Chemical Engineering Thermodynamics
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Lecture – 24
Fugacity

Hello and welcome back. In this lecture, today we are going to look at a quantity called as Fugacity. Fugacity comes from a root word which means the tendency to escape and this has been developed to characterize vapor liquid equilibrium in an easier fashion. Before we get into details of fugacity, let us quickly revise what we have done so far.

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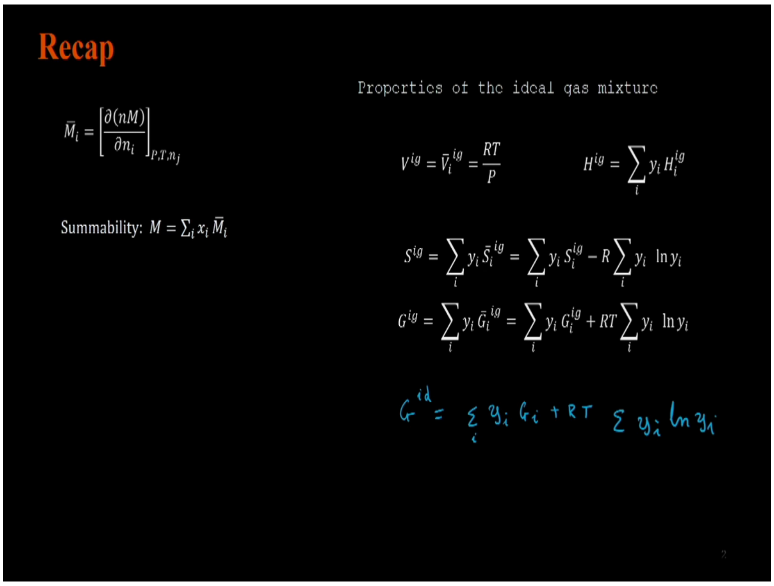

Recap

$$\bar{M}_i = \left[\frac{\partial(nM)}{\partial n_i}\right]_{P,T,n_j}$$

Summability: $M = \sum_i x_i \bar{M}_i$

Properties of the ideal gas mixture

$$V^{ig} = \bar{V}_i^{ig} = \frac{RT}{P} \qquad H^{ig} = \sum_i y_i H_i^{ig}$$

$$S^{ig} = \sum_i y_i \bar{S}_i^{ig} = \sum_i y_i S_i^{ig} - R\sum_i y_i \ln y_i$$

$$G^{ig} = \sum_i y_i \bar{G}_i^{ig} = \sum_i y_i G_i^{ig} + RT\sum_i y_i \ln y_i$$

$$G^{id} = \sum_i y_i G_i + RT \sum y_i \ln y_i$$

We are looking at solution thermodynamics or thermodynamics of mixtures of chemical species we talked about partial molar properties, we talked about how the total property of a mixture is related to the partial molar property, we looked at properties of ideal gas mixtures and we also defined an ideal solution which has similar characteristics as that of an ideal gas mixture. For example, G for an ideal solution is same as it is counterpart for the ideal gas mixture.

So, G for an ideal solution is sigma y i G i for the pure species plus RT sigma y i ln y i and based on this we can derive the other thermodynamic properties such as the entropy for an ideal solution enthalpy and volume for an ideal solution as well as we have defined a host of other thermodynamic properties such as a property changes upon mixing etcetera.

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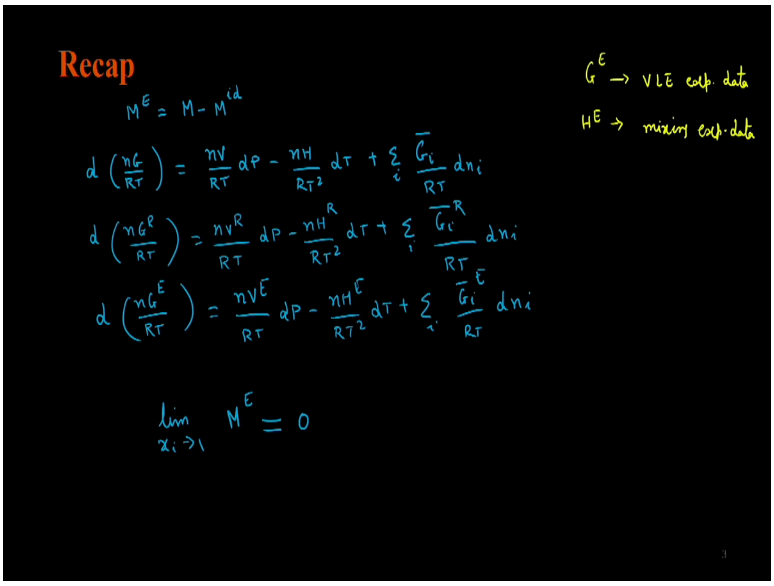

Recap

$$M^E = M - M^{id}$$

$$d\left(\frac{nG}{RT}\right) = \frac{nV}{RT}dP - \frac{nH}{RT^2}dT + \sum_i \frac{\bar{G}_i}{RT}dn_i$$

$$d\left(\frac{nG^R}{RT}\right) = \frac{nV^R}{RT}dP - \frac{nH^R}{RT^2}dT + \sum_i \frac{\bar{G}_i^R}{RT}dn_i$$

$$d\left(\frac{nG^E}{RT}\right) = \frac{nV^E}{RT}dP - \frac{nH^E}{RT^2}dT + \sum_i \frac{\bar{G}_i^E}{RT}dn_i$$

$$\lim_{x_i \to 1} M^E = 0$$

$G^E \to$ VLE exp. data

$H^E \to$ mixing exp. data

In addition to this in the previous lecture we have also looked at a quantity known as an excess property which is essentially the deviation from the ideal solution behavior, we defined it as for any thermodynamic property we defined it as m minus M ideal. We also looked at the fundamental property relations in terms of Gibbs free energy as the generating function d nG by RT we said is nV by RT dP minus nH by RT square dT plus sigma over i let us write it as G i bar by RT d n i.

