TERNARY PHASE DIAGRAMS

An Introduction

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Credit for scanning the phase diagrams:
Brenden Croom

Utility of Ternary Phase Diagrams

- **Glass compositions**
- **Refractories**
- **Aluminum alloys**
- **Stainless steels**
- **Solder metallurgy**
- **Several other applications**

References on Ternary Phase Diagrams

A. Prince, Alloy Phase Equilibria, Elsevier Publishing Company, New York, 1966

D. R. F. West, Ternary Equilibrium Diagrams, Chapman and Hall, New York, 1982

G. Masing, Ternary Systems, Reinhold Publishing Company, New York, 1944

C. G. Bergeron and S. H. Risbud, Introduction to Phase Equilibria in Ceramics, The American Ceramic Society, Ohio, 1984

M. F. Berard and D. R. Wilder, Fundamentals of Phase Equilibria in Ceramic Systems, R.A.N. Publishers, Ohio, 1990

F. N. Rhines, Phase Diagrams in Metallurgy, McGraw-Hill, New York, 1956

A. Reisman, Phase Equilibria, Academic Press, 1970

What are Ternary Phase Diagrams?

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.

The 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”

Some Important Terms

- **Overall composition**
- **Number of phases**
- **Chemical composition of individual phases**
- **Amount of each phase**
- **Solidification sequence**

Overall Composition - 1

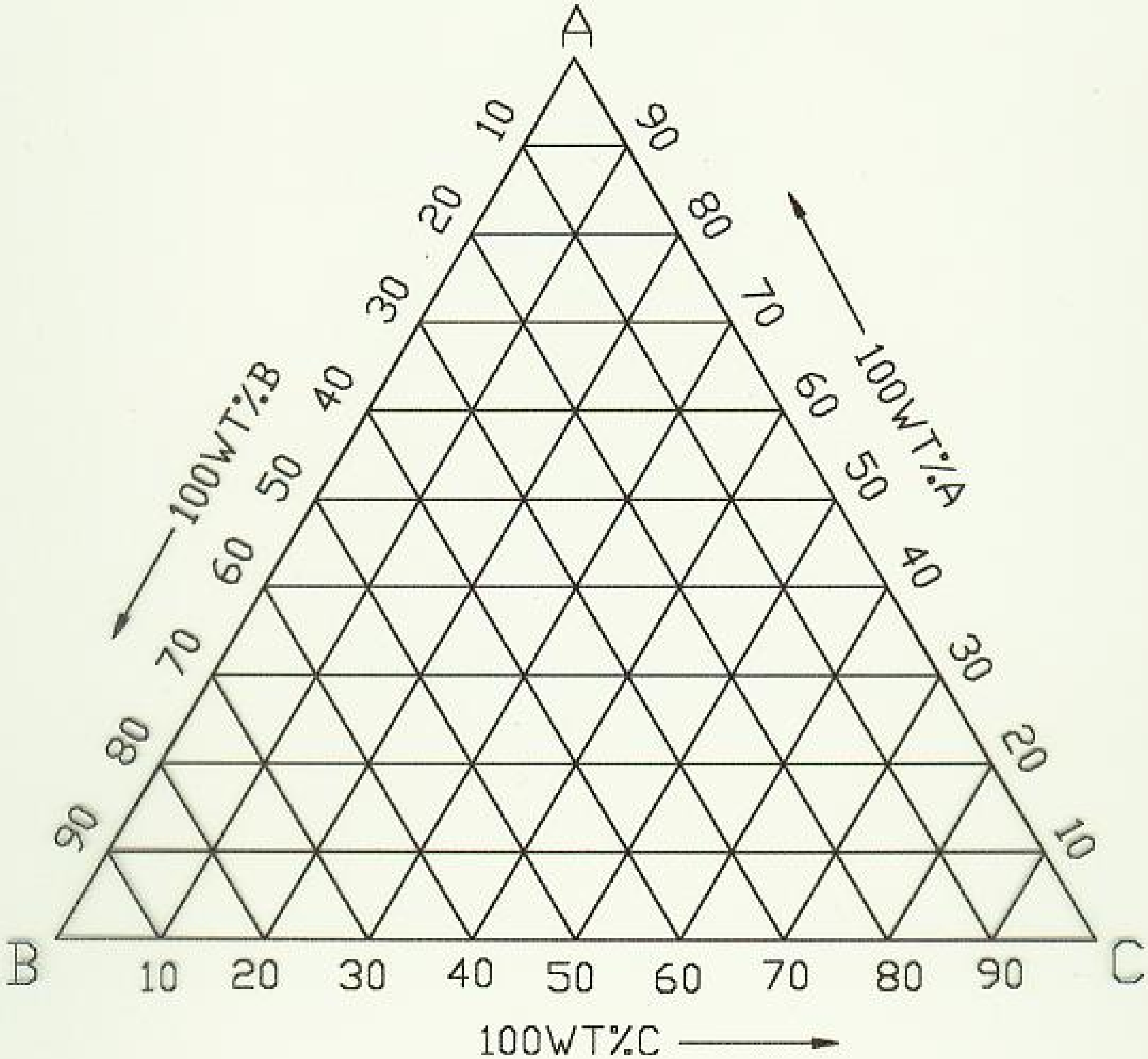
The concentration of each of the three components

Can be expressed as either “wt. %” or “molar %”

Sum of the concentration of the three components must add up to 100%

The Gibbs Triangle is always used to determine the overall composition

The Gibbs Triangle: An equilateral triangle on which the pure components are represented by each corner



The Gibbs Triangle

Overall Composition - 2

There are three ways of determining the overall composition

<u>**Method 1**</u>

Refer to Figures OC1 and OC2

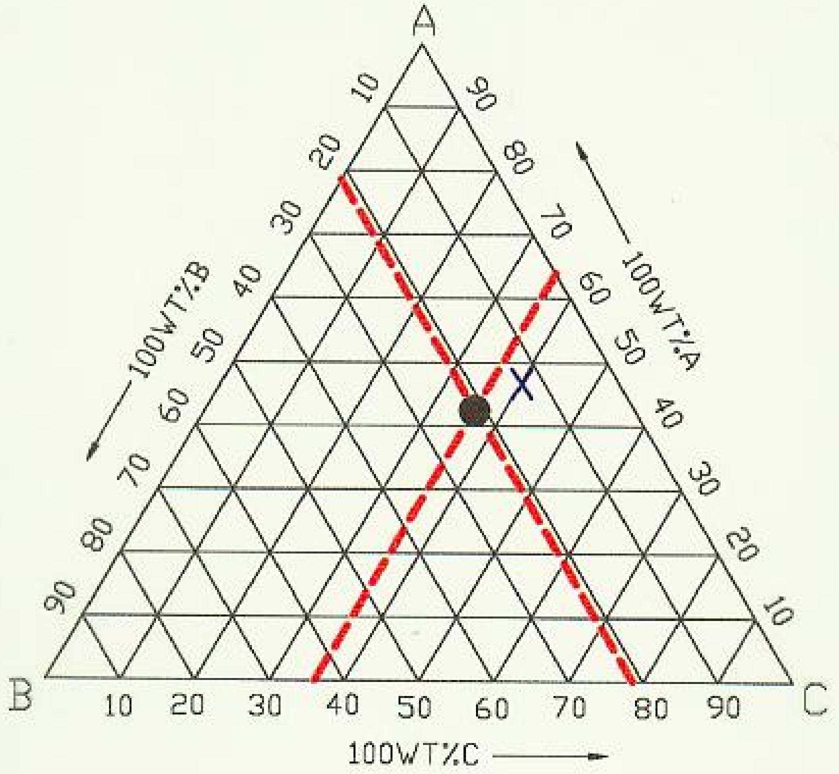
Let the overall composition be represented by the point X

Draw lines passing through X, and parallel to each of the sides

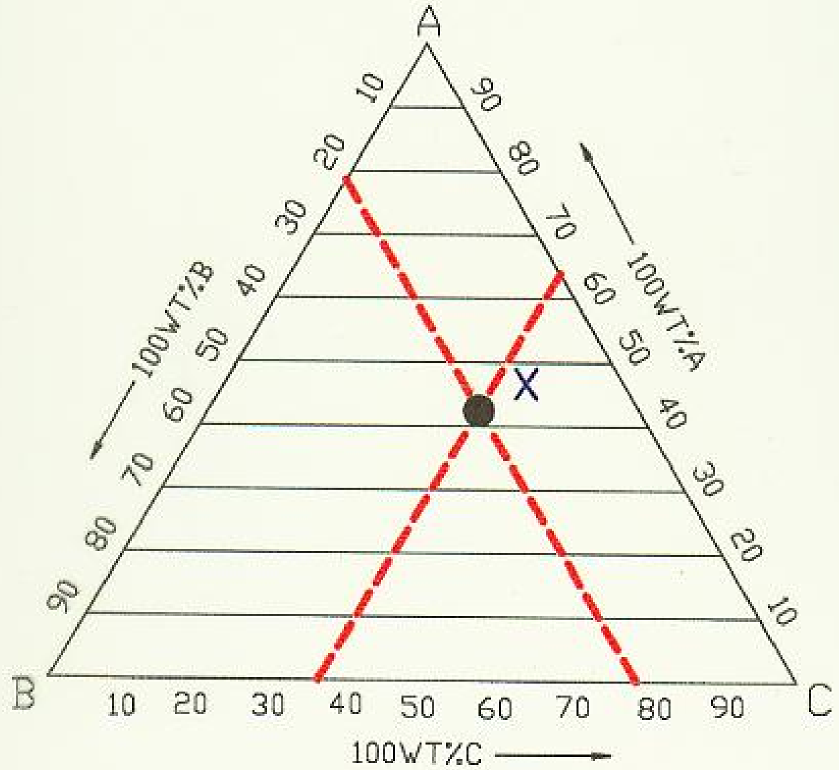
Where the line A'C' intersects the side AB tells us the concentration of component B in X

The concentrations of A and C, in X, can be determined in an identical manner

OC1:



OC2:



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Overall Composition - 3

<u>Method Two</u>:

Draw lines through X, parallel to the sides of the Gibbs Triangle

A'C' intersects AB at A'

B'C" intersects AB at B'

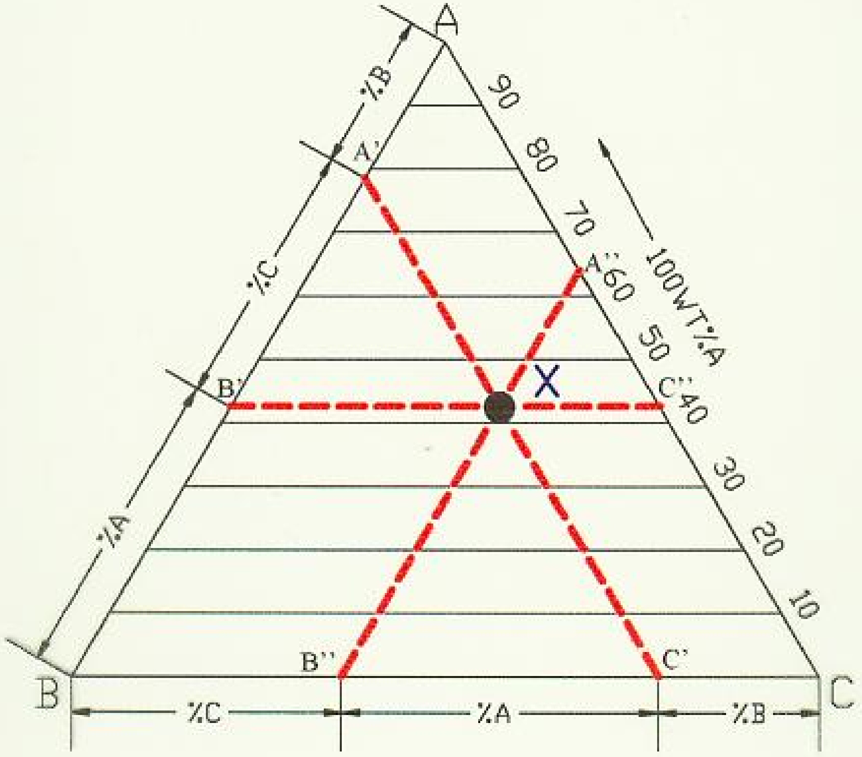
Concentration of B = AA'

Concentration of C = A'B'

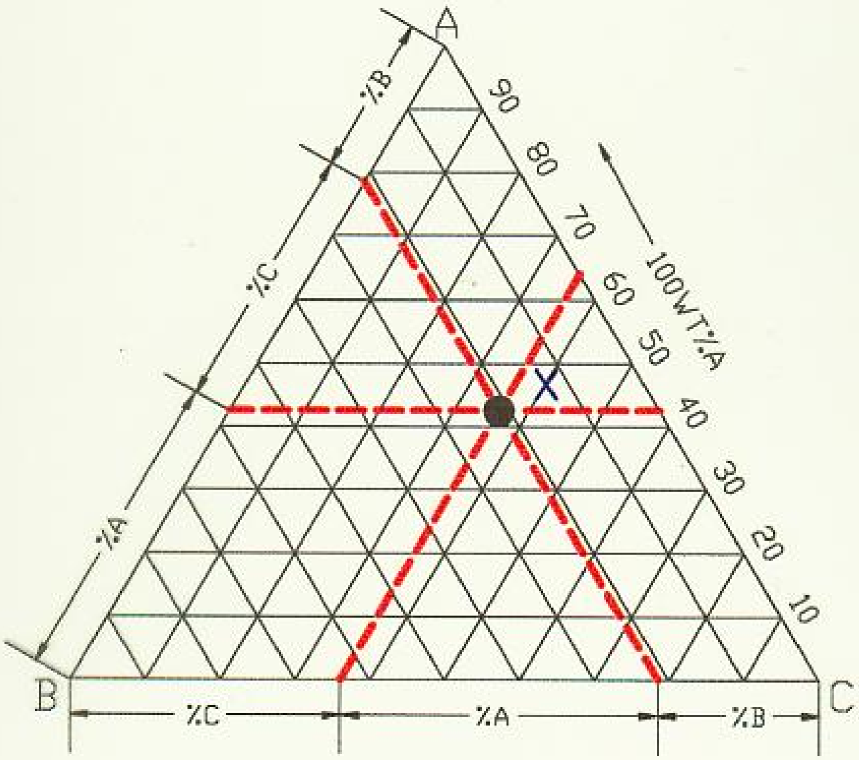
Concentration of A = B'B

This method can be somewhat confusing, and is not recommended

DIVISN1:



DIVISN2:



Overall Composition - 4

<u>Method 3</u>

Application of the Inverse Lever Rule

Draw straight lines from each corner, through X

$$\%A = \frac{AX}{AM} \qquad \%B = \frac{BX}{BN} \qquad \%C = \frac{CX}{CL}$$

Important Note:

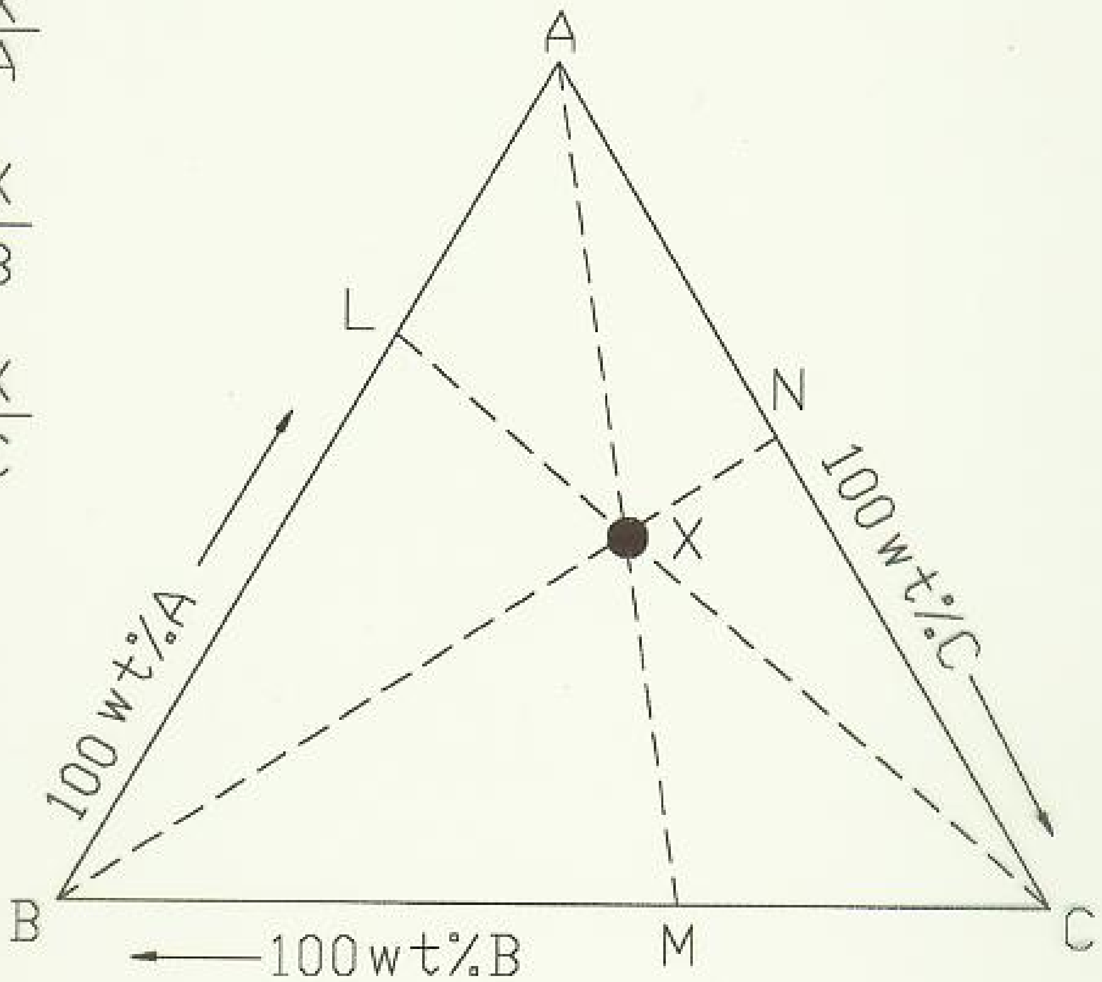
Always determine the concentration of the components independently, then check by adding them up to obtain 100%

RATIOCMP:

$$\%A = \frac{MX}{MA}$$

$$\%B = \frac{NX}{NB}$$

$$\%C = \frac{LX}{LC}$$

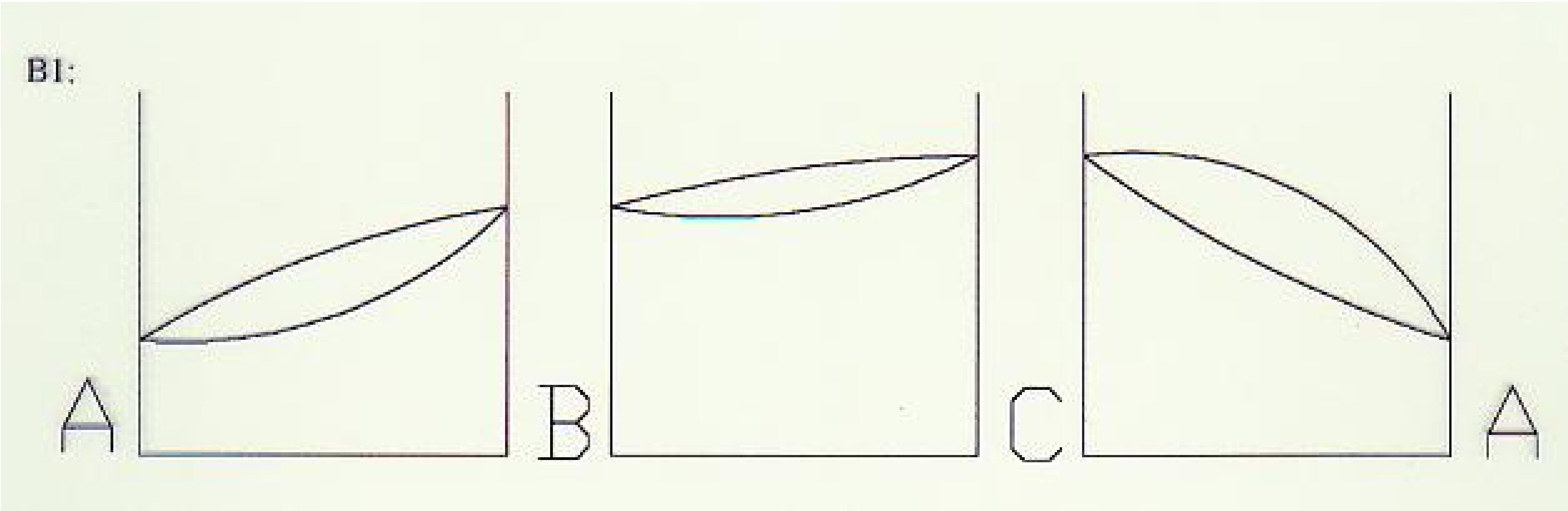


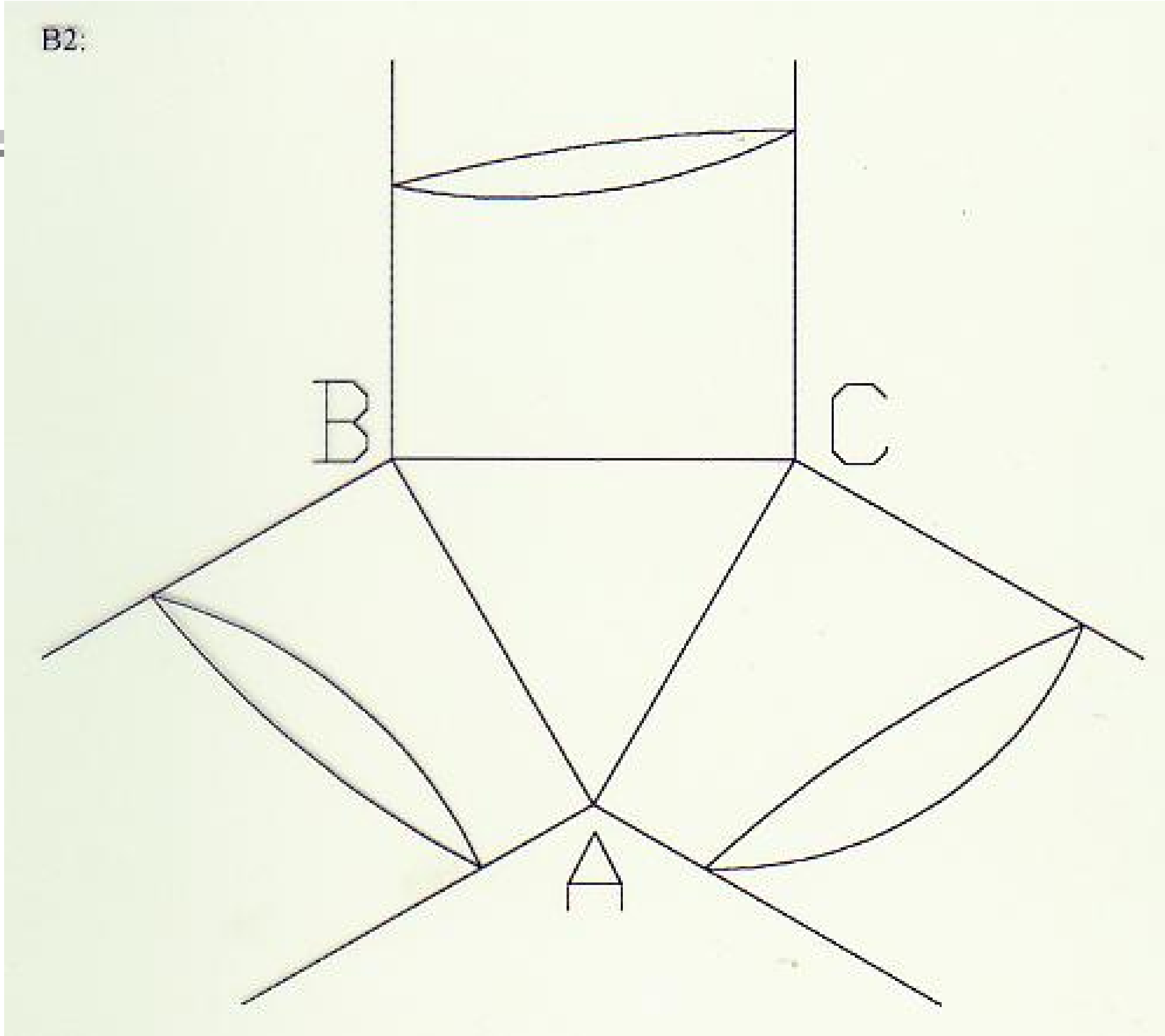
Ternary Isomorphous System

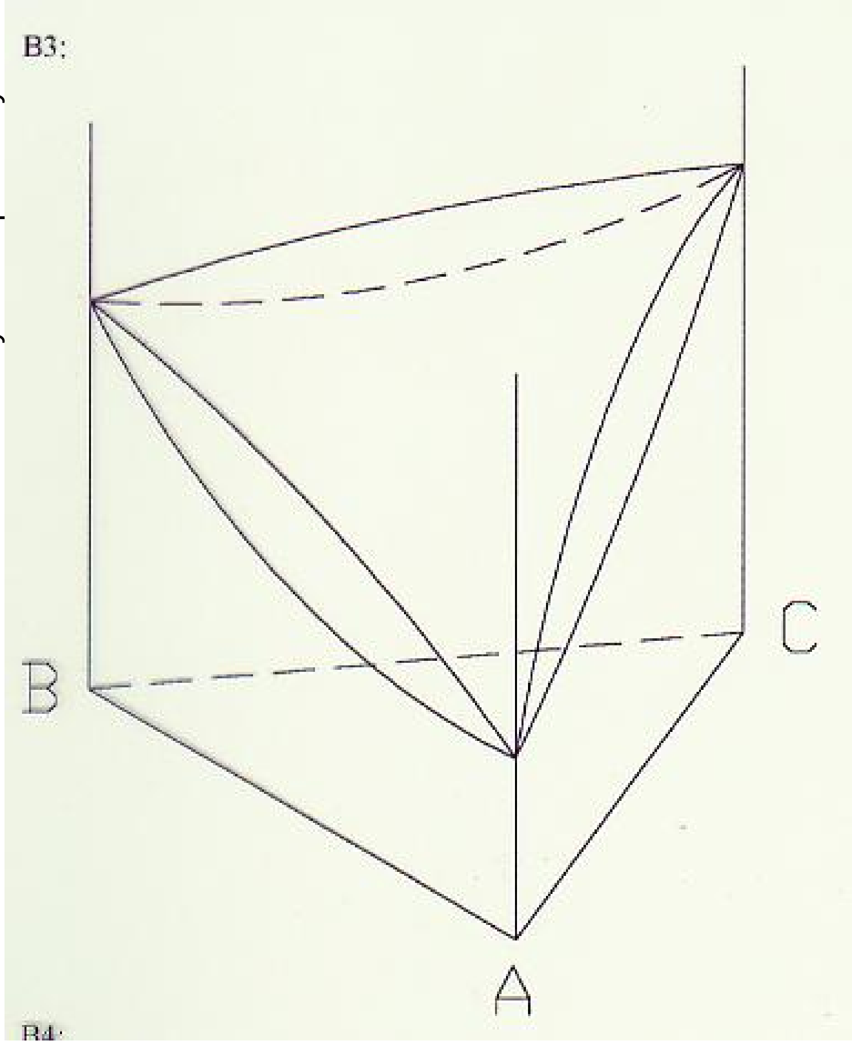
<u>Isomorphous System</u>: A system (ternary in this case) that has only one solid phase. All components are totally soluble in the other components. The ternary system is therefore made up of three binaries that exhibit total solid solubility

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

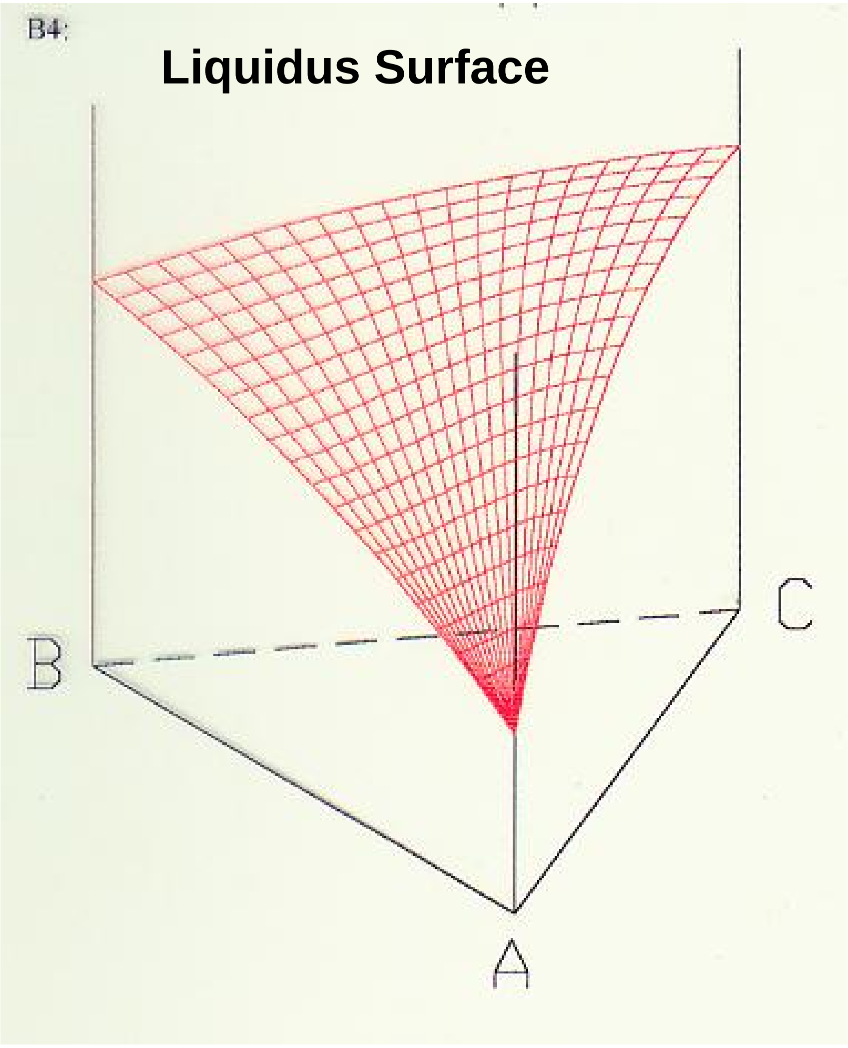
<u>The Solidus Surface</u>: A plot of the temperatures below which a (homogeneous) solid phase forms for any given overall composition


B1:
A
B
C
A


B2:
B
C
A

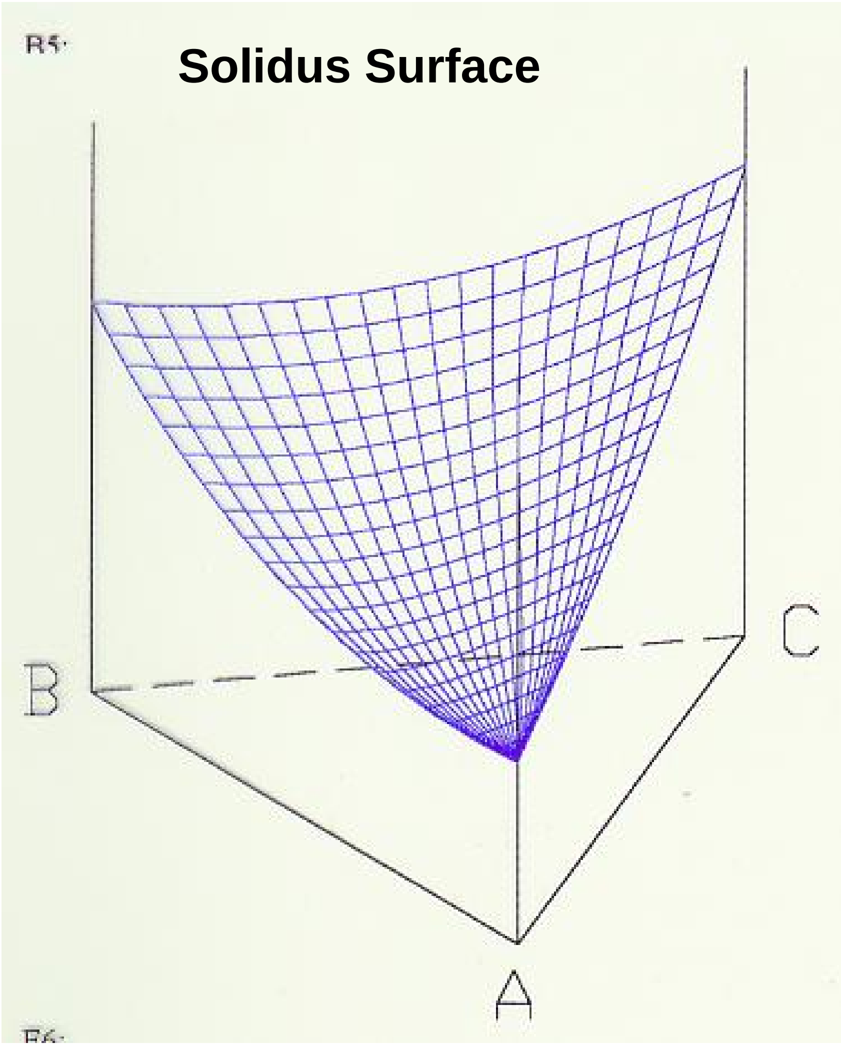


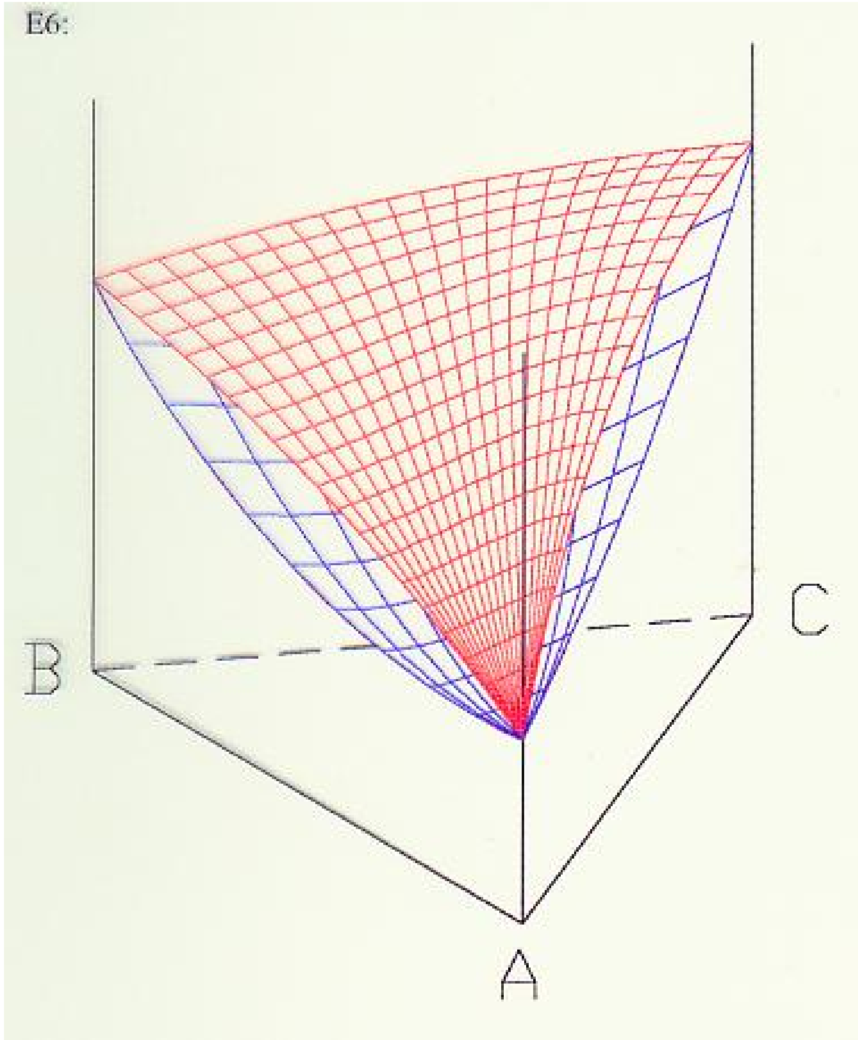
B3:
B
C
A
B4:

