Fundamentals of Materials Processing (Part–1)
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Lecture Number 04
Thermodynamics of Solidification

Okay so welcome back. Now we are getting into the higher drive, now in the higher gear.

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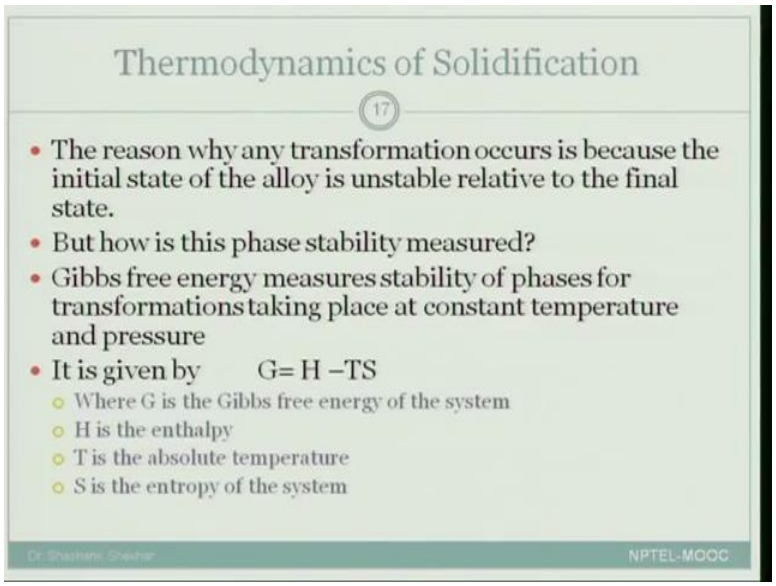

So we are starting with thermodynamics of solidification. Now, the reason why any transformation occurs is because the initial state of the alloy is unstable relative to the final state. But for example, liquid to solid, when you cool down the temperature, solid state is more stable. But how is this stability measured, that is a big question. It is not really big when you talk in terms of thermodynamics, there is the quantity 'Gibbs Free Energy' which measures the stability of phases, for transformations taking place at constant temperature and pressure, and it is given by G equal to H minus TS, where G is the Gibbs Free Energy of the system, H is the enthalpy, T is the absolute temperature in Kelvin, and S is the entropy of the system.

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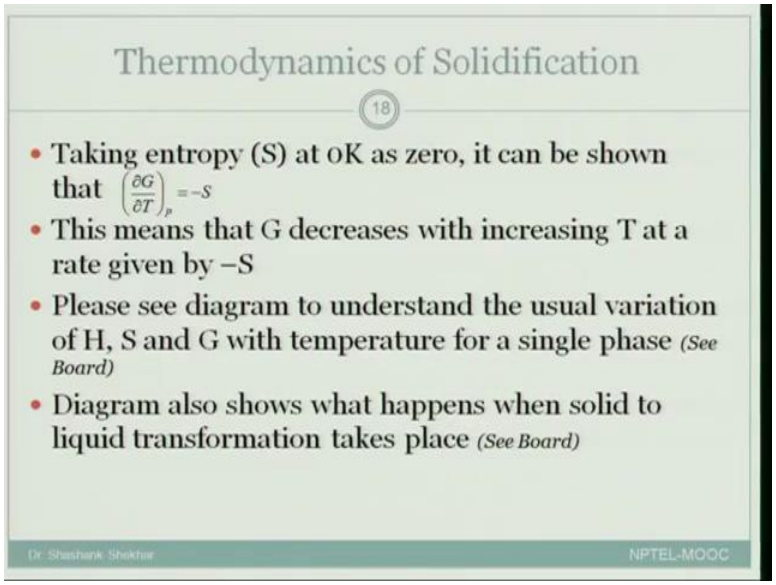

Now if we take entropy S, which is given by the quantity S has 0 at 0 Kelvin, then it can be shown that del G over del T, that is the gradient of free energy with respect to temperature is minus S. This means that G decreases with increase in temperature at a rate given by minus S. So now, let us look at what this means.

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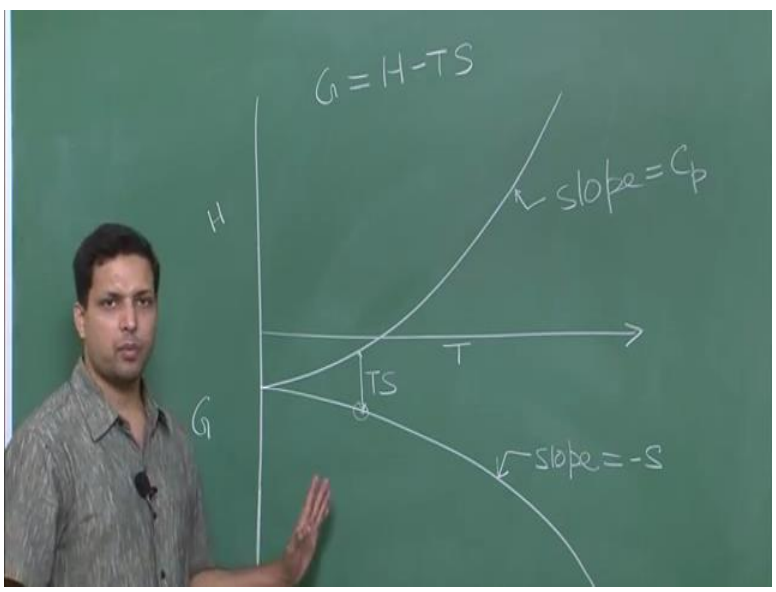

