2009 fall

Phase Transformation of Materials

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Contents for previous class

- Binary phase diagrams

각 온도의 G-X 관계 도식 ⟺ T-X 관계 도식으로 plot

합금의 평형조성 ⟶ 주어진 온도에서 얻은 자유에너지 곡선으로 얻음

평형은 온도변화에 따라 어떻게 변화되어 가는가?

1) Simple Phase Diagrams

2) Systems with miscibility gap

4) Simple Eutectic Systems

3) Ordered Alloys

5) Phase diagrams containing intermediate phases

- Gibbs Phase Rule

$F = C - P + 2$ (from T, P)

Contents for today's class

- **Effect of Temperature on Solid Solubility**
- **Equilibrium Vacancy Concentration**
- **Influence of Interfaces on Equilibrium**
- **Ternary Equilibrium: Ternary Phase Diagram**

Effect of T on solid solubility

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

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

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

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

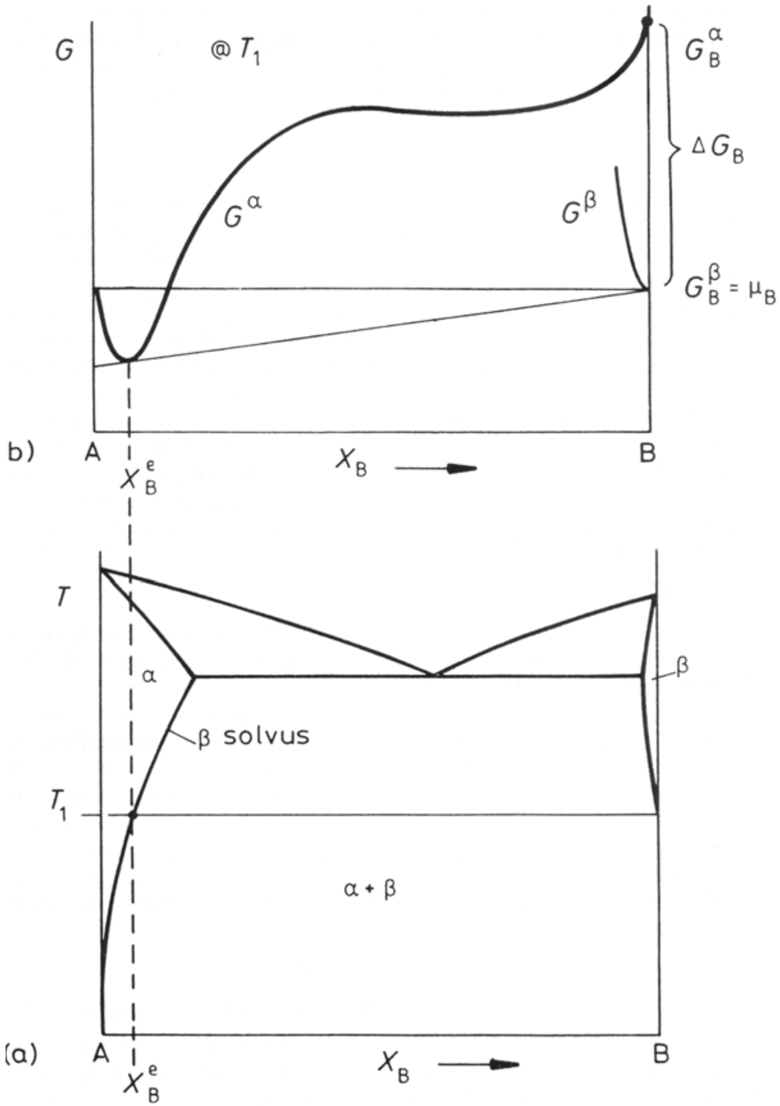


Fig. 1.36 Solubility of B in A.

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

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

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

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

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

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

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

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

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

Equilibrium Vacancy Concentration

$$\Delta G = \Delta H - T\Delta S$$

- **Vacancies increase the internal energy of crystalline metal due to broken bonds formation.**

$$\Delta H \cong \Delta H_V X_V$$

- Vacancies increase entropy because they change the **thermal vibration frequency** and also the **configurational entropy**.

- Total entropy change is thus

$$\Delta S = \Delta S_V X_V - R\{X_V \ln X_V + (1 - X_V)\ln(1 - X_V)\}$$

The molar free energy of the crystal containing X_v mol of vacancies

$$G = G_A + \Delta G = G_A + \Delta H_V X_V - T\Delta S_V X_V + RT\{X_V \ln X_V + (1 - X_V)\ln(1 - X_V)\}$$

➡ **With this information, estimate the equilibrium vacancy concentration.**

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

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

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

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

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

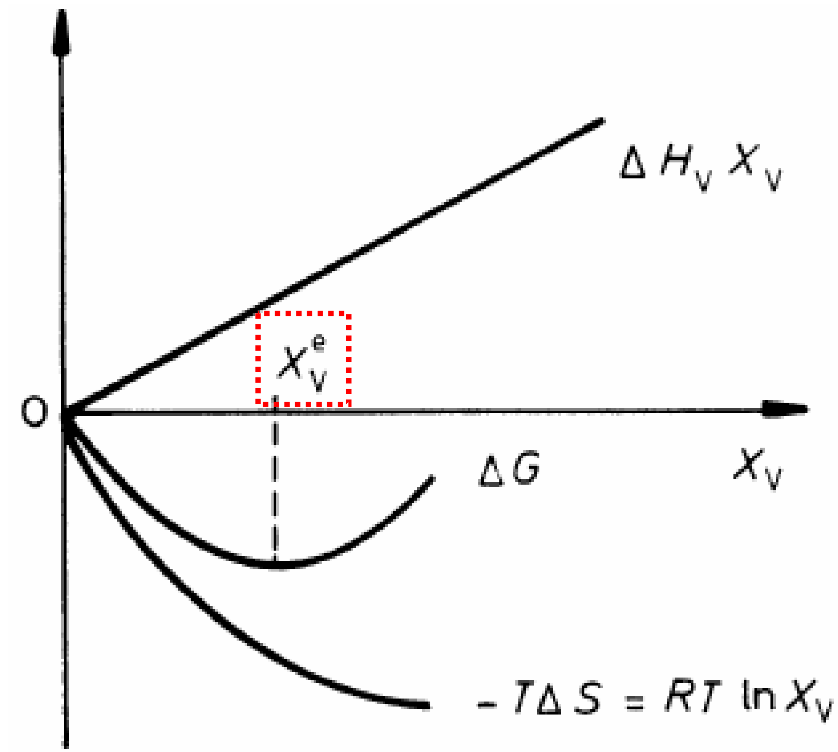


Fig. 1.37 Equilibrium vacancy concentration.

- **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**

Interface (α/β)=γ

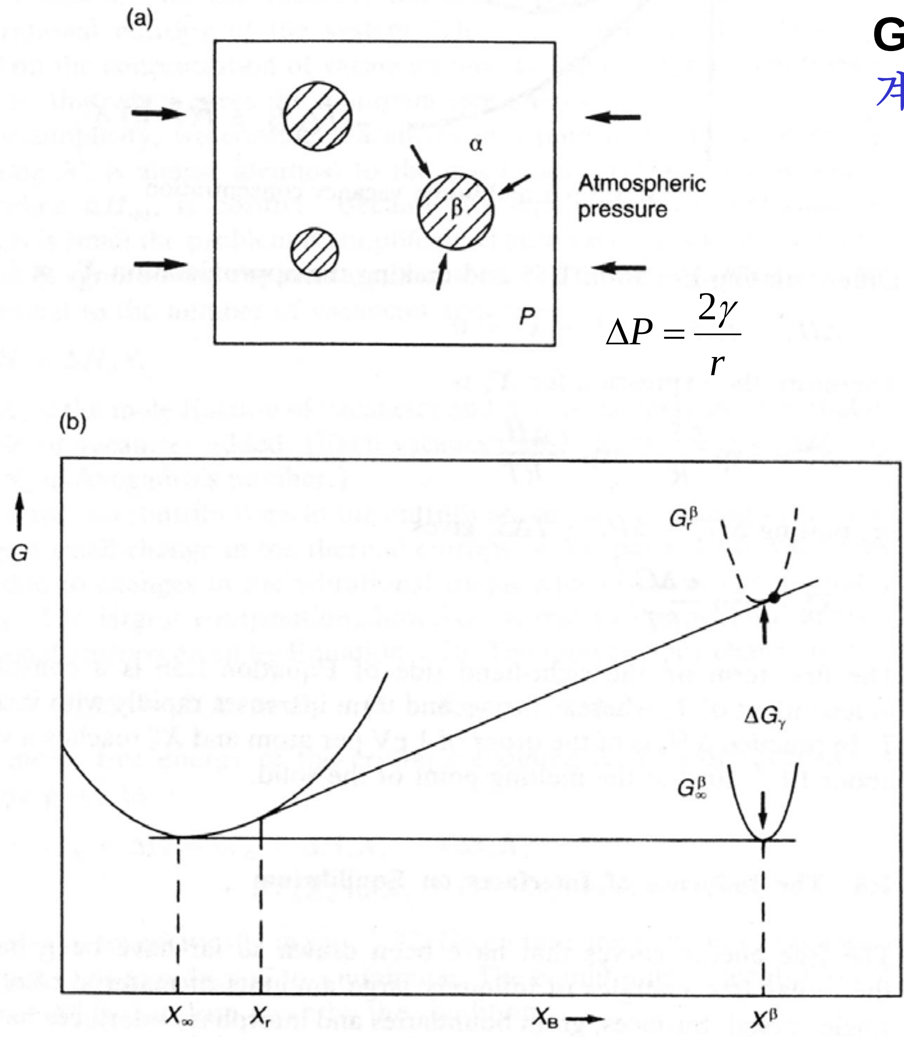


Fig. 1.38 The effect of interfacial energy on the solubility of small particles.

$$\Delta G = \frac{2\gamma V_m}{r}$$ 의 effect

Gibbs-Thomson effect:

계면에너지로 인해 자유에너지가 증가하는 현상

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

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

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

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

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

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

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

r=10nm 이면 10% 증가

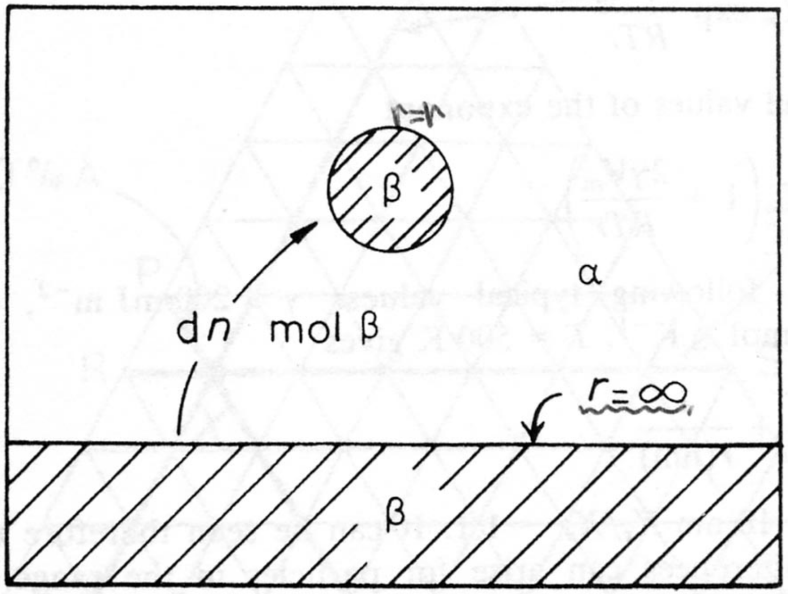


Fig. 1.39 Transfer of dn mol of β from large to a small particle.

$$\Delta G = \frac{2\gamma V_m}{r} \qquad \Delta G \cong \frac{L\Delta T}{T_m}$$

$$r^* = \frac{2\gamma}{\Delta G_V} = \frac{2\gamma T_m}{L\Delta T}$$

$$\Delta T \uparrow, r^* \downarrow$$

β formation in α

β Nucleation & growth in α

Interface (α/β) : size barrier

composition barrier

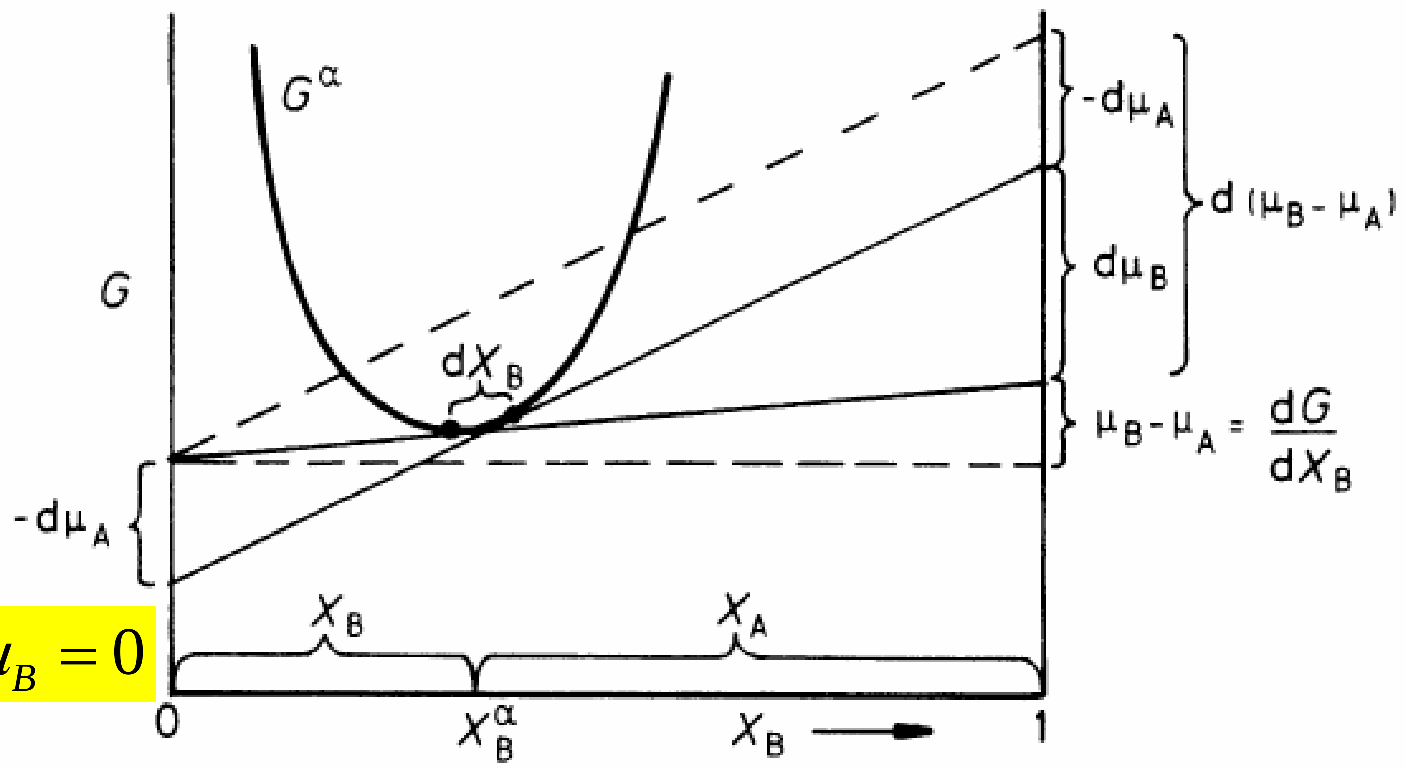
Undercooling이 클수록 **r***가 작다

→ Nucleation ↑β 상의 수

➔ size barrier (r*)

Additional Thermodynamic Relationships for Binary Solutions

➡ 조성 변화로 인한 화학퍼텐셜의 변화 계산: **Gibbs-Duhem 식**



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

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

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

The Gibbs-Duhem Equation

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

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, $\Omega = 0,$

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

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

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

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

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

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

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

Driving force: precipitation

* Consider the chemical potential of component *B* in phase *alpha* compared to *B* in *beta*. This difference, labeled as ΔG_n on the right of the lower diagram is the driving force (expressed as energy per mole, in this case).

* To convert to *energy/volume*, divide by the molar volume for *beta*: $\Delta G_V = \Delta G_n / V_m$.

Driving force for the reaction : ΔG_0

Driving force for nucleation : ΔG_n

Because the first nuclei of beta to appear do not ignificantly change the composition of the parent material

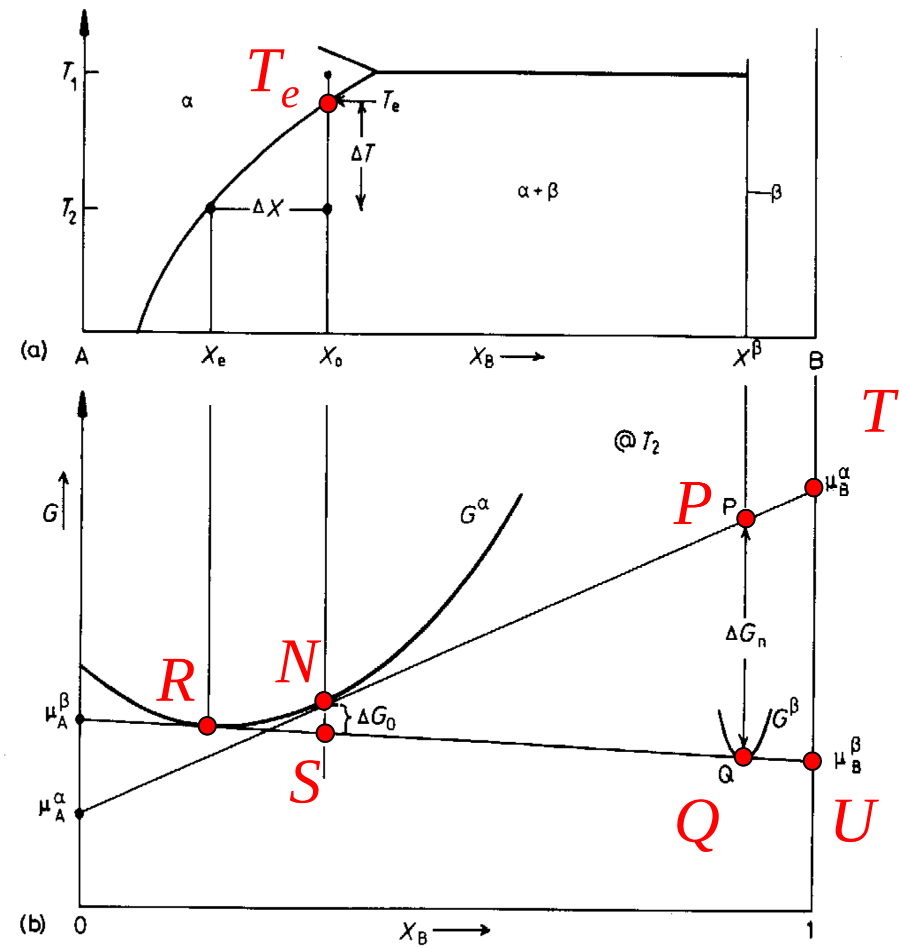


Fig. 5.3 Free energy changes during precipitation. The driving force for the first precipitates to nucleate is $\Delta G_n = \Delta G_v V_m$. ΔG_0 is the total decrease in free energy when precipitation is complete and equilibrium has been reached.

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:

$F = C + 1 - P$

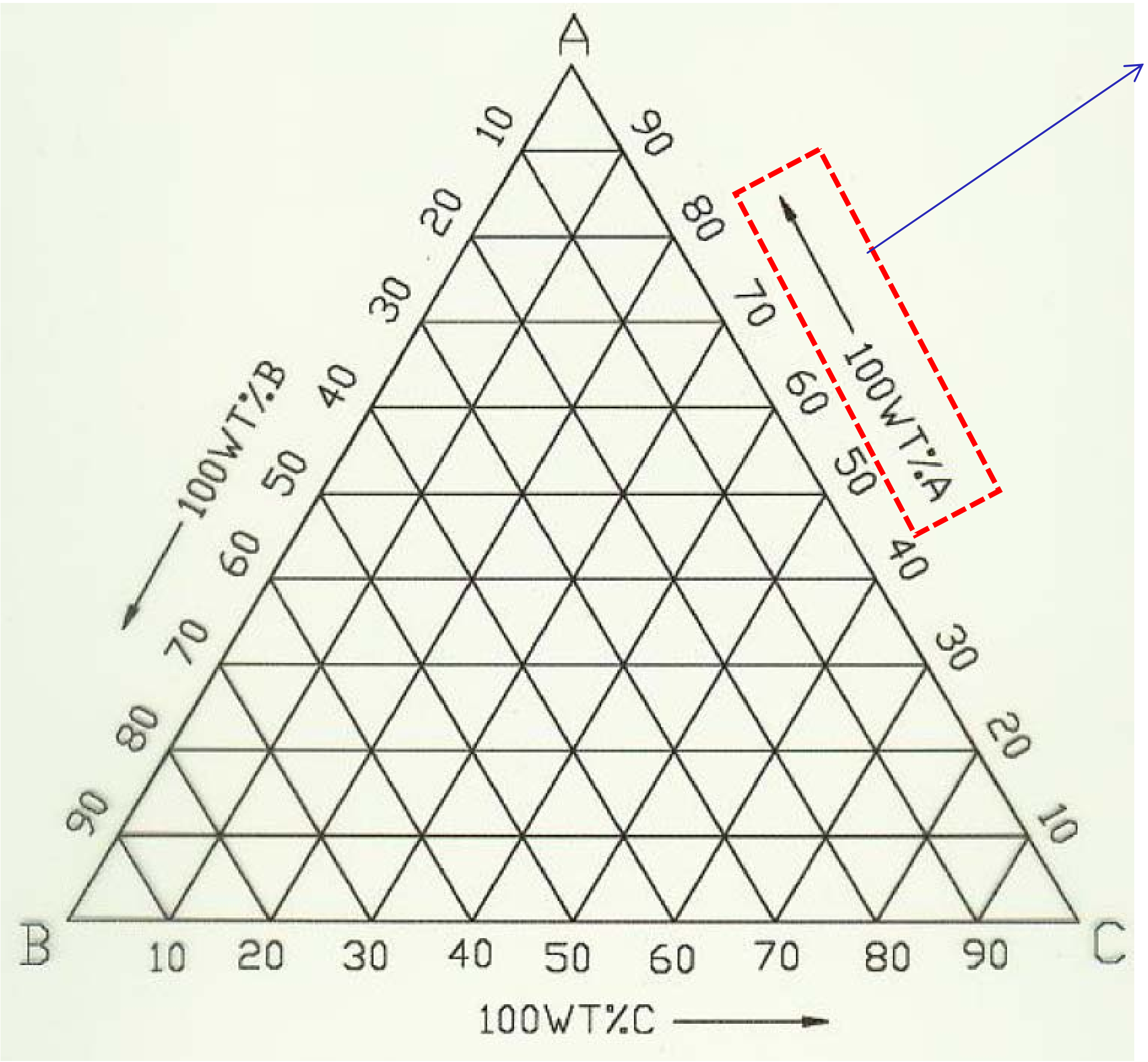
For C = 3, the maximum number of phases will co-exist when F = 0

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.

