2021 Spring

“Phase Equilibria *in* Materials”

04.06.2021

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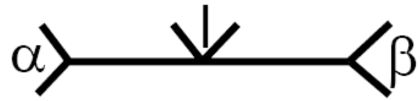
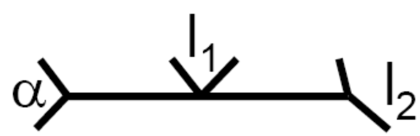
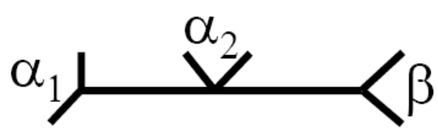
Review of Invariant Binary Reactions

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

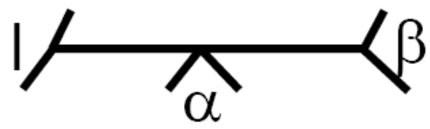
Metatectic reaction: $\beta \leftrightarrow L + \alpha$ **Ex. Co-Os, Co-Re, Co-Ru**

Review of Invariant Binary Reactions

Peritectic Type

Peritectic

$l + \beta \rightleftarrows \alpha$



Fe-C

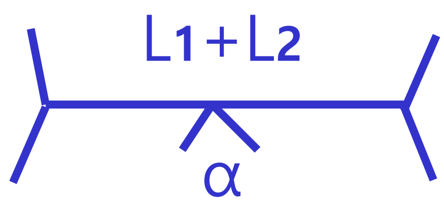
Peritectoid

$\alpha + \beta \rightleftarrows \gamma$

Cu-Al

Syntectic reaction

Liquid1+Liquid2 ↔ α



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

On cooling two phases going to one phase

MIDTERM: 23rd April (Friday) 2 PM – 5 PM,

33 Dong 330 & 331 Ho

※ I will post your designated seat in front of the classroom on the day of the test.

Scopes: Text ~ page 117/ Teaching note ~10

and Homeworks

Chapter 8.
Ternary Phase Diagrams
Two-Phase Equilibrium

What are ternary phase diagram?

Diagrams that represent the equilibrium between the various phases that are formed between three components, as a function of temperature.

Normally, pressure is not a viable variable in ternary phase diagram construction, and is therefore held constant at 1 atm.

www.sjsu.edu/faculty/selvaduray/page/phase/ternary_p_d.pdf

8.1 INTRODUCTION

$G=f$(comp., temp.)

→ Ternary system : A, B, C

→ $G=X_AG_A+X_BG_B+X_CG_C+aX_AX_B+bX_BX_C+cX_CX_A+RT(X_A\ln X_A+X_B\ln X_B+X_C\ln X_C)$

Gibbs phase rule : P=(C+2)-F   For isobaric systems : P=(C+1)-F

For C=3,

① f=3, trivariant equil, p=1 (one phase equilibrium)

② f=2, bivariant equil, p=2 (two phase equilibrium)

③ f=1, monovaiant equil, p=3 (three phase equilibrium)

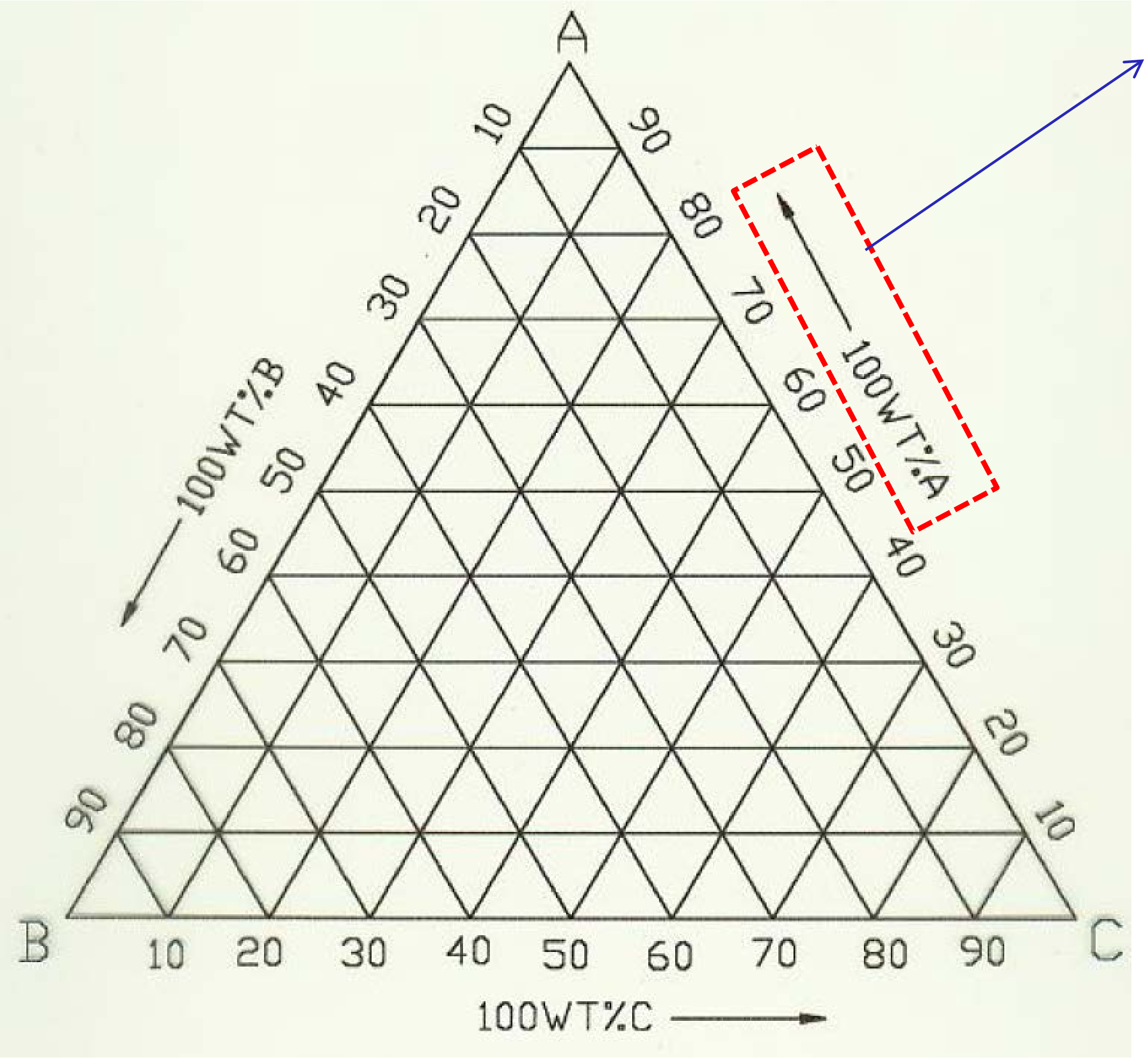
$$\begin{array}{lll}
\alpha \rightleftharpoons \beta + \gamma, & \alpha \rightleftharpoons \beta + l, & \alpha \rightleftharpoons l_1 + l_2 \\
l_1 \rightleftharpoons l_2 + l_3, & l_1 \rightleftharpoons \alpha + l_2, & l \rightleftharpoons \alpha + \beta \\
\alpha + \beta \rightleftharpoons \gamma, & \alpha + \beta \rightleftharpoons l, & l_1 + l_2 \rightleftharpoons l_3 \\
l_1 + l_2 \rightleftharpoons \alpha, & l_1 + \alpha \rightleftharpoons l_2, & l + \alpha \rightleftharpoons \beta.
\end{array}$$

④ f=0, invariant equil, p=4 (four phase equilibrium)

$$\begin{array}{lll}
\alpha \rightleftharpoons \beta + \gamma + \delta, & \alpha + \beta \rightleftharpoons \gamma + \delta, & \alpha + \beta + \gamma \rightleftharpoons \delta \\
l_1 \rightleftharpoons l_2 + l_3 + l_4, & l_1 + l_2 \rightleftharpoons l_3 + l_4, & l_1 + l_2 + l_3 \rightleftharpoons l_4 \\
l \rightleftharpoons \alpha + \beta + \gamma, & l + \alpha \rightleftharpoons \beta + \gamma, & l + \alpha + \beta \rightleftharpoons \gamma \\
l_1 \rightleftharpoons l_2 + \alpha + \beta, & l_1 + l_2 \rightleftharpoons \alpha + \beta, & l_1 + l_2 + \alpha \rightleftharpoons \beta \\
l_1 \rightleftharpoons l_2 + l_3 + \alpha, & l_1 + l_2 \rightleftharpoons l_3 + \alpha, & l_1 + l_2 + l_3 \rightleftharpoons \alpha \\
\alpha \rightleftharpoons l_1 + l_2 + l_3, & \alpha + l_1 \rightleftharpoons l_2 + l_3, & \alpha + l_1 + l_2 \rightleftharpoons l_3 \\
\alpha \rightleftharpoons \beta + l_1 + l_2, & \alpha + \beta \rightleftharpoons l_1 + l_2, & \alpha + \beta + l_1 \rightleftharpoons l_2 \\
\alpha \rightleftharpoons \beta + \gamma + l, & \alpha + \beta \rightleftharpoons \gamma + l, & \alpha + \beta + \gamma \rightleftharpoons l \\
 & l_1 + \alpha \rightleftharpoons l_2 + \beta. &
\end{array}$$

Gibbs Triangle

An Equilateral triangle on which the pure components are represented by each corner.

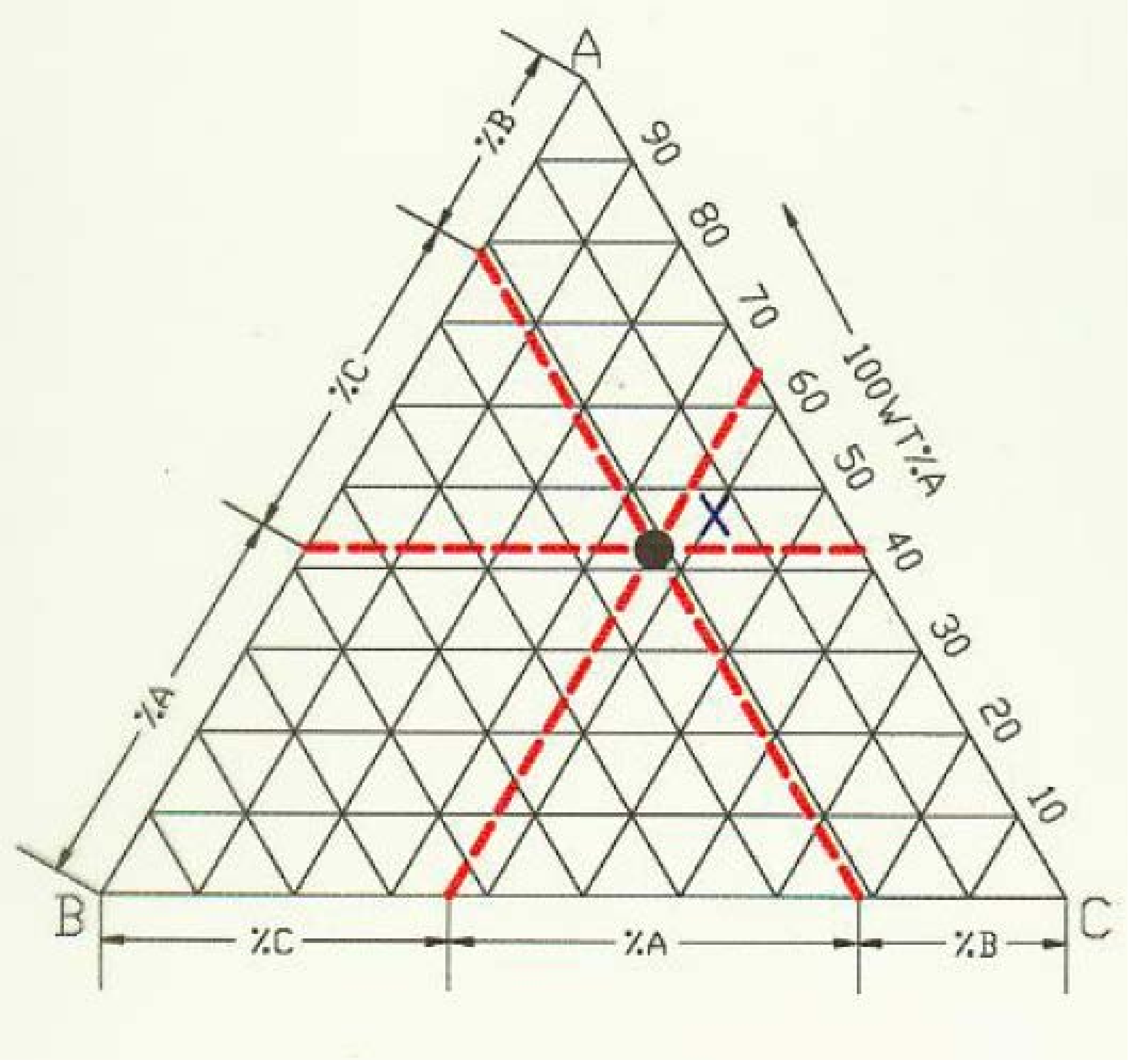


Concentration can be expressed as either "wt. %" or "at.% = molar %".

$$X_A+X_B+X_C = 1$$

Used to determine the overall composition

Overall Composition



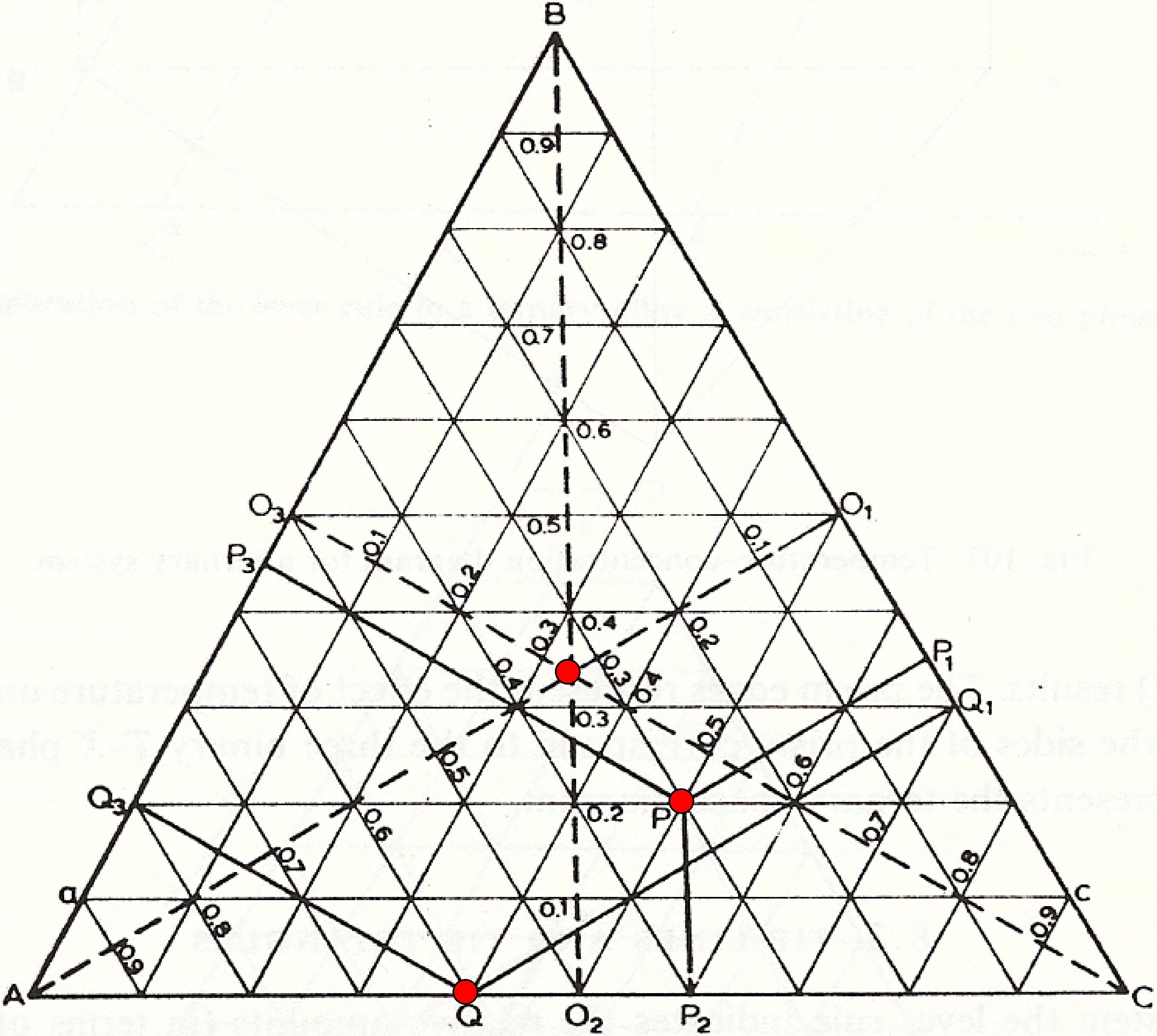
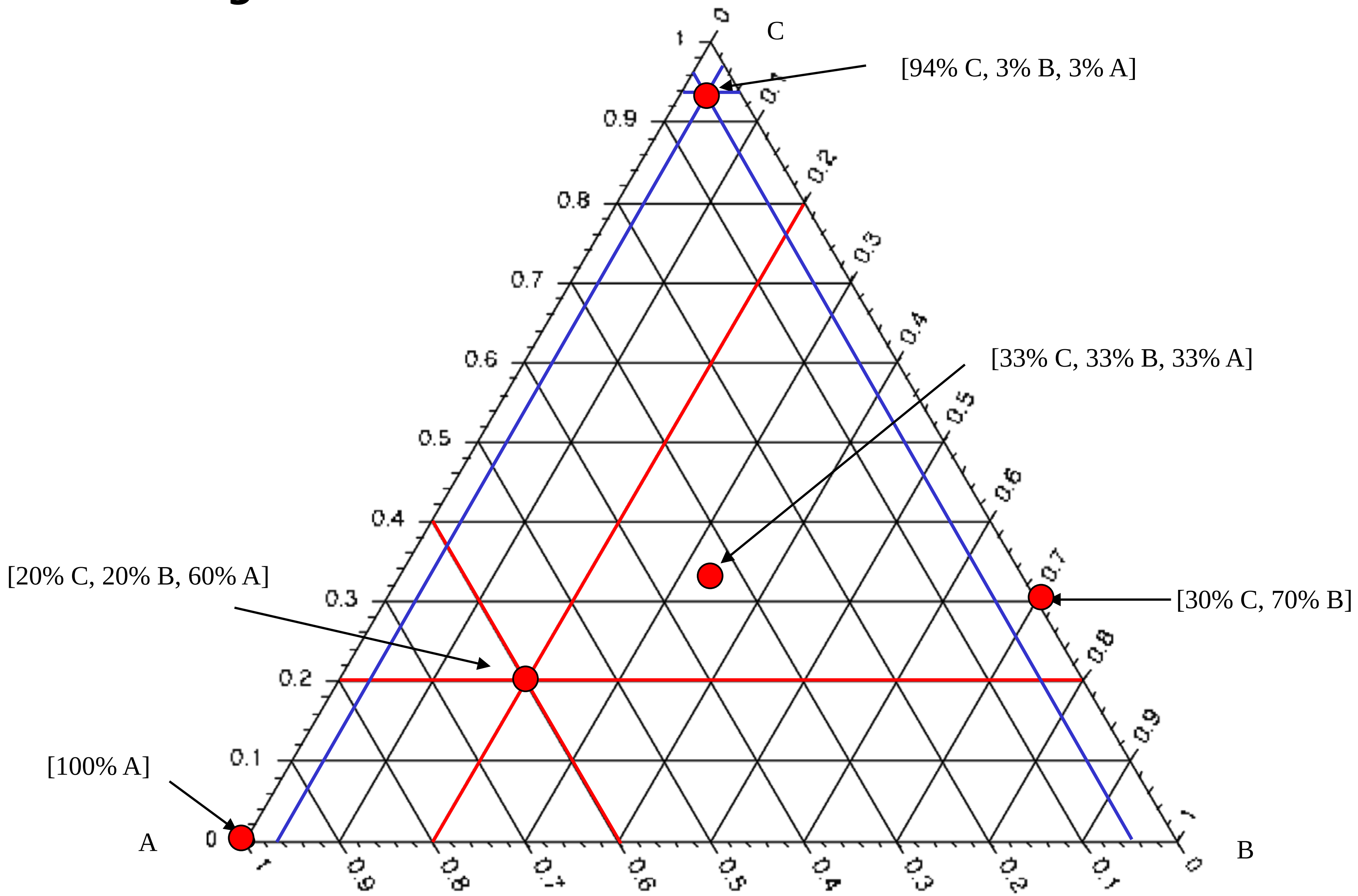


Fig. 106. Plotting of alloy compositions in ternary systems.

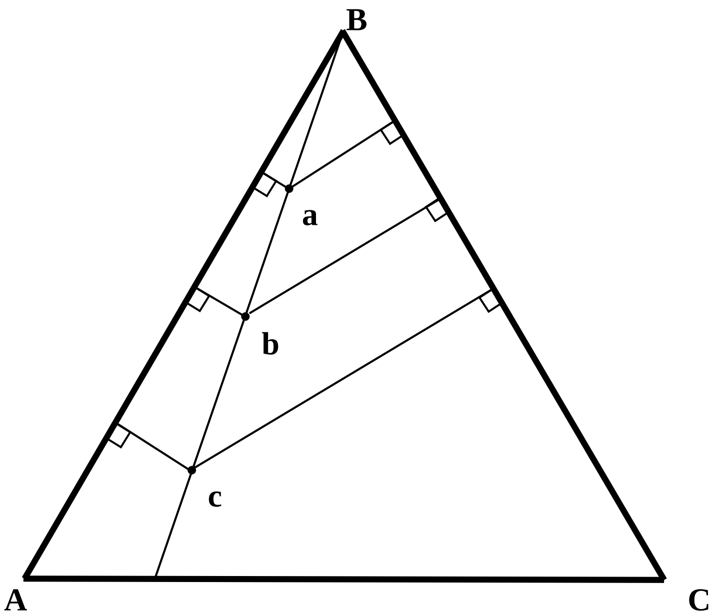
8.2 REPRESENTATION OF TERNARY SYSTEMS

Gibbs triangle



8.2 REPRESENTATION OF TERNARY SYSTEMS

Gibbs triangle



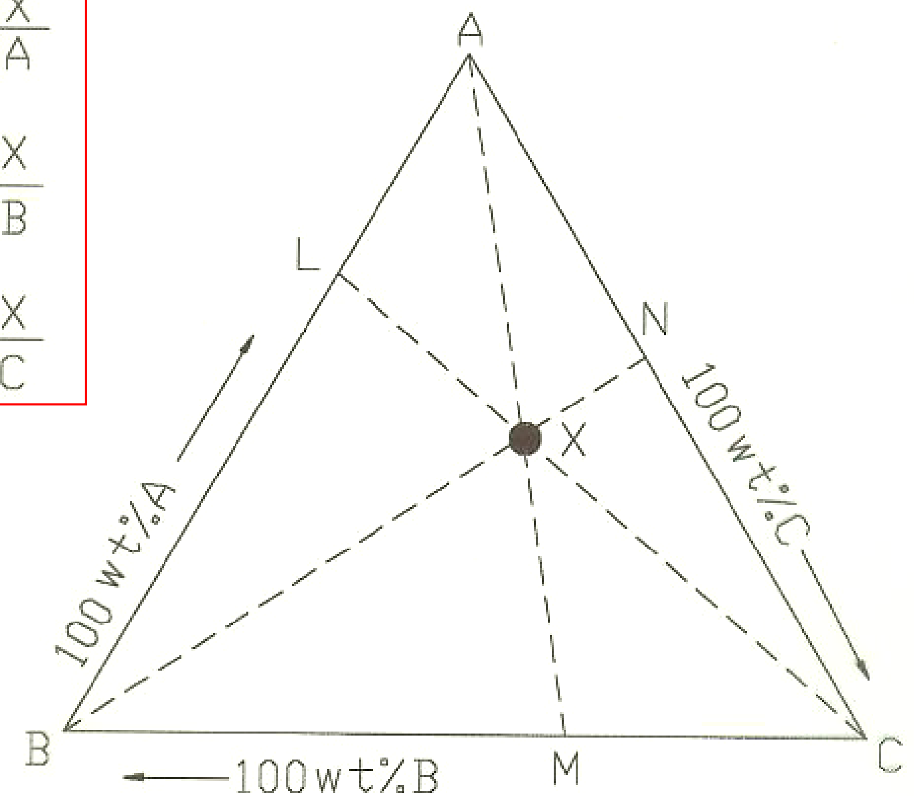
→ Ratio of X_C/X_A is same at a, b, c.

2) Overall Composition of X alloy

$$\%A = \frac{MX}{MA}$$

$$\%B = \frac{NX}{NB}$$

$$\%C = \frac{LX}{LC}$$

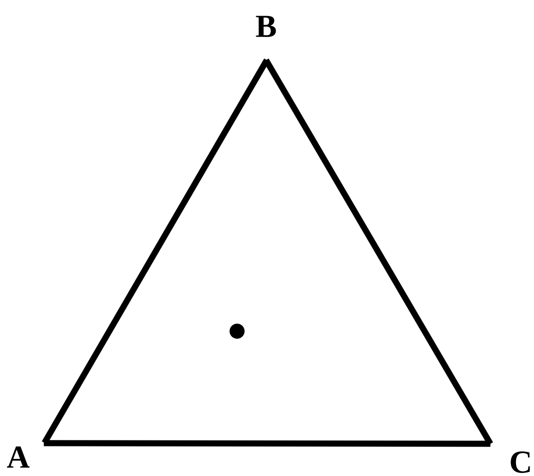


According to Triangle congruence condition

8.3 TIE LINES AND TIE TRIANGLES

Isothermal section

P=1



P=2 **Tie line :** 2 phase equilibrium

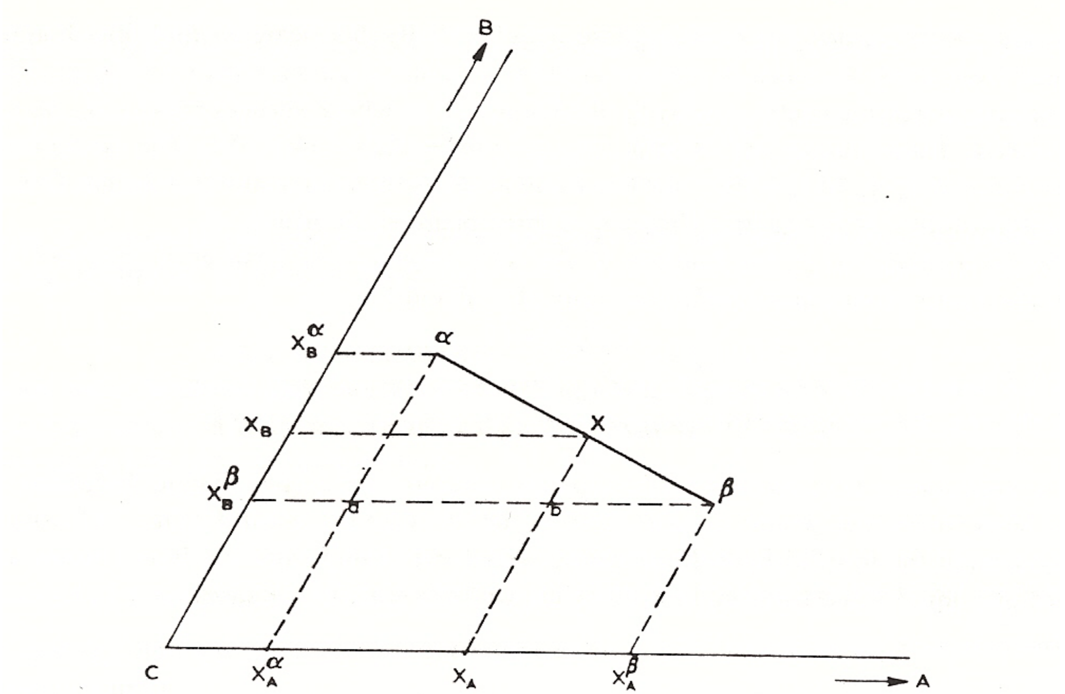
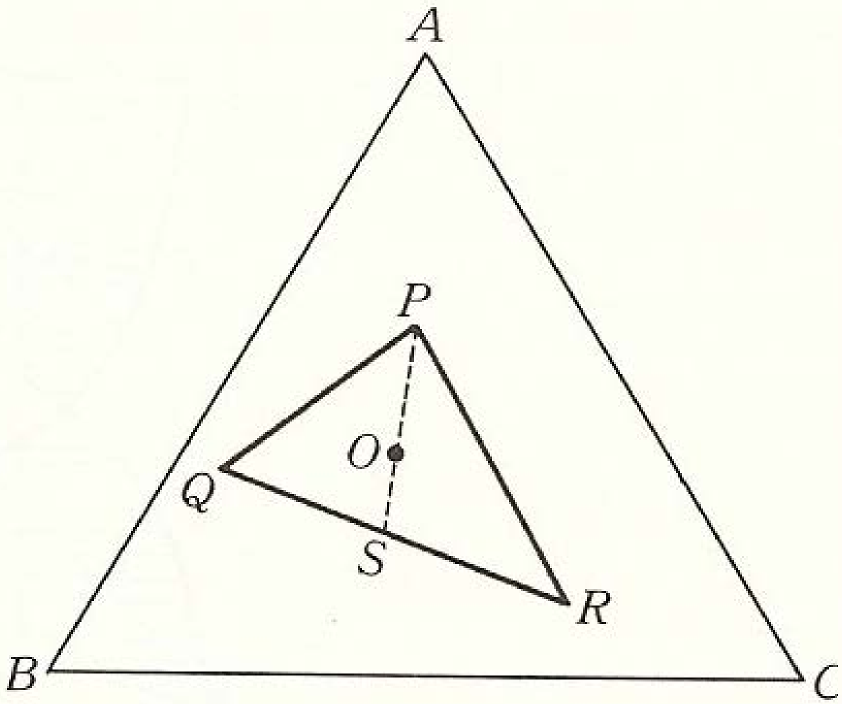


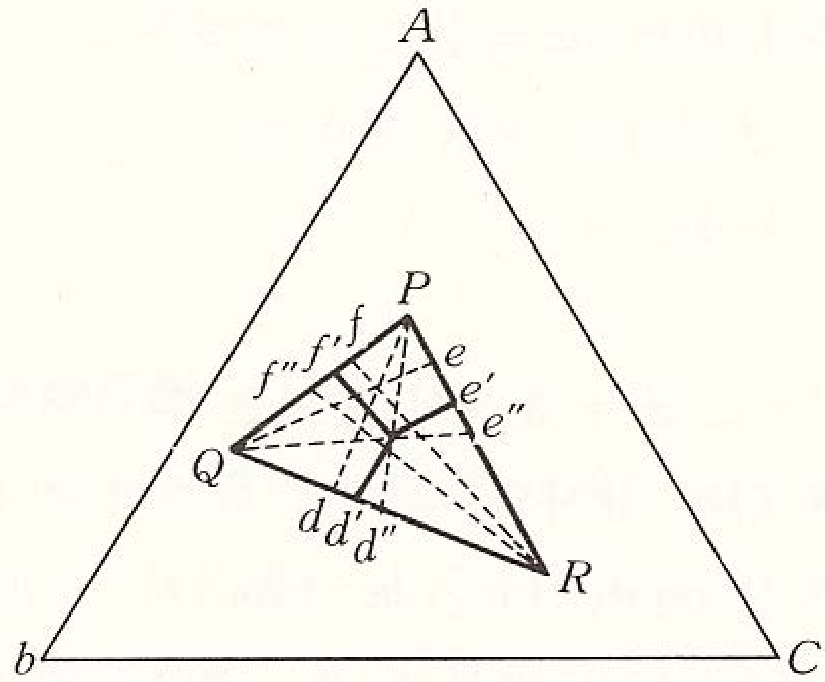
Fig. 108. Application of the lever rule to a ternary alloy *X* consisting of the two phases *α* and *β*.

$$m_\alpha : m_\beta = X\beta : \alpha X = b\beta : ab$$

8.3 TIE LINES AND TIE TRIANGLES

P=3 Tie triangle : 3 phase equil.



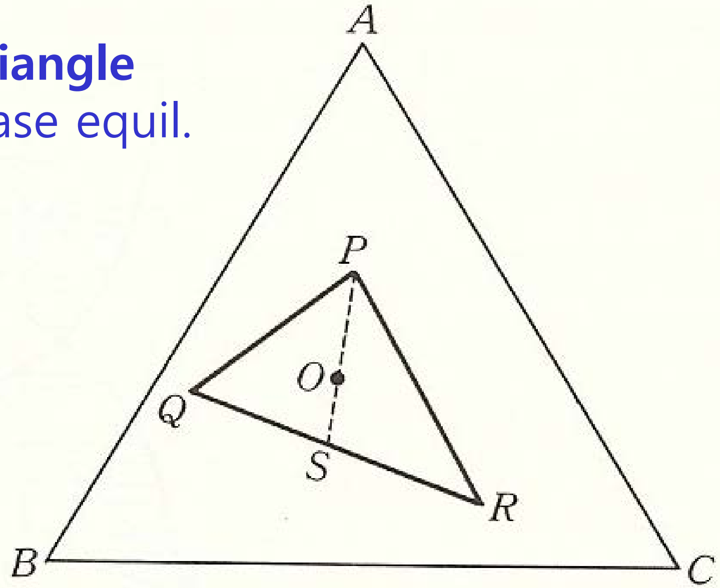


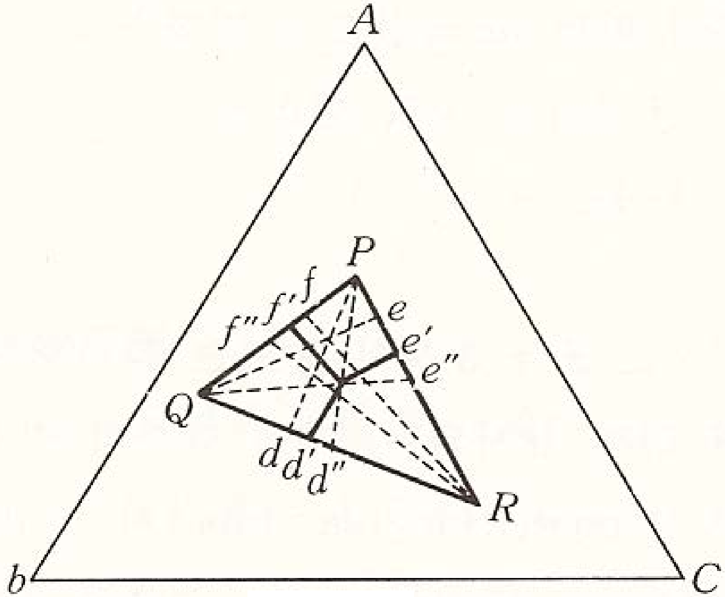
P contents: Q contents: R contents $= \dfrac{Od'}{Pd} : \dfrac{Oe'}{Qe} : \dfrac{Of'}{Rf}$

$$= \frac{Od''}{Pd''} : \frac{Oe''}{Qe''} : \frac{Of''}{Rf''}$$

Incentive Homework 7: derive the above relationships in tie triangle

Tie triangle
: 3 phase equil.





P contents in O alloy

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

S composition in O alloy

$$S\,\% = \frac{PO}{PS} \times 100$$

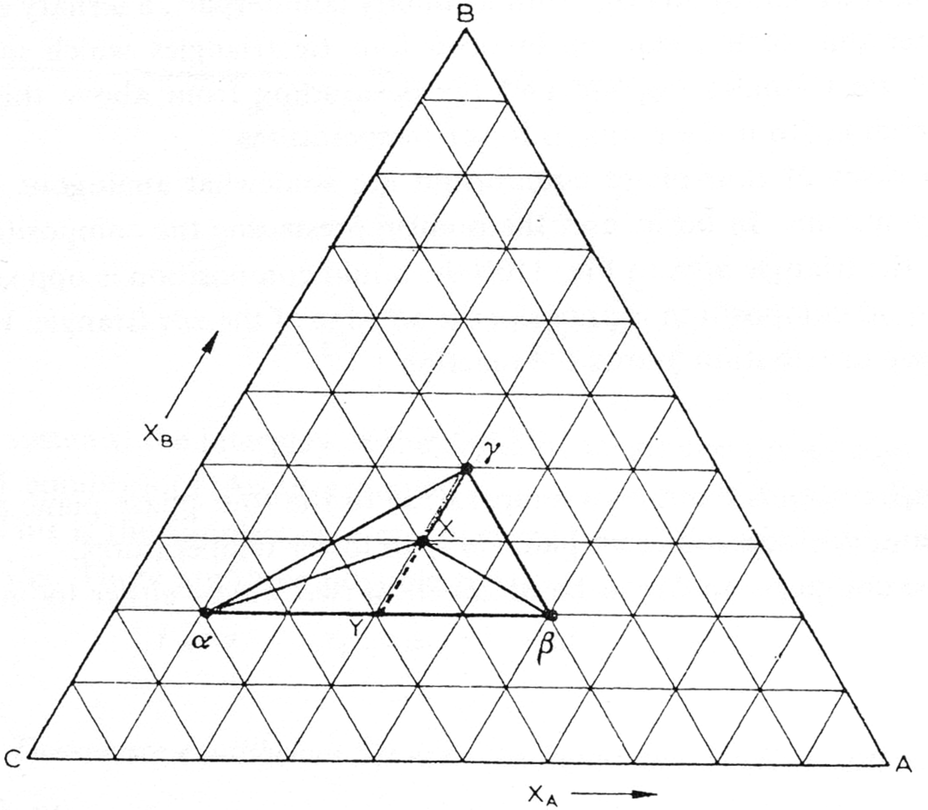
S composition = Q alloy + R alloy (tie line), Q contents and R contents in O alloy

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

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

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%

8.3 TIE LINES AND TIE TRIANGLES

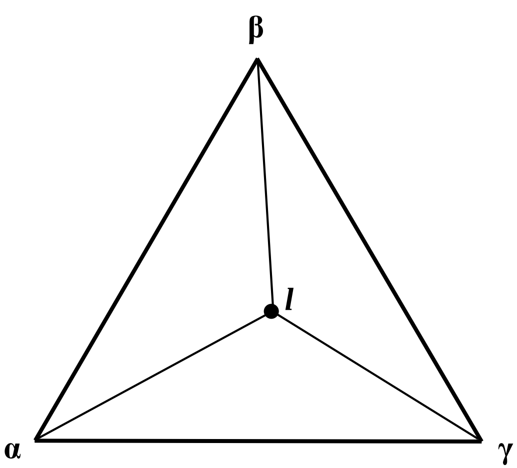
P=4

4 phase equil. → f=0 → invariant reaction

① **Ternary eutectic** : L → α + β + γ

② **Ternary peritectic** : L + α + β → γ
L + α → β + γ

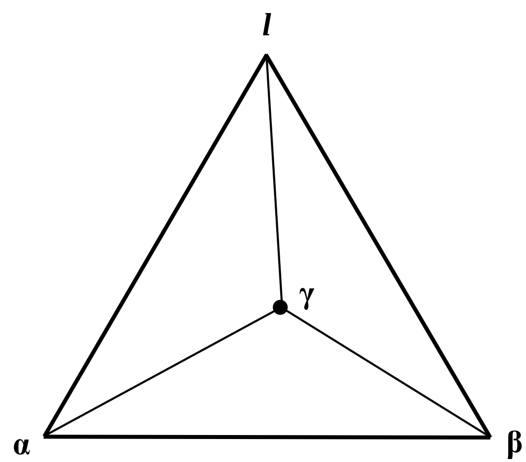
Ternary eutectic



αβ*l* & αγ*l* & βγ*l* → αβγ*l* → αβγ

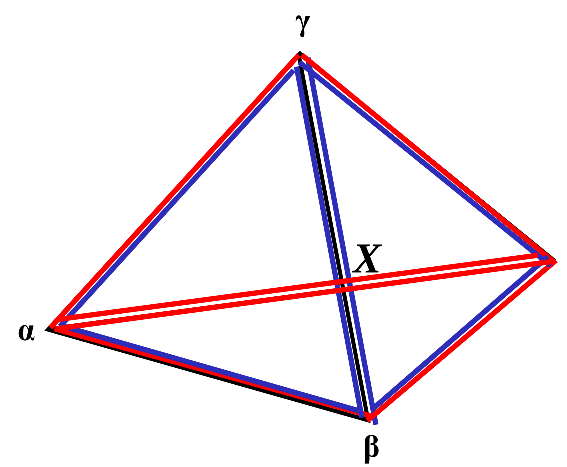
Ternary peritectic

L + α + β → γ



αβγ & αγ*l* & βγ*l* → αβγ*l* → γ

L + α → β + γ



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

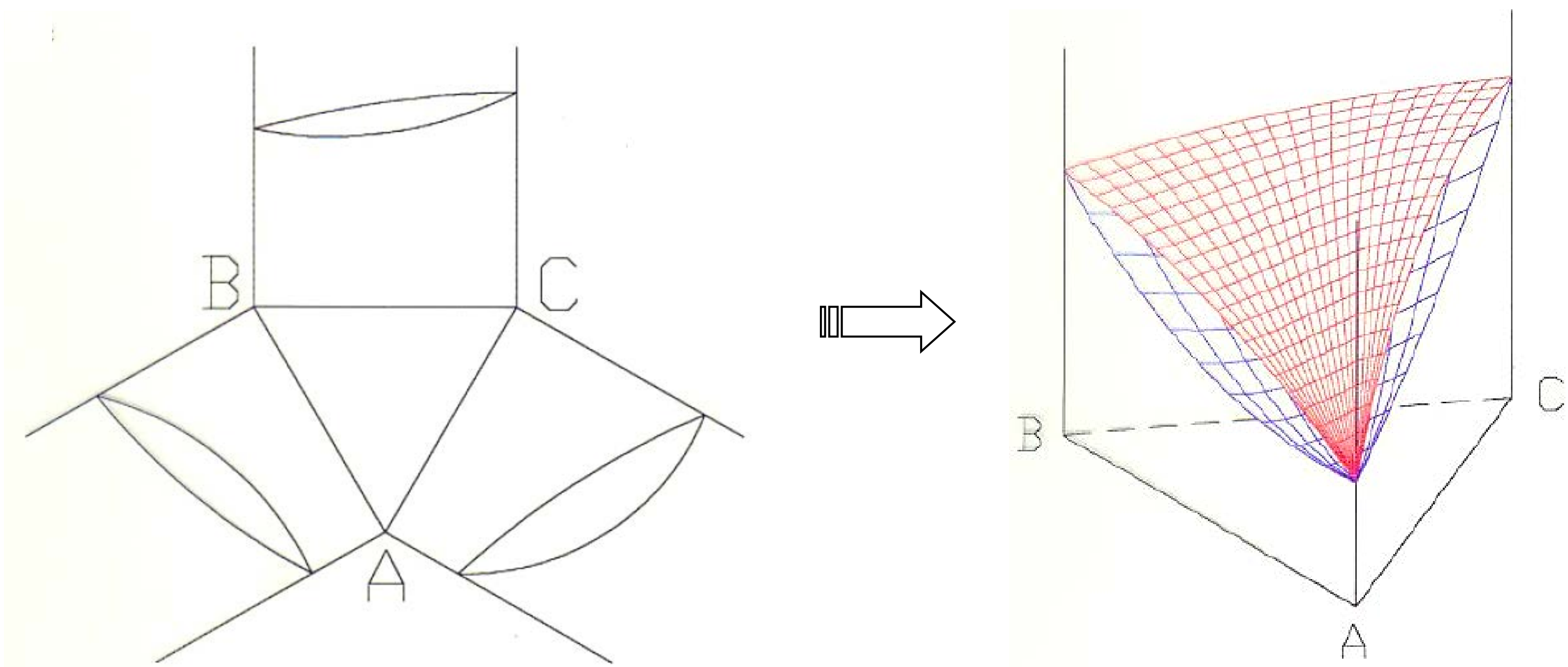
αβ*l* & αγ*l* → αβγ*l* → αβγ & βγ*l*

8.4 TWO-PHASE EQUILIBRIUM

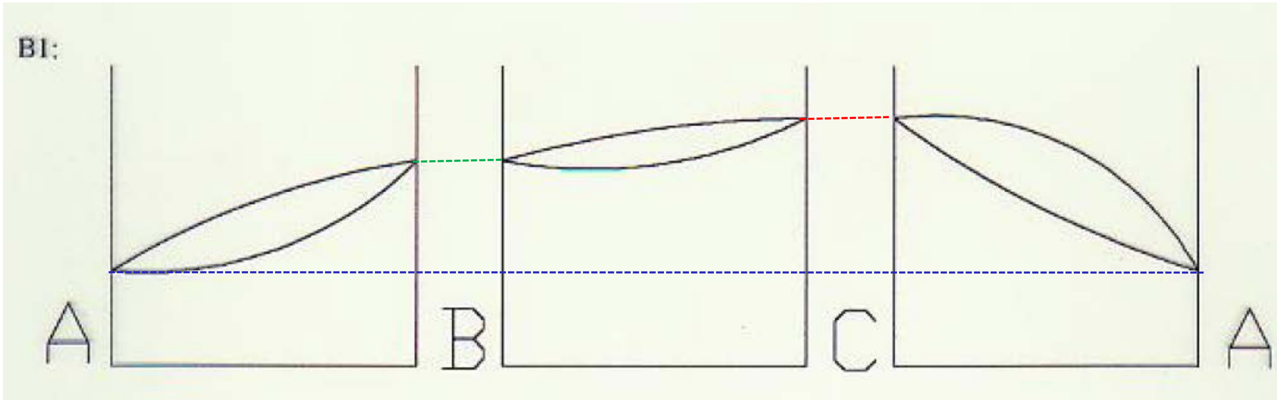
8.4.1 Two-phase equilibrium between the liquid and a solid solution

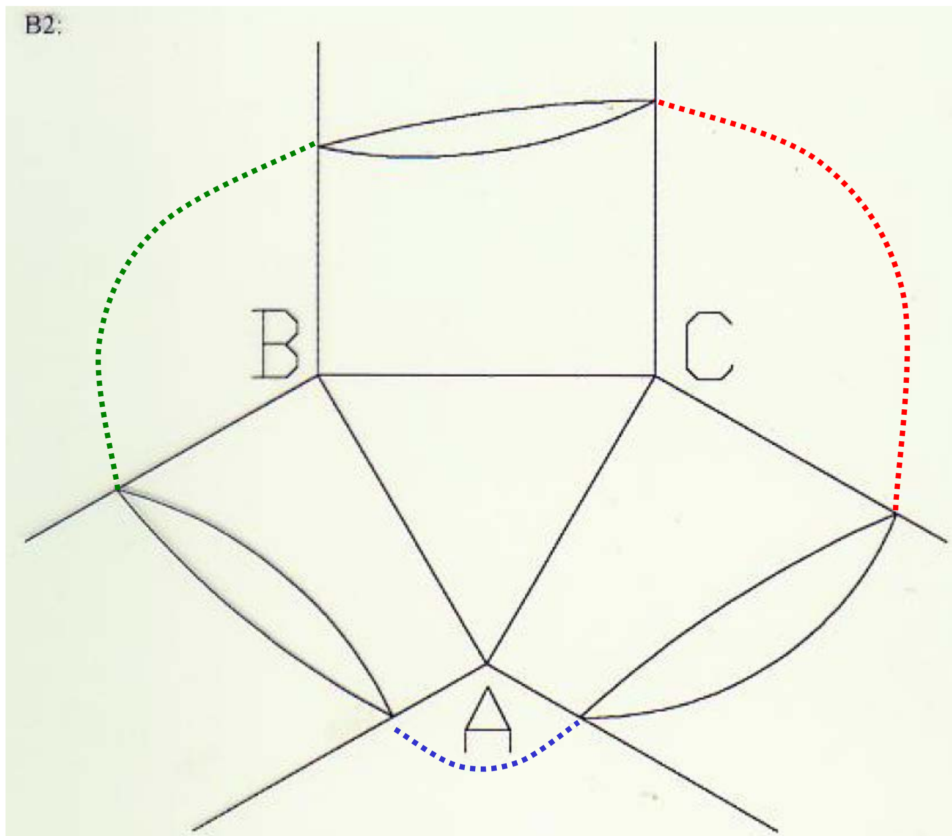
Ternary isomorphous system

A system that has only one solid phase. All components are totally soluble in the other components. The ternary system is therefore made up of three binaries that exhibit total solid solubility.

