Chemical Engineering Thermodynamics
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Lecture - 35
Gamma/Phi Formulation

Hello and welcome back. So, in the previous videos we were looking at a solving the phase equilibrium problem. We started off with ideal solution approach wherein we have used Raoult's law, to solve the phase equilibrium problem and then we have introduced the activity coefficients and models for activity coefficients so that we can solve the phase equilibrium problem using those concepts. After that we have looked at alternative methods to solve the phase equilibrium problem using what are known as the k charts or the deep (Refer Time: 01:05) charts. The first discussion today will involve what is known as a Gamma Phi Formulation.

So, if we recall the phase equilibrium relation we have used so far involving the activity coefficients is known as the modified form of the Raoult's law, wherein the vapour fugacity is sorry. If you recall the phase equilibrium relation we have used so far is known as the modified Raoult's law wherein the vapour fugacity is written in terms of the partial pressure y i P and the liquid fugacity is written as x i, gamma i, P i sat. So, the gamma i captures the non-ideal solution behaviour of the liquid phase let us call that as equation 1. Now, this comes with the assumption, the other assumptions for Raoult's law except.

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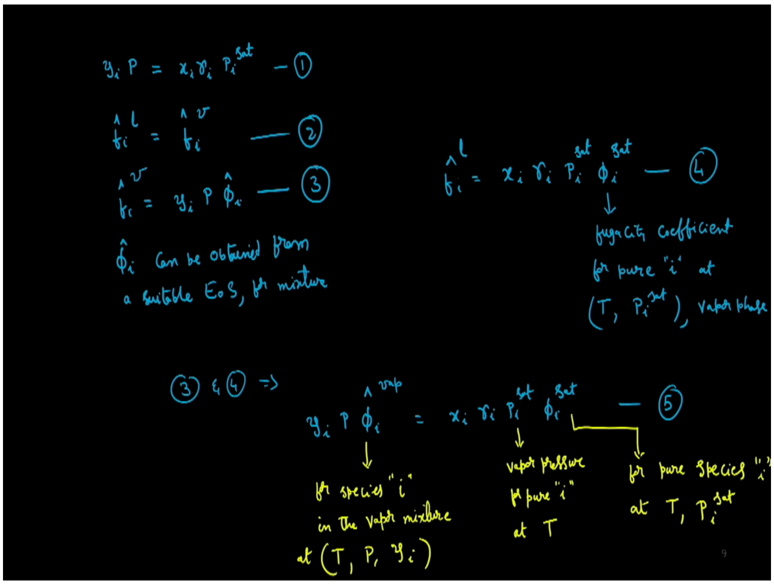

$y_i P = x_i \gamma_i P_i^{sat}$ — ①

$\hat{f}_i^{l} = \hat{f}_i^{v}$ — ②

$\hat{f}_i^{v} = y_i P \hat{\phi}_i$ — ③

$\hat{\phi}_i$ can be obtained from a suitable EoS, for mixture

$\hat{f}_i^{l} = x_i \gamma_i P_i^{sat} \phi_i^{sat}$ — ④

ϕ_i^{sat} ↓ fugacity coefficient for pure "i" at (T, P_i^{sat}), vapor phase

③ & ④ ⇒

$y_i P \hat{\phi}_i^{vap} = x_i \gamma_i P_i^{sat} \phi_i^{sat}$ — ⑤

$\hat{\phi}_i^{vap}$ ↓ for species "i" in the vapor mixture at (T, P, y_i)

P_i^{sat} ↓ vapor pressure for pure "i" at T

ϕ_i^{sat} ↓ for pure species "i" at T, P_i^{sat}

Now, this comes with the assumption that the vapour phase is ideal gas like. So, that the vapour mixture behaves as an ideal gas as well as the individual species behave as ideal gas at the saturation conditions, so that we just get P i sat on right hand side of this expression.

What if the vapour phase is not ideal? Well, if the vapour phase is not ideal then we start with the phase equilibrium relation which says the fugacity of the liquid phase is equal to the fugacity of the vapour phase. And the fugacity of the vapour phase, if it is not an ideal gas is essentially y i times P times phi i hat, and phi i hat can be obtained from a suitable equation of state. Let us say (Refer Time: 03:19) equation of state for the mixture, right. This is for the vapour phase fugacity.

