Chemical Engineering Thermodynamics
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Lecture - 33
Phase Equilibrium (VLE) Calculations for Non-ideal Solutions

Hello and welcome back. In the previous video, we were looking at phase equilibrium calculations using Raoult's law which is essentially for ideal solutions where, the activity coefficient is going to be 1. In this video we will look at Phase equilibrium Calculations for Non-ideal Solutions. So, there is a excess Gibbs free energy model which we will use to calculate the activity coefficients. And hence, the calculations are going to be a little bit more lengthier and involved than the Raoult's law; type of an approach, but the essential idea is still are going to remain the same.

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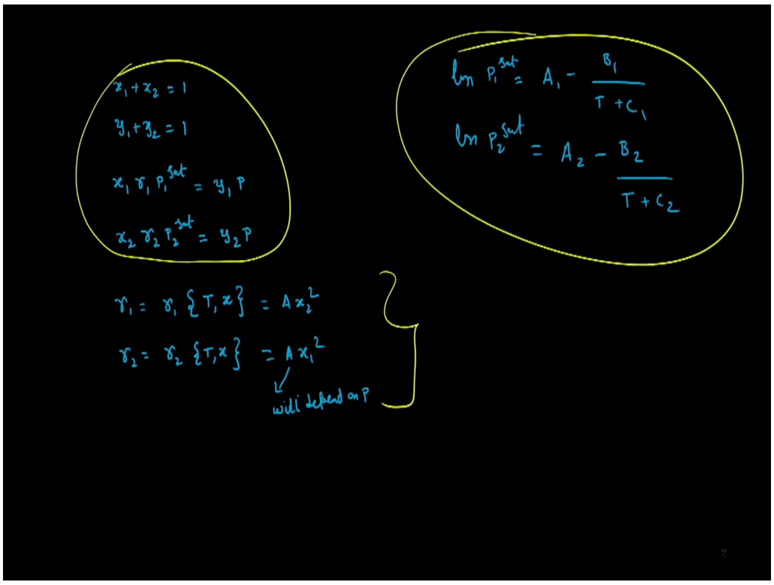

$x_1 + x_2 = 1$

$y_1 + y_2 = 1$

$x_1 \gamma_1 P_1^{sat} = y_1 P$

$x_2 \gamma_2 P_2^{sat} = y_2 P$

$\ln P_1^{sat} = A_1 - \frac{B_1}{T + C_1}$

$\ln P_2^{sat} = A_2 - \frac{B_2}{T + C_2}$

$\gamma_1 = \gamma_1 \{T, x\} = A x_2^2$

$\gamma_2 = \gamma_2 \{T, x\} = A x_1^2$

will depend on P

So, if we think about it there isn't much difference; the set of equations are going to be identical I will write a set of equations for binary mixture x 1 plus x 2 is going to be equal to 1 y 1 plus y 2 is going to be equal to 1. This is these are the two closure equations the phase equilibrium relations involved for non-ideal solutions, if we assume that the gas phase is ideals. When I say the gas phases ideal we mean it is ideal gas like, then the only non-ideality is due to mixing of the liquids which will change the phase equilibrium relation to x 1 gamma 1 P 1 sat will be equal to y 1 P. And, for the other component the fugacity of the liquid phase is going to be x 2 gamma 2 times P 2 sat that would equal the fugacity of the vapor.

Because, its ideal gas like that would be its partial pressure or y 2 times P. So, these are the 4 set of equations that we have; now in addition to the Raoult's law as you can see the two additional variables that appear in these equations are gamma 1 and gamma 2. If you recall at a given temperature and pressure gamma 1 is a function of mole fraction, it is a weak function of pressure and it is a functional mole fractions. So, it will depend on temperature and mole fraction that functionality with respective pressure is something which we can ignore. We have similarly gamma 2 will be a function of both temperature and x and in addition to this.

So, once I have these functionalities for example, if it is a molecules type of equation then it is A x 2 square and this one will be something like A x 1 square where, A itself will depend on pressure. It can be any of those models we looked at in the previous videos like a two suffix modulus equation or a Wilson's equation and RTL equation; any of those models can be used depending on the system we are looking at. And in addition to this of course, for the pure components the most popular by and large the most popular approach is to use the Antoine equation.

So, if we have the Antoine constants for component 1 and component 2 then we calculate these vapor pressures using those Antoine constant sorry, this should have been T plus C 1 and T plus C 2. So, once the temperature is given and the parameters for the Antoine equation are known I can calculate P 1 sat or I can use these two equations in combination with all these other equations to find whatever are going to be the unknowns. So, as you can see the first four equations and this equation are almost identical to what we have used in in the Raoult's law case except that in I get two additional equations now, to model the non-ideality of the liquid phase that will reflect as gamma 1 and gamma 2 in Raoult's law of course, these values were 1.

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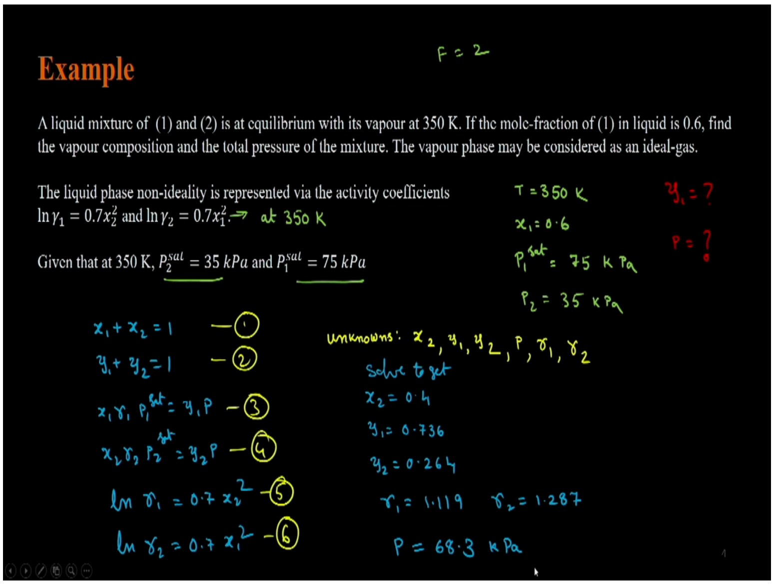

Example

$F = 2$

A liquid mixture of (1) and (2) is at equilibrium with its vapour at 350 K. If the mole-fraction of (1) in liquid is 0.6, find the vapour composition and the total pressure of the mixture. The vapour phase may be considered as an ideal-gas.

