Principles of Physical Metallurgy

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Lecture No. #25

Ternary Phase Diagram

Good morning. Last few classes, we have been discussing about phase equilibria in a binary system.

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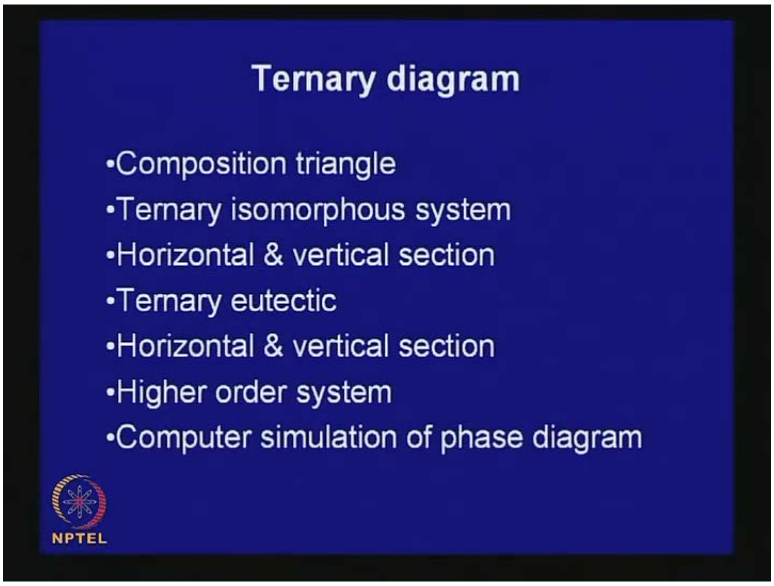

And we looked at several types of binary equlibria phase equilibria that are possible, and in binary system, we have seen at maximum number of phases that can stay in equilibrium is three. Now, today we will look at phase equilibria in a ternary component, where number of component is three, and let us see, under this case what we are going to consider. Say in a two-dimensional space, the representation of composition was quite simple, we can construct the diagram easily. But when we go to a next higher order, we need to define a method of representing composition. We will talk about composition triangle. How do we represent composition in a ternary system?

We will look at ternary isomorphous system. We will look at some of the 2 D representation of ternary diagram. This is done through different sections, like horizontal and vertical sections. We will look at one ternary system, where we have eutectic reaction at ternary eutectic. We will look at horizontal, and vertical sections of this ternary eutectic system, and from this we will see that complication, if you go to higher order, it will be impossible to represent it in a 2 D. There the only way we can extend or understand phase equilibria is through mathematical models or computer simulation. So, this is what we are going to cover today.

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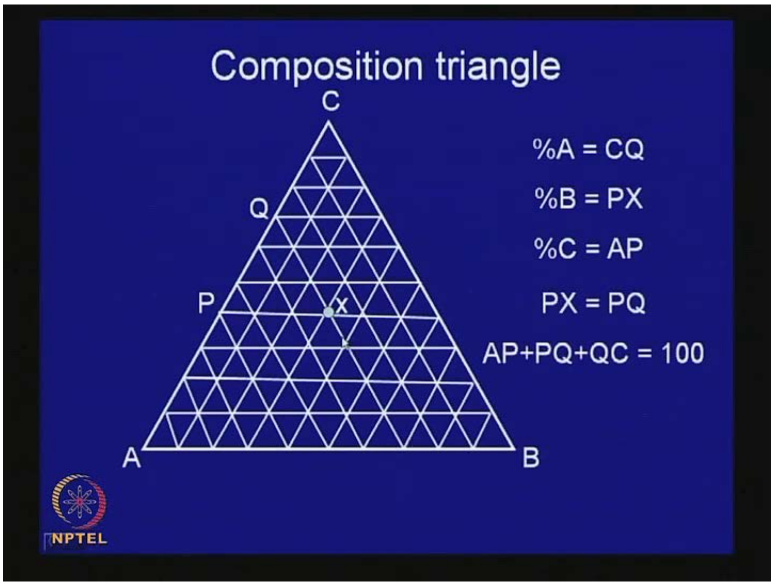

Let us begin this lecture with composition triangle, which is shown over here. So, we use a an an equilateral triangle, where each corner this corner represents pure A; this corner represents pure B; this corner represents pure C. And now, say this triangle we can construct like in a 2 D graph; several these lines can be constructed and these lines, which represent composition and somewhere we will come to it little later. And say like these lines, which are drawn at equi distance; they represent actually the percentage. See like here, if you look at this point, percentage C is 0. Say, suppose we go to the next let us say it is 10, 20, 30, 40, 50, 60; likewise it becomes 100 over here.

And the same way these lines, which are drawn parallel to the side opposite to vertex A. So, that is C be parallel to this. These lines represent percentage A. Similarly, lines drawn parallel to the side opposite vertex B; so that means A C. All these lines parallel to A C, they represent percentage B and this end is 100 percent; this end is 0. So, now let us look at how do you represents. So, what will be the composition of this particular point? Now, here you can read it easily. Say, suppose you want to read what is the percentage

A, so here this we we you will read from this end. So, here it is 0, 10, 20, 30. So, A is 30. Similarly, how much is B?

B, you check up from here 0, 10, 20, 30. Now, you check up that whether that how much is C. So, C should therefore be 40, 30 30; it makes 60; C should be 40. Let us see what is c. So, you check up from here. This is 0, 10, 20, 30, 40; that means you add up all; you get 100. So, infact this is easily seen over here; that means percentage A is represented by that this to this; so actually it is C Q. Similarly, percentage B is represented by P X, which is actually equal to… So, this is an equilateral triangle. So, P X equal to P Q and percentage C is A P from here; from this point to this point, which is equal to A P. So, therefore you know you add all these up, it comes to 100.

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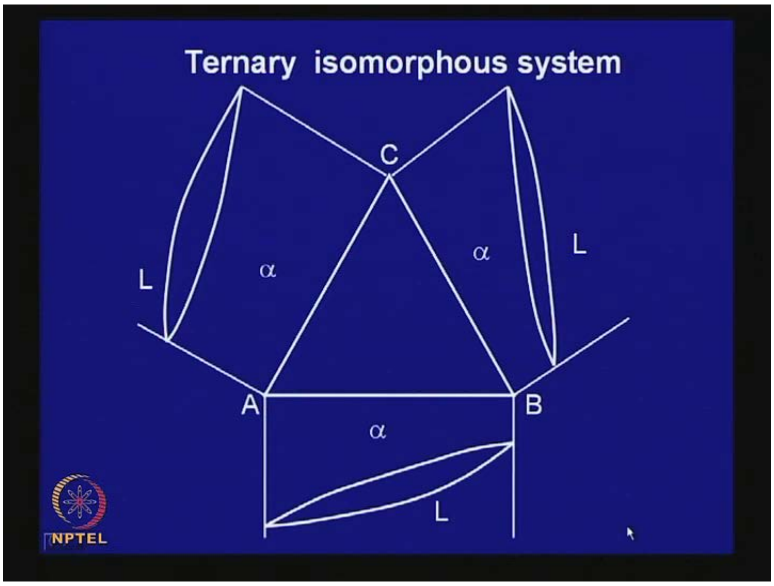

Now, having done this let us look at a ternary isomorphous system; now which is shown over here. Say, this is the composition triangle. Now, in this case you each of the binary system also must have must be an isomorphous system, which is shown here. See we have opened up; I mean we are trying to represent this in 2 D. So, this is the composition triangle. This point is pure A. Now, on this if you draw a perpendicular and here a perpendicular and draw the binary phase diagram between A and C. This portion is liquid; this is the solid solution, alpha. Similarly, we do the same thing over here. So, this melting point so this melting point on this, they are exactly seen.

