Module 25

Ternary Phase Diagram

Lecture 25

Ternary Phase Diagram

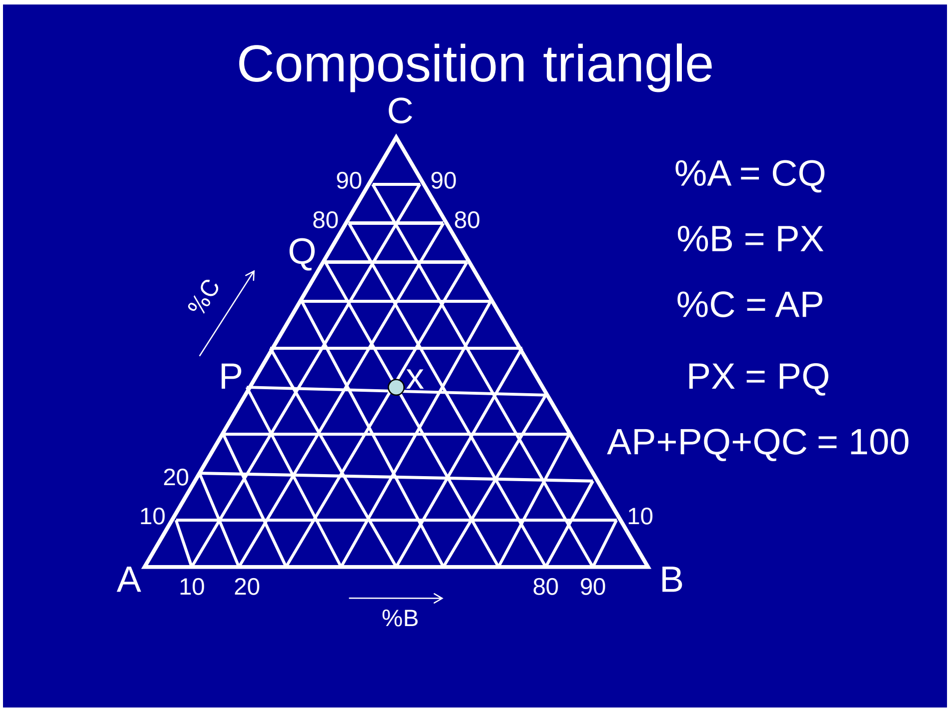
Keywords: Composition triangle, ternary isomorphous system, vertical & horizontal section, ternary eutectic

Introduction

We are now familiar with binary phase diagrams. It is like a map in a two dimensional space representing temperature and composition where there are several domains separated by boundaries. Within each domain a particular phase or at best a maximum of 2 phases can coexist. It may also have isotherms representing 3 phase equilibrium. We have looked at different types of hypothetical phase diagrams and a specific binary phase diagram representing iron – carbon system. Phase diagrams help us interpret the structures of metal and alloys. This gives a rough estimate of its properties as well. However, most commercial alloys have more than two components. This is where we need higher orders of phase diagram. Let us first look at ternary diagram which is used to represent the stability of different phases if the alloy consists of 3 components.

Composition triangle:

In a binary phase diagram the horizontal axis is used to represent the composition. This is enough because we need to specify the amount of one component only. The amount of the other is obtained by subtracting it from 100. In a ternary system we need to specify the amounts of two components. Therefore we need two axes. The amount of the third can be obtained by subtracting the sum total of the two from100. This is best done using a composition triangle. This is illustrated in slide 1.

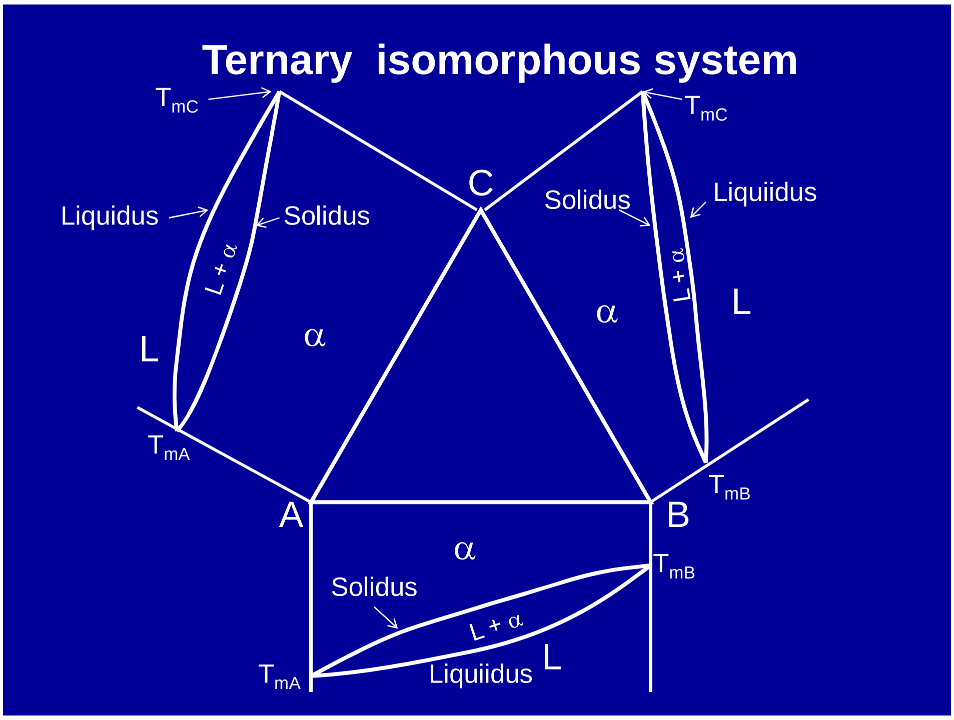


Slide 1

An equilateral triangle is used to represent the composition of a ternary alloy. Slide 1 shows such a triangle. Three vertices are named after the three components A, B & C. These three points represent 100% A, B and C respectively. The three sides of the triangle represent the compositions of the 3 binary alloys. At every point on the line BC (the side opposite the vertex A) has 0% A. The each side of the triangle has been subdivided into 10 parts by a set of points. Join these as shown in slide 1. The entire space is now divided into a set of small equilateral triangles. These can be further subdivided depending on the needs. Smaller divisions are needed for more precise location of the composition of the alloy. Let us consider an alloy represented by the point X as shown in the slide. What is its composition? How could this be read from the diagram? For example % A is read by measuring the distance from the side (BC) opposite the vertex A. It is equal to 30% (=CQ). Note that the lines are drawn at intervals of 10%. % B is read from the side AC. This is equal to 30% (=PX). %C is read from the side AB. This is equal to 40% (=AP). Note that the sum of the three is 100.

