Chemical Engineering Thermodynamics
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Lecture 41
Fugacity coefficient for mixtures

Welcome back in the last class we talked about fugacity coefficient and particularly we also demonstrated the expression for fugacity coefficient if it is based on van der Waals equational state for the mixtures.

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So if you look at the expressions we have two expressions which we came up with one where the it's a pressure explicit equation so one here was simply V i P by RT minus one and the other one was infinity to V RT by V minus del P by Del N TP and j not equal to i d v minus T l n z so this is something if you have information of the volumetric data we can use that in this case we have to use pressure explicit equation or state so these are the two expressions which we came up with for the last and in the last class.

So let me just little bit of put thoughts on our this particular fugacity coefficient which we came up with so by definition we say fugacity coefficient is nothing but the following fugacity of i divided by partial pressure or we can write like this f i is equal to Phi i yi P. Now this is the fugacity coefficient of component i in the mixture sometimes we make an approximation that Phi i we approximate this to be a Phi I of that of a pure fluid and if that is the case then I can use this phi I

as f i pure divided by P in that case f i is y i f i pure so this is an approximation and sometimes we call it Lewis fugacity rule.
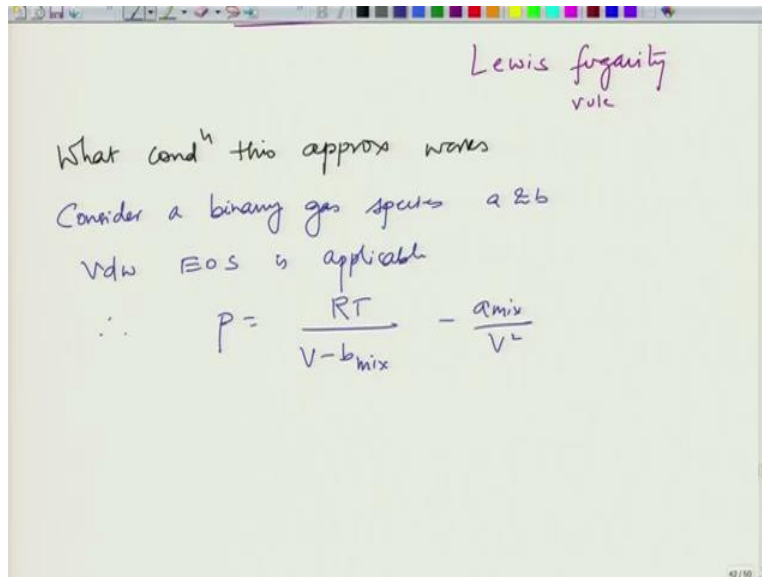
$$\ln \phi_i = \int_0^P \frac{\left(\frac{V_i P}{RT} - 1\right) dP}{P}$$

$$\ln \phi_i = \int_\infty^V \left[\frac{RT}{V} - \left(\frac{\partial P}{\partial N_i}\right)_{T,P,N_i,\phi_i}\right] dV - RT \ln Z$$

$$\frac{f_i}{y_i P} = \phi_i \quad or \quad f_i = \phi_i y_i P$$

$$f_i = y_i \, f_{i,pure} \quad Lewis \; Fugacity \; Rule$$

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It's also called Lewis fugacity rule and so question is like you know when this rule will be applicable let us try to understand that what condition where you can approximate fugacity of a component i in a mixture as a simply a mole fraction of that component multiplied by fugacity of the component i for the pure liquid for that the same temperature and pressure so something which we can approximate in some conditions so let us look at it. So in order to explain let me consider a binary gas species A and B and if we assuming this boundary guess let us assume that also that van der Waals equation of state is applicable.
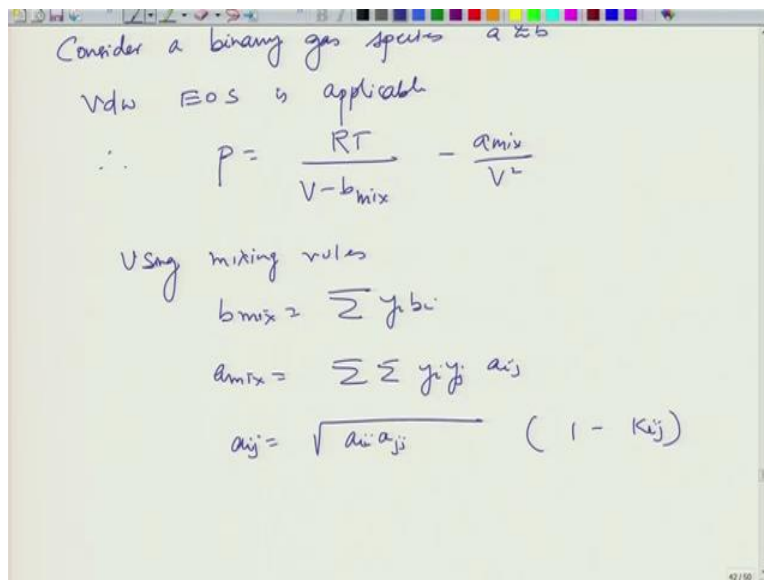
$$VDW\ EOS\ is\ applicable \quad P = \frac{RT}{V - b_{mix}} - \frac{a_{mix}}{V^2}$$

