Phase Equilibria in Materials(Nature and Properties of Materials-II)
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Lecture - 12
Solubility Limits for 2-phase Co-existence

So, we will now begin with lecture number 12. So, welcome you all, so we will just recap the last lecture, in the last lecture we looked at what other phases are present in the real system.

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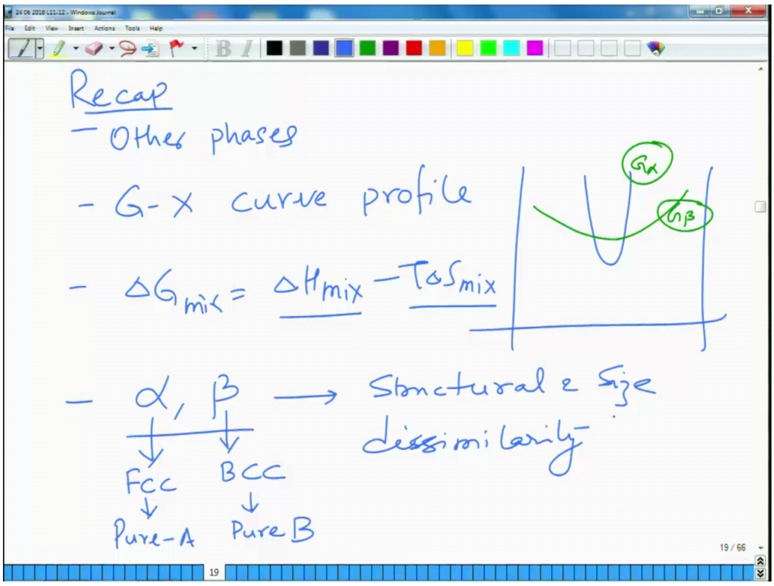

Recap

- Other phases
- G-X curve profile
- $\Delta G_{mix} = \underline{\Delta H_{mix}} - \underline{T\Delta S_{mix}}$
- α, β → Structural & Size dissimilarity

α ↓ FCC ↓ Pure-A

β ↓ BCC ↓ Pure B

So, other phases so, we looked at intermetallic phases and we reach out ordered phases that are present and then we looked at the free energy composition curve profile. So, we looked at whether, so the phases with fixed composition or(Refer Time: 00:52) composition tolerances have a shallow GX curve as compared to phases which have more tolerance for composition fluctuations.

So, you can have free energy composition curves like this or you can have energy composition curves like this which is determined by the. So, this is let say G alpha this is G beta. So, this is more of a ordered phase whereas, this is more of a solid solution kind of phase, which has which has larger composition fluctuation more shallower GX curve. So, this is what we and this is and also the then the transition between ordered and disordered phases are the function of temperature is governed by changes in you can say delta G mix is equal to delta H mix minus T delta S mix and it is the competition between these two which determines which phase is stable at which temperature.

And then we looked at we started with our discussion on equilibrium heterogeneous systems. So, we introduced two phases alpha and beta. So, alpha is a FCC structured phase so, a pure A has FCC structure pure B has BCC structure and they do not have similar structure, which means there is a structural and size dissimilarity. So, what we want to see is that how do free energy profiles of these two phases compete with each other to give rise to a phase coexistence.

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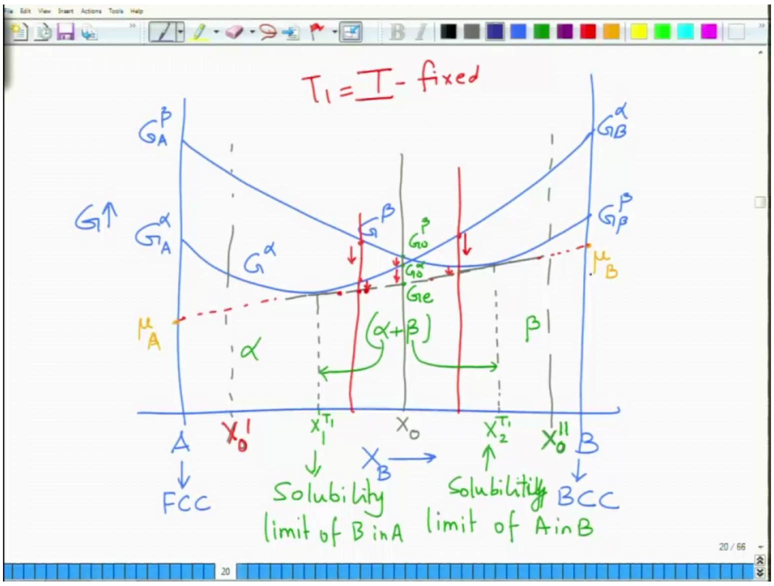

So, we saw that we have a scenario like this so, this is G X curve. So, you have one phase with free energy curve like this another phase with free energy curve like that. So, this is let us say G alpha this is G beta. So, this is basically G A in alpha this is G A this is G B in alpha this is G A in beta and this is G B in beta. So, we can see that G A alpha is lower than G B beta because the structure of pure A is FCC which is more stable as compared to BCC whereas, B being BCC phase is more stable in the beta phase form than the alpha phase form which is FCC. So, as far as this is concerned this is your A FCC and pure B BCC communication.