Ternary isomorphous system:

Let us consider a ternary system consisting of 3 components A, B & C. These are soluble in all proportions in both liquid and solid state. This is the characteristic of an isomorphous system. Slide 2 shows the nature of the respective binary phase diagrams.



Slide 2

The solid solution is represented as α. L is the liquid. T_{mA} is the melting point of A. T_{mB} is the melting point of B and T_{mC} is the melting point of C. Here the entire sketch is shown on a plane. For example to represent the binary AB system the axis representing temperature is perpendicular to AB. To visualize how the ternary diagram would look like rotate the respective binary diagrams by 90° about the respective sides of the base ABC. For example rotate the binary diagram for the system AB about B by 90°. Note that the temperature axis now is vertical. The plane joining the three binary liquidus lines is the surface representing the liquidus of the ternary system. In the same manner the surface joining the three solidus lines is the ternary solidus. Figure 1 gives a 3D view of the ternary phase diagram of this system.

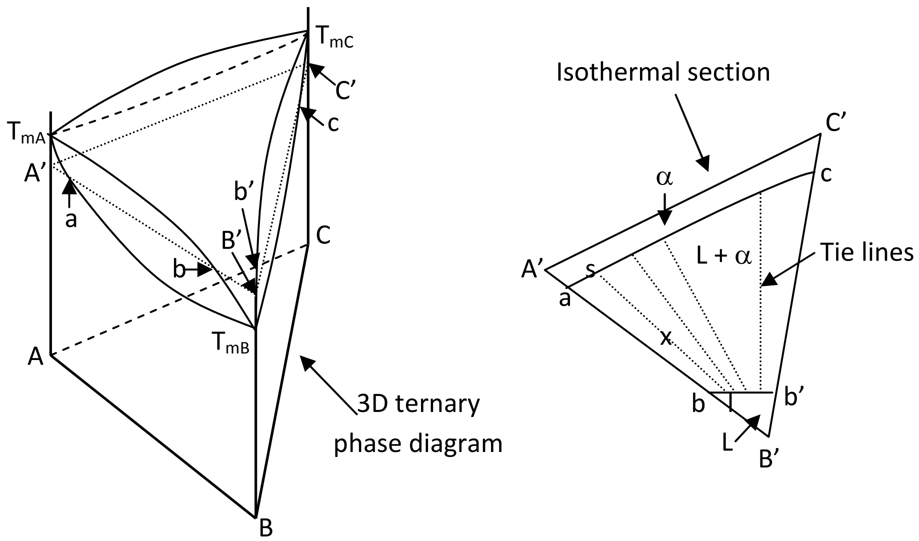


Fig: 1

The sketch on the left in fig 1 is the 3D view of the phase diagram. The base ABC is the composition triangle. The vertical lines represent temperatures. The top surface joining the melting points of the three components is the liquidus surface. There is a similar surface beneath this passing through the points T_{mA}, T_{mB} & T_{mC}. This is the solidus surface. The 3D sketch as above is not a convenient way to represent ternary phase diagrams. In order to have a quantitative insight often these are represented by sectional views. These are isothermal and vertical sections. The sketch on the right of fig 1 gives an isothermal section of the 3D phase diagram. The A'B'C' intersects the liquidus and solidus planes along the lines bb' and ac (see fig 1). They appear as a pair of curves in the isothermal section. The region between the two is the two phase field. Within this both liquid and solid can coexist. The dotted lines in this field are known the tie lines. Note that they appear to emanate from the point B'. The points of intersection of the tie line with the liquidus and the solidus are the compositions of the liquid and solid that can coexist at this temperature.

Let us apply Gibbs phase rule (P + F = C + 1) to the two phase field in a ternary diagram. Note that the number of phases = P = 2, number of components = C = 3. Therefore degree of freedom = F = 2. What does this mean? It means that two phase equilibrium can have only two independent variables. Let us assume that one of this is the temperature. What is the second variable? It is the gross composition of the alloy. The compositions of the two phases that can coexist at this temperature are defined by the points of intersection of tie line passing through the point denoting the gross composition of the alloy with the corresponding liquidus and the solidus. As an illustration the composition is marked as x on a tie line in Fig 1. The compositions of the two phases are fixed by s & l. Or else you can fix the composition of one of the two phases. For example if you fix s the composition of the liquid l is also defined by the point l, the point of intersection of the tie line and the liquidus. Like binary phase diagram you could use lever rule to find the amounts of liquid and solid in a two phase field if the composition of the alloy is known. Consider the alloy x on the tie line joining 'sl' in Fig 1. The ratio of the amounts of liquid and solid is given by sx/lx.

The isothermal section can give you the compositions of liquid and solid that can coexist at a given temperature. It gives no idea about the temperature range over which two phases can coexist. You need vertical sections to know about these. You can have several types of vertical sections. This is shown in Fig 2.