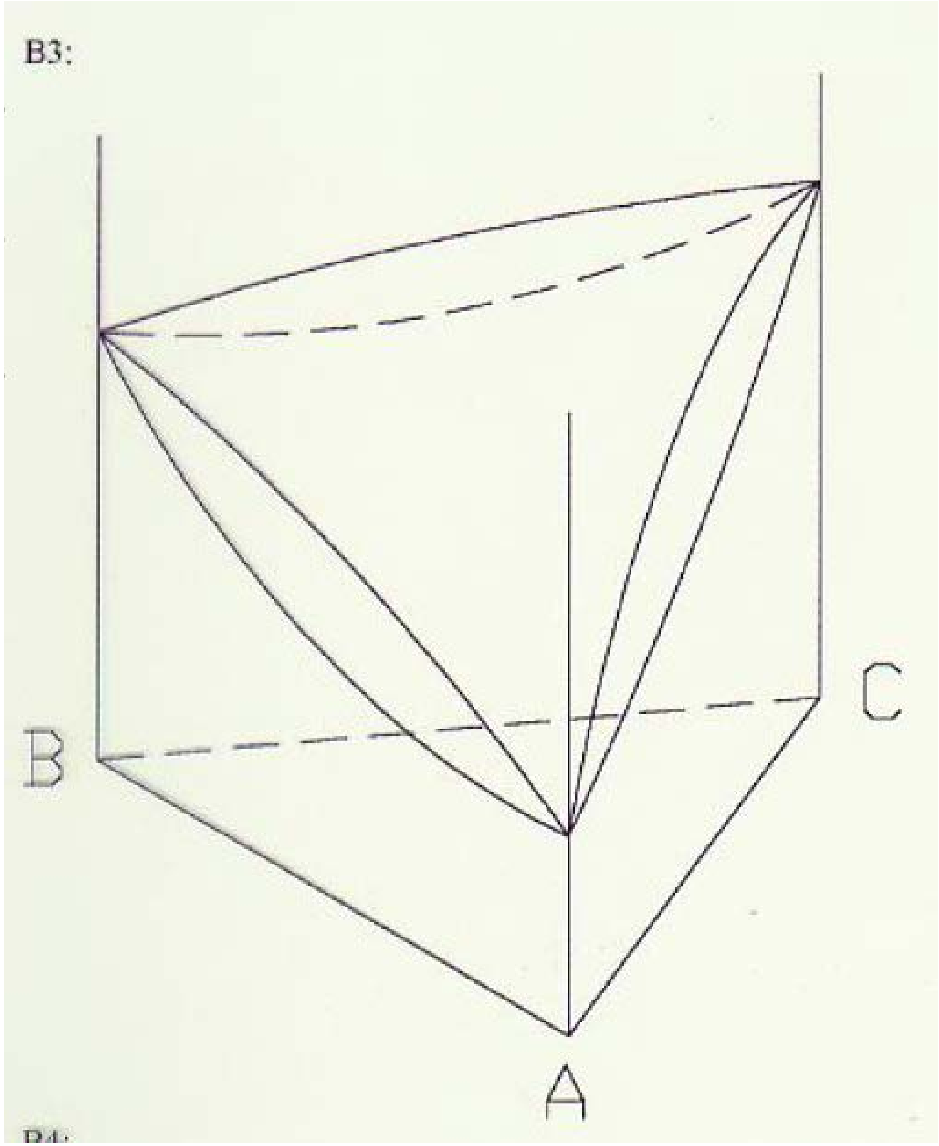


Ternary Isomorphous System

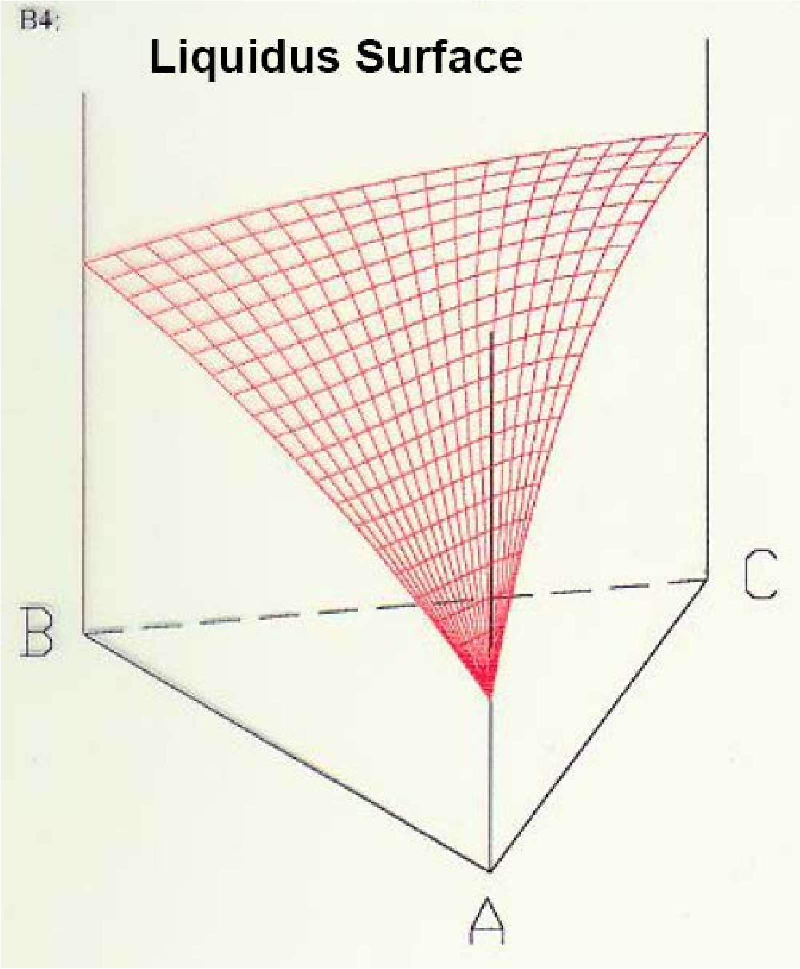




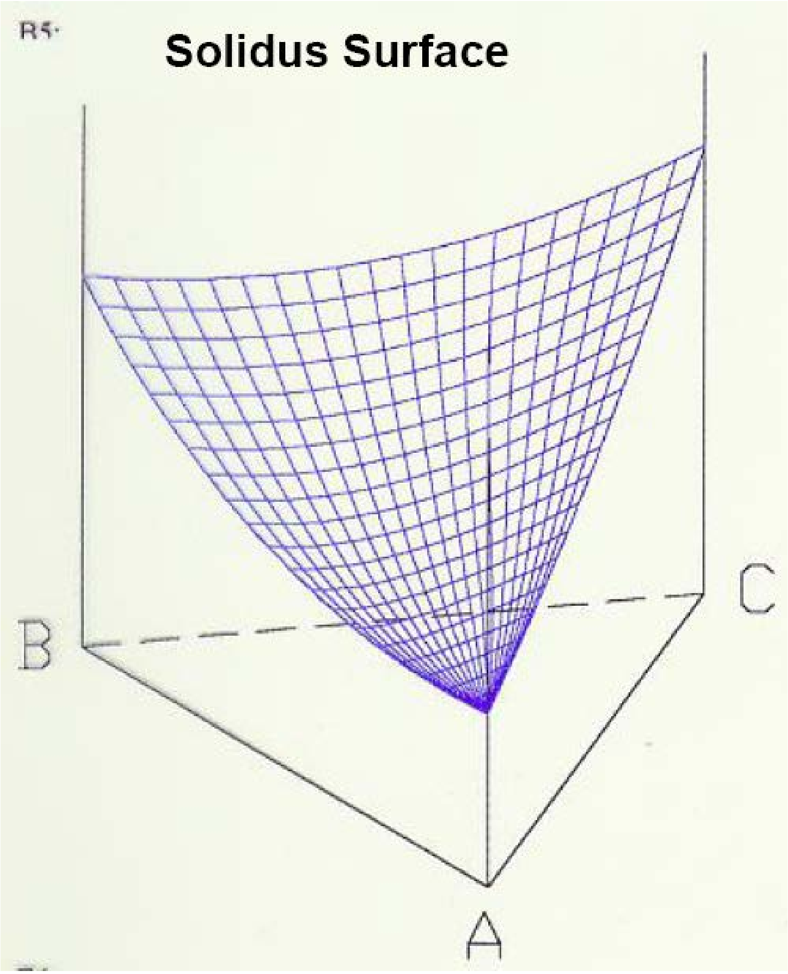
Ternary Isomorphous System



Ternary Isomorphous System

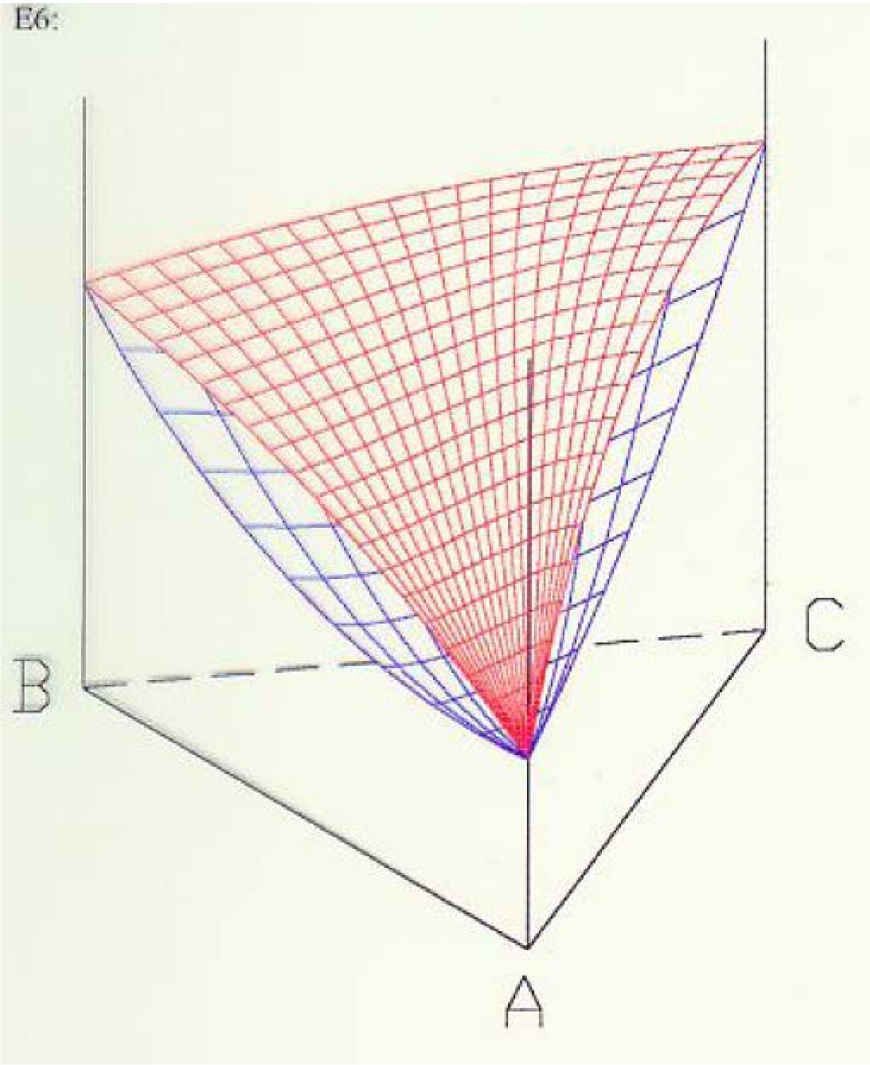


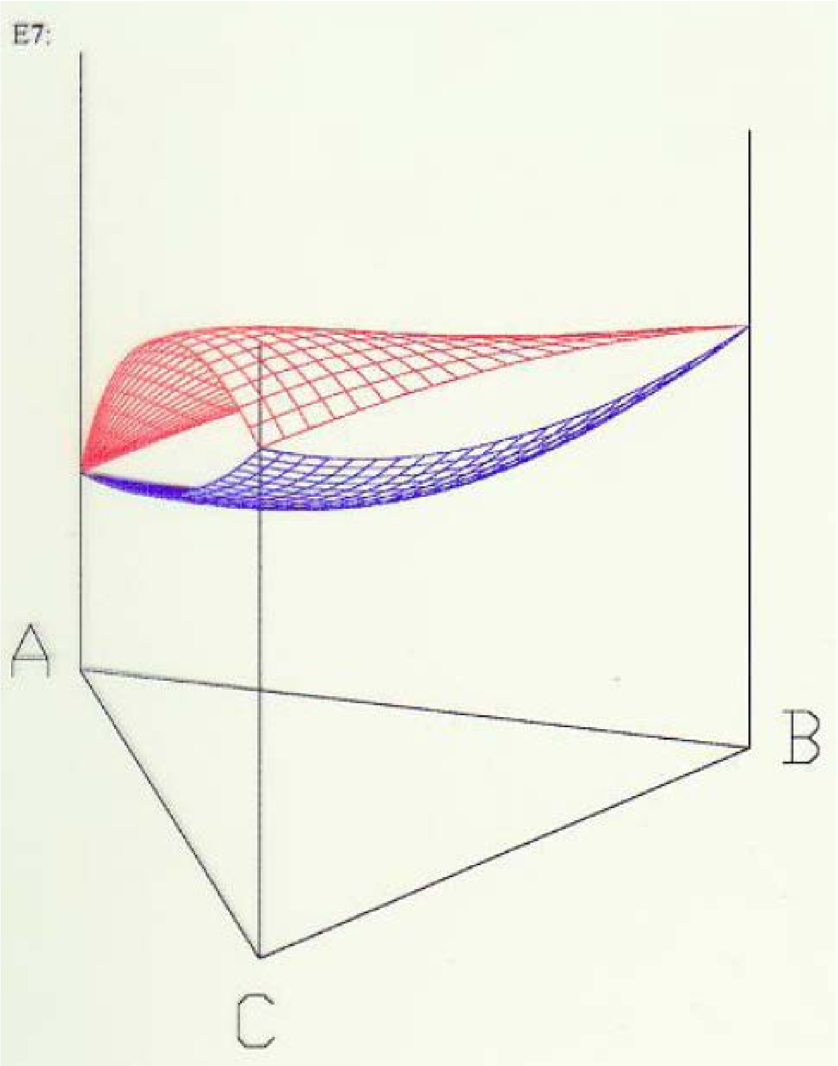
A plot of the temperatures above which a homogeneous liquid forms for any given overall composition.



A plot of the temperatures below which a homogeneous solid phase forms for any given overall composition.

Ternary Isomorphous System





Ternary Phase Diagram: three dimensional models

How to show in 2-dim. space?

① **Projection (liquidus & solidus surface, solid solubility)**

② **Isothermal section**

③ **Vertical section**

④ **Polythermal projection**

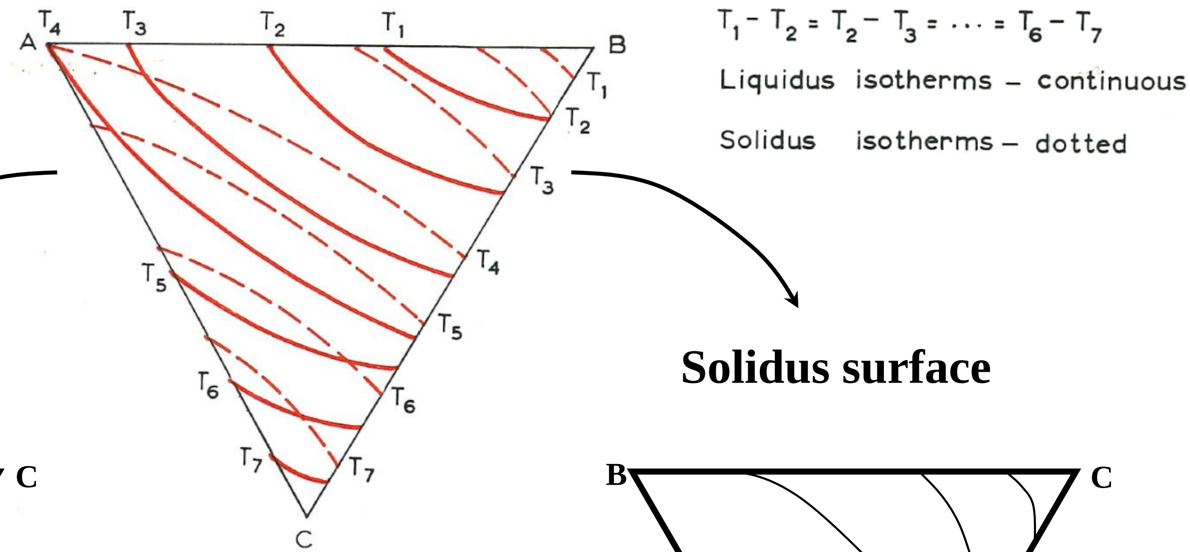
H8: find a good example & submit ppt file by email

8.4 TWO-PHASE EQUILIBRIUM

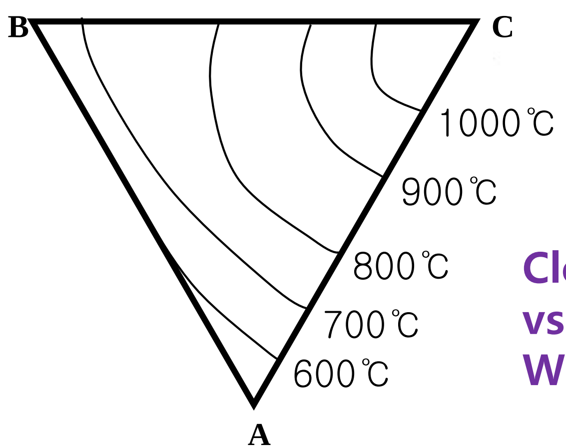
8.4.1 Two-phase equilibrium between the liquid and a solid solution

① Projection (liquidus & solidus surface)

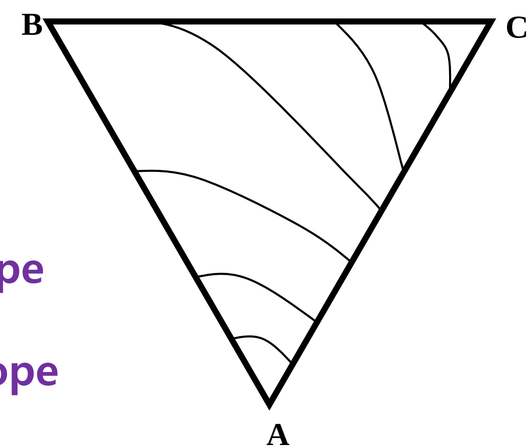
→ **No information on 2 phase region**



Liquidus surface



Solidus surface



Close spacing → steep slope
vs
Wide spacing → gentle slope

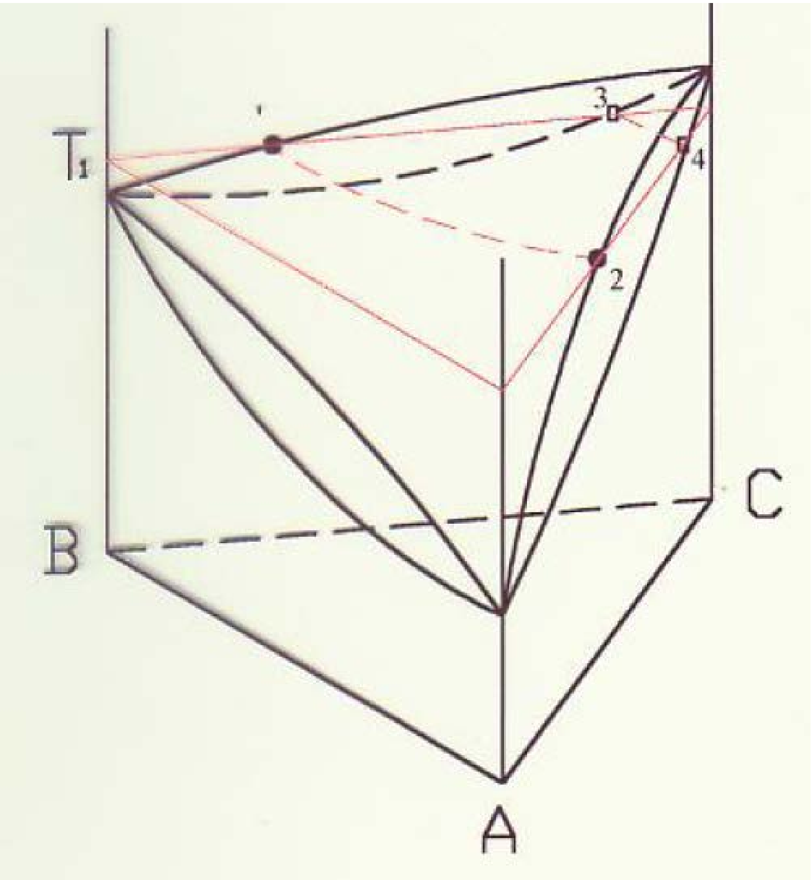
Projections of the liquidus surface are often useful in conveying a clear impression of the <u>shape of the surface</u> and indicating, by <u>folds and valleys, the presence of ternary invariant reactions</u>.

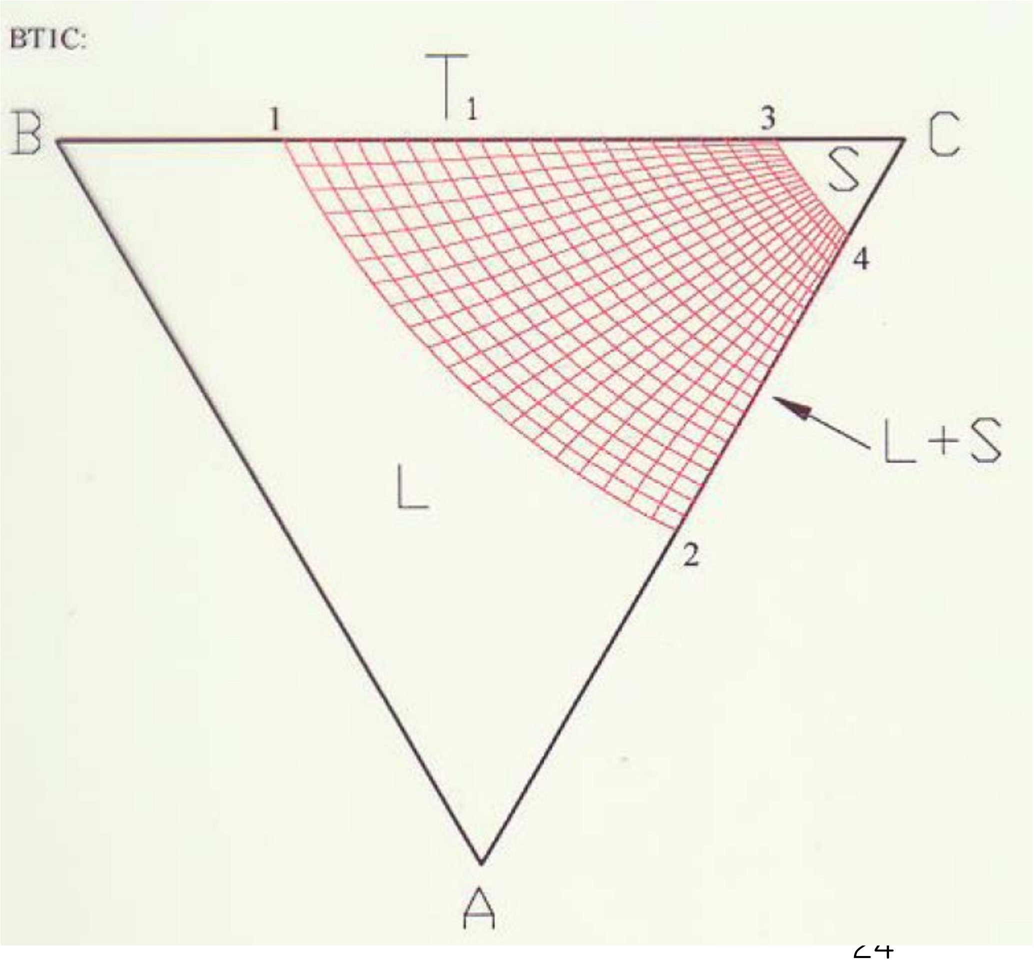
8.4 TWO-PHASE EQUILIBRIUM

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

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

Ternary Isomorphous System





8.4 TWO-PHASE EQUILIBRIUM

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

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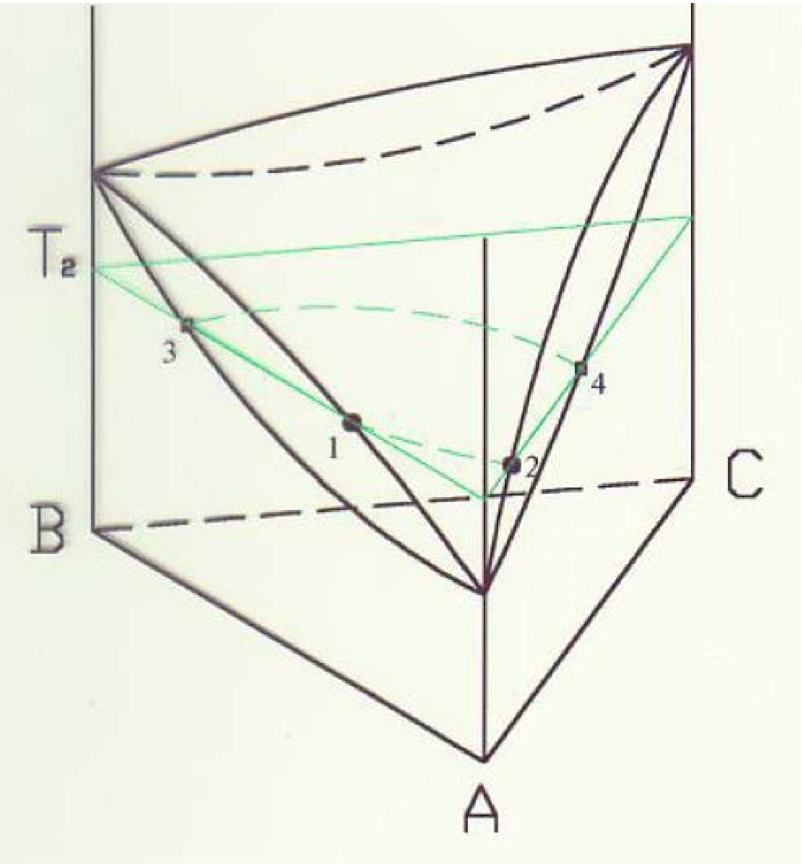
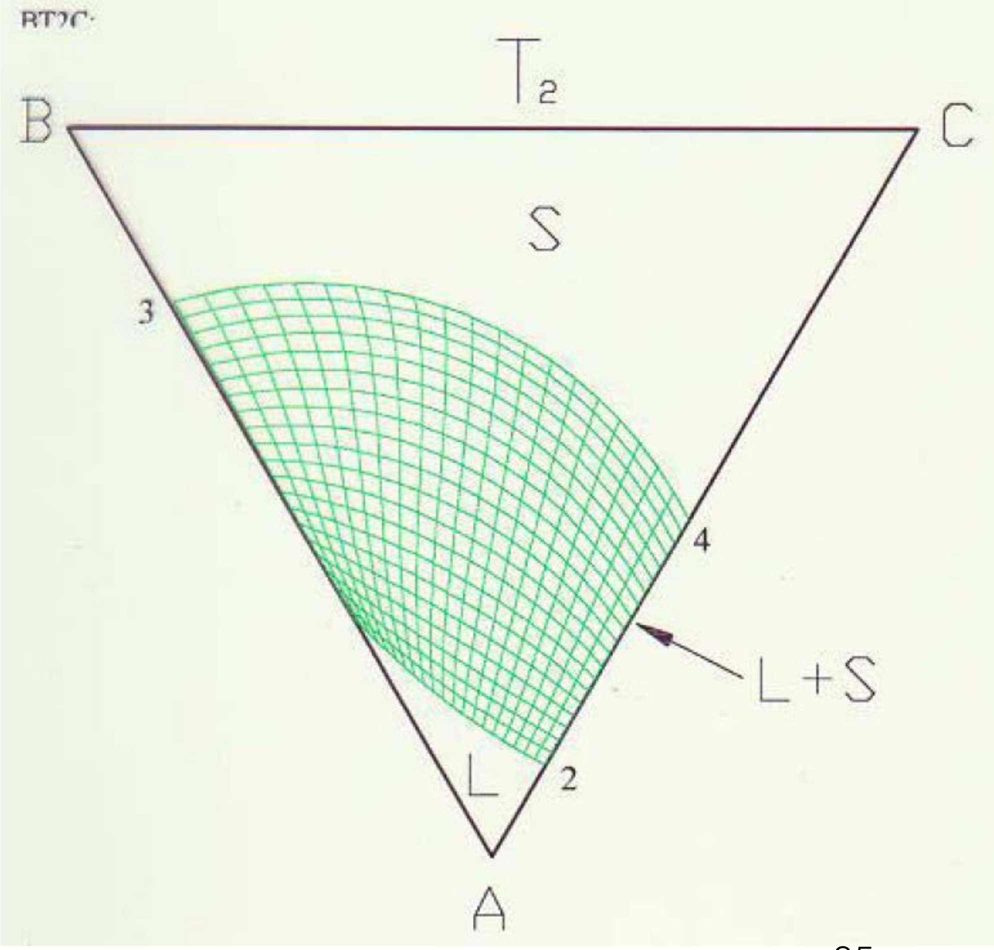
Ternary Isomorphous System





Ternary Isomorphous System

Isothermal section → F = C - P

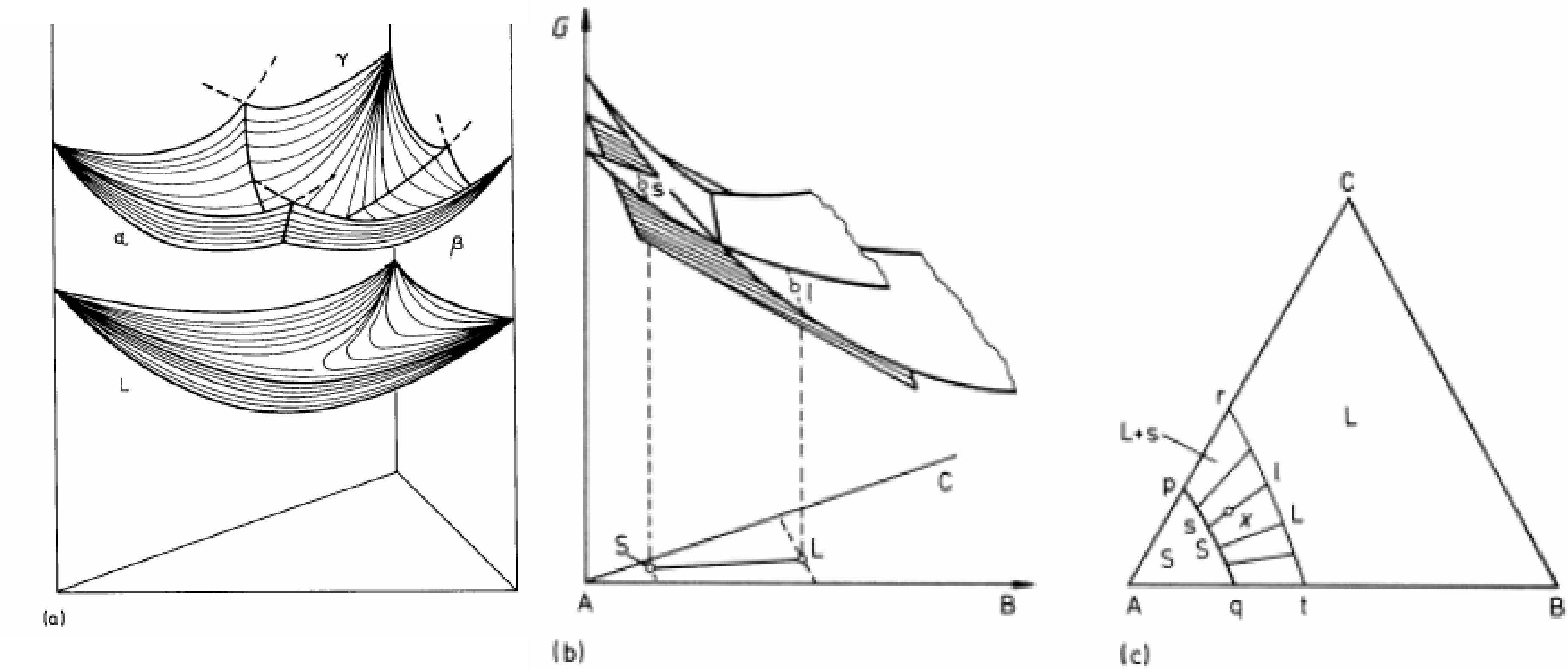
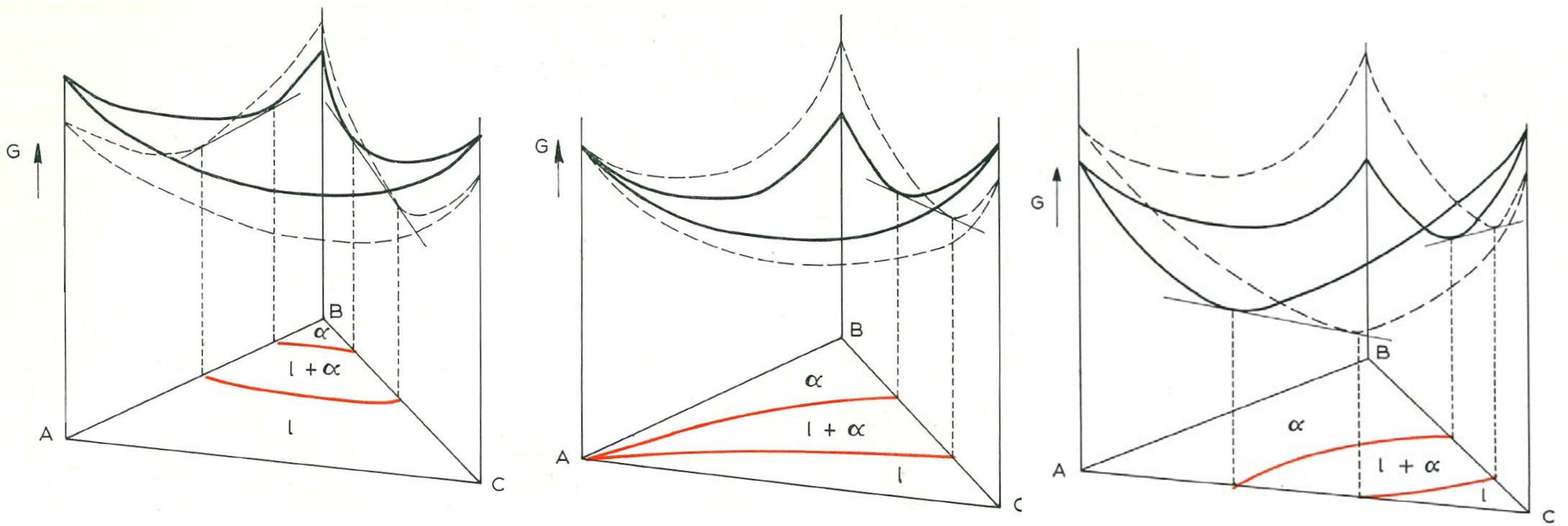


Fig. 1.41 (a) Free energies of a liquid and three solid phases of a ternary system.

Ternary Isomorphous System

Isothermal section → F = C - P



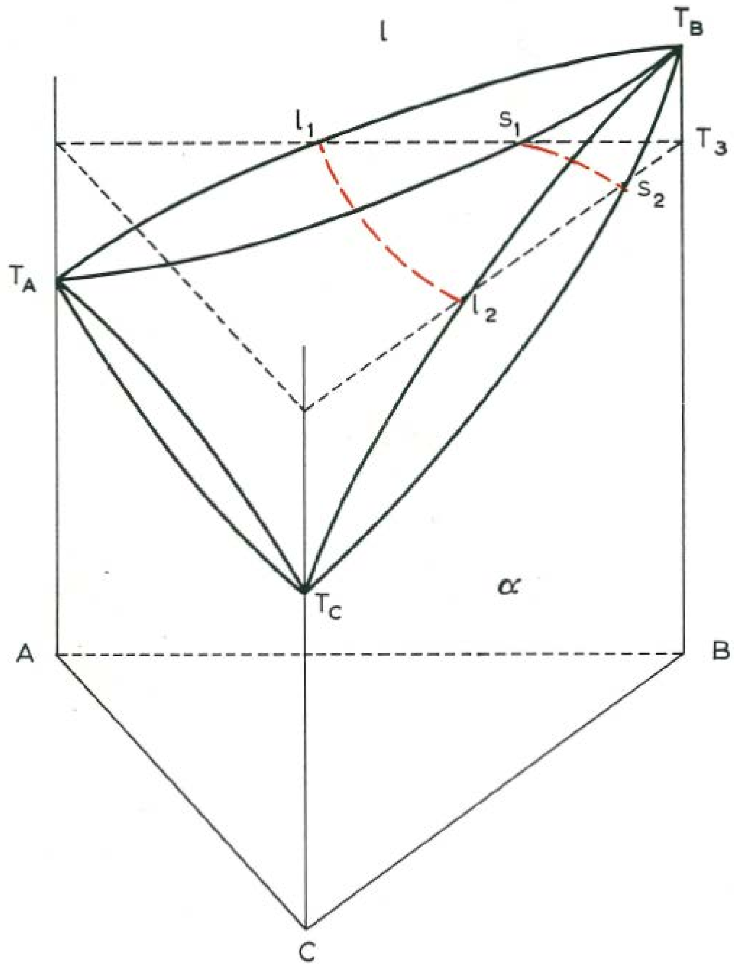
124. Illustration of the equilibria in Fig. 111 by means of free energy surfaces for the liquid and α phases at various temperatures, (a) between T_B and T_A, (b) at T_A, and (c) between T_A and T_C.
– – – – – –, liquid free energy surface; ————, α free energy surface.

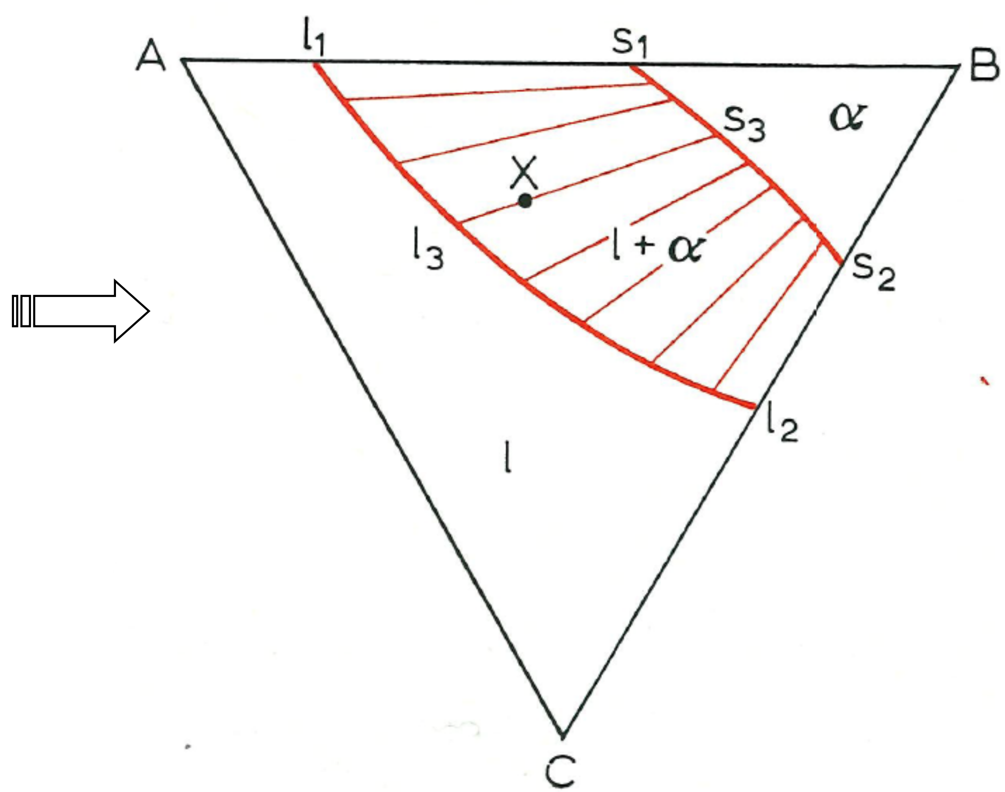
8.4 TWO-PHASE EQUILIBRIUM

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

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

Ternary Isomorphous System





8.4 TWO-PHASE EQUILIBRIUM

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

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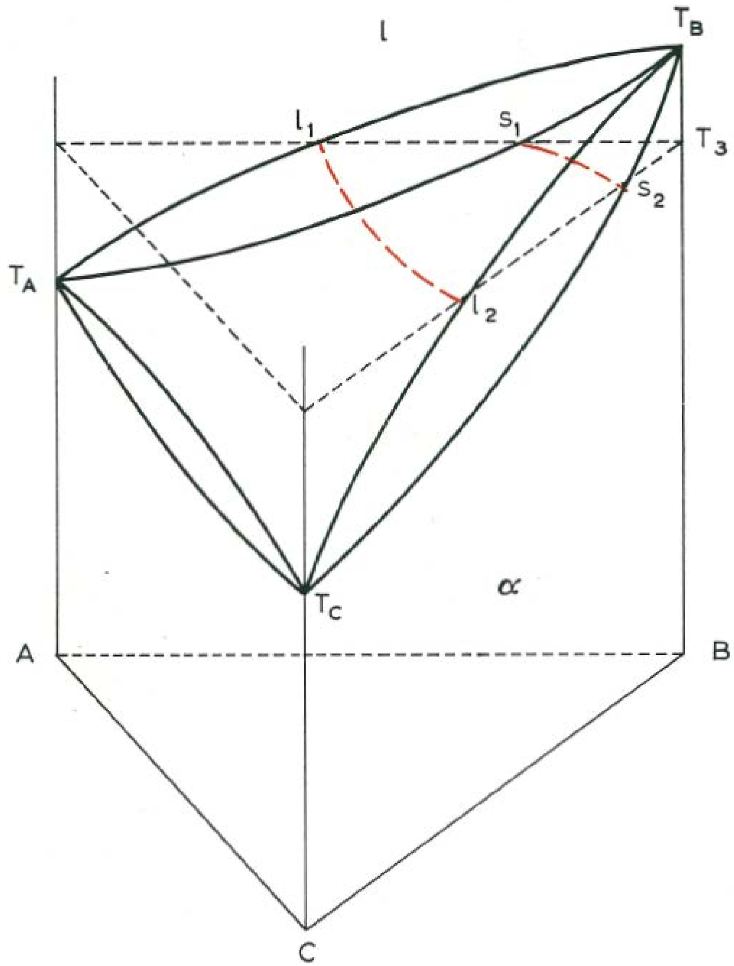
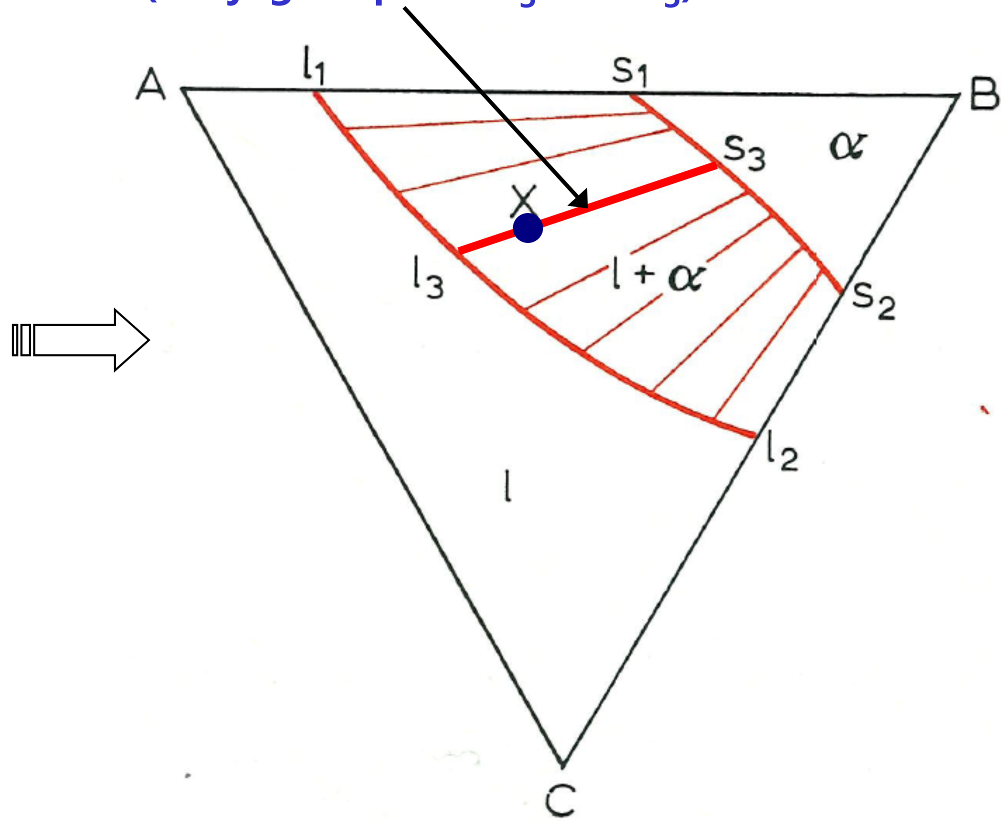
Ternary Isomorphous System





8.4 TWO-PHASE EQUILIBRIUM

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

How decide position of tie lines?

→ by experiment

→ impossible!

