

**Advanced Metallurgical Thermodynamics**  
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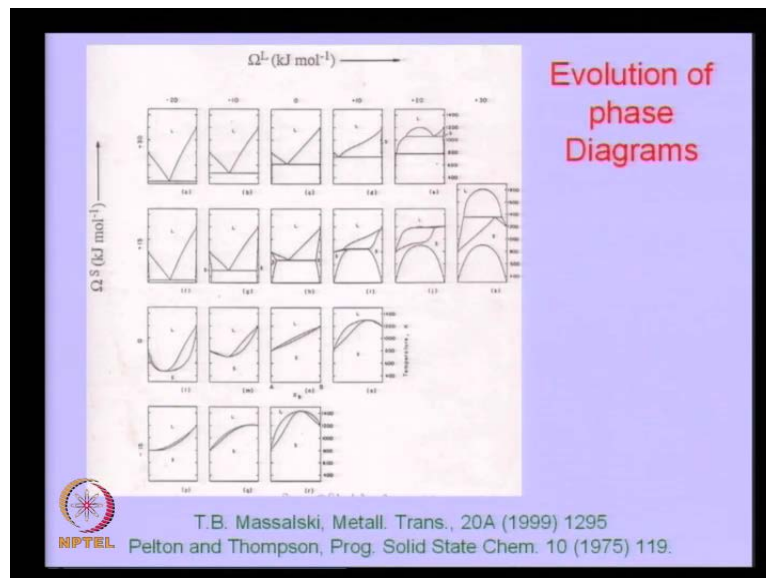
**Module No. # 01**

**Lecture No. # 08**

**Evolution of Phase Diagrams, Miscibility gap**

Last class, we were talking about the evolution phase diagram based on thermodynamic principles. We took up two parameters, which are basically the  $\Omega^s$  and the  $\Omega^l$ , which is nothing but, the interaction parameter in the liquid between A and B and interaction parameter in the solid between A and B, and used them to basically see how phase diagram evolve from a isomorphous system. And you get isomorphous system, when both of them are close to 0, and as you start varying one, keeping the other one fixed, how the phase diagram evolves, so we will try to see that.

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And today, I just had brought you image from one of the reference as you can see here, this is from T.B. Massalski, published in Metall Trans in 1999, which gives you a flayer of how really the phase diagram evolves; actually I was talking about that. You can see

here, on the left axis you have the  $\omega_s$  and on the top, which is the X axis is the  $\omega_l$ , and you see how as you start varying these things, how various from phase diagrams come. And you see, when you take both of them as 0 0, that is what ends of the view of the isomorphous system. And if you keep  $\omega_l$  as 0 and keep decrease, or keep the  $\omega_s$  as 0, keep decreasing the  $\omega_l$ , make  $\omega_l$  more and more negative, you see when it is minus 10 and when it is minus 20, what you see? You start seeing pseudo eutectic phase diagram evolves, so the liquid becomes more and more stable, so the liquidus curve starts plunging down.

And, as you start seeing, you see more and more of liquid stability there. And on the other side, keeping the same, the  $\omega_s$  as 0, and let us say, increase the  $\omega_l$  to positive side, again you see that, you start seeing that, because the moment  $\omega_l$  is positive and  $\omega_s$  is 0, that means solid is more stable than the liquid, and as a result solid stability regime increases and you start seeing a congruent melting phase develops. And similar thing can also happen when **omega l is**  $\omega_s$  is negative. For example, keeping  $\omega_l$  as constant at 0, and if you make the  $\omega_s$  negative, this is what you see in the diagram below, where you see the moment you have minus 15 for the  $\omega_s$ , you again start seeing for the same  $\omega_l$  being kept as 0, so you see the concrete melting task evolving.

So, you can see that, we can have **either** this under the ideal conditions. You can have a pseudo eutectic type, when the liquid is more stable; when the solid is more stable, you start getting what is called the concrete melting, which is an indication of the formation of the inter metallic. And if this becomes stronger, that means, if the  $\omega_s$  becomes more and more negative, you would actually see that inter metallic starts actually evolving inside the phase diagram. And this is as far as either the  $\omega_l$  being negative or  $\omega_s$  being negative, but if you think if  $\omega_s$  is positive, what is going to happen? Keeping the  $\omega_l$  as 0 and if you start making it positive, for example you see, this is plus 15 and everything is kilojoules per mole, all the numbers that we are talking are basically the enthalpy unit because  $\omega_s$  is nothing but, the enthalpy unit, because it is an interaction parameter and that multiplied by X A and X B will give you the actually enthalpy of mixing.

So, it will have the same unit for the enthalpy, which is nothing but kilojoules per mole. So, you can see here, if you keep this as 0 and then make  $\omega_s$  as positive 15, you

start developing eutectic. And we saw yesterday how this eutectic actually develops because of the miscibility gap, and the miscibility gap and the liquid of plunging down, side downwards and both of them meeting, both the liquidus, solidus and the miscibility gap meeting. Basically, what you see down is this, it is the miscibility gap and this is the liquid of both of them merging to each other, and you will get that. Now, if you keep this as constant and let us say make  $\omega_1$  more and more negative, you see that liquid is becoming more and more stable with respect to the solid and as a result, the eutectic temperature starts falling.

You will see the same thing can be also seen, if you want to increase the  $\omega_s$  keeping the  $\omega_1$  the same. For example, if you keep the  $\omega_1$  as 0 and increase the  $\omega_s$  to plus 30, what you see here is that, the terminal solubility vanished on both the sides and you will also see the liquid is coming down. Like this we will be able to see, how various and similarly, if you keep this as 0 and make **it** this as plus 30 and make this more and more negative, similar thing happens. So, as the liquid becomes more and more stable by making the  $\omega_1$  more and more negative, you see that the liquidus line comes down, that means the eutectic becomes more and more deep eutectic.

