Thermodynamics And Kinetics Of Materials

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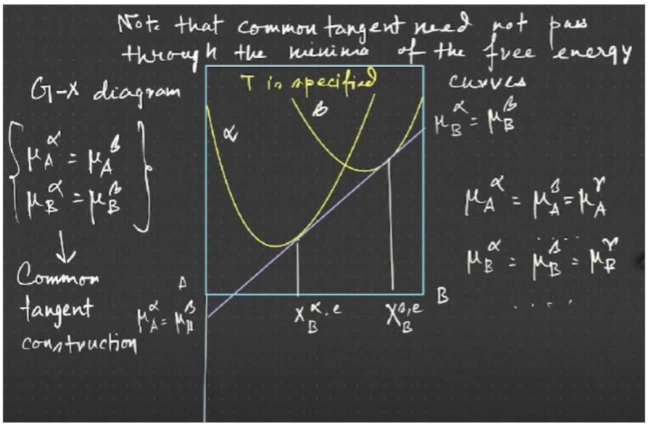
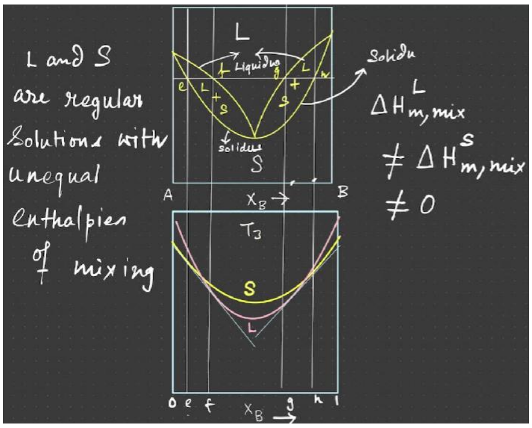
Lecture 35

Thermodynamics of phase diagrams - G-x curves

Have a look at this case where liquid and solid are regular solutions. So, we looked at the compound energy construction and we also looked at compound energy construction basically gives you the chemical equilibrium conditions at a given temperature. This is done at a given temperature. Remember, here some T is specified, T is specified. When we are drawing the free energy composition diagram, we already know that T. So, T is specified and you have alpha and beta and you can see that it is not really the common tangent basically tells you a condition where mu a alpha equals to mu a beta and mu a alpha equals to mu beta and at the where the interest the common tangent.





the points touches the curves, the points touches the curves if I look at that point. So, this point for example or this point for example basically gives me the equilibrium compositions of the alpha and beta phases that are in equilibrium, like alpha and beta are in equilibrium. So, XB alpha equilibrium is the composition of the alpha phase that is in equilibrium with the beta phase. Similarly, XB beta equilibrium this composition is basically the composition that is of beta phase that is in equilibrium with the alpha phase.

So, basically it gives you a solution, a graphical solution of these equations, of these equations it gives you a direct graphical solution. We can look at more complex diagrams also to look at an estimate the graphical solutions for example, here liquid and solid. So, if you look at that liquid and solid, there are two phases liquid and solid. But you can see this diagram is quite complex because you have L plus S here, E plus L plus S here and there is only one point where it changes, continuous one point where it changes. L plus S as regular solution, so this is where you have the pure liquid and then you have solid.

Now, if you look at that at temperature T3, you have one composition E, then F, F is the composition of the solid phase in equilibrium with the liquid, so F is the composition of the liquid phase, this is the liquidus, this is a liquidus line, this is liquidus. So, basically if I tell what are the liquidus lines, so basically I can basically easily tell what are the liquidus lines. So, this is liquidus and similarly this is also liquidus, right. So, this is also liquidus, right, this is the liquidus line, these two are the liquidus lines. this is your solidus line.

Solidus basically is separate, so basically you have, so if you look at that, you have this solidus line here, and this is also solidus. So, now if you look at the compositions f and g represent, so if we look at f and g I am going the other way. So, F and G represent the equilibrium compositions of the liquid phase that are in equilibrium with the solid phase. So, F for example, is the composition of liquid phase that is in equilibrium with the solid phase at the solid phase with composition E. Similarly, G is the composition of the liquid phase that is in equilibrium with the solid phase with composition H right here G and H is a tie line.

So, you have a tie line G H and then you have a tie line E F. So, E F the two endpoints are the equilibrium compositions for liquid and the solid phases and these tie line basically is the equilibrium of the solid phase and this is equilibrium of the liquid phase right. Now, if you look at that if you see that these are both regular solutions with unequal enthalpies of mixing. So, if you see unequal enthalpies of mixing means your your regular solution models will be different, slightly different, right? They will have different shapes. For example, this solid curve has a different curvature than a liquid curve, right? The liquid curve, the liquid curve that you have has a different curvature, than the solid curve, right.