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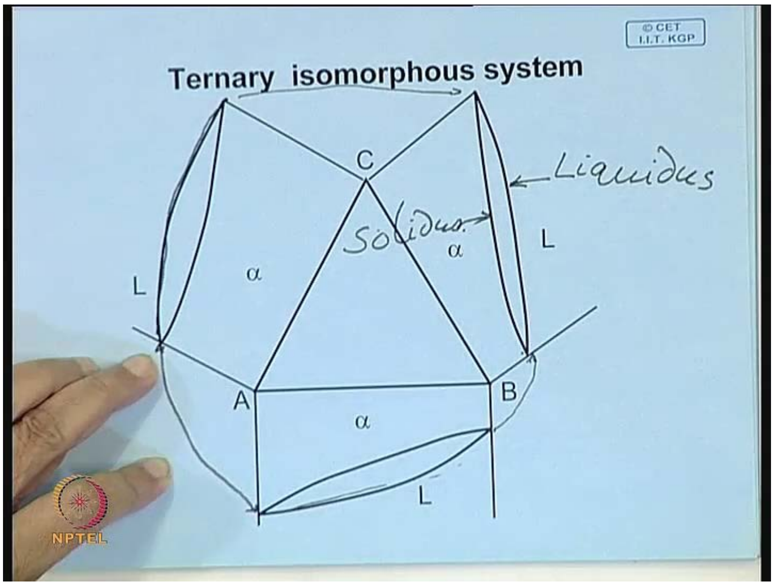

So, if you say suppose here you cut this diagram and try to fold it up. So, what will happen? Then this point and this point, they are exactly same; they will meet each other. Similarly, you cut out this portion and then this and this point, they will join together and similarly, these two. So, what you will have if you do these. You cut out this portion; draw this on a 2 D diagram; cut out this portion; fold it along this and make this vertical. Then this point will join here; this point will join with this and these two points will come over one another. And in that case in a 3 D, what you will have? You will have one surface top surface, which is made up of these liquidus line. This line is liquidus and this line is solidus. So, this liquidus represents the temperature at which, solidification begins and here solidus represents the temperature at which, solidification is completed.

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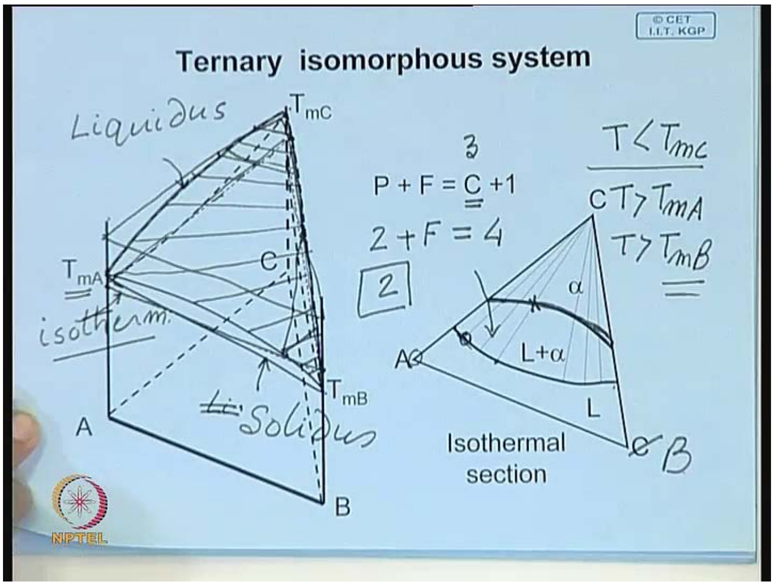

And now let us see how does this 3 D diagram look like; which is shown over here. Now, if you do this folding, so this is the top surface this is the top surface, which is drawn by firm line. So, what you so whatever you see, say this line say this line these are let us say different isotherms. So, this is the top surface, which represents… the surface this top surface represents liquidus. Similarly, you can think of that bottom surface joining this liquidus line sorry this solidus line. This is the solidus line and the other solidus line, which will not be visible in a 3 D. It is covered by the top surface and if you join these bottom surfaces; so this line, this line and this line, so it will generate a curved surface and this surface is called solidus.

So, you see 3 D, it is now quite difficult to now visualize that at particular composition and particular temperature what will this system consist of. For this, what we do? We visualize we take certain sections. Say, suppose we try and draw an isothermal section say at this particular temperature. Imagine, this is lower than this triangle; this plane. We draw a plane horizontal plane; horizontal plane means an isothermal plane. So, this this vertical axis represents temperature; this is melting point of A and this is an isotherm. This is a plane; this dotted line here this represents a plane, which intersects this temperature axis below melting point of A; below melting point of C.

But it meets the other axis above melting point of B. In that case, clearly you can see say here this will towards this. So, it will intersect. Where does it intersect these two surfaces; which is shown over here. Now, look at so one (( )) we will find the… When this surface cuts like this, I think there is some A C portion will be solid. So, it will one side; this one will cut this solidus line. So, this is A and C. So, this plane first this is that solidus line; this is B and B end, A B end is still liquid. So, this part here it intersect somewhere here; maybe here and similarly here; so which is drawn over here along. So, this portion is yet to solidify; whereas, this part has solidified.

And this is the region and you will get a region, where I think that is this diagram actually represents a section somewhere above the melting point of A; somewhere here. So, that means this temperature is lower than melting point of C. But this temperature is greater than melting point of A. It will also greater than melting point of B. So, here you can see this will section; see this part is the liquidus and the bottom part is the solidus and this portion, this side it will be liquid. Now, here look at this condition where two phases are coexisting together. If you apply phase rule and what do you get? Now, this is a ternary system; number of components, this is 3; so this equal to 4. Now, number of phases coexisting, P is 2.

So, therefore degree of freedom here is 2. Now, one we are fixing the temperature. By fixing the temperature also, we are not able to define this two phase region, unless we put there is one more variable with needs to be fixed up, which is the sty line. So, that means either you have to fix up say my liquid has this composition. Then you will be able to calculate what is the composition of the solid, which solid becomes fixed or else you have to say that solid has this composition; then the liquid becomes fixed. So, this is so therefore, I mean so this we will see later, when we will talk about how we can apply the principle of thermodynamics to calculate this phase diagram.

