2017 Fall

"Phase Transformation *in* Materials"

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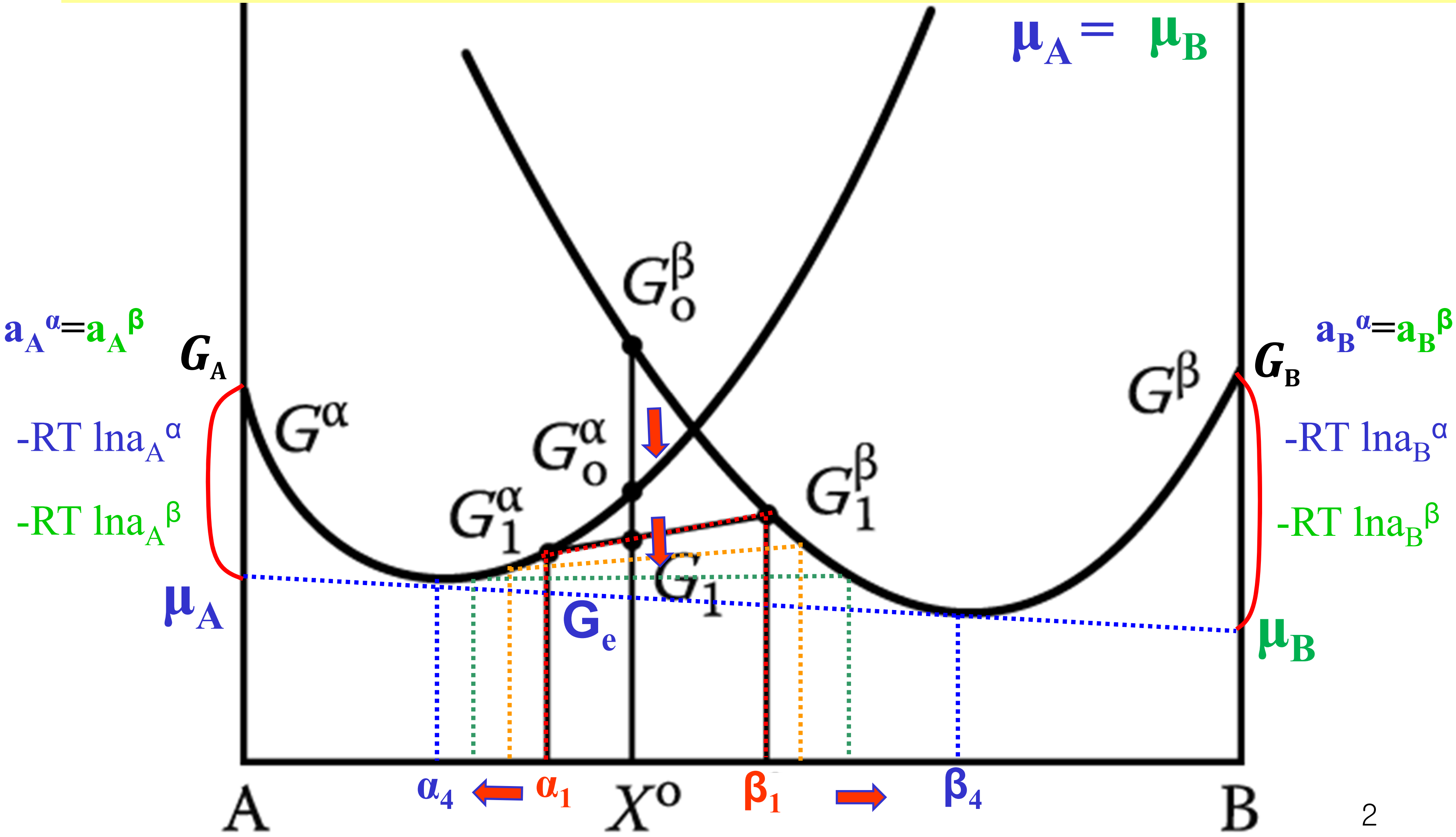
Equilibrium in Heterogeneous Systems

In X^0, $G_0^\beta > G_0^\alpha > G_1$ ➡ $\alpha + \beta$ separation ➡ unified chemical potential

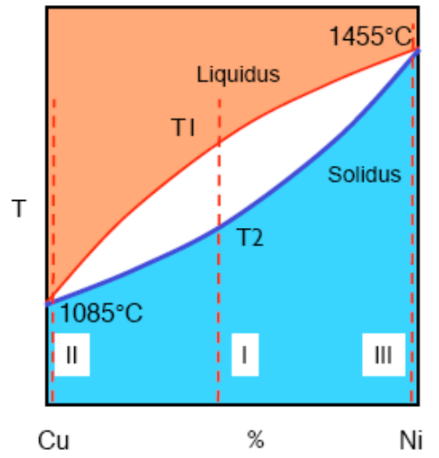


- Binary phase diagrams

1) Simple Phase Diagrams

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

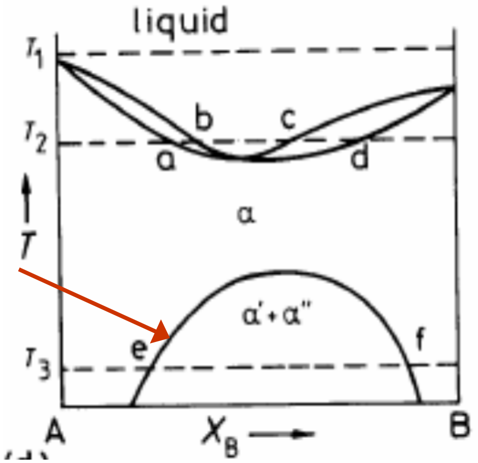
Assume: (1) completely miscible in solid and liquid.
(2) Both are ideal soln.



2) Variant of the simple phase diagram

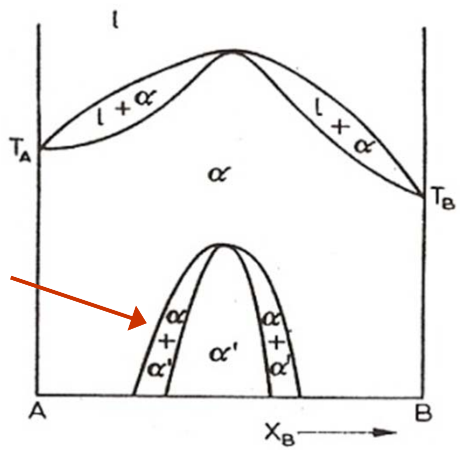
$$\Delta H^{\alpha}_{mix} > \Delta H^{l}_{mix} > 0$$

miscibility gab

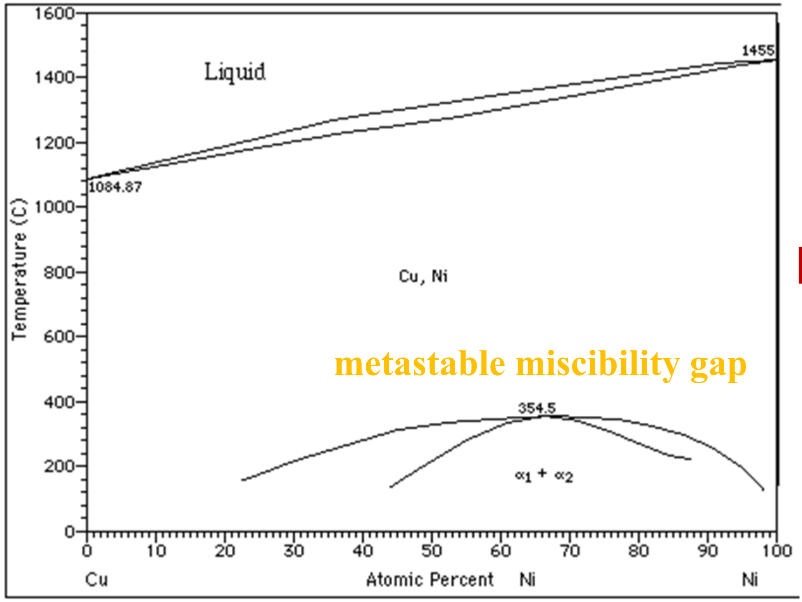


$$\Delta H^{\alpha}_{mix} < \Delta H^{l}_{mix} < 0$$

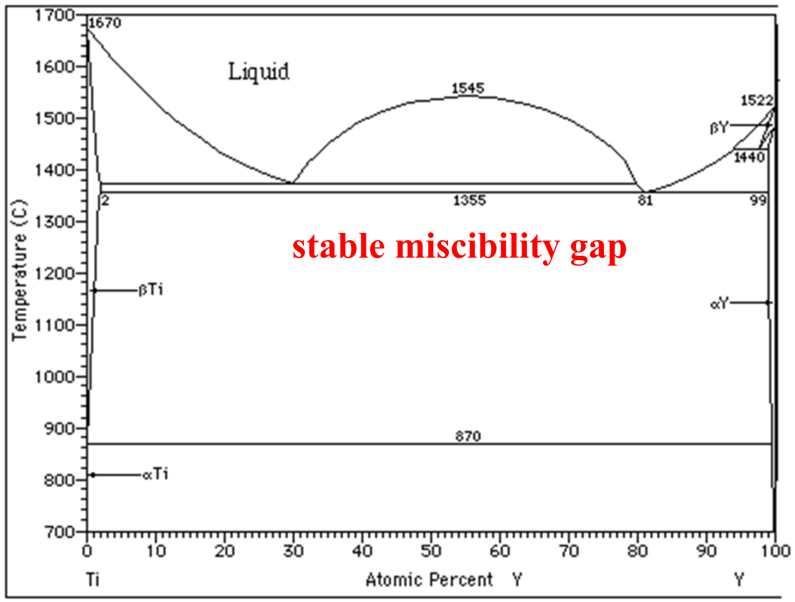
Ordered phase



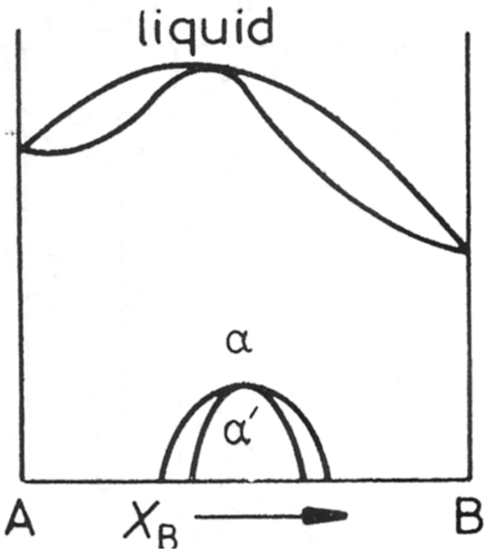
$\Delta H^{S}_{mix} > 0$: **Solid solution → solid state phase separation (two solid solutions)**

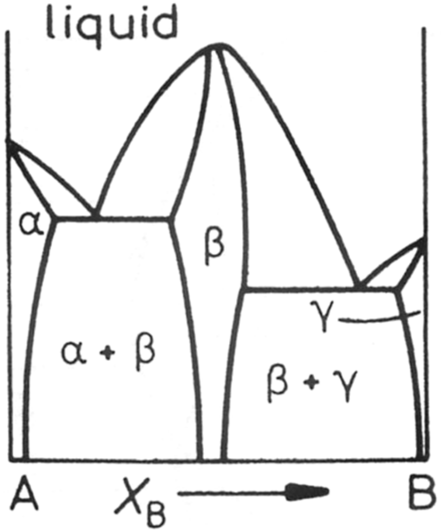


$\Delta H^{S}_{mix} >> 0$: **liquid state phase separation (up to two liquid solutions)**

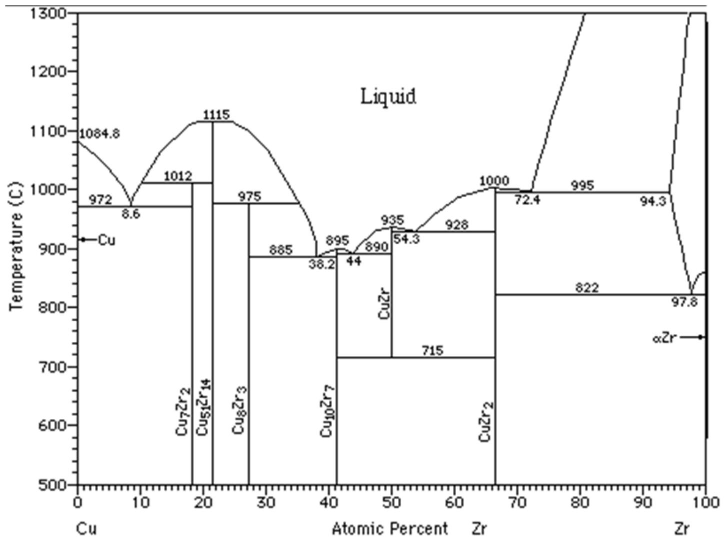


$\Delta H^{S}_{mix} < 0$: **Solid solution → ordered phase**





$\Delta H^{S}_{mix} << 0$: **Compound : AB, A_2B…**



Summary I : Binary phase diagrams

1) Simple Phase Diagrams

Both are ideal soln. → 1) Variation of temp.: $G^L > G^s$ 2) Decrease of curvature of G curve
(∵ decrease of $-T\Delta S_{mix}$ effect)

2) Systems with miscibility gap

$$\Delta H^L_{mix} = 0 \quad \Delta H^S_{mix} > 0$$

1)Variation of temp.: $G^L > G^s$ 2)Decrease of curvature of G curve + Shape change of G curve by H

4) Simple Eutectic Systems

$$\Delta H^L_{mix} = 0 \quad \Delta H^S_{mix} >> 0$$

→ miscibility gap extends to the melting temperature.

3) Ordered Alloys

$$\Delta H^L_{mix} = 0 \quad \Delta H^S_{mix} < 0$$

$\Delta H_{mix} < 0$ → A atoms and B atoms like each other. → Ordered alloy at low T
$\Delta H_{mix} << 0$ → The ordered state can extend to the melting temperature.

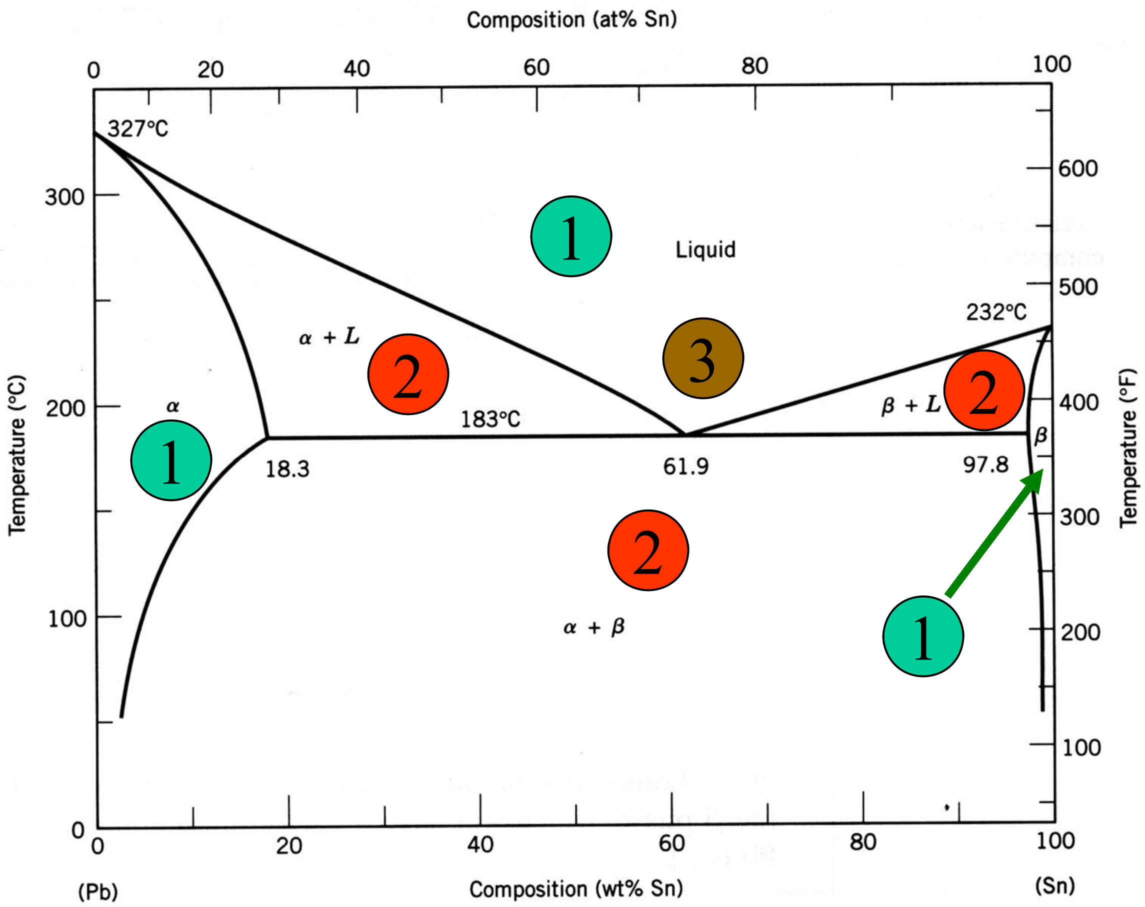
5) Phase diagrams containing intermediate phases

Stable composition ≠ Minimum G with stoichiometric composition

The Gibbs Phase Rule

For Constant Pressure,

P + F = C + 1



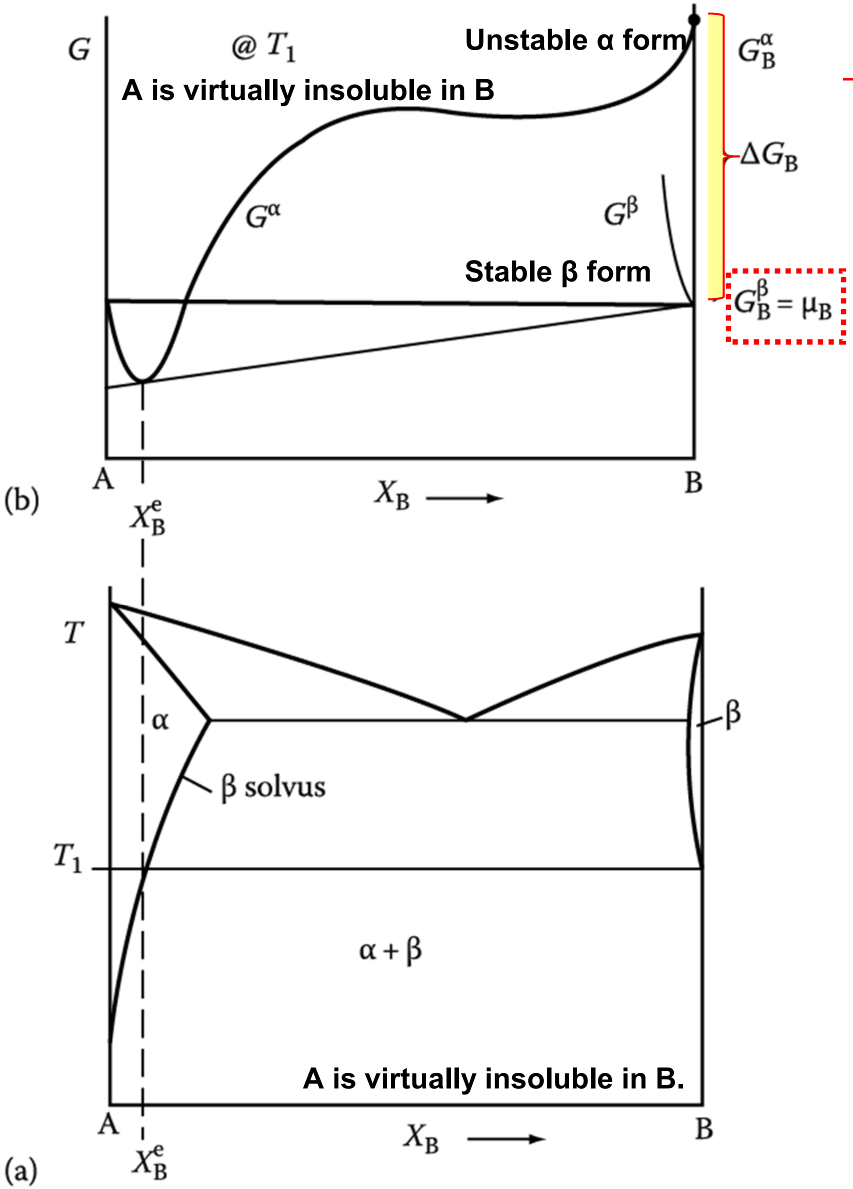
1 **single phase**
F = C - P + 1
= 2 - 1 + 1
= 2
can vary T and composition independently

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

1.5.7 Effect of T on solid solubility

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



$$\mu_B^\alpha = {}^oG_B^\alpha + \Omega(1-X_B)^2 + RT\ln X_B = \mu_B^\beta \simeq {}^oG_B^\beta$$

$$\Delta G_B^{\beta\to\alpha} = {}^0G_B^\alpha - {}^oG_B^\beta = {}^oG_B^\alpha - \mu_B^\beta = {}^oG_B^\alpha - \mu_B^\alpha$$

$${}^oG_B^\alpha - \mu_B^\alpha = -\Omega(1-X_B)^2 - RT\ln X_B$$

$$\Delta G_B^{\beta\to\alpha} = -\Omega(1-X_B)^2 - RT\ln X_B$$

$$RT\ln X_B = -\Delta G_B^{\beta\to\alpha} - \Omega(1-X_B)^2$$

$$(here, X_B^e << 1)$$

$$RT\ln X_B^e = -\Delta G_B^{\beta\to\alpha} - \Omega$$

$$>> \quad X_B^e = \exp\left(-\frac{\Delta G_B^{\beta\to\alpha} + \Omega}{RT}\right)$$

$$\Delta G_B^{\beta\to\alpha} = \Delta H_B^{\beta\to\alpha} - T\Delta S_B^{\beta\to\alpha} \text{ 이므로}$$

$$X_B^e = \exp\left(\frac{\Delta S_B^{\beta\to\alpha}}{R}\right)\exp\left(-\frac{\Delta H_B^{\beta\to\alpha} + \Omega}{RT}\right)$$

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

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

***Q* : heat absorbed (enthalpy) when 1 mole of β dissolves in A rich α as a dilute solution.**

* Limiting forms of eutectic phase diagram

The solubility of one metal in another may be so low.

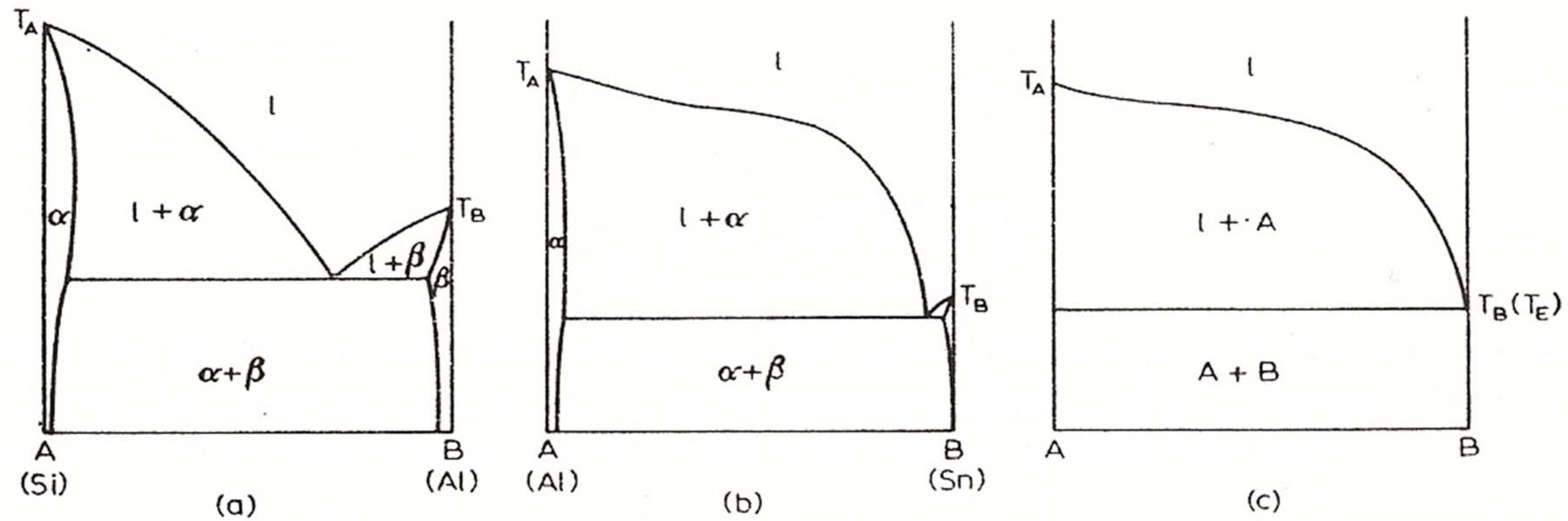


Fig. 53. Evolution of the limiting form of a binary eutectic phase diagram.

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

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.