The liquid phase non-ideality is represented via the activity coefficients $\ln\gamma_1 = 0.7x_2^2$ and $\ln\gamma_2 = 0.7x_1^2$. $\rightarrow$ at 350 K

Given that at 350 K, $P_2^{sat} = 35\ kPa$ and $P_1^{sat} = 75\ kPa$

$T = 350\ K$

$x_1 = 0.6$

$P_1^{sat} = 75\ kPa$

$P_2 = 35\ kPa$

$y_1 = ?$

$P = ?$

$x_1 + x_2 = 1 \quad — ①$

$y_1 + y_2 = 1 \quad — ②$

$x_1 \gamma_1 P_1^{sat} = y_1 P \quad — ③$

$x_2 \gamma_2 P_2^{sat} = y_2 P \quad — ④$

$\ln\gamma_1 = 0.7 x_2^2 \quad — ⑤$

$\ln\gamma_2 = 0.7 x_1^2 \quad — ⑥$

unknowns: $x_2, y_1, y_2, P, \gamma_1, \gamma_2$

solve to get

$x_2 = 0.4$

$y_1 = 0.736$

$y_2 = 0.264$

$\gamma_1 = 1.119 \quad \gamma_2 = 1.287$

$P = 68.3\ kPa$

Now, once we understand this basic idea and the strategy, the approach is almost going to remain identical to what we have done; nevertheless let us solve a few examples based on non-ideal liquid phase. So, I have a liquid mixture of 1 and 2 in equilibrium with its vapor at 350 Kelvin. So, the temperature is given, temperature is 350 Kelvin and mole fractions mole fraction of the liquid is given x 1 is 0.6.

In addition the vapor pressures for P 1 sat and P 2 sat are given. So, we do not have to go and use Antoine equation or Antoine constant because, we do not know what 1 and 2 are in any case, we are just going to take the given data. So, P 1 sat is 75 kilo Pascal's P 2 sat is 35 kilo Pascal. So, we are going to use that information in our calculations directly instead of taking the Antoine Raoult, and P 2 sat is 35 kilo Pascal's that is just right.

Now, in addition what we want to find is the vapor phase composition y and the total pressure of the mixture P. And, we can consider the vapor phase to be ideal, but the liquid phase non-ideality or the activity coefficients are given by the two expressions you have seen therefore, ln gamma 1 and and ln gamma 2. So, once this information is available we will write the set of equations we want to work with the closure equations x 1 plus x 2 is 1 y 1 plus y 2 is 1 right and then x 1 gamma 1 P 1 sat is y 1 P x 2 gamma 2 P 2 sat is y 2 P.

And the model for the activity coefficients ln gamma 1 is 0.7 times x 2 square ln gamma 2 is 0.7 times x 1 square right. Now, if you actually think about it if you do a degree of freedom analysis apply the phase rule the degrees of freedom for this system are still by the way 2. And, the two variables we need are given to us the temperature which in turn manifests as the vapor pressure in these calculations and of course, the constant a 0.7 should be at this particular temperature.

This should be at 350 Kelvin, if this data is for other temperature we will not be able to use it for this temperature because, that constant a is a function of both temperature and mole fraction as we said sorry that constant a is a function of temperature; so obviously, that that needs to be at the same temperature. Now, we have 6 equations here 1 2 3 4 5 and 6 equations and the unknowns in this equation x 1 is known.

So, x 2 is not known y 1 y 2 that is 3 unknowns total pressure P gamma 1 and gamma 2 these are all my unknowns right, everything else in these 6 equations we know. So, we solve these 6 equations for the these are 6 independent equations of course, with all these 6 equations for the 6 unknowns to get what we want it turns out that x 2 obviously, in easiest one out of these x 2 will turn out to be 0.4 y 1 is 0.736 y 2.

So, we solve these 6 equations y 2 is 0.264, gamma 1 right gamma 1 in this case turns out to be 1.119 gamma 2 happens to be 1.287. And finally, the pressure P is 68.3 kilo Pascal's. This is the result I get by solving these 6 equations for the 6 unknowns. Some of these exercises we can do by hand, we can eliminate some equations, find the unknowns and then substitute and go about the calculation to get probably all the unknowns, but some of these equations are quite intensive to solve. So, we might need help of a software right.

But, essentially we want to formulate the problem as if we have these many independent equations, these many unknowns we solve them to get the unknowns and then take the data whatever data we need from there. So, as you can see in this case right when activity coefficients are not unity they are significantly different than unity, then as you can see in this case the activity coefficients are not unity. They are significantly different from unity of course, and hence the Raoult's law probably would not have worked to give us the correct picture for such a scenario.

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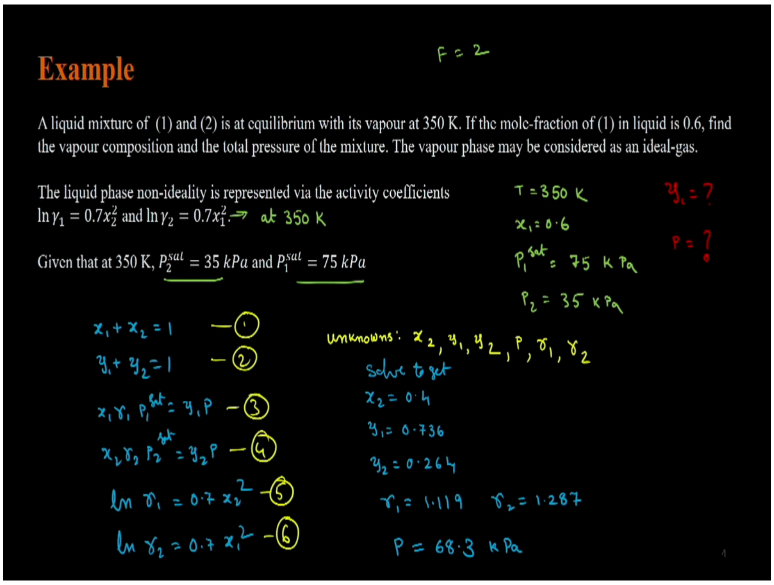

Example

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Given that at 350 K, $\underline{P_2^{sat} = 35\ kPa}$ and $\underline{P_1^{sat} = 75\ kPa}$

$T = 350$ K

$x_1 = 0.6$

$P_1^{sat} = 75$ kPa

$P_2 = 35$ kPa

$y_1 = ?$

$P = ?$

$x_1 + x_2 = 1 \quad — ①$

$y_1 + y_2 = 1 \quad — ②$

$x_1 \gamma_1 P_1^{sat} = y_1 P \quad — ③$

$x_2 \gamma_2 P_2^{sat} = y_2 P \quad — ④$

$\ln \gamma_1 = 0.7 x_2^2 \quad — ⑤$

$\ln \gamma_2 = 0.7 x_1^2 \quad — ⑥$

unknowns: $x_2, y_1, y_2, P, \gamma_1, \gamma_2$

solve to get

$x_2 = 0.4$

$y_1 = 0.736$

$y_2 = 0.264$

$\gamma_1 = 1.119 \quad \gamma_2 = 1.287$

$P = 68.3$ kPa

Now, let us move on right and try to solve another example. I have a similar problem, this time the vapor mole fraction is given to us y 1 is 0.9, the temperature is 350 Kelvin and at that temperature P 1 sat is 75 kilo Pascal's P 2 sat is 35 kilo Pascal's. Temperature is 350 Kelvin and the mole fractions are related by the same expression as earlier. And like I said of course, those the activity coefficients are given by the same expressions as earlier and like I said those activity coefficients are applicable at the temperature of interest in this case 350 Kelvin.

