Chemical Engineering Thermodynamics
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Lecture - 27
Partial Molar Properties and Fugacity

Hello, and welcome back, in the previous lectures, we looked at solution thermodynamics and we defined what are known as partial molar properties, we looked at several relations amongst the partial molar properties and then we looked at the phase equilibrium problem in detail where we said the chemical potential for each of the species in a phase needs to be same. So, to be able to solve the phase equilibrium problem we equate the chemical potentials, but it turns out that chemical potential is an abstract concept and to be able to relate it better to physical reality we brought in a new quantity which is known as fugacity.

What we will do in this lecture today is look at some examples trying to calculate partial molar properties given a sum of the partial molar properties, calculate other partial molar properties and also how to calculate fugacity of a pure species given an equation of state. We will look at a few more examples we have done some examples in the previous lectures, let us look at a few more examples in this lecture.

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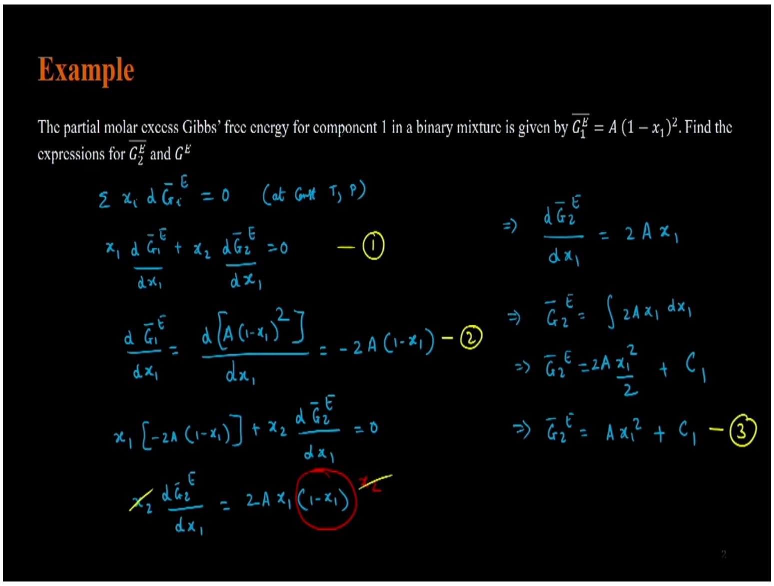

Example

The partial molar excess Gibbs' free energy for component 1 in a binary mixture is given by $\overline{G_1^E} = A(1-x_1)^2$. Find the expressions for $\overline{G_2^E}$ and G^E

$\sum x_i \, d\bar{G}_i^E = 0$ (at Cnst T, P)

$x_1 \frac{d\bar{G}_1^E}{dx_1} + x_2 \frac{d\bar{G}_2^E}{dx_1} = 0$ — ①

$\frac{d\bar{G}_1^E}{dx_1} = \frac{d\left[A(1-x_1)^2\right]}{dx_1} = -2A(1-x_1)$ — ②

$x_1\left[-2A(1-x_1)\right] + x_2 \frac{d\bar{G}_2^E}{dx_1} = 0$

$\cancel{x_2} \frac{d\bar{G}_2^E}{dx_1} = 2Ax_1 \boxed{(1-x_1)} \cancel{x_2}$

$\Rightarrow \frac{d\bar{G}_2^E}{dx_1} = 2Ax_1$

$\Rightarrow \bar{G}_2^E = \int 2Ax_1 \, dx_1$

$\Rightarrow \bar{G}_2^E = 2A\frac{x_1^2}{2} + C_1$

$\Rightarrow \bar{G}_2^E = Ax_1^2 + C_1$ — ③

So, to begin with; we are given the partial molar excess Gibbs free energy for component 1 in a binary mixture that is G 1 bar etcetera; remember this superscript E stands for excess quantity G is the Gibbs free energy the subscript 1 is for component 1 and the over bar on top of this indicates the partial molar property. So, in that sense G 1 bar E is the partial molar excess Gibbs free energy for component 1. We are given a relation for this in terms of A, a parameter A and the composition x 1.

So, in that sense a is a quantity which will depend on temperature and pressure of the mixture, but then for now we are looking at a given temperature and pressure G 1 bar E is given to be A times 1 minus x 1 whole square and we need to find expressions at the same conditions for G 2 bar E and the excess Gibbs free energy G E let us see how we can solve this problem.

Now, if you recall the way the two excess quantities are related to one another, G 1 bar E and G 2 bar E are related to one another at constant temperature and pressure is we are the Gibbs-Duhem equation which says x 1 d G 1 bar E plus x 2 d G 2 bar E equals 0 or sigma x i d G i bar E is 0. This is true at constant temperature and pressure. So, we will maintain the temperature and pressure conditions constant. At these conditions we want to know how G 1 bar E and G 2 bar E are related to one another.

So, if I expand this for a binary mixture it will be like I said x 1 d G one bar E plus x 2 d G 2 bar E is 0 and both G 1 bar E and G 2 bar E at these conditions of temperature and pressure are going to be functions of mole fraction. So, we will take this derivative with respect to one of the two mole fractions let us say x 1. So, Gibbs-Duhem equation now will read x 1 d G 1 bar E by d x 1 plus x 2 d G 2 bar E over d x 1 equals 0.

So, since I know G 1 bar E, I can use this relation and try to calculate G 2 bar E, let us see how we do that. Now, let me try to find the derivative first d of G 1 bar E over d x 1 from the given equation is derivative of A times 1 minus x 1 whole square, right; over d x 1. A is a parameter that is independent of composition so, we can bring that out. So, this will be 2 times or negative 2 times A times 1 minus x 1 the negative sign is because x 1 has a negative sign in front. So, this is the derivative I am looking at, right.

Let us give these equations some numbers. Let me call this as equation 1 and this is equation 2. What I will do is I will put the result from equation 2 into equation 1, right then equation 1 becomes x 1 times negative 2 A into 1 minus x 1 plus x 2 d G 2 bar E over d x 1 equals 0. I can substitute or I can simplify this equation and it will become x 2 d G 2 bar E over d x 1 is going to be the negative sign we will take it to the other side. So, it will be 2 A x 1 1 minus x 1 and remember 1 minus x 1 in here is since it is a binary mixture this is x 2 and that x 2 will cancel out with this x 2.

So, in effect what I will have is derivative of G 2 bar E over d x 1 is going to be simply 2 A x 1. This is the derivative I am looking at. Now, if I am interested in G 2 bar E; I can integrate this equation with respect to x 1 ah. So, this becomes G 2 bar E is going to be integral of 2 A x 1 d x 1. If I integrate it will be A times x 1 squared over 2 and then I have a 2 there plus some constant. Let us call that as C 1 and that makes G 2 bar E to be equal to A x 1 square plus a constant C 1.

We will come back and look at how to calculate this constant C 1, but that is the form of the expression we are looking at for G 2 bar A. Now, remember when we say constant it is a constant that is independent of composition because the integration is being performed with respect to composition; it might depend on temperature and pressure just as A can, right.

