Thermodynamics of Fluid Phase Equilibria
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Lecture – 17
Stability Criteria

Now, we are going to talk about stability criteria.

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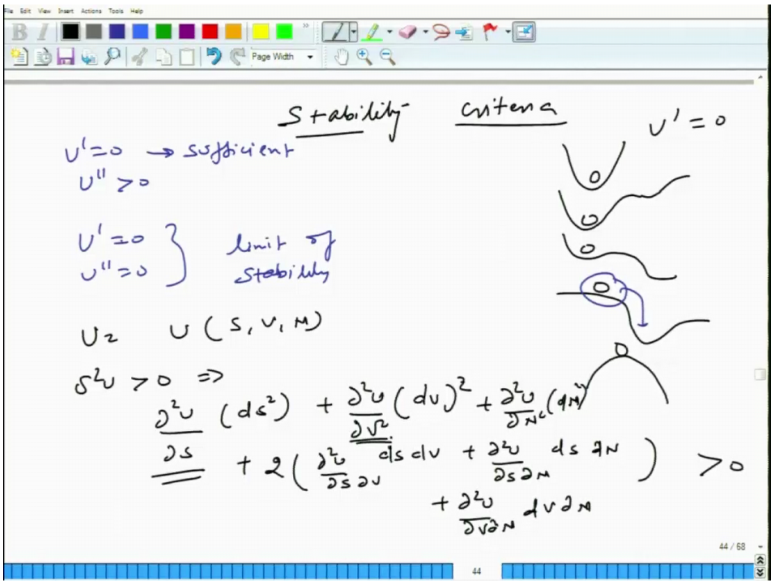

Stability criteria

$U' = 0 \rightarrow$ sufficient

$U'' > 0$

$\left.\begin{array}{l} U' = 0 \\ U'' = 0 \end{array}\right\}$ limit of stability

$U = U(S, V, N)$

$$\delta^2 U > 0 \Rightarrow \frac{\partial^2 U}{\partial S}(dS^2) + \frac{\partial^2 U}{\partial V^2}(dV)^2 + \frac{\partial^2 U}{\partial N^2}(dN^2) + 2\left(\frac{\partial^2 U}{\partial S \partial V} dS\, dV + \frac{\partial^2 U}{\partial S \partial N} dS\, dN + \frac{\partial^2 U}{\partial V \partial N} dV\, dN\right) > 0$$

$U' = 0$

And we all are aware of stability from mechanical perspective. So, for example, for an equilibrium system, a ball would be stable in such a scenario, this is let us say a function represented by energy a variable ok. Then you could have other scenario something like this, something like this, something like this, ok, something like this, ok. Now of course, we know that if this is a energy profile then of course in this case U, the first derivative of U is going to be 0, ok. This is not a sufficient condition and then you need to come up with another one. So, U equal to 0 and U double derivative should be equal to 0 in order to have a minimum ok. So, this is not sufficient.

So, in this case particularly you know this is going to be if you partible slightly is going to move to this direction ok. So, this becomes a limit of stability beyond this is unstable, ok. If you change the little bit curvature is going to be unstable. So, these are limit up till where it can reach or there is a limit which is defined by nothing but in this case also is defined by the second derivative of U to be 0, where you can say this is the region of beyond which there is a region of unstable or instability will arise in the system ok.

So, the limit is given by basically these 2 conditions. So, this is the limit of stability. Again, if you look at these variables this one first derivative is 0 and as well as the second derivative is greater than 0. In this case also, the first derivative is 0 and second derivative is also 0. So, this brings up conditions there beyond this of course, is going to be unstable and this is what we are going to use it.

So, let me just consider a simple example we will just take it U first that U is a function of S V N and what we are interested is basically for the case of a stability we need the second derivative has to be greater than 0 into the word you need this condition all right. Now, since this is a function of S V, I can write this as sum of various different second order derivatives plus 2 times the mixed derivatives just for the completion, I am going to write it some of you already know this, but it is just to make sure that we are on the same point.

Now, what we are interested is that this expression of course, is greater than 0 and if one of the variable is or let us say keeping the 2 variables fixed if one of the variable is positive of here changing one of the variable keeping the other fixed. For example, if you are changing S keeping V and N fixed, then this means that this this second derivative will be greater than 0, ok. Similarly, if we are keeping S and N fixed this means this has to be greater than 0 ok. So, using these concepts you can come up with this expression.