So, as we as you are saying that on this pure A phases FCC structure, so pure A that is alpha is FCC structure the free energy of A and alpha form is lower as compared to free energy of A in beta form. So, that is why you see G alpha to be lower than GF GB GA beta similarly G B beta is lower than GB alpha implying that beta phase BCC structured beta phase is more stable as compared to alpha phase.

Now, let us look at the phase existence. So, what happens in this plot is now you can see that it is very clear on the left side as you go closer to A that A is more stable the free energy of alpha phase is lower than beta phase, if you go to right side you see that free energy of beta phase is lower than lower than free energy of alpha phase which is more stable.

What happens in the intermediate composition? So, that is where the problem is what happens when these two curves cross over and what happens in the region which are edges into this crossover. So, for this to tackle with this problem what we do is that so, let me just write it here ok, the sake of so for the purpose of clarity or simplicity I draw a common tangent between these two curves ok, and let us say the overall alloy composition is this, this is my overall alloy composition X naught.

Now, this is one composition you can have another composition of the alloy here let us say X naught prime and you can have another composition of the alloy here which is X naught double prime. So, you can have three alloys one with composition X naught second with composition X naught prime third with composition X naught double prime.

Now, what happens for let us look at first X naught prime let me label it with different color X naught prime. So, at this composition G A alpha is lower than G B beta and the phase that is stable at this composition at a fixed temperature let us say T is fixed ok. So, T is equal to T 1 so, T 1 temperature X naught prime composition will result in formation of single phase structure that is alpha phase. So, basically this alpha phase is solid solution of B in A. So, it has majority component as A minority component as B and it crystallizes in the structure which is similar to the structure of pure A that is FCC phase. This continues until this point at which the tangent to the curve G alpha is there.

If you go in the right side the curve now beyond the intersection of tangent with the G beta curve in this regime let me label this as green in this regime the free energy of beta phase is lower than the free energy of alpha phase as a result now alloy crystallizes in this regime in beta phase structure that is BCC structured. So, on the left you have alpha phase region on the right you have beta phase region. So, in this you have alpha in this you have beta.

What happens in the intermediate composition ranges? In the intermediate composition ranges in the vicinity of crossover so, suppose your alloy composition X naught then what you need to do is that if these two free energy curves are in this drawn in this fashion. So, that they are one is shifted with respect to the other in one region and in other region it is down, then you need to find a common tangent and we need to we draw a common tangent in such a manner that the point at which tangent touches G alpha curve if you take the in if you if you drop if you take a if you draw vertical line on the X axis from that curve this is let say composition X T 1. So, we can say that this is let us say X 2 T 1 ok, these are the compositions within which you will have. So, this line if you look at free energy of beta phase this was that free energy of alpha phase which was that, but the mixture free energy would be this.

So, what happens in this case is within this regime you will have a mixture of alpha and beta phase. So, alpha phase of composition this boundary beta phase of composition this boundary and these two phases will coexist with each other with lower free energy than either of G alpha and G beta ok. So, as a result within this composition you have a two say two phase mixture.

So, if so, now, let me reiterate it again, when you have these two phases which have overlapping and free energy curves with crossovers at certain places. In this case the principle is to draw a common tangent and that common tangent allows you to divide the phase free energy composition diagram in various regions in which you can see which is the single phase region which is the two phase region. So, what we see here is we see a single phase region alpha below composition X 1 T 1.

So, anything below X 1 T 1 will be in single phase alpha form for instance X naught prime a single phase alpha alloy similarly X naught double prime which is above X 2 T 1 and in this region alloy will exist in the beta phase form which is bcc structured between these two ends X 1 T 1 and X 2 T 2 which is the solubility limit which defines the solubility limit of B in A and solubility. So, this is solubility limit of B in A and this is solubility limit of A in B. So, between these two regions what exists is the co to a co phase coexistence of alpha and beta with alpha phase composition going to be given by this boundary and beta phase composition going to be given by this boundary.

So, now let us so, we what we do here is basically the if you look at the free energy a profiling the free energy drops from this point let us say this is G naught beta, this is G naught alpha and what you have here is G equilibrium the equilibrium free energy is lower than G naught alpha and G naught beta. So, for any composition if you draw another composition for instance here if you draw for this region all of them will show decrease infinity from here to here to here to here and then here to here. So, your free energy is given by free energy line one this line ok.

