Advanced Thermodynamics
Prof. Nanda Kishore
Department of Chemical Engineering
Indian Institute of Technology Guwahati, India

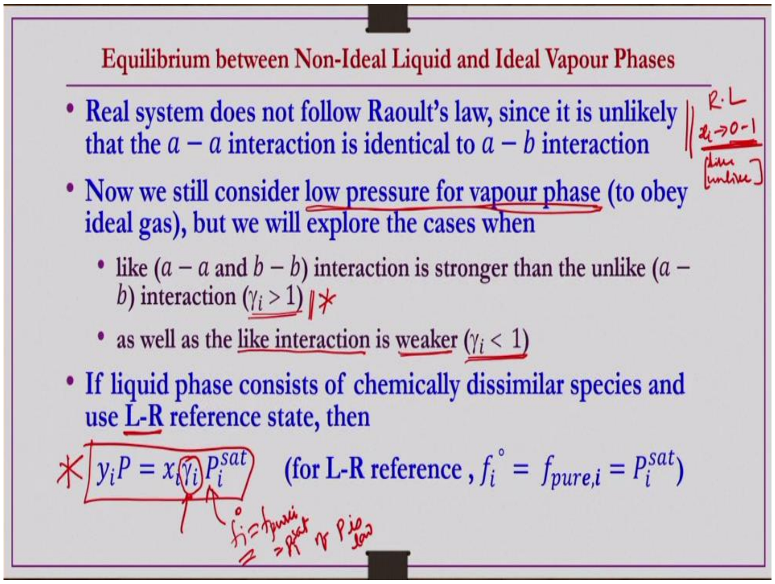
Lecture-24
Vapour - Liquid Equilibrium-2

Welcome to the MOOC course advanced thermodynamics the title of this lecture is vapour liquid equilibrium part 2. This is a continuation of our previous lecture in the previous lecture we have discussed several aspects of vapour liquid equilibrium, especially when both the phases are obeying a kind of ideal behavior. So, phase diagram how to do the dew point calculations bubble point calculations etc. those things we have seen.

Now in this lecture what we will be doing? We will be taking the same vapour liquid equilibrium case but when one of these phases exhibit as some kind of non-ideality. Or both the phases exhibit some amount of non ideality then how to bring in the non-ideality of you know either of the phases in the equations and then how to solve those equations in order to get the equilibrium composition of a multi component mixture when these phases obey non-ideality so, that is what we see.

So, now, what we do? First we start with a kind of non-ideality in liquid phase only, that is we take low pressure case, so, that the vapour phase still be behaving a kind of ideal, but the interactions among the molecules in the liquid phase are not you know, similar to each other for different possible interactions. So, that you know liquid phase is showing a kind of non-ideality, that case will be taking first.

(Refer Slide Time: 01:59)



Equilibrium between Non-Ideal Liquid and Ideal Vapour Phases

- Real system does not follow Raoult's law, since it is unlikely that the $a-a$ interaction is identical to $a-b$ interaction
- Now we still consider low pressure for vapour phase (to obey ideal gas), but we will explore the cases when
  - like ($a-a$ and $b-b$) interaction is stronger than the unlike ($a-b$) interaction ($\gamma_i > 1$) | *
  - as well as the like interaction is weaker ($\gamma_i < 1$)
- If liquid phase consists of chemically dissimilar species and use L-R reference state, then

$$* \boxed{y_i P = x_i \gamma_i P_i^{sat}} \quad (\text{for L-R reference}, f_i^\circ = f_{pure,i} = P_i^{sat})$$

So, equilibrium between non-ideal liquid and ideal vapour phases the real system does not follow Raoult's law, since it is unlikely that a-a interactions are quite identical to a-b interactions that is not possible in general. Actually this Raoult's law what does it mean? It says that you know a liquid is ideal in the entire range of x_i varying from 0 to 1 actually Lewis's fugacity rule say that the liquid obeys the ideal behavior in the limit $x_i \to 1$ whereas the Henry's law says that liquid obeys ideal behavior in the limit of $x_i \to 0$.

Whereas Raoult's law says that liquid obeys ideal behavior in the entire range of x_i from 0 to 1. So when you are saying for the entire enough x_i from 0 to 1, if the liquid is showing ideal behavior. That means indirectly you are saying that the like interactions and then unlike interactions are similar, then only it is possible and that liquid is in a liquid solution liquid mixture whatever is there that can be ideal only when like in unlike interactions are quite similar to each other for the entire range of x_i that is that then only it is possible.

But that is not true in most of the cases, in many cases it is not possible that you know in the entire range of x_i that liquid may be showing ideal behavior. That means in the entire range of x_i whatever the like interactions are a-a interactions and unlike interactions or a weak kind of interactions are there they cannot be quite similar to each other in the entire range of x_i. So, that means obviously, that liquid will start showing some kind of non ideality.

So, now what we do we take a low pressure. For vapour phase for the vapour or gas phase if the pressure is low, then we have seen that the vapour are that particular gas phase whatever is said that would be displaying a kind of ideal behavior. So, directly taking non-ideality of both vapour and liquid phases may become mathematically complicated to solve the problem. So, that is the reason we are starting with this case where we are taking the vapour phases ideal and then in order to have a vapour phase ideal.

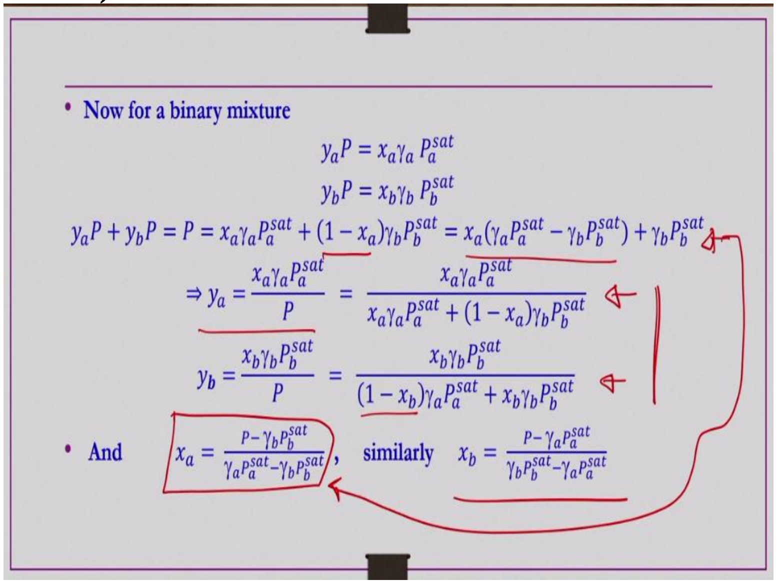
What is the essential criteria that you should maintain in the operational conditions that do your operation pressure should be low. If your operational pressure is low our system pressure is low then you can say that your vapour phase is ideal that case will take but we will be exploring the cases for the liquid phase 2 different cases when like interaction that is a-a interactions or b-b interactions or both of them are stronger than the unlike interaction that is a-b interactions.

So, if like interactions are stronger then we call it positive deviation from ideal behavior. Under such conditions activity coefficient is > 1 in general. So, that is what we see. So why it is > 1, what happens under these conditions etc. those things will take. And then we will also take the case where the like interactions like a-a interactions or b-b interactions or both a-a and b-b interactions are weaker than the unlike interactions, something like a-b interactions.

So under such conditions, the activity coefficient in general is < 1 and then we call such kind of system deviating negative deviation from ideal behavior. So either of the cases we will take and then see how to solve the problems. If the liquid phase consists of chemically dissimilar species and the L R reference state is taken, then we have already seen that $y_i P = x_i \gamma_i f_i^0$ and then chemically dissimilar species and then we are taking L R reference state. So, then we know that f_i^0 whatever $x_i \gamma_i f_i^0$ is there, f_i^0 should be $f_{\text{pure } i}$.

If you take L R Lewis Randal reference state and then $f_{\text{pure } i}$ is nothing but P_i^{sat} if pressure is low. So, that is what we have already seen in the previous lecture, only additional thing compared to the previous lecture is that now there is a non-ideality in the liquid phase and then that non-ideality has been brought in terms of γ_i. In this problem now we explored in detail in order to find out equilibrium combination y_i versus x_i let us say pressure and temperature are given.

(Refer Slide Time: 06:56)



- Now for a binary mixture

$$y_aP = x_a\gamma_a P_a^{sat}$$

$$y_bP = x_b\gamma_b P_b^{sat}$$

$$y_aP + y_bP = P = x_a\gamma_aP_a^{sat} + (1-x_a)\gamma_bP_b^{sat} = x_a(\gamma_aP_a^{sat} - \gamma_bP_b^{sat}) + \gamma_bP_b^{sat}$$

$$\Rightarrow y_a = \frac{x_a\gamma_aP_a^{sat}}{P} = \frac{x_a\gamma_aP_a^{sat}}{x_a\gamma_aP_a^{sat} + (1-x_a)\gamma_bP_b^{sat}}$$

$$y_b = \frac{x_b\gamma_bP_b^{sat}}{P} = \frac{x_b\gamma_bP_b^{sat}}{(1-x_b)\gamma_aP_a^{sat} + x_b\gamma_bP_b^{sat}}$$

- And $\boxed{x_a = \frac{P-\gamma_bP_b^{sat}}{\gamma_aP_a^{sat}-\gamma_bP_b^{sat}}}$, similarly $x_b = \frac{P-\gamma_aP_a^{sat}}{\gamma_bP_b^{sat}-\gamma_aP_a^{sat}}$

So now for a binary mixture if you write this way y_a P = x_a γ_a $P_a^{sat}$for binary mixture of a and b components, then we have y_a p = x_a γ_a P_a^{sat} then y_b P = x_b γ_b P_b^{sat}. If you add them together (y_a + y_b) P is nothing but P = x_a γ_a P_a^{sat}+x_b we can write as write it as (1 − x_a) γ_b P_b^{sat}. So, this you can write x_a (γ_a P_a^{sat} − γ_b P_b^{sat})+γ_b P_b^{sat}.

