2015 Fall

"Phase Transformation *in* Materials"

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Eun Soo Park

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

- Equilibrium in Heterogeneous Systems

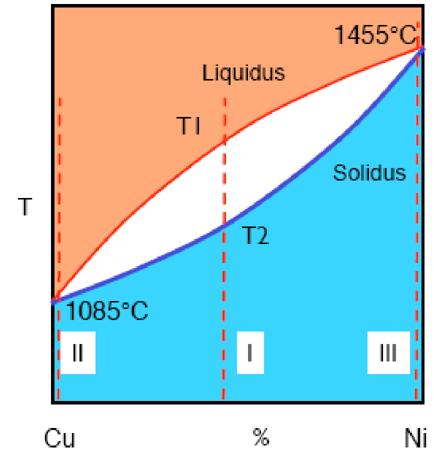
$G_0^{\beta} > G_0^{\alpha} > G_0^{\alpha+\beta}$ ➡ $\alpha + \beta$ separation ➡ unified chemical potential

- Binary phase diagrams

1) Simple Phase Diagrams

$\Delta H^{L}_{mix} = 0 \;\; \Delta H^{S}_{mix} = 0$

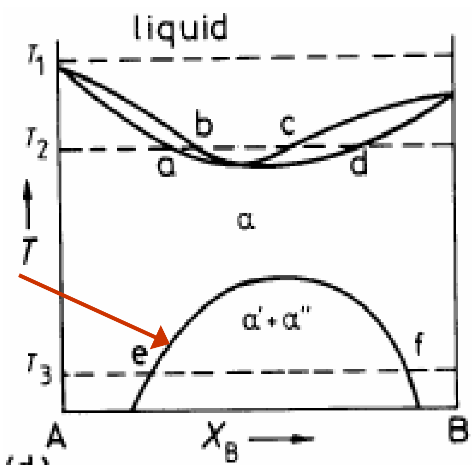
Assume: (1) completely miscible in solid and liquid.
(2) Both are ideal soln.



2) Variant of the simple phase diagram

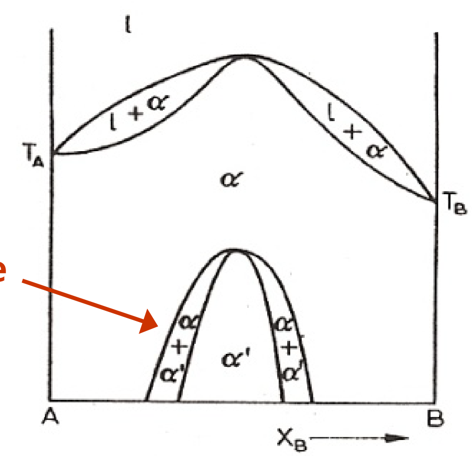
$\Delta H^{\alpha}_{mix} > \Delta H^{l}_{mix} > 0$

miscibility gab

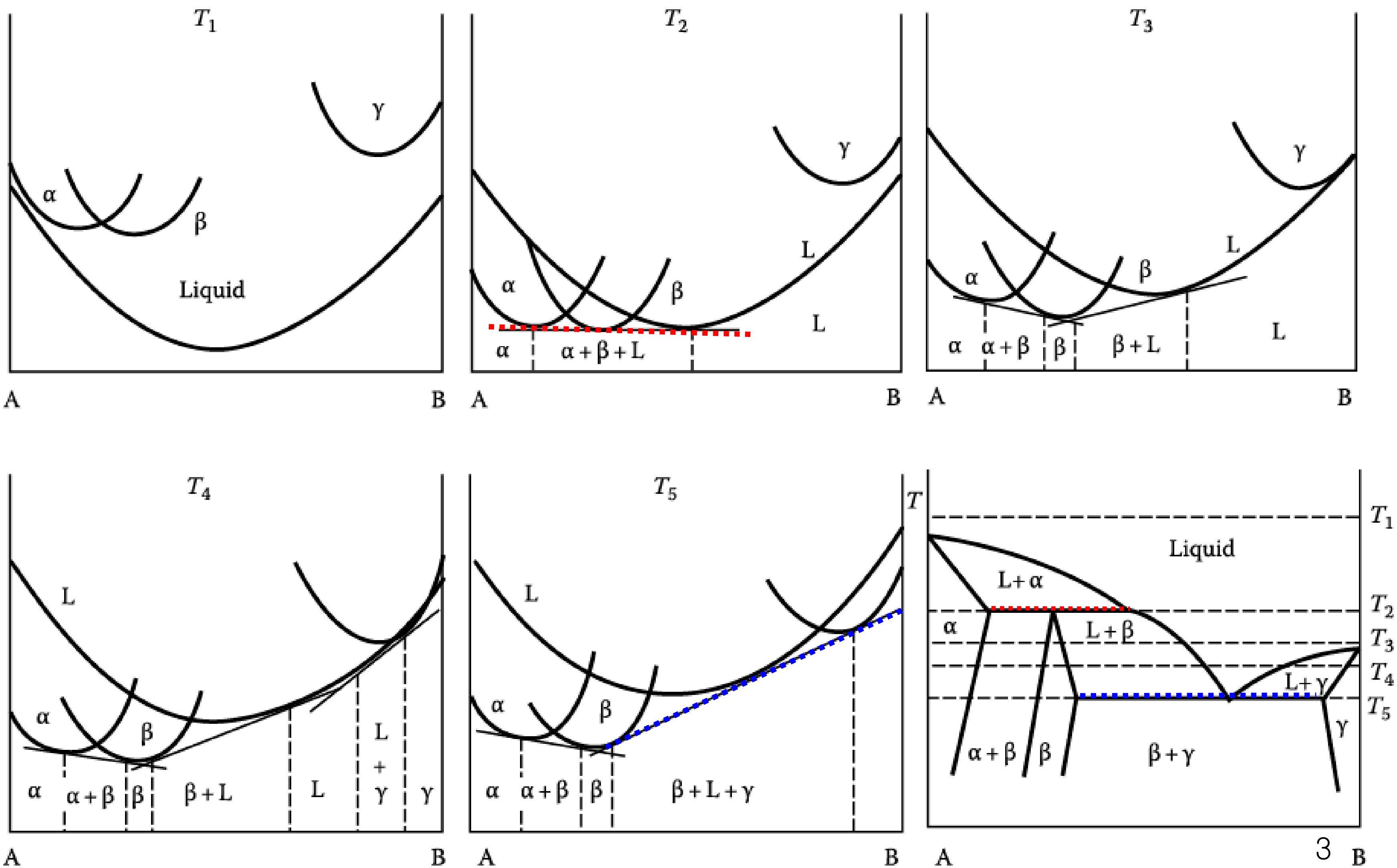


$\Delta H^{\alpha}_{mix} < \Delta H^{l}_{mix} < 0$

Ordered phase



5) Phase diagrams containing intermediate phases



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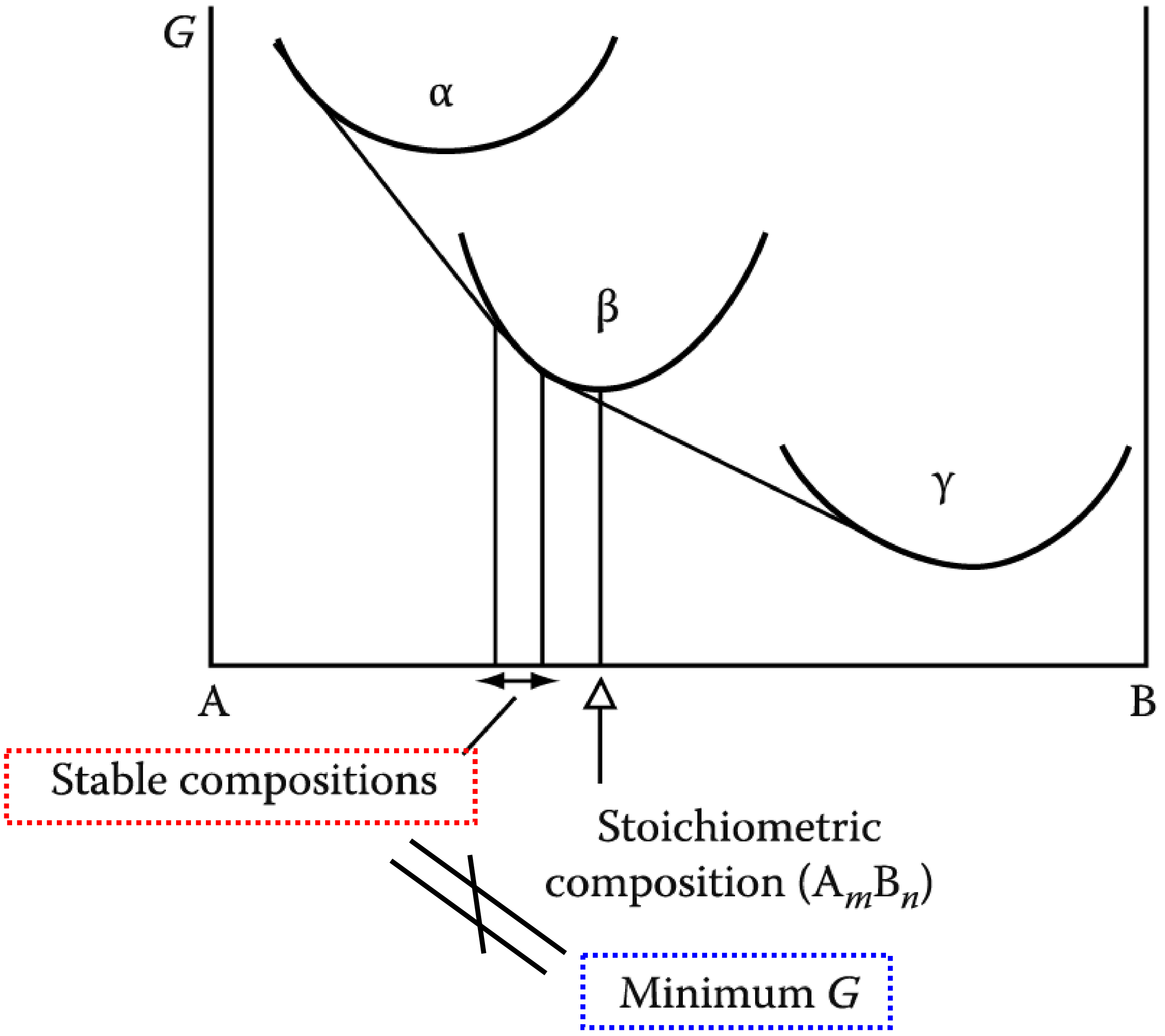
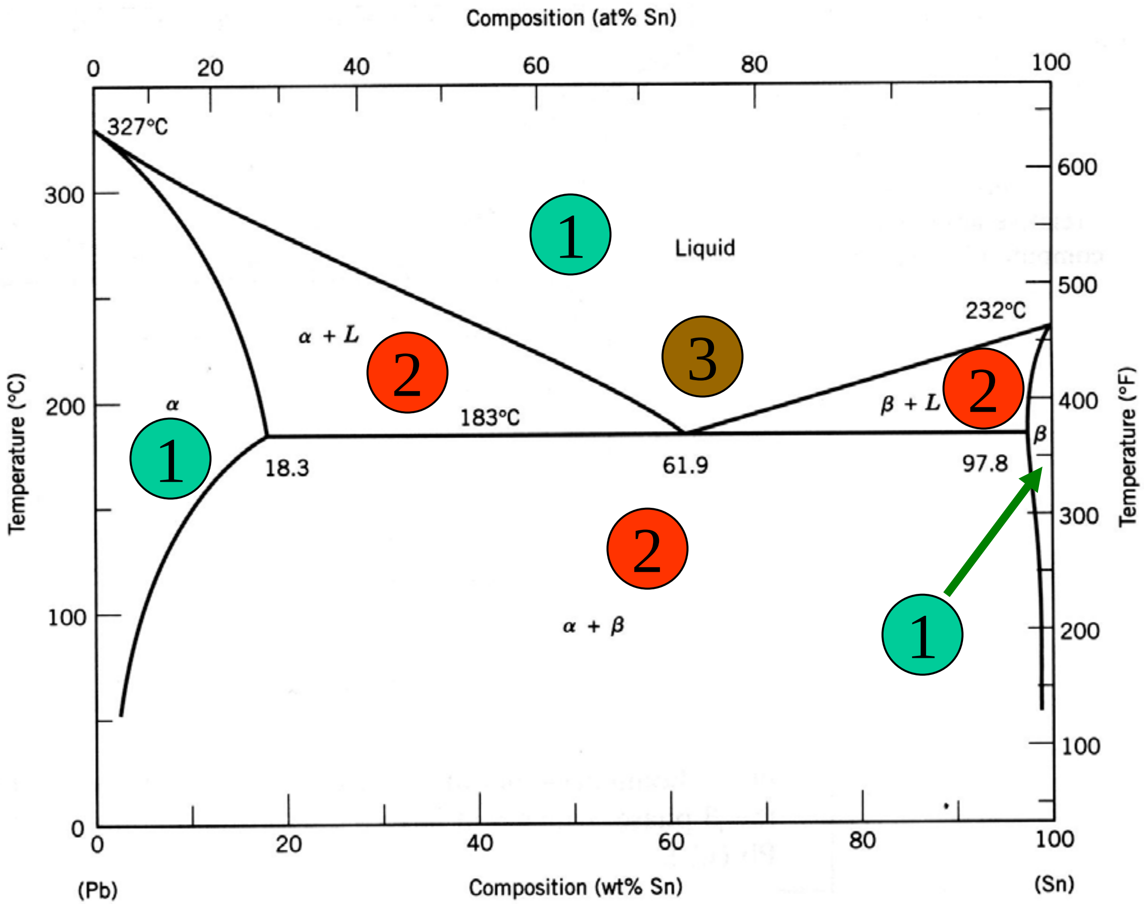


The Gibbs Phase Rule

For Constant Pressure,

$P + F = C + 1$



1 **single phase**
$F = C - P + 1$
$= 2 - 1 + 1$
$= 2$
can vary T and composition independently

2 **two phase**
$F = C - P + 1$
$= 2 - 2 + 1$
$= 1$
can vary T *or* composition

3 **eutectic point**
$F = C - P + 1$
$= 2 - 3 + 1$
$= 0$
can't vary T or composition

* Vacancies increase the internal energy and entropy → Gibb's free energy

Equilibrium concentration X_V^e will be that which gives the minimum free energy.

: adjust so as to reduce G to a minimum

at equilibrium $$\left(\frac{dG}{dX_V}\right)_{X_V = X_V^e} = 0$$

$$\Delta H_V - T\Delta S_V + RT \ln X_V^e = 0$$

A constant ~3, independent of T **Rapidly increases with increasing T**

$$X_V^e = \exp\frac{\Delta S_V}{R} \cdot \exp\frac{-\Delta H_V}{RT}$$

putting $\Delta G_V = \Delta H_V - T\Delta S_V$

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

- **In practice, ΔH_V is of the order of 1 eV per atom and X_V^e reaches a value of about 10^{-4}~10^{-3} at the melting point of the solid**

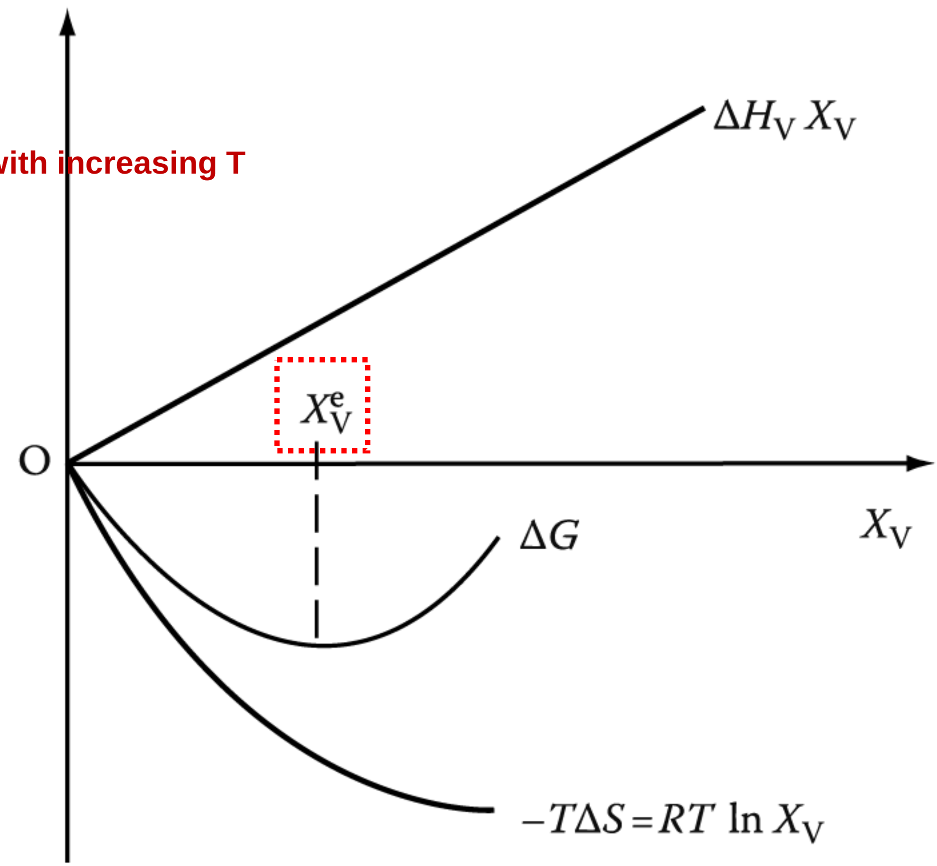
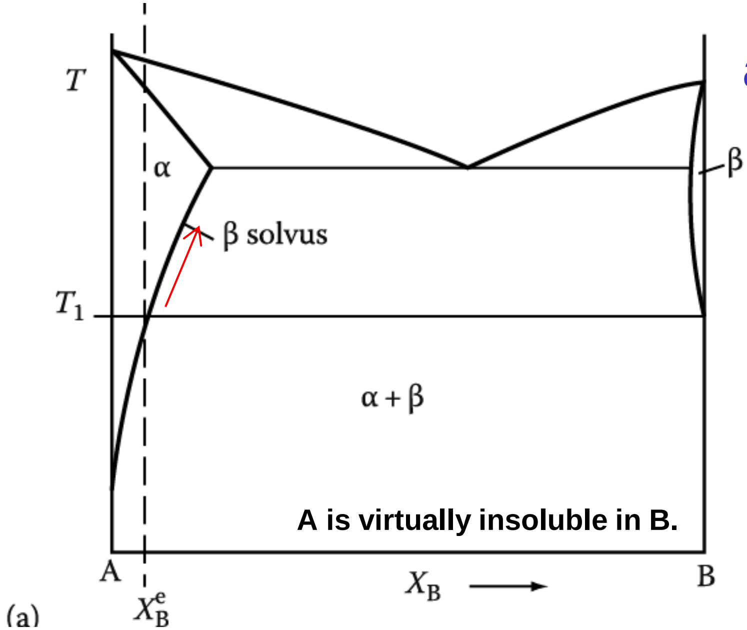


Fig. 1.37 Equilibrium vacancy concentration.

: adjust so as to reduce G to a minimum



a. Effect of T on solid solubility

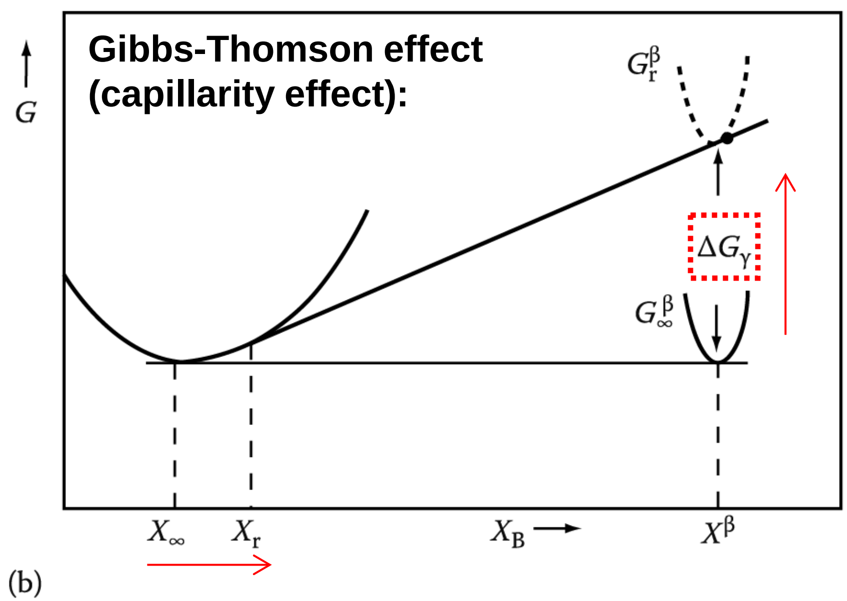
$$X_B^e = A\exp\left\{-\frac{Q}{RT}\right\}$$

a) $T\uparrow \Rightarrow X_B^e \uparrow$

b) **It is interesting to note that, except at absolute zero, X_B^e can never be equal to zero, that is, no two compo -nents are ever completely insoluble in each other.**

" T↓ →Solid solution α→ precipitate β "

b. Influence of Interfaces on Equilibrium: extra ΔG



$$\Delta G = \Delta P \cdot V \Rightarrow \Delta G = \frac{2\gamma V_m}{r}$$

For small values of the exponent,

$$\frac{X_B^{r=r}}{X_B^{r=\infty}} = \exp\left(\frac{2\gamma V_m}{RTr}\right) \approx 1 + \frac{2\gamma V_m}{RTr}$$

Ex) **γ=200mJ/m², V_m=10⁻⁵ m³,T=500K**

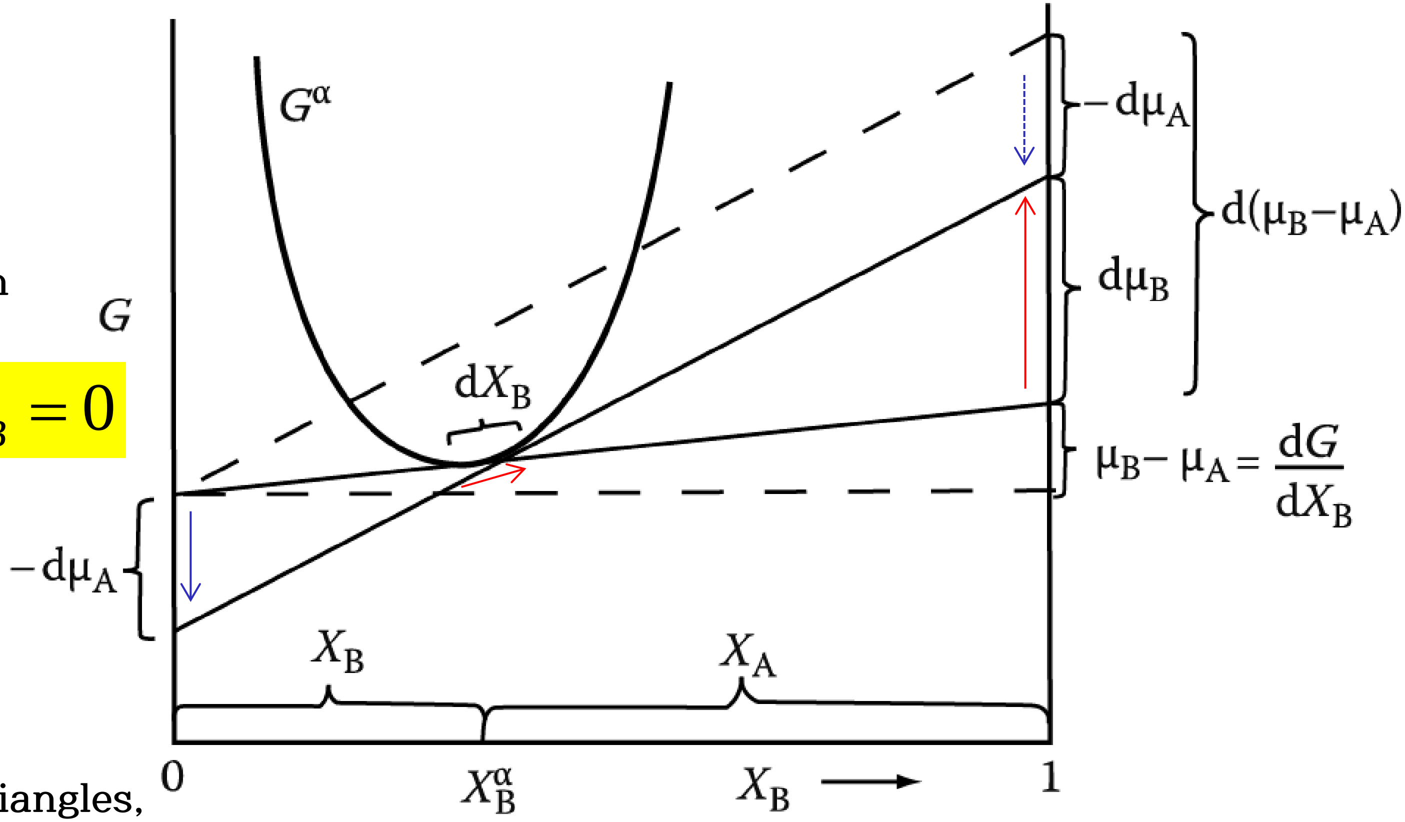
$$\frac{X_r}{X_\infty} = 1 + \frac{1}{r(nm)}$$