Rules for tie line

(i) Slope gradually changes.

(ii) Tie lines cannot intersect.

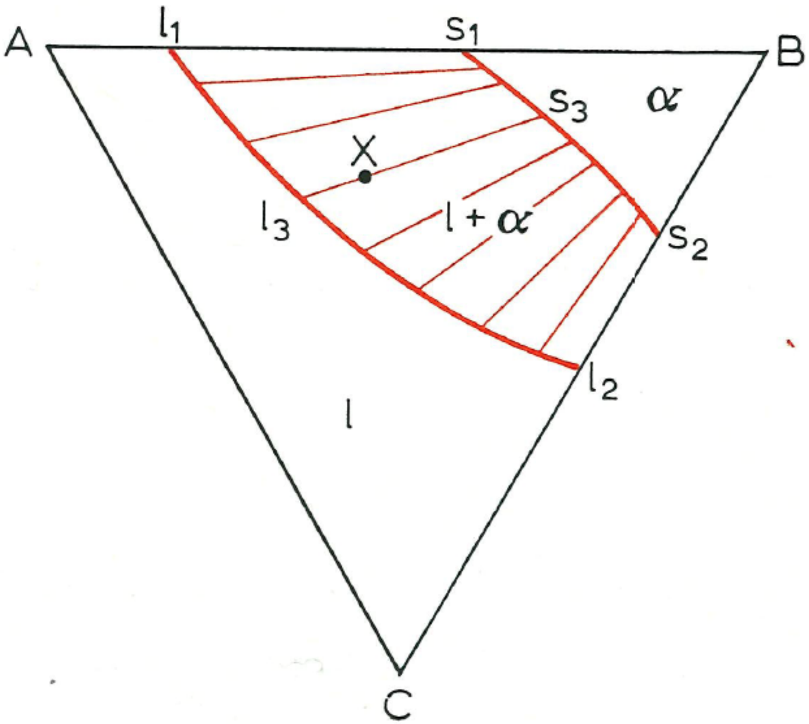
(iii) Extension of tie line cannot intersect the vertex of triangle.

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

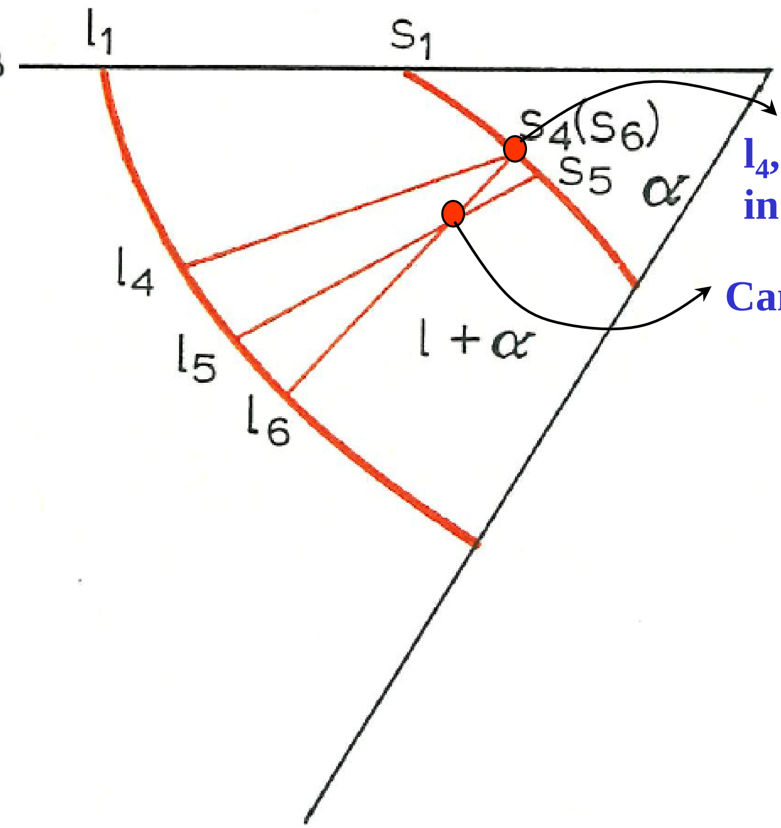
8.4 TWO-PHASE EQUILIBRIUM

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

(i) Slope gradually changes.



(ii) Tie lines cannot intersect at constant temperature.



l_4, $s_{4(6)}$, l_6 are in equil.

Cannot happen.

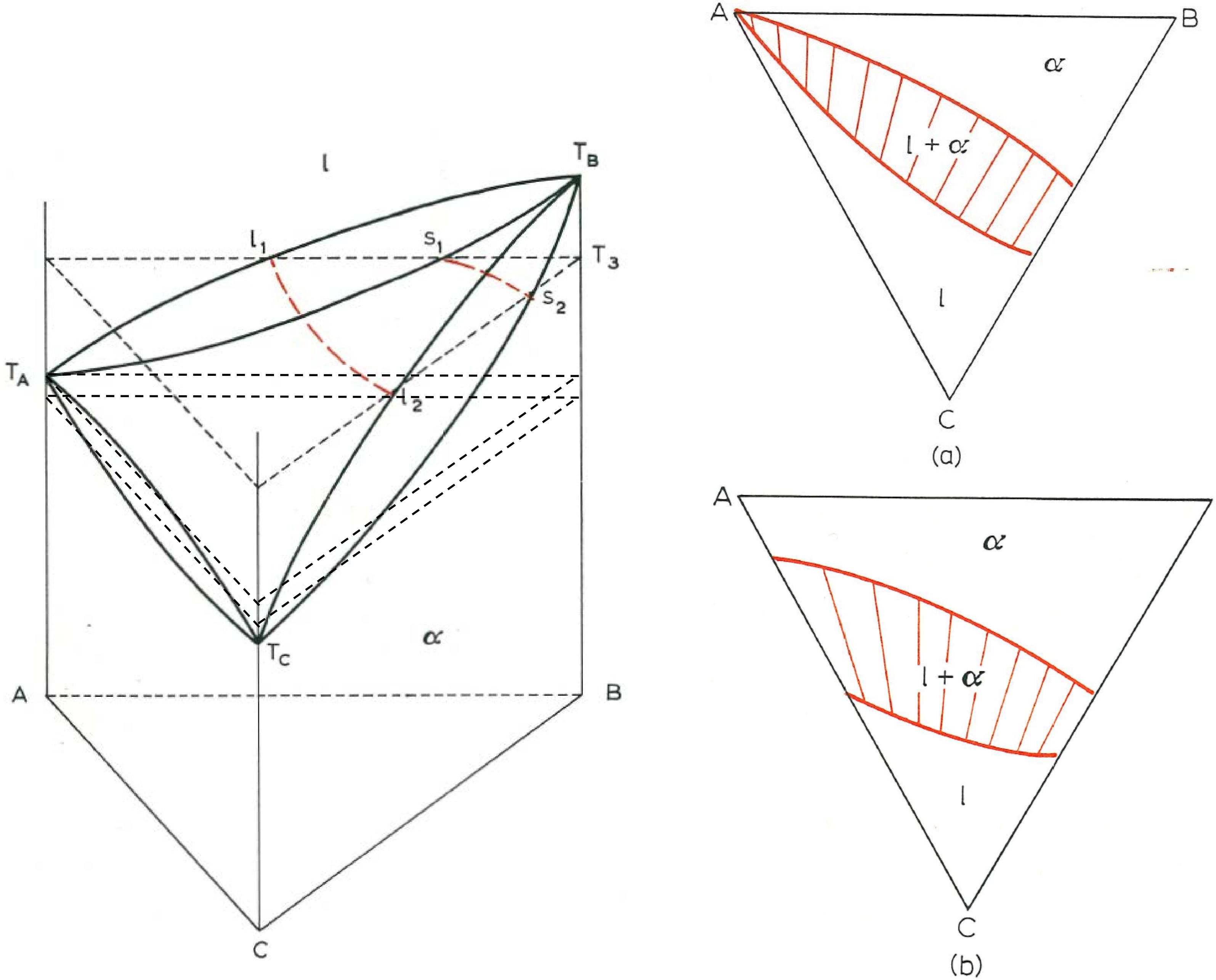
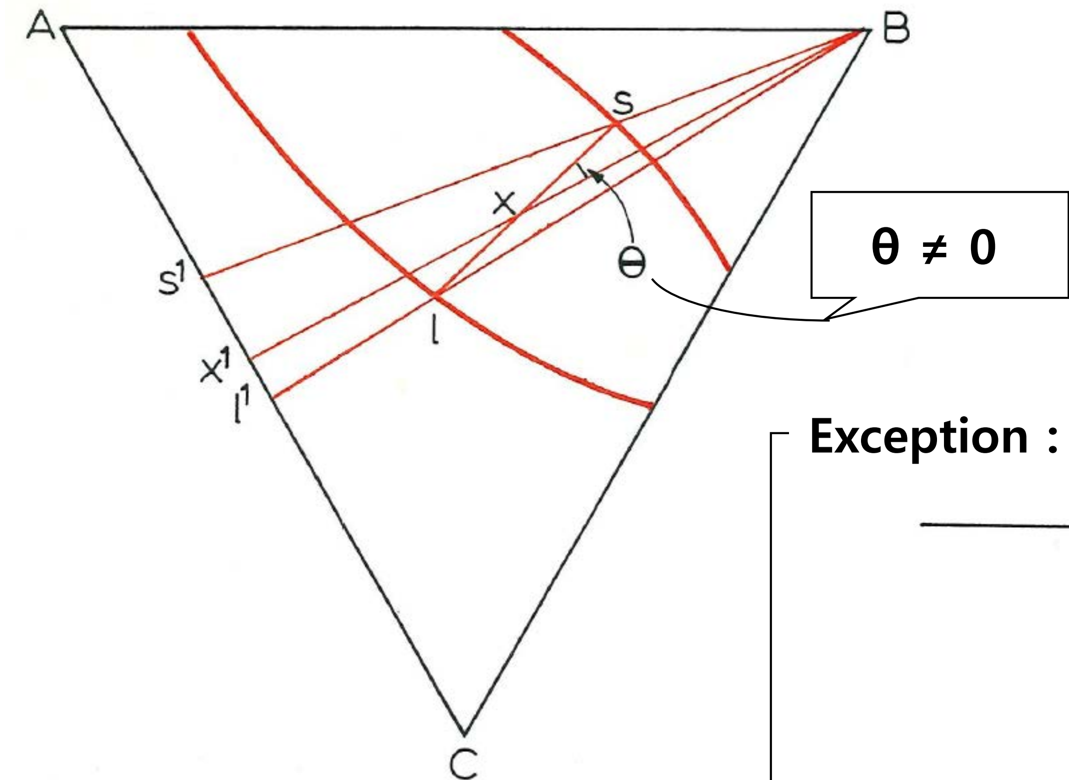


Fig. 116. Isothermal sections through Fig. 111 at (a) T_A, and (b) between T_A and T_C.

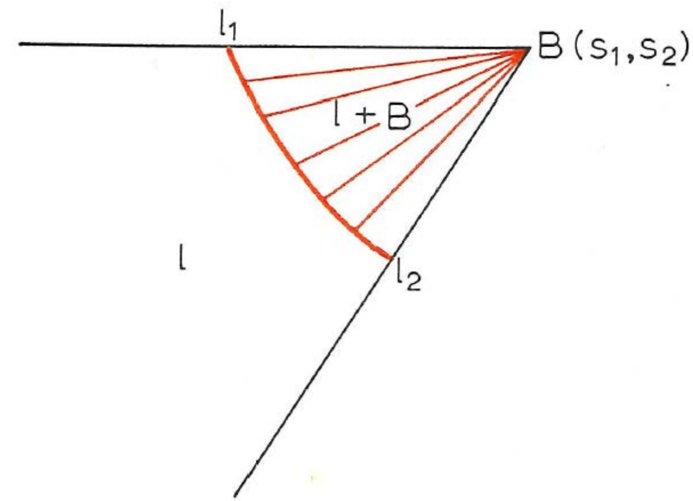
8.4 TWO-PHASE EQUILIBRIUM

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

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



Exception : solubility is infinitely small.

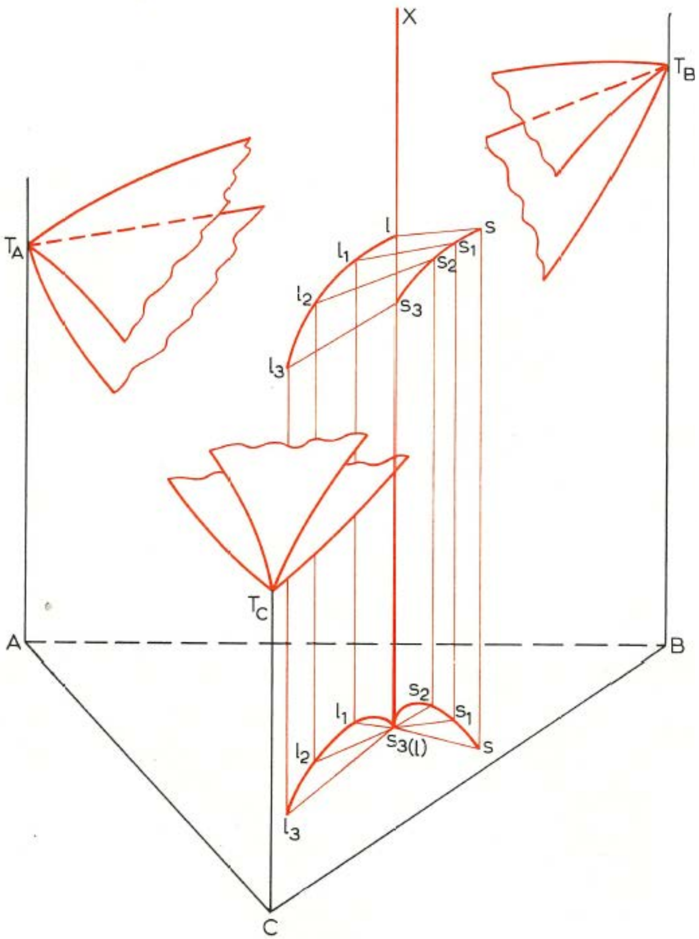


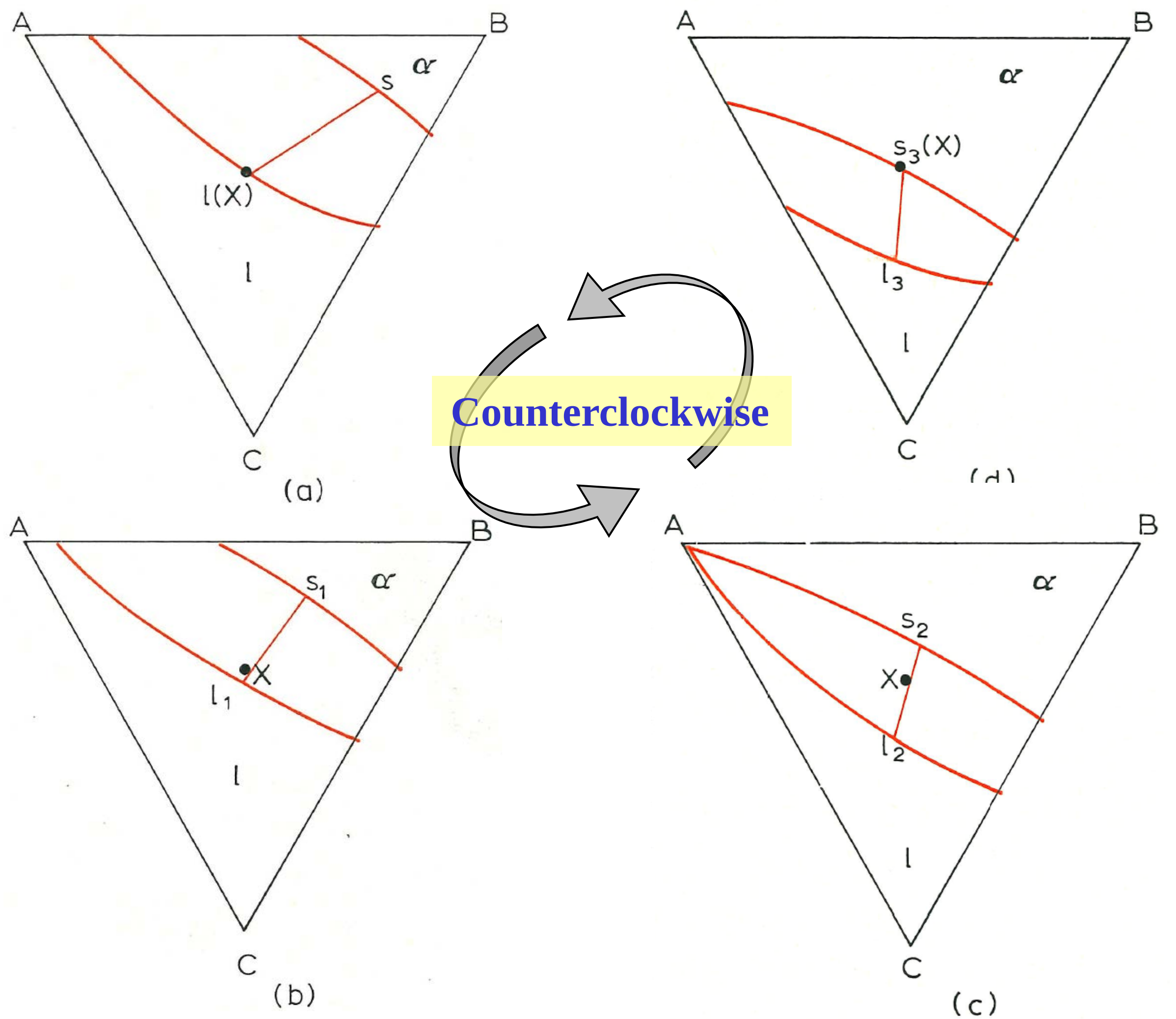
8.4 TWO-PHASE EQUILIBRIUM

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

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

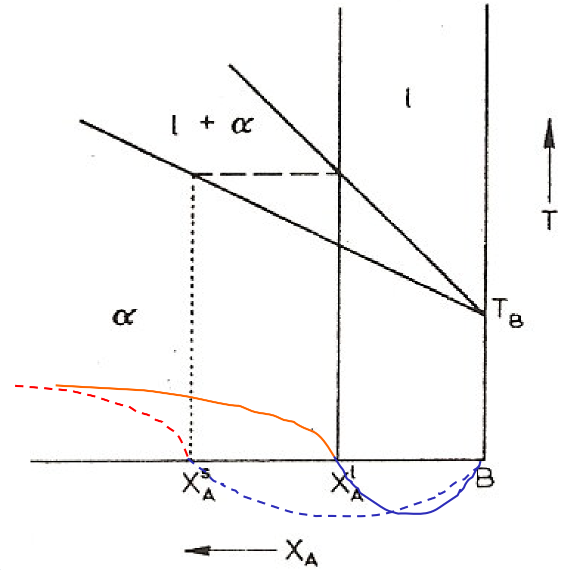
: Clockwise or counterclockwise





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

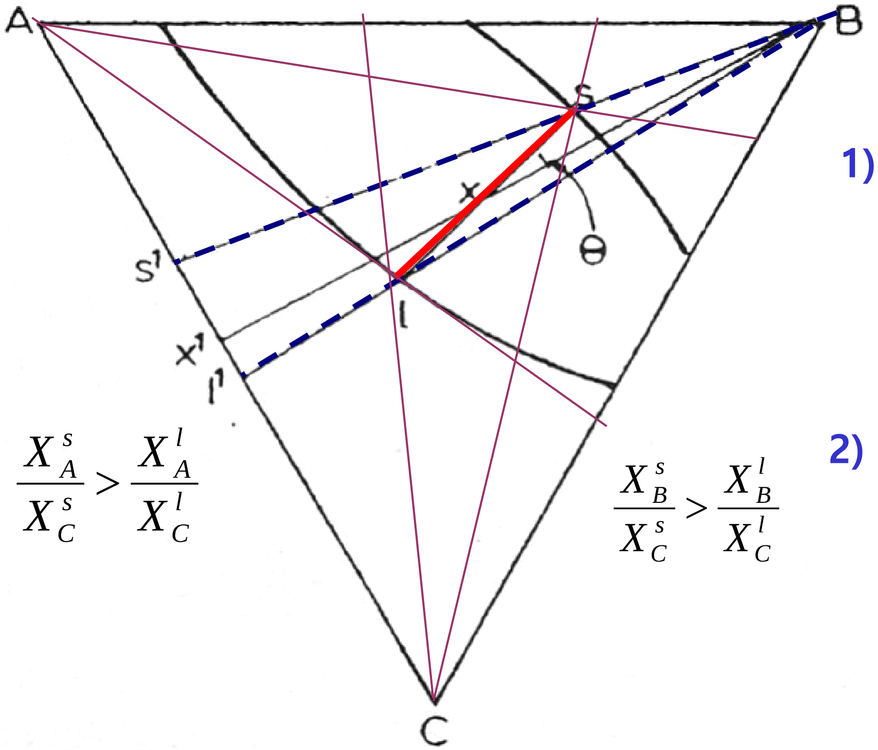
$$\frac{X_A^S}{X_A^S + X_B^S - X_A^S} > \frac{X_A^l}{X_A^l + X_B^l - X_A^l}$$

Therefore,

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

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,



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

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

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

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

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

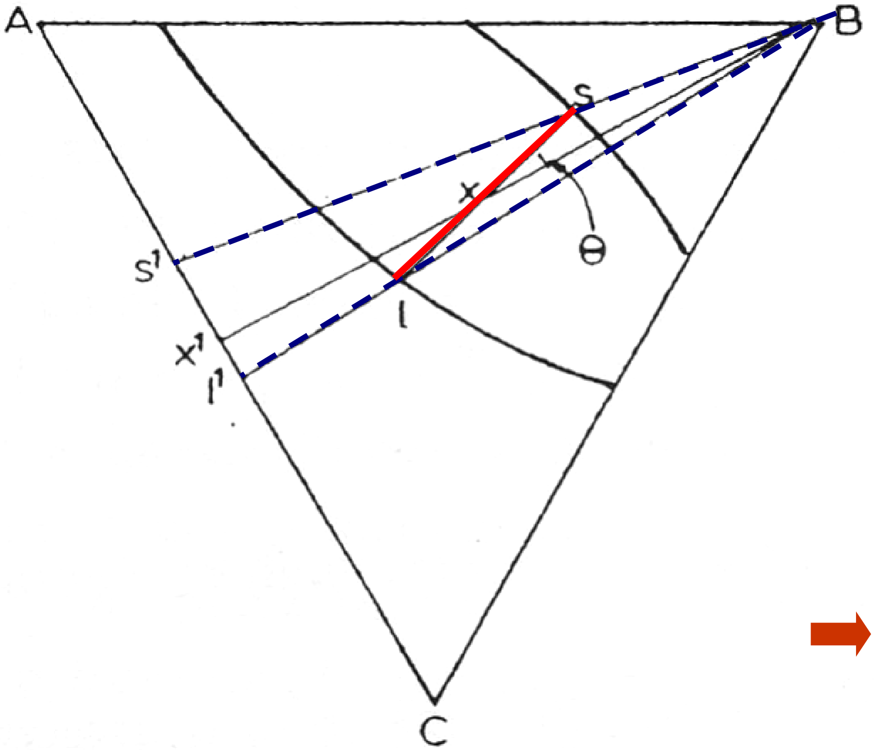
$$\frac{s^1C}{s^1A} > \frac{l^1C}{l^1A} \quad \text{and} \quad \frac{X_A^s}{X_C^s} > \frac{X_A^l}{X_C^l}$$

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

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

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

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



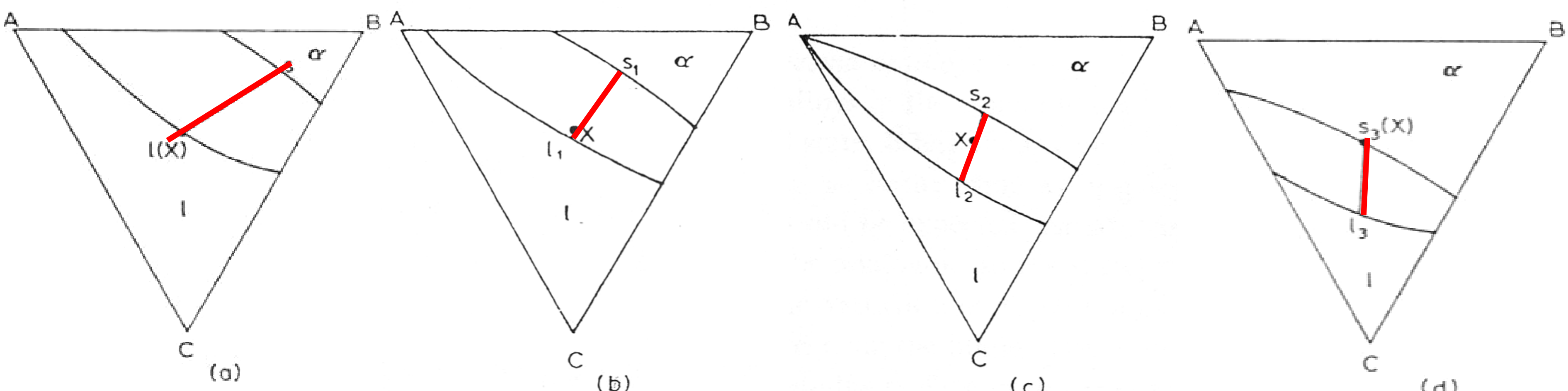
The tie line *ls* is rotated anticlockwise by an angle Θ relative to the line Bx^1.

If Θ = 0

then $$X_A^S / X_C^S = X_A^l / X_C^l$$

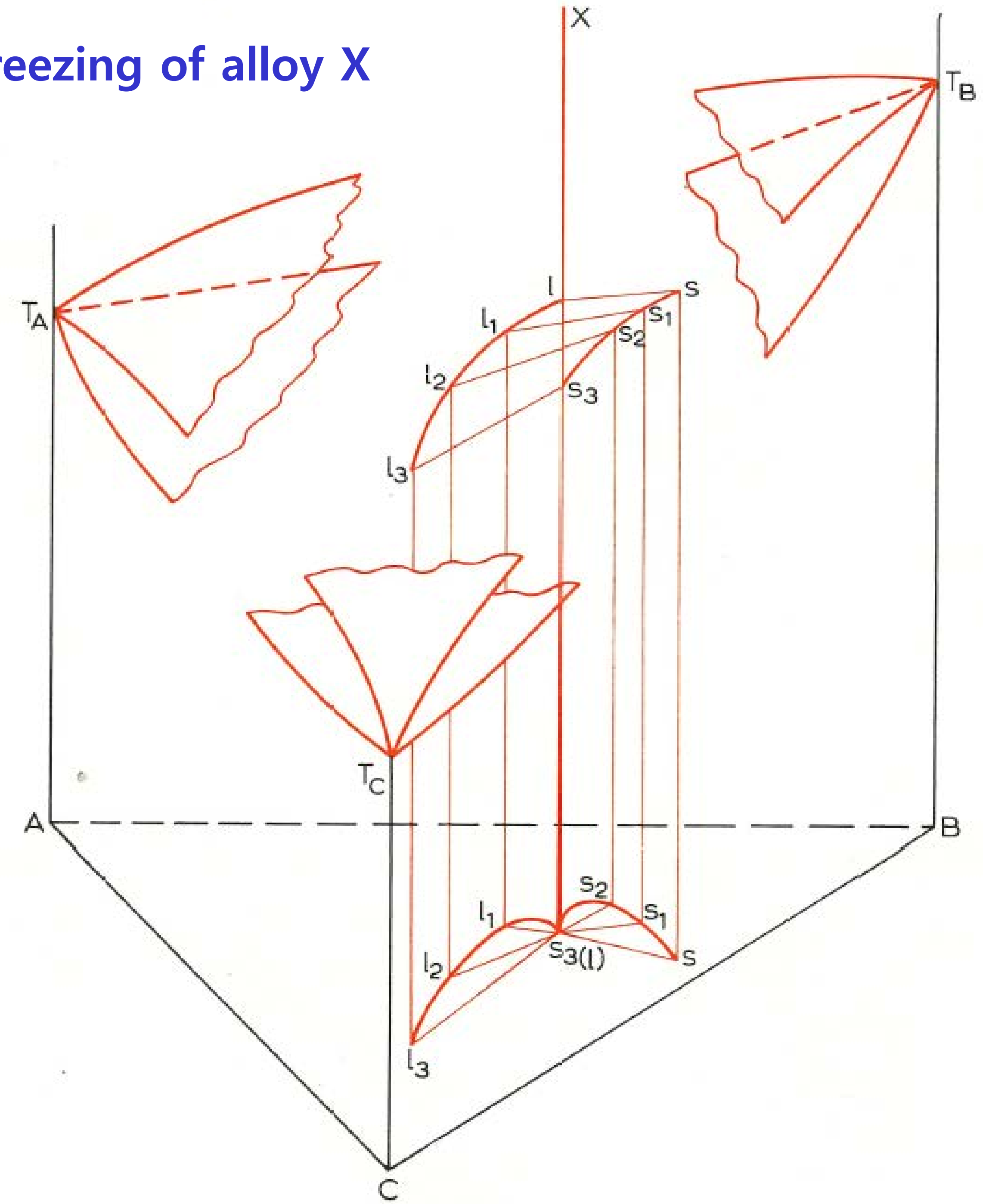
in contradiction to Konovalov's Rule.

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

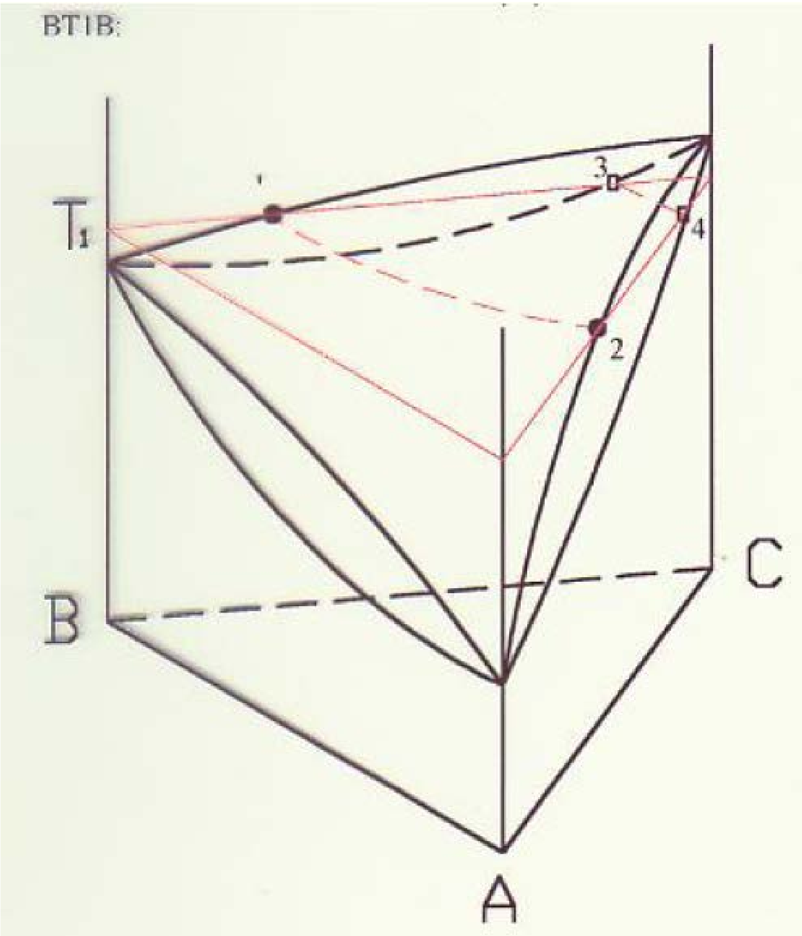


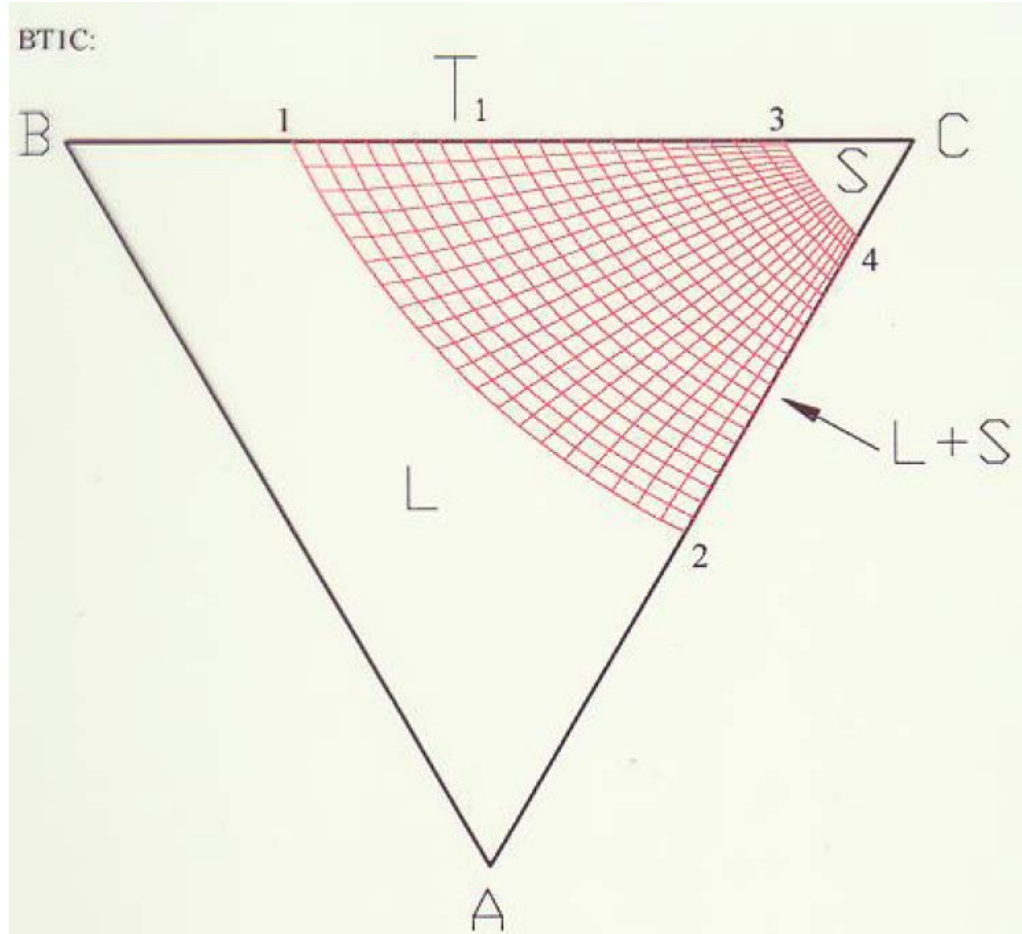
Counterclockwise rotation

Equilibrium freezing of alloy X

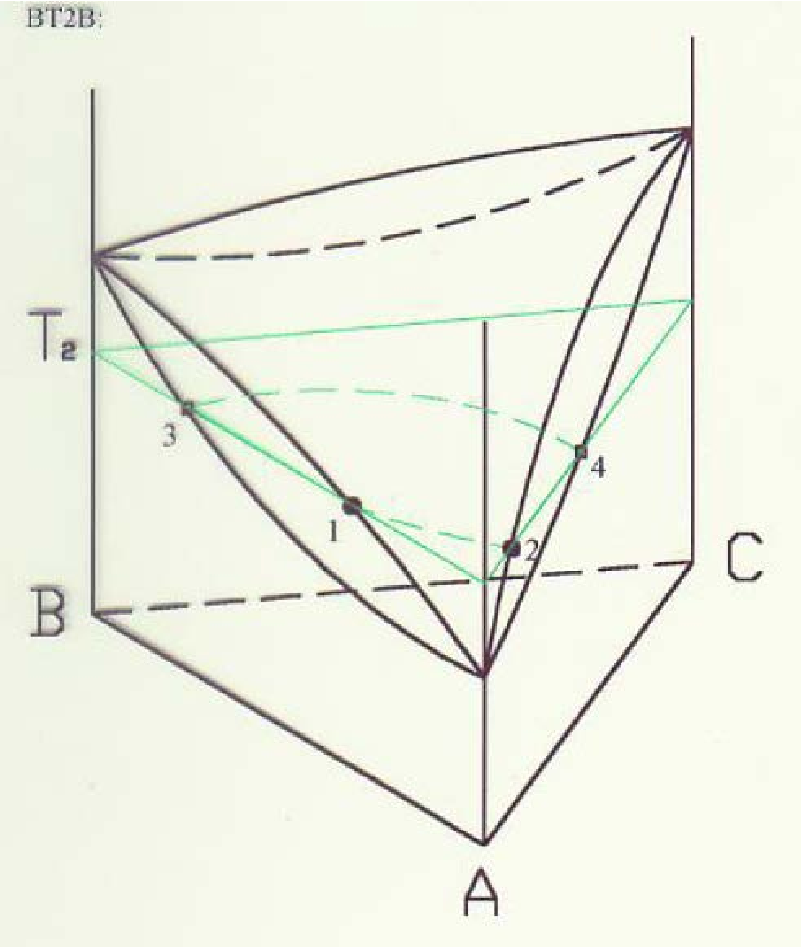


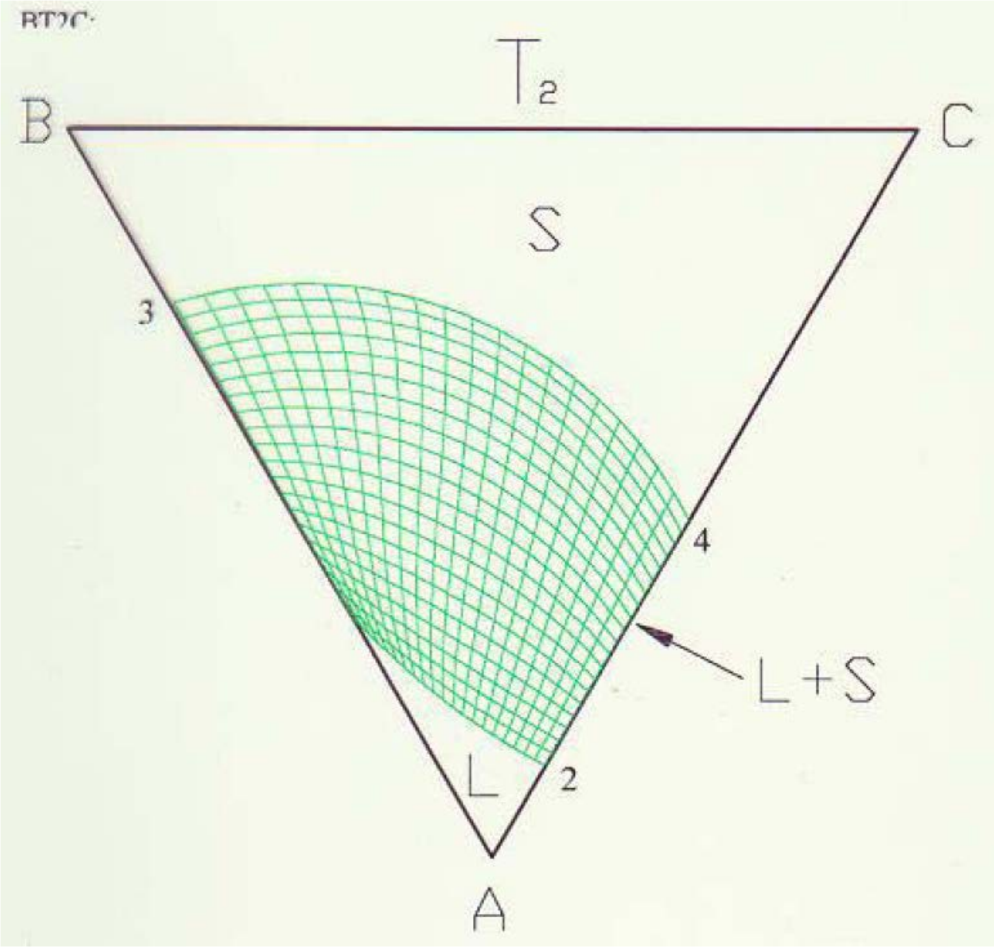
Counterclockwise rotation





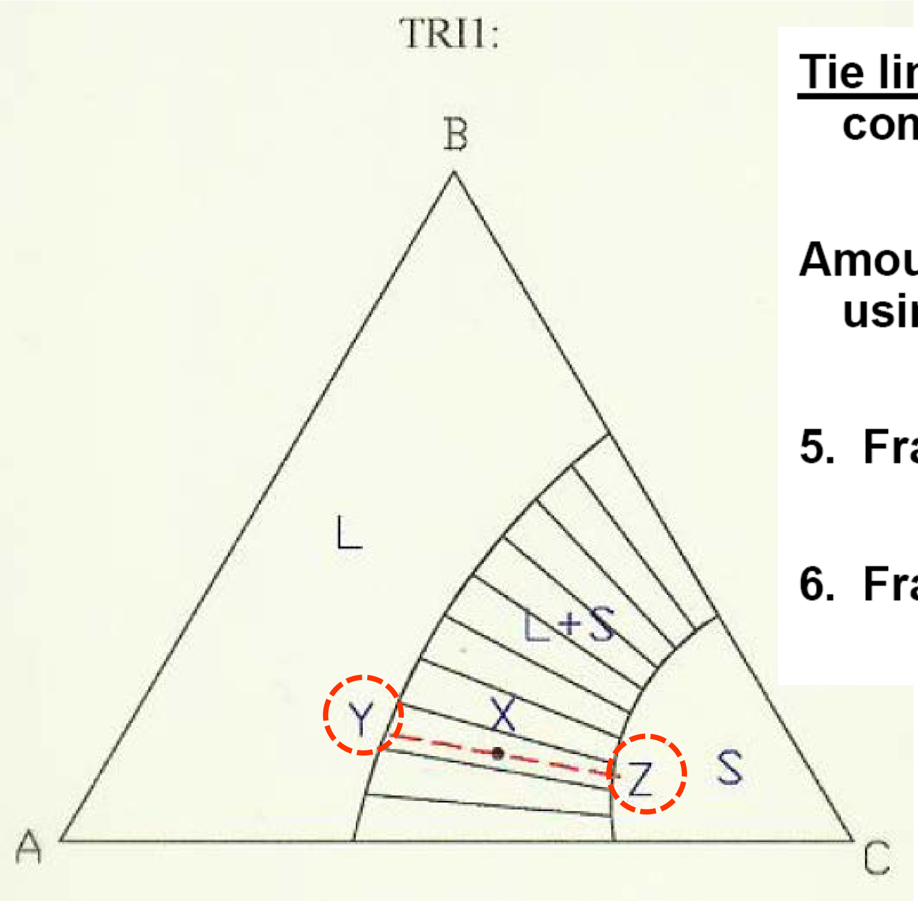
Counterclockwise rotation





Ternary Isomorphous System

Locate overall composition using Gibbs triangle



Tie line: A straight line joining any two ternary compositions

Amount of each phase present is determined by using the Inverse Lever Rule

5. Fraction of solid = YX/YZ

6. Fraction of liquid = ZX/YZ

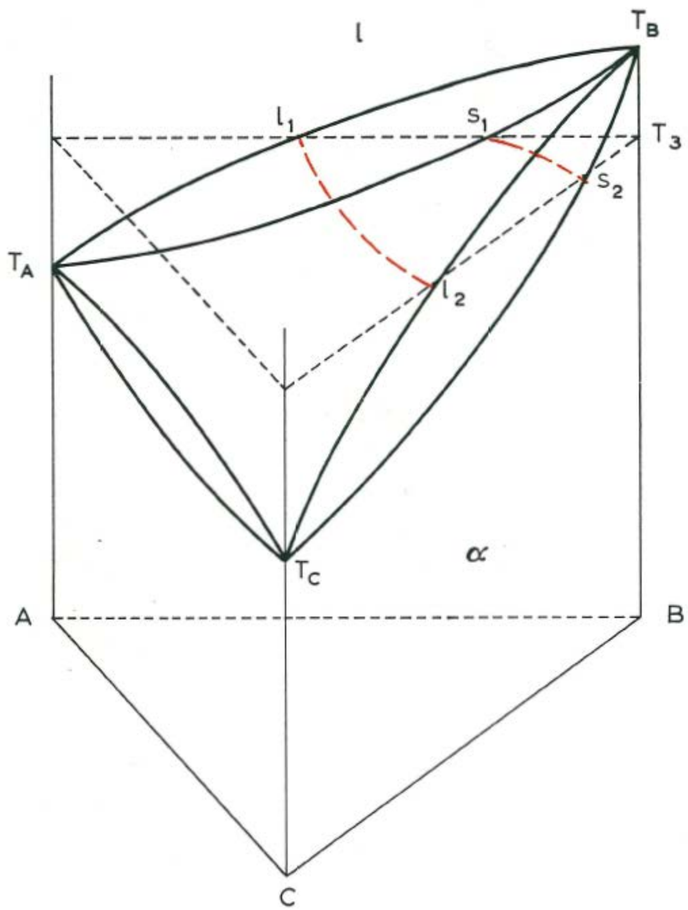
8.4 TWO-PHASE EQUILIBRIUM

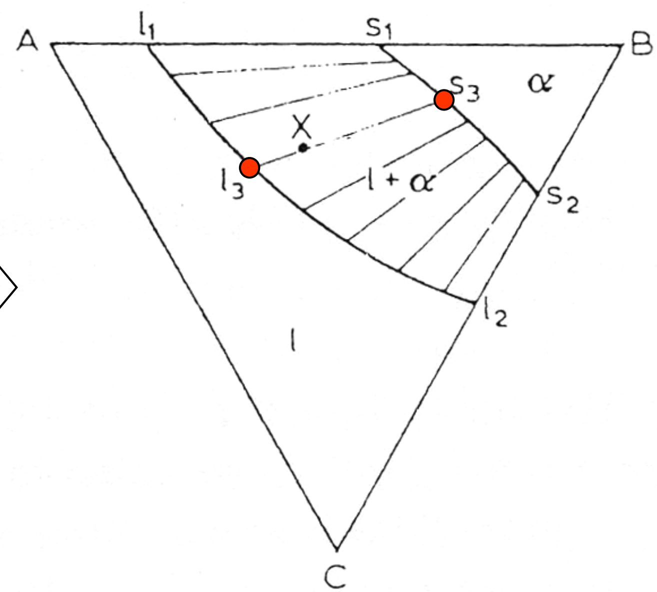
8.4.1 Two-phase equilibrium between the liquid and a solid solution

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)