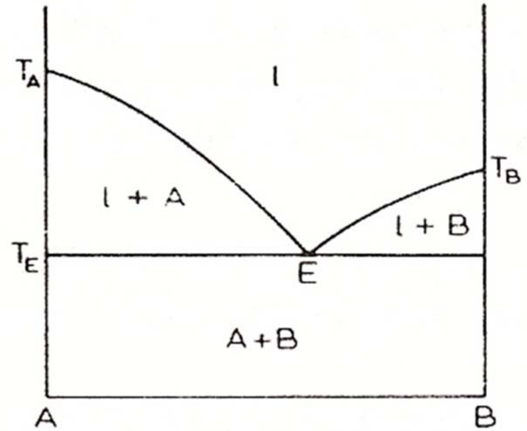


Fig. 54. Impossible form of a binary eutectic phase diagram.

a) 평형에 미치는 공공의 영향

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

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

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

- **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**

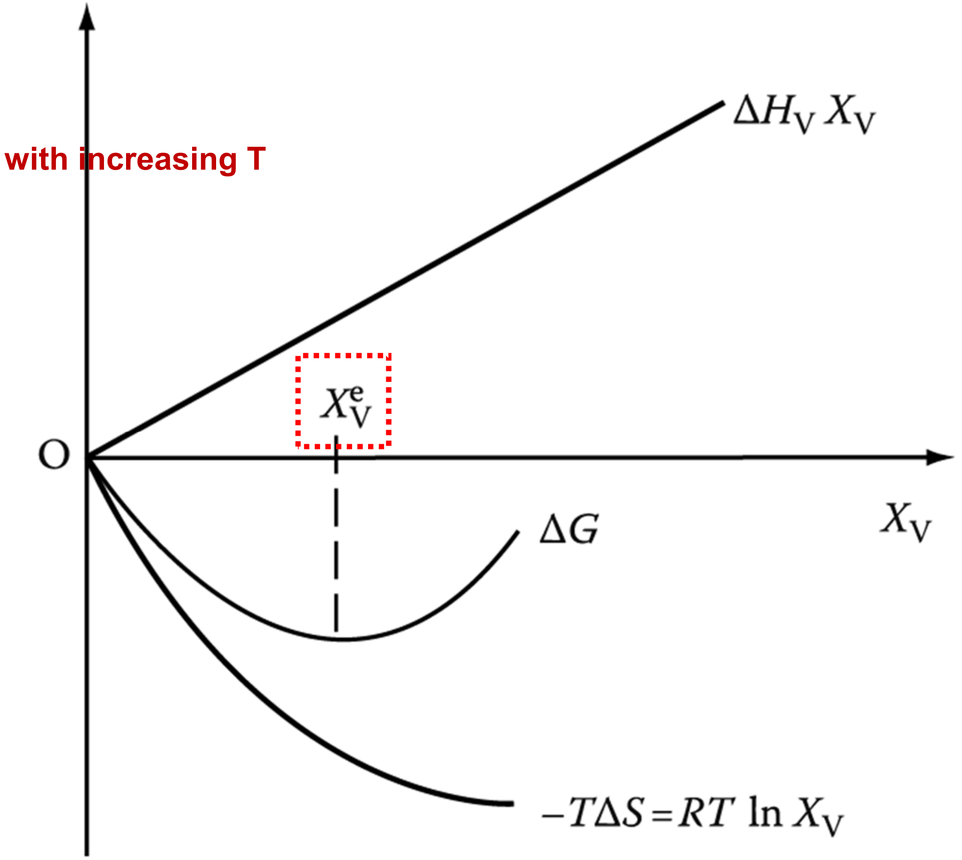


Fig. 1.37 Equilibrium vacancy concentration.

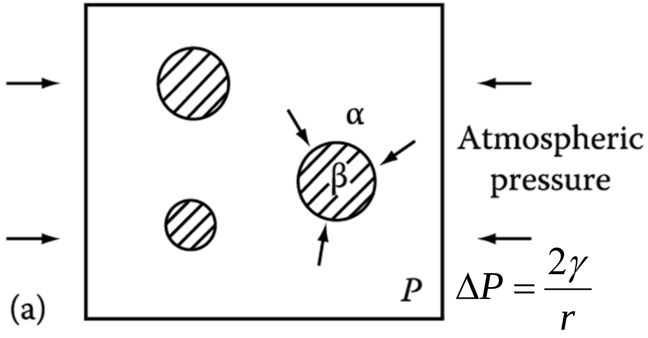
: adjust so as to reduce G to a minimum

The G curves so far have been based on the molar Gs of infinitely large amounts of material of a perfect single crystal. Surfaces, GBs and interphase interfaces have been ignored.

1.6 Influence of Interfaces on Equilibrium - b) 평형에 미치는 계면의 영향

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

Extra pressure ΔP due to curvature of the **α/β**



The concept of a pressure difference is very useful <u>for spherical liquid particles</u>, but it is less convenient in solids (often nonspherical shape).

$$dG = \Delta G_\gamma dn = \gamma dA \qquad \Delta G_\gamma = \gamma dA/dn$$

Since n=4πr³/3V$_m$ and A = 4πr² $\Delta G = \frac{2\gamma V_m}{r}$

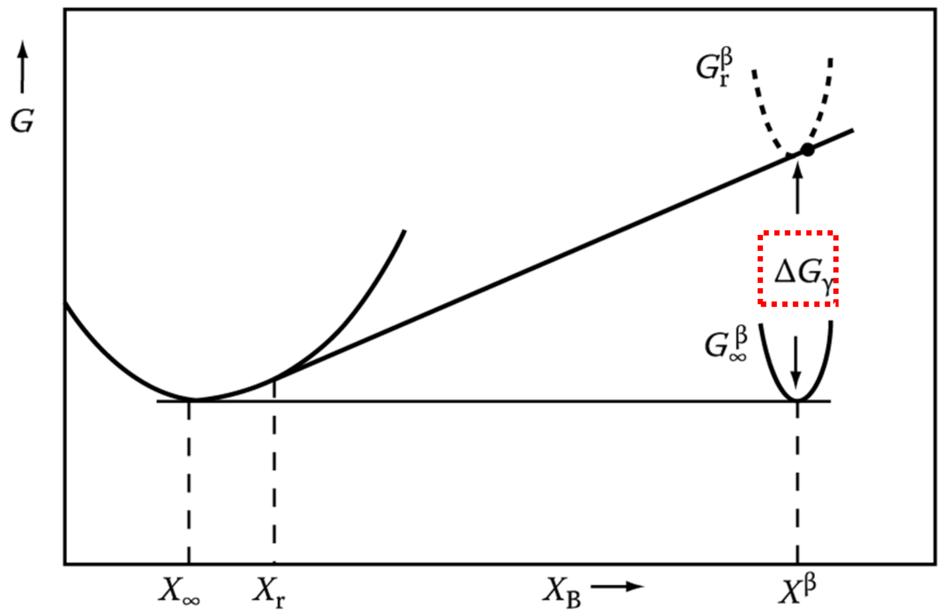


Fig. 1.38 The effect of interfacial E on the solubility of small particle

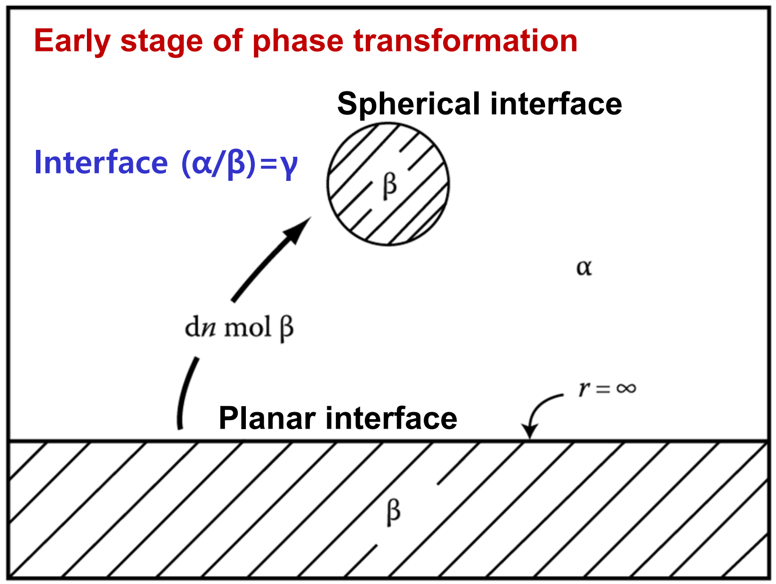


Fig. 1.39 Transfer of dn mol of β from large to a small particle.

Gibbs-Thomson effect (capillarity effect):

Free energy increase due to interfacial energy

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

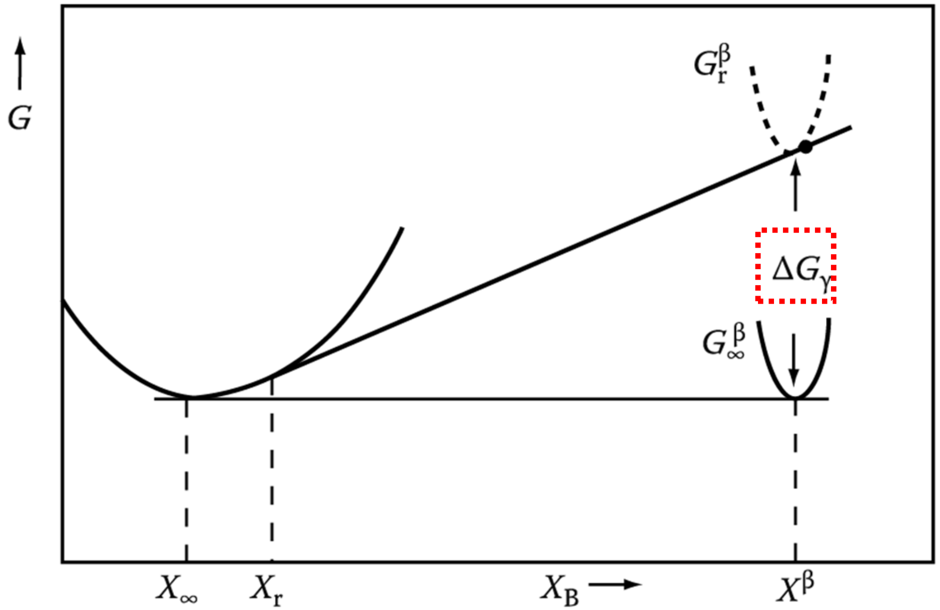
$$X_B^e = \exp(-\frac{\Delta G_B + \Omega}{RT})$$

$$X_B^{r=\infty} = \exp(-\frac{\Delta G_B + \Omega}{RT})$$

$$X_B^{r=r} = \exp(-\frac{\Delta G_B + \Omega - 2\gamma V_m / r}{RT})$$

$$= X_B^{r=\infty} \exp(\frac{2\gamma V_m}{RTr})$$

Quite large solubility differences can arise for particles in the range r=1-100 nm. However, for particles visible in the light microscope (r>1um) capillarity effects are very small.



(b)

Fig. 1.38 The effect of interfacial energy on the solubility of small particles.

For small values of the exponent,

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

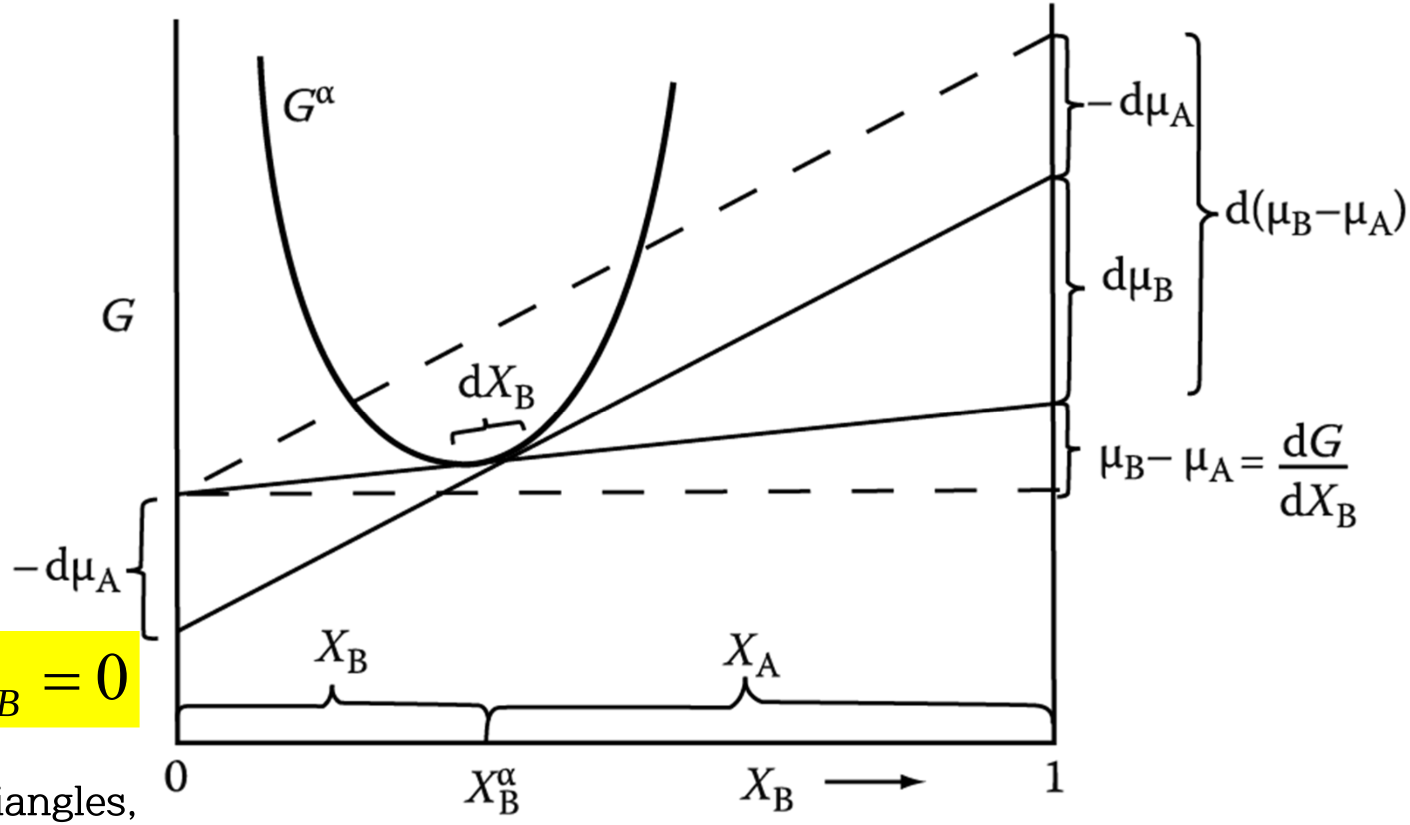
Ex) **γ=200mJ/m^2, V_m=10^{-5} m^3,T=500K**

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

For r=10 nm, solubility~10% increase

1.8 Additional Thermodynamic Relationships for Binary Solutions

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



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

Comparing two similar triangles,

$$-\frac{d\mu_A}{X_B} = \frac{d\mu_B}{X_A} = \frac{d(\mu_B-\mu_A)}{1} \Leftarrow \frac{dG}{dX_B} = \frac{\mu_B-\mu_A}{1}$$

, $\frac{d^2G/dX^2}{d^2G/dX_B^2=d^2G/dX_A^2}$

Substituting right side Eq.
& Multiply X_AX_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

Additional Thermodynamic Relationships for Binary Solutions

The Gibbs-Duhem Equation
합금조성의 미소변화 (dX)로 인한 화학퍼텐셜의 미소변화(**dμ**) 를 계산

be able to calculate the change in chemical potential (dμ) that result from a change in alloy composition (dX).

① **For a regular solution,**

$$G = X_A G_A + X_B G_B + \Omega X_A X_B + RT(X_A \ln X_A + X_B \ln X_B)$$

$$\frac{d^2G}{dX^2} = \frac{RT}{X_A X_B} - 2\Omega$$

For a ideal solution, $\Omega = 0,$

$$\frac{d^2G}{dX^2} = \frac{RT}{X_A X_B}$$

② **Different form Eq. 1.65**

$$\mu_B = G_B + RT\ln a_B = G_B + RT\ln \gamma_B X_B$$

$\gamma_B = a_B/X_B$

Differentiating With respect to X_B,

$$\frac{d\mu_B}{dX_B} = \frac{RT}{X_B}\left\{1 + \frac{X_B}{\gamma_B}\frac{d\gamma_B}{dX_B}\right\} = \frac{RT}{X_B}\left\{1 + \frac{d\ln\gamma_B}{d\ln X_B}\right\}$$

$$\frac{d\mu_B}{dX_B} = \frac{RT}{X_B}\left\{1 + \frac{X_B}{\gamma_B}\frac{d\gamma_B}{dX_B}\right\} = \frac{RT}{X_B}\left\{1 + \frac{d\ln\gamma_B}{d\ln X_B}\right\}$$ **Eq. 1.69**

a similar relationship can be derived for $d\mu_A/dX_B$

$$-X_A d\mu_A = X_B d\mu_B = RT\left\{1 + \frac{d\ln\gamma_A}{d\ln X_A}\right\}dX_B = RT\left\{1 + \frac{d\ln\gamma_B}{d\ln X_B}\right\}dX_B$$ **Eq. 1.70**

$$-X_A d\mu_A = X_B d\mu_B = X_A X_B \frac{d^2G}{dX^2}dX_B$$ **Eq. 1.65**

The Gibbs-Duhem Equation

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

be able to calculate the change in chemical potential (dμ) that result from a change in alloy composition (dX).

Total Free Energy Decrease per Mole of Nuclei ΔG_0

: 변태를 위한 전체 구동력/핵생성을 위한 구동력은 아님

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)

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

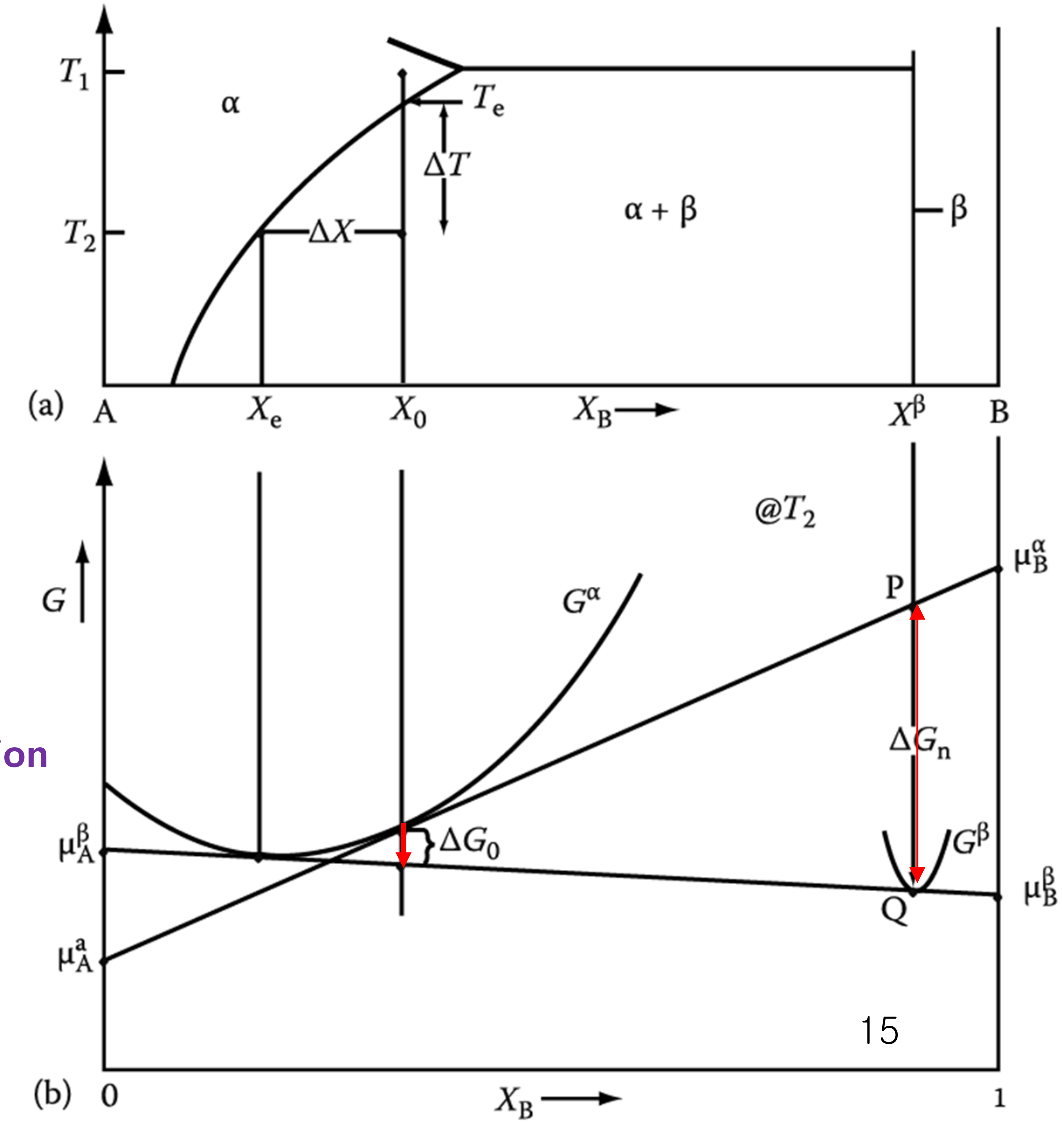
: driving force for β precipitation

For dilute solutions,

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

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

∝ undercooling below T_e



Summary II: Binary phase diagrams

- **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.

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

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

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:

$F = C + 1 - P$

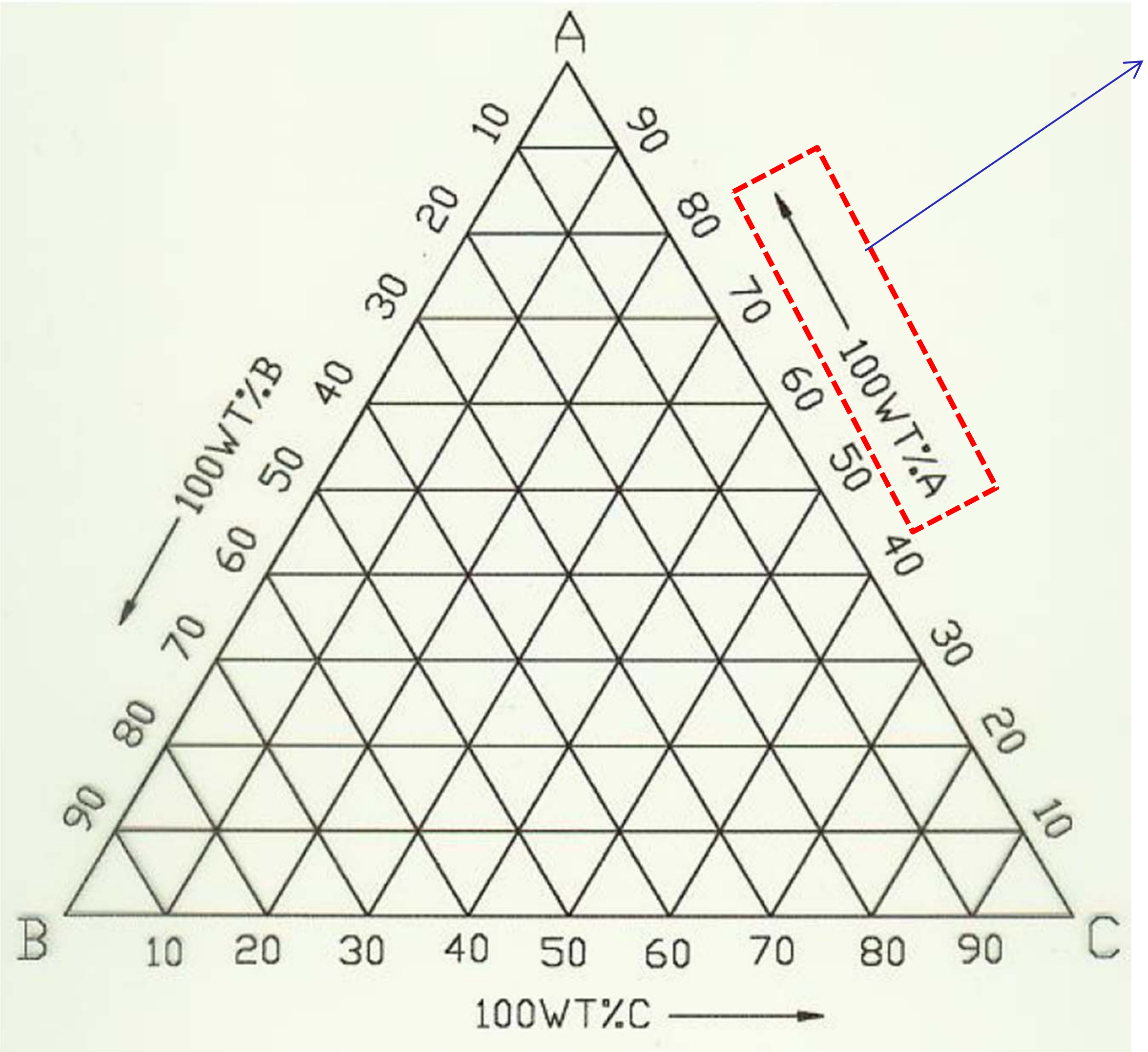
For $C = 3$, the maximum number of phases will co-exist when $F = 0$

$P = 4$ 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.

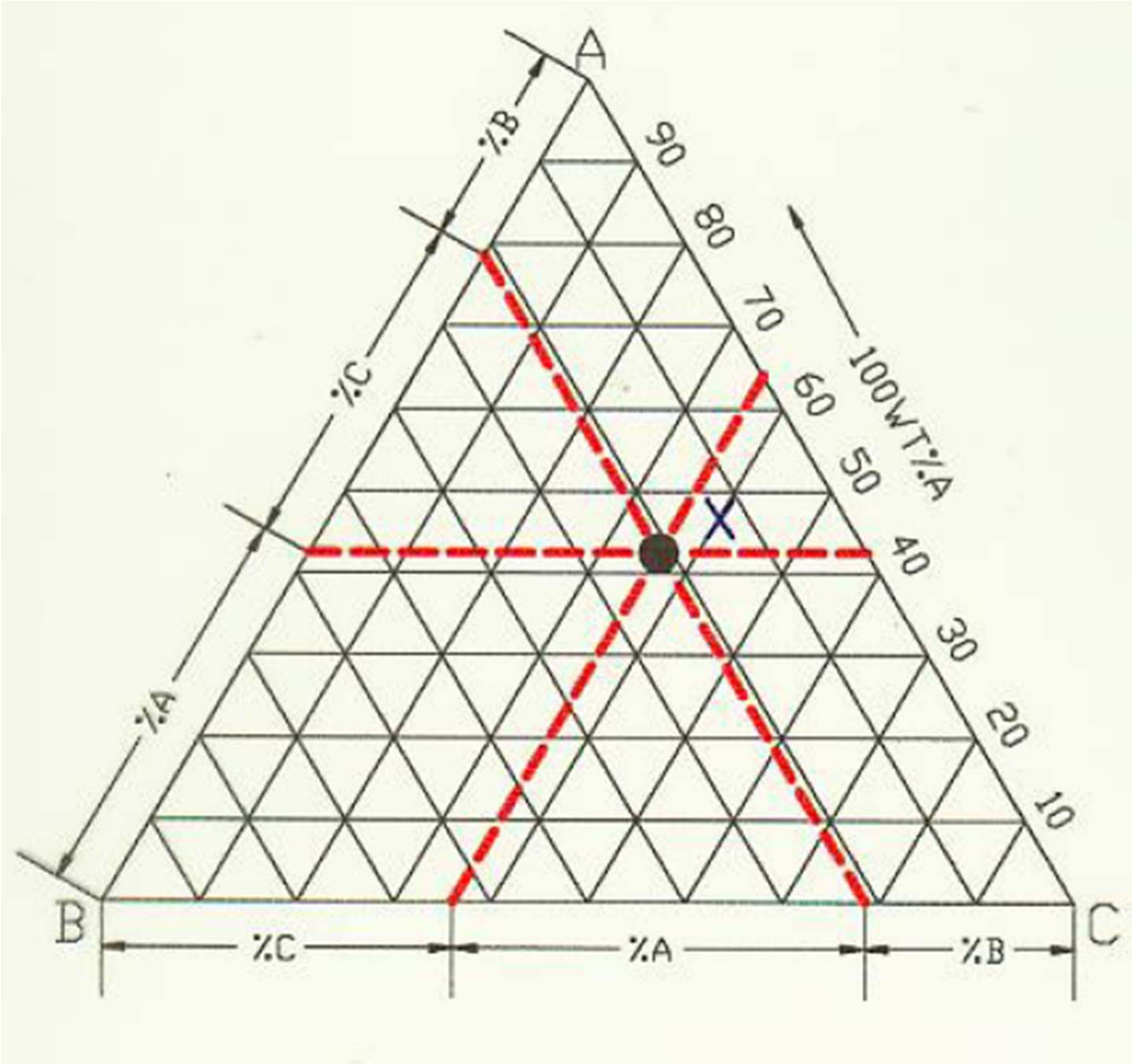


Concentration can be expressed as either "wt. %" or "at.% = molar %".

