Phase Equilibria in Materials (Nature and Properties of Materials - II)
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Lecture - 13
Phase Diagram Formation: Binary Solution

So now, let us today we begin a new lecture, lecture 13. So, welcome you all. So, in the last lecture we talked about, let me revisit the last lecture. In the last lecture we talked about, how equilibrium and heterogeneous system exists. So, basically we started with our discussion on equilibrium in heterogeneous systems.

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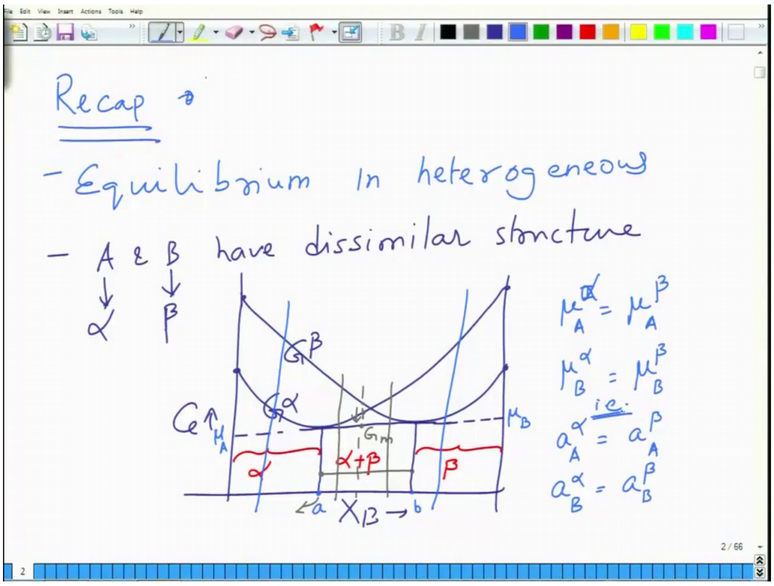

Recap :

- Equilibrium in heterogeneous
- A & B have dissimilar structure

$A \rightarrow \alpha$, $B \rightarrow \beta$

$\mu_A^\alpha = \mu_A^\beta$

$\mu_B^\alpha = \mu_B^\beta$

i.e.

$a_A^\alpha = a_A^\beta$

$a_B^\alpha = a_B^\beta$

So, which basically, meant that we no longer relying on the definition of, ideal solution. So, you may have situations where A and B have dissimilar structure, which means, they do not make a complete solid solution. So, as a result there are two phases which may exist.

So, for instance, there may be one phase, alpha phase which has a structure of pure A and the beta phase which has a structure of pure B. It could be FCC BCC whatever and it is the when these two phases will eventually end up having their own free energy curves. So, you will have free energy curve for A and you will have a free energy curve for B. So, this is alpha beta sorry this is for G beta this is G alpha.

So, hypothetically speaking you might have A and B as well, but when, when you are on A rich composition, then G alpha is lower than G beta and when you are on B rich compositions, G beta is lower than G alpha making alpha and beta more stable. And, in the intermediate compositions, in near the crossovers you have to draw a common tangent and this common tangent defines the boundary up to which single phases can exist on either A rich side and B rich side.

So, in this region; so, this will be alpha, this would be beta and in between you will have a two-phase mixture alpha plus beta whose free energy, so, if you have this overall composition, like this then the free energy of this mixture will be this, which is G mixture as compared to this or that. So, free energy is going down and stabilized at this point.

So; and the composition of alpha phase is given by, so, you have two phases alpha and beta, the relative proportion of alpha and beta will be determined by the composition. So, if you have this composition the alpha and beta proportions will be different, if you have this composition alpha and beta proportionately different. However, whatever the proportion of alpha and beta, may be the composition of alpha that is amount of B in alpha, would be determined by intersection of this horizontal. With this line this is the, composition of alpha phase and this is the composition of beta phase.