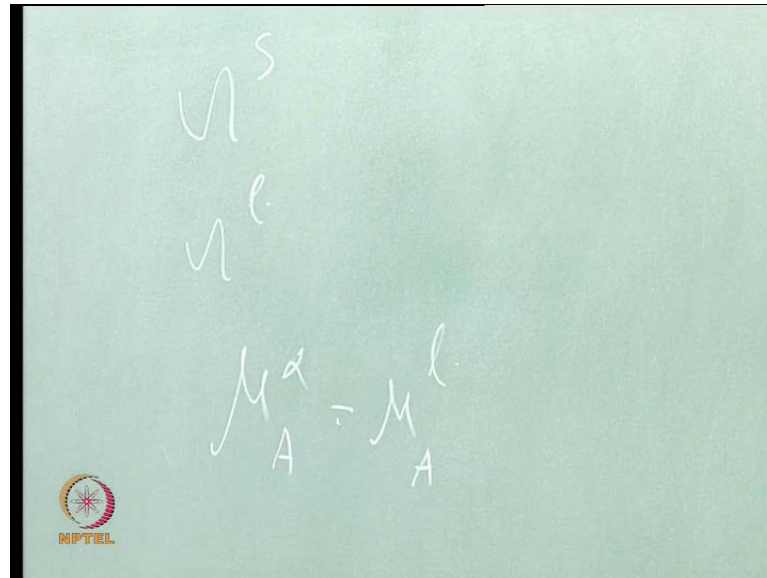
Yesterday, I also gave you an idea of how to quantitatively measure, how deeply the eutectic is with respect to basically, we take the melting points of two pure metals and then find out what is the melting point of mixture of the two pure metals at the eutectic composition, and take down what is the eutectic temperature; and the difference between this two will give you a measure of the deeper eutectics, and of course, it has to be normalized with respect to the melting point of the mixture and that is what we have seen in the last class.

Now, if you see that, if the  $\omega_1$  becomes positive, so far we have seen whether the  $\omega_s$  is positive and the  $\omega_1$  is either 0 or negative, and if you make the  $\omega_1$ , start making the  $\omega_1$  positive, then you start seeing that development of the monotectic phase diagram. You start seeing a miscibility gap inside the liquid, not only the solid also will have miscibility gap, but also the liquid will have the miscibility gap and you start developing either the monotectic or the syntectic kind of phase diagrams.

That is how you see all the phase diagrams can be, in fact though this is schematically shown in principle, one can calculate all these phase diagrams simply by just varying the

two parameters. And whole calculation is based on what we have seen, the equilibrium principle, which is nothing but, the chemical potential of A in alpha is equal to chemical potential of A in liquid.

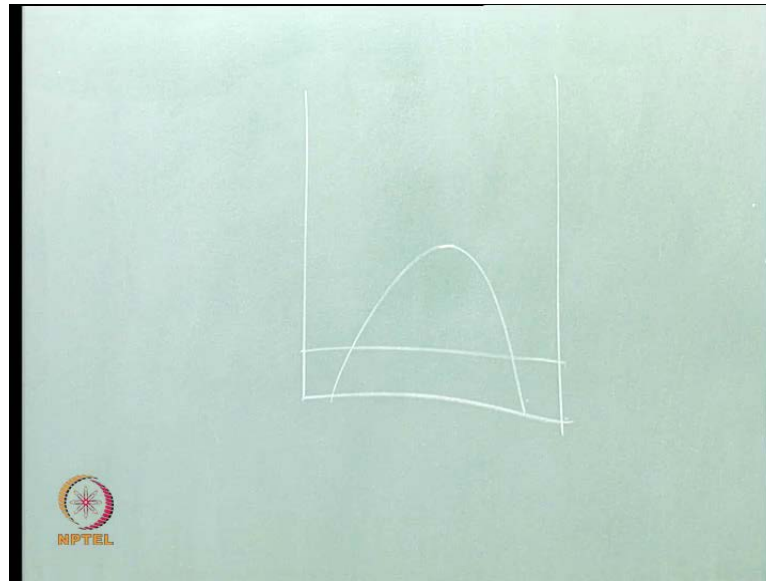
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And if you use this as the starting point for your equilibrium, from that, you can find out at each temperature, what is the liquidus composition, what is solidus composition, and from that, we can come across all this. And in case there is third phase to be evolved, for example, in case of eutectic or in case of monotectic, you have three phases coming into picture, and you would see how to deal with those three phases. By considering third phase, and that is what we are going to see today, what happens, how do I consider the third phase?

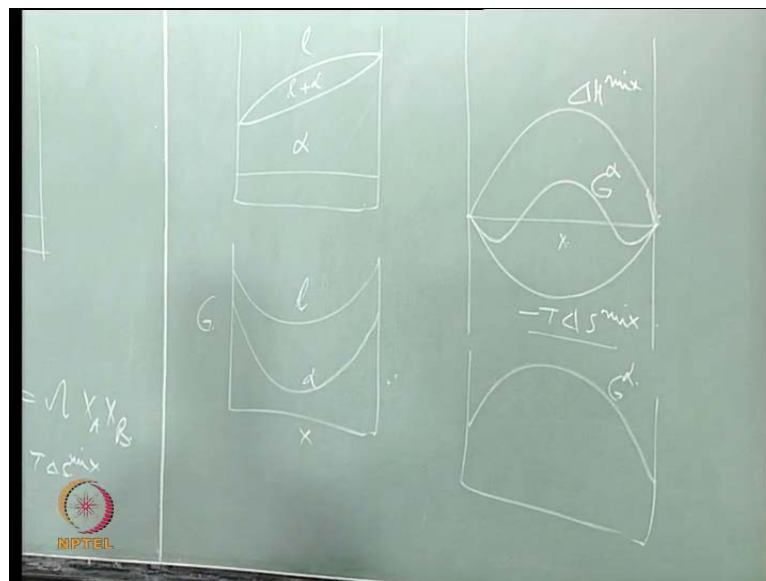
At the moment, we have been talking about only two phases, omega s and omega l, and how do I consider that third phase. And that is what we will see today, and that also will give you an idea of how to understand the miscibility gap.