For r=10 nm, solubility~10% increase

Gibbs-Duhem equation: Calculate the change in (dμ) that results from a change in (dX)

Gibbs-Duhem equation for a binary solution

$$X_A d\mu_A + X_B d\mu_B = 0$$



Comparing two similar triangles,

$$-\frac{d\mu_A}{X_B} = \frac{d\mu_B}{X_A} = \frac{d(\mu_B - \mu_A)}{1} \Leftarrow \frac{dG}{dX_B} = \frac{\mu_B - \mu_A}{1}, \quad \frac{d^2G/dX^2}{d^2G/dX_B^2 = d^2G/dX_A^2}$$

Substituting right side Eq. & Multiply $X_A X_B$

$$-X_A d\mu_A = X_B d\mu_B = X_A X_B \frac{d^2G}{dX^2} dX_B$$

Eq. 1.65

" Gibbs-Duhem Equation "

X_A, X_B vs. $d\mu_A$, $d\mu_B$

γ_A, γ_B

a_A, a_B

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

Total Free Energy Decrease per Mole of Nuclei ΔG_0

: Driving force for phase transformation of system

Driving Force for Precipitate Nucleation $\boxed{\alpha \rightarrow \alpha + \beta}$ 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)

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

$$\boxed{\Delta G_V} = \frac{\Delta G_n}{V_m}$$ *per unit volume of* β

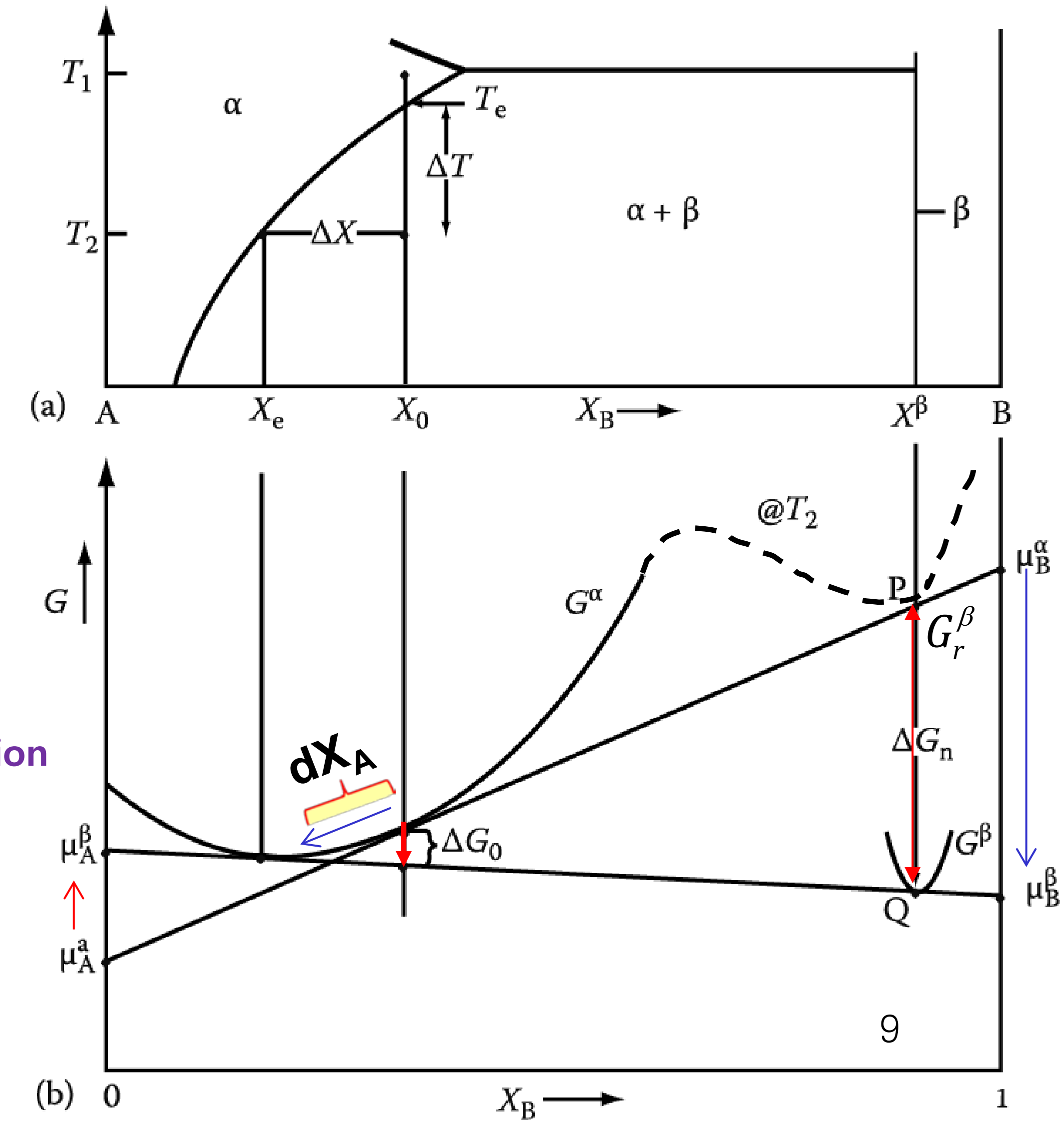
: driving force for β precipitation

For dilute solutions,

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

$$\boxed{\Delta G_V \propto \Delta X \propto \Delta T}$$

∝ undercooling below T_e



Contents for today's class

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:

$F = C + 1 - P$

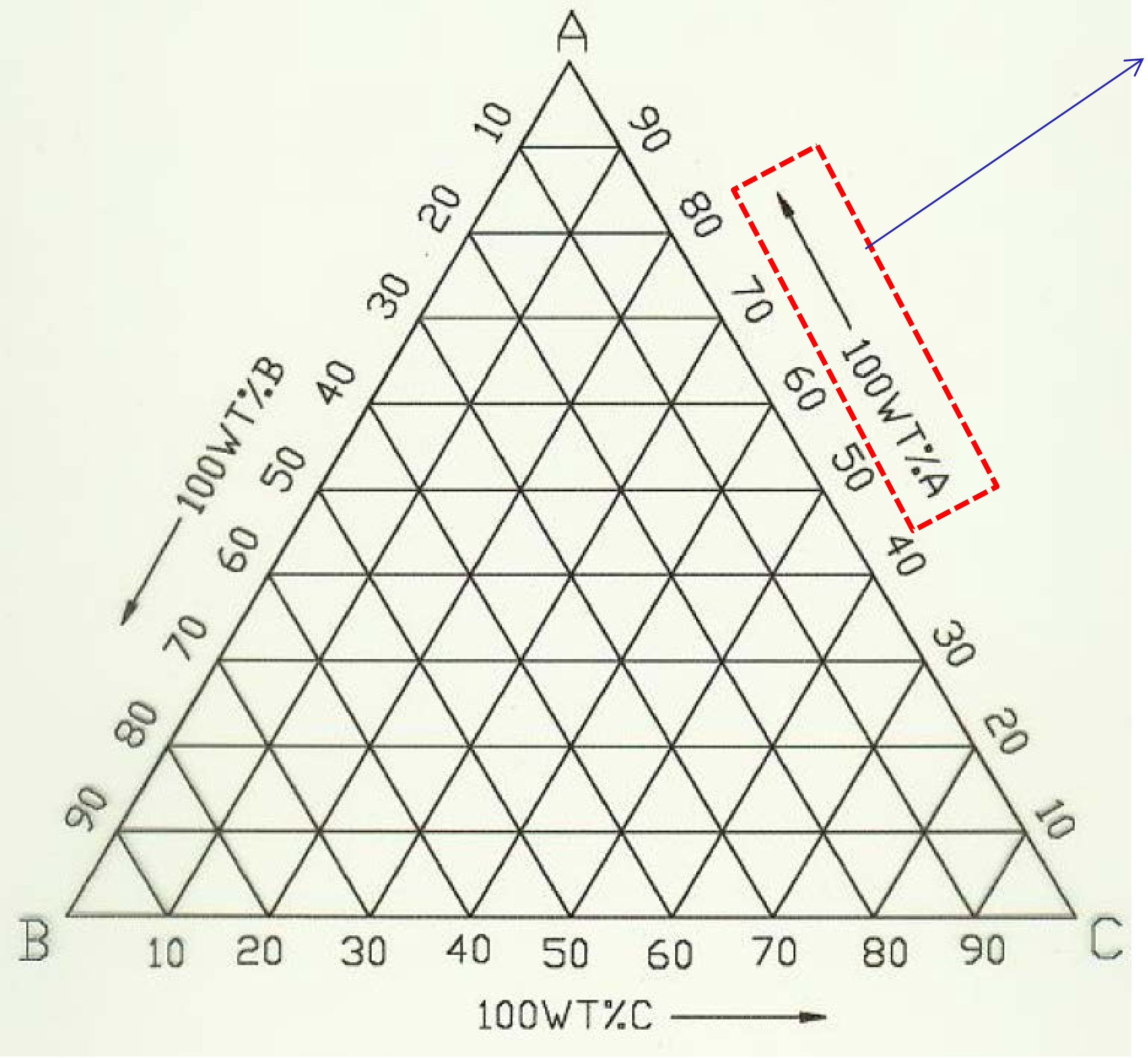
For $C = 3$, the maximum number of phases will co-exist when $F = 0$

$P = 4$ 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.

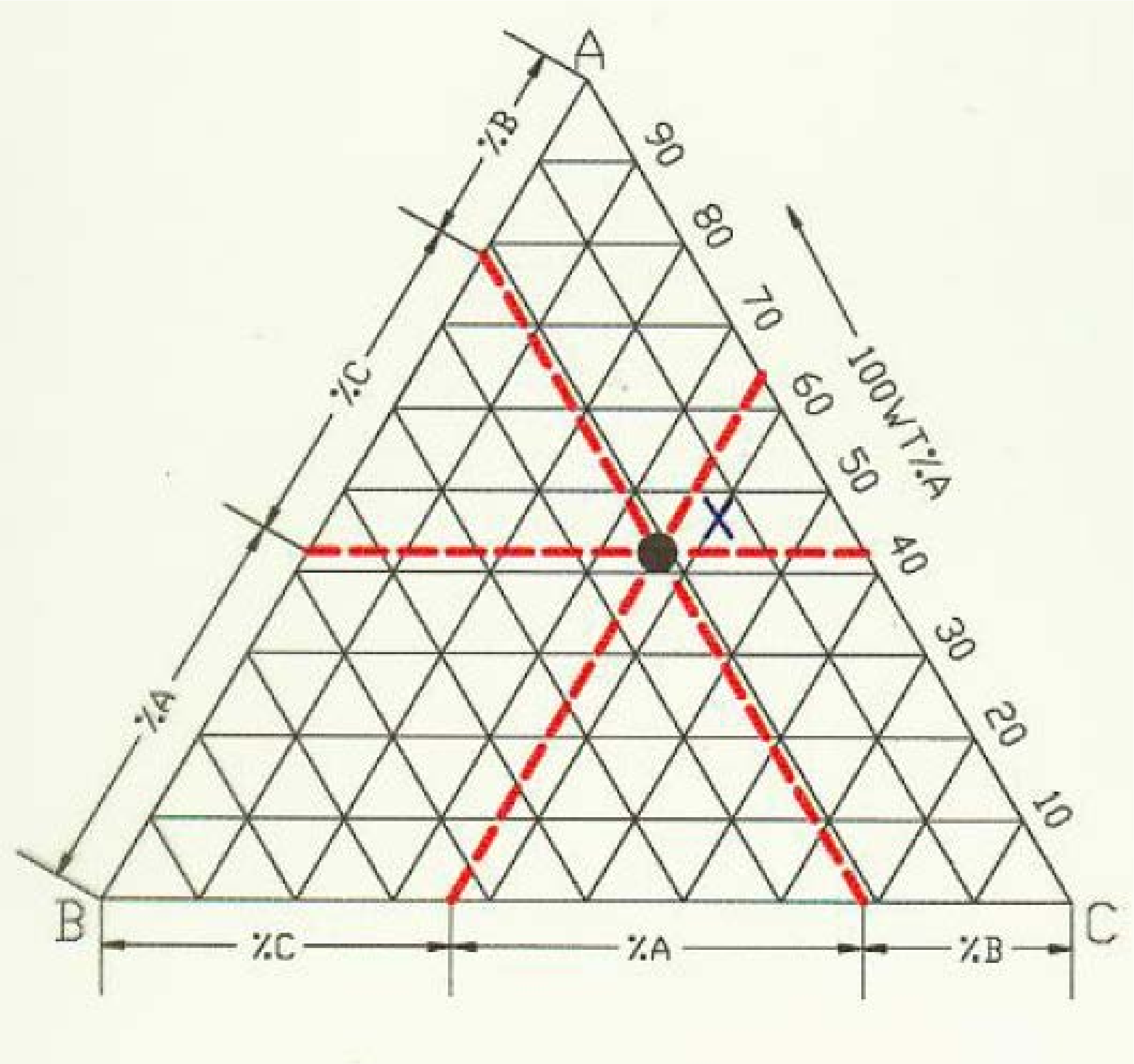


Concentration can be expressed as either "wt. %" or "at.% = molar %".

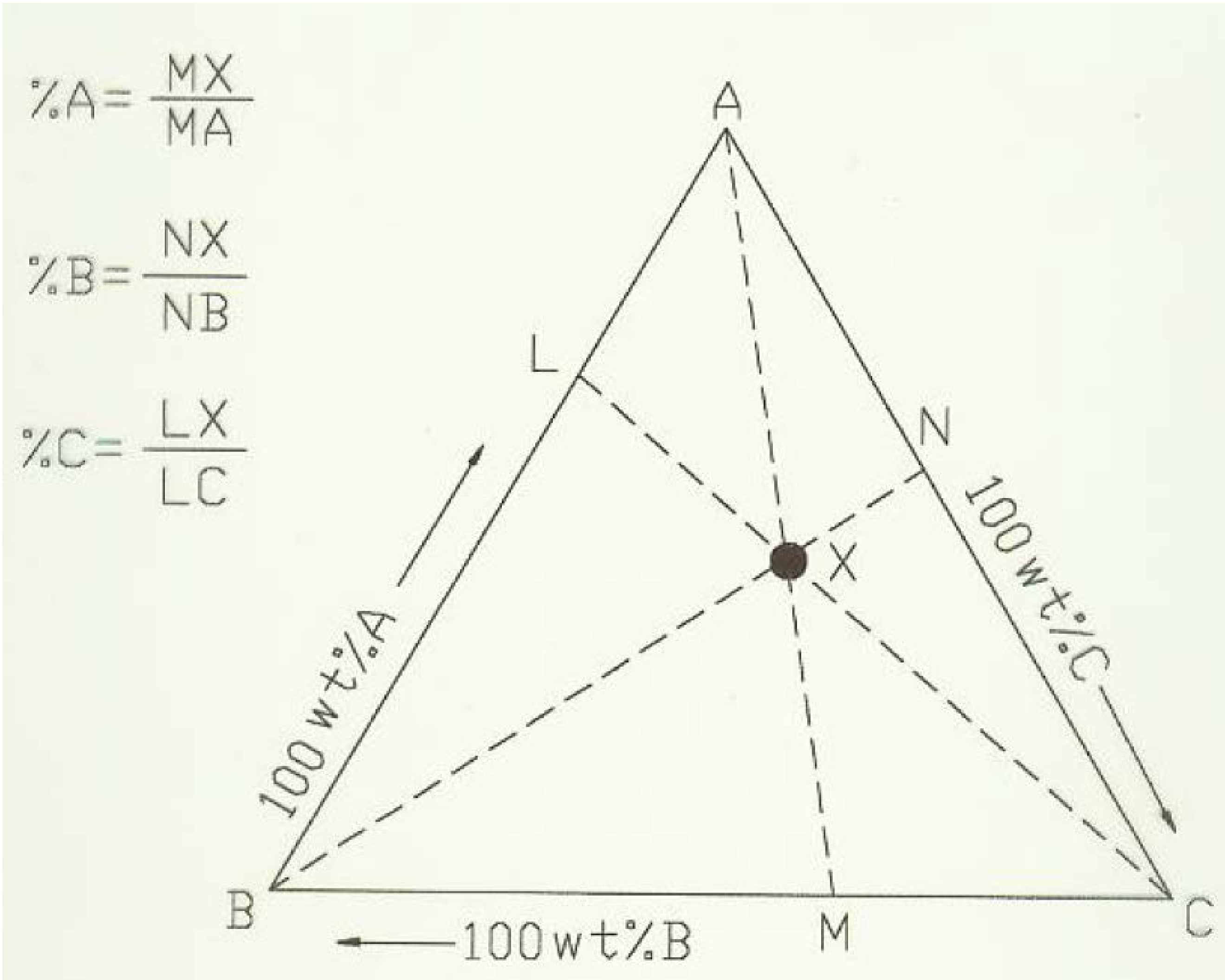
$$X_A+X_B+X_C = 1$$

Used to determine the overall composition

Overall Composition



Overall Composition



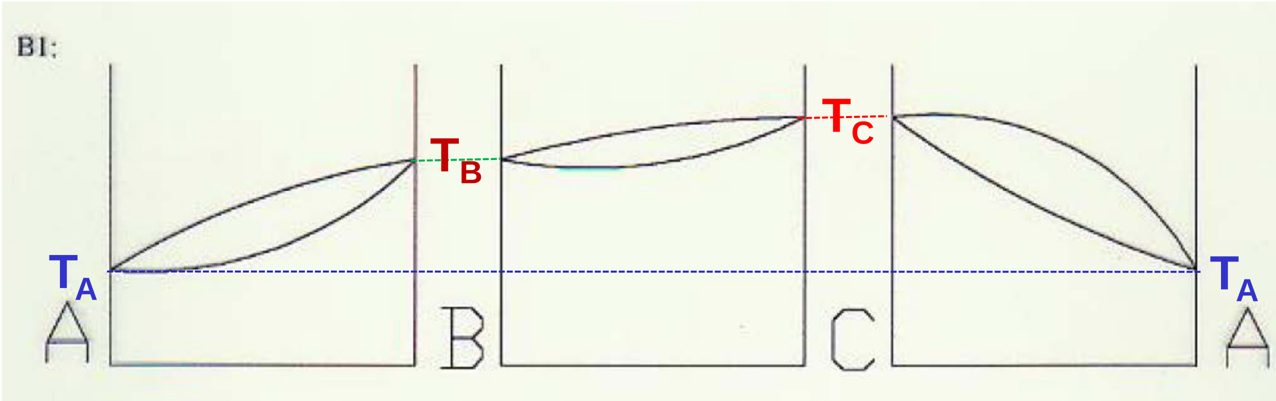
Ternary Isomorphous System

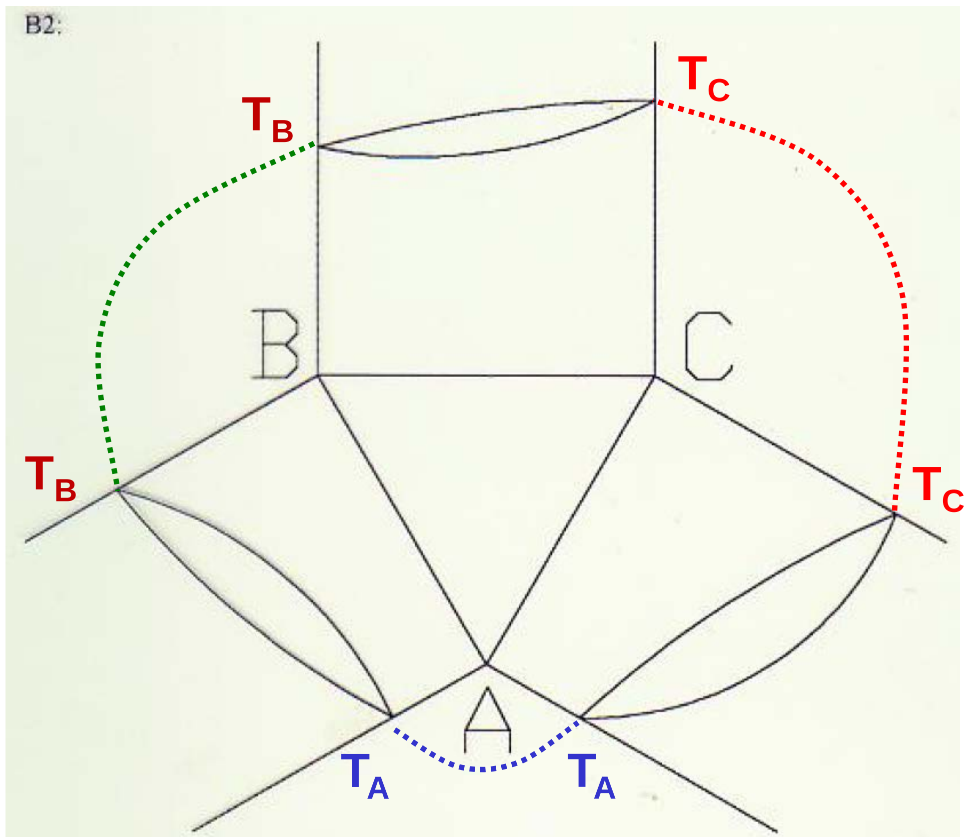
<u>Isomorphous System</u>: A system (ternary in this case) that has only one solid phase. All components are totally soluble in the other components. The ternary system is therefore made up of three binaries that exhibit total solid solubility.

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

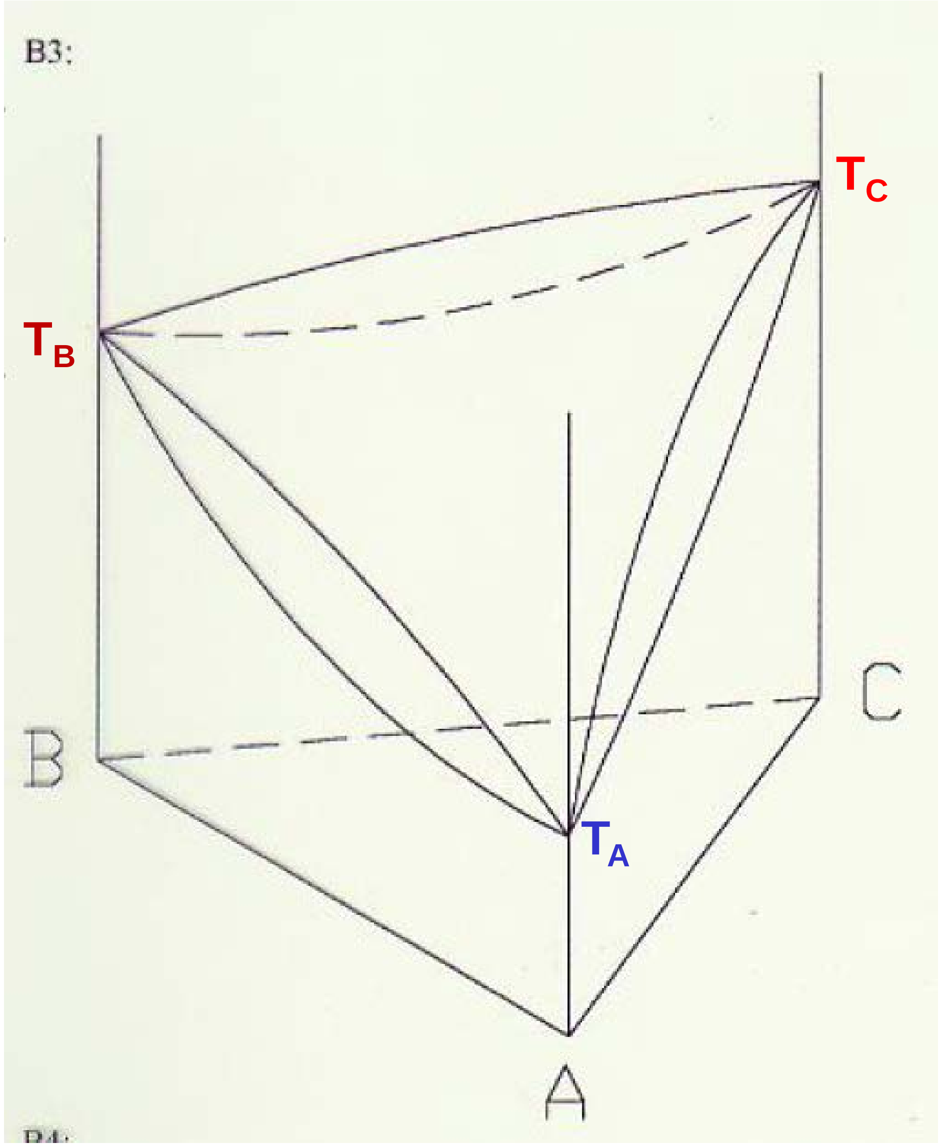
<u>The Solidus Surface</u>: A plot of the temperatures below which a (homogeneous) solid phase forms for any given overall composition.

