Advanced Thermodynamics
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Lecture -29
Vapor - Liquid - Liquid Equilibrium - 2

Welcome to the MOOCs course advanced thermodynamics data of this lecture is vapor-liquid-liquid equilibrium part 2. In the previous lecture what we have seen different T-x-y phase diagrams of VLLE system that is where you know, we have one vapor and then 2 liquid phases are coexisting. So how their T-x-y diagrams would look like at a given pressure and then if you change the pressure how they are going to change those things we have already seen, in detail in the previous lecture.

We have also seen how to obtain equilibrium composition of this VLLE system with equations and then how we can segregate this equations in order to solve this VLLE problems, especially when the pressure is low to moderate that is what we have seen. So now in this particular lecture, we will be taking a few example problems and then we try to draw phase diagrams for this system from this example problem.

Before going into the details of solving this problems will be recapitulating the equation part of equilibrium composition measurement for this VLLE problems that will be having a kind of recapitulation.

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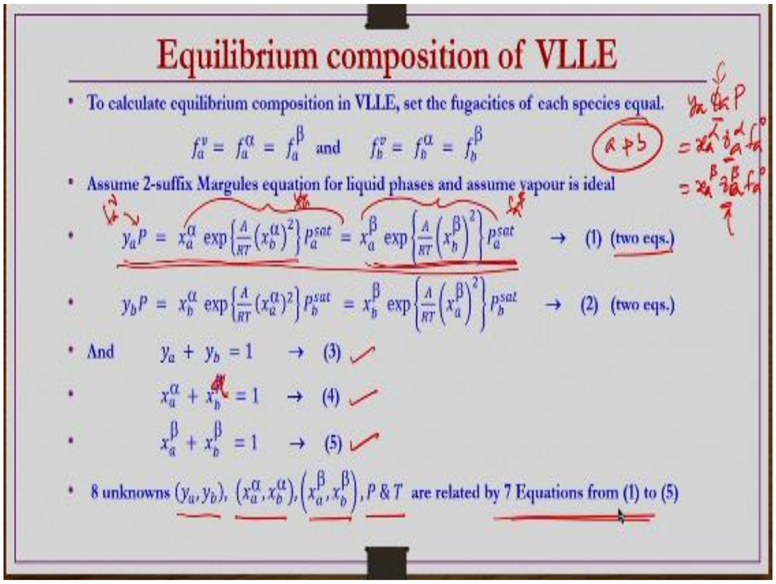

Equilibrium composition of VLLE

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

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

a + b

$y_a \phi_a P = x_a^\alpha \gamma_a^\alpha f_a^0 = x_a^\beta \gamma_a^\beta f_a^0$

- 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)

Equilibrium composition of VLLE, so to calculate the equilibrium composition in VLLE, what we have to do we have to set the fugacities of each species equal. So that if you do $f_a^v = f_a^\alpha = f_a^\beta$ and then $f_b^v = f_b^\alpha = f_b^\beta$. We are taking only binary system having a and b components. Now this we know that $f_a^v = f_a^\alpha = f_a^\beta$. So then if you write generalized one $y_a\ \phi_a\ P = x_a^\alpha\ \gamma_a^\alpha\ f_a^0 = x_a^\beta\ \gamma_a^\beta\ f_a^0$ this thing.

So now depending on the phase whether it is ideal or non-ideal, so this ϕ_a and γ_a terms should be there. So if it is ideal phase, so then I know this can be taken out. If it is non-ideal, accordingly corresponding equation, depending on which model have been used for a describing the non-ideality of the vapor phase accordingly ϕ_a expression will come into the picture.

And accordingly which model for excess Gibbs energy is used to describe the non-ideality of the liquid phase. So accordingly this $\gamma_a^\beta\ \gamma_a^\alpha$ expression would come into the picture. So if you have non-ideality in all 3 phases solving this equation will become very difficult because all these equations are non-linear, highly non-linear and then obtaining composition by hand calculation become very difficult.

So one can write and kind of algorithm and then solve them and also there are few programs available. So that we can use and then obtain this composition. Equilibrium composition for this such kind of non-ideal non-linear systems. However for simplicity we take now vapor phase as a kind of ideal phase and then liquid phase non-ideality described by 2 suffix Margules equation that simplicity we take and then we assume the pressure is low to moderate and then do a few example problems?

Then you assume 2 suffix Margules equation for liquid phase and then vapor phase as a kind of ideal phase then we have for component a this expression y_aP = x_a^α exp $\frac{A(x_b^\alpha)^2}{RT}$ P_a^{sat} = x_a^β exp $\frac{A(x_b^\beta)^2}{RT}$ P_a^{sat}. So this part is nothing but f_a^β this middle part is nothing but f_a^α and this is nothing but f_a^v.

Which is we have written for component a. So, there are 2 independent equation. 1st term = the middle term one independent equation then 1st term equal to the 3rd term is other independent relation or you can take the 2nd and 3rd terms are equal as a kind of independent equation, if 2 are independent third one cannot be taken as independent. So 2 equations are there. Similarly for component b if you write you have 2 equations like this.

So 4 equations and then in addition to that one the mole fraction of summation of mole fraction of all the components should be equal in each phase. So these 3 relation because 3 phases are there for vapor phase, for α liquid phase and then for β liquid phase, this should be x_a^α, x_b^α. $x_a^\alpha + x_b^\alpha = 1$. So now we have how many unknowns y_a, y_b, x_a^α, x_b^α, x_a^β, x_b^β, P and T are the unknowns.

So depending on the like, you know phases are existing and depending on the component you can use the Gibbs phase rule to find out the minimum degrees of freedom. So accordingly those now depending on the degrees of freedom you can fix those many independent variables and then remaining independent variables, you can calculate using this equations. Here at this 8 variables are related by this 7 equations.

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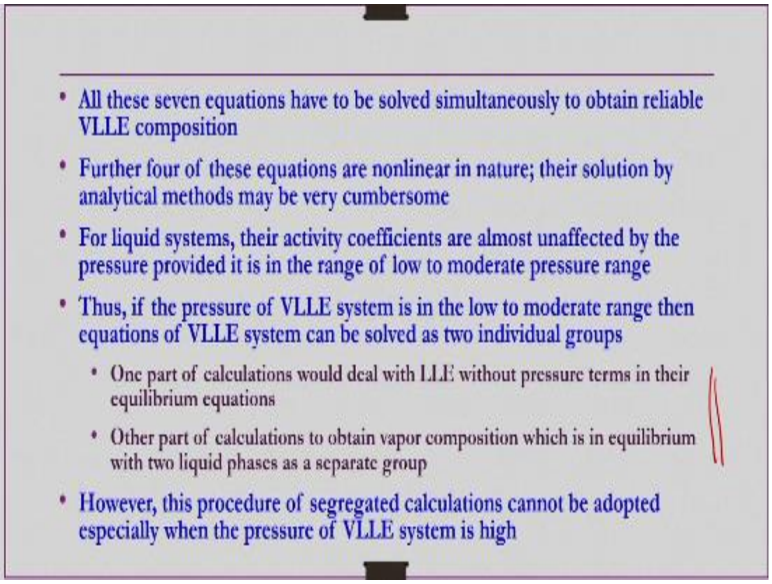

- All these seven equations have to be solved simultaneously to obtain reliable VLLE composition
- Further four of these equations are nonlinear in nature; their solution by analytical methods may be very cumbersome
- For liquid systems, their activity coefficients are almost unaffected by the pressure 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 become very cumbersome. For liquid system their activity coefficients are almost unaffected by the pressure provided it is in the range of low to moderate pressure that we already know. Making use of that benefit that liquid phase non-ideality or activity coefficients of liquid phase are independent of the pressure.