For now, we will hang on to this equation 3, what we will do next is try to calculate the total excess Gibbs or the molar excess Gibbs free energy G E, not the partial molar, but the molar excess Gibbs free energy of the mixture G E first and once we calculate G E we will try to look at properties of G E and see if we can estimate or if you can say something about this constant C 1.

So, we will move on to the next step for now. To get the molar property of the mixture G E; we will use what we call as this summability relation earlier.

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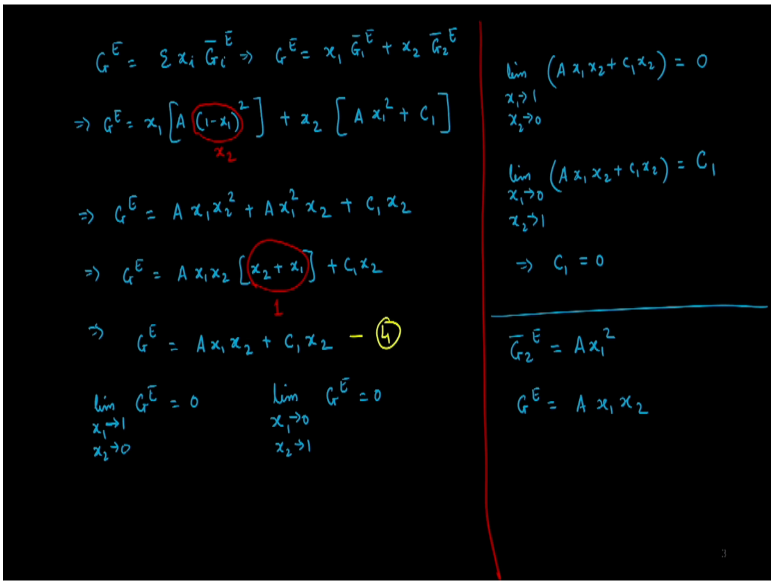

$$G^E = \sum x_i \bar{G}_i^E \Rightarrow G^E = x_1 \bar{G}_1^E + x_2 \bar{G}_2^E$$

$$\Rightarrow G^E = x_1\left[A \underbrace{(1-x_1)}_{x_2}{}^2\right] + x_2\left[A x_1^2 + C_1\right]$$

$$\Rightarrow G^E = A x_1 x_2^2 + A x_1^2 x_2 + C_1 x_2$$

$$\Rightarrow G^E = A x_1 x_2 \left[\underbrace{x_2 + x_1}_{1}\right] + C_1 x_2$$

$$\Rightarrow G^E = A x_1 x_2 + C_1 x_2 \quad - (4)$$

$$\lim_{\substack{x_1 \to 1 \\ x_2 \to 0}} G^E = 0 \qquad \lim_{\substack{x_1 \to 0 \\ x_2 \to 1}} G^E = 0$$

$$\lim_{\substack{x_1 \to 1 \\ x_2 \to 0}} (A x_1 x_2 + C_1 x_2) = 0$$

$$\lim_{\substack{x_1 \to 0 \\ x_2 \to 1}} (A x_1 x_2 + C_1 x_2) = C_1$$

$$\Rightarrow C_1 = 0$$

$$\bar{G}_2^E = A x_1^2$$

$$G^E = A x_1 x_2$$

And, if you recall for a multi component mixture; the summability relation is given by sigma x i G i bar E; sum of the partial molar properties weighted with the appropriate mole fractions. Now, for a binary mixture which is our case of interest here, it will be x 1 G 1 bar E plus x 2 G 2 bar E. This is the excess Gibbs free energy for the mixture. I have expressions for both G 1 bar E and G 2 bar E. So, let me bring those two equations here.

So, G E is going to be x 1 times G 1 bar E is A times 1 minus x 1 whole squared plus x 2 G 2 bar E is A times x 1 squared plus the constant C 1. Now remember we said this quantity in the first term this quantity here is x 2 because it is a binary mixture x 1 plus x 2 is 1. So, what this will make is G E is going to be equal to A times x 1 x 2 squared plus A times x 1 squared x 2 from the second term plus the constant C 1 times x 2. This would be the final expression I have for the excess Gibbs free energy of the mixture, right.

I can simplify this a little bit more G E is going to be A times x 1 x 2 from the first two terms for times x 2 plus x 1 plus C 1 times x 2 and because this is a binary mixture again x 1 plus x 2 is simply 1. So, that equation will then simplify to G E is going to be A times x 1 x 2 plus the constant C 1 times x 2 this is my expression for the total Gibbs free energy of the mixture 4. Let us call that as equation 4.

Now, we still have the constant C 1 in there which we could not get from the earlier integration. Let us see if I can estimate it now. Recall one of the behaviour for excess properties. We said the excess properties at both the pure component limits x 1 going to 1 or x 2 going to 1; the excess property needs to go to 0 because it is mostly made of either pure 1 or pure 2. If that be the case limit right limit of x 1 going to 0; G E or let us say x 1 going to 1, this will be the pure component limit for 1 which means x 2 is going to 0; G E should be equal to 0 and limit of x 1 going to 0 which is x 2 going to 1. This is pure component limit for to G E should be 0 again at both these limits the excess property should go to 0.

Now, if I apply these two requirements to equation 4, right let us see what happens; limit of x 1 going to 1, x 2 going to 0 G E is A x 1 x 2 plus C 1 x 2 and this will be since x 2 appears in both the terms and it is going to 0, this will go to 0. So, no problem with the first limit, it will be obeyed with by equation 4. If I look at the second limit limit of x 1 going to 0, x 2 going to 1; G E again is the x 1 x 2 plus C 1 x 2 from equation 4 x 1 is going to 0. So, the first term disappears x 2 is going to 1. So, the second term will be C 1 and by the requirement for an excess property this has to be 0 which implies the only way it can go to 0 is if this value of C 1 will be 0. So, that is how we estimate the constant C 1 it needs to be 0 in this scenario.

So, once we have the C 1 value I can go back and write both the partial molar property G 2 bar E from equation 3; if you look at equation 3 it is A x 1 square plus C 1 and now C 1 is determined to be 0. So, G 2 bar E will be simply A x 1 squared; will be simply A x 1 squared and G E the molar excess Gibbs free energy is going to be simply A times x 1 x 2. So, these are the two expressions we are looking at or we wanted to solve in this particular problem.

So, again essentially what we are using is relating the partial molar properties why are the Gibbs-Duhem equation it needs to be satisfied always. We are also imposing the thermodynamic requirements for the limits of at the limits of both the pure components the excess property should go to 0 and that is how we obtain the constant C 1 and the summability relation always needs to be obeyed, that is how we got G E from G 1 bar E and G 2 bar E. So, that summarizes the approach to solving this particular problem.