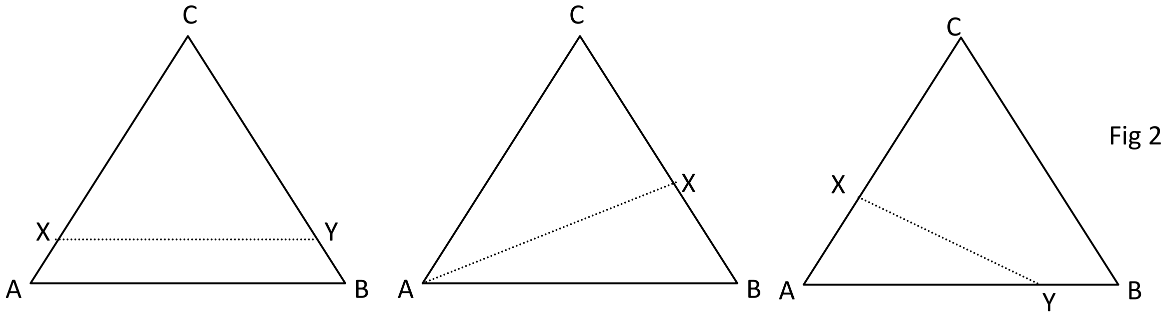


Fig 2

Figure 2 shows the orientations lines XY & AX on the composition triangle. An imaginary vertical plane passing through these would intersect the surfaces representing the solidus and the liquidus. The trace of these on a plane is the vertical section of the ternary diagram.

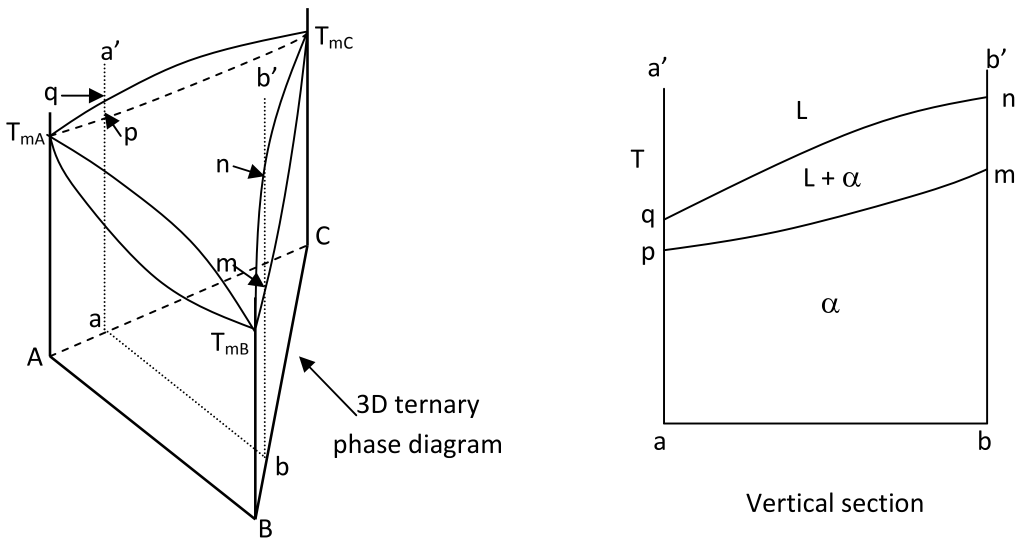
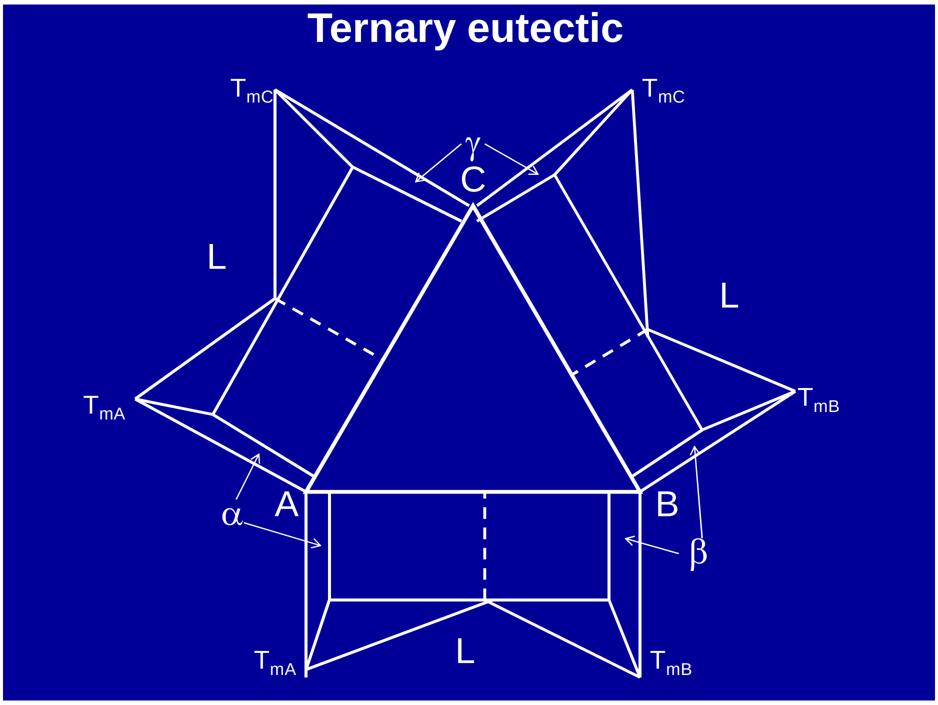


Fig: 3

The sketch on the left of fig 3 gives a 3D ternary phase diagram of an isomorphous system. The sketch on the right gives a vertical section of the same. The vertical plane is represented by /abb'a'/ in the 3D ternary diagram. Note the points of intersections of the line aa' (normal to the plane ABC) with the solidus and the liquidus . These are p & q. The points of intersection of the line bb' are m & n. The locations of these are marked on the line aa' and bb' as p, q, m & n in the sketch on the right. Get the points of intersections of a set of vertical lines between points a & b on the ternary diagram to draw the lines representing the liquidus and the solidus in the diagram on the right. This is how a vertical section can be drawn (see fig 3).