In addition we can also write similar equations for the residual Gibbs free energy. All the quantities change into residual quantities in this case and we get this by subtracting an analogous equation for ideal gas plus sigma over i G i bar R which is partial molar residual Gibbs free energy d n i. And if we subtract the ideal solution equation from this what we get is d n G E by RT from the first equation of course, is nV E by RT dP minus nH E by RT square dT plus sigma over i G i bar E by RT d n i. And based on this we can write a host of derivatives such as derivative of n G over RT with respect to temperature will be negative nH by RT square and so on of course, that derivative is taken at constant pressure and composition.

So, we looked at the similarities between the residual properties and excess properties and we also talked about the nature of excess properties we said at the pure component limit x i going to 1 M E the excess property should go to 0 because it will hit the pure component limit both M and M for the ideal solution approach the pure component limit, so, that difference will go to 0. This is true at all the corresponding pure component limits for each of the species.

In addition we also said that there is no other thermodynamic restriction for variation of G E or H E with composition we have seen that G E can be positive or negative depending on whether the system has positive deviations from ideal solution behavior or negative deviations from ideal solution behavior. We also said that H E, can be greater than or less than G E it can be a positive quantity negative quantity and it can have a wide variety of behavior as we have seen in the previous lecture.

Now, the task in front of us is to be able to characterize the behavior of mixtures or solutions and to be able to do that we have introduced a quantity known as excess quantity which is essentially the deviation from ideal solution behavior and to be able to characterize excess quantity we want to use Gibbs free energy as the generative function or G E as the generating function. And if you recall in the last class we said G E is obtained from vapor liquid equilibrium experimental data. It is obtained from experimental data for vapor liquid equilibrium.

In addition, H E is obtained from mixing data or experimental data for mixing of two chemical species. If that be the case to be able to understand the behavior of systems which are not ideal we want to quantify the excess quantity or excess Gibbs free energy, we need to understand the vapor liquid equilibrium behavior of substances or mixture of substances. So, to be able to do that let us quickly recall what we discussed about vapor liquid equilibrium.

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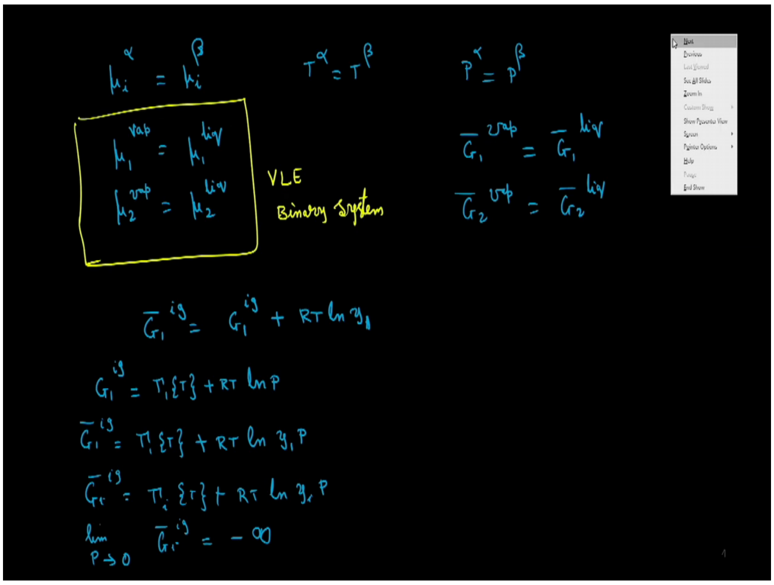

$$\mu_i^{\alpha} = \mu_i^{\beta} \qquad T^{\alpha} = T^{\beta} \qquad P^{\alpha} = P^{\beta}$$

$$\boxed{\begin{aligned} \mu_1^{vap} &= \mu_1^{liq} \\ \mu_2^{vap} &= \mu_2^{liq} \end{aligned}}$$

VLE

Binary System

$$\bar{G}_1^{vap} = \bar{G}_1^{liq}$$

$$\bar{G}_2^{vap} = \bar{G}_2^{liq}$$

$$\bar{G}_1^{ig} = G_1^{ig} + RT \ln y_1$$

$$G_1^{ig} = \Gamma_1\{T\} + RT \ln P$$

$$\bar{G}_1^{ig} = \Gamma_1\{T\} + RT \ln y_1 P$$

$$\bar{G}_i^{ig} = \Gamma_i\{T\} + RT \ln y_i P$$

$$\lim_{P \to 0} \bar{G}_i^{ig} = -\infty$$

We said then there is 2 phases that are in equilibrium with each other then the chemical potential for each of the species in the 2 phases alpha and beta needs to be same and this is true for all the chemical species i that are present in the 2 phases. And this characterizes equilibrium in addition to the equality of temperatures in both the phases and equality of pressures in both the phases.