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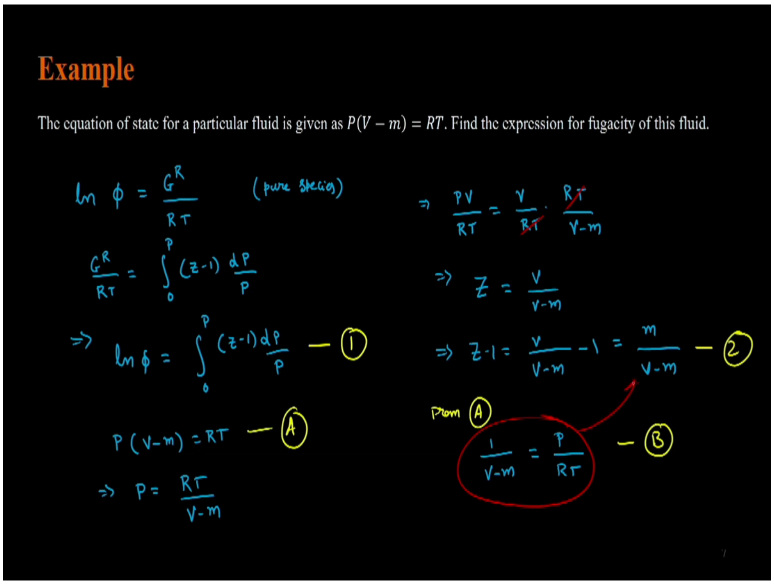

Example

The equation of state for a particular fluid is given as $P(V-m) = RT$. Find the expression for fugacity of this fluid.

$$\ln \phi = \frac{G^R}{RT} \quad (\text{pure species})$$

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

$$\Rightarrow \ln \phi = \int_0^P (Z-1)\frac{dP}{P} \quad — ①$$

$$P(V-m) = RT \quad — Ⓐ$$

$$\Rightarrow P = \frac{RT}{V-m}$$

$$\Rightarrow \frac{PV}{RT} = \frac{V}{R\cancel{T}} \cdot \frac{R\cancel{T}}{V-m}$$

$$\Rightarrow Z = \frac{V}{V-m}$$

$$\Rightarrow Z-1 = \frac{V}{V-m} - 1 = \frac{m}{V-m} \quad — ②$$

From Ⓐ

$$\frac{1}{V-m} = \frac{P}{RT} \quad — Ⓑ$$

Let us look at another example. So, in this problem we are interested in deriving an expression for fugacity given the equation of state. Equation of state is given as P times V minus m is RT. Remember that for an ideal gas PV is RT. For this particular gas the equation of state is P times V minus m as RT and we are interested in deriving an expression for fugacity.

Now, if you recall to do that the way we handle this particular problem is to write the expression for the fugacity coefficient ln phi and it turns out that this fugacity coefficient ln phi is related to the residual Gibbs free energy G R over RT. Now, this is for of course, a pure speciesand since it is just related to the residual Gibbs free energy the way we have handled it earlier if you recall what we did for a virial equation of state is write the residual Gibbs free energy in terms of the integral 0 to P Z minus 1 dP over P; Z is the compressibility factor and which we get from the equation of state and then we need to integrate that Z minus 1 by P from 0 to P.

So, what this essentially implies then is that the fugacity coefficient ln phi is also going to be given by the same expression Z minus 1 dP over P. So, then to obtain fugacity we first calculate the fugacity coefficient and then since fugacity coefficient is f over P; I can go back and write an expression for fugacity. First let us solve for the fugacity coefficient from the given equation of state.

So, I am going to a start from this expression or equation 1 which relates the fugacity coefficient to the compressibility factor what I will do is take the given equation of state and see if I can derive an expression for the compressibility factor. P times V minus m is RT which implies P is going to be RT by V minus V minus m. So, this implies PV over RT is going to be V by RT times RT by V minus m and if I cancel RT out, what I am left with is on the left hand side PV by RT is Z and on the right hand side RT cancels out and what I have left is V by V minus m. And, since I am interested in Z minus 1 it turns out to be V by V minus m minus 1 which will be m over V minus m, right. So, this is the value for Z minus 1.

Now, I am going to use this expression for Z minus 1 in equation 1, but the challenge is that equation 1 is in terms of pressure and equation 2 which gives me an expression for Z minus 1 is in terms of volume. So, I cannot directly use this in 1; what I need to do rather is convert equation 2 in terms of pressure somehow and then put it back in equation 1. Let us see how I do that.

Now, remember the equation of state itself is given by this expression here, let us call that as expression A. So, from A; 1 over V minus m is going to be P over RT, right, let us call that as B. So, I am just rewriting the given equation of state to get 1 over V minus m; let us call that as B now what I will do is I will put B in equation 2. So, essentially this is what I am going to I am going to a take this equation here and put it in this expression for Z minus 1 over there.

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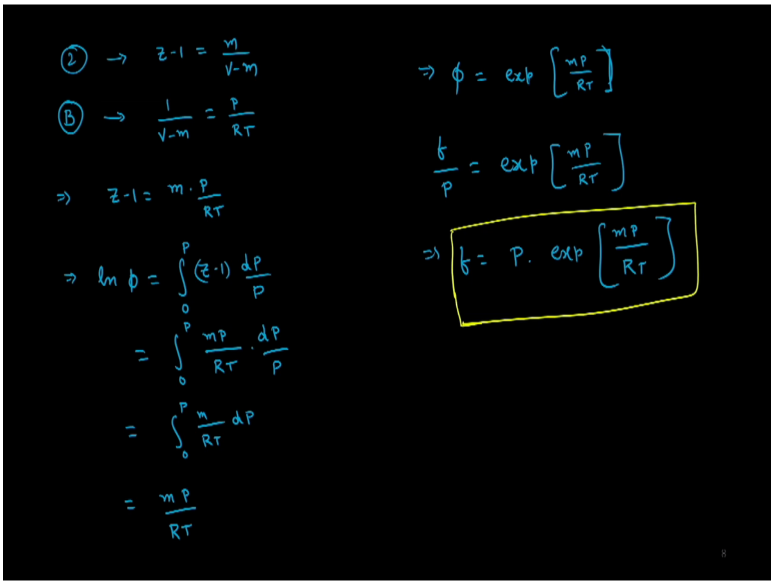

② $\rightarrow$ $Z-1 = \frac{m}{V-m}$

Ⓑ $\rightarrow$ $\frac{1}{V-m} = \frac{P}{RT}$

$\Rightarrow Z-1 = m \cdot \frac{P}{RT}$

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

$$= \int_0^P \frac{mP}{RT} \cdot \frac{dP}{P}$$

$$= \int_0^P \frac{m}{RT} dP$$

$$= \frac{mP}{RT}$$

$$\Rightarrow \phi = \exp\left[\frac{mP}{RT}\right]$$

$$\frac{f}{P} = \exp\left[\frac{mP}{RT}\right]$$

$$\Rightarrow \boxed{f = P.\ \exp\left[\frac{mP}{RT}\right]}$$

If I do that write equation 2 reads Z minus 1 is m by V minus m equation B reads 1 by V minus m is 1 by V minus m is P over RT right. So, I am going to put B in equation 2 which implies Z minus 1 is going to be m times 1 by V minus m is P over RT.

