Advanced Thermodynamics
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Lecture -28
Vapour - Liquid - Liquid Equilibrium

Welcome to the MOOCs course, Advanced Thermodynamics. The title of this lecture is vapour-liquid-liquid equilibrium. Till now what we have seen? We have seen a vapour phase a liquid phase being in equilibrium they are co-existing, and they are in equilibrium. So then how to find out their equilibrium composition. That is what we have seen and then also we have seen a case where two partially miscible liquid systems or liquid phases are co-existing and they are at equilibrium.

So then, how to find out the equilibrium composition of those liquid-liquid equilibrium systems? Those things we have seen but now in this particular lecture what we are going to discuss is that, is it possible that the vapour phase and two partially miscible liquid phases are co-existing. So that VLE, LLE both of them are there in addition to that VLLE is also there that is vapour-liquid-liquid equilibrium, two liquid phases and one vapour phase are in equilibrium.

They are coexisting and they are in equilibrium. So then how to obtain their equilibrium composition that is one thing and then other thing important thing that how this phase diagrams of this VLLE systems look like. VLE systems and then LLC system we have seen the phase diagram system etcetera how they look like those things we have seen but now we have to see for this VLLE system how the phase diagram would look like. So, let us consider three phases: one vapour and two liquid phases are co-existing and are in equilibrium.

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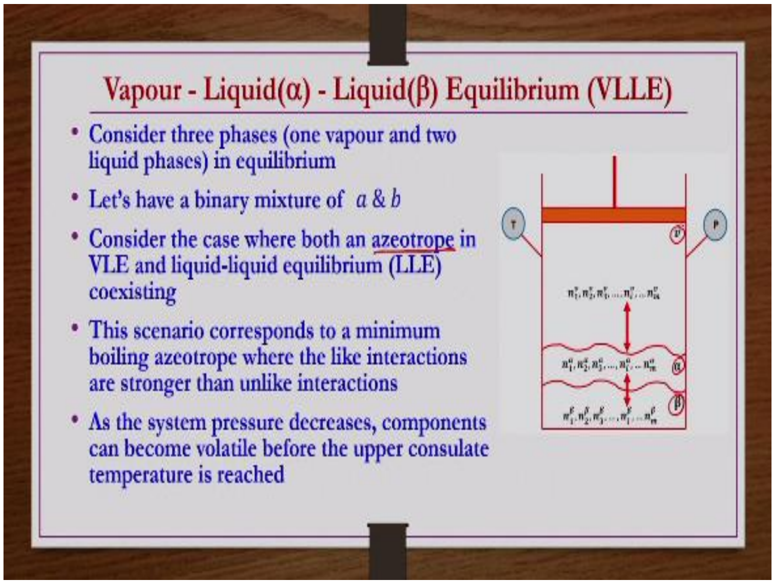

Vapour - Liquid(α) - Liquid(β) Equilibrium (VLLE)

- Consider three phases (one vapour and two liquid phases) in equilibrium
- Let's have a binary mixture of a & b
- Consider the case where both an azeotrope in VLE and liquid-liquid equilibrium (LLE) coexisting
- This scenario corresponds to a minimum boiling azeotrope where the like interactions are stronger than unlike interactions
- As the system pressure decreases, components can become volatile before the upper consulate temperature is reached

So let us say we have a close system as shown here in this picture there is a vapour phase which is designated as v and there is a liquid phase designated as α phase. There is another liquid phase which is designated as β. So, these three phases are co-existing and each of them are having n number of components. n_1, n_2, n_3, n_i, n_m are the moles of those number of components from component 1 to m.

And then they are given a superscript like β, α, v. They indicate n for different phase, let us say n_1^v, n_2^v, n_3^v, and so on so n_m^v are nothing but the number of moles of each component that are present in the vapour phase at equilibrium. And then n_1^α, n_2^α, n_3^α and so on so n_m^α are nothing but the number of moles of each of these components that are present in liquid phase α.

Similarly, n_1^β, n_2^β, n_3^β and so on so n_m^β are nothing but number of moles of these m number of components that are present in liquid β phase. All of them are co-existing in a close system and then all of them are at equilibrium and then the temperature of the system is T and the pressure of the system is P. So that is what we have. So similar like, whatever system that we have taken VLE there one liquid phase and one vapour phase are coexisting.

Those calculations we have seen, so now here, one vapour phase but two liquid phases are co-existing, and they are in equilibrium. So, while doing the calculation we will be taking the generalized cases anyway, but for simplicity what we start with a binary system. We consider a binary system a mixture of component a and b. Then consider the case where both an azeotrope in VLE and LLE co-existing.

So, this having azeotrope is not a kind of compulsory at all, but we start with that kind of system. So that it is easy to understand. Later on in the next class will be taking a few example problems where we will be having VLE system without an azeotrope but still there will be kind of VLLE case. Later, on in the next lecture what will be doing? We will be taking a problem, and then we try to draw the phase diagram.

So we realize that without any azeotrope also if there is a VLE then also it is possible that you know, VLLE system is possible, but for simplicity in order to understand VLLE we start taking discussing the case having LLE and then VLE but VLE having azeotrope as well. So, this scenario corresponds to a minimum boiling azeotrope where the like interactions are stronger than the unlike interactions.

Why, minimum boiling azeotrope that also I explain schematically in the next slide. As the system pressure decreases components can become volatile before the upper consolute temperature is reached.

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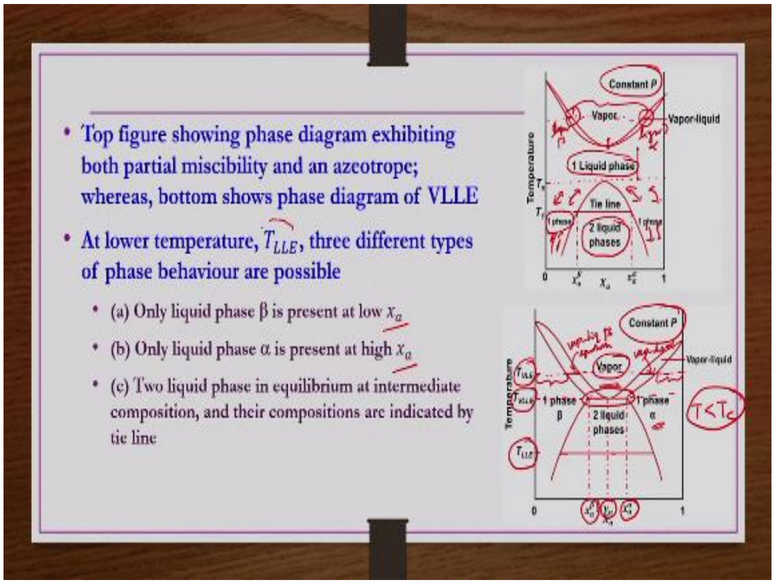

- Top figure showing phase diagram exhibiting both partial miscibility and an azeotrope; whereas, bottom shows phase diagram of VLLE
- At lower temperature, T_{LLE}, three different types of phase behaviour are possible
  - (a) Only liquid phase β is present at low x_a
  - (b) Only liquid phase α is present at high x_a
  - (c) Two liquid phase in equilibrium at intermediate composition, and their compositions are indicated by tie line

So, let us have these, T-x y diagram temperature versus mole fraction diagram if we have here. So now here we can say this T_u this upper consolute temperature is there. So above this temperature only one liquid phase is existing as in LLE case. Below this T_u the temperature system, temperature is below this one let us say T_1 so then two liquid phases are coexisting they are partially miscible, and they are at equilibrium and they are co-existing.

