Chemical Engineering Thermodynamics

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Lecture - 34
VLE Diagrams
Azeotrope
K-Values

Hello and welcome back. So, far we looked at vapor liquid equilibrium calculations, we have done a vapor liquid equilibrium calculations using Raoult's law, where the both the liquid and the vapor phase are assumed to be ideal gas like an ideal solution like. And we have extended it to non ideal solutions where we have excess Gibbs free energy, the activity coefficients that account for the non-ideality of the liquid phase and then we have incorporated the model for the activity coefficients into our VLE calculations.

What we will do today is quickly look at vapor liquid equilibrium diagrams more commonly known as P-x-y and T-x-y diagrams, we use them in now routinely in a separation processes design. And then, we look at a special case of a vapor liquid equilibrium which involves what is known as azeotrope; as it turns out when mixtures form azeotrope, it is not possible to separate them by simple distillation techniques. So, they are an important class of mixtures which we need to focus on when we design distillation processes for such mixtures. And finally, we are going to look at alternate ways of VLE calculations using what are known as deep research charts or K-values.

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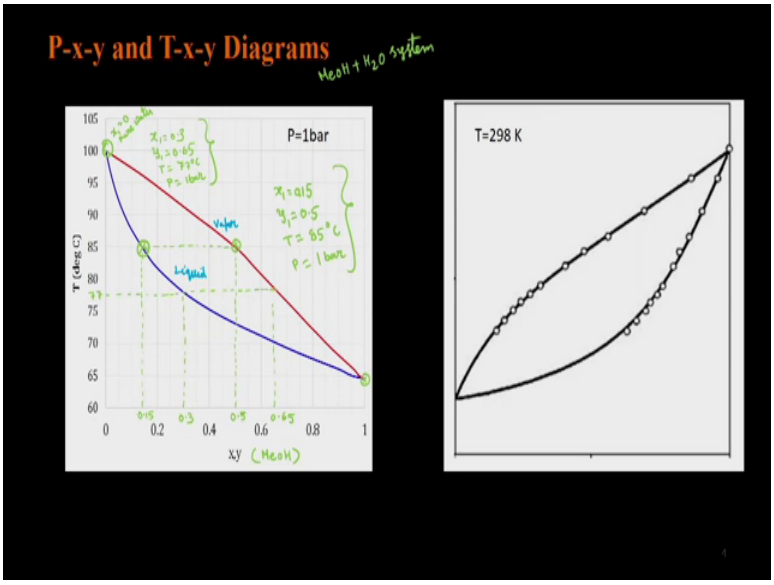

P-x-y and T-x-y Diagrams

So, let us get started with what are known as VLE diagrams or P-x-y and T–x-y diagrams. The figure I have on the left is for methanol water system, on the x axis we have the mole fraction and on the y axis we have the temperature right and this is a figure for the system at a pressure total pressure of 1 bar. There are two curves on this figure as you can see; the one in blue and another one in a red. The blue curve indicates what is known as the liquid line and the red curve indicates what is known as the vapor line, alright.

So, essentially at a given temperature, let us say 85 degrees centigrade, let me pick another color for this temperature 85 degree centigrade. The mole fraction of the liquid is going to be somewhere over there and the mole fraction of the vapor that is going to be in equilibrium with this liquid will be obtained because equilibrium indicates are both vapor and liquid are at the same temperature. We take the same temperature 85 degree centigrade, extend it all the way to the vapor curve and then read the mole fraction for the vapor curve at the same temperature.

So, what this tells me is a liquid with a mole fraction of 0.18 will be in equilibrium with a mole fraction of about 0.5, I am sorry this is not 1.8, this is about 0.15 will be in equilibrium with a vapor of mole fraction of about 0.5 right. So, both the curves need to be read at the same temperature and we call this as a T-x-y curve because it is taken at a constant pressure and for different temperatures we have different equilibrium values for the corresponding liquid and a vapor.

So, x 1 is 0.15 y 1 is 0.5 the temperature is 85 degree centigrade and the pressure is 1 bar, these are the equilibrium conditions for the system. I can also read equilibrium at a different temperature. Let us say at a temperature of about 0.3 for x and the corresponding vapor temperature for the sorry vapor mole fraction for this will be about 0.65 alright and the temperature is maybe 77. So, another set of conditions I can read from the curve are x 1 is 0.3, y 1 is 0.65, the temperature is 77 degree centigrade and the pressure is 1 bar.

So, as you can see for any condition I note or read of this chart, the total pressure of the system is always 1 bar the liquid and vapor mole fractions and the corresponding temp equilibrium temperatures are going to be different and so on alright. What happens at the pure component limit for example, this is x and y maybe we should note that we mean methanol here x and y for which component in this case it turns out to be for methanol and this is like I said m for methanol and water system the x and y mole fractions, x 1 and y 1, we are reading of the chart are for methanol.

So, when x 1 is 0 which is at this end all the way here, x 1 is 0 which means it is pure water and as you know of at about 1 bar the corresponding temperature saturation temperature for pure water is about 100 degree centigrade, water boils at 100 degree centigrade and 1 bar. And similarly, at the other pure component limit which is about here the corresponding saturation temperature is 65 indicating methanol boils at 65 degrees and 1 bar alright. So, those are the corresponding saturation temperatures you can also think of it as at 65 degree centigrade, the vapor pressure is 1 bar for methanol at 100 degree centigrade, the vapor pressure is 1 bar for water.

But as far as the pressure is concerned because the figure is for a total pressure of 1 bar that stays constant, we can have different compositions for each of the two liquids in the corresponding temperatures of course, are going to be different. This is something which we can read of a T-x-y diagram as we call it. The other interesting thing is this, there is a region within the figure where we have two phases a vapor phase and a liquid phase and there are also regions in this figure where we only have a single phase.

The ones I showed so far or the temperatures I have picked so far always fall in the two phase region, alright.

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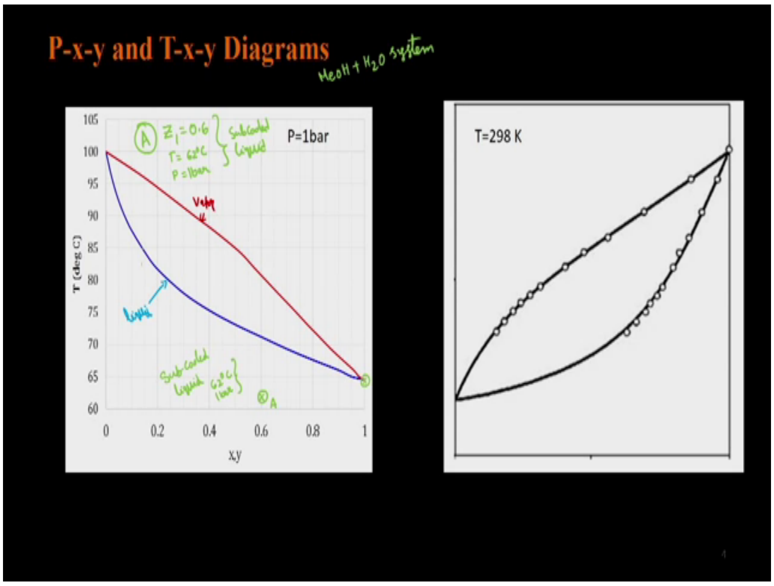

P-x-y and T-x-y Diagrams

Let us remember what we said the red one is the vapor curve and the blue one is the liquid curve. So, this is vapor curve and this is liquid curve. So, the temperatures I picked earlier always fell within the two phase region, but let us say I pick a temperature somewhere below 65 alright. Let us let us pick a temperature right over there. Let us use a different color for that.