So let us say, let me plot both G and H, and on the x-axis, I have temperature. On the, since H is positive, and G is negative, so I will, although this y-axis is energy, but on the positive side we will have H, on the most of the time, and negative side we will have G. Over here, H will vary

something like this; H will also be increasing with temperature, and G will be decreasing with temperature. And if, like we said, del G over del T is equal to minus S, it means that slope is equal to minus S. Although I did not describe, but you can also say that slope is here is equal to Cp, which is the heat capacity.

Now over here; let me write that equation, G equal to H minus TS. So if this is H, this is the difference TS, and therefore you get at this particular temperature, this will be your G. So this will be your G equal to H minus TS. This will be the total Gibbs free energy for a single phase at different temperature. Now here no transformation is taking place. Now let us say that some transformation is taking place. So, we will modify it a little bit.

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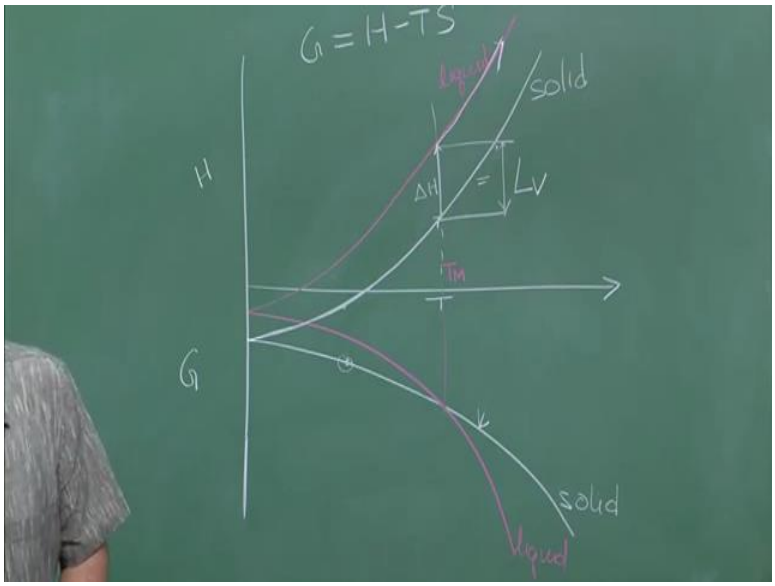

Now we will assume that the drawing that I have drawn, this is only for solid. And we will add over here. So what do we see? So this is the liquid, now we have two phases for the same component; one is solid, the other is liquid. So let me write it with white. Now what do we see first thing here is that G for the (tot), which is the total energy for liquid decreases or comes below that of solid at a particular temperature. So what should that temperature be? You must have guessed it; it is the melting temperature. So at the melting temperature, if you are above the melting temperature, liquid has lower energy; and if you are less than the melting temperature, sorry, I said it wrong; if you are above the melting temperature, the free energy for liquid is

smaller, and if you are less than the melting temperature, free energy of solid is lower. And therefore this is the stable phase.

So in terms of H, what will happen? So for example, if we are increasing the temperature, so you will be over here. You will have to apply this much of energy, which is what; which is nothing but the latent heat. So this delta H is also the latent heat. So this is how the solid or the phase free energy change would look like for solid to liquid and liquid to solid transformation.

So, let us get back to the slide. Over here we have already seen how the variation of H, S and G with temperature will look like for a single phase, which was the earlier diagram, and then we showed the diagram, what happens when solid to liquid transformation takes place. But this is still a single component, and with only two phases possible, which is solid and liquid. Now, let us add some complexity to be able to understand what will happen in a little bit more complex condition.

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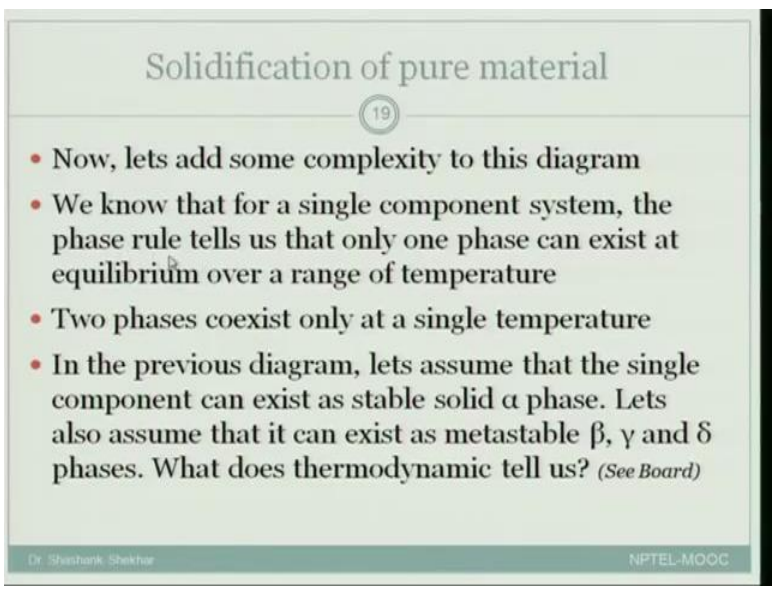

So what is the complexity hat we will add? Now we know that, when we have a single component, which is the case, we will still (ex) we will still continue with that. We will continue with single component. The phase rule tells us that only one phase can exist at equilibrium over a range of temperature. However, two phases can co-exist at a single temperature. Now in the previous diagram let us add that the single component can exist as a stable solid alpha phase; and

along with that, there will be some metastable phases, beta, gamma and delta. So now, we will redraw it to look like.