And another thing which this curve shows you if you extend this further the intersection of this line what does it tell you the intersection the intersection of this line is basically the chemical potential. So, this is for instance mu A and this is for instance mu B thus. So, what this tells you is that you have chemical potential of A on this side you have chemical potential of B on this side and since you have a common tangent to G alpha and G beta what it means is that chemical potential of A in alpha is equal to chemical potential of A in beta and chemical potential of B in alpha is equal to chemical potential of B in beta.

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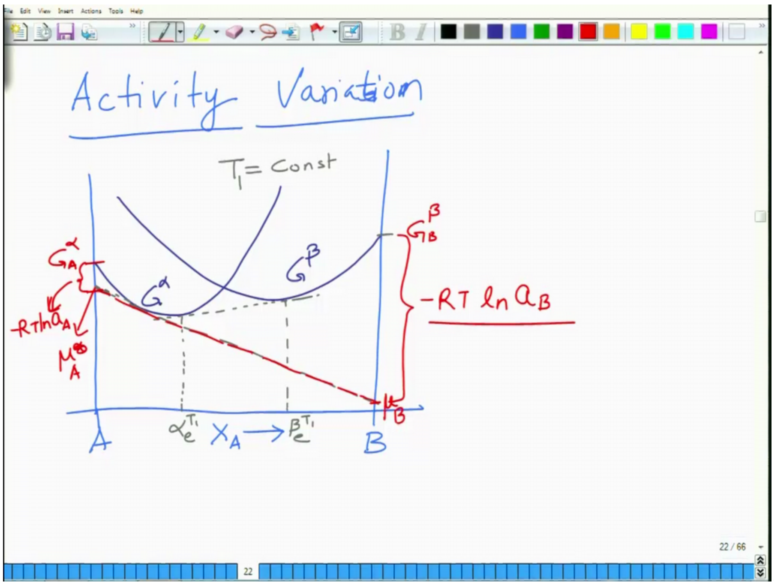

So, now let us now look at how does the activity vary because activity is the signature of chemical potential activity variation X A. So, if I draw now two vases so, let us say this is G alpha this is G beta. So, G alpha and G beta the two phase equilibrium is given by the common tangent. So, this is let us say alpha e beta e at temperature T ok, T is constant so, it is a T 1 ok.

And the so, if you now look at the for example, you want to look at the variation in activity you need to draw a common tangent. So, for common tangent let us say I take this particular point ok, let me use a different colour. So, if I now determine what is the so, this is basically the chemical potential right, this is G A alpha this is G B beta this is that this is mu A alpha and this is mu B this is mu A let us say mu B ok.

The differences between this is minus RT ln a A and difference between this is minus RT ln a B. Now, so, this is what is the activity let us say so, if you now draw the activity profile if you draw the activity profile.

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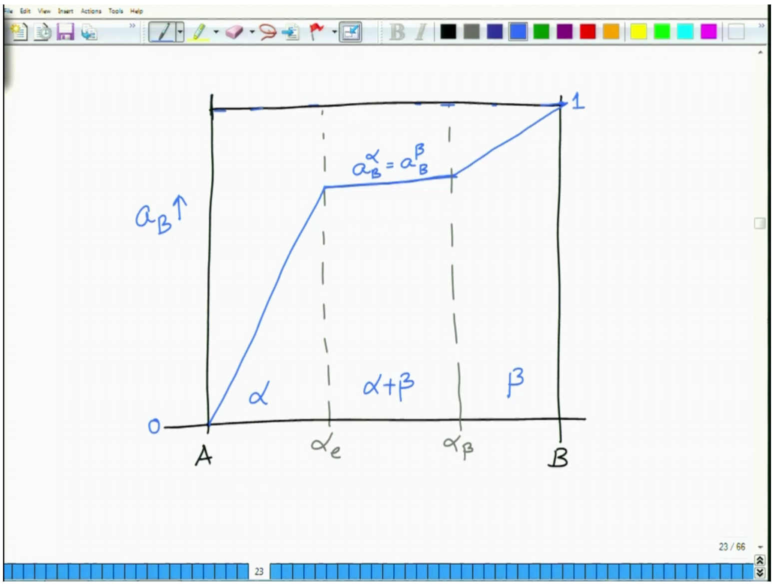

So, if I draw so, let us say corresponding to these two figures. So, this is alpha e this is alpha beta. So, this is A this is b so, I draw two vertical lines. So, this is alpha e this is alpha beta

So, let us first draw a B activity of B, now activity is same as chemical potential. So, what it says is that within the so, in we know that in this you have alpha in this region you have beta then in between you have alpha plus beta. So, what it says is that the activity of pure A of course so, when you have pure A activity of B is equal to 0 then you have pure B the activity is equal to 1. So, this is the top line ok, this is the top line which is activity is equal to 1 in between the activity of A activity of B in alpha must be equal to activity of B in beta.

