

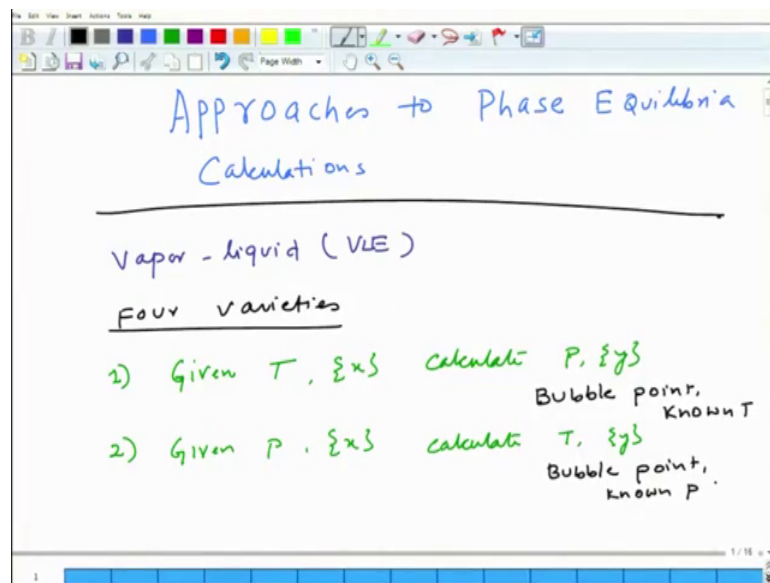
Thermodynamics of Fluid Phase Equilibria
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Lecture - 29
Approaches to Phase Equilibria Calculations

Welcome back. In this lecture we will continue the phase equilibria from thermodynamic volumetric data; that means, thermodynamic property from volumetric data, but in particular today we will look into the approaches to phase equilibria calculations we consider a very simple case ok.

So, to illustrate it we consider simple vapor liquid, that is VLE vapor liquid equilibria.

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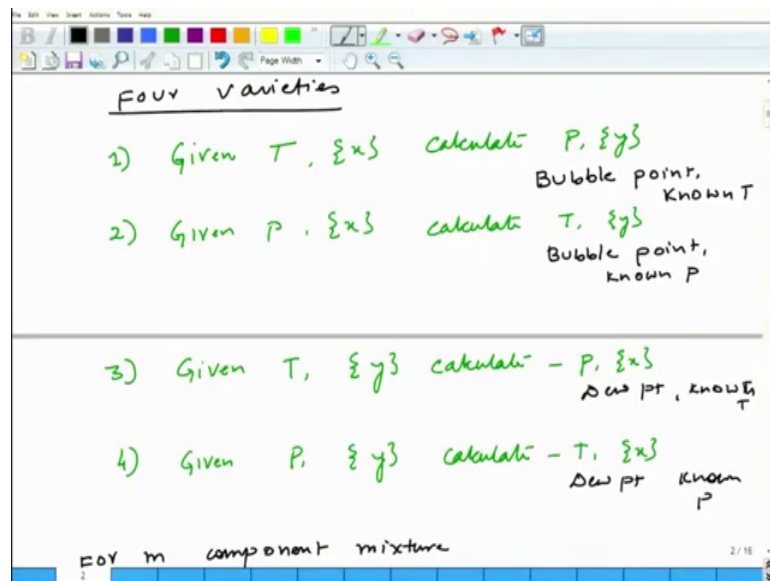
Now, there could be many possibilities in order to simplify it we will consider 4 cases. So, let me just write down the 4 cases. Usually it comes in these 4 variables of 4 different varieties ok. So, there could be 4 different varieties of phase equilibria kind of calculations. So, what it depends on? It depends on what kind of data which we have ok. Sometimes you may have only the liquid compositions, sometimes you may have only the vapor compositions, sometimes you have temperature, but not pressure information sometimes pressure, but not temperature information and so forth.

So, let me just write down and, so one first could be let us say given temperature and liquid composition calculate pressure and vapor composition. What kind of a point it is like? Calculation is called what? Bubble point, because the bubble of vapor. So, you are basically calculating the composition which means when is vapor forms, right.

So, these kinds of calculations are called bubble point for known T temperature is known right, ok. Now, let us continue for another case where given pressure and liquid composition calculate temperature and composition. So, this is again bubble point, but known P, alright. So, these are the two possibilities.

The other possibilities when the composition of the vapor phase; are given and you have been asked to calculate the composition of the liquid phase in such case that would be dew point.

