Chemical Engineering Thermodynamics
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Lecture - 37
LLE and VLLE

Hello and welcome back. In the previous lectures we looked at the condition for stability of a liquid mixture and when an immiscibility sets into a liquid mixture. The other equilibria we want to look at is a Vapor-Liquid-Liquid-Equilibrium.

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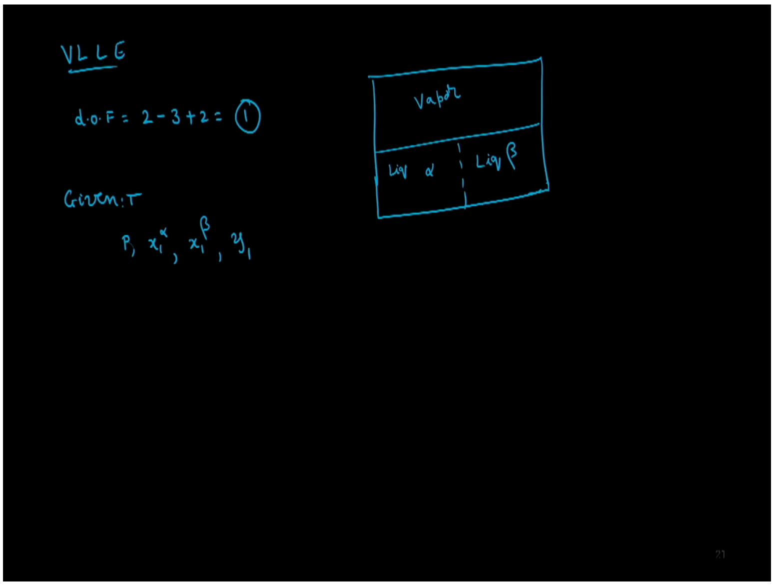

VLLE

$\text{d.o.F} = 2-3+2 = ①$

Given: T

$P, x_1^{\alpha}, x_1^{\beta}, y_1$

In case of a vapour-liquid-liquid-equilibrium, what happens is, there is a liquid mixture which is immiscible. So, we end up having two phases in the liquid mixture and we have a single vapor phase above it which is in equilibrium.

Now, if we look at this there is an alpha phase for the liquid, a beta phase for the liquid and a vapor phase. Now, let us say that we have two components in this particular system. The degrees of freedom will be 2 components minus the number of phases which is 3 plus 2. So, that is just 1. So, the degree of freedom for this particular binary mixture exhibiting a vapour-liquid-liquid equilibrium is 1.

So, if the temperature is given then the pressure and the mole fractions in the alpha phase, beta phase and the vapor are fixed. So, given T for example, any; it could be any of the variables, but let us say temperature is known. Then the pressure x 1 in the alpha phase which of course, means x 2 in the alpha phase, x 1 in the beta phase and y 1 all the four variables are going to be fixed. We just have 1 degree of freedom. So, we have chosen T, everything else should be fixed according to the phase rule. So, let us see how we can solve a problem for a vapour-liquid-liquid equilibrium.

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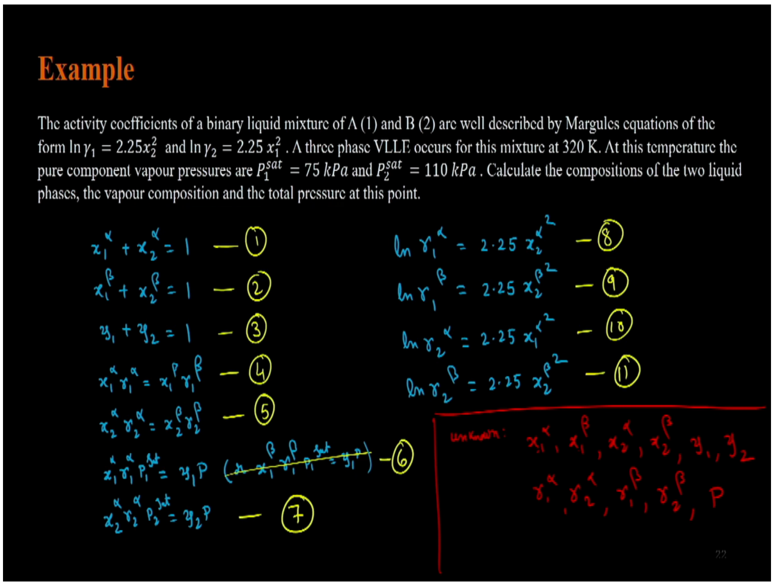