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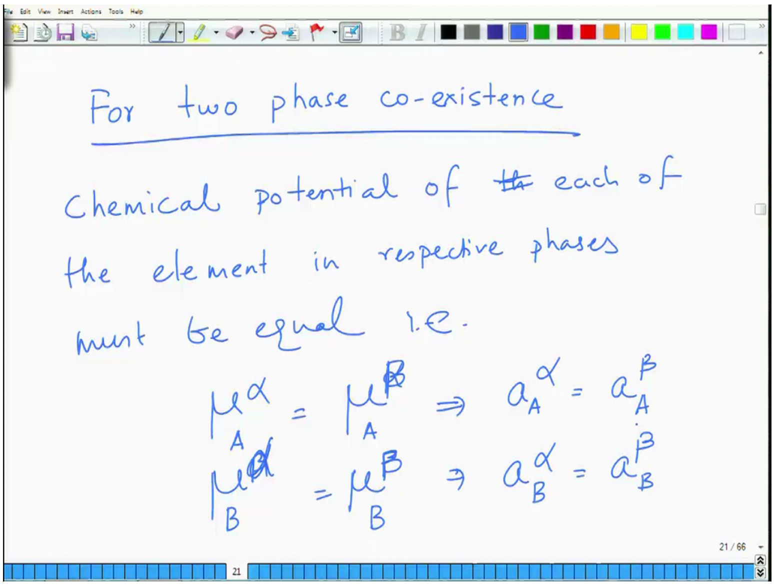

For two phase co-existence

Chemical potential of ~~the~~ each of the element in respective phases must be equal i.e.

$$\mu_A^{\alpha} = \mu_A^{\beta} \Rightarrow a_A^{\alpha} = a_A^{\beta}$$

$$\mu_B^{\alpha} = \mu_B^{\beta} \Rightarrow a_B^{\alpha} = a_B^{\beta}$$

So, we want to say that chemical potential of A in alpha is equal to chemical potential of A in beta similarly chemical potential of B in alpha is same as chemical potential of B in beta and that is what it means in terms of activity and activity of A in alpha is same as activity of A in beta and activity of B in alpha is same as activity of B in beta. So, chemical potential of each of the element in respective phases must be equal that is mu A alpha is equal to mu A beta and mu B alpha is equal to mu B beta which is which implies a A alpha is equal to a A beta and a B alpha is equal to A B beta.

So, if I now plot here so, since the activity. So, this is the a B alpha is equal to a B beta and in other regions it goes like this. So, this is the variation of activity.

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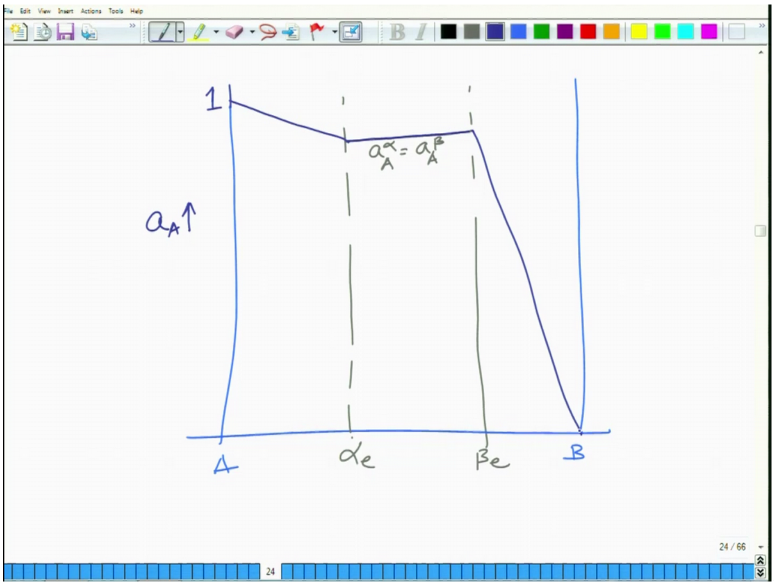

Similarly when you plot the activity variation for a A again you have to draw these two lines alpha e beta e. So, again you will have a region in which a A alpha will be equal to a A beta and now for pure a it would be 1. So, it will start from 1 so, this is a A here and then it will go through plateau and before it goes to before it goes to 0 and this is 0 this is how to faithfully quick equilibrium will be, so for.