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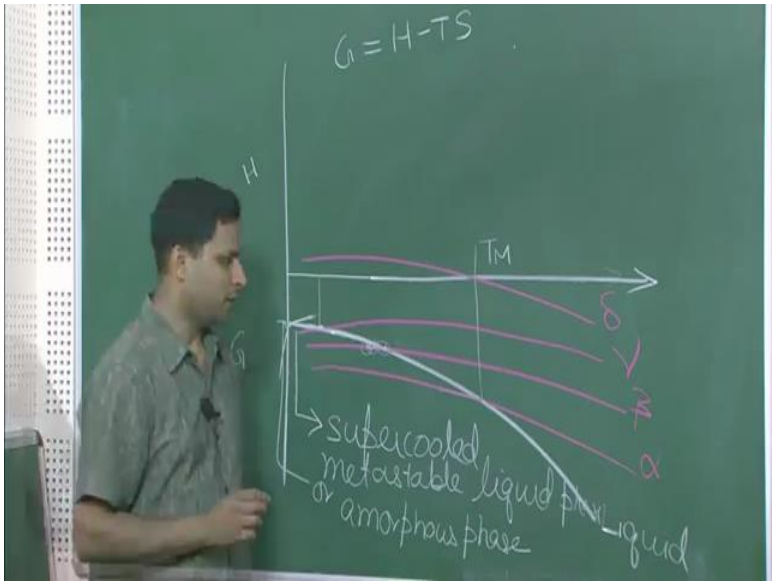

So let us say this is still our liquid, and we are now drawing only the G curve, we do not want to draw H, we just want to see what happens when there are more than one phases that can exist at for a particular component. So, let us say, there is this alpha phase; so this is the G plot or the free energy plot for alpha plot, for the alpha phase. Now the same material, let us say can also exist as beta; so this is how the plot ill look like; and let us say this same plot can, same material can also exist as another phase gamma. But that is not all; there is still another phase that can exist, but it does not intersect with the liquid phase and let us say this is delta. So now what does this thermodynamics tells us about all this?

Okay. So now let us say we are coming from a temperature higher, high enough. There, liquid is the stable phase. So we are in the liquid state, and we keep reducing the temperature. So this is the temperature at which ideally you would have expected solidification into alpha phase. So, alpha phase should start to nucleate over here, but it is quite possible and it is practiceable that you can suppress nucleation of alpha phase. So instead of going to the solid the stable alpha phase, you will still maintain super-cooled liquid, and you may get to a temperature where liquid to beta phase transformation takes place.

So, at this particular temperature, if you keep keep going to a lower temperature, and beta nucleation takes place, it is possible that you may get beta phases; and this will be as good reversible process as the formation of alpha phases will be. However the beta phase that forms, it can further breakdown back into alpha phase, but that is not what we are looking into, we are just trying to understand what happens to liquid phase when we keep reducing the temperature. Now if we are able to reduce or suppress nucleation of beta phase also, then we get even further super-cooled liquid and we may get gamma phase. We may start to get gamma phase at this particular temperature.

And again like I said earlier, we may even be able to suppress this, in which case what we get is a super-cooled metastable liquid phase. If it has enough viscosity; if it has its viscosity is low enough, or it may transform to amorphous phase. What is interesting here is that since the liquid curve does not intersect with the delta curve, there is no way that you will get transformation from liquid to delta. You may get from liquid to alpha, if alpha nucleation takes place; if you suppress it, you may get beta; if you suppress even this, you may get liquid to gamma. But there is now way that liquid can be transformed into delta because liquid and delta G curves do not intersect at any point.

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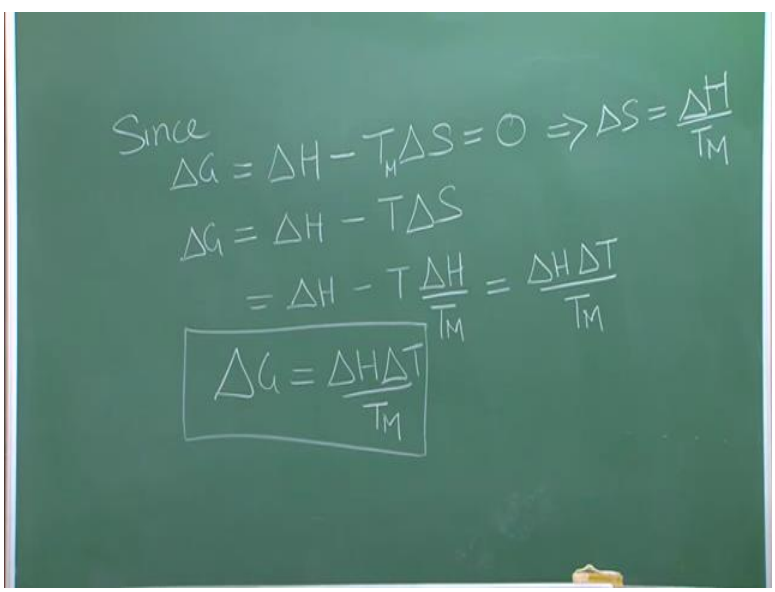

Now another important thing is that, since delta G, which is for transformation from one phase to another; let us say, we are looking at a single component, liquid to a stable phase transformation.