$$Using\ mixing\ rules \quad b_{mix} = \sum y_i b_i$$

$$a_{mix} = \sum\sum y_i y_j a_{ij}$$

$$a_{ij} = \sqrt{a_{ii}a_{jj}}(1 - K_{ij})$$

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Now if you use the mixing rules then I can write the B mix as summation y i b i and a mix as double summation y i y j a i j where a i j is geometric mean of a i i and a j j then we multiply by 1 minus K i j the factor. So if you use this expression and obtain the fugacity of component a without going into the details of the derivation let me just put down the expression so that we can understand at what conditions we are going to get that Lewis fugacity rule.

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$$\ln \varphi_i = \int_0^P \left(\frac{\bar{V}_i P}{RT} - 1 \right) \frac{dP}{P}$$

$$\ln \varphi_i = \int_\infty^V \left[\frac{RT}{V} - \left(\frac{\partial P}{\partial N_i} \right)_{T,P,N_j,\, \ne i} \right] dv \; - RT \ln z$$

$$\frac{f_i}{y_i P} = \varphi_i \quad \text{or} \quad f_i = \varphi_i \, y_i \, P$$

$$\varphi_{i,\,pure} = \frac{f_{i,\,pure}}{P}$$

$$\therefore \boxed{f_i = y_i \, f_{i,\,pure}} \qquad \text{Approximation}$$

So I write like this f f a and y a f a pure I can also say a vapor because since I am using y I am just ignoring that at this point. So this is f y a f a pure and then finally we get in term exponential which has the falling component you have this under square a this coefficient interaction strength coefficient energetic coefficient here a of a minus a of b square y b square P RT square so this is the term which we are going to get.

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For Lewis fugacity rule to hold

1) $P \to 0$
   $T \to \infty$ $\bigg\}$ ideal gas

2) $y_a \to 0$
   Comp a is present in large excess

3) $\sqrt{a_a} = \sqrt{a_b}$
   → Chemical nature of species a is similar to that of species b

Now the Lewis fugacity rule says they are following that you have y i is equal to y f i is equal to y i multiply by f i pure so this is the term here f a is equal to y a multiplied by f a pure which essentially means for the sake of Lewis fugacity rule or Lewis fugacity rule implies that if it is

valid then this must be one if Lewis fugacity rule is applicable. This is based on van der Waal equation of state.

Now from here we can figure it out the conditions for which this particular exponential term approaches towards one. So for Lewis fugacity rule to hold what we need, we need well the pressure goes to 0 essentially this will be one so pressure should approach toward 0 what about temperature well temperature can if temperatures infinite also this will lead to that condition so temperature should approach towards infinity and these two conditions indicate that this is nothing but the ideal gas so for ideal gas this particular expression should hold that means this particular expression should go towards one for ideal gas. What about other condition so we do have other possibilities for example if y b is 0 or approaches as 0 then also this particular term will approach towards one.

So let me put this as condition one this is condition one the condition two is y b approaches towards 0 which essentially means component a is present in large access, which means b is extremely dilute that is the condition for the mixture and the third is the following, that if this term itself is 0 or if this under root square a is equal to under root square of a or b then this exponential term will approach towards one.

So this would also lead to the same exponential term approaching towards one so this will be the condition also so we have three conditions and these conditions particularly indicates that the interaction nature of component a is that of similar to that of a component b which essentially means that the species are very similar in nature.

