Chemical Engineering Thermodynamics
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Lecture - 26
Fugacity

So far we looked at calculation of Fugacity and fugacity coefficient using virial equation of state. We have also used Licastro tables to calculate these quantities, but they have a limited range of pressures over which they can be applied as you know; how do we calculate fugacity and fugacity coefficient at other conditions how do we do that for liquids. To answer that question we can go back and revisit our discussion on cubic equation of state.

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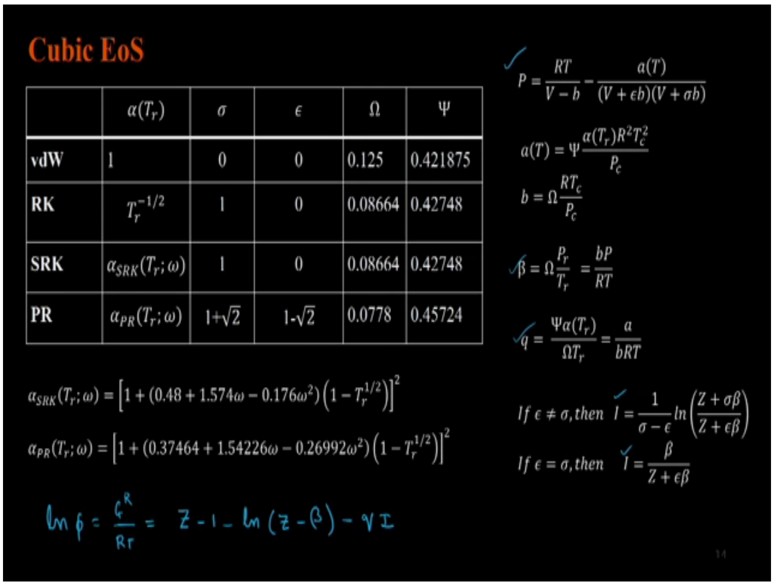

Cubic EoS

	$\alpha(T_r)$	σ	ϵ	Ω	Ψ
vdW	1	0	0	0.125	0.421875
RK	$T_r^{-1/2}$	1	0	0.08664	0.42748
SRK	$\alpha_{SRK}(T_r;\omega)$	1	0	0.08664	0.42748
PR	$\alpha_{PR}(T_r;\omega)$	$1+\sqrt{2}$	$1-\sqrt{2}$	0.0778	0.45724

$$\alpha_{SRK}(T_r;\omega) = \left[1 + (0.48 + 1.574\omega - 0.176\omega^2)\left(1 - T_r^{1/2}\right)\right]^2$$

$$\alpha_{PR}(T_r;\omega) = \left[1 + (0.37464 + 1.54226\omega - 0.26992\omega^2)\left(1 - T_r^{1/2}\right)\right]^2$$

$$\ln\phi = \frac{G^R}{RT} = Z - 1 - \ln(Z - \beta) - qI$$

$$P = \frac{RT}{V-b} - \frac{a(T)}{(V+\epsilon b)(V+\sigma b)}$$

$$a(T) = \Psi\frac{\alpha(T_r)R^2T_c^2}{P_c}$$

$$b = \Omega\frac{RT_c}{P_c}$$

$$\beta = \Omega\frac{P_r}{T_r} = \frac{bP}{RT}$$

$$q = \frac{\Psi\alpha(T_r)}{\Omega T_r} = \frac{a}{bRT}$$

$$If\ \epsilon \neq \sigma, then\ I = \frac{1}{\sigma - \epsilon}\ln\left(\frac{Z+\sigma\beta}{Z+\epsilon\beta}\right)$$

$$If\ \epsilon = \sigma, then\ I = \frac{\beta}{Z+\epsilon\beta}$$

And if you recall for a variety of cubic equations we have a general expression that we have used right. The general cubic equation of state is given by the expression I have in here. P is RT by V minus b minus a by a quadratic in V. The parameters for the equation of state a in some cases we will depend on temperature in some cases they may not as in case of van der Waals equation or Redlich Kwong equation they will not depend on temperature part. In general it is a function of temperature, b is only dependent on the critical properties and from that we calculate a host of parameters based on these 2 parameters a and b.

And we can use cubic equation of state as we have seen in our earlier discussion to calculate the molar volume or the compressibility factor Z. We have also used it to calculate the residual properties such as residual enthalpy, residual entropy and residual Gibbs free energy we have developed expressions for those. What we will do is use those expressions and also try to calculate fugacity and fugacity coefficient.

If you recall we said that the fugacity coefficient ln phi for pure species is G R by RT and this equals for a cubic equation of state Z minus 1 minus ln of Z minus beta minus q times I and Z is the compressibility factor at the condition we are looking at beta q and I are given in the expressions here beta q and I depending on whether we have the same value for epsilon and sigma or different values for them. So, once I know a cubic equation of state and given a temperature and pressure I can calculate the compressibility factor and all the other parameters that are listed in here and use those to calculate the fugacity or the fugacity coefficient.

Let us try to demonstrate this calculation using an example, but before we do that I should emphasize that this is a cubic equation of state which means at certain conditions it may have 3 real roots corresponding to the vapour like root, the liquid like root and the metastable state and in that case we have 3 values for compressibility factor Z. So, which 1 do I use for calculating the fugacity coefficient? The answer lies in the fact that what fugacity coefficient am I trying to calculate. If I am trying to calculate fugacity coefficient on the for the liquid then I will use the liquid like root, if I am trying to calculate fugacity coefficient for the vapour then I will use the vapour like root; having said that lets try to demonstrate this calculation in one example.

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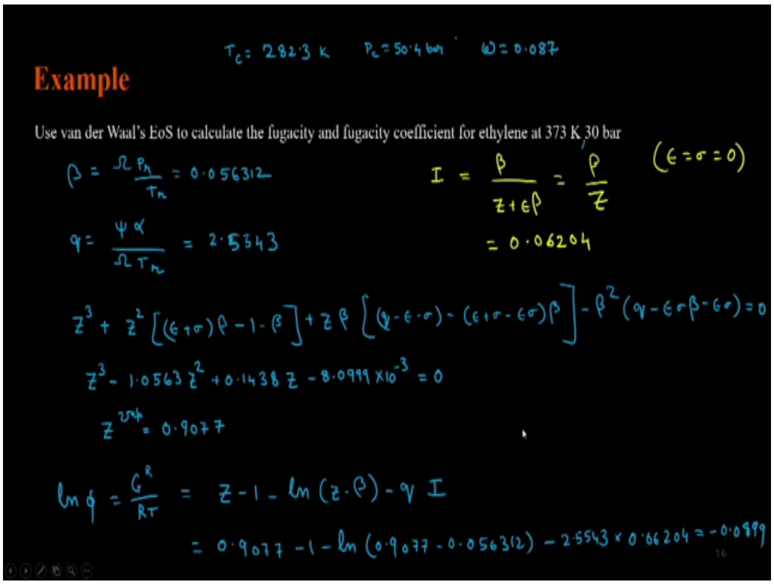