So then whatever the equation number 1 and 2 that we have given that is the equilibrium relations for VLLE problem for both the components that you can segregate in 2 parts. You can segregate in 2 parts and then 1 part you can solve the equations only taking the LLE terms and then solving the LLE composition exactly the similar way as we have done pure LLE problem where there is no vapor phase at all the only 2 liquid phases are coexisting.

Once you have this LLE composition, that you can use and then you find out vapor composition so that all these 3 phases composition you can find out wherever 2 liquid composition you will be finally obtaining. But this segregating approach you can use only if the pressure is low to moderate you cannot use it if the pressure is high. So this is what we have seen in previous lecture, it is a kind of recapitulation.

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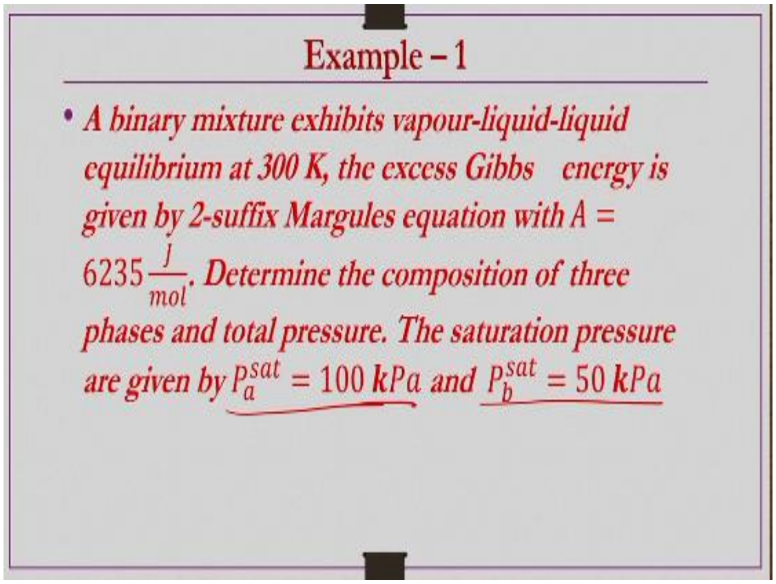

Example – 1

- A binary mixture exhibits vapour-liquid-liquid equilibrium at 300 K, the excess Gibbs energy is given by 2-suffix Margules equation with A = 6235 $\frac{J}{mol}$. Determine the composition of three phases and total pressure. The saturation pressure are given by $P_a^{sat} = 100\ kPa$ and $P_b^{sat} = 50\ kPa$

So now what we have we will take an example problem, a binary mixture exhibit vapor liquid liquid equilibrium at 300 K, the excess gives energy is given by 2-suffix Margules equation with A = 6235 Joules per mole. Determine the composition of 3 phases and total pressure this saturation pressures are given as P_a^{sat} 100 kilopascals and P_b^{sat} 50 kilopascals that is 1 bar or it is approximately 1 bar $P_a^{sat}$and P_b^{sat} is approximately 0.5 bar.

So they are saturation pressure are very low so then what we can say the activity coefficients of these system of this whatever they do liquids are they here taken binary mixtures, so they can be treated as independent of pressure because this saturation pressures are low for these 2 components. We can treat the activity coefficients of this liquid system as independent of pressure.

So then that we can have a kind of segregation of LLE part from vapor part in the equilibrium relations of VLLE and then solve the equations as we have described previous slides.

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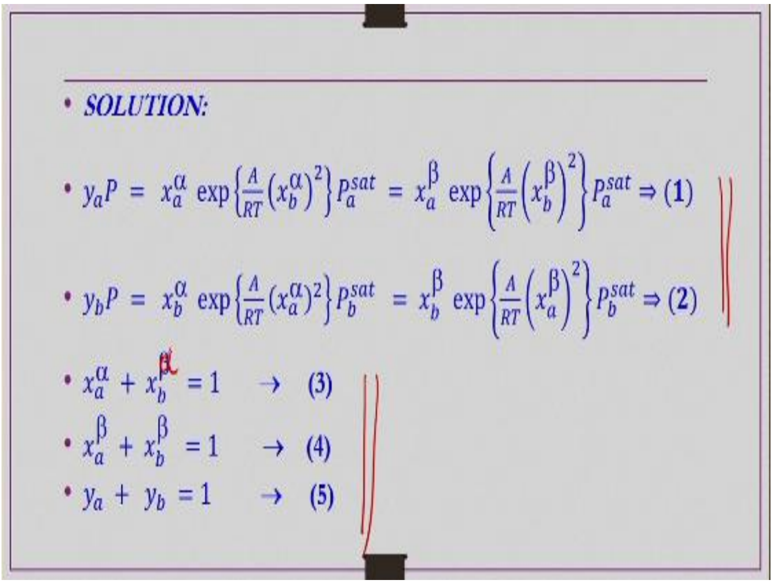

- ***SOLUTION:***
- $y_aP = x_a^{\alpha} \exp\left\{\frac{A}{RT}(x_b^{\alpha})^2\right\}P_a^{sat} = x_a^{\beta} \exp\left\{\frac{A}{RT}\left(x_b^{\beta}\right)^2\right\}P_a^{sat} \Rightarrow \mathbf{(1)}$
- $y_bP = x_b^{\alpha} \exp\left\{\frac{A}{RT}(x_a^{\alpha})^2\right\}P_b^{sat} = x_b^{\beta} \exp\left\{\frac{A}{RT}\left(x_a^{\beta}\right)^2\right\}P_b^{sat} \Rightarrow \mathbf{(2)}$
- $x_a^{\alpha} + x_b^{\cancel{\beta}\alpha} = 1 \quad \rightarrow \quad (3)$
- $x_a^{\beta} + x_b^{\beta} = 1 \quad \rightarrow \quad (4)$
- $y_a + y_b = 1 \quad \rightarrow \quad (5)$

So we have for component a and then component b we have this relations. Now for liquid α phase $x_a^{\alpha} + x_b^{\alpha}$ should be 1 and then a liquid β phase $x_a^{\beta} + x_b^{\beta}$ should be 1 and for the vapor phase $y_a + y_b$ should be 1, these are the relations. So how to solve them? We have to solve these equations non-linear equations in accordance with these things and this equation should be satisfied then only we can say the reliable solution.

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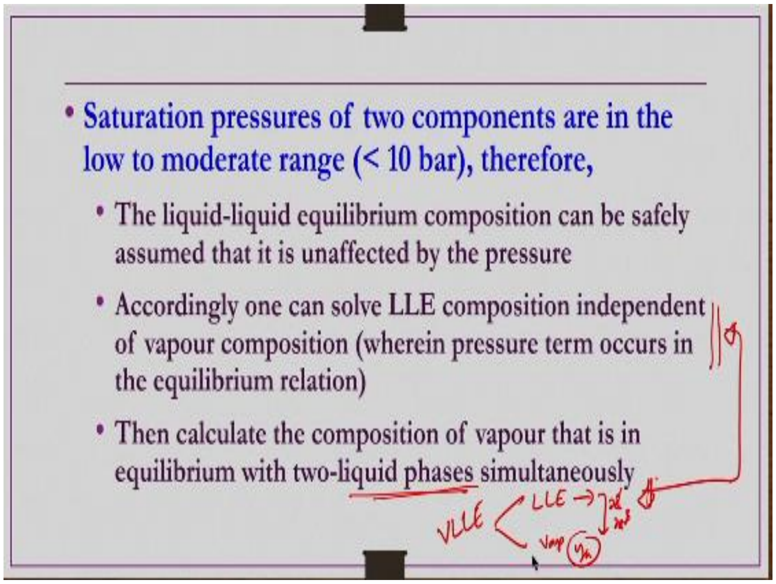

- Saturation pressures of two components are in the low to moderate range (< 10 bar), therefore,
  - The liquid-liquid equilibrium composition can be safely assumed that it is unaffected by the pressure
  - Accordingly one can solve LLE composition independent of vapour composition (wherein pressure term occurs in the equilibrium relation)
  - Then calculate the composition of vapour that is in equilibrium with two-liquid phases simultaneously

Saturation pressures of 2 components are in the low to moderate range therefore the liquid-liquid equilibrium composition can be safely assumed that it is unaffected by the pressure. Accordingly one can solve LLE composition independent of vapor composition wherein the pressure term occurs in the equilibrium relation in this equation number 1 and 2, whatever every term in the previous slide.