Only then we will of course, be able to use this data; in addition what we want to find in this case is the liquid composition x and the total pressure P. So, this is going to be a dew P calculation in our terminology and for the dew P calculation, since the temperature is known it is easy to find the vapor pressures P 1 sat and P 2 sat; in this case it is already given to us now.

For this problem we write the exact same set of equations as we did earlier, nothing is going to change those 6 equations are going to remain exact identical. In fact, the model for activity coefficient also happens to be same. So, x 1 P 1 sat gamma 1 is going to be y 1 P that is the phase equilibrium relation for 1 x 2 P 2 sat gamma 2 is y 2 P the phase equilibrium relation for component 2. And, then the model for activity coefficients ln gamma 1 is 0.7 x 2 squared ln gamma 2 is 0.7 x 1 squared.

Now, these are the 6 equations I have exactly as earlier, the only thing that is different now is what is known and what is unknown. In this case the unknown is out of these is y 2 which is trivial of course, then x 1 x 2 P gamma 1 and gamma 2; those are my 6 unknowns everything else is known. P 1 sat P 2 sat are known y 1 is known right. So now, I solve these 6 equation 6 independent equations for the 6 unknowns and it turns out that the values I get are as follows y 2 is of course, 0.1 x 1 is 0.877 x 2 is 0.123 gamma 1 is 1.01 gamma 2 is 1.011 gamma 2 is 1.713.

And the total pressure P in this case happens to be 73.9 kilo Pascal's 73.9 kilo Pascal's right. So, nothing has changed we just have a different set of unknowns, but the same set of equations to solve and this is where we end up with. Now, there are two or three things that are interesting to note in here from the previous example. The previous problem is the same model same parameters etcetera. In this case when the liquid composition is 0.6 x 1 is 0.6 gamma 1 is 1.1 not 19 and gamma 2 is 1.287.

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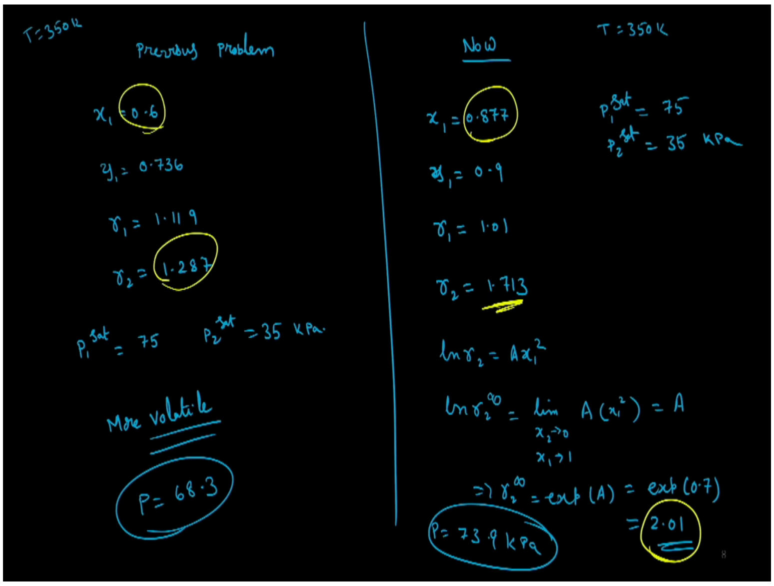

$T = 350\,K$

Previous problem

$x_1 = 0.6$

$y_1 = 0.736$

$\gamma_1 = 1.119$

$\gamma_2 = 1.287$

$P_1^{sat} = 75 \quad P_2^{sat} = 35\ kPa.$

More volatile

$P = 68.3$

Now

$T = 350\,K$

$x_1 = 0.877$

$y_1 = 0.9$

$\gamma_1 = 1.01$

$\gamma_2 = 1.713$

$P_1^{sat} = 75$

$P_2^{sat} = 35\ kPa$

$\ln \gamma_2 = A x_1^2$

$\ln \gamma_2^{\infty} = \lim_{\substack{x_2 \to 0 \\ x_1 \to 1}} A(x_1^2) = A$

$\Rightarrow \gamma_2^{\infty} = \exp(A) = \exp(0.7)$

$= 2.01$

$P = 73.9\ kPa$

So, what I will do is I will quickly list that, for the previous problem because both of these problems are same; based on the same set of chemical species in the same activity coefficient models right. In the previous problem x 1 is 0.6 in this problem x 1 we got was 0.877 right, as x 1 increases the liquid phase mole fraction increases so, does the vapor phase mole fraction right. And, if you can recall y 1 earlier was 0.736 and y 1 now is 0.9 although y 1 is given and we found x 1.

But, essentially at equilibrium this is what it is, in both cases the temperature is 350 Kelvin, pressure is of course, different right. So, as x 1 increased y 1 increased and if you look at gamma 1 it is even more interesting it is 1.119 earlier. And, as x 1 increases we are approaching the pure component limit for 1 which means gamma 1 has to decrease and go closer to unity and that is what happens when x 1 is 0.877.

Now, gamma 1 is 1.01, now what happens for gamma 2 then? Gamma 2 earlier was 1.287 and gamma 2 now is 1.713. In fact in fact, based on this model which is ln gamma 2 is A x 1 squared right based on this model ln gamma 2 infinity is essentially limit of x 2 going to 0 or x 1 going to 1 A times x 1 squared. So, that will turn out to be A which means gamma 2 infinity is going to be exponential of this quantity A which happens to be 0.7 in our example.

So, that exponential of 0.7 is 2.01. So, essentially at the pure component limit as we keep increasing x 1 as keep decreasing x 2 we are at x 1 of 0.877 here. But, as x 1 approaches unity the pure component 1 for 1 the infinite dilution activity coefficient for 2 gamma 2 infinity will approach a value of 2.01. That is why when x 1 changed from 0.6 here to 0.877, here gamma 2 has increased from 1.287 towards this value of 2.01.

