

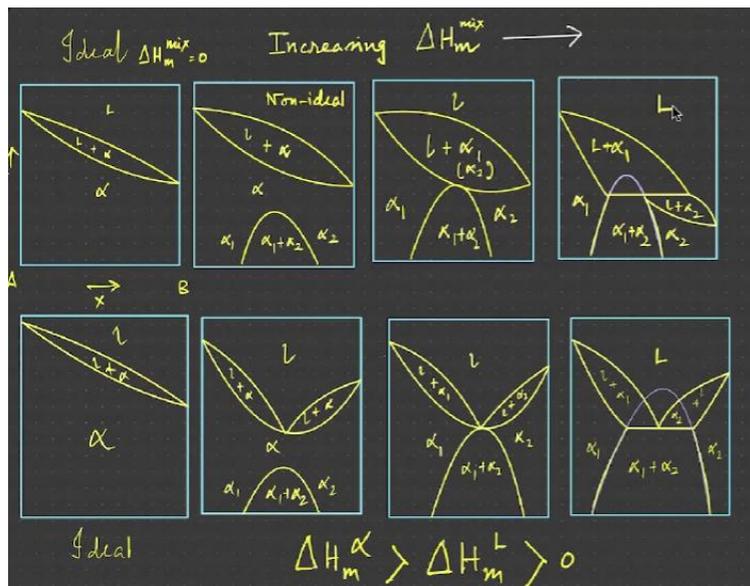
Thermodynamics And Kinetics Of Materials

Prof. Saswata Bhattacharya
 Dept of Materials Science and Metallurgical Engineering,
 IIT Hyderabad

Lecture 34

Binary alloy phase diagrams - intermediate phases and miscibility gap

So, as I was telling about this predictive and type 3 diagrams and type 4 diagrams, we looked at different types of diagrams. Like type 4, I have not yet gone. So, I am looking at type 3, but you need to understand that from type 2, we can basically go to type 3 in this way that you have ideality. So, when you are looking at these lens diagrams, For example, your liquid and then you have this lens like region where you have liquid plus solid solution, alpha solid solution. So, this is like liquid plus alpha solid solution and this is also a solid solution. So, basically alpha is your solid basically, alpha is your solid.

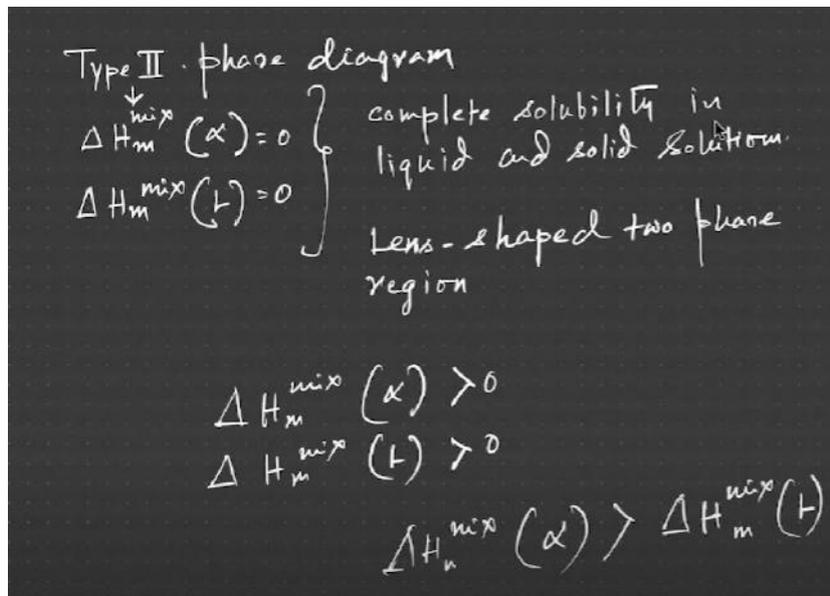


Now, this here in the liquid it is infinitely miscible, A and B are infinitely soluble. In the alpha also, in the solid solution also, A and B are infinitely soluble, right? They are completely soluble. So, in this case, you can basically use an ideal solution concept for describing liquid and alpha. So, liquid can be described as an ideal solution, alpha can be described as an ideal solution, right? And basically, in such a case, what you will have, you have this lens shape, you have this lens shape.

two-phase region, right, this is this lens shaped two-phase region, right, it looks like a lens where this is A, pure A, this is the pure A melting point, this is pure B melting point. Now, however, when you want to go into this type 3 type of phase diagrams, type 3 phase diagrams

like eutectic and pre-tectic phase diagrams, then you require to introduce non-ideal. Now, when I talked about ideal solution, what did we tell? We told that the enthalpy of mixing is equal to 0. So, if we look at non-ideal or if you want to introduce non-ideal, we have to change the enthalpy of mixing and the enthalpy of mixing in the liquid and the solid will not be equal. So, basically if I think of this that in the solid phase the enthalpy of mixing is more than in the liquid phase and in both cases the enthalpy of mixing is positive.

So, basically what I am looking at is we are taking enthalpy of mixing is positive. in both liquid and solid solutions. So, enthalpy of mixing is positive in both liquid and solid solutions. So, that is what I am talking about. So, basically if the enthalpy of mixing is positive in both liquid and solid solutions and k, so if enthalpy of mixing, so please look at this condition, so have a look at this condition, $\Delta H_m^{\text{mix}}(\alpha) > 0$, $\Delta H_m^{\text{mix}}(\text{L}) > 0$, in addition they are unequal that means $\Delta H_m^{\text{mix}}(\alpha) > \Delta H_m^{\text{mix}}(\text{L})$.