Ternary Isomorphous System





Ternary Isomorphous System



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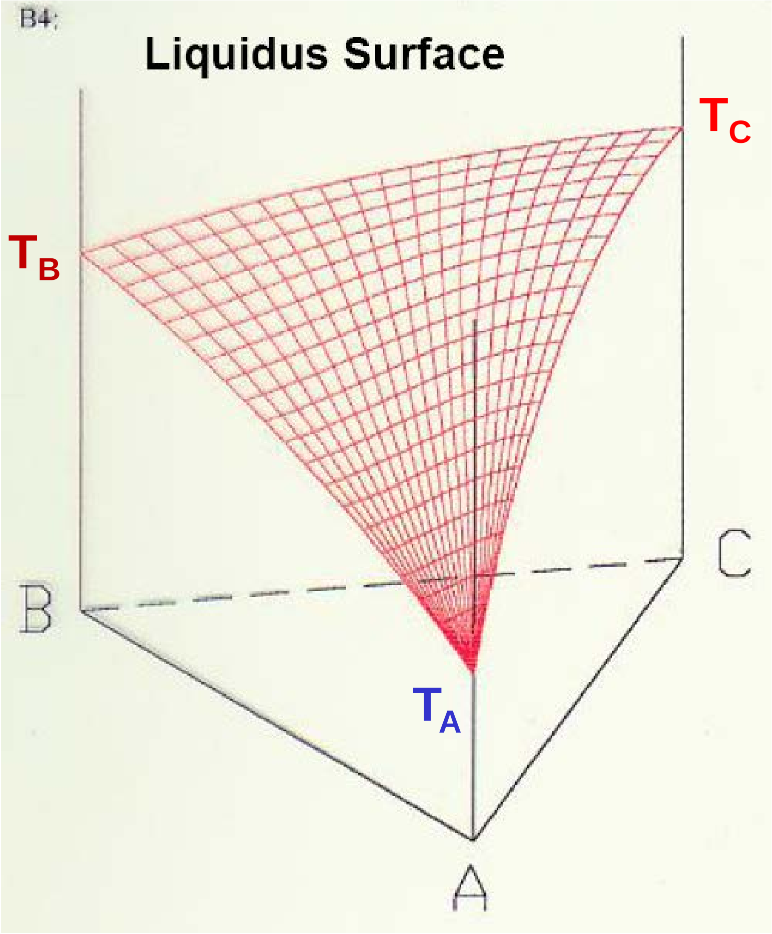

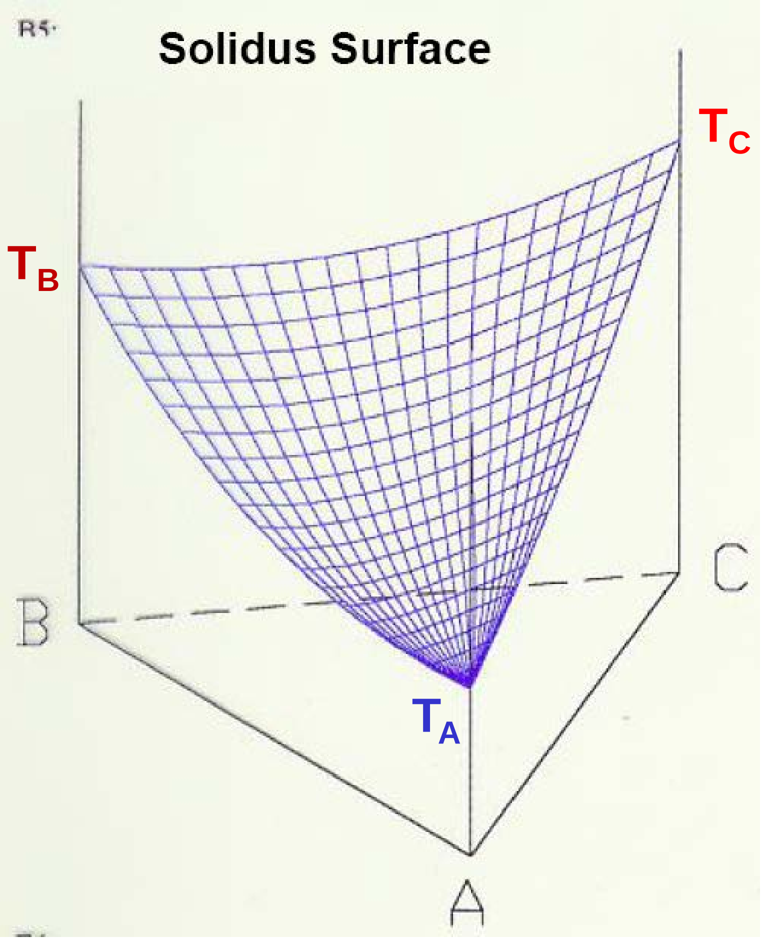

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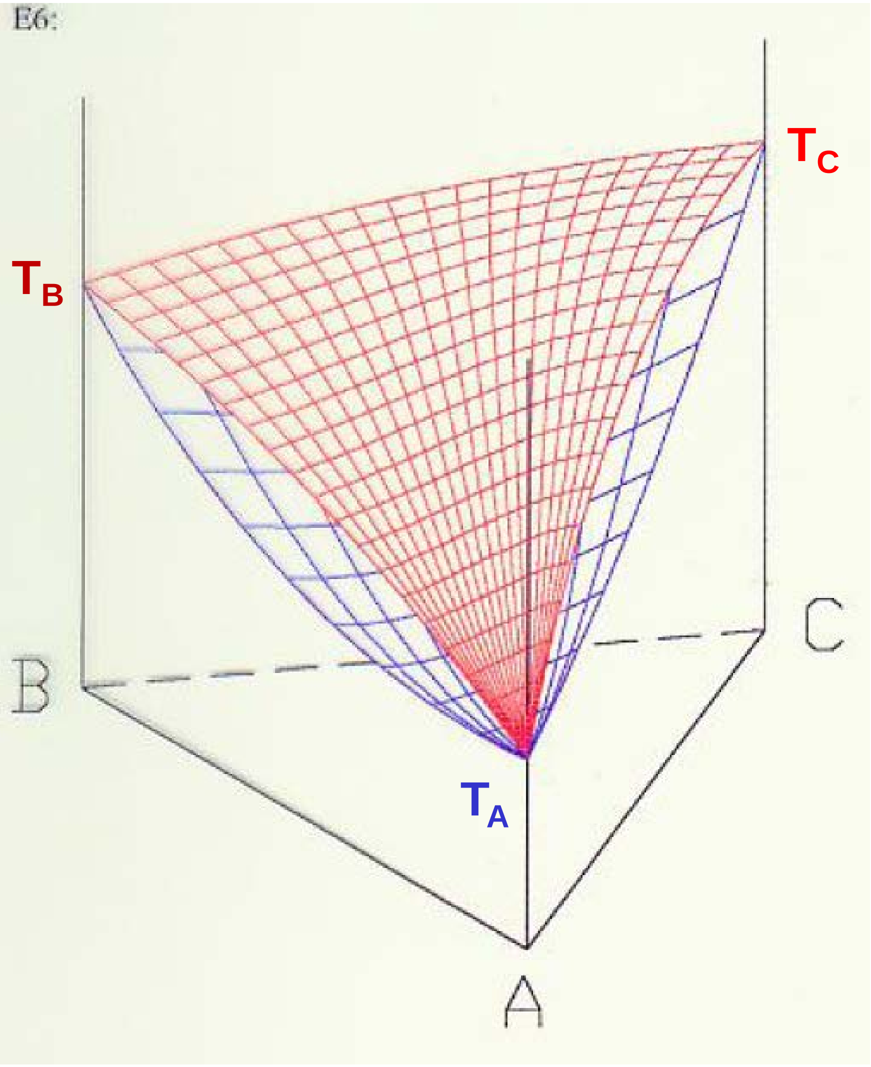
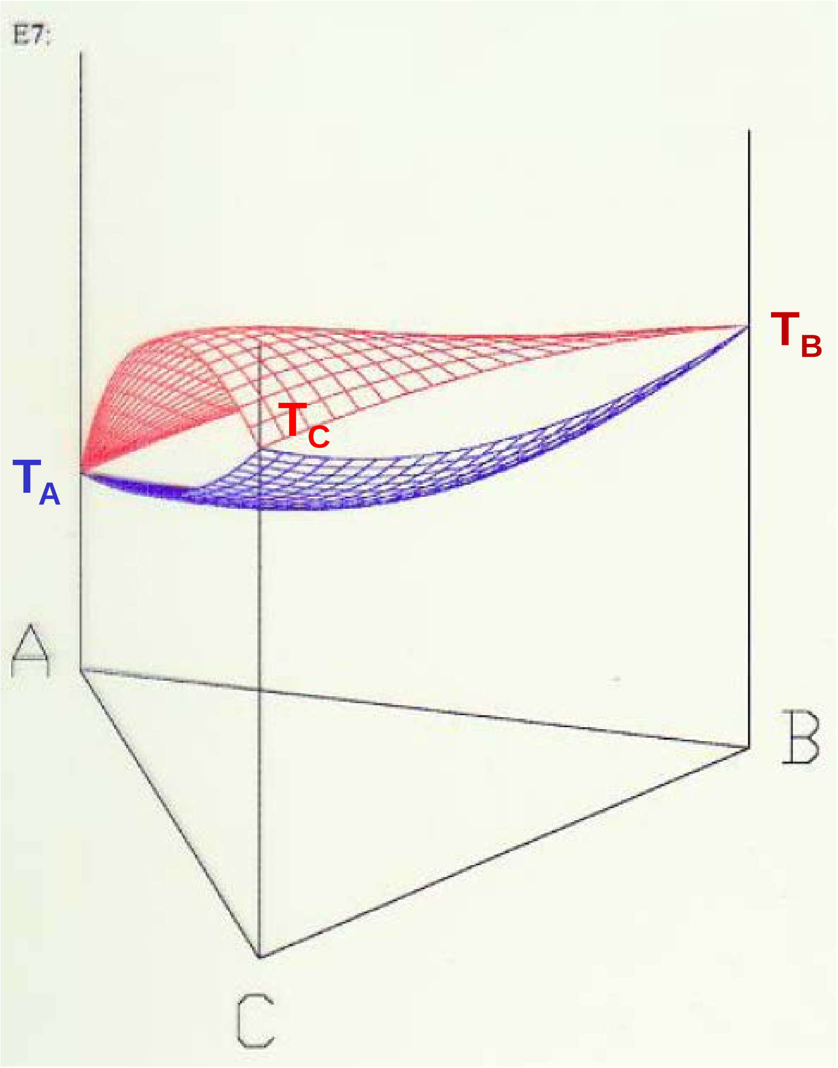
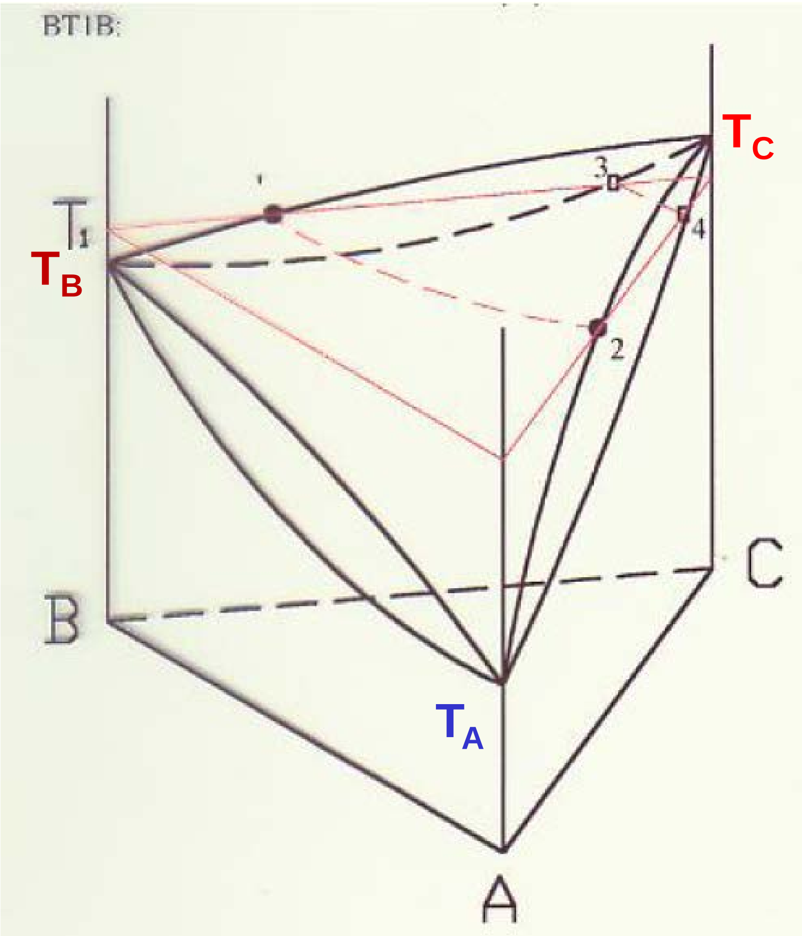
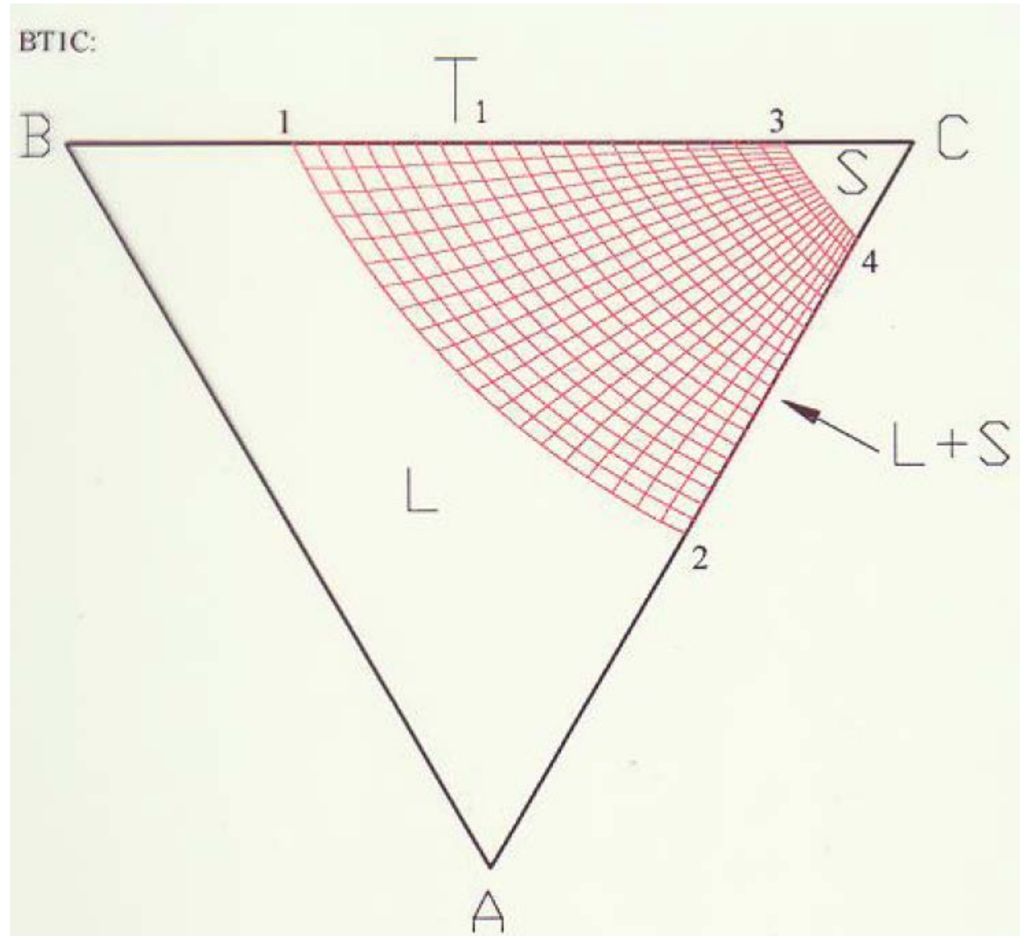




