2019 Spring

"Phase Equilibria *in* Materials"

04.15.2019

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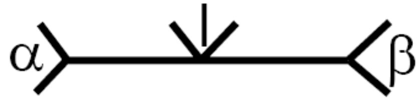
Review of Invariant Binary Reactions

Eutectic Type

Eutectic

$l \rightleftarrows \alpha + \beta$



Al-Si, Fe-C

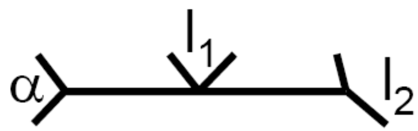
Eutectoid

$\gamma \rightleftarrows \alpha + \beta$

Fe-C

Monotectic

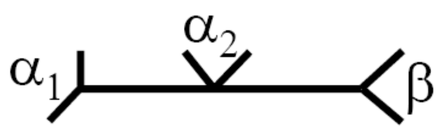
$l_1 \rightleftarrows \alpha + l_2$



Cu-Pb

Monotectoid

$\alpha_2 \rightleftarrows \alpha_1 + \beta$



Al-Zn, Ti-V

On cooling one phase going to two phases

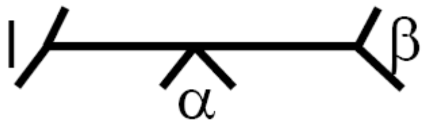
Metatectic reaction: $\beta \leftrightarrow L + \alpha$ **Ex. Co-Os, Co-Re, Co-Ru**

Review of Invariant Binary Reactions

Peritectic Type

Peritectic

$l + \beta \rightleftarrows \alpha$



Fe-C

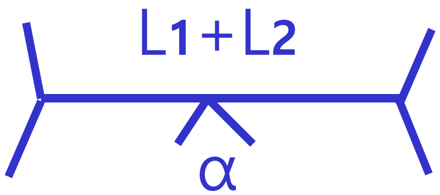
Peritectoid

$\alpha + \beta \rightleftarrows \gamma$

Cu-Al

Syntectic reaction

$Liquid_1 + Liquid_2 \leftrightarrow \alpha$



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

On cooling two phases going to one phase

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) $l_1 \rightleftharpoons l_2$, $l \rightleftharpoons \alpha$, and $\alpha \rightleftharpoons \beta$.

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

$\alpha \rightleftharpoons \beta + \gamma$, $l_1 \rightleftharpoons l_2 + l_3$, $\alpha + \beta \rightleftharpoons \gamma$, $l_1 + l_2 \rightleftharpoons \alpha$,

$\alpha \rightleftharpoons \beta + l$, $l_1 \rightleftharpoons \alpha + l_2$, $\alpha + \beta \rightleftharpoons l$, $l_1 + \alpha \rightleftharpoons l_2$,

$\alpha \rightleftharpoons l_1 + l_2$, $l \rightleftharpoons \alpha + \beta$, $l_1 + l_2 \rightleftharpoons l_3$, $l + \alpha \rightleftharpoons \beta$.

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

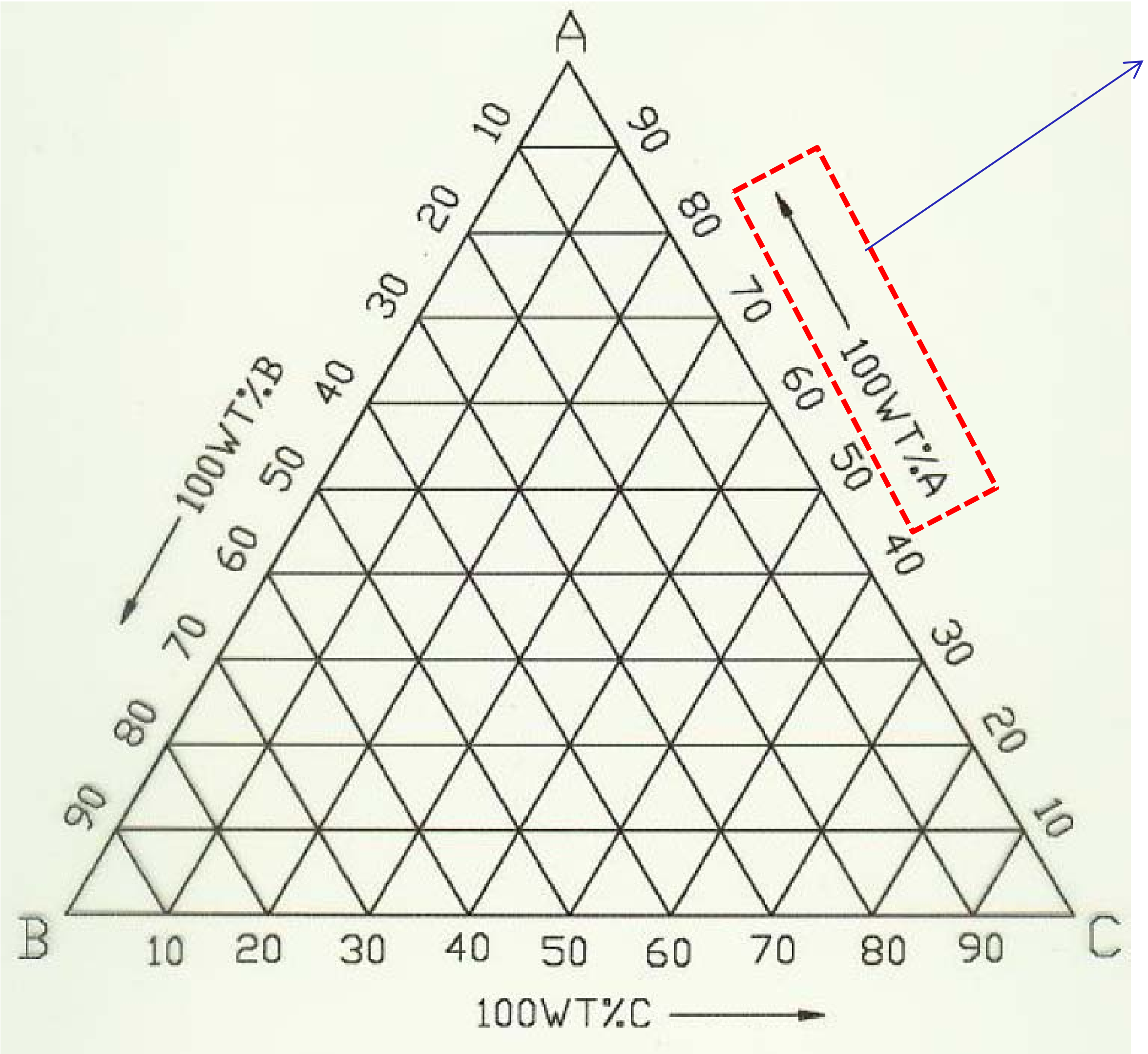
$\alpha \rightleftharpoons \beta + \gamma + \delta$, $l_1 \rightleftharpoons l_2 + l_3 + l_4$, $l \rightleftharpoons \alpha + \beta + \gamma$, $l_1 \rightleftharpoons l_2 + \alpha + \beta$, $l_1 \rightleftharpoons l_2 + l_3 + \alpha$, $\alpha \rightleftharpoons l_1 + l_2 + l_3$, $\alpha \rightleftharpoons \beta + l_1 + l_2$, $\alpha \rightleftharpoons \beta + \gamma + l$,

$\alpha + \beta \rightleftharpoons \gamma + \delta$, $l_1 + l_2 \rightleftharpoons l_3 + l_4$, $l + \alpha \rightleftharpoons \beta + \gamma$, $l_1 + l_2 \rightleftharpoons \alpha + \beta$, $l_1 + l_2 \rightleftharpoons l_3 + \alpha$, $\alpha + l_1 \rightleftharpoons l_2 + l_3$, $\alpha + \beta \rightleftharpoons l_1 + l_2$, $\alpha + \beta \rightleftharpoons \gamma + l$, $l_1 + \alpha \rightleftharpoons l_2 + \beta$.

$\alpha + \beta + \gamma \rightleftharpoons \delta$, $l_1 + l_2 + l_3 \rightleftharpoons l_4$, $l + \alpha + \beta \rightleftharpoons \gamma$, $l_1 + l_2 + \alpha \rightleftharpoons \beta$, $l_1 + l_2 + l_3 \rightleftharpoons \alpha$, $\alpha + l_1 + l_2 \rightleftharpoons l_3$, $\alpha + \beta + l_1 \rightleftharpoons l_2$, $\alpha + \beta + \gamma \rightleftharpoons l$

Gibbs Triangle

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

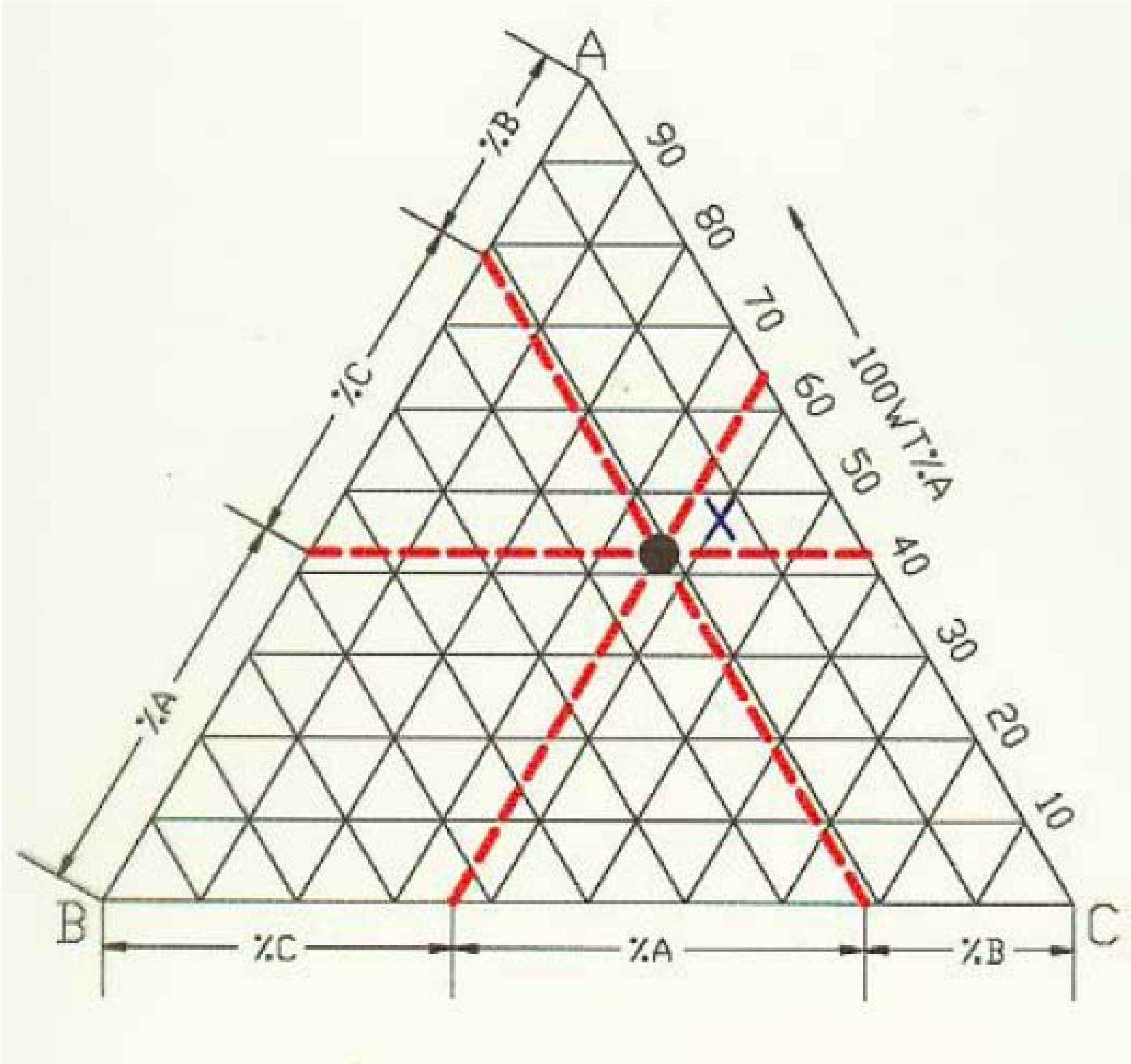


Concentration can be expressed as either "wt. %" or "at.% = molar %".

$$X_A+X_B+X_C = 1$$

Used to determine the overall composition

Overall Composition



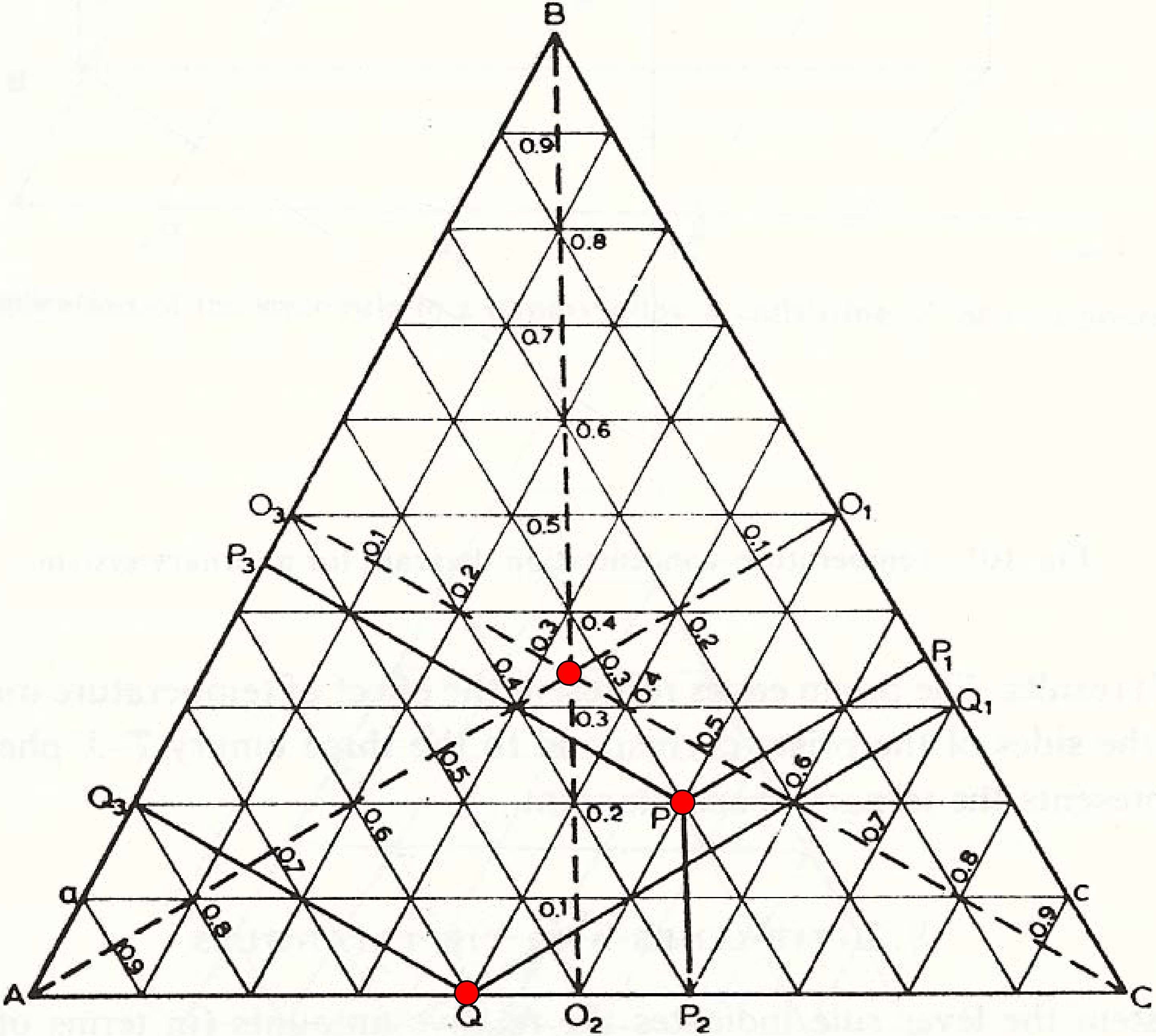
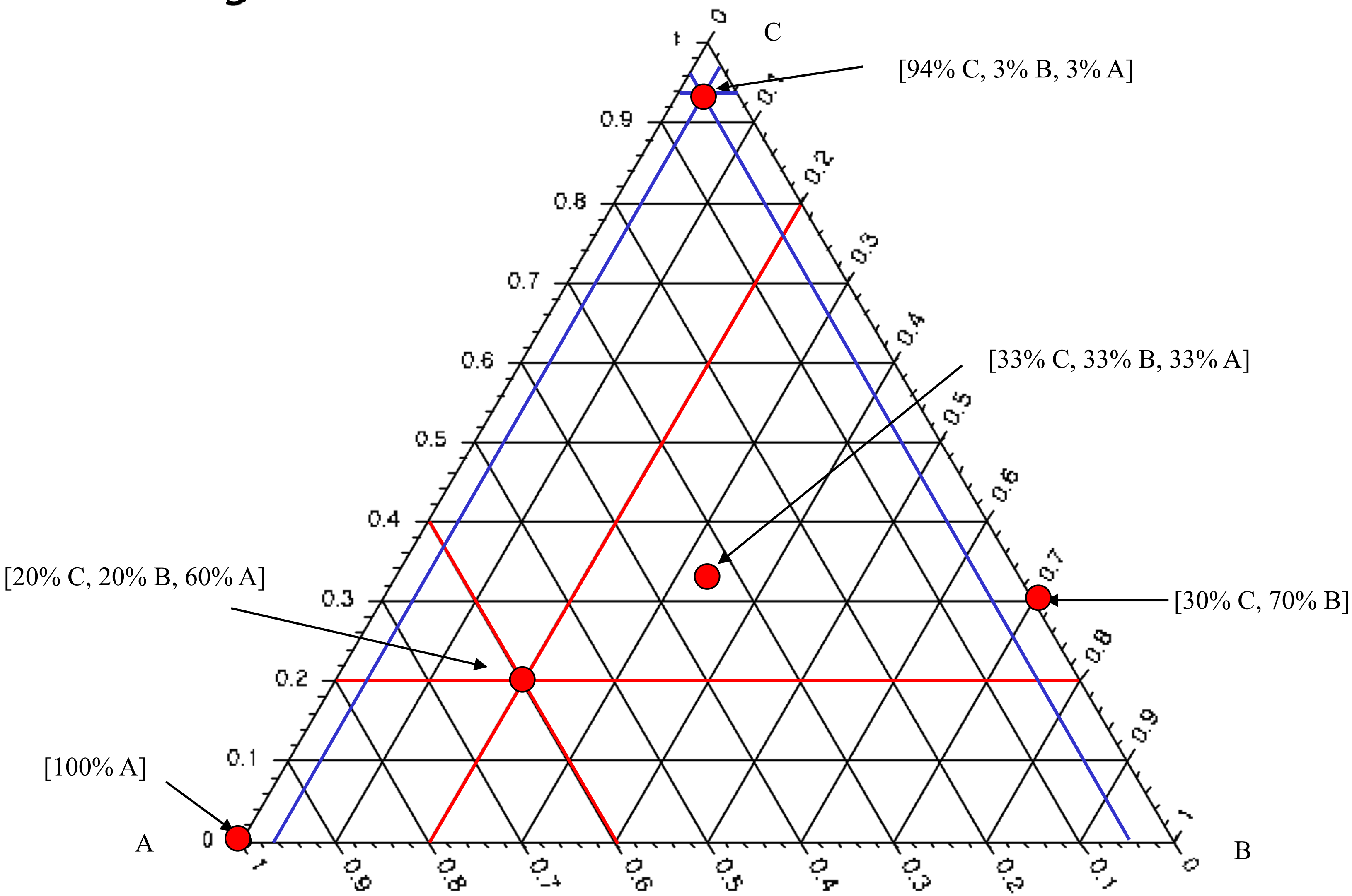


Fig. 106. Plotting of alloy compositions in ternary systems.

