2018 Fall

"Phase Transformation *in* Materials"

09.27.2018

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Contents for previous class:

- **Gibbs Phase Rule** $F = C - P + 1$ **(constant pressure)**

  Gibbs' Phase Rule allows us to construct phase diagram to represent and interpret phase equilibria in heterogeneous geologic systems.

- **Effect of Temperature on Solid Solubility**

$$X_B^e = A\exp\left\{-\frac{Q}{RT}\right\}$$ **a)** $T \uparrow \Rightarrow X_B^e \uparrow$ **b)** X_B^e **can never be equal to zero.**

- **Equilibrium Vacancy Concentration**

$$X_V^e = \exp\frac{-\Delta G_V}{RT}$$

- **Influence of Interfaces on Equilibrium**

$$\Delta G = \frac{2\gamma V_m}{r}$$ **Gibbs-Thomson effect**

- **Gibbs-Duhem Equation:** **Be able to calculate the change in chemical potential that result from a change in alloy composition.**

$$X_A X_B \frac{d^2 G}{dX^2} = RT\left\{1 + \frac{d\ln\gamma_A}{d\ln X_A}\right\} = RT\left\{1 + \frac{d\ln\gamma_B}{d\ln X_B}\right\}$$

합금조성의 미소변화 (dX)로 인한 화학퍼텐셜의 미소변화(**dμ**) 를 계산

Total Free Energy Decrease per Mole of Nuclei $\Delta G_0 = -V\Delta G_V + A\gamma + V\Delta G_s$

: 변태를 위한 전체 구동력/핵생성을 위한 구동력은 아님

Chapter 5.1

Driving Force for Precipitate Nucleation $\alpha \rightarrow \alpha + \beta$ ΔG_V

$$\Delta G_1 = \mu_A^{\alpha} X_A^{\beta} + \mu_B^{\alpha} X_B^{\beta}$$

: Decrease of total free E of system by removing a small amount of material with the nucleus composition (X_B^{β}) (P point)

$$\Delta G_2 = \mu_A^{\beta} X_A^{\beta} + \mu_B^{\beta} X_B^{\beta}$$

: Increase of total free E of system by forming β phase with composition X_B^{β} (Q point)

$$\Delta G_n = \Delta G_2 - \Delta G_1$$ (length PQ)

$$\Delta G_V = \frac{\Delta G_n}{V_m} \quad per\ unit\ volume\ of\ \beta$$

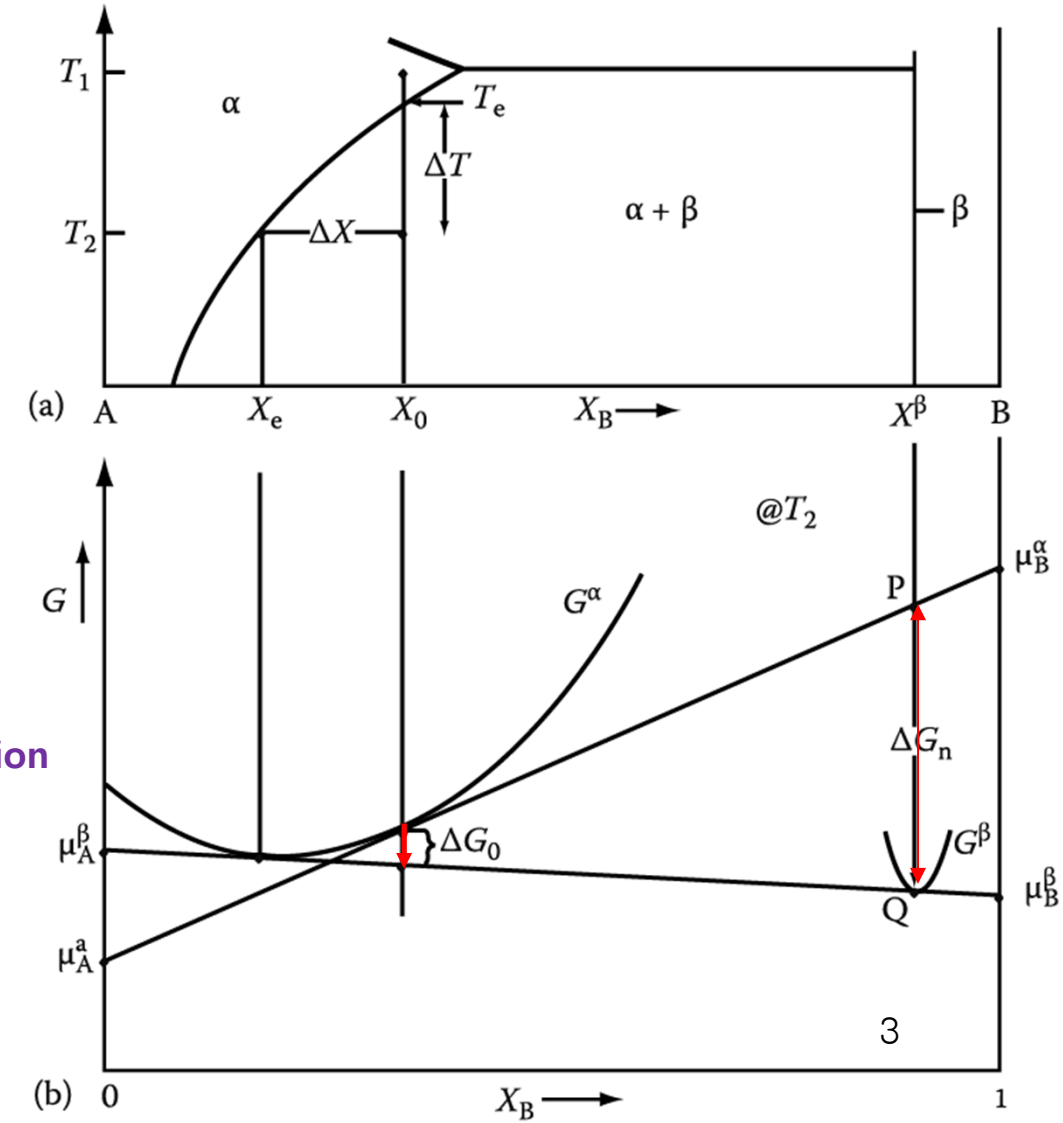
: driving force for β precipitation

For dilute solutions,

$$\Delta G_V \propto \Delta X \quad where\ \Delta X = X_0 - X_e$$

$$\Delta G_V \propto \Delta X \propto \Delta T$$

∝undercooling below T_e



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

Gibbs Phase Rule for 3-component Systems

$F = C + 2 - P$

For isobaric systems:

$F = C + 1 - P$

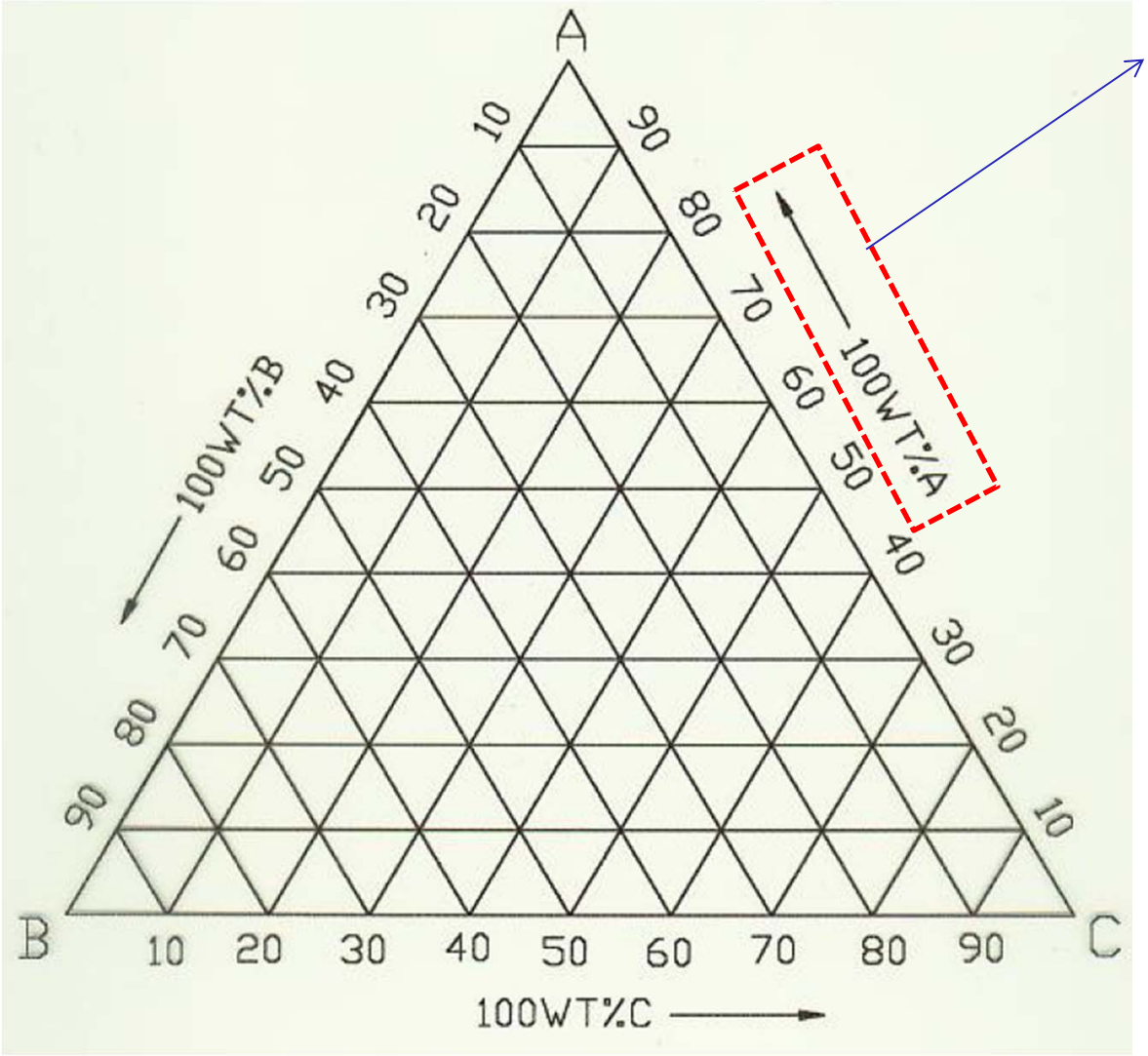
For C = 3, the maximum number of phases will co-exist when F = 0

P = 4 when C = 3 and F = 0

Components are “independent components”

Gibbs Triangle

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

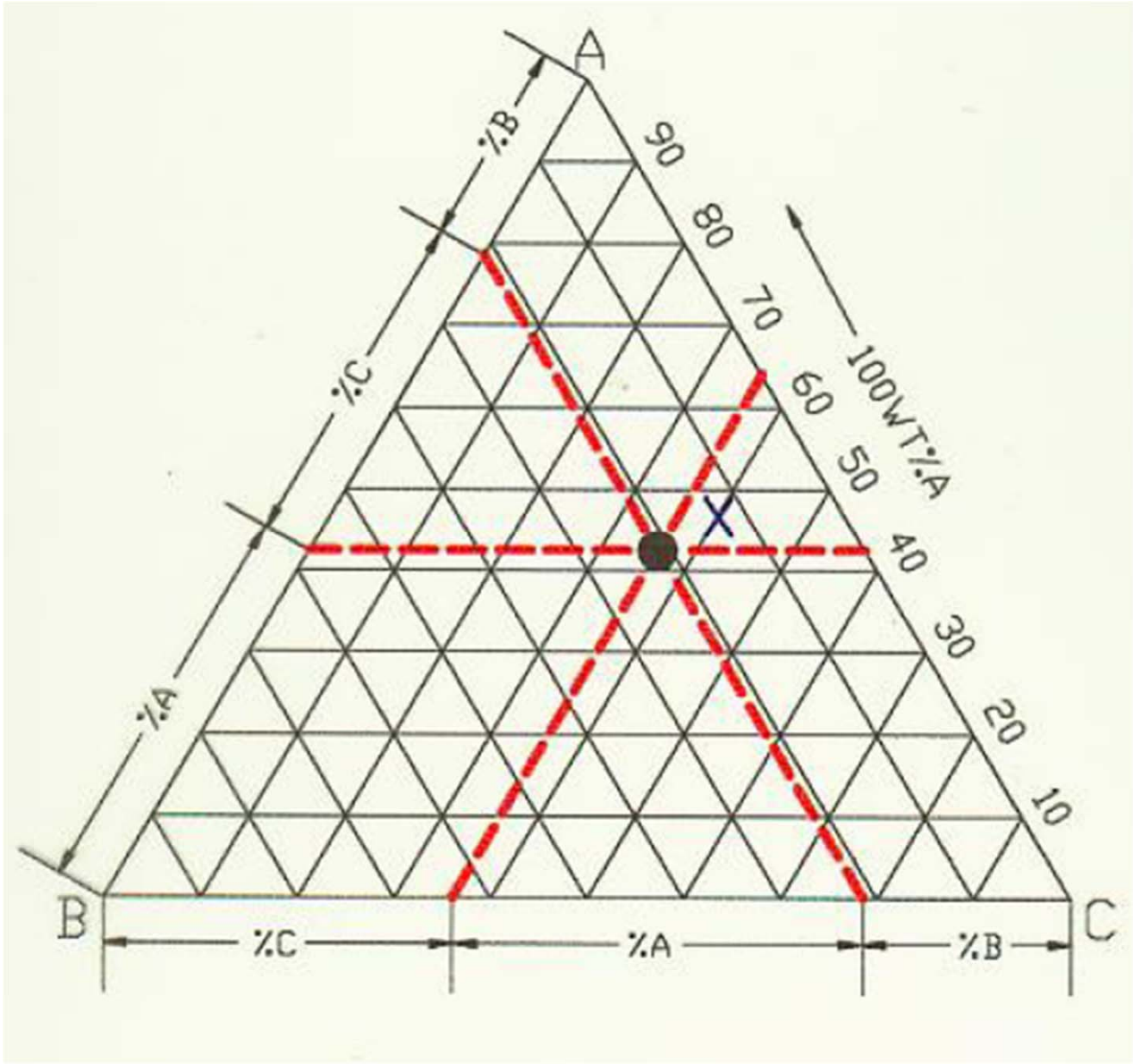


Concentration can be expressed as either "wt. %" or "at.% = molar %".

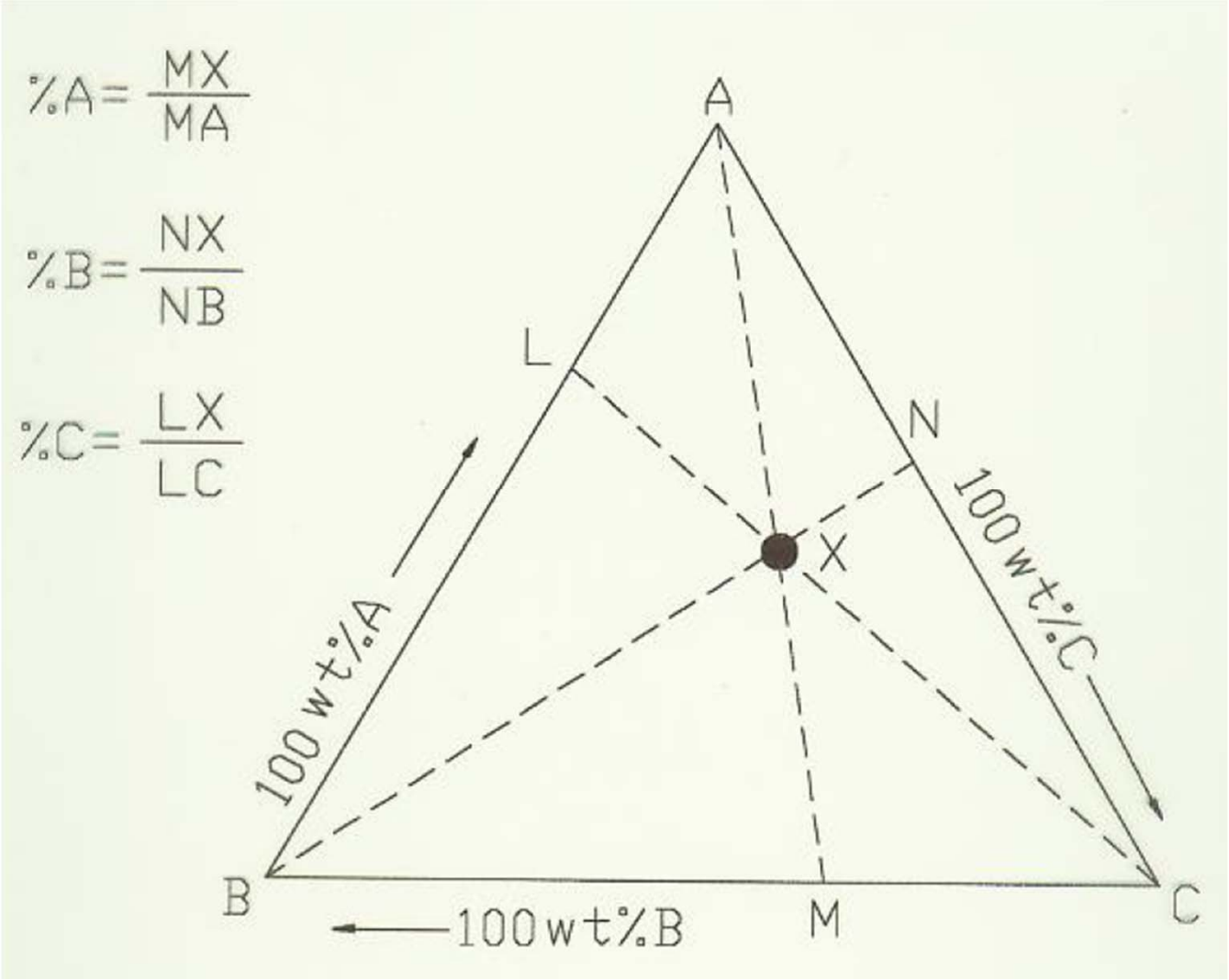
$$X_A+X_B+X_C = 1$$

Used to determine the overall composition

Overall Composition



Overall Composition



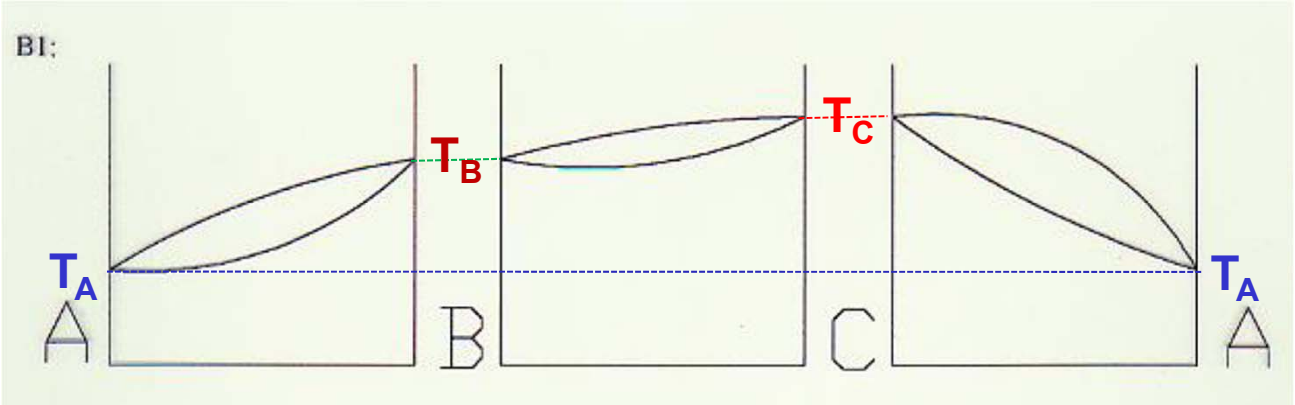
Ternary Isomorphous System

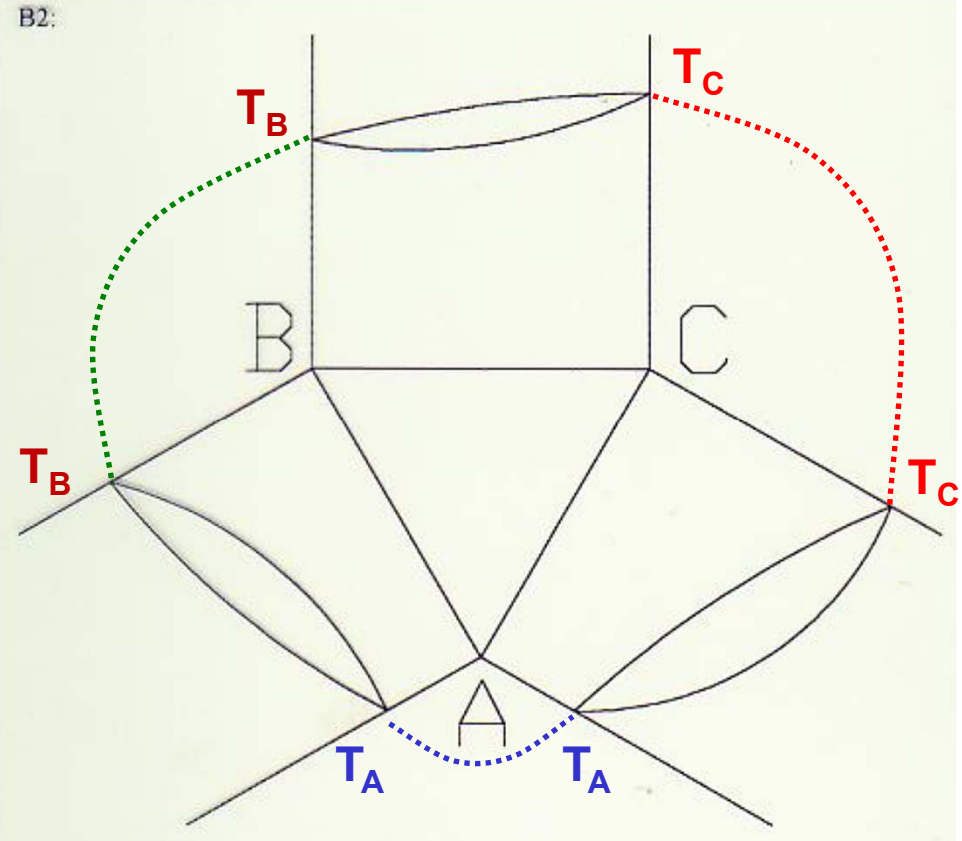
Isomorphous System: A system (ternary in this case) that has only one solid phase. All components are totally soluble in the other components. The ternary system is therefore made up of three binaries that exhibit total solid solubility.

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

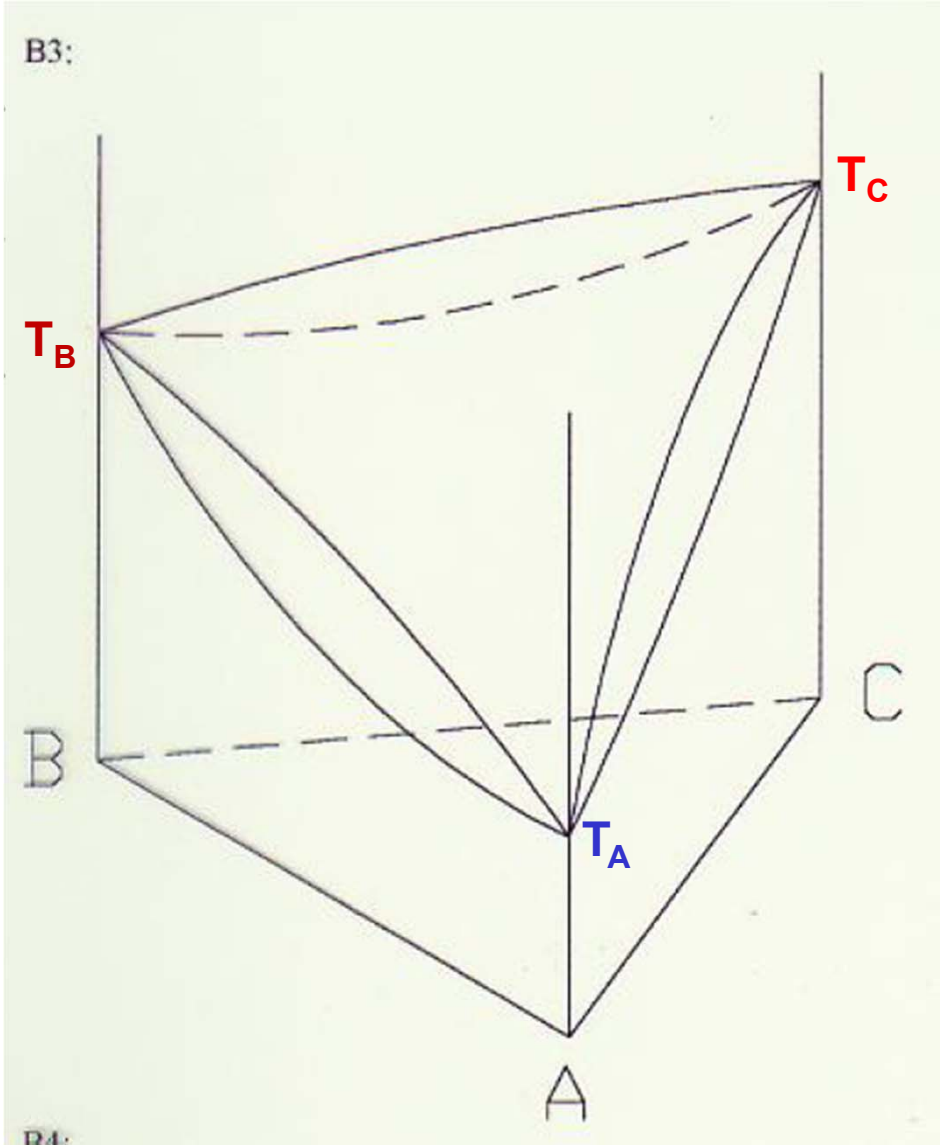
The Solidus Surface: A plot of the temperatures below which a (homogeneous) solid phase forms for any given overall composition.