Now, for the liquid phase fugacity it is x i, gamma i, to account for non-ideal solution behaviour, but P i sat is the fugacity at the saturation condition. If it is not ideal gas then we have to correct for that non-ideality of the vapour phase at saturation condition and we do that by introducing phi i sat. This phi i sat essentially is the fugacity coefficient for the pure species. Remember the all of these are pure species; the mixture comes in the mixture non-ideality comes in through the activity coefficient. So, P i sat is the fugacity coefficient for pure i at the temperature and its vapour pressure which is P i sat, right and this could be the vapour phase fugacity, right.

So, again this vapour phase fugacity for pure species can be obtained via a suitable equation of state. So now, if I combine both of these right then I get y i P phi i hat for the vapour is going to be equal to x i gamma i, P i sat phi i sat at the saturation condition for a pure species, right. So, this is the phase equilibrium relation that corrects for non-ideal gas behaviour of the vapour phase.

Now, again recall that this is for species i in the vapour mixture and because the vapour mixture is at a mole fraction of y i this will be at T, P and y i, right. This is the vapour pressure for pure i, for pure species i at the temperature T and this is for pure species i again, this is the fugacity coefficient for pure species i at the saturation conditions which are essentially t and P i sat.

So, what we have done is rewritten the Raoult's law or the modified Raoult's law. Now, accounting for the vapour phase non-idealities, the only additional information we need then to solve equation 5 are appropriate equations of state that can calculate the fugacity coefficients in the mixture as well as previously coefficient at the saturation conditions for the pure species. At moderate pressures in the vapour phase as we have seen earlier; obviously, we can use a virial equation of state. So, what we will do as an example next involves such a calculation.

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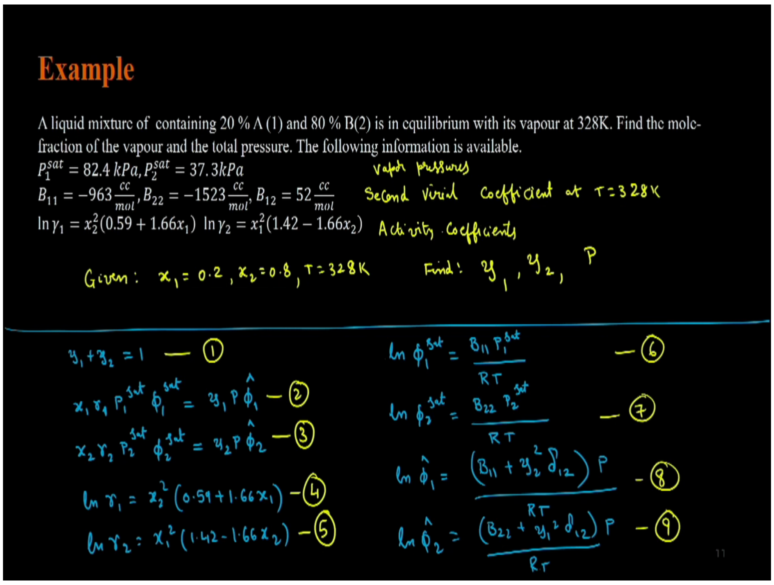

Example

A liquid mixture of containing 20 % A (1) and 80 % B(2) is in equilibrium with its vapour at 328K. Find the mole-fraction of the vapour and the total pressure. The following information is available.

$P_1^{sat} = 82.4\, kPa, P_2^{sat} = 37.3 kPa$ vapor pressures

$B_{11} = -963 \frac{cc}{mol}, B_{22} = -1523 \frac{cc}{mol}, B_{12} = 52 \frac{cc}{mol}$ Second virial coefficient at T = 328 K

$\ln \gamma_1 = x_2^2(0.59 + 1.66x_1)$ $\ln \gamma_2 = x_1^2(1.42 - 1.66x_2)$ Activity coefficients

Given: $x_1 = 0.2$, $x_2 = 0.8$, $T = 328K$ Find: y_1, y_2, P

$y_1 + y_2 = 1$ — ①

$x_1 \gamma_1 P_1^{sat} \phi_1^{sat} = y_1 P \hat{\phi}_1$ — ②

$x_2 \gamma_2 P_2^{sat} \phi_2^{sat} = y_2 P \hat{\phi}_2$ — ③

$\ln \gamma_1 = x_2^2 (0.59 + 1.66 x_1)$ — ④

$\ln \gamma_2 = x_1^2 (1.42 - 1.66 x_2)$ — ⑤

$\ln \phi_1^{sat} = \frac{B_{11} P_1^{sat}}{RT}$ — ⑥

$\ln \phi_2^{sat} = \frac{B_{22} P_2^{sat}}{RT}$ — ⑦

$\ln \hat{\phi}_1 = \frac{(B_{11} + y_2^2 \delta_{12}) P}{RT}$ — ⑧

$\ln \hat{\phi}_2 = \frac{(B_{22} + y_1^2 \delta_{12}) P}{RT}$ — ⑨

So, we have a liquid mixture of two species A and B that is in equilibrium with its vapour at 328 Kelvin. We want to find the mole fraction of the vapour and the total pressure and we are given the following additional information. So, if you recall B 11, B 22 the second virial coefficients for pure species and B 12 is the sec cross virial coefficient.