Now, if I do that, if I pick a temperature here, what is the condition? Will it fall in a 2 phase region, what is the composition of the vapor or the liquid that is in equilibrium with one another well as it turns out, this region below the 2 phase region, not below the blue curve is what we call as a sub cooled liquid. We cannot have a vapor liquid equilibrium at this condition.

This is a sub cooled liquid at let us say 62 degree centigrade and 1 bar. This liquid mixture has a overall mole fraction. So, let us not remember we used the variable z to indicate the overall mole fraction. The overall mole fraction of this mixture is 0.6 I do not know if it is vapor or liquid, but like I said because it is below the blue curve once I look at the figure I can decide that it is below the blue curve. So, it is going to be in the liquid phase or in a sub cooled liquid state at 1 bar and 62 degree centigrade.

This is sub cooled liquid. Let us give a name to this point A, this is where we are alright write there ok. So, this is a sub cooled liquid.

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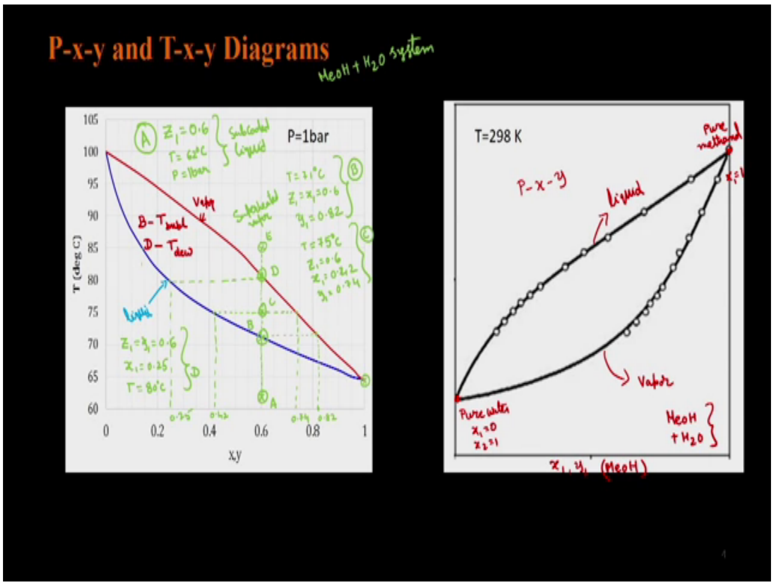

P-x-y and T-x-y Diagrams

Now, if I keep increasing the temperature for this mixture. I am going to the overall mole fraction is still going to the same I take it in a vessel and then everything is in this sub cooled liquid state if I keep increasing the temperature. Eventually, I will reach this point B right and this point B falls on the liquid curve, but then I have hit the blue curve which corresponds to the 2 phase envelope. So, there will be that first bubble of vapor which is formed and the mole fraction for that first bubble of vapor is going to be whatever we read at that temperature on the vapor curve.

So, the overall mole fraction z is 0.6. By the time I reach this temperature let us say 71 degree centigrade, there is just that one bubble of vapor that is formed, the overall mole fraction is going to be equal to the liquid mole fraction which is still 0.6, but then that one bubble of vapor which forms is going to have a mole fraction of about 0.82 let us say corresponding to what I read here, alright.

And the total pressure is still 1 bar by the way. So, I am not going to keep writing that and this is going to be the state of the liquid at point B. I can keep heating it, if I heat it and reach 75 degree centigrade. The overall mole fraction is still going to be 0.6, the overall mole fraction in this case is going to be mole fraction of the liquid phase plus mole fraction of the vapor phase or the total moles in the both the liquid and the vapor put together for component one divided by the total moles in the liquid and vapor both the components right.

So, that overall mole fraction is still 0.6 because that is what I have taken in the vessel, but then the temperature now is 75 degree centigrade. The overall mole fraction would not change, it is 0.6, but the mole fraction of the liquid and vapor are going to change if they if we achieve equilibrium at that condition. The mole fraction of the liquid and the vapor, this is going to be the liquid mole fraction let us say 0.42 and this is going to be the vapor mole fraction about 0.74. So, liquid mole fraction is 0.42 and the vapor mole fraction is 0.74, this is for point C there.

I can keep doing that, I will make different mixtures or I will make mixtures with different liquid and vapor mole fractions, but the overall mole fraction is going to remain the same. So, the way we achieve it is the corresponding liquid fraction or the amount in the liquid phase to the amount in the vapor phase is going to be different. In fact, it is given by the length of the line segments here going from C to the red curve and C to the blue curve, but that is for a different time.

Now, once we understand that and then I can keep increasing this temperature all the way until this point D here alright. And when I am at point D, I am on the vapor curve and the overall mole fraction as you can see here will be same as the mole fraction of the vapor phase because this point D corresponds to the mole fraction of the vapor as well. So, C 1 will be equal to y 1 is 0.6 which means almost everything is in the vapor phase except for that one drop in the liquid phase whose mole fraction is going to be given by what I read of here which is about 0.25.

So, x 1 is going to be 0.25 and then the temperature when we achieve this is going to be about 80 degree centigrade, this is corresponding to point D. So, at 0.5, the mole fraction of the vapor phase will be same as the overall mole fraction which we started with except for a very small amount of liquid that is in equilibrium with this vapor. That small amount of liquid will have a mole fraction of 0.25 alright and we are at point D now, 80 degree centigrade.

I can increase the temperature even further and when I do that, what I end up with is only vapor because I just had that last drop of liquid and once I increase the temperature even that last drop of liquid is going to evaporate and then all I have is the vapor phase and this vapor is what we call as superheated vapor.

So, we started with from point A, where we are in a sub cooled liquid state increase the temperature reached this point B where we found that first bubble of vapor, moved all the way through the 2 phase region where we had different ratios of vapor to liquid and the corresponding equilibrium mole fractions whatever they turn out to be. And then eventually we reached point D where we had that last drop of liquid and eventually we move into the superheated vapor phase.

