Lecture – 6
Fugacity from Volumetric Data - 2

Welcome to the MOOCs course advanced thermodynamics. The title of this lecture is Fugacity from Volumetric Data part 2. Since this is a continuation of previous lecture, we will be having a recapitulation of what we have discussed in previous lecture.

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In the previous class, we derived fugacity coefficient from volumetric data information in the pressure explicit form or with temperature and volume as independent variables, okay? Those fugacity coefficient expressions we have derived for component i of a mixture we derived it as

$RT \ln \phi_i = RT \ln\left(\frac{f_i}{y_i P}\right) = \int_V^\infty \left[\left(\frac{\partial P}{\partial n_i}\right)_{T,V,n_j} - \frac{RT}{V}\right] dV$ - RT ln z. This is what we have derived for a

component i of a mixture.

If that component is a pure component, then for a pure component i we have derived it as

$RT \ln \left(\frac{f_i}{P}\right)_{pure\ i} = \int_V^\infty \left(\frac{P}{n_i} - \frac{RT}{V}\right) dV$ - RT ln z + RT (z - 1), where z is the compressibility factor

of the system, it is given by $\frac{PV}{RT}$, okay? So, now, what we do? We take a few equations of state and then try to derive the fugacity coefficient of a component i in a mixture as well as a fugacity coefficient of a pure component i. Those things we will take now.

Fugacity of a component in a mixture according to van der Waal's equation

- Consider a mixture whose volumetric properties are described by van der Waal's equation:

$$P = \frac{RT}{v-b} - \frac{a}{v^2} \qquad (60)$$

Where v = molar volume of mixture = V/n_T and a, b = constants depends on composition

- Substitute $v = \frac{V}{n_T}$ in equation (60) $\Rightarrow P = \frac{n_T RT}{V-n_T b} - \frac{n_T^2 \cdot a}{V^2}$ $\qquad (61)$

- $\left(\frac{\partial P}{\partial n_i}\right)_{T,V,n_j} = \frac{\partial}{\partial n_i}\left(\frac{n_T RT}{V-n_T b}\right) - \frac{1}{V^2}\frac{\partial}{\partial n_i}(n_T^2 \cdot a) = \frac{RT\left[(V-n_T b)\frac{\partial}{\partial n_i}(n_T) - n_T \frac{\partial}{\partial n_i}(V-n_T b)\right]}{(V-n_T b)^2} - \frac{1}{V^2}\frac{\partial}{\partial n_i}(n_T^2 \cdot a)$

$$= \frac{RT\left[(V-n_T b)(1) - n_T\left(0 - \frac{\partial}{\partial n_i}(n_T b)\right)\right]}{(V-n_T b)^2} - \frac{1}{V^2}\frac{\partial}{\partial n_i}(n_T^2 \cdot a)$$

$$= \frac{RT}{(V-n_T b)} + \frac{n_T RT \frac{\partial}{\partial n_i}(n_T b)}{(V-n_T b)^2} - \frac{1}{V^2}\frac{\partial}{\partial n_i}(n_T^2 \cdot a) \Rightarrow (62)$$

So, fugacity coefficient of the component in a mixture according to Van der Waal's equation. Consider a mixture whose volumetric properties are described by Van der Waal's equation given as $P = \frac{RT}{v-b} - \frac{a}{v^2}$. Now, here if the Van der Waal's equation is in this form, this equation we cannot write as a kind of volume explicit form, right? So, then we have to take the generalized fugacity expressions in terms of pressure explicit form volumetric data whatever available.

That means, from this equation, we have to write in a pressured explicit form, indeed it is already given in a pressure explicit form. So, for this equation, first we have to convert the molar volume into the total volume and then we have to find out a, b constant for the mixtures because a and b are the Van der Waal's constant and these are for the mixture because this equation is given for the mixture. So, those things we have to find out and then we have to find out $\left(\frac{\partial P}{\partial n_i}\right)_{T,V,n_j}$ and then substitute in equation number 53 of previous lecture that you know

RT ln $\phi_i = \int_V^\infty \left(\left(\frac{\partial P}{\partial n_i}\right)_{T,V,n_j} - \frac{RT}{V}\right) + $ RT ln z, that expression.

In that equation, in place of $\left(\frac{\partial P}{\partial n_i}\right)_{T,V,n_j}$, whatever $\left(\frac{\partial P}{\partial n_i}\right)_{T,V,n_j}$ we will get from this equation that we have to substitute and simplify, okay? That is what we are going to do now, okay? First convert this equation in terms of total volumes by replacing molar volume by total volume divided by the total number of moles n_T and a and b are the Van der Waal's constant and they

are dependent on the composition. That means, for pure gases, they are experimentally available a_1, a_2, etc. b_1, b_2, etc. are available for pure components 1, 2, etc., right?

So, when we mix them together 1, 2, etc., component. Then obviously different composition will give different gases mixture. So, for that mixture, this a, b constant we have to obtain and these a, b constants are functions of the composition of the mixture, okay? So, those things also we have to see now. First part will take only converting it in terms of total volume, right? So when we do this one by replacing v by $\frac{V}{n_T}$ and then simplifying, then we will have this equation, right?

So now we need $\left(\frac{\partial P}{\partial n_i}\right)_{T,V,n_j}$ in order to substitute in equation number 53. Remember for last couple of lectures and this lecture, equation numbers I am maintaining sequentially, so that it should not be confused, okay? So this first equation of this lecture is 60, okay? Because until the previous lecture, we had an equation number 59, okay? So now here, $\left(\frac{\partial P}{\partial n_i}\right)_{T,V,n_j}$ this I am doing because this lecture and the previous 2 lectures are connected one to other lecture, one way or other way, so that is the reason I am maintaining this equation number in a sequential manner for all 3 lectures.

So now for this equation of state in a pressure explicit form, what we will do? We will do $\left(\frac{\partial P}{\partial n_i}\right)_{T,V,n_j}$ that means $\frac{\partial}{\partial n_i}$ of this first term $-\frac{1}{V^2}\frac{\partial}{\partial n_i}(a \cdot n_T^2)$, right? So, here what is this a, b is, we know that it depends on the composition, right? So that means y_i, y_j, etc., it depends. So, that means it is dependent on n_i. So, we have to differentiate this one, we cannot take it as a constant because it is dependent on the composition. So, what is that a for a mixture that we do not know.

So, for the time being, we will not be able to differentiate this one. Similarly, same is true for b. So, now, what we do? RT part of this differentiation is constant because you know all these calculations we are doing at constant temperature and composition, n_T we have to differentiate with respect to n_i, okay? So, differentiation of this one is you know here $(V - n_T b)^2$ and then RT is constant then $(V - n_T b)\frac{\partial}{\partial n_i}(n_T) - n_T \cdot \frac{\partial}{\partial n_i}(V - n_T b)$, $-\frac{1}{V^2}\frac{\partial}{\partial n_i}(n_T^2 \cdot a)$ would be as it is.