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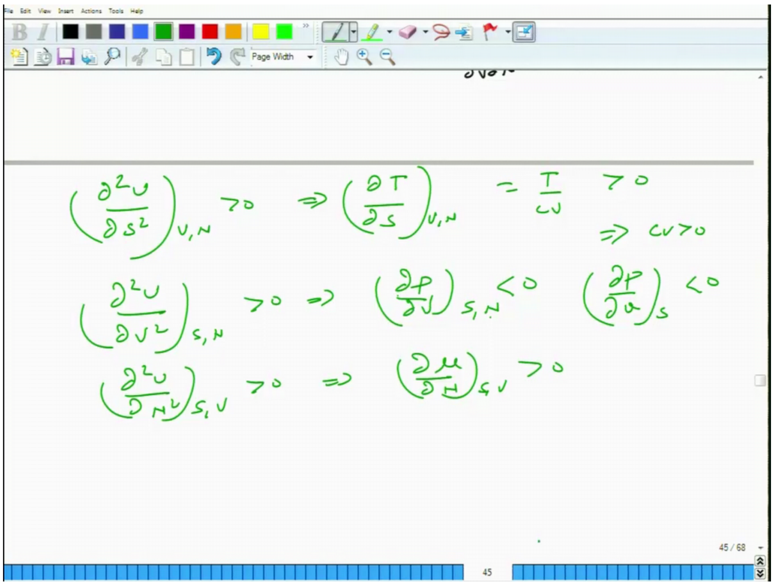

$$\left(\frac{\partial^2 U}{\partial S^2}\right)_{V,N} > 0 \Rightarrow \left(\frac{\partial T}{\partial S}\right)_{V,N} = \frac{T}{C_V} > 0$$

$$\Rightarrow C_V > 0$$

$$\left(\frac{\partial^2 U}{\partial V^2}\right)_{S,N} > 0 \Rightarrow \left(\frac{\partial P}{\partial V}\right)_{S,N} < 0 \quad \left(\frac{\partial P}{\partial v}\right)_{S} < 0$$

$$\left(\frac{\partial^2 U}{\partial N^2}\right)_{S,V} > 0 \Rightarrow \left(\frac{\partial \mu}{\partial N}\right)_{S,V} > 0$$

This is nothing but del T by del S because del U by del S is nothing but T and this is nothing but T by CV and this has to be greater than 0 which means because T by definition has to be greater than 0 which means CV is greater than 0, ok. Similarly you can show del U by del V is minus of del P by del V that missense has reversed. So, this is this shows that the pressure if you change the increase the volume the pressure will decrease ok.

You can also write this expression as del P by molar volume ok, we are taking the N inside which means basically everything is in the molar quantity the other thing is chemical potential, this has to be greater than 0. So, if we increase the amount of moles present in the system, the chemical potential should also increase that is what it tells that is a condition of stability if the chemical potential decreases which means is basically unstable that is what it tells you that ok.

So, it gives you the behaviour. So, if somebody is asked you what will be the condition of stability for the pressure if you the volume is increasing automatically, it means something that the pressure or decrease or the way if the volume is compressing decreasing which means the pressure is also increasing is. So, there is intuition for you and then there is a thermodynamic relation which also tells you the same thing, right.

I can actually extend this exercise for other cases or. So, I am not going to derive anything.

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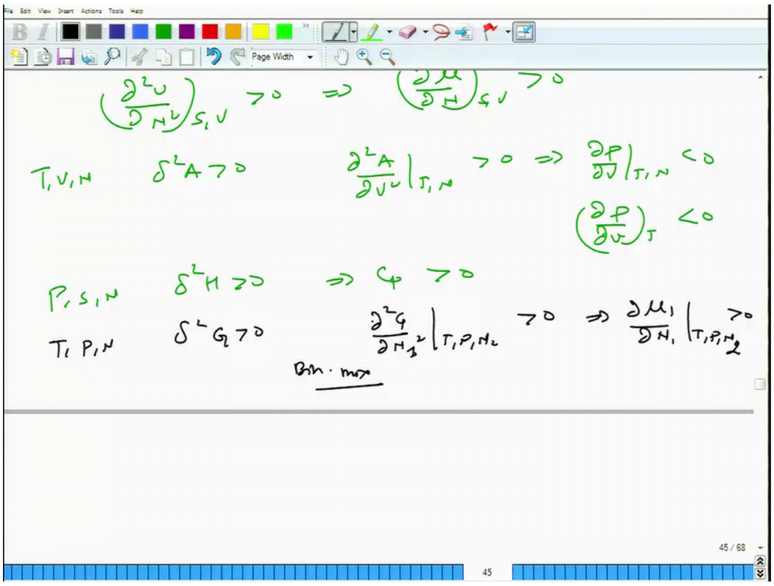

