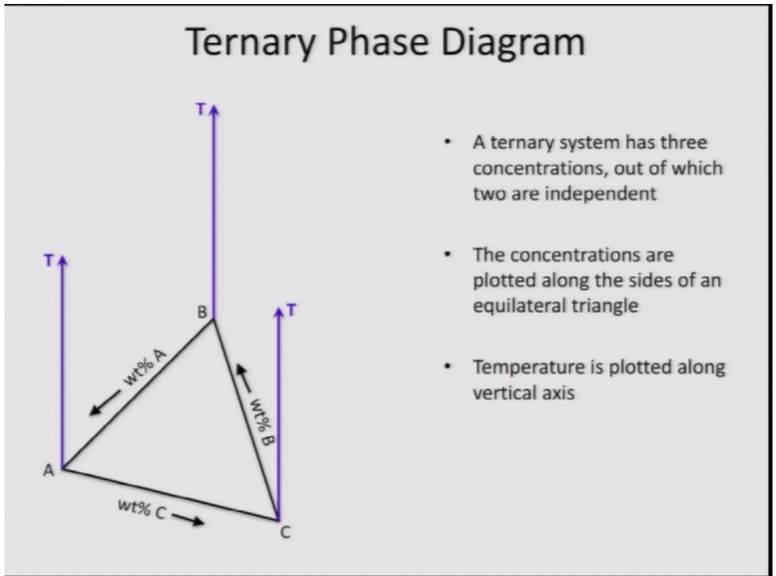
Diffusion in Multicomponent Solids
Professor. Kaustubh Kulkarni
Department of Material Science and Engineering
Indian Institute of Technology, Kanpur
Lecture No. 49
A Brief Introduction to Ternary Phase Diagrams

Welcome to the forty ninth lecture of the open course on diffusion in multi-component solids. In this lecture I have briefly given an introduction of ternary phase diagrams through the perspective of our class, isothermal sections or isotherms are very important and hence the primary focus in this lecture is to illustrate how to read ternary isotherms. I have also presented an example of a ternary isotherm of copper-nickel-zinc system.

So, far we have studied diffusion in single phase systems or we have studied single phase diffusion, which means the terminal alloys which were used for diffusion couple both had same phases to start with and there was no new phase forming during the course of the diffusion. Next few classes we would study multiphase diffusion. In multiphase diffusion either we start with two terminal alloys which have two different phases or even if we start with two terminal alloys having the same phases during the course of diffusion a new phase or a multiphase layer forms in the diffusion zone.

While studying multiphase diffusion we would often refer to ternary isotherms and hence in this lecture I would like to briefly introduce to ternary phase diagrams, with the focus on how to read ternary isotherm, because that is more important through our class' perspective.

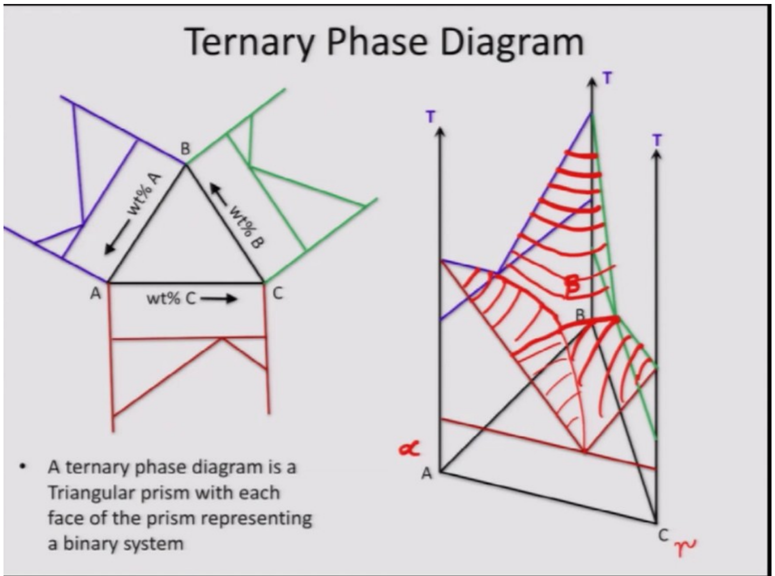
(Refer Slide Time: 01:55)



In a binary system there are two concentration variables out of which only one is independent and hence a ternary phase diagram has to be plotted in 3 dimensions in which temperature is plotted on a vertical axis and two independent concentration variables on the horizontal axis. Typically this is how a ternary phase diagram is plotted. At the base of the diagram there is an equilateral triangle which represents three concentration variables.

