Thermodynamics of Fluid Phase Equilibria
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Lecture - 30
Traditional Approaches to Phase Equilibria Calculations

So, welcome back. In this lecture I am going to spend time to illustrate the use of traditional approach for calculating phase equilibria method that is phi gamma approach ok. So, let us start again by looking at the definition or the expression for fugacity ok. So, let me first write down the fugacity expression for vapor phase.

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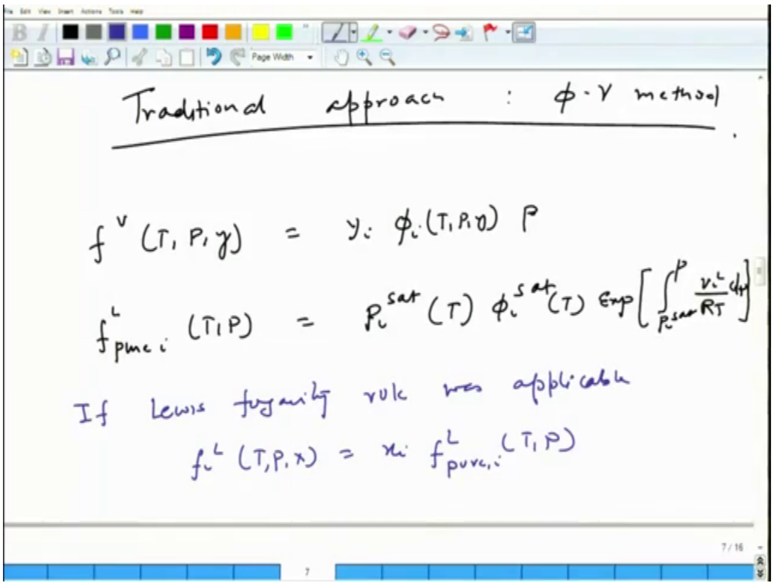

Traditional approach : $\phi \cdot \gamma$ method

$$f^V(T,P,y) = y_i\,\phi_i(T,P,y)\,P$$

$$f^L_{pure\,i}(T,P) = P_i^{sat}(T)\,\phi_i^{sat}(T)\,\mathrm{Exp}\left[\int_{P_i^{sat}}^{P}\frac{v_i^L}{RT}\,dP\right]$$

If Lewis fugacity rule was applicable

$$f_i^L(T,P,x) = x_i\,f^L_{pure,i}(T,P)$$

So, y i multiplied by P would be a simple Lewis fugacity rule, but then we multiply phi i also which is a correction to this, which is nothing, but fugacity coefficient. Now, this fugacity coefficient also depends on temperature pressure and composition. So, I am going to write that ok.

Now, this traditional approach phi gamma approach which we say makes use of different models or for liquid and for vapor ok. So, we will try to make use of this. Let me just first build the base for that for liquid we know that f L pure i temperature pressure is P i sat T phi i sat again a T and then you have this pointing correction exponential from P i sat to P V i L that is molar volume liquid RT dp if. So, what we are going to do is a bit deviate from this an ask this question if Lewis fugacity rule were applicable, rule was applicable then we would have f i L T P x as x i times fugacity of liquid pure i T P right that is what the fugacity rule says.

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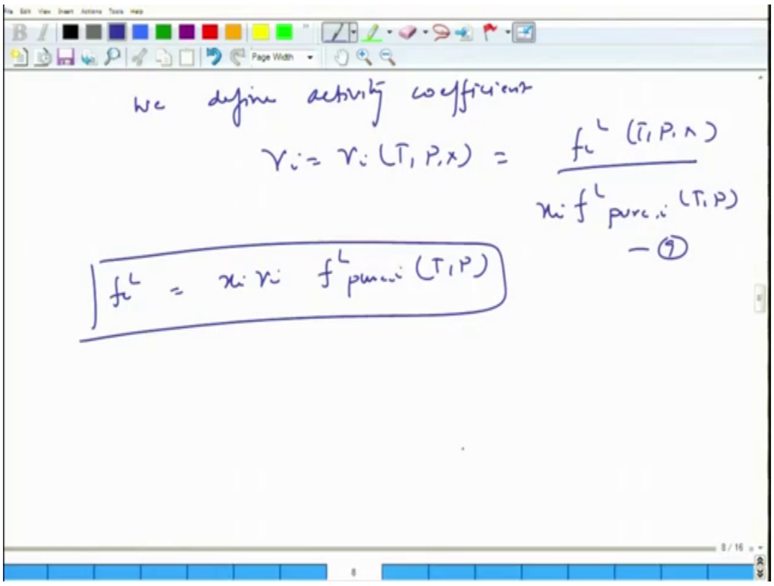

We define activity coefficient

$$\gamma_i = \gamma_i(T,P,x) = \frac{f_i^L(T,P,x)}{x_i f^L_{pure,i}(T,P)} \quad -⑨$$

$$\boxed{f_i^L = x_i \gamma_i f^L_{pure,i}(T,P)}$$

And thus we have defined earlier also and then I am going to define it again that in general we defined activity coefficient which basically nothing but illustrate the deviation from this Lewis fugacity rule ok.