So, basically other, in other words what are we looking at is basically this. that in the, so basically from lens, lens is type 2, right, lens is type 2. From type 2, if I have to go to type 3 phase diagram, then first of all ΔH_m , in type 2 you have ΔH_m that is enthalpy of mixing, molar enthalpy of mixing for the So, ΔH_m^{mix} for the alpha phase say for example, for alpha is 0 and ΔH_m^{mix} . So, this is for the ideal lens like conditions, this is for type 2. So, this is for type 2, but for type 3 what you are telling basically, so this is type 2.

or where you have, so this is where you have complete solubility in liquid and solid solutions. And in such case you get type II phase diagram. And also, one of the things that it looks, it has a shape, a lens, these are, these phase diagrams are typically lens shaped, where you have a lens shaped region, lens shaped two-phase region. Now, if you make ΔH_m^{mix} for alpha greater than 0, as well as ΔH_m^{mix} for liquid greater than 0. In addition, you are also

telling that $\Delta H_m^{\text{mix}}(\alpha)$ is greater than $\Delta H_m^{\text{mix}}(\text{liquid})$, so basically the enthalpy of mixing, ΔH_m^{mix} means molar enthalpy of mixing.

for the liquid solution. So, molar enthalpy of mixing of the solid solution is greater than the molar enthalpy of molar enthalpy of mixing of the liquid solution. The molar enthalpy of mixing the liquid solution is less than the molar enthalpy of mixing the solid solution of A and B and both are positive. That means $\Delta H_m^{\text{mix}}(\alpha)$ is equal to 0 that is enthalpy of mixing, enthalpy of molar enthalpy of mixing the alpha phase is equal to 0 in the liquid phase is equal to 0 and that in the alpha phase is greater than that of the liquid phase and both are greater than 0, in such case what you get is deviation from identity or you get non-ideal. So, this is like increasing ΔH_m^{mix} means this is also non-ideal.

So, today if I tell that this is non-ideal, this is not, that is wrong, this is also non-ideal, this is increasingly non-ideal and this is also non-ideal. So, we can tell this direction increasing ΔH_m^{mix} is a mix and also increasing non ideal. So, increasing deviation from ideal is basically towards the from left to right. So, here you have ideal Now, you see in a non-ideal system at a lower temperature, remember this is temperature axis, this is temperature axis. So, at a lower temperature, you basically have this alpha phase which can now phase separate into alpha 1 plus alpha 2.

So, alpha can phase separate into alpha 1 plus alpha 2. at a temperature that is below a critical temperature. So, say there is a critical temperature T_{CR} , below that T_{CR} you have alpha 1 plus alpha 2 coexistence and here you have alpha 1, here you have alpha 2. with increasing means it make it more positive make $\Delta H_m^{\text{mix}}(\alpha)$ more positive if I make $\Delta H_m^{\text{mix}}(\alpha)$ there is a molar enthalpy of mixing. So, this is ΔH_m^{mix} remember this is ΔH_m^{mix} and this is also ΔH_m^{mix} .

So, $\Delta H_m^{\text{mix}}(\alpha)$ or $\Delta H_m^{\text{mix}}(\text{liquid})$ if we make them more positive or particularly if we make So, in this case alpha goes to alpha 1 plus alpha 2. So, if we can make the molar free energy of mixing more positive, more positive, then basically what we are trying to say is that the critical temperature. So, basically the critical temperature is such that of the phase diagram is such that miscibility gap. So, the miscibility gap region meets the lens like region, right, meets this two phase co-existence region of liquid and alpha or liquid and alpha 1 and liquid and alpha, it can be liquid alpha 1 or liquid plus alpha 2. Now, it is basically meeting here.

Now, you can see that this is meeting here, the miscibility gap meets here. Now, if it goes further, so you may increase it further, what you will see is that this is the gap now enters the lens. It is entering the lens and then the lens converts into a region like this. The lens converts into a region like this, right? This is the region that where the lens converts and this one, basically if you see this one, And you see the miscibility gap has entered. So, this is the purple colored line is the metastable portion.

It is the metastable portion of miscibility gap. This is with increasing ΔH_M mix that is increasing molar enthalpy of mixing and molar enthalpy of, remember two things. One is increasing molar enthalpy of mixing and molar enthalpy of mixing has to be positive. if you as you have shown is regular solution that if molar enthalpy of mixing is sufficiently positive then only you get something called a miscibility gap right we have already shown that so basically remember this point okay that we have discussed previously now if you see you have this α_1 plus α_2 here but you see now this guy has gone inside the lens and the lens has now converted into a two-phase region L plus α_1 . So, you have L plus α_1 and then you have α_1 and α_1 plus α_2 , L plus α_2 and α_2 and again this is like a point.

But please remember that there is this metastable submerged miscibility gap, right. This miscibility gap has entered the lens and it has converted with increasing non-identity or increasing positive enthalpy of mixing of the solid solution. You basically have entered into a regime where the miscibility gap has become metastable and what you have got is a peritectic phase diagram or a peritectic reaction, right. At this point, at this point, if you look at this point, say for example, call this P, so this is a peritectic reaction. So, type 3 you have looked at peritectic phase diagram, just previously we looked at peritectic phase diagram, but we also looked at eutectic phase diagram, is it also possible for eutectic phase diagram, indeed it is because again you see you start with ideal, you increase the enthalpy of mixing and it is positive.

So, you can see that enthalpy of mixing of the α phase that is the solid phase is more positive than for the liquid phase and as a result you have this miscibility gap, right. And not only this miscibility gap, now this lens has broken into two pieces. If you see that it has not really broken, this red line is continuous. So, this is basically a continuous, but it has now changed its curvature, right, near it has changed its curvature. So, it has, it is, it looks like a double lens, right.

You have one lens here and you have one lens here and you have one region, a very small region where there is a change in curvature, a rapid change in curvature that is happening and then this Again, the liquidus, so the liquidus has changed this way, right. It looks like two L plus α regions separated by one L region, right, here. And then there is equilibrium with

alpha and below a certain temperature again, below the critical temperature again, alpha converts to alpha 1 plus alpha 2, right. That is the transformation inside the miscellaneuous gap. Now, think of this, you make it more positive, you make ΔH_m more positive, then basically this miscellaneuous gap grows, right, it grows.

So, that is what I am talking about. See for example, it has grown here, it has grown here. So, you can see here it has grown. So, it has grown and it has touched this point. Now once it has touched this point, you see basically there is a coexistence of liquid alpha 1 and alpha 2.

