

Phase Equilibria in Materials(Nature and Properties of Materials - II)
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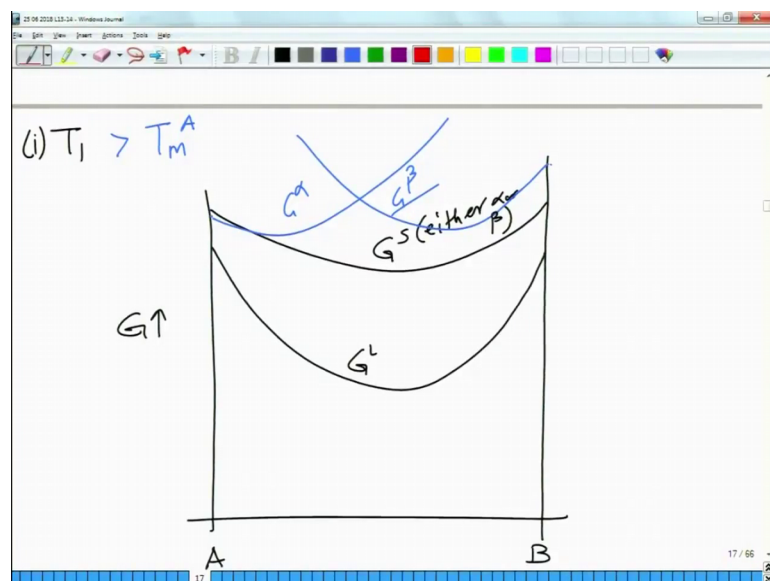
Lecture - 15
Phase Diagram Construction: Eutectic Phase

Welcome again all of you. So, this is a lecture 15 of Phase Equilibria module. So, let me just recap what we were doing in the last class because we left intermittently. So, we started looking, so, in couple of lectures where we started looking at Phase Equilibria and Heterogeneous System and we were taking examples in as far as binary solutions are concerned.

So, first we had a look at you know systems with complete miscibility in each other that is in both liquid and solid state of A and B which means A and B make a random solid solution in solid state. As a result the phase diagram that you get for that kind of A B system is isomorphous system for example, copper nickel system.

Now, the next system that we were looking at was system in which A and B have partial solid solubility which means A can accommodate some amount of B and B can accommodate some amount of A before super saturation happens. And as a result, it has profound influence on the free energy composition landscape which leads to changes in the phase diagram construction. So, let me just now go back to what we were doing.

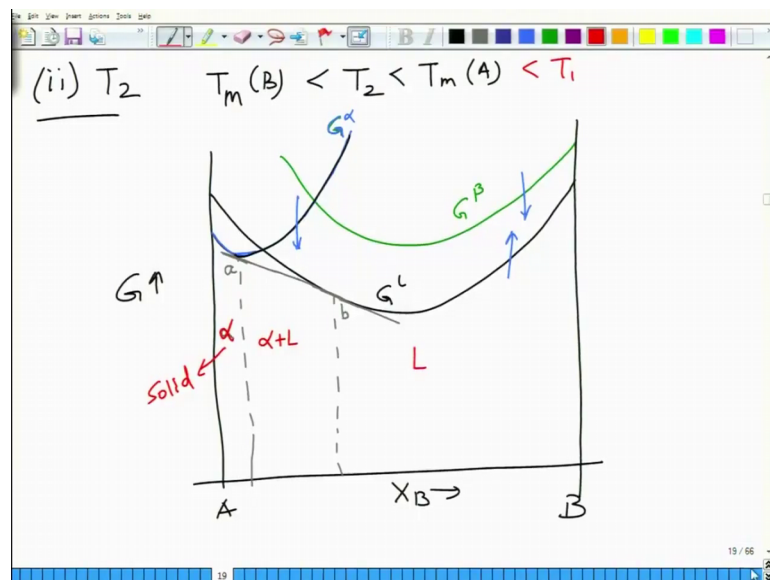
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So, this was the first thing that we did. So, we have two elements A and B, a melting point of A is higher than that of B. And what we have here is we have first temperature T_1 which is higher than the melting point of A. As a result, since we can see that since it's temperature at which is higher than the melting point of both the phases, both the elements, we are going to have liquid phase which is stable than the solid phase could be mixture of two solid phases. So, in this case, it would be mixture of two solid phases.

So, what we are going to draw is G alpha and G beta and both are going to be above the liquid phase. So, in this regime liquid will be the most stable phase as far as T_1 is concerned at T_2 temperature which is intermediate between; which is the intermediate temperature between the melting point of A and melting point of B.

