2009 fall

# Advanced Physical Metallurgy

# "Phase Equilibria in Materials"

11. 12. 2009

Eun Soo Park

Office: 33-316
Telephone: 880-7221
Email: espark@snu.ac.kr
Office hours: by an appointment

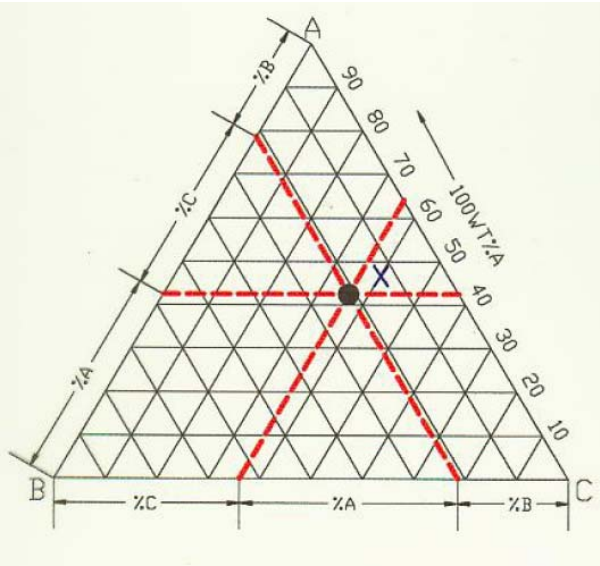
# Contents for previous class "Ternary Phase diagram"

## Ternary system: A, B, C

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

**Overall Composition →** Gibbs triangle

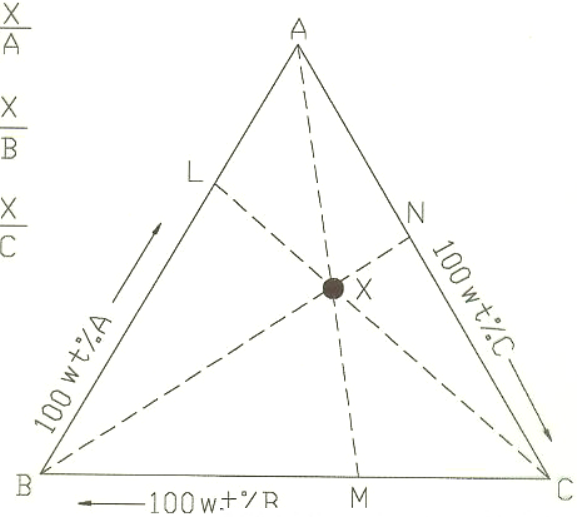
**Tie triangle : 3 phase equil.**

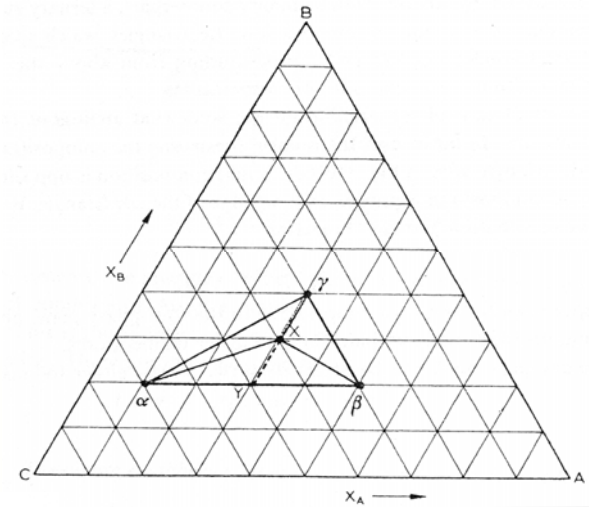



$$\%A = \frac{MX}{MA}$$

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

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



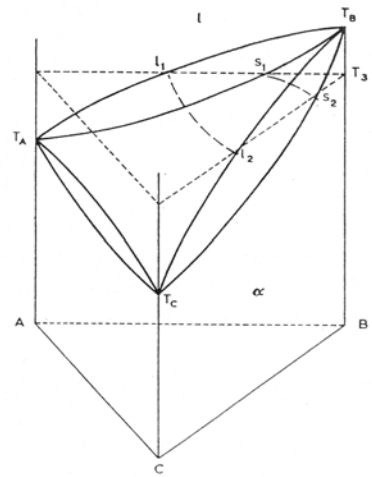

## Ternary isomorphous system

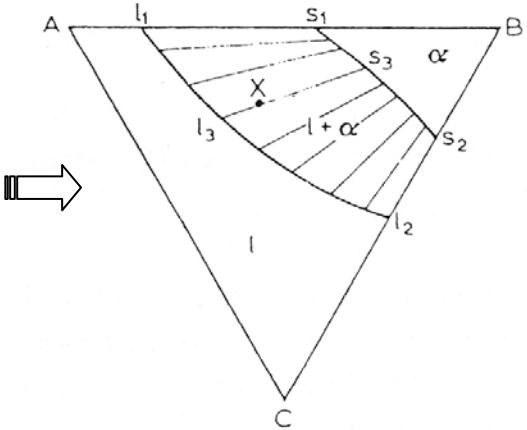
**How to show in 2-dim. space?**

① Projection (liquidus & solidus surface)

② Isothermal section

③ Vertical section



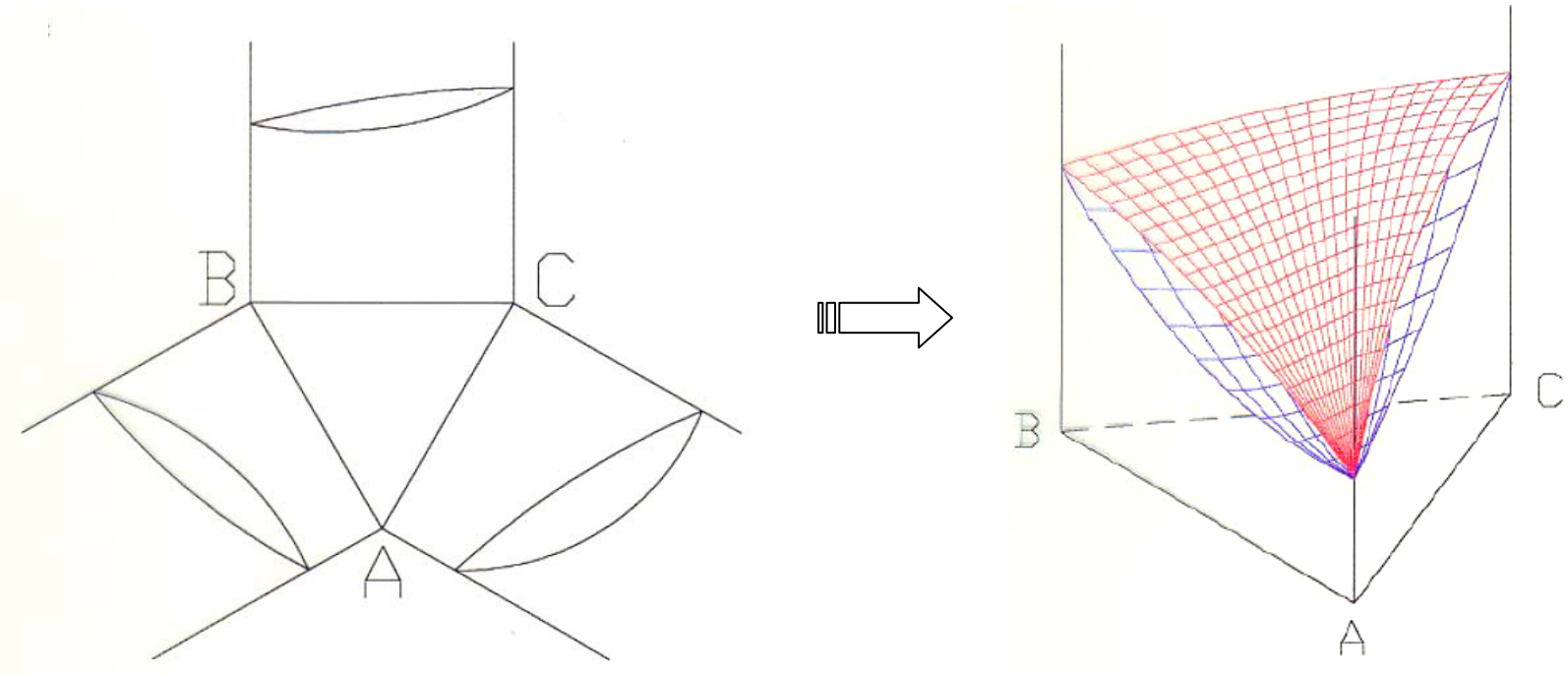



# 8.4 TWO-PHASE EQUILIBRIUM

## 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.



## How to show in 2-dim. space?

① Projection (liquidus & solidus surface)

② Isothermal section

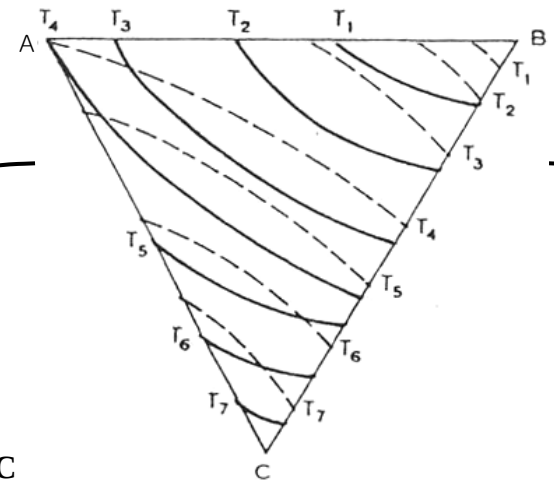
③ Vertical section

# 8.4 TWO-PHASE EQUILIBRIUM

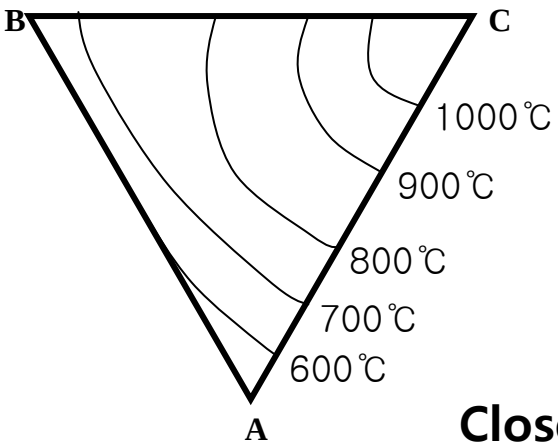
## 8.4.1 Two-phase equilibrium between the liquid and a solid solution

① **Projection** (liquidus & solidus surface)