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Yesterday, somebody was asking me, sir if this is the miscibility gap, how does this gets closed? What is thermodynamic behind it? We will also see today, **how** what is thermodynamics behind this, the miscibility gap getting closed at higher temperature and why does it kept closed. To understand this, what we see is, how does the free energy curve looks like at the temperature does.

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For example, you take a system which is an isomorphous system and draw free energy curve at the temperature, how does free energy curve look like? If I draw it, this is G

verses  $X$  we are talking and at this temperature, what is stable? Solid alpha is stable, this is liquid and this is liquid plus alpha, so alpha is more stable, very easy. So, as a result, I will see the free energy curve for alpha which looks like this and of course, there will be a free energy curve for the liquid which is something like this, this is liquid, this is alpha, Am I right. And this free energy curve is expressed in terms of the free energy expression that we have given earlier, where  $G_{\alpha}$  is  $X_A G_A$  plus  $X_B G_B$  plus  $\Delta H_{\text{mixing}}$  plus  $R T X_A \ln X_A$  plus  $X_B \ln X_B$ ; so that expression which we have given can be used to calculate this free energy. This is all fine, the moment you see a miscibility gap here, how does this free energy curve is going to change?

The difference between this and this system is that, in this system the  $\omega$  is positive, right. So, there is a positive interaction between the A and B; that means, A and B do not attract each other, they repel each other. The moment this is positive, what happens to  $\Delta H_{\text{mixing}}$ ,  $\Delta H_{\text{mixing}}$  is positive. Because,  $\Delta H_{\text{mixing}}$  is nothing but,  $\omega$  into  $X_A X_B$  regular solution model, as long as I assume that regular solution model is varied. So, this is also positive, if this is positive, if that is positive then, you would see that, if I try to draw, you will see that if I plot, that  $\Delta H_{\text{mixing}}$  as a function of composition, you will see that  $\Delta H_{\text{mixing}}$  curve will be something like this (Refer Slide Time: 11:00), this is  $\Delta H_{\text{mixing}}$ , am I right.

So, once it is like that, and you have that,  $T \Delta H_{\text{mixing}}$  curve minus  $T$  into  $\Delta S_{\text{mixing}}$ , which is the second part of the free energy of mixing will always be negative. The only difference is, depending on the temperature of this, this value is going to depend; this value, how large absolutely it is, or how small absolutely it is, depends on what is the  $T$ . Because,  $\Delta S_{\text{mixing}}$  is only a function of composition, it is a symmetric function we have seen that,  $X_A \ln X_A$  plus  $X_B \ln X_B$  plus  $X_B$ .

So, as a result, this is going to be solely dependent on the temperature and as a result, at room temperature if I am considering, where the temperature is not too high, you would see that possibly this particular value,  $T \Delta S_{\text{mixing}}$  is lower than the  $\Delta H_{\text{mixing}}$ . For a certain case, as long as  $\Delta S_{\text{mixing}}$  value, the maximum value of  $\Delta S_{\text{mixing}}$  is smaller than the minimum value of  $T \Delta S_{\text{mixing}}$ , you would see that the  $\Delta G_{\text{mixing}}$  which is nothing but,  $\Delta H_{\text{mixing}}$  minus  $T$  into  $\Delta S_{\text{mixing}}$ . If this is positive, which what we have seen here, but its absolute value if it is smaller than this negative value, then the  $\Delta G_{\text{mixing}}$  is still negative. So, the  $\Delta G_{\text{mixing}}$  is still negative

then, free energy curve will be having a curve downwards. I have seen how, drawn here, it will be like that, the moment this value is higher than this **u t**, that the free energy curve will look.

If I draw free energy curve, the free energy curve would look something like this. Assuming that the  $G_A$ ,  $G_B$  is 0, we can always assume the standard stage. The free energy of that, the free energy would be 0, as an extreme case of course, it may not be 0. If I assume that  $G_A$  is equal to 0,  $G_B$  equal to 0, that  $X_A G_A$  plus  $X_B G_B$  term vanishes for schematic case, we can guess that assume it 0. So, once that vanishes, then I can write this as  $G_{\alpha}$ , but at the same time you may say, sir why not **it will go** the free energy curve go like this, when this is going to be higher than this, why should it half?

And in place implication like that, why not it goes like this?

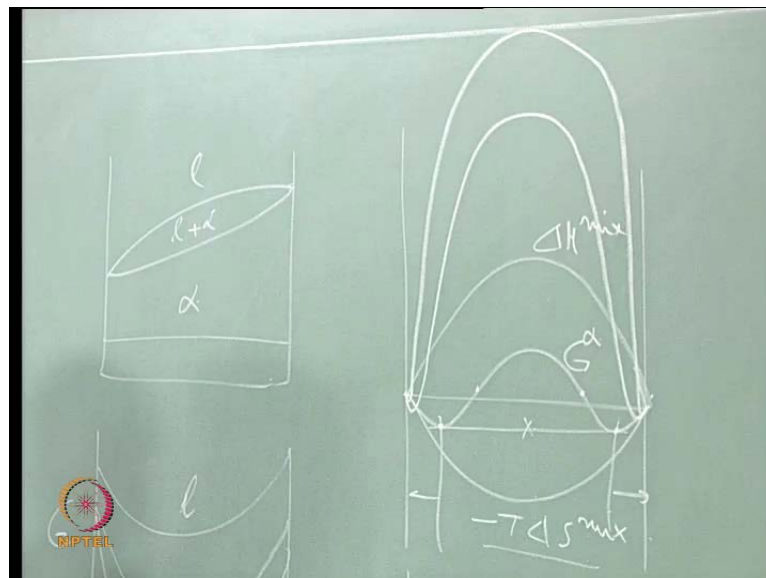
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That is where, we have seen in one of the pervious classes, that free energy expression which is here,  $X_A G_A$ . Even if you assume that the pure method terms are not there and simply put  $\omega X_A X_B$  plus  $R T X_A L N X_A$  plus  $X_B L N X_B$  and differentiate this and find out the **do**  $G_{\alpha}$  half **do**  $X_B$  and find out what is the value of at  $X_A$  equal to 1 and  $X_B$  equal to 1, you see that this is minus infinity. I hope all of you have done this assignment and submitted to me.