Slide 3

Ternary eutectic:

Let us consider a ternary alloy consisting of three components A, B & C. The 3 binary alloys form 3 different eutectics. These are shown along the respective sides of the composition triangle as shown in slide 3. The terminal solid solutions are represented as α, β & γ. Let the binary eutectic temperatures be denoted as $T_{\alpha\beta}$, $T_{\beta\gamma}$ and $T_{\gamma\alpha}$. The ternary eutectic represents 4 phase equilibrium where a liquid transforms into a mixture of 3 phases. This is represented as:

$$L = \alpha + \beta + \gamma \qquad (1)$$

Recall Gibbs phase rule (P + F = C + 1). The number of phases = 4, the number of components = C = 3. Therefore the degree of freedom = F = 0. This means such equilibrium can exist only at a fixed temperature between 4 phases having fixed compositions. Let the eutectic temperature be represented as T_E. Since each of the four phases should have fixed compositions let these be represented as α_E, β_E and γ_E. An isothermal section at the eutectic transformation temperature would therefore look like the sketch given in Fig 4. Note that E represents the composition of the liquid which could remain in equilibrium with solids α_E, β_E and γ_E at the eutectic temperature.

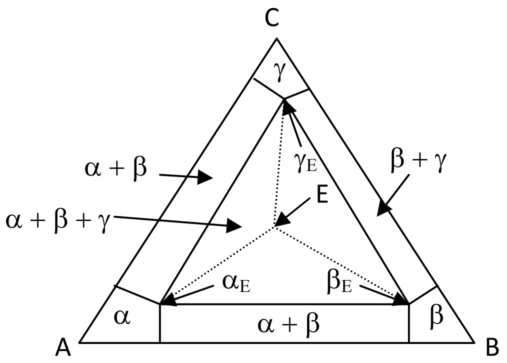
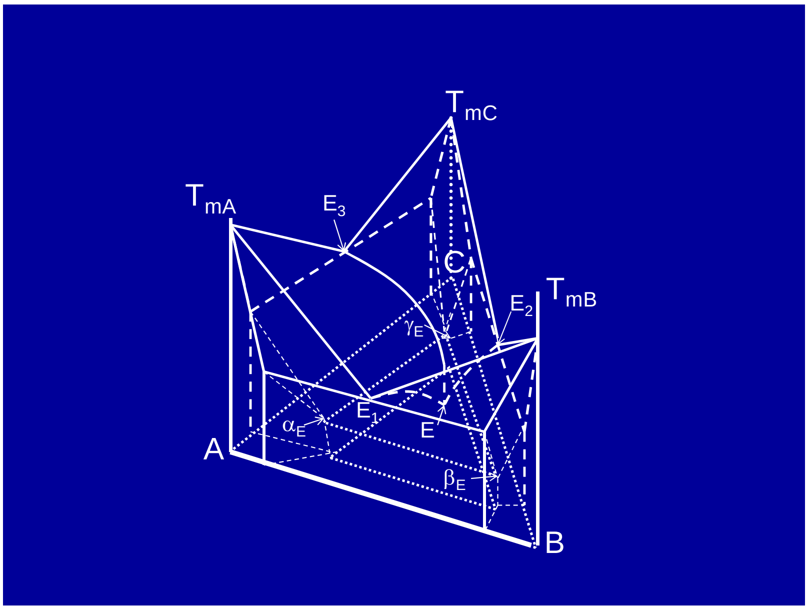


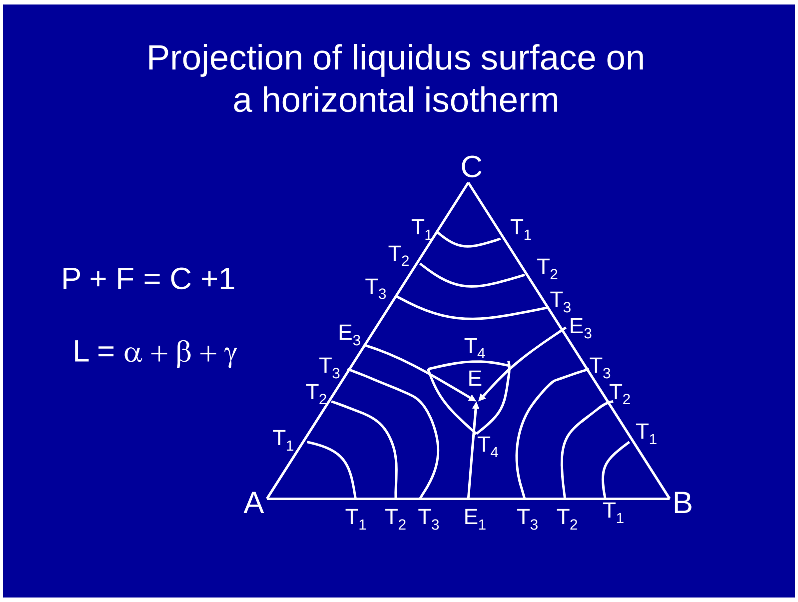
Fig 4

Imagine that the 3 binary eutectic phase diagrams shown in slide 3 are rotated by 90° about the respective edges of the composition triangle so that the temperature axes become perpendicular to the base. This gives a three dimensional view of the ternary diagram. It is shown in slide 4.