So, at this temperature if you want to find out the mole fraction of a component in each of these two partial immiscible systems. So, then you have to draw a tie line at this temperature and then corresponding you can find out. So, this x_a, this greater larger mole fraction set probably you can have a one liquid phase after this envelope that liquid phase is rich in component a. So that is usually we call it α phase.

And then the lower mole fraction side whichever you know, having excess smaller one. So, which these smaller and then out of this envelope which wherever this single liquid phase is there so that is usually referred as β liquid phase. So now here out of this envelope depends on the composition not only just upper consolute temperature, you can see depends on the composition, the temperature both.

So, there is a possibility that be a kind of single liquid phase, that liquid phase may be rich in component a one phase. And then another phase may be rich component b that is possible and then but within this envelope we can have a both the phases coexisting that is LLE is existing that is liquid-liquid equilibrium is existing between two liquid phase α phase and β phase or liquid phase one or liquid phase two like that whatever you get call it.

But if the temperature is above this upper consolute temperature, then you will have only single liquid phase. Even if the temperature is less than the upper consolute temperature there would be some region depends on the mole fraction, depends on this x_a value there may be single phase is possible. That single phase, one side lower x_a side, the single phase is usually β liquid phase and then higher x_a is usually α liquid phase that is what we have.

Now if the temperature further away above this T_u temperature upper consolute temperature. Let us assume there is a kind of vapour liquid equilibrium is also there, vaporization of a volatile component is taking place and then there is a kind of vapor liquid equilibrium is also taking place. So now you can see here this VLE curve whatever shown here. So that is having you know azeotropic composition at this point just for indication I showed.

So, it is not any exact phase diagram of any system or at any pressure or that any temperature or just for understanding we are doing. We will be taking one example case also, real case where we can have such kind of system as well. So now here we can have, if you draw a kind of line here like this. So, what you can have. So here you have the liquid β phase, liquid phase, only are having.

So, but this is β phase and then in between you can have a kind of vapour liquid equilibrium between vapour and then liquid β. Here again, you can have an in this region again. You can have a kind of a vapour liquid equilibrium but vapour and then α liquid would be there here vapour and then β liquid would be there in the left side and the right hand side that is larger α we have α liquid.

And then now you can see as mole fraction increases after this point, this only vapor is existing for large range of intermediate mole fraction. Then again vapour liquid equilibrium is there then after this again extreme large values of x_a we have only single liquid phase. So, this kind of systems are there. So, all this thing we are doing this T-x y diagram at constant pressure. So now assume the conditions are such a way that these two are intersecting.

This LLE curve and then VLE curve; VLE curve is having different behavior here. v liquid β phase diagram upto this azeotrope and from this point what we have, v liquid α equilibrium curve phase diagram for that vapour and then α liquid combination that we are having in the right side. Now if these VLE with an azeotrope whatever we have shown that one and then this LLC curve intersecting what will happen?

That will see now in the previous slide we were talking about minimum boiling azeotrope because of this region in order to explain this one we have taken a minimum boiling azeotropic mixture that we have taken. Because under such conditions intersection of these two phases is possible if you tune the parameters appropriately that again we are going to see that is the reason we are taking the case minimum boiling azeotrope.

So that it is possible to have a kind of imaginary kind of situation where you know intersection of this LLE and then VLE curves can take place. So now here the azeotrope and the temperature of the system or the boiling temperature of the mixture is less than the boiling temperature of both components a and b. So that is the reason it is a minimum boiling azeotrope. So, for this reason in order to have the intersection of this LLE and VLE curves.

We have taken minimum boiling azeotrope case we have taken. Now when we have intersection of this thing at the same, some constant pressure, what is that let us not worry. So, then we have like this, again, here also exactly we can see here, this intersection has taken place before. This temperature of the system reaches the upper consolute temperature, the pressure is adjusted such a way, that are the pressure is low enough such a way.

That some of the component or whichever is the mole volatile component is there that is vapourized and then VLE system is also taking place in addition to LLE. So, before there is LLE obviously this we can see here at the temperature T_{LLE} within this envelope, whatever is there within this envelope. We have LLE of the system and then here before this usually, this we have this kind of system.

So before it reaches the upper consolute temperature, you know vapour is reduced such a way that more volatile component is vaporized and then VLE is also started and then that VLE behavior and then LLE behavior are coinciding with each other so that we can have this kind of picture here. So again, at the temperature T less than when the temperature is small enough that is T_{LLE}. Then we can have a kind of liquid-liquid behavior.

Where two liquid phases are coexisting if the temperature is large that is T_{VLE} then there will be again VLE is existing. So now here within this region with both depending on the composition as well as the depending on the temperature within this region what we have? We have single liquid phase, that liquid phase we call it let us say β. Similarly, here also within this envelope this region.

What we can have depending on the temperature and then composition which is falling in this region? We can have one single phase liquid that is α. And then within this envelope as usual like in LLE we have two liquid phases coexisting that is α and then β phases. Let us say at this, if this is the, at this point if you wanted to know the composition of these two coexisting liquid phases.

So, you can draw a tie line and at the corresponding temperature and then find out towards the right side or the higher x_a side what we have? A phase mole fraction will be having and then towards the lower x_a side will be having β phase small fraction of that particular component. Let us say a if you do, T versus x_a, if you see here larger x_a side whatever this tie line is intersecting with this curve here.

So let us this curve here if you have so this should be your; if you do the, find out the composition, so this would be your x_a^α but at this TLE temperature and this should be your x_a^β. That is again a T_{LLE} temperature because at T_{LLE} temperature we draw a kind of tie line and then we found the composition. So, let us say at this temperature if you wanted some other temperature higher than the T_{LLE} here.

But still within the range where we can have two phases, so then again corresponding this should be your x_a^α and then this should be x_a^β so like this you can find out the composition. So now what we can see here at higher temperature, that is let us say T_{VLE} at this temperature if you draw a tie line here. So depending on the mole fraction if the mole fraction is smaller and then temperature at this temperature mole fraction is up to this range.

Then we have a pure liquid phase one liquid phase is not pure only single liquid phase is there that is liquid phase β and after that vapour and then liquid β phase equilibrium is there and then after that again, if you further increase the mole fraction at this for the same tie line at temperature T_{VLE} further increasingly mole fraction after this point then you can have only pure, not pure you will be having only single vapour phase.