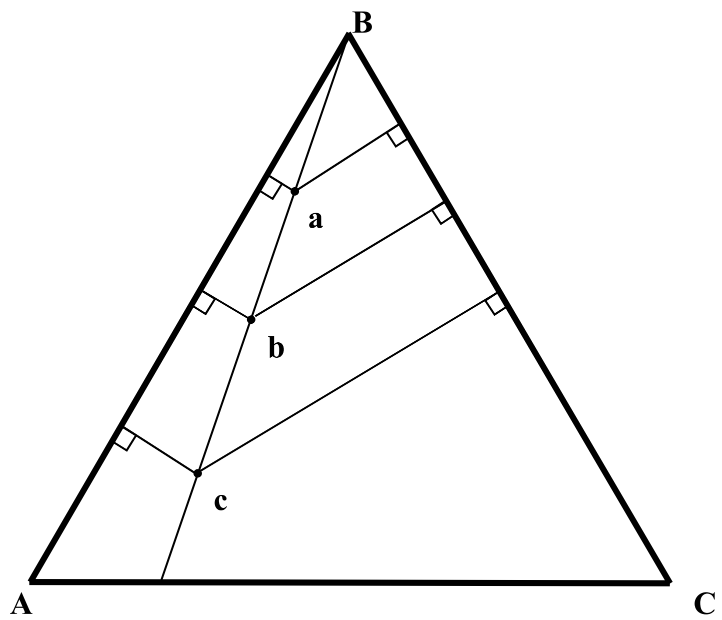
8.2 REPRESENTATION OF TERNARY SYSTEMS

Gibbs triangle



8.2 REPRESENTATION OF TERNARY SYSTEMS

Gibbs triangle



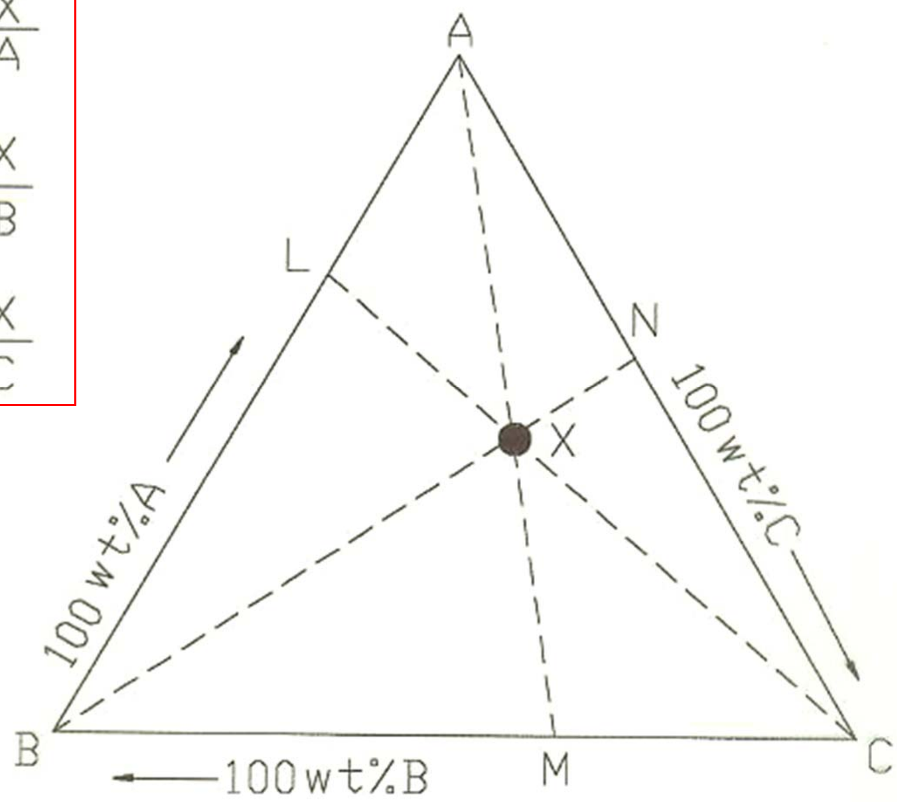
→ Ratio of X_C/X_A is same at a, b, c.

2) Overall Composition of X alloy

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

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

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

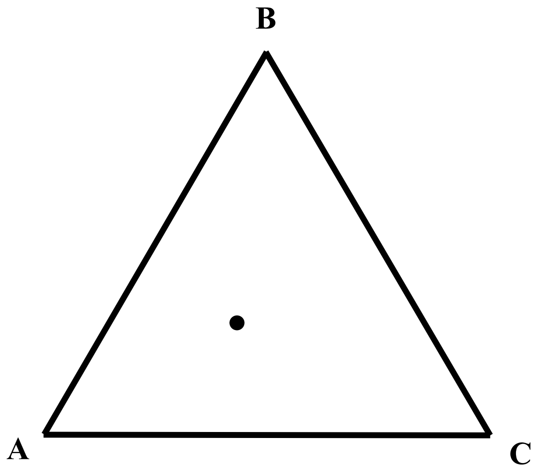


According to Triangle congruence condition

8.3 TIE LINES AND TIE TRIANGLES

Isothermal section

P=1



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

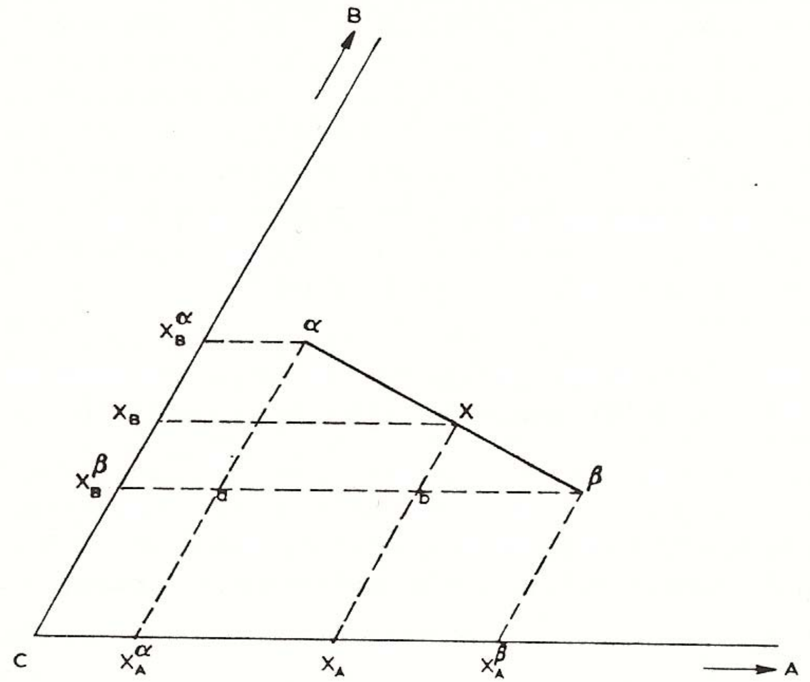
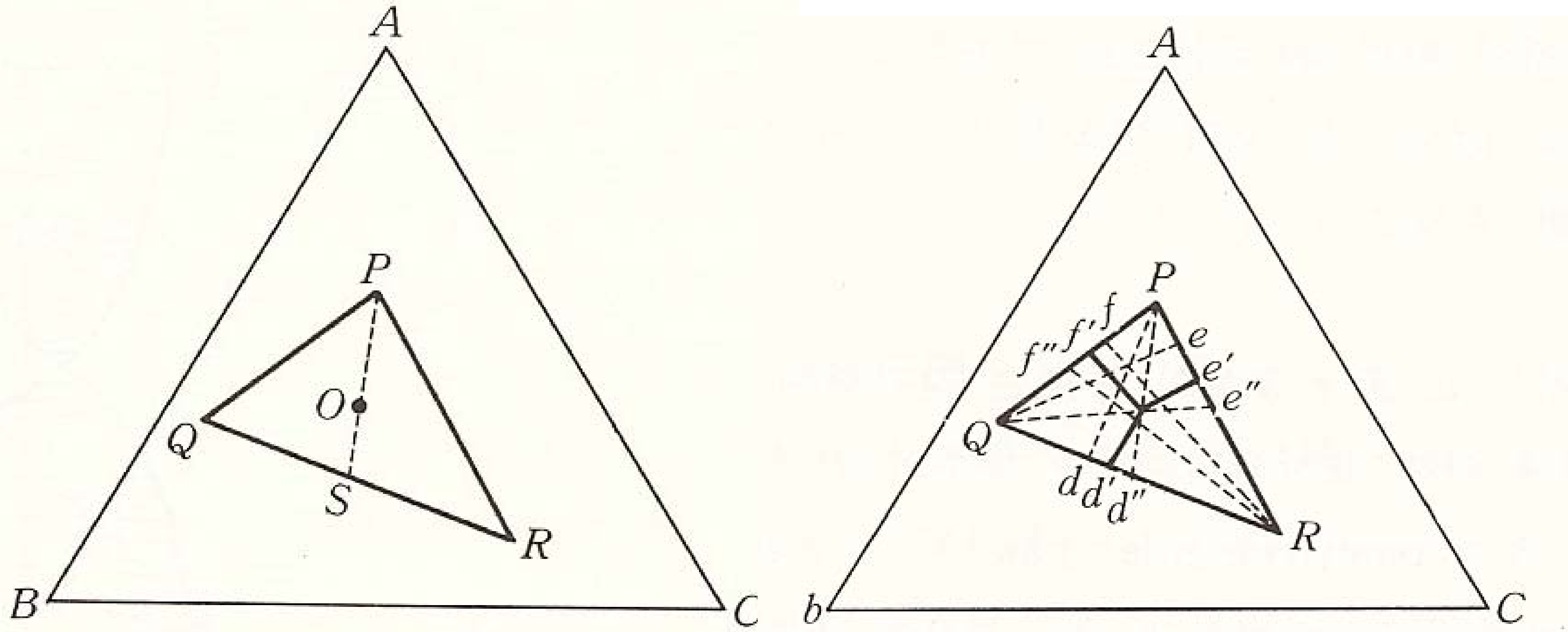


Fig. 108. Application of the lever rule to a ternary alloy *X* consisting of the two phases α and β.

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

8.3 TIE LINES AND TIE TRIANGLES

P=3 Tie triangle : 3 phase equil.

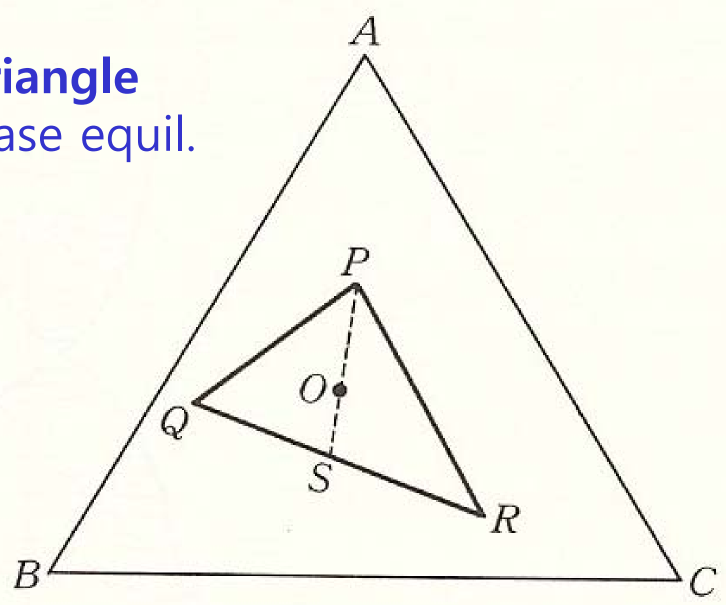


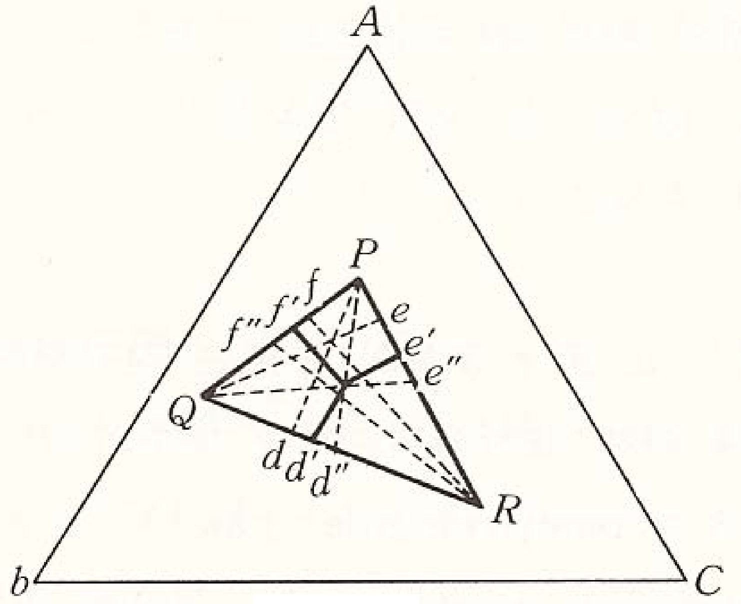
P contents: Q contents: R contents $= \frac{Od'}{Pd} : \frac{Oe'}{Qe} : \frac{Of'}{Rf}$

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

Incentive Homework 6: 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

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

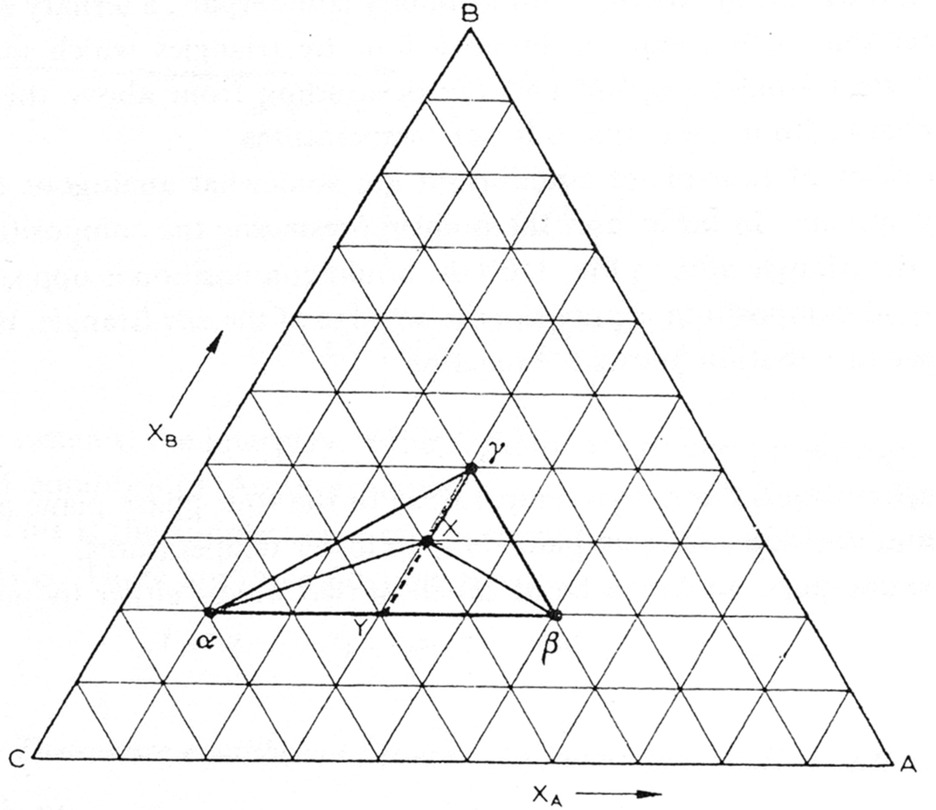
S composition = Q alloy + R alloy (tie line), Q contents and R contents in O alloy

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

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

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

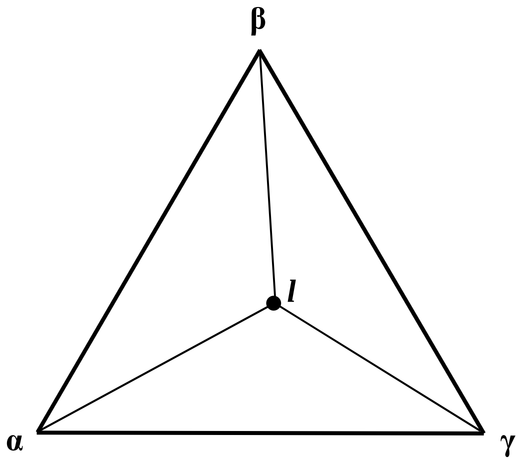
P=4

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

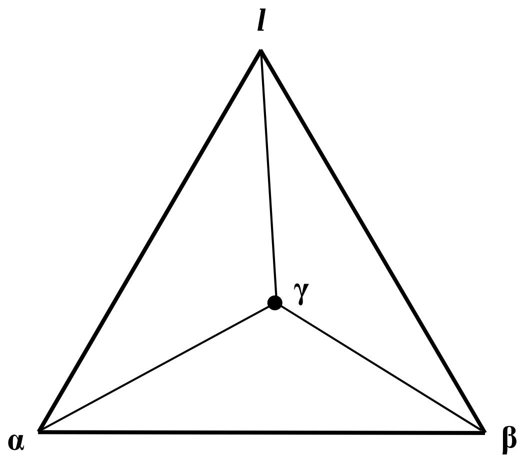
Ternary eutectic



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

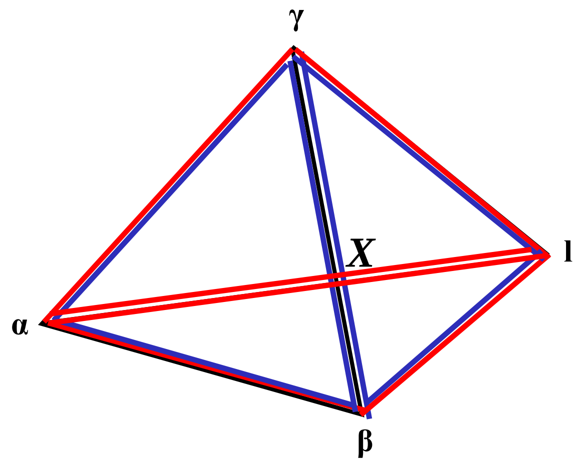
Ternary peritectic

L + α + β → γ



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

L + α → β + γ



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

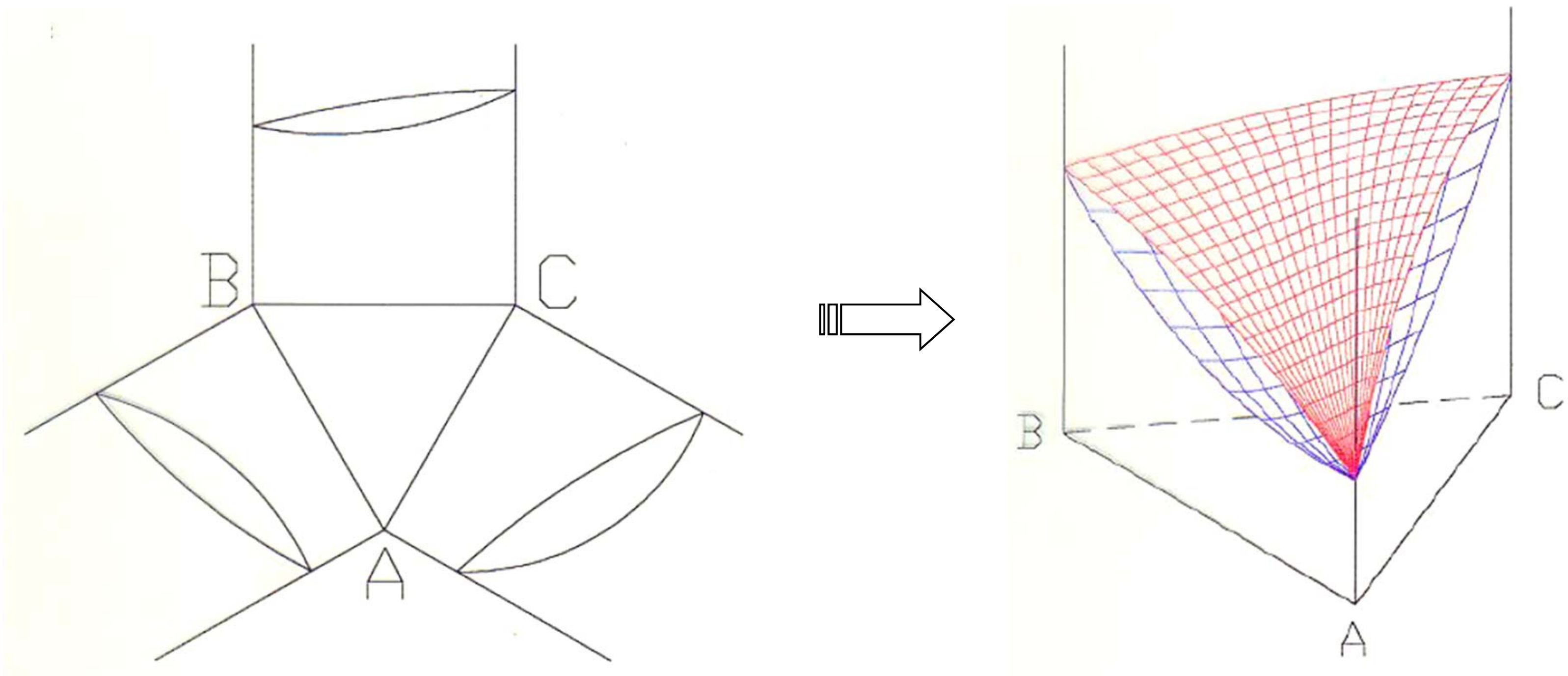
$\alpha\beta l$ & $\alpha\gamma l \rightarrow \alpha\beta\gamma l \rightarrow \alpha\beta\gamma$ & $\beta\gamma l$

8.4 TWO-PHASE EQUILIBRIUM

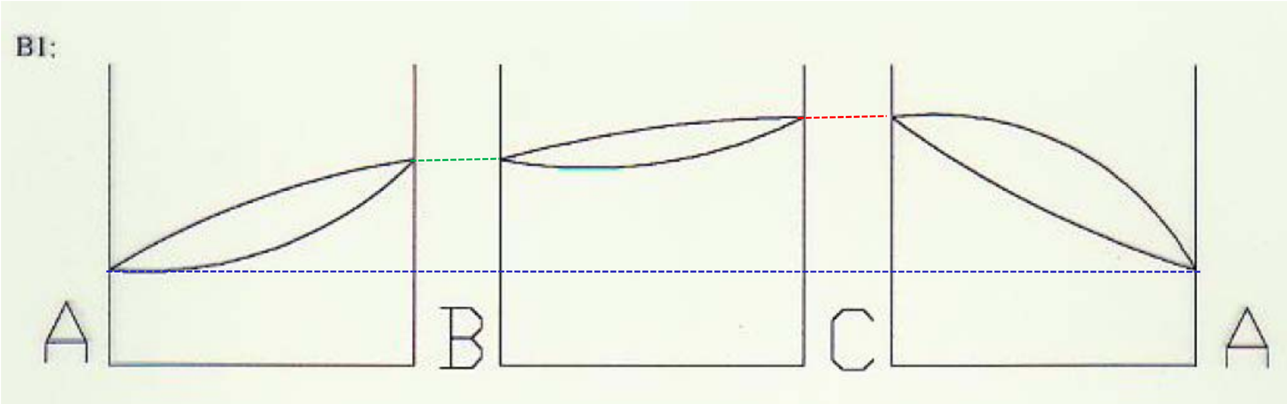
8.4.1 Two-phase equilibrium between the liquid and a solid solution

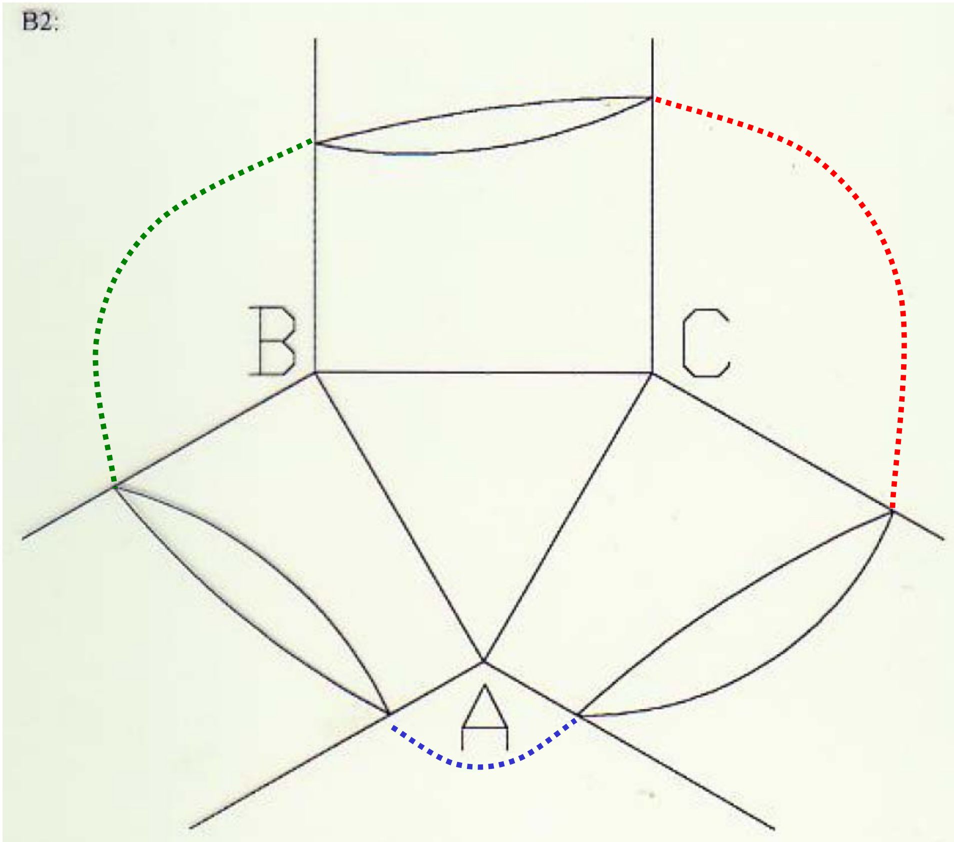
Ternary isomorphous system

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.

