2020 Spring

Advanced Solidification

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Chapter 1 Introduction of Solidification

Melting and Crystallization are Thermodynamic Transitions

(1st order transition)

Melting Temp. (T_m) $\Delta G = 0$ 1) G_L versus G_S 2) Interfacial free energy

↕

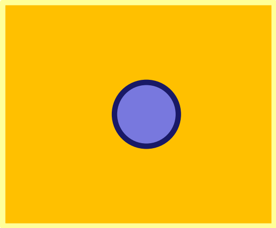
Glass transition is kinetic Transitions

(pseudo 2nd order transition)

Glass transition (T_g) "Internal" time scale ≈ "external" time scale

Melting and Crystallization are Thermodynamic Transitions

Solidification: Liquid → Solid



<Thermodynamic>

- Interfacial energy ⇨ ΔT_N

Liquid T_m Undercooled Liquid Solid

No superheating required!

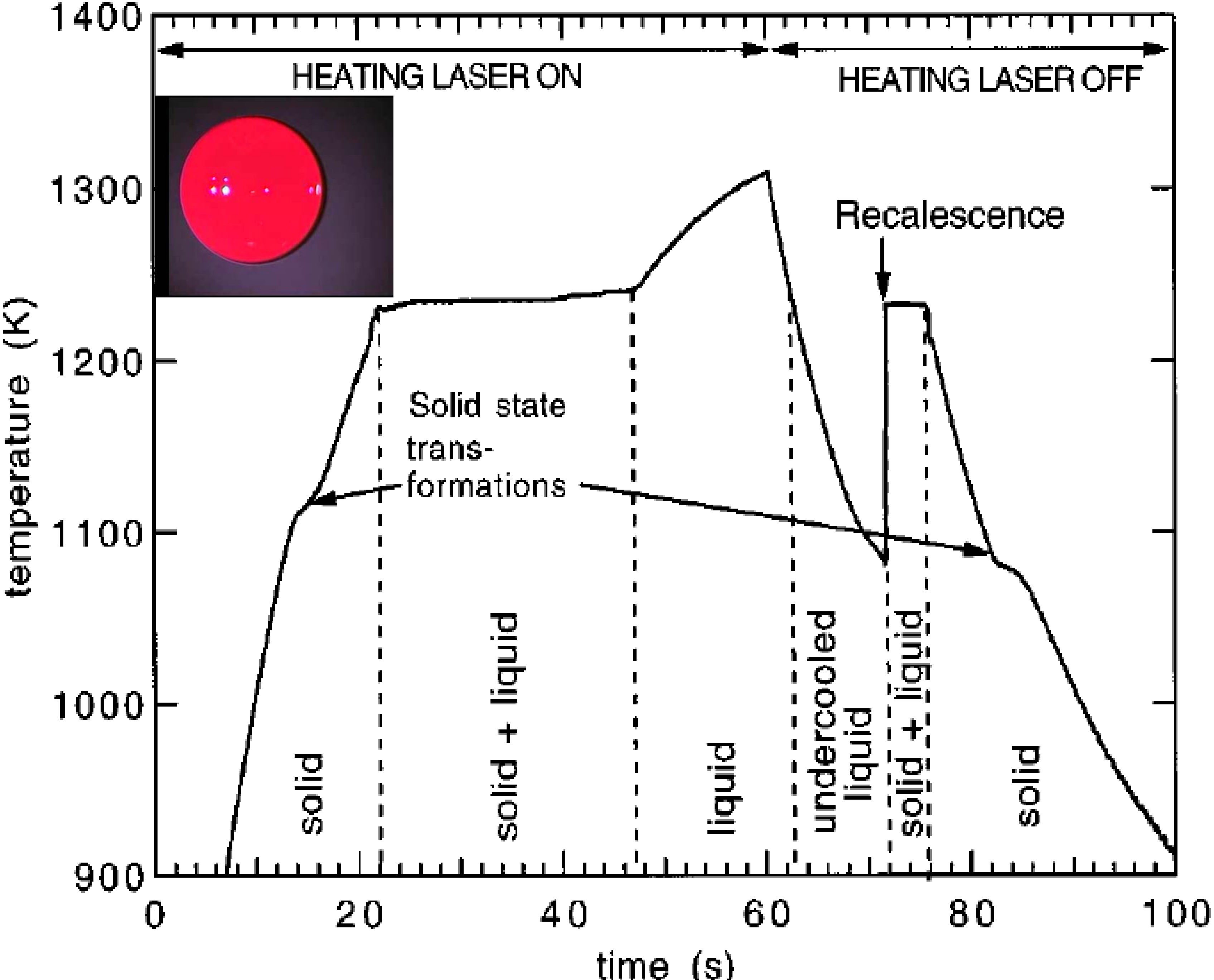
vapor

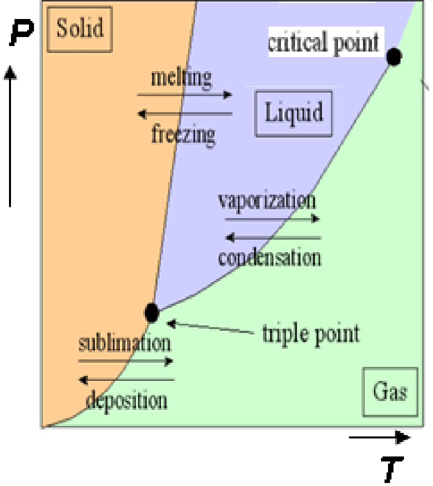
- Interfacial energy ⇨ No ΔT_N

$$\gamma_{SL} + \gamma_{LV} < \gamma_{SV}$$

Melting: Liquid ← Solid

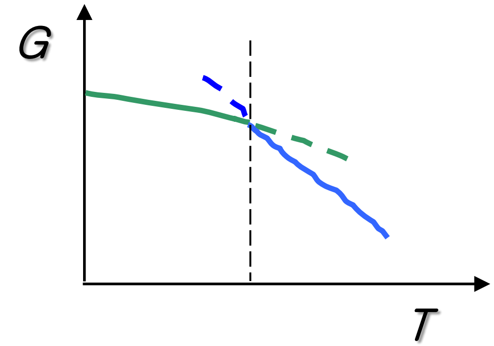
Incentive Homework 1:
Example of Superheating (PPT 3 pages)


HEATING LASER ON
HEATING LASER OFF
Recalescence
Solid state trans-formations
solid
solid + liquid
liquid
undercooled liquid
solid + liquid
solid
temperature (K)
time (s)
1400
1300
1200
1100
1000
900
0
20
40
60
80
100



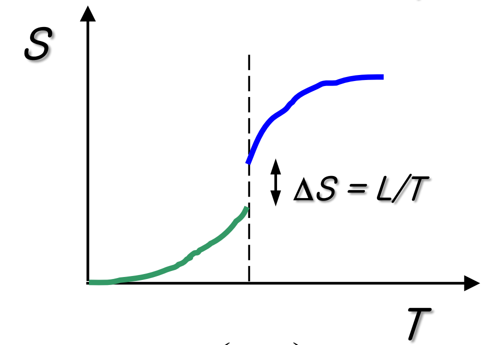
The First-Order Transitions

Latent heat
Energy barrier
Discontinuous entropy, heat capacity



- First Order Phase Transition at T_T:
  - G is continuous at T_T
  - First derivatives of G (V, S, H) are discontinuous at T_T

$$V = \left(\frac{\partial G}{\partial P}\right)_T \qquad S = -\left(\frac{\partial G}{\partial T}\right)_P \qquad H = G - T\left(\frac{\partial G}{\partial T}\right)_P$$

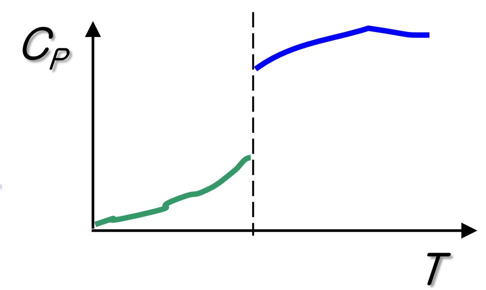


  - Second derivatives of G (α, β, C_p) are discontinuous at T_T

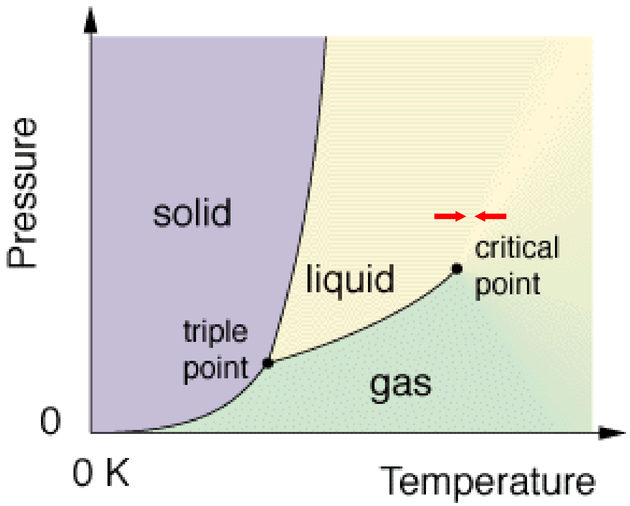
$$C_P = \left(\frac{\partial H}{\partial T}\right)_P \qquad \alpha = \frac{1}{V}\left(\frac{\partial V}{\partial T}\right)_P \qquad \beta = \frac{-1}{V}\left(\frac{\partial V}{\partial P}\right)_T$$

Heat capacity at constant P or V | **Coefficient of Thermal expansion** | **Compressibility at constant T or S**

$$C_P = T\left(\frac{\partial S}{\partial T}\right)_{P,N}$$

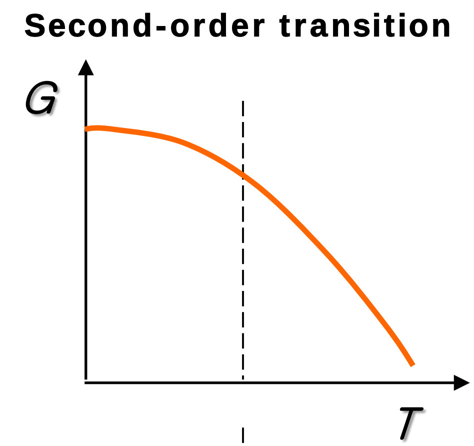


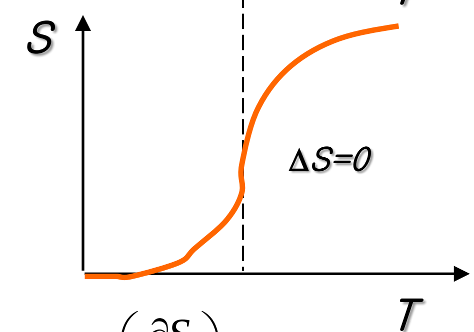
  - Examples: Vaporization, Condensation, Fusion, Crystallization, Sublimation.



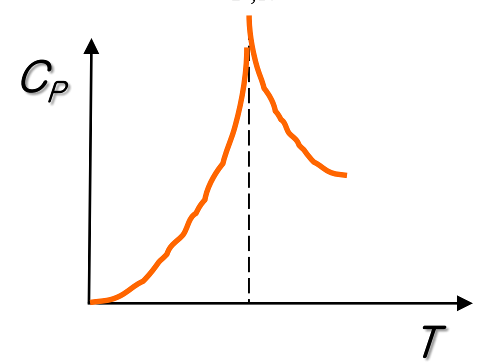
The Second Order Transition

No Latent heat
Continuous entropy





$$C_P = T\left(\frac{\partial S}{\partial T}\right)_{P,N} \rightarrow \infty$$



- Second Order Phase Transition at T_T:
  - G is continuous at T_T
  - First derivatives of G (V, S, H) are continuous at T_T

$$V = \left(\frac{\partial G}{\partial P}\right)_T \qquad S = -\left(\frac{\partial G}{\partial T}\right)_P \qquad H = G - T\left(\frac{\partial G}{\partial T}\right)_P$$

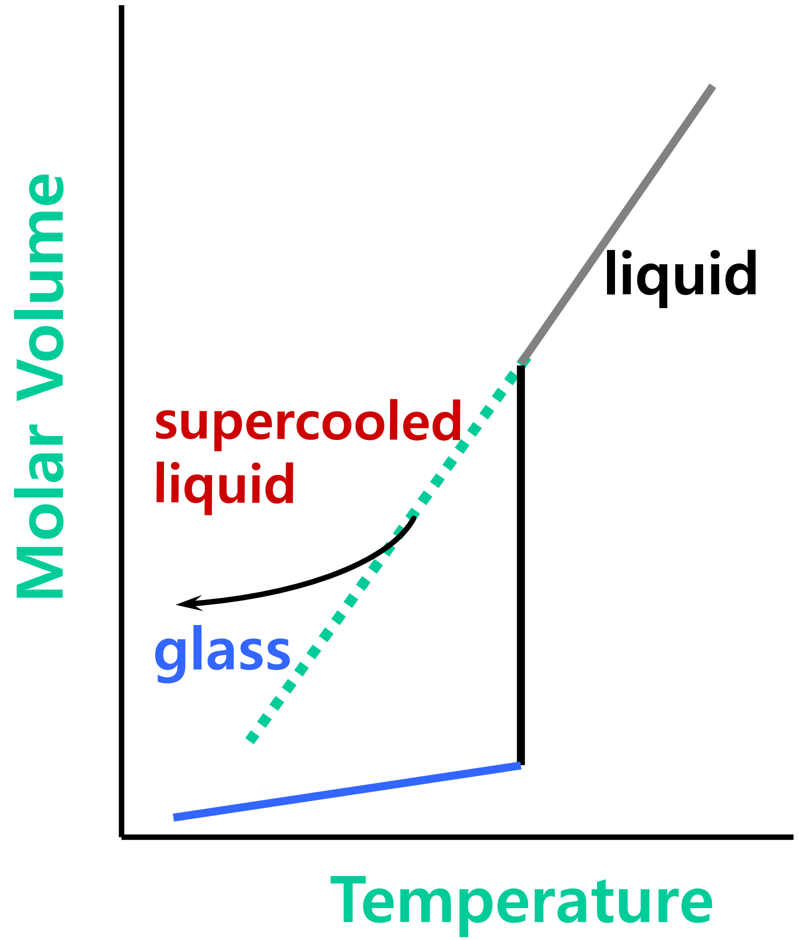
  - Second derivatives of G (α, β, C_p) are discontinuous at T_T

$$C_P = \left(\frac{\partial H}{\partial T}\right)_P \qquad \alpha = \frac{1}{V}\left(\frac{\partial V}{\partial T}\right)_P \qquad \beta = \frac{-1}{V}\left(\frac{\partial V}{\partial P}\right)_T$$

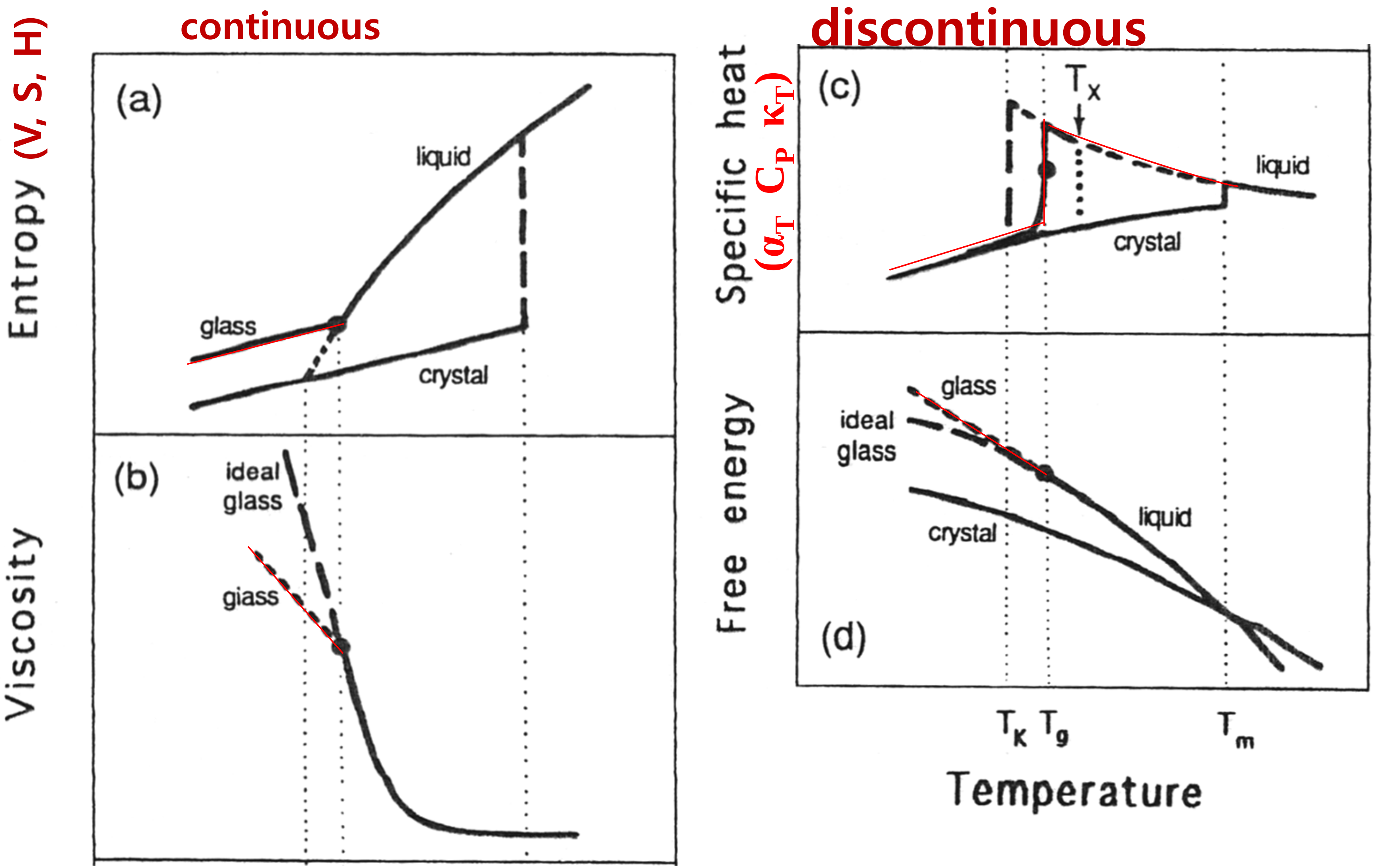
  - Examples: Order-Disorder Transitions in Metal Alloys, Onset of Ferromagnetism, Ferroelectricity, Superconductivity.

Glass Formation is Controlled by Kinetics

- Glass-forming liquids are those that are able to "by-pass" the melting point, T_m
- Liquid may have a "high viscosity" that makes it difficult for atoms of the liquid to diffuse (rearrange) into the crystalline structure
- Liquid maybe cooled so fast that it does not have enough time to crystallize
- Two time scales are present
  - (1)"Internal" time scale controlled by the viscosity (bonding) of the liquid for atom/molecule arrangement
  - (2) "External" timescale controlled by the cooling rate of the liquid



Glass transition
(1) ≈ (2)

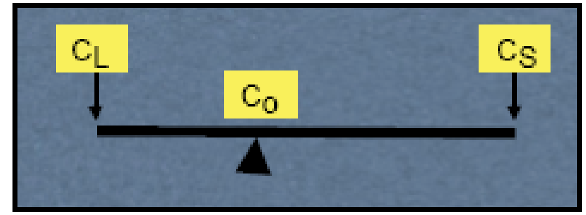


Schematic of the glass transition showing the effects of temperature on the entropy, viscosity, specific heat, and free energy. T_x is the crystallization onset temperature.

Q1. Types of Melting (L → S)

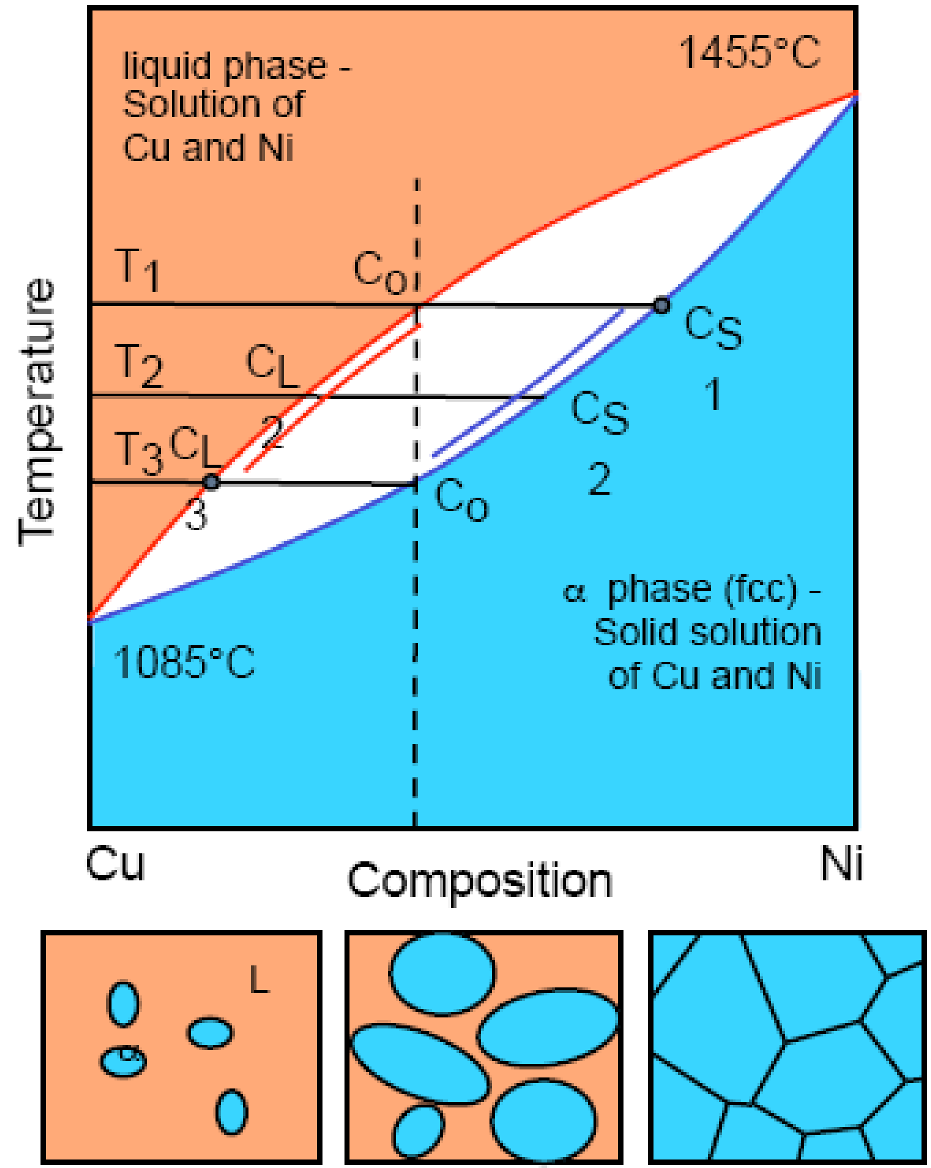
Binary phase diagrams

- Simple Phase Diagrams



The simplest type of binary phase diagrams is the isomorphous system, in which the two constituents form a continuous solid solution over the entire composition range. An example is the Ni-Cu system.

Solidification of alloy C_o starts on cooing at T_1. The first solid formed has a composition of C_{s1} and the liquid C_o. On further cooling the solid particles grow larger in size and change their composition to C_{s2} and then C_o, following the solidus whereas the liquid decrease in volume and changes its composition from C_o to C_{L3} following the liquidus. The solidification completes at T_3.

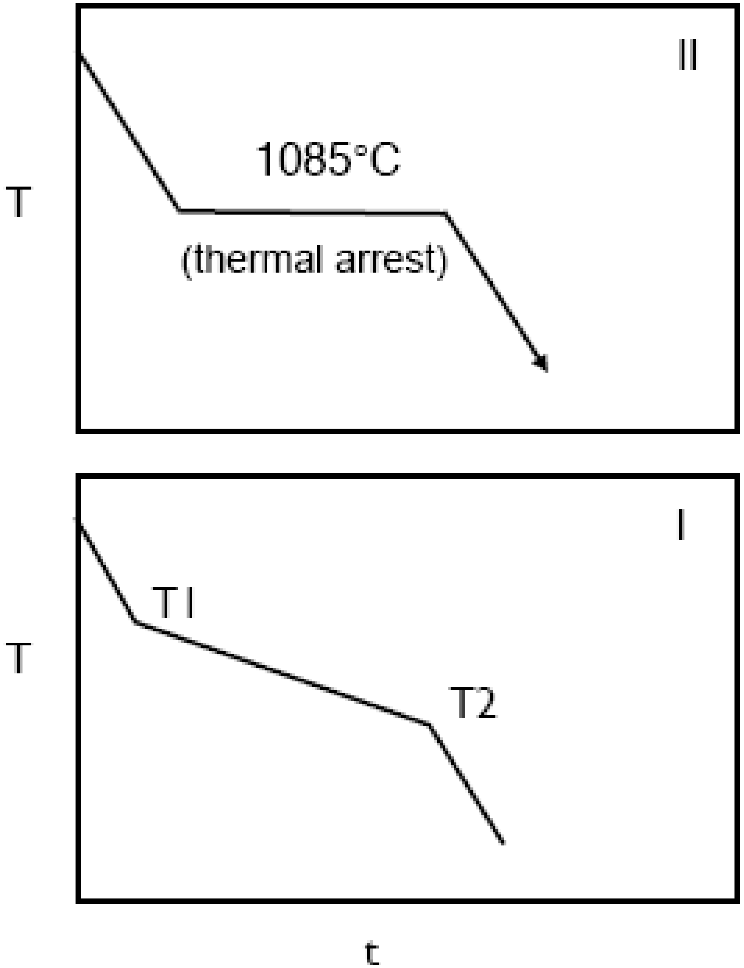


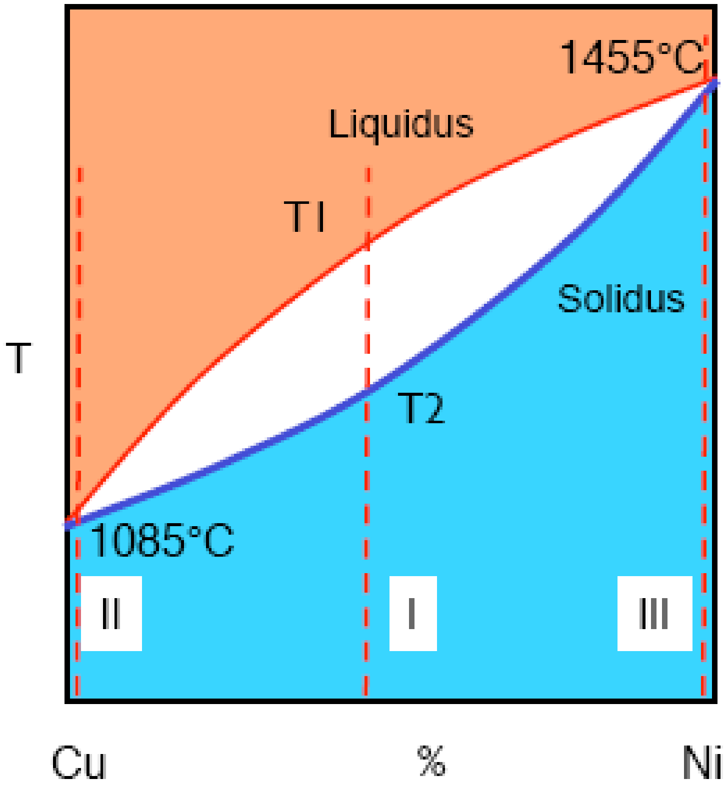
Melting Point

Metal	Melting Point Fahrenheit	Centigrade	Kelvin
Aluminum	1220	660	933
Beryllium	2340	1280	1553
Chromium	3430	1890	2163
Cobalt	2723	1495	1768
Columbium	4380	2415	2688
Copper	1981	1083	1356
Gallium	86	30	303
Germanium	1760	958	1231
Gold	1945	1063	1336
Indium	314	156	429
Iridium	4449	2454	2727
Iron	2802	1539	1812
Lead	621	327	600
Lithium	367	186	459
Magnesium	1202	650	923
Mercury	−38	−39	234
Molybdenum	4760	2625	2898
Nickel	2651	1455	1728
Osmium	4900	2700	2973
Platinum	3224	1774	2047
Plutonium	1184	640	913
Radium	1300	700	973
Rhodium	3570	1966	2239
Silicon	2605	1430	1703
Silver	1761	961	1234
Sodium	208	98	371
Tantalum	5425	2996	3269
Tin	449	232	505
Titanium	3300	1820	2093
Tungsten	6170	3410	3683
Uranium	2065	1130	1403
Vanadium	3150	1735	2008
Zinc	787	419	692
Zirconium	3200	1750	2023

Cooling Curves

determination of Phase diagrams





Q2. Types of Melting (L → S)

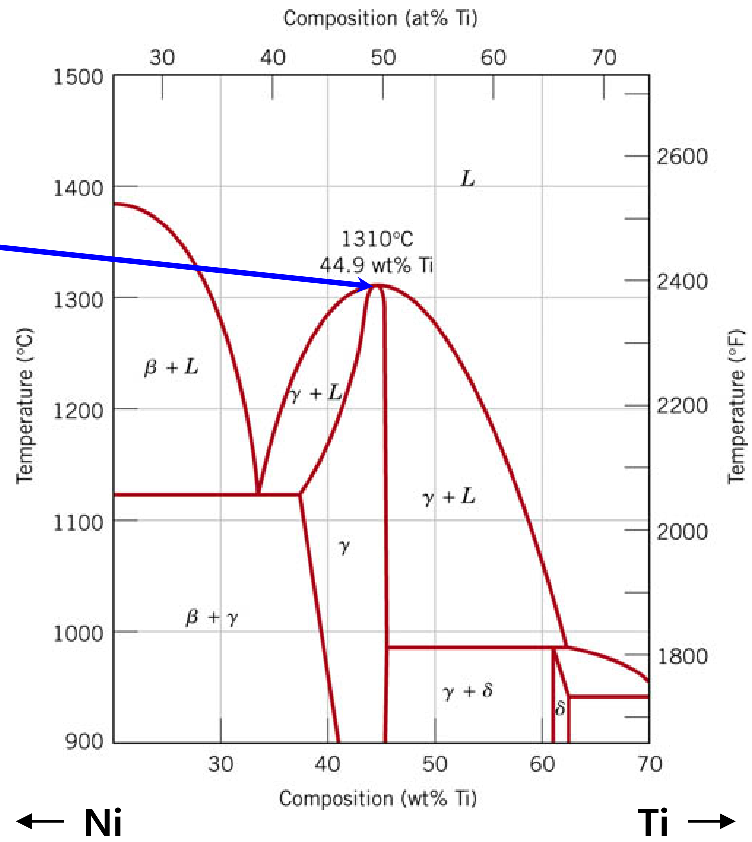
Congruent vs Incongruent

Congruent vs Incongruent

Congruent phase transformations: no compositional change associated with transformation

Examples:

- Allotropic phase transformations
- Melting points of pure metals
- Congruent Melting Point



Incongruent phase transformation: at least one phase will experience change in composition

Examples:

- Melting in isomorphous alloys
- Eutectic reactions
- Pertectic Reactions
- Eutectoid reactions

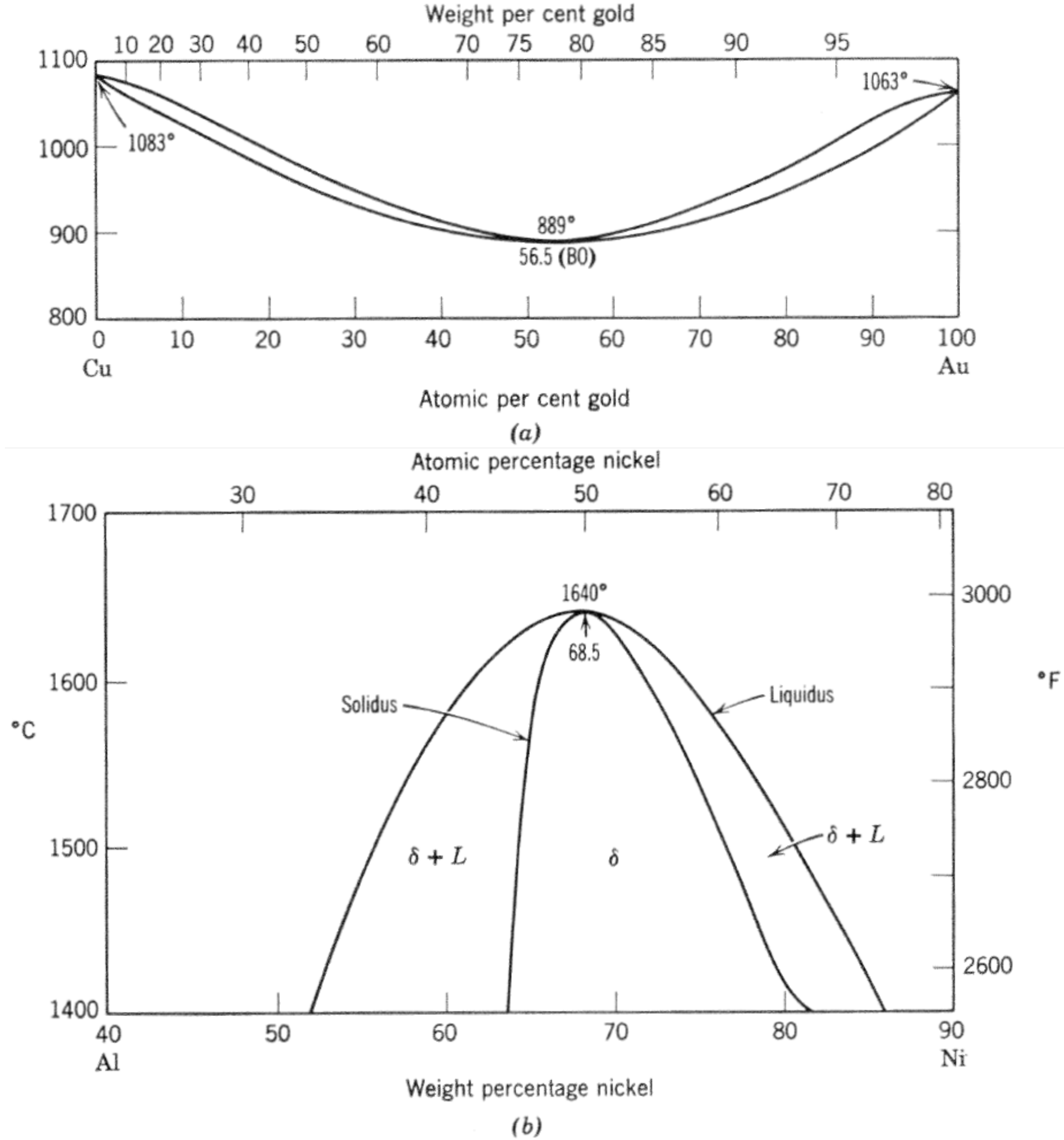


Fig. 1.3. Congruently melting alloys. (*a*) Minimum type, (*b*) maximum type. [Part (*a*) from Ref. 2, p. 199; part (*b*) from Ref. 4, p. 1164. Both used by permission.]