Now, recall that we said at point D we will get the first bubble of vapor. So, that point B is what we call as the bubble point temperature right. So, let me write that B is the bubble point temperature and point D where we have that last drop of liquid is what we call as the dew point temperature T dew alright and anything in between we are in the 2 phase region.

So, this is discussion on the T-x-y diagram where the pressure is constant at 1 bar. I can make a similar argument for the P-x-y diagram right, this is drawn at a single temperature, the temperature turns out to be 298 Kelvin in this case. The only difference is going to be the top curve in here will correspond to the liquid and the bottom curve here will correspond to the vapor that is the only difference between the T-x-y and the P-x-y diagram. So, I will leave it for you to think over why the top curve represents a liquid here and the bottom curve represents a vapor. Still remember that we are talking about x 1 and y 1 corresponding to the mole fraction of methanol and this is still for methanol plus water system.

So, we are looking at the same system at a different temperature and the pressures are going to vary starting from a low pressure here where there is this is pure water right as you recall we said at this end this is pure water because x 1 is 0. So, x 2 is 1 and at this end here this is pure methanol right because x 1 is 1, alright. So, I will leave it for you to think over why the top curve represents the liquid curve and the bottom curve represents the vapor and the bottom one represents that for the vapor. So, now this is about P-x-y and T-x-y diagrams of course, these diagrams are nice looking for methanol water system.

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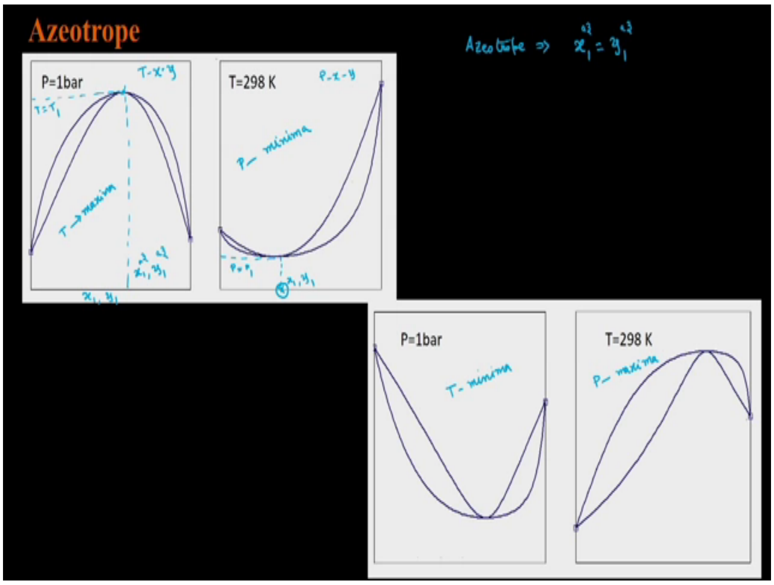
Azeotrope

But then, it is not the case for some other systems alright and these systems where the curves look something like what I have shown here alright are known as systems that exhibit azeotrope, alright. So, the first thing I guess is to define what we mean by an azeotrope and by azeotrope we mean the mole fractions of the vapor and the liquid are same in that particular at that particular condition. So, for example, if you look at the figure on the top, so let us say the pressure here is sorry this is at a pressure of one bar the temperature here is T 1.

So, at a temperature of t 1 and a pressure of 1 bar, this particular system this of course, is x 1 y 1 and this is the temperature sorry. So, this is the T-x-y curve alright and this is the P-x-y curve. Now, when the two vapor and liquid curves meet one another at any point at that particular temperature they form what is known as an azeotrope and if you think about it corresponding to that temperature, if we were to read what the composition of the vapor and the liquid that are in equilibrium with one another is then it is going to be exactly same because the curves are meeting one another right.

Let us call that as x 1 azeotrope and y 1 azeotrope right at this particular point corresponding to the temperature T 1, both the x and y values are going to be same and hence we form what is known as an azeotrope. The trick being if you think about it where if I were to distill methanol and water mixture, methanol the mole fraction of methanol in the vapor phase is going to be higher as we have seen in the previous slide, but if any of the mixtures forms an azeotrope and I make a vapor from this mixture, it is composition is going to be exactly same as that of the liquid composition which means there is no I cannot separate that particular mixture at the given conditions because vapor mole fraction is going to be identical to that of the liquid mole fraction.

I can look at it on a t a P-x-y diagram as well it is the same system, but now we have it on a P-x-y diagram. So, at this pressure at this pressure of P 1, this particular mixture forms an azeotrope and the compositions of course, are going to be obtained by this value here for x 1 and y 1.

Now, what we observe here is a maxima for temperature and a minima for pressure when this azeotrope is form. On the other hand, we can have a minima for temperature and a maxima for pressure. So, I guess what I am trying to give as a take away message is that this P-x-y and T-x-y curves can come in a variety of shapes we can form azeotropes where the liquid and the vapor compositions are going to be same.

We can have a maxima in this curve or a minima in this curve depending on the system we are looking at and it turns out that Raoult's law for ideal systems cannot predict the formation of azeotropes, but some of the other equations including the Margule's equation or Wilson's equation and RTL equations such as these can of course, predict formation of azeotrope for some of the mixtures.

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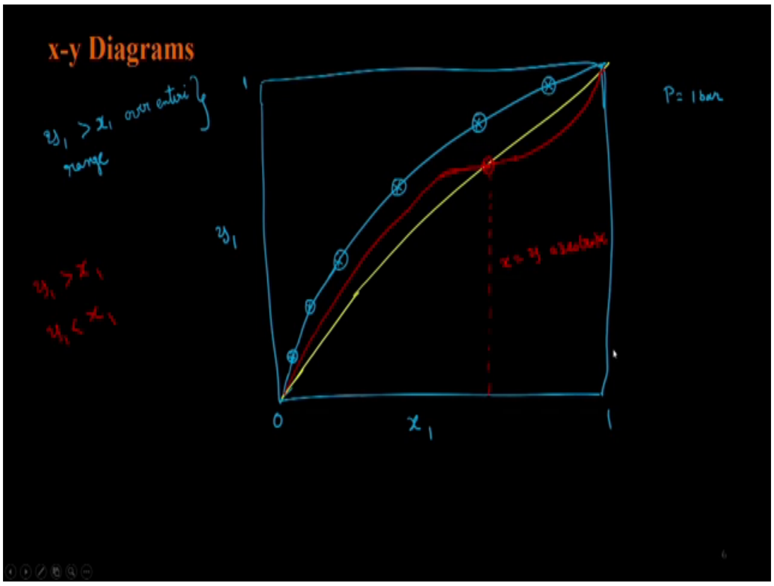

x-y Diagrams

What we looked at in the previous slide is what is known as a P-x-y or a T-x-y diagram of course, we also have what is known as an x, y diagram and in an x, y diagram as the name indicates all we do is simply plot alright x versus y, the x being the mole fraction of one of the components in the liquid phase, y being the mole fraction of that component in the vapor phase way either plot it at a constant pressure or at a constant temperature let us say we plot it at a constant pressure of 1 bar. Then as we change the temperature, we get a value for x right and the corresponding vapor composition which is in equilibrium with this x is y we plot that as x y.