So, these are the second virial coefficients at the temperature of interest which is 328 Kelvin. These are the vapour pressures P 1 sat and P 2 sat, and these are the activity coefficients gamma 1 and gamma 2, our expressions for activity coefficients, right. So, we have this information and we want to calculate what we are given is x 1 is 0.2, obviously, x 2 is 0.8, the temperature is 328 Kelvin and what we have to find is y i or rather let us write them out this is a binary mixture so we have y 1, y 2 and the total pressure P. This is what we have to find.

So, let us see how we try to solve this problem. What I will do as I have been doing. So, far is try to list all the equations that are suitable, see how many unknowns I have and then solve the set of algebraic equations to get the necessary unknowns. So, let us start writing the equations I have. I want y 1 and y 2, so the first equation I would write is the closure equation which reads y 1 plus y 2 is 1, that is my equation 1, right. Then the phase equilibrium relation for component 1 which will be x 1, gamma 1, P 1 sat, P 1 sat the fugacity coefficient at the saturation condition will be y 1 P phi 1 hat. This will be equation 2. Then equation 3 will be the phase equilibrium relation for component 2 which will be x 2 gamma 2 phi 2 sat is at times phi 2 that is y 2 P phi 2 hat. This will be equation 3.

Now, I know P 1 sat and P 2 sat, the vapour pressures I know x 1 and x 2 I have to write equations for the activity coefficients gamma 1 and gamma 2. Those are already given. So, ln gamma 1 is x 2 square 0.59 plus 1.66 x 1. This will be equation 4. And ln gamma 2 will be x 1 squared 1.42 minus 1.66 x 2. This will be equation 5, right.

And let us see what other equations I can write. We also need expressions for the fugacity coefficients at the saturation conditions and fugacity efficient in the mixture. So, let us write them down. If you recall for pure species using virial equation of state the fugacity coefficient is given by the expression ln P 1 at the saturation condition is B 11. The second virial coefficient for pure one times the pressure in this case it will be the saturation condition pressure which is P 1 sat over RT, and similarly ln phi 2 sat is for pure species again this time for 2 will be B 22, the second virial coefficient for 2 times the appropriate pressure at which we need phi 2 sat in this case it will be vapour pressure for 2 which is P 2 sat over RT.

And then when we move on to mixtures, we have ln P 1 hat this will be the fugacity coefficient for one in the mixture which is given as B 11 plus y 2 squared delta 12 times P over RT and ln phi 2 hat is B 22 plus y 1 square delta 12 over RT times P. This will be my equations 6 through 9. Remember that we have derived these expressions 8 and 9 or we have looked at these expressions 8 and 9 when we were using virial equation of state for the mixtures. I suggest that you go back and look at those videos if you wanted to revise that concept again.

Now, once we have these 9 equations the only other thing that is left which we did not write an equation for is that delta 12 and again this is discussed when we talked about the second virial coefficient for the mixtures.

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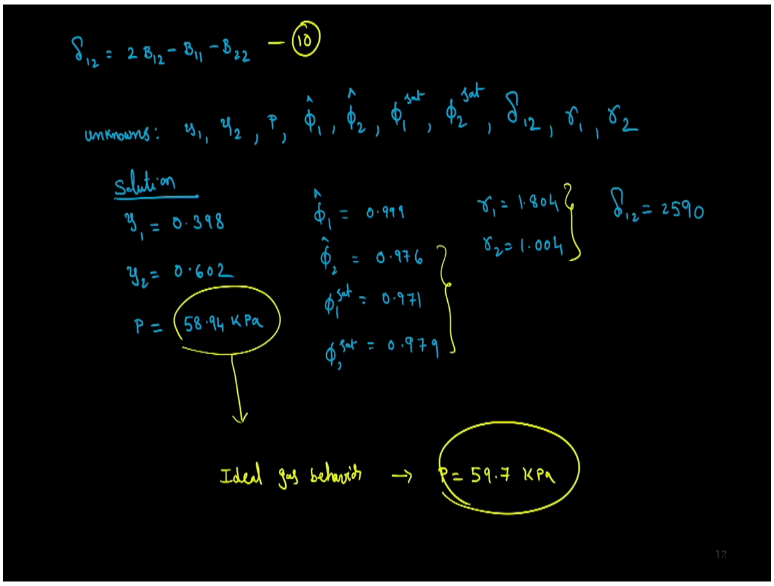

