

Chemical Engineering Thermodynamics
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Lecture 31
Equation of State (continued)

Hi, in today's lecture we are going to continue taking the understanding of what we have covered in the last lecture on equation of state and corresponding state principle with some examples. So, we have also listed a compressibility chart for use.

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Virial Equation in concentration

Show that a Taylor series expansion for the compressibility factor, z , about temperature, T , and concentration, $c = 1/v$, gives the form of the virial equation shown in Equation (4.26).

$$z = \frac{Pv}{RT} = 1 + \frac{B}{v} + \frac{C}{v^2} + \frac{D}{v^3} + \dots$$

$$z = f(T, c)$$

Taylor expansion at $c=0$

$$z = f(T, c=0) + \left. \frac{\partial f(T, c)}{\partial c} \right|_{c=0} c + \left. \frac{\partial^2 f(T, c)}{\partial c^2} \right|_{c=0} \frac{c^2}{2!} + \left. \frac{\partial^3 f(T, c)}{\partial c^3} \right|_{c=0} \frac{c^3}{3!} + \dots$$

So, let us start with this question, which is a Virial equation, however in the concentration. So the question says that you know show that a Taylor series expansion for the compressibility factor z , about temperature T and concentration C which is equal to 1 by molar volume gives the form of the virial equation shown in the equation 4.6, which basically referring to the text book here, that is chorus key.

$$z = \frac{Pv}{RT} = 1 + \frac{B}{v} + \frac{C}{v^2} + \frac{D}{v^3} + \dots$$

$$z = f(T, c)$$

Taylor expansion at $c = 0$:

$$z = f(T, c = 0) + \left. \frac{\partial f(T, c)}{\partial c} \right|_{c=0} c + \left. \frac{\partial^2 f(T, c)}{\partial c^2} \right|_{c=0} \frac{c^2}{2!} + \left. \frac{\partial^3 f(T, c)}{\partial c^3} \right|_{c=0} \frac{c^3}{3!} + \dots$$

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$$f(T, c) = z(T, c) = \frac{Pv}{RT} = 1 = \frac{P}{cRT}$$

all gases \rightarrow I.G.

$$z = 1 + \left. \frac{\partial f(T, c)}{\partial c} \right|_{c=0} c + \frac{\partial^2 f(T, c)}{\partial c^2} \bigg|_{c=0} \frac{c^2}{2!} + \dots$$

$$z = \frac{P}{cRT} = 1 + Bc + Cc^2 + Dc^3$$

$$B = \left. \frac{\partial f}{\partial c} \right|_{c=0} \quad ; \quad C = \frac{1}{2!} \left. \frac{\partial^2 f}{\partial c^2} \right|_{c=0}$$

So let us look at the also what happens to this function at c equal to 0, which is nothing but Z T c equal to 0 this means that we are talking about 1 by V goes to 0. Now, this means basically the density is extremely low, so all gases will tend towards ideal gas.

$$f(T, c = 0) = z(T, c = 0) = \frac{Pv}{RT} = 1 = \frac{P}{cRT}$$

$$z = 1 + \frac{\partial f(T, c)}{\partial c} \bigg|_{c=0} c + \frac{\partial^2 f(T, c)}{\partial c^2} \bigg|_{c=0} \frac{c^2}{2!} + \dots$$

$$z = \frac{P}{cRT} = 1 + Bc + Cc^2 + Dc^3 \quad ; \quad B = \frac{\partial f(T, c)}{\partial c} \bigg|_{c=0} \quad ; \quad C = \frac{1}{2!} \frac{\partial^2 f(T, c)}{\partial c^2} \bigg|_{c=0}$$

So one can clearly see that is since we have taken this function as of derivative of c. This B C Ds would be dependent on temperature. At the c equal to 0 and hence these are only dependent to these coefficients are only depend on temperature. That is something which we have already discussed about. So this is just an illustration of how one can also write or develop this kind of equation of state for solution phase as well, or in general for some concentration of the gases.

But note that this B C and D are more fundamental in nature and the origin comes from the statistical mechanics approach. B again is nothing but the second virial coefficient which essentially reflect how two body interactions contribute to the equation of state or in general to

the pressure or compressibility here c would be that when you have three particles or three body interactions, how that contributes to the Z and D is for full body interaction and so forth.