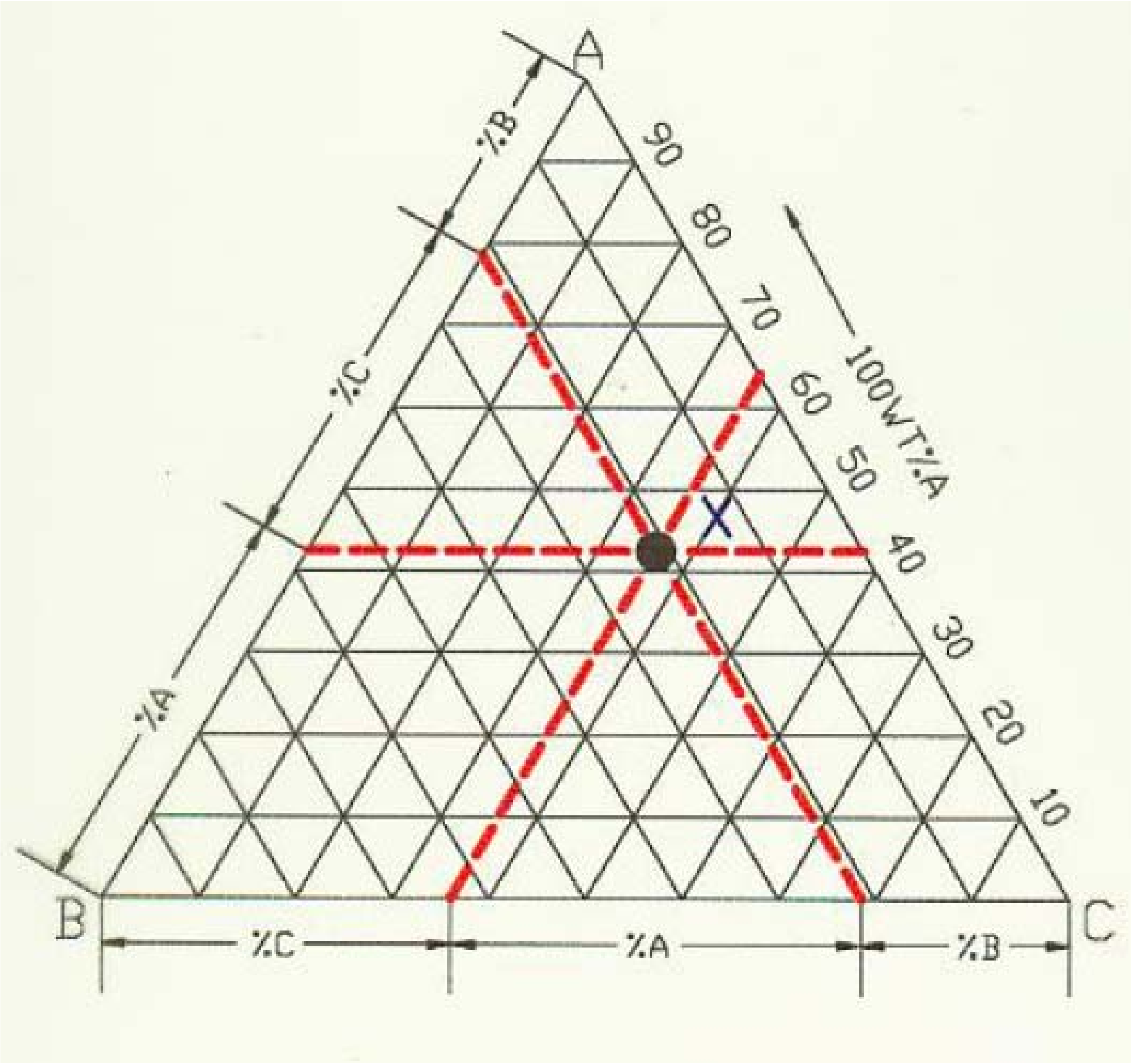


Concentration can be expressed as either "wt. %" or "at.% = molar %".

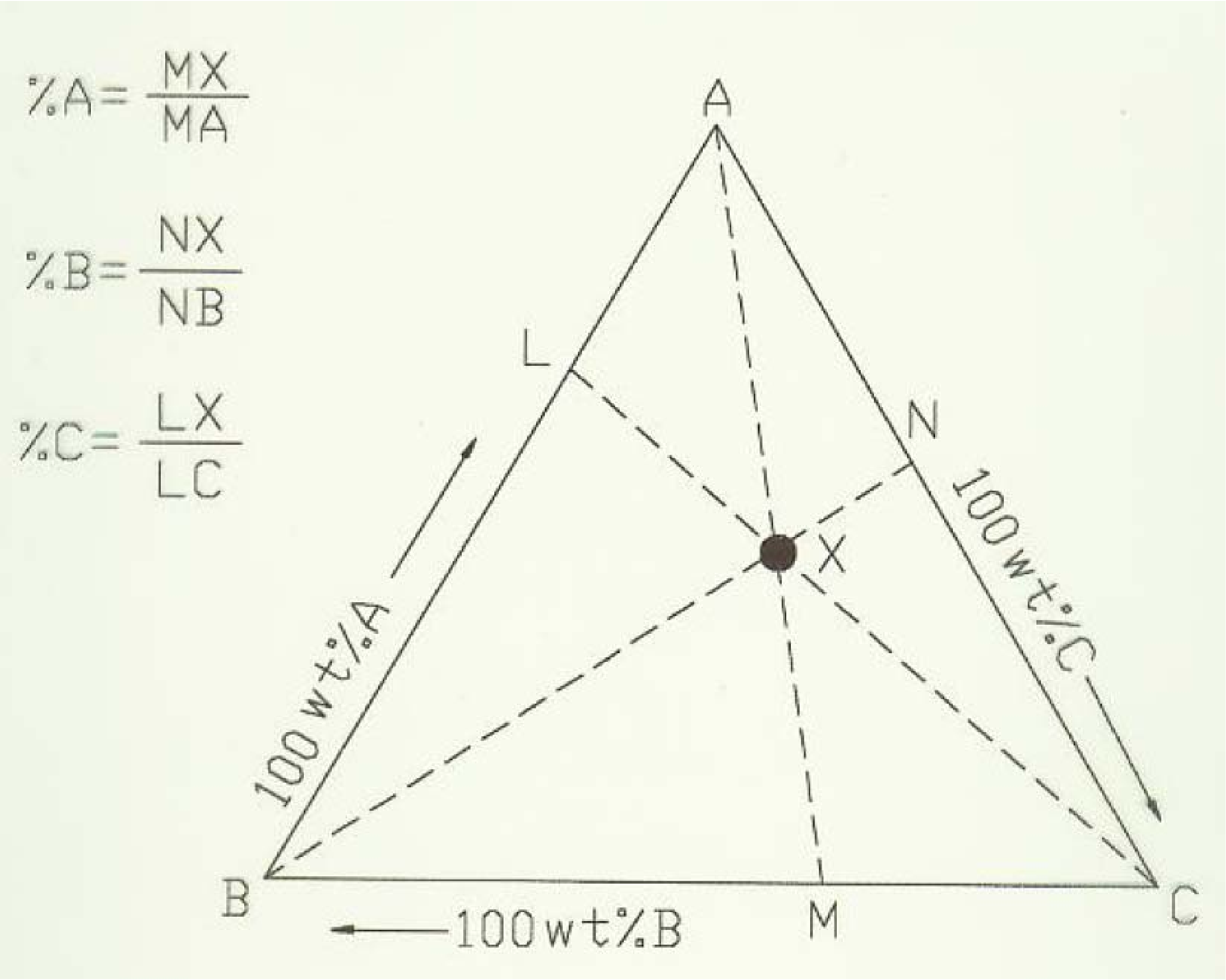
$$X_A+X_B+X_C = 1$$

Used to determine the overall composition

Overall Composition



Overall Composition



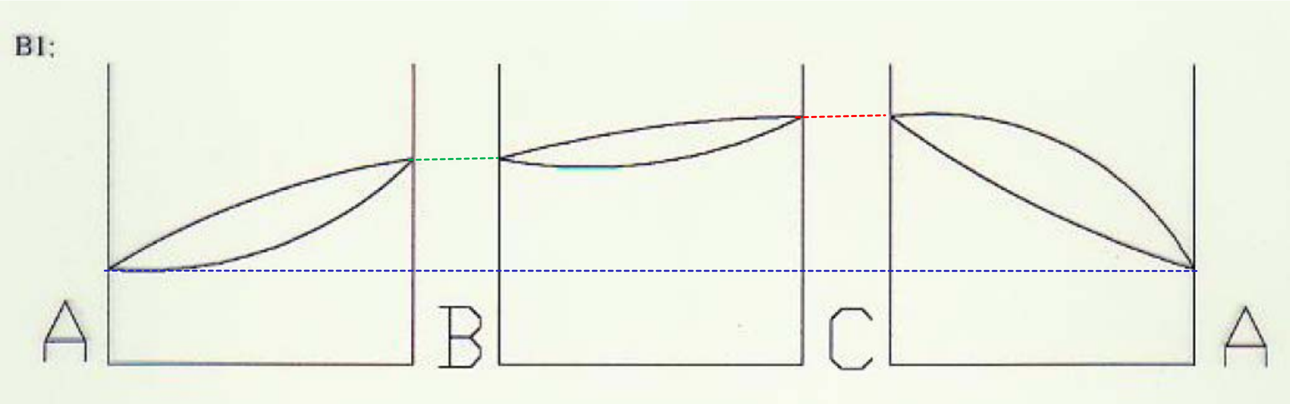
Ternary Isomorphous System

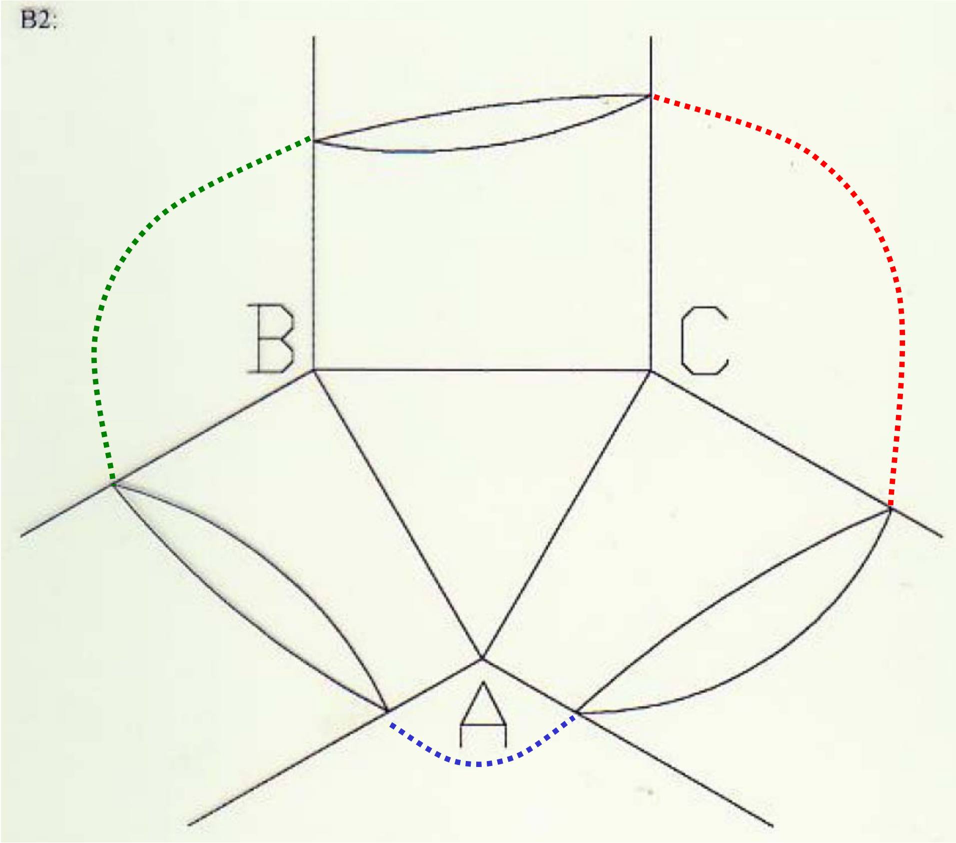
Isomorphous System: A system (ternary in this case) that has only one solid phase. All components are totally soluble in the other components. The ternary system is therefore made up of three binaries that exhibit total solid solubility

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





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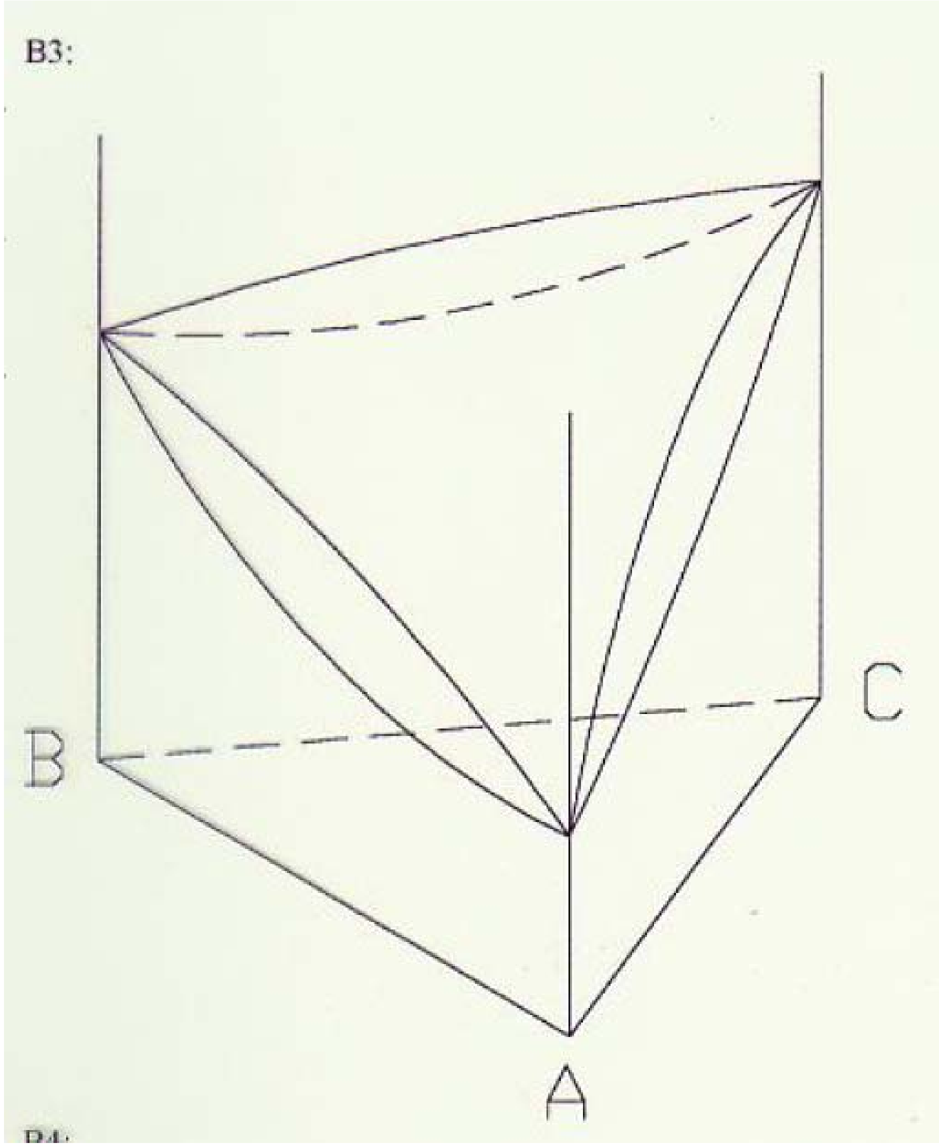