Then calculate the composition of vapor that is in equilibrium with the 2 liquid phases simultaneously for whose composition we have already obtained by this LLE calculations. So this VLLE problem what we are doing we are segregating as first LLE problem finding out their composition and then using this composition that is $x_a^\alpha$and then x_a^βthat we are using and then finding out the vapor composition that is y_a that way we are doing.

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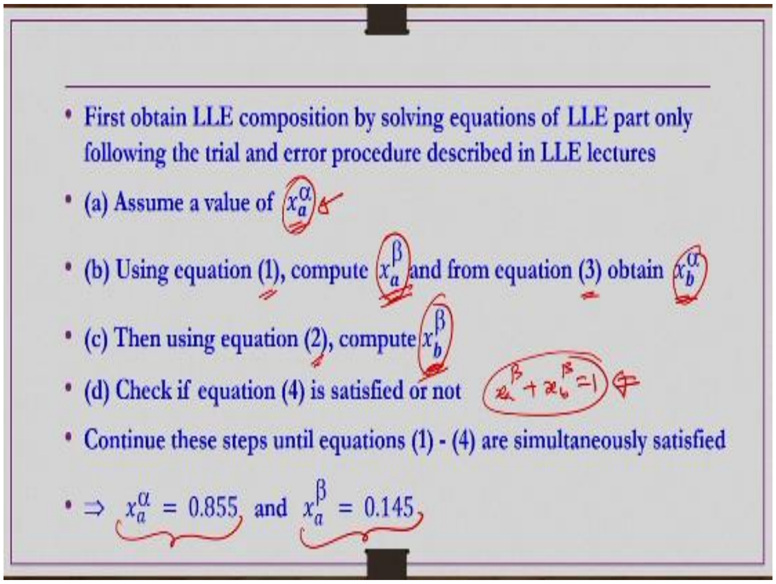

- First obtain LLE composition by solving equations of LLE part only following the trial and error procedure described in LLE lectures
- (a) Assume a value of x_a^α
- (b) Using equation (1), compute x_a^β and from equation (3) obtain x_b^α
- (c) Then using equation (2), compute x_b^β
- (d) Check if equation (4) is satisfied or not $x_a^\beta + x_b^\beta = 1$
- Continue these steps until equations (1) - (4) are simultaneously satisfied
- $\Rightarrow \underbrace{x_a^\alpha = 0.855}$ and $\underbrace{x_a^\beta = 0.145}$

Because the pressure is in the low to moderate range. So first obtain the LLE composition by solving equations of LLE part only following the trial and error solution procedure described in LLE lectures. What we have done there, we have to assume a value of $x_a^\alpha$and then using equation 1 in the previous slide I have written, compute $x_a^\beta$and then from equation 3 you obtain, what is x_b^α.

Then using equation 2 you computex_b^β, so now all the values are obtained x_a^α, x_b^α, x_a^β, x_b^β you have got, though it is starting assumed values. Then you have to check if equation 4 is satisfied or not that is $x_a^\beta + x_b^\beta = 1$ or not, this is what we have to check. Why we have to check because this x_a^β and x_b^βwe are calculating this using equation 1 and 2 which are the primary equations of LLE.

So if this obtain x_a^β and then x_b^β when you add them together if it is coming close to 1 then assume the value of x_a^α is reliable and then that can be taken as a solution. Other ways what you have to do you are to assume another value of x_a^α and then repeat the calculation until this equation satisfies. Continue these steps until equations 1, 2, 4 are simultaneously satisfied.

So then when you do this thing then you will find x_a^α = 0.855 for this problem and then x_a^β you will be getting 0.145 for this problem.

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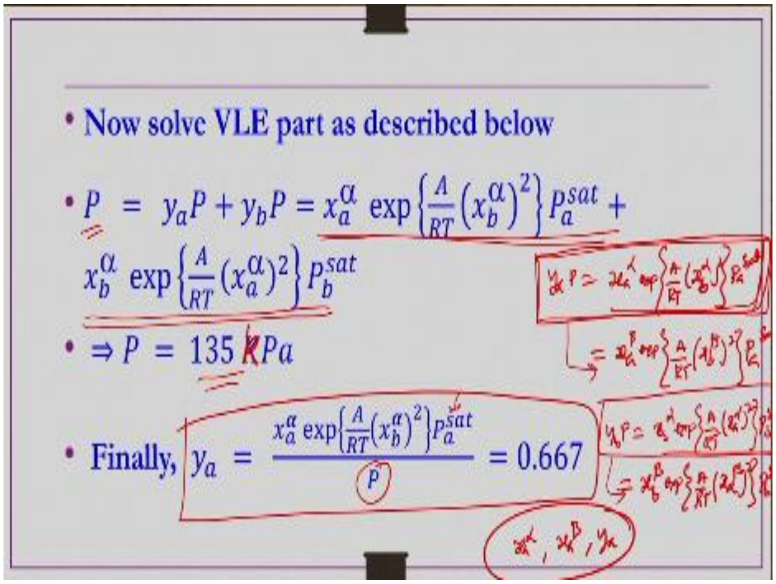

- Now solve VLE part as described below
- $P = y_a P + y_b P = x_a^\alpha \exp\left\{\frac{A}{RT}\left(x_b^\alpha\right)^2\right\} P_a^{sat} + x_b^\alpha \exp\left\{\frac{A}{RT}\left(x_a^\alpha\right)^2\right\} P_b^{sat}$
- $\Rightarrow P = 135\ kPa$
- Finally, $y_a = \dfrac{x_a^\alpha \exp\left\{\frac{A}{RT}\left(x_b^\alpha\right)^2\right\} P_a^{sat}}{P} = 0.667$

$y_a P = x_a^\alpha \exp\left\{\frac{A}{RT}(x_b^\alpha)^2\right\} P_a^{sat}$

$= x_a^\beta \exp\left\{\frac{A}{RT}(x_b^\beta)^2\right\} P_a$

$y_b P = x_b^\alpha \exp\left\{\frac{A}{RT}(x_a^\alpha)^2\right\}$

$= x_b^\beta \exp\left\{\frac{A}{RT}(x_a^\beta)^2\right\}$

x^α, x^β, y_a

So now solve VLE part as described below, so what you can do you can take this equation, 2 equations are there whatever P = y_a P + y_b P = this one + this one. Whatever the equation number 1 and 2 are there, if you add them together then we have this equation. Because that we have written for component a and component b as well. So we are taking for the component a part for that you can do.

You can take, I mean like we can take this vapor and then α liquid phase part that we have taken. So you can take vapor and then β liquid phase also and then similarly you can find out the pressure. So then you will get P = 135 kilopascal and then y_a = $\frac{x_a^\alpha exp\{\frac{A}{RT}(x_b^\alpha)^2\} P_a^{sat}}{P}$ = 0.667, so that is your equating this equation probably i will write again. So y_a P = $x_a^\alpha exp\left\{\frac{A}{RT}(x_b^\alpha)^2\right\} P_a^{sat}$ is there and then this is also equals to $x_a^\beta exp\left\{\frac{A}{RT}\left(x_b^\beta\right)^2\right\}P_a^{sat}\ x_a^\beta$. This is one equation for component 1 and similarly if you write for the component 2 that is y_b P = $x_b^\alpha exp\left\{\frac{A}{RT}(x_a^\alpha)^2\right\}P_b^{sat}$ = $x_b^\beta exp\left\{\frac{A}{RT}\left(x_a^\beta\right)^2\right\}P_b^{sat}$.