There will not be any liquid phase and then further if you increase mole fraction at the same temperature towards the larger this small fraction side. So then here we have this vapor and then liquid α equilibrium is there and then further if you increase the mole fraction at the same temperature what happens we have again one liquid phase α is there. So, at one single temperature you can see depending on the composition there is a region.

Where only a liquid β phase is that there is a region, where there is a vapor and then liquid β equilibrium is there and then there is other range of a mole fraction where there is only vapour phase is there and then there is other range of mole fraction where this vapor and then liquid α equilibrium and then there is another range of mole fraction at higher x_a values. We have only one single liquid phase that is α phase.

So all these things are possible in this VLE but at this temperature at VLLE that we call it VLLE because here this VLE and then this LLE curves are intersecting and then we have a kind of line not necessarily there will be line there will may be kind of more complicated things are also possible. So, at this temperature all these two liquid phases whatever the two liquid phases, they are co-existing at because this envelope includes the region of LLE.

So, this line is with the LLE and then this line is also, includes the vapor composition again. It is also therefore the vapor part also, so it is a combined existing this region this particular region at this temperature VLLE what we are having? We are having this vapor and then two liquid phases at equilibrium. And then if you draw a tie line at this temperature T_{VLLE}. So, whichever is the larger mole fraction side is there that is the mole fraction of that component in α liquid phase.

And then whichever is the lower x_a side is there, a lower side for mole fraction is there. That is the mole fraction of that particular component in the β phase and then whatever in between this vapour that is coinciding with the vapor line at that point, whatever the composition is there, that is the, composition of that particular that is the mole fraction of that particular component in the vapour phases and all these three are in equilibrium with each other.

So, this is the case of a one particular VLLE that is one vapor and then two liquid phases are in equilibrium. So, this is the case where minimum boiling azeotrope is there so then you can easily visualize the co-existing of these three phases one vapour and two liquid phases, but not necessarily all VLE should be looking like this. In the next lecture, we will be taking a problem and then will be discussing how this P-x-y diagram, look like and then there you will be finding that there is no azeotrope present at all.

So more complicated than these things are also possible, for simplicity for easy understanding we have taken this case. So at lower temperature T_{LLE} three different types of phase behavior are possible only liquid phase β that is possible at lower x_a and then only liquid phase α that is present at higher x_a side and then two liquid phase in equilibrium at intermediate composition and their composition are indicated by the tie line as have explained here that is there.

This is all it, lower temperature T_{LLE}, lower in this and how much lower we cannot say that is lower than the upper consolute temperature that way we can take with related to the upper consolute temperature less than the upper consolute temperature at certain location. T, temperature, if you see that T_{LLE} that we are indicating.

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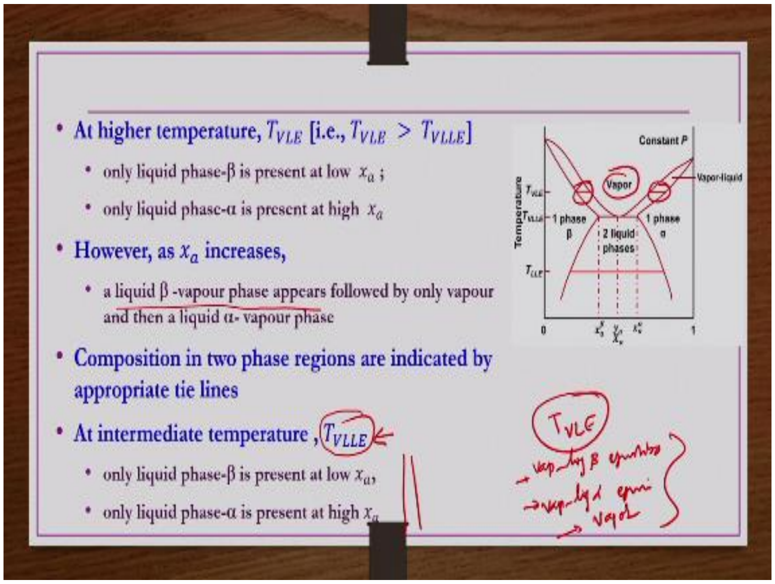

- At higher temperature, T_{VLE} [i.e., $T_{VLE} > T_{VLLE}$]
  - only liquid phase-β is present at low x_a ;
  - only liquid phase-α is present at high x_a
- However, as x_a increases,
  - a liquid β -vapour phase appears followed by only vapour and then a liquid α- vapour phase
- Composition in two phase regions are indicated by appropriate tie lines
- At intermediate temperature , T_{VLLE}
  - only liquid phase-β is present at low x_a,
  - only liquid phase-α is present at high x_a

So now the same diagram I have shown here also for easy understanding. So, at higher temperature T_{VLE} that is T_{VLE} is greater than T_{VLLE} then what we can have? We can have only liquid β. That is again at low x_a side and then only liquid α that is again at high x_a side and then however as x a increases from small x_a or lower x_a to higher x_a then a liquid β and vapor phase that co-existing that is this region followed by only vapour phase that is this one, and then a liquid α and then vapour phase that is this region is possible.

After this lower x_a range where only liquid β phase is there and then before that higher x_a range where only α liquid phase is there in between these two regions we have three different kind of behaviors we can see. 2 VLE behaviors that is vapour and then liquid β VLE then only vapour then another VLE that is vapour and then liquid α VLE that we can have. As already described and then composition in two phase regions are indicated by appropriate tie lines anyway at intermediate temperature.

This T_{VLLE} is that, we call it as a kind of intermediate temperature only liquid phase β is presented low x_a and then only liquid phase α is presented high x_a. What does it mean by there is no region where only vapor is forming or there is no region where vapour and then liquid equilibrium whatever we have seen? At T_{VLE} this one and then vapor liquid α equilibrium.

And then pure and not pure and then only vapour phase whatever these things that we have seen at T_{VLE} they are not present at temperature this T_{VLLE}. When there is three phases or coexisting so then this will be absent for this case.

