Chemical Engineering Thermodynamics

Prof. Sasidhar Gumma
Department of Chemical Engineering
Indian Institute of Technology, Guwahati

Lecture - 28
Fugacity

Hello and welcome back, in the previous lectures were talking about Fugacity. We looked at the need for using fugacity in phase equilibrium calculations.

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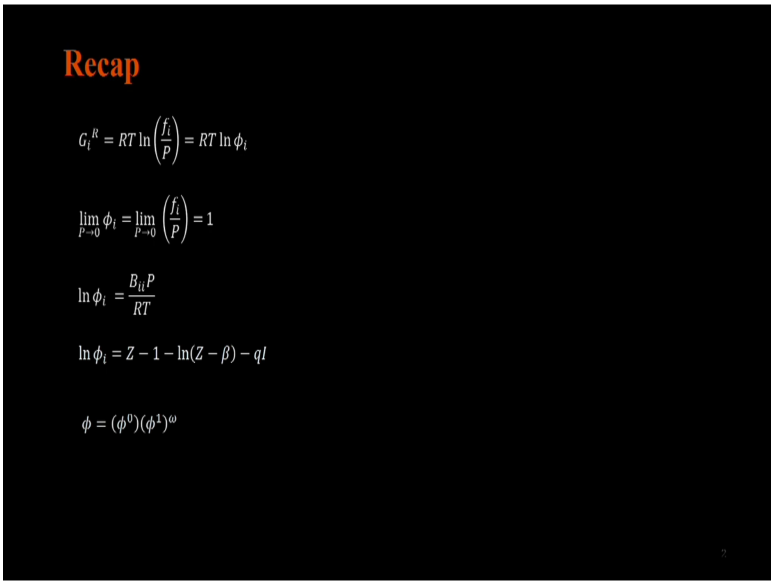

Recap

$$G_i^R = RT\ln\left(\frac{f_i}{P}\right) = RT\ln\phi_i$$

$$\lim_{P\to 0}\phi_i = \lim_{P\to 0}\left(\frac{f_i}{P}\right) = 1$$

$$\ln\phi_i = \frac{B_{ii}P}{RT}$$

$$\ln\phi_i = Z - 1 - \ln(Z-\beta) - qI$$

$$\phi = (\phi^0)(\phi^1)^{\omega}$$

We said that in at phase equilibrium just like chemical potentials of a species in each of the phases is equal, the fugacity also will be equal we related it to the Gibbs free energy or the residual Gibbs free energy. We also defined fugacity coefficient as a ratio of fugacity to pressure or partial pressure in case of mixtures. And we said that as the limit P approaches 0 the fugacity coefficient will approach unity and the fugacity itself will approach the pressure.

We looked at how to use various equations of state to calculate fugacity in case of pure species, we have used the virial equation of state, we have also used a cubic equation of state to calculate fugacity and even the Lee Kesler tables for fugacity coefficients.

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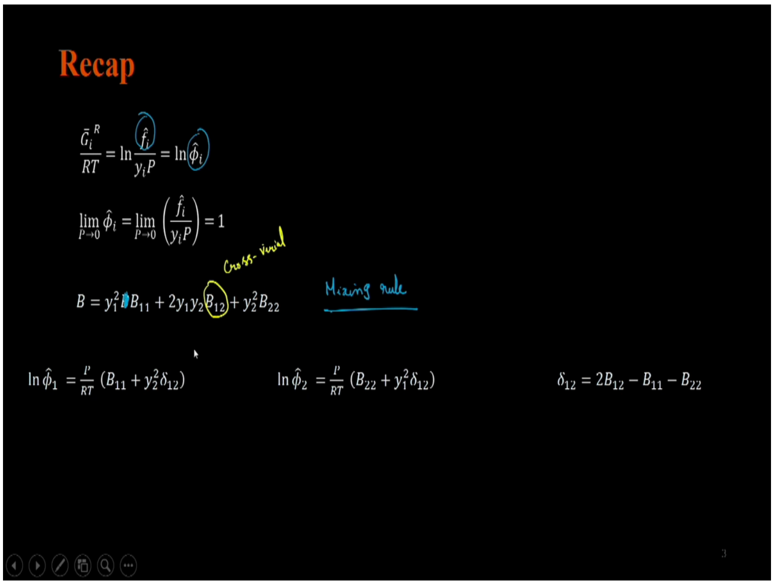

Recap

$$\frac{\bar{G}_i^R}{RT} = \ln\frac{\hat{f}_i}{y_i P} = \ln\hat{\phi}_i$$

$$\lim_{P\to 0}\hat{\phi}_i = \lim_{P\to 0}\left(\frac{\hat{f}_i}{y_i P}\right) = 1$$

Cross-virial

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

Mixing rule

$$\ln\hat{\phi}_1 = \frac{P}{RT}(B_{11} + y_2^2\delta_{12}) \qquad \ln\hat{\phi}_2 = \frac{P}{RT}(B_{22} + y_1^2\delta_{12}) \qquad \delta_{12} = 2B_{12} - B_{11} - B_{22}$$

In case of mixtures, we defined what is known as fi hat, the fugacity of species i in the mixture or phi i hat the fugacity coefficient for species i in the mixture and related it to the partial molar Gibbs free energy the residual partial molar Gibbs free energy G i bar R. And in case of the mixture we said as the zero pressure limit, the fugacity will approach the partial pressure of that particular species.