And we are somewhere here 1.7 and we keep increasing that it will hit this limit of 2.01 at the pure component limit of x 1 going to 1. So, that is what it is also the in terms of the pressures, what about I can guess P 1 sat is if you recall at this temperature P 1 sat is 75. P 2 sat for both cases is 35 right because, the temperature is same and the species are same P 1 sat and P 2 sat are same it is 35 kilo Pascal’s right.

Now, in this case as x 1 increases we are increasing the liquid phase mole fraction for component 1, component 1 happens to be the more volatile component. Its vapor pressure is more so, its volatility is more. So, it is the more volatile component and because we have a liquid richer in more volatile component, the total pressure of the mixture at the same temperature is going to be higher right. And, that is why if you recall the total pressure earlier was in the first problem 68.3 and in the second problem it is 73.9 kilo Pascal’s this is the total pressure.

Because, we have a liquid mixture richer in more volatile component the total pressure of this mixture also will go up. So, these are things which you would expect, but then now once we work with the numbers it is easier to appreciate these facts and then when we see experimental data that does not obey such trends, we can raise a red flag then right. So, that is the reason we discuss such trends, now let us try to work on another example.

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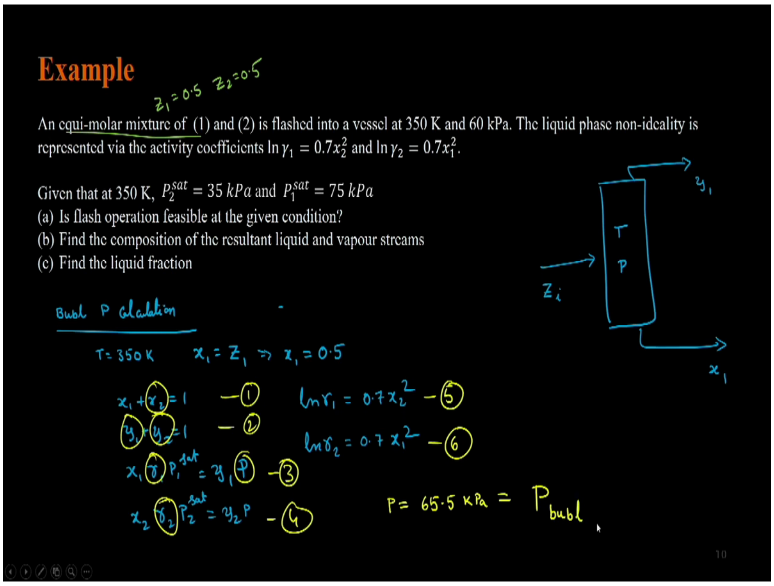

Example

$z_1 = 0.5$ $z_2 = 0.5$

An equi-molar mixture of (1) and (2) is flashed into a vessel at 350 K and 60 kPa. The liquid phase non-ideality is represented via the activity coefficients $\ln \gamma_1 = 0.7x_2^2$ and $\ln \gamma_2 = 0.7x_1^2$.

Given that at 350 K, $P_2^{sat} = 35\ kPa$ and $P_1^{sat} = 75\ kPa$

(a) Is flash operation feasible at the given condition?

(b) Find the composition of the resultant liquid and vapour streams

(c) Find the liquid fraction

Bubl P Calculation

$T = 350\,K \qquad x_1 = z_1 \Rightarrow x_1 = 0.5$

$x_1 + x_2 = 1 \quad - ①$

$y_1 + y_2 = 1 \quad - ②$

$x_1 \gamma_1 P_1^{sat} = y_1 P \quad - ③$

$x_2 \gamma_2 P_2^{sat} = y_2 P \quad - ④$

$\ln \gamma_1 = 0.7 x_2^2 \quad - ⑤$

$\ln \gamma_2 = 0.7 x_1^2 \quad - ⑥$

$P = 65.5\ kPa = P_{bubl}$

So, in this problem we have a flash operation and a equi-molar liquid mixture, an equi-molar mixture I am sorry is flashed into a vessel at 350 Kelvin and 60 kilo Pascal's. The liquid phase non-ideality is represented via the activity coefficients given by the same expressions as we looked at earlier and the vapor pressures at the temperature are of course given. So, we need to first of all figure out if this operation is feasible and then find the resultant composition of the liquid and vapor streams we get from this operation.

And finally, the liquid fraction we will get out of the flash vessel; if you recall if flash operation involves taking a feed and pushing in to a flash vessel which is maintained at a constant temperature and pressure. We get a liquid stream and a vapor stream out of this with compositions x 1 and y 1. We call the composition of the feed as z i if you recall, when we try to solve such a problem using Raoult's law approach.

So, this is a similar problem and to solve this problem we solve the phase equilibrium relations and other expressions we have used earlier. But to answer the first question is the flash operation feasible at the given condition, if you recall when we worked with Raoult's law we said the feasibility of a flash operation is determined by finding what we as the dew point pressure and the and the bubble point pressure. The first thing to do is to find the dew point pressure.

So, to check the feasibility of an operation if you recall when to check the feasibility of an operation flash operation, when we have worked with Raoult’s law we said the way we do that is we take the feed mole fraction and set it equal to the mole fraction of the liquid mixture once and vapor mixture once, do a dew P or a bubble P calculation and get the total pressure. Now so, let us do a bubble P calculation, for a bubble P calculation the temperature is 350 Kelvin and we want x the mole fraction of the liquid phase.

So, what we will do is we will set it equal to the overall mole fraction of the feed which is z 1 which implies x 1 in this case will be equal to 0.5, since it is n equi-molar mixture; maybe we should write that out here right z 1 is 0.5 and z 2 also is equal to 0.5. Now, when we do this and do a bubble P calculation the equations we are looking at then are x 1 plus x 2 is 1 y 1 plus y 2 is 1 x 1 gamma 1 P 1 sat is y 1 P x 2 gamma 2 P 2 sat is y 2 P, ln gamma 1 is 0.7 times x 2 square ln gamma 2 is 0.7 times x 1 square.

Now, I solve this; now I solve these 6 equations to get these 6 unknowns, let me highlight the unknowns here x 2 is an unknown y 1 and y 2 are unknowns gamma 1 and gamma 2 are unknowns 1 2 3 4 5 and the total pressure P. Once I solve these 6 equations to get the 6 unknowns I get a pressure and the vapor mole fraction in this case the liquid mole fraction is the feed mole fraction. And, once I do that the pressure I get turns out to be the pressure I get turns out to be 65.5 kilo Pascal’s and we call this as the bubble point pressure.