Example

The activity coefficients of a binary liquid mixture of A (1) and B (2) are well described by Margules equations of the form $\ln \gamma_1 = 2.25x_2^2$ and $\ln \gamma_2 = 2.25\, x_1^2$. A three phase VLLE occurs for this mixture at 320 K. At this temperature the pure component vapour pressures are $P_1^{sat} = 75\ kPa$ and $P_2^{sat} = 110\ kPa$. Calculate the compositions of the two liquid phases, the vapour composition and the total pressure at this point.

$x_1^\alpha + x_2^\alpha = 1$ — ①

$x_1^\beta + x_2^\beta = 1$ — ②

$y_1 + y_2 = 1$ — ③

$x_1^\alpha \gamma_1^\alpha = x_1^\beta \gamma_1^\beta$ — ④

$x_2^\alpha \gamma_2^\alpha = x_2^\beta \gamma_2^\beta$ — ⑤

$x_1^\alpha \gamma_1^\alpha P_1^{sat} = y_1 P \quad (\cancel{x_1^\beta \gamma_1^\beta P_1^{sat} = y_1 P})$ — ⑥

$x_2^\alpha \gamma_2^\alpha P_2^{sat} = y_2 P$ — ⑦

$\ln \gamma_1^\alpha = 2.25\, {x_2^\alpha}^2$ — ⑧

$\ln \gamma_1^\beta = 2.25\, {x_2^\beta}^2$ — ⑨

$\ln \gamma_2^\alpha = 2.25\, {x_1^\alpha}^2$ — ⑩

$\ln \gamma_2^\beta = 2.25\, {x_2^\beta}^2$ — ⑪

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

The activity coefficients of a binary liquid mixture are given Margules type of equation ln gamma 1 and ln gamma 2 are given there. A three phase VLLE occurs for this particular mixture at 320 Kelvin. And the vapor pressures of the pure components at this temperature are given. And what we are interested in calculating is the compositions of the two liquid phases, the vapor phase and the total pressure at the three phase point.

Now, to solve this particular equation we want to write all the equations that are appropriate. Let us see; let us start with the easiest ones. The closure equations x 1 for the alpha phase plus x 2 for the alpha phase need to be equal to 1; x 1 for the beta phase plus x 2 for the beta phase need to be equal to 1. And the vapor compositions y 1 plus y 2 needs to be equal to 1 of course. And for the liquid-liquid equilibrium, x 1 in the alpha phase gamma 1 in the alpha phase should be equal to x 1 in the beta phase gamma 1 in the beta phase.

Similarly, for component 2, x 2 in the alpha phase gamma 2 in the alpha phase should be equal to x 2 in the beta phase times gamma 2 in the beta phase. There is also an equilibrium between the vapor phase and the liquid phase so, x 1 gamma 1 P 1 at the saturation condition should be equal to y 1 times P. Notice that this equation is identical to, sorry x 1 alpha gamma 1 alpha. Notice that this equation is identical to x 1 beta gamma 1 beta P 1 sat equal to y 1 P.

We could use either one of the two equations and that is because x 1 alpha gamma 1 alpha is identical to x 1 beta gamma 1 beta via equation 4. So, we could write the equilibrium between the alpha phase of the liquid and vapour or the beta phase of the liquid and vapour. It really does not matter which one we choose. So, we are going to ignore this and we will just use the alpha phase for the vapor for convenience. It does not matter which one we choose. So, that will be my equation 6. And I can write a similar phase equilibrium relation between component 2 in the alpha phase and the vapor phase for component 2, y 2 P.