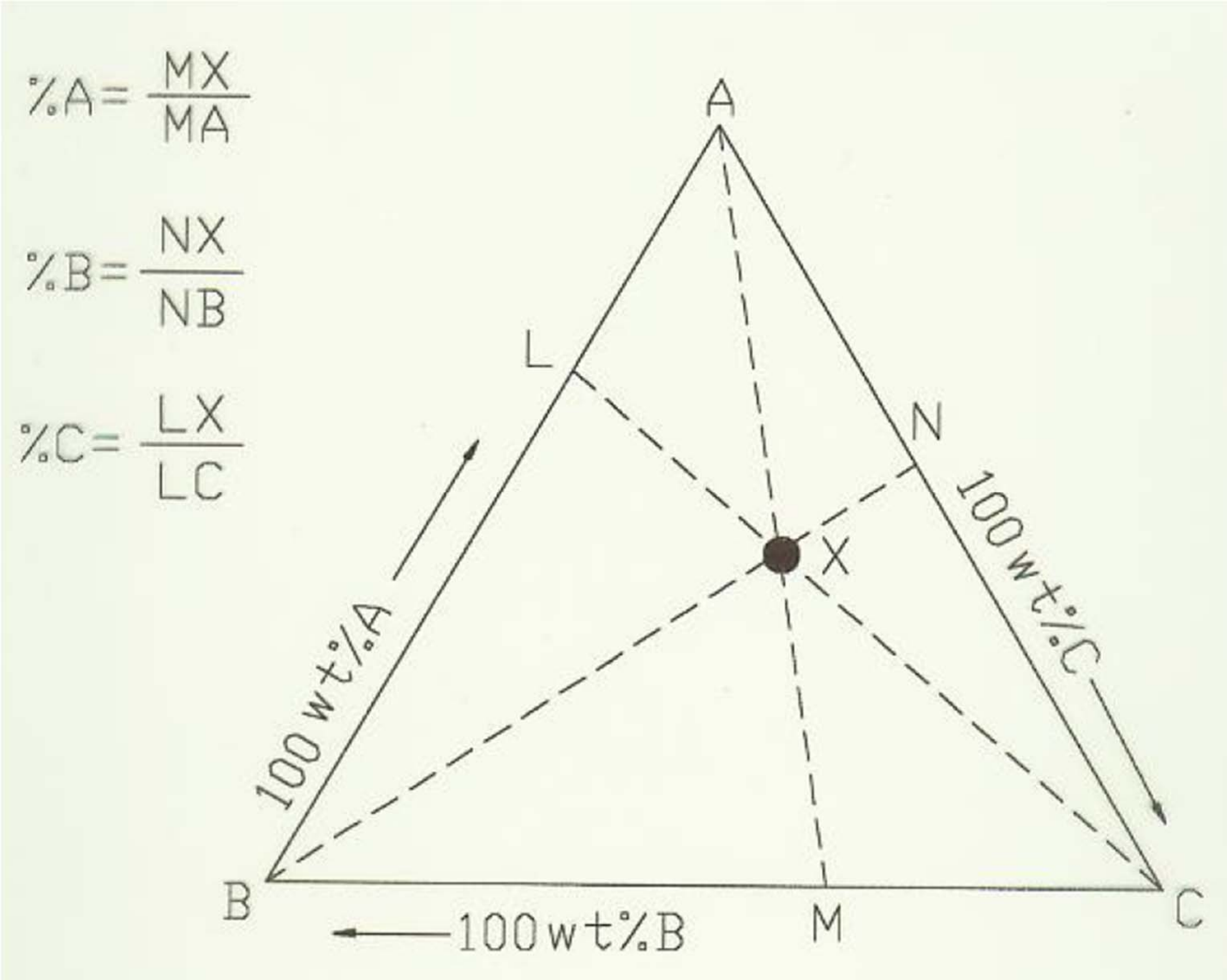
$$X_A+X_B+X_C = 1$$

Used to determine the overall composition

Overall Composition



Overall Composition



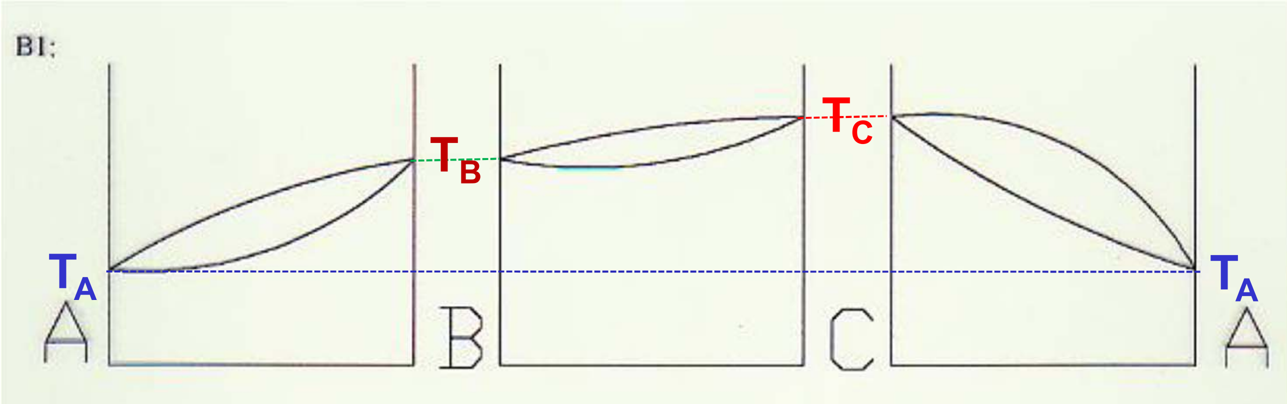
Ternary Isomorphous System

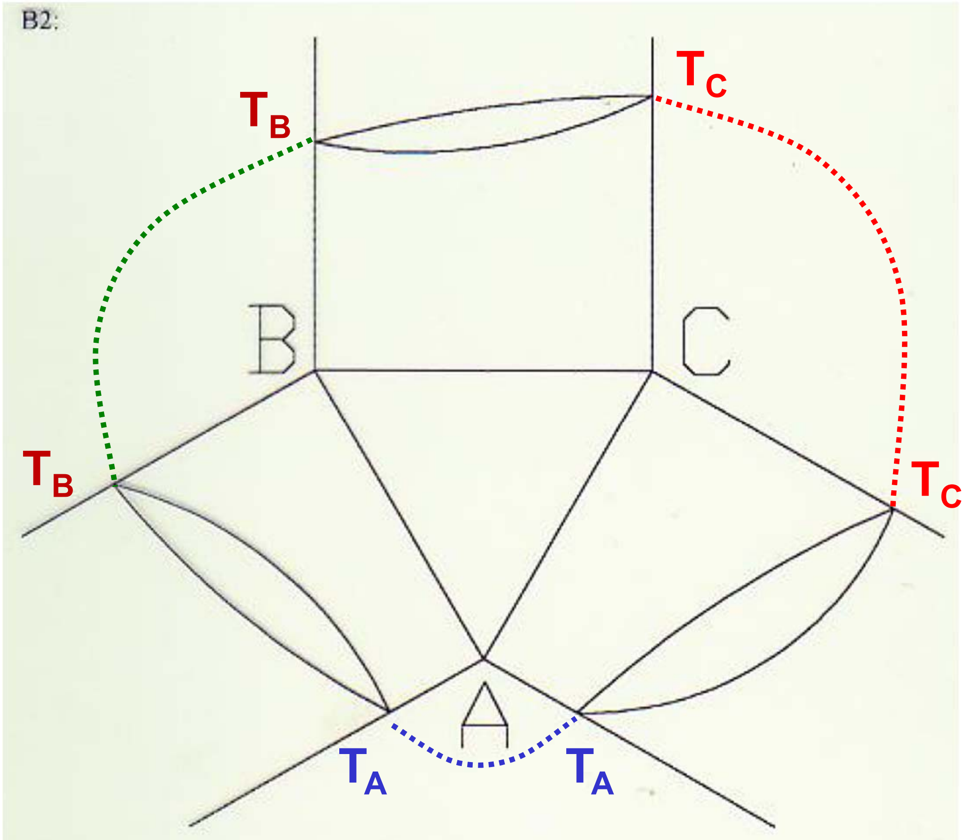
Isomorphous System: A system (ternary in this case) that has only one solid phase. All components are totally soluble in the other components. The ternary system is therefore made up of three binaries that exhibit total solid solubility.

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

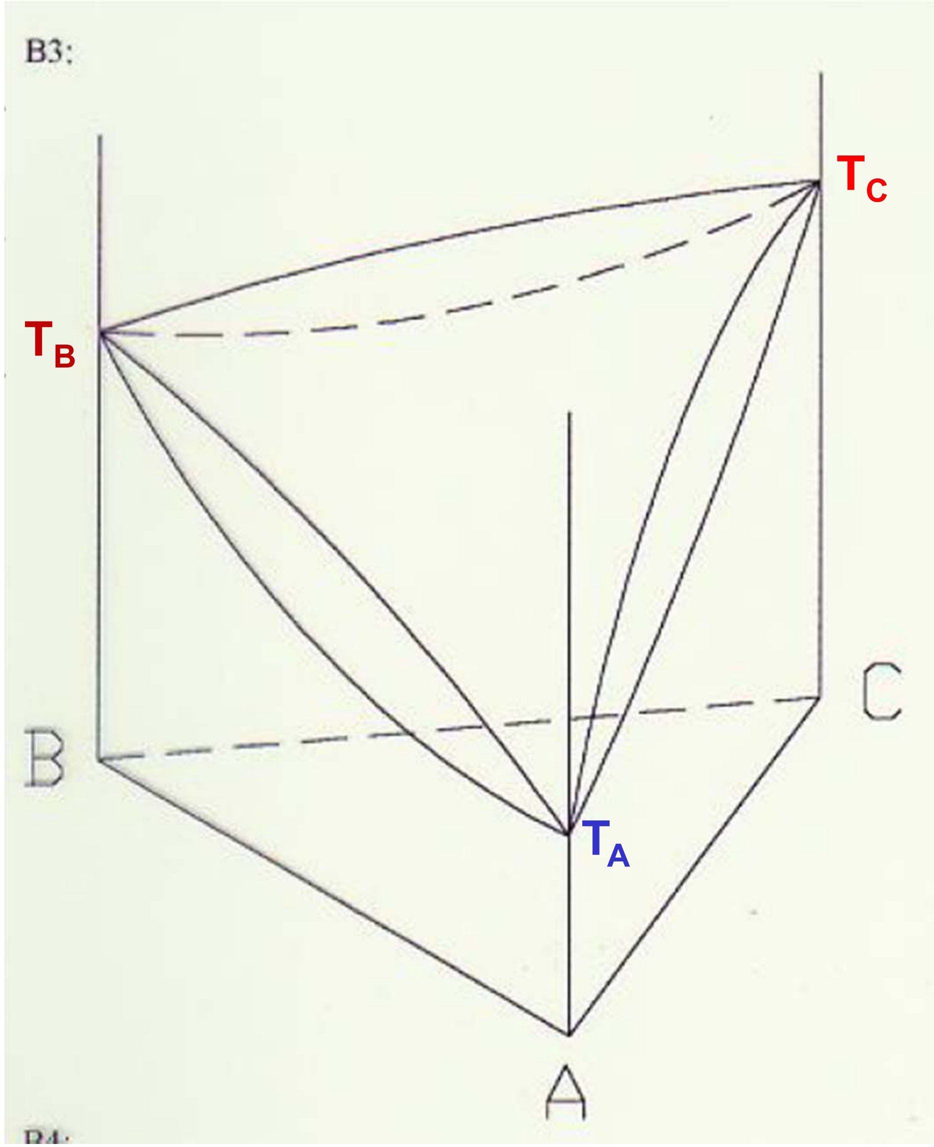
The Solidus Surface: A plot of the temperatures below which a (homogeneous) solid phase forms for any given overall composition.