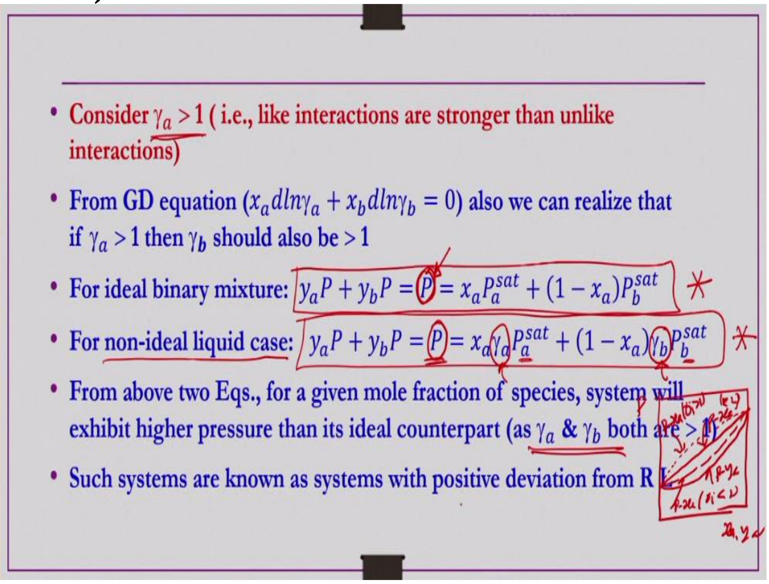
So, now, from this equation x_a you can find out if your pressure and temperature is known by $x_a = \frac{P-\gamma_bP_b^{sat}}{\gamma_bP_a^{sat}-\gamma_bP_b^{sat}}$. So, by using this equation you can find out. If x_a known then simply $y_a = \frac{x_a\gamma_aP_a^{sat}}{P}$ if x_a is known then γ_a is also known. So, that can be found and provided that constants of you know of the constants associated with the excess Gibbs energy for that liquid phase unknown.

So, then γ_a is also known that means, if you know the x_a. So, $\frac{x_a\gamma_aP_a^{sat}}{P}$if you do you know then y_a. So, this is what this equation you can use for finding out x_a to find in order to find out y_a. So, y_b similarly is nothing but $\frac{x_b\gamma_bP_b^{sat}}{P}$ that is $\frac{x_b\gamma_bP_b^{sat}}{(1-x_b)\gamma_aP_a^{sat}+x_b\gamma_bP_b^{sat}}$. So, these 2 equations can be used find out y_a or y_b or both on. So, these 2 equations can be used to find out the vapour phase mole fraction.

So, x_a as I already mentioned you can find out from this equation that is $\frac{P-\gamma_bP_b^{sat}}{\gamma_bP_a^{sat}-\gamma_bP_b^{sat}}$. Similarly x_b you can find it out as by rearranging this equation in terms of x_b then you will find

$x_b = \frac{P-\gamma_a P_a^{sat}}{\gamma_b P_b^{sat}-\gamma_a P_a^{sat}}$. So, these are the equation one can use to solve the problems in order to get the equilibrium composition of vapour liquid equilibrium case especially leaving liquid phase displaying some amount of non ideality whereas, vapour phase being still ideal because the pressure is low that case we take.

(Refer Slide Time: 10:03)



- Consider $\gamma_a > 1$ (i.e., like interactions are stronger than unlike interactions)
- From GD equation ($x_a dln\gamma_a + x_b dln\gamma_b = 0$) also we can realize that if $\gamma_a > 1$ then γ_b should also be > 1
- For ideal binary mixture: $y_aP + y_bP = P = x_aP_a^{sat} + (1-x_a)P_b^{sat}$ *
- For non-ideal liquid case: $y_aP + y_bP = P = x_a\gamma_aP_a^{sat} + (1-x_a)\gamma_bP_b^{sat}$ *
- From above two Eqs., for a given mole fraction of species, system will exhibit higher pressure than its ideal counterpart (as γ_a & γ_b both are > 1)
- Such systems are known as systems with positive deviation from RL

So, now what we do we have taken the non-reality in the liquid phase. So, for the liquid phase non ideality can be represented by 2 cases $\gamma_i > 1$ that is positive deviation from ideal behaviour or like interactions are stronger than the unlike interactions. So, that case will take and then see how the calculations can be proceed. So, from gives the GD equation that is (x_a dln γ_a + x_b dln γ_b = 0) from this equation if you know that because x_a x_b < 1 or at the max they can be 1.

So, from here if you have $\gamma_a > 1$, so, this equation, from this equation you also realise that $\gamma_b > 1$. So, what does it mean by let us say for binary mixture when both phases are displaying ideal behavior, so, in the previous lecture, we have seen this equation that is $y_a P + y_b P = P = x_a P_a^{sat} + (1 - x_a) P_b^{sat}$. Now, for the today's case were non ideal liquid phases that vapour phase is still ideal, but the liquid phase is non ideal.

And then and that non ideality also we have taken that γ_a is > 1 then the corresponding equation in the previous slide we have written this 1 that is $y_a P + y_b P = P = x_a \gamma_a P_a^{sat} + (1 - x_a) \gamma_b P_b^{sat}$. So, now here γ_a and then γ_b are coming into the picture because liquid phase's non-ideal and now we have seen here for a given temperature this $P_a^{sat} P_b^{sat}$ are in any way constant.

Now what we do we see the pressure how are they for ideal case that is when both phases are ideal and then 1 phase is ideal other phase liquid phase is non ideal then how the pressure would be different, by comparing these 2 equation that is what we can understand. So, a given temperature $P_a^{sat} P_b^{sat}$ are known and in general they are positive and then x_a and $1 - x_a$ are known kind of thing.

So, now, whatever the x_a P_a^{sat} and then $(1 - x_a)$ P_b^{sat} are the values it is having if your $\gamma_a > 1$ and then $\gamma_b > 1$ then you can realise that the second case where the liquid phase is having non ideality, the pressure the total pressure is going to be higher than the corresponding pressure in the its ideal liquid phase counterpart. So, that means in this case whatever the pressure is there in the ideal behaviour case.

That would be smaller than the pressure in the case of this non ideal liquid phase provided this $\gamma_a > 1$ if $\gamma_a > 1$ then $\gamma_b > 1$ for the binary mixture according to Gibbs-Duhem equations. So, what does it mean? So, if you remember that P-x-y diagram that we have seen in the previous lecture, P x_a versus y_a if you draw, so, what we have seen we have seen a kind of a P x_a curve like this and then P y_a curve like this.

This is what we have seen, this is for you know ideal liquid this is for the ideal liquid phase. But now, what happens in this case if pressure is going to be more, if the liquid phase is showing non ideality and then the liquid phase non ideality is having such a way that like interactions are stronger that is $\gamma_i > 1$. So, the pressure is going to be higher than the corresponding pressure of ideal liquid phase.

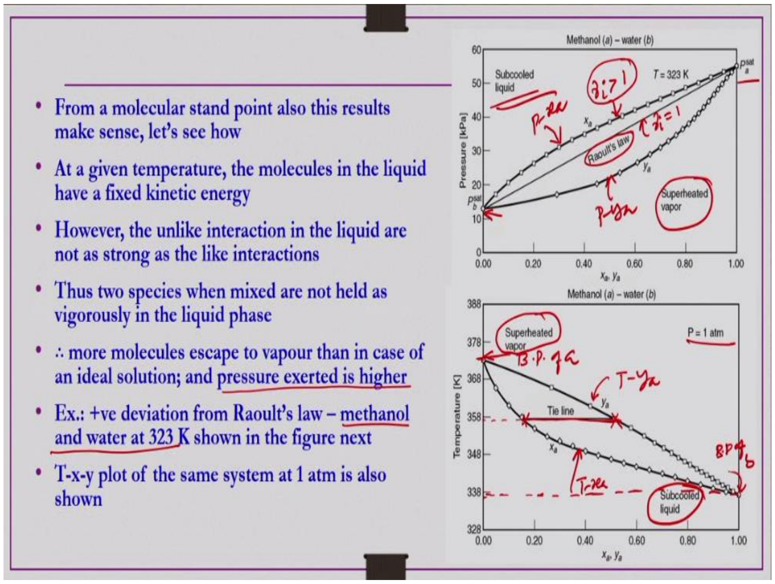
So, then obviously, these corresponding P x_a curve for this case is going to be like this, it is not going to be straight line like in the previous case that we have seen. So, that is what it means. So, in the Raoult's law when the liquid phase is also ideal, so, then we have a P x_a curve as a kind of straight line. But in the case of non ideal liquid this P x_a curve is not going to be straight line because in this case we have taken like interactions are stronger.

So, then γ_a γ_b both are > 1 so the corresponding pressure here is going to be higher than the, it is counterpart ideal liquid pressure. This is what let us say what happens if the like interactions are weaker or $\gamma_i < 1$. So, then from this equation if γ_a γ_b are < 1. So, for a given x_a P_a^{sat}combination and then x_b P_b^{sat}combination the corresponding pressure that is going to have here in the non ideal liquid is going to be lower than it is an ideal counterpart.

So, that means, under such conditions we may have you know the P x_a curve like this. So, this is again P x_a curve but $\gamma_i < 1$ and then this is also P x_a curve but $\gamma_i > 1$. Whereas the solid straight line is also P x_a curve but $\gamma_i = 1$ that is ideal liquid. So, that is the difference that you can realize from here. So, from above to equation for a given mole fraction of species system.

Will exhibit higher pressure than its ideal counterpart, because first case we are taking γ_a and γ_b both are > 1. So, such systems are known as systems with positive deviation from ideal behavior or positive deviation from Raoult's law.

(Refer Slide Time: 16:33)



- From a molecular stand point also this results make sense, let's see how
- At a given temperature, the molecules in the liquid have a fixed kinetic energy
- However, the unlike interaction in the liquid are not as strong as the like interactions
- Thus two species when mixed are not held as vigorously in the liquid phase
- ∴ more molecules escape to vapour than in case of an ideal solution; and pressure exerted is higher
- Ex.: +ve deviation from Raoult's law – methanol and water at 323 K shown in the figure next
- T-x-y plot of the same system at 1 atm is also shown

From a molecule standpoint also this results make sense, because what happens at a given temperature the molecules in the liquid have a fixed kinetic energy. However, the unlike interaction in the liquid are not as strong as the like interactions. Let us say any solution liquid solution, pure solution if you take the like interactions are going to be very strong in general but if you add some other component to this pure component then there will be unlike interactions as well in addition to a-a and b-b kind of like interaction.

There will be a kind of unlike a-b interactions would also be there, but the case is that in general the a-a interactions or b-b interactions are going to be much stronger than the unlike a-b interactions. So, if the unlike interactions are not stronger then obviously, its tendency to escape from the liquid phase and to join or go into the vapour phase is going to be very high compared to the case of you know pure liquid cases. So, that is what it means. So, the unlike interactions in the liquid are not as strong as in the like interactions.

This 2 species when mixed are not held as vigorously in the liquid phase as they are in the pure solution form or pure form before adding together or before making a kind of liquid solution. Therefore, more molecules escape to vapour than in the case of an ideal solution and obviously, pressure exerted is higher. If more and more molecules are going into the vapour phase, then obviously, the pressure of this system is going to increase gradually.

And then because of that one whatever that P x_a curve that we have seen that is going to have a kind of, you know pressure showing higher than the corresponding pressure by ideal behaviour. So, one example we are showing here positive deviation from Raoult's law, methanol and water system, if you take it 323 Kelvin, then it will be having it will be showing positive deviation from Raoult's law. So, corresponding T-x-y plot also we have shown at 1 atmosphere for the same system.