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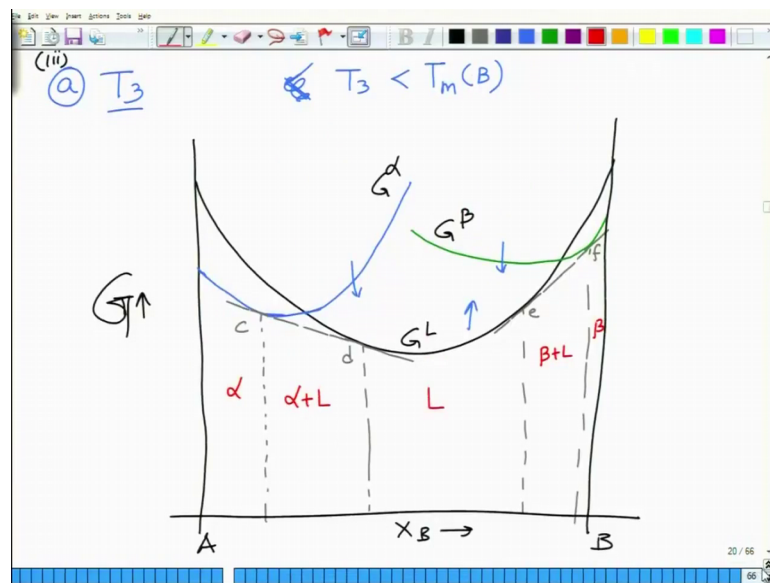


So, of course, it is lower than T_1 , but it is also lower than T_m of A, I have not drawn the phase E composition plot for T_2 is temperature being equal to T_m of A which is similar to what we do in the last example.

So, T_2 is between melting points of A and B. So, as a result what you have is you have since temperature is higher than the melting point of B and lower than the melting point of A alpha phase which is the solid solution of B in A or and which has a similar structure as of pure a starts to stabilize. So, the free energy of alpha phase lowers with respect to free energy of liquid, but the free energy of beta phases still high which has a structure same as B. And as a result, we form two phase region on the A rich side.

So, on the A rich side when you are below point A. So, we first what we drew was we did was, we do a common tangent between G^α and G^L . And the intersection of tangent with the point where tangent touches the G^α and G^L curves, we denote them as A and B. Below the composition A it is all alpha which is solid state. So, alpha will be solid. After A, but below B composition you will have two phase region that is alpha plus liquid and above B composition, you will have only liquid state. So, we have alpha liquid, alpha followed by alpha plus liquid followed by liquid.

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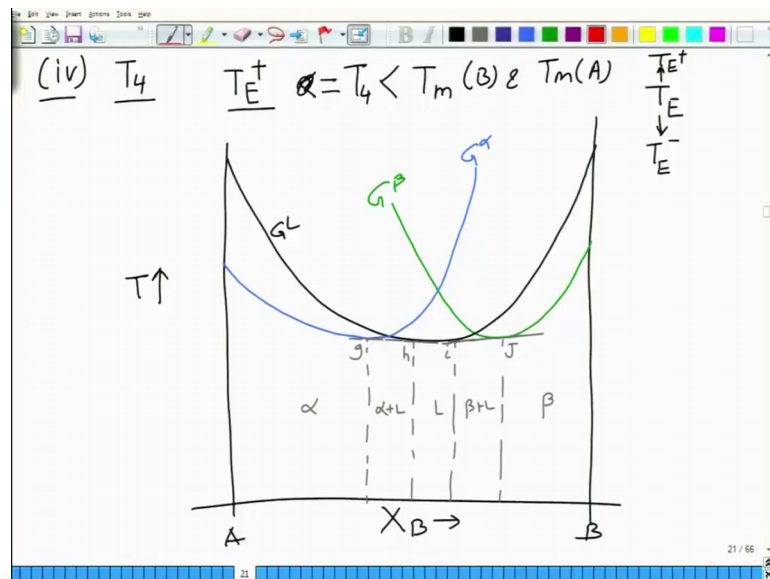
And then we go to temperature T_3 which is lower than the melting point of B. So, this is now lower than the melting point of B. So, what we have here is both alpha and beta curves are shifted further down with respect to G^L curve. And as a result, what you have here is, as a result what you have here is you have formation of two, two phase regions on the two sides of the curve. So, you, we again draw the common tangent between liquid plot and the solid plots.

So we denote them the, that the points wet engines touch as c d e f. So, below c on the aided side is the phase field alpha, above c, but below d is the two phase region alpha plus liquid. And then we have liquid because in this region liquid free energy is lower than both alpha and beta. And again we reach a, region which is bound by two points e and f which are again the between the common tangent points. So, this is beta plus liquid

on the right far right on the beaded side, when the composition is beyond f which is the b rich region, we have beta phase stabilizing.