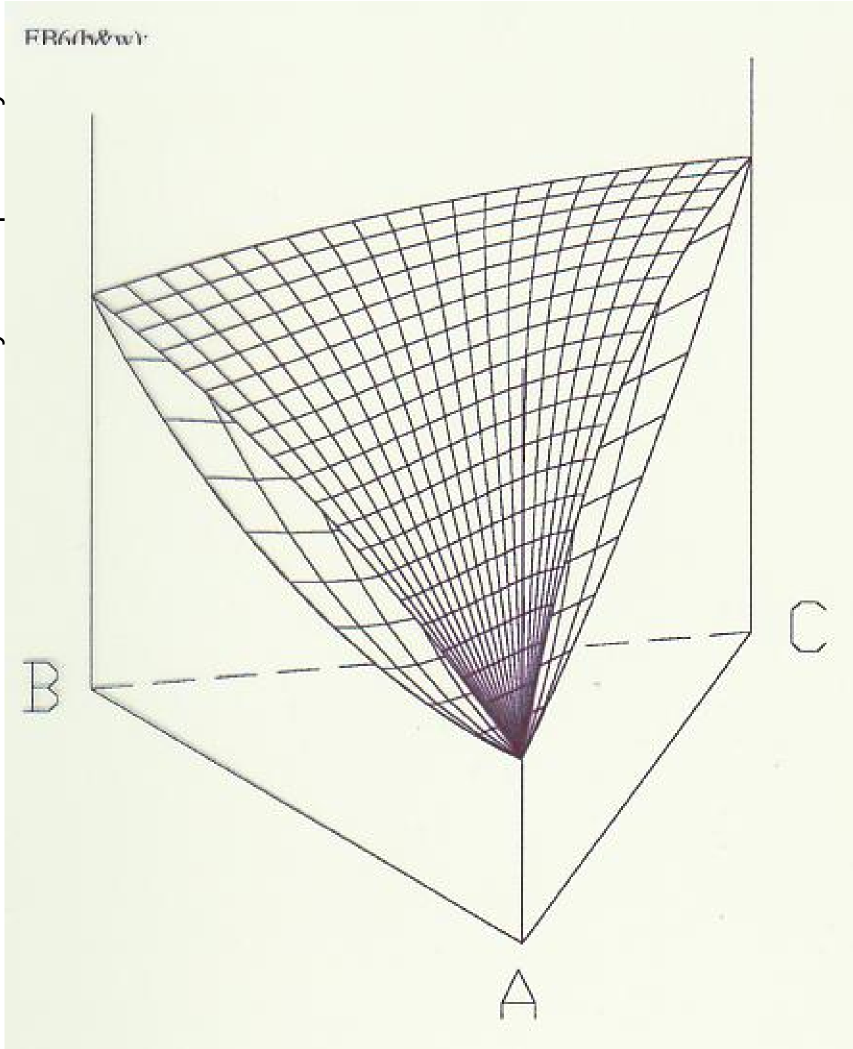


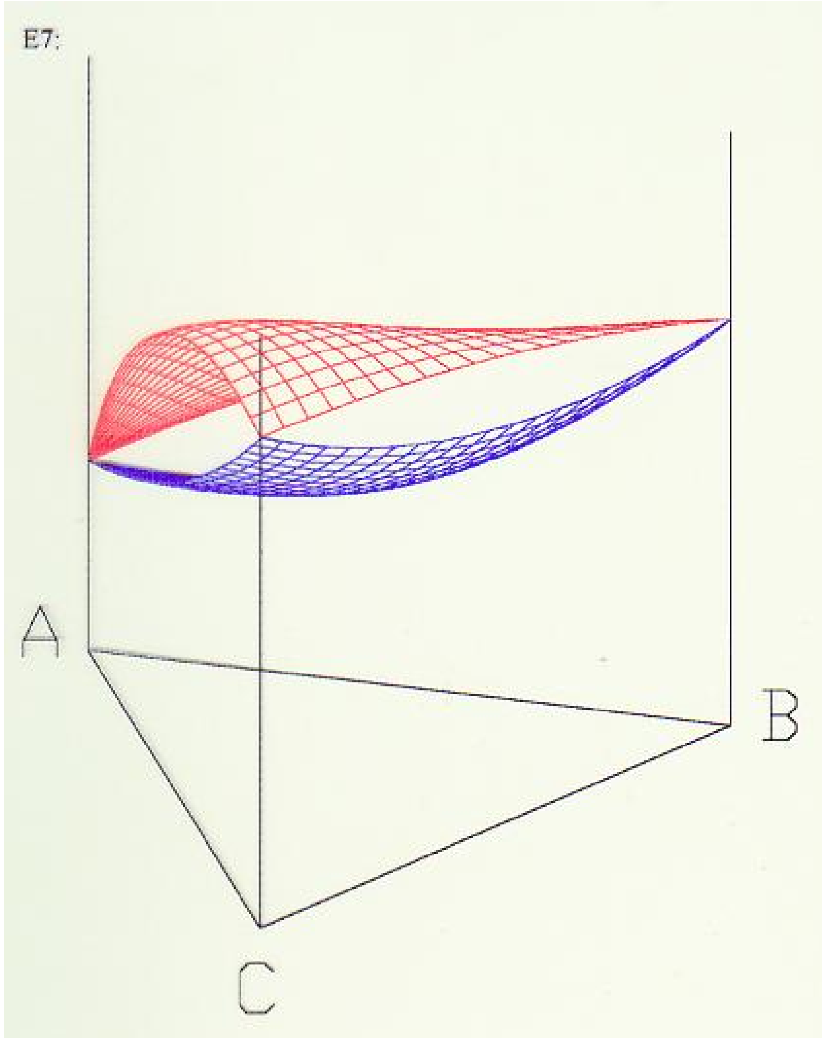
B4:
Liquidus Surface
B
C
A

Solidus Surface



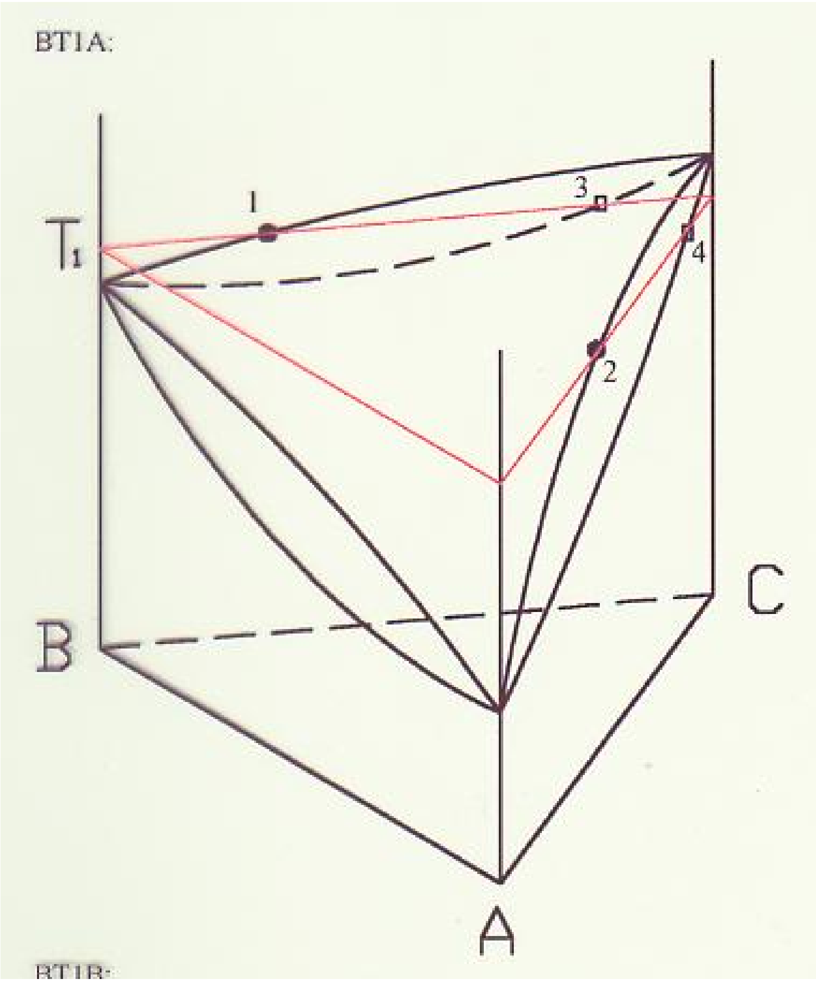


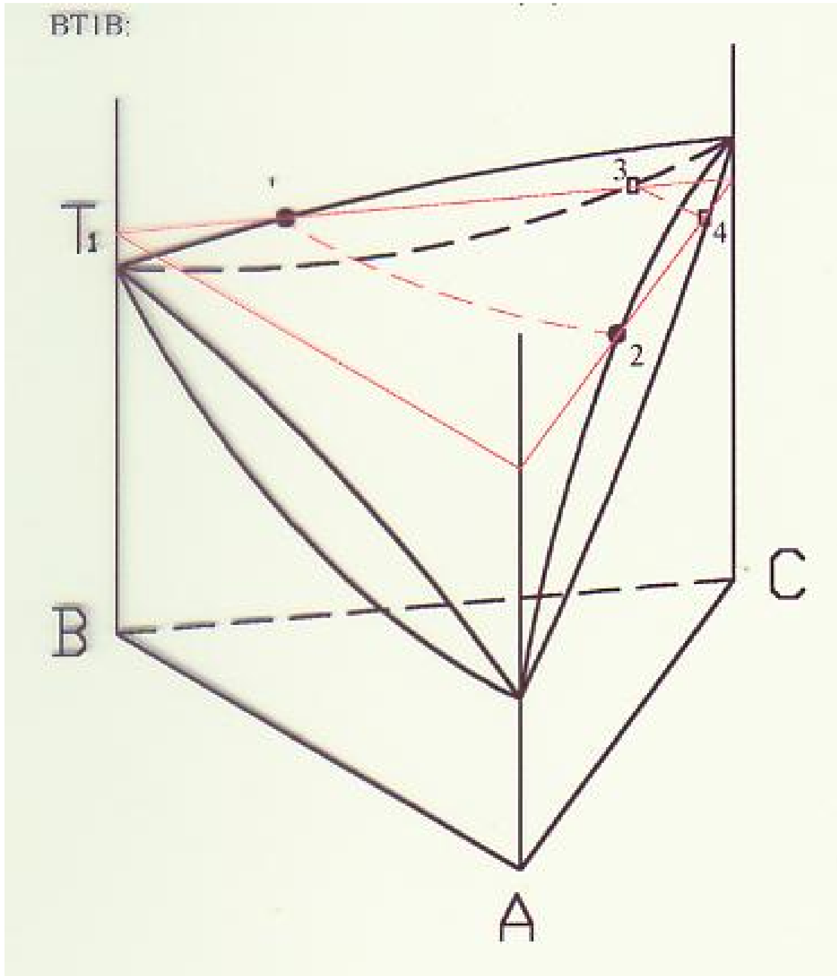

B
C
A


E7:
A
B
C

Ternary Isomorphous System

- **Isothermal Section**: A "horizontal" section of a ternary phase diagram obtained by cutting through the space diagram at a specified temperature
- Refer to Figures BT1A, BT1B and BT1C
- Identify temperature of interest, T_1 here
- Draw the horizontal, intersecting the liquidus and solidus surfaces at points 1, 2, 3 & 4
- Connect points 1 & 2 with curvature reflecting the liquidus surface
- Connect points 3 & 4 with curvature reflecting the solidus surface


BT1A:
T1
1
3
4
2
B
C
A


BT1B:
3
T1
4
2
B
C
A

Ternary Isomorphous System

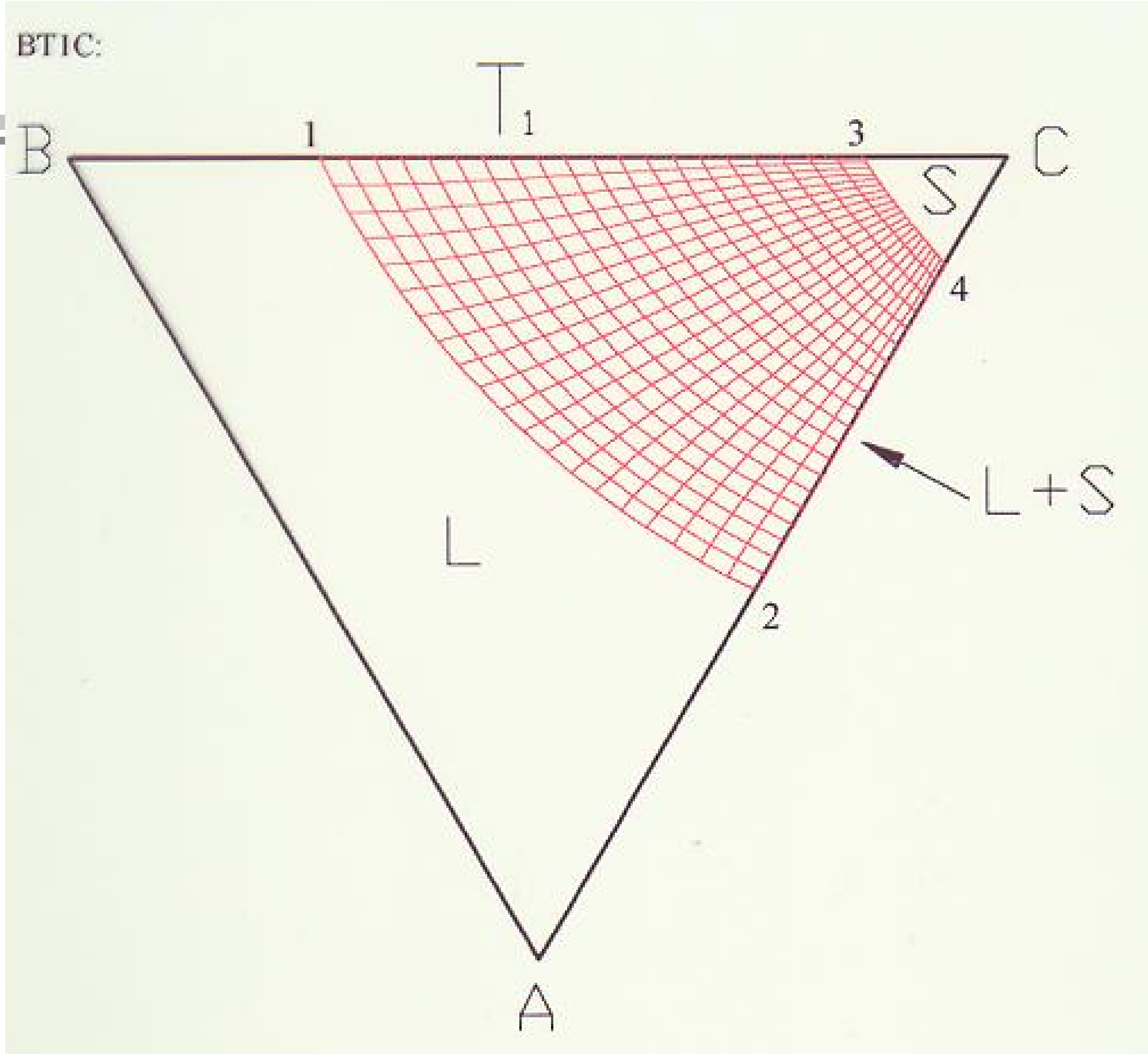
The line connecting points 1 & 2 represents the intersection of the isotherm with the liquidus surface

The line connecting points 3 & 4 represents the intersection of the isotherm with the solidus surface

Area A-B-1-2: homogeneous liquid phase

Area C-3-4: homogeneous solid phase

Area 1-2-3-4: two phase region - liquid + solid


BTIC:
T1
1
3
B
C
S
4
L+S
L
2
A

Ternary Isomorphous System

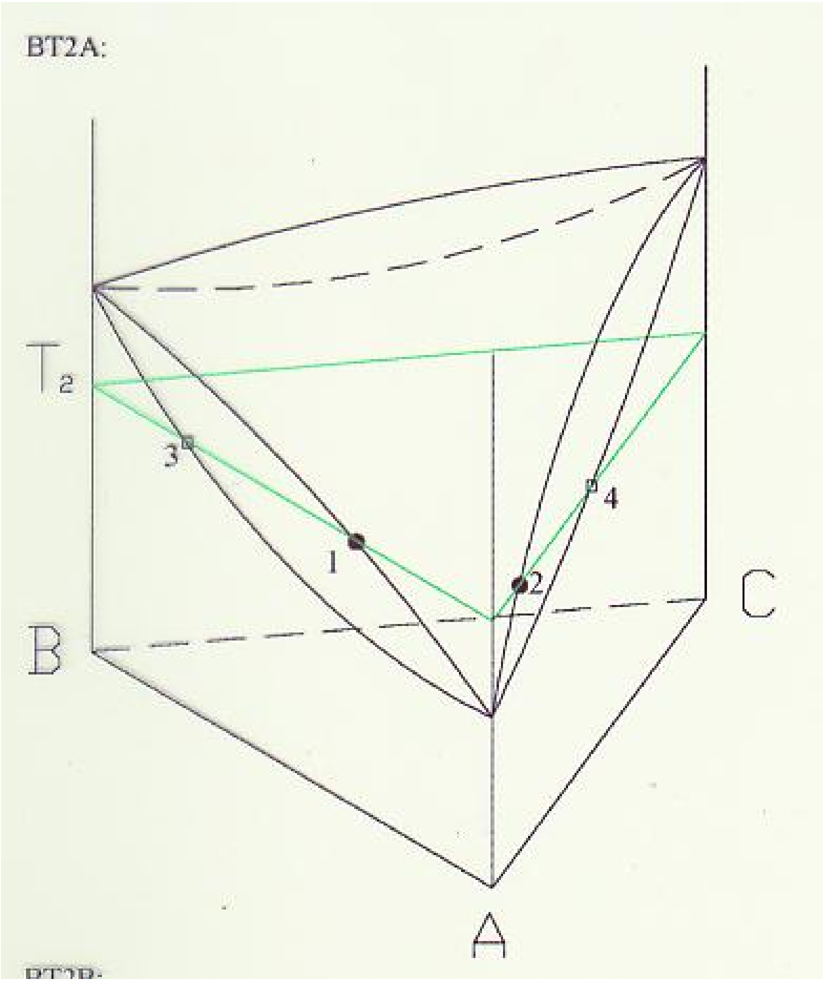
<u>Isothermal Section</u> - continued

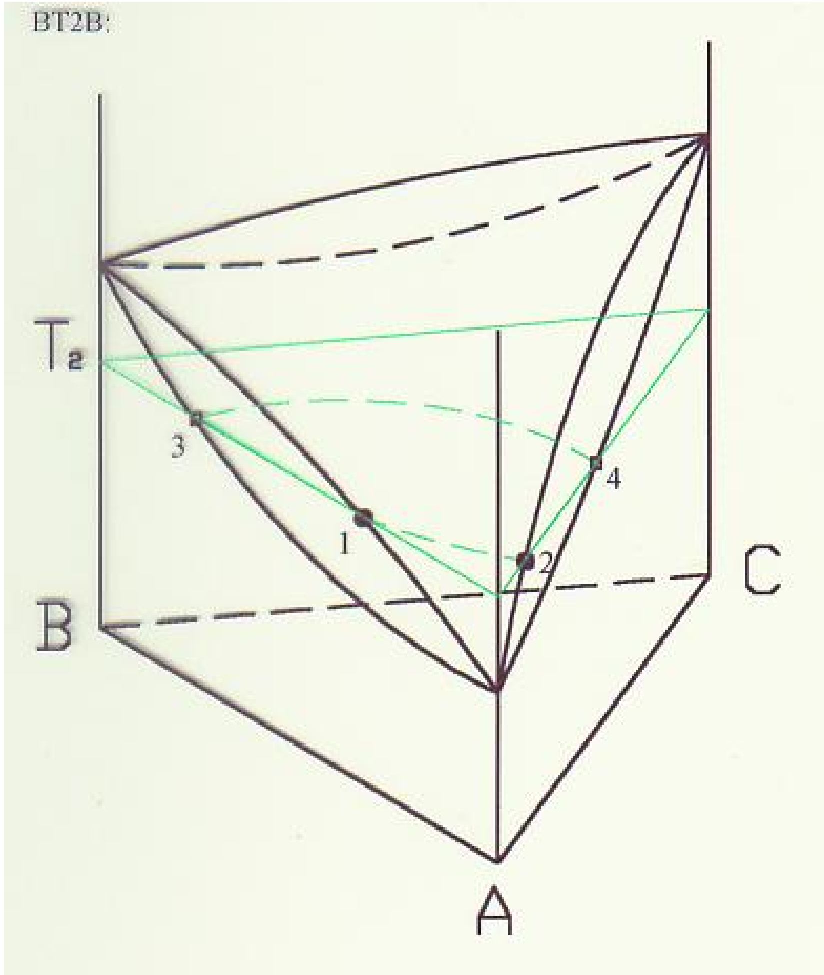
Temperature = T_2, below melting points of A & B, but above melting point of C

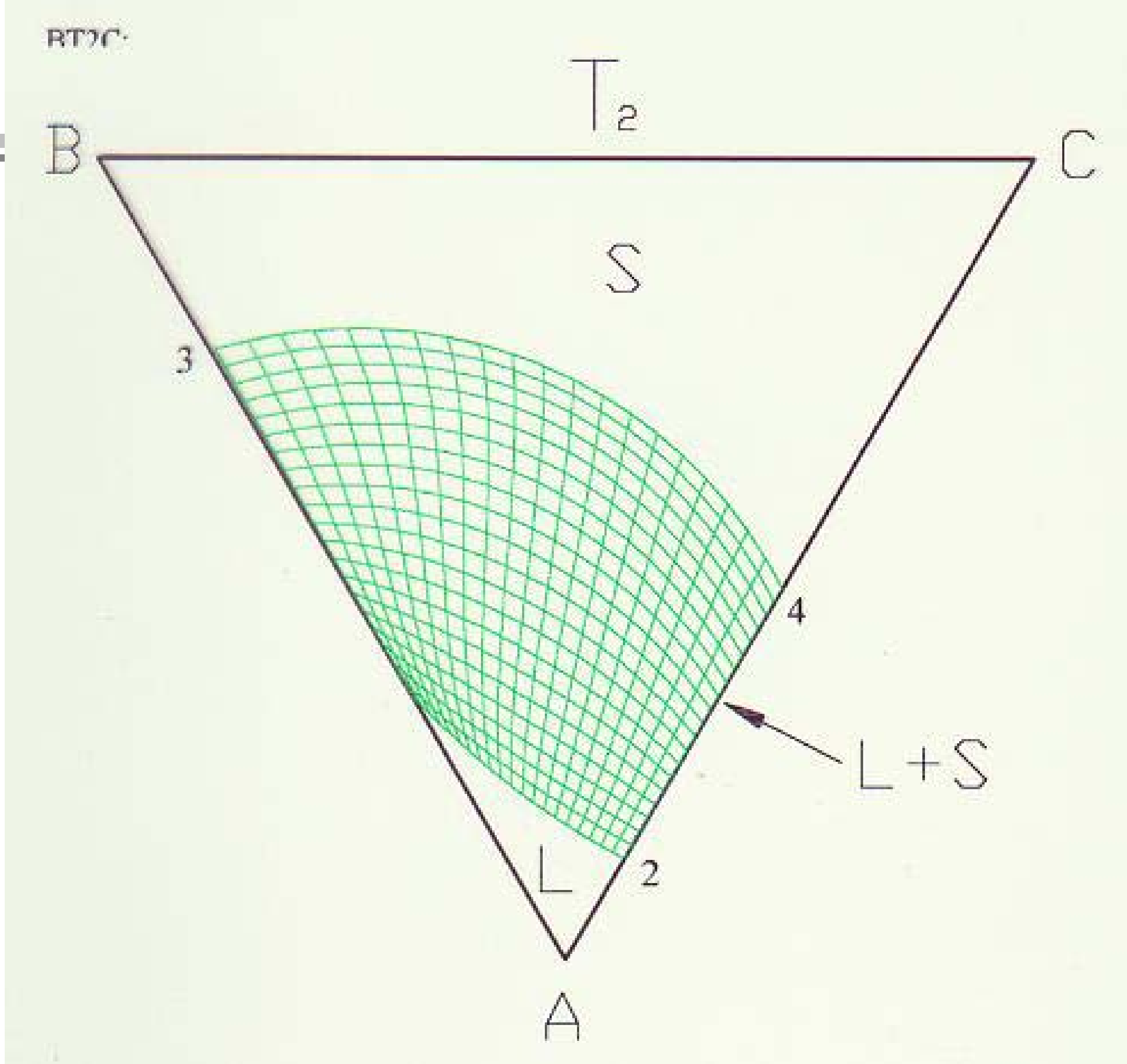
Area A-1-2: homogeneous liquid phase

Area B-C-4-3: homogeneous solid phase

Area 1-2-3-4: two phase region - liquid + solid


BT2A:
T2
3
4
1
2
B
C
A


BT2B:
T2
3
4
1
2
B
C
A


T2
B
C
S
3
4
L+S
L
2
A

Ternary Isomorphous System

Determination of:

(a) Chemical composition of phases present

(b) Amount of each phase present

when the overall composition is in a two phase region

Ternary Isomorphous System

1. **Locate overall composition using the Gibbs triangle**
2. **Draw tie-line passing through X, to intersect the phase boundaries at Y and Z**
3. **The chemical composition of the liquid phase is given by the location of the point Y within the Gibbs Triangle**
4. **The chemical composition of the solid phase is given by the location of the point Z within the Gibbs Triangle**

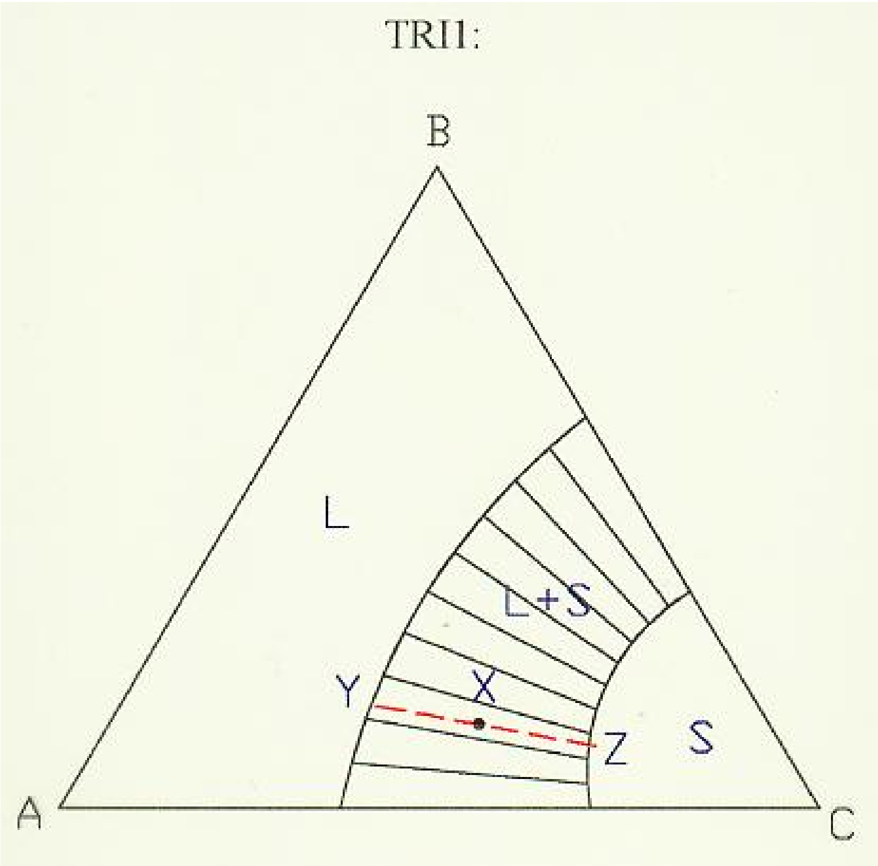
Ternary Isomorphous System

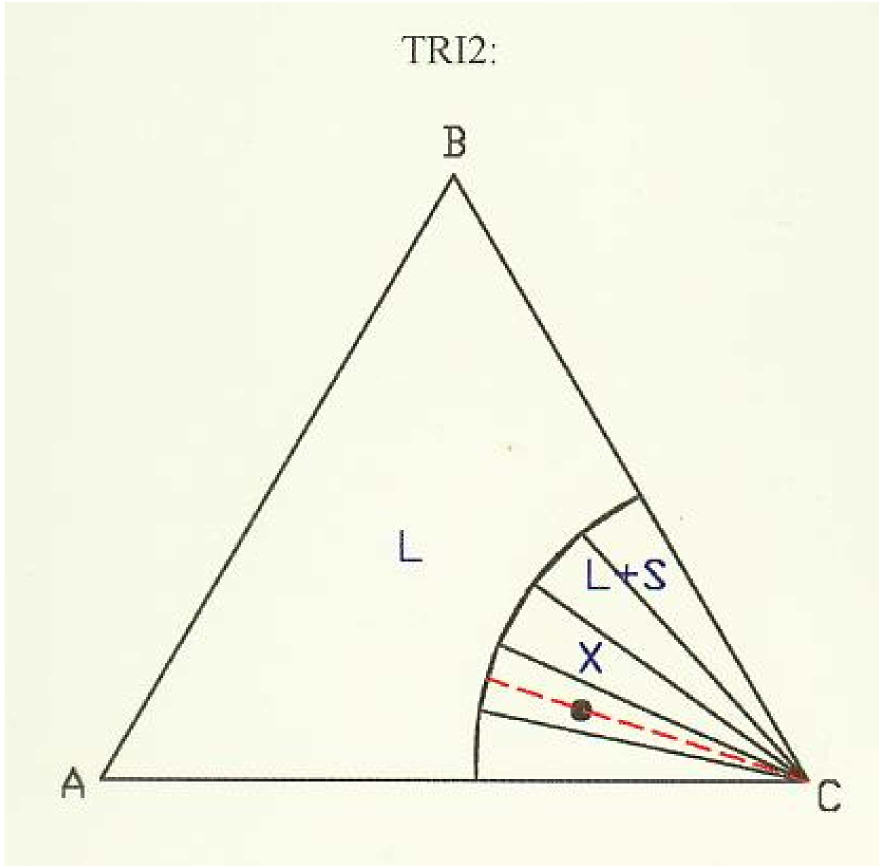
<u>Tie line</u>: A straight line joining any two ternary compositions

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


TRI1:
B
L
L+S
Y
X
Z
S
A
C


TRI2:
B
L
L+S
X
A
C

Ternary Isomorphous System

Drawing tie-lines in two phase regions

1. **The directions of tie lines vary gradually from that of one boundary tie line to that of the other, without crossing each other**
2. **They must run between two one-phase regions**
3. **Except for the two bounding tie-lines, they are not necessarily pointed toward the corners of the compositional triangle**

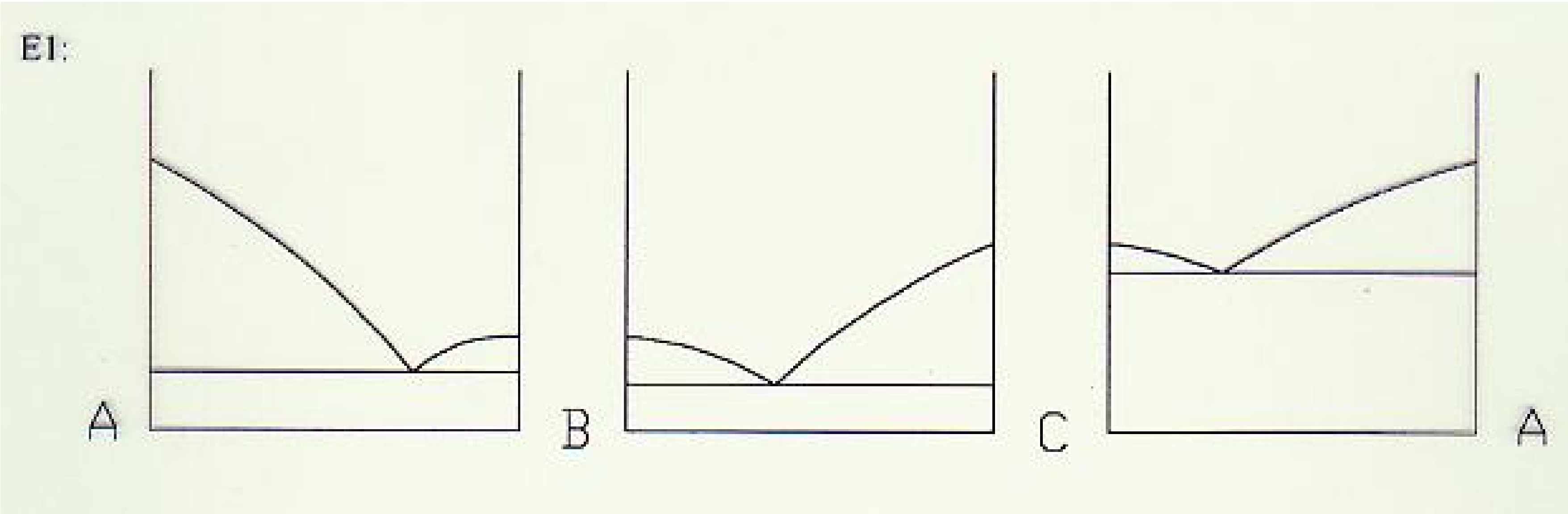
Ternary Eutectic System
(No Solid Solubility)

The Ternary Eutectic Reaction:

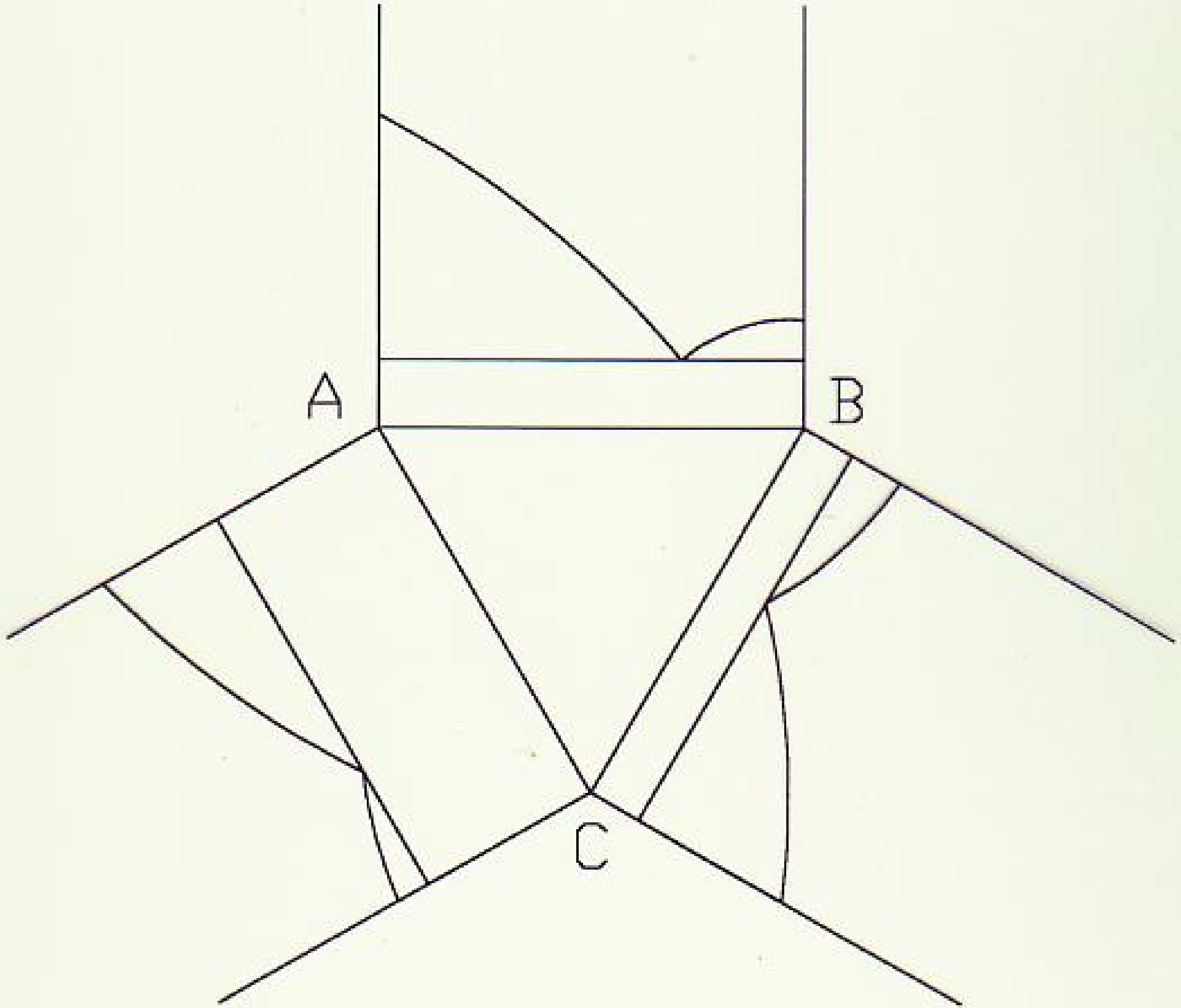
L = $\alpha + \beta + \gamma$

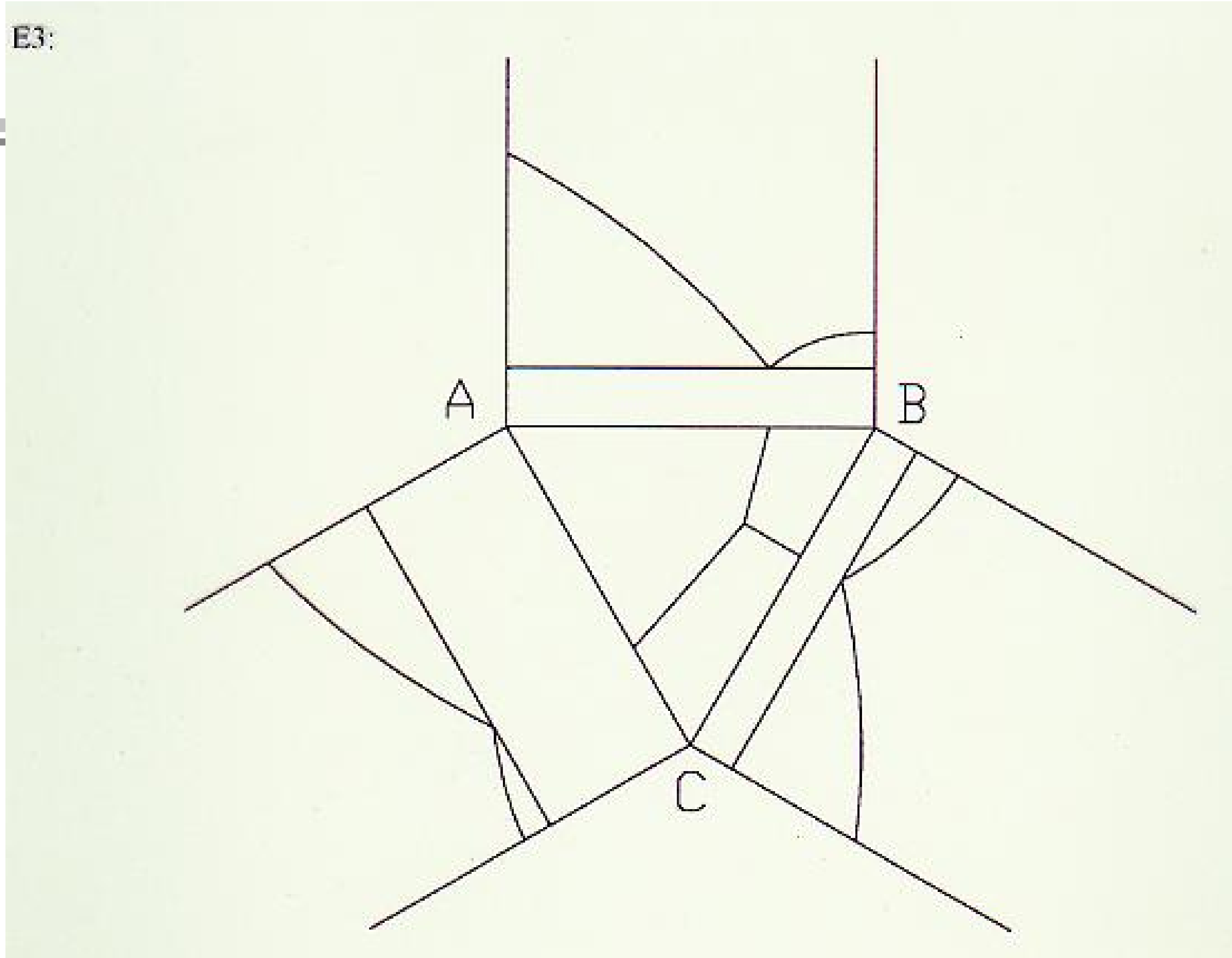
A liquid phase solidifies into three separate solid phases