To be able to calculate fugacity of mixture species in a mixture using virial equation of state, we said that we need what is known as a Mixing rule to be able to calculate the virial coefficient B for the mixture it is related to the individual virial coefficients B 1 1, B 2 2 the mole fraction y 1 as well as an additional virial coefficient B 1 2 which we called as the Cross Virial coefficient. And once we have the information about these virial coefficients, now we can use the relations shown here to calculate the fugacity of the species in the mixture we can also extend this formula to multi component mixtures, now what we have shown here is for a binary mixture.

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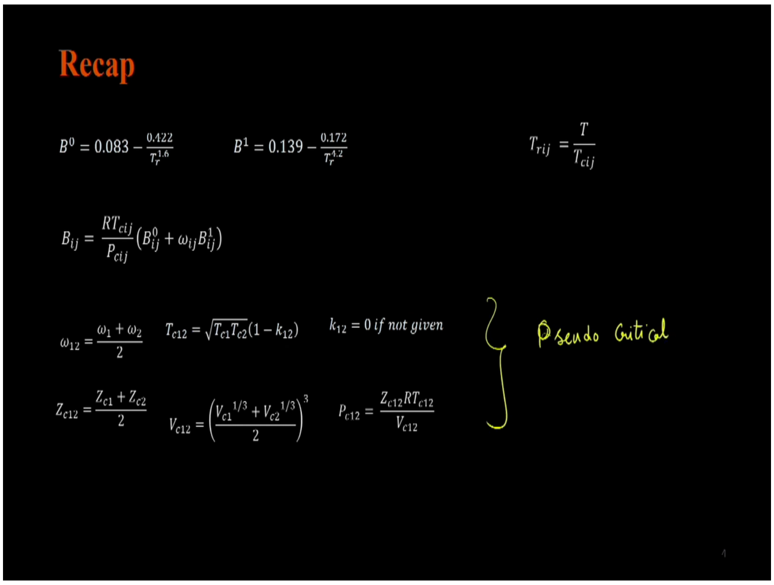

Recap

$$B^0 = 0.083 - \frac{0.422}{T_r^{1.6}} \qquad B^1 = 0.139 - \frac{0.172}{T_r^{4.2}} \qquad T_{rij} = \frac{T}{T_{cij}}$$

$$B_{ij} = \frac{RT_{cij}}{P_{cij}}\left(B_{ij}^0 + \omega_{ij}B_{ij}^1\right)$$

$$\left.\begin{array}{lll} \omega_{12} = \dfrac{\omega_1 + \omega_2}{2} & T_{c12} = \sqrt{T_{c1}T_{c2}}(1 - k_{12}) & k_{12} = 0 \textit{ if not given} \\ Z_{c12} = \dfrac{Z_{c1} + Z_{c2}}{2} & V_{c12} = \left(\dfrac{{V_{c1}}^{1/3} + {V_{c2}}^{1/3}}{2}\right)^3 & P_{c12} = \dfrac{Z_{c12}RT_{c12}}{V_{c12}} \end{array}\right\}$$

Pseudo Critical

Now, pure virial coefficients and the cross virial coefficient can be obtained from experiments or from the theory of corresponding states for example, using correlations such as these for B naught and B 1 which are related to the reduced temperature and once we have B naught and B 1, I can calculate B i j if i equals j then we have the pure species of second virial coefficient. If i is not equal to j, then we have what is known as the cross virial coefficient. And to be able to calculate B i j the cross virial coefficient we can use what are known as the combining rules to obtain the Pseudo Critical constants or the Pseudo Critical parameters such as T c 1 to omega 1 to the compressibility factor, the volume etcetera from which we calculate the pressure and once we have this information I can calculate the cross virial coefficient B 1 2. We have used this in an experiment and calculated the fugacity coefficient for species in a mixture.

What we will do today is look at how to calculate fugacity coefficient of species in a mixture using cubic equation of state.

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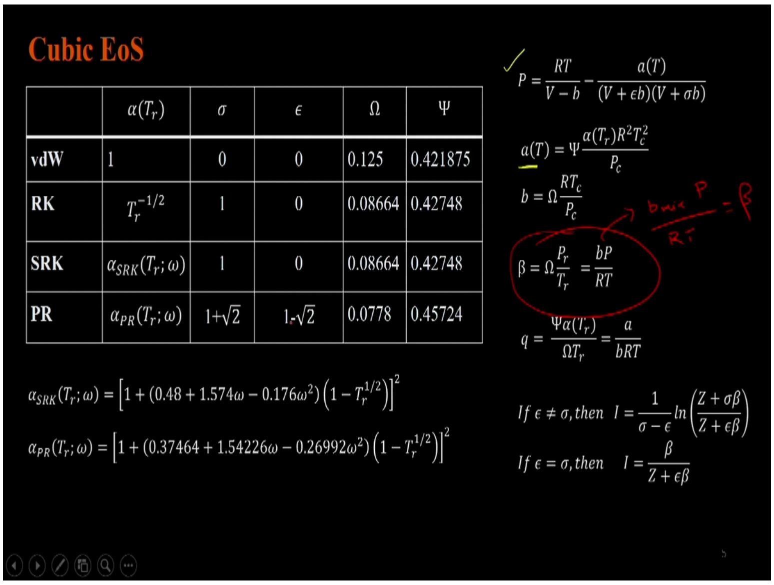

Cubic EoS

	$\alpha(T_r)$	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

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

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

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

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

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

$$\boxed{\beta = \Omega \frac{P_r}{T_r} = \frac{bP}{RT}} \rightarrow \frac{b_{mix} P}{RT} = \beta$$

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

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

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

If you recall, we have used a variety of cubic equations of state the van der Waals, Redlich-Kwong, Peng-Robinson Soave Redlich-Kwong etcetera each one of them can be written in a generic form as shown here with several parameters a b etcetera listed in there. In case of SRK and Peng-Robinson, we have an additional parameter alpha which will give a functionality to the parameter a in terms of the temperature or the reduced temperature and the eccentric factor omega.