Now, I change the temperature the vapor in liquid equilibrium will be established at this pressure of 1 bar, but at a different compositions for x and y that composition is going to be right there and so on. Now, I can fill this curve and it may look something like that alright, for methanol and water system. Now, the thing to note in here is that if I draw this diagonal and remember both x and y go from 0 to 1 in terms of mole fractions right, 0 to 1 for x 1 and 0 to 1 for y 1, this diagonal in here represents the line which is x equal to y. So, anything about the diagonal like the x, y curve I have drawn here for these points indicates that y is greater than x. So, we are likely to find that component 1, y 1 is greater than x 1 over the entire range alright.

So, what it means is that we are going to find component 1 in the vapor phase more as opposed to that in the liquid phase or it is more volatile component. Now, it does not have to be such a nice curve as in case of methanol and water system. In fact, if the system forms an azeotrope as in the previous example we have not seen then what happens to this x, y diagram is it goes for a part of the region, it goes above the yellow line and for the other part it drops down and goes below the yellow line. So, in a part of the region we have y 1 greater than x 1 and in another part y 1 is less than x 1, but then there is a point where it crosses the yellow line or x equal to y line alright. So, at that point of course, x equals y and we have an azeotrope alright.

So, this is formation of azeotrope indicated on a x, y diagram. So, diagram such as these are helpful to understand the behavior of a system over a range of temperatures or pressures and they are routinely used in a design of separation processes like I said. Now, let us take this message forward because these are so important.

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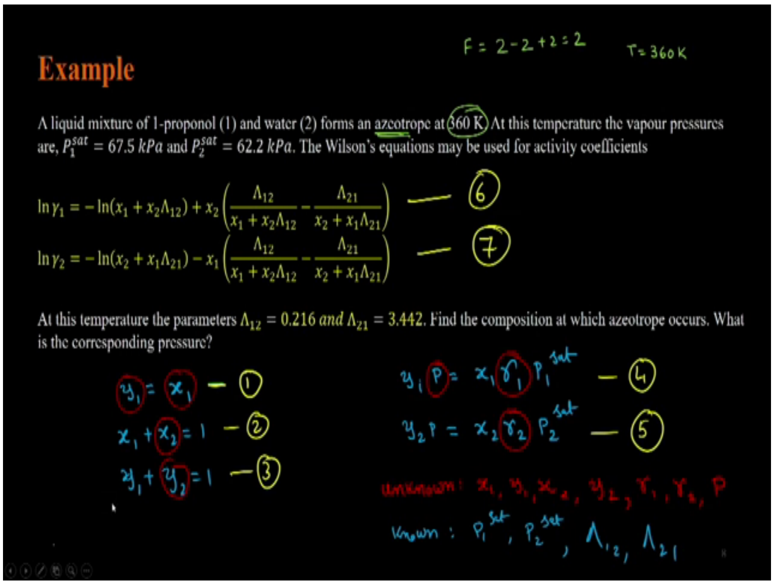

$F = 2-2+2 = 2$ $T = 360\,K$

Example

A liquid mixture of 1-proponol (1) and water (2) forms an azeotrope at 360 K. At this temperature the vapour pressures are, $P_1^{sat} = 67.5\ kPa$ and $P_2^{sat} = 62.2\ kPa$. The Wilson's equations may be used for activity coefficients

$$\ln\gamma_1 = -\ln(x_1 + x_2\Lambda_{12}) + x_2\left(\frac{\Lambda_{12}}{x_1 + x_2\Lambda_{12}} - \frac{\Lambda_{21}}{x_2 + x_1\Lambda_{21}}\right) \quad —⑥$$

$$\ln\gamma_2 = -\ln(x_2 + x_1\Lambda_{21}) - x_1\left(\frac{\Lambda_{12}}{x_1 + x_2\Lambda_{12}} - \frac{\Lambda_{21}}{x_2 + x_1\Lambda_{21}}\right) \quad —⑦$$

At this temperature the parameters $\Lambda_{12} = 0.216$ *and* $\Lambda_{21} = 3.442$. Find the composition at which azeotrope occurs. What is the corresponding pressure?

$y_1 = x_1$ — ①

$x_1 + x_2 = 1$ — ②

$y_1 + y_2 = 1$ — ③

$y_1 P = x_1 \gamma_1 P_1^{sat}$ — ④

$y_2 P = x_2 \gamma_2 P_2^{sat}$ — ⑤

Unknown: $x_1, y_1, x_2, y_2, \gamma_1, \gamma_2, P$

Known: $P_1^{sat}, P_2^{sat}, \Lambda_{12}, \Lambda_{21}$

Let us see if we can calculate the formation of an azeotrope, it turns out that a liquid mixture of propanol and water forms an azeotrope at 360 Kelvin. At this temperature, the vapor pressure is for both 1 and 2 are given and the activity coefficients are modeled using Wilson's equations, the model for activity coefficients are given in there and the parameters for the Wilson's equation lambda 1 2 and lambda 2 1 the values for those two parameters are also given.

The question is find the composition at which the azeotrope occurs, what is the corresponding pressure at which it occurs? Now, let us take a minute and see what information we have. So far we have dealt with vapor liquid equilibrium calculations alright and in vapor liquid equilibrium calculations this is a binary mixture and we have 2 phases vapor and liquid phase and like we did earlier.

If I calculate the degrees of freedom for this system, it turns out that degrees of freedom is going to be two components minus two phases plus 2 which is 2, I have two degrees of freedom and the only thing that is given to me in this particular problem is the temperature I have fixed only one variable temperature, 360 Kelvin. I do not know the pressure neither I know the composition of the vapor phase or the liquid phase.

So, in that sense all the degrees of freedom are 2, I only have one variable, but then I have some other information additional information about the system. I know that the system forms an azeotrope at these conditions and once it forms an azeotrope and what;

that means, if it forms an azeotrope is that the mole fraction of the vapor and the liquid phases at the condition I am looking at are equal or y 1 equals x 1 and because it is a binary system whether I write y 1 equals x 1 or y 2 equals x 2, it really does not matter, they are identical equations. So, we will just write one of those equations. So, this is an additional equation which is an outcome of the azeotrope formation. In addition to this equation, I can write the other equations we routinely right.