For example, liquid to alpha phase transformation; and this is TM, which we can say this is the TM, and let us forget the other phases. There is just one relation that we may look into. Now this, add transformation, at the temperature of transformation, we can say this is 0. At any other temperature, this will not be 0, and we can write like this. So from here, we get delta H by TM; and if we put it over here, we get. So, delta G can be written as, for small amount of under-cooling, delta G can be written like this. This is a good relation that you may like to remember and use it later on. Okay so that is about a single component system.

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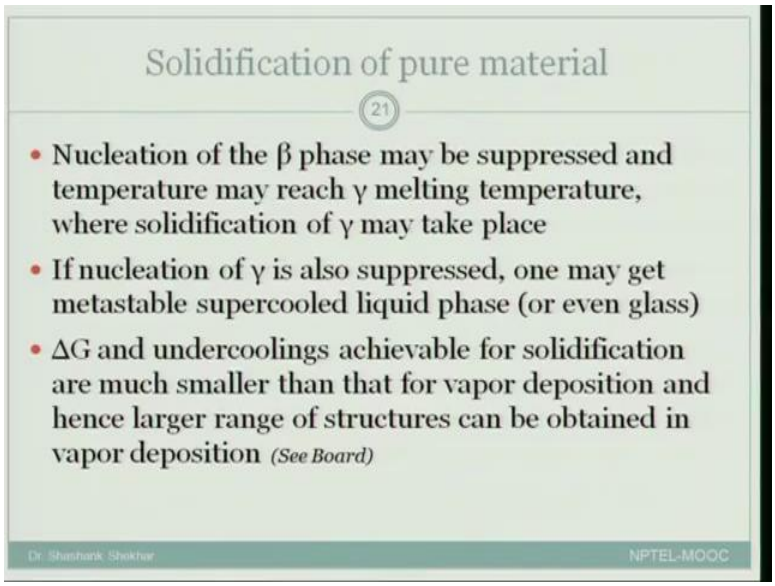

just let let me rephrase what we have already discussed. Nucleation of beta phase may be suppressed, and temperature may reach gamma melting temperature, where (solidification) solidification of gamma may take place. If nucleation of gamma is also suppressed, one may get metastable super-cooled liquid phase, or even glass or amorphous phase. Now delta G and under under-cooling is achievable for for solidification. Now you look at this equation, why I said this is important is because in regular solidification process, this quantity, delta T by TM that you can obtain, is very small.

Which means, the under-cooling is small, as well as the delta G that you are able to get is very small. But, if you do get this process or you (so) if you make solidification from vapour deposition, you can get very large values of delta T by TM, which means you get very large

under-coolings, as well as very large driving forces, which means that you will be able to get very large range of structures.

For example, in the previous case that we were talking about earlier, you had alpha, beta and gamma phases, so by using some vapour (())(13:48) deposition technique or other non-conventional technique where you get very large delta G, you can get other structures which are not possible using usual solidification techniques. So now that was about a single component system where we had, first we had only single phase, then we had two phases.

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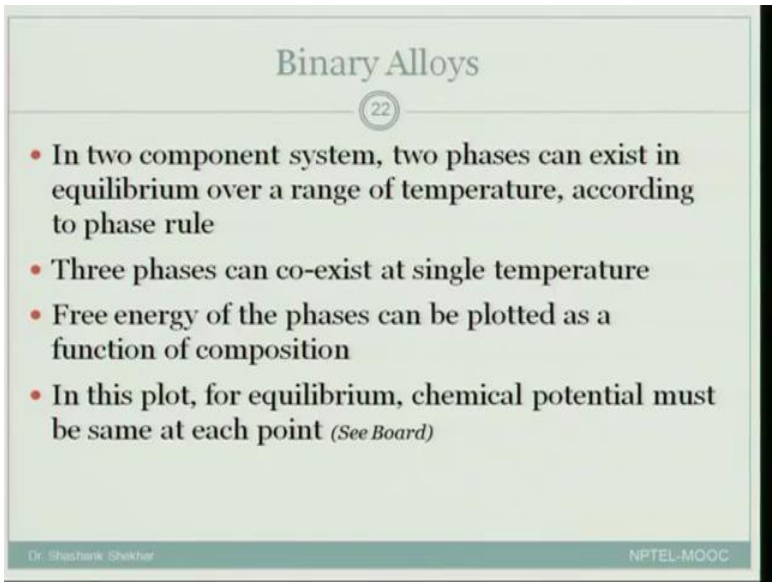

Now let us add a little bit complexity to this; now we will have two phases, have two components. So the two components, how (will) how will the two components look like. The two phases can exist in equilibrium over a range of temperature, according to phase rule. So we know that when we have two phases, there can be two components; in the two components system, we can have two phases that can exist in a range of temperature. But three phases can only exist at one particular temperature. Now the free energy or the phases can be plotted as a function of composition. However this is not sufficient, and you may need to use what is called as chemical potential, because it is the chemical potential that must be same at each point if we are talking about the equilibrium condition.