Ternary Isomorphous System

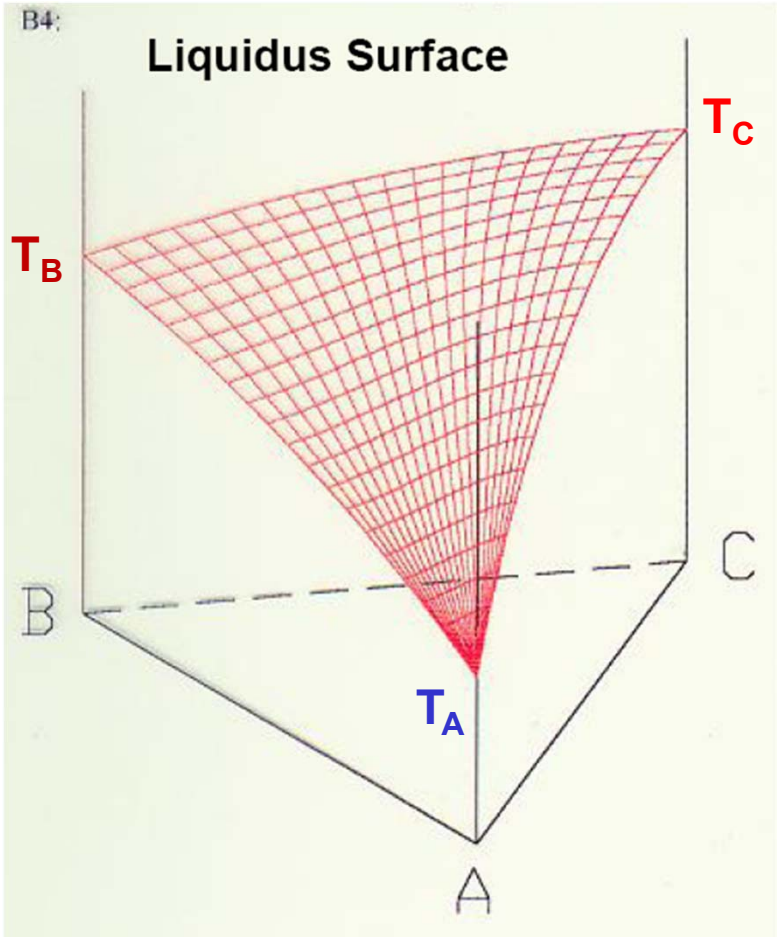


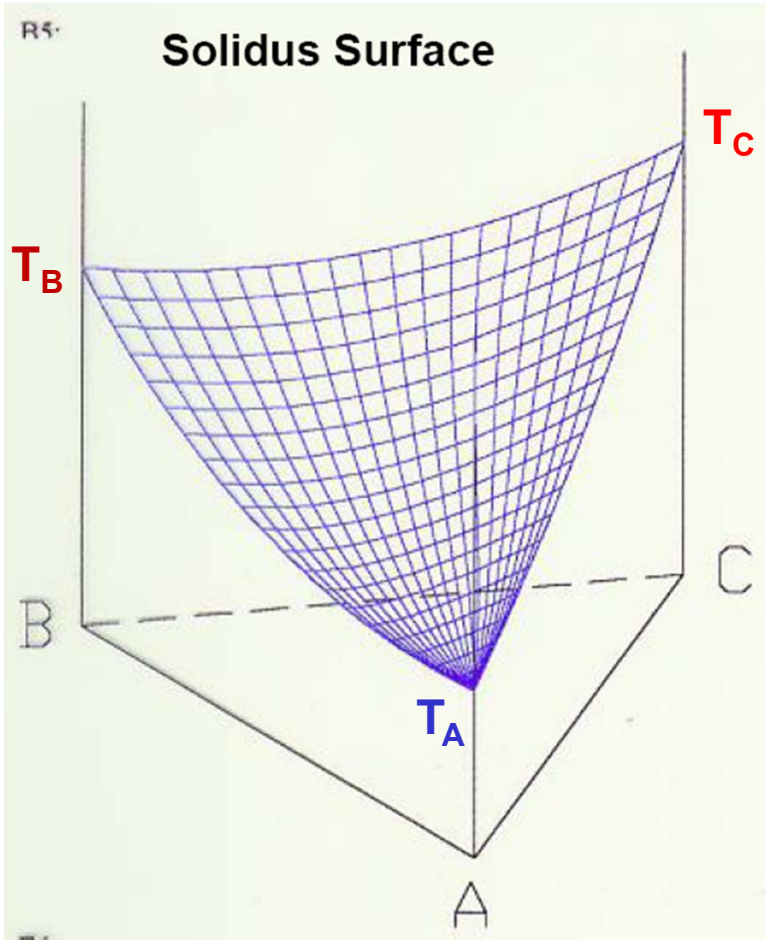


Ternary Isomorphous System

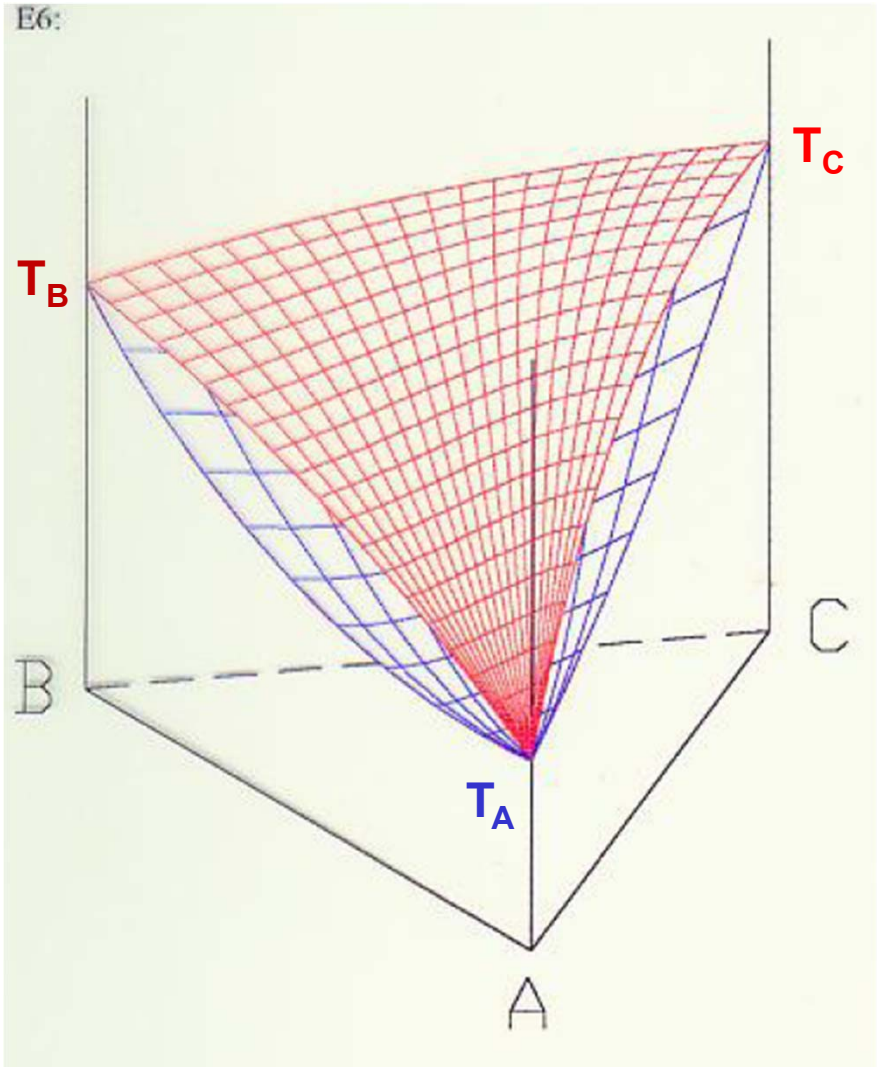


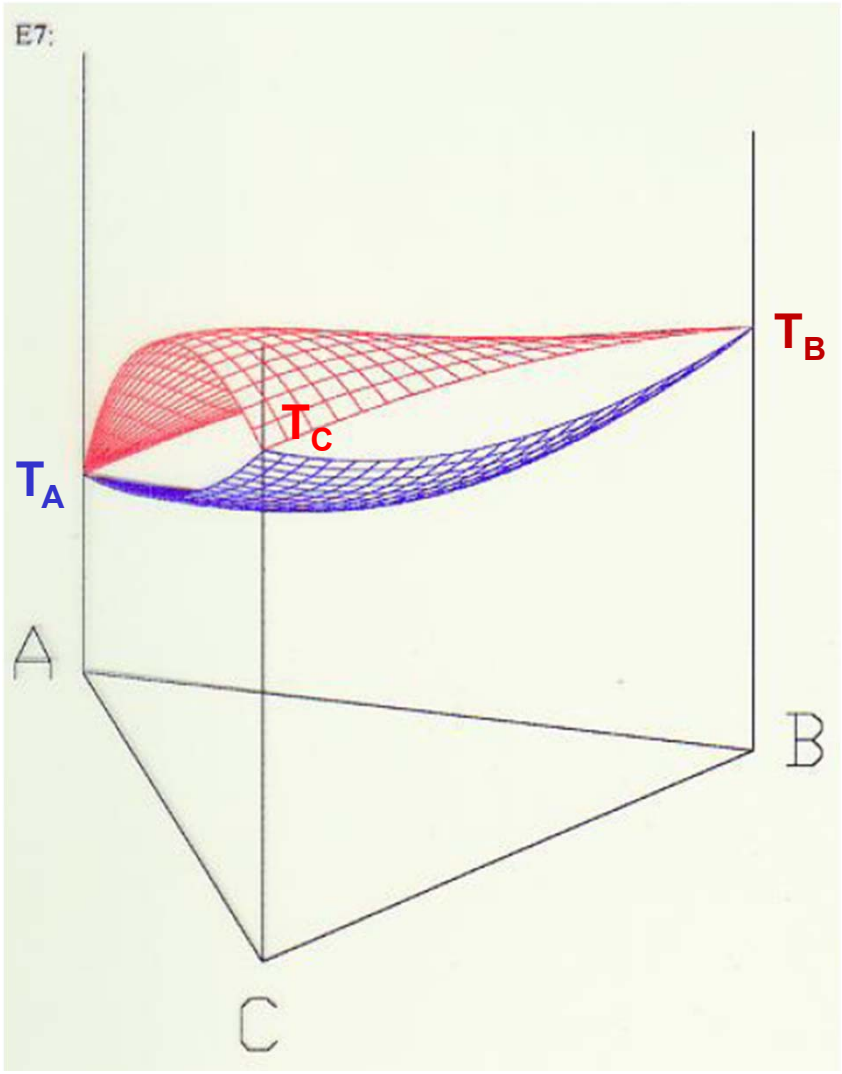
Ternary Isomorphous System





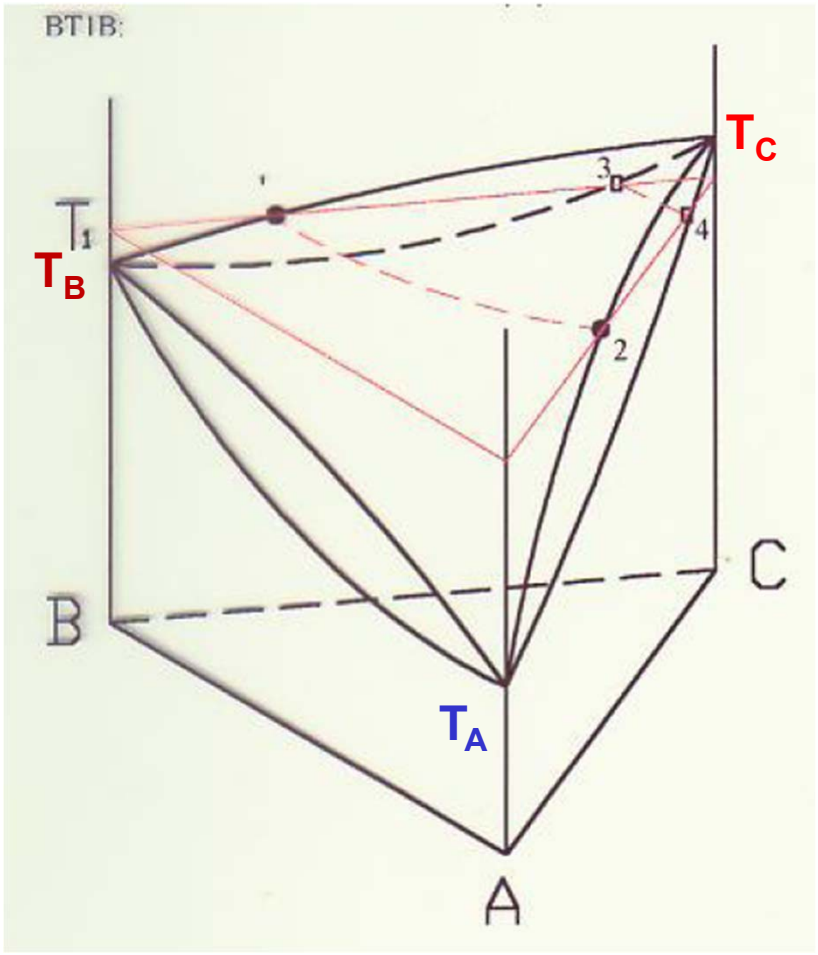
Ternary Isomorphous System

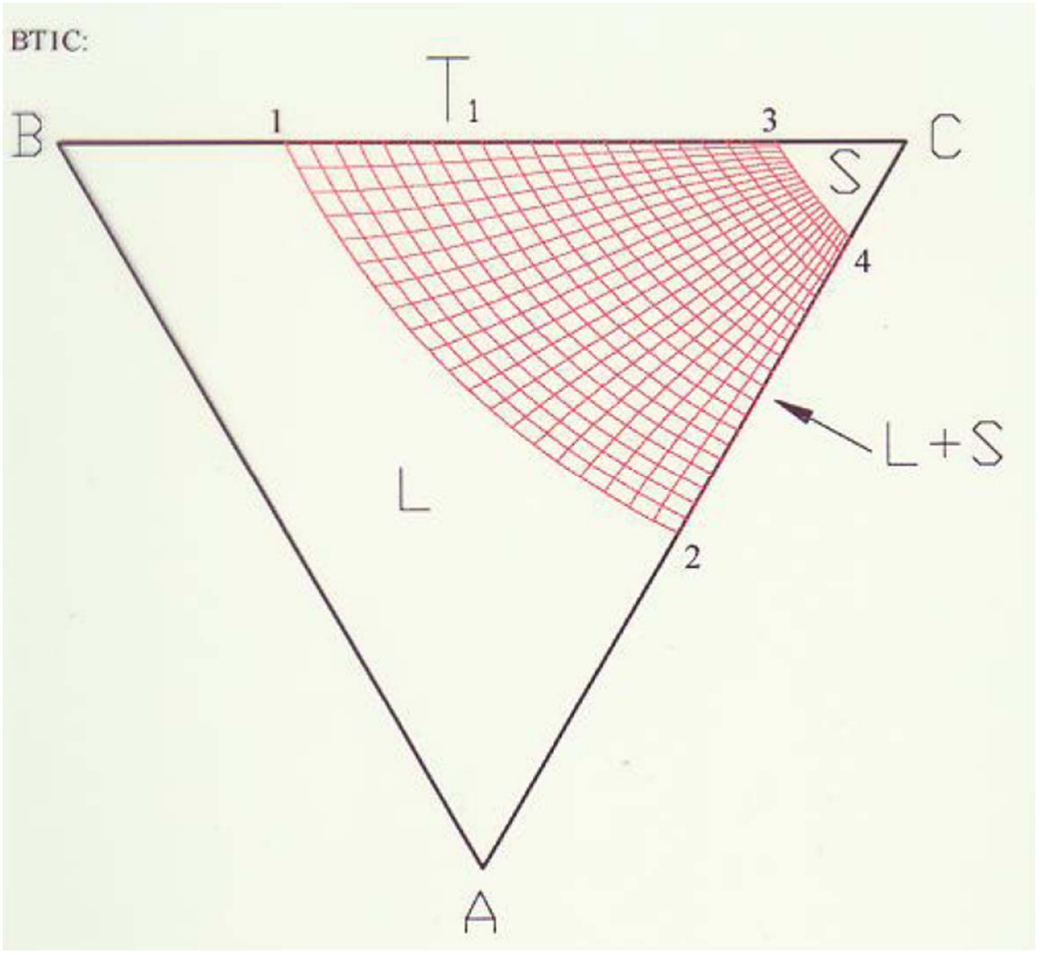




Ternary Isomorphous System

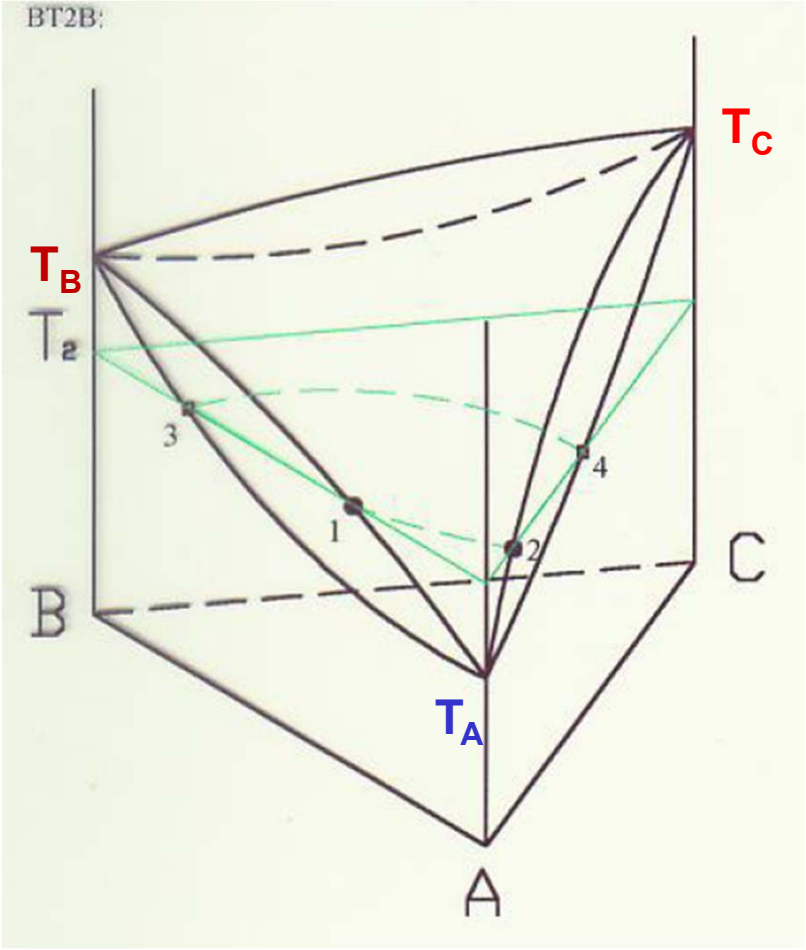
Isothermal section → F = C - P

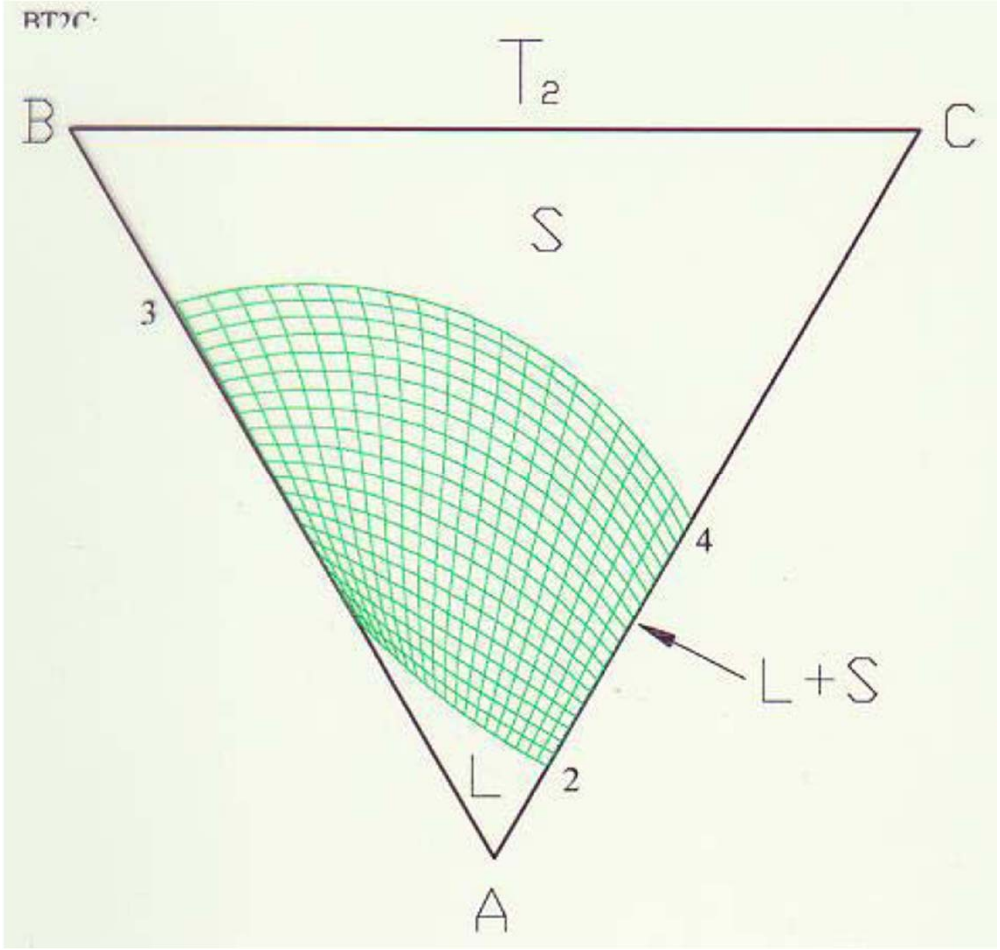




Ternary Isomorphous System

Isothermal section





Ternary Isomorphous System

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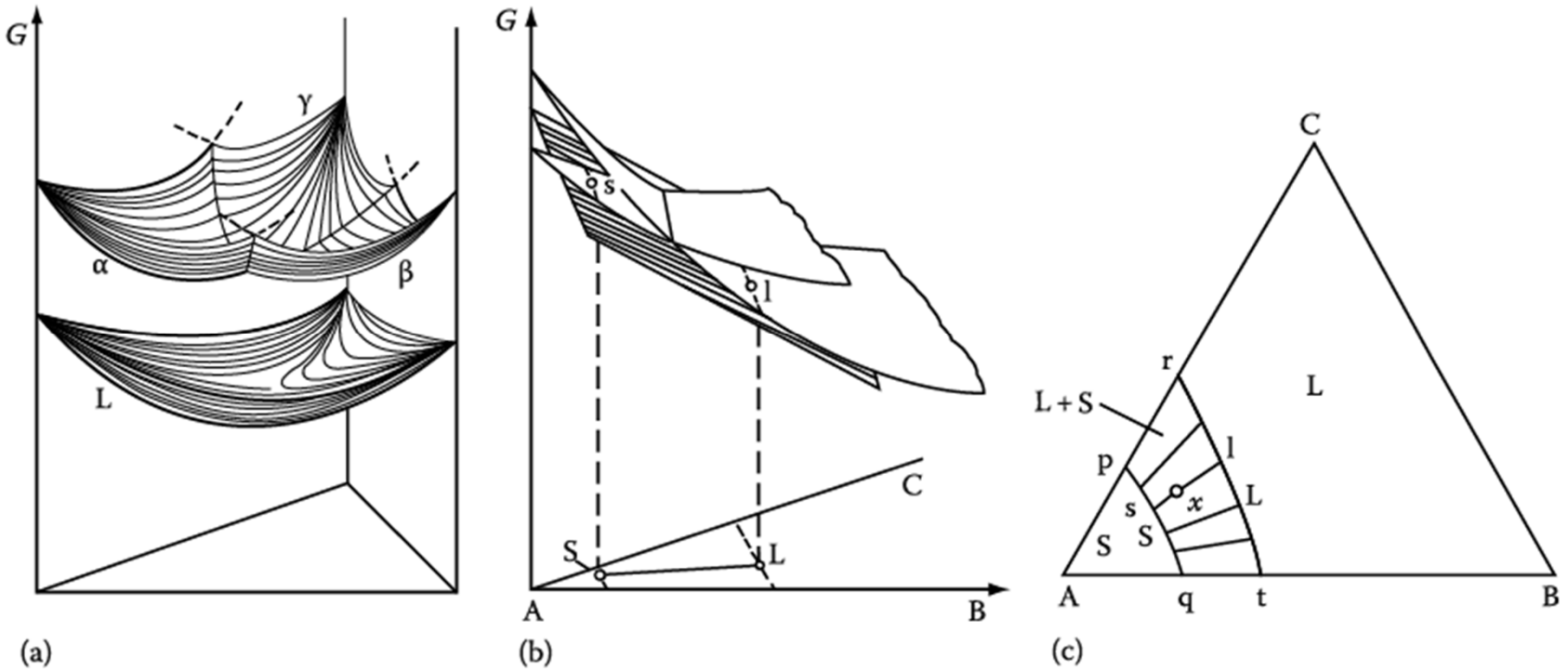


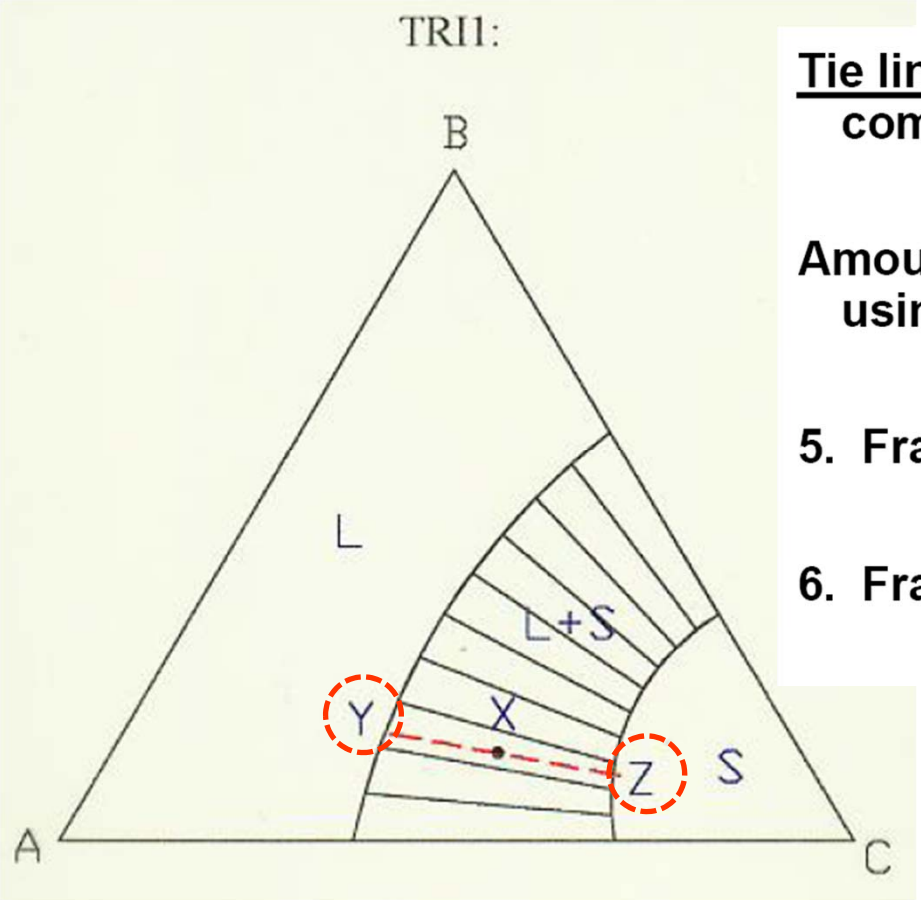
Fig. 1.41 (a) Free energy surface of a liquid and three solid phases of a ternary system.

