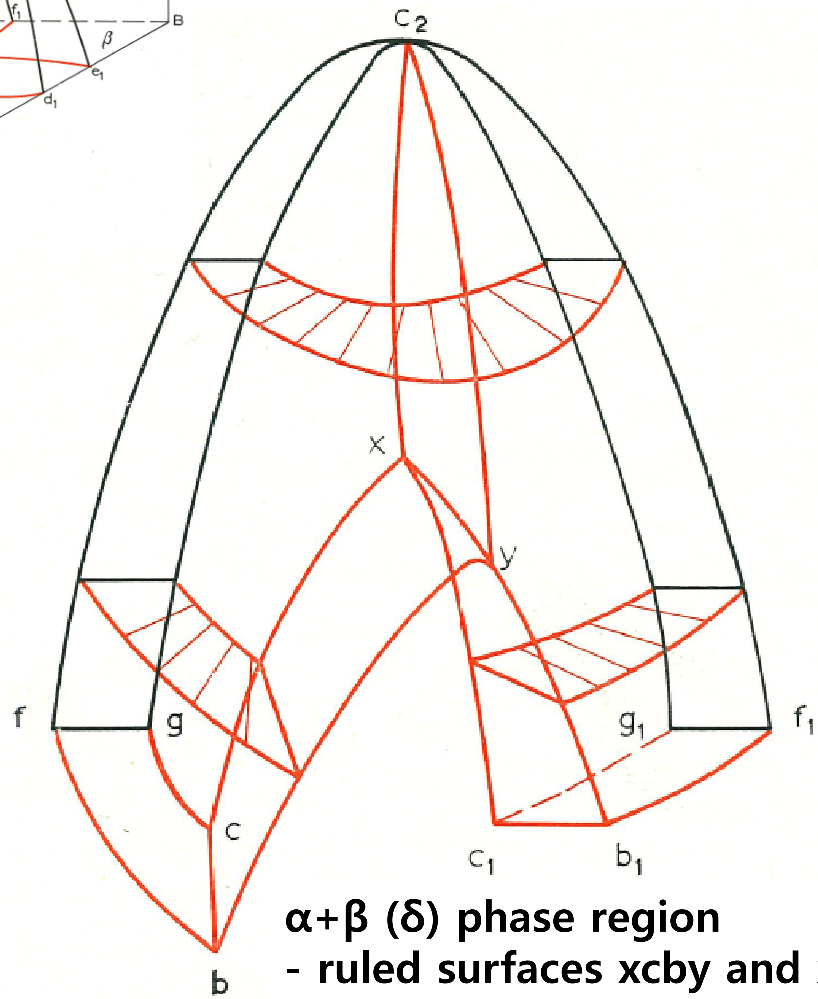


$T_3 < T_{xyz}$ (T_2)

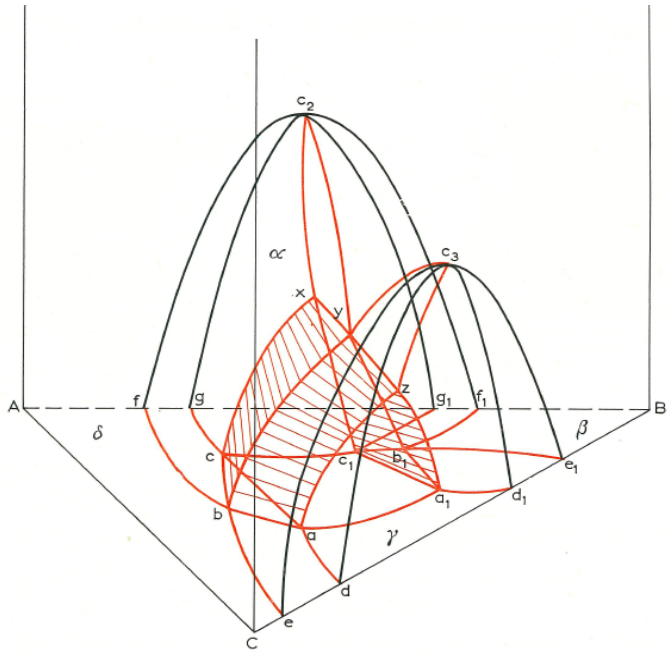


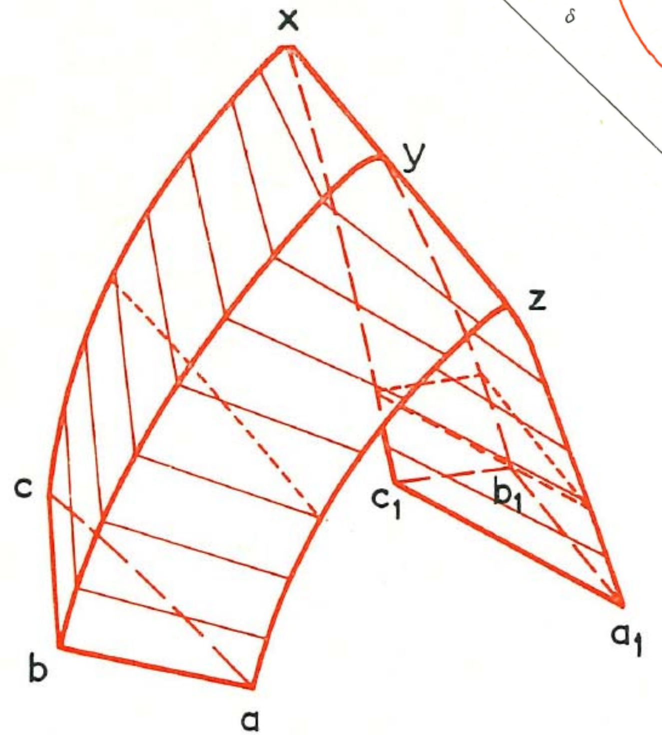


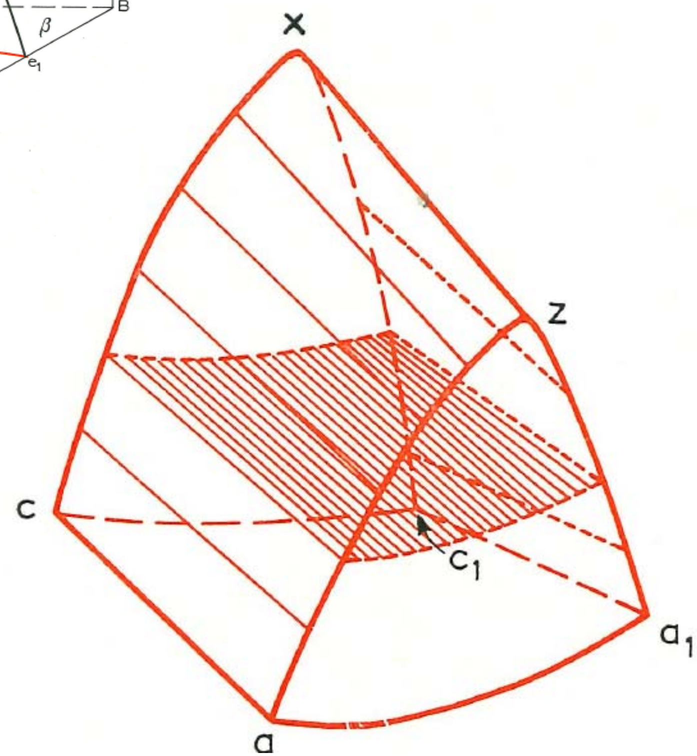
α phase region



α+β (δ) phase region
- ruled surfaces xcby and xc_1b_1y







α+β(δ)+γ phase region
-ruled surfaces xcby, ybaz, xcaz,
xc_1b_1y, yb_1a_1z and xc_1a_1z

α+ γ phase region
- ruled surfaces xcaz and xc_1a_1z

"Ternary Phase diagram"

" Two phase equilibrium (f = 2)"

1) <u>Two-phase equilibrium</u> between the liquid and a solid solution
2) Ternary <u>two-phase equilibrium</u> with a saddle point
3) <u>Two-phase equilibrium</u> between solid or liquid solutions: $\alpha_1 \rightleftarrows \alpha_2$ or $l_1 \rightleftarrows l_2$

Miscibility gap

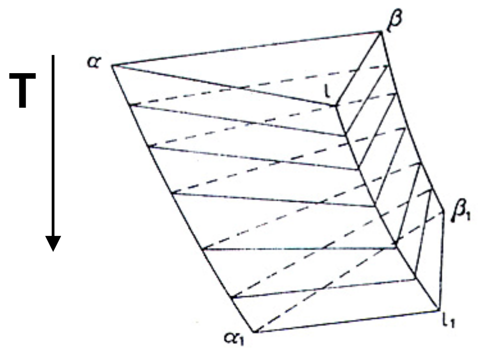
* Tie lines are not parallel to the binary tie line.