So, the previous 1 whatever it is shown here so, there also if it is exhibiting methanol water system, then we have this straight line this straight line where $\gamma_i = 1$. So, if this system is having positive deviation from Raoult's law then because of that non ideality whatever the molecules are there they are having more tendency to go into the vapour phase and because of that one pressure increases and then whatever the deviation is there that deviation is called as a kind of positive deviation from Raoult's law.

So, that occurs when γ_i is > 1 or positive deviation like this. Rest everything is same as we have discussed in the previous lecture that you know about this P x_a curve we are having sub cooled liquid and then below this P y_a curve we are having superheated vapour in between these 2 curves whatever the enclosed area is there that is the region where both vapour liquid are coexisting and they are at equilibrium.

And then this curve P x_a curve is also known as the kind of bubble point curve because that is the point at which first bubble forms from the liquid states as you gradually decrease the pressure and then this P y_a curve is also known as the dew point curve, because, when you gradually compress the vapour by increasing the pressure at constant temperature this is the point, this P y_a curve is the point laying on the P y_a curve would be 1 at which first dew point is forming from the superheated vapour.

So, that is the reason it is known as dew point curve that P y_a curve also whatever the P y_a curve that is also known as the dew point curve. So, rest everything is same only thing that we have this γ_i > 1. So, accordingly there is a kind of a higher pressure compared to the corresponding ideal liquid case. So, we have not seen any T-x-y plot. So, far the comparison purpose has shown T-x-y plot of the same methanol water system but at 1 atmosphere. So, temperature versus x_a y_a is shown here.

So, here so, since it is T-x-y record so, the vapour phase you know would be having the, you know vapour phase will form at higher temperatures. So, then the above curve or whatever is the that is known as the T y_a curve whereas T in the P x_a curve it is below curve or whatever the below line instead that is P y_a curve and then liquid phase would be existing at the lower temperature that is the region T x_a is a below curve whereas the liquid phase at fixed temperature.

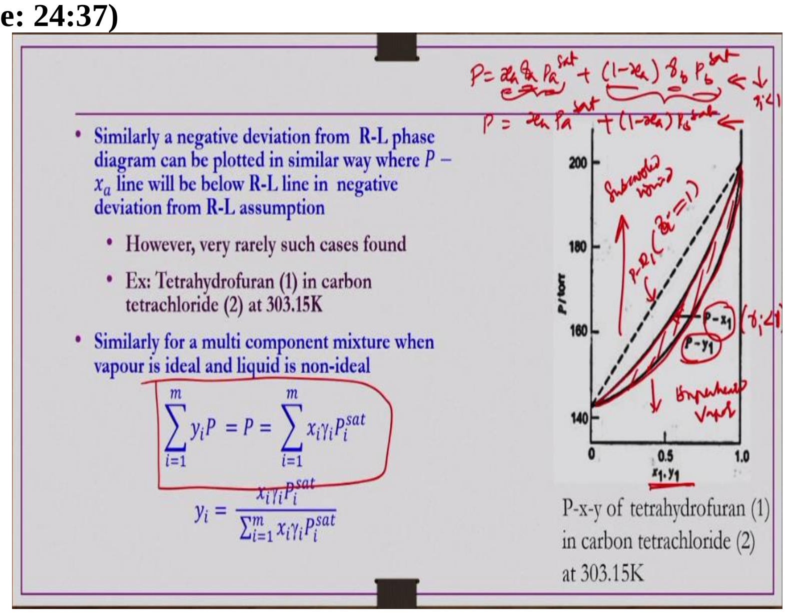
Will have it higher pressure it by gradually increasing the higher pressure the time will be getting the condensed phase or compressed liquid phase that you can here. That is the reason that is been a step and then here this is known as the P_b^{sat} in P x_a curve and then this is known as P_a^{sat}, corresponding values. But whereas here now here it is nothing but boiling point of a and then corresponding this value whatever is there that should be boiling point of component b.

So, now methanol water, water boiling point is 100 degrees centigrade so, then there is the region 373 Kelvin is shown as kind of boiling point of that point. So, this T y_a curve whichever intersects upper end of Y axis is you know, it is a boiling point of component and wherever the lower end of T y_a curve intersecting with this Y axis is known as the other side of the Y axis is known as the boiling point of component b.

And so, now in between we have a kind of, you know, between these 2 and curves, whatever the enclosed area is that area, it is both having both vapour and liquid phases. Above this T y_a curve now, we have the superheated vapour and then below this T x_a curve we are having sub cooled liquid and rest everything is same as in corresponding P-x-y diagram. Because here now here this is let us say tail end if you take so, this is the constant temperature it is joining tying up the 2 combinations of you know equilibrium phases.

This y_a and x_a correspondingly. So, similarly here also we can find out you know what is the bubble point composition, dew point composition etc. all those things we can find out from the T-x-y diagram as well as we have done from T-x-y diagram in the previous case. So, this is about the positive deviation from ideality or positive deviation from the Raoult's law.

(Refer Slide Time: 24:37)



$P = x_a \gamma_a P_a^{sat} + (1-x_a)\gamma_b P_b^{sat}$ ← ↓ $\gamma_i < 1$

$P = x_a P_a^{sat} + (1-x_a) P_b^{sat}$ ←

- Similarly a negative deviation from R-L phase diagram can be plotted in similar way where $P - x_a$ line will be below R-L line in negative deviation from R-L assumption
  - However, very rarely such cases found
  - Ex: Tetrahydrofuran (1) in carbon tetrachloride (2) at 303.15K
- Similarly for a multi component mixture when vapour is ideal and liquid is non-ideal

$$\sum_{i=1}^{m} y_i P = P = \sum_{i=1}^{m} x_i \gamma_i P_i^{sat}$$

$$y_i = \frac{x_i \gamma_i P_i^{sat}}{\sum_{i=1}^{m} x_i \gamma_i P_i^{sat}}$$

P-x-y of tetrahydrofuran (1) in carbon tetrachloride (2) at 303.15K

So, what if we have a negative deviation, negative deviation from Raoult's law can be plotted in a similar way where P x_a line will be below R L line in negative deviation from R L assumption.

Because, whatever that equation is you write $P = x_a \gamma_a P_a^{sat} + (1 - x_a) \gamma_b P_b^{sat}$. So, now, if $\gamma_a < 1$ γ_b is also going to be < 1. So, then whatever the value of $x_a P_a^{sat}$ and then $x_b P_b^{sat}$ are there if you are multiplying these 2 individual terms by some number which is having < 1.

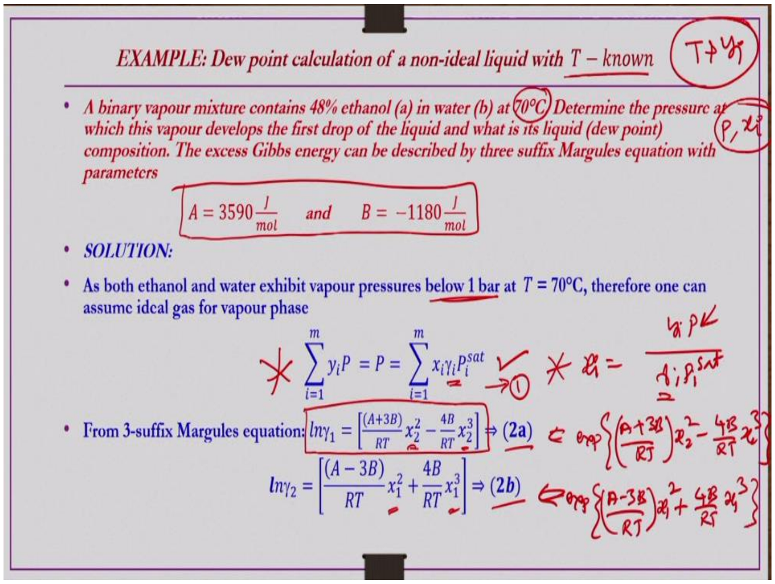
So, the overall pressure is going to be < its corresponding pressure whatever the ideal pressure or the ideal case pressure that is $x_a P_a^{sat} + (1 - x_a) P_b^{sat}$. So, compared to this 1, in this case, it is pressure is going to be less because here $\gamma_a < 1$ negative deviation from ideal behavior. But such cases are very rare because we know that the like interactions that is a-a interaction or b-b interactions are both a-a b-b interactions are stronger than the unlike interaction.

Something like a-b interactions in general for most of the cases. That is the reason you know the tendency of the molecules to escape from the liquid phase is higher to go and join the vapour phase there will be very rare cases that you know the tendency of this molecules the tendency of these molecules would be less and then bind together with some other foreign materials you know much stronger that is unlike interactions being strong is a very rare case in general. However, there are few system.

So, for example, if you take tetrahydrofuran in carbon tetrachloride at 303.15 Kelvin, then we can have you know, negative deviation from Raoult's law like this. So, now here pressure versus or P versus x_1 y_1 if you do this is the case P x_1 but $\gamma_i = 1$. Now here this case, this curve or whatever is there this is nothing but again P x_1, but here γ_i is < 1 that is the reason the pressure is < the corresponding ideal liquid pressure. And then this other curve is you know, like P y_1 curve.

Below this P y_1 curve, what we will be having we will be having a superheated vapour because it is a P-x-y diagram. And then above this P x_1 curve, we will be having sub cooled liquid and then whatever this enclosed area between these P x_1 and P y_1 is there that is the region where both vapour and liquid phases are coexisting and that equilibrium. Similarly for a multi component mixture when vapor phase is ideal and then liquid phase is non ideal then we have this equation we can extend it to the multiple component mixture having m number of components then y_i P you can find out from this equation like this.

(Refer Slide Time: 28:28)



EXAMPLE: Dew point calculation of a non-ideal liquid with $\underline{T - \text{known}}$ $\boxed{T + y_i}$

- A binary vapour mixture contains 48% ethanol (a) in water (b) at $\boxed{70°C}$ Determine the pressure at which this vapour develops the first drop of the liquid and what is its liquid (dew point) composition. The excess Gibbs energy can be described by three suffix Margules equation with parameters $\boxed{P, x_i}$

$$\boxed{A = 3590 \frac{J}{mol} \quad \text{and} \quad B = -1180 \frac{J}{mol}}$$

- **SOLUTION:**
- As both ethanol and water exhibit vapour pressures $\underline{\text{below 1 bar}}$ at $T = 70°C$, therefore one can assume ideal gas for vapour phase

$$* \sum_{i=1}^{m} y_i P = P = \sum_{i=1}^{m} x_i \underline{\gamma_i} P_i^{sat} \checkmark \rightarrow ① \quad * \; x_i = \frac{y_i P \swarrow}{\underline{\gamma_i} P_i^{sat}}$$

- From 3-suffix Margules equation: $\boxed{ln\gamma_1 = \left[\frac{(A+3B)}{RT} x_2^2 - \frac{4B}{RT} x_2^3\right]} \Rightarrow \underline{(2a)} \quad \Leftarrow \exp\left\{\left(\frac{A+3B}{RT}\right) x_2^2 - \frac{4B}{RT} x_2^3\right\}$

$$ln\gamma_2 = \left[\frac{(A-3B)}{RT} x_1^2 + \frac{4B}{RT} x_1^3\right] \Rightarrow \underline{(2b)} \quad \Leftarrow \exp\left\{\left(\frac{A-3B}{RT}\right) x_1^2 + \frac{4B}{RT} x_1^3\right\}$$

So, now what we do? We take an example problem dew point calculation of a non ideal liquid with T known a binary vapour mixture contains 48% ethanol in water at 70 degrees Centigrade. So, T and y_i are given. Determine the pressure at which this vapour develops the first drop of the liquid and what is its liquid or dew point composition. So pressure at which first drop of liquid forms from this vapour mixture.