So, this is the equilibrium composition of alpha phase, that is this is the maximum amount of B, that can exist in A. Similarly, this is the equilibrium composition of beta phase which is in coexistence with alpha phase. If the alloy composition was somewhere in this two-phase region and this means that this is the maximum amount of A that can be present in B, stabilizing the beta phase

So, depending upon, where you are in the solid solution, if you are in these regions, then you will stable. So, if you have a composition somewhere here or if you have a composition you have here. So, you will stabilize alpha phase or beta phase depending upon whether you in the right or the left, but between these two points, the point a and point b, you are going to stabilize only here alpha plus beta phases mixture, ok; if the free energy curves were like this, and we also looked at the activity. So, what this basically meant is that, the common tangent is nothing, but the chemical potential. So, this is mu A and this is mu B.

So, basically, what it means is that mu A in phase one, that is alpha is equal to mu A in beta, similarly, mu B in alpha is equal to mu B in beta. So, this is the equality, which has to be maintained for two-phase quote equilibrium to coexist, and what this means, basically, is that a A in alpha activity of a A alpha is equal to activity of a A beta and activity of B in alpha is equal to activity of B in beta. So, we can say i e, ok.

So, basically, A is A has a similar level of activity in both alpha and beta for two-phase equilibrium to exist. Similarly, B has similar level of activity in alpha and beta phases for two-phase equilibrium to equilibrium to exist. Now, what we were doing at the end was we were trying to make, we were trying to construct phase diagram on the basis of these free energy composition curves you stop somewhere in the middle. So, we will revisit that exercise again.

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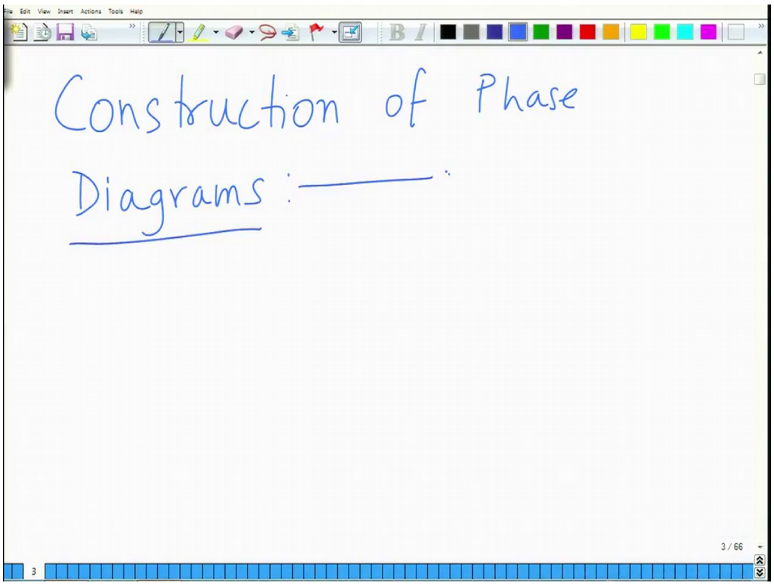

Construction of Phase

Diagrams :

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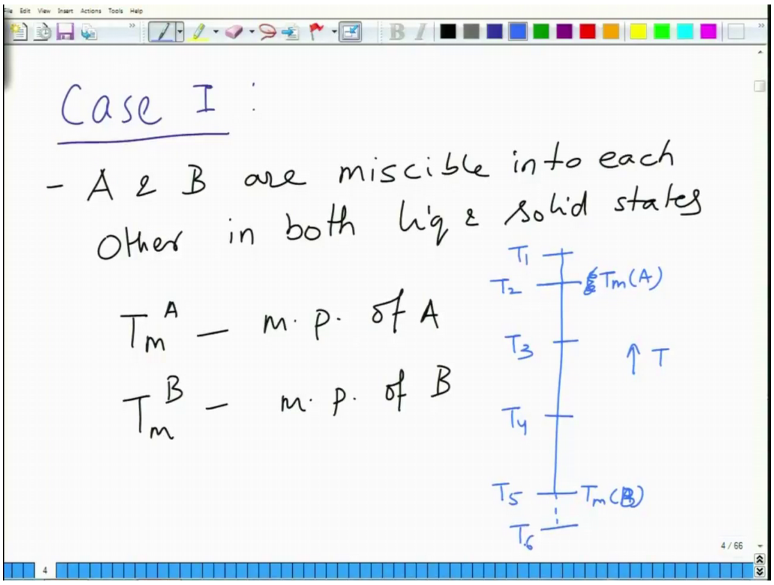

Case I :

- A & B are miscible into each other in both liq & solid states

T_m^A — m. p. of A

T_m^B — m. p. of B

So, what we will do is now we will start Construction of Phase Diagrams, ok. So, in this case, first we will take case I; case I says that, A and B are miscible into each other, in both liquid and solid states. So, basically, when we say Construction of Phase Diagram, right now, we are looking only at binary.