So, triangle ABC here is an equilateral triangle, corners A, B and C represent 100 percent of pure elements A, B and C and on the vertical axis temperature is represented. The sides of the triangle represent the binary compositions, so side BA represent binary composition of system BA, AC represents the binary composition of the system AC and BC represents the binary composition of BC.

(Refer Slide Time: 03:16)

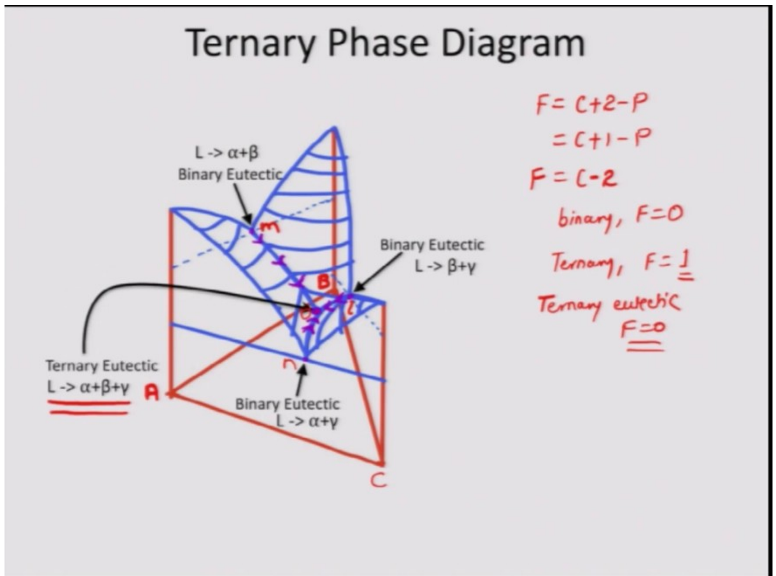


So, I have shown the base of the ternary phase diagram here. This is usually referred to as the ternary triangle or a Gibbs triangle, we will see how the compositions can be read on this ternary triangle, but before that I would like to explain how the ternary phase diagram is constructed. So, in this triangle each of the edges represent binary systems, let us simply consider the simple eutectics.

So, let us assume that all 3 of the binaries are simple eutectic systems and I have shown these simple eutectics on the sides, so this is the eutectic system AB, this one is eutectic system BC and this is the eutectic system AC. If I make this binary phase diagrams stand vertically on the respective edges and extend various phase fields into the ternary compositions, it will form a ternary phase diagram. Remember any composition that lies inside the triangle is a ternary composition. So, if I make this binary phase diagrams stand up on the edges it would look something like this, I have not shown the extension of the phases on this diagram into the ternary compositions as yet. Since all 3 systems are simple eutectics, there are 4 phases in all on this phase diagram. The 3 solid solutions αwhich is basically pure A, β which is pure B and γwhich is pure C. And the fourth phase is liquid, we can see there are 3 eutectic points one for AB, one for BC and one for AC here, so if we extend the liquidus of all the binary phase diagrams into the ternary composition range, then it will form basically the liquidus surface of the ternary phase diagram ABC.

So, if I roughly extend, this is basically the liquidus surface. If I mark the isothermal sections on this liquidus surfaces, so this is how the ternary phase diagram ABC would look like from the top. So, basically a ternary phase diagram is a triangular prism with each phase of the prism representing a binary system.

(Refer Slide Time: 07:10)



I have redrawn this ternary phase diagram here, we can note there are 3 binary eutectics here, a binary eutectic is a 3 phase equilibrium and these 3 eutectics are one on the binary system. Let us write the ABC corners here, in binary AB the eutectic reaction is liquid going to $\alpha+\beta$, in BC the eutectic reaction is liquid giving $\beta+\gamma$ and in AC it is liquid giving $\alpha+\gamma$.