So, one is slightly less spread, another is more spread, but a liquid for example has slightly more depth in the middle and solid has slightly less depth in the middle, it is like is less, it is more shallow, solid curve, solid range curve looks more shallow and liquid range curve looks more deep. And, but why does this happen? Why are the shapes so different? The shapes are different because the models are different and also in these models, the the enthalpies of mixing or molar enthalpies of mixing are unequal so as a result if you see that you will again see that once we do this so you have this solid curve here right you have this solid curve here so if you look at the solid curve you have this this here and you have the liquid curve here and then you have this tannins, right. So, the liquid curve is given in pink, the solid curve is given in yellow and as you can see solid curve is more shallow than liquid, right at the, at the, at the, at the the equi-atomic composition or at or near the equi-atomic composition and also they have different curvatures. So, as a result, if you see the tangent construction here, you will see that you get into this G and H here and if you do the tangent construction here, you can see this blue curve, you can see this blue curve, this blue line that we have. So, this is the blue line and this is another tangent that we have.

And so, from these tangents you can basically tell that this tangent basically gives me the, this is the going to be my composition of the liquid phase in equilibrium with the composition, with solid phase denoted by E, right. So, this is the composition of the liquid phase denoted by F, right, this is F. And this is the composition that is, so again it comes from, you can see E and F basically gives you the points where the common tangent touches the yellow and the pink curve. The pink curve is the free energy of the liquid and the yellow curve is the solid. And again, you have on the other side, you have again this blue curve, this blue line which is a common tangent line, this blue line is a common tangent line and it intersects or it touches, it cannot intersect, right, it touches the liquid curve here at G and the solid curve here at H, right.

So, it touches it at H. So, if I look So, I think that G is like this place, done. So, now we have to also understand another very important point that is the liquid and solid, that is I have this text. You have this liquid free energies and solid free energies. In all these free energies, we always use some standard state.

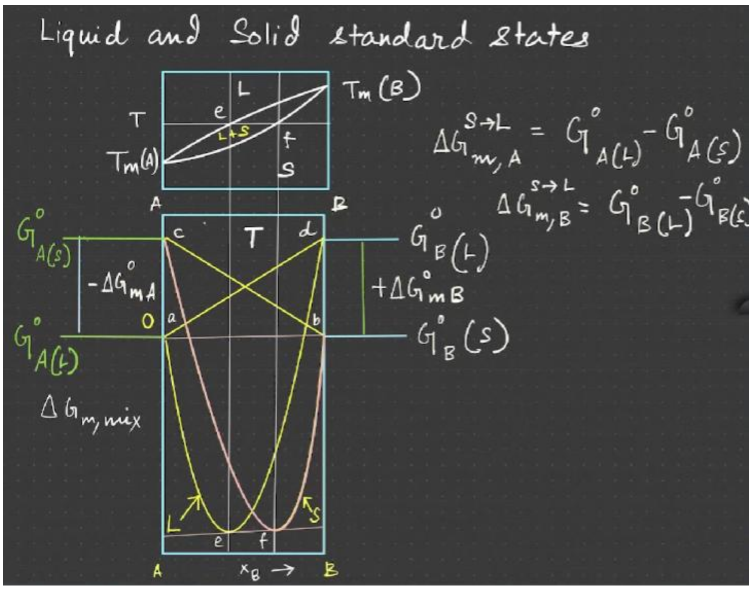
If you see the case here, Tm of A is less than Tm of E. Tm of A is less than Tm of E, that is the melting point of A. So, in this diagram very quickly, is less than T. Now, I am looking at a temperature T, say this temperature. Now, we have this liquid plus solid equilibrium and we have these two free nets.

If you look at this very carefully, this is the liquid free net. See, this is the, this curve, this curve extending from here goes up to here is the liquid free net. And this curve extending from here up to here is the solid free in fact if you want I can basically replace the solid free energy So, pink is basically the solid one and the pink is basically the solid one and yellow is basically the liquid one. Now, if you see that you have two points here that is this you are drawing at some temperature T, this is what you are drawing at some temperature T. Now, at this temperature if you look at that at this temperature is above TMA, this temperature is above TMA that means at this temperature the pure A should be liquid.

So, at this temperature pure A, pure A the liquid pure A free energy is here. because here you have basically a liquid phase, right. So basically at this temperature, at this temperature T, the liquid phase free energy is less than the solid phase free energy for pure A, right. For pure A, pure A solid, the free energy is more than pure A liquid at this temperature, right. So basically solid to liquid if you look at, solid to liquid if you look at, so this is like the melting condition solid has a higher free energy and liquid has a lower free energy.