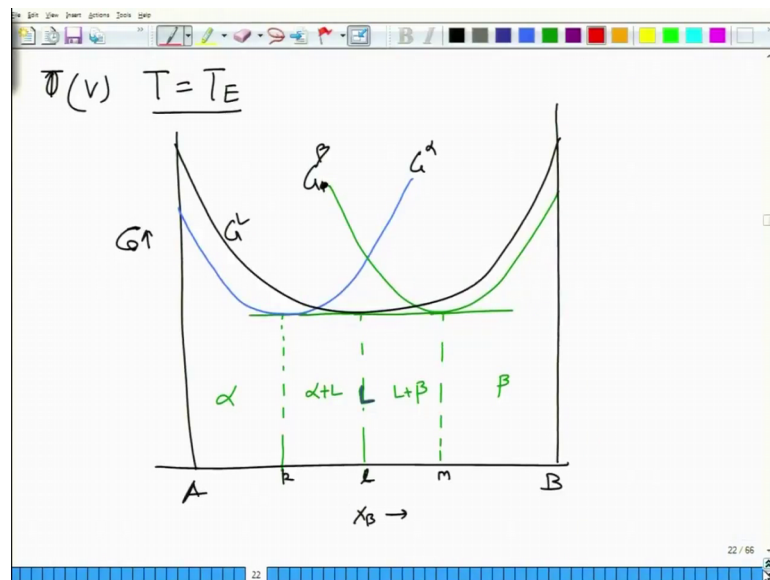
So, you can see how the phase evolution has happened from complete liquid to first the formation of alpha and alpha plus liquid for and alpha region. Now to alpha alpha plus liquid, liquid beta plus liquid and beta so, you have complete five phase fields here. And then, we move on to a temperature T_4 which is lower than both melting points of A and B, but it is slightly higher than the a specific temperature called as eutectic temperature and this eutectic temperature is this is a temperature, I will explain later what it is.

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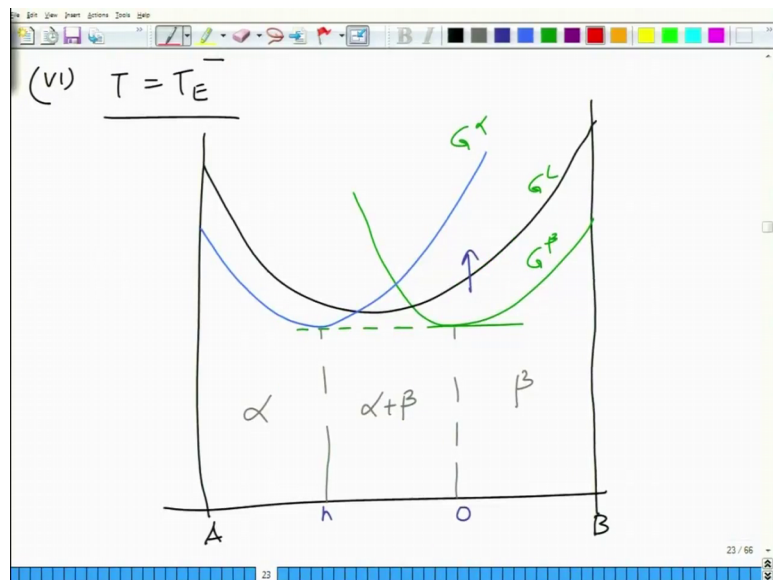
But let us say it is T_4 plus so, at this temperature the minima's of all the three phases that is alpha liquid and beta are almost at the same level, since temperatures slightly higher than the T_4 plus the, that alpha and beta minimizer slightly shifted up with respect to liquid. So, we draw a common tangent again. So, it is alpha, alpha plus liquid, liquid region a shank quite a bit and then beta plus liquid and then beta. So, again these points are denoted as g h i J.