So, we are looking at binary A B kind of diagrams. And so, they are completely miscible into each other melting point of A is Tm A and melting point of B is Tm B. And, so, they make two phases which is solid and liquid and the relative variation of these solid and liquid free energy curves, with respect to temperature will determine, what phase existence will happen in these systems.

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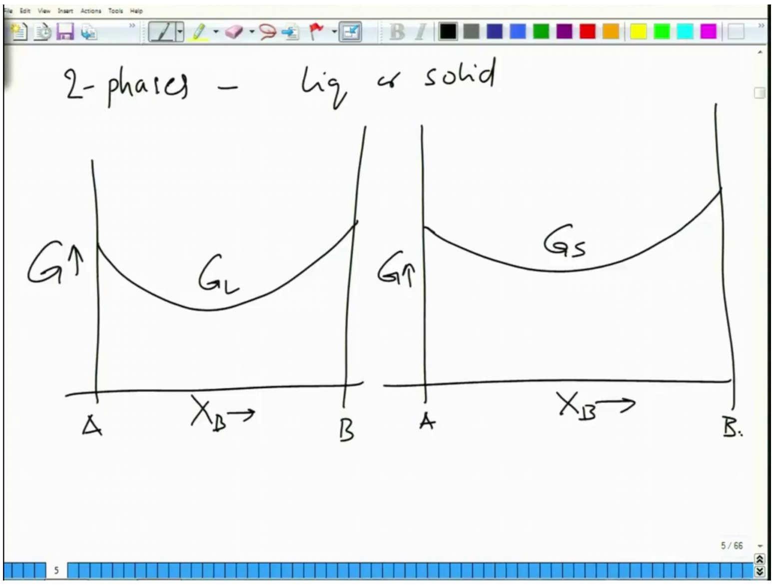

2- phases – liq or solid

So, let us look at; so, initially you will have; so, let us consider two phases they exist only in two phases, that is liquid or solid. So, the free energy of liquid is let say like this so, this is GL and you may have another free energy curve for solid which may be little shallower as compared to alright.

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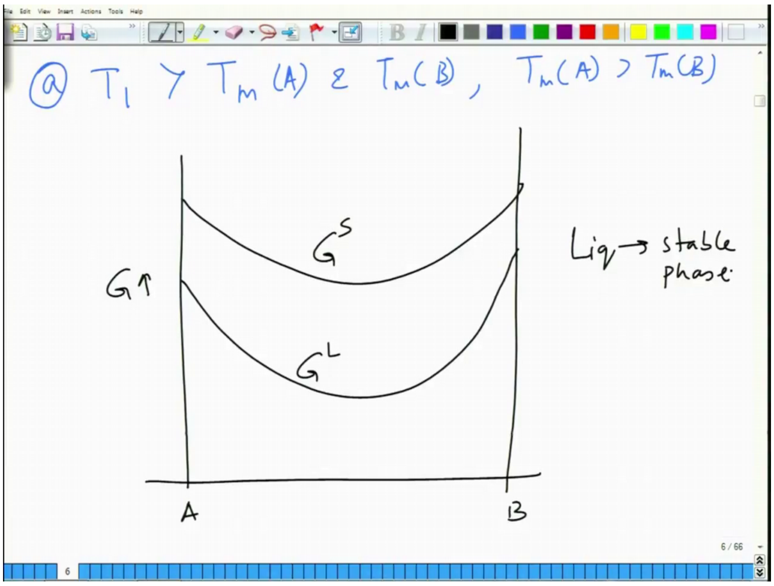

@ $T_1 > T_m(A)$ & $T_m(B)$, $T_m(A) > T_m(B)$

Liq → stable phase

Now, let us begin with few, let us look at a few cases or a few instances of temperature. So, first let us look at, at temperature T 1 which is greater than Tm A and Tm B both, and we say that Tm A is higher than Tm B. So, in such a situation, when temperature is higher than melting point of both A and B, when you construct the free energy composition plot. So, this we have drawn in the next last class. So, we will not spend too much time on it.