Ternary Isomorphous System

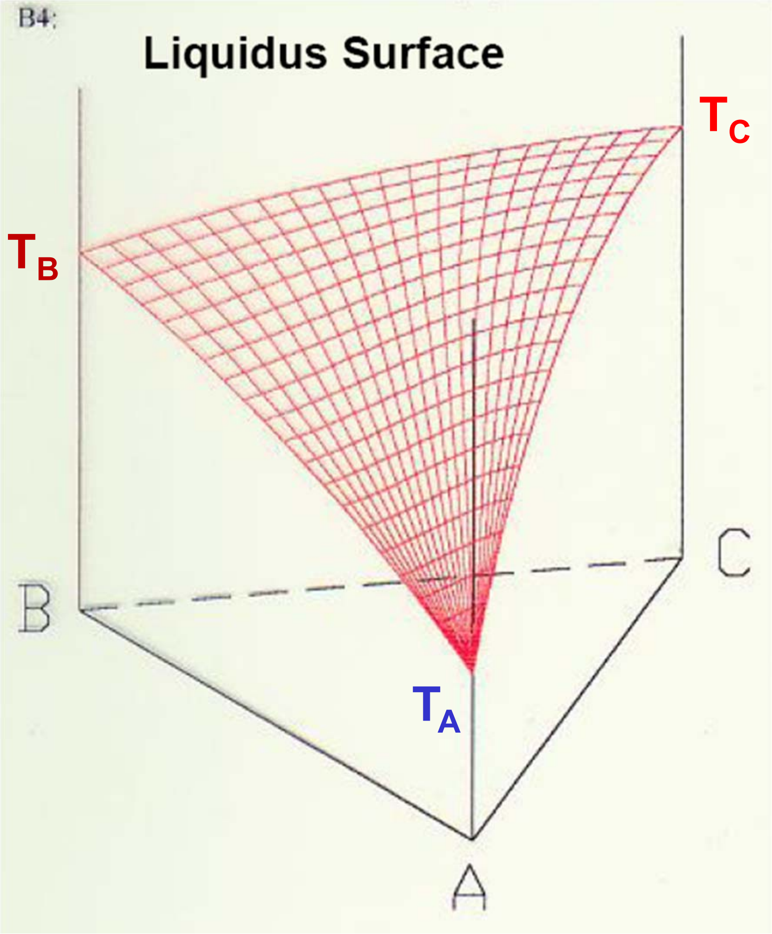


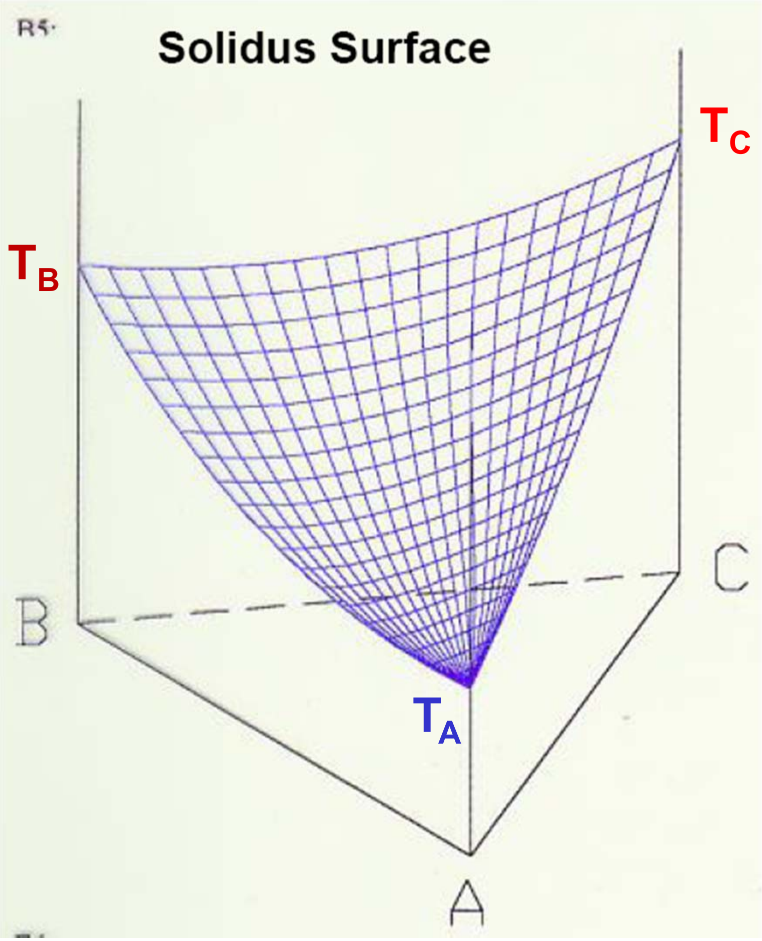


Ternary Isomorphous System

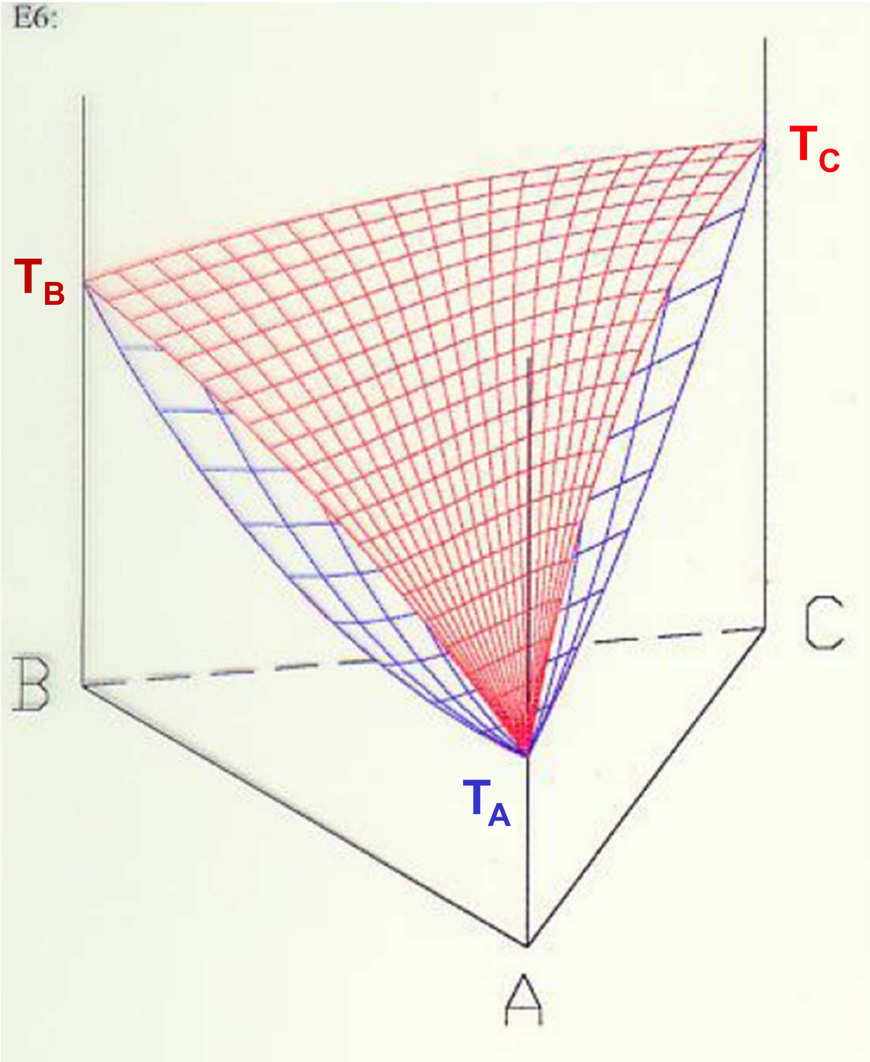


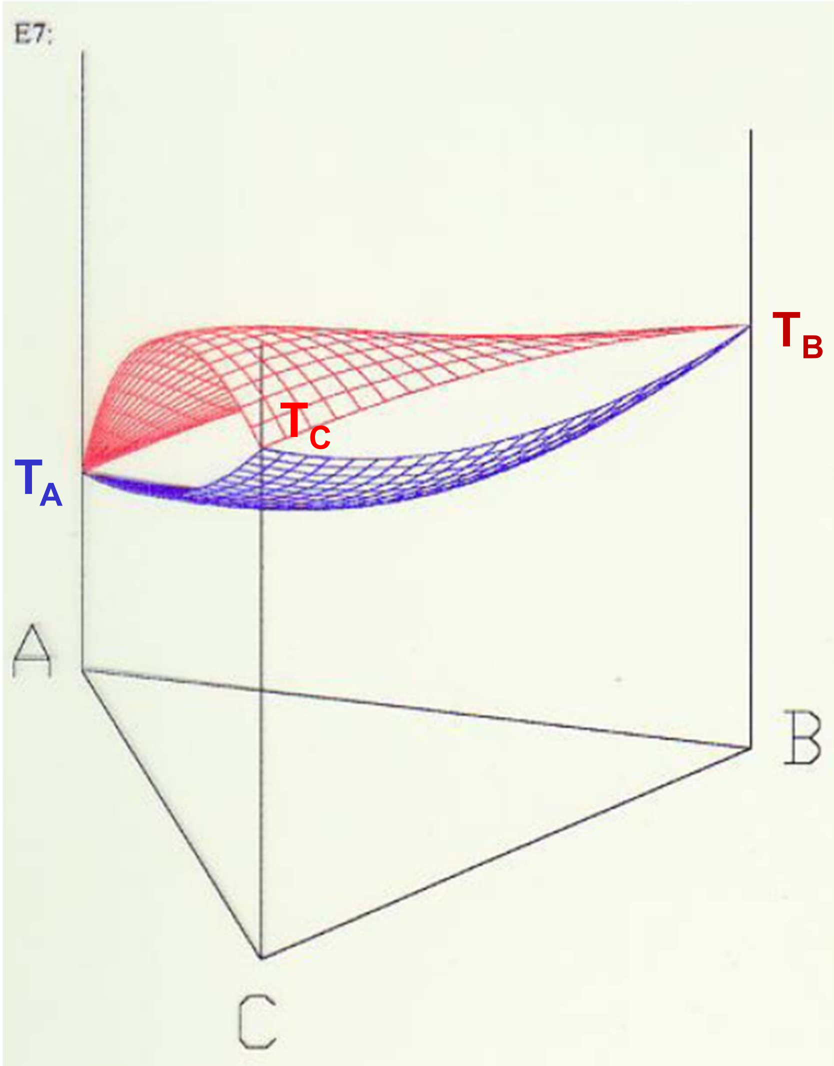
Ternary Isomorphous System





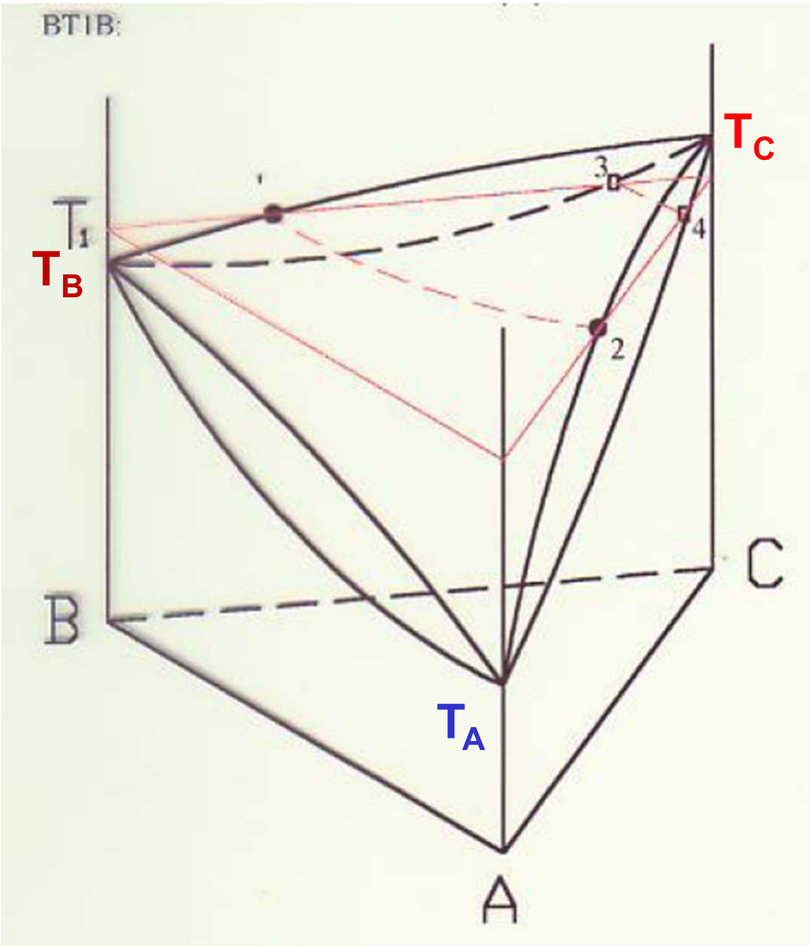
Ternary Isomorphous System

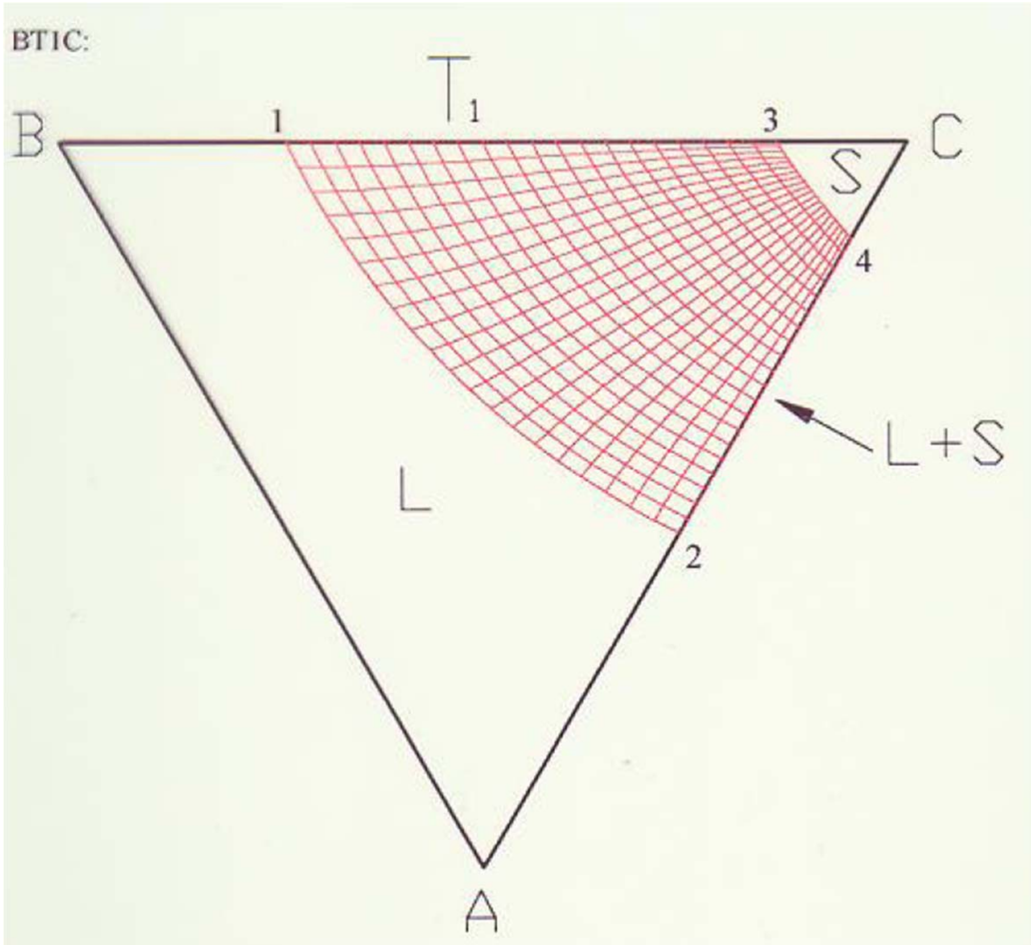




Ternary Isomorphous System

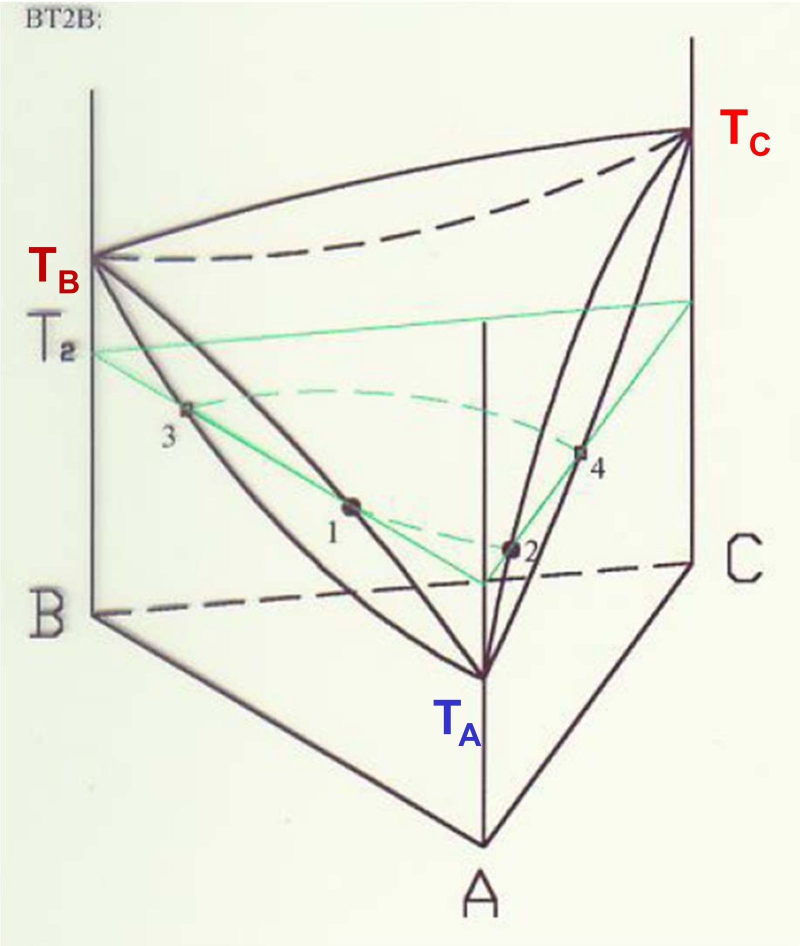
Isothermal section → F = C - P

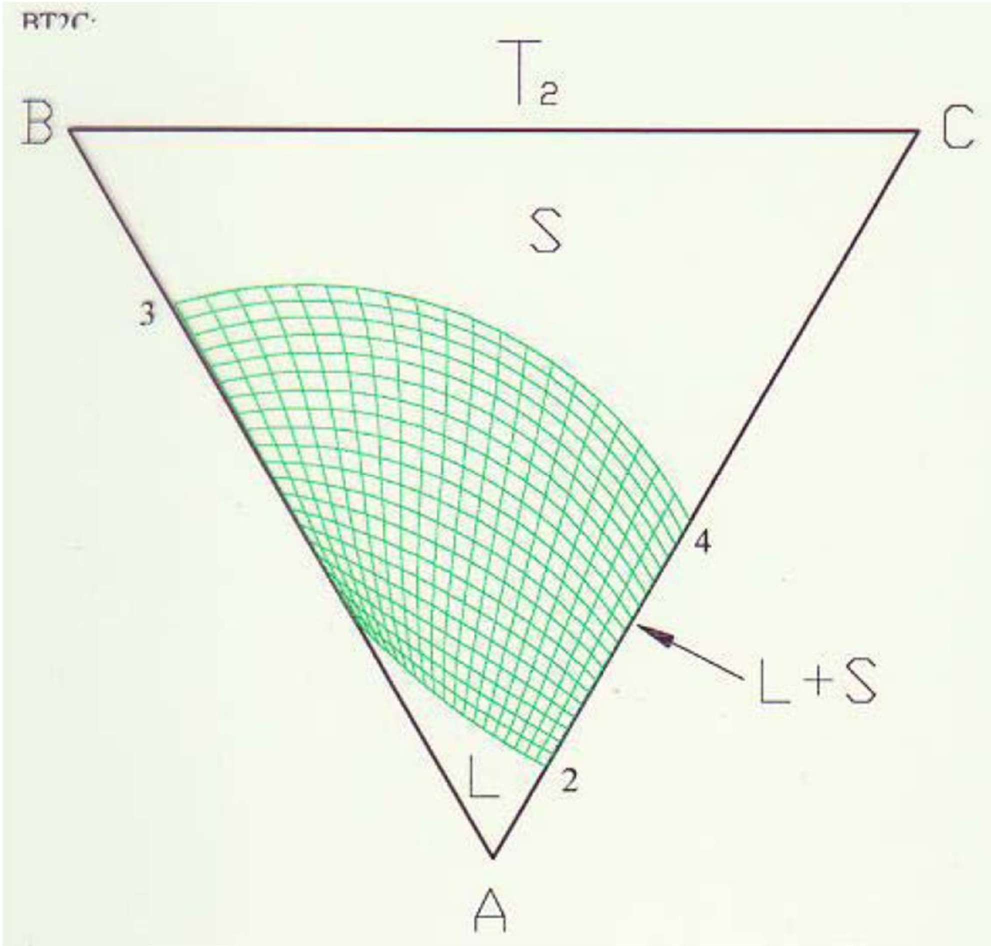




Ternary Isomorphous System

Isothermal section





Ternary Isomorphous System

Isothermal section → $F = C - P$

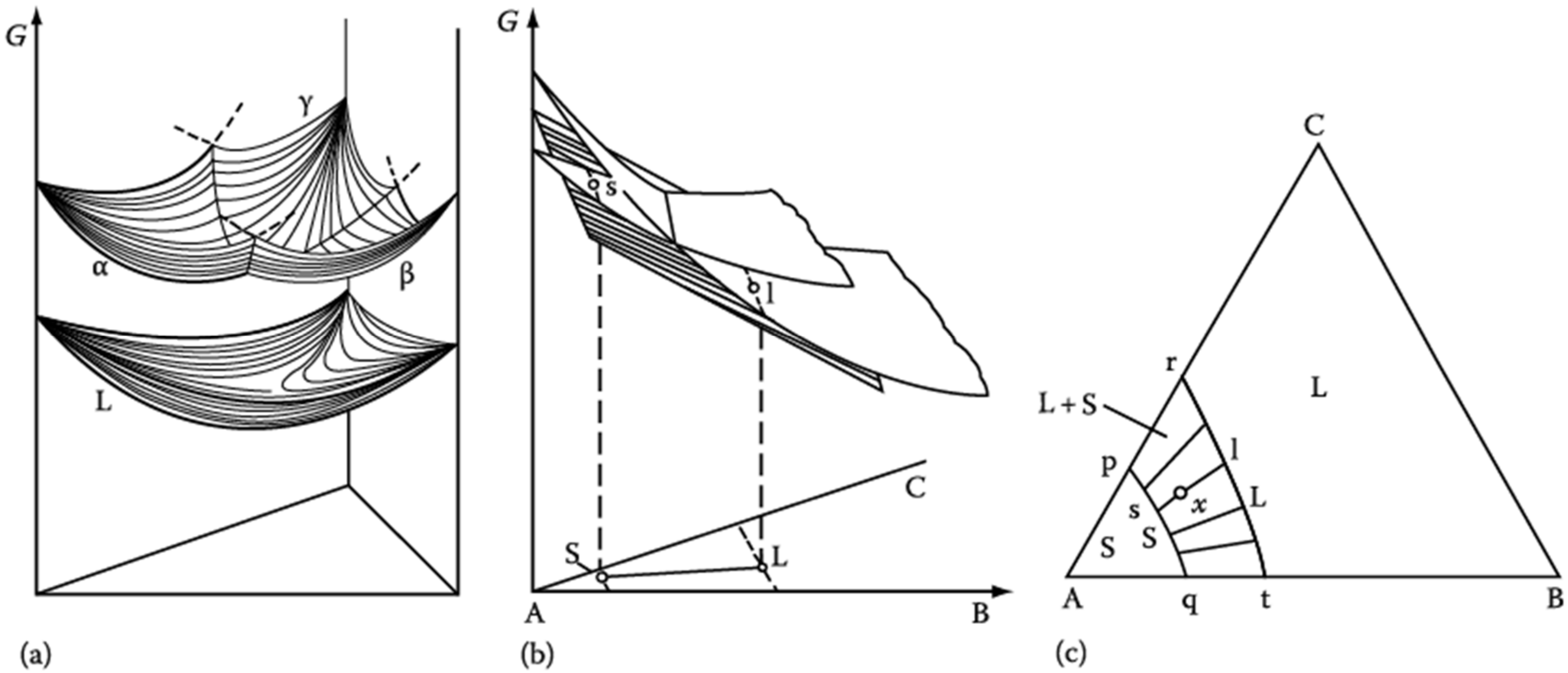


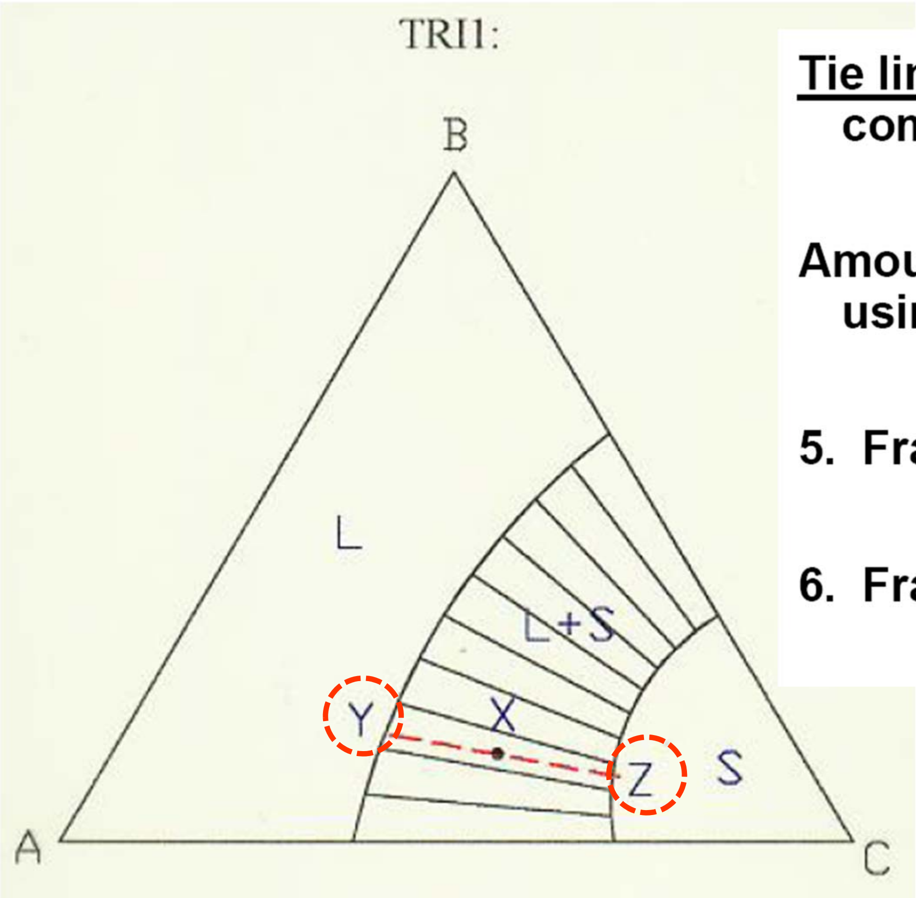
Fig. 1.41 (a) Free energy surface of a liquid and three solid phases of a ternary system.

(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:

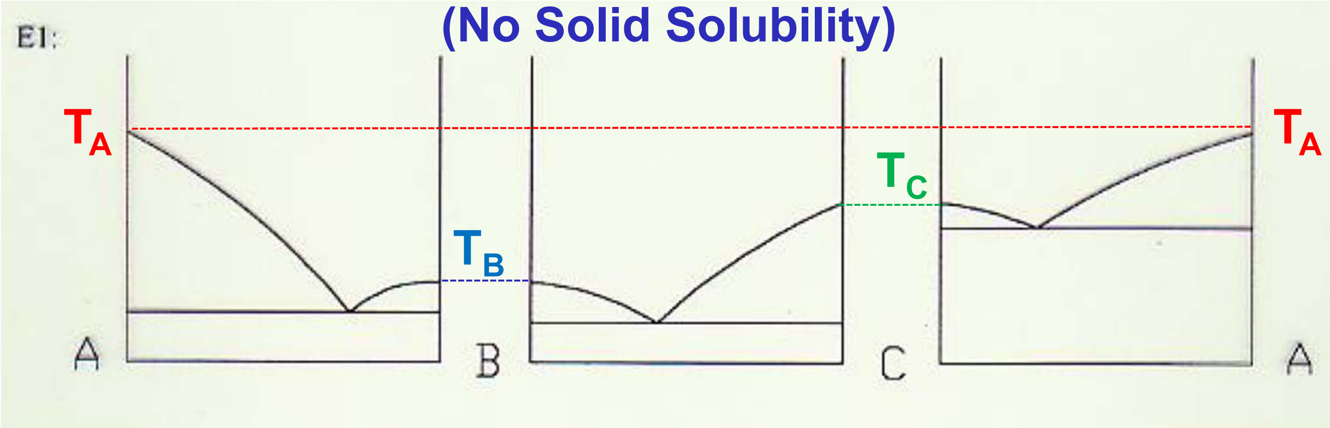
$$L = \alpha + \beta + \gamma$$

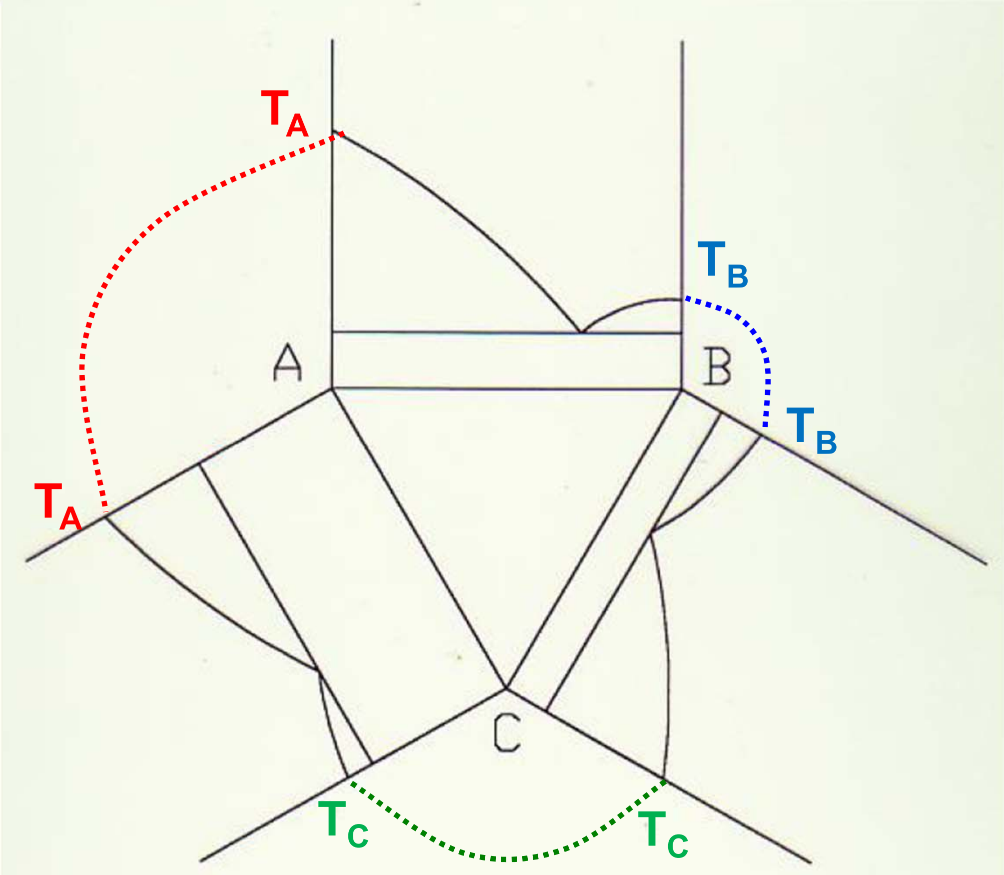
A liquid phase solidifies into three separate solid phases

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

Ternary Eutectic System

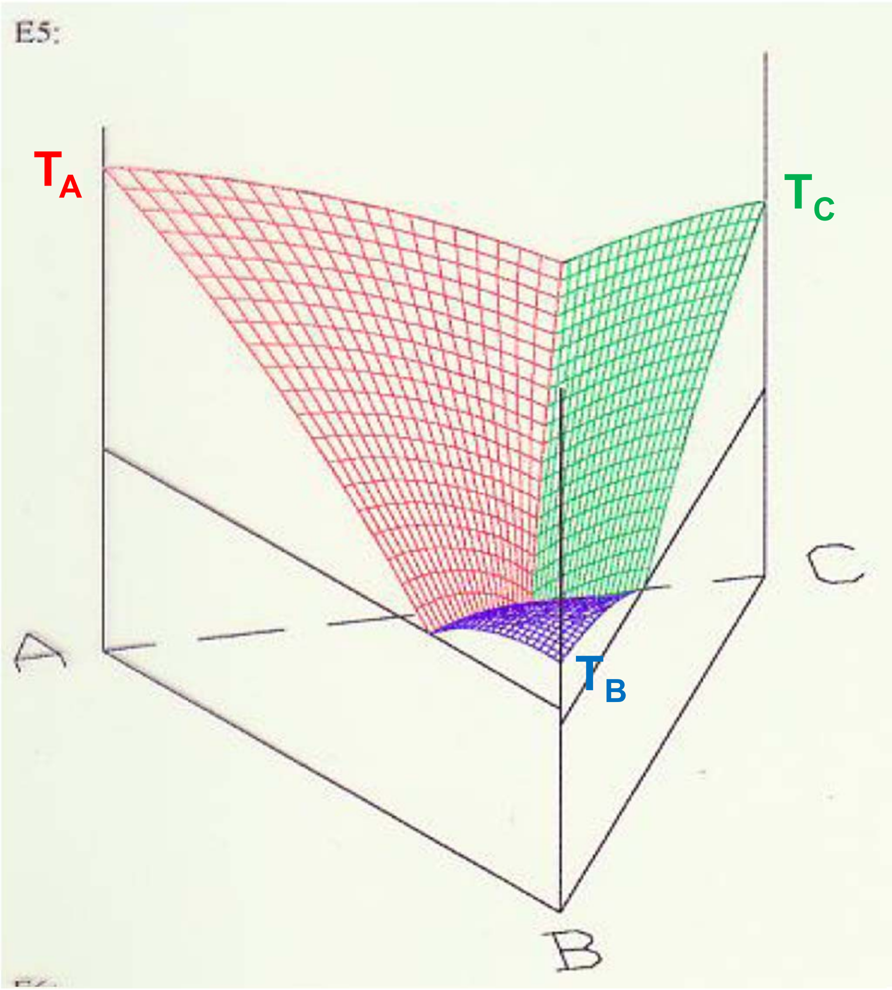
(No Solid Solubility)



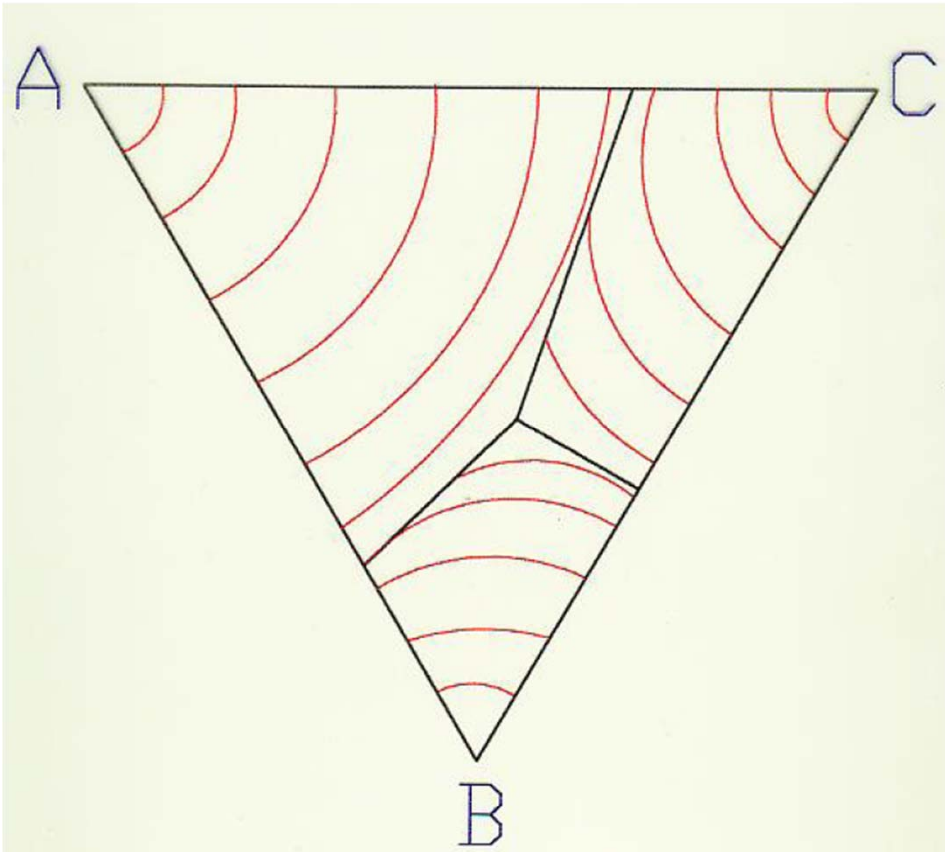


Ternary Eutectic System

(No Solid Solubility)