You see that it is minus infinity and as result, let me say the slope of the free energy curve as a function of composition, irrespective of what is the omega value. However, large positive or however large negative it is, this is bound to be negative and it is minus infinity. And because, it is minus infinity on both sides of the free energy diagram, in terms of the composition you see that the free energy has to form because, the negative in the free energy curve should have a slope which is minus infinity towards this end and towards this end, the only difference that you see when you keep on increasing this positive. If this is negative, there is no problem at all; if this is negative, what is going to happen? This curve is going to become more and more deeper down.

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You will see that this curve will go down more and more if omega is negative. Omega being negative is not a problem at all the free energy curve is not going to change.

Much expecting that the shape remains the same, the absolutely values are going to change. But, if this value is positive and depending on how large this value is, you would see that this free energy curve could in a ultimate case, could even be like this or could even become drop a little and then suppose become like this. If the delta omega value is highly positive, then you see it drops by a small extent and then starts rising and this drop is because of this. So, you would see in all the cases, it will never start from 0 and starts rising.



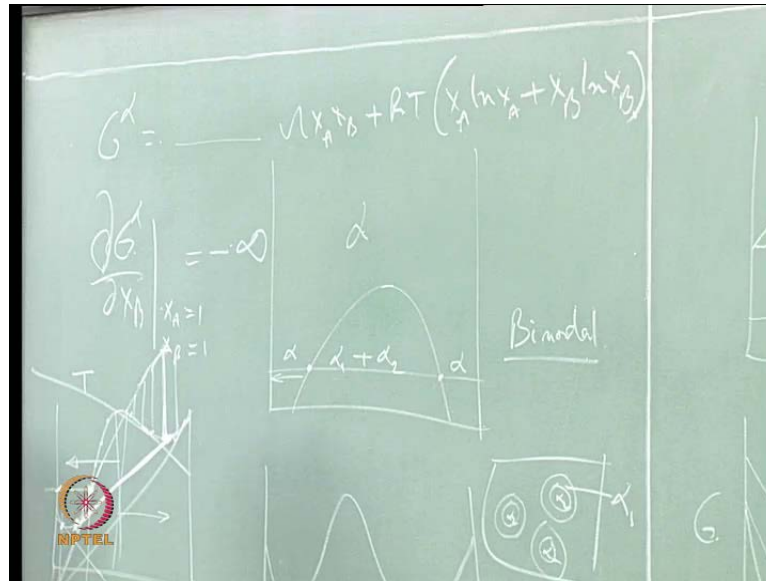
So, it has to have a drop and how small it is, how **how** measurable it is depends on the sensitivity of your measuring instrument. But, in principle, thermodynamically and in fundamentally it has to come down and that is what you see here. And the moment you see a curve like this, I can stop talking in terms of what is called common tangent because, this curve is one single curve. But, it as an inflection, the slope of it is changing at this point. In fact, will come to this point **this** later, they are called spinodal points and when we talk about spinodal transmission, we will try to understand that in greater detail. But, the moment you see a free energy curve like this, then I can start talking about **(( ))**.

If I start drawing a tangent, you will see at one stage, there can be tangent, which is something like this, which is a tangent for the both the ends. And this particular tangent, where **where** you see that 2 points there, these 2 points are nothing but, the equilibrium compositions of the original face, which is now decomposing into 2 phases. Because of this limitation of the omega is being positive that A and B are not able to dissolve into each other. So, there are forces to segregate **((y))** A dissolve into B to some extent. B dissolves into A to some extent and they are not able to completely dissolve to the extent to which A dissolves into B and B dissolves into A can be obtained from this common tangent. So, that means, basically what you see, these 2 points at this temperature are nothing but, these 2 points from this free energy curve.

And that is why we call this, we have composition of alpha 1 and composition of alpha 2, incidentally you call this as alpha 1 plus alpha 2, and you do not call them alpha and beta basically because, both are same structure. It is actually one single phase which is decomposing into two with the structure remaining the same, expecting the composition being different. So, as a result, the whole thing is alpha and alpha splitting into two phases, one having A rich composition, another having a B rich composition; and that is how you see that it will have. We will know more about this as we go to spinodal and try to understand why spinodal decomposition looks like that. Now, if you look at what should happen if this is a free energy curve, if that is the free energy curve which is leading to this situation of alpha 1 having this composition, alpha 2 having this composition at this particular temperature.

And mind you, I have associated that if I am on this side, **if I am on this side**, what does it mean? You remember that, maybe I will draw this in a greater detail for you to understand, why this splitting has to occur.

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For example, imagine a case something like this and you have a common tangent, which is something like this. And I Mind you, common tangent does not mean it has to be always horizontal, the free energy curve could be like this, could also be like that; though generally, **for the most of the** in most of text books where shown like this. If it is not that, it has to be a horizontal.

So, if you take a case of this composition **composition** to the left of it, and draw a tangent which goes and hit somewhere here, you would see that the whole free energy curve, **the whole free energy curve** is above this tangent. And in comparison, if I take a composition here and draw a tangent to that, assume that this is the tangent, this is the point. You see that if this is the tangent for that particular composition I am taking, a alpha of that particular composition. You see that, beyond this particular composition, you see that there are certain compositions which have lower free energy than that corresponding to this tangent.

That means, these compositions are stable compositions because, their free energy is lower. So, they can in principle come out of this particular composition. So, if I take alpha of this composition, in principle alpha half alpha, that composition is not stable. Why because, in principle, I can even show what is the free energy of this **free energy of this** and if I take 2 phase mixture of alpha 1 plus alpha 2 of the same composition, that 2 phase mixture has a free energy which is given by this. Because this is the common

tangent, if I draw that line, any 2 phase mixture, whenever you draw a 2 phase mixture, the free energy of a mixture can be always found out by the line joining two free energy curves per energy points. So, if this is per energy of the alpha, one of the equilibrium composition and if this is the free energy for the alpha 2 of the equilibrium composition, then the line joining this two will give you the free energy.