* Congruent transformations

Congruent transformation:

(a) and (b): a melting point minimum, a melting point maximum, and a critical temperature associated with a order-disorder transformation

(c) and (d): formation of an intermediate phase (next page)

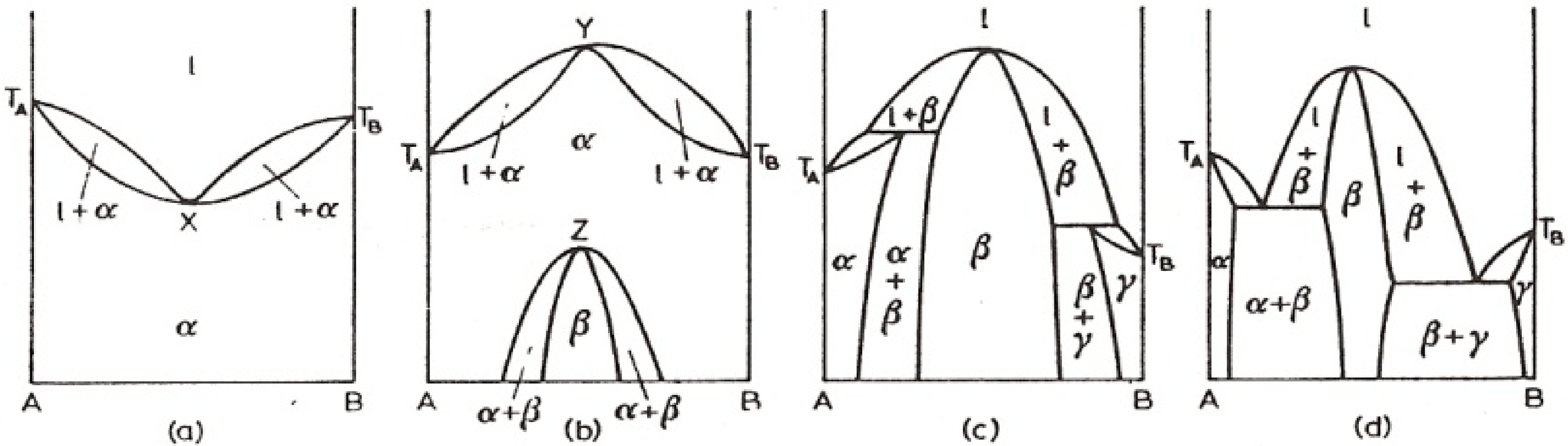


Fig. 76. Examples of congruent transformations.

* Congruent transformations

: More usual type of congruently-melting intermediate phase

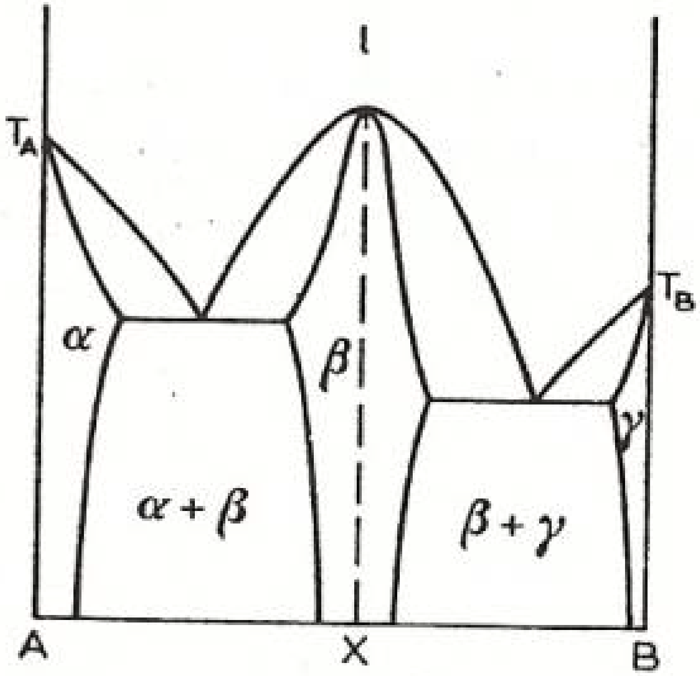
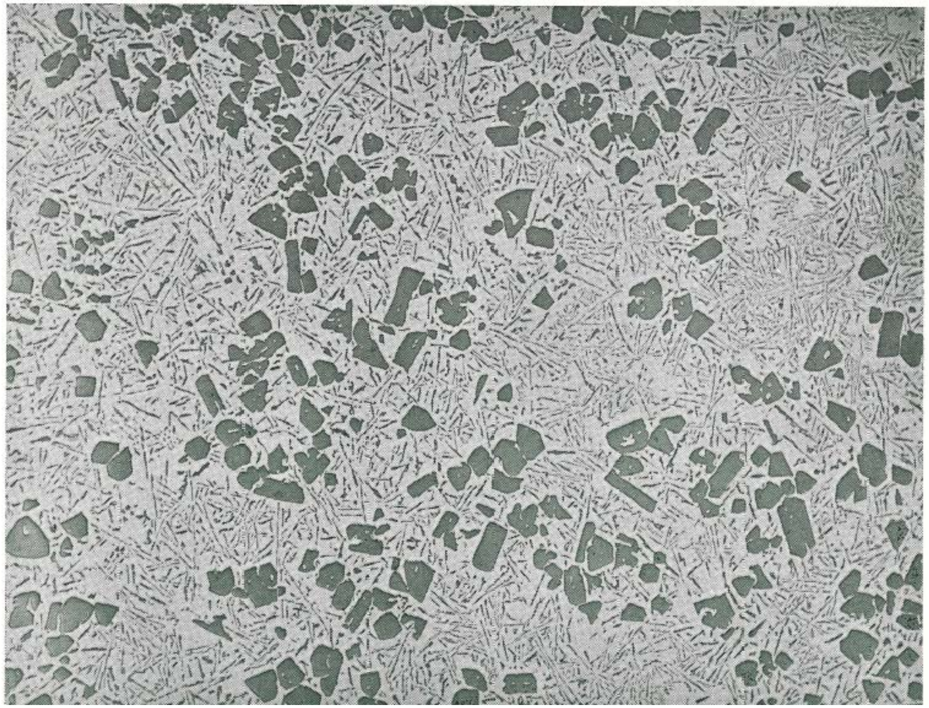


Fig. 78. Phase diagram with a congruent intermediate phase.

→ Partial phase diagram A-X and X-B



Microstructure of a cast Al-22% Si alloy
showing polyhedra of primary Si in eutectic matrix

: Similar with eutectic alloy system/ primary β phase with well-formed crystal facets (does not form dendrite structure)

In many cases, X = normal valency compound such as Mg_2Si, Mg_2Sn, Mg_2Pb

or Laves phase, particularly stable compounds

: More usual type of congruently-melting intermediate phase

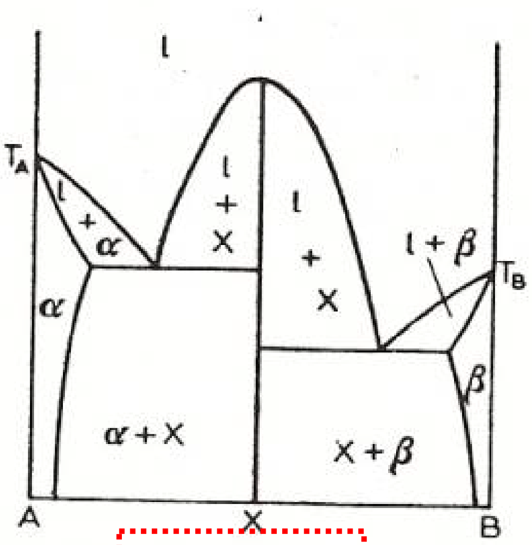
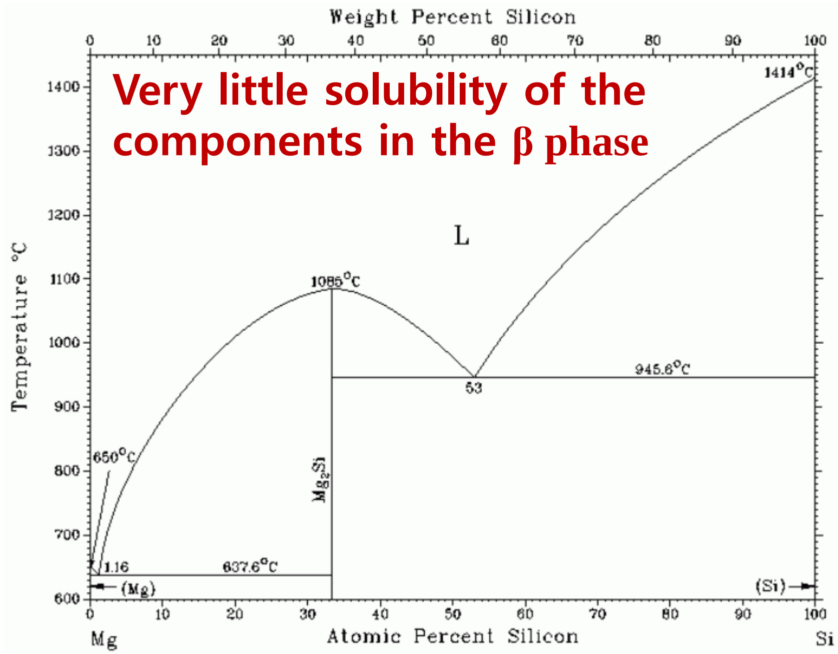
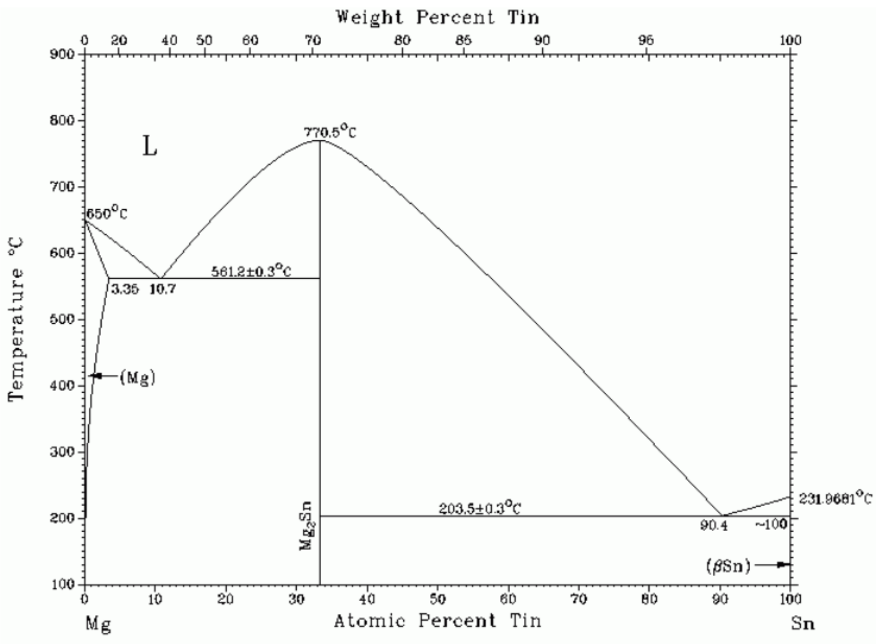
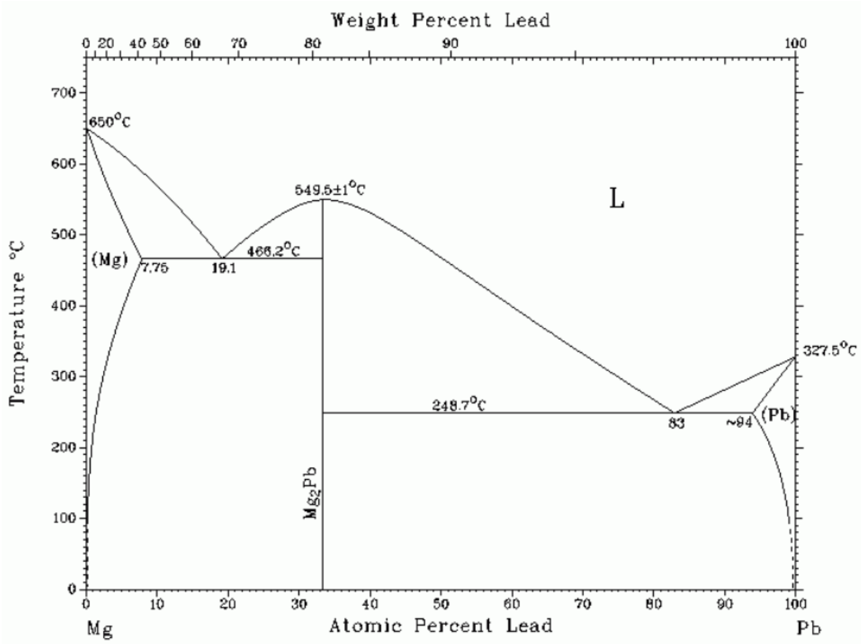


Fig. 79. Limiting case of Fig. 78.



Very little solubility of the components in the β phase



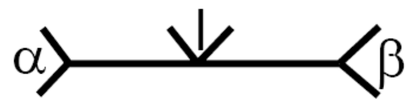


Review of Invariant Binary Reactions

Eutectic Type

Eutectic

$l \rightleftarrows \alpha + \beta$



Al-Si, Fe-C

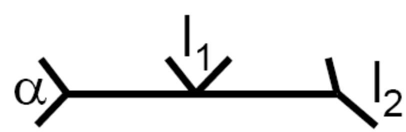
Eutectoid

$\gamma \rightleftarrows \alpha + \beta$

Fe-C

Monotectic

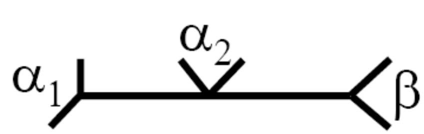
$l_1 \rightleftarrows \alpha + l_2$



Cu-Pb

Monotectoid

$\alpha_2 \rightleftarrows \alpha_1 + \beta$



Al-Zn, Ti-V

On cooling one phase going to two phases

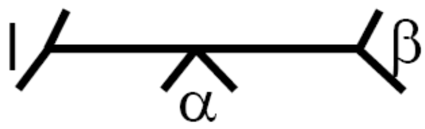
Metatectic reaction: $\beta \leftrightarrow L + \alpha$ **Ex. Co-Os, Co-Re, Co-Ru**

Review of Invariant Binary Reactions

Peritectic Type

Peritectic

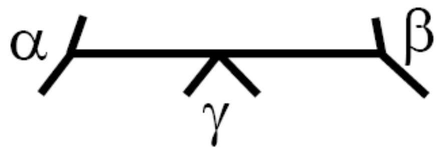
$l + \beta \rightleftarrows \alpha$



Fe-C

Peritectoid

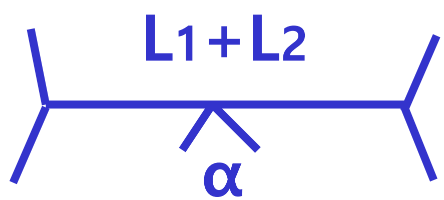
$\alpha + \beta \rightleftarrows \gamma$



Cu-Al

Synthetic reaction

$Liquid_1 + Liquid_2 \leftrightarrow \alpha$



K-Zn, Na-Zn, K-Pb, Pb-U, Ca-Cd

On cooling two phases going to one phase

a) Eutectic reaction

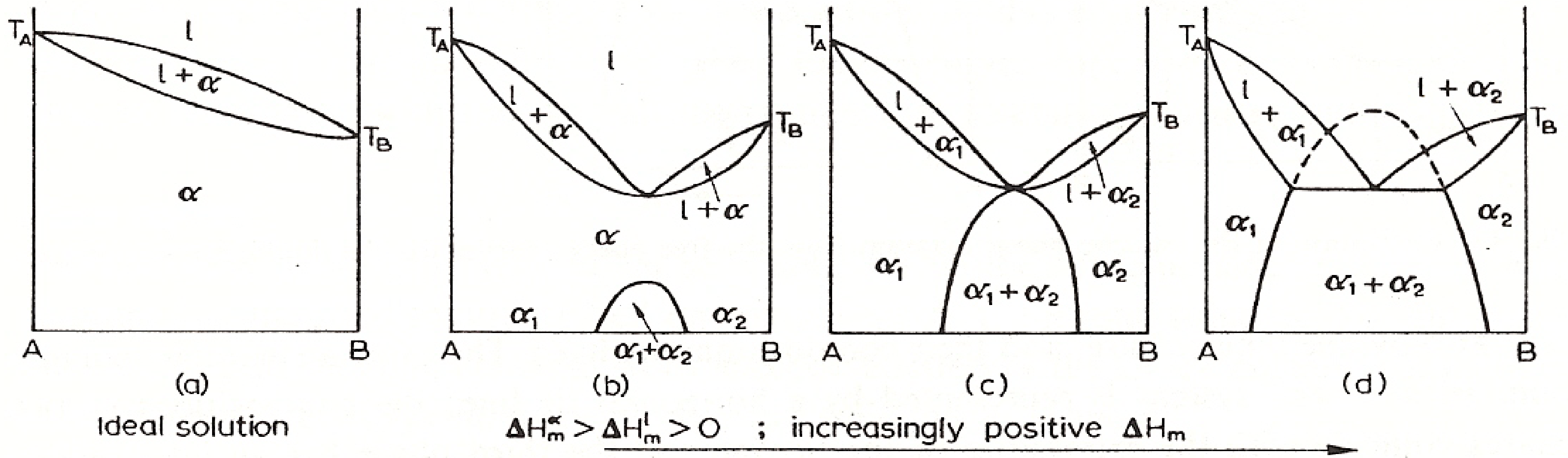


Fig. 43. Effect of increasingly positive departure from ideality in changing the phase diagram for a continuous series of solutions to a eutectic-type.

b) Peritectic reaction

Considerable difference between the melting points

$$\Delta H_{mix}^{\alpha} > \Delta H_{mix}^{l} > 0$$

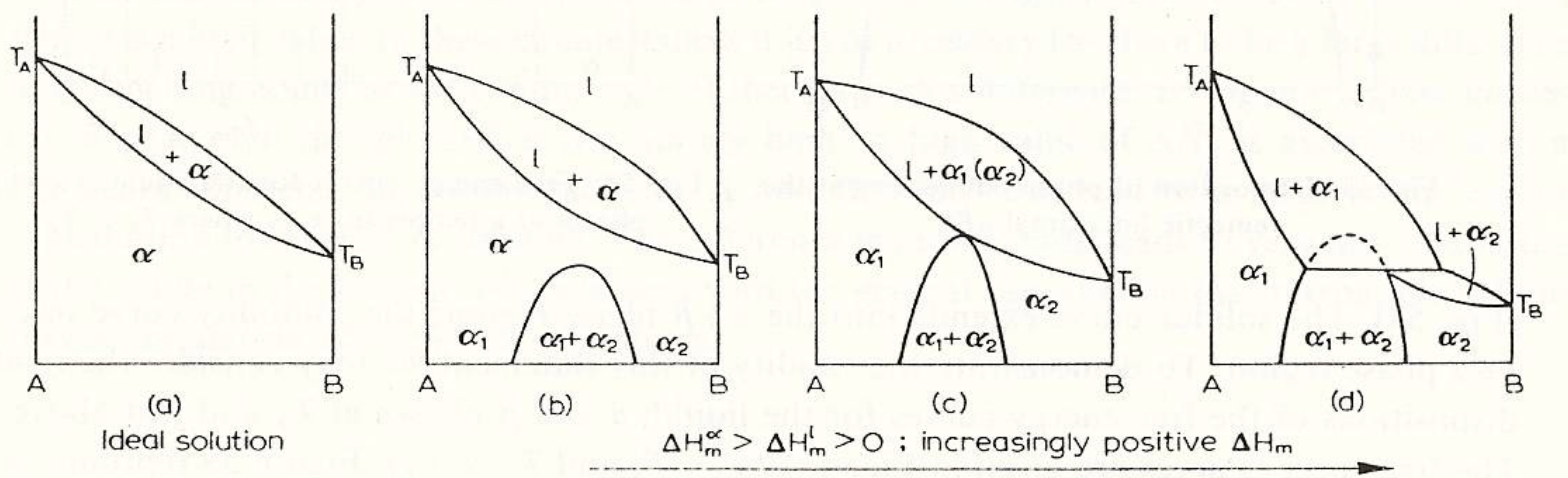
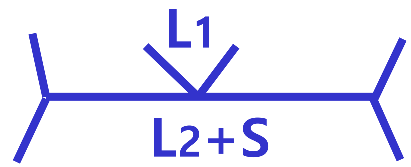
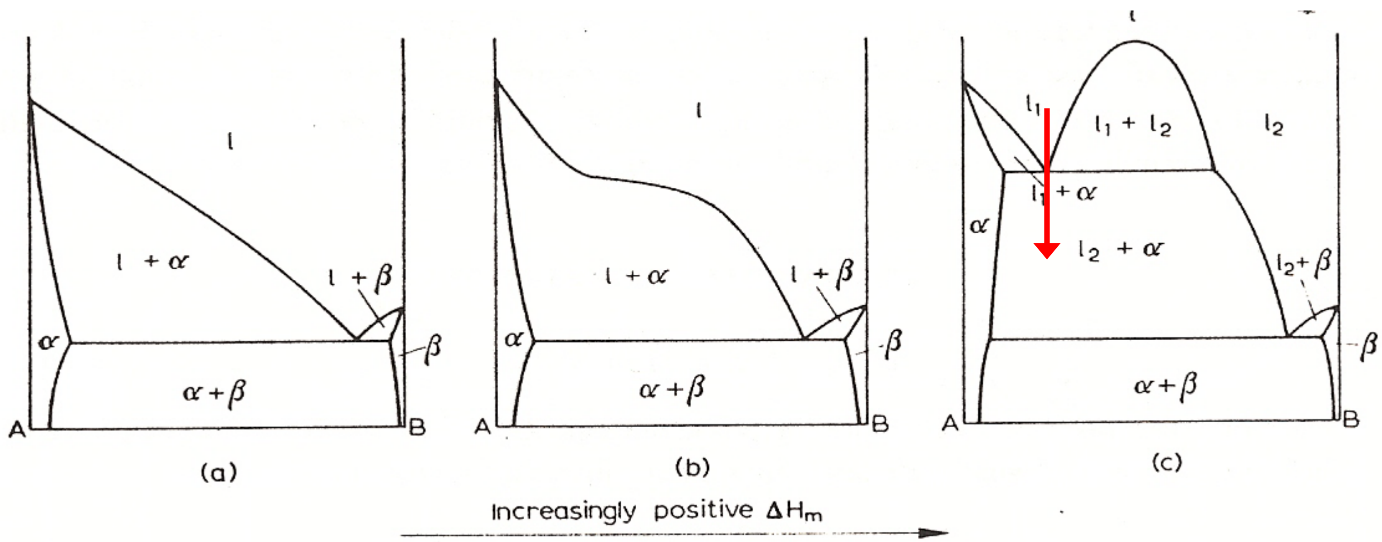


Fig. 61. Effect of increasingly positive departure from ideality in changing the phase diagram from a continuous series of solutions to a peritectic-type.

c) Monotectic reaction:

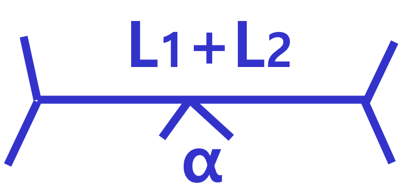


Liquid1 ↔Liquid2+ Solid

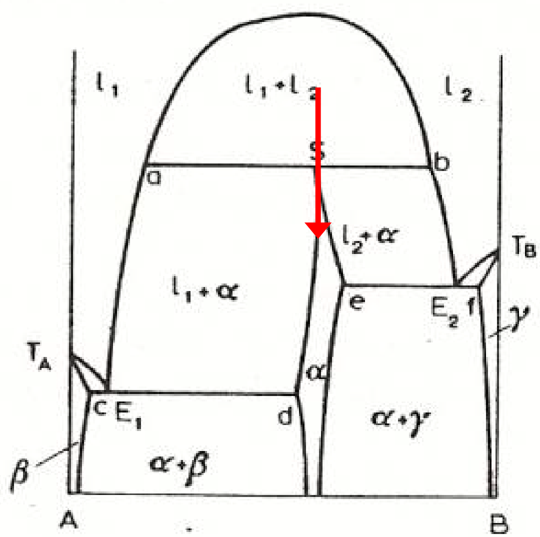


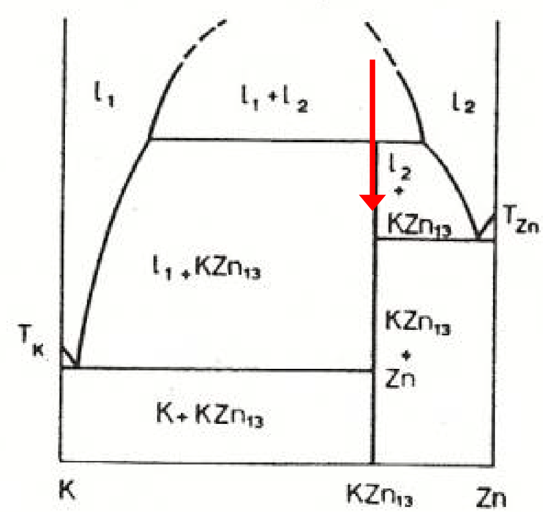
d) Synthetic reaction

Liquid1+Liquid2 ↔ α



K-Zn, Na-Zn,
K-Pb, Pb-U, Ca-Cd





e) Metatectic reaction: $\beta \leftrightarrow L + \alpha$ Ex. Co-Os, Co-Re and Co-Ru

(Both α and β are allotropes of A)

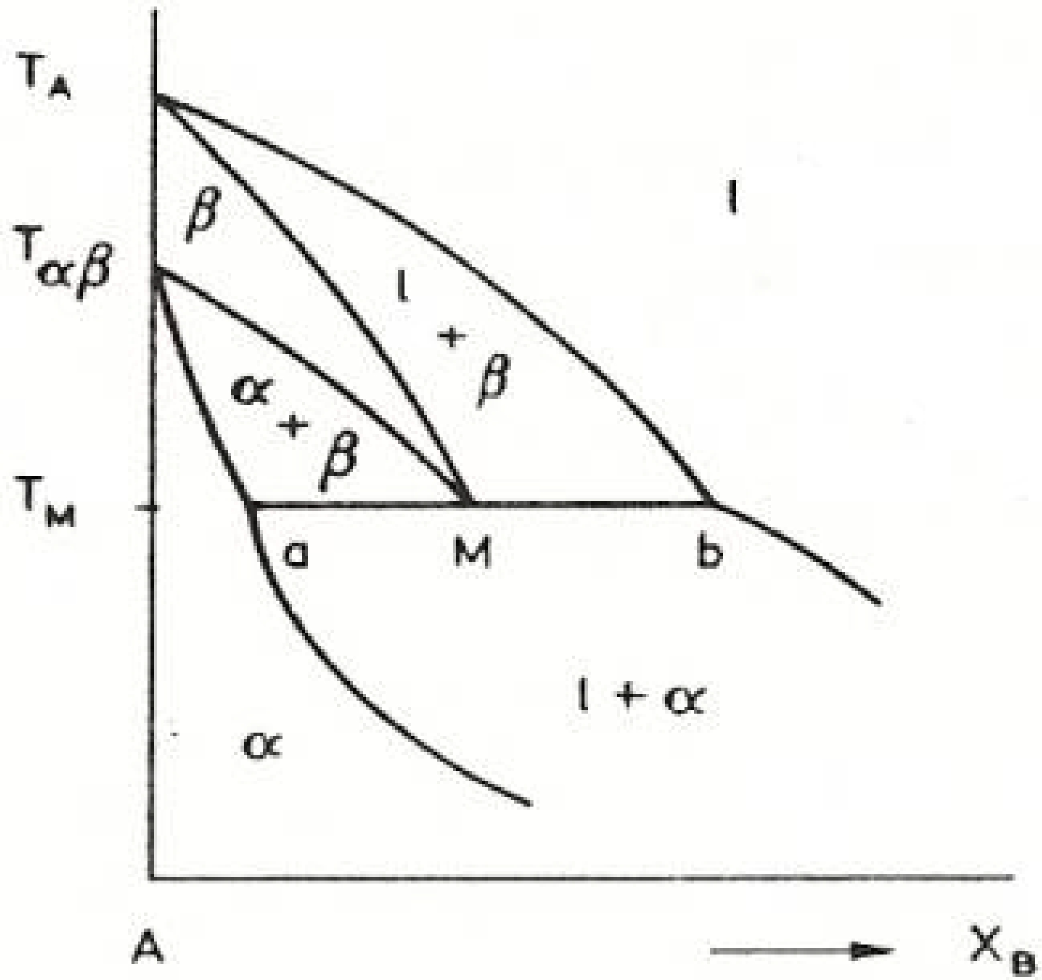


Fig. 103. The metatectic reaction.

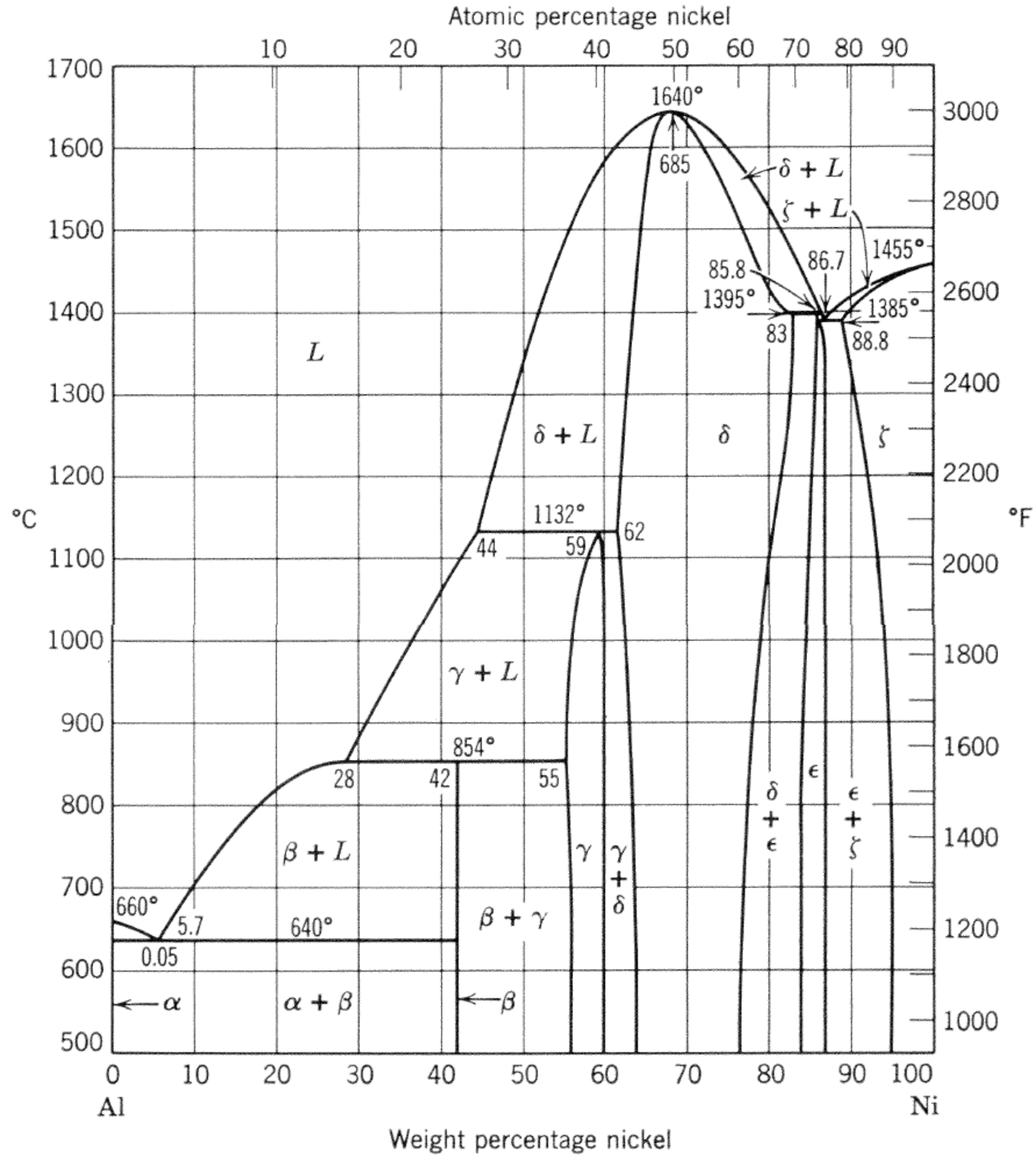
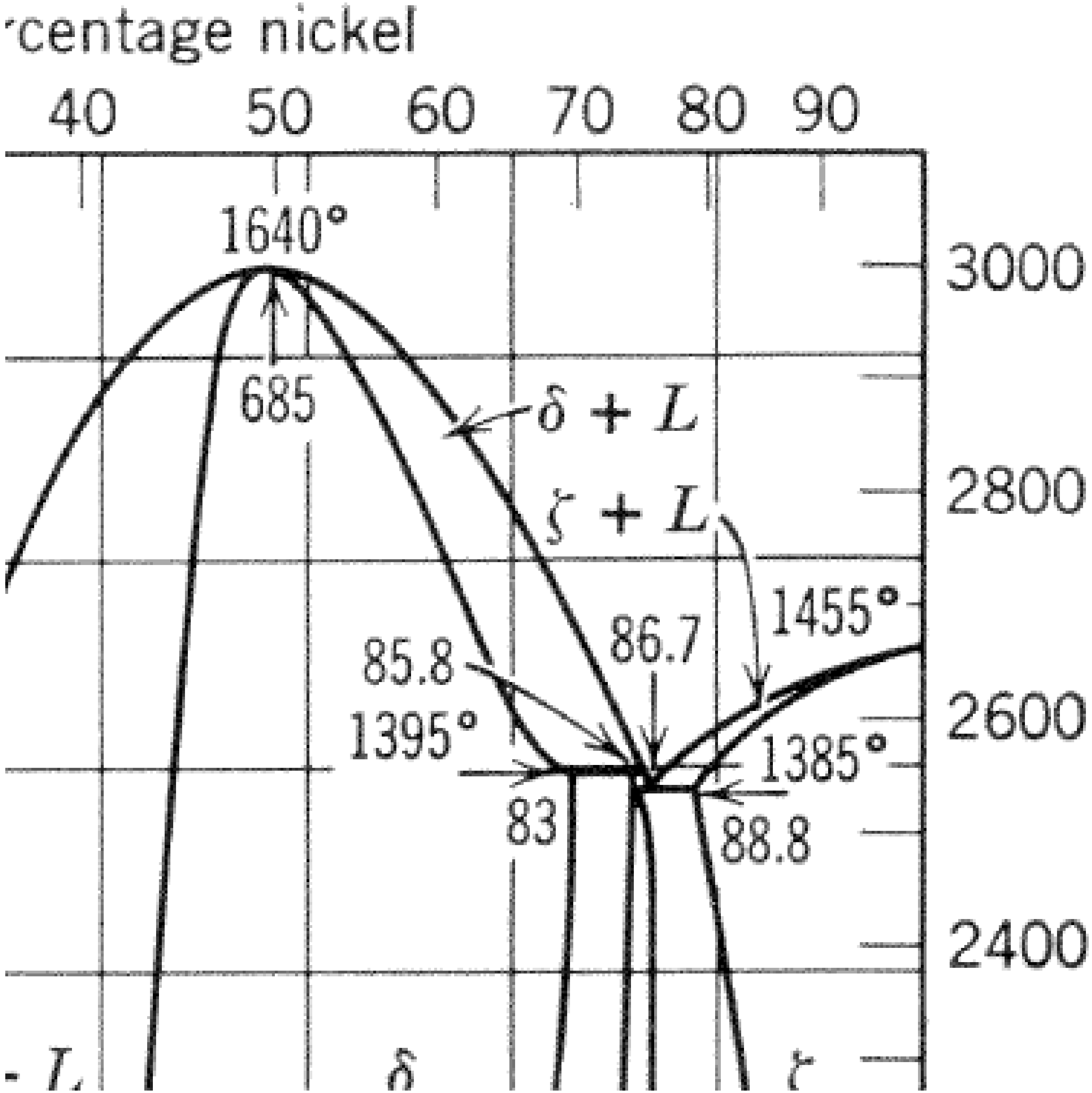


Fig. 1.7. Liquidus and solidus curves for the Aluminum-nickel system. (From Ref. 4, p. 1164. Used by permission.)


centage nickel
40
50
60
70
80
90
1640°
685
δ + L
ζ + L
3000
2800
2600
2400
1455°
86.7
85.8
1395°
1385°
83
88.8
δ
ζ

1.4 Gas-Metal Equilibrium

Two main types of gas-metal equilibrium: (a) those in which the liquid and the solid each take the form of (liquid/solid) solutions, and (b) those in which a compound phase is formed.