So, now I have rewritten Z minus 1 in terms of P alone. So, I can easily use this equation in one to be able to integrate Z minus 1 with respect to P,. So, ln phi is from equation 1 is integral 0 to P Z minus of 1 dP over P because Z minus 1 is m times P over RT this will be 0 to P m times P over RT dP over P and. So, that is essentially integral 0 to P m over RT dP, the parameter m R and T are independent of pressure. So, they can come out and this integral evaluates to simply mP over RT. So, that is the expression we have for ln phi and if you recall this is exactly identical to a virial equation of state with only the second virial coefficient.

Now, once I have expression for ln phi I can calculate phi which is going to be exponential of mP over RT and I can write phi as f over P would be fugacity coefficient is fugacity over the pressure. So, the fugacity itself is going to be the pressure times exponential of mP over RT. So, that is the expression I am looking at for this particular scenario. Expression for fugacity in terms of the given equation of state; the pressure, the temperature and the parameter for the equation of state which is m.

So, there are a couple of tricks we have done to get this solution. The first thing is relate the fugacity to Gibbs free energy and because of the residual Gibbs free energy and because we already know the expression for residual Gibbs free energy in terms of the parameters for equation of state I can rewrite ln phi in terms of Z that is the first thing we have done and once we went on to obtain an expression for Z minus 1 as in equation 2 we realize that I cannot use equation 2 directly in equation 1 because equation 1 is integration with respect to pressure equation 2 is something we have in terms of volume.

These are simple equations, so, it is easy to perform the mathematical manipulation here to rewrite 2 in terms of pressure which is what we have done. We have rewritten the given equation of state to get 1 over V minus m in terms of the pressure alone without involving any volume. Once I have that in equation B, I can go back rewrite the suppression for Z minus 1; compressibility factor minus 1 in terms of P alone and once I have it only in terms of P; I can come back and integrate this expression only in terms of P, obtain the final result and then calculate the fugacity coefficient followed by the value for fugacity.

Now, if it is not easy to do this manipulation and obtain an expression for Z minus 1 only in terms of P then it will not be possible to do this particular integration and we will have to resort to other methods. Remember, we have done something like that for residual Gibbs free energy when there is a cubic equation of state. There we write the expression for residual Gibbs free energy in terms of volume only without bringing in the pressure. So, it is important to have everything inside this integral for residual Gibbs free energy or the fugacity coefficient either only in terms of pressure without involving the volume or only in terms of volume without involving the pressure. It is important to have it in one or the other way then we can go ahead and perform the integration to obtain the result we are interested in.

So, that completes this particular problem. Let us move on to the next one.

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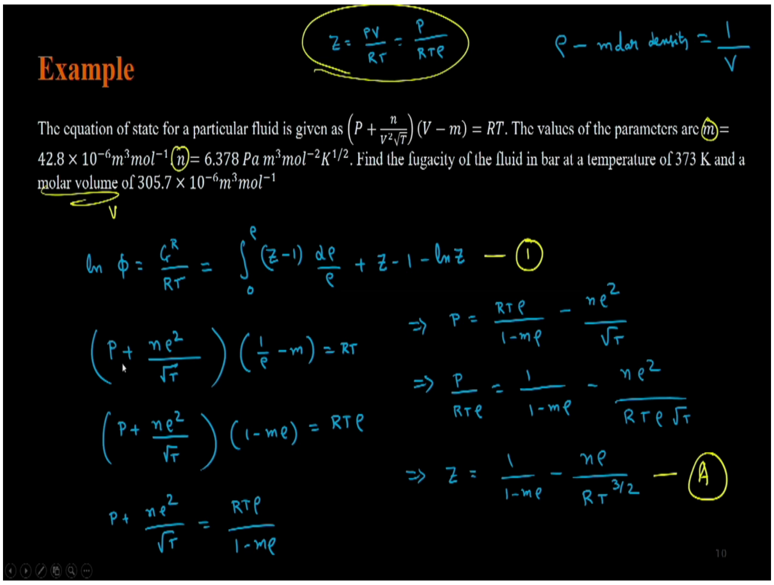

Example

$Z = \frac{PV}{RT} = \frac{P}{RT\rho}$

ρ – molar density $= \frac{1}{V}$

The equation of state for a particular fluid is given as $\left(P + \frac{n}{V^2\sqrt{T}}\right)(V - m) = RT$. The values of the parameters are $m =$ $42.8 \times 10^{-6} m^3 mol^{-1}$ $n = 6.378\ Pa\ m^3 mol^{-2} K^{1/2}$. Find the fugacity of the fluid in bar at a temperature of 373 K and a molar volume of $305.7 \times 10^{-6} m^3 mol^{-1}$

V

$$\ln\phi = \frac{G^R}{RT} = \int_0^{\rho} (Z-1)\frac{d\rho}{\rho} + Z - 1 - \ln Z \quad — ①$$

$$\left(P + \frac{n\rho^2}{\sqrt{T}}\right)\left(\frac{1}{\rho} - m\right) = RT$$

$$\left(P + \frac{n\rho^2}{\sqrt{T}}\right)(1 - m\rho) = RT\rho$$

$$P + \frac{n\rho^2}{\sqrt{T}} = \frac{RT\rho}{1 - m\rho}$$

$$\Rightarrow P = \frac{RT\rho}{1-m\rho} - \frac{n\rho^2}{\sqrt{T}}$$

$$\Rightarrow \frac{P}{RT\rho} = \frac{1}{1-m\rho} - \frac{n\rho^2}{RT\rho\sqrt{T}}$$

$$\Rightarrow Z = \frac{1}{1-m\rho} - \frac{n\rho}{RT^{3/2}} \quad — Ⓐ$$

Here we have an equation of state which is something similar to the previous expression with an additional term added to P here. P plus n by V square square root of T times V minus m is RT this is our equation of state. The values of the parameters m and m, m and n for this particular equation of state are given to us. What we are interested in is finding the fugacity of the particular fluid in bar at a given temperature which is 373 Kelvin and the molar volume is 305 10 power minus 6 meter cube per mole. So, the temperature and molar volume are given to us. Once temperature and molar volume are given we can always go back and use the equation of state to find the pressure, but so, everything else is fixed of course, because it is a pure species, but for now what we are interested in is calculating the fugacity of the fluid given this particular equation of state.

Let us see how we solve this particular problem. What we will do again is try to write the equation for fugacity coefficient first right and let us write that ln phi is G R over RT. And, now as in the previous problem I can use an expression for G R over RT in terms of the compressibility factor Z, but then I should be able to write the final expression inside the integral only in terms of pressure which is not going to be possible in this scenario because it is cubic in volume.