Now, $\frac{\partial}{\partial n_i}$ is nothing but 1 and then the $\frac{\partial}{\partial n_i}(V - n_Tb)$ is nothing but $0 - \frac{\partial}{\partial n_i}n_Tb$. This b also we do not know for the mixture, but it depends on the composition, so it has to be evaluated once we find out what is that b depending on the composition. Same is true for the second term, so that we are keeping as it is. So further, this we can simplify as $\frac{RT}{V - n_T b}$ and then this term $\frac{n_T RT \frac{\partial}{\partial n_i}(n_T b)}{(V - n_T b)^2}$ - $\frac{1}{V^2}\frac{\partial}{\partial n_i}(n_T^2 \cdot a)$ is as it is.

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Now, this term we will be substituting in equation number 53 here. This is the equation number 53. This is the equation for fugacity of component i, if the equation of state is given in a pressure explicit form, right? So, now here this $\frac{\partial P}{\partial n_i}$ is nothing but this term just we had - $\frac{RT}{V}$ is as it is and then - RT ln z is as it is. Integration of this part is nothing but ln[V - n_Tb]. Integration of this part that is integral of $\frac{1}{(V - n_T b)^2} = -\frac{1}{V - n_T b}$.

Then here also integral of $\frac{1}{V^2} = -\frac{1}{V}$ and then integral of $\frac{1}{V}$ is nothing but ln V, right? And then these limits V to ∞ are there. Here we must remember this n_Tb, n_T, a, b, T, etc., are independent of volume. So, while doing the integration, we can take them as a constant. Now, what we do? These 2 ln terms will join together, so that we can have this RT ln $\frac{V - n_T b}{V}$ as one term and then remaining terms we are keeping as it is without doing anything, okay?

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- For $V \to \infty \Rightarrow \ln\left(\frac{V - n_T b}{V}\right) \to 0$; $\frac{1}{(V - n_T b)} \to 0$ and $\frac{1}{V} \to 0$ (64)
- $\therefore$ Eq. (63) reduces

$$RT \ln \frac{f_i}{y_i P} = RT \ln \frac{V}{V - n_T b} - n_T RT \left[\frac{\partial}{\partial n_i}(n_T b)\right] \frac{1}{(V - n_T b)} + \frac{\partial(n_T^2 a)}{\partial n_i} \frac{1}{V} - RT \ln z$$

(65)

- In order to make use of equation (65) to calculate the fugacity one has to make assumptions concerning the composition dependence of constants "a" and "b"
- These assumptions are not made based on thermodynamic arguments but must be obtained from molecular consideration

Now, limiting condition we have to do. This $\ln \frac{V - n_T b}{V}$ should be tending to 0 if V tends to ∞.

Because if you take ln, the same thing you can write $\frac{1 - \frac{n_T b}{V}}{1}$, right? I am just, you know, taking V common from the numerator and denominator and canceling out. So, now, if V tends to ∞, so $\frac{1}{V}$ should be tending to 0, so ln of $\frac{1}{1} = 0$. So, that is what we get, okay? So, other two limits $\frac{1}{V - n_T b}$ should be tending to 0 and $\frac{1}{V}$ should also be tending to 0 if V tends to ∞.

When you substitute these limits, the previous expression reduces to this particular form, okay? This here, we have substituted only limiting conditions whatever the V tends to some finite V and then V tends to ∞, okay? Now, this equation is useful only when we know what is this $\frac{\partial}{\partial n_i}(n_T^2 a)$ and then we know $\frac{\partial}{\partial n_i}(n_T b)$, then only this equation is useful, otherwise this equation is as good as nothing has been done. So, these equations we already understood this b and a are dependent on the composition.

So, we have to make some assumptions on how this a and b are dependent on the composition, and these assumptions cannot be made based on the thermodynamic principles or thermodynamics understanding, but they can be made only based on the molecular considerations, right?

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- Suppose m components in the mixture with spherical molecules one can interpret b as follows

$$b^{1/3} = \sum_{i=1}^{m} y_i b_i^{1/3} \qquad (66)$$

- Other way, average the molecular volume directly as $b = \sum_{i}^{m} y_i b_i$ (67)
- At moderate densities, for mixtures those molecules are not too dissimilar in size the particular mixing rule used for "b" does not significantly affects the results
- However, fugacity of a component is a mixture is sensitive to mixing rule used for constant "a"
- If we interpret "a" as a term that reflects the strength of attraction between two molecules, then for a mixture we may want to express "a" by averaging overall molecular pairs, then $a = \sum_{i=1}^{m} \sum_{j=1}^{m} y_i y_j a_{ij} \Rightarrow (68)$
- and for $i \neq j$, $\Rightarrow a_{ij} = \sqrt{a_i a_j} \Rightarrow (69)$

So, what we do? We see a few mixing rules. Suppose m components in the mixture with spherical molecules one can interpret b as follows as $b^{\frac{1}{3}} = \sum_{i=1}^{m} y_i\, b_i^{1/3}$. Now, this b_i is nothing but the constant b of ith species if it is in the pure form, okay? Because this we know a_i, b_i, etc., are available when the component is in pure form, okay? So, for pure form, they are available from experiments. So, if you wanted to know the mixtures, so then we can use this as one of the mixing rule for b.

There are many other mixing rules. If you take another mixing rule for b is like this. $b = \sum_{i=1}^{m} y_i\, b_i$, again b_i is for, the b constant for pure component i and then y_i is nothing but that particular composition of a component i in the mixture, okay? But it has been found by so many studies that whether we use this b expression or this expression usually the results may not be affected much. Fugacity calculation especially may not be affected much especially at moderate densities.

So, any of these 2 we can use, but what kind of mixing rule are you using in order to find out the a constant for the mixture, it strongly influences the final results especially fugacity results. So, one should be very careful while choosing mixing rule for a. So, if we interpret a as a term that reflects the strength of attraction between 2 molecules indeed this out of this a and b constants, a sometime indicates or the terms with a are indicating something like attractive forces, whereas the other terms with the b terms, etc., those indicates repulsive forces, okay?

So, for a, this is one of the mixing rules that is a $= \sum_{i=1}^{m} \sum_{j=1}^{m} y_i y_j a_{ij}$ and then if $i \neq j$, then $a_{ij} = \sqrt{a_i a_j}$. If i = j, then $a_{ij} = a_i a_i$ that is a_i simply if i = j or a_j if you read a_{jj} kind of thing, okay? So, now we use these mixing rules and then further we simplify the equation that we have derived for fugacity coefficient in previous slide, okay?

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So, then this is actually previous equation 65 that we derived in previous equation. Now, we will be using some assumptions for $n_T b$ first. So, in place of b, we are using this $\sum_{i=1}^{m} y_i b_i$ mixing rule, okay? And then a let us keep it as it is. Then this remaining terms wherever this V terms are there, numerator and denominator I am dividing by n_T, right? So that there will not be any change and further in the next step wherever $\frac{V}{n_T}$ is there I can write it as a molar volume v, okay? So that is what I am doing here.