So, what you will have is free energy of liquid being. So, this is G liquid, this is G solid; so, free energy of liquid is lower all throughout the composition range. As a result, liquid is the stable phase at equilibrium at temperature T 1 alright. So, remember that ok.

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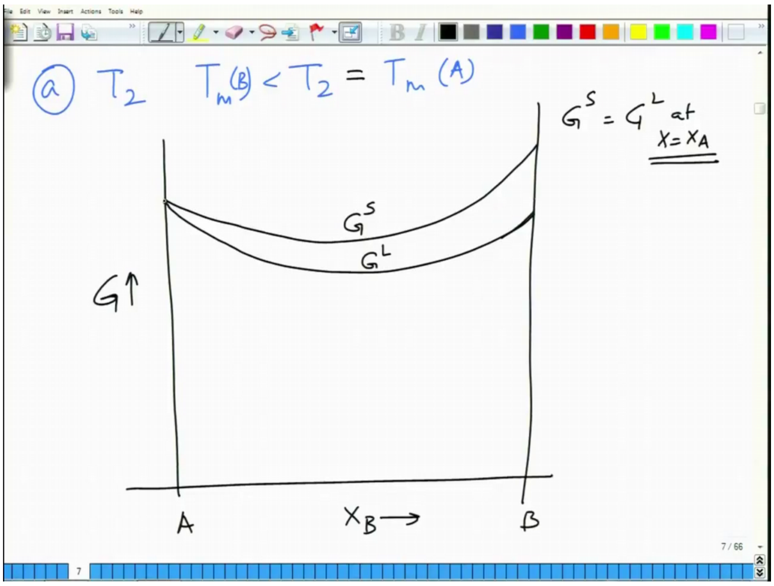

So that, now, add temperature T 2, let us define this T 2 as T 2 is lower than Tm of A, but its higher than Tm of B. Under such circumstances, what happens is that or maybe first, take a condition in which it is equal to Tm of A. Now, what it means is that for, let us say, this is A this is B, so, this is XB and this is G, alright.

So, now temperature is; so, temperature is equal to melting point of A, which means the free energy of solid should be free energy of liquid, at X is equal to X A for pure A right ? Sorry-sorry, this should be GL this should be GS. So, free energy of solid must be equal to free energy of liquid at X is equal to X A that is for pure A. So, this is where, let us say, we are this is, the free energy of liquid and free energy of solid.

So, but all throughout the composition range, since Tm is lower than B. So, the free energy curves are something like this ok. So, this is your GS this is your GL. So, except at pure A. Everywhere else the free energy of liquid is lower than free energy of solid.

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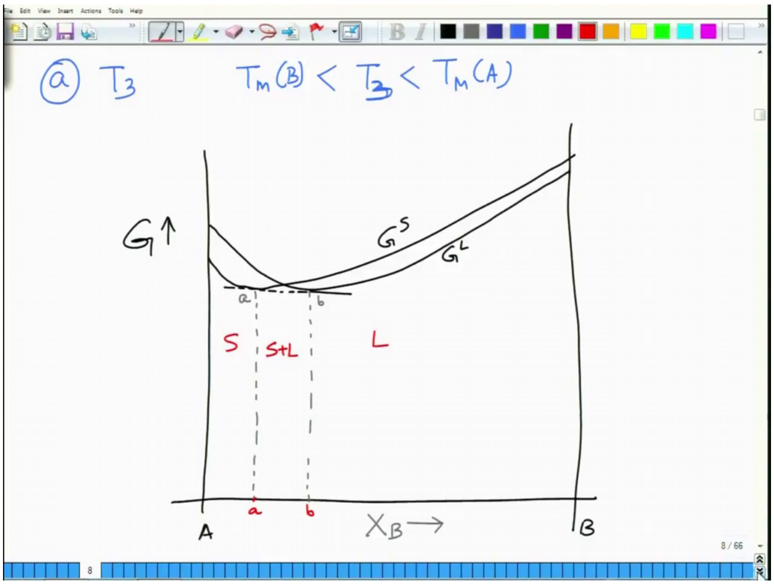

Now, let us look at the third scenario. Now, at temperature T3, now T3 is lower than Tm A, but it is higher than Tm B, all right. So, my temperature scale is like this. So, I have a temperature scale system temperature. So, somewhere here, I have Tm A, sorry Tm B and somewhere here I have Tm A and this is our temperature increasing ok.