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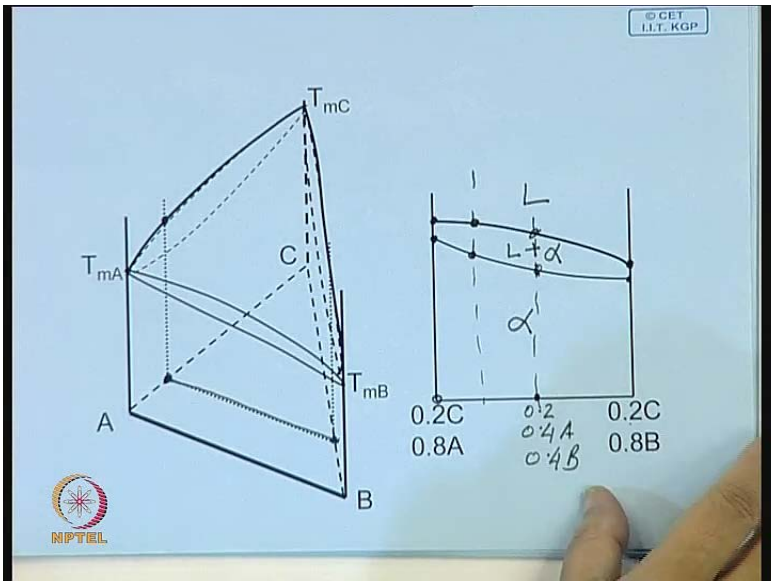

Now, next let us (( )) and see that how will the vertical section look like. Now, here in this diagram think about a vertical plane, which intersects this composition A C at this point; which is let us say this point, which is 20 percent C, 80 percent A. Similarly, this point is let us say 20 percent C, 80 percent B. Now, if you construct this, you will see that at the highest temperature, it intersects here excuse me which is shown over here. And then, this is where solidification begins and this is where the solidification is complete and this portion is liquid; this is alpha; this is liquid plus alpha.

So, same way here also you will find, it will intersect liquidus surface here and the solidus surface at this and in between here at any composition you can say that any composition. So, this is your this is where the solidification starts; this is where temperature where solidification is complete and all along this composition line, the percentage C is same. What is changing is the ratio of A and B. So, here it is 80 percent A; here it is 80 percent B; somewhere in between it may be 0.2, 0.4 A, 0.4 B. So, there you can read from this diagram; this melting range of that particular alloy.

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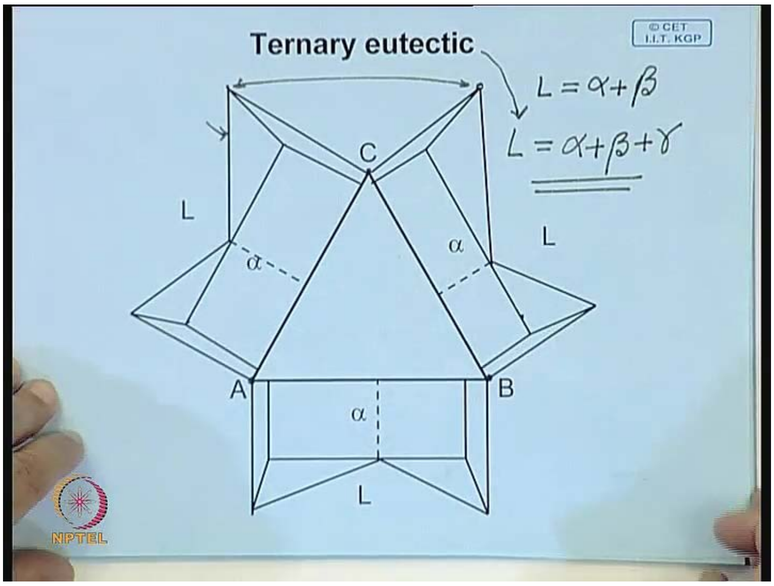

Now, let us see take up the case of a simple ternary eutectic. Now, see in a ternary eutectic what happens in a binary eutectic. We have seen that a liquid breaks down into two solids; alpha and beta. Now, in case of a ternary eutectic, there will be liquid of a particular composition will decompose at the same temperature into a mixture of three solid. This is ternary eutectic this is the ternary eutectic. Now, let us see that how do we construct a ternary eutectic diagram. Now, here let us take up a case, where each of these binary; they are simple binary eutectic. This is the binary eutectic isotherm.

This is the binary eutectic isotherm for system A B. This is the binary eutectic temperature for the system B C and this is the binary eutectic temperature for the system A C. Now, here also what you do is here also you cut out this portion and fold it along this line and now, you imagine this is the liquidus line. Now, this point will join with this. So, one liquidus surface will drop down from that vertex that C like this. Similarly, another liquidus surface will drop down from that vertex at A somewhere here. Similarly, the third one from the melting point of B and they will all meet at that eutectic point and which is shown here.

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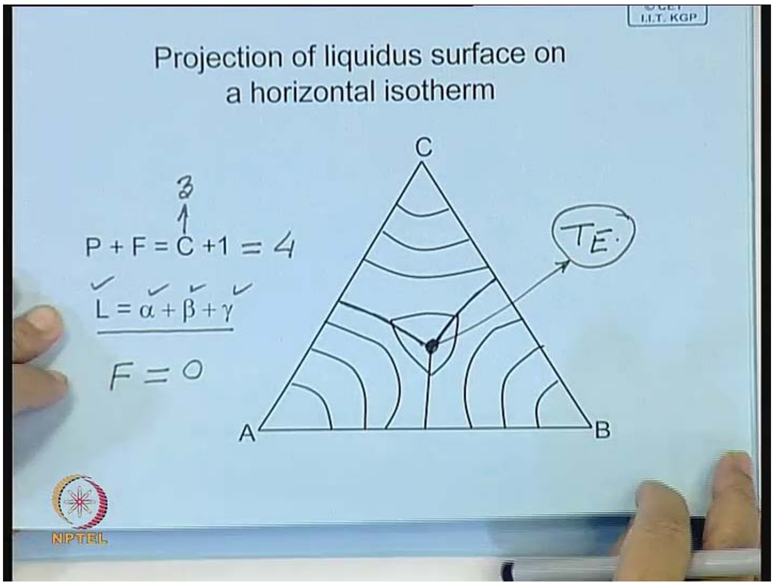

So, that means this is the liquidus surface. This is the projection of the liquidus surface on an horizontal plane. If you look from the top of this, it will look like as if; this is a surface which is coming down. This is a surface which is coming down from the point over A; at the melting point of A like this and like this and they will all meet along these lines; these curves. Along these curves, they will meet and this is the ternary eutectic point. This point is the ternary eutectic ternary eutectic. Now, in a ternary eutectic if you apply in this case; so this is the temperature, it will take place at a definite fixed temperature and the composition of alpha, beta, gamma will be fixed.