So what have I done, I have taken only this part of 2 equations and then added them together then I have this equation y_a P + y_b P so that is nothing but P into y_a + y_b that is P and then equals to this particular part of you know from component a this particular part and then from component b this particular part. You can do other way also y_a P you can take equal to this part and then y_b P you can take equal to this part and then the obtained pressure you can get the same thing.

And then for y_a again, once I found P, I have used only this part of the equation to find out this y_a. That is $\frac{x_a^\alpha exp\left\{\frac{A}{RT}(x_b^\alpha)^2\right\}P_a^{sat}}{P}$ when I substitute all these values because P_a^{sat}, P_a^{sat}values are given in the problem x_a^α, x_a^βwe have already found so x_b^α $x_b^\beta$are found anyway A is also given temperature is also given everything is known and then pressure we just now found it as 135 kilopascals, so then it comes out to be 0.667 so pressures kilopascal, small k should be there.

So this is how we can see, now x_a^αwe found. So x_a^β we found and then y_a also found, that is all 3 phases α liquid, β liquid and the vapor phase are coexisting and they are at equilibrium and then coexisting and equilibrium so their composition we have found doing this way by segregating, so this is how we can solve this problem.

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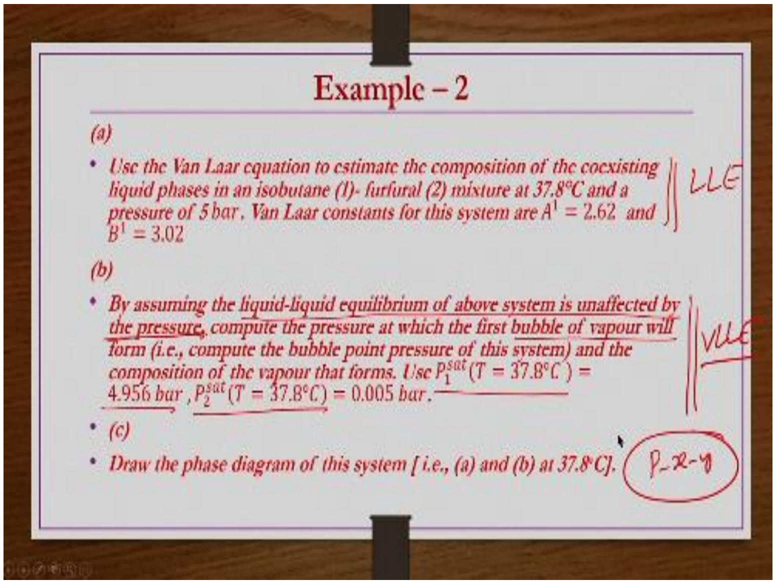

Example – 2

(a)

- *Use the Van Laar equation to estimate the composition of the coexisting liquid phases in an isobutane (1)- furfural (2) mixture at 37.8°C and a pressure of 5 bar. Van Laar constants for this system are $A^1 = 2.62$ and $B^1 = 3.02$*

LLE

(b)

- *By assuming the liquid-liquid equilibrium of above system is unaffected by the pressure, compute the pressure at which the first bubble of vapour will form (i.e., compute the bubble point pressure of this system) and the composition of the vapour that forms. Use $P_1^{sat}(T = 37.8°C) =$ 4.956 bar, $P_2^{sat}(T = 37.8°C) = 0.005$ bar.*

VLLE

- *(c)*
- *Draw the phase diagram of this system [i.e., (a) and (b) at 37.8°C].*

P-x-y

Now what we do we take another example problem. Use the Van Laar equation to estimate the composition of the coexisting liquid phases in an iso-butane and furfural mixture at 37.8 degree centigrade and a pressure of 5 bar. Van Laar constants for this system are given as A^1 is nothing but 2.62 and B^1 is nothing but 3.02. So that is first part that is only LLE part is there, there is no vapor.

In the second part by assuming the liquid-liquid equilibrium of above system is unaffected by pressure it is given already given so we do not need to make an assumption or we do not need to check out the vapor pressure saturation pressures or the total pressure of the system. This already given that assuming the LLE of above system is unaffected by the pressure, compute the pressure at which the first bubble of vapor will form that is computing the bubble point pressure of this system is required and also composition of the vapor that forms.

P_1^{sat} at this temperature and then P_2^{sat} at the same 37.8 degree centigrade are given P_1^{sat} is 4.956 bar and then P_2^{sat} is 0.005. The saturation pressures are anyway very small so then obviously the activity coefficients of liquid phases are the LLE behavior will be unaffected by the pressure. So now here this is VLLE part coming into picture, but VLLE part is such a way that LLE part can be segregated from the vapor part in solving this problem.

Because LLE part is unaffected by the pressure that is already given and also you have to draw the phase diagram of this system that is we have to draw P-x-y diagram for this system.

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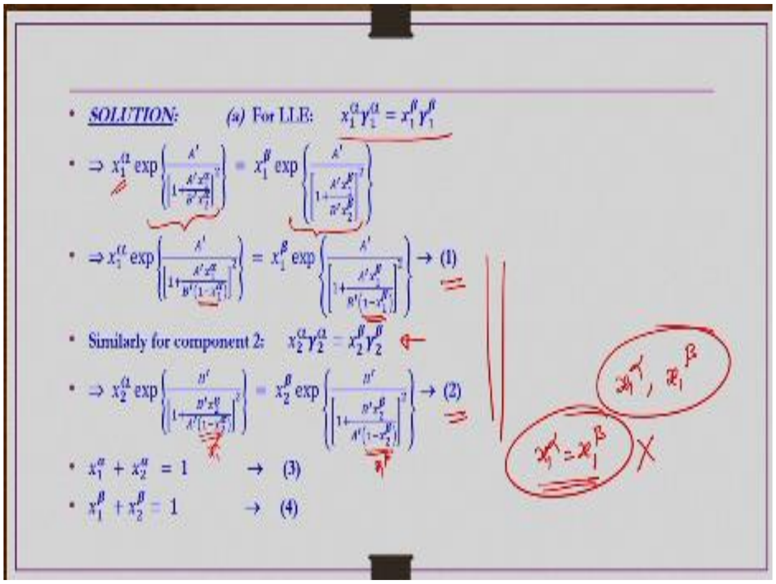

- ***SOLUTION:*** *(a)* For LLE: $x_1^\alpha\gamma_1^\alpha = x_1^\beta\gamma_1^\beta$
- $\Rightarrow x_1^\alpha \exp\left\{\frac{A'}{\left[1+\frac{A'x_1^\alpha}{B'x_2^\alpha}\right]^2}\right\} = x_1^\beta \exp\left\{\frac{A'}{\left[1+\frac{A'x_1^\beta}{B'x_2^\beta}\right]^2}\right\}$
- $\Rightarrow x_1^\alpha \exp\left\{\frac{A'}{\left[1+\frac{A'x_1^\alpha}{B'(1-x_1^\alpha)}\right]^2}\right\} = x_1^\beta \exp\left\{\frac{A'}{\left[1+\frac{A'x_1^\beta}{B'(1-x_1^\beta)}\right]^2}\right\} \rightarrow (1)$
- Similarly for component 2: $x_2^\alpha\gamma_2^\alpha = x_2^\beta\gamma_2^\beta$
- $\Rightarrow x_2^\alpha \exp\left\{\frac{B'}{\left[1+\frac{B'x_2^\alpha}{A'(1-x_2^\alpha)}\right]^2}\right\} = x_2^\beta \exp\left\{\frac{B'}{\left[1+\frac{B'x_2^\beta}{A'(1-x_2^\beta)}\right]^2}\right\} \rightarrow (2)$
- $x_1^\alpha + x_2^\alpha = 1 \quad \rightarrow \quad (3)$
- $x_1^\beta + x_2^\beta = 1 \quad \rightarrow \quad (4)$

x_1^α, x_1^β

$x_1^\alpha = x_1^\beta$ X

So for LLE component 1 and 2 take $x_1^\alpha\gamma_1^\alpha = x_1^\beta\gamma_1^\beta$ for component 1, so x_1^α and then γ_1^α for Van Laar equation is nothing but exp $\left\{\frac{A'}{\left[1+\frac{A'x_1^\alpha}{B'x_2^\alpha}\right]^2}\right\}$ = x_1^β and then γ_1^β is nothing but exp $\left\{\frac{A'}{\left[1+\frac{A'x_1^\beta}{B'x_2^\beta}\right]^2}\right\}$.