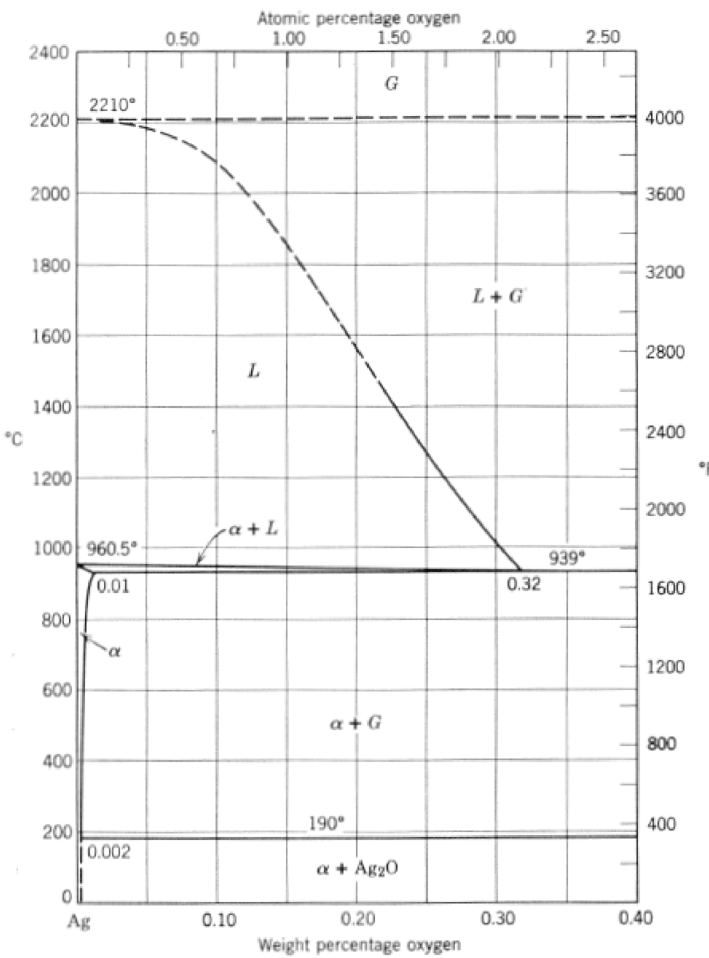


Fig. 1.8. Silver-oxygen phase diagram. (From Ref. 4, p. 1152.)

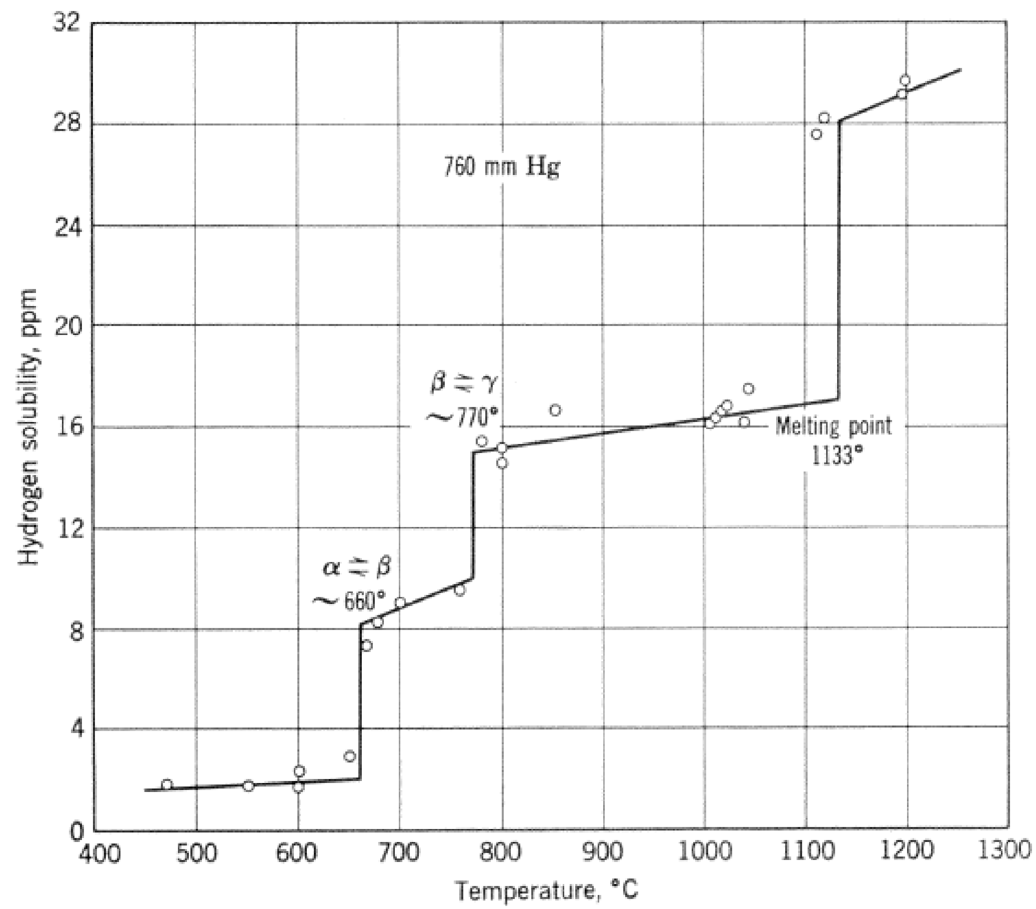


Fig. 1.9. Uranium-hydrogen phase diagram. (From Ref. 2, p. 803. Used by permission.)

Q3. Pressure effect of melting

Pressure Effects

The melting point of a pure element or compound is a constant, but it does vary slightly with pressure. This is because the application of a pressure tends to favor the formation of the phase (solid or liquid) which has the smaller specific volume. Most metals expand on melting, the solid being the denser phase. Increase of pressure, therefore, in such cases, raises the melting point. On the other hand, some substances, including water, gallium, germanium, silicon, and bismuth contract on melting. Pressure lowers the melting point of such materials. The change of melting point corresponding to a change in pressure of one atmosphere can be calculated from the Clapeyron equation:

$$\frac{\Delta T}{\Delta P} = \frac{T_E(V_2 - V_1)}{L}$$

in which ΔT is the change of melting point in centigrade degrees resulting from a change of pressure ΔP in dynes/cm^2; T_E is the melting point (absolute); V_1 and V_2 are the volumes of 1 gm of solid and liquid respectively; and L is the latent heat of fusion in ergs/gm.

Pressure Effects $\frac{\Delta T}{\Delta P} = \frac{T_E(V_2 - V_1)}{L}$

The equilibrium temperatures discussed so far only apply at a specific pressure (1 atm, say). At other pressures the equilibrium temperatures will differ.

If α & β phase are equilibrium,

$$dG^{\alpha} = V^{\alpha}dP - S^{\alpha}dT$$

$$dG^{\beta} = V^{\beta}dP - S^{\beta}dT$$

At equilibrium,

$$dG^{\alpha} = dG^{\beta}$$

$$\left(\frac{dP}{dT}\right)_{eq} = \frac{S^{\beta} - S^{\alpha}}{V^{\beta} - V^{\alpha}} = \frac{\Delta S}{\Delta V}$$

$$Here \quad \Delta S = \frac{\Delta H}{T_{eq}},$$

**** Clausius-Clapeyron Relation*** : $\left(\frac{dP}{dT}\right)_{eq} = \frac{\Delta H}{T_{eq}\Delta V}$

(applies to all coexistence curves)

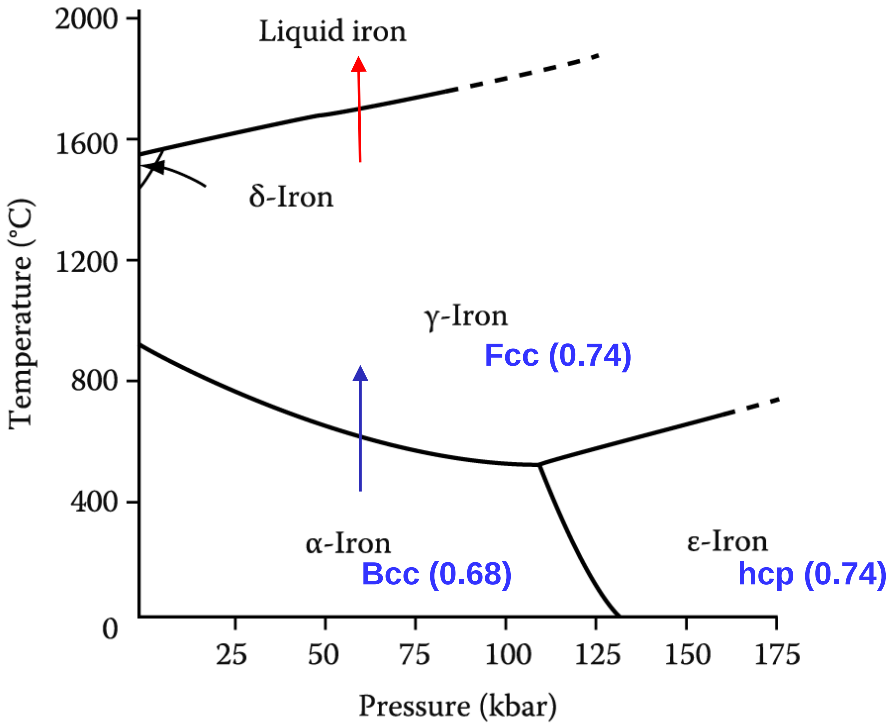


Fig. 1.5 Effect of pressure on the equilibrium phase diagram for pure iron

For, γ →liquid; ΔV (+), ΔH(+)

$$\left(\frac{dP}{dT}\right) = \frac{\Delta H}{T_{eq}\Delta V} > 0$$

For, α→γ ; ΔV (-), ΔH(+)

$$\left(\frac{dP}{dT}\right) = \frac{\Delta H}{T_{eq}\Delta V} < 0$$

$$\left(\frac{\partial G}{\partial P}\right)_T = V$$

Q4. Ternary Phase Diagram

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: (constant pressure)

$F = C + 1 - P$

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"

"Ternary Phase diagram"

G=f(comp., temp.)

→ Ternary system : A, B, C

→ $G = X_A G_A + X_B G_B + X_C G_C + aX_A X_B + bX_B X_C + cX_C X_A + RT(X_A \ln X_A + X_B \ln X_B + X_C \ln X_C)$

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

For C=3,

① f=3, trivariant equil, p=1 (one phase equilibrium)

② f=2, bivariant equil, p=2 (two phase equilibrium)

③ f=1, monovaiant equil, p=3
(three phase equilibrium)

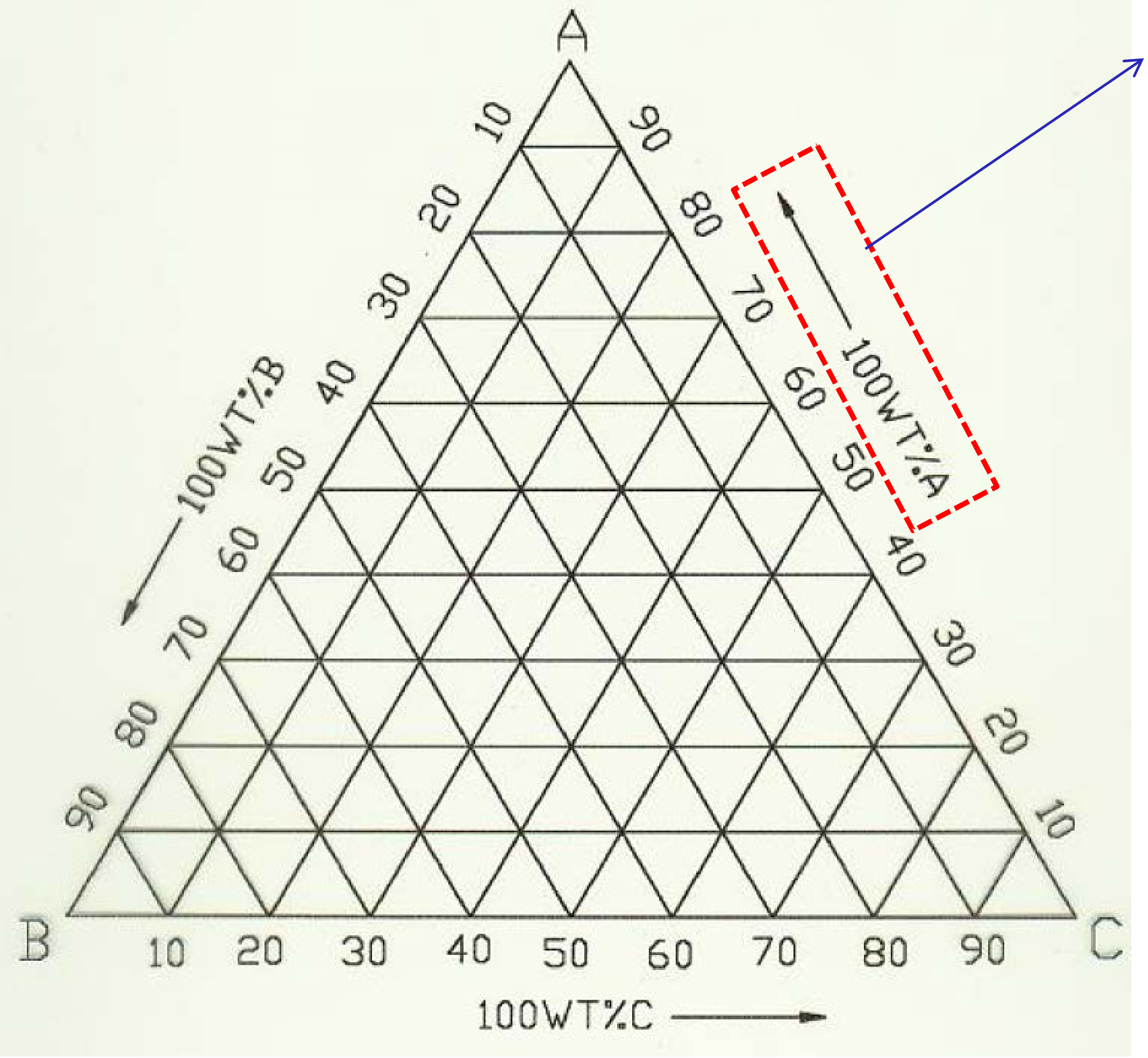
$\alpha \rightleftharpoons \beta + \gamma,$	$\alpha \rightleftharpoons \beta + l,$	$\alpha \rightleftharpoons l_1 + l_2$
$l_1 \rightleftharpoons l_2 + l_3,$	$l_1 \rightleftharpoons \alpha + l_2,$	$l \rightleftharpoons \alpha + \beta$
$\alpha + \beta \rightleftharpoons \gamma,$	$\alpha + \beta \rightleftharpoons l,$	$l_1 + l_2 \rightleftharpoons l_3$
$l_1 + l_2 \rightleftharpoons \alpha,$	$l_1 + \alpha \rightleftharpoons l_2,$	$l + \alpha \rightleftharpoons \beta.$

④ f=0, invariant equil, p=4
(four phase equilibrium)

$\alpha \rightleftharpoons \beta + \gamma + \delta,$	$\alpha + \beta \rightleftharpoons \gamma + \delta,$	$\alpha + \beta + \gamma \rightleftharpoons \delta$
$l_1 \rightleftharpoons l_2 + l_3 + l_4,$	$l_1 + l_2 \rightleftharpoons l_3 + l_4,$	$l_1 + l_2 + l_3 \rightleftharpoons l_4$
$l \rightleftharpoons \alpha + \beta + \gamma,$	$l + \alpha \rightleftharpoons \beta + \gamma.$	$l + \alpha + \beta \rightleftharpoons \gamma$
$l_1 \rightleftharpoons l_2 + \alpha + \beta,$	$l_1 + l_2 \rightleftharpoons \alpha + \beta,$	$l_1 + l_2 + \alpha \rightleftharpoons \beta$
$l_1 \rightleftharpoons l_2 + l_3 + \alpha,$	$l_1 + l_2 \rightleftharpoons l_3 + \alpha,$	$l_1 + l_2 + l_3 \rightleftharpoons \alpha$
$\alpha \rightleftharpoons l_1 + l_2 + l_3,$	$\alpha + l_1 \rightleftharpoons l_2 + l_3,$	$\alpha + l_1 + l_2 \rightleftharpoons l_3$
$\alpha \rightleftharpoons \beta + l_1 + l_2,$	$\alpha + \beta \rightleftharpoons l_1 + l_2,$	$\alpha + \beta + l_1 \rightleftharpoons l_2$
$\alpha \rightleftharpoons \beta + \gamma + l,$	$\alpha + \beta \rightleftharpoons \gamma + l,$	$\alpha + \beta + \gamma \rightleftharpoons l$
	$l_1 + \alpha \rightleftharpoons l_2 + \beta.$	

Gibbs Triangle

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

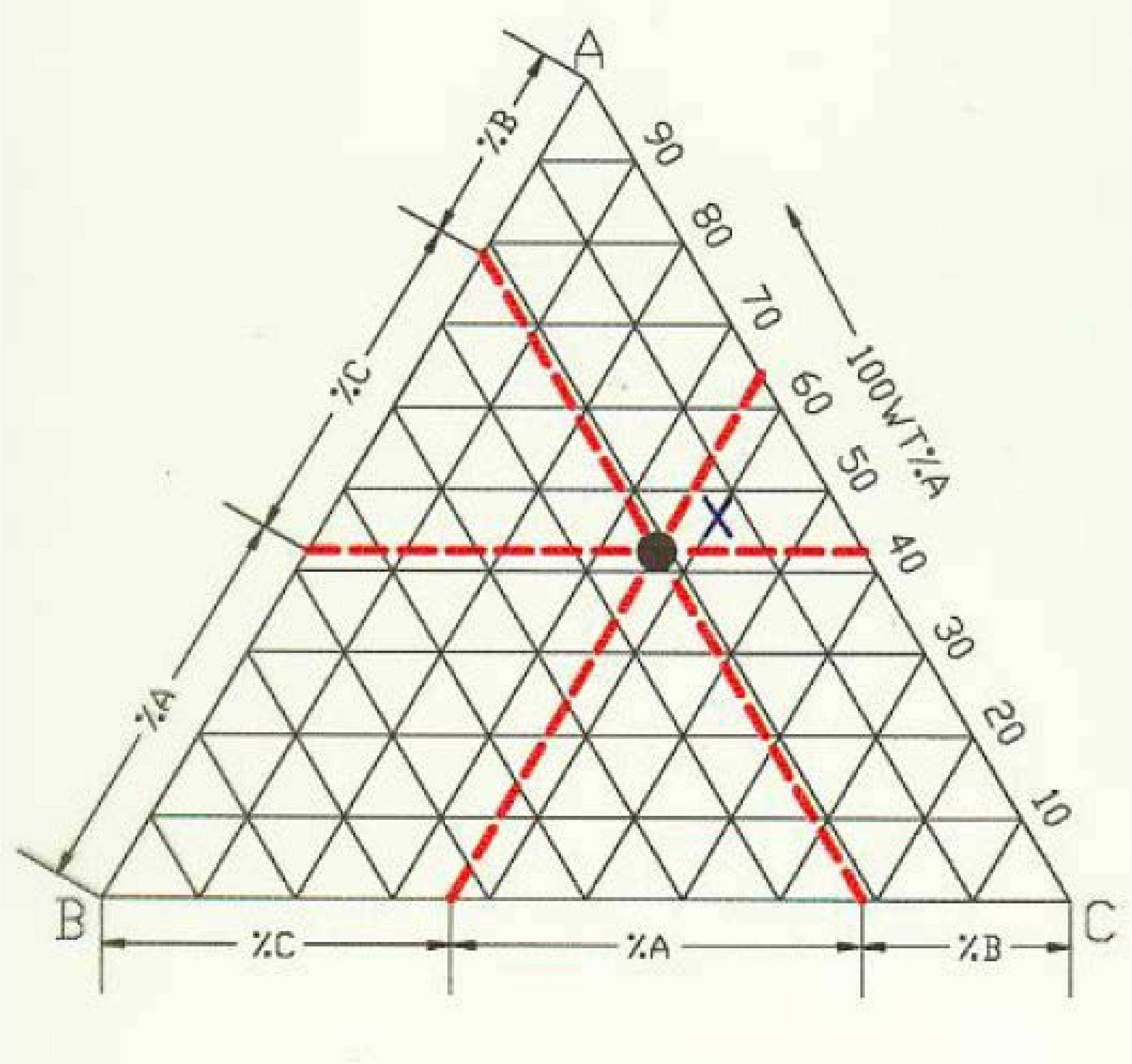


Concentration can be expressed as either "wt. %" or "at.% = molar %".

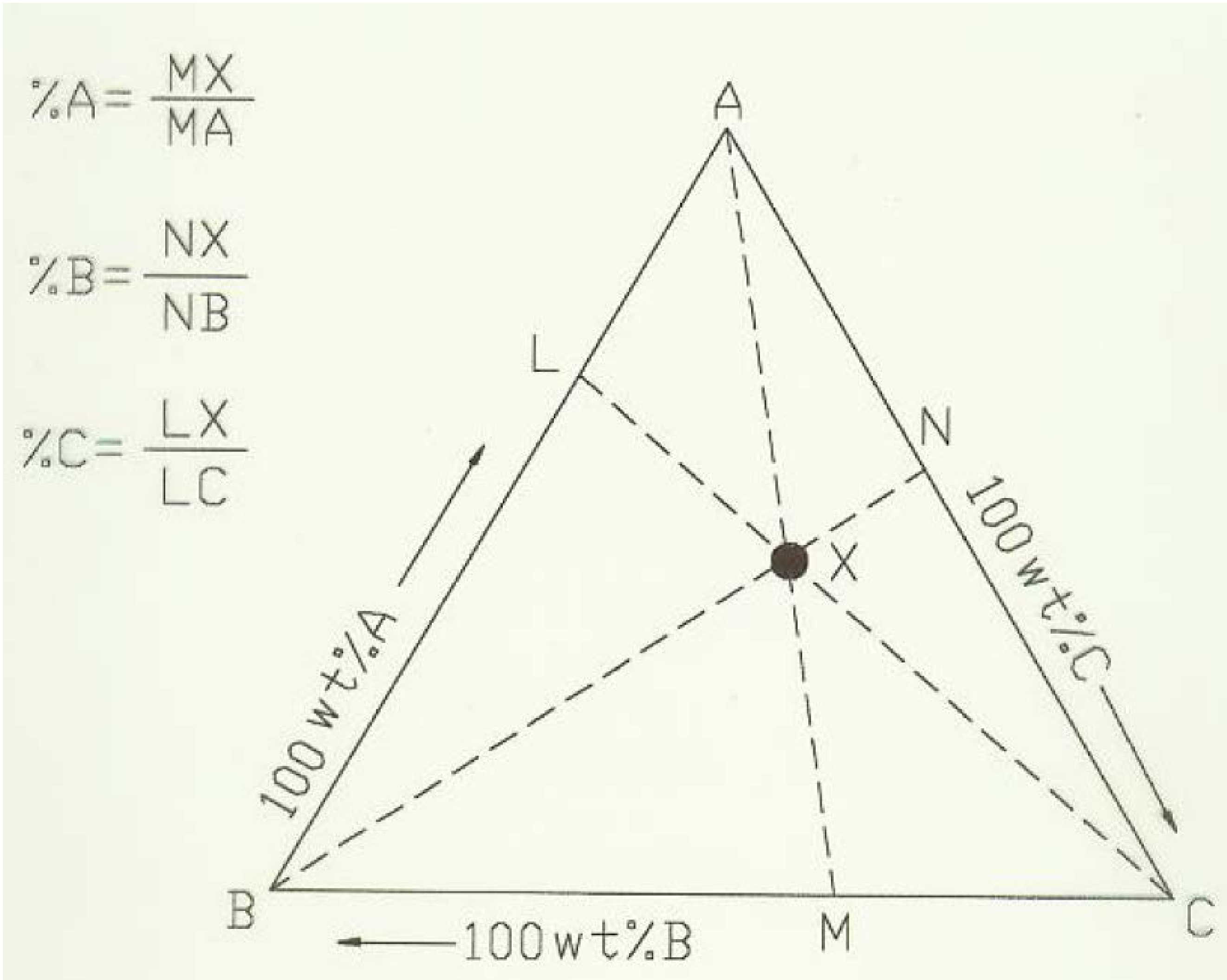
$$X_A + X_B + X_C = 1$$

Used to determine the overall composition

Overall Composition



Overall Composition



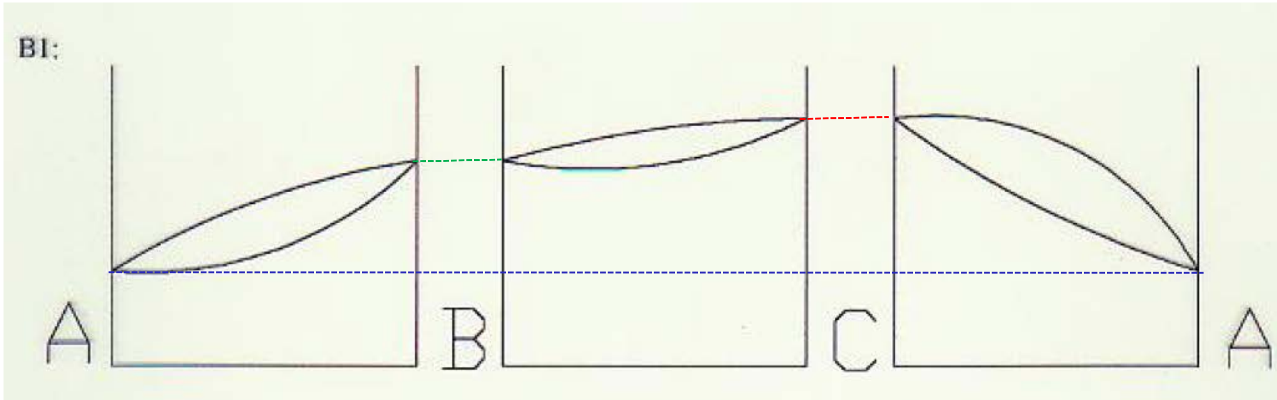
Ternary Isomorphous System

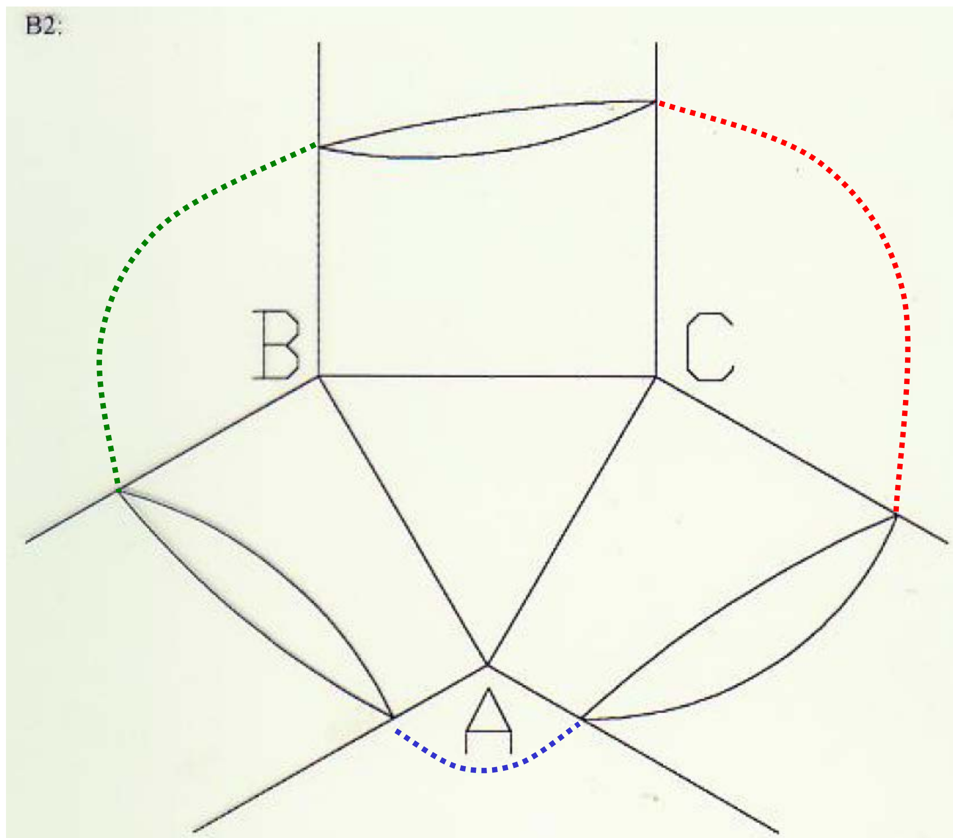
Isomorphous System: A system (ternary in this case) that has only one solid phase. **All components are totally soluble in the other components.** The ternary system is therefore made up of three binaries that exhibit total solid solubility.

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

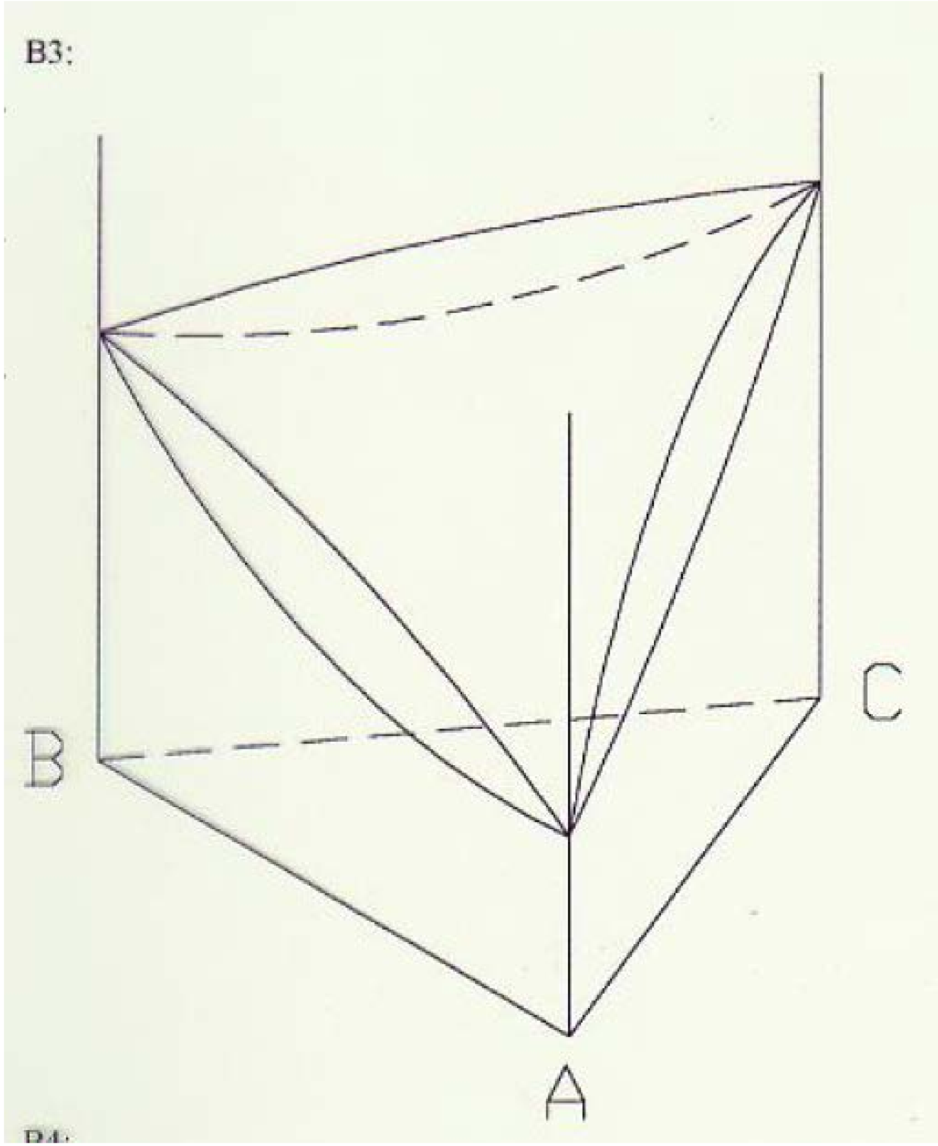
The Solidus Surface: A plot of the temperatures below which a (homogeneous) solid phase forms for any given overall composition.