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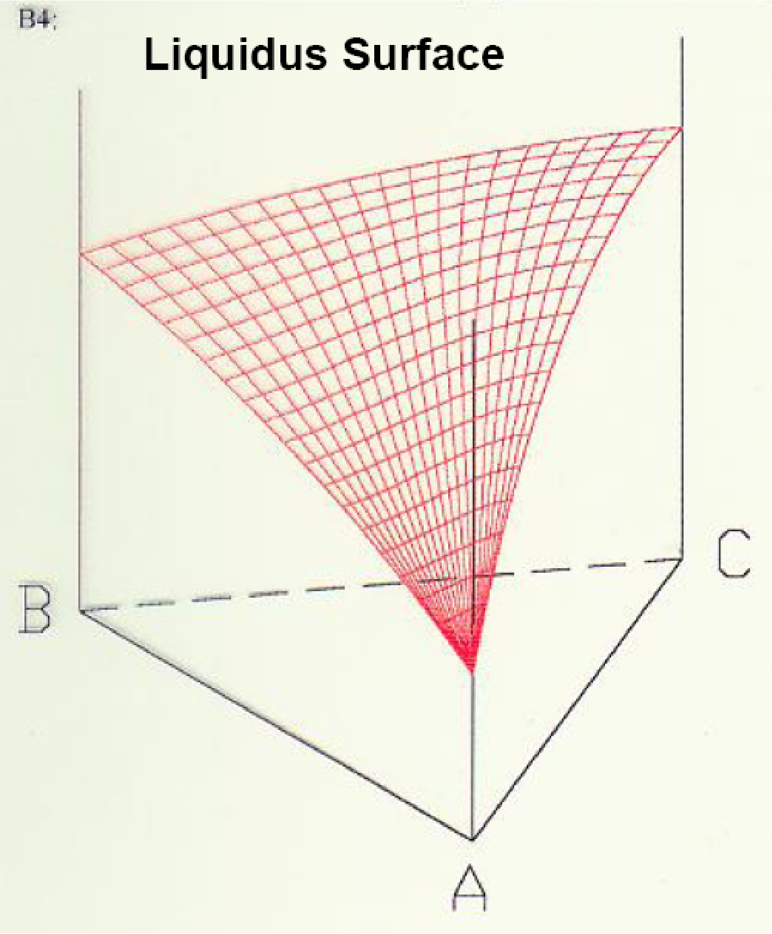
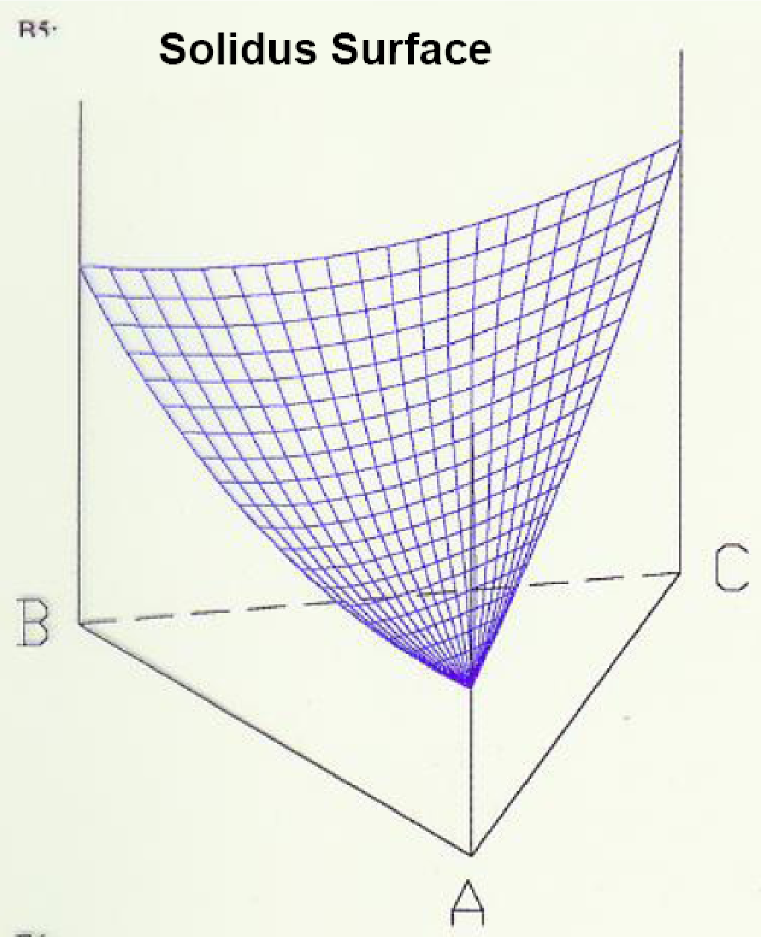
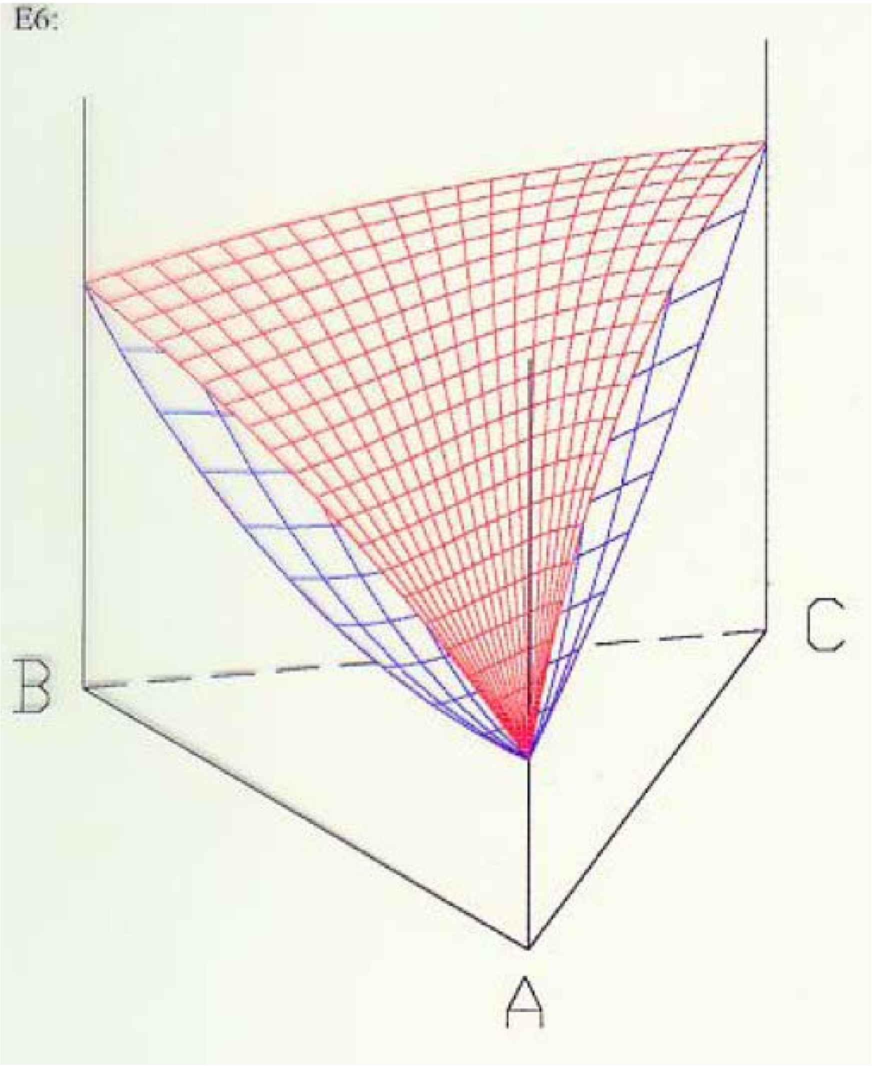
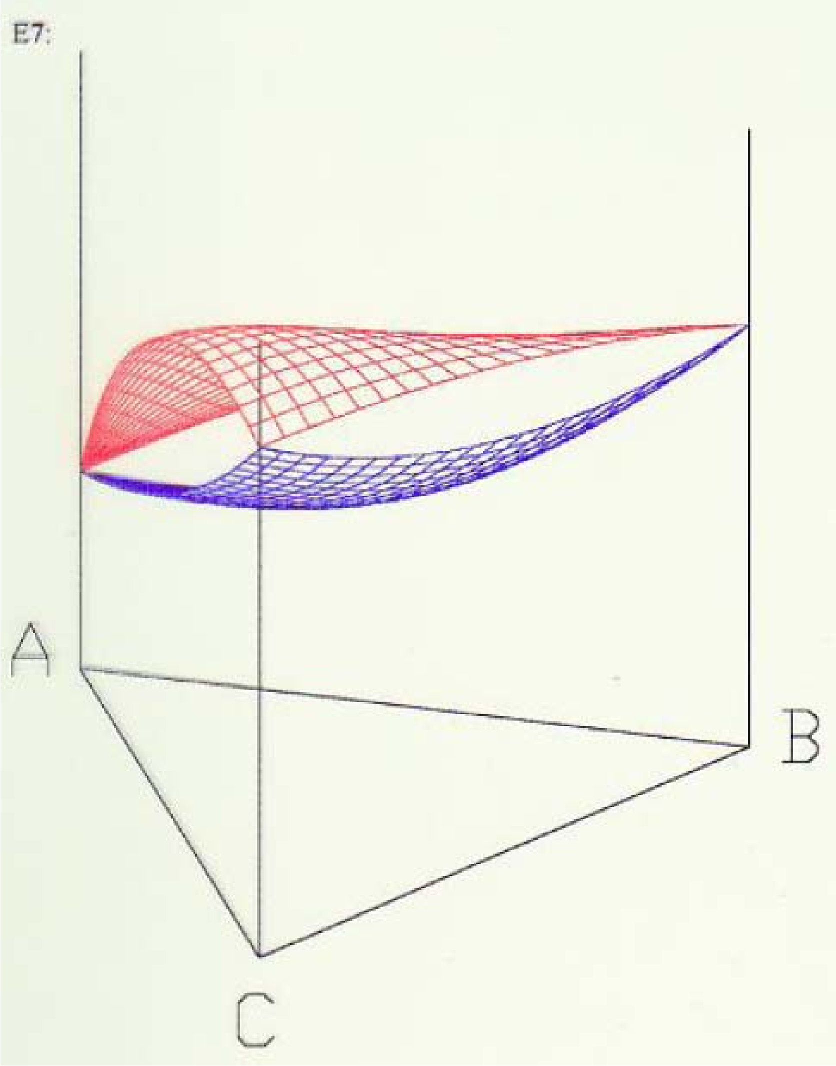




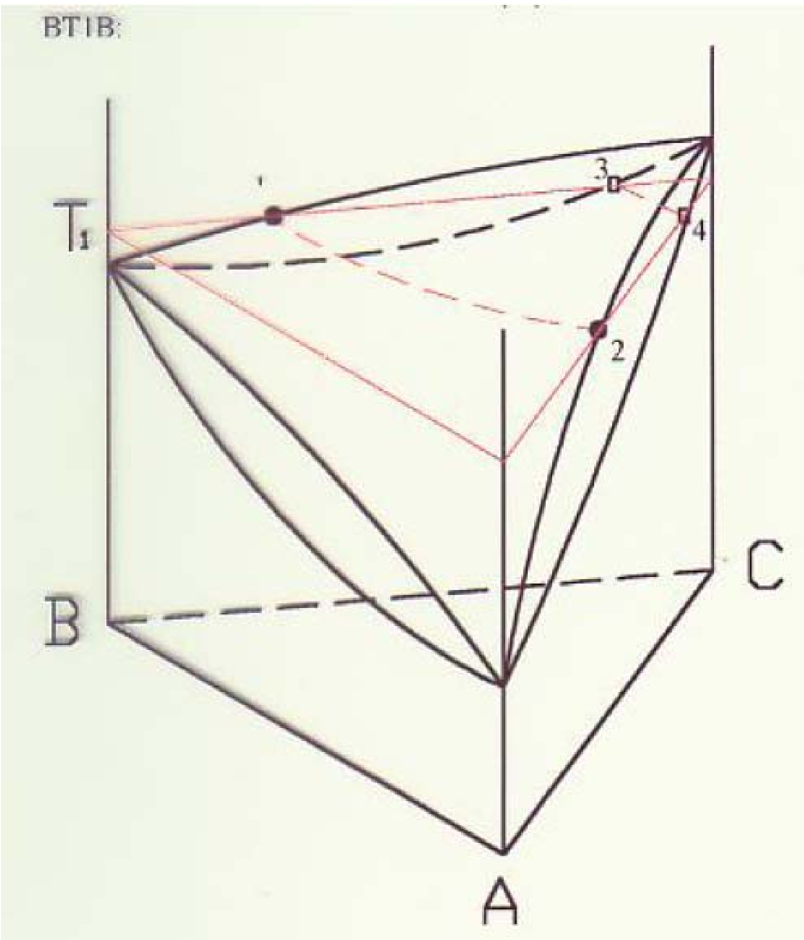
Ternary Isomorphous System

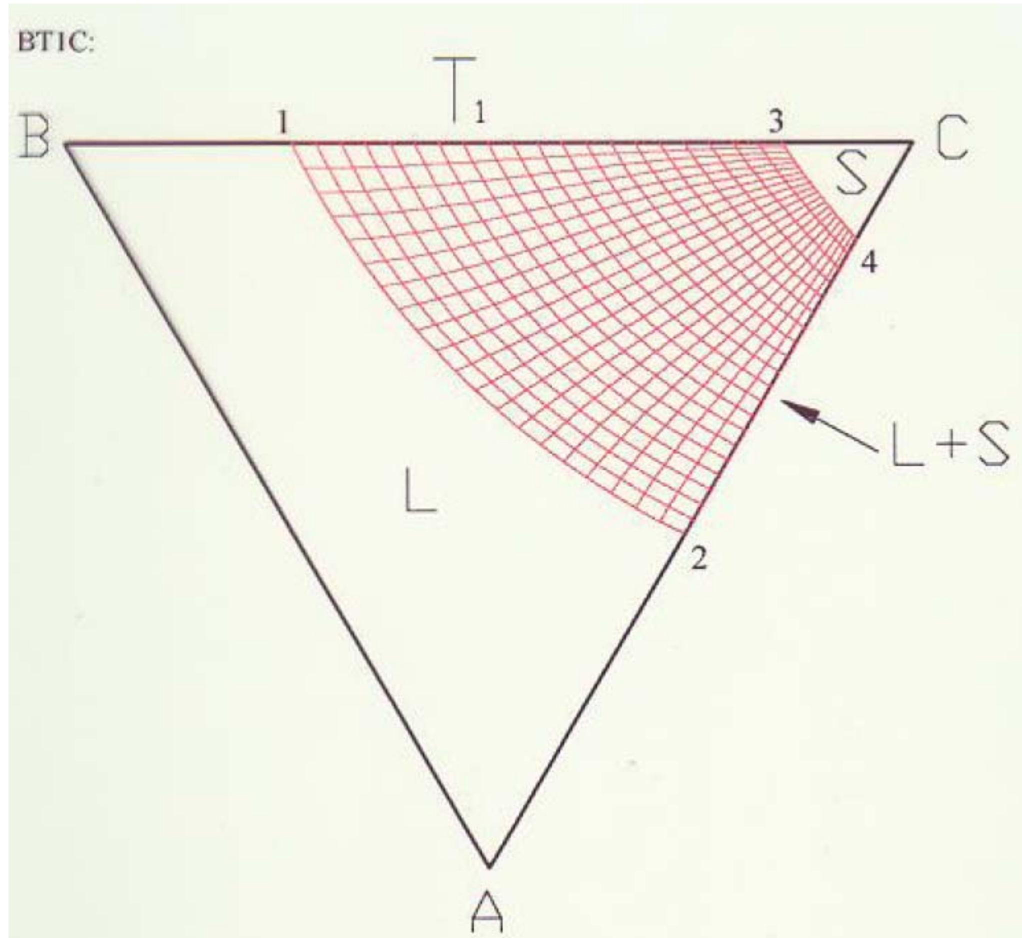




Ternary Isomorphous System

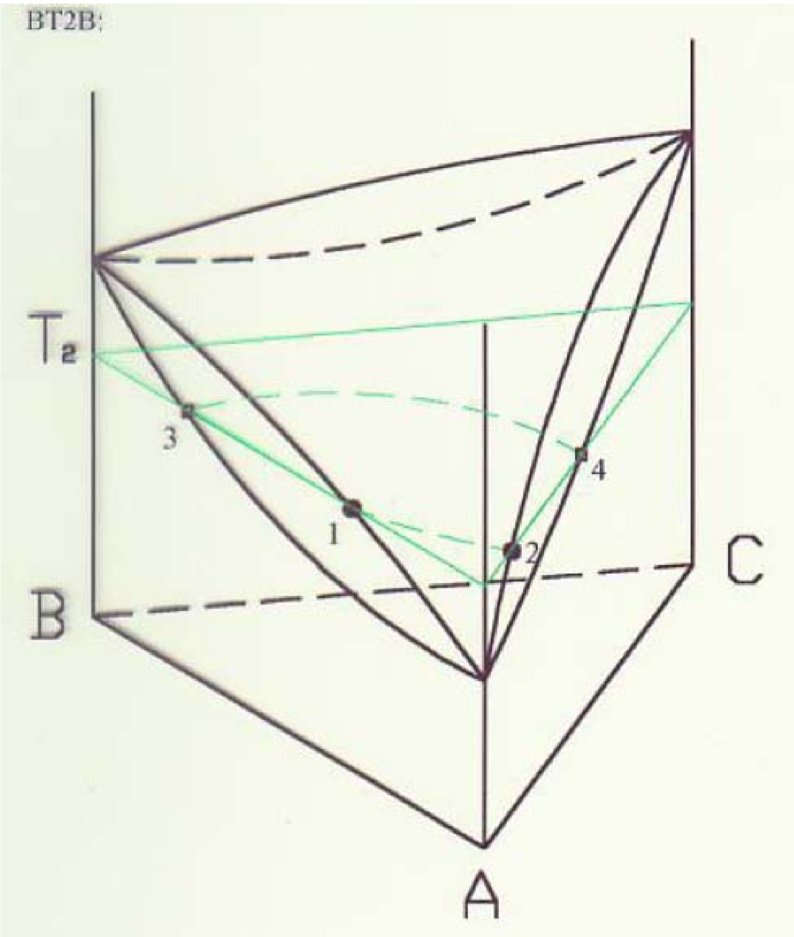
Isothermal section → $F = C - P$

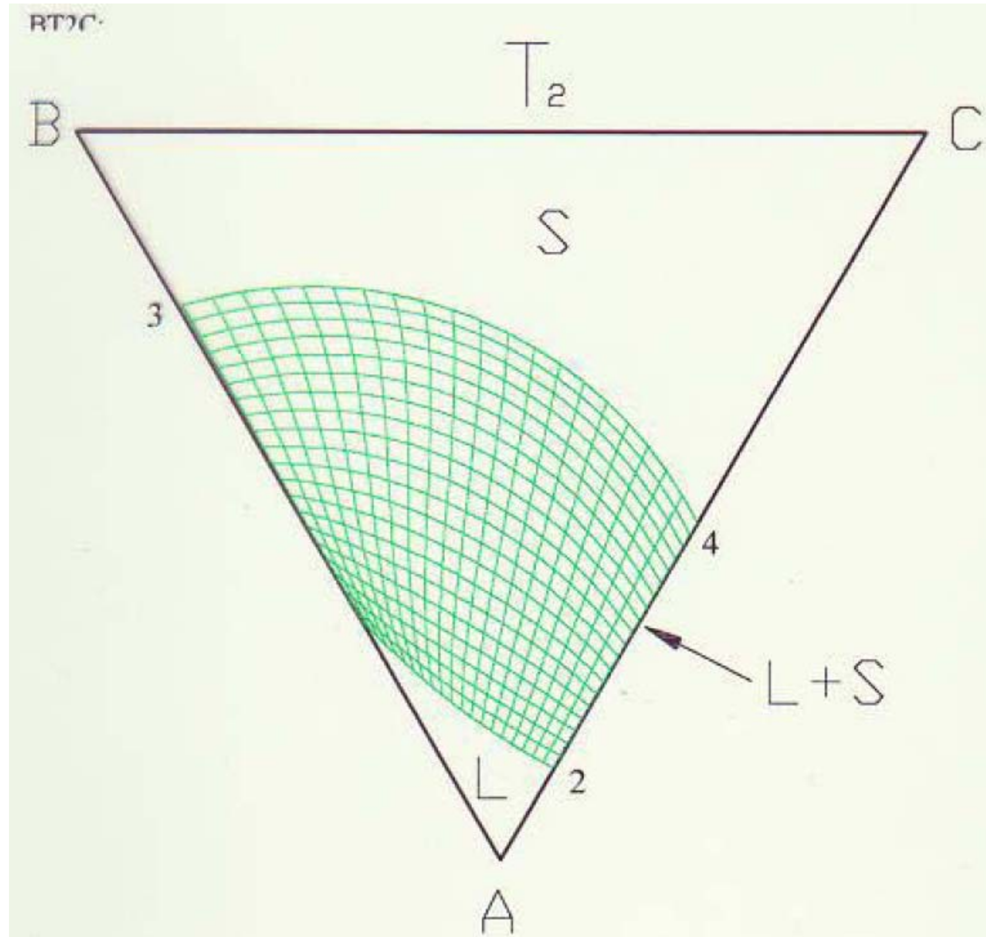




Ternary Isomorphous System

Isothermal section





Ternary Isomorphous System

Isothermal section → F = C - P

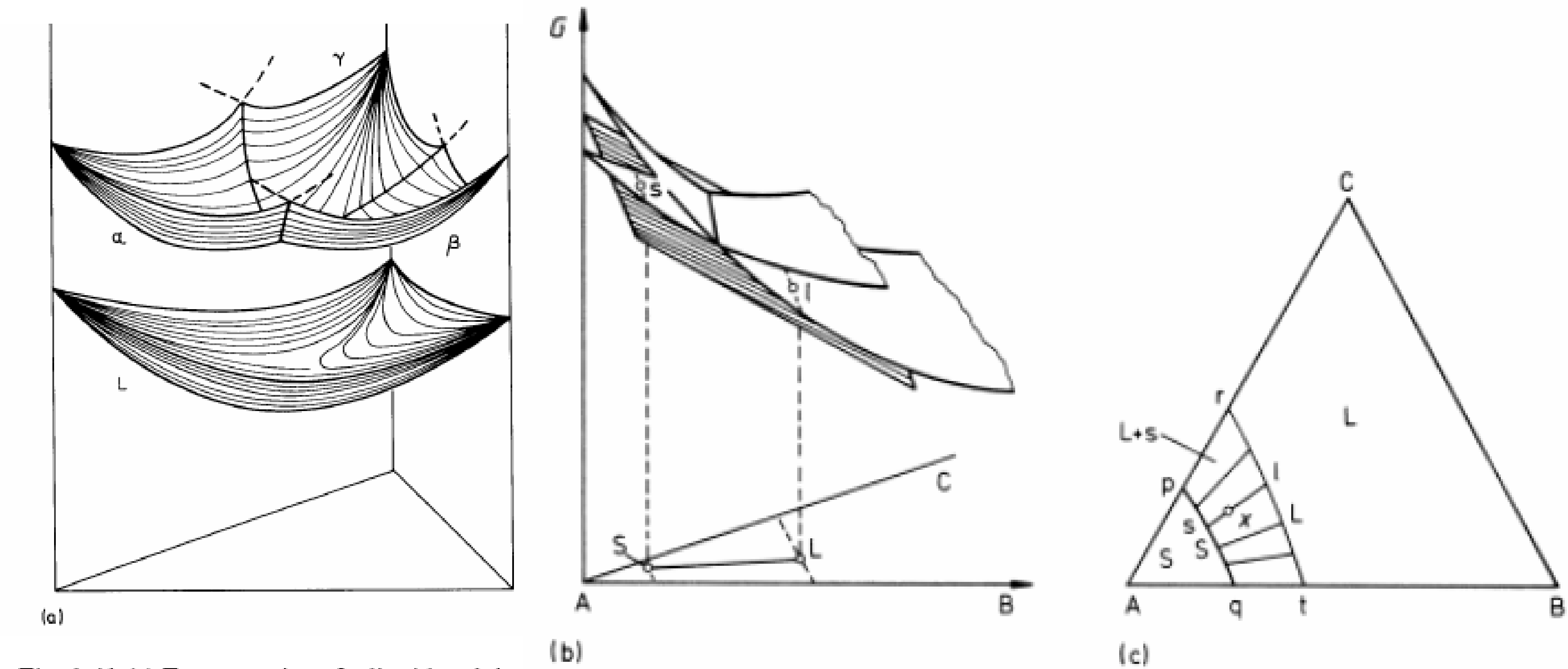
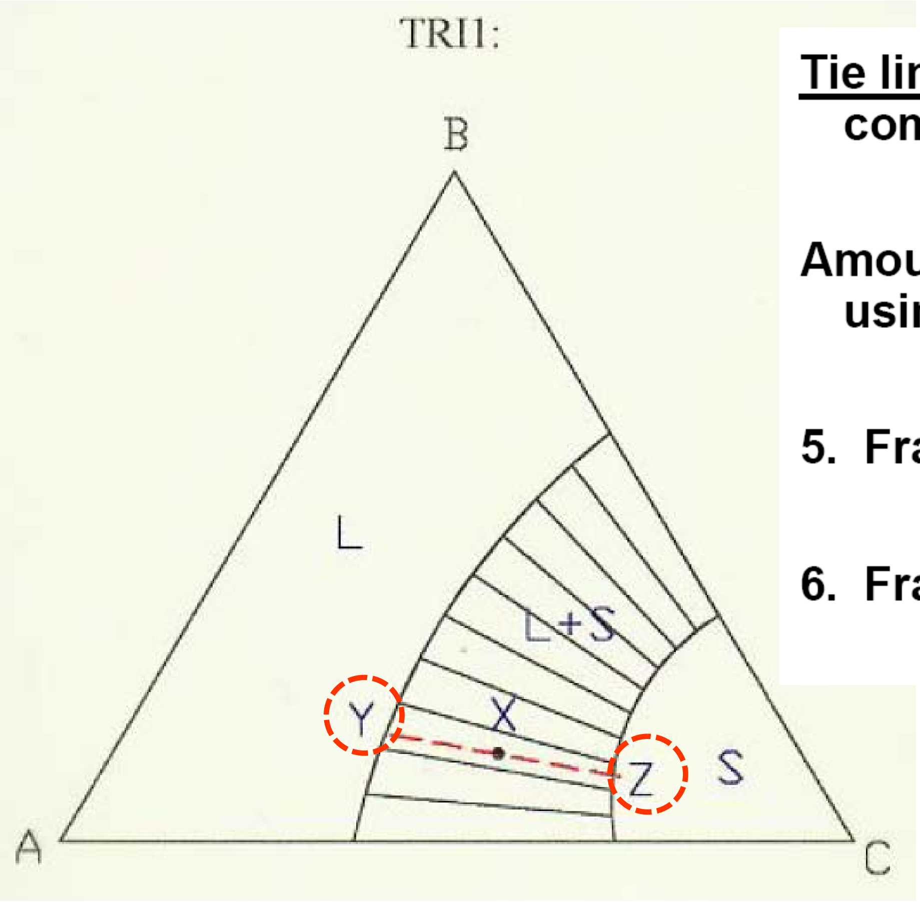


Fig. 1.41 (a) Free energies of a liquid and three solid phases of a ternary system.