In a binary phase diagram, a eutectic is an invariant that is because of the constraints put by the Gibbs phase rule. So, if I write the equation for Gibbs phase rule it says:

$$F=C+2-P$$

Since I am considering phase diagram at constant pressure, so this would be:

$$F=C+1-P$$

In a binary eutectic there are 3 phases in equilibrium, so we have for 3 phase equilibrium:

$$F=C+1-3=C-2$$

So, this shows that:

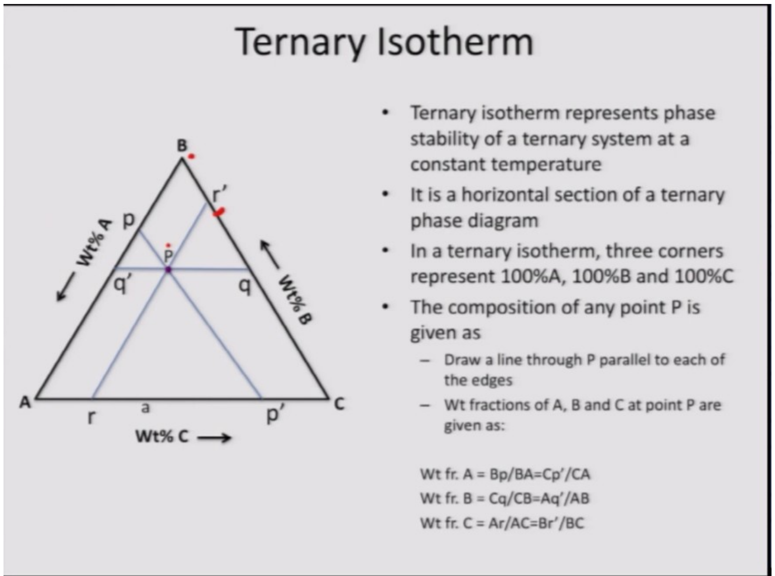
$$For\ binary\ , F=0$$

that means there is 0 degree of freedom for a eutectic equilibrium on a binary phase diagram. However, in ternary since $C=3$, so we still have one degree of freedom, $F=1$ and hence a binary eutectic in a ternary phase diagram solidifies over a range of temperature. I have highlighted the ranges of three different binary eutectics by the arrows here. So, if I denote these lines as let us call this m this n and this binary eutectic point as L where the three lines intersect is point o, so the line $mo, no \wedge Lo$ which are going down represent the solidification ranges of binary eutectics including phases $\alpha\ \beta$ and $\beta\ \gamma$ and $\alpha\ \gamma$ respectively, the three binary eutectics intersect at this point o and it represents a ternary eutectic, a ternary eutectic has 4 phases in equilibrium.

So, this ternary eutectic o represents the reaction: $L \rightarrow \alpha+\beta+\gamma$. If I apply Gibbs phase rule for ternary eutectic here, we will see $F=0$ that means on a ternary phase diagram a ternary eutectic or a 4 phase equilibrium represents an invariant, that means it occurs at a single composition and single temperature. And hence, a ternary eutectic solidifies at a single constant temperature.

Now, this is a very simple case where we considered all three binaries to be simple eutectics, but there may be a number of intermediate phases forming in each of the binary system, also there may be some ternary phases which may be forming and hence the ternary phase diagrams may become very complicated. However, for this class we are not interested in studying the ternary phase diagrams in depth, but we are only interested in knowing how to read ternary isotherms, so that we can use it later on in when we study multiphase diffusion. So, I would now briefly introduce you to how to read ternary isotherms.

(Refer Slide Time: 11:25)