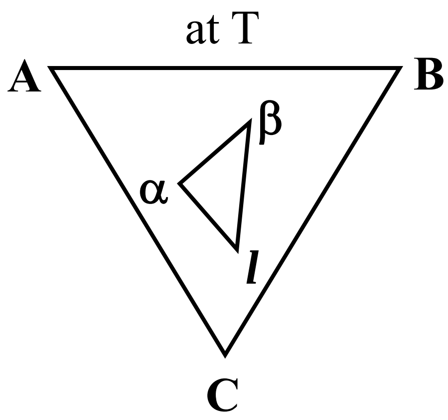
- Addition of C to a heterogeneous mixture of A & B in a ratio corresponding to the distribution of C

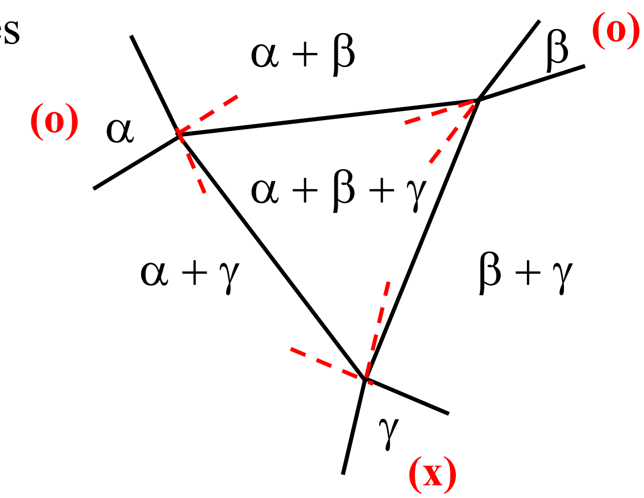
" Three phase equilibrium (f =1)"

• Tie triangle

vertex of tie triangle
→ composition of three phases







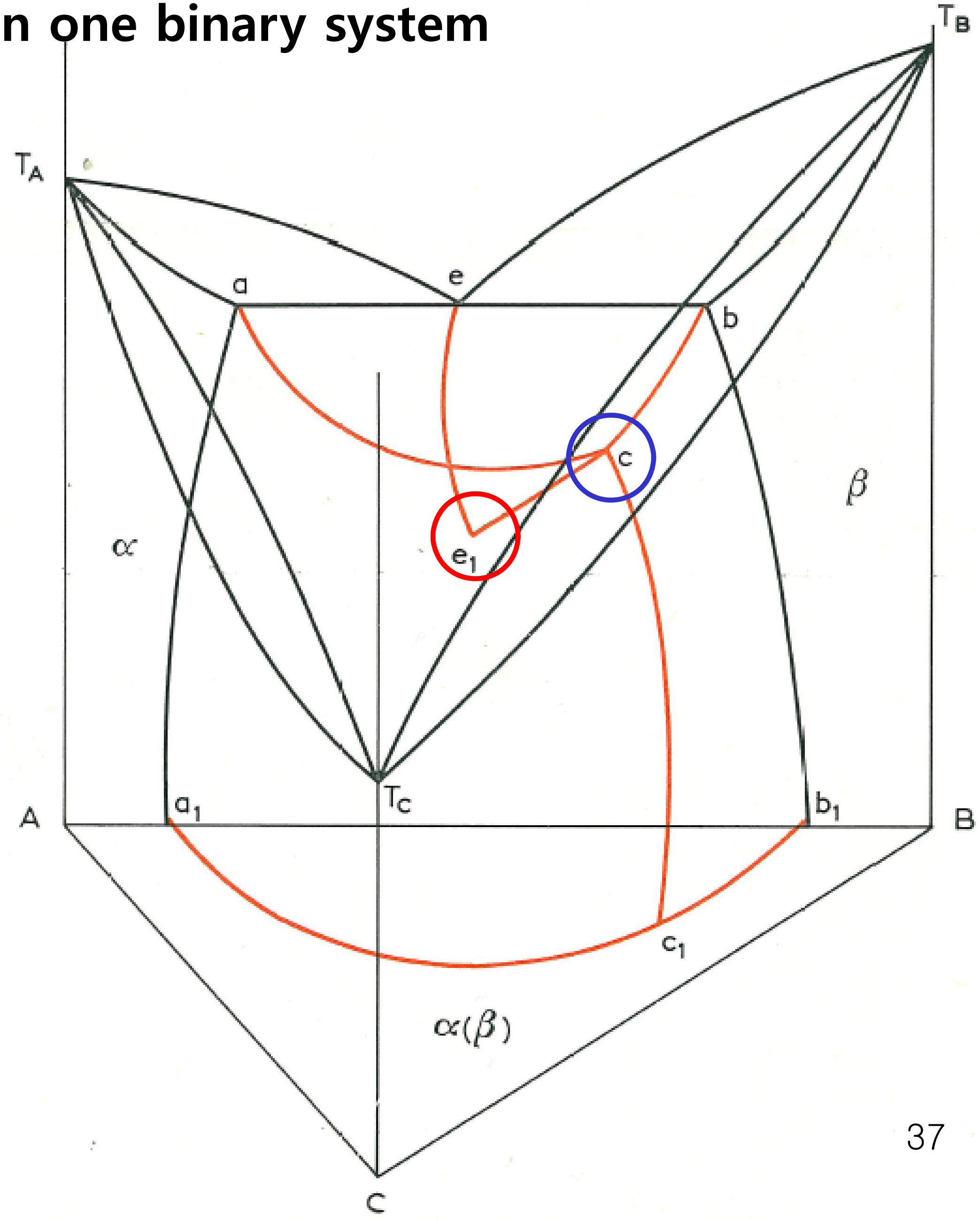
① Coalescence of miscibility gap and two phase region

② Coalescence of two two-phase region

9.3. THREE-PHASE EQUILIBRIUM INVOLVING EUTECTIC REACTIONS

9.3.1. A eutectic solubility gap in one binary system

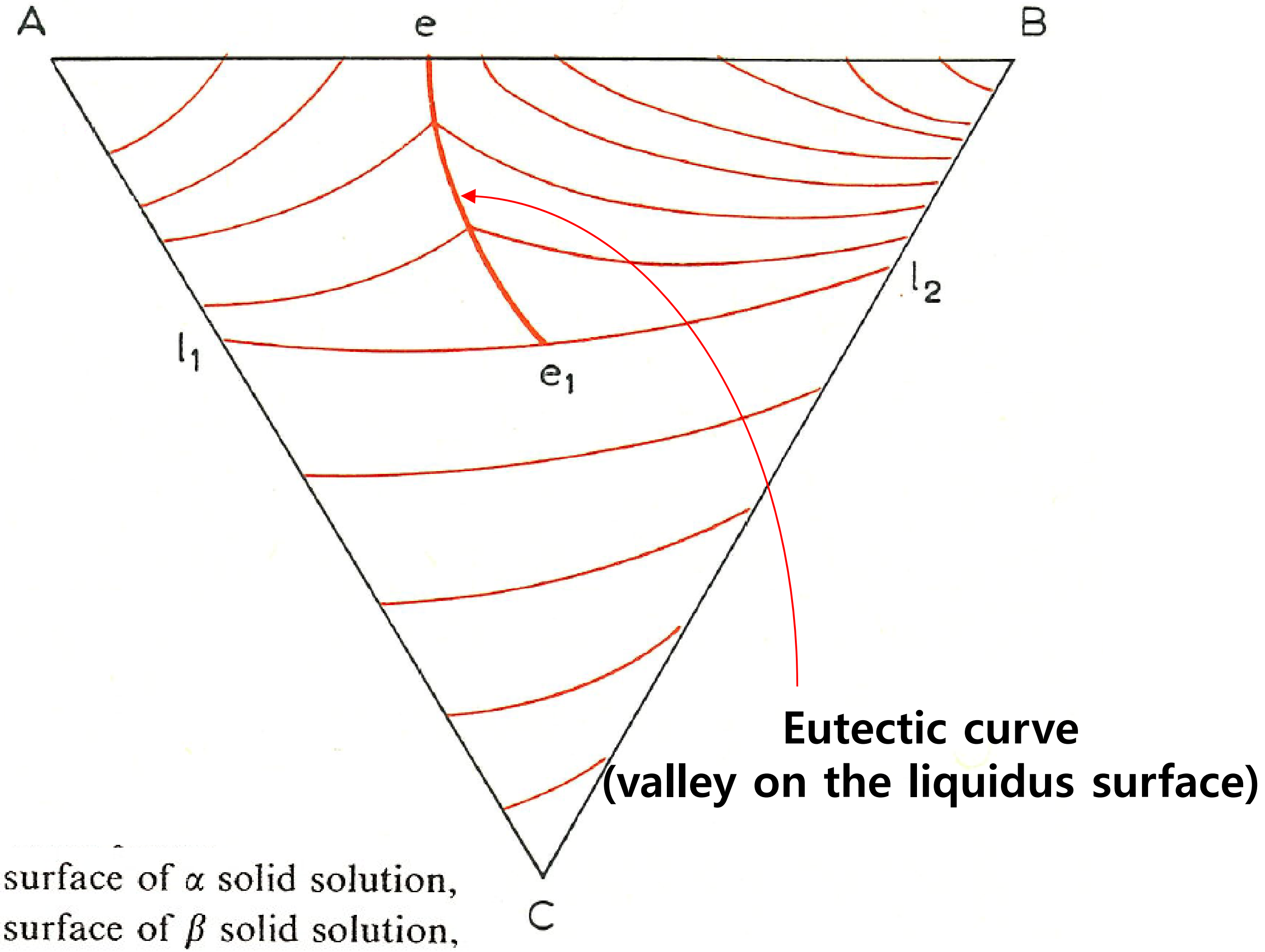
- One binary eutectic : AB
  Complete solid solution : BC, AC