Ternary Isomorphous System

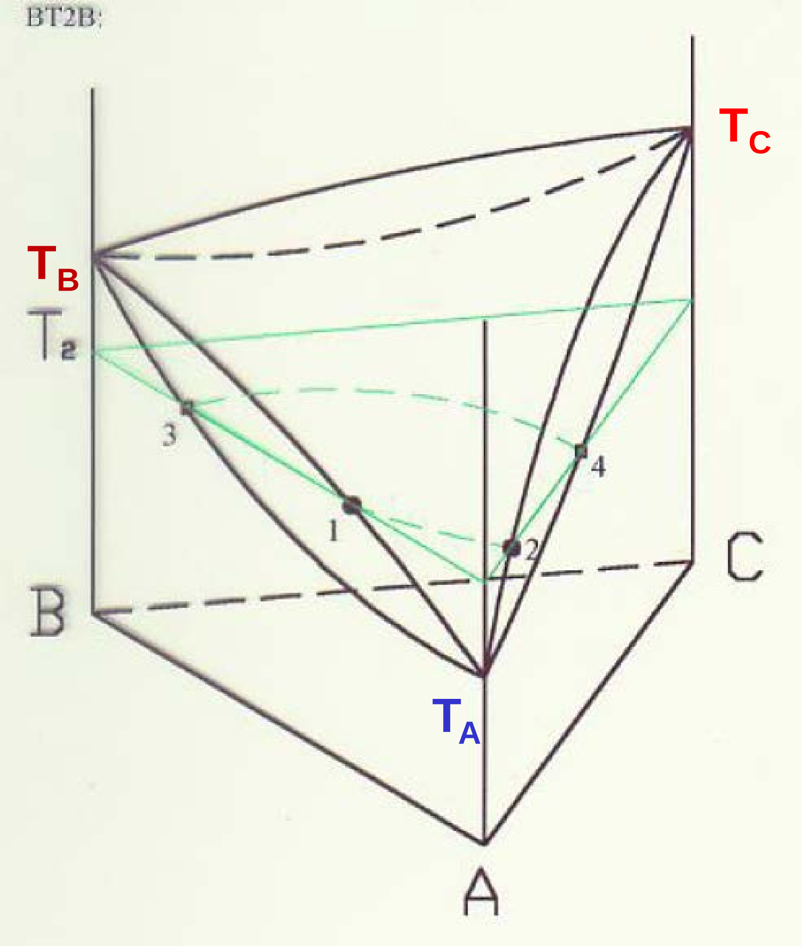
Isothermal section → F = C - P

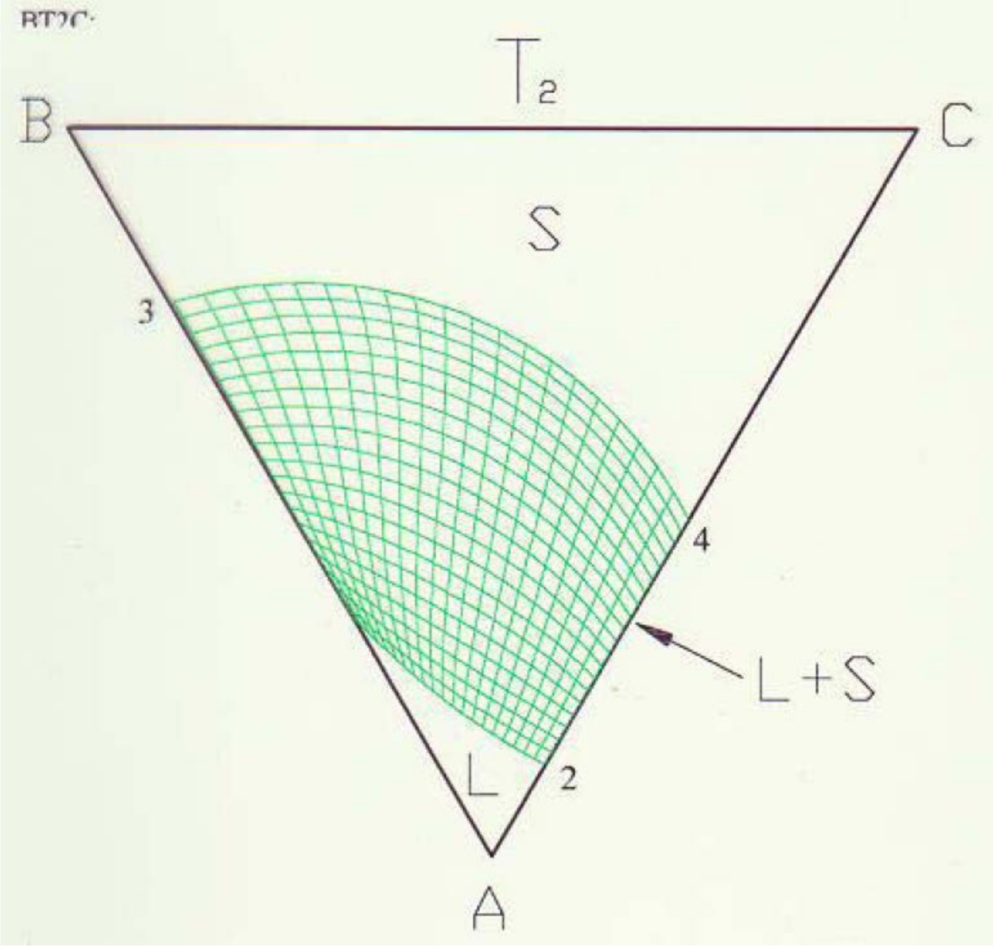




Ternary Isomorphous System

Isothermal section





Ternary Isomorphous System

Isothermal section → F = C - P

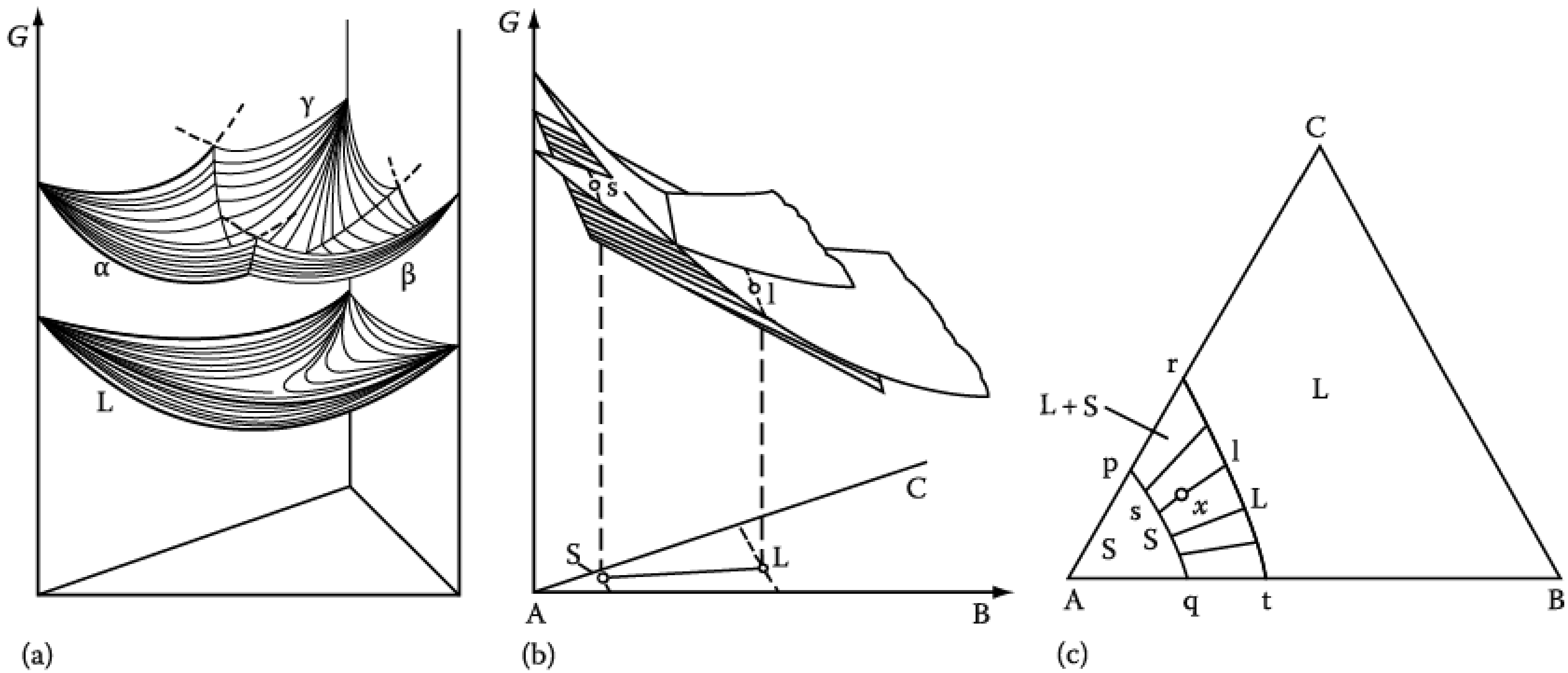


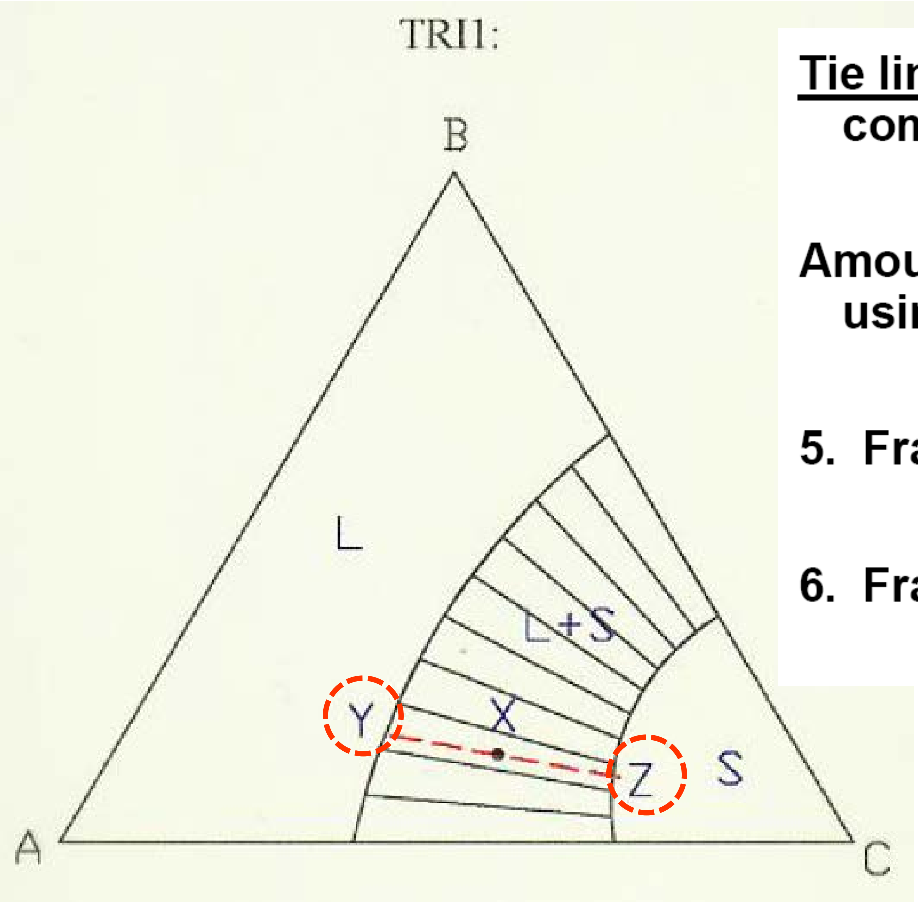
Fig. 1.41 (a) Free energy surface of a liquid and three solid phases of a ternary system.

(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:

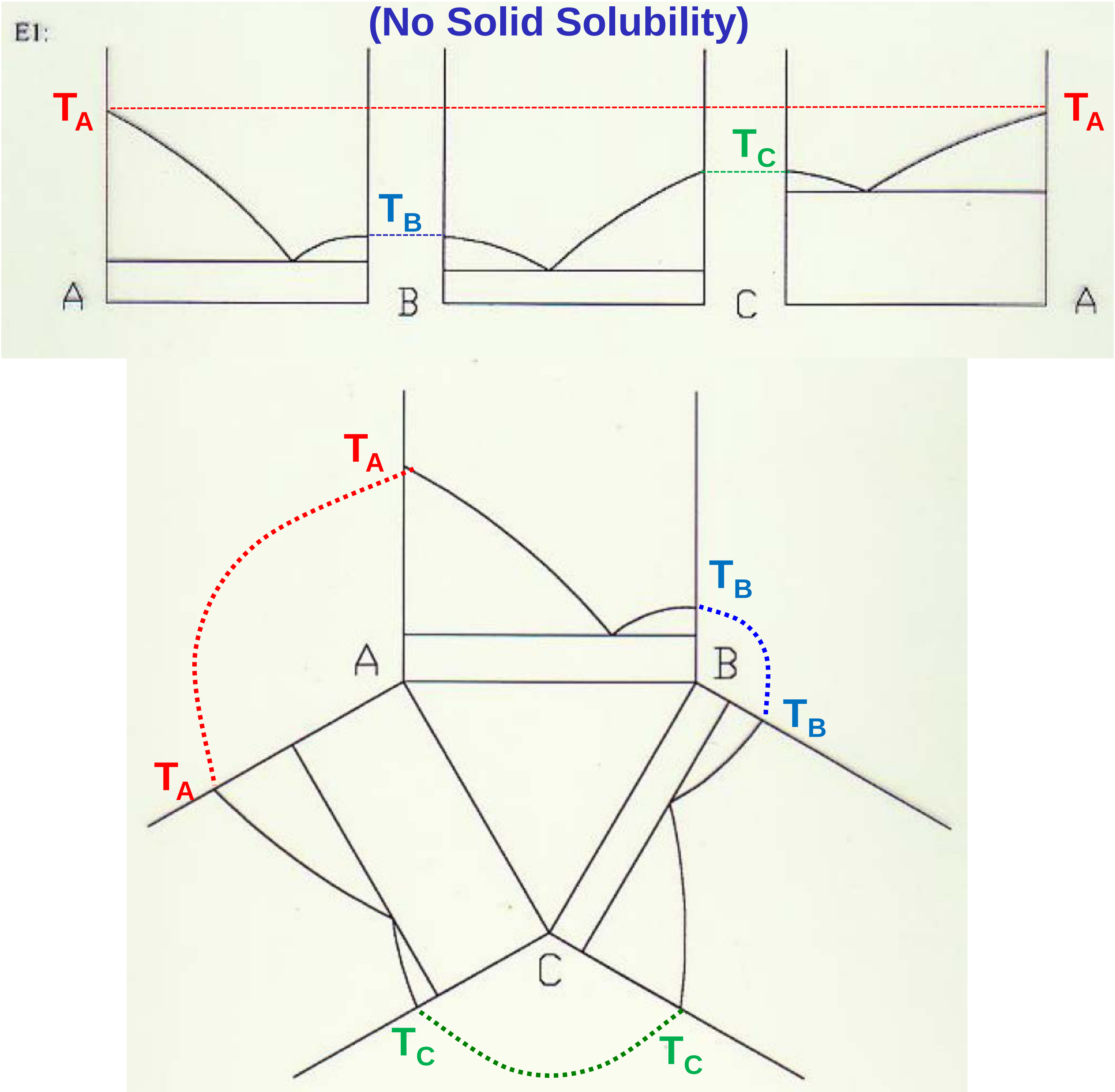
$$\boxed{\mathbf{L} = \alpha + \beta + \gamma}$$

A liquid phase solidifies into three separate solid phases

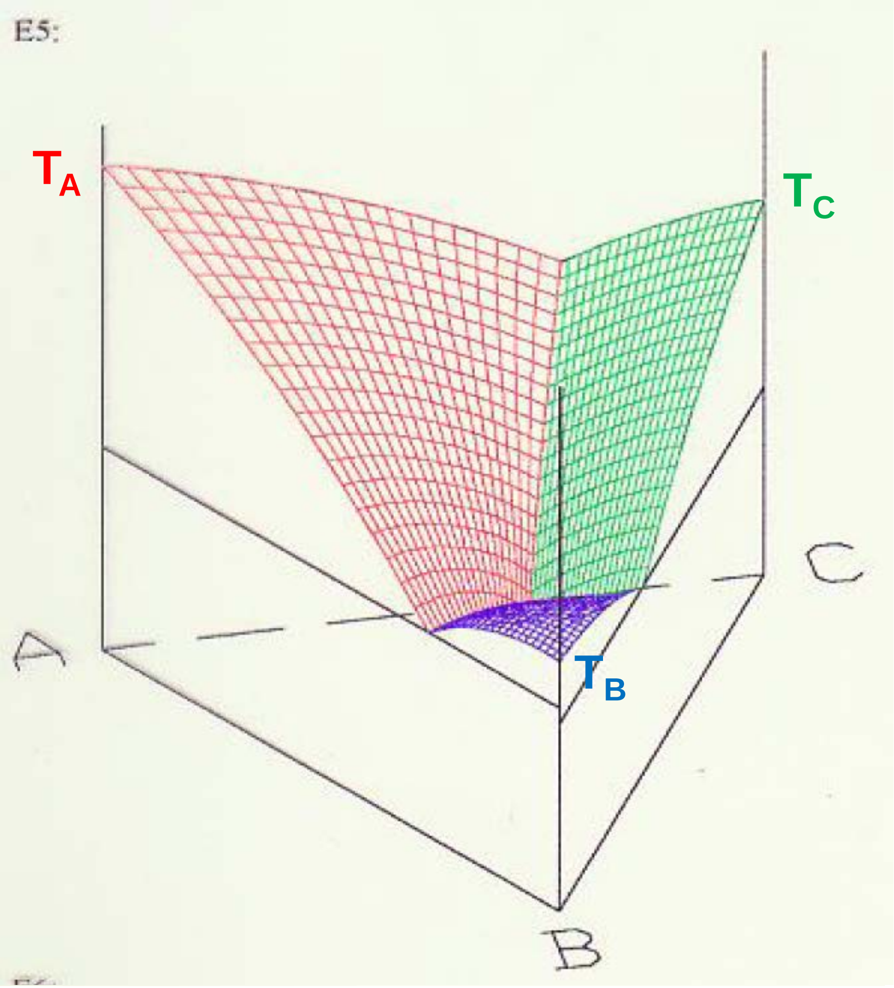
Made up of three binary eutectic systems, all of which exhibit no solid solubility

Ternary Eutectic System

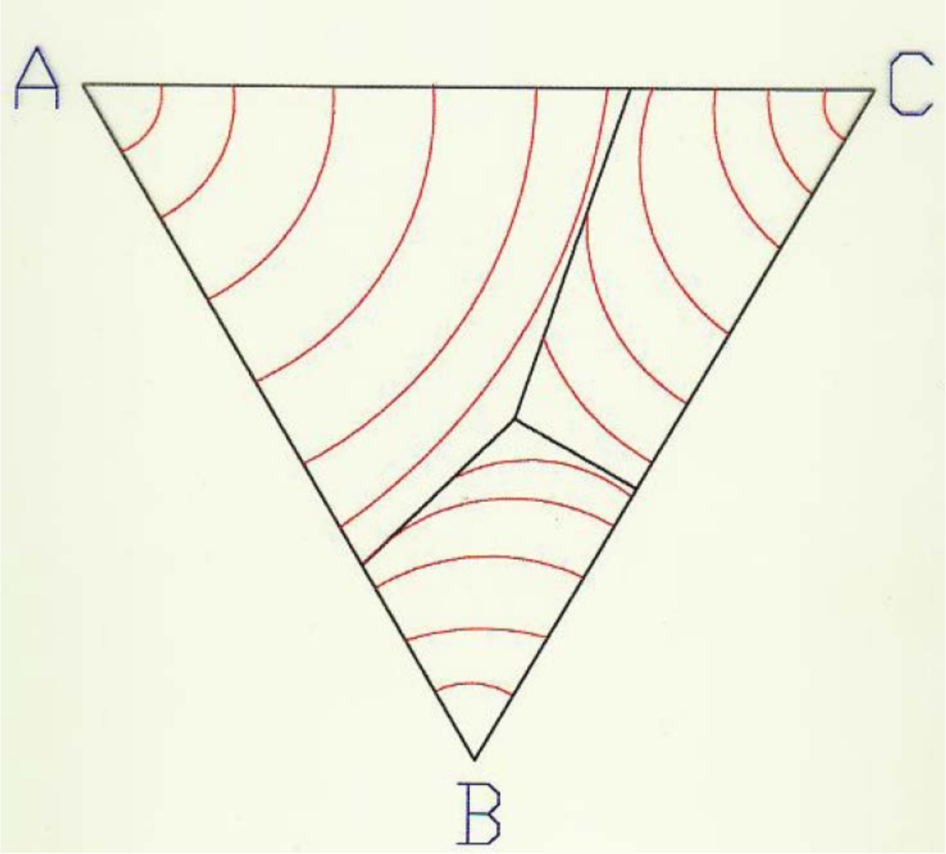
(No Solid Solubility)



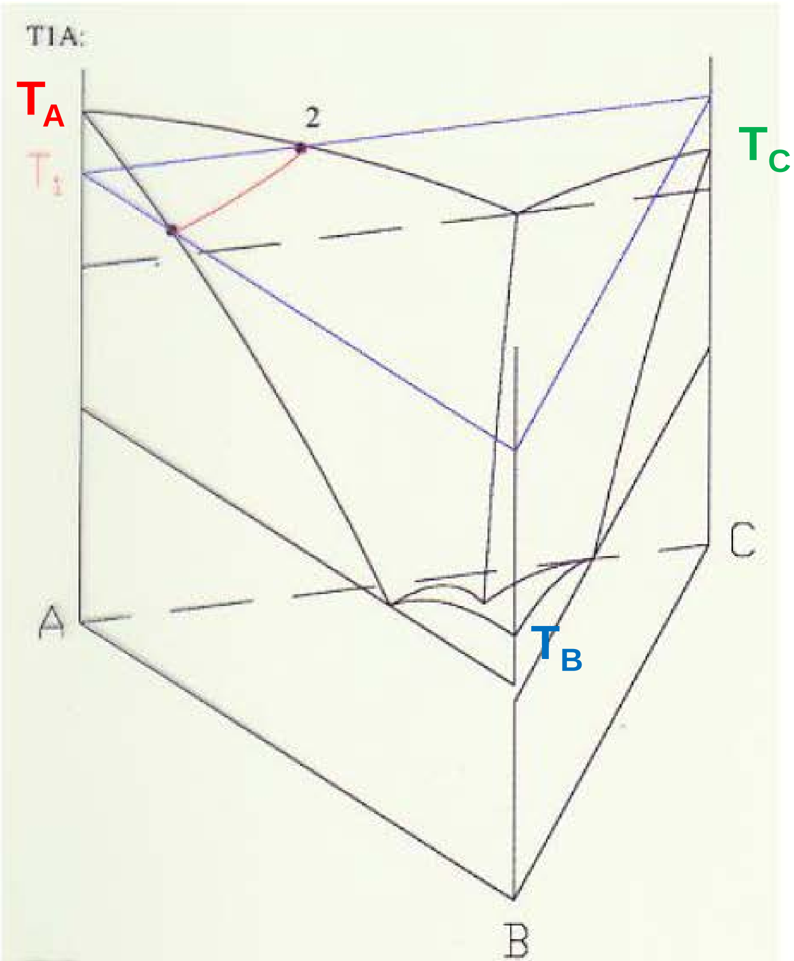
Ternary Eutectic System
(No Solid Solubility)

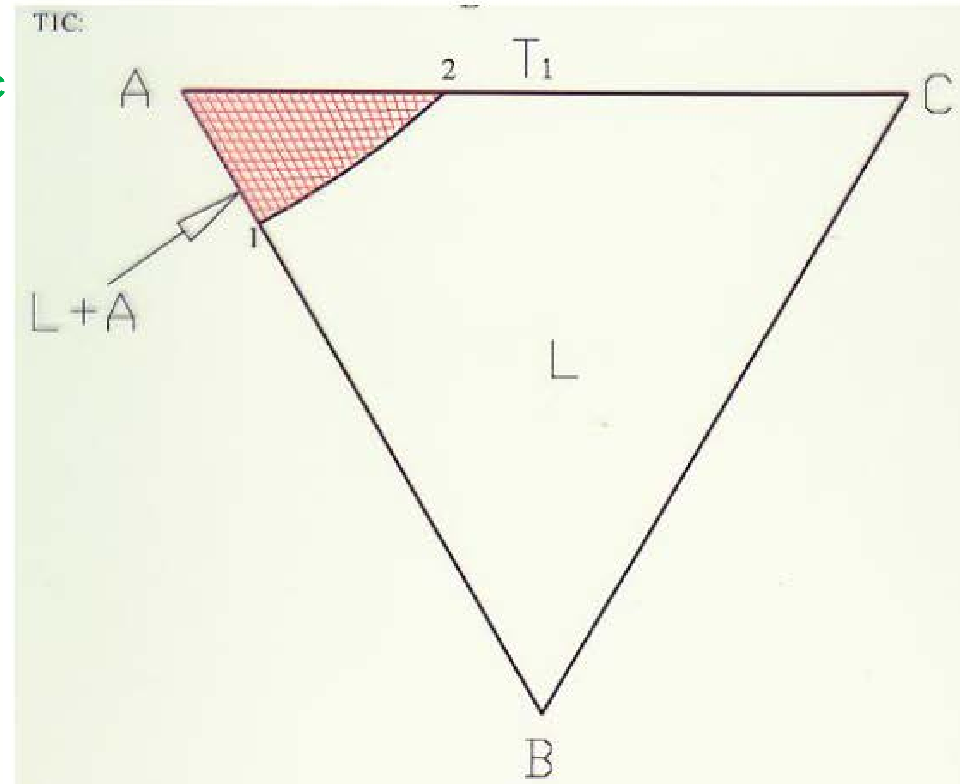


Liquidus projection

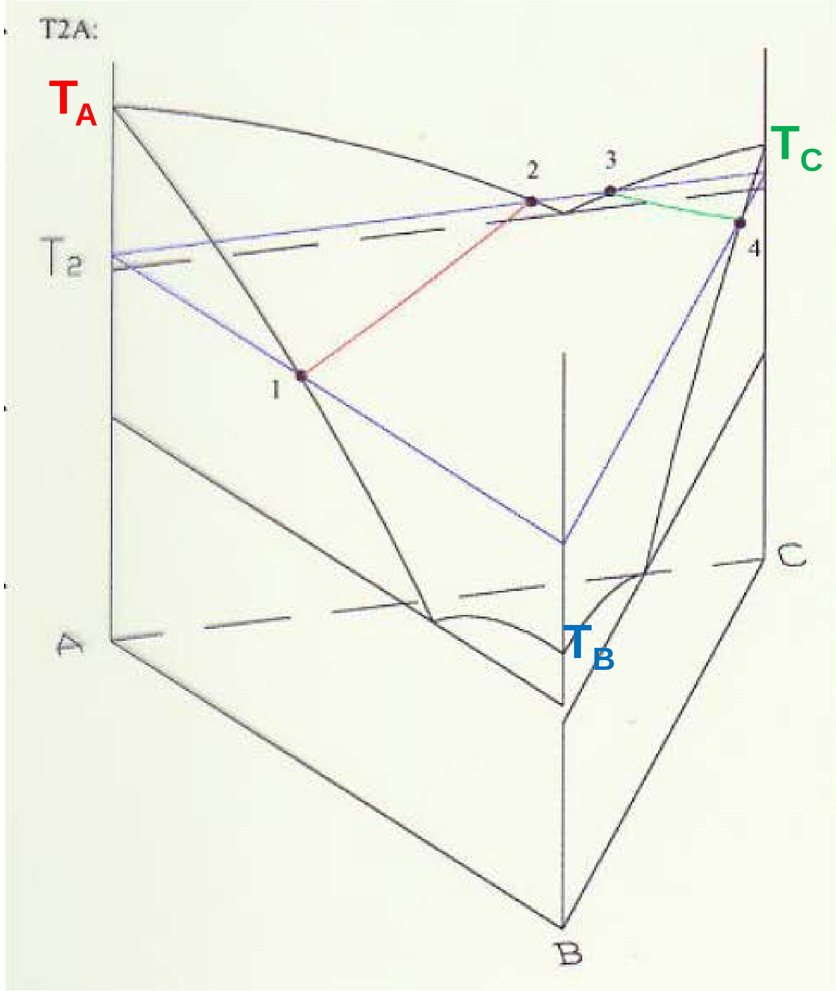


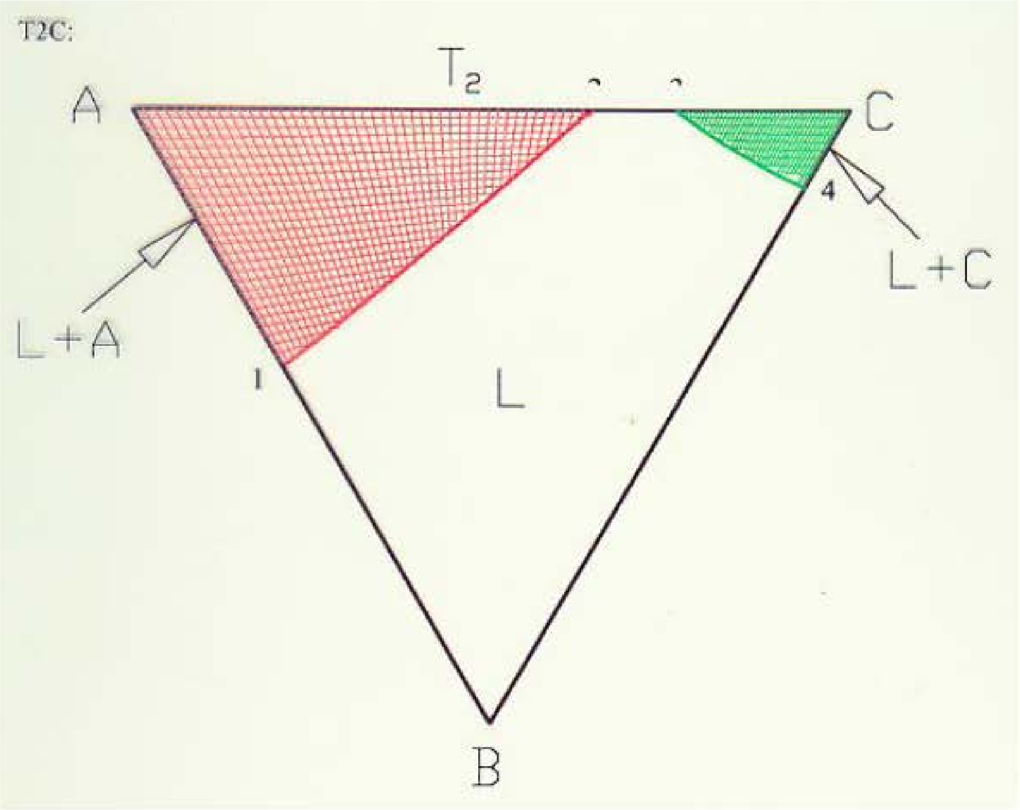
Ternary Eutectic System
(No Solid Solubility)





Ternary Eutectic System
(No Solid Solubility)