And then what is the corresponding composition of that liquid drop that is P x_i we have to find out the excess Gibbs energy can be described by three suffix Margules equation with parameters A and B given like this. For the liquid phase it said in the problem it is mentioned that three suffix Margules equation is sufficient to display or you know is a three suffix Margules equation is sufficient to represent the non ideality of the liquid phase that is what mentioned in the problem, but about the vapour phase it is not mentioned.

And then we cannot know whether it is ideal or non ideal because the pressure is also not known. So, under such conditions we have to make some kind of assumptions 1 has assumption is that no details are given. So, then you can take the ideal behaviour but logically also we have to think how it is possible is it going to be that assumption is going to be reliable or not. So, then what we have to see at this 70 degrees centigrade because our system is at 70 degrees centigrade at 70 degrees centigrade.

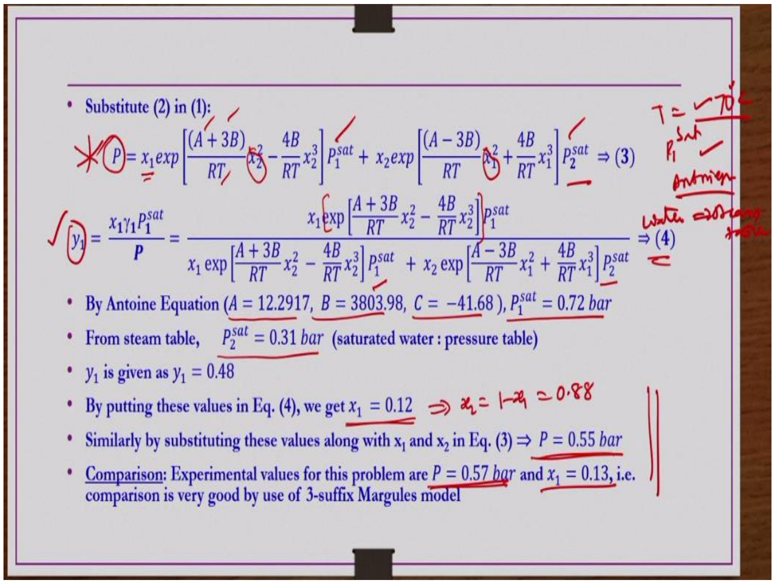
We can know the vapour pressure of this pure component ethanol and water and then in general at 70 degrees centigrade the vapour pressure of these 2 components is below 1 bar. If the vapour pressure is very small then it is possible that the vapour mixture that is found because of these 2 component is going to be having the pressure smaller pressure and then pressure is small so, then we can take ideal gas assumption without any difficulty and then that will not induce much error at all.

So, if the vapour phase is ideal then we have $y_a P = x_a \gamma_a P_a^{sat}$ and $y_b P = x_b \gamma_b P_b^{sat}$ so that generalized when we have written here, so γ_i that 3 suffix Margules equation we have to use that is given. So for 3 suffix Margules equation $\ln \gamma_i = \left[\frac{(A+3B)}{RT} x_j^2 - \frac{4B}{RT} x_j^3\right]$ if it is mixture of i j and component. If it is mixture of 1 and 2 component then $\ln \gamma_1 = \left[\frac{(A+3B)}{RT} x_2^2 - \frac{4B}{RT} x_2^3\right]$. Similarly, $\ln \gamma_2 = \left[\frac{(A+3B)}{RT} x_1^2 - \frac{4B}{RT} x_1^3\right]$.

Now, here this equation if you wanted to solve, because this equation you need you know you need to know what x_i is. So, x_i is nothing but simply you know $\frac{y_i P}{\gamma_i P_i^{sat}}$ and then $P = \sum x_i \gamma_i P_i^{sat}$. So, that P is not known and then x_i is also not known. So, then until and unless you know x_i you cannot know the P. So, we will see how to solve this problem. So, but we have to go step by step. So, γ_i you can you calculate because A and B are given T is given but x_i is not given that is x_1 x_2 is not given.

So, we have to write this equation for 2 component system and then see if we can overcome this difficulty. So, this equation whatever equation number 2 we have this is your equation number 1. So, whatever the equation number 2 that is 2a 2b γ_1 is nothing but exponential of $\left[\frac{(A+3B)}{RT} x_2^2 - \frac{4B}{RT} x_2^3\right]$, this is γ_1. Similarly, γ_2 is exponential of $\left[\frac{(A+3B)}{RT} x_1^2 - \frac{4B}{RT} x_1^3\right]$. So, this if you substitute here in equation number 1 in place of γ_i.

(Refer Slide Time: 33:45)



- Substitute (2) in (1):

$$P = x_1 exp\left[\frac{(A+3B)}{RT}x_2^2 - \frac{4B}{RT}x_2^3\right]P_1^{sat} + x_2 exp\left[\frac{(A-3B)}{RT}x_1^2 + \frac{4B}{RT}x_1^3\right]P_2^{sat} \Rightarrow (3)$$

$$y_1 = \frac{x_1\gamma_1 P_1^{sat}}{P} = \frac{x_1 \exp\left[\frac{A+3B}{RT}x_2^2 - \frac{4B}{RT}x_2^3\right]P_1^{sat}}{x_1 \exp\left[\frac{A+3B}{RT}x_2^2 - \frac{4B}{RT}x_2^3\right]P_1^{sat} + x_2 \exp\left[\frac{A-3B}{RT}x_1^2 + \frac{4B}{RT}x_1^3\right]P_2^{sat}} \Rightarrow (4)$$

$T = 70°C$

P_1^{sat} ✓

Antoine

water → steam table

- By Antoine Equation ($A = 12.2917$, $B = 3803.98$, $C = -41.68$), $P_1^{sat} = 0.72\ bar$
- From steam table, $P_2^{sat} = 0.31\ bar$ (saturated water : pressure table)
- y_1 is given as $y_1 = 0.48$
- By putting these values in Eq. (4), we get $x_1 = 0.12$ $\Rightarrow x_2 = 1 - x_1 \simeq 0.88$
- Similarly by substituting these values along with x_1 and x_2 in Eq. (3) ⇒ $P = 0.55\ bar$
- Comparison: Experimental values for this problem are $P = 0.57\ bar$ and $x_1 = 0.13$, i.e. comparison is very good by use of 3-suffix Margules model

Then we have B = x_a, P = x_1 but we because we are having the labels 1 and 2 for these components. So, if you substitute equation 2 in equation 1 then P = x_1 in place of γ_1 and we have written this one P_1^{sat}+ x_2 in place of γ_2 we have written this one P_2^{sat}. So, now here in this equation A B are known temperature is given, P_1^{sat}you can find out because temperature is given then P_1^{sat}can be known Antoine equation.

If it is water then from steam tables also we can know what the saturation pressure of the water system at T equals to is given at temperature of 70 degrees centigrade. So, those things are known only thing unknown is x_1 or x_2 here in the right hand side but left hand side P is also not known. But left hand side P is also not known. So, we cannot solve this equation directly. So, what we do we write expression for y_i, $y_i = \frac{x_i\gamma_i P_i^{sat}}{P}$, y_i is given so y_1 if you write $y_1 = \frac{x_1\gamma_1 P_1^{sat}}{P}$.

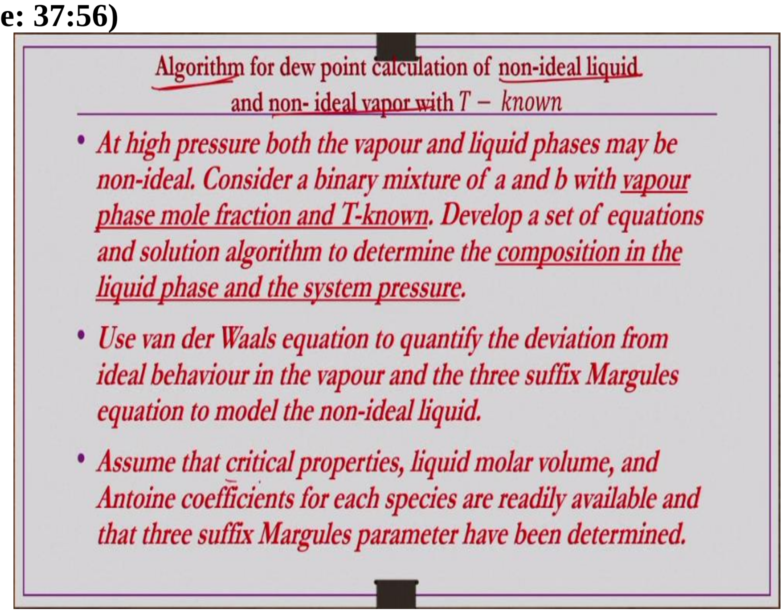
So, then you have this equation x_1 and then this particular thing is nothing but $\frac{\gamma_1 P_1^{sat}}{P}$is nothing but this equation number 3 from P, we are having P = this one. Similarly, for y_2 also you can write like this, but now, this equation we see left hand side y_1 is known, right hand side A B T are known $P_1^{sat} P_2^{sat}$you can know from the Antoine equations or steam tables, so, only is unknown is the x_1 or x_2 that is $1 - x_1$. So, in this equation for internal that is for the first component Antoine constants A B C are given here.

So, by using Antoine equation, you can find out the saturation pressure of first component as 0.72 bar and from the steam tables for water at 70 degrees centigrade, you can find it out P_2^{sat} as 0.31 bar. So, P_1^{sat} P_2^{sat} is also known. So, everything is known in equation number 4 except x_1 or 1 minus x_1 in place of x_2. So, that you if you substitute these values $y_1 = 0.48$ and then P_1^{sat} is 0.72 P_2^{sat} so, that is 0.31 and then A and B whatever given values and then T is 70 degrees centigrade etc.

That you substitute in equation number 4 you will get after simplification x_1 is 0.12 that means, you know if you x_1 is known, then x_2 is also known as 1 minus x_1 is nothing but 0.88. So, both x_1 and x_2 are known. So, these values if you substitute in equation number 3 along with that A B, constants P_1^{sat} P_2^{sat} and temperature and then solve then you will find it out the pressure P is going to be 0.55 bar.