$T_c = 282.3$ K $\quad P_c = 50.4$ bar $\quad \omega = 0.087$

Example

Use van der Waal's EoS to calculate the fugacity and fugacity coefficient for ethylene at 373 K, 30 bar

$$\beta = \frac{\Omega P_r}{T_r} = 0.056312$$

$$q = \frac{\psi \alpha}{\Omega T_r} = 2.5343$$

$$I = \frac{\beta}{Z + \epsilon\beta} = \frac{\beta}{Z} \qquad (\epsilon = \sigma = 0)$$

$$= 0.06204$$

$$Z^3 + Z^2\left[(\epsilon+\sigma)\beta - 1 - \beta\right] + Z\beta\left[(q - \epsilon - \sigma) - (\epsilon + \sigma - \epsilon\sigma)\beta\right] - \beta^2(q - \epsilon\sigma\beta - \epsilon\sigma) = 0$$

$$Z^3 - 1.0563Z^2 + 0.1438Z - 8.0999 \times 10^{-3} = 0$$

$$Z^{vap} = 0.9077$$

$$\ln\phi = \frac{G^R}{RT} = Z - 1 - \ln(Z - \beta) - qI$$

$$= 0.9077 - 1 - \ln(0.9077 - 0.056312) - 2.5543 \times 0.06204 = -0.0899$$

So, in this problem we are interested in calculating fugacity and fugacity coefficient for ethylene at 373 Kelvin in 30 bar using van der Waals equation of state. To be able to use the equation of state the first thing we need are the critical conditions critical constants T c and P c. For ethylene if you recall T c was 282.3 Kelvin, P c was 50.4 bar and omega is 0.087. At the given conditions I can use the equation of state parameters listed in here and calculate beta and q, turns out for this condition beta is going to be omega P r over T r and this value turns out to be 0.056312; q is psi alpha by omega T r and for this particular case the value turns out to be 2.5543. Remember alpha for van der Waals equation of state is 1.

Now, once I have beta and q the next thing we want to do is calculate the compressibility factor at the given conditions. And to calculate the compressibility factor if you recall what we did was to solve the cubic in Z right and the cubic in Z had this form. This is a lengthy expression we can actually get rid of epsilon and betas, epsilons and sigmas for van der Waals equation of state and the equation actually looks much simpler than this once we do that, but I am writing it for sake of generality.

Once we do that this is the cubic in Z we want to a solve. We can simplify this and substitute the values of beta q epsilon and sigma. For van der Waals equation of state both epsilon and sigmas are 0 if you recall from the table and once we do that we get the coefficients for this cube polynomial and it turns out to be Z cube plus rather in this case minus 1.0563Z square plus 0.1438 Z minus 8.099 10 power negative 3; this equals 0.

This is the cubic in Z we get for the equation of state. We can solve this cubic to obtain the 3 roots and in this particular case it turns out that only 1 root is real and that real root of course, corresponds to the vapour like volume because its much closer to 1 and that value turns out to be 0.90774 Z, the compressibility factor. Once I have that value I can go back and calculate G R by RT or ln phi which is Z minus 1 minus ln Z minus beta minus q times I.

So, I have beta I have q I have Z what I do not have is I and for van der Waals equation of state epsilon is sigma. So, I is beta by Z plus epsilon beta right which is essentially beta by Z since epsilon equals sigma equals 0 for van der Waals equation of state. So, this value once I have Z I can calculate this value and this value turns out to be 0.06204 that is the value of I. Once I have I can put everything back in this expression for ln phi.

So, it will be 0.9077 minus 1 minus ln of 0.9077 minus 0.056312 minus 2.5543 times 0.06204 and this equals ln phi which is negative 0.0899. This is the value of ln phi we will get by simplifying the numericals and once we have ln phi I can calculate phi.

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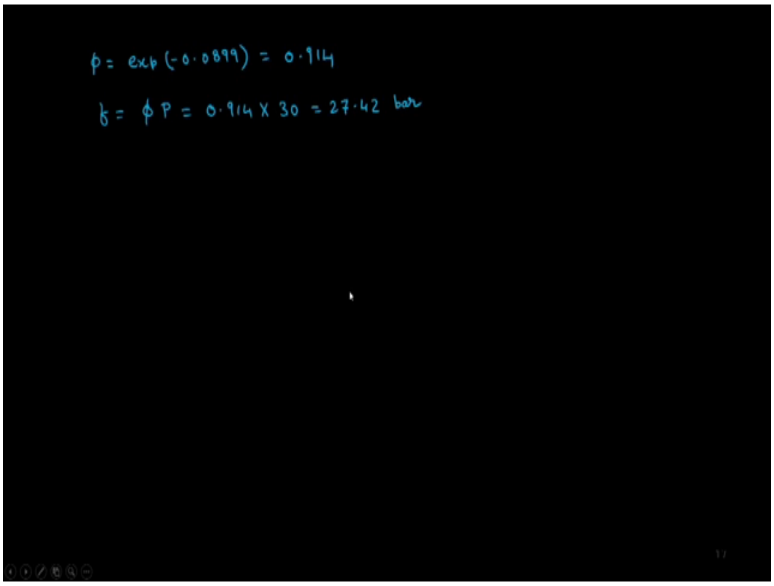

$\phi = \exp(-0.0899) = 0.914$

$f = \phi P = 0.914 \times 30 = 27.42$ bar

It will be exponential of negative 0.0899 that is the value of ln phi this is 0.914 and once I have phi I can calculate the fugacity f it will be 0.914 times 30 bar which is 27.42 bar.

So, I can use a cubic equation of state and calculate fugacity. We almost follow exact same procedure as we did for calculation of the residual properties in particular residual Gibbs free energy and then from there we can calculate the fugacity. So, that demonstrates the use of cubic equation of state for calculation of fugacity.

Now, what we have done so far is looked at using a variety of PVT equations to calculate the fugacity and fugacity coefficient of pure species. In fact, the last approach we have used for cubic equation of state can also calculate the fugacity of pure liquid if I use the liquid like volume or liquid like compressibility factor from the cubic equation of state solution if that exists at the given condition of course. Next what will try to do is try to extend our discussion to fugacity of species in the mixture.