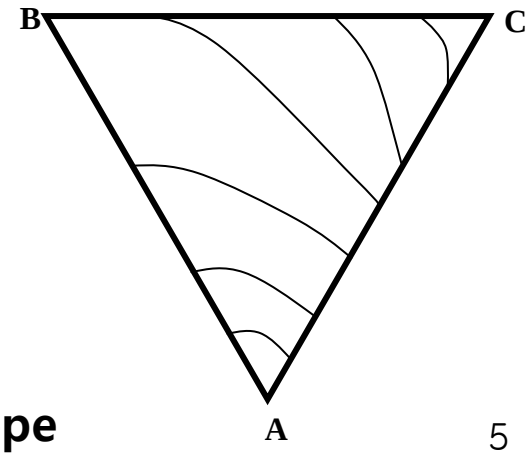
→ **No information on 2 phase region**




**Liquidus surface**




**Solidus surface**



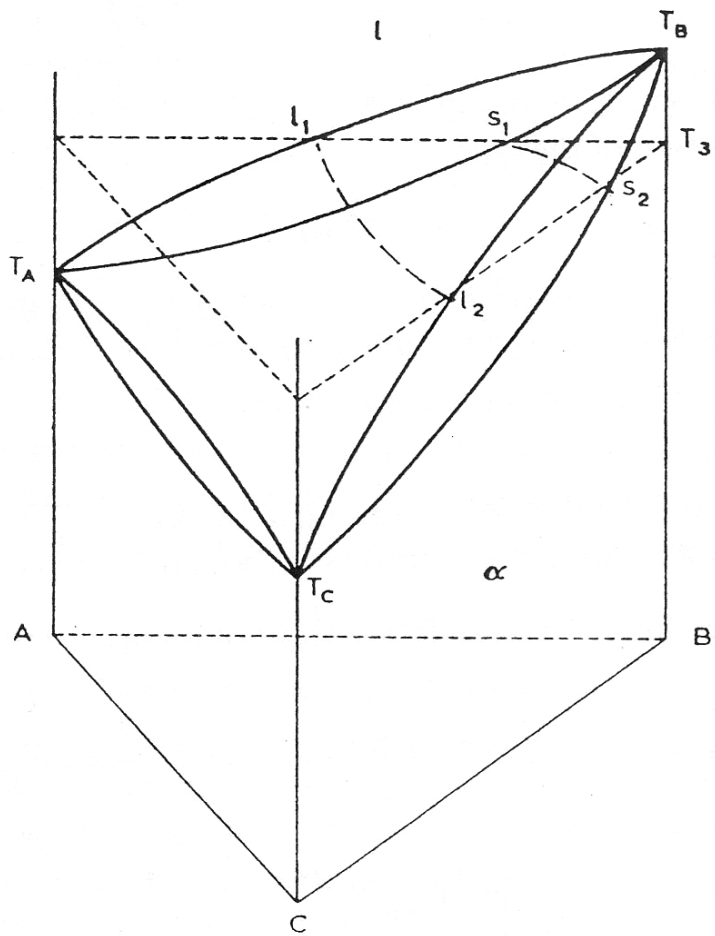

**Close spacing → steep slope**

# 8.4 TWO-PHASE EQUILIBRIUM

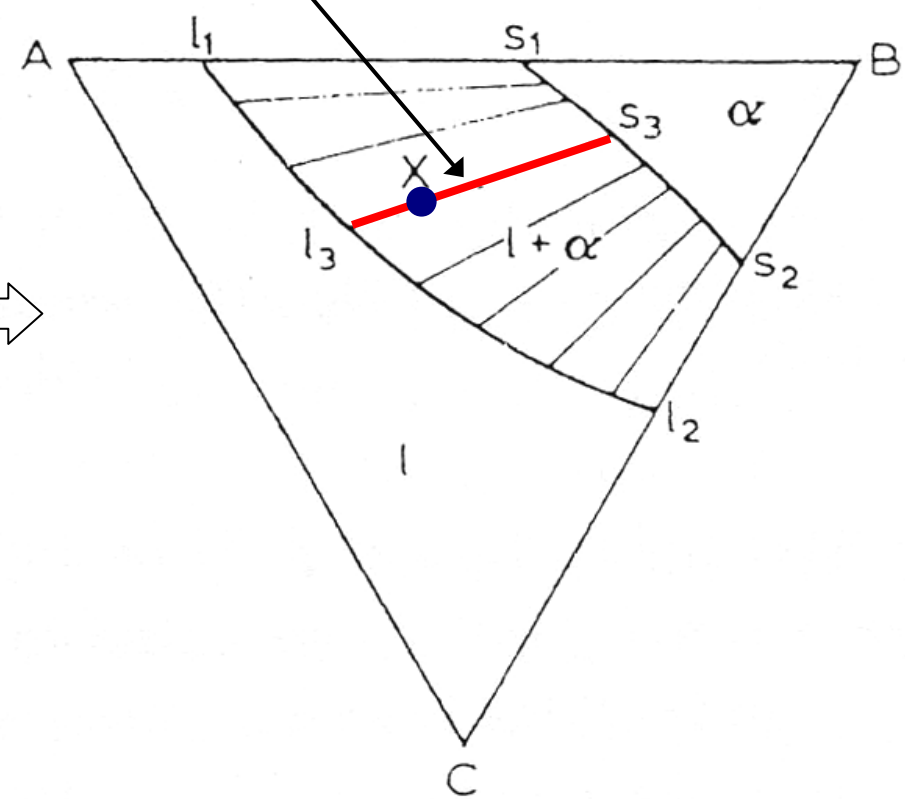
## 8.4.1 Two-phase equilibrium between the liquid and a solid solution

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

**Ternary Isomorphous System**




**Tie line $l_3s_3$**
**(conjugate phase $l_3$ and $s_3$)**



# 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.

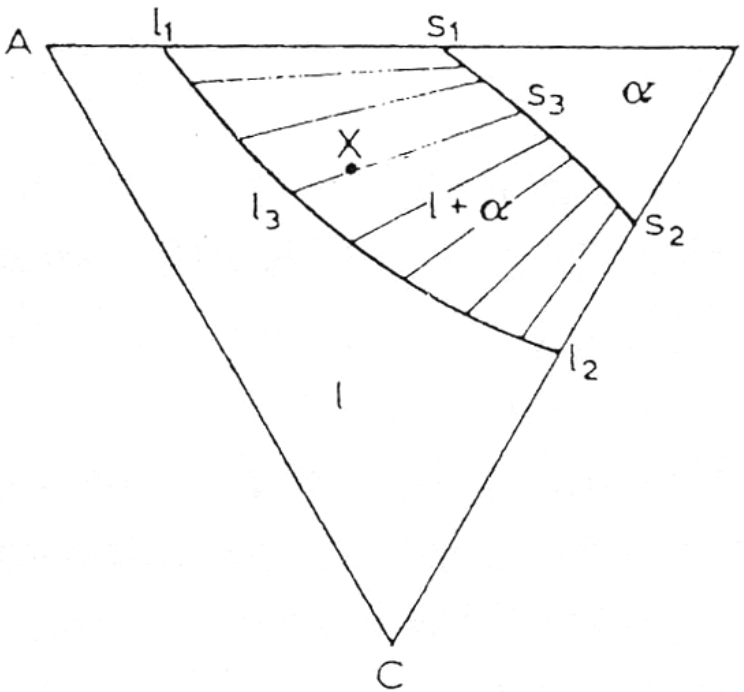
(iii) Extension of tie line cannot intersect the vertex of triangle.

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

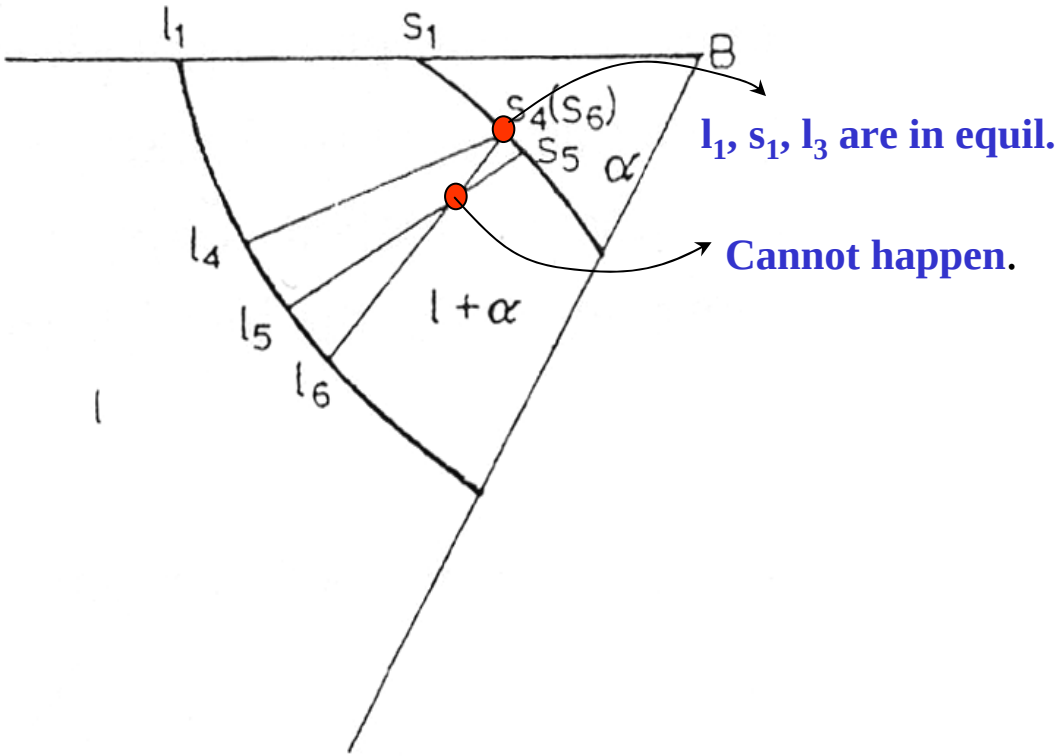
# 8.4 TWO-PHASE EQUILIBRIUM

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

**(i) Slope gradually changes.**



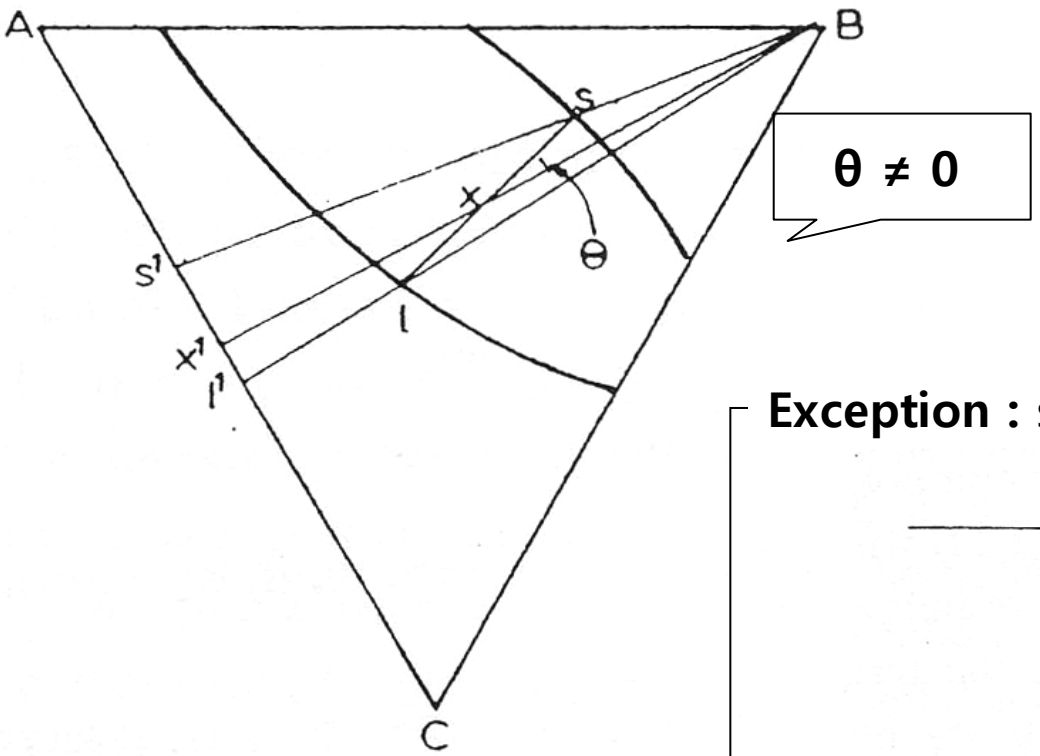

**(ii) Tie lines cannot intersect.**



# 8.4 TWO-PHASE EQUILIBRIUM

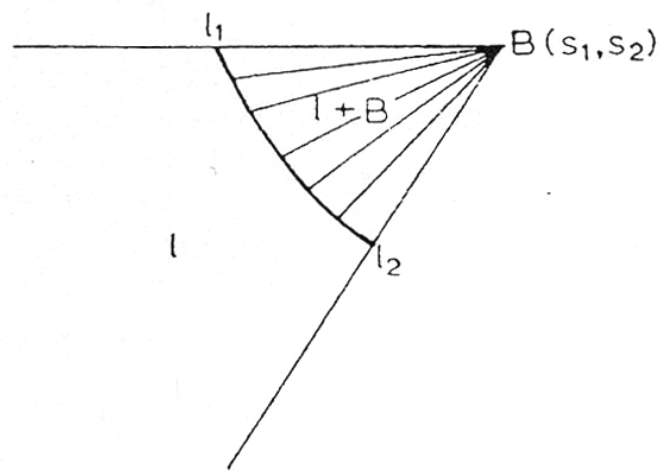
## 8.4.1 Two-phase equilibrium between the liquid and a solid solution

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




$\theta \neq 0$

**Exception :** solubility is infinitely small.

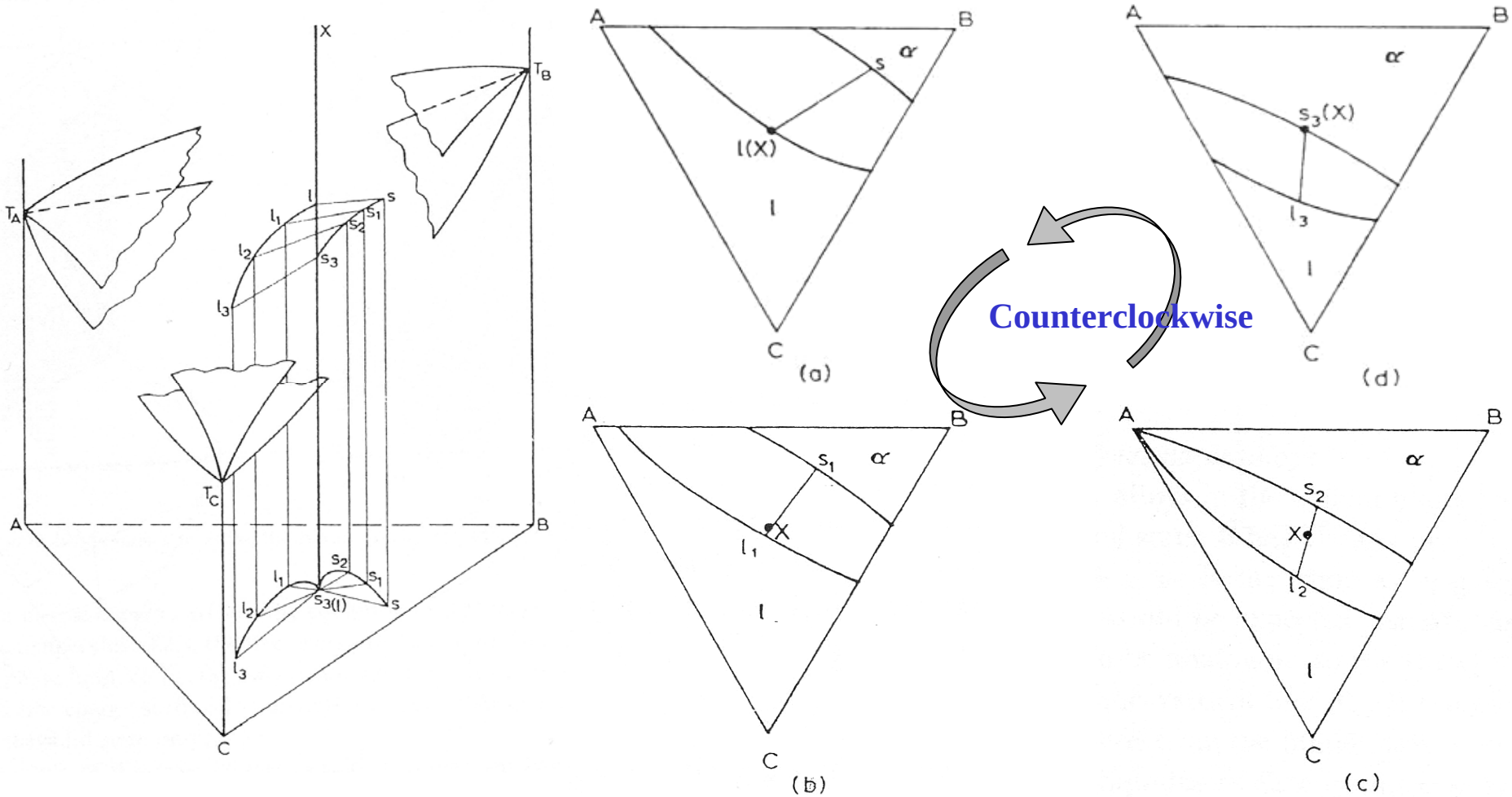


# 8.4 TWO-PHASE EQUILIBRIUM

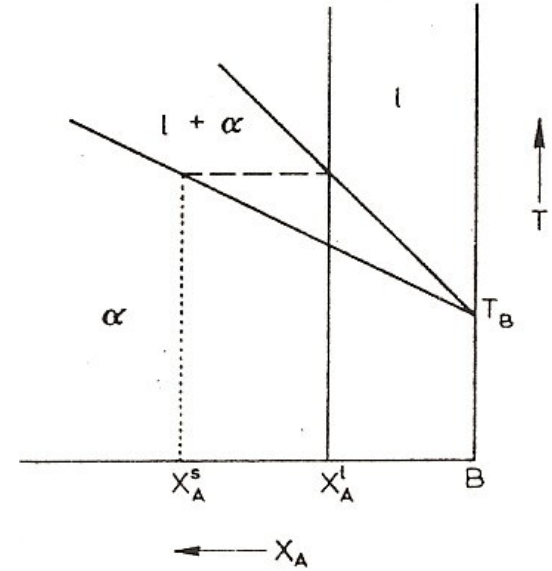
## 8.4.1 Two-phase equilibrium between the liquid and a solid solution