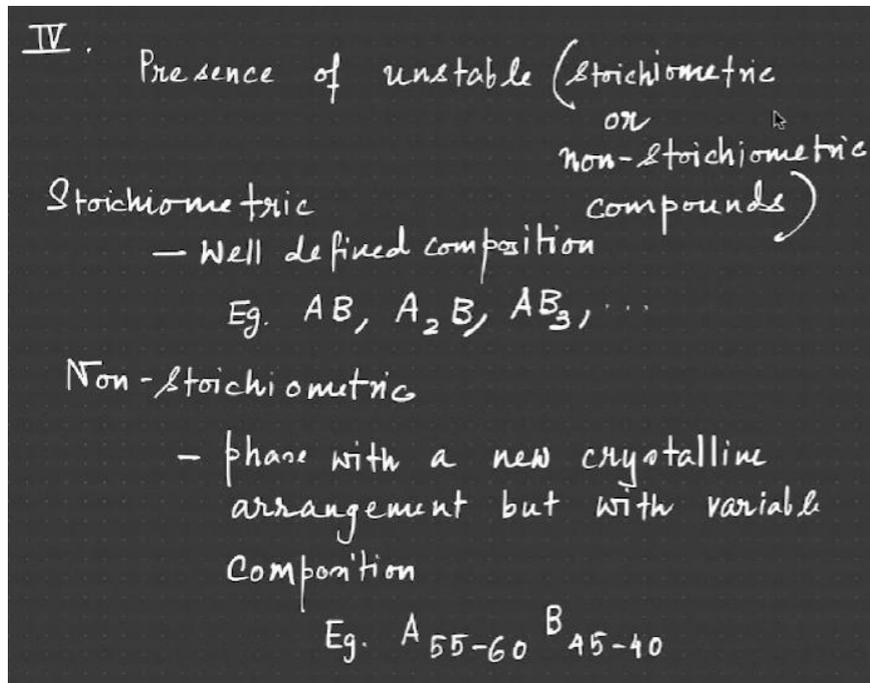
there is no alpha anymore, you see once the point has been touched, you have alpha 1, alpha 2 and liquid. You do not have alpha anymore, right, previously you had an alpha solution, again below a critical temperature, this alpha transform to alpha 1 plus alpha 2. Now, there is, now as you make it more and more positive, ΔH_m more and more positive, ΔH_m liquid more and more positive, particularly this gap. So, if you make it more and more positive, you will see that the miscibility gap now touches exactly one point and at that point liquid alpha 1 and alpha 2 coexist. Now see you cannot have more than three phase coexistence in a binary solution according to Gibbs phase rule because if you have more than three phase coexistence then basically your degree of freedom goes to minus 1.

You should have a maximum phase coexistence that you can have in a binary solution is three phases. like we have read this invariant reactions like the pyrotechnic reaction or the eutectic reaction. Now, you can see that if the miscibility gap progresses further with increase in ΔH_m , increasing that, increasing the molar enthalpy of mixing of the alpha phase, if your, if your miscibility gap enters, now the miscibility gap enters or advances further, right, it advances further. So, at higher temperatures also, There is a miscibility gap. Basically, you have a miscibility gap.

Now, at a higher temperature, your $T_{critical}$ is increasing. Now, your $T_{critical}$ has increased somewhere here, say. So, basically, your miscibility gap will now go like this, right? And exactly that is what I have drawn. Now, you see this miscibility gap, this portion of the miscibility gap now becomes metastatic. If liquid phase is absent, then you can basically think of this miscibility gap, this submerged miscibility gap.

Otherwise, it is simple eutectic reaction where you have L here, you have L plus alpha 1 here, L plus alpha 2 here and this is the eutectic point and at the eutectic composition and temperature, L transforms to alpha 1 plus alpha 2. It is a mixture of two phases, alpha 1 and alpha 2. This is how a phase diagram involves as a function of non-ideality and the non, where

the non-ideality is introduced by making the enthalpy of mixing positive for both the solid and the liquid phases and also making them unequal such that the enthalpy of mixing of the solid phase is more than that of that in the liquid phase and we are considering a binary . So, you can see the evolution of phase diagram or phase stability map. So once you have done that, now we will quickly go through the type IV and type V phase diagnosis.



Type IV phase diagnosis, basically you have an unstable stoichiometric or non-stoichiometric compound. Unstable means, so stoichiometric compound what does stoichiometric compound means it has a very fixed and well defined composition for example AB AB contains 50 atomic percent A 50 atomic percent B right AB cannot be obtained or AB if you have a fixed composition AB there is no other combination of A and B 50 atomic percent 50 atomic percent other than 50 50 you have no other atomic composition that will produce this AB compound similarly A to B you have one-third, so you have one-third B and two-third A. So, basically two-third of the atoms will belong, will be of A and one-third of the atoms will be of B and that basically will be exactly two-third is to one-third. So, that is 2 is to 1 and this A to B formula does not change or AB_3 , AB_3 means you have one-fourth A and three-fourth B. So, these are stoichiometric well-defined, stoichiometric well-defined compositions.

However, there are also non-stoichiometric intermediate compounds that can form, which has a new crystalline arrangement other than the terminal solid solutions, they have new crystalline arrangements. So, think of the eutectic diagram inside, if you insert a phase boundary within the eutectic diagram in the two-phase region, that is an intermediate phase, but that intermediate phase should have a different, should new crystalline arrangement and, but it will also have variable composition. Now, if you are non-stationary, non-stationary means the compound has variable composition. Say for example, A, so this is a compound, a non-stationary compound

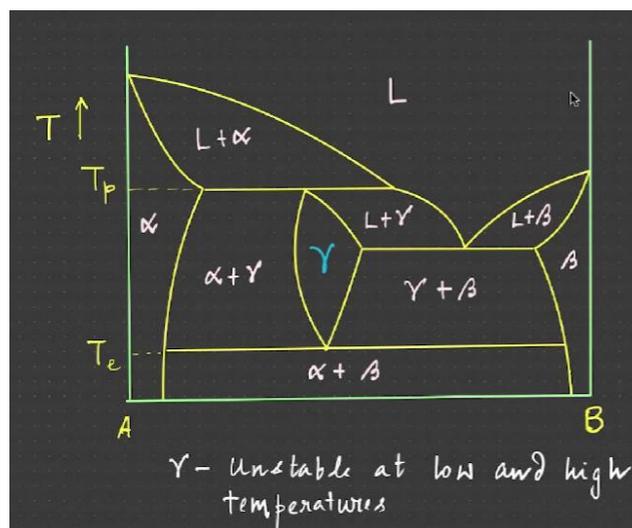
where A can vary between 55 and 60 and B can vary between 45 and 40, right. A can vary between 45 and 60 and B can vary between 45 and 40 atomic percent, right.

So, in A is 55 atomic percent, say for example, B is 45 atomic percent. If A is 60 and a percent, B is like 40 and a percent. So, A can vary between 55 and 60. So, basically you have some solubility in this non-stoichiometric compound of B. So, you have a varying solubility of B in this non-stoichiometric phase.

So, in stoichiometric, it is exactly, it is like a line compound and here it is again a phase region. This is a phase region and here it is like a line compound. So, this is a line compound. So, let me write here and here it is again area.