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

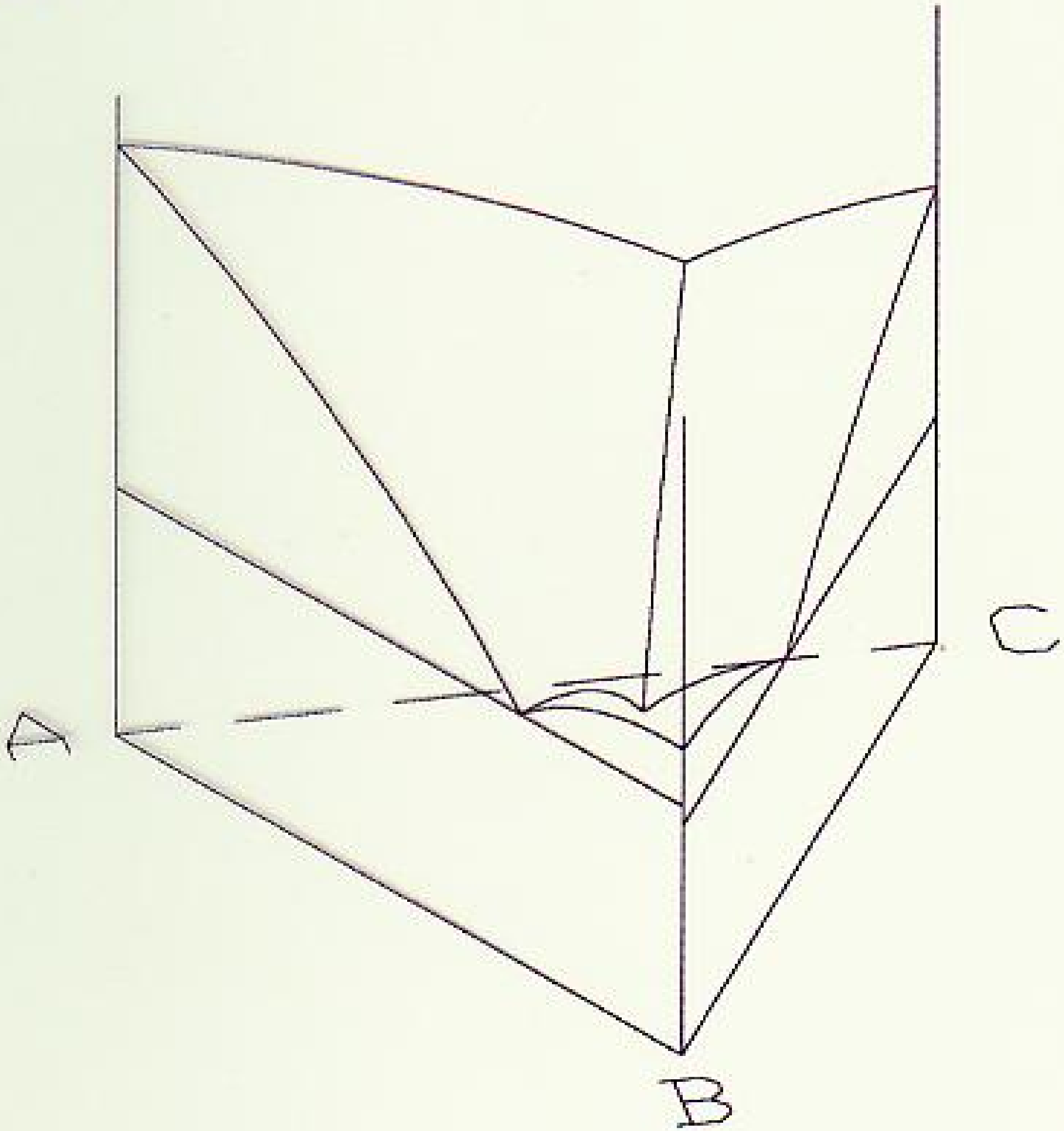

E1:
A
B
C
A

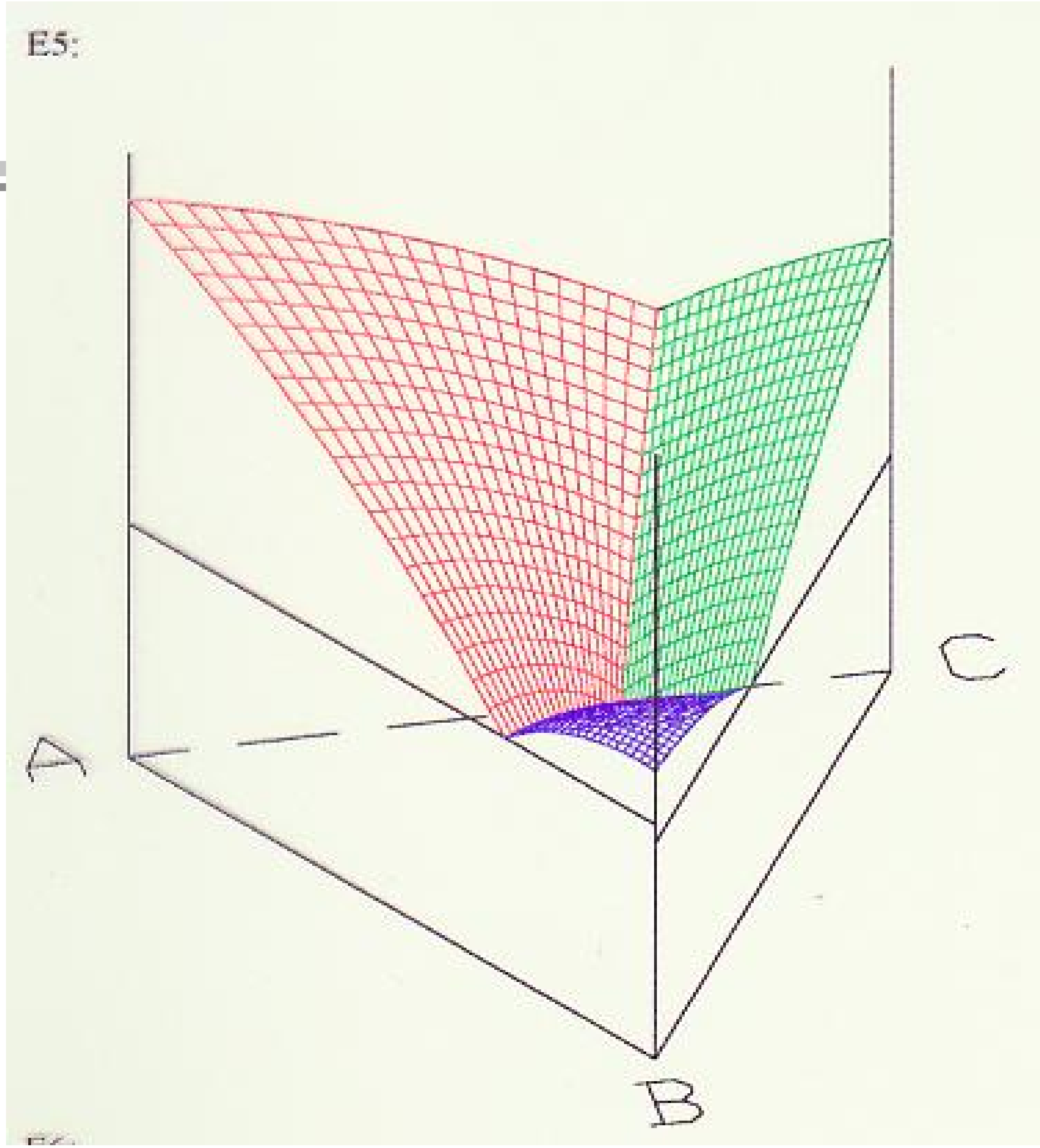
E2:

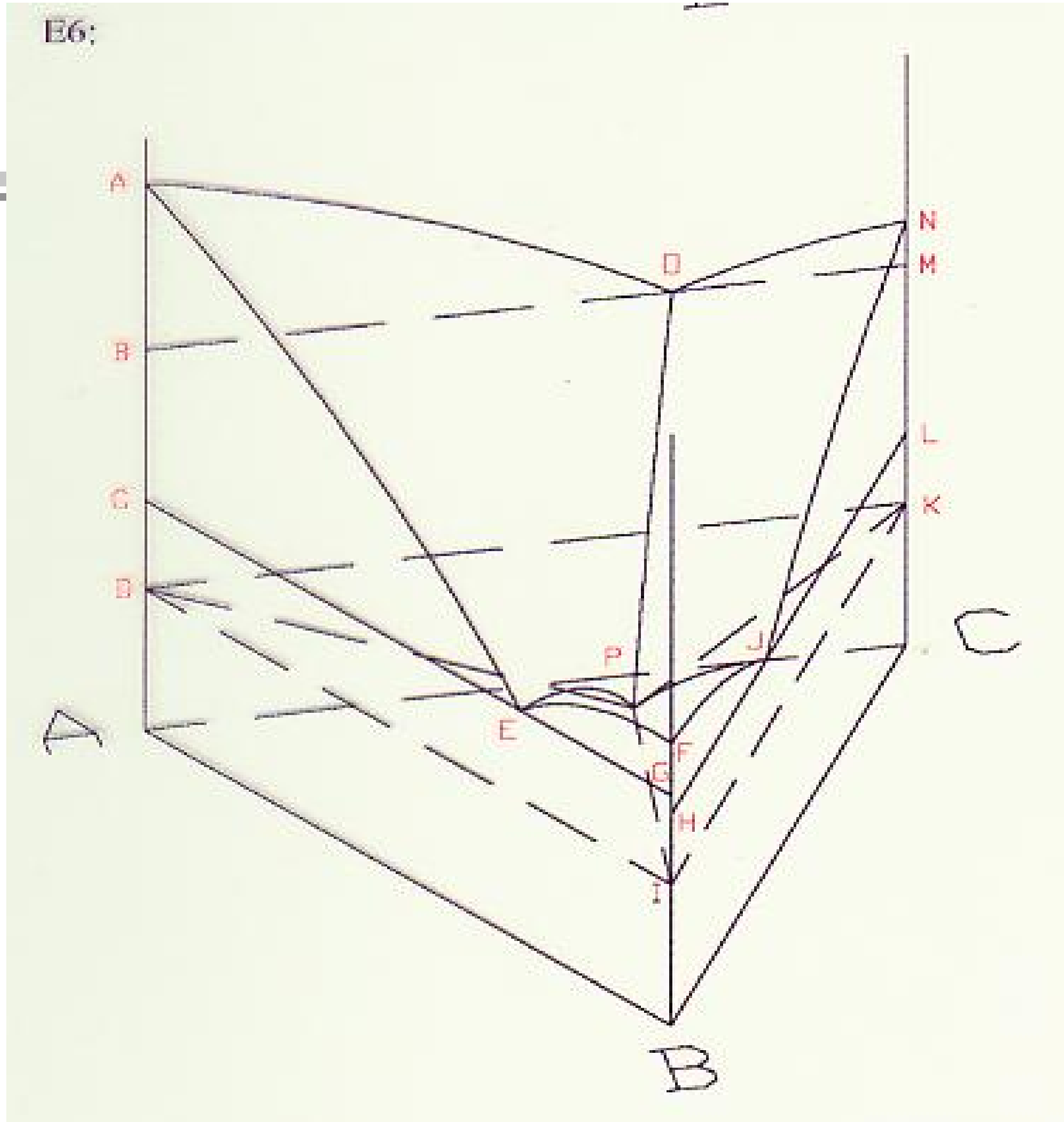



E3:
A
B
C

E4:




E5:
A
B
C


E6:
A
B
C
D
D
N
M
L
K
P
J
E
F
G
H
I
A
B
C

Ternary Eutectic System
(No Solid Solubility)

Phase regions:

Homogeneous liquid phase

Liquid + one solid phase

Liquid + two solid phases

Three solid phases

Ternary Eutectic System
(No Solid Solubility)

<u>The Liquidus Surface</u>

The liquidus surface "dips down" somewhere in the middle, to the ternary eutectic point, which would be at a temperature lower than all three binary eutectic temperatures

All points in space, above the liquidus surface, represent the existence of a homogeneous liquid phase

All points in space, below the liquidus surface, represent the existence of two or more phases (*more on this later*)

Ternary Eutectic System
(No Solid Solubility)

<u>The Liquidus Surface</u> (continued)

The Liquidus Projection - a projection of the liquidus surface onto a plane, with indications of isotherms and phase regions

The liquidus surface also represents the boundary between the single phase liquid region and the (liquid + one solid phase) regions

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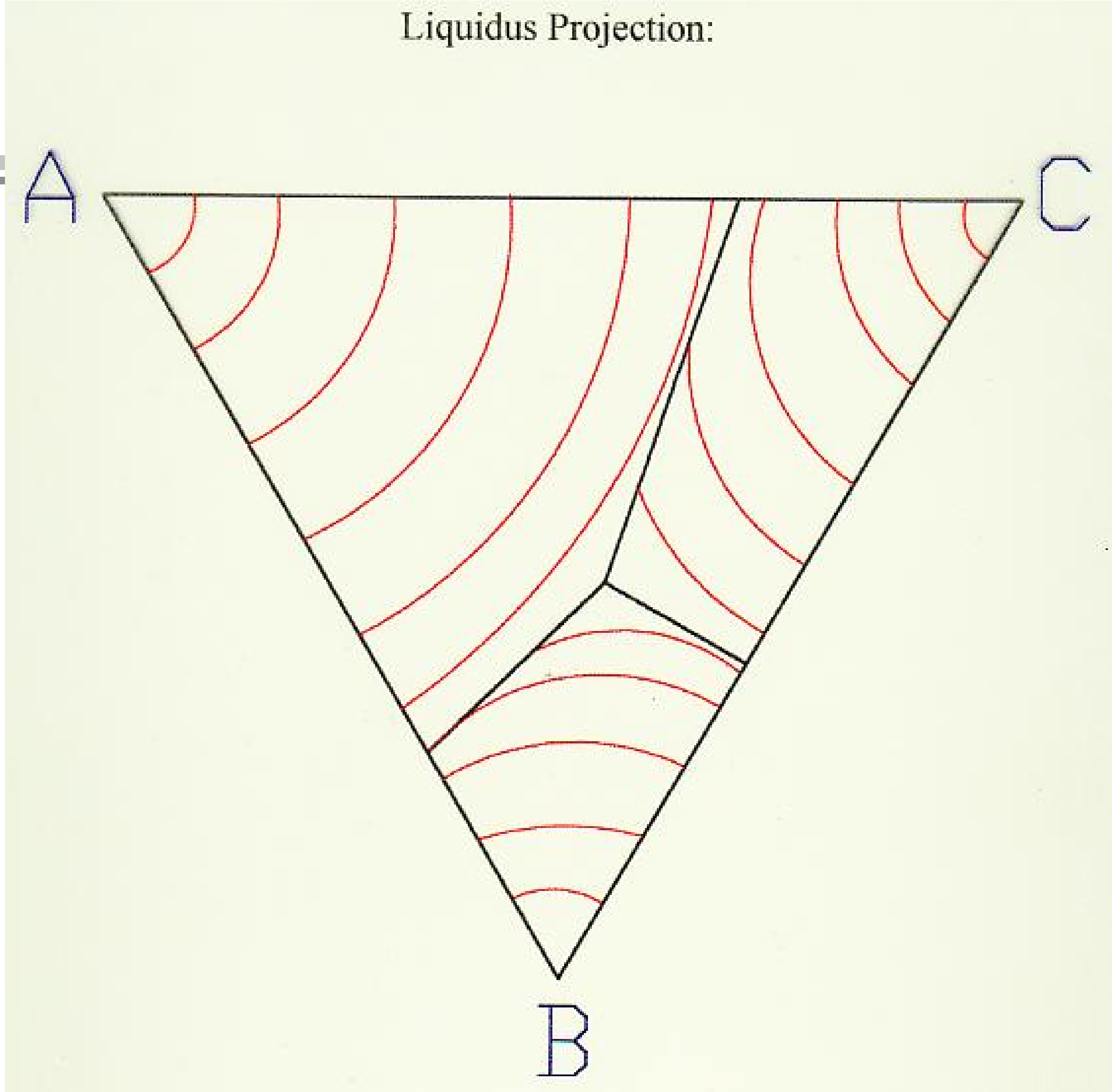

Liquidus Projection:
A
C
B

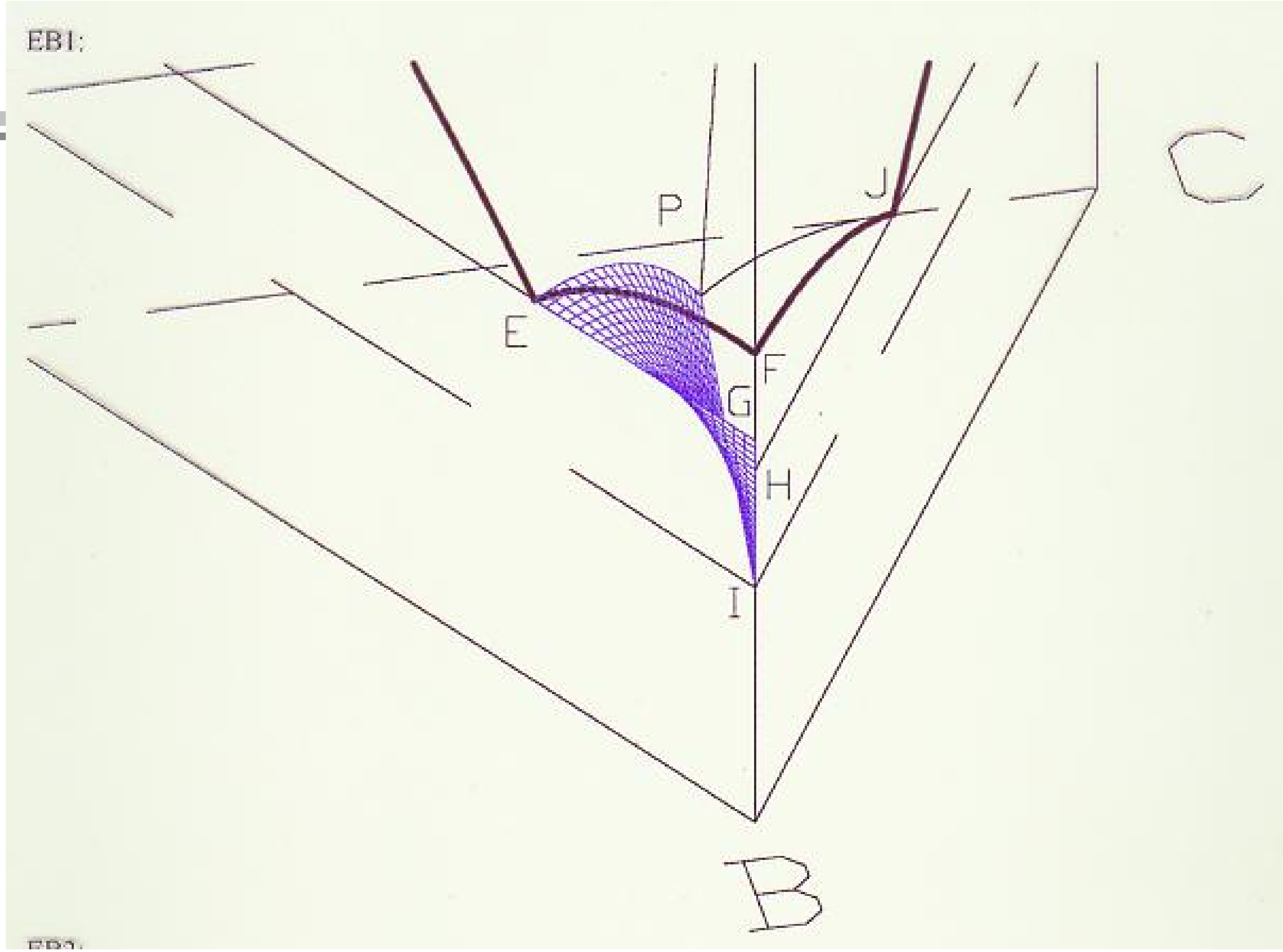
Ternary Eutectic System
(No Solid Solubility)

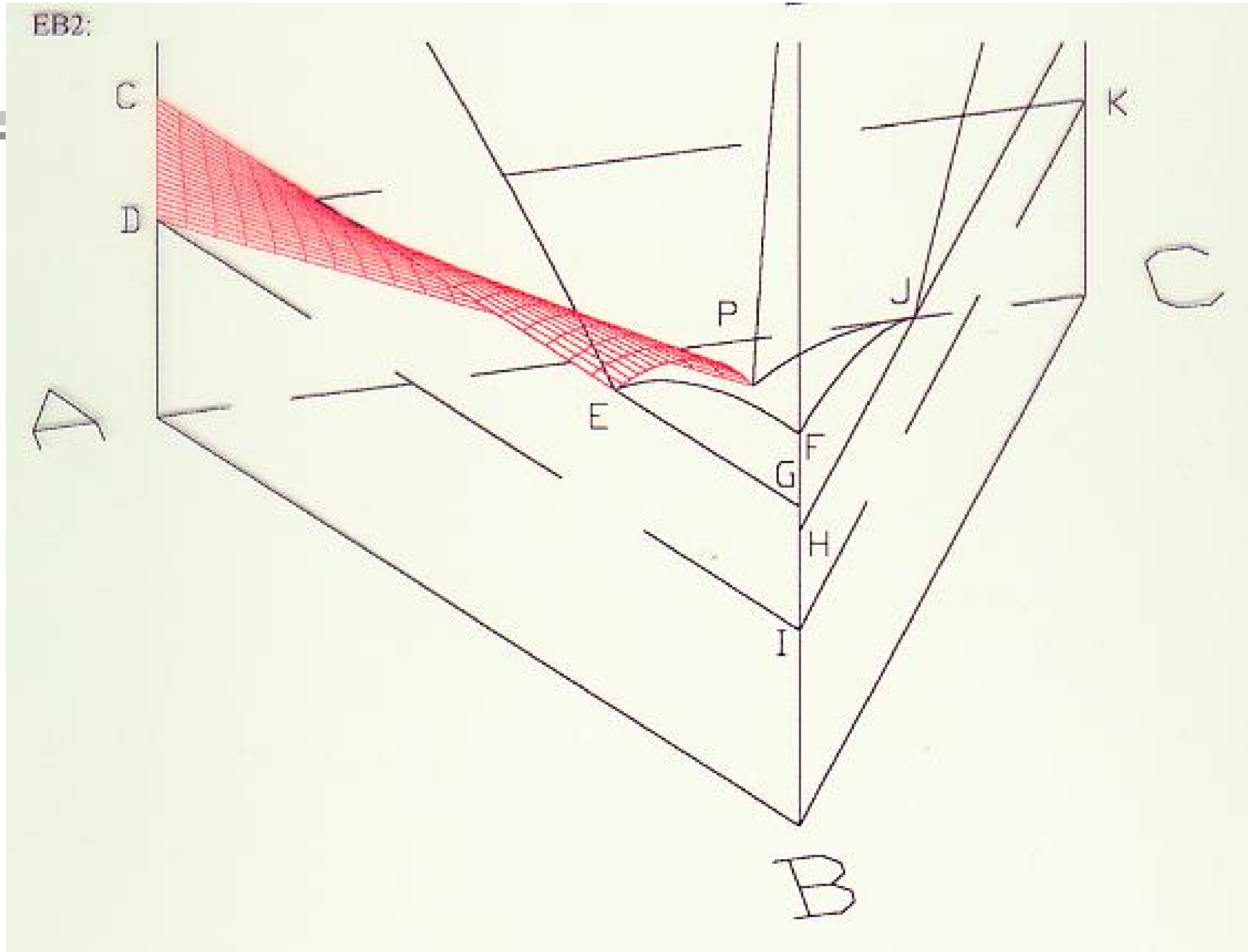
Boundaries between 2 phase regions & 3 phase regions

With reference to Figure EB1:

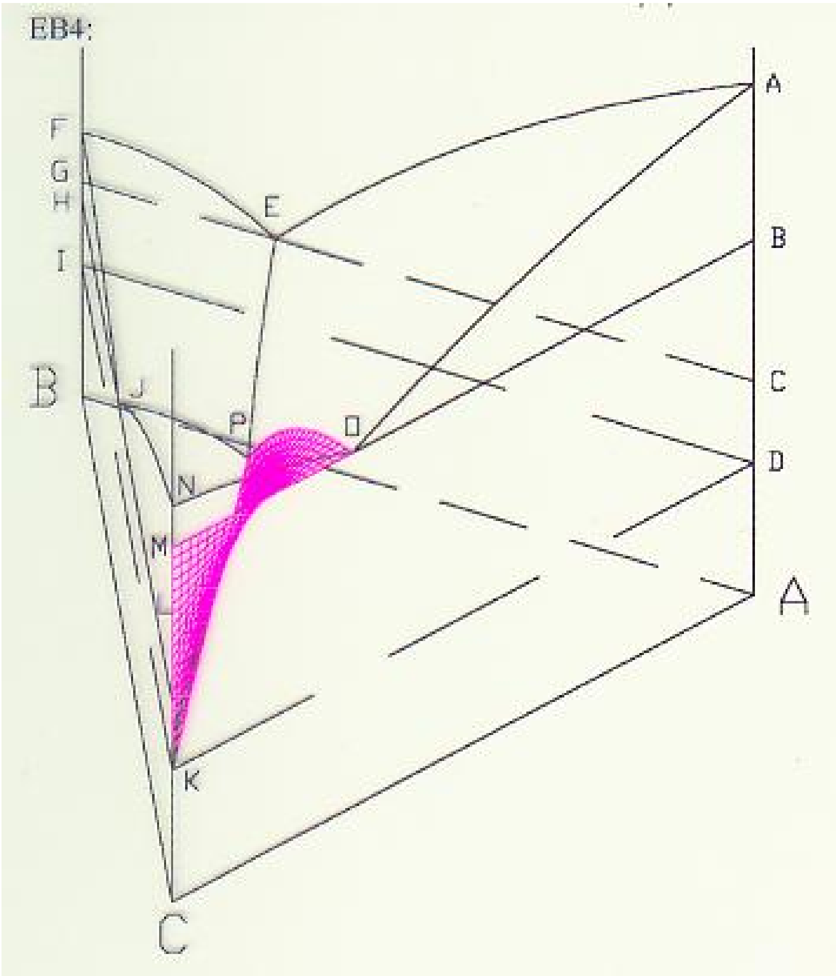
The surface P-E-F-J represents the boundary between the liquid region and the (liquid + one solid phase) region

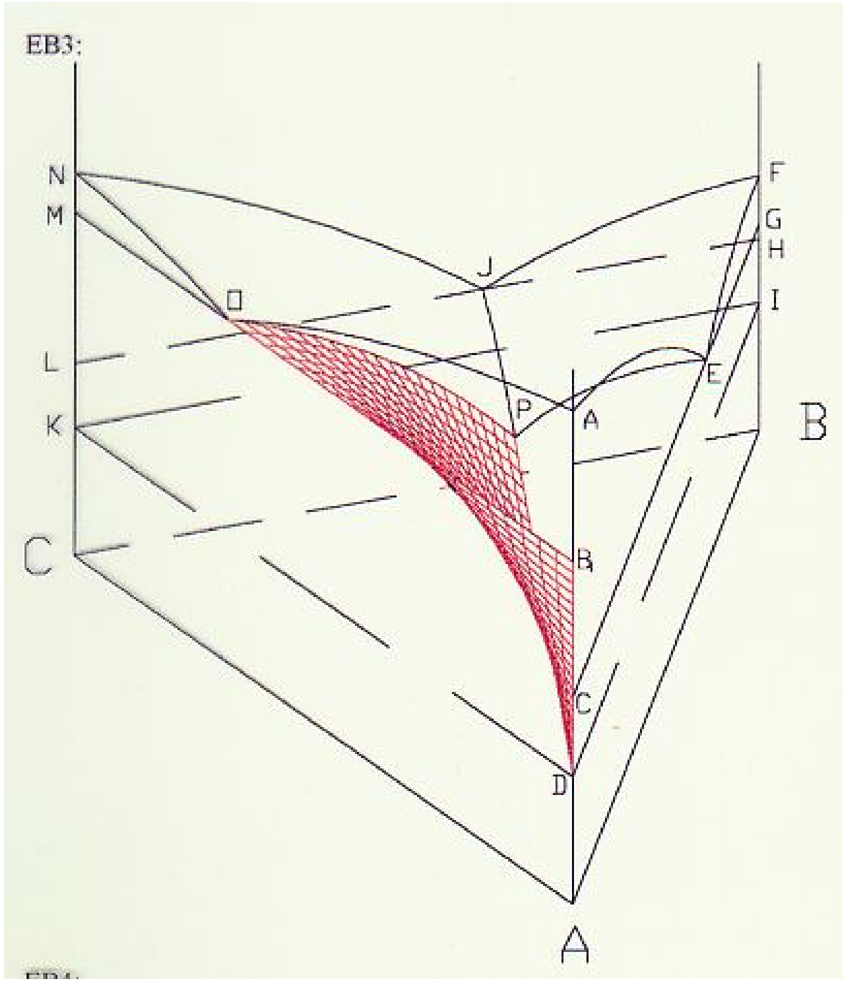
The surfaces P-E-G-I-P and P-J-H-I-J-P represent the boundary between the (liquid + one solid phase) region and the (liquid + two solid phases) regions

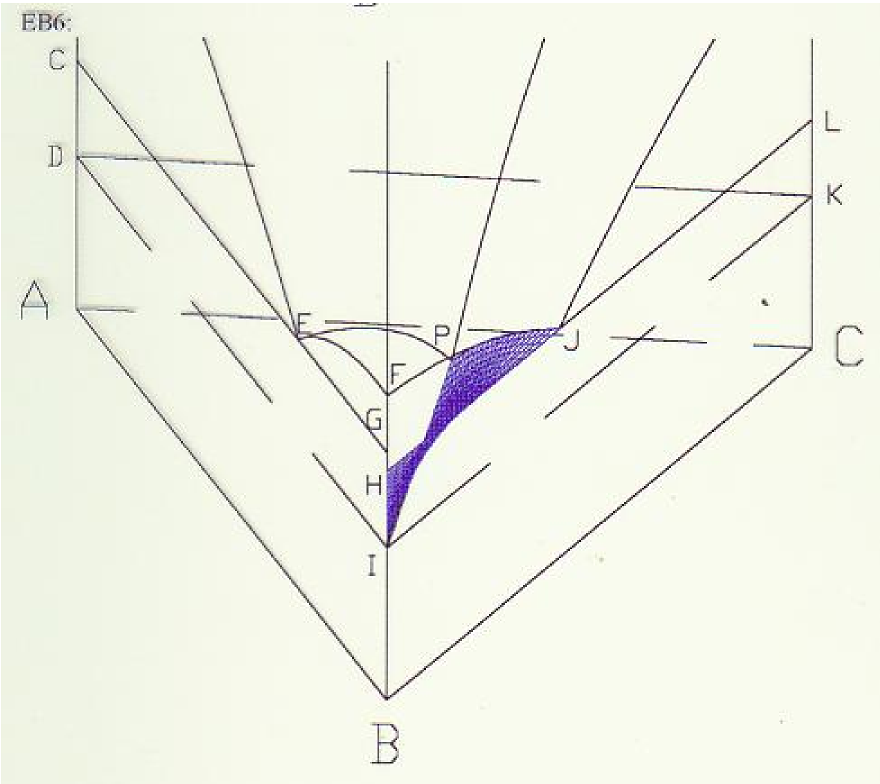

EB1:
P
J
C
E
F
G
H
I
B

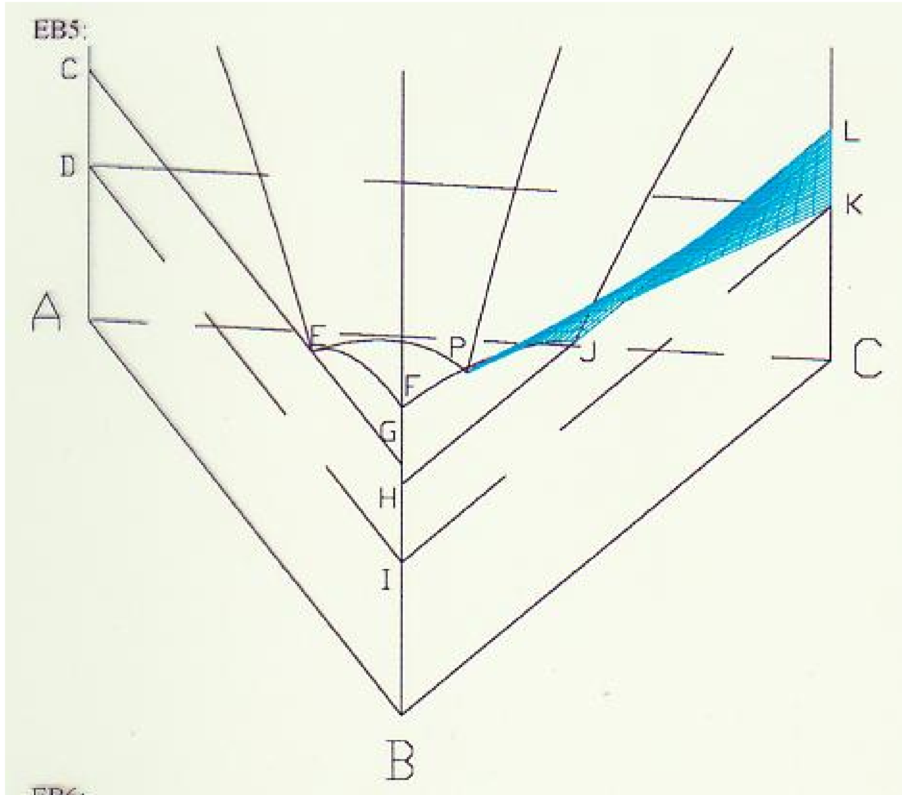

EB2:
C
D
A
E
P
J
K
C
F
G
H
I
B

Ternary Eutectic System – No Solid Solubility

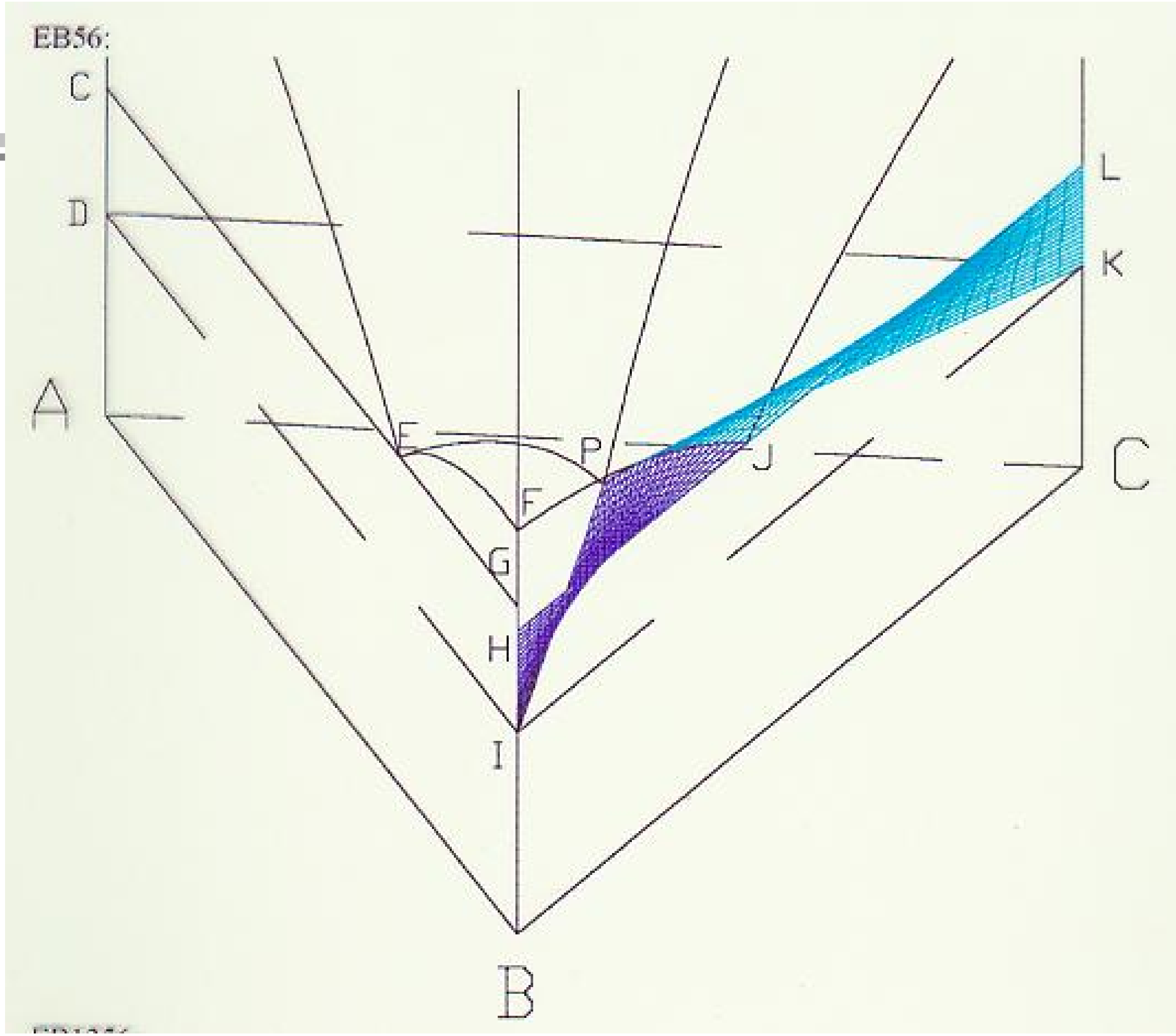


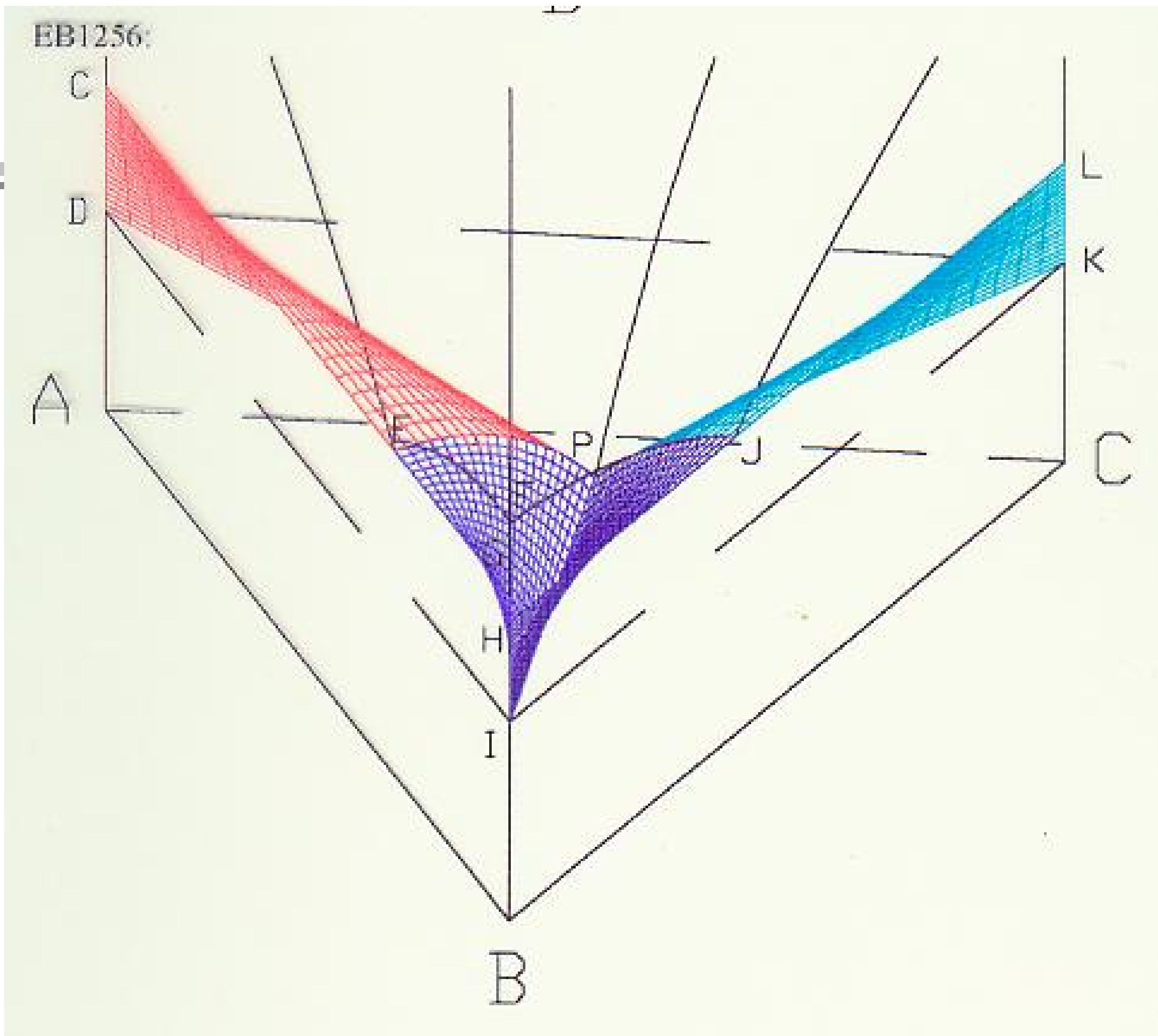



EB6:
C
D
A
E
P
J
F
G
H
I
B
L
K
C


EB5:
C
D
A
E
P
J
F
G
H
I
B
L
K
C

Ternary Eutectic System – No Solid Solubility




EB1256:
C
D
A
E
F
G
H
I
P
J
L
K
C
B

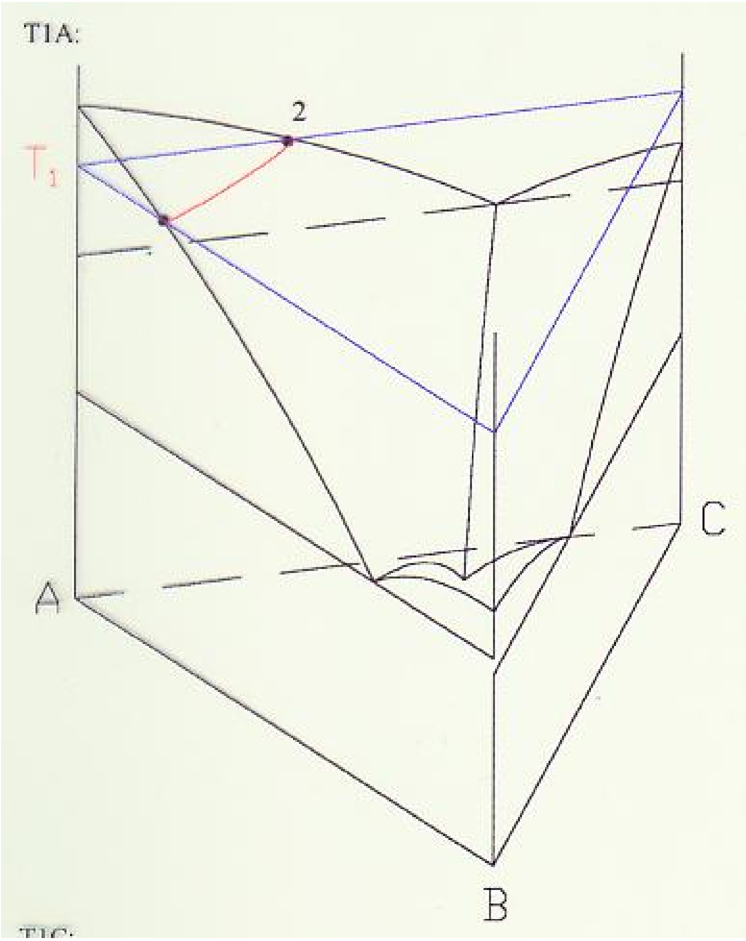
Ternary Eutectic System
(No Solid Solubility)