The first one being well, the second one I should say now is x 1 plus x 2 is 1, that is the closure equation for liquid mole fractions and y 1 plus y 2 is one that is the closure equation for vapor mole fractions. Let us number them that is 2, that is 3. Now, I can also write the phase equilibrium relations y 1 P is x 1 gamma 1 P 1 sat I have P 1 sat and P 2 sat directly given to me otherwise I can use antoine equations to get P 1 sat and P 2 sat at the temperature of interest in this case they are given to me readily. This turns out to be equation 4, and I can write another phase equilibrium relation for component 2 which is x 2 gamma 2 P 2 sat equals y 2 times P that turns out to be my equation 5, alright.

These are the 5 equations I have and let us see how many unknowns I have in this particular set of equations I am going to use this. I do not know y 1, I do not know x 1 2 right, I do not know y 2, I do not know x 2 that is 4, I do not know the total pressure that is 5, I do not know gamma 1, I do not know gamma 2. So, 1, 2, 3, 4, 5, 6 and 7 unknowns, I know P 1 sat and P 2 sat. So, I did not count them seven unknowns and I have five equations, but then if you think about it there are two additional equations, one each for gamma 1 and gamma 2 alright.

So, let me number these equations given to me for gamma 1 and gamma 2 that is 6 and that is 7. So, now, I have 7 equations and 7 unknowns let me write them down. The unknowns are x 1, y 1, x 2, y 2 gamma 1, gamma 2 and P all of these are unknown and what is known to me is P 1 sat, P 2 sat, lambda 1 2, the parameter for the Wilsons equation these are the four things I know and everything else pretty much is unknown in this set of equations, seven equations you see here.

So, the trick then is to be able to solve these seven equations and obtain the seven unknowns we are looking at. We can use any equation solver any suitable software to achieve this task. In fact, I have been telling it since the beginning, the major challenge is to be able to formulate the problem right once we do that we can always use a suitable software to solve the system of simultaneous equations and obtain the solution for such a system. But in certain cases, it might be easier to reduce these larger set of equations into a smaller number which we can handle in a software probably much more easily.

For example, if you think about it, I am going to start working with 4 and 5. Like I said we do not have to do this if you can use the software directly and use the solve the seven equations we are good, but then sometimes it helps to reduce the set of equations and look at what exactly is happening.

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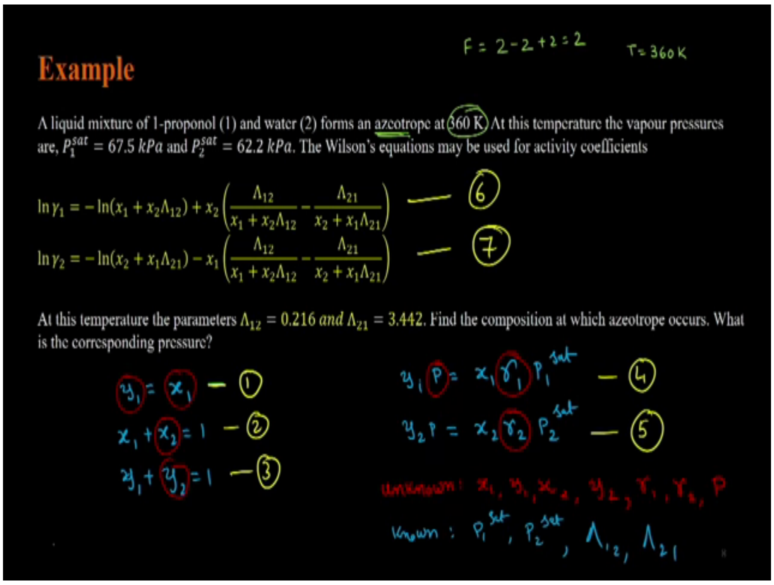

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unknown: $x_1, y_1, x_2, y_2, \gamma_1, \gamma_2, P$

Known: $P_1^{sat}, P_2^{sat}, \Lambda_{12}, \Lambda_{21}$

For example, let me work with equations 4 and 5 here x 1 gamma 1 P 1 sat is y 1 p, this is equation 4 and x 1 is y 1, that was equation 1. So, I can use equation 1 in 4 which means x 1 equals y 1. So, this one will cancel out and I have gamma 1 P 1 sat is P alright.

Similarly, for equation 5, I can write x 2 gamma 2 P 2 sat is y 2 P and because x 1 is y 1 it also implies x 2 is y 2 hence gamma 2 P 2 sat will be equal to P and once I have these two equations, both of them equal P which means gamma 1 P 1 sat is gamma 2 P 2 sat I have the values of P 1 sat and P 2 sat readily available to me alright.

So, if I take these equations here right and use the values of P 1 sat and P 2 sat, so let me write the expression for gamma 1, it is exponential of negative l n x 1 plus x 2 lambda 1 2 plus x 2 times lambda 1 2 over x 1 plus x 2 lambda 1 2 minus lambda 2 1 by x 2 plus x 1 lambda 2 1. This is gamma 1 and the P 1 sat value well, let me just write it as P 1 sat here this will equal exponential of minus l n x 2 plus x 1 lambda 2 1 minus x 1 lambda 1 2 by x 1 plus x 2 lambda 1 2 minus lambda 2 1 by x 2 plus x 1 lambda 2 1 times P 2 sat.

So, I can reduce these set of equations into let me give this a number, equation 8 you see here and this equation 8 is in terms of quantities. I know the only thing I do not know in this equation 8 is x 1. In fact, if you think about it I can replace x 2 everywhere in this equation 8 where the x 1 and once I do that, the only thing that I do not know in this equation 8 is x 1, I have knowledge of P 1 sat P 2 sat lambda 1 2 and lambda 2 1, I know everything in this equation 8 except x 1. So, I can solve for x 1 1 equation 1 unknown once I get x 1 as it turns out for this particular problem, the value of x 1 we get by solving equation 8 alone is let me write it is 0.352.

And once I have x 1, I can go back use each of these equations to get gamma 1 gamma 2 right, I can once I have x 1, I can calculate x 2 use equation 6 and 7 to calculate gamma 1 and gamma 2 and then I can go back and calculate the total pressure etcetera. So, I did that exercise.