So, we will have to use the other expression we have derived earlier for the residual Gibbs free energy and that expression if you recall was in terms of the density and it is written as integral of 0 to rho. The density rho which is inverse of the molar volume; Z minus 1 d rho over rho plus Z minus 1 minus ln Z. This is the expression we have written for residual Gibbs free energy when we had a cubic equation of state. We will use that expression here.

Now, this is a cubic equation of state, but it does not fall in one of those four equations of state cubic equations of state we had in the table. Although we can rewrite in that form with a little bit of manipulation it is much easier we handle it directly ah. The only four equations of state we had in the table were Van der Waals, Redlich-Kwong, Soave-Redlich-Kwong and Peng-Robinson and this does not fall in one of those four categories. So, what we will do is take the expression for the residual Gibbs free energy directly in terms of density and try to use the equation of state and integrate to get an expression for ln phi. Once we have the expression we will plug in the numbers calculate the fugacity coefficient, and hence the fugacity, alright.

So, this is the expression we start with right G R over RT is this integral. So, to be able to do the integration then I need to write Z minus 1 only in terms of density and I need to eliminate the pressure completely and remember like I said density is 1 over the molar volume. So, what I will first do is rather write the equation of state in terms of density rather instead of the volume.

So, P plus n times rho square because 1 over V square is rho squared the density is inverse of molar volume square root of T 1 over rho minus m. So, m is molar density maybe we should write it down. Sorry, rho is molar density right rho is molar density and this is 1 over V that is the expression we are using to rewrite the equation of state this is RT; RT, right.

So, if you rewrite this particular expression then P plus n rho squared over square root of T times 1 minus m rho is going to be RT rho, right and what we are interested in is the compressibility factor Z. So, let us see if I can derive an expression for Z. now, Z is PV over RT as you know and this is going to be P over RT rho then in terms of density. So, we are interested in deriving an expression for this. So, what I will do is rewrite the equation of state. Let us let us move this to the top Z is PV over RT. So, that is going to be in terms of density it will be P over RT rho.

So, we will rewrite this P plus n rho squared over square root of T is going to be RT rho over 1 minus m rho and that implies P is going to be RT rho over 1 minus m row minus m row square by square root of T and since we are interested in d what I will do is divide this by RT rho on both sides. P over RT rho is going to be 1 over 1 minus m rho; RT rho in the numerator and denominator get cancelled minus and rho squared over RT rho square root T. So, this would be Z will be equal to 1 by 1 minus m rho minus n rho by RT to the power 3 over 2. I notice that I have cancelled the rho in the denominator with one of the rho in the numerator. So, that leaves row in the numerator and then T times root T is T to the power 3 by 2.

So, this is the expression we have for Z the compressibility factor from the given equation of state we are interested in the integral Z minus 1 d rho over rho what I will do is from this I will first calculate Z minus 1.

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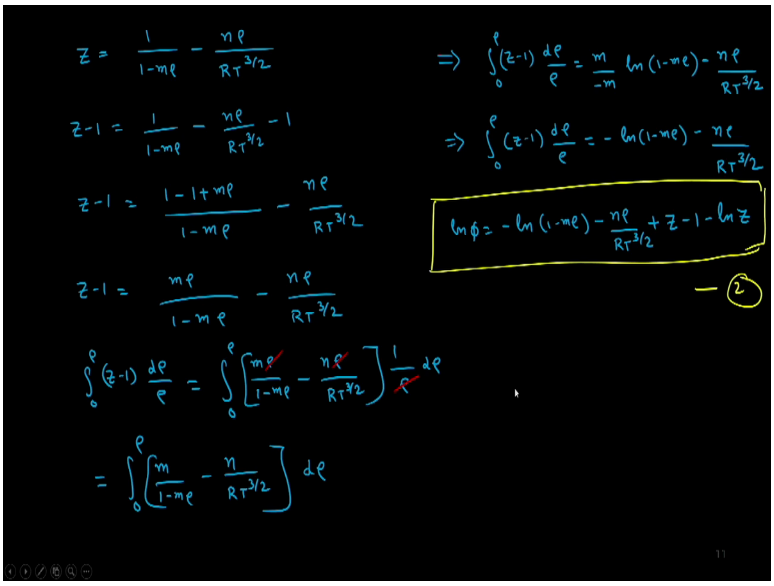

$$Z = \frac{1}{1-m\rho} - \frac{n\rho}{RT^{3/2}}$$

$$Z-1 = \frac{1}{1-m\rho} - \frac{n\rho}{RT^{3/2}} - 1$$

$$Z-1 = \frac{1-1+m\rho}{1-m\rho} - \frac{n\rho}{RT^{3/2}}$$

$$Z-1 = \frac{m\rho}{1-m\rho} - \frac{n\rho}{RT^{3/2}}$$

$$\int_0^\rho (Z-1)\frac{d\rho}{\rho} = \int_0^\rho \left[\frac{m\cancel{\rho}}{1-m\rho} - \frac{n\cancel{\rho}}{RT^{3/2}}\right]\frac{1}{\cancel{\rho}}\,d\rho$$

$$= \int_0^\rho \left[\frac{m}{1-m\rho} - \frac{n}{RT^{3/2}}\right] d\rho$$

$$\Rightarrow \int_0^\rho (Z-1)\frac{d\rho}{\rho} = \frac{m}{-m}\ln(1-m\rho) - \frac{n\rho}{RT^{3/2}}$$

$$\Rightarrow \int_0^\rho (Z-1)\frac{d\rho}{\rho} = -\ln(1-m\rho) - \frac{n\rho}{RT^{3/2}}$$

$$\boxed{\ln\phi = -\ln(1-m\rho) - \frac{n\rho}{RT^{3/2}} + Z - 1 - \ln Z} \quad \text{— ②}$$

So, let us rewrite that expression we had for Z. Z is 1 by 1 minus m rho minus n rho by RT to the power 3 over 2. Z minus 1 is going to be 1 by 1 minus m rho minus n rho by RT to the power 3 over 2 minus 1. So, that would be 1 minus 1 plus m rho by 1 minus m rho I am combining the first and the last terms RT to the power 3 over 2. So, Z minus 1 then is going to be m rho by 1 minus m rho minus n rho by RT to the power 3 by 2.

Now, notice that Z minus 1, I have written it only in terms of the density there is no pressure term at all. So, it is rather easy to integrate. Now, the first term I have an equation for the residual Gibbs free energy or the fugacity coefficient is integral of Z minus 1 d rho over rho. So, let me handle that first term. Integral of 0 to rho Z minus of 1 d rho over rho is going to be integral of 0 to rho m rho by 1 minus m rho minus n rho by RT to the power 3 over 2 1 by rho T rho, right and that will simplify to integral 0 to rho m by 1 minus m rho minus n by RT to the power 3 over 2 d rho. The rho here will get cancelled with this rhos. So, that is the expression I have for the integral.