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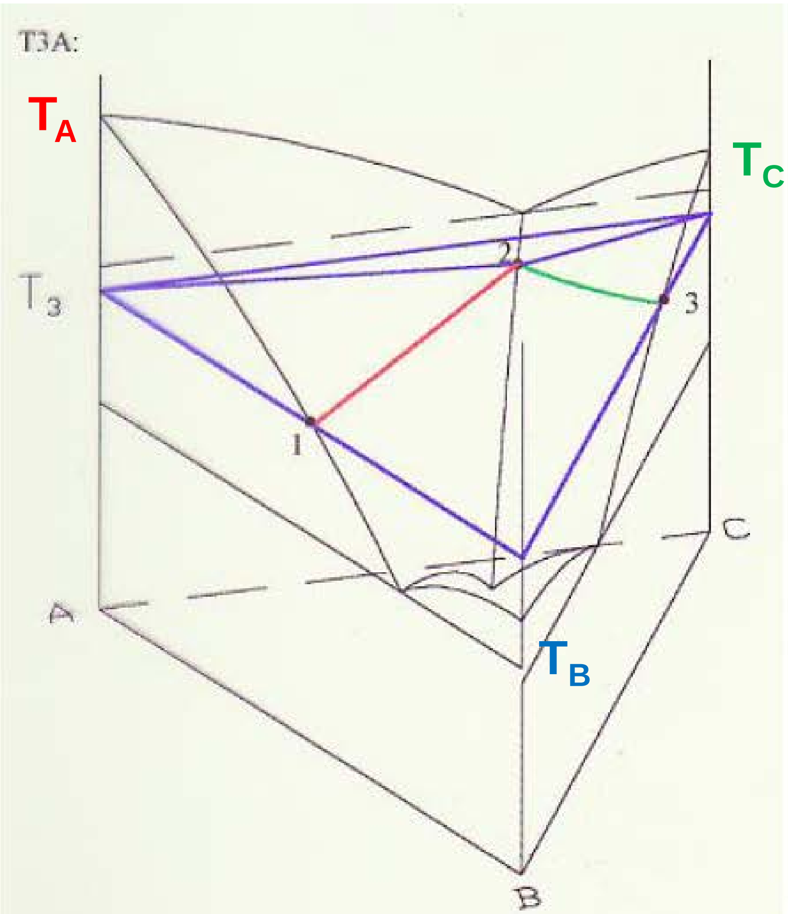

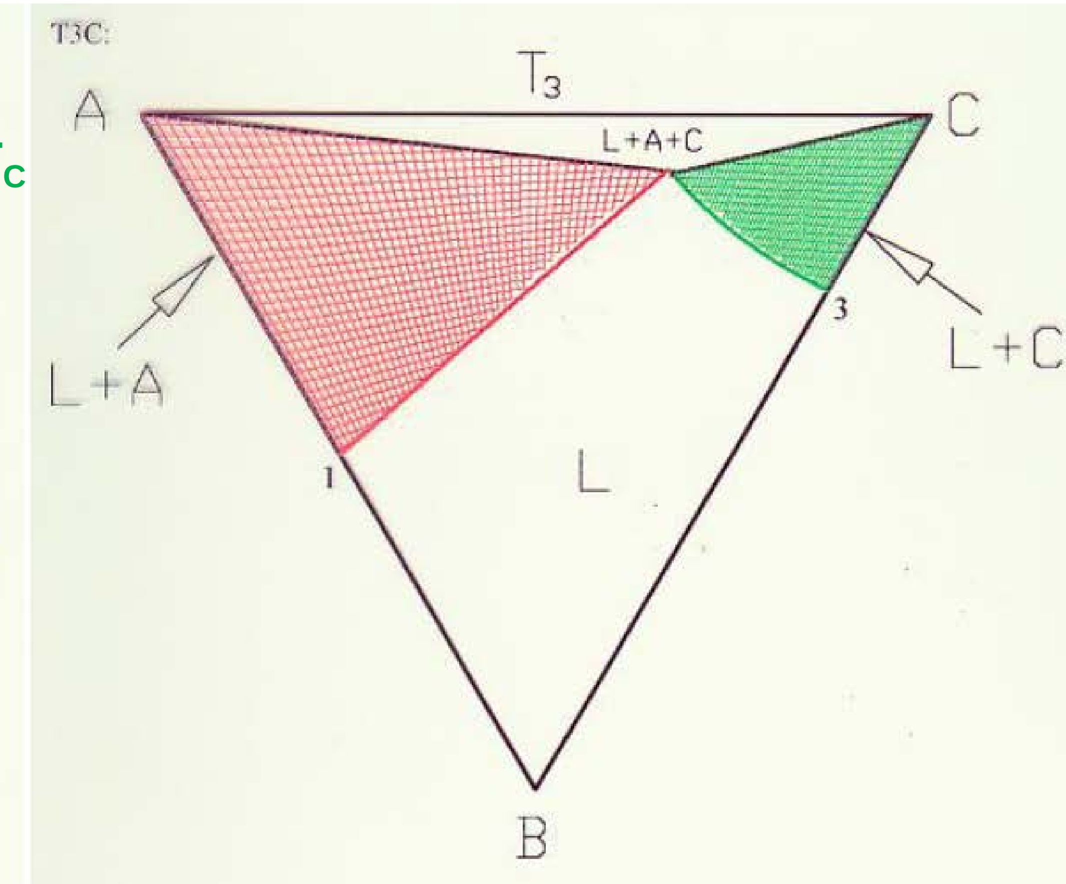

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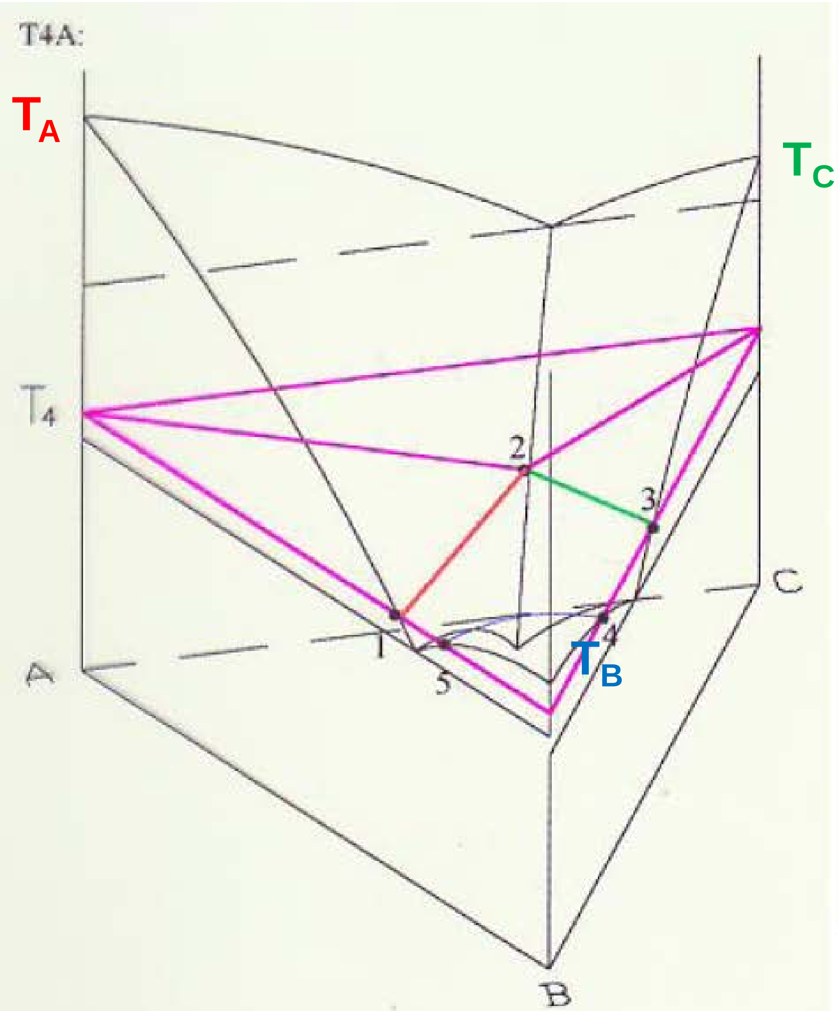

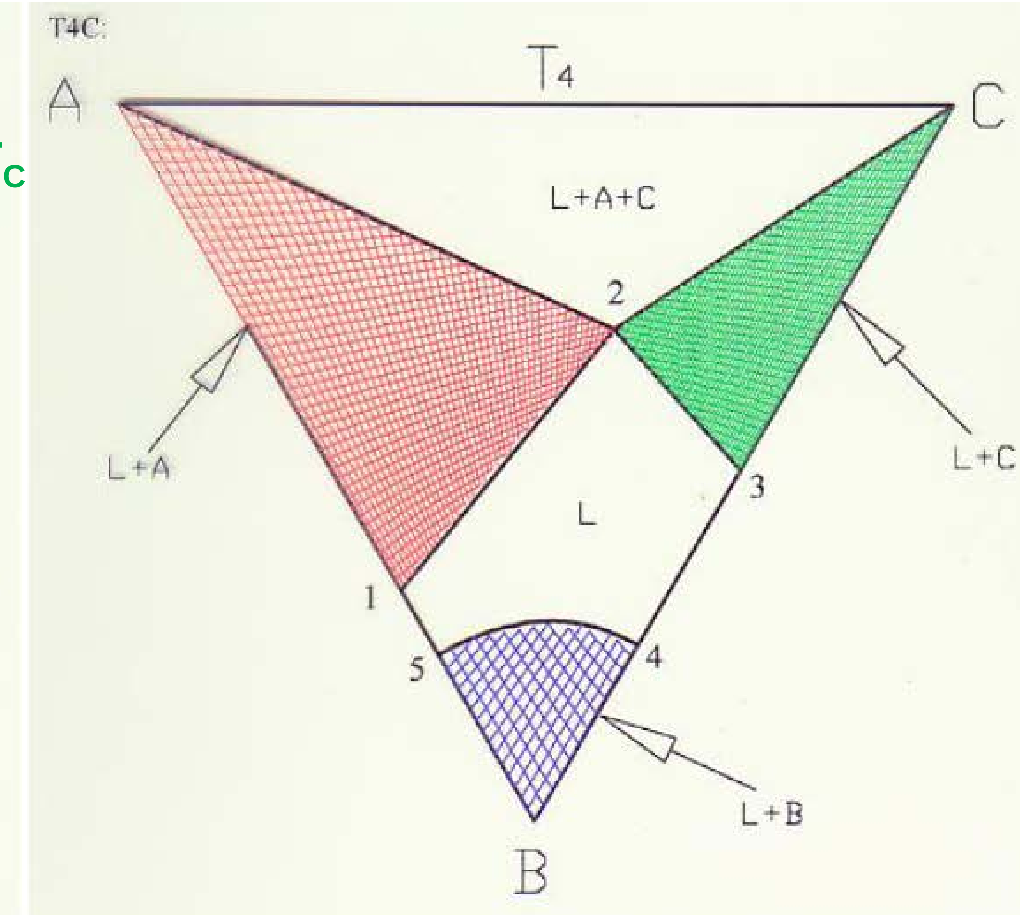

Ternary Eutectic System

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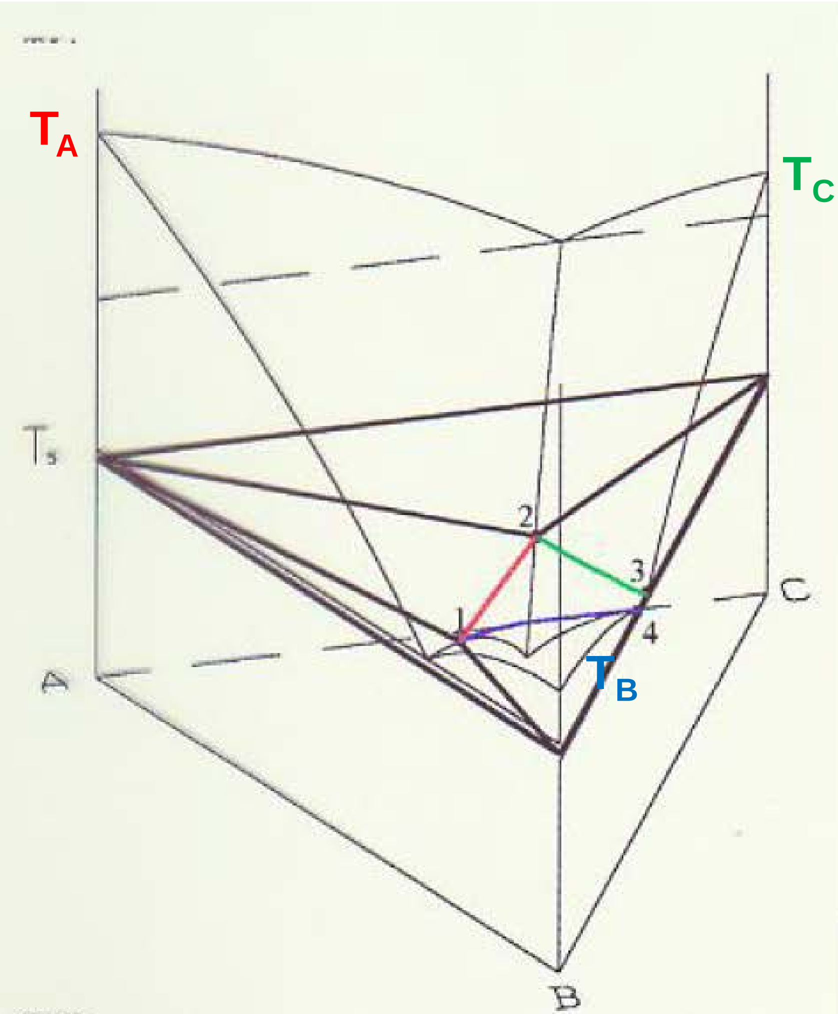

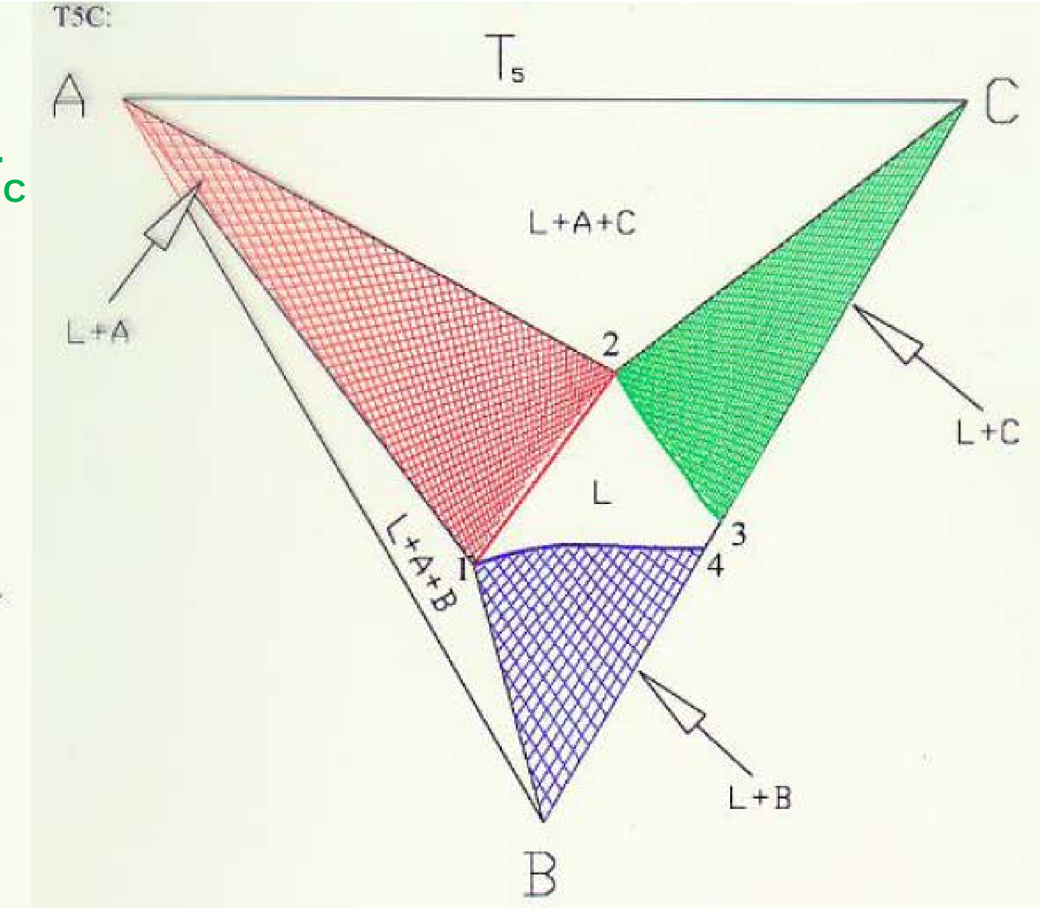

Ternary Eutectic System

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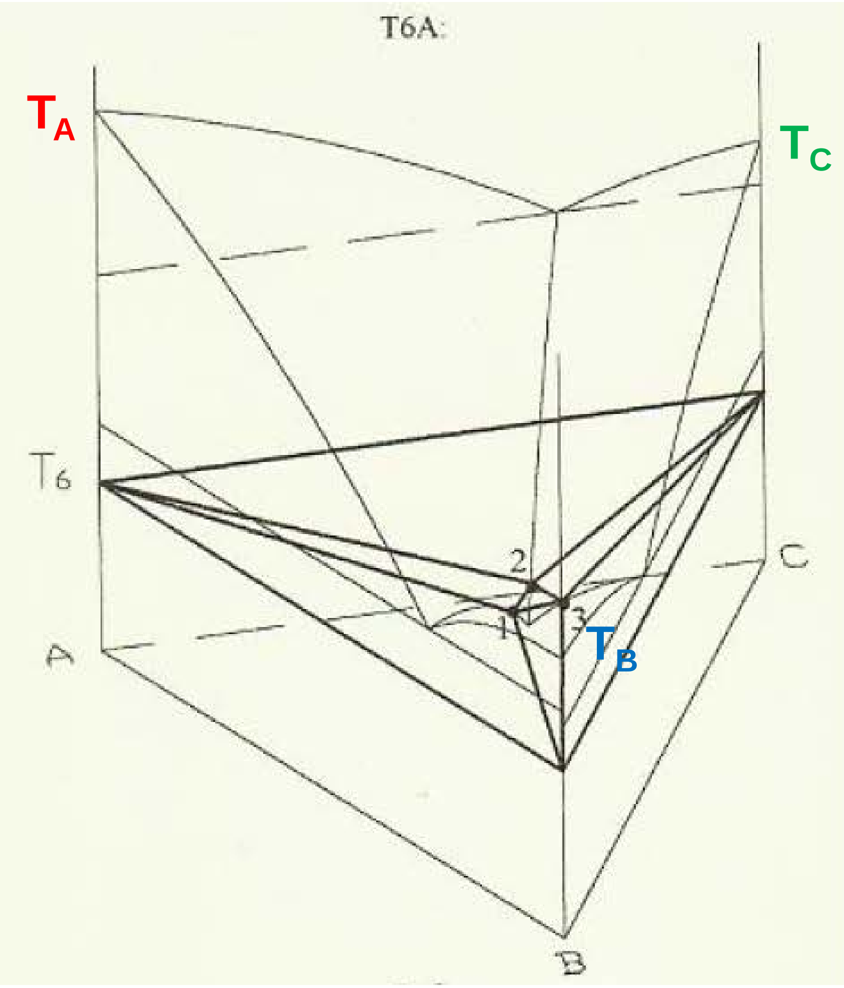
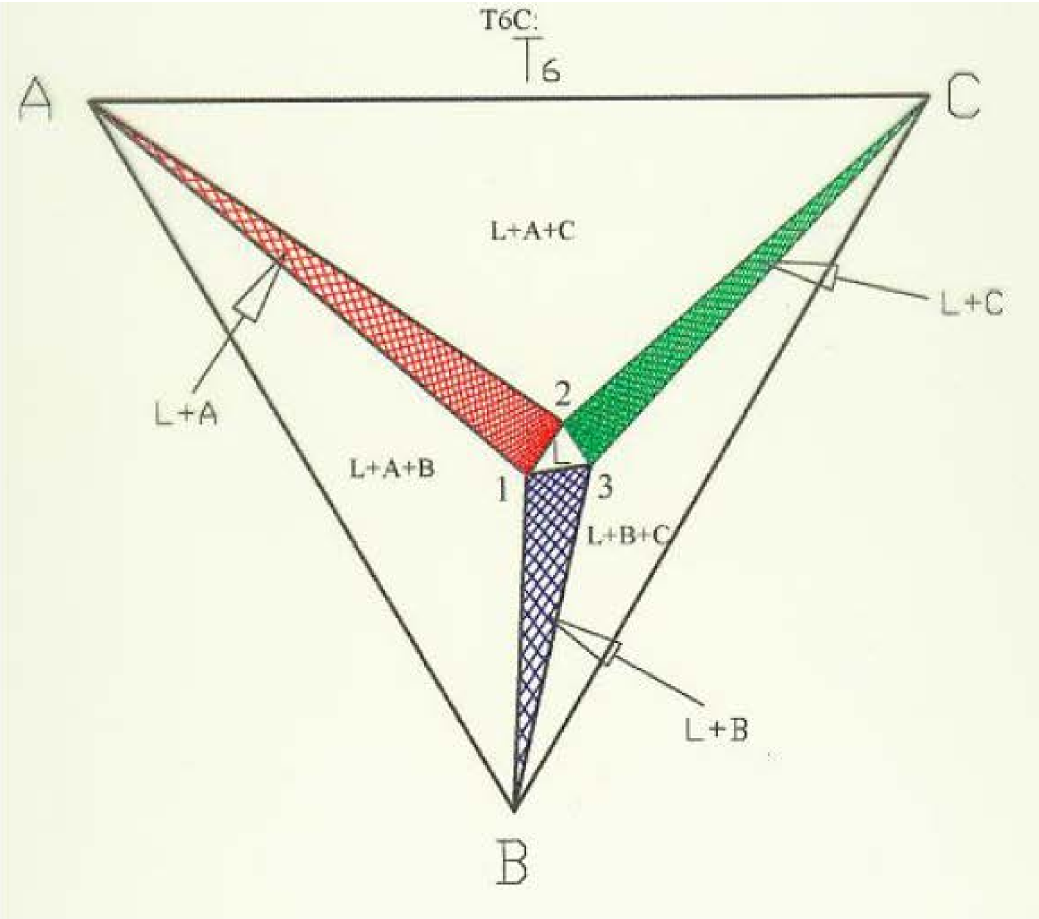
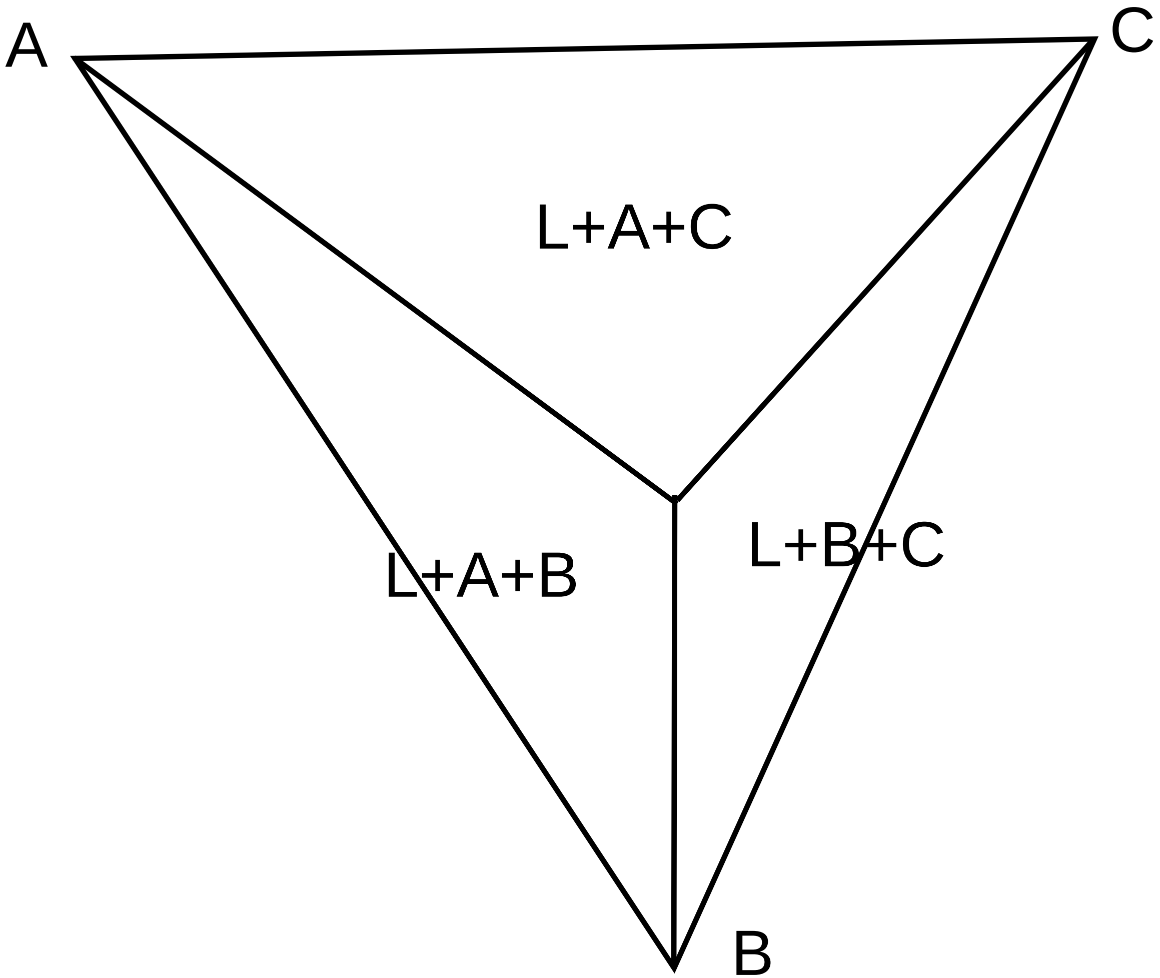




Ternary Eutectic System

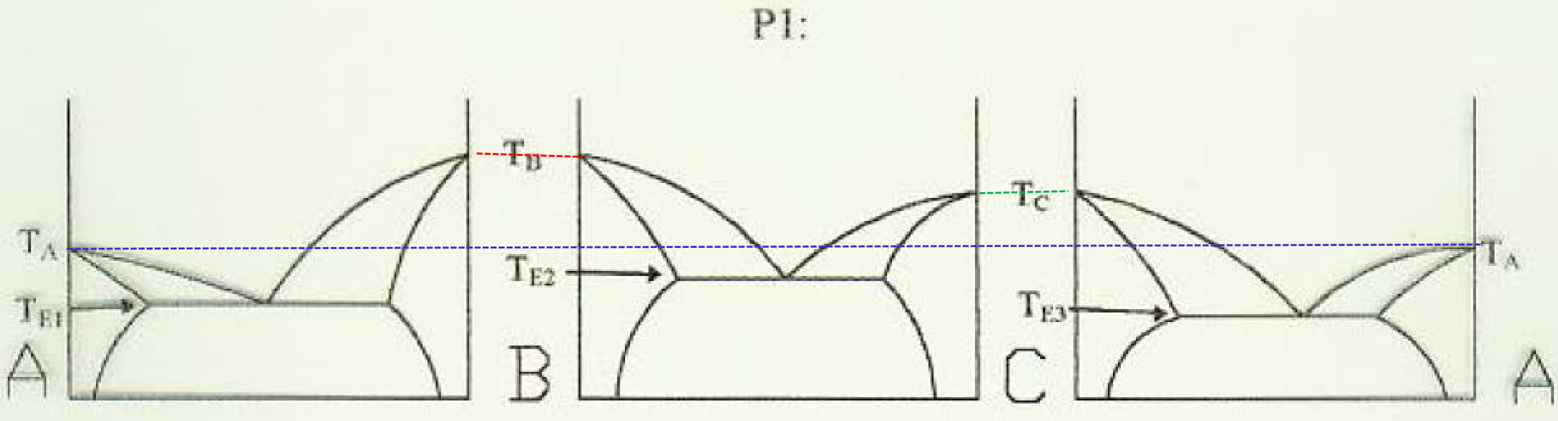
(No Solid Solubility)

T= ternary eutectic temp.