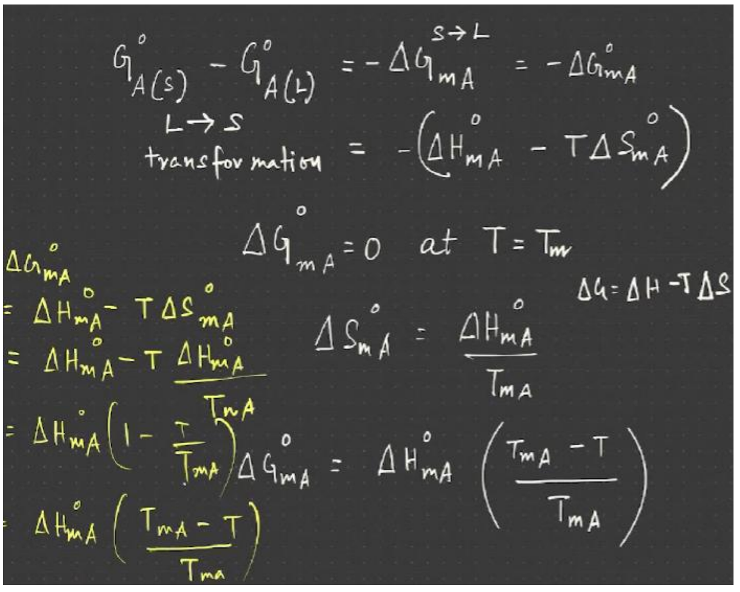
So, liquid, solid to liquid means GA, GA0 liquid minus GA0 solid, but GA0 liquid is already less than GA0 solid that means it has to be negative. So, delta GMA solid to liquid is basically GA0 liquid minus GA0 solid, which is basically, which is basically negative. So, basically, That is what I have written, right? So, this is more, this is more than this guy or this is less, this, the GA0 liquid is less, right? GA0 liquid is less than GA0 solid. As a result, this guy has to be negative, right? Now, if you look at B, if you look at B, TMB, that is the melting point of B is higher. So, basically, solid here will have a lower frequency.

The solid here will have a lower frequency. So, solid has a lower frequency here and the liquid has a higher frequency here. So, basically, if you consistently look at this delta G0m, that is the molar free energy for pure B, right, 0 and B basically tells you it is for pure B, then delta G0b from solid to liquid is basically, again, liquid, solid to liquid, right, final minus initial, so liquid minus solid, right, G0b liquid minus G0b solid, right, G0b liquid is basically higher than higher value, right, at temperature T, G0B liquid has a higher, greater value than G0B solid. So, basically G0B liquid is greater than G0B solid at temperature T. However, G0A liquid is less than G0A solid at temperature, at the same temperature T, right, because of the melting point differences, because T lies in between TMA and TMB, that is the melting points of LB.



Now, what should you choose as standard state? You can choose anything, you can choose The reference tend to be anything. It can be A in solid and B in liquid or it can be A liquid and B solid. So it depends on both A and B in the liquid state. That's also possible. Only thing you have to be very, very systematic and careful when you calculate right remember one thing whatever be your reference state your common tangent construction does not change common tangent construction remains as it is right whatever be your reference state only your reference state it should be consistent say for example for the liquid if i take A in the liquid form and B in the solid form to be the standard state, then basically A in the liquid form and B in the solid form has to be in the standard state also for the solid phase.

I cannot switch standard states from phase to phase. So, for the liquid phase, if I tell A liquid and pure A liquid is my standard state and pure B solid is my standard state, then for my alpha phase or for my solid phase, also I have to do exactly the same that pure A liquid is my standard state for A and pure B solid is my standard state for B at this stage. So, that is exactly what I am trying to say. So, basically if I tell solid to, so this is like liquid to solid transformation. So, it is like a freezing transformation.



So, where you have solid to liquid, G0 solid, but remember this is positive, G0 solid is greater than G0 liquid because liquid has a lower frequency at this temperature. So, G0 solid minus G0 liquid is minus of delta GMA solid to liquid is minus delta G0M. So, it is basically G liquid, so minus of delta G0 ma. By the way, minus delta G0 ma is basically, so if you see this, this is positive, right, positive and this is negative and so there should be, this guy has to be negative, right. So, delta G ma itself is negative.