So, by comparison experimental results for this system is that P is 0.57 bar and x_1 is 0.13 and then we can see that it matches really well with experimental results. That means, this three suffix Margules equation is much reliable to reproduce experimental results for such kind of systems like water ethanol etc.

(Refer Slide Time: 37:56)



Algorithm for dew point calculation of non-ideal liquid and non- ideal vapor with $T -$ known

- *At high pressure both the vapour and liquid phases may be non-ideal. Consider a binary mixture of a and b with vapour phase mole fraction and T-known. Develop a set of equations and solution algorithm to determine the composition in the liquid phase and the system pressure.*
- *Use van der Waals equation to quantify the deviation from ideal behaviour in the vapour and the three suffix Margules equation to model the non-ideal liquid.*
- *Assume that critical properties, liquid molar volume, and Antoine coefficients for each species are readily available and that three suffix Margules parameter have been determined.*

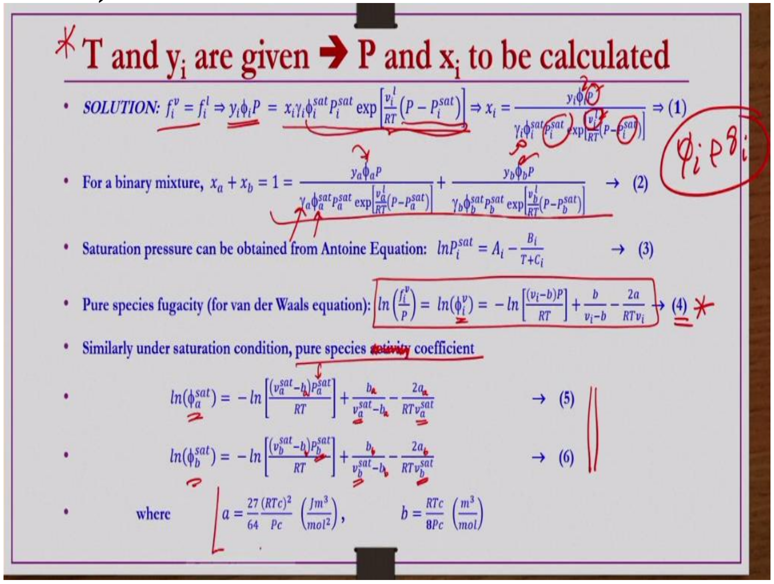
Now we have algorithm for dew point calculation of non ideal liquid and non-ideal vapour phase also I am directly saying the algorithm because when both vapour and liquid phases are having non ideality. That means we are working at a high pressure systems then you know what happens the equations would be become more complicated and then one has to go for a kind of iterative calculations as we are describing now. So, this is the other extreme case of both the phases displaying ideal behavior.

Now, in this case we are taking non ideal behavior for both vapour and liquid phase, if you are saying that the vapour phase is non ideal that means, by default you are saying that pressure is not low pressure is high. So, that you cannot avoid the non ideality in the vapour phase. So, when you say the non idealities there in the both phases you have to depict, you have to show or represent the equation by which the non ideality of each phase is represented that you have to mention.

So, what we do we take a case where the vapour phase non idealities represented by Van der Waals equation because such equations we have extensively used in previous lectures where we wanted to find out the fugacities of fugacity coefficient because no vapour phase is also non ideal. So, view how to have the information about the figures to coefficient as well and then for the liquid phase what we do we go by the three suffix Margules equation which we just know found, we just now have used.

Then, we assume that the critical properties liquid molar volume and Antoine coefficients for each species are readily available, in addition to 3 suffix Margules parameters A and B. So, first we list out all the equations.

(Refer Slide Time: 39:46)



* T and y_i are given ➔ P and x_i to be calculated

- SOLUTION: $f_i^v = f_i^l \Rightarrow y_i\phi_i P = x_i\gamma_i\phi_i^{sat}P_i^{sat}\exp\left[\frac{v_i^l}{RT}(P-P_i^{sat})\right] \Rightarrow x_i = \frac{y_i\phi_i P}{\gamma_i\phi_i^{sat}P_i^{sat}\exp\left[\frac{v_i^l}{RT}(P-P_i^{sat})\right]} \Rightarrow (1)$
- For a binary mixture, $x_a + x_b = 1 = \frac{y_a\phi_a P}{\gamma_a\phi_a^{sat}P_a^{sat}\exp\left[\frac{v_a^l}{RT}(P-P_a^{sat})\right]} + \frac{y_b\phi_b P}{\gamma_b\phi_b^{sat}P_b^{sat}\exp\left[\frac{v_b^l}{RT}(P-P_b^{sat})\right]} \rightarrow (2)$
- Saturation pressure can be obtained from Antoine Equation: $lnP_i^{sat} = A_i - \frac{B_i}{T+C_i} \rightarrow (3)$
- Pure species fugacity (for van der Waals equation): $\boxed{ln\left(\frac{f_i^v}{P}\right) = ln(\phi_i^v) = -ln\left[\frac{(v_i-b)P}{RT}\right] + \frac{b}{v_i-b} - \frac{2a}{RTv_i}} \rightarrow (4)$ *
- Similarly under saturation condition, pure species ~~activity~~ coefficient
- $ln(\phi_a^{sat}) = -ln\left[\frac{(v_a^{sat}-b_a)P_a^{sat}}{RT}\right] + \frac{b_a}{v_a^{sat}-b_a} - \frac{2a_a}{RTv_a^{sat}} \rightarrow (5)$
- $ln(\phi_b^{sat}) = -ln\left[\frac{(v_b^{sat}-b_b)P_b^{sat}}{RT}\right] + \frac{b_b}{v_b^{sat}-b_b} - \frac{2a_b}{RTv_b^{sat}} \rightarrow (6)$
- where $a = \frac{27}{64}\frac{(RTc)^2}{Pc}\left(\frac{Jm^3}{mol^2}\right)$, $b = \frac{RTc}{8Pc}\left(\frac{m^3}{mol}\right)$

$\phi_i P \gamma_i$

So, in this case T and y_i are given. So, you have to find out P and x_i. The process that we are going to start can be used for any combination any 2 nodes and then remaining 2 unknowns you can find out for a binary mixture. So, for the binary mixture, we are going to do this algorithm development. So, we know that $f_i^v = f_i^l$ that means, f_i^v is nothing but $y_i\,\phi_i\,P$ and $f_i^l = x_i\,\gamma_i\,f_i^0$ and then f_i^0, if at high pressures, we have seen that $f_i^0 = \phi_i^{sat}\ P_i^{sat}\exp\left[\int_{P_i^s}^{P}\frac{v_i^l}{RT}dP\right]$.

And then if this v_i^l is independent of ΔP then we can write it as $\left[\int_{P_i^s}^{P}\frac{v_i^l}{RT}dP\right]$ we can write it as $\frac{v_i^l}{RT}\Delta P$ that is $P - P_i^{sat}$. So, this is also we have seen. So, now, x_i you how to find out so, $x_i = \frac{y_i\phi_i P}{\gamma_i\phi_i^{sat}P_i^{sat}exp\left[\frac{v_i^l}{RT}(P-P_i^{sat})\right]}$. So, now in order to find out these things, you need to know several things first of all pressure is not known here and then this ϕ_i that is also not known though Van der Waals equation it is mentioned.

So, if you remember figures the coefficient for Van der Waals equation of state. So, there are also pressure term is there. So, this is pressure that is also not known and then this activity γ_i, so, we know it is function of composition of the liquid phase. So, that is also not known x_i that is what we are finding out. So, temperature is given so, P_i^{sat} you can know and then it is mentioned that the molar volumes etc. all are given. So, P_i^{sat} you can find out because Antione constants are available that is what it says.

So, these things having difficulty now you know this ϕ_i and then γ_i both of them you know having terms which are not no like pressure and the composition. So, this equation if you write for a binary system it is going to be become kind of complicated equation to do hand calculation one has to go for several iterations. So, this for binary system if you write $x_a = \frac{y_a\phi_a P}{\gamma_a\phi_a^{sat}P_a^{sat}exp\left[\frac{v_a^l}{RT}(P-P_a^{sat})\right]}$ like that.

$x_b = \frac{y_b\phi_b P}{\gamma_b\phi_b^{sat}P_b^{sat}exp\left[\frac{v_b^l}{RT}(P-P_b^{sat})\right]}$ then add them together. So, then we have this summation this equation number 2 now we write expression for individual this ϕ_a^{sat} ϕ_a and then this γ_a $\phi_b^{sat}\phi_b$ and then this γ_b because it is mentioned that the non-ideality in the vapour phase is described by Van der Waals equation. So, corresponding fugacity expressions we can use and then liquid phase non-ideality can be described by 3 suffix Margules equation, it is given in the problem.

So for 3 suffix Margules equation activity coefficients γ expressions we already know. So, we can write them. Saturation pressure can be obtained from the Antoine equation. That is ln $P_i^{sat} = A_i - \frac{B_i}{T(K)+C_i}$, T is in Kelvin and then P_i^{sat} in bar. For pure species fugacity for Vander Waals equation, equation our state this is what we have already derived in one of our previous lecture this is pure species fugacity, obeying the Vander Waals equation and then there is a pressure term.

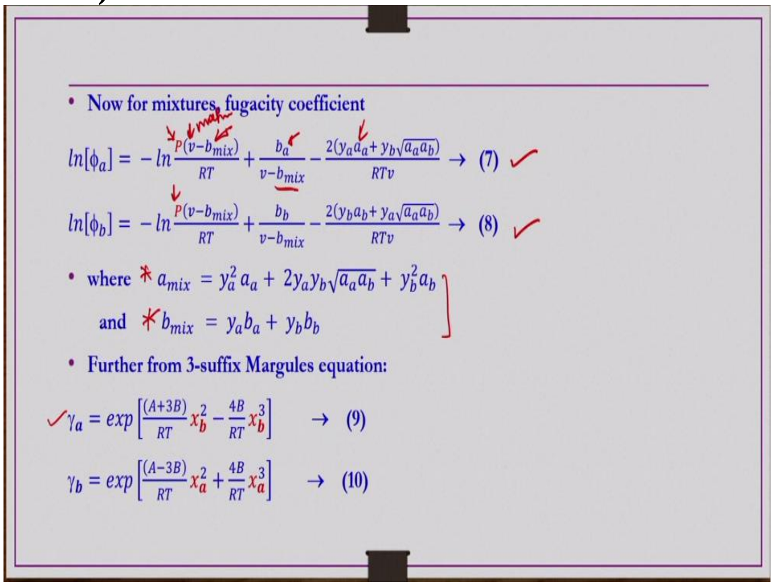
So, in this pressure term if you substitute, in place of pressure if you substitute saturation pressure so, then this fugacity is nothing but the fugacity of a saturated vapour phase. So, that means, under saturation condition pure species fugacity coefficient we can find it out as ln $\phi_a^{sat} = -ln\left[\frac{(v_a^{sat}-b)P_a^{sat}}{RT}\right] + \frac{b}{v_a^{sat}-b} - \frac{2a}{RTv_a^{sat}}$. Only thing what we have done, in this equation number 4, wherever v_i is there we have written v_a^{sat} and then wherever P is there we have written P_a^{sat}.