Then so, this part now will become in terms of molar volume that is $\frac{v}{v-b}$ and then same here $\frac{1}{v-b}$ and then here this $\sum_{i=1}^{m} y_i b_i$, y_i I can write $\frac{n_i}{n_T}$, so n_T and this n_T will be cancelled out, $\sum_{i=1}^{m} n_i b_i$ would be there, okay? This term we are keeping as it is. Further what I am doing this RT whatever RT is there that I have already cancelled out from all the terms, right okay? So that here we get $\frac{1}{VRT}$ anyway, okay? That RT term has been brought to the right hand side.

So wherever RT was there in the numerator that has been canceled out by denominator RT, wherever there was no RT, so then this RT is coming in the denominator, okay? Next, we know that $\frac{\partial}{\partial n_i} b_i n_i$ is nothing but bi, okay? $\frac{b_i}{v-b}$ term we will be getting and then remaining terms we

are keeping as it is, okay? So now, what we do? In the next step, we try to find out this one. So, this one what we do, we do for a binary component, right?

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For a binary component mixing rule for a is nothing but $y_1^2\, a_1 + 2\, y_1\, y_2\, \sqrt{a_1 a_2} + y_2^2\, a_2$. I am writing it for binary mixture only. y_1 is the mole fraction of component 1, y_2 is mole fraction of component 2, a_1 is constant a for pure component 1, a_2 is constant a for pure component 2, right? Then $\frac{\partial}{\partial n_1}(n_T^2\, a)$, I am doing for first component in the binary mixture for simplicity. So, then this here wherever y_1 is there, I am writing $\frac{n_1}{n_T}$ and then wherever y_2 is there I am writing $\frac{n_2}{n_T}$.

So, then in place of a, this is what I have. So, this n_T^2, n_T^2 we can cancel out. Then if you differentiate from differentiation on the first term, we will get $2\, n_1\, a_1$ is constant. Differentiation of second term I will get $2\, n_2$ and then $\sqrt{a_1 a_2}$ is constant and then third term is 0, differentiation of third term is 0. So, then from these 2 terms, $2\, \sqrt{a_1}$, I am taking common. So, then I can have $n_1\, \sqrt{a_1} + n_2\, \sqrt{a_2}$.

The purpose of doing this differentiation for binary component is that now we can generalize this one to the multi-component mixture easily. This we can write for multi-component mixture as $2\sqrt{a_i}\,\{\sum_{j=1}^{m} n_j\sqrt{a_j}\}$. So, this one we can substitute in the previous expression. Previous

expression here what we had, we had $\frac{\partial}{\partial n_i} n_T^2$. a in this place and divided by $\frac{V}{RT}$ was there. So, in place of $\frac{\partial}{\partial n_i} n_T^2$ here, we are writing $2\sqrt{a_i} \left\{ \sum_{j=1}^{m} n_j \sqrt{a_j} \right\}$.

So now this term further next what I am doing, I am dividing by n_T, both numerator and denominator I am dividing by n_T. So that $\frac{n_i}{n_T}$ I can write it as y_j and then V by n_T I can write it as v molar volume, rest all other terms we are keeping same without changing anything. So, this is the expression for fugacity component of i in a mixture if equation of state of the mixture is given in a pressure explicit form according to Van der Waal's equation of state, right? And then z is nothing but compressibility of the mixture that is nothing but $\frac{PV}{RT}$.

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Example – 1

- A pure gas is described by Redlich - Kwong equation of state by $P = \dfrac{RT}{v-b} - \dfrac{a}{v(v+b)\sqrt{T}}$ where a & b are constants. Obtain expression for its fugacity

- Solution: $P = \dfrac{RT}{v-b} - \dfrac{a}{v(v+b)\sqrt{T}} \rightarrow \dfrac{P}{n_i} = \dfrac{RT}{V-bn_i} - \dfrac{an_i}{V(V+n_ib)\sqrt{T}}$

$$\int_V^\infty \left(\frac{P}{n_i} - \frac{RT}{V} \right) dV = \int_V^\infty \left[\frac{RT}{V-bn_i} - \frac{an_i}{\sqrt{T}} \left(\frac{1}{V} - \frac{1}{V+n_ib} \right) \frac{1}{n_ib} \right] dV - \int_V^\infty \frac{RT}{V} dV$$

$$= RT \ln(V-bn_i) \Big|_V^\infty - \frac{a}{b\sqrt{T}} [\ln V - \ln(V+n_ib)]_V^\infty - RT \ln V \Big|_V^\infty$$

$$= RT \ln(V-bn_i) \Big|_V^\infty - \frac{a}{b\sqrt{T}} \ln \left[\frac{V}{V+n_ib} \right]_V^\infty - RT \ln V \Big|_V^\infty$$

$$\int_V^\infty \left(\frac{P}{n_i} - \frac{RT}{V} \right) dV = RT \ln \frac{(V-bn_i)}{V} \Big|_V^\infty - \frac{a}{b\sqrt{T}} \ln \left[\frac{V}{V+n_ib} \right]_V^\infty = -RT \ln \frac{V-bn_i}{V} + \frac{a}{b\sqrt{T}} \ln \frac{V}{V+n_ib}$$

Now, we take Redlich-Kwong equation as a kind of example. We take a pure component whose equation of state is described by Redlich-Kwong equation and it is given by $P = \frac{RT}{v-b} - \frac{a}{v(v+b)\sqrt{T}}$, where a and b are constants, so these are for the pure components. So, it is a pure component, so we do not need to worry about the mixture. So, we have to find out f_pure i, so that is $\int_V^\infty \left(\frac{P}{n_i} - \frac{RT}{V} \right)$ dV - RT ln z + RT (z − 1) that is what we have to find out.

In that equation $\frac{P}{n_i}$ we have to find out what it is and then what is $\frac{P}{n_i}$ according to Redlich-Kwong equation we have to find out and substitute in that equation. So, P, first what I am doing? I am dividing this equation both side by n_i, okay? And then wherever this, let us say first term, this term I am doing $\frac{RT}{v-b} . \frac{1}{n_i}$ is there. So, this one I can write RT, molar volume into

number of moles is nothing but total volume (V - bn$_i$). Similar rearrangement if I do for the second term, then I can get $\frac{an_i}{V(V + n_i\, b)\sqrt{T}}$, okay?

Now, this expression what I will be doing next step? I will be separating $\frac{1}{V(V + n_i\, b)}$ in 2 term so that I can do integration easily, right? So, that I do $\frac{an_i}{\sqrt{T}}$ is constant and then this term $\frac{1}{V(V + n_i\, b)}$ if I write in 2 terms, I can write it as $\left(\frac{1}{V} - \frac{1}{(V + n_i\, b)}\right)\frac{1}{(n_i\, b)}$, which is same as $\frac{1}{V(V + n_i\, b)}$, right? So, now this n$_i$, this n$_i$ I can cancel out, whereas the remaining terms are the same. So, this is actually we need $\int_V^\infty \left(\frac{P}{n_i} - \frac{RT}{V}\right) dV$.