So, this becomes positive, right, because this is greater. So, as this is greater, so this has to be negative to make it positive. Now, this is liquid to solid transformation. Now, this you can basically tell that delta G minus delta G 0 ma is minus of this delta G is delta H minus T delta S. So, that is what I am writing delta H 0 ma.

So, basically this is the molar enthalpy molar free enthalpy sorry molar enthalpy of mixing molar enthalpy of pure molar enthalpy of pure A. So, this is molar enthalpy of pure A and this is molar entropy of pure A. right. This is molar enthalpy. So, this is the molar enthalpy of mixing or change in molar enthalpy of molar enthalpy for POA, but it transfers from liquid to solid or from liquid, right.

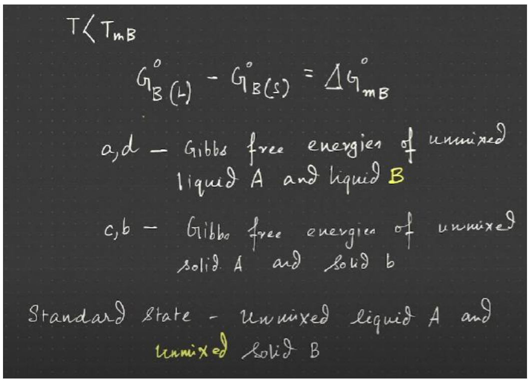
So, basically, when I am looking at that, so, when I am doing delta GMA solid to liquid, so, basically, we are looking at melting, right. We are looking at melting. So, basically, this is equals to minus delta HGMA, there is a enthalpy of that is the change in enthalpy or change in molar enthalpy or molar enthalpy associated with this solid to liquid translation. Again, this is the molar entropy associated with solid to liquid translation of pure A, solid to liquid translation of pure A. So, that is why we put a 0 here in the superscript.

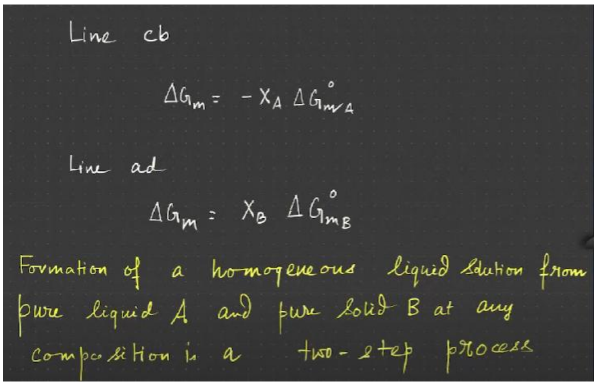
At T equal to Tm, solid and liquid are coexisting. So, at T equal to Tm, delta Gm is 0. Delta Gm is 0 has to be equal to 0 at T equal to Tm. Now, if that is so, if you now put it here, so this is 0.

0 is this minus this. So, basically, if I can write delta S0m, that is the molar entropy of pure air, the molar entropy of pure air in solid-liquid transformation, right, molar entropy of pure air during solutability transformation is basically a ratio between the molar enthalpy of pure air by the melting point of air, right, molar enthalpy of pure air by the melting point of air, right. Now, this is your entropy because this has to be 0 at the melting point, right, TMA is the melting temperature, here TMA is the melting of pure air. Now, if that is so, I am just putting it here. So, basically delta h m a 0 minus t delta s m a 0 and delta h m a 0 minus t delta h m a 0 by del t from here, from this equation you are getting that, from this equation you are getting this one. So, if you have that, this can be made common and you get 1 minus t by T m a which is basically T m a minus t by T m a, fantastic.

So, we got the delta G 0 m a as T m a minus t by T m a. Now, if you can see here T m a is basically T m a is basically less than T. So, T m a minus T is negative. So, basically delta G 0 m a is negative by itself.

So, this means solid to liquid. So, if it is liquid to solid transformation, then it becomes possible because again and again liquid has lower free energy than this P over T. On the other hand, T is less than T m a. So, there the liquid has So, the solid has less free energy. So, solid has lesser free energy while liquid has more free energy.





So, basically delta G 0 m B is positive. Because if you look at the liquid and solid, so this is liquid, liquid has a higher energy. So, this is delta G0 and B is positive, delta G0 and B is positive. Now, you have AD, which are the gives free energies of unmixed liquid A and liquid B. So, this is A and B are unmixed liquid A and liquid B, A and B. right and C and B right A B B and C or C and B are the states of unmixed solid A and solid B.