Talking about a vapor and liquid equilibrium then and if we have two components then mu 1 in the vapor phase should be equal to mu 1 in the liquid phase, mu 2 for component 2 in the vapor phase should be equal to mu 2 for component 2 in the liquid phase. This is for a binary system of two species in equilibrium VLE for a binary system.

Now, I can write chemical potentials also in terms of partial molar Gibbs free energies. This also means that G 1 bar in the vapor phase should be equal to G 1 bar in the liquid phase and G 2 bar in the vapor phase should be equal to G 2 bar in the liquid phase. Let us take a minute and look at what G 1 bar and G 2 bar in the vapor and liquid phases are in any phase for that matter. If you recall for an ideal gas G 1 bar for an ideal gas was G 1 for the ideal gas of the pure species at the same temperature and pressure plus RT ln y i or y 1.

So, G 1 I G will be gamma 1 some constant for that species plus RT ln p and G 1 bar ig then will be gamma 1 T plus RT ln y 1 p and for any species i of course, this will be G i ig will be gamma i T plus RT ln y i P. As pressure goes to 0, the only way this equation will be satisfied is if this partial molar Gibbs free energy G i bar ig goes to negative infinity only then this particular equation will be satisfied.

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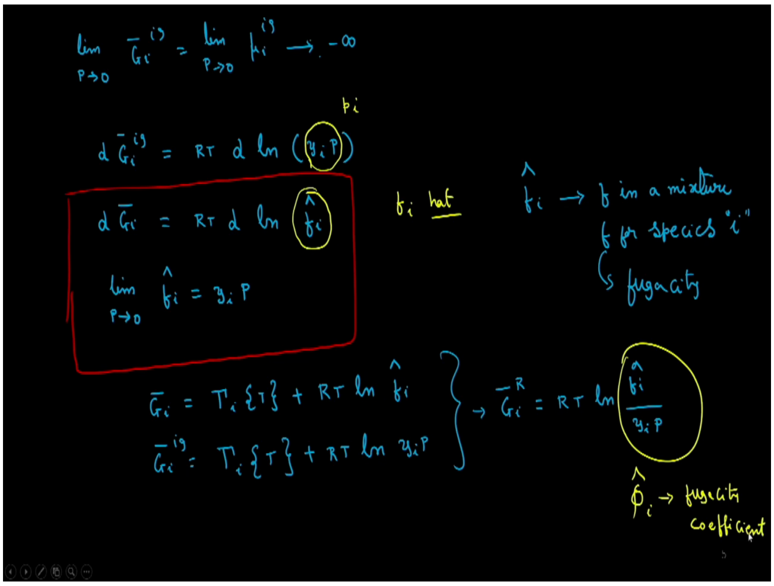

$$\lim_{P\to 0} \bar{G}_i^{ig} = \lim_{P\to 0} \mu_i^{ig} \to -\infty$$

p_i

$$d\bar{G}_i^{ig} = RT\, d\ln(y_i P)$$

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

$$\lim_{P\to 0} \hat{f}_i = y_i P$$

f_i hat

$\hat{f}_i \to$ f in a mixture

f for species "i"

↳ fugacity

$$\left.\begin{aligned} \bar{G}_i &= \Gamma_i\{T\} + RT\ln \hat{f}_i \\ \bar{G}_i^{ig} &= \Gamma_i\{T\} + RT\ln y_i P \end{aligned}\right\} \to \bar{G}_i^R = RT\ln \frac{\hat{f}_i}{y_i P}$$

$\hat{\phi}_i \to$ fugacity coefficient

So, this is true in general for any chemical species the limit at 0 pressure both G i bar ig hence the chemical potential mu i ig will approach negative infinity. So, in that sense chemical potential is not a convenient function to use or easily relate to. So, what we rather do is try to define a quantity which is not so abstract and to be able to do that we resort back to the equation we started with dG ig or dG i bar ig is RT d ln y i P for an ideal gas this equation is true.

What we do is for a real gas we will write an analogous equation d G i bar for any gas, so, for any substance for that matter not just gas is written as RT d ln fi hat. So, what I am doing is replacing the partial pressure in the ideal gas y i times P is the partial pressure P i with a quantity called as f i hat. The hat is the hat I put on top of f i of course, right f i and a hat and it indicates that we are talking about the quantity f in a mixture. F for species i because of the subscript i and this quantity f is what we call as fugacity and like I said at the beginning of this lecture fugacity generally means the tendency to escape and in relation to vapor liquid equilibrium as we will see greater the fugacity greater is the tendency of that species to stay in the vapor phase and hence the name.

So, this is the definition for fugacity of species i in the mixture and to be able to complete the definition we need to define a limit and that limit turns out to be the limit at the 0 pressure we say that at limit as P goes to 0 f i hat will be y i times P it will approach the ideal gas limit. That is how we complete the definition for fugacity of species i.

So, these two equations right here put together define the fugacity of species i in the mixture which we are calling it as f i hat. We use a hat instead of the bar we have used for partial molar properties such as partial molar Gibbs free energy here because f i hat is not a partial molar property, but we are still talking about a species i in the mixture. So, differentiate it from a partial molar property we are using a hat instead of the over bar as in case of partial molar properties.