So, this term is $\frac{P}{n_i}$, this term is $\frac{RT}{V}$ as it is, as a separate term I have written, right? Further if you integrate this equation, now what we will have? The integration of first term is nothing but RT ln (V - bn$_i$) because b and n$_i$ are independent of V. So we can treat them as constant while doing the integration. Similarly, integration of this part is ln V - ln (V + n$_i$ b) and then integration of $\frac{1}{V}$ is nothing but ln V and then limits are V to ∞. So, V to ∞ we substitute here, substitution we will do later.

Now, what we do? We combine these two terms as ln A- ln B = ln A by B form. So, $\ln\frac{V}{(V + n_i\, b)}$ we are having here and then RT ln V is as it is. Now, in the next step what I have done. The first ln term and the last ln V term I have clubbed together as ln $\frac{V - bn_i}{V}$ form and then this term is as it is without any change. So, now RT ln $\frac{V - bn_i}{V}$, I can write by substituting this limits ∞,+ $\frac{a}{b\sqrt{T}}\, ln\, \frac{V}{(V + n_i\, b)}$.

Here it was -, here it was +, so now it is reverse - and + because you know upper limit when V tends to ∞, both these two terms are tending to 0. So, lower limits when V = V, then we get the negative symbol here when substituting the limits.

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- We have $RT \ln\left(\frac{f}{P}\right)_{pure\,i} = \int_V^\infty \left(\frac{P}{n_i} - \frac{RT}{V}\right)dV - RT\ln(z) + RT(z-1)$

$$RT \ln\left(\frac{f}{P}\right)_{pure\,i} = -RT\ln\left(\frac{V-bn_i}{V}\right) + \frac{a}{b\sqrt{T}}\ln\left(\frac{V}{V+n_ib}\right) - RT\ln z + RT(z-1)$$

$$\ln\left(\frac{f}{P}\right)_{pure\,i} = \ln\left(\frac{v}{v-b}\right) + \frac{a}{RT^{3/2}b}\ln\left(\frac{v}{v+b}\right) - \ln z + (z-1)$$

- But $z = \frac{Pv}{RT} = \frac{v}{v-b} - \frac{a}{RT^{3/2}(v+b)} \Rightarrow z-1 = \frac{v}{v-b} - 1 - \frac{a}{RT^{3/2}(v+b)}$

$$\Rightarrow z-1 = \frac{b}{v-b} - \frac{a}{RT^{3/2}(v+b)}$$

$$\text{and } \ln z = \ln\left[\left(\frac{v}{v-b}\right) - \frac{a}{RT^{3/2}(v+b)}\right]$$

So, we have for RT ln $\left(\frac{f}{P}\right)_{\text{pure i}}$, this expression we derived. So, in this place for Redlich-Kwong equation what is integral $\int_V^\infty \left(\frac{P}{n_i} - \frac{RT}{V}\right)dV$ that we just derived? So, that one is nothing but this one, okay? Just now we derived for Redlich-Kwong equation $\int_V^\infty \left(\frac{P}{n_i} - \frac{RT}{V}\right)dV$ is nothing but this one, okay? And then remaining the - RT ln z + RT (z - 1) we are keeping as it is.

So, this RT if I can cancel out and then wherever this V terms are there, so both numerator and denominators I am dividing by n_T, so that $\frac{V}{n_i}$ or $\frac{V}{n_T}$ is same. $\frac{V}{n_i}$, I can write it as v molar volume here also the same thing and then here also same thing, we do not get any additional terms, rather this multiplication whatever n_i's are there they will be cancelled out because we are dividing by n_i both numerator and denominators, right? So now, next step what we have to do?

What is this z we have to find out? Because this ln z + (z – 1), whatever these terms are there, there we can substitute, z is nothing but $\frac{Pv}{RT}$. So Redlich-Kwong equation if you rearrange in terms of $\frac{Pv}{RT}$ = then remaining terms would be $\frac{v}{v-b}$ - $\frac{a}{RT^{3/2}(v+b)}$ this is what we get, z - 1 is nothing but this term - 1, okay? So, that if you do the LCM, you will get $\frac{b}{v-b}$ as first term and then second term would be as it is. Then ln z would be ln of $\frac{v}{v-b}$ - $\frac{a}{RT^{3/2}(v+b)}$ this is what you get. So, these 2 terms you can substitute here for these 2 cases.

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$$\ln\left(\frac{f}{P}\right)_{pure\ i} = \ln\left(\frac{v}{v-b}\right) + \frac{a}{RT^{3/2}b}\ln\left(\frac{v}{v+b}\right) + \left(\frac{b}{v-b}\right) - \frac{a}{RT^{3/2}(v+b)} - \ln\left[\left(\frac{v}{v-b}\right) - \frac{a}{RT^{3/2}(v+b)}\right]$$

$$= \left(\frac{b}{v-b}\right) - \frac{a}{RT^{3/2}(v+b)} + \frac{a}{RT^{3/2}}\ln\left(\frac{v}{v+b}\right) - \ln\left[\frac{\frac{v}{v-b} - \frac{a}{RT^{3/2}(v+b)}}{\left(\frac{v}{v-b}\right)}\right]$$

$$\ln\left(\frac{f}{P}\right)_{pure\ i} = \left(\frac{b}{v-b}\right) - \frac{a}{RT^{3/2}}\ln\left(\frac{v}{v+b}\right) - \frac{a}{RT^{3/2}(v+b)} - \ln\left[1 - \frac{a}{RT^{3/2}(v+b)}\left(\frac{v-b}{v}\right)\right]$$

But $P = \frac{RT}{v-b} - \frac{a}{v\sqrt{T}(v+b)} \Rightarrow \frac{P(v-b)}{RT} = 1 - \frac{a(v-b)}{RT^{3/2}v(v+b)}$

$$\therefore \ln\left[1 - \frac{a(v-b)}{RT^{3/2}v(v+b)}\right] = \ln\left[\frac{P(v-b)}{RT}\right]$$

When you do this one, you will get z - 1 is this one and then ln z is this part, remaining first two terms are as it is, we are not changing them. This is z - 1 term and this term is ln of z term, right? So, now what we do? This particular ln term and then this particular ln term that is first and last ln terms. I am writing ln A - ln B = ln A by B form, so then I get this particular term and then remaining terms are as it is, right? Next step, this I can further simplify as $1 - \frac{a}{RT^{3/2}(v+b)}$ $\frac{v-b}{v}$, this is what I get by simplifying this particular term, right?

Then, we have equation of state given like this. I am further simplifying what is this, can we simplify further so that it will be having less number of term that is what I am doing. So, this equation if I rearrange, this is the Redlich-Kwong equation, equation of state for pure component it is given. If I rearrange this equation $\frac{P(v-b)}{RT}$, then I will get this one as 1 - $\frac{a(v-b)}{RT^{3/2}v(v+b)}$, which is nothing but this term ln term. So, in place of ln of this term, I can write ln of $\frac{P(v-b)}{RT}$, so that I will be doing here in the next step.