(b) A tangential plane construction to the free energy surfaces defined equilibrium between s and l in the ternary system

(c) Isothermal section through a ternary phase diagram

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

Ternary Eutectic System
(No Solid Solubility)

The Ternary Eutectic Reaction:

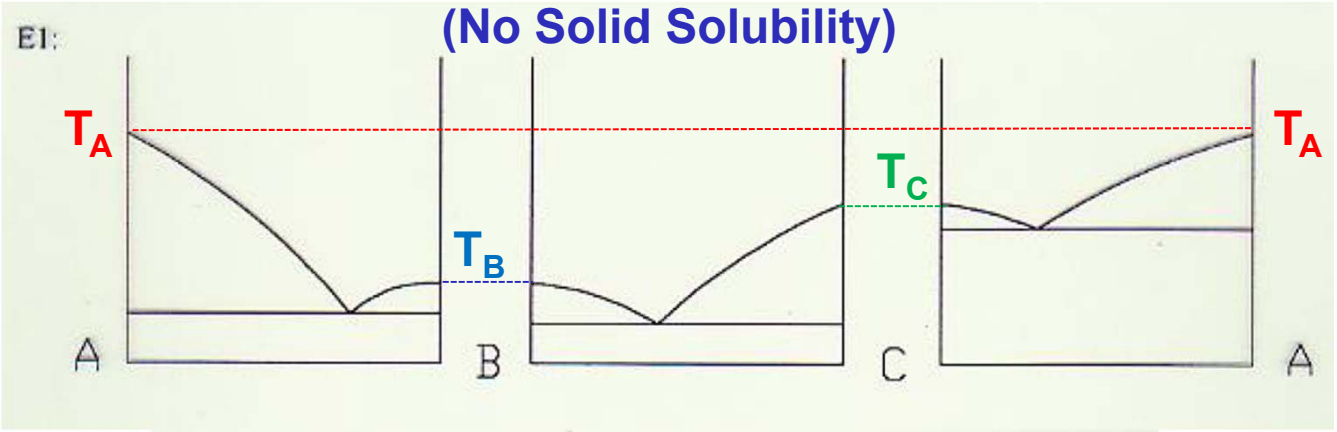
$$L = \alpha + \beta + \gamma$$

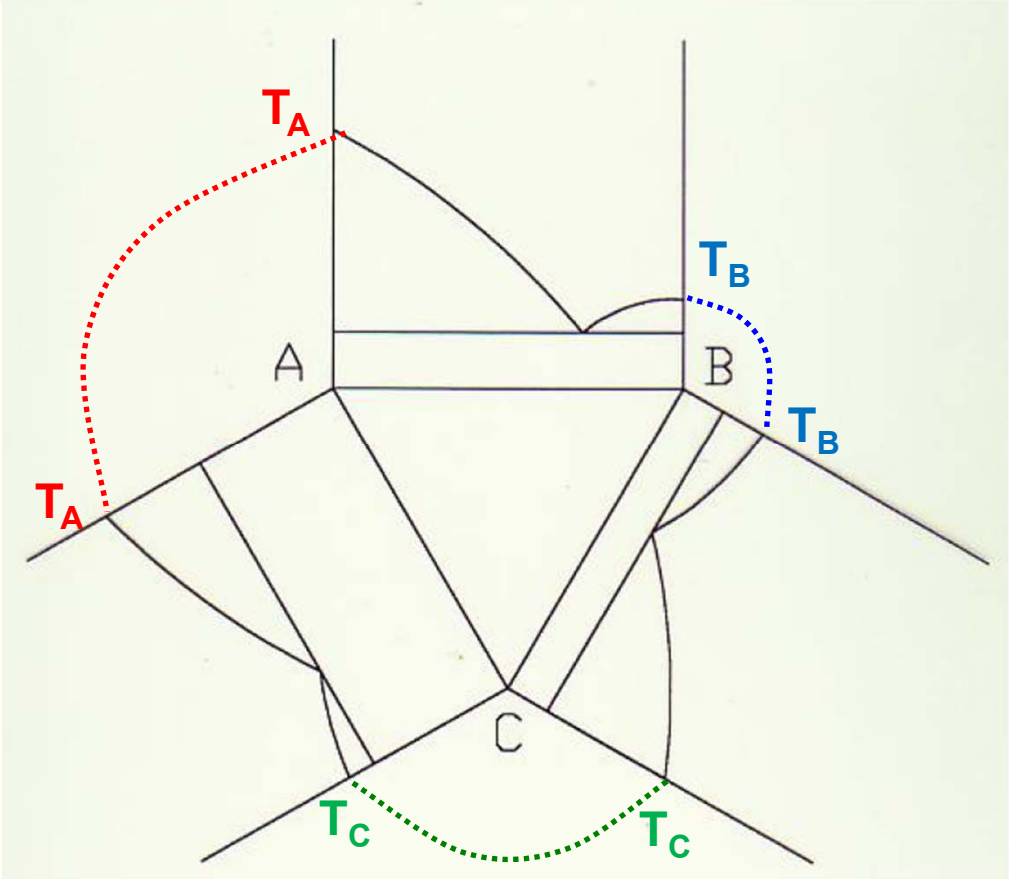
A liquid phase solidifies into three separate solid phases

Made up of three binary eutectic systems, all of which exhibit no solid solubility

Ternary Eutectic System

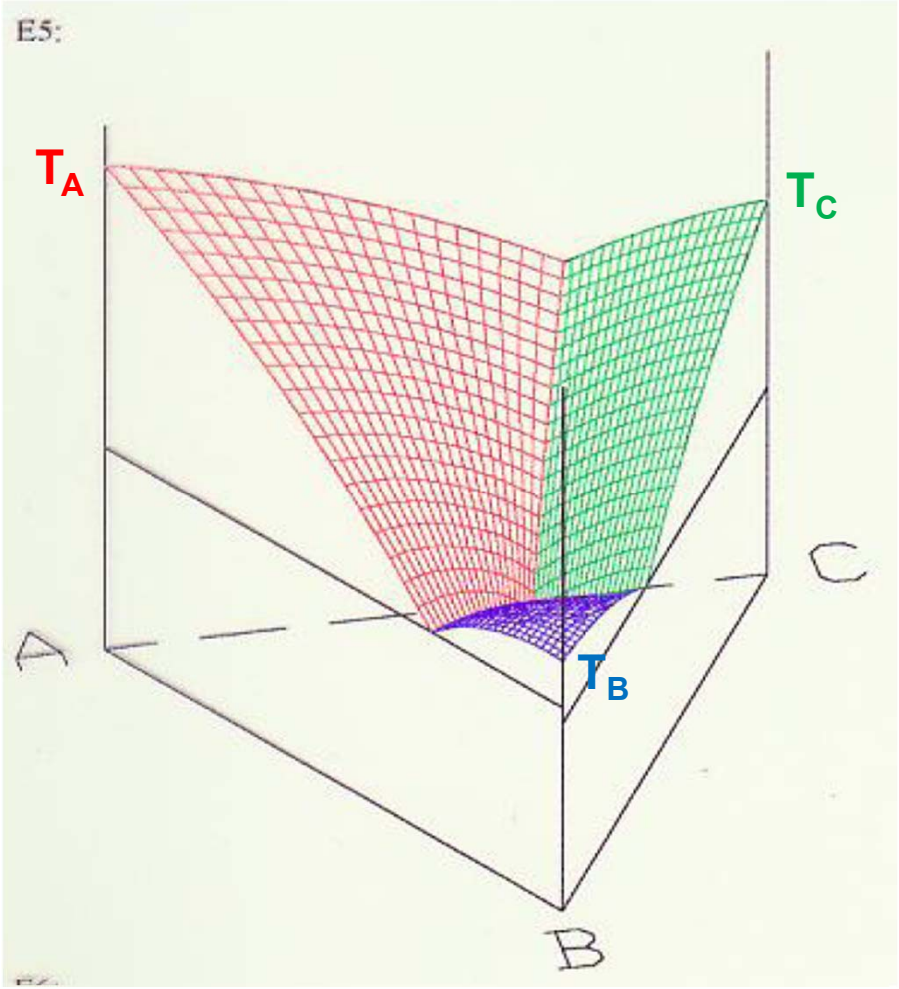
(No Solid Solubility)



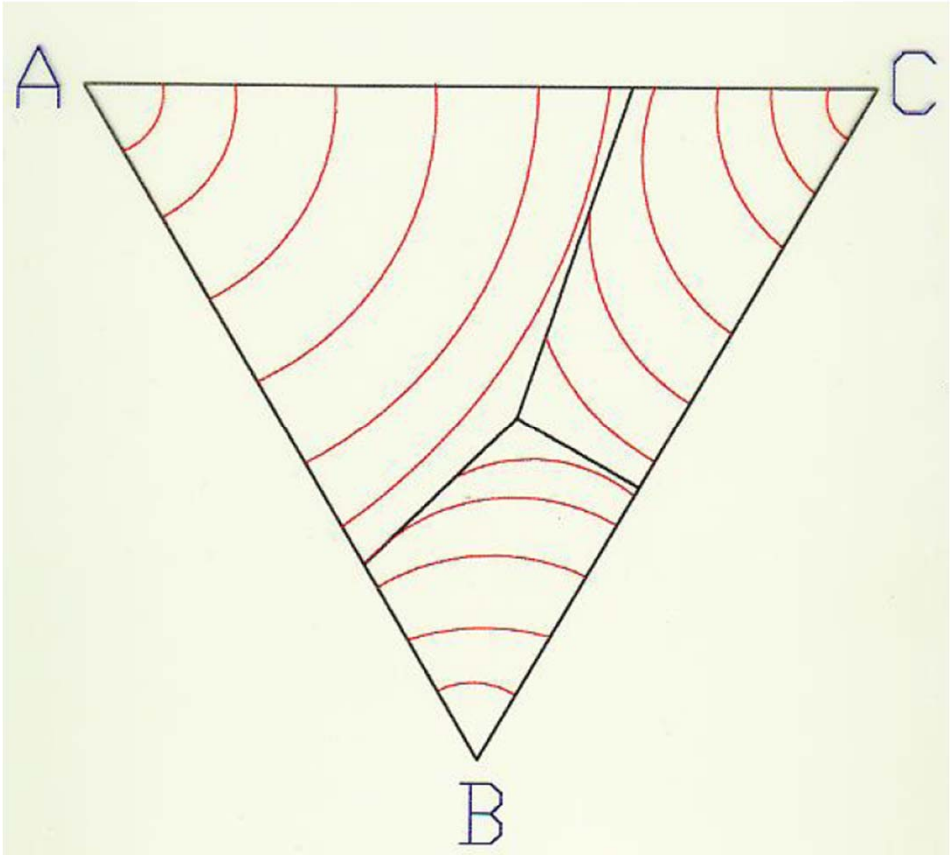


Ternary Eutectic System

(No Solid Solubility)

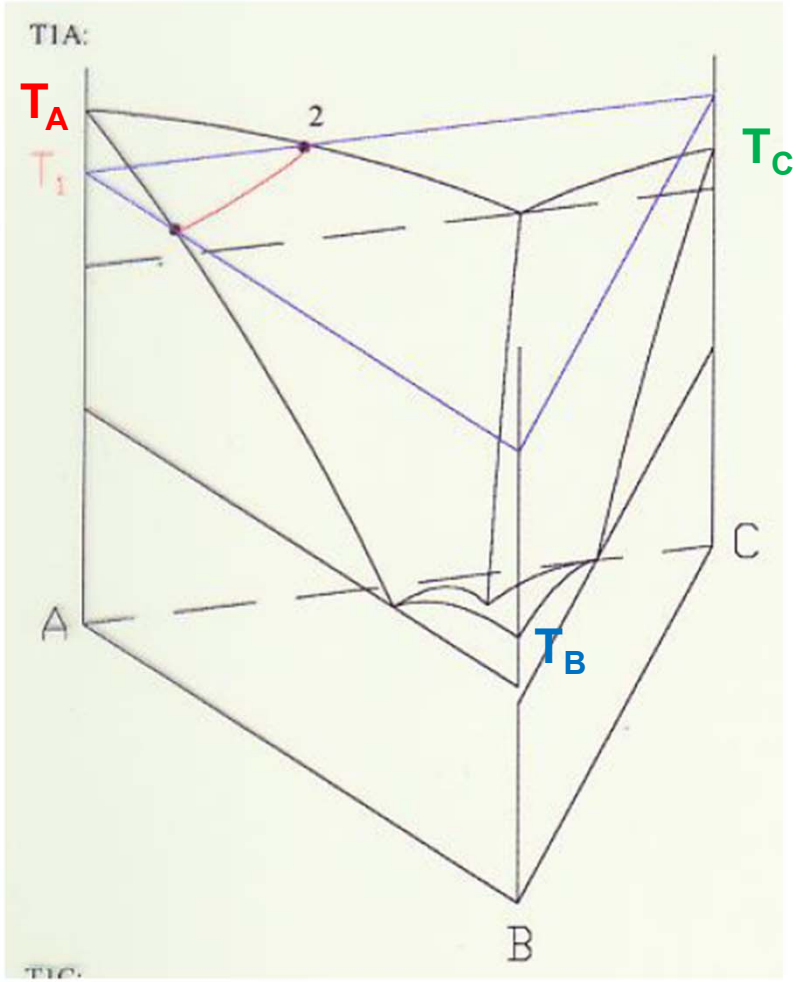


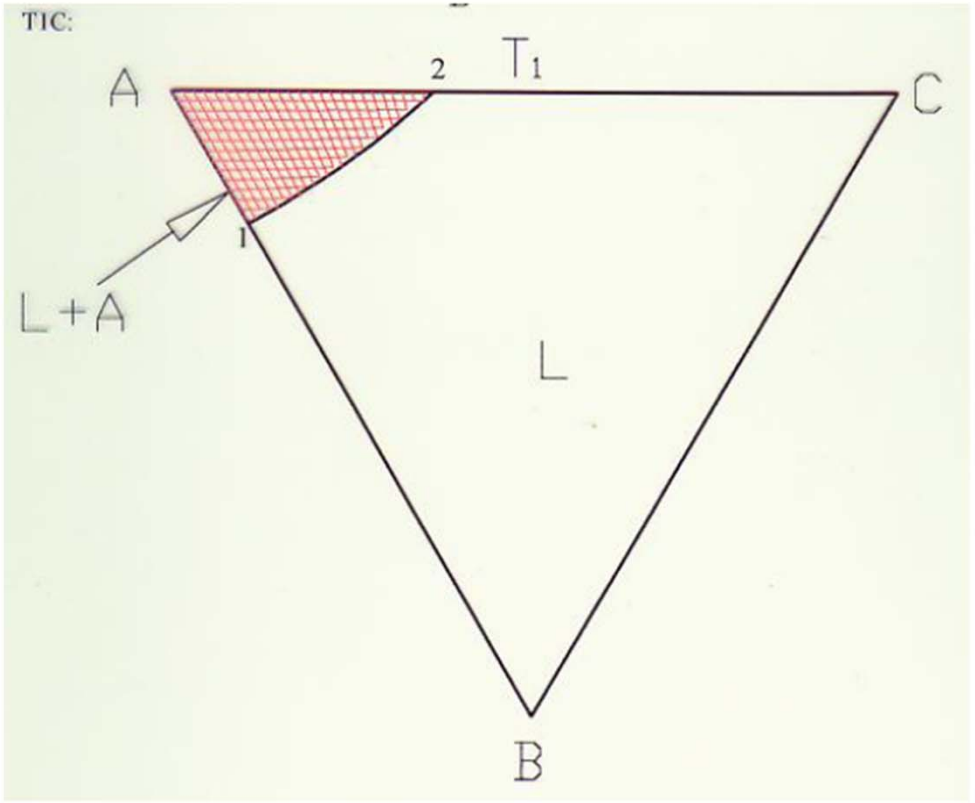
Liquidus projection



Ternary Eutectic System

(No Solid Solubility)





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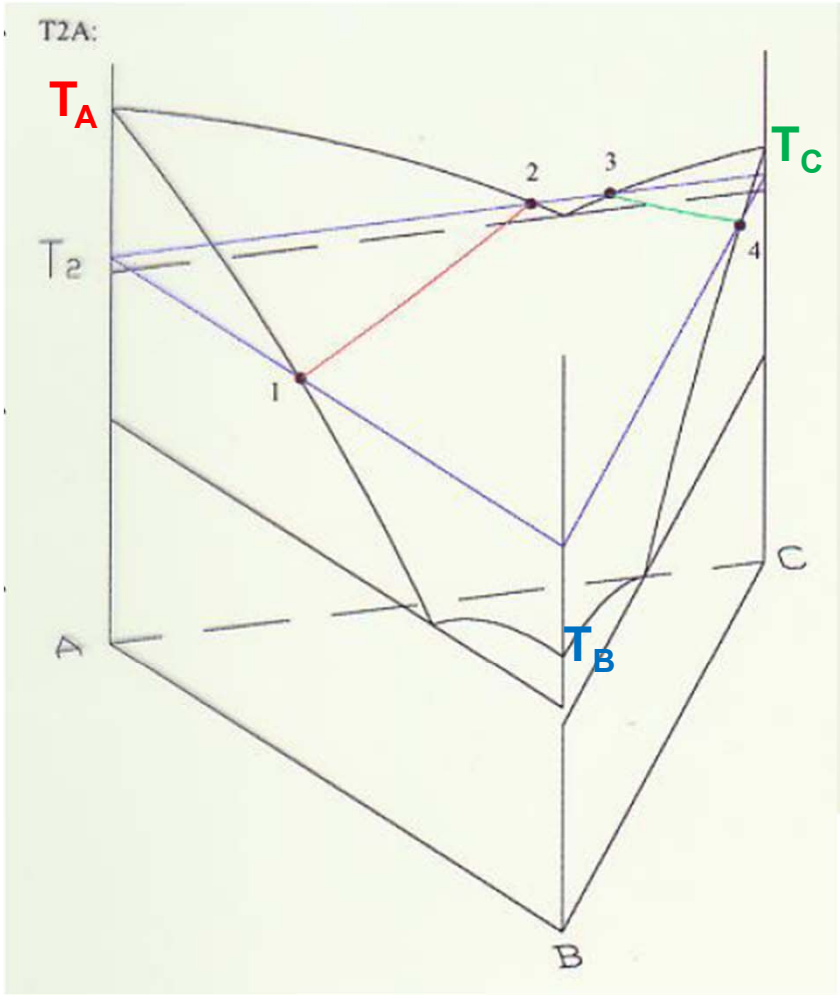
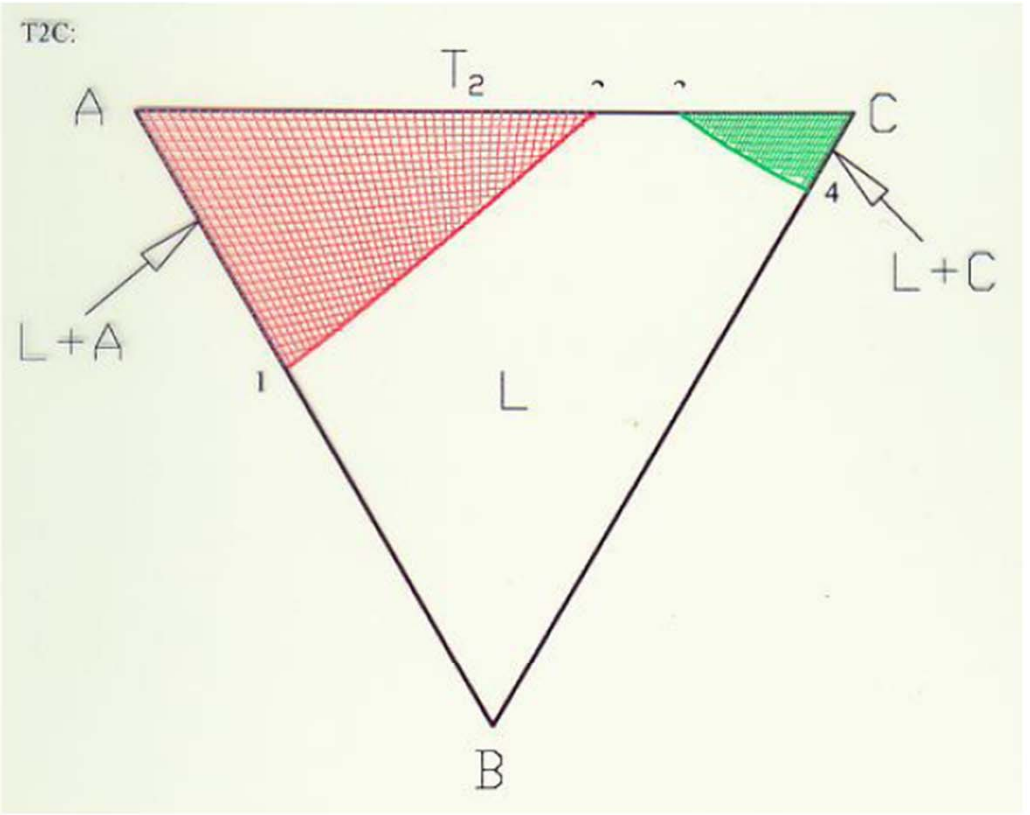
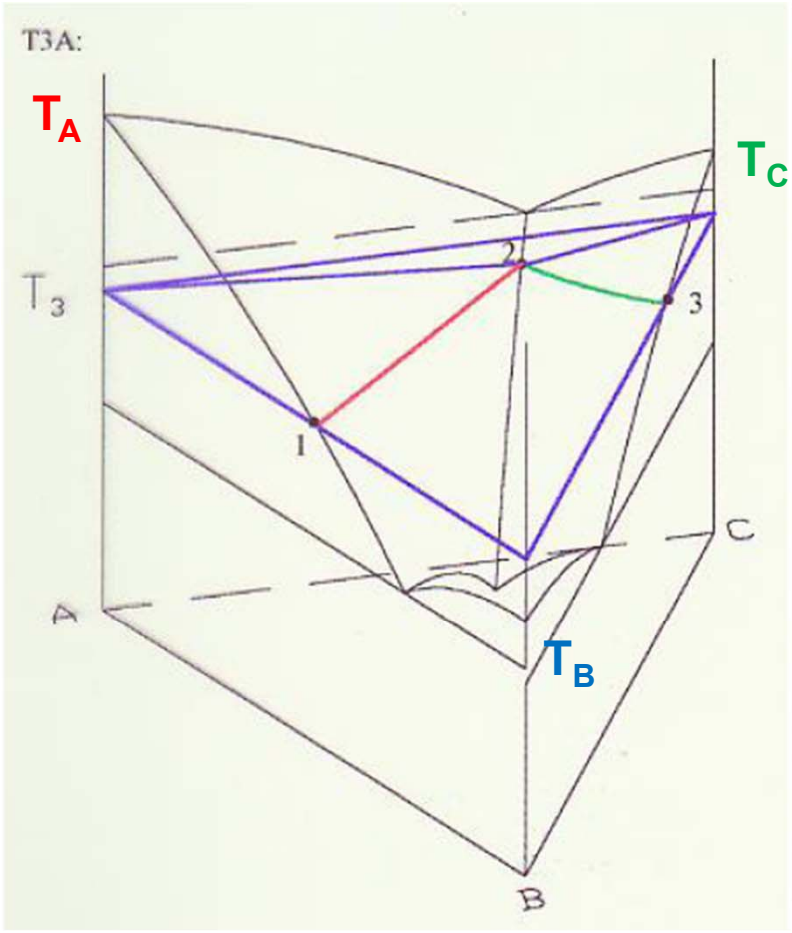
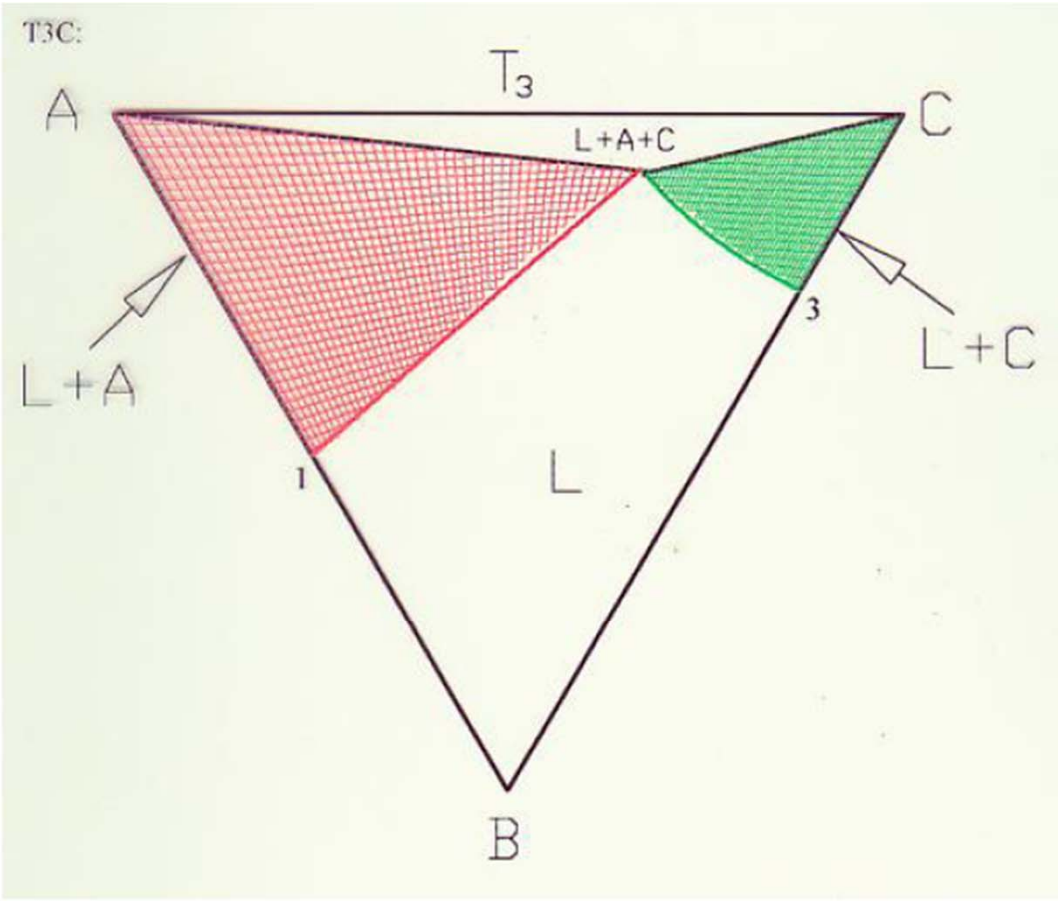