This is basically the ideal liquid will behave like Lewis fugacity expressions ok. So, this we defined activity coefficient gamma i is equal to gamma i T P x which is nothing but f i L T P x divided by f L pure i T P and as well as x i. This is 6 7 and 8 and this is basically 9, yes. Lewis fugacity rule becomes the basis for getting the rose law. So, Lewis fugacity is nothing, but it tells you the system is behaves like ideal system ok.

So, now, given this expression of gamma you can write down f i L as nothing, but x i gamma i f L pure i at T and P since it is pure there is no composition ok. And now, I can plug in the expression of f L pure which is this at a given temperature pressure away from the P side right. So, now, I can plug in and I get an expression which is the following gamma i.

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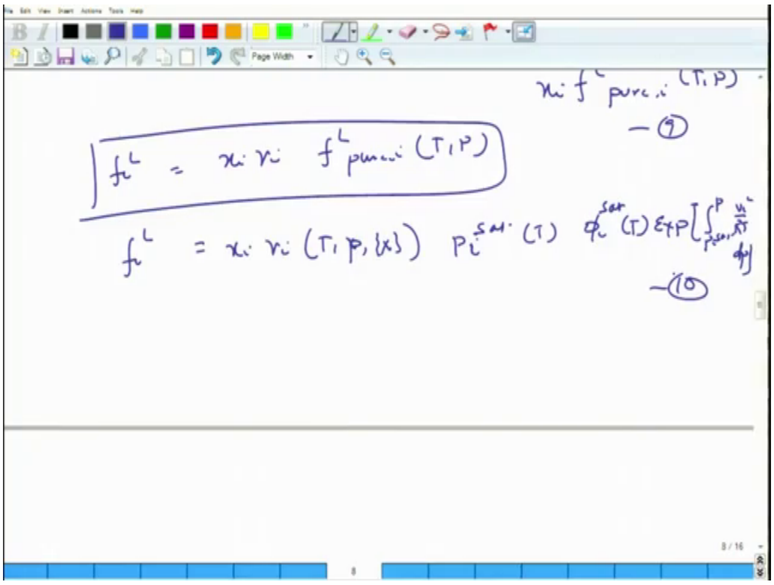

$x_i f^L_{pure,i}(T,P)$ — ⑨

$$\boxed{f_i^L = x_i \gamma_i f^L_{pure,i}(T,P)}$$

$$f_i^L = x_i \gamma_i (T,P,\{x\})\, P_i^{sat}(T)\, \phi_i^{sat}(T) \exp\left[\int_{P_i^{sat}}^{P} \frac{v_i^L}{RT} dP\right]$$ — ⑩

Now, gamma i since f L is depends on f T P f gamma i also depends on T P x. So, gamma i which depends on T P x when I am writing here x basically the thing, but composition ok, P i sat temperature phi sat temperature and exponential P i sat P vl T and dp ok.

Now, this is my f L right this is my question 10. Now, given this expression and given the fact that you have written this already for this which is for vapor right. Now, for it for condition of equality you need fugacity should be same in the vapor and phase; that means, you can equate equation 6 and equation 10.

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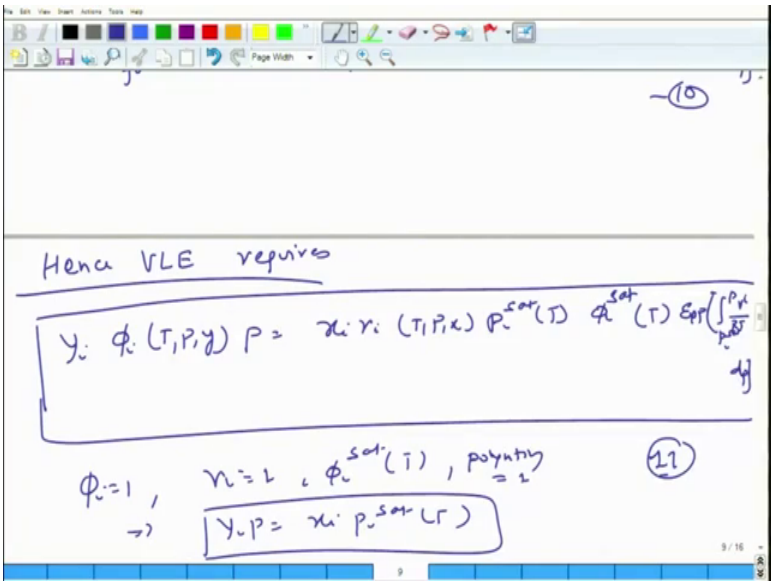

— ⑩

Hence VLE requires

$$\boxed{y_i \phi_i (T,P,y) P = x_i \gamma_i (T,P,x) P_i^{sat}(T)\, \phi_i^{sat}(T) \exp\left(\int_{P_i^{sat}}^{P} \frac{v_i^L}{RT} dP\right)}$$ ⑪

$\phi_i = 1$, $\gamma_i = 1$, $\phi_i^{sat}(T)$, poynting $= 1$

$\rightarrow \boxed{y_i P = x_i P_i^{sat}(T)}$

So, you get an final expression hence VLE requires the following condition to be met which is y i phi i T P x y P is gamma i this T P x P i sat T phi i sat T and exponential term ok, it is not be clear, but you got the idea. This is nothing but the pointing correction. So, this is the final expression of this from here you can you can also get the Rose law by considering phi i to be 1 ok.