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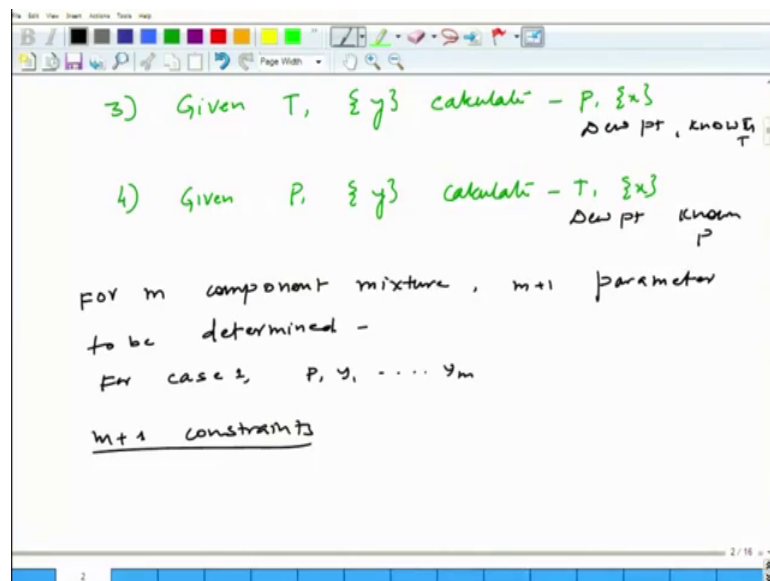
Because when the first drop of liquid forms ok, but depending on what conditions available it could be known temperature or known pressure. So, I am going to just write down that calculate P T x. So, this is dew point known T and this is dew point known pressure ok. So, these are the simple mechanism. Now, the question is how do calculate when you have any one of this situation ok. So, you know the number of variables you know the constraints. So, let us now, write down and see how we can approach or develop this methodology to solve such a problem.

So, considering that it is a mixture ok, still we say vapor liquid system, but it is a mixture and. So, for m component mixture for m component mixture how many parameters we have to find? We have m component mixture. How many parameters we need to evaluate for any of this? Unknowns are.

Student: M.

M minus 2 so, but the temperature so; unknowns are pressure and the composition, right. So, in general you have to evaluate m plus 1 parameter ok. Some may be dependent because y's are m and P is 1. So, m plus 1 parameter need to be evaluated which are nothing but P let us say in one of the case, for the case of 1 for case 1 we have P y 1 y m ok. So, these are the number of variables.

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So, let me just write down the number of constraints also in this. So, what are the number of constraints? We say that m is basically the number degree of freedom that is what we are saying it, right. So, let me also put it. So, so here m plus 1 constraints are there. Why is that? See remember how we have evaluated or determined the Gibbs phase rule we made use of equilibrium condition.

Now, in this case the number of constraints are basically the equality, temperatures are going to be constant. We do not have to bother about temperature pressure, we do not have to bother about it we can simply use chemical potential or the fugacity.

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For m component mixture, $m+1$ parameter
to be determined -
For case 2, P, y_1, \dots, y_m
 $m+1$ constraints $f_i^L(T, P, x_i) = f_i^V(T, P, y_i)$
 $\sum y_i = 1$ $i=1 \dots m$ - (2) - (1)

For dew point calculations
 $(m+1)$ st constraint $\sum x_i = 1$

2

So, let me write down there m components; that means, the m equations for fugacity. So, if the temperature, pressure and composition this would be f_i^L vapor again temperature, pressure and where i is equal to 1 to m . So, there are m equations for each of them in addition since y 's are connected where y_i is equal to 1. So, these are how many constant $m+1$ constraints ok. Now, similarly for dew point calculations so, this way is for bubble point calculation for dew point calculation that was case 3 and 4 the m plus or $m+1$ constraint is summation x_i is equal to 1 right ok.

Now, this equation let me write down the equation since so that I can make use of it later. So, this equation let say is 1, this is 2.

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$(m+1)$ st constraint $\sum x_i = 1$
 applicable when f is known as a function of $T, P, z/y$
 when f is known as a function of T, v, z comp
 $f_i^L = f_i(T, v^L, x_i) = f_i(T, v^V, y_i)$
 $P(T, v^L, x_i) = P(T, v^V, y_i)$
 $P_0 - P_f \rightarrow \gamma$

So, question 1 and 2 if you look at it together basically equation one these are applicable when the fugacity is known as a function of temperature and pressure is not it and composition, f is known as a function of T, P and x or composition x or y ok.