So this equations for the γ for Van Laar equation that we have already derived in previous lectures. This A' B' are given only thing that we have to find out what is this x_1^α and x_1^β these things you have to find out, this is for component 1. Similarly if you write for component 2 before writing component 2 what we do, we write this entire equation in terms of x_1 so wherever x_2 is there we will be writing 1 - x_1.

So that this entire equation is in terms of x_1^α and x_1^β because rest everything is given A', B' etc. are given or A_1, B_1 are given. So now for component 2 similarly LLE relation if you write is nothing but $x_2^\alpha\ \gamma_2^\alpha = x_2^\beta\ \gamma_2^\beta$. That is x_2^α exp $\left\{\frac{B'}{\left[1+\frac{B'x_2^\alpha}{A'(1-x_2^\alpha)}\right]^2}\right\}$.

But you know I am writing x_1^α is nothing but 1 - x_2^α so that this entire equation is in terms of x_2^α, and this part is square of this part is there = x_2^β and then γ_2^β is nothing but exp $\left\{\frac{B'}{\left[1+\frac{B' x_2^\beta}{A' x_1^\beta}\right]^2}\right\}$ I am writing 1 - x_2^β. So that this entire equation is in terms of x_2^α and x_2^β.

So now we have 2 equations and then 2 unknowns. x_1^α and then x_1^β because if x_1^α is known x_2^α is anyway known, x_1^β is known x_2^β be any way known for a binary system. So this equation may not be sufficient because if you solve only this equation by taking that $x_1^\alpha = x_1^\beta$ any value of x_1 in α phase and β phase if you take and then equate them then this equation would be satisfied as we have already seen.

But that is not the correct solution because that should also satisfy this equation $x_1^\alpha + x_2^\alpha = 1$ and $x_1^\beta + x_2^\beta = 1$. Obviously in equations exponential terms are there non-linear equations are there very difficult to solve. So one can use the numerical tools that are available to solve this equations or one can go for trial and error solution method as we have seen previously.

So all these equations 1, 2, 3 and 4 how to be simultaneously solved in order to get the solution and then all this equations you know, solving analytical is very difficult so one can apply numerical methods to get this solutions or otherwise one can follow the trial under approach that we have already discussed. So the same thing we are going to follow here again.

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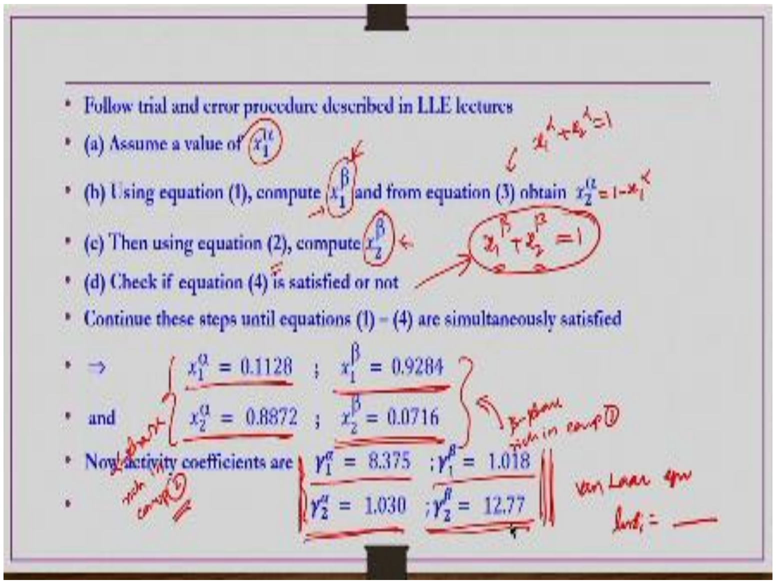

- Follow trial and error procedure described in LLE lectures
- (a) Assume a value of x_1^α
- (b) Using equation (1), compute x_1^β and from equation (3) obtain $x_2^\alpha = 1 - x_1^\alpha$
- (c) Then using equation (2), compute x_2^β
- (d) Check if equation (4) is satisfied or not
- Continue these steps until equations (1) – (4) are simultaneously satisfied
- ⇒ $x_1^\alpha = 0.1128$; $x_1^\beta = 0.9284$
- and $x_2^\alpha = 0.8872$; $x_2^\beta = 0.0716$
- Now activity coefficients are $\gamma_1^\alpha = 8.375$; $\gamma_1^\beta = 1.018$
- $\gamma_2^\alpha = 1.030$; $\gamma_2^\beta = 12.77$

$x_1^\alpha + x_2^\alpha = 1$

$x_1^\beta + x_2^\beta = 1$

β-phase rich in comp ①

α-phase rich in comp ②

Van Laar eqn

$\ln \gamma_i =$ —

So follow trial and error pressure described in LLE lectures that is first assumed a value of x_1^α then solve equation number 1 to get x_1^β. And then from equation 3, equation 3 is nothing but $x_1^\alpha + x_2^\alpha = 1$. So x_1^α we have already assumed so x_2^α you can find it all what is 1 - x_1^α. So that is x_2^α. Once you know, x_2^α using that x_2^α. You can solve this equation number 2 to get x_2^β.

So x_1^α we assume and then $x_1^\beta x_2^\beta$ we calculated. So now this x_1^β, actually x_1^β and then this x_2^β when you add them together they should come equals to 1, but now what we are doing we are getting this x_1^β and then x_2^β we are calculating from 2 different equations. So that is the reason we have to check now $x_1^\beta + x_2^\beta = 1$ is it coming equals to 1 or not.

If it is coming equals to 1 then solution is reliable are assumed x_1^α is reliable and then obtained x_1^β is correct value. If that is not coming to 1 then we have to repeat these steps, check if equation 4 is satisfied or not, equation 4 is nothing but this $x_1^\beta + x_2^\beta = 1$. So if this equation 4 is not satisfied by independently finding out x_1^β and then x_2^β from 2 different equation.

And then by adding them together if they are not coming equals to 1 that means that it assumed value of x_1^α is not correct and then we have to update this x_1^α or assume another value of x_1^α and then continue the pressure till we satisfy this equation. Continue these steps until equations 1 to 4 are simultaneously satisfied and then get the answer. So when you follow this procedure then you can find out $x_1^\alpha$is nothing but 0.1128 and $x_1^\beta$is nothing but 0.9284.

Similarly $x_2^\alpha$is nothing but 0.8872 and then $x_2^\beta$is nothing but 0.0716. What we can understand from this solutions this α phase is rich in component 2, whereas this β phase rich in component 1. The component 1 is almost 92 or 93 % in β phase, whereas component 1 is very small in α phase and the α phase component 2 is very rich almost 88, 89% of moles of that the α phase are of component 2.