So, if you consider phi i to be 1 which is basically the idols condition of the vapor gamma to be 1 again ideal solution, and then you can consider again phi i sat to be when assuming the saturated vapor fugacity is 1 which means again is ideal and then you can consider pointing correction to be 1 y i P is x i which is nothing, but Rose law all right.

Now, so, let us take this and we can consider a system which are of a similar type let us say case of benzene and toluene ok.

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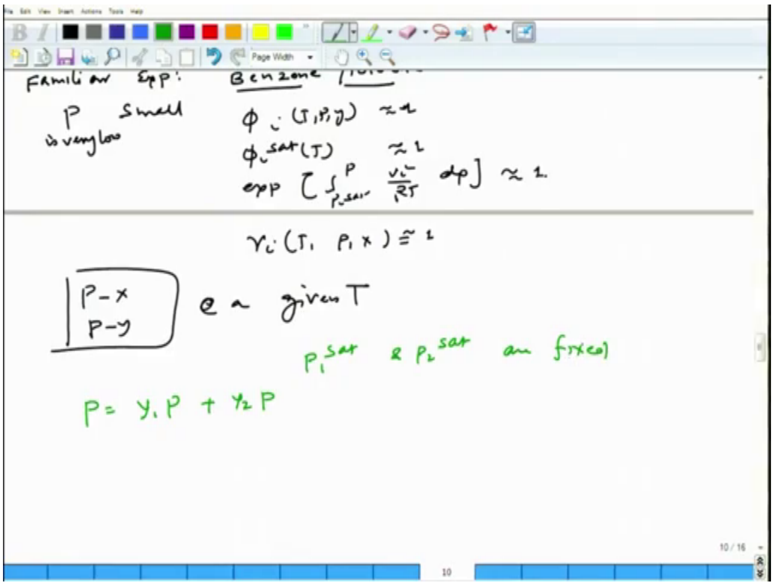

Familiar Exp: Benzene / Toluene

P small is very low

$\phi_i(T,P,y) \approx 1$

$\phi_i^{sat}(T) \approx 1$

$\exp\left[\int_{P_i^{sat}}^{P} \frac{v_i}{RT}\,dp\right] \approx 1$

$\gamma_i(T, P, x) \cong 1$

$\boxed{\begin{matrix} P-x \\ P-y \end{matrix}}$ @ a given T

P_1^{sat} & P_2^{sat} are fixed

$P = y_1 P + y_2 P$

This is a familiar case again we are considering pressures to be small this familiar example is the one which we have similar kind of molecule similar sizes which in this case let us say is benzene toluene ok.

And my question is that can we find out for such a system pressure versus composition plots for paper case and for liquid case. So, assuming these pressures are small if pressures are small and we have already considered pressure is very low and we know what the kind of approximation we can make operation low pressures ideal gas is idle vapor phase b we can behave like an idol. So, phi i T P y for vapor and as well as phi sat T both we can approximate to 1 since it is a low pressure the exponential P i sat till P this is also we can approximate.

Now, since benzene and toluene have similar chemical nature and type in sizes we can also approximate gamma T P x ok. So, we got this same cross expression ok. So, these are the basic assumptions which we have made, but it depends on what kind of system we can do. Now, let us try to come up with an expression where we can draw it also. So, what we interested is basically? P x curve and P y curve this is what we are interested at a given temperature ok, at a given T ok.

So, let us consider P. Now, P is nothing, but y i y i P. So, that is y P plus y 2 P because it is a binary mixture ok. So, P is equal to y 1 P and y 2 P temperature is fixed for a given temperature we know the P sat is are going to be fixed because this is for the pure system P 1s sat is for the pure system. So, which means basically P 1 sat and P 2 sat are fixed ok.