Let us see what you get if you apply phase rule. Now, here this component this is 3; so this is 4. Now, how many faces you have in equilibrium? Now, number of phase when this eutectic reaction takes place; 4 phases are coexisting. Now, if 4 phases are coexisting, in that case your degree of freedom this becomes 0; that means composition of liquid and each of these solid phase will be fixed. And later on, we will see we will do a simple a solver problem to show how to find out that eutectic temperature. Assuming the solution liquid solution to be ideal and assuming there is no solubility in solid state.

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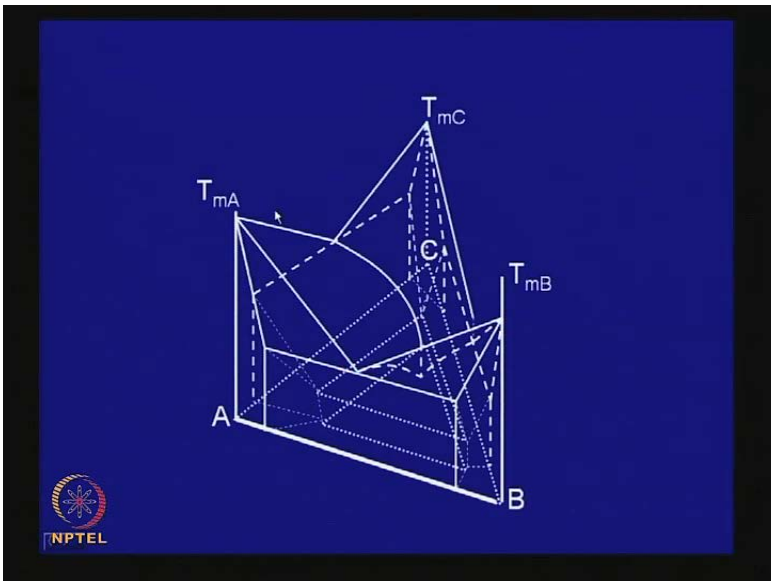

Now, let us look at this diagram the nature of this diagram, which is… Here these are the three axis; here you look at this is the liquidus surface, which is coming down from that melting point. Say on this line is the T m A is the melting point of A. This is the liquidus surface; this line similarly consisting of this.

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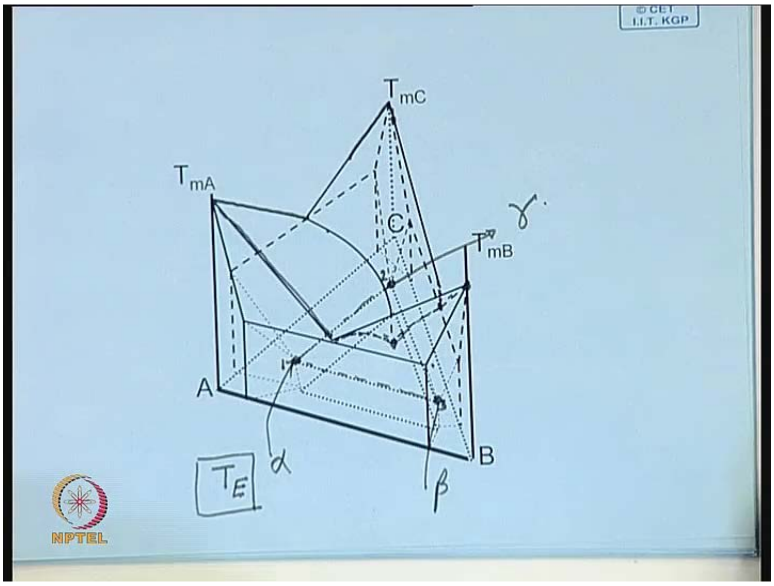

So, in this if you look at here this line, this surface, this, this; then this line, this surface; this is one phase; liquidus phase. Similarly, there will be one consisting of this, this and then this, then this, this. Similarly, a third surface will be from a melting point of B and two of these they will meet along a line like this; a curve like this. Similarly, this surface one coming down from melting point of B and one coming down from the point T m A; they will meet along this. So, there will be a three curves along which, these surfaces will meet and inside I have drawn this is the isotherm; this triangle say 1, 2, 3. This you can say this is the temperature eutectic temperature; that is isotherm at eutectic temperature, where all these are meeting and these are the fixed composition. This is the alpha; this is beta and this is gamma and they have fixed composition. So, at this temperature T E that equilibrium there will be equilibrium between liquid of specific composition with three solids of specific composition; that is 1, 2, 3.

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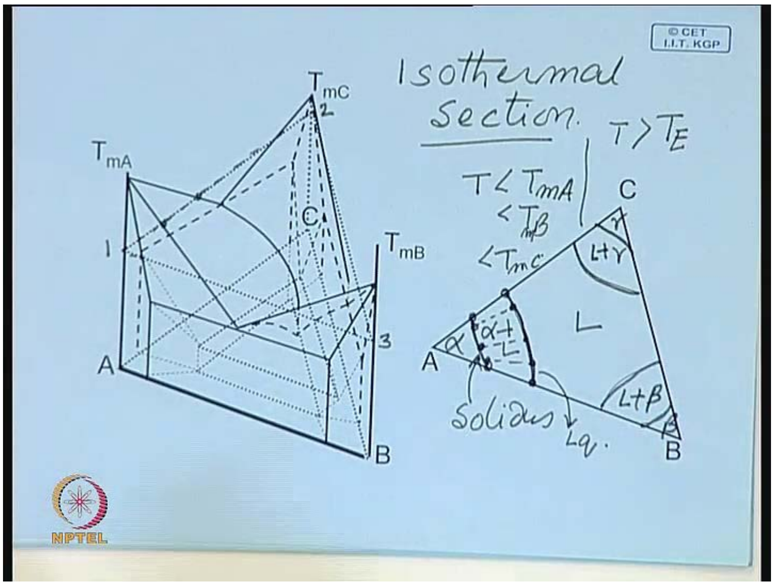

Now, let us try and construct say sectional diagrams. Now, let us look at one isothermal isothermal section isothermal section and we are taking it at a temperature T, which is lower than each of these melting temperature. This is lower than melting point of A; this is also lower than melting point of B and lower than melting point of C. But it is greater than the eutectic temperature. Now, here in that case, this is the plane here which is drawn; this is the plane. So, 1; this is 2; this is 3. So, here you can see this plane will intersect this somewhere here; this line somewhere here. So, this is the liquidus line, A end.

So, this is one point; this is one point. So, this is the liquidus line. So, you get this is the liquidus line. Similarly, this plane will intersect this line here. Similarly and similarly, the solidus this and there will be another here; so these two and this will be the solidus.