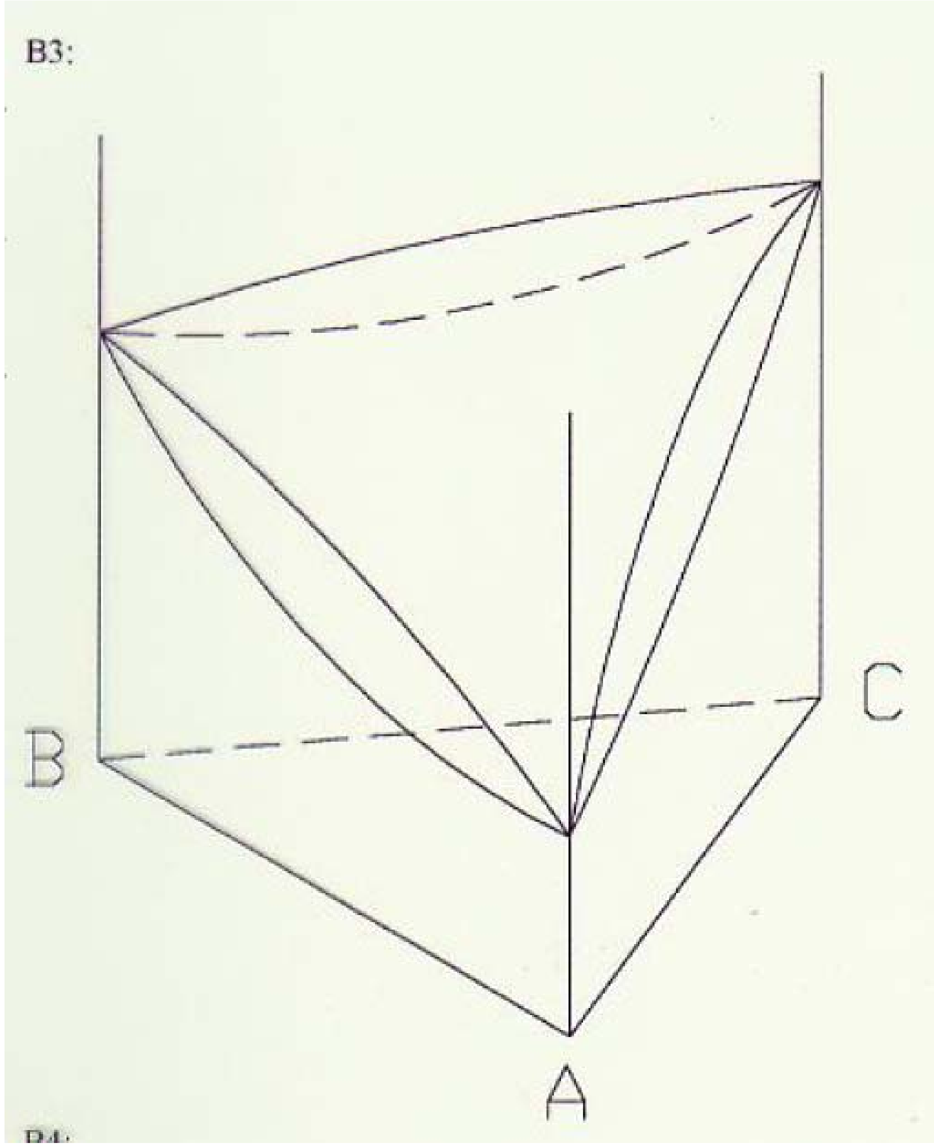


Ternary Isomorphous System

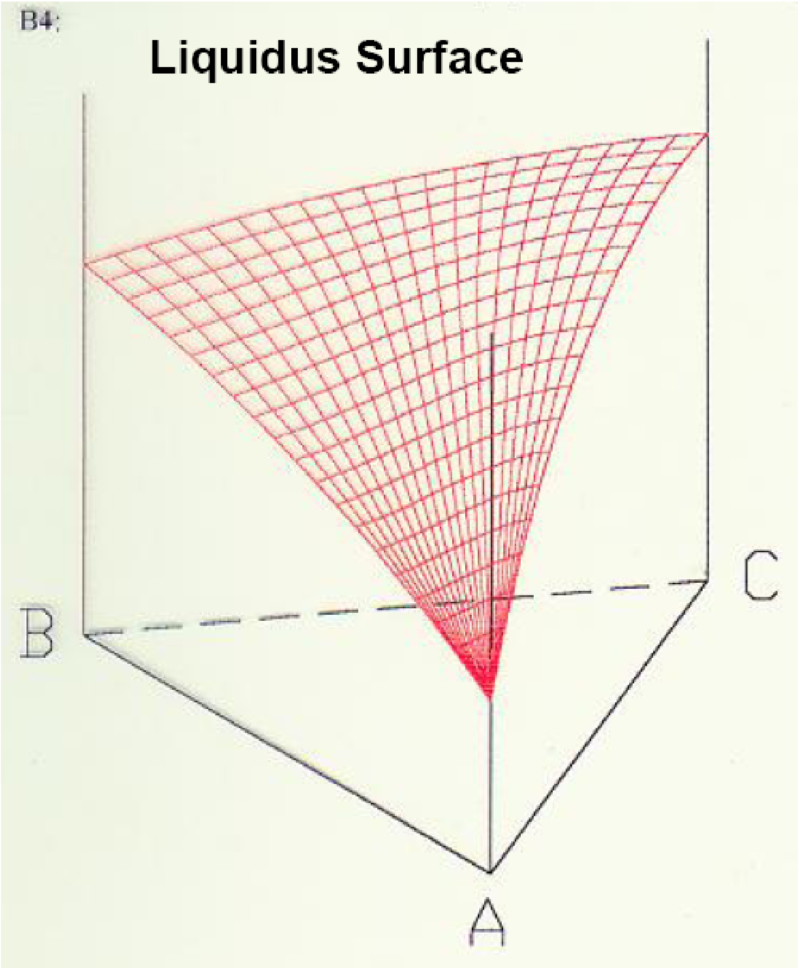




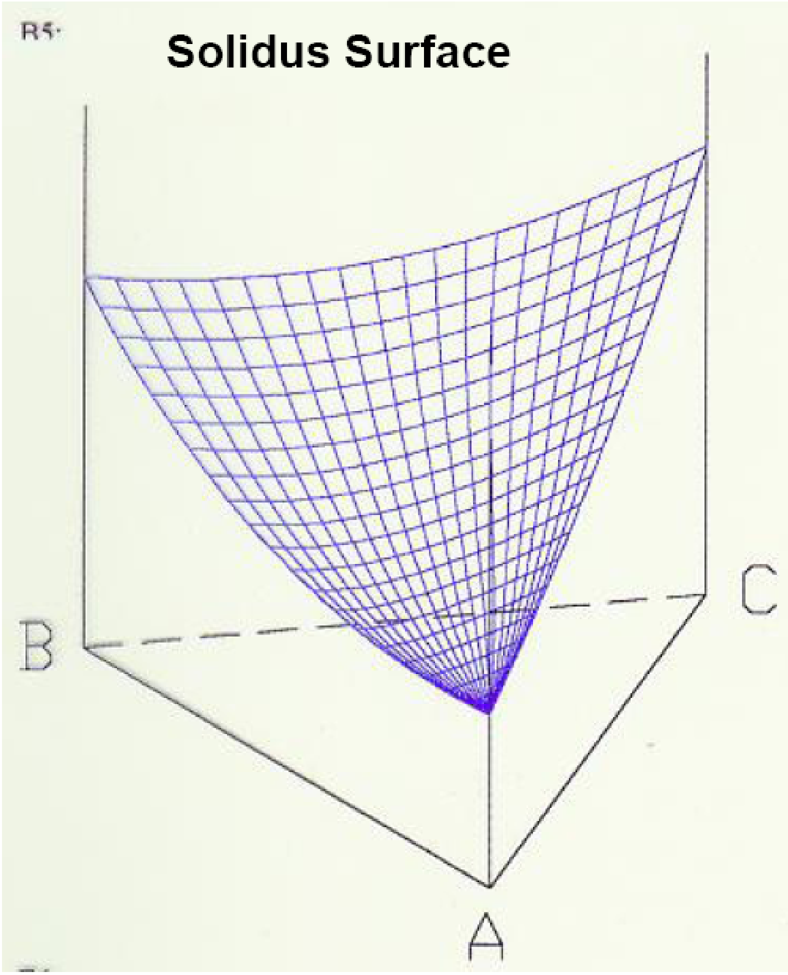
Ternary Isomorphous System



Ternary Isomorphous System

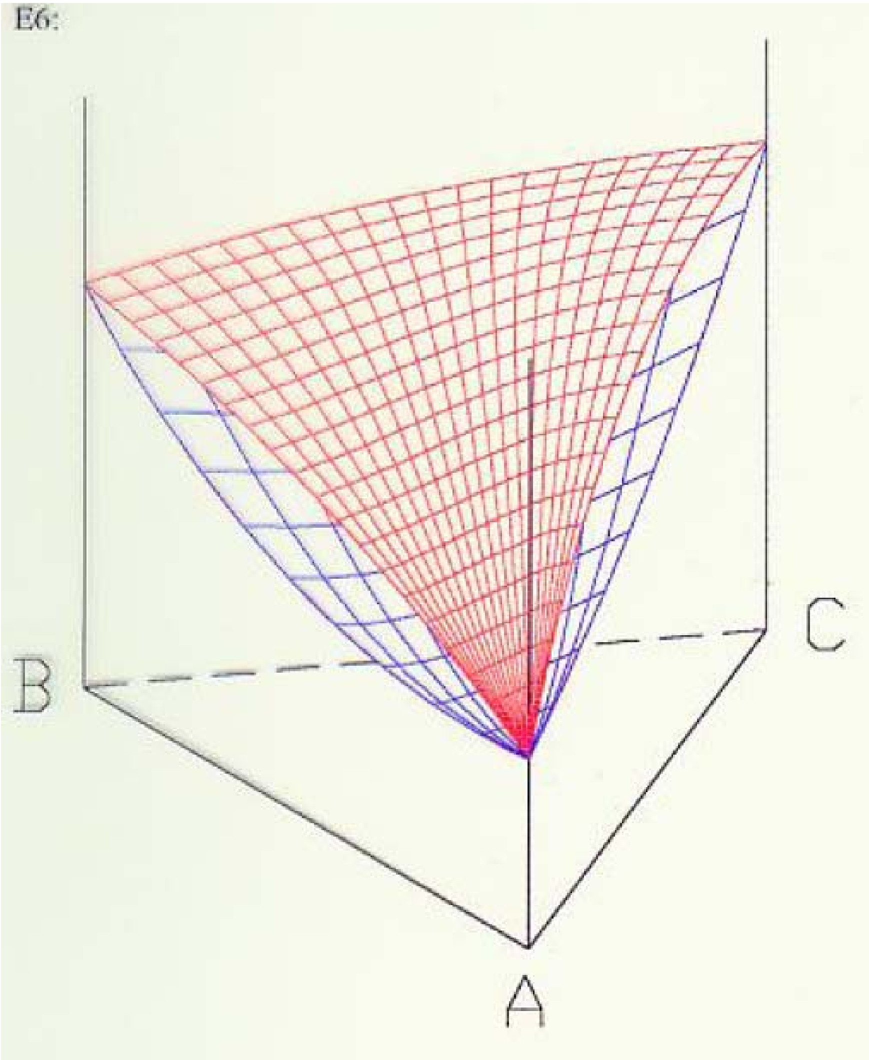


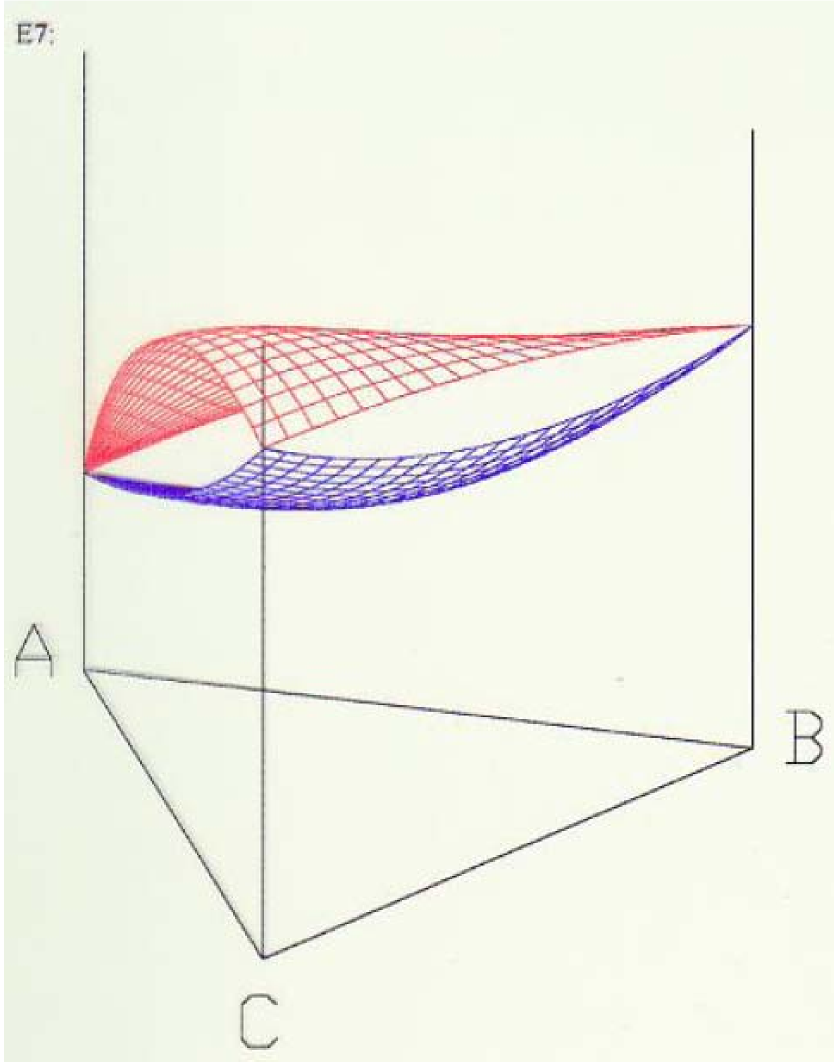
A plot of the temperatures above which a homogeneous liquid forms for any given overall composition.



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**

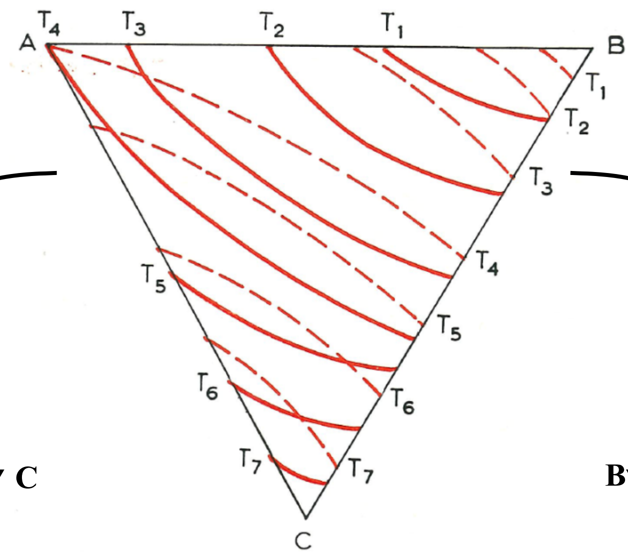
H7: find a good example & submit ppt file by email

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

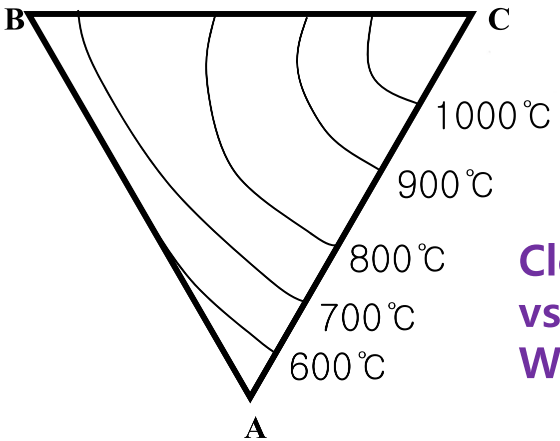


$T_1 - T_2 = T_2 - T_3 = \cdots = T_6 - T_7$

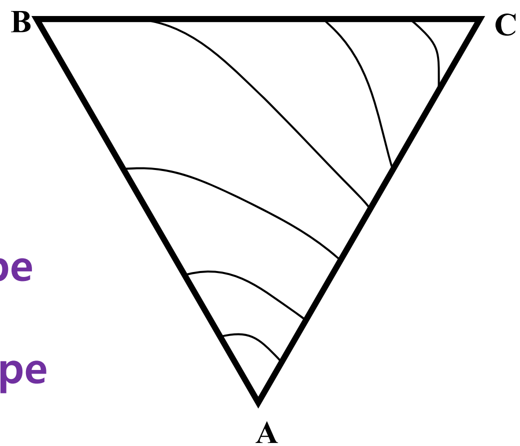
Liquidus isotherms – continuous

Solidus isotherms – dotted

Liquidus surface



Solidus surface



Close spacing → steep slope
vs
Wide spacing → gentle slope

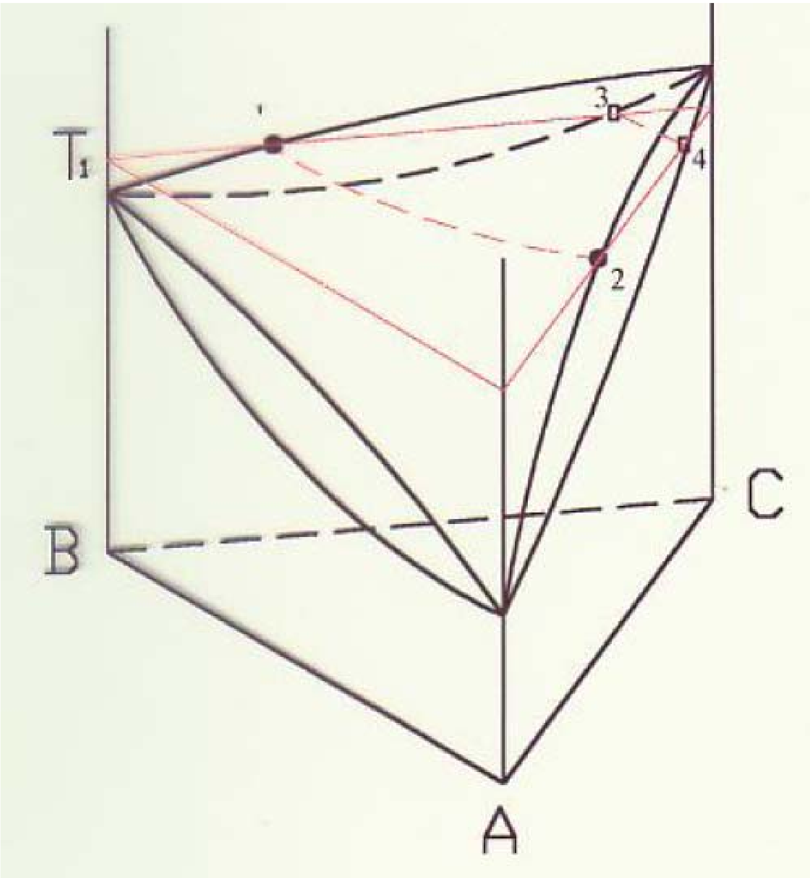
Projections of the liquidus surface are often useful in conveying a clear impression of the <u>shape of the surface</u> and indicating, by <u>folds and valleys, the presence of ternary invariant reactions</u>.