Ternary Isomorphous System

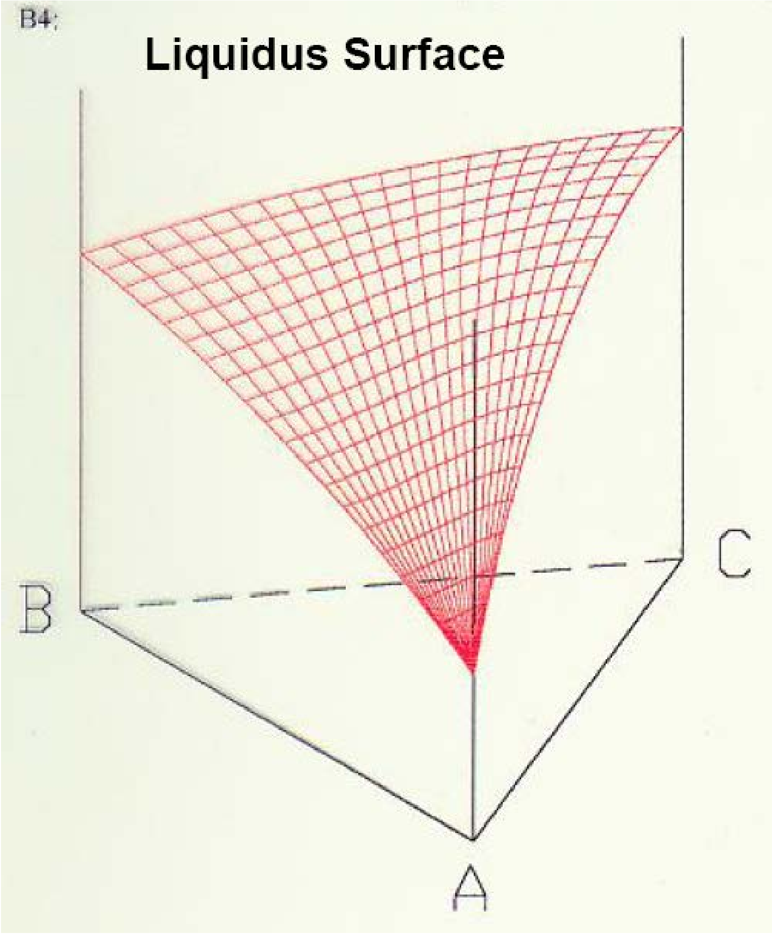


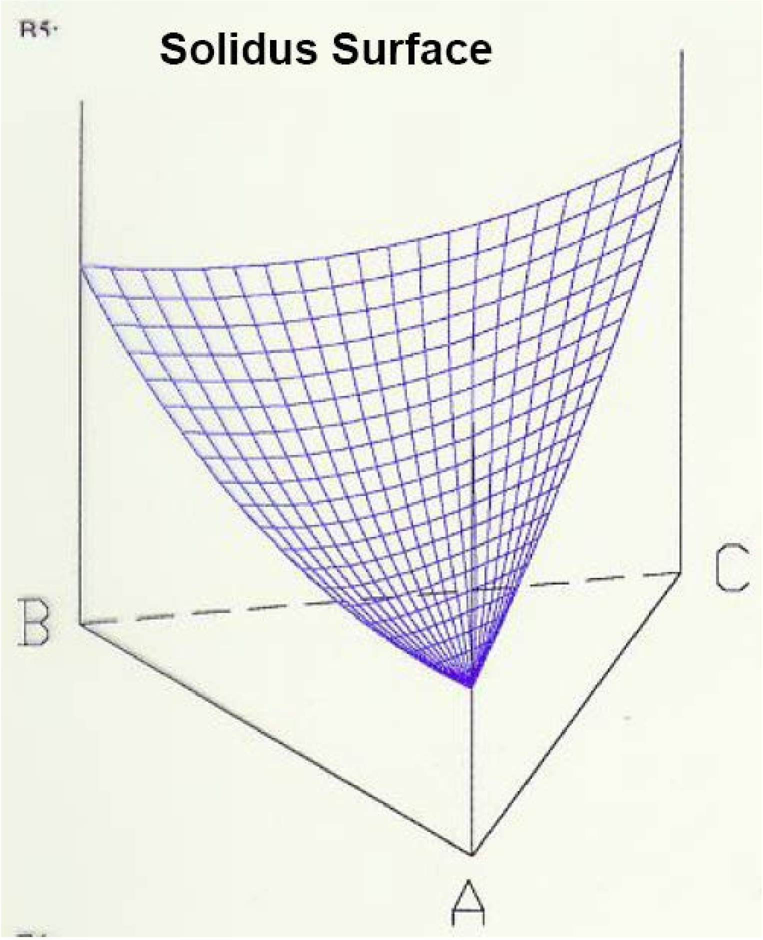


Ternary Isomorphous System

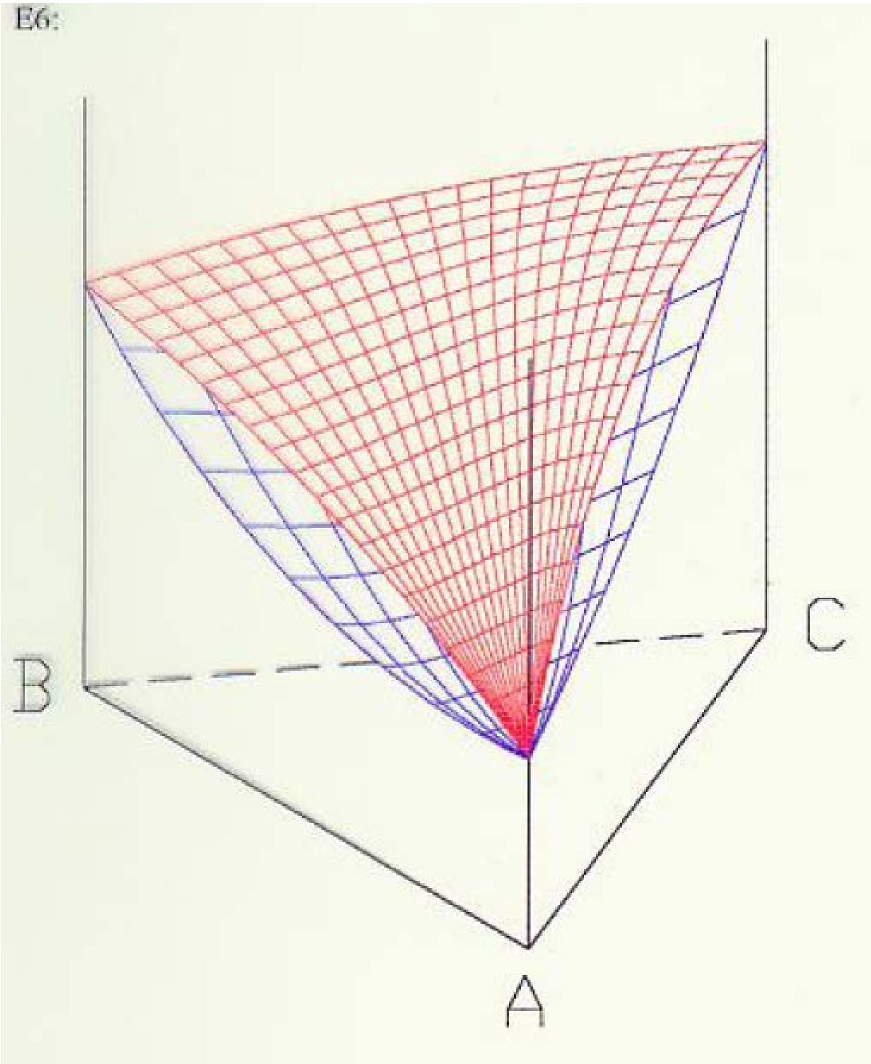


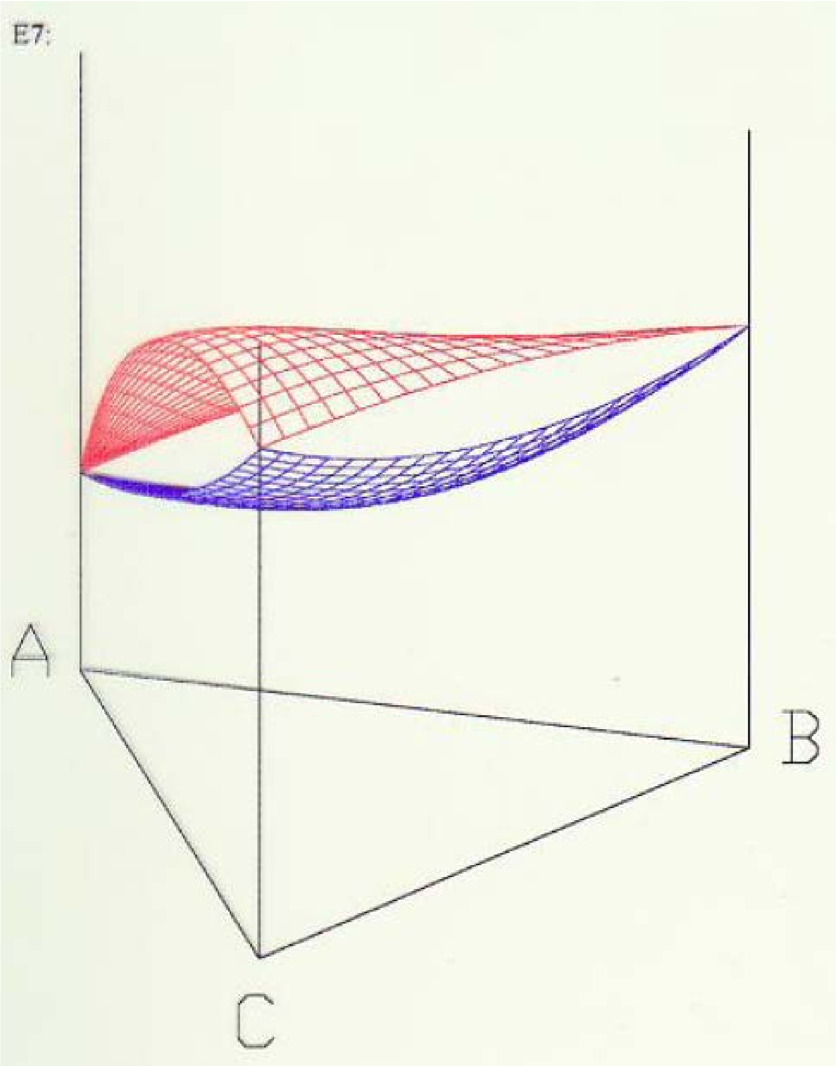
Ternary Isomorphous System





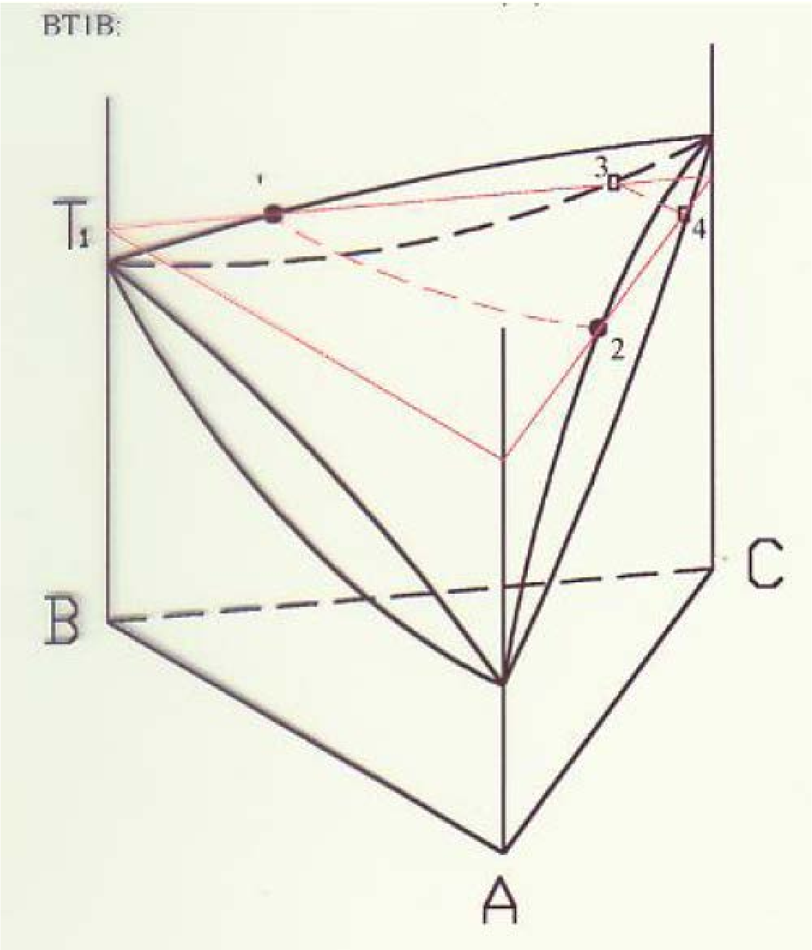
Ternary Isomorphous System

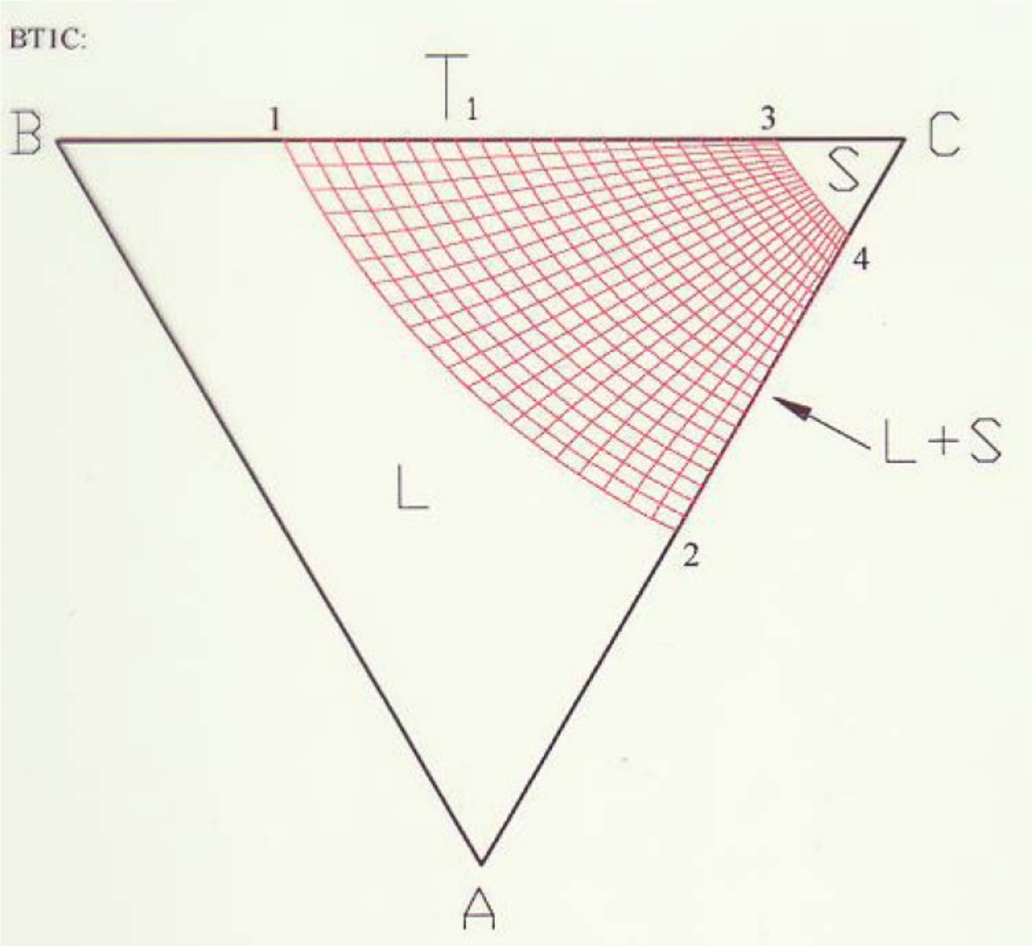




Ternary Isomorphous System

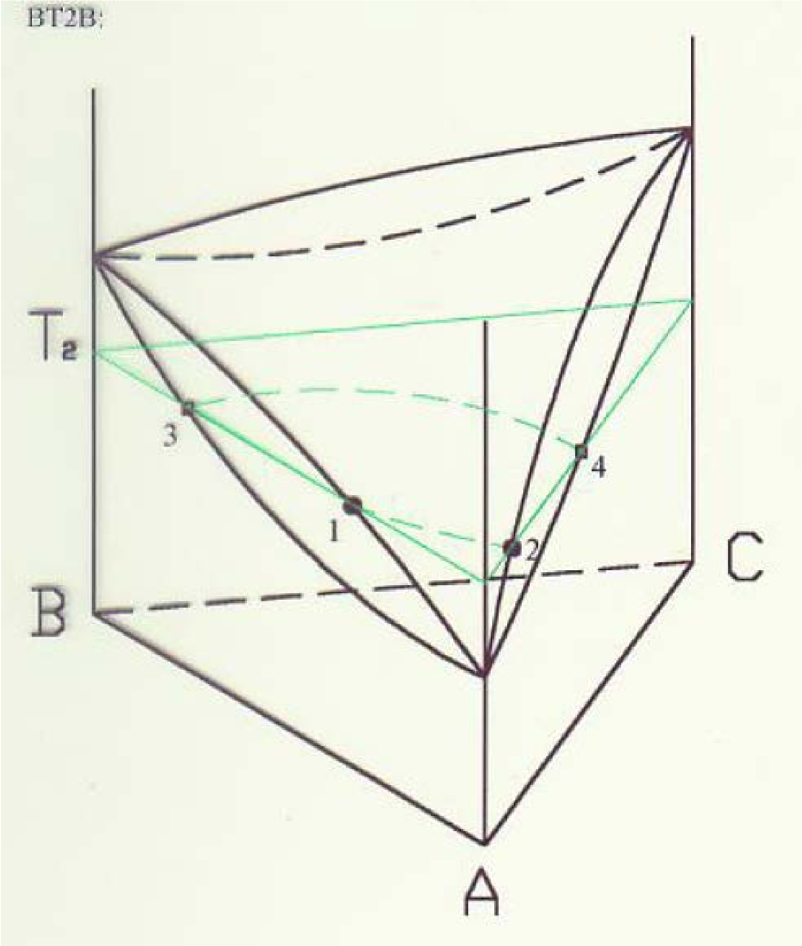
Isothermal section → F = C - P

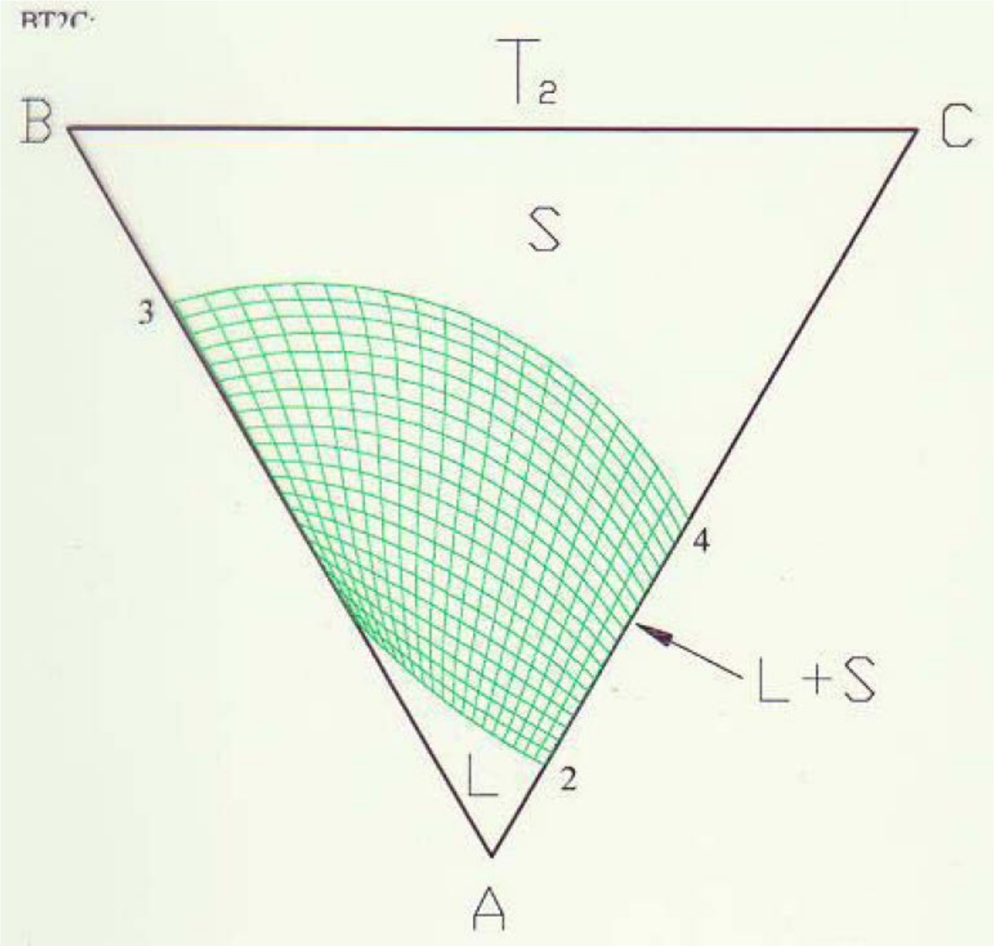




Ternary Isomorphous System

Isothermal section





Ternary Isomorphous System

Isothermal section → F = C - P

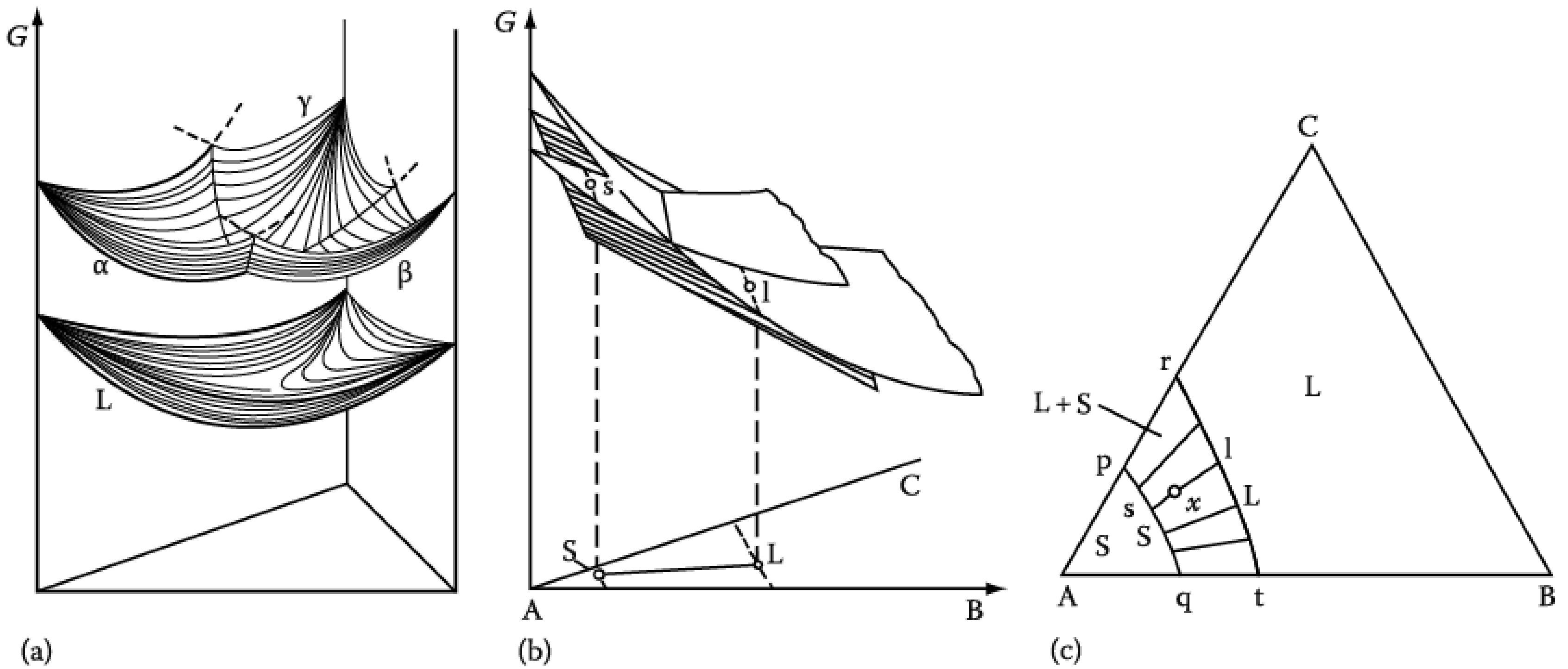


Fig. 1.41 (a) Free energies of a liquid and three solid phases of a ternary system.

Ternary Eutectic System
(No Solid Solubility)

The Ternary Eutectic Reaction:

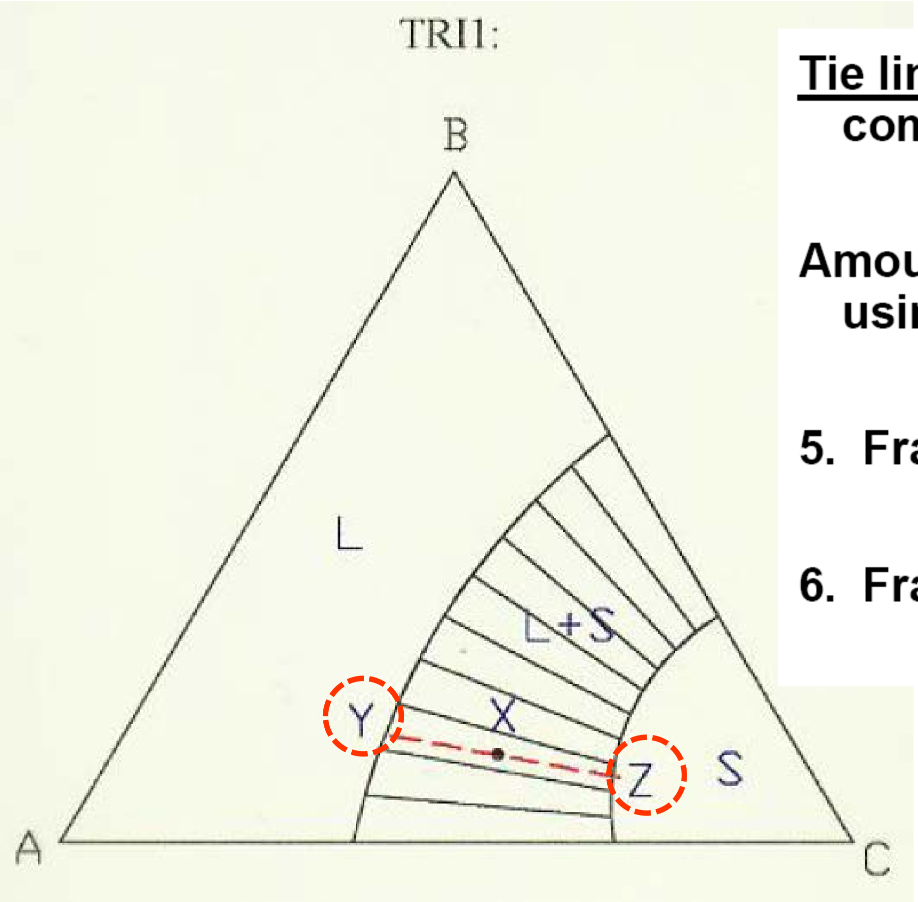
$$L = \alpha + \beta + \gamma$$

A liquid phase solidifies into three separate solid phases

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

Ternary Isomorphous System

Locate overall composition using Gibbs triangle



<u>Tie line</u>: A straight line joining any two ternary compositions

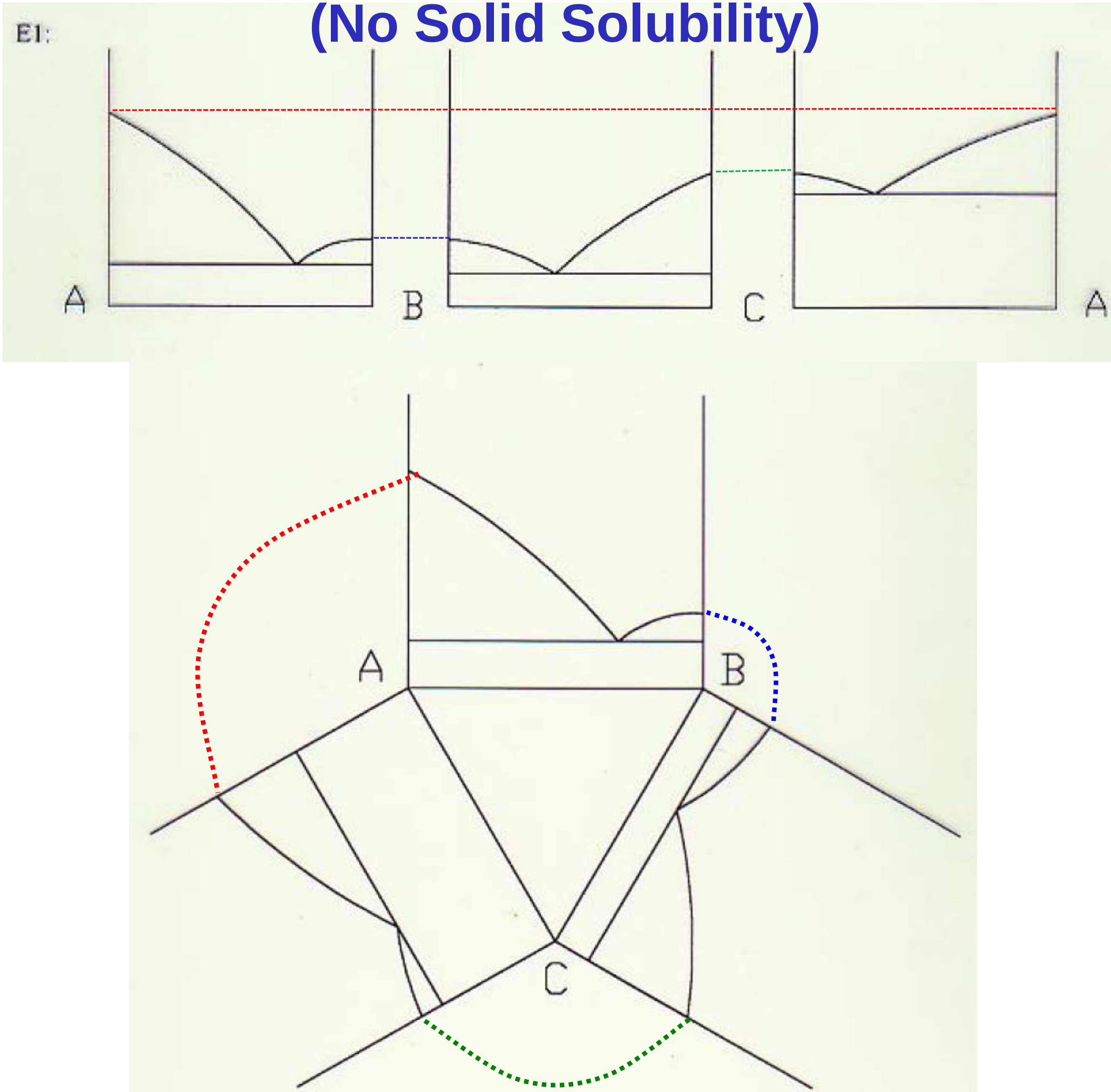
Amount of each phase present is determined by using the Inverse Lever Rule