If I have a phase mixture of alpha 1 and alpha 2 with different amounts of alpha 1 and alpha 2, what is the free energy for such a mixture can be always obtained by this line. It is simple rule of mixture and if that is the case here, the 2 phase mixture here has a lower free energy dynamics and because 2 phase mixture has a lower free energy than this, you would see instead of single phase existing, for this particular alive composition it would like to exist tablet 2 phase mixture. And that is what you see if you draw a tangent, you see that the phase here which is B rich phase, having compositions of all this composition. Anyone of the composition can, in principle enucleate from this particular ((alien)) because, this a line has a higher free energy than the 2 phase picture, which one will actually enucleate we will see when we talk about what is called spinodal.

We will know more details about it, which phase should actually form and in principle usually the word form is the one which have the highest driving force. And the highest driving force you can obtain by the difference between this and this will give you the highest driving force. As a result, that is the composition which is went to enucleate. We will know more about it when we go spinodal, but at the moment, you can understand that, if I take this particular a line composition, a composition of this, you see that none of this particular compositions have free energy lower than this line. As a result, none of them can enucleate from an alpha of this composition that means what? The alpha of single phase alpha is stable at this particular composition, but if I take this particular composition, single phase alpha is not stable, it wants to split into two, which is alpha 1 plus alpha 2 and alpha 2 will enucleate out of that alpha.

And whatever alpha is left out is what we start calling it as alpha 1 because, the moment you see that alpha 2 of this particular composition enucleate, then immediately there has to be an equilibrium between that alpha 2 and alpha. For example, if you have an alpha from which alpha 2 have enucleate, this alpha 2 as to be in equal with alpha. What particular composition of that can be equilibrium with this alpha 2 if you try to look at. If this is alpha 2, the composition of alpha that can be in equilibrium with alpha 2 is only

this composition because, the 1 that can come as common tangent. When you draw a common tangent, you would see where **where** this common tangent attaches the alpha; that is, this composition that alone can be in equilibrium with this alpha 2. You cannot have this particular composition in equilibrium with this alpha 2 because, I cannot have a common tangent between that and this, it is not possible to have common tangent.

That means what? That means, what the moment alpha 2 comes out of alpha, the composition of alpha surrounding this particular alpha 2 change. And it actually it becomes poorer in B and richer in A. Why does it become poorer in B? Because, it is alpha 2, which is rich in B is coming out of alpha. Other result, the alpha which is surrounding that will loss B atoms because, all the B atoms are coming together and forming A alpha 2 phase. And because alpha 2 phase is coming out the alpha, which is around that will lower its B atoms and other result, the composition of alpha stood towards pure A side such that, that particular alpha becomes **e** equilibrium with the alpha 2. So, that alpha which you see it around this, alpha 2 will start calling it as alpha 1. So, now that alpha, which is so far away from this alpha 1 and alpha 2, you may still have alpha.

Having this particular composition until the whole the reaction is complete. At the beginning of the reaction, you will see the alpha 2 will come out and around this alpha 2, always you will have alpha having a composition which is **which is** decided by this common tangent. And that is what you will call as alpha 1 and this is what we call it as alpha 2; alpha 2 is B rich and alpha 1 is A rich and this is how you see this happening. And similarly, if I choose a composition here for the alpha, again you will see that if I draw a tangent there, you will see all this free energy point. That means free energy of any of this composition is higher than this tangent, so other result, nothing can come out of that particular alpha. So, single phase alpha is stable at that, everything we are talking is at a particular temperature.

See, because free energy composition diagram is always drawn at a fixed temperature, we are talking at the temperature, let say that temperature is this temperature. So, at this temperature to the left of this point, single phase alpha is stable to the right of this point. Again, single phase alpha is stable, that is what this free energy curve tells me and between this 2 point single phase, alpha is not stable and that is why whether I choose this composition or choose this composition, if I draw a tangent here, you will see all the

composition to the left of this; tell precipitate out of this. So, that means, from alpha alpha 1 will precipitate and everything will be ((inverse)) of water. we are talk. So far, once alpha 1 comes out, alpha 1 is a rich place. Other result the A atoms from alpha how to come together and form the A rich alpha 1 phase, and other result A atoms in the alpha surrounding the alpha 1 will deplete in the A atoms and that becomes alpha 2.

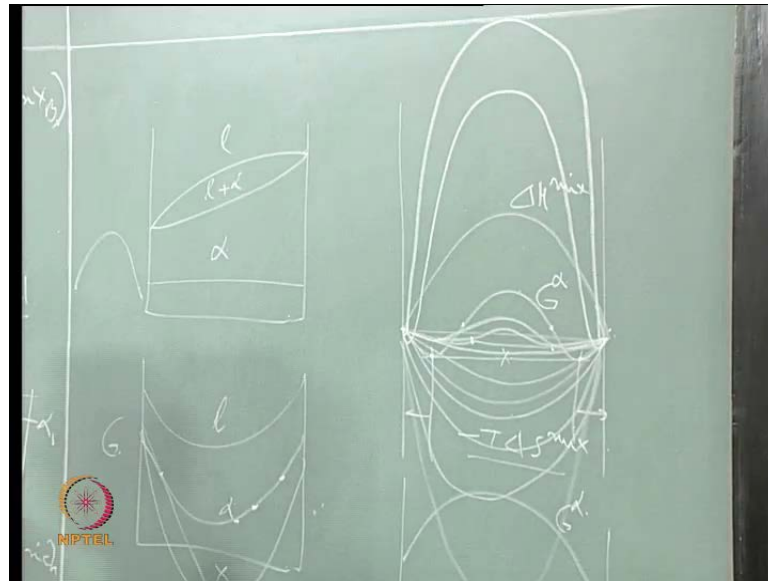
So, will have alpha 1 surrounded by alpha 2; in the previous case, it is alpha 2 surrounded by alpha 1. So, depending on whether you have, taking a A rich composition or B rich composition, this is what will happen. This keeps on happening until you reach the whole composition of alpha 1 and alpha 2 reach these two compositions, this is what the free energy concept tells you. At that temperature that these are the only two compositions that can be equilibrium, no other composition can be equilibrium. So slowly, you see that the alpha composition changes and the alpha 2 composition remain. What it is, according to the phase diagram? According to the p n composition, that the remaining whole alpha vanished and you will have alpha 2 growing at the existence of alpha. And you would have alpha plus alpha 2 and alpha 1 at the end of this.