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

: Clockwise or counterclockwise



**This rotation coincides with the direction of highest melting point component to the lowest.**




**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

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

$$X_A^S > X_A^l$$

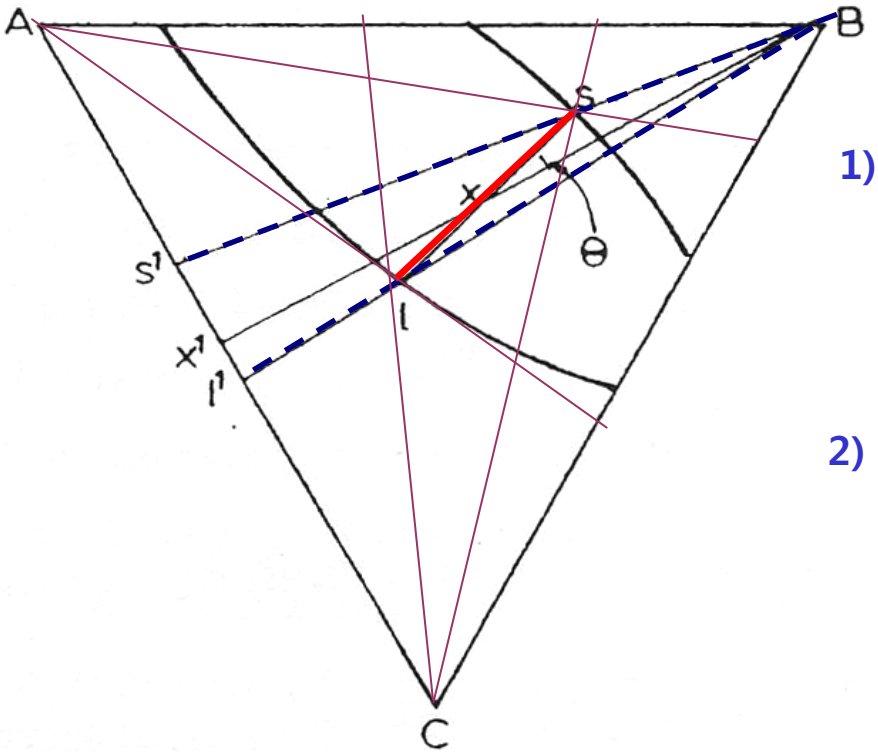
and

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

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.**




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

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

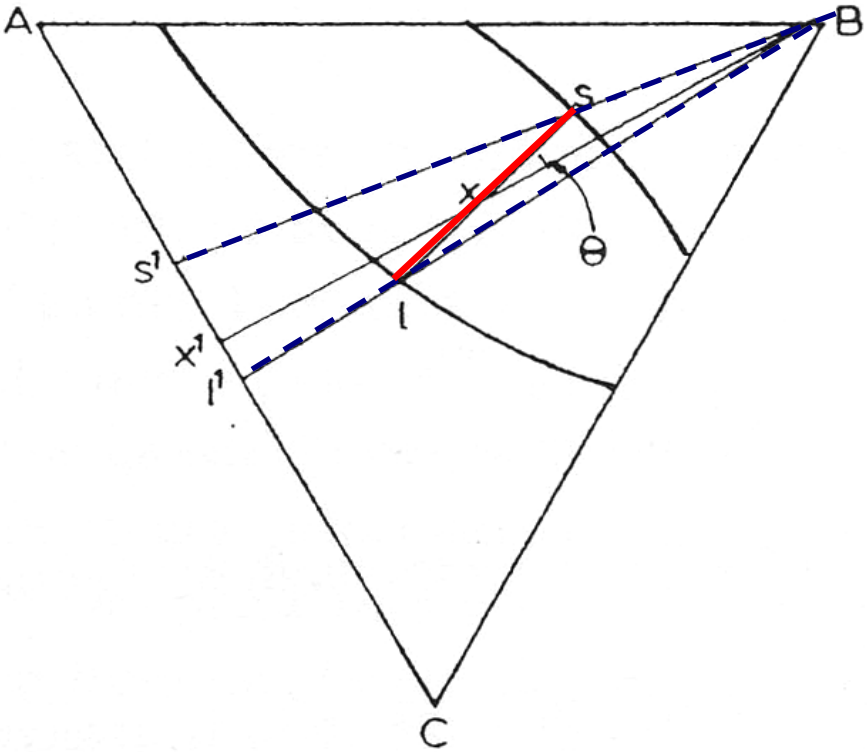
$$\frac{s^1 C}{s^1 A} > \frac{l^1 C}{l^1 A} \quad \text{and} \quad \frac{X_A^s}{X_C^s} > \frac{X_A^l}{X_C^l}$$

**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**



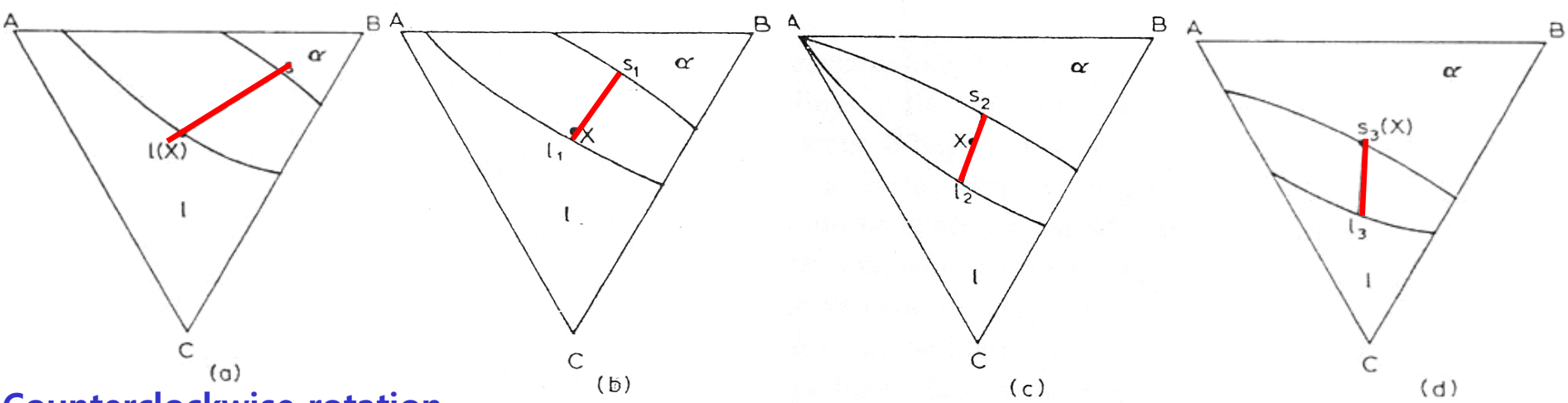

**The tie line ls is rotated anticlockwise by an angle Θ relative to the line Bx[1].**

$$\Theta = 0$$

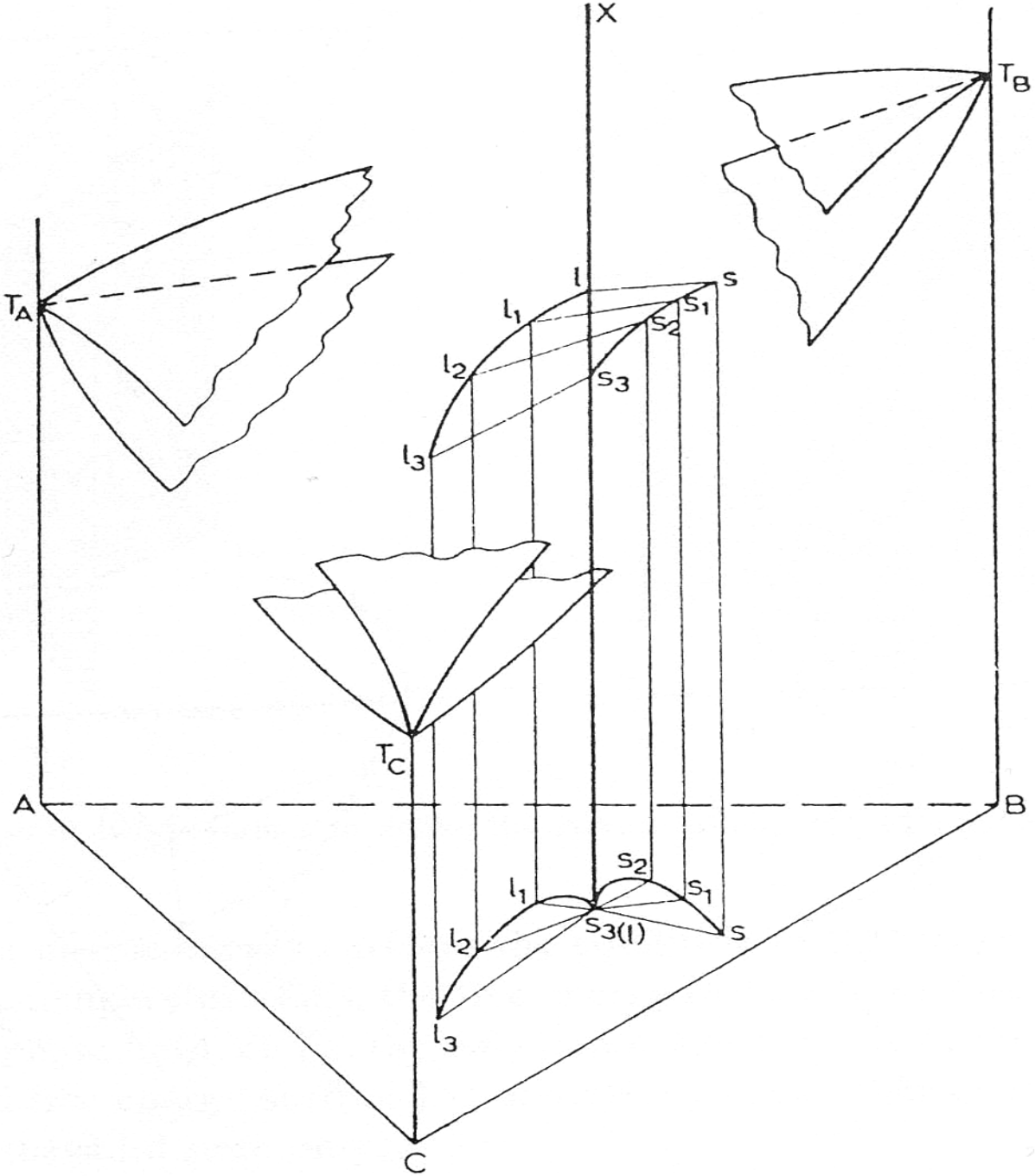
*then* $$X_A^S / X_C^S = X_A^l / X_C^l$$