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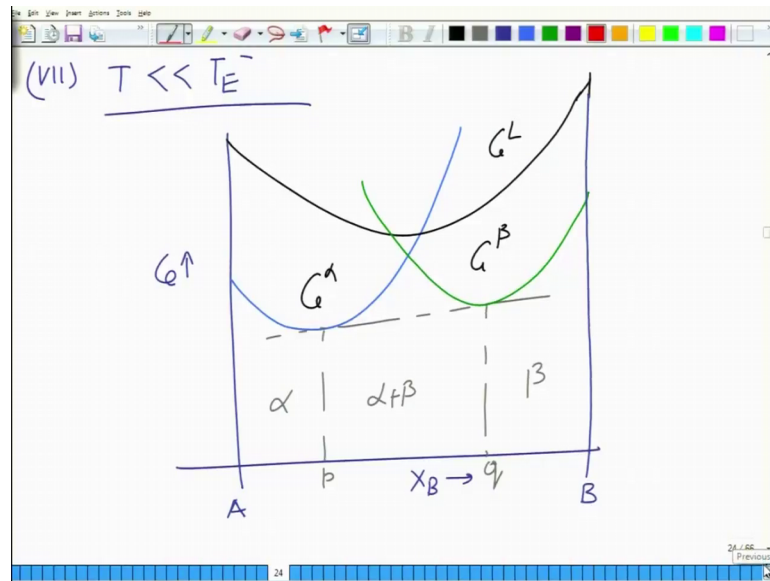
And then we looked at T is equal to T_E which is the eutectic temperature, a specific temperature at which all the three phases are in equilibrium. Now, this is where we have all the three minimas on a flat line. So, what we have is alpha, alpha plus liquid, liquid denoted just by a straight line, liquid plus beta and beta phase.

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A moment you go to slightly below the eutectic temperature the liquid curve shoots up goes up with respect to alpha and beta. And what we have is a two phase equilibrium alpha, alpha plus beta and beta.

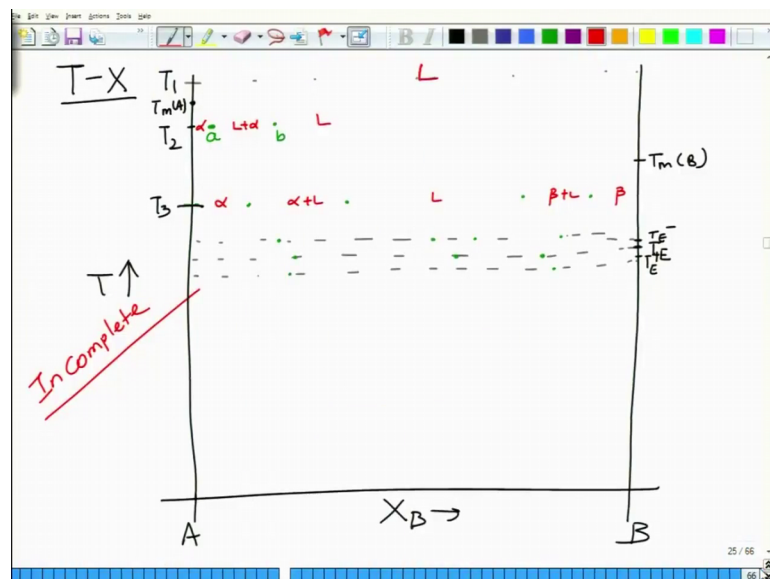
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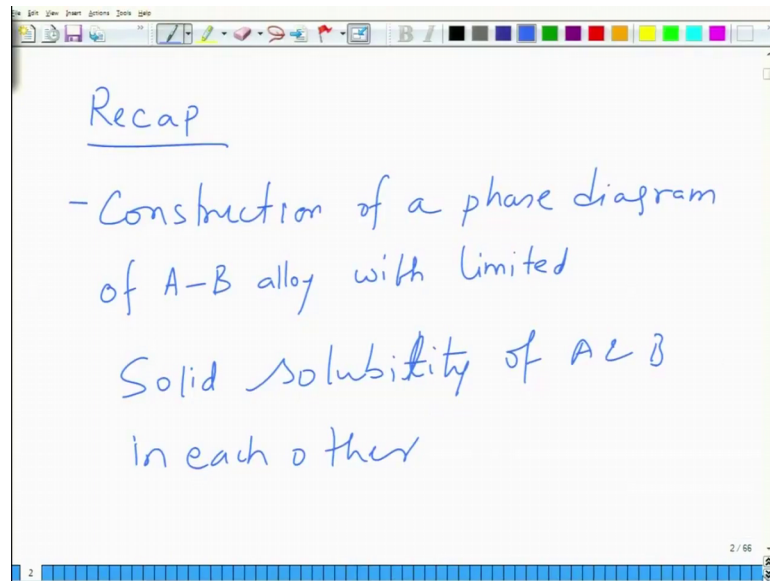
And then when you go to further lower temperatures, what we have is widening of this alpha plus beta regime and alpha and beta again narrow down little bit because of decreasing solid solubility in the solid phase.