$$\left(\frac{\partial^2 U}{\partial N^2}\right)_{S,V} > 0 \Rightarrow \left(\frac{\partial \mu}{\partial N}\right)_{S,V} > 0$$

$$T,V,N \qquad \delta^2 A > 0 \qquad \left.\frac{\partial^2 A}{\partial V^2}\right|_{T,N} > 0 \Rightarrow \left.\frac{\partial P}{\partial V}\right|_{T,N} < 0$$

$$\left(\frac{\partial P}{\partial V}\right)_T < 0$$

$$P,S,N \qquad \delta^2 H > 0 \Rightarrow C_p > 0$$

$$T,P,N \qquad \delta^2 G > 0 \qquad \left.\frac{\partial^2 G}{\partial N_1^2}\right|_{T,P,N_2} > 0 \Rightarrow \left.\frac{\partial \mu_1}{\partial N_1}\right|_{T,P,N_2} > 0$$

Bin. mix

For the case of T V N ok, del of square a must be greater than 0 for stability which means del square for the case of let us say, I am keeping temp T and unfixed it means del P by del V T N should be less than 0, it gives you the same expression it gives you the del P by del V at T is greater than 0, exactly, the same expression; what you have got another way for the case of P S N or S P N, you can show that this will lead to the expression Cp greater than 0 for the case of T P, you will get del square g del then for the case of let us say binary mixture this must be greater than 0 which means basically tells you that 2 greater than 0 ok. So, this is let us say for the binary mixture ok.

So, these are the analysis you can do in order to find out the variables for the for the stability and this is extremely useful for calculating the phase equilibria for mixtures, you will be using this information to find out which region is basically stable region in which region is unstable region. Now, I will try to ask a question here with an example that; now that you have got this expression depending on what variables you have kept you got phase different expressions all right. So, there has to be some equivalence of the expressions irrespective of whatever the variables you fix some expression should be same. So, this we can illustrate in by an example..

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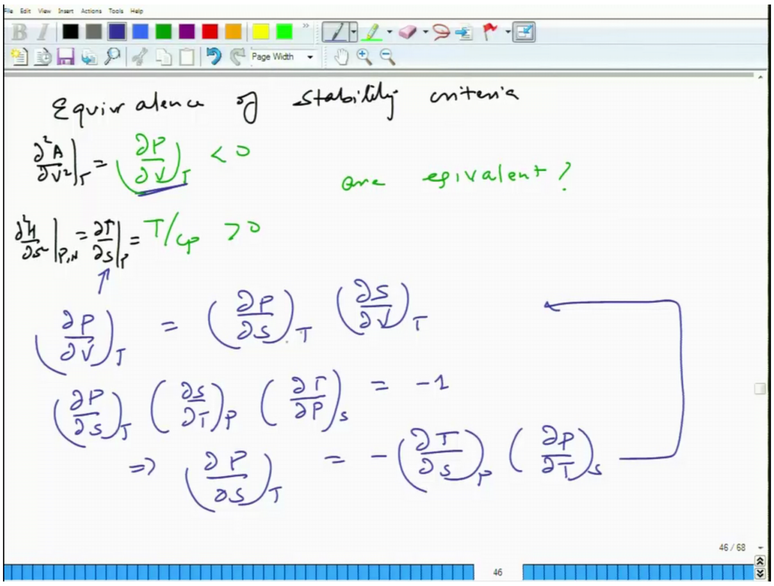

Equivalence of stability criteria

$$\left.\frac{\partial^2 A}{\partial V^2}\right|_T = \left(\frac{\partial P}{\partial V}\right)_T < 0$$

are equivalent ?

$$\left.\frac{\partial^2 H}{\partial S^2}\right|_{P,N} = \left.\frac{\partial T}{\partial S}\right|_P = T/c_p > 0$$

$$\left(\frac{\partial P}{\partial V}\right)_T = \left(\frac{\partial P}{\partial S}\right)_T \left(\frac{\partial S}{\partial V}\right)_T$$

$$\left(\frac{\partial P}{\partial S}\right)_T \left(\frac{\partial S}{\partial T}\right)_P \left(\frac{\partial T}{\partial P}\right)_S = -1$$

$$\Rightarrow \left(\frac{\partial P}{\partial S}\right)_T = -\left(\frac{\partial T}{\partial S}\right)_P \left(\frac{\partial P}{\partial T}\right)_S$$

So, the question is how to demonstrate equivalence of stability criteria and what we interested is to show that there is this expression and this expression are equivalent ok.