**in contradiction to Konovalov's Rule.**

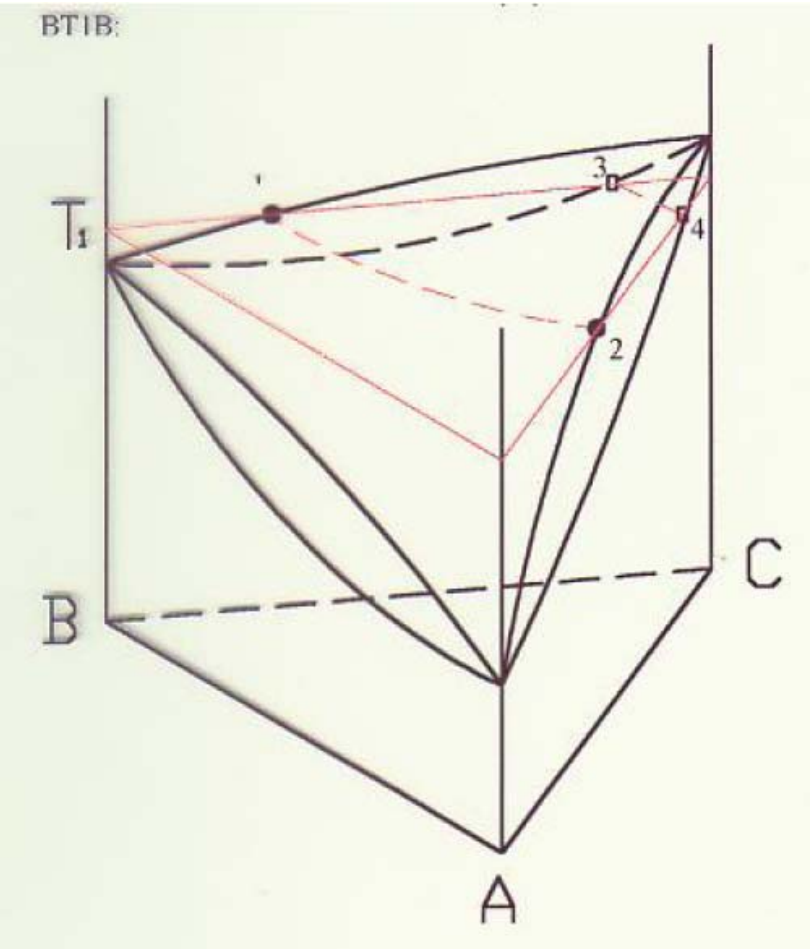
➡ **Tie lines when produced do not intersect the corner of the concentration triangle.**

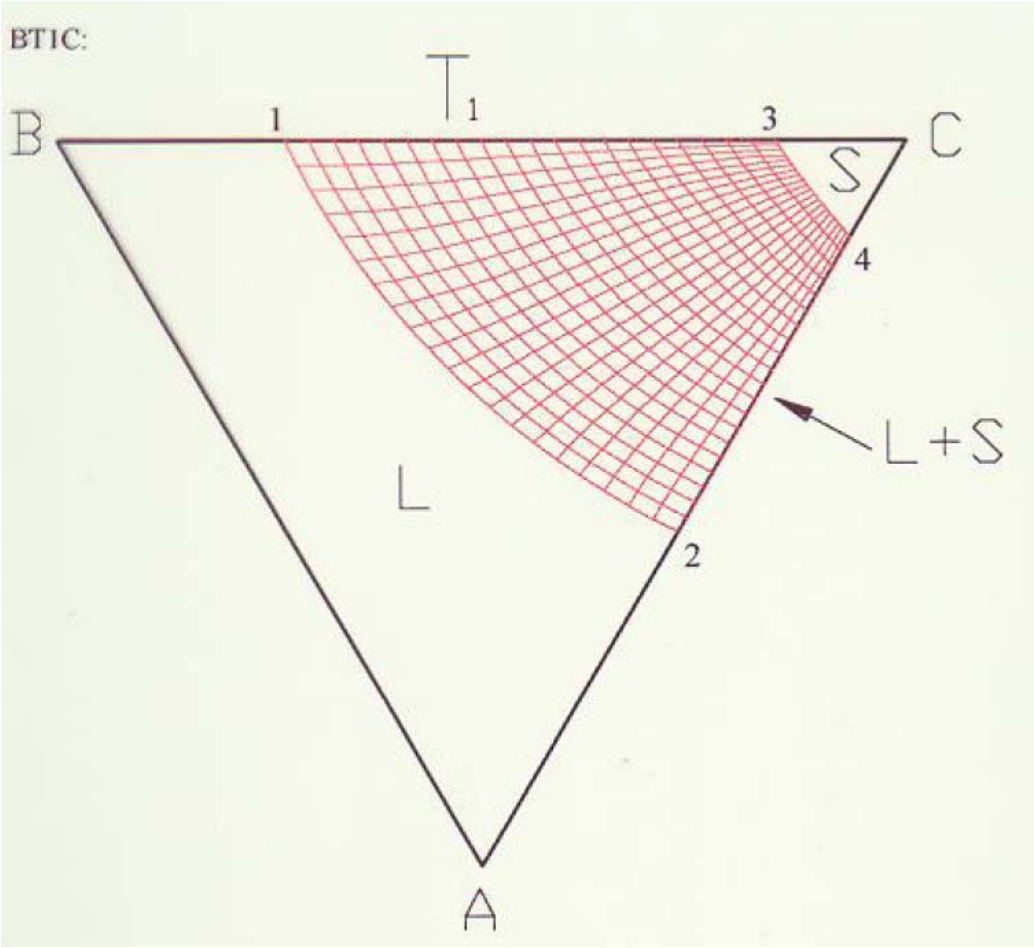



**Counterclockwise rotation**

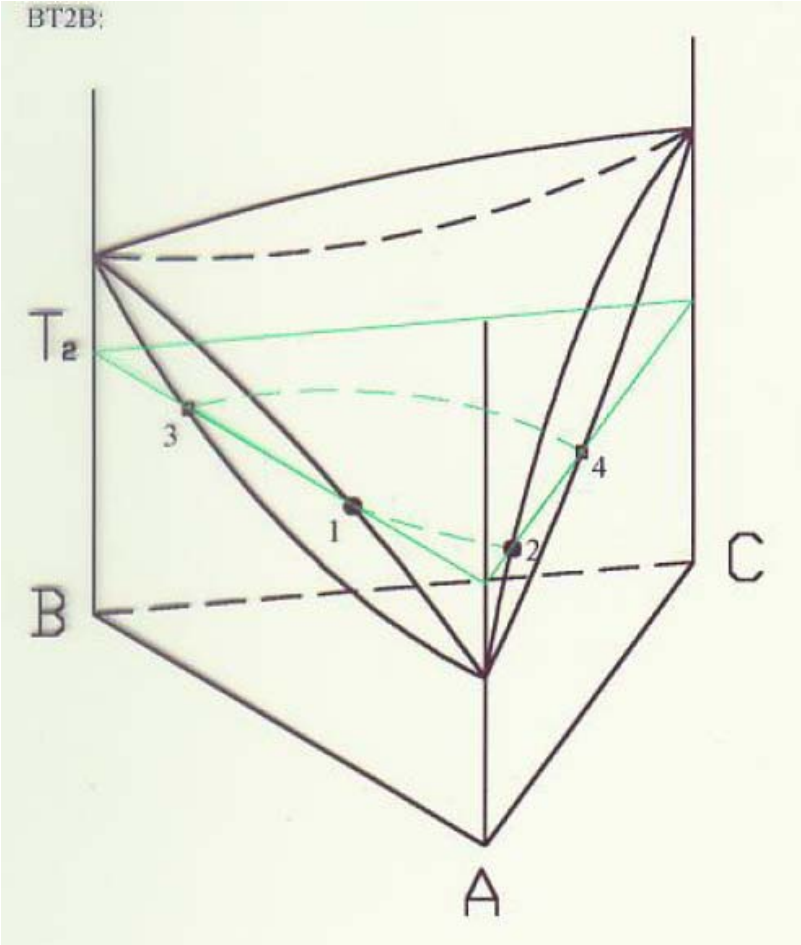

X
$T_B$
$T_A$
l
s
$l_1$
$s_1$
$s_2$
$l_2$
$s_3$
$l_3$
$T_C$
A
B
$s_2$
$l_1$
$s_1$
$l_2$
$s_{3(l)}$
s
$l_3$
C