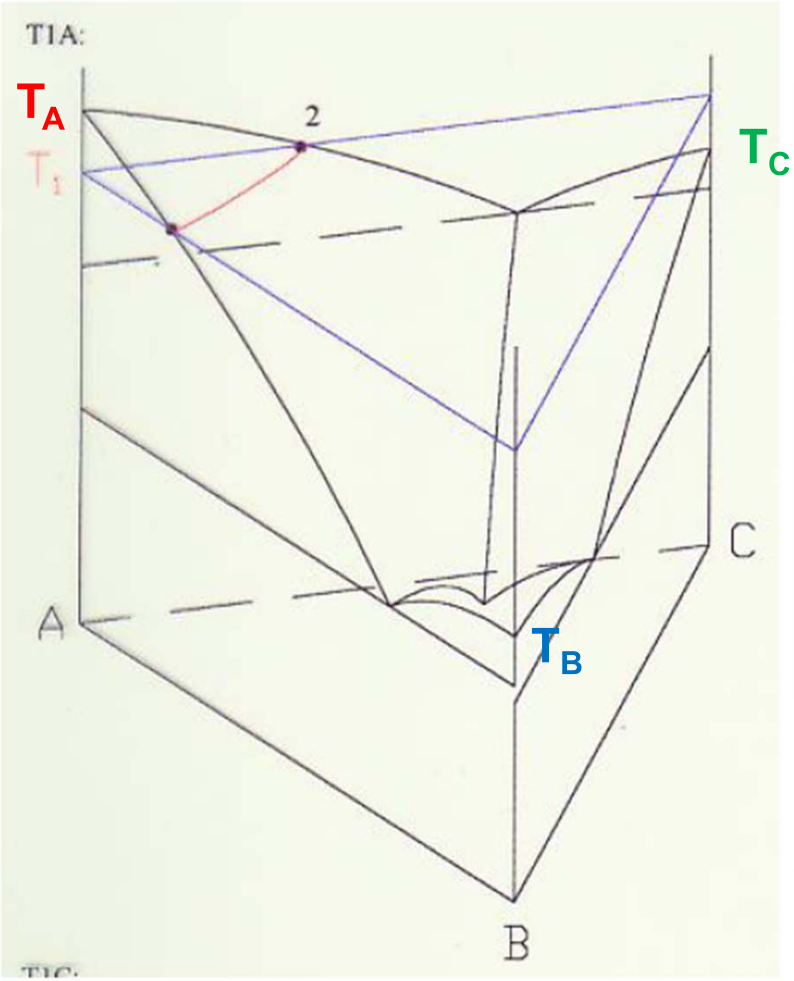


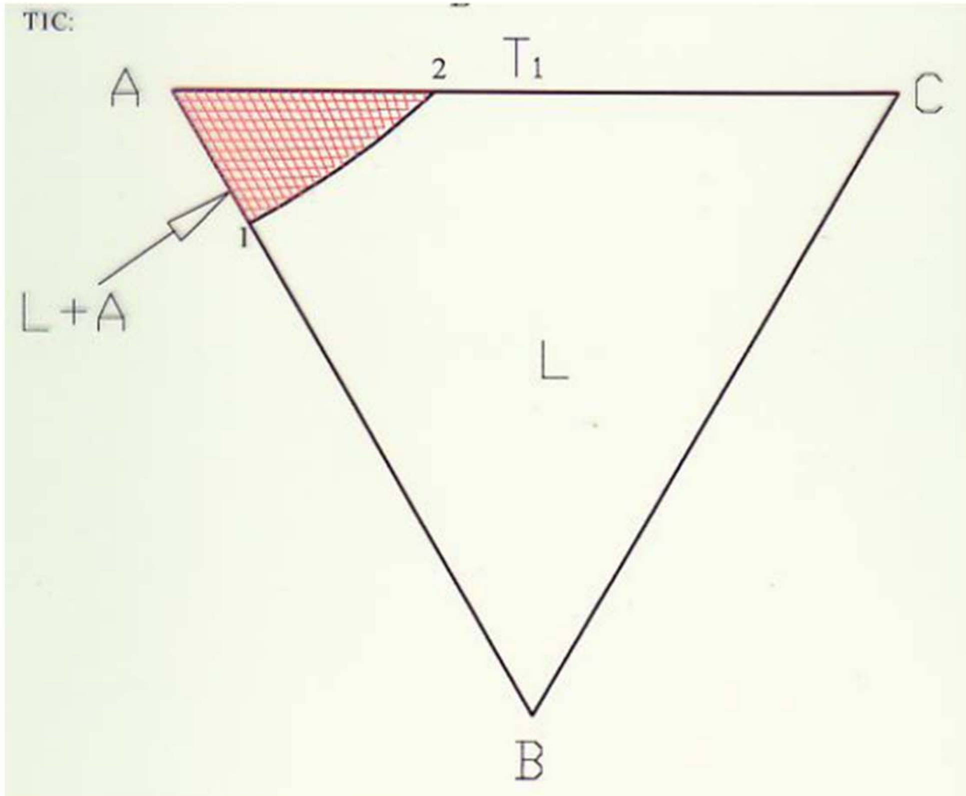
Liquidus projection



Ternary Eutectic System

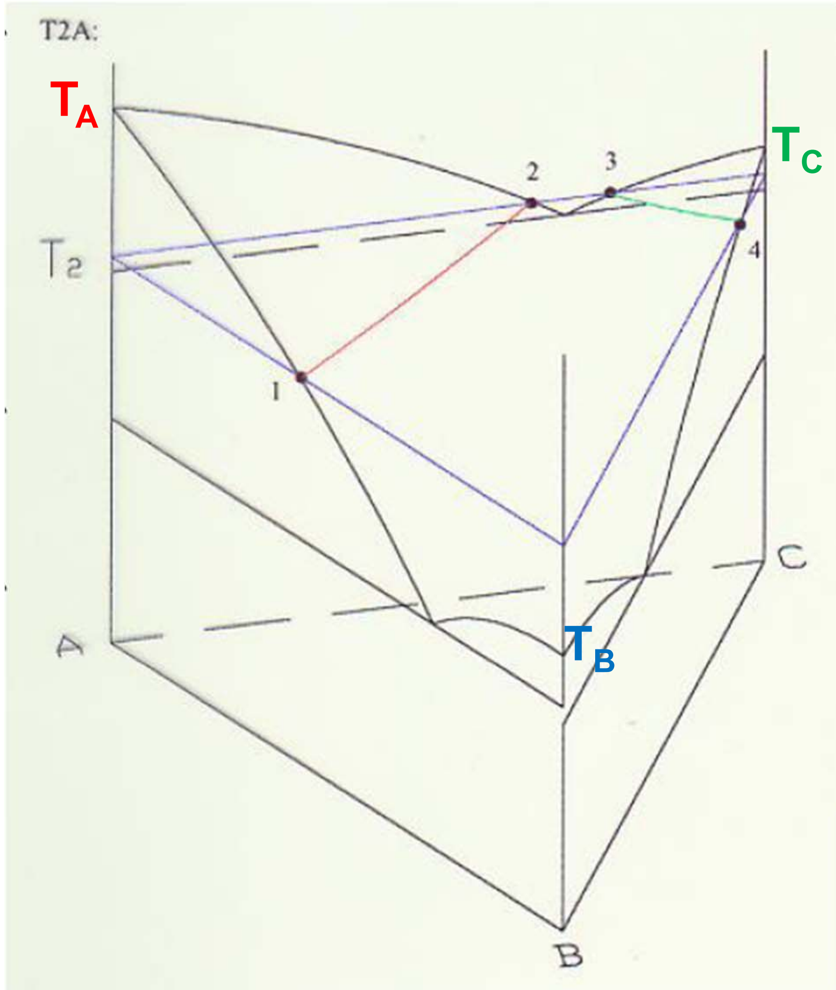
(No Solid Solubility)

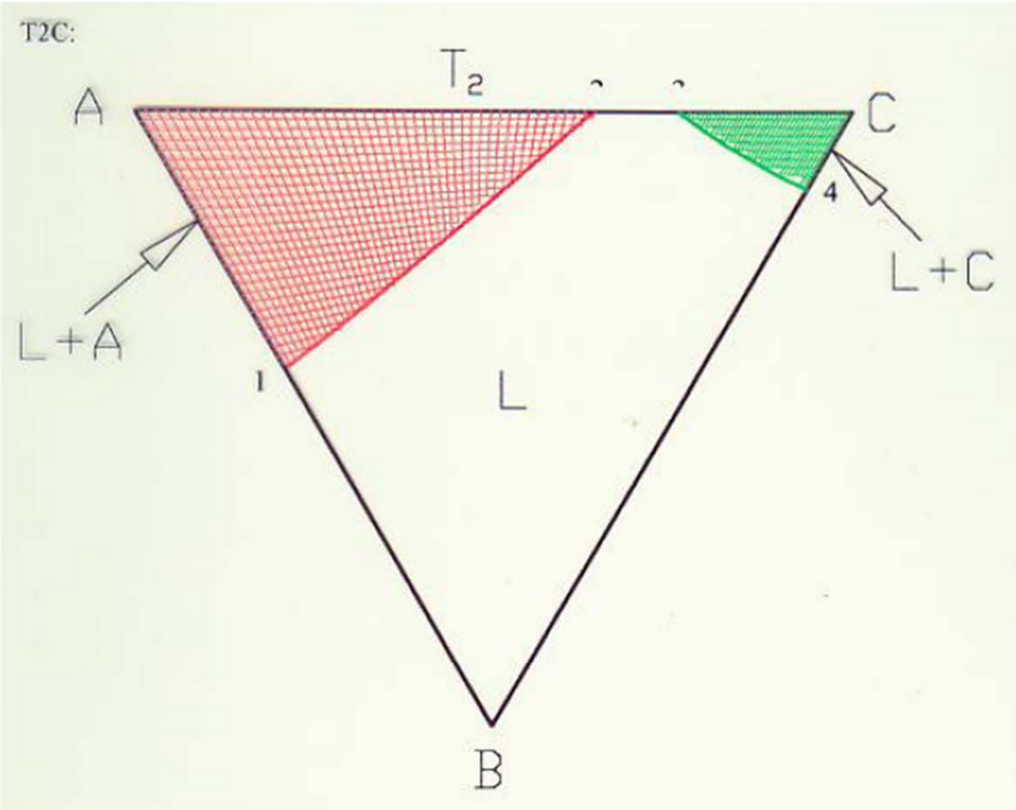




Ternary Eutectic System

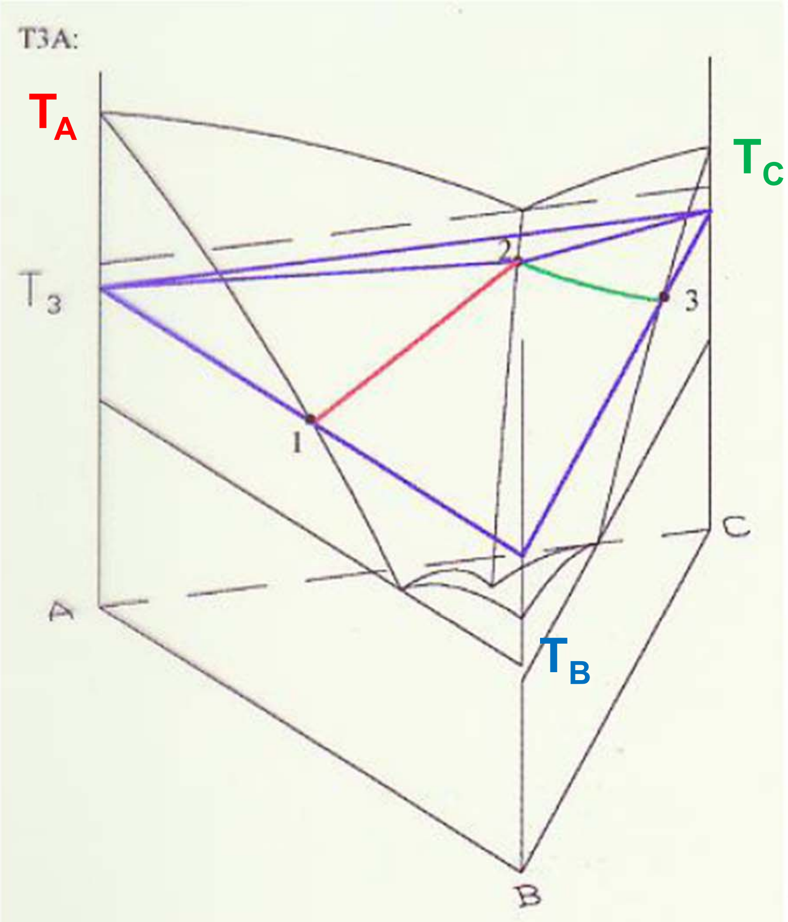
(No Solid Solubility)

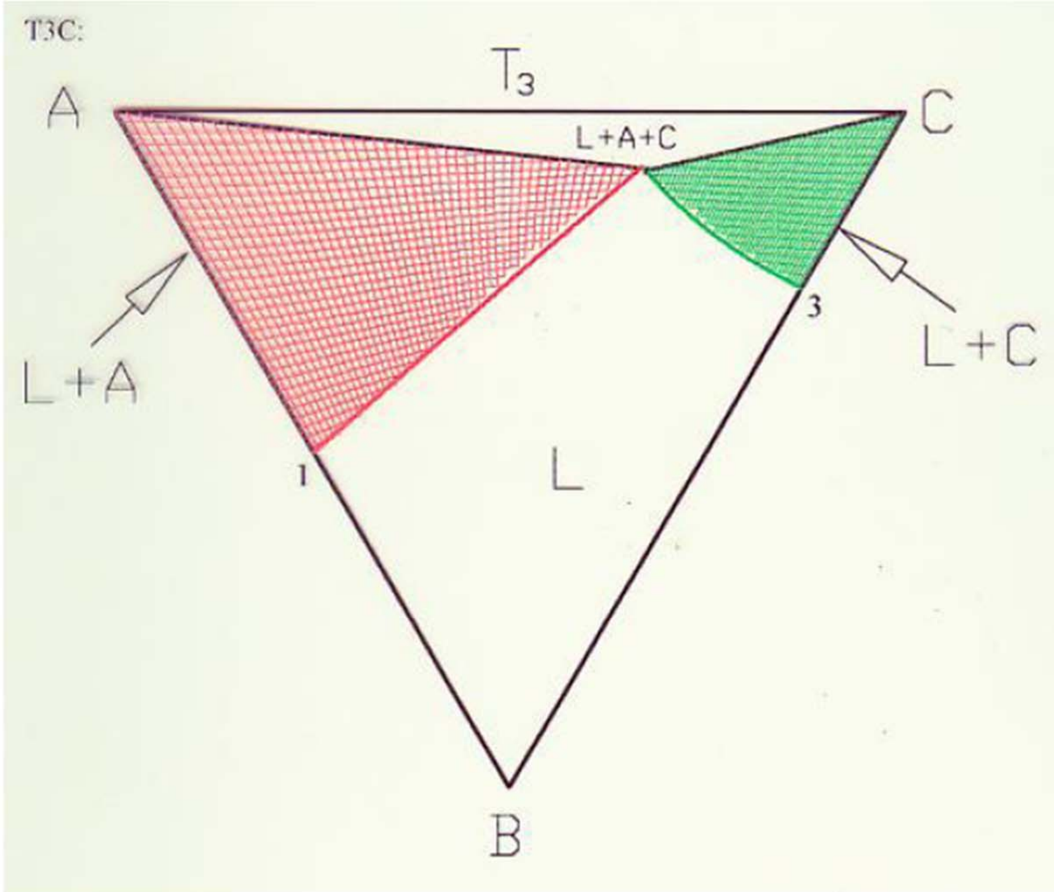




Ternary Eutectic System

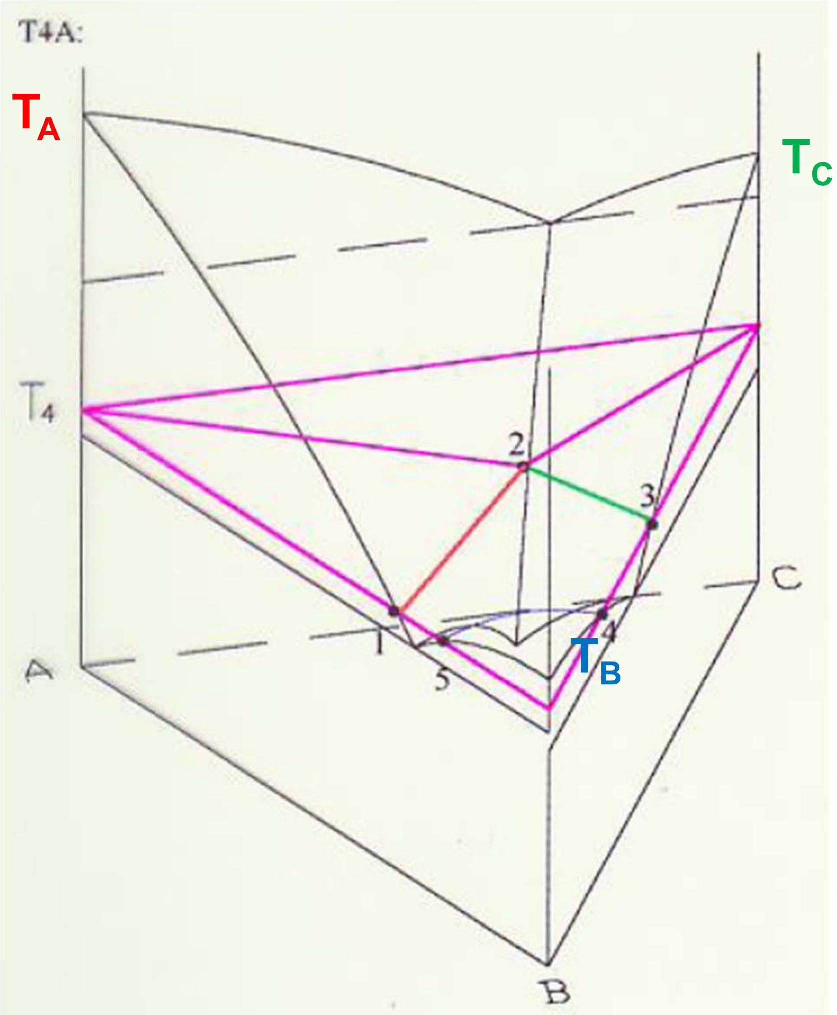
(No Solid Solubility)

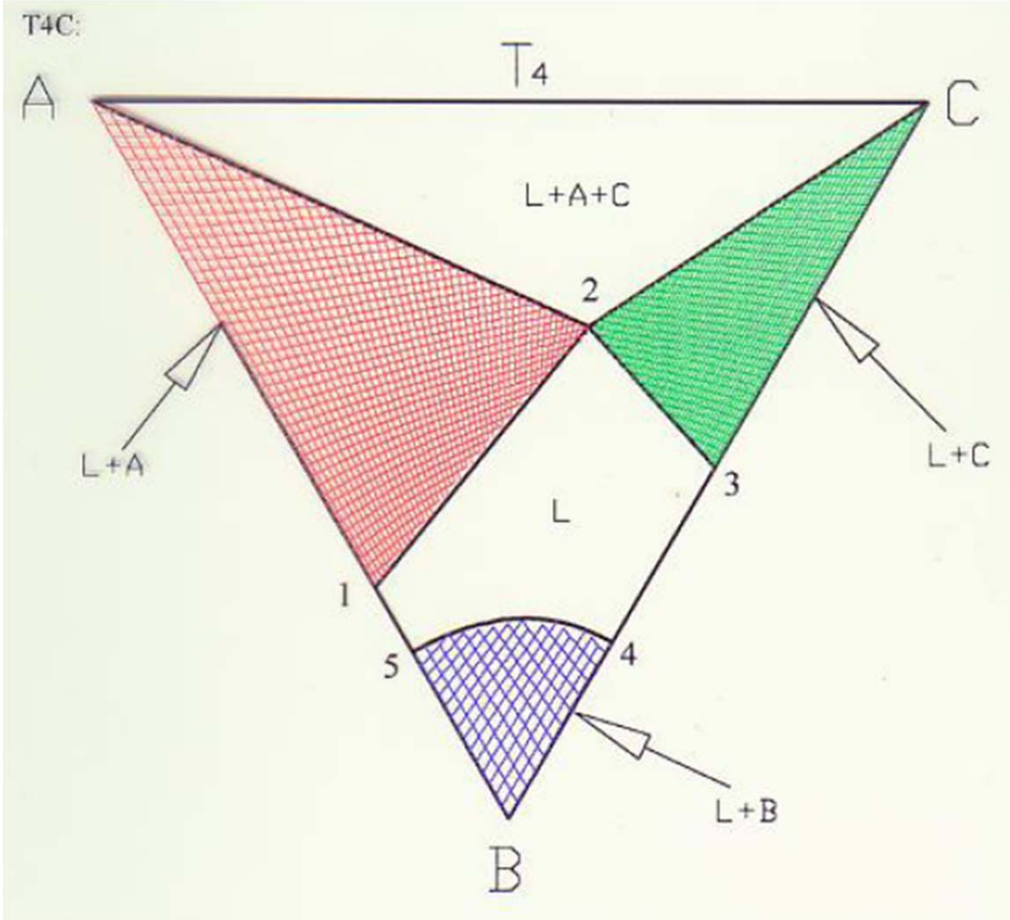




Ternary Eutectic System

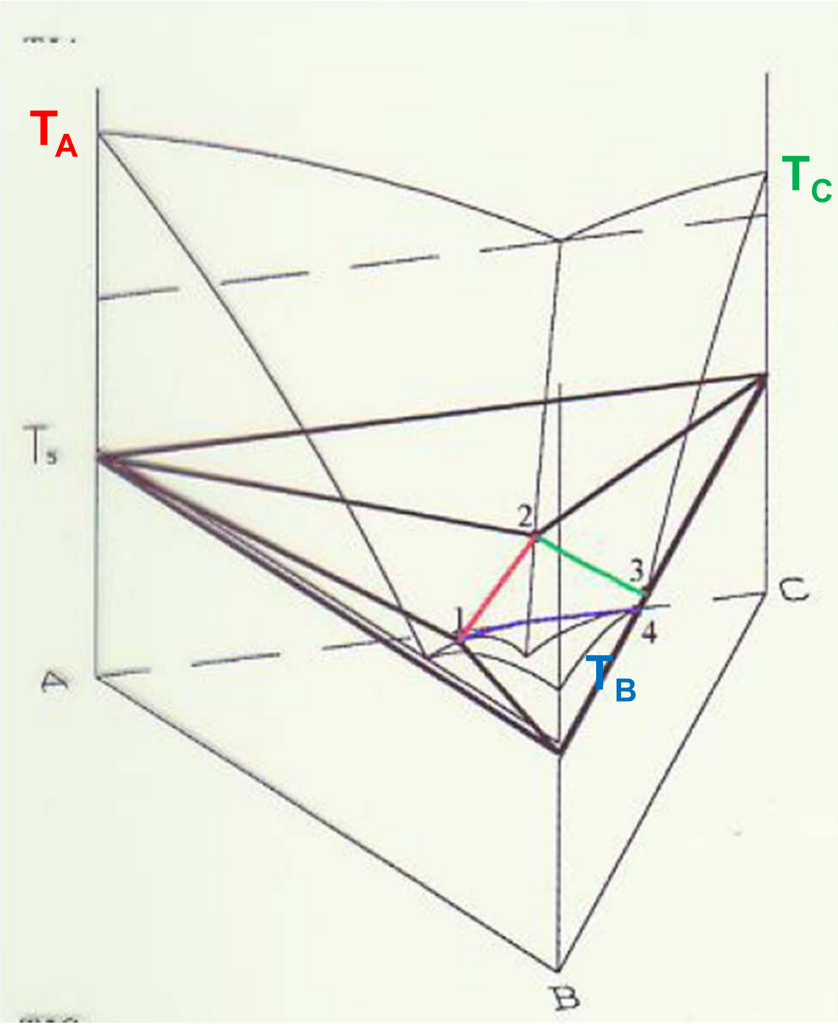
(No Solid Solubility)

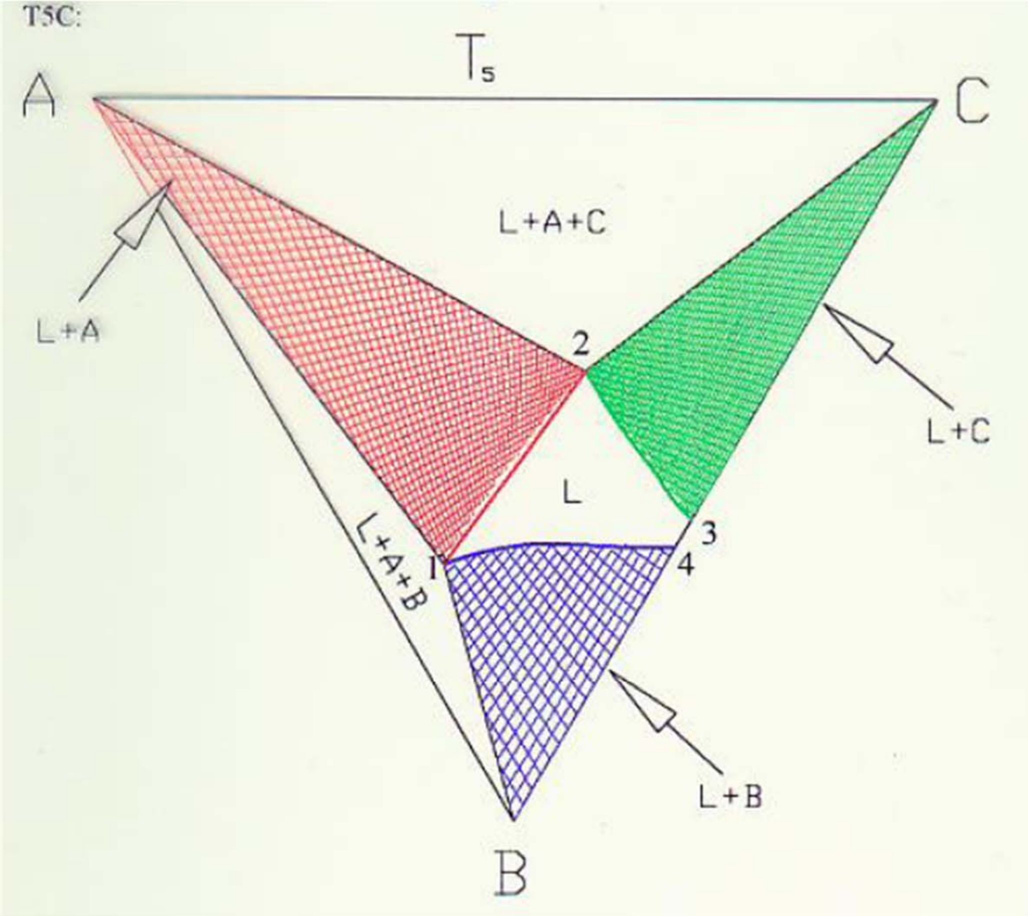




Ternary Eutectic System

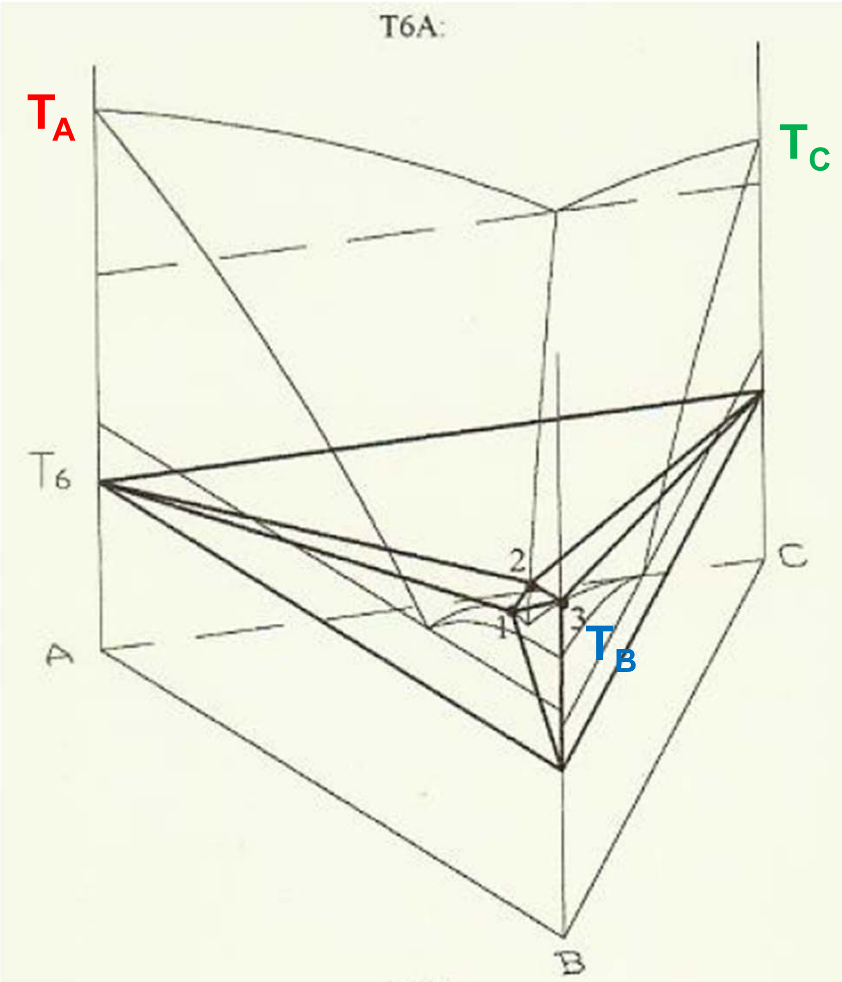
(No Solid Solubility)