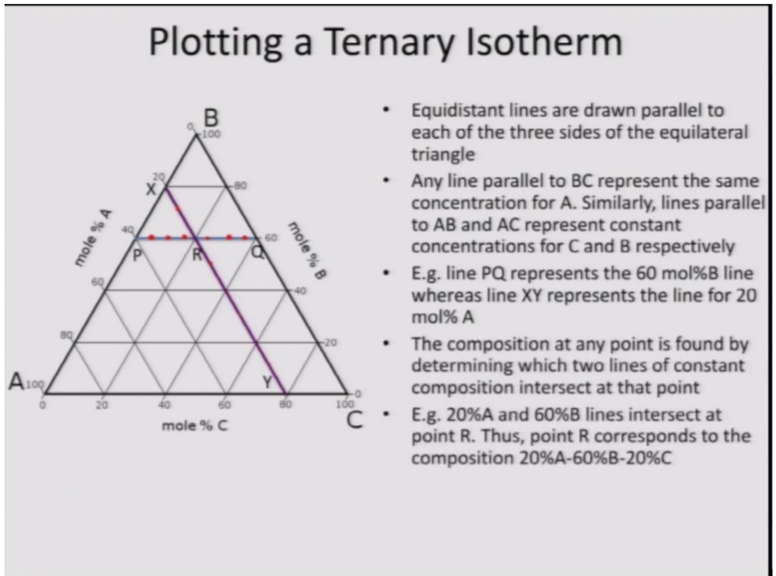


As the name suggests a ternary isotherm is nothing but an isothermal section of a ternary phase diagram. And since a ternary phase diagram is a triangular prism and isothermal section should be an equilateral triangle. And I have shown one such triangle here ABC. Now, how to read the composition of a point inside a Gibbs triangle? So, let us consider an example of point p here. For doing this I have to first draw three lines passing through point p and which are parallel to the three edges of the triangle.

So, I have drawn line pp' which is parallel to side BC, qq' parallel to side AC and rr' parallel to side AB. The compositions can be expressed either in weight fraction, weight percent or mole fraction or more percent. In this case here I have shown the compositions in weight percent. So, the weight percent of component A in the alloy with composition p is found by finding the ratio of lengths of Bp and the length BA, or equivalently finding the length Cp' and taking the ratio with the length CA.

Similarly, the concentration of B in the alloy p is the ratio of lengths Aq' with the length AB or equivalently the ratio of length Cq with the length CB and the concentration of C is the ratio of length Ar and length AC or the ratio of Br' and BC. There are only two independent concentration variables in ternary. So, the third concentration need not be evaluated this way, because the third concentration variables would simply be a dependent variable. So, the concentration of C can also be evaluated as $1 - weight\,fraction\,of\,A - weight\,fraction\,of\,B$. For ease of reading the sides of the Gibbs triangle are usually divided in equal divisions, so that we can mark the compositions easily.

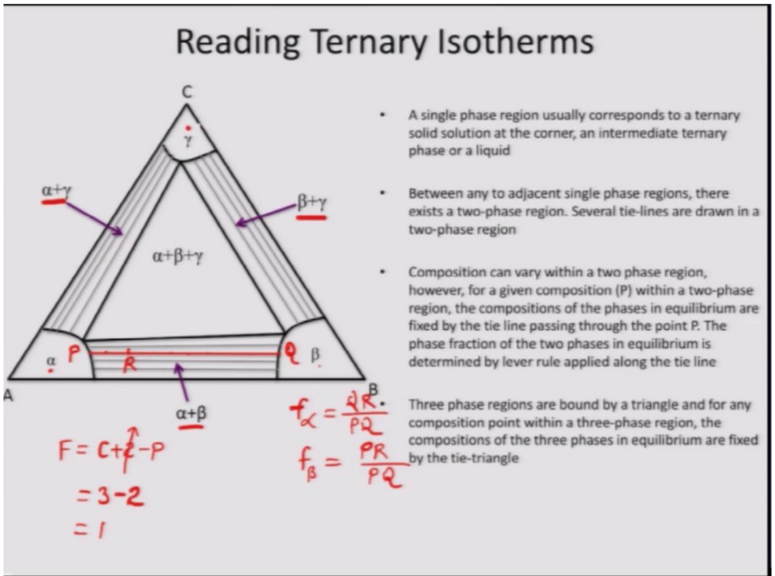
(Refer Slide Time: 14:15)



So, I have shown it on this triangle here ABC and I have shown the divisions for 20 mole percent here. As I said unit can be mole percent or weight percent, one has to be consistent throughout the phase diagram. Note that any line parallel to an edge represents a constant concentration line for an element which is opposite to that edge. So, for example if we consider line PQ, it is a line on which the concentration of B is constant, more specifically line PQ here represents 60 mole percent B line, so any alloy that lies on this line PQ has concentration of B as 60 mole percent.

Similarly, there is another line I have shown XY which is parallel to line BC. Any alloy that lies on line XY has a constant concentration of A which is 20 mole percent of A. Now, PQ and XY they intersect at point R and so the composition of alloy R would be 60 mole percent of B, 20 mole percent of A and $100-60-20$, which is 20 mole percent of C. This is how we can read the composition in a ternary triangle. So, I have covered all these points.

(Refer Slide Time: 16:08)



Now, when there are more phases present, ternary isotherm may become little more complicated, one example I have shown here in this case all the binaries have terminal solid solubility. So again I have shown the ternary system ABC, if you consider A rich corner both the binary AB and AC have some terminal solid solubility on the A rich inside, that is C is soluble in A to some extent, B is soluble in A to some extent and a corresponding phase is labelled as α. And this solubility also extends to some extent into the ternary compositions. And hence on the A rich side you will see there is a single-phase solid solution α.