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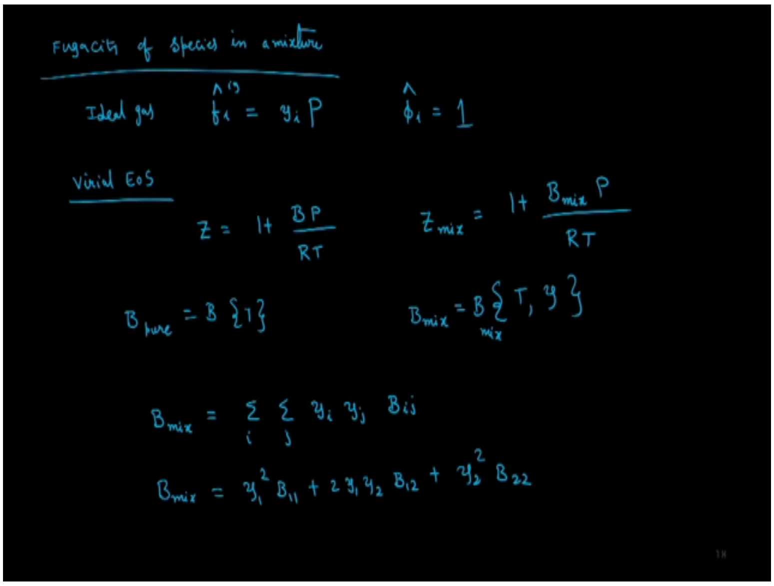

Fugacity of species in a mixture

Ideal gas $\hat{f}_i^{ig} = y_i P$ $\hat{\phi}_i = 1$

Virial EoS

$Z = 1 + \frac{BP}{RT}$ $Z_{mix} = 1 + \frac{B_{mix} P}{RT}$

$B_{pure} = B\{T\}$ $B_{mix} = B_{mix}\{T, y\}$

$B_{mix} = \sum_i \sum_j y_i y_j B_{ij}$

$B_{mix} = y_1^2 B_{11} + 2 y_1 y_2 B_{12} + y_2^2 B_{22}$

For an ideal gas mixture of course, recall that f i hat will be equal to the partial pressures. So, it will be y i times P because phi i hat for an ideal gas mixture needs to be equal to 1.

Next easiest equation of state we can use is a virial equation of state. The first thing we need to answer is how does or how we can write? Virial equation of state for a mixture a virial equation of state using only the second virial coefficient is written as Z is 1 plus BP over RT this was for a pure species. I can write an analogue as equation for a mixture. The compressibility factor for the mixture is going to be B for the mixture P over RT. Recall that the second virial coefficient in case of a pure species is only a function of temperature.

B pure is only a function of temperature. In case of a mixture obviously, it will be a function of temperature as well as the mole fraction because its gas let us call it as y. So, it will be a function of both the temperature and mole fraction one can actually derive an expression for B mixture from statistical mechanics and it turns out that B for the mixture is given by this expression here. In a multi component mixture it is sigma over i sigma over j y i y j B i j.

Now if I expand these summations for a binary mixture it turns out to be B mix is y 1 squared B11 plus 2 y 1 y 2 B12 plus y 2 squared B22. Now, if you notice the expression for b mixture contains 3 virial coefficients in addition to the mole fractions.

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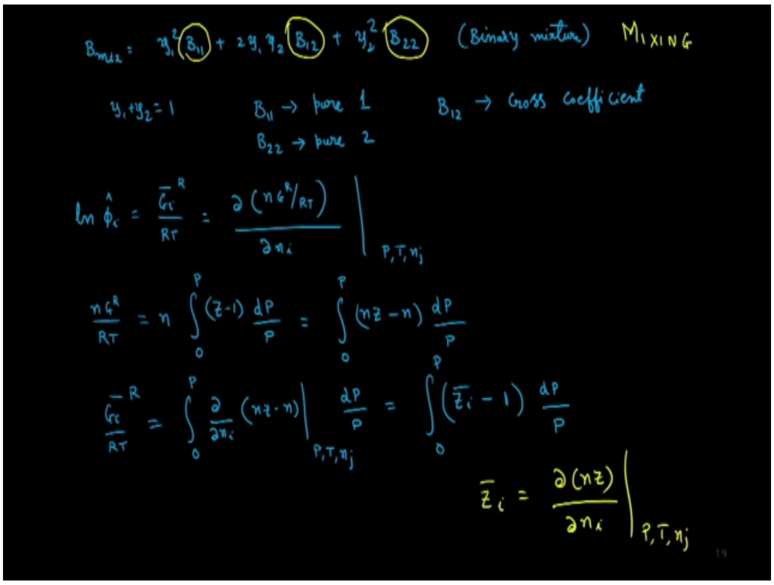

$$B_{mix} = y_1^2 \boxed{B_{11}} + 2 y_1 y_2 \boxed{B_{12}} + y_2^2 \boxed{B_{22}}$$ (Binary mixture) MIXING

$y_1 + y_2 = 1$

$B_{11} \rightarrow$ pure 1

$B_{22} \rightarrow$ pure 2

$B_{12} \rightarrow$ Cross coefficient

$$\ln \hat{\phi}_i = \frac{\bar{G}_i^R}{RT} = \left.\frac{\partial (n G^R/RT)}{\partial n_i}\right|_{P,T,n_j}$$

$$\frac{n G^R}{RT} = n \int_0^P (Z-1) \frac{dP}{P} = \int_0^P (nZ - n) \frac{dP}{P}$$

$$\frac{\bar{G}_i^R}{RT} = \int_0^P \left.\frac{\partial}{\partial n_i} (nZ - n)\right|_{P,T,n_j} \frac{dP}{P} = \int_0^P (\bar{Z}_i - 1) \frac{dP}{P}$$

$$\bar{Z}_i = \left.\frac{\partial (nZ)}{\partial n_i}\right|_{P,T,n_j}$$

Lets rewrite that equation again B mix is y 1 squared B 1 1 plus 2 y 1 y 2 2 B 12 plus y 2 squared B 2 2; this is a binary mixture. In a binary mixture; obviously, y 1 plus y 2 is 1 and given a mole fraction we can calculate the other one. The other thing that appears in this expression is virial coefficients three of them; B 11, B 22 and B 12. B 11 and B 22 are the pure virial or the virial coefficients for the pure species 1 and 2 respectively. B 12 is what is called as a cross coefficient for a mixture of 1 and 2. We will come back and see how one can calculate B 1 2, but for now, it suffices to say it is also a virial coefficient that depends only on temperature.

The composition dependency for the mixture is given by the expression we have on the top, we call this as a mixing rule because we are writing a property for a mixture we call this as a mixing rule. This is how we mix the virial coefficients to obtain virial coefficient for the mixture. This mixing rule contains 3 virial coefficients B 11 for pure 1, B 2 2 for pure 2 and B 12 which is the cross virial coefficient.