$\delta_{12} = 2B_{12} - B_{11} - B_{22}$ — ⑩

unknowns: $y_1, y_2, P, \hat{\phi}_1, \hat{\phi}_2, \phi_1^{sat}, \phi_2^{sat}, \delta_{12}, \gamma_1, \gamma_2$

Solution

$y_1 = 0.398$

$y_2 = 0.602$

$P = \boxed{58.94 \text{ KPa}}$

$\hat{\phi}_1 = 0.999$

$\hat{\phi}_2 = 0.976$

$\phi_1^{sat} = 0.971$

$\phi_2^{sat} = 0.979$

$\gamma_1 = 1.804$

$\gamma_2 = 1.004$

$\delta_{12} = 2590$

Ideal gas behavior → $\boxed{P = 59.7 \text{ KPa}}$

It turns out that for a binary mixture delta 12 is defined as 2 times the cross virial coefficient B 12 minus B 11 minus B 22. So, let us write this as equation, equation 10. Now, if I want to list all the unknowns in these equations, let us look at the previous one. I have to find y 1 and y 2, so y 1, y 2 and P are unknown to begin with right, y 1, y 2, P, then the fugacity coefficients of 1 and 2 in the mixture vapour mixture, the fugacity coefficient at the saturation conditions and the delta 12. So, we have 1, 2, 3, 4, 5, 6, 7, 8 unknowns so far.

And the other two unknowns of course, are the activity coefficients gamma 1 and gamma 2 those are also unknown gamma 1 and gamma 2. So, that makes it a system of 10 equations and these 10 unknowns, we can reduce the number of equations by suitable substitutions and algebraic manipulations whichever way you choose to do it or use the software to solve for the 10 equations. Whatever we end up doing we can actually get values for each of these unknown variables. And let me write the final solution I have for this set of equations.

It turns out that what we get is y 1 turns out to be 0.398, y 2 is 0.602 obviously, the total pressure P is 58.94 kilo Pascals, then we have the fugacity coefficients phi 1 hat, phi 2 hat, phi 1 sat and phi 2 sat. These numbers turn out to be 0.999 and 0.976, 0.971 and 0.979.

The activity coefficients gamma 1 is 1.804 and gamma 2 is 1.004 and finally, delta 12 turns out to be 2590, right. So, these are the final values we get for all the unknowns. What is of interest here is to note that the gas is not exactly ideal there is about a 3 percent deviation from ideality, if these values for the fugacity coefficients were unity then of course, it is an ideal gas behaviour So, the vapour phase does deviate from ideality somewhat. Obviously, the solution is non-ideal in terms of the liquid mixture, right.

And of course, once we solve for everything we get a value for pressure which is actually different from if we assumed an ideal gas like vapour behaviour. If we assumed an ideal gas behaviour, but included the activity coefficients the total pressure one would get is 59.7 kilo Pascal's. So, this is slightly different from what we actually have when we include the vapour phase non-ideality.

So, depending on the second virial coefficients and how much deviation we have in terms of a non-ideal gas vapour like behaviour there would be a difference in the solution we get obviously. Nevertheless, the point of this exercise is that if one wishes to include the vapour phase non-ideality it can be done with the same set of equations and slight modifications to those. So, with that we demonstrated the example of gamma phi formulation for solving the phase equilibrium problem. What we will do next is actually use an equation of state approach to solve the phase equilibrium problem.