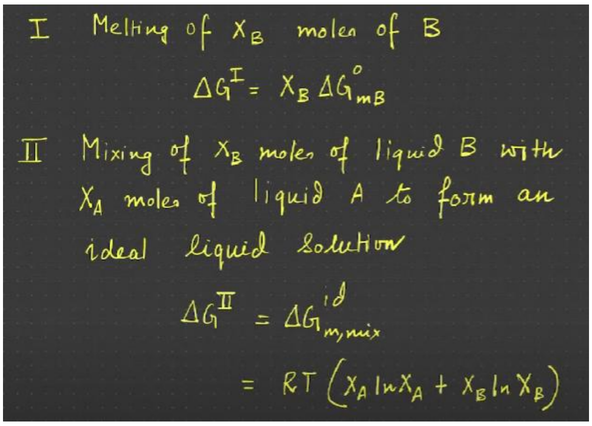
Now standard state you can use anything but we are we are using unmixed solid liquid A and unmixed solid B. Now if that is so now you see one very important thing here so minus delta GMA 0 Now, if you see when x A equal to 1, you have the difference is minus delta G m A 0. Now, I am looking at the equation of line C B. Now, if you see, if I go further, if I go further down, say for example here, it will be minus delta G m A 0 times the minus delta g m s 0 times the composition. So, basically at this point, so basically the composition of A, this it will vary as composition of A.

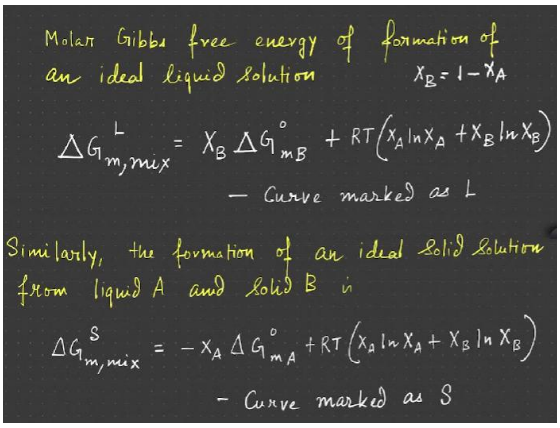
So, because composition of A varies from 100 here to 0 here. So, basically it is varying with the, so basically if you look at the C-B line, you see the C-A and you see this line distance here, this distance this, this and all. So, ultimately basically As you can see here, the line C D, the equation is very simple, delta g m A 0 times x A, times x A because x A is 1 here and x A becomes 0 here, x A is 1 here, here x A is 1 and here becomes 0. So, this is your delta g m is 0. So, delta g m is 0 into x A and x A is 0, x A is equal to 100 or x A equal to 1 in the, when you have pure A and it goes to 0 as you have pure B, as you move towards pure B.

So, basically the equation becomes x A times minus excepting delta G M L C O, this minus is because delta G M L C O by itself is negative I am putting a minus minus delta G M L C O. So, basically that is what I have written and similarly for line A D. if you look at line AD, so this is the one, plus delta G0 MB, if you look at the line AD, you see at DB, delta G0 MB is full, otherwise it becomes smaller and smaller. So, if you look at this, if you look at this, if you look at this, the values become smaller and smaller. So, this is delta G0 MB that is the for the pure B, liquid to solid transformation, we are writing delta g g of B.

So, liquid to solid transformation remember or solid to liquid transformation, so we are writing this. Now, once we have written this, it has to be multiplied with, so basically if I look at the A D line, it will be multiplied with x B. So, this is very very common sense and you can understand, right. Line A D the equation is, the line A D the equation is this. And now, if you see the formation of homogeneous liquid solution from pure liquid A and pure solid B at any composition is a two-step process.

How? Because if you have liquid A and solid B, it is a two-step process. What is the two-step process? First thing is XB because it has to become, it has to go to the liquid step. So, the first thing is melting of XB moles of B. Now, when you multiply, so delta G0 MB is basically from solid to liquid transformation.