Slide 4

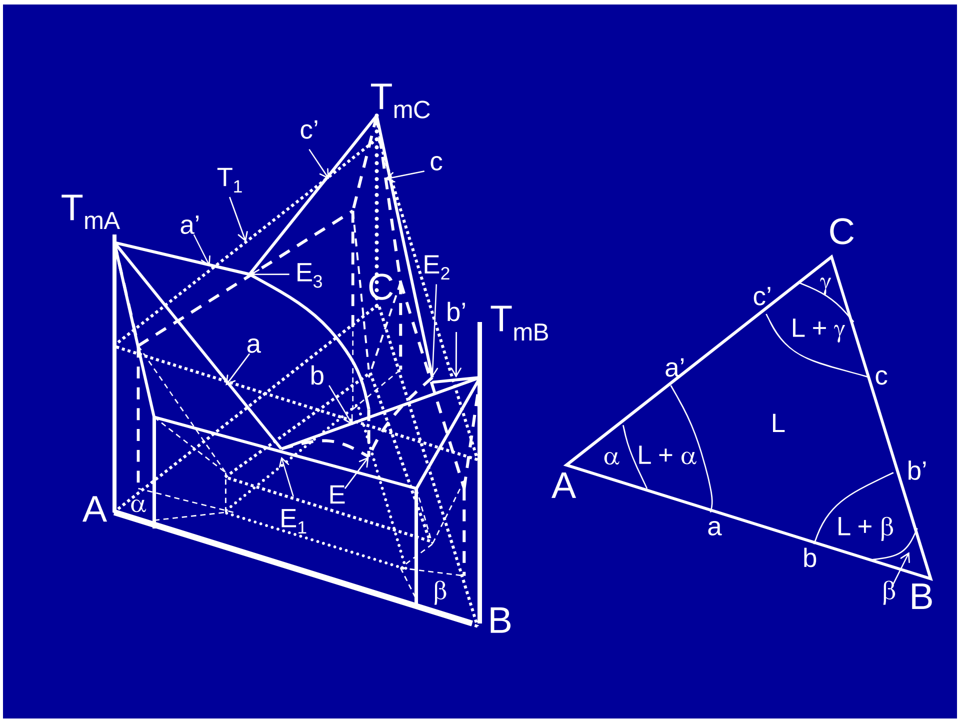
Look at the top surface of the liquidus. It has 3 curved segments. These are T_{mA} E_1 E E_3, T_{mB} E_2 E E_1 & T_{mC} E_2 E E_3. Its appearance from the top would look like the sketch in slide 5. The curved lines are the temperature contours (trace of the isothermal planes with the surface representing the liquidus.



Slide 5

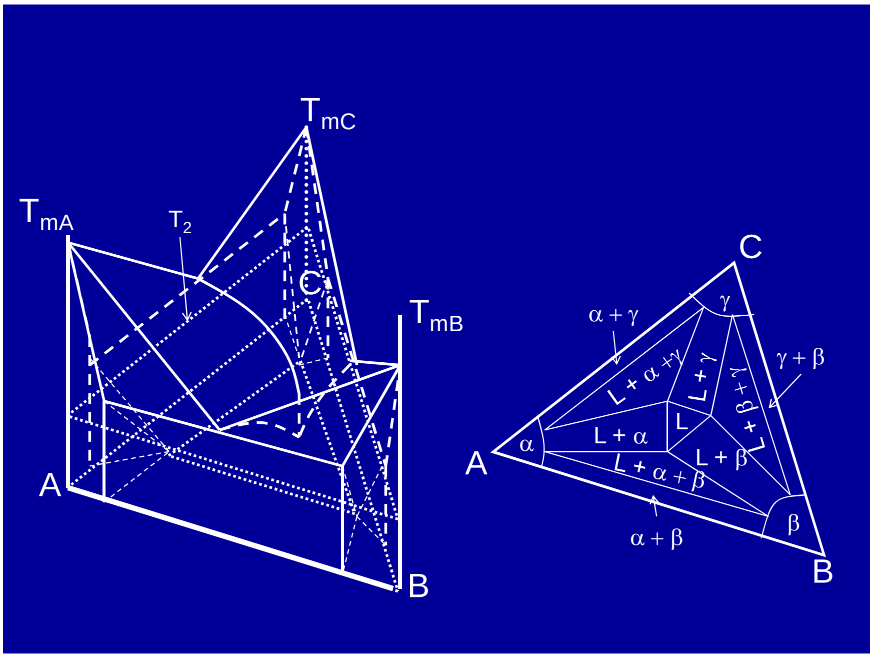
The temperature contours are marked as T_1, T_2, $T_{3,}$ & T_4. Note that $T_1 > T_2 > T_3 > T_{4.}$ E denotes the eutectic where 4 phases can co-exist. The eutectic is the last liquid to solidify. The curves E_1E denotes the curve along which the liquidus surface coming down from the melting points of A & B intersect.

3D representation is often difficult to interpret. Isothermal sections are used to represent the domains of expected phases as a function of composition. Slide 6 gives a typical sectional the ternary eutectic diagram by a plane at $T = T_1$.



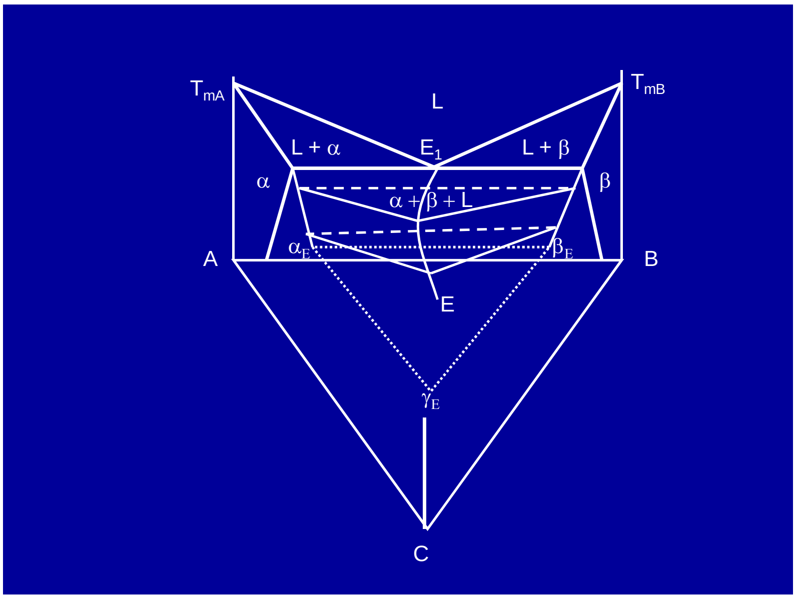
Slide 6

Slide 7 gives an isothermal section of the ternary diagram at a temperature (T_2) lower than all the 3 binary eutectic temperatures but higher than that of the ternary eutectic.