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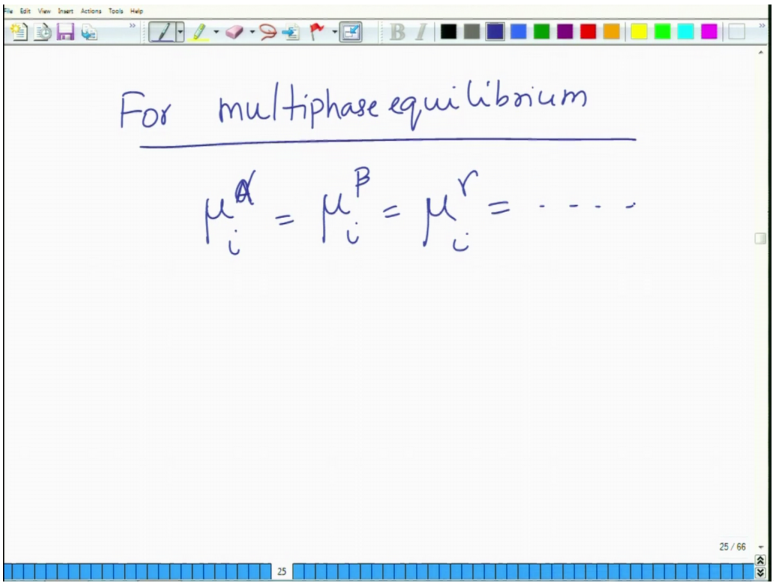
For multiphase equilibrium

$$\mu_i^\alpha = \mu_i^\beta = \mu_i^\gamma = \dots$$

For multi phase equilibrium we can say that mu i in A is equal to mu i so, mu i alpha is equal to mu i beta mu i gamma and so, on and so, forth. So, this is how the chemical potential equality has to be maintained across the free energy landscape. Now, let us say let us build a phase diagram now ok. So, we now go to building a phase diagram based on this free energy composition concept.

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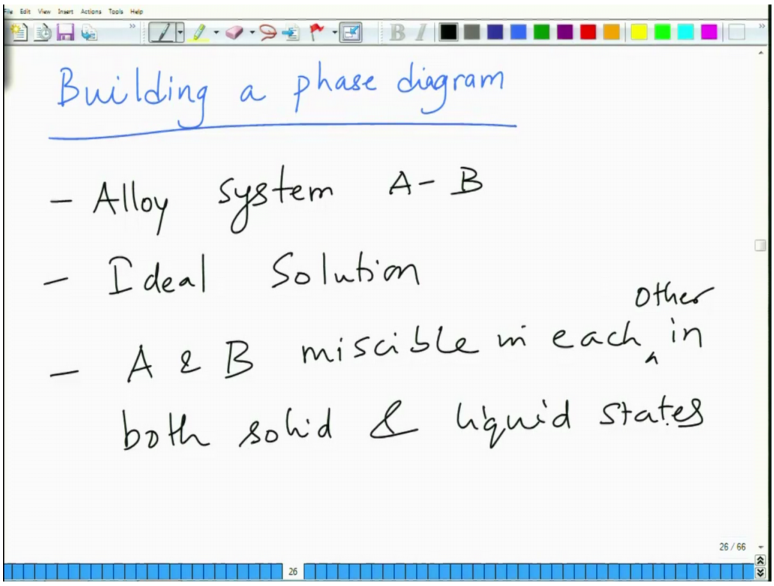

Building a phase diagram

- Alloy system A- B
- Ideal Solution
- A & B miscible in each other in both solid & liquid states

So, so, we have said that the free energy so, we have said that chemical potential must be equal for each element in two different phases and that is obeyed by activity as well ok. So, basically now let us look at two sys[tem]- let us look at Alloy System A B it is an ideal solution. So, A and B are miscible in each other in both solid and liquid states ok.

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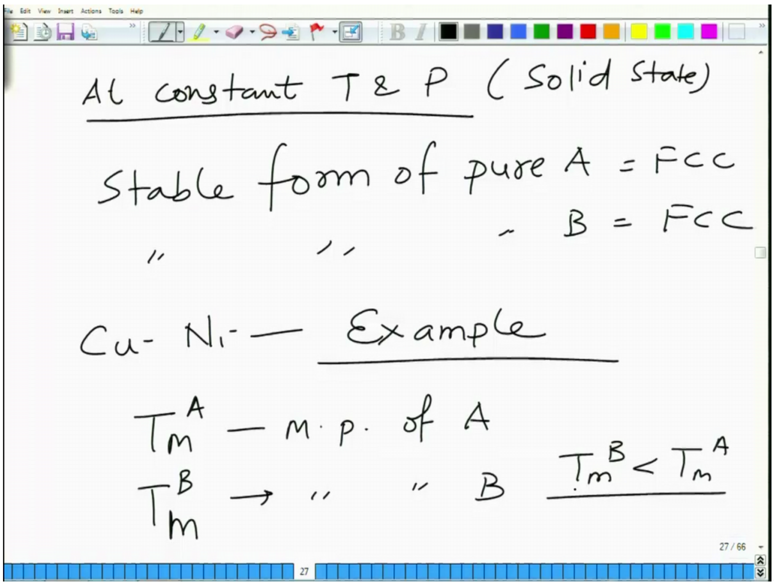