Now, we want to construct a phase diagram having got this information. So, that is what we will do in the next today's, today's lecture, we started doing in the last class, but unfortunately we did not have enough time. So, this is what we were doing, we will now take it up in today's class.

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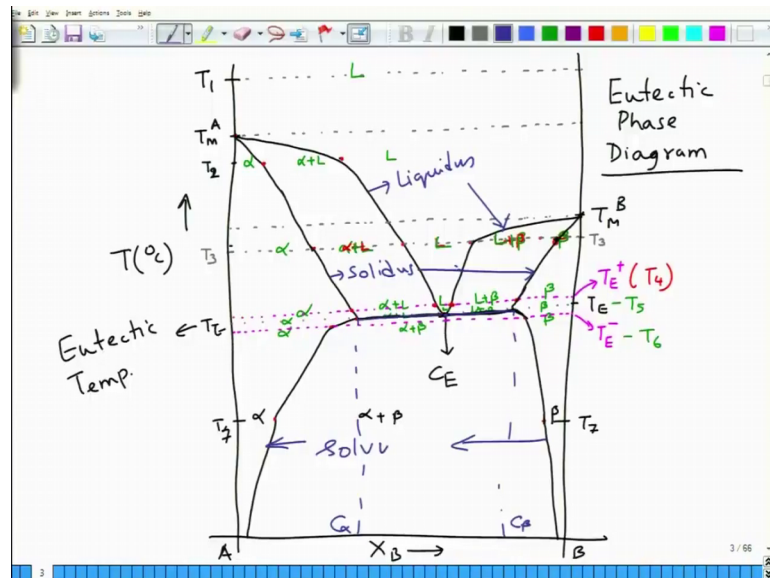


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So, basically recap was construction of a phase diagram of A B alloy with limited solid solubility of A and B in each other which is because of you know structural differences, size difference, valance differences and so on and so forth, but they do not have vast difference in the melting point.

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So, now let us make this, right. So, this is pure A, pure B, we go from here X_B and this is the temperature axis. So, this could be the degree centigrade or Kelvin depending upon how you want to. So, let us say, first we look at a temperature T_1 . So, let us say this is,

let us identify a few temperatures $T_m A$, let us say this is $T_m B$ and let us say this is another temperature, let me this is another temperature T_E . So, let me draw a few lines here. So, this is T_1 line, this is $T_m A$ line, this $T_m B$ line, this is T_E line and let me draw the T_E plus and T_E minus a little sorry, wrong colour. So, this is T_E minus and that was T_E plus and this is T_E minus. So, this would be T_E plus and this would be T_E minus, all right. And they are not very straight, but pardon me for that.

So, first thing that we observed was we had a T_1 , everything was liquid. At a temperature T_2 which is between $T_m A$ and so, of course, at $T_m A$ both solid and liquid phases will be in equilibrium. At temperature T_1 , we had alpha region somewhere here followed by liquid region. So, this is, now let us label it, this is alpha, alpha plus liquid and liquid and let us mark these points as red.

The first one is here, last another one would be at somewhere here. Now, at T_2 temperature, now this is a T_1 sorry, this is a T_2 , this is T_2 , T_3 was a temperature, let me see where the T_3 was. So, let me mark these temperatures as well T_4 , T_5 and T_6 . So, T_3 was lower than the melting point of B, let us go back here, T_3 was lower than melting point of B. So, this would be T_3 . So, let us say, this is T_3 , let me draw again a horizontal line at T_3 .

Now, at T_3 what we will have is, so, this is point A B, now we will have c d e f. So, let me choose red colour. So, my next point is we are at T_3 . So, we are somewhere here in terms of the other point c. So, we have alpha. So, this is alpha, followed by we will have alpha plus liquid, followed by we will have liquid, followed by we will have. So, this is beta and this is liquid plus and beta. And now we are near another point. So, now, we are T_4 , so, this is T_4 . So, when we go to T_4 , this point is somewhere here.

So, let for the sake of simplicity, let us move these points a little bit so, that they fall in a, they fall on a nice curve. So, it would be somewhere, somewhere here. So, if, I now make the other points that will be somewhere here, this would be somewhere here, this would be somewhere here and this would be somewhere here. So, this is again, so, this is alpha plus liquid, liquid liquid plus beta, beta this is again alpha, alpha plus liquid, this is liquid, this is liquid plus beta, beta.

And, now we go to T_5 . So, at T_5 there is only one point for liquid, this is liquid and this is alpha. So, what we have here is alpha, alpha plus liquid, liquid. And then when we go

to beta, when we go to T 6, which is this temperature, it is alpha and beta have shifted little bit here. So, what you have is alpha beta and you have alpha plus beta and here you had alpha, alpha plus liquid, liquid here liquid plus beta and beta.