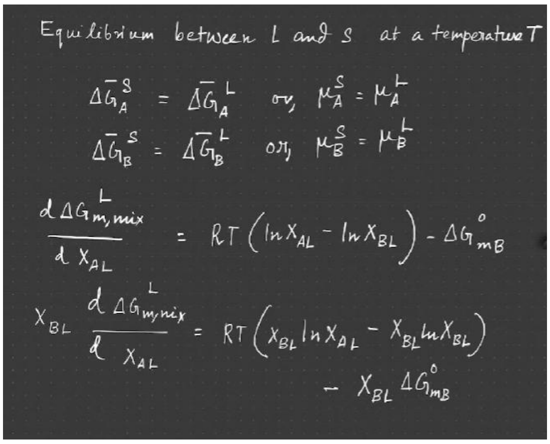


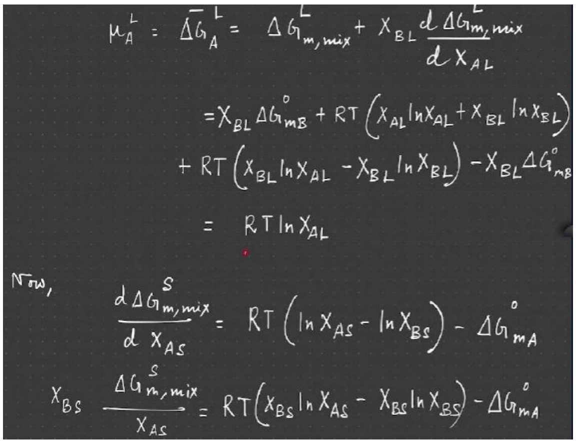


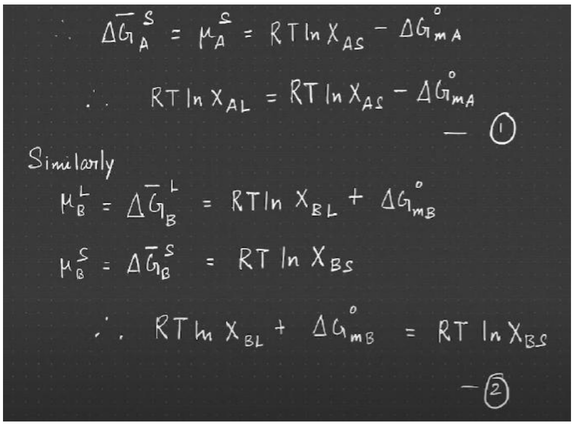
solid to liquid transformation, right. So, basically if I look at that solid to liquid transformation, which is basically, now if you see the solid to liquid transformation, please understand, so this is the solid and it goes to liquid, right. So, you require to apply, so basically you have to apply energy because liquid has a higher, higher energy than solid, right because T is basically less than T of T, right. So, now if that is so, you have this term, so you have where is that, this term that is the first step which is basically xB times delta, so xB is the formula composition of alloy, so melting of xB moles of B, so composition of alloy is xB, so xB times delta G0 mB. Now and then mixing of this XB modes of liquid or XB atoms of liquid, XB modes of liquid B with XA modes of liquid A to form an ideal liquid solution which is basically delta G ideal mix which is RT XLA XA plus XA beta XA. Now if you have that, then you have and you also know, so basically now molar key strain energy of formation of an ideal liquid solution is basically you just add it together, right.

You add steps 1 and 2. So, you have like delta G1 plus delta G2 and so this becomes x B delta G0 m B. So, this is the term because the first term and the second term is like this, okay. And this is the equation of the curve markers. This is the equation of the curve markers. Similarly, for an ideal solid solution, from liquid A and solve B, again you have to freeze the liquid, you have to freeze the liquid, you have to freeze the liquid, again you have to minus XA delta G0 MA, which is basically your time plus RT XA delta XA plus RT XB.

So, here, so in the case of ideal solved solution, A has to be frozen, so which is basically given by this expression. So, basically it is solid to liquid translation. So, solid to liquid. So, minus of delta G ma or delta minus of delta G 0 ma.