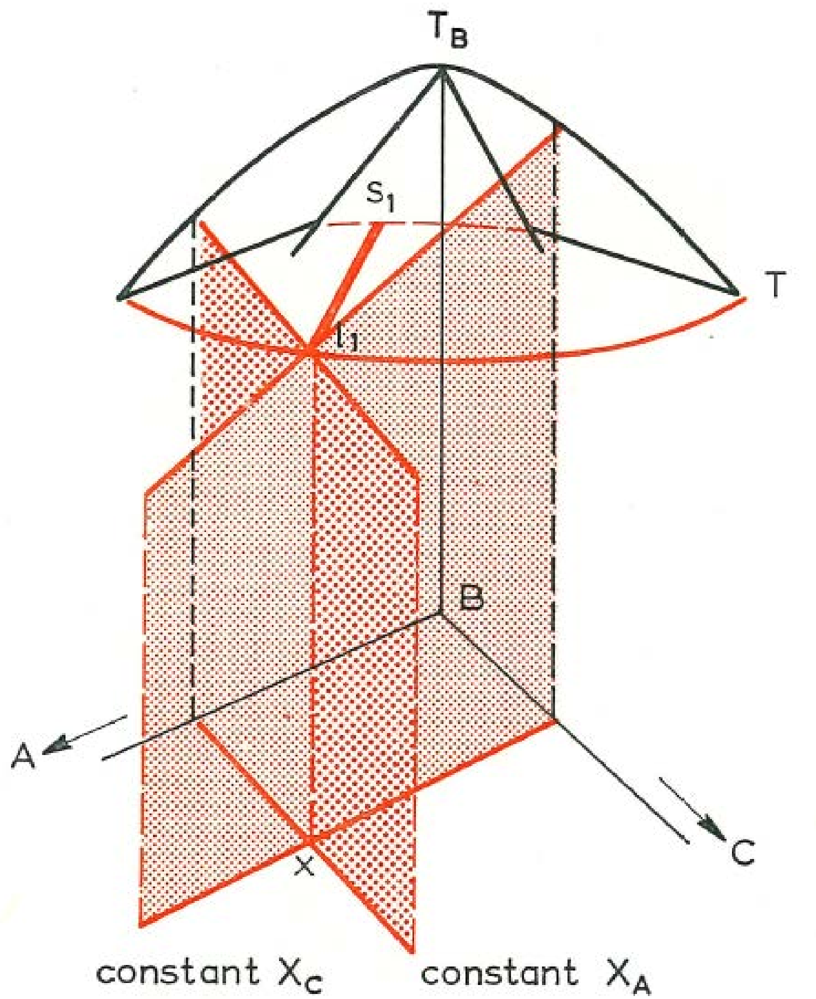
→ Tie line

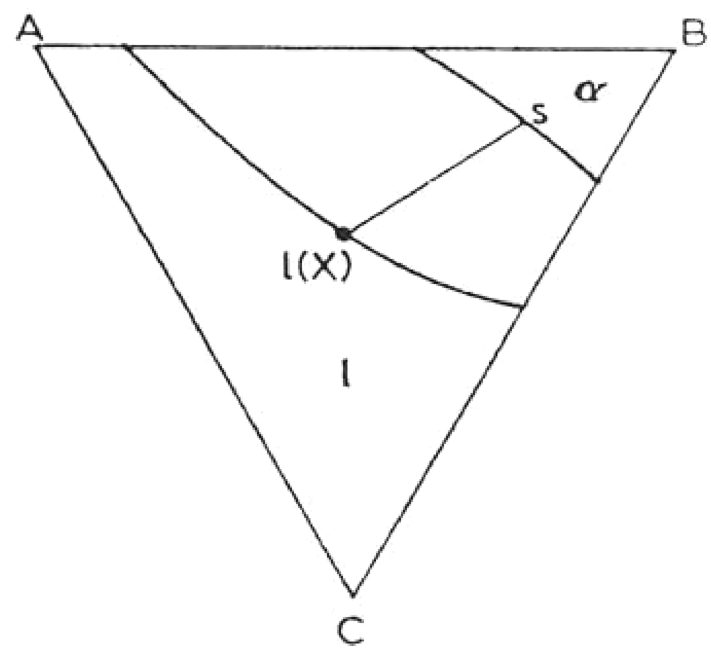
→ Comp. of solid (X_A^α, X_B^α, X_C^α)

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

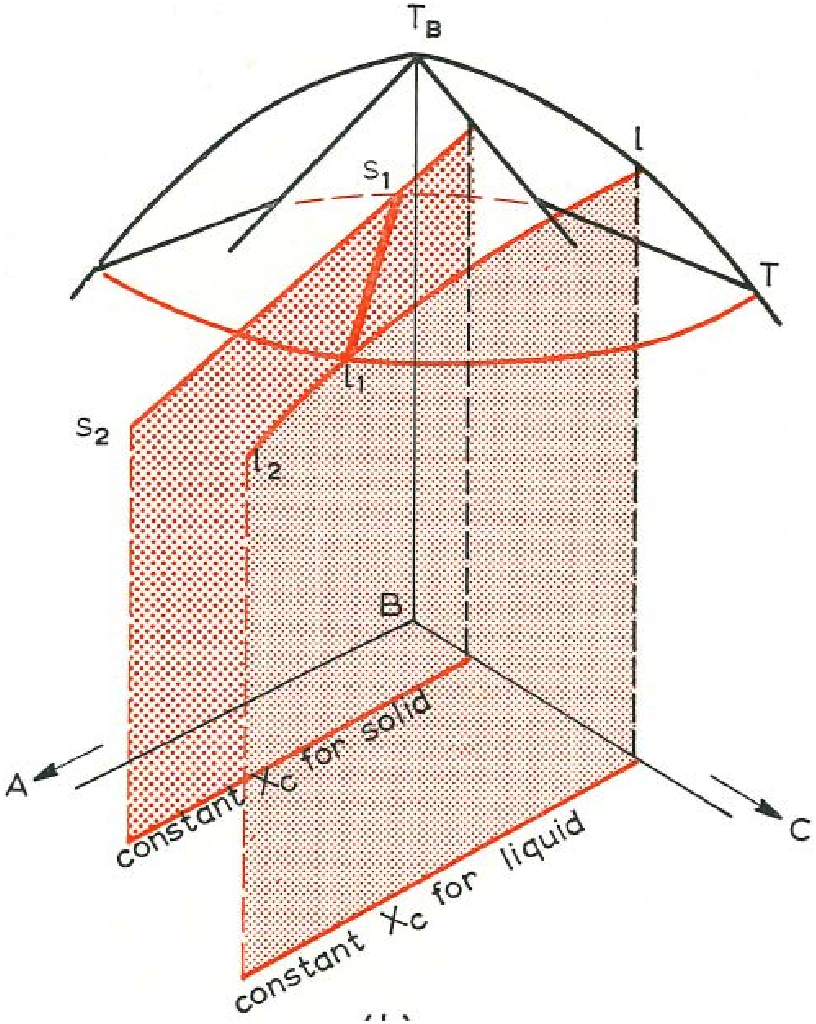
→ Temp. T

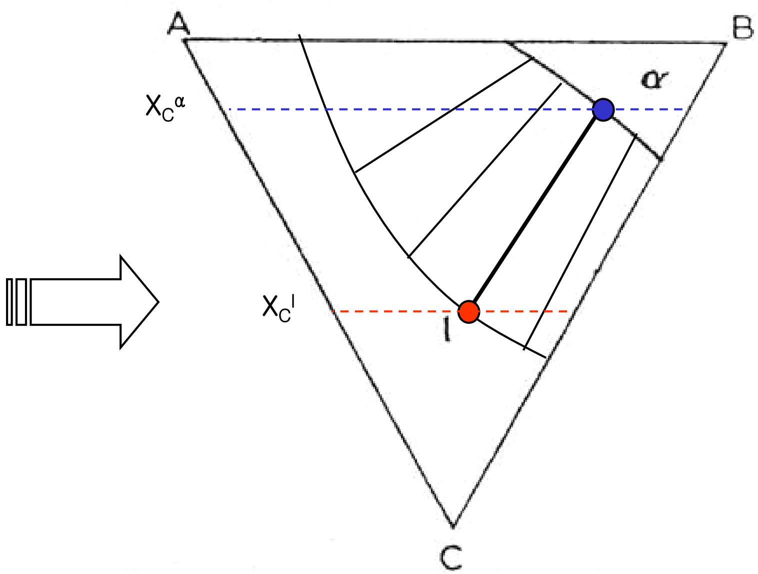
→ Two phase region

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>

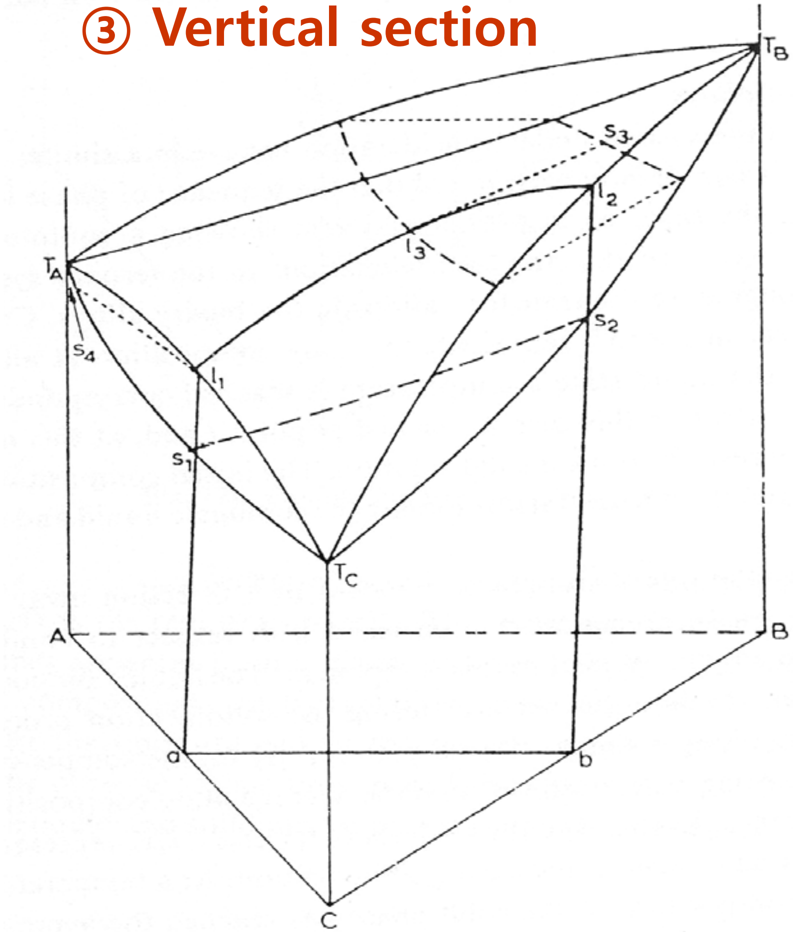
→ Temperature, tie line

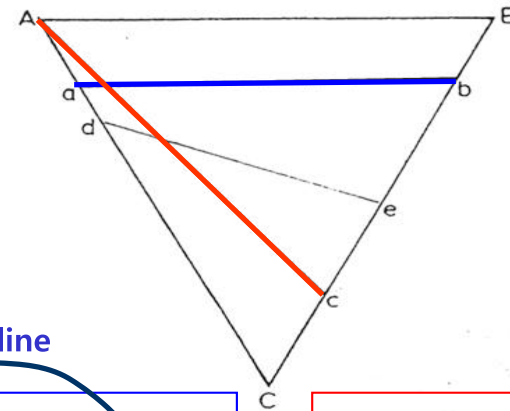
→ Composition of liq. & sol.

8.4 TWO-PHASE EQUILIBRIUM

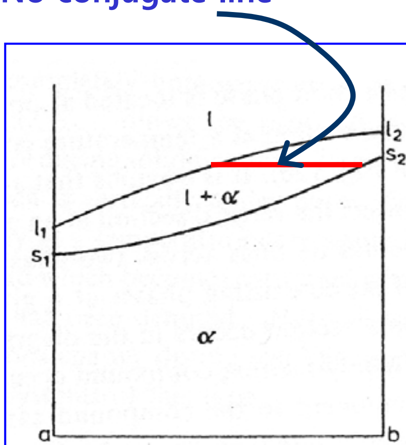
8.4.1 Two-phase equilibrium between the liquid and a solid solution

③ Vertical section

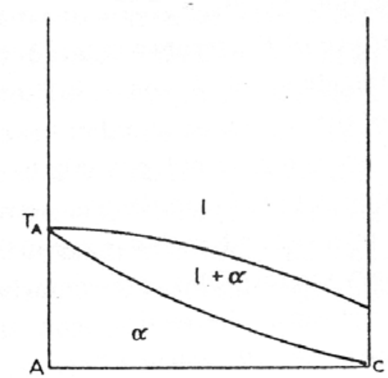




No tie line &
No conjugate line



Paralleled to binary (AB)



Cut through vertex

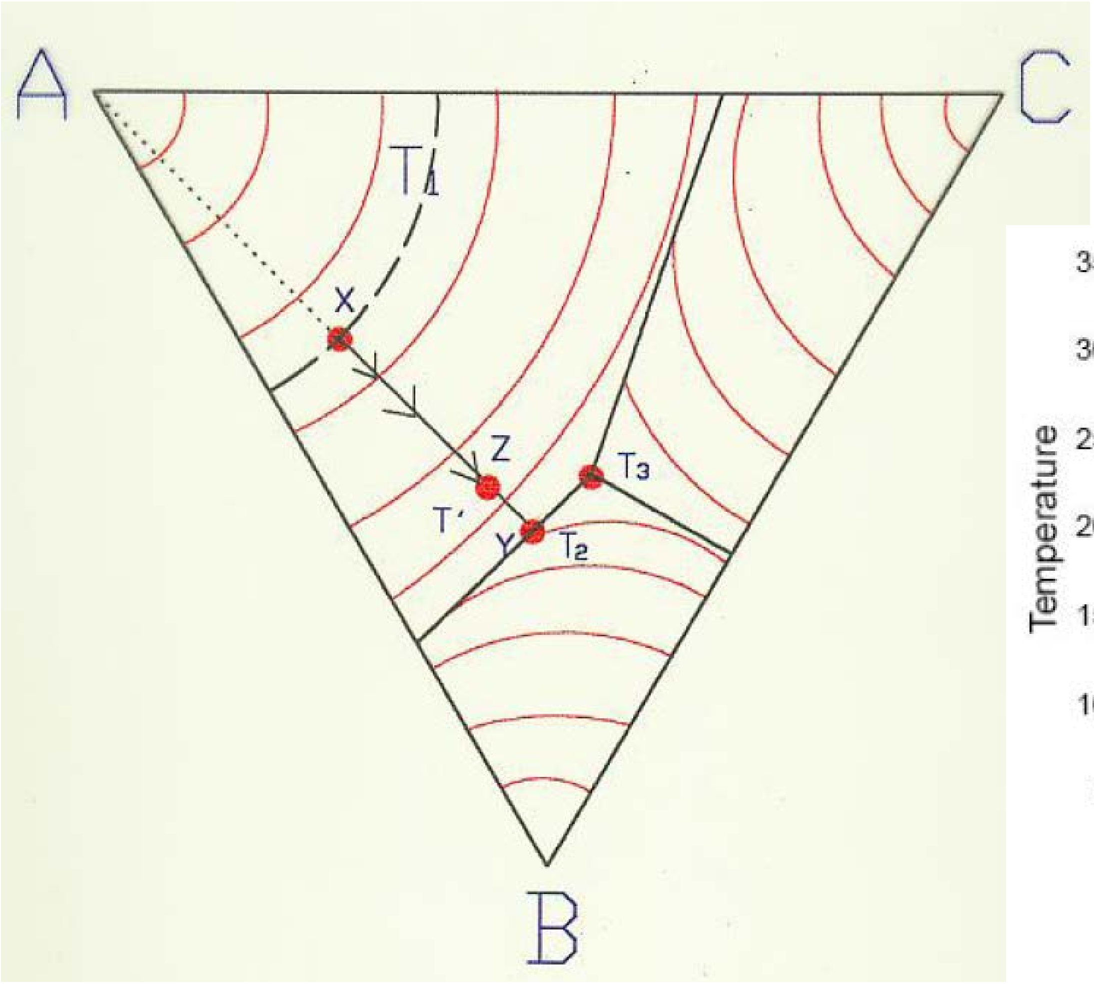
① **Useful for effect of 3rd alloying element**

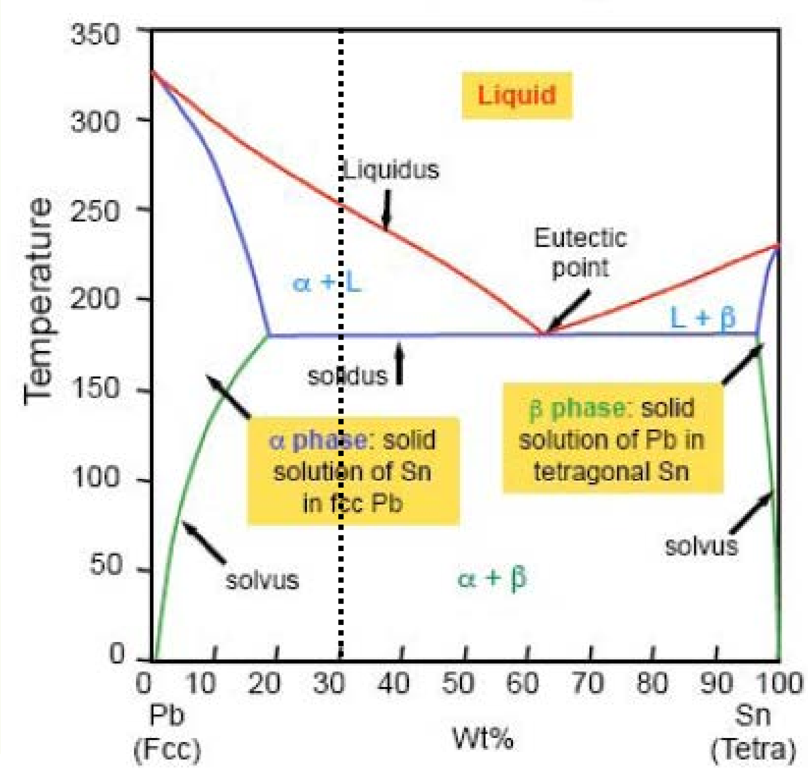
However, it is not possible to draw horizontal tie lines across two-phase regions in vertical sections to indicate the true compositions of the co-existing phases at a given temperature.

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

Ternary Eutectic System

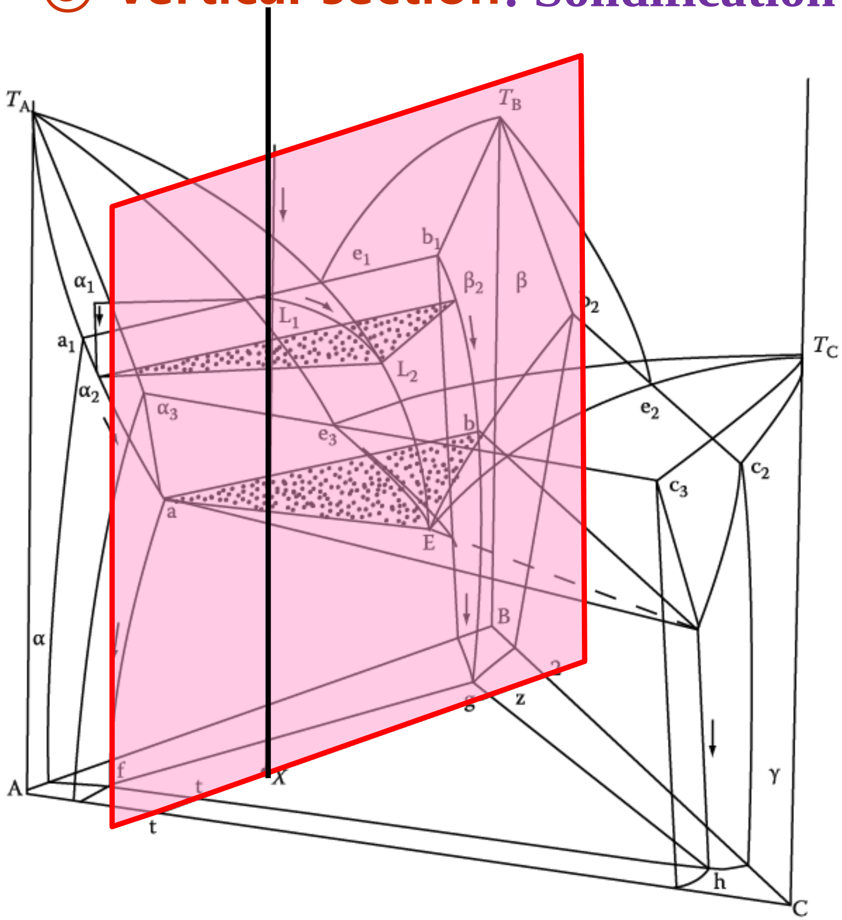
: Solidification Sequence

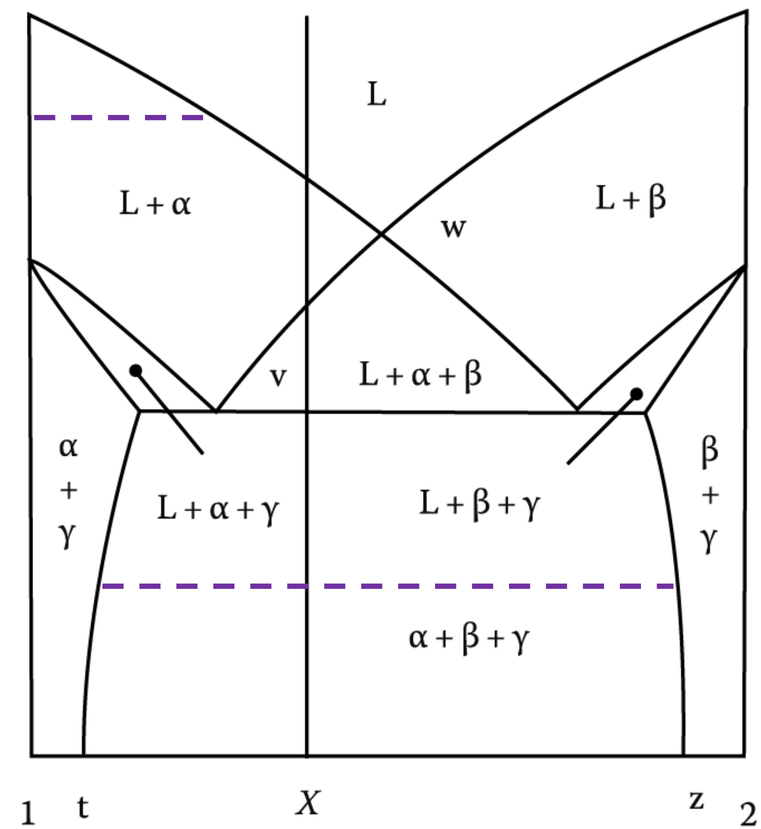




Ternary Eutectic System

③ Vertical section: Solidification Sequence



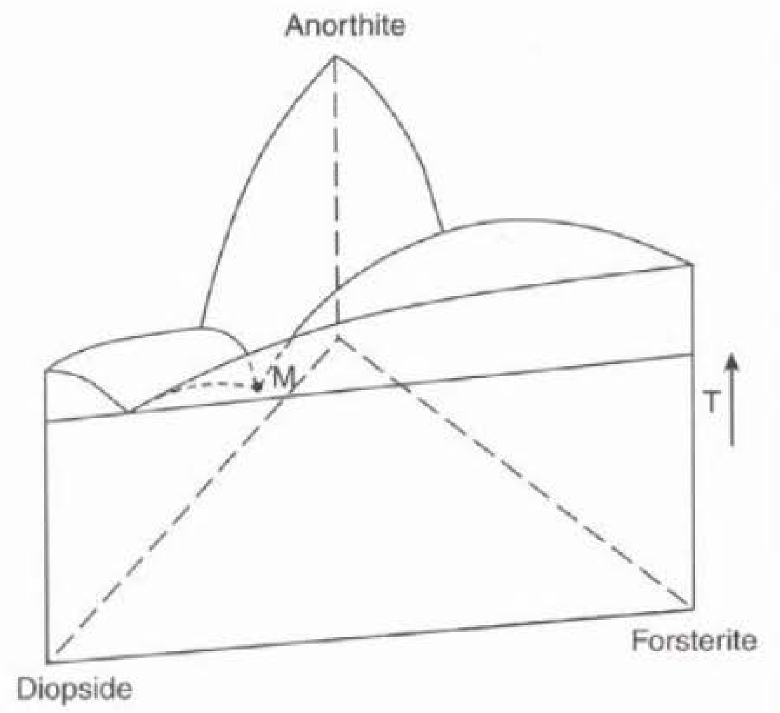


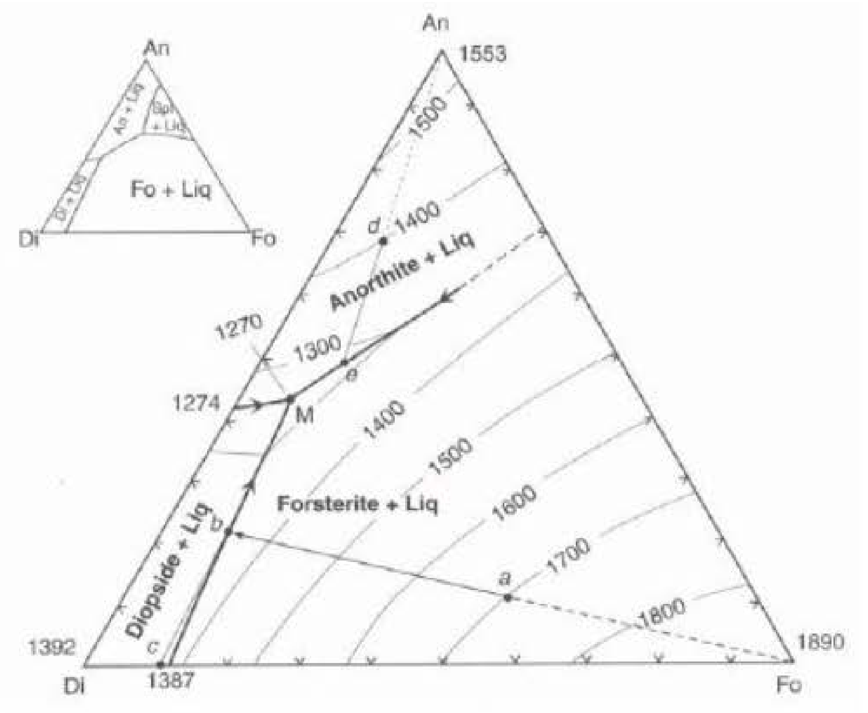
* The horizontal lines are not tie lines.
  (no compositional information)

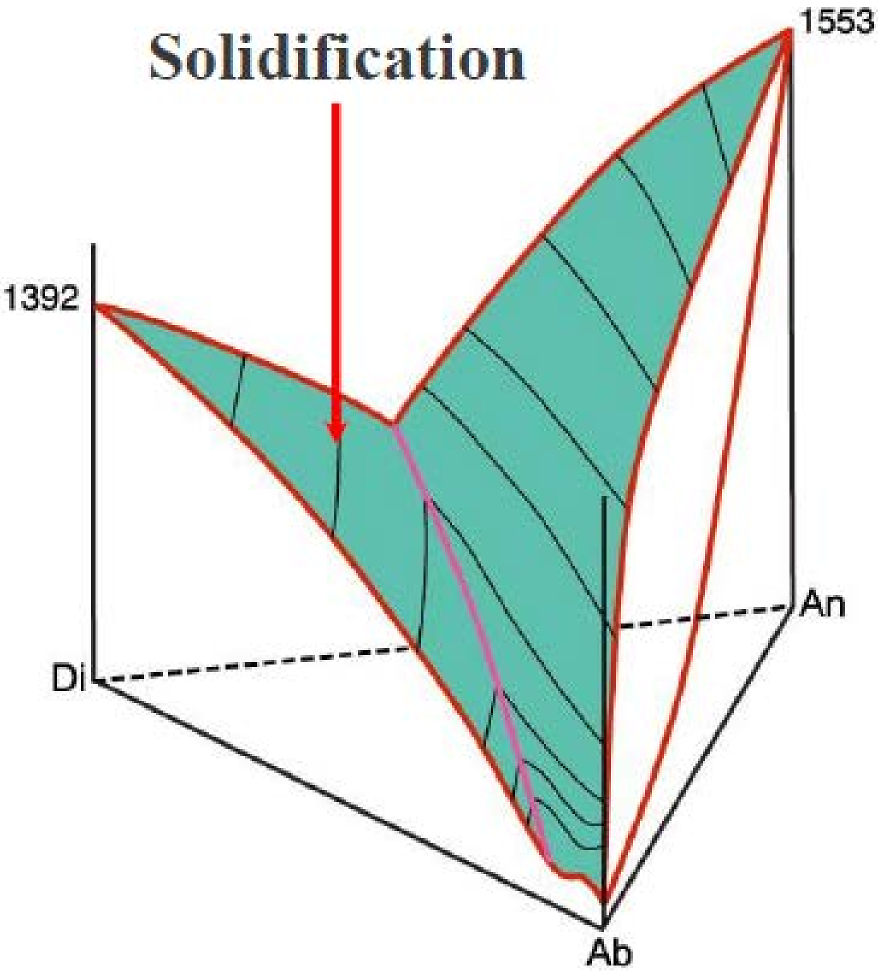
* Information for equilibrium phases at different tempeatures

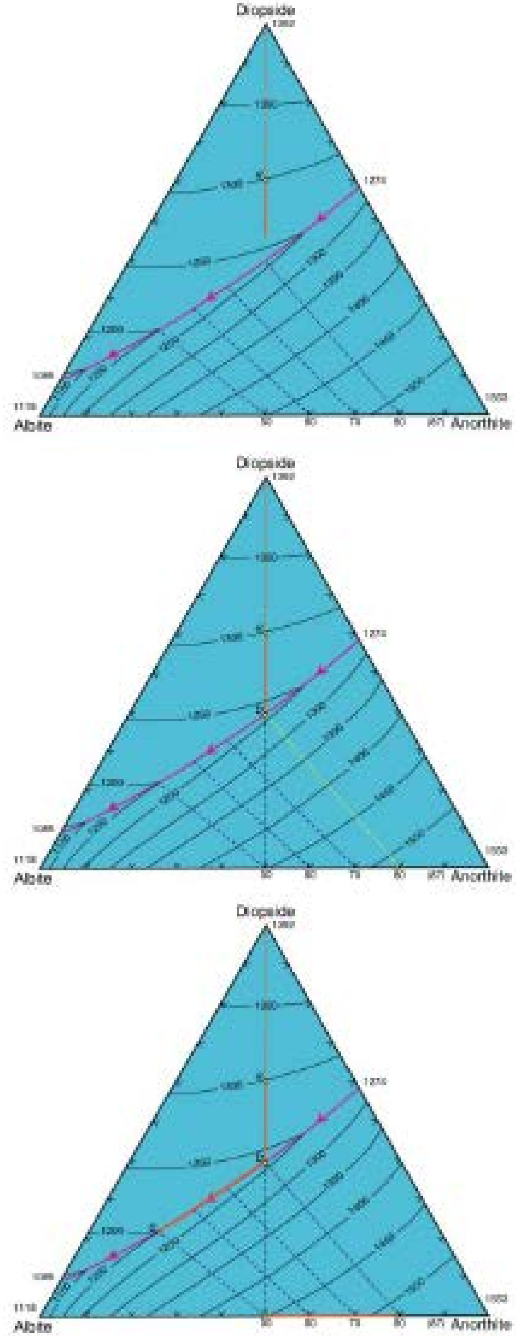
④ Polythermal projection

In order to follow the course of solidification of a ternary alloy, assuming equilibrium is maintained at all temperatures, it is useful to plot the liquidus surface contours.

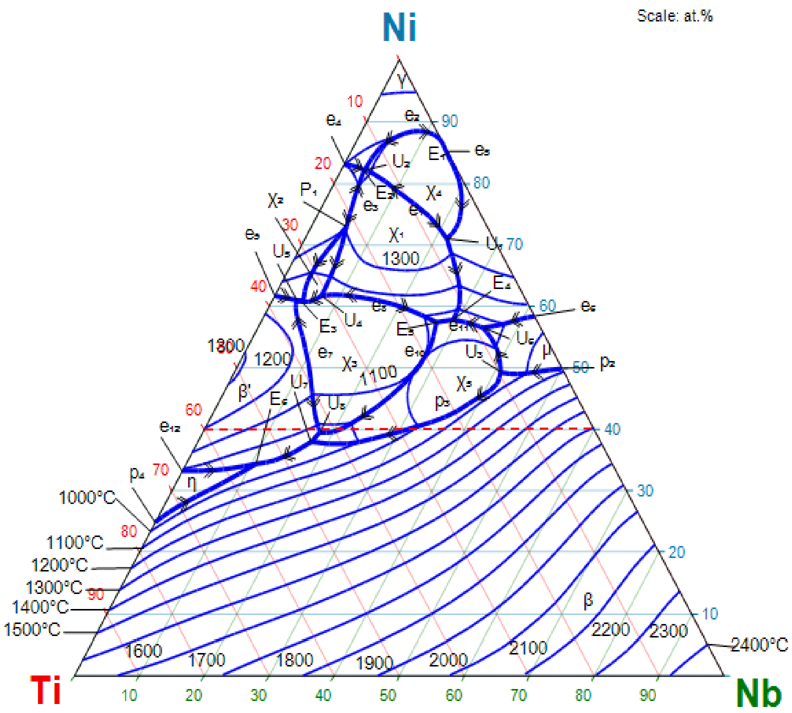




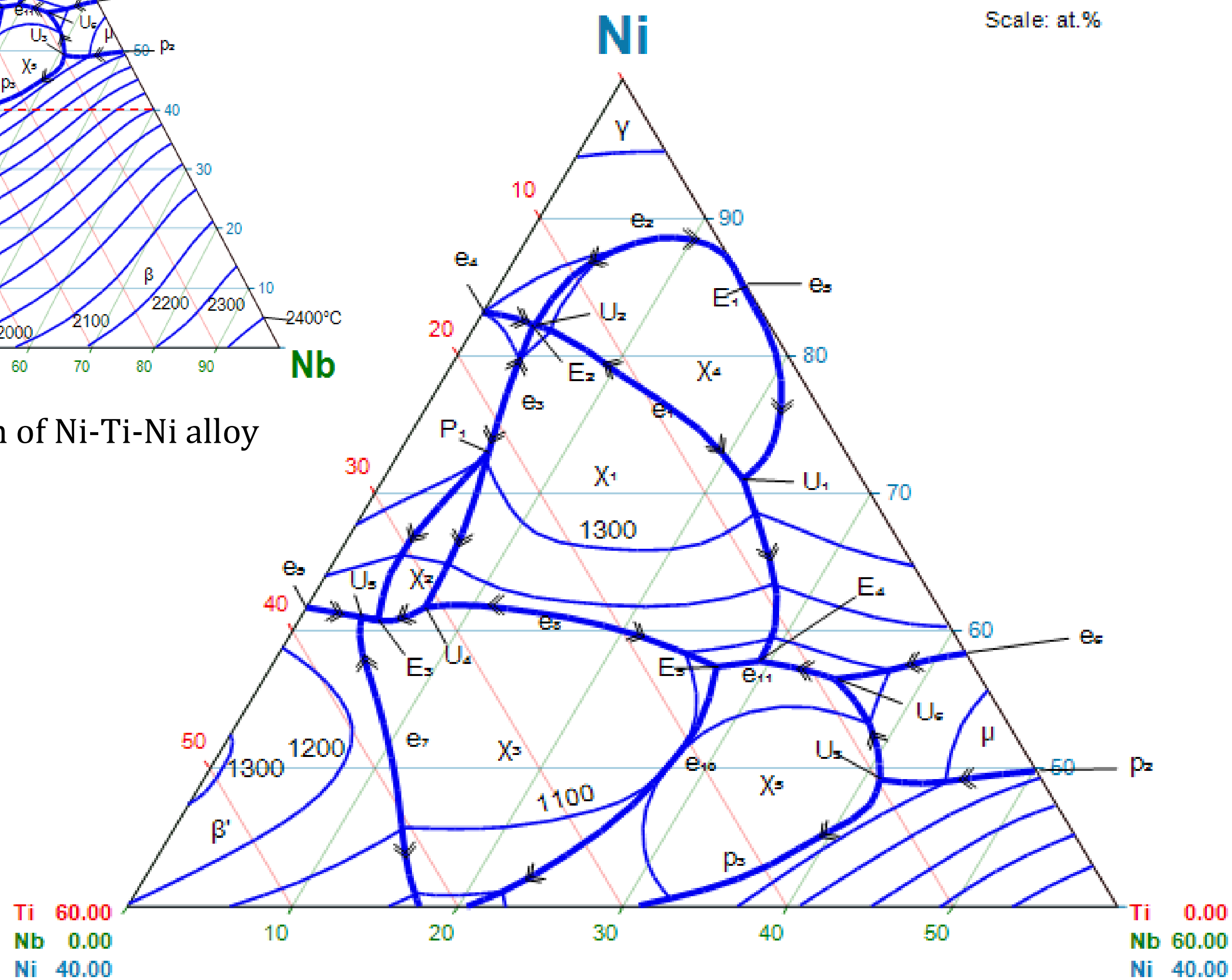




Liquidus phase concentration change during the solidification



Liquidus projection of Ni-Ti-Ni alloy



Enlarged part of the liquidus projection of Ni-Ti-Ni alloy

2021 Spring

"Phase Equilibria *in* Materials"

04.08.2021

Eun Soo Park

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

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.

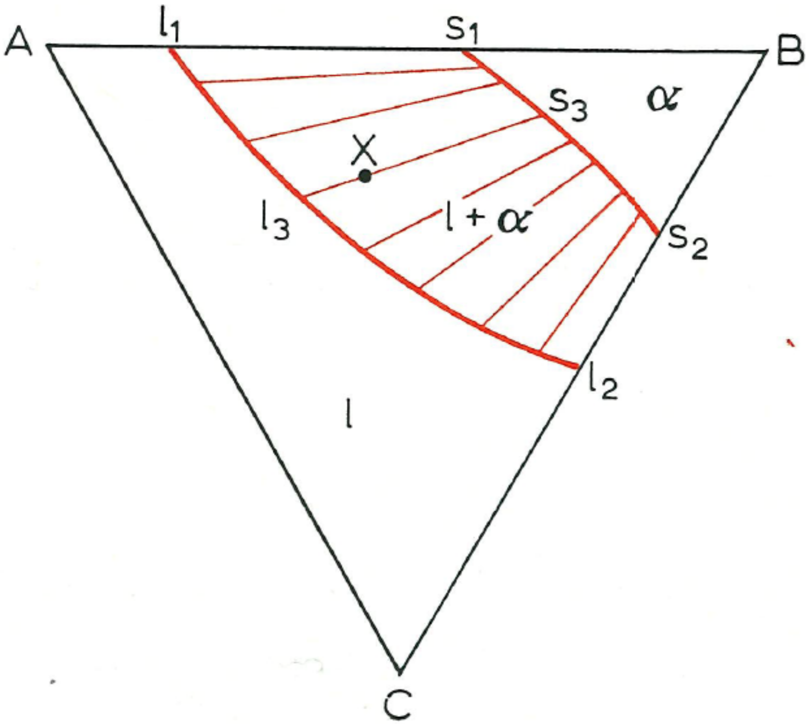
④ **Polythermal projection**

8.4 TWO-PHASE EQUILIBRIUM

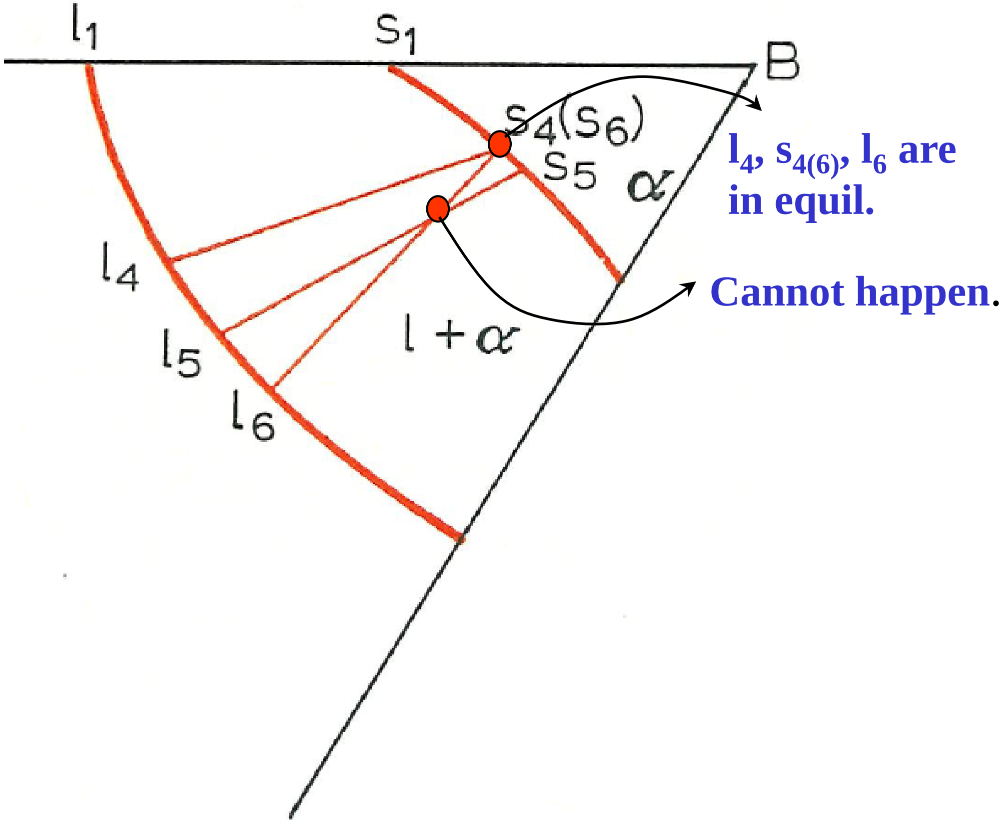
8.4.1 Two-phase equilibrium between the liquid and a solid solution

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

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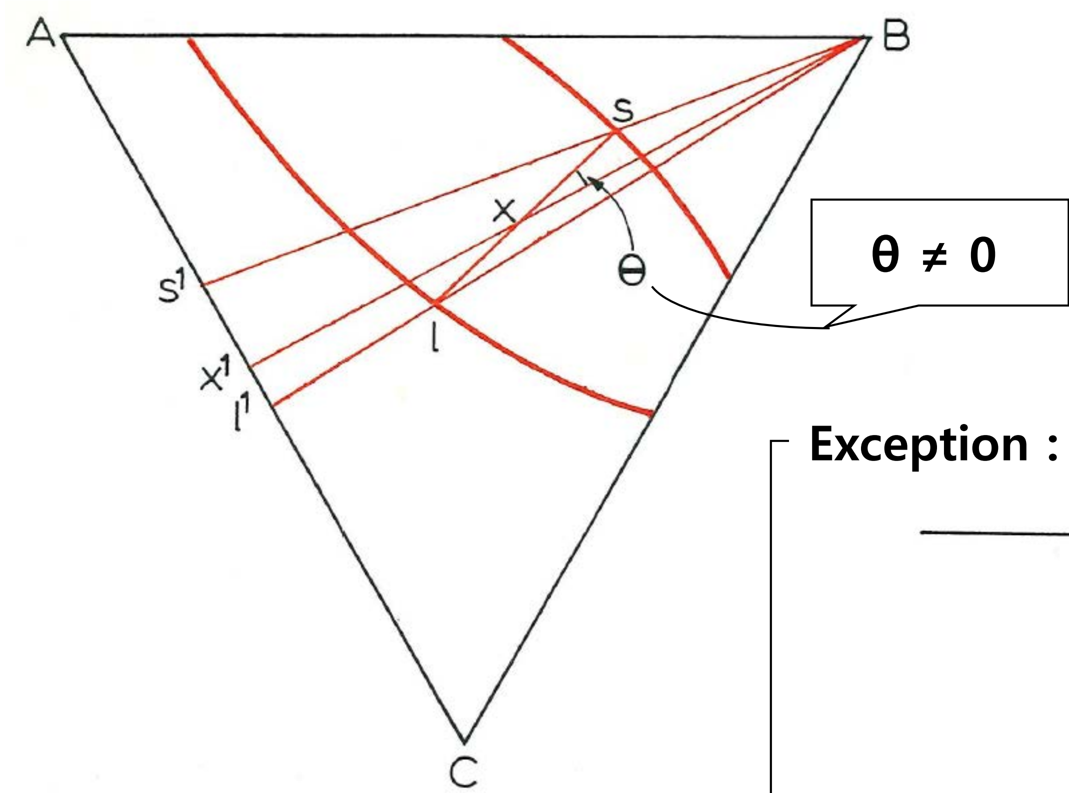

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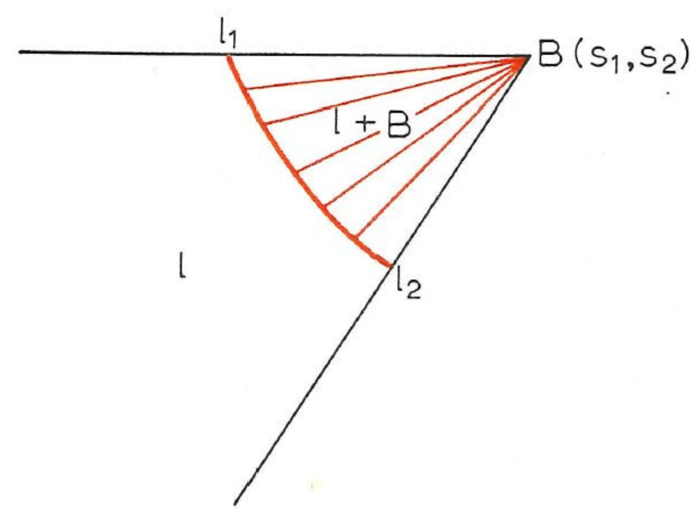