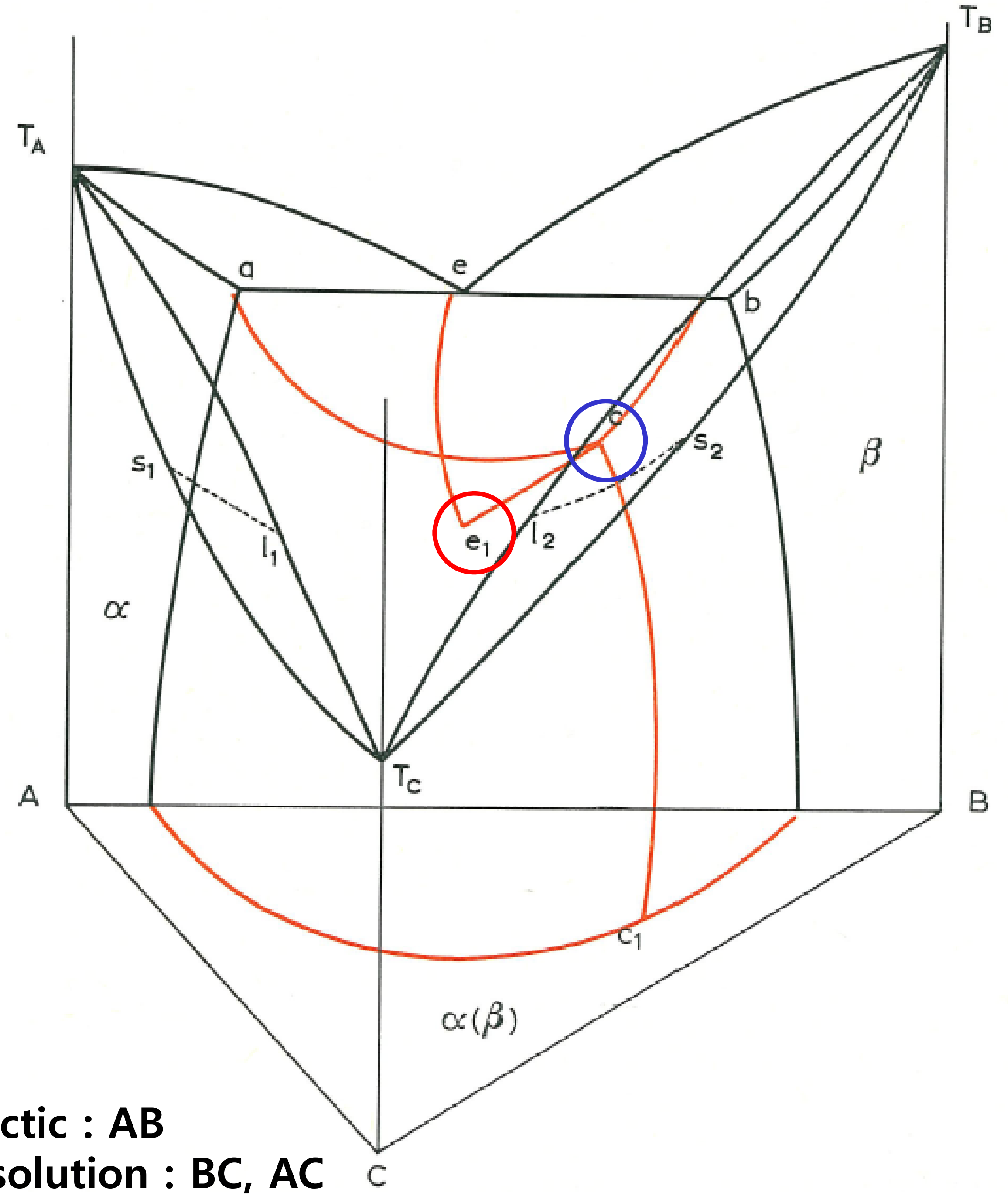
9.3. THREE-PHASE EQUILIBRIUM INVOLVING EUTECTIC REACTIONS

- **Polythermal Projection**

The liquidus surface



$T_A e e_1 l_1 T_A$ – the liquidus surface of α solid solution,
$T_B e e_1 l_2 T_B$ – the liquidus surface of β solid solution,
$l_1 e_1 l_2 T_C l_1$ – the liquidus surface of $\alpha(\beta)$ solid solution.

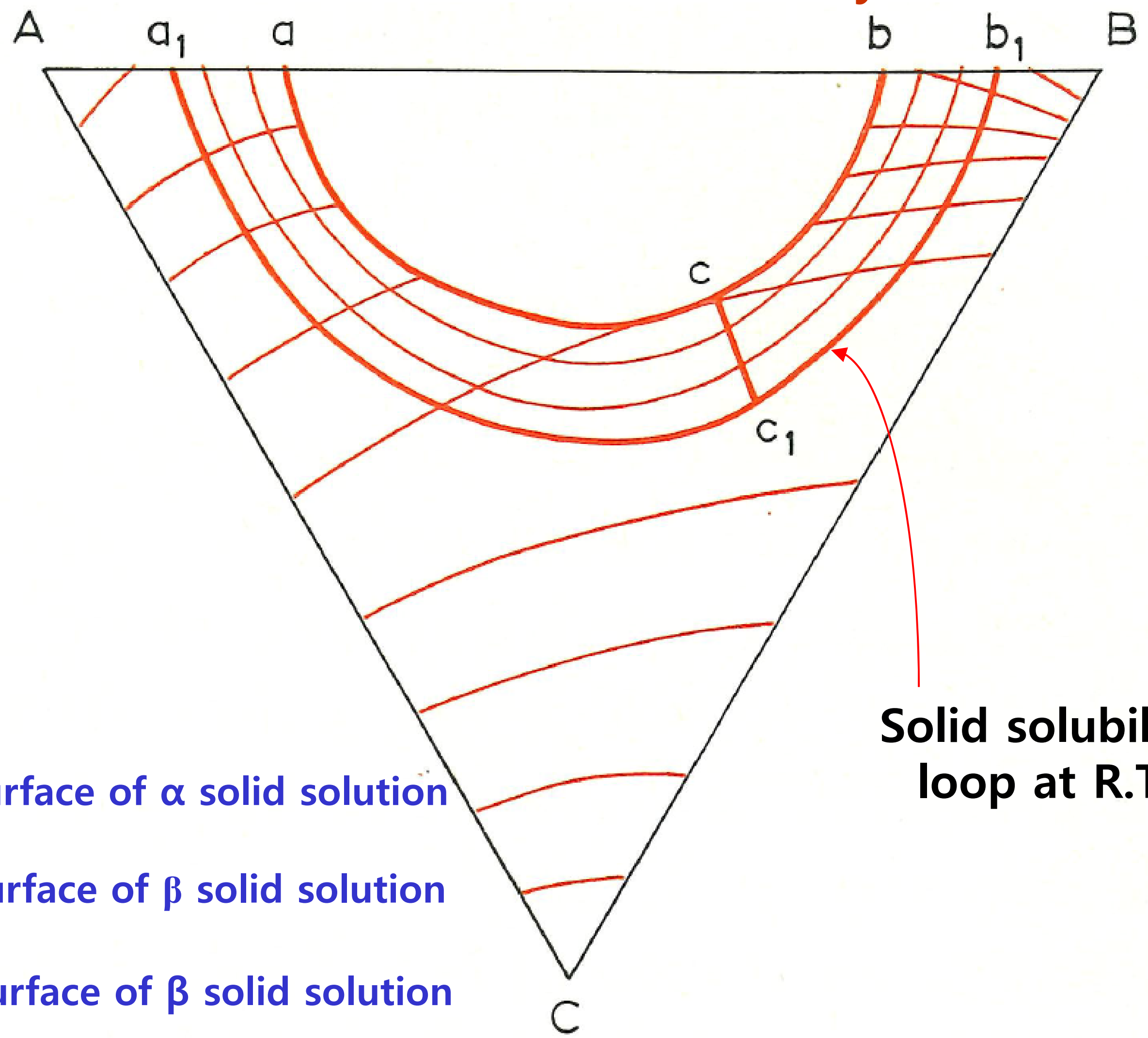


- **One binary eutectic : AB**
  Complete solid solution : BC, AC

9.3. THREE-PHASE EQUILIBRIUM INVOLVING EUTECTIC REACTIONS

- **Polythermal Projection**

The solidus surface and the solubility surface

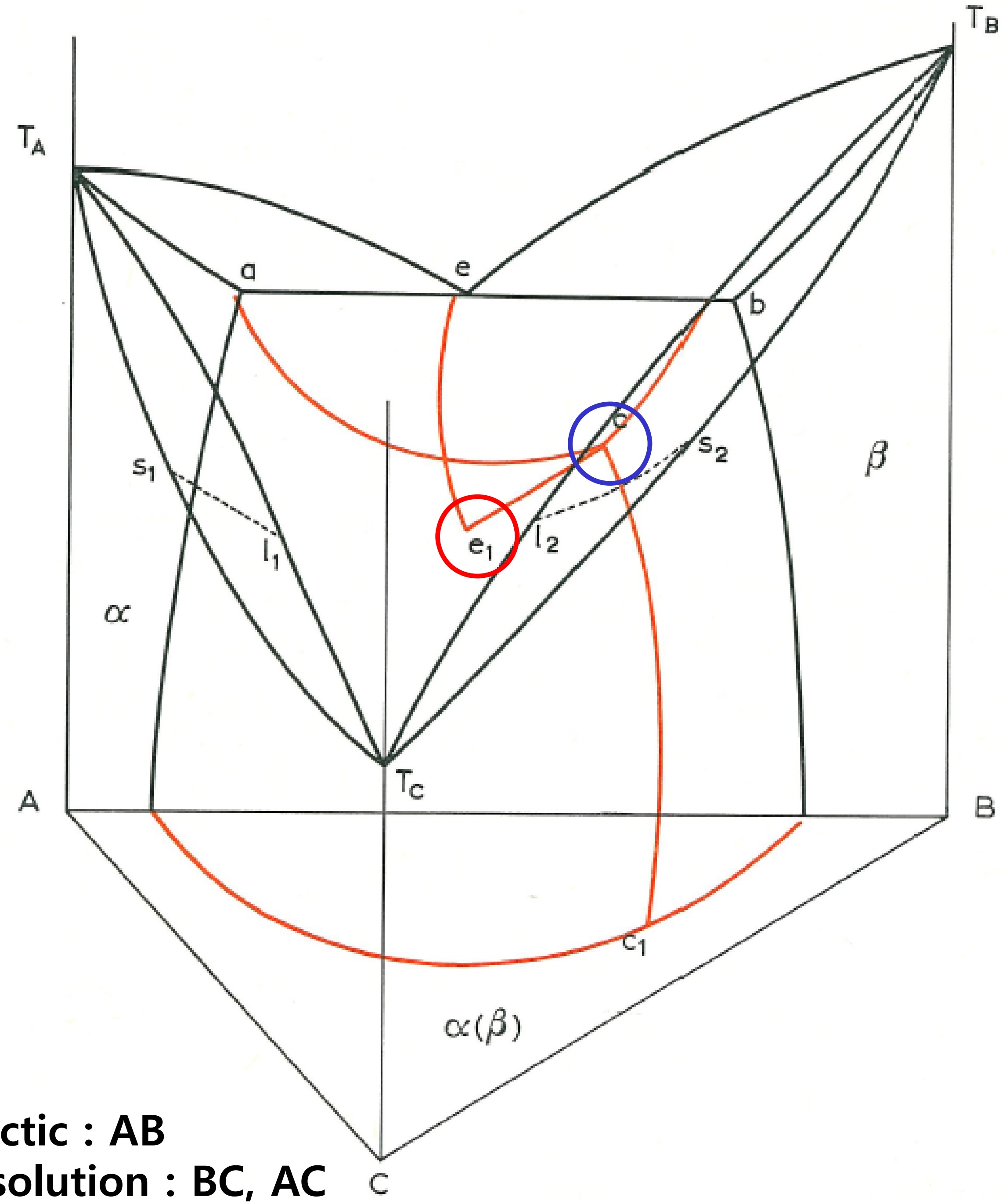


Solid solubility loop at R.T.