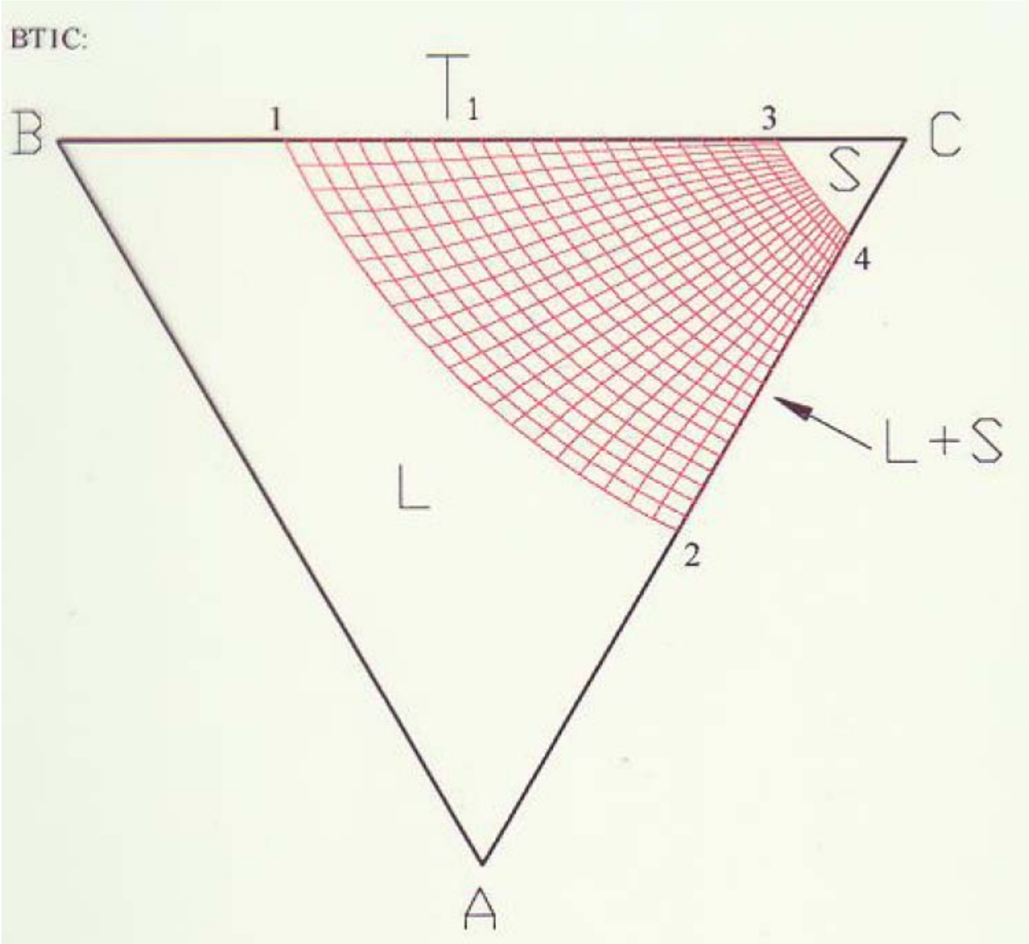
8.4 TWO-PHASE EQUILIBRIUM

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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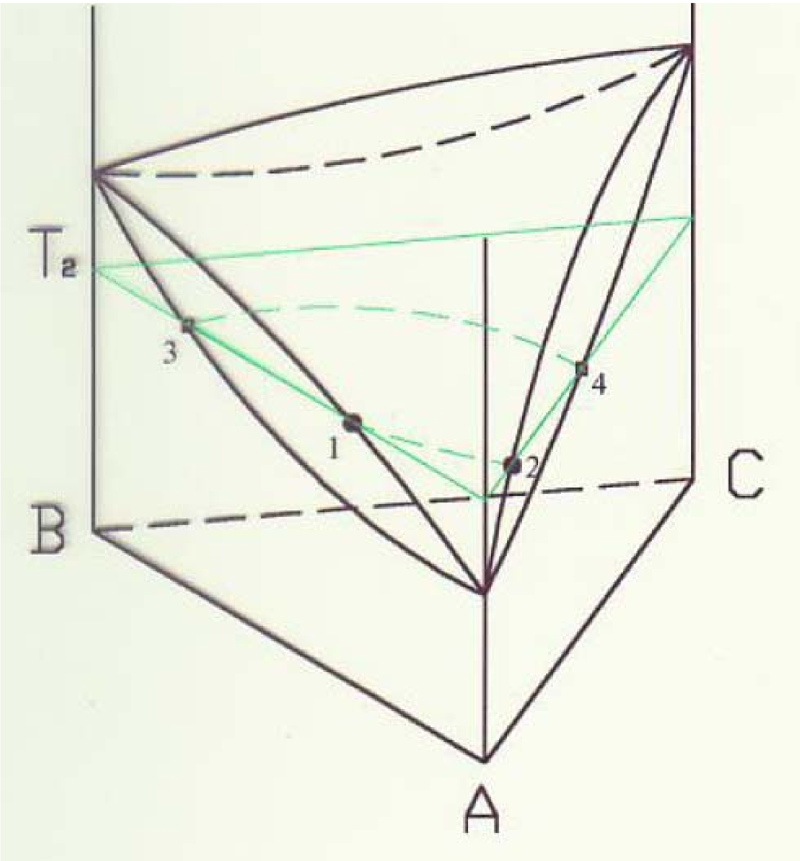
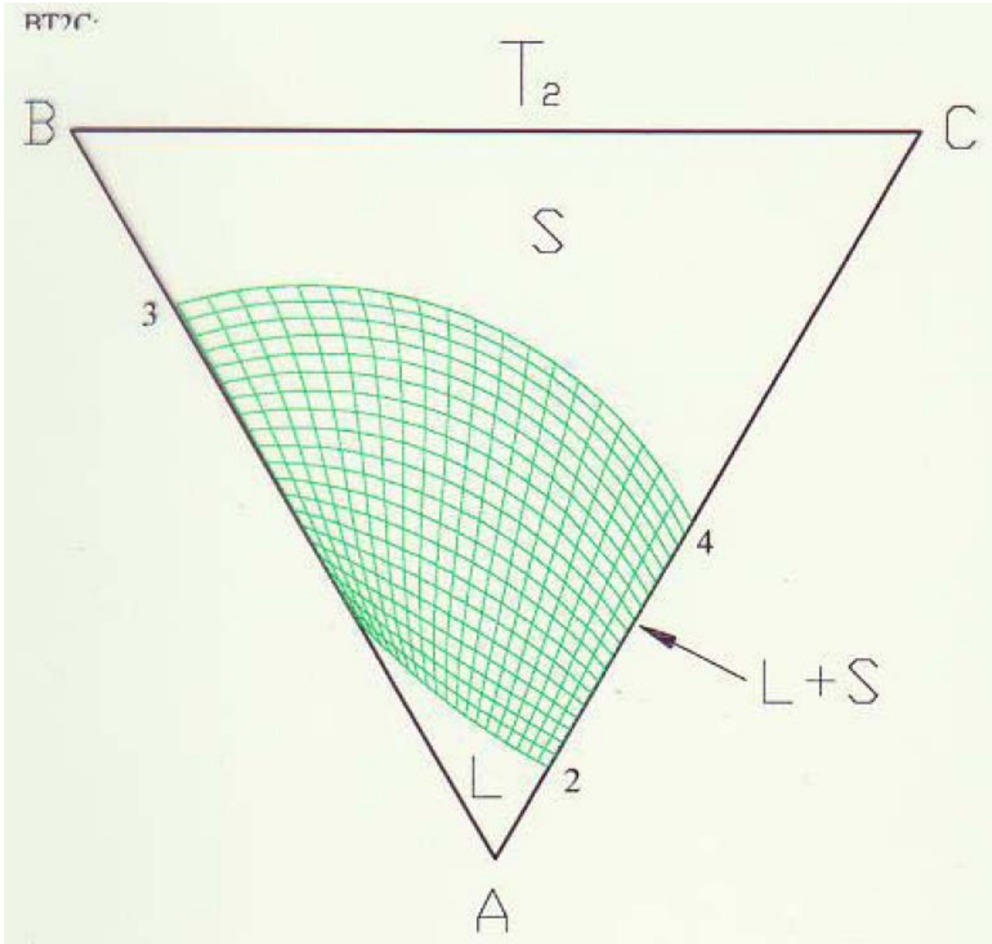
Ternary Isomorphous System





Ternary Isomorphous System

Isothermal section → F = C - P

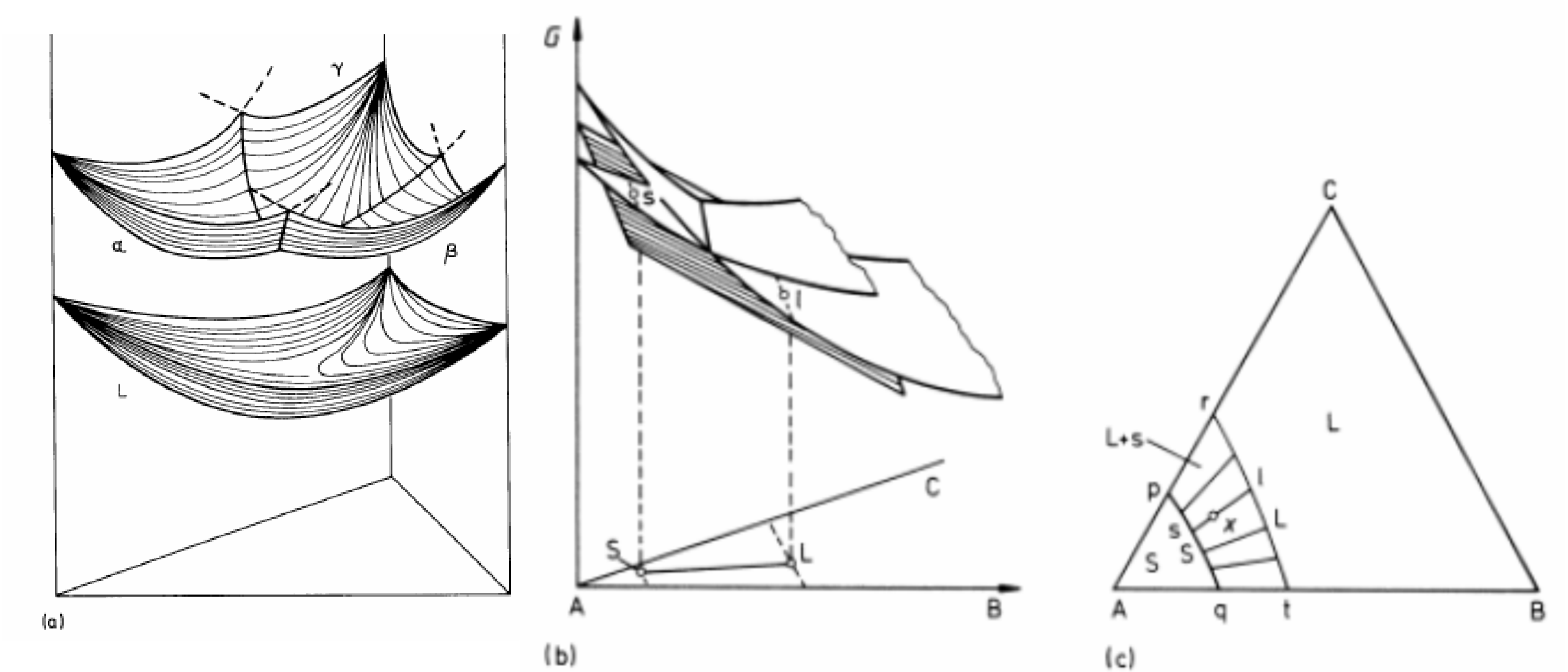
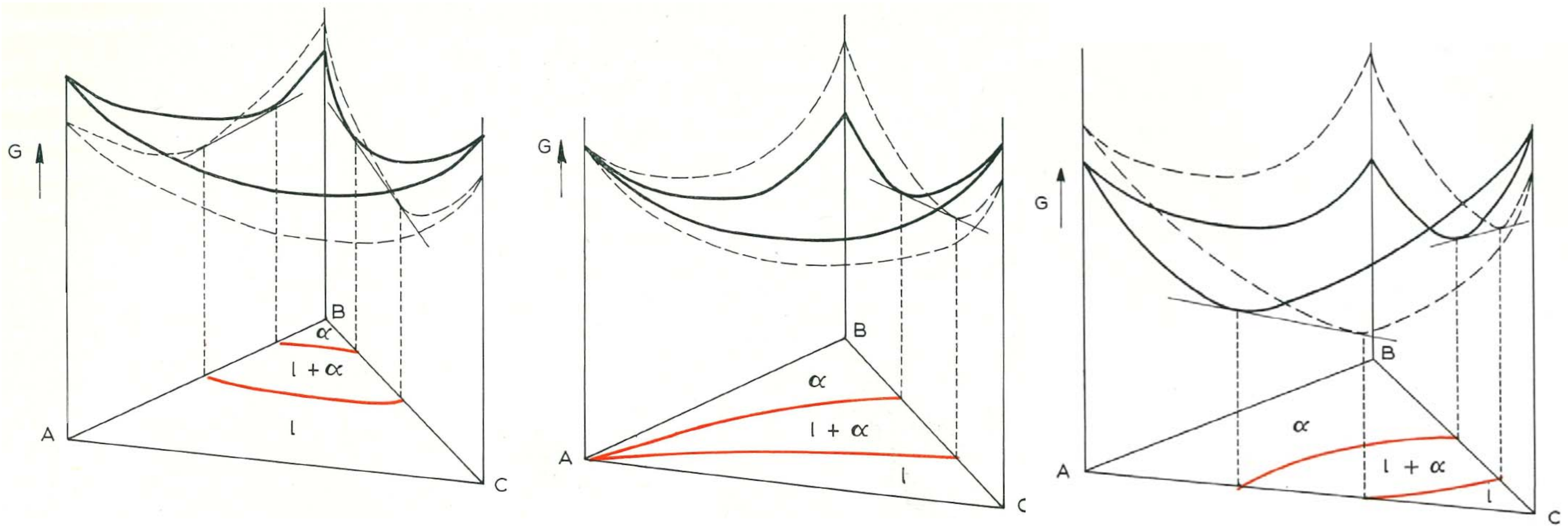


Fig. 1.41 (a) Free energies of a liquid and three solid phases of a ternary system.

Ternary Isomorphous System

Isothermal section → F = C - P



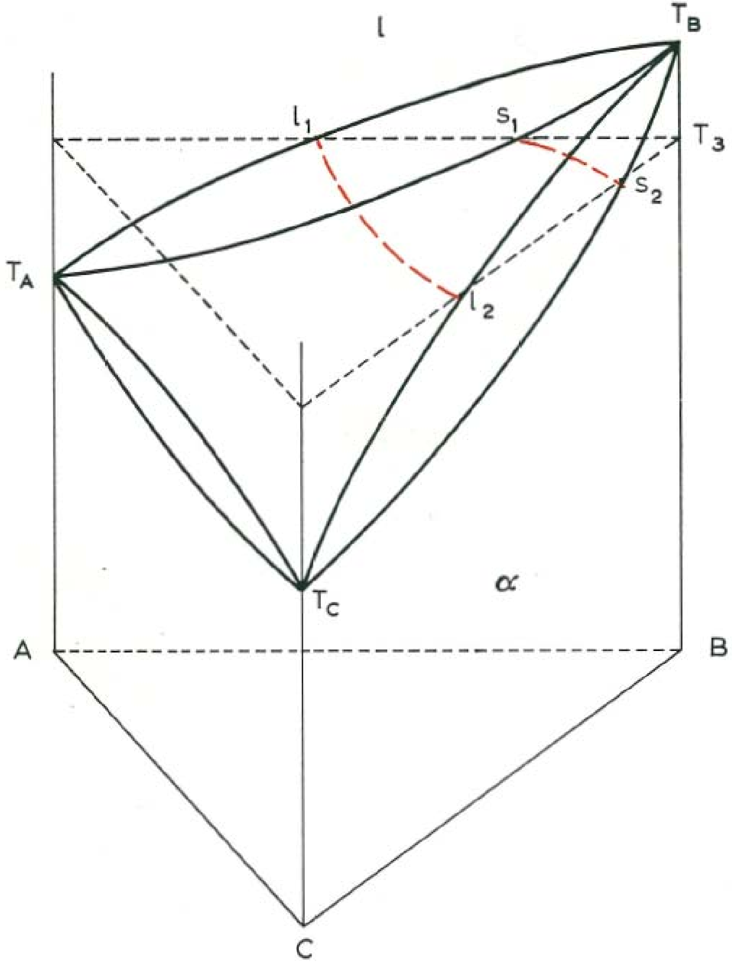
124. Illustration of the equilibria in Fig. 111 by means of free energy surfaces for the liquid and α phases at various temperatures, (a) between T_B and T_A, (b) at T_A, and (c) between T_A and T_C. ------, liquid free energy surface; ———, α free energy surface.

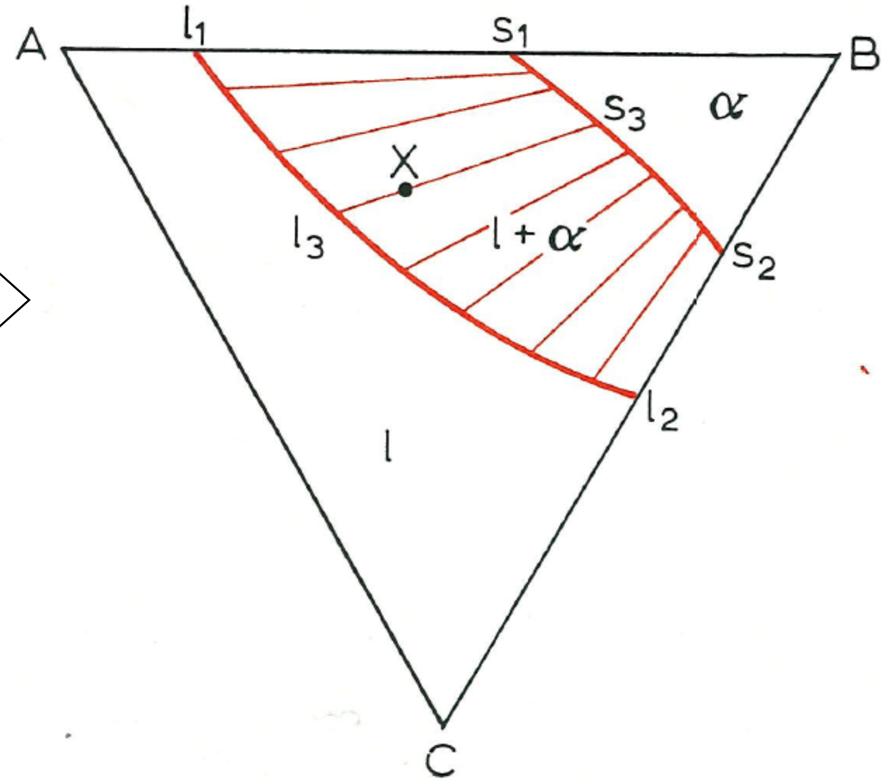
8.4 TWO-PHASE EQUILIBRIUM

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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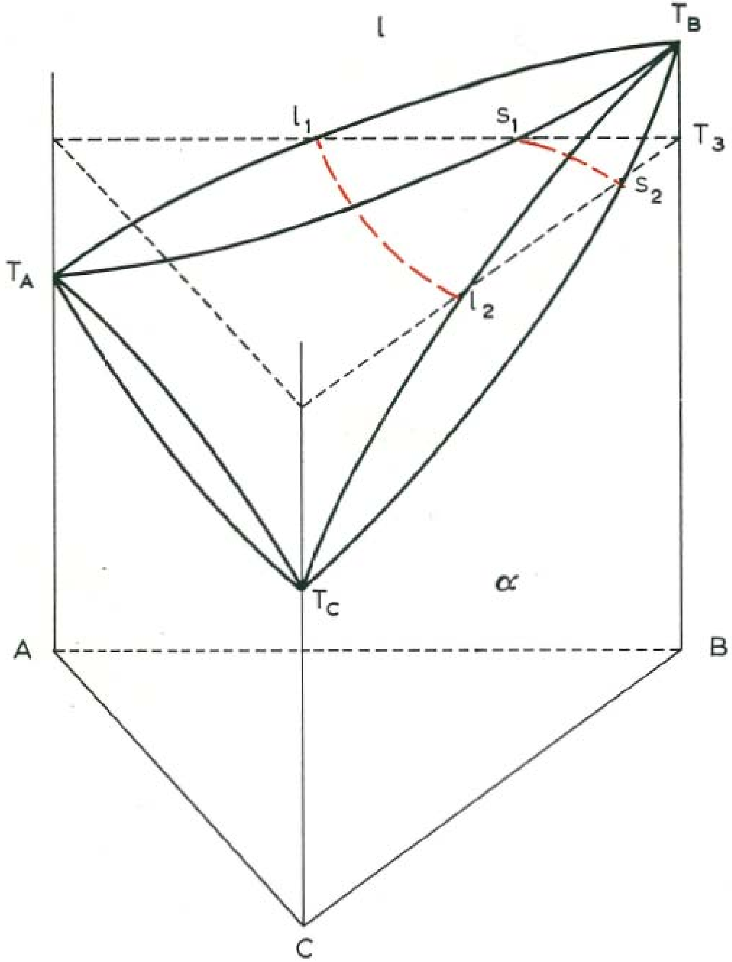
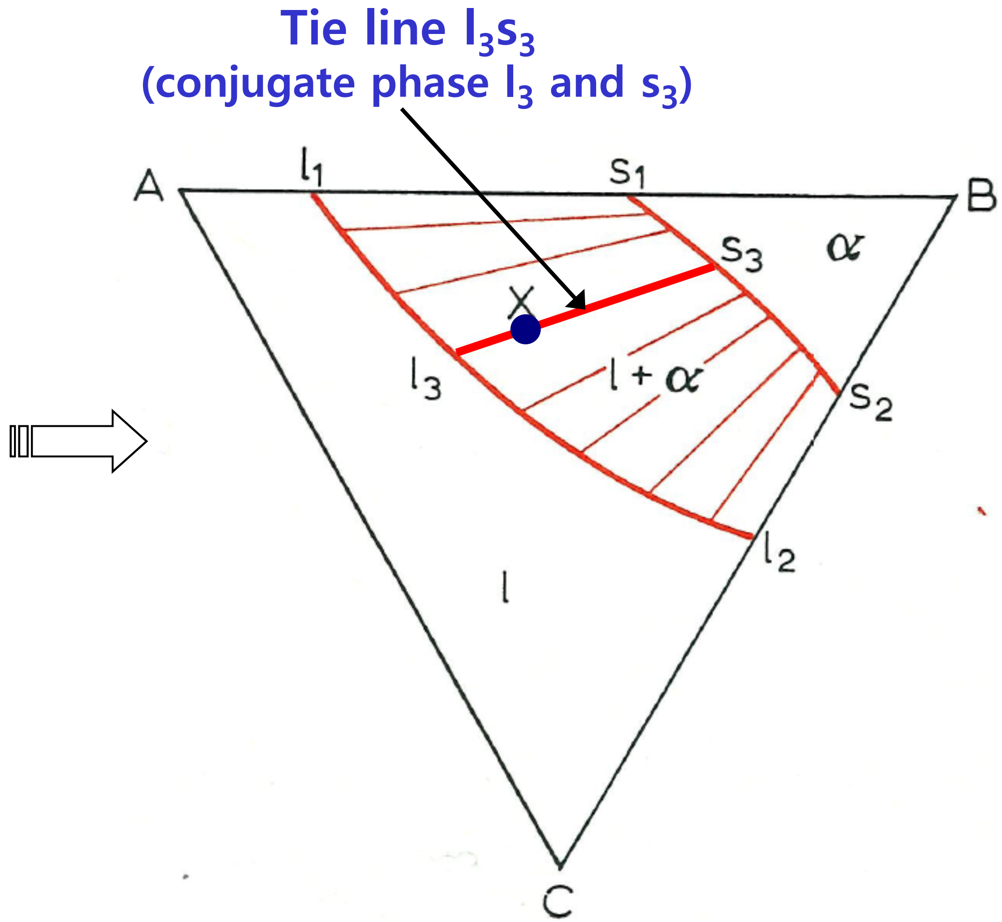
Ternary Isomorphous System





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.