So, if one of them is 0 the other one should be 0; something like that. So, this is to show this these 2 equivalent saying this is equivalent to saying this the other one. So, we will try to solve this and again we have to go back to the basic definition. So, this is nothing but del square H by del S square because this is del T by del S at constant p.

So, I will just consider for the pure system and which is del del square H by del S square at constant PM and this is nothing but del square a by del V square constant e ok. So, what we had try to do here is we try to make use of the fact that there is a inter entropy which is coming here in this expression and. So, we can try to introduce entropy in and relate this expression to the entropy changes in the entropy so; that means, interest introducing a new variable which we can you do that using chain rules.

So, del P by del V at constant T can be written as del P by del S at constant T and del S by del V at constant T now we have this P S T, you have three variables. So, now, we can use x y z minus 1 row ok. So, we have del P by del S T del S by del T P del T by del P. So, this must be P S S T T P this must be;

Student: Minus 1.

Minus 1, ok, this must be minus 1. So, now, from here I get del P by del S at constant T ok. So, with this I plug in here this expression can be now replaced by this..

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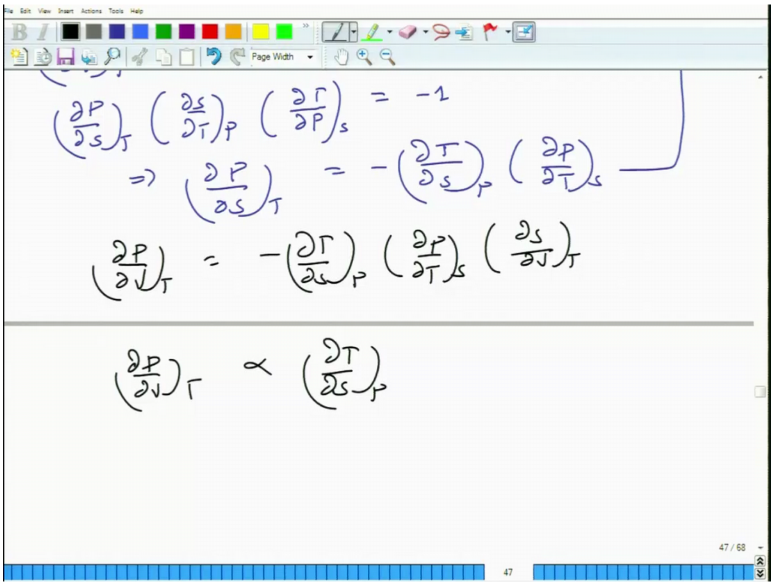

$$\left(\frac{\partial P}{\partial S}\right)_T \left(\frac{\partial S}{\partial T}\right)_P \left(\frac{\partial T}{\partial P}\right)_S = -1$$

$$\Rightarrow \left(\frac{\partial P}{\partial S}\right)_T = -\left(\frac{\partial T}{\partial S}\right)_P \left(\frac{\partial P}{\partial T}\right)_S$$

$$\left(\frac{\partial P}{\partial V}\right)_T = -\left(\frac{\partial T}{\partial S}\right)_P \left(\frac{\partial P}{\partial T}\right)_S \left(\frac{\partial S}{\partial V}\right)_T$$

$$\left(\frac{\partial P}{\partial V}\right)_T \propto \left(\frac{\partial T}{\partial S}\right)_P$$

So, I get del P by del V at constant T is minus del T by del S at constant P del P by del T at constant S and del S by del V T ok. So, I have this expression, now this is what we actually wanted to get because you see this was this expression and this part was del T by del S at constant P. So, we got an expression which tells you this left hand side is proportional to T by Cp ok.

So, this is what our intention was to get del P by del V T is proportional to del T by del S p ok. So, this means that this condition of stability criteria or the stability criteria is basically equivalent if one is 0 basically the other would be also 0 now this is this this criteria are quite important also. So, I will just make use of this criterias for understanding the criticality also and then will stop this lecture.

So, let us take a case of vapour liquid 2 phase system or vapour liquid phase diagram on a P V diagram ok.