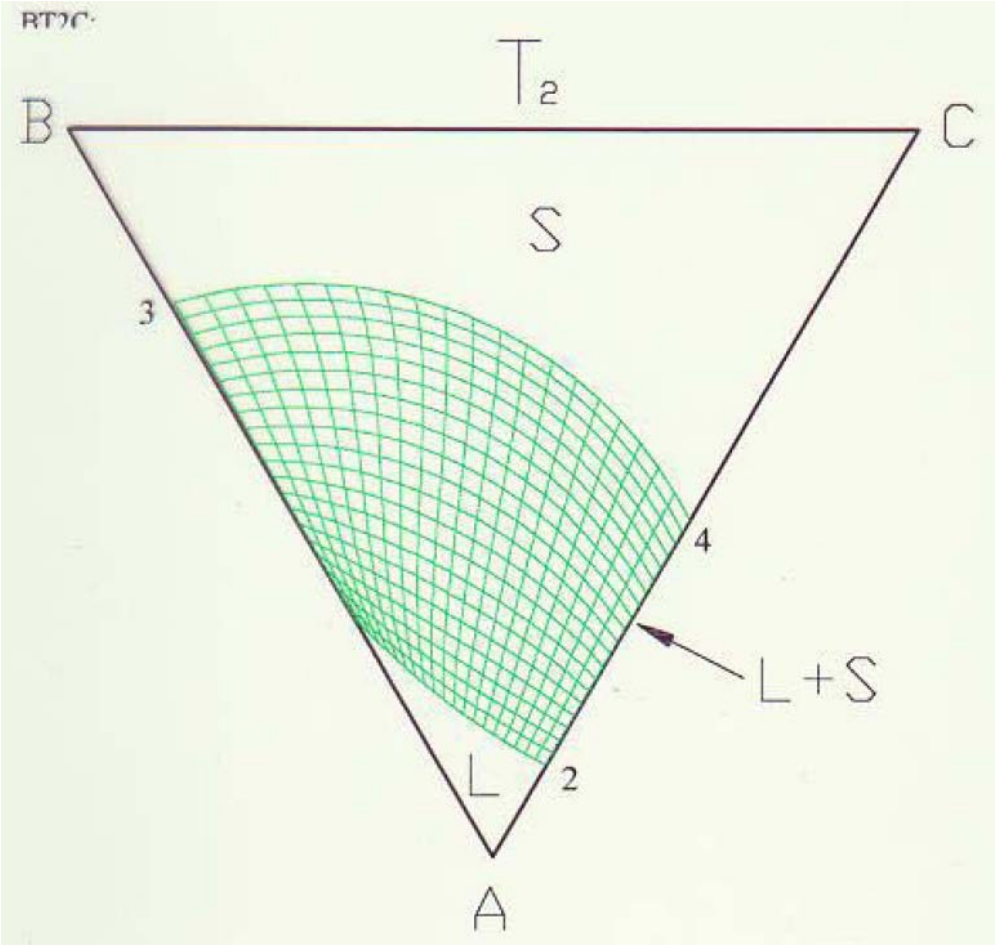
# Counterclockwise rotation



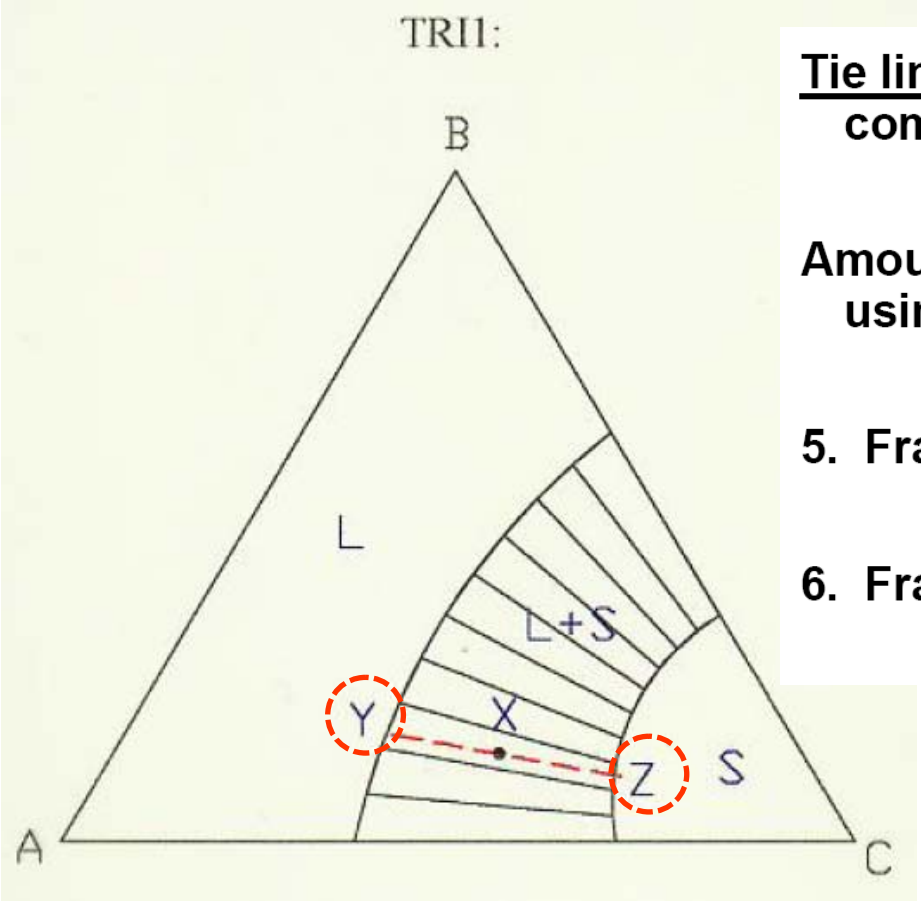
# Counterclockwise rotation



# Ternary Isomorphous System

## Locate overall composition using Gibbs triangle




<u>Tie line</u>: 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

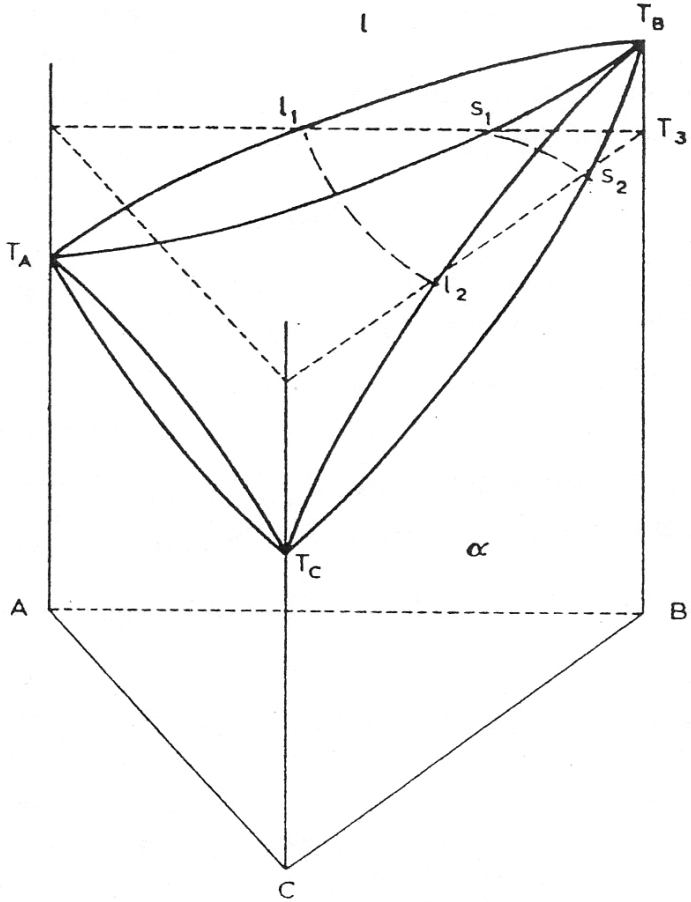
# 8.4 TWO-PHASE EQUILIBRIUM

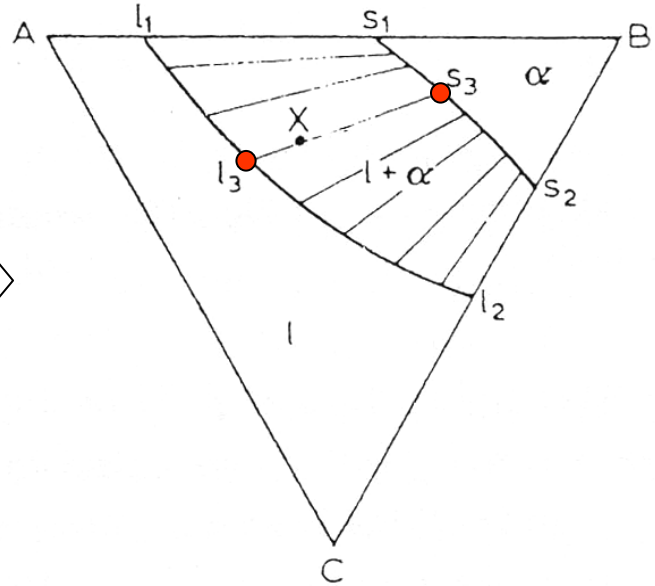
## 8.4.1 Two-phase equilibrium between the liquid and a solid solution

**Two phase equilibrium ( f = 2 )**

→ T, $X_A^l$, $X_B^l$ ($X_C^l$), $X_A^\alpha$, $X_B^\alpha$ ($X_C^\alpha$)

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




→ Comp. of liq ( $X_B^l$, $X_C^l$ )

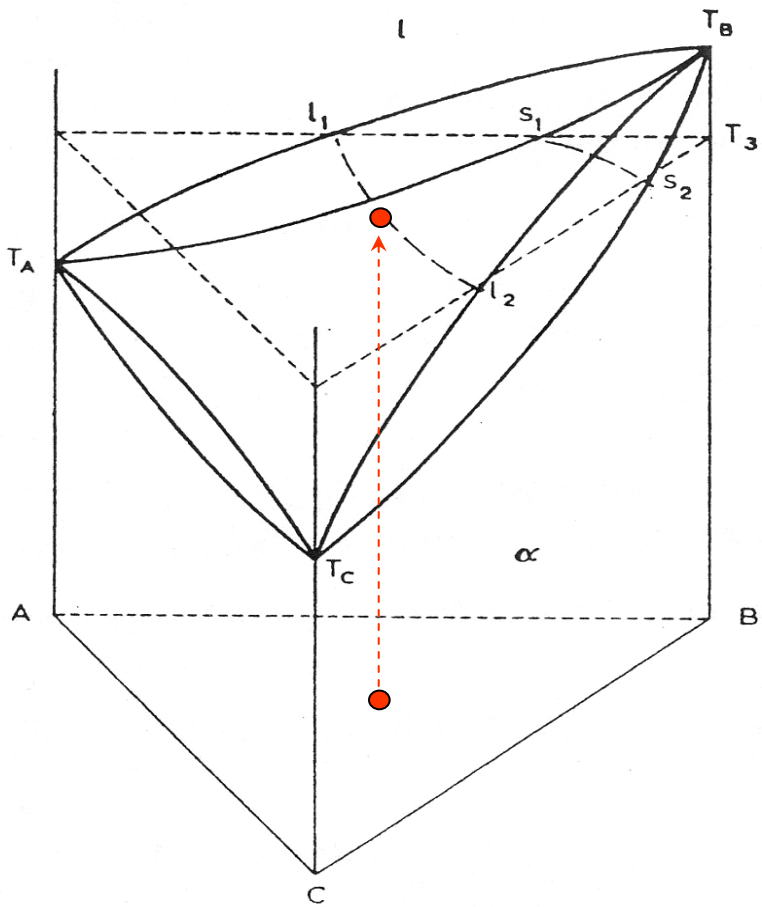
→ Tie line

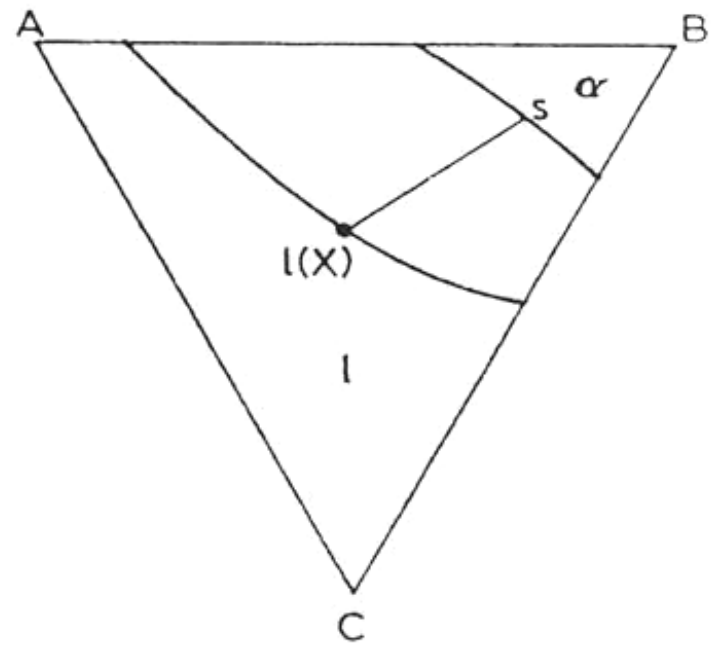
→ Comp. of solid ( $X_A^\alpha$, $X_B^\alpha$, $X_C^\alpha$ )

# 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

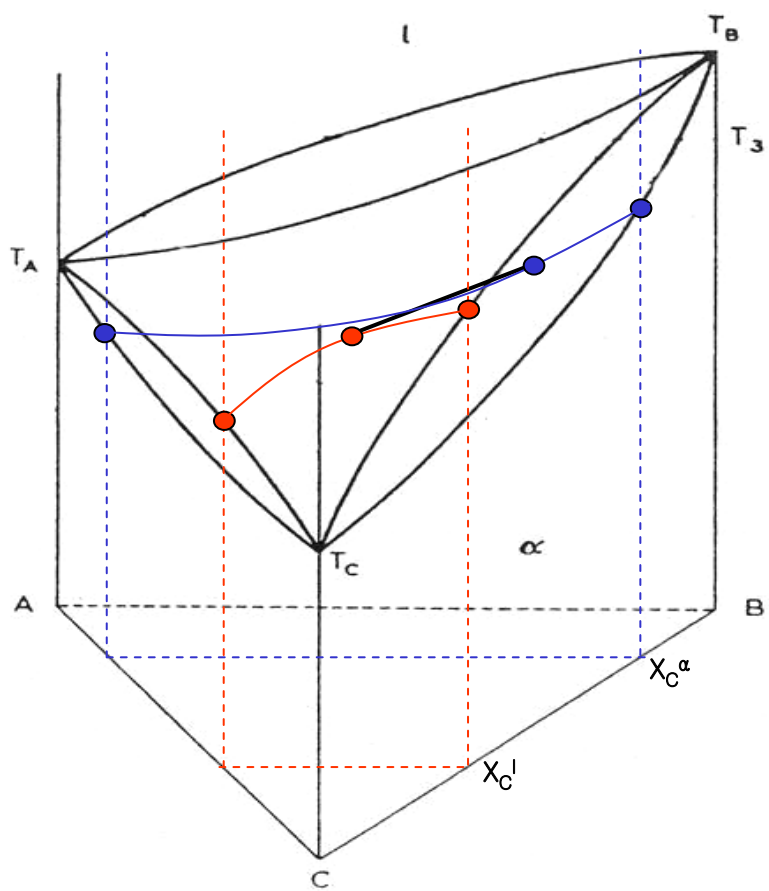
→ Temp. T

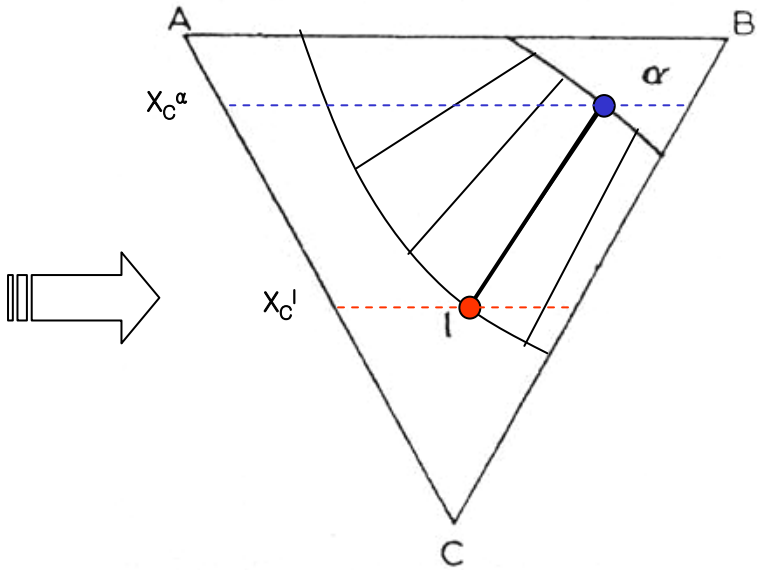
→ Two phase region

# 8.4 TWO-PHASE EQUILIBRIUM

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

③ If we know $X_C^l$, $X_C^\alpha$, we can know composition of liq & sol.




→ $X_c^\alpha$ & $X_C^l$ come closer

→ Will intersect at only one point.

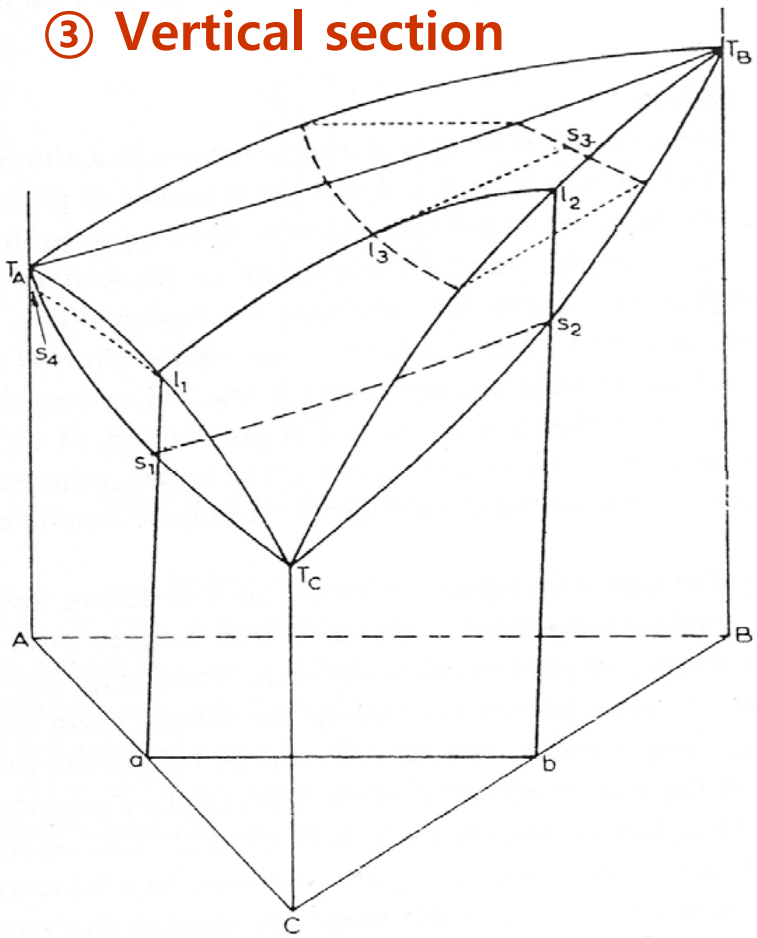
→ Temperature, tie line

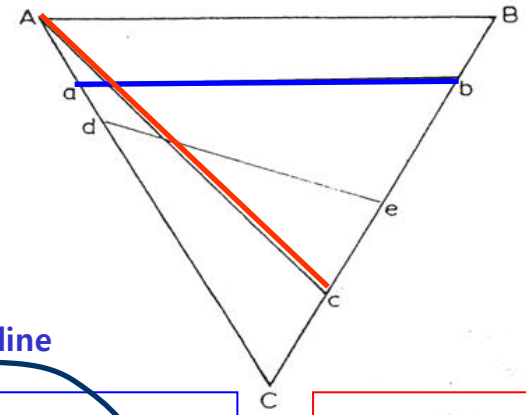
→ Composition of liq. & sol.