Similarly, on the B rich side there is a single-phase region β and on C rich side there is a single-phase region γ. Between any two adjacent single-phase regions there has to be a two phase region. So, between α and γ, we have $\alpha+\gamma$, between α and β we have $\alpha+\beta$ and between β and γ we have $\beta+\gamma$, you will see there are multiple parallel looking lines plotted in each of the two phase regions. These are nothing but tie lines. A tie line joins the two compositions which are in equilibrium.

So, if I consider this red tie line here shown in $\alpha+\beta$ region, let us call this line as PQ. If you select any composition, let us say R here along this tie line, at this temperature the alloy R exist in two stable phases, alloy R exist as a two phase mixture, one phase α with composition P and the other phase β with composition Q. If I change the alloy composition anywhere along this tie line the phase compositions remains same. The only thing that change are the phase fractions of α and β. And we can find a phase fraction by applying lever rule.

So, if I want to find the phase fraction of α at composition R it would be simply:

$$f_\alpha = \frac{QR}{PQ}$$

and phase fraction of β would be:

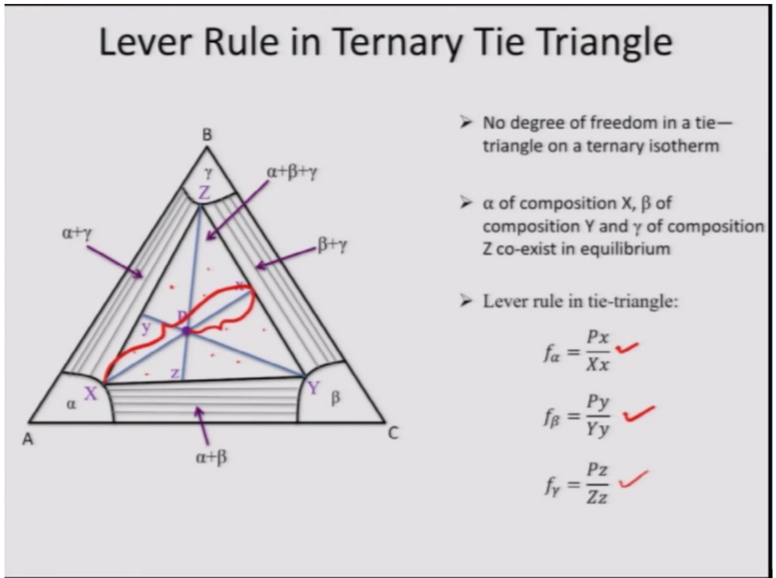
$$f_\beta = \frac{PR}{PQ}$$

length PR over length PQ. Now, when I consider binary phase diagram at a given temperature, I can draw only one tie line, but on a ternary isotherm I can see there are multiple tie lines in the same two phase region. So, if I apply Gibbs phase rule here, I can write:

$$F = C + 2 - P$$

Since the phase diagram is always at constant pressure and since I am considering an isotherm or isothermal section of the phase diagram, I am holding temperature also constant and so I do not need to consider factor 2, for a ternary C is 3 and a two phase region P is equal to 2 and so F is equal to 1. So, in two phase region on a ternary isotherm there is 1 degree of freedom and hence there are multiple tie lines. There is also a 3-phase region here that you can see $\alpha + \beta + \gamma$ and now I will talk about this three phase region.

(Refer Slide Time: 20:41)