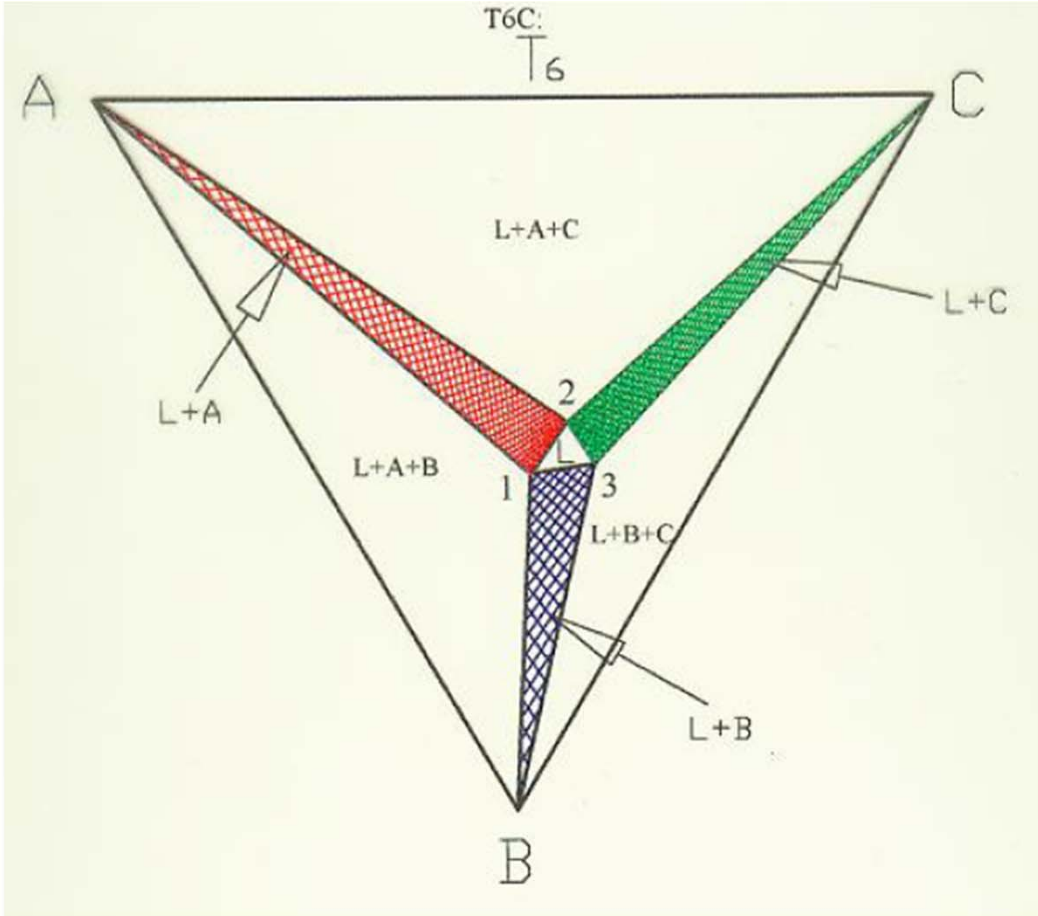




Ternary Eutectic System

(No Solid Solubility)

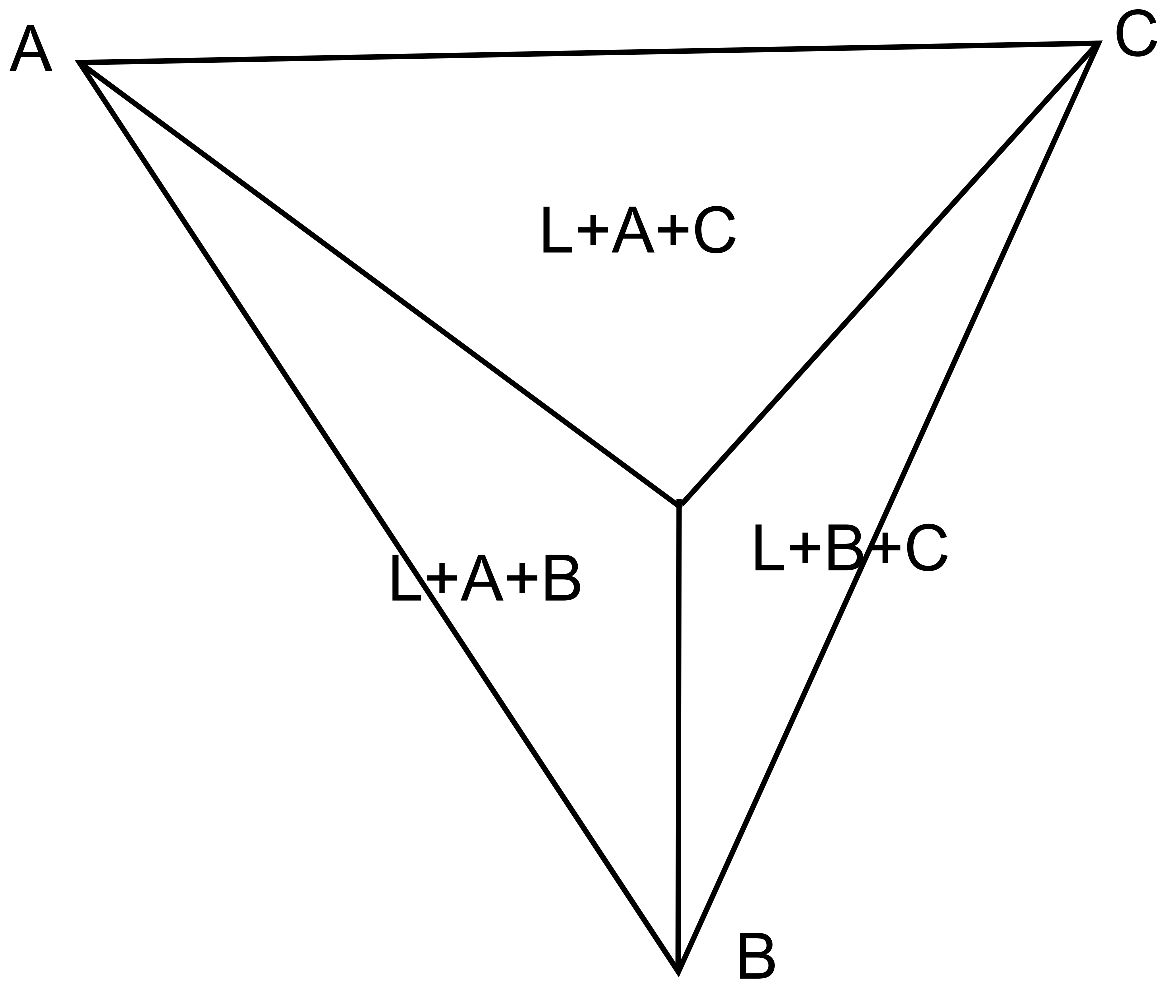




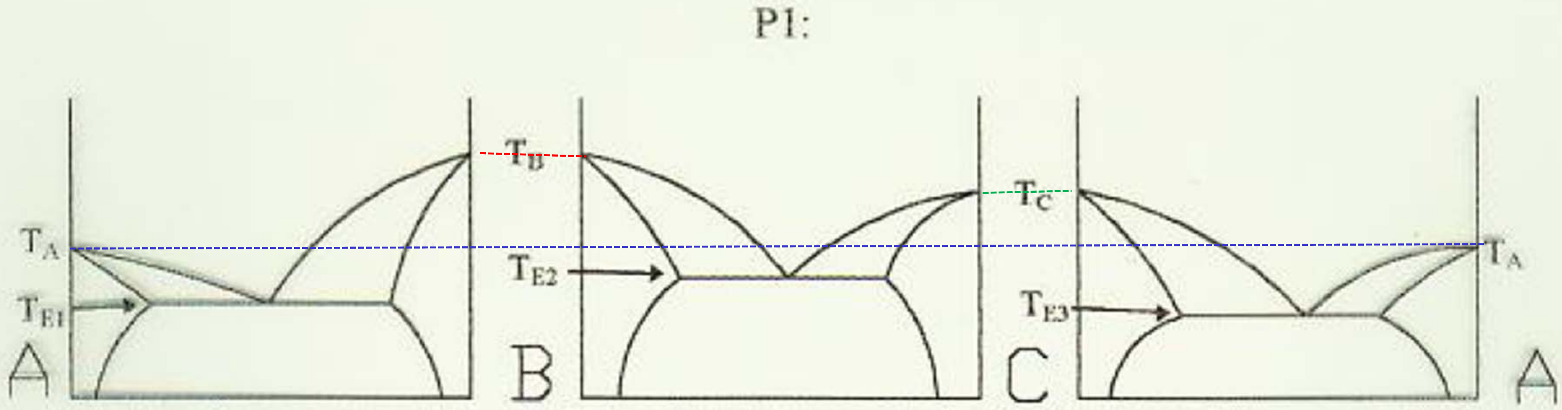
Ternary Eutectic System

(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

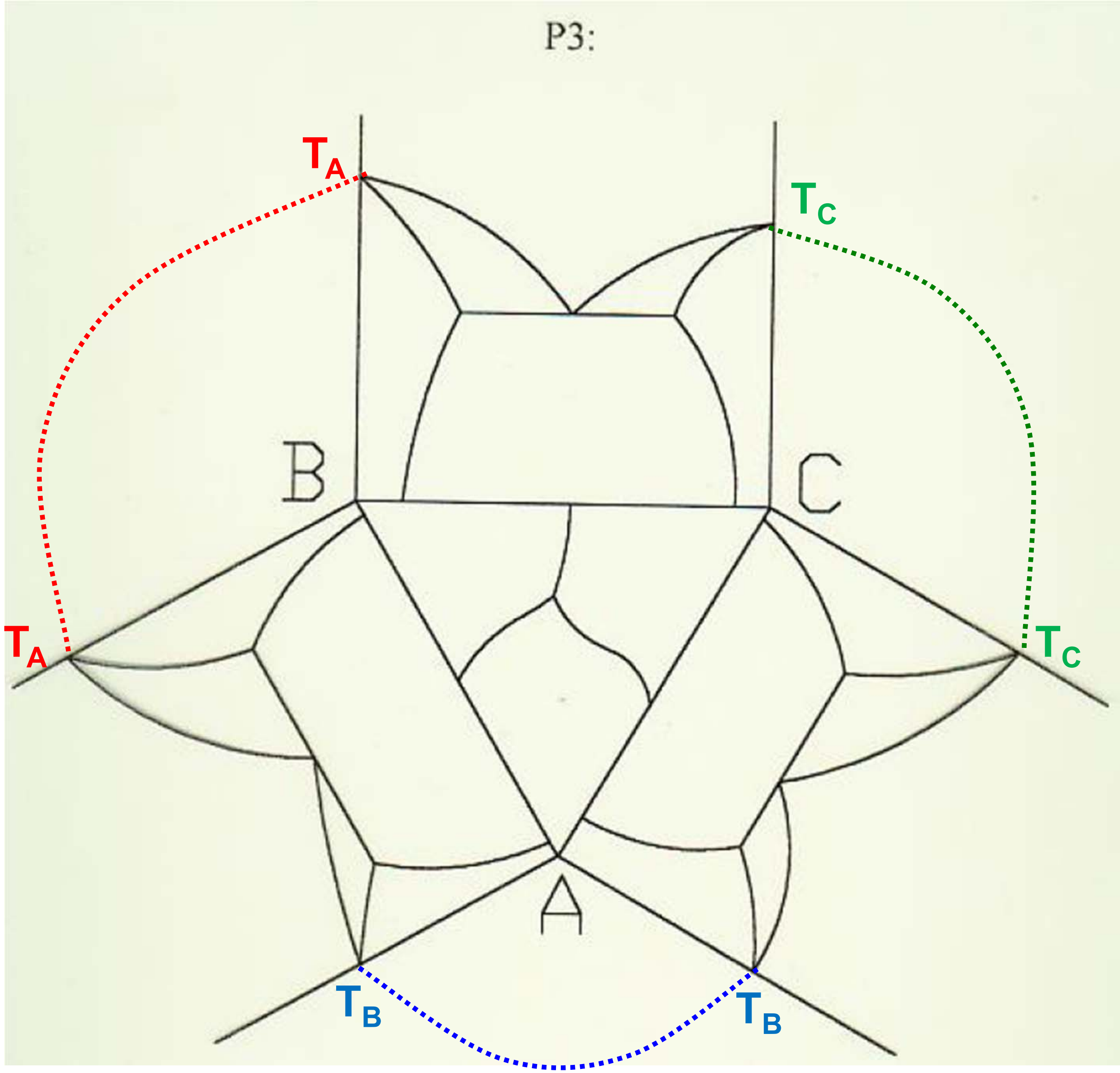
T_C: Melting Point Of Material C

T_{E1}: Eutectic Temperature Of A-B

T_{E2}: Eutectic Temperature Of B-C

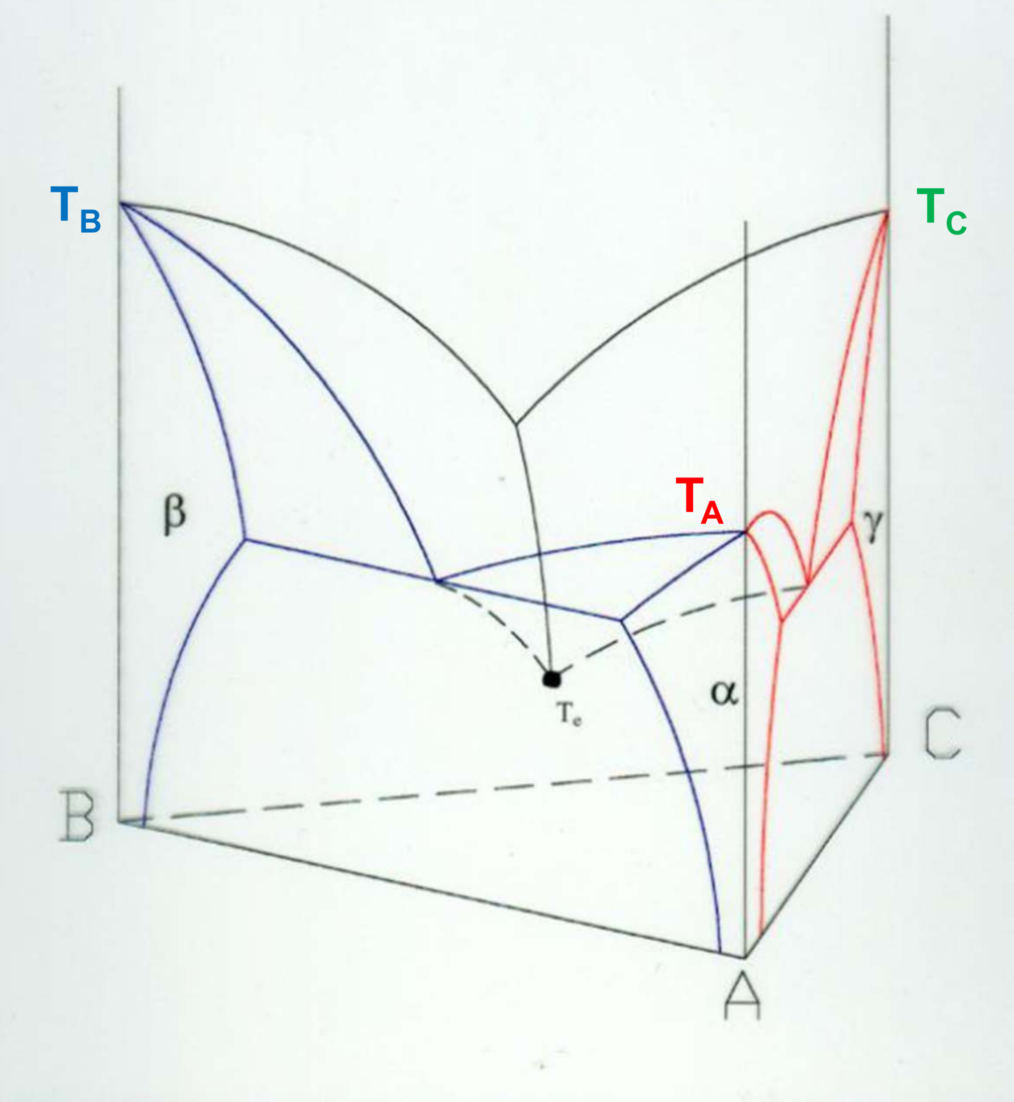
T_{E3}: Eutectic Temperature Of C-A

Ternary Eutectic System
(with Solid Solubility)

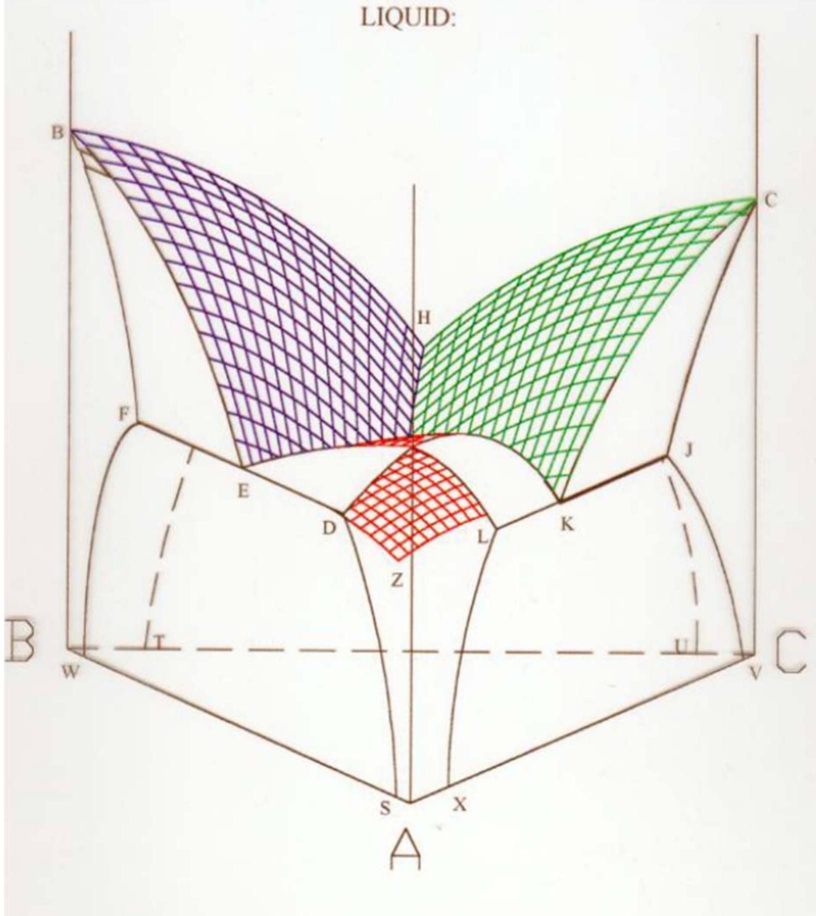


Ternary Eutectic System

(with Solid Solubility)

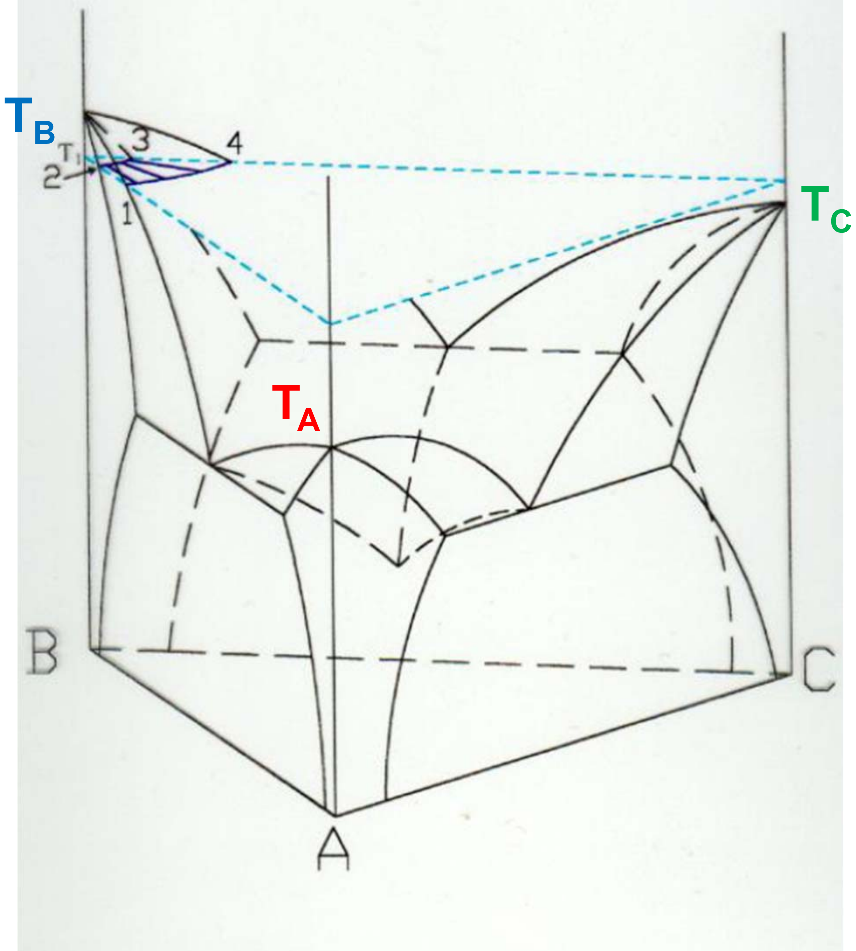


Main outline of Ternary Phase Diagram with Ternary Eutectic (T_e) and Solid Single Phase Regions Shown

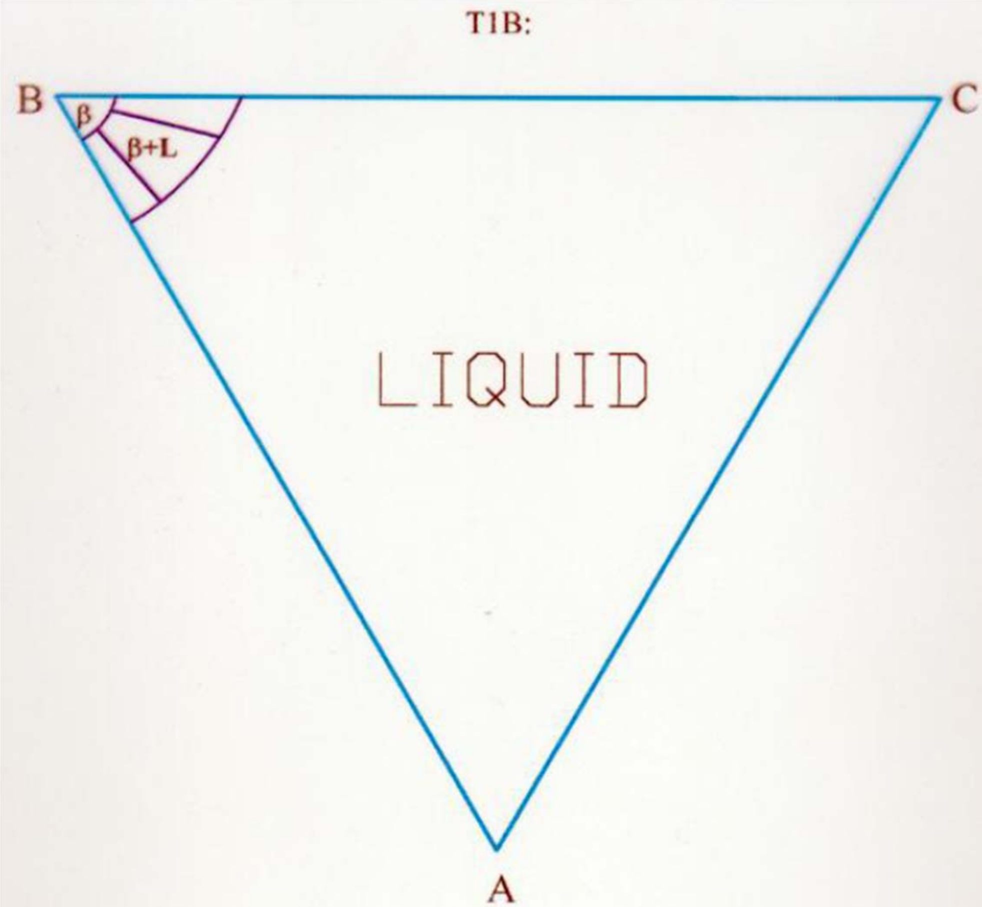


All Liquidus surfaces (α+L-Red, β+L-Purple, γ+L-Green)