All the three of them are functions only of temperature. When we try to solve a problem will come back and talk about how one can get B 1 2, but for now we will carry this discussion forward and see how we can actually calculate fugacity coefficient and fugacity of species in a mixture given these 3 virial coefficients B 1, B 2 2 and B 1 2. To do that what we have to do is go back to the definition of fugacity coefficient. Remember that ln phi i hat is G i bar R over RT. So, this is the derivative of n G R by RT with respect to n i at P T and n j right.

Now, n G R by RT by itself is n times G R by RT if you recall is integral 0 to P Z minus 1 d P by P. So, derivative of this with respect to n i is what we are interested in. Let us take an inside. It will be n Z minus n d P by p. So, G i bar R by RT then will be derivative of this with respect to n i. So, we can take the derivative into the integral. It will be derivative with respect to n i of n Z minus n at P T and n j d P over P and that will be integral 0 to P derivative of n Z over n i we can call it as partial molar compressibility factor for i Z i bar minus derivative of n with respect to n i if you recall is 1 d P.

Now, what I am interested in is then finding Z i bar or the derivative of n Z with respect to n i; derivative of n Z with respect to n i at P T and n j. To do that lets write use an equation of state. In this case we are interested in using virial equation of state.

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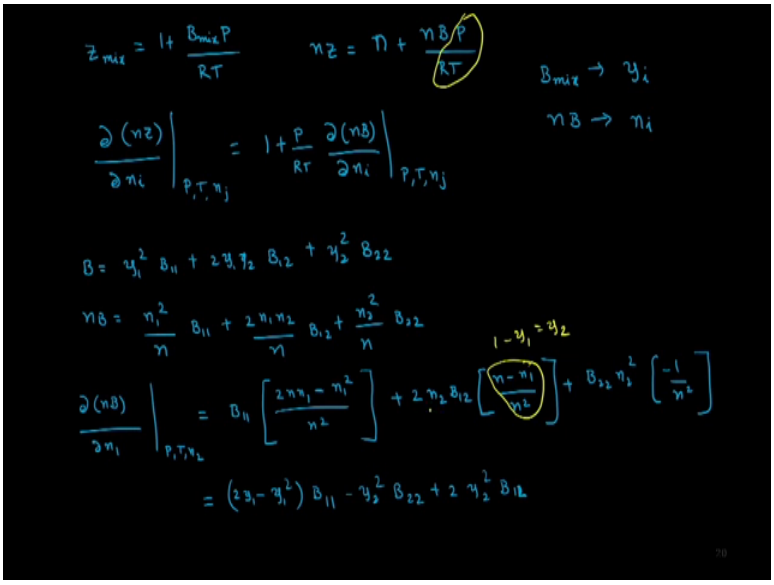

$$Z_{mix} = 1 + \frac{B_{mix}P}{RT} \qquad nZ = n + \frac{nBP}{RT}$$

$$B_{mix} \to y_i$$

$$nB \to n_i$$

$$\left.\frac{\partial(nZ)}{\partial n_i}\right|_{P,T,n_j} = 1 + \frac{P}{RT}\left.\frac{\partial(nB)}{\partial n_i}\right|_{P,T,n_j}$$

$$B = y_1^2 B_{11} + 2y_1y_2B_{12} + y_2^2B_{22}$$

$$nB = \frac{n_1^2}{n}B_{11} + \frac{2n_1n_2}{n}B_{12} + \frac{n_2^2}{n}B_{22}$$

$$1 - y_1 = y_2$$

$$\left.\frac{\partial(nB)}{\partial n_1}\right|_{P,T,n_2} = B_{11}\left[\frac{2nn_1 - n_1^2}{n^2}\right] + 2n_2B_{12}\left[\frac{n-n_1}{n^2}\right] + B_{22}n_2^2\left[\frac{-1}{n^2}\right]$$

$$= (2y_1 - y_1^2)B_{11} - y_2^2B_{22} + 2y_2^2B_{12}$$

If you recall for virial equation of state Z makes is 1 plus B max over RT times P right and n times Z and just omitting the subscript. Mixture of course we are talking about a mixture is simply n plus n plus n times B may B P over RT and the derivative of this quantity with respect to n i at P T and n j is going to be 1 plus the temperature and pressure are constant. So, I can take those out of the derivative which means I can get P by RT out of that derivative. So, what I will have left is P over RT derivative of n B with respect to n i and P T and n j. Recall that B for the mixture is a function of y i

So, n B will be a function of n i. So, that is why I did not take be out of that derivative although the temperature is constant for a mixture B itself is going to be a function of the mole fraction or n B will be a function of n i. So, then what I am looking at is trying to obtain a derivative of n B with respect to n i and P T at P T and n j. Once I do that I can easily get the fugacity coefficient for species i.

So, what we will do is consider a binary mixture to demonstrate how we do this and then we can generalize the result we obtain. For a binary mixture we said B is y 1 squared B 11 plus 2 y 1 y 2 B 12 plus y 2 squared B 2 2; n times B is going to be n 1 squared over n times B 1 1 plus 2 n 1 n 2. When we take the derivative with respect to n i right, remember that we want to convert all the mole fractions in to number of moles n 1’s n 2’s and ns right. We cannot leave mole fractions in there because we are taking derivative with respect to n 1 or n 2.

So, what I did is converted y 1 squared by n squared and multiplied it with n. So, that what I will have left is n 1 square over n B 1 one plus 2 n 1 n 2 over n B 12 plus n 2 squared over n B 2 2.

So, now I have converted everything in terms of moles there is no mole fraction left on the right hand side. Now I need to take a derivative with respect to let us say n 1, then derivative of n B with respect to n 1 because there are only 2 components what I am holding constant is n 2 T and P of course, this value will be I am holding n 2 constant. So, this value will be B 1 1 times 2 n n 1 minus derivative of n with respect to n 1 is 1.

So, it is n 1 squared over n squared plus 2 times n 2 is constant B 12 is constant what I have left inside to take the derivative is n 1 over m derivative of n 1 over n with respect to n 1 will be n minus n 1 over n square plus finally, what I have is B 2 2 n 2 squared and derivative of 1 over n with respect to n 1 will be negative 1 over n squared. I can simplify this and if you see I can rewrite all the ns and n 1's in terms of the mole fraction y 1 back. So, what I get finally, is going to be 2 y 1 minus y 1 squared B 11 minus y 2 squared B 2 2 plus 2 y 2 squared B 1 2. Notice that this will be 1 minus y 1 which is y 2 this y 2 multiplied with sorry this will be 1 minus y 1 by n.