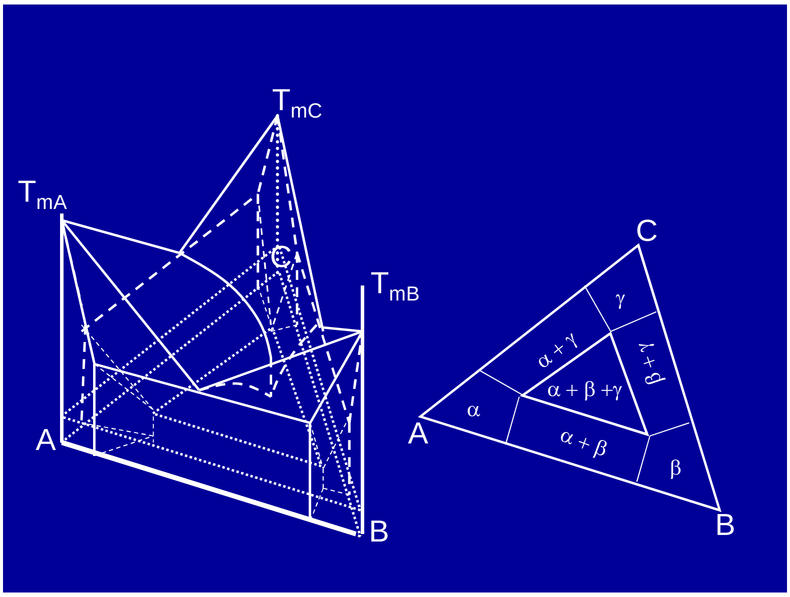
Slide 7

Slide 8 would help you appreciate the origin of the triangular shaped three phase regions in the isothermal section shown in slide 7. Only a part of the 3D ternary diagram is shown. The triangle $\alpha_E\beta_E\gamma_E$ is the plane denoting the ternary eutectic reaction isotherm. The point E is the composition of the eutectic (the last liquid to solidify).

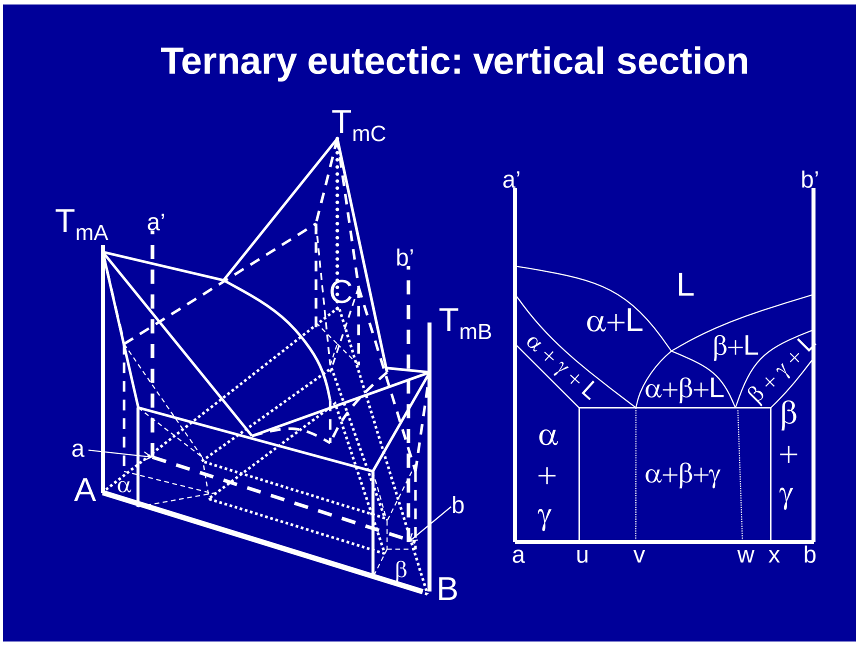


Slide 8

Slide 9 shows an isothermal section at a temperature lower than the ternary eutectic. Only the alloy having a definite composition E will solidify as a mixture of three phases called ternary eutectic. The regions away from this point may have all the three phases having different structural features. There may be primary phase, binary eutectic and ternary eutectic. The vertical section such as the one given in slide 10 shows how the structure would vary as move from point a to b.

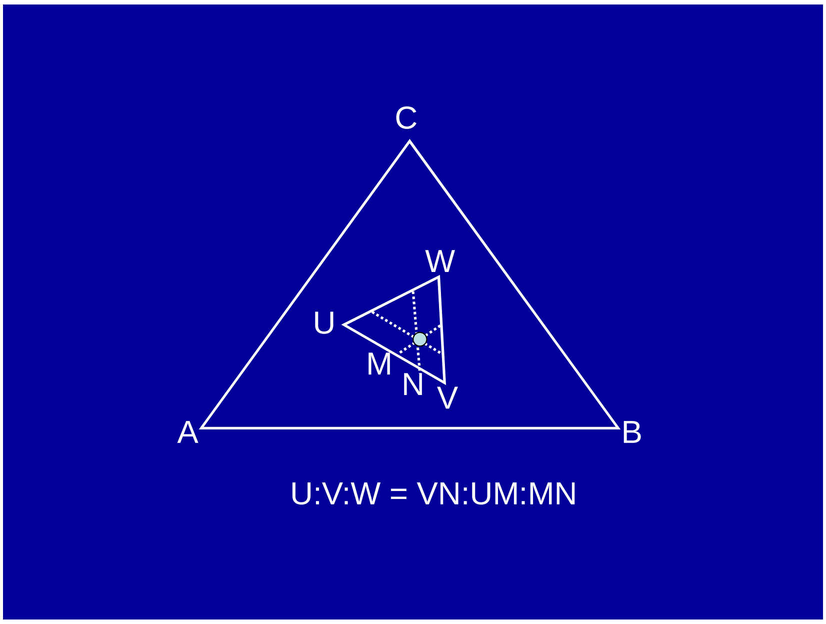


Slide 9



Slide 10

The sketch on the left in slide 10 is the 3D view of the ternary phase diagram. The sketch on the right is the vertical section along the plane a'abb'. If the alloy composition lies between a & u it would consist of primary α and binary eutectic $\alpha+\gamma$. If it is between u & v it would have primary α, binary eutectic $(\alpha+\gamma)$ and ternary eutectic. Between v & w the alloy will have binary eutectic $(\alpha+\beta)$ and ternary eutectic & so on.