We will know more about it when we go to the spinodal, but at the moment, what you need to understand is that this is how we will know that this. Any composition that I choose higher here, here you see all this composition have higher free energy than at 2 phase mixture; the 2 phase mixture composition given by this, and as a result, a 2 phase mixture is more stable in this between these two points, and in these two points are called bimodal points. We will talk about this again, when we come to spinodal decomposition. So, what you see is that, you will see between this two is the alpha 1 and alpha 2. And we call it as alpha 1 and alpha 2 because both of them have the same structure; we do not call them as alpha and beta. So, the moment you will bring in a beta, that means, we are talking about different. So, this is how you see this happens. Now, what should happen if I increase the temperature, what should happen?

If I increase the temperature, this delta s mixing, is it a function of temperature? Actually yes, and no, according this it is actually no. But, we if you carefully look at this omega, omega is what interaction parameter; it tells you actually about how strong is the A B bound; whether A and B attract each other or repel each other and this bound energy are in principles, function of temperature. So, in principle, there are models that are available where omega is consider as a temperature function and if you go to cal pad geranial's

and cal pad, the book that I have told you half minutes burns out book, you will see their omega is also taken as a function of temperature. But for the most of the basic thermodynamic understanding, people consider this to be constant. If this is constant, the only temperature function is this and **this being** the whole thing being negative, because this whole thing is minus  $T \Delta s_{\text{mixing}}$  so, this whole thing being negative.

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So, you would see that this keeps on going more and more negative. As I increase the temperature, as it becomes more and more negative, what you see, because this is fix  $\Delta s_{\text{mixing}}$  is fix and this is becoming more and more negative; you see you will reach a stage where this free energy curve changes from this shape to this shape. You would actually see that, this free energy curve slowly starts becoming like this and then it further becomes like this because, this pump start decreasing.

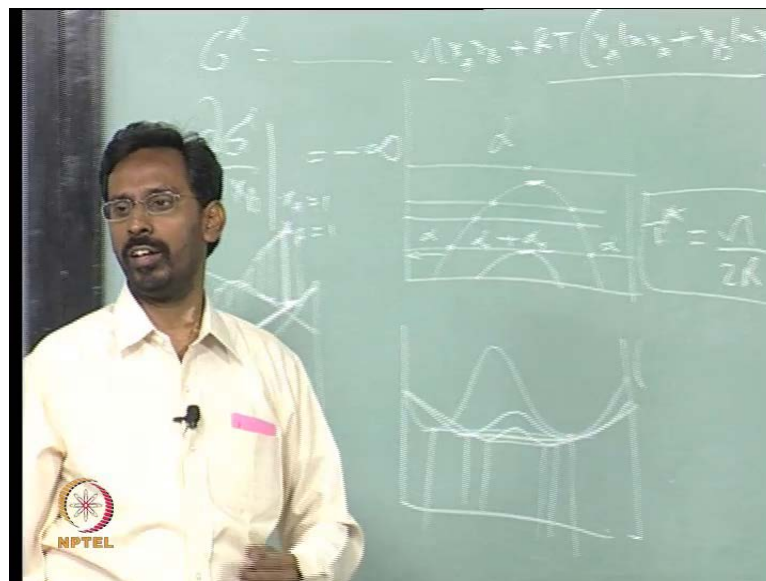
Because, the negative value of the entropy of mixing is becoming more and more, and you would see at some stage, the free energy curve like this. And be **((hound))** the temperature, the free energy curve becomes more and more negative again because, this is much more negative, you can see that just looking at the  $T \Delta s_{\text{mixing}}$ . So, we can understand how this free energy curve, which has a con K con X mixed, is getting converted to one single type of free energy, which indicates stability. We will also talk about how stability is related to this, when we come to the point of spinodal. So, this is an indication of instability for free energy, we will see why it so, when we come to

spinodal decomposition. At the moment, you just leave it. So, the moment you see that this free energy curve that means, there is any, for example, if you take any point here, a composition here or here or here or here.

If I draw a tangent, what does that tell me? That is, all points are free energy points. That means, at any given composition, free energy of all this composition is above the top tangent. So, there is no chance for any other composition to precipitate out of alpha of this composition. I can see it from all the composition, anywhere I choose a composition, draw a tangent, you would see all the whole free energy curve is above that of the tangent. Because it is the above the tangent, there is no chance for this. That is why this free energy curve indicates its single phase is stable and that is the reason why, above this particular temperature, if you come to this temperature, you will see the free energy curve becomes like this. And that basically means that, this has to merge.

You will also see, as you go to higher and higher temperature, this composition starts coming closer and that is what you seen here. Also, as you go from this to anything like this, for example, if you see there are too many curves here that may confuse you. For example, if I take this free energy curve, draw a common tangent, you would see, may be I will show you here.

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If you see, this is **a this** decreasing like this, and draw again a common tangent, you would see this points would be inside these two points; that means the equilibrium

composition. The bimodal points are shifting towards each other as the temperature increase, and to an extent that you would see that, slowly they start coming closer and closer to an extent that at some stage, both become margin to each other and become one point.

