Lecture – 47
Stability of the Fluid Phases

Welcome back. Now, I am going to start describing how to connect the access functions access function and partial miscibility to understand the stability of the phase ok.

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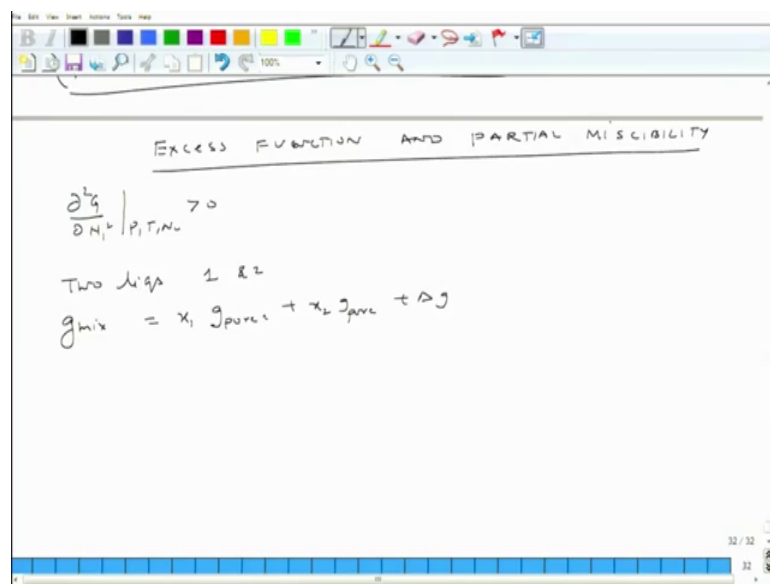
So, the reason we are trying to understand this is because our interest is to understand whether the system is stable or not. Now, for stability if you recall we always talked about the second derivative of the free energies to be greater than 0 ok. So, in other word if you have a make sure then your interest is basically to look at second derivative function and this must be 0 for stable phase ok.

So, let us consider system here where you have a mixture two of two liquids let us say 1 and 2, ok. Now, you can write down this total g of mix as simply the component of contribution from the pure phase plus the change upon mixing, ok.

Now, let me just draw this that this particular function, if you look at here with respect to n this is equivalently you can also look at instead of just del of g you can also look at del of delta g ok. So, del of delta g also is equivalent statement if you were looking at it here.

So, let me just draw an interesting curve here. So, what we interested is something like this. So, this is basically I am plotting del mix g here ok.

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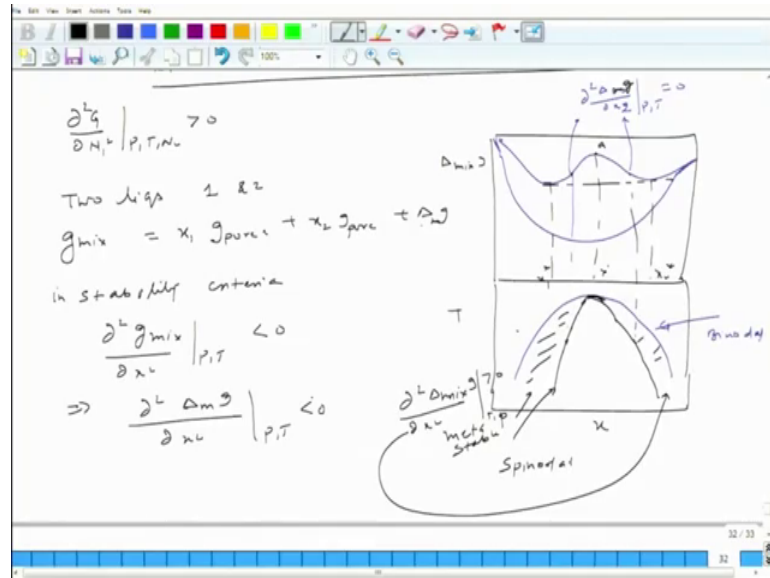
As a function of composition and beneath here we have temperature versus composition right. So, typically when you look at if you recall your simple vapour liquid concept phase diagram then usually this is kind of a curve where this is your binodal curve ok, and we always talk about what would be the typical free energy at this point the second derivative. So, since it is this. So, you would expect that del of any mixture delta g with respect to composition would be also greater than 0 at this case because these are the stable phase ok.

So, correspondingly at T 1 you may have something like this here pretty much stable phase they where is concave up ok. Now, if you increase the temperature you may see something like this, something like this ok. Now, this part here if you look at it this part the second derivative x 2 at this pressure and temperature will be 0 here also it will be 0 right ok. Now, this corresponds to somewhere here where I am going to draw and this corresponds to some point here at this temperature this two points.