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:

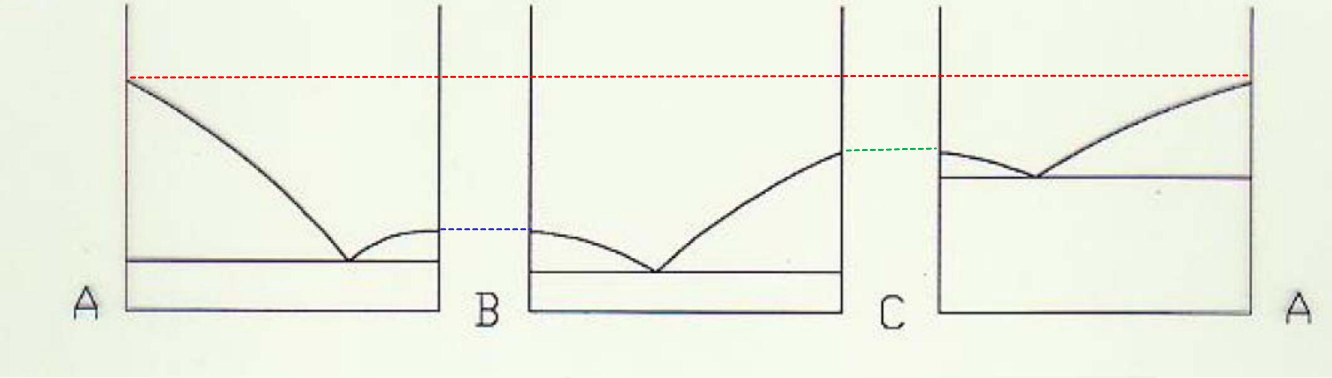
$$L = \alpha + \beta + \gamma$$

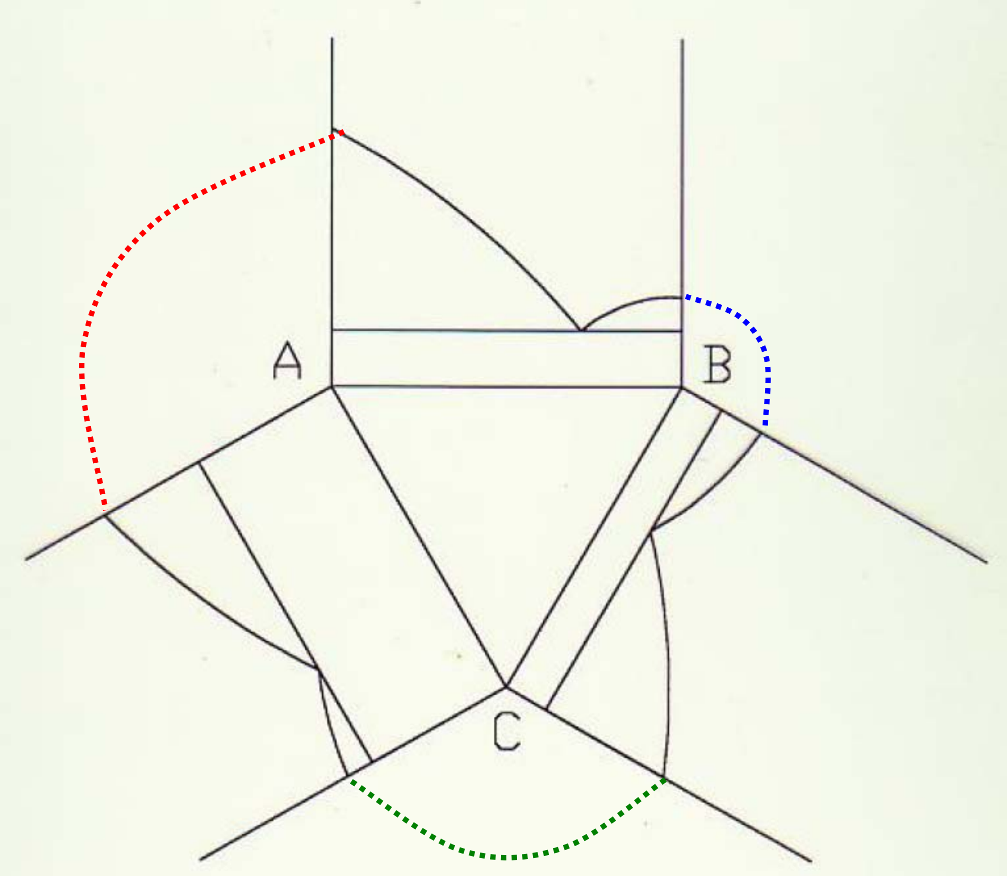
A liquid phase solidifies into three separate solid phases

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

Ternary Eutectic System

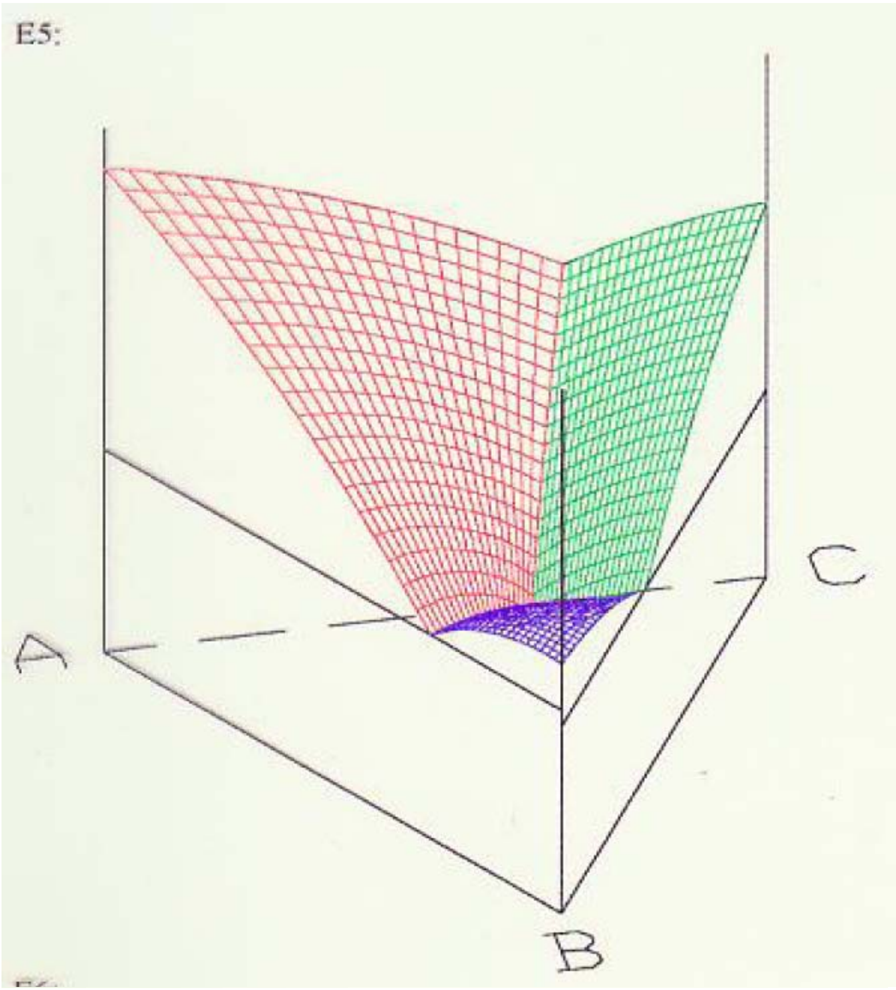
(No Solid Solubility)



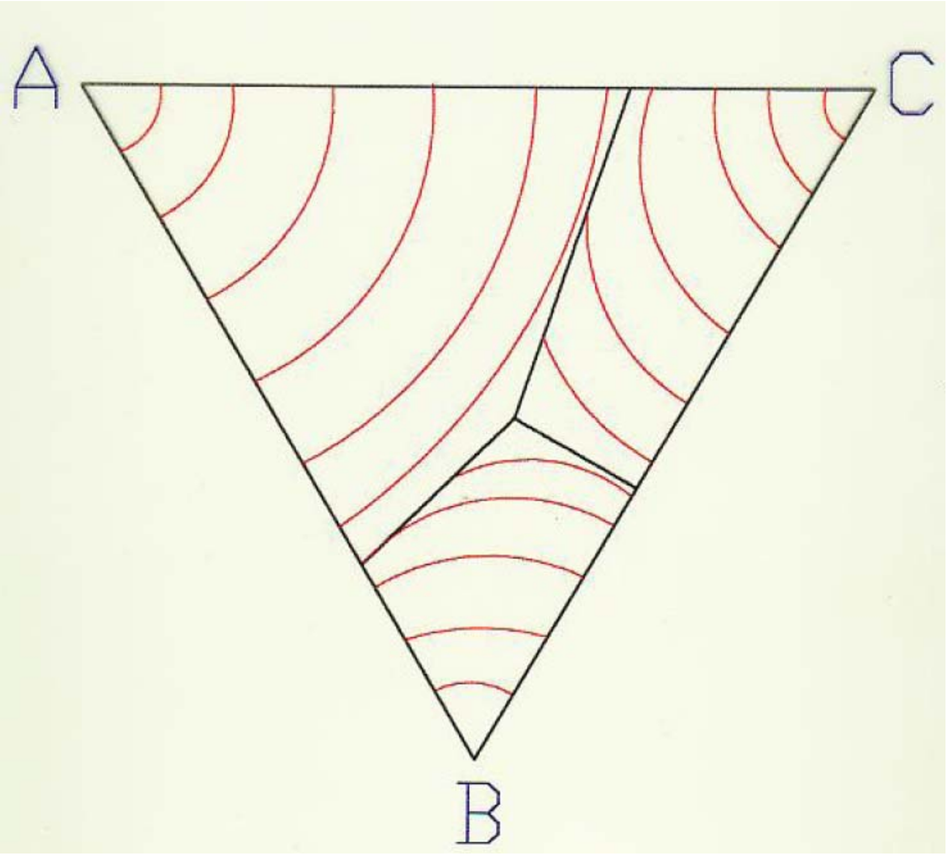


Ternary Eutectic System

(No Solid Solubility)

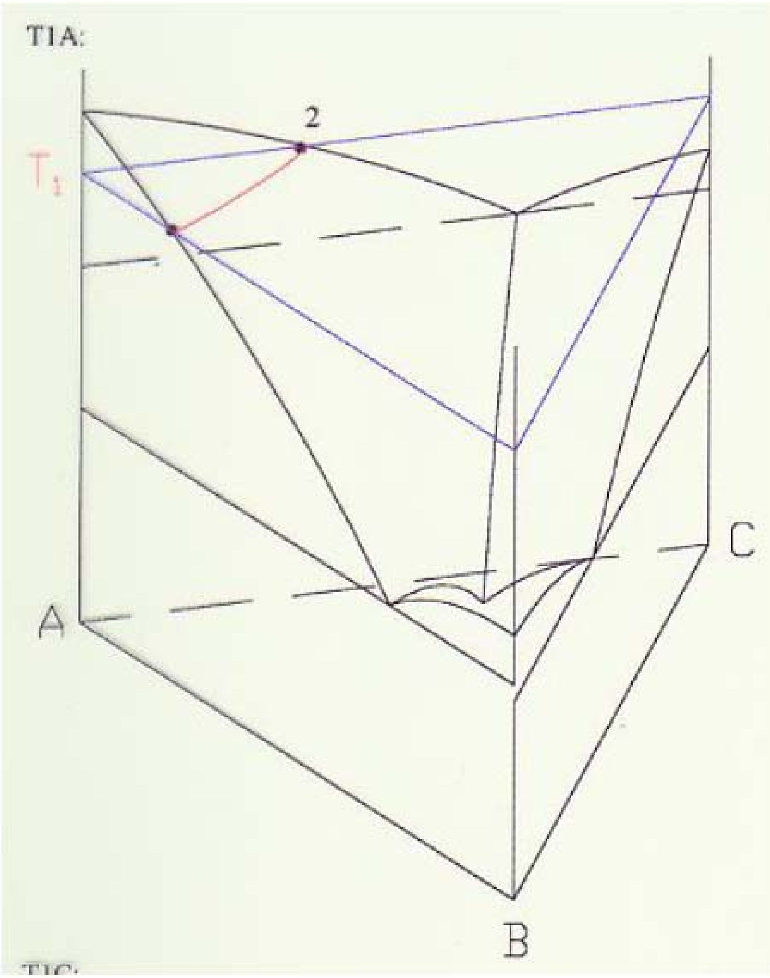


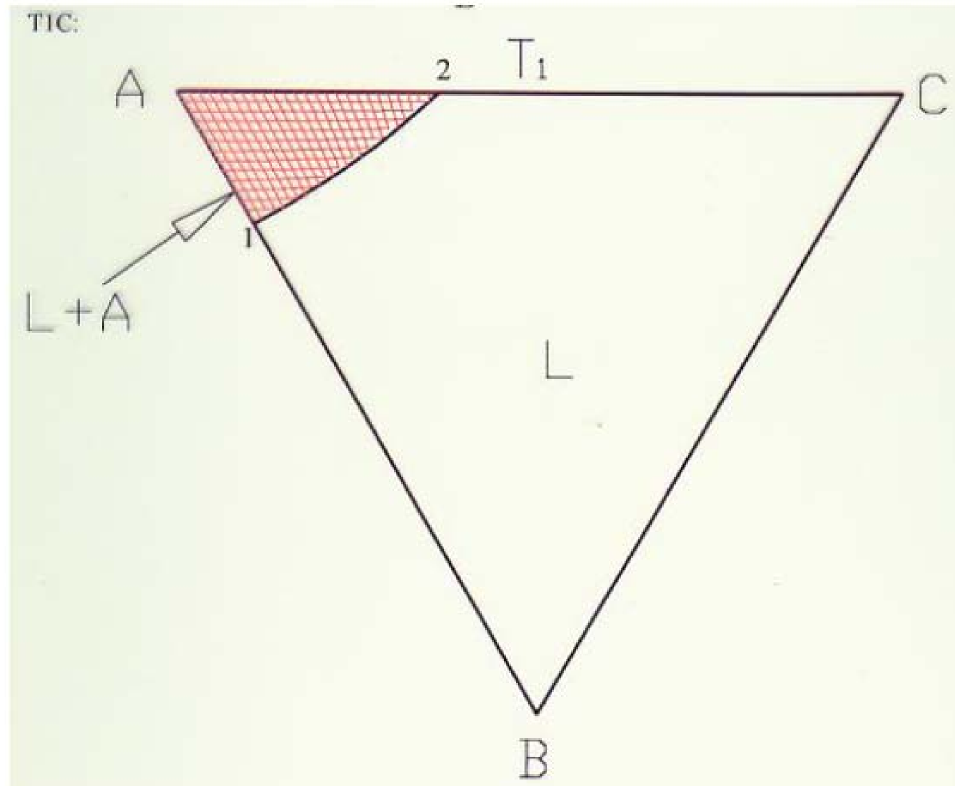
Liquidus projection



Ternary Eutectic System

(No Solid Solubility)





Ternary Eutectic System

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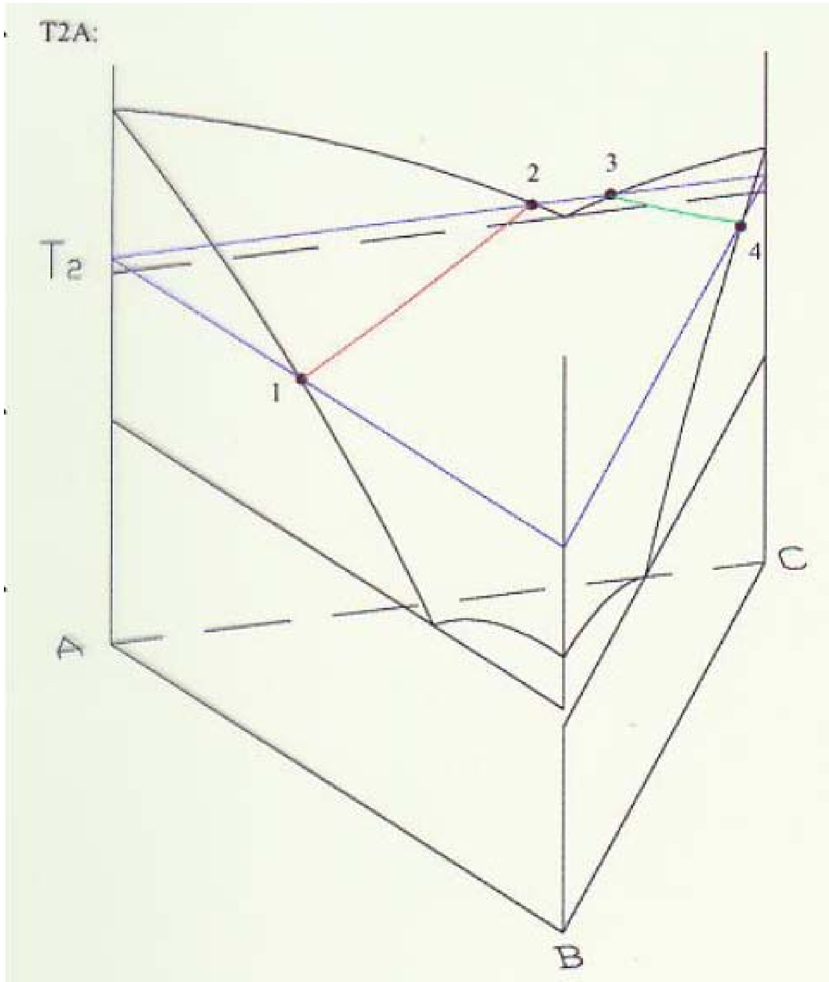
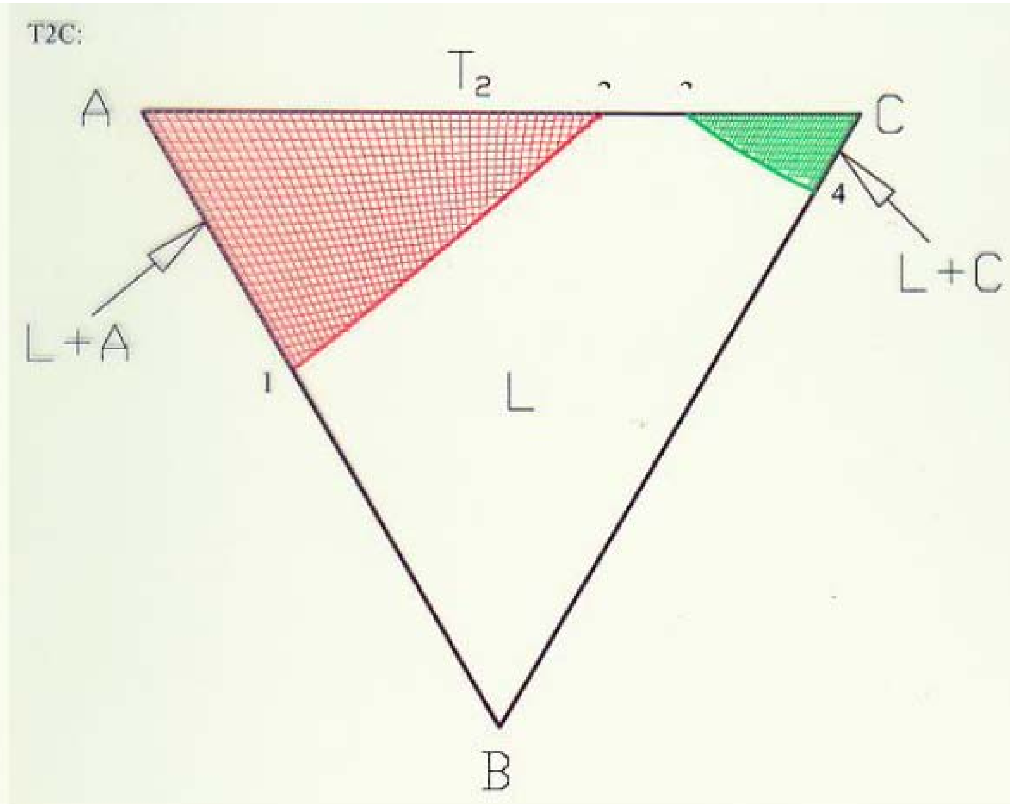
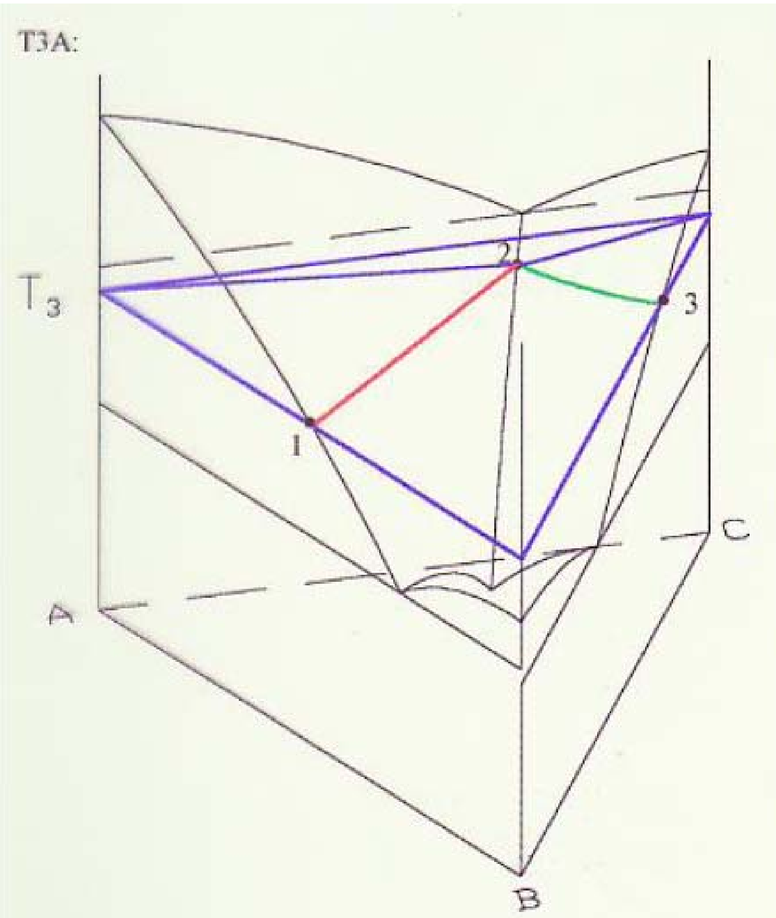
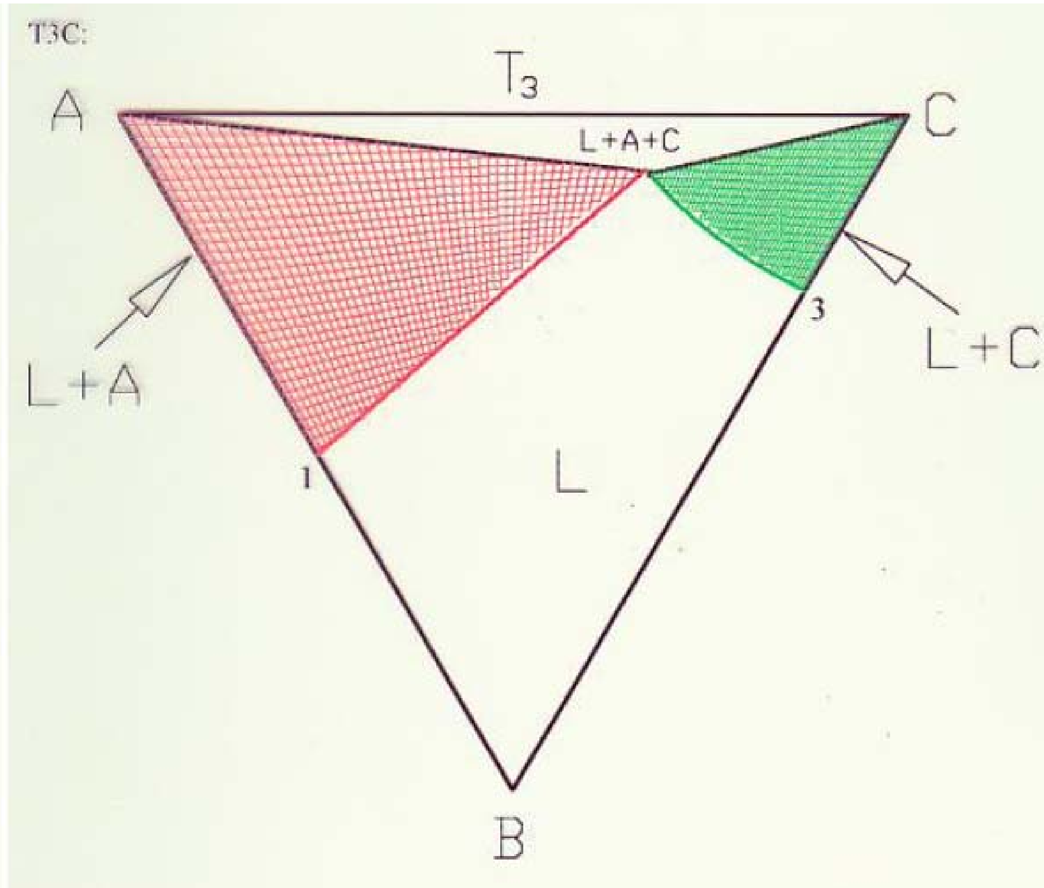