Similarly, for ϕ_b^{sat} ln $\phi_b^{sat} = -ln\left[\frac{(v_b^{sat}-b)P_b^{sat}}{RT}\right] + \frac{b}{v_b^{sat}-b} - \frac{2a}{RTv_b^{sat}}$. Here also in place of v_i, what we have done in equation number 4, in place of v_i we have written v_b^{sat} and in place of pressure P we have written now P_b^{sat}. Remember this equations, that is equation number 4 itself is for pure species, So, equation numbers 5 and 6 also for pure species A and B.

So, when we are say the pure species, so, whatever these Van der Waals constant A B are there for their for the pure component so, this b is nothing but b_a pure component a, it is constant b and then this is a nothing but is a suffix a that is constant a for pure component a. So, that it is explicitly you do not need to write every time. So, then the second 1 also we can read this b_b, b is nothing but for the pure component b so b suffix b you can write like this and then this a is nothing for pure component b,

So, a_b so, these are explicit now, at this level we already understand what this a and b constant for pure and then mixture if you are not writing. So, anyway we are writing here to pure species fugacity coefficient. So, ϕ_a^{sat} ϕ_b^{sat}. So, corresponding a and b should be pure component a and b values. So, this a and b we can find it out from this critical temperature critical pressure. In the problem it is also mentioned that critical parameters are already available.

(Refer Slide Time: 46:45)



- Now for mixtures, fugacity coefficient

$$ln[\phi_a] = -ln\frac{P(v-b_{mix})}{RT} + \frac{b_a}{v-b_{mix}} - \frac{2(y_a a_a + y_b\sqrt{a_a a_b})}{RTv} \rightarrow (7) ✓$$

$$ln[\phi_b] = -ln\frac{P(v-b_{mix})}{RT} + \frac{b_b}{v-b_{mix}} - \frac{2(y_b a_b + y_a\sqrt{a_a a_b})}{RTv} \rightarrow (8) ✓$$

- where * $a_{mix} = y_a^2 a_a + 2y_a y_b\sqrt{a_a a_b} + y_b^2 a_b$

  and * $b_{mix} = y_a b_a + y_b b_b$

- Further from 3-suffix Margules equation:

$$✓\gamma_a = exp\left[\frac{(A+3B)}{RT}x_b^2 - \frac{4B}{RT}x_b^3\right] \rightarrow (9)$$

$$\gamma_b = exp\left[\frac{(A-3B)}{RT}x_a^2 + \frac{4B}{RT}x_a^3\right] \rightarrow (10)$$

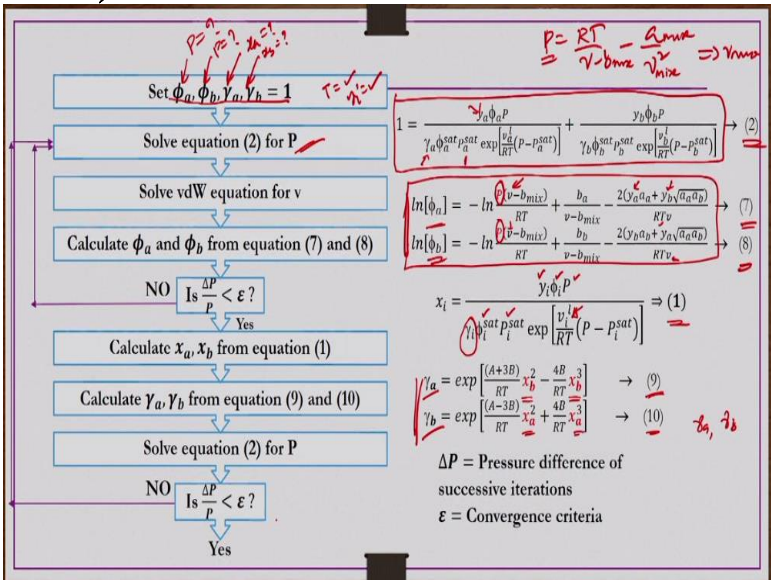
So, for the mixture fugacity coefficient we have already seen ln ϕ_a is nothing but this expression we have derived ln ϕ_b is nothing but this expression we have derived. We have derived for a component i in the mixture, a generalized one. So, this is what we have written. So, now here this v is nothing but for the mixture. Now, b is the mixture and this here b_a "a" we have to specifically mentioned because now it is for the mixture.

So, b_a is for the pure component a, whatever b constant is there and then b mixture is that whatever the b constant for the mixture similarly, a_a or a_b whatever written here like this and then pressure we have to find out that is not known that is the reason I highlighted in red color font. Here in this equation wherever we need probably a_{mixt}, and then b_{mixt}. So, this mixing though we have used. I am not writing them explicitly again.

So, further from three suffix Margules equation, we have this γ_a = exp$\left[\frac{(A+3B)}{RT}x_b^2 - \frac{4B}{RT}x_b^3\right]$ and then γ_b = exp$\left[\frac{(A+3B)}{RT}x_a^2 - \frac{4B}{RT}x_a^3\right]$. So, here this x_a x_b are not known, that is the reason I have highlighted them in bold font again. Now, if you wanted to solve the equation number 1 the big equation that we have written, so what do you need to know you need to know P as well as x_i both of them are not known.

And then we have to do several iterations so that for different combinations of P and x_i that equation satisfies so rather doing hand calculations several iteration, it is better to kind of small programme doing you kind of you know, small programming and then 1 can easily calculate for that we can have a kind of algorithm here.

(Refer Slide Time: 48:52)



Set $\phi_a, \phi_b, \gamma_a, \gamma_b = 1$

Solve equation (2) for P

Solve vdW equation for v

Calculate ϕ_a and ϕ_b from equation (7) and (8)

Is $\frac{\Delta P}{P} < \varepsilon$?

Calculate x_a, x_b from equation (1)

Calculate γ_a, γ_b from equation (9) and (10)

Solve equation (2) for P

Is $\frac{\Delta P}{P} < \varepsilon$?

$$1 = \frac{y_a\phi_a P}{\gamma_a\phi_a^{sat}P_a^{sat}\exp\left[\frac{v_a^l}{RT}(P-P_a^{sat})\right]} + \frac{y_b\phi_b P}{\gamma_b\phi_b^{sat}P_b^{sat}\exp\left[\frac{v_b^l}{RT}(P-P_b^{sat})\right]} \rightarrow (2)$$

$$ln[\phi_a] = -ln\frac{P(v-b_{mix})}{RT} + \frac{b_a}{v-b_{mix}} - \frac{2(y_a a_a + y_b\sqrt{a_a a_b})}{RTv} \rightarrow (7)$$

$$ln[\phi_b] = -ln\frac{P(v-b_{mix})}{RT} + \frac{b_b}{v-b_{mix}} - \frac{2(y_b a_b + y_a\sqrt{a_a a_b})}{RTv} \rightarrow (8)$$

$$x_i = \frac{y_i\phi_i P}{\gamma_i\phi_i^{sat}P_i^{sat}\exp\left[\frac{v_i^l}{RT}(P-P_i^{sat})\right]} \Rightarrow (1)$$

$$\gamma_a = exp\left[\frac{(A+3B)}{RT}x_b^2 - \frac{4B}{RT}x_b^3\right] \rightarrow (9)$$

$$\gamma_b = exp\left[\frac{(A-3B)}{RT}x_a^2 + \frac{4B}{RT}x_a^3\right] \rightarrow (10)$$

ΔP = Pressure difference of successive iterations

ε = Convergence criteria

So what we do, we do not know what is ϕ_a ϕ_b because if you wanted to know ϕ_a ϕ_b you should know is pressure you do not know γ_a γ_b because if you need to know γ_a γ_b what is x_a what is x_b you have to know you do not know. So, what we do we set this ϕ_a ϕ_b γ_a γ_b all of them are equals to 1 and then T is given y_i is also given that is y_a y_b are given.

So, now, in this equation you have to find out pressure phi as the first iteration that is you know y_a is given ϕ_a ϕ_b we are taking 1 and then ϕ_a^{sat}we have already calculated for a given temperature case and P_a^{sat} also we can calculate γ_a we are taking 1. So, in the right hand side except the pressure everything is known. Everything is known because ϕ_a ϕ_b γ_a γ_b we are taking = 2. As the first assumption, so, pressure you can find out once the pressure is known, then P = $\frac{\text{RT}}{v-b} - \frac{a}{v^2}$.

This equation you can find out, this is Van der Waals equation, this equation you can find out this equation you can use to find out v_{mixt} because no pressure you have already found as part of first iteration. Because we mixture is also known is required because in this ln ϕ_a next step that is you know, we update actually we update ϕ_a ϕ_b values, remember where the pressure terms are coming only in the fugacity terms are the expression for the fugacity.

Whereas, the composition is coming into the picture in the terms related to the activity coefficient, so, since pressure is already found, so, whatever the assumed fugacity coefficients are there that will be updating by solving this equation 7 and 8. In the 7 and 8 now, after first iteration P is known and then v_{mixt} you are finding out from the equation of state that is given that is Van der Waals equation of statistics. So, v_{mixt} is also known in a and b constants are known.

So, b_{mixt} a_{mixt} you can find out and then y_a y_b are given, T is given. So, v you just find out so, everything is known in the right hand side after first iteration. So, after first iteration what is ϕ_a ϕ_b you can calculate using this equation number 7 and 8 equation number as are same as in previous slides. So, once this 7 and 8 equations are solved to get the ϕ_a and ϕ_b then equation number 1 that is $x_i = \frac{y_i \phi_i P}{\gamma_i \phi_i^{sat} P_i^{sat} exp\left[\frac{v_i^l}{RT}(P - P_i^{sat})\right]}$.

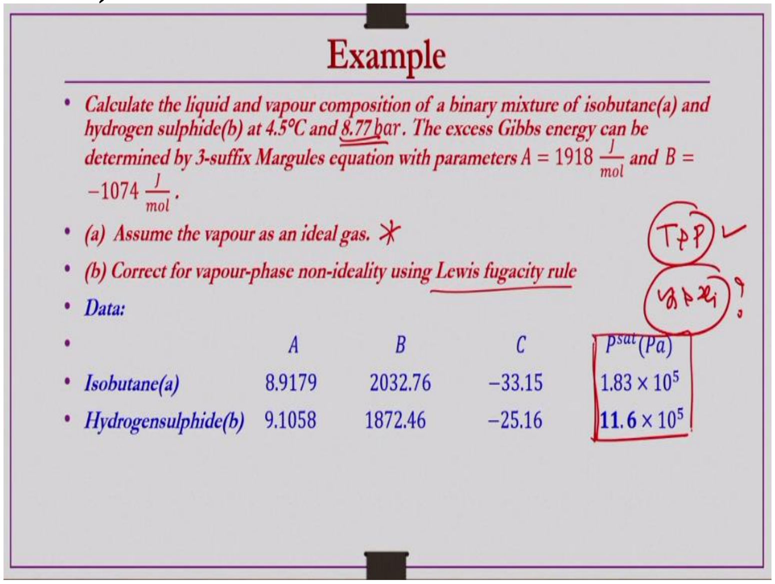
So, this equation number 1 can solve to get the x_i because y_i is known ϕ_a ϕ_b, you just updated after first iterations. P is also you have the first iteration ϕ_i^{sat}that is already known P_i^{sat} is already known, γ_i is you are taking as = 1 as the first assumption. So v_i^l etc. are known that is where the assumption of the problem or the statement of the problem says. So, everything is known except the γ_i which already we have taken as = 1 as a part of first iteration this is all part of first iteration.