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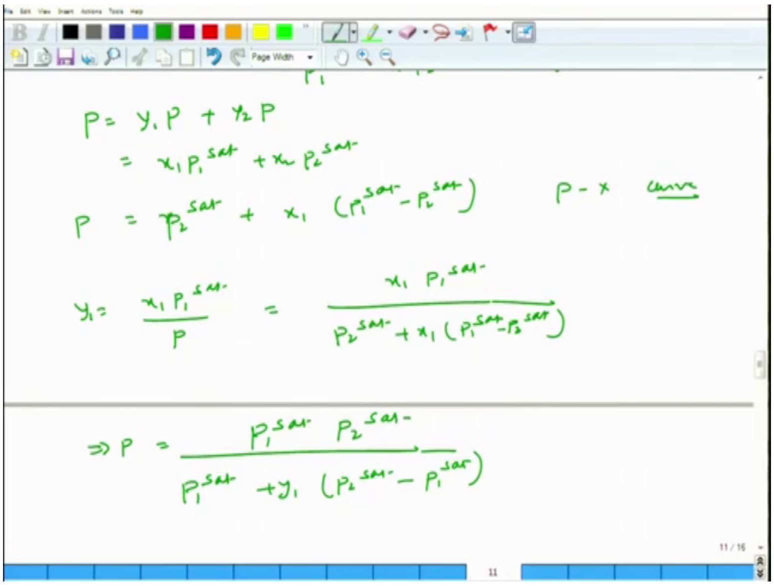

$$P = y_1 P + y_2 P$$

$$= x_1 P_1^{sat} + x_2 P_2^{sat}$$

$$P = P_2^{sat} + x_1 (P_1^{sat} - P_2^{sat}) \qquad P-x \quad \underline{\text{curve}}$$

$$y_1 = \frac{x_1 P_1^{sat}}{P} = \frac{x_1 P_1^{sat}}{P_2^{sat} + x_1 (P_1^{sat} - P_2^{sat})}$$

$$\Rightarrow P = \frac{P_1^{sat} P_2^{sat}}{P_1^{sat} + y_1 (P_2^{sat} - P_1^{sat})}$$

So now, I can write this as x 1 P 1 sat plus x 2 P 2 sat I can also write as P P 2 sat plus x 1 P 1 sat minus P 1 P 2 sat this is your P x curve which is a linear clearly right ok.

Now, my interest is P y curve. So, I can write y 1 as x 1 P 1 sat divided by P i will start with this. Now, this I can write as P as P 2 sat plus x 1 P 1 sat minus P 2 sat and this is x 1 P 1 sat ok. You rearrange this. If you rearrange this what you get? P you can be shown we can show this bit more exercises P can be shown as P 1 sat P 2 sat divided by P 1 sat y 1 P 2 sat minus P 1 sat ok. So, you can actually really do a little bit of exercise here because for each of them you can write x 1 P 1 sat you can write it as y 1 P right and x x 1 P 2 x 1 can be written as in terms of x 2 and you can redo this exercise to get this expression.

So, these two expressions which you got P x and P y you can plot it and if you plot this is how it looks like ok.

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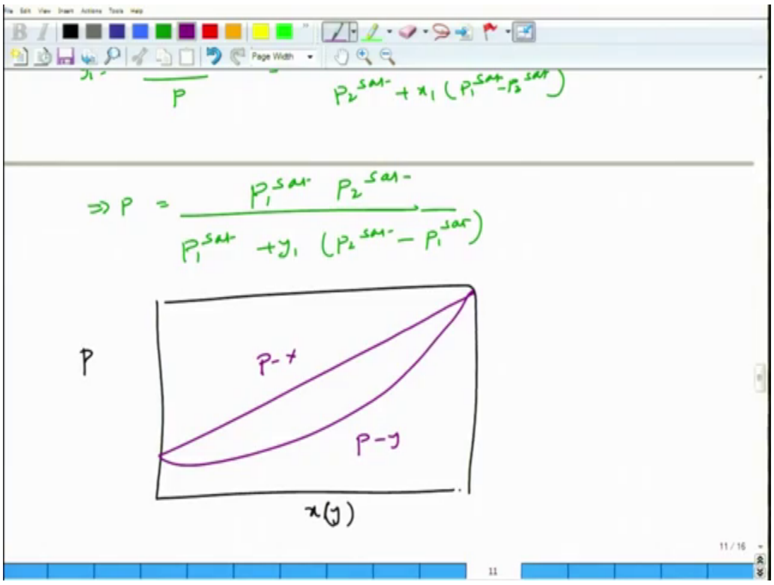

P $\quad P_2^{sat} + x_1 (P_1^{sat} - P_2^{sat})$

$$\Rightarrow P = \frac{P_1^{sat} \; P_2^{sat}}{P_1^{sat} + y_1 \, (P_2^{sat} - P_1^{sat})}$$

So, this is your pressure this is your x 1 or y instead of dividing it I will say x or y right and this is how it looks. So, for the case of this system I get this kind of expression ok. So, of course, this linear will be P x and this would be your P y ok. So, this is the example based on Cross law, but the approximation which we have made of course, is a spacial approximation it is not valid for all the systems.

So, if you do not you know let us assume that you have equation the state available with you. So, you can make use of equation of state to solve the problem instead of just making such an approximation ok. So, let me try also that example.