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- **Now**

$$\ln\left(\frac{f}{P}\right)_{pure\ i} = \left(\frac{b}{v-b}\right) + \frac{a}{RT^{3/2}b}\ln\left(\frac{v}{v+b}\right) - \frac{a}{RT^{3/2}(v+b)} - \ln\left[\frac{P(v-b)}{RT}\right]$$

$$\ln\left(\frac{f}{P} \times \frac{P(v-b)}{RT}\right) = \left(\frac{b}{v-b}\right) + \frac{a}{RT^{3/2}b}\ln\left(\frac{v}{v+b}\right) - \frac{a}{RT^{3/2}(v+b)}$$

$$\left(\frac{f}{P}\right)_{pure\ i} \times \frac{P(v-b)}{RT} = \exp\left\{\left(\frac{b}{v-b}\right) + \frac{a}{RT^{3/2}b}\ln\left(\frac{v}{v+b}\right) - \frac{a}{RT^{3/2}(v+b)}\right\}$$

$$\left(\frac{f}{P}\right)_{pure\ i} = \frac{RT}{P(v-b)}\exp\left\{\left(\frac{b}{v-b}\right) - \frac{a}{RT^{3/2}(v+b)} + \frac{a}{RT^{3/2}b}\ln\left(\frac{v}{v+b}\right)\right\} \quad *$$

ϕ_i, E.O.S $\rightarrow$ $V = -$, $P = -$

$f_{pure\ i} \rightarrow \phi_i \Leftarrow V = F_V(T, P, n_1, n_2$

$f_{pure\ i} \rightarrow \phi_i \Leftarrow P = F_P(T, V, n_1, n_2$

So in place of that particular term, I am writing $\frac{P(v-b)}{RT}$ here. Now what I do? Last term of RHS, I am taking to the left hand side. Then I can have this $\ln\left(\frac{f}{P}\right)_{pure\ i} + \ln\frac{P(v-b)}{RT}$. So, ln of A + ln of B = ln of A * B form, I can write. So then, I have written $\ln\left(\frac{f}{P}\right)\frac{P(v-b)}{RT}$, and then in the right hand side terms I am keeping as it is without any change. So now I can take exponential by taking off ln because I want expression for $f_{pure\ i}$. So, then this is what I am having.

That means $\left(\frac{f}{P}\right)_{pure\ i}$, I can write it as $\frac{RT}{P(v-b)}$ exponential of this term as it is, okay? So, now we have a final expression for fugacity of pure component i if the equation of state is described by Redlich-Kwong equation and then that is given in a pressure explicit form, then the fugacity of the pure component is nothing but this one. So, now, we have taken 2 examples. One is like you know we take a mixture whose equation of state is described by Van der Waal's equation.

So, that equation we have written in a pressure explicit form and then we found what is ϕ_i expression for the component i in the mixture. Then we have taken a pure component, but the equation of state is Redlich-Kwong equation and then that Redlich-Kwong equation is given in a pressure explicit form. For that case what is the fugacity of pure component i that is $f_{pure\ i}$ is this one, this is what we have derived, okay? Now what we have? We have this V as function of temperature, pressure, and then composition, so and so, then we have a certain expression for ϕ_i and $f_{pure\ i}$.

This is what we derived in one of the previous lecture and then in this lecture we have this equation of state as a pressure explicit form as a function of temperature, volume, n_1, and n_2 and composition so on so. So, in the previous case temperature and pressure as independent variables, so there by keeping temperature constant we could find out what is the effect of a change in pressure, what is the effect of change in pressure that would be occurring in ϕ_i and $f_{pure\ i}$ that we have seen.

In today's lecture, temperature and volume as independent variable, so at constant temperature by changing the volume how much change in the ϕ_i and then $f_{pure\ i}$ occurring, those things we have seen in this particular lecture, okay? Now, what we do, let us say you have one equation of state and then you can write that one as a volume explicit form as well as the pressure explicit form, right? So, then both these equations will provide us the same ϕ_i or $f_{pure\ i}$ or not are different equation that we have to crosscheck.

Indeed, they have to provide the same expression, then only these derivations are correct, generalized expression that we have derived for the fugacity coefficient of component i or fugacity of pure component i. They can be correct are reliable only when you take one equation of state but that equation of state you write as a kind of volume explicit form and pressure explicit form and then you derive corresponding fugacity coefficients and then crosscheck.

If you are getting same thing, then they are correct, otherwise you might have made some kind of mistakes that is what you would be realizing, okay? That we crosscheck now.

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Whether volume explicit and pressure explicit forms give same expression for fugacity or not that is what we check. So, already in one of the previous lecture, we have taken Van der Waal's equation in volume explicit form. Van der Waal's expression is given by this PV = RT + $\left(b - \frac{a}{RT}\right)$P, right? And then we found ϕ_1 we have taken for the binary mixtures a ϕ_1 we found this equation 34 in lecture number 4 and then for $f_{\text{pure 1}}$, we found this equation 35 in the same lecture number 4, right?

From these two, we derived $f_1 = y_1\ f_{\text{pure 1}}\ \exp\left[\frac{\left(a_1^{1/2} - a_2^{1/2}\right)^2 y_2^2 P}{(RT)^2}\right]$, this is what we have derived. Now the same equation of state, we will write it in a pressure explicit form, okay? So, these 2, 34, 35 and 36 these equations we got when we wrote this equation of state in a volume explicit form, but the same expression now we will write in pressure explicit form like this and then we will be using equation number 53 and 54 in order to get ϕ_1 and then $f_{\text{pure 1}}$ and then check whether are we getting these expressions or not.

If the equation of state is same and whether are you writing the equation of state is volume explicit form or pressure explicit form, you should get the same fugacity expression, right? So, these things and 34, 35 we have anyway derived now, using the pressure explicit form of same equation of state we will be doing for, what is ln, ϕ_1, $f_{\text{pure 1}}$, etc., those things we evaluate and then check. We should get same expression, otherwise we are making some mistakes either in derivation or applying the derivation here for these equations of state, okay?

So, this PV = RT $+\left(b - \frac{a}{RT}\right)$, this expression if I write pressure explicit form this is what I get. What I have done? This $\left(b - \frac{a}{RT}\right)$ P that term I have taken to the left hand side and P, I have taken common, then I have done the LCM and then rearranged it, P is one side and all other terms other side. Also, what I have done in place of molar volume v, I have written $\frac{V}{n_T}$, right? For ϕ_1, I have to find out $\frac{\partial P}{\partial n_1}$ because RT ln ϕ_1 is nothing but $\int_V^\infty \left(\frac{\partial P}{\partial n_1} - \frac{RT}{V}\right)dV$ - RT ln z. So, $\frac{\partial P}{\partial n_1}$ we have to find out.