Ternary Eutectic System

(with Solid Solubility)



T_A: Melting Point Of Material A

T_B: Melting Point Of Material B

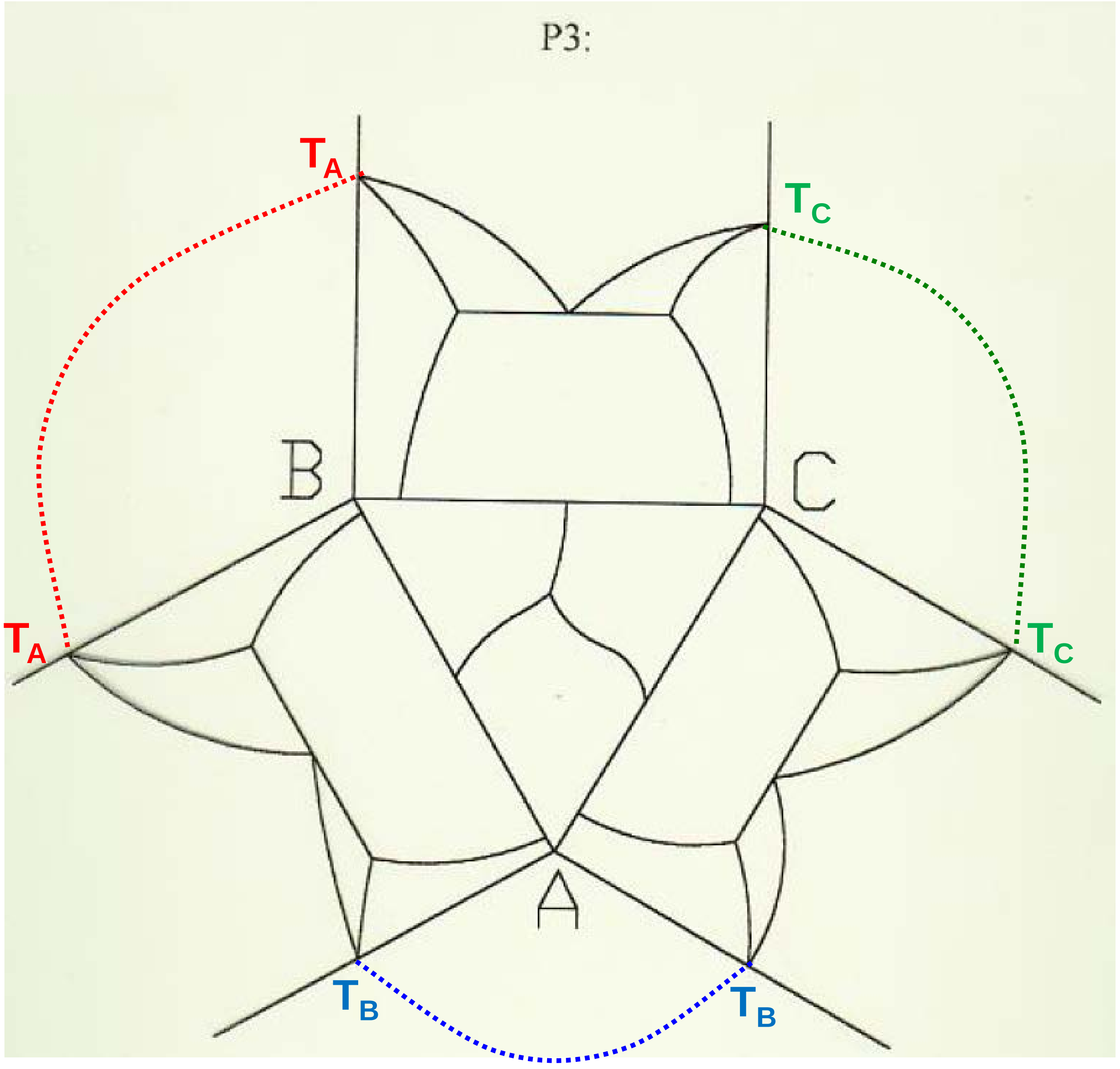
T_C: Melting Point Of Material C

T_{E1}: Eutectic Temperature Of A-B

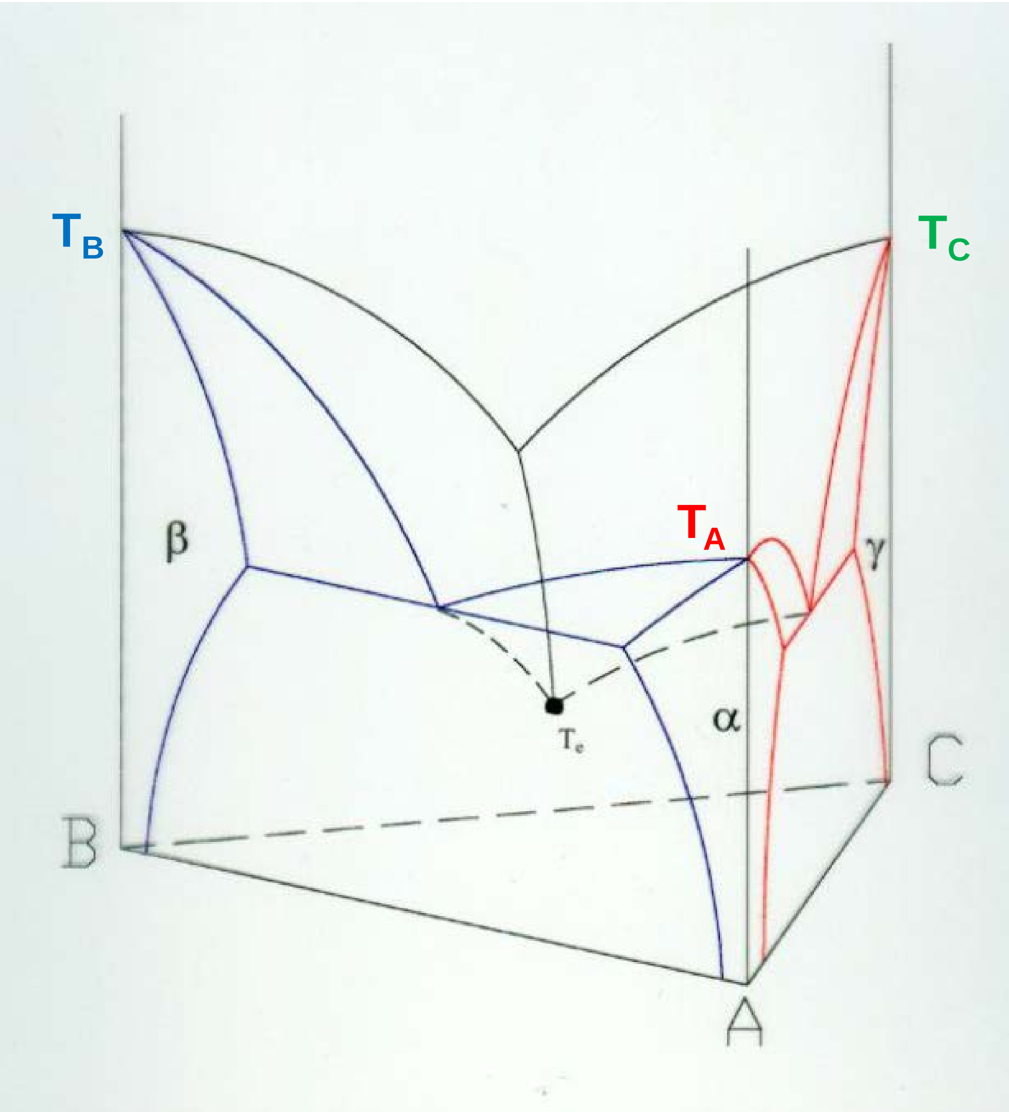
T_{E2}: Eutectic Temperature Of B-C

T_{E3}: Eutectic Temperature Of C-A

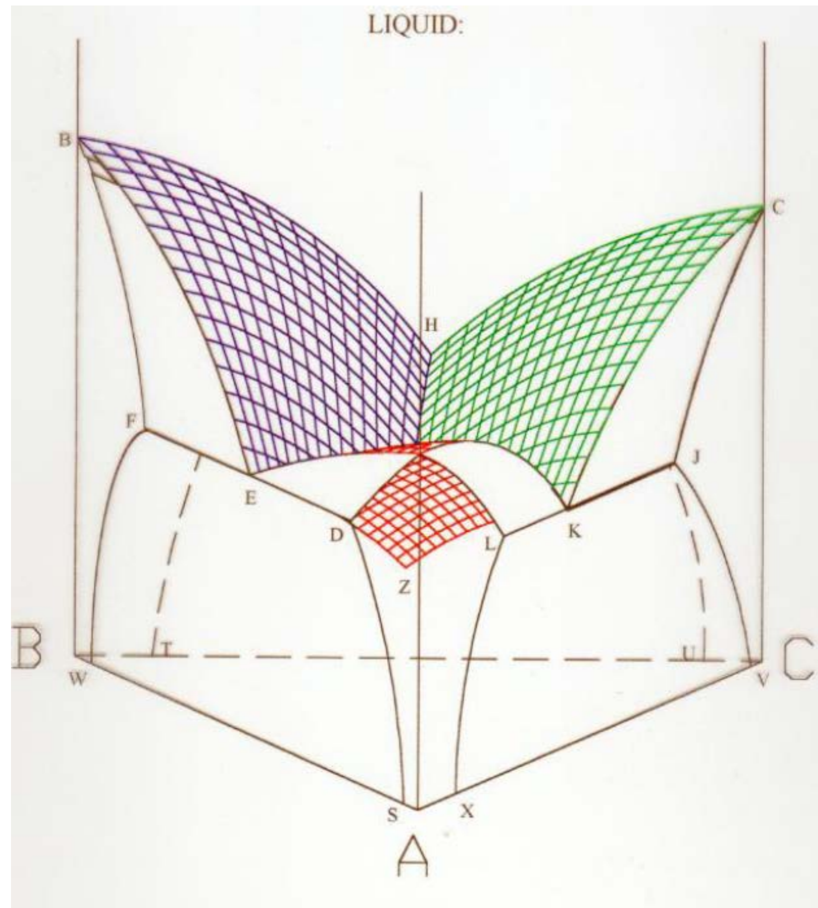
Ternary Eutectic System
(with Solid Solubility)



Ternary Eutectic System
(with Solid Solubility)

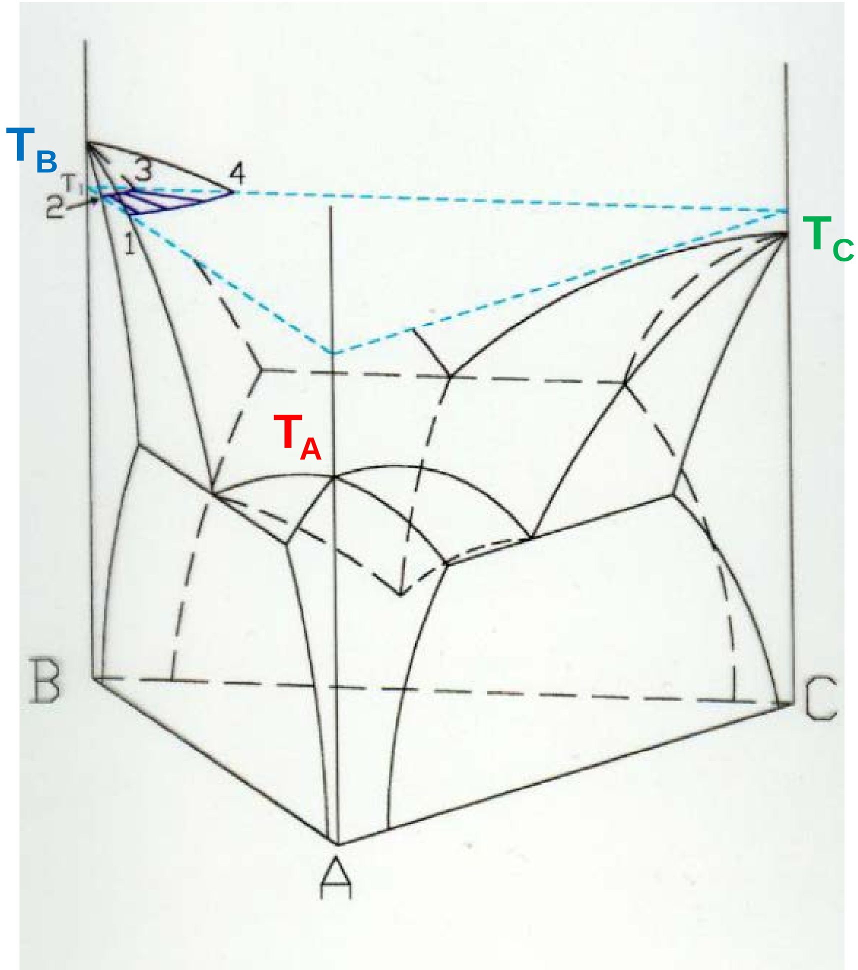


Main outline of Ternary Phase Diagram with Ternary Eutectic (T_e) and Solid Single Phase Regions Shown

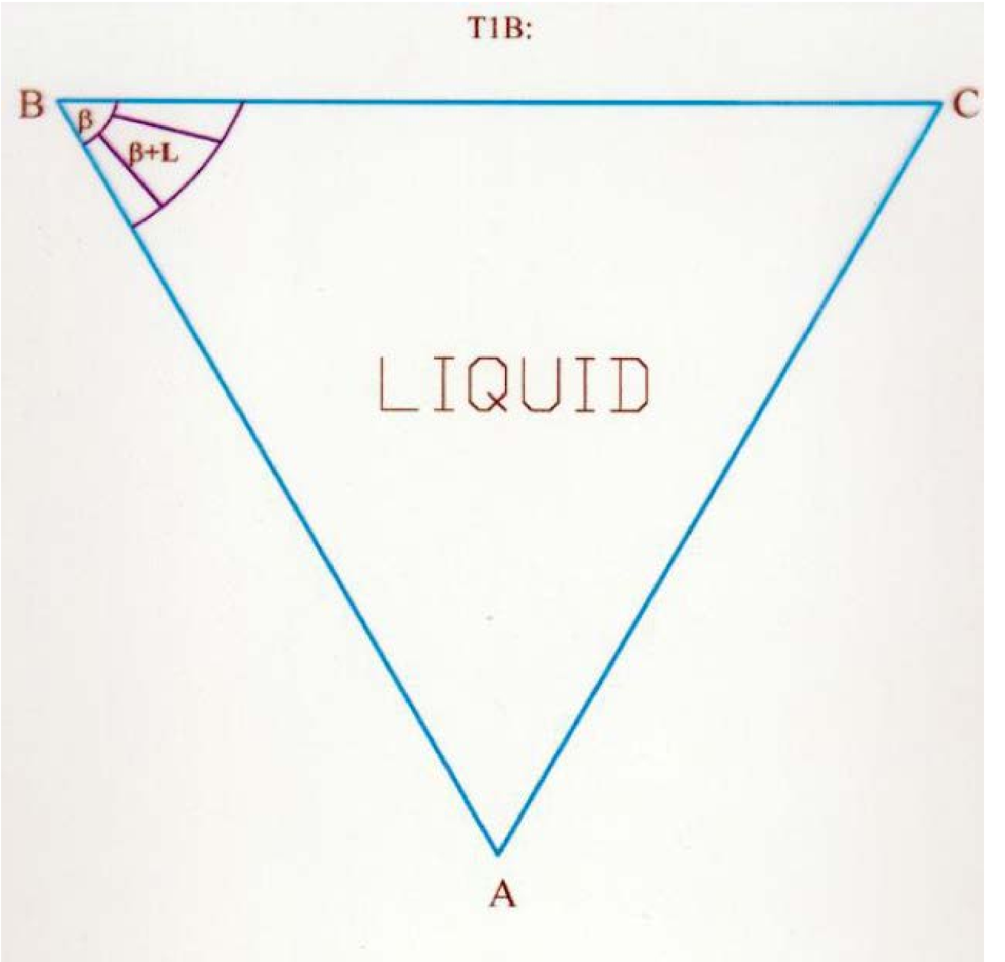


All Liquidus surfaces (α+L-Red, β+L-Purple, γ+L-Green)

Ternary Eutectic System
(with Solid Solubility)



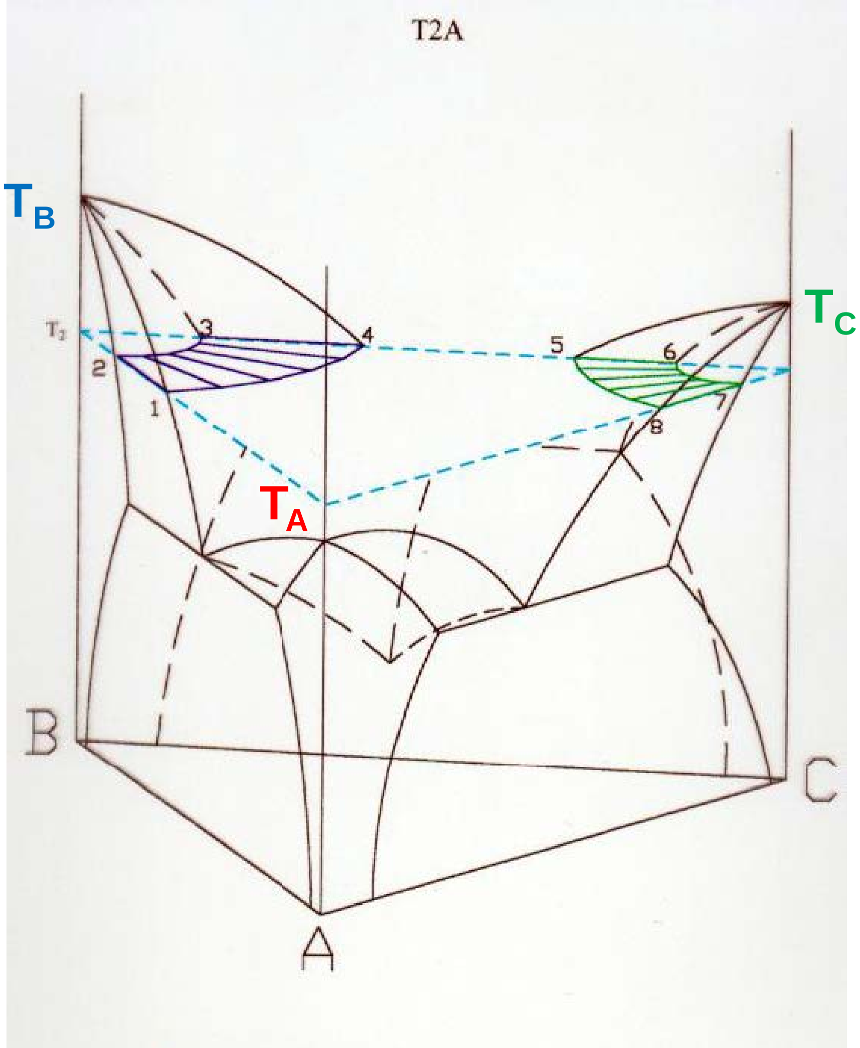
Temperature Slice At $T_1 < T_B$, But $>T_A$, T_C



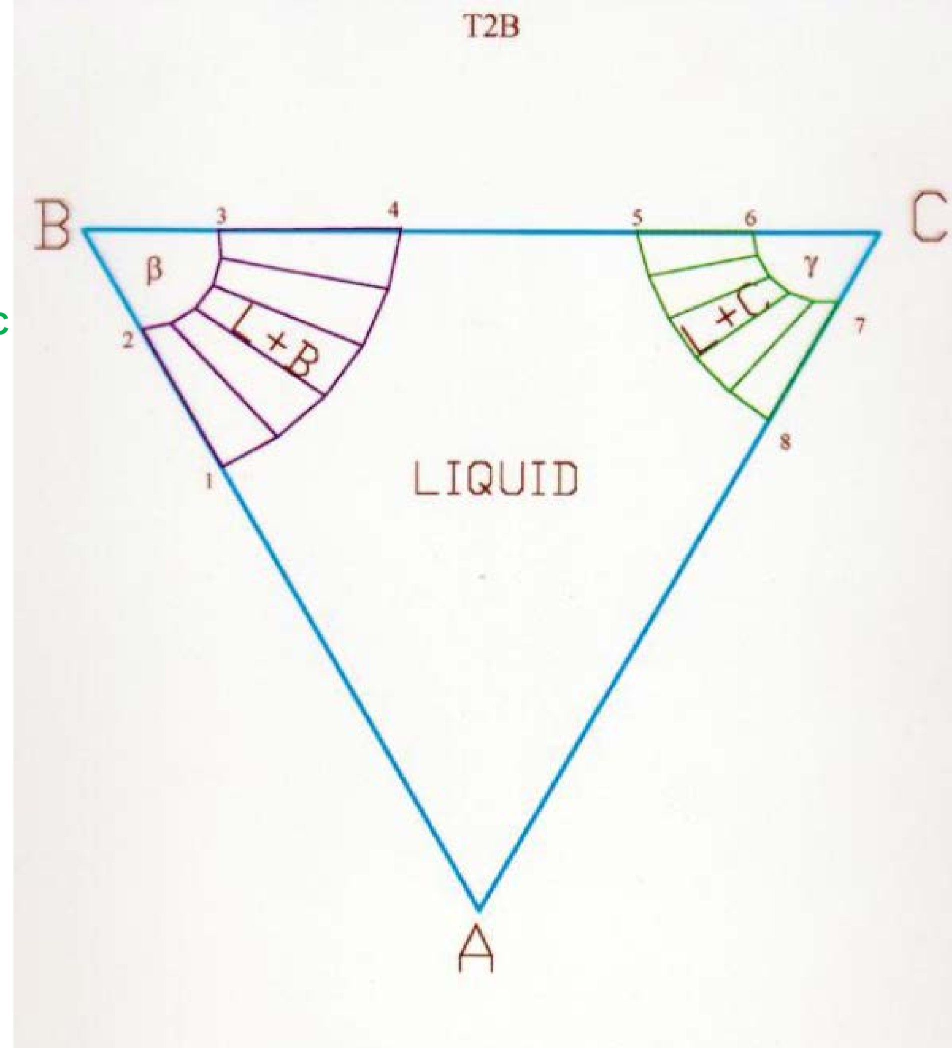
Isothermal Section At $T=T_1$

Ternary Eutectic System

(with Solid Solubility)