So, these two relations here complete the definition for fugacity right and if you observe these two equations closely the first equation is G i bar like I said earlier in can be written as some constant for that species i at the temperature of interest plus RT ln f i hat and for an ideal gas I can write an equation because it is only dependent on temperature and the species that constant is still going to be the same plus RT ln y i P for an ideal gas.

And if I subtract one from the other what I get on the left hand side is G i bar R or the partial molar residual Gibbs free energy and on the right hand side we have RT ln f i hat over y i P, right and this quantity here on the right hand side f i hat over y i P is called as phi i hat corresponding to f i hat we have a phi i hat which is the fugacity coefficient. It is essentially the ratio of fugacity to the partial pressure and we call it as the fugacity coefficient.

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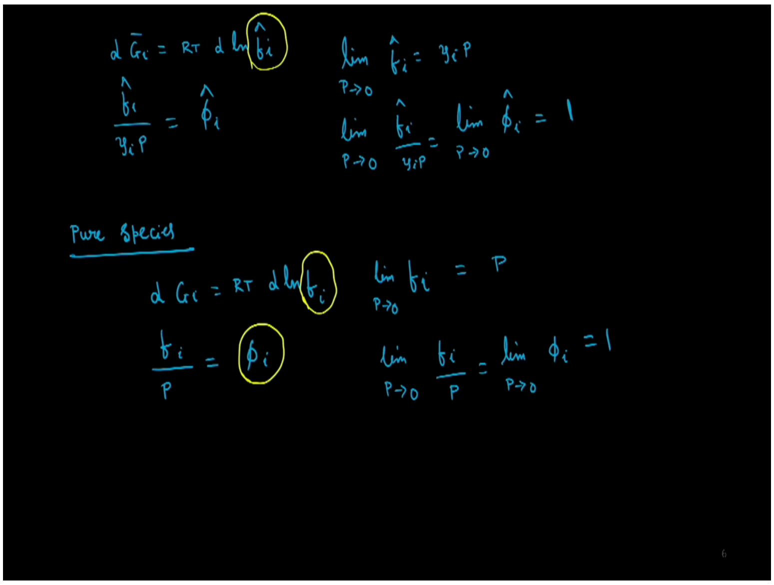

$$d\bar{G}_i = RT\, d\ln \boxed{\hat{f}_i} \qquad \lim_{P\to 0} \hat{f}_i = y_i P$$

$$\frac{\hat{f}_i}{y_i P} = \hat{\phi}_i \qquad \lim_{P\to 0} \frac{\hat{f}_i}{y_i P} = \lim_{P\to 0} \hat{\phi}_i = 1$$

Pure Species

$$dG_i = RT\, d\ln \boxed{f_i} \qquad \lim_{P\to 0} f_i = P$$

$$\frac{f_i}{P} = \boxed{\phi_i} \qquad \lim_{P\to 0} \frac{f_i}{P} = \lim_{P\to 0} \phi_i = 1$$

So, what we have now then is two equations one is d G i bar is RT d ln f i hat and f i hat over y I P is what we are calling as phi i hat and in addition limit of P going to 0 f i hat is y i P or limit of P going to 0 f i hat over y i P is limit P going to 0 phi i hat for the fugacity coefficient and this value is 1, right. So, the fugacity coefficient of species at the 0 pressure limit is going to be 1.

In addition to this once we have written these equations for a mixture we can also write corresponding equations for pure species d G i is RT d ln f; f over P for pure species y is 1. So, f over P is f i over P is phi i and limit of P going to 0 f i will be equal to P and limit of P going to 0 f i over P will be limit of P going to 0 phi i and it will still be 1.

Now, notice the analogy between the two for a mixture or for a pure species we have analogues equations except that we are replacing the fugacity of species i in the mixture f i hat with the fugacity of the pure species, I am sorry I should have written a i here fugacity of the pure species f i and because it is a pure species d G i bar will be same as d G i and the fugacity coefficient will be phi instead of phi i hat. So, the equations are otherwise analogues they will reduce to pure component equations as y i goes to 1 of course.

In addition to this what is the advantage of using fugacity for vapor liquid equilibrium calculations?

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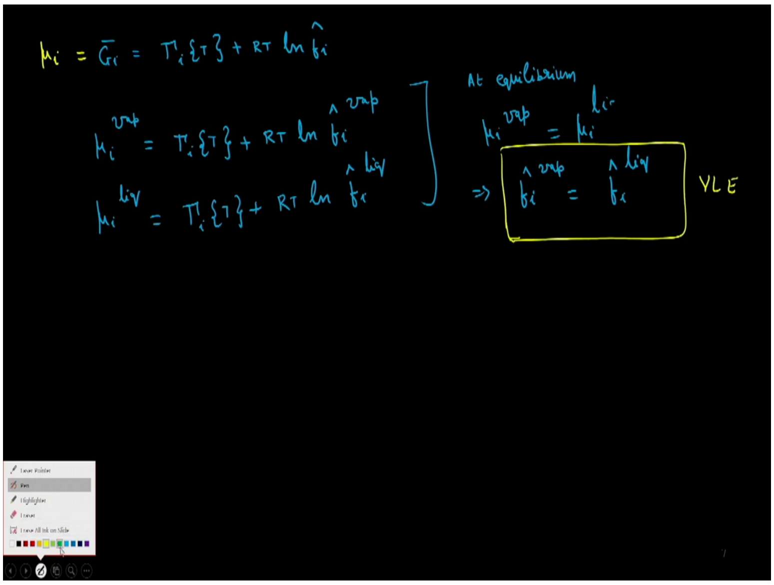

$$\mu_i = \bar{G}_i = \Gamma_i\{T\} + RT \ln \hat{f}_i$$

$$\left.\begin{aligned} \mu_i^{vap} &= \Gamma_i\{T\} + RT \ln \hat{f}_i^{vap} \\ \mu_i^{liq} &= \Gamma_i\{T\} + RT \ln \hat{f}_i^{liq} \end{aligned}\right]$$