When we have also seen that the fugacity can be also related in terms of the molar volume. So, when the information is available not in terms of just pressure, but in terms of let us say molar volume, then we can write the same expression as f_i^L is equal to $f_i(T, v^L, x_i)$ is equal to $f_i(T, v^V, y_i)$ this is for i is equal to 1 to m ok. So, this is useful when f is known as T, V and composition then this is more convenient to write it, in such case when you write it we also write the pressure also because pressure in the both the phases particularly in the pressure along this scalar version of it is temperature V, L, x should be same as ok. So, remember pressure is basically tensile component in a variable.

So, the trace of it or the diagonal average value of the diagonal version is basically going to be a hydrostatic pressure all that is the pressure which is felt by the single phase, but at the interface only the normal component of the interface would be particularly based on the force balance. But overall the pressure felt by the vapor should be same as this. So, this is a condition assuming that of course, there is no gravity effect. So, this is something which we consider.

Student: (Refer Time: 10:42).

See, we what we say is the falling because this the pressure which talking about is basically the scalar version of it. So, mechanically the pressure only at the interface will be fixed ok. But the same pressure this is the same pressure here in the in the in the your face here would be same in the rest of the component ok. The normal pressure would be same as a within the face in other word if this question is very interesting. So, if you look at two phases here you have alpha and beta. So, this component is going to be same right and this component transition pressure will be little different you know varying in order to have interfacial tension. But we are talking about this pressure here only that this would be the one.

But the reason is that this pressure when you go away from the interface across here all this pressure will be same is not it, so that means, if I plot a pressure profile the normal pressure will be like this across the interface if I plot it pressure as a function of distance and if you are taking a distance like this the normal pressure will be this for all of it ok. Whereas, the tangential pressure the one which is the other component of the pressure will be something like this there will be deviation has to be mirror image, something like this ok.

So, this is the region which will be this is the region which basically is the interfacial region right because of this changes in the normal pressure and tangential pressure, the surface tension, gets out of it in the sense there is a this contributes to the surface tension rise, but otherwise in the bulk region; that means, somewhere here. So, this is let us say interfacial region then this bulk region the normal pressure and tangential pressure the same in these conditions this holds this pressure will be ok. So, since view address that question. Now, let me also consider the other thing. So, pressure will be written as this.

Now, depending on whether is a bubble point calculation or dew point calculation you are going to write it like this, this is going to be bubble point. You are calculating the bubble point which essentially means you do not know the vapor phase composition ok.

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$\Sigma \gamma_i = 1$ (bubble pt)
 $\Sigma x_i = 1$ (dew pt)

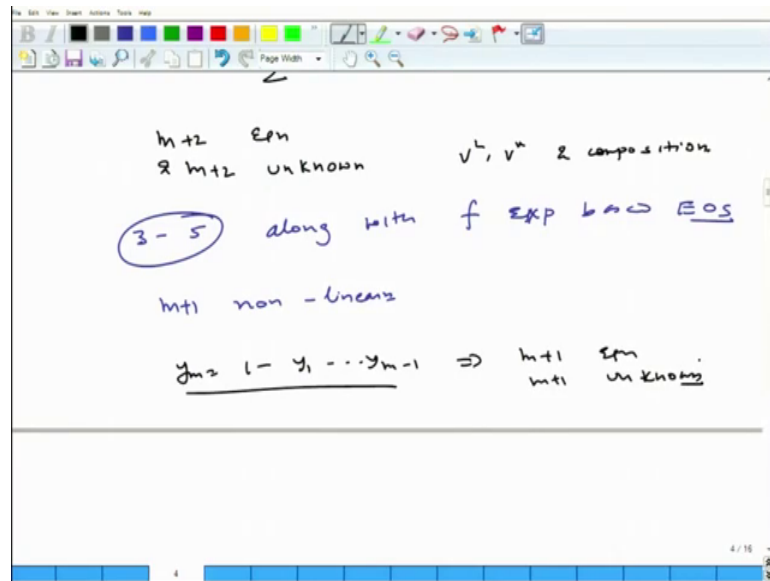
E7 2 22 applicable known as fu of T, P, Σy
 when f is known as T, v, & comp
 $f_i^L = f_i(T, v^L, x_i) = f_i(T, v^V, y_i)$
 $P(T, v^L, \Sigma x) = P(T, v^V, \Sigma y)$

Diagrams showing pressure (P) vs volume (v) for bubble and dew point calculations. The bubble point diagram shows a horizontal line at pressure P_b intersecting the bubble point curve. The dew point diagram shows a horizontal line at pressure P_d intersecting the dew point curve. A green arrow labeled $P_b - P_d \rightarrow \gamma$ indicates the pressure difference.