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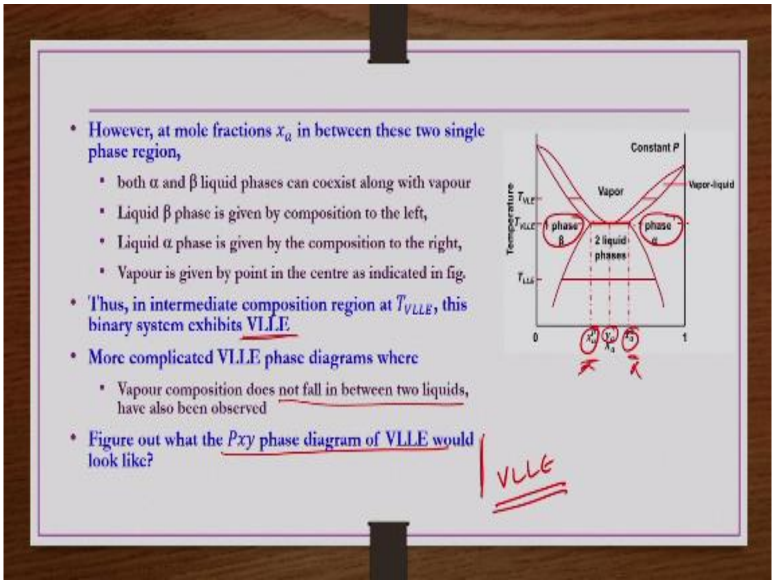

- However, at mole fractions x_a in between these two single phase region,
  - both α and β liquid phases can coexist along with vapour
  - Liquid β phase is given by composition to the left,
  - Liquid α phase is given by the composition to the right,
  - Vapour is given by point in the centre as indicated in fig.
- Thus, in intermediate composition region at T_{VLLE}, this binary system exhibits VLLE
- More complicated VLLE phase diagrams where
  - Vapour composition does not fall in between two liquids, have also been observed
- Figure out what the Pxy phase diagram of VLLE would look like?

So the same picture I have drawn a once again, so however as mole fraction x_a in between these two single phase regions that is this β liquid phase and then β α phase both α and β liquid phases can coexist along with the vapor between this two region as x_a increases. So liquid β phase is given by composition on the left side, so this is one and then liquid α phase is given by the composition to the right that is x_a^α here at this tie-line.

Let us say if you draw tie-line at T_{VLLE} so then we have this one compositions. Liquid phase compositions, you can find out like this, this will be α phase α liquid phase composition this would be β phase liquid composition. Vapor is given by point in the center as indicated in the figure here this y_a is the vapor phase composition. So, all these three phases one vapour and then two liquid phases are co-existing at this T_{VLLE}.

So thus, in intermediate composition region, at T_{VLLE} this binary system exhibits vapour-liquid-liquid equilibrium, that is one vapour phase and then two liquid phases are at equilibrium. So more complicated VLE phase diagrams where vapor composition does not fall in between two liquids have also been observed so we are not going into those details as of now any way. Figure out what the P-x-y phase diagram of VLLE would look like that you can try.

But however next class I am going to solve a problem to draw this P-x-y diagram for that particular problem. So, but however, you can also try think how P-x-y diagram may look like for a VLLE system.

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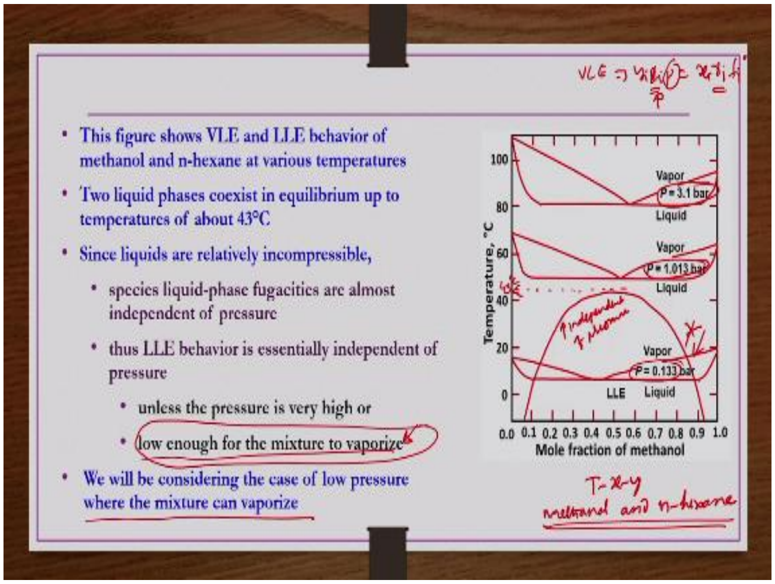

$VLE \Rightarrow y_i \hat{\phi}_i P = x_i \gamma_i f_i$

- This figure shows VLE and LLE behavior of methanol and n-hexane at various temperatures
- Two liquid phases coexist in equilibrium up to temperatures of about 43°C
- Since liquids are relatively incompressible,
  - species liquid-phase fugacities are almost independent of pressure
  - thus LLE behavior is essentially independent of pressure
    - unless the pressure is very high or
    - low enough for the mixture to vaporize
- We will be considering the case of low pressure where the mixture can vaporize

T-x-y
methanol and n-hexane

So now what we see, we take an example of methanol and n-hexane system. And then for this one, we try to draw T-x-y diagram at different pressures. Anyway, temperature we are varying and to in order to see but we also change the pressure at different pressures we try to have the system and then if you draw, we can have a picture like this. What we understand the activity coefficients etc. of a liquid system are independent of the pressure provided the pressure is in low to moderate range.

That is what we already understood, that is what we are already know that means if you do not have very high pressure then the LLE behavior is not affected by the pressure, that is what we can say. But if the temperature is lower than the upper consolute temperature and then pressure is in low to moderate range then there will be a kind of LLE is possible. So that LLE shown here which is independent of pressure.

Because we are calling it like, you know low to moderate range of pressure only in that range only we are doing it. Now if the pressure is very low what happens? Whichever is the more volatile component is there out of these two that will be vaporizing and then there is a VLLE is also possible and then we know this from VLE calculation the equilibrium compositions are functions of pressure.

How this pressure is changing? Why that is VLE what we have seen. $y_i \phi_i P = x_i \gamma_i f_i^0$. This γ_i is independent of pressure but ϕ_i here is dependent on, this also we found as function of pressure and then composition this again the pressure term is here. So that means the vapor composition part is not independent of the pressure. So that means VLE phase diagram would be different if you draw a different pressures.

The same T-x-y diagram, whatever you are drawing here. If you draw a different pressures targeting the VLE behavior of the same system, so then you have the different curves and then different curves are shown here at the low pressure is this one bottom one and then 1.013 bar it is a middle one and then the top one at 3.1 bar. Whereas the LLE behavior is independent of pressure, so then for all the cases we are having only one particular envelope.

Because this LLE curve we have drawn for the case where the upper consolute temperature has not reached. For those cases we have drawn here, before reaching the upper consolute temperature, whatever the LLE behavior is there that we have drawn and then that is independent of the pressure. So, this figure shows VLE and LLE behavior of methanol and n-hexane at various temperature it is exactly the same way.

Whatever we have done the previous thing, but only thing that we are taking an example and then trying to come to that state where we have this VLLE curves directly. Previously generalized one we have taken the directly now we step by step we do this VLE evaluation and LLE evaluation and then see how we can come out to the case where we can have VLLE as well.