Chemical nature species a similar to that of species b. So these are these are the conditions for which Lewis fugacity rule is applicable. So let me now try to extend this exercise and particularly try to find out the fugacity of let us say liquid phase. So because we have been talking about fugacity in the gas phase, now let me just talk about the fugacity of liquid phase particularly for the pure case.
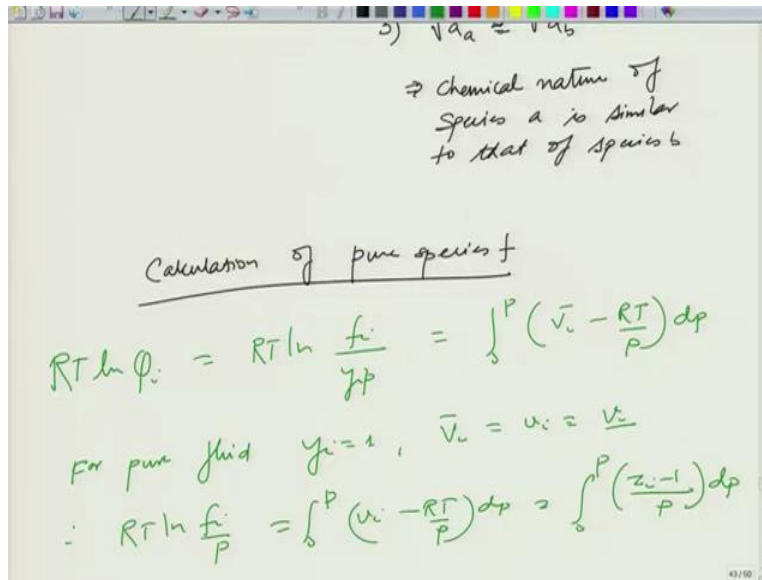
So we can use the same expression and obtain the fugacity for the, of a pure species.

$$RT \ln \phi_i = RT \ln \frac{f_i}{y_i P} = \int_0^P \left(\overline{V_i} - \frac{RT}{P} \right) dP$$

$$For\ pure\ fluid\ y_i = 1, \overline{V_i} = v_i = \underline{V_i}$$

$$RT \ln \frac{f_i}{P} = \int_0^P \left(v_i - \frac{RT}{P} \right) dP = \int_0^P \frac{Z_i - 1}{P} dP$$

So we do have this two so that is a good now considering or breaking into two parts. So let me add first put down the question so what we are interested is to find out the fugacity of let us say this, so this may be our phase diagram and what we are trying to find out is fugacity of a point here at a given temperature which is isotherm here and this is of course our p of ice at T. P is of component i are pure in this case is a pure phase at a temperature T. So we are interested here is the fugacity at this point so how do we calculate it so what we are interested is basically RT ln f of liquid pure component at temperature t and p so this is t and this is your basically b here.

So we are interested in this point., so this point which is at T and P. So I can now look at this expression f l by P by P here and if you look at here this 0 to P here is something like corresponds to pressure which is v is equal to infinity so somewhere far from the right hand side here and going to this point and then there is a phase transition and then we are talking about integral from this point to this point so i would like to break this here from here to here so it's like 0 to P i sat vi minus RT by P dp plus P i sat to P vi minus RT by P.

$$RT ln \frac{f_{pure,i}^L(T,P)}{P}$$

$$= \int_0^{P_i^{sat}} \left(V_i - \frac{RT}{P} \right) dP$$

$$+ \int_{P_i^S}^{P} \left(V_i - \frac{RT}{P} \right) dP = RT ln \frac{f_i^S(T)}{P_i^S(T)} + \int_{P_i^S}^{P} v_i dP - \int_{P_i^S}^{P} \frac{RT}{P} dP$$

Now one of the important thing which we are trying to do is the that we are looking at from here to here at this point this since the fugacities are same here because of the fact that the fugacity of component i is same as in the liquid phase and the vapor phase because of the equality because chemical potential should be same indicates the fugacity should be same that means this contribution from here to here is not from here to here the contribution is basically in 0 and we are not bothered by this phase transition at this point.