This is the liquidus and here you will have alpha plus liquid and here you can also draw tie lines. So, you have to fix specify the temperature of the solid, which will be equilibrium with the liquid. So, similarly there will be such two phase region on each of these three ends. This will be liquid plus gamma; this portion is liquid; this is alpha; this is beta; this is gamma; this is liquid plus beta.

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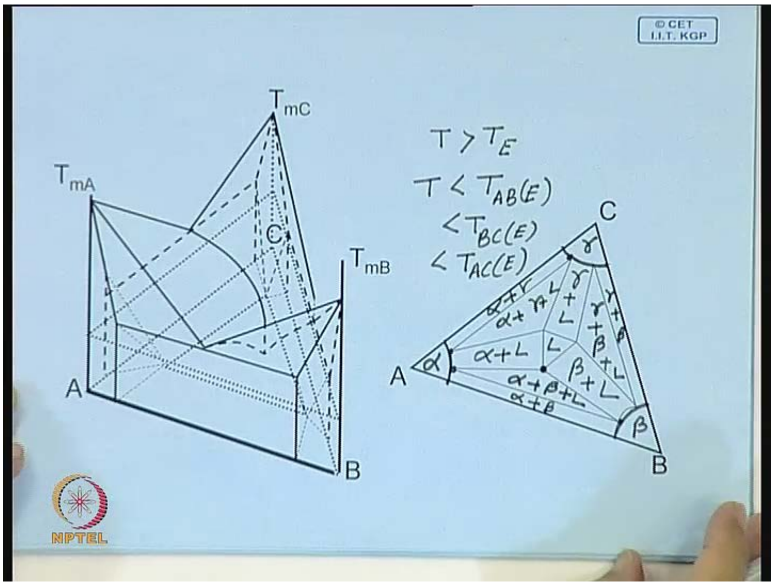

Now, let us see having done this let us look at the isothermal section at a temperature, which is lower than each of these three eutectic temperatures. There are three binary eutectic temperatures. So, we are taking a section at a temperature, which are lower than the binary eutectics of each of these three systems. But higher than the ternary eutectic isotherm, say little over the temperature is little greater than the ternary eutectic. But it is temperature is less than each of these binary eutectic, say A B eutectic or it is less than B C eutectic; less than A C eutectic temperature. Now, here it is very easy to visualize; because each of these end A B C, there will be a region where it will be single phase. So, this is alpha; this is beta; this is gamma. Now, similarly here there will be some of these points. There will be regions, where there will be only alpha and beta coexisting.

See the end; say we are taking say suppose here this will be alpha plus beta and this is the portion, which is liquid. This portion will be alpha plus gamma; this portion will be gamma plus beta. Now, here we will see that why this type of a triangular region should exist. This portion will be alpha beta liquid. So, this is the composition of alpha beta and this is the composition of the liquids. Now, this portion will be alpha gamma liquid; this portion will be gamma beta plus liquid and these regions will be binary region; alpha plus liquid. This will be gamma plus liquid; this will be beta plus liquid. So, in the same way I think it is possible to construct or visualize from this type of a ternary eutectic diagram or you can construct a model and try and verify whether you get this kind of horizontal sections.

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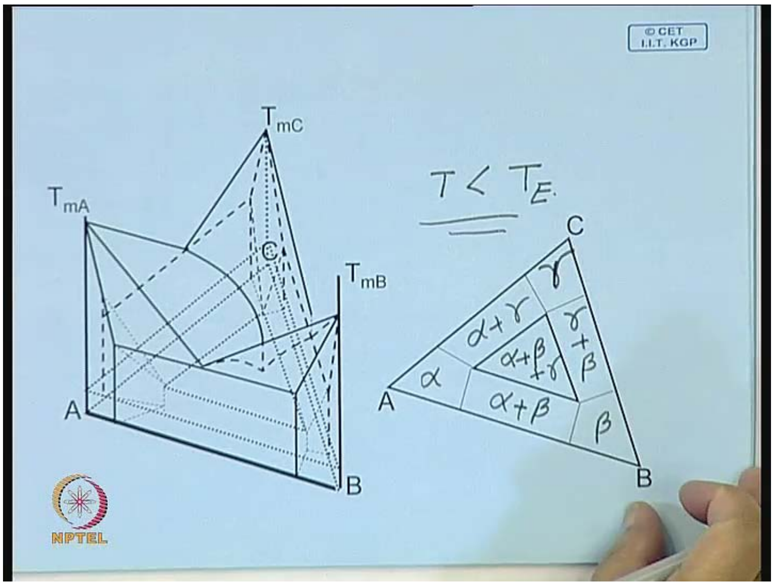

And here is the horizontal section at a temperature below the eutectic temperature. So, that means this horizontal section is below the ternary eutectic; let us say at room temperature. This is the alpha end; this is the beta; this is gamma; this is alpha plus gamma; this is alpha plus beta; this is gamma plus beta. And in this region, you have the eutectic; that is ternary eutectic will be there in this region; alpha beta gamma. This portion you will get binary eutectic alpha gamma, gamma beta.

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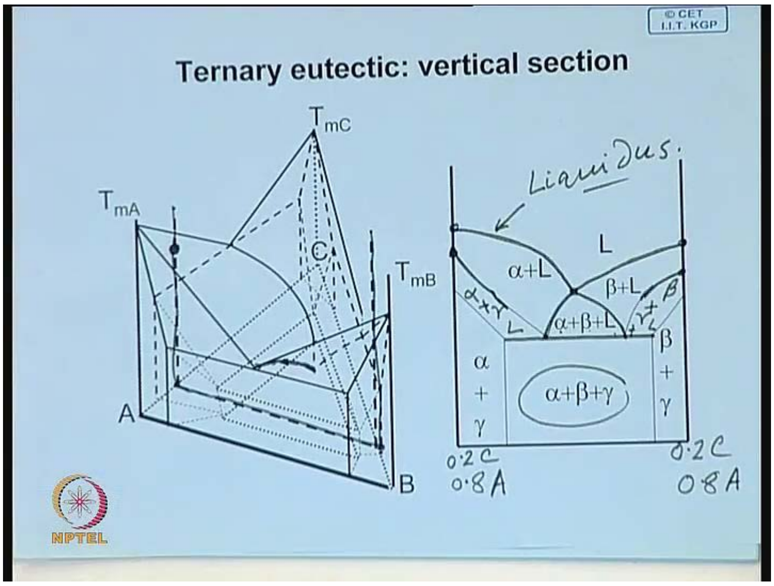

Now, let us try to understand how can be draw a vertical section. So, for that it is the three phase region; that is between that binary eutectic to ternary eutectic. It is a necessary to visualize what is the nature of this zone and we will see in the next two diagrams. Say, here it is the exactly the same diagram we have drawn here and we are trying to construct a vertical section, which is taken from along the vertical plane constructed on this line. And to construct this, we have now to visualize where these surfaces are intersected. Say, here first one is very easy to see that one; say this is the point that liquidus surface is intersected. Let us say this is 80 percent 0.8 A, 0.2 C; this end therefore will be 0.2 C, 0.8 A.