So, we are choosing, we have chosen temperature first T1, then we have chosen T2, which is equal to T1 a then we will choose T 3 which is somewhere here, we will choose another T4 and this will be T 5 and then we will go down once more. Here, we will choose T 6, ok, this is how the strategy is going to be.

So, we are now at T 3, which is lower than the melting point of A, but higher than the melting point of B. So, the free energy composition curve in such a situation is something like that. So, these are hypothetical free energy composition curves, if the change situations can be very different. So, what you obtain in the phase diagram can be very different.

So, in this case, what happens is that, I mean you are at a temperature, that is; so, we will have a situation something like this, then we have a situation something like that. So, here what happens is that when you are, the temperature is lower than the melting point of A, but higher than the melting point of B, in that case, in certain parts of the, free energy composition curves, this GS is lower than GL, whereas, in rest of the composition landscape your GL is lower than GS.

So, you can see, that in this region solid seems to be more stable, in this region liquid seems to be more stable. In between, you need to draw a common tangent which is this and if I correspond, if I take a projection of these points on the x axis, let us say, these are point a and b in corresponding to composition of B. So, this is XB alright; so, this is; let us say, A and B which are composition of which are XB, values certain XB values ok. So, this is a temperature T3.

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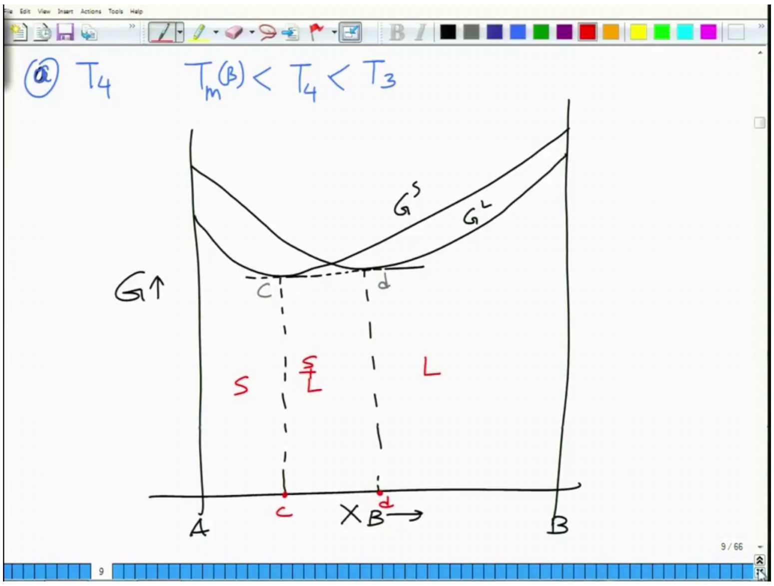

Now, we go to a temperature T4 and this T4, as I have told you, is less than T3, but is higher than again Tm of B, alright. So, when I, now make a plot of G X; so, I, let me make in black, the sake of consistency A B, X B this is G.

So now, what happens is that, the free energy of liquid, so, this further shift to right. So, this is GS this is G L and these two points are, points, we had point a b and now this will be point c and d. So, we can see that, with respect to previous figure A and B have shifted slightly to the right, because of the shift of free energy curves in such a fashion ah. So, that both are shifting to the right.