Ternary Eutectic System

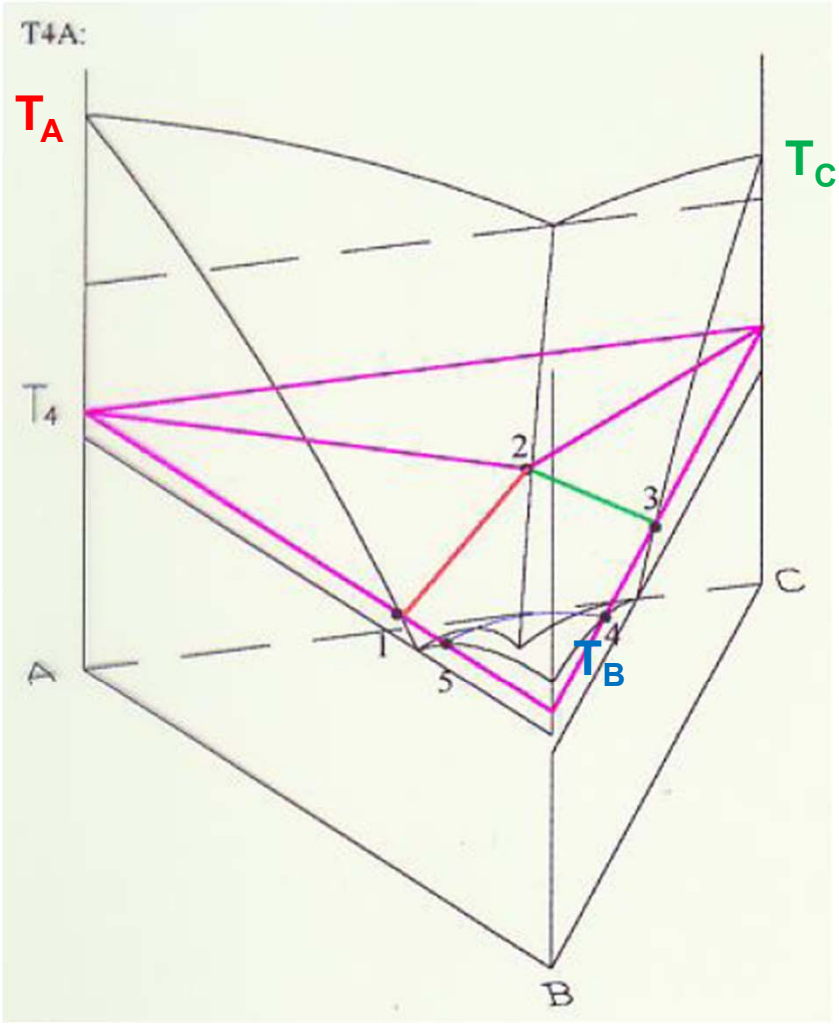
(No Solid Solubility)

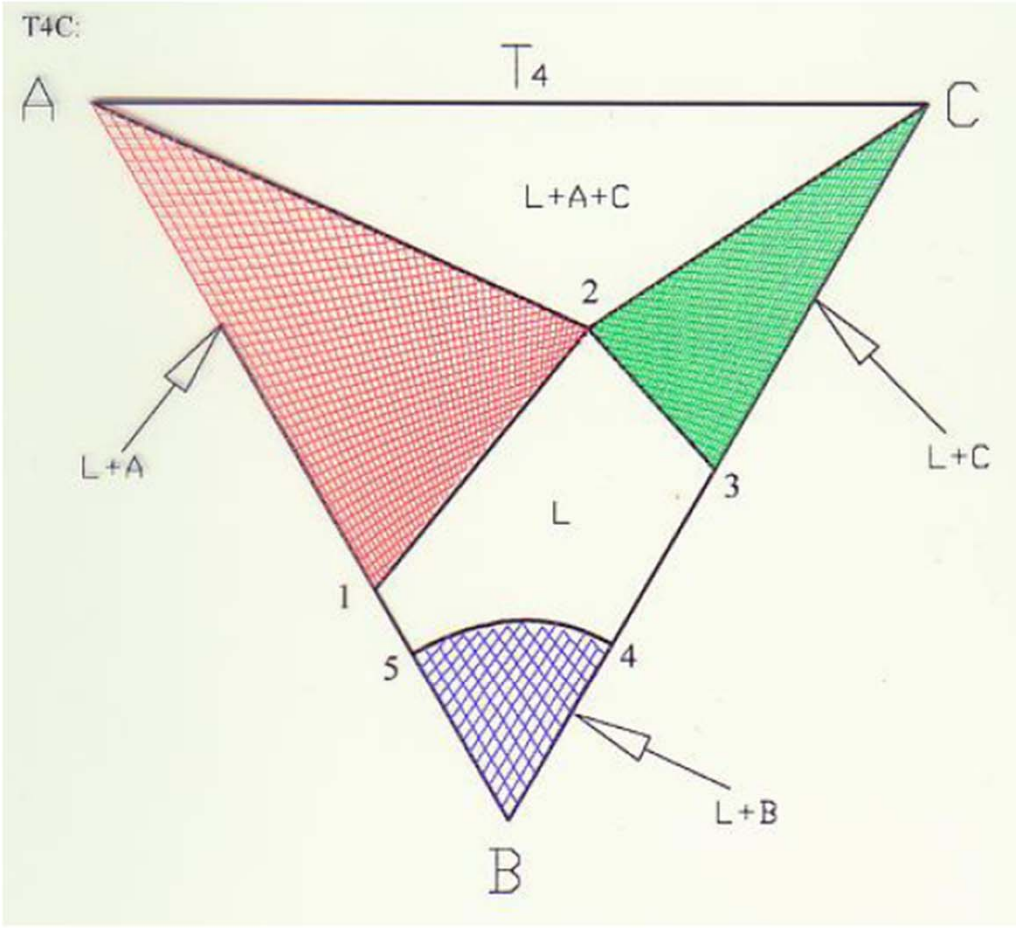




Ternary Eutectic System

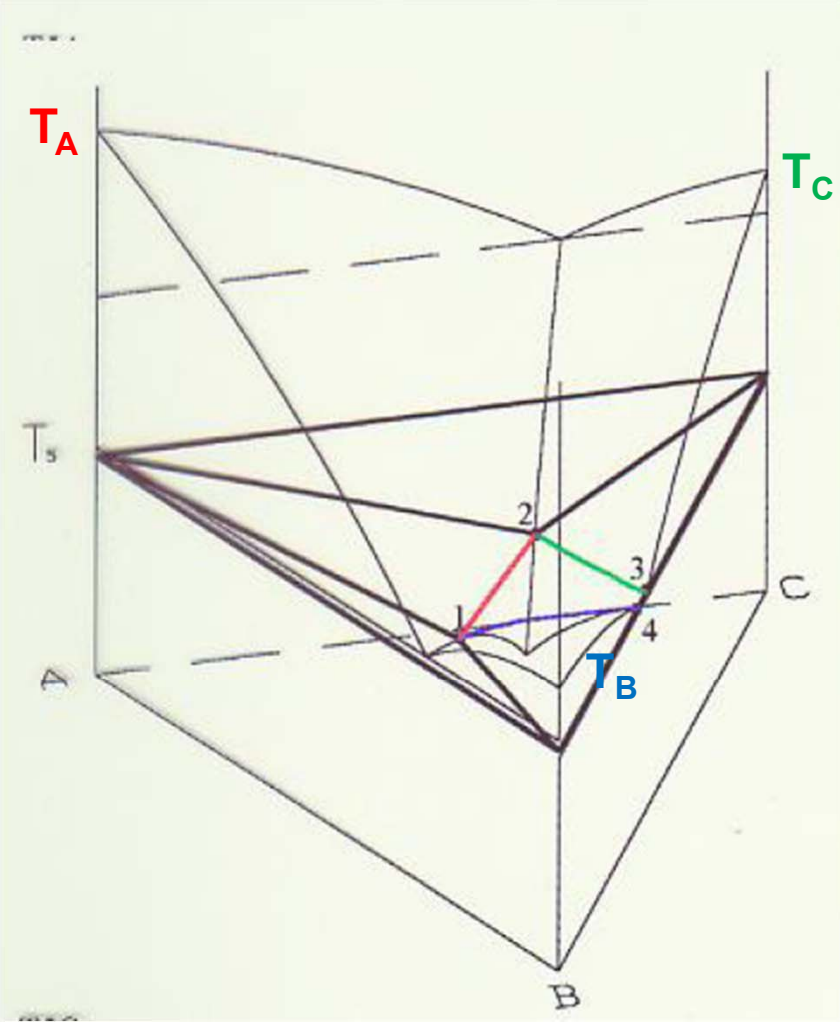
(No Solid Solubility)

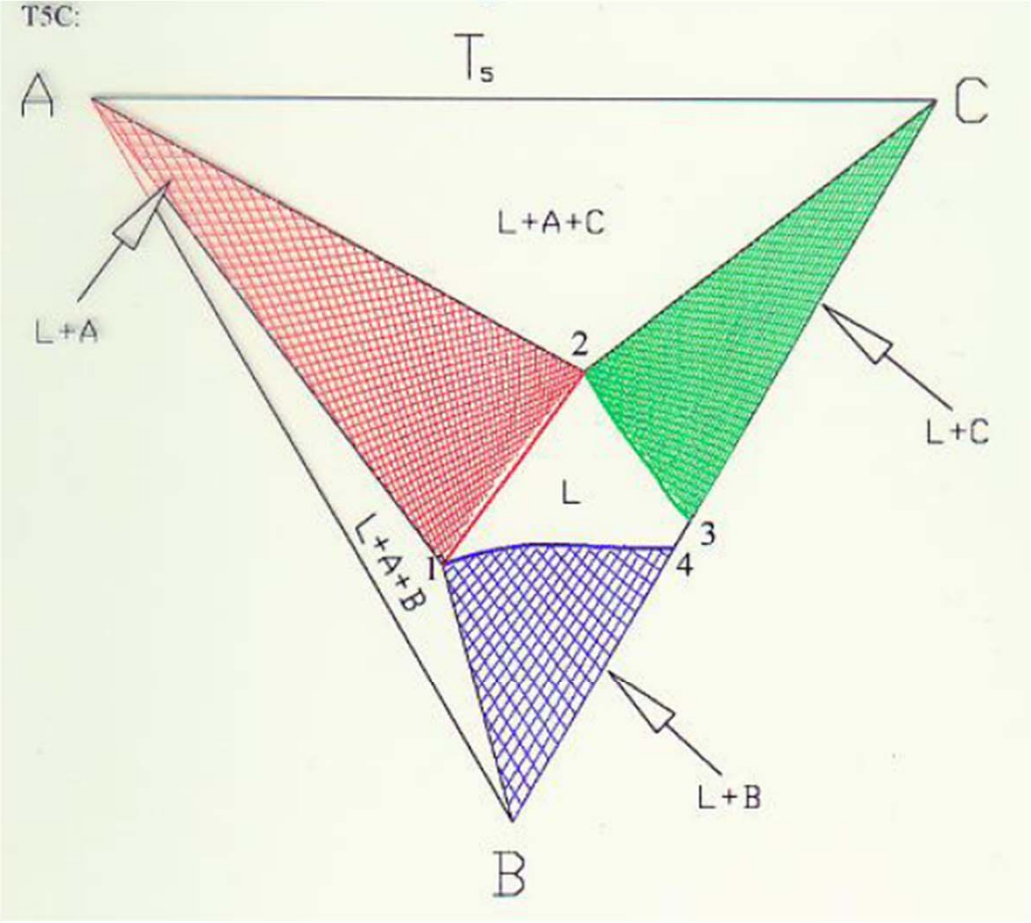




Ternary Eutectic System

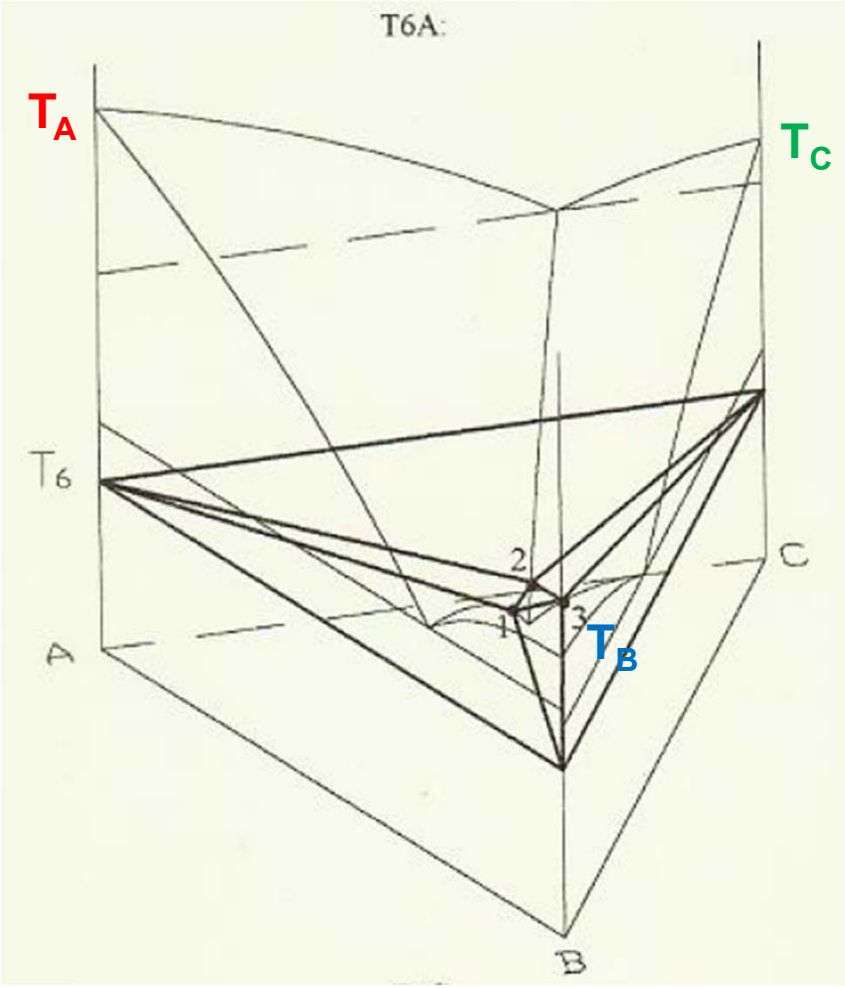
(No Solid Solubility)

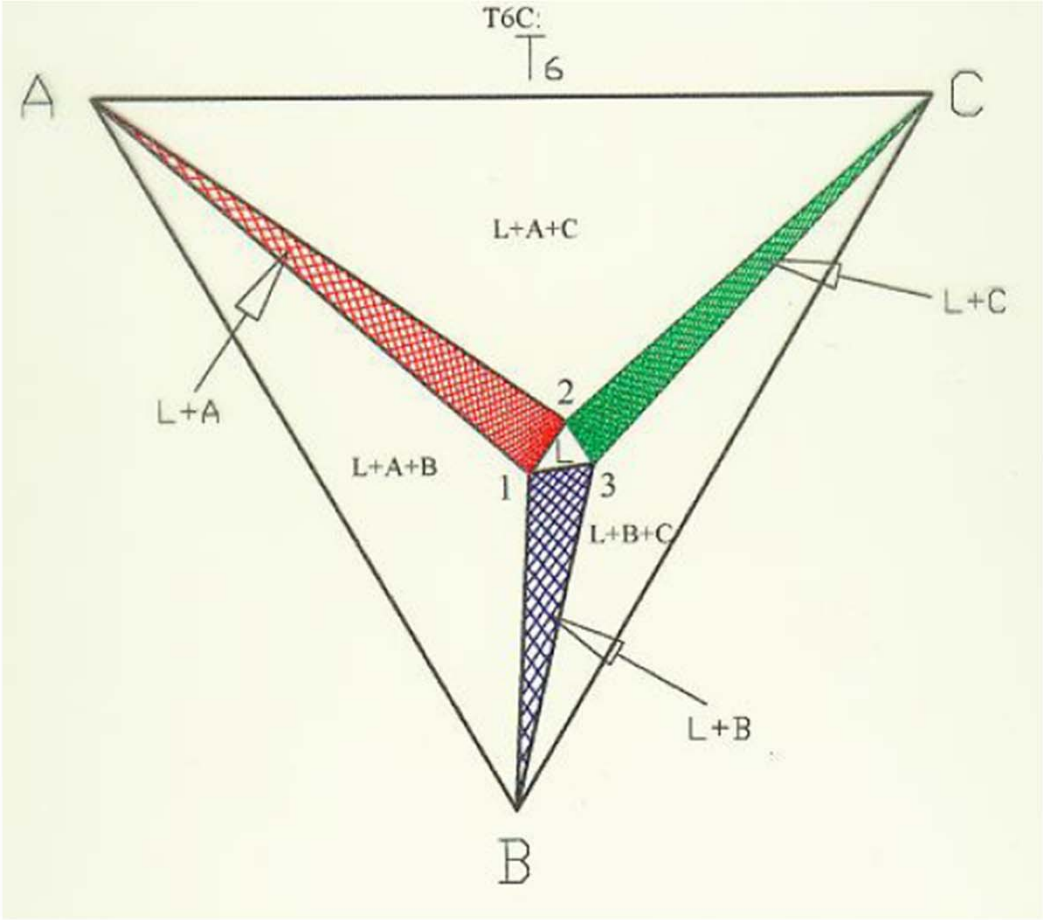




Ternary Eutectic System

(No Solid Solubility)

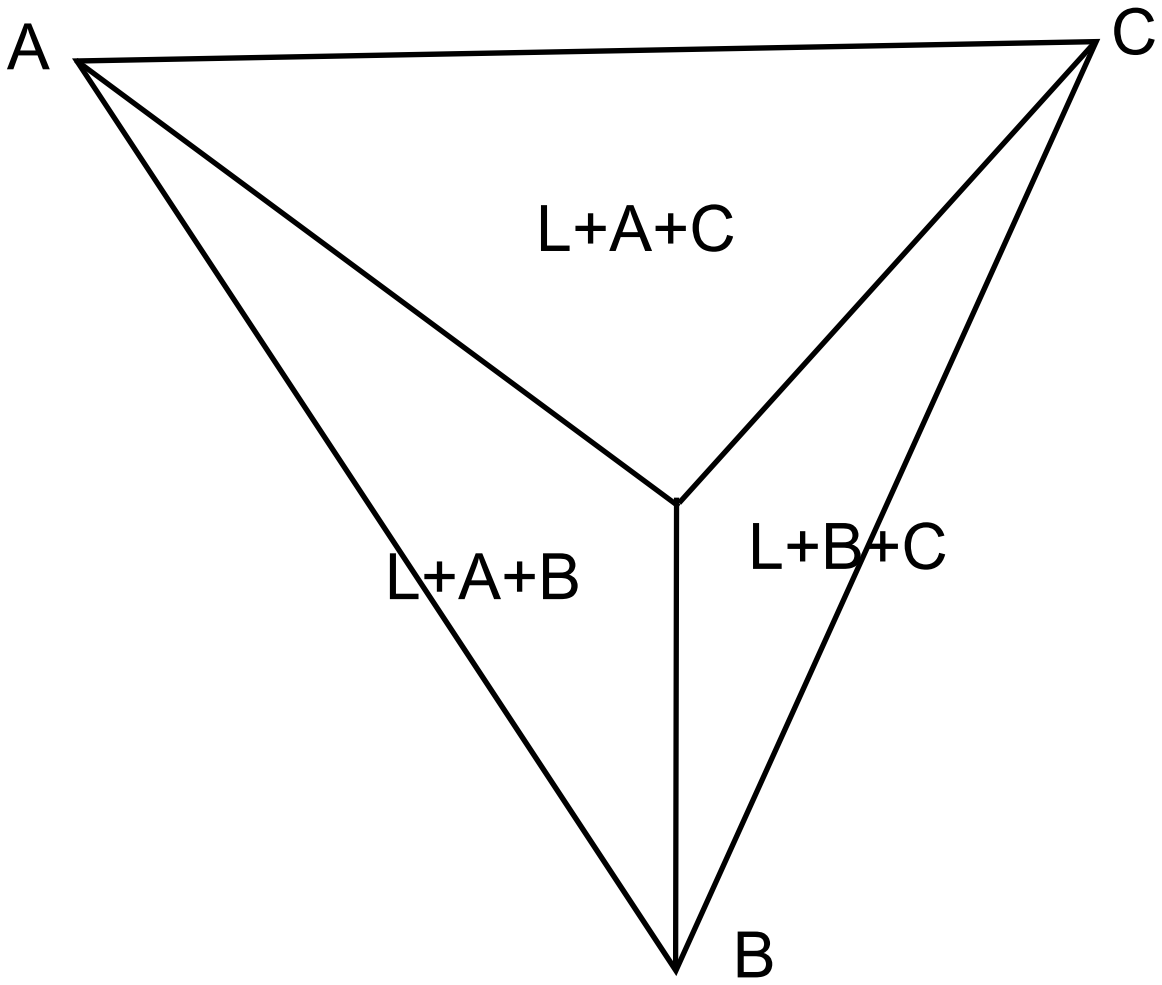




Ternary Eutectic System

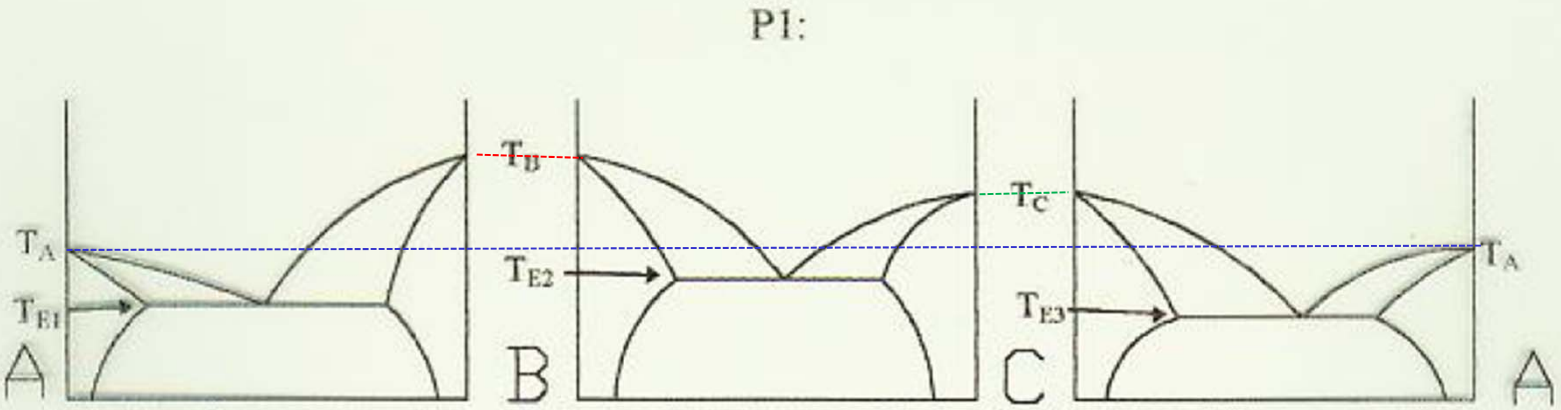
(No Solid Solubility)

T= ternary eutectic temp.