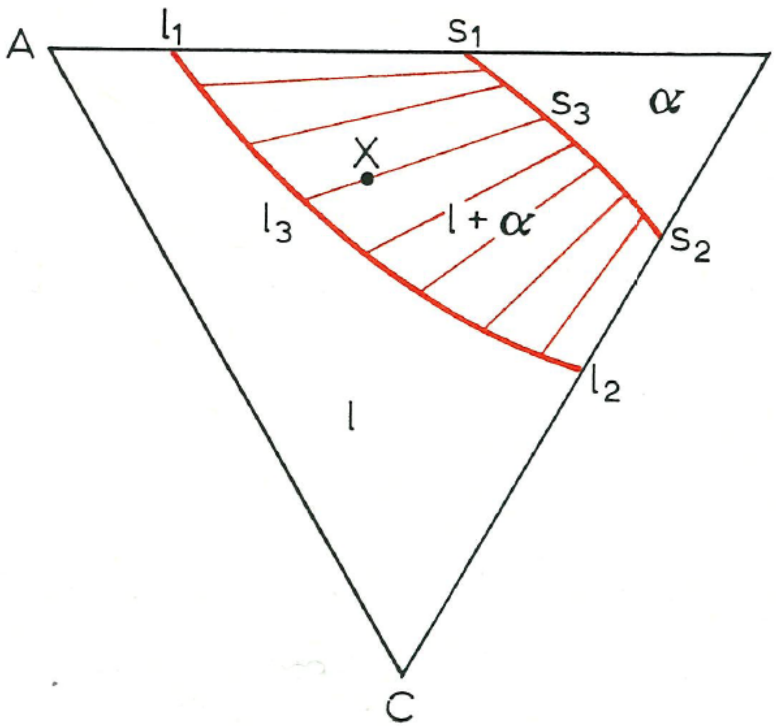
(iii) Extension of tie line cannot intersect the vertex of triangle.

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

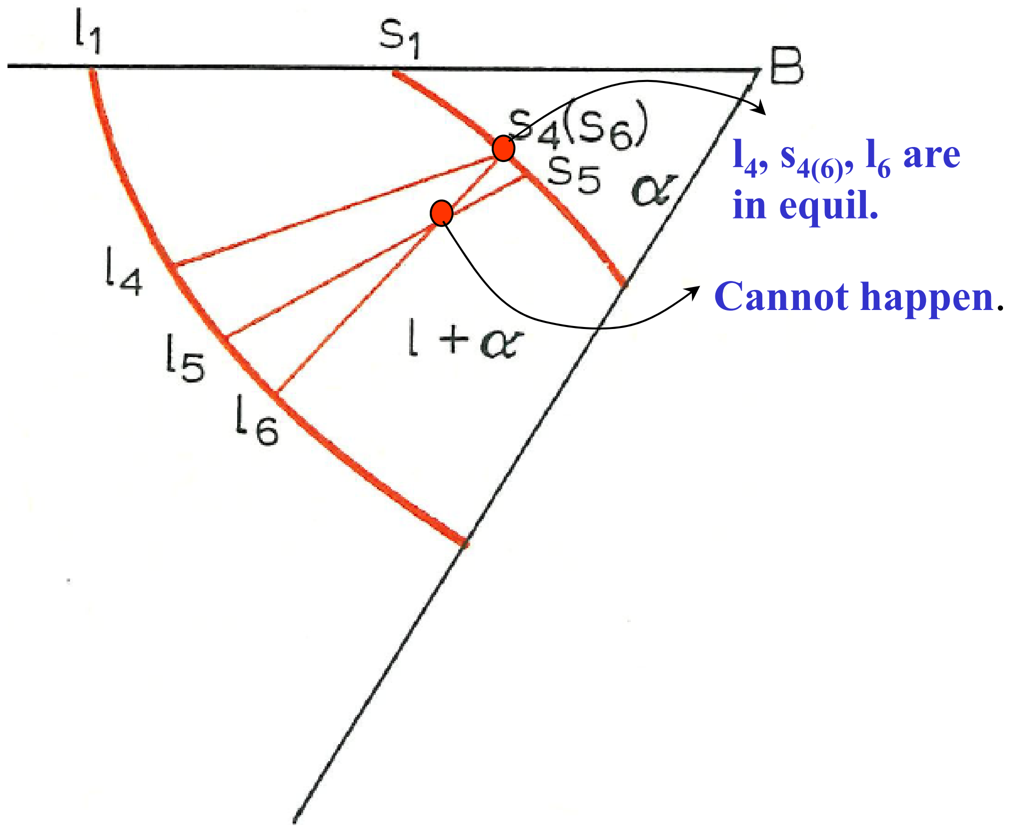
8.4 TWO-PHASE EQUILIBRIUM

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.



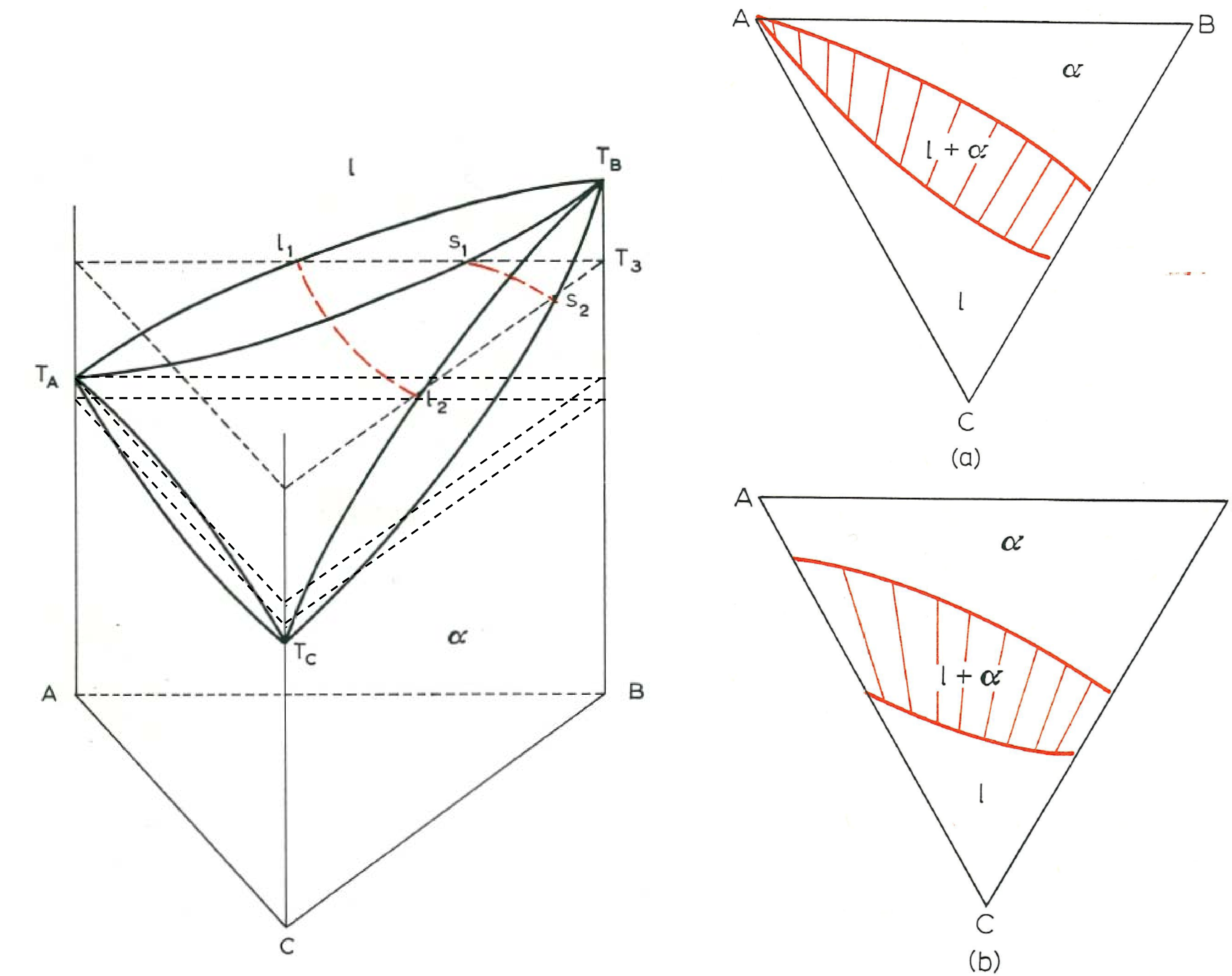
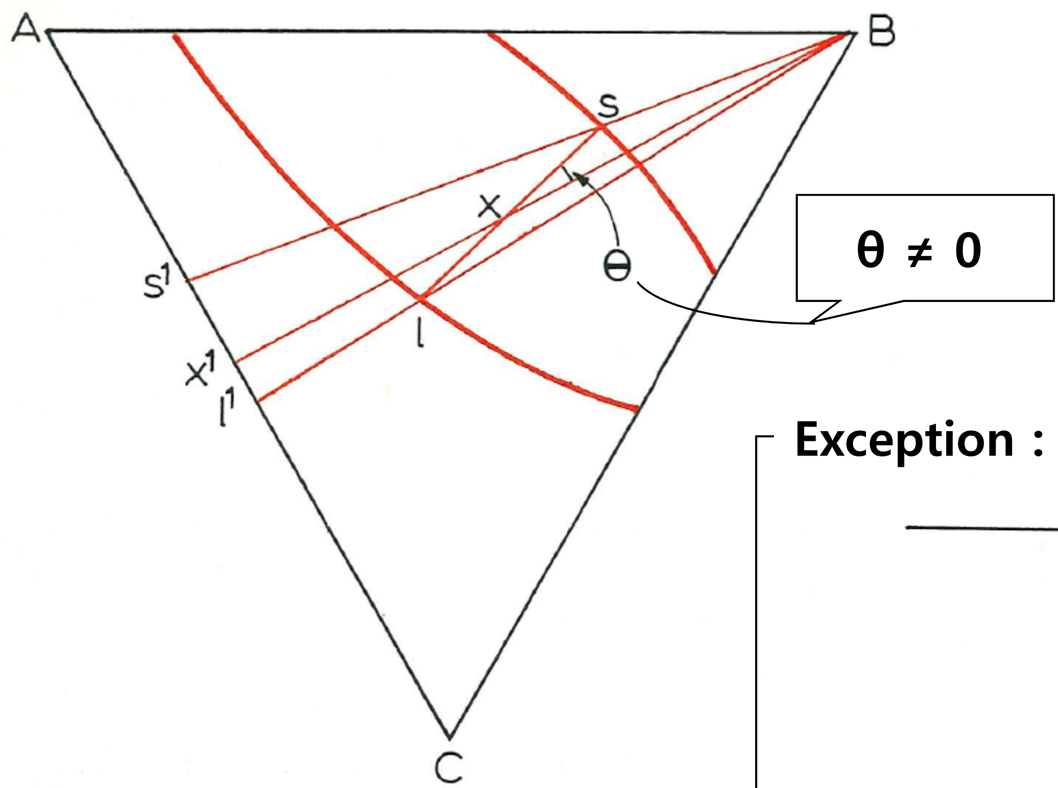


Fig. 116. Isothermal sections through Fig. 111 at (a) T_A, and (b) between T_A and T_C.

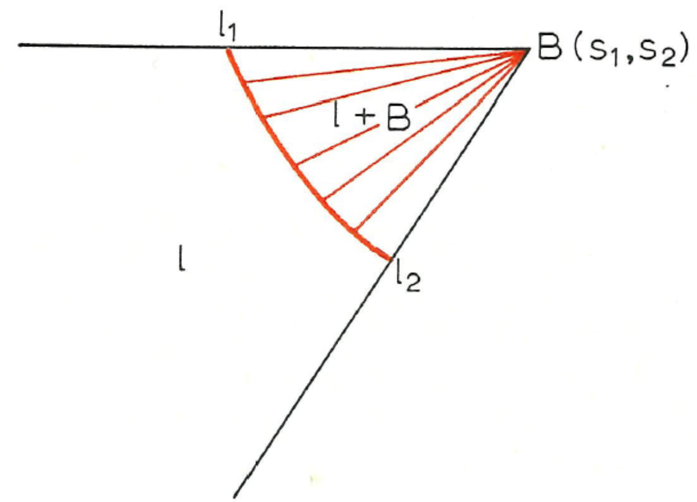
8.4 TWO-PHASE EQUILIBRIUM

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.

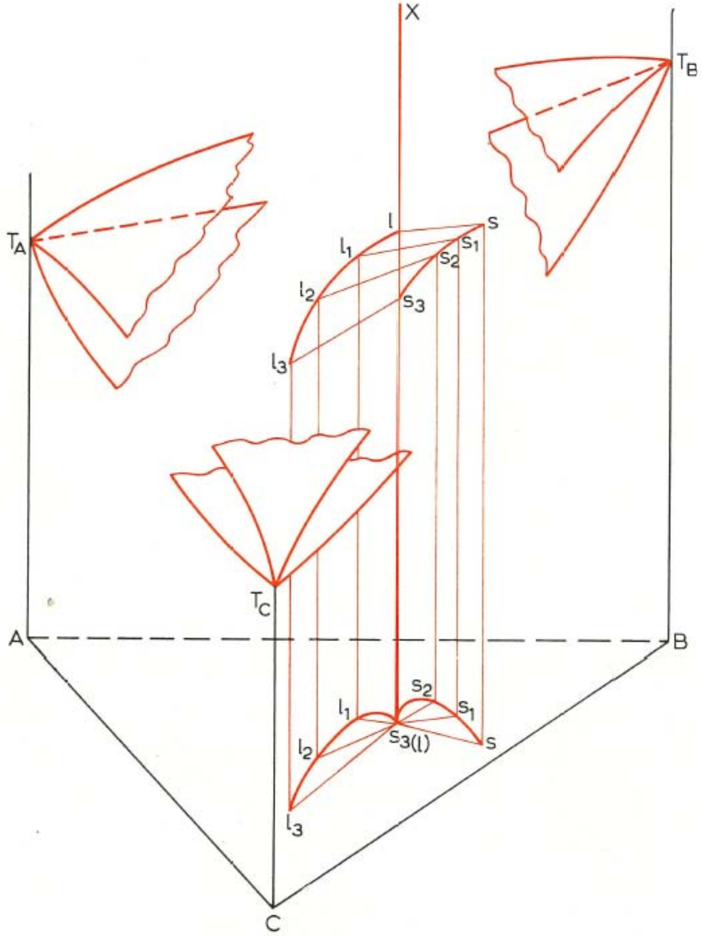


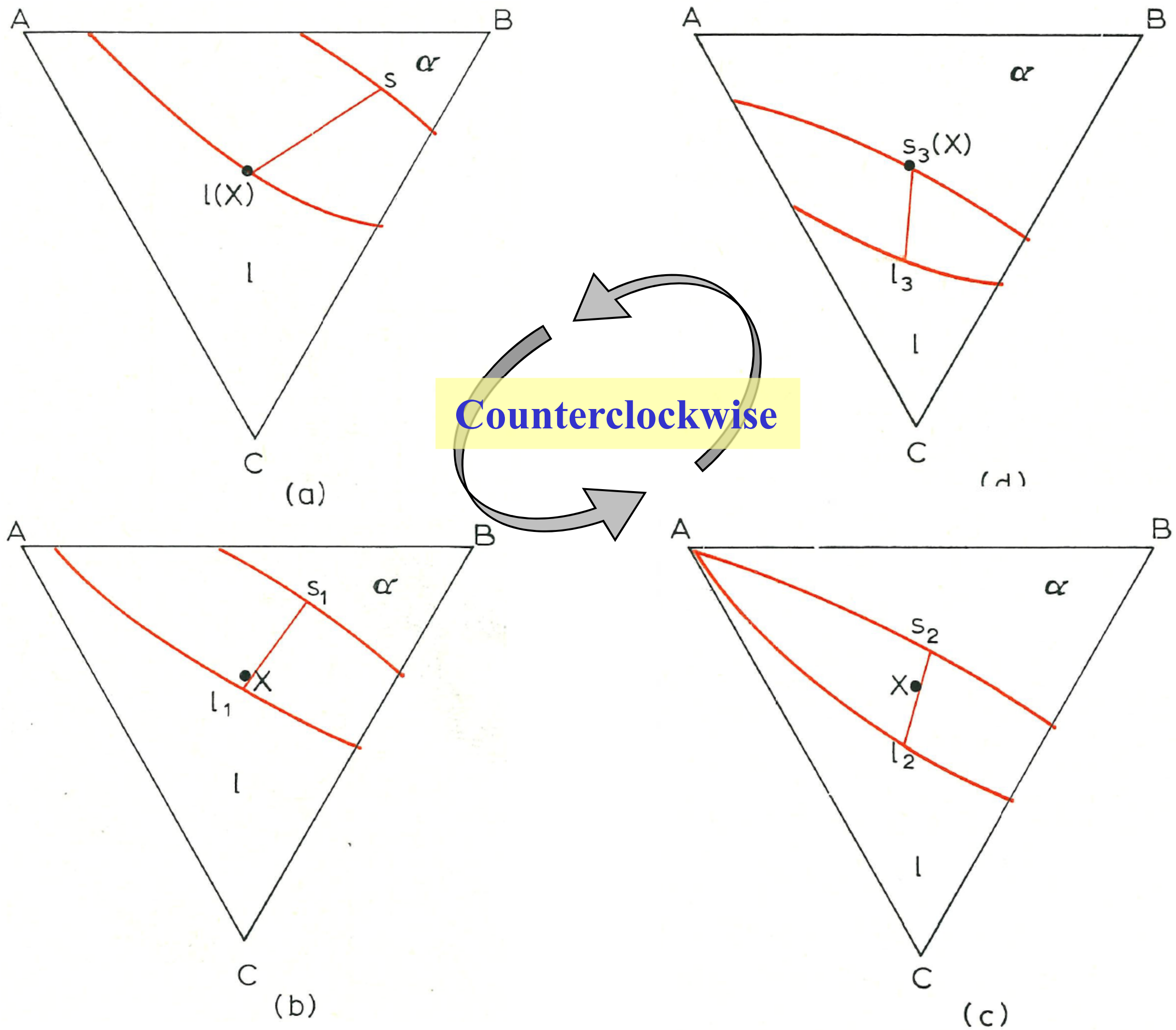
8.4 TWO-PHASE EQUILIBRIUM

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)