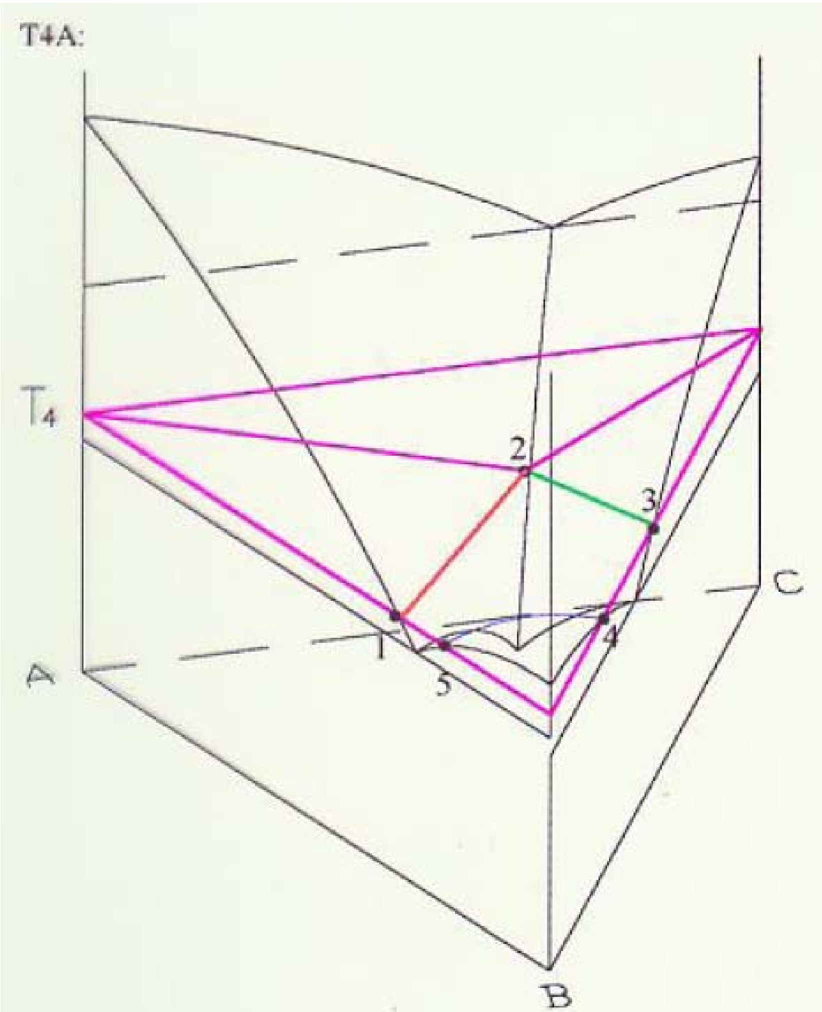
Ternary Eutectic System
(No Solid Solubility)

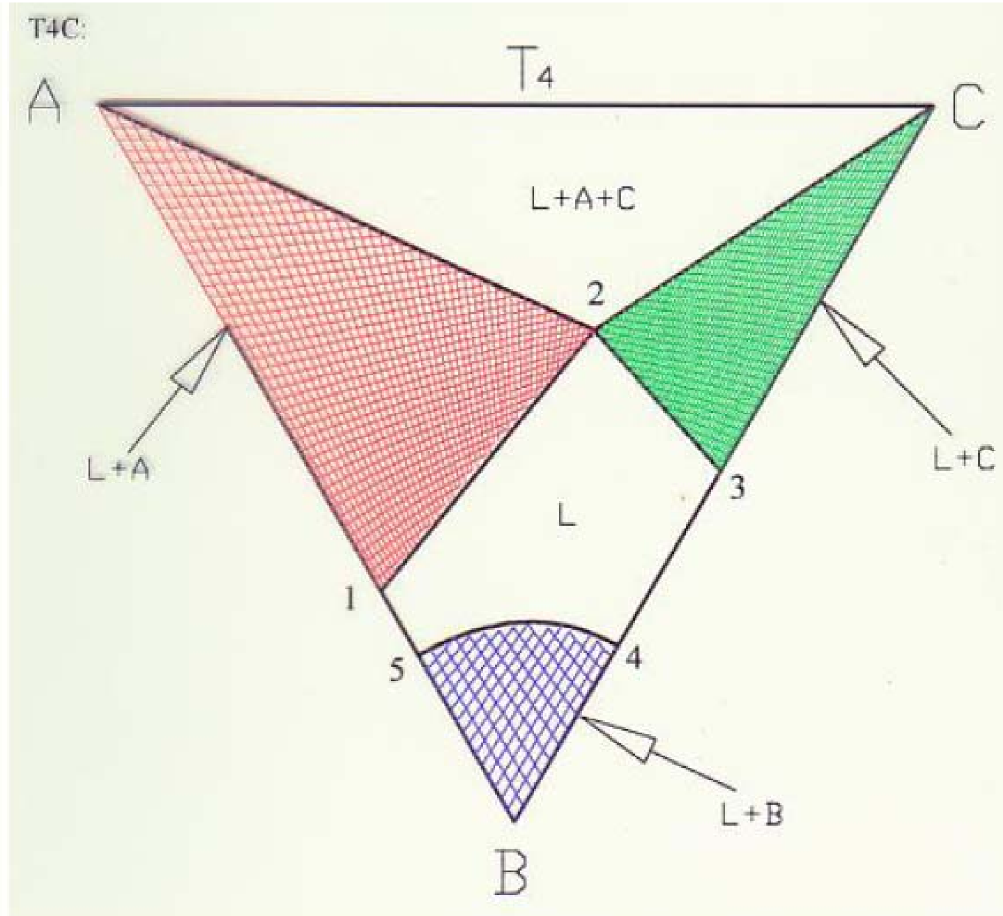




Ternary Eutectic System

(No Solid Solubility)





Ternary Eutectic System
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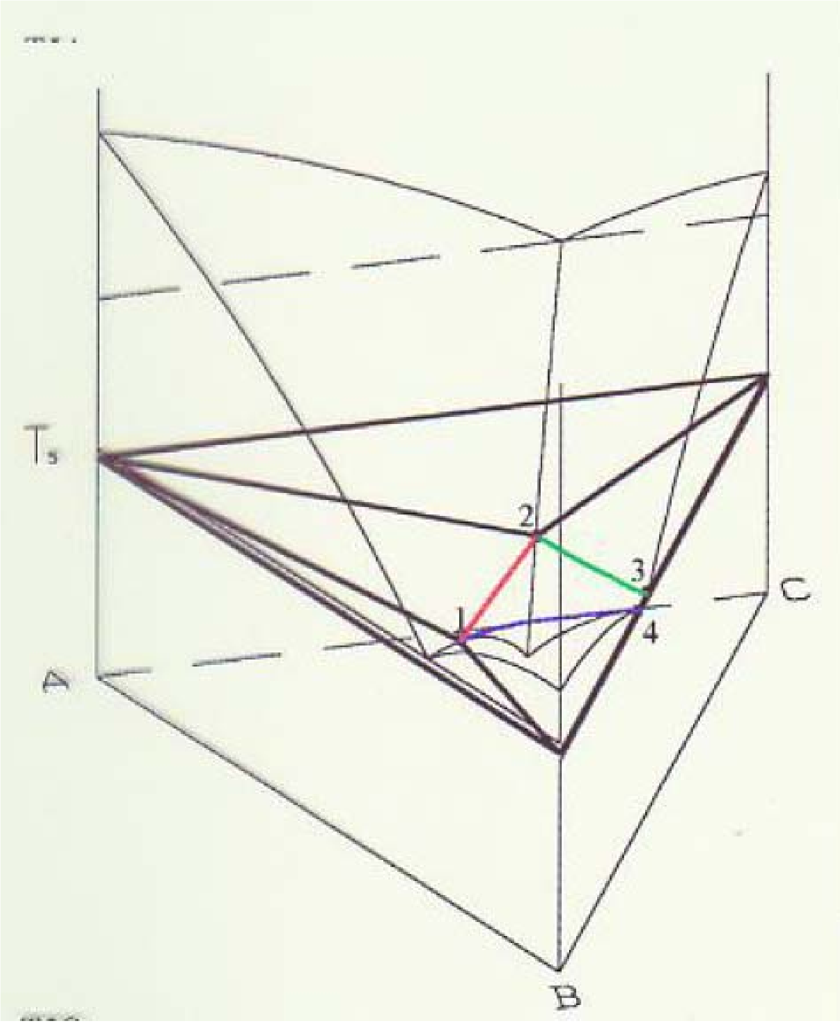
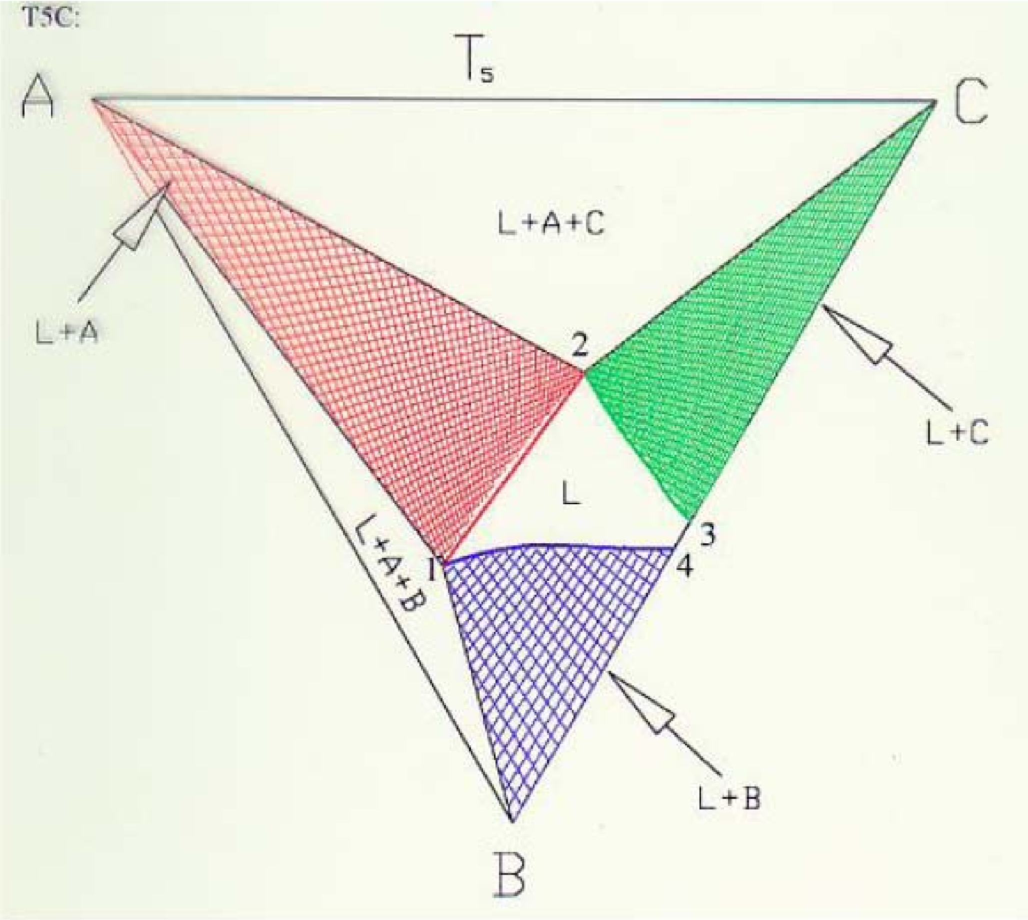
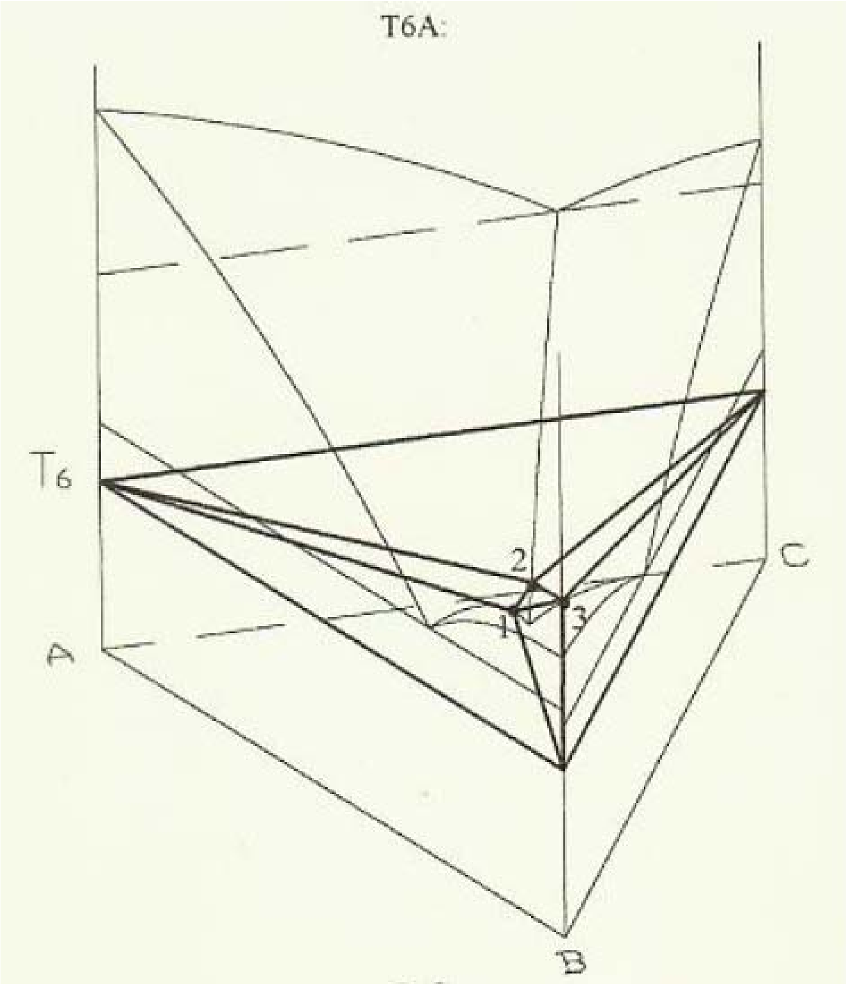
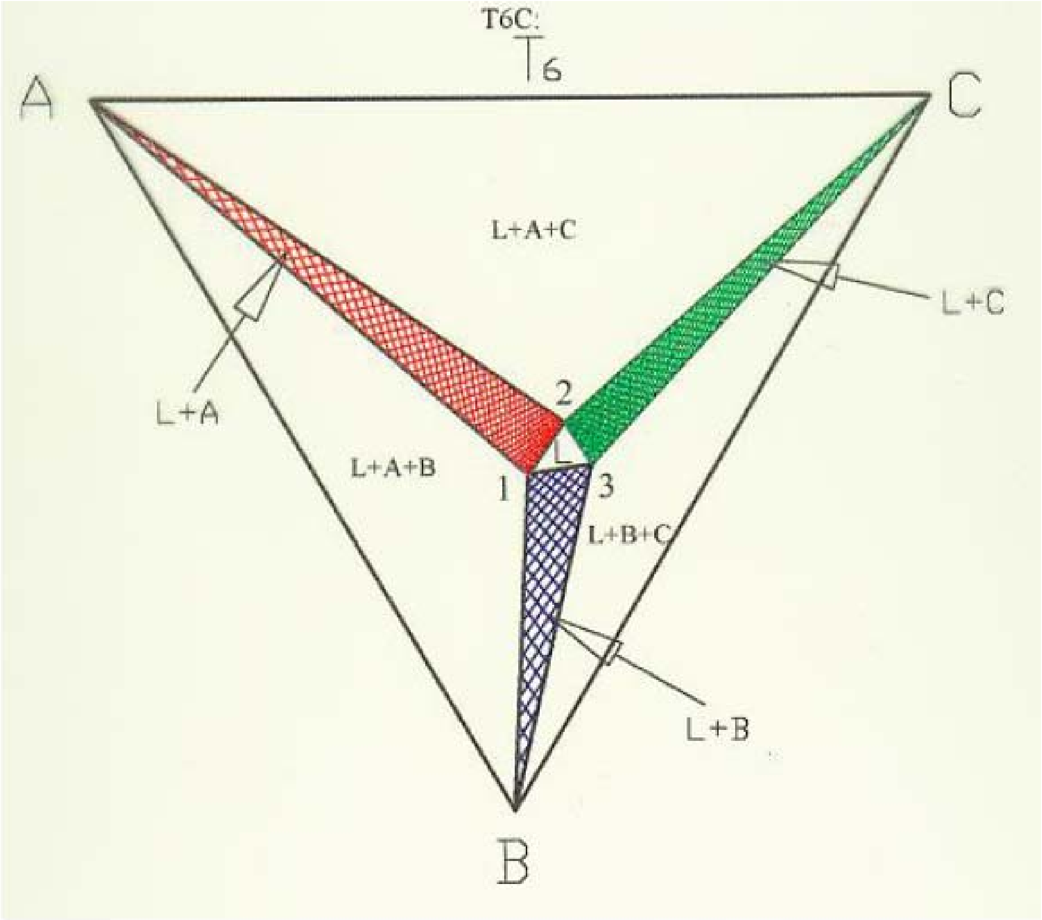




Ternary Eutectic System

(No Solid Solubility)