8.4 TWO-PHASE EQUILIBRIUM

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

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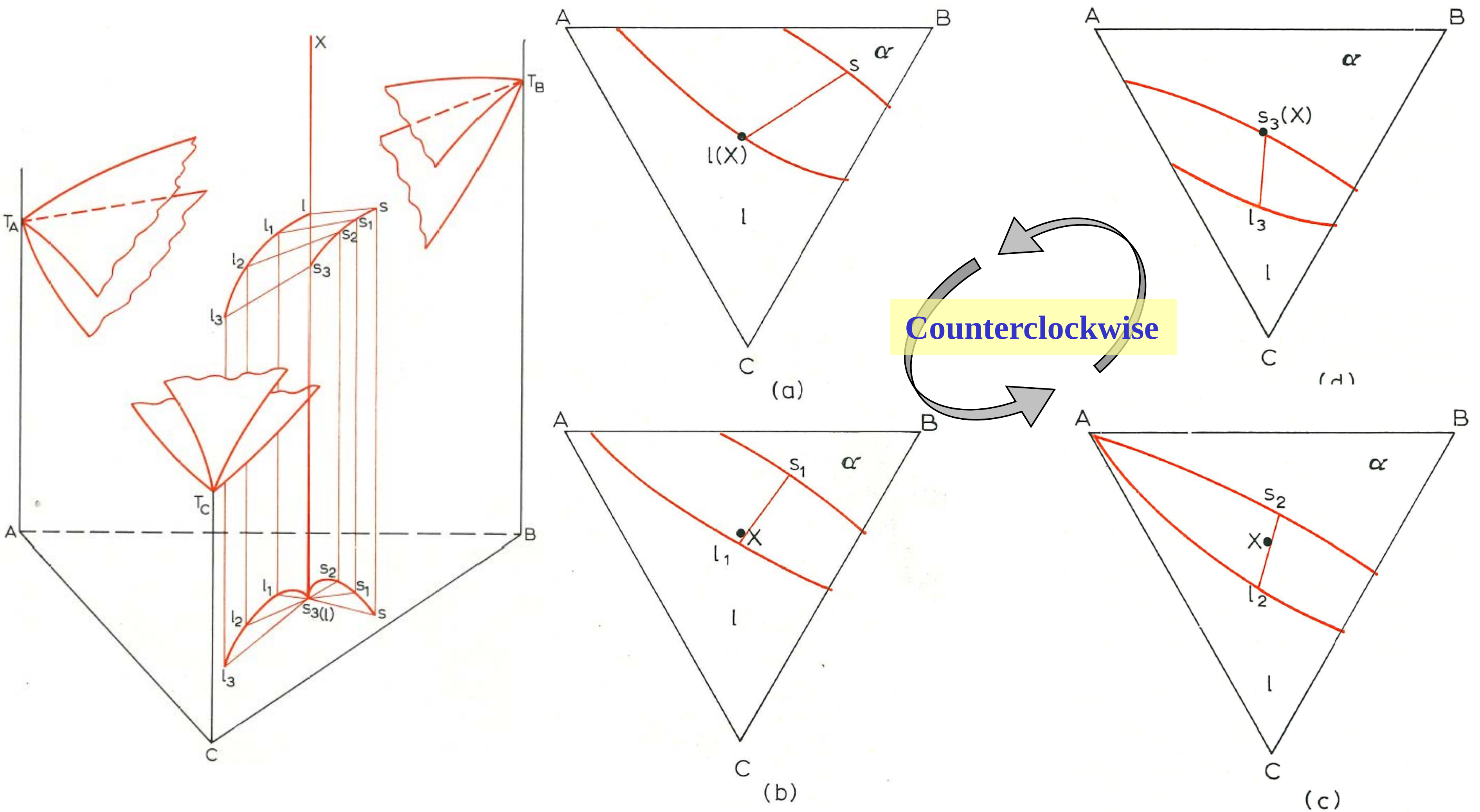

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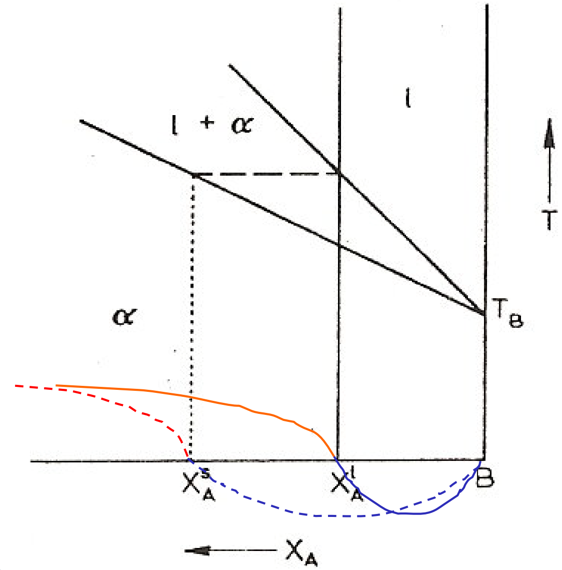
: Solid is always richer than the melt with which it is in equilibrium in that component which raises the melting point when added to the system.



$$X_A^S > X_A^l$$

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

then

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$$X_A^S > X_A^l$$

and

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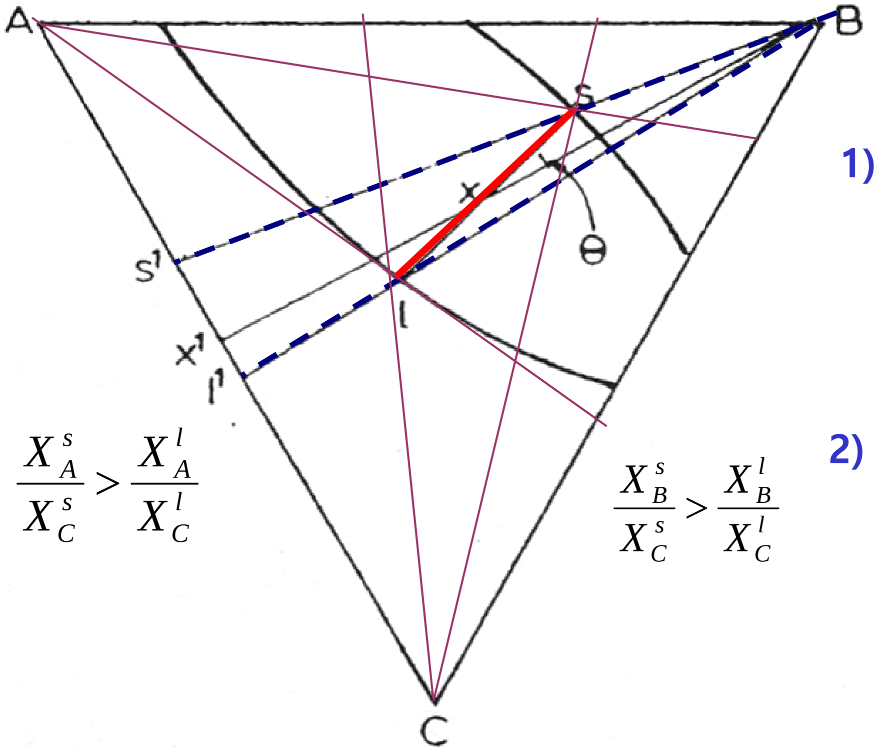
Therefore,

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

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,



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

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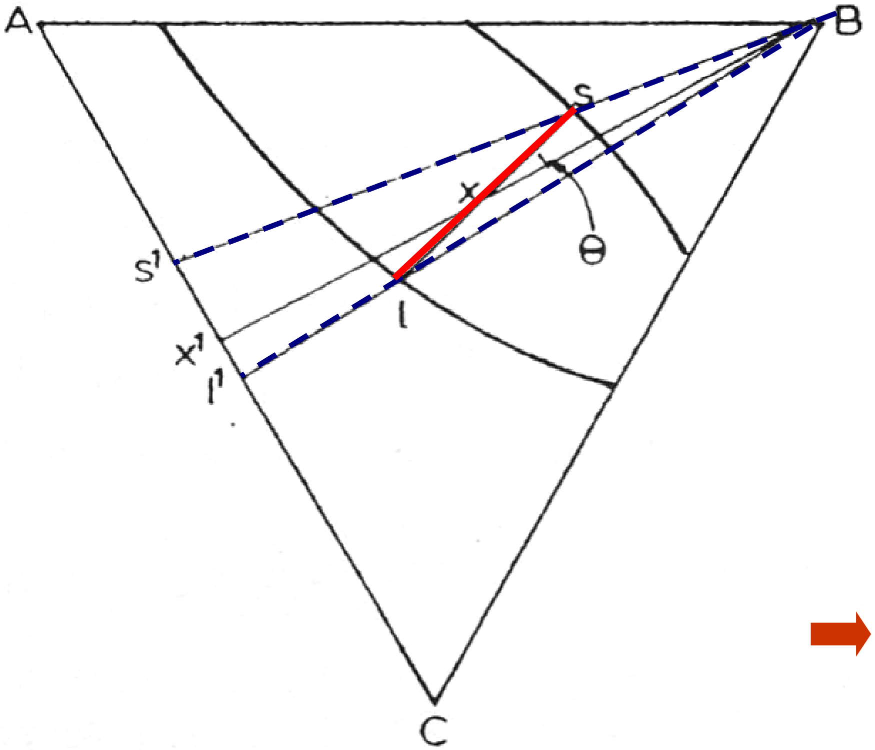
$$\frac{s^1C}{s^1A} > \frac{l^1C}{l^1A} \quad \text{and} \quad \frac{X_A^s}{X_C^s} > \frac{X_A^l}{X_C^l}$$

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

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

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

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



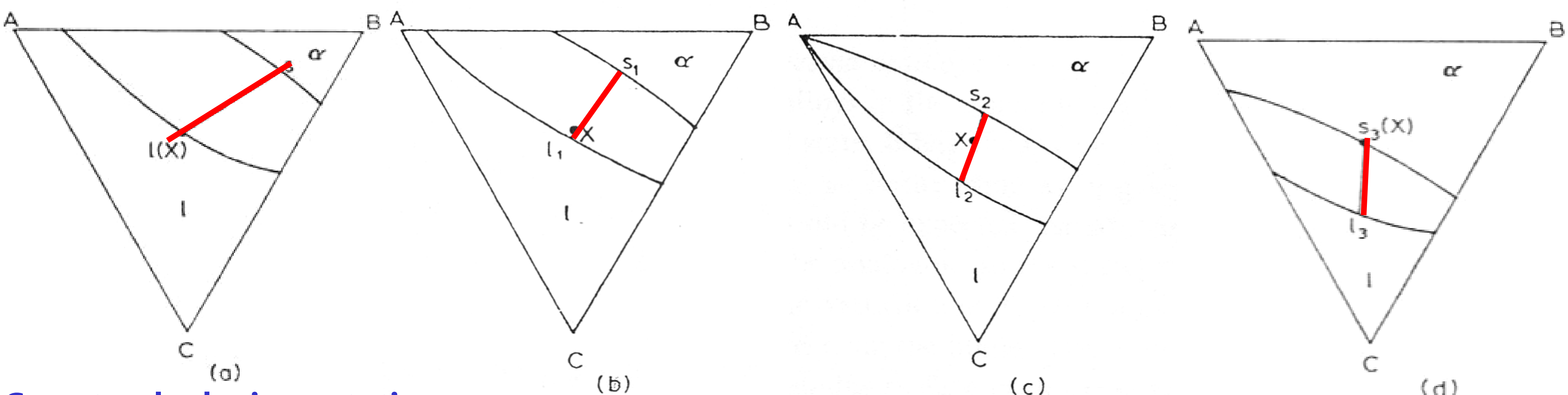
The tie line *ls* is rotated anticlockwise by an angle Θ relative to the line Bx[1].

If Θ = 0

then $$X_A^S / X_C^S = X_A^l / X_C^l$$

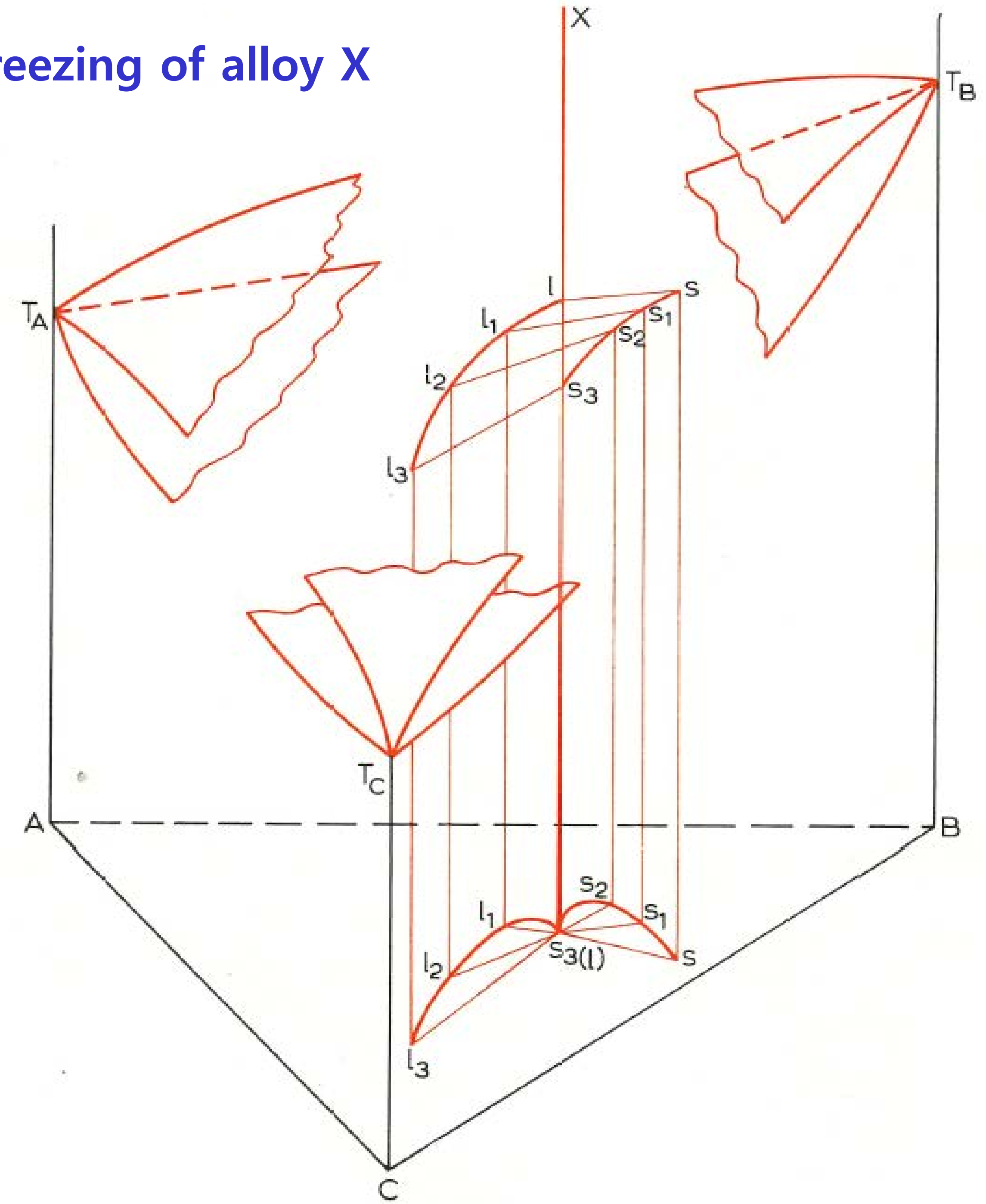
in contradiction to Konovalov's Rule.

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



Counterclockwise rotation

Equilibrium freezing of alloy X



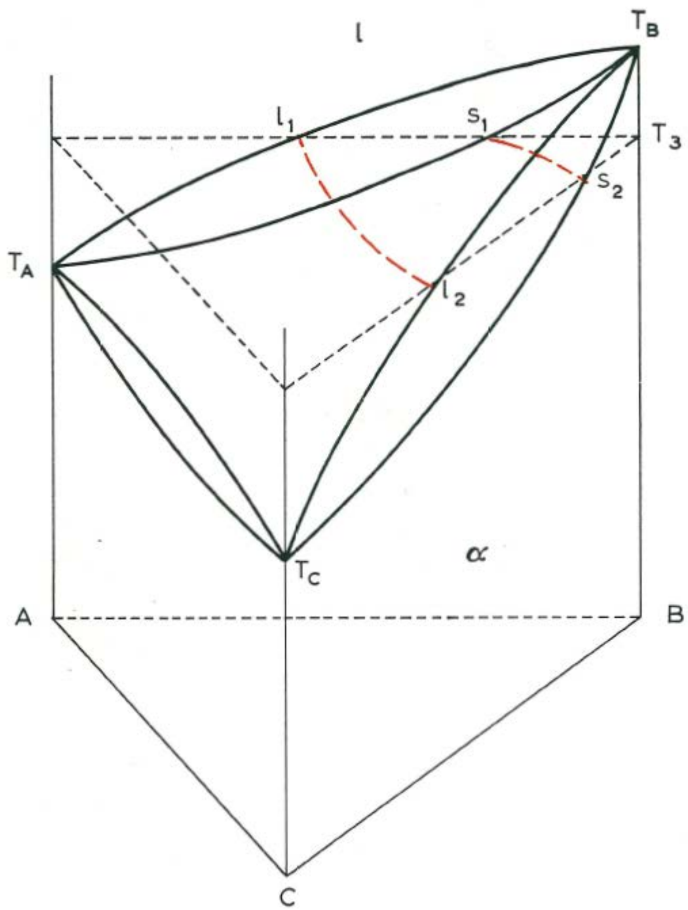
8.4 TWO-PHASE EQUILIBRIUM

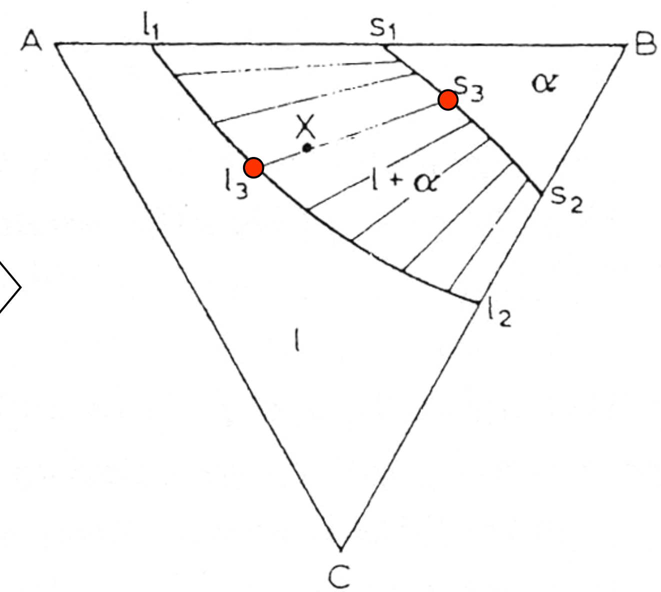
8.4.1 Two-phase equilibrium between the liquid and a solid solution

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)

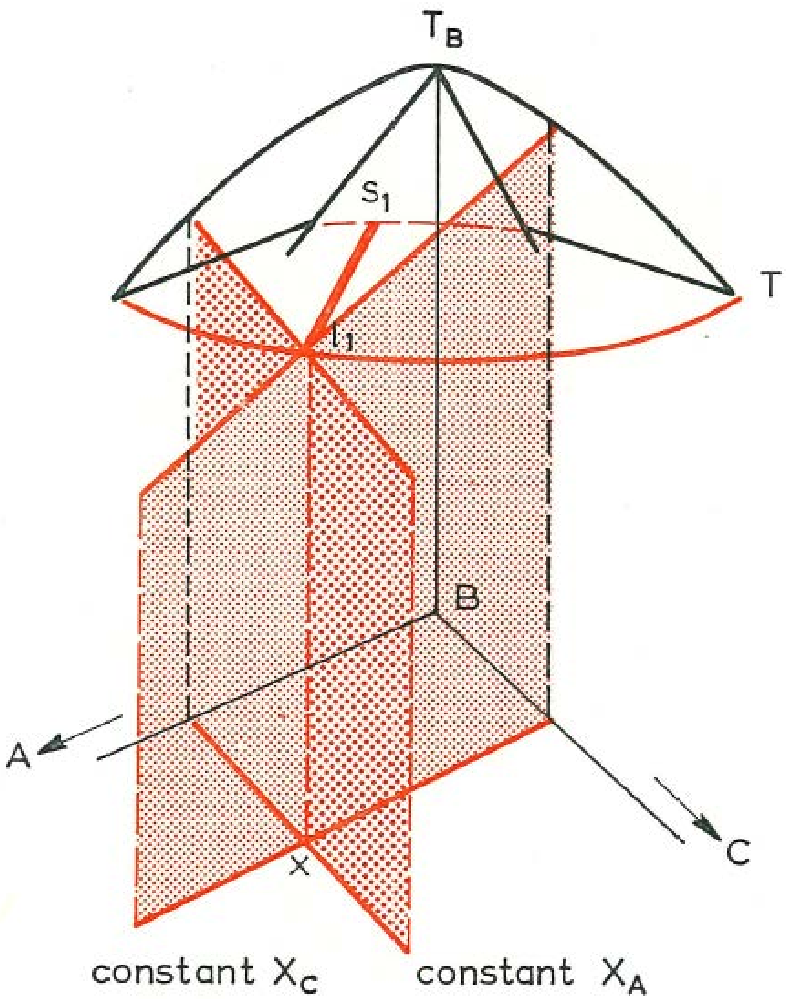
→ Tie line

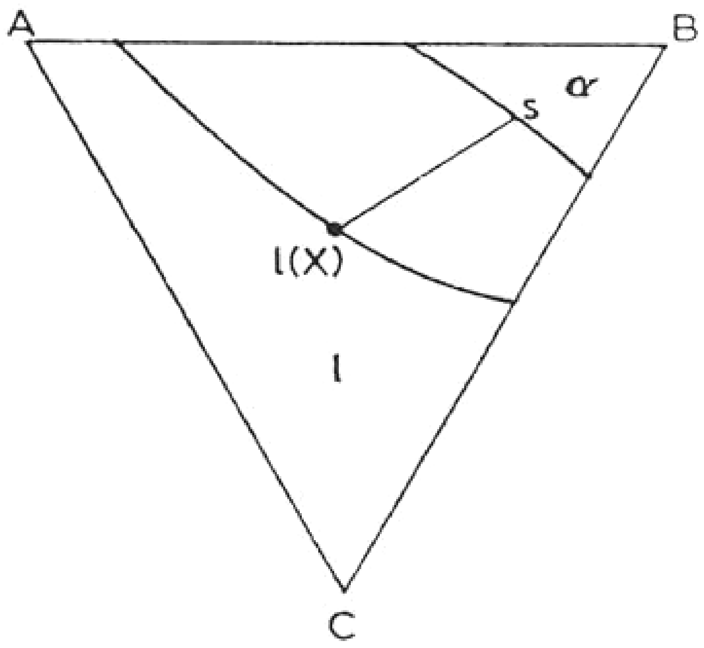
→ Comp. of solid (X_A^α, X_B^α, X_C^α)

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

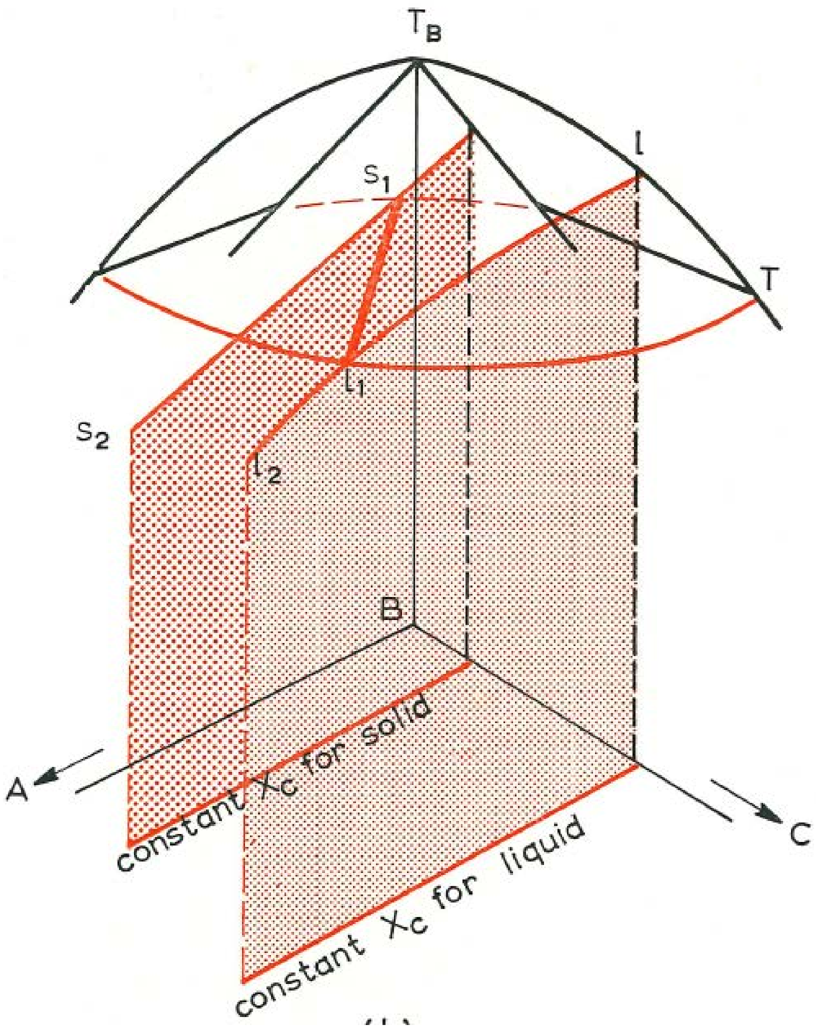
→ Temp. T

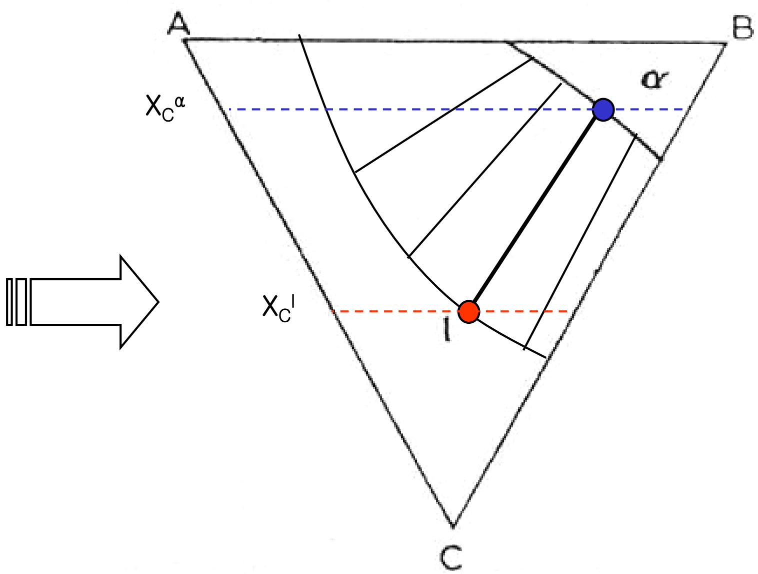
→ Two phase region

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

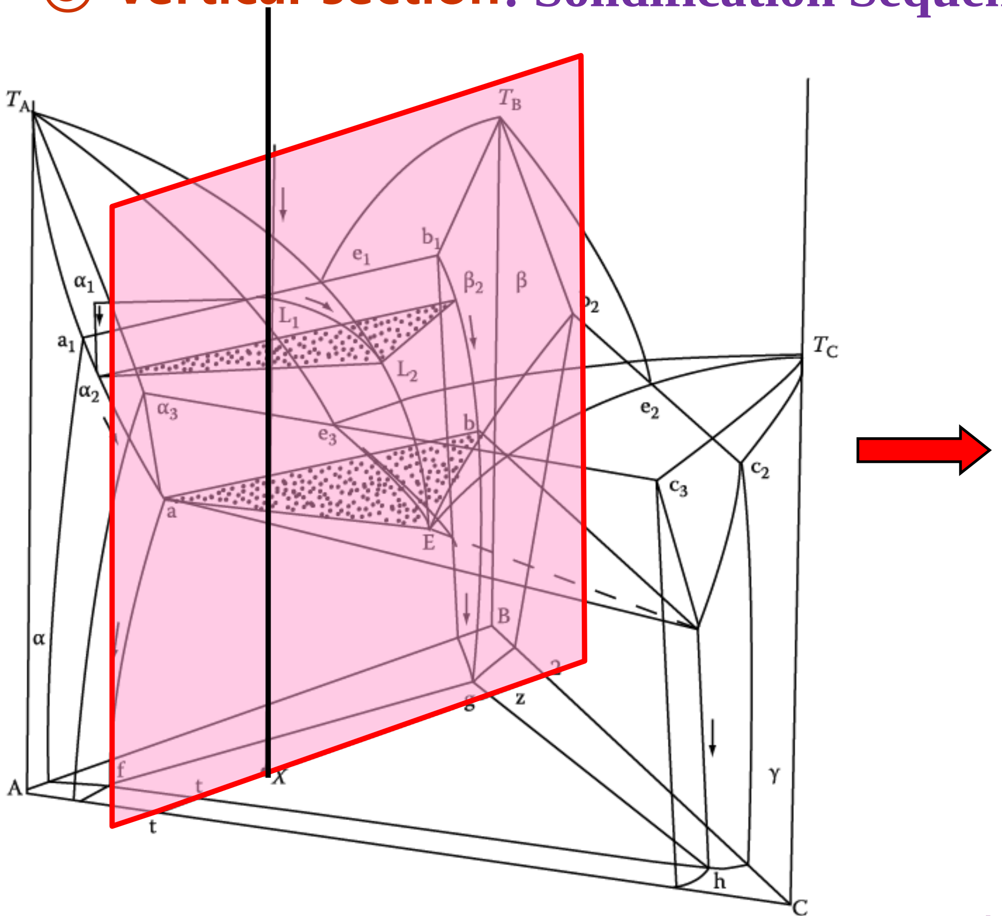
→ <u>will intersect at only one point.</u>

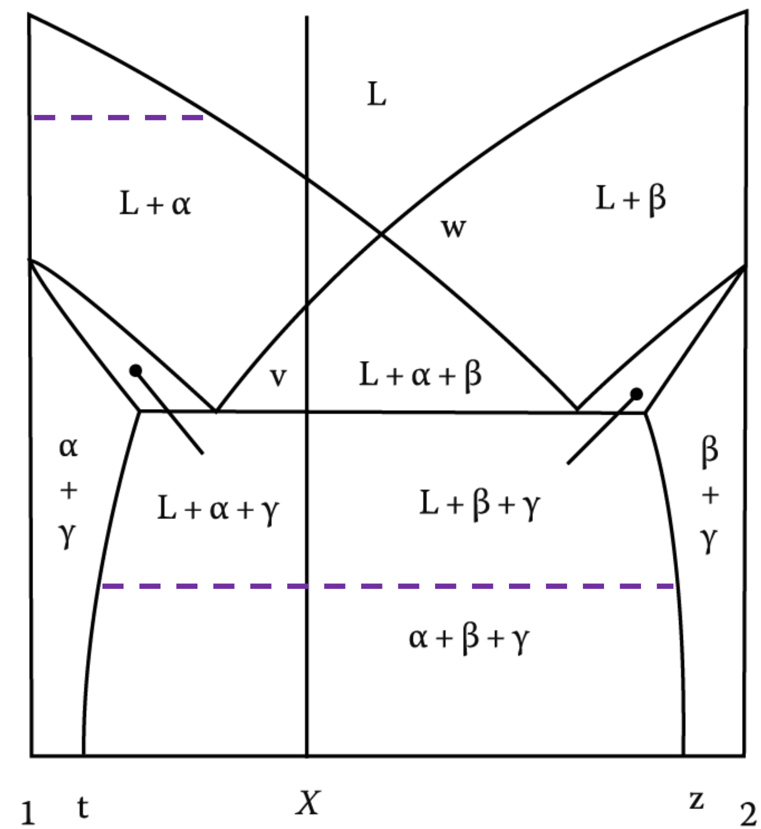
→ Temperature, tie line

→ Composition of liq. & sol.

Ternary Eutectic System

③ Vertical section: Solidification Sequence





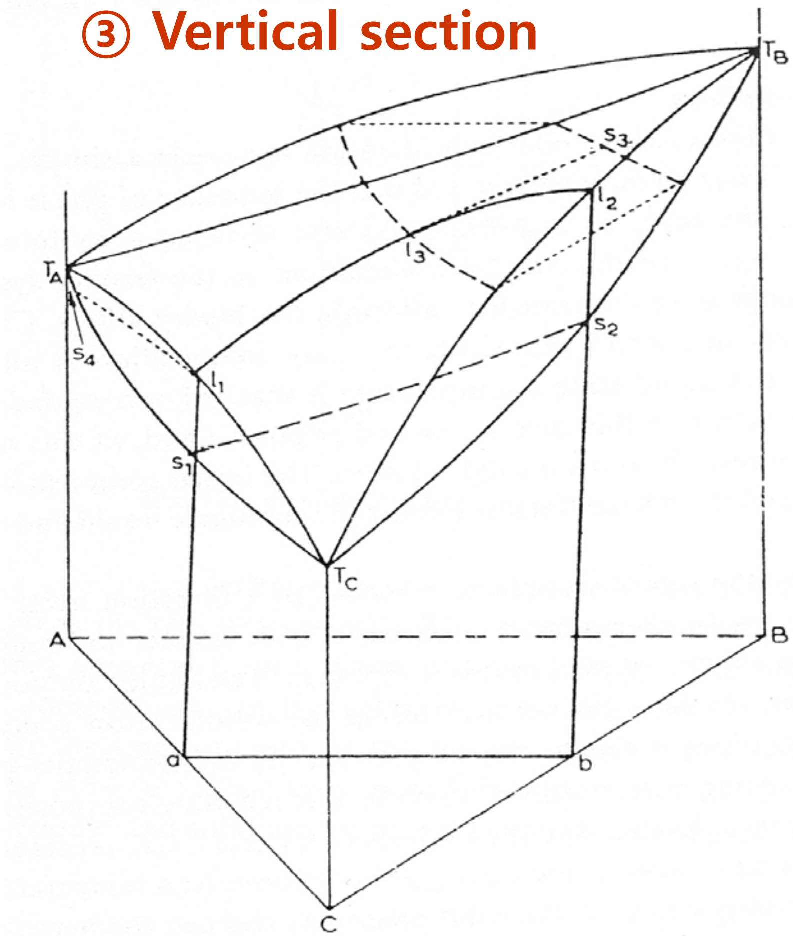
* The horizontal lines are not tie lines.
(no compositional information)

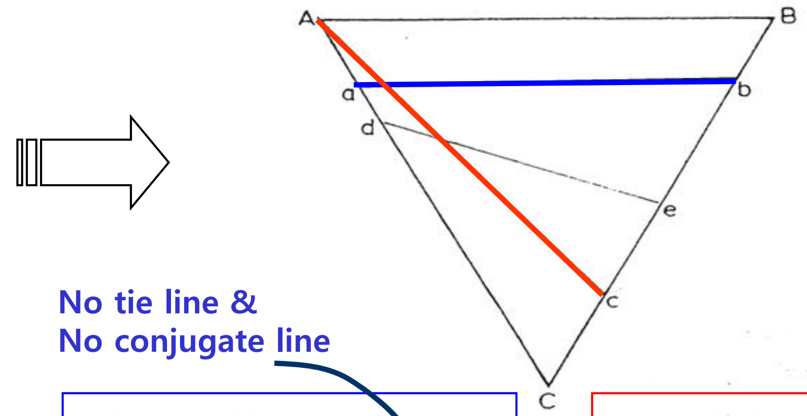
* Information for equilibrium phases at different tempeatures

8.4 TWO-PHASE EQUILIBRIUM

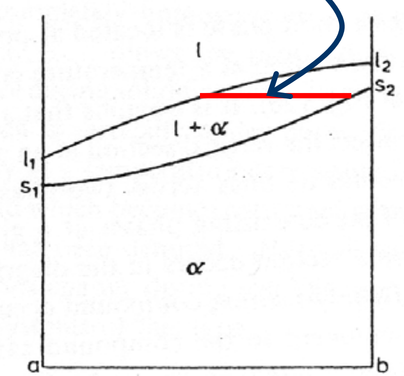
8.4.1 Two-phase equilibrium between the liquid and a solid solution

③ Vertical section

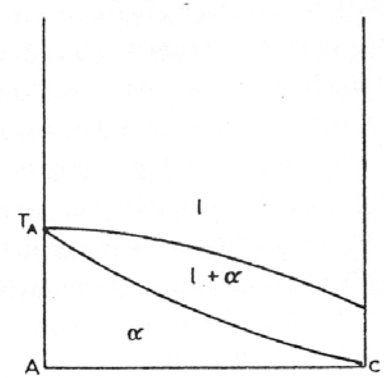




No tie line &
No conjugate line



Paralleled to binary (AB)



Cut through vertex

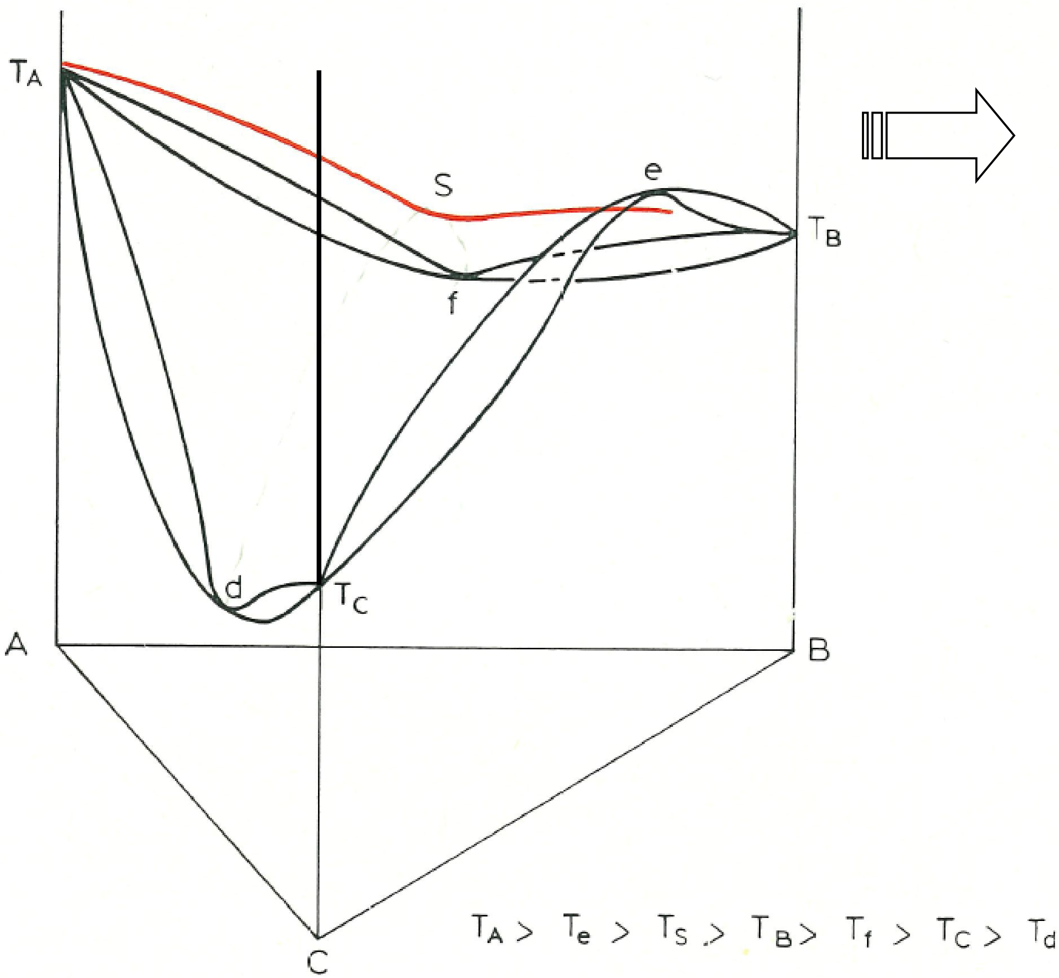
① **Useful for effect of 3rd alloying element**

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.

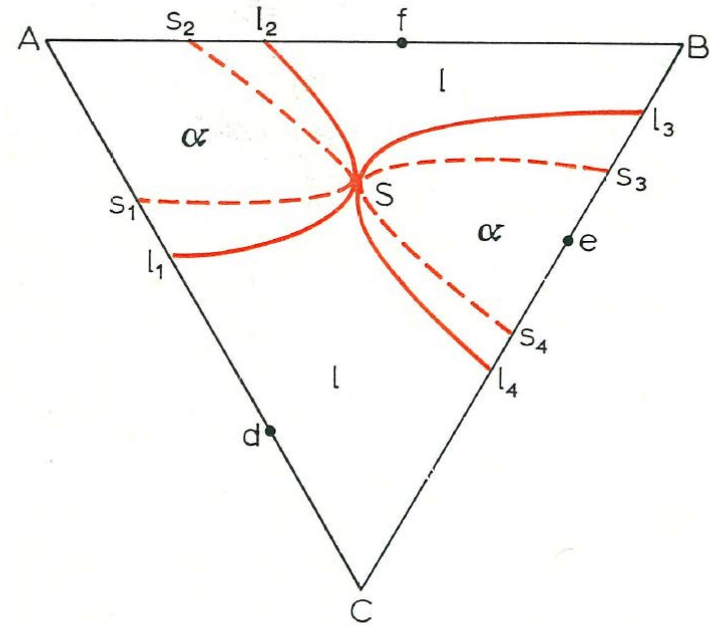
② **Pseudobinary section: the section from the 3rd component to the compound (congruently-melting compound) can then be a binary section**

8.4.2 Variants of the phase diagram
(more complex system)

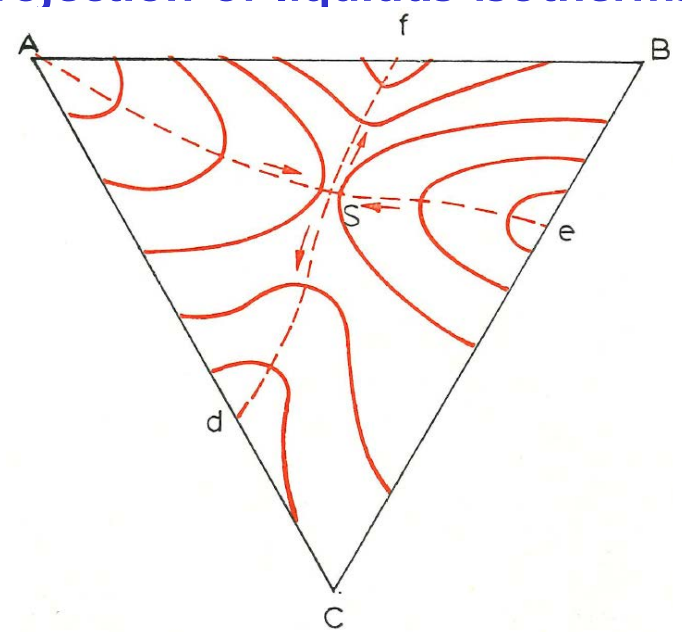
* Ternary two-phase equilibrium
with a saddle point



Isothermal section ($T=T_s$)



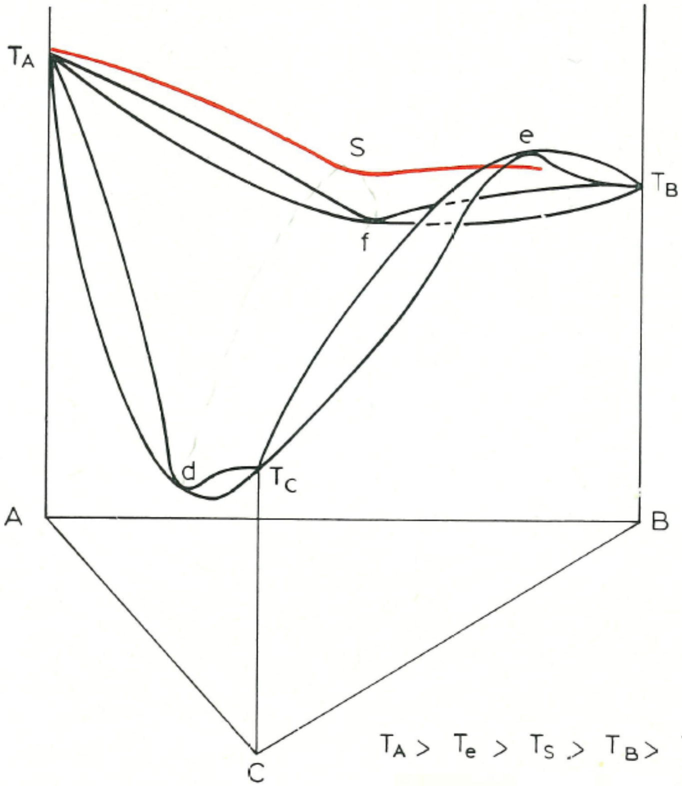
Projection of liquidus isotherms

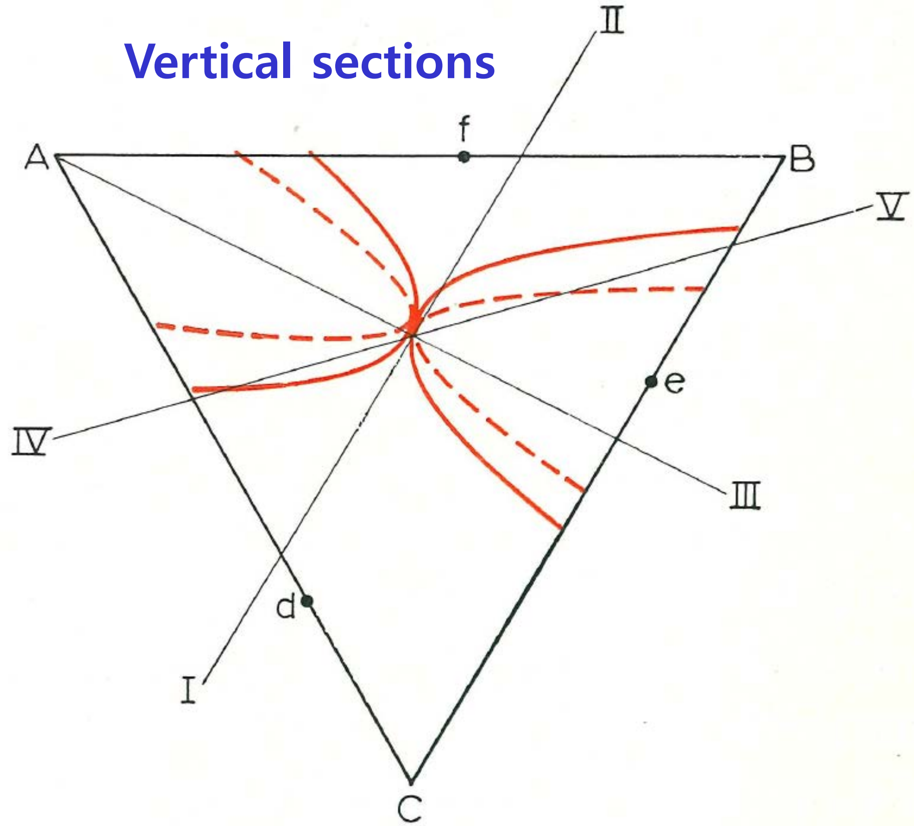


S : saddle pt. where liquidus & solidus surfaces meet

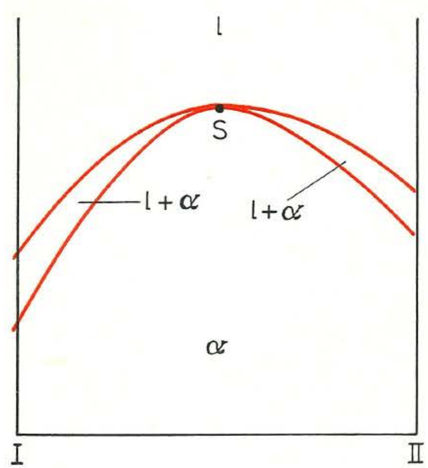
8.4.2 Variants of the phase diagram
(more complex system)