So, two liquid phases coexist in equilibrium up to temperature of about 43 degrees centigrade. So below that we have a kind of LLE two liquid phase coexisting. Since liquids are relatively incompressible as I said. Species liquid phase fugacities are almost independent of pressure. Thus, LLE behavior is essentially independent of pressure so that we are having only one LLE. Whether you draw it at 0.113 bar or that is whether you obtain this LLE behavior whether at 0.133 bar or at 1.013 bar or 3.1 bar, you will be getting the same curve.

Superimposing into one to each other because the pressure is in the lower range of the pressure only not even the moderate range, 3 less than 10 bar we can say as a kind of lower range pressure in general. So that is the region LLE curve we are having only one curve. That is because independent of pressure unless the pressure is very high so if the pressure is very high then this non ideality of a liquid phase is also going to be affected by the pressure.

Those things we have not taken or other ways if you have the pressure is low for the mixture to vaporize our other ways if you have the case, pressure is low enough for the mixture to vaporize. Though the temperature you maintain the low temperature but the pressure is also a very low then one of the components may be vaporizing and vapour liquid equilibrium may also be possible. So exactly what we are doing now will be taking this case.

That is will be taking the case of this one and then discussing in detail, so now we will be considering the case of low pressure where the mixture can vaporize.

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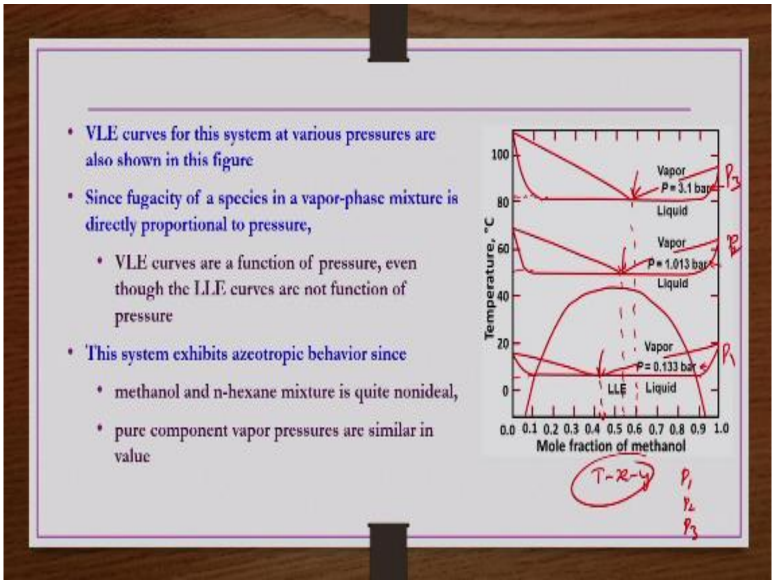

- VLE curves for this system at various pressures are also shown in this figure
- Since fugacity of a species in a vapor-phase mixture is directly proportional to pressure,
  - VLE curves are a function of pressure, even though the LLE curves are not function of pressure
- This system exhibits azeotropic behavior since
  - methanol and n-hexane mixture is quite nonideal,
  - pure component vapor pressures are similar in value

So same figure once again VLE curves for the system at various pressure are also shown in this figure that is at the different pressures 0.133 bar, 1.013 bar and then 3.1 bar there VLE behavior is also shown since fugacity of species in vapour phase mixture is directly proportional to pressure. VLE curves are function of pressure even though LLE are not function of pressure. So, because the vapour phase mixture, you know, because the fugacity of species is directly proportional to pressure.

In the case of vapour phase the fugacity of species is directly proportional to the pressure that is the region we are having different VLE curves if you change the pressure. Though, it is T-x-y curve but at different pressures. P_1, P_2, P_3, if you call it P_1, we are having this one P_2, we are having this behavior P_3 we are having this behavior. The shape wise phase diagram shape is they are looking similar.

But composition and temperature wise they are very different from one other. Whereas LLE we are having only one curve at all the pressures because it is independent of the pressure. We have taken the pressure is such a way that this system exhibits azeotropic behavior. Because now here whether this pressure is low pressure I mean, whatever the pressure you have taken there is a azeotropic behavior but only thing the azeotropic composition are different each case

And then corresponding temperatures are also different in each case. Why it is having? Because this methanol n-hexane mixture is quite non ideal and also the vapor pressure of this methanol and also the vapor pressure of these two components are very much close to each other. That is the reason it is possible that azeotrope may exist and then that we can see all the pressure that we have considered here.

Only thing that if you change the pressure the azeotrope composition is changing and then corresponding, minimum boiling azeotropic behavior is there so the corresponding temperature is also changed. One case it is around 5 degree centigrade another case it is around 50 degrees centigrade. Another case it is around 80 degree centigrade, as you increase the pressure from P_1 to P_2 to P_3.

And then composition of azeotropic mixture is decreasing. For P_1 case it is approximately 0.4 per for P_2 case approximately 0.54 and then for P_3 case it is approximately 0.6.

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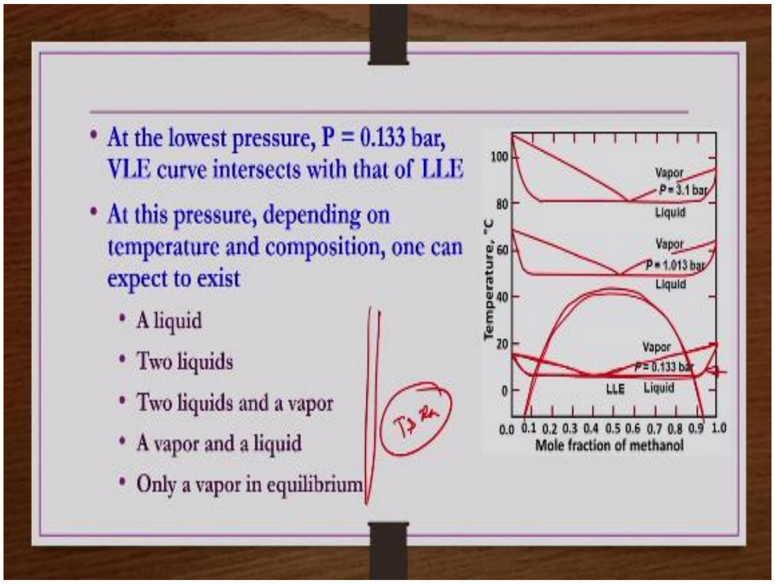

- At the lowest pressure, P = 0.133 bar, VLE curve intersects with that of LLE
- At this pressure, depending on temperature and composition, one can expect to exist
  - A liquid
  - Two liquids
  - Two liquids and a vapor
  - A vapor and a liquid
  - Only a vapor in equilibrium

So, the same picture is shown here again, so at the lowest pressure that is at this case 0.113 bar VLE curve intersect with that of LLE that we can see here. So, this is LLE part and then this is the corresponding VLE at this pressure they are intersecting now. So, at this pressure depending on the temperature and composition one can expect to exist only one liquid phase, two liquid phases also possible and then two liquids under vapor is also possible.