At equilibrium

$$\mu_i^{vap} = \mu_i^{li}$$

$$\Rightarrow \boxed{\hat{f}_i^{vap} = \hat{f}_i^{liq}} \quad VLE$$

If you think about it G i bar is some constant plus RT ln f i and recall that G i bar is same as the chemical potential mu i. Now, if I write these equations for the vapor and the liquid phases then mu i in the vapor phase is gamma i which is a function only of temperature. It will not depend on the phase it will depend only on the species as long as the species i is same it will simply be gamma i T plus RT ln f i hat the fugacity of that species i in the vapor mixture.

Similarly, mu i in the liquid phase is going to be same constant plus RT ln f i hat in the liquid mixture and because at equilibrium mu i hat vapor is mu i hat and because at equilibrium mu i vapor is mu i liquid from these two equations what we get is f i hat in the vapor phase, the fugacity of species i in the vapor mixture should equal the fugacity of species i in the liquid mixture. So, instead of relating the vapor liquid equilibrium we had if you chemical potentials what we have achieved by introducing fugacity is that the fugacity of these species in the vapor and liquid mixtures are going to be same for a VLE right.

So, in that sense we can probably easily relate to these quantities and these quantities are well behaved even at the limit of 0 pressure, as we have seen the fugacity is boil down to partial pressures, in a pure component it is simple the pressure, etcetera. So, we can relate to fugacity in an easier fashion than to chemical potential probably. If that be the case to be able to characterize the vapor liquid equilibrium behavior we can work with fugacity is provided we know how to calculate fugacities. How does one calculate fugacity of a species?

So, by the way to be able to calculate fugacity, let us go back to it is definition and ask a question what is fugacity of species in an ideal gas? So, first let us talk about fugacity of an ideal gas.

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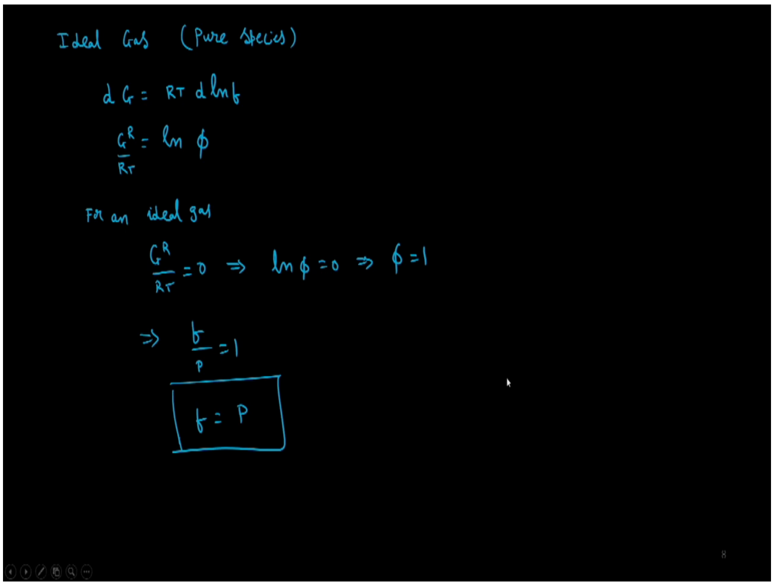

Ideal Gas (Pure Species)

$$dG = RT\, d\ln f$$

$$\frac{G^R}{RT} = \ln \phi$$

For an ideal gas

$$\frac{G^R}{RT} = 0 \Rightarrow \ln \phi = 0 \Rightarrow \phi = 1$$

$$\Rightarrow \frac{f}{P} = 1$$

$$\boxed{f = P}$$

Let us say we have a pure species in an ideal gas state by definition fugacity is d G is RT d ln f and we want to calculate this quantity an dG R or G R by RT is ln phi, right. This is for pure species we can use a subscript i, but because there is only one species we will just ignore the subscript.

So, the residual Gibbs free energy is related to the fugacity coefficient phi we have this equation. For an ideal gas G R by RT is 0, because there is no residual property which means that ln phi is 0 or the fugacity coefficient is 1 because the fugacity coefficient is 1, f by P is 1 or f is equal to P for an ideal gas. This will hold because the residual Gibbs free energy for an ideal gas of course, is 0.