So, this is a line compound. and here it is like area or region, you can call it. It is a new single phase field. Now, this single phase field has a composition which varies where A varies between 35 and 60 atomic percent while B varies between 45 and 40 atomic percent. So, this is one example where it is unstable. See, basically if you look at this, there is a eutectic here.

If you look at this, there is a eutectic here and there is a peritectic here and you have this intermediate gamma phase. If you look at this, you have this intermediate gamma phase, you have liquid, liquid plus alpha. So, immediately whenever you mark a phase diagram, you first look at or identify the single phase regions. For example, this is a single phase region with degree of freedom 2 and we mark it as alpha. Single phase region with degree of freedom 2, mark it as beta.



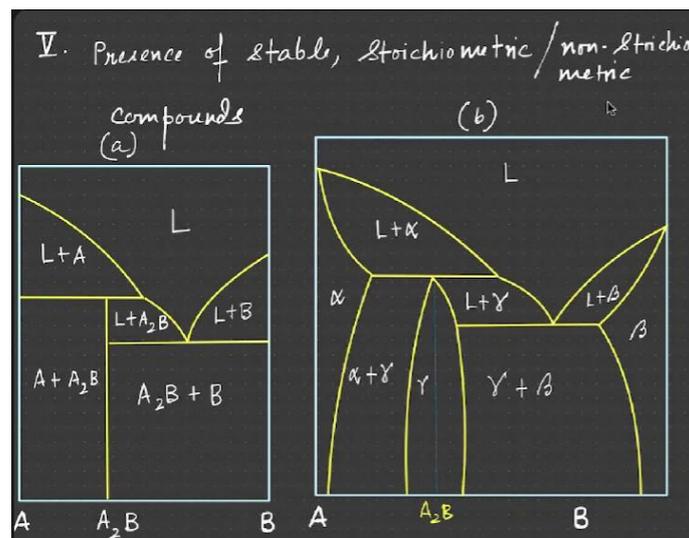
Single phase region with degree of freedom to market as L. Now, why L here? Why not L here? Why L here, not here? This is because liquid will generally form at a temperature higher

than the solid, right? Because solid requires heat to convert to liquid, right? So, liquid will always be at, stable at higher temperatures. Now, you see, you also have now another single phase field called gamma. Now, this gamma is basically appearing somewhere in between alpha and beta. Now, if you see this gamma, there is one interesting point that I want to tell you, that above T_p , gamma is gone, right? Gamma has converted to L plus alpha.

And below T_e , gamma has converted to alpha plus beta. So, this is an unstable compound. And so, unstable because it is not stable at all temperatures. It is not stable. So, it is basically, what does unstable mean? Unstable means, so, means, so, these are unstable, right? It has upper temperature limit for stability as well as a lower temperature limit, right.

So, basically if I go below T , it does not remain as gamma, but it changes to alpha plus beta. Alpha plus beta are the terminal solutions, right. Gamma changes to alpha plus beta. By the way, this transformation is gamma to alpha plus beta is called eutectoid transformation, right.

It is very similar to eutectic transformation. So, you have this gamma phase and you have again this particular temperature T_b . at which you can see here you have gamma phase, you have alpha phase and you have beta phase. So, you have degree of freedom equal to 0 and basically what I am telling is the gamma phase has a different crystal structure than either alpha or beta, right, that is the point. So, but gamma phase is an intermediate phase, but it is also having a limited solubility because if you are within T_p and T_e , within T_p and T_e it exists, but above T_p does not exist or below T_e it does not exist. we come to another phase diagram which is called presence of stable.



So, stable means it may not be stable at high temperatures, but it has to be stable at one temperature. For example, if I look at this lime compound A to B, So, I look at a stoichiometric case and I look at a non-stoichiometric case. So, if I look at a line compound A to B, so basically

you have L and you have your A, so L plus A and then A plus A to B, A to B to B and this is the line of A to B, this is the line of A to B. Now as you can see A to B basically solid, this A to B solid when it changes to liquid basically the composition of A to B has been disturbed because now the composition as soon as it enters here then it has this composition, this and the pure B composition.

Now again you go, so instead of going there you go here. Again, you have this two-phase composition, right? Your liquid phase composition is changing. So, that means it is an incongruently melting compound. A to B is an incongruently melting compound because when it melts, the composition of the solid state and the composition of the liquid state are not all the same, right? The liquid composition has changed from A to B, right? A to B was the solid line compound composition, but as soon as it changes to liquid, the liquid composition has changed, right? So, this is a line compound, this is what I am calling a line compound because it is a line, this is exactly the situation of A to B. However, you may have an A to B as a central structure, you can look at the blue line here, a blue faint line I have drawn.

But if you look at this, this is based on A to B. This gamma structure is based on A to B, but gamma has now some solubility. How? And some limited solubility. Why? See, A to B is in the middle, but it can be slightly different from A to B, right? So, at this point, you can have difference in A to B. And so, if it is slightly different, so what does this mean? This means that gamma, although is a non-stoichiometric compound based on A to B, in gamma, the composition of A can change and composition of B can change within a limit or within a range.

That is the point. So, if at any given temperature, for example, if I look at the gamma phase field, you cannot draw any tie line here. Remember, you cannot draw, it is a single phase field. Now, if you look at gamma region, gamma region exactly behaves like A to B. Only thing, it is a region, while A to B is a line region.

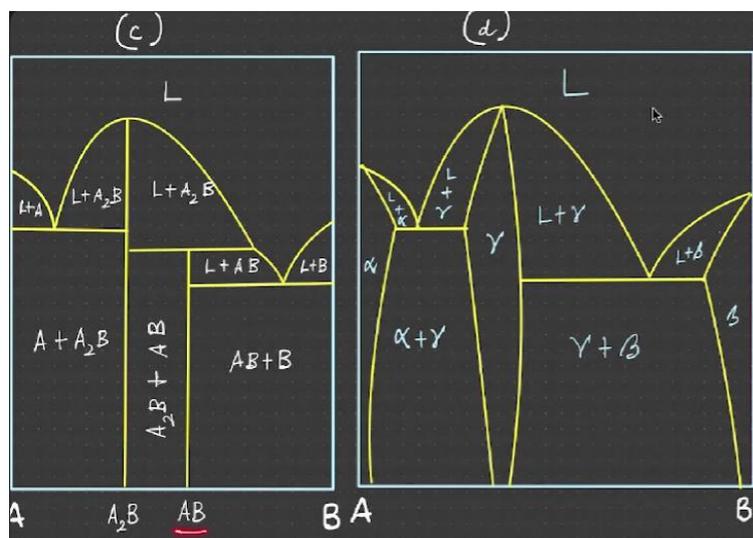
A to B is a line compound, but gamma is an intermediate region. And remember, as you go down the temperature, gamma is quite stable. Similar is for A to B. However, when gamma melts, or if gamma, say for example, the gamma goes here, and that wants to go into the two-phase region of liquid plus alpha, what will happen? You will have gamma and then gamma should go to liquid plus alpha. So, what will basically happen is the gamma will melt at a different composition, right, it will not melt at the original composition that we have.