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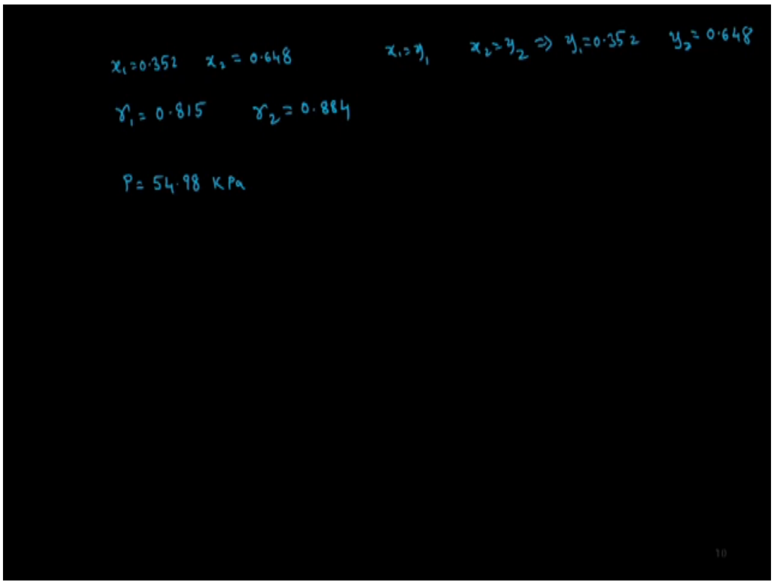

$x_1 = 0.352$ $x_2 = 0.648$ $x_1 = y_1$ $x_2 = y_2 \Rightarrow y_1 = 0.352$ $y_2 = 0.648$

$\gamma_1 = 0.815$ $\gamma_2 = 0.884$

$P = 54.98$ KPa

And let me give you some final numbers x 1 like I said is 0.352. So, x 2 is going to be 0.648. Now, since x 1 is y 1 and x 2 is y 2, this also implies y 1 is 0.352 and y 2 is 0.648 alright. That is the meaning of having an azeotrope, x 1 will be y 1 and x 2 will be y 2.

The values for gamma 1 is 0.815 and gamma 2 is 0.884. The value I get for the total pressure P is 54.98 kilo Pascals. So, we said we had seven unknowns, alright. So, let us see if we got all our unknowns 1, 2, 3, 4, 5, 6 and 7 unknowns. Those are our 7 unknowns, we obtained by solving the 7 equations, we reduce this set of seven equations into a single equation.

So, that it is easily workable, but once we finish that we can go back and calculate each of the unknown quantities in the original set of equations. So, this is how we can use the activity coefficient models along with the phase equilibrium relations to obtain at what conditions an azeotrope will occur in a given system.

Of course, like I said, this is just an example we could have to solve the example with a different activity coefficient model if we did not have the vapor pressures we could have used Antoine constants and so on. We can build up on what we have done in this particular example.

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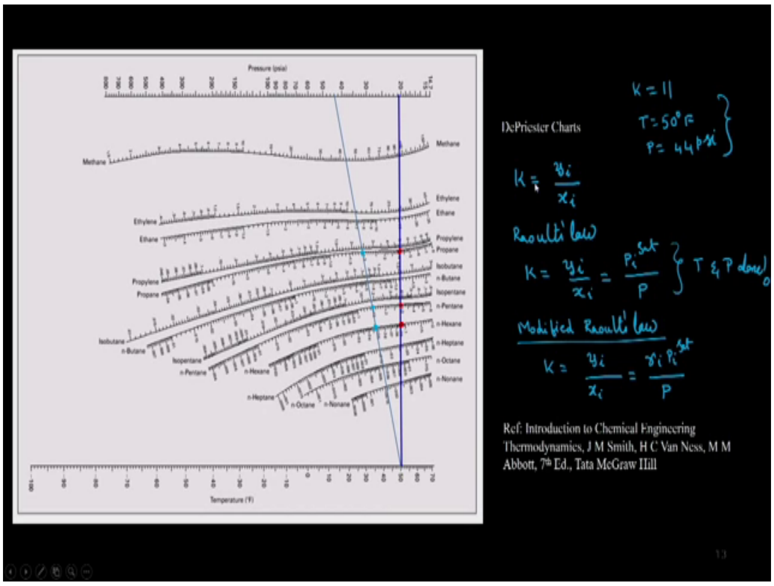

DePriester Charts

K = 11

T = 50°F

P = 44 psi

$K = \frac{y_i}{x_i}$

Raoult's law

$K = \frac{y_i}{x_i} = \frac{P_i^{sat}}{P}$ } T & P done

Modified Raoult's law

$K = \frac{y_i}{x_i} = \frac{\gamma_i P_i^{sat}}{P}$

Ref: Introduction to Chemical Engineering Thermodynamics, J M Smith, H C Van Ness, M M Abbott, 7th Ed., Tata McGraw Hill

Now, let us talk about solving vapor liquid equilibrium problems in an alternative way. The chart you see here is what is known as depriester chart and what the depriester chart does is give us the values of what is known as the K factor which is essentially the ratio of mole fraction in the vapor to that in the liquid y i over x i and this K factor is given as a function of temperature and pressure on this chart. At the bottom I have the temperature in Fahrenheit, at the top I have the pressure in PSI and what we do is we draw a line joining the given temperature and pressure and once we do that this line intersects the curves for various components that are shown in this particular chart.

So, for example, we have a set of hydrocarbons in this chart methane, ethylene, ethane, propylene, propane, butane, pentane etcetera. At the given temperature and pressure, we draw the we join those temperature and pressure conditions given to us and when it intersects the curves for each of the species the point of intersection for each species we can read a value on the curve. For example, for ethylene the value I can I read here is about 11.

So, the K value for ethylene is 11 at 50 degree Fahrenheit and a pressure of 44 PSI. So, at these conditions if the temperature and pressure are given to me, then I can join the temperature and pressure 50 here, 44 here and then pick the curve for ethylene and read the number of the chart. So, you see small numbers in here. So, that number on the chart turns out to be 11 for ethylene. That is how I get a K value at the given temperature and pressure conditions for the species indicated on the chart.

So, once we have the K value, it turns out it is easy to work with vapor liquid equilibrium problems. If you think about it, strictly speaking if Raoult's law is a applicable, K value is y i over x i which means it is the vapor pressure over the total pressure of the system right x i times P i sat will be y I times P which is the phase equilibrium relation for Raoult's law. So, the K factor will also equal the ratio of the vapor pressure to the total pressure and since vapor pressure is only dependent on temperature for that species, this essentially the K factor will depend on T and P alone alright.

On the other hand, if we use what we call as the modified Raoult's law that incorporates the non ideality of the liquid mixture, then K value is going to be y i over x i gamma i well sorry it is still y i over x i. So, that is gamma i P i sat over P. So, we have an additional functionality of the activity coefficient which of course, in turn depends on x. So, strictly speaking if the liquid phase is non ideal, then K value is going to be a function of mole fraction also. But then one can use an average value of the activity coefficient over the entire mole fraction range and come up with a reasonable estimate for the K value which is more or less applicable over the entire range of mole fractions.

This type of an approach works when the species are similar in chemical nature such as hydrocarbons which in fact, follow Raoult's law very closely the activity coefficients are pretty small and then we can sorry the activity coefficients are pretty close to unity and such an approach will be workable. Let us see how I can use this depriester chart to solve a problem.