And a vapor and a liquid one single liquid is also possible and only vapour also possible, all these may be depending on the temperature and then composition. Any of this may possible and they may be in equilibrium.

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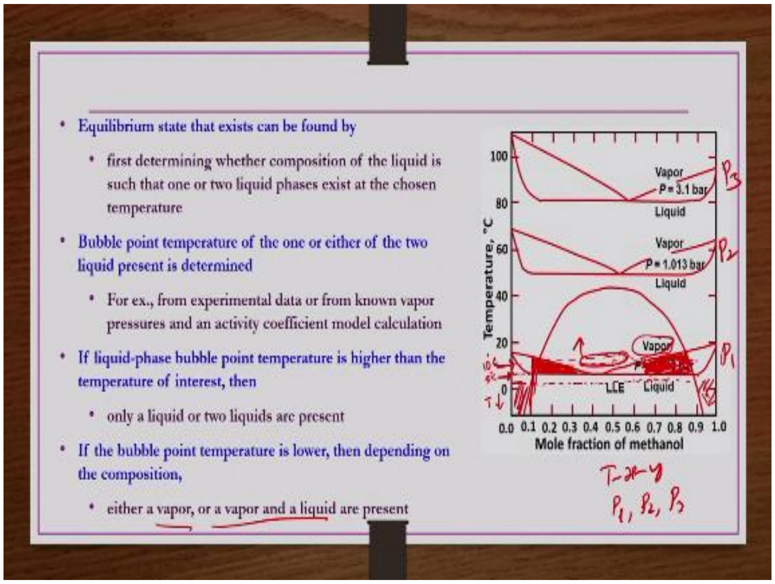

- Equilibrium state that exists can be found by
  - first determining whether composition of the liquid is such that one or two liquid phases exist at the chosen temperature
- Bubble point temperature of the one or either of the two liquid present is determined
  - For ex., from experimental data or from known vapor pressures and an activity coefficient model calculation
- If liquid-phase bubble point temperature is higher than the temperature of interest, then
  - only a liquid or two liquids are present
- If the bubble point temperature is lower, then depending on the composition,
  - either a vapor, or a vapor and a liquid are present

So now same T-x-y diagram for this methanol and n-hexane mixture is shown here at different pressures P_1, P_2, P_3, this is I am calling P_1, this is am calling P_2, this am calling P_3. So, equilibrium state that exists can be found by first determining whether the composition of the liquid is such that one or two liquid phases exists at the chosen temperature, that is one thing you have to do.

And then bubble point temperature of the one or either of the two liquid present has to be determined because based on that one only we can say whether one liquid phase is existing or two liquid phases are existing with equilibrium or one liquid and two vapor or one liquid and or one vapor and two liquids are coexisting at equilibrium from all those things you can know only when you find out these things.

So especially this bubble point temperature that will help us how to determine for a given composition, which all these phases are existing. So how to find out the bubble point temperature, for example, from experimental data or from known vapour pressures and an activity coefficient model calculations one can determine this bubble point temperature for the given system.

Then if liquid phase bubble point temperature is higher than the temperature of interest. Bubble point temperature now this is the VLE, so let us say VLE part, if you take this path, so above this one we have the vapors here, and then below this one we have liquid. So, let us say if you take this one at this point one composition, this is the corresponding temperature where the first bubble is forming below that it is and the liquid phase.

If the temperature of your interest is less than this temperature, less than this bubble point temperature or the bubble time point temperature is higher than your interest temperature. Interested temperature may be let us say you have this, 2 degrees centigrade here. So, within this one you can have only one liquid phase, or two liquids are present if you like this temperature and then composition is also within point one.

So then only one liquid phase is possible, at this temperature if your composition is higher, so then two liquid phases are possible at this same temperature of 2 degrees centigrade which is lower than the bubble point temperature of liquid phase. So, then all this your two liquid phases are existing. Further higher mole fraction, but this same temperature of 2 degrees centigrade only one liquid phase is existing that is possible.

Now if the bubble point temperature is lower then, depending on the composition, so that is, this is the bubble point temperature and then our interested temperature is something here. Now it is approximately how much? 10 degrees centigrade, earlier approximately 2 degrees centigrade. So now bubble point temperature is approximately something like 5 degree centigrade now here at the same composition.

So, now again depending on the composition at this temperature your temperature of interest is higher than the bubble point temperature or bubble point temperature is lower than the temperature of your interest then depending on the composition, you can either have a pure vapour at this if you draw tie-line like this. So, you can have either a vapour in this region, only vapour phase we are having. Or vapour liquid equilibrium may be there in this region.

That is also possible, depending on the composition so at this bubble point temperature we have found this composition. So after this we are having only one particular, because this is the bubble point temperature and then higher temperature we are taking than the bubble point temperature depending on the composition, you can have a VLE behavior are a only vapour behavior or again, you can have a kind of vapor region here again in this region.

So, all this is possible depending on the composition that only either a vapour or a vapour-liquid are present that is all possible here. So, this is how you can find out.

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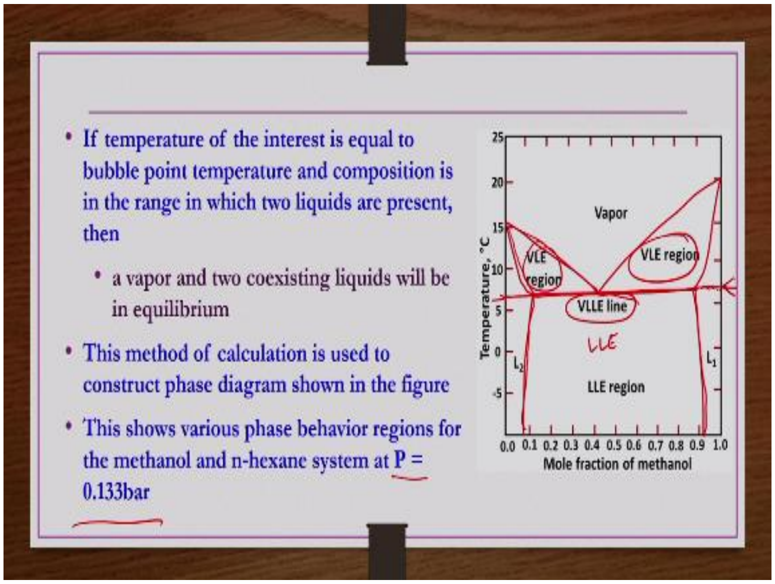

- If temperature of the interest is equal to bubble point temperature and composition is in the range in which two liquids are present, then
  - a vapor and two coexisting liquids will be in equilibrium
- This method of calculation is used to construct phase diagram shown in the figure
- This shows various phase behavior regions for the methanol and n-hexane system at P = 0.133bar

So let us say if your temperature of interest = the bubble point temperature and composition is in the range in which two liquids are present then we can have a kind of VLE behavior where a vapor and two coexisting liquids will be in equilibrium. So, let us say this one at this particular this thing, if you see here. So, this all this liquid this envelope whatever this envelope ie there that is for the LLE part.