So, I can obtain the derivative of n B with respect to n 1. This can be further simplified to put it in a general form. It turns out that this value of derivative of n B with respect to n 1 at P T and n 2 can be written as B 11 plus y 2 square delta 12.

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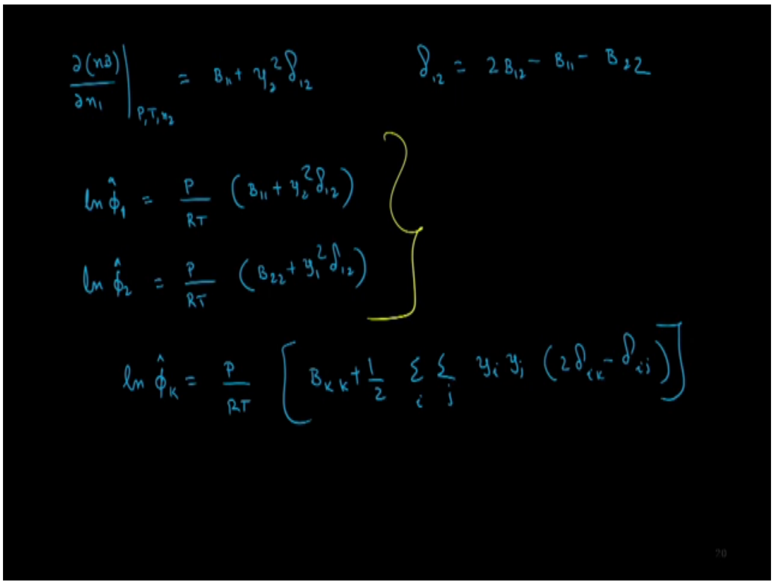

$$\left.\frac{\partial(nB)}{\partial n_1}\right|_{P,T,n_2} = B_{11} + y_2^2\delta_{12} \qquad \delta_{12} = 2B_{12} - B_{11} - B_{22}$$

$$\left.\begin{aligned} \ln\hat{\phi}_1 &= \frac{P}{RT}\left(B_{11} + y_2^2\delta_{12}\right) \\ \ln\hat{\phi}_2 &= \frac{P}{RT}\left(B_{22} + y_1^2\delta_{12}\right) \end{aligned}\right\}$$

$$\ln\hat{\phi}_k = \frac{P}{RT}\left[B_{kk} + \frac{1}{2}\sum_i\sum_j y_i y_j \left(2\delta_{ik} - \delta_{ij}\right)\right]$$

This delta 12 is given by 2 B 12 minus B 11 minus B we can further simplify that right. And once we have this value I can easily write ln phi 1 hat this is P over RT times derivative of n B with respect to n 1 which is B 11 plus y 2 square delta 12 and ln phi 2 hat is going to be P over RT B 2 2 y 1 square delta 1 2.

In general for a multi component mixture ln phi k hat is written as P over RT B k k plus half double sigma i j y i y j to delta i k minus delta i j. This is a general expression for a multi component mixture, but for our discussion here it suffices to say that these expressions for binary mixtures should be sufficient.

So, what we have done essentially is derived an expression for fugacity coefficient in a binary mixture in terms of the virial coefficients B 11 B 2 2 and delta 12 which includes the cross virial coefficient B 12 in addition to temperature and pressure. So, given the virial coefficients we can readily obtained the fugacity coefficient of the species. So, this expression here gives us the fugacity coefficient of species in a binary mixture or in generally multi component mixture relating it to the pure component virial coefficients and the cross virial coefficient B i j. One question still remains unanswered.

How do we obtain the cross virial coefficient B i j or B 1 2? One can obtain them from experiments if we study the behaviour of the mixture. If not we resort to empirical means to obtain this cross virial coefficient B 1 2. One of the ways that is proposed is to use what are known as pseudo critical constants.

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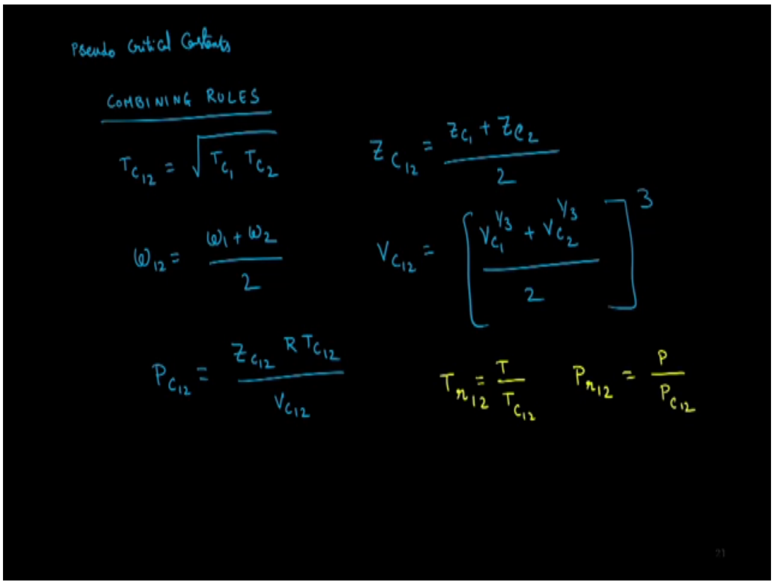

Pseudo Critical Constants

COMBINING RULES

$$T_{c_{12}} = \sqrt{T_{c_1} T_{c_2}}$$

$$Z_{c_{12}} = \frac{Z_{c_1} + Z_{c_2}}{2}$$

$$\omega_{12} = \frac{\omega_1 + \omega_2}{2}$$

$$V_{c_{12}} = \left[\frac{V_{c_1}^{1/3} + V_{c_2}^{1/3}}{2}\right]^3$$

$$P_{c_{12}} = \frac{Z_{c_{12}} R T_{c_{12}}}{V_{c_{12}}}$$

$$T_{r_{12}} = \frac{T}{T_{c_{12}}} \qquad P_{r_{12}} = \frac{P}{P_{c_{12}}}$$

To obtain pseudo critical constants we use a set of what are known as combining rules, differentiate them from the mixing rules we have used to obtain the properties of a mixture for example, B mix and in combining rules what we have do is use empirical formulae to calculate these pseudo critical constants.

So, these combining rules give us pseudo critical constants and by pseudo critical constants what we mean is that we obtain the constant T c 12 using the pure component T c 1 and T c 2 we are this formula. Similarly we take the arithmetic mean for obtaining the compressibility factor at the critical condition G Z c 12 and the eccentric factor omega 12 both of them are given by their respective arithmetic means and the volume V c 12 is given as arithmetic mean of their cube roots.