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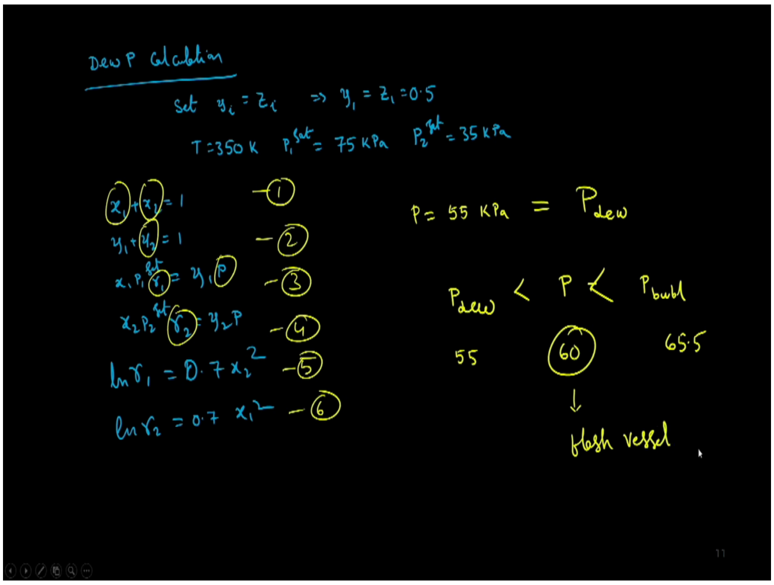

Dew P Calculation

Set $y_i = z_i \Rightarrow y_1 = z_1 = 0.5$

$T = 350\ K \quad P_1^{sat} = 75\ KPa \quad P_2^{sat} = 35\ KPa$

$x_1 + x_2 = 1$ — ①

$y_1 + y_2 = 1$ — ②

$x_1 P_1^{sat} \gamma_1 = y_1 P$ — ③

$x_2 P_2^{sat} \gamma_2 = y_2 P$ — ④

$\ln \gamma_1 = 0.7\, x_2^2$ — ⑤

$\ln \gamma_2 = 0.7\, x_1^2$ — ⑥

$P = 55\ KPa = P_{dew}$

$P_{dew} < P < P_{bubl}$

55 60 65.5

$\downarrow$

flash vessel

I perform a similar exercise for a dew P calculation, in a dew P calculation we set y i equal to z i which implies y 1 for us will be z 1 or 0.5, the temperatures and is 350 Kelvin which means P 1 sat and P 2 sat at this temperature are what they are given to us, it is 35 kilo Pascal. And, we solve the same set of equations I am not going to rewrite them, but it is the same set of 6 equations; well we will solve the same set of 6 equations as earlier. Let us write them anyway x 1 plus x 2 is 1 y 1 plus y 2 is 1 x 1 P 1 sat is gamma 1 is y 1 P x 2 P 2 sat gamma 2 is y 2 P gamma 1 or ln gamma 1 is 0.7 x 2 square ln gamma 2 is 0.7 x 1 square.

And, when we have this because I know y 1 the unknowns in this set of equations are x 1 x 2 y 2 P gamma 1 and gamma 2. Those are my 6 unknowns which I get by solving these 6 equations and when I complete this exercise the value I get for pressure is a 55 kilo Pascal's and we call this as the dew point pressure. Now, we got the dew point pressure and the bubble point pressure for this operation and as you see the dew point pressure is less than the pressure we are working with the flash vessel which is less than the bubble point pressure. The numbers are 55 here 65.5 for the bubble point we got earlier and the flash vessel is operating at an intermediate pressure.

So, because the flash vessel is operating at an intermediate pressure it is possible or the operation is feasible. Now, having answered that question right the flash vessel is operating at 60 kilo Pascal's which is intermediate pressure. So, the operation itself is feasible. Now, having answered that question we want to find the composition of the resultant liquid and vapor streams. Now, when we look at the flash vessel it is operating at a certain temperature and pressure.

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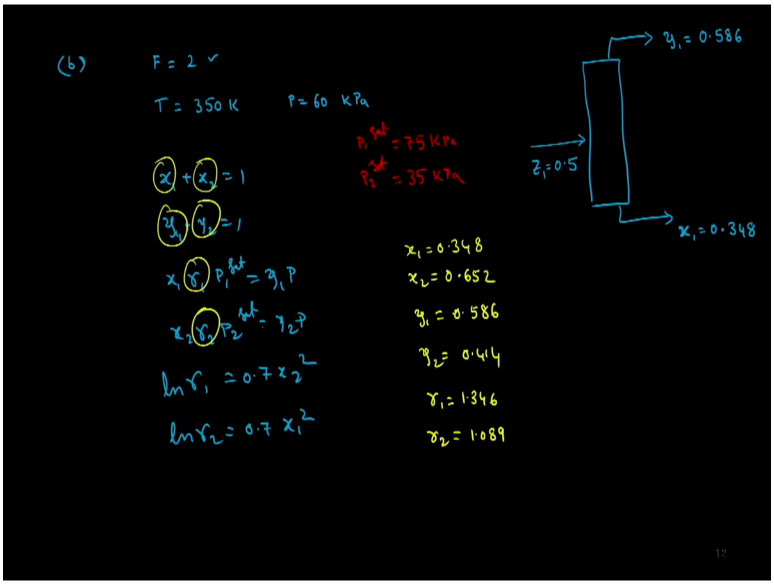

(b) $F = 2$ ✓

$T = 350\ K$ $P = 60\ kPa$

$P_1^{sat} = 75\ kPa$

$P_2^{sat} = 35\ kPa$

$x_1 + x_2 = 1$

$y_1 + y_2 = 1$

$x_1 \gamma_1 P_1^{sat} = y_1 P$

$x_2 \gamma_2 P_2^{sat} = y_2 P$

$\ln \gamma_1 = 0.7 x_2^2$

$\ln \gamma_2 = 0.7 x_1^2$

$x_1 = 0.348$

$x_2 = 0.652$

$y_1 = 0.586$

$y_2 = 0.414$

$\gamma_1 = 1.346$

$\gamma_2 = 1.089$

So, let us try to solve part b, again the degrees of freedom for this system it is a binary system 2 phases. So, degrees of freedom is 2, I just need to get 2 variables to fix the state of the system. I just need to have 2 variables to fix the state of the system which turned out to be the temperature at 350 Kelvin and the pressure at 60 kilo Pascal's in this case. These are the conditions at which the flash vessel is operating.