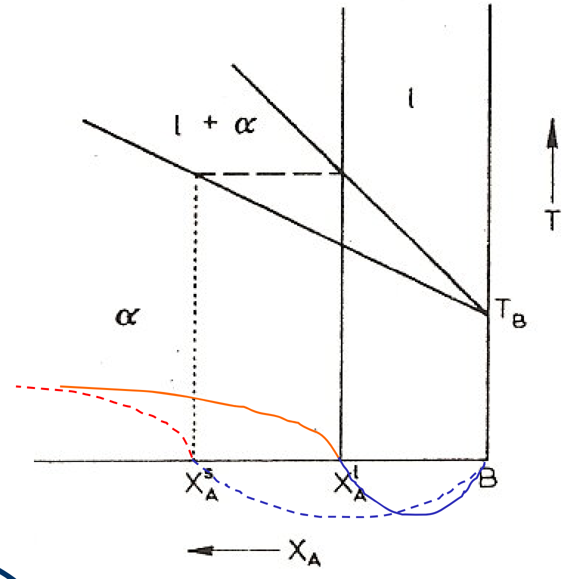
: Clockwise or counterclockwise





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

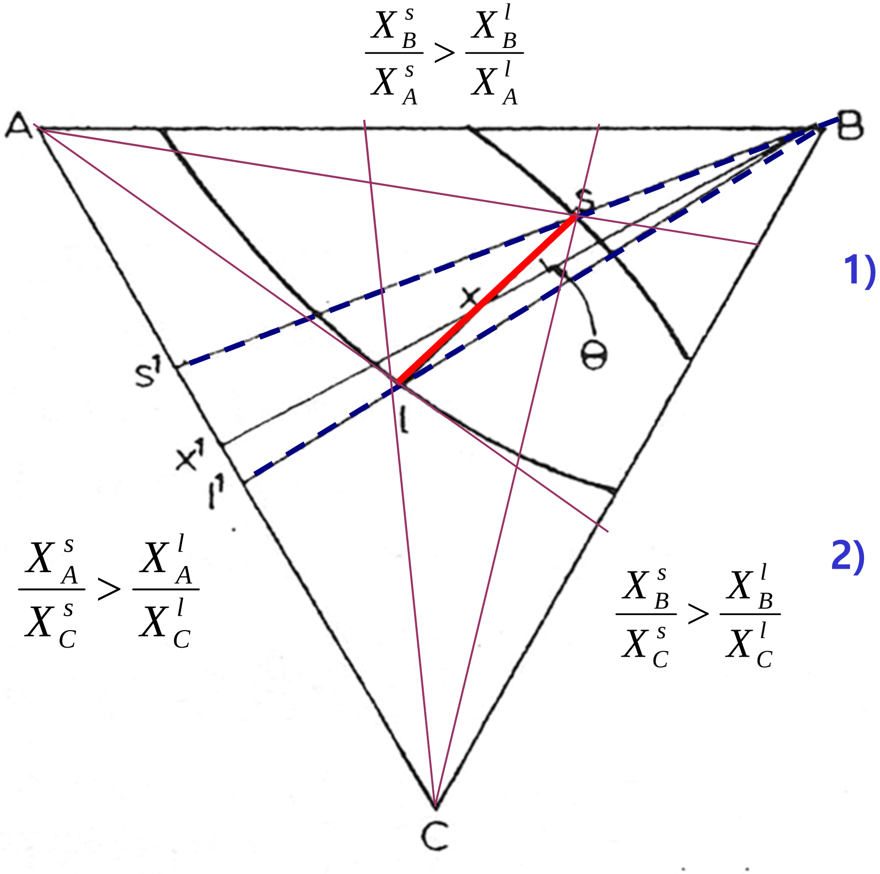
$$\frac{X_A^S}{X_A^S + X_B^S - X_A^S} > \frac{X_A^l}{X_A^l + X_B^l - X_A^l}$$

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,



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

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

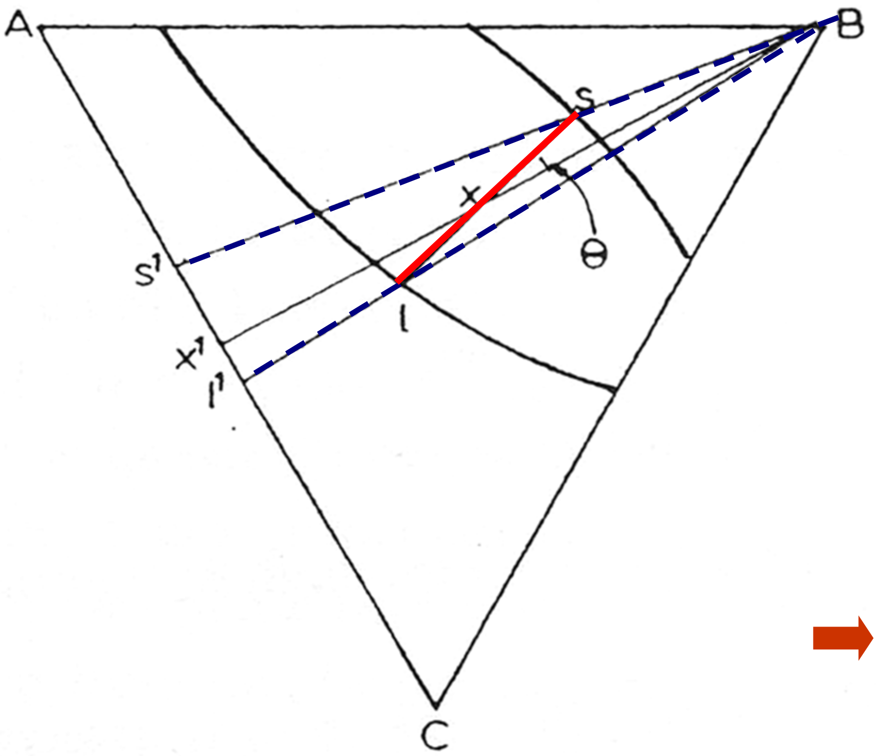
$$\frac{s^1C}{s^1A} > \frac{l^1C}{l^1A} \quad \text{and} \quad \frac{X_A^s}{X_C^s} > \frac{X_A^l}{X_C^l}$$

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



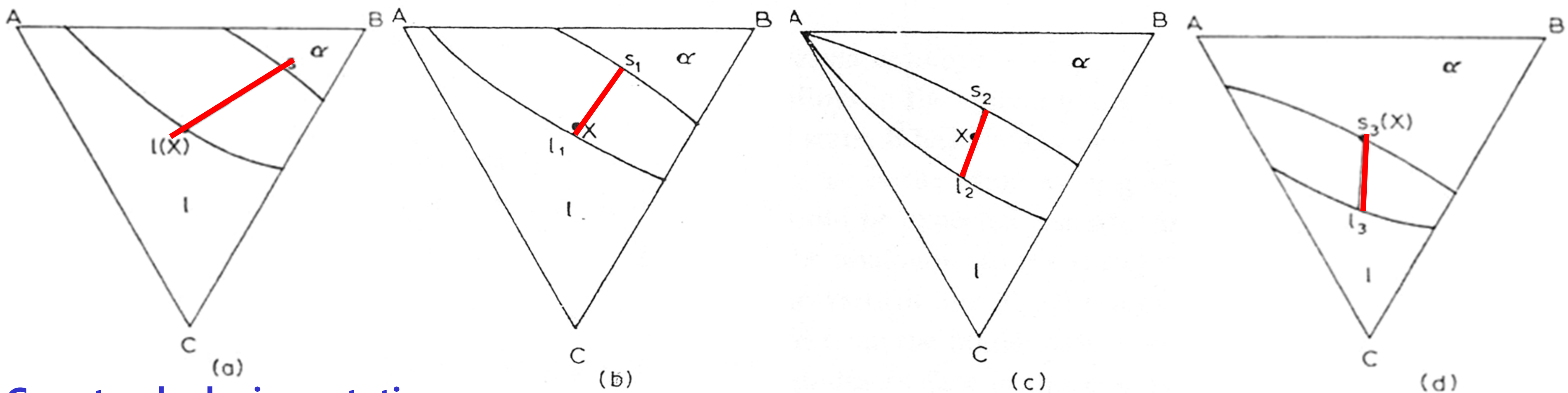
The tie line *ls* is rotated anticlockwise by an angle Θ relative to the line Bx[1].

If Θ = 0

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

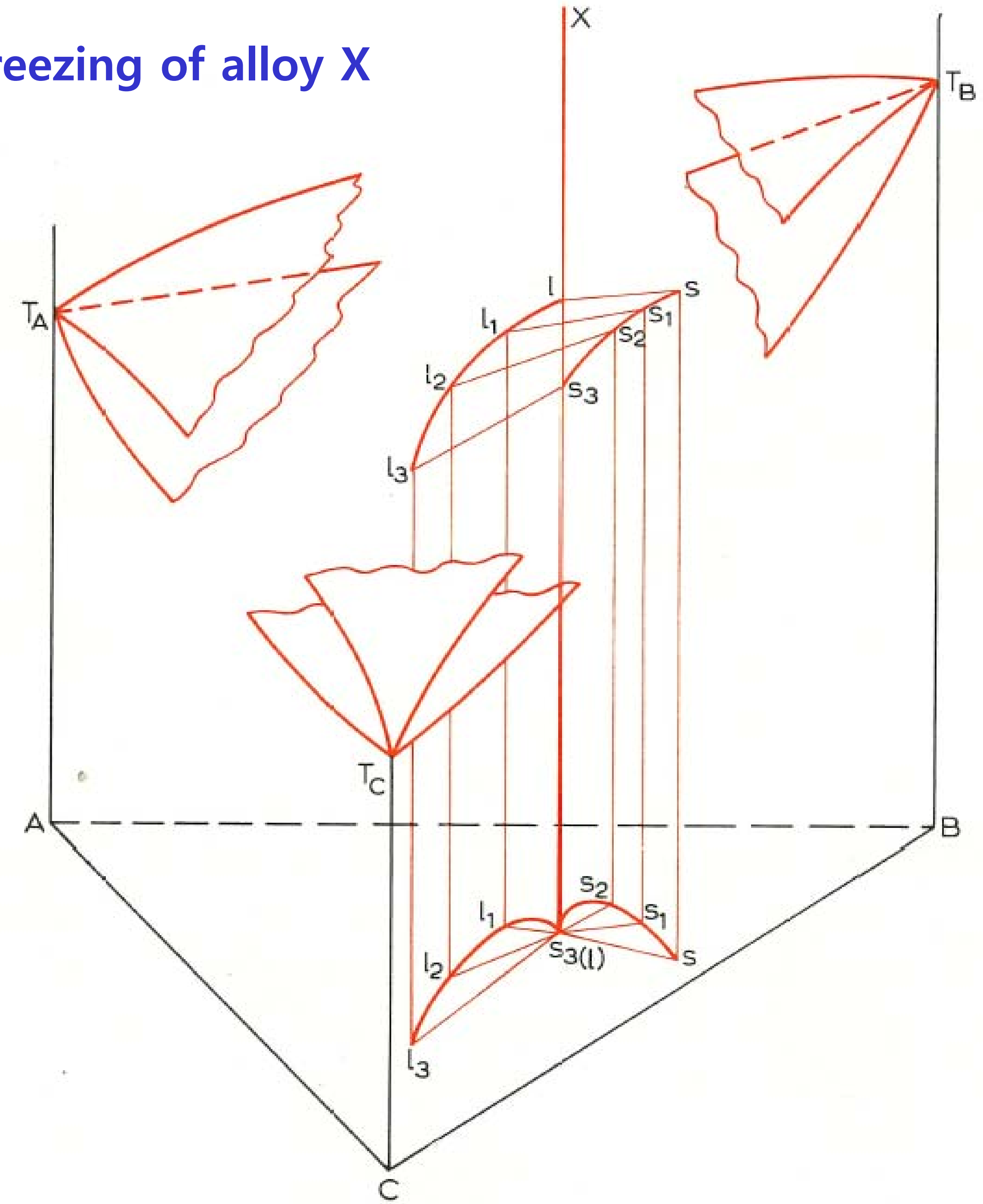
in contradiction to Konovalov's Rule.