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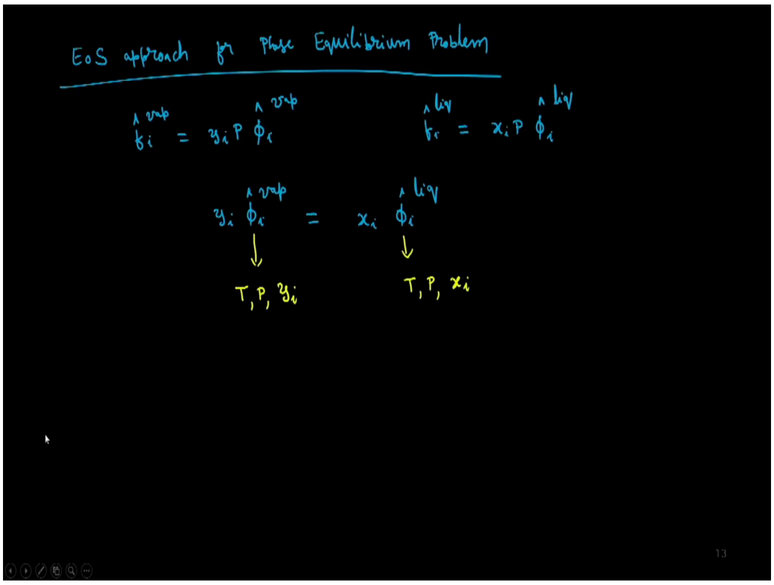

EoS approach for Phase Equilibrium Problem

$\hat{f}_i^{vap} = y_i P \hat{\phi}_i^{vap}$ $\qquad$ $\hat{f}_i^{liq} = x_i P \hat{\phi}_i^{liq}$

$$\underset{\displaystyle T, P, y_i}{\underset{\downarrow}{y_i \hat{\phi}_i^{vap}}} = \underset{\displaystyle T, P, x_i}{\underset{\downarrow}{x_i \hat{\phi}_i^{liq}}}$$

If you recall when we have used a cubic equation of state, we said that this cubic equation of state can in fact represent the vapour phase region as well as the liquid phase region. If that be the case right; one can actually use an equation of state to calculate the fugacity in the liquid phase as well, right. So, for example, the way we are writing fugacity in the vapour phase using an equation of state is it is the partial pressure times the fugacity coefficient in the mixture. This is the vapour mixture; obviously, why is the mole fraction in the vapour phase.

I can write a similar expression for the liquid phase fugacity also instead of resorting to activity coefficients and vapour pressures I can actually write this as the partial pressure in the liquid phase multiplied with the fugacity coefficient of the liquid which is phi i hat liquid, right.

And equilibrium criteria requires that these two fugacities be equal which implies y i times phi i hat vapour should be equal to x i times phi i hat liquid. The only trick here is that I need to have a suitable equation of state which can describe the liquid phase behaviour. Obviously, virial equation of state is not applicable for liquids, so we cannot use video equation of state for the liquid phase fugacity, but a suitable cubic equation of state might be useful to calculate the liquid phase fugacity coefficients and the phase and solve the phase equilibrium problem using such an approach.

But I need to mention though that one should remember this fugacity coefficient of the vapour is a function of temperature, pressure and the mole fraction in the liquid phase which is y i. And the fugacity coefficient of the liquid is a function of temperature, pressure and mole fraction of the liquid x i, right. And the way we write the fugacity coefficients depends on the equation of state cubic equation of state we use. I suggest that you go back to the videos and look at calculating the fugacity coefficient of a species in the mixture using a cubic equation of state.

When we have solved an example for calculating the fugacity coefficient of a species in the mixture using cubic equation of state, we have demonstrated it for vapour phase, but a exactly similar approach is applicable to liquid phase also. One only needs to consider the root for the cubic equation of state that is appropriate for the liquid as long as we do that all the other calculations remain exactly the same. So, let us quickly write the set of equations then we need to solve to get all the unknowns using an equation of state type of an approach.

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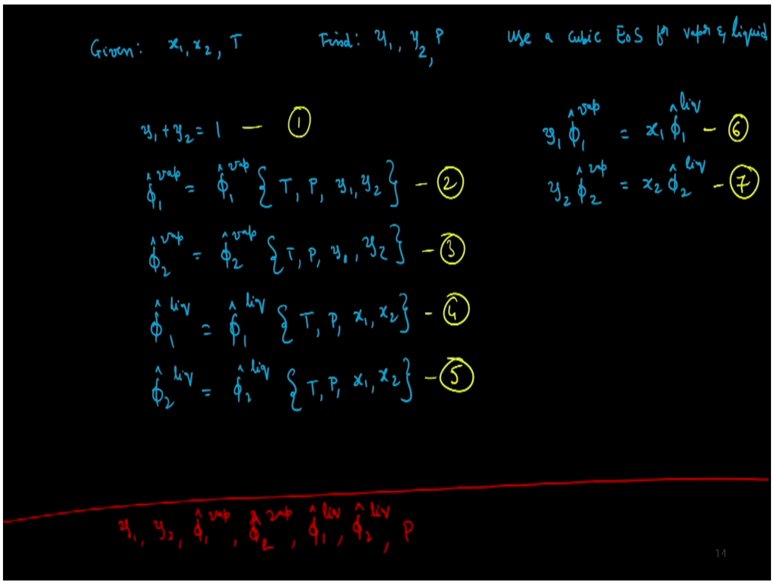