5. Fraction of solid = YX/YZ

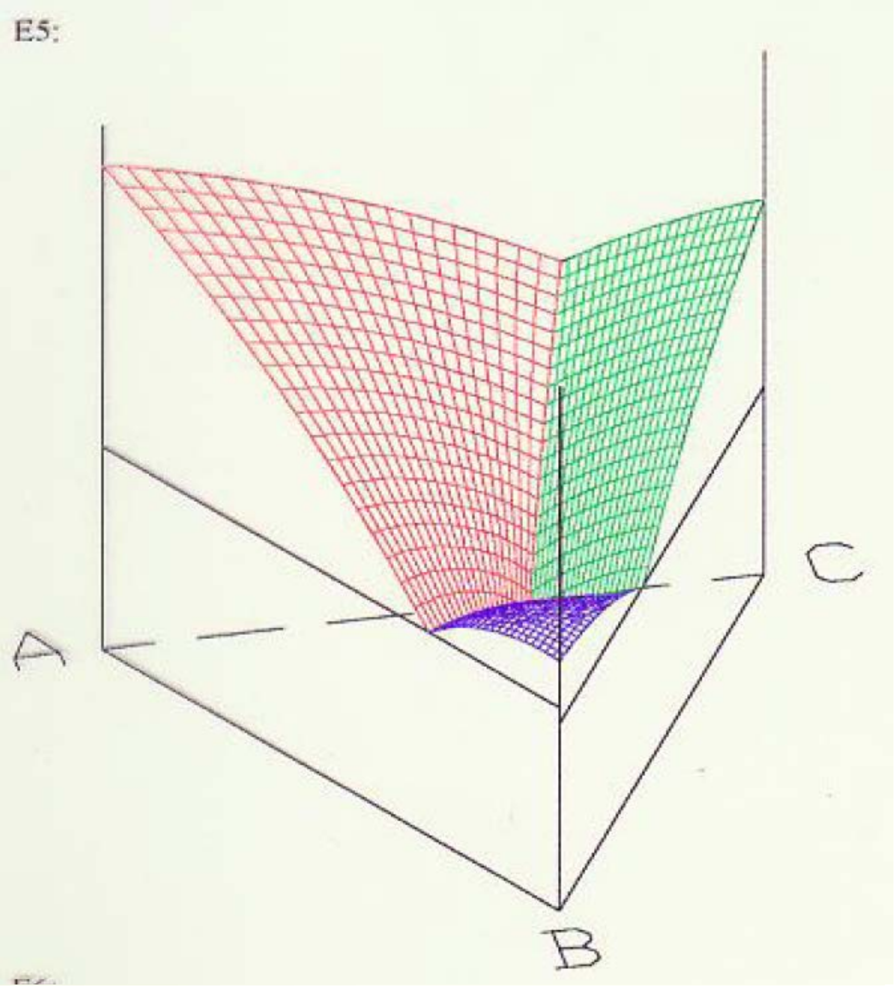
6. Fraction of liquid = ZX/YZ

Ternary Eutectic System

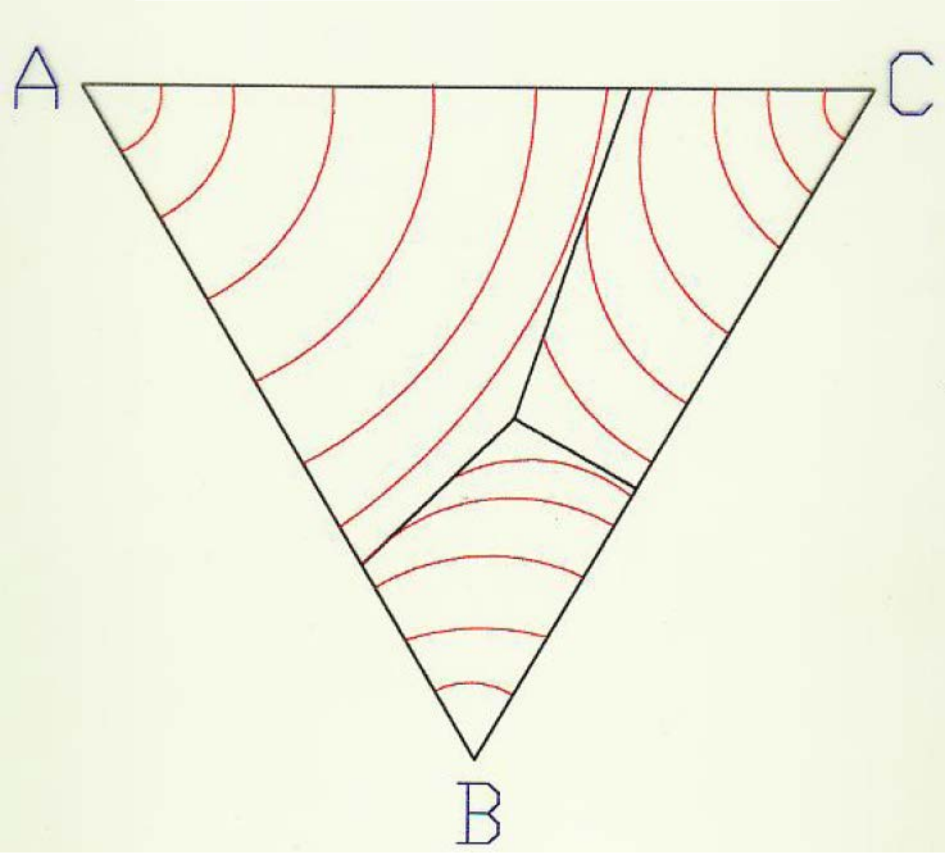
(No Solid Solubility)



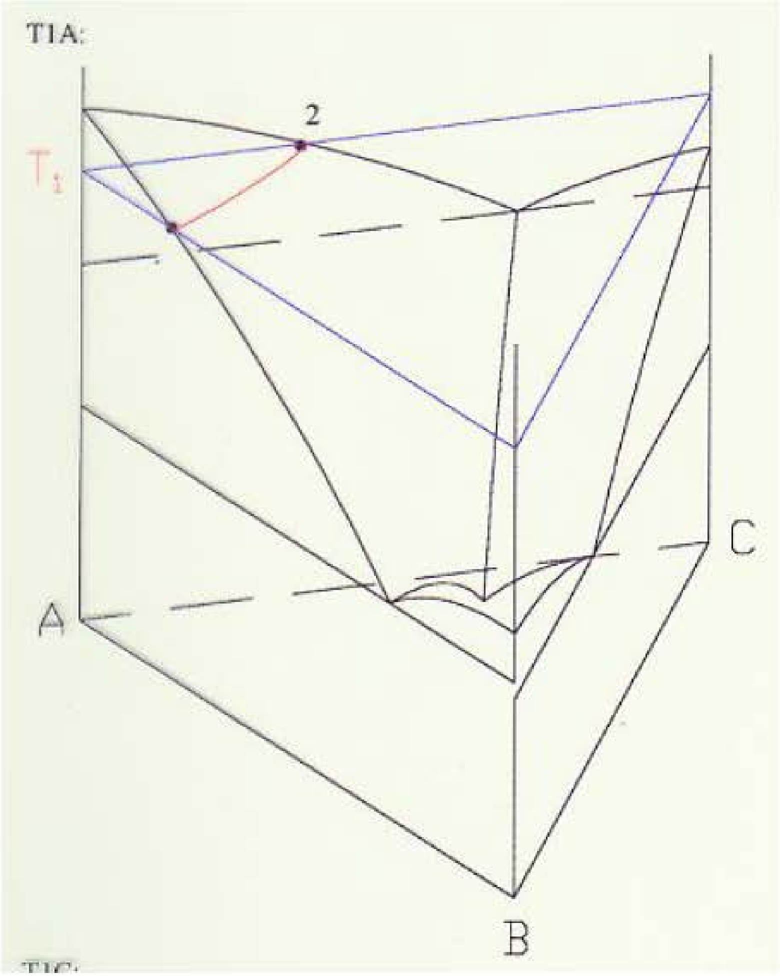
Ternary Eutectic System
(No Solid Solubility)



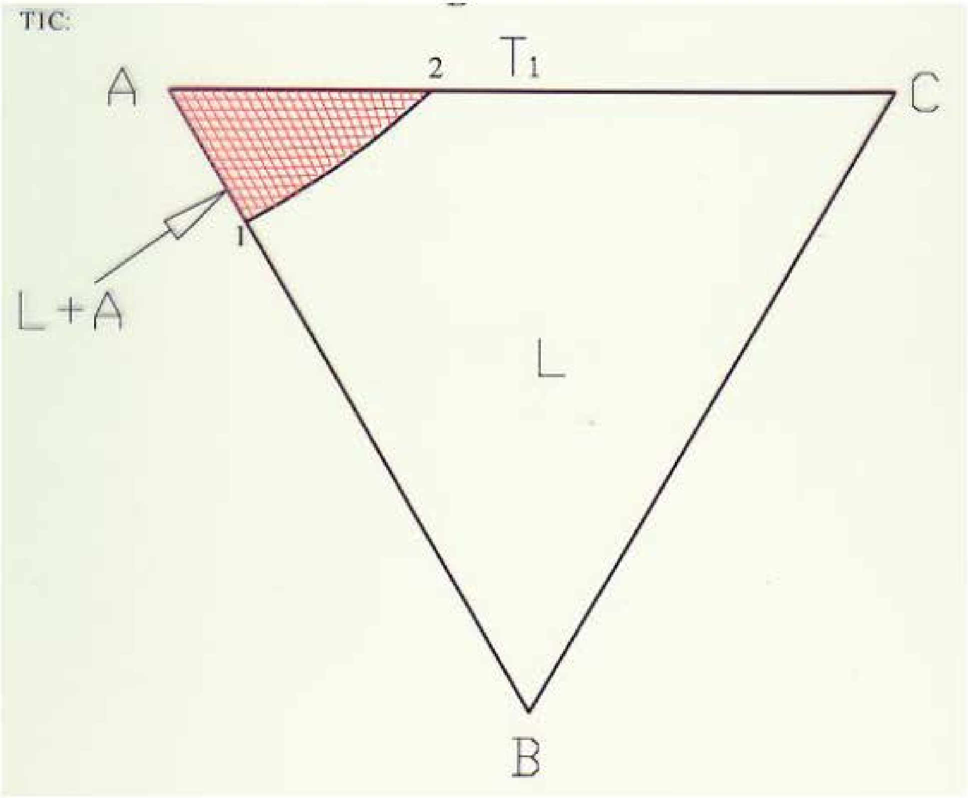
Liquidus projection



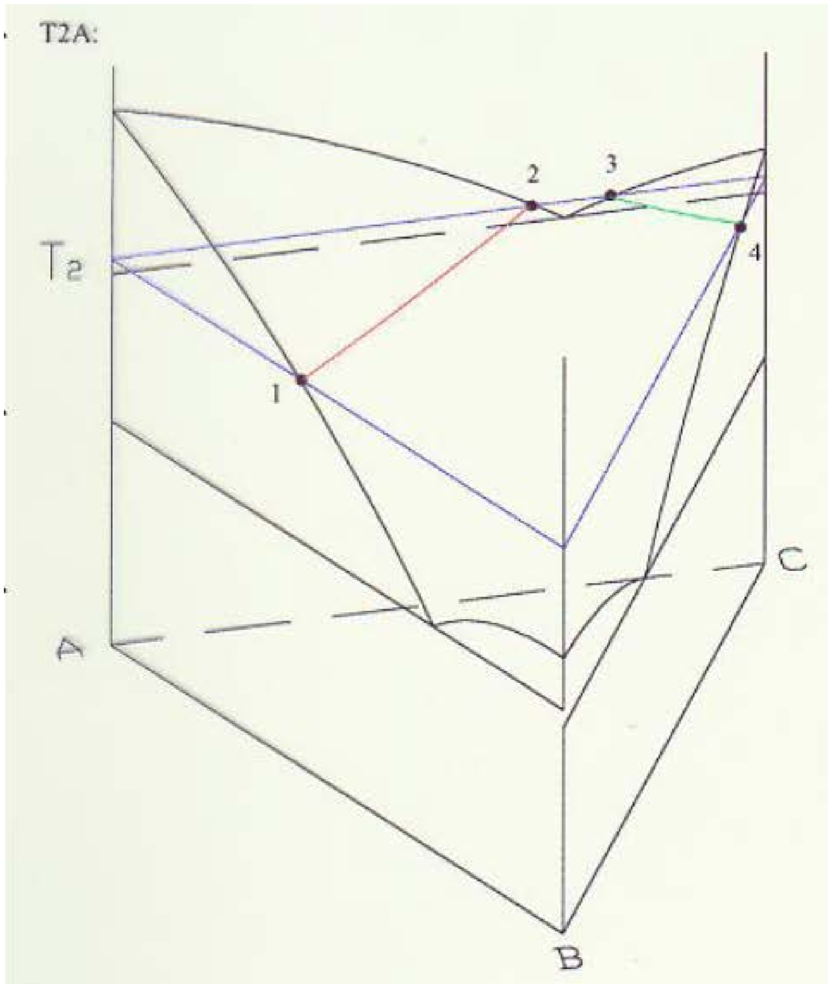
Ternary Eutectic System
(No Solid Solubility)

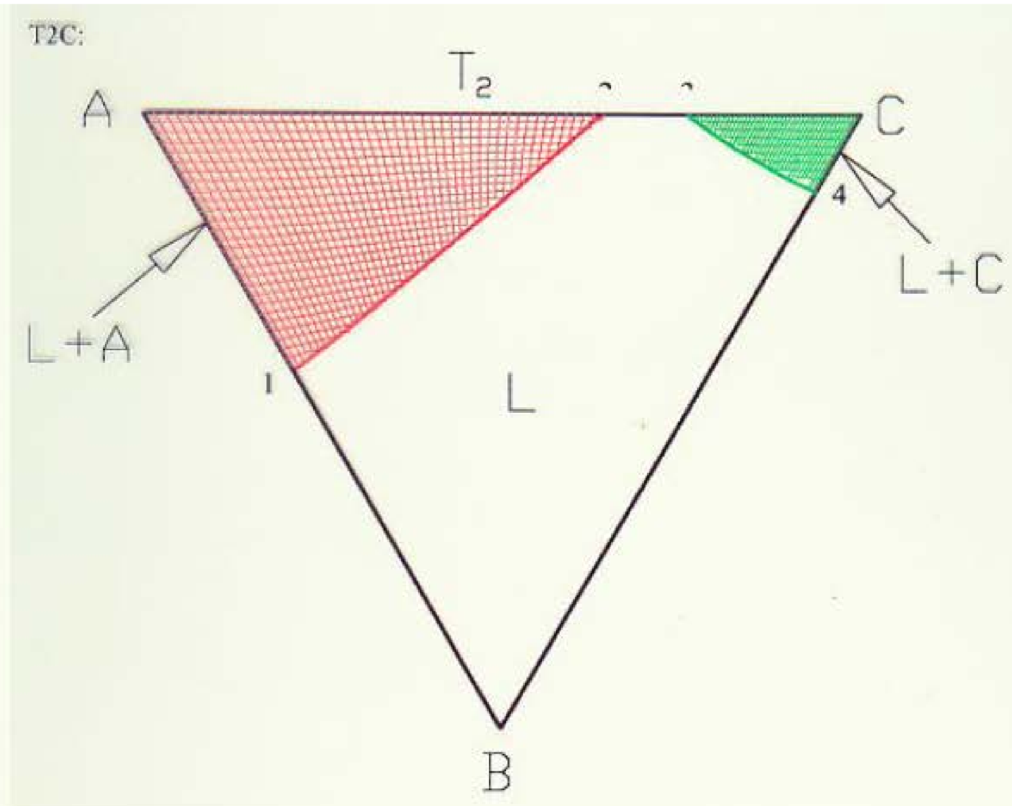


*** Isothermal section**

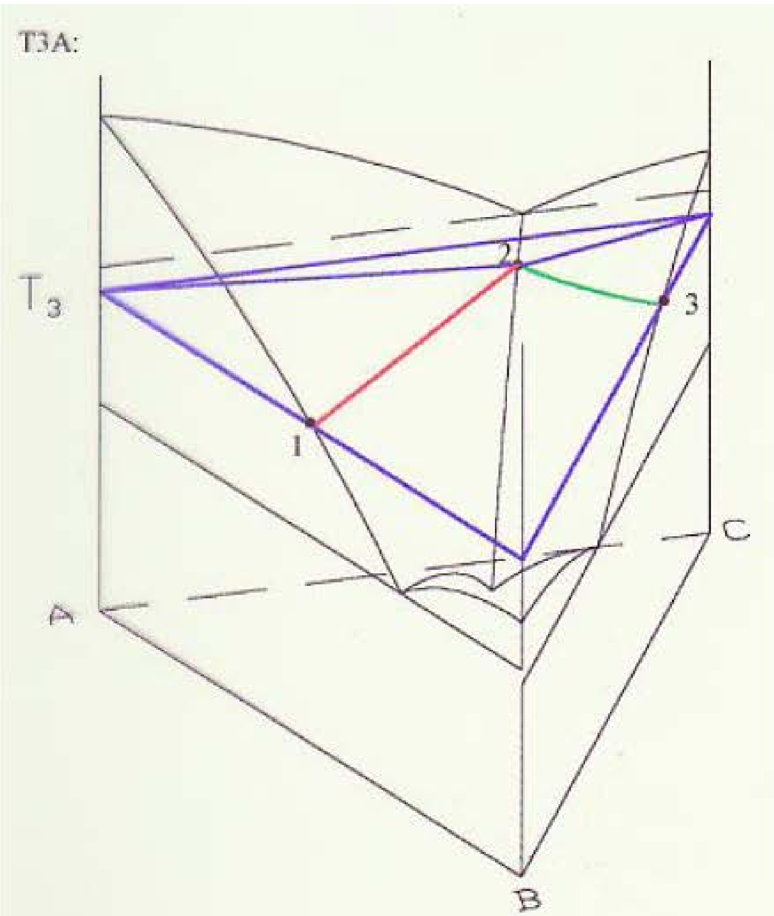


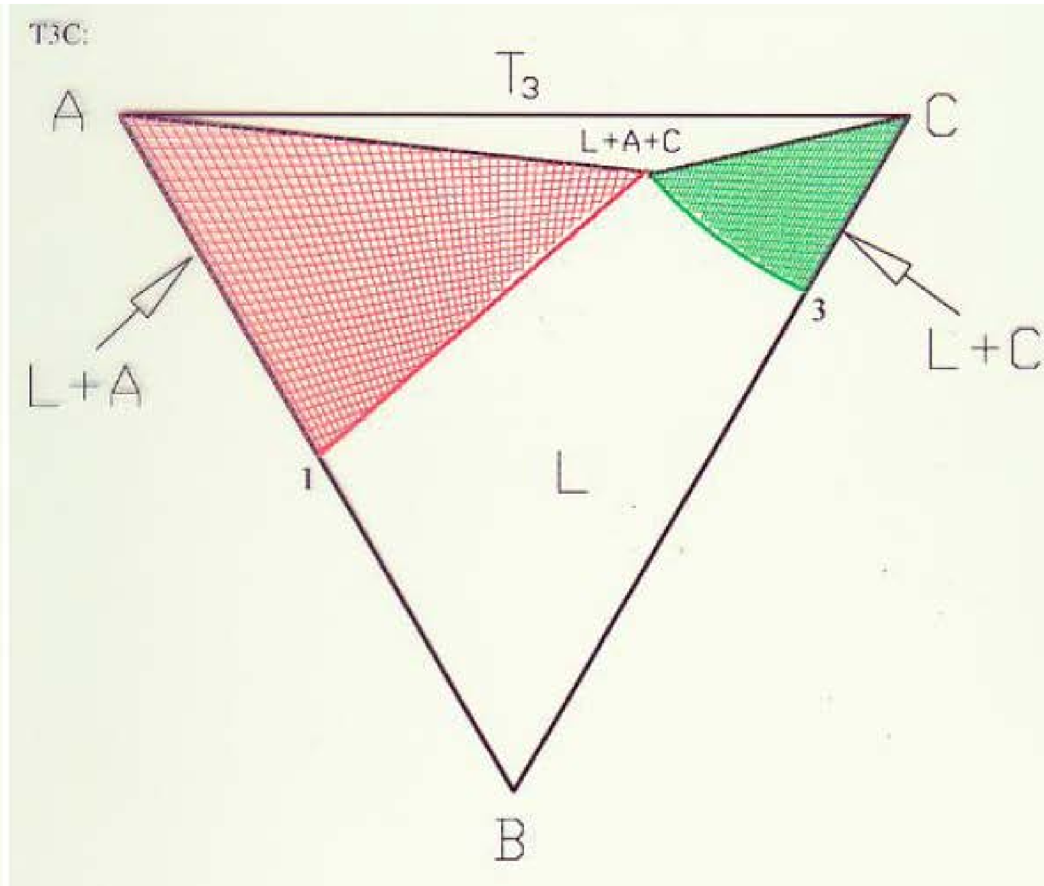
Ternary Eutectic System
(No Solid Solubility)



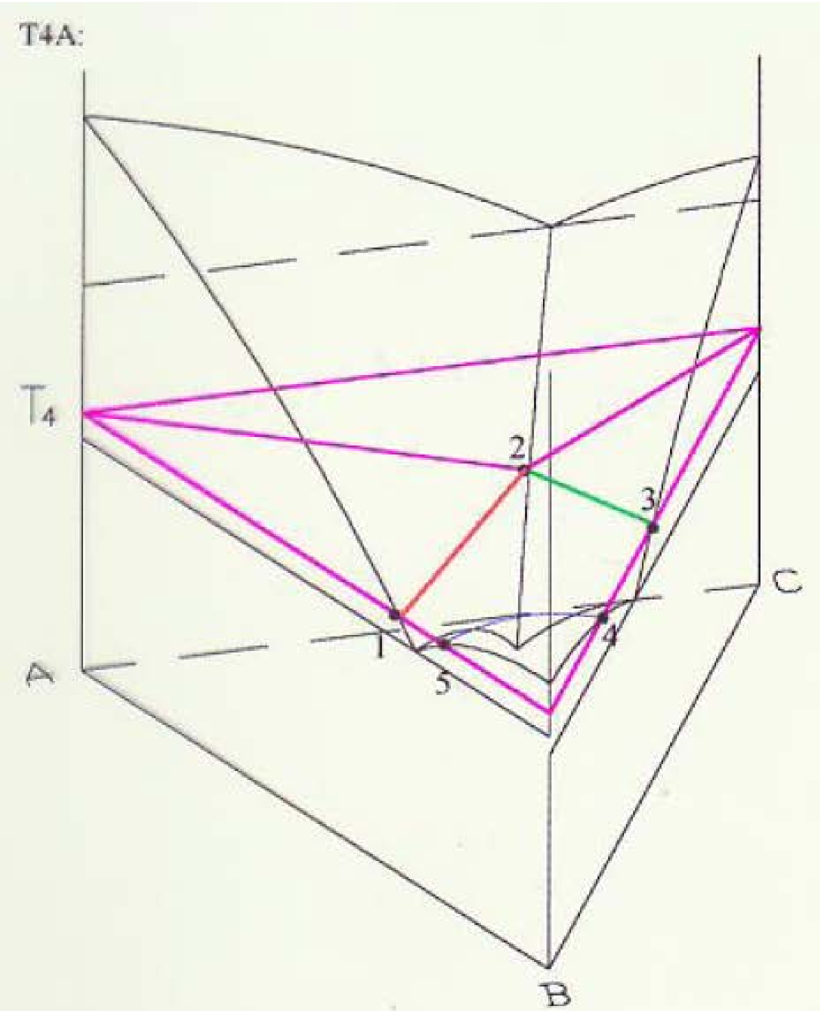


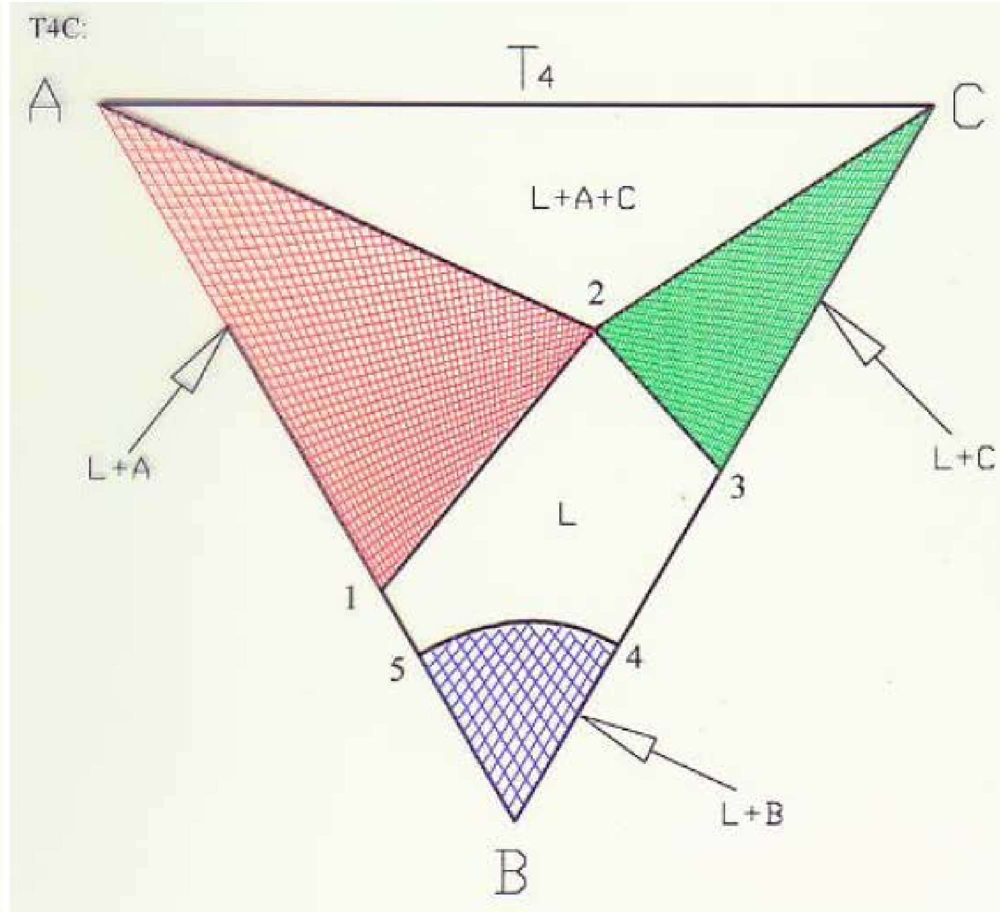
Ternary Eutectic System
(No Solid Solubility)



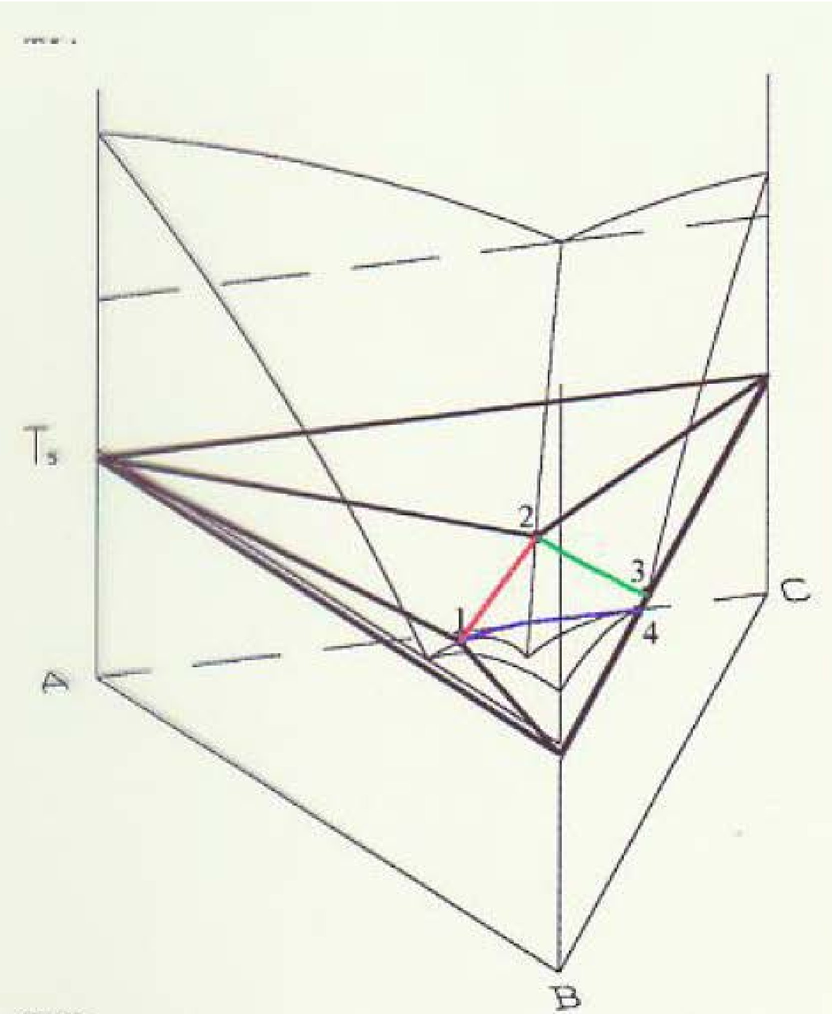


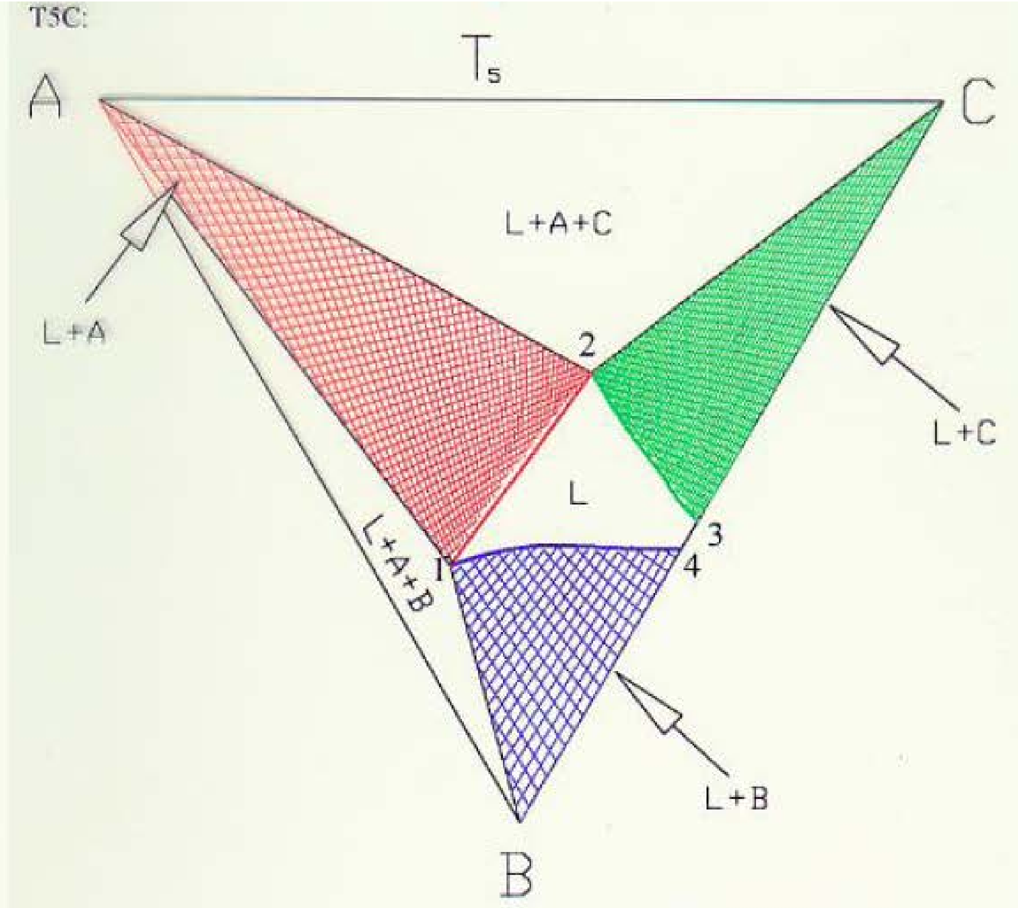
Ternary Eutectic System
(No Solid Solubility)



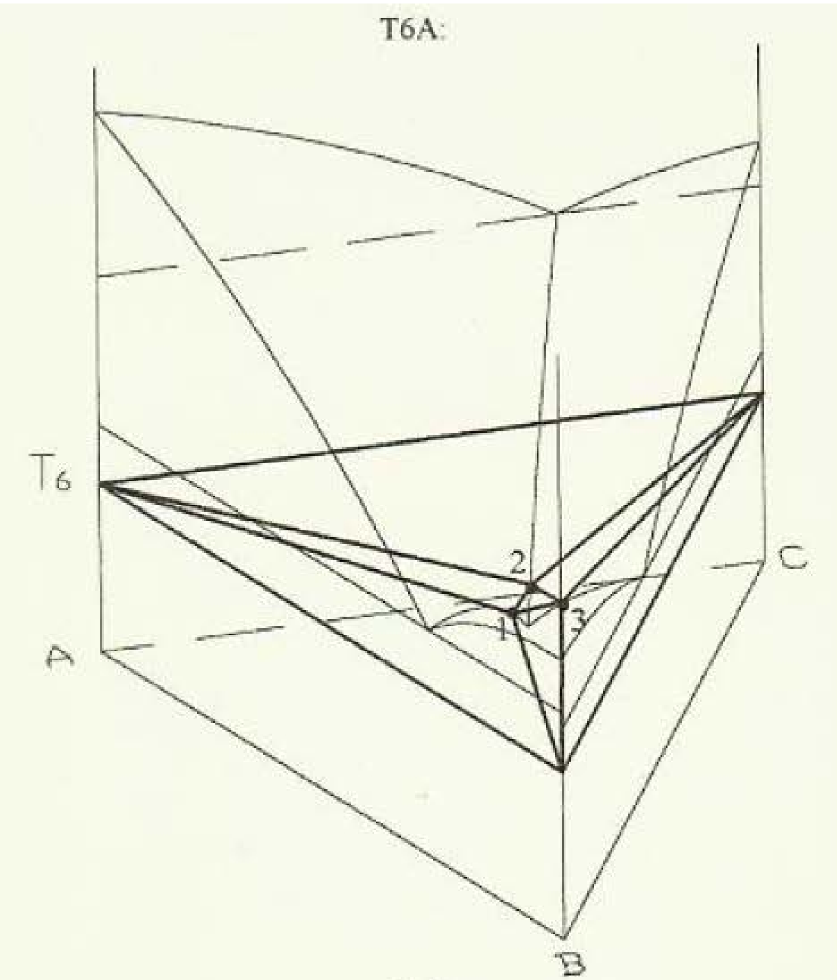


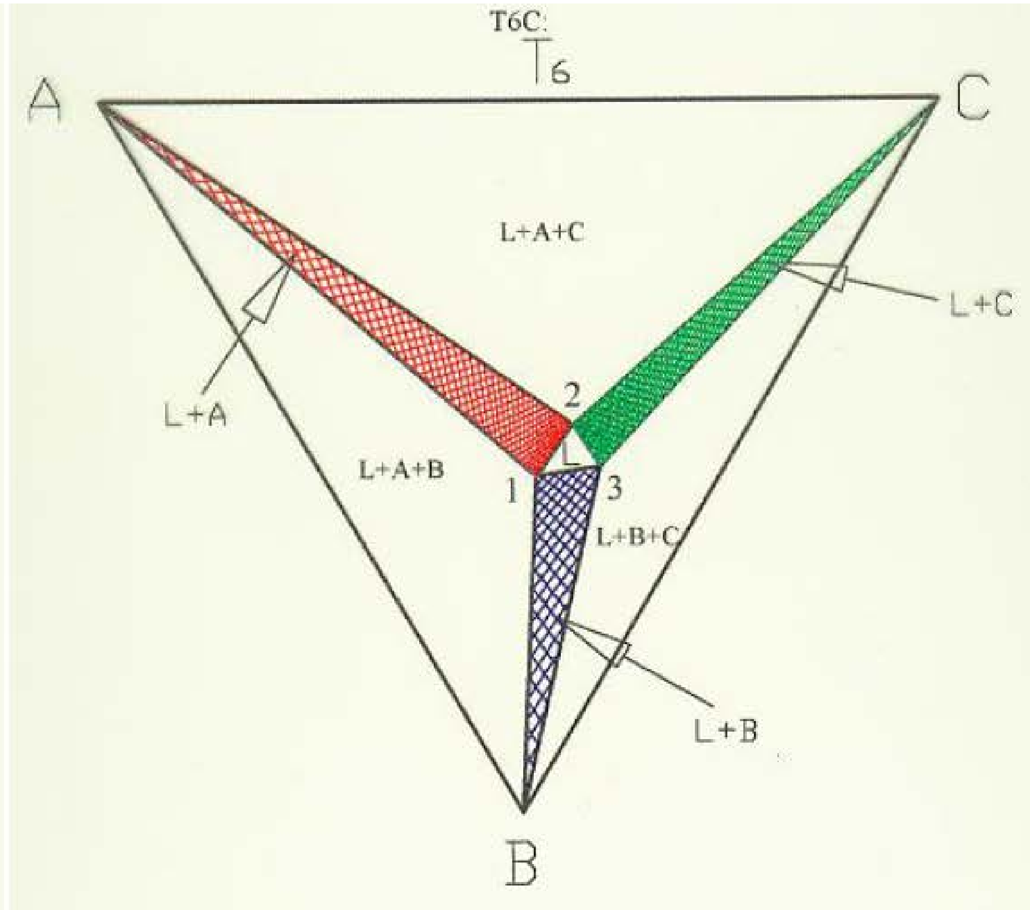
Ternary Eutectic System
(No Solid Solubility)