# 8.4 TWO-PHASE EQUILIBRIUM

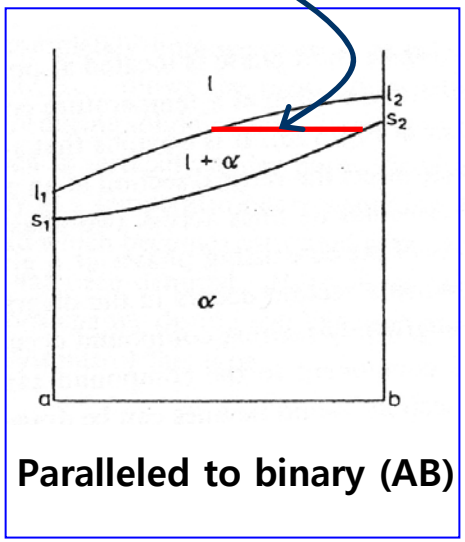
## 8.4.1 Two-phase equilibrium between the liquid and a solid solution

### ③ Vertical section

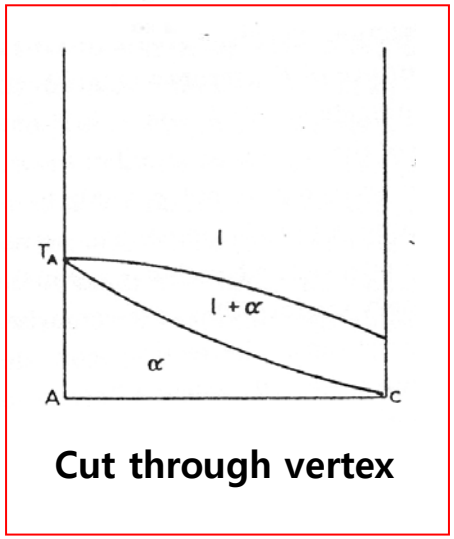



No tie line &
No conjugate line




Paralleled to binary (AB)




Cut through vertex

① Useful for effect of 3rd alloying element

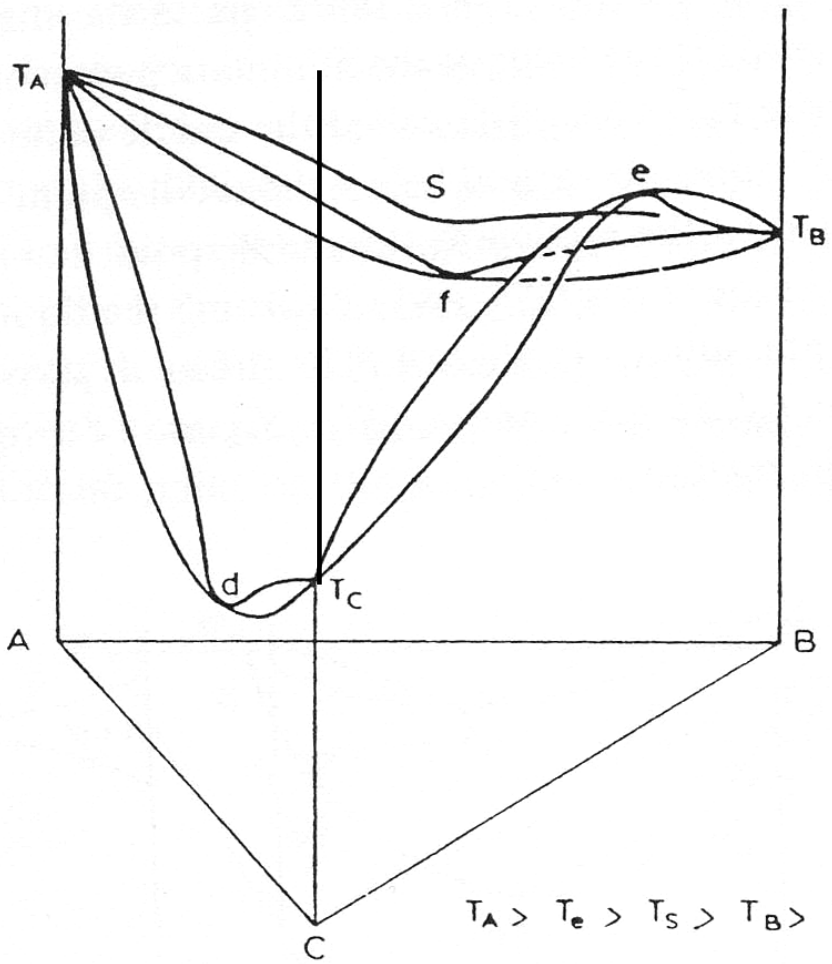
However, it is not possible to draw horizontal tie lines across two-phase regions in vertical sections to indicate the true compositions of the co-existing phases at a given temperature.

② Congruent melting phase

: composition does not change when liq. ↔ sol. transform occurs.

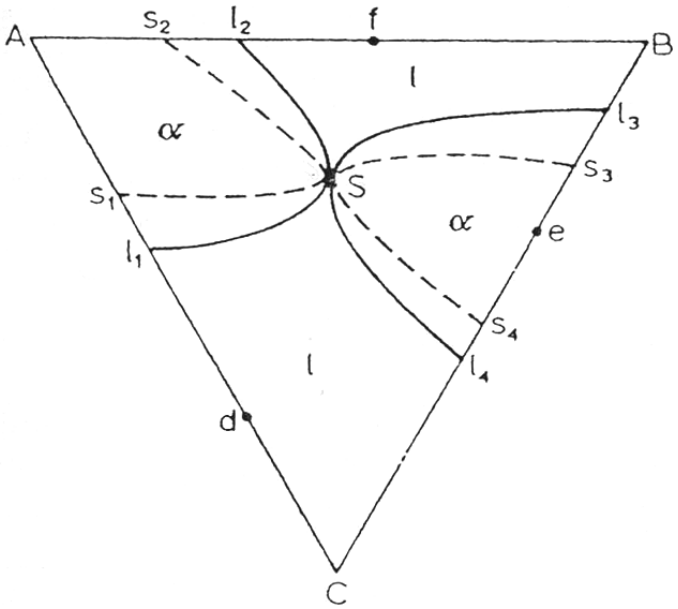
# 8.4.2 Variants of the phase diagram
(more complex system)

## Ternary two-phase equilibrium with a saddle point

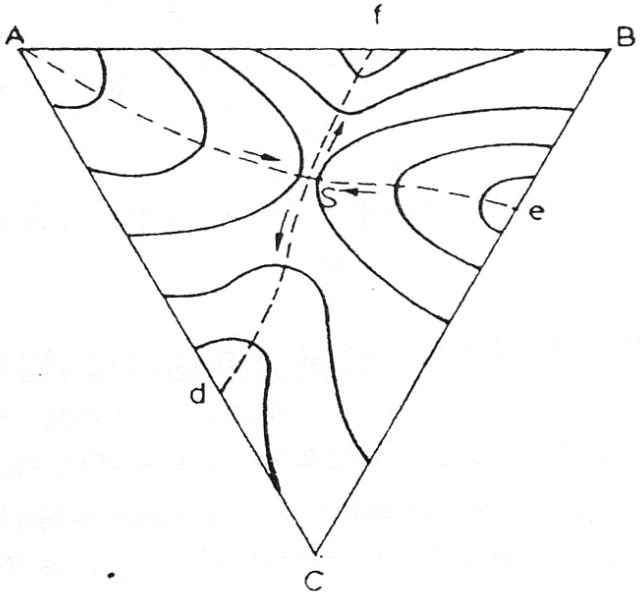



$T_A > T_e > T_S > T_B > T_f > T_C > T_d$

## Isothermal section ($T=T_s$)

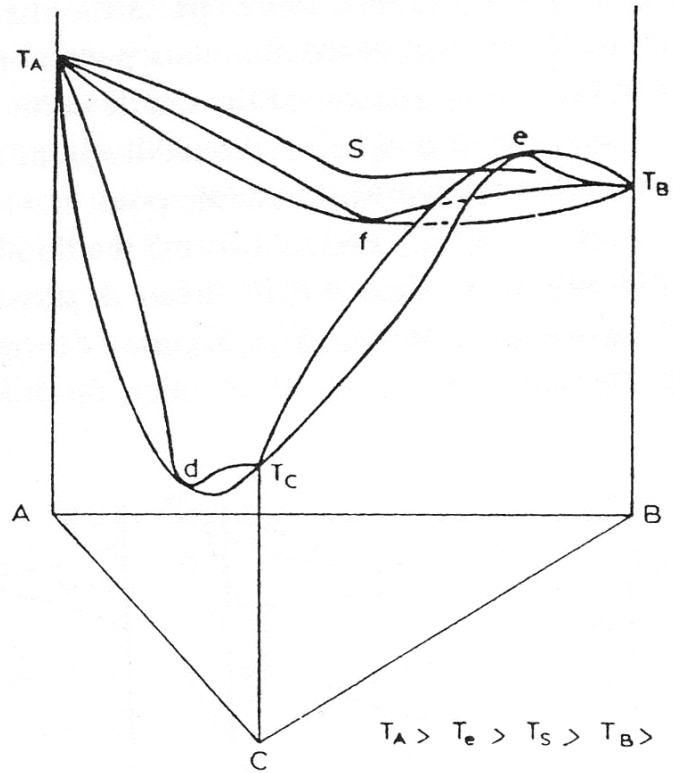



## Projection of liquidus isotherms



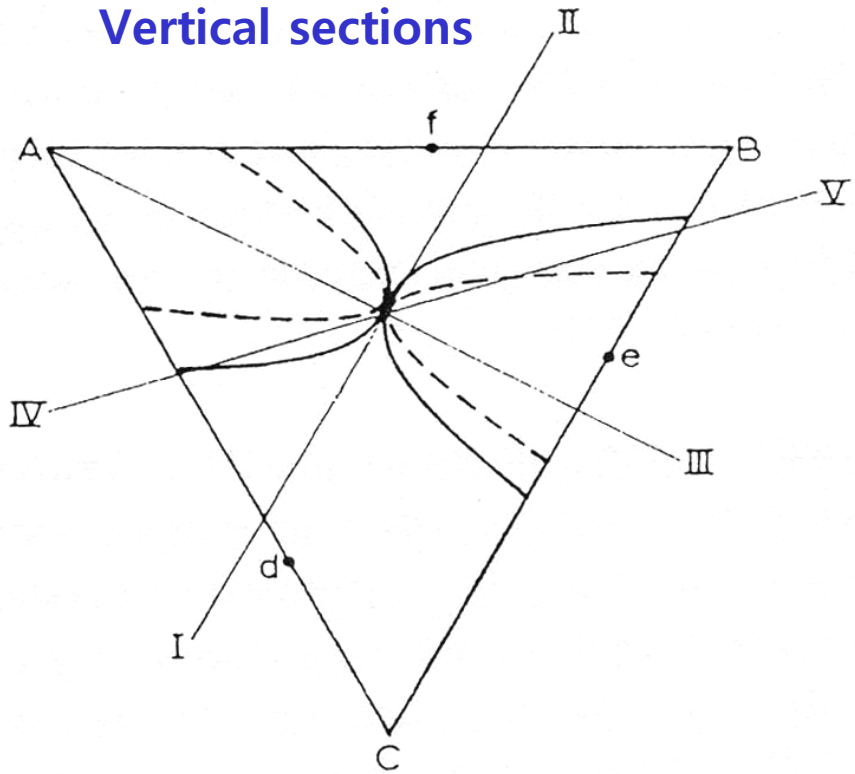

**S : saddle pt. where liquidus & solidus surfaces meet**

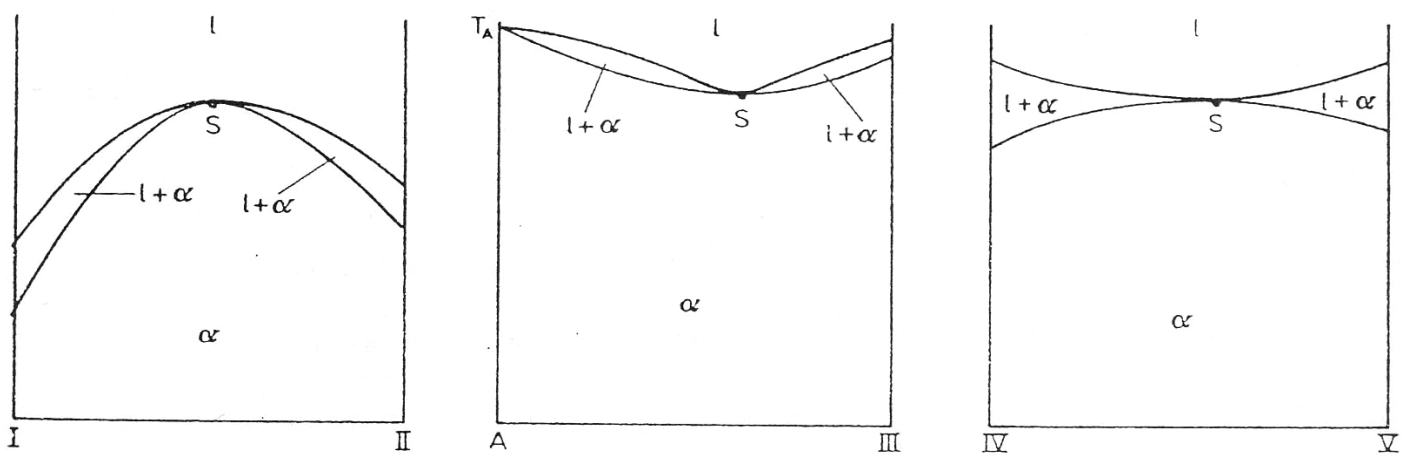
# 8.4.2 Variants of the phase diagram
## (more complex system)