Now, we have used this cubic equation of state successfully to calculate the fugacity of pure species, but for a mixture, what we need is just like in case of virial equation of state, I need Mixing Rules right I need mixing rules to be able to apply these cubic equations of state as well for a mixture.

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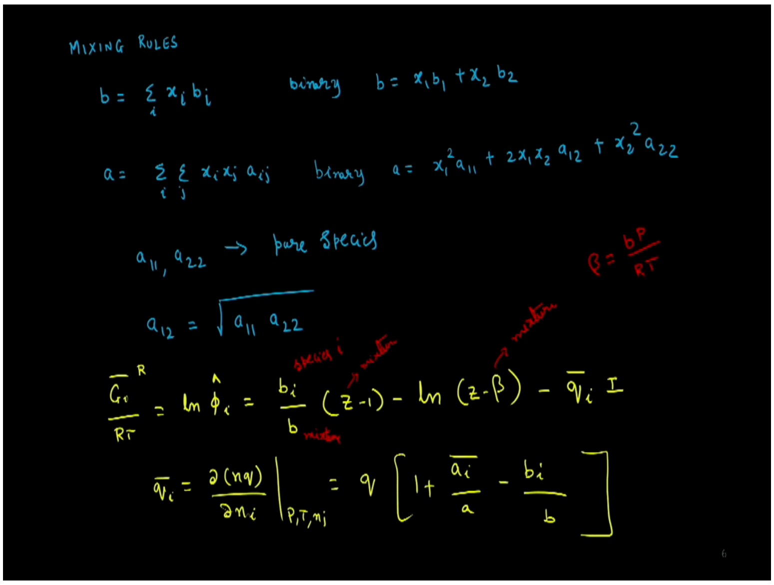

MIXING RULES

$b = \sum_i x_i b_i$ binary $b = x_1 b_1 + x_2 b_2$

$a = \sum_i \sum_j x_i x_j a_{ij}$ binary $a = x_1^2 a_{11} + 2x_1 x_2 a_{12} + x_2^2 a_{22}$

a_{11}, a_{22} → pure species

$\beta = \frac{bP}{RT}$

$a_{12} = \sqrt{a_{11} a_{22}}$

$$\frac{\bar{G}_i^R}{RT} = \ln \hat{\phi}_i = \frac{\overset{\text{species } i}{b_i}}{\underset{\text{mixture}}{b}} (\overset{\text{mixture}}{Z} - 1) - \ln (Z - \overset{\text{mixture}}{\beta}) - \bar{q}_i I$$

$$\bar{q}_i = \left. \frac{\partial (nq)}{\partial n_i} \right|_{P,T,n_j} = q \left[1 + \frac{\bar{a}_i}{a} - \frac{b_i}{b} \right]$$

The mixing rules we are going to use are what are what is known as a linear mixing rule for b. I am going to write b indicating it is a parameter for the mixture, it is related to the individual pure species mixing rules via this equation x i b i sigma of x i b i. So, for a binary it reduces to b is x 1 b 1 plus x 2 b 2.

Similarly, the parameter a we use a quadratic mixing rule i j x i x j a i j and for a binary this reduces to x 1 squared a 1 1 plus 2 x 1 x 2 a 1 2 plus x 2 squared a 2 2.

As usual a 1 1 and a 2 2 are the a's for pure species 1 and 2 and a 1 2 is the cross parameter and for this particular scenario we will get it we are a combining rule and the combining rule we use to get a 1 2 is square root of a 1 1 times a 2 2 right.

Once we have a 1 1, a 2 2 and a 1 2 from the combining rule, I can apply it if I know the mole fraction in the mixing rule and get the a for the mixture. So, these are the mixing rules we will use for a cubic equation of state right.

Once I have this information I can work through the math to obtain the partial molar Gibbs free energy G i bar by R T which in turn is related to the fugacity coefficient of species i in the mixture l n phi i hat we will not go through the math, but we will write the final expression it turns out to b i over b Z minus 1 minus l n Z minus beta minus q i bar o times i and q i bar here is given as the derivative of n q with respect to n i at P, T, n j and this in turn boils down to q times 1 plus a i bar over a minus b i by b.