So, you find out what is x_i. After finding out the x_i in pressure you can individually let us check whether the Δ P by P is $< \varepsilon$ or not Δ P is nothing but the difference in pressures after 2 successive iterations. So, if it is $< \varepsilon$ then you can proceed to the next level calculation or otherwise you get back to this previous step, you know where you are solving the pressure again. So, once x_i is known that means x_a x_b are known.

So, then equation number 9 and 10 you can use to solve this γ_a γ_b because x_a x_b are known a and b constants are given for 3 suffix Margules equation. So, now, after first iteration you have the updated γ_a γ_b also. So, now, you go back to the equation number 2 to solve again as the second iteration part of second iteration you find out P what is pressure like that you have to continue these calculation until this $\frac{\Delta P}{P}$ is < some epsilon value, which is used for the convergence criteria.

So, this is one can make a kind of algorithm to do you know solving the equilibrium composition for vapour liquid equilibrium problems when both vapour and liquid phases display non-ideality, you can understand from this tan calculations are a bit difficult but however can be doable.

(Refer Slide Time: 54:30)



Example

- Calculate the liquid and vapour composition of a binary mixture of isobutane(a) and hydrogen sulphide(b) at 4.5°C and 8.77 bar. The excess Gibbs energy can be determined by 3-suffix Margules equation with parameters $A = 1918 \frac{J}{mol}$ and $B = -1074 \frac{J}{mol}$.
- (a) Assume the vapour as an ideal gas. *
- (b) Correct for vapour-phase non-ideality using Lewis fugacity rule
- Data:

	A	B	C	$P^{sat}(Pa)$
Isobutane(a)	8.9179	2032.76	−33.15	1.83×10^5
Hydrogensulphide(b)	9.1058	1872.46	−25.16	11.6×10^5

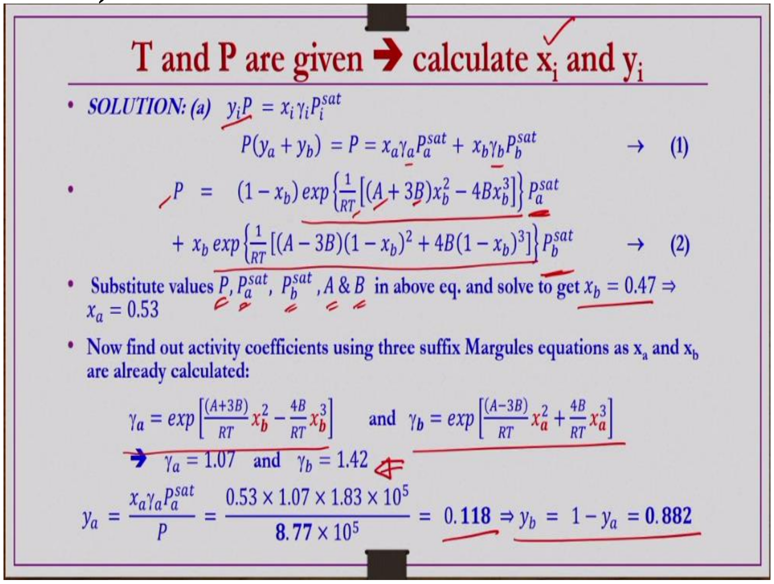
T, P ✓

y_i, x_i ?

So, one last example problem we take now, before winding up. Calculate the liquid and vapour compression of a binary mixture of iso-butane and hydrogen sulphide at 4.5 degrees centigrade and 8.77 bar so, the pressure is still low, it is not very low but still low. It is not very high to take that you know vapour phase as a kind of non ideal. Excess Gibbs energy can be determined by three suffix Margules equation with parameter say us and be given.

So, assumed as vapour phase as an ideal gas that is itself is mentioned first part of the solution, second part of the solution correct for vapour phase non ideality using Lewis fugacity. So, under such conditions you have to find out you know x_i and then y_i known here T and P are given y_i and x_i you how to find out under 2 different assumptions. First assumption is that the vapour phase is ideal second assumption is that vapour phase non idealities are represented or corrected using the Lewis fugacity. So, data that is entered constants are given for 2 components the corresponding saturation pressure we can obtain Antione equations like this.

(Refer Slide Time: 55:56)



T and P are given ➔ calculate x_i and y_i

- *SOLUTION: (a)* $y_i P = x_i \gamma_i P_i^{sat}$

$$P(y_a + y_b) = P = x_a \gamma_a P_a^{sat} + x_b \gamma_b P_b^{sat} \quad \rightarrow \quad (1)$$

- $$P = (1 - x_b)\exp\left\{\frac{1}{RT}\left[(A+3B)x_b^2 - 4Bx_b^3\right]\right\} P_a^{sat} + x_b \exp\left\{\frac{1}{RT}\left[(A-3B)(1-x_b)^2 + 4B(1-x_b)^3\right]\right\} P_b^{sat} \quad \rightarrow \quad (2)$$
- Substitute values $P, P_a^{sat}, P_b^{sat}, A$ & B in above eq. and solve to get $x_b = 0.47 \Rightarrow x_a = 0.53$
- Now find out activity coefficients using three suffix Margules equations as x_a and x_b are already calculated:

$$\gamma_a = \exp\left[\frac{(A+3B)}{RT}x_b^2 - \frac{4B}{RT}x_b^3\right] \quad \text{and} \quad \gamma_b = \exp\left[\frac{(A-3B)}{RT}x_a^2 + \frac{4B}{RT}x_a^3\right]$$

➔ $\gamma_a = 1.07$ and $\gamma_b = 1.42$

$$y_a = \frac{x_a \gamma_a P_a^{sat}}{P} = \frac{0.53 \times 1.07 \times 1.83 \times 10^5}{8.77 \times 10^5} = 0.118 \Rightarrow y_b = 1 - y_a = 0.882$$

So, first case we take y_i P = x_i γ_i P_i^{sat} since vapour phase is ideal first case. So, there is no ϕ_i term coming into the left hand side here. So, if you write for both the components and then add them together we can have P y_a + P y_b that is nothing but P = x_a γ_a P_a^{sat} + x_b γ_b P_b^{sat}. So, this P_a^{sat} are known P_b^{sat} are known that γ_a γ_b are represented by 3 suffix Margules equation.

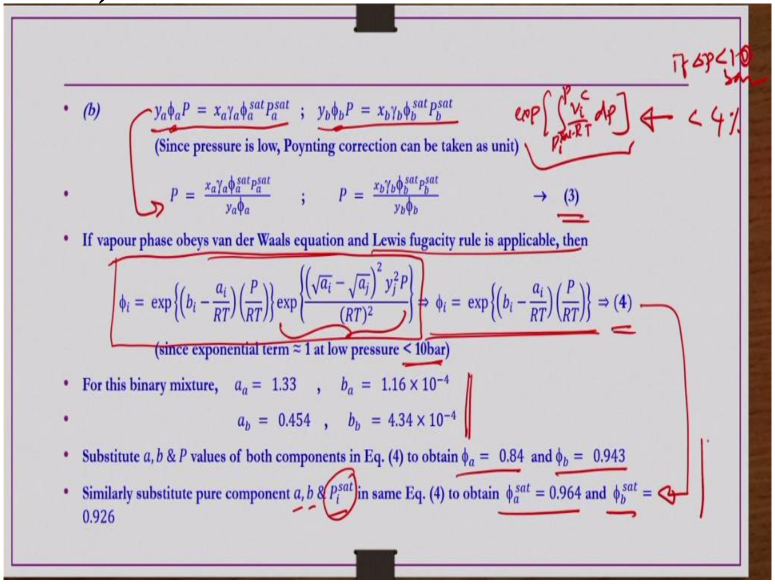
So, this they can be written as exponential of this term for γ_a and then exponential of this term for γ_b. This a and b constants are given. Temperature is also given pressure is also given. So, what is the unknown here in this equation only x_b is the unknown. So, here P known given P_a^{sat} we just obtained P_b^{sat} we obtained a and b constant for 3 suffix Margules equation are given. So, if you substitute all of this in the above equation and solve, then you will find out x_b = 0.47 that means, x_a = 0.53.

So, out of y_i and x_i you already found, what is x_i? Now, y_i we have to find out. So, for y_i to find out you have that x_i γ_i P_a^{sat} by P that means, γ_i you have to find out since x_a x_b are already calculated just now, in the first step of this problem. So, γ_a γ_b you can calculate using this expression now, because x_a x_b we already calculated and then A B constants of three suffix Margules equations are given T is given.

So, everything in the right hand side is known so then γ_a you can find it out as 1.07 γ_b you can find it out as 1.42 and then you can see now γ_i is > 1 that means like interactions are stronger, are this system is showing the liquid phase non idealities such a way that non ideality positive deviation from Raoult's law is exhibiting. That this liquid phase showing the positive deviation from the Raoult's law that is what we can understand from these things.

So, once γ_a γ_b are also known, then you can find out $y_a = \frac{\gamma_a x_a P_a^{sat}}{P}$. So, that comes to be 0.118 and then y_b is nothing but $1 - y_a$ that comes out to be 0.882. So, now y_a is also formed. So, the first part of the problem is done when the vapour phase is displaying ideal behavior.