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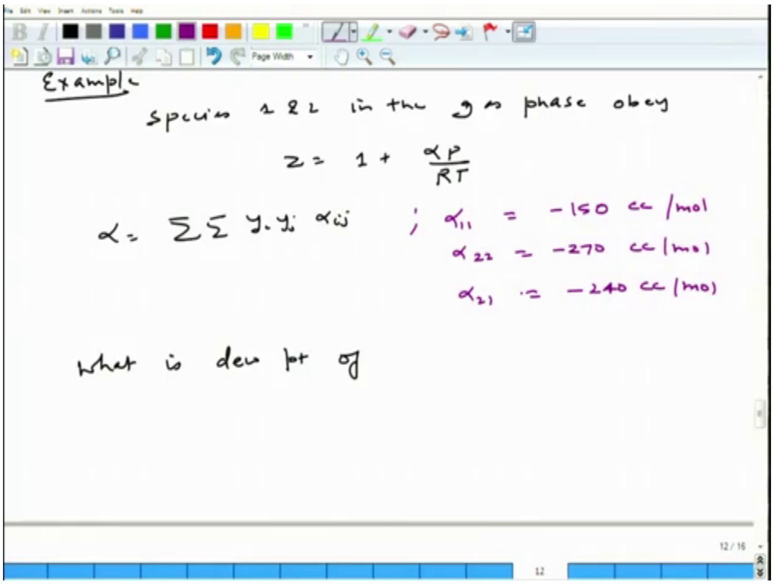

Example

species 1 & 2 in the gas phase obey

$$z = 1 + \frac{\alpha P}{RT}$$

$\alpha = \sum \sum y_i y_j \alpha_{ij}$; $\alpha_{11} = -150$ cc/mol

$\alpha_{22} = -270$ cc/mol

$\alpha_{21} = -240$ cc/mol

what is dew pt of

So, here the example is related to, this is example which states that the species 1 and 2 in the gas phase obey the following equation where. So, z is nothing, but the compressibility alpha is summation y y j alpha ij since it is a binary mixture we know this how to sum it up easily. And we need 3 we need 3 variables because if it is a binary mixture we need alpha 12 which is minus 150 cubic centimetre per mole, alpha 22 which is minus 270 cubic centimetre per mole, alpha 21 which is minus 240 cubic centimetre per mole ok.

So, what is the question? The question is what is the dew point symmetric this must have been alpha 11 Alpha 11 is minus 150 cubic centimetre per mole, alpha 22 is minus 270 cubic centimetre per mole, left 21 is minus 240 cubic centimetre per mole alpha 21 is basically nothing, but alpha 12. So, what is the dew point of a 60-40 mixture at pressure is 20 atmosphere, ok.

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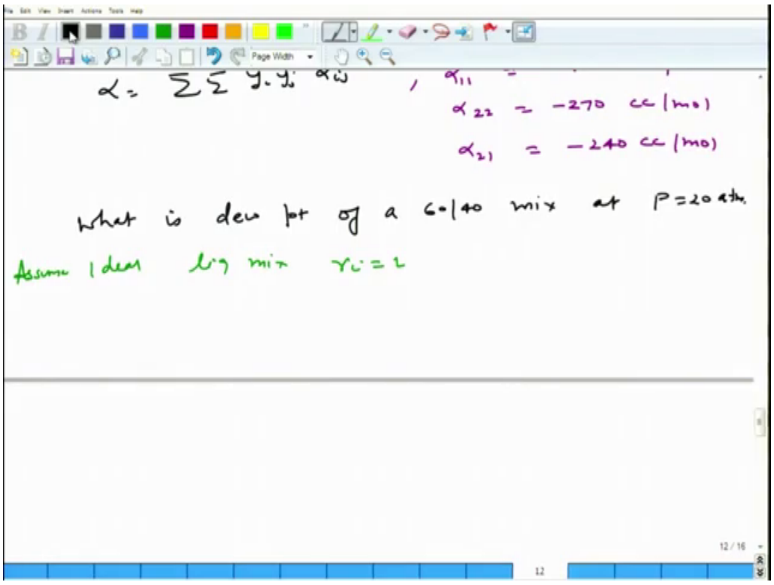

$\alpha = \sum \sum y_i y_j \alpha_{ij}$, $\alpha_{11} =$

$\alpha_{22} = -270$ cc/mol

$\alpha_{21} = -240$ cc/mol

what is dew pt of a 60/40 mix at P = 20 atm

Assume ideal liq mix $\gamma_i = 1$

Now, what we have been given what you have been asked is basically that we know you can make use of idle solution. So, we can assume ideal liquid mixture which means basically gamma i is basically 0. So, gammas are 0. What are other things which we have been given? What other things which are given to us is the relation of pressure and temperature for the vapor phase in terms of the following expression which is. What are these expression? Sent to an equation ok, alright.