Slide 11

Slide 11 illustrates the method of estimating the amounts of phases in a 3 phase region. The sketch in slide 11 shows a triangle UVW where three phases viz. U, V & W can coexist. Let the alloy composition be represented by the point within UVW. Draw 3 lines parallel to the three sides of the triangle UVW but passing through the point as shown in the sketch. The amounts of the three phases are given by U:V:W = VN:UM:MN.

Higher order phase diagrams:

Binary phase diagrams can be drawn easily in a two dimensional space. We need a three dimensional space to represent ternary diagrams. However commercial alloys may have much more than 3 alloy elements. It would be impossible to represent this in a physical space. However they may be mathematically represented in a higher order space. Let us consider an isomorphous system consisting of n alloy elements. The elements have unlimited solubility in both solid and liquid state. Gibbs free energy is a measure of the stability of a phase. The free energy of a solution is given by the sum total of the individual free energy of the components and the free energy of mixing. In an isomorphous system there are only two different constituents the solid (α) and the liquid (L). The free energies of the two are given by the following set of equations:

$$G^L = \sum_{i=1}^{n} N_i^L G_i^L + RT \sum_{i=1}^{n} N_i^L \, ln a_i^L \qquad (2)$$

$$G^\alpha = \sum_{i=1}^{n} N_i^\alpha G_i^\alpha + RT \sum_{i=1}^{n} N_i^\alpha \, ln a_i^\alpha \qquad (3)$$

For simplicity let us assume that the solutions are ideal so that the activity can be taken to be equal to the respective mole fractions $\left(a_i^L = N_i^L\right)$. Recall the expressions used to calculate binary isomorphous phase diagram from the thermodynamic properties of the two components. This can be extended to a ternary isomorphous system as follows:

$$lnN_A^\alpha = lnN_A^l + \frac{\Delta H_{mA}}{R}\left(\frac{1}{T} - \frac{1}{T_{mA}}\right) = lnN_A^l + F_A \qquad (4)$$

$$lnN_B^\alpha = lnN_B^l + \frac{\Delta H_{mB}}{R}\left(\frac{1}{T} - \frac{1}{T_{mB}}\right) = lnN_B^l + F_B \qquad (5)$$

$$lnN_C^\alpha = lnN_C^l + \frac{\Delta H_{mC}}{R}\left(\frac{1}{T} - \frac{1}{T_{mC}}\right) = lnN_C^l + F_C \qquad (6)$$

$$N_A^\alpha + N_B^\alpha + N_C^\alpha = 1 \qquad (7)$$

$$N_A^L + N_B^L + N_C^L = 1 \qquad (8)$$

To find the compositions of the liquid and solid that can coexist at a temperature we need to know the melting point and the latent heats of fusion of the three components. Therefore at a given temperature T the functions F_A, F_B, & F_C can be calculated. Note that there are six unknowns $(N_A^\alpha, N_{B,}^\alpha N_C^\alpha, N_A^L, N_{B,}^L N_C^L)$. But there are only 5 equations. To solve it we need another equation. At a given temperature we can have at best two phases. Let the weight fraction of solid (α) be W_α and that of the liquid (L) be W_L. The total free energy of the system can therefore be represented as:

$$G^T = W_L G^L + W_\alpha G^\alpha \qquad (9)$$

$$W_\alpha + W_L = 1 \qquad (10)$$

Let us now evolve a strategy to minimize the total free energy. For a given composition of the solid use the equation set 4-6 to find the composition of the liquid. Once these are known the free energies of the solid and the liquid can be estimated. Find what combination of the weight fraction solid and weight fraction liquid the total free energy is the lowest. This is how W_α & W_L at every point of the composition triangle can be estimated.

The same concept can be extended to a ternary eutectic system as well. Let us find the temperature at which eutectic reaction would take place in a ternary system consisting of three metals A, B & C. Assume that they are miscible in all proportion in the liquid state but they are insoluble in the solid state. Recall the expressions that were used to find the eutectic temperature in a binary system. In a ternary system we would have an additional equation. These are given in slide 12 along with the data used to estimate the eutectic temperature.

Ternary eutectic: Estimation of eutectic temperature

$$\bar{G}_A^\alpha = RT \ln N_A^l + \frac{\Delta H_{mA} \Delta T_{mA}}{T}$$

$$\bar{G}_B^\beta = RT \ln N_B^l + \frac{\Delta H_{mB} \Delta T_{mB}}{T}$$

$$\bar{G}_C^\gamma = RT \ln N_C^l + \frac{\Delta H_{mC} \Delta T_{mC}}{T}$$

T_{mA}	1200
ΔH_{mA}	10000
T_{mB}	1000
ΔH_{mB}	10000
T_{mC}	800
ΔH_{mC}	10000

T	NA	NB	NC
511.3015	0.257968	0.315455	0.426577

Slide 12

The solids are assumed to be immiscible. Therefore the partial molar free energies of the components are equal to zero ($\bar{G}_A^\alpha = \bar{G}_B^\beta = \bar{G}_C^\gamma = 0$). We have 4 unknowns. These are the eutectic temperature and the composition of the eutectic liquid (N_A^l, N_B^l, N_C^l). Note that we have another equation that the atom fraction A, B & C in the liquid is equal to 1. The table in slide 12 gives a set of values for the melting points and latent heats of fusion of the three metals. This can be solved using a simple iterative scheme using spreadsheet. If the melting points and the latent heats of fusion of the three components are identical the eutectic composition will be given by $N_A = N_B = N_C = 0.333$.