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$$f(r, \infty) = Z(T, c=0) = \frac{Pv}{RT} = 1 = \frac{P}{cRT}$$

$V_c \rightarrow 0$
all gas \rightarrow I.G.

$$Z = 1 + \frac{\partial f(T, c)}{\partial c} \Big|_{c=0} c + \frac{\partial^2 f(T, c)}{\partial c^2} \Big|_{c=0} \frac{c^2}{2!} + \dots$$

$$Z = \frac{P}{cRT} = 1 + Bc + Cc^2 + Dc^3 + \dots$$

$\frac{\partial f}{\partial c} \Big|_{c=0}$ $\frac{1}{2!} \frac{\partial^2 f}{\partial c^2} \Big|_{c=0}$

So something which is more profound and more correct and thus it also provides way to address inter molecular interactions. You can also get the idea, what would be a typical interaction between two particles. So one can calculate the V 's from the experiment and make use of this experiment to valuate effective interactions, but at low densities.

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Calculation of the Second Virial Coefficient from Hard Sphere Potential

$$B = 2\pi N_A \int_0^\infty \left(1 - e^{-\frac{\Gamma(r)}{kT}}\right) r^2 dr$$

$$= 2\pi N_A \left[\int_0^\sigma r^2 dr + \int_\sigma^\infty \left(1 - e^{-\frac{\Gamma(r)}{kT}}\right) r^2 dr \right]$$

$$= 2\pi N_A \left. \frac{r^3}{3} \right|_0^\sigma$$

$$B_{HS} = \frac{2\pi N_A \sigma^3}{3}$$

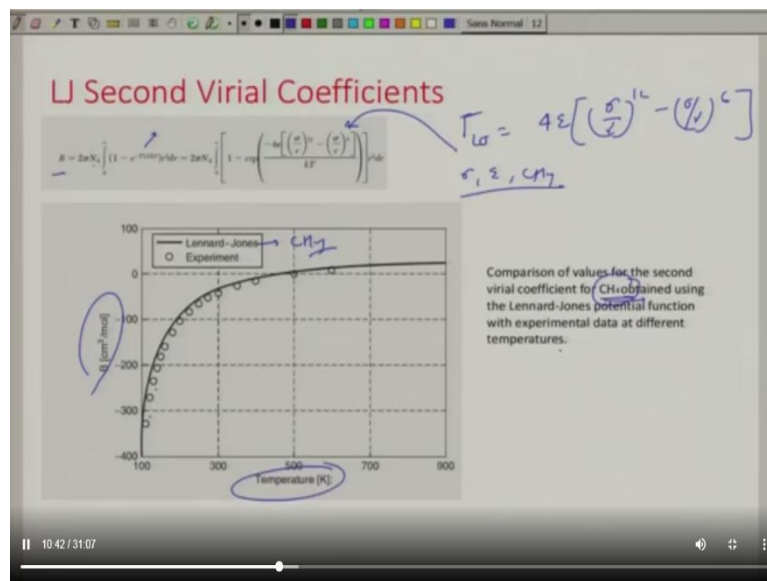
So let me just continue with this exercise and now we can take up a problem where second virial coefficient for the hard sphere potential is to be evaluated.

$$B = 2\pi N_A \int_0^\infty \left(1 - e^{-\frac{\Gamma(r)}{kT}}\right) r^2 dr = 2\pi N_A \left[\int_0^\sigma r^2 dr + \int_\sigma^\infty \left(1 - e^{-\frac{\Gamma(r)}{kT}}\right) r^2 dr \right] = \frac{2\pi N_A r^3}{3} \Big|_0^\infty$$

$$B_{HS} = \frac{2}{3} \pi N_A \sigma^3$$

So this is your B for hard sphere and similarly, you can actually calculate the virial coefficient second virial coefficient for many different potential models which are identical available. For example, you can calculate that for Lennard Jones. So the land potentials exponential 6 and so forth.

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$$\Gamma_{L\sigma} = 4\epsilon \left[\left(\frac{\sigma}{r} \right)^{12} - \left(\frac{\sigma}{r} \right)^6 \right]$$

So as I said, we can calculate the second virial coefficient for other potentials. So Lennard Jones could be one. So, here again. I am trying to describe the same expression B is $2 \pi N A \int_0$ to infinity $1 - \frac{e^{-\epsilon \left(\left(\frac{\sigma}{r} \right)^{12} - \left(\frac{\sigma}{r} \right)^6 \right)}}{kT}$ $r^2 dr$. Now, for L J this is going to be this, so this we plug in here and now subsequently, you have to also try to integrate this and that becomes a little tricky but nevertheless you can obtain the values of B as a function of r for depending on different molecules.