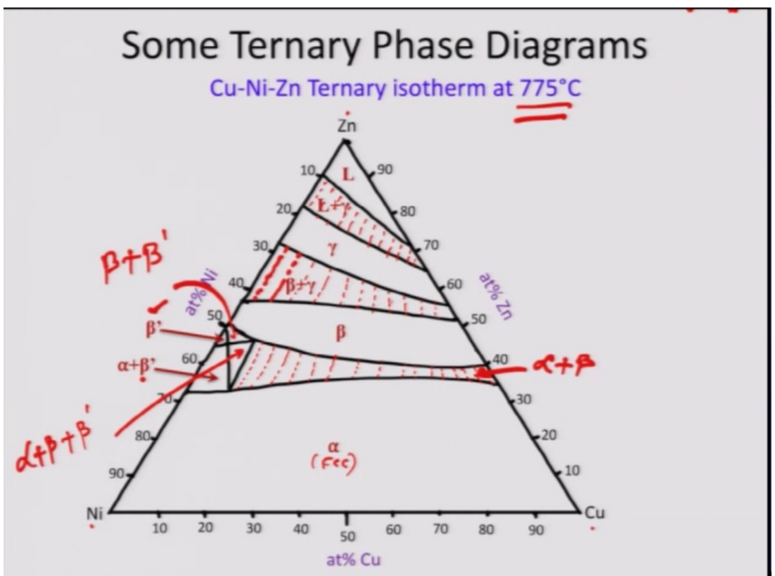
If I apply the Gibbs phase rule to the three-phase region obviously on a ternary isotherm the degree of freedom becomes 0, that means if there exist 3 phases in equilibrium at a constant temperature, their compositions are fixed. In other words, if I select any composition in this three phase region which is denoted by X, Y, Z here I know that there exist three phases in equilibrium: α with composition X, β with composition Y and γ with composition Z. And again that is because the degree of freedom in the three phase region is 0 on a ternary isotherm.

With change in composition within this 3 phase region the only thing that will change are the phase fractions of individual phases, the compositions of the phases remain same. Here, the degree of freedom is 0, hence the three phase region on a ternary isotherm is usually triangle. The corners of the triangle represent the equilibrium composition of the 3 phases, the only thing that changes with alloy composition within this triangle is the phase fraction. With change in alloy composition within the triangle the phase fractions of 3 phases will change, but the compositions of the phases will be still constant.

So, how do we find phase fractions? Again we can apply the Lever rule as applicable, to the Tie triangle. So, if I consider point P here, in order to determine the phase fractions in alloy with composition P, I have to first draw 3 lines which pass through point P and one of the corners of the tie triangle. So, I have drawn the 3 lines passing through P, it is X to small x, Y to small y and Z to small z and a phase fraction of phase α is then given by the ratio of length PX and lengthXx, $\frac{PX}{Xx}$.

Similarly, the phase fraction of β is length P small y over length Yy, $\frac{PY}{Yy}$and the phase fraction of γ would be $\frac{PZ}{Zz}$. This is how ternary phase diagram can be read. Now, there may be intermediate phases forming and we may have more complicated looking ternary isotherms. One such example, not so complicated though, but having intermediate phases I have shown here.

(Refer Slide Time: 23:43)



This is a ternary isotherm of copper-nickel-zinc at 775 ℃, this is not a very accurate isotherm and I am just showing the schematic which I have drawn. You can see the 3 corners nickel, copper and zinc; we know at 775 degree centigrade copper nickel system shows complete miscibility and that miscibility extends quite a bit into the ternary composition range and hence we see a big α FCC phase field here, then there are multiple intermediate phases both in nickel-zinc binary and copper-zinc binary and they show complete miscibility, couple of them, β for example and γ.

And of course at 775 degree centigrade zinc exist as stable liquid and so on the zinc rich corner we can see the single phase region of liquid or L. Similarly, there is a small composition range of a phase $\beta^{'}$on the nickel-zinc binary, this $\beta^{'}$ exhibits a small solubility for copper and hence there is a small region of $\beta^{'}$. Between any two adjacent single phase regions there would be two phase region and so we can see the two phase region $\alpha+\beta$ here, then $\beta+\gamma$, $liquid+\gamma$, similarly we have $\alpha+\beta^{'}$ here, this one here is $\beta+\beta^{'}$.

Each of the two-phase region we can draw the tie lines which would roughly look like this, so in $\alpha+\beta$ a tie lines may look like this, in $\beta+\gamma$ it may look like this, $liquid+\gamma$ the tie lines basically join the equilibrium compositions of the two phases in equilibrium. Now, for the precise tie lines one needs to experimentally determine those, but these tie lines would roughly look like this. There also exists one three phase region here, so there is a tie triangle here which is basically the 3 phase equilibrium of $\alpha+\beta+\beta^{'}$.

So, this is the Copper-Nickel-Zinc ternary isotherm at 775 degree centigrade, there may exist more such intermediate phases which may not show the complete solid solubility as exhibited by this β and γ here and we can have more and more complicated ternary isotherms. We will do some of them in the exercise; this was just an example that I wanted to show so that you know how to read ternary isotherms. I will stop here today. Thank you.