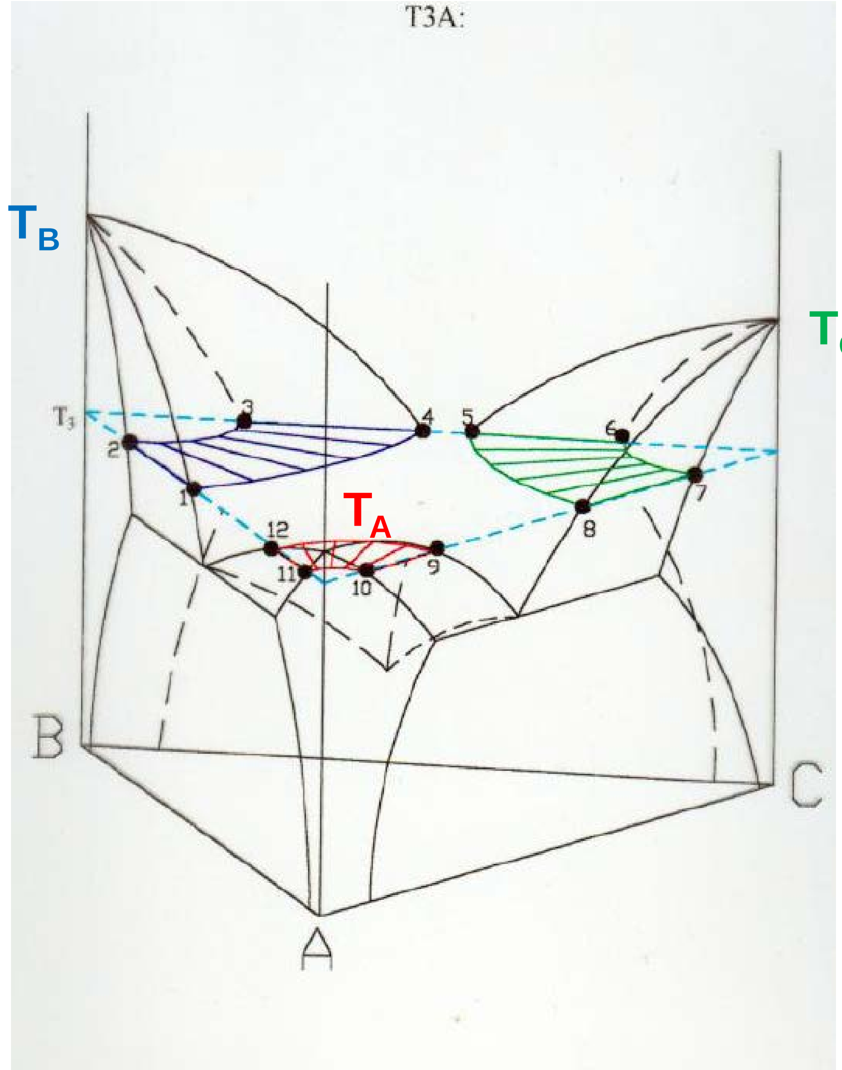
Temperature Slice At $T_2 > T_A$ But, $T_2 < T_B, T_C$



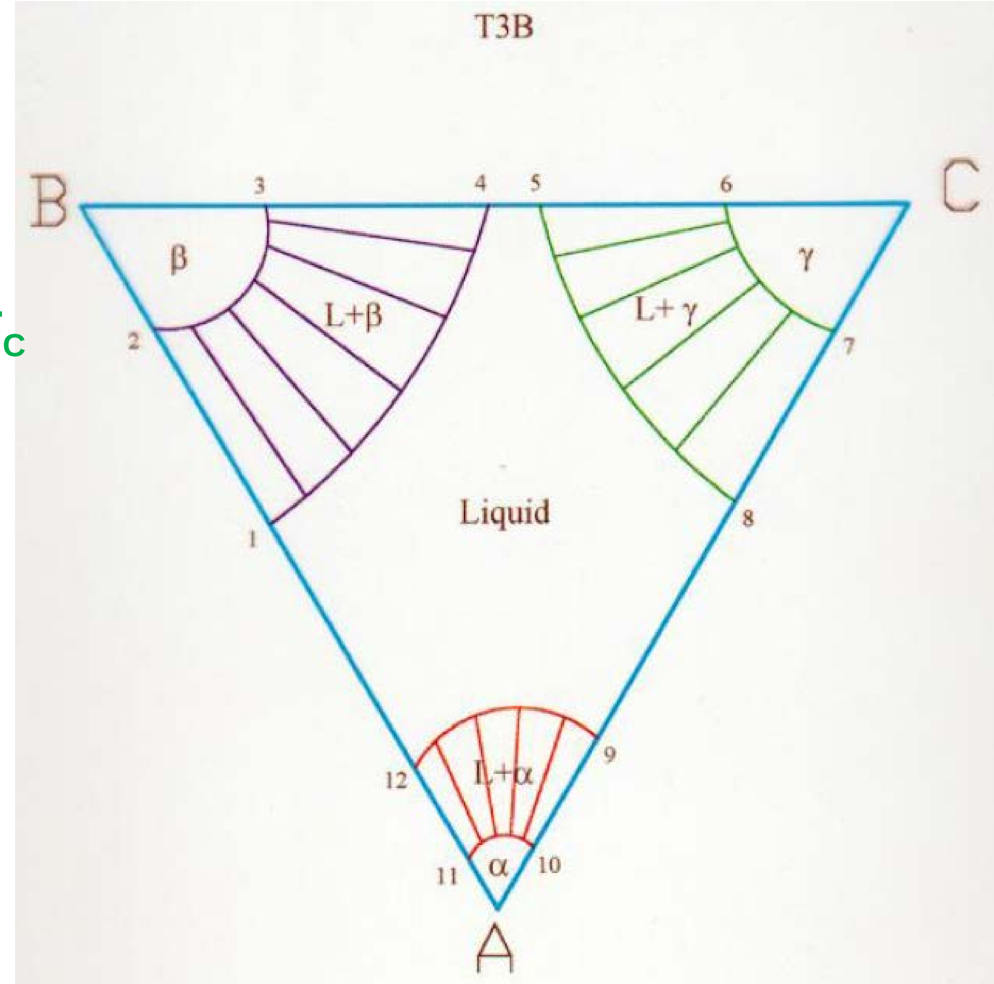
Isothermal Section At $T = T_2$

Ternary Eutectic System

(with Solid Solubility)

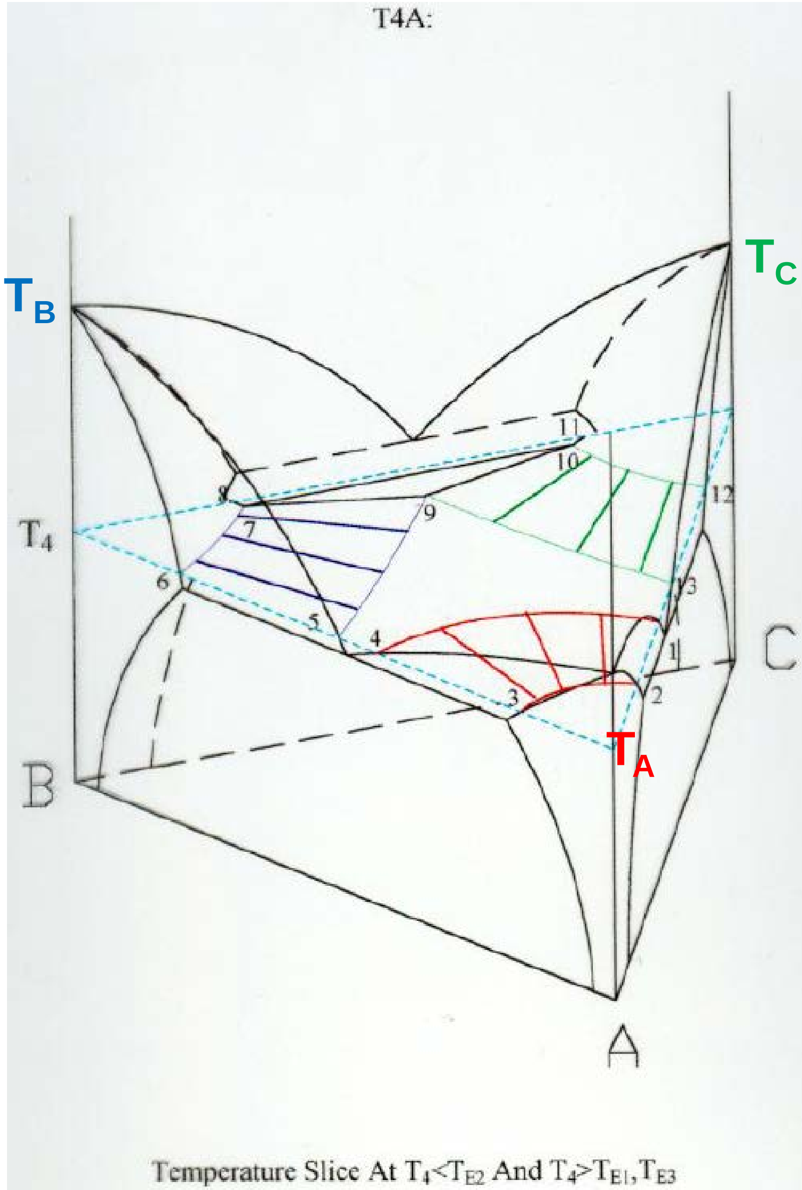


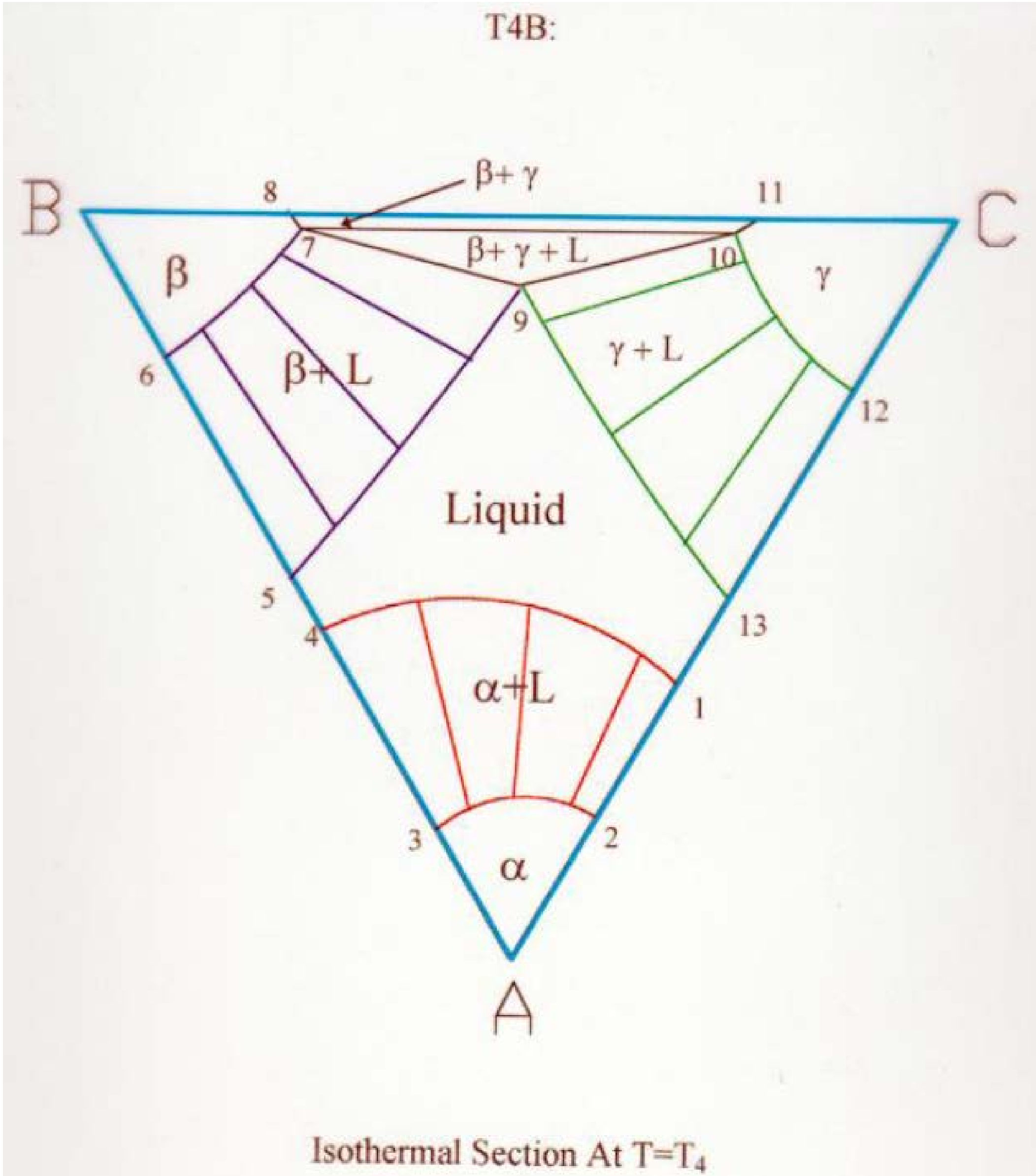
Temperature Slice At $T_3 < T_A, T_B, T_C$, But $T3 > T_{E1}, T_{E2}, T_{E3}$



Isothermal Section At $T= T_3$

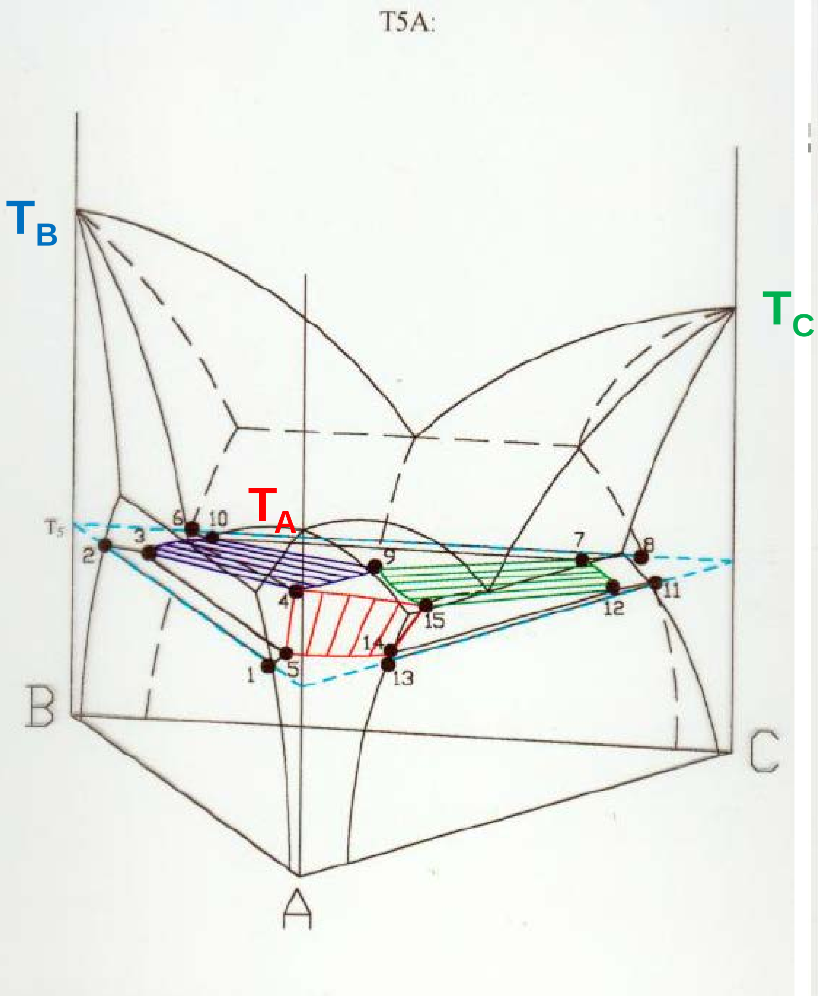
Ternary Eutectic System
(with Solid Solubility)



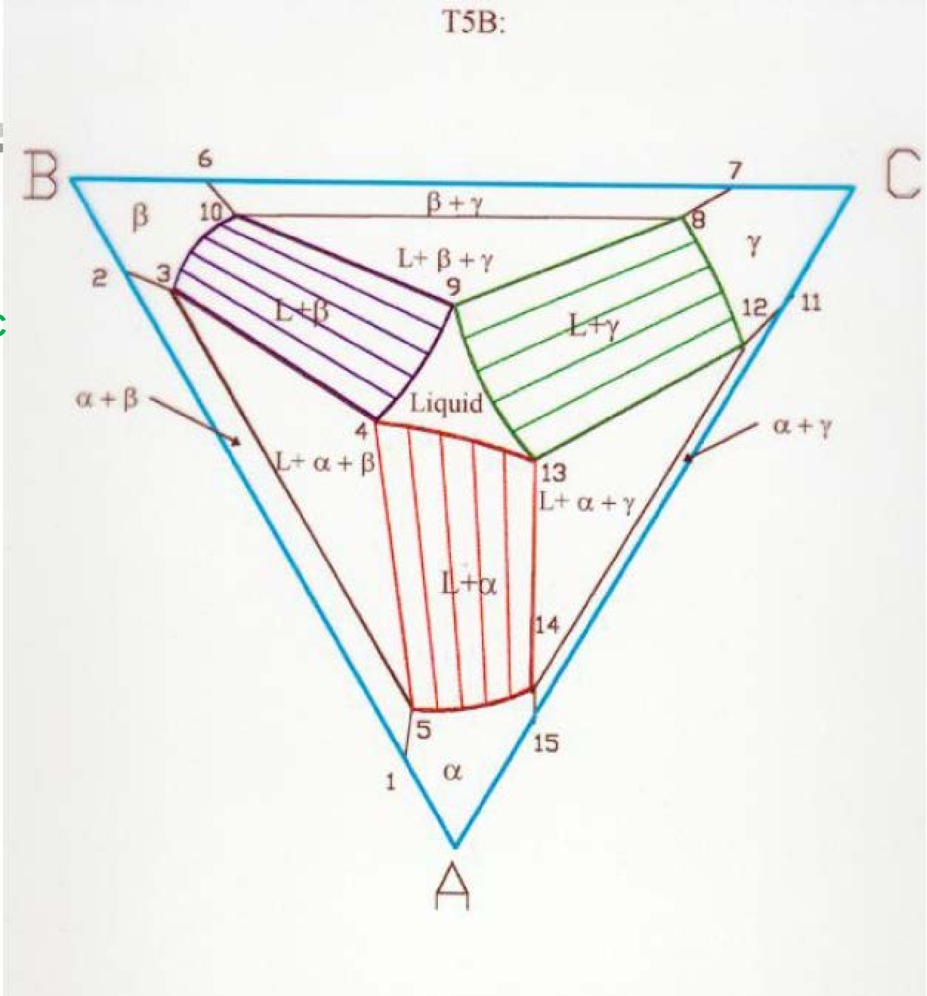


Ternary Eutectic System

(with Solid Solubility)