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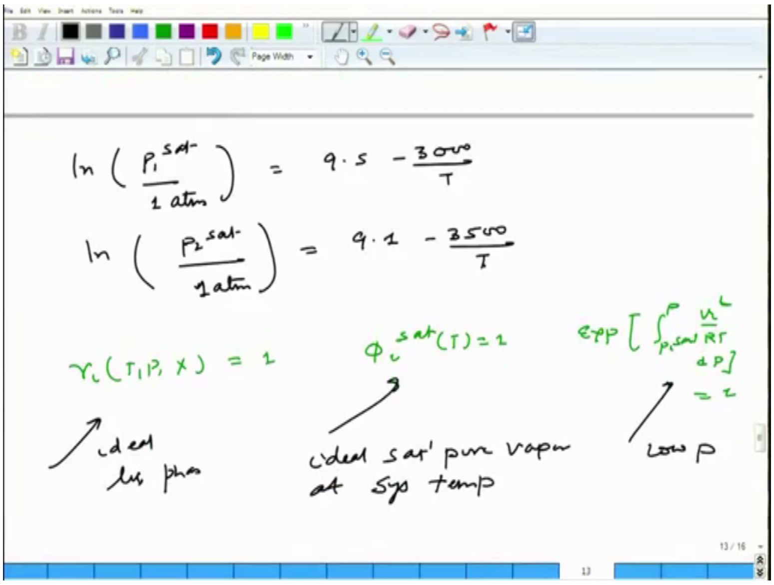

$$\ln\left(\frac{P_1^{sat}}{1\ atm}\right) = 9.5 - \frac{3000}{T}$$

$$\ln\left(\frac{P_2^{sat}}{1\ atm}\right) = 9.1 - \frac{3500}{T}$$

$\gamma_i(T, P, x) = 1$ ideal liq phase

$\phi_i^{sat}(T) = 1$ ideal sat' pure vapor at sys temp

$\exp\left[\int_{P_i^{sat}}^{P} \frac{v^L}{RT} dP\right] = 1$ Low P

So, the question is now, well the posed z is given alphas are known 40-60 gamma and all this information. So, how do we go about it? From where we should start? We must start first from the our definition of the equality conditions right here.

Student: (Refer Time: 16:50).

Right. So, this is one. What about this? Fugacity we have to worry about it. But what about this? And of course, we have pointing correction. Now, what we can do is we can start with certain assumptions, we can we also have to make certain assumptions what we are going to say is the following. That of course, we have been given that gamma i is going to be 0 1.

So, gamma i T P x is 1 ok, we assume that phi i sat is 1 ok; that means, idle saturated pure vapor because this is for the pure vapor right, pure vapor at system temperature and then you have this point in correction phi sat P v L RT dp ok. So, this is for ideal liquid phase this is for ideal saturated vapor pure vapor at our system temperature and this is the low pressure ok. So, this is the assumption.

If we do that what we as a the low pressure because 20 atmosphere is still resembly low pressure. Now, we obtain the following expression y i phi i T P y pressure and this is equal to x i P i sat. So, this is our final expression ok.

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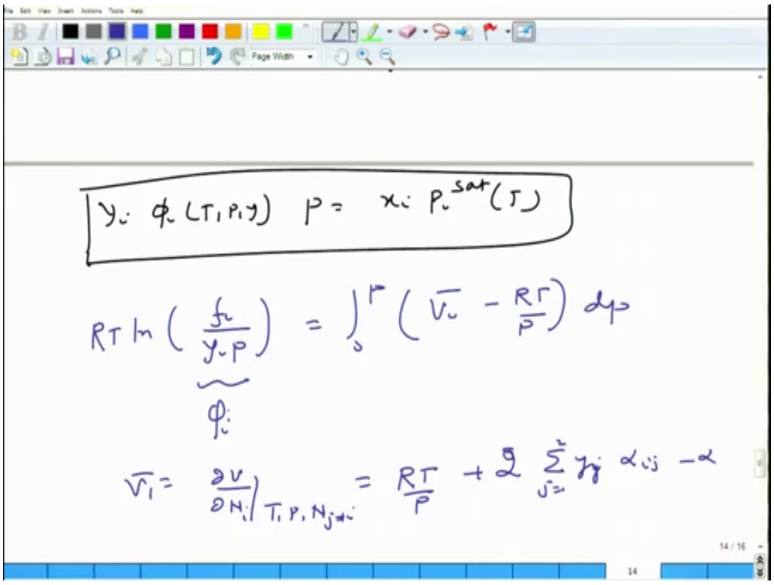

$$\boxed{y_i \, \phi_i (T, P, y) \, P = x_i \, P_i^{sat}(T)}$$

$$RT \ln \underbrace{\left(\frac{f_i}{y_i P} \right)}_{\phi_i} = \int_0^P \left(\bar{V}_i - \frac{RT}{P} \right) dp$$

$$\bar{V}_1 = \left. \frac{\partial V}{\partial N_i} \right|_{T, P, N_{j \neq i}} = \frac{RT}{P} + 2 \sum_{j=1}^{2} y_j \, \alpha_{ij} - \alpha$$

Now, from where, what else we can do? What else we can find out? We have to find out well that phi i. So, we can avail the expression which we have written for fugacity which related to the volumetric you know partial molar volumes. So, we can actually write down the following expression now. Recall that we have T fi or phi which is nothing, but a f i divided by P 0 to P V i bar minus right. So, now, because the reason why we made use of is because this is nothing, but what is this?