Ternary Eutectic System

(with Solid Solubility)



T_A: Melting Point Of Material A

T_B: Melting Point Of Material B

T_C: Melting Point Of Material C

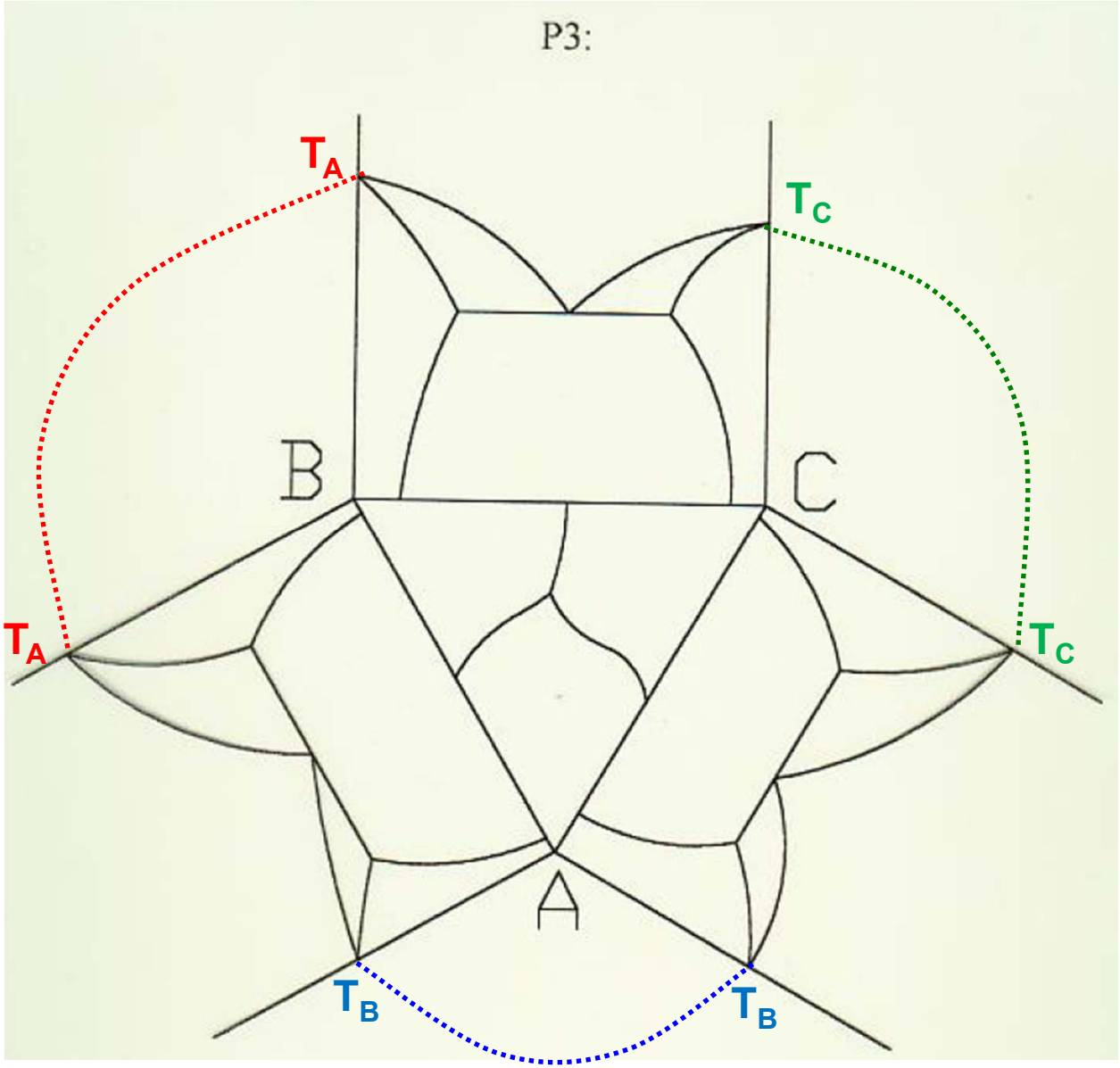
T_{E1}: Eutectic Temperature Of A-B

T_{E2}: Eutectic Temperature Of B-C

T_{E3}: Eutectic Temperature Of C-A

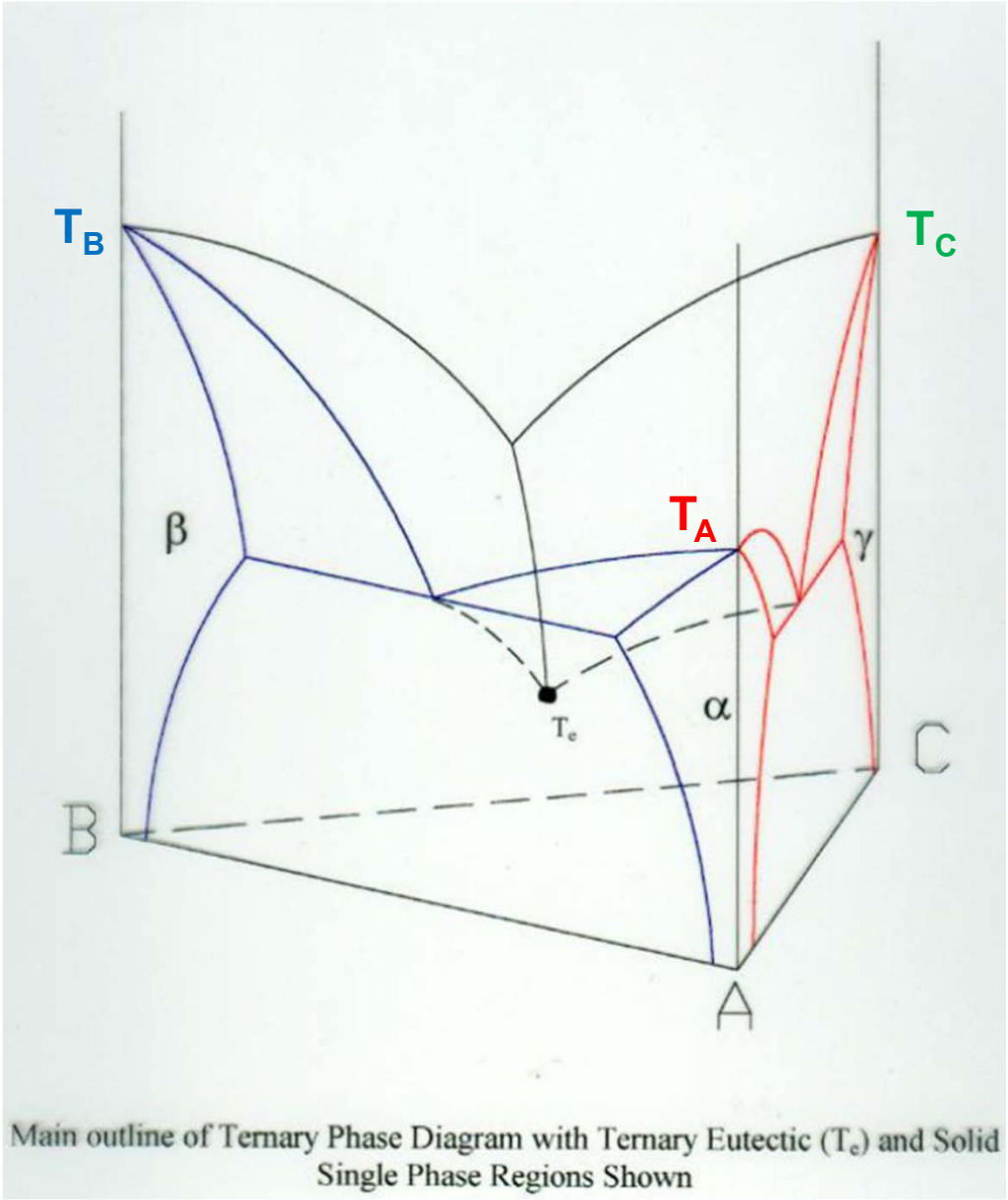
Ternary Eutectic System

(with Solid Solubility)

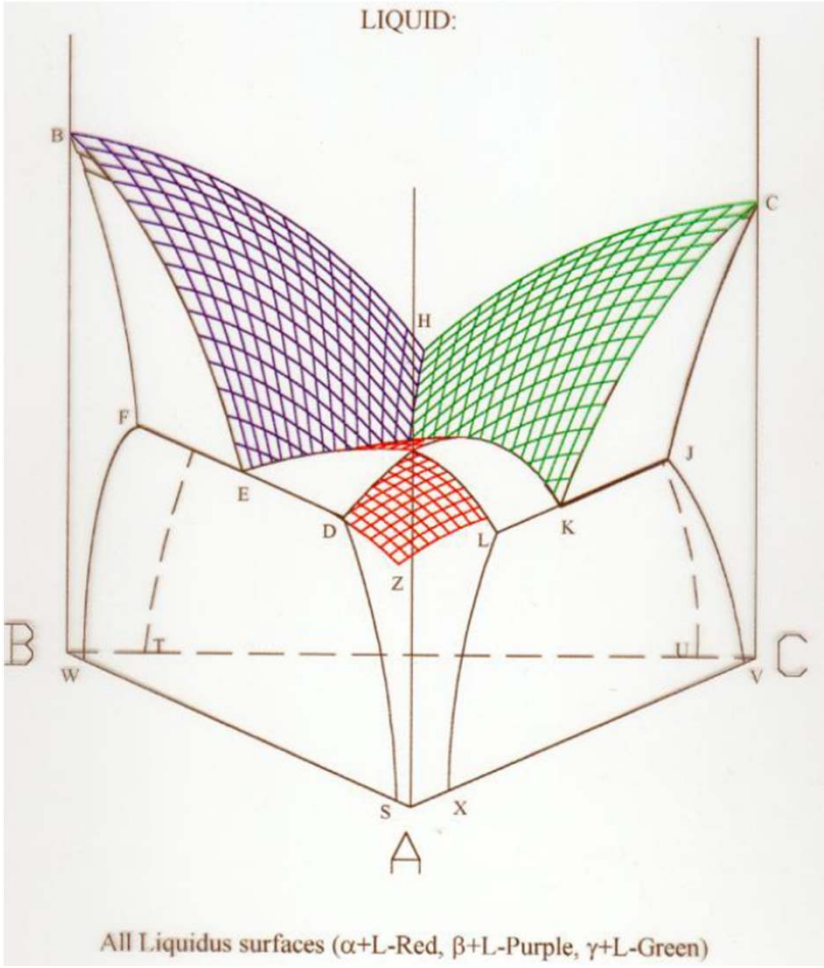


Ternary Eutectic System

(with Solid Solubility)

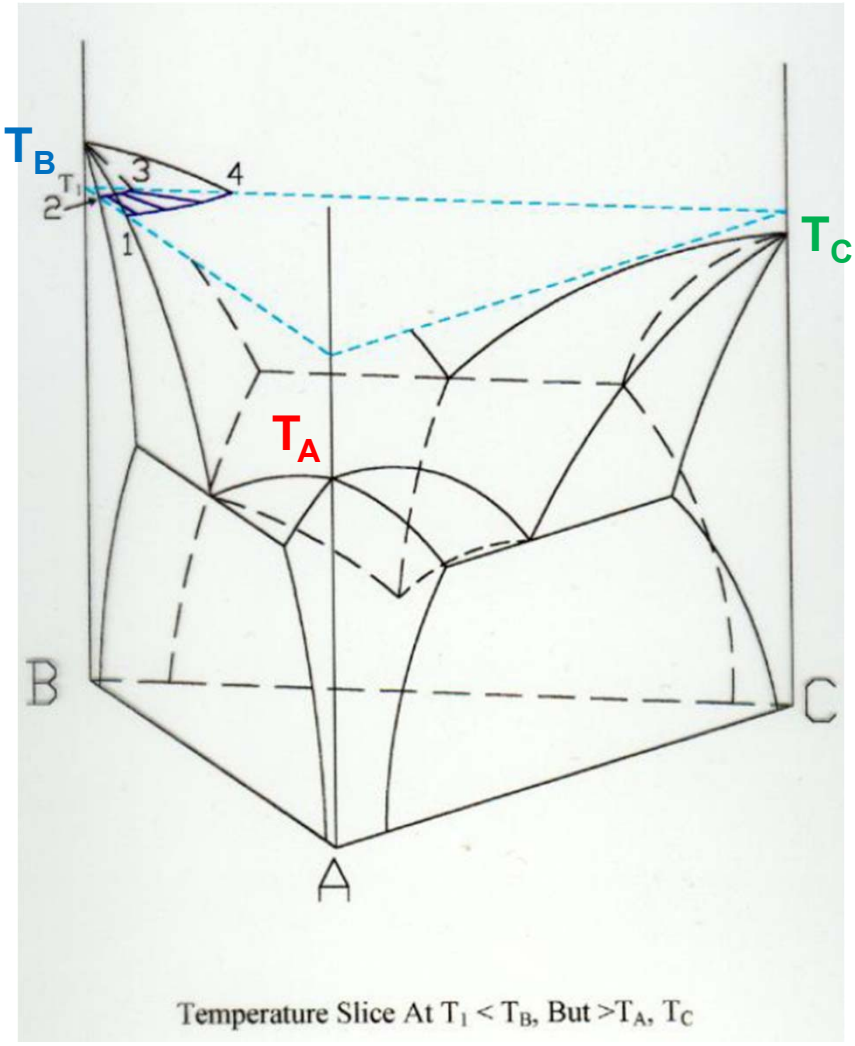


Main outline of Ternary Phase Diagram with Ternary Eutectic (T_e) and Solid Single Phase Regions Shown

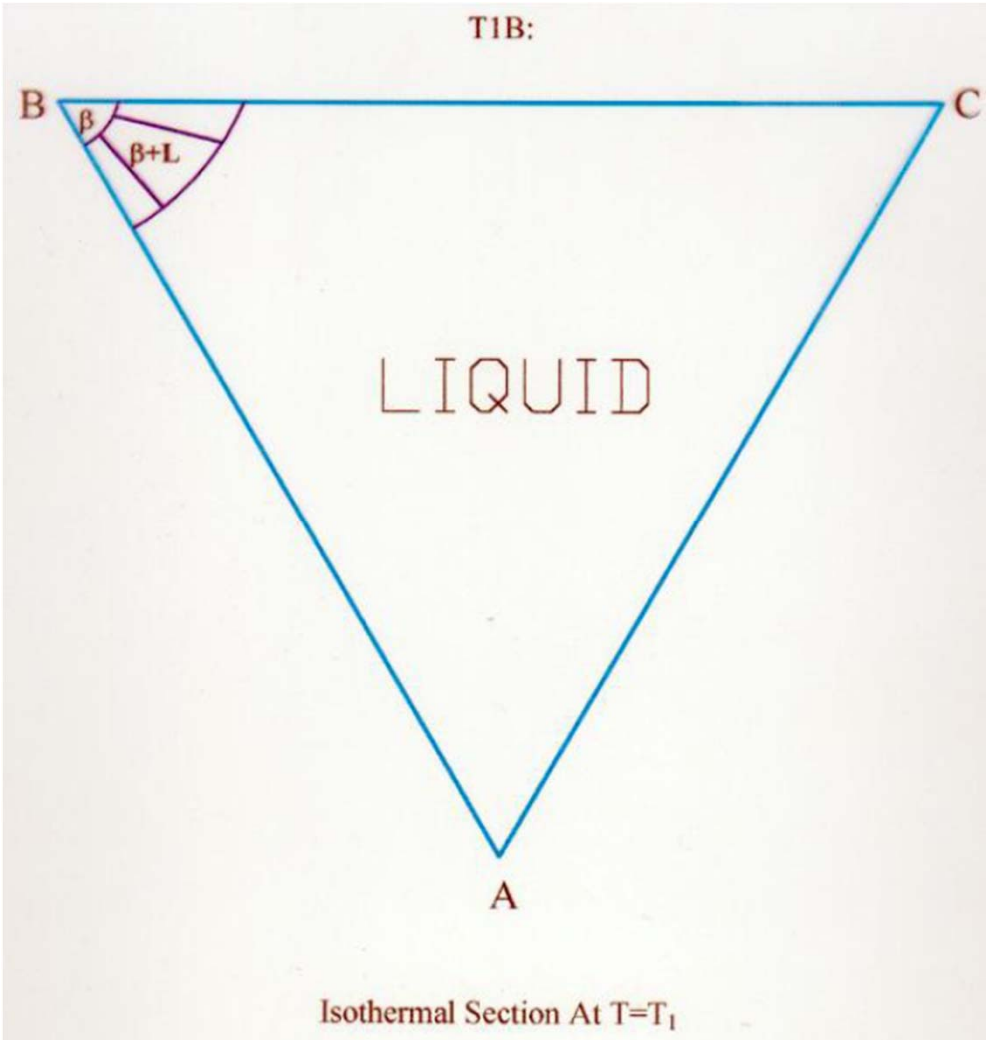


All Liquidus surfaces (α+L-Red, β+L-Purple, γ+L-Green)

Ternary Eutectic System
(with Solid Solubility)



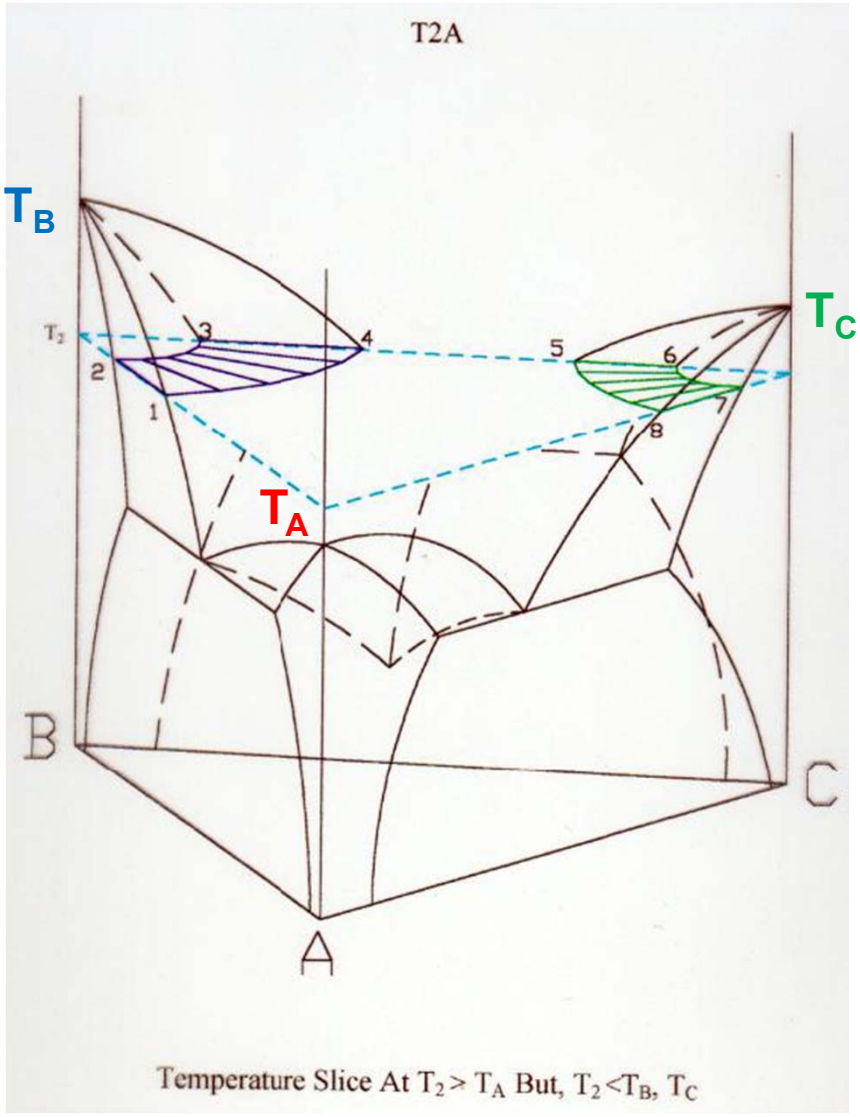
Temperature Slice At $T_1 < T_B$, But $> T_A$, T_C



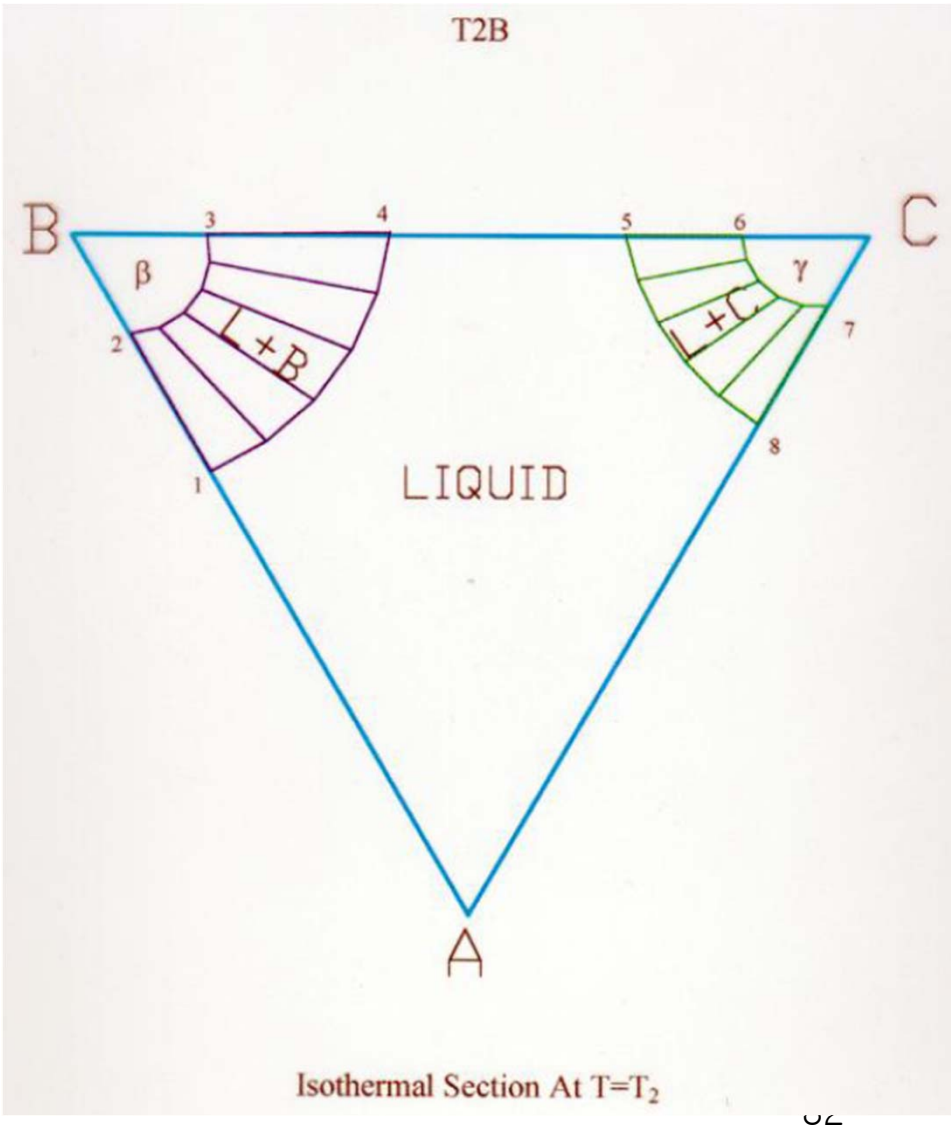
Isothermal Section At $T=T_1$

Ternary Eutectic System

(with Solid Solubility)



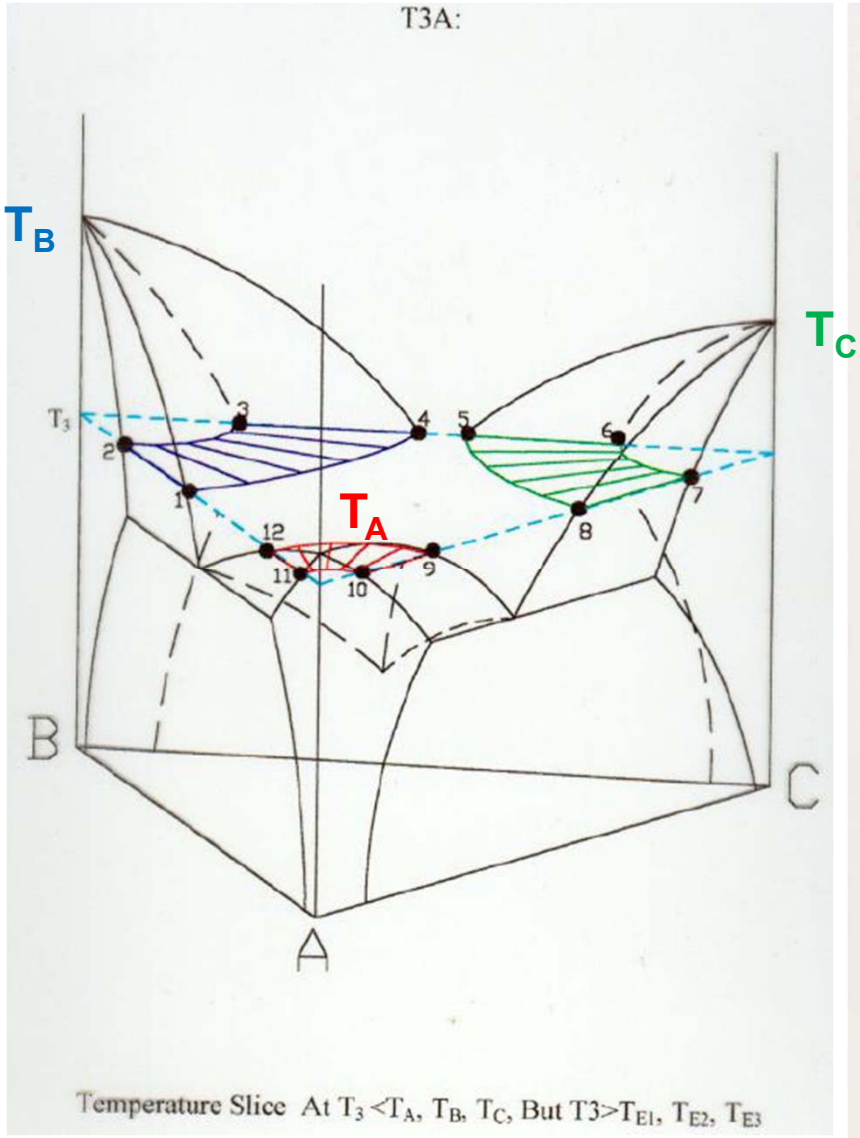
Temperature Slice At $T_2 > T_A$ But, $T_2 < T_B$, T_C

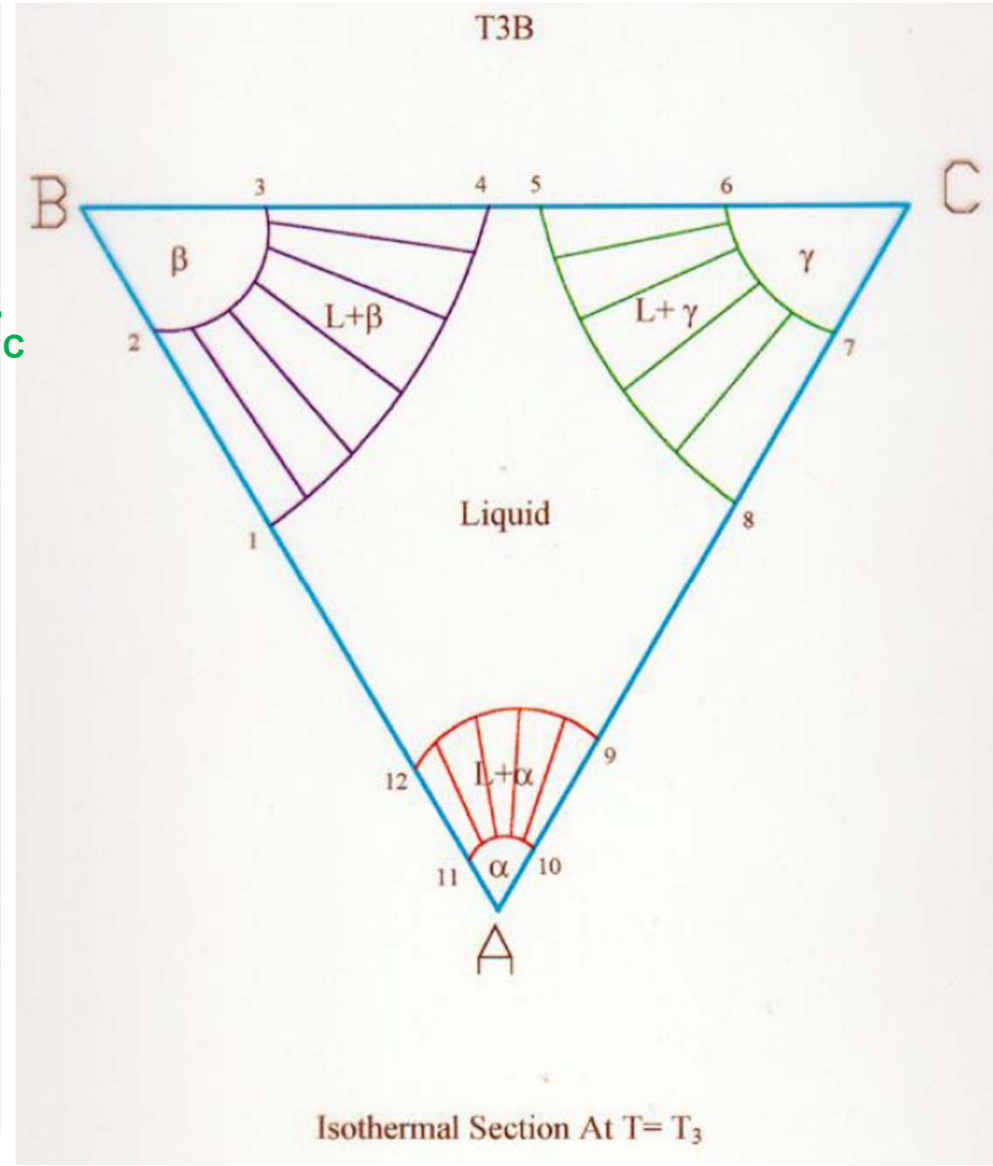


Isothermal Section At $T=T_2$

Ternary Eutectic System

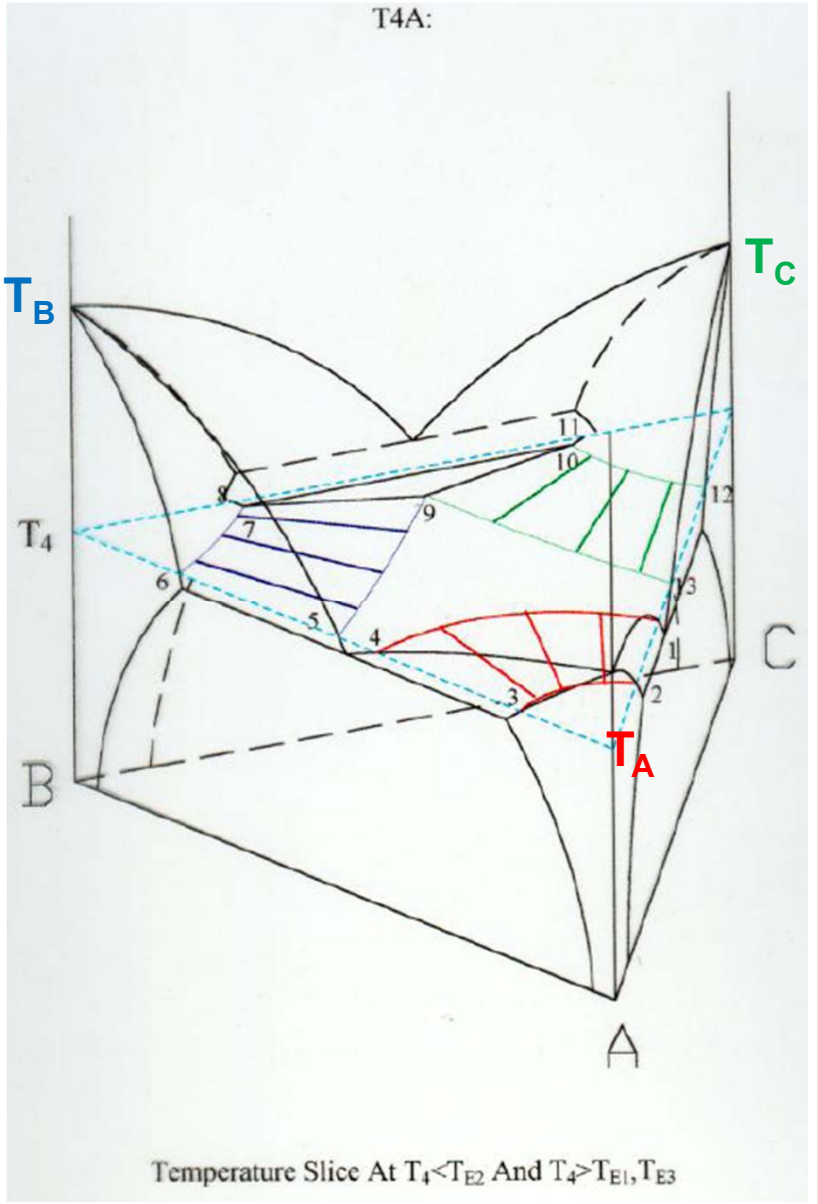
(with Solid Solubility)