Now, so this point we can easily visualize and then these two liquidus line, they will drop down like this. This also will come like this and meet somewhere on this along that curve, where both the surfaces are meeting. So, this two; it is easy to visualize. So, this is the liquidus. So, this is the point where it intersects; this vertical plane intersects this curve that this curve along which, these two liquidus surface intersect. Now, to understand what will happen beneath this temperature region. So, obviously there will also be a temperature here. It will intersect the solidus here and this will be the curve, which will follow the intersection with the solidus line; solidus surface.

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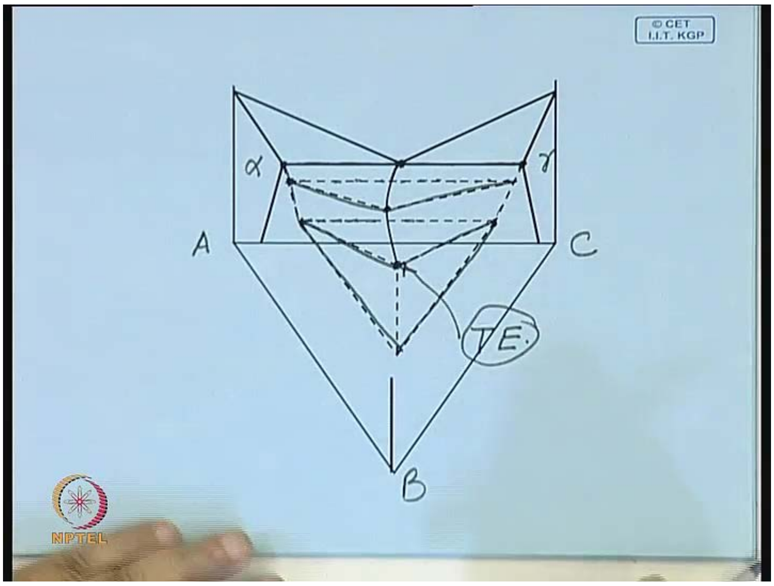

Now to visualize that, you think about; here in this diagram, we have removed this portion just to understand what is the nature of this three phase region. So, this let us say this this is two part; only just change that orientation a bit. Say, suppose this is A; this is C; this is B. So, this is a binary eutectic between A and C. This portion is alpha; this portion is gamma. Now, look at this here; here binary eutectic this is a line. Now, when this surface comes down, it follows it builds a surface a curved surface comes a sting of which comes down to that eutectic isotherm; this point. This represents that eutectic isotherm; this triangle; this is the eutectic isotherm.

This I am still drawing is a dotted line, which you would not be able to see. Now, this surface this point comes down and meets along at this point, which is the ternary eutectic. This is the ternary eutectic T E; ternary eutectic point and this point represent solubility limit and this solvus line it also comes and meets the isotherm at this point. Now, you see in that case what you generate here. This is one isotherm; this is one point; this is intersecting here; this is intersecting. So, this kind of a triangular region and this are the dotted line, which which is behind you. Similarly, this is you know that at this point it just meets that eutectic isotherm.

So, this type of a triangular that plane it just comes down and meets that ternary meets at ternary eutectic isotherm. So, with this we come back to this diagram. (Refer Slide Time: 31:16) So, what it shows is below this point; this is that section valid and this is the ternary that isotherm and this will meet at this point. If I come back, similarly there will be similar surface, which is coming down from that A B eutectic and they are meeting at this point. So, somewhere here they will meet and this isotherm here they will meet. So, that vertical section will something look like this (Refer Slide Time: 31:16) and which is what is drawn here.

Alpha beta liquid; this is that and this side will be alpha gamma liquid. This side will be beta plus gamma plus liquid and this is that eutectic reaction isotherm. And after this, you will have the remaining liquid is solidify as ternary eutectic. But you will have primary phases. Depending on where you are located, you will have some primary alpha; you will also have some binary eutectic and ternary eutectic. So, this this is how it is possible to construct the both horizontal and vertical sections of a phase diagram. But the problem comes you know real systems are never just binary or ternary. See, even simple any alloy you take, you may have 3, 4, 5 alloy elements present.

Now, in that case how do you extend that concept to a normal a common a basically a binary I mean higher order systems, where number of components will be much larger; there will be larger than 3. Definitely as the ternary diagram, it is possible to visualize or construct a diagram in a three dimensional space. But even if you go to a quaternary system, it will now become impossible to do so. And only way you can we do this and do some calculation is in mathematical space and imaginary say n dimensional space and how we will look at some example how it is done just the basic principles.

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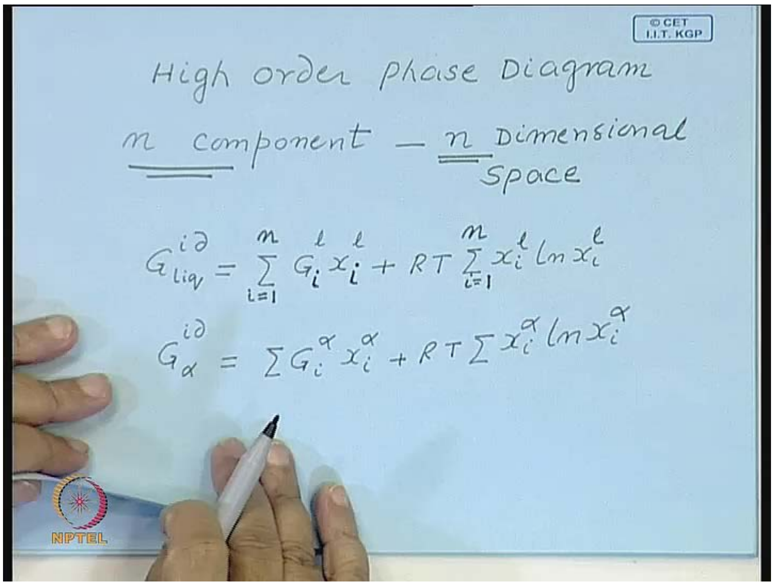

So, higher order phase diagram, where n is the number of component; you need n dimensional space to construct a diagram. Now, let us see even if a simple isomorphous system; if we are trying to construct a phase diagram using mathematical techniques, how do we proceed. We looked at it; say suppose we say that i represent a particular component and this i extends from let us say 1 to n. And if we assume the solutions are ideal solution, then we can say that the free energy of the system that mixture will be represented by these. These are the standard state free energy. This is the free energy of mixing. Similarly, you will have a similar expression for solid. So, such expression it is possible to write down and say suppose we consider an isomorphous system in n dimensional space and it is possible to do and visualize, if such a system exists what will be the phase composition at particular temperature.