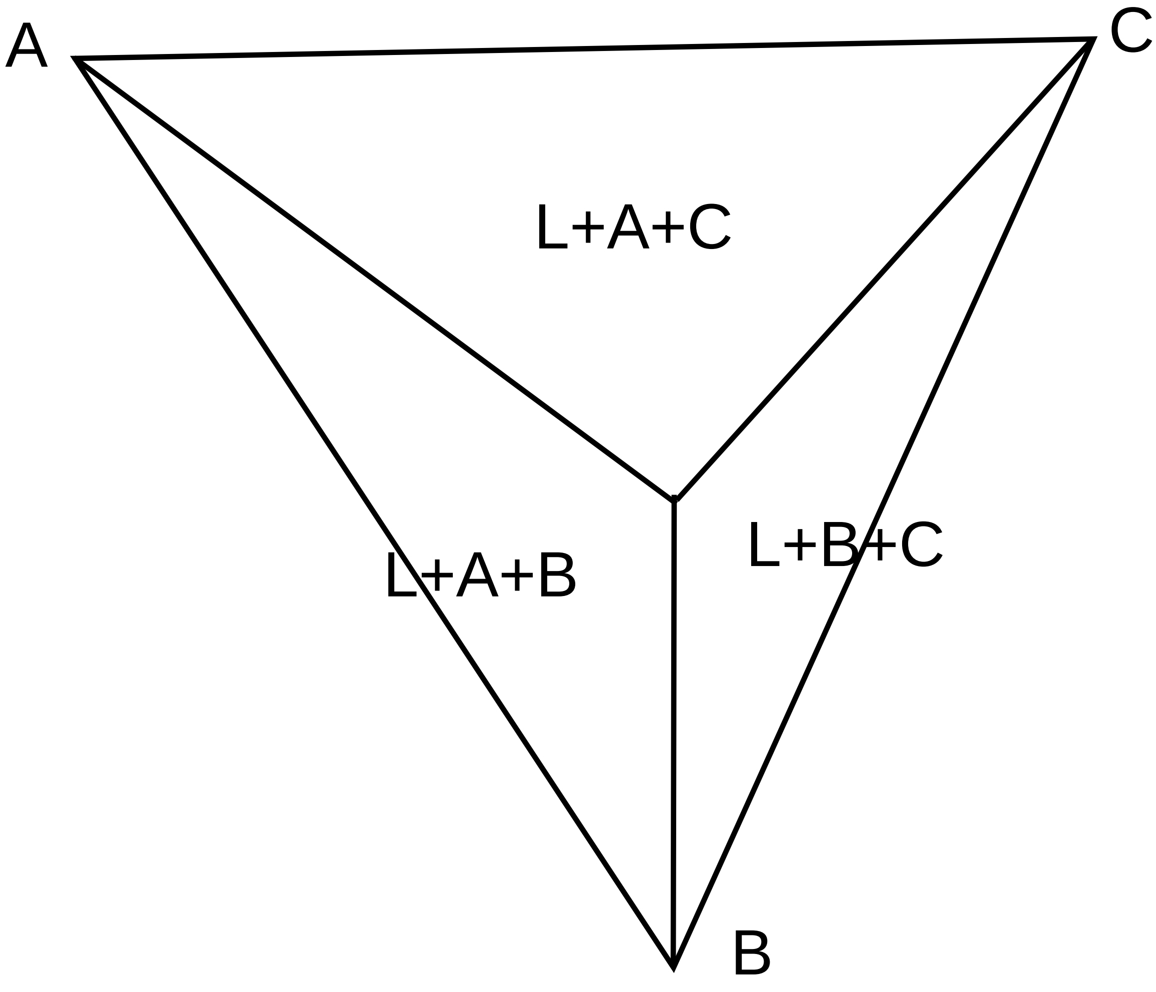
Ternary Eutectic System
(No Solid Solubility)



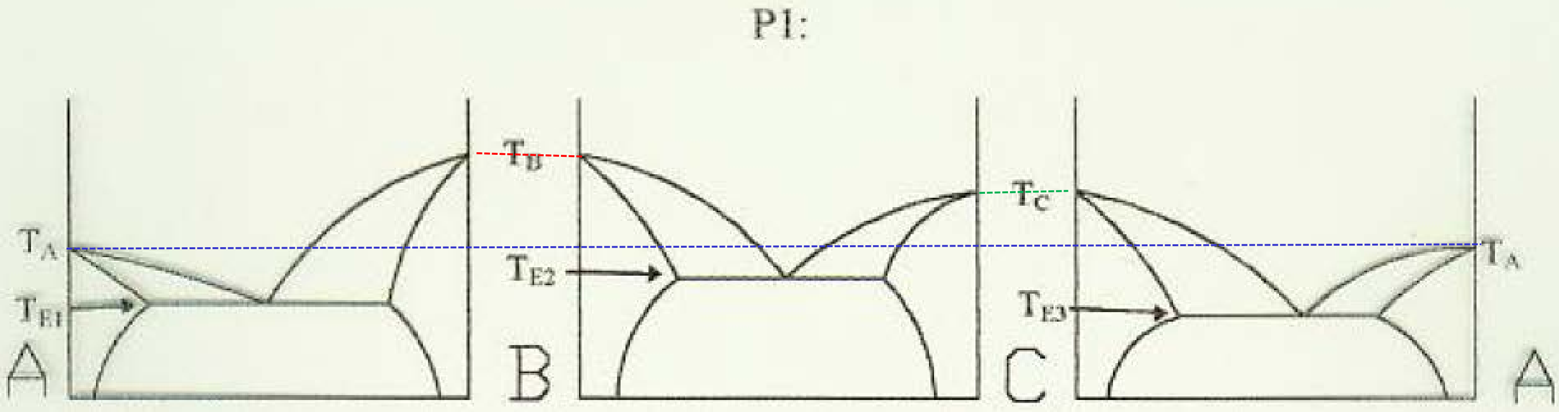


Ternary Eutectic System
(No Solid Solubility)

T= ternary eutectic temp.



Ternary Eutectic System
(with Solid Solubility)



T_A: Melting Point Of Material A

T_B: Melting Point Of Material B

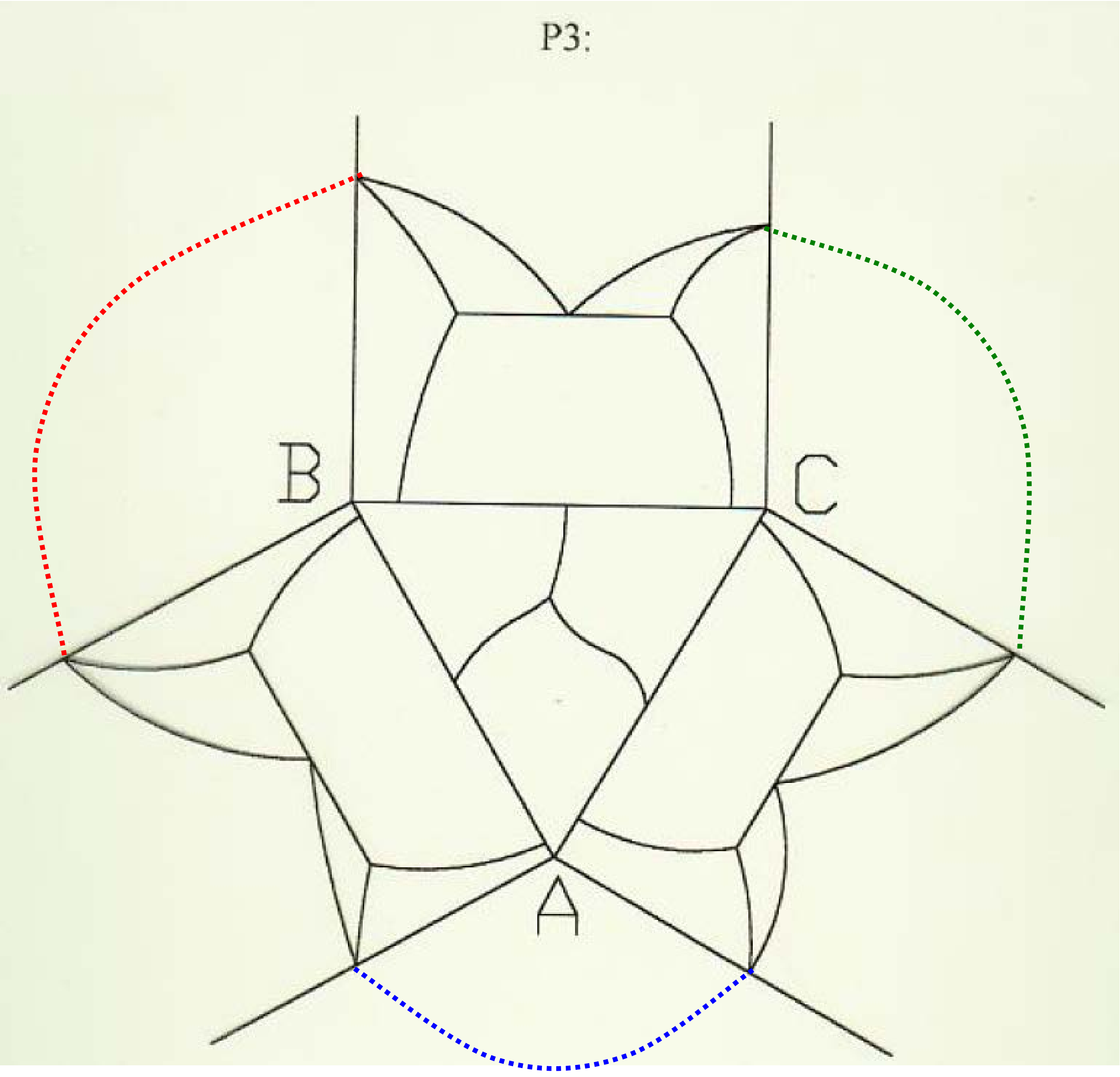
T_C: Melting Point Of Material C

T_{E1}: Eutectic Temperature Of A-B

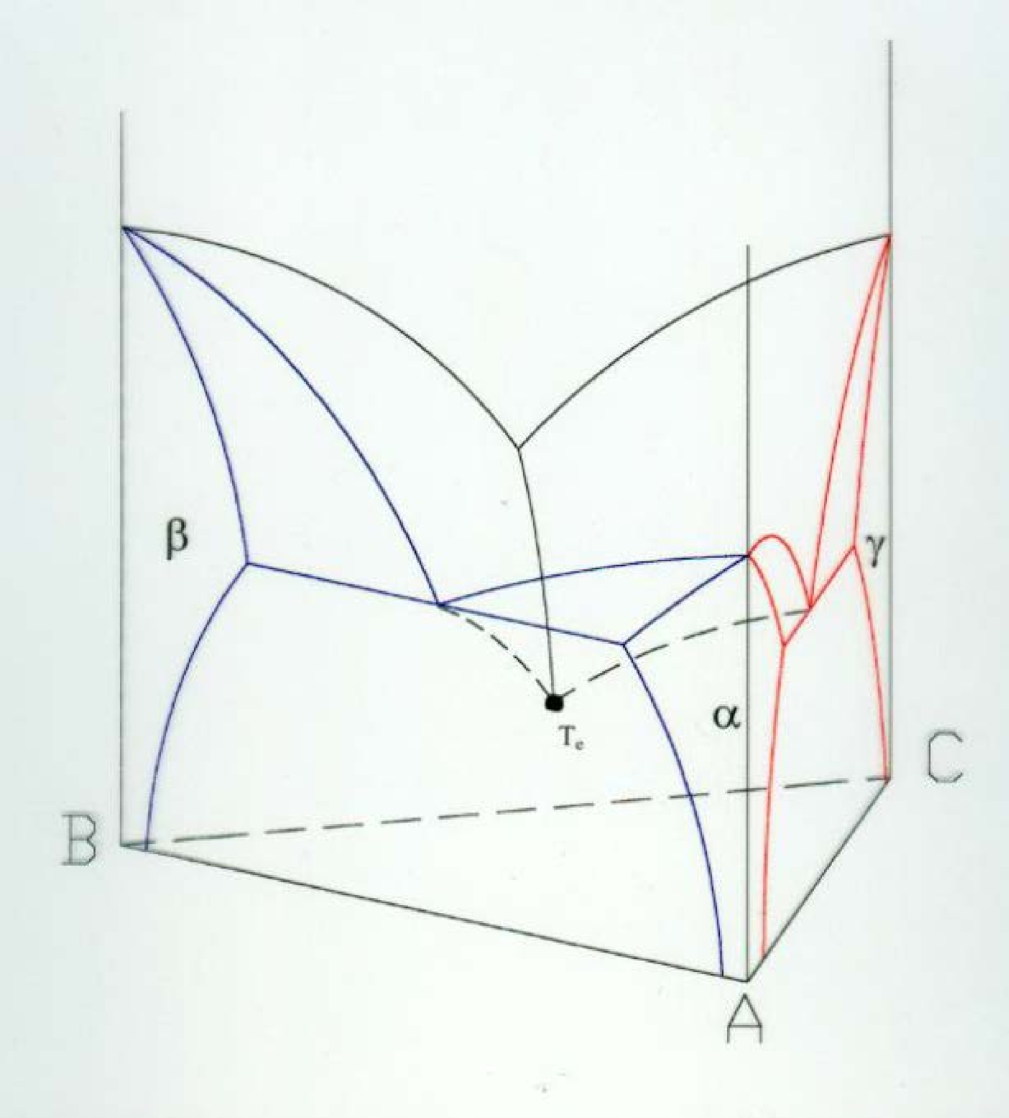
T_{E2}: Eutectic Temperature Of B-C

T_{E3}: Eutectic Temperature Of C-A

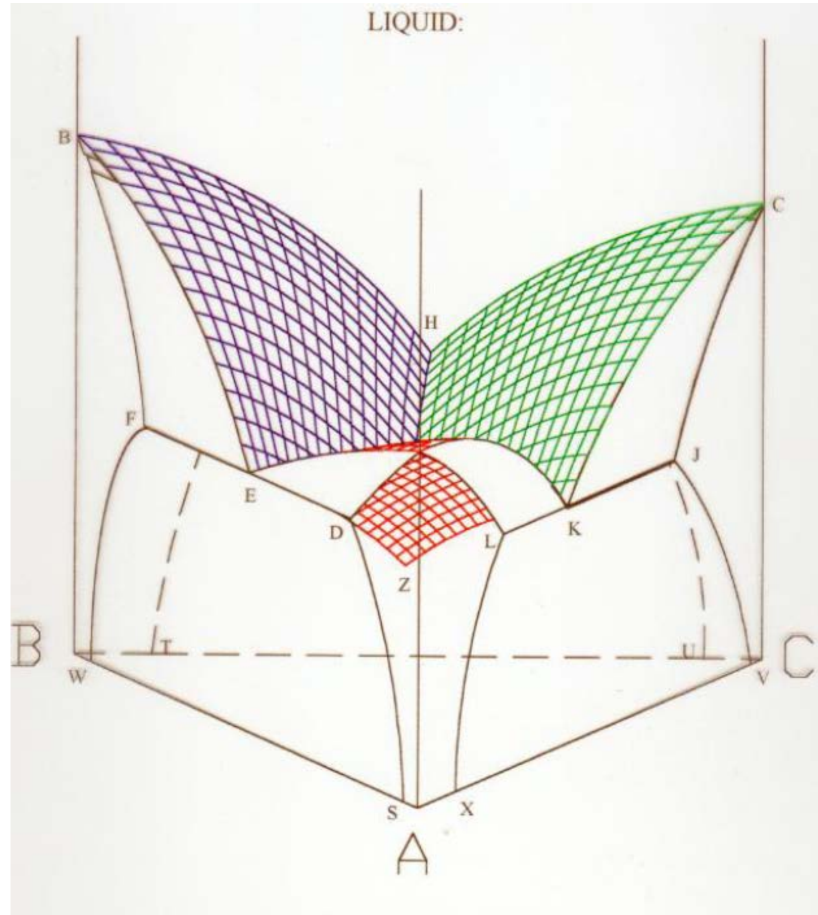
Ternary Eutectic System
(with Solid Solubility)



Ternary Eutectic System
(with Solid Solubility)

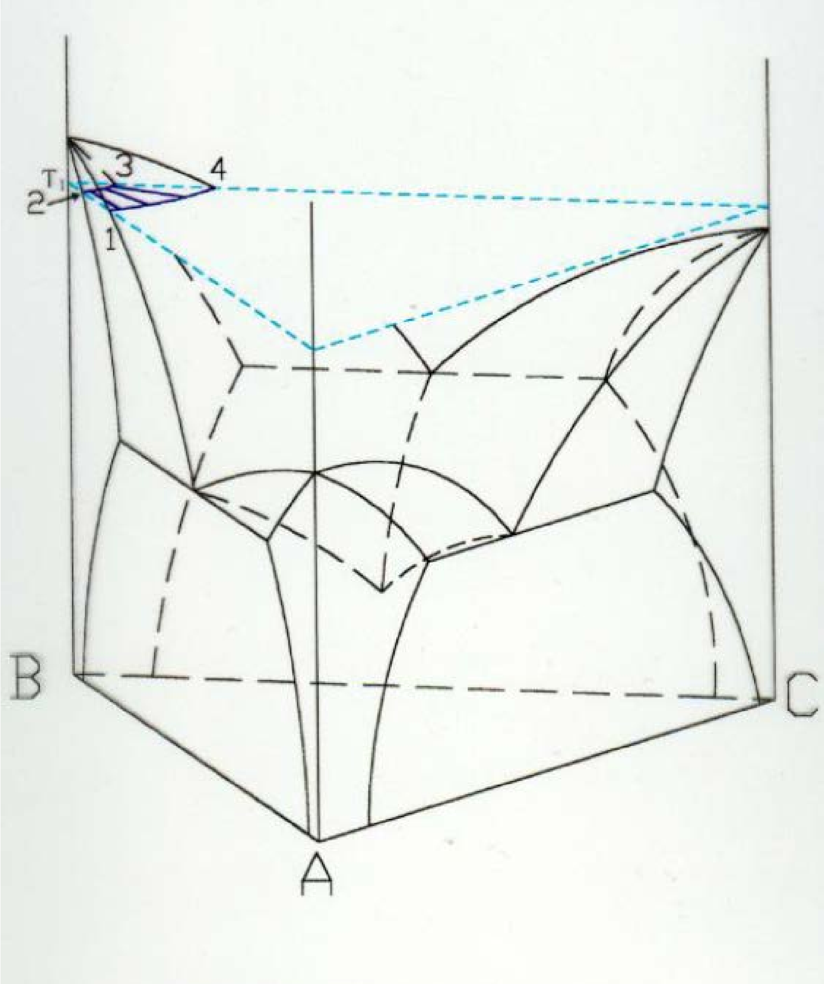


Main outline of Ternary Phase Diagram with Ternary Eutectic (T_e) and Solid Single Phase Regions Shown

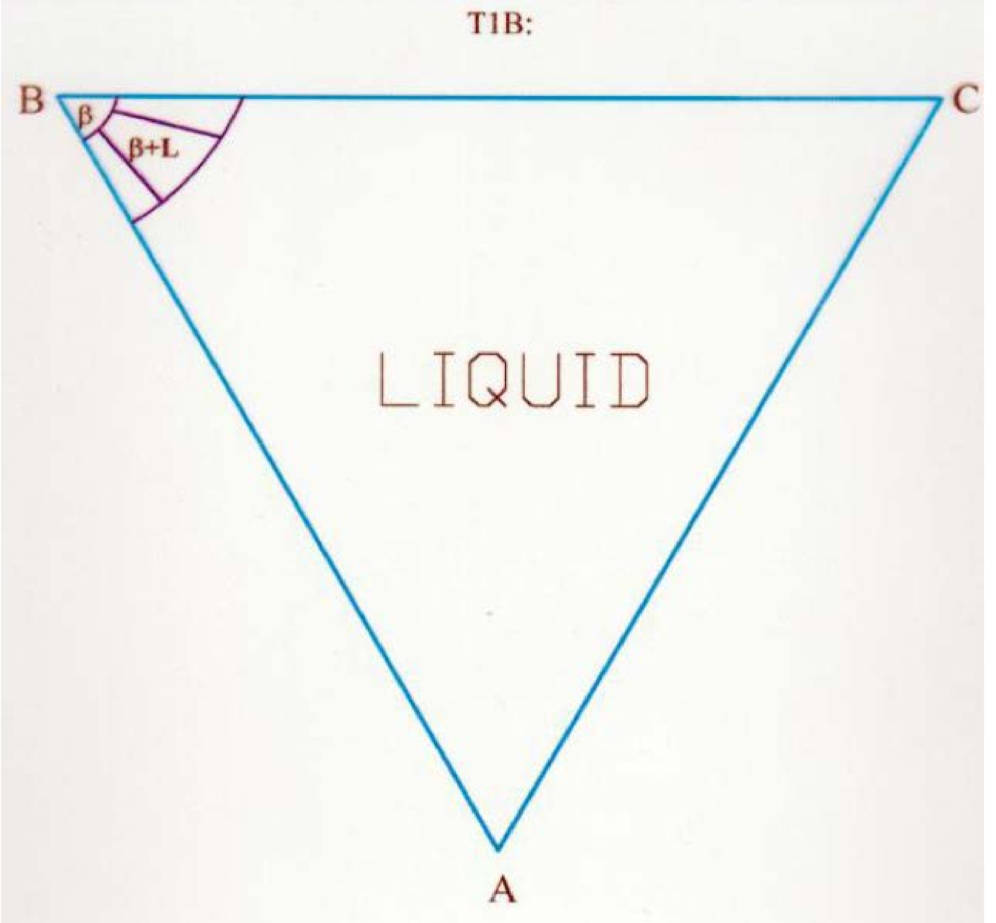


All Liquidus surfaces (α+L-Red, β+L-Purple, γ+L-Green)

Ternary Eutectic System
(with Solid Solubility)

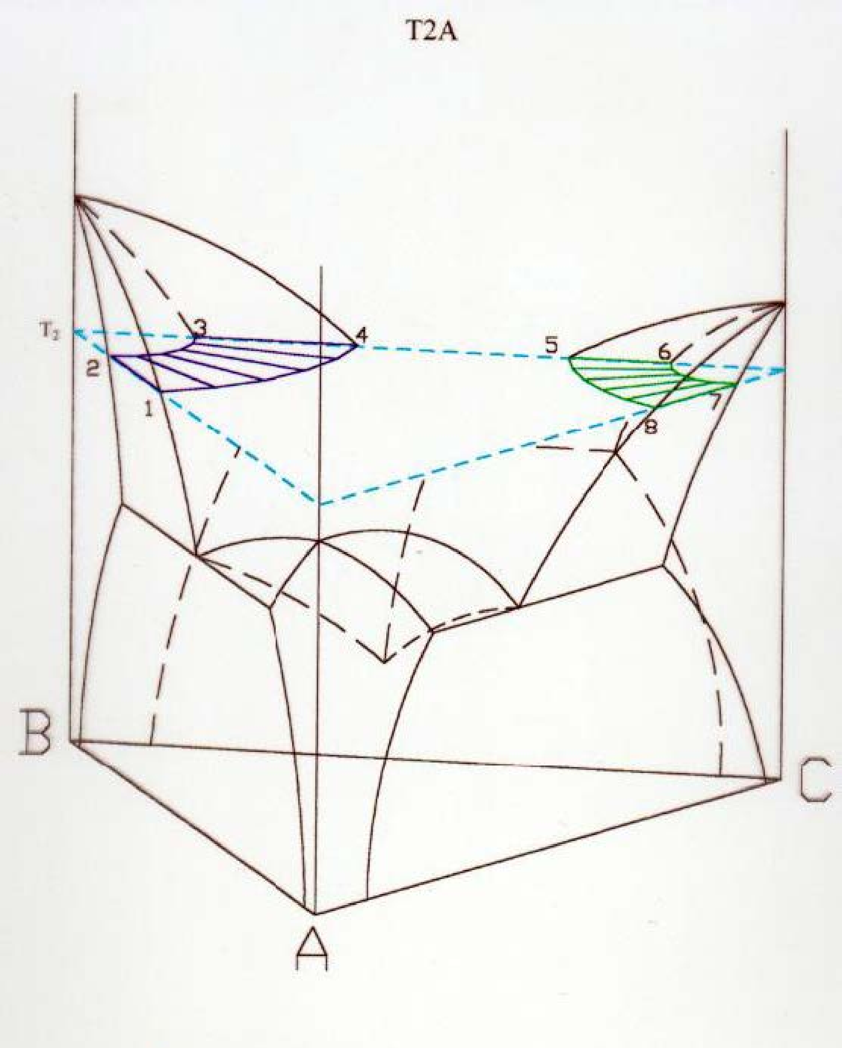


Temperature Slice At $T_1 < T_B$, But $>T_A$, T_C

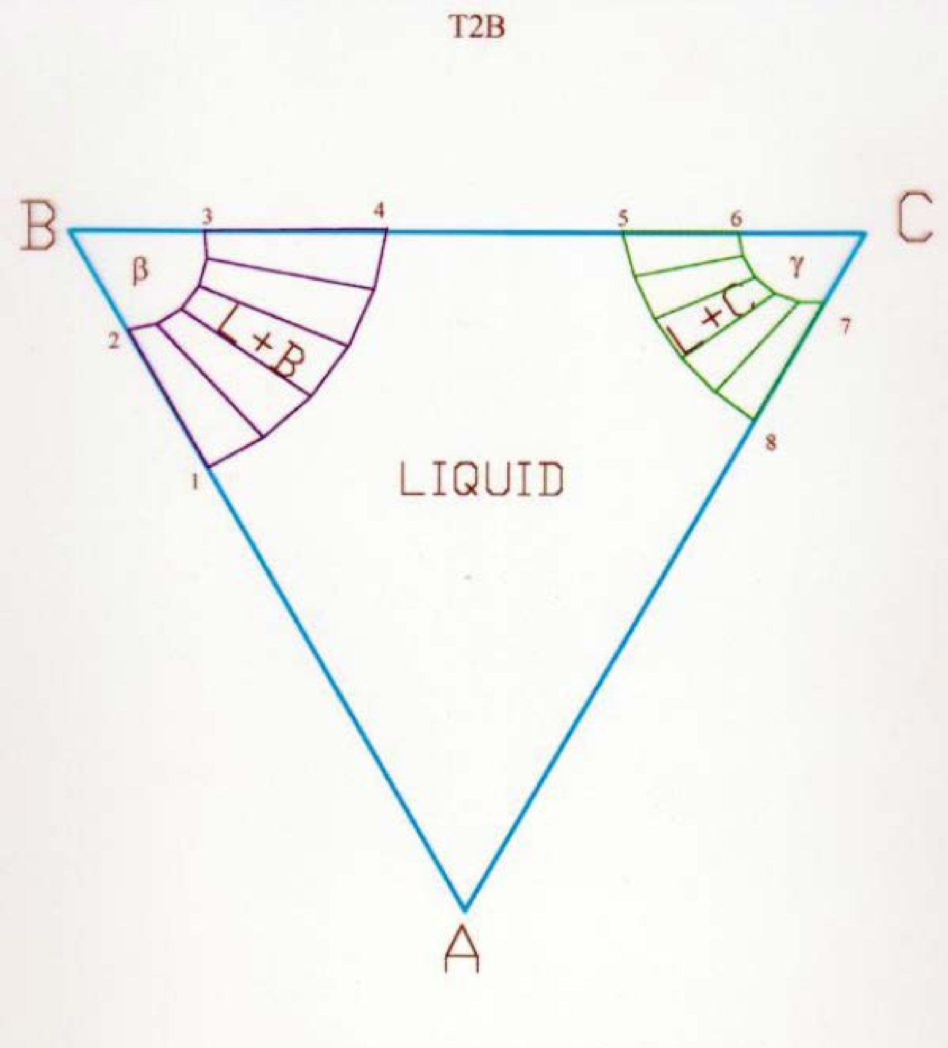


Isothermal Section At $T=T_1$

Ternary Eutectic System
(with Solid Solubility)



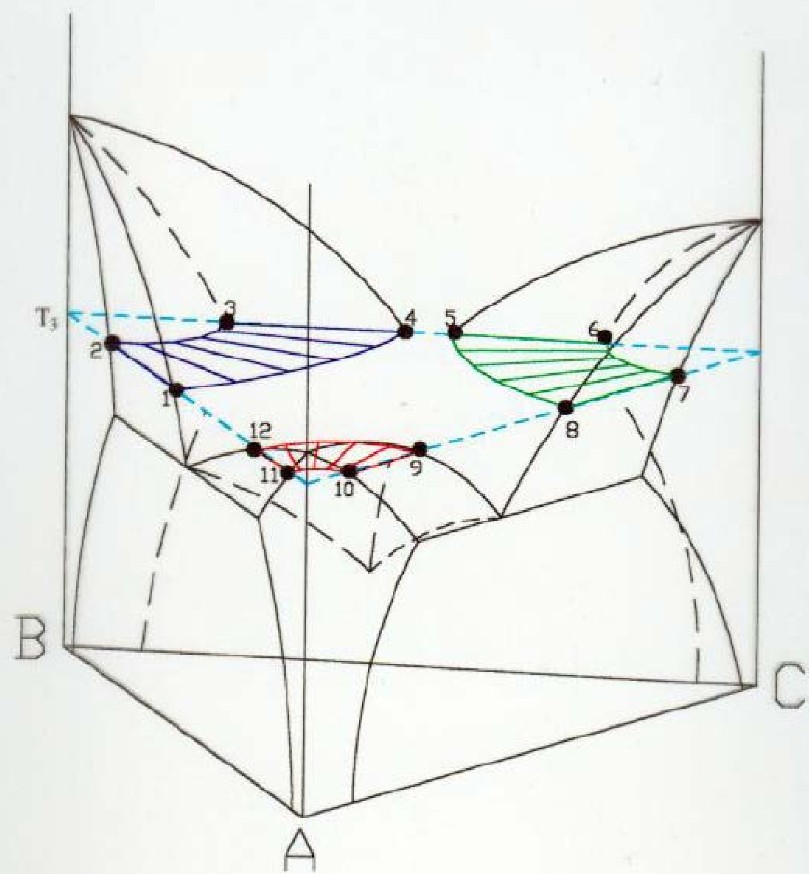
Temperature Slice At $T_2 > T_A$ But, $T_2 < T_B$, T_C



Isothermal Section At $T=T_2$

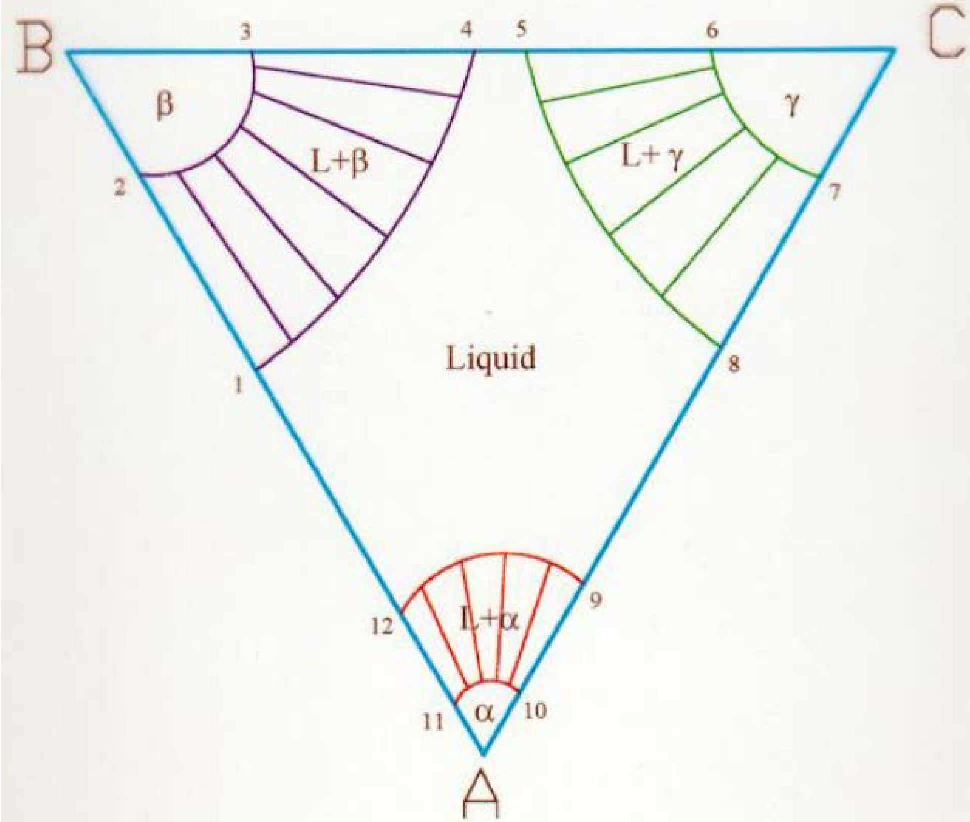
Ternary Eutectic System
(with Solid Solubility)

T3A:



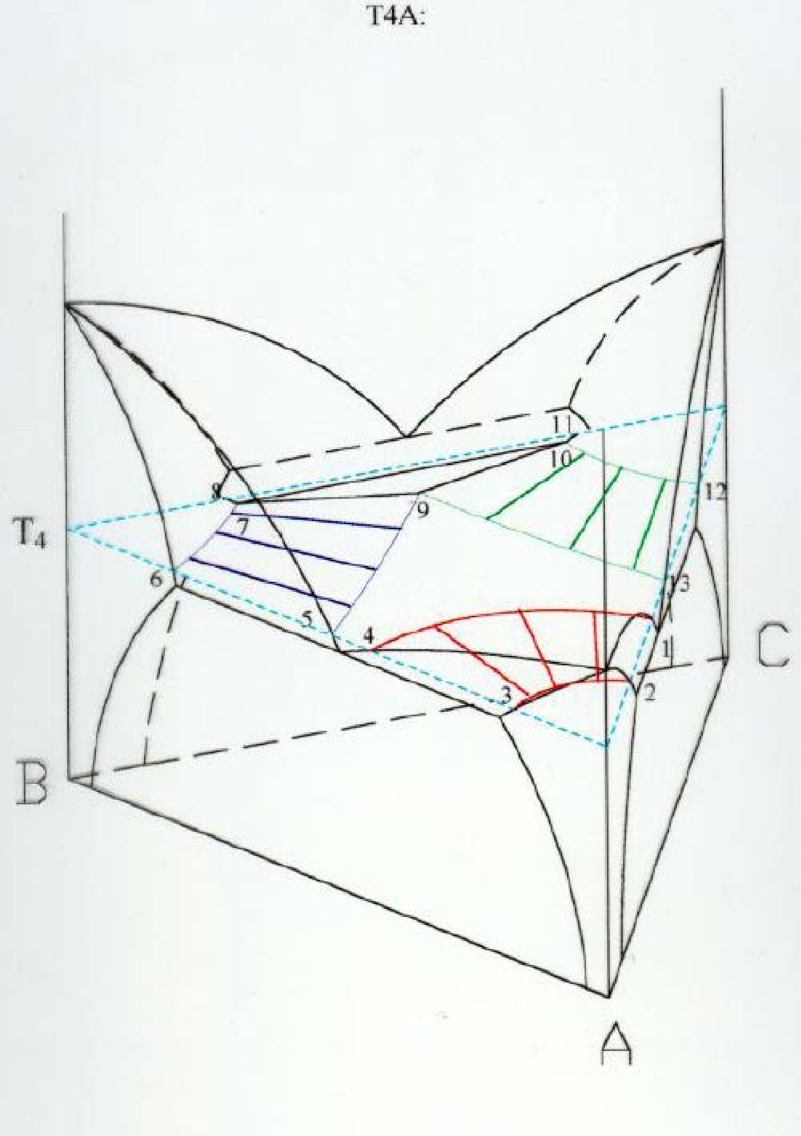
Temperature Slice At $T_3 < T_A, T_B, T_C$, But $T3 > T_{E1}, T_{E2}, T_{E3}$

T3B

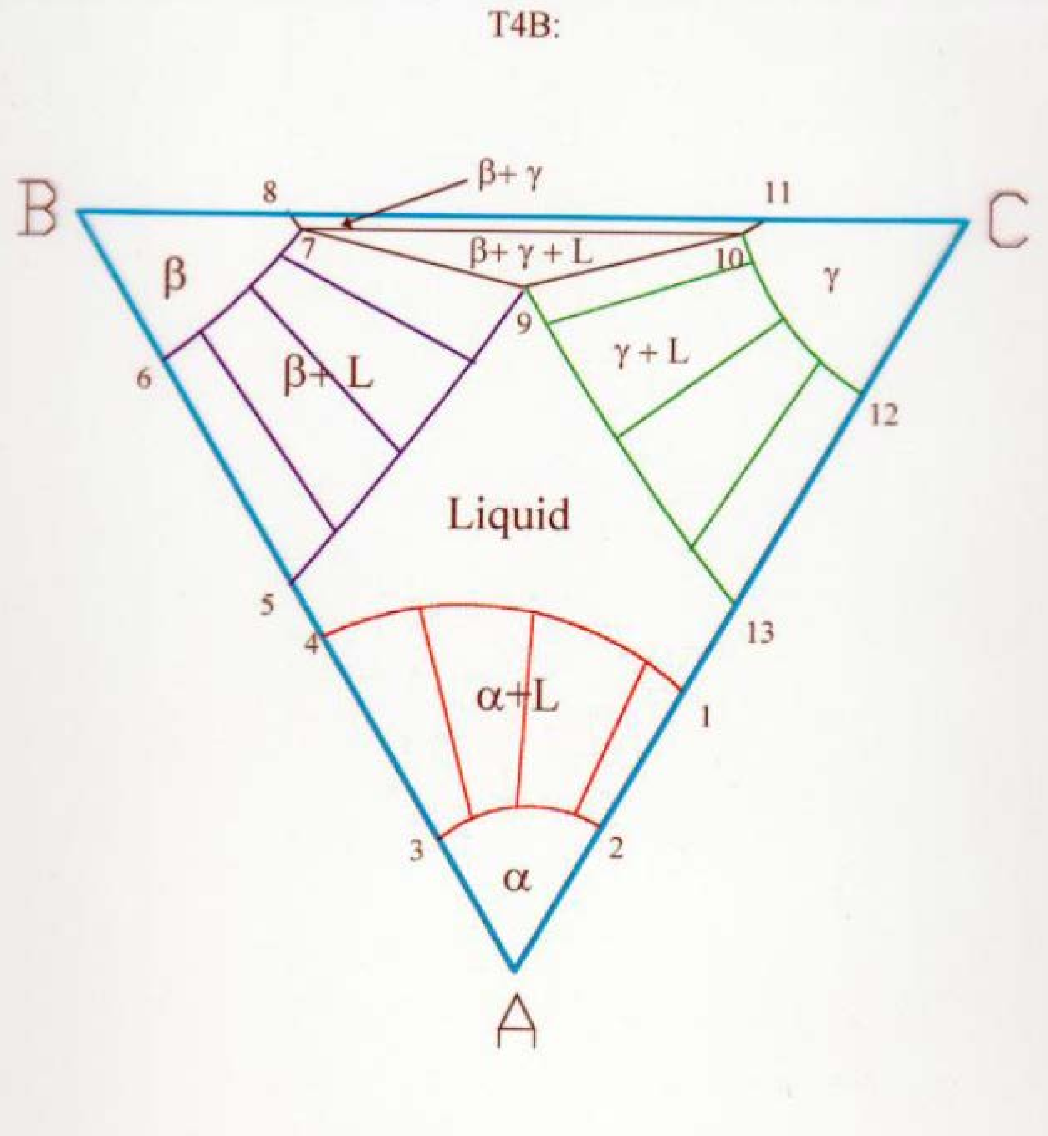


Isothermal Section At $T = T_3$

Ternary Eutectic System
(with Solid Solubility)



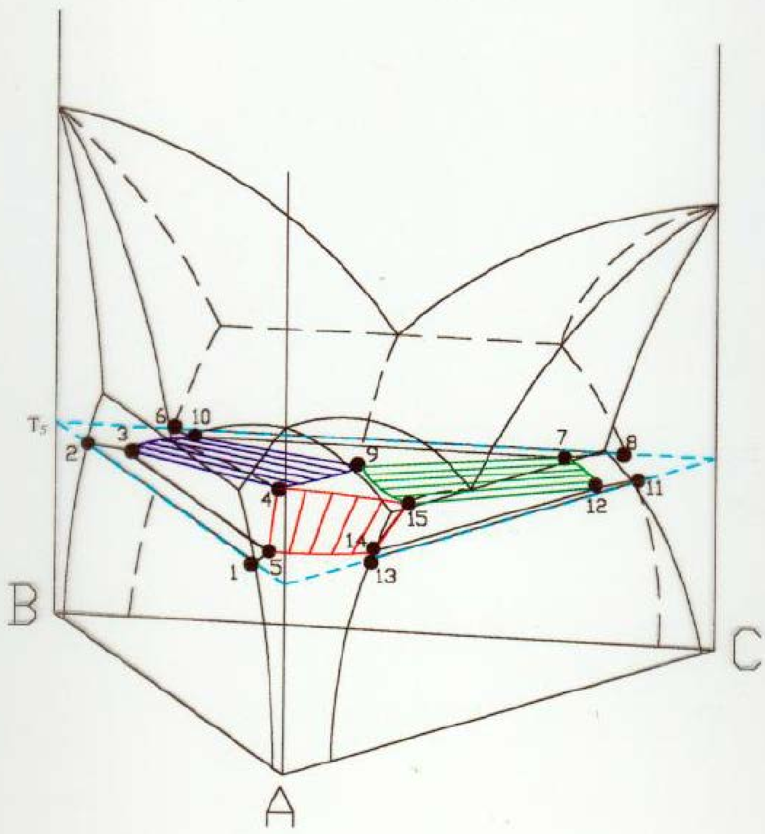
Temperature Slice At $T_4<T_{E2}$ And $T_4>T_{E1},T_{E3}$



Isothermal Section At $T=T_4$

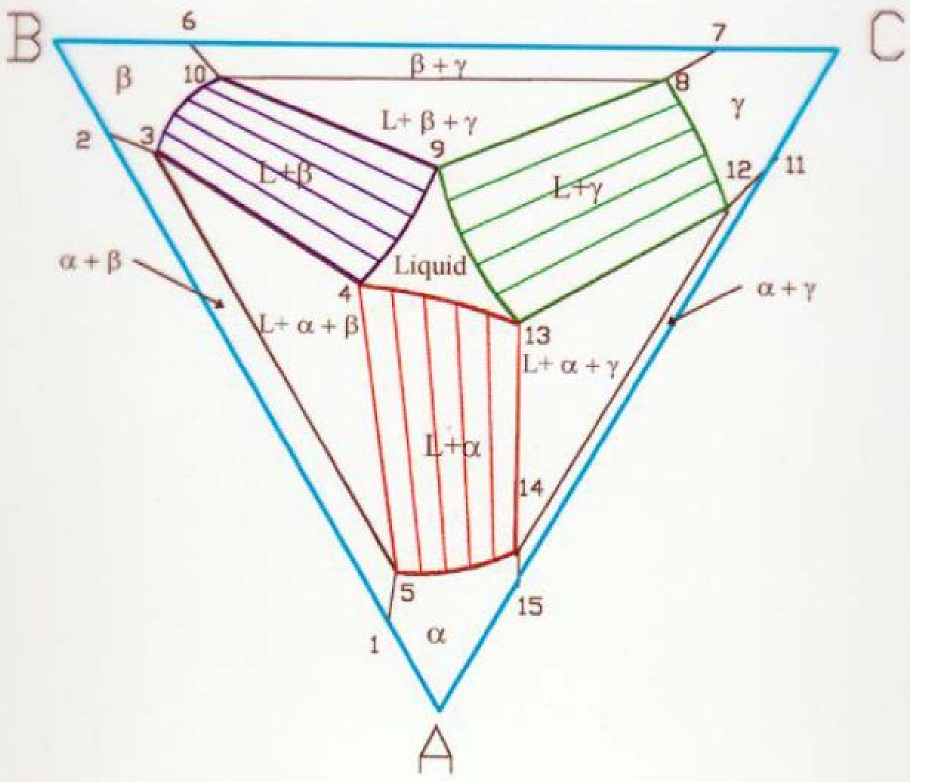
Ternary Eutectic System
(with Solid Solubility)

T5A:



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

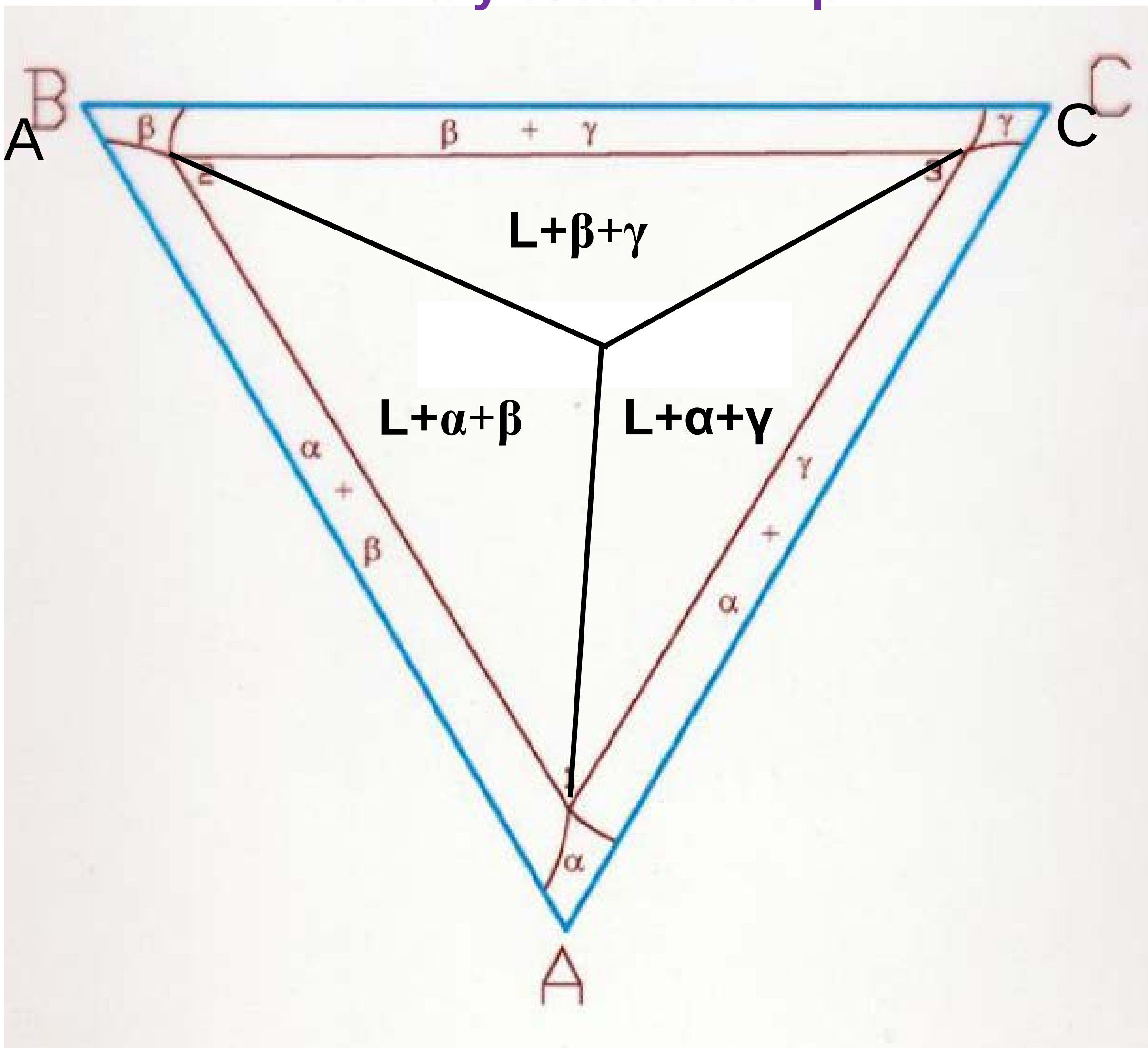
T5B:



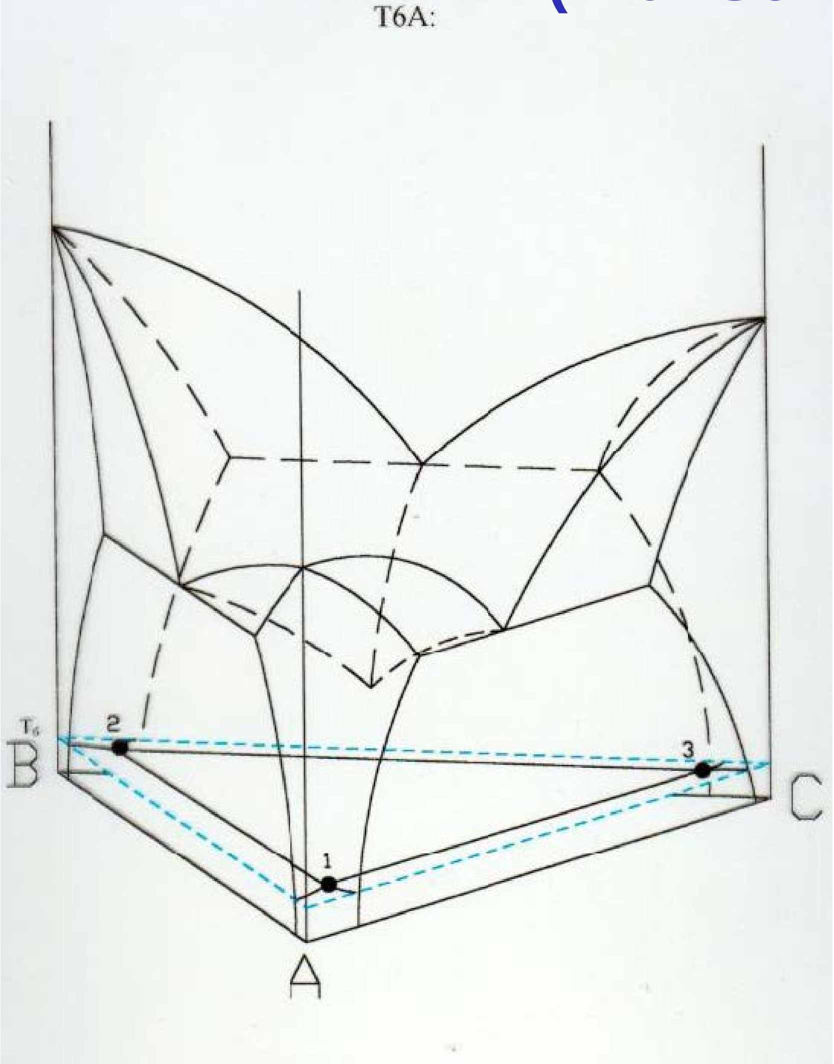
Isothermal Section At $T=T_5$

Ternary Eutectic System
(with Solid Solubility)

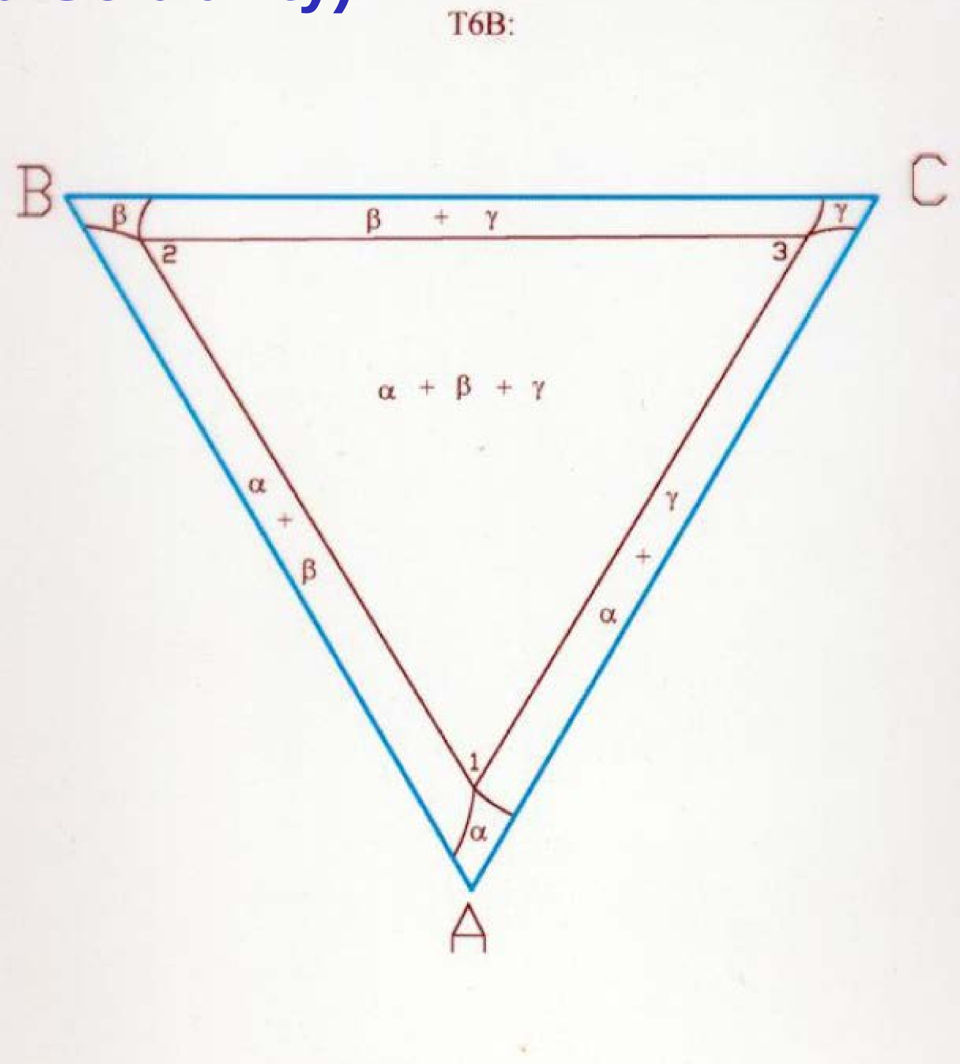
T= ternary eutectic temp.



Ternary Eutectic System
(with Solid Solubility)



Temperature Slice at $T_6 < T_E$



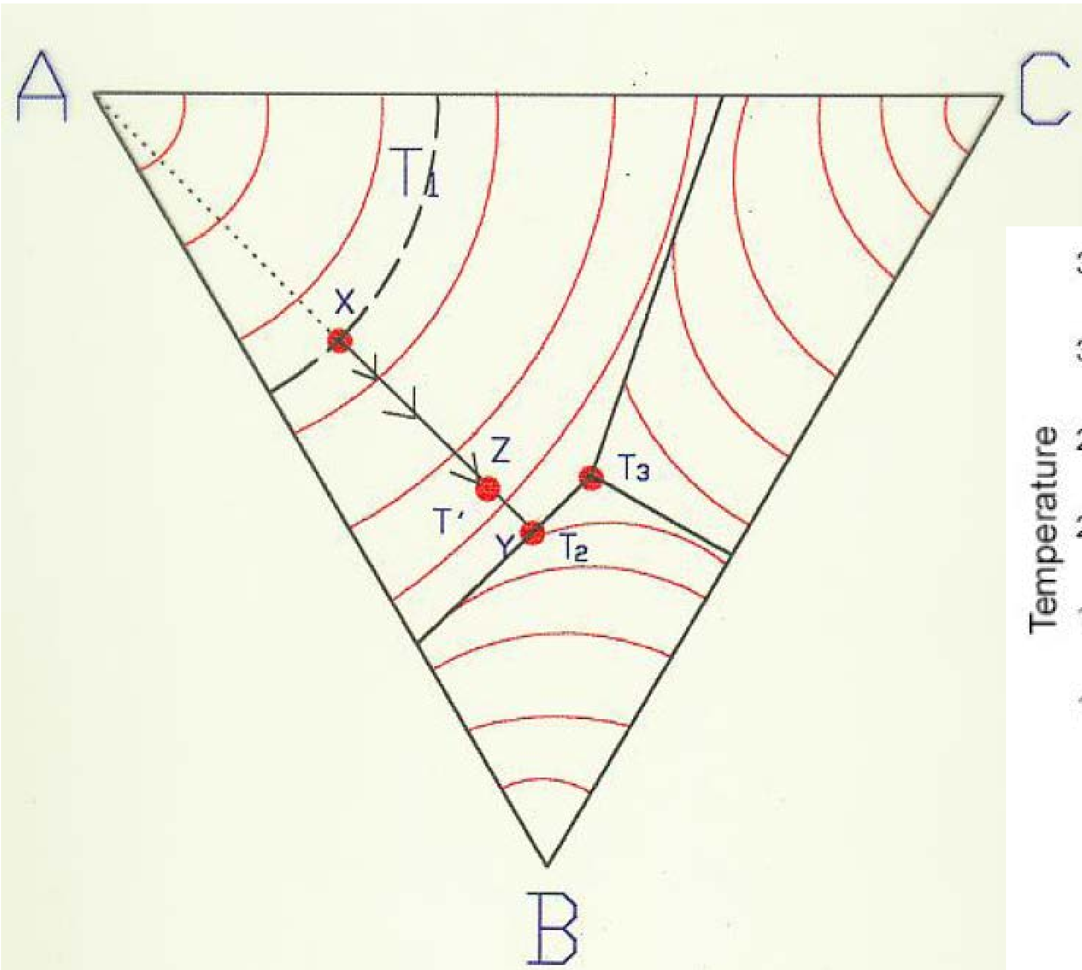
Isothermal Section At $T=T_6$

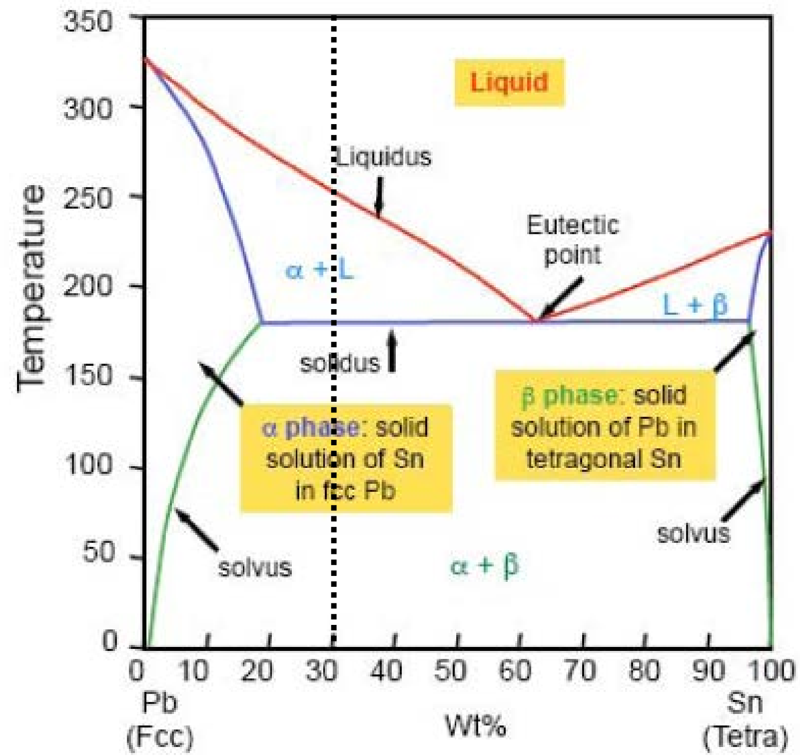
정해솔 학생 제공 자료 참조: 실제 isothermal section의 온도에 따른 변화

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

Ternary Eutectic System

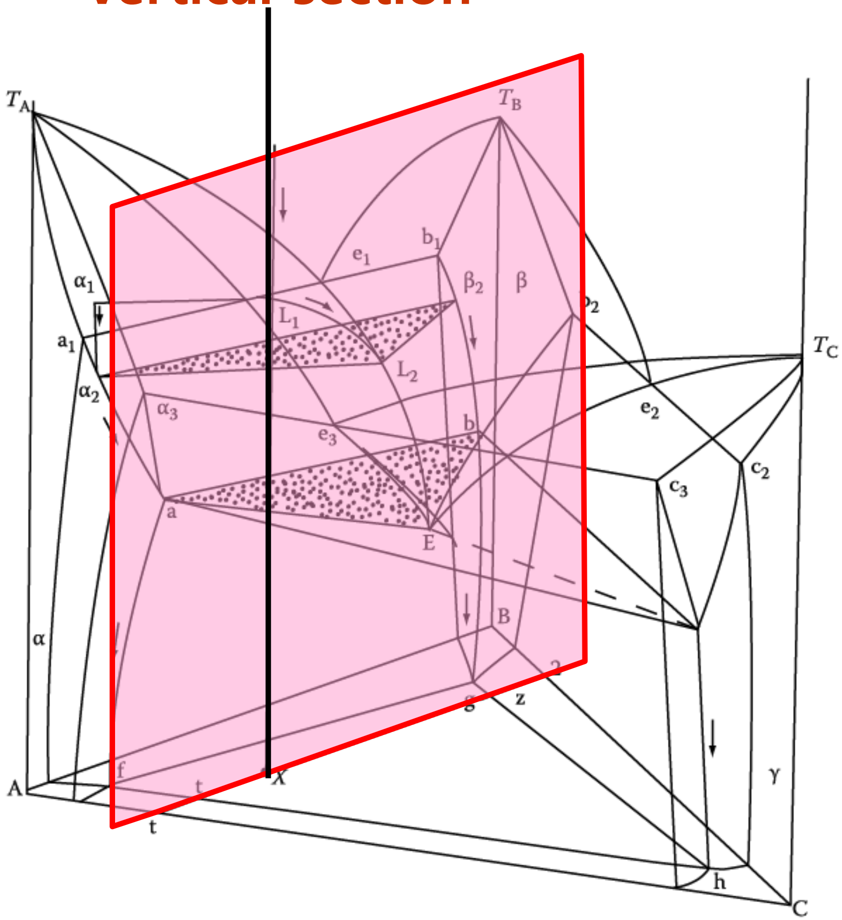
Solidification Sequence

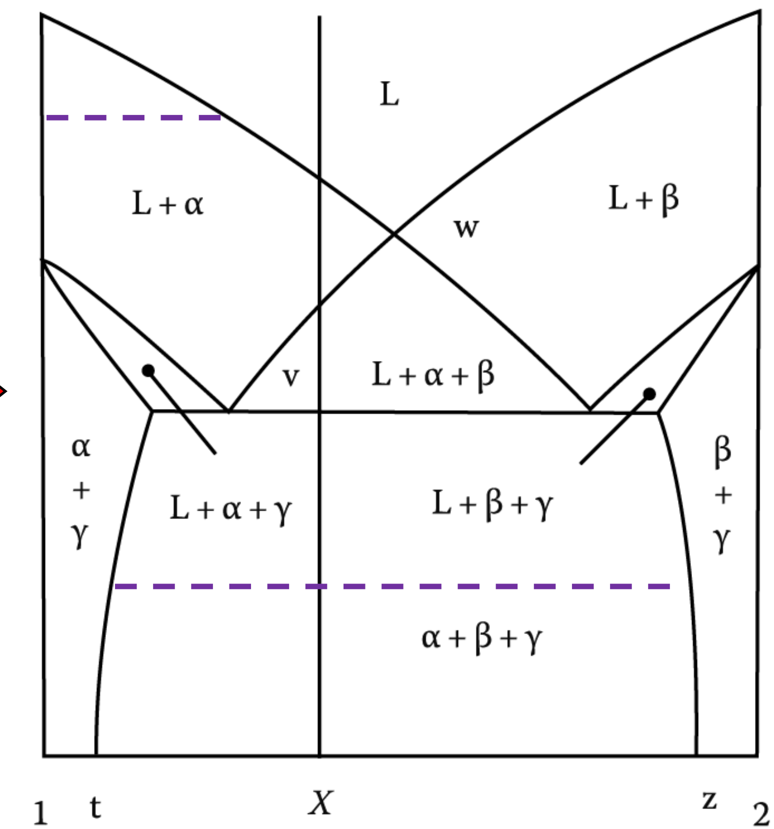




Ternary Eutectic System

* Vertical section

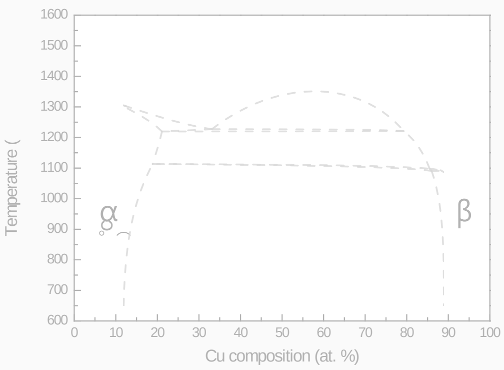




* The horizontal lines are not tie lines.
  (no compositional information)

* Information for equilibrium phases at different tempeatures

Construction of pseudo-binary phase diagram

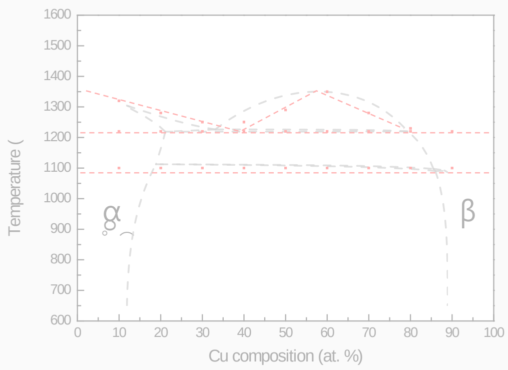


Thermodynamic calculation

- Expecting approximation of phase diagram

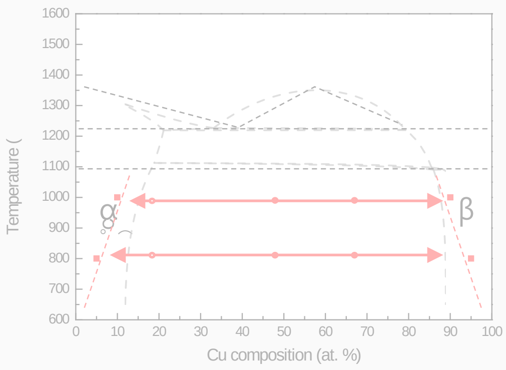
X-ray diffraction

- Determination of phases



TGA/DSC

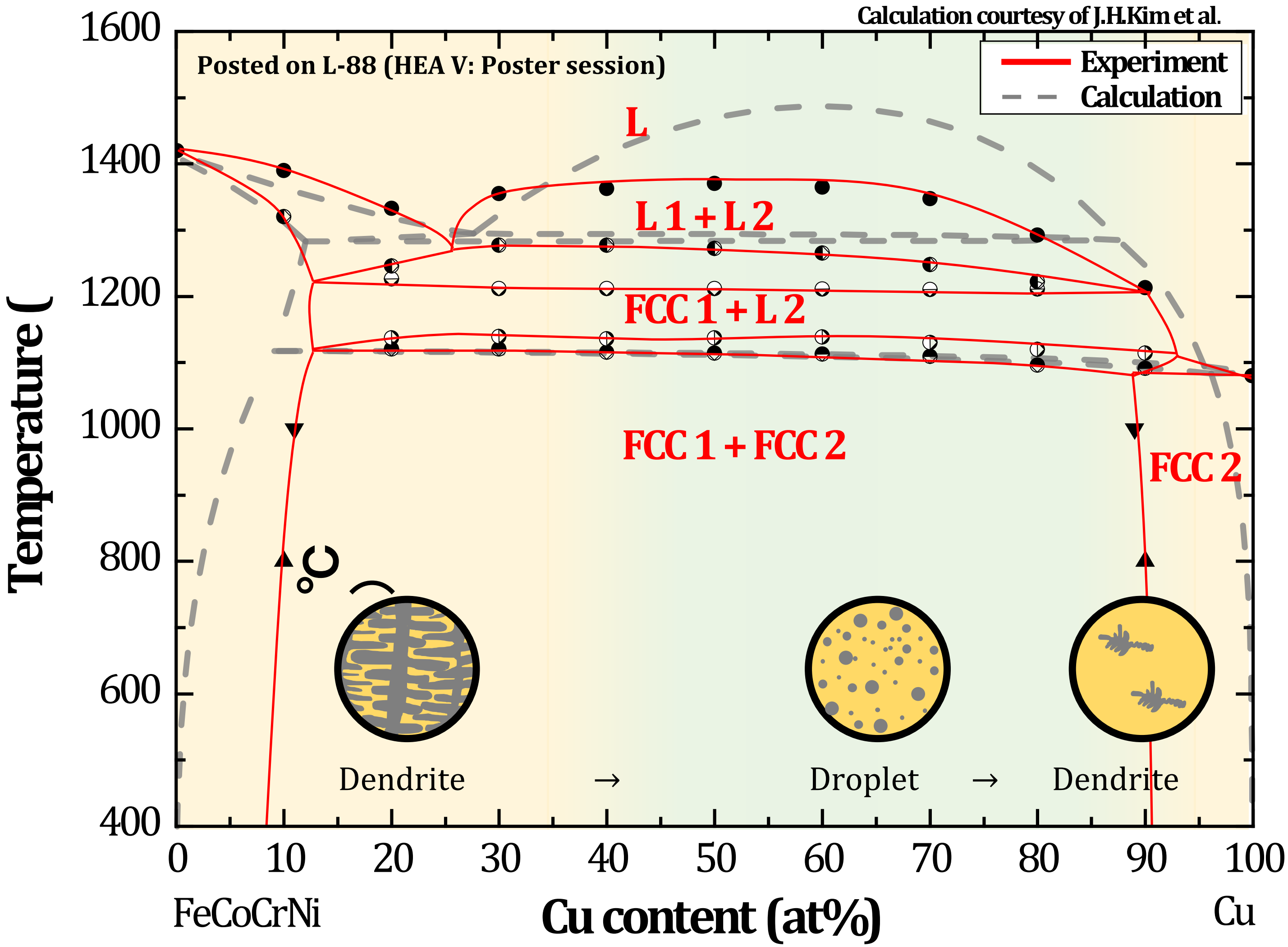
- Finding out temperatures of phase transformations
- Confirming invariant reaction points



FE-EPMA

- Investigation of equilibrium composition at each temperature

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



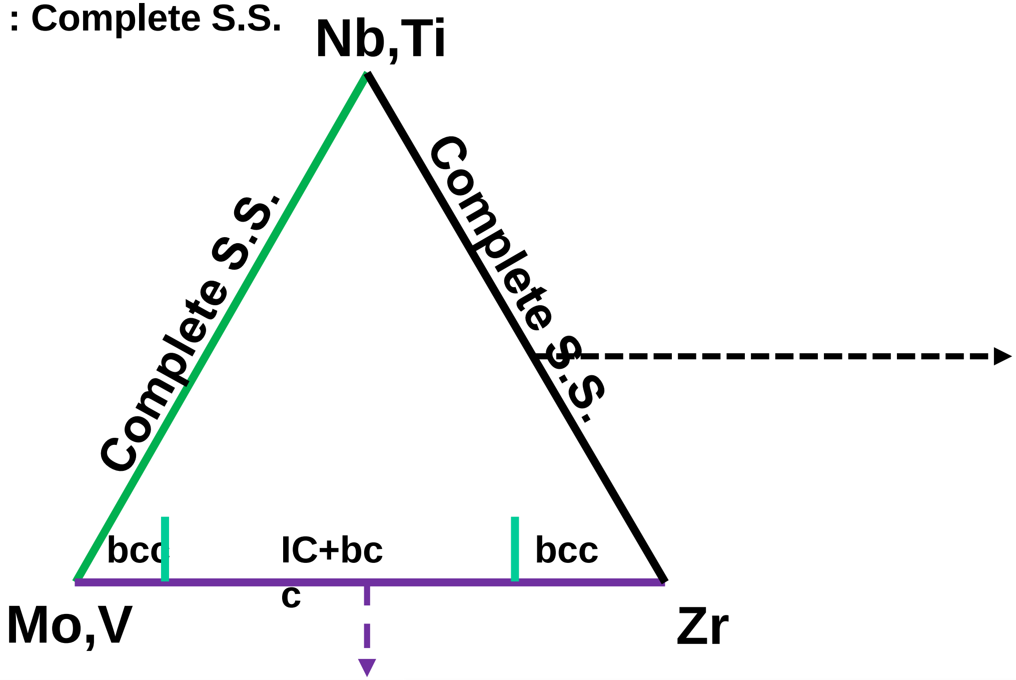
- Pseudo-binary system between FeCoCrNi and Cu shows monotectic reaction having liquid separation region.