And whatever is leaving the flash vessel the assumption is that these two streams are going to be at equilibrium, at the same conditions as that in the flash vessel. So, those two variables are given to us. So, I should be able to calculate x 1 and y 1 at these conditions. Now, I will write the same set of equations again x 1 plus x 2 is 1 y 1 plus y 2 is 1 x 1 gamma 1 P 1 sat is y 1 P x 2 gamma 2 P 2 sat is y 2 P gamma 1 or ln gamma 1 is 0.7 x 2 squared ln gamma 2 is 0.7 x 1 squared.

Having written these 6 equations next task is to identify what are unknowns. In this case once the temperature and pressure is fixed P 1 sat and P 2 sat are fixed which are given to us 73 sorry, 75 kilo Pascal's and P 2 sat is 35 kilo Pascal's. These two numbers are given because of the temperature and the unknowns are x 1 x 2 y 1 y 2 gamma 1 gamma 2. Those are my 6 unknowns everything else is known in this particular set of 6 equations. I find these 6 unknowns and the values I have are x 1 is 0.247 y 1 is 0.5, I am sorry and the values and the values I have are x 1 is 0.348 x 2 is 0.652 of course, y 1 is 0.586 y 2 is 0.414.

So, those are the 4 variables gamma 1 and gamma 2 of course, can be written gamma 1 is 1.346 and gamma 2 is 1.089. If you look at these numbers it is also obvious that we are sending an equi-molar mixture with a mole fraction of 0.5. And, the vapor is richer in the more volatile component; in this case the more volatile component is the one which has a higher vapor pressure which is 1. So, the vapor has a mole fraction which is greater than that of the feed and the liquid has a mole fraction that is lower than that of the feed. So, we are going to find more volatile component more in the vapor phase; obviously, and low less in the liquid phase. So, we can find the vapor and liquid compositions for this flash operation.

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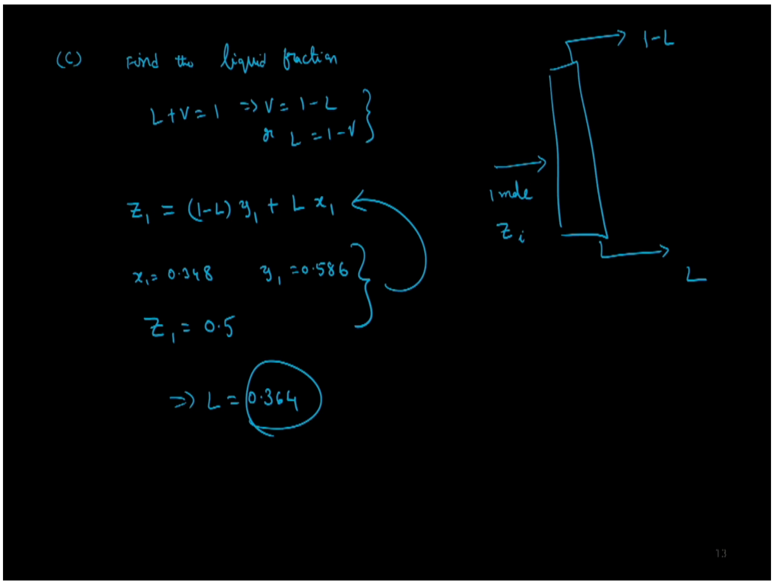

(c) Find the liquid fraction

$$\left.\begin{aligned} L+V=1 \Rightarrow V &= 1-L \\ \text{or } L &= 1-V \end{aligned}\right\}$$

$$z_1 = (1-L)\,y_1 + L\,x_1$$

$$\left.\begin{aligned} x_1 = 0.348 \quad & y_1 = 0.586 \\ z_1 = 0.5 & \end{aligned}\right\}$$

$$\Rightarrow L = \boxed{0.364}$$

The next thing to do is find the liquid fraction. Now, if you recall the way we have defined liquid and vapor fractions is for 1 mole of feed, the mole fraction z i; V is the vapor L is the liquid. So, the overall balance will be L plus V is 1. So, I can call this as 1 minus V or this as 1 minus L whichever way you look at it right, V is 1 minus L or L is 1 minus V right. Now, in this case I want the liquid fraction so, I will leave the variable L there and get rid of V that is easier to work with. So, liquid is L vapor is 1 minus L for 1 mole of feed. And, a component balance for 1 will yield z 1 times 1 mole will be equal to 1 minus L times y 1 that is the vapor mole fraction L times x 1.

This is the equation I want to solve and I already have x 1 and y 1 values from the previous step right x 1 and y 1 values from this step; I am going to use those. I know that x 1 is 0.348 y 1 is 0.586 and z of course, is the feed composition which is 0.5. Once I use these 3 values here I can find L and in this case L turns out to be 0.364. So, for every mole of vapor that we feed into the liquid mixture we get 0.364 moles of liquid and 0.636 moles of vapor that is how we work on a flash problem. So, this part essentially is exactly identical to what we have done in the Raoult's law case. The only thing we are taking from the previous step are the values for x 1 and y 1 which of course, in involve the activity coefficient calculations.

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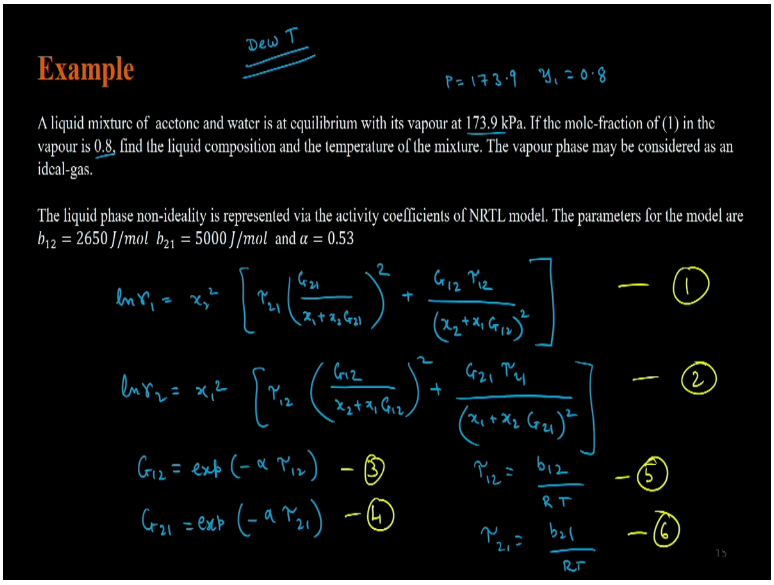

Example

Dew T

$P = 173.9 \quad y_1 = 0.8$

A liquid mixture of acetone and water is at equilibrium with its vapour at 173.9 kPa. If the mole-fraction of (1) in the vapour is 0.8, find the liquid composition and the temperature of the mixture. The vapour phase may be considered as an ideal-gas.