Given: x_1, x_2, T

Find: y_1, y_2, P

Use a cubic EoS for vapor & liquid

$y_1 + y_2 = 1$ — ①

$\hat{\phi}_1^{vap} = \hat{\phi}_1^{vap}\{T, P, y_1, y_2\}$ – ②

$\hat{\phi}_2^{vap} = \hat{\phi}_2^{vap}\{T, P, y_1, y_2\}$ – ③

$\hat{\phi}_1^{liq} = \hat{\phi}_1^{liq}\{T, P, x_1, x_2\}$ – ④

$\hat{\phi}_2^{liq} = \hat{\phi}_2^{liq}\{T, P, x_1, x_2\}$ – ⑤

$y_1 \hat{\phi}_1^{vap} = x_1 \hat{\phi}_1^{liq}$ – ⑥

$y_2 \hat{\phi}_2^{vap} = x_2 \hat{\phi}_2^{liq}$ – ⑦

$y_1, y_2, \hat{\phi}_1^{vap}, \hat{\phi}_2^{vap}, \hat{\phi}_1^{liq}, \hat{\phi}_2^{liq}, P$

So, for example let us say we are given, let us consider a binary mixture. We are given x 1, x 2 and the temperature t just like the previous problem we did we want to find y 1, y 2 and p, but this time using a cubic equation of state. We want to use a cubic equation of state for vapour and the liquid phases.

So, if one wants to do that then the first thing we want to do is write the suitable set of equations that we are looking at because we want to find y 1 and y 2, I would write the closure equation for this which reads y 1 plus y 2 is 1, right. The other set of equations would be phi 1 hat in the vapour phase is going to be a function, a suitable function or the expression that is suitable for that particular equation of state for the fugacity coefficient of the mixture and we notice that this is a function of temperature, pressure and the mole fraction of the vapour which is y 1 and y 2.

Similarly, phi 2 hat vapour is going to be a function of the temperature the pressure y 1 and y 2 the mole fraction of the vapour phase. For the liquid phase phi 2 hat liquid is going to be sorry, phi 1 hat liquid is going to be phi 1 hat liquid that is dependent on the temperature, pressure and the mole fractions for the liquid phase which are x 1 and x 2. The similarly for the component two it will be a function that will involve T, P, x 1 and x 2. So, these are my 5 equations, right.

And let us list the unknowns here. The unknowns I have are y 1, y 2, phi 1 hat vapour, phi 2 hat vapour, phi 1 hat liquid, and phi 2 hat liquid right also the pressure is unknown. So, I have 1, 2, 3, 4, 5, 6, 7 equations, we have written 5 so far and the other two equations of course, involve the quality of fugacities and in terms of the variables we are using for this particular approach we would have it as phi y 1 phi 1 hat vapour times the pressure is x 1 phi 1 hat liquid times the pressure. So, that pressure drops out from both sides that is equation 6. And similarly, for component 2 it will be vapour is x 2 phi 2 hat sorry, phi hat well yeah vapour is going to be x 2 free to add liquid. So, those are the other two equations we are looking at. So, now, I have 7 equations and I can solve these 7 equations for these 7 unknowns.

The catch of course, again like I said is in finding an appropriate equation of state that can describe the vapour phase behaviour and one that can describe the liquid phase behaviour. And remember the challenge in finding an appropriate equation of state for the liquid mixture is that it needs to be applicable over the entire range of pressures from 0 to P, and the compositions we are looking at only then we would be able to calculate the fugacity of the liquid mixture using this type of an approach.

So, the essential ideas are still the same. We want to equate the fugacities and write a system of equations as many as are necessary to get all the unknowns we have. Once we do that we can solve the mathematical problem and come up with a solution to the phase equilibrium problem. Of course, all of these discussions we had can be readily extended to a multi component mixture. We are always talking about a binary mixture, but one can extend these ideas to a multi component mixture it only involves writing additional equations for the other components that are involved, right.

So, with that we end the discussion for the solution of the phase equilibrium problem involving vapour and liquid phases. What we will do next is look at liquid and liquid equilibrium. We will talk about that in the next video.

Thank you.