So, it will have a different alpha solid solution consistency. So, basically the composition of alpha solid solution will vary, right, because it is given by a tie line. For example, if I just looked at these tie lines here, So, this triangle or this triangle.

So, I have drawn just two. So, basically I have drawn this. So, one. So as you can see, this gamma when it melts, basically continuously changes the composition of the liquid, the composition of the alpha phase. So there is, so basically the gamma, whatever composition it started with, it can be like A55. So it is based on the A to B structure.

That's what I can say. The gamma is based on A to B structure. However, it has some limited solubility of A and B, right? So basically, if I look at this temperature, If I look at some temperature, say for example, let us look at a temperature like this. If you look at this temperature, first thing, first. See, you can only draw So, now if you look at this, the gamma composition basically that is equilibrium with alpha is given by, so this is some temperature say for example, let us call this temperature say T is 1. Now at T 1, you have gamma beta equilibrium as well as alpha gamma equilibrium. So, you basically know the phase boundary compositions, you know the phase boundary compositions.

So, basically you are looking at the phase boundary compositions here. And so you have basically gamma in equilibrium with alpha, gamma in equilibrium with beta. But as you go above, as you go up the temperatures, if you as you go above, if you go above, then basically you go like this. basically the liquid phase that falls will have a different composition than gamma phase, right. It will have, so any composition, I can take some composition here, even if I take some composition here, as you go here, say for example this temperature, you basically have now a liquid composition which is different. You go to this temperature, you have a liquid composition which is different.



You do not, so basically what does that mean? It means that again this is an incongruently melting solid. Now, let us look at a congruently melting solid case where again we are looking at two compounds, two line compounds. One is called AB, another is called AB is like 50A, 50B, another is A to B. so now if you look at that A2B extends from some room temperature or nearby room temperature it goes on and on and on and on until hits the liquid so basically A2B when it converts to liquid A2B itself when it converts to liquid the composition of A to B does not change, liquid also has the same composition A to B and these are called congruently melting compounds.

These are called congruently melting compounds. In fact, you also have a incongruently melting, see you have an eutectic compound here, you have an eutectic here. You have because you see the diagram here, so you have an eutectic here, you have again So, basically you have a peritectic here and again you have some eutectic L plus AB, L plus B is AB plus B, but the point that I want to make here is that this compound AB is incongruently melting solid, it is an incongruently melting, as soon as you enter here basically what you are basically seeing is the composition. And now again you go here, now you see there is a change in composition. So, basically you have to, we have to remember what is, so basically AB is incongruently melting while A2B is congruently melting. Now again we can think of some solubility and we can think of like it is not exactly line compound but a phase bound.

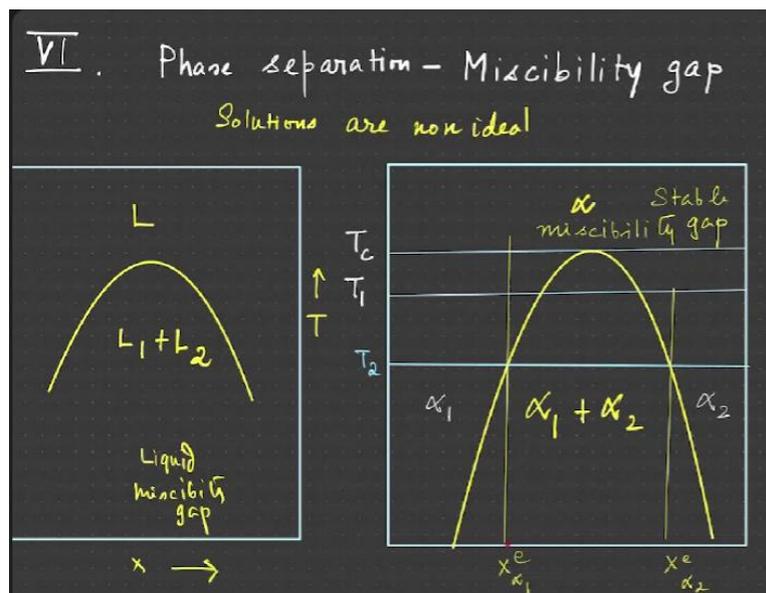
So, basically if you look at this gamma phase which has a different structure from alpha and beta and this gamma phase basically is based on this A to B composition but A is now allowed to vary within some limits and B is now allowed to vary within some limits as a result. So, as a result, what you see is this gamma phase forms, but now if you go to this A to B composition within the gamma phase and again extend the horizontal line, you will basically see that you have ended up with the melting of this composition. Say for example, if I take this guy, if I take it out, so let us look at this. So, let me just do one thing, just do one thing.

Now, let us have, so this is called a convertible metal solid. So, basically for this convertible metal solid which lies in the gamma region basically converts to L, basically converts to So, you basically have now type 4 phase, type 5 phase diagram. Again, here as you can see type 5 means intermediate phases that are stable and extend at, extend on either side. It can extend on the liquid side or it can extend towards the room temperature side. But only thing is the previous one, type 3 was having this, type 4 was having this problem or that it is stable within a temperature range. However, if you look at this carefully, If you look at this carefully where I have drawn, basically what you see is that it is a congruently melting solid for the given or specified composition.

So, that given or specified composition here is based on A to B. So, this is basically, this is nothing but This is the A to B combination. Now, you have type 6 phase diagram which is basically a very important phase diagram. We have already introduced that. This is called miscibility gap and this happens when you use a regular solution model or some non-ideal model. In a non-ideal model, you are basically telling that there is a finite ΔH mixing in the liquid state or as well as in the solid state.