And, if I simplify that integral what I will end up with what I will end up with is integral of 0 to rho Z minus of 1 d rho over rho is going to be the integral of the first term will be m by minus m ln of 1 minus m rho and integral of the second term is going to be n rho by RT to the power 3 over 2. That will be the value of the integral and if you simplify that it will be integral of 0 to rho Z minus of 1 d rho over rho is going to be negative ln 1 minus m rho minus m rho by RT to the power 3 over 2, right.

So, this is the final in expression for the integral evaluated in terms of densities for the given equation of state. What we will do is, take this expression and put it in equation 1 to get an expression for ln; ln phi. So, ln phi then is going to be the integral value minus ln 1 minus m rho minus n rho by RT to the power 3 over 2 plus Z minus 1 minus ln Z. This is the final expression we have for the fugacity coefficient, let us call that as equation 2.

Now, if you look at this equation all we have all we have is the densities and the compressibility factors that appear on the on the right hand side. Now, to be able to calculate a numerical value than I need both the density as well as the compressibility factor Z, alright. So, let us see what numbers are given to us. I have the values of the parameters m and n here. I have mm I have and what I am given is the molar volume V. So, I need to use this expression 1 over V to calculate the density rho. I do not have I do not have the compressibility factor, but what I can do you is use this expression rewritten form of equation of state let us call that as A; I can use this expression A to calculate the compressibility factor Z and again A involves only the temperature and the density apart from the two parameters m and n.

So, that is going to be our strategy then from the given values of the temperature m and n as well as the molar volume we will convert it into density once we have these we can calculate the compressibility factor Z in terms of A from equation A and then we will use that value of Z and the density and the other given values to calculate ln phi, alright.

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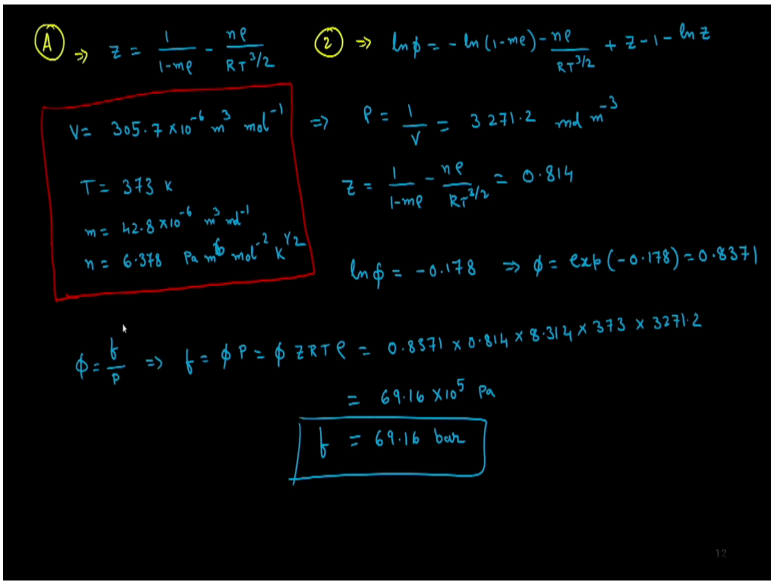

$$Ⓐ \Rightarrow Z = \frac{1}{1-m\rho} - \frac{n\rho}{RT^{3/2}} \qquad ② \Rightarrow \ln\phi = -\ln(1-m\rho) - \frac{n\rho}{RT^{3/2}} + Z - 1 - \ln Z$$

$$\boxed{\begin{array}{l} V = 305.7 \times 10^{-6}\ m^3\ mol^{-1} \\ T = 373\ K \\ m = 42.8 \times 10^{-6}\ m^3\ mol^{-1} \\ n = 6.378\ Pa\ m^6\ mol^{-2}\ K^{1/2} \end{array}} \Rightarrow \rho = \frac{1}{V} = 3271.2\ mol\ m^{-3}$$

$$Z = \frac{1}{1-m\rho} - \frac{n\rho}{RT^{3/2}} = 0.814$$

$$\ln\phi = -0.178 \Rightarrow \phi = \exp(-0.178) = 0.8371$$

$$\phi = \frac{f}{P} \Rightarrow f = \phi P = \phi Z R T \rho = 0.8371 \times 0.814 \times 8.314 \times 373 \times 3271.2$$

$$= 69.16 \times 10^5\ Pa$$

$$\boxed{f = 69.16\ bar}$$

So, let us then rewrite these two equations on the next slide. Equation A is a rewritten form of the given equation of state in terms of the compressibility factor Z is 1 by 1 minus m row minus n rho by RT to the power 3 over 2; 1 by 1 minus m rho minus n rho by RT to the power 3 over 2. And, equation 2 we had an expression for ln phi and it is given as ln phi equals minus ln 1 minus m rho minus n rho by RT to the power 3 over 2, right plus Z minus 1 minus ln ln Z. So, this is equation 2 for the fugacity coefficient.

So, from the given data we need to calculate the density and the compressibility factor then. The given data say is the molar volume V is 305.7 into 10 to the power negative 6 meter cube per mole. What this implies is the density rho is going to be 1 over the molar volume and that value evaluates to be 3271.2 moles per meter cube. So, we are simply taking the inverse of the molar volume to get the molar density or rho. Once I have rho we also know the temperature T is given to be 373 Kelvin.

So, what I will do is I will put them in a box. We are also given the two parameters m and n. We will use SI units throughout. So, m is 42.8 and n is 6.378 into 10 power minus 6 meter cube per mole Pascal meter cube per mole inverse Kelvin; meter cube mole Pascal meter cube meter power 6 and mole to the power 2 Kelvin to the power half. These are the values given to us. So, I will just put them in this box so that we know that these are the given this is the given data and from this data what I have calculated is the density rho first.

The second thing we will calculate is use this density to calculate Z, from equation 2 it is 1 by 1 minus m rho minus n rho by RT to the power 3 over 2 and this turns out to be 0.8145 substitute the numerical values. Once I have Z and rho I can go back and use equation 2 to calculate ln phi and that value of ln phi from equation 2 turns out to be negative 0.78, right negative 0.178 and what that means, is phi is going to be e to the power of this value negative 0.178 the turns out to be 0.8371. So, I have calculated the value of the fugacity coefficient from the given information.

The next thing we are interested in is in calculating the fugacity and recall that phi is f over P which implies the fugacity f is going to be the fugacity coefficient times the pressure. I have the fugacity coefficient, but I do not have the value for the pressure P, right and what we will do is we will either use the given equation of state or I can use the use the expression for the or the value of the compressibility factor to calculate the fugacity coefficient, right.

And, if you recall remember that the compressibility factor is related to the pressure. It is Z RT rho right; pressure is Z RT rho I have values of everything else. So, what we will do is write this as phi times Z RT rho. I have values for everything now 0.8371 times Z is 0.814 times R is 8.314 times T is 373 times rho is 3271.2. And, if you simplify the numerical value it turns out to be 69.16 into 10 power 5 Pascals or 69.16 bar. So, that is the value of fugacity I am looking for.