Essentially we are taking some sort of a arithmetic mean of the size of the particular molecule we are considering and finally, P c 12 is since P V is Z RT P c 12 will be given by this equation here. So, these are the empirical combining rules we use if we do not have any experimental data to calculate B 1 2. Once we define the pseudo critical parameters using these combining rules what we can do is obtain T r 12 and P r 1 2.

Now, I have T c 12 and P c 1 2. So, T r 12 is going to be T over T c 12 this will be P over P c 1 2. So, once I have this combining rules I can use it to calculate the reduced temperature T r 12 given as T over T c 1 2. Once I have T r 1 2, I can use this reduced temperature T r 12 to calculate B 12 or the cross virial coefficient. The way we do that is use the theorem of corresponding states.

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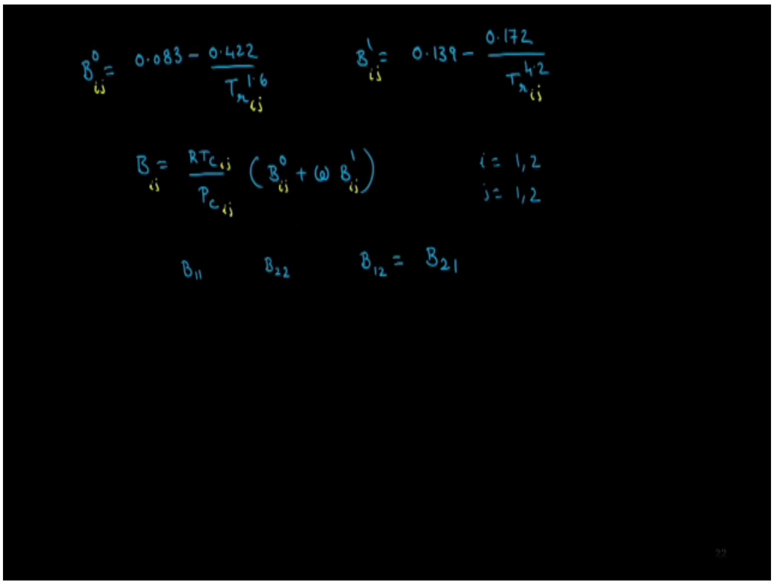

$$B^0_{ij} = 0.083 - \frac{0.422}{T_{r_{ij}}^{1.6}} \qquad B^1_{ij} = 0.139 - \frac{0.172}{T_{r_{ij}}^{4.2}}$$

$$B_{ij} = \frac{RT_{c_{ij}}}{P_{c_{ij}}}\left(B^0_{ij} + \omega B^1_{ij}\right) \qquad \begin{array}{l} i = 1,2 \\ j = 1,2 \end{array}$$

$$B_{11} \qquad B_{22} \qquad B_{12} = B_{21}$$

And in one of the previous problems we calculated B naught we are this correlation and B 1 using this correlation right. And we combined B naught and B 1 to obtain the virial coefficient B. We did this for a pure species right and we said B is RT c by P c B naught plus omega B 1. What we will do? We will use the same correlations, but this time to obtain the cross virial coefficient B 1 2. The way we do that is we will write a general expression for i j right in an analogous equation and so, let us simply use that subscript here.

To get i j what we will do is use the reduced temperature T r i j in these 2 equations and what we get is B naught i j and B 1 i j and we use those B naught i js and B 1 i js along with T c i j and P c i j to obtain B i j and the values of i and j in a binary mixture can be 12 j also can be 1 2.

So, I can use these equations to obtain all the 3 virial coefficients; B 11 if i equal to j equals 1 then what i get is B 1 1; if i equals j equals 2 what i get is B 2 2; if i is 1 and j is 2 what i get is B 1 2. Of course, in this formulation the idea is that B 12 is going to be equal to B 2 1. So, whether i is 2 and j is 1 or j is 2 or i is 1 we obtain the same values. So, B 12 is essentially B 2 1 both of them are identical.

So, this is how we will obtain our cross burial coefficient. Let us demonstrate this using an example.

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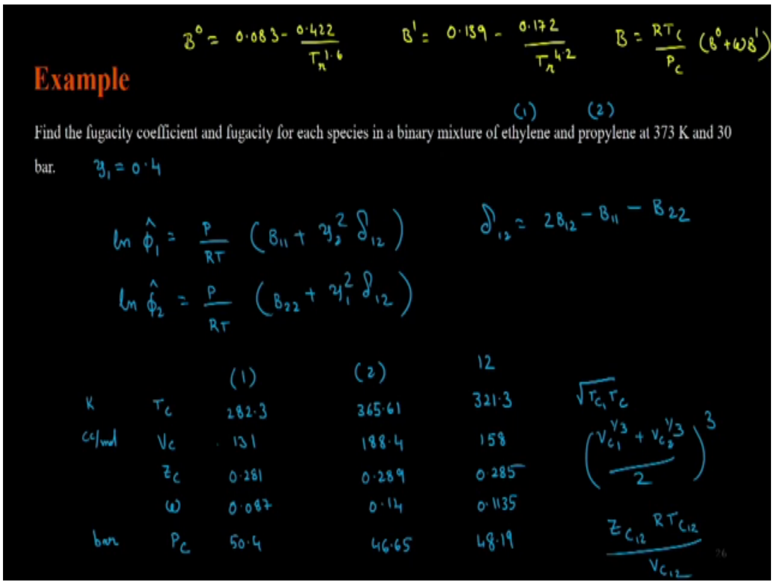

$$B^0 = 0.083 - \frac{0.422}{T_r^{1.6}} \qquad B^1 = 0.139 - \frac{0.172}{T_r^{4.2}} \qquad B = \frac{RT_c}{P_c}(B^0 + \omega B^1)$$

Example

Find the fugacity coefficient and fugacity for each species in a binary mixture of ethylene (1) and propylene (2) at 373 K and 30 bar. $y_1 = 0.4$

$$\ln \hat{\phi}_1 = \frac{P}{RT}\left(B_{11} + y_2^2 \delta_{12}\right) \qquad \delta_{12} = 2B_{12} - B_{11} - B_{22}$$

$$\ln \hat{\phi}_2 = \frac{P}{RT}\left(B_{22} + y_1^2 \delta_{12}\right)$$

		(1)	(2)	12	
K	T_c	282.3	365.61	321.3	$\sqrt{T_{c_1} T_{c_2}}$
cc/mol	V_c	131	188.4	158	$\left(\frac{V_{c_1}^{1/3} + V_{c_2}^{1/3}}{2}\right)^3$
	Z_c	0.281	0.289	0.285	
	ω	0.087	0.14	0.1135	
bar	P_c	50.4	46.65	48.19	$\frac{Z_{c_{12}} RT_{c_{12}}}{V_{c_{12}}}$

We want to find the fugacity coefficient and fugacity for each species in a binary mixture of ethylene and propylene at 373 Kelvin and 30 bar. We should of course, have been given and a value for the composition of this mixture without that we cannot obtain the fugacity coefficient right.