So, you see this is a liquid miscibility gap or liquid miscibility gap where you have one liquid which is you have one liquid which is phase separating to 11 percent, right. So, this is called a liquid density gap. So, you see liquid density gap as well as if you look at this diagram, if you look at this diagram, you see α is a α basically is a solution. Now, if you see there is a P_c or critical temperature P_c , right, at below which the The α phase separates spontaneously into α_1 and α_2 .

It phase separates. Basically, we can tell it phase separates α_1 and α_2 . In the possibility gap gain gain, there is a catch to basically distinguish between whether the phase separation is spontaneous or it is non-spontaneous, right. So, basically what I am trying to say, here I am not looking at phase transformation, but I am looking at So, this diagram basically tells you that if you have a homogeneous solid phase α and there is a critical temperature below which the α can phase separate into α_1 and α_2 . Only thing that you have to remember is that α_1 and α_2 , α_1 and α_2 . In this case, when you have a central gap, you assume them to be structurally same. Basically, α_1 , if α is FCC, α_1 , so it's like silver-copper mixture. So, if you think of a silver-copper alloy, silver is FCC, copper is FCC, so α is FCC.



But now, when α decomposes into α_1 and α_2 , which one is like HG rich solution or silver rich solution or another is copper rich solution, you will basically see that α you

will basically see that alpha 1 and alpha 2 also possesses the same crystal structure, possesses the same crystal structure as the parent alpha case. So, and also again, if you look at some temperature T_2 , just for convenience, if you look at some temperature T_2 , you can see that, so this, if I have to mark this, this is basically pure alpha 1, this is pure alpha 2. So, basically if I have to mark this, so this is the composition, or this is the composition of coexistence of alpha 1 and alpha 2. So, there is this equilibrium, right. So, the coexistence, the equilibrium of alpha 1 and alpha 2 occurs at this composition and this composition, right, $x \in \alpha_1$ and $x \in \alpha_2$, right, at these compositions at this temperature.

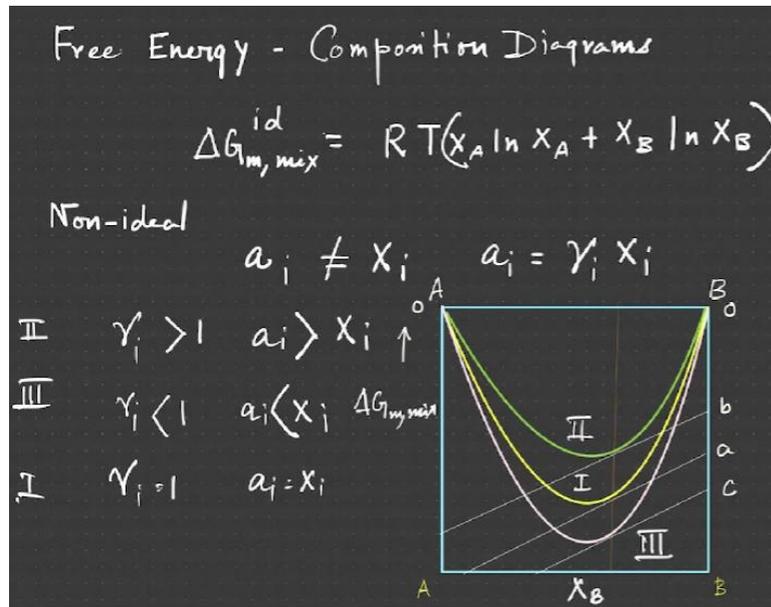
now as you can see here it is clear now that this miscibility gap now if you have a eutectic phase diagram there is always a submerged metastable miscibility gap if you can basically somehow suppress the function of liquid then you will have basically so you will have alpha which is metastable and this alpha changes to alpha 1 plus alpha 2. Currently, what you see is not a metastable microstructure, but if you follow this exactly the yellow lines, basically $L \rightarrow \alpha_1 + \alpha_2$ will still happen. However, the mode of decomposition will be different, right, $L \rightarrow \alpha_1 + \alpha_2$, the mode of dissipation will be different. However, you please note that this submerged miscibility gap helps us understand why some phase separation happens in such, during such transformation, during transformations like pre-technique transformation, pre-technique transformation and so on, in a spin order, right? So this miscellaneous gap, this submerged miscellaneous gap or metastatic miscellaneous gap that we find when we reject L, When we reject L or we suppress L or liquid and we basically tell that it is alpha, alpha 1 and alpha 2 are the phases.

Alpha is the phase above a critical temperature. Again, remember the concept of critical temperature. This is very important. So, this is our critical temperature say. Now, at this critical temperature, at this critical temperature the alpha phase as well as the alpha 1 phase and the alpha 2 phase can coexist.

Again, we are suppressing L. So, alpha is the metastable parent phase and alpha 1 plus alpha 2 is still not metastable, but basically alpha 1 plus alpha 2, these are basically the stable phase separated phases, right, which are isostructure, but not isocompositional. They are different compositionally, but they are similar structure, correct. So, you have the submerged metastable miscibility gap, right. you note that this is a submerged metastable miscibility gap. So, metastable means if the formation of liquid is suppressed and you form this alpha solid solution which is a metastable solid solution at this temperature.

then below this critical temperature it will face. So, we are done. Now, we look at, very quickly we look at the free energy composition diagram. We start with the free energy composition diagram and remember this free energy composition diagram from there you can explain the

phase diagram or phase stability maps. Why? Because free energy composition diagram tells you in some way. See, for example, already we know from free energy convolution diagram that at any point you can draw a tangent and you have the Stanley intercept method and the intercepts basically give you the chemical potentials of the species, species A and species B, we know that. Also another thing we know that for ideal, delta Gm makes ideal will only contain the entropy term and it will be parametric.