So, let us quickly summarize this problem what we have done to obtain the value of the fugacity. We have taken the equation of state; we realized that this equation of state cannot be written only in terms of pressure because it is cubic in volume. So, we have decided to use equation 1 for GR by RT which is same as ln phi and we have written the given equation of state in terms of density and obtain the value for the compressibility factor Z and hence Z minus 1. Once we get that value we ensured that Z minus 1 is only in terms of density. So, that I can go back and use equation 1 to do the integration we integrated it in terms of density and then used it to obtain the expression for ln phi.

Once we have the expression we have to calculate the numerical value. So, we use the given data to obtain to obtain these numerical values we had to do a couple of manipulations; 1; to calculate density from the given molar volume. 2; to calculate the compressibility factor using the equation of state and finally, to calculate fugacity we realize that we did not have the pressure, we rewrite it in terms of the compressibility factor Z. So, that we have pressure and from that we calculate the fugacity. So, that completes this particular problem.

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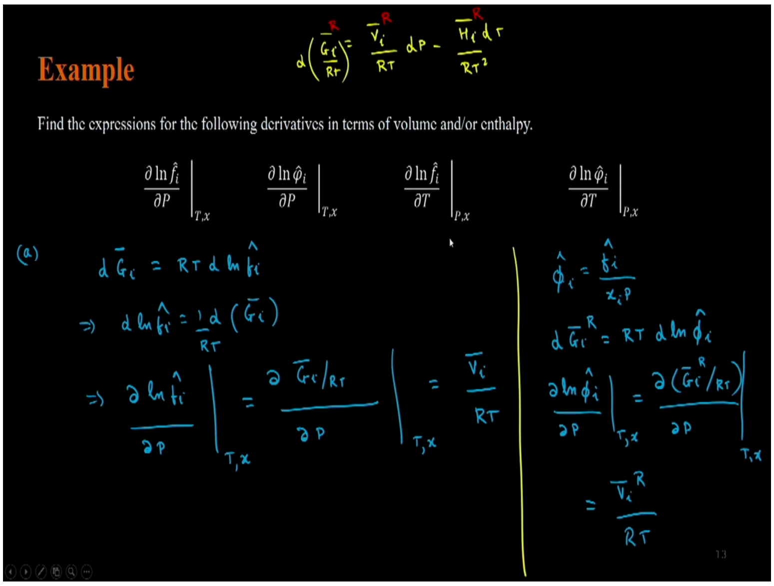

Example

$$d\left(\frac{\bar{G}_i^R}{RT}\right) = \frac{\bar{V}_i^R}{RT}\,dP - \frac{\bar{H}_i^R\,dT}{RT^2}$$

Find the expressions for the following derivatives in terms of volume and/or enthalpy.

$$\left.\frac{\partial \ln \hat{f}_i}{\partial P}\right|_{T,x} \qquad \left.\frac{\partial \ln \hat{\varphi}_i}{\partial P}\right|_{T,x} \qquad \left.\frac{\partial \ln \hat{f}_i}{\partial T}\right|_{P,x} \qquad \left.\frac{\partial \ln \hat{\varphi}_i}{\partial T}\right|_{P,x}$$

(a)

$$d\bar{G}_i = RT\,d\ln \hat{f}_i$$

$$\Rightarrow d\ln \hat{f}_i = \frac{1}{RT}\,d\left(\bar{G}_i\right)$$

$$\Rightarrow \left.\frac{\partial \ln \hat{f}_i}{\partial P}\right|_{T,x} = \left.\frac{\partial\, \bar{G}_i/RT}{\partial P}\right|_{T,x} = \frac{\bar{V}_i}{RT}$$

$$\hat{\phi}_i = \frac{\hat{f}_i}{x_i P}$$

$$d\bar{G}_i^R = RT\,d\ln \hat{\phi}_i$$

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

$$= \frac{\bar{V}_i^R}{RT}$$

Let us look at another example. What we are interested in is getting expressions for the following derivatives in terms of volume or enthalpy. ln f i hat right if you recall ln f i hat is defined by this derivative d G i is RT d ln f i hat. The fugacity of species i in the mixture f i hat is related to the Gibbs free energy G i d G i bar or the partial molar Gibbs free energy d G i bar, right; that is how we define the fugacity. It is related to the chemical potential. This comes directly from the definition for fugacity of species i in the mixture.

Now, if I take the derivative with respect to pressure at constant temperature and x right, the other way of writing it is d ln f i hat is simply d of G i bar 1 over RT. Now, if I am taking the derivative of this with respect to the pressure at constant temperature and x derivative of ln f i hat over pressure at constant temperature and x and because temperature is constant it can go into the derivative. So, it will be derivative of G i bar over RT over pressure at constant T and x.

And, if you recall the fundamental property relation which I will write on the top here; we said d G i bar is V i bar or d G i bar over RT is V i bar over RT dP minus H i bar over RT square d T plus sigma mu i d n i. This is the one of the forms of the fundamental property relations which we have written earlier this is actually derivative of the total value G i bar over RT.

So, now if I am interested in this derivative with respect to P at T and x, T; well, I am sorry this should have been not d n i bar sigma mu i d x i, right we are writing the molar properties. So, this would be rather x i. Now if I take the derivative with respect to T and x then the second and the third terms drop out and the derivative with respect to pressure will simply be V i bar over RT and since this also happens to be the derivative for ln of f i hat over P that is what we have, right. This is for part A, right.

Now, if I look at part B, it is not the derivative for the fugacity, but rather it is the derivative for the fugacity coefficient. Now, if you recall derivative now if you recall the fugacity coefficient phi i hat is related to f i hat we have this equation y i P or x i P since we are writing using x for mole fraction let us write it as x i P, right. Now, then the G i bar R will be related to d ln phi i hat, right. So, the residual Gibbs for free energy will be related to the fugacity coefficient or sorry, the partial molar residual Gibbs free energy rather would be related to the fugacity coefficient whereas, the partial molar Gibbs free energy is going to be related to the fugacity itself. So, that is all that is the only difference.

And, once we identify that difference I could write the fundamental property relation for residual Gibbs free energy also and that would simply add on a residual term on the top, right, a residual term there at constant T and x this term drops out anyway, right. That is the fundamental property relation at constant composition for a system and hence the derivative with respect to pressure will simply be and hence the derivative of ln phi i hat with respect to pressure at constant T and x will be derivative of G i bar R over RT with respect to pressure at constant T and x and that will simply be V i bar R over RT.

So, the essential difference between the two derivatives the first and the second one for fugacity, the other one for fugacity coefficient is that the first case it is the molar; partial molar volume V i bar over RT and in the second case it is residual partial molar volume which is V i bar R over RT, that is the only difference between these two derivatives.