The liquid phase non-ideality is represented via the activity coefficients of NRTL model. The parameters for the model are $b_{12} = 2650\,J/mol$ $b_{21} = 5000\,J/mol$ and $\alpha = 0.53$

$$\ln\gamma_1 = x_2^2\left[\tau_{21}\left(\frac{G_{21}}{x_1+x_2G_{21}}\right)^2 + \frac{G_{12}\tau_{12}}{(x_2+x_1G_{12})^2}\right] \quad — ①$$

$$\ln\gamma_2 = x_1^2\left[\tau_{12}\left(\frac{G_{12}}{x_2+x_1G_{12}}\right)^2 + \frac{G_{21}\tau_{21}}{(x_1+x_2G_{21})^2}\right] \quad — ②$$

$$G_{12} = \exp(-\alpha\tau_{12}) \quad — ③ \qquad \tau_{12} = \frac{b_{12}}{RT} \quad — ⑤$$

$$G_{21} = \exp(-\alpha\tau_{21}) \quad — ④ \qquad \tau_{21} = \frac{b_{21}}{RT} \quad — ⑥$$

Now, all the models; now all the problems or examples we looked at so far involve simple models for activity coefficients although that does not have to be the case right. We can use more complicated models, as in this case we want to use an NRTL model, a non-random 2 liquid theory model, the parameters for the model b 1 2 and b 2 1 are given. And the total pressure of the mixture is given P is 173.9 and the vapor mole fraction is given y 1 is 0.8. And, the vapor mole fraction is given y 1 is 0.8; what we are interested in finding out is the temperature and the liquid composition.

So, it will be a Dew T calculation, but we are using a NRTL model to solve this problem. This is a liquid mixture of acetone and water and because, the temperature is unknown we also do not have information on the pure component vapor pressures. But, first let us write the model equations themselves ok, that might be a good start. Let us write the model equations, for NRTL model it turns out the following equations hold, but first let us write the model equations themselves. For NRTL model it turns out that the following equations hold ln gamma 1 is given by this expression here x 2 squared tau 2 1; you can refer any standard textbook or a good source to get these model equations.

It might be a little lengthy to work and obtain the equations directly from the excess Gibbs free energy x 1 G 1 2 whole square right and ln gamma 2 turns out to be x 1 squared tau 1 2 G 1 2 by x 2 plus x 1 G 1 2 whole squared plus G 2 1 tau 2 1 by x 1 plus x 2 and G 2 1 whole squared. So, let us start numbering these equations if there will be a lot of them. So, let us start numbering to write it from the beginning. These are the two equations for the activity coefficients right. I do not know what G 1 2 and G 2 1 are in fact, they are given from the model.

G 1 2 is exponential of negative alpha tau 1 2 G 2 1 is exponential of negative alpha tau 2 1. Notice that alpha is given to us, but we still do not know what tau 1 to n tau 2 1 are and it turns out that tau 1 2 is related to b 1 2; we have the equation by RT and tau 2 1 is b 2 1 over RT. So, I am going to number these equations as well 5 and 6 right, these are 6 equations so far we have written just for the activity coefficient models and various combinations of those. But, that we know the other parameters we know b 1 2, we know R is the universal gas constant, we know the value for alpha.

Now, the pressure and y 1 are also given to us, of course in these expressions what we have is x 1 and x 2 the mole fractions of the liquid phase which we do not have information about. But, what we do know is the pressure and y 1.

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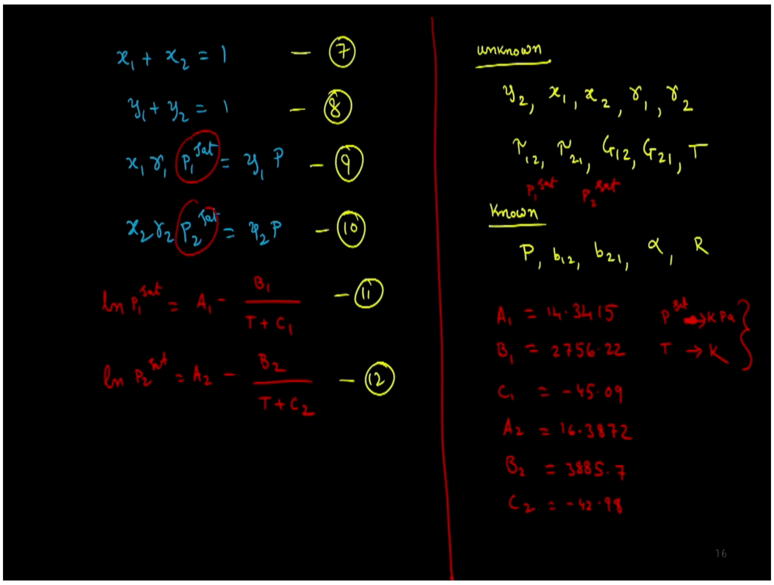

$x_1 + x_2 = 1$ — ⑦

$y_1 + y_2 = 1$ — ⑧

$x_1 \gamma_1 P_1^{sat} = y_1 P$ — ⑨

$x_2 \gamma_2 P_2^{sat} = y_2 P$ — ⑩

$\ln P_1^{sat} = A_1 - \frac{B_1}{T + C_1}$ — ⑪

$\ln P_2^{sat} = A_2 - \frac{B_2}{T + C_2}$ — ⑫

unknown

$y_2, x_1, x_2, \gamma_1, \gamma_2$

$\tau_{12}, \tau_{21}, G_{12}, G_{21}, T$

P_1^{sat} P_2^{sat}

Known

$P, b_{12}, b_{21}, \alpha, R$

$A_1 = 14.3415$

$B_1 = 2756.22$

$C_1 = -45.09$

$A_2 = 16.3872$

$B_2 = 3885.7$

$C_2 = -42.98$

$P^{sat} \rightarrow kPa$

$T \rightarrow K$

So, let us write the other set of equations we can work with, we know we have our closure equations x 1 plus x 2 is 1 y 1 plus y 2 is 1. And, from the activity coefficients we calculate using the NRTL model, we can use them in phase equilibrium relations x 1 gamma 1 P 1 sat is going to be equal to y 1 P x 2 gamma 2 P 2 sat is going to be equal to y 2 P alright. So, this will be my equation 7 8 9 10, of 10 equations so, far let us see if I can write all the unknowns on the side y 1 is given. So, technically because we are using y 1 plus y 2 is 1 we mean that y 2 we do not know.