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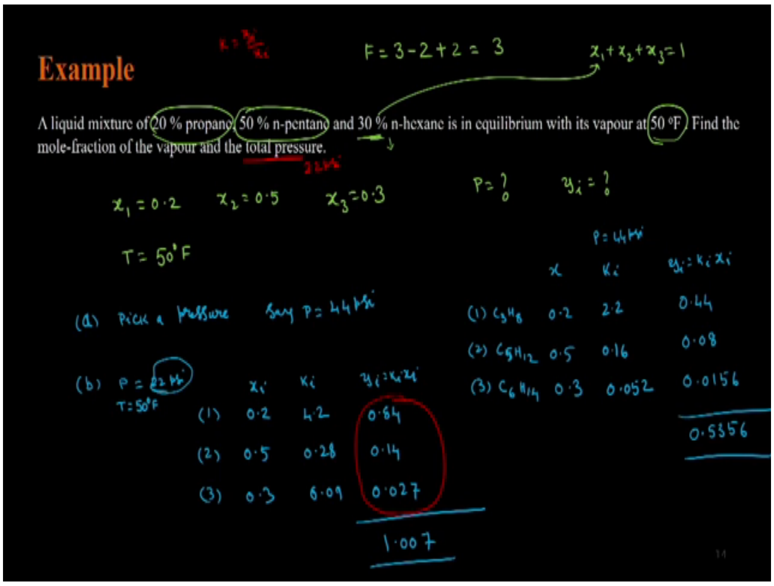

Example

A liquid mixture of 20 % propane, 50 % n-pentane and 30 % n-hexane is in equilibrium with its vapour at 50 °F. Find the mole-fraction of the vapour and the total pressure.

$F = 3 - 2 + 2 = 3$

$x_1 + x_2 + x_3 = 1$

$x_1 = 0.2 \quad x_2 = 0.5 \quad x_3 = 0.3$

$P = ? \quad y_i = ?$

$T = 50°F$

(a) Pick a pressure Say $P = 44$ psi

(b) $P = 22$ psi, $T = 50°F$

	x_i	K_i	$y_i = K_i x_i$
(1)	0.2	4.2	0.84
(2)	0.5	0.28	0.14
(3)	0.3	0.09	0.027
			1.007

$P = 44$ psi

	x	K_i	$y_i = K_i x_i$
(1) C_3H_8	0.2	2.2	0.44
(2) C_5H_{12}	0.5	0.16	0.08
(3) C_6H_{14}	0.3	0.052	0.0156
			0.5356

In here, we have a liquid mixture of propane; pentane and n-hexane in equilibrium with it is vapor at 50 degrees Fahrenheit. What we want to find is the mole fraction of the vapor and the total pressure. So, the first thing I do is find the degrees of freedom and see if there is enough information given so that I can solve the problem. For this particular, for this particular system I am looking at the degrees of freedom is the number of components in this case it is a ternary mixture I have three components minus the number of phases I have vapor and liquid phases and plus 2. So, that turns out to be three degrees of freedom. So, I should be given three independent information.

50 degrees Fahrenheit that is 1 and I have 2 mole fractions, propane and pentane. Now this is not over defined we do not have four informations that 30 percent n hexane is an additional information anyway. Once it is a ternary mixture and I have propane and pentane in the given amounts, then obviously, hexane has to be 30 percent because it has to satisfy that equation which reads x 1 plus x 2 plus x 3 is 1. The mole fractions of all the three components put together have to go to 1. So, it relates to that equation. So, in

that sense, the system is not over defined I still only have three pieces of information given to me.

Now, so let us call propane as 1, x 1 is 0.2, x 2 is 0.5 and; obviously, x 3 is 0.3. What I do know is that the temperature is 50 degrees Fahrenheit. What I do not know is the pressure and the compositions in the vapor phase y i. So, what we will do is to be able to use depriester charts to solve this problem, the easiest way is to pick a pressure. This can come from experience or so, what we do to solve this problem using depriester charts is first pick a pressure right, this can come from experience and once we pick a pressure let us pick a 44 PSI for this problem.

Once I pick that pressure, I have the temperature available to me, I have picked the pressure, will go back to depriester charts here 50 degree Fahrenheit, 44 is the light blue curve I have drawn here and at this condition temperature and pressure conditions I can read the K values of the chart right. I need K value for propane which is about there the K value for n pentane is write about there and n hexane is write about there.

So, I pick these three values and let me write them alright. So, I have x i or let us make a table alright that is the easiest way to do these problems we will make a table for 1, it is C 3 H 8, 2 is C 4 well C 5 H 12 and 3 is C 6 H 14; alright I have the values of x given to me 0.2, 0.5 and 0.3. At a pressure of 44 PSI, the K values I read off the chart turn out to be 2.2, 0.16 and 0.052. Once I have the K values because K is y over x alright K is y over x alright y is K times x i. So, I can calculate y I as K i times x i for each of the species and as it turns out this value is going to be 0.44, 0.08 for this and 0.0156 for this. And if I sum these K values sorry y i values for the three species, it turns out that this sum is 0.5356.

Obviously, the sum of mole fractions has to add up to unity which is not the case at this given condition. So, it means that the pressure I have picked initially is not correct. So, my guess is not correct, I have to revise my estimate for the pressure alright. We can do that, go back and then pick another pressure this time let us pick about 22 psi shown by the dark blue line in this particular curve on this particular chart and then I read the values again for each of the three species, right about there, there and there. And I will write these values again, alright. So, let me revise this oh let us make another table.

Let us write these values again. So, 1, 2 and 3, x i is 0.2, 0.5 and 0.3 K is at 22 psi and a temperature is still the same 50 degree Fahrenheit. These turn out to be 4.2, 0.28 and 0.09. And if I find the corresponding y is which is K i times x i, they turn out to be 0.84, 0.14 and 0.027 and if I add them, they sum to 10.007 which is pretty close to 1. So, this is a decent estimate for the pressure alright 22 psi.

So, hence the solution to this problem is the total pressure will be 22 psi and the mole fractions in the vapor phase are going to be these numbers 0.84, 0.14 and 0.027. So, that is the solution to this problem using K chart. We did not need Antoine constants to calculate the vapor pressures, we do not have to work through the phase equilibrium relations and things like that because most of it is coming via the K values in this particular case. So, this is an alternate approach, but essentially the underlying principle is still the same ok.