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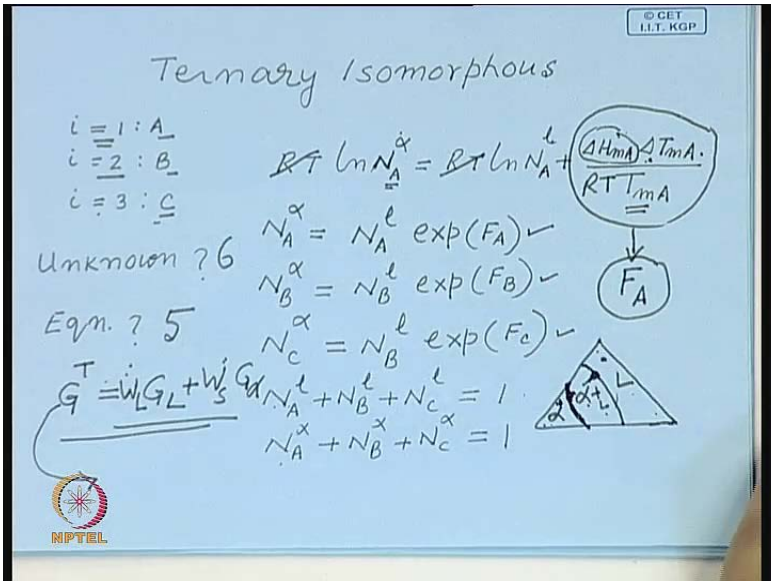

Now, in extension of this say suppose we look at ternary isomorphous system. Say suppose i 1 represents A; i 2 represents B; i 3 represents C. We had done the similar calculations for binary; extend the same thing to a ternary system. If you look back your lecture, if you equilibri at the chemical potential of A in solid and liquid, it is possible to write down; that is equilibrium that is chemical potential of A in solid that is alpha. N A is the mole atom fraction A in alpha. This is equal to this. N A l is atom fraction A in liquid. This is the enthalpy change of melting or fusion. This is the temperature difference between the temperature of interest and the melting point.

And T m A is the melting point of A and what we have seen? We have introduced divide all this R T and we said that this you assume that suppose this is a function A, which depends only on the thermodynamic characteristic; that is enthalpy of fusion or latent heat of fusion; the melting point and the universal gas constant and that temperature. So, this in that case, you can simply write this expression in this form. So, this is when you equate chemical potential of A in alpha and liquid to the same thing equating chemical potential of B, this is the second equation; this is the third equation.

And parallelly, we also have that atom fraction; if you add up A B C in liquid, it should be equal to 1. If you add this up, it should be equal to 1. So, now look at how many unknowns we have. We have say each of these A, B, C, N A, N B, N C; they are unknowns. So, you have 6 unknowns. But how many equations do we have? We only have 5 equations. So, therefore a few one to solve this; it is impossible to solve. So, that is why you know if you look at this composition triangle at a particular temperature, if you are able if you want to solve this; say suppose we have seen at a particular temperature, this side let us say alpha; this side is liquid; this is alpha plus liquid.

You want to find out at particular composition, which phases more stable. How can you do it? So, in that case the best we to do it is to construct or find out that free energy, which will be a mixture of say weight fraction of let us say alpha; the total free energy. This total will be the free energy of let us say this is the liquid and this is weight fraction liquid plus weight fraction solid the free energy of alpha, you construct this. Now, you try and find out. You change these weights and try and see and minimize and what values of these weight fraction is this minimum and this can be done in a computer usually.

So, what you have to do? You are trying to solve at every point on this composition triangle and find out which combination of that percentage of certain phases. Suppose, here you will find if it is 100 percent solid, then the free energy is minimum. Here, if you find that 100 percent only if it is 100 percent liquid, it is that free energy is minimum. But in between you will find, you have to say that here it will vary. I mean so similarly, you will be able to find out here both can coexist. In that case, you can construct this boundary. So, this is how the computation or phase equilibria problem is solved in a higher order space. Now, if you extend the same thing in the case of eutectic, what will you have?

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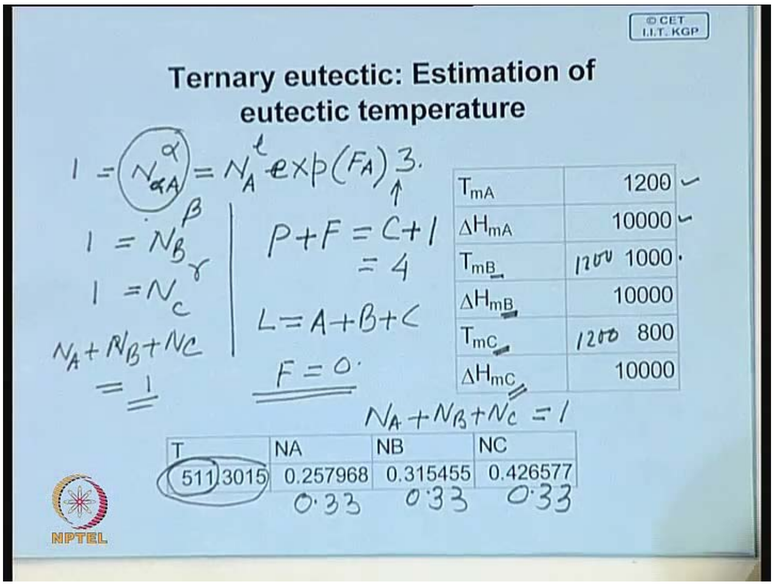

Now, in that case what you can do? Following the exactly there similar case in a ternary eutectic, what you can write at that eutectic temperature. Let us say just above that eutectic temperature, say you can equate say N A in alpha; this will be equal to N A liquid plus that any liquid; then exponential F A. So, you will have the three such equations you have three such equations and you will also have and here let us try and simplify it even for there. We assume that alpha is pure A. So, that means we assume this is equal to 1. Similarly, N B beta this is equal to 1; N C gamma equal to 1. So, that means what we are assuming that liquids in the liquid state A B C, they form an ideal solution; whereas, in solid state they are totally insoluble in each other.

And in that case, if you take up let us say some numerical values. This is the melting point of A; this is this is the latent heat of fusion for A. This is melting point of B; this is latent heat of fusion for B. This is melting point C of C; this is latent heat of fusion of C. Now, in that case now let us see what you have here? You have if you apply the phase rule, we have seen that P plus F equal to C plus 1. So, here this number of component is 3; so this is equal to 4 and here liquid is breaks down into three solid mixture of three solid. So, you have a situation, where four phases are coexisting. So, therefore degree of freedom equal to 0. So, that means not only I mean this can happen only if the temperature is fixed temperature and therefore, it should be possible to calculate the temperature in principle and this is what we shown over here.