So, this is called spinodal ok, where this is the line which corresponds to the second derivative of the guess free energy 0. This range here is our outside is a stable phase and this is actually the meta stable part where the second derivative here at the temperature is

pressure is greater than greater than 0 ok, in both the case, here this is also true this is also true.

Now, looking at here again if you look at it here, this is your point A. So, basically this is, so what is happening? This is concave up which is stable concave down. So, if you have a system concave up it will try to segregate in such a way that it will end up somewhere here, phase separate segregate such that the composition is closer to this part. So, this is your composition initial composition it may segregate in such a way that it becomes x 1 star x 2 star ok. So, and this of course, can be connected by a tangent correspondingly, so this is something which one can prove it also.

So, the instability criteria is dealt second derivative of g mix x square P T less than 0. This also implies that second derivative of delta m part here g by del x square it is less than 0 ok. So, this is something which comes directly from this analysis.

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Now, let us try to introduce an access function. So, let us define g E with respect to the access means with respect to idle solution ok. So, it is going to be g mix ok, minus RT x 1 ln x 1 plus x 2 ln x 2 minus x 1 g pure minus x 2 g pure 2 ok. So, this is the g of x all right. I am going to take second derivative for this plus, so if it is an in unstable then this will happen this condition will meet, is not it. So, if you use this you can show that this condition is equivalent this. So, this is for instability.

Why I have to do that? Why I have to change this thing to g E and again I take the second derivative since this is going to be less than 0, I rearranged, so this is what I get. So, this is why I have to come of this expression because g E can be connected to activity another thing other models and that is a reason. But this depends primarily on the way it is. So, if you change this system to some other thing you may not see this kind of curve you may see this kind of curve also. So, it primarily depends on the molecular nature of the system individual components.

We have introduced the access function in this way with respect to the idle solution and then we got this expression because of course, the second derivative of this with respect to x is going to be less than 0 for instability. So, we write and write in this form and now, I have a expression in terms of g x ok. So, for idle solution what is a g x? 1 to be 0 right because that is with respect to idle solution right the g x is 0 this will be for call x value which essentially say there inequality. So, if this is 0 that means, inequality is never over it for idle solution. You will not see these things because all these are positive ok.

So that means, the idle solution is always stable and cannot exhibit any phase phase separation or splitting right always stable ok. Now, let us try to understand a bit more by considering a model ok. So, let us consider the one constant Margules model where the model is a is equal to A x 1, A x 2, right. So, the question is what would be the variable A for which this stable phase exists or in other word what would be the variable A for which the phase or the system will be unstable. So, we can plug in here we can take the second derivative right T P, this is going to be. So, I can write this in terms of x 1, A x 1 1 minus x 1. So, this is going to be minus of 2 A, ok.

Now, 2 minus 2 A plus RT this term should be greater less than 0 then this will give us a condition of A.

So, I can write this or minus 2 A plus RT 1 by x 1 plus by x 2 ok, less than 0 or 2 A greater than RT by x 1 x 2. So, if you plot this RT by x 1 x 2 as a function of x it will look like this where this is nothing, but minimum value is going to be 4 RT ok.

So, what is the smallest value we satisfy the above inequality? Value of A which satisfies the above inequality it is going to be 2 RT right and the corresponding composition would be right this is the critical composition right. So, you are saying that A should be may be satisfy the inequality it should be this is point greater than 2 RT right ok.

So, this is a very simple exercise which you have done. Of course, you can actually use some other models also and come up with the parameters which for the for which stable or unstable phase occurs ok.

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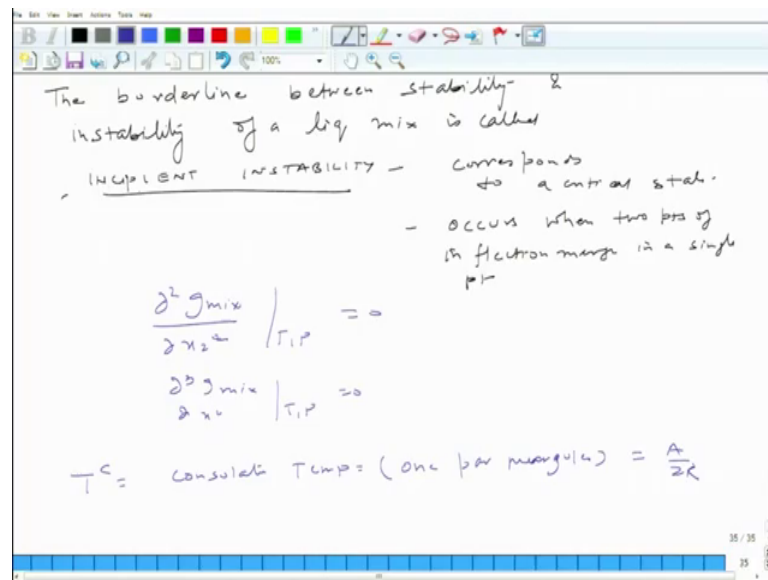
So, essentially what it tells this A characterize the stable and unstable phase. So, there is a border line between this stability and instability, and this border line is called sometimes incipient instability ok. So, it is like more or less it also gives you the idea of the critical state at which this things will serve will not be stable or something like that.