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

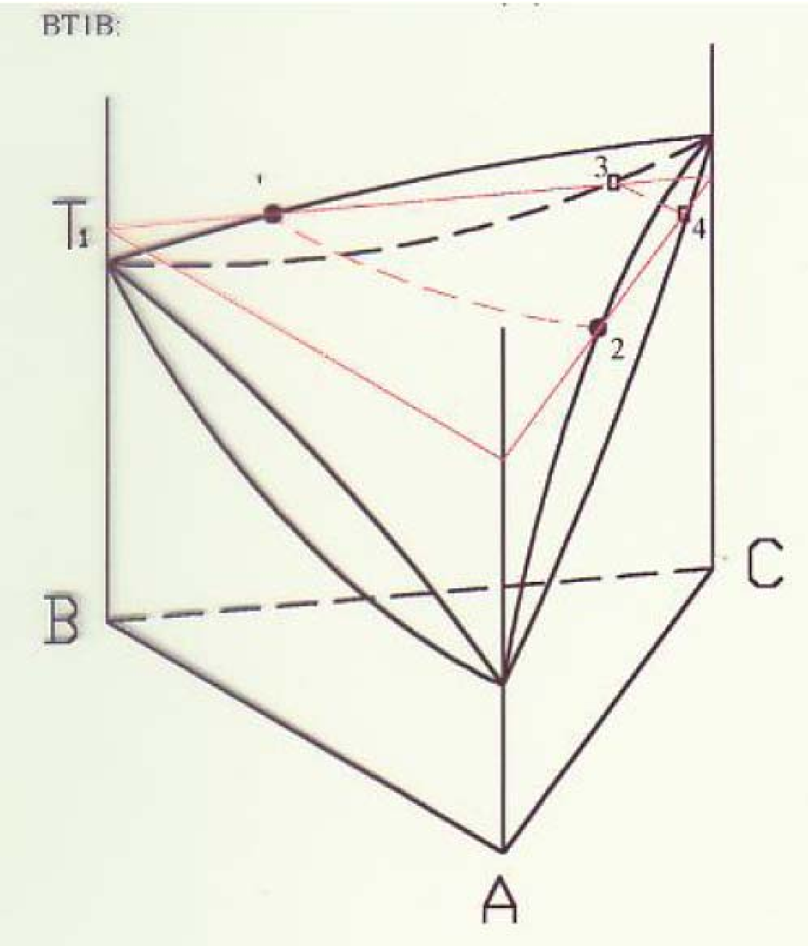


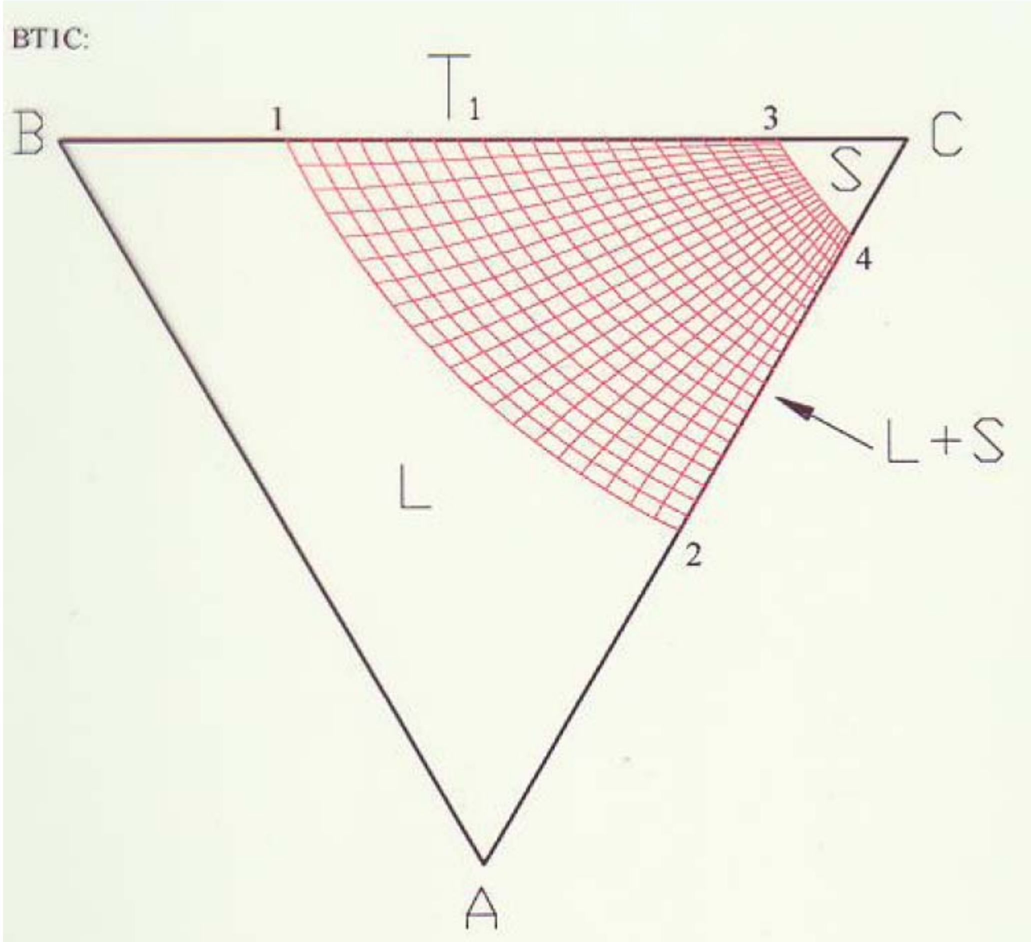
Counterclockwise rotation

Equilibrium freezing of alloy X

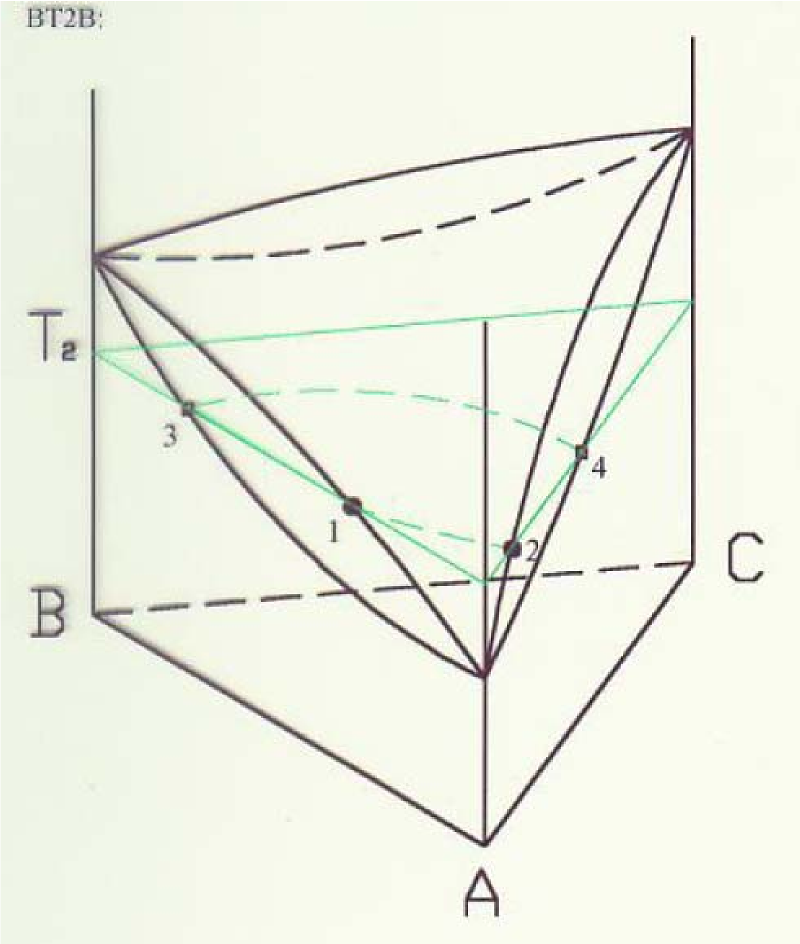


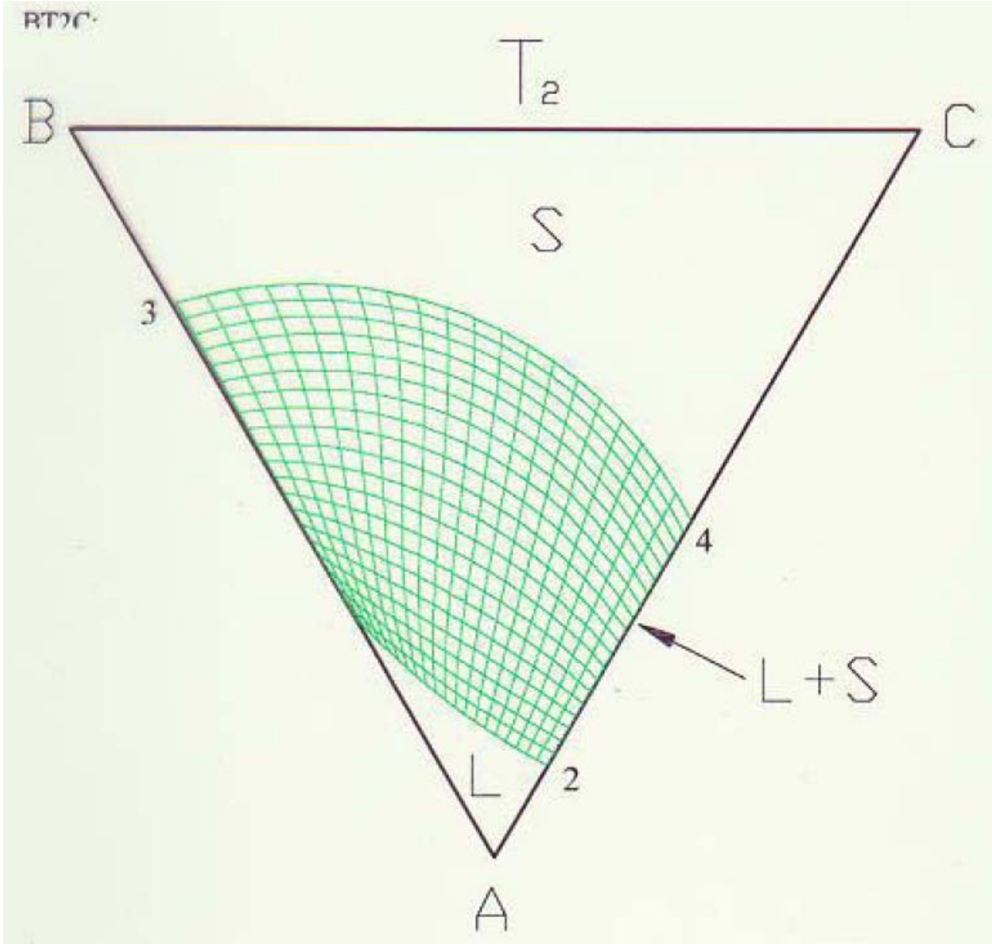
Counterclockwise rotation





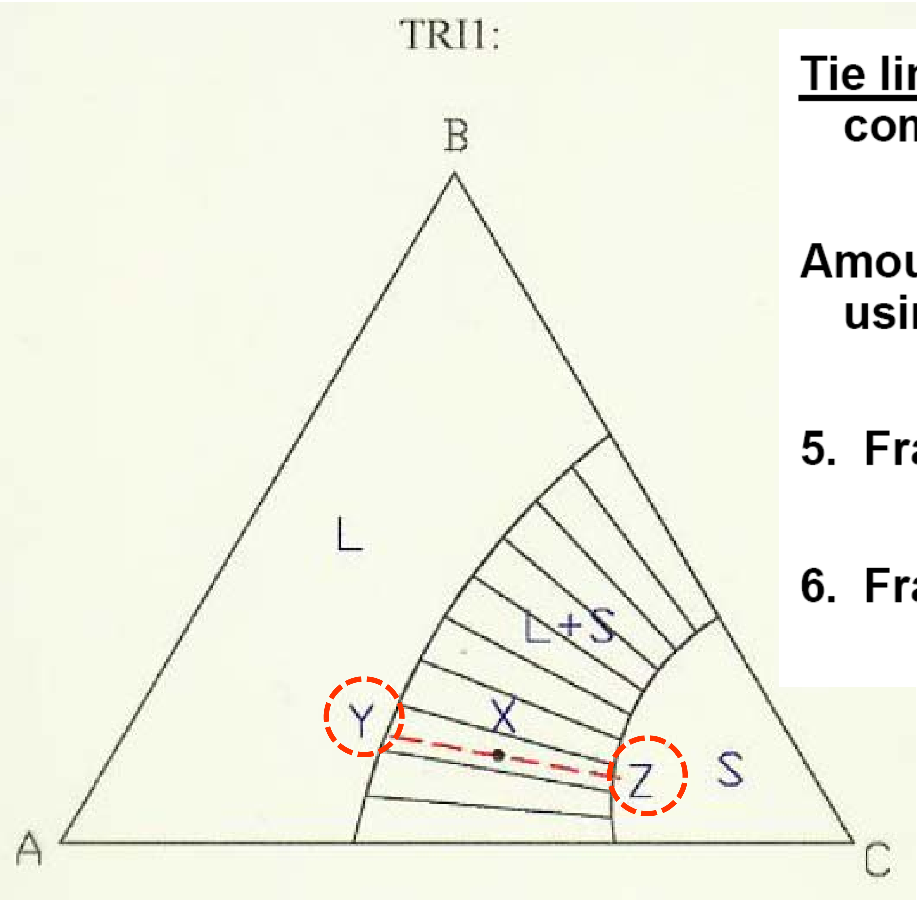
Counterclockwise rotation





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

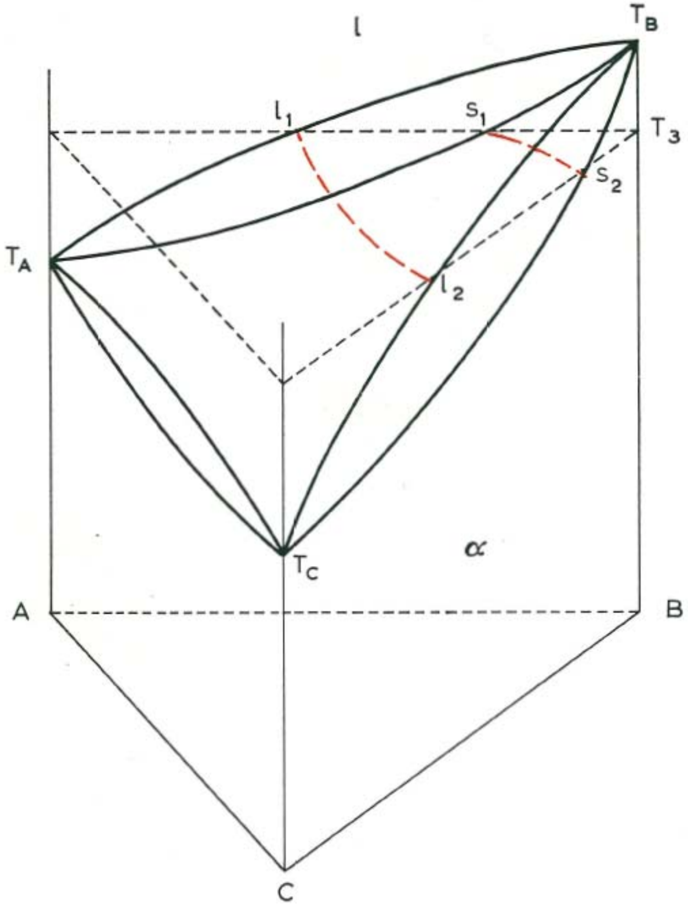
8.4 TWO-PHASE EQUILIBRIUM

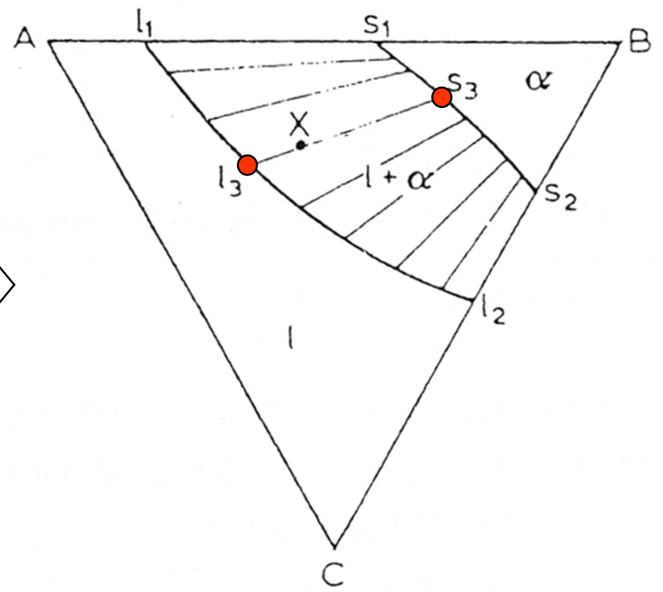
8.4.1 Two-phase equilibrium between the liquid and a solid solution

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)

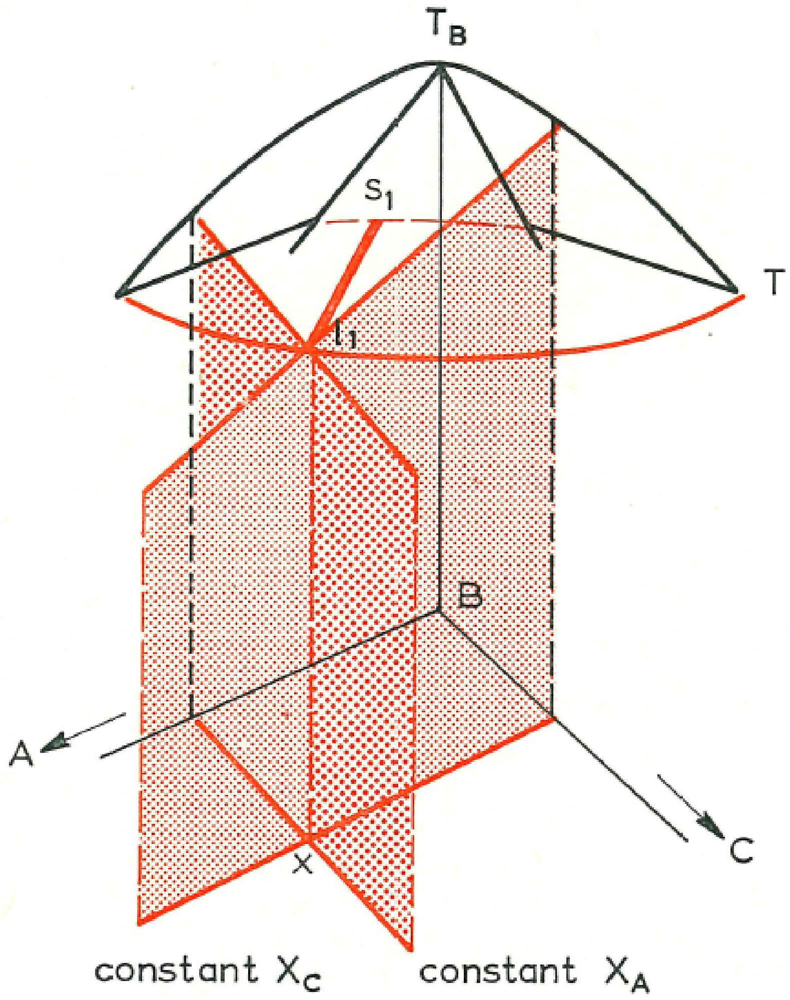
→ Tie line

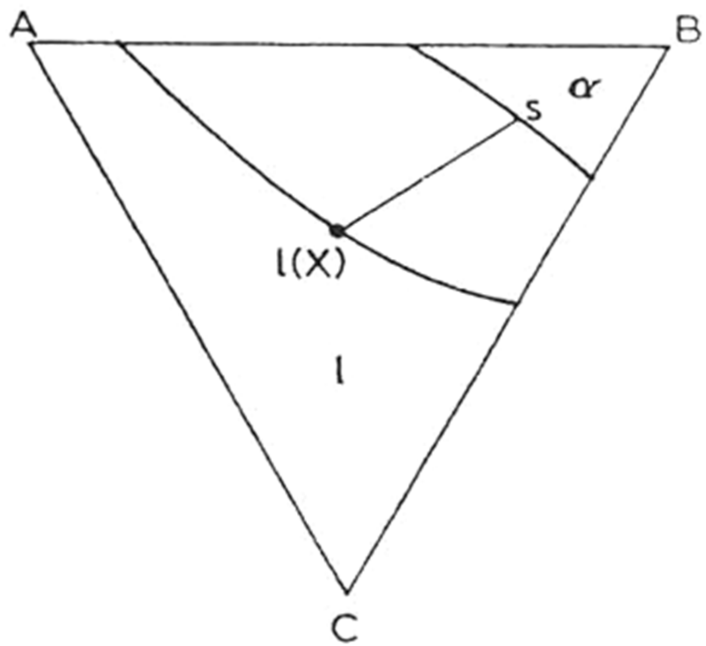
→ Comp. of solid (X_A^α, X_B^α, X_C^α)

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

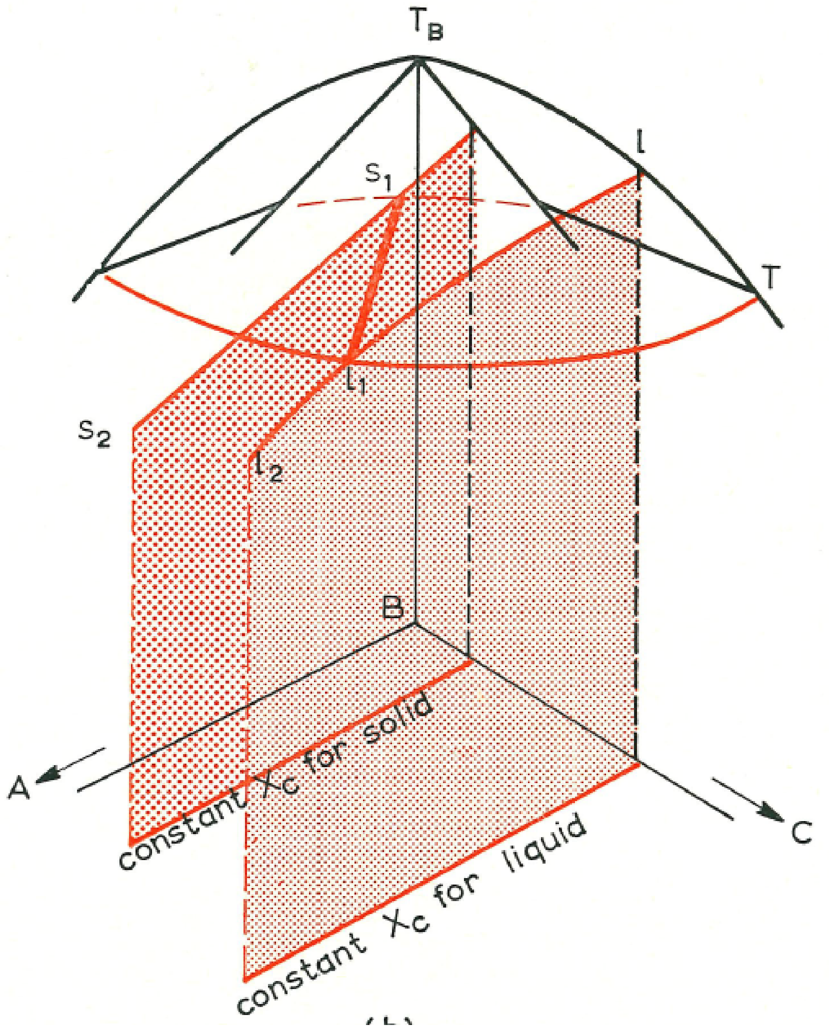
→ Temp. T

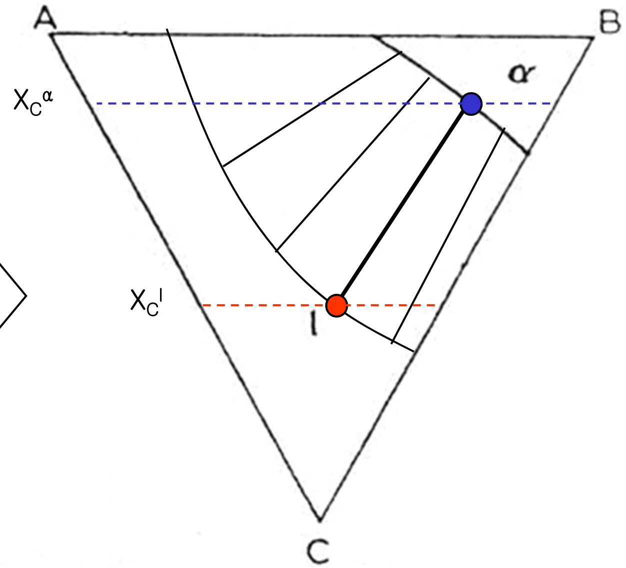
→ Two phase region

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>

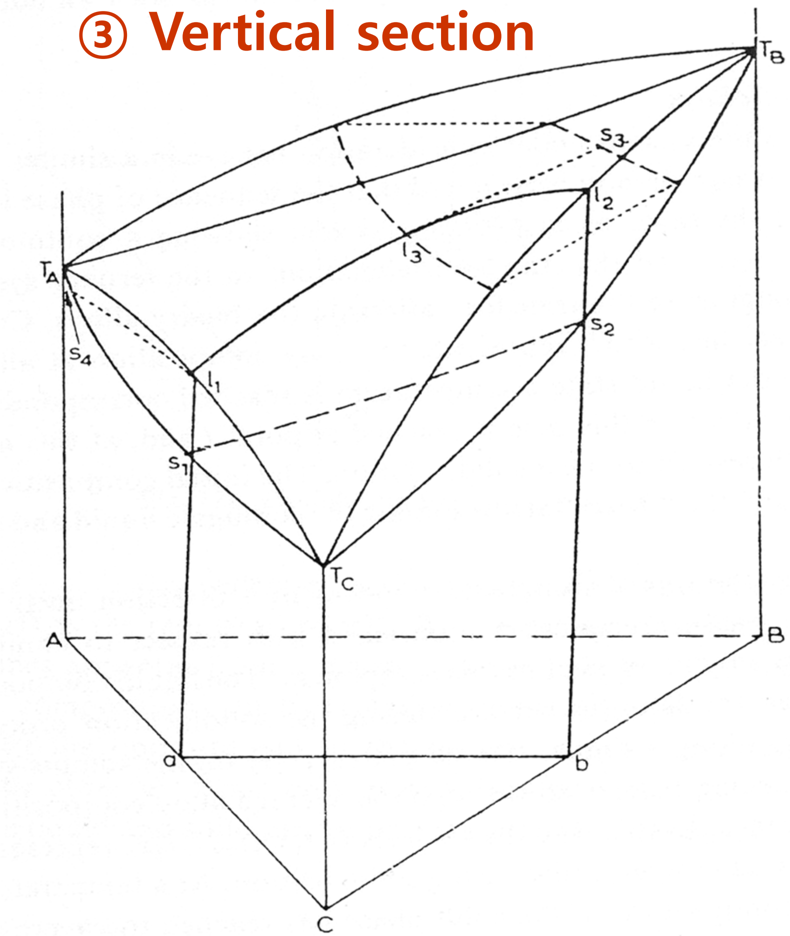
→ Temperature, tie line

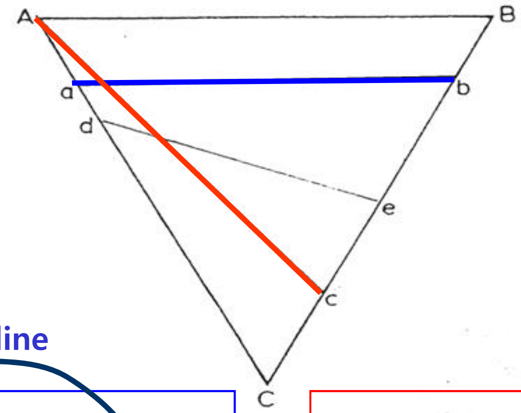
→ Composition of liq. & sol.

8.4 TWO-PHASE EQUILIBRIUM

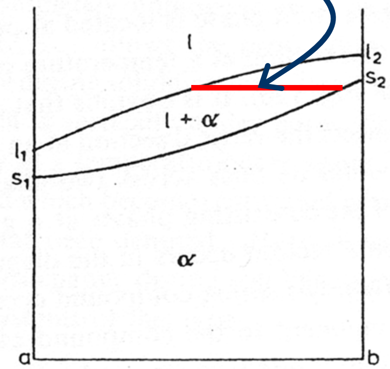
8.4.1 Two-phase equilibrium between the liquid and a solid solution

③ Vertical section

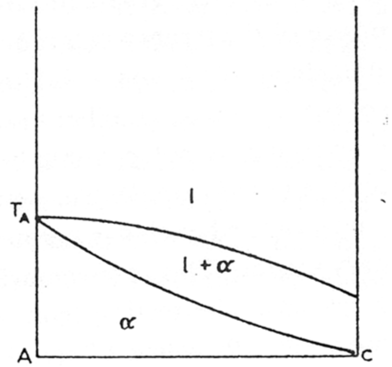




No tie line &
No conjugate line



Paralleled to binary (AB)



Cut through vertex

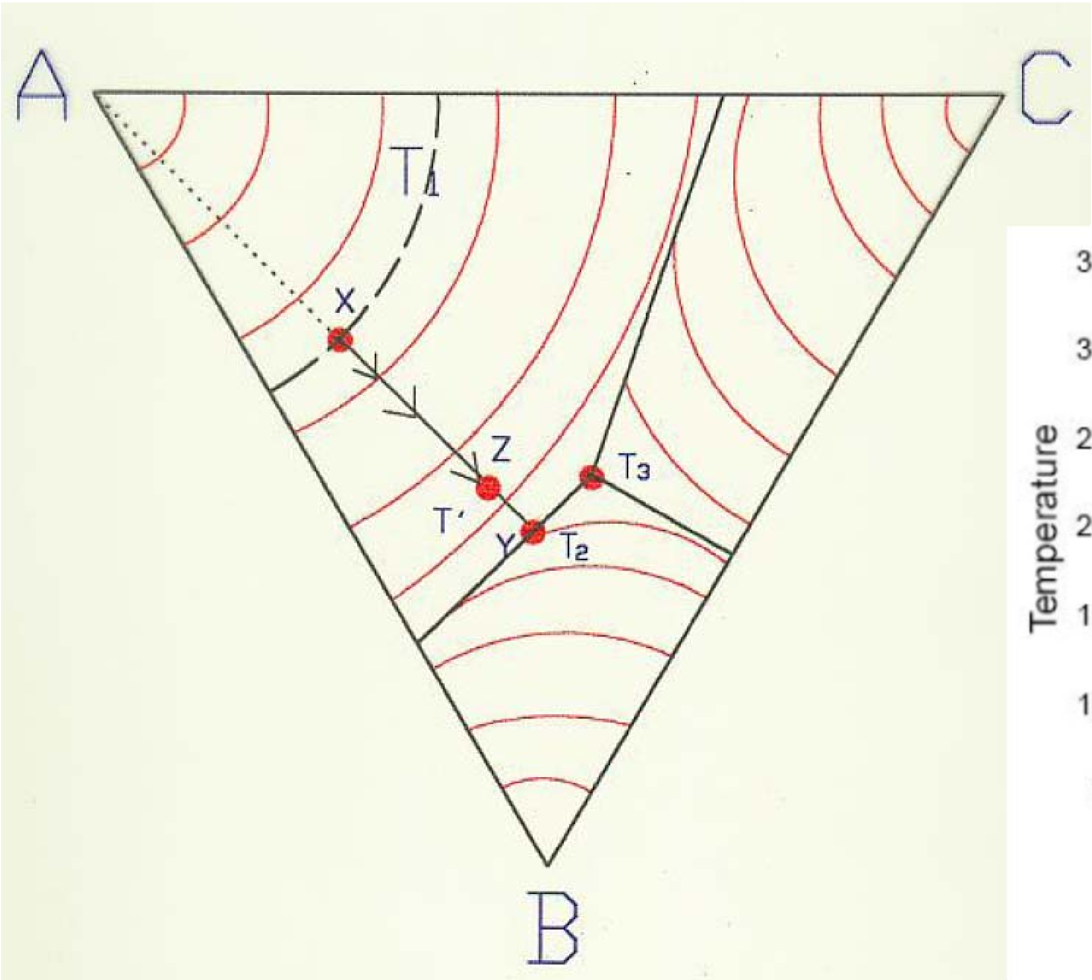
① Useful for effect of 3rd alloying element

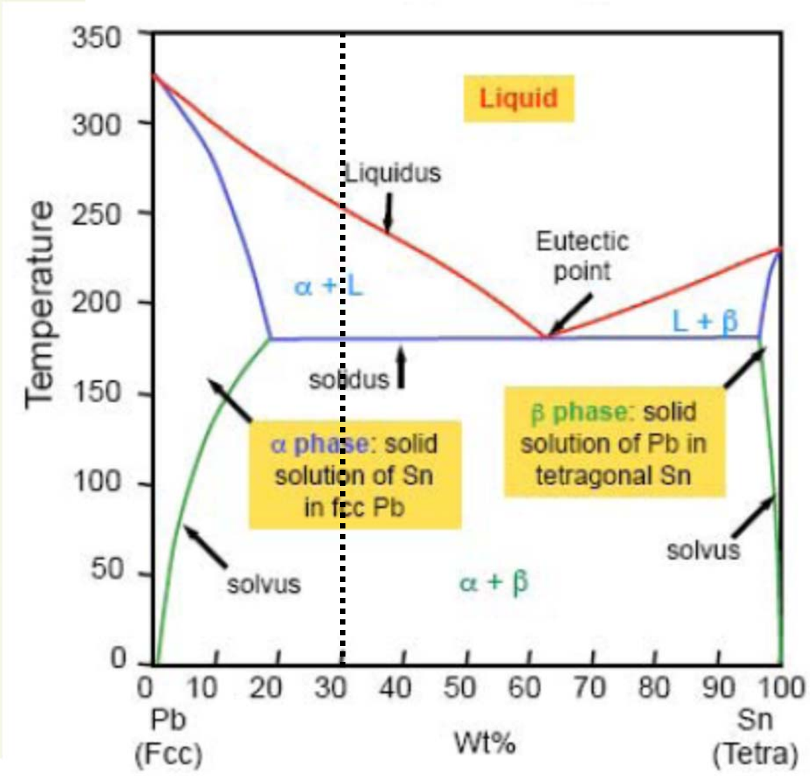
However, it is not possible to draw horizontal tie lines across two-phase regions in vertical sections to indicate the true compositions of the co-existing phases at a given temperature.