Ternary Eutectic System
(with Solid Solubility)

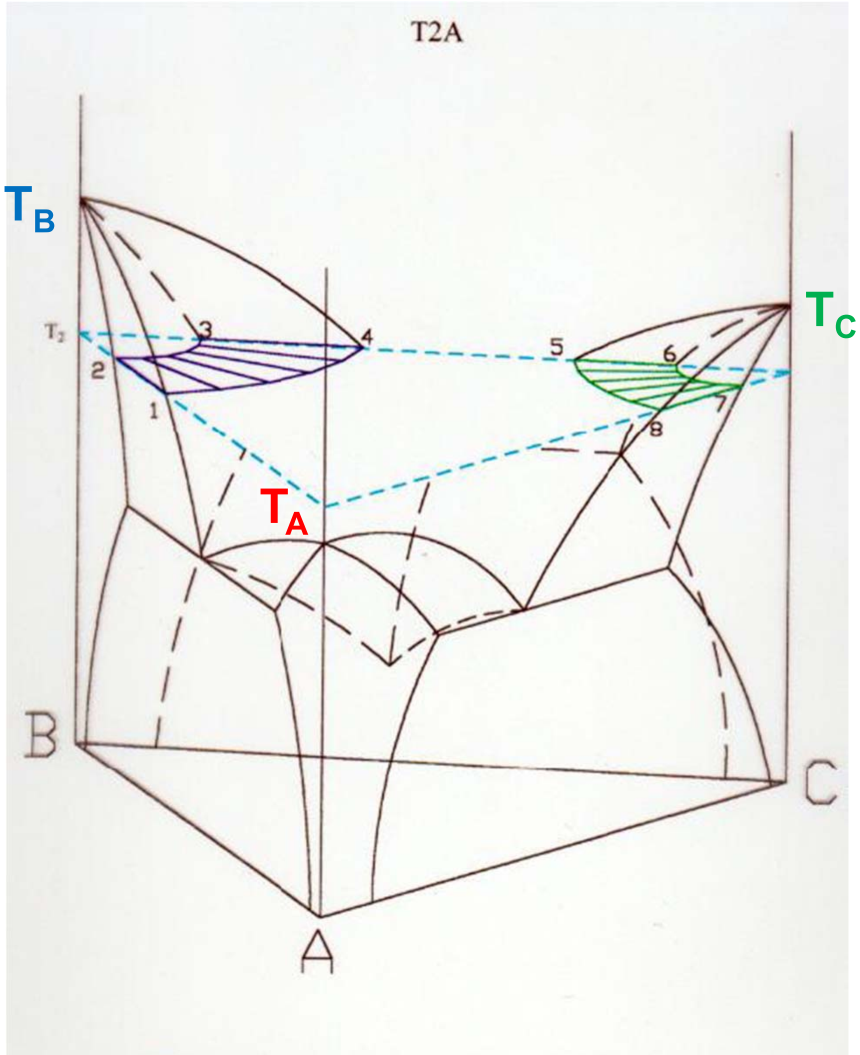


Temperature Slice At $T_1 < T_B$, But $>T_A$, T_C

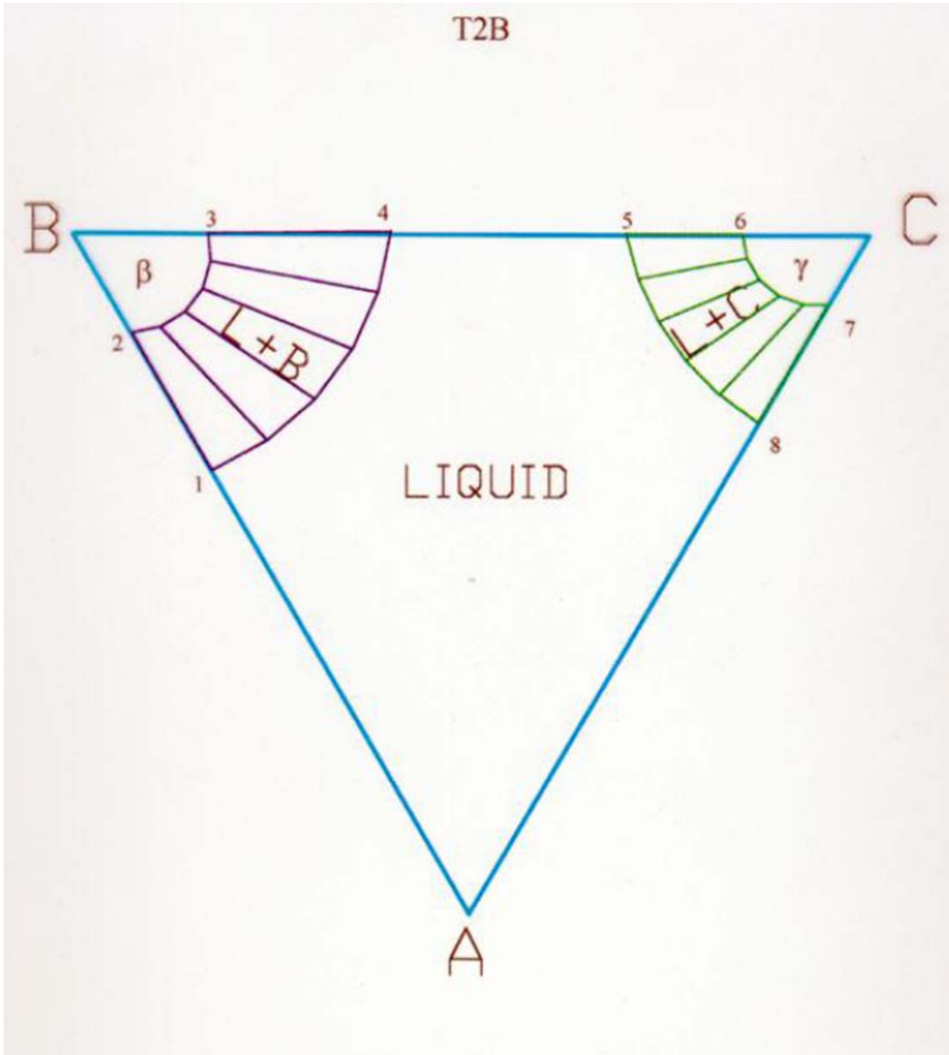


Isothermal Section At $T=T_1$

Ternary Eutectic System
(with Solid Solubility)

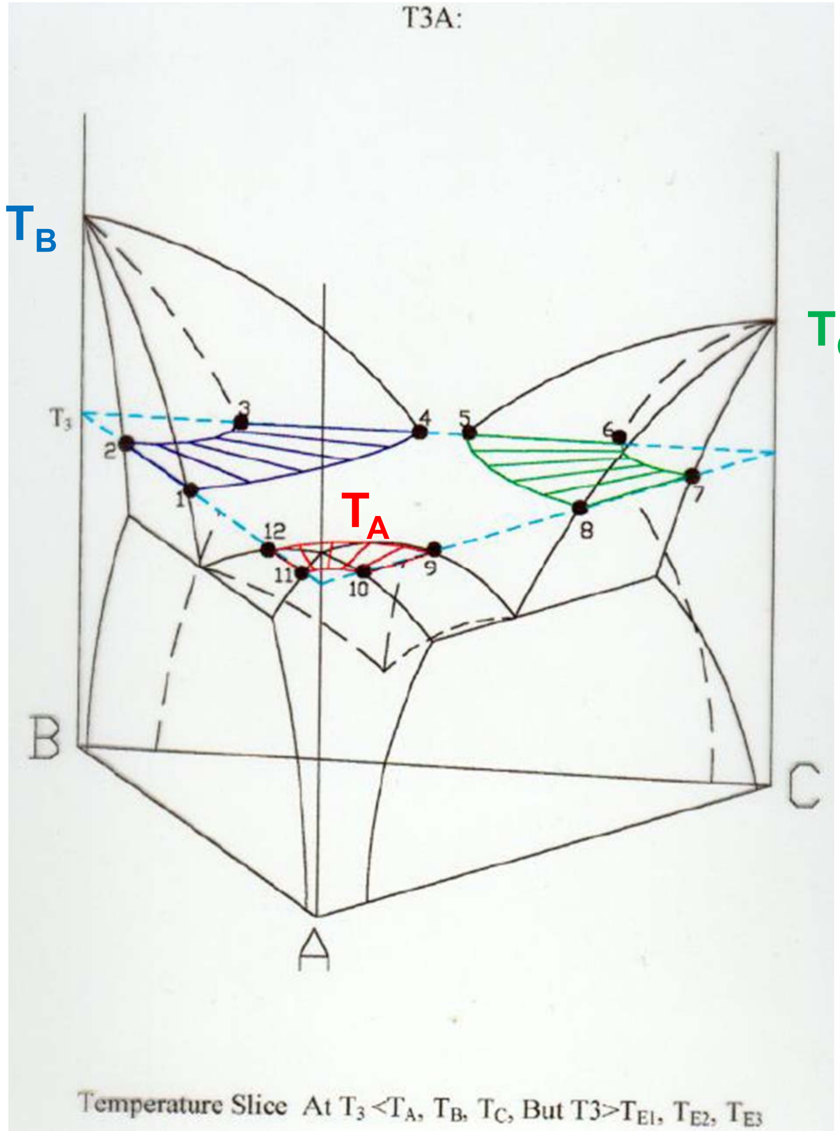


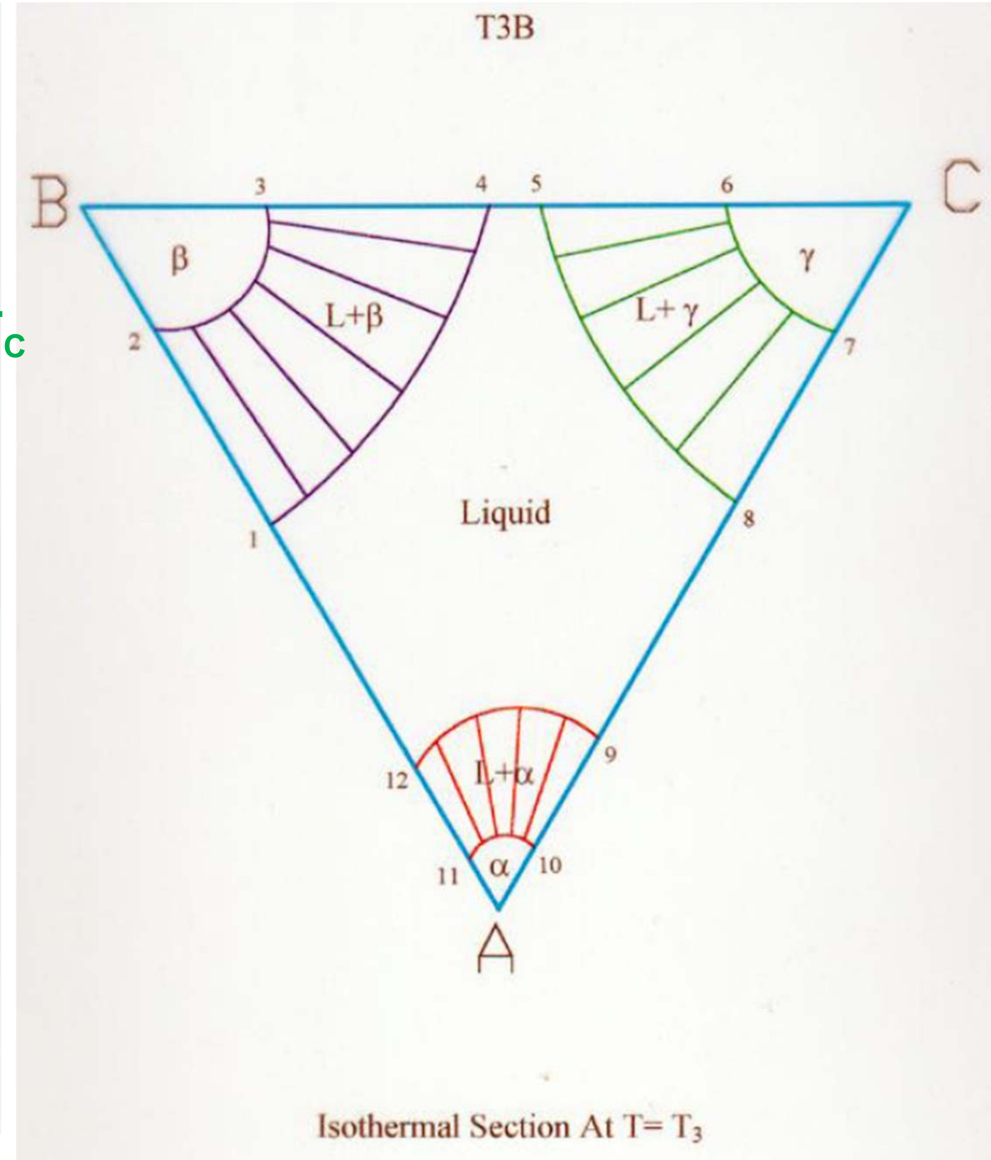
Temperature Slice At $T_2 > T_A$ But, $T_2 < T_B$, T_C



Isothermal Section At $T=T_2$

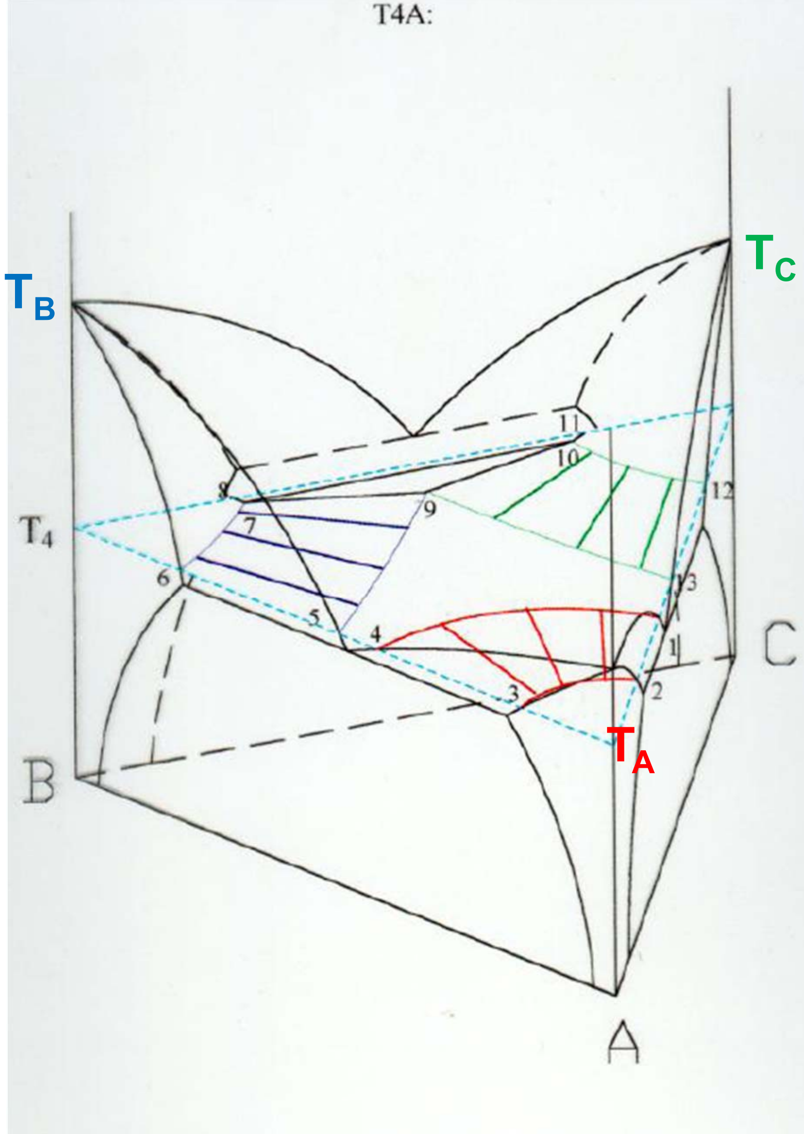
Ternary Eutectic System
(with Solid Solubility)



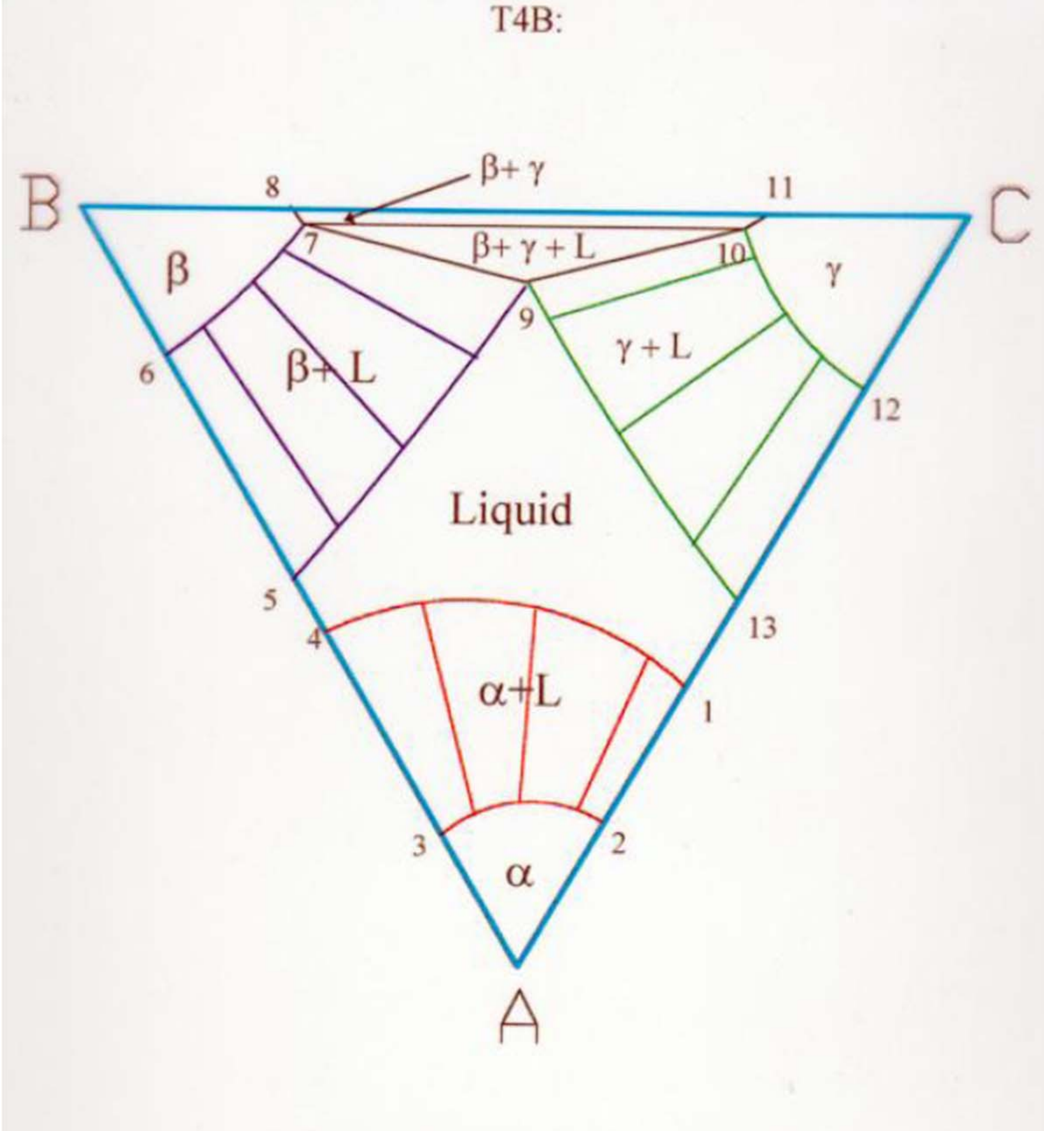


Ternary Eutectic System

(with Solid Solubility)



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

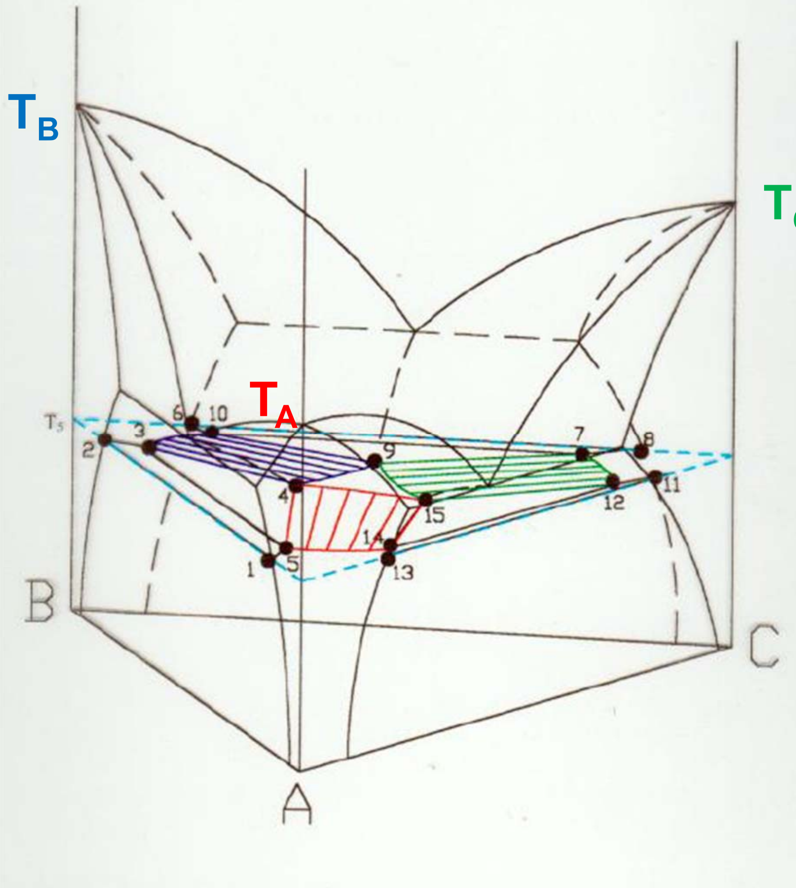


Isothermal Section At $T=T_4$

Ternary Eutectic System

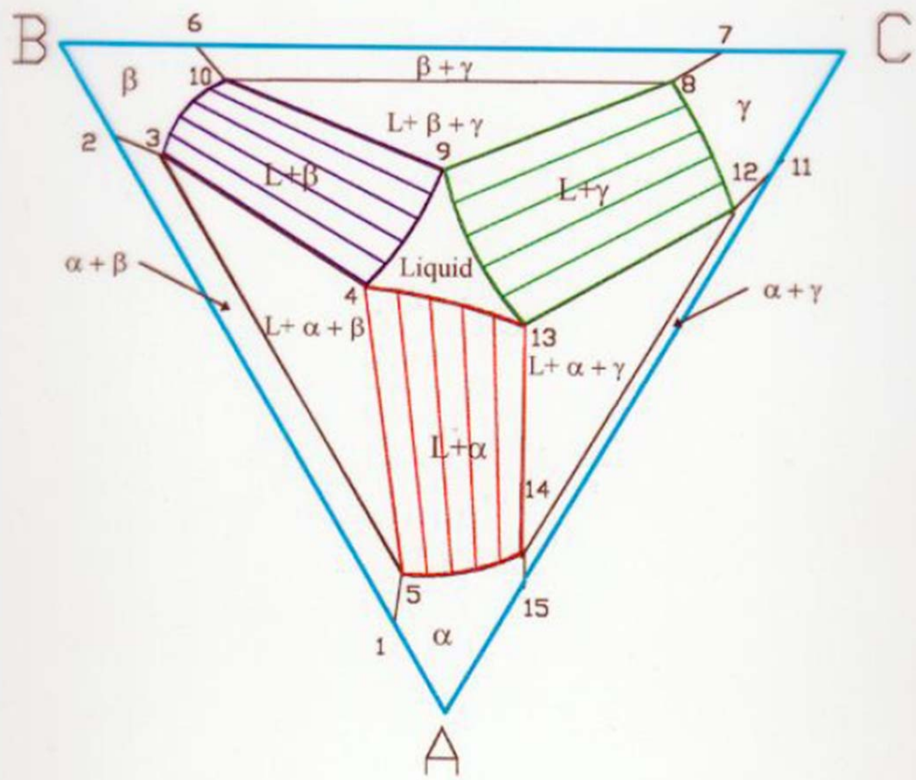
(with Solid Solubility)

T5A:



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

T5B:

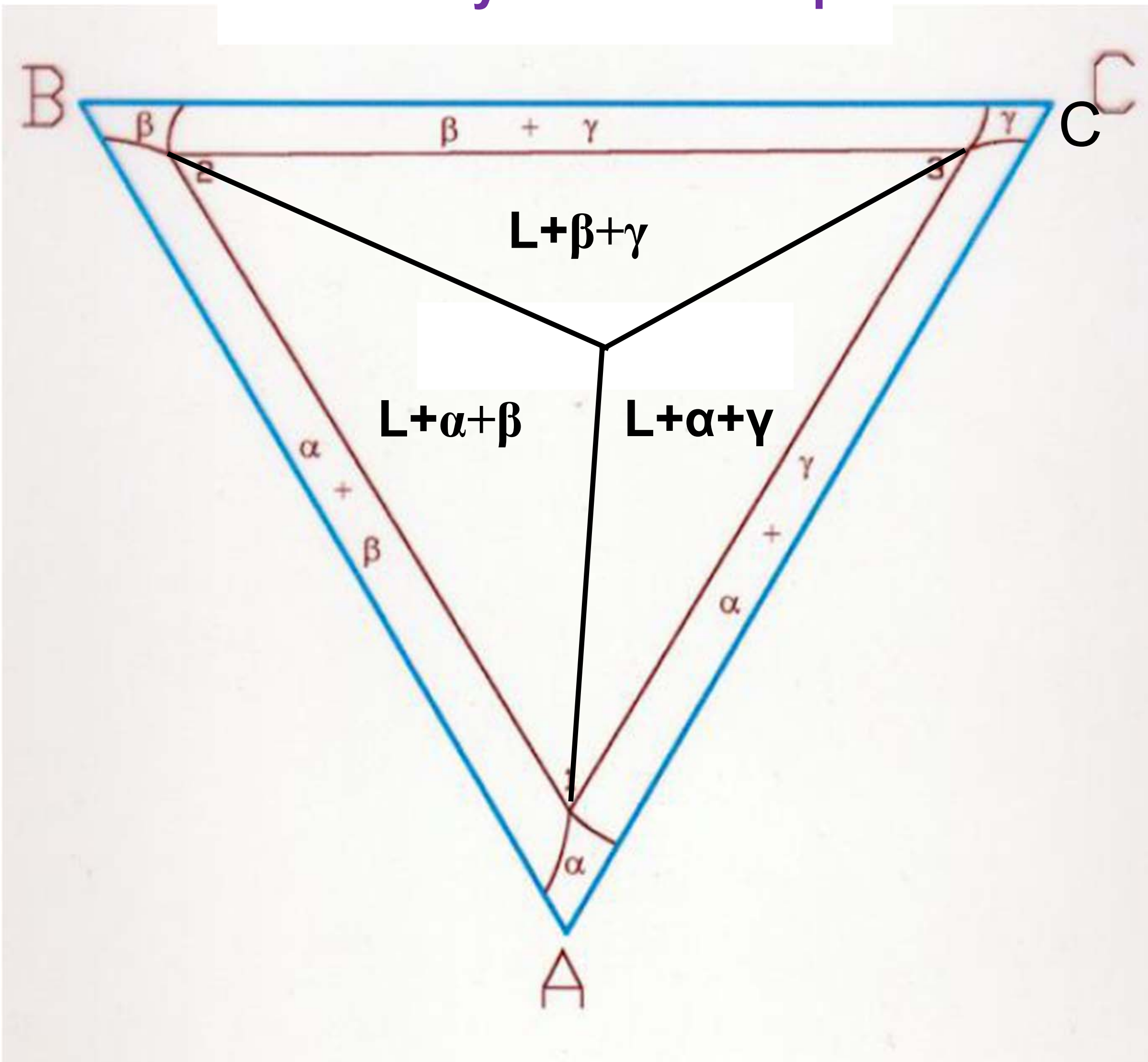


Isothermal Section At $T = T_5$

Ternary Eutectic System

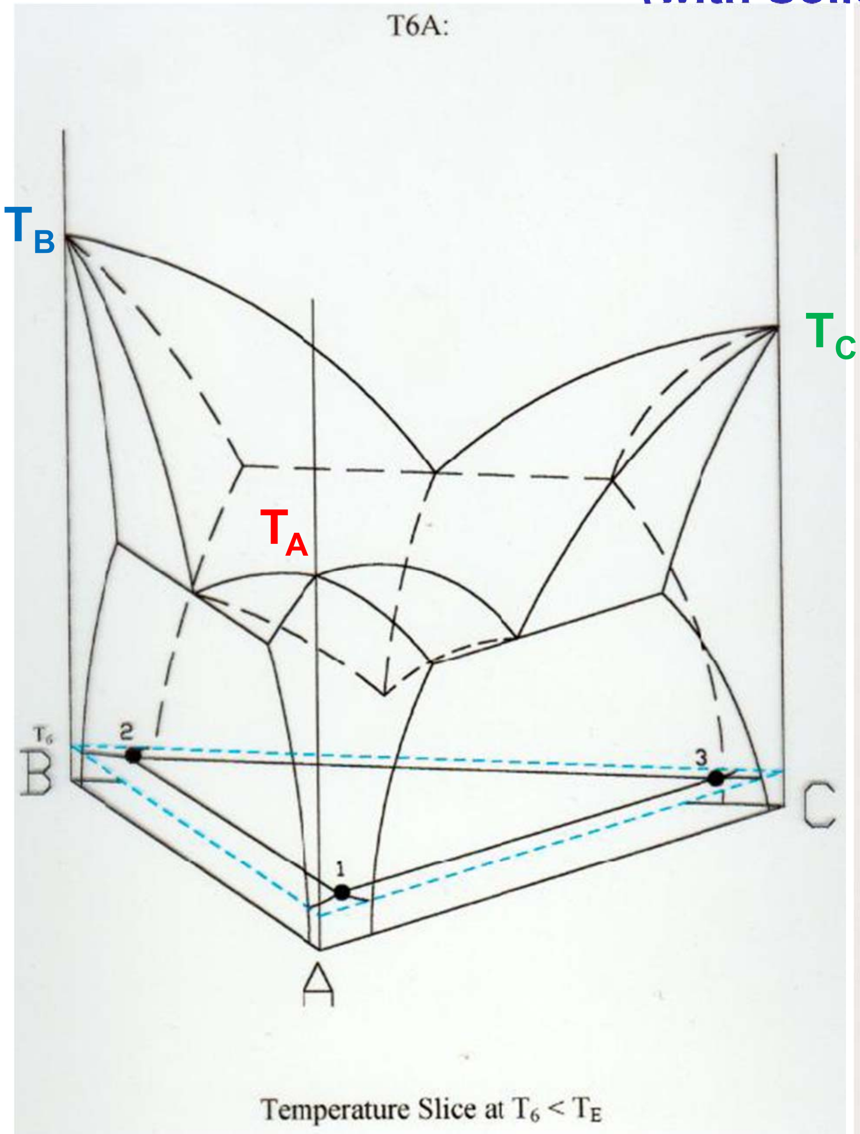
(with Solid Solubility)

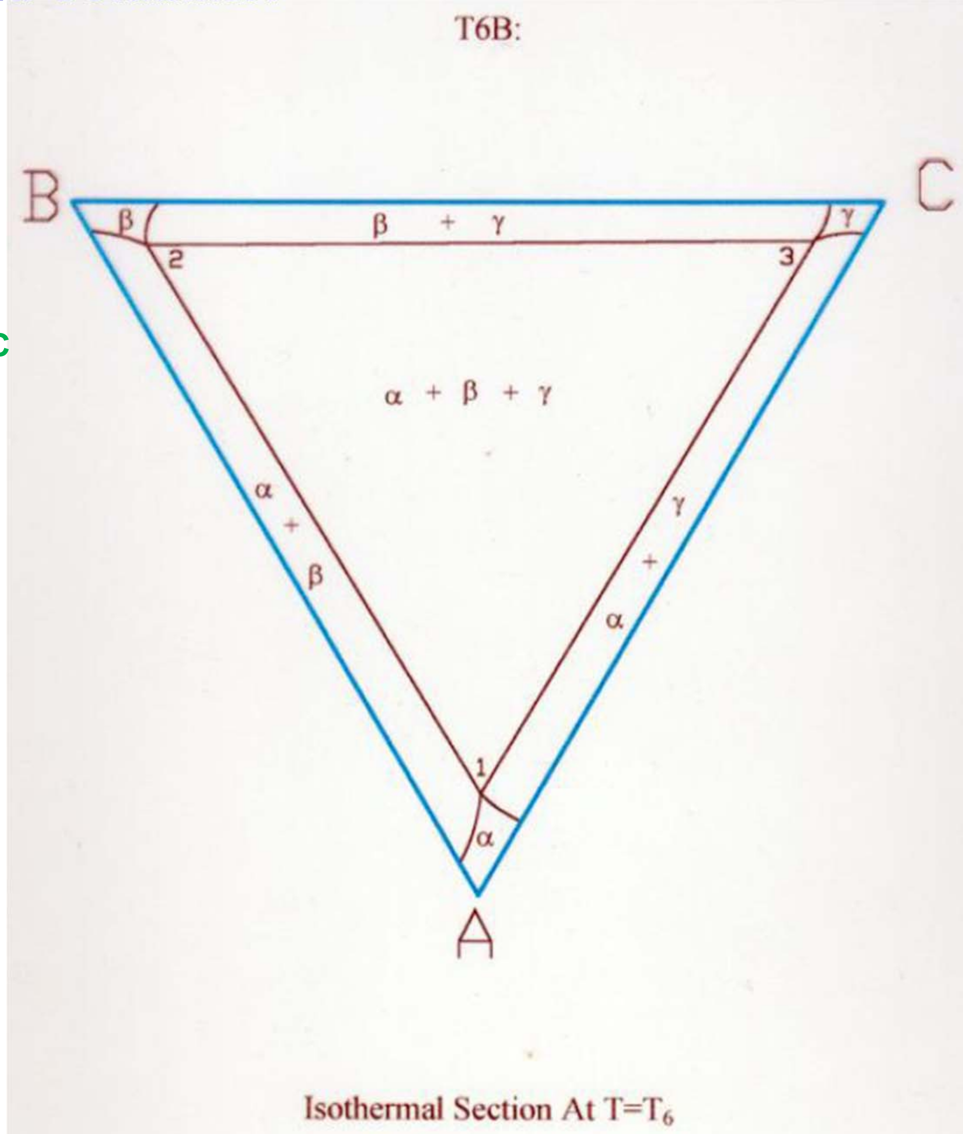
T= ternary eutectic temp.



Ternary Eutectic System

(with Solid Solubility)



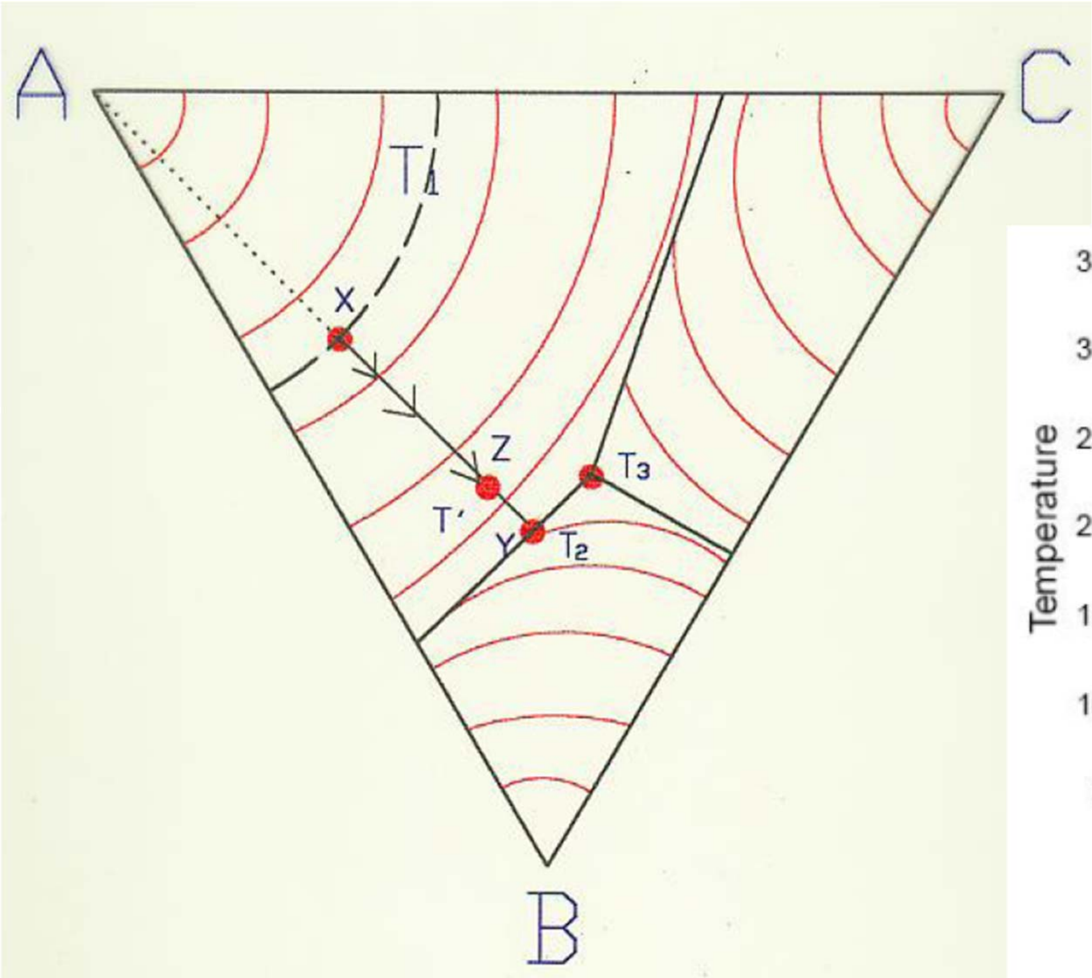


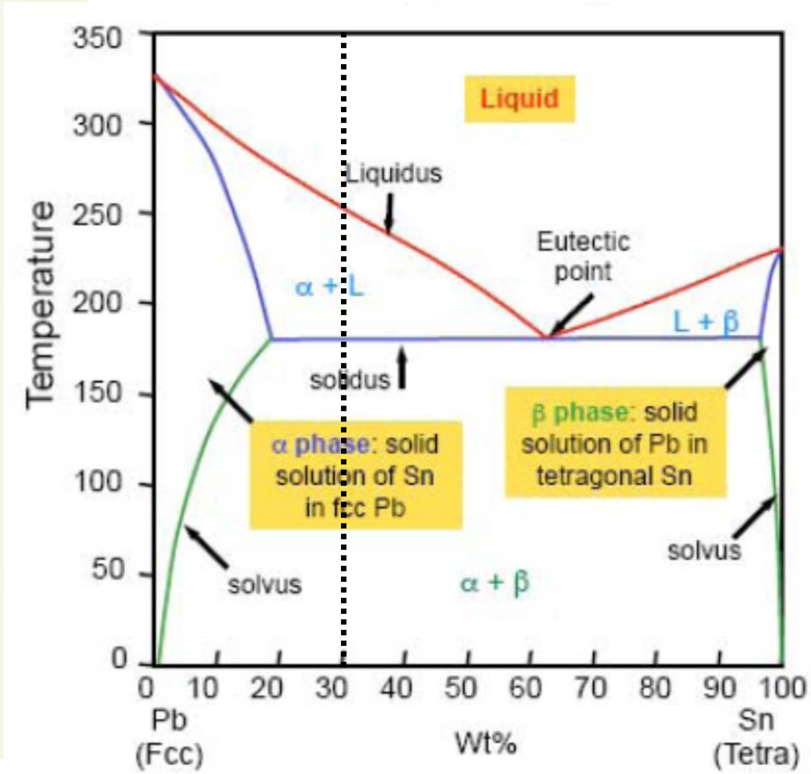
정해솔 학생 제공 자료 참조: 실제 isothermal section의 온도에 따른 변화

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

Ternary Eutectic System

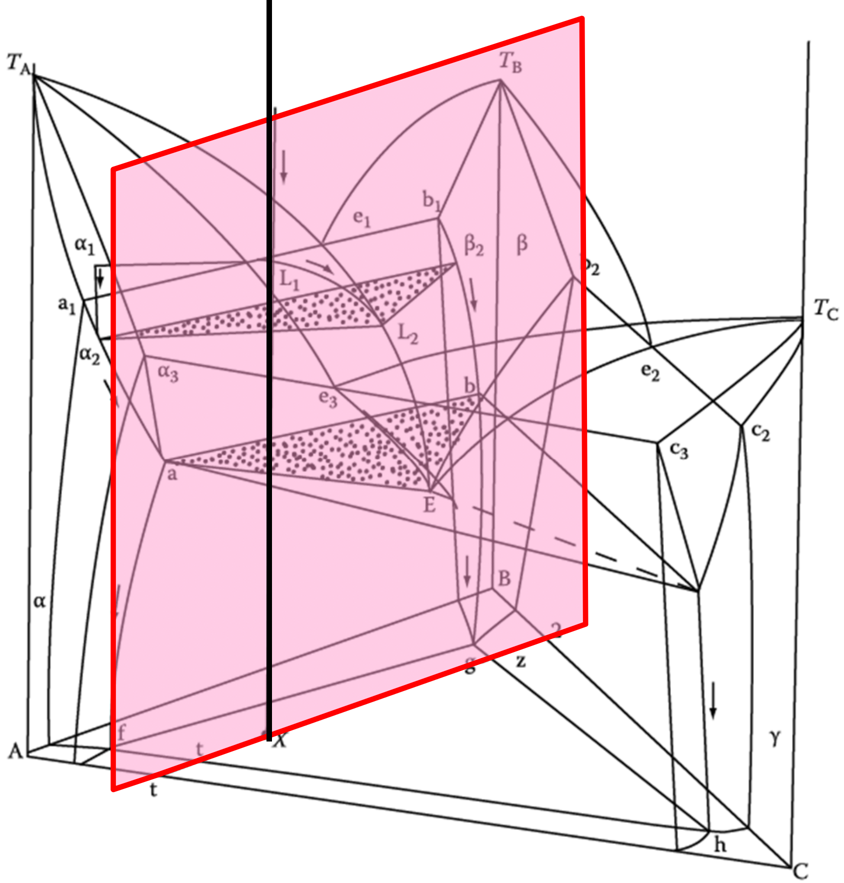
3) Solidification Sequence: liquidus surface

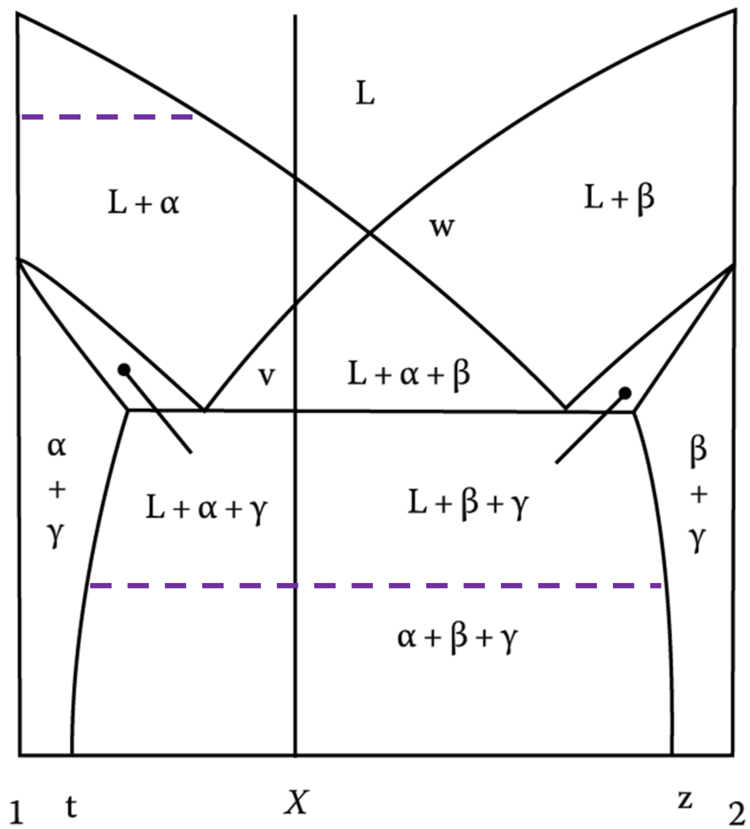




Ternary Eutectic System

*** Vertical section**





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

* Information for equilibrium phases at different tempeatures

< Quaternary phase Diagrams >

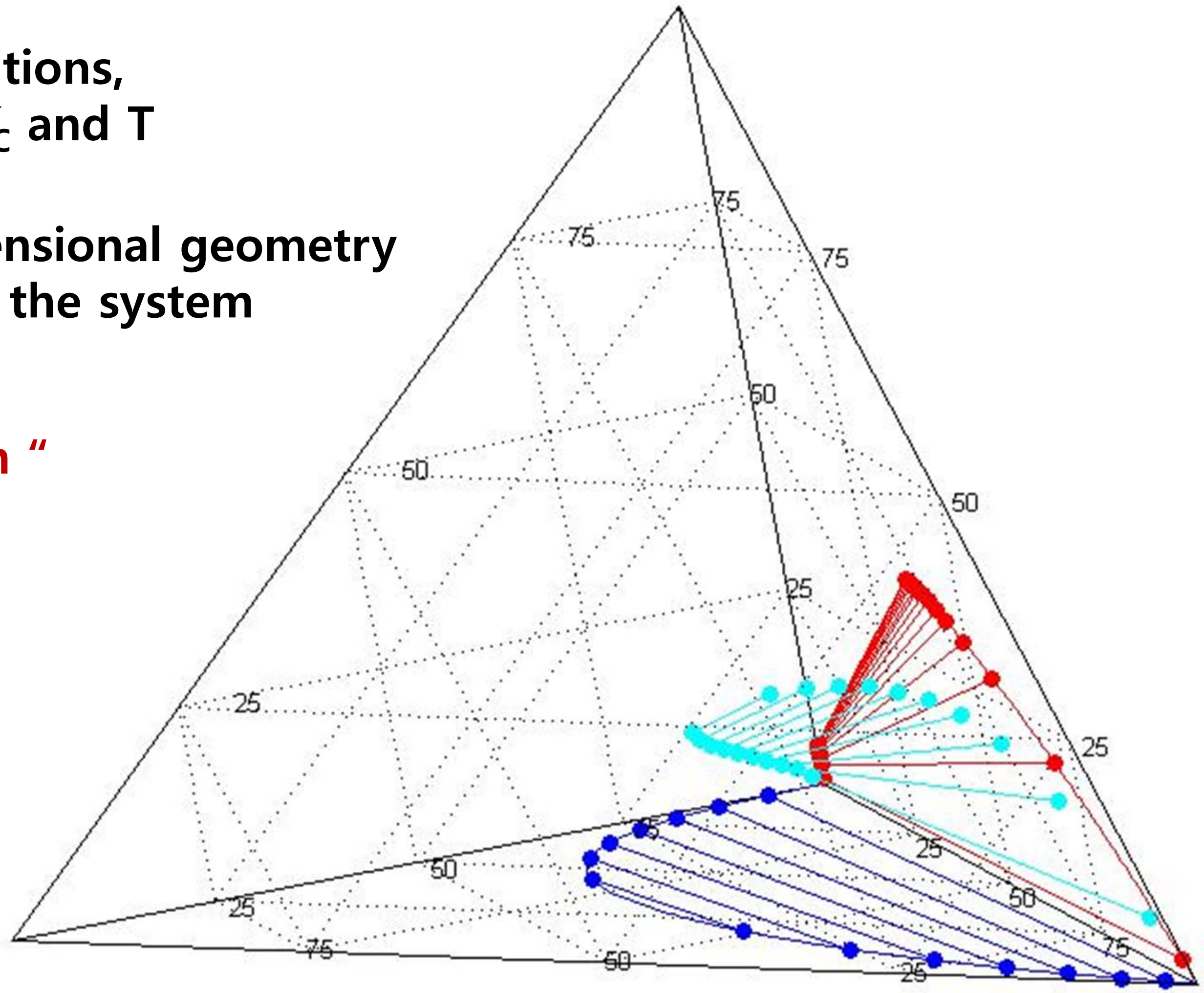
Four components: A, B, C, D

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

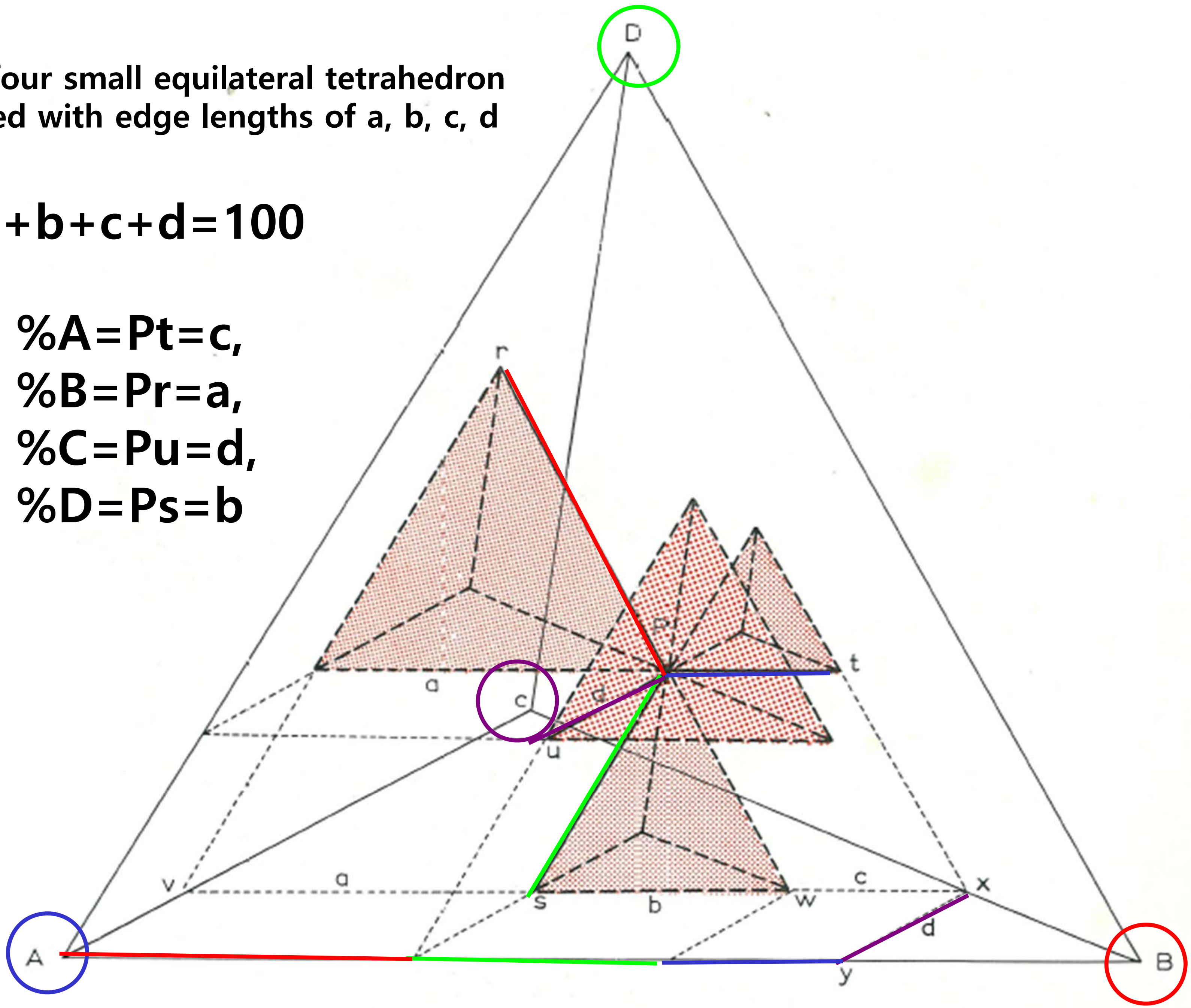


Fig. 247. Representation of a quaternary system by an equilateral tetrahedron.

*** Incentive Homework 1**

Please submit ternary phase diagram model which can clearly express 3D structure of ternary system by October 16 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!!