So that is α phase is rich in component 2 and then β phase is rich in component 1. So now we have to find out activity coefficients also because the how to use them for calculating this y_a composition as well so γ_1^αyou can get 8.375 and γ_1^β 1.018 and then γ_2^α 1.030 and then γ_2^β12.77, these are using the Van Laar equations.

Van Laar equations, whatever ln γ expression that we have in terms of A', B' so they can be used for both phases, α and β phases and then simply substitution of this x_1^α $x_2^\alpha x_1^\beta x_2^\beta$ etc. in those equations, you can substitute and then get this equation. At the beginning of this solution of this problem, we have this equation detail. So there you can simply substitute thisγ_1^α.

And whatever the x_2^α information is required that you substitute because A', B' are anyway given. Similarly for the case of γ_1^βwhatever the x_2^β information is required that you got already so you substitute because here also A', B' are known same A', B' are there. Similarly γ_2^α γ_2^β also you can find out. So now for VLLE what we can have.

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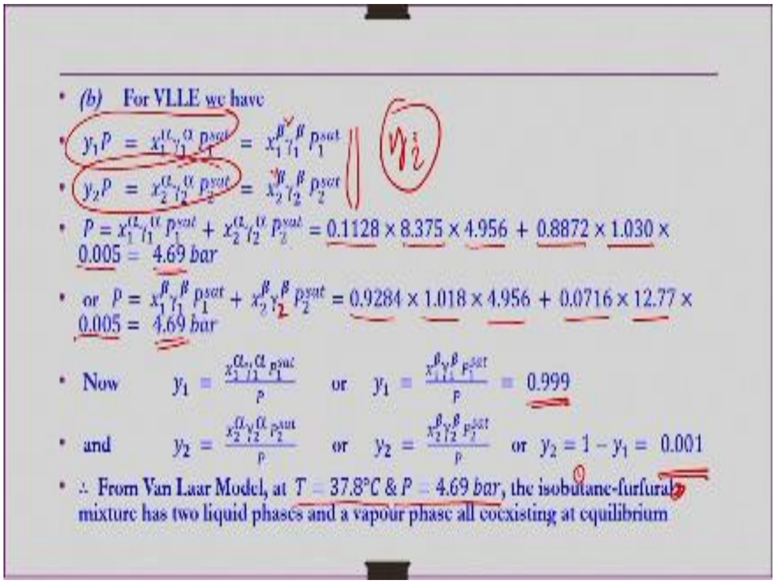

- (b) For VLLE we have
- $y_1P = x_1^{\alpha}\gamma_1^{\alpha}P_1^{sat} = x_1^{\beta}\gamma_1^{\beta}P_1^{sat}$
- $y_2P = x_2^{\alpha}\gamma_2^{\alpha}P_2^{sat} = x_2^{\beta}\gamma_2^{\beta}P_2^{sat}$

γ_i

- $P = x_1^{\alpha}\gamma_1^{\alpha}P_1^{sat} + x_2^{\alpha}\gamma_2^{\alpha}P_2^{sat} = 0.1128 \times 8.375 \times 4.956 + 0.8872 \times 1.030 \times 0.005 = 4.69\ bar$
- or $P = x_1^{\beta}\gamma_1^{\beta}P_1^{sat} + x_2^{\beta}\gamma_2^{\beta}P_2^{sat} = 0.9284 \times 1.018 \times 4.956 + 0.0716 \times 12.77 \times 0.005 = 4.69\ bar$
- Now $y_1 = \frac{x_2^{\alpha}\gamma_1^{\alpha}P_1^{sat}}{P}$ or $y_1 = \frac{x_1^{\beta}\gamma_1^{\beta}P_1^{sat}}{P} = 0.999$
- and $y_2 = \frac{x_2^{\alpha}\gamma_2^{\alpha}P_2^{sat}}{P}$ or $y_2 = \frac{x_2^{\beta}\gamma_2^{\beta}P_2^{sat}}{P}$ or $y_2 = 1 - y_1 = 0.001$
- ∴ From Van Laar Model, at $T = 37.8°C$ & $P = 4.69\ bar$, the isobutane-furfural mixture has two liquid phases and a vapour phase all coexisting at equilibrium

We can have $y_1P = x_1^{\alpha}\ \gamma_1^{\alpha}\ P_1^{sat} = x_1^{\beta}\ \gamma_1^{\beta} P_1^{sat}$. So this is for the component 1. Similarly for component 2 if you have $y_2P = x_2^{\alpha}\ \gamma_2^{\alpha}\ P_2^{sat} = x_2^{\beta}\ \gamma_2^{\beta}\ P_2^{sat}$. So this is nothing but f_l^v will be this is nothing but f_l^{α} this particular part and this particular part is nothing but f_l^{β}.

Similarly this particular part is nothing but f_2^{β}. This particular path is nothing but f_2^{α}. This particular part is nothing but f_2^v which are at equilibrium and coexisting. Now, if you wanted to find out this y_1, or y_2, you need to know P that is now given. So first what you have to do you have to find out what is the pressure? So for that what you can do, you can add these 2 parts $y_1P = x_1^{\alpha}\ \gamma_1^{\alpha} P_1^{sat}$ + the other equation $y_2P = x_2^{\alpha}\ \gamma_2^{\alpha} P_2^{sat}$.

So then we get, so when you add these 2 then we have $y_1P + y_2P$, that is nothing but $P = x_1^{\alpha}, \gamma_1^{\alpha}\ P_1^{sat}\ + x_2^{\alpha}\ \gamma_2^{\alpha}\ P_2^{sat}$. So x_1^{α} you find out this one, γ_1^{α} you obtain this one. P_1^{sat} is given this one and the next 2 α you obtained as this one and then γ to α you obtained it as this one and then P_2^{sat} is given as this one when you substitute all these things you will get 4.69 bar.

You can add these 2 parts also you can add that is why y_iP part if you equate with this β phase equations then also you can get that is P = or $y_1P + y_2P$ is nothing but P and then that equals to $x_1^{\beta}\ \gamma_1^{\beta} P_1^{sat} + x_2^{\beta}\ \gamma_2^{\beta}\ P_2^{sat}$ this one also you can do. x_1^{β} you got it as 0.9234, x_1^{β} this is what you got. P_1^{sat} it is given 4.956 and then x_2^{β} you obtain this one and then γ_1^{β} you obtained it as and then

γ_2^β you obtained as 12.77 and then P_2^{sat} is given as 0.005 then also you are getting 4.69 bar.

Either way you can get it, so once the pressure is known then you can use either this part of the equation or this part of the equation. Any equation you can use and then find out the y_2 because in these 2 equations now only unknown is y_n that is y_1, y_2, if one is known another one can be known so y_1 you can write it as $\frac{x_1^\alpha \gamma_1^\alpha P_1^{sat}}{P}$ or $\frac{x_1^\beta \gamma_1^\beta P_1^{sat}}{P}$.

Also you can do when you do you will get 0.999. So at this pressure the vapor is almost pure in component 1. Only small amount of negligible amount of component 2 is there in the vapor phase. So y_2^α you can get $\frac{x_2^\alpha \gamma_2^\alpha P_2^{sat}}{P}$ or $\frac{x_2^\beta \gamma_2^\beta P_2^{sat}}{P}$ you can do then you can get y_2 as 0.001 or you can simply do 1 - y_1 then you will get y_2 as 0.001.

So now equilibrium composition of VLLE also we obtained. We obtain the equilibrium composition of VLLE part as well. So now what we have to do. We have to draw phase diagram, so from Van Laar model it is 37.8 degrees centigrade and 4.69 bar, the iso-butane that is component 1 and then furfural mixture that is component 2 has 2 liquid phases and a vapor phase all coexisting at equilibrium. Though the vapor phase is having you know, almost pure iso-butane.