So that is there so that is valid for this, liquids also and then that is also this point is also common point or this line is whatever this tie line. Let us say if I draw here, so this tie line is corresponding tie line is common for both the LLE part as well as the two VLE regions as well. So that is the region this line, whatever is there that we call it as a VLLE line. So now you can see it is quite similar as whatever the T-x-y diagram for VLLE system.

That we have taken previously but without an example, so this is with an example, we are mentioning. So, this method of calculation is used to construct a phase diagram as shown in the picture and then this shows various phase behavior regions for methanol and n-hexane system at 0.133 bar. So now depending on the composition and depending on the temperature you can find out.

Whether one liquid is existing or two liquid phases are existing or two liquids are one way per existing or one liquid and vapour is existing all that you can find out from this phase diagram. So, this is how one can construct the phase diagram behaviour. So now how to find out the equilibrium composition of VLE? So next part is calculation methods of equilibrium composition of VLLE problems. So, equilibrium composition of VLLE.

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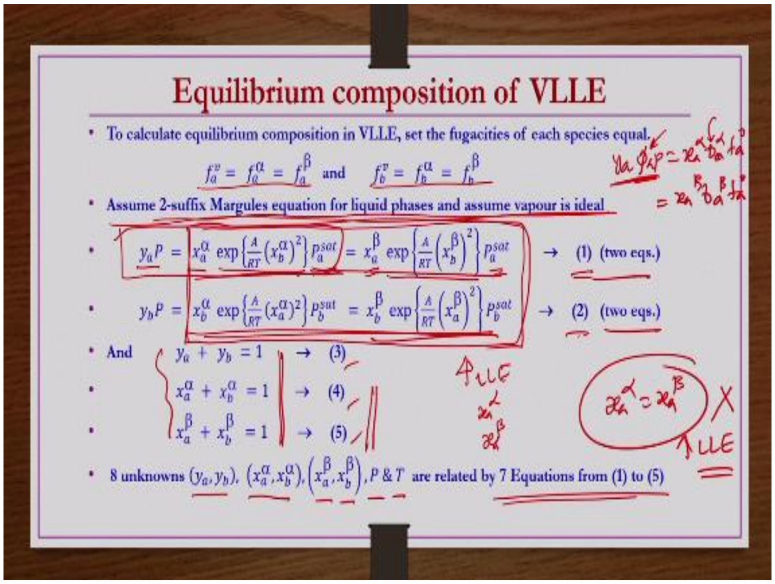

Equilibrium composition of VLLE

- To calculate equilibrium composition in VLLE, set the fugacities of each species equal.

$$f_a^v = f_a^\alpha = f_a^\beta \quad \text{and} \quad f_b^v = f_b^\alpha = f_b^\beta$$

- Assume 2-suffix Margules equation for liquid phases and assume vapour is ideal
- $y_a P = x_a^\alpha \exp\left\{\frac{A}{RT}(x_b^\alpha)^2\right\} P_a^{sat} = x_a^\beta \exp\left\{\frac{A}{RT}\left(x_b^\beta\right)^2\right\} P_a^{sat}$ → (1) (two eqs.)
- $y_b P = x_b^\alpha \exp\left\{\frac{A}{RT}(x_a^\alpha)^2\right\} P_b^{sat} = x_b^\beta \exp\left\{\frac{A}{RT}\left(x_a^\beta\right)^2\right\} P_b^{sat}$ → (2) (two eqs.)
- And $y_a + y_b = 1$ → (3)
- $x_a^\alpha + x_b^\alpha = 1$ → (4)
- $x_a^\beta + x_b^\beta = 1$ → (5)
- 8 unknowns (y_a, y_b), (x_a^α, x_b^α), $\left(x_a^\beta, x_b^\beta\right)$, P & T are related by 7 Equations from (1) to (5)

$y_a \phi_a P = x_a^\alpha \gamma_a^\alpha f_a^o$

$= x_a^\beta \gamma_a^\beta f_a^o$

4LLE

x_a^α

x_a^β

$x_a^\alpha = x_a^\beta$ X

LLE

So, this going to be straight forward mathematically as we have seen for VLE and LLE. So to calculate equilibrium composition in VLLE obviously the fugacity of each species should be equal in all three phases so far component a we can now $f_a^v = f_a^\alpha = f_a^\beta$ similarly for component b also we can have like this. Then assume 2-suffix Margules equation for the liquid phase and assume vapour phase ideal.

So, these things we are taking because this, equations now you are going to realize that very complicated and very difficult to solve analytically. There may be approximate solutions are possible better can be done by numerical solutions, especially if the pressure is high then one has to go for the numerical solution. So, for simplicity in order to write these equations now, what we have to write? What is f_a^v?

If you take non ideality everywhere then y_a ϕ_a P $=x_a^\alpha\ \gamma_a^\alpha\ f_a^0 = x_a^\beta,\ \gamma_a^\beta\ f_a^0$ this is what you should have. So, what is this γ? We should know what this ϕ_a is then only we can write equation. So, ϕ_a there are many relations are there. So, for simplicity, we are taking ideal behavior and then γ_a also different models are available activity coefficient models that we have already seen.

So, first simplicity, we have taken 2-suffix Margules equation, which is simplest one, where γ is nothing but exponential of $\frac{Ax_b}{RT}$, where γ_a is nothing but $\frac{Ax_b^2}{RT}$. So that is the region for simplicity we have taken these two for liquid phase, non-ideality. We have taken 2-suffix Margules equation and then for vapor phase we are not taking non ideality at all, we are taking ideal behaviour. If non ideality is there than similar way, we have to do calculation any way.

So, for this condition if you write for component a so y_a P $=x_a^\alpha$ exp $\frac{A(x_b^\alpha)^2}{RT}$ and then $f_a^0$is nothing but P_a^{sat} because pressure is low to moderate pressure cases we are doing and then $=f_a^\beta$that is x_a^β exp $\frac{A\left(x_b^\beta\right)^2}{RT}$ and then multiplied by P_a^{sat} f_a^0 is again P_a^{sat} this is for the component a.

Similarly, for component b you can write like this. So now how many equations are there here? So, this is one equation and then the other one is other equation. So, two equations we can take independently and then here also two equations independently one can take. So, two equations are there, four equations and then we have this $y_a + y_b$ =one and then for α and then β phases $x_a + x_b = 1$ these three equations are there.

So total 7 equations are there, so then how many unknowns are there? y_a, y_b, x_a^α, x_b^α, x_a^β, x_b^β, P and T. Out of this variables how many of them are independent variables? And then in order to find out these independent variables what should be the degree of rhythm? That you can calculate and accordingly you can use this, equations for solving for solving the equilibrium composition.