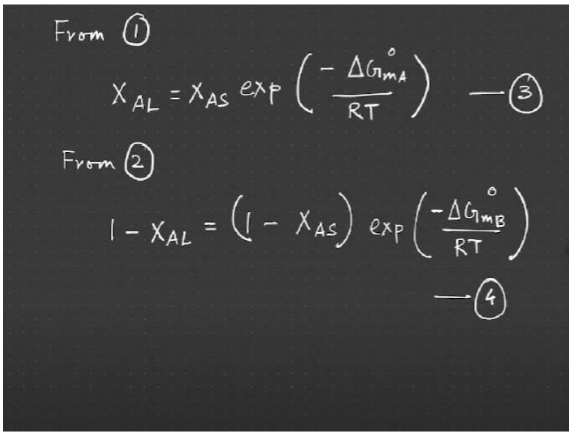


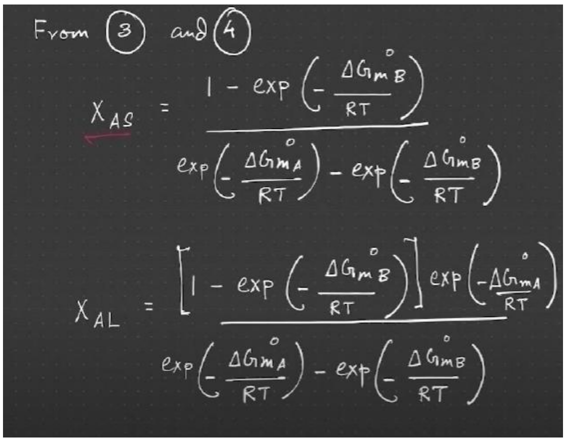


So, basically that is the idea. So, minus of delta G 0 ma. minus X A delta G 0 m A plus R T X A m X A plus R T X B m X A. Now, if you look at the equilibrium, you have to see that this is like mu A S equals mu A L and mu B S equals mu B L or you can also write this. This is the partial molar free energy of component A in the solid state, shag should be equal to partial molar free energy of component A in the liquid state, similarly for B. Now, you have the mu A, the equation, the mu A equation is you have d delta g dx, d delta g dx which is basically coming from here, right.

So, you already know d delta g liquid, right. this is the molar free energy of mixing for the liquid solution, this is the molar free energy of mixing for the solid solution. Now, if I know this, I also know its derivative right, d delta g dx I know and we know that formula. So, the formula is delta g minus x into d delta g dx. So, basically if I know the formula, so what is mu L liquid, mu L liquid is this, delta G liquid plus X bl times d delta G dxA.

Now, if I have that, so basically dXA liquid. Now, if I have that, we do a little manipulation, so basically we get R Tl xA. So, for solid also, if I have a look at solid and if you do that, you basically get RT ln Xa S minus delta G0 L. So, basically you get RT, so if you equate them, you basically get RT ln Xa L equals to RT ln Xa S minus delta G0 L. Similarly, for mu L, you have RT ln Xb L plus delta G0 Mb and for mu Bs, it will be RT ln Xb S. So, this is equation 1, this is Basically, if you have these two equations, you can basically get the mole fraction of A or composition of A in the liquid.





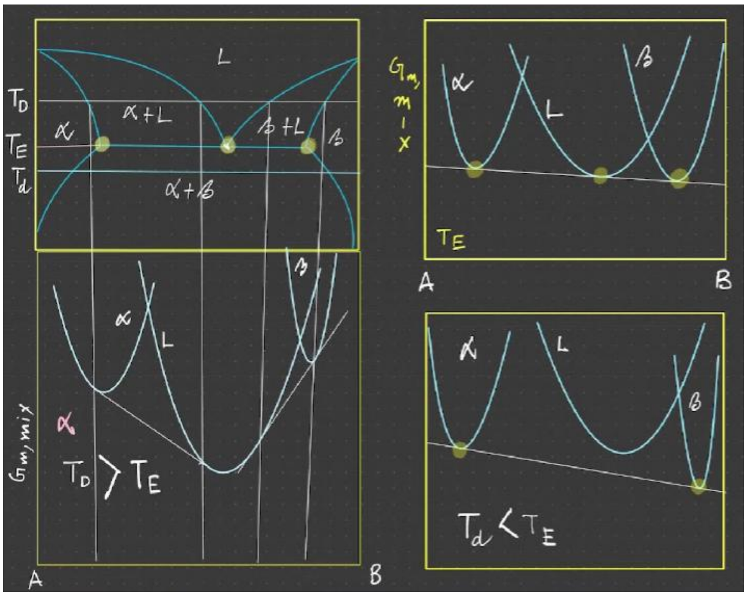
xAl basically ignores the composition of A in liquid which is equal to composition of A in solid times exponential minus delta gm 0 by RT minus delta gm 0 by RT. And 1 minus x L is 1 minus x A x, so that is from 2 into exponential minus delta G 0 m B by r. So, that is the idea. So, this is basically 1 minus x L is nothing but x B L.

So, you have x B L. So, x B L equals to x B S exponential minus delta G 0 m B by r. Now, from 3 and 4, so this is your 3 and this is your 4, basically you can write XAS and XAL. So, basically X, so if I know this, so XAL and XAS, right, so basically XAS and XAL. So, you know 3 and 4 and you know XAS and you know XAS and you know XAL, right.

So, if I want to do this, we can further simplify it. How do I simplify it? Because you have x a l and x a s and you have two equations, you have this equation and you have this equation. If you want to eliminate it is nothing but x a l by x a s which is exponential minus and so 1 minus x a l by 1 minus x a s which is this equation. So, basically if you have that you can do a little bit of manipulation to get say S to be mon minus exponential minus delta g 0 m 0 b by RT into divided by exponential minus delta g 0 m by RT and minus of exponential of minus delta g m 0 b by RT. So, basically you get the composition of the composition of A in solid and you also can get composition of A in liquid.