(Refer Slide Time: 58:59)



If $\Delta P < 10$ bar

- (b) $y_a\phi_a P = x_a\gamma_a\phi_a^{sat}P_a^{sat}$; $y_b\phi_b P = x_b\gamma_b\phi_b^{sat}P_b^{sat}$ $\exp\left[\int_{P_i^{sat}}^{P}\frac{v_i^c}{RT}dP\right] \leftarrow < 4\%$

  (Since pressure is low, Poynting correction can be taken as unit)
- $P = \frac{x_a\gamma_a\phi_a^{sat}P_a^{sat}}{y_a\phi_a}$; $P = \frac{x_b\gamma_b\phi_b^{sat}P_b^{sat}}{y_b\phi_b}$ → (3)
- If vapour phase obeys van der Waals equation and Lewis fugacity rule is applicable, then

  $$\phi_i = \exp\left\{\left(b_i - \frac{a_i}{RT}\right)\left(\frac{P}{RT}\right)\right\}\exp\left\{\frac{\left(\sqrt{a_i}-\sqrt{a_j}\right)^2 y_j^2 P}{(RT)^2}\right\} \Rightarrow \phi_i = \exp\left\{\left(b_i - \frac{a_i}{RT}\right)\left(\frac{P}{RT}\right)\right\} \Rightarrow (4)$$

  (since exponential term ≈ 1 at low pressure < 10bar)
- For this binary mixture, $a_a = 1.33$, $b_a = 1.16 \times 10^{-4}$
- $a_b = 0.454$, $b_b = 4.34 \times 10^{-4}$
- Substitute a, b & P values of both components in Eq. (4) to obtain $\phi_a = 0.84$ and $\phi_b = 0.943$
- Similarly substitute pure component a, b & P_i^{sat} in same Eq. (4) to obtain $\phi_a^{sat} = 0.964$ and $\phi_b^{sat} = 0.926$

Second part of the problem Lewis fugacity rule is used to correct the vapour phase non-ideality. So, phi$_a$ phi$_b$ terms should be coming for both components when we write this equation y_a ϕ_a P = x_a γ_a $\phi_a^{sat} P_a^{sat}$ said that equation for you if you write for the 2 components a and b then you can have this equation, but of course it is also it should also have $\exp\left[\int_{P_i^s}^{P}\frac{v_i^c}{RT}dP\right]$.

This poynting correction, this should come should also be multiplied for both of these terms but we have seen the pressure is small 8.77 bar though it is not very small but it is small enough that is < 10 bars something like that then we have seen this exponential term induces error < 4% or something like that, that is what we have already seen if Δ P is < 10 bar itself is 8.77, but we have seen. So, this under such conditions what happens you know, if the Δ P is small and then $v_i^c$is < 100 cc per mole in 1 of the previous lecture.

We have seen that this exponential term is going to induce difference < 4% on d. So, that means, you can take off this exponential term poynting correction term can be taken as unit because its contribution is very small and then including term unnecessarily increase the calculations. So, from these 2 equations what we can write P = $\frac{x_a \gamma_a \phi_a^{sat} P_a^{sat}}{y_a \phi_a}$ and then P = $\frac{x_b \gamma_b \phi_b^{sat} P_b^{sat}}{y_b \phi_b}$, this is what we can have.

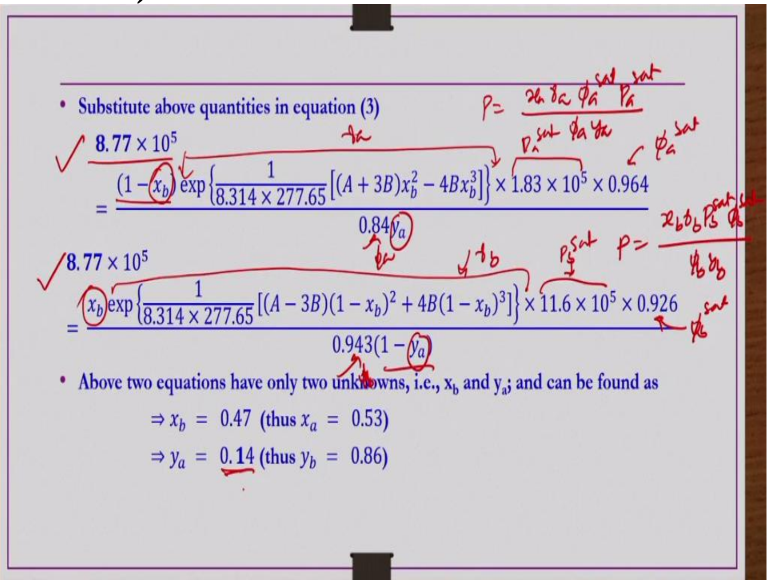
Now in vapour phase Van der Waals equation is I mean, it is given that vapour phase obeys the Van der Waals equation of state and then Lewis fugacity rule is applicable in order to convert its non-ideality or in order to correct for the non ideality vapour phase that is given. So, in one of the previous lecture for Van der Waals equation of state combined with the Lewis fugacity rule phi a we have found it like this, but in this exponential term is going to be very small for the case where the pressure is small so, that we take it as exponential of this term if we take it as 1.

So, that we can have only first term this will also reduce some amount of work so ϕ_i = $\exp\left\{\left(b_i - \frac{a_i}{RT}\right)\left(\frac{P}{RT}\right)\right\}$ this is what we can have. So, this second exponential correction we are taking off, because the pressure is very small 8.77 bar only, it is not very small pressure is small though it is not very high. So, it may be having some value, but it is not going to induce much error. Exponential term can be taken approximately 1 at low pressures < 10 bar.

So, for this binary mixture from the literature this a and b constants of Van der Waals equation of state are given like this. So, substitute this a, b and P in this equation number 4 to get ϕ_a and ϕ_b as 0.84 and then 0.943. So, in this equation number 4 one more thing is known and then a, b and then P_i^{sat}rather P if you substitute P_i^{sat}in this equation number 4 then you will get $\phi_a^{sat}$and ϕ_b^{sat}because this equation is valid for the entire range of pressure that we have taken 0 to P and $P_i^{sat}$is somewhere in between of this.

So, then we have in this equation in place of P if you substitute P_i^{sat} values then we will get ϕ^{sat} fugacity coefficient of a saturated vapour conditions. So, now, these values you know in this equation number 3 except y_a x_a and then γ_a γ_b everything are known. So, one can solve for those equations.

(Refer Slide Time: 01:03:53)



- Substitute above quantities in equation (3)

$$P = \frac{x_a \gamma_a \phi_a^{sat} P_a^{sat}}{\phi_a y_a}$$

$$\frac{8.77 \times 10^5}{} = \frac{(1 - x_b)\exp\left\{\frac{1}{8.314 \times 277.65}\left[(A + 3B)x_b^2 - 4Bx_b^3\right]\right\} \times 1.83 \times 10^5 \times 0.964}{0.84 y_a}$$

$$P = \frac{x_b \gamma_b P_b^{sat} \phi_b^{sat}}{\phi_b y_b}$$

$$8.77 \times 10^5 = \frac{x_b \exp\left\{\frac{1}{8.314 \times 277.65}\left[(A - 3B)(1 - x_b)^2 + 4B(1 - x_b)^3\right]\right\} \times 11.6 \times 10^5 \times 0.926}{0.943(1 - y_a)}$$

- Above two equations have only two unknowns, i.e., x_b and y_a; and can be found as

$\Rightarrow x_b = 0.47$ (thus $x_a = 0.53$)

$\Rightarrow y_a = 0.14$ (thus $y_b = 0.86$)

Now by using, by substituting these quantities in equation number 3, equation number 3 is nothing but P = $\frac{x_a \gamma_a \phi_a^{sat} P_a^{sat}}{y_a \phi_a}$. So, this is x_a is nothing but 1 − x_b writing P is nothing but 8.77 bar that is we have written in Pascal and this exponential term whatever is there that is nothing better from here to here it is nothing but γ_a and this is nothing but P_a^{sat} and this is nothing but ϕ_a^{sat} that we just find out and then this is nothing but ϕ_a.

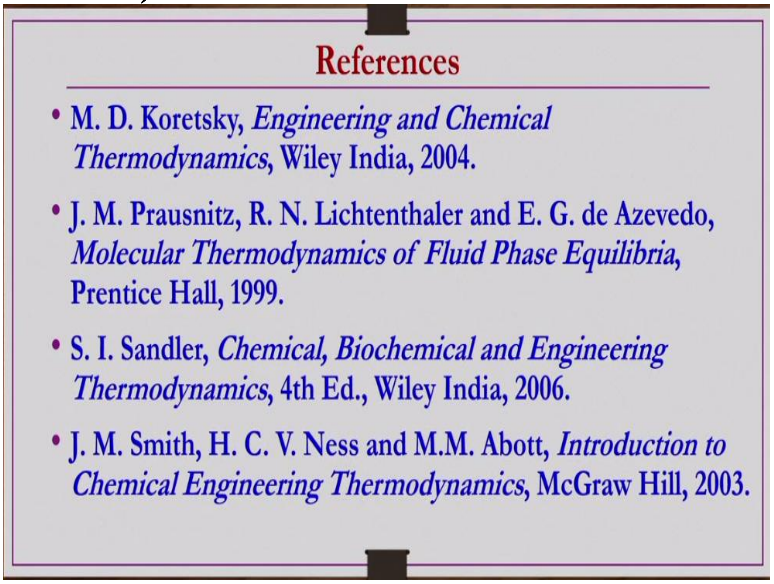
Similarly, for second component also if you write we have this equation. So, now in these 2 equations, what are the unknowns' x_b and then y_a. 2 equations we are having for writing you know component a, we have got this equation, this equation when we write for the component we got this equation by writing for component b that is P = $\frac{x_b \gamma_b \phi_b^{sat} P_b^{sat}}{y_b \phi_b}$, this is what we are having.

So, here this is x_b and then this exponential term is nothing but γ_b this is nothing but P_b^{sat} and this is nothing but ϕ_b^{sat} and this is nothing but ϕ_b and then in place of y_b I am writing 1 − y_a. So, 2 equations 2 unknowns are there you can solve this equation without any difficulty. And then when you solve this equation, you will find out x_b is still going to be 0.47 like in the previous case, but y_a is going to be 0.14.

So, y_a is going to be changed and changing y_a is 0.14 because now y_a that is vapour phase we brought in the non ideality through the Lewis fugacity. So, this is how you can find out any vapour liquid problem, whether having 1 phase identity or both phase ideality or 1 phase non ideal or both phase non ideal whatever the situation is a vapour liquid equilibrium problems corresponding equilibrium compositions you can find out using the problems that we have done till now, whether it is bubble point calculation or dew point calculation without any difficulty.

We can solve them provided required information is available that is something that can turn constants etc. saturation pressures etc. and then this constant associated with the equation of state or you know constant associated with the excess molar Gibbs energy etc. those kind of thing if you know so, then you can find out the equilibrium composition of vapour liquid equilibrium problems without any difficulty references for this lecture are given here.

(Refer Slide Time: 01:07:30)



References

- M. D. Koretsky, *Engineering and Chemical Thermodynamics*, Wiley India, 2004.
- J. M. Prausnitz, R. N. Lichtenthaler and E. G. de Azevedo, *Molecular Thermodynamics of Fluid Phase Equilibria*, Prentice Hall, 1999.
- S. I. Sandler, *Chemical, Biochemical and Engineering Thermodynamics*, 4th Ed., Wiley India, 2006.
- J. M. Smith, H. C. V. Ness and M.M. Abott, *Introduction to Chemical Engineering Thermodynamics*, McGraw Hill, 2003.

But this is the book that have followed for this entire lecture. Thank you.