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

Ternary Eutectic System

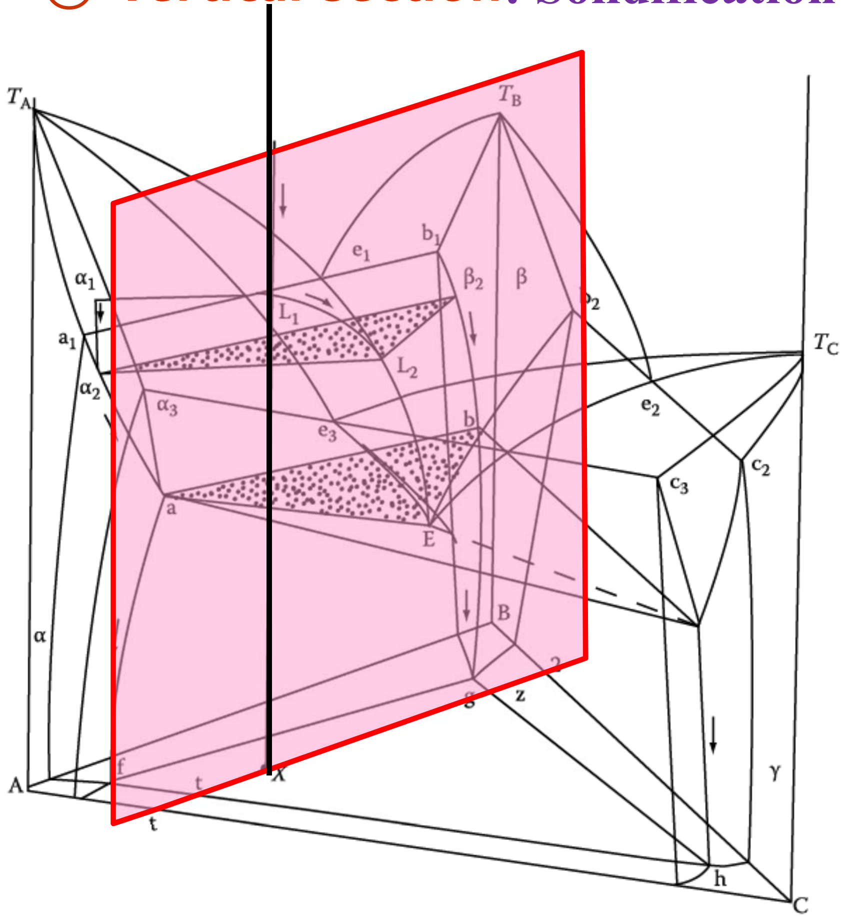
: Solidification Sequence

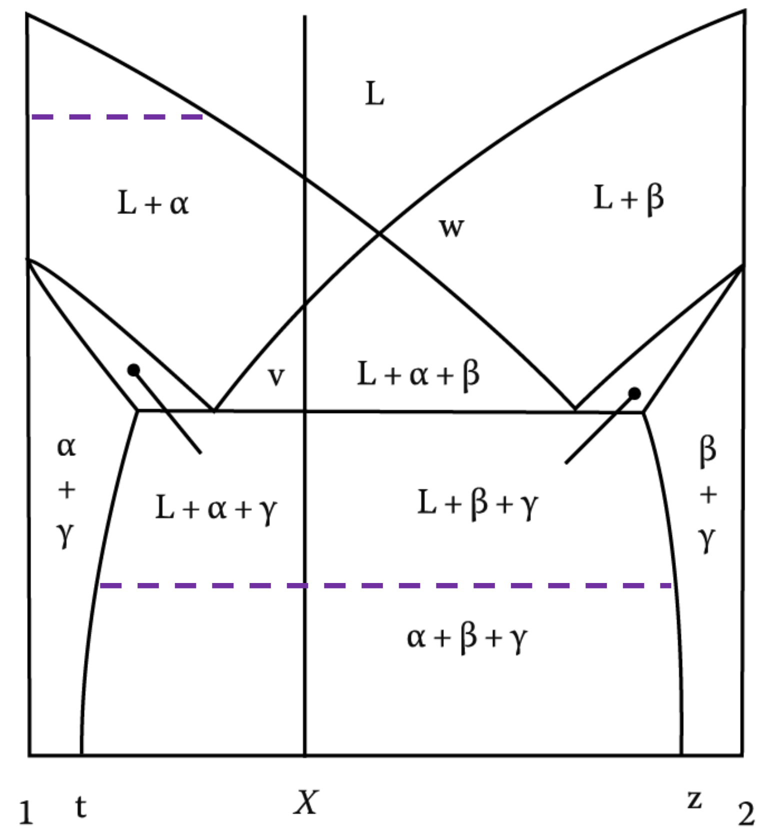




Ternary Eutectic System

③ Vertical section: Solidification Sequence



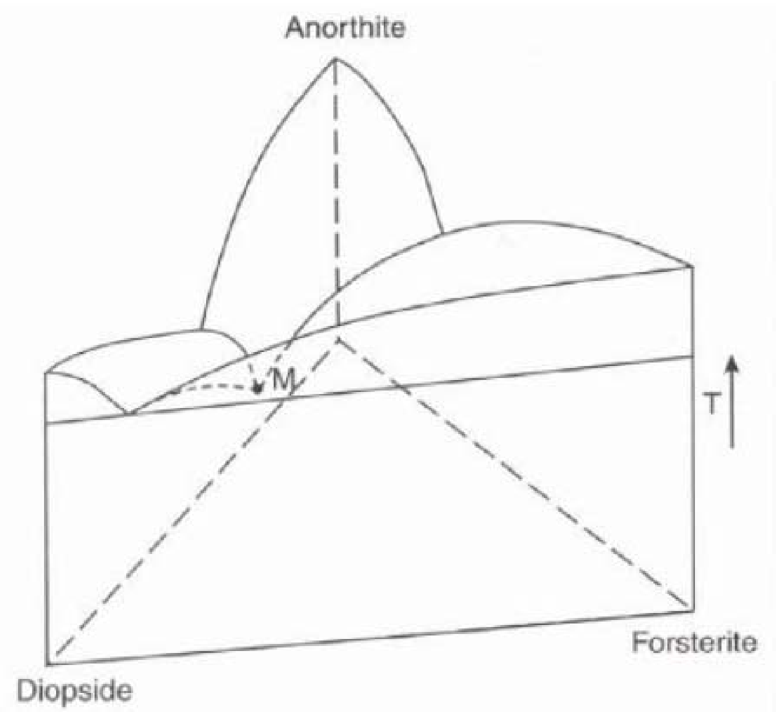


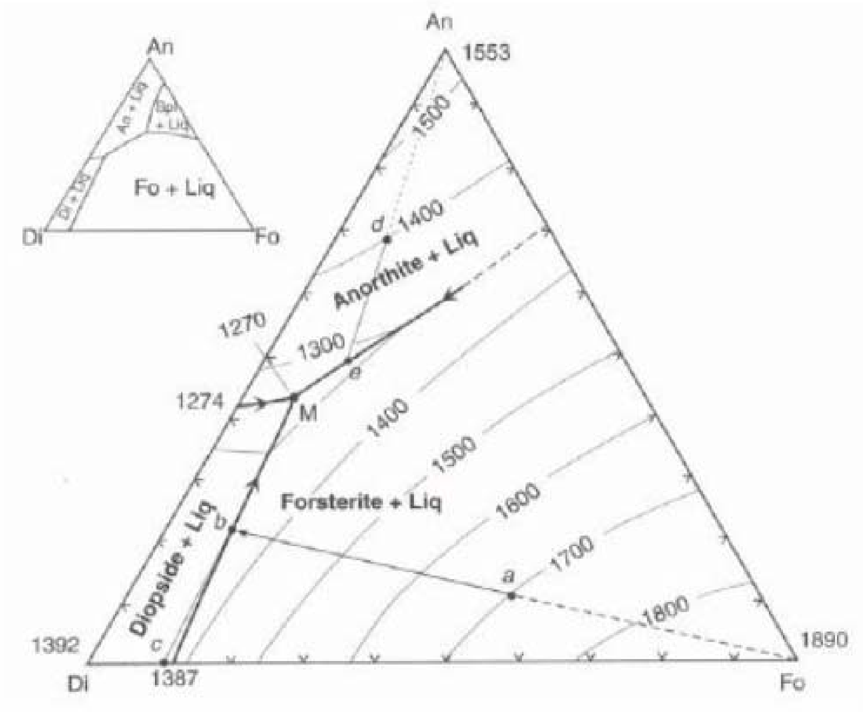
* The horizontal lines are not tie lines.
(no compositional information)

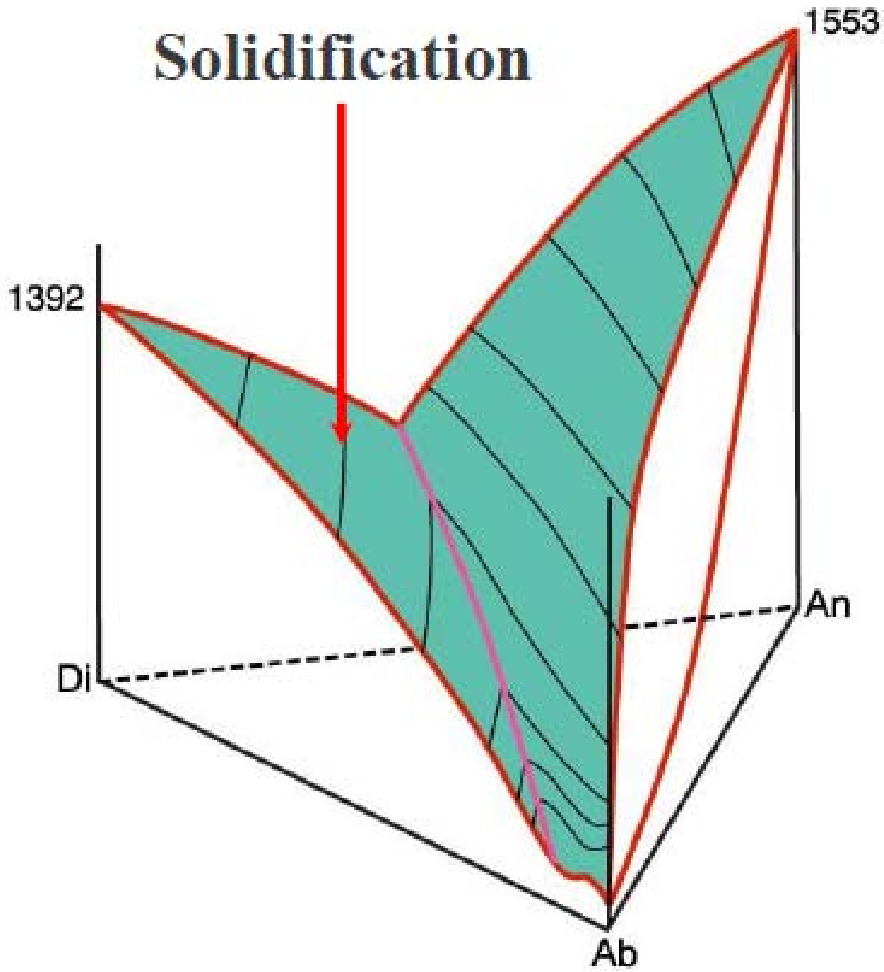
* Information for equilibrium phases at different tempeatures

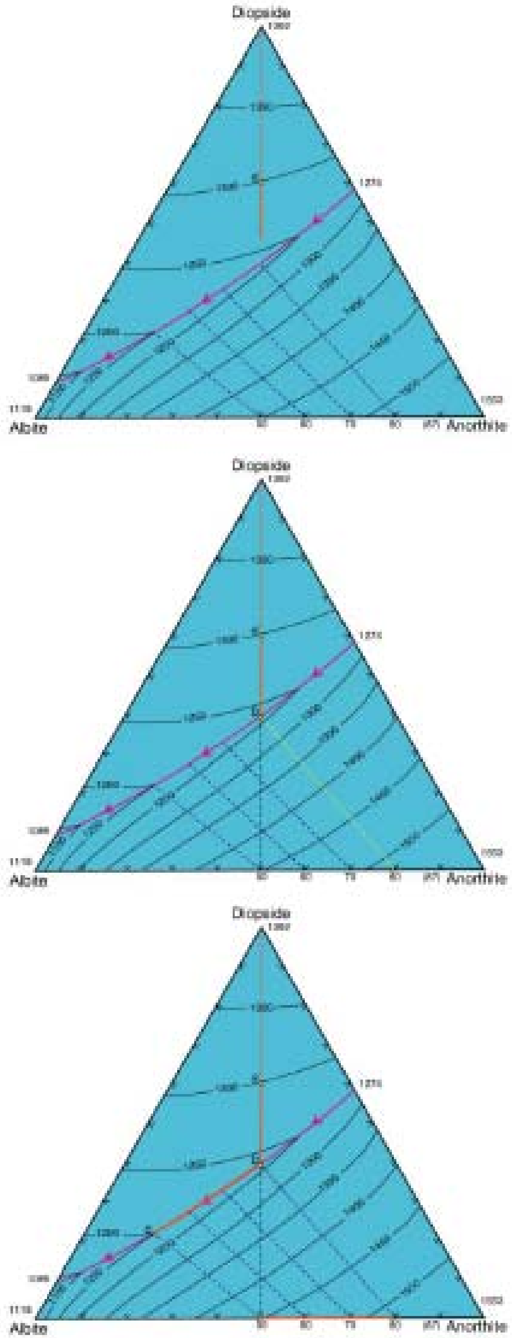
④ Polythermal projection

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.

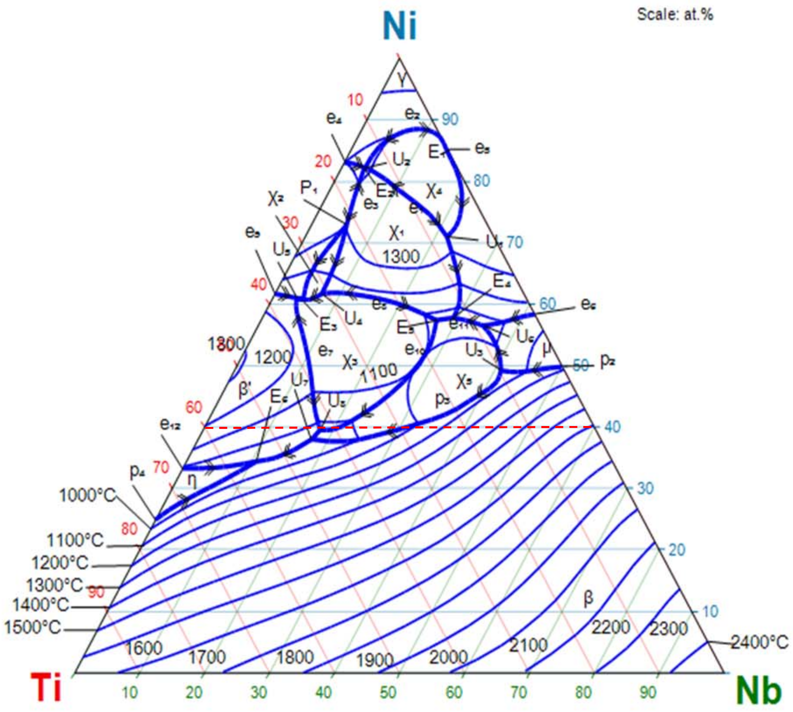




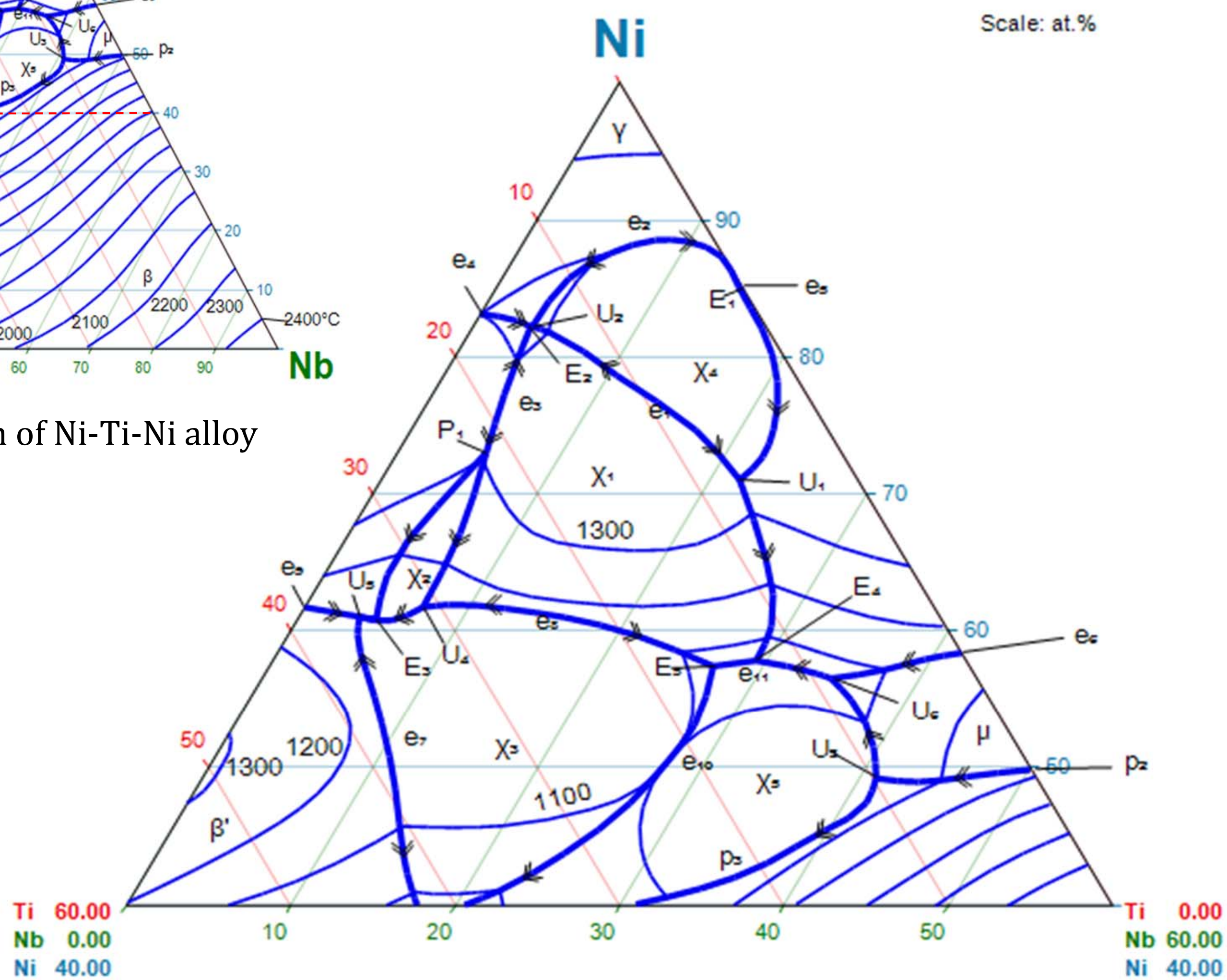




Liquidus phase concentration change during the solidification



Liquidus projection of Ni-Ti-Ni alloy



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