You can also come up with a reduced B also where this can be in a reduced distance for example, and similarly ϵ can be taken to the left hand side and B can be for the reduced value of B can be plotted. But in this case we are just taking the σ and ϵ of CH_4 , which is available from the textbook tables and as well as an IST tables are available as well. So you making use of that, you can calculate the analytical form of B as a function of temperature for CH_4 and then this information for CH_4 is for the B is available, and this is something which V is drawn as a symbols here and you can clearly see how beautifully it is in line with the analytical expression.

So, something which we can make use of it that an analytical forms particularly for a spherical particles non polar molecules. The B 's are the second virial coefficients are extremely correct from the analytical expressions. Something which clearly sees we can see it from this exercise.

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Compressibility chart

A unique generalized relation of compressibility factor as a function of reduced temperature and pressure for similar kind of molecules.

Its useful to have it in the form of graphs or table.

In general

$$z = z^{(0)} + \omega z^{(1)}$$

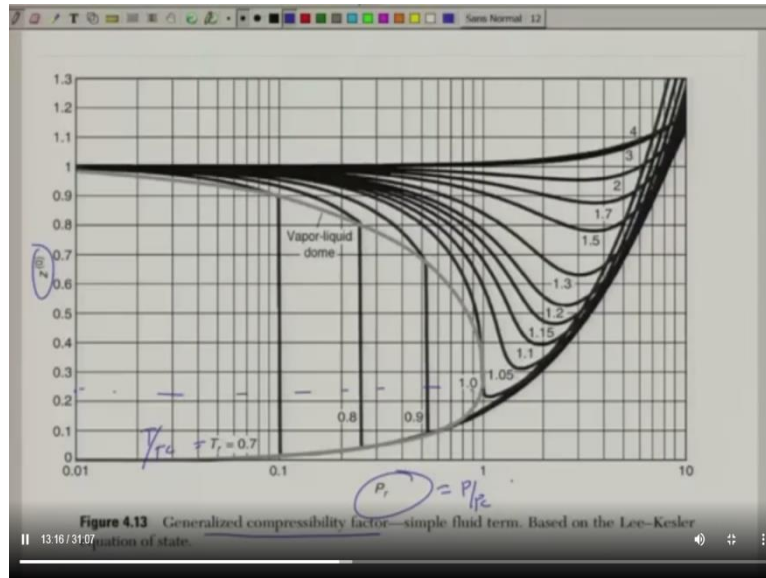
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$$z = z^{(0)} + \omega z^{(1)}$$

So we have also gone through the compressibility chart earlier which is discussed the reduced Cross Penn State principal and the concept has been made use of it by using those Crossman step is principal particularly for the compressibility factor, which generalize the relation as a function of a reduced temperature and pressure for similar kind of molecules. So I usually it is very useful if it is in the form of graphs or tables. In general one can write as we have already discussed that a compressibility factor can be written as the two parts one, which is due to the spherical nature or non polar nature of the particle.

And the second part comes where it is the polar nature or the non spherical nature are basically added here. So this is usually this should be zero for particles such as argon methane and so forth. But if you have a quite a significant polarizable molecules and the shapes are not spherical in nature then essentially you will have W's non 0 and as well as there will be Z. So now let us see how it looks like as far as the diagrams are concerned or graphs are concerned.