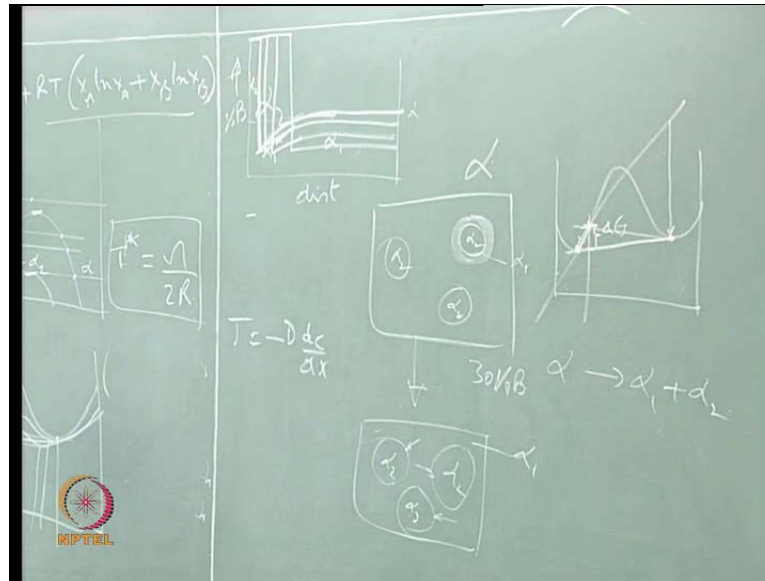
That is, this point that you see here, and that temperature in principle. How do I calculate the temperature, can you tell me? Can I calculate the temperature; it should be very easy, what is the temperature? Where it should happen, you simply equate this with this, simply equate this with this you can find out what is the T and again that is not sufficient; something else we have to do. Equate and put one boundary conditions X A equal to X B because, both this functions being cemetery, this actually happens at 50.

So, equate this to this, and then take X A equal to 0.5 and X B equal to 0.5. And once you take that, you would be able to find out this T, which is this. In fact, you would see when you calculate this, later you would see this will become equal into that. We call it as T star and T star is  $\omega$  by 2 R, one can do this calculation and so, the higher the omega value, is the higher the omega value is the higher will be the T star. That is what yesterday when we are talking about, as I increase the omega more and more or in other words, as I increase the size factor more and more, you would see that this temperature increases, initially it was the miscibility gap was like this.

Then the miscibility gap has become like this, so this temperature has gone up. When I increase the omega, this temperature goes up and that is what you see this happening. So, like this, we can in principle find out how this miscibility gap closes that temperature and this miscibility gap closes can be easily found out by equating this with this. And finally, (( ))... In fact, it is not so simple. Also, we will see as we go along, when we go spinodal, there is also another way to find out by taking the second differential of the free energy. How to do that? We will see when we go to the spinodal at the moment you take it this way, this is clear know, let us now look at, yes.



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Let us see, this is all alpha, starting with alpha we are talking of a situation where a free energy curve is like this. We are talking of a composition like this, it is the starting composition. Let it be 20 percent or 30 percent B, that is alpha and in this alpha now, alpha 2 having this particular composition as enucleated. This is **this is** alpha 2 which is enucleated and that as how much this as much more be content is in it. And how does this **enculturation** occur? Where another question is, you say sir, alpha is continuing only 30 percent B and if it 30 percent B, then how can in a 30 percent B, which is uniformly 30 percent B.

Suddenly, you will have a nucleus of the alpha 2 which as 70 percent B coming out. This is where you need to understand that every liquid or solid, you at any given temperature, there always are vibrations. There are always atoms moving and there are always clusters of varying composition though, over all the composition is 30 percent. You can have a small region which is few nanometer regions, for even the less than nanometer region, where the atoms are more concentrated in terms of either A or B. But, the question is, according to thermodynamic mix, **atom in given temperature (( ))**. If this alpha is not stable, then those clusters which have A B content of this would get stabilize suddenly and that particular clusters will start growing; that is what we call it as R star, this how you will liquid to solid.

Cross machine, you may ask, since liquid is completely random, how does suddenly solid nucleate? Because, there is a short range order inside the liquid and inside the short range order, you see some clusters having a particular cluster structure. They may be 100 atom clusters, 10 atom clusters, and 1000 atom clusters, different **different** sizes do exist, and once a particular size of the cluster has the value of the  $R^*$  for that particular temperature, that particular cluster starts growing. So, let us assume that there are clusters.

So, that B has nucleated. How it has nucleated, let us not bother about it now. Once it is nucleated, this is  $\alpha_2$ , now this particular  $\alpha_2$ , can it be in equilibrium with this  $\alpha_1$ ? It is not possible, because I cannot draw a common tangent between these two, impossible, yes, so this.

It is inside  $\alpha_1$ , because this  $\alpha_2$  is stable, it has a low free energy with respect to that  $\alpha_1$ , **with respect to that  $\alpha_1$** , because it has a low free energy. So, it tries to come out, but once it comes out, because this cannot be the only way this  $\alpha_2$  can be stable, either to dissolve that into the matrix or change the  $\alpha_1$  around its composition such that it can exist with that. **this way cannot** If you want to be friendly with somebody, you change your attitude or change your friend. So that, you are in a kind of harmony with the other friend, exactly the same way here. So, if you want the  $\alpha_2$  to be alive, it can be alive only if  $\alpha_1$  around it changes its composition such that, you can have a common tangent between those two, that  $\alpha_1$  alone can be in equilibrium with  $\alpha_2$ .

So, as a result, because, already from the  $\alpha_1$  B atoms have come together to form  $\alpha_2$ , then obviously, this  $\alpha_1$  has given out some B atoms. Because it has given out some B atoms, its B atoms will decrease. So, in small domain, **in a small domain** like this, the B atoms have decreased and when they have decreased, that means, the pre composition of  $\alpha_1$  has that actually started moving in this direction only. At least, a small reason it might not have happened in the whole  $\alpha_1$ , but at least just around  $\alpha_2$ , it will happen. And that particular small reason around this, I will call it as  $\alpha_1$  and that composition will reach this particular composition so that this  $\alpha_2$  can be alive, otherwise,  $\alpha_2$  cannot be alive. It has to dissolve; that this is the major problem, that is why we will see  $\alpha_1$ .

And now, what should happen in future? This  $\alpha_1$   $\alpha_2$  is there, then  $\alpha_1$  is also there. So, finally, at this temperature, in principle, what is stable is only  $\alpha_1$  plus

alpha 2 and what is the driving force for that? The driving force is this minus this, is the delta G that is the delta G for the alpha. To give you alpha 1 plus alpha 2, that is the driving force. So, driving force is available, the only thing that you need is, you need diffusion so that diffusion takes place. And **what should** what you will see is, this alpha slowly vanishes, the alpha having this composition because, it is not stable. It slowly starts giving out the B atoms more and more so that, alpha 2 starts growing.