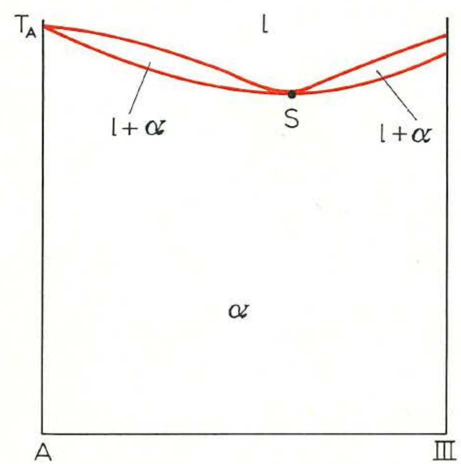
Vertical sections

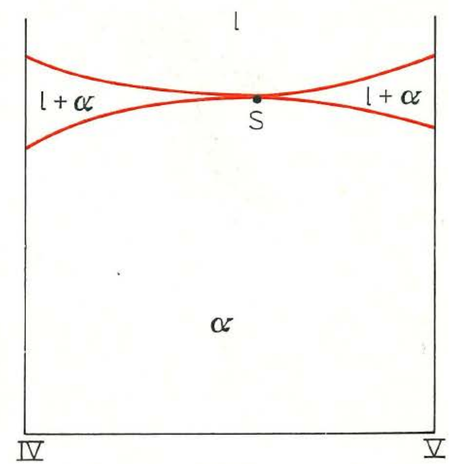




$T_A > T_e > T_S > T_B > T_f > T_C > T_d$





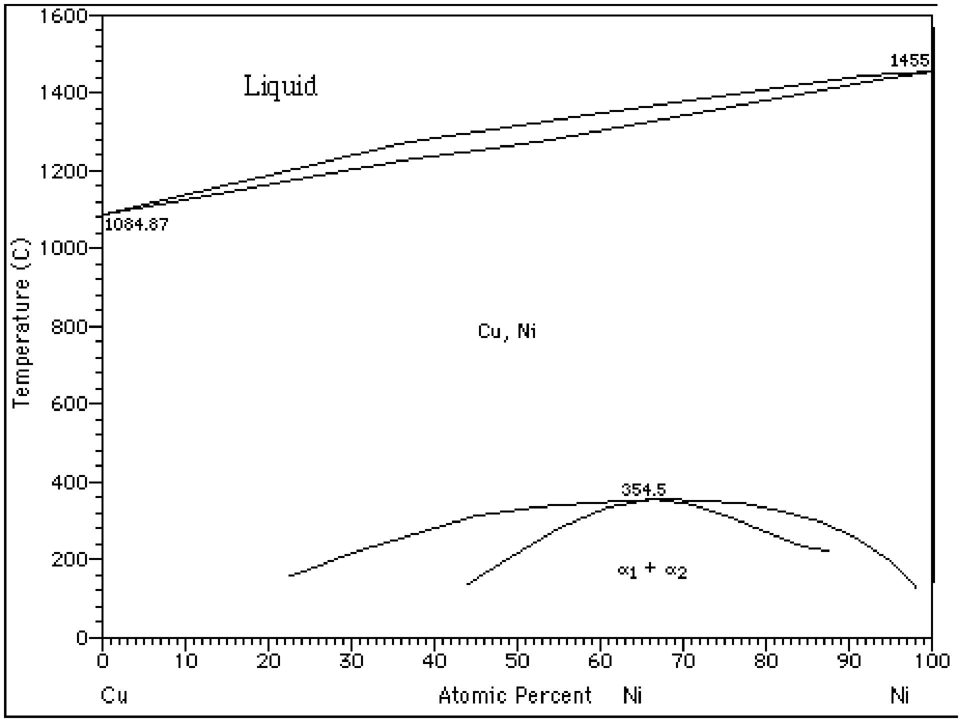


8.4 TWO-PHASE EQUILIBRIUM

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

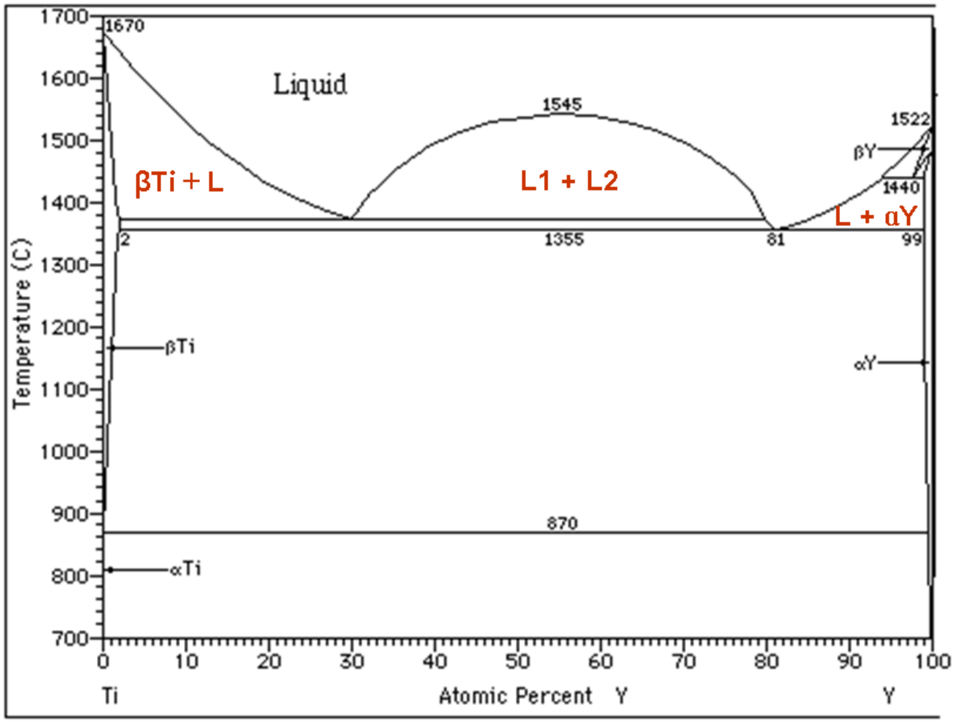
Miscibility gap

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



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

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



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

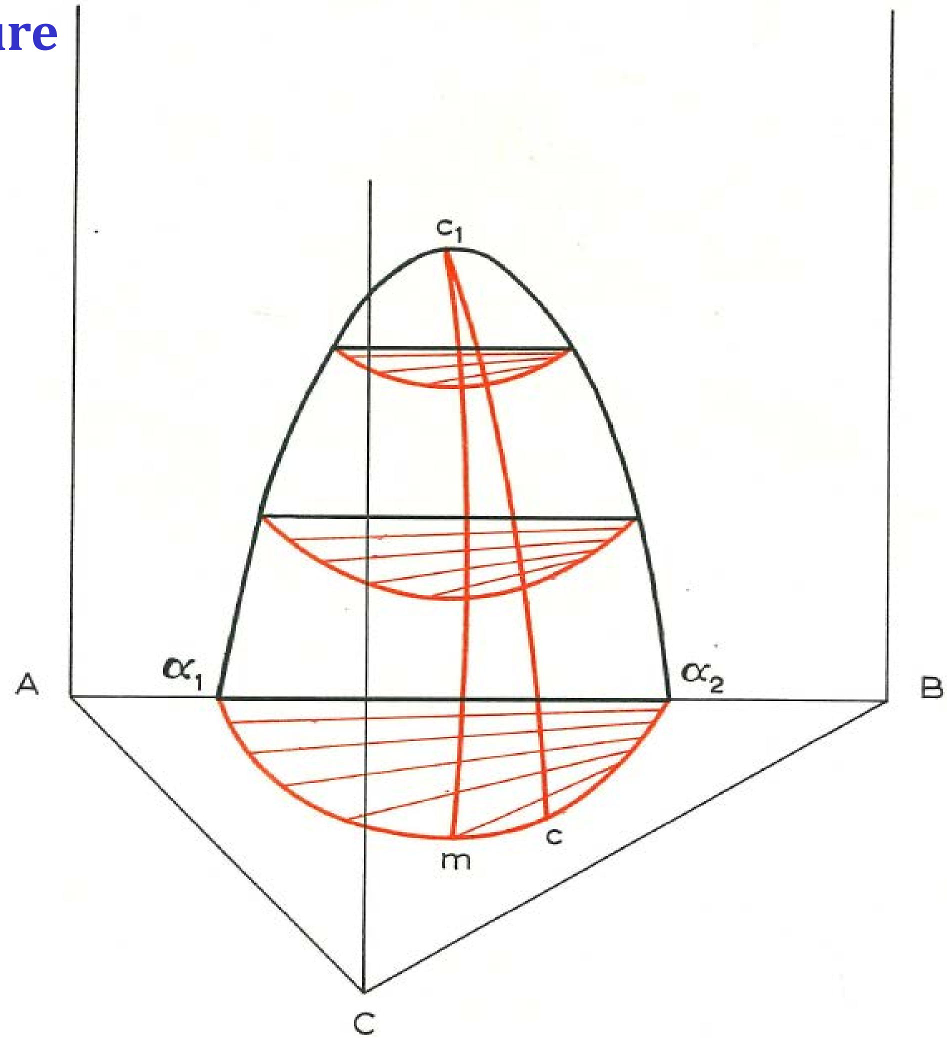
8.4 TWO-PHASE EQUILIBRIUM

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



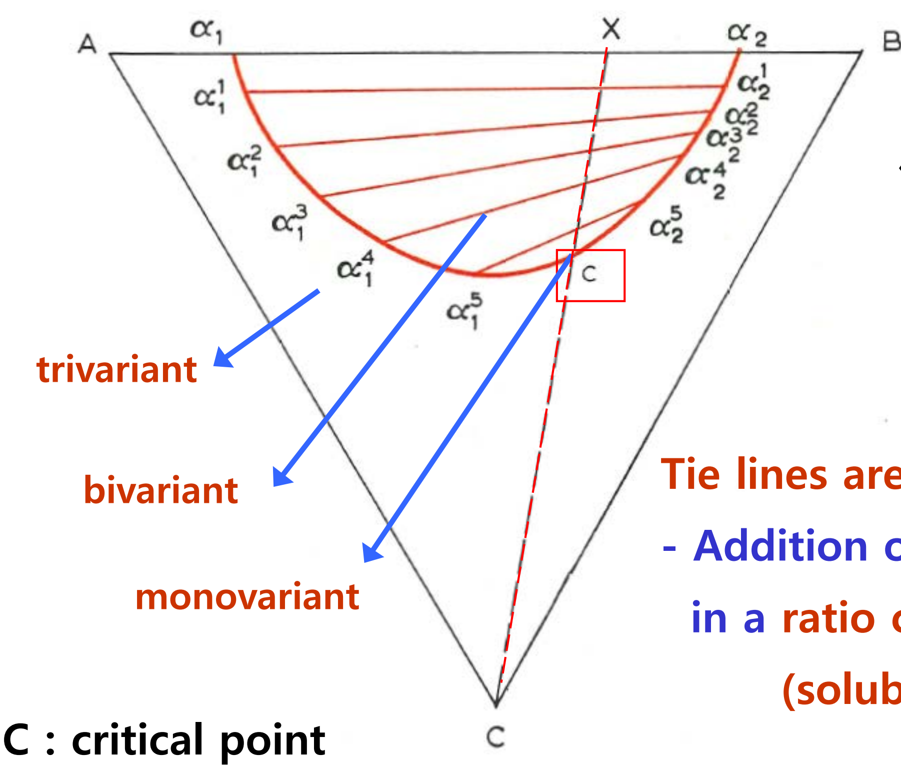
8.4 TWO-PHASE EQUILIBRIUM

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

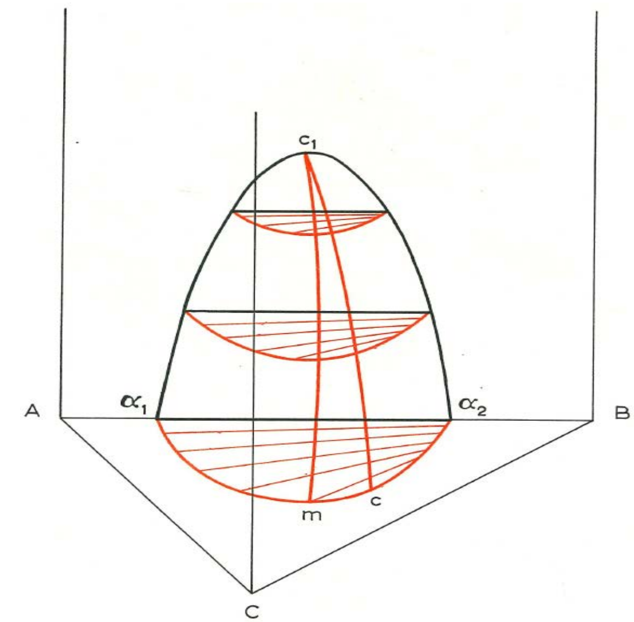
Miscibility gap

a. Ternary system with only a binary critical point

- Isothermal section at room temp.



C : critical point



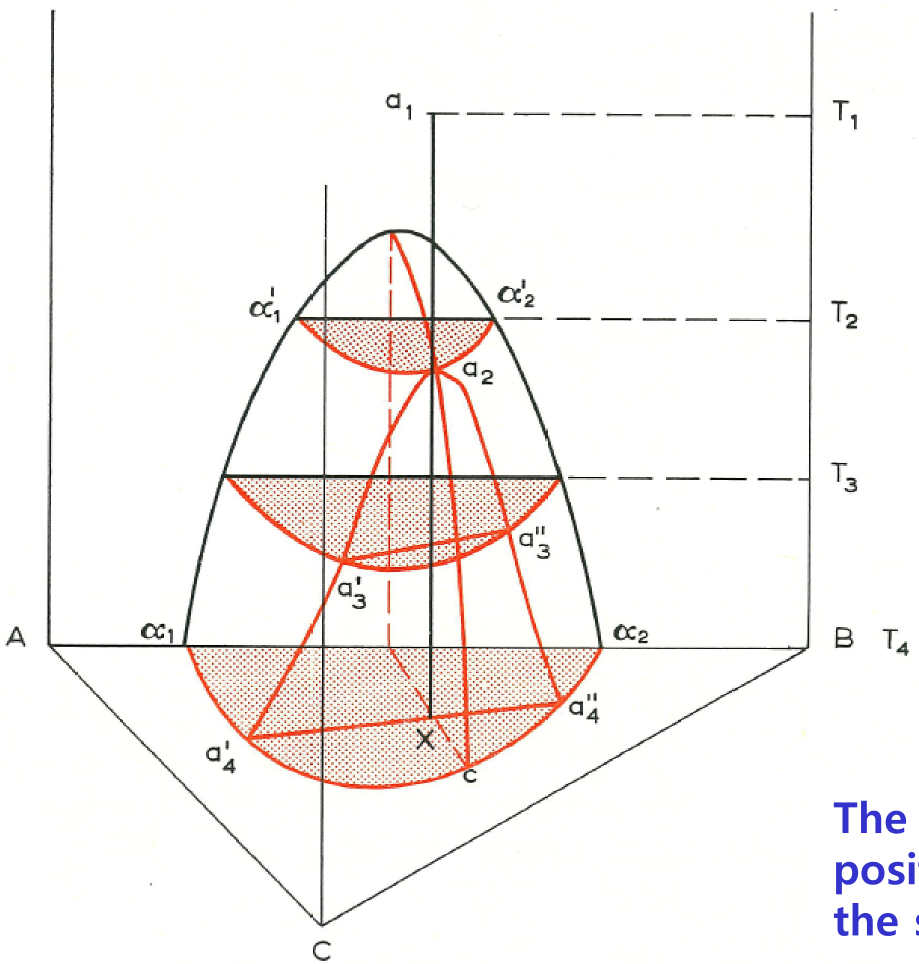
Tie lines are not parallel to the binary tie line.

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

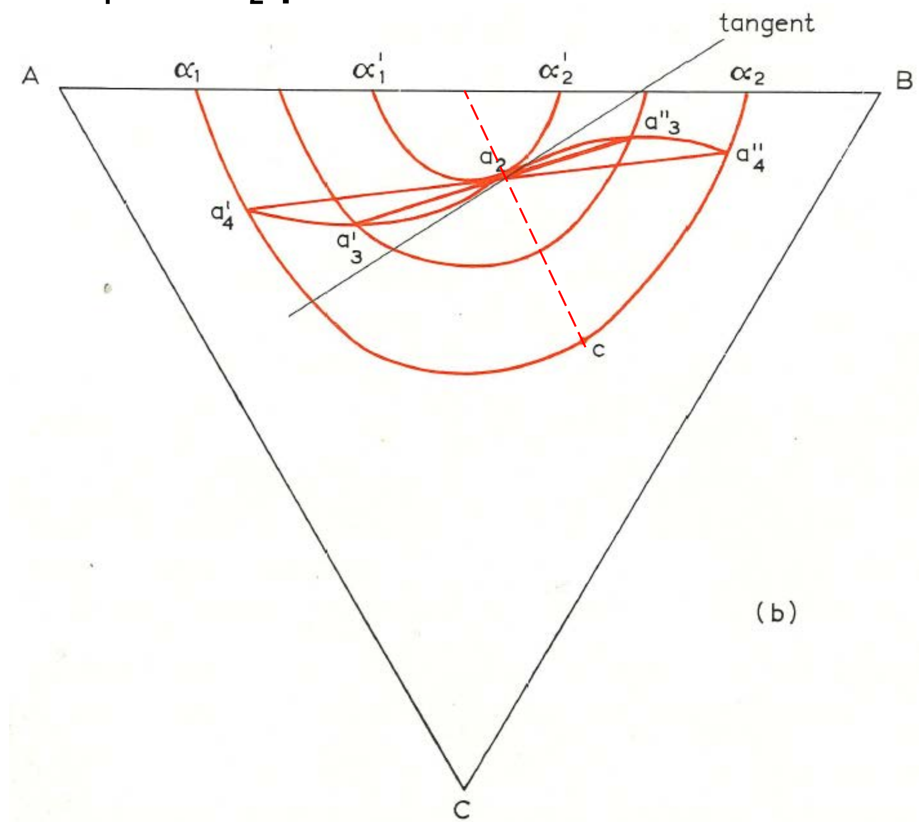
(Max. point, m ≠ critical point, c in most cases)

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

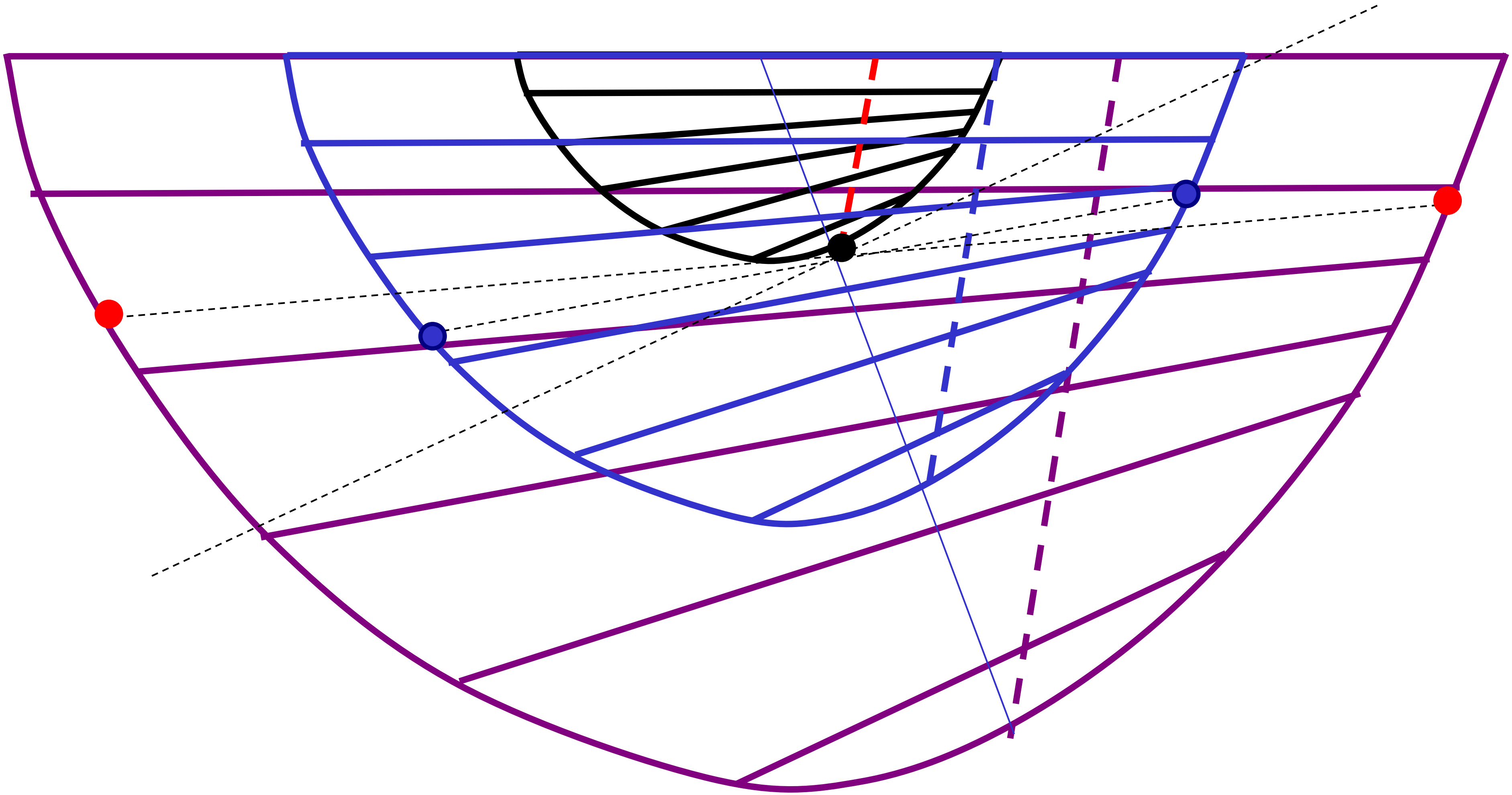


(b) Changes in composition of the co-exisitng α_1 and α_2 phases

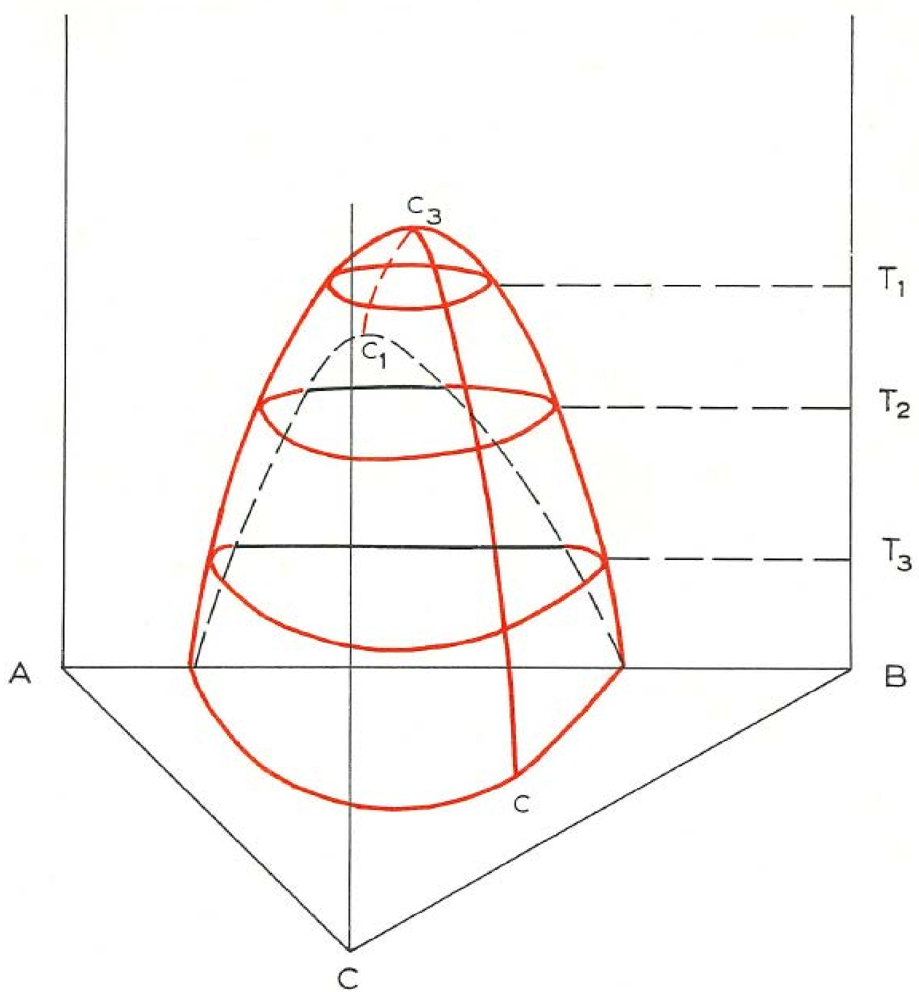


The course of the curves is defined by the relative position of the tie lines which skew round towards the side AB as the temperature decreases.

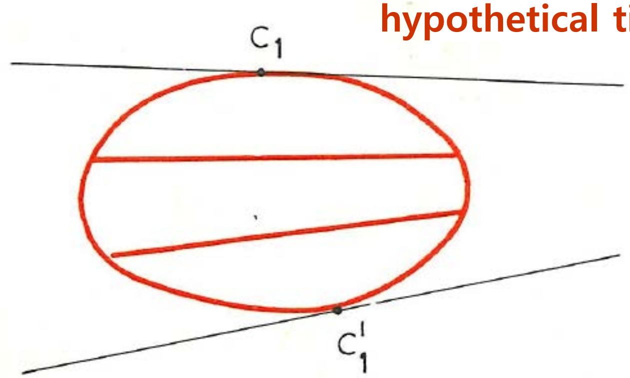
➡ Curves changes along a line which is tangential to the solubility curve



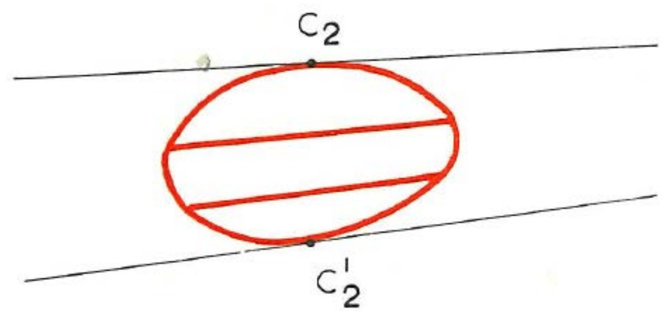
b. A ternary system with a binary and a ternary critical point



Isotherms



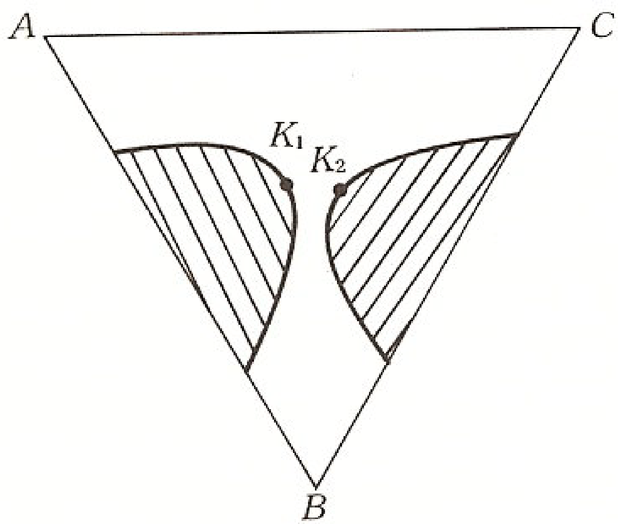
(a) The binary critical point temperature

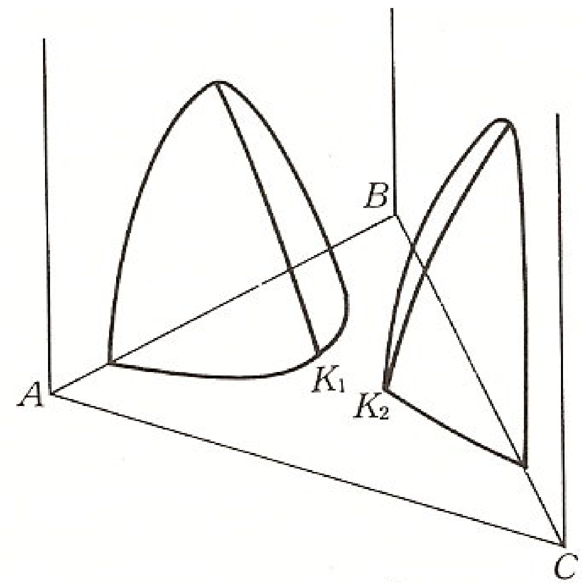


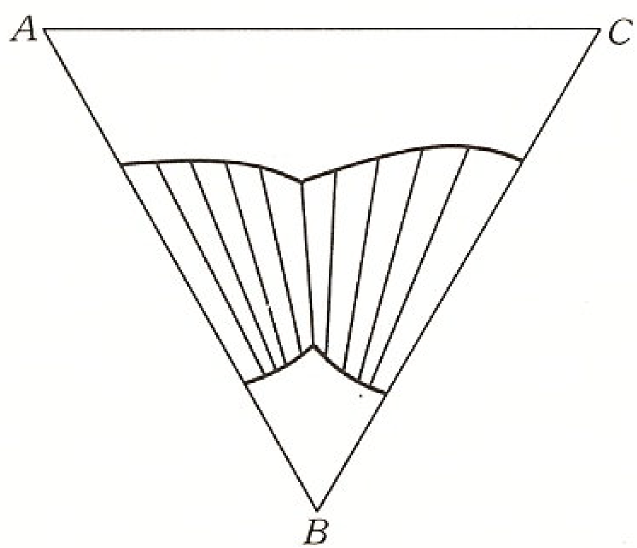
(b) A temperature between c_1 and c_3

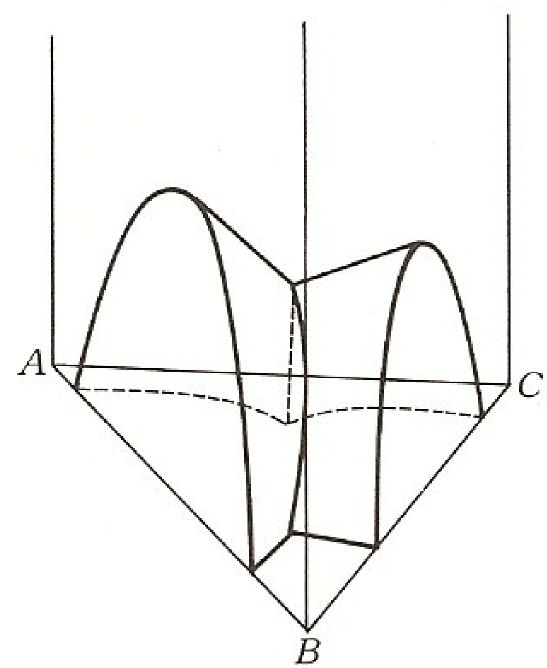
(c) The ternary critical point temperature

c. ternary system with two miscibility gaps

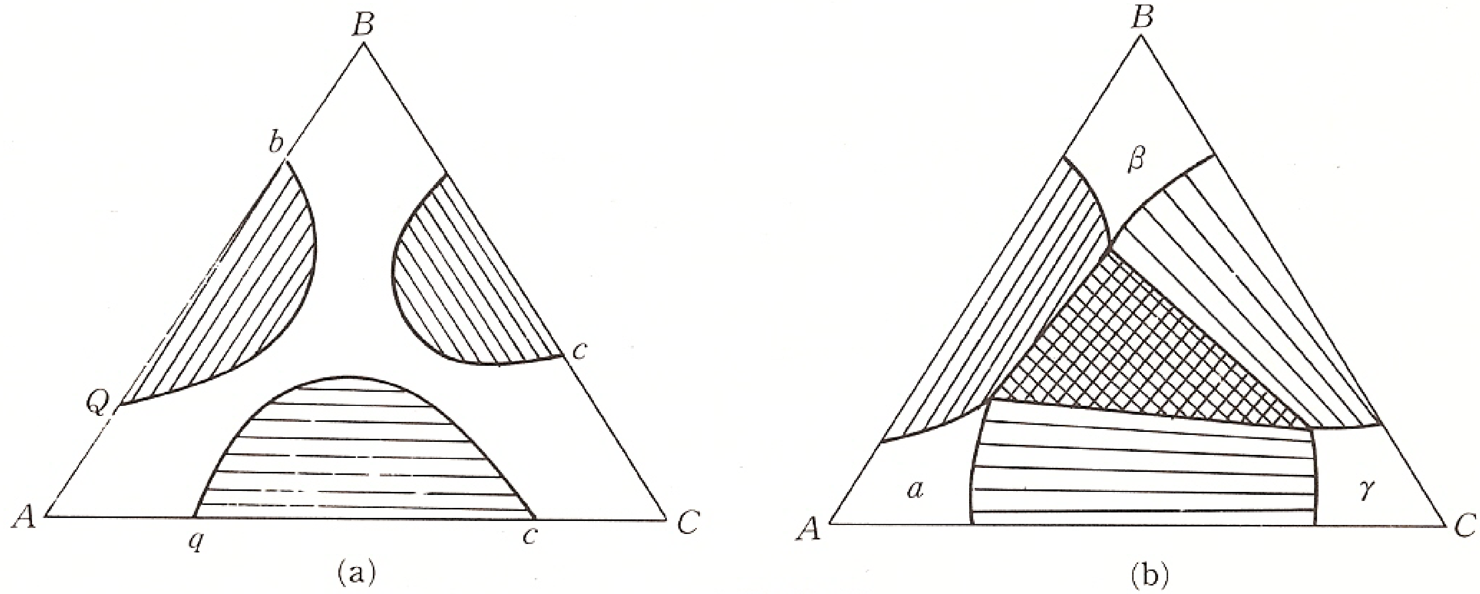




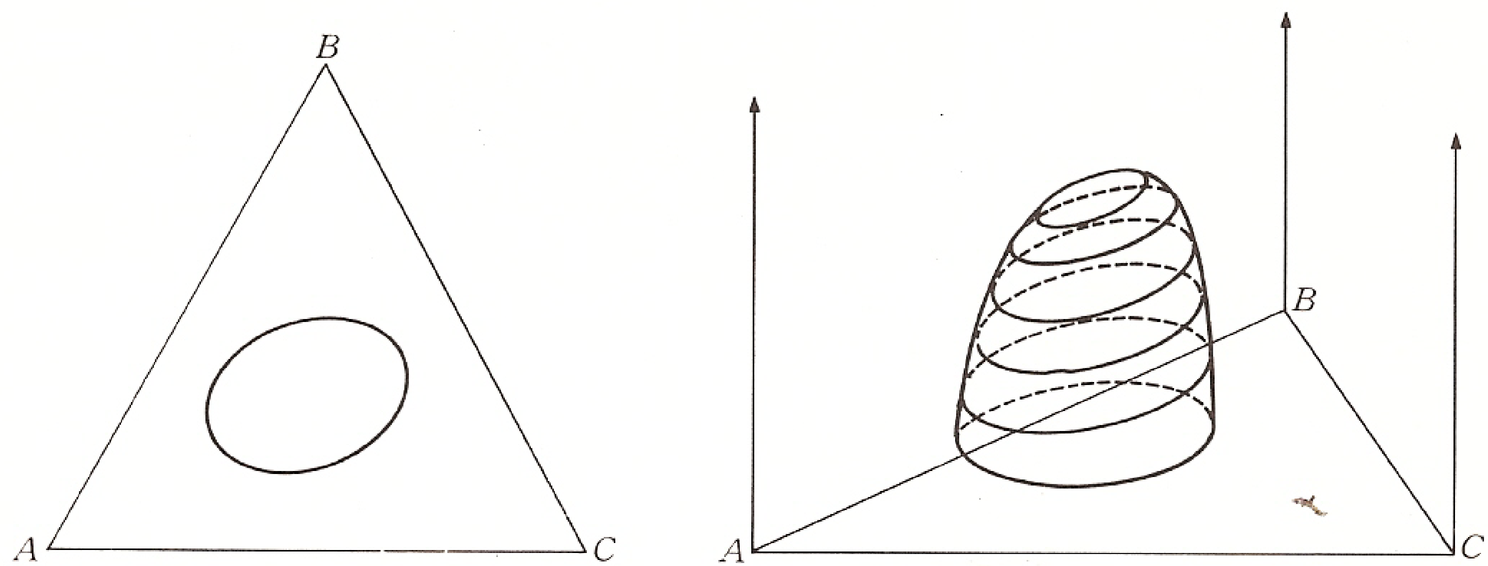




c. Ternary system with three miscibility gaps



d. Ternary system with miscibility gap in three component region



Chapter 9. Ternary phase Diagrams

Three-Phase Equilibrium

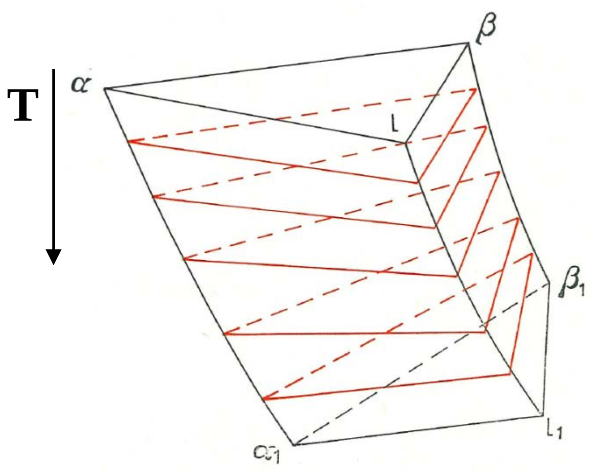
9.1. PROPERTIES OF THREE-PHASE TIE TRIANGLES

Two phase equil. (f = 2)

- ideal system
- liquidus max. (or min.)
- miscibility gap

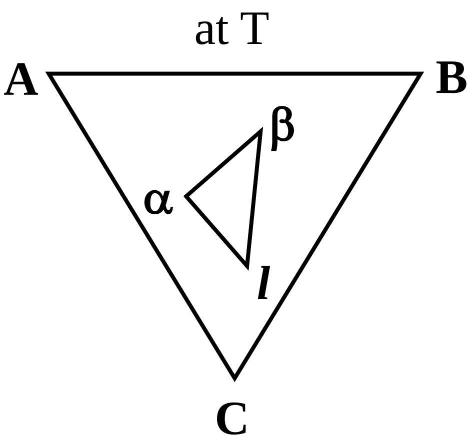
Three phase equil. (f = 1)

• **Tie triangle**

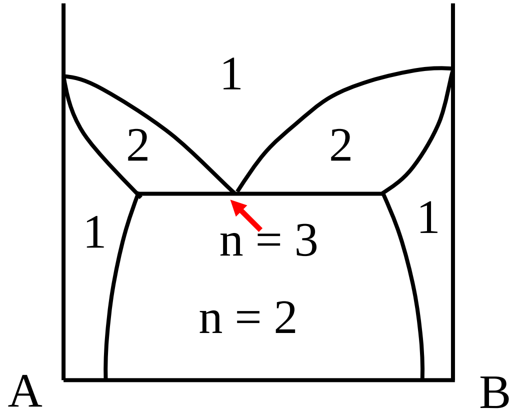


① vertex of tie triangle

→ composition of three phases

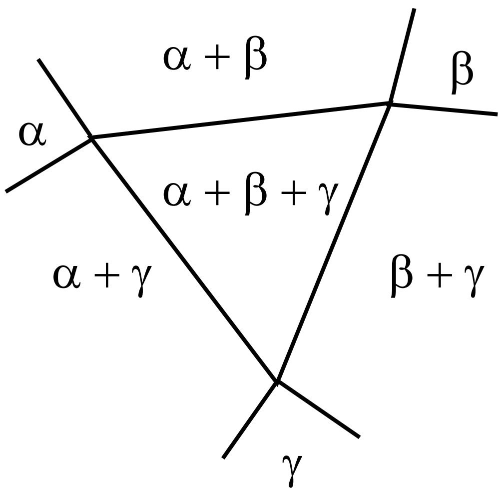


cf) *n* phase region is surrounded by
$n \pm 1$ phase region



9.1. PROPERTIES OF THREE-PHASE TIE TRIANGLES

② **tie triangle will be surrounded by 2 phase region**

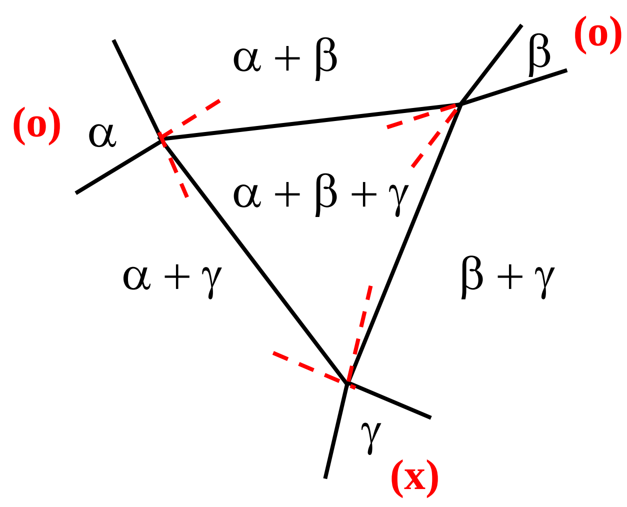


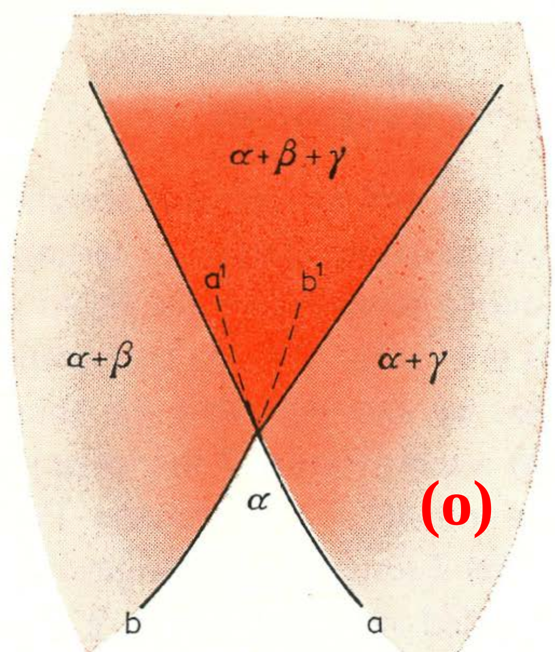
③ **at vertex, single phase region will exist.**

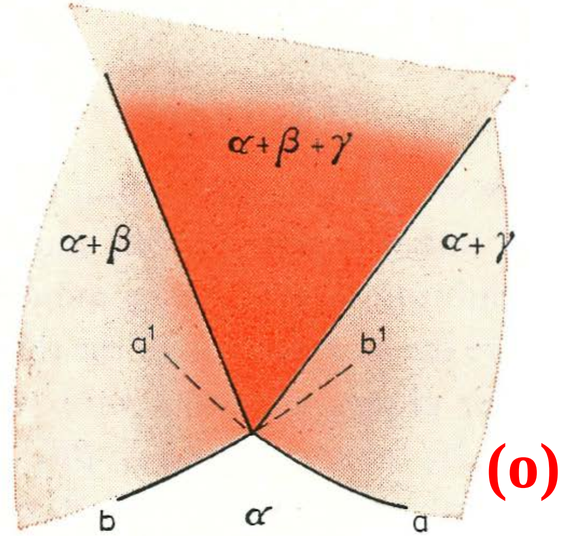
④ **rule for phase boundary between single and two phase regions**

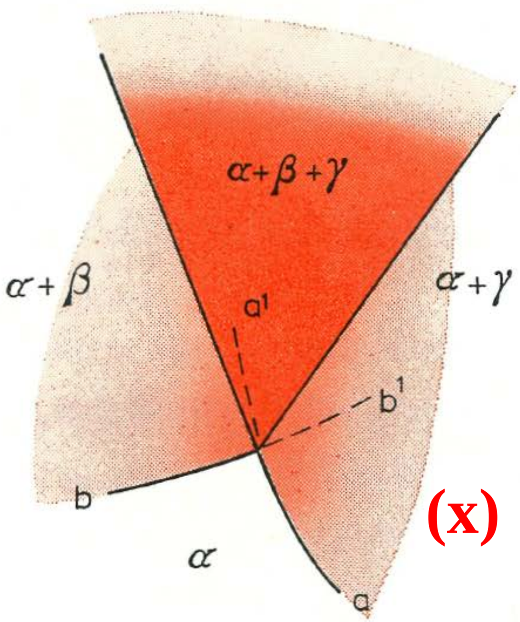
- extension of boundary (two)

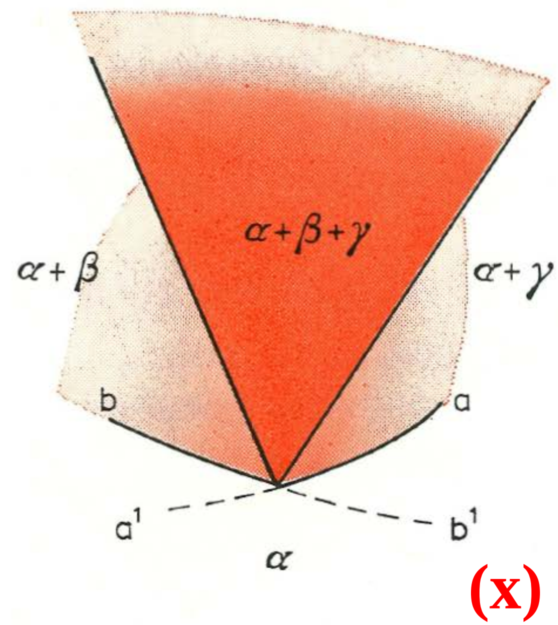
→ **both should toward outside the triangle or inside the triangle**




α+β+γ
a¹
b¹
α+β
α+γ
α
b
a
(o)


α+β+γ
α+β
α+γ
a¹
b¹
b
α
a
(o)


α+β+γ
α+β
α+γ
a¹
b¹
b
α
a
(x)


α+β+γ
α+β
α+γ
b
a
a¹
b¹
α
(x)

9.2. THREE-PHASE EQUILIBRIUM

① Coalescence of miscibility gap and two phase region

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

"critical point meet two phase region"

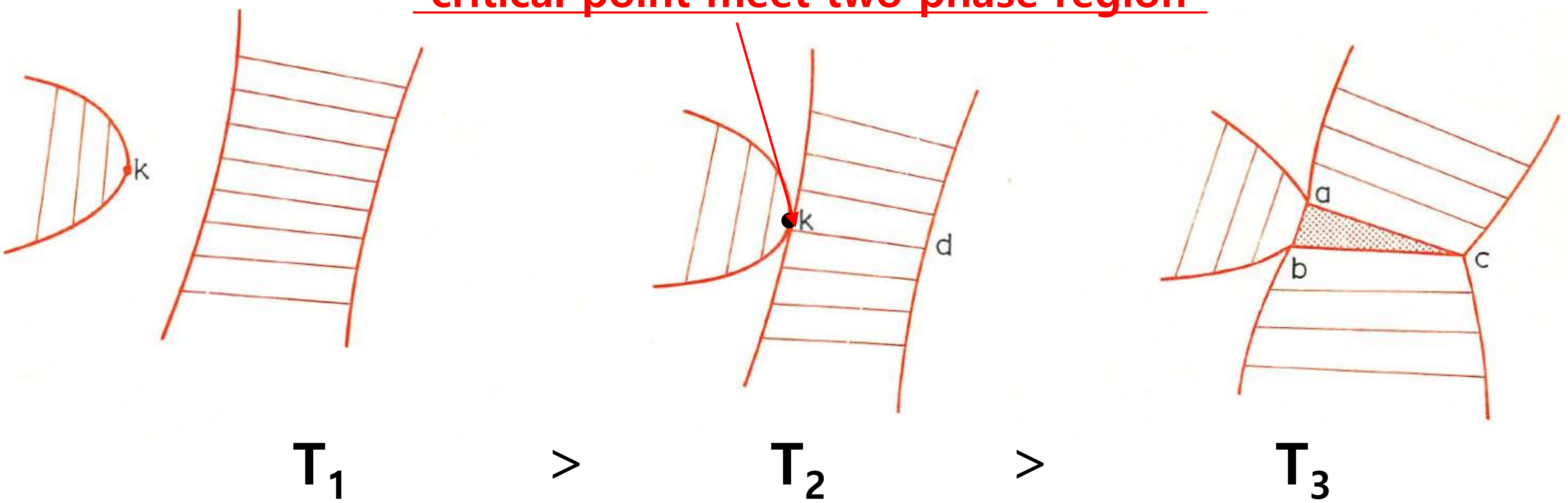
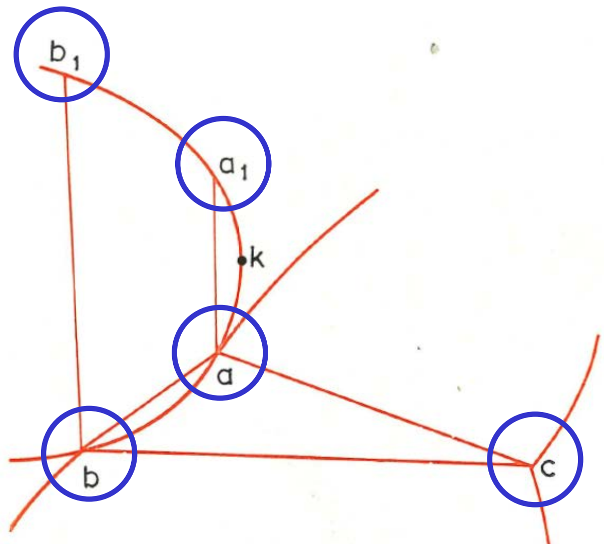


Fig. 136. Production of a ternary three-phase equilibrium by the coalescence of two two-phase regions

9.2. THREE-PHASE EQUILIBRIUM

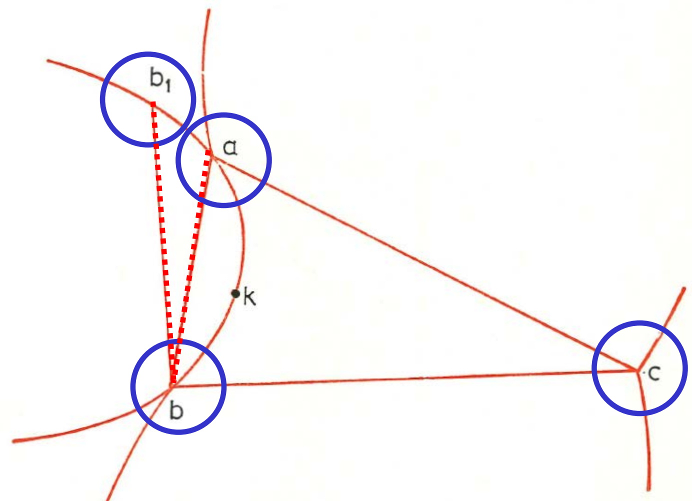
① Coalescence of miscibility gap and two phase region

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



Five phase equilibrium: this is impossible.