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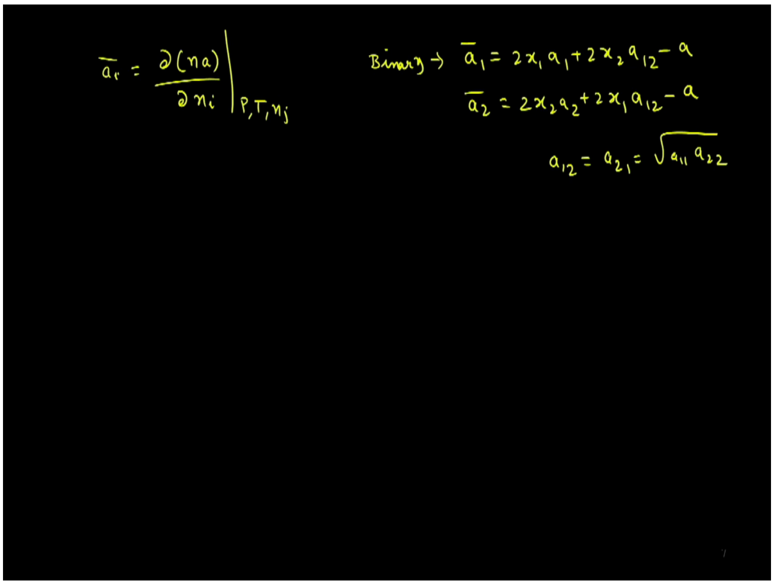

$$\bar{a}_i = \left.\frac{\partial(na)}{\partial n_i}\right|_{P,T,n_j}$$

Binary → $\bar{a}_1 = 2x_1a_1 + 2x_2a_{12} - a$

$\bar{a}_2 = 2x_2a_2 + 2x_1a_{12} - a$

$a_{12} = a_{21} = \sqrt{a_{11}a_{22}}$

And finally, a i bar again is a partial molar a. So, we will write it as derivative of n times a over n i at P T and n j. For a binary this simplifies to a 1 bar is 2 x 1 a 1 plus 2 x 2 a 1 2 minus a a 2 bar is 2 x 2 a 2 plus 2 x 1 a 1 2 minus a because of the definition we have used note that a 1 2 is going to be equal to a 2 1 both of them are square root of a 1 1 a 2 2 right.

So, with this what we have if you look at the formula from the previous slide, I have an expression for l n of the fugacity coefficient phi i hat it is given in terms of b i which is b for species i over b which is b for the mixture maybe I should write that here to bring more clarity this is for species i, this is for the mixture. If I don't have any subscript it is for the mixture. If I have a subscript it is for that particular species, then this is also for the mixture, this is also for the mixture and if you recall beta was b times P over R T.

If you look at this here beta is b times P over R T. So, I use b for the mixture times P over R T that will give me beta, that beta is for the mixture I again is given by these two definitions here I have Z which is for the mixture beta for the mixture and sigma and epsilon come from the equation of state I choose and finally, q i bar times q i bar is given by the expression here which in turn has a and b the partial molar a and a and b for the mixture b i is for the species i and the partial molar a itself is given by the definition here and we can reduce it in terms of a 1's and a 1 2's for a binary mixture right?

So, once I have this information I should be able to calculate the fugacity of species i in the mixture. Things will be a little clear if we start working with one example and see how we can calculate each of the quantities we need.

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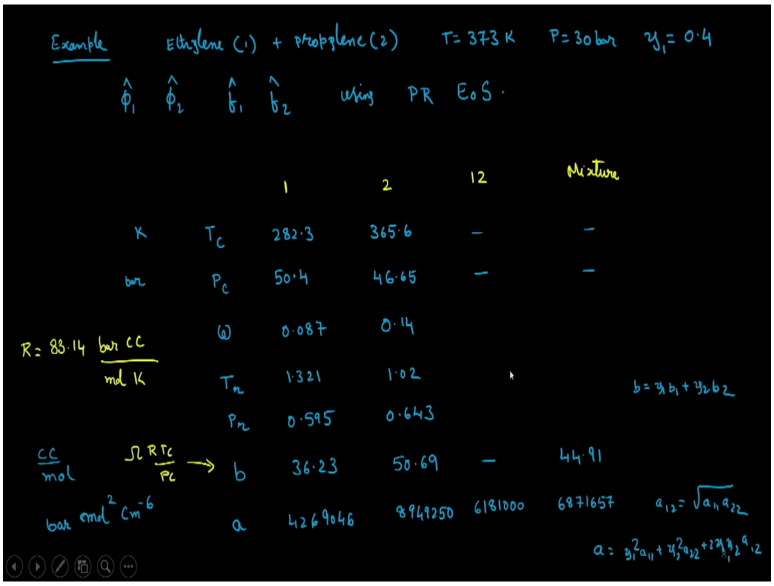

Example Ethylene (1) + propylene (2) $T = 373\ K$ $P = 30\ bar$ $y_1 = 0.4$

$\hat{\phi}_1$ $\hat{\phi}_2$ $\hat{f}_1$ $\hat{f}_2$ using PR EoS.

		1	2	12	Mixture
K	T_c	282.3	365.6	–	–
bar	P_c	50.4	46.65	–	–
	ω	0.087	0.14		
	T_r	1.321	1.02		
	P_r	0.595	0.643		
$\frac{cc}{mol}$ $\Omega \frac{RT_c}{P_c} \rightarrow$	b	36.23	50.69	–	44.91
bar mol^2 cm^{-6}	a	4269046	8949250	6181000	6871657

$R = 83.14 \frac{bar\ cc}{mol\ K}$

$b = y_1 b_1 + y_2 b_2$

$a_{12} = \sqrt{a_{11} a_{22}}$

$a = y_1^2 a_{11} + y_2^2 a_{22} + 2 y_1 y_2 a_{12}$

So, let us work on a problem. Let us say I have a mixture of ethylene let us call this as 1 plus propylene let us call this as 2 at a temperature of 373 Kelvin the pressure is 30 bar and the mole fraction y 1 is 0.4.