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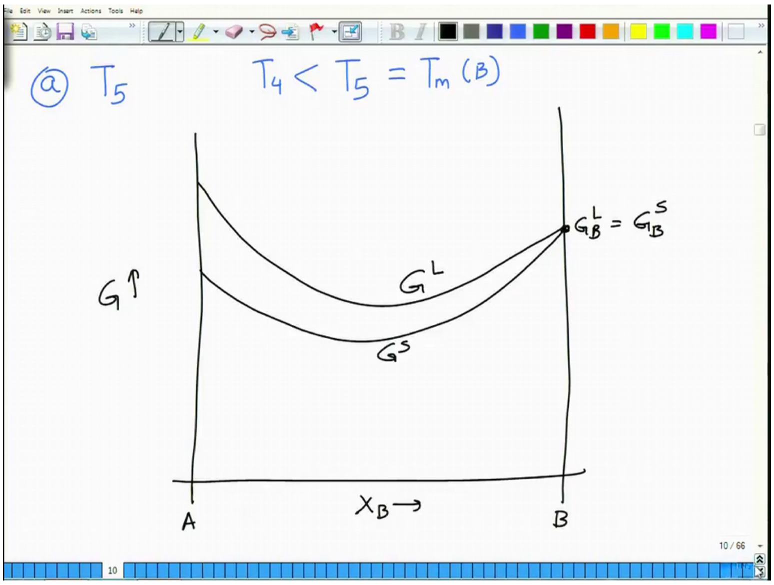

@ T_5 $T_4 < T_5 = T_m(B)$

Now, at temperature T5, at temperature T5, now this T5; so, look at the previous slides, one of the previous slides T5 is same as Tm of B. So, what we are standing here, now is T5 is equal to Tm of B, so; obviously, it is higher than T 4 ok. So, when I, now draw the free energy versus composition plot; so, this is capital A this is G, alright.

So, now when I make this; so, I can see that, now B is melting point is lower than that of solid and that of a as a result except at melting point of B. So, except at pure B the free energy of. So, except at this point which is, G B l is equal to G B S. Everywhere else GS is lower than G l and when you go to a temperature T 6 which is lower than T5, then as you understand, we are in the completely solid.

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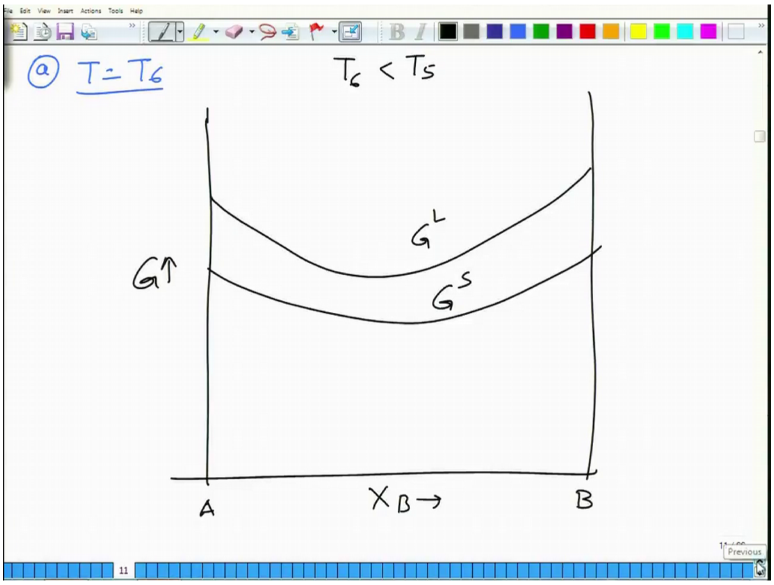

So, the condition here is A and B are miscible into each other. So, they follow sort of, pretty neat behaviour. So, now, what happens is that just G l is higher than GS for both pure A at all compositions.