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$$\Rightarrow P = \frac{n_T (RT)^2}{[(V - bn_T)RT + an_T]}$$

$$\frac{\partial p}{\partial n_1} = \frac{[(V-bn_T)RT + an_T](RT)^2(1) - n_T(RT)^2\left[0 - \frac{\partial}{\partial n_1}(bn_T)RT + \frac{\partial}{\partial n_1}(an_T)\right]}{[(V-bn_T)RT + an_T]^2}$$

$$\Rightarrow \frac{\partial p}{\partial n_1} = \frac{(RT)^2}{[(V-bn_T)RT + an_T]} - \frac{n_T(RT)^2\left\{\frac{\partial}{\partial n_1}(bn_T)RT + \frac{\partial}{\partial n_1}(an_T)\right\}}{[(V-bn_T)RT + an_T]^2}$$

- But $\frac{\partial}{\partial n_1}(bn_T) = \frac{\partial}{\partial n_1}(n_1 b_1 + n_2 b_2) = b_1$

- And $\frac{\partial}{\partial n_1}(an_T) = \frac{\partial}{\partial n_1}\frac{n_T(n_1^2 a_1 + 2n_1 n_2 \sqrt{a_1 a_2} + n_2^2 a_2)}{n_T^2}$

$$\frac{\partial}{\partial n_1}(an_T) = \frac{n_T(2n_1 a_1 + 2n_2\sqrt{a_1 a_2} + 0) - (n_1^2 a_1 + 2n_1 n_2\sqrt{a_1 a_2} + n_2^2 a_2)(1)}{n_T^2}$$

$$\frac{2n_1 a_1}{n_T} = 2n_1 a_1 \qquad \frac{2n_2\sqrt{a_1 a_2}\ n_T}{n_T} = 2n_2\sqrt{a_1 a_2}$$

So, this is the P in pressure explicit form, Van der Waal's equation is this one. So, this one $\frac{\partial P}{\partial n_i}$ is simply you know d of $\frac{x}{y}$ form. So, that if you do and then simplify we get here this expression for $\frac{\partial P}{\partial n_1}$, okay? So, here RT whole square is a kind of constant term that I can take constant. So, $\frac{n_T}{[(V-bn_T)RT + an_T]}$, this one I have to differentiate. So, $[(V - bn_T)RT + an_T]^2$ is as it is. Then this $[(V - bn_T)RT + an_T](RT)^2$, $\frac{\partial}{\partial n_1}(n_T)$ is nothing but 1 - n_T $(RT)^2$ and $\frac{\partial}{\partial n_1}$ (V - bn$_1$)RT + an$_T$ is nothing but $\frac{\partial}{\partial n_1}$V = 0 and then $\frac{\partial}{\partial n_1}$ b n$_T$ we do not know.

Unless we use mixing rule, we cannot find out what is b and what is a and $\frac{\partial}{\partial n_1}$a n$_T$ we are keeping as it is because this a and b are dependent on this composition. So, we have to use the mixing rule. So, now, this differentiation I am writing in 2 terms like this, okay? Then, we will be using $\frac{\partial}{\partial n_1}$b n$_T$ as we are using this b while using this pressure explicit form derivation when we do mixing rules, we have to use same one as we have used for the volume explicit form.

For the volume explicit form b we have written as sigma b$_i$ y$_i$, b$_i$ is nothing but constant b for pure component i, okay? So, like that b$_1$, b$_2$ you have to get for the pure components. Then you have to write b = b$_1$ y$_1$ + b$_2$ y$_2$ and then y$_1$ y$_2$ I am writing it as $\frac{n_1}{n_T}$ and $\frac{n_2}{n_T}$. So, b n$_T$ is nothing but b$_1$ n$_1$ + b$_2$ n$_2$. We are doing for the binary mixture because same Van der Waal's equation when we have taken as a kind of a volume explicit form we have done for binary mixture as a starting point.

So, $\frac{\partial}{\partial n_1} b \, n_T$ is nothing but $\frac{\partial}{\partial n_1}$ ($n_1 \, b_1 + n_2 \, b_2$) which is nothing but b_1 according to mixing rule that we have taken, okay? So, similarly, $\frac{\partial}{\partial n_1}$ a n_T, a we are using this, we have used a for the mixture is equal to $y_1^2 \, a_1 + 2 \, y_1 \, y_2 \, \sqrt{a_1 a_2} + y_2^2 \, a_2$ we have to use because the same mixing rule we have used when we have done the same problem using the volume explicit form. So, here also when you write $y_1 = \frac{n_1}{n_T}$ and then $y_2 = \frac{n_2}{n_T}$, then we have this expression.

So, that mixing rule for a if you use, this is what you get. So, now we are differentiating this particular thing. So, now what I can do? I can cancel out n_T and then n_T^2 and then when I differentiate denominator n_T^2 will be there n_T and then differentiation of this term is $2 \, n_1 \, a_1 + 2 \, n_2 \, \sqrt{a_1 a_2} + 0$ - this a part whatever and then differentiation of n_T with respect to n_1 is 1, okay? This part if I write it here $2 \, n_1 \, a_1 \frac{n_T}{n_T^2}$, I can write it as $\frac{2 n_1 a_1}{n_T}$. So, that is $2 \, y_1 \, a_1$ and then similarly for this term, I can write it as $\frac{2 n_2 \sqrt{a_1 a_2} n_T}{n_T^2}$. So, this n_T and then square of this one is cancelled out, so $2 \, y_2 \, \sqrt{a_1 a_2}$ I can write, right? And then this term I will be writing this is nothing but simply a, $a_1 \, y_1^2 + 2 \, y_1 \, y_2 \, \sqrt{a_1 a_2} + y_2^2 \, a_2$, this is nothing but this one. So, this is nothing but a, okay?

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So that if I do, I get $2 \, y_1 \, a_1$ first term + $2 \, y_2 \, \sqrt{a_1 a_2}$ second term and then third term - a. So, - a anyway we can write, we have to write in this form. So, next part what I am doing? I will be doing from all y_1 terms together y_2 terms together I am writing here. So, first this term and this

term, from these 2 terms $a_1 y_1$ I have taken common and then from these 2 terms, I have taken $2\sqrt{a_1 a_2}y_2$ as common, then I have this one.

In the next step, $2 - y_1$, I can write it as $1 + y_2$ because y_1 is nothing but $1 - y_2$ and then y_1, I can write $1 - y_2$, right? So, this $1 - y_1$, I can write y_2. So, in place of $\frac{\partial}{\partial n_1}a\, n_T$, you can write it as $a_1 - (\sqrt{a_1} - \sqrt{a_2})^2 . y_2^2$.

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That if you write in that particular term, so, this is what we will get, okay? This is what we have in place of $\frac{\partial P}{\partial n_i}$ by substituting whatever this particular term is nothing but $\frac{\partial}{\partial n_1} a\, n_T$ that is what we had now, okay? And this particular term is nothing but $\frac{\partial}{\partial n_1} b\, n_T$. Then further if you rearrange these terms and then integrate like this, so then you will have integration of this term is nothing but ln of the same term, then integration of $\frac{1}{V}$ is ln V.