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



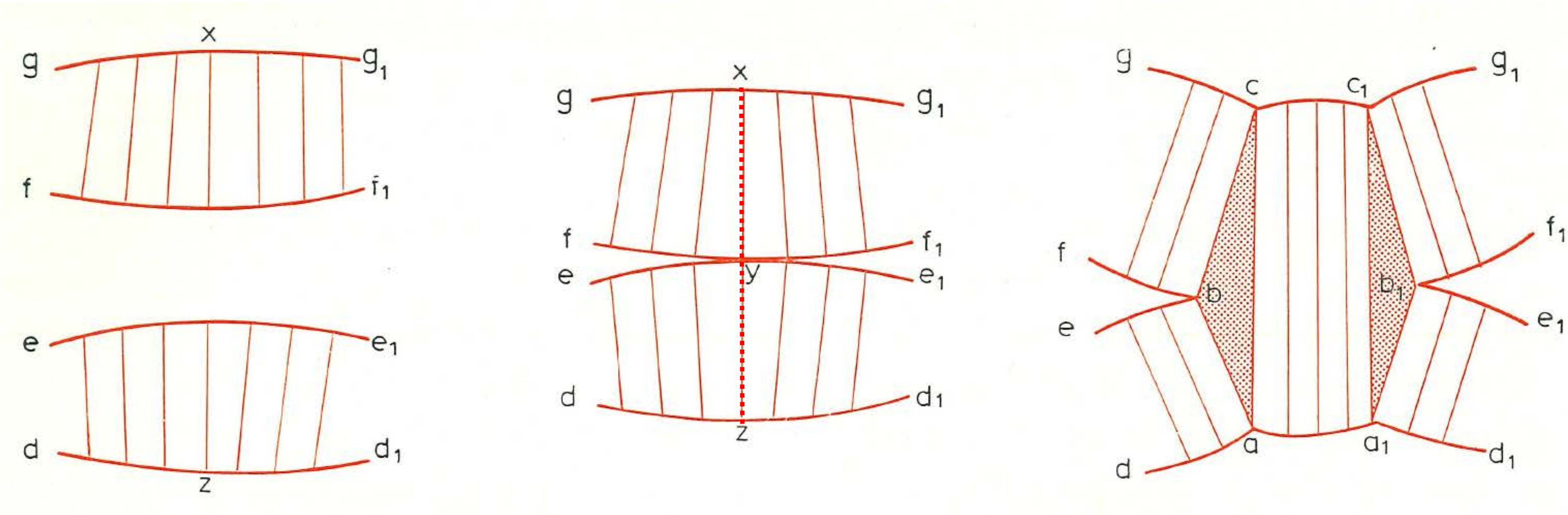
impossible condition of two tie lines: ab and bb_1

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*.

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

9.2. THREE-PHASE EQUILIBRIUM

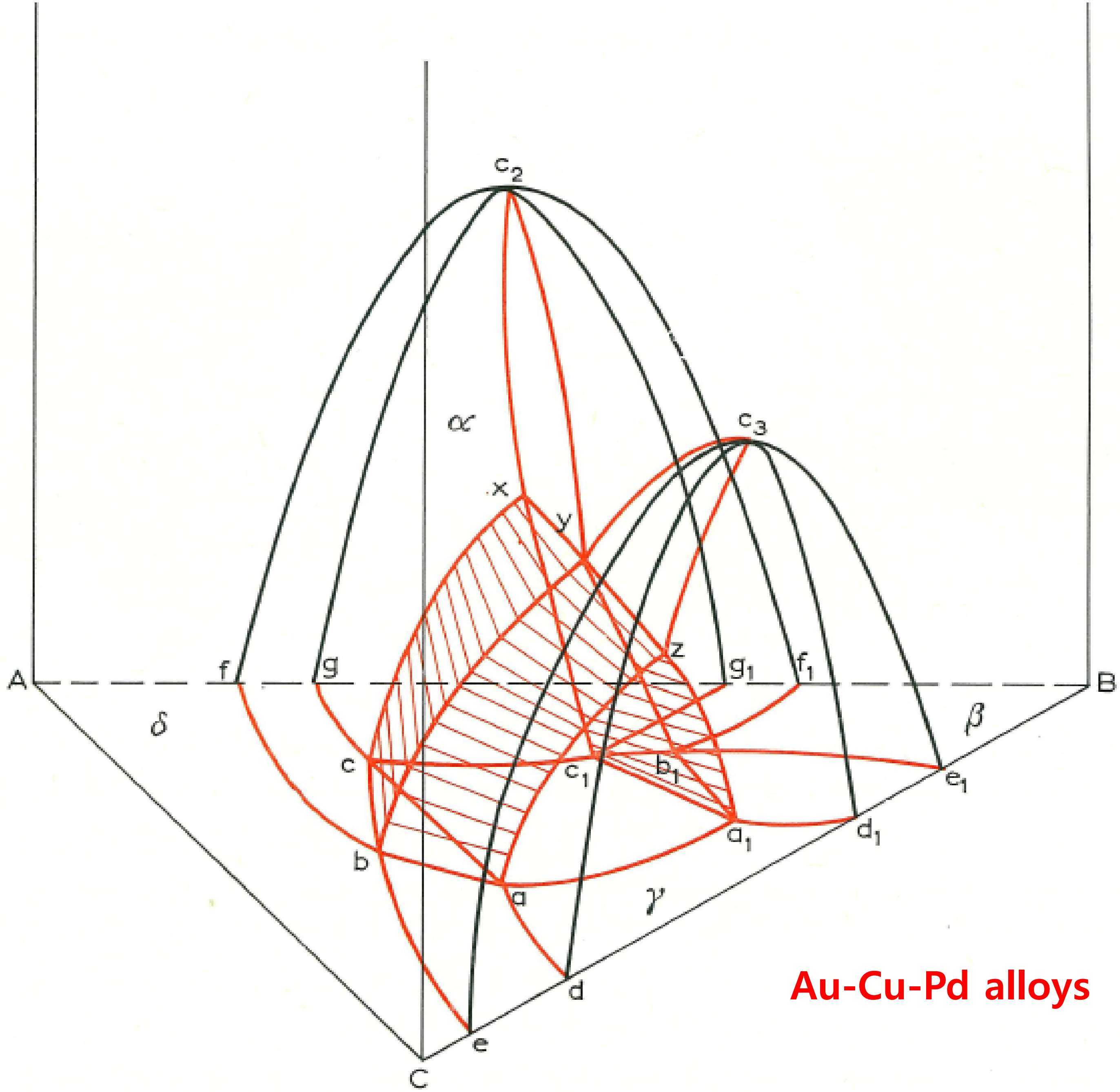
② Coalescence of two two-phase region



T_1 > T_2 > T_3

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

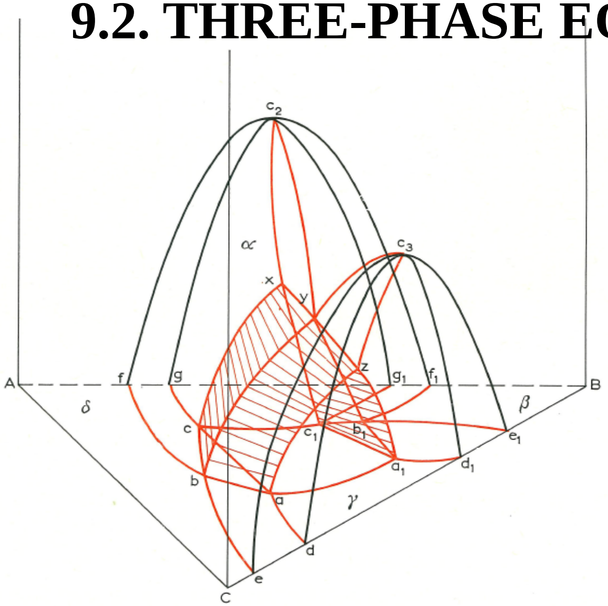
Fig. 138. Alternative method to Fig. 136 for the production of a ternary three-phase equilibrium by the coalescence of two two-phase regions

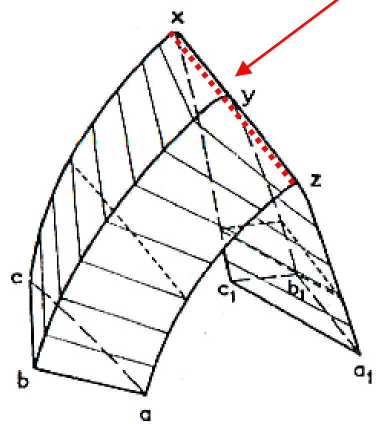


Au-Cu-Pd alloys

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

9.2. THREE-PHASE EQUILIBRIUM

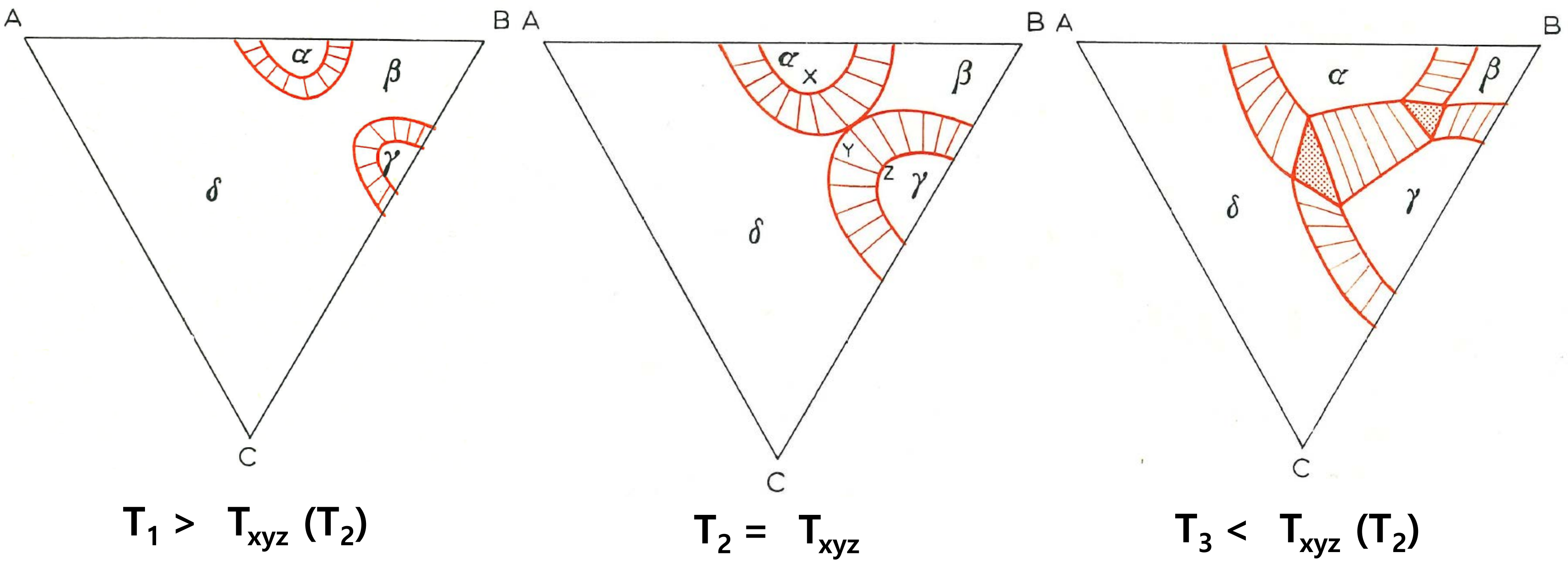


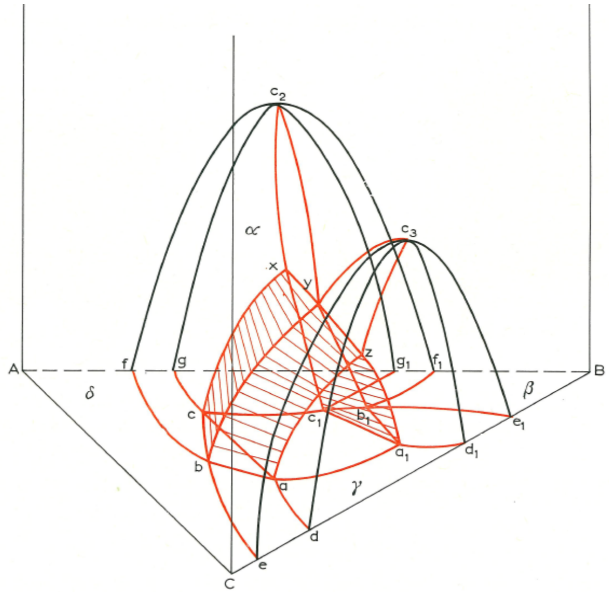


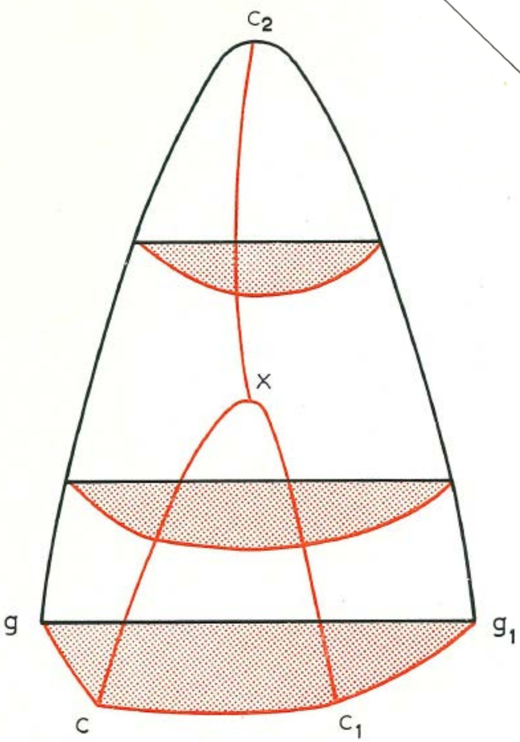
→ *n* component system, reaction between *n* phases occur then the temperature is max or min

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

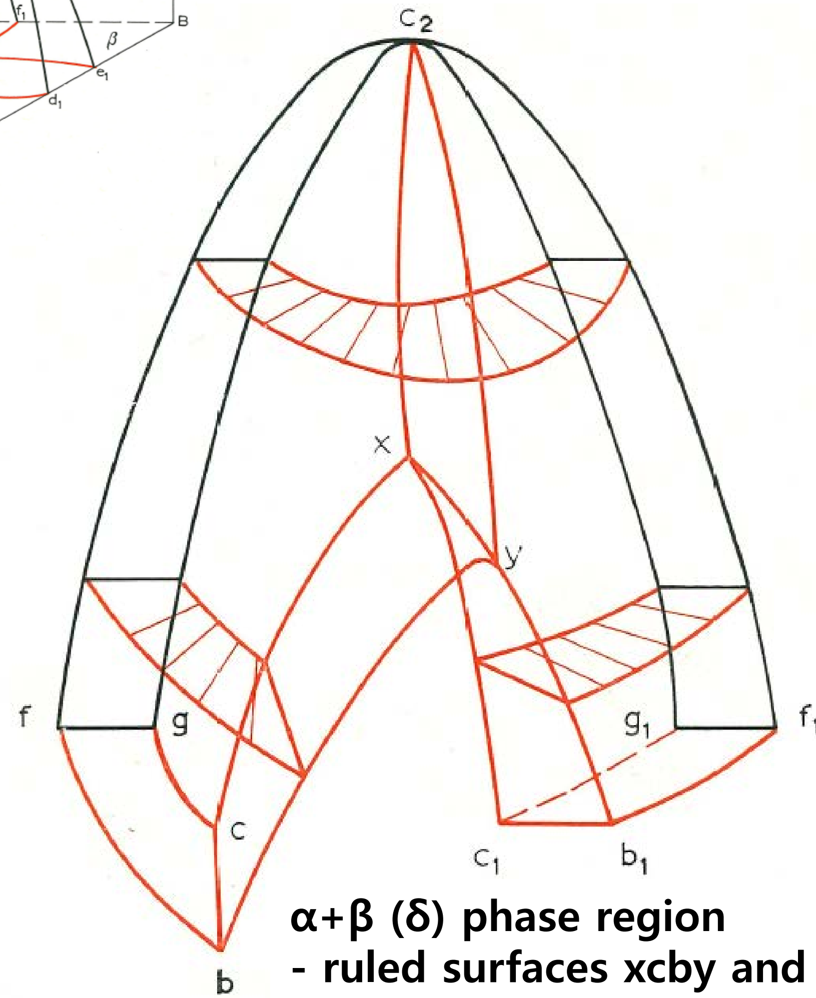
Three isothermal sections



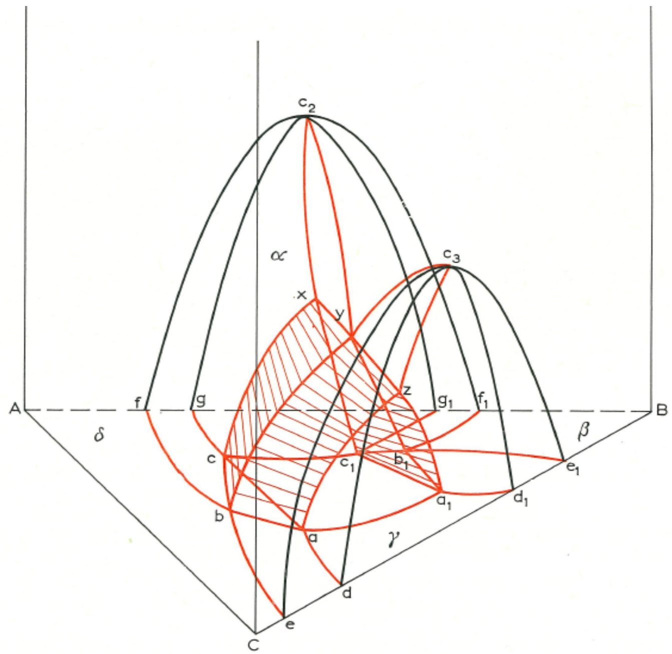


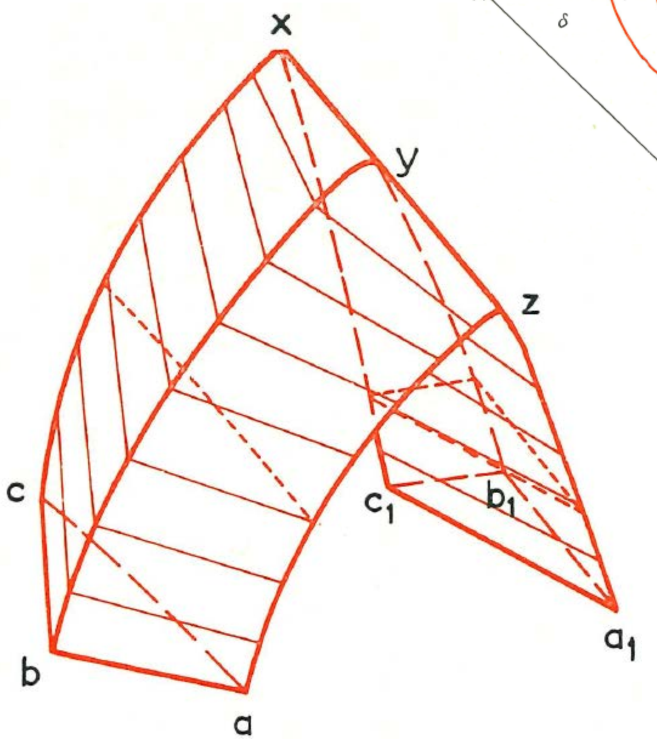


α phase region

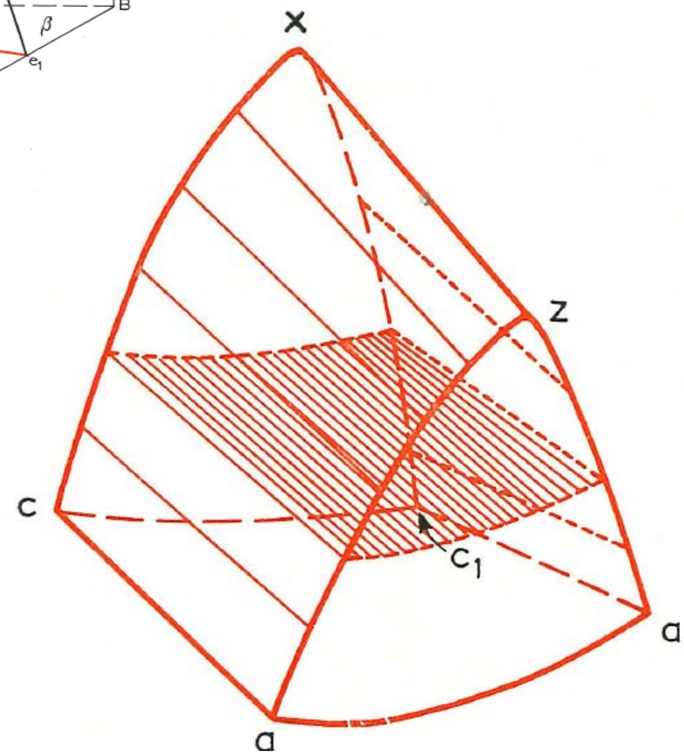


α+β (δ) phase region
- ruled surfaces xcby and xc_1b_1y





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) 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 $l_1 \rightleftarrows l_2$

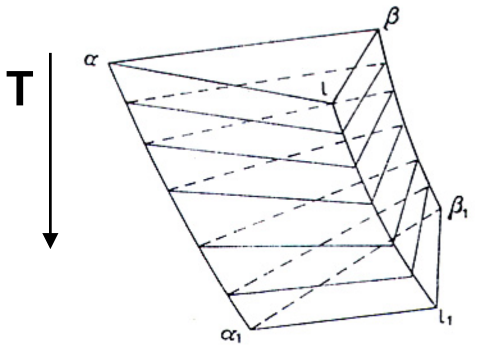
Miscibility gap

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

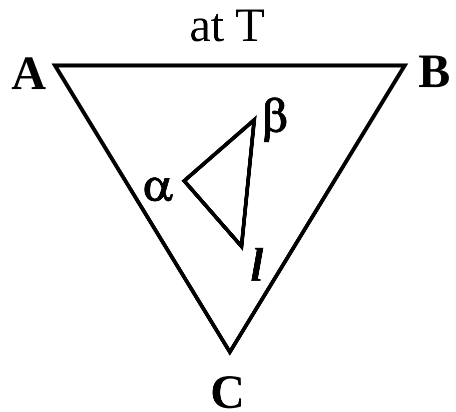
- Addition of C to a heterogeneous mixture of A & B in a ratio corresponding to the distribution of C

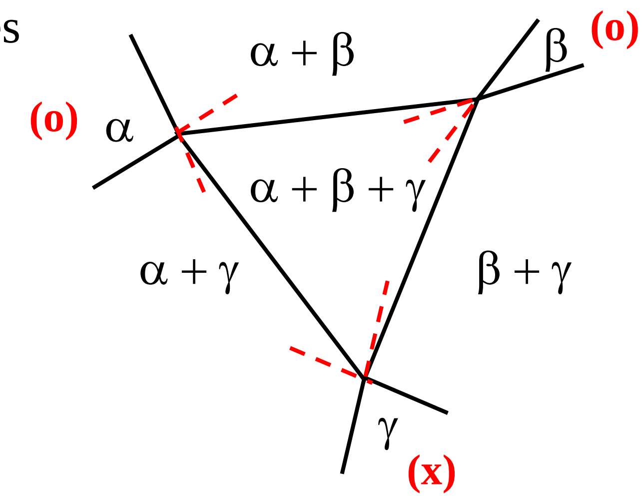
" Three phase equilibrium (f =1)"

• Tie triangle



vertex of tie triangle
→ composition of three phases





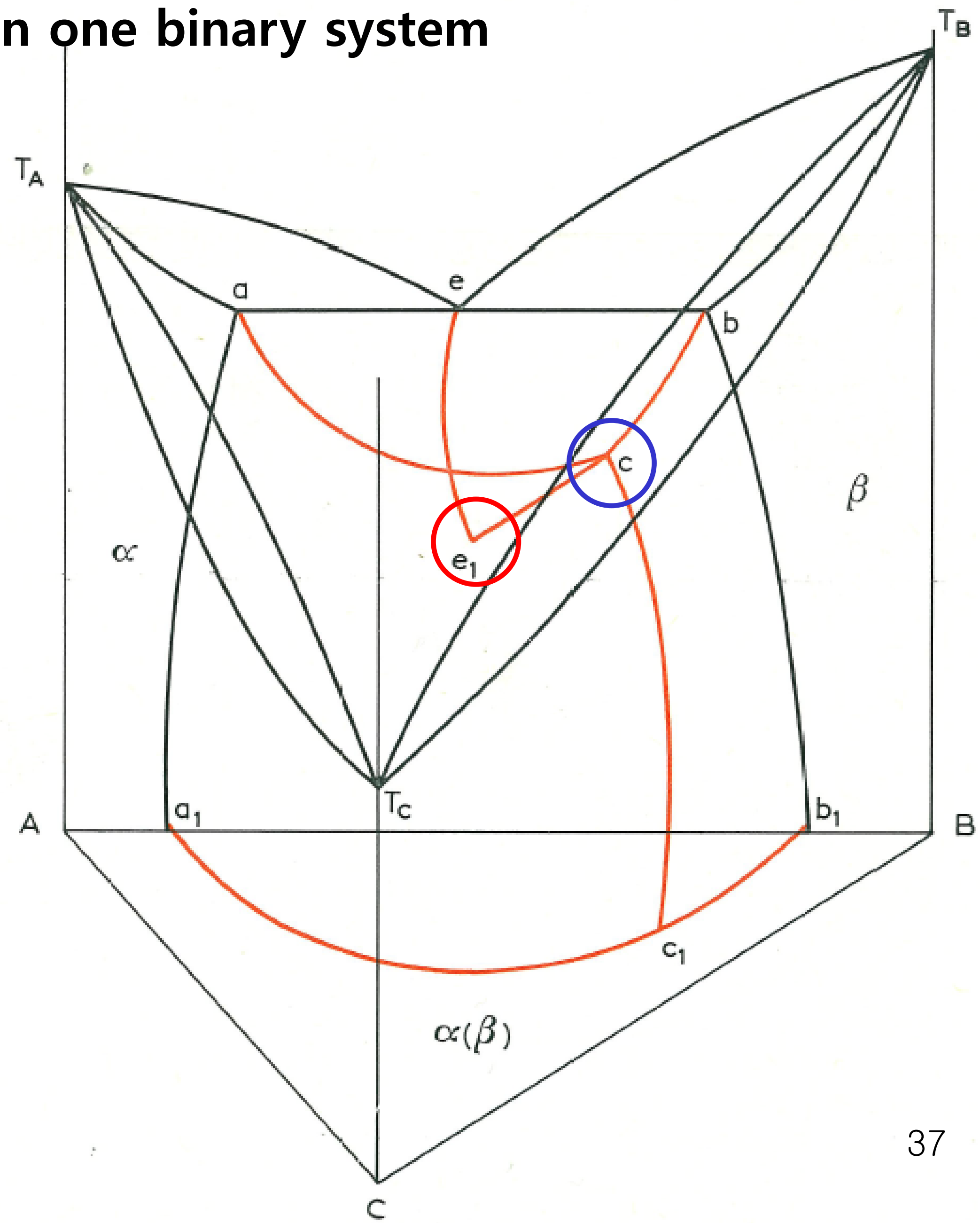
① Coalescence of miscibility gap and two phase region

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

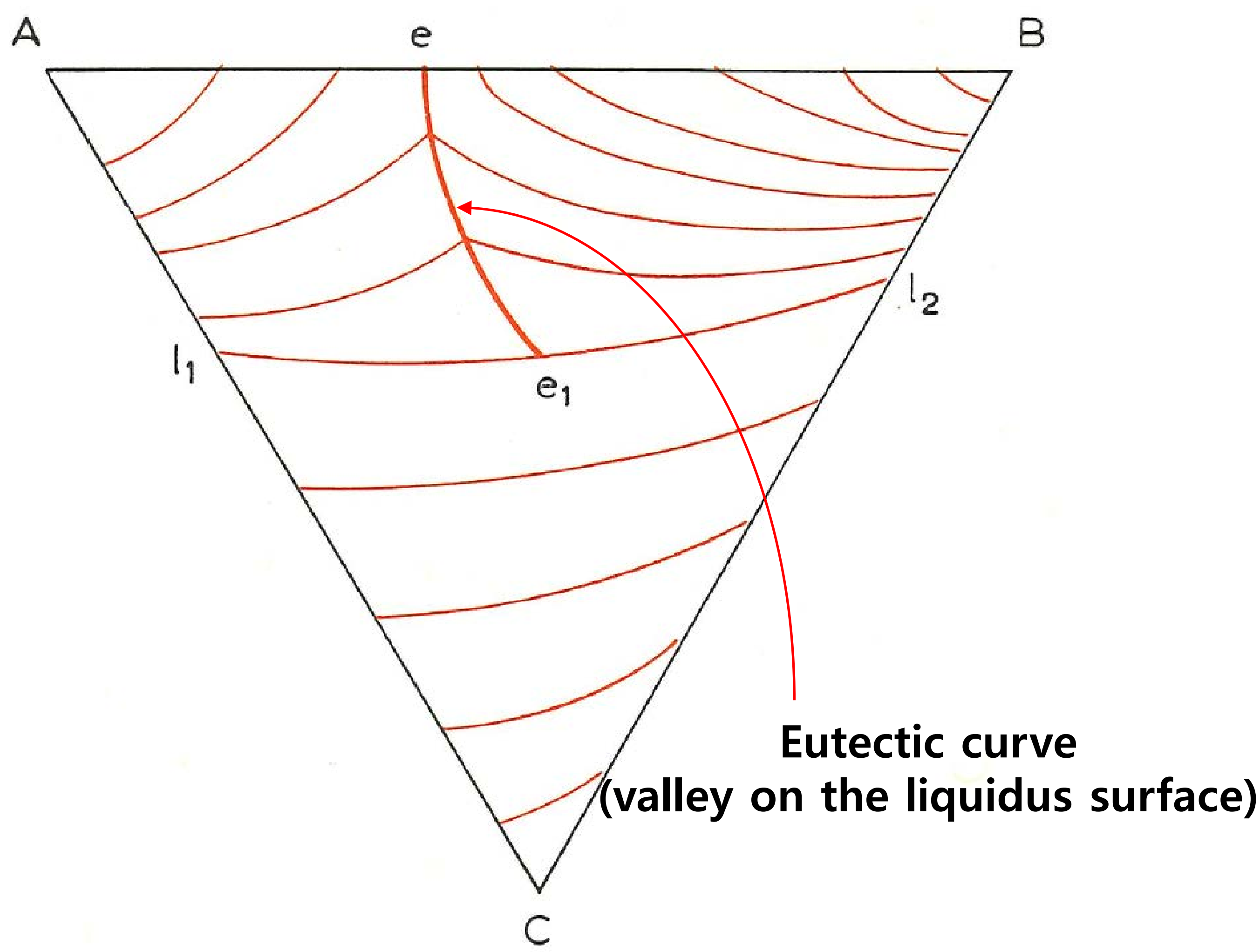
- **One binary eutectic : AB**
  Complete solid solution : BC, AC

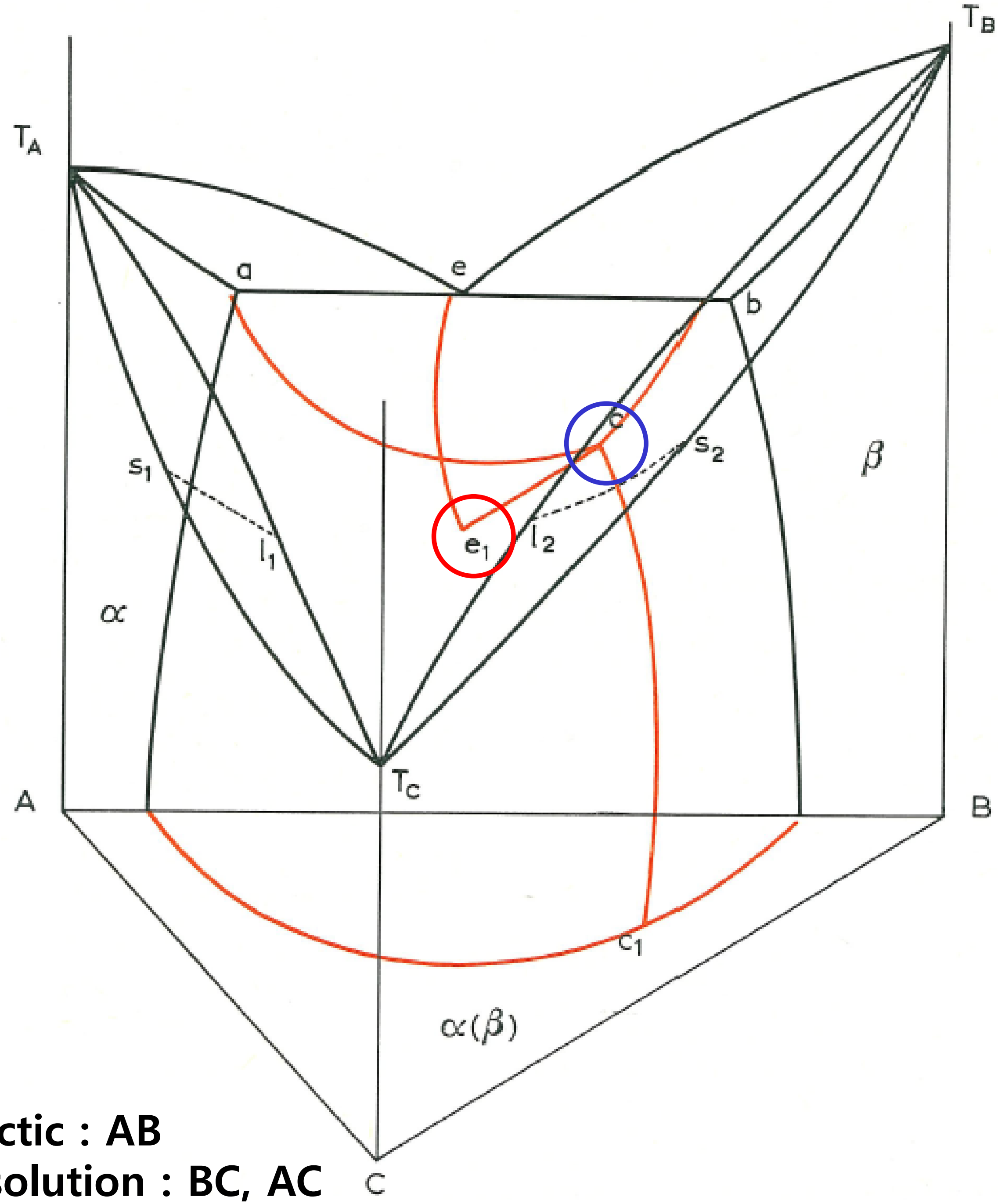


9.3. THREE-PHASE EQUILIBRIUM INVOLVING EUTECTIC REACTIONS

- **Polythermal Projection**

The liquidus surface



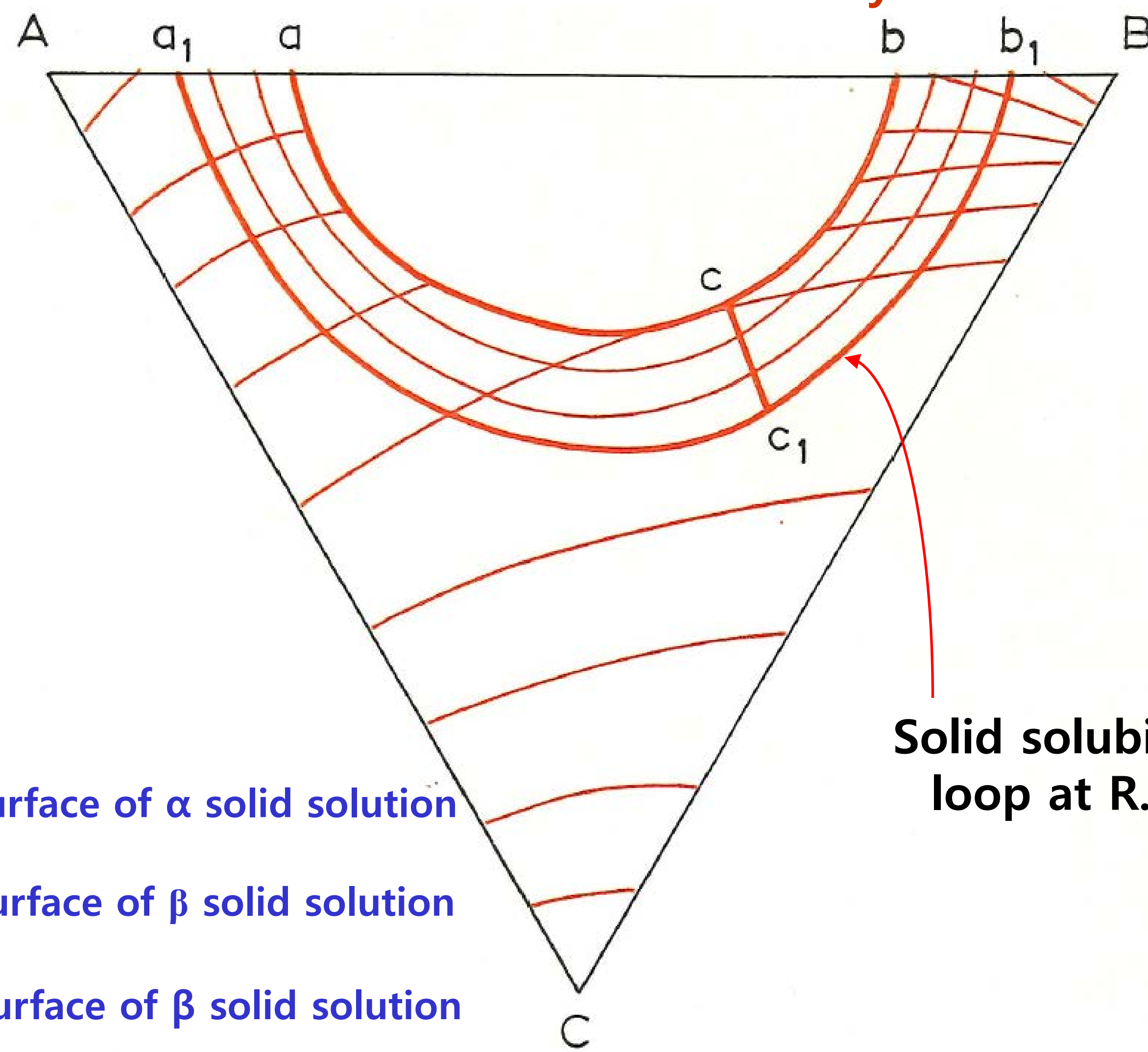


- **One binary eutectic : AB**
  Complete solid solution : BC, AC

9.3. THREE-PHASE EQUILIBRIUM INVOLVING EUTECTIC REACTIONS

- **Polythermal Projection**

The solidus surface and the solubility surface

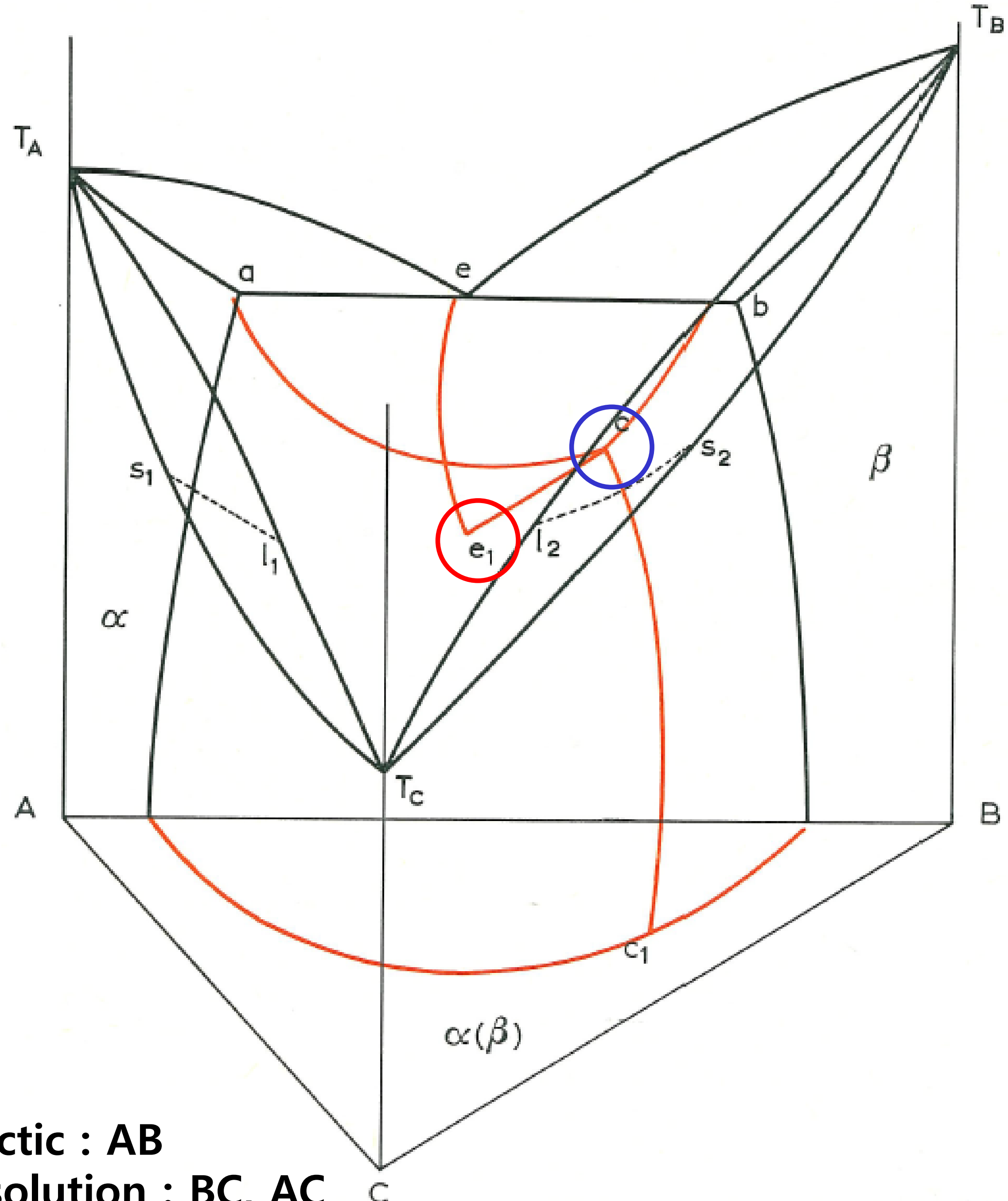


Solid solubility loop at R.T.