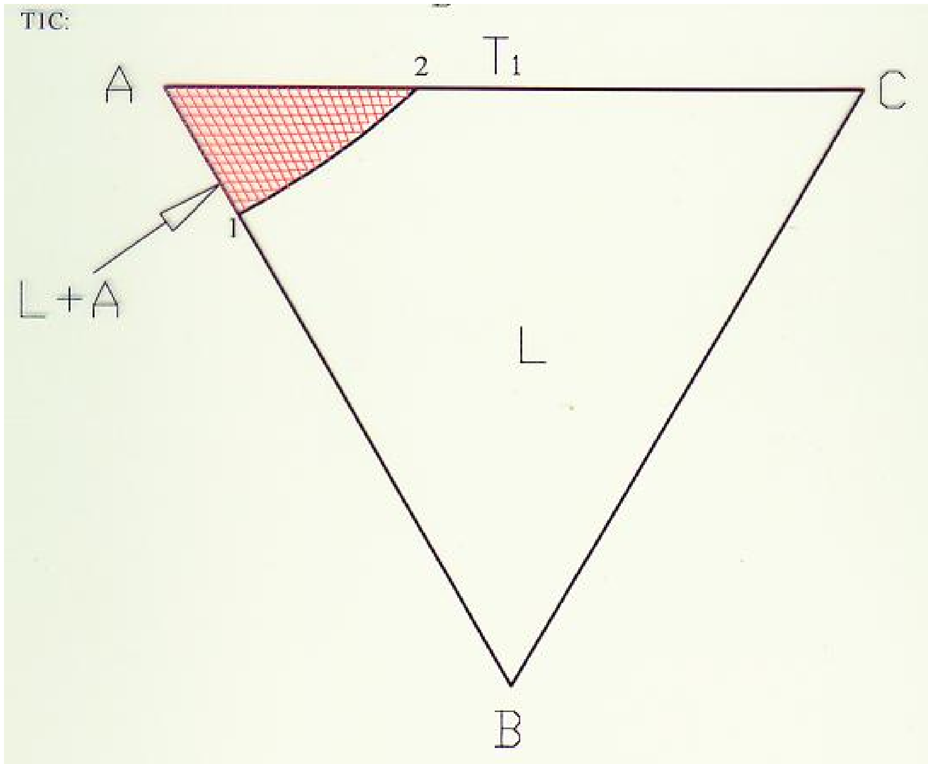
Isothermal Section at T_1, below melting point of A, but above melting points of B and C

We have two regions: a region of "liquid" and a region of "liquid + A"

The boundary between these two regions is a line, the curvature of which is in accordance with the liquidus surface

Ternary Eutectic System – No Solid Solubility





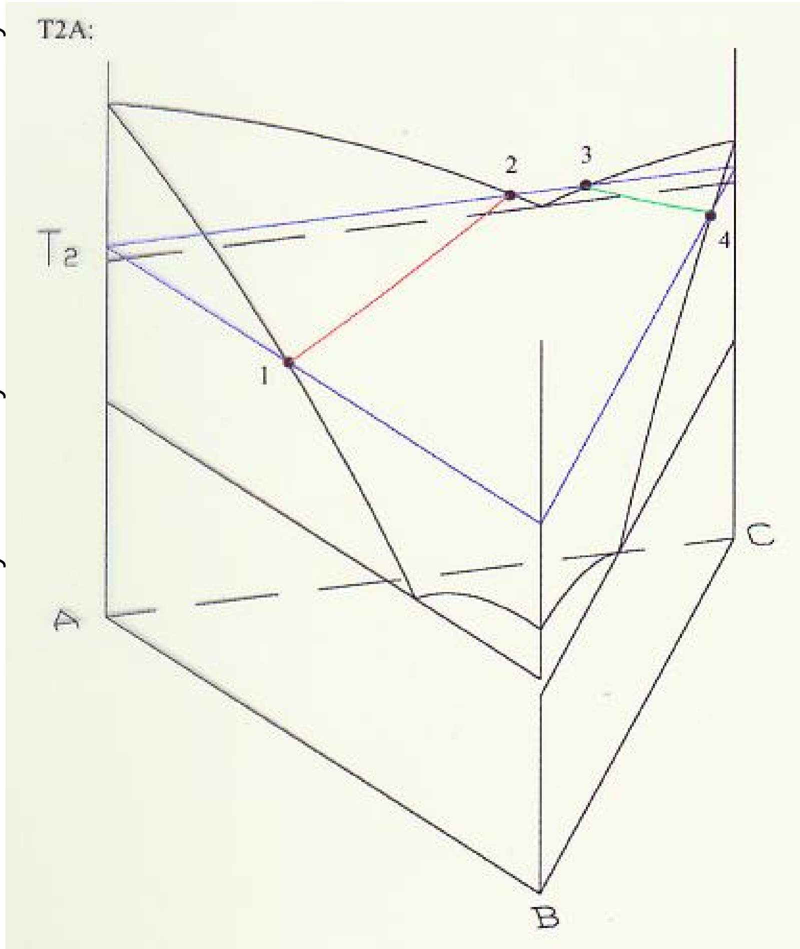
Ternary Eutectic System
(No Solid Solubility)

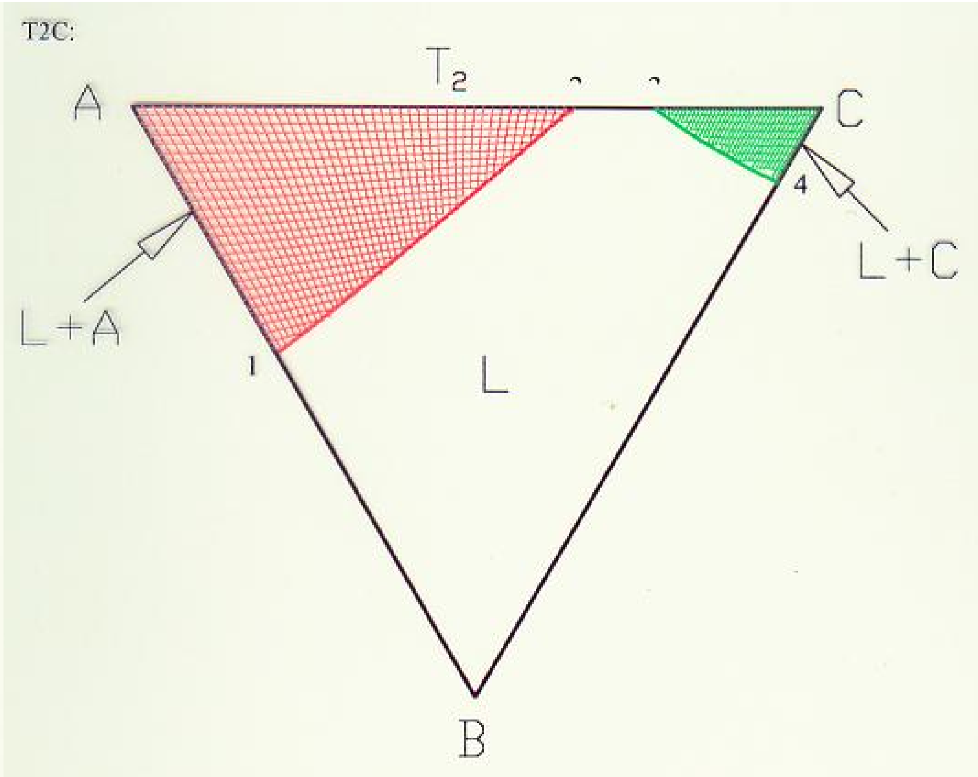
Isothermal Section at T_2, below the melting points of A and C, but above the melting point of B, and above the eutectic temperature of the system A-C

This isothermal section has three regions - L, L+A, and L + C

The boundary between L and L+A is determined by where the isothermal plane cuts the liquidus surface

Ternary Eutectic System – No Solid Solubility



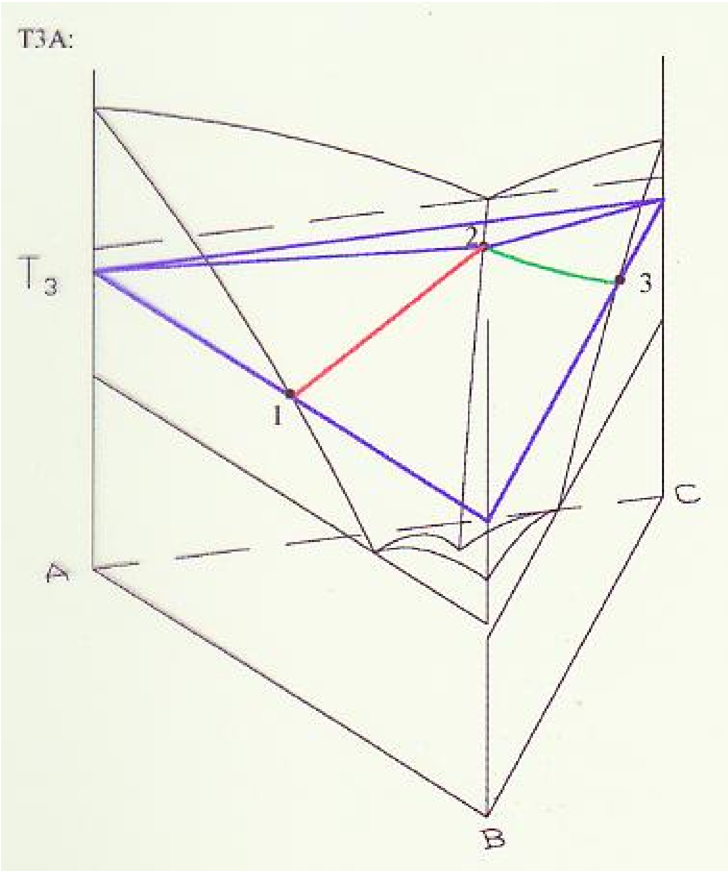


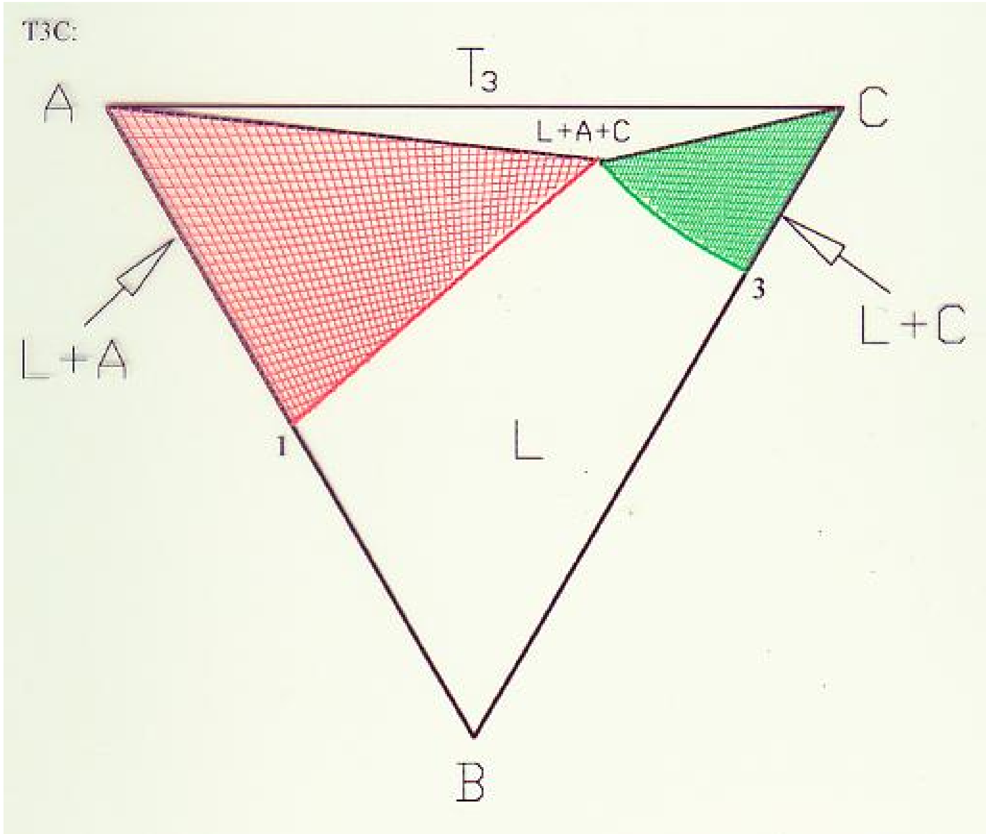
Ternary Eutectic System
(No Solid Solubility)

Isothermal section at temperature T_3, below the eutectic temperature of the system A-C, but still above the melting point of B

The isothermal section now has four regions: L, L+A, L + C, L + A + C

Note that points 2 and 4 have converged and moved into the Gibbs Triangle; this represents the path that connects the A-C eutectic point to the ternary eutectic point


T3A:
T3
2
3
1
A
B
C


T3C:
T3
A
C
L+A+C
L+A
L+C
L
1
3
B

Ternary Eutectic System
(No Solid Solubility)

The boundaries between the one-phase and two-phase regions, and the two-phase and three-phase regions are lines, <u>but</u> the one-phase region and the three-phase region meet at a point

The three-phase region is a triangle - called a <u>tie-triangle</u>

Law of Adjoining Phases

(for isothermal sections of ternary phase diagrams)

$R_1 = R - D^- - D^+ >= 0$

R_1: dimension of boundary between neighboring phase regions; 0 for point contact, 1 for line contact and 2 for surface contact

R: dimension of the concerned diagram or section of a diagram; for an isothermal section of a ternary, R = 2

D^-: number of phases that <u>disappear</u> when crossing the boundary from one phase region to another

D^+: number of phases that <u>appear</u> when crossing the boundary from one phase region to another

Law of Adjoining Phases
(continued)

1-phase region with 2-phase region: line

1-phase region with 3-phase region: point

2-phase region with 3-phase region: tie-line

2-phase region with 2-phase region: point

1-phase region with 1-phase region: point

Ternary Eutectic System
(No Solid Solubility)

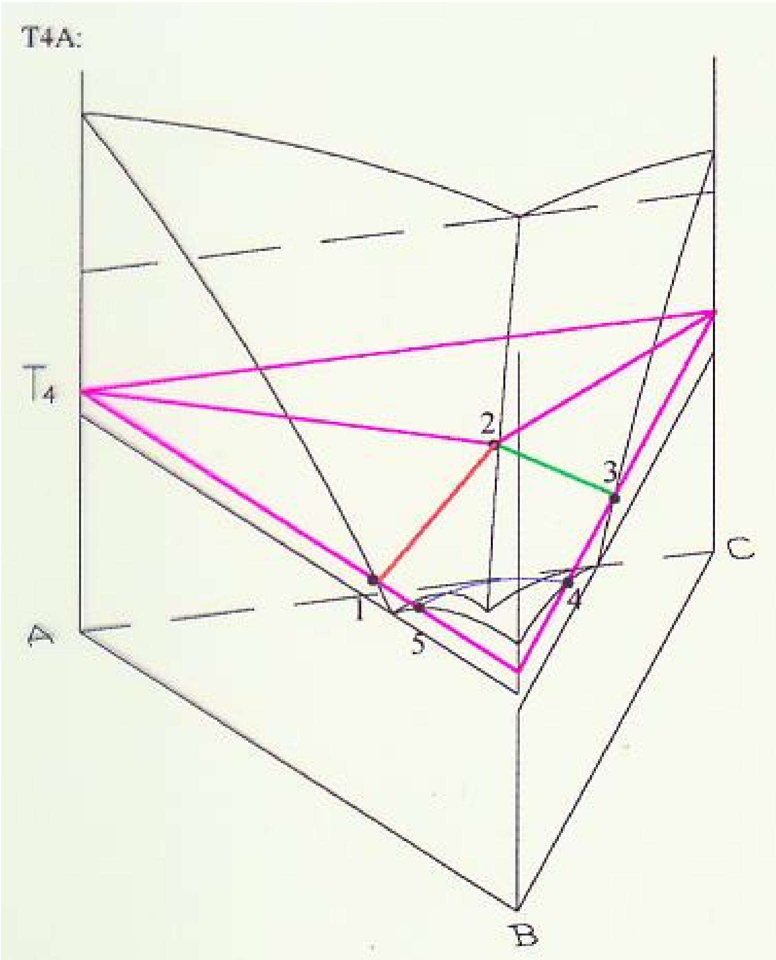
Isothermal section at temperature T_4, below the melting points of A, B and C, and below the eutectic temperature of the A-C system, but above the A-B and B-C eutectic temperatures

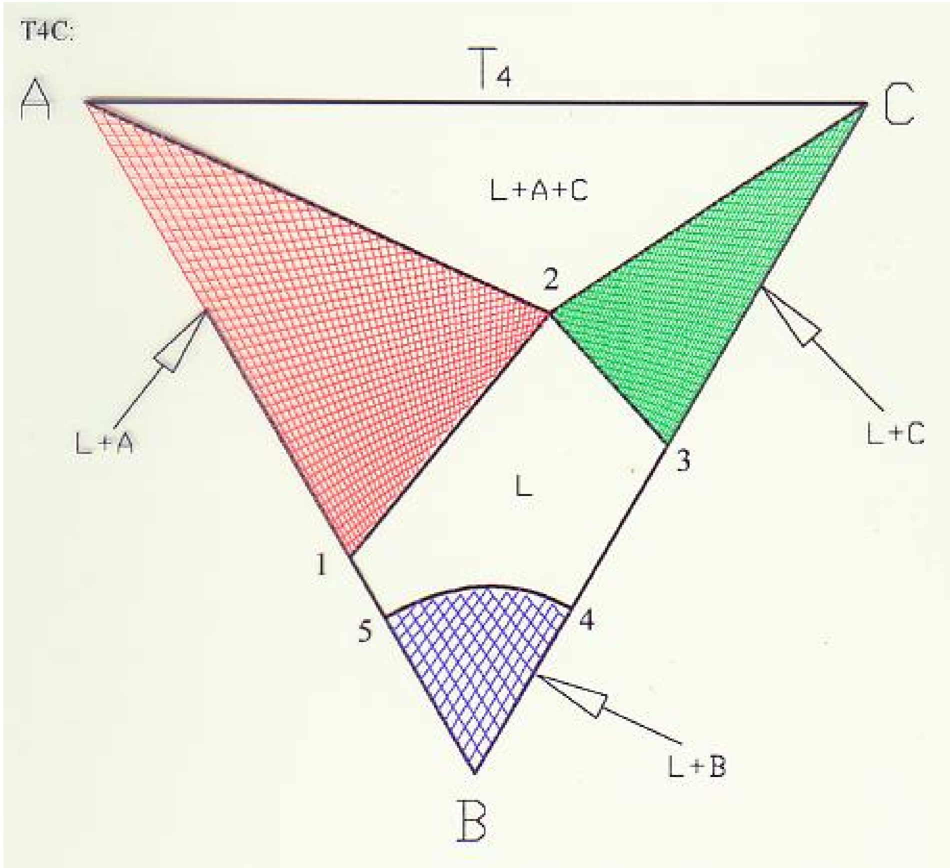
The isothermal section now has five regions:

L, L+A, L+B, L+C, L+A+C

Point 2 has moved further into the Gibbs Triangle, towards the ternary eutectic point

Ternary Eutectic System – No Solid Solubility





Ternary Eutectic System
(No Solid Solubility)

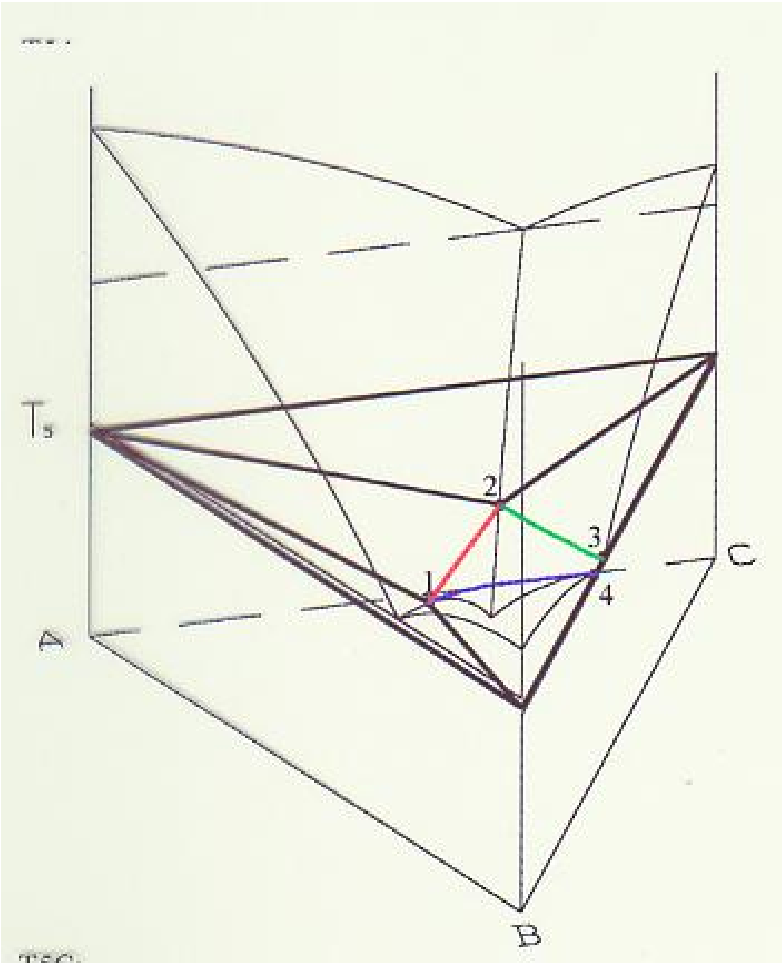
Isothermal section at temperature T_5, above the eutectic temperature of the B-C system, but below all other melting points and eutectic points

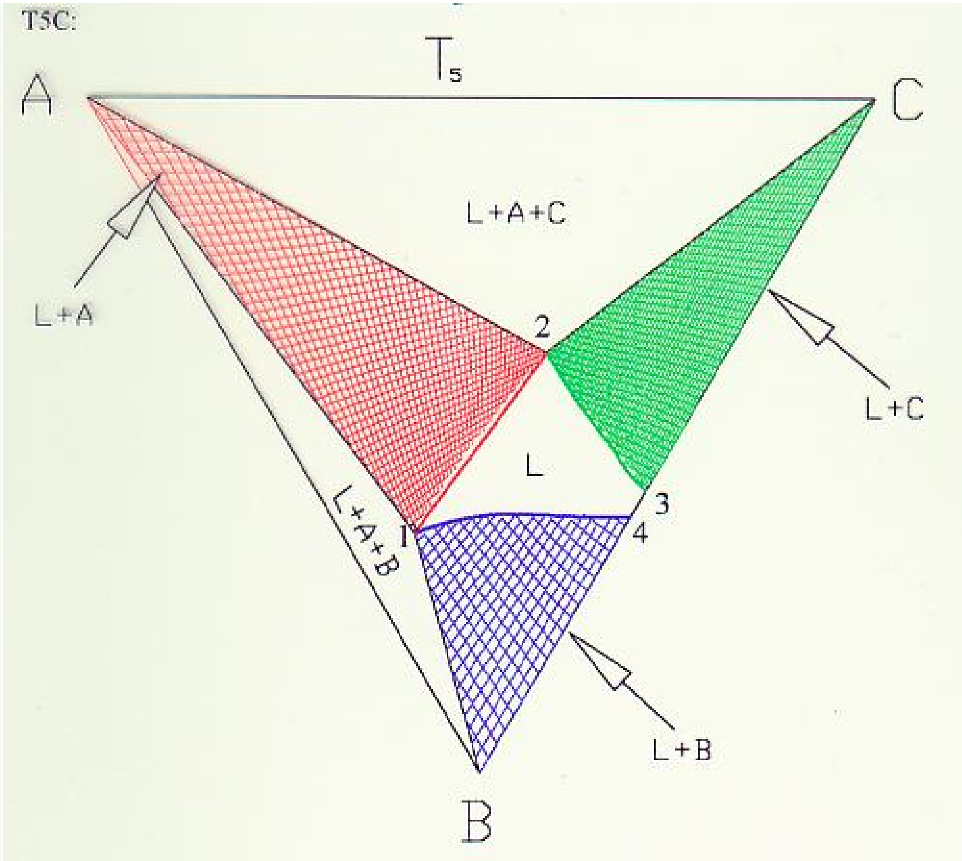
The isothermal section now has six regions:

L, L+A, L+B, L+C, L+A+B, L+A+C

In addition to Point 2, Point 1 has also moved into the Gibbs Triangle, towards the ternary eutectic

Ternary Eutectic System – No Solid Solubility





Ternary Eutectic System
(No Solid Solubility)

Isothermal section at temperature T_6, above the ternary eutectic temperature, but below all other melting points and eutectic points

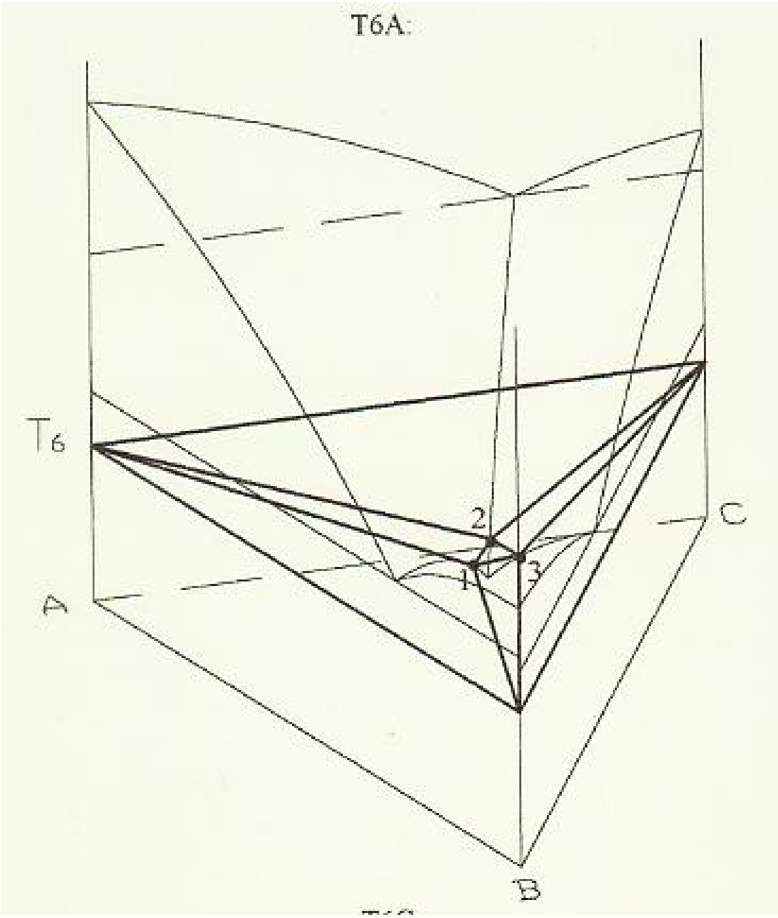
The isothermal section now has seven regions:

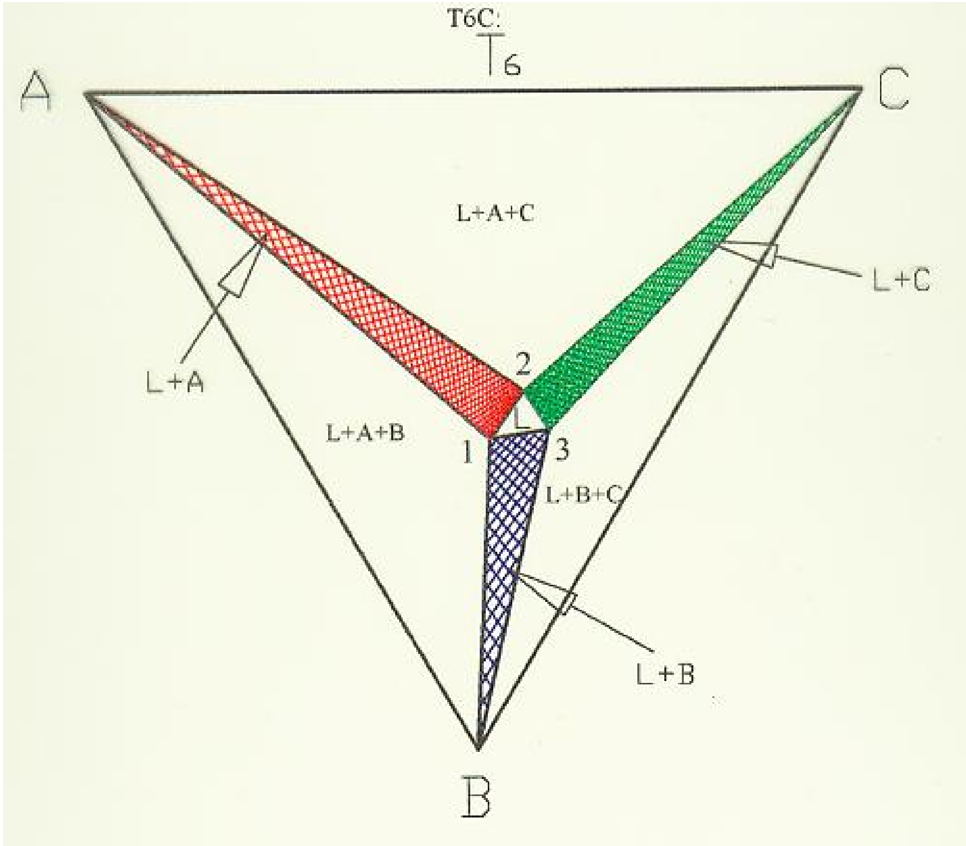
L, L+A, L+B, L+C, L+A+B, L+A+C, L+B+C

In addition to Points 1 & 2, Point 3 has also moved into the Gibbs Triangle, towards the ternary eutectic

Note that the liquid regions is slowly converging towards the ternary eutectic point

Ternary Eutectic System – No Solid Solubility





Ternary Eutectic System
(No Solid Solubility)

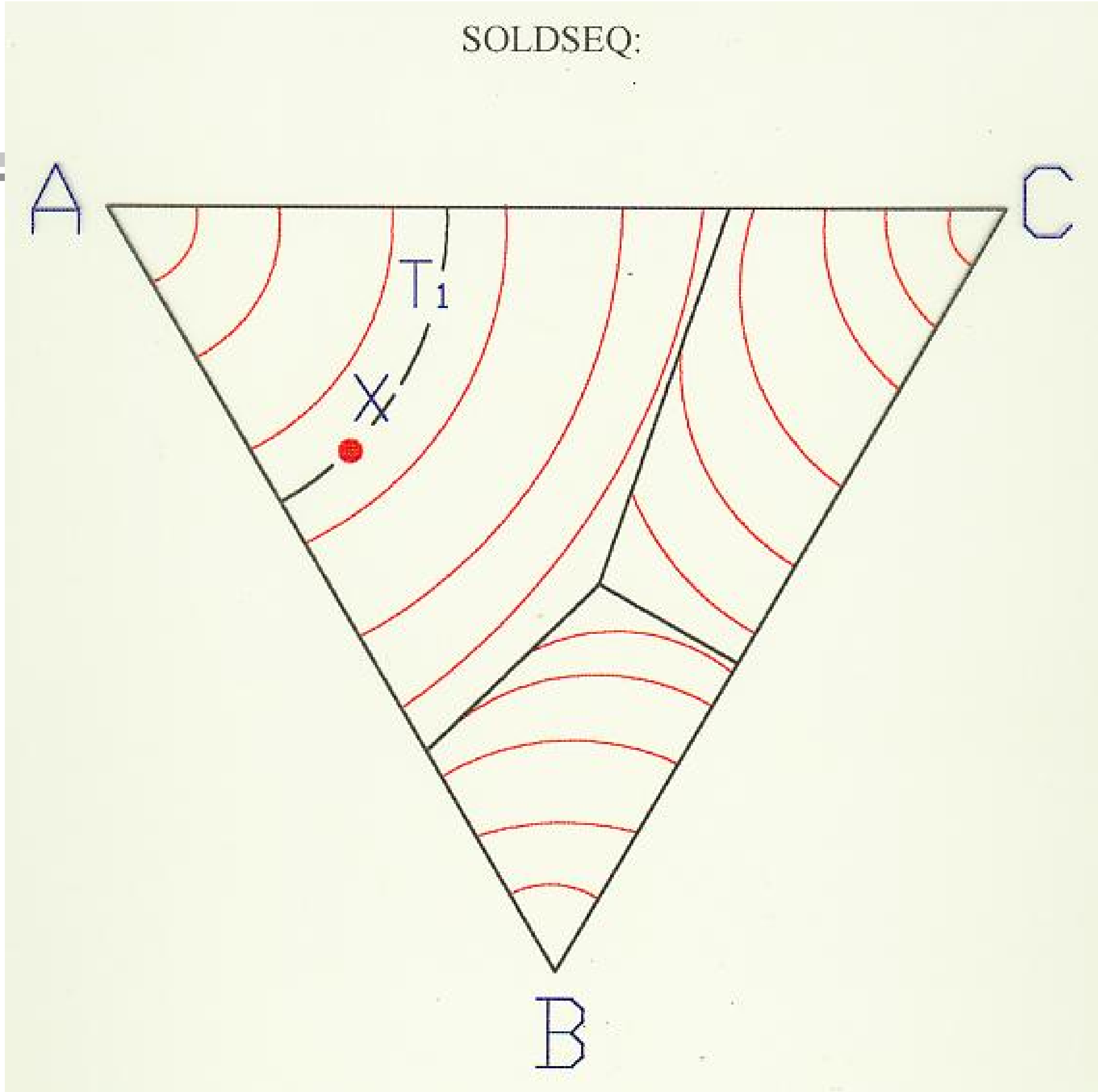
Solidification Sequence

Given an overall composition, determine the sequence of solidification, assuming equilibrium conditions

Let the overall composition be given by the point X

Imagine a line, orthogonal to the plane of the liquidus projection, passing through X

Let this line intersect the liquidus surface at a temperature T_1


SOLDSEQ:
A
C
B
T1
X

Ternary Eutectic System
(No Solid Solubility)

Solidification Sequence (continued)

For all temperatures $T > T_1$, there is one homogeneous liquid phase

Solidification begins when $T = T_1$

The first solid to appear is: A

Ternary Eutectic System
(No Solid Solubility)

Solidification Sequence (continued)

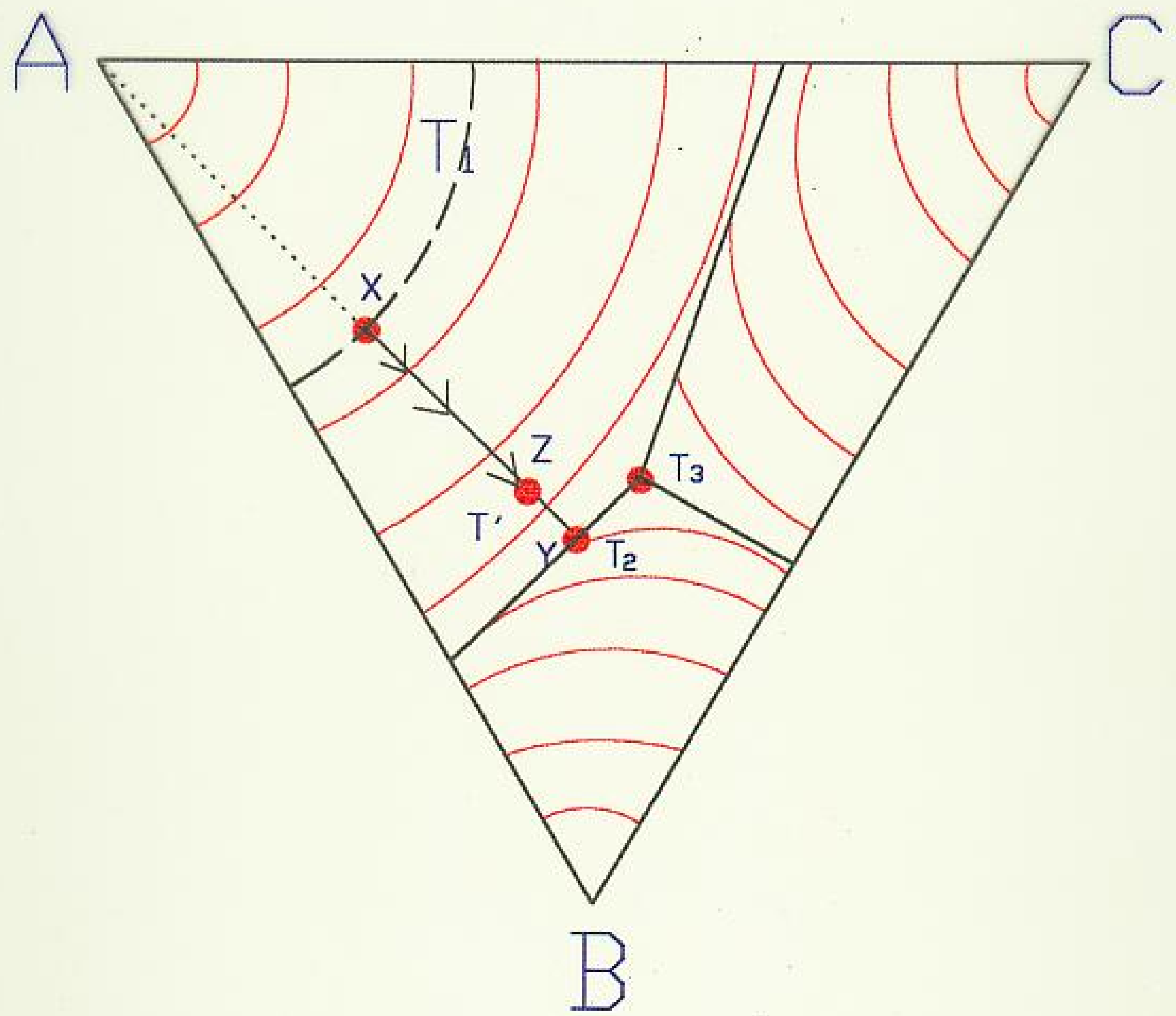
When $T < T_1$, then precipitation of A occurs

As the temperature drops, the composition of the liquid phase "travels" along the line XY, on the liquidus surface, towards Y.