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

**Vertical sections**



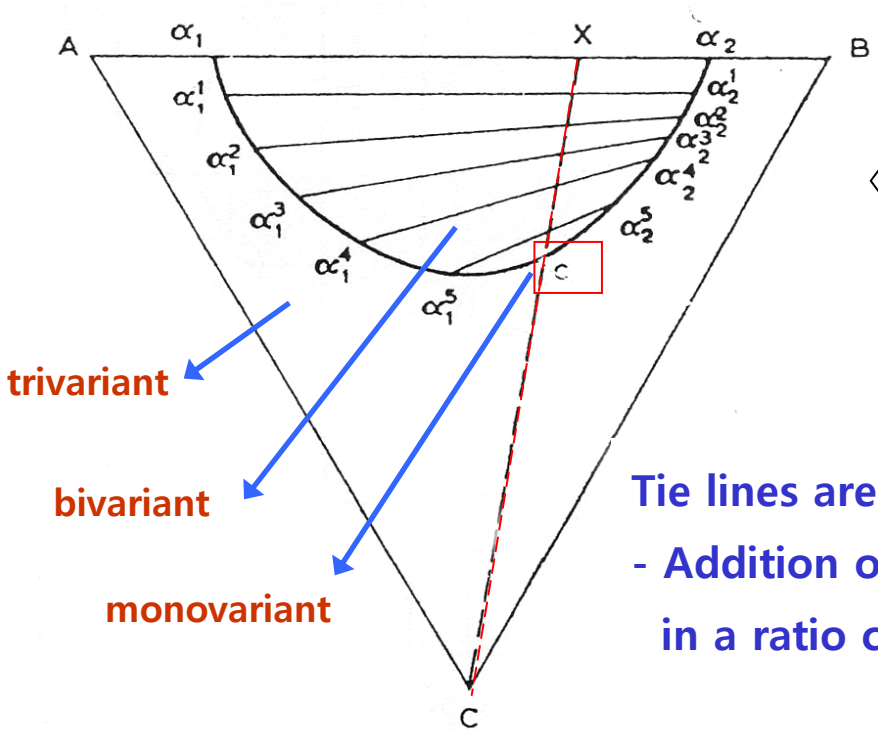
# 8.4 TWO-PHASE EQUILIBRIUM

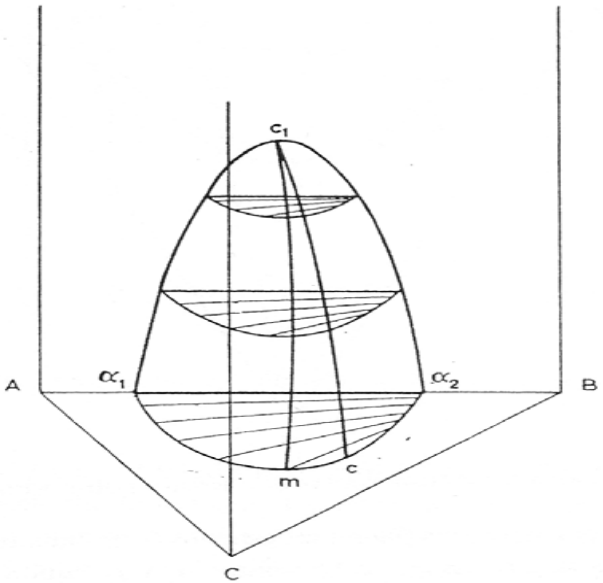
## 8.4.3. Two-phase equilibrium between solid or liquid solutions: $\alpha_1 \rightleftarrows \alpha_2$ or $l_1 \rightleftarrows l_2$

**Miscibility gap**

- **A ternary system with only a binary critical point**

  - **Isothermal section at room temp.**




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

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

**C : critical point**

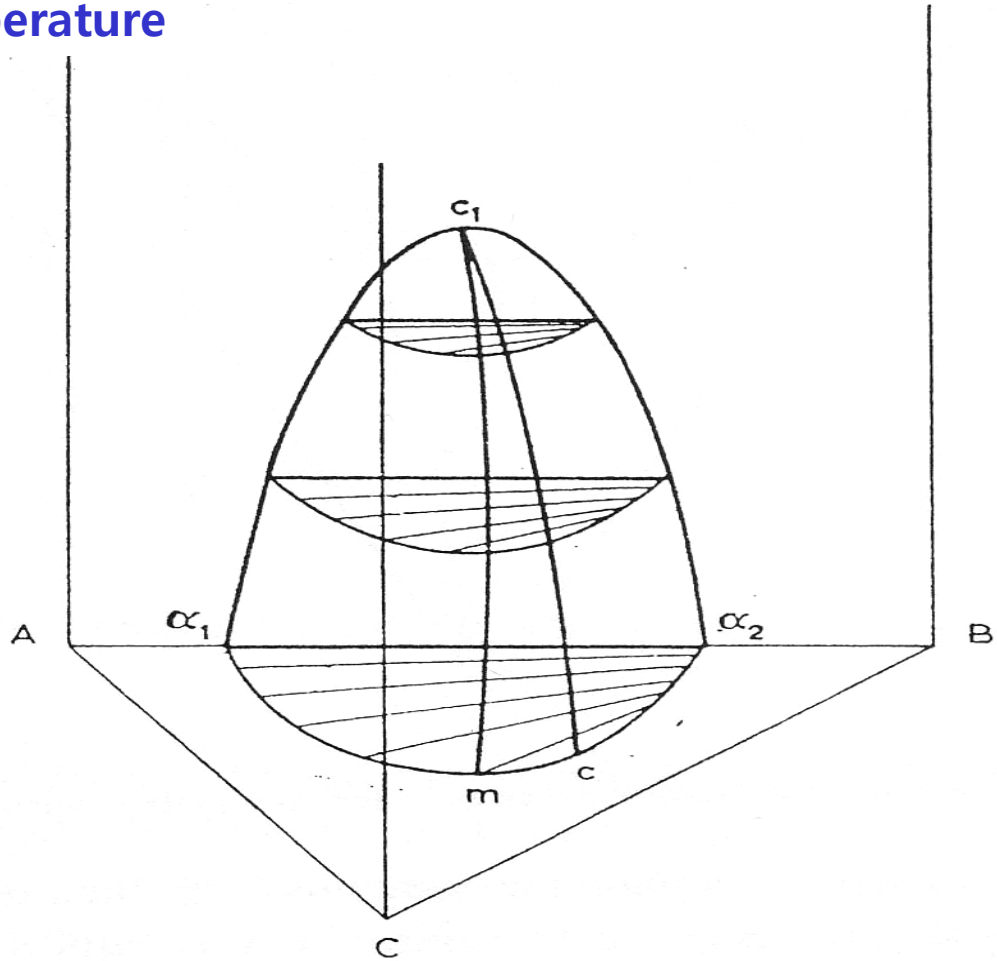
**( Max. point ≠ critical point in most cases )**

# 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**

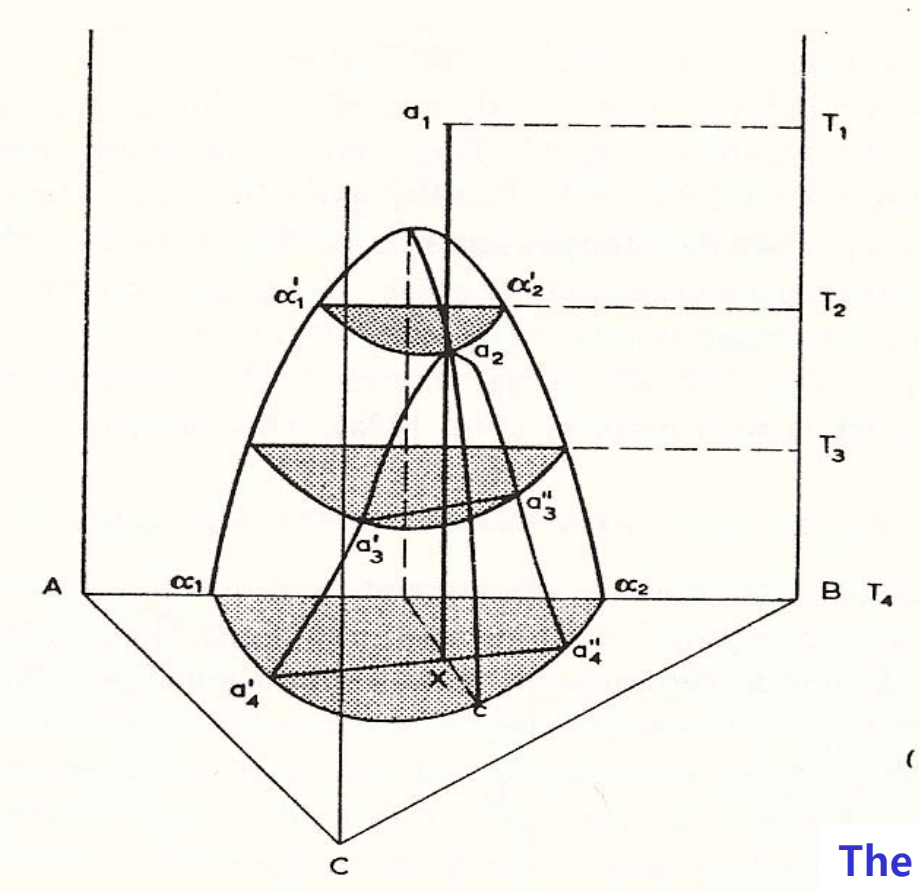
- **A ternary system with a closed miscibility gap associated with a binary critical point $c_1$**
  - **effect of temperature**

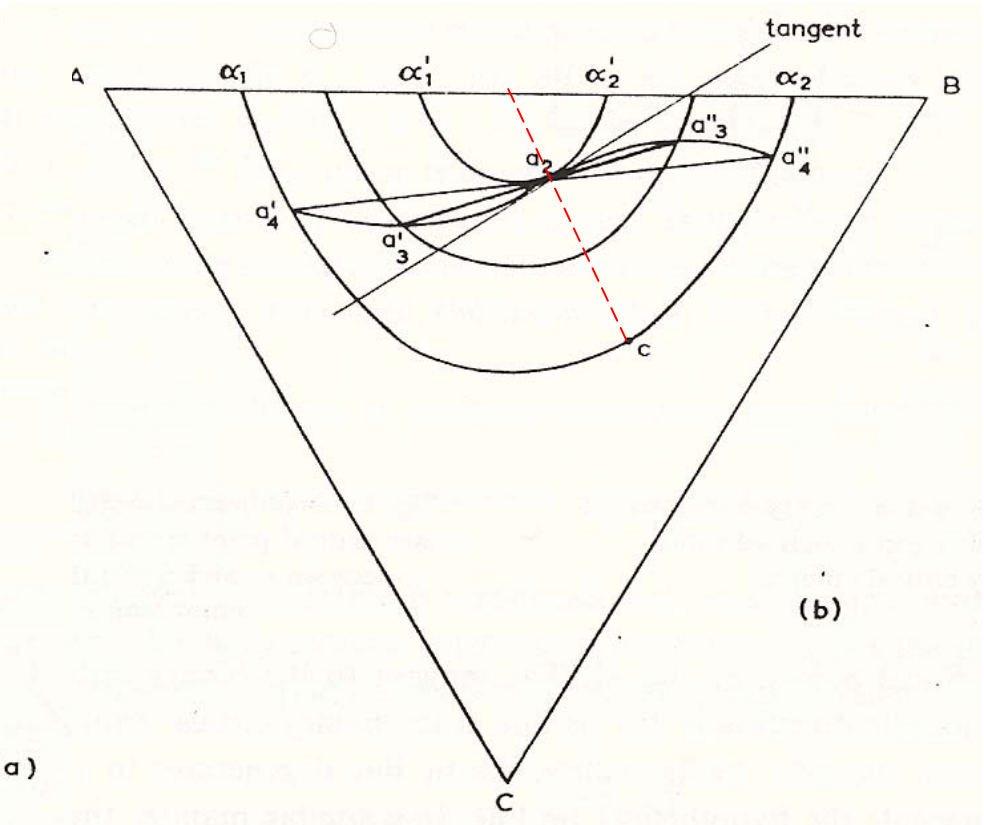


## 8.4.3. Two-phase equilibrium between solid or liquid solutions: $\alpha_1 \rightleftarrows \alpha_2$ or $l_1 \rightleftarrows l_2$