So that is why I do not have any terms specifically covering this part because that is not contributing to the integral. So it is a 0 to Pi sat and Pi sat to P so essentially from here to here and here to here. Now I try to expand it now if you look at this part first term this is going to be RT l n fi s at that particular temperature and Ps that is P sat at the temperature plus integral of P sat integral of P sat here I am putting it i here, to P and this is the first part is now vi d p considering is a pure component. So I will just remove this part here and consider this as a small v. So vi p minus r minus integral of minus integral of RT by P dp Ps P.
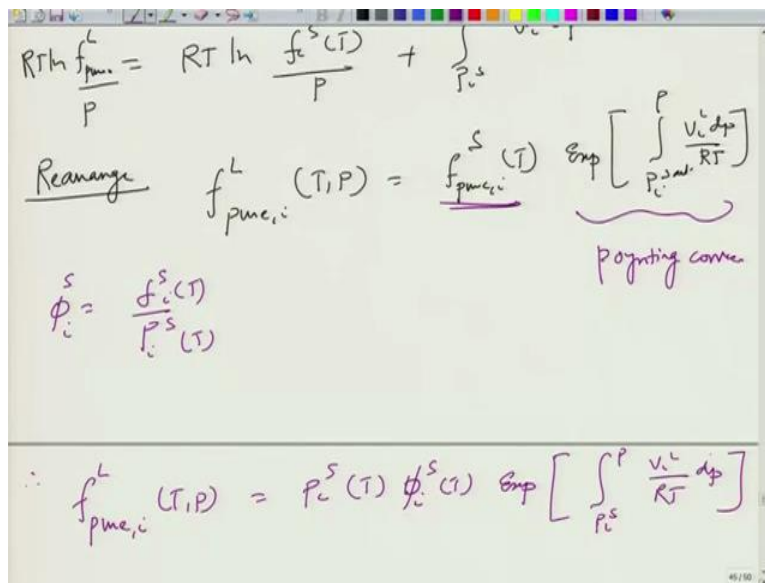
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Now this one would be RT l n P by P i s, so this and this because of being negative here sign here this will cancel this part and the P will become b will come to the denominator. So I can write this right hand side as RT ln fi sat T divided by P plus P i sat by p vi now this vi here is basically the region which corresponds to the liquid part.

So I am going to put simply this as indicating or differentiating that this is a molar volume corresponds to the liquid region of the fluid now with this my left hand side now is remains the same though RT ln f L pure i divided by P. Now I can now simplify this expression so if I rearrange I get f of L pure i TP, because P will cancel here so it will remain here is f pure i because it's all pure action at this point S T exponential integral of P is sat P vi l d p and then of course RT should be also part of it because you have to divide by RT. So I put it in their RT. So this is the expression which I get so essentially tells you that a fugacity in the liquid state at a given temperature and pressure is nothing but fugacity of the pure substance saturation condition multiplied by the term called exponential integral for Pi sat to P which is nothing but the Poynting correction.

$$RTln\frac{f^L_{pure,i}}{P} = RTln\frac{f^S_i(T)}{P} + \int_{P^S_i}^{P} v^L_i dP - RTln\frac{P}{P^S_i}$$

$$Rearranging, \ f^L_{pure,i}(T,P) = f^S_{pure,i}(T) \exp[\int_{P^{sat}_i}^{P} \frac{v^L_i}{RT} dP] \qquad Poynting \ correction$$

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So this term is we are going to get is going to say pointing correction now i can simplify a little bit more by considering the fact that this by definition can be written as your using the fugacity coefficient that by figure fugacity coefficient is f by P. So, if it is a sat then this is nothing but sat at that particular temperature so then this is going to be sat and of course this is a pure component

i so I am going to put i here and this is i. So, therefore, f of l pure i at that T and P is Pi s T phi i S T and then this exponential Poynting correction.

$$\phi_i^S = \frac{f_i^S(T)}{P_i^S(T)}$$

$$f_{pure,i}^L(T,P) = P_i^S(T)\phi_i^S(T)\exp\left[\int_{P_i^{sat}}^{P} \frac{v_i^L}{RT}dP\right]$$

$$f^L_{pme,i}(T,P) = P^S_i(T) \, \phi^S_i(T) \, \exp\left[\int_{P^S_i}^{P} \frac{v^L_i}{RT} \, dp\right]$$

At low P

$$\phi^S_i \approx 1$$

Poynting correction ≈ 1

$$\boxed{f^L_i = P^S_i}$$

So pointing correction often would be this would be negligible because if the liquids often incompressible and hence this at low pressure phi i s is going to be 1 and this term pointing correction we are going to consider is 1 therefore at low p we can write simply as f of i l is nothing fi sat .So most of most of the cases for the liquid will be ignoring these pointing corrections to simplify the problems if it is available anyway if the pressures are high then you are going to consider this pointing correction but if the pressures are low you can ignore this pointing correction terms

$$At\ low\ P,\ \ \phi^S_i \approx 1\ \ \ Poynting\ correction \approx 1$$

$$f^L_i = P^S_i$$

At this point, I think we are done with the concepts of the fugacity and the fugacity coefficients and we have used the ideal gas mixture to start with I defined a bit of the how to take it the fugacity to the liquid phase as well in the next class we will going to start ideal liquid or mixtures to and basically the reference point for the liquids and how do we take care of that. So, I will describe a bit using the foundation what we have taken here for the ideal gas mixtures we will be starting the ideal gas idle liquid mixtures and essentially will build up a buildup upon a new way to address those concepts. So, with that I will stop here now and I will see you in the next lecture.