Let the temperature at Y be T_2

At temperatures of $T_2 < T < T_1$, there are two phases in equilibrium - A and L

PATH:



Ternary Eutectic System
(No Solid Solubility)

Solidification Sequence (continued)

In order to determine the amount of each phase present, we need to fix the temperature first.

Let T = T', being at point Z

We use the Inverse Lever Rule

Fraction of L = AX/AZ

Fraction of A = XZ/AZ

Chemical composition of the liquid phase is determined by the composition of point Z within the Gibbs Triangle

Ternary Eutectic System
(No Solid Solubility)

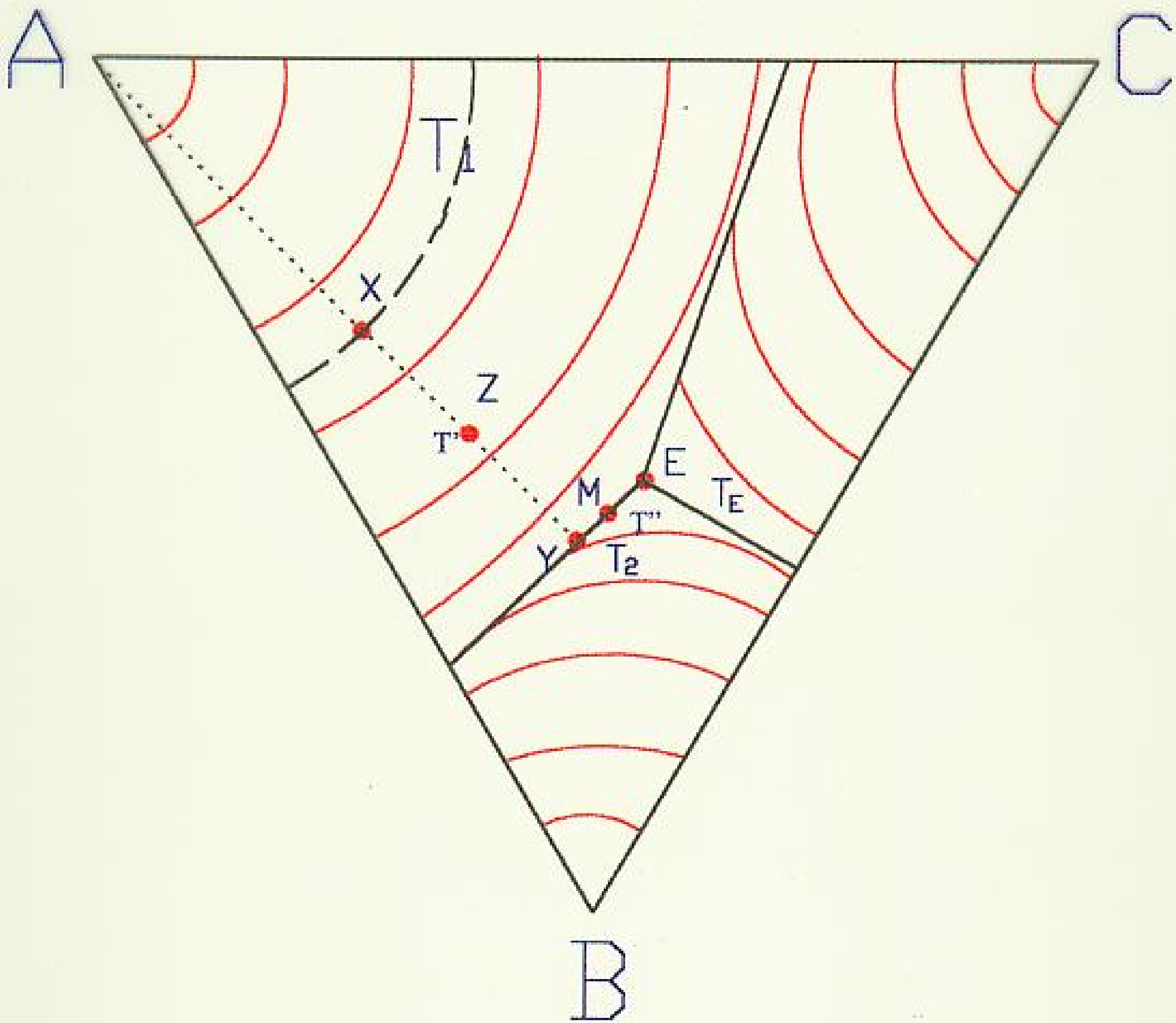
Solidification Sequence (continued)

At point Y, where $T = T_2$, the second solid phase, B, begins to precipitate

Over the temperature range of $T_2 > T > T_E$:

- **The solid phases A and B exist in equilibrium with L**
- **Both solid phases, A and B, coprecipitate as the temperature is lowered**

PATH2:



Ternary Eutectic System
(No Solid Solubility)

<u>Solidification Sequence</u> (continued)

Analysis when T = T", i.e., at point M

Composition of L is given by the composition of M within the Gibbs Triangle

How do we determine the amounts of A, B and L?

Let temperature T" correspond to the point M

Ternary Eutectic System
(No Solid Solubility)

Solidification Sequence (continued)

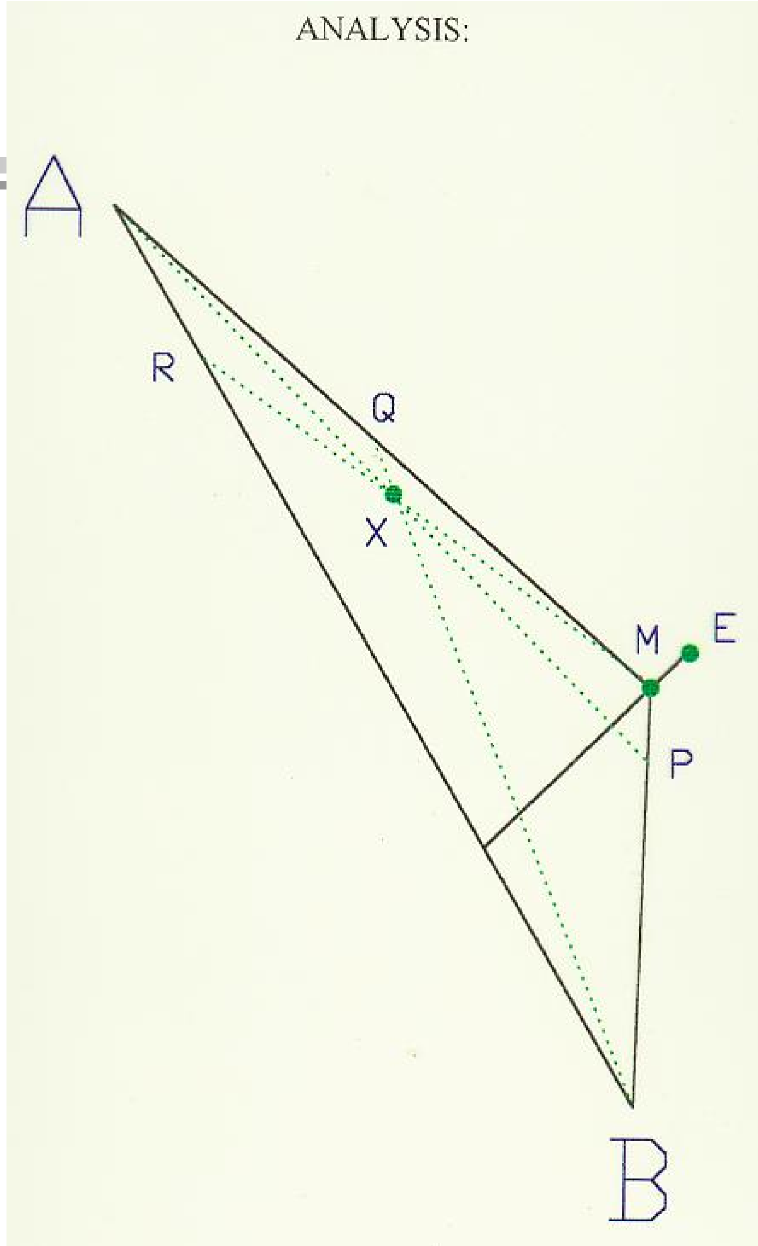
Construct the triangle A-B-M

This triangle is a ternary system in which the overall composition X can be represented in terms of the three constituents

Fraction of A = *PX/PA*

Fraction of B = *QX/QB*

Fraction of L = *RX/RM*

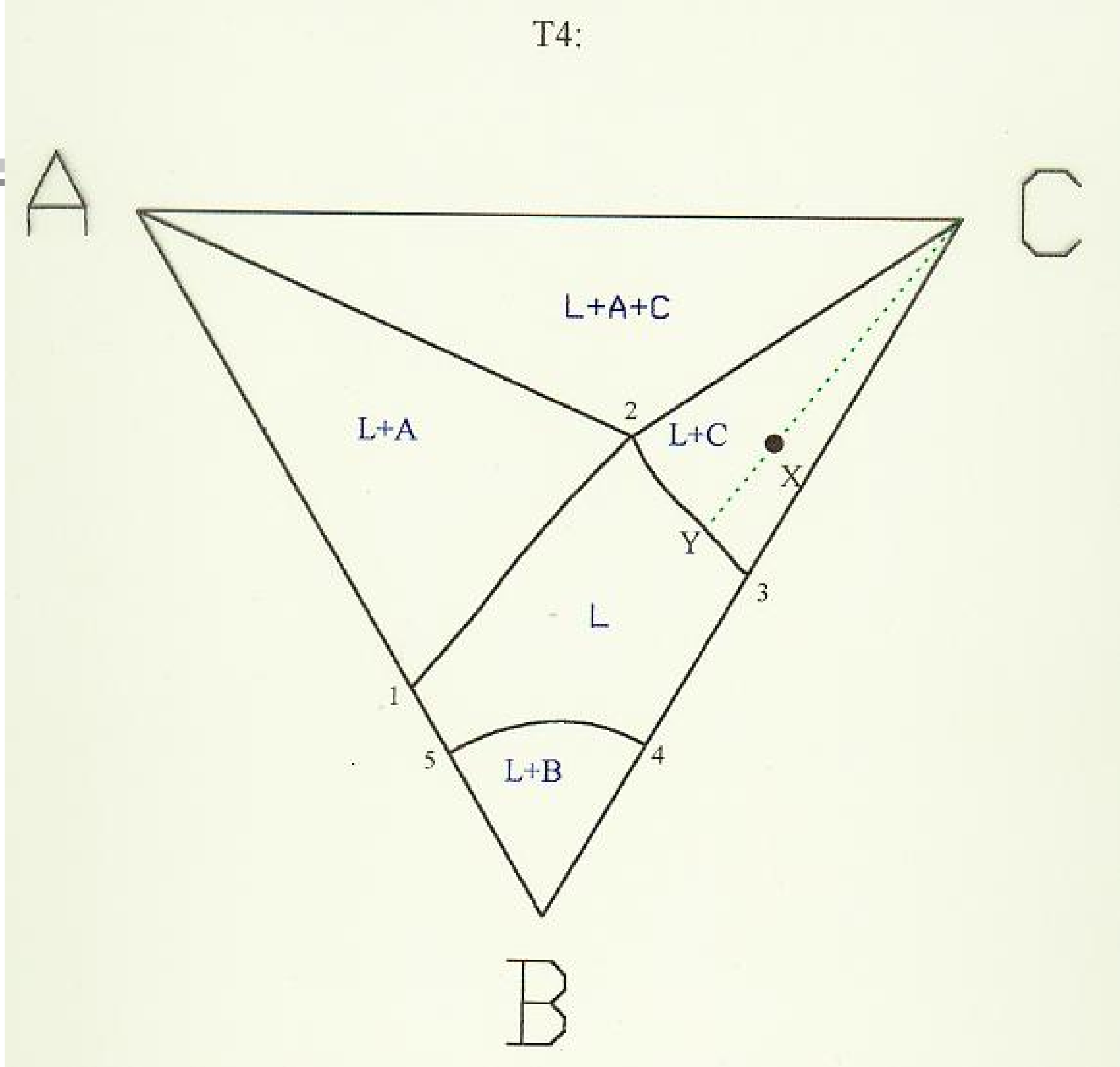

ANALYSIS:
A
R
Q
X
M
E
P
B

Ternary Eutectic System
(No Solid Solubility)

Phase analysis at a given temperature

Isothermal Section at $T = T_4$ will be used as reference

For all overall compositions that fall within the region marked L, the chemical composition of the liquid phase is the same as the overall composition


T4:
A
C
B
L+A+C
L+A
L+C
L
L+B
X
Y
1
2
3
4
5

Ternary Eutectic System
(No Solid Solubility)

Phase analysis at a given temperature

If the overall composition falls within a two phase region, e.g., L + C, then:

1. Locate the position of the overall composition, X, within the Gibbs Triangle

2. Draw tie lines, in this case connecting point C to line 2-3, and passing through X, and intersecting line 2-3 at Y

3. Use the Inverse Lever Rule to determine the amounts of L and C

Fraction of L = *CX/CY*

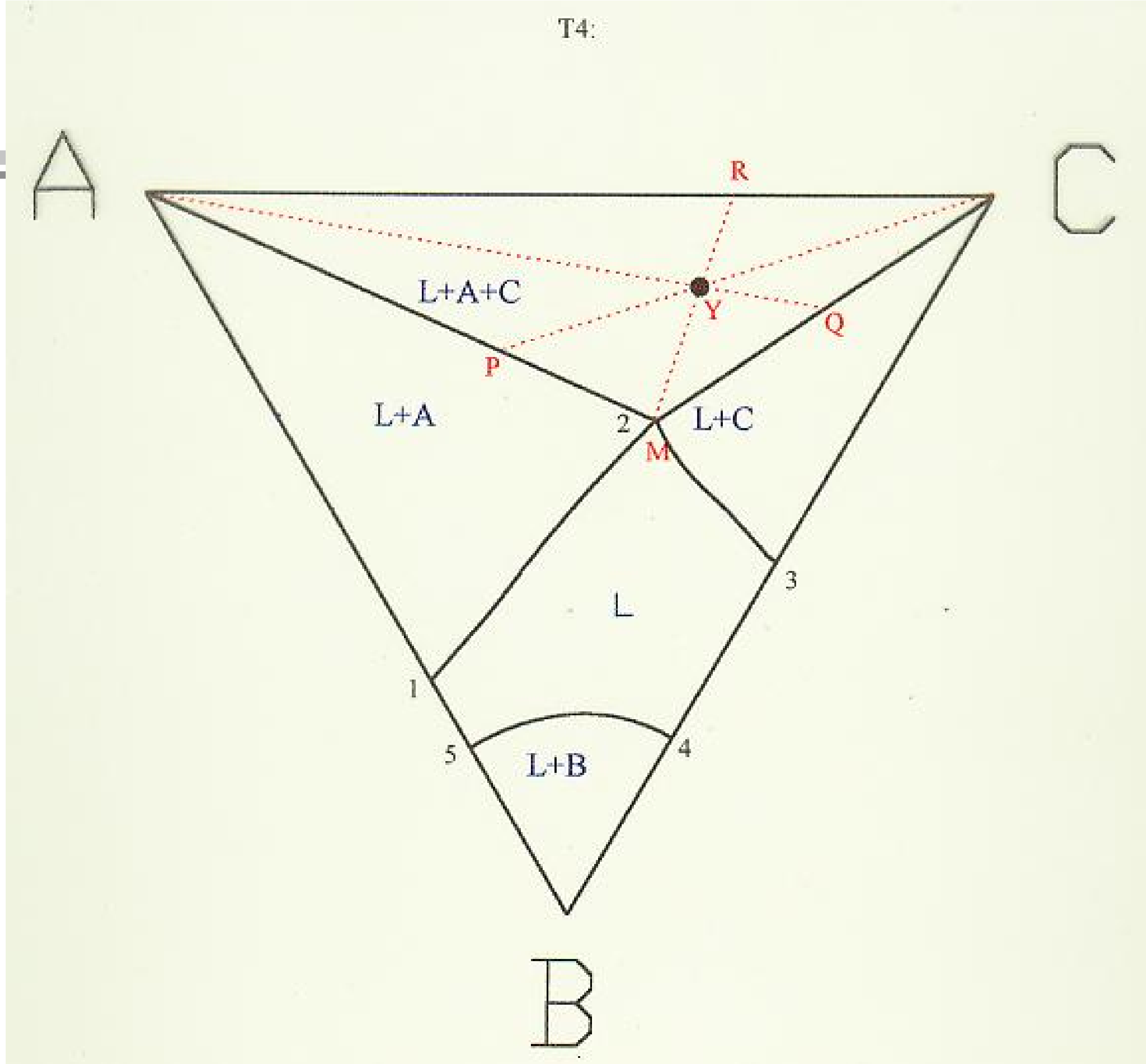
Fraction of C = *YX/CY*

Ternary Eutectic System
(No Solid Solubility)

<u>Phase analysis at a given temperature</u>

The chemical composition of C in this case is 100% C

The chemical composition of L is given by determining the composition the point Y represents within the Gibbs Triangle


T4:
A
C
B
R
L+A+C
Y
Q
P
L+A
2
L+C
M
3
L
1
5
4
L+B

Ternary Eutectic System
(No Solid Solubility)

Phase analysis at a given temperature

If the overall composition falls within a three phase region, e.g., L + A + C

1. Locate the position of the overall composition, Y, within the Gibbs Triangle

2. Construct the following straight lines:

A-Y-Q, M-Y-R and C-Y-P

3. Use the Inverse Lever Rule to determine the amounts of L, A and C

Fraction of A = QY/QA

Fraction of C = PY/PC

Fraction of L = YR/MR

Ternary Eutectic System
(No Solid Solubility)

Phase analysis at a given temperature

The chemical composition of A in this case is 100% A

The chemical composition of C in this case is 100% C

The chemical composition of L is given by determining the composition the point Y represents within the Gibbs Triangle

Some Useful Rules regarding Phase Diagrams

***The Boundary Rule*: Any p-phase region can be bounded only by regions containing p +/- 1 phases, where p denotes the number of phases.**

***The Boundary Curvature Rule*: Boundaries of one-phase regions must meet with curvatures such that the boundaries extrapolate into the adjacent two-phase regions.**

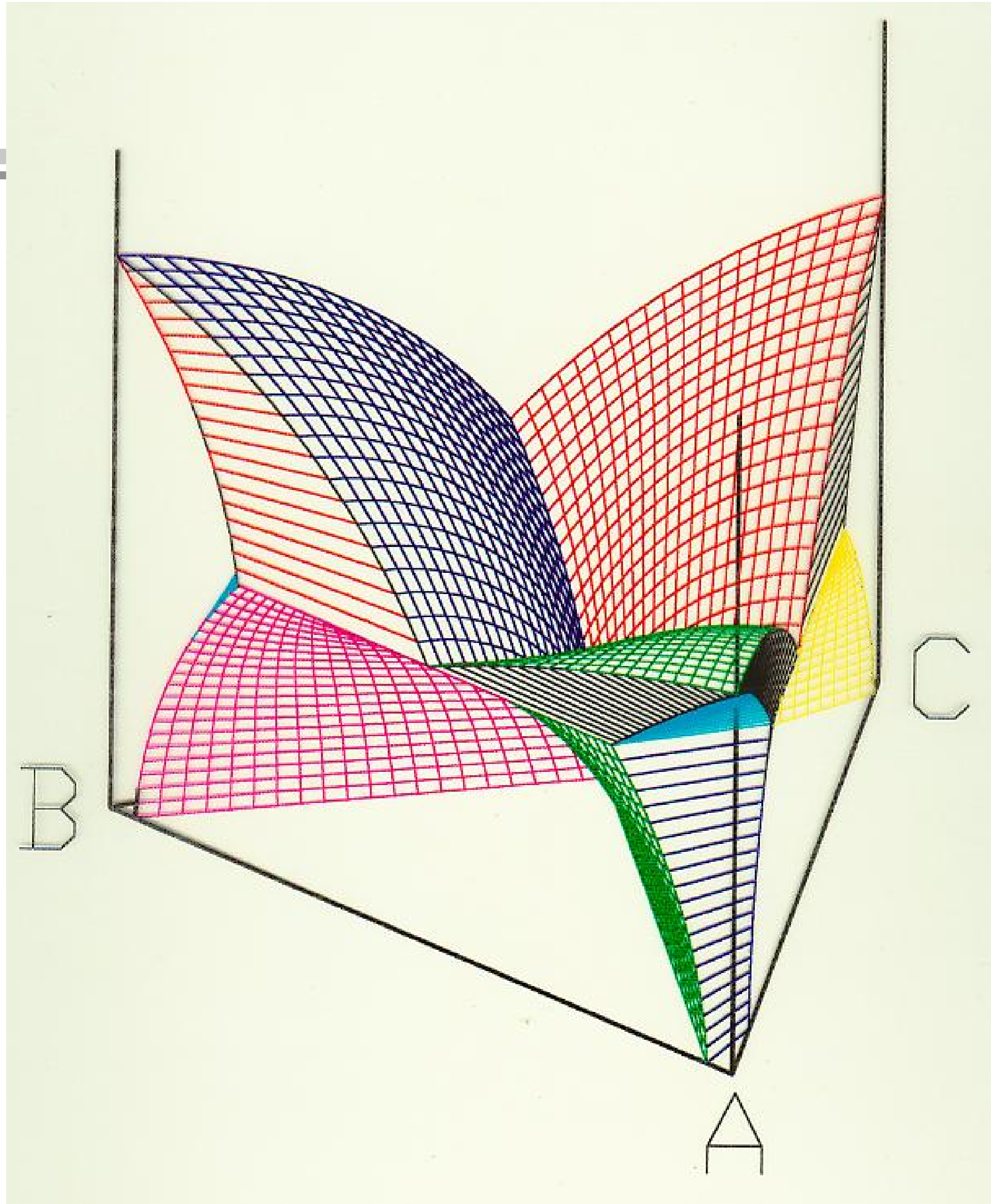
***The Solubility Rule*: All components are soluble to some degree in all phases**

Ternary Eutectic System

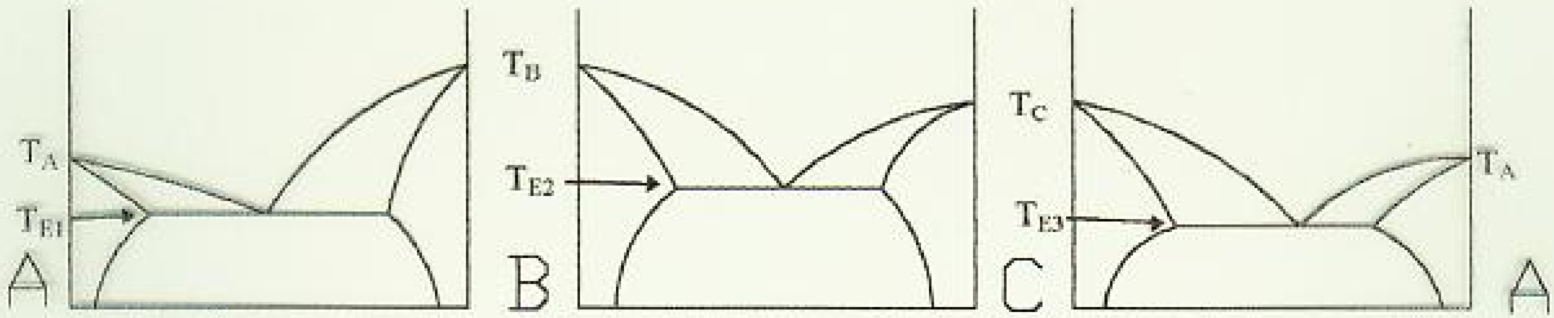
(With Solid Solubility)

G. Selvaduray - SJSU - Oct 2004

Ternary Eutectic System – With Solid Solubility



P1:



T_A: Melting Point Of Material A

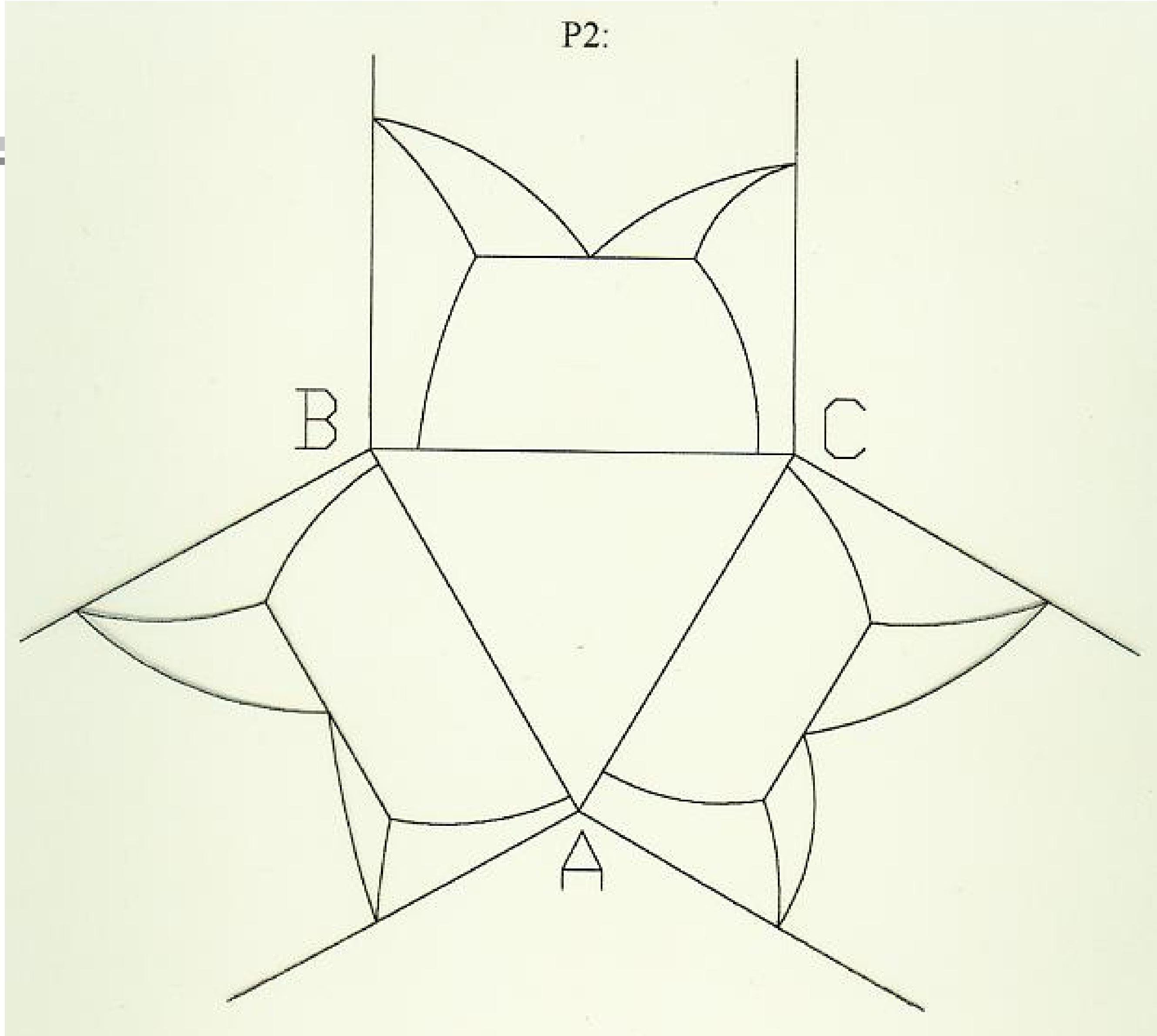
T_B: Melting Point Of Material B

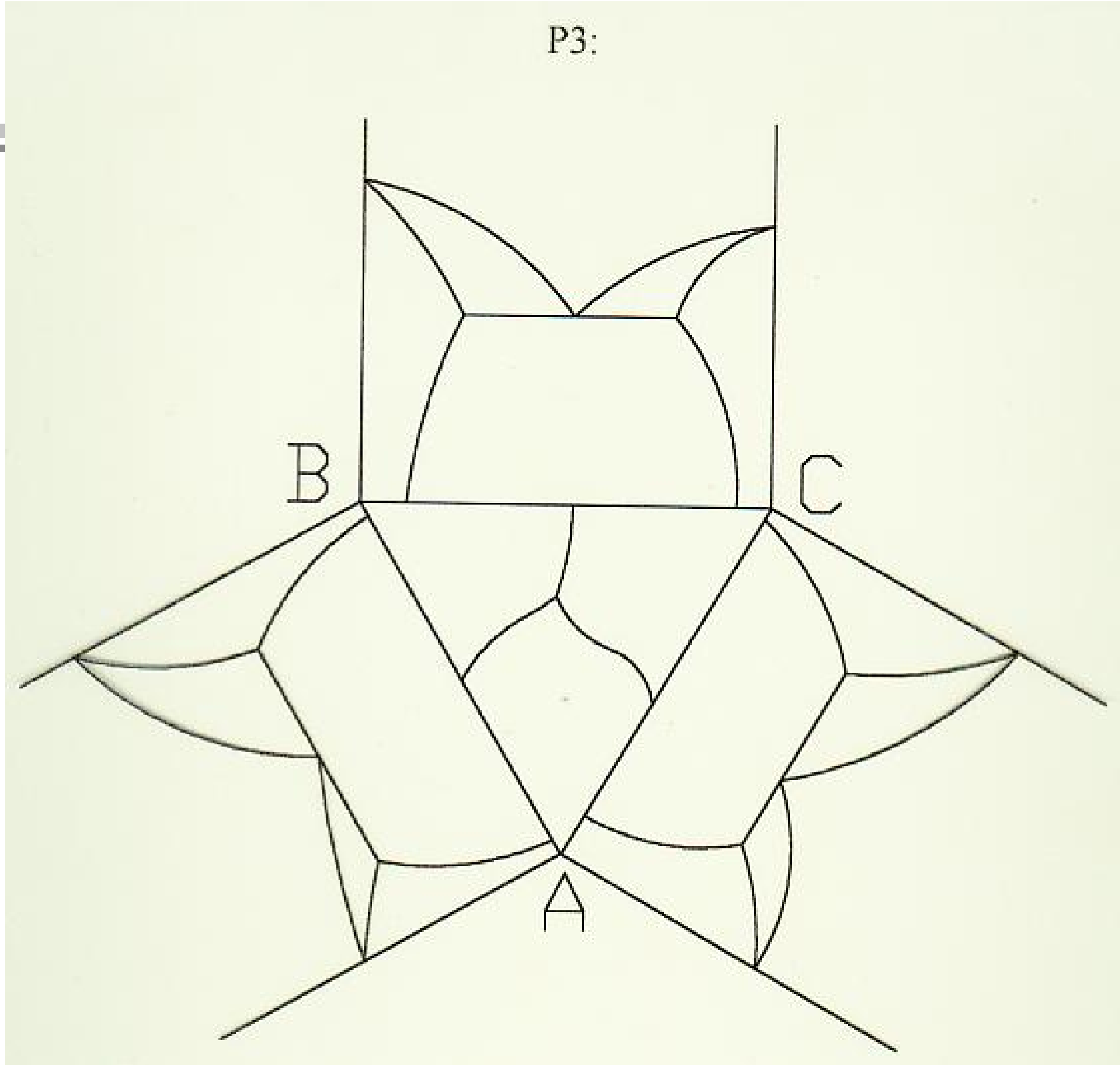
T_C: Melting Point Of Material C

T_{E1}: Eutectic Temperature Of A-B

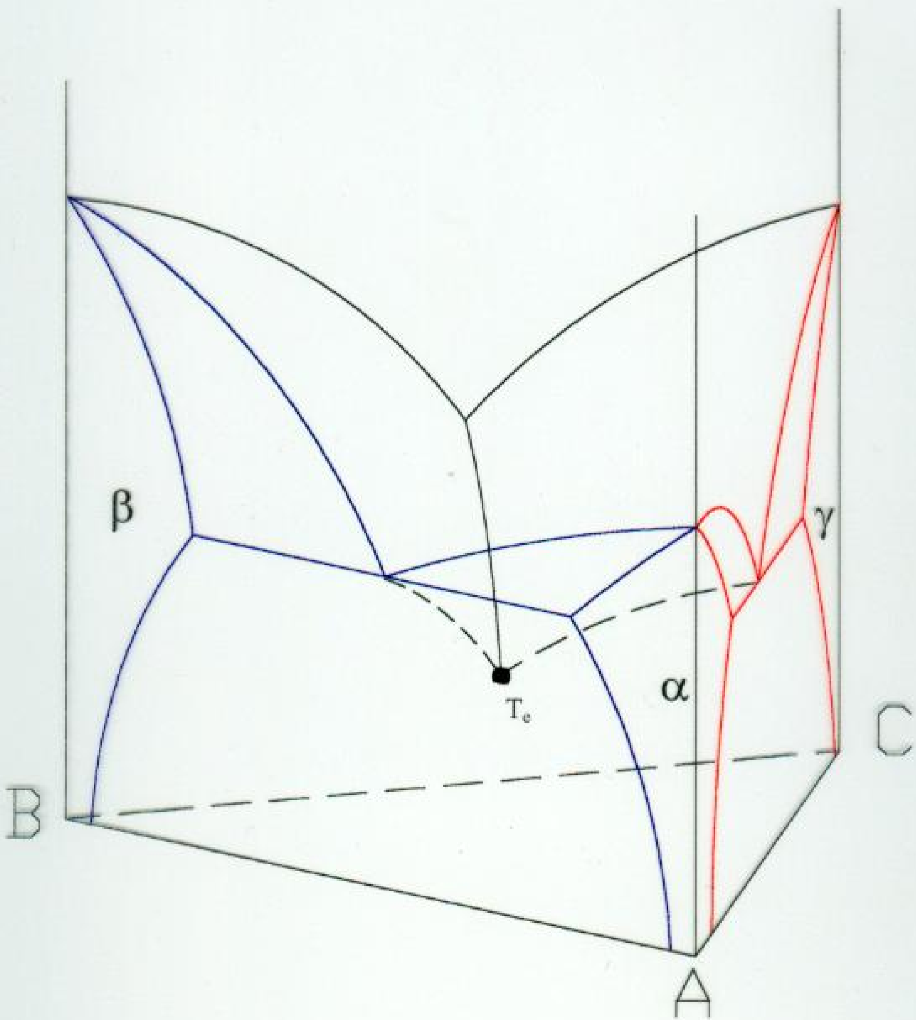
T_{E2}: Eutectic Temperature Of B-C

T_{E3}: Eutectic Temperature Of C-A

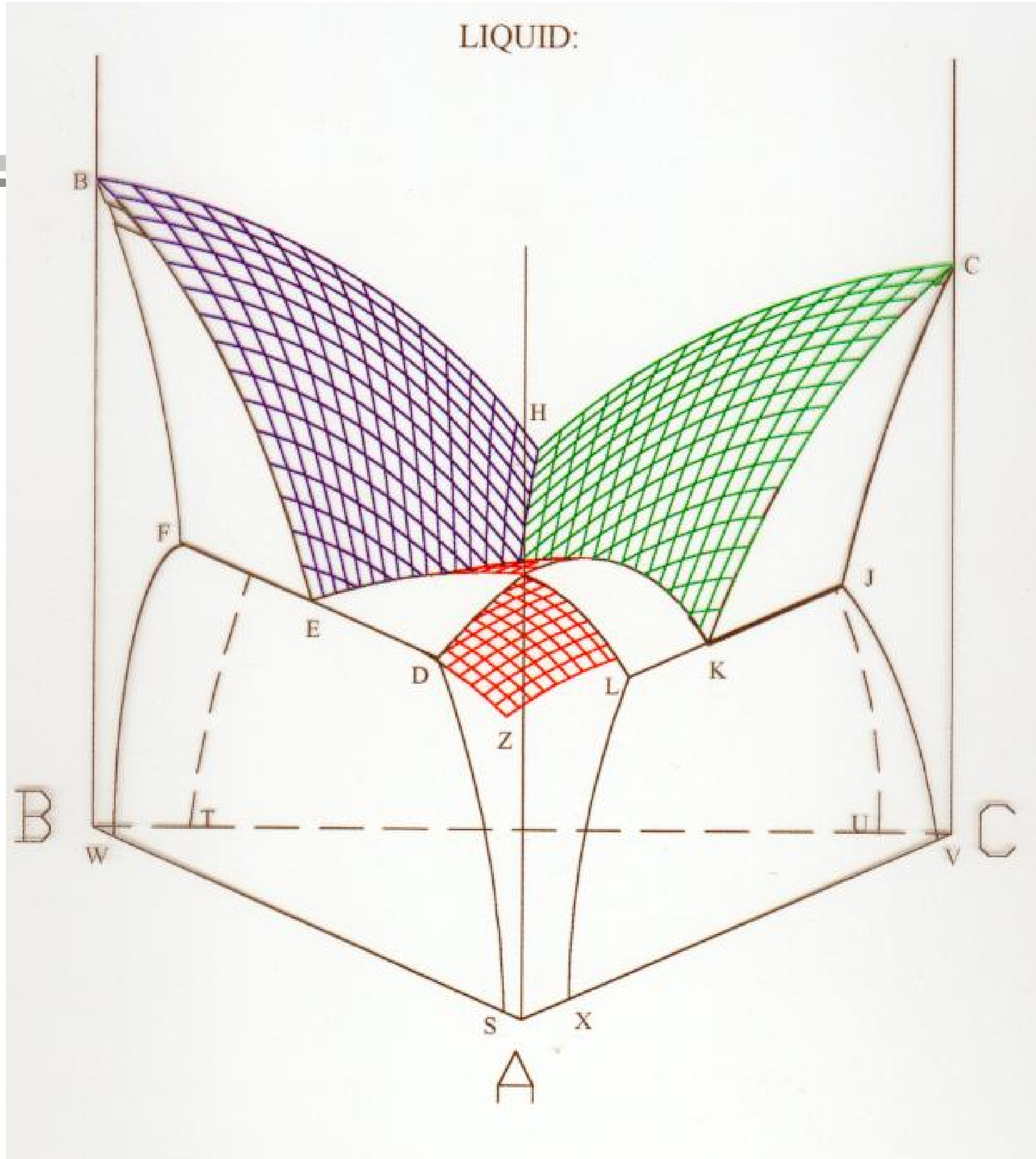

P2:
B
C
A


P3:
B
C
A

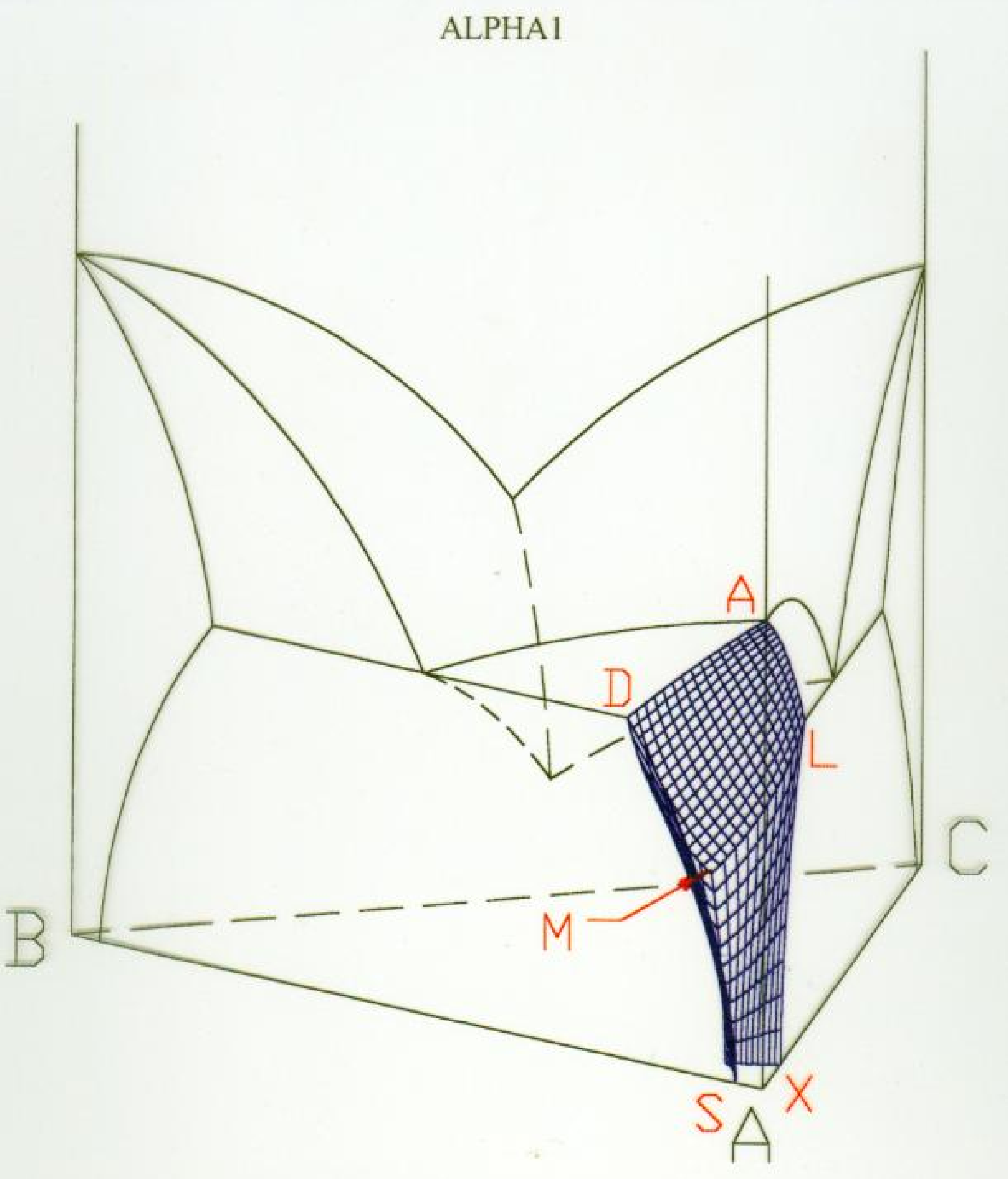
P4:



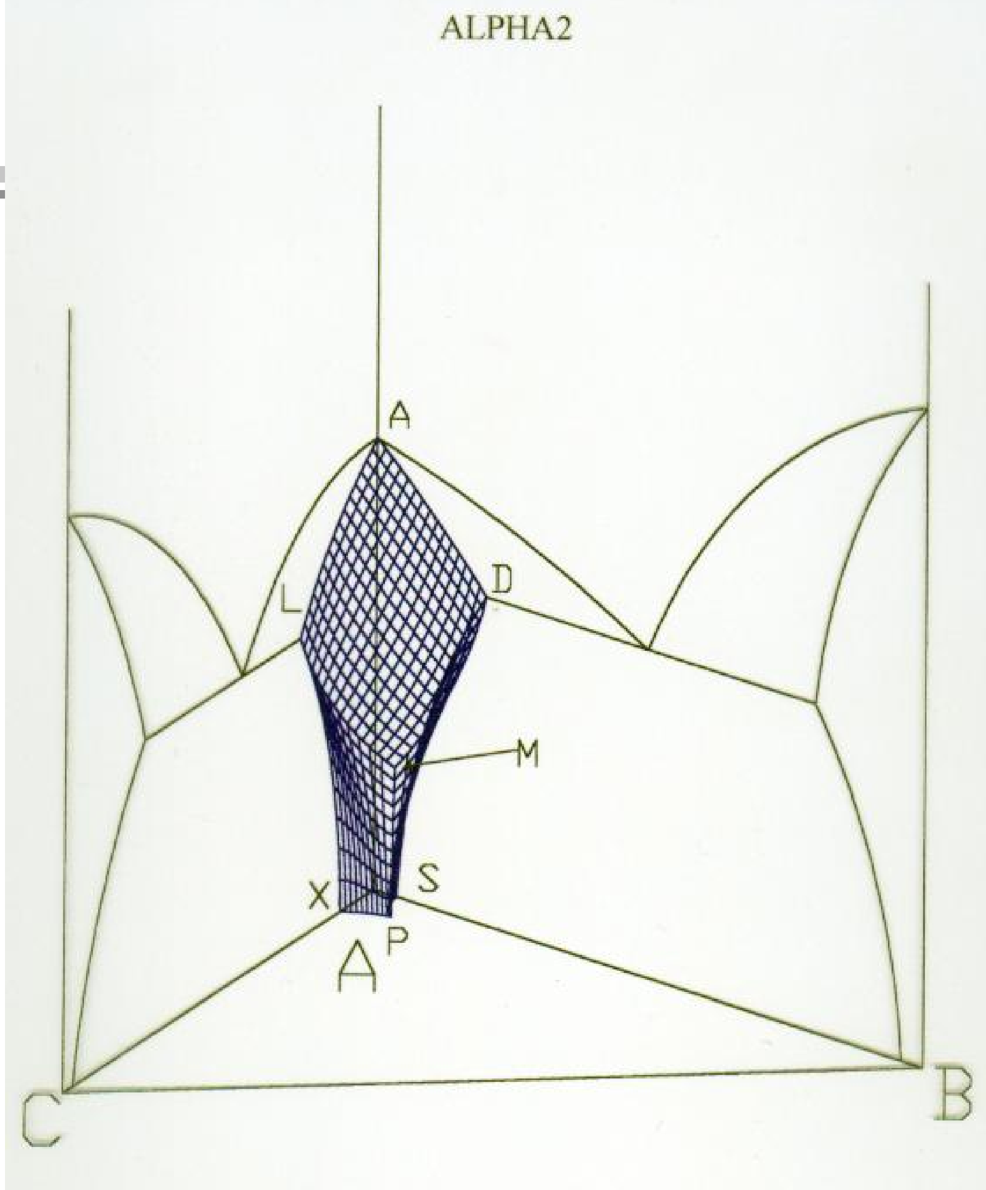
Main outline of Ternary Phase Diagram with Ternary Eutectic (T_e) and Solid Single Phase Regions Shown



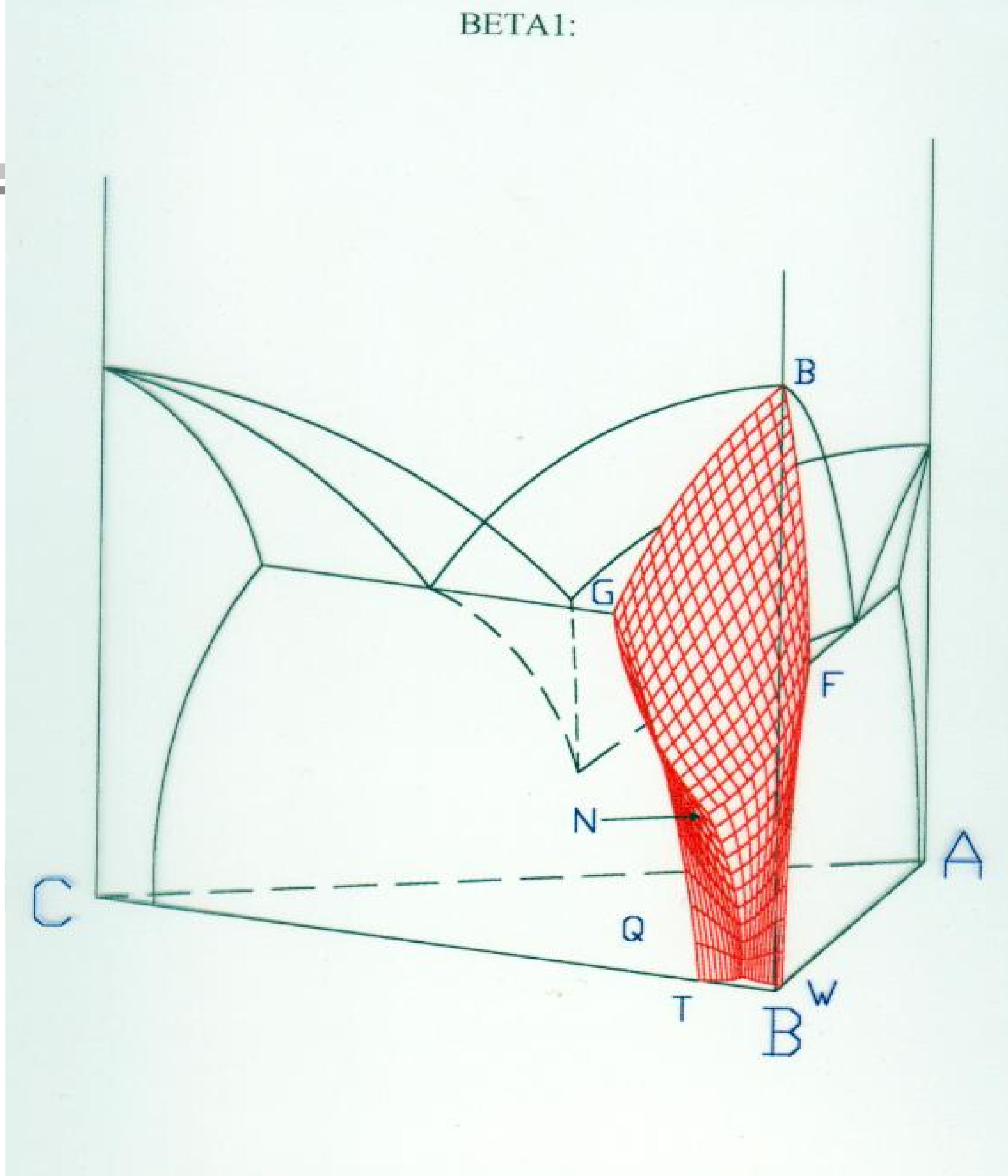
All Liquidus surfaces (α+L-Red, β+L-Purple, γ+L-Green)



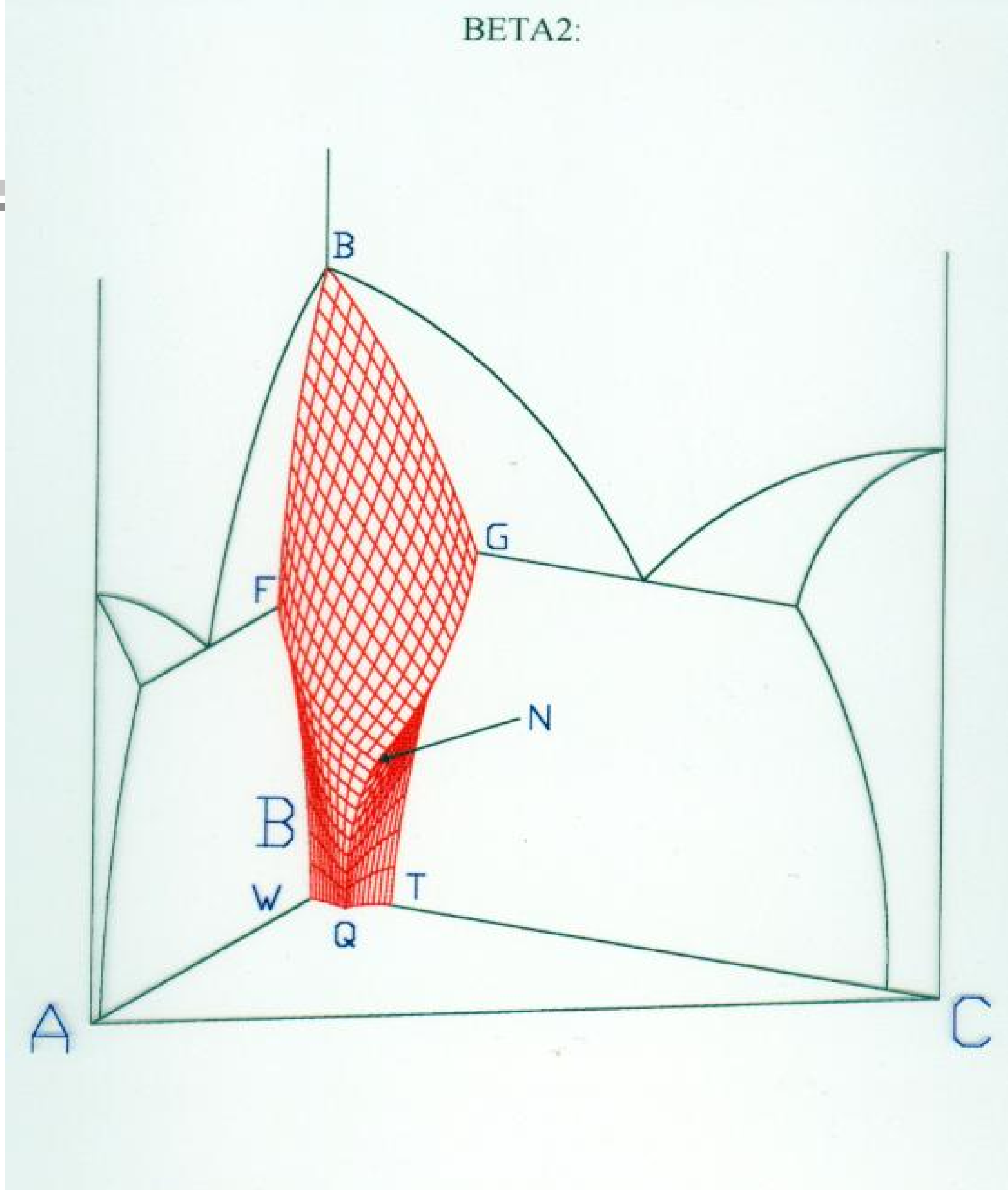
Single Phase Region (α) Viewed From Corner A.



Single Phase Region (α) Viewed From Side C-B

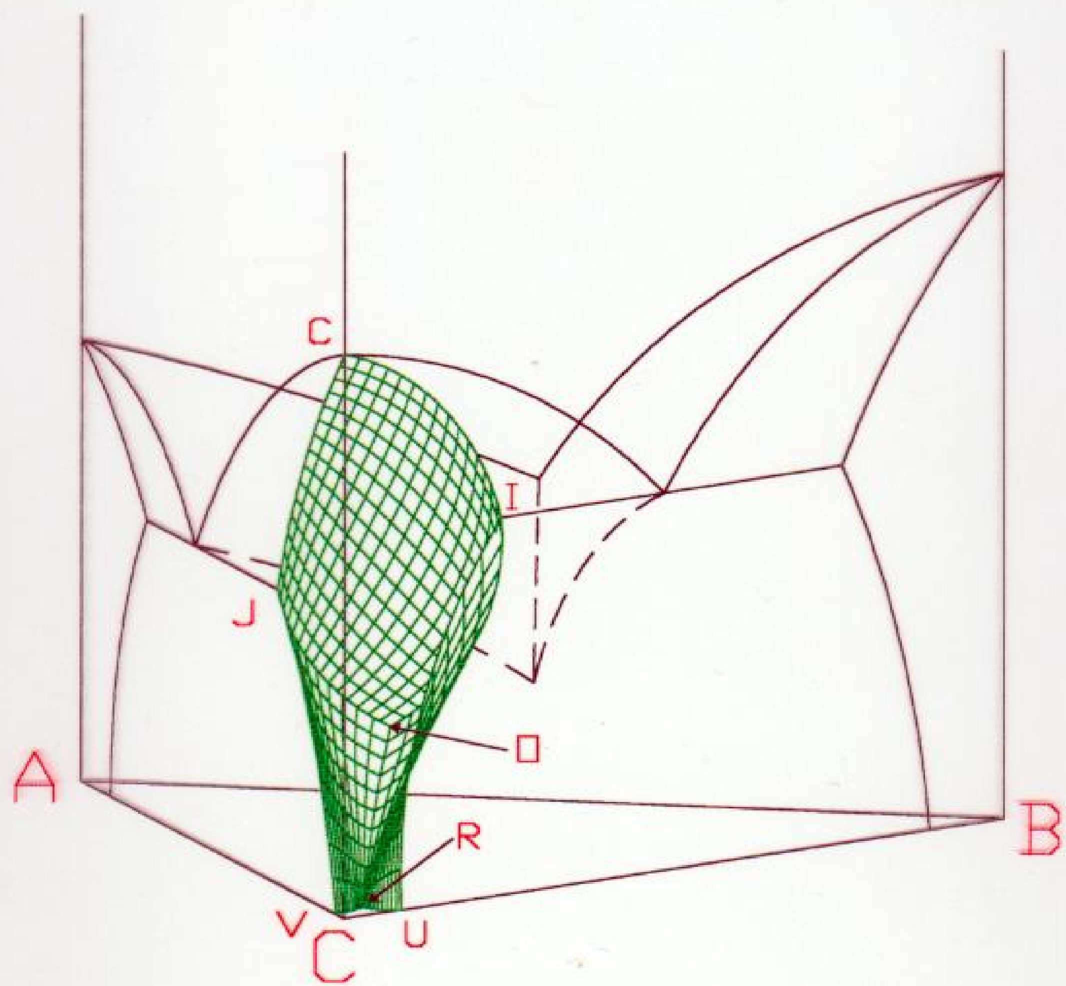


Single Phase Region (β) Viewed From Corner B.



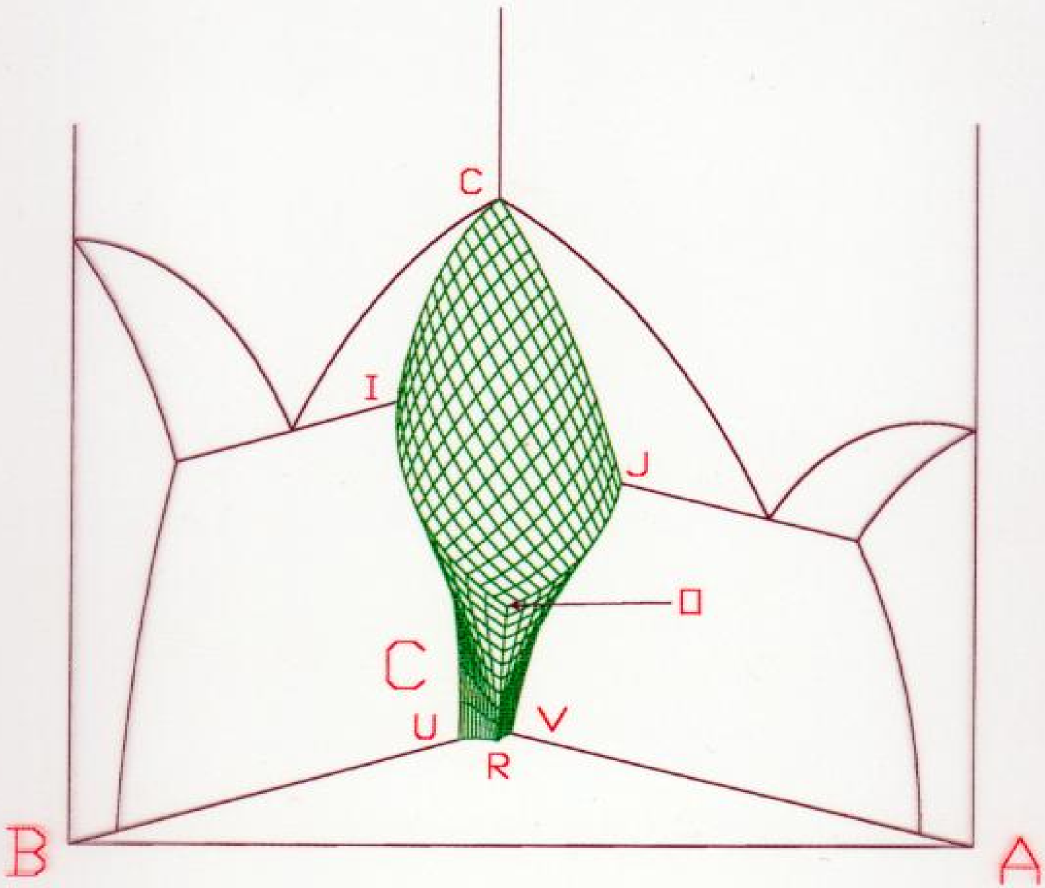
Single Phase Region (β) Viewed From Side A-C.

GAMMA1:

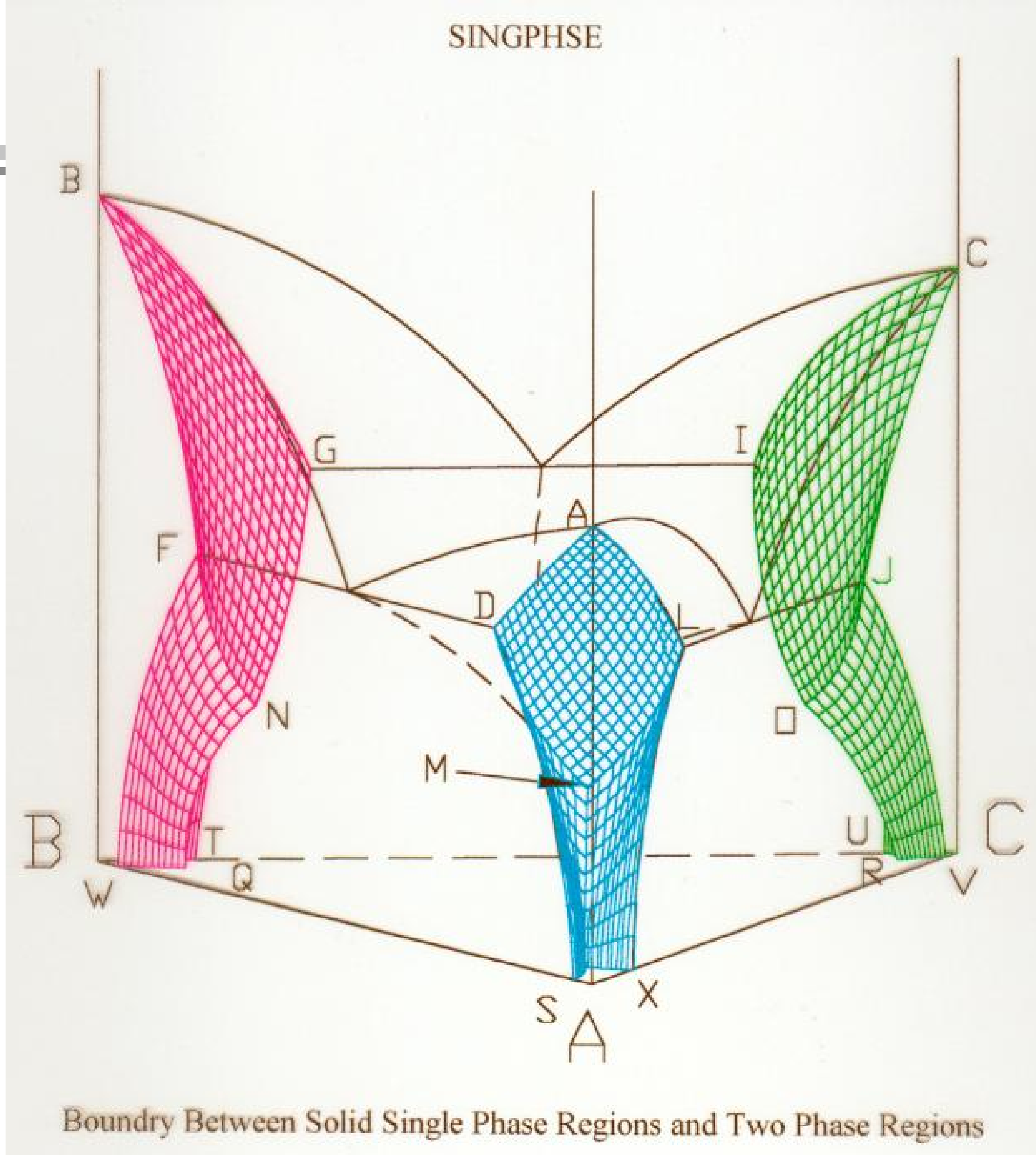


Single Phase Region (γ) Viewed From Corner C.

GAMMA2:

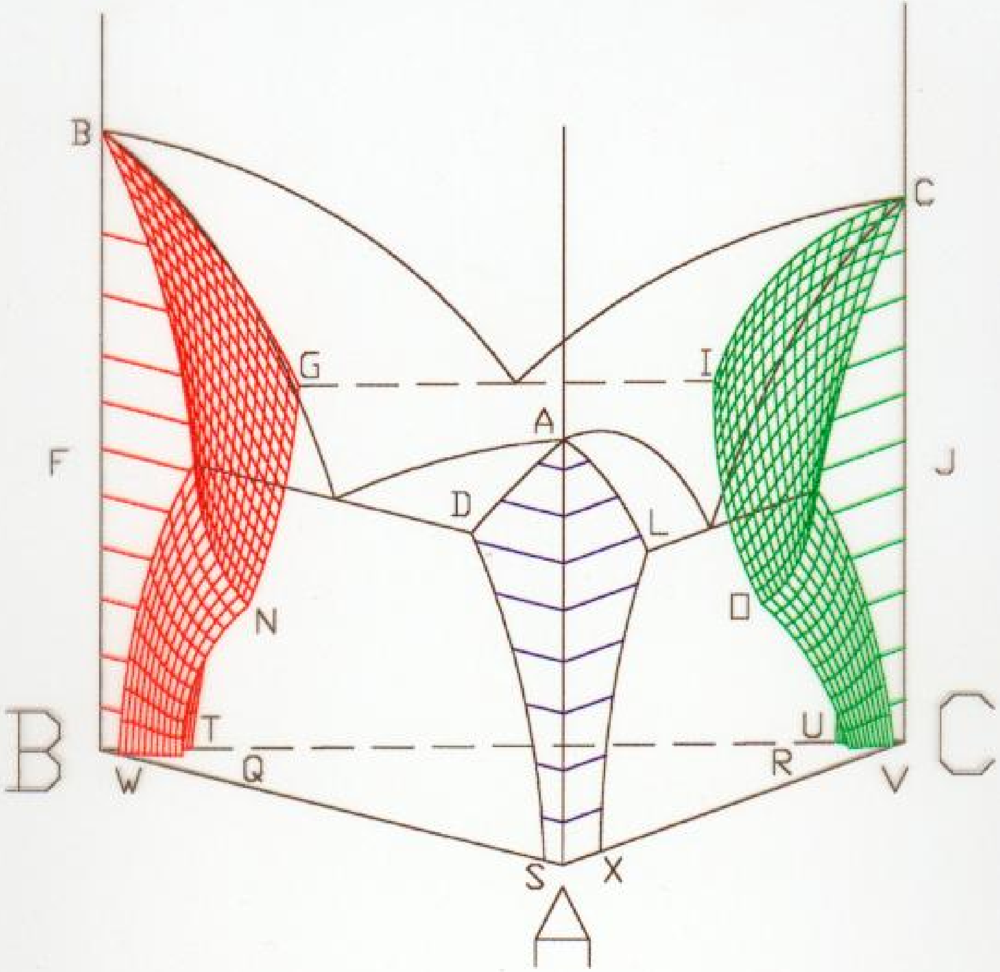


Single Phase Region (γ) Viewed From Side B-A



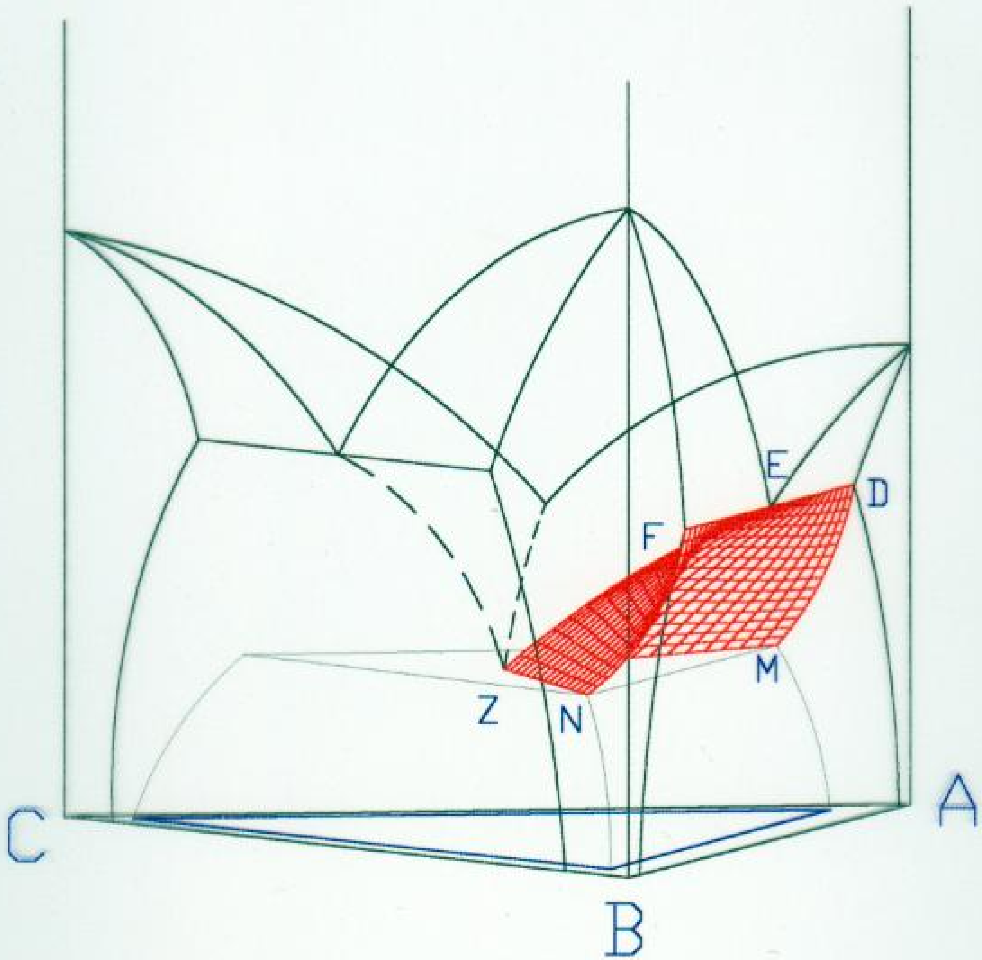
Boundry Between Solid Single Phase Regions and Two Phase Regions

SNGPSE2:



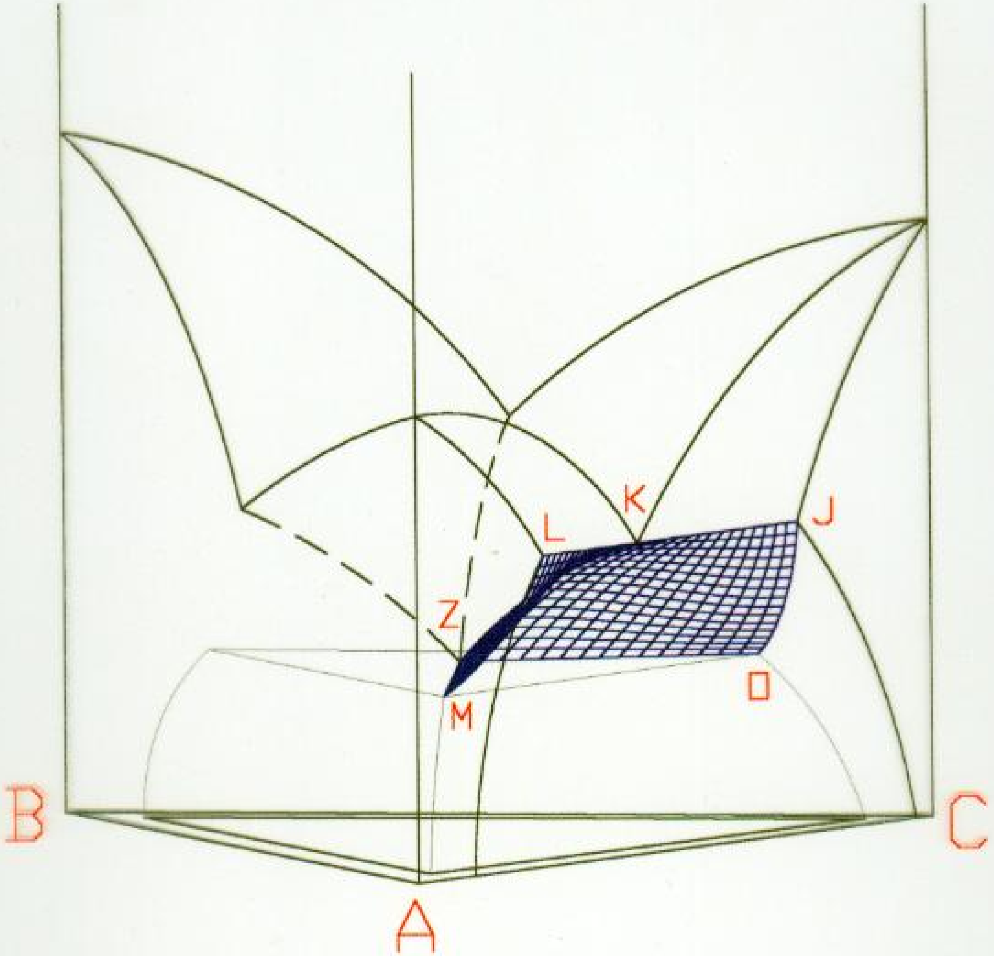
Single Phase Regions: α, β, γ

APBPL:



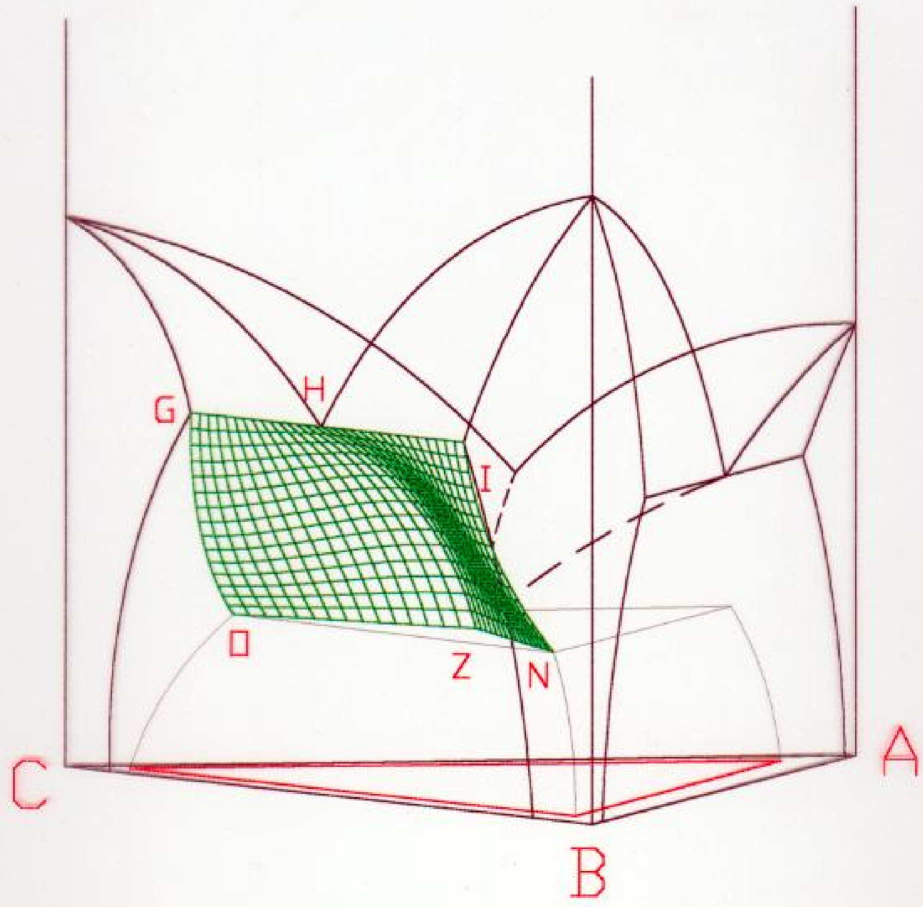
Three Phase Region: 2-Solids & 1-Liquid Phase (α+β+L)

APCPL:

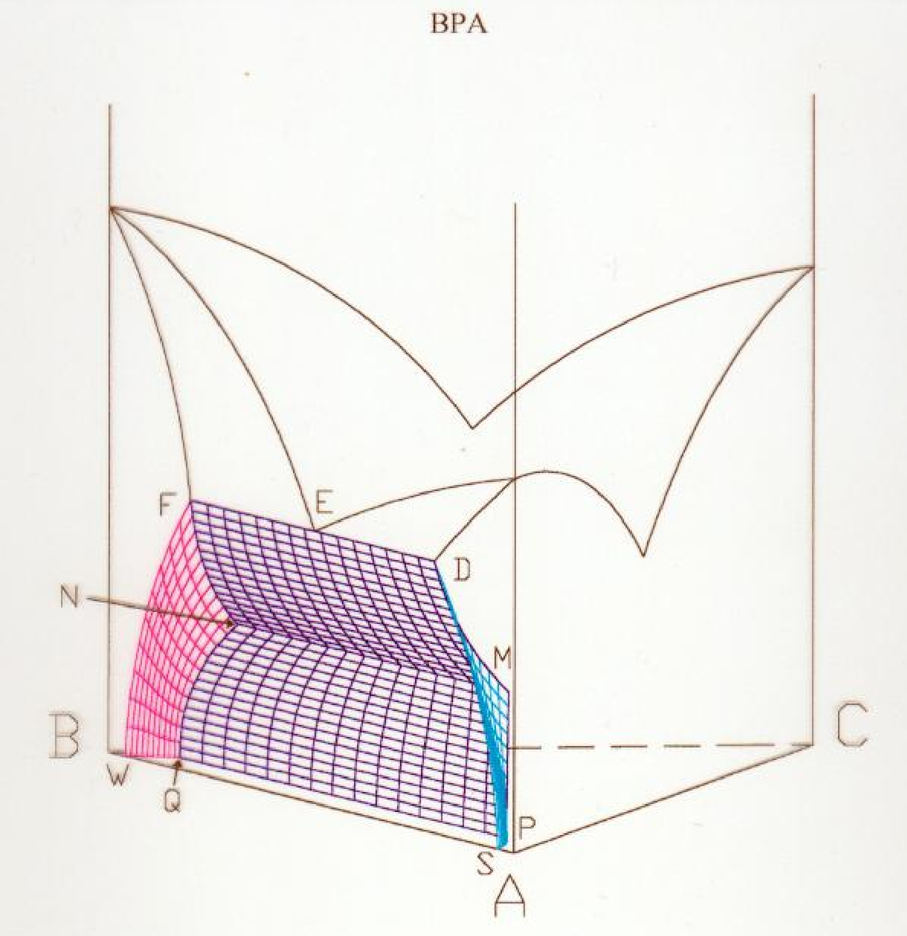


Three Phase Region: 2-Solids & 1-Liquid Phase ($\alpha + \gamma + L$)

BPCPL:

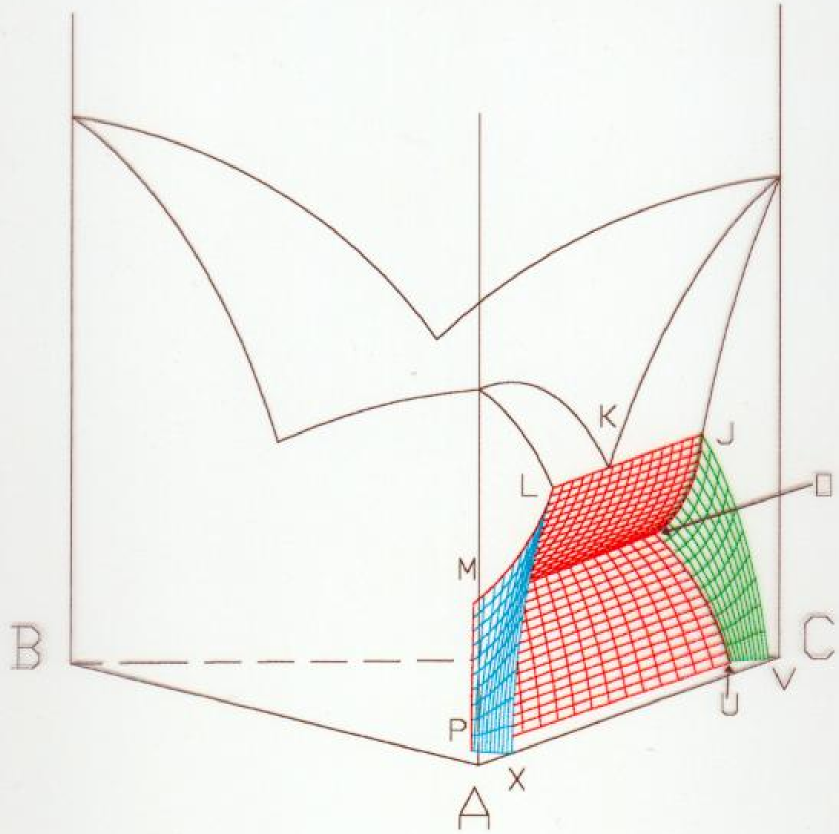


Three Phase Region: 2-Solids & 1-Liquid Phase (β+ γ +L)



Two Phase Region of α and β
DMPS: Boundry of α-β Region and α Region
FNQW: Boundry of α-β Region and β Region
FEDMN: Boundry of α-β Region and 3-Phase (2 Solids-1 Liquid) Region
NMPQ: Boundry of α-β Region and 3 Phase (3 Solids) Region

APC



Two Phase Region of α and γ

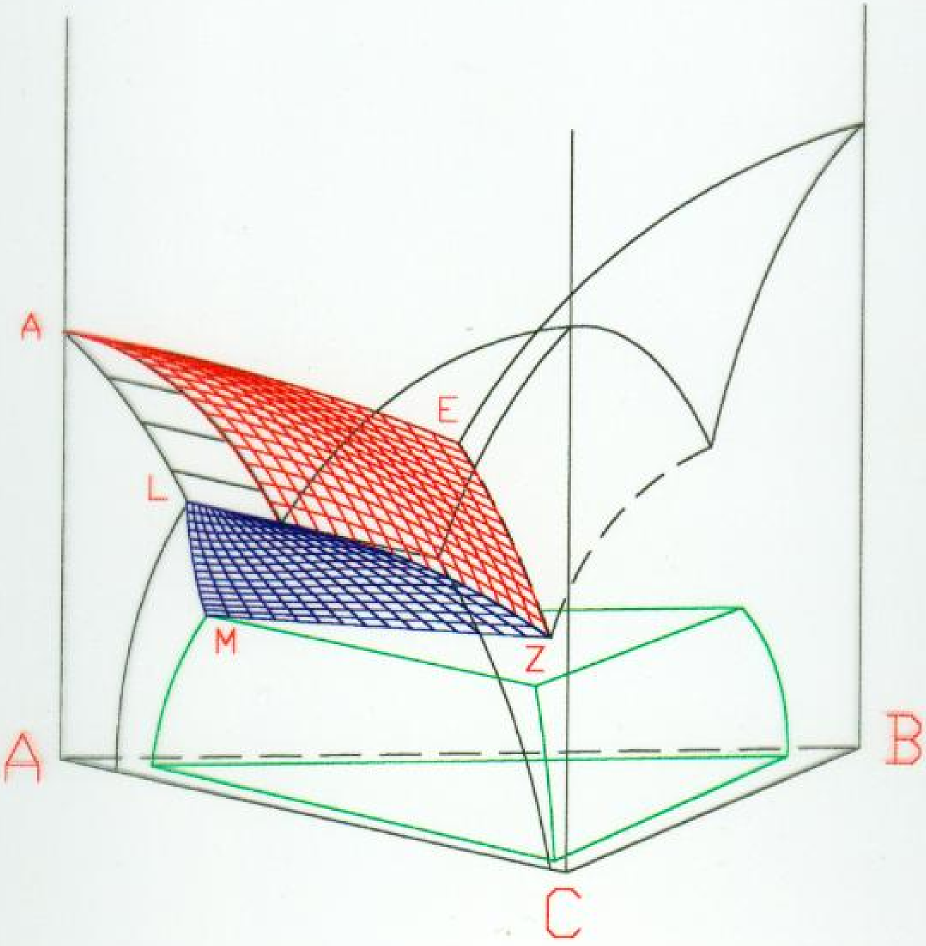
LMPX: Boundry of α-γ Region and α Region

JOUV: Boundry of α-γ Region and γ Region

LKJOM: Boundry of α-γ Region and 3-Phase (2 Solids-1 Liquid) Region

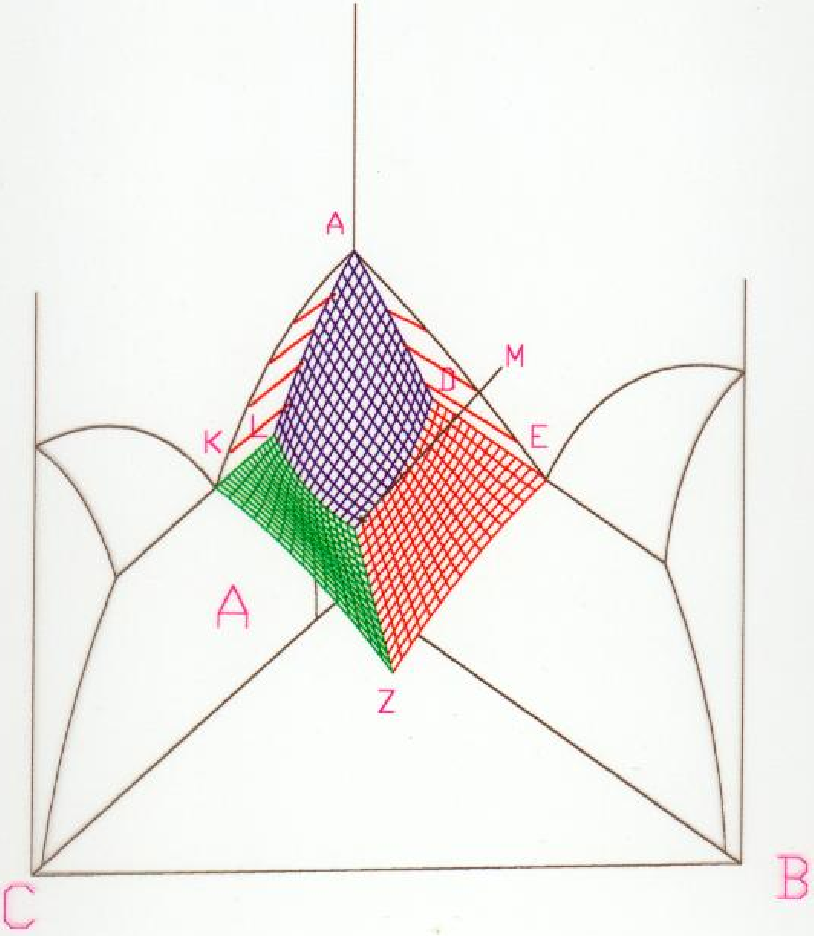
MOPU: Boundry of α-γ Region and 3 Phase (3 Solids) Region

APL1



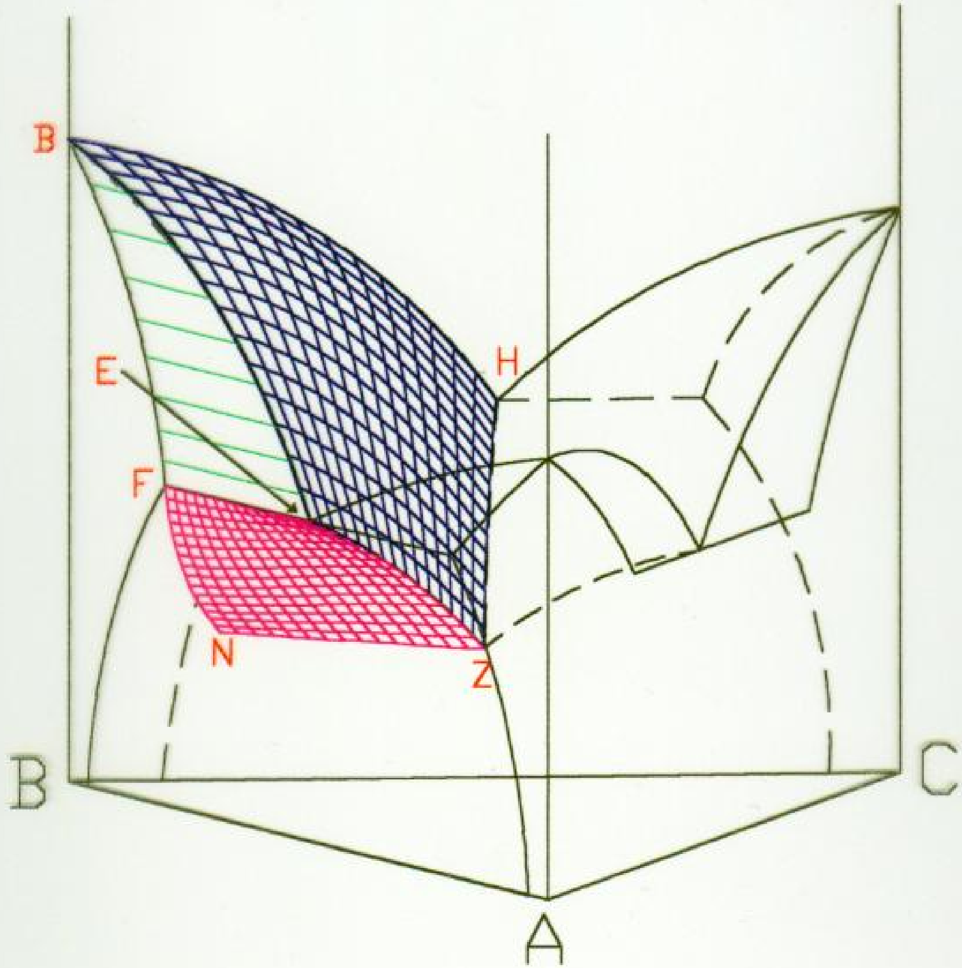
Two Phase Region of $\alpha + L$

APL2:



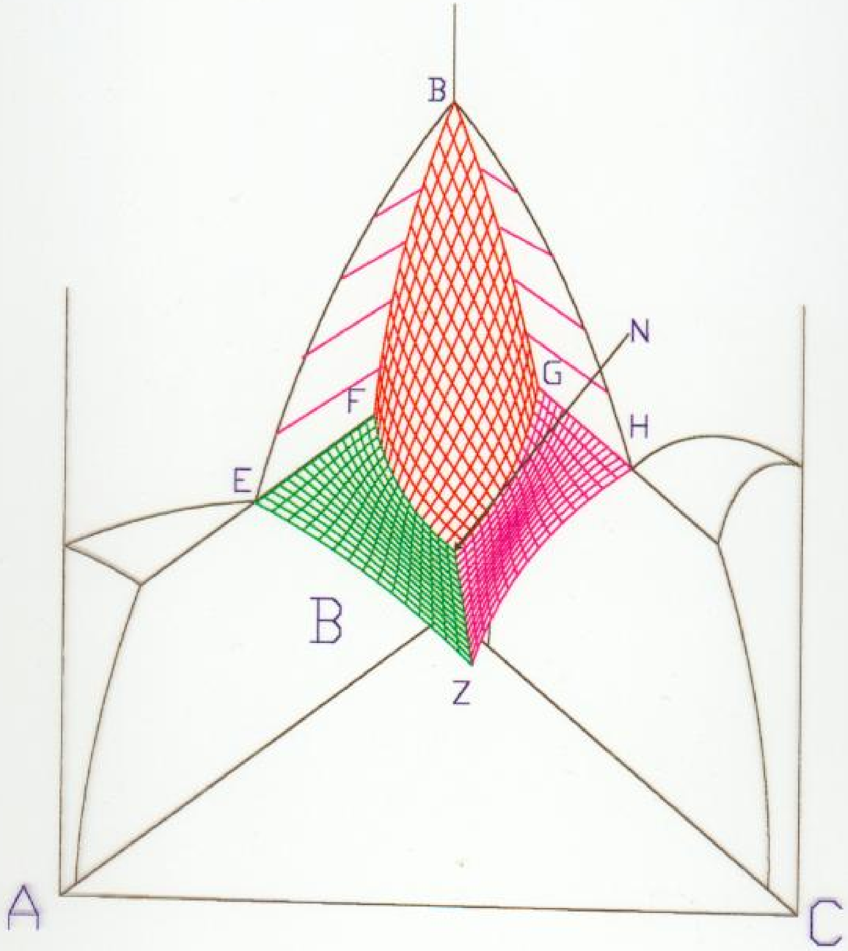
Two Phase Region of α + L Without Liquidous Surface

BPL1:



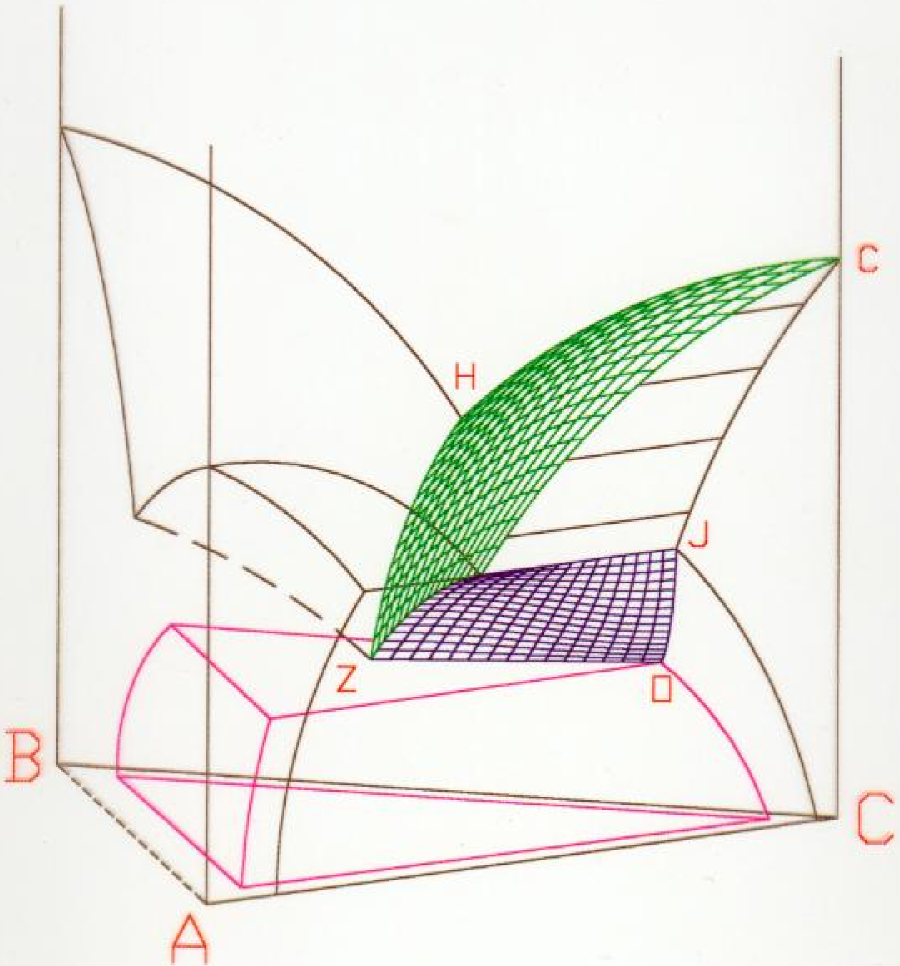
Two Phase Region of $\beta + L$

BPL2:



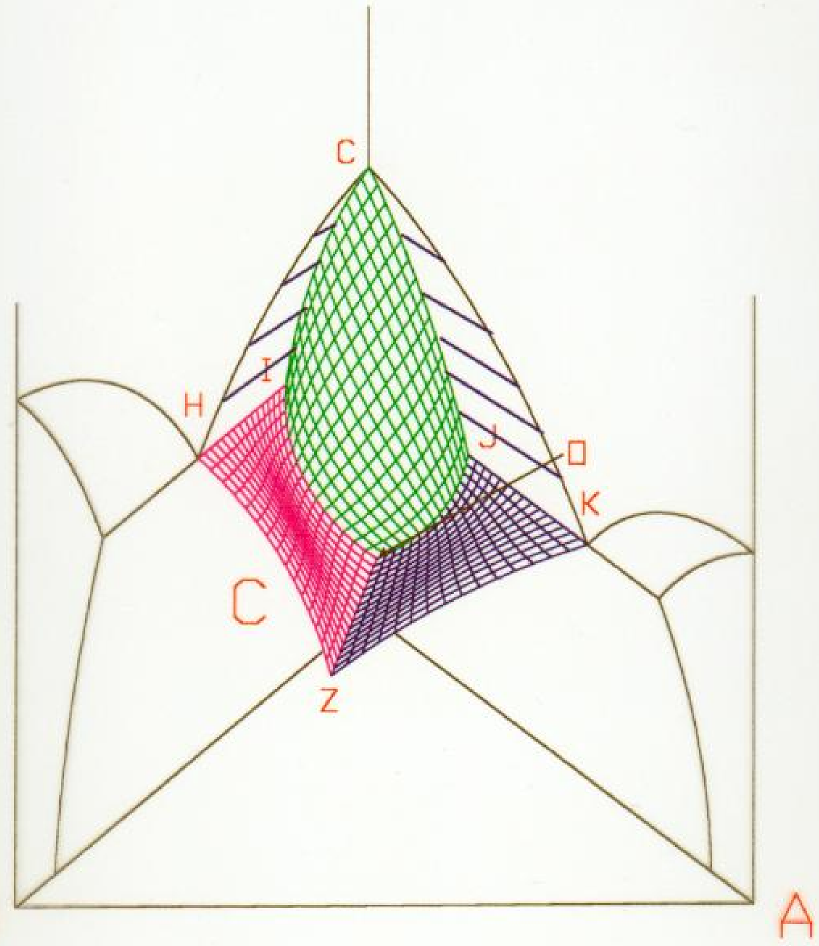
Two Phase Region of β + L Without Liquidous Surface

CPL1:



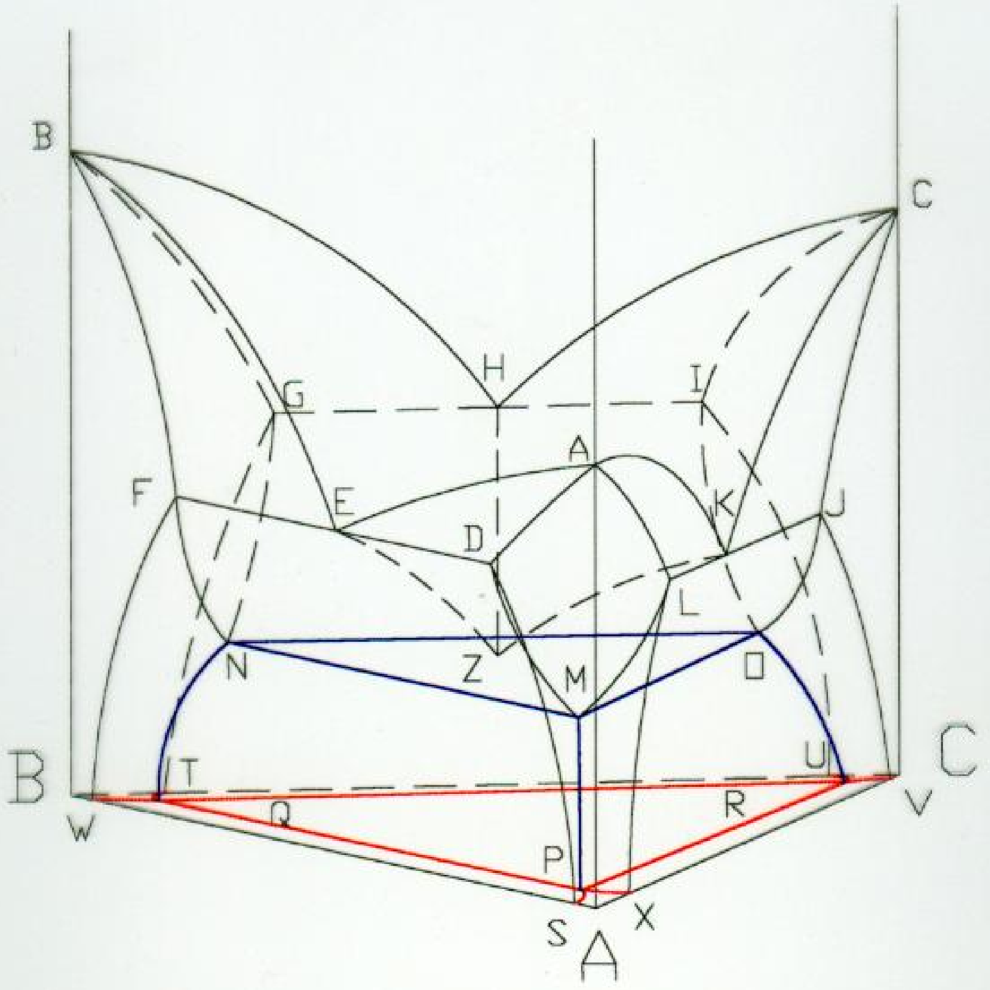
Two Phase Region $\gamma + L$

CPL2:



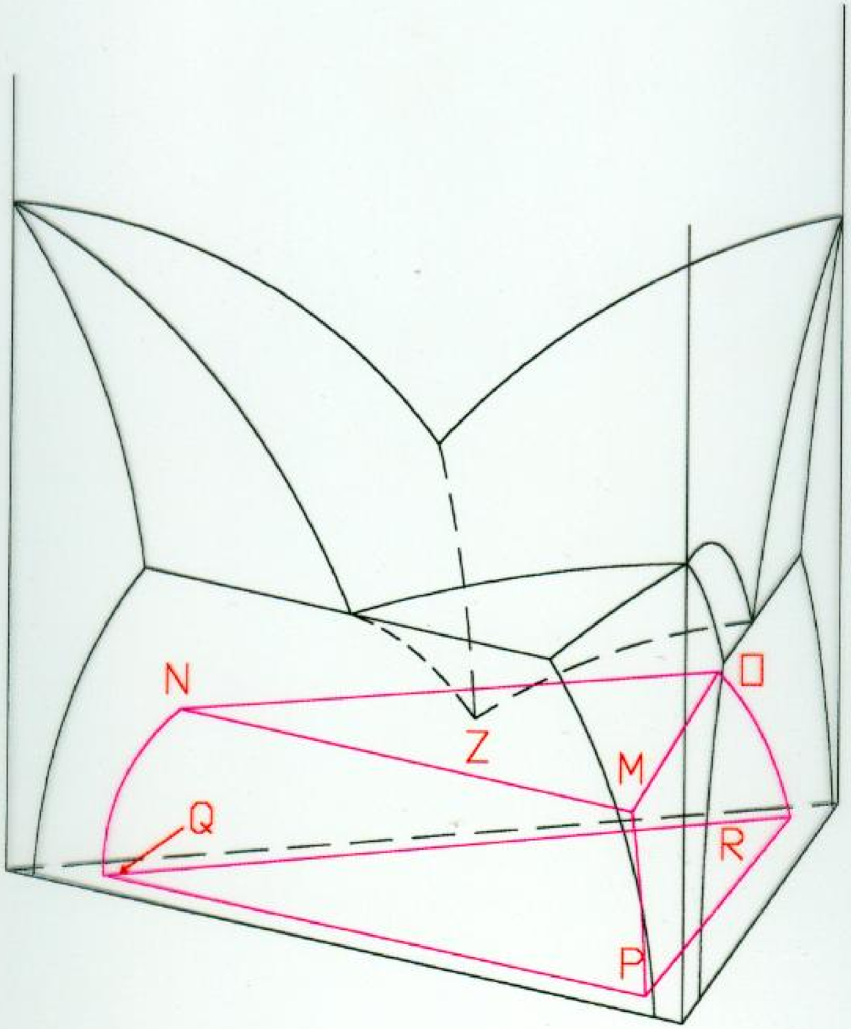
Two Phase Region of $\gamma + L$ Without Liquidous Surface

P6



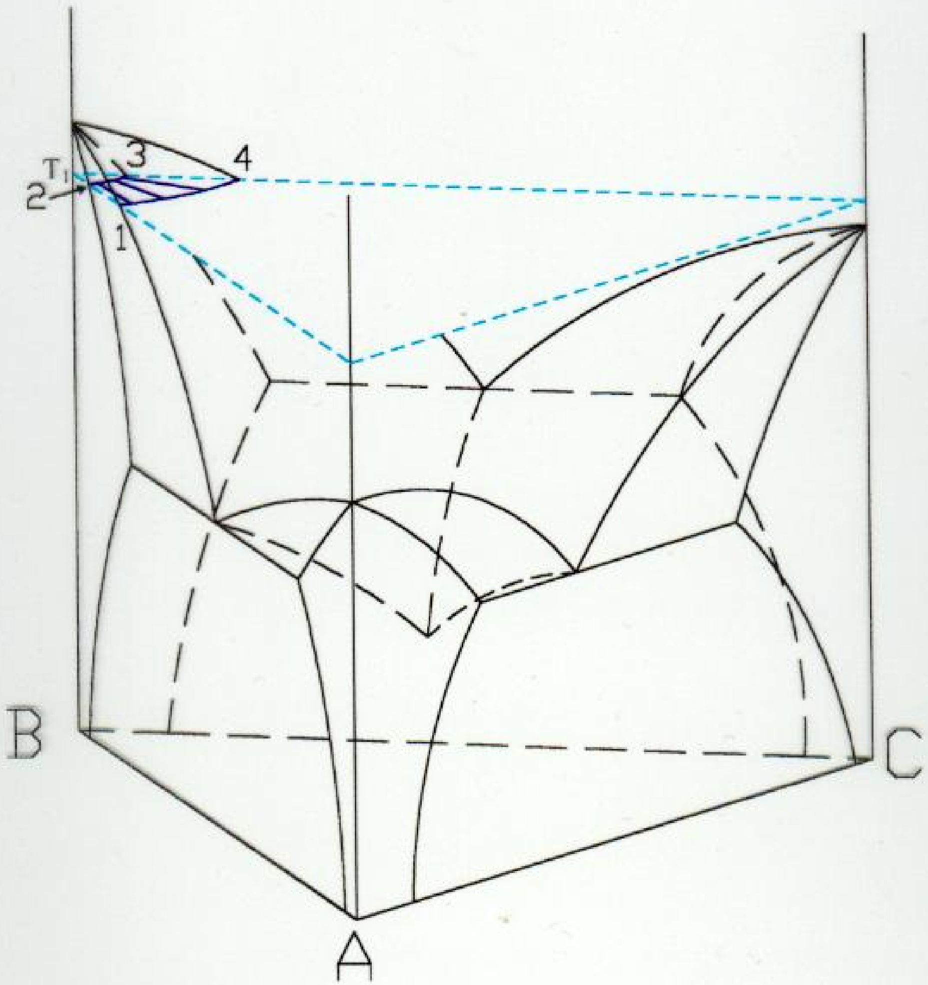
Ternary Phase Diagram with three phase region of $\alpha + \beta + \gamma$ outlined

THREPHSE

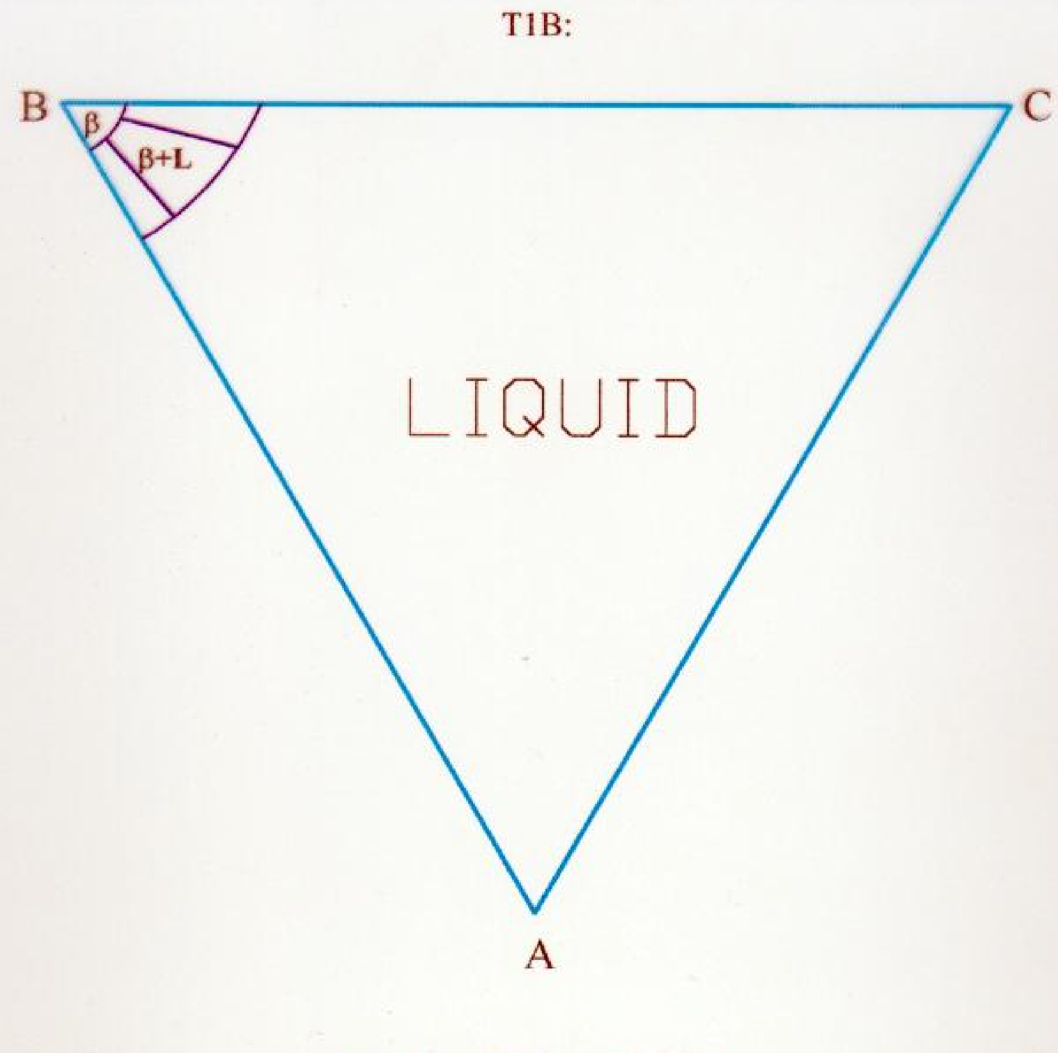


Three phase region that consists of $\alpha + \beta + \gamma$ (All Solids)

T1A:

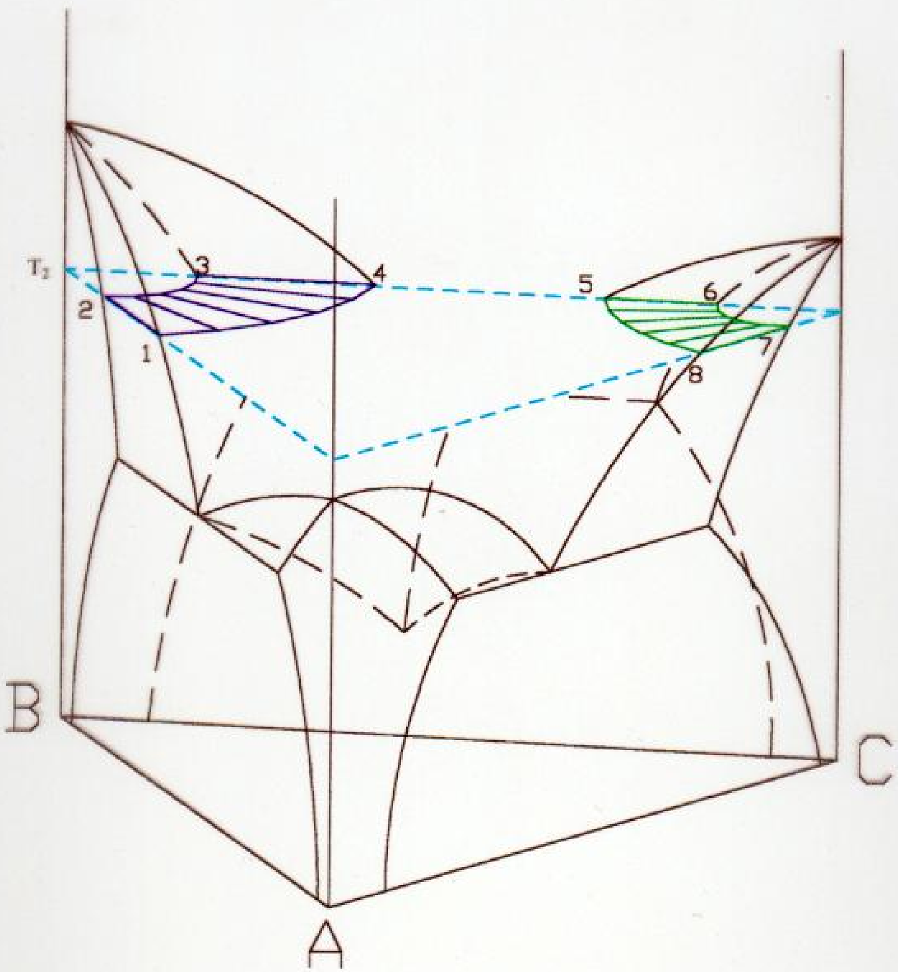


Temperature Slice At $T_1 < T_B$, But $>T_A$, T_C

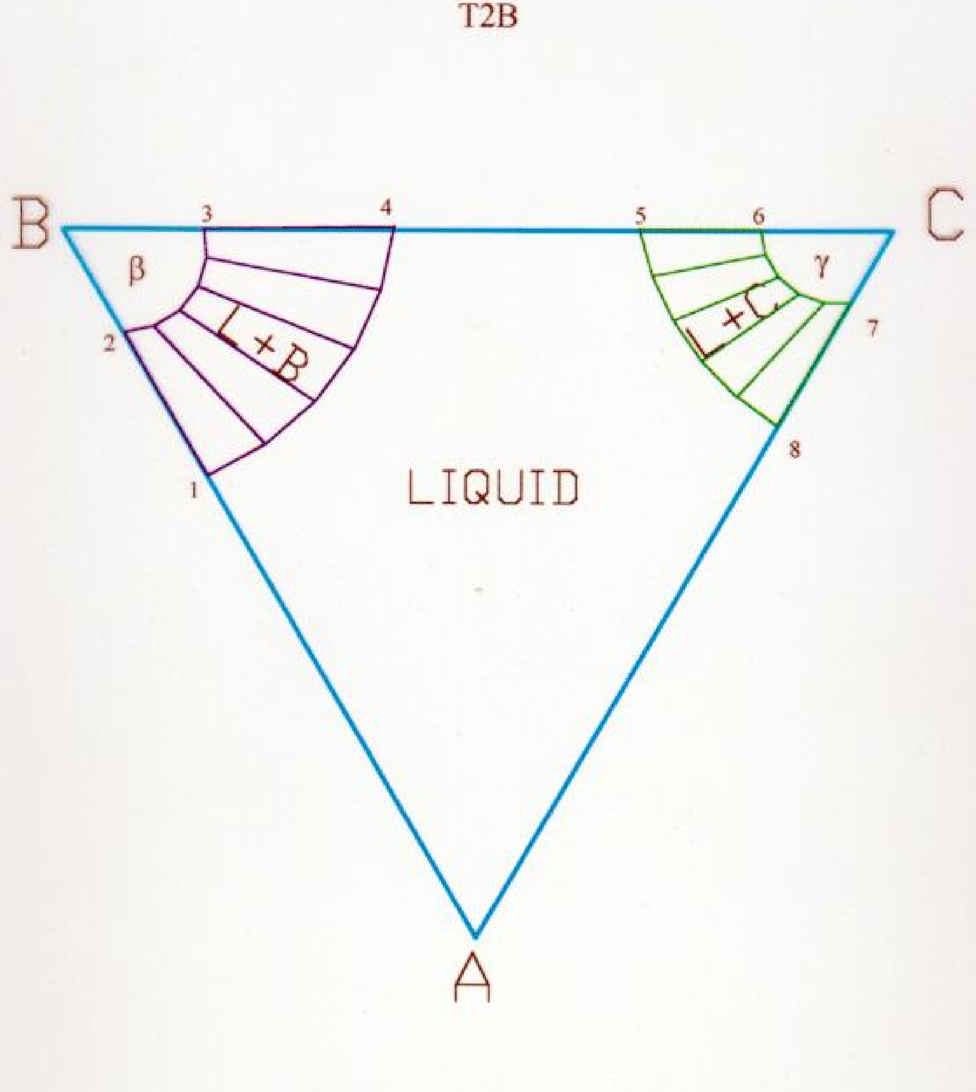


Isothermal Section At $T=T_1$

T2A

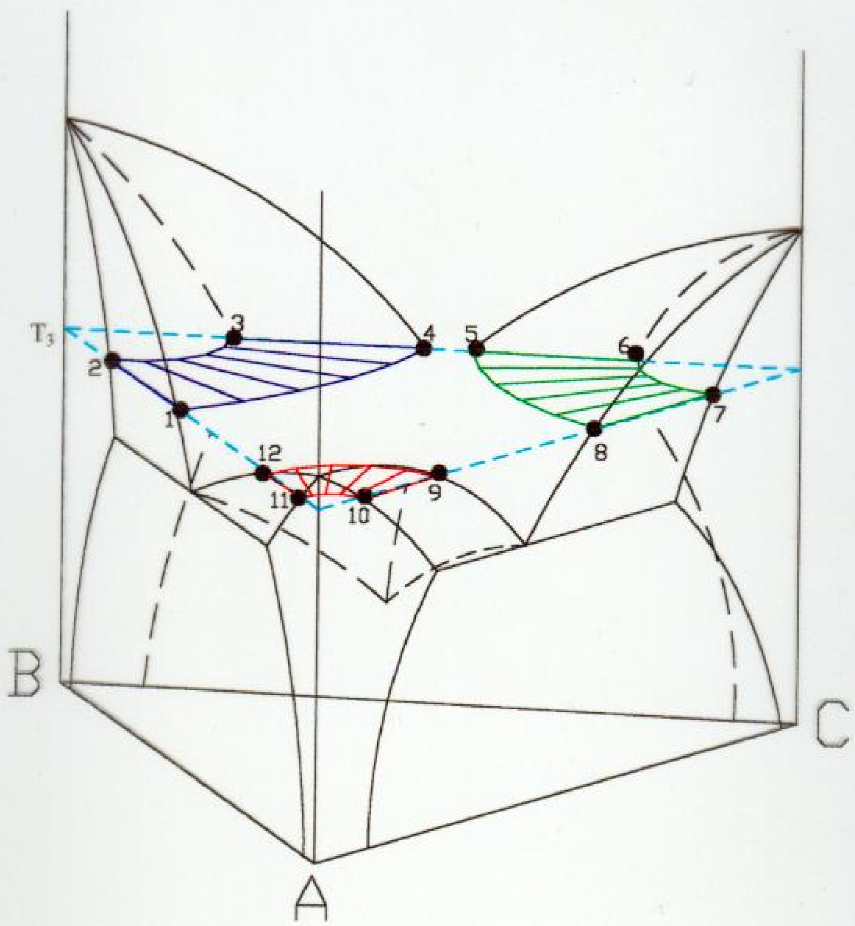


Temperature Slice At $T_2 > T_A$ But, $T_2 < T_B$, T_C

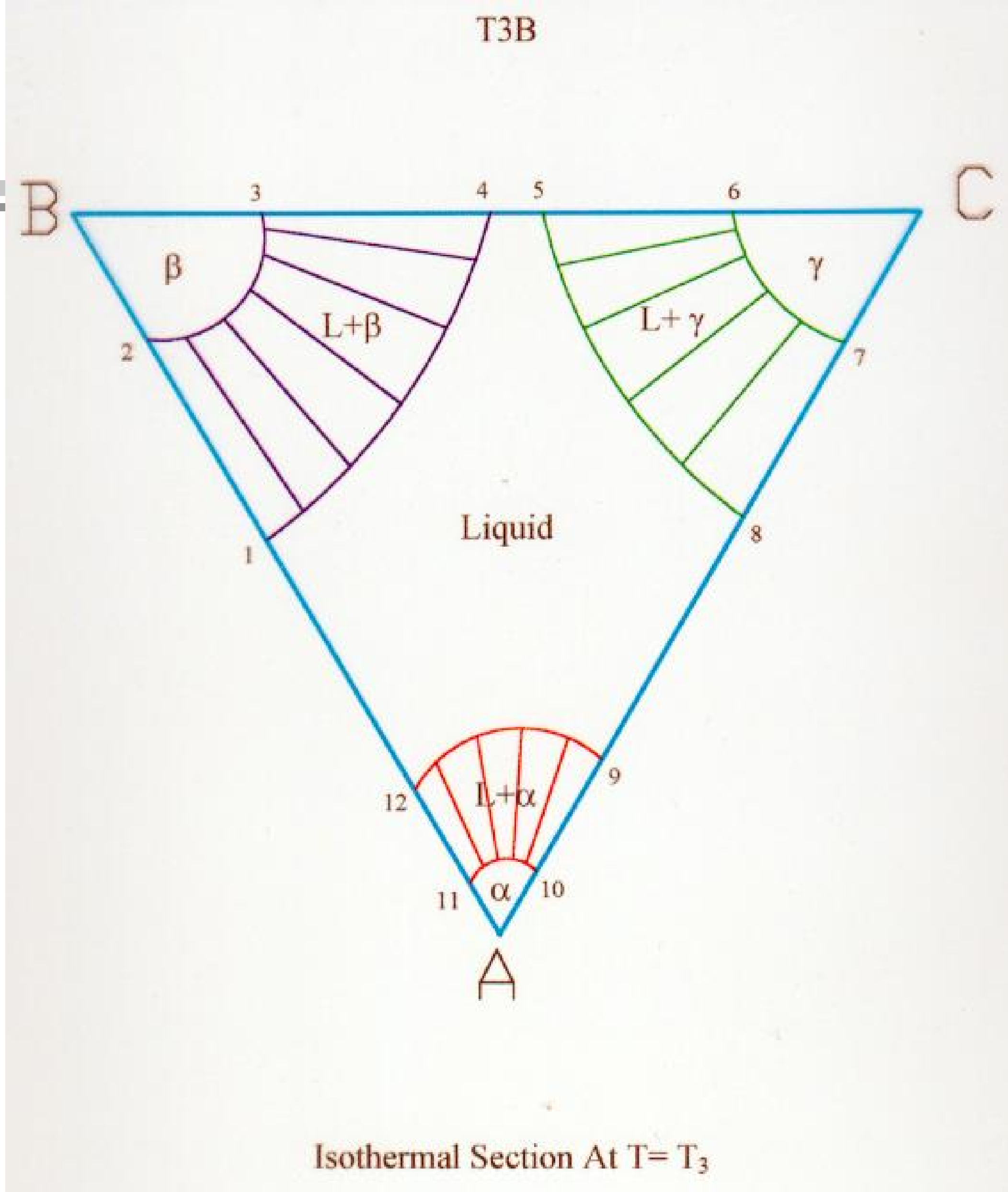


Isothermal Section At $T=T_2$

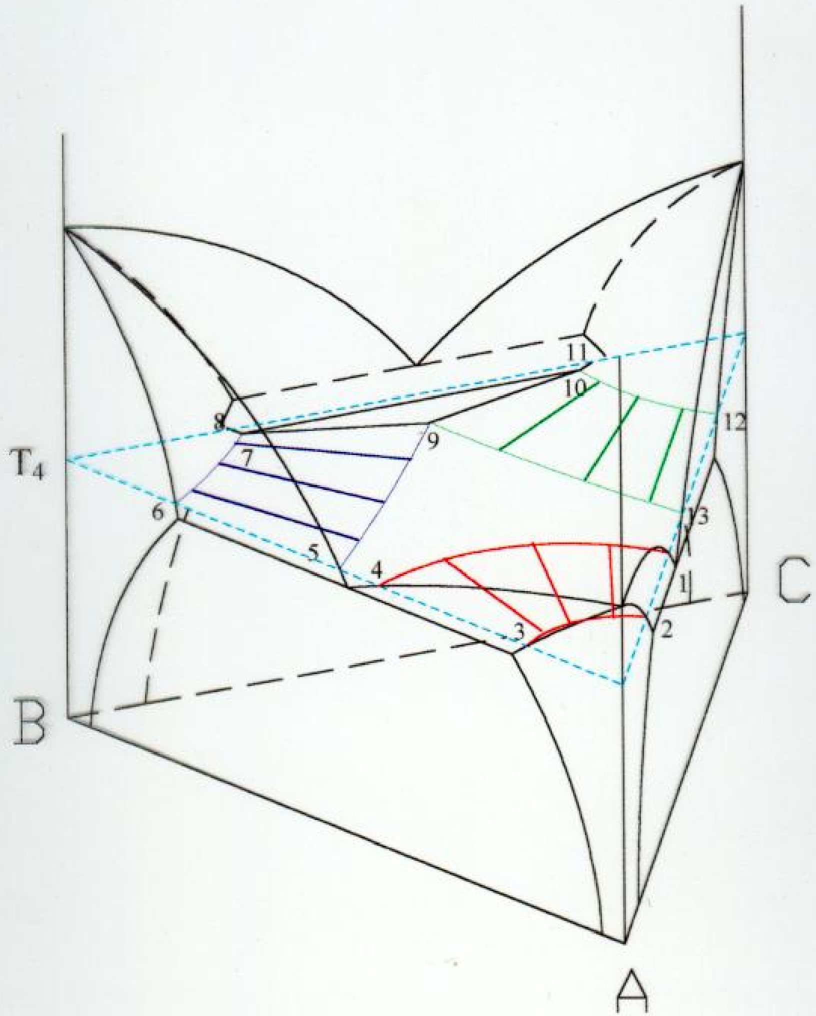
T3A:



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

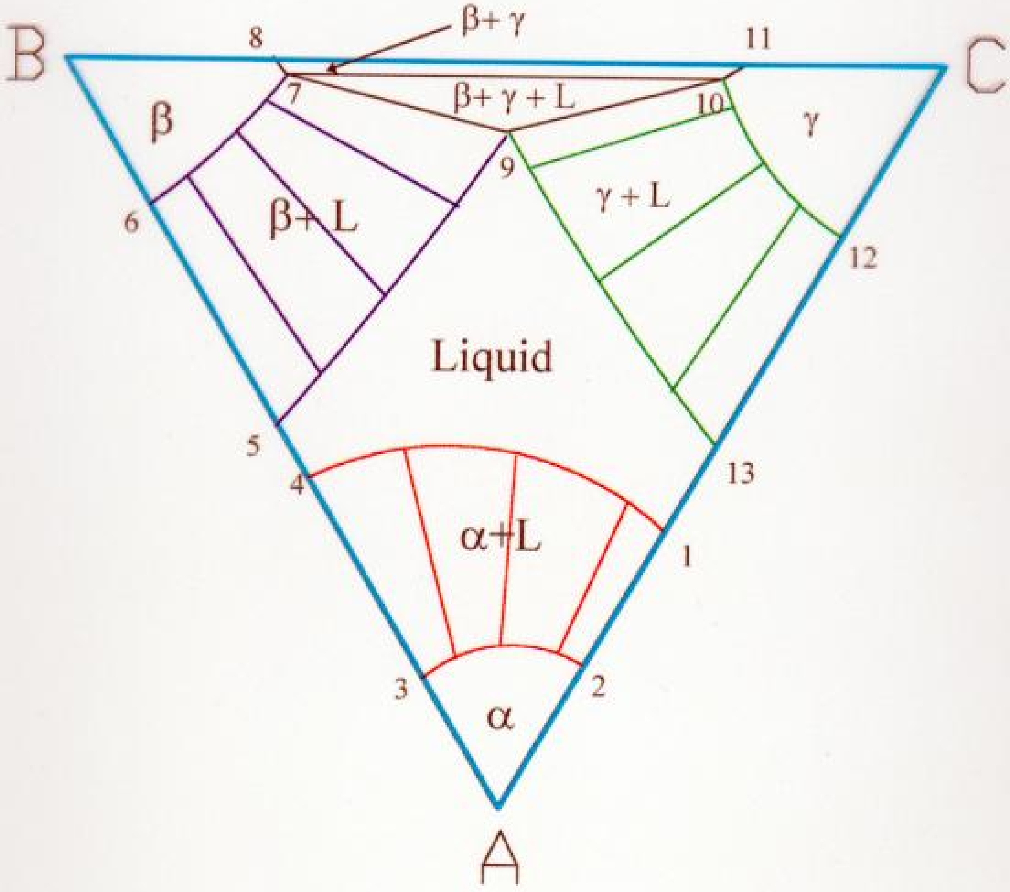

T3B
B
C
A
3
4
5
6
β
L+β
L+ γ
γ
2
7
1
8
Liquid
L+α
α
9
10
11
12
Isothermal Section At T= T3

T4A:



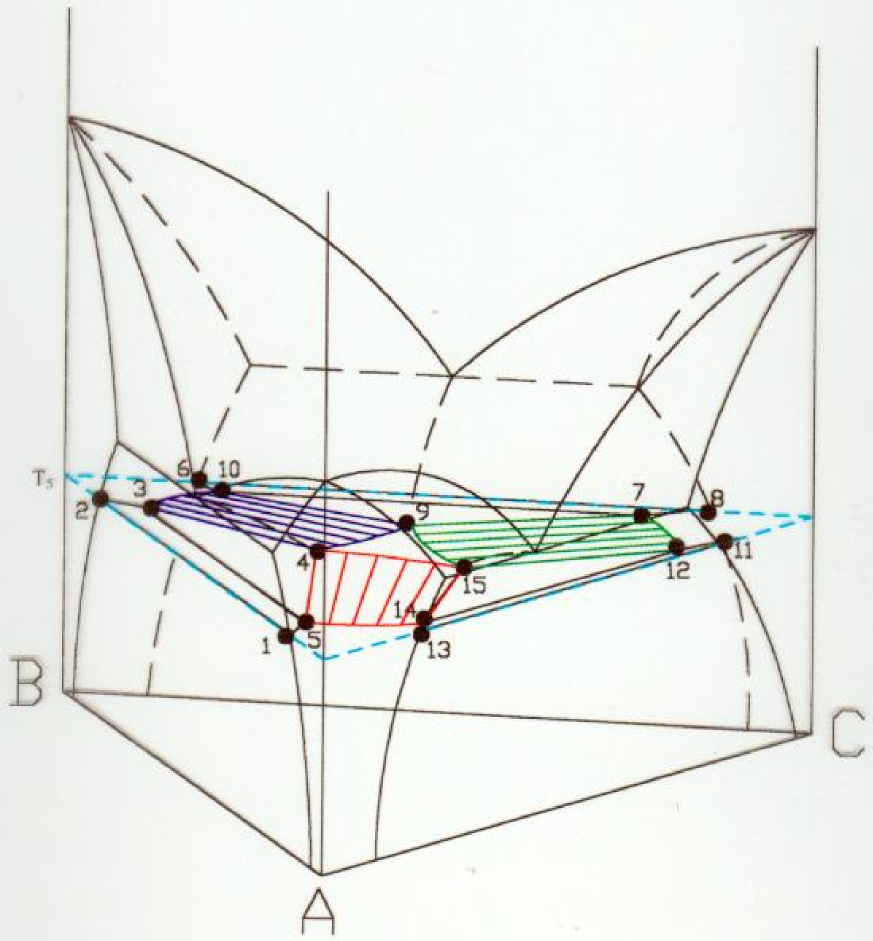
Temperature Slice At $T_4 < T_{E2}$ And $T_4 > T_{E1}, T_{E3}$

T4B:



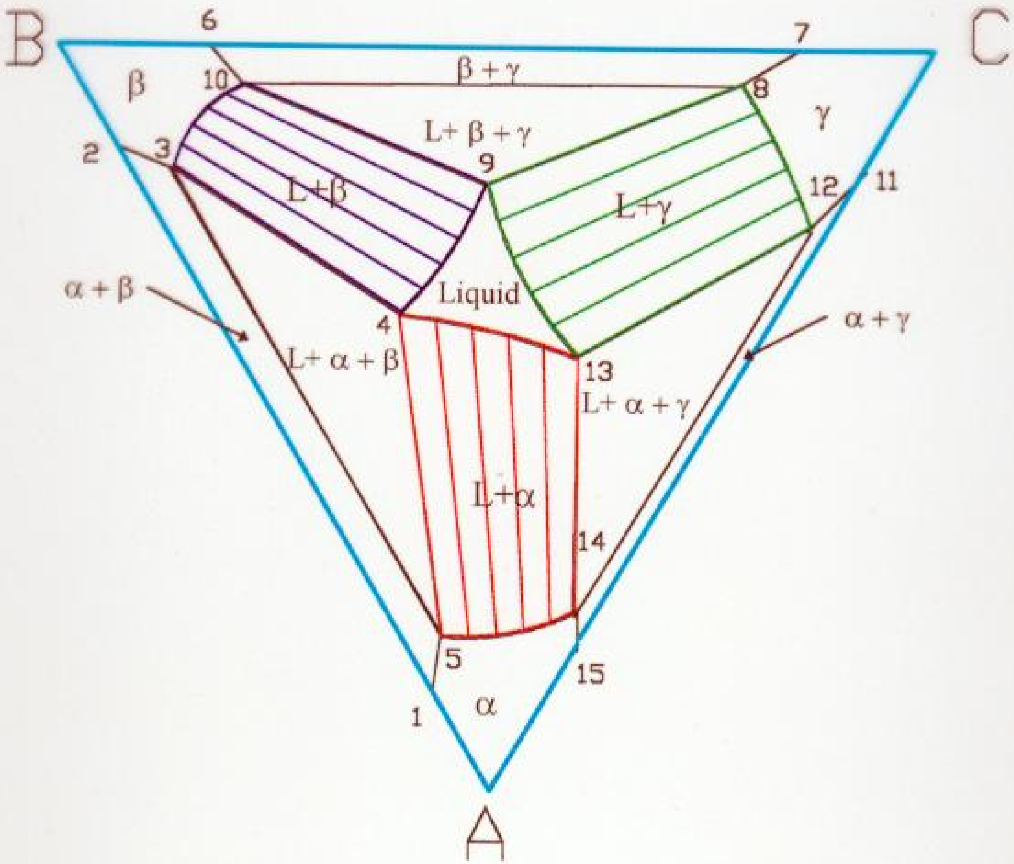
Isothermal Section At $T=T_4$

T5A:



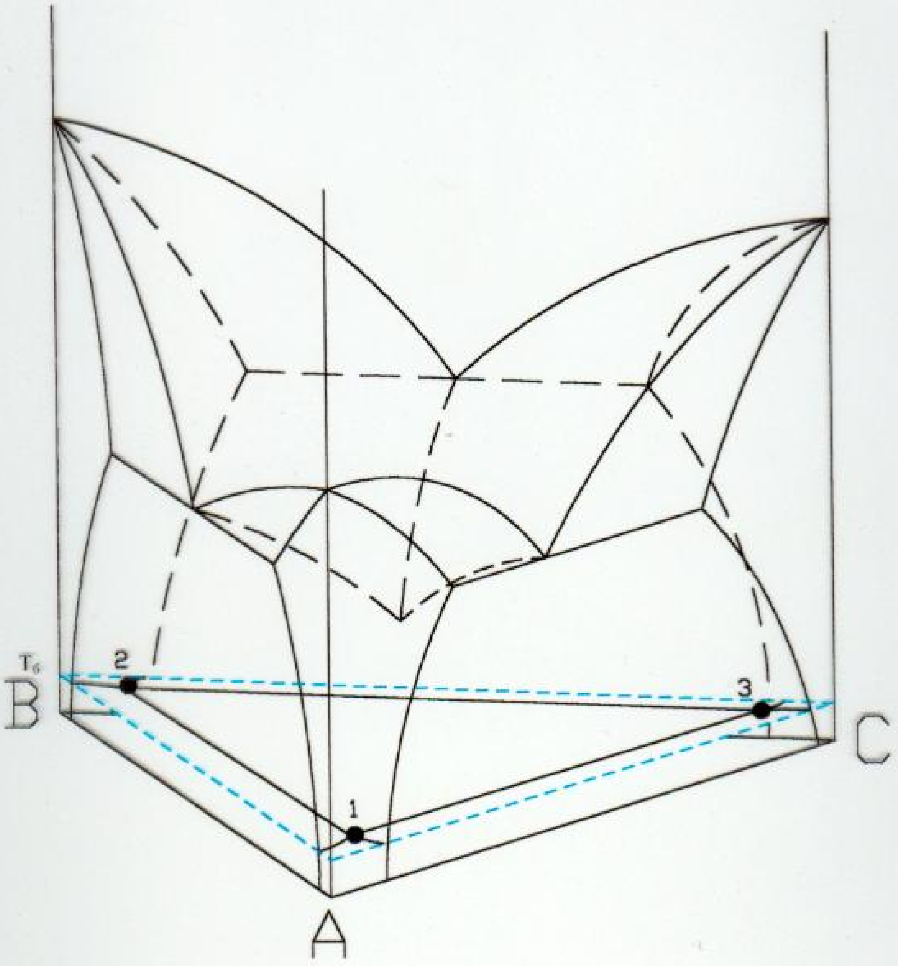
Temperature Slice Below All Binary Eutectics But, Above The Ternary Eutectic

T5B:



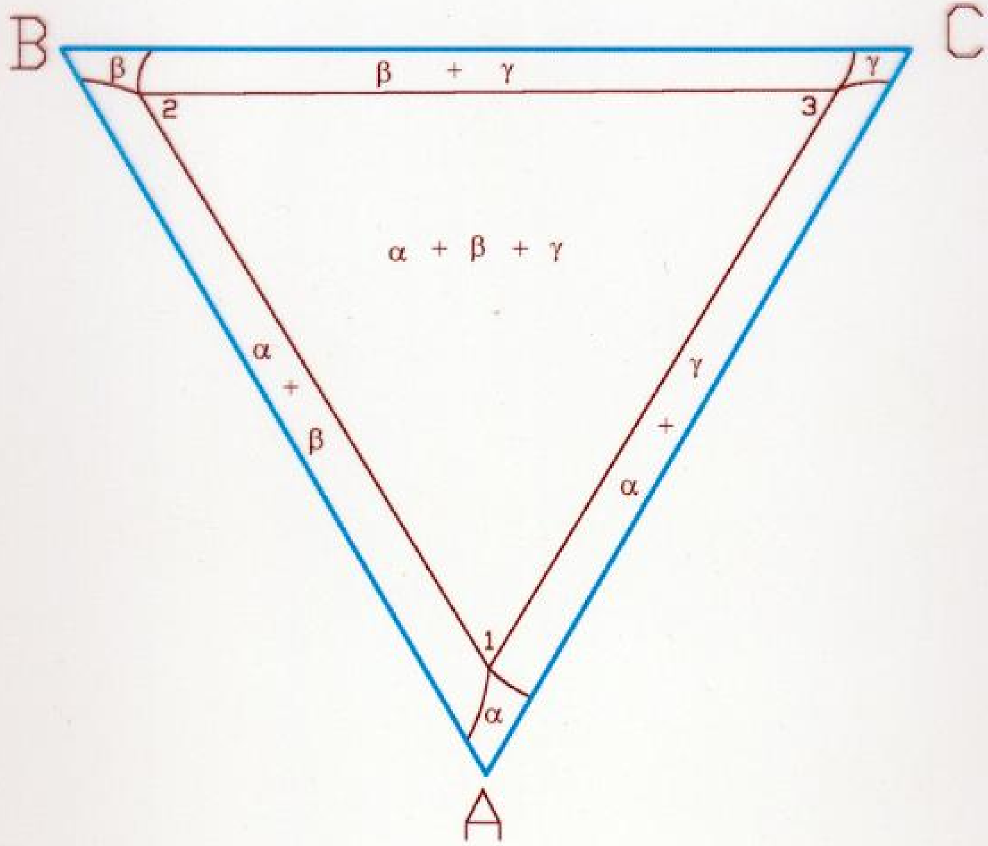
Isothermal Section At $T=T_5$

T6A:



Temperature Slice at $T_6 < T_E$

T6B:



Isothermal Section At T=T_6

Alamade Lines

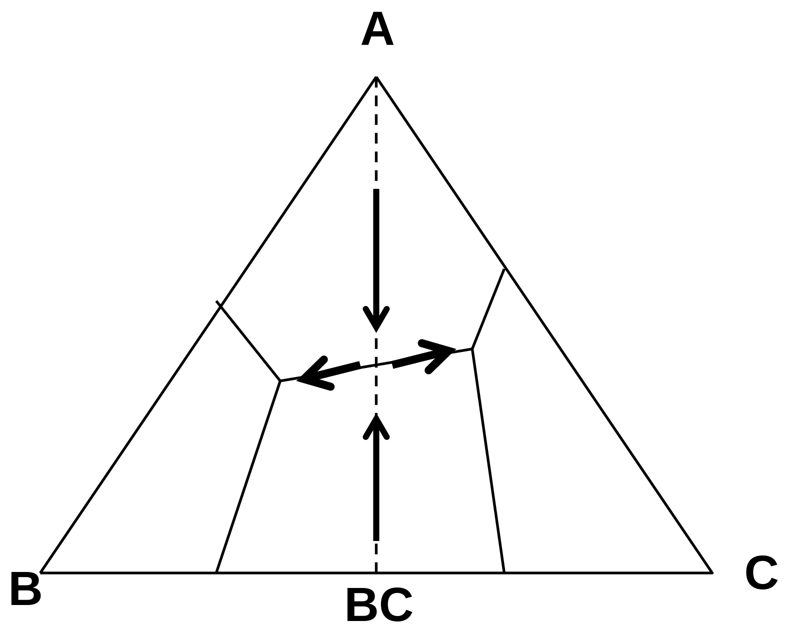
A join connecting the composition of the primary crystals of two areas having a common boundary line.

<u>Alkamade Theorem</u>: The intersection of a boundary line with its Corresponding Alkamade line represents a temperature maximum on that boundary line and a temperature minimum on the Alkamade Line.

Alkamade lines never cross one another

Source: Bergeron & Risbud

Alamade Lines



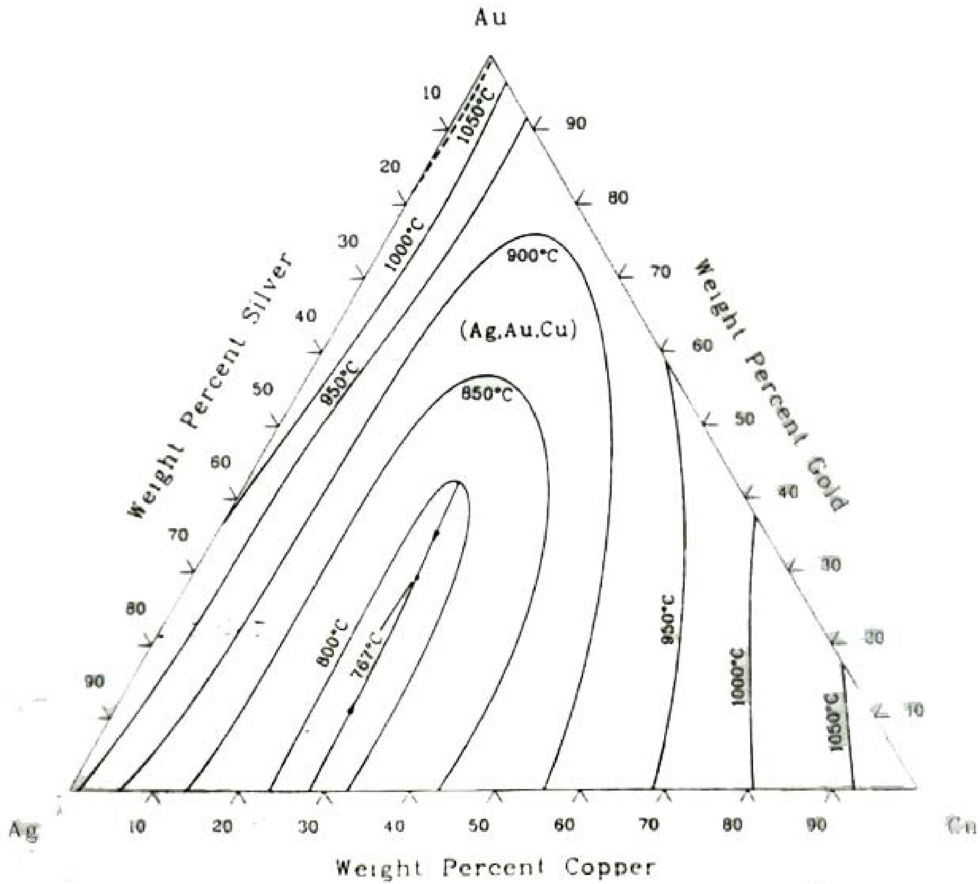
Alkamade Lines:

A-B B-C C-A

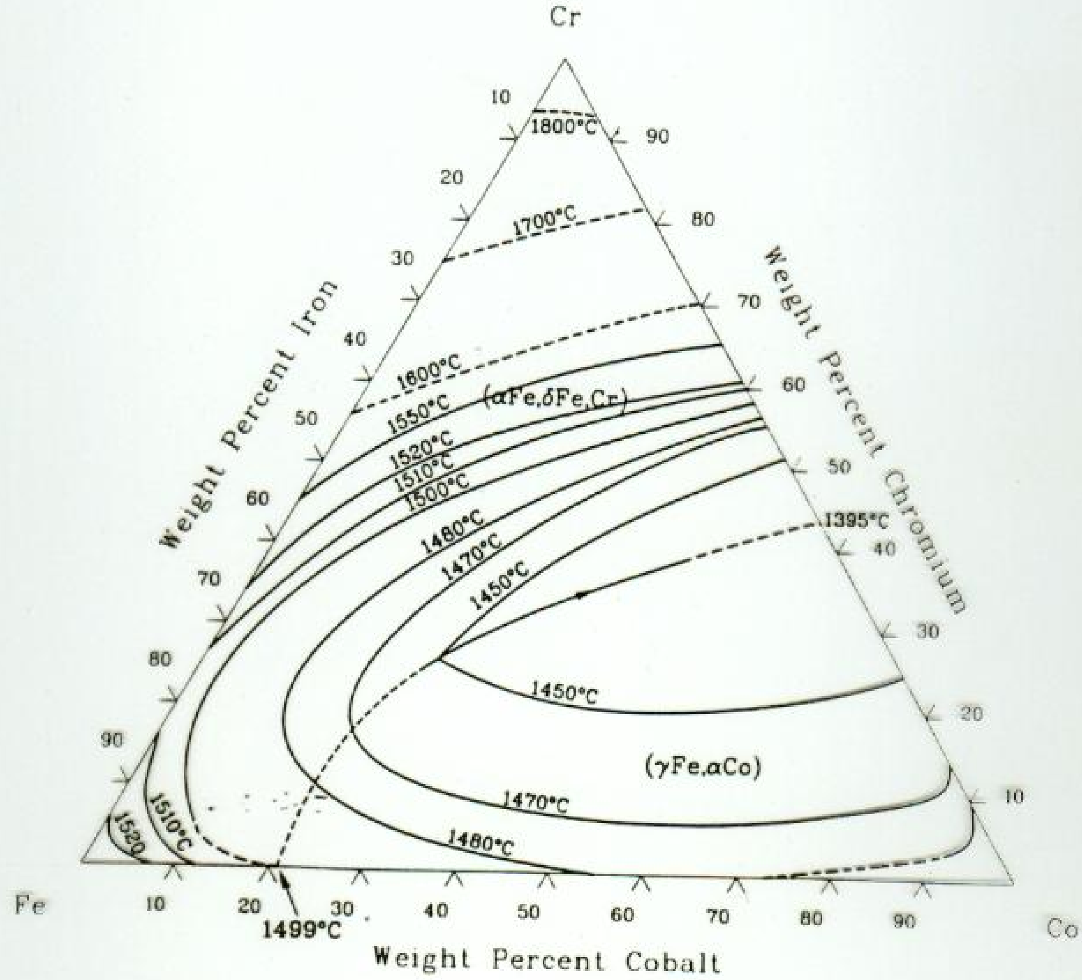
B-BC BC-C

A-BC

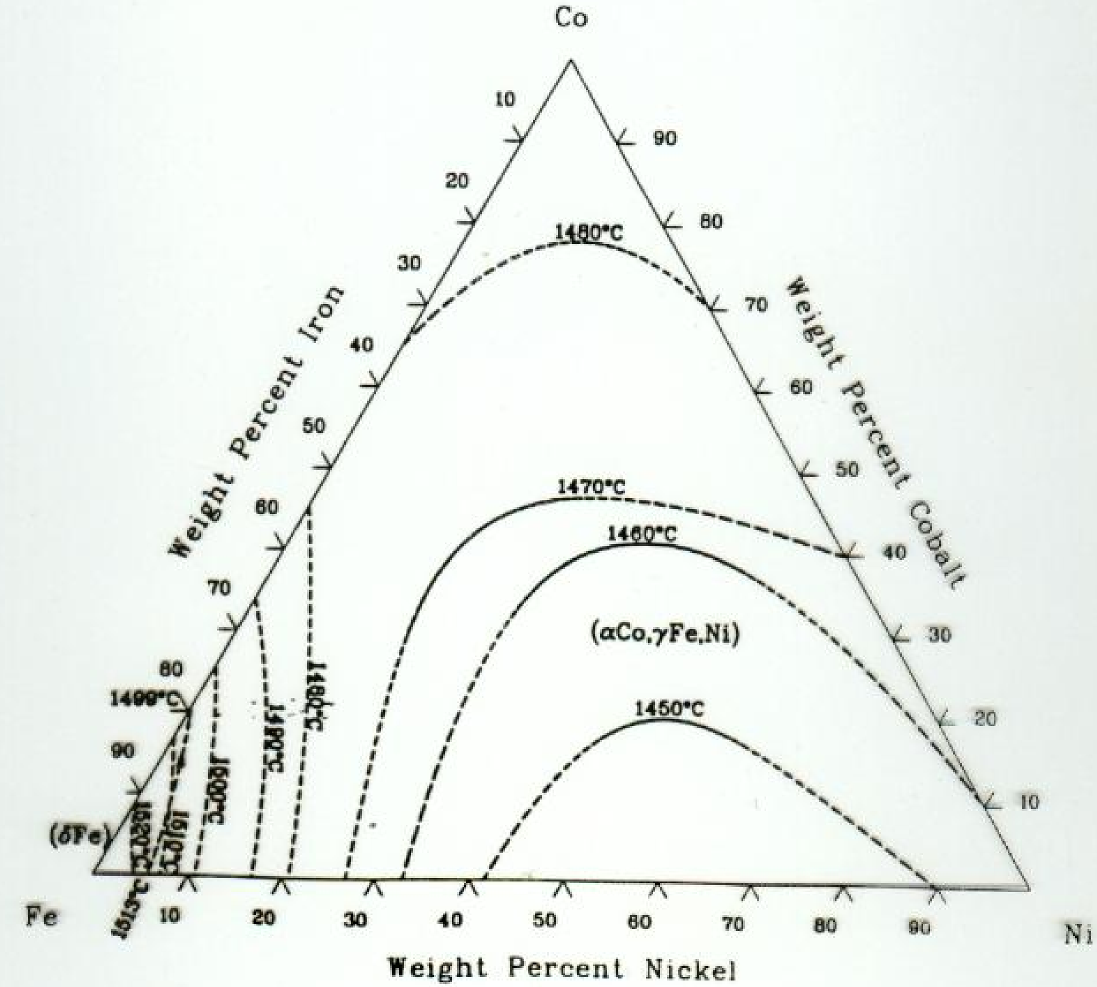
Ag-Au-Cu liquidus projection [90Pri]



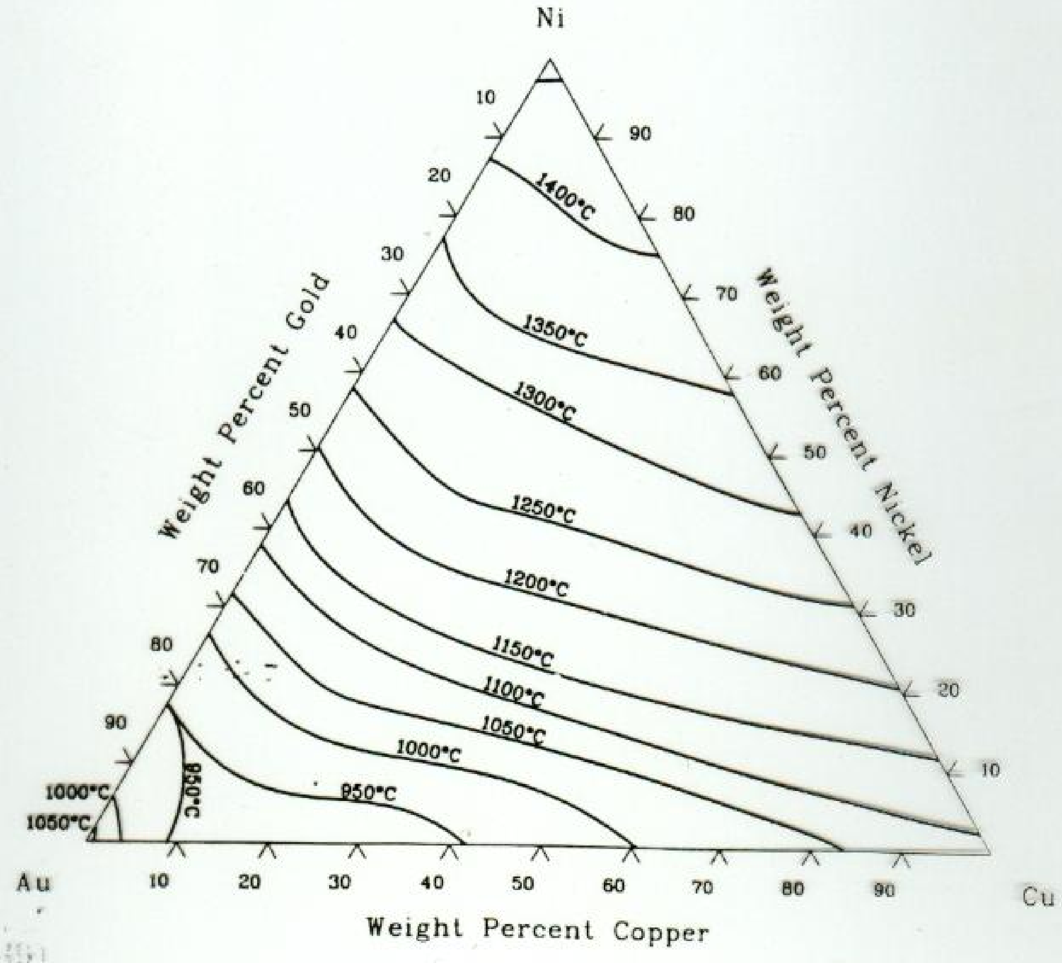
Co-Cr-Fe liquidus projection [88Ray]



Co-Fe-Ni liquidus projection [88Ray]



Au-Cu-Ni liquidus projection [90Pri]



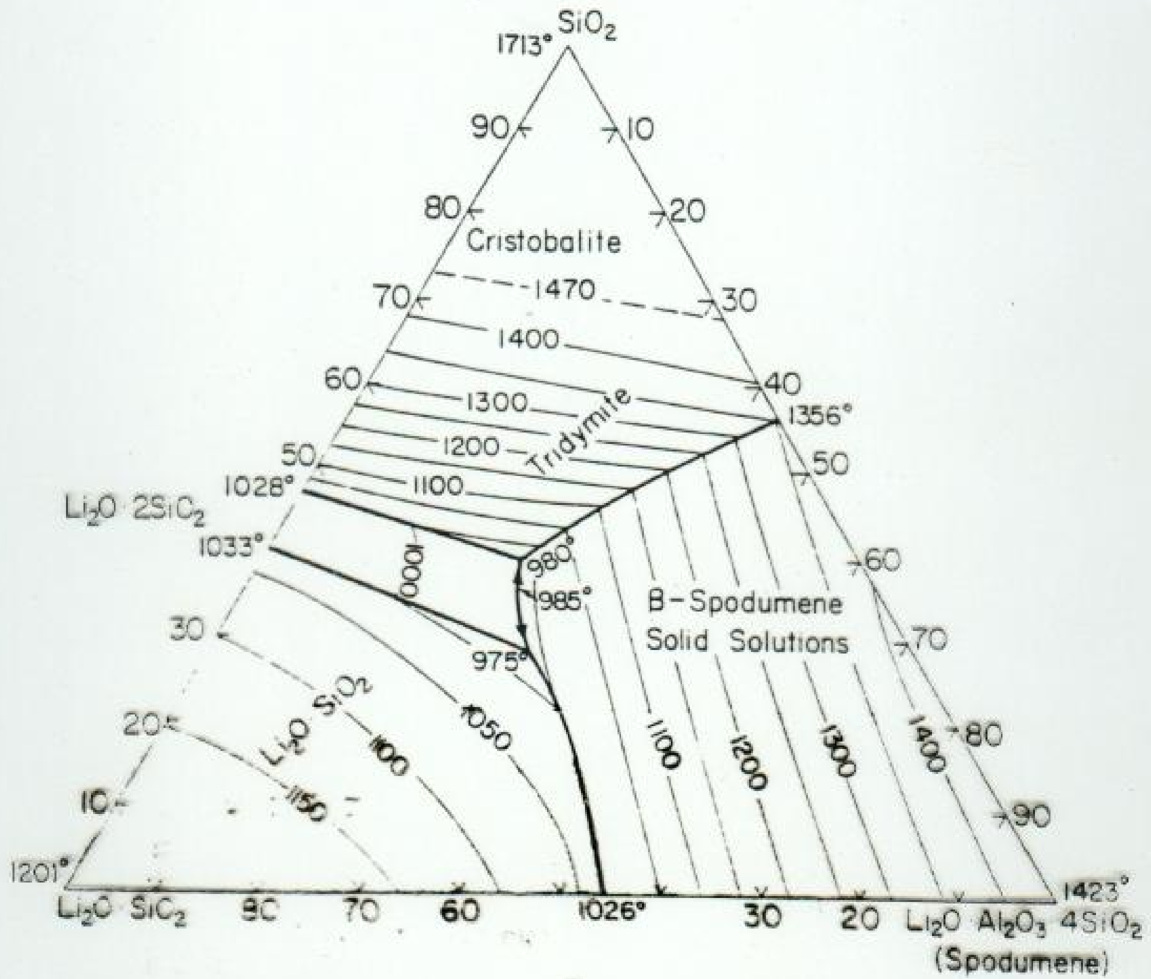


FIG. 450.—System $Li_2O \cdot SiO_2$–$Li_2O \cdot Al_2O_3 \cdot 4SiO_2$–$SiO_2$.

Rustum Roy and E. F. Osborn, *J. Am. Chem. Soc.*, **71** [6] 2092 (1949).