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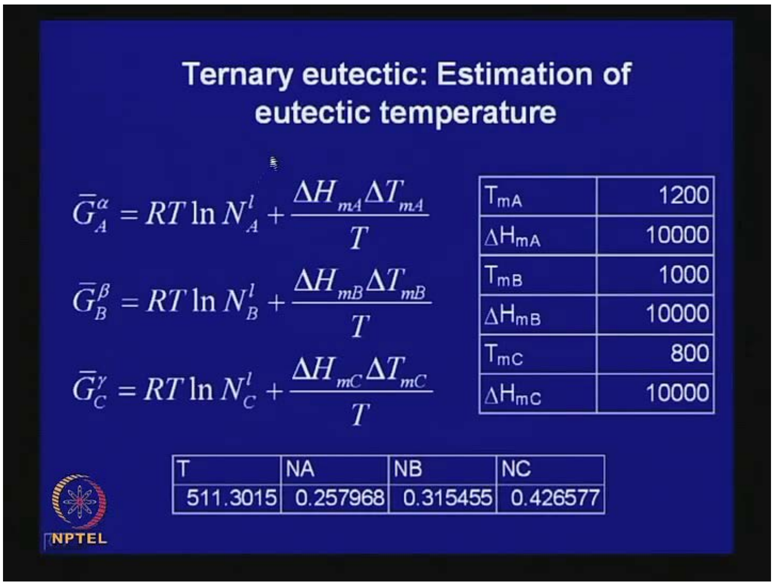

If you equate this ternary eutectic that estimation of that eutectic temperature, these are the three equations. Now, here you assume that this portion; this is equal to this is 0; you can say that the the this equal to 0. This is a stable phase; it is pure A; this is 0. And in that case, what you need to do? Here you see (Refer Slide Time: 46:16) this is N A plus N B plus N C; they represent atom fraction A B C in liquid; they should be 1. So, what you need to do? You need to iterate. It is a simple iteration process. You change this temperature; only unknown is this temperature here. Now, change this temperature to satisfy that is N A plus N B plus N C equal to 1. If you do this, you will get this exact temperature in this particular case is this. Now, you try if you make all this equal; if you make this, this, this temperature, this also you make 12000; this also you make 12000, then you will find all these points N A, N B, N C they all will be equal one third, one third, one third. Now, I will one point is…

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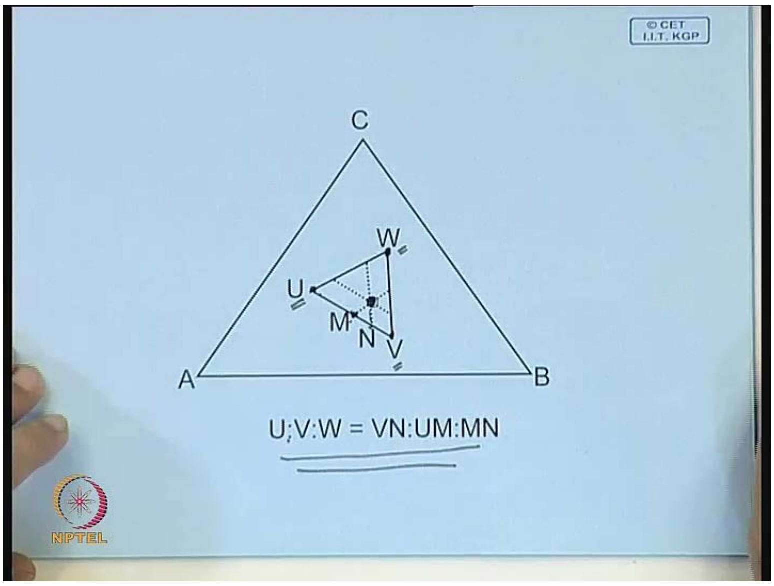

Here if you see this, you will be situation; you will come up with situations, where you often have to in this in this ternary diagram or in a multi component system. You often may have to apply that material balance here; say where three phases are coexisting. So, our multiple phases are coexisting. How you do it? So, here also the principle will be exactly similar to that of that composition triangle concept that we have seen and which is shown over here. This is say suppose U V W and you have an alloy of this composition. And so what will be the percentage of these phases U V W?

So, they will be present in this ratio U V W. Now, look at how much is W. So, W will be proportional to w will be proportional to this to this part. So, W will be proportional to here to here and these three will construct constitute an equilateral triangle. So, here also you can imagine; so you draw lines, which are parallel to each of these lines. So, W is equal to this from here to here, which is equal to M N. Similarly, V V is equal to from here; U N is equal to V and U is equal to V N; so, which is shown over here.

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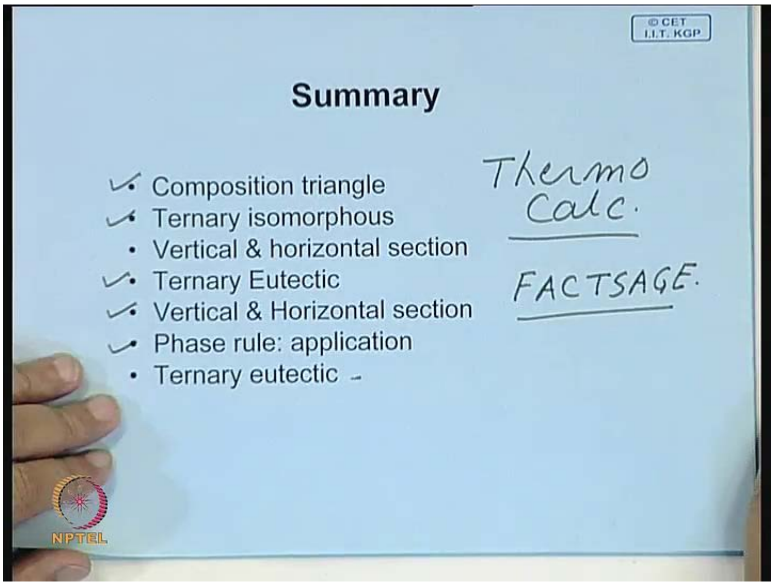

So, with this therefore we now finish. I mean just seen the case of that equilibria in a multi component system. We looked at ternary system in detail and higher order system becomes much more complicated and which certain simplifying assumption and assuming solution model like ideal solution model. I just said it is possible to calculate that ternary eutectic temperature in in a in a very specific system. We did that calculation and same thing can be used for higher order systems. And infact, there are now it is thermodynamic data basis; using that program, which minimizes that by minimizing free energy; that minimization of free energy concept, it gives you solutions that in certain composition phases. With the available thermodynamic data what is the expected number of type of phases and their composition it is possible to calculate.

And two very common these packages; they are known as one is a thermocalc, FACTSAGE; there may be others also. So, in short what we looked at today? We looked at composition triangle, looked at ternary isomorphous diagram, we looked at vertical and horizontal sections, we looked at ternary eutectic, we looked at its several vertical and horizontal sections. We applied phase rule to see that whether it is applicable here. We looked at ternary eutectic calculation has been done, and we also looked at how this concept can be extended to understand equilibrium in higher order systems. And there in all probability you have to resolve to thermodynamic data basis with solvers, which are there are commercial packages available like thermocalc, FACTSAGE. Thank you very much.