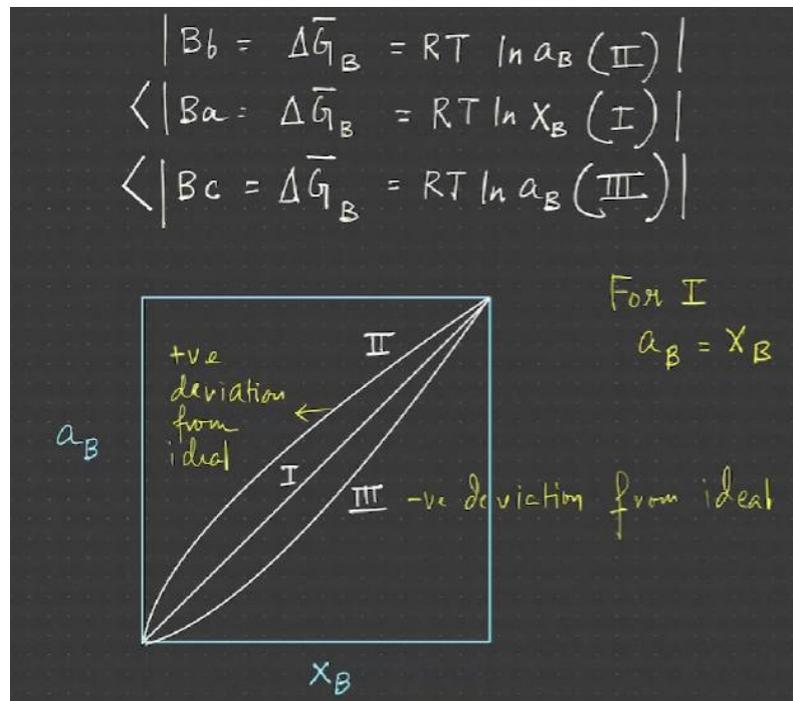


Now, if see if it is non-ideal, A_i is not equal to ψ_i . But if it is ideal, then A_i equals to $\gamma_i x_i$. Now, if you see γ_i is greater than 1, this is type 2. So, type 1, when I have this 1, the free energy 1, here basically we are telling that ΔH_{mix} is 0, ΔH_{mix} or a molar enthalpy of mixing is 0. So, basically 1 is the ideal, it is the free energy of the ideal solution. 1 corresponds to the free energy of the ideal solution, 2 corresponds to the free energy of a solution which deviates from ideality, but the deviation is positive that is γ_i , γ_i is the activation coefficient mean 2 is greater than 1.

In type 2 phase diagram, in the type 2 free energy diagram, that is basically this when I mark 2, this is 2 and this 2 corresponds to this free energy, this green free energy. The green free energy shows positive deviation, positive deviation from the ideal case and this positive deviation means γ_i is greater than 1 and a_i is greater than x_i . Now, if you look at curve 3, the curve 3 basically represents a negative deviation from idealities. Idealities begin by Raoult's law, A_i equal to x_i , but in general where γ_i equal to 1, but A_i equals to $\gamma_i x_i$.

So, if you see the type 3, the third, the marked as 3, not type, we call it level. So, the free energy corresponds to level 3, the free energy corresponds to level 3. If you look at that, you will see that at any point, Here, in type 3, γ_i is less than 1, right? You are basically falling

below 1, right? You are falling below 1. So, as a result, if you are below 1, if you are below 1, that means there is a negative deviation from identity. So, this gives you a negative deviation and this gives you a positive deviation from identity. This gives you a negative deviation from identity, right? And negative deviation means gamma is less than 1.



Positive deviation means gamma is greater than 1. Ideal, there is no deviation means gamma equal to 1. So, that is right. Now, if you see, you have BB, BA and BC. So, you can basically write BB is nothing but the intercept delta GB bar or BB.

BB is also delta GB bar. BA is also delta GB bar and BC is also delta GB bar. But this is delta GB bar for BB is delta GB bar for type 2. If you see $RT \ln AB$, so delta Gb bar is the partial molar free energy of mixing associated with the beta, associated with B, like partial molar free energy of mixing associated with B. So, delta Gb bar is $RT \ln AB$, right. So, this is basically AB corresponding to 2, right. 2 means where gamma I is greater than 1, gamma I is greater than 1 or gamma B you can write is greater than 1.

Now, in this case, for the case R, BA, BA is the intercept, right, this BA, what is this BA intercept? This intercept basically gives you mu B, right, for the ideal solution, right, this is basically delta GB bar equals to mu B, okay, and this mu B is for the ideal solution, right, we are doing it for some ideal solution. So, then this is the ideal solution, so here activity is equal to mole fraction, these are non-ideal. So, here remember this is basically BC and this is basically BB and you can immediately see that BB that is the intercept BB is larger than BC.

So, it has a negative deviation from ideal. So, Raoult's law if you write AB versus XB. So, this is again a recollection of the previous lecture. If you see that you have this 45 degree line and where a b equal to x b. Now, the deviation can be positive and the deviation can be negative, right. But Raoult's law tells basically it is a straight line, right. And as soon as there is deviation, that means gamma is not equal to 1, you will start seeing either a positive deviation or negative deviation.

So, 3 gives you negative deviation from ideal condition and 2 gives you negative deviation from, positive deviation from ideal condition. Now, we come to a very important concept called free energy, the equilibrium, chemical equilibrium equilibrium very easily. So, if we look at this, you have these two free energies. We can say at temperature T1, at temperature T1, I am drawing the free energy curves for two phases.

There is a liquid-solid coexistence. If you have a liquid-solid coexistence, then basically at temperature T1, we are drawing say for example, the free energy composition curve. Now, if you are looking at the free energy composition curve at temperature T1, T1 is fixed, you have the liquid curve, this is the liquid free energy, we are assuming again this is ideal solution. So, liquid has some parabolic shape, liquid free energy and the solid free energy, it is $RT \ln x_a$ plus x_b . So, liquid and solid, if you look at liquid this is the liquid and this is the solid.

So, this is your solid free energy and this is your liquid free energy. Now, if you see for any given composition I can draw a tangent. Now, if I draw a tangent to the liquid phase what do you get? I will get the on the on the left hand side we will basically get for the liquid phase we will get μ_a liquid, we will get μ_a liquid and you will also get μ_b liquid. Are you seeing that? So, you have μ_a , this is basically the diagram. So, you have μ_a liquid and you have μ_b liquid. Similarly, if I look at the solid free energy curve, the solid curve, the solid free energy curve, then we are looking at, this is the solid free energy curve.