Now, let us try to connect the dots. So, when we try to connect the dots, so, the first dot is something like this, this and this. It is not very straight as it should be. So, on that first let us so, you will have to pardon me little bit for this kind of boundaries turning curvy they are not so, curvy in reality and have this kind of.

So, let us say this point is this, this is the beta point. And then we connect a lower temperature, this is for lower temperature part, just one second to this lower temperature part. And then we had a T 7, where alpha and beta shifted even. So, this could be let say T 7. So, at T 7, it was here, let say it is here and when we connect the dots, it would be somewhere here, something like that.

So, what you will have is here. So, this is the T E line, up to this point liquid and beta coexist and liquid and solid coexist. After this line only solid phases coexist. And within this region, so, if you, you can take this further down, it will come like this, if you had more energy curves. So, this is that T 7 alpha, alpha plus beta and beta.

So, if you look at the phase diagram, now what we have established here is you have a liquid phase here, liquid phase as a temperature decreases, liquid phase first forms into alpha plus liquid then as a for this composition, if you had this composition liquid phase will convert into beta first and this liquid plus beta will slowly, slowly convert into alpha plus beta.

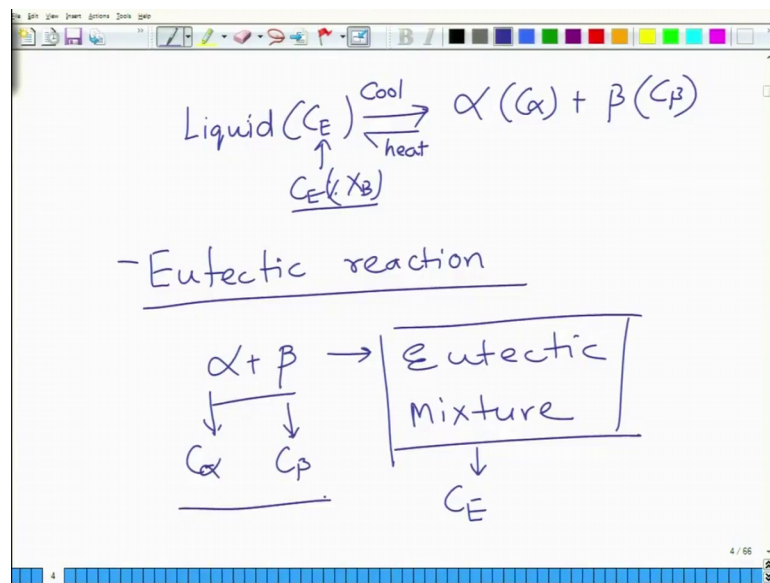
So, you form this kind of phase diagram where you have two regions of complete solid on the right and left, these are called as terminal solid solutions of alpha and beta, solid solution of B in A and A and B. On the high temperature side, you have liquid only. In the intermediate temperatures and intermediate compositions, what you have is a two phase region liquid plus alpha and liquid plus solid.

Unlike isomorphous system, there are two liquid plus solid regions, one is liquid plus solid, one second is the liquid plus solid two alpha or beta. And then at lower temperatures and intermediate compositions, you do not have alpha and beta alone, you have a mixture of alpha and beta.

And there is a specific temperature at which is called as T_E , which we call as eutectic temperature. At this temperature, liquid of this composition which is called as C_E , the eutectic composition directly transforms into two solid phases alpha and beta and this temperature is lower than the both melting point end of A and B.

So, this kind of phase diagram that we obtain when A and B have limited solid solubility into each other, but their melting points are not vastly different this is called as a eutectic phase diagram.

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And basically what happens is that so, this phase diagram is characterized by phase reaction in which liquid of composition C_E . So, C_E is basically C_E percentage of X B. So, it is in the mole percent of X B transforms into solid phase alpha of composition C_α and transforms in to beta phase which is composition of C_β . So, this is, I would say C_α and this I would say is C_β and this is C_E . So, this is at this temperature.