Then integration of this term is nothing but this particular same term because all this b_1, a_1, a_1 a_2, y_2, b, etc., except this particular term, denominator term, in the numerator everything is constant, so numerator is as it is and then denominator a square term is there, so - 1 by whatever this $(V - b\, n_T) + \frac{an_T}{RT}$ that we will be getting by integrating it. So, limits V to ∞ we can substitute for all these 3 terms.

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- $\int_V^\infty \left(\frac{\partial P}{\partial n_1} - \frac{RT}{V}\right) dV = RT\ln\left[\frac{V}{(V-bn_T)+\frac{an_T}{RT}}\right] - \frac{n_T\left[-b_1RT + a_1 - (\sqrt{a_1}-\sqrt{a_2})^2 y_2^2\right]}{\left((V-bn_T)+\frac{an_T}{RT}\right)}$

$\frac{V}{n_T} = v$

- $\boxed{= RT\ln\left[\frac{vRT}{(v-b)RT+a}\right] - \frac{RT\left[-b_1RT + a_1 - (\sqrt{a_1}-\sqrt{a_2})^2 y_2^2\right]}{\left((v-b)RT+a\right)}}$

- We have $RT\ln\frac{f_1}{y_1 P} = \int_V^\infty \left(\frac{\partial p}{\partial n_1} - \frac{RT}{V}\right) dv - RT\ln(z)$

- $RT\ln\frac{f_1}{y_1 P} = RT\ln\left[\frac{vRT}{(v-b)RT+a}\right] - \frac{RT\left[-b_1RT + a_1 - (\sqrt{a_1}-\sqrt{a_2})^2 y_2^2\right]}{\left((v-b)RT+a\right)} - RT\ln\left(\frac{Pv}{RT}\right)$

$RT\ln\frac{f_1}{y_1 P} = RT\left\{\ln\left[\frac{vRT}{(v-b)RT+a} \times \frac{RT}{Pv}\right] + \frac{\left\{b_1RT - a_1 + (\sqrt{a_1}-\sqrt{a_2})^2 y_2^2\right\}}{(v-b)RT+a}\right\}$

- But from $Pv = RT + \left(b - \frac{a}{RT}\right)P \Rightarrow v = \frac{RT}{P} + b - \frac{a}{RT} \Rightarrow v - b + \frac{a}{RT} = \frac{RT}{P}$

$\Rightarrow (v-b)RT + a = \frac{(RT)^2}{P}$

When we substitute these limits, we will be having this particular form, okay? Further you can simplify by dividing the numerator and the denominator of both the terms by n_T, so that $\frac{V}{n_T}$, I can write v, molar volume, so that is what we have done here. So, then, this particular term $\int_V^\infty \left(\frac{P}{n_i} - \frac{RT}{V}\right)$ in that equation number 53. $RT\ln\frac{f_1}{y_1 P} = \int_V^\infty \left(\frac{\partial P}{\partial n_1} - \frac{RT}{V}\right) dv$ RT ln z if it is pressure explicit form, if the equation of state is pressure explicit form.

This one we just derived here. So that will be substituting here now. Then we substitute, you will get this particular term and then RT ln z as it is, ln z, I am writing $\frac{Pv}{RT}$. So, we will have this term. So first ln term and then last ln term, I combined it as this term, okay? So this (v – b) RT + a, I have written in red because from equation of state PV = RT + $\left(b - \frac{a}{RT}\right)$ P, this is the equation of state. If you rearrange this equation, then v – b + $\frac{a}{RT}$, you will be getting $\frac{RT}{P}$ that means, (v – b) RT + a is nothing but $\frac{(RT)^2}{P}$. So, wherever this red font (v – b) RT + a is there, there I can substitute $\frac{(RT)^2}{P}$.

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When I substitute this one here, $\frac{(RT)^2}{P}$ in the denominator, so then that I can write $\frac{P}{(RT)^2}$. Here also in the denominator $(RT)^2/P$, I have written. So now, what we can see? This is RT, then RT, $(RT)^2$ cancel out, Pv and then Pv cancel out. So, ln of 1 is there. So the first term is ln of 1 is 0 and then remaining term is like this. I am just writing, first I am splitting it in two terms. So, this $\frac{b_1\,RT-a_1}{(RT)^2/P}$ that one term and then remaining $(\sqrt{a_1}-\sqrt{a_2})^2\,\frac{y_2^2 P}{(RT)^2/P}$ by P that I am writing as a second term.

That means, $\ln\frac{f_1}{y_1 P} = \left(b_1 - \frac{a_1}{RT}\right)\frac{P}{RT} + (\sqrt{a_1} - \sqrt{a_2})^2\,\frac{y_2^2 P}{(RT)^2/P}$. That means $f_1 = y_1 P$ exponential of this term and then exponential of this term, and then this is if you recollect, crosscheck, it is the same expression when we have used Van der Waal's equation as a kind of volume explicit form. Now, we have crosschecked the fugacity coefficient generalized expressions are correct whether we use volume explicit form or pressure explicit form of the equation of state, they will give the same answer for any equation of state.

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$$f_{pure\,i} = P\,\exp\left\{\left(b - \frac{a}{RT}\right)\frac{P}{RT}\right\}$$

- For pure component, in pressure explicit form:

$$Pv = RT + \left(b - \frac{a}{RT}\right)P \Rightarrow \frac{pv}{RT} - 1 = \left(b - \frac{a}{RT}\right)\frac{P}{RT} \checkmark$$

$$\Rightarrow P = \frac{RT}{(v-b) + \frac{a}{RT}} \Rightarrow \frac{P}{n_i} = \frac{RT}{\left[(v-b) + \frac{a}{RT}\right]n_i} \Rightarrow \frac{P}{n_i} = \frac{RT}{(V - bn_i) + an_i/RT}$$

$$\cdot \int_V^\infty \left(\frac{P}{n_i} - \frac{RT}{V}\right)dV = \int_V^\infty \left(\frac{RT}{(V-bn_i)+an_i/RT} - \frac{RT}{V}\right)dV$$

$$= RT\ln\left[(V - bn_i) + \frac{an_i}{RT}\right]_V^\infty - RT\ln V\Big|_V^\infty$$

$$= RT\ln\left[\frac{V}{(V - bn_i) + an_i/RT}\right] = RT\ln\left[\frac{v}{(v) - b) + a/RT}\right] = RT\ln\left[\frac{vRT}{(v-b)RT + a}\right]$$

So, for a pure component i if the equation of state is available in pressure explicit form, then what is the fugacity of pure component i for the Van der Waals equation of state that we have taken. We have taken this Van der Waal's equation of state $Pv = RT + \left(b - \frac{a}{RT}\right)P$, right? So, for this equation of state we have already written as a kind of volume explicit form and then we obtained fugacity of that pure component i, right? And then we got that one answer as $f_{pure\,i} = P\,\exp\left(b - \frac{a}{RT}\right)\frac{P}{RT}$.