So, it is basically also suggests that it corresponds to a critical state ok, this is the border line right. It also one can find out by looking at the second and third order. So, basically it occurs when two points of inflection merge into single point ok. Well, this may look very complicated statement here, but in a simple way this is characterized by looking at simply the second order should be 0 or third order to be 0 that is what it looks like this.

Now, in this case the consulate temperature is another statement which another variables which we would like to emphasize. Now, for example, T c which is we call it consulate temperature for the one parameter Margules equation is given by A by 2 R. So, recall that this was the minimum value of A. So, the T which corresponds to such a thing would be the critical temperature which we call in this kind of system as consulate temperature ok.

So, now, I will try to use this one parameter Margules equation to describe different kind of phase diagram which we obtained for different conditions ok. So, I am going to describe different ways the A could be for different system.
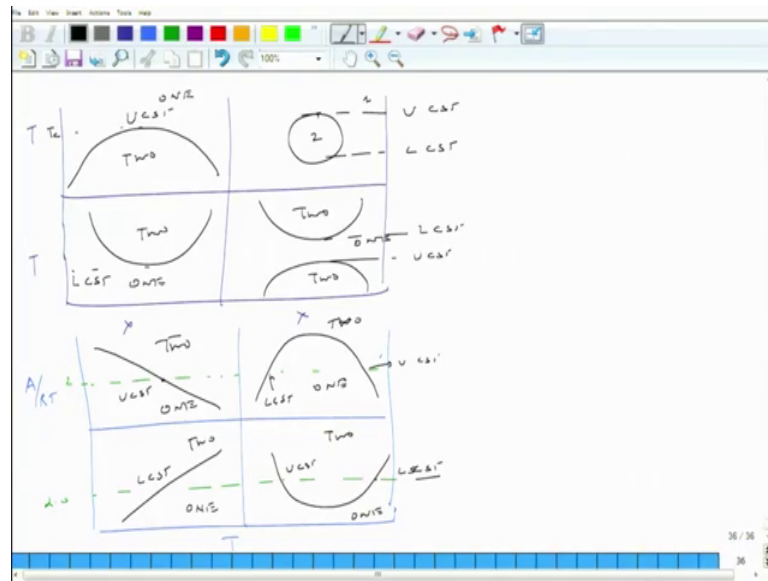
So, let me first draw temperature versus composition and what we have here is something like this, this, this ok. So, in this case this is a two phase, this is a one phase, this is nothing but T c and this is called upper critical solution temperature UCST ok. This is again two phase this is one phase all right.

So, here this is your UCST and this is your LCST ok. Here is two phase this is one phase, this is call LCST ok. This is two phase, this is two phase, this is one phase and this is the little bit interesting because this is called LCST and this is called UCST. The curvature top the way it is their concave down would be UCST.

The corresponding a values which allows this kind of this phase diagram let me draw that for now. So, it is going to be T and we are talking about A by RT ok. In a A by RT is two when you are talking about the conditions are the minimum value for the instability ok. So, let me draw here this is the two value ok. So, this is your value.

So, this is the temperature which is not corresponding to UCST this two, this is one ok, this is the one we have, the other one is going to be like this and this is another one ok. So, this one would be your LCST, this one is your UCST. Again this is this is two phase up, this is one phase ok, this is two phase, this is one phase.

So, this is corresponding to LCST, this is UCST, and this is UCST and this is your LCST. So, it is not always that LCST has to be lower than the UCST because I think this the

way it is done is basically the way the curvatures, but anyway the point was basically that this A, the nature of the A with respect to temperature governs the way the phase diagrams are and this is something were very simple system tells you this such a complicated phase diagram all right.

So, I hope that you got an idea of the way we calculate the instability and how we can relate g access ok; a different models can be used to identify the conditions for which this phase diagram or phase separation occurs.

So, with this I will stop and the next lecture I am going to start theory of solutions.

So, see you in the next lecture.