These are the conditions given to me and I am interested in calculating phi 1 hat, phi 2 hat, the fugacity of species 1 in coefficients for species 1 and 2 as well as the fugacity for the species 1 and 2 in the mixture using let us say Peng-Robinson equation of state we have not used this equation of state so far less. So, let us use that in this particular example this is what I want to calculate.

To do this calculation we will run through a series of steps and follow the procedure given to us so, what I will do is I will list some quantities for 1, species 1 for species 2 if there is any cross coefficient for 1 2 and finally, for the mixture. Alright, let us start working with some of these quantities. First one I will try to row get from a handbook is T c, the critical temperature for ethylene it is 282.3, for propylene it is 365.6, we do not need it for 1 2 or the mixture Pc is 50.4 this is in bar, this is in Kelvin of course, and for 2 it is 46.65 bar I do not need these using a equation of state we get got 1 2, P c 1 2 or T c 1

2 and we used virial equation of state the pseudo critical parameters for cubic equation of state we do not need those numbers

Then the accentric factor omega 0.087 and 0.14. Using this T c, I can get T r as 1.321 and 1.02 I can get P r as 0595 and 0.643. In addition I can get b if you look at this equation b is omega R T c over P c. I have T c, I have P c, I can use a value for R and omega for Peng-Robinson equation of state is this number here.

So, that is b, I need to calculate. So, let us write that equation here it is omega T c over P c that is what I am trying to calculate I have T c, P c and in appropriate units I should be using R as 83.14 bar CC per mole Kelvin. When I do that the value of b, I will get is 36.23 for 1, 50.69 for 2 there is no 1 2, but for the mixture I will use the combining rule x 1 b 1 plus x 2 b 2 right? So, this value here is going to be 44.91.

Well I should say because this is a vapor mixture I am going to let us say call it as y 1 b 1 plus y 2 b 2 we do not know if it is a vapor or a liquid mixture then we can use x 1 to be the mole fraction in a more general sense, but it really does not matter as long as we stick to the same notation.

So, once I have b, the next thing I would like to calculate is a if you go back and look at our table a is given by this expression here which requires psi alpha R squared T c square over P c. So, we run through this calculation the first thing I will calculate is alpha for Peng-Robinson equation of state which is this number here right it needs omega and the reduced temperature. Once I have the reduced temperature and omega I can calculate alpha, I will plug that alpha in here the psi for Peng-Rrobinson is given here and I get psi, I get alpha from the equation here and R square T c square over P c everything else is known.

So, once I finish that calculation this is the number I have for a again I am working with a R of n bar c c per mole per Kelvin and the value of a I get for 1 is 4269046, b is 8949250, a 1 2 is square root of a 1 1 a 2 2 that number turns out to be 618100, well 618100, 3 zeroes there and for the mixture it is a quadratic mixing rule this value turns out to be 6871657, a is x 1 squared a 1 1 or rather since we are using wise here it’s y 1 square a 1 1 y 2 square a 2 2 plus 2 y 1 y 2 a 1 2 that is the equation I have used to get a for the mixture right?

So, these are the numbers I have for a and b, notice the units for b in this case are going to be same as that of the volume. So, a b is going to be in c c per mol and a is going to be bar mol square centimeter to the power negative 6. These are the units for a.

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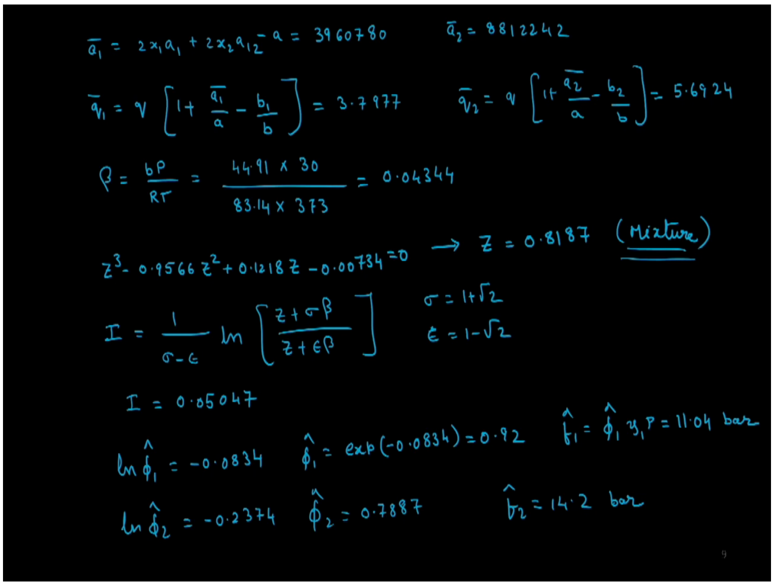