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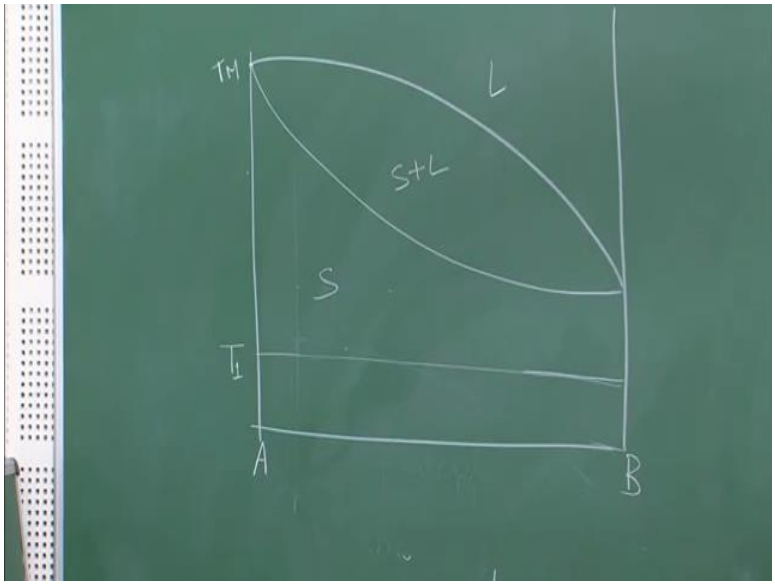

So, let us get back to this, in terms of the diagram. So let us take a very simple binary phase system, which is miscible in each other. So the two components we are talking about are A and B. This is a very simple system and over here, this is some temperature, let us call it TM, and we will first consider a temperature very low enough, where only one system exists; so let us call it T1. This is the region where both solid and liquid exist; so this is the solid region, this is the solid plus liquid region, and this is the liquid region.

So this is a phase diagram for a two-component system. Now how does the free energy plot look like for let us say this particular temperature, where we have only one phase existing for two components? Remember, we are not talking about single component anymore; we have two components. The two components, it can be two different elements, it can be two different compounds, it can be two (diff) any two different entities. So now, it is important to see how the free energy plots look like.

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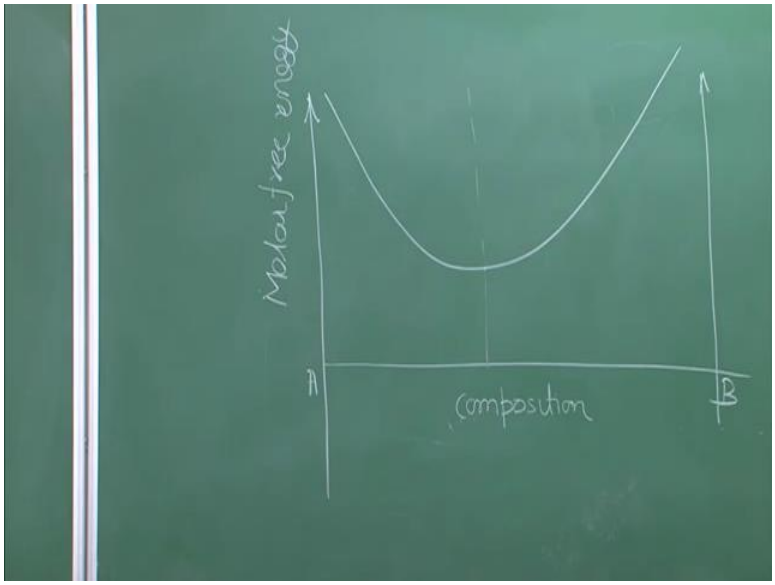

So usually, when we are plotting this, we use the term molar free energy to denote energy in terms of per unit mole, and since solid phase is the only phase that can exist, so what here we have B, so on the x-axis basically you have composition. So this tells you the overall change in the energy, Gibbs free energy of the system which has two components A and B. Now, like I said earlier, this is good enough as a system; but what about the energy for individual system. We want to know what is the energy, free energy for A, what is the free energy for B; and for that, we need to invoke what is called as chemical potential.

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So what is chemical potential? We will describe it okay, we will describe it over here. So we are talking about mu A. So this is the equation that gives the value of chemical potential nutrition A, meaning, this is the change in the overall energy of the system when you add a small amount, a small mole of A; basically a change in the ratio of A and B, because we are talking about moles of A. So you are changing the ratio of A and B. So while you, I had this small amount of A; what is the change in the Gibbs free energy, overall system, free energy of the overall system; that is what is called as the chemical potential.

