Chemical Engineering Thermodynamics Professor Jayant K. Singh Department of Chemical Engineering Indian Institute of Technology, Kanpur Lecture -40 Fugacity coefficient in terms of measurable properties

Okay, welcome back. Last class we ended with the derivation of the fugacity coefficient. In fact, we defined the fugacity coefficient. The, ended the class asking simple question that how do we relate the fugacity coefficient or in general fugacity to measurable quantities?

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So, this is what we are going to do today. We will start with the basic definition that we know, which is the following that, del GI bar GP at temperature and number of moles constant is related to VI bar. So, this is something which we know and this is also del UI, by del P, okay. So, this comes directly from the definition of it. You can consider this a straight forward that, this is nothing.

But if you look at the pure component, partial derivative G with respect to P is basically V, and hence, we just extending that like by putting a bar here, which we have done in the earlier case also, and they are shown that this is feasible. Now based on the definition of the chemical potential, UI minus U is nothing but a LN FI. I can write this as, okay. And this is nothing but of course a VI bar, okay.

So now using this information, I can integrate this term here. What I can get is the following some temperature. Let us say because we are integrating with respect to pressure, then is P2 and I am putting composition here. And this is same here. So, I put it let us say 2 indicate that this is corresponds to 2 and this corresponds to 1, and this will be your integral of P1 to P2 VI DP, alright. So, this will be the integral if you take the, this, this expression. So, what we have to do is how we have to correct this thing to the fugacity coefficient.

$$
\frac{\partial \overline{G_i}}{\partial P}|_{T,\{N\}} = \overline{v_i} = \frac{\partial \mu_i}{\partial P}|_{T,\{N\}}
$$

$$
\overline{V_i} = \frac{RT\partial \ln f_i}{\partial P}|_{T,\{N\}}
$$

$$
RT \ln \frac{f_{i,2}(T, P_2, \{x\})}{f_{i,1}(T, P_1, \{x\})} = \int_{P_1}^{P_2} \overline{V_i} dP
$$

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So, consider the following case, consider that P1 approaches to 0. So, in that case, I can write it like this, TLN FI, T and I am going to right now P2 as, the P2 as a P there to make it a bit generic. So, this will be your P and the difference is FI, T, P goes to 0 and then this is X, okay. So that means this basically goes to 0. So, this, again, again make it bit generic here, where I can write like this that P1 corresponds to P goes to 0. So, the left-hand side is this and the righthand side be your 0 to P, VI, DP, right. So, this is something which I can write.

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 $P_1 = 0; P_2 = P$

$$
RT \ln \frac{f_i(T, P, \{x\})}{f_i(T, P \to 0, \{x\})} = \int_0^P \overline{V_i} dP
$$

$$
Applying \, IG: \quad RT \ln \frac{f_i^{IG}(T, P, \{x\})}{f_i^{IG}(T, P \rightarrow 0, \{x\})} = \int_0^P \overline{V_i}^{IG} dP
$$

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Subtract:
$$
RT \ln \frac{f_i(T, P, \{x\})}{f_i(T, P - 0, \{x\})} = RT \ln \frac{f_i^{IG}(T, P, \{x\})}{f_i^{IG}(T, P - 0, \{x\})} = \int_{0}^{P} (\overline{V_i} - \overline{V_i}^{IG}) dP
$$

\n
$$
= \int_{0}^{e} (\overline{V_i} - \overline{V_i}^{IG}) dP
$$
\n
$$
= \int_{0}^{e} (\overline{V_i} - \overline{V_i}^{IG}) dP
$$

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So, what about the left-hand side? So, the left-hand side can be now simplified a bit because if you take this RT common, then I can get the following in FI T, P, X, FI T, P 0 X, right, and this is a log here. So essentially the negative here, and I can write this as FI ideal gas T, P 0.

And FI ideal gas T, P, right. So, this would be also approaching towards ideal gas. Why? Because pressure is approaching towards 0 and hence all the systems will behave like an ideal gas, particularly the, the gas mixtures will behave like an ideal gas and hence this value. We can cancel it, okay, because they will behave similarly.