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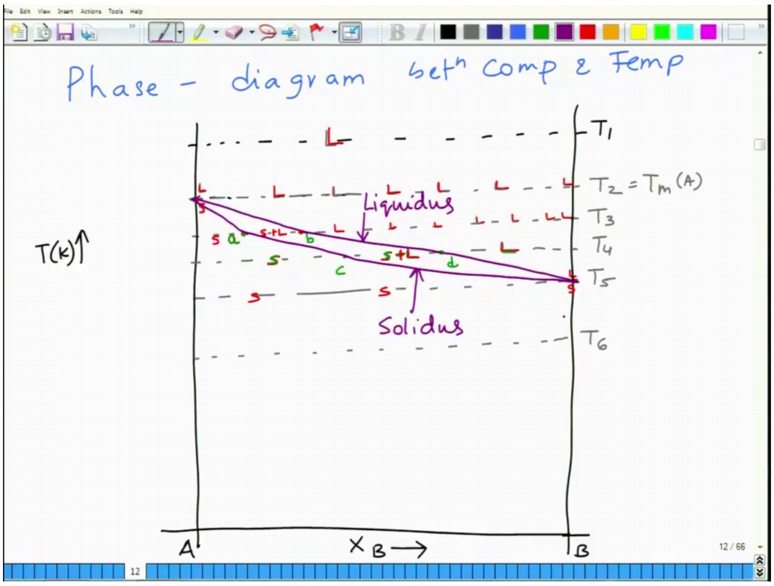
Phase - diagram bet^n comp & Temp

So now, let us reconstruct our phase, now let us construct the phase diagram ok. Now, construct the phase diagram between composition and temperature. So, what we do is that we draw a different plot here, alright. So, we have pure A pure B and this is X B varying to the right.

Now, at T1 so, at temperature T1 so, we, we first define the temperatures alright. So, this is; so, y axis is the temperature axis in Kelvin or degree centigrade. Whatever, this is T1, let us say let me use the grey line, I think, it is much more T2. Let us say, this is T3 T4 and somewhere here is T5 and then we have T6. So, we had only liquid phase at T1. So, it is all across the case, it is liquid, ok.

So, along this line at all compositions we had only liquid phase at T2. T 2 was equal to Tm of A. So, if you go to previous slides, T2 is equal to Tm of A except here. At this point, that is at pure A solid and liquid coexisted, but everywhere else it was liquid. So, if i go back here; so, at this point we will have liquid and solid, but everywhere else we will have liquid all right. So, let us say, this is liquid everywhere, it is liquid except at this point, where liquid and solid coexisted below. This will be solid, hope this will be liquid.

Now, let us go to T3. T3, what we saw was we had solid existing in this region. So, this is solid, this is liquid and this is solid plus liquid and boundary of solid is here. So, solid of composition this A is in equilibrium with liquid of composition B in the two-phase region. Whereas, below A and B it was only. So, this is A, this is B. So, below A and B, only solid existed below A only solid existed above B only liquid existed and between A and B, you had only solid plus liquid.

So, let us go back to this plot. So, let us say two hypothetical points a and b are here. So, this is a; let us say, this is B. So, here we had only solid here we had only solid plus liquid and here it will be liquid all throughout now all right. So, this is A, let me just define a different colour. This is a, this is b and similarly, if you now go to T4we had two different points c and d.

So, again, in this region you had solid, in this region you had solid plus liquid and, in this region, you have liquid. So, this point is c this point at d. So, if your composition is lower than c you only had solid phase. If your composition is above d you only had liquid phase between c and d, you will only have solid and liquid coexist. You will have mixture of solid and liquid. Solid composition will be given by c and liquid composition will be given by d that proportions will be, proportions will be worked out. Later, we will see how the proportion changes as a function of composition.

So, if I now take these two points; so, let us say, this is c, maybe getting a little, let us just zoom in a little bit ok. So, let us say, this is c somewhere here and this is d ok. So, this is c this is d, before c you had solid within these two, you had solid plus liquid and now you had all liquid. So, solid, solid plus liquid and then you had liquid and then when you go to T5, which is this temperature except at this point which is pure B everywhere else we had solid.

So, there is a similar to what you had at, T2. So, at this point we will only have liquid solid below this and above this temperature, but everywhere else it will be solid. So, here it will be solid-solid and now what we do is that, we join these lines. So, we had one solid liquid line here, we had one solid liquid line here and we join this two ends with different boundaries of, so let see, where with the separate. So, one track is this which is b d and let us connect it to this point and then another track is this a c and this point.

So, we can see that, between these two bounds you have solid plus liquid region above this bound, above the top bound is the liquid region and below the bottom bound you had a solid region. So, these are the phase boundaries. So, the first one, the top one is called as liquidus and the bottom one is called as solidus.