Student: Phi, phi.

This is phi right so, but we have been given this also right the compressibility. So, with compressibility we can directly use here rearranging this term and we can obtain our our values is little tricky because it takes time to do that. Now, V i bar is del V by del N i T P; T P and rest of the rest of the N i N j not equal to N i ok.

So, this given this expression of compressibility you can show that which is actually you know multiple step derivation that this is equal to is 2 times summation y alpha ij in this case yj j is equal to 1 to 2 minus alpha ok. Alpha is basically the sum of providers right. So, this I am I am these I am not deriving it this you can you can find it out by doing the exercise ok.

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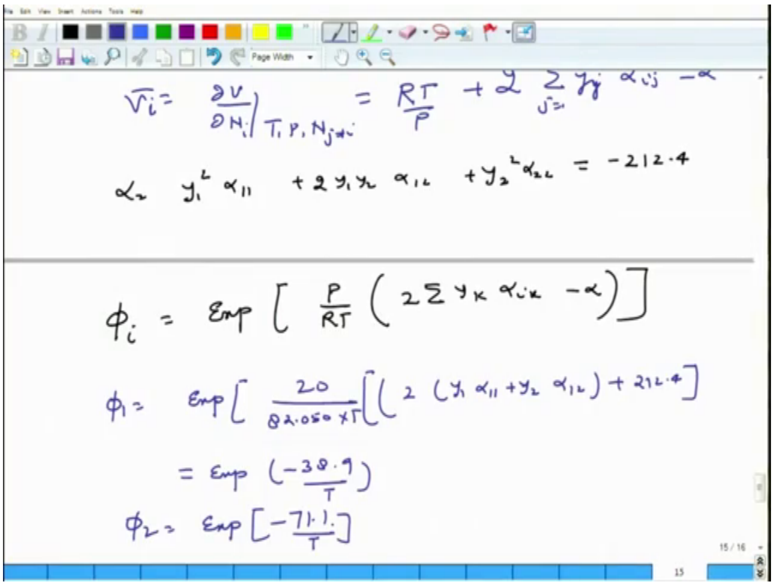

$$\bar{V}_i = \left.\frac{\partial V}{\partial N_i}\right|_{T, P, N_{j \neq i}} = \frac{RT}{P} + 2 \sum_{j=1} y_j \alpha_{ij} - \alpha$$

$$\alpha = y_1^2 \alpha_{11} + 2 y_1 y_2 \alpha_{12} + y_2^2 \alpha_{22} = -212.4$$

$$\phi_i = \mathrm{Exp}\left[\frac{P}{RT} \left(2 \sum y_k \alpha_{ik} - \alpha \right) \right]$$

$$\phi_1 = \mathrm{Exp}\left[\frac{20}{82.050 \times T} \left[\left(2 \left(y_1 \alpha_{11} + y_2 \alpha_{12} \right) + 212.4 \right] \right.\right.$$

$$= \mathrm{Exp}\left(-\frac{38.9}{T} \right)$$

$$\phi_2 = \mathrm{Exp}\left[-\frac{71.1}{T} \right]$$

What is alpha here? Alpha is y 1 square 11 plus 2 y 1 y 2, alpha 12 plus y 2 alpha 22 you can plug in these values of y's because and as well as alpha because you know this y's are given to you this becomes 212.4 ok. Now, phi is the expression of phi based on this when you plug in there is nothing it comes out to be exponential P by RT to summation y that is k because this i remember this is i. So, with the here I am putting y k alpha i k minus alpha this is the expression which comes out to be after plugging this V i bar if you plug in the equation you get this expression of phi i.

Now, with this information you can write down phi 1 and phi 2. So, phi 1 is going to be exponential 20 is the pressure we are going to put it in the way the units are in atmospheric unit the r and 2 times y 1 alpha 11 plus y 2 alpha 12 plus 212.4 which is alpha this comes out to be exponential minus 38.9 by T similarly phi 2 is exponential minus 70.1 by T ok.

So, for the case of species one this we can write y 1 phi 1 right. So, this is species 1. Now, you can plug in these expressions, all right.