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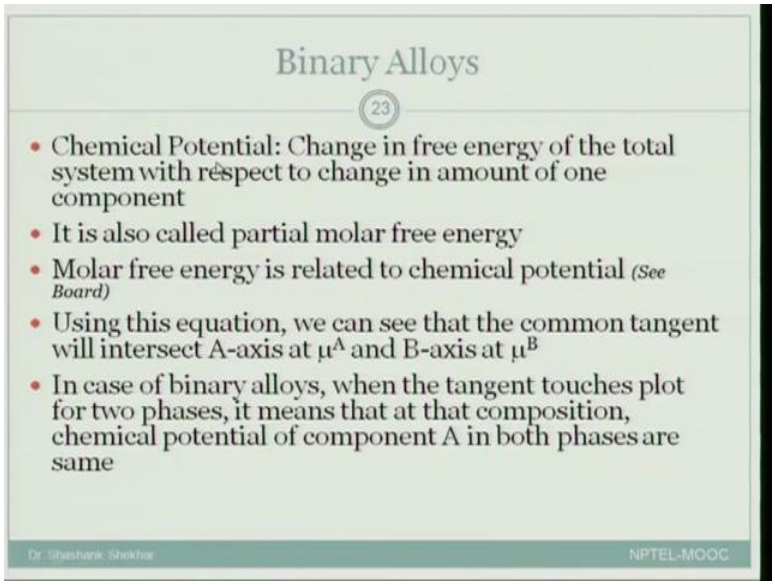

So, let me get back to the slide over here. In the slide, as you would see, chemical potential is change in free energy of the total system with respect to change in amount of one component. It is also called ‘partial molar free energy’. Now this molar free energy is related to chemical potential, meaning the free energy that we have described over here; this, this can be related to the overall chemical the the chemical potential of the overall system; sorry the chemical potential can be related to the Gibbs free energy of the total system, which is given like this.

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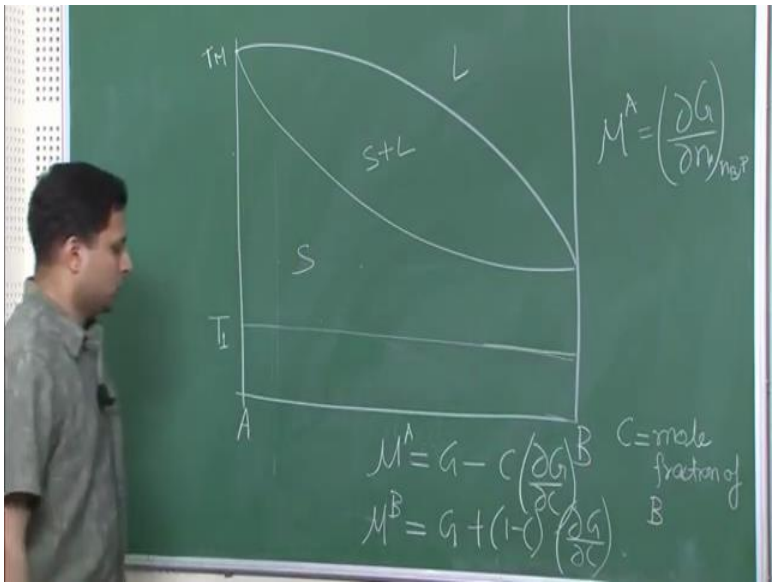

So this is the chemical potential for A, where C is the mole fraction of B. So this is the chemical potential of A, this is the overall free energy of the system; so both of them are related over here, and these are the two equations that we get for the chemical potential. Now if you look at these two equations, you would realize, that what it is saying is that you can obtain the chemical free potential for each of these system from the plot.

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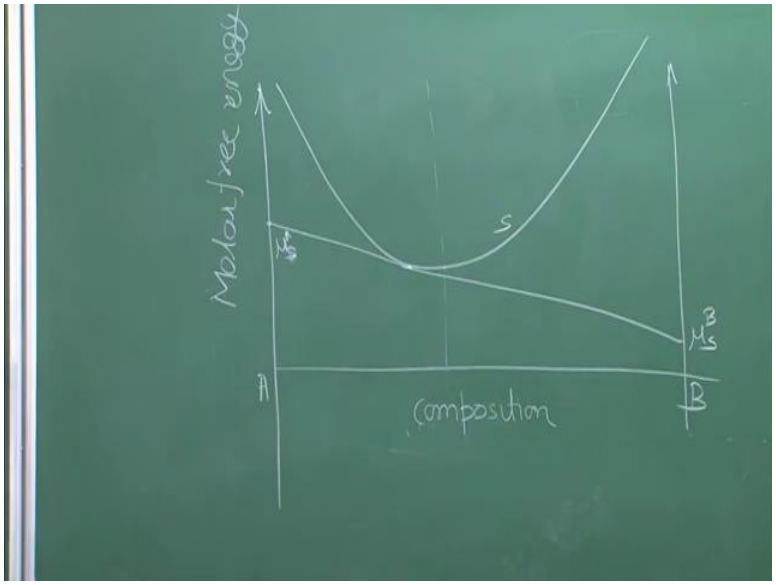

For example, let us say if I am at this particular point; all I know, if I want to know the chemical free potential, I need to draw a tangent over here. And this tangent will give me the chemical free potential, the chemical potential for component A, in this particular phase, whatever is this phase. let us say this is the solid phase. So we will denote by superscript A, which is the chemical potential of the component mu; so mu so this is mu A, meaning chemical potential of A in the solid phase S. And over here, this is a chemical potential of B in the phase S, which is solid.