So, let us say y 1 is 0.4 in this particular problem and 1 stands for ethylene 2 stands for propylene. So, then lets restate the problem. We want to obtain the fugacity and fugacity coefficient for each species in a binary mixture of ethylene and propylene. Ethylene being 1 and propylene is 2. The mole fraction of ethylene in this mixture y 1 is 0.1. We want to use virial equation of state to do this particular calculation.

So, we are going to use the formulae we wrote earlier. B naught we want to obtain it using this equation, P 1 using this equation these are the 2 virial coefficient coefficients related to the temperature or reduced temperature and B of course, is RT c by P c B naught plus omega B 1.

We can use it to obtain all the 3 virial coefficients 11 12 and 2 2 right. So, if you recall we said that the fugacity coefficient ln phi 1 hat is P over RT B 11 plus y 2 square delta 12 and ln phi 2 hat in the binary mixture phi over RT B 2 2 plus y 1 square delta 12 and delta 12 was 2 B 12 minus B 11 minus B 2 2.

So, to obtain the fugacity coefficients phi 1 hat and phi 2 hat for ethylene and propylene I need the temperature and pressure which are given to me the composition y 1 and y 2 which is also known. So, all I do not know to use those equations are the virial coefficients B 11 B 2 2 and delta 12 which of course, needs B 12. So, once I have these 3 virial coefficients I can come back and use these 3 virial coefficients along with the other information in these 2 equations to get the fugacity coefficients of the 2 species.

So, then my first task is to obtain the 3 virial coefficients and we are going to use the equations listed about to obtain B naught B 1 and hence B i j, I do that. B naught and B 1 for the pure species 1 and 2 are easy to obtain, but for the cross virial coefficient B 12 I need the pseudo critical parameters 2 we will use the combining rules we talked about earlier to get those values.

First let us list ethylene, propylene and the pseudo constant 1 2. Lets list each of the critical parameters T c, let us talk about T c, V c, Z c, omega and finally, P c. T c for ethylene is 282.3 Kelvin; for propylene it is 365.61 Kelvin and T c 12 321.3 this is square root of T c 1 and T c 2; V c in c c per mole maybe I should write the units here this is c c per mole these 2 are dimensionless and this will be n bar ok. V c is 131; for 2 it is 188.4.

And using the combining rule we get V c 12 as 158; this was V c 1 to the power one third plus V c 2 to the power one-third over 2 whole cube. If you recall Z c and omega are same the arithmetic averages this is 0.281; this is 0.289 and average of that is Z c 12 which is 0.285 and omega this is 0.087; this is 0.14 and average of that is 0.1135 and finally, P c is 50.4; this is 46.65 and once we have all the other parameters T c V c Z c, we can calculate P c as Z c 12 R T c 12 by V c 12 and this turns out to be 48.19; this is the value of P c 1 2. So, now once I have the critical parameters for 1 1, 2 2 and 12 I can calculate the reduced temperature first.

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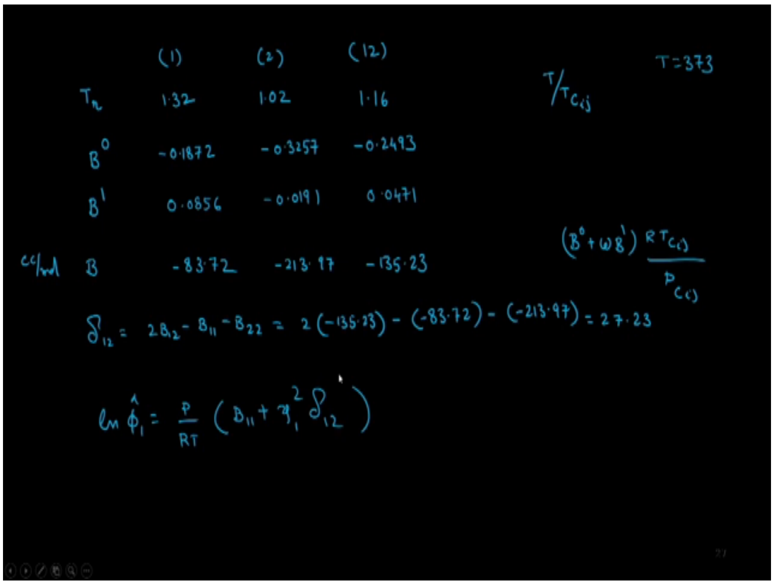

	(1)	(2)	(12)
T_r	1.32	1.02	1.16
B^0	-0.1872	-0.3257	-0.2493
B^1	0.0856	-0.0191	0.0471
cc/mol B	-83.72	-213.97	-135.23

$T/T_{c_{ij}}$

$T=373$

$$\left(B^0+\omega B^1\right)\frac{RT_{c_{ij}}}{P_{c_{ij}}}$$

$$\delta_{12}=2B_{12}-B_{11}-B_{22}=2(-135.23)-(-83.72)-(-213.97)=27.23$$

$$\ln\hat{\phi}_1=\frac{P}{RT}\left(B_{11}+y_1^2\delta_{12}\right)$$

So, I am going to formulate a similar table again for 1 2. The reduced temperature is going to be T over T c i j and in this case it will be 1.32. Remember that T c is 370 T is 373 Kelvin. So, T over T c I 11 is 1.32 this is 1.02 and this will be 1.16 and using this T I can calculate B naught and B 1 this will be negative 0.1872 this will be negative 0.3257.

And this will be negative 0.2493. B 1 is 0.0856 negative 0.0191 and 0.0471. Once I have B naught and B 1 I can calculate B which is B naught plus omega B 1 times R T c i j by P c i j. I will use that expression to calculate B and in this case B turns out to be negative 83.72. This is in c c per mole negative 213.97 and negative 1305.23. Once I have B right and I have obtained recall that I have obtained B naught and B 1 using the formula we listed here in terms of T r right and then B of course.

Once I have B 11 which is negative 83.7 to B 2 2 which is negative 213.97 and B 12 which is negative 1305.23 I can calculate delta 12 which is 2 B 12 minus B 11 minus B 2 2, that will be 2 times negative 135.23 then minus minus 83.72 minus minus 213. 97 and this value turns out to be positive 27.23. Once I have delta 12 I can calculate ln phi 1 hat and ln phi 2 hat. I will go back to this equation here to calculate ln phi 1 hat and phi 2 hat these 2 equations.

Now, I have B 11 delta 12 P over RT right. So, ln phi 1 hat is going to be P over RT times B 11 plus y 2 square delta 12 I am sorry y 1 square delta 12 right. Now its y 2 squared delta 12.