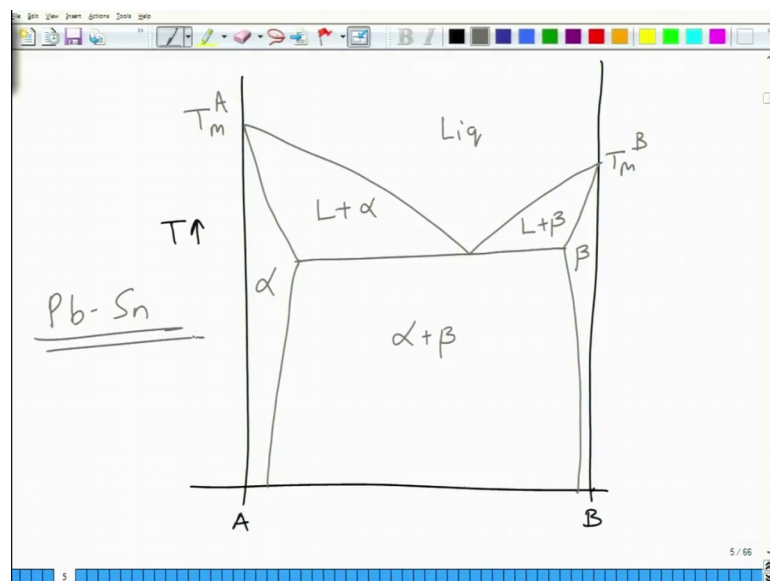
So, I will tell you now, how the microstructure evolves later on. So, this is at cooling you can also heat it. So, it is a reversible process and then alpha plus beta which exists at this composition will convert into liquid, of composition C_E . So, this is, what is the characteristics of this phase diagram, it is called as eutectic phase diagram. And this reaction is called as eutectic reaction. And it is at this temperature, you can see the three phases coexist at this line, you can see that at this point liquid and alpha plus beta all

three coexist, it was which was marked by which was marked by free energy minimum being at the same height, at the same level for all the three phases.

So, at this point your three phases coexist together whereas, in the other regions you can see that in this region liquid phase exists in this region alpha phase exists in this region beta. So, there are three single phase regions and then there are three two phase regions this is the this is the region between alpha plus liquid there is a region between liquid and beta which is liquid plus beta. And the region between two solid phases alpha plus beta.

Again the terminology wise, this boundary is called as liquidus which is the boundary between liquid and the first solid, both of these are liquidus, these are solidus. And these two boundaries are called as solvus, mixture of alpha and beta is called as Eutectic mixture. And eutectic mixture, the overall composition of this mixture will be same as C E, but alpha will be of composition C alpha and beta will be of composition C beta, we will discuss this phase diagram a little later in terms of how the phase is evolved.

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So, the previous one was the phase diagram that we constructed which was not very neat as far as drawing was concerned. So, what you will obtain is something like this. So, this would be the liquid region, this would be liquid plus alpha, this would be alpha, this would be alpha plus beta liquid plus beta and this would be beta. So, this looks like more neat diagrams and this is T_m of B, this is T_m of A. So, this would be a eutectic phase

diagram. And these alpha and beta can have different structures, but alpha and beta can also have similar structures alpha 1 and alpha 2 for instance.

So, this phase diagram for example, you have systems like Latin alloy which is a very important soldering material, it follows this kind of phase diagram. So, other than these two kinds of phase diagram that we discussed, one is the isomorphous phase diagram. We evolve them on the basis of free energy composition changes. You can have other diagrams as well. For instance you can have situations where you can have high free energy of mixing.

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Systems with a miscibility Gap

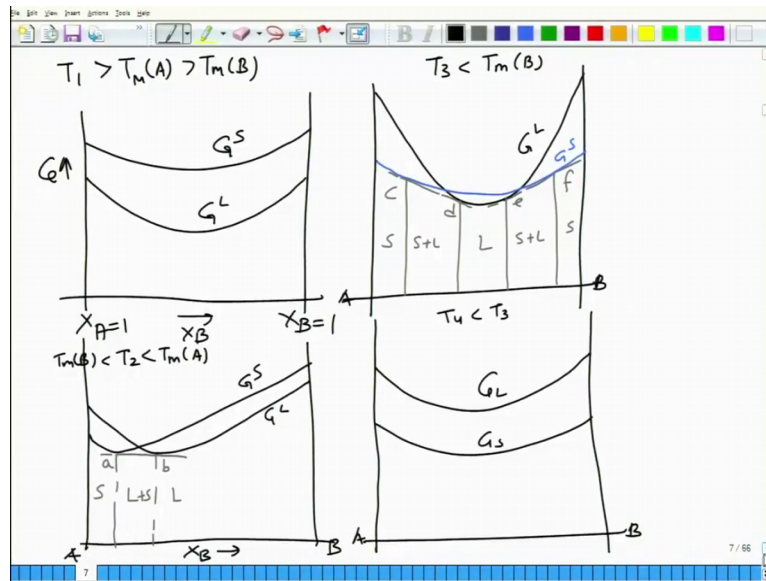
$$\Delta H_{\text{mix}}(s) > \Delta H_{\text{mix}}(L) = 0$$

⇒ A and B are soluble in liquid
but may not be in the solid state

For instance, we can have systems which have you can have systems with the miscibility gap. So, miscibility gap now what I would do is that, I would take a reverse approach here. So, system so, the miscibility gap means for these materials delta H mix and solid state is larger than delta H mixed in liquid state which is equal to 0.