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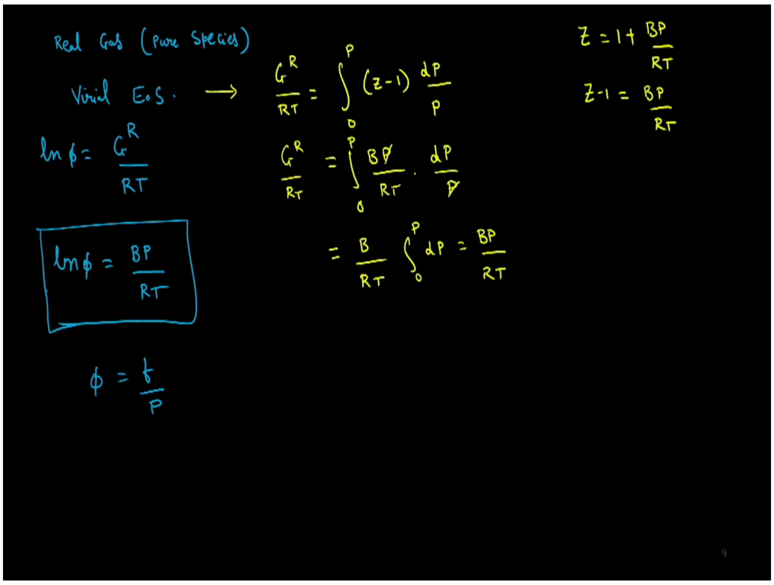

Real Gas (Pure Species)

Virial E.S. $\longrightarrow$ $\frac{G^R}{RT} = \int_0^P (z-1)\frac{dP}{P}$

$\ln\phi = \frac{G^R}{RT}$

$\frac{G^R}{RT} = \int_0^P \frac{B\cancel{P}}{RT}\cdot\frac{dP}{\cancel{P}}$

$= \frac{B}{RT}\int_0^P dP = \frac{BP}{RT}$

$\boxed{\ln\phi = \frac{BP}{RT}}$

$\phi = \frac{f}{P}$

$z = 1 + \frac{BP}{RT}$

$z - 1 = \frac{BP}{RT}$

Now, if we have a scenario where the residual Gibbs free energy is not 0, if the gas is not ideal, so, let us talk about a real gas and we are still talking about pure species, but let us talk about a real gas which obeys virial equation of state. Then, by definition ln phi is G R over RT I am talking about pure species.

So, like I said I am ignoring the subscript i, ln phi is G R over RT and if it obeys virial equation of state if you recall how we calculated the residual properties G R over RT was integral 0 to P, the compressibility factor z minus 1 dP over P, that was the relation for G R over RT. And for virial equation of state z is 1 plus BP over RT using only the second virial coefficient or z minus 1 is BP over RT.

So, this integral will then be BP over RT times dP over P. These two get cancelled; the second virial coefficient is function only of temperature. So, I can take everything out of that integral sign because there only functions of temperature B over RT integral 0 to P dP or this will be BP over RT. So, G R over RT is essentially BP over RT using virial equation of state or ln phi is going to be simply BP over RT. Once I have phi I can calculate the fugacity coefficient if I know the pressure.

So, if I have virial equation of state and I know the second virial coefficient then I can easily calculate the fugacity for pure species right. Let us work on one quick example using this idea.

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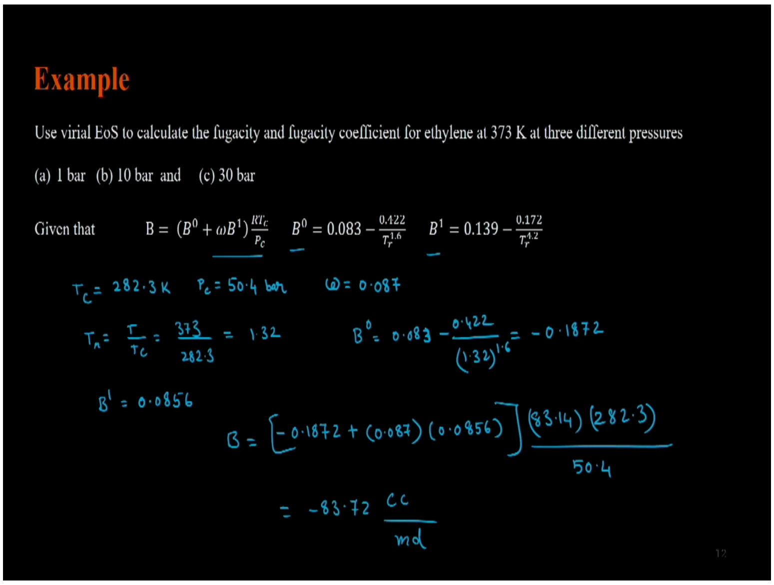

Example

Use virial EoS to calculate the fugacity and fugacity coefficient for ethylene at 373 K at three different pressures

(a) 1 bar (b) 10 bar and (c) 30 bar

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

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

$T_r = \frac{T}{T_c} = \frac{373}{282.3} = 1.32$ $B^0 = 0.083 - \frac{0.422}{(1.32)^{1.6}} = -0.1872$

$B^1 = 0.0856$

$$B = \left[-0.1872 + (0.087)(0.0856)\right]\frac{(83.14)(282.3)}{50.4}$$

$$= -83.72\ \frac{cc}{mol}$$

We have a virial equation of state and we want to calculate the fugacity and fugacity coefficient for ethylene at 373 Kelvin one temperature and three different pressures; 1 bar, 10 bar and 30 bar. And the second virial coefficient for this particular compound is given by the relations shown here we first need to calculate two quantities B naught and B 1 which are related to the reduced temperature and once I have the two quantities and I know the critical constants I can go back and calculate the second virial coefficient.