At constant T & P (Solid State)

Stable form of pure A = FCC
" " " B = FCC

Cu- Ni — Example

T_m^A — m.p. of A
T_m^B → " " B

$T_m^B < T_m^A$

So, first what we should do is that lets say at constant temperature and pressure ok. Stable form of so, in the solid state of course, pure A is let us say FCC and a stable form of your B lets say is also FCC. So, this is something which is very well obeyed by let us say copper nickel system this ideal solid solution that you make. So, they are miscible into each other both liquid and solid state in the melting point of A is Tm A melting point of B is melting point of B. Let us say that Tm B is lower than Tm A ok.

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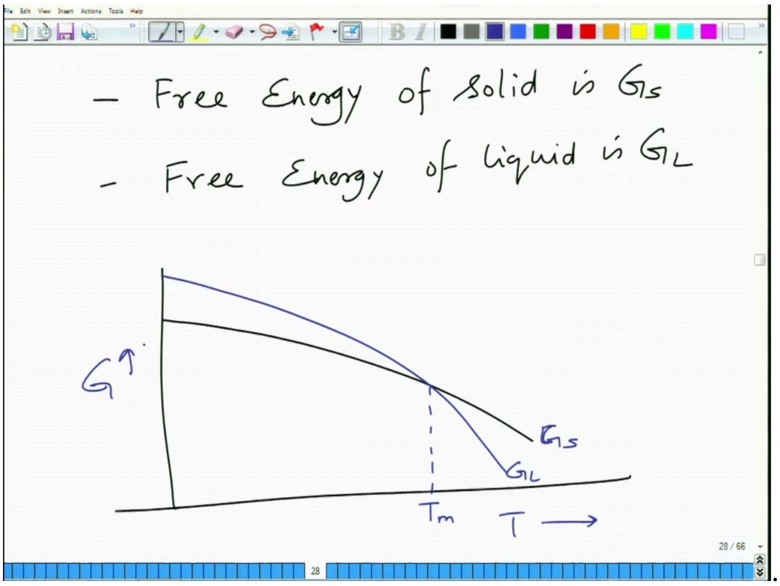

- Free Energy of Solid is G_s
- Free Energy of Liquid is G_L

And let us say the free energy of solid is Gs free energy of liquid is GL ok, and we know that free energy a variation free energy of solid goes like that, free energy of liquid drops even further. So, this is GL this is G s and this represents what we call it as a melting point. So, this is true for both alpha and beta phases this is G this is T the free energy of solid decreases as your liquid decreases, but free energy of liquid decreases much more sharply as compared to free energy of solid.

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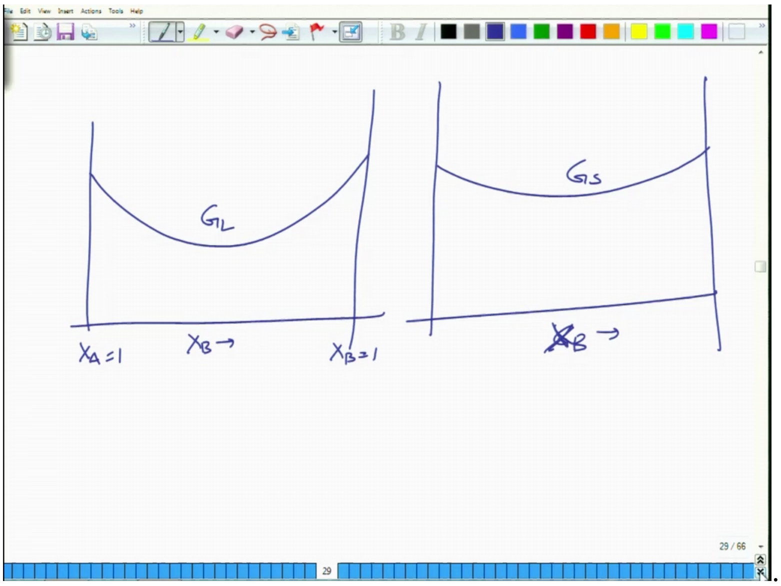

So, now let us look at so, when and when you plot the free energy of solid and liquid phases they are something like this. So, this is GL and this is Gs fairly similar curve GL is Gs is more you can say shallower as compared to that. So, this is XB and this is Gs now it is the relative movement of GL and Gs with respect to each other that will determine the stability of various phases.