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$$
\frac{1}{2} \pi \sum_{i=1}^{n} \frac{1}{2} \pi \sum_{j=1}^{n} \frac{1}{2} \pi \sum_{j=1}^{n}
$$

0

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RTIM $f_c(T_1P, \frac{f_1}{f_1})$ = $RTln \varphi$ = $\begin{tabular}{|c|c|c|c|c|} \hline \multicolumn{3}{|c|}{\textbf{O} & \mathbb{R}} & \mathbb{R} \\ \hline \multicolumn{3}{|c|}{\textbf{O} & \mathbb{R}} & \mathbb{R} \\ \hline \multicolumn{3}{|c|}{\textbf{O} & \mathbb{R}} & \mathbb{R} \\ \hline \multicolumn{3}{|c|}{\textbf{O} & \mathbb{R}} & \mathbb{R} & \mathbb{R} \\ \hline \multicolumn{3}{|c|}{\textbf{O} & \mathbb{R}} & \mathbb{R} & \mathbb{R} \\ \hline \multicolumn{$ \times Ξ = $\frac{1}{2}$ = $\frac{1}{2}$ $0₀$ BWA $2 + 2$

So at this point, I am just considering this, X is just a composition, which by the way, I have used earlier, mostly Y, right. So we can replace this by saying it to be Y here. So we will just try to replace it, okay. So we will just try to replace this to avoid confusion. So basically it means that we are going to consider, just Y as a symbol for the gas phase. So that's what I am trying to now correct it here.

So this should have been the written here Y, just to be consistent with the rest of the, our, right up, okay. Okay, so you have this, expression now finally, which is that the RT LN ratio of this fugacity of the, a component in the gas mixture with respect to that of the ideal gas. And that is equal to 0 to P VI minus VI ideal gas, which is nothing but 0 to P VI minus RT by P DP, right? So now I can write this because we know that for fugacity of component in ideal gas mixture is nothing but the proportional to the pressure or it is partial pressure in the sense.

So FI IG is nothing but partial pressure. So I can write like YI and P. So therefore, I can write down this expression is RT LN FI by YIP. This is RT LN by definition, this is nothing but FI, right. This is nothing but FI and this equal to 0 to P VI bar minus RT by P DP, okay.

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So this is useful when, when you have explicit information. So useful for explicit information of the volume as a function of P and, and T, right. But not useful, for not, for pressure-based equation simplicity. So, this equation is, will be used easily for the case of when you have the information like this.

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$$
\frac{\frac{1}{2} \pi \frac{1}{2} \pi \frac
$$

But if it is equational state, which is the pressure explicit, then it will not be useful, then we have to find a different way. Okay, so I can also simplify this expression in terms of a compressibility factor. So I can write this as LN Phi I, okay and 0 to P VI P divided by RT minus 1, DP by P like this also I can write it out, okay.

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For the case of a pure fluid, for pure fluid, this would be LN Phi is equal to 0 to P, Z minus 1 DP by P, right. So this would, this would be the case for the pure fluid. So I can write this expression in terms of ZI also. So I can write like this as a ZI minus one DP by P. One can also write this expression in terms of the reduced expression.

So it could be written as like say L Phi is PR some ideal to PR ZI minus 1, DPR by PR. So one can also write in this form of reduced expression or reduced variable.

$$
\ln \phi = \int_0^P \frac{(z-1)dP}{P}
$$

$$
Reduced\ variable: \ln \phi_i = \int_{P_{Y_{ideal}}}^{P_Y} \frac{[z_i - 1]dP_Y}{P_Y}
$$

Now just the way we have tried to use as a compressibility factor, using some kind of a chart which was based on some equational state, typically leak as slur equational state. We can also use the similar kind of concert for getting fugacity coefficient. So, so we can use some chart for obtaining the fugacity coefficient, okay. And though it is not very popular, but still one can obtain it if the charts are given to you, okay. So, let us assume that if we use equational state based on Lee Kesler, okay and integrate the right-hand side.

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fogauly conflictions $+$ f_{σ} $Chart$ Coode -1 & integral $Lec - Keslet$ EOS ₽ we use $R.H.S$ $Log \theta$ Carrietion term. $log \varphi$ $log \varphi_c = log \varphi^{(0)} + \omega log \varphi^{(1)}$ $T_{r, R} \rightarrow \varphi^{(0)}$, $\ell \varphi^{(4)}$ \bullet 8 $\frac{1}{10}$ b **ORDOOMA MP B at 4** SASPM

So, depending on the equation of state, you can get two kind of a log form, one is a log Phi 0 and the other one is log Phi of 1, which is nothing but the correction term. As we have done for Z, okay, where the Z1 was the one which took care of a non-spherical nature of the molecule. Similarly, here, Phi 1 also corresponds to those kinds of a correction term, okay.