Again I could have written this equation for beta phase. It really does not matter. That will be my equation 7 and then I have expressions for the activity coefficients themselves, gamma 1 alpha is going to be 2.25 or this is actually ln gamma 1 alpha is 2.25 x 2 for the alpha phase is squared, ln gamma 1 in the beta is 2.25 x 2 in the beta phase squared, ln gamma 2 in the alpha phase is 2.25 x 1 in the alpha phase squared. And ln gamma 2 in the beta phase is 2.25 x 2 in the beta phase squared. So, these are my equations 8 through 11.

Now, I have 11 equations and let us count the number of unknowns, x 1 alpha, x 1 beta, x 2 alpha, x 2 beta, y 1, y 2, then gamma 1 alpha, gamma 2 alpha, gamma 1 beta, gamma 2 beta and the total pressure and the total pressure P. So, that will be 1, 2, 3, 4, 5, 6, 7, 8, 9, 10 and 11 unknowns. So, we solve this set of 11 equations to obtain the 11 unknowns and we should have our result.

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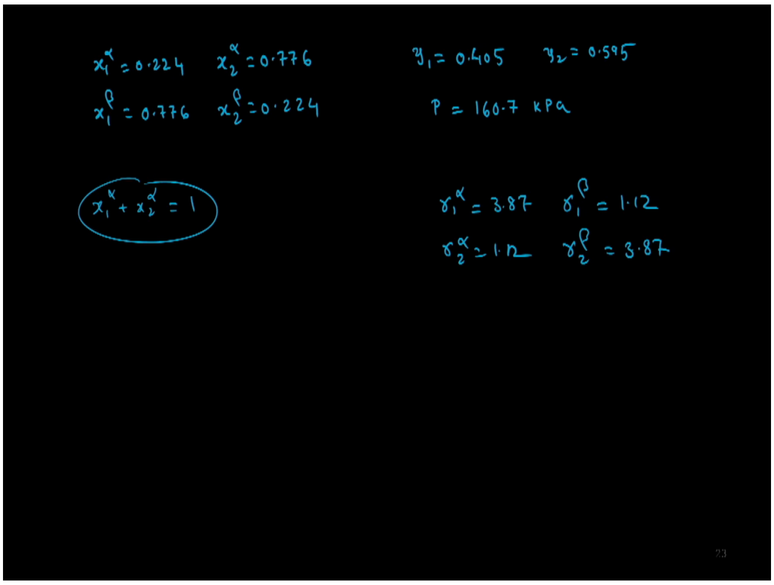

$x_1^\alpha = 0.224$ $x_2^\alpha = 0.776$ $y_1 = 0.405$ $y_2 = 0.595$

$x_1^\beta = 0.776$ $x_2^\beta = 0.224$ $P = 160.7$ kPa

$\boxed{x_1^\alpha + x_2^\alpha = 1}$

$\gamma_1^\alpha = 3.87$ $\gamma_1^\beta = 1.12$

$\gamma_2^\alpha = 1.12$ $\gamma_2^\beta = 3.87$

It turns out that the numbers I have are, x 1 alpha is 0.224. So, for the alpha phase the component 2 will be 0.776. And in the beta phase x 1 is 0.776 which means in the beta phase x 2 will be 0.224. I will come back to these numbers in a minute.

But let us write the other results, y 1 is 0.405, y 2 is 0.595. The total pressure P turns out to be a 160.7 kilo Pascal's. the corresponding activity coefficient values or gamma 1 alpha is 3.87, gamma 1 beta is 1.12, gamma 2 alpha is 1.12 and gamma 2 beta is 3.87. Notice that the only requirement according to the closure equation is x 1 alpha plus x 2 alpha should be equal to 1.

Although, in here it looks as if x 1 alpha plus x 1 beta is 1, it is not a thermodynamic requirement. It just so happens because of the symmetry of the Margules equation we have used for the activity coefficients. So, we want to keep that in mind. This is this does not always have to be true. So, this is how we handle a vapor-liquid-liquid-equilibrium problem. With that we end the video lecture for today. When we come back in the next video we are going to look at reaction equilibrium.

Thank you.