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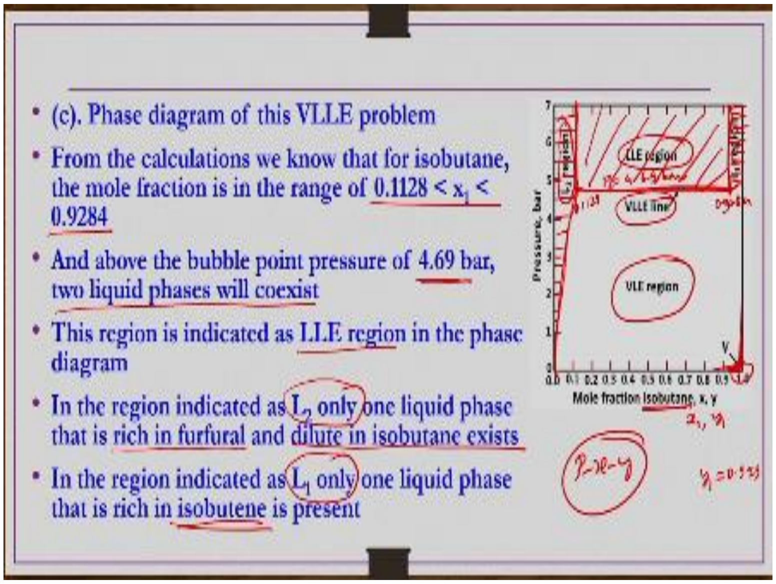

- (c). Phase diagram of this VLLE problem
- From the calculations we know that for isobutane, the mole fraction is in the range of $0.1128 < x_1 < 0.9284$
- And above the bubble point pressure of 4.69 bar, two liquid phases will coexist
- This region is indicated as LLE region in the phase diagram
- In the region indicated as L_2 only one liquid phase that is rich in furfural and dilute in isobutane exists
- In the region indicated as L_1 only one liquid phase that is rich in isobutene is present

So now will be drawing phase diagram of the system. The pressure that we got 4.69 bar so there this one that line so from the calculation we know that for iso-butane so as x_1 we are plotting, x_1 and then y_1 we are plotting P versus x_1, y_1 that is what we are calculating because temperature is fixed pressure. I know we can find out for different x_1, y_1, x_2, y_2 for different phases. A and β liquid phases and then vapor phase also we can know the calculation from this equation and then you can draw this figure.

The iso-butane mole fraction we have seen that it is changing in the range of 0.1128 to 0.9284 and above the bubble point pressure of 4.69 bar only 2 liquid phases will exist so first that is what we try to locate, we try to have the line, you know up to this part, you know what we have we line up for P = 4.69 bar system pressure. And then we locate a mole fraction 0.1128 and then 0.9284 and then above this pressure we know only liquid phases would be there and then 2 liquids are co-existing.

So above this pressure LLE region would be there, so draw a line from here like this at point small fraction 0.1128 and then 0.9284 here and then along this tie line pressure. So this region will be having only LLE region. Below this region we will be having VLLE region and then this line is nothing but VLLE line and then we know this L_2 region small in this iso-butane fraction is rich in the other components.

So this other component is whatever furfural so this region, whatever this is there x liquid 2 regions that is you know, furfural region. So whatever the reason above this pressure of 4.69 bar is there that is LLE region indicated as LLE region in the phase diagram. This is how we can construct this phase diagrams and then the reason indicated as L_2 only whatever this region is there, so that region only 1 liquid phase is existing that is region for furfural that is the 2nd component and dilute in iso-butane rich in furfural and dilute in isobutene.

So that region we are calling L_2 regions, so that line from here 0.1122 is 0 you can draw a line it is not exactly 0 whatever 0.012 composition that is there that we have found and the calculation that line, so what is almost close to 0 so this line you can combine like here. So this entire region now you have liquid 2 region are β liquid phase or second liquid phase which is region furfural.

And then whatever the reason L_1 is there that is rich in isobutene so you can see this region and entire region is L_1 is rich in isobutene. So this is what we can have so this L_l region is rich in isobutene because larger x_1 side because you are plotting isobutene and so larger that is it pure liquid is there and then there is a vapor phase also that vapor phase is there only you know, y_1 0.999 almost touching this right scale here.

So only this small region there is a vapor only this small region close to this corner right corner here you have a vapor phase. So now you can have this P-x-y diagram in constant temperature.

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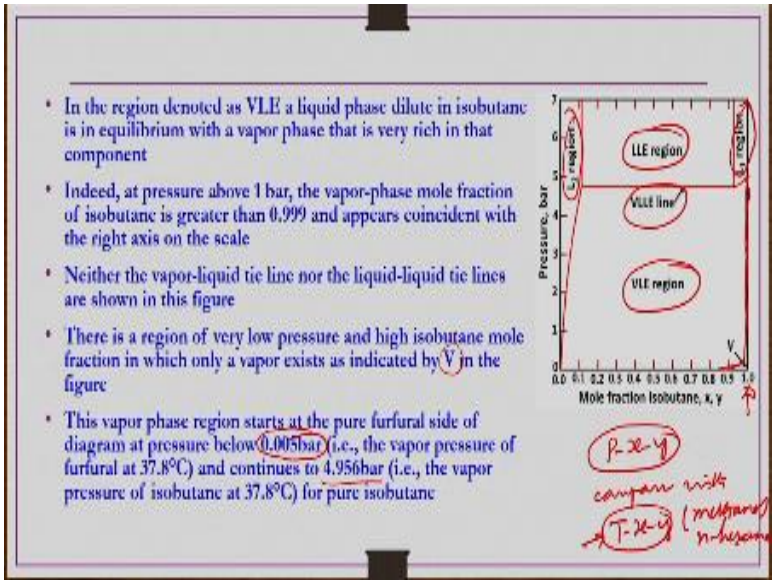

- In the region denoted as VLE a liquid phase dilute in isobutane is in equilibrium with a vapor phase that is very rich in that component
- Indeed, at pressure above 1 bar, the vapor-phase mole fraction of isobutane is greater than 0.999 and appears coincident with the right axis on the scale
- Neither the vapor-liquid tie line nor the liquid-liquid tie lines are shown in this figure
- There is a region of very low pressure and high isobutane mole fraction in which only a vapor exists as indicated by V in the figure
- This vapor phase region starts at the pure furfural side of diagram at pressure below 0.005bar (i.e., the vapor pressure of furfural at 37.8°C) and continues to 4.956bar (i.e., the vapor pressure of isobutane at 37.8°C) for pure isobutane

So in the region denoted VLE a liquid phase dilute in isobutene is in equilibrium with a vapor phase that is rich in that component, so this, that is the VLE region. So now we indicated a LLE region we indicated the furfural rich liquid region, we indicated the isobutene rich liquid region and then we indicated the VLE region also which is where vapor, you know, is in equilibrium with a liquid phase which is diluting isobutene that is what we can see.

That also indicated so indeed at pressure above 1 bar the vapor phase mole fraction is mole fraction of iso-butane is greater than 0.111 and appears coinciding with the right axis on the scale shown here. So neither the vapor-liquid tie line nor the liquid-liquid tie-lines are shown because we are interested in trying to phase diagram. So that at any given constant pressure a horizontal line if you draw so that tie lines accordingly there are different phase compositions you can find it out.

So now here you can compare. So there is a region of very low pressure and high iso-butane mole fraction in which only vapor exists as indicated by V here in the corner. Because y_1, we know it is 0.999, so that is the region it is there in this part. This vapor phase region starts at the pure furfural side of diagram at pressure below 0.005 bar that is the vapor pressure of furfural and continues to up to almost 5 bars that is 4.956 bar that is the vapor pressure of iso-butane for pure isobutene.