$T_A s_1 c a T_A$ - the solidus surface of α solid solution

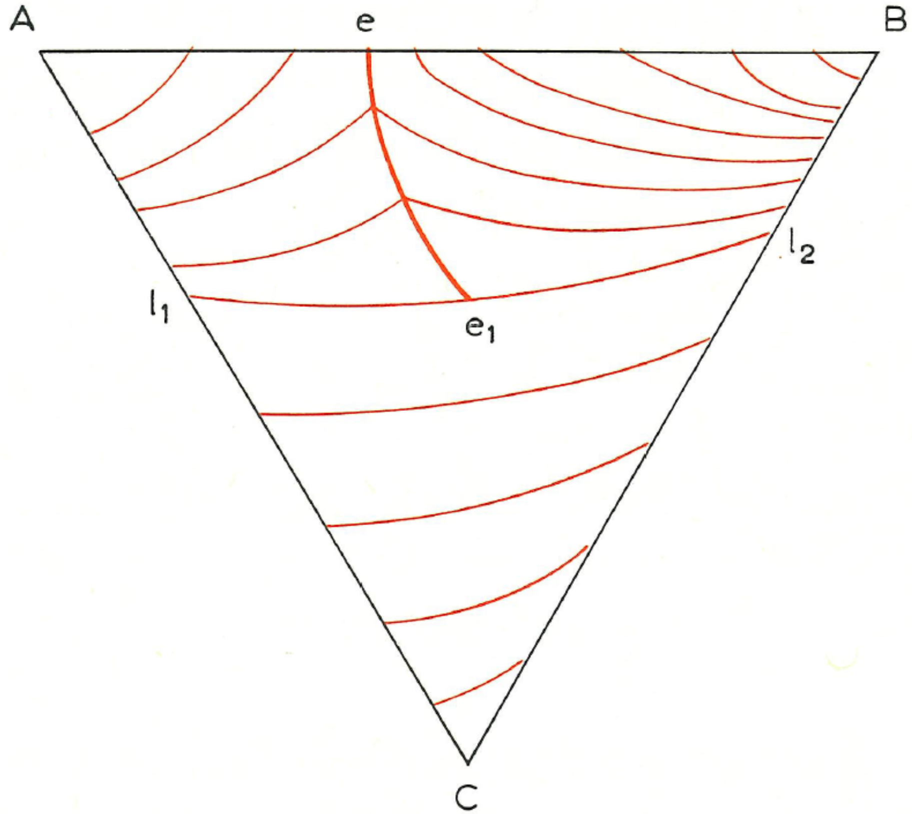
$T_B s_2 c b T_B$ - the solidus surface of β solid solution

$T_c s_1 c s_2 T_c$ - the solidus surface of β solid solution

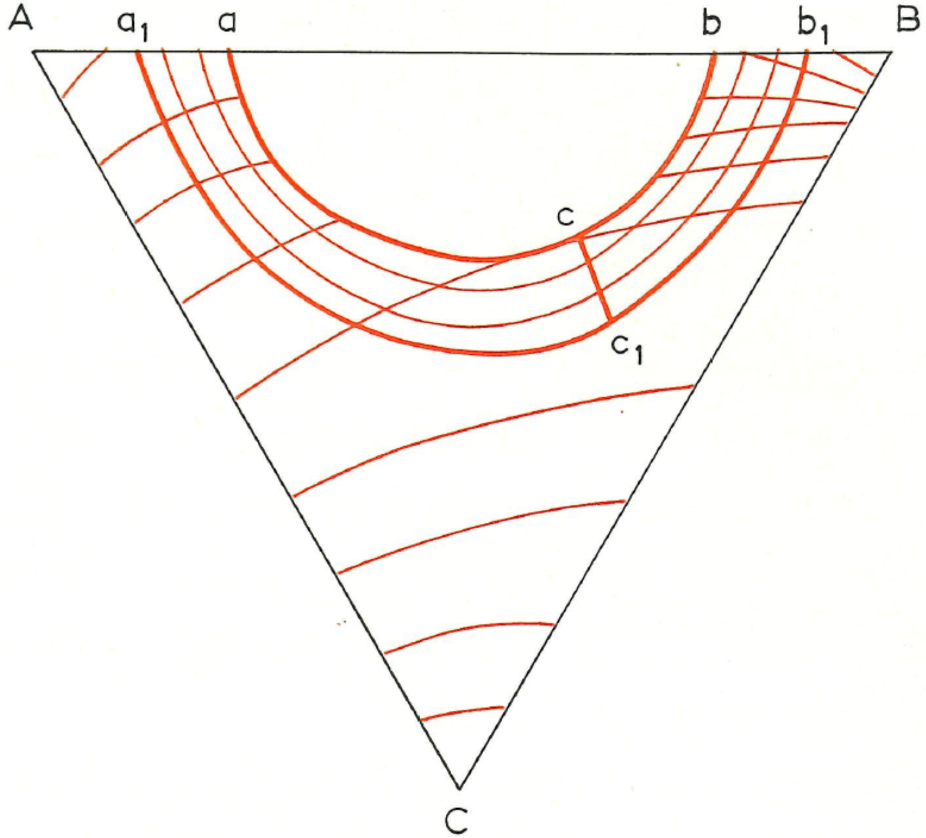


- **One binary eutectic : AB**
  Complete solid solution : BC, AC

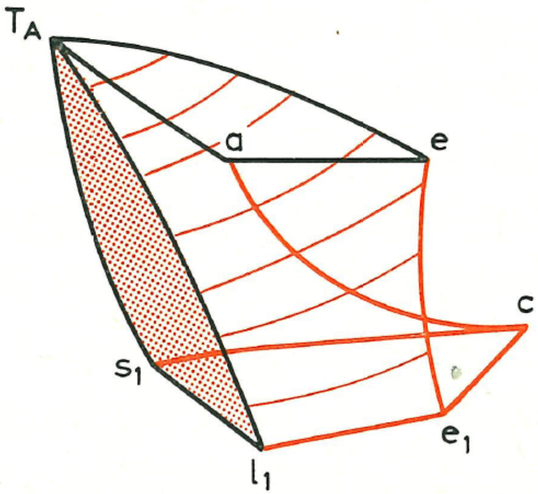
The liquidus surface



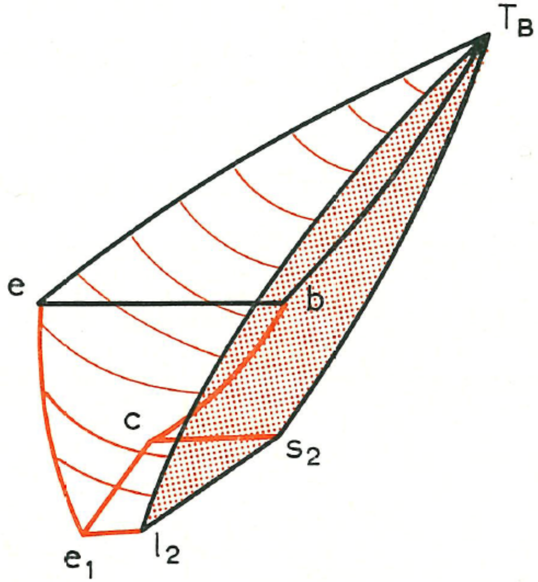
The solidus surface and the solubility surface