And throughout as you can see the second virial coefficient will only be functions of the reduced temperature or temperature and the critical properties, nothing else. So, it will only depend on temperature for that matter and the pressure changes from 1 to 10 to 30 bar B is not going to change. So, what we will do is first calculate this quantity B so that I can then use it for all the 3 pressures to be able to do that we need the critical properties so that I can calculate T R. Let us use a suitable reference and obtain the critical properties for ethylene turns out for ethylene the critical temperature is 282.3 Kelvin and the critical pressure is 50.4 bar and the eccentric factor omega is 0.087.

Once I have these three I can calculate the reduced temperature it is T over T c or 373 over 282.3. So, this will be 1.32, then once I have the reduced temperature I can calculate B naught which is 0.083 minus 0.422 divided by 1.32 to the power 1.6 and this value turns out to be negative 0.1872. Similarly, B 1 is going to be 0.0856 and once I have B naught and B 1 I can calculate B it will be negative 0.18724 B naught plus the eccentric factor 0.087 times B 1 which is 0.0856 times R which is 83.14 bar cc per mole per Kelvin times T c is 282.3 Kelvin over P c which is 50.4 bar and once we use these units what we get is a value of B as negative 83.72 cc per mole.

So, now I have the value for the second virial coefficient from the given correlations. Once I have this value I can use this B to calculate the residual Gibbs free energy the fugacity coefficient and hence the fugacity.

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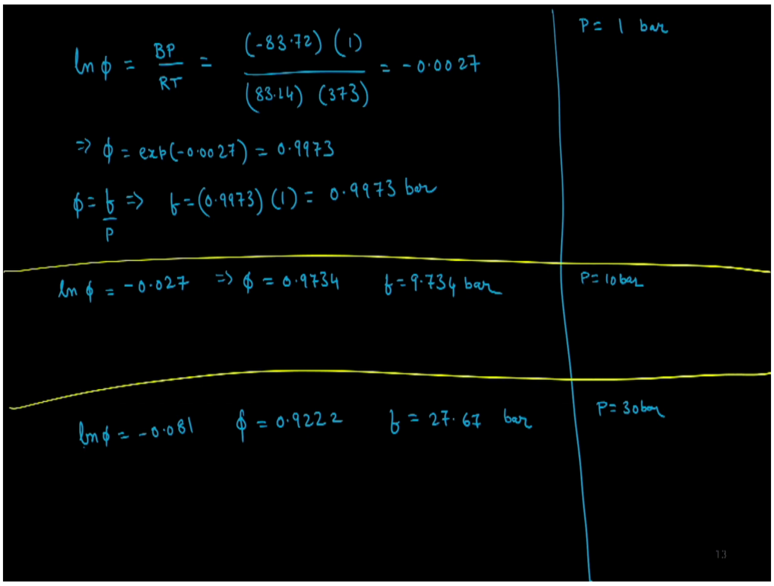

$\ln\phi = \frac{BP}{RT} = \frac{(-83.72)(1)}{(83.14)(373)} = -0.0027$

$\Rightarrow \phi = \exp(-0.0027) = 0.9973$

$\phi = \frac{f}{P} \Rightarrow f = (0.9973)(1) = 0.9973$ bar

$P = 1$ bar

$\ln\phi = -0.027 \Rightarrow \phi = 0.9734 \quad f = 9.734$ bar

$P = 10$ bar

$\ln\phi = -0.081 \quad \phi = 0.9222 \quad f = 27.67$ bar

$P = 30$ bar

If you recall both the residual Gibbs free energy and ln phi are same or residual Gibbs free energy G R by RT and ln phi are same and they are equal BP over RT for virial equation of state using only the second virial coefficient. And once I have the value for B which is negative 83.72 cc per mole I just need to be careful with the units the pressure we have 3 different conditions for which we are interested in calculating ln phi.

First one is one bar over 83.14 and 373 Kelvin right and for this value it turns out that ln phi is 0.0027 and I take an exponential of that we get phi which turns out to be 0.9973 and f if you recall is phi is f over P which implies f is going to be 0.9973 times the pressure which is 1 bar.

So, the units for fugacity of course, are going to be same as that of pressure. So, that will be 0.9973 bar I can do it at 10 bar and the values I get are ln phi is negative 0.027 and phi will be 0.9734 and f is going to be 9.734 bar. I can repeat the calculation at 30 bar ln phi is going to be negative 0.081, phi is going to be 0.922 and f is going to be 27.67 bar. As you can see once the pressure increases we are moving away from 0, the ideal gas behavior and hence the fugacity coefficient phi moves further away from 1 and the fugacity itself f is going to move further away from pressure P and that is what is happening as we increase the pressure from 1 bar to 10 bar to 30 bar. This is how we can use a virial equation of state to calculate fugacity of pure species.