So in that case, if you are able to obtain this thing from the chart given to you in terms of PR and same for the case of 0 and 1 that means the one without, with series, simple systems and for the one which has a non-spherical and other kind of Charles system, then you should be able to find out log of Phi I as simple addition of 0 plus the eccentric factor multiplied by Phi of 1, okay. The process remains the same as we have done earlier. So, you obtain TR, PR and from there you obtain Phi 0 and Phi 1, okay.

$$
\log \phi_i = \log \phi^0 + \omega \log \phi^1
$$

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<u>PERSONAL BRANCH</u> **Continued State** $RT\ln \rho_i = \int_{0}^{P} (\bar{v}_{u} - \bar{v}_{u}^{IG}) d\rho$
 $P = \frac{ZRT}{V} = \frac{ZRT}{V}$ $dp = \frac{RT}{V} dz = \frac{2RT}{V} dy$
 $RThq_i = \int_0^P \sqrt{v} dy = \int \frac{RT}{P} dz$ $= \int^p \overline{v} \, d\varphi = \int \frac{RT}{p} \left[\frac{RT}{2} \, dz - \frac{2\pi r}{2} \, dz \right]$ OORD
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So that is something which there in the text book which we have using for this particular course. Now the question is that if, if the information for us is not given in explicit form of volume as it is written here, then this particular expression which we have derived is not of use. So, what you do in case of an equation of state, in pressure explicit. So, we need to come up with a better way to do that and let us try to derive it, okay.

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$$
\frac{1}{2} \pi r^2 \sin \frac{2\pi x}{3}
$$
\n
$$
\frac{d\rho}{d\theta} = \frac{RT}{\frac{V}{L}} \frac{dz}{d\theta} = \frac{2RT}{\frac{V^2}{L}} \frac{d\theta}{d\theta}
$$
\n
$$
R^2 \ln \rho_{\theta} = \int \frac{RT}{\sqrt{L}} \frac{dz}{d\theta} = \int \frac{RT}{\theta} \left(\frac{RT}{\sqrt{L}} \frac{dz}{d\theta} - \frac{2RT}{\frac{V^2}{L}} \frac{dz}{d\theta} \right)
$$
\n
$$
= \int \sqrt{r_0} dr = \int \frac{RT}{2} \left(\frac{RT}{\sqrt{L}} \frac{dz}{d\theta} - \frac{2RT}{\frac{V^2}{L}} \frac{dz}{d\theta} \right)
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= \int \sqrt{r_0} dr = \int \frac{RT}{2} \frac{dz}{d\theta} + RT \int \frac{dx}{d\theta} \frac{dx}{d\theta}
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= \int \sqrt{r_0} dr = \int \frac{RT}{2} \frac{dz}{d\theta} + RT \int \frac{dx}{d\theta}
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= \int \frac{dx}{d\theta} \frac{dx}{d\theta} + RT \int \frac{dx}{d\theta} = \int \frac{dx}{d\theta} \frac{dx}{d\theta}
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= \int \frac{RT}{2} \frac{dx}{d\theta} + RT \int \frac{dx}{d\theta} = \int \frac{RT}{2} \frac{dx}{d\theta} =
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$$
RT \ln \phi_i = \int_0^P \left(\overline{V}_i - \overline{V}_i^{IG} \right) dP
$$

$$
P = \frac{ZRT}{v}
$$

\n
$$
dP = \frac{RT}{V} dZ - \frac{ZRT}{V^2} d\underline{V}
$$

\n
$$
RT\ln \phi_i = \int_0^P \overline{V}_i dP - \int \frac{RT}{P} dP = \int_0^P \overline{V}_i dP - \int \frac{RT}{P} \left[\frac{RT}{V} dZ - \frac{ZRT}{V^2} d\underline{V} \right]
$$

\n
$$
RT\ln \phi_i = \int_0^P \overline{V}_i dP - \int_1^Z \frac{RT}{Z} dZ + RT \int_\infty^{\frac{V}{L}} \frac{dV}{V}
$$

You can, you can expand this and then you will get, the same expressions, 0 to P VI bar DP minus, minus RT and this is going to PV by RT is nothing but Z. So either Z will come here and this will be Z. So if you multiply this by that, that is going to be plus, because there is a minus here, so plus RT we can say this is 1 by P that comes out here multiplied by ZRT by V DV, okay.

So this is how we are going to get this expression, okay. So now look at it carefully. So what we have is, this term ZRT by V is nothing but P, okay. So this one, that gets cancelled with this, right. So I have now expression of 0 to P VI bar DP minus RT by Z DZ. Since pressure is from 0 to P, Z is going to be some 1 to Z. And what about the volume? Volume here is going to be from infinity to some V bar, okay. So this is the expression which we got if you expand the, the term here.

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Now we need to further simplify this, okay. So, one of the things which we need to do is to, because here, for example, this, if you look at it, this can be written as simply RT, LN Z, right. If you have an expression, okay, someone, something like in DV. So, so how do you get that? Okay, so when we look at this, then we realize also that well VI is nothing but a del V by del NI, T, P NJ not equal to I, right.

Now if you consider a cyclic relation between a del V by del NI, DP del P by del V T and del NI by del P, that, V. This must be minus 1, right. So here, this is something which, because we are keeping the NI is constant in this case only the pressure and the volumes are changing. So if NI is a constant, if temperature is constant, then essentially this can be written as DP by DV, okay. If that is a case, then I can write this as del V by del, del NI, okay, and DP is nothing but minus del P by del NI, DV. So, now I got expression of VI. This is nothing but VI. So VI DP is nothing but minus of this term, okay.