So, all these 8 unknowns are related by this, 7 equations, 2 and 2, 4 here and then 5, 6, 7 equations. Now even for liquid-liquid equilibrium, we have seen when there is this y_a P, part only this liquid-liquid equilibrium part is there. We have seen this solving this calculation is very tough. We have our several methodologies, numerical approaches are there. They can be used to solve this problems.

Now these two relations are also in equilibrium with a vapour phase, so y_a P are y_a phi_a P will also come into the picture if there is a non-ideality for the time being we have not taken the non-ideality anyway here. So then one has to write an algorithm accordingly and then solve the problem. Satisfying all these three conditions and then we should also make sure that the trivial solutions whatever $x_a^\alpha = x_a^\beta$ if you take then all these equations are satisfying in the case of LLE.

This we are saying but that is not correct solution anyway. So that you can realize if this, equations are also satisfying or not. So, for simplicity what we do? Will be assuming the pressure is low, if the pressure is low then we know this activity coefficients etc. are independent of the pressure. So, then we can segregate this problem first we can solve the LLE part of the problem solving only this part.

Without worrying about what is this y_a P, because now we know these, part any of these things are independent of pressure this equation number one and two. Whatever this box one are given, that independent of the pressure if you take the pressure is low to moderate range. So, this part you can take it as a kind of LLE part and then find out what is x_a^α and then x_a^β? If x_a is known x_b can be easily known.

Satisfying these conditions exactly the same way that we have done in previous LLE lecture. Once we have this, calculations of x_a^α and x_a^β then either by taking this part or by taking the first and last term of this equation, you can solve the vapour composition part as well. Where the pressure is also coming into the picture, so that segregating we can do here, in the case of VLLE.

Remember this segregating of this equation has a separate LLE problem and then VLLE problem. Only when the pressure is low to moderate if the pressure is high, we cannot do that one and then we have to go for a numerical, solutions.

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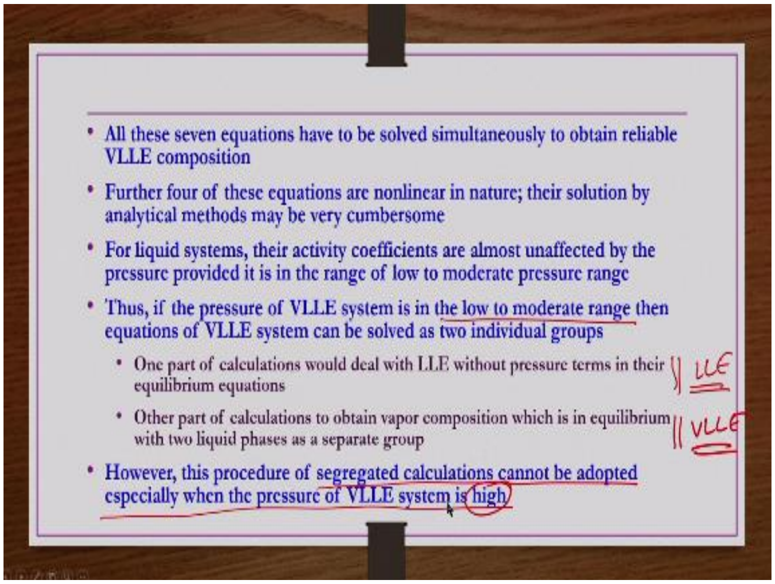

- All these seven equations have to be solved simultaneously to obtain reliable VLLE composition
- Further four of these equations are nonlinear in nature; their solution by analytical methods may be very cumbersome
- For liquid systems, their activity coefficients are almost unaffected by the pressure provided it is in the range of low to moderate pressure range
- Thus, if the pressure of VLLE system is in the low to moderate range then equations of VLLE system can be solved as two individual groups
  - One part of calculations would deal with LLE without pressure terms in their equilibrium equations
  - Other part of calculations to obtain vapor composition which is in equilibrium with two liquid phases as a separate group
- However, this procedure of segregated calculations cannot be adopted especially when the pressure of VLLE system is high

All these 7 equations how to be solved simultaneously to obtain reliable VLLE composition. Further 4 of these equations are non-linear in nature their solution by analytical methods may be very cumbersome, obviously we see how much nonlinear are they. For liquid systems, their activity coefficients are almost unaffected by the pressure provided it is in the range of low to moderate pressure range.

Thus, if the pressure of VLLE system is in the low to moderate range then equations of VLE system can be solved as two individual groups. First group calculations would deal with LLE without pressure terms in their equilibrium equations that is equation number one and two, you will not be taking the first term y_a P terms you will not be taking. And then the remaining x_a^α+ x_b^α=1 and then x_a^β+ x_b^β=1 should also be maintained.

Exactly the same way as LLE problems that we have solved in previous lectures. Other part of the calculation to obtain vapour composition, which is an equilibrium with the two liquid phases as a separate group. We will be taking some example problems to understand how this calculation can be done in the next class anyway. So, however, this procedure of segregated calculations cannot be adopted especially when the pressure of VLLE system is very high. This approach we can follow only the pressure when the pressure is low to moderate.

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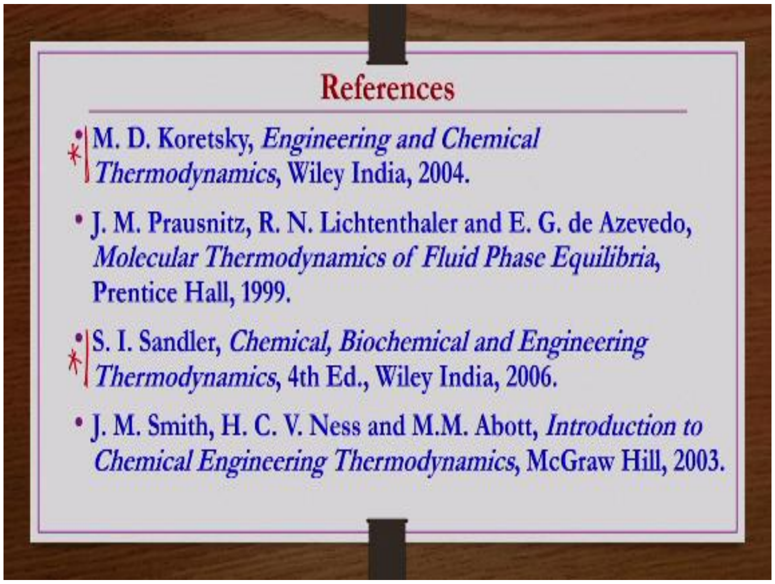

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References for this lecture are given here; Engineering and chemical thermodynamics by Koretsky. Molecular Thermodynamics of fluid phase Equilibria Prausnitz et al. Chemical, Biochemical and Engineering Thermodynamics by Sandler, Introduction to Chemical Engineering Thermodynamics by Smith et al. So, the references for this lecture of primarily these two books Sandler and Koretsky especially this Sandler book is a very good reference book for VLLE phase diagrams as well as the calculations. Thank you.