$\bar{a}_1 = 2x_1a_1 + 2x_2a_{12} - a = 3960780$ $\quad \bar{a}_2 = 8812242$

$\bar{q}_1 = q\left[1 + \frac{\bar{a}_1}{a} - \frac{b_1}{b}\right] = 3.7977$ $\quad \bar{q}_2 = q\left[1 + \frac{\bar{a}_2}{a} - \frac{b_2}{b}\right] = 5.6924$

$$\beta = \frac{bP}{RT} = \frac{44.91 \times 30}{83.14 \times 373} = 0.04344$$

$Z^3 - 0.9566Z^2 + 0.1218Z - 0.00734 = 0 \longrightarrow Z = 0.8187$ $\underline{\underline{(\text{Mixture})}}$

$I = \frac{1}{\sigma - \epsilon} \ln\left[\frac{Z + \sigma\beta}{Z + \epsilon\beta}\right]$ $\quad \sigma = 1 + \sqrt{2}$, $\epsilon = 1 - \sqrt{2}$

$I = 0.05047$

$\ln\hat{\phi}_1 = -0.0834$ $\quad \hat{\phi}_1 = \exp(-0.0834) = 0.92$ $\quad \hat{f}_1 = \hat{\phi}_1 y_1 P = 11.04$ bar

$\ln\hat{\phi}_2 = -0.2374$ $\quad \hat{\phi}_2 = 0.7887$ $\quad \hat{f}_2 = 14.2$ bar

So, with these numbers I can go to the next step in my calculation which is calculating the partial molar values for a 1 bar and a 2 bar. a 1 bar if you recall is 2 x 1 a 1 plus 2 x 2 a 1 2 minus a in this case I have all the numbers I need. So, I can calculate this numerical value to be this much and similarly a 2 bar is going to be 8812242.

Once I have a 1 bar and a 2 bar, I can calculate q right 1 bar turn it is q times 1 plus a 1 bar by a minus b 1 by b. So, this value here turns out to be 3.7977 and similarly q 2 bar is q 1 plus a 2 bar over a minus b 2 by b which works out to be 5.6924. The other thing I need in these calculations is beta which is b P over R T.

We already have b for the mixture from the previous slide the value we had was 44.91, the pressure here is 30 bar R is 83.14 times 373 this value works out to be 0.04344 4 beta. Once I have all of this if you look at the equation we have here for l n phi i hat, I have b i b beta q 1 bar and q 2 bar of course.

What I do not have is i and the value for z or the compressibility factor and if you recall i also is related to z. So, I think the next step to in this calculation is to find the value of z at the given conditions. To find the value of z the compressibility factor at the given temperature and pressure, if you recall what we need to do is solve the cubic equation we get and obtain the roots of that cubic equation. The cubic equation in this case right let us show that cubic equation once for sake of well we do not have it here.

So, that cubic equation in this case works out to be z cube minus 0.9566 z square plus point 0.1218 z minus point 0.00734 equals 0 and the roots of this cubic there is only one real root the other two are imaginary the real root works out to be point 0.8187. That is the compressibility factor at the given conditions temperature and pressure conditions right using the values of a for the mixture this is for the mixture. So, when I get the coefficients for this cubic equation, I have used a and b for the mixture and then once I get the coefficients I can find the root to be done. So, this is for the mixture let us highlight that.

So, once I have z for the mixture, I can go back and calculate i which is 1 by sigma minus epsilon l n of z plus sigma times beta z plus epsilon times beta. For Peng-Robinson sigma is 1 plus square root of 2 epsilon is 1 minus square root of 2, I have the value of z, I have the value of beta. So, I can plug all those numbers in to get a value for I which turns out to be 0.05047 in this case.

Now, once I have I and Z, I have everything I need to calculate the fugacity coefficient, l n phi 1 hat now turns out to be 0.0834. So, phi 1 hat is going to be exponential of that value, 0834 which is 0.92 and f 1 hat is going to be phi 1 hat times the partial pressure y 1 P which is 11.04 bar and l n phi 2 hat for propylene is 2374, phi 2 hat is 0.7887 and f 2 hat works out to be 14.2 bar.

So, this is how we use a cubic equation of state to calculate the fugacity coefficient and fugacity of species in a binary mixture of course, we can extend this to a multi component mixture. So, what we have done so far is demonstrated the need for fugacity and tried to calculate fugacity using a variety of approaches virial equation of state the Lee Kesler tables we have used a cubic equation of state both for mixtures as well as pure species. There is one other interesting way to calculate fugacity for liquids or condensed phases right.

Now, if you recall, when we calculate fugacity using virial equation of state it is mostly applicable only to vapors until moderate pressures. If I am going to use a cubic equation of state to calculate fugacity of course, I can if at the given conditions the equation of state yields a liquid like root then I can use that equation of state to calculate the fugacity of the liquid. So, we have a scenario now where I can use virial equation of state to calculate fugacity of a gas or a vapor but that is applicable only up till moderate pressures.

The only approach that probably will work for calculating fugacity of a liquid in whatever we have looked at so far is using a cubic equation of state. If I have a cubic equation of state and I get and that yields me a liquid like root, then I can use it to calculate the fugacity of the liquid. I can use the liquid like root for the compressibility factor z and extend whatever calculations we have done so far to calculate the fugacity of the liquid.

But then for that approach to work the equation of state needs to be applicable over the entire range of pressures from zero pressure to the pressure of our interest. If it is not sufficient, if the cubic equation of state only works for the pressure we are looking at, it should work for the entire range because the equation we have obtained is actually via an integration from zero pressure to the pressure P of interest right

So, unless we are able to find such an equation of state which is applicable over the entire range of pressures, we will not end up with a correct value for fugacity or fugacity coefficient using a cubic equation of state. The other way to calculate fugacity of a liquid we are talking about pure liquids here.