Similarly, this is dew point ok. So, in this case if you notice you have a fugacity for known values of T and V and composition, but the number of variables have increased for such a case if you write this the number of variables r is it N plus 1 or is it more its m plus 2 because you have volume also we need to find out.

You do not know the volume, you do not know the pressure and of course, the compositions of the relevant phase where there is a bubble point or dew point calculation. So, the number of variables are now, m plus two and number of constraint has also increased because we have added this one the additional term of pressure; that means, number of constraint is also m plus 2. So, you can solve this such a problem, ok.

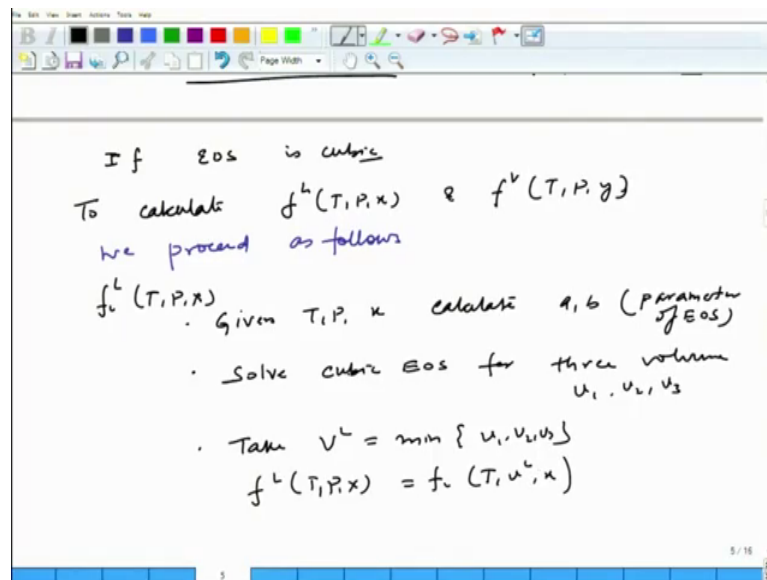
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So, this would be a V I V b and composition ok. Now, this is you let me write down the equation numbers. So, this is that say 3, 4 and this is 5. So, now, if you use this 3 to 5 equation along with along with fugacity expressions based on earlier which we have discussed equation of state that that was discussed last you know like the last lecture, then you can try to solve this expressions ok.

So, this will give us m plus 1 non-linear equation and one linear equation ok. You can drop this also, you can drop you can you make use of this and write represent let us say for the case of summation y_i equal to 1 you can write simply y_m is equal to 1 minus y_1, y_2, \dots, y_{m-1} . So, with this expression if you plug in there you get m plus 1 equation with m plus 1 unknowns ok. But these are all non-linear equation.

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So, assuming that the equation of state which we are trying to use is basically cubic, if equation of state is cubic then we actually can write this expression which we have written here in terms of the earlier expression this is ok. So, how we can do that? Let me just write down this because at the end what we are trying to do is we are trying to calculate fugacity as a function of temperature, pressure, and composition.

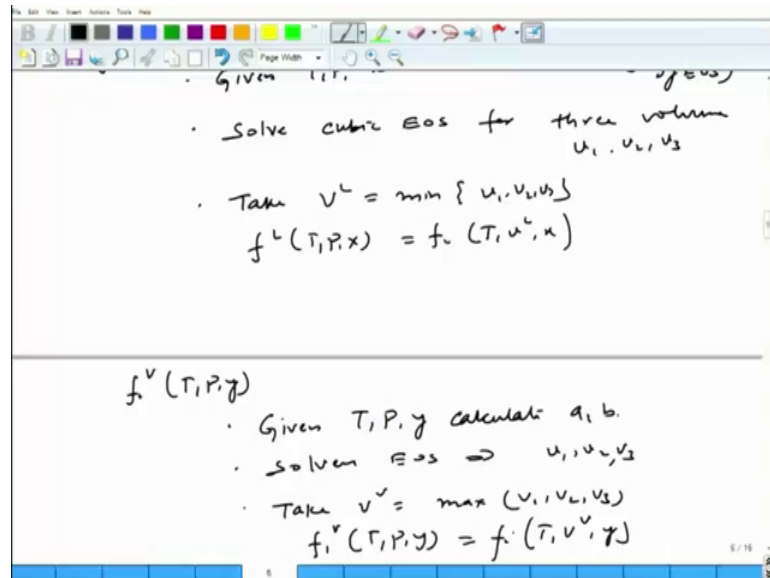
So, given the data available is basically on the volumetric form and the molar volumes have fugacity dependence on molar volume is known which if not in from the experiment we can make use of equation of state. And then you can try to use it to solve it in order to obtain the fugacity in terms of temperature and pressure and composition.