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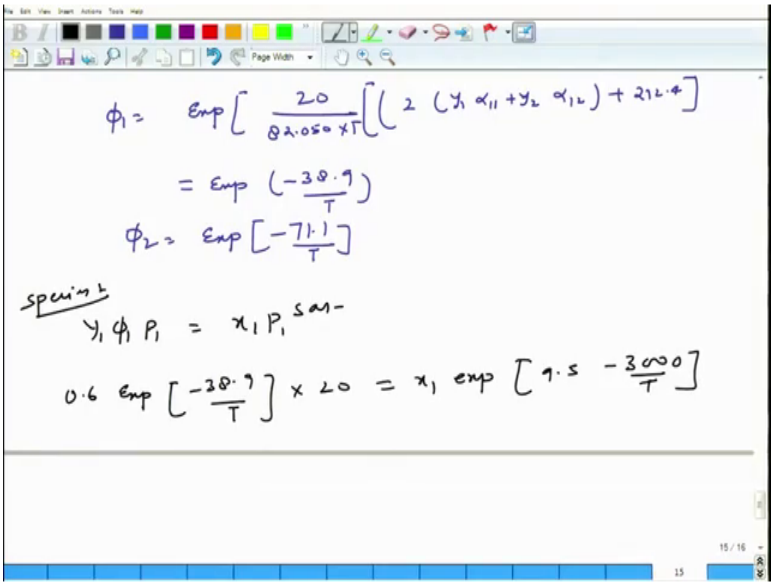

$$\phi_1 = \text{Exp}\left[\frac{20}{82.050 \times T}\left[\left(2\,(y_1\alpha_{11} + y_2\alpha_{12}\right) + 212.4\right]\right.$$

$$= \text{Exp}\left(-\frac{38.9}{T}\right)$$

$$\phi_2 = \text{Exp}\left[-\frac{71.1}{T}\right]$$

species 1

$$y_1\phi_1 P_1 = x_1 P_1^{sat}$$

$$0.6\ \text{Exp}\left[-\frac{38.9}{T}\right] \times 20 = x_1 \exp\left[9.5 - \frac{3000}{T}\right]$$

So, you have 0.6 exponential. So, we are considering species 1.6 species to 0.4, 0.6 exponential minus 38.9 by T multiplied by 20 again in that specific term this is exponent and this x 1 and what about P 1 sat P 1 sat is since from the entire expression we have this information right. So, we can plug in there ok. So, this is the value for species 2 I am going to write directly, ok.

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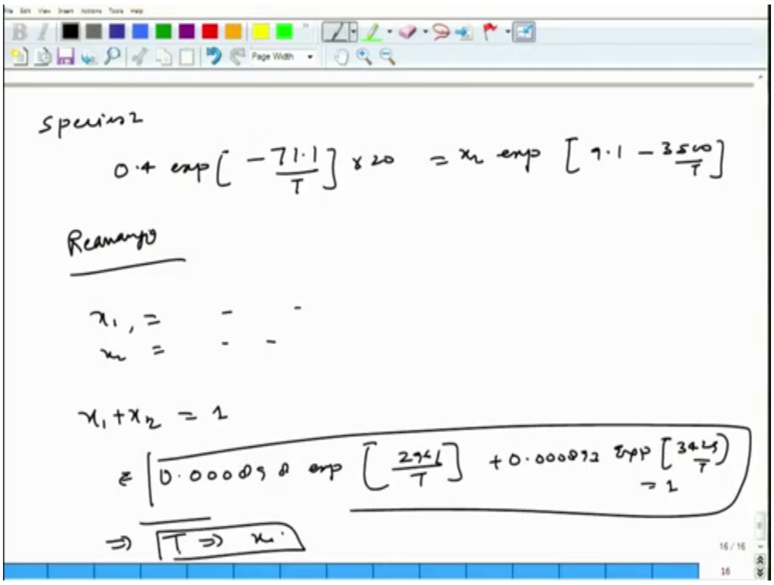

Species 2

$$0.4 \exp\left[-\frac{71.1}{T}\right] \times 20 = x_2 \exp\left[9.1 - \frac{3500}{T}\right]$$

Rearrange

$x_1 = \text{-} \quad \text{-}$

$x_2 = \text{-} \quad \text{-}$

$x_1 + x_2 = 1$

$$\boxed{0.000098 \exp\left[\frac{2961}{T}\right] + 0.000983 \exp\left[\frac{3429}{T}\right] = 1}$$

$\Rightarrow \boxed{T \Rightarrow x_i}$

For a species 2, 0.4 exponential minus 71.1 by T multiplied by 20 this is x 2 exponential 9.1 minus 3500 by T. Now, these two expressions we can rearrange ok.

Student: (Refer Time: 24:34).

If you rearrange expression we get x 1 and x 2 as a function of expressions right. So, you can rearrange right take a and then we can make use of the fact that x 1 plus x 2 is equal to be one which in this case is 0.00098 exponential this term which is 2961 by T plus 0.000983 exponential 3429 by T is equal to 1. Now, it is very straightforward this is the expression you can plug in this in excel and find out the temperature once you find out the temperature you plug back and get your expression of x and t. So, thus you can use any equal excel sheet or writer program and obtain from here temperature once you obtain you get your excise ok.

So, this is a very simple way of doing this exercise. I hope you really understood the procedure of doing such a problem. But we will be looking at more algorithmic ways in the next lecture for obtaining it more complex conditions where the approximations are not so straightforward using phi gamma approach.

So, I will see you in the next lecture.