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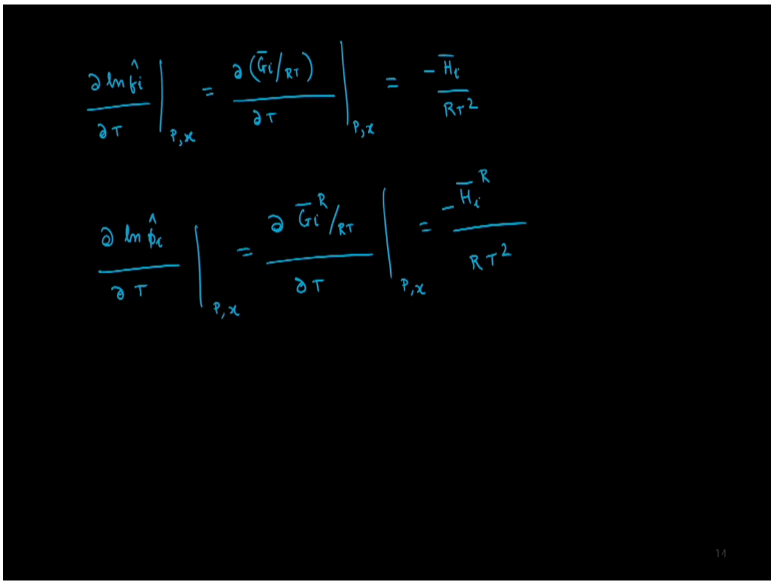

$$\left.\frac{\partial \ln \hat{f}_i}{\partial T}\right|_{P,x} = \left.\frac{\partial (\bar{G}_i/RT)}{\partial T}\right|_{P,x} = \frac{-\bar{H}_i}{RT^2}$$

$$\left.\frac{\partial \ln \hat{\phi}_i}{\partial T}\right|_{P,x} = \left.\frac{\partial \bar{G}_i^R/RT}{\partial T}\right|_{P,x} = \frac{-\bar{H}_i^R}{RT^2}$$

Now, the third and the fourth derivatives are with respect to temperatures. I am interested in the derivative of ln f i hat over temperature at constant P and x. And, again we will identify this as the derivative of G i bar over RT with respect to temperature at constant P and x just like we did before the derivative with respect to pressure. This time it is with respect to temperature, but it is still related to the derivative of G i bar by RT and because of the fundamental property relation this derivative would turn out to be negative of H i bar over RT square, right.

So, the derivative with respect to temperature for the algorithm of fugacity of fugacity is H i bar over RT square and similarly, for fugacity coefficient just like the earlier scenario for pressure it will be the derivative of G i bar R over RT with respect to temperature at constant P and x and that will be H i bar R the residual partial molar enthalpy over RT square negative H i bar R over RT squared.

So, these are the four derivatives we are interested in. All of them can be obtained readily from the fundamental property relation and identifying that fugacity or fugacity coefficient are related to the partial molar Gibbs free energy or residual partial molar Gibbs free energy.

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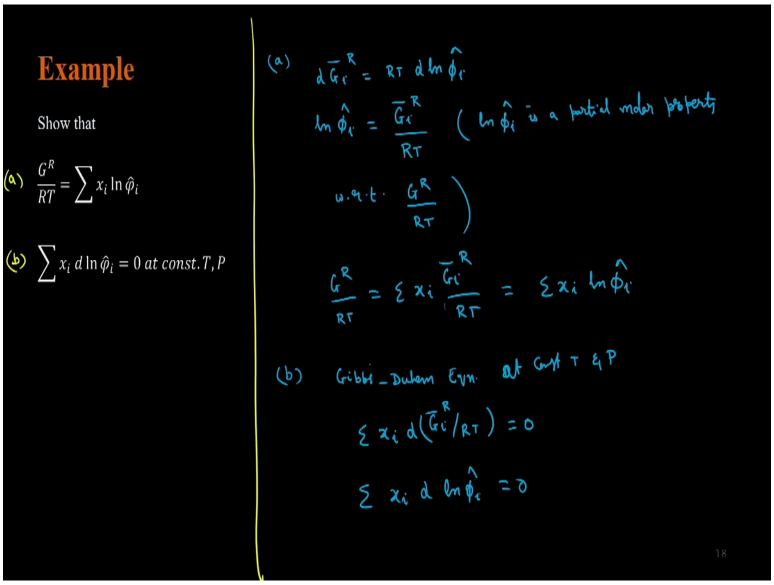

Example

Show that

(a) $\frac{G^R}{RT} = \sum x_i \ln \hat{\varphi}_i$

(b) $\sum x_i \, d \ln \hat{\varphi}_i = 0$ at const. T, P

(a) $d\bar{G}_i^R = RT \, d \ln \hat{\phi}_i$

$\ln \hat{\phi}_i = \frac{\bar{G}_i^R}{RT}$ ($\ln \hat{\phi}_i$ is a partial molar property w.r.t. $\frac{G^R}{RT}$)

$\frac{G^R}{RT} = \sum x_i \frac{\bar{G}_i^R}{RT} = \sum x_i \ln \hat{\phi}_i$

(b) Gibbs-Duhem Eqn. at const T & P

$\sum x_i \, d(\bar{G}_i^R/RT) = 0$

$\sum x_i \, d \ln \hat{\phi}_i = 0$

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Let us solve one last problem for today before we wind up. We want to show that the residual Gibbs free energy G R by RT is sigma x i ln phi i hat and the second part we want to show that sigma x i d ln phi i hat at constant T and P is 0. Let us see how we do that. It is almost; it is very easy if we recall what we have done in the previous problem. So, let us give this some numbers a and b. Let us look at part a first.

Now, recall that d G i bar R the residual Gibbs free energy is related to the fugacity coefficient via this relation, right and by definition we make sure that for ideal gas the residual Gibbs free energy is 0. So, by definition ideal gas the fugacity coefficient will be equal to 1. So, if we take that then essentially ln phi i hat is G i bar R over RT, right. ln phi i hat is a partial molar property with respect to G R over RT.

So, I can write that G R over RT is a mobility relation is sigma x i G i bar R over RT and I can replace this G i bar over RT with ln phi i. So, it will become x i ln phi i hat. So, that is how we did have this particular expression essentially it is the part that we identify ln phi i hat is a partial molar property just like G i bar R over RT and it is related to G R over RT. So, we use the summability relation to obtain this particular expression. Once we identify this the second part is almost straight forward ln phi i hat is a partial molar property and by Gibbs-Duhem equation at constant temperature and pressure sigma x i d m i bar in this case let us say the partial molar property we are interested in is the residual Gibbs free energy G i bar R over RT needs to be equal to 0, right.

Since G i bar R over RT is a partial molar property sigma x i the derivative of that should be equal to 0 at constant temperature and pressure we are the Gibbs-Duhem equation. And, because we have identified d G i bar R over RT as d ln phi i hat, it simply means that sigma x i d ln phi i hat also needs to be equal to 0 at constant temperature and pressure. So, this automatically follows from the definition of the fugacity coefficient and the Gibbs-Duhem equation.

So, that completes this particular problem. Thank you for watching this video today. We will come back in the next class and talk; continue our discussion on solution thermodynamics.

Thank you.