So, basically A and B are soluble in liquid phase, but may not be in the solid state. So, I will not spend too much time on it, I will just go through a few phase boundaries.

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So, for example, we can have scenario in which let us say at a temperature T_1 which is greater than the melting point of let us say $T_m(B)$ is higher than $T_m(A)$ which is higher than $T_m(B)$, this is the scenario.

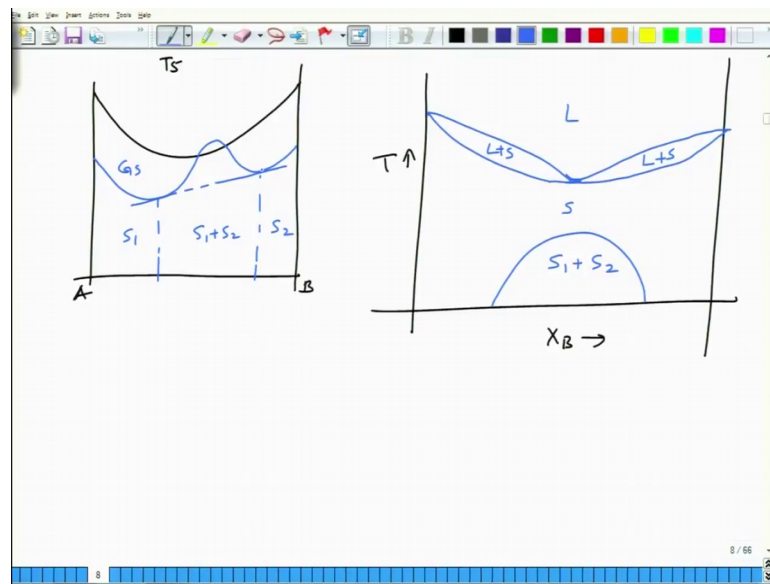
The first scenario is like this, T_1 . So, you have X_A , X_B . And let us say the scenario is something like this, you have G^S and you have G^L , this G then you come to a temperature, different temperature. At this temperature the free energy curve shifts a bit. So, you have this is the free energy curve of solid phase, this is the free energy curve of liquid phase. So, this temperature T_2 is lower than T_m of A , but higher than T_m of B . So, this will redraw it. So, you had, there is a free energy of solid phase, it is free energy of liquid phase. So, G^S , G^L that is the common tangent that we draw, this is solid, this is liquid plus solid and this is liquid so, this is A , this is B .

Now, you come to another temperature $A B$ and this temperature is T_3 which is lower than T_m of B . So, what you have a situation like this, you have free energy oops not very neat. So, this is G^L , I draw the solid phases little differently solid phases, but like this.

So, this is G^S and then you draw the common tangent now, you can draw the common tangent here and you can draw a common tangent here. So, this is four points. So, you will have solid, you will have solid plus liquid, you will have liquid, solid plus liquid and solid.

So, this is let us say c d e f, you lower the temperature further down and let us say you reach a temperature T_4 which is lower than T_3 . At this temperature your G S, G L p. So, up to this point it sounds all right. Now, it seems a bit strange, then in one sense that you had single phase region liquid followed by two, two phase, one two phase region and then you had two, two phase regions somewhere in between the solid. So, the liquid phase is liquidus and solidus are little different.

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Now, let us go to a temperature T_5 . So, at T_5 a liquidus is something like this and solidus, solid free energy curve changes a bit, solid free energy curve takes this form. So, now, the solid has basically phase separated into different composition. So, this is S_1 , S_1 plus S_2 and S_2 .

So, when you construct the phase diagram for such a system, the phase diagram, I will not get into details of now phase diagrams unlike in T and X_B , what you will have is something like this you have. So, you have liquid, liquid plus solid, liquid plus solid. And then at lower temperatures and here also you had solid, but then this solid has broken at two decomposed into two different solids at. So, you can see that the free energy curve or solid develops a curvature here, a negative curvature at this point at which temperature at phase separates into two solid phases.

So, I will stop here at this point, what we have looked at is basically the eutectic phase diagram and phase diagram of a system in which solid is immiscible in the solid will A

and B are immiscible in the solid phase itself. We will come back to a few more variations of phase diagrams in the next lecture.

Thank you.