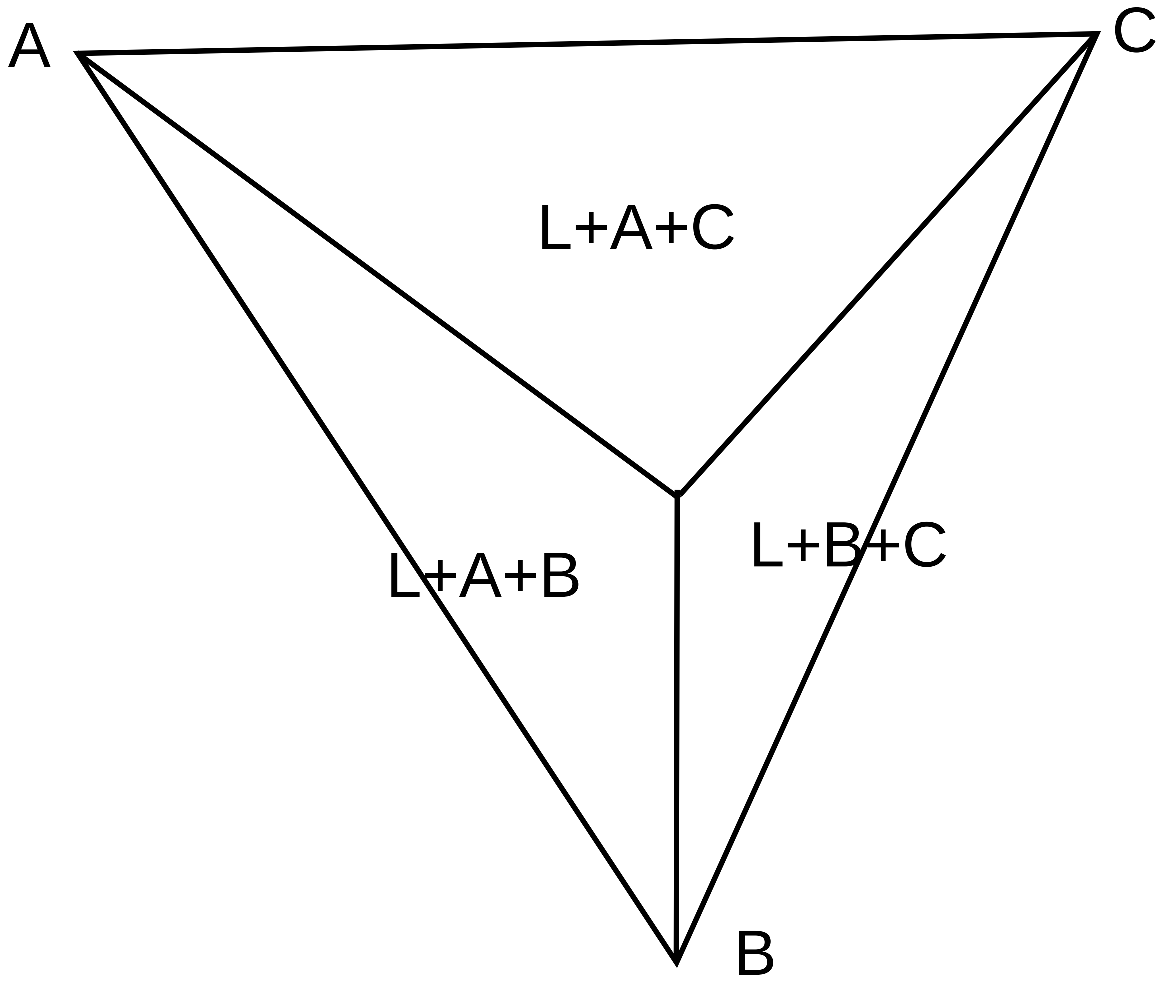




Ternary Eutectic System

(No Solid Solubility)

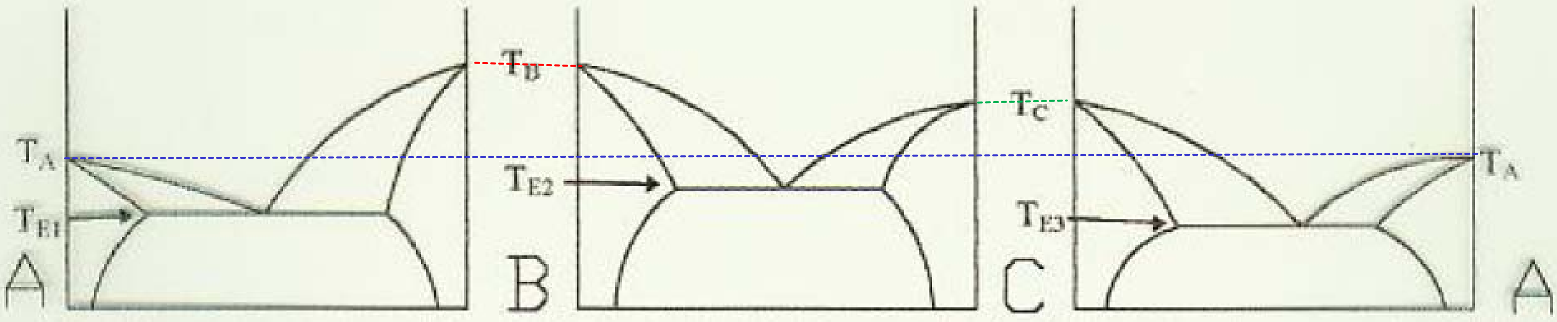
T= ternary eutectic temp.



Ternary Eutectic System

(with Solid Solubility)

P1:



T_A: Melting Point Of Material A

T_B: Melting Point Of Material B

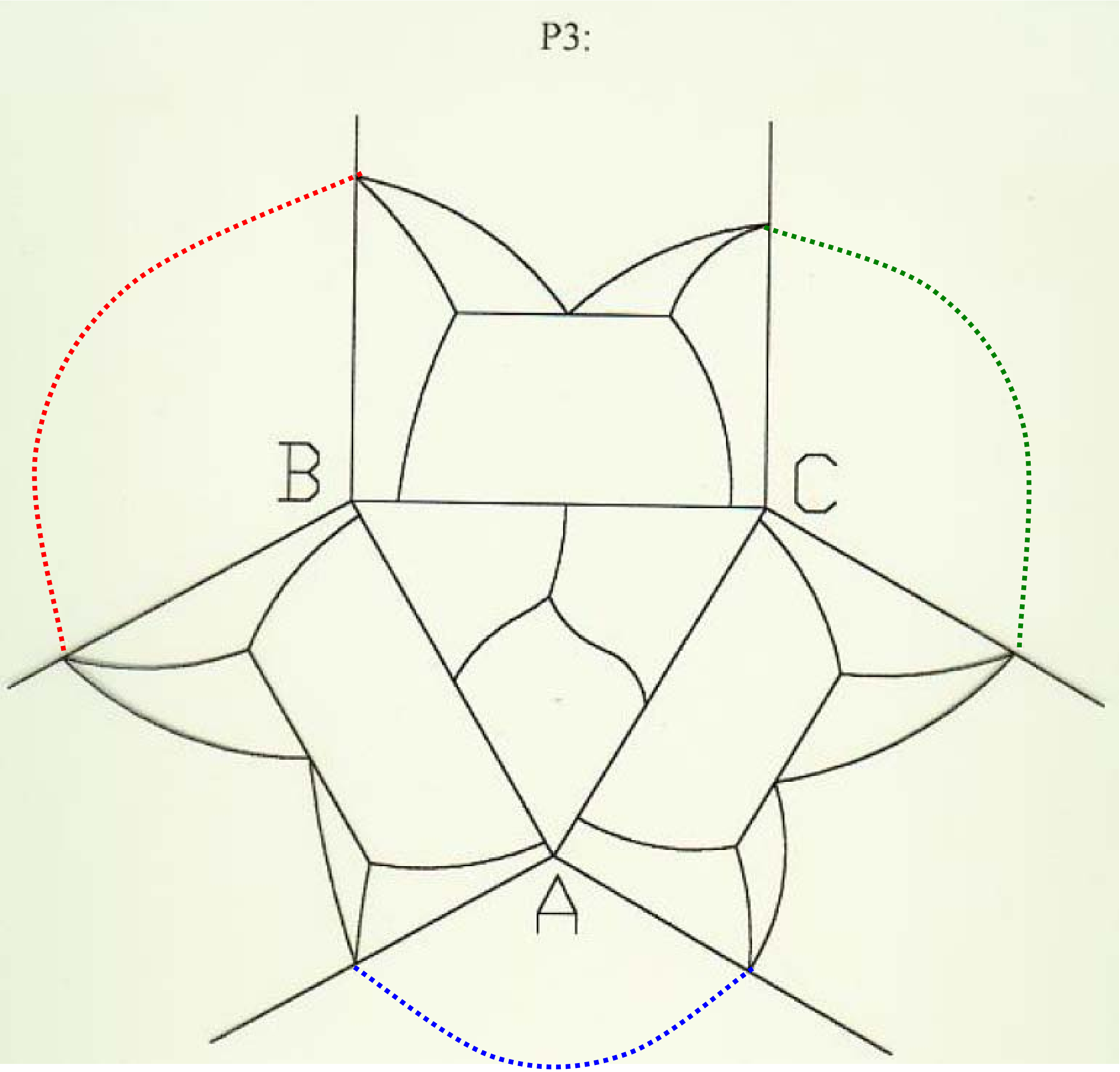
T_C: Melting Point Of Material C

T_{E1}: Eutectic Temperature Of A-B

T_{E2}: Eutectic Temperature Of B-C

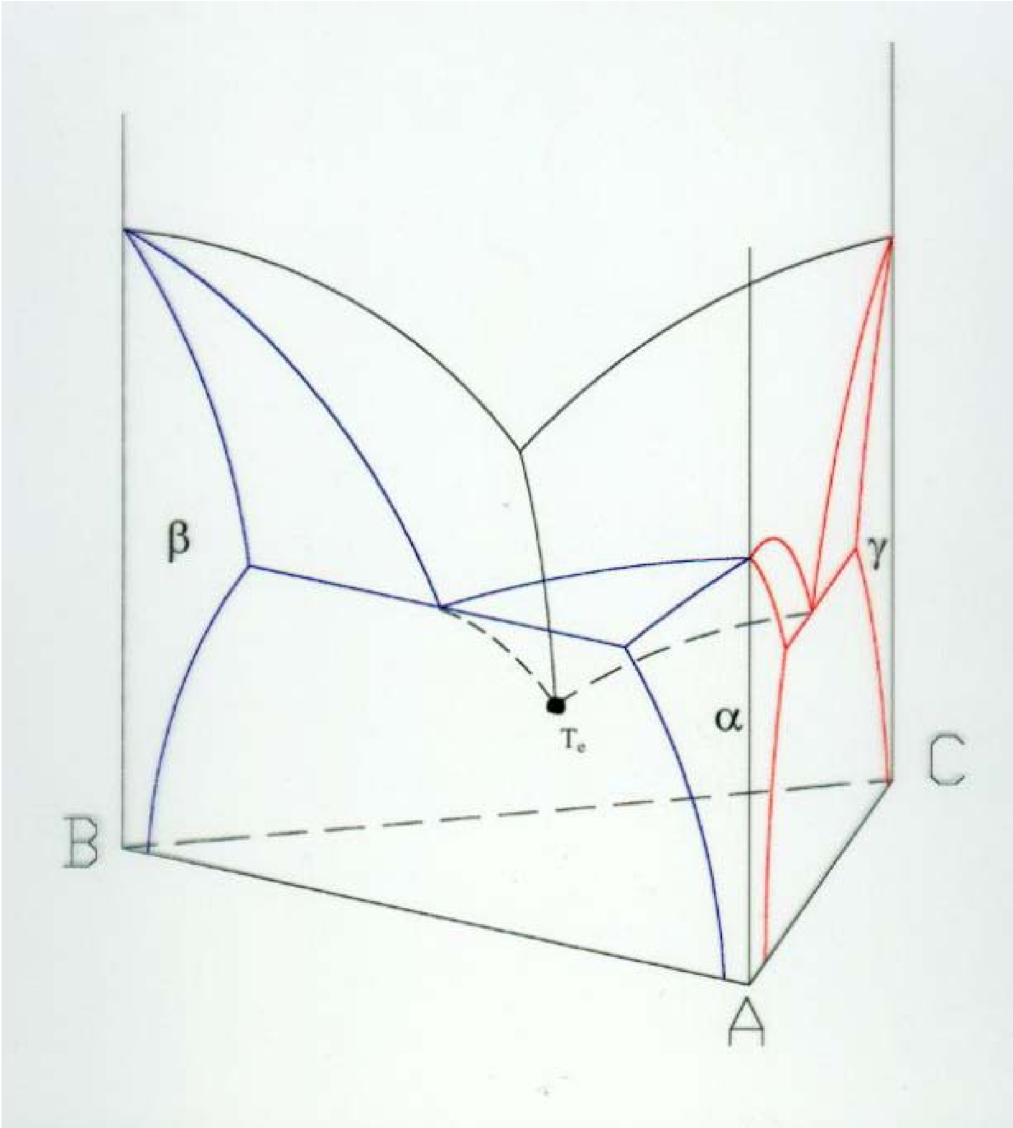
T_{E3}: Eutectic Temperature Of C-A

Ternary Eutectic System
(with Solid Solubility)

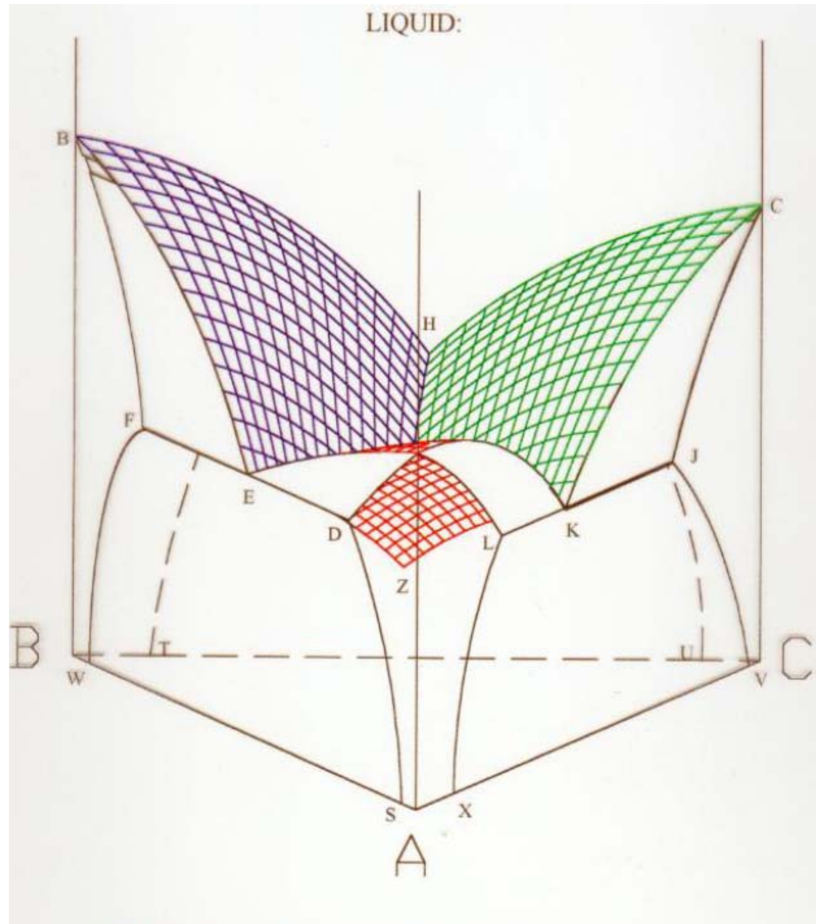


Ternary Eutectic System

(with Solid Solubility)

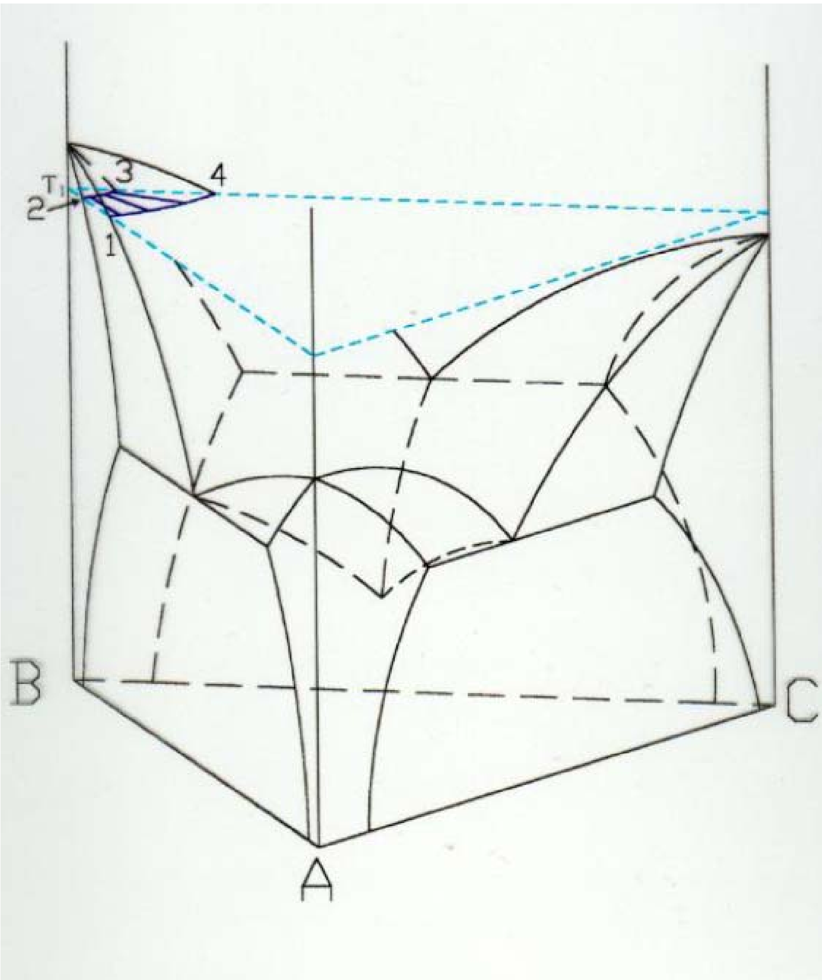


Main outline of Ternary Phase Diagram with Ternary Eutectic (T_e) and Solid Single Phase Regions Shown

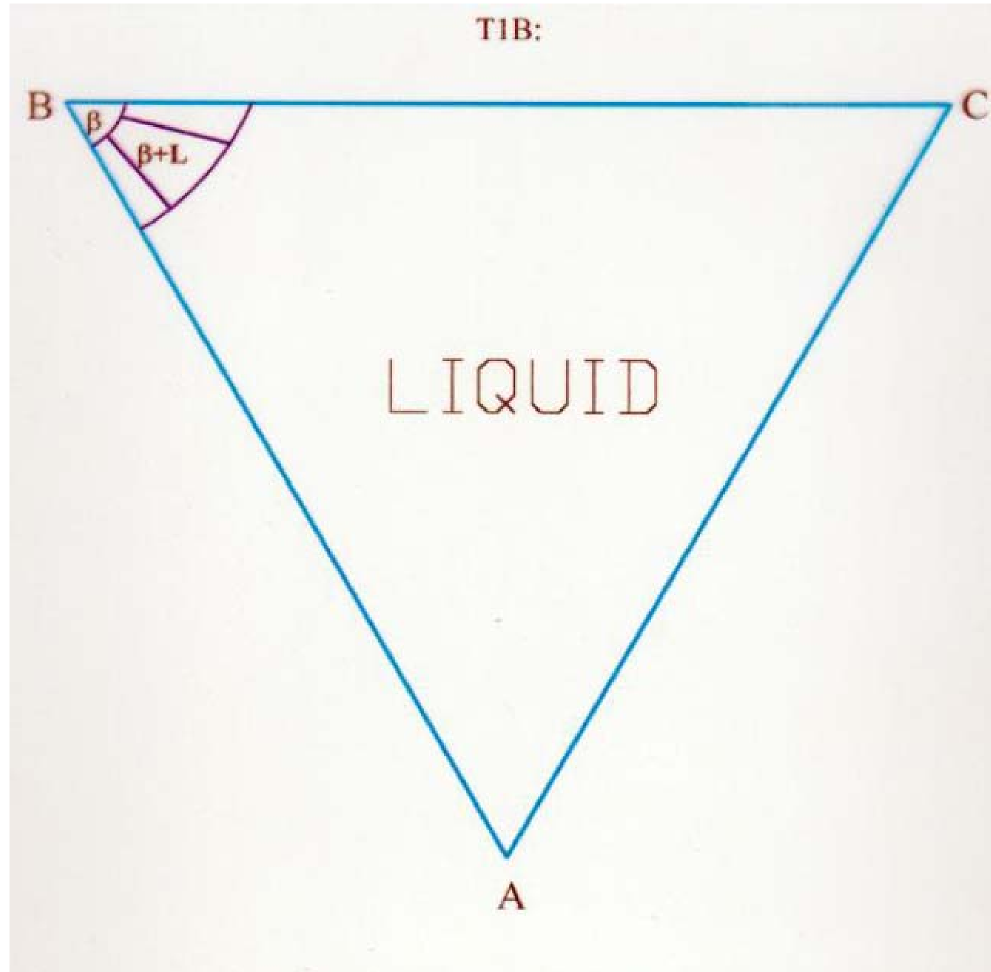


All Liquidus surfaces (α+L-Red, β+L-Purple, γ+L-Green)

Ternary Eutectic System
(with Solid Solubility)