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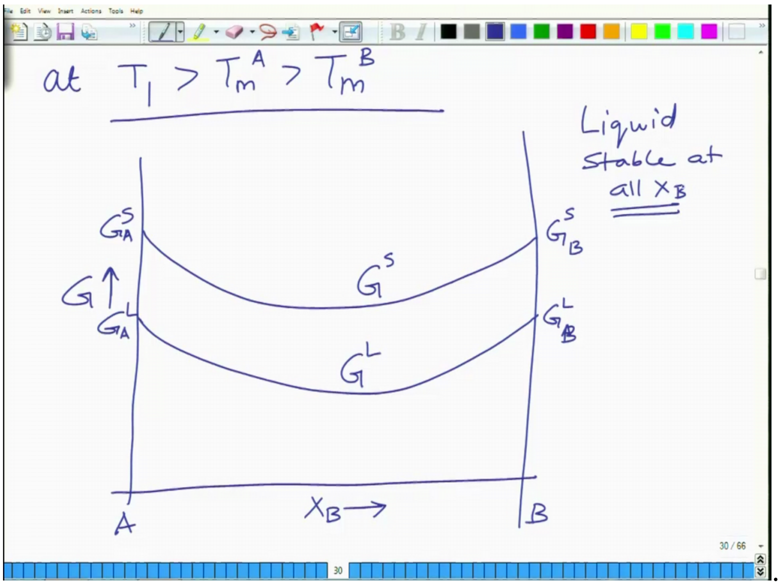

So, let us first look at a temperature T which is greater than T m of A which is greater than T m of B so, this is T 1. So, in this regime this is A this is B X B and this is G B. So, what we say in this phase is we say that G. So, in this phase when the temperature is higher than the melting point of A and B the free energy of liquid has got to be lower than range of solid as a result this is G L and this is Gs. So, this is G A L this is GA S so, I will just make subscripts are written above. So, this is Gs this is G L this is G BS this is G A and G B L ok. So, this tells me that all throughout the range liquid is stable so, which means liquid stable at all X B.

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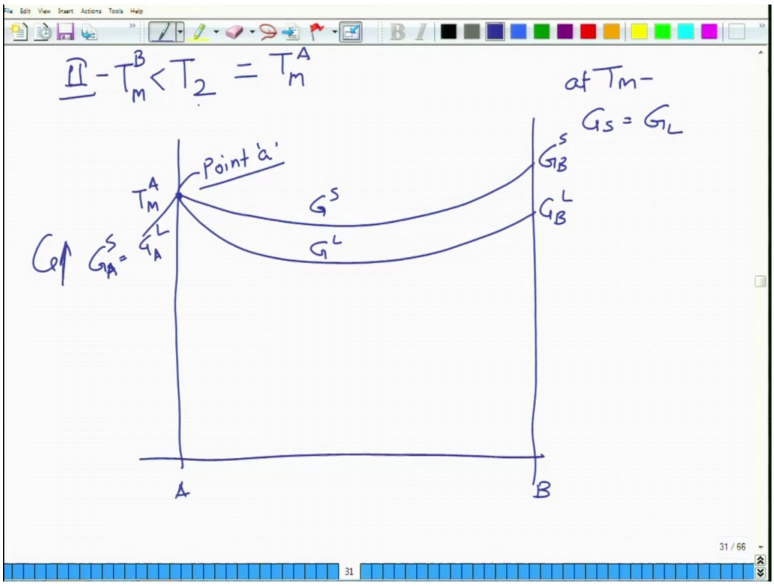

Now, let us come to second scenario where there is a temperature T 2 which is equal to melting point of A, but as bigger than melting point of B ok, in this scenario again lets draw the phase curve. So, when the melting point when we are standing at the melting point at Tm if we know that Gs is equal to Gl. So, which means for A this is A this is B for A the free energy curve will be coinciding. So, this is Gs this is G L this is Tm A at this point G S G A S is equal to G A L and this is GB S and this is GB L let us say this is point a ok, we again see that nearly for all compositions G L is lower than G s, but at pure A G L is equal to Gs.