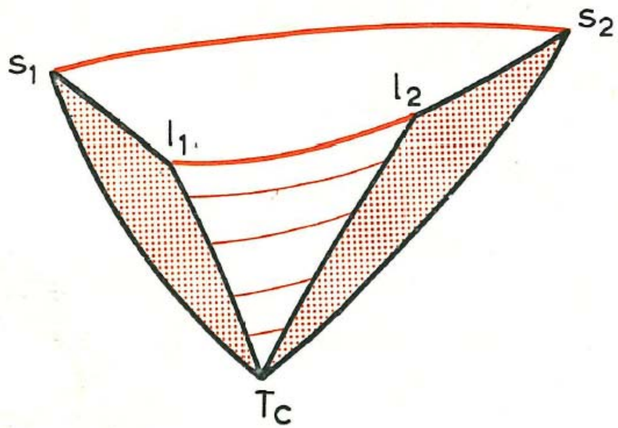
The two-phase regions



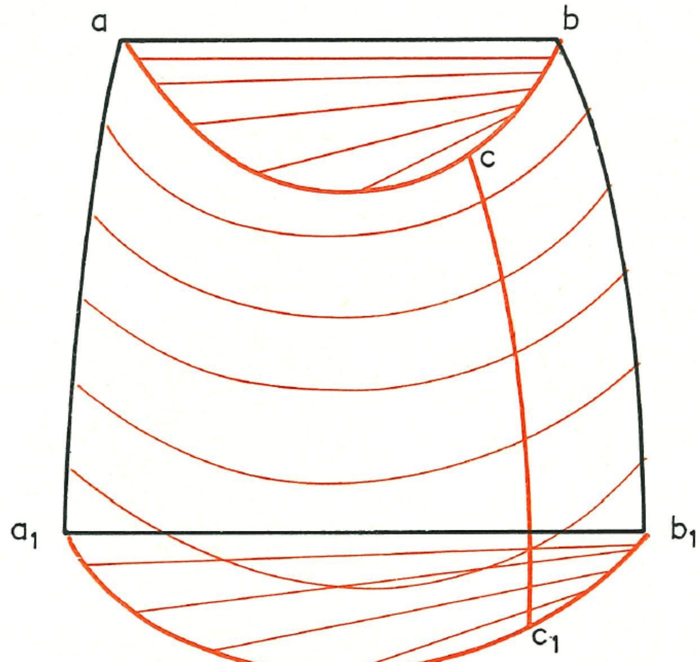
L+α phase region



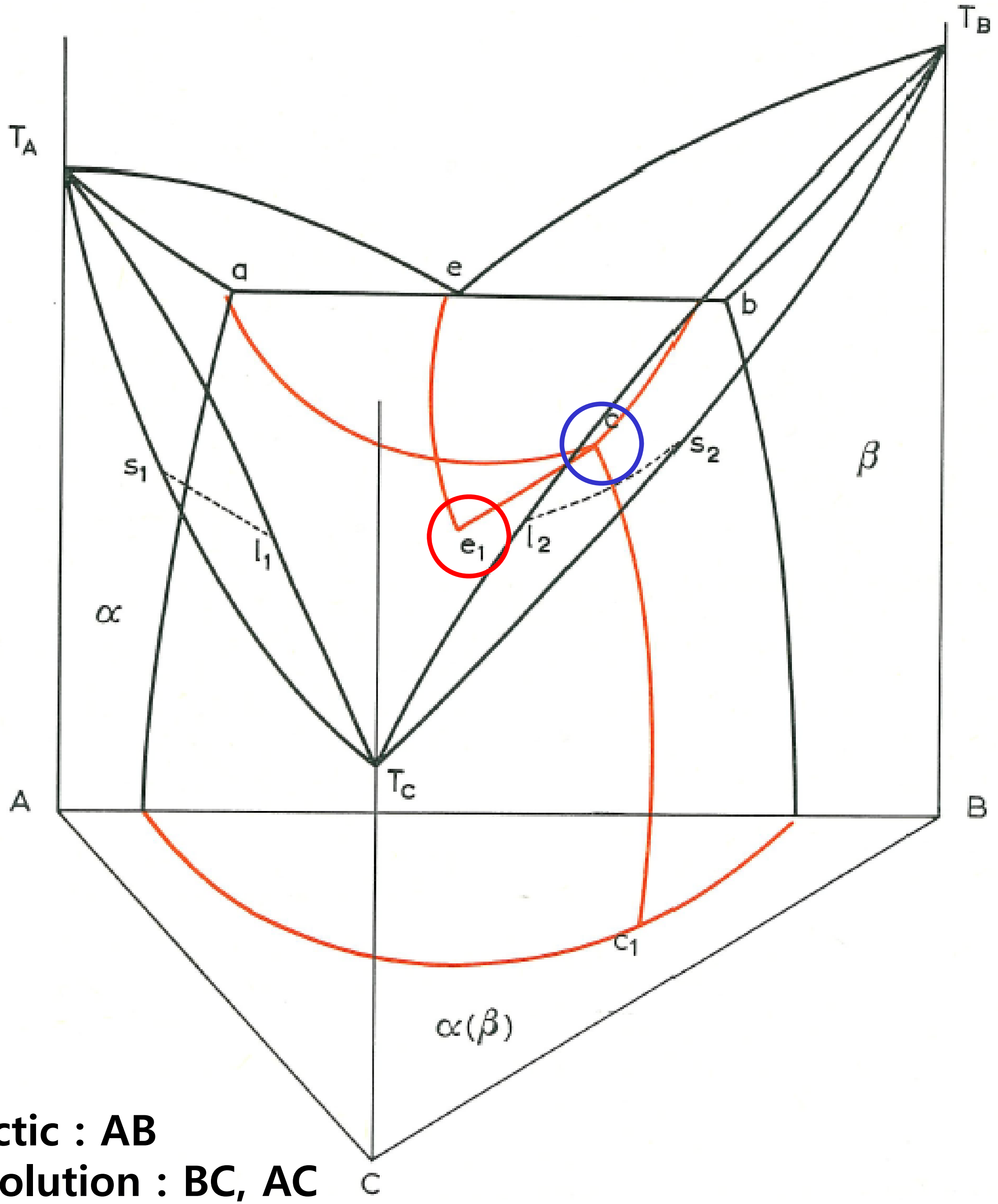
L+β phase region



L+α(β) phase region



α+β phase region

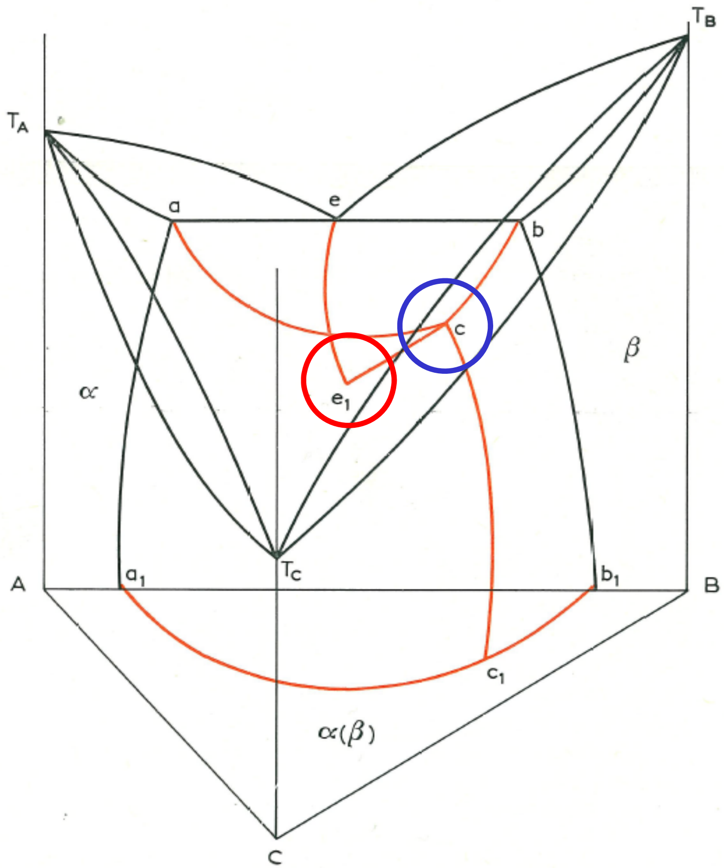


- **One binary eutectic : AB**
  Complete solid solution : BC, AC

9.3. THREE-PHASE EQUILIBRIUM INVOLVING EUTECTIC REACTIONS

9.3.1. A eutectic solubility gap in one binary system

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



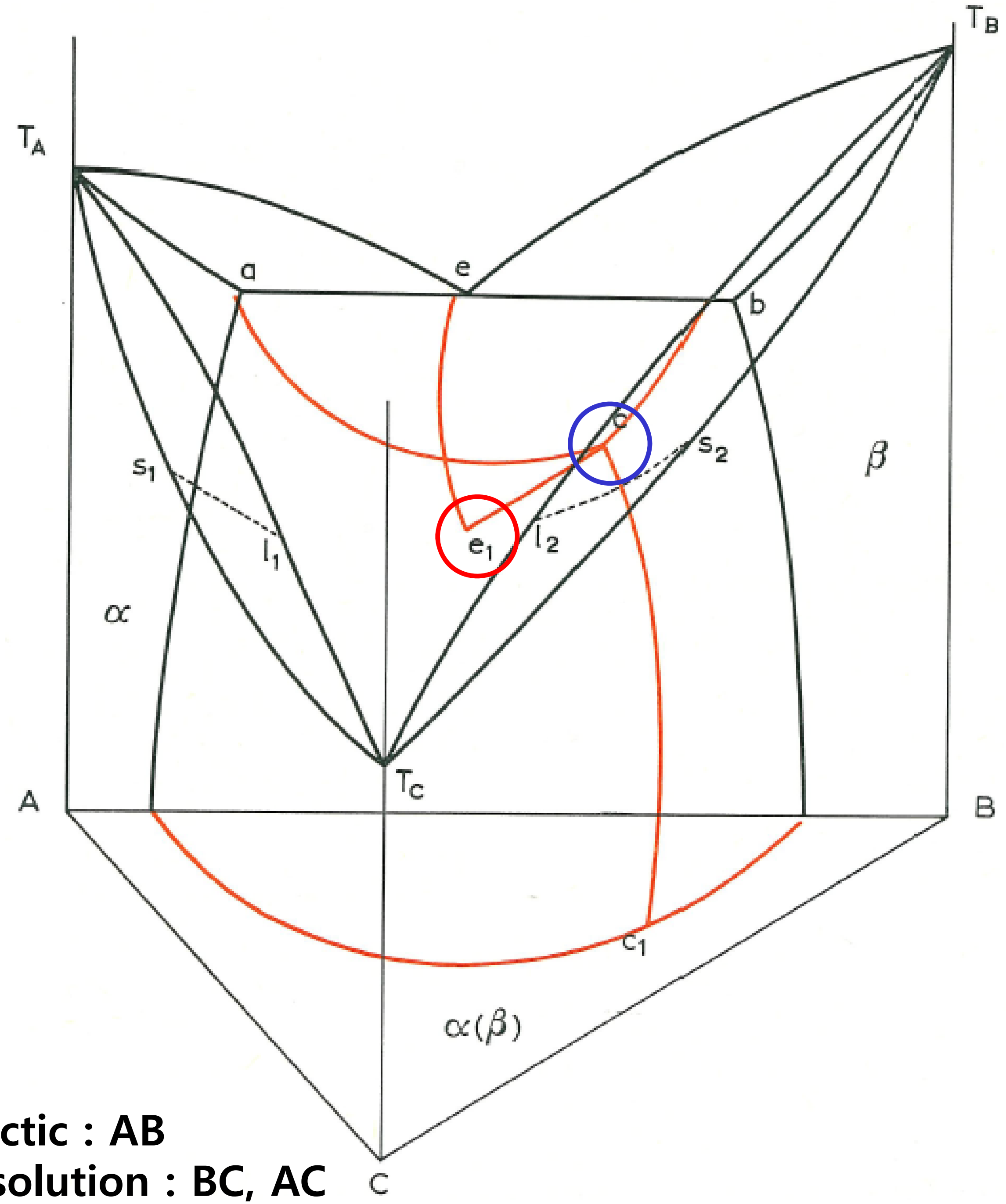
- **Closed solid solubility loop**
  → minimum critical point c
  : ternary α and β phases become indistinguishable.