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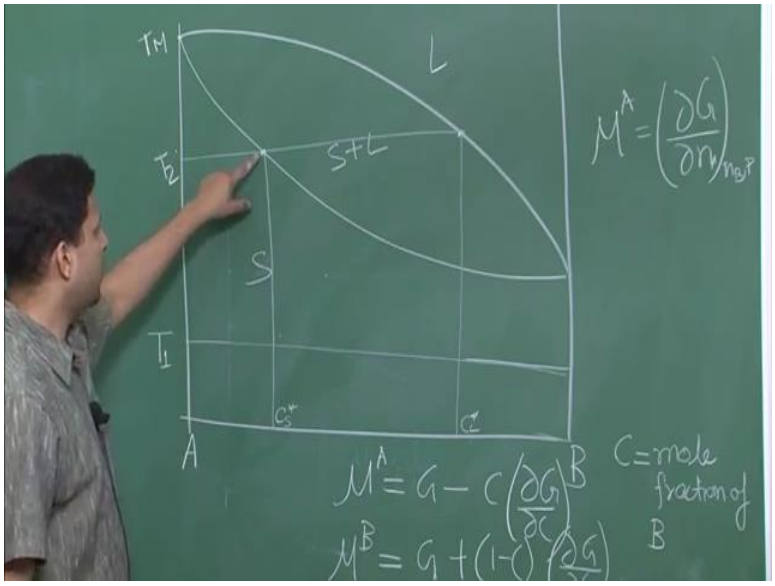

Now let us say, so this is how this energy plot would look like at a temperature where you have only one phase existing which is the solid phase. Now let us say we are at some particular temperature T2. So over here, you have two different; you have two different components, solid and liquid, and there are some specific or you can say critical concentration, which we will see, is relate, we will be able to relate over there. So this is the concentration CS star over there, and this is the concentration CL star over here. Now since we have two different phases, we will also have two different plots. So this will be the free energy plot for liquid.

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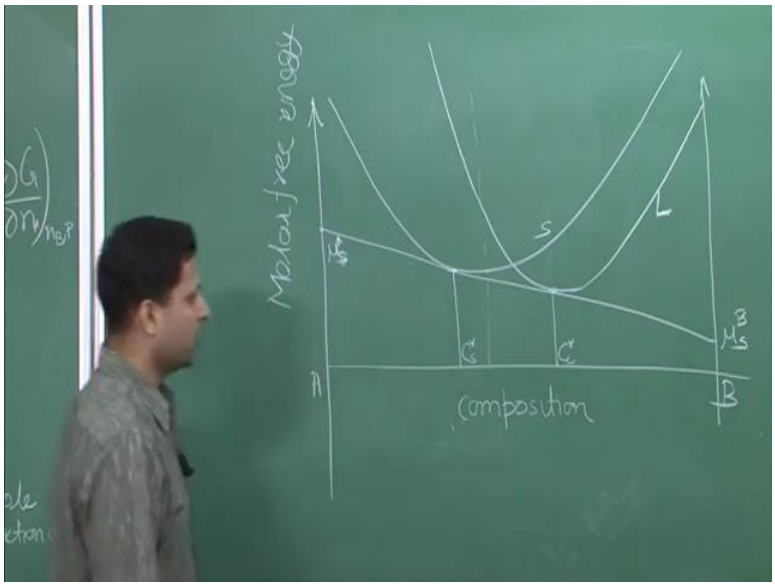

And in fact, because we have selected a range where both solid and liquid are stable, it means that a common tangent must cross from both of these, and the common tangent, the points at which it will cross will give you the critical or the concentration which will be formed when these two exist together. So in this region where we have both solid and liquid, the concentration of solid will be CS star, concentration of liquid will be CL star, and it is given by this common tangent system. So we get so this chemical potential allows us to get the CS star and CL star values in a very simplified manner, specially if you are if you can, if you look at the equation which allows us to draw the common tangent.

So, just to sarize what I said, it also says that chemical potential of compound, of component A in solid and liquid are same; so for example, when we draw a common tangent, it says that at this

particular when this this common tangent which is over here, the chemical potential of A in solid is same as the chemical potential of A in liquid.

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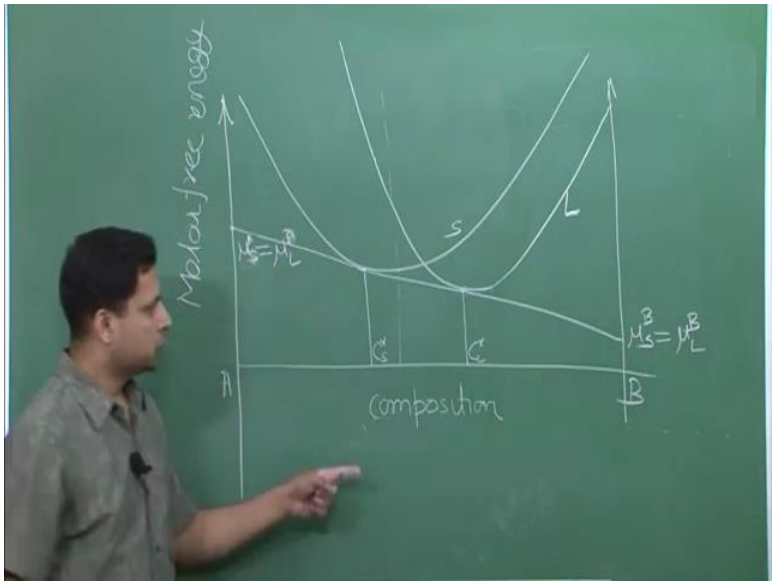

So, if I; so the chemical potential of B in solid is same as chemical potential of B in liquid, and that is why they are existing together, they can co-exist. Similarly, chemical potential of A in solid is same as chemical potential of A in liquid, and therefore they can co-exist.