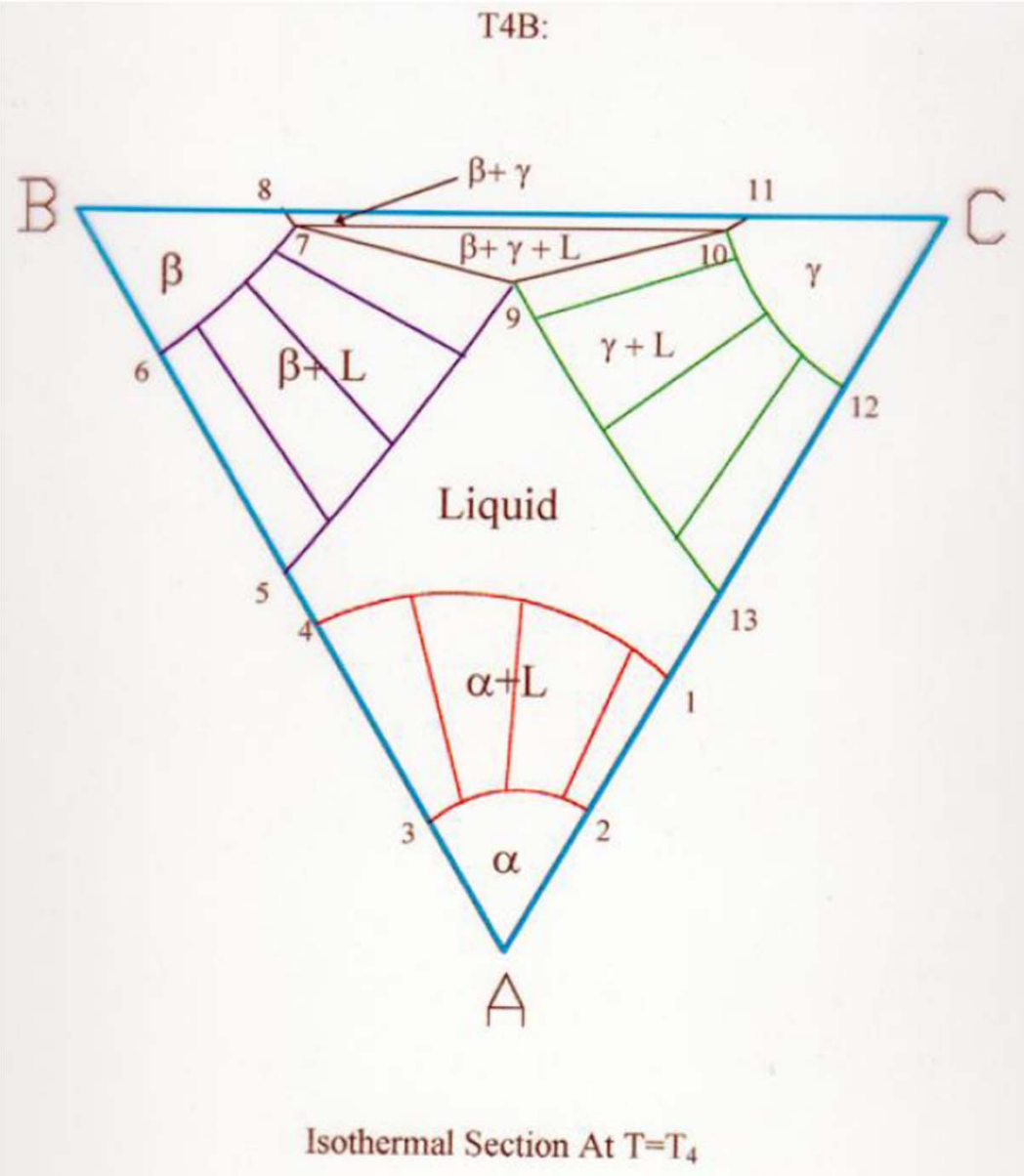


Ternary Eutectic System

(with Solid Solubility)

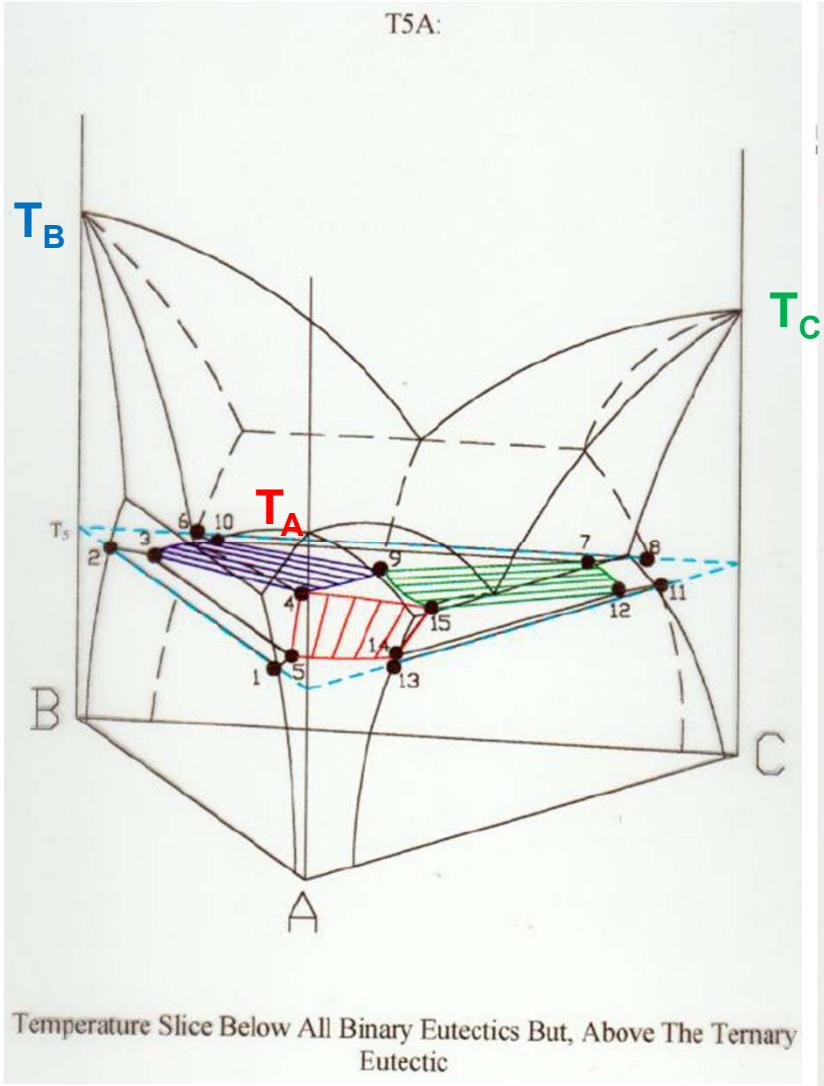


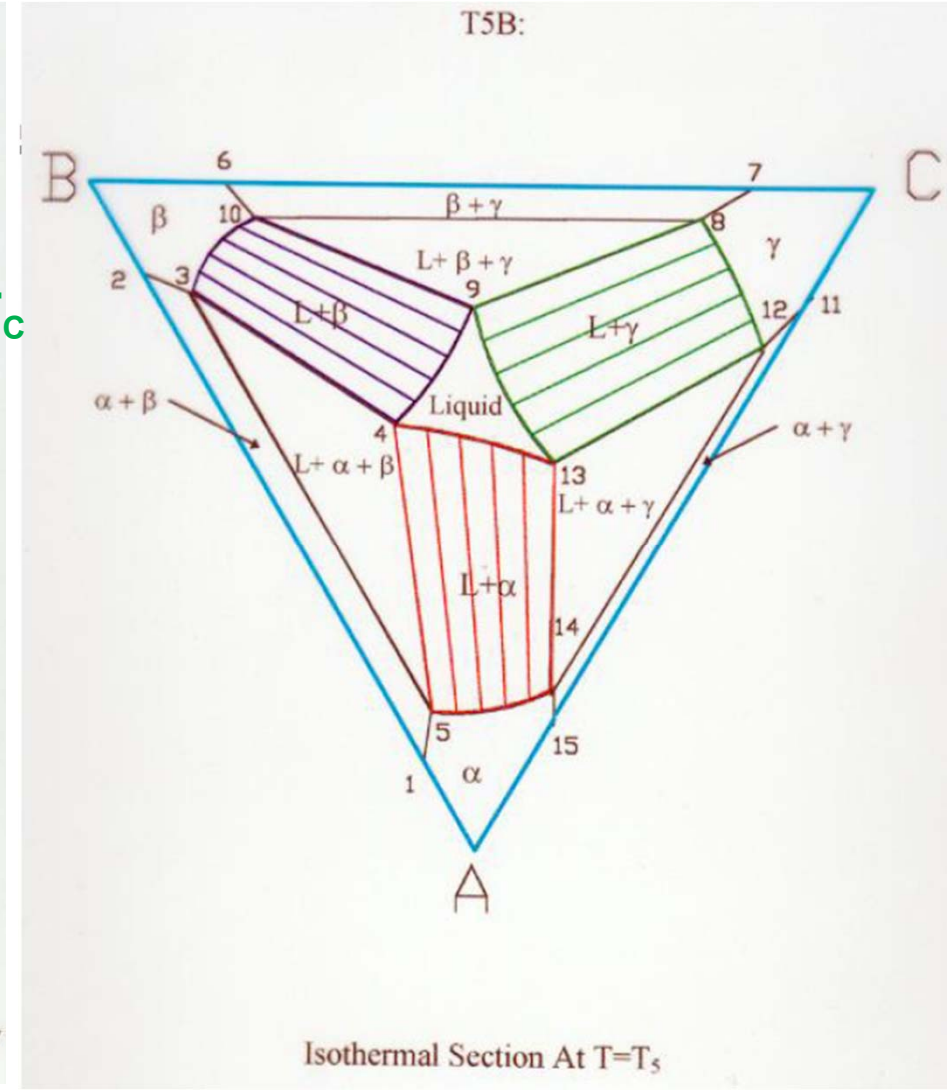
Temperature Slice At $T_4<T_{E2}$ And $T_4>T_{E1},T_{E3}$



Isothermal Section At $T=T_4$

Ternary Eutectic System
(with Solid Solubility)

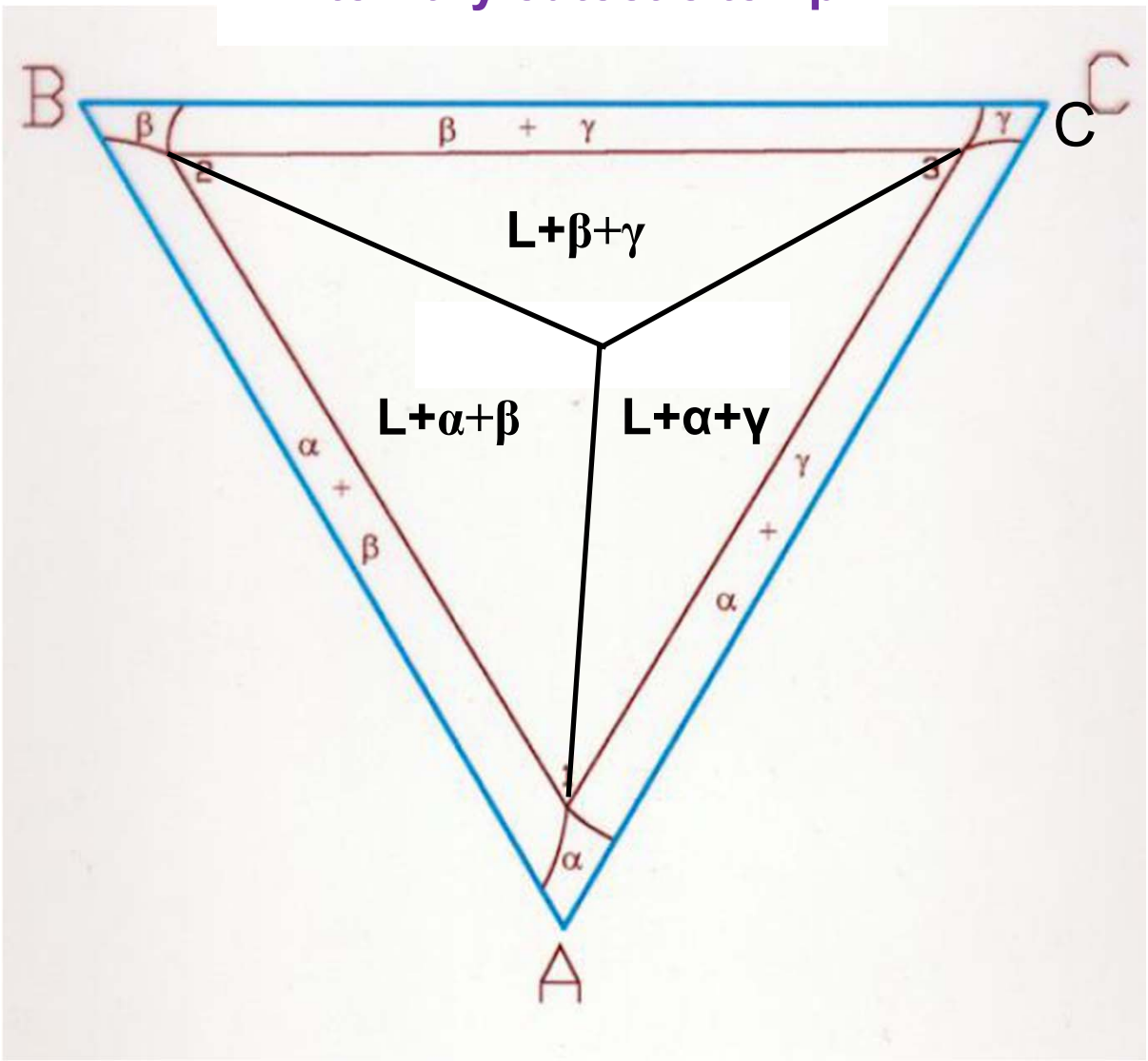




Ternary Eutectic System

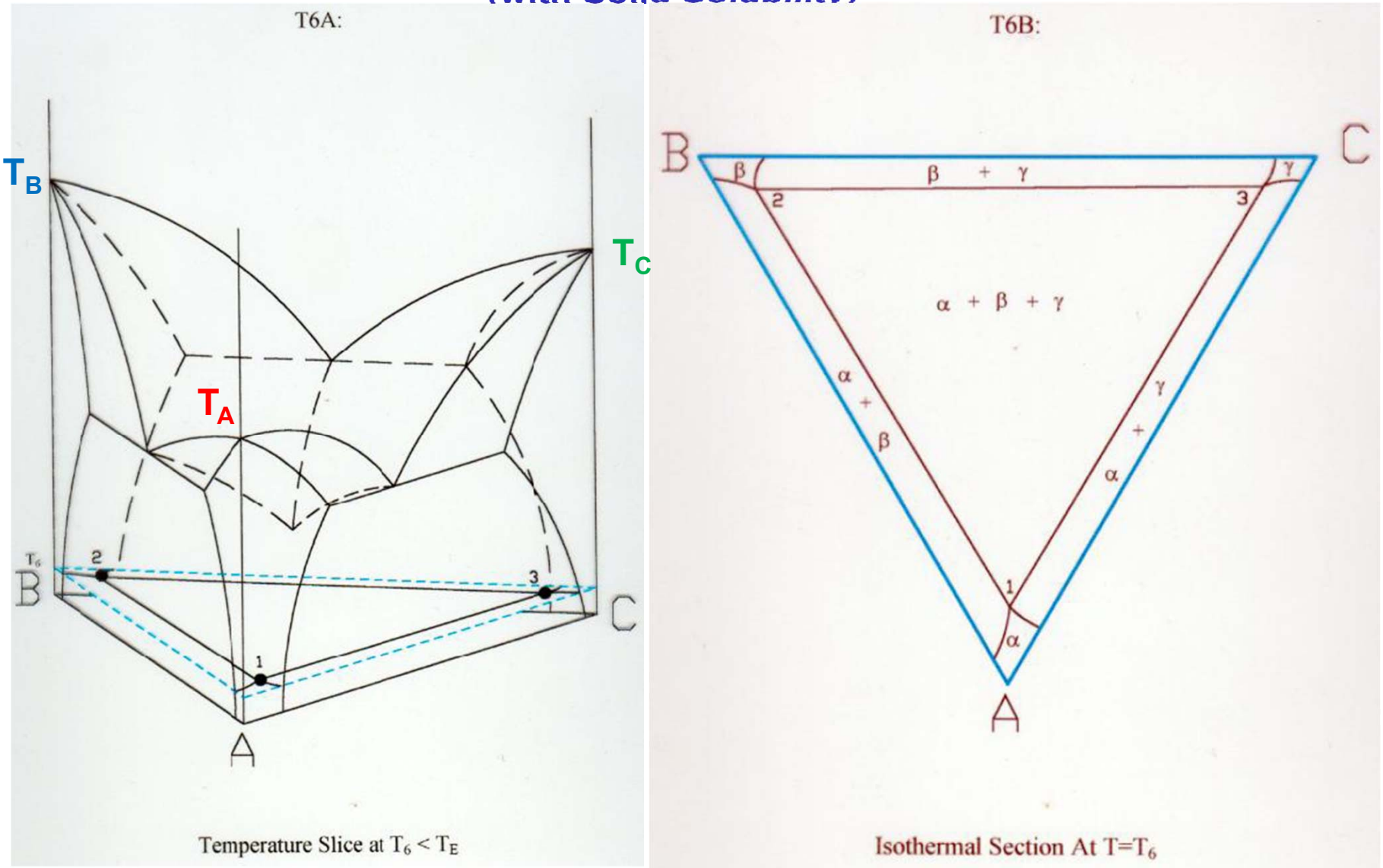
(with Solid Solubility)

T= ternary eutectic temp.



Ternary Eutectic System

(with Solid Solubility)

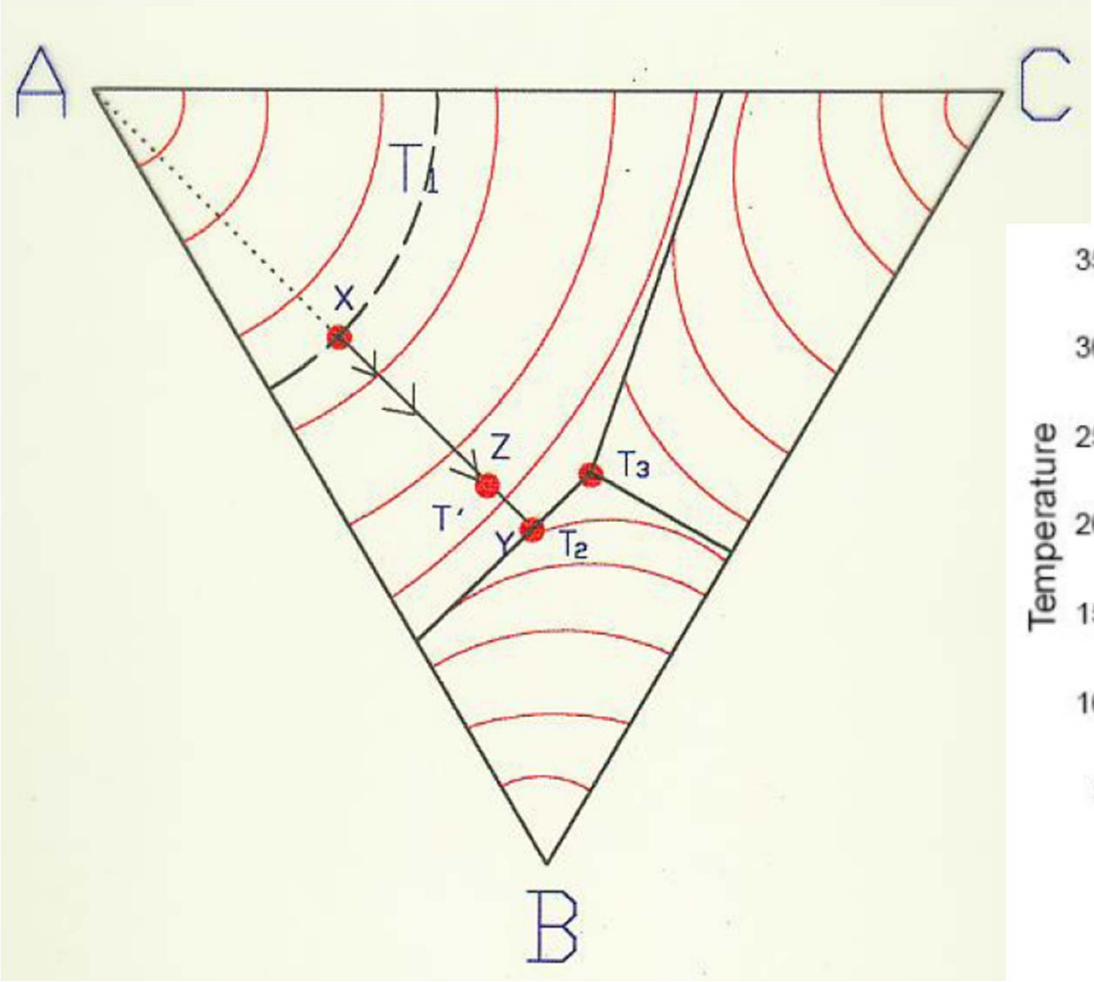


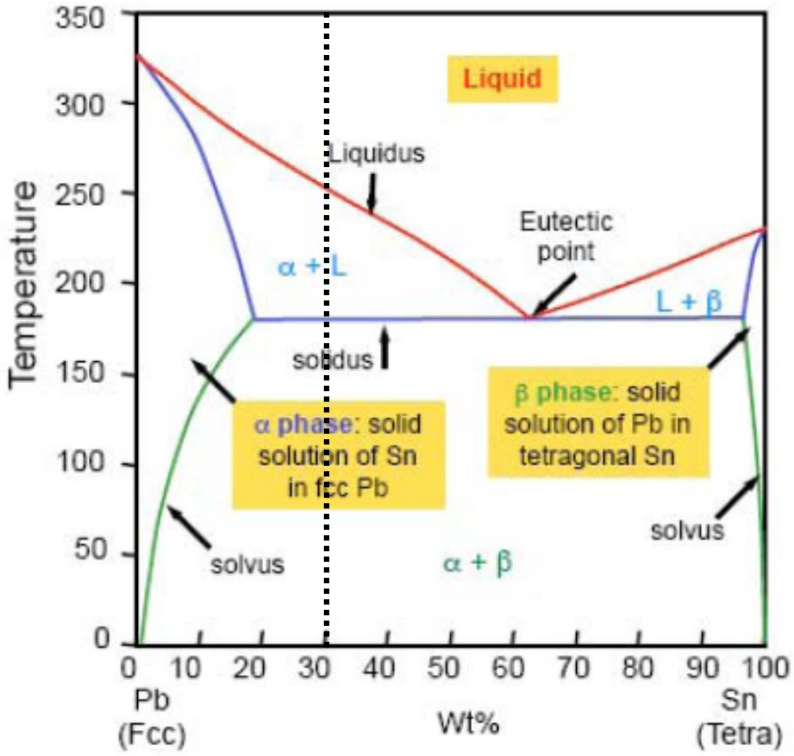
정해솔 학생 제공 자료 참조: 실제 isothermal section의 온도에 따른 변화

http://www.youtube.com/watch?v=yzhVomAdetM

Ternary Eutectic System

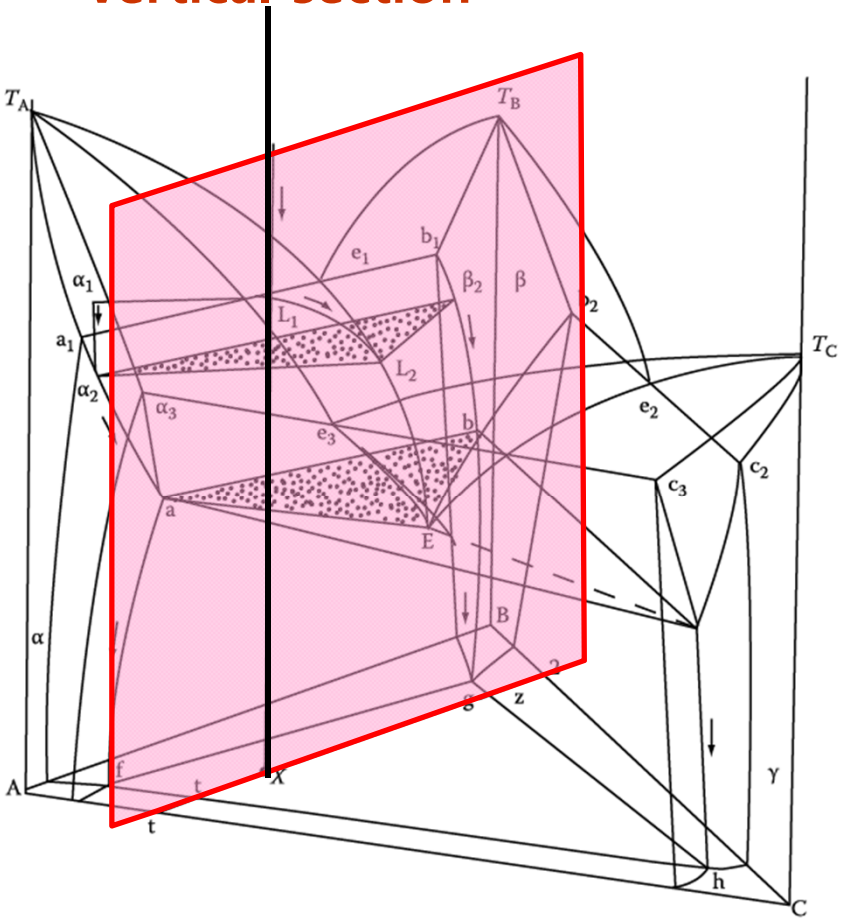
3) Solidification Sequence: liquidus surface