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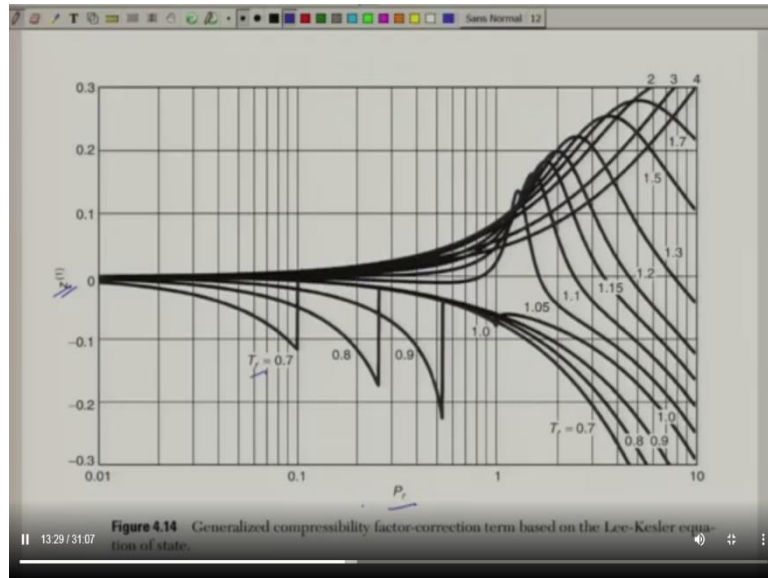


$$Pr = \frac{P}{P_c} ; Tr = \frac{T}{T_c}$$

So this is a simple Z 0 part are generalized compressibility factor for simple fluids and you can see here, there are two things one is your Pr and the Tr. So essentially the idea, is that for a given molecule you first calculate Pr. Pr is nothing but P by P C. Similarly T is T r is nothing but T by T C. So you obtain the critical property of a molecule. And from there you obtain your PC and TC and subsequently you get Pr and Tr.

Now in order to find Z zero we can take one of those things. For example you if you are if you evaluate the PI which turns out to be let us say 1 it you can draw a straight line and corresponding to Tr. You can get it something like for example, in this case if it is 1 I am here. This is the intersection with this T I is equal to 1 and from here I can draw again a horizontal line to get my Z 0. Now, this may be very cumbersome, and that is why a table is also generated in order to avoid manual error or estimating from the graph.

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So this is the corresponding Z of 1 which would depend on again P_r and T_r . Again, this generalized compressibility factor. And this is the correction term because of the spherical and the polar nature of the molecule again, you do the same thing. The corresponding table is available in the textbook course key where it is C1. Table C 1 and C 2 corresponds to figure 4.13 and 4.14.

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T_c, P_c

Example

Calculate the volume occupied by 10 kg of butane at 50 bar and 60°C using the Redlich-Kwong equation and the generalized compressibility charts.

$$P = \frac{RT}{v-b} - \frac{a}{T^{1/2}v(v+b)}$$

We first find the Redlich-Kwong parameters a and b using critical properties:

$$a = \frac{0.42748R^2T_c^{2.5}}{P_c} = 29.08 \left[\frac{\text{JK}^{1/2}\text{m}^3}{\text{mol}^2} \right] \text{ and } b = \frac{0.08664RT_c}{P_c} = 8.09 \times 10^{-5} \left[\frac{\text{m}^3}{\text{mol}} \right]$$

$$v = 1.2 \times 10^{-4} \left[\frac{\text{m}^3}{\text{mol}} \right] \quad \text{By Trial and Error}$$

15:38 / 31:07 $\frac{10}{0.0812} \times 1.20 \times 10^{-4} = 0.021 \text{ [m}^3\text{]}$

$$P = \frac{RT}{v-b} - \frac{a}{T^{1/2}v(v+b)}$$

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Now let us try to make use of it some examples and this is related to generalized compressibility chart and as well as the equation of state. So the question here is calculate the volume occupied by 10 kg of butane at 50 bar and 60 degree celsius using the R K equation and also compare that with the generalized compressibility chart. Now, if you look at R K equation, it is the usual the first part characterized by exclusion volume and then the attractive term.

So this is the attractive term now A and B are related to the critical properties and it is written here. So essentially for the butane the idea is to get first TC and PC which we can get it from the test book appendix tables or you can also get it from the NIST table that is from the web and then obtain your a and then b. Once you obtain in the a and b, then you plug in there. So for the given temperature and the pressure that means you know the pressure and you know the temperature and as well as a and b.

Now the question is what would be the be V. So this is a cubic equation. So, one way is to do a trial and error in this way that becomes much easier. So you keep doing your trial and error until you get a value which you can do it in Excel sheet and the value which comes out to be is 1.2 into 10 to power minus 4 meter cube per mole. Now from here we can get the volume by

scaling, by multiplying with the mass here or number of moles basically. So, it should be the mass a divided by the molecular weight of the butane so that is this part multiplied by molar