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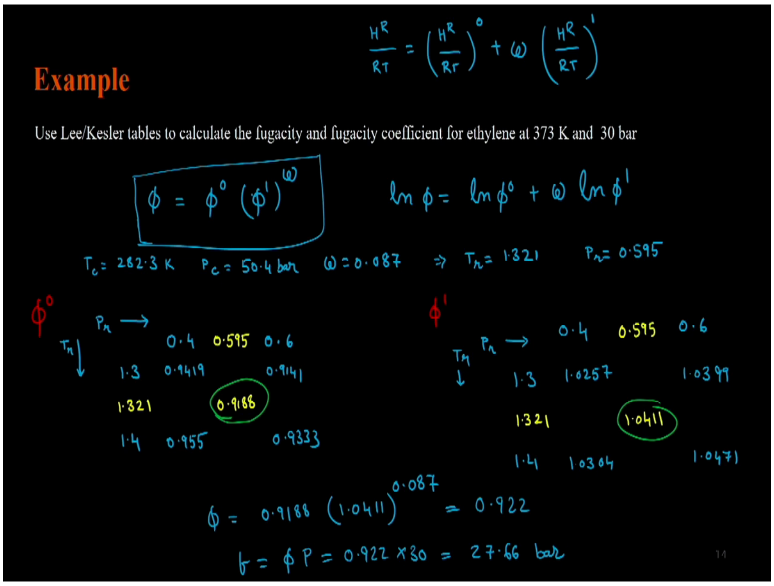

Example

$$\frac{H^R}{RT} = \left(\frac{H^R}{RT}\right)^0 + \omega \left(\frac{H^R}{RT}\right)^1$$

Use Lee/Kesler tables to calculate the fugacity and fugacity coefficient for ethylene at 373 K and 30 bar

$$\boxed{\phi = \phi^0 (\phi^1)^{\omega}} \qquad \ln \phi = \ln \phi^0 + \omega \ln \phi^1$$

$T_c = 282.3$ K $\quad P_c = 50.4$ bar $\quad \omega = 0.087 \Rightarrow T_r = 1.321 \quad P_r = 0.595$

ϕ^0

$T_r \downarrow$ \ $P_r \rightarrow$	0.4	0.595	0.6
1.3	0.9419		0.9141
1.321		0.9188	
1.4	0.955		0.9333

ϕ^1

$T_r \downarrow$ \ $P_r \rightarrow$	0.4	0.595	0.6
1.3	1.0257		1.0399
1.321		1.0411	
1.4	1.0304		1.0471

$$\phi = 0.9188\,(1.0411)^{0.087} = 0.922$$

$$f = \phi P = 0.922 \times 30 = 27.66 \text{ bar}$$

Now, recall we have used Lee Kesler tables to calculate the residual properties the residual enthalpy and the residual entropy. So, these Lee Kesler tables also exist for calculation of fugacity and fugacity coefficient. If you recall they are based on Pitzer correlations which arise from theorem of corresponding states.

And we said species which have which are at the same reduced conditions reduced temperature and reduced pressure with the same value of eccentric factor omega behave similarly. One of the ways we have used Lee Kesler table to calculate the residual enthalpy is by calculating H R by RT via two quantities H R by RT 0 plus and H R by RT 1. Both these quantities can be obtained in two different tables at the given reduced conditions T r and P r and then the total H R by RT was sum of these two the second quantity of course, multiplied with the eccentric factor omega.

Similar tables also exist for calculation of fugacity coefficient, essentially it is related to residual Gibbs free energy, right. So, and the way we use Lee Kesler tables is again calculating two quantities and phi naught and phi 1 or looking up for two quantities phi naught and phi one in the Lee Kesler tables at the given reduced conditions T r and P r and then calculating phi the fugacity coefficient using the relation phi is phi naught phi 1 times phi 1 to the power omega. Actually what it is ln phi is going to be ln phi naught plus omega times ln phi 1 ln phi of course, is the residual Gibbs free energy G R by RT. So, we combine them with omega and then if you get rid of the logarithms what we end up with is a relation like this.

So, this is how we are going to use Lee Kesler tables for calculation of fugacity coefficients. Let us try to solve this particular problem using this idea. We are interested in calculating the fugacity coefficient again for ethylene at 373 Kelvin and 30 bar at these conditions. The first thing we have to do is calculate T r and P r if you recall in the previous problem we said T c for ethylene is 282.3 Kelvin P c is 50.4 bar and omega is 0.087.

And what this means is T r is going to be T over T c, it is going to be 1.32; P r is going to be P over P c which is going to be 0.595. At these conditions in fact, it is 1.321 and at these conditions we are interested in calculate or looking up the Lee Kesler tables for a value of phi naught and for phi 1. As usual Lee Kesler tables are listed at discrete steps. The ones I have used the reduced pressure it is listed at 0.4 and 0.6 for reduced temperature it is listed at 1.3 and 1.4. What we are interested in is something in between 1.3 to 1 and 0.595, right.

So, if you recall we need to do a double linear interpolation. So, first let us write what we have at the conditions listed in the table 9419, 0.9141, 0.955 and 0.933. We can do a double linear interpolation and end up with a value of 0.9188, this is for the quantity phi naught. This will give us a quick estimate if we want to do a more rigorous calculation we will also involve phi 1. I look up for these four values in the table and then do a double linear interpolation and once I do that I will end up with the value of phi 1 at the desired conditions right.

So, these are the two quantities I am looking at the desired conditions phi naught and phi 1. I will combine them using the eccentric factor omega to get phi 0.9188 times 1.0411 to the power 0.087 and this value turns out to be 0.922 and once I have phi f is going to be phi times the pressure and in this case the pressure is 30 bar. So, it will be 0.922 times 30 which turns out to be 27.66 bar.

So, using the tables we can also estimate fugacity of the pure species. So, we have looked at virial equation of state to estimate the fugacity of pure species, we have used the Lee Kesler tables to estimate the fugacity coefficient and hence the fugacity for pure species. When we come back in the next lecture, we will look at how to estimate fugacity coefficient using cubic equation of state and then extend this discussion to a mixture of chemical species.

Thank you.