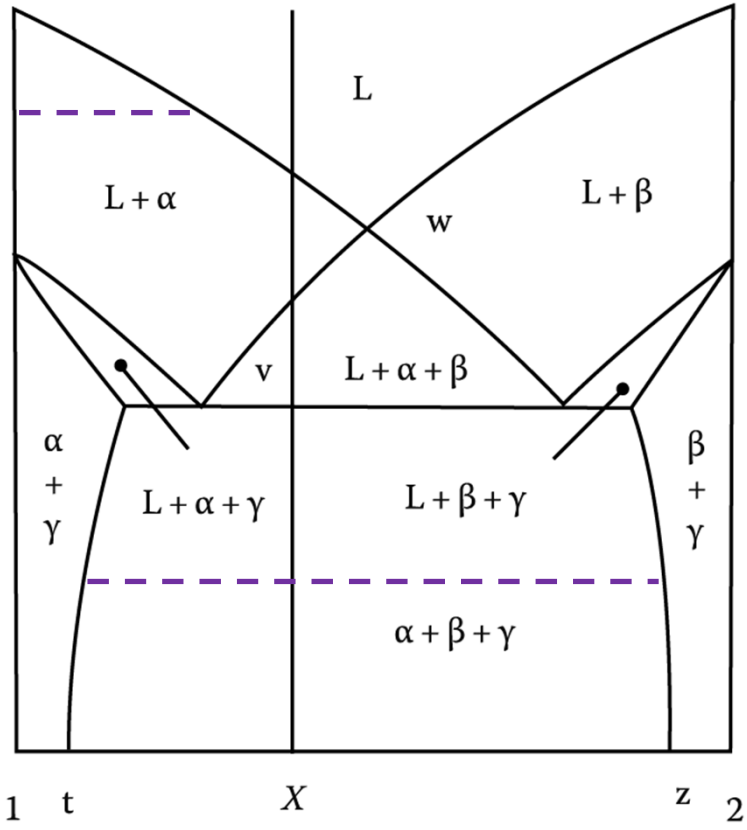




Ternary Eutectic System

* Vertical section





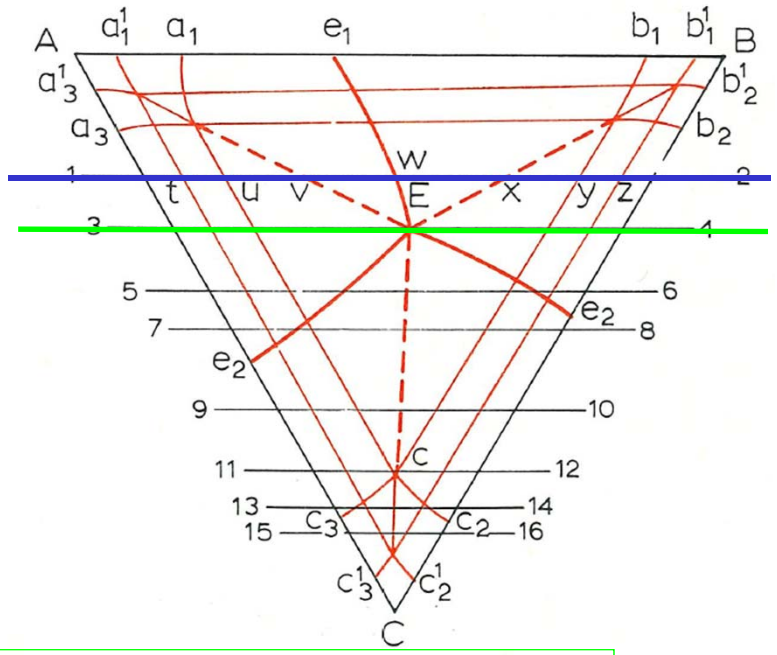
* The horizontal lines are not tie lines. (no compositional information)

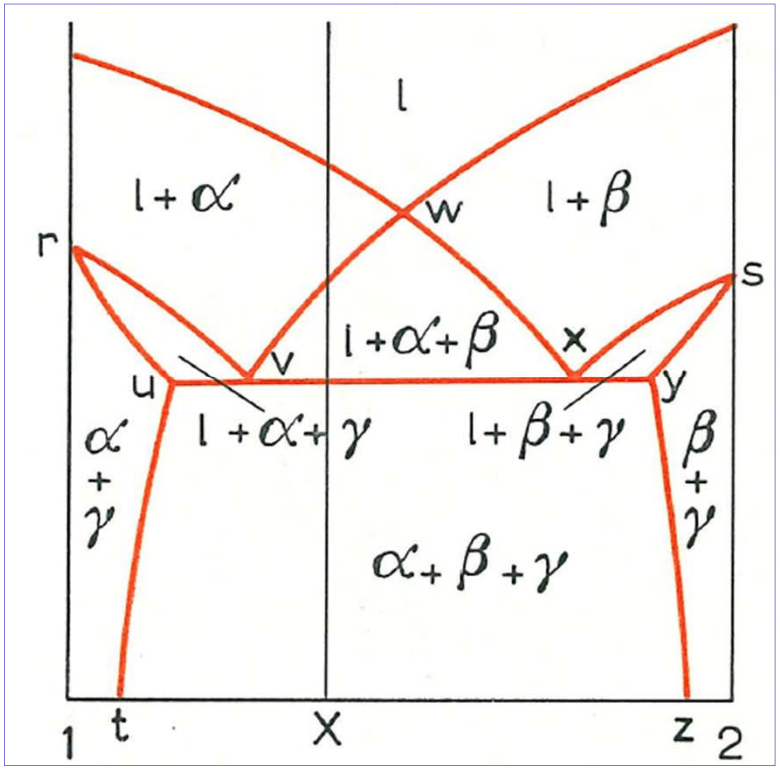
* Information for equilibrium phases at different tempeatures

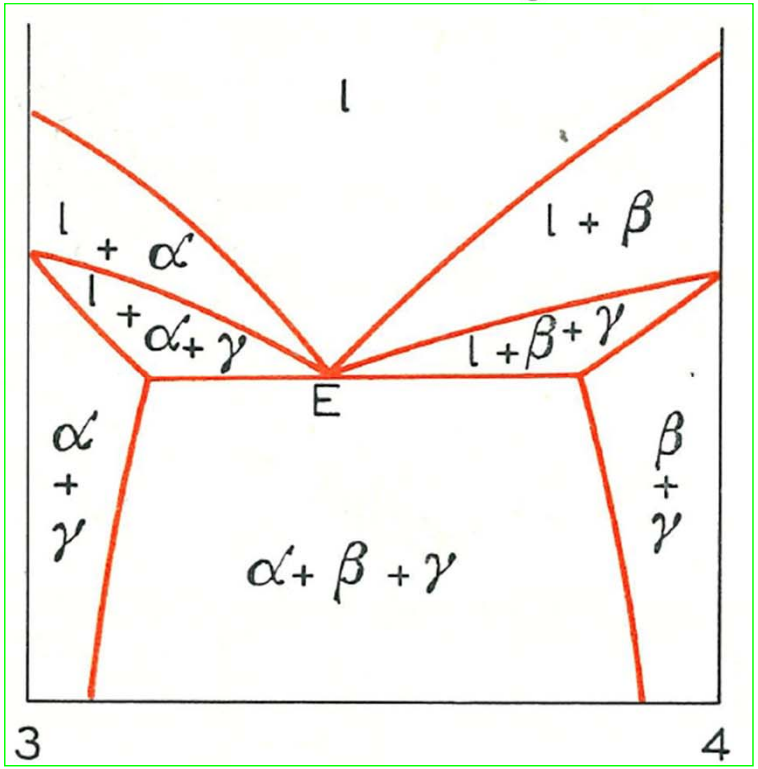
10.1. THE EUTECTIC EQUILIBRIUM

$(l = \alpha + \beta + \gamma)$

Vertical section **Location of vertical section**

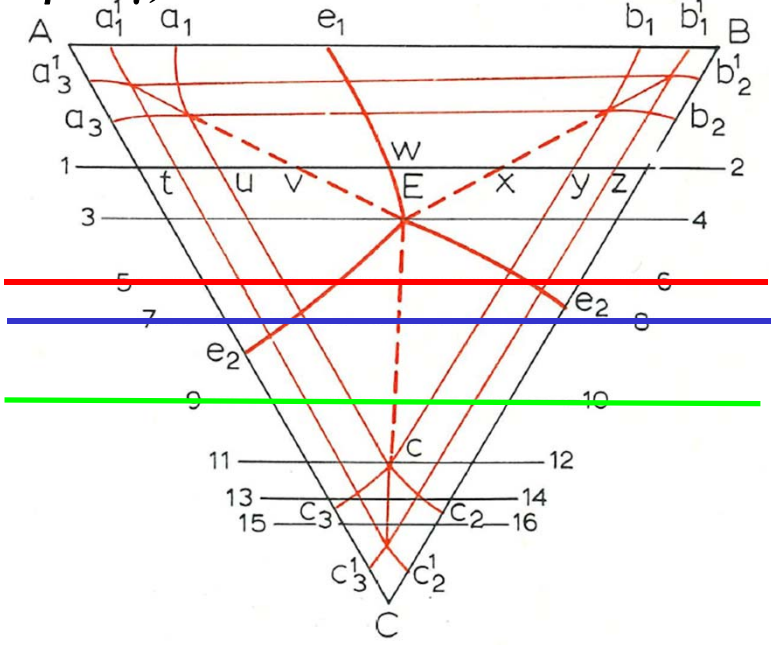


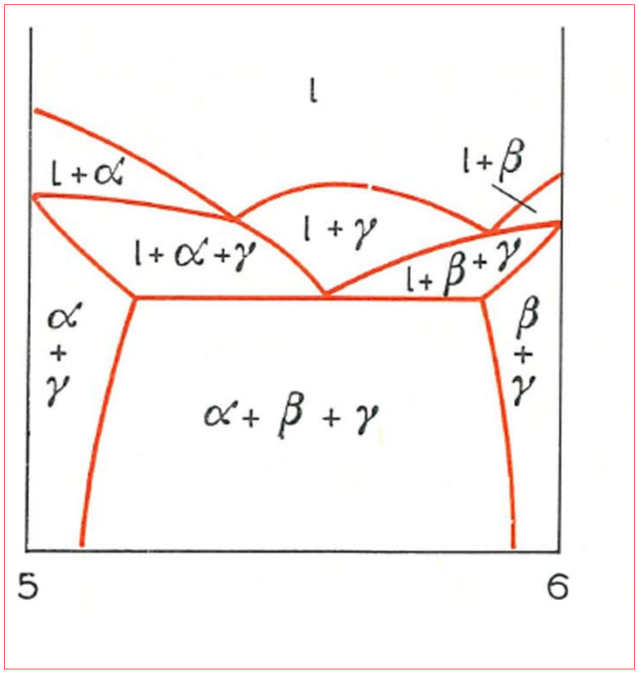


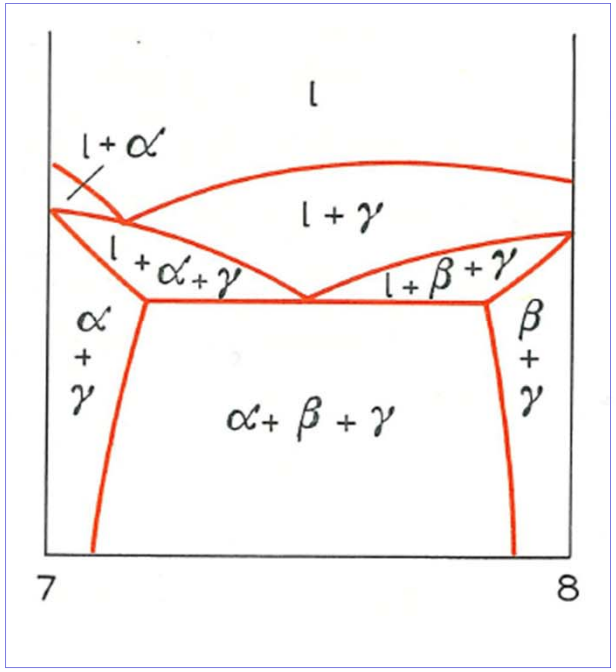


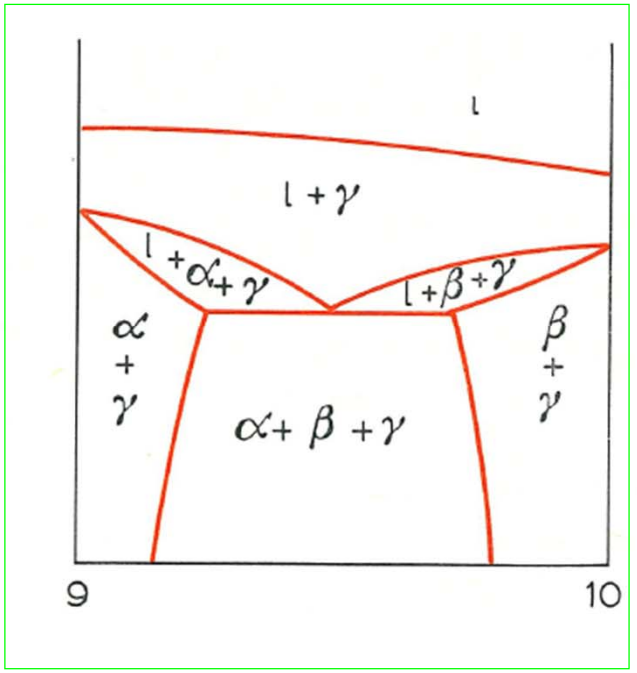
10.1. THE EUTECTIC EQUILIBRIUM ($l = \alpha + \beta + \gamma$)

Vertical section **Location of vertical section**



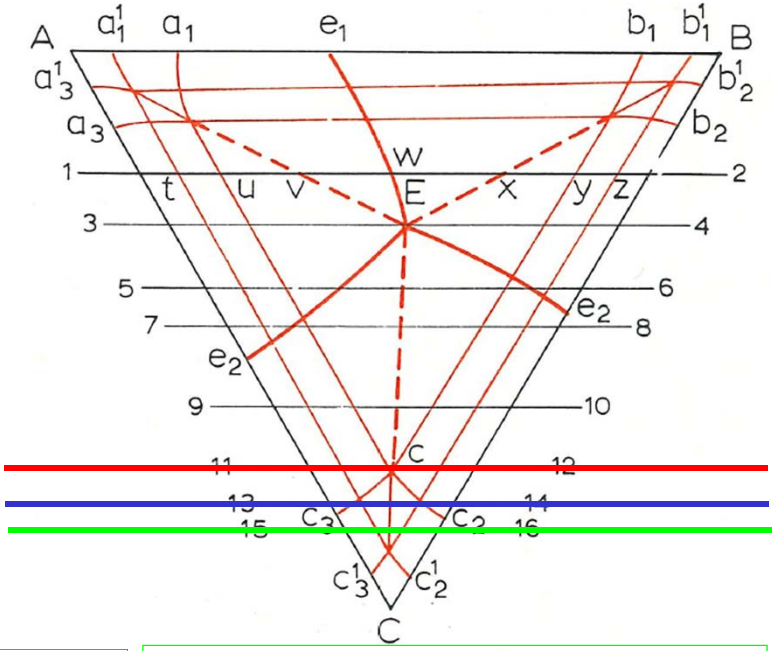


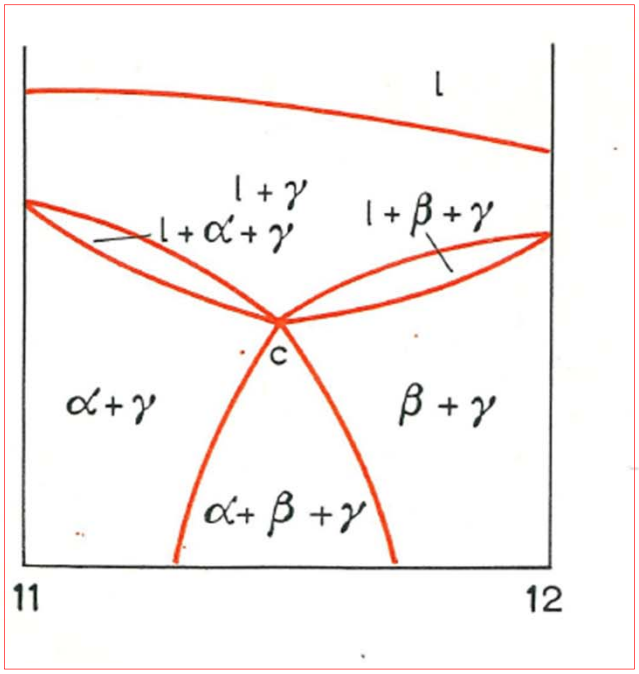


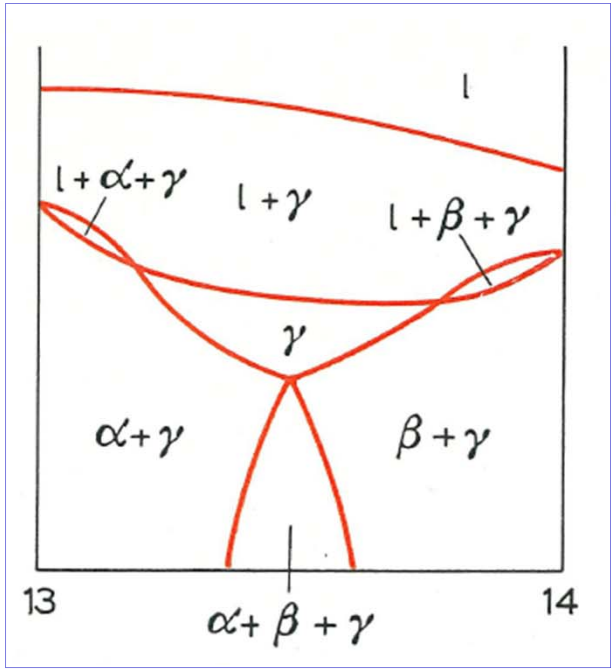


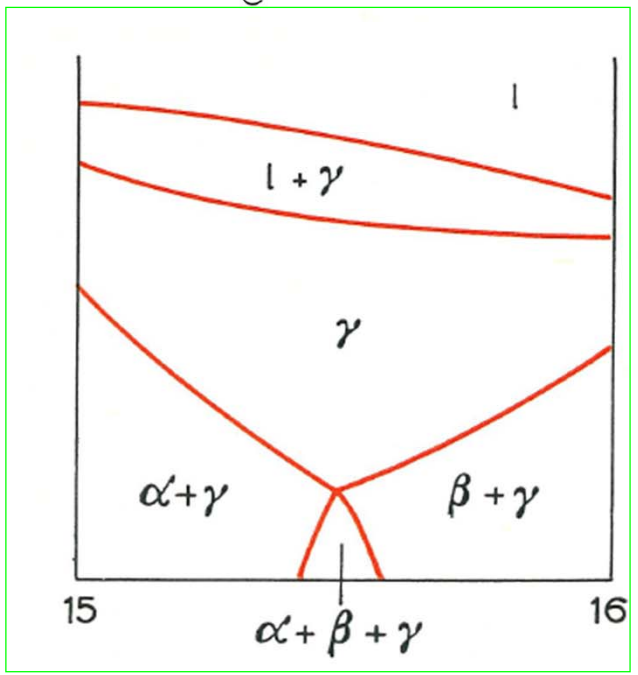
10.1. THE EUTECTIC EQUILIBRIUM ($l = \alpha + \beta + \gamma$)

Vertical section **Location of vertical section**









< Quaternary phase Diagrams >

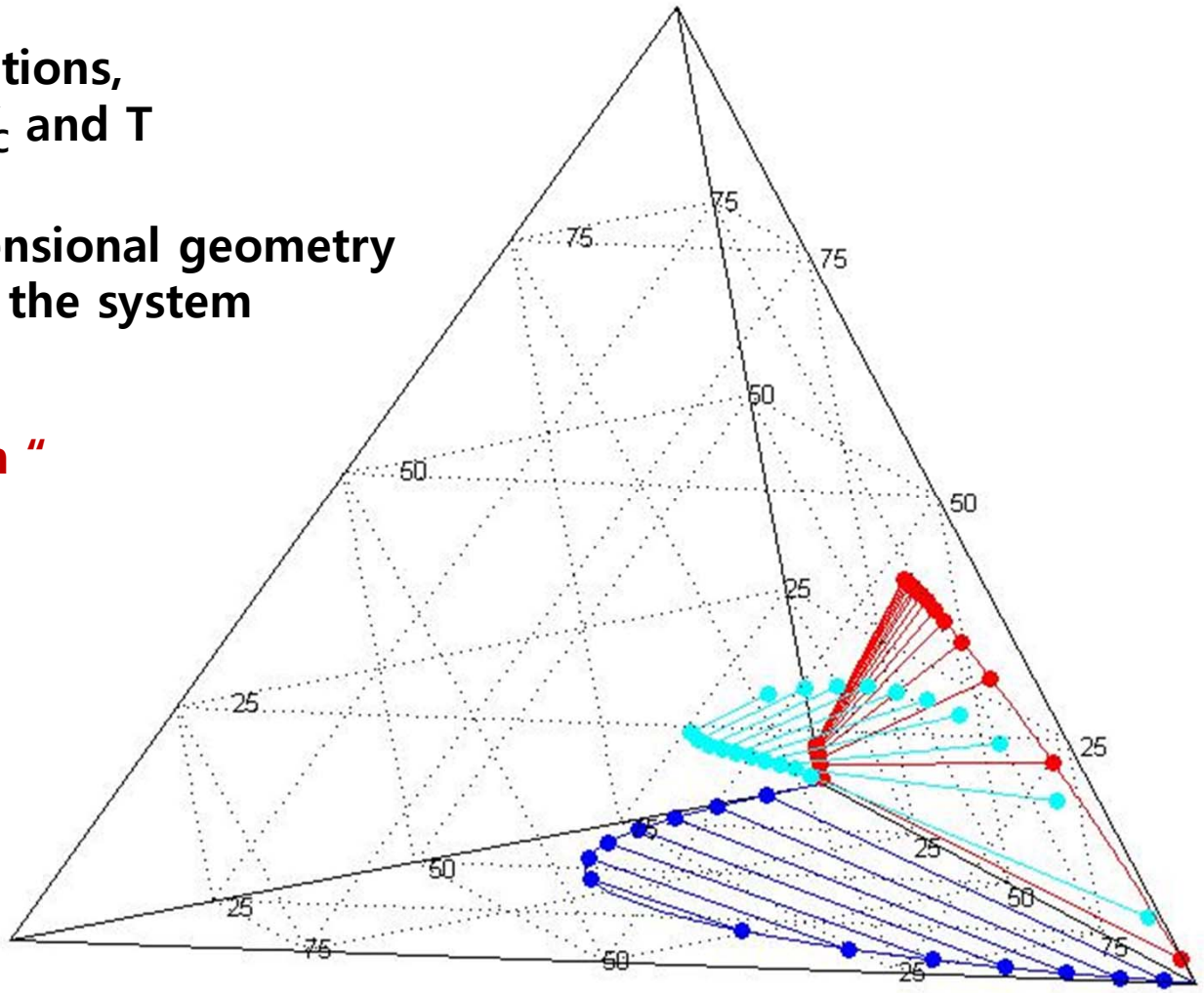
Four components: A, B, C, D

Assuming isobaric conditions,
Four variables: X_A, X_B, X_C and T

A difficulty of four-dimensional geometry
→ further restriction on the system

Most common figure:
" equilateral tetrahedron "

- **4 pure components**
- **6 binary systems**
- **4 ternary systems**
- **A quarternary system**



* Draw four small equilateral tetrahedron
→ formed with edge lengths of a, b, c, d

$$a+b+c+d=100$$

$$\%A=Pt=c,$$
$$\%B=Pr=a,$$
$$\%C=Pu=d,$$
$$\%D=Ps=b$$

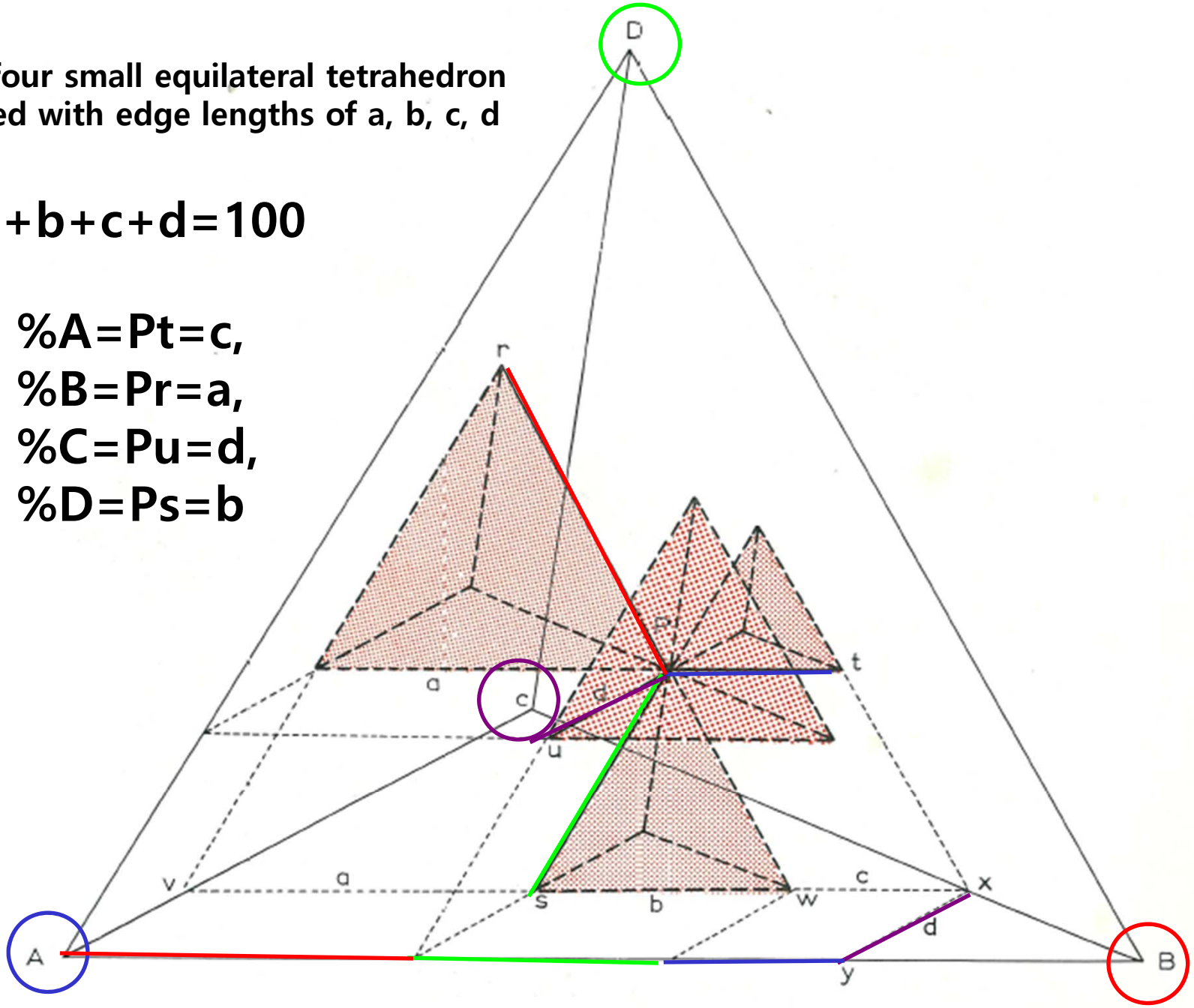
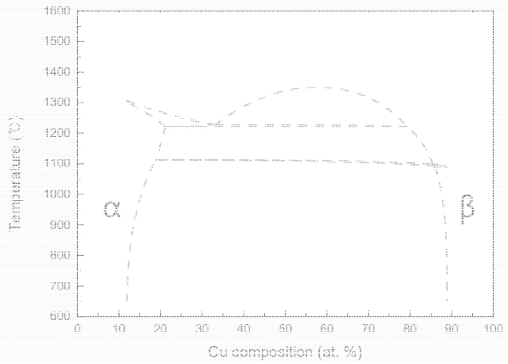


Fig. 247. Representation of a quaternary system by an equilateral tetrahedron.