So this region this now this line you can see a very, almost touching this wall and then this line goes up to almost 5 bars like this. So this is vapor region. So now here what we can see if you compare this T-x-y diagram of Methanol n-hexane system, we can see there we in T-x-y diagram we have already seen in the previous lecture there was a kind of azeotrope minimum boiling azeotrope mixture this one at the given conditions.

But here in this P-x-y diagram there is no azeotrope at all because the vapor pressure of this iso-butane and then furfural are very much different from each other. So though there is a non-ideality in this iso-butane and furfural system. The vapor pressure of these components are far away from each other, so that is the reason there is no azeotrope here but still we have a kind of VLLE. So the reason which is operating LLE and then VLLE region here.

The straight line is whatever is there that is the VLLE line. So it is not necessary that we should always have a kind of azeotrope in order to have a kind of VLLE, it is not required. That is it is not necessary to have azeotrope in VLLE in order to have VLE considering with LLE before the temperature of the system rich in the upper constant temperature. That is not required that is as a one simple case they have taken in the previous lecture and discussed.

As already mentioned in previous lecture, different types of complicated phase diagrams may also possible. Now what we do quickly before winding up this lecture we have a comparison of whatever the phase diagrams we have seen in couple of minutes and then wind up the lecture.

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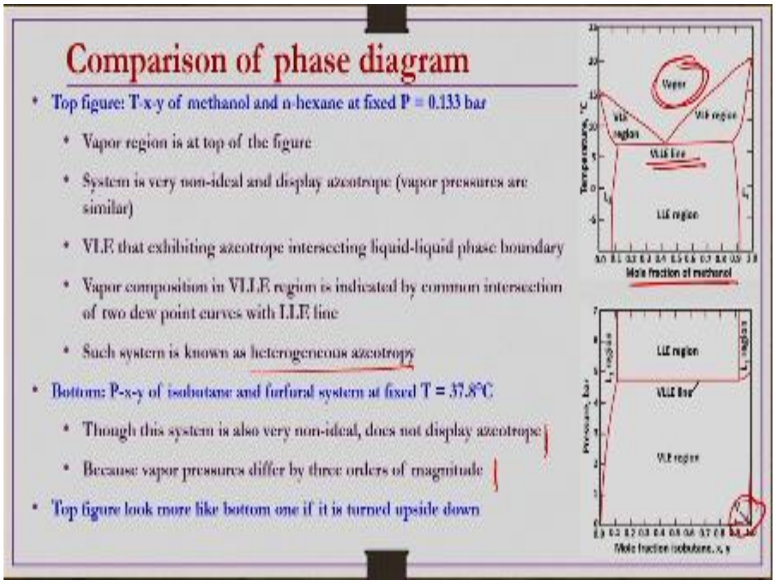

Comparison of phase diagram

- Top figure: T-x-y of methanol and n-hexane at fixed P = 0.133 bar
  - Vapor region is at top of the figure
  - System is very non-ideal and display azeotrope (vapor pressures are similar)
  - VLE that exhibiting azeotrope intersecting liquid-liquid phase boundary
  - Vapor composition in VLLE region is indicated by common intersection of two dew point curves with LLE line
  - Such system is known as heterogeneous azeotropy
- Bottom: P-x-y of isobutane and furfural system at fixed T = 37.8°C
  - Though this system is also very non-ideal, does not display azeotrope
  - Because vapor pressures differ by three orders of magnitude
- Top figure look more like bottom one if it is turned upside down

Comparison of phase diagram. T-x-y diagram that we have drawn for Methanol n-hexane system in previous lecture is given here. T-x-y of Methanol n-hexane at fixed pressure of 0.133 bar is given shown here and then bottom figure indicates the P-x-y diagram of whatever the iso-butane and then furfural that we have just taken example problem we solve the problem and then draw this phase diagram.

So we are comparing these two. Bottom one is P-x-y of isobutene and furfural system and fixed temperature of 37.8 degree centigrade. In the T-x-y diagram here vapor region is at the top of the figure obviously. Because this is T-x-y and then whereas the vapor region here is T-x-y region at top. Whereas in P-x-y diagram the region is in the bottom at the lower pressure side. Then the system in T-x-y diagram system is very non ideal and display azeotrope because vapor pressure so far methanol n-hexane are almost close to each other.

They are very much similar to each other and close to each other, so that is the reason here azeotrope here. But in case of isobutene and furfural system though the system is non ideal, there is no azeotrope here, because vapor pressure of these 2 components differs from each other by order of 3 of magnitude. So because of this very different vapor pressure even though there is non-ideality in the system of isobutene and furfural, there is no azeotrope formation here.

Azeotrope formation may take place in general if this vapor pressure in the components are very close to each other and then VLE that exhibiting azeotrope intersecting the liquid-liquid phase boundary here in this case of T-x-y diagram and then we are having a kind of a VLLE line in the case of T-x-y diagram and then vapor composition VLE region is indicated by comma intersection of 2 dew point curves with LLE line.

As already discussed such system is known as heterogeneous azeotrope. Now further what we can do if you compare, if you do upside down of one of this figure you can see other one. So let us say the top figure T-x-y if you put it upside down you can see a kind of bottom figure you can get but without azeotrope in the bottom. So top figure look like bottom one if it is turned upside down and then there is no azeotrope kind of thing.

So finally this is how we can solve the problems associated with the vapor-liquid-liquid equilibrium and then construct phase diagram and then depending on the temperature and composition or depending on the pressure and composition one can indicate the different regions single liquid regions, two liquids region, vapor liquid region etc. all those things one can do.

And remember all these calculations we have done for the cases where the pressure is in low to moderate range, so that we can segregate the governing VLLE equations in 2 parts. LLE is independent of the pressure part and then solve the LLE composition independent of the pressure and then using the LLE composition you can find out the vapor composition so that we can find out the composition of all 3 phases that is 1 vapor phase and 2 liquid phase which are co-existing and at equilibrium.

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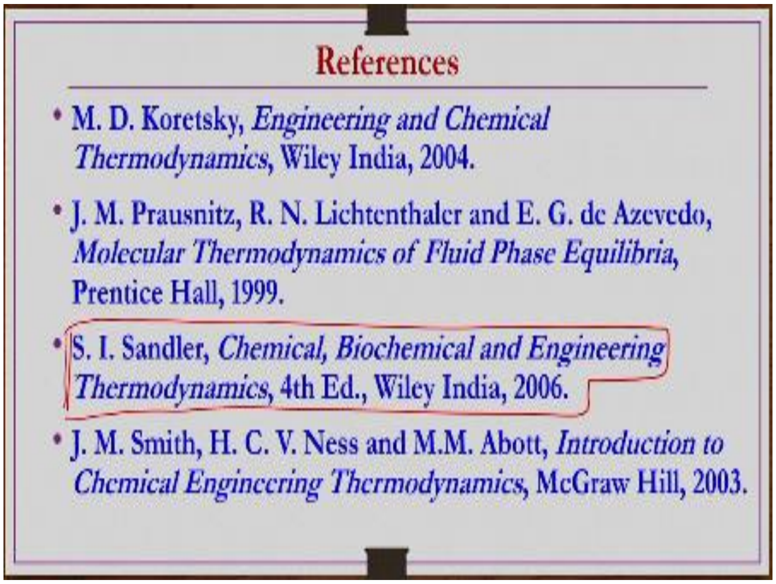

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So the references for this lecture are given here Engineering and chemical thermodynamics by Koretsky, Molecular Thermodynamics of Fluid Phase Equilibria by Prausnitz et al, Chemical biochemical and engineering Thermodynamics by Sandler and then Introduction to Chemical engineering thermodynamics by Smith et al. This entire lecture is prepared from this reference books that is Sandler. Chemical Biochemical and Engineering Thermodynamics by Sandler including the example problem discussed also the same in this particular reference book. Thank you.