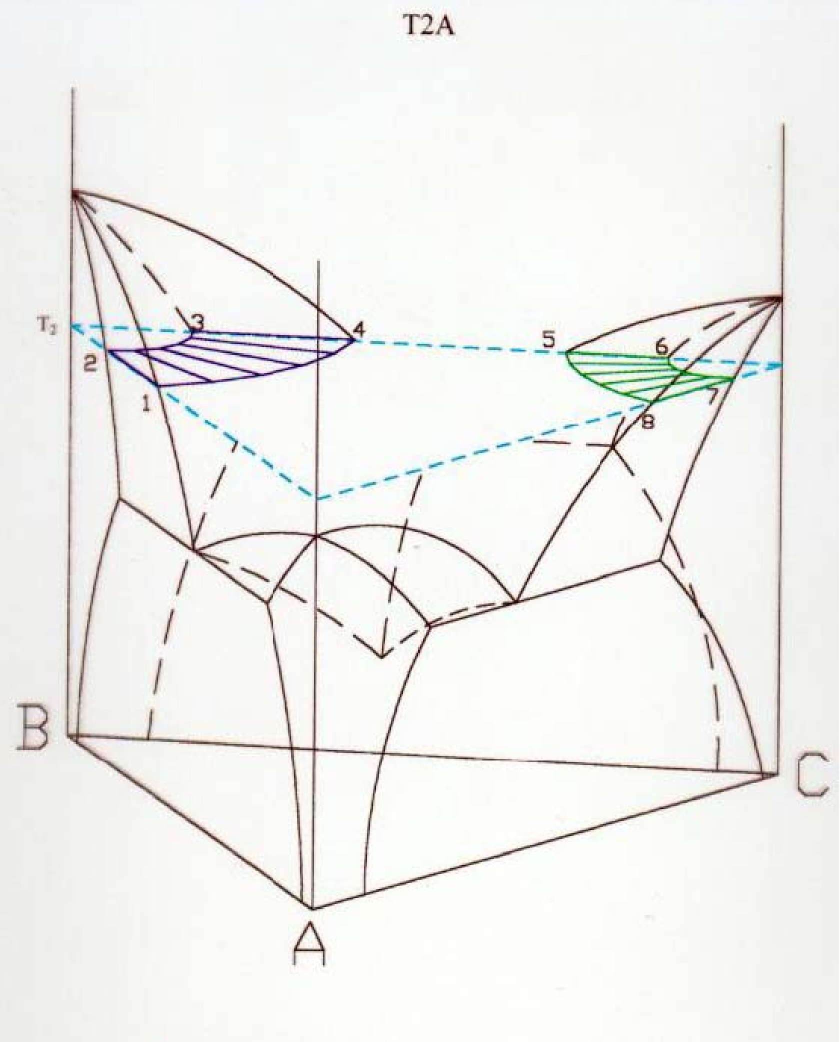


Temperature Slice At $T_1 < T_B$, But $> T_A$, T_C

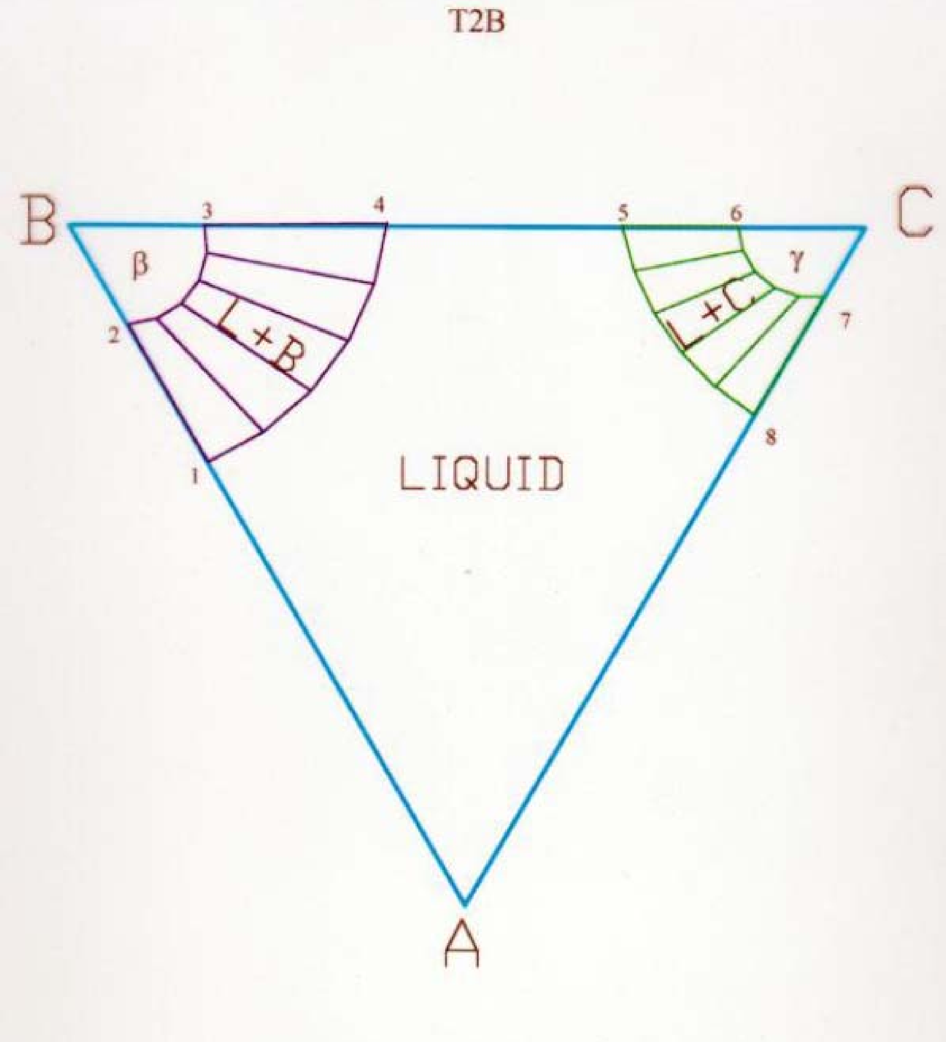


Isothermal Section At $T = T_1$

Ternary Eutectic System
(with Solid Solubility)

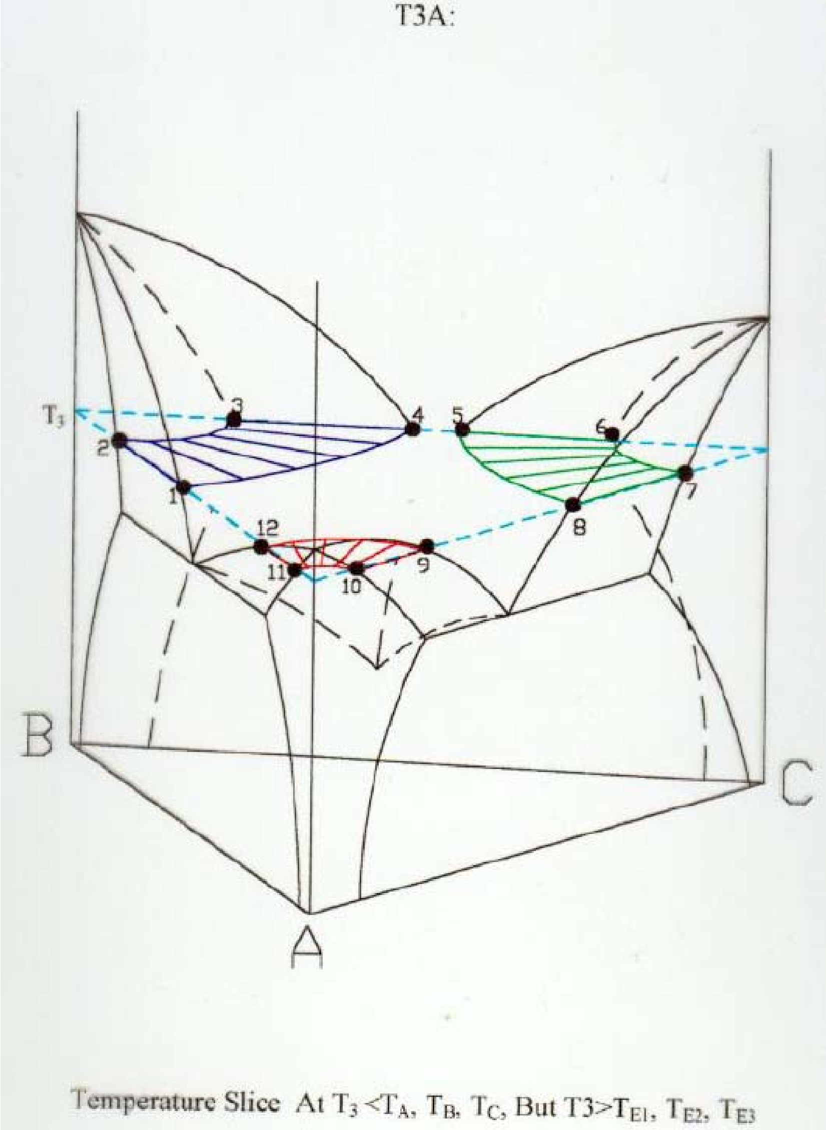


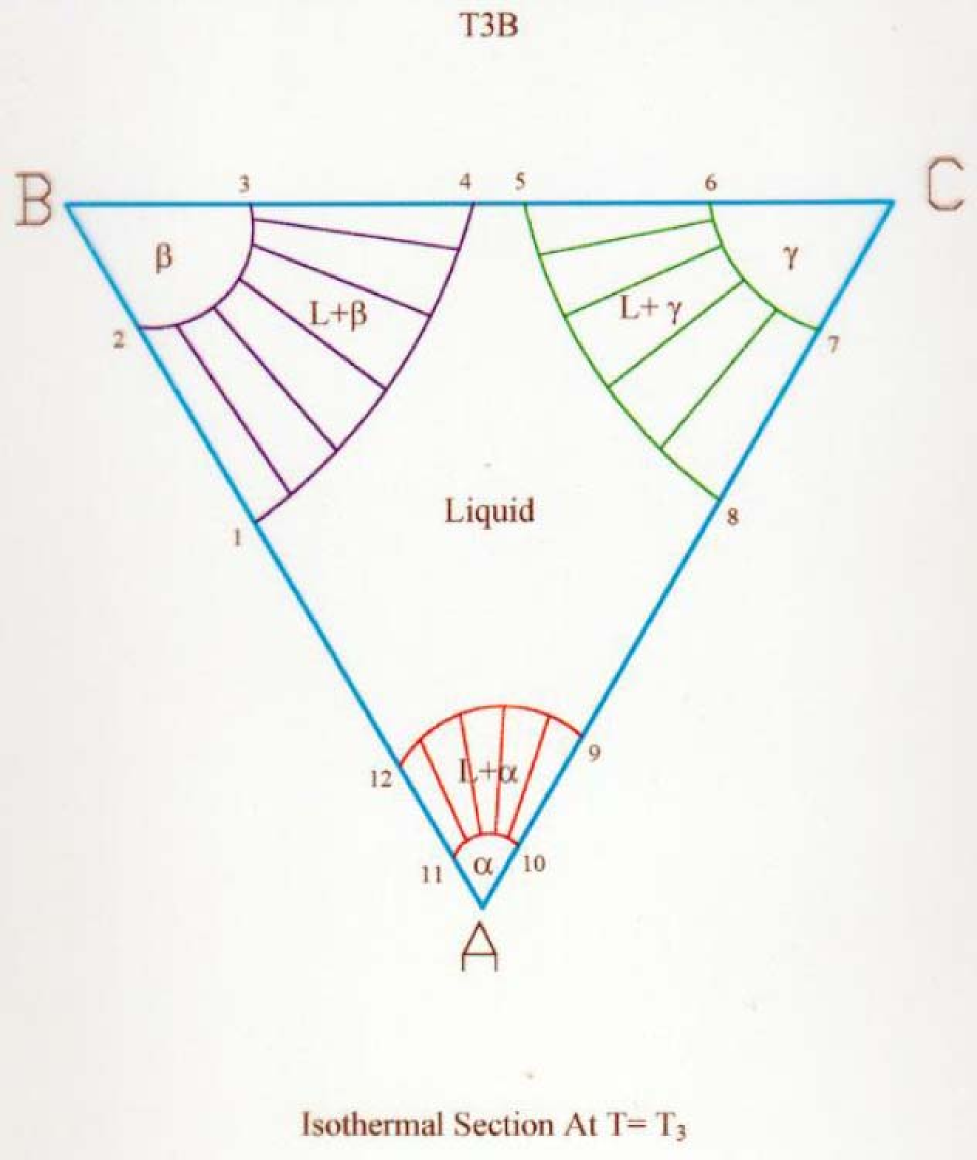
Temperature Slice At $T_2 > T_A$ But, $T_2 < T_B$, T_C



Isothermal Section At $T = T_2$

Ternary Eutectic System
(with Solid Solubility)

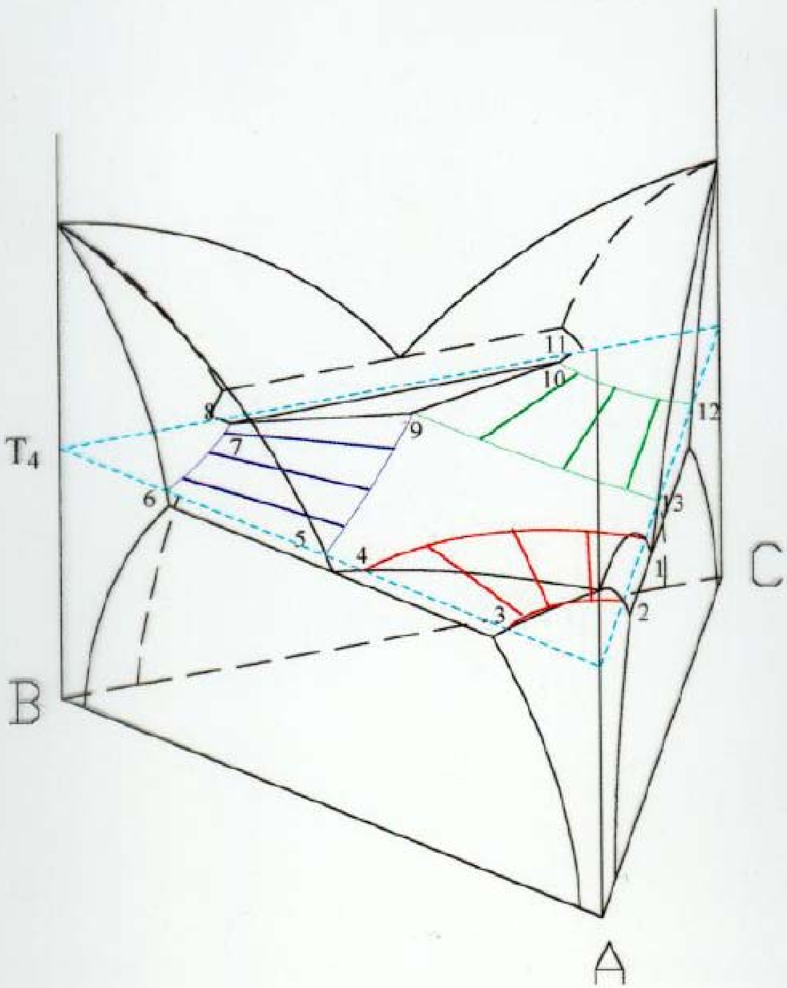




Ternary Eutectic System

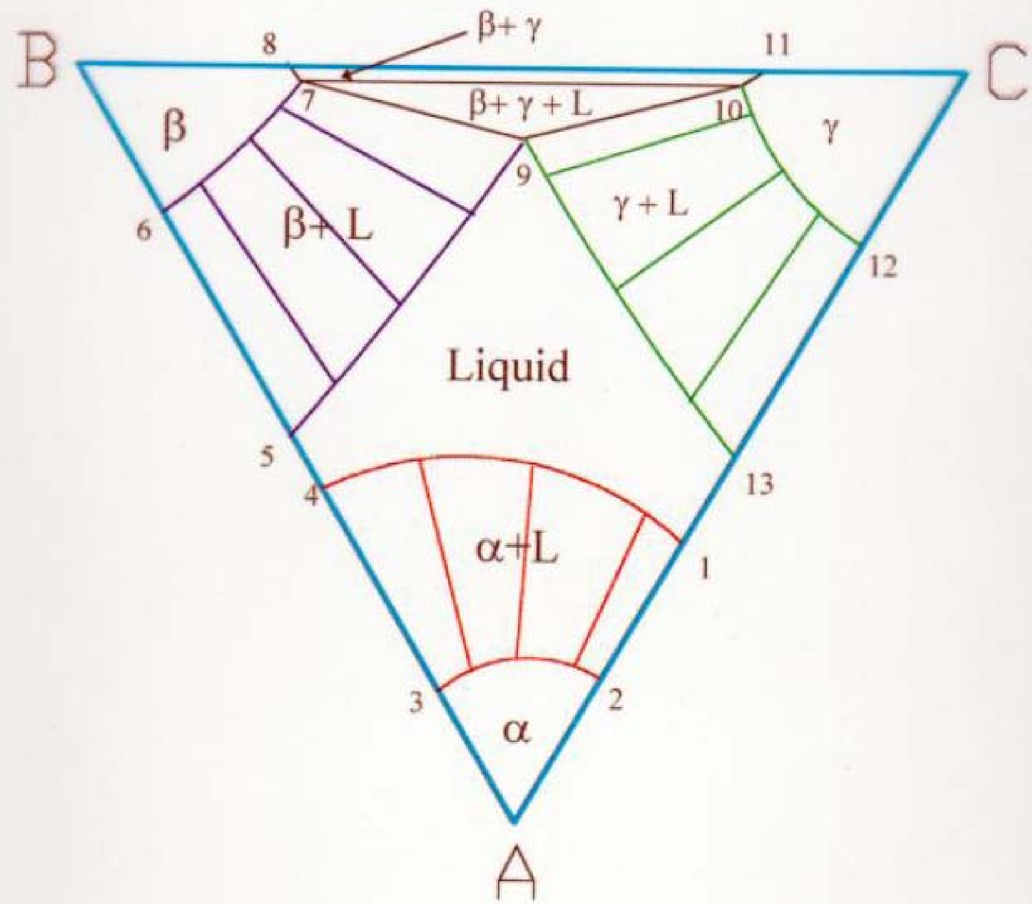
(with Solid Solubility)

T4A:



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

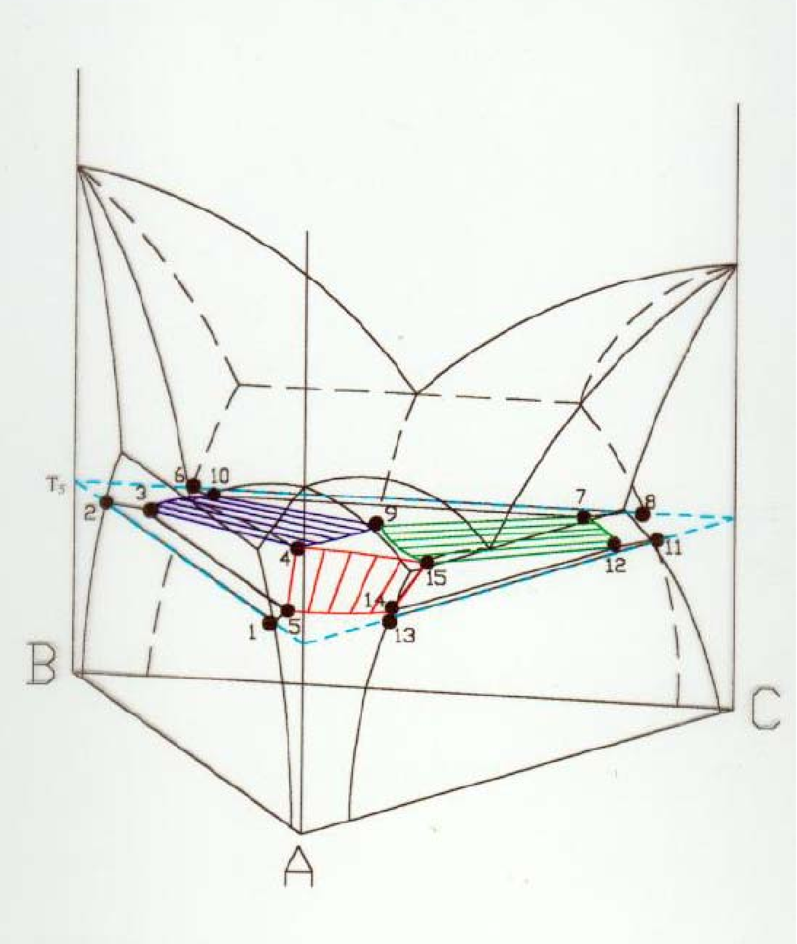
T4B:



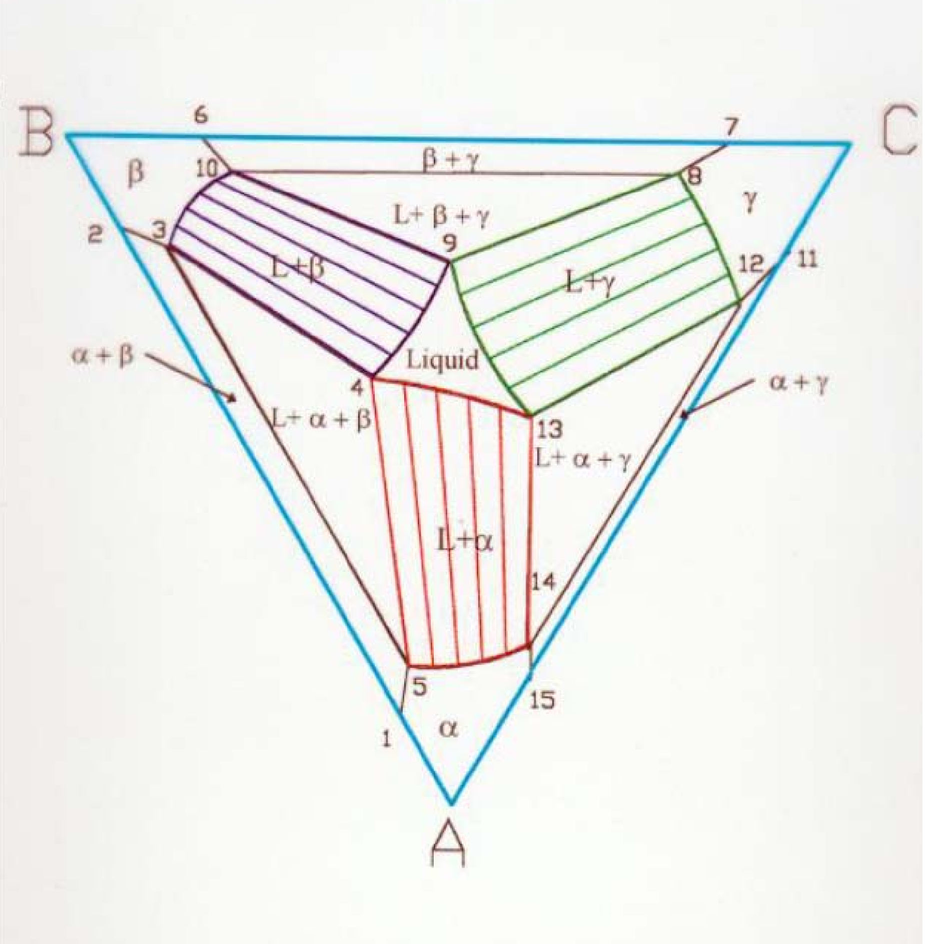
Isothermal Section At $T = T_4$

Ternary Eutectic System

(with Solid Solubility)



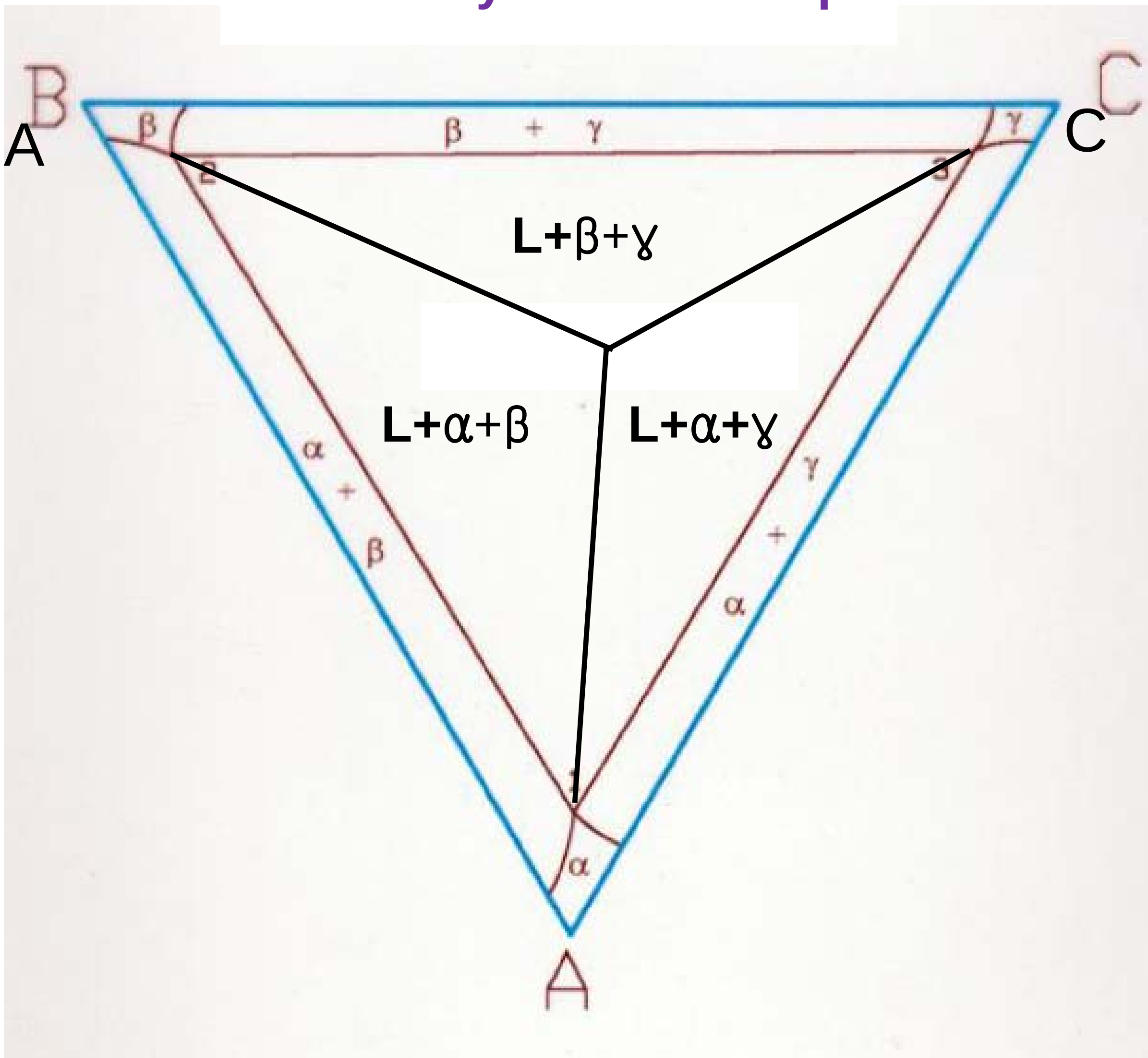
Temperature Slice Below All Binary Eutectics But, Above The Ternary Eutectic



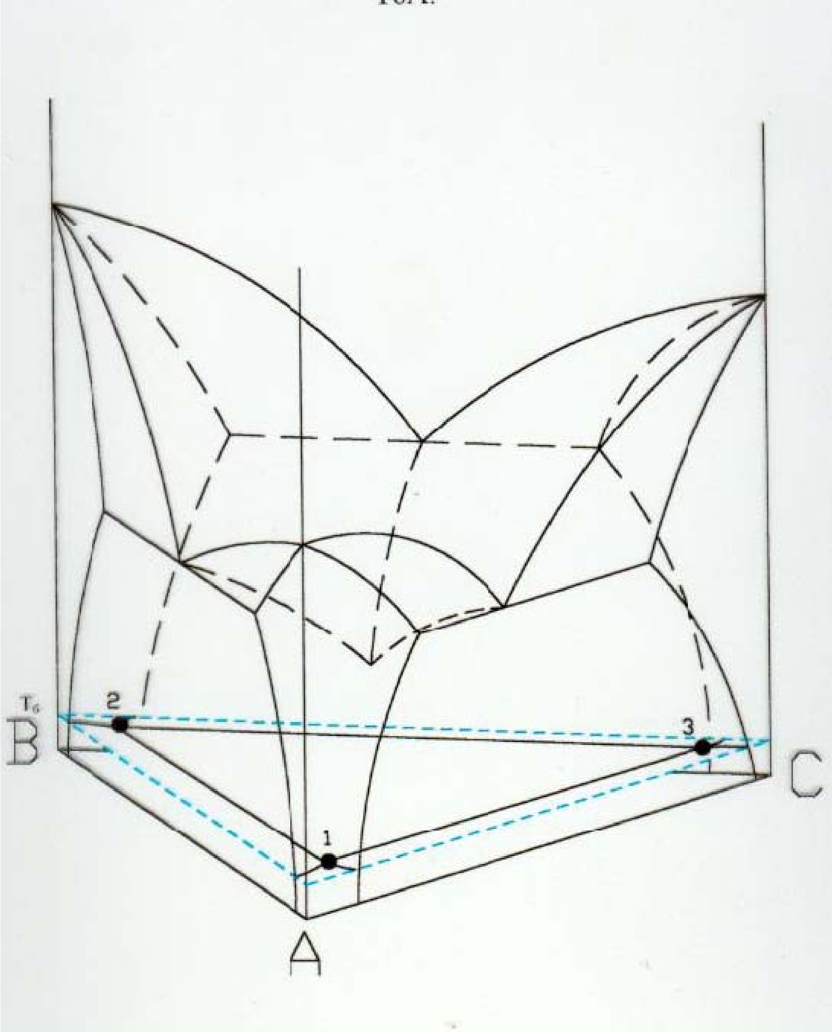
Isothermal Section At $T=T_5$

Ternary Eutectic System
(with Solid Solubility)

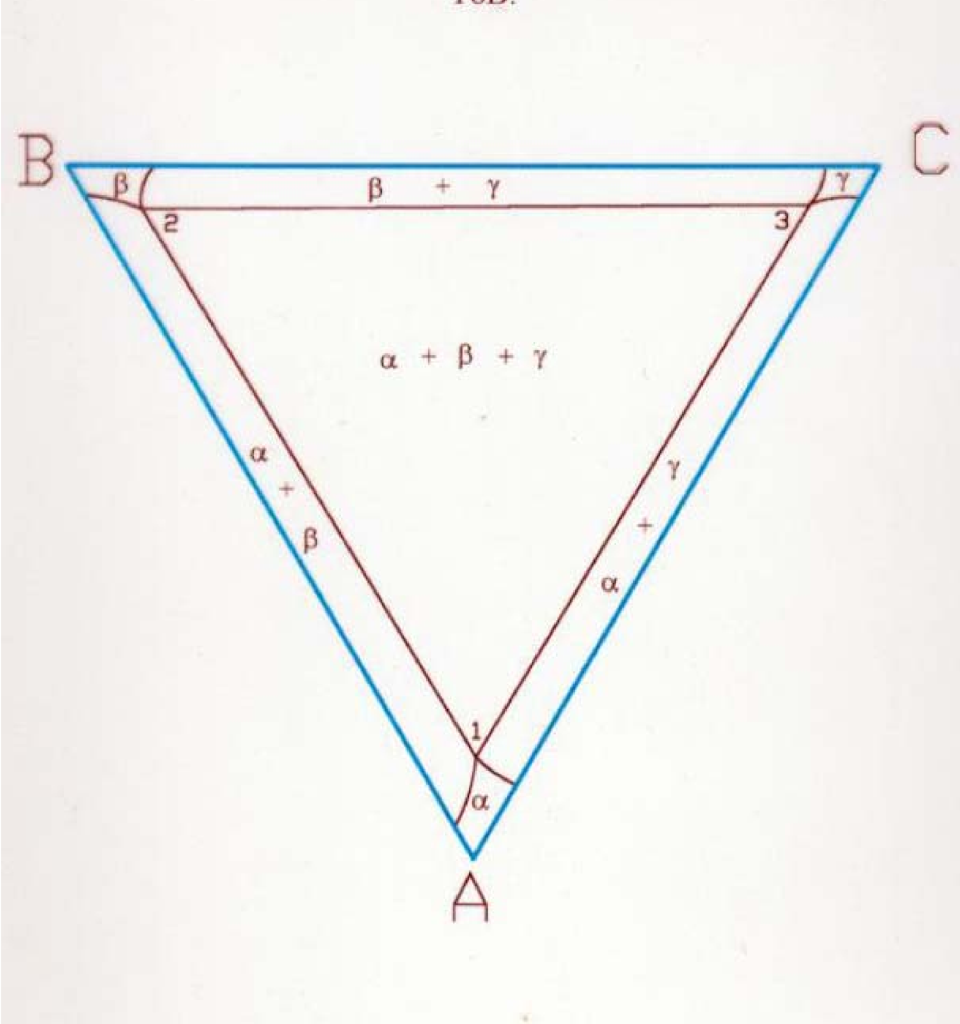
T= ternary eutectic temp.



Ternary Eutectic System
(with Solid Solubility)



Temperature Slice at $T_6 < T_E$



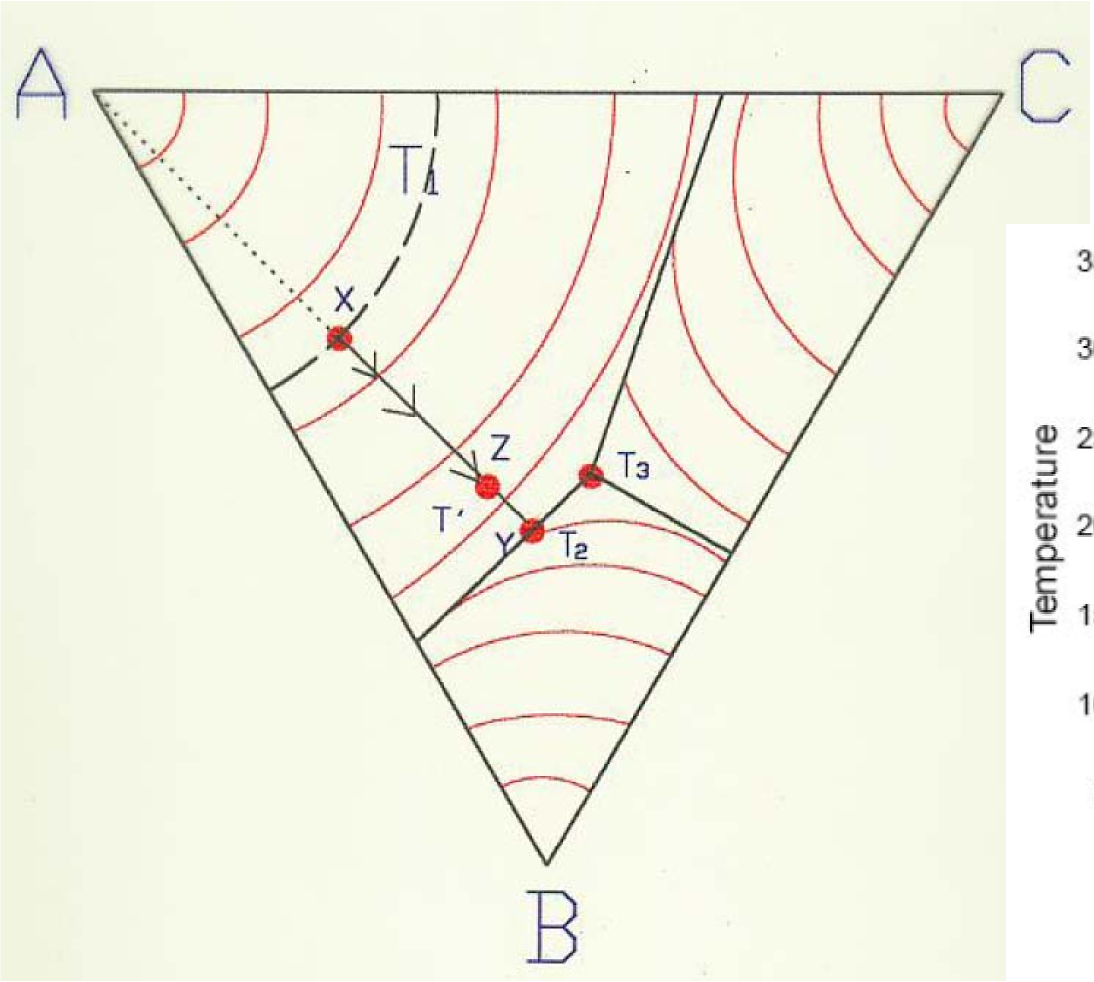
Isothermal Section At $T=T_6$

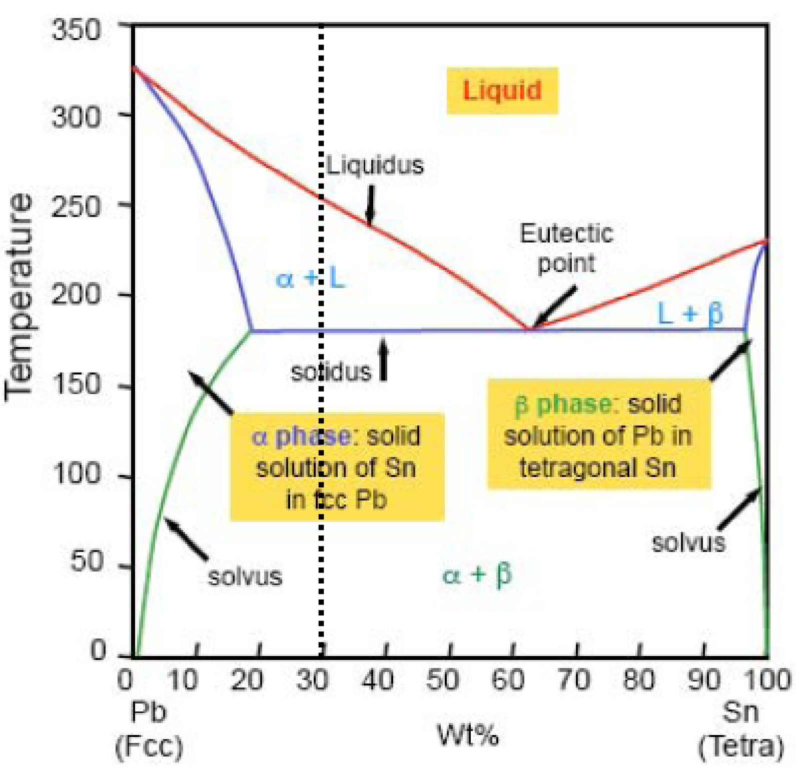
정해솔 학생 제공 자료 참조: 실제 isothermal section의 온도에 따른 변화

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

Ternary Eutectic System

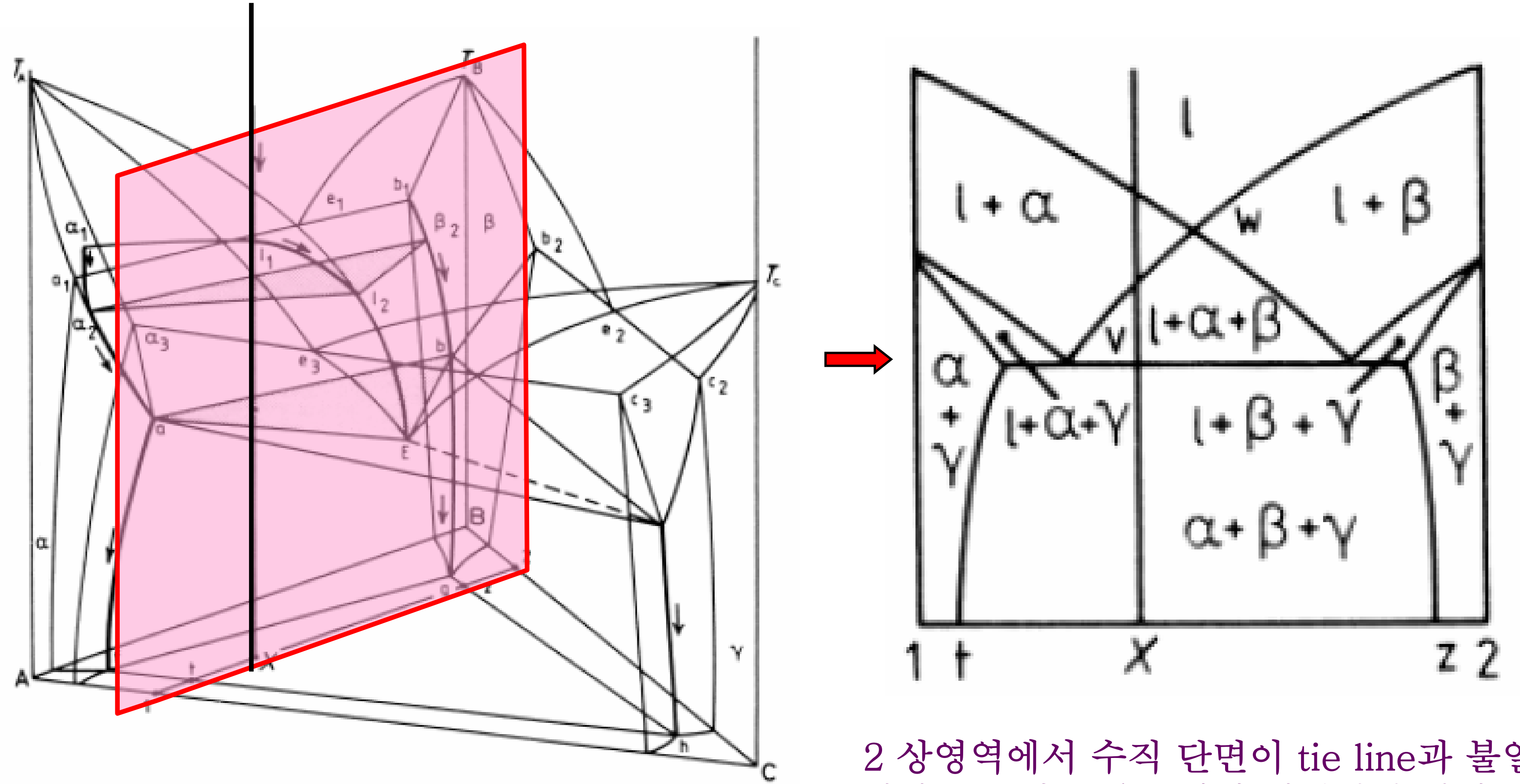
Solidification Sequence





Ternary Eutectic System

Solidification Sequence



2 상영역에서 수직 단면이 tie line과 불일치하므로 다른 온도에서 평형상만 나타내고 조성은 표시할 수 없음.

Quarternary의 평형상태를 기하학적으로 표시한 그림

4성분원소들 가운데서 임의의 3성분의 농도가 독립적으로 변할 수 있는 함수이므로 여러가지 조성의 Quar-ternary alloy은 공간적으로 표시된다. 3원계의 조성은 정4면체의 면상에, 그리고 4원계 합금의 조성은 정4면체의 내부공간에 표시된다. 합금의 조성은 정4면체의 기하학적성질에 의하여 결정된다. 4원계에서 상조성을 결정하기 위하여 lever rule을 이용한다. 4원합금의 변태과정을 고찰할 때 정4면체안의 추상적인 4차원 투영을 이용한다.