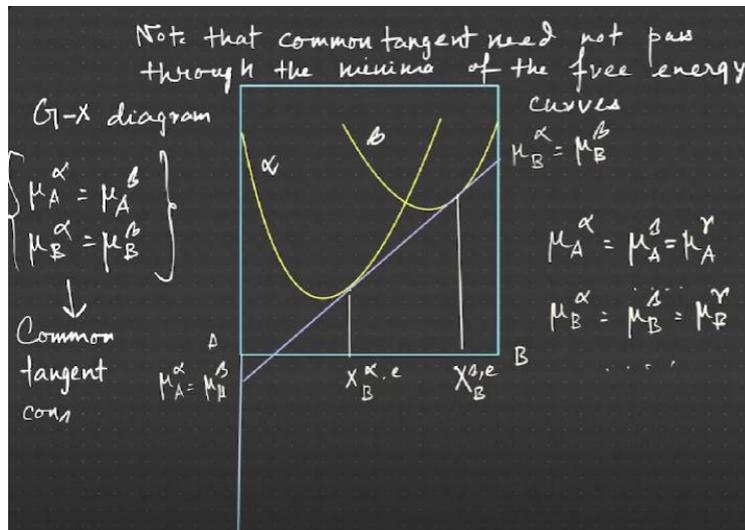
And basically, again we are drawing some tangent, some arbitrary tangent. Again, the intercepts basically gives me, so do not be confused. So, I will do one thing. I will just write it with a different color. So, basically, μ_A solid and this is μ_B solid. Now, if you see if I want to have a liquid solid equilibrium like two phase coexistence means, two phase coexistence means They are at equilibrium.

Two phase coexistence means they are at equilibrium. Liquid and solid are at equilibrium. Now, if I want to see the equilibrium graphically, how do I do that? Because you have two tangents. Now, you have to remember that you have μ_A solid, you have μ_A liquid, you

have μ_B solid and μ_B liquid. How do you basically find the equilibrium? So, you remember at equilibrium, at equilibrium means here I am talking about chemical potential of each species. So, basically at chemical equilibrium condition is μ_A solid equals to μ_A liquid another is μ_B solid equals to μ_B liquid that is the chemical equilibrium the well known chemical equilibrium condition.

So, now if you look at that If you look at this, then there is an interesting point that I want to tell. So, basically μ_s solid that you have here has to be equal to μ_n equal. μ_b solid has to be equal to μ_b equal. How is it possible? If we have a common intercept. Now, for common intercept, we require common tangent between these two curves.

Now, think of this white line, this white tangent line. This white line basically exactly does that. It creates a common tangent. Now, this is the common tangent. If you go to this intersect, you will see basically μ_A liquid equal to μ_A solid and μ_B liquid equals and on this side, it tells μ_B liquid equal to μ_B solid. So, you understood the common tangent is basically a graphical way of assessing the chemical equilibrium by solving these equations that μ_A is, μ_A solid equals to μ_A liquid and μ_A solid equals to μ_B liquid. If I solve these equations, what do I get? We get the compositions corresponding to E and F, compositions corresponding to E and F.



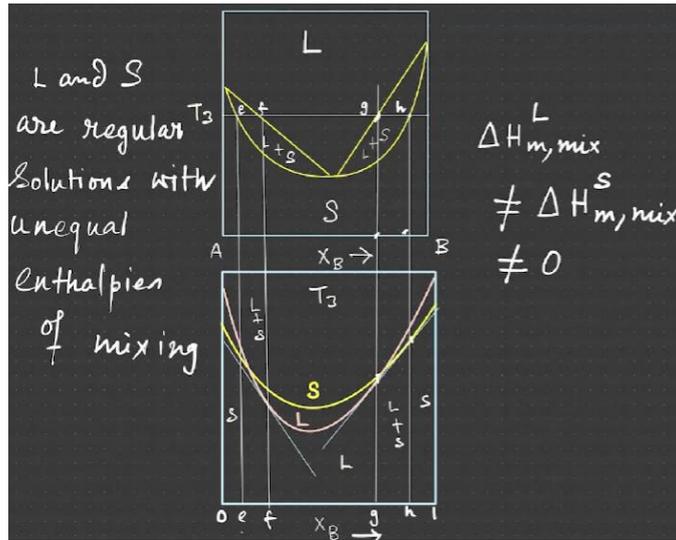
So, basically if I know the liquid solution model and the solid solution model, I can basically calculate, I can basically calculate the equilibrium. we can basically calculate the equivalent. So, what we looked at or learnt today is this common tangent construction. And finally, we have to remember, so this common tangent construction again, you should not, you should remember, note that common tangents need not pass through the minimum of the cost.

So, this is the minimum of the free energy cost. So, this is basically, this is also called, you know, G-X diagram. And this is also called, this is called common tangent construction. And note that the common tangent did not pass the minimum of the free energy curves, right. Only if the minima are at the same level, the minima are at exactly the same level, then you will have a horizontal common tangent, right. But otherwise, if you see here, you have alpha phase and beta phase that are in equilibrium. If you look at alpha phase and beta phase in equilibrium and you want to use a common tangent construction which I have done, this purple line basically gives you the common tangent.

You see your minima are here somewhere, but the common tangents are here, right. This gives you the, this indicates the composition of the alpha and beta phases in equilibrium, right. This is basically X_B alpha equilibrium with beta. So, X_B alpha, this is basically X_B alpha composition that is equilibrium with beta and this is X_B beta equilibrium. So, equilibrium that when I am looking at this equilibrium, we can tell alpha beta equilibrium and this beta alpha equilibrium, right. So, basically what we are trying to say is that the equilibrium, the common tangent points, the common tangent where the common tangent touches these two curves, these two points basically correspond to the equilibrium compositions.

These two points basically correspond to the the solution of these two equations like $\mu_A^\alpha = \mu_A^\beta$ and $\mu_B^\alpha = \mu_B^\beta$. That is what is embodied. So, that is what is embodied in the common tangent construction. So, common tangent basically tells you a graphical way of estimating the equilibrium compositions.

In fact, I have a Python notebook which I will show. So, basically this is the common tangent. So, this is graphical common tangent construction. The basis is this equilibrium conditions. So, note that I will discuss further that we will discuss another very important idea. So, before that I will just quickly, I will quickly finish this lecture. here with this that liquid and solid if they are regular solutions with unequal enthalpy mixing you often have a phase diagram where you basically have this liquid solid.



So, you can this is the something like you have two lenses here. So, you have two lenses here like this and then like this and you basically can see here that this is like a liquid-solid region and then again there is a liquid-solid region and then there is one small point which is basically where it is turning right, it is turning. In fact, the way it should be drawn is not this, but remember this is a problem of the drawing here this act in general this is much smoother okay so basically if you look at that We can, yeah. So, I will come to this in the next lecture. I will come to this in the next lecture and I will explain to you that when you basically estimate liquid and solid to be regular solutions, you will see there is a definition of viability which I have discussed already and you can look at how this quantum construction can be used to basically find the compositions of the phases that have any equilibrium. So, that is something that you can see in the next lecture.