- **l → α + β in ternary composition range**
  → three phase region

- **Along ac : α composition**
  along bc : β composition
  → l along ee_1
  → e_1 & c should be at same temperature

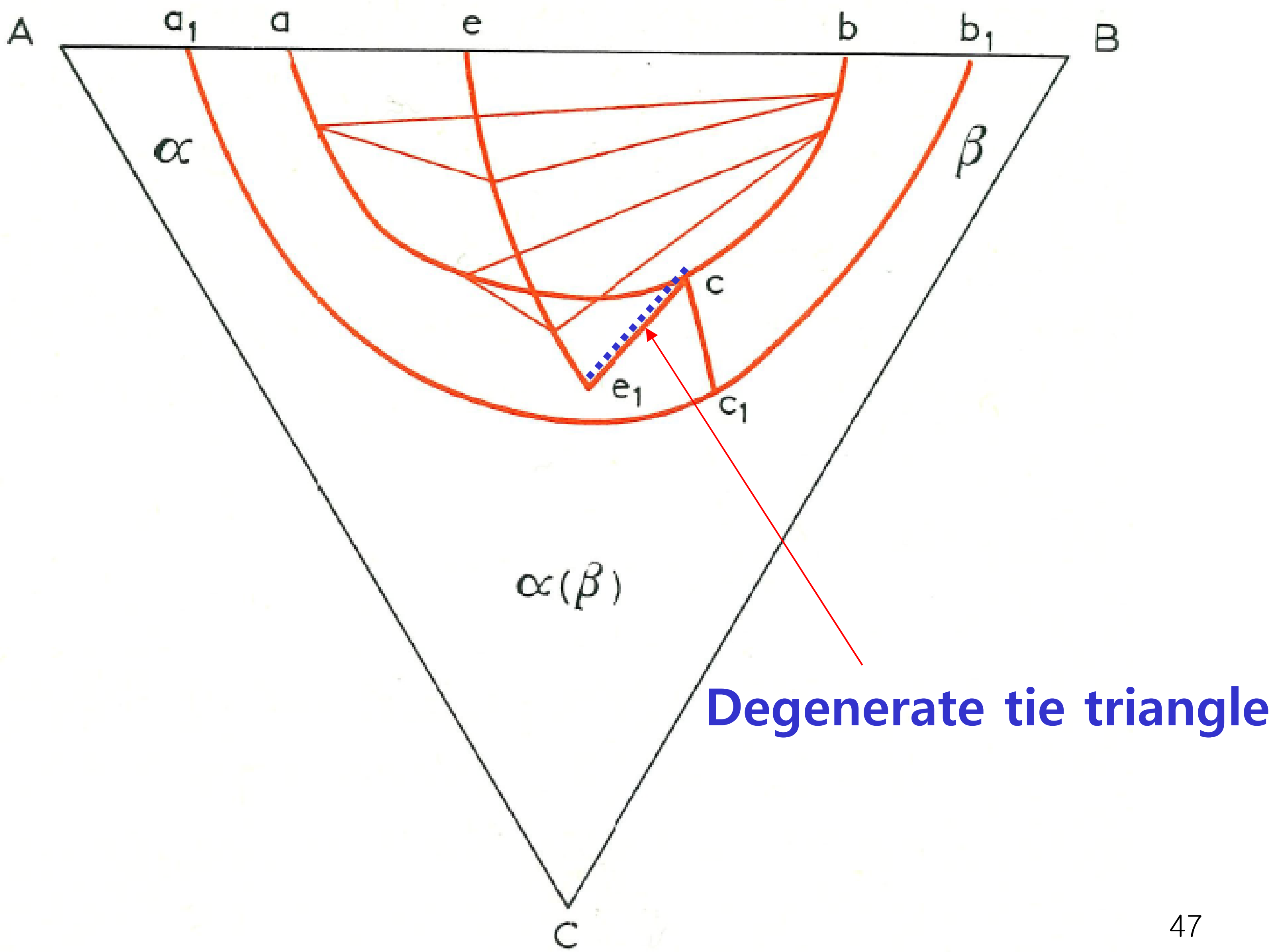
- **Three phase region will start**
  at binary eutectic temp.

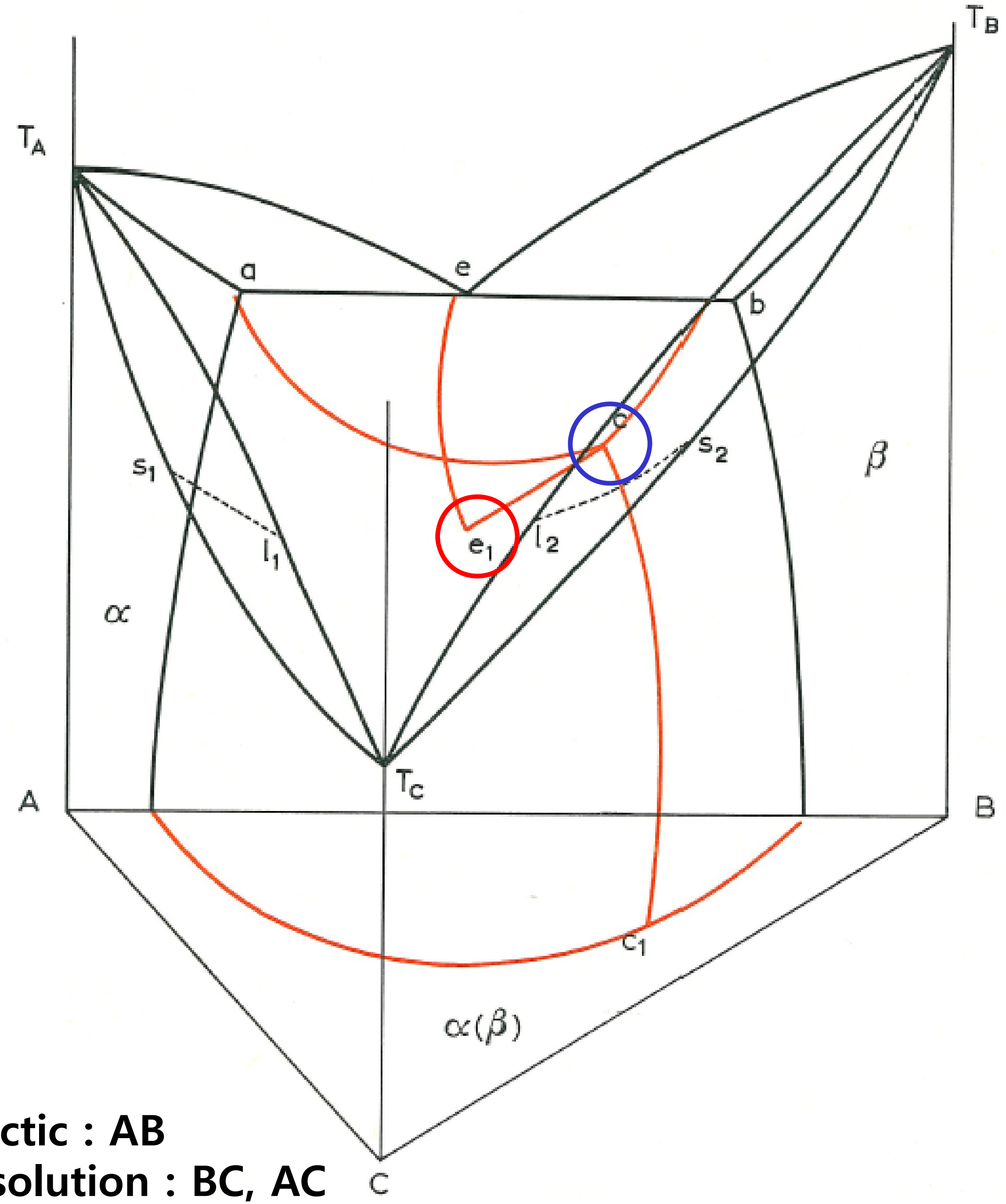
- **Three phase region will end at e_1c temp.**