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

(b) Changes in composition of the co-exisitng $\alpha_1$ and $\alpha_2$ phases

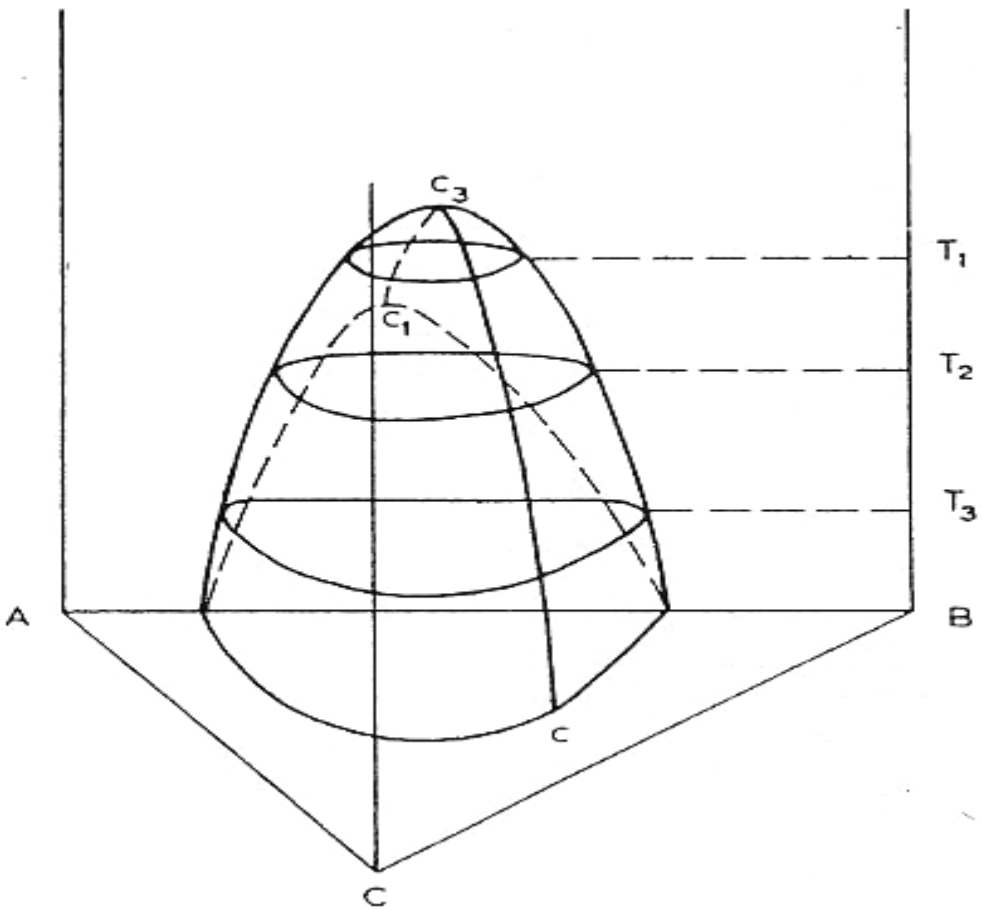


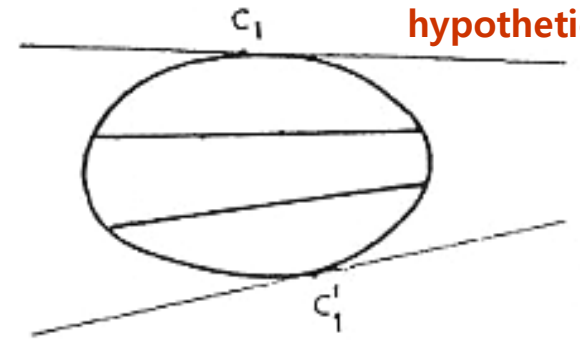

The course of the curves is defined by the relative position of the tie lines which skew round towards the side AB as the temperature decreases.

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

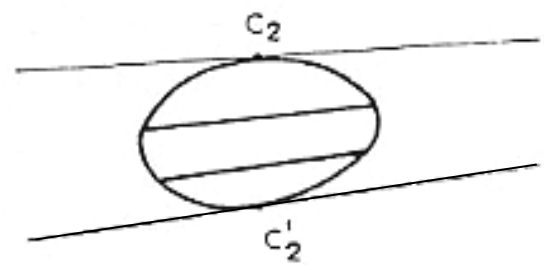
- **A ternary system with a binary and a ternary critical point**



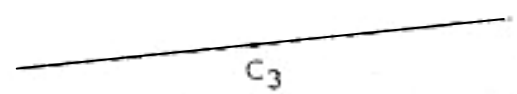

## Isotherms




(a) The binary critical point temperature

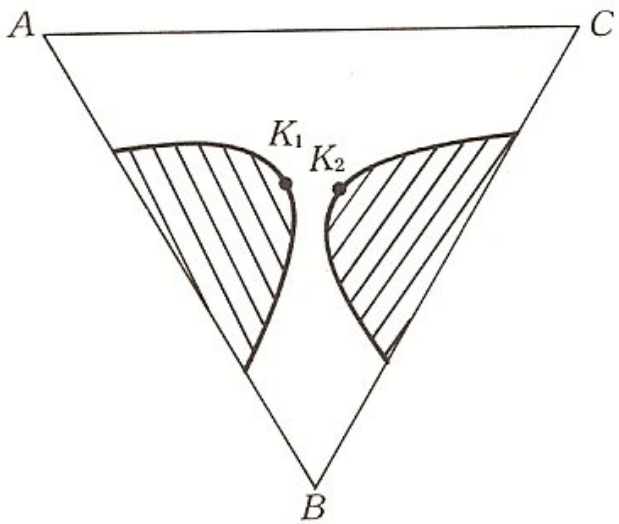


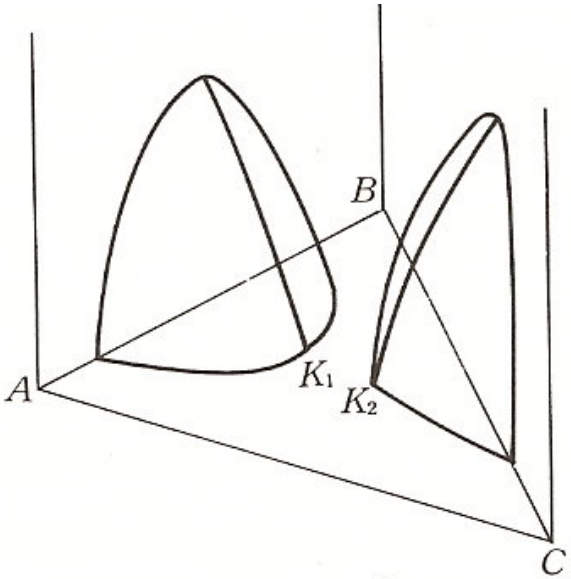

(b) A temperature between $c_1$ and $c_3$

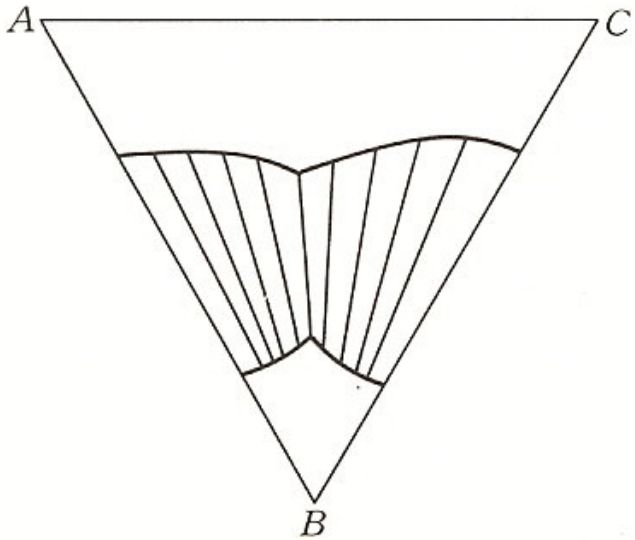


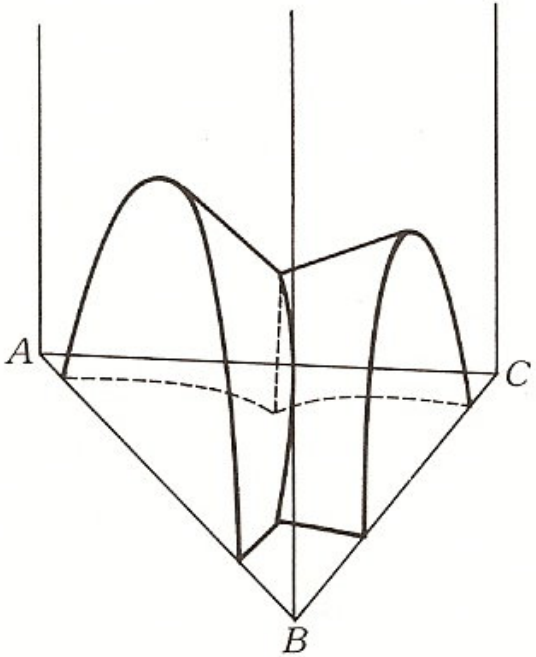

(c) The ternary critical point temperature

- **A ternary system with two miscibility gaps**

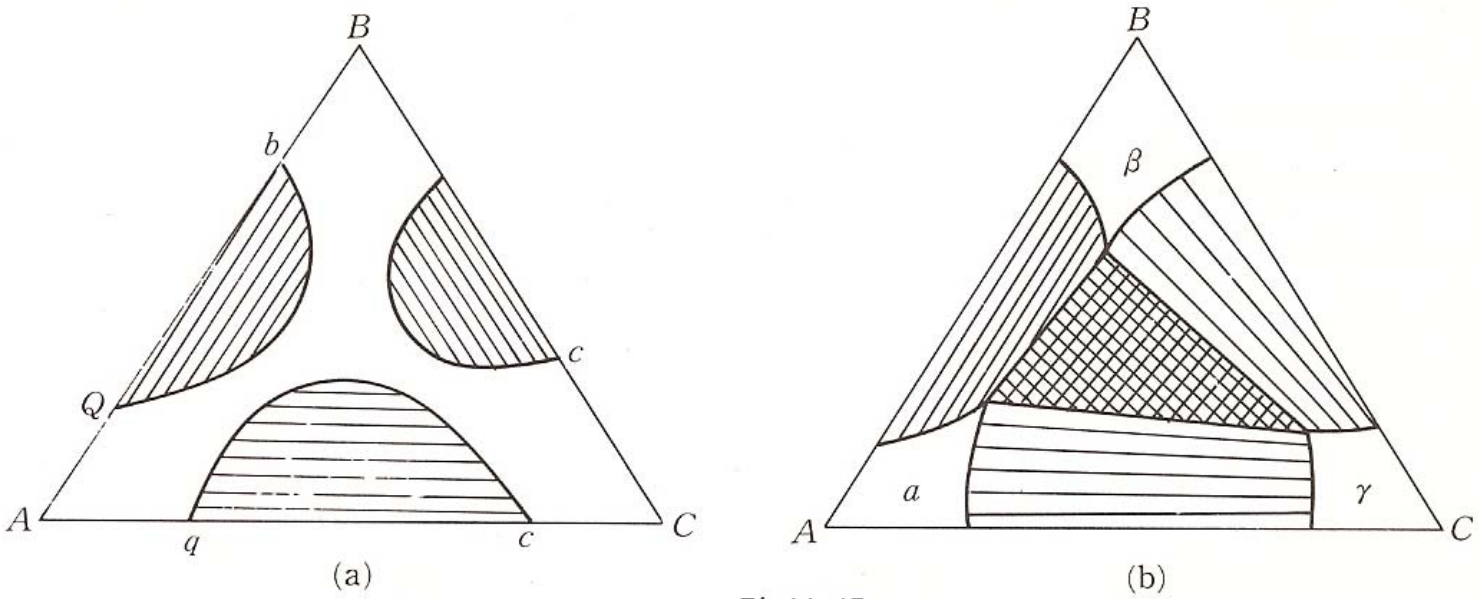


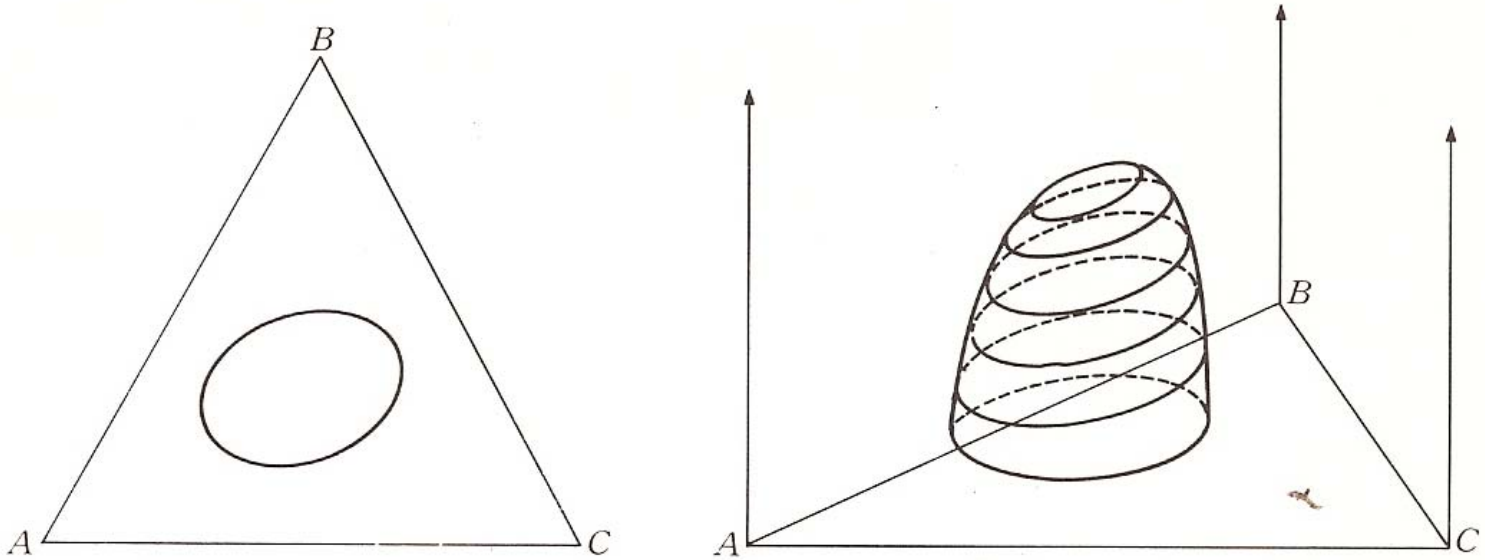



- **A ternary system with three miscibility gaps**




- **A ternary system with miscibility gap in three component region**