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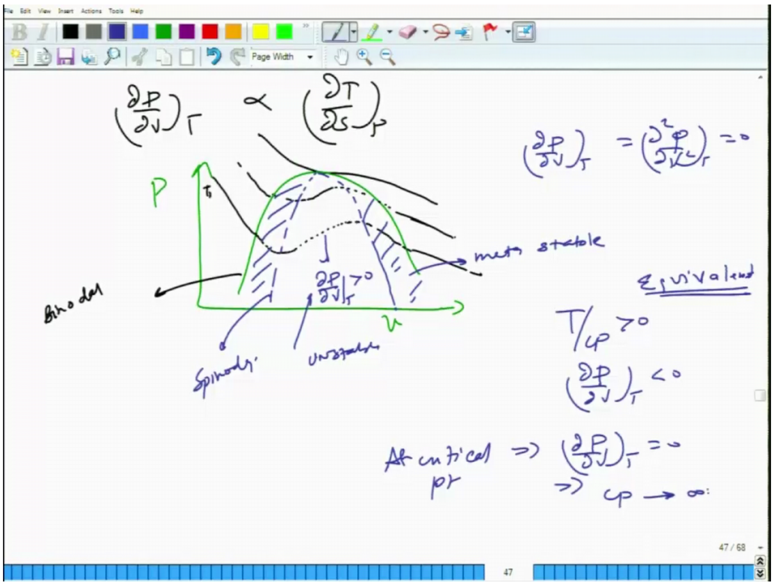

$$\left(\frac{\partial P}{\partial V}\right)_T \propto \left(\frac{\partial T}{\partial S}\right)_P$$

$$\left(\frac{\partial P}{\partial V}\right)_T = \left(\frac{\partial^2 P}{\partial V^2}\right)_T = 0$$

$$\left.\frac{\partial P}{\partial V}\right|_T > 0$$

Equivalent

$$T/C_P > 0$$

$$\left(\frac{\partial P}{\partial V}\right)_T < 0$$

At critical pt $\Rightarrow \left(\frac{\partial P}{\partial V}\right)_T = 0$

$\Rightarrow C_P \to \infty$

So, this is our binodal or this is the basically the saturation vapour and liquid lines ok, I can draw the isotherms ok. So, this can actually go here and it may not directly reach to the other part because it could depending on the rate at which you are controlling the experiment it can actually go into this regions. So, what we see is the following something like this is one temperature and similarly this is it not the temperature and so forth, you will get this which is a critical point.

So this is sometimes called binodal these lines this green curve is called binodal Thai lands can be drawn on this and then there is something called spinodal. Spinodal actually is the one where you are getting this point where this is this part is reaching minimum ok; that means, I mean this is the region where this is maximum ok. So, this is your spinodal. So, what you see from this part to this part is there is a slope is positive at constant T when slope is positive; what it means from our condition criteria the del P by del V should be less than 0 which means this is the region where it is unstable.

Student: Unstable.

So, what we did is the case where this is 0. This point del P by del V is 0 here as well as well as here because there is the minimum it is the maximum. So, we are trying to connect these dots and then you connect we got this blue curve and this becomes the limit of stability and this region is your metastable region and this region is unstable region and this is a critical point at critical point we know the first derivative and second derivative has to be 0 right. So, del P by del V at T is equal to del square p by T all right now we also know that these 2 terms which we just derived that T by Cp should be greater than 0 for stability and as well as del P by del V should be less than 0..

So, this must be an equivalent stability criteria ok, but at the critical point what happens this is 0 which essentially means at critical point since these are equivalent criteria at critical point if this is 0 implies Cp should go to infinity right Cp should be infinity ok. So, if you measure Cp as a function of temperature or function of this that at critical point you should see it should increase to very large values right now what happens to also in at near critical point that fluctuations ok. The density fluctuates any thermodynamic properties fluctuates which are not controlled for a temperature volume an N fixed other thermodynamic variables should fluctuate.

So, at critical point the density fluctuations are quite high when you keep the temperature below let us say a critical point the fluctuations are smaller or equivalent to its molecular diameter and that is why for a 2 phase system, you could you see very clearly in the separation between 2 phase, but now when you take the temperature to the critical point what happens the fluctuations are more much more than the molecular size.

So, they fluctuate. So, much that at critical point they overlap the one phase is fluctuating. So, when the overlap the distinct boundary is lost and that is where this milky appearance comes into this if you do the experiment you can easily find out the phase separation by looking at just an image of it below critical point, but at critical point you will not be able to find any specific phase separation. So, the reason why we went through is we wanted to understand the stability criteria and its usage in in various different application there is a equivalence of criteria and thus this leads to certain conditions which we can make use of to find out whether the system is stable though I have explained it in terms of only the pure system, but of course, you can extend that to also mixtures..

So, we will stop here and I will continue in the next lecture we will describe a bit of equilibrium conditions that gives you a phase reverse of forth ok. So, I will see you in the next lecture.