Temperature Slice Below All Binary Eutectics But, Above The Ternary Eutectic

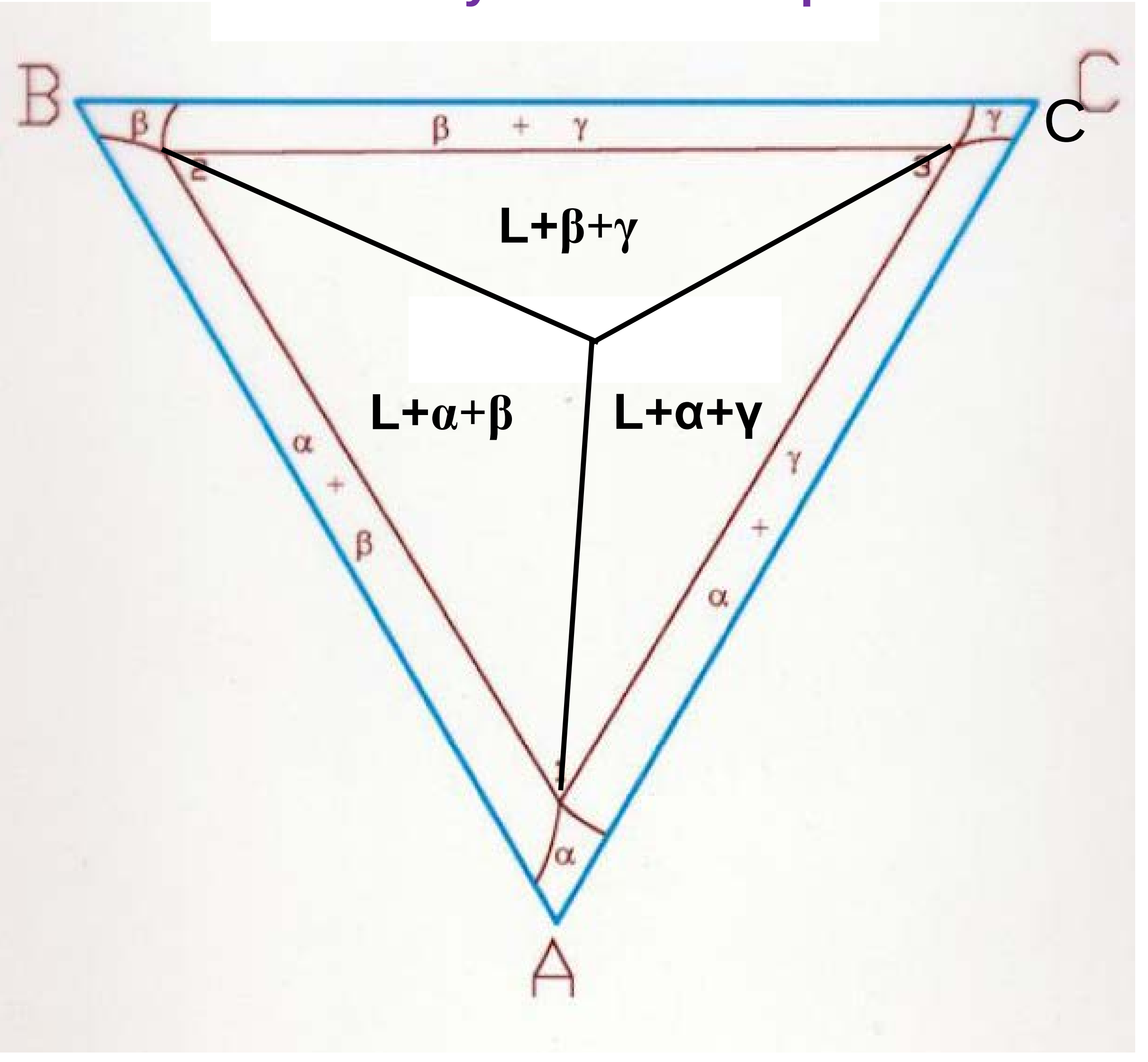


Isothermal Section At $T=T_5$

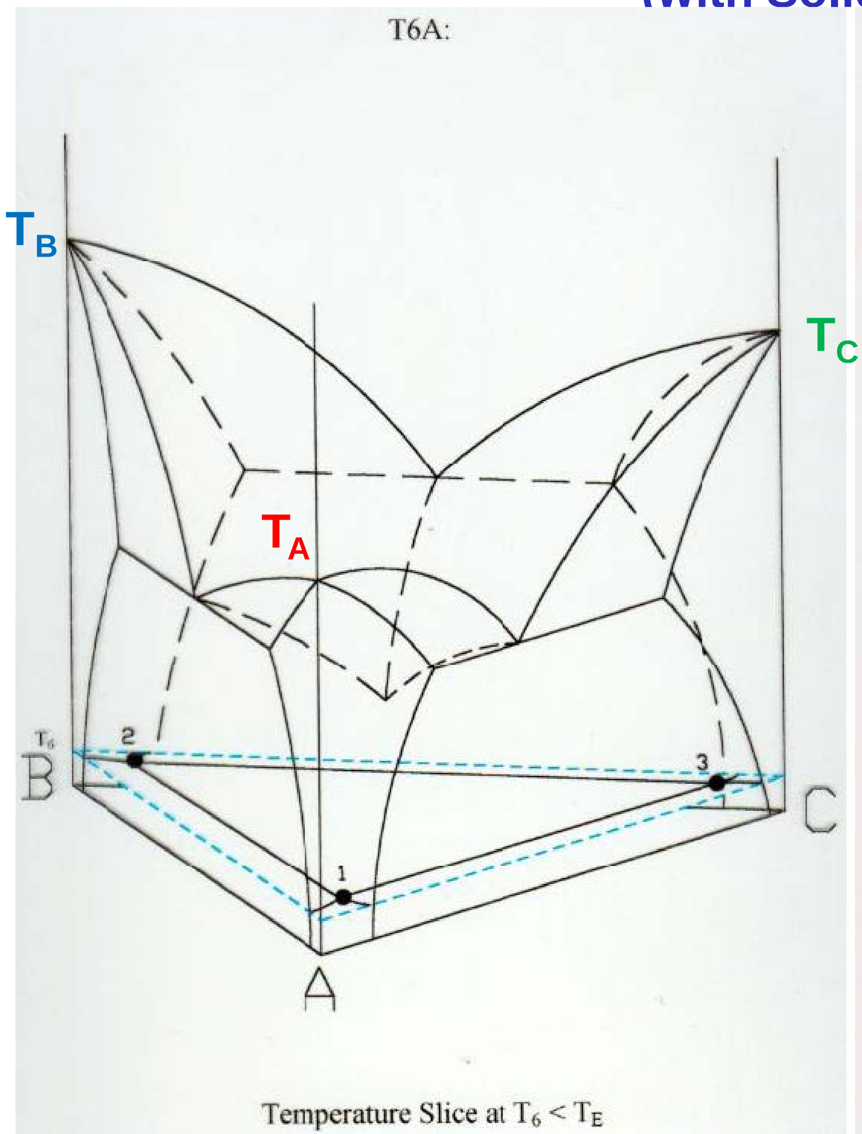
Ternary Eutectic System

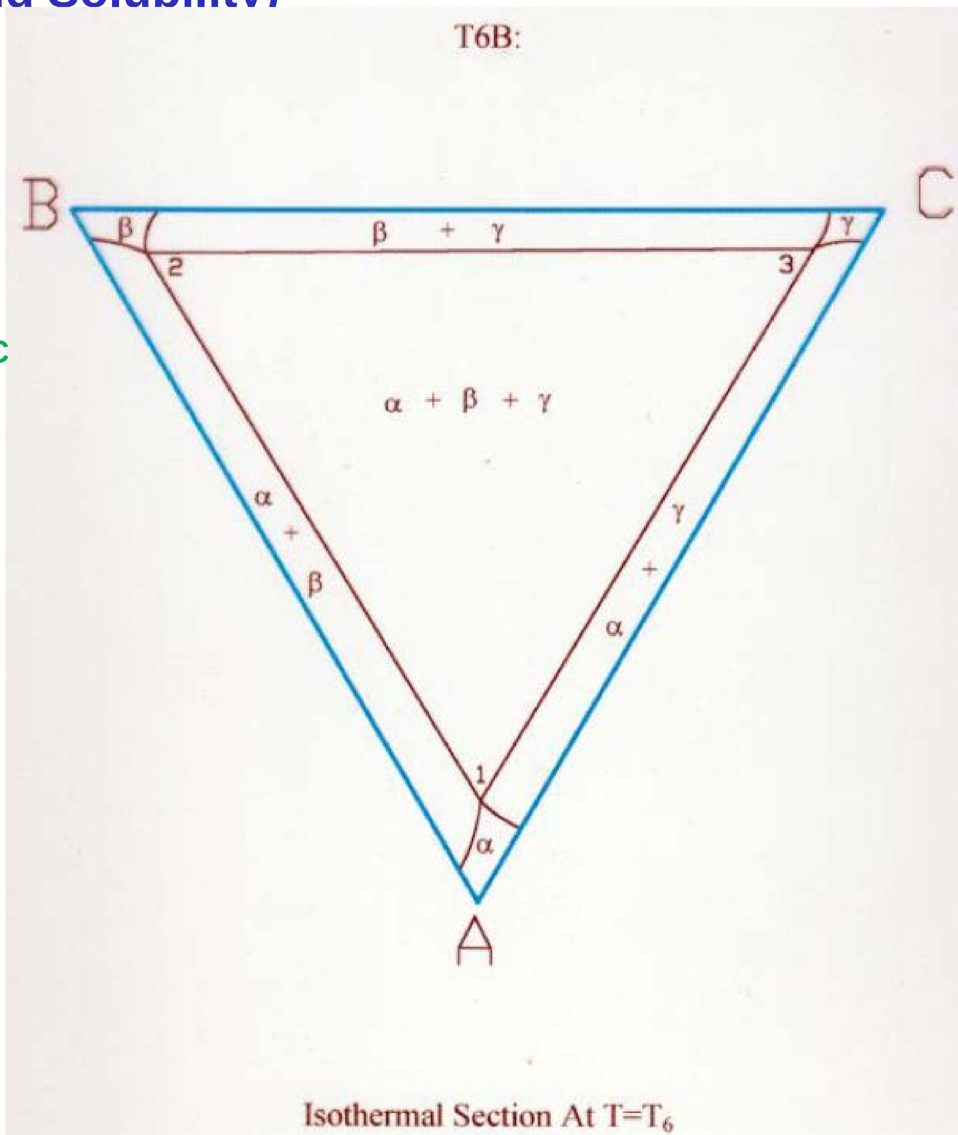
(with Solid Solubility)

T= ternary eutectic temp.



Ternary Eutectic System
(with Solid Solubility)

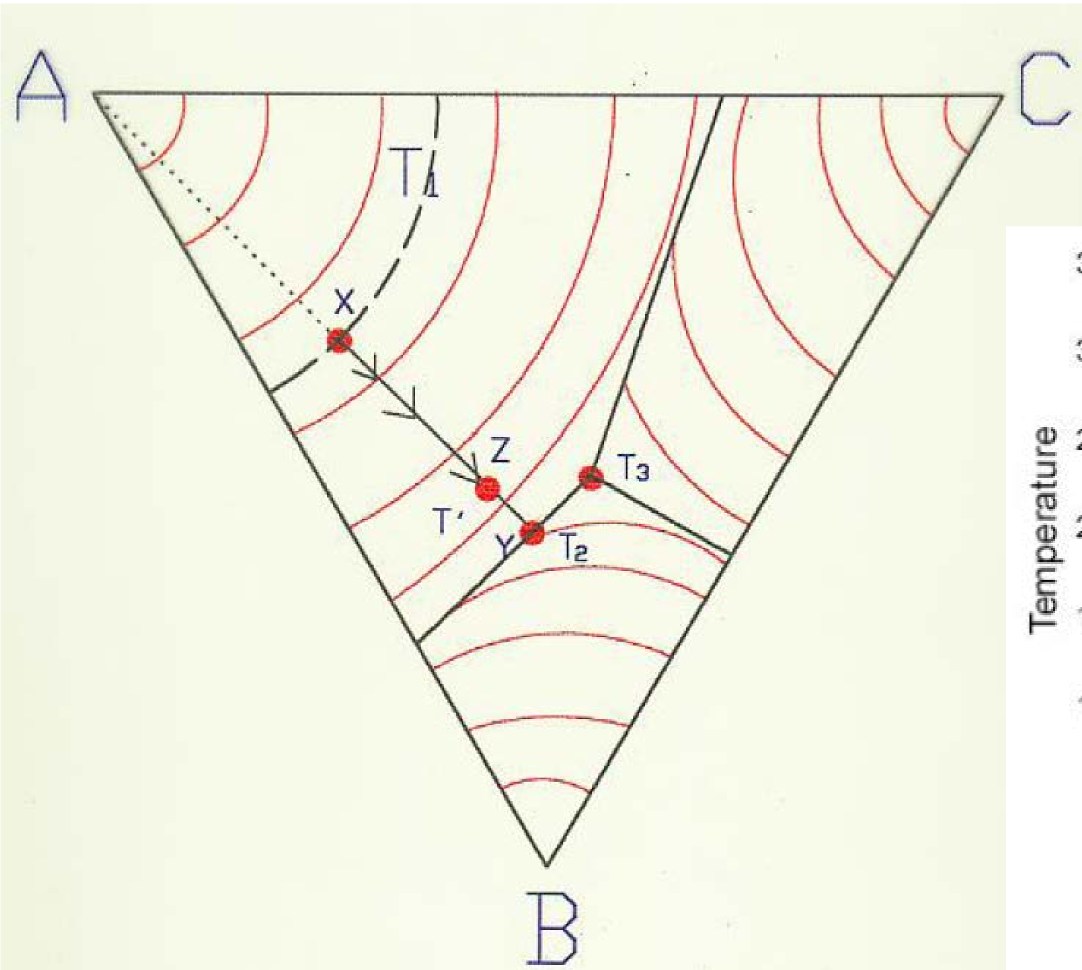


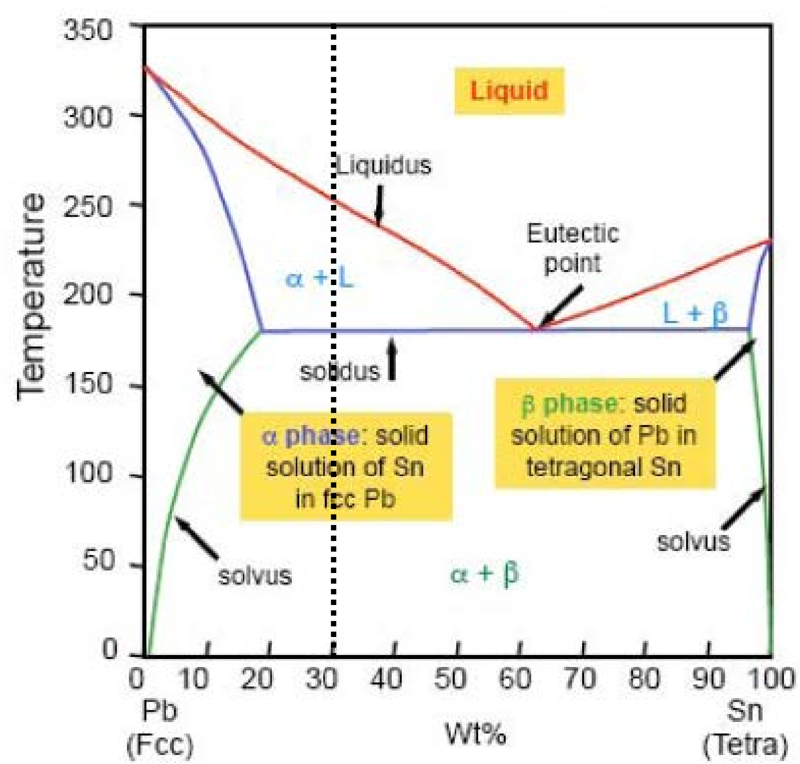


정해솔 학생 제공 자료 참조: 실제 isothermal section의 온도에 따른 변화
http://www.youtube.com/watch?v=yzhVomAdetM

Ternary Eutectic System

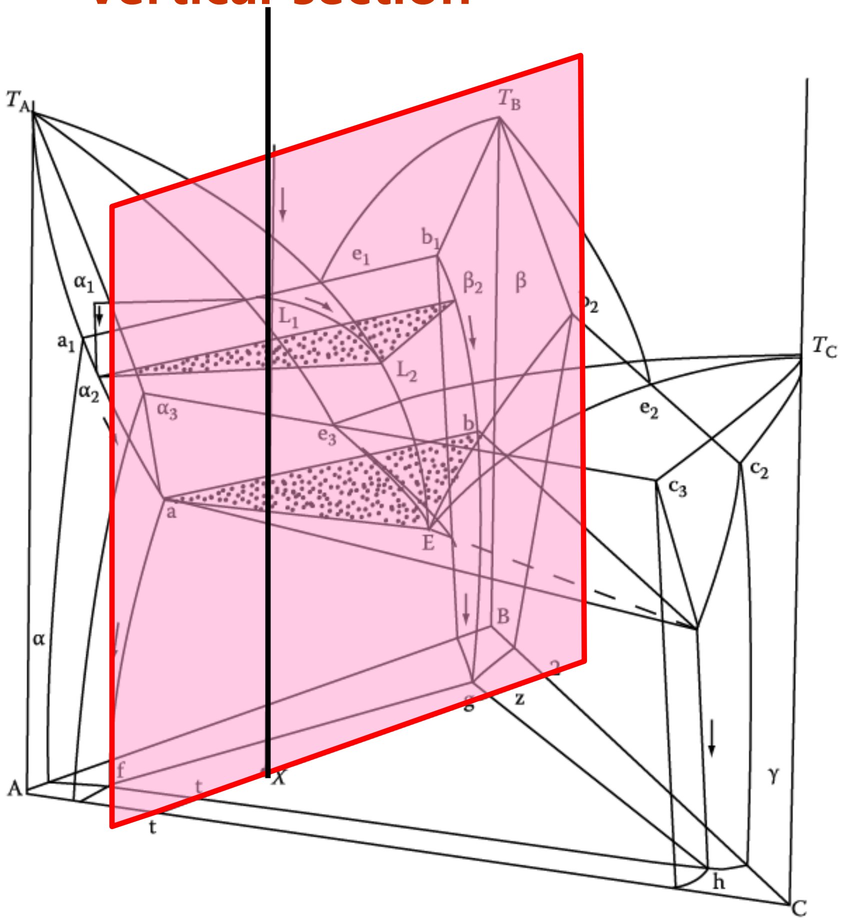
3) Solidification Sequence: liquidus surface

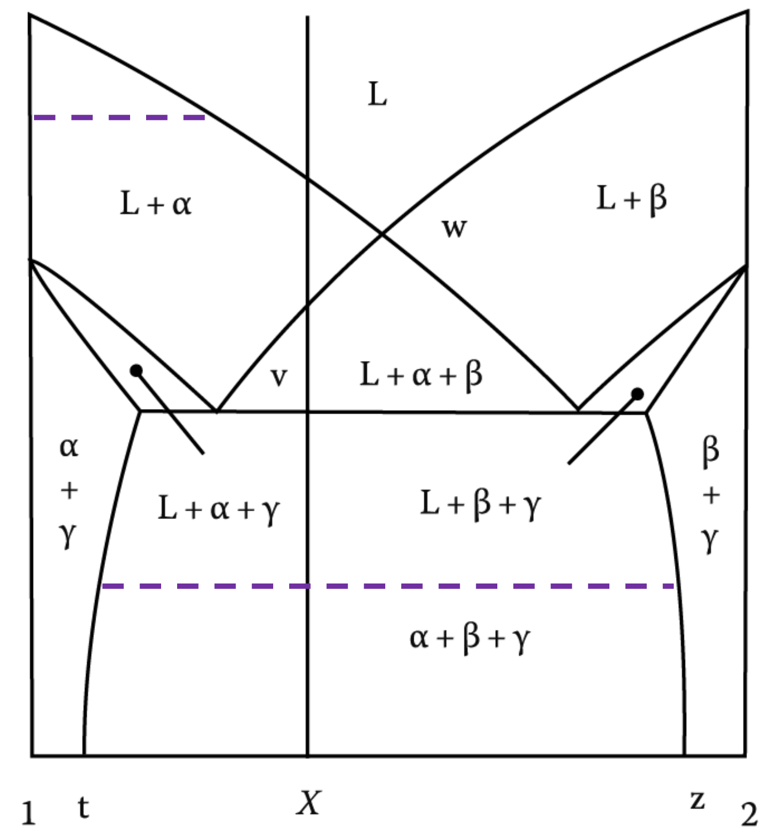




Ternary Eutectic System

* Vertical section





* The horizontal lines are not tie lines.
  (no compositional information)
* Information for equilibrium phases at different tempeatures

< Quaternary phase Diagrams >

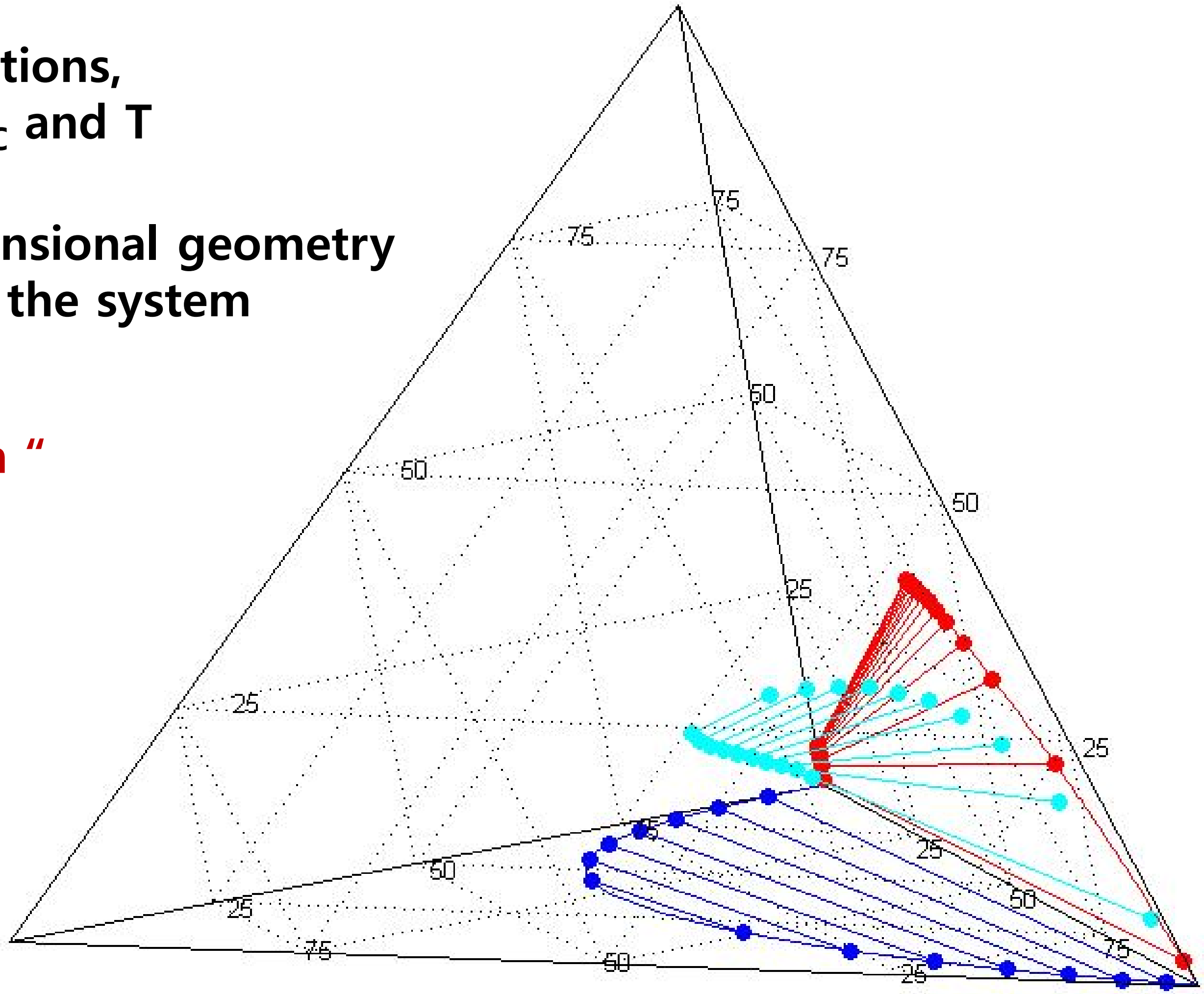
Four components: A, B, C, D

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

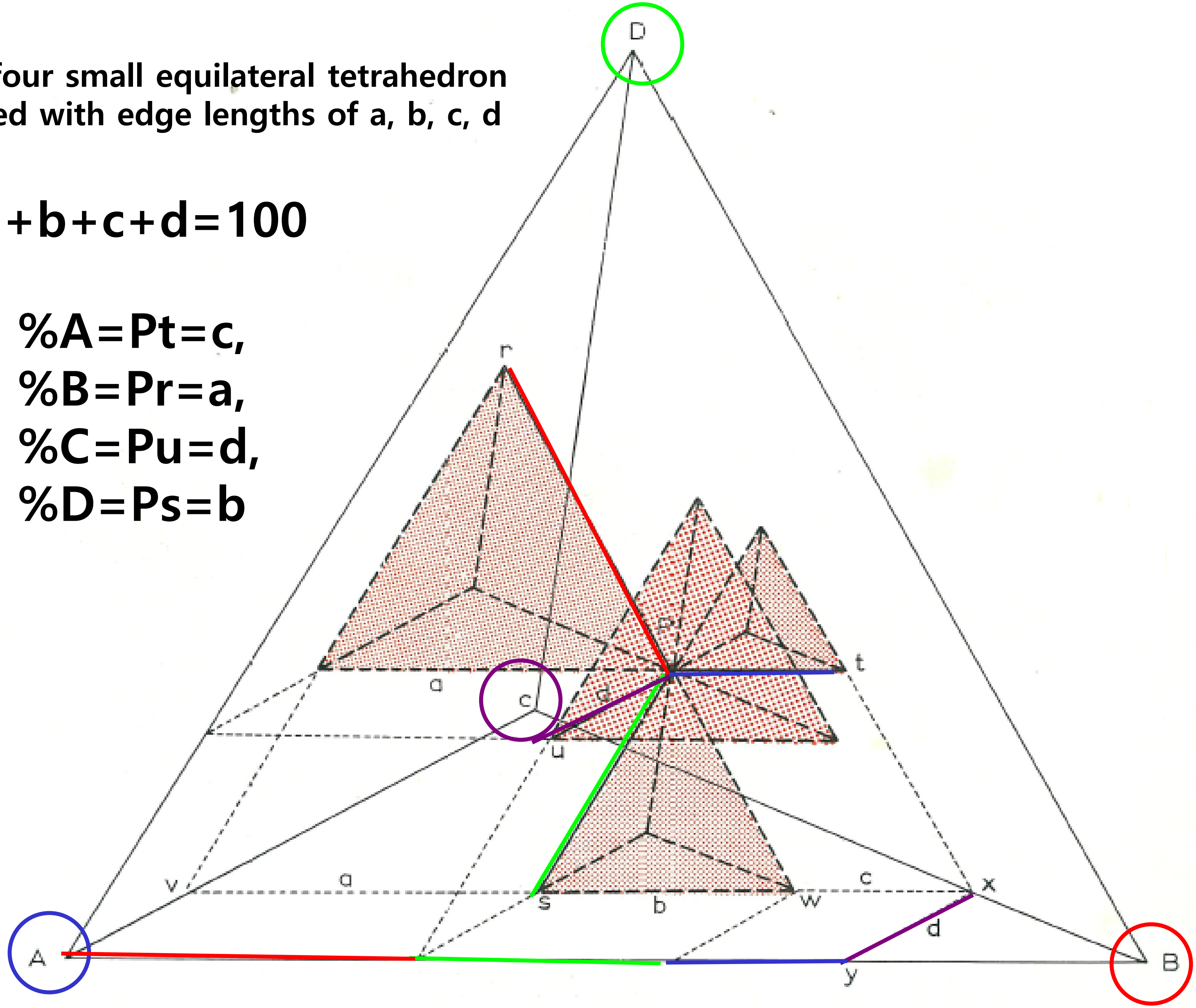


Fig. 247. Representation of a quaternary system by an equilateral tetrahedron.

*** Incentive Homework 1**

Please submit ternary phase diagram model which can clearly express 3D structure of ternary system by October 17 in Bldg. 33-313.
You can submit the model individually or with a small group under 3 persons.

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

Good Luck!!