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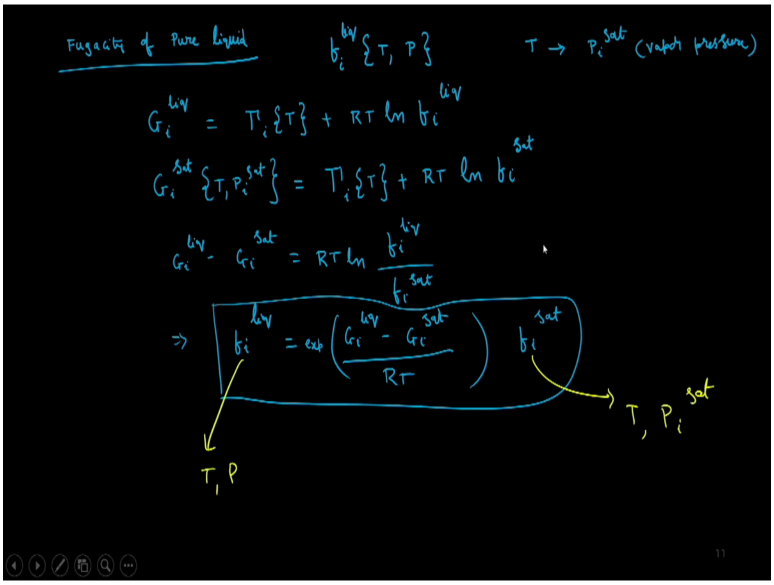

Fugacity of Pure Liquid

$f_i^{liq}\{T, P\}$ $T \rightarrow P_i^{sat}$ (vapor pressure)

$$G_i^{liq} = \Gamma_i\{T\} + RT \ln f_i^{liq}$$

$$G_i^{sat}\{T, P_i^{sat}\} = \Gamma_i\{T\} + RT \ln f_i^{sat}$$

$$G_i^{liq} - G_i^{sat} = RT \ln \frac{f_i^{liq}}{f_i^{sat}}$$

$$\Rightarrow \boxed{f_i^{liq} = \exp\left(\frac{G_i^{liq} - G_i^{sat}}{RT}\right) f_i^{sat}}$$

So, what we do is we use the concept of vapor liquid equilibrium to calculate the fugacity of pure liquid. Let us say I am interested in fugacity of liquid at a certain temperature and pressure P this is pure liquid. So, it depends only on, the fugacity will depend only on temperature and pressure. Let us call this as liquid right this is what I am interested in calculating.

Now, this fugacity of liquid let us give us subscript i so that we are talking about species i although it is pure component will be related to the Gibbs free energy of the liquid G i liquid via this equation some constant plus R T l n f i and at the saturation condition at this temperature T let the vapor pressure be P i sat for this liquid. At the saturation condition that is G i sat which is at T and P i sat right at this condition of T and P i sat, let's say the Gibbs free energy is G i sat at this condition because the temperature is same the constant is still going to be same plus R T l n f i sat. Now if I subtract one from the other, then it turns out that G i liquid minus G i sat is R T l n f i liquid over f i sat.

So, what this means is that the fugacity of liquid at a temperature T and pressure P we will be G i liquid minus G i sat over R T exponential of this multiplied with f i sat right.

So, the fugacity of liquid at any temperature T and pressure P will be related to the fugacity at temperature T and pressure P i sat we are this equation.

Now, there is two things I want to add on top of this equation.

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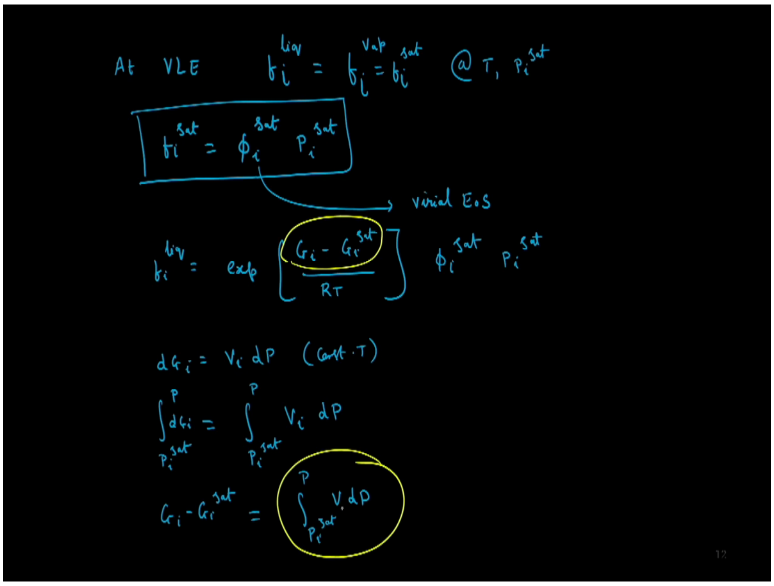