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

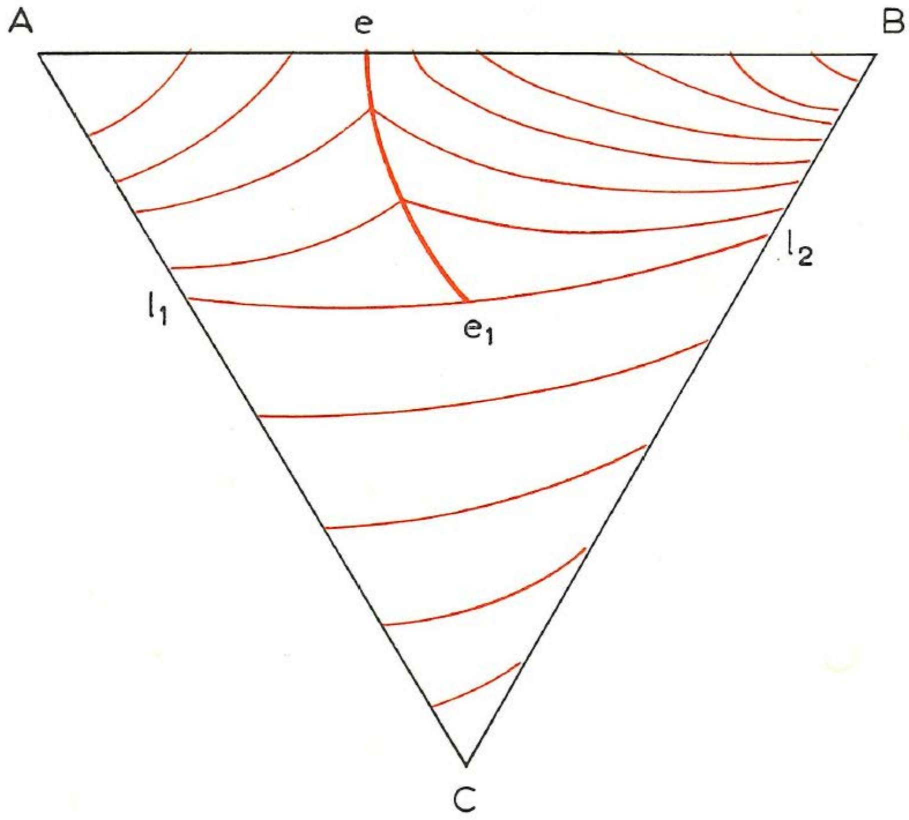
$T_B s_2 c b T_B$- the solidus surface of β solid solution

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

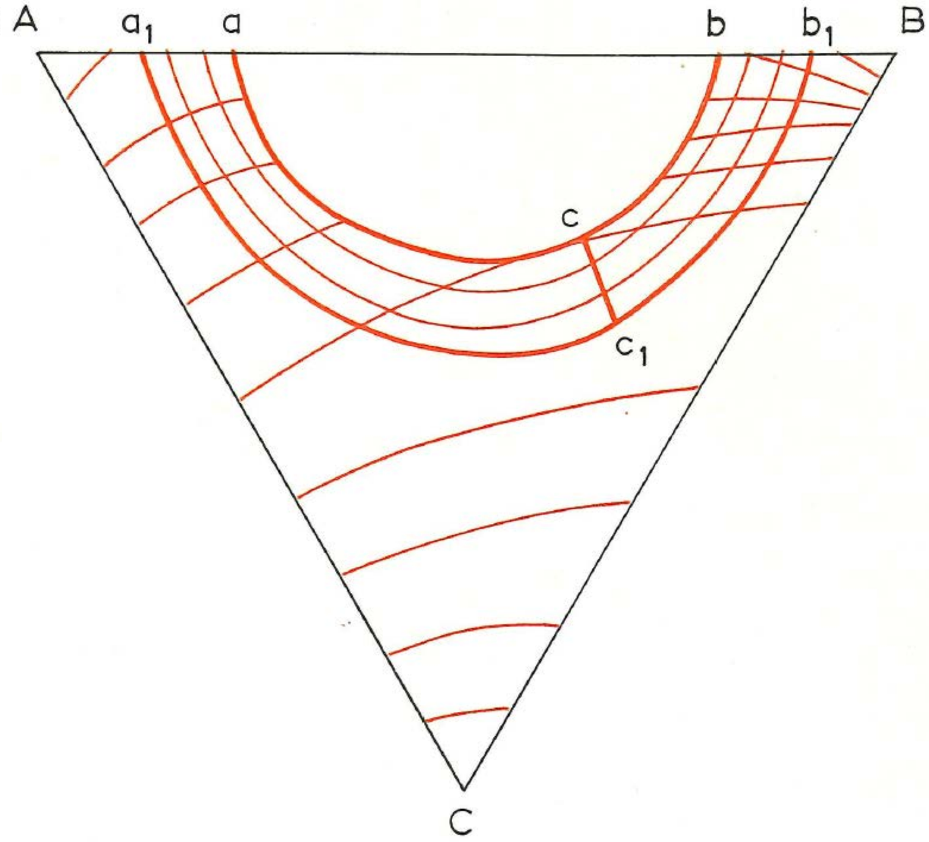


- **One binary eutectic : AB**
  Complete solid solution : BC, AC

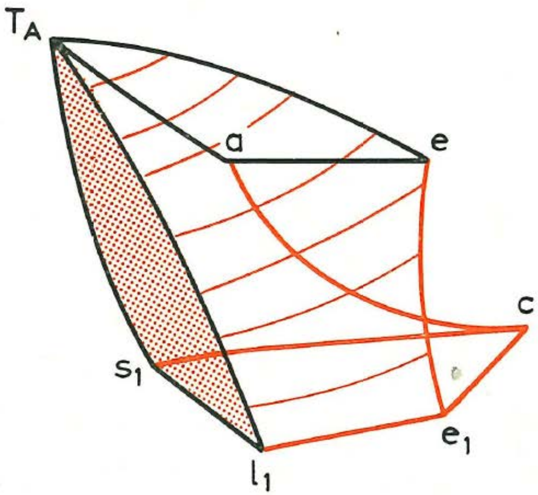
The liquidus surface



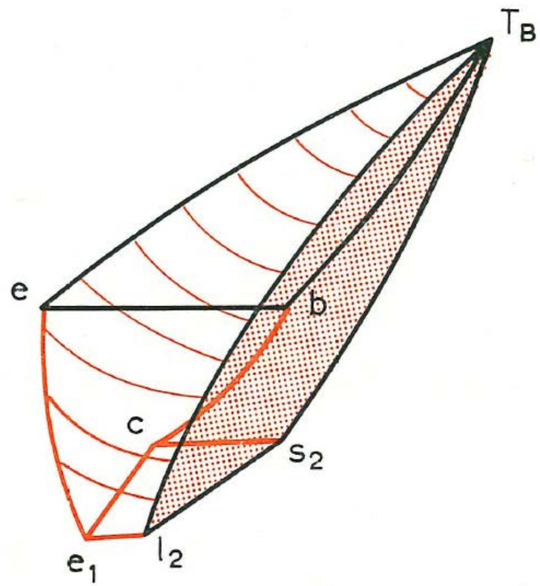
The solidus surface and the solubility surface



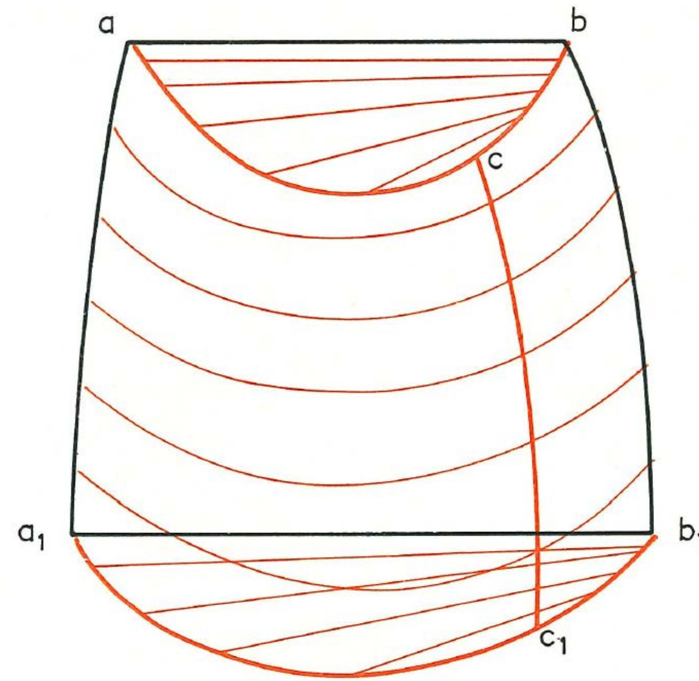
The two-phase regions



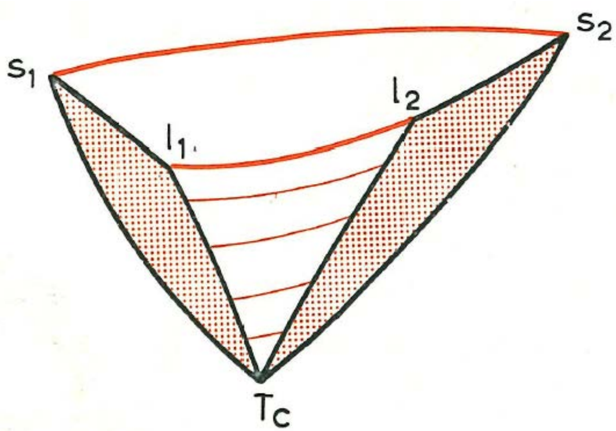
L+α phase region



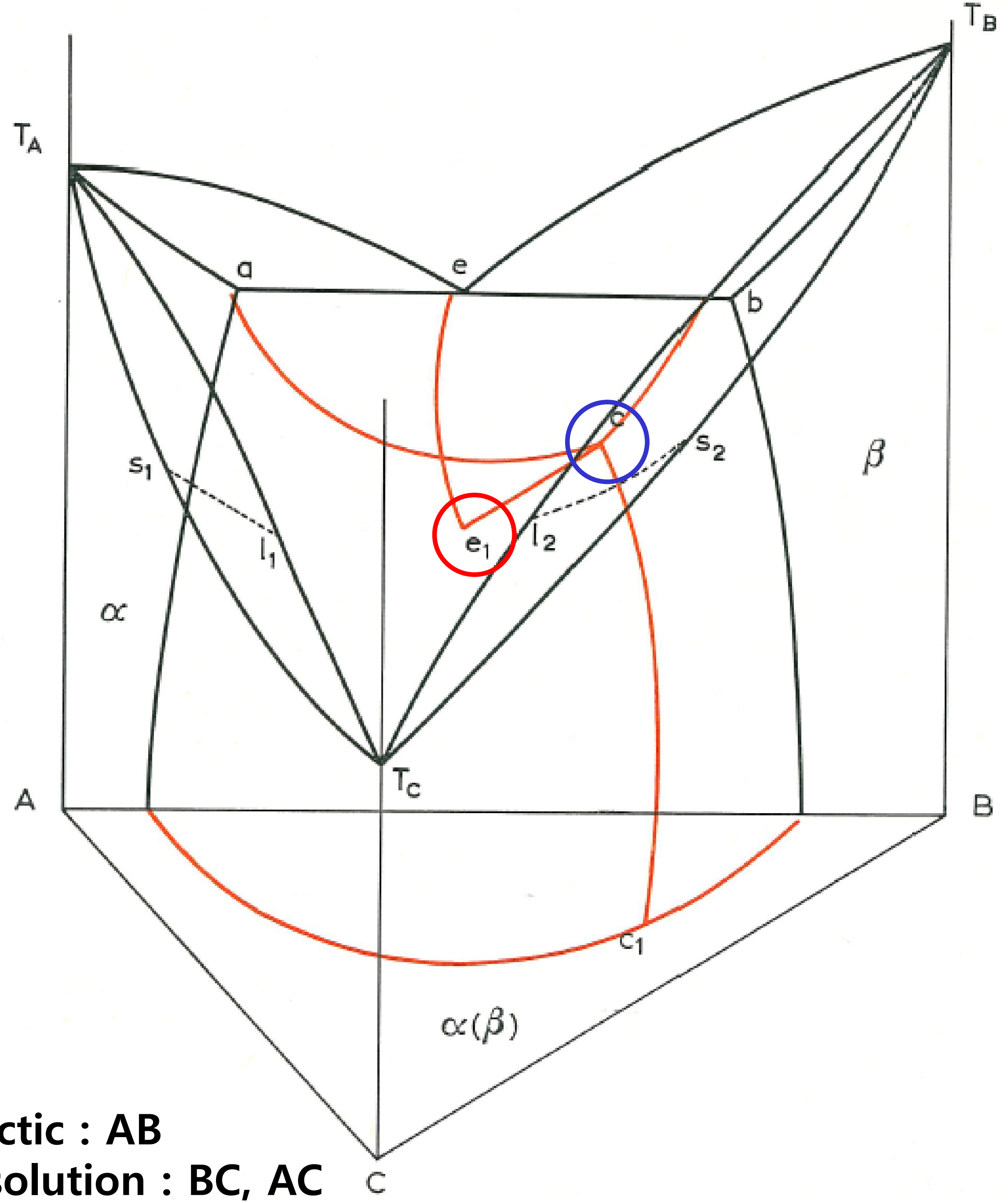
L+β phase region



α+β phase region



L+α(β) phase region

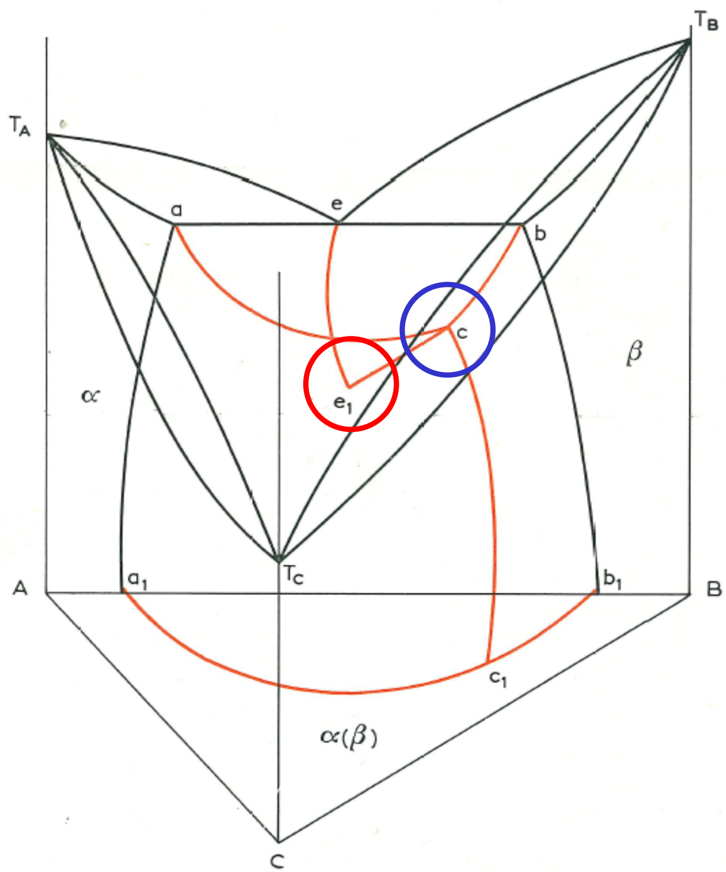


- **One binary eutectic : AB**
  Complete solid solution : BC, AC

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



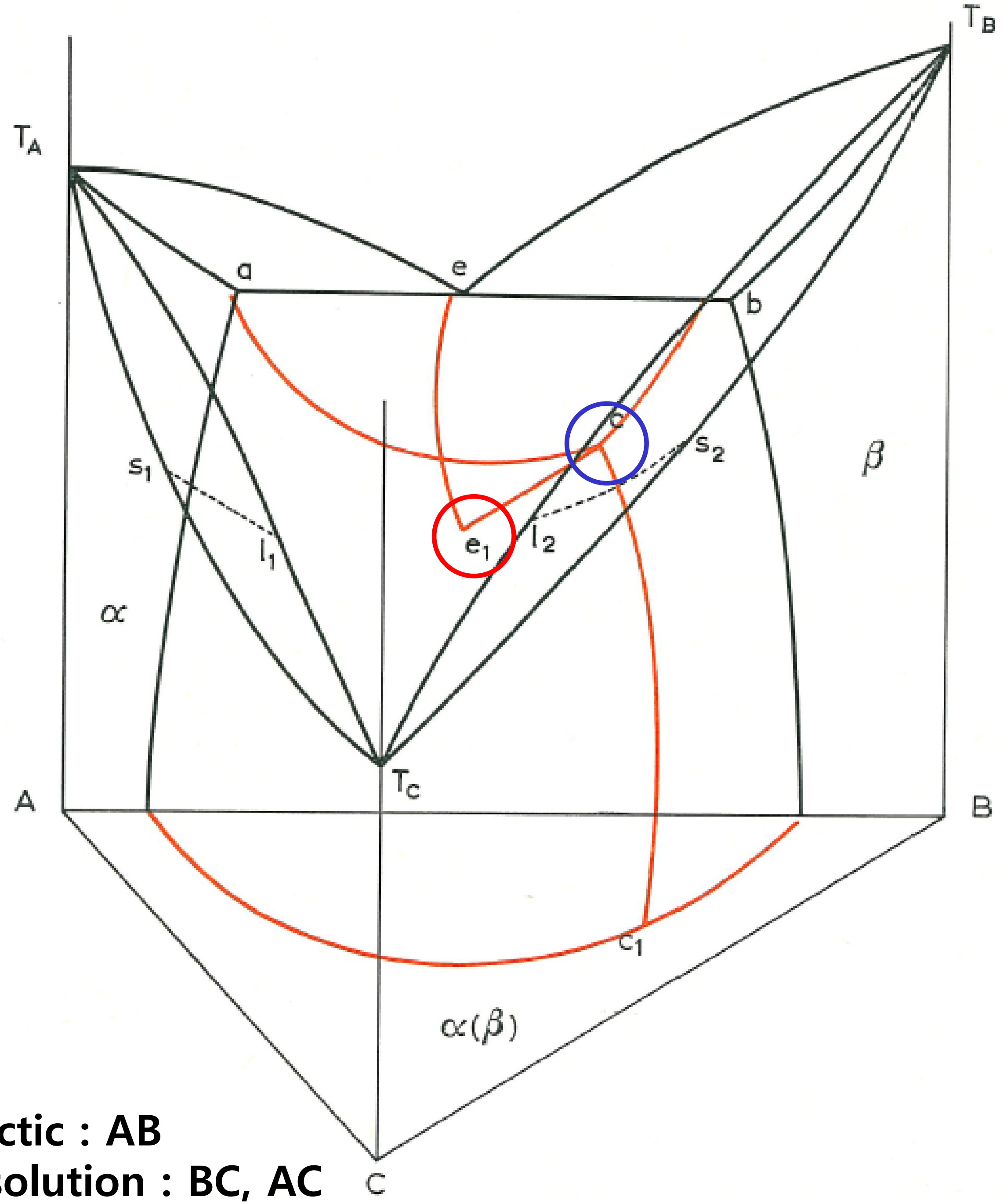
- Closed solid solubility loop
  → minimum critical point c
  : ternary α and β phases become indistinguishable.

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

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

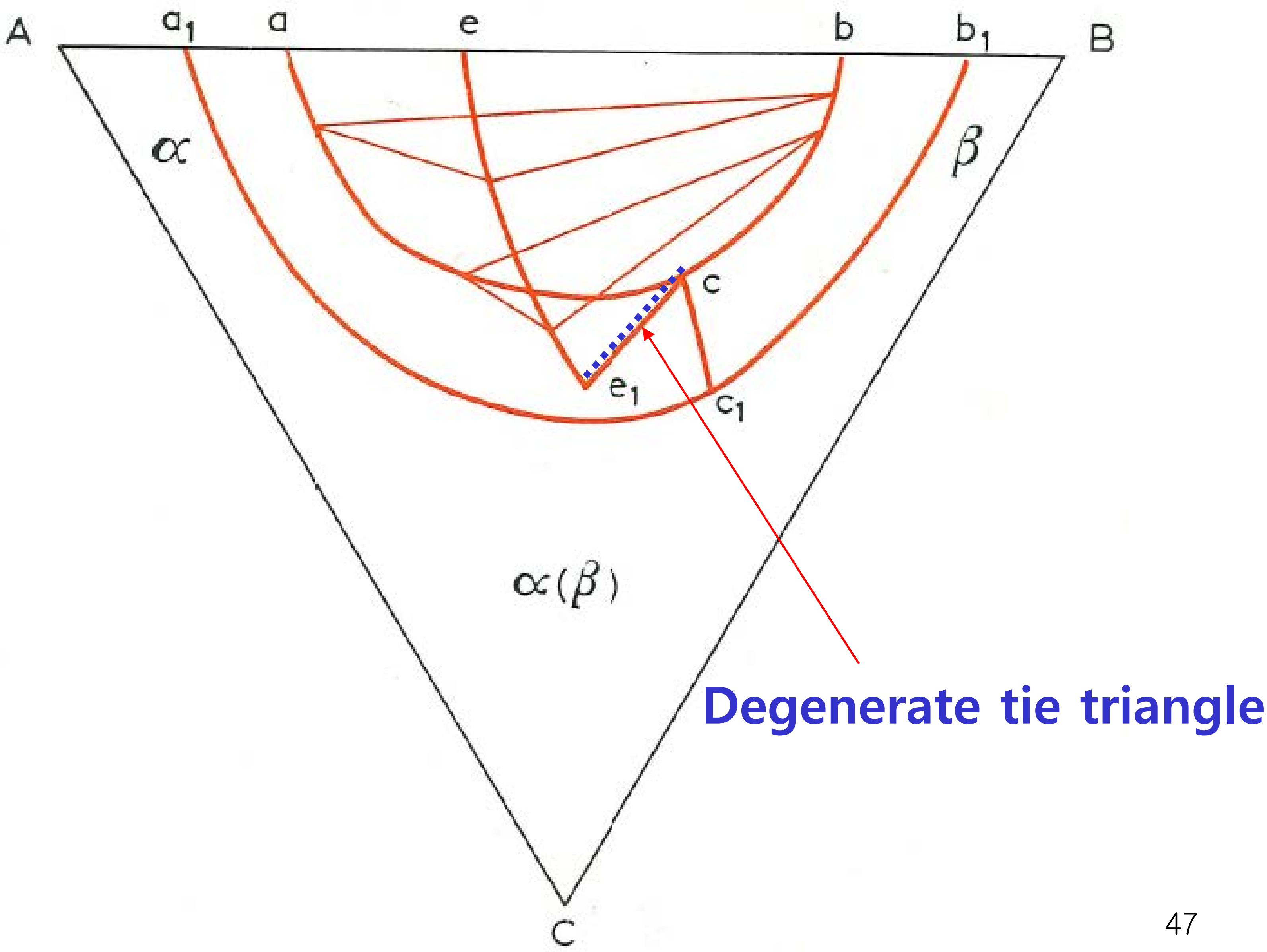
- Three phase region will start
  at binary eutectic temp.

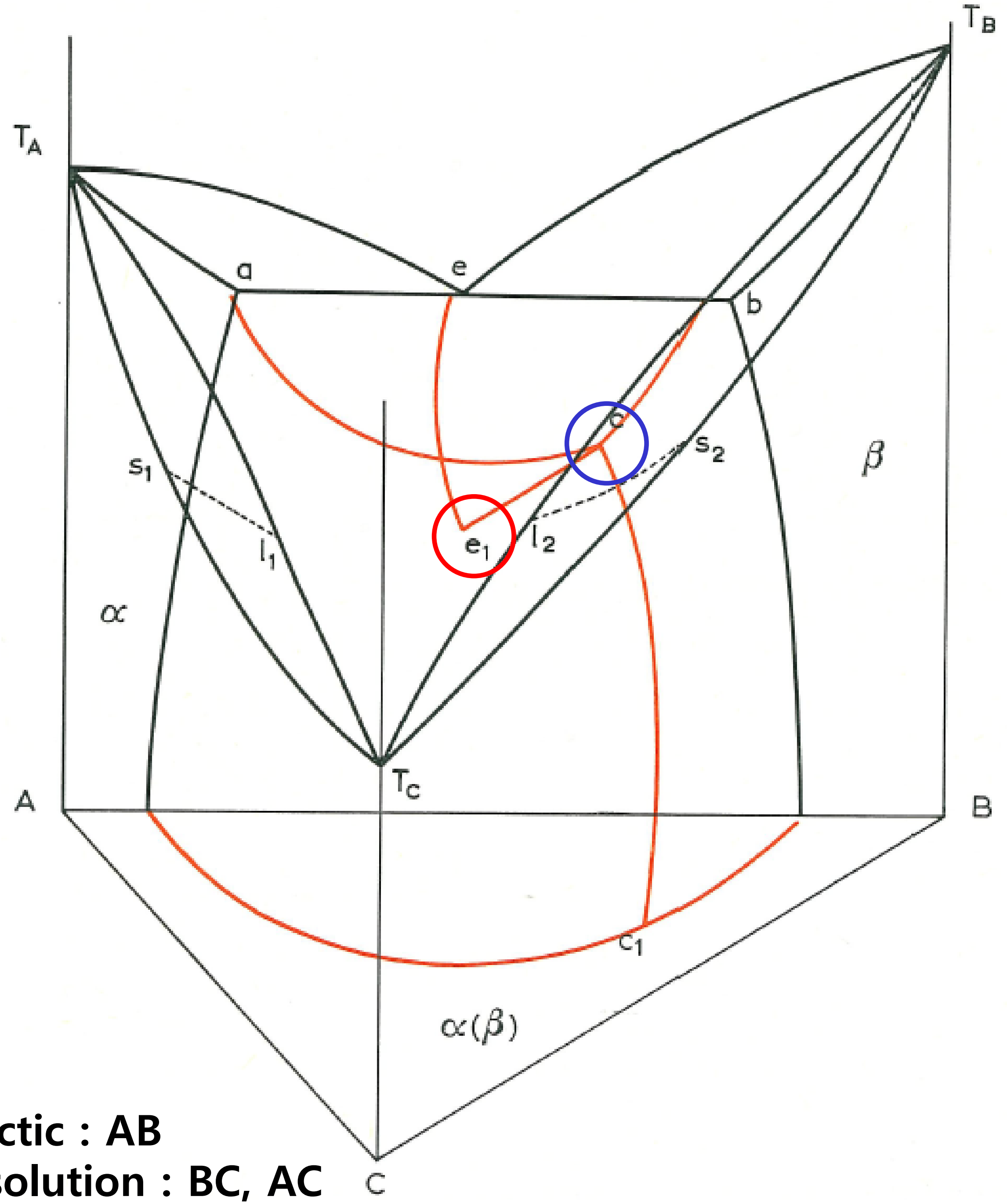
- Three phase region will end at e_1c temp.



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

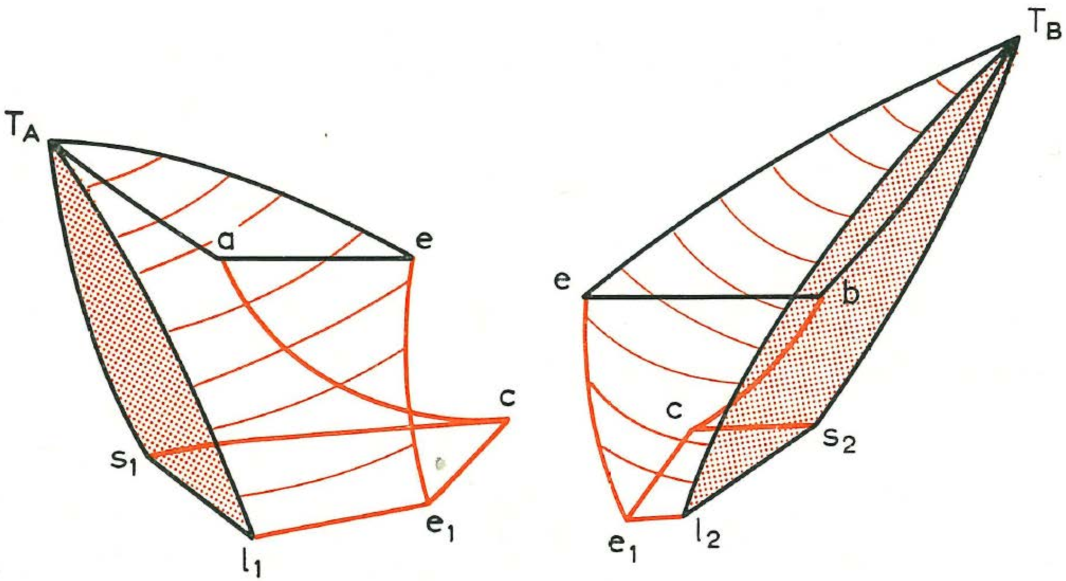
• **Projection on concentration triangle ABC**

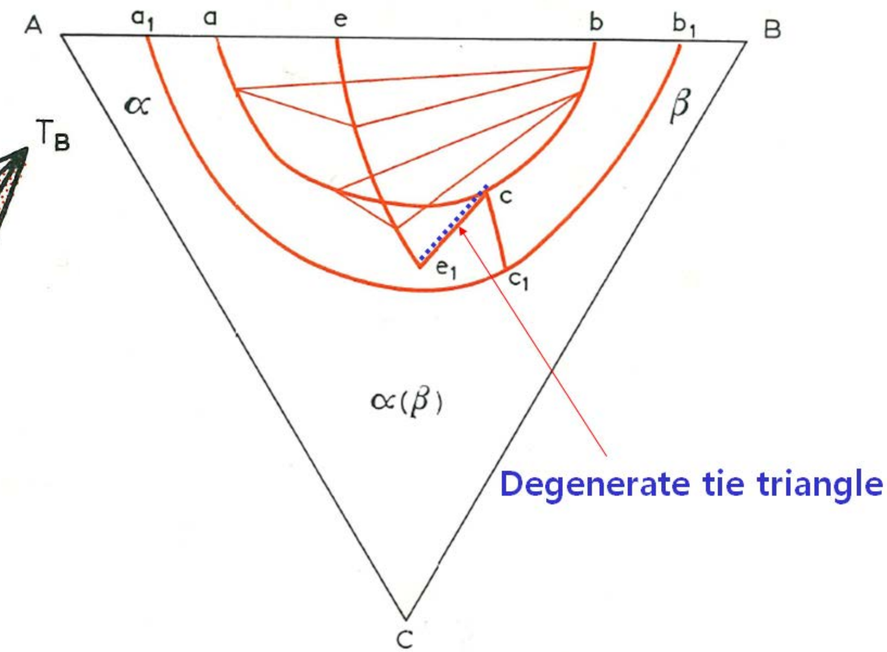


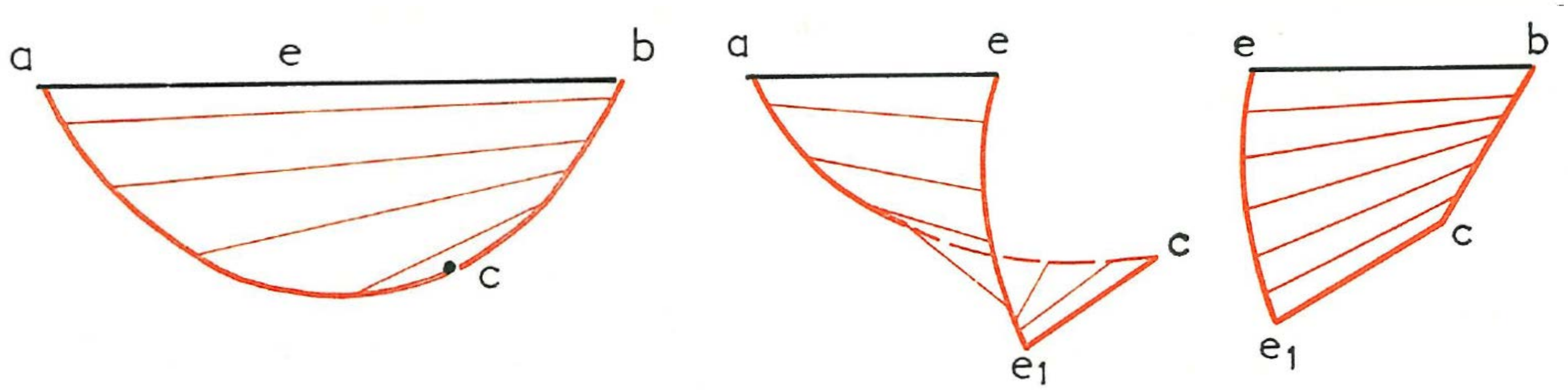


- **One binary eutectic : AB**
  Complete solid solution : BC, AC

The three-phase regions





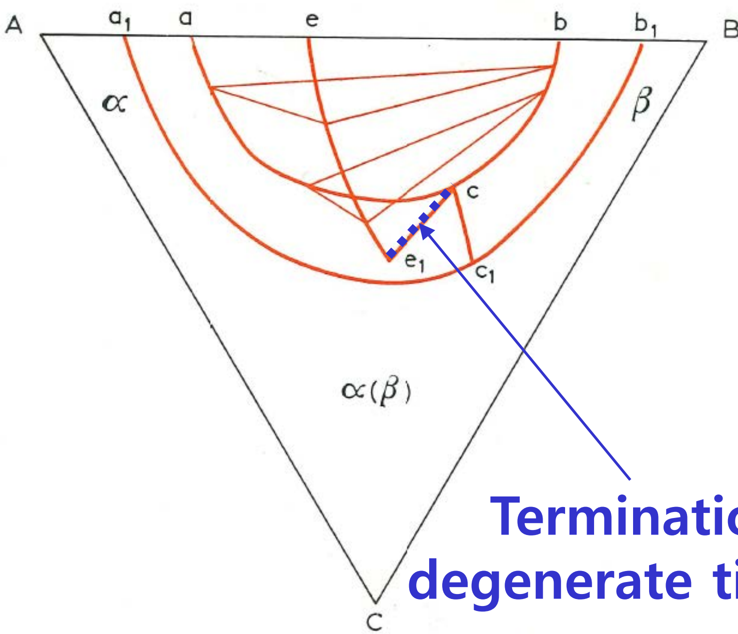


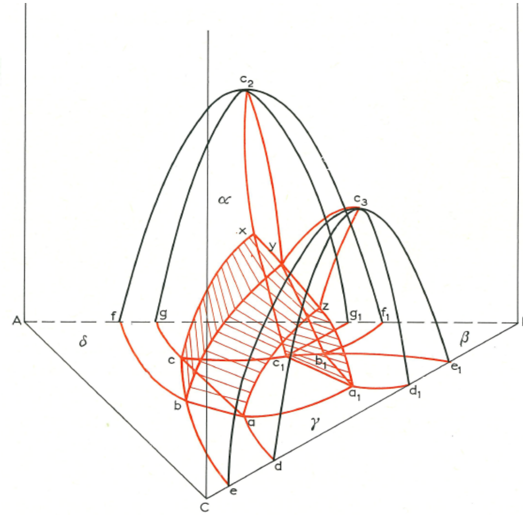
(a) (b) (c)

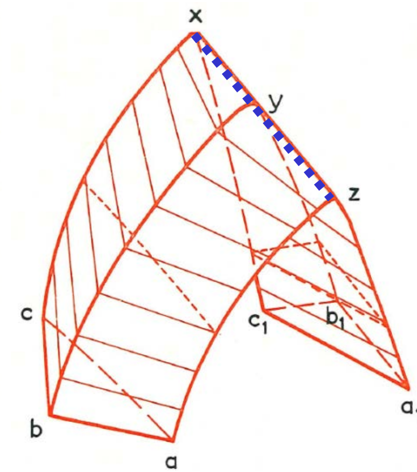
Fig. 147. The ruled surfaces bounding the three-phase ($l+\alpha+\beta$) region in Fig. 142. (a) The $\alpha\beta$ ruled surface; (b) the $l\alpha$ ruled surface; (c) the $l\beta$ ruled surface.

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

(a)



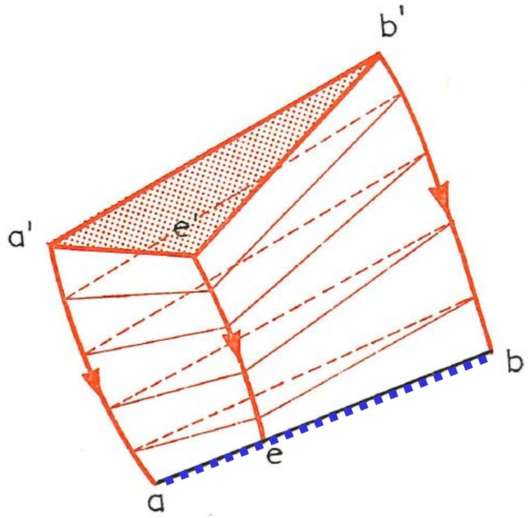


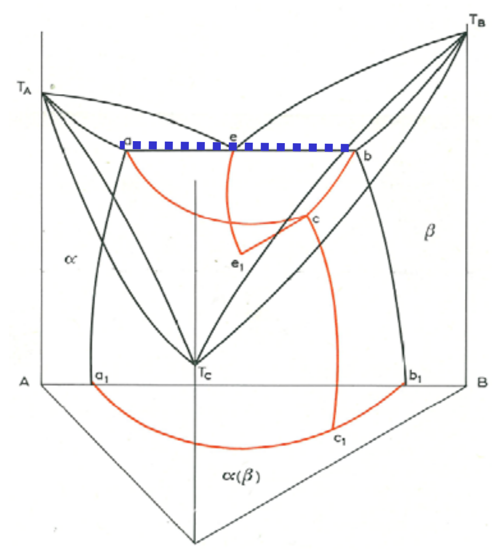


Termination at a degenerate tie triangle

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

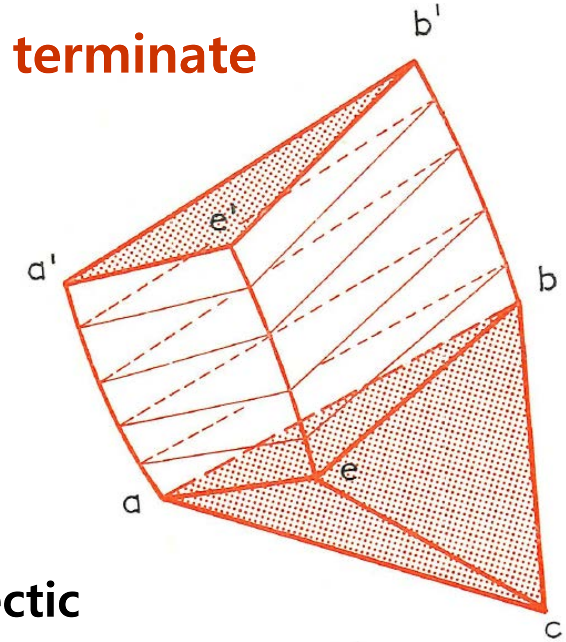
(b) Termination at a reaction isotherm



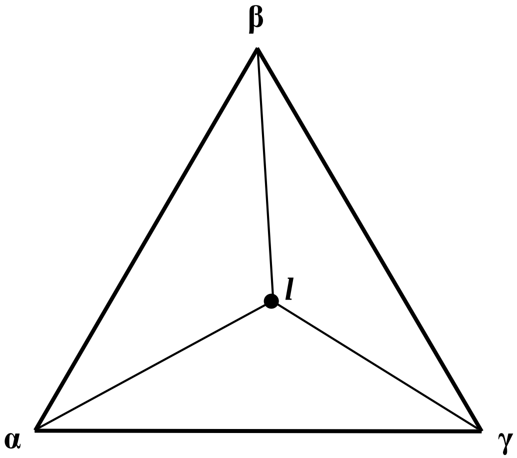


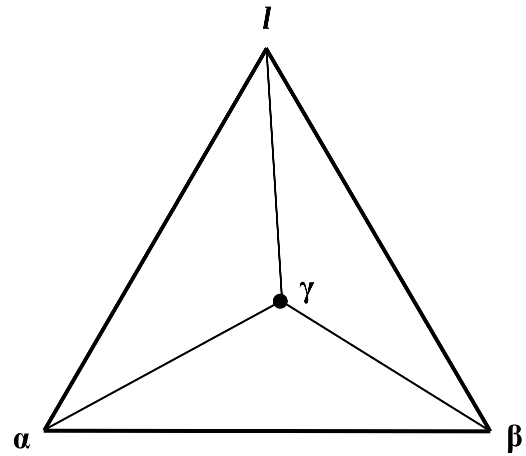
The ways in which three phase regions terminate in ternary systems:

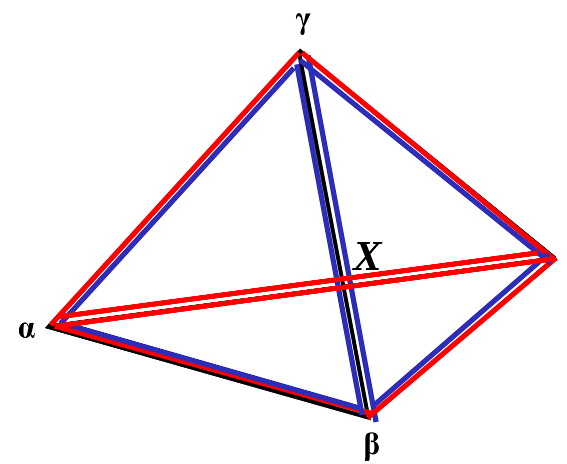
(c) Termination at a four-phase plane



Ternary eutectic	Ternary peritectic	
$L \rightarrow \alpha + \beta + \gamma$	$L + \alpha + \beta \rightarrow \gamma$	$L + \alpha \rightarrow \beta + \gamma$







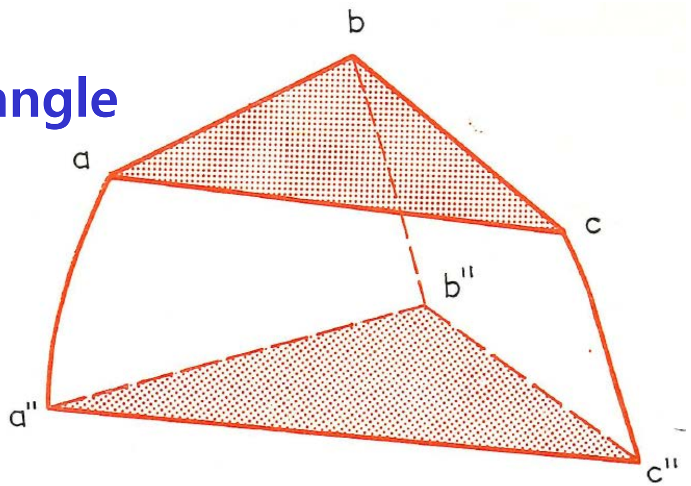
$\alpha\beta l$ & $\alpha\gamma l$ & $\beta\gamma l \rightarrow \alpha\beta\gamma l \rightarrow \alpha\beta\gamma$

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

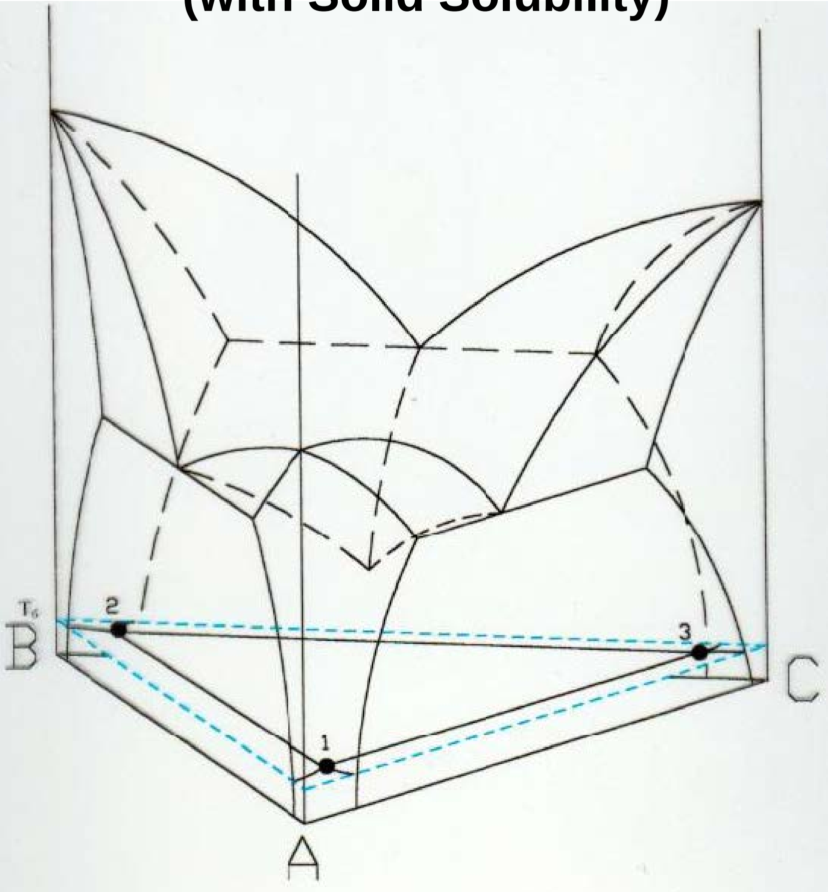
$$\frac{m_\alpha}{m_l} = \frac{Xl}{\alpha X} \quad \text{and} \quad \frac{m_\beta}{m_\gamma} = \frac{\gamma X}{X\beta}$$

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

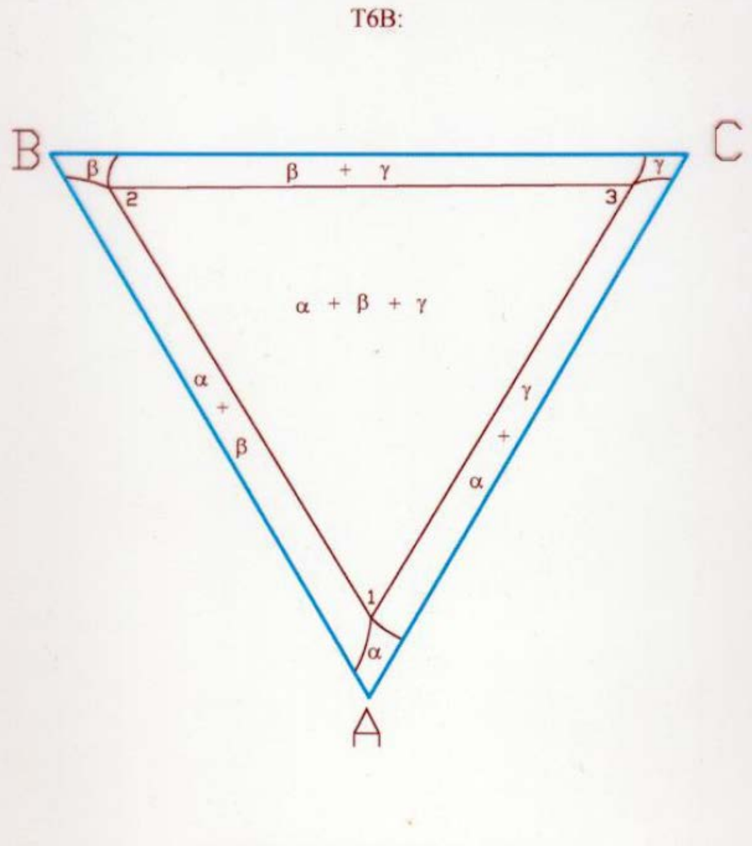
(d) Termination on the concentration triangle



Ternary Eutectic System
(with Solid Solubility)



Temperature Slice at $T_6 < T_E$



Isothermal Section At $T=T_6$