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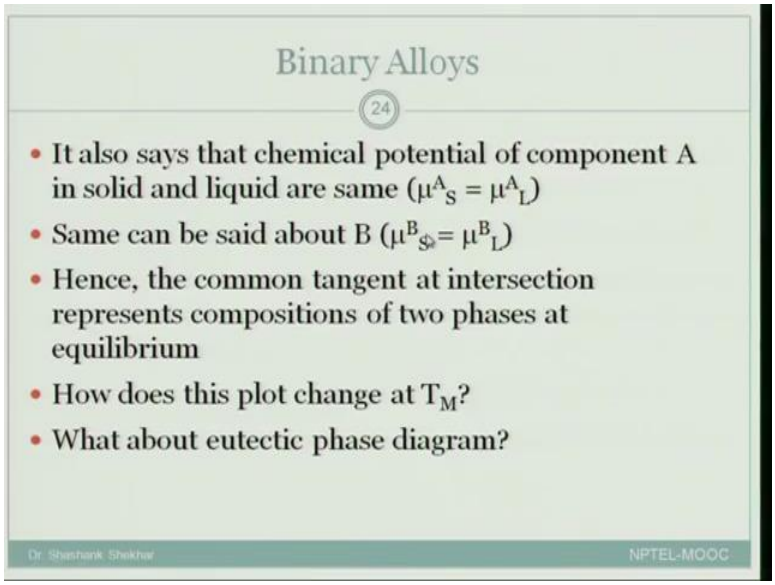

So same can be said about B; mu BS is equal to mu BL. Hence the common tangent at intersection represents composition of two phases at equilibrium. How does this plot change at TM? Now, what will happen if we are now looking at this particular temperature? What, how will this plot look like? That is a question that you should ask yourself, but we will since this is a simpler question, we will draw it over here.

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So now we are drawing at T equal to TM. Or actually we are just a little above TM, because even at TM, we will have both solid and liquid; so, for the sake of simplicity, let us assume that we are just above TM, which means that there is only liquid and there is no solid, so there will be no intersection of solid and liquid when we draw this free energy diagram, and you will get only liquid for all compositions.

Now this was a very simple phase diagram that we were looking at. What I would like you to try on your own is to find out how this phase diagram would look like, or the, sorry the free energy diagram would look like for a little bit more complicated system which is eutectic system.

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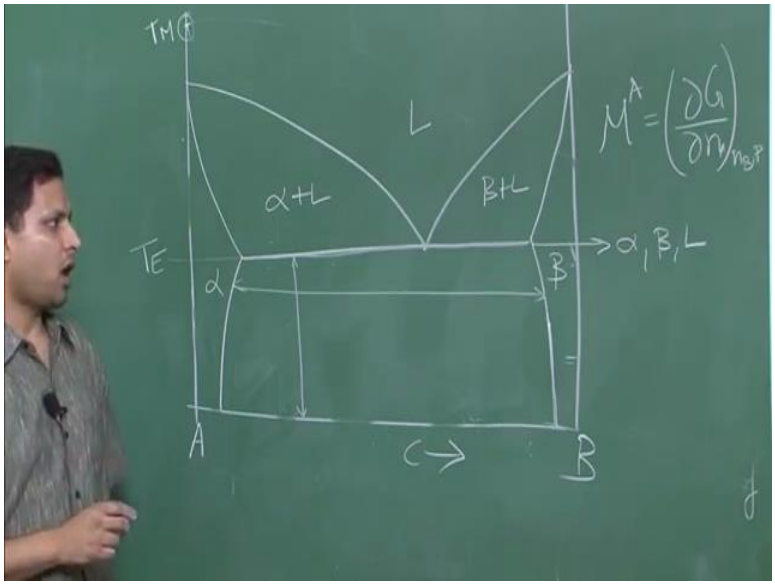

So this is your composition, which is basically mole fraction of B. On here, you are pure A; on here, you are pure B. These are the two different phases; let us say alpha and beta, and over here you will have beta plus liquid; here you have alpha plus liquid; here you have liquid. Now if you are talking about temperature range and composition range; over here, you can see that two different phases can co-exist. And it is for a wide range of temperature, as we would expect from the phase rule. But if we come to this particular temperature which is a T-eutectic, you would have three different phases existing together, which are alpha, beta and liquid.

Now, you should try and draw the free energy diagram for a system like this at a temperature like this; how it would look like, and what will be the common tangent that you need to draw over there. Try doing that, and we will end this part over here. Thank you.