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$$
\overline{V}_{i} = \frac{\partial v}{\partial N_{i}}|_{T,P,N_{j\neq i}} \quad \left(\frac{\partial v}{\partial N_{i}}\right)_{T,P} \left(\frac{\partial P}{\partial v}\right)_{T,\{N_{i}\}} \left(\frac{\partial N_{i}}{\partial P}\right)_{T,v} = -1
$$
\n
$$
\left(\frac{\partial v}{\partial \mu_{i}}\right) dP = -\left(\frac{\partial P}{\partial N_{i}}\right) dv
$$
\n
$$
RT \ln \phi_{i} = -\int \left(\frac{\partial P}{\partial N_{i}}\right)_{dv} - RT \ln Z + RT \int \frac{dV}{V}
$$
\n
$$
RT \ln \phi_{i} = \int_{\infty}^{V} \left[\frac{RT}{V} - \left(\frac{\partial P}{\partial N_{i}}\right)_{T,P,N_{j\neq i}}\right] dV - RT \ln Z
$$

So that is now the final expression which we got and which can be used when you have pressure based. Equational state of pressure explicit equation of state, okay. So, let us consider a simple application.

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So, if you are asked to find out the, let us say, fugacity of a mixture, which can be represented by a wonder wall equational states, and how do you do that now? So let us now first, you know, use this expression to, to come up with an expression for a fugacity for wonder wall equational state mixture. So this is the simple application. Consider, consider this vander wall, equational state for a mixture, okay.

Consider *vdw EOS*:
$$
P = \frac{RT}{\underline{V} - b_{mix}} - \frac{a_{mix}}{\underline{V}^2}
$$

$$
a_{mix} = \sum \sum a_{ij} x_i x_j \quad a_{ii} = a_i
$$

$$
a_{ij} = a_{ji} = \sqrt{a_i a_j} (1 - k_{ij})
$$

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$$
b_{mix} = \sum_{i=1}^{n} x_i b_i
$$

$$
P = \frac{RT}{\underline{V} - \sum x_i b_i} - \frac{\sum \sum a_{ij} x_i x_j}{\underline{V}^2}
$$

$$
P=\frac{RTN}{V-\sum N_ib_i}-\frac{\sum \sum a_{ij}N_iN_j}{V^2}=\frac{RT}{V-\sum N_kb_k}+\frac{RTNb_i}{(V-\sum N_kb_k)^2}-\frac{2\sum a_{ik}N_k}{V^2}
$$

So that is my equational state, okay. I can also convert this thing into number of moles.

And why do I need that? Because if you look at it, this is one of the constraints. If you want to find out the, because this is pressure explicitly equational state. So you need to find out the partial derivative with the pressure, with respect to NI. And for that you need these expressions in terms of NI, so this is your RT. I can now write like this and here then the total number of moles will come into the picture.

And of course, this will go and now instead of XI, I will have minus summation NI BI, okay. And this is going to be, by the way, this is must be double summation. So this will be a double summation AIJ NI NJ V square, right. So if you take the derivative of del P by del NI of this, okay, some, so one can come up with an expression here.

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------- $b_{\text{max}} = \sum_{k=1}^{n} x_{k} b_{k}$ -55 $\frac{RTN}{\sqrt{-2N_{i}b_{i}}}\$ \mathcal{D} $\frac{RT}{V - \sum_{k} N_{k} b_{k}} + \frac{RT N b_{k}}{(V - Z N_{k} b_{k})}$ **OROOCWE** $-20 - 0 = 0$

So if you take a, take a with respect to NI the value may will be RT, V minus summation and some NK, BK plus RTN BI, V minus summation NK Bk square minus 2 summation AIK, NK V square. So I am not going to discuss drive completely, but you are going to get this kind of expressions. And now this expression has to be put it in here in order to obtain the RT LN Phi of corresponding to the vander wall equational state.

And that's how you are going to write it completely these expressions, okay. So that becomes a little cumbersome, but this is how you are going to get if you put all this details, to obtain the fugacity coefficient, okay. Okay, so I think at this point, this is what we wanted to cover to explain how to obtain fugacity relations with the volume, with the, with the thermodynamic properties. And I hope that, this illustration helped you or at least clarifies that, the expressions are going to be different when it is volume explicit, information when it is there or when it is pressure explicit information and does need to be aware of, the problem statement.

And based on that one would be taking the right kind of expressions, to obtain the, the fugacity coefficients. In the next class, we will take it further to try to understand the fugacity. The approximations related to the, I know, gas phase and subsequently will take up the ideal mixtures the, for that before the liquid phase, okay. So, with that, I will close today's class and we will see you next time.