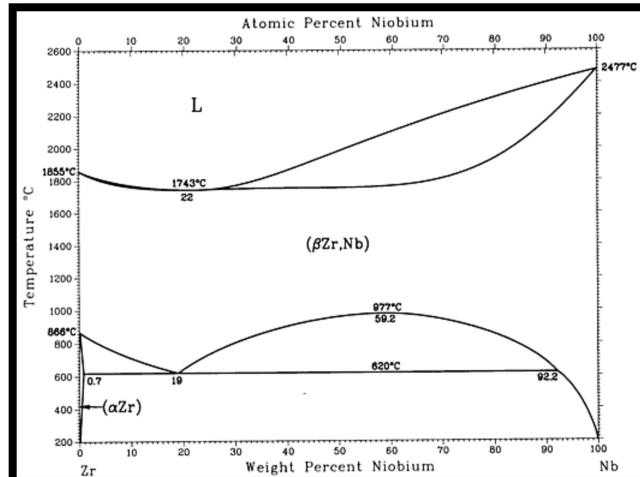
MoVNbTiZr: Construction of pseudo-ternary phase diagram

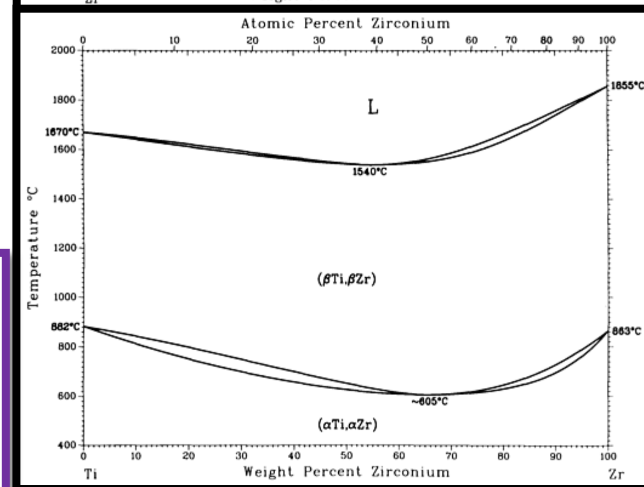
Mo, V, Nb, Ti : Complete S.S.

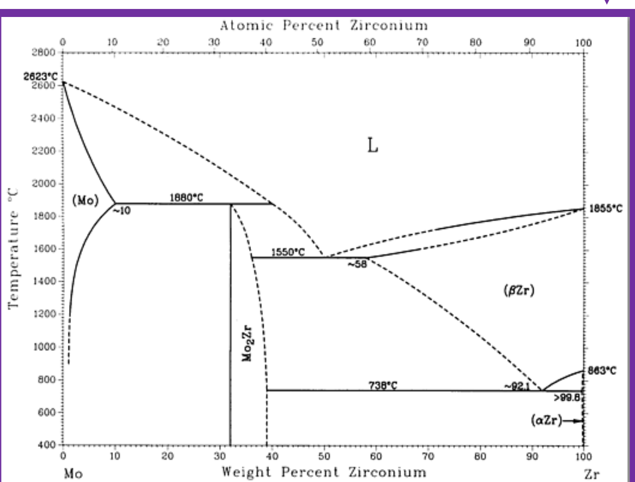
V-Zr, Mo-Zr

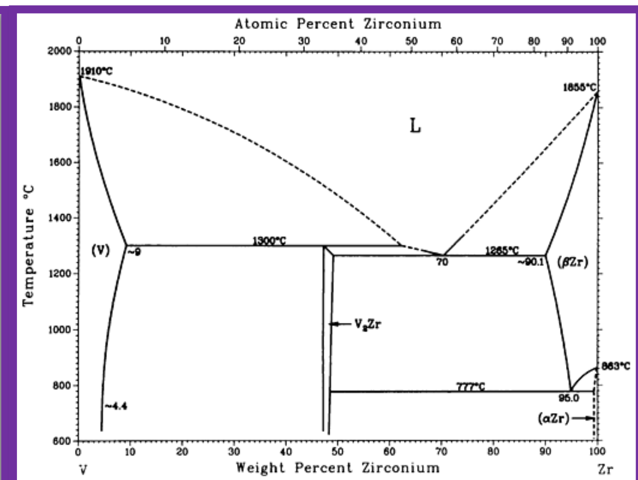
Ti-Zr, Nb-Zr



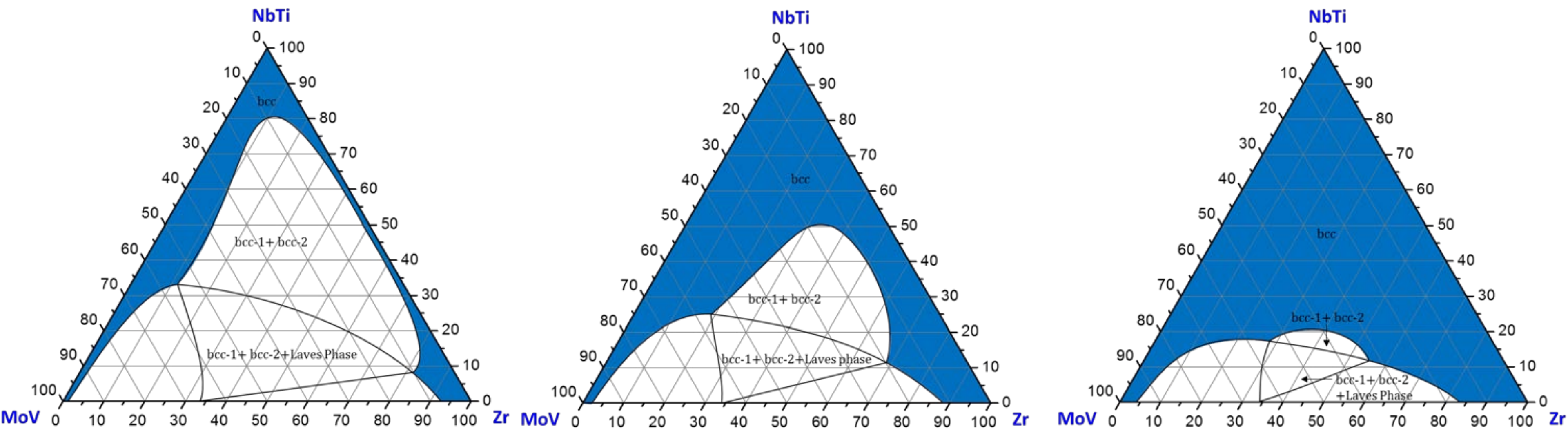








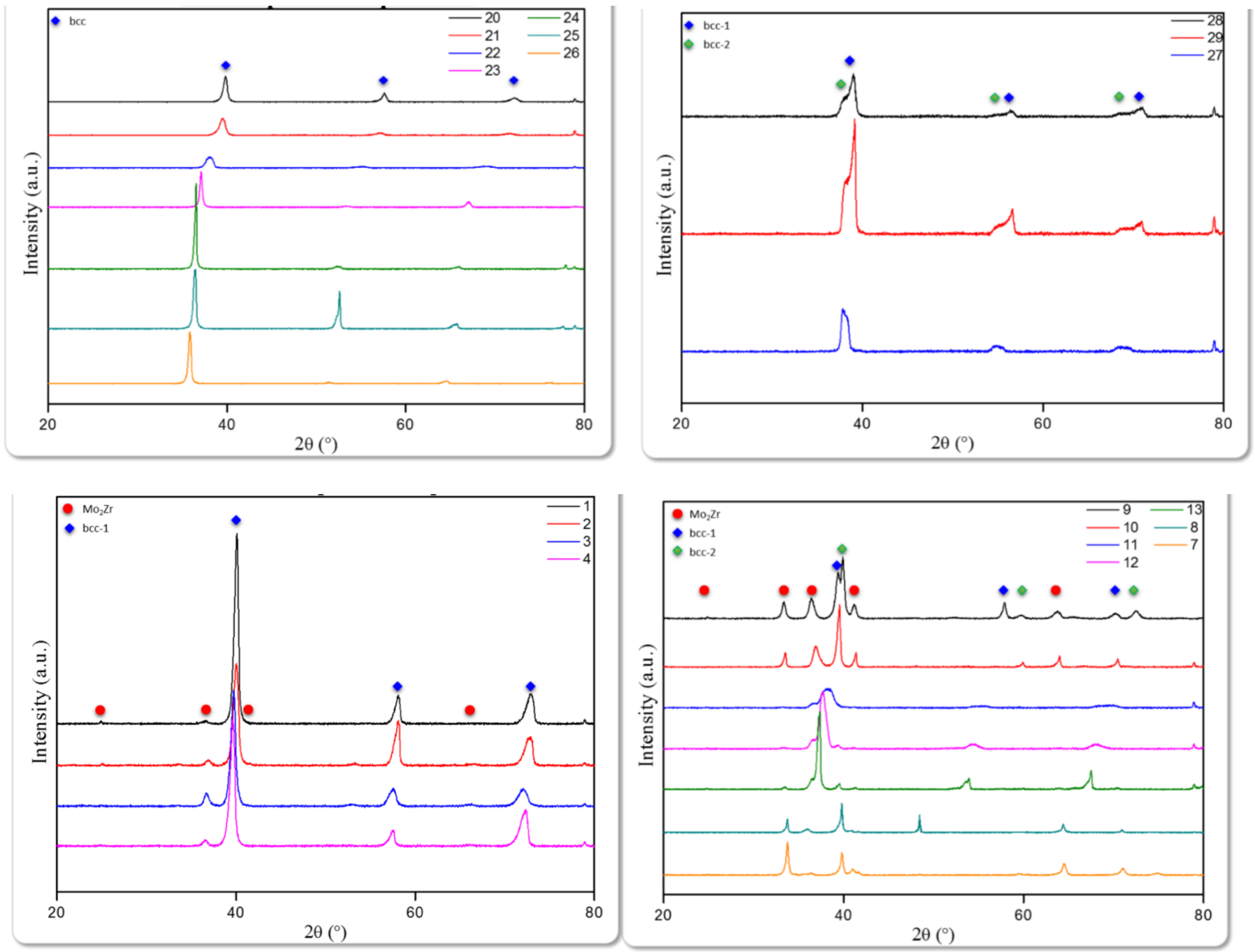
TiNbMoVZr: Construction of pseudo-ternary phase diagram



1100K 1300K 1500K

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

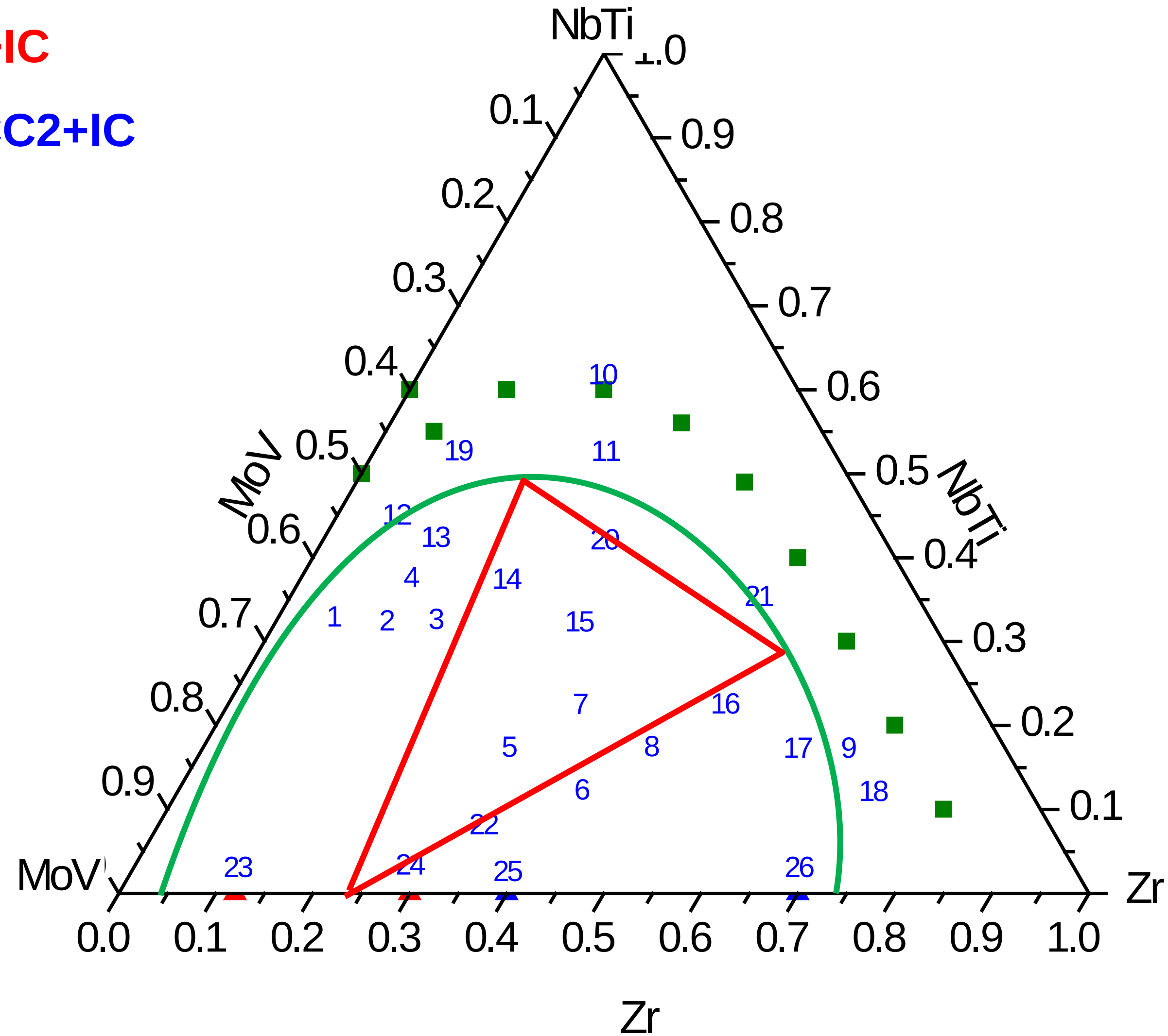
Construction of pseudo-ternary phase diagram

BCC1+BCC2+IC

BCC1+IC / BCC2+IC

BCC1+BCC2

Single BCC



Find single phase region without intermetallic compounds

Homework 2: Please find ternary phase diagram in the literature. And explain the detail for the phase diagram in your word. (within 3 pages PPT)

< Quaternary phase Diagrams >

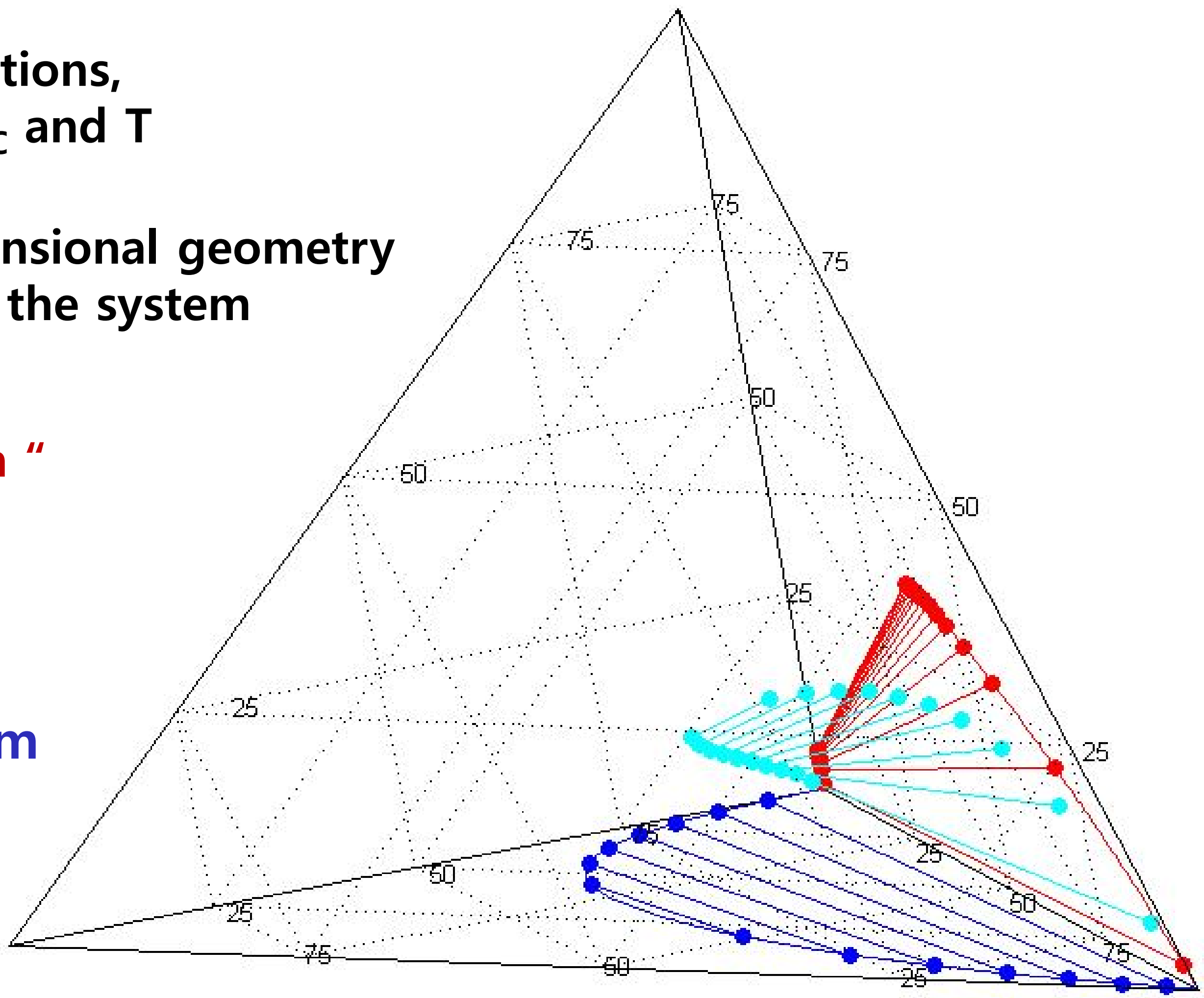
Four components: A, B, C, D

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

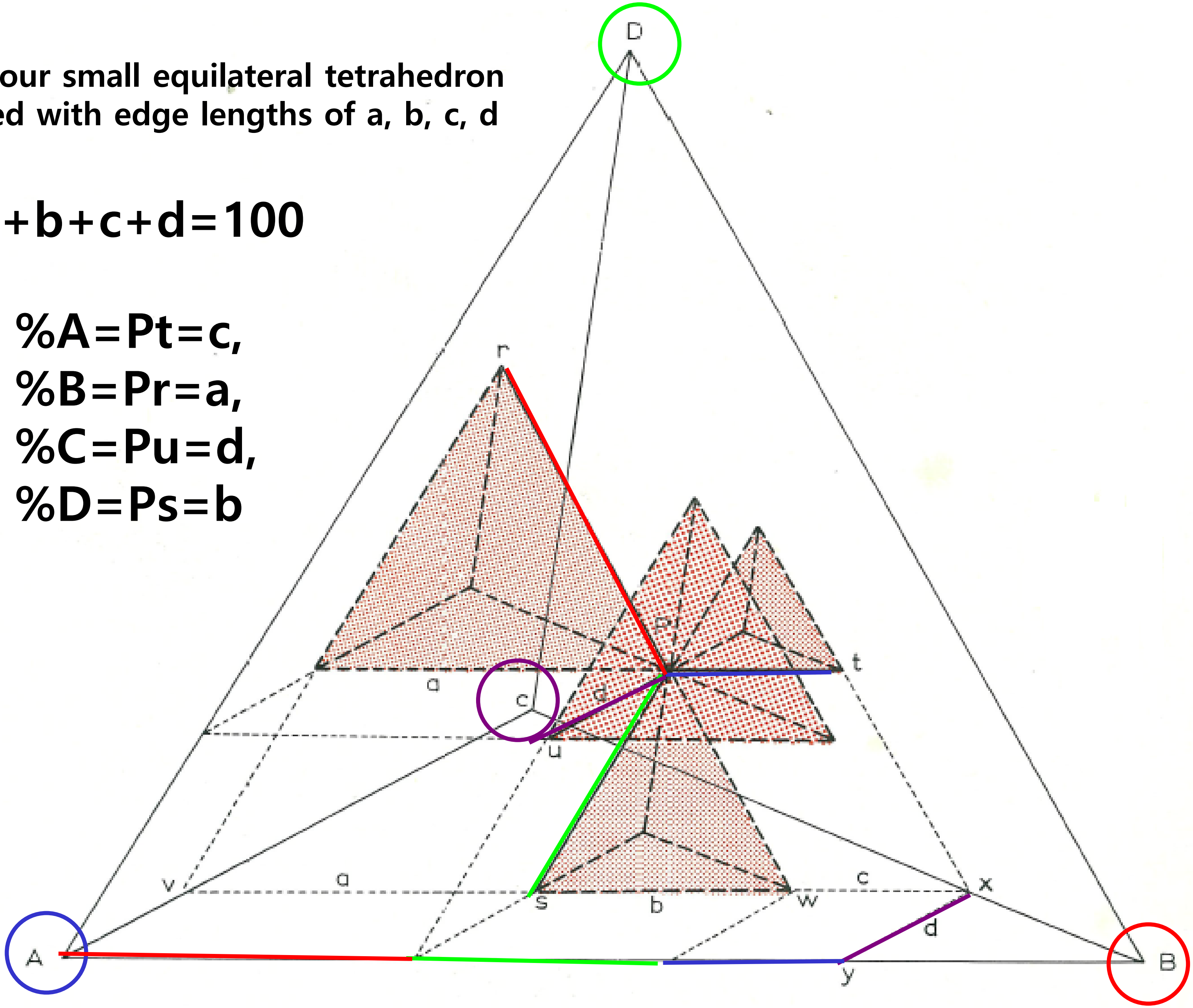


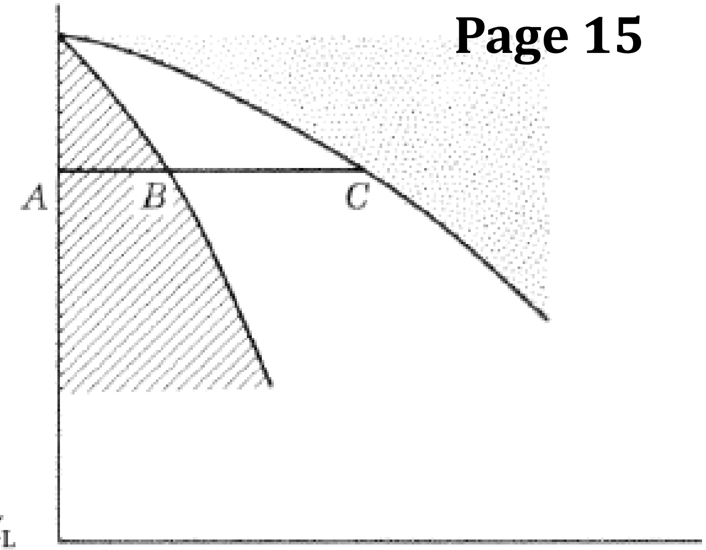
Fig. 247. Representation of a quaternary system by an equilateral tetrahedron.

Q5. Distribution coefficient & Van't Hoff equation

Page 15

1.7 The Distribution coefficient

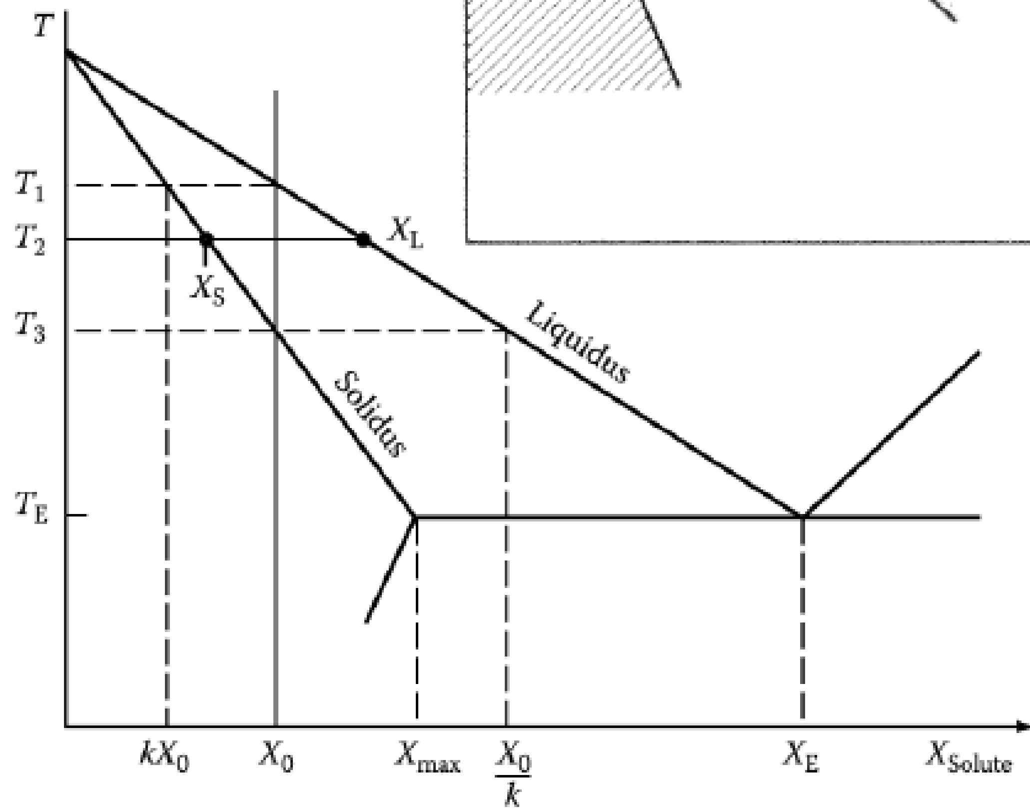
$$k_0 = \frac{X_S}{X_L} = AB/AC < 1$$



k_0 : Eq. distribution coefficient

X : mole fraction of solute

In this phase diagram of straight solidus and liquidus, k_0 is independent of T.



A hypothetical phase diagram

$k_0 = X_S/X_L$ is constant.

1.7 The Distribution coefficient

Van't Hoff equation: $$\frac{dC_L}{dT_L} - \frac{dC_S}{dT_S} = \frac{L}{RT_E^2}$$

Van't Hoff equation relates the change in the equilibrium constant, K_{eq}, of a chemical reaction to the change in temperature , T, given the standard enthalpy change ΔH, for the process. The equation has been widely utilized to explore the changes in state functions in the thermodynamic system.

1.7 The Distribution coefficient

Van't Hoff equation: $$\frac{dC_L}{dT_L} - \frac{dC_S}{dT_S} = \frac{L}{RT_E^2}$$

- A useful method of checking the accuracy of the slope dC_s/dT_s of the solidus line from that of the liquidus (which is more reliable)
- This equation applies strictly only at very low concentrations.

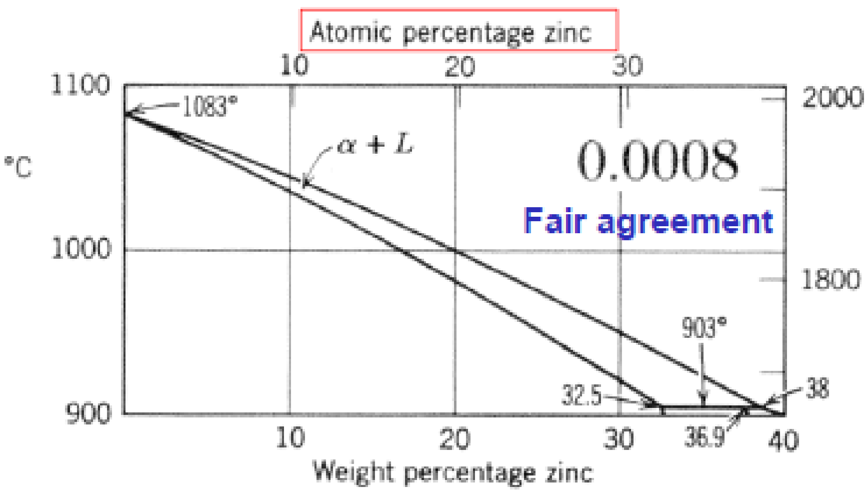
In the case of copper, $$\frac{dC_L}{dT_L} - \frac{dC_S}{dT_S} = 0.0009$$

Atomic weight = 63.5

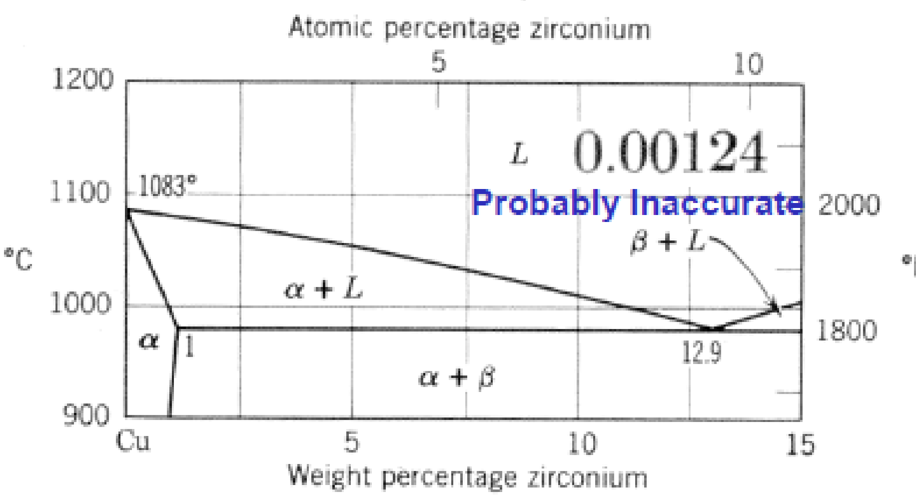
L = 50.6 cal/gm or 3280 cal/mole

Melting point = 1083°C = 1356°K

R = 1.98 cal/mole °K



$$\frac{dC_L}{dT_L} = 0.0028 \quad \text{and} \quad \frac{dC_S}{dT_S} = 0.0020$$



0.00133 and 0.00009 atomic per cent per degree

➡ It is probable that the solidus curve is inaccurate.