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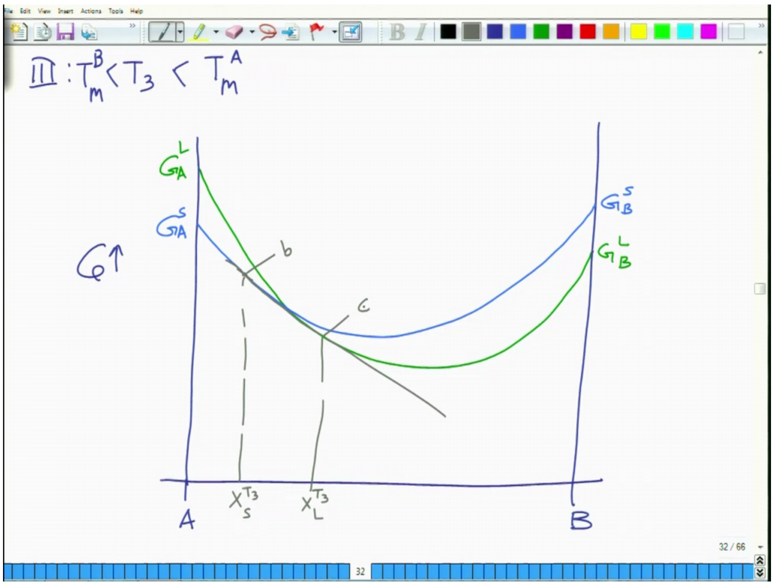

$\text{III} : T_m^B < T_3 < T_m^A$

Let us move to another point T 3, T 3 is now lower than Tm of A, but it is bigger than Tm of B. So, at this point what will happen is so, this is G. So, now, at this temperature we are at a temperature which is lower than melting point of A which means for A solid phase is more stable as compared to liquid phase whereas, for B the liquid phase is more stable has come in a solid phase. So, now, these two free energies as you can understand they will start crossing with respect to each other.

So, if you plot so, this is let us say for this is let us say for solid ok, now for solid this is G A S this is GB S. So, solid free energy now has to be lower than the liquid free energy for the A. So, which means the other free energy curve will start at this point and will cross over this curve somewhere here such that G B L is lower than GB S, but G A L is higher than. So, you can say that you can see now in certain region your solid free energy is lower than that of liquid free energy whereas, in the other part your liquid free energy is lower than the solid free energy.

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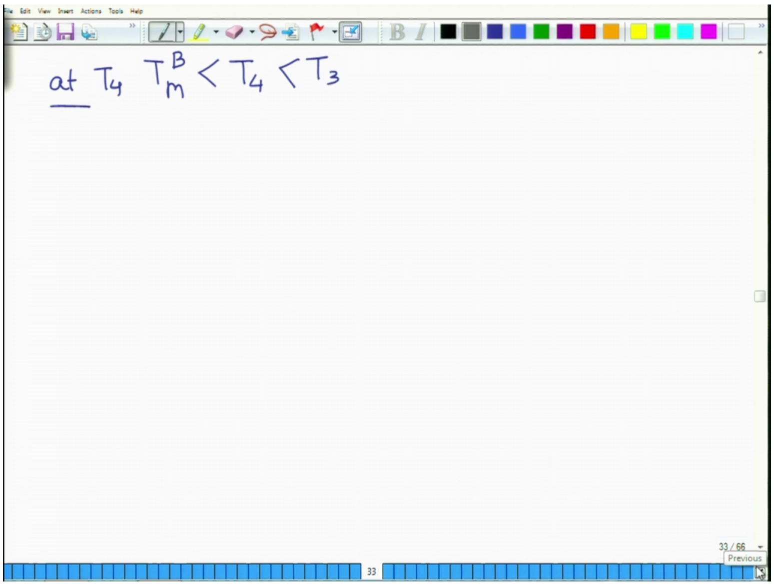

at T_4 $T_m^B < T_4 < T_3$

Let us now take it further at T 4. So, T 4 is greater than T 3 T 4 is smaller than T 3, but it is still bigger than TmB. So, what we do is that in the in this slide, we draw on our common tangent. So, using the same principle that we applied earlier, so, this is the common tangent. So, let us say this is X s T 3 and this is X LT 3 ok, and this point is point b one b and this is point c.

So, what we will do is that now we will stop here, we will do the further analysis in the next class, but what we have seen in this class is we have learned how to draw a free energy phase diagrams for. So, if I come from the beginning, what I said was when you have when you have two phases with different structures these phases will have overlap of free energy curves in such a fashion. So, that on one side you will have one single phase region on the other side you will have another single phase region in between the relative shift of these free energy curves which will determine what phases will coexist with each other.

And then we said that for two phase coexistence the mandatory requirement is that chemical potential of each of the element in respective phases must be equal, that is mu A alpha should be equal to mu A beta and mu B alpha is equal to mu B beta and that is obvious from the tangent that is draw from drawn from this line.

So, the common tangent says that the common tangent is nothing, but the chemical potential and this says that the chemical potential of A and B in two phases A in two phases and B in two phases must be equal, so, we will stop here.

Thank you.