At VLE $\quad f_i^{liq} = f_i^{vap} = f_i^{sat} \quad @ \; T, \; P_i^{sat}$

$$\boxed{f_i^{sat} = \phi_i^{sat} \; P_i^{sat}}$$

$\phi_i^{sat} \rightarrow$ virial E.o.S

$$f_i^{liq} = \exp\left[\frac{G_i - G_i^{sat}}{RT}\right] \phi_i^{sat} \; P_i^{sat}$$

$$dG_i = V_i \, dP \quad (\text{Const.} \, T)$$

$$\int_{P_i^{sat}}^{P} dG_i = \int_{P_i^{sat}}^{P} V_i \, dP$$

$$G_i - G_i^{sat} = \int_{P_i^{sat}}^{P} V_i \, dP$$

The first thing is at vapor liquid equilibrium, recall that the chemical potentials the Gibbs free energies and hence the fugacity of the pure species are going to be equal right and we are talking about vapor pressure P i sat. So, at T and P i sat the vapor and liquid are in equilibrium and the fugacity at this condition are going to be same. So, I am simply going to call this fugacity value as f i sat right. It does not matter whether I am talking about the liquid phase or the vapor phase, the fugacity is same we are simply going to call it as the fugacity of saturated vapor or saturated liquid we will simply say f i sat right.

This f i sat will be related to the fugacity coefficient at this condition phi i sat times the vapor pressure P i sat right. And it is easy to calculate the vapor phase fugacity like we have seen we can use the second virial coefficient, we can use cubic equation of state whatever it is at the saturation condition to calculate phi i sat. The simplest way of course, is to use the virial equation of state that is same.

So, I can calculate the fugacity at the saturation condition using virial equation of state and so the previous equation f i liquid will be exponential of G i minus G i at the saturation condition over R T right times phi i sat times P i sat.

Now let us see what I can do with this equation. G i minus G i sat recall that d G i is V i d P as long as the temperature is constant. I can integrate this from P i sat to P, this will be integral of P i sat to P V i d P. I am integrating it over the liquid phase from the saturation condition to the pressure P of interest right. When I do this on the left hand side I have G i minus G i sat, on the right hand side it is integral of P i sat to P V d P.

So, what I can do is I can replace this thing here in terms of Gibbs free energies with the integral of V d P or V i d P.

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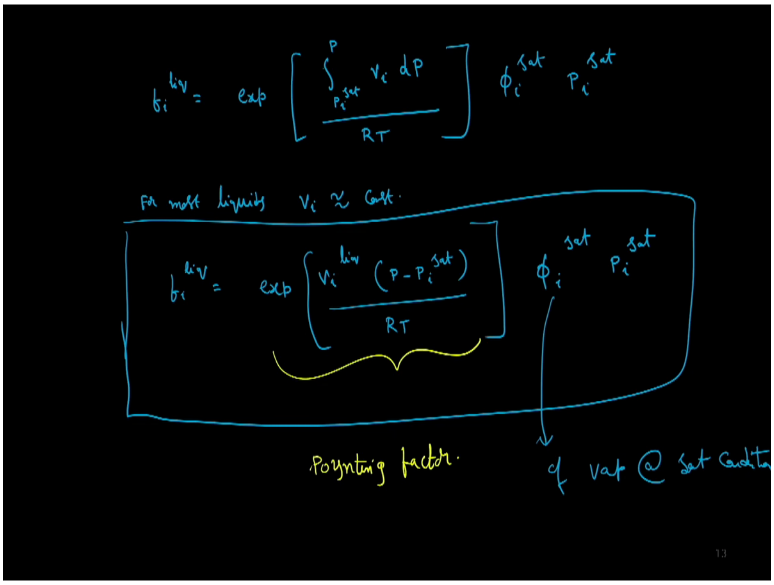

$$f_i^{liq} = \exp\left[\frac{\int_{P_i^{sat}}^{P} V_i \, dP}{RT}\right] \phi_i^{sat} \, P_i^{sat}$$

For most liquids $V_i \approx$ Const.

$$\boxed{f_i^{liq} = \underbrace{\exp\left[\frac{V_i^{liq}\left(P - P_i^{sat}\right)}{RT}\right]}_{\text{Poynting factor.}} \underset{\phi \text{ vap @ Sat Condit}}{\underbrace{\phi_i^{sat}}} \, P_i^{sat}}$$

So, essentially that equation now boils down to f i liquid is going to be exponential of integral P i sat to P V i d P over R T times phi i sat times P i sat. The vapor pressure multiplied with the fugacity coefficient at the saturation condition multiplied with the exponential term in here.

For most liquids, over moderate changes in pressure from P i sat to P, V i is fairly constant. So, I can take that out of the integral sign there in which case this equation will reduce to exponential of V i liquid times integral of d P will be P so, that definite integral will be P minus P i sat over R T exponential of this term.

This is a fair approximation, if P is not too far away from P i sat over moderate changes the liquid can be considered fairly incompressible, the volume will be more or less constant it can come out of the integral and that equation reduces to this form.

So, what this equation allows me to do is to calculate the fugacity of a liquid from known information and the fugacity coefficient of vapor at saturation condition. So, if I can calculate fugacity of vapor at the saturation condition, I can use this equation and calculate the fugacity of liquid at an elevated pressure P. This term, exponential term in here is known as Poynting.

So, we have used the vapor liquid equilibrium concept to come up with an alternate way to calculate fugacity of species of pure species in the liquid phase. We will come back and try to work on one example using the Poynting factor to correct the fugacity of liquid in the next lecture.

Thank you.