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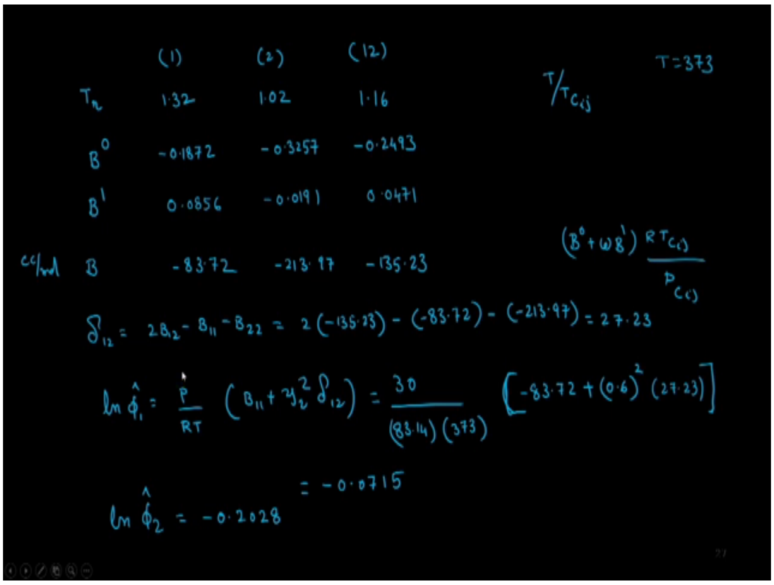

$T = 373$

$T/T_{c_{ij}}$

		(1)	(2)	(12)
	T_r	1.32	1.02	1.16
	B^0	-0.1872	-0.3257	-0.2493
	B^1	0.0856	-0.0191	0.0471
cc/mol	B	-83.72	-213.97	-135.23

$$(B^0 + \omega B^1)\frac{RT_{c_{ij}}}{P_{c_{ij}}}$$

$$\delta_{12} = 2B_{12} - B_{11} - B_{22} = 2(-135.23) - (-83.72) - (-213.97) = 27.23$$

$$\ln \hat{\phi}_1 = \frac{P}{RT}\left(B_{11} + y_2^2 \delta_{12}\right) = \frac{30}{(83.14)(373)}\left[-83.72 + (0.6)^2 (27.23)\right]$$

$$= -0.0715$$

$$\ln \hat{\phi}_2 = -0.2028$$

So, once I have all those quantities I can write ln phi 1 hat write; ln phi 1 hat is going to be P over RT B 11 plus y 2 squared delta 12 that will be the pressure here is 30 bar R is 83.14 in bar c c per mole per Kelvin.

This is 373 Kelvin times B 11 which is negative 83.72 plus y 2 squared which is 0.6; y 1 is 0.4. So, y 2 is 0.6 whole squared delta 12 is 27.23 and if I simplify that what I end up with is negative 0.0715 and similarly ln phi 2 hat is going to be negative 0.2028.

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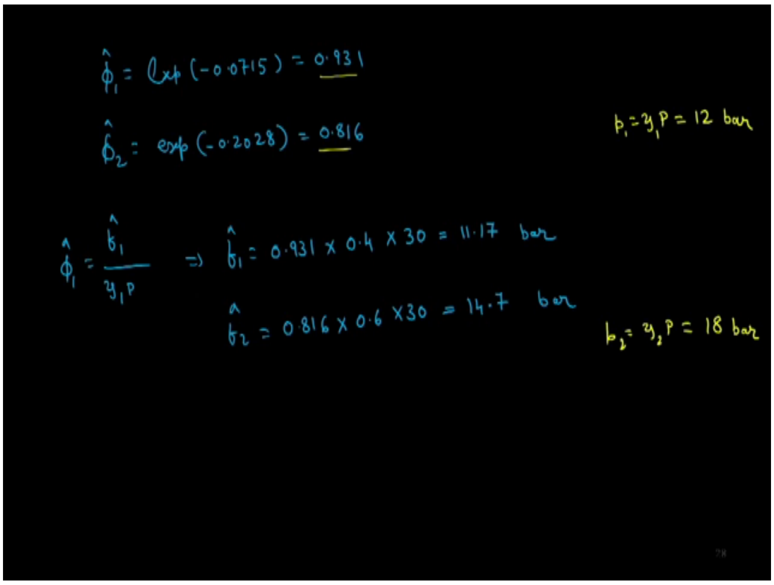

$$\hat{\phi}_1 = \exp(-0.0715) = \underline{0.931}$$

$$\hat{\phi}_2 = \exp(-0.2028) = \underline{0.816}$$

$p_1 = y_1 P = 12$ bar

$$\hat{\phi}_1 = \frac{\hat{f}_1}{y_1 P} \Rightarrow \hat{f}_1 = 0.931 \times 0.4 \times 30 = 11.17 \text{ bar}$$

$$\hat{f}_2 = 0.816 \times 0.6 \times 30 = 14.7 \text{ bar}$$

$p_2 = y_2 P = 18$ bar

Once I have ln phi 1 hat and phi 2 hat I can calculate the fugacity coefficients in the mixture, phi 1 hat is going to be exponential of negative 0.0715 which turns out to be 0.931 and phi 2 hat is going to be exponential of negative 0.2028 which turns out to be 0.816 and f 1 hat by y 1 P this is phi 1 hat which means f 1 hat is going to be 0.931 times y 1 which is 0.4 times 30. So, that would be 11.17 and similarly f 2 hat is going to be phi 2 hat which is 0.816 times y 2 which is 0.6 times B 30 which is 14.7 bar.

So, we go through the series of steps, first to calculate the cross virial coefficient and the pure component virial coefficients after obtaining the pseudo critical parameters using the combining rules and once we do that rest of it is pretty straightforward to calculate the fugacity coefficient and hence the fugacity of species 1 and 2 in the mixture. Now, notice that at in this particular mixture the partial pressure P 1 is y 1 P that is about 12 bar and P 2 is y 2 P that is about 18 bar. So, as opposed to the partial pressure 12 bar the fugacity of species 1 is about 11.1 bar because of the non ideality and f 2 hat as opposed to 18 bar is about 14.7 bar.

So, that the values of the fugacity coefficients or the fugacity is in that sense demonstrate how far away we are from ideal gas behaviour. So, that completes our discussion on fugacity coefficients of gases using virial equation of state. When we come back in the next video, we are going to try to use a cubic equation of stage to calculate the fugacity species sorry fugacity coefficient of species in the mixture and following that we will look at other methods to calculate fugacity of liquids.

Thank you and see you in the next lecture.