So, what this shows you is that, if you know the free energy composition curves at different temperatures, you can mark the phase boundaries that is the boundary between solid and liquid boundary between liquid and liquid plus solid and so on and so, forth at different temperatures and when you connect the points together you can draw a phase diagram. So, this is the simple binary phase diagrams where A and B are miscible into each other.

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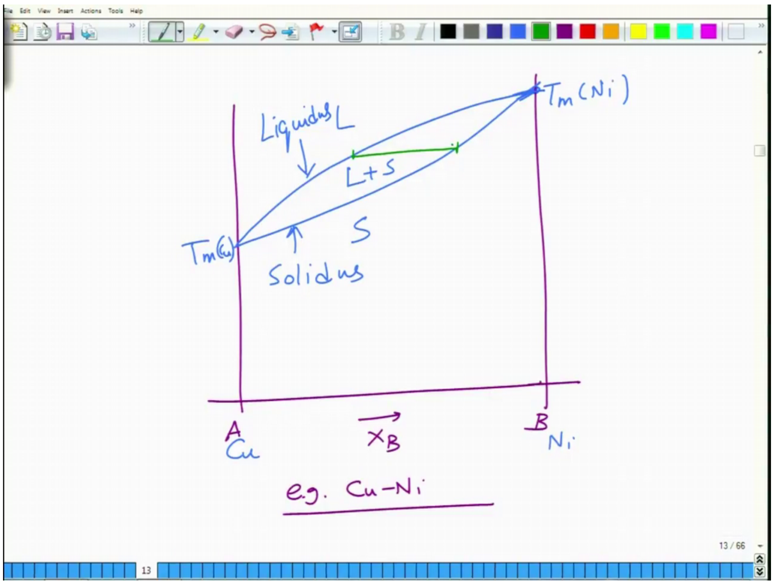

So, what you have here is so, in reality, so in reality, it will look a little neater than this. So, if you draw our real phase diagram where A and B are miscible into each other, example for example, is Copper-Nickel system, Copper-Nickel are very nicely miscible into each other. So, if it is pure copper if this is pure nickel then the system looks something like that sorry. So, this is Tm Nickel this is Tm Copper. Above this, it is all liquid between this it is liquid and solid and here it is all solid. So, this is solidus and this is liquidus.

So, this can be as I showed you in the previous slide. If you take free energy composition plots at various temperatures, you can join the dots together you can join that. You can first mark the dots, which are basically representation of which basically, represent the boundary between two different phase regions. For instance, in this case at temperature T2 this point was boundary between liquid and solid. So, below this point you will have liquid above this point you will have solid and at this point both of them coexisted right.

If you come to temperature T3 solid and liquid both coexisted, but below if your composition was below A, it will be only solid if your composition was above B, it was completely liquid between A and B, it will be solid plus liquid. Now, if you come to temperature T4 your composition, if it was below c 3 you would have 100 percent solid. If it was above d you will have 100 percent liquid between c and d if your composition was you will have mixture of solid and liquid, and then you we went down to temperature T5 and at T5 liquid and solid both coexisted only for pure B. For every other composition, the solid was more stable. So, this is in opposite of what we saw at T2; at T 2 only for pure a liquid and solid coexisted, but everywhere else on the composition landscape is all liquid.

So, when you connect, now the phase, how do you connect the boundaries now? So, you connect the dots, where liquid separates a two-phase region and you connect the dots where solid separates a two-phase region. So, when you connect the dots here, you get a two-phase region, in which you will have only solid and liquid coexisting with each other.

And, this will be basically a simple binary diagram, where two elements have complete solubility solid solubility into each other the melting points are not vastly different that still structures are similar. And, they make an extended solid soluble solid solution in both liquid and solid state, the boundaries between liquidus liquid and liquid plus solid region is called as liquidus.

The phase boundary between solid and liquid plus solid is called as solidus and between liquid and solidus liquidus and solidus you have a two-phase region of solid and liquid and, the composition of liquid and solid phases is governed by these horizontal lines, I will come upon, I will talk about those things a little later ok. So, we will stop here and we will take some more examples in the next class. Next lecture before we move on to further aspects of phase diagrams.

Thank you.