And as alpha gives out more and more B atoms, what happens? The alpha becomes poorer in B and so that whole of alpha, so after sometime you would see a situation like this that the alpha 2s have grown. These are all alpha 2s because, the B atoms are coming, **continues** and flowing into the alpha 2 from the alpha, and as they flow into this, you would see alpha 2 increases and the remaining alpha completely becomes alpha 1. So, you will have alpha 1 matrix and alpha 2 precipitate in this type and this can be seen in very easily if you look at the gradient between this and this. Why does there is gradient come, for example, you can see the moment you see a situation, I see a case where everything is alpha, **everything is alpha** with a certain composition usually.

Suddenly, you see a beta. I am in, alpha 2 comes out; if the alpha 2 comes out, alpha 2 have much higher composition then the alpha has in it. So, as result, this is, if I call this as alpha 2 which is coming out, the remaining is alpha, but this alpha 2 cannot be in equilibrium with this alpha. So, what is that, it can be in equilibrium with? So, it is this value. So, you will see that alpha 2 will be in equilibrium alpha having a composition which is much lower than this alpha. So, you will see that, this will be actually, if I draw the concentration profile, it looks like, this is the alpha, this is the alpha 1, this is the alpha 2. So, you see a concentration profile something like this, just listen to alpha 2, alpha will have a lower composition.

But again, from the alpha 2, alpha will have the same composition with which you have started. Now, what happen is, if you see, there is a gradient  $c$  (**or**), B atoms are more in this. Everything I am talking in terms of percentage B, as a function of distance. So, initially everything is alpha and inside the alpha 2 has come out and alpha 2 has higher B content. And because of this, alpha 2 has to be alive; it can be in equilibrium with alpha having a lower B content than what it is. That what you see this is **the al** starting alpha, this is alpha composition which is lower than the thing. So, now, you see there is a gradient, because there is a gradient, you would start seeing the B atoms are flowing

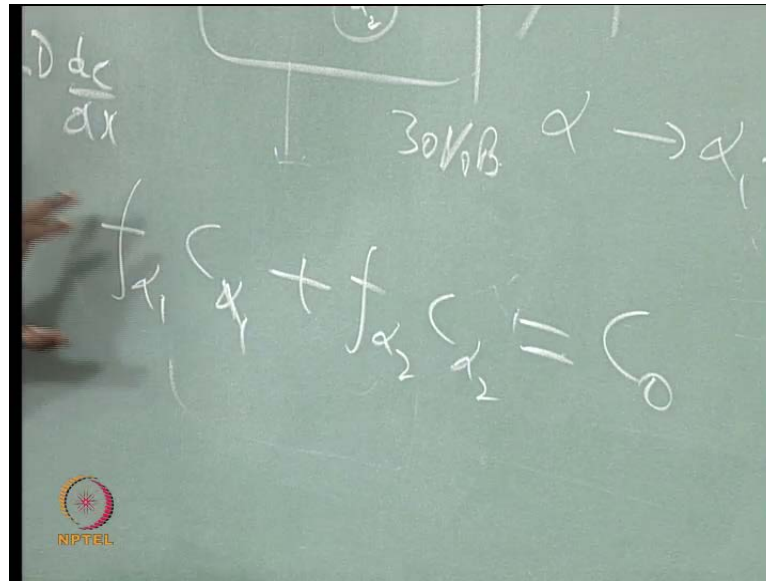
from this alpha towards this. Then what should happen? Slowly, this will grow; this will start growing more and more.

But **will this change**, will this composition change? This composition is equilibrium composition of alpha 1 in equilibrium with the alpha 2, so that cannot change. Then, as this grows, something else should happen. What should happen? Amount of alpha **amount of** we are not talking about amount, now we are talking about in terms of concentration, anything should happen. Of course, amount of alpha will decrease because, the alpha 2 is increasing, alpha will decrease; anything else should happen to the composition of alpha will go down. So, as a result, you see that this curve or this course, you would see a situation. Well, it becomes **well** this B content in the alpha has to come down, because it is giving away.

It is like reservoir, giving the B atoms to the alpha 2. As you keep on giving more and more atoms to alpha 2, the amount of B atoms in alpha should come down. So, this particular value comes down and as this comes down, you will see a situation where finally, the whole alpha around this alpha 2 will have alpha 1 composition. Then, will call this whole thing as alpha 2 alpha 1, this as alpha 2. So, now, it is alpha 2 and alpha 1. Of course, kinetically if I look at it, because if this is happening as the composition is decreasing, the gradient is coming down. That means  $d c$  by  $d x$  is coming down; you know that  $J$  is minus  $B$  into  $d c$  by  $d x$ , if the  $d c$  by  $d x$  coming down, then what should happen? The cluster should, so the reaction is slow down, so the growth of alpha 2 will slow down with time; that is fine.

But thermodynamically, finally, it should come to this and that is how you see that remaining alpha will be called now, not as a alpha, it will called as alpha 1. So, that is how you see one single alpha has become alpha 1 plus alpha 2. When the same thing can happen in a different fashion in spinodal, we will know how it will happen, when we come to spinodal. You can see that, this is how **prating** take place, and as you increase the temperature, this how you see this gets closed up. I think with this we will close for today. I want to say the fact, another concept, which will start in the next class. Obviously, that **not** balance has to be maintained. So, because the mass balance has to be maintained, the only thing is, we can write an expression now.

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The fraction of alpha 1 into the composition of alpha 1 plus the fraction of alpha 2 into the composition of alpha 2 should be equivalent to  $m_i C_{\text{naught}}$  which I have started. So, the amounts of alpha 1 and alpha 2 will be adjusted in such way that, these compositions will give you a particular amount. So, **we can**, this is how actually our lever rule comes. How to do get lever rule? It is only this.