The method described above is generic. It can be extended to higher order systems. The approach is similar even in the cases where the solutions do not follow Raoult's law. The appropriate solution model or data on activity coefficients are to be included in the expressions defining the equilibrium between respective phases. In short more numbers of thermodynamic parameters are to be taken into account. Several extensive computer databases on a wide range of materials are now available. They are linked with solvers and post processors which can generate and display different forms of phase stability diagrams on binary, ternary or higher order system. Two of the most widely used packages for generating phase diagrams are Thermocalc & Factsage. These are equipped with user friendly computer interfaces with adequate help levels. They are being widely used to evaluate multi-component phase diagrams. The packages may differ in details. However all of them are based on the concept of minimization of Gibbs free energy.

Summary:

In this module we have learnt ternary phase diagrams. This gives a geometrical display of the domains of the stability of various phases as a function of temperature and composition. An equilateral triangle is used to represent the composition of the alloy. The transformation temperatures are displayed on the lines perpendicular to the point representing the alloy. We looked at the basic features of a ternary isomorphous and a ternary eutectic system. 3D representation is often difficult to use. Isothermal & vertical sections are more convenient to use. The former gives a display of the domains where different phases are to be found at a given temperature. The latter gives the transformation temperatures for a set of alloys along a line on the composition triangle. A number of such diagrams were presented. The problem associated with display of phase diagrams of higher order systems was discussed. It can only be represented mathematically in a higher order space. How to assess the stability of various phases in such a system has been discussed.

Exercise:

1. Sketch a composition triangle to represent composition of a ternary alloy and locate the alloys having following compositions (a) 20A 40B 40C (b) 60A20B20C

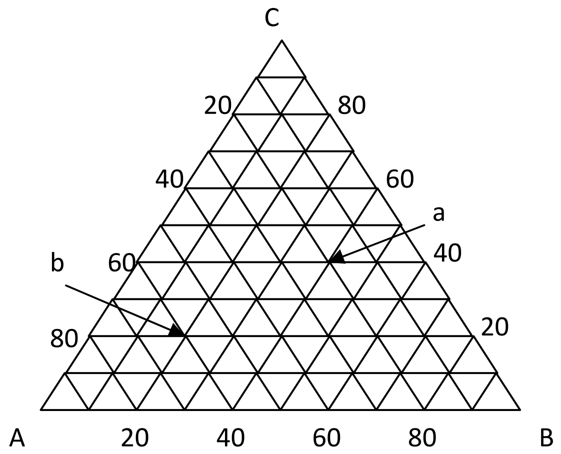
2. In a ternary system estimate amount of α & β in an alloy having 22.5%A, 23.5%B, 50%C at a given temperature T where three phases a, b and liquid are in equilibrium. Composition of these three phases are liquid: 15A 15B70C, α: 60A20B20C, β:20A40B20C

3. Find out the composition of the alloy which has 50% α & 50% β at temperature T for sytem described in problem 2.

4. A ternary system consisting of three metals A, B & C has two binary eutectics; one between A & B and the other between B & C and one binary isomorphous system between A & C. The system has two terminal solid solutions (α and β). Assume that the temperature of binary eutectic between A & B is higher than that of B & C. (a) Sketch a space model of this system indicating single phase, two phase and three phase regions. (b) Sketch an isothermal section at a temperature where there are single phase, two phase and three phase regions. (c) Sketch a vertical section passing through B and the midpoint between A & C of the composition triangle.

Answer:

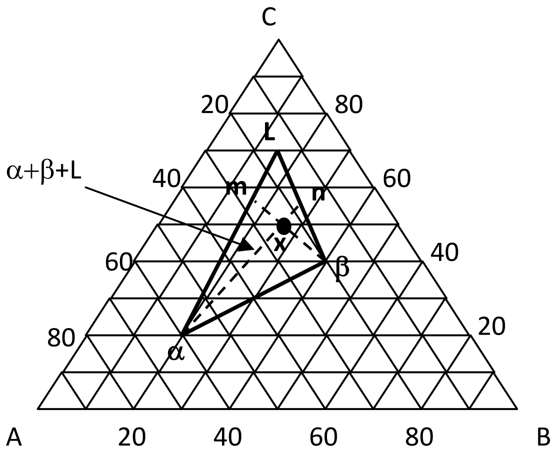
1.



2. Isothermal section at temperature T is given in the following figure. Alloy composition is represented by point x. This lies within a triangle whose vertices denote the composition of α, β and liquid. Join the points α & β with x and extend these lines to meet the opposite side at points m & n. Measure the lengths αn, xn, βm &xm.

$$\%\alpha = \frac{xn}{\alpha n} \times 100$$

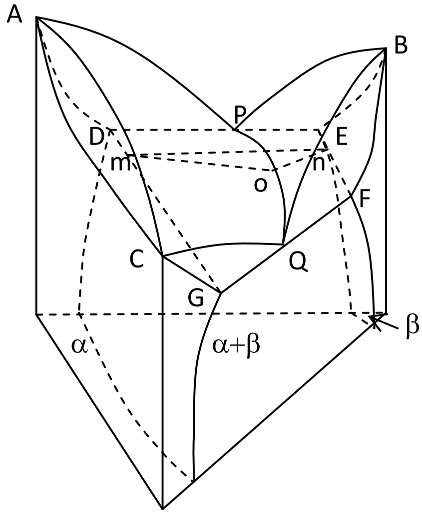
$$\%\beta = \frac{xm}{\beta m} \times 100$$



3. Alloy having 50% $\alpha + 50\%\ \beta$ is the mid point of tie line $\alpha\beta$ of the above diagram. In this case it is 40%A 30%B 30%C

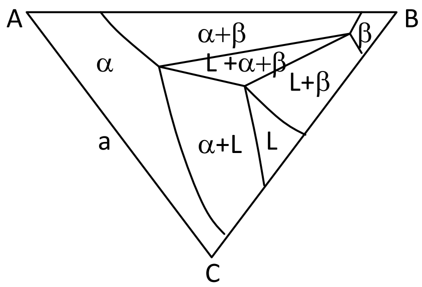
4. Sketch of the 3-D model of this system:

(a)



Note: line joining eutectic point P with Q is above the surface joining DEFG. There is a surface joining lines DE with FG passing through line PQ. Triangle mno is a section of the region between these two surfaces.

(b)



(c)