Construction of pseudo-binary phase diagram for multi-component alloy system

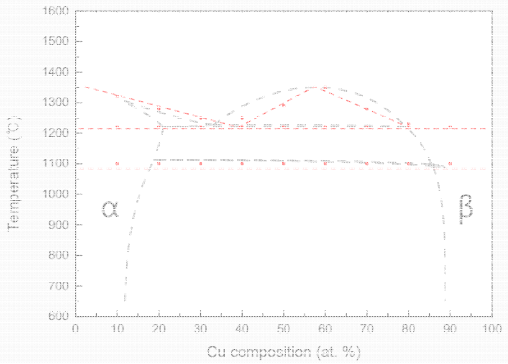


Thermodynamic calculation

- Expecting approximation of phase diagram

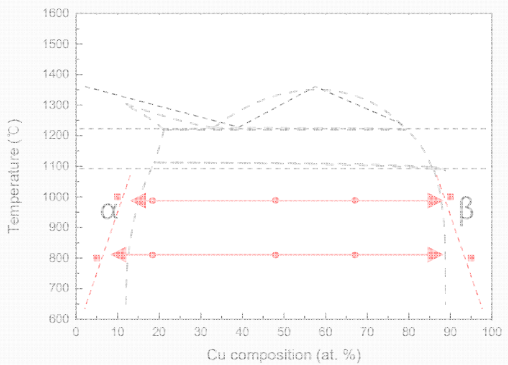
X-ray diffraction

- Determination of phases



TGA/DSC

- Finding out temperatures of phase transformations
- Confirming invariant reaction points

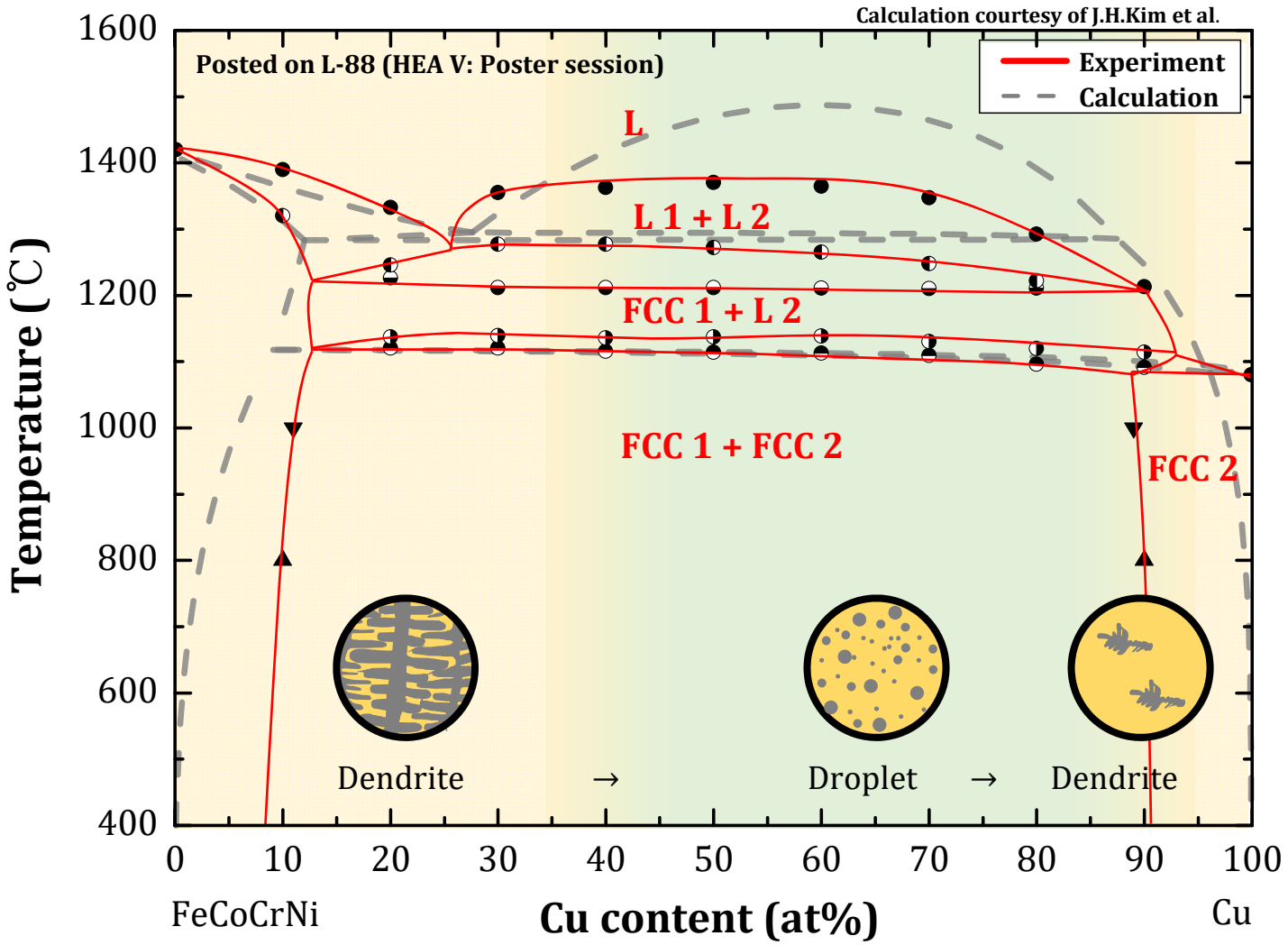


FE-EPMA

- Investigation of equilibrium composition at each temperature

➢ Phase diagram was expected to optimize composition and microstructure of phase separating HEA

Pseudo-binary phase diagram of PS-HEA



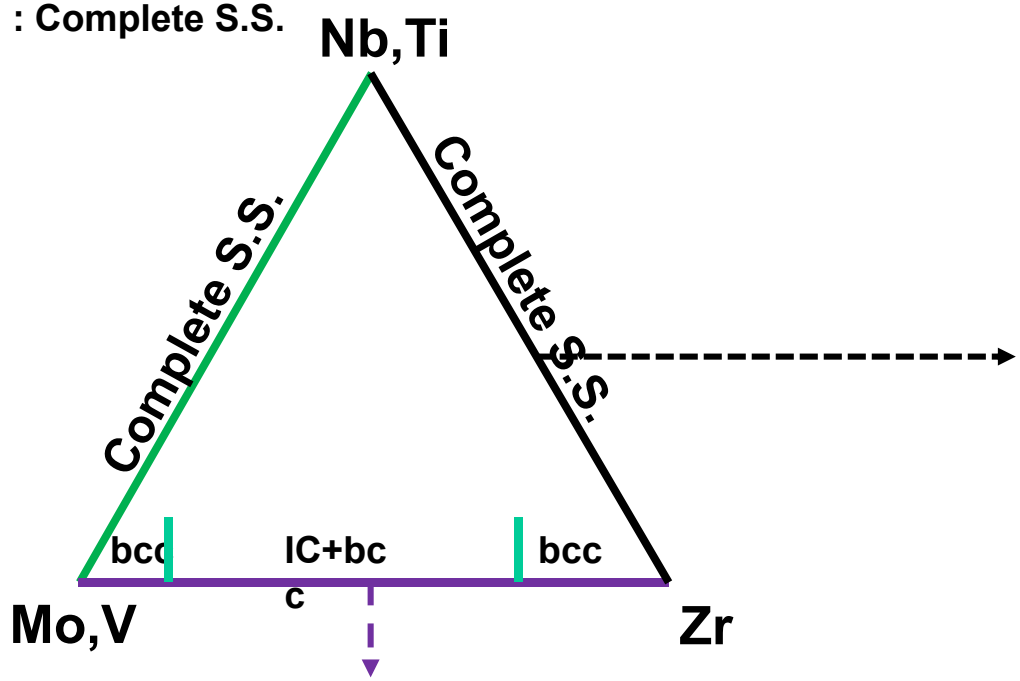
- Pseudo-binary system between FeCoCrNi and Cu shows monotectic reaction having liquid separation region.

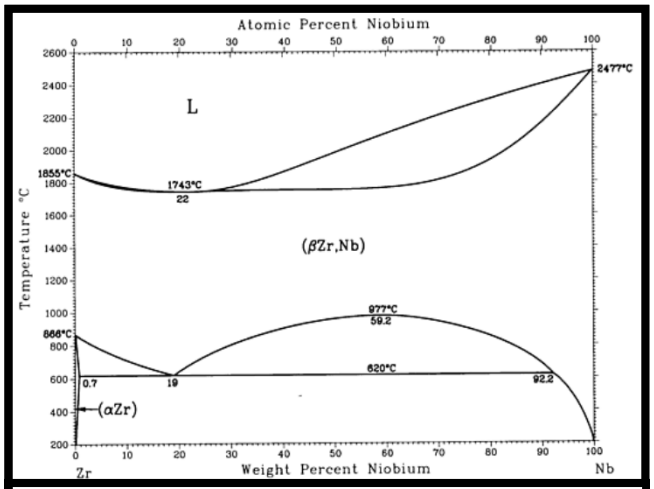
MoVNbTiZr: Construction of pseudo-ternary phase diagram

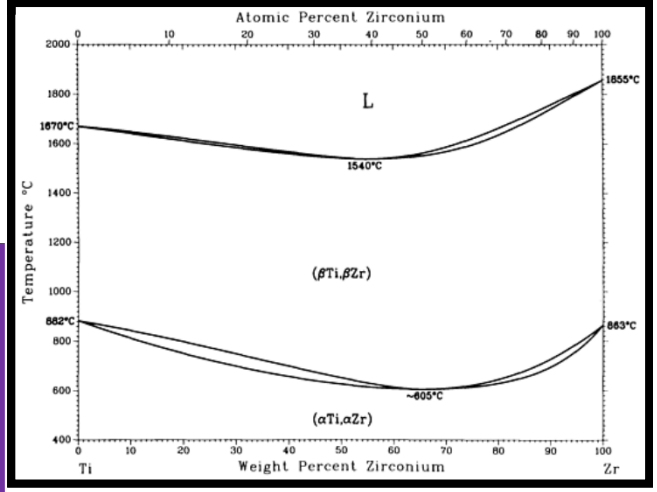
Mo, V, Nb, Ti : Complete S.S.

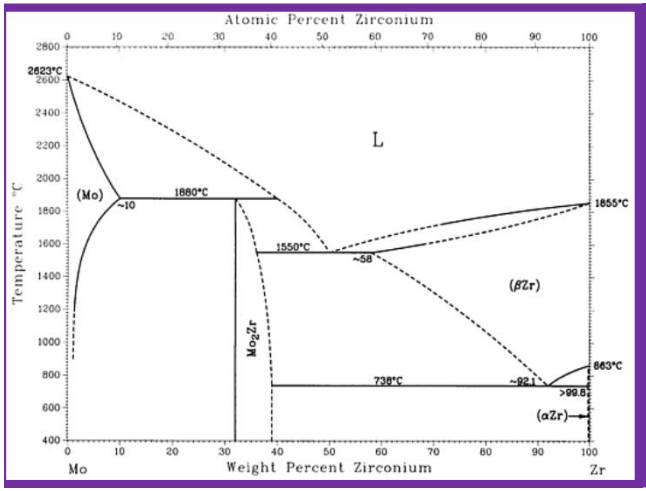
V-Zr, Mo-Zr

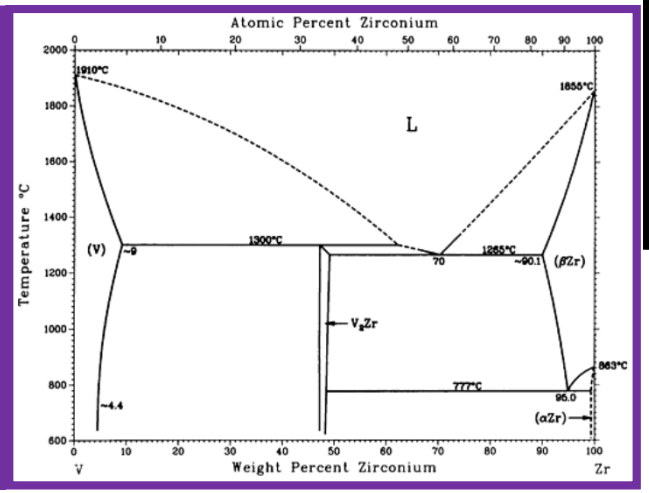
Ti-Zr, Nb-Zr



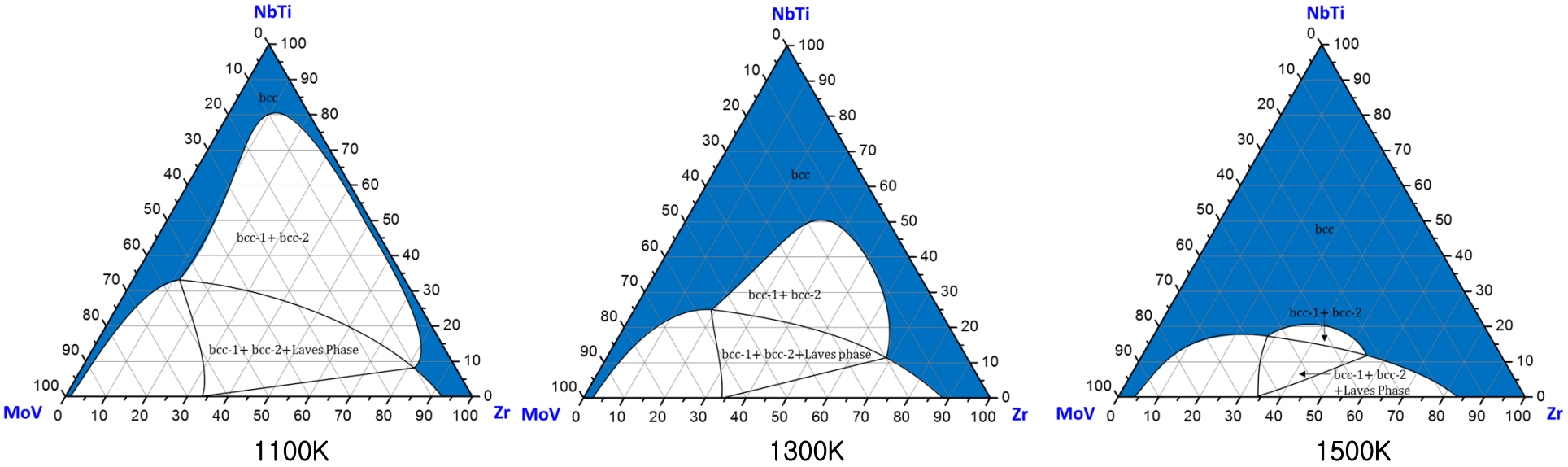






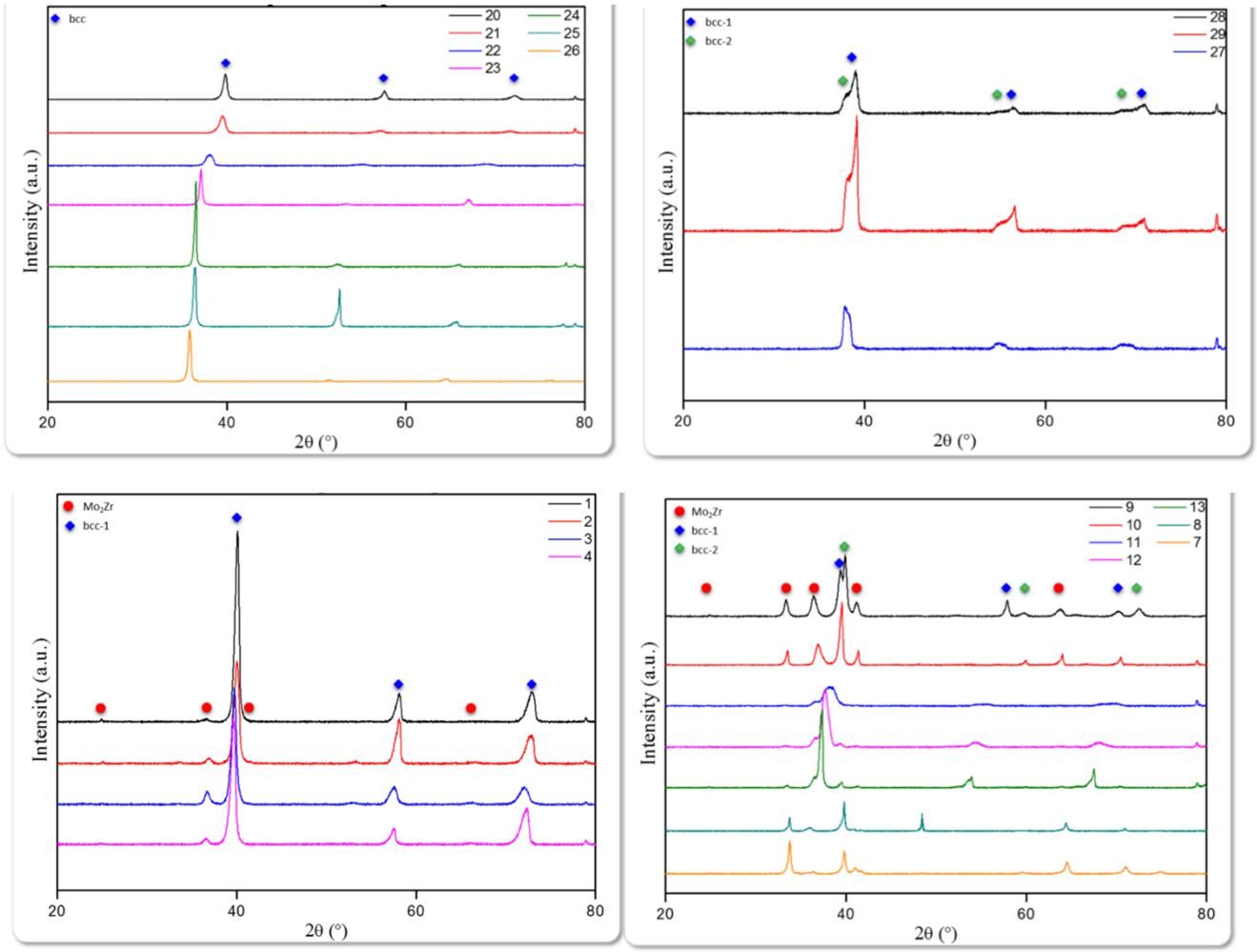


TiNbMoVZr: Construction of pseudo-ternary phase diagram



Calculated pseudo-ternary isothermal sections of the MoNbTiVZr system

MoVNbTiZr: Construction of pseudo-ternary phase diagram



X-ray diffraction analysis of the as-cast samples

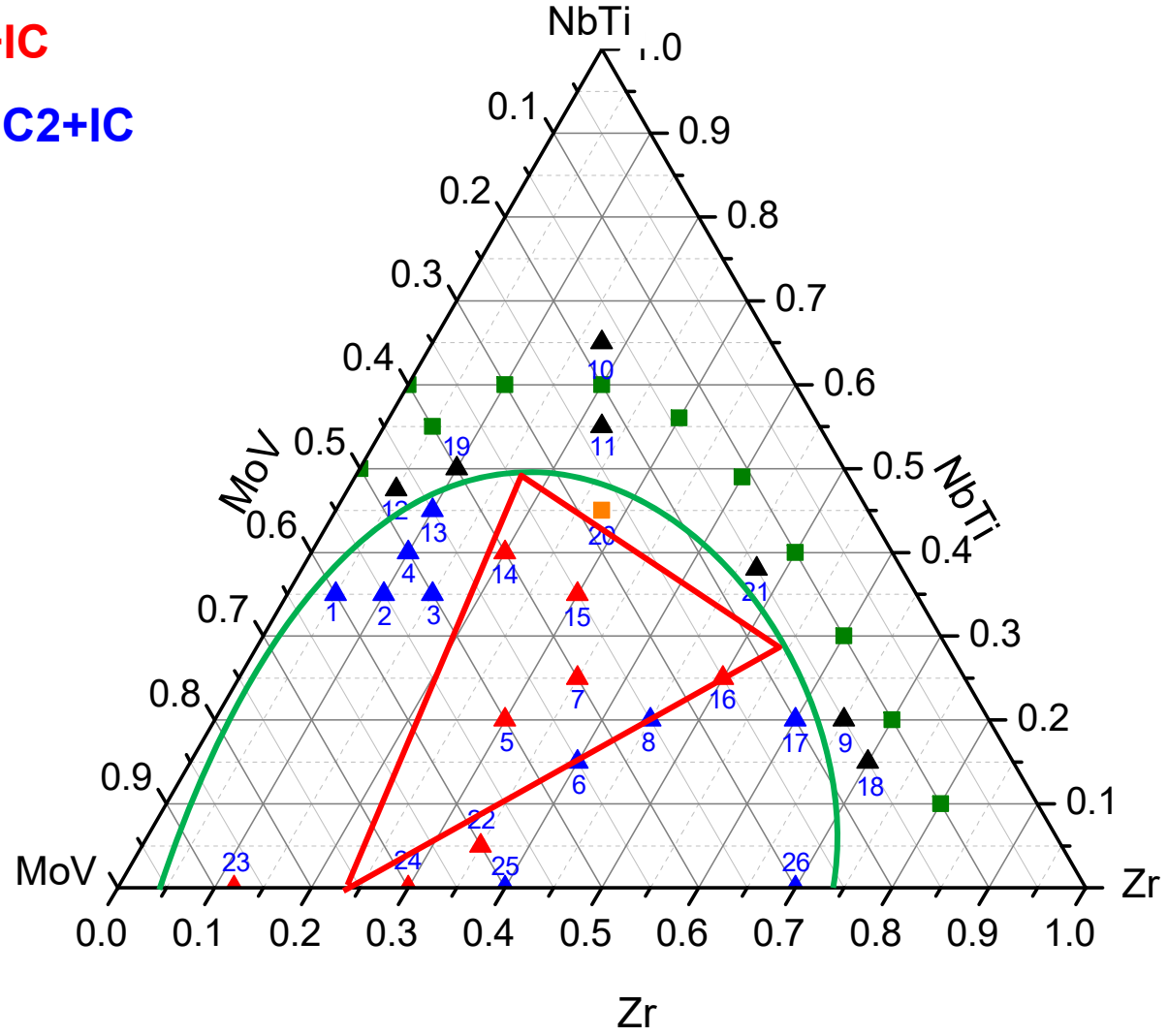
Construction of pseudo-ternary phase diagram

BCC1+BCC2+IC

BCC1+IC / BCC2+IC

BCC1+BCC2

Single BCC



Find single phase region without intermetallic compounds

Homework1 :

Please explain how to calculate muti-component phase diagram reflecting excess Gibbs energy based on session 1.9. (within 3 pages PPT)

*** Incentive Homework 1**

Please submit ternary phase diagram model which can clearly express 3D structure of ternary system by October 12 in Bldg. 33-313.
You can submit the model individually or with a small group under 2 persons.

*** Homework 2 : Exercises 1 (pages 61-63)**

Good Luck!!