This is what we have already got it, but if the same equation of state if I write it as a kind of pressure explicit form and then obtain a fugacity coefficient of the pure component i, am I getting the same thing or not that is what crosschecking we have done. We have already done for a component i in a mixture, now we are taking the same concept same equation of state but pure component, so that to make sure whether the derivations or whether generalized fugacity coefficient expressions are correct, are they applicable for a given equation of state.

Whether I use volume explicit form or pressure explicit form are they giving same answer or not that is what we are verifying. So, for a component i in a mixture we have already done, so far a pure component i we are doing for the equation of state given by Van der Waal's equation. So, now we need a z - 1 somewhere in the generalized expression for fugacity of pure component i, so that z is it is nothing but $\frac{Pv}{RT}$ so that I am writing $\frac{Pv}{RT}$ - 1 from this equation is nothing but $\left(b - \frac{a}{RT}\right)\frac{P}{RT}$.

Now this equation of state what I am doing? I am doing kind of pressure the explicit form. I have written like a pressure explicit form like this and then I am dividing both sides by n_i because I need integral $\frac{P}{n_i}$ dV information so that to substitute in generalized fugacity expression, right? So then now here, v * n_i is nothing but V that is total volume and then - b n_i $+\frac{an_i}{RT}$, this is what we are getting. So we need $\int_V^\infty \left(\frac{P}{n_i} - \frac{RT}{V}\right) dV$. So $\frac{P}{n_i}$ is this term - $\frac{RT}{V}$.

Here in this equation a, b, R are the constant, okay? And temperature also we are doing all these expressions at constant temperature and composition. So, they are independent of the volume. So, when we do the integration of these things ln of this term and then ln of this term we will get, there is RT manipulation and the limits V to ∞. Now, this RT you can take common and then it is in the form of ln A - ln B, so you can write ln A by B form and then substitute limits V to ∞.

You will get RT ln $\left[\frac{V}{(V-bn_i)+an_i/RT}\right]$ and now again inside this ln term, now what I am doing? I am dividing both numerator and denominator by n_i so that $\frac{V}{n_i}$ I can write it as v that is molar volume. Then I have the same equation RT ln $\left[\frac{v}{(v-b)+a/RT}\right]$ that I can write RT ln $\left[\frac{vRT}{(v-b)RT+a}\right]$.

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This expression we can substitute here in generalized expression for fugacity coefficient of pure component i. So, in place of $\int_V^\infty \left(\frac{P}{n_i} - \frac{RT}{V}\right) dV$ whatever we got, we substitute here, z also we have found, z - 1 also we have found. So those things we substitute here, right? So, this

particular term is nothing but $\int_V^\infty \left(\frac{P}{n_i} - \frac{RT}{V}\right) dV$ just we derived and then RT ln z, z we are writing $\frac{Pv}{RT}$ and z - 1 we have seen from the equation of state is nothing but $\left(b - \frac{a}{RT}\right)\frac{P}{RT}$.

From the same equation of state we have seen this $(v - b)RT + a$ is nothing but $\frac{(RT)^2}{P}$, so that we can substitute here, okay? And then this ln A - ln B form is there ln A by B form, I can write. So, then $\frac{vRT}{(RT)^2/P} / \frac{Pv}{RT}$, so that I can write $* \frac{RT}{Pv}$. So, here $(RT)^2$, here $(RT)^2$ is cancelled out. Here v, here v cancel out and then this P, this P will be cancelled out, so that we have ln of 1 that is 0, so only term is remaining is this term.

That means $\ln \left(\frac{f_i}{P}\right)_{pure\,i} = \left(b - \frac{a}{RT}\right)\frac{P}{RT}$ or $f_{pure\,i} = P \exp\left\{\left(b - \frac{a}{RT}\right)\frac{P}{RT}\right\}$. So, now by taking pressure explicit form also, we got the pure component fugacity same as the one that we got by taking the equation of state in a volume explicit form and using corresponding generalized fugacity relation, right? So, what does it mean? Whether you take the equation of state volume explicit form or pressure explicit form, when you use the corresponding generalized fugacity relations, then you will be getting the same answer whether it is component i in a mixture or whether it is a pure component i.

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So, that is in summary if you have the equation of state in volume explicit form, then for a component i in the mixture, you can use this equation. If the component is pure component i, then you can use this equation to get the fugacity of the pure component i, but if you have the equation of state in pressure explicit form, then for a component i in the mixture you can use this equation to get the fugacity coefficient of component i in the mixture, and then if the

component is pure component i, then you can use this last expression to get the fugacity of that particular component in a pure form, okay?

So, let us say whether that is whether you use this equation or you use this equation, you get the same answer. Sometimes what happens the equations of state are such a way that you can write either in a volume explicit form or pressure explicit form, mostly most of the equations of state are available in pressure explicit form. So, it is more convenient to use this expression, right? Similarly, for pure components also whether you use this equation or you use this equation, you will be getting same as pure i expression, okay?

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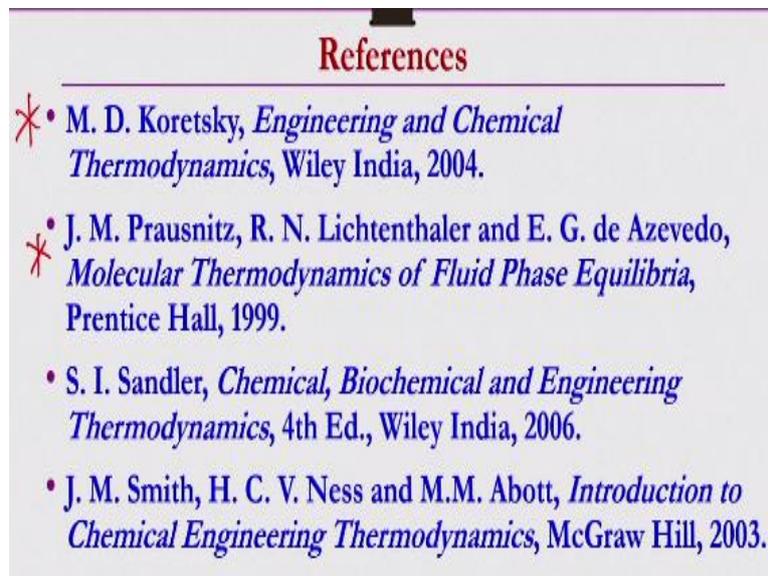
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* S. I. Sandler, *Chemical, Biochemical and Engineering Thermodynamics*, 4th Ed., Wiley India, 2006.

* J. M. Smith, H. C. V. Ness and M.M. Abott, *Introduction to Chemical Engineering Thermodynamics*, McGraw Hill, 2003.

The references for this lecture are given here. Engineering and Chemical Thermodynamics by Koretsky. Molecular Thermodynamics of Fluid Phase Equilibria by Prausnitz et al. Chemical, Biochemical and Engineering Thermodynamics by Sandler. Introduction to Chemical Engineering Thermodynamics by Smith et al. Most of the details of the today's lecture as well as the previous 2 lectures can be found from these 2 reference books.

Thank you.