So, how do we do that? To calculate f and f^V , temperature, pressure, v we proceed as follows ok. For case of liquid T, P, x since we have to evaluate this we I am going to write down the algorithm a simple algorithm how we are going to do that. Given T, P, x calculate the equation of state variables which is usually a and b , if it is a cubic equation these are parameters of equation of state then solve cubic equation of state for 3 volumes right, you are going to get 3 volumes and you have to find out let us say let me just write down V_1, V_2, V_3 .

Now, for the case of liquid you take V^L as the minimum value of this right. So, in such case you can write $f^L(T, P, x)$ is equal to $f_i(T, V^L, x)$ ok. So, what we have done is basically we made use of an equation of state could be van der Waals equation of state could be

other equation of state. So, all these are cubic equation state solve it you obtain 3 values of V 's take the molar volume of liquid which corresponds to the minimum value of it ok. So, that is to get $f^L(T, P, x)$.

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Now, what about $f^V(T, P, y)$? So, this is again we can think of that we can write down the algorithm given T, P, y calculate again a, b that is parameter for a question of state solve equation of state leading to 3 values then.

Student: (Refer Time: 20:13).

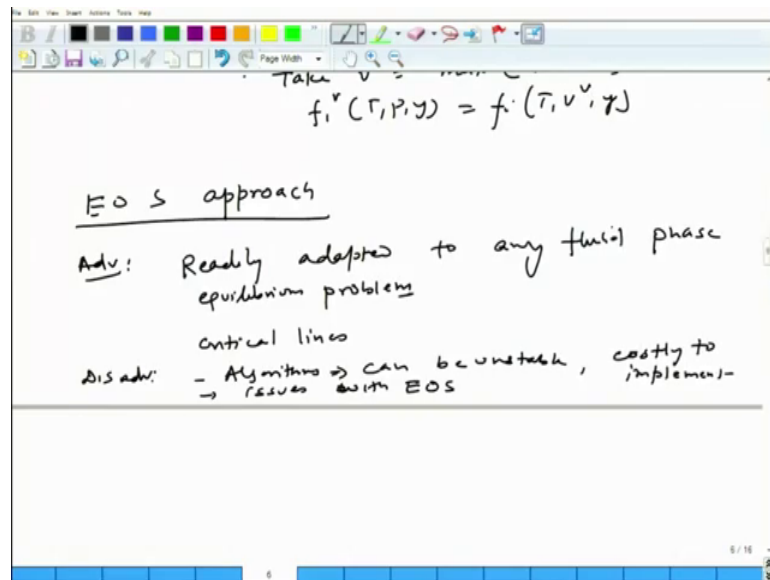
You write; we are going to take the molar volume of vapor has maximum value among these 3 and thus we get $f^V(T, P, y)$ has f^L ok.

Student: Sir, why are you taking minimum (Refer Time: 20:40) maximum (Refer Time: 20:40).

It is a good question, because of since for the vapor liquid equilibrium you have a vapor which is going to be a max having the molar volume much more than the liquid and since you are using the equation of state for a given temperature and pressure you are going to get different values. So, the least value stable values positive value will be for corresponding to the liquid and then maximum largest positive value would be correspond to the vapour. This comes directly from the equation of state the way the equation state diagrams are.

So, we are making use of that and understanding from that point of view that this would be separated largely by much bigger differences, and since there is only one possible value. So, you will see that the roots are going to be having some some imaginary values also you have to ignore that you have to take onto the real values.

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So, let me just make a concluding remark as far as equation state approach is concerned. So, this is equation of state approach ok. Now, the advantage is that you can readily adapt or make use of any of you can use this approach for any fluid having an equation of state. So that means, readily adapted to any fluid phase equilibria phase equilibrium problem. So, this is one of the advantage you can find out even the critical lines for the mixture using this approach. What are the problems related to equation of state? Because of the non-linearity of this set of equations the way you solve could lead to unstable situations also ok. So, numerical lead become unstable. So, there is finding such a solution in making use of equation of state could be problem.

In addition since the equation states are you know may for many systems are not well developed then it is it as a limitations with respect to the quality of equation of state which are using for a given system thus it limits the way or the use of it.

So, this is the disadvantage. So, the algorithms can be unstable right and may be costly to implement. So, algorithms can lead to instability costly to implement which means it may time you take time to finish the job right and we have a problem of equation of state

ok, issues with equation of state ok. So, this is not the best approach to solve the vapor liquid equilibria for mixtures there are other methodology such as phi gamma approach which I am going to take in the next lecture, ok.

So, see you in the next lecture.