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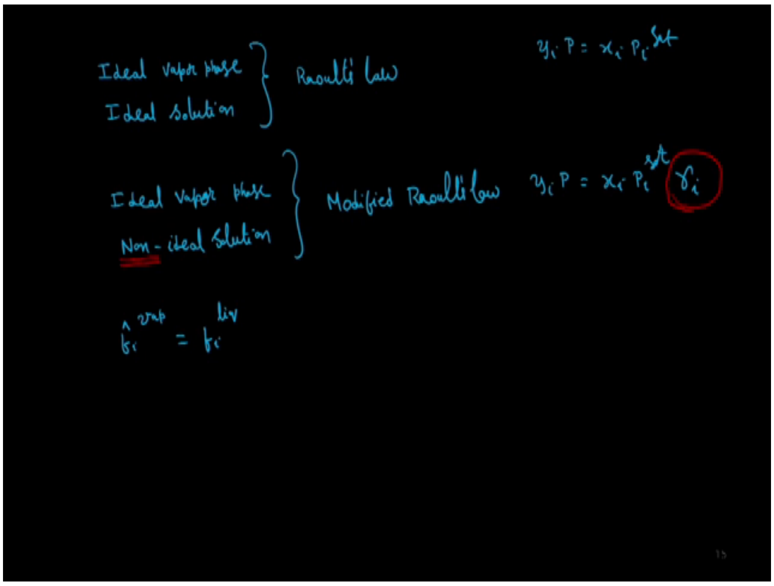

Ideal vapor phase
Ideal solution
} Raoult's law $y_i \cdot P = x_i \cdot P_i^{sat}$

Ideal vapor phase
Non-ideal solution
} Modified Raoult's law $y_i P = x_i \cdot P_i^{sat} \boxed{\gamma_i}$

$\hat{f}_i^{vap} = f_i^{liq}$

So, the examples we looked at so far involve ideal vapor phase, which means that the vapor phase behaves as if it is an ideal gas when the liquid mixture also behaves as an ideal solution we have used Raoult's law, when the mixture liquid mixture behaves as a non-ideal solution we have used the modified Raoult's law.

The essential difference between these two approaches is that we included the activity coefficient in the case of non ideal solutions, but in certain cases the vapor phase might also be non-ideal, meaning it does not have to behave as an ideal gas. If the vapor phase is non-ideal, how do we write? The phase equilibrium relation for such systems to answer that question we resort to the phase equilibrium relation in terms of fugacities, it reads the fugacity of the liquid should be equal to the fugacity of the vapor alright.

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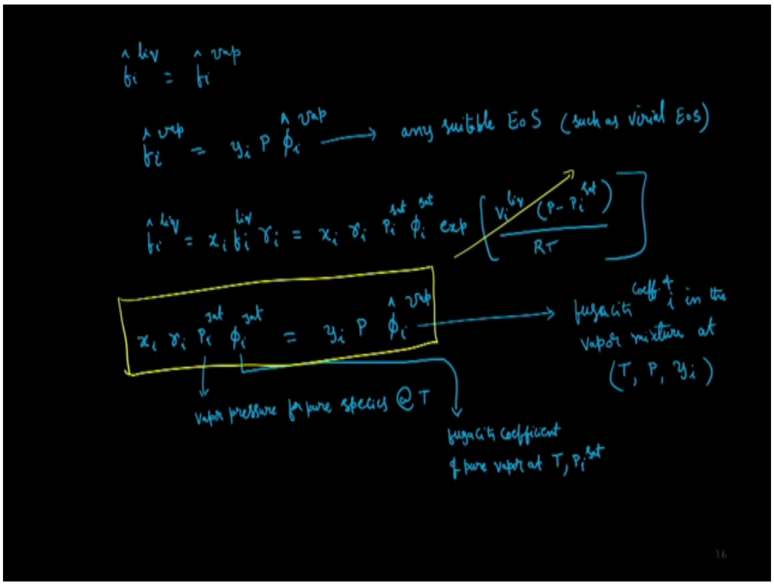

$$\hat{f}_i^{liq} = \hat{f}_i^{vap}$$

$$\hat{f}_i^{vap} = y_i P \hat{\phi}_i^{vap} \longrightarrow \text{any suitable EoS (such as virial EoS)}$$

$$\hat{f}_i^{liq} = x_i f_i^{liq} \gamma_i = x_i \gamma_i P_i^{sat} \phi_i^{sat} \cancel{\exp\left[\frac{V_i^{liq}(P - P_i^{sat})}{RT}\right]}$$

$$\boxed{x_i \gamma_i P_i^{sat} \phi_i^{sat} = y_i P \hat{\phi}_i^{vap}}$$

P_i^{sat} → vapor pressure for pure species @ T

ϕ_i^{sat} → fugacity coefficient of pure vapor at T, P_i^{sat}

$\hat{\phi}_i^{vap}$ → fugacity coeff. of i in the vapor mixture at (T, P, y_i)

We will start from there and we will write the fugacity for each of the phases without assuming that the vapor phase is ideal. Now, the fugacity of the vapor, if we do not assume that the vapor phase is ideal is then y i times P times the fugacity coefficient for that species in the vapor phase. And how do we get this? We can get this from any suitable equation of state such as the radial equation of state for example, right. So, once I use an equation of state, I can calculate the fugacity of the species in the vapor mixture and use it to calculate the fugacity of the vapor.

So, instead of y i p, it will be y i P times phi I hat vapor and for fugacity of the liquid remember we account an ideal solution will have fugacity of the liquid to be x i times f for the pure liquid or f i and the non-ideality we have incorporated using the activity coefficient which is gamma i alright.

Now, we converted the fugacity of the liquid pure liquid into it is vapor pressure and a pointing correction factor x i gamma i, the fugacity at the saturation conditions which is P i sat times the pointing correction factor exponential of V i liquid P minus P i sat over R T. This is how we calculate the fugacity of the liquid. And in this calculation, the fugacity at the saturation condition is assumed to be it is vapor pressure. That would be the case if the vapor is ideal. If the vapor does not behave as an ideal gas, then we have to account for the non ideality of the vapor phase and we do that by incorporating a fugacity coefficient for that species i at the at the saturation conditions.

Now, whether we choose to leave the pointing correction factor as it is or we choose to ignore it depends on the difference P minus P i sat, for now let us ignore that part. And if we do that the phase equilibrium relation will become x i gamma i P i sat phi i sat will equal y i P phi i hat vapor. So, this is the revised phase equilibrium relation that accounts for non ideality of the vapor phase.

Now, recall that P i sat is the vapor pressure for pure species at the temperature of interest T and this quantity is the fugacity coefficient of pure vapor at T and P i sat. So, it will depend on the temperature and of course, the pressure P i sat and this quantity is fugacity of i in the vapor mixture, sorry this is not fugacity fugacity coefficient of i in the vapor mixture and because it is in the mixture it will depend on the temperature, pressure and the mole fraction y I alright.

So, this is the revised phase equilibrium relation which involves the activity coefficients to account for non ideality of the liquid phase and fugacity coefficients to account for the non ideality of the vapor phase and we call this as the gamma phi formulation. So, if you look at it, it is almost identical to the equations we have been using so far for phase equilibrium calculations except that an additional fugacity coefficient term is incorporated into this equation to account for non ideality of the vapor phases. So, with that, we end the lecture today when we come back in the next video, we will look at solving one or two problems based on these ideas and then take it forward.

Thank you.