We do not know x 1, we do not know x 2, we do not know gamma 1, we do not know gamma 2; well let us also list the known values now since we are at it we know the pressure P so, far that is what it is. Let us go to the previous one, in here I do not know tau 1 2 and tau 2 1, I do not know G 1 2 and G 2 1. I am going to use the equations we wrote there, but we do not know the numerical values as of now. So, it is tau 1 2, tau 1 G 1 2 G 2 1 and in those expressions what I do know are b 1 2 R and alpha and b 2 1 of course, what I know are b 1 2 b 2 1 alpha of course, R is the universal gas constant.

So, let us see how many equations I have 10 equations, I have 1 2 3 4 5 6 7 8 9. What did we miss? G 1 2 G 2 1 tau 1 2 tau 2 1 that is 4 of them well I know b 1 2 and b 2 1 I know b 1 2 and b 2 1 I know alpha, I know R I know P right; I do not know the temperature here which is in terms of tau 1 2 and tau 2 1. So, that is something I do not know yet of course, the temperature. So, those are the 10 unknowns and I know these equations, but if you pay a closer attention to these equations we also have the vapor pressures, technically we do not know them because we do not know the temperature.

So, we also do not know P 1 sat and P 2 sat. So now, in addition to those 10 variables the vapor pressures are two more variables. So, I have 12 unknowns the others are what I know. Now, to get vapor pressures if you recall we can use Antoine constants right. So, what we will do is write these expressions for P 1 sat in terms of Antoine constants A 1 minus B 1 by T plus C 1 ln of P 2 sat is A 2 minus B 2 by T plus C 2. Once I write those two equations now, I have 12 equations and 12 unknowns which I can solve using any suitable software and I have my result. Of course, I need to know I need to know the Antoine constants to be able to do that so, A 1 B 1 C 1.

Well, let us write them oh I have taken these numbers from a handbook that is not given as a part of the problem, but they are taken from a handbook. So, I will give you those numbers, if you cannot find them you can work with these numbers. For 1 this is 14.3415 B is 2756.22, C is negative 45.09, for 2 this is 16.3872 is water 1 is acetone 3885.7. This is negative 42.98, P sat is in kilo Pascal's and the temperature is in Kelvin and that is a natural logarithm.

So, once we use these parameters we should be able to get the vapor pressure at a given temperature. So, the trick then is to we can simplify this set of equations, do some substitutions, make them into a smaller set, but essentially what we are looking at is these 12 equations and the 12 unknowns I have listed here. We solve for these 12 equations and 12 unknowns to get what we want and as it turns out the numbers look something like this.

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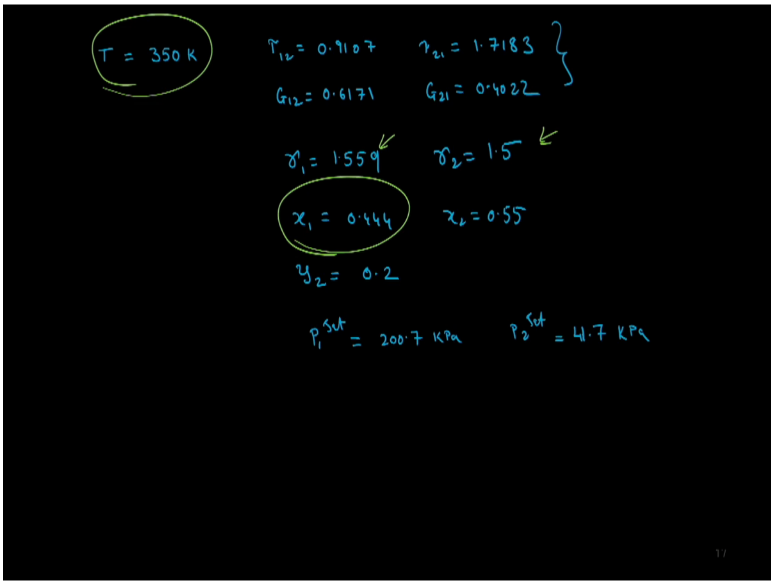

$T = 350\ K$

$\tau_{12} = 0.9107$ $\tau_{21} = 1.7183$

$G_{12} = 0.6171$ $G_{21} = 0.4022$

$\gamma_1 = 1.559$ $\gamma_2 = 1.5$

$x_1 = 0.444$ $x_2 = 0.55$

$y_2 = 0.2$

$P_1^{sat} = 200.7\ KPa$ $P_2^{sat} = 41.7\ KPa$

The temperature I get is 350 Kelvin, at this temperature tau 1 2 I have is 0.9107, tau 2 1 I have is 1.7183 G 1 2; remember in NRTL model G 1 2 and G 2 1 have nothing to do with the Gibbs free energy that we usually talk about. They are just a part of this equation parameter list 0.6171 and G 2 1 is 0.4022. And, once I have these 2 I can go back and calculate gamma 1, this case turns out to be 1.559 and gamma 2 turns out to be 1.5. Of course, to calculate gamma 1 we also need x right, x turns out to be 0.444 and x 2 turns out to be 0.556.

We said we have 12 unknowns, how many did we write so far? 1 2 3 4 5 6 7 8 9, we are still missing 3 of them. The other one of course, is y 2 which simply happens to be 0.2, that is 10 we still have two more to go well P 1 sat and P 2 sat from Antoine equation; at the given condition P 1 sat is 200.7 for acetone that is more volatile component and P 2 sat is 41.7 kilo Pascal's. So, as you can see we saw the earlier set of 12 equations to get these 12 unknowns 1 2 3 4 5 6 7 8 9 10 11 and 12. So, that completes the solution to this problem.

We can take whatever data we need from here, usually what we are interested is not the auxiliary variable tau 1 2's and G 1 2's, but rather you know the mole fractions of the vapor phase is what has been asked and the temperature T right. I am sorry usually what we are interested in as in this case is the mole fraction of the liquid this is a Dew T calculations. So, we are interested in mole fraction of the liquid x 1 and the temperature

T others are obviously, very variables that arise out of this calculation. Of course, activity coefficients are something we pay attention to, they are significantly different from one indicating the non-ideality of this particular mixture for acetone and water.

So, the vapor liquid equilibrium calculations essentially we worked with the same set of equations. They can be more complicated or less complicated as in case of Raoult's law but, essentially we work with the same set of equations to perform various calculations; a Dew P, Dew T, flash calculation etcetera. When we come back in the next class we look at other ways of performing these vapor liquid equilibrium calculations, especially in a hydro carbon especially those involving hydrocarbons; wherein there are other methods that we can use in a easier way.

Thank you.