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

- **Projection on concentration triangle ABC**





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

The three-phase regions

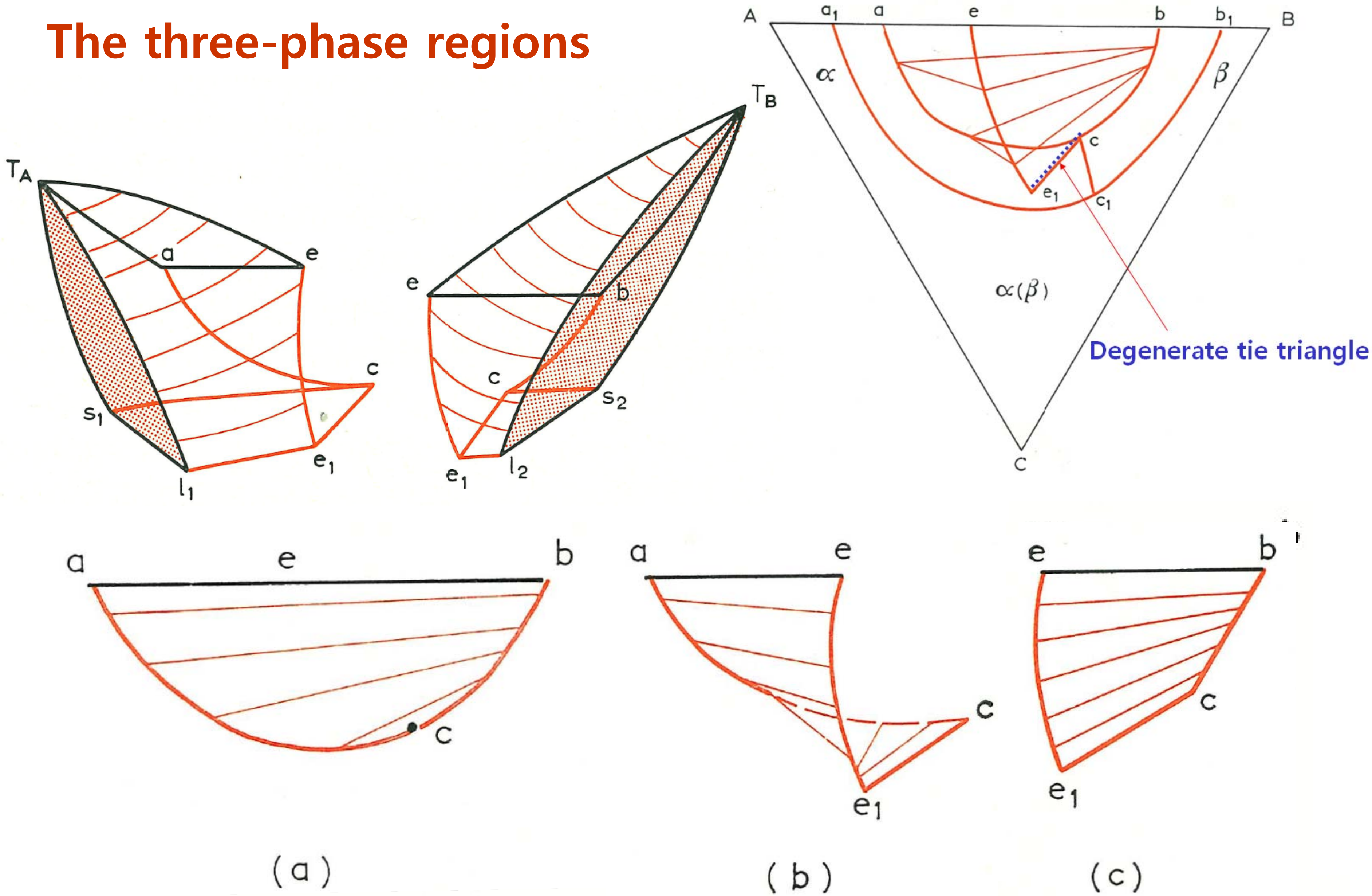
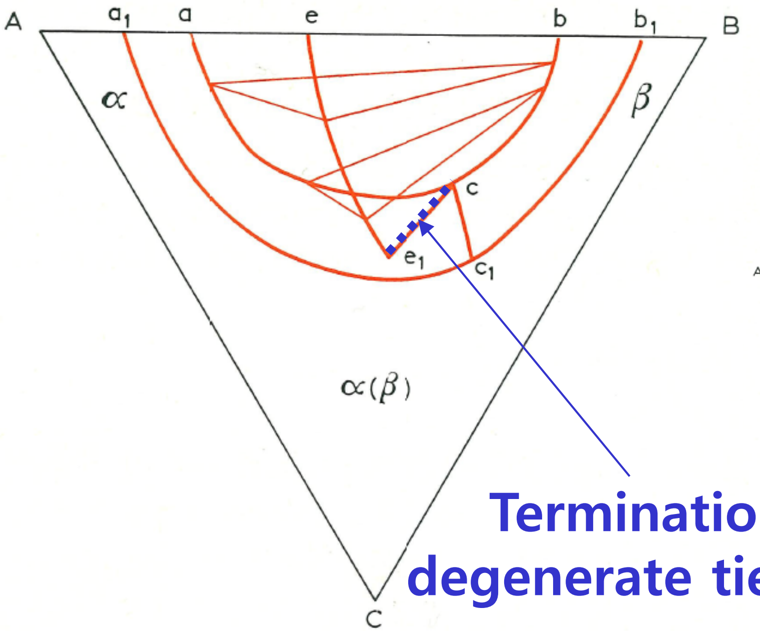


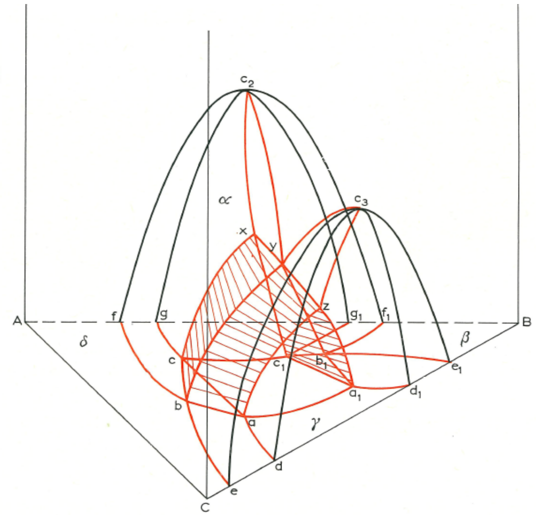
Fig. 147. The ruled surfaces bounding the three-phase ($l+\alpha+\beta$) region in Fig. 142. (a) The $\alpha\beta$ ruled surface; (b) the $l\alpha$ ruled surface; (c) the $l\beta$ ruled surface.

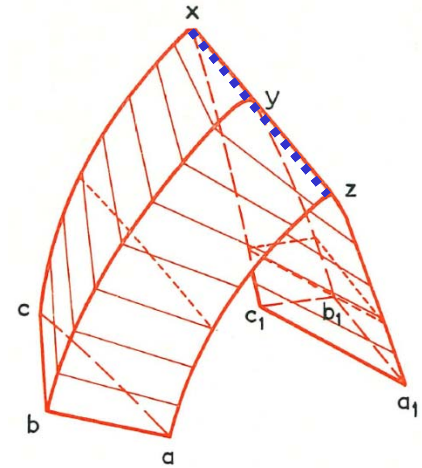
The ways in which three phase regions terminate in ternary systems:

(a)



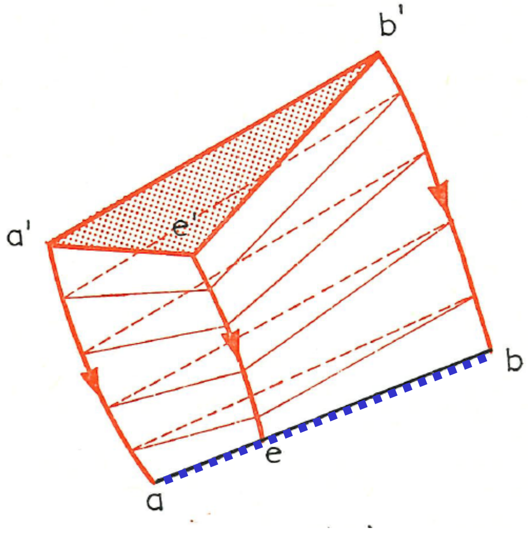
Termination at a degenerate tie triangle

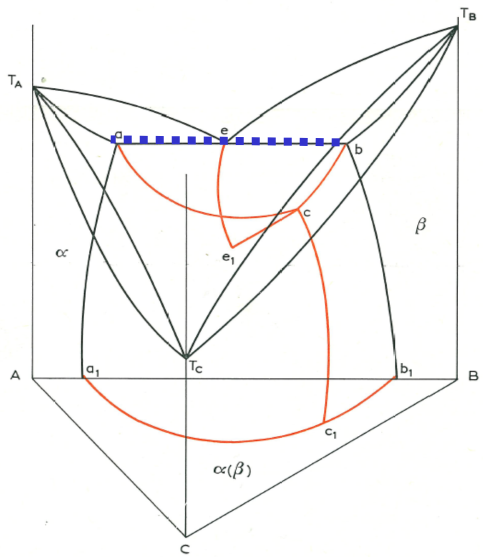




→ **ternary system, 3 phases are in a straight line as three points.**

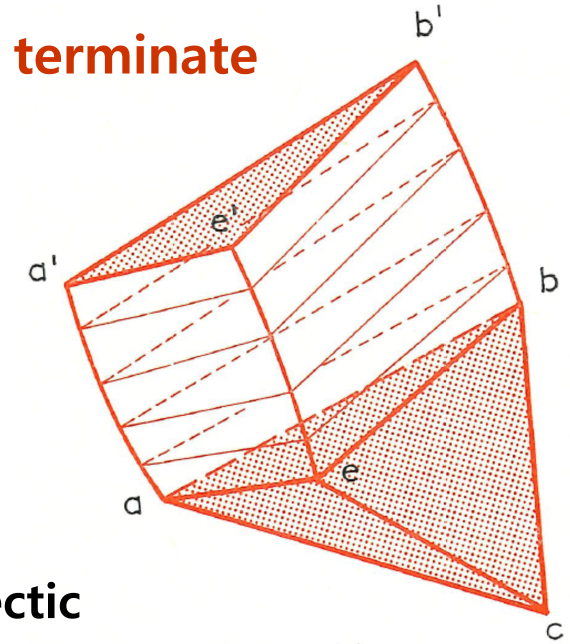
(b) Termination at a reaction isotherm





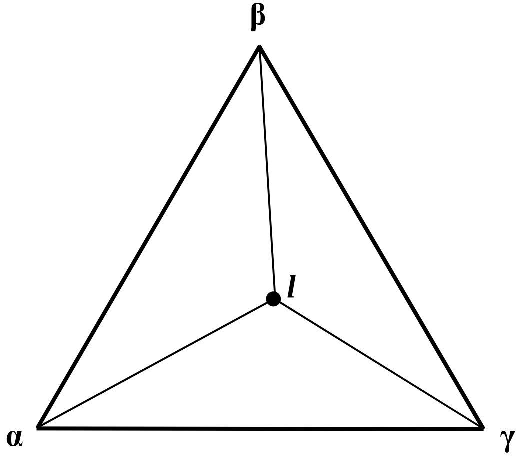
The ways in which three phase regions terminate in ternary systems:

(c) Termination at a four-phase plane



Ternary eutectic

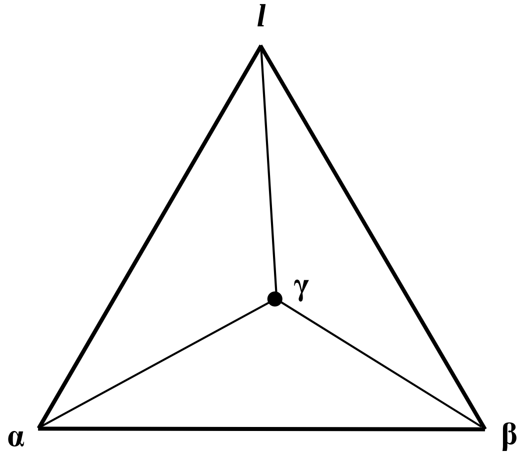
L → α + β + γ



$\alpha\beta l$ & $\alpha\gamma l$ & $\beta\gamma l \rightarrow \alpha\beta\gamma l \rightarrow \alpha\beta\gamma$

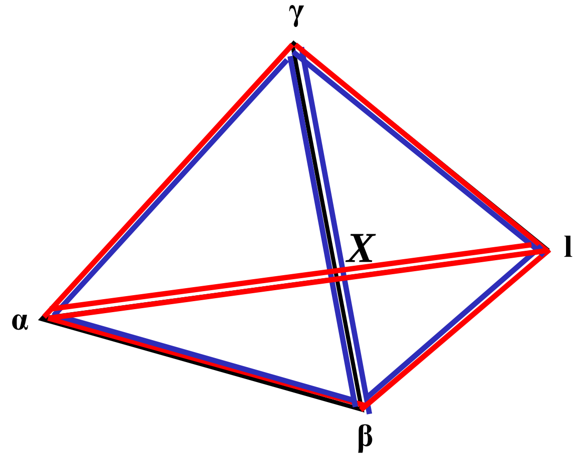
Ternary peritectic

L + α + β → γ



$\alpha\beta\gamma$ & $\alpha\gamma l$ & $\beta\gamma l \rightarrow \alpha\beta\gamma l \rightarrow \gamma$

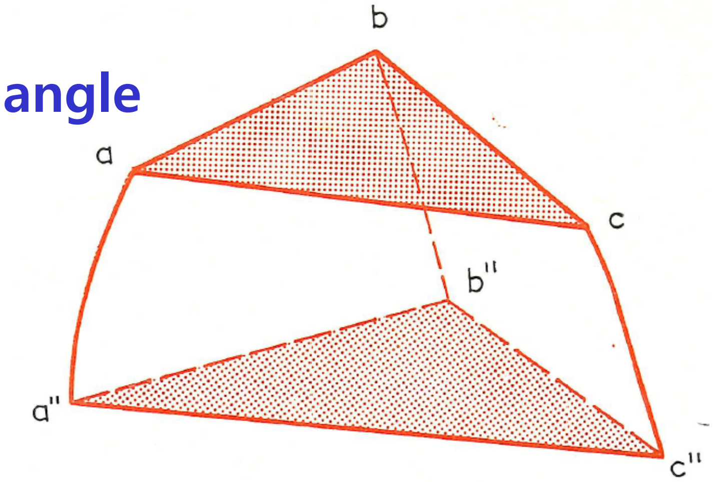
L + α → β + γ



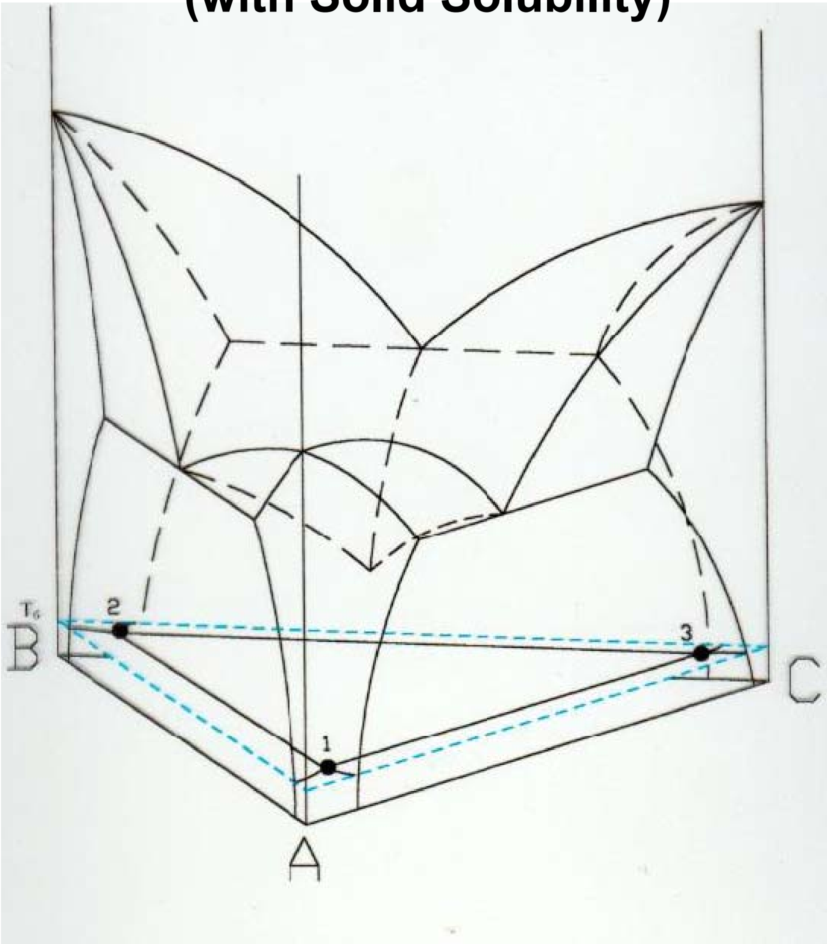
$$\frac{m_\alpha}{m_l} = \frac{Xl}{\alpha X} \quad \text{and} \quad \frac{m_\beta}{m_\gamma} = \frac{\gamma X}{X\beta}$$

$$\boxed{\alpha\beta l} \;\&\; \boxed{\alpha\gamma l} \rightarrow \alpha\beta\gamma l \rightarrow \boxed{\alpha\beta\gamma} \;\&\; \boxed{\beta\gamma l}$$

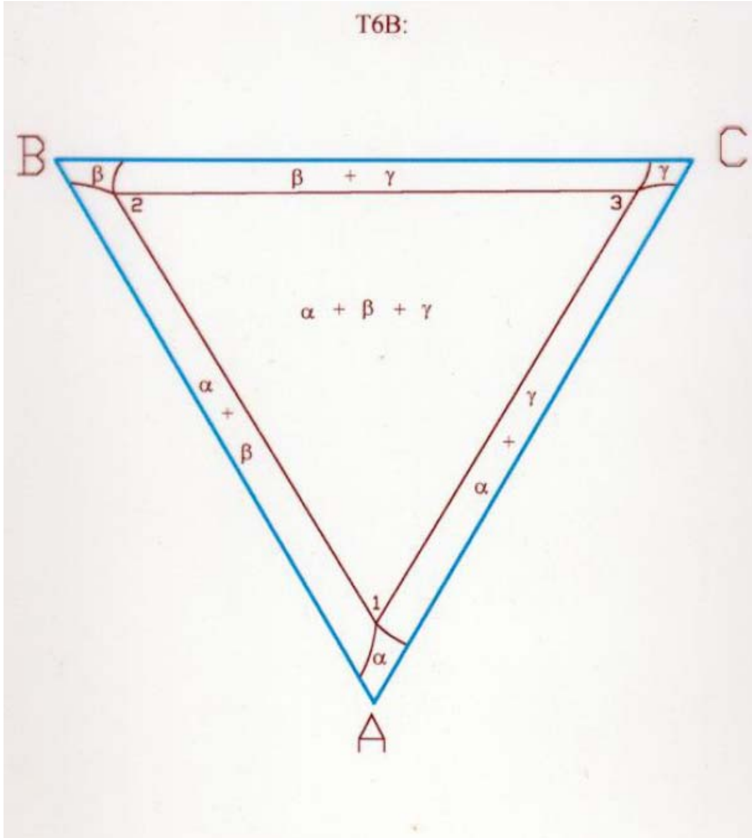
(d) Termination on the concentration triangle



Ternary Eutectic System
(with Solid Solubility)



Temperature Slice at $T_6 < T_E$



Isothermal Section At $T=T_6$