Now, how do you do this manipulation? The idea is very simple. The idea is very simple. You have 1 and 2. From 1 and 2, you are basically writing xal and xas. So, basically if you know these two equations, there are two equations and there are two unknowns.

One is xal, another is xas. These are the two unknowns. Now, if you have these two unknowns, if you have these two unknowns x a l and 1 minus x a l and you have x a s and 1 minus x a s two unknowns two equations you are basically doing a little bit of manipulation. So, basically you can write 1 minus x a l plus x a l is 1 and you have x a s exponential minus g m a 0 by r t and 1 minus x a s exponential delta g m b 0 by r t and this is equals to So, basically from there you can obtain XAS and XAL. So, this is just a little bit of engineering manipulation. Now, once you have done such manipulation, now you can basically look at the, so what you got is basically the concentration A, you have got the concentration of A. So, basically you have got XAS in terms of, so you know T, you know this guy and so you know with temperature how the composition of A in solid will change and A in liquid will change.



So, if you know that, you also know basically the B in solid and B in liquid. So, basically you know the equations of the liquidus and the solidus. This gives me the equation of the, so this gives me the equation of the solidus. So, this is the solidus line as a function of Xs versus T, you get Xs versus T and this So, this is how you can basically explain the equations and you see if you have an, so one thing I wanted to tell you that if you do this free energy composition diagrams, you can basically analyze any equilibrium. Say for example, if I have this eutectic, if I have eutectic point, so basically at If I just look at Te, at temperature Te, you see alpha, so basically this is this point, this point tells that this is the alpha liquid and beta consistence. But this is the composition, so this is where it comes in handy, this is the composition of liquid, this is the composition of beta and this is the composition of alpha at the temperature.

At the eutectic temperature, this is the composition of liquid, this is the composition of beta, and this is the composition of alpha. As you can see, composition of liquid is between composition of alpha and composition of beta, unlike in the peritectic. Now, if you have that, you have the alpha free energy, you have the liquid free energy, and you have the beta free energy, all of them will fall on the same common tangent at P. And this basically corresponds to this point, this basically corresponds to this point, and this composition corresponds to this point.

So, this is at T. Now, if you go below T, say for example at T d, you will see at T d you have only alpha and beta. So, the liquid basically just goes up. Liquid does not remain in the component.

So, you have the alpha composition. So, you have the alpha composition. and the beta composition. There is no liquid because the liquid has gone up, right. Liquid does not come in the common tangent. So, basically at T d you have only this phase and this phase, the alpha phase and beta phase and these are your compositions and this is exactly the compositions that you have, right.

And say for example, this is T small d, this small d is basically below T. So, T d is basically less than T d and this T d is greater than Now, in this case what you will see, you will have alpha phase as well as the liquid phase. So, basically you see you have alpha liquid. So, this is the liquid composition, this is the liquid composition in equilibrium. So, this is the liquid composition in equilibrium, this is the alpha composition in equilibrium.

And you have again, a pure liquid region. So, this is basically as you can see here that after that, so after this there is a gap, right, there is a gap. So, this is the pure liquid region and then again you get into beta plus liquid region. So, this is basically marked by these two points, right, these two points in the temple. So, these two points basically mark these and these two points.

You can see this point and this point are the same as this point and this point. And you basically get the liquid beta equilibrium. And then finally, you have, so beyond this point, beyond this point, you have pure beta. And before this point, before this point, you have pure alpha. So, alpha, alpha plus liquid, liquid, tight alpha, you have alpha, alpha plus liquid, then liquid, then beta plus.

So, again, this gives you aqua resistance beta plus liquid. So, this is the region of beta plus liquid. and this is the region. So, you can just do one thing, you can just extend this point.

So, if you extend this point, you can extend this point. So, you can now mark them. you can now mark them. So, this is alpha, this is alpha plus liquid and this is liquid and then this is liquid plus beta and then beta. So, basically you can see that at T e mu A l equals to mu A alpha equals to mu A beta or we can do it for mu B l, mu B alpha, mu B beta. So, you have four equations. So, if you look at, very similarly, if you look at the pre-technique composition, then again you have this beta composition, you have the liquid composition, but here you see the liquid composition, see alpha, beta and liquid, all of them follow the same component, all of them at the predicate point, at this reaction point alpha, beta and liquid.

But beta composition, see here the beta composition is between alpha composition and the liquid composition. Alpha composition, liquid composition, beta composition. So, beta composition is So, this is exactly. So, next we will discuss the criteria for phase stability in the next lecture, 12-week lecture. We will start with the criteria for phase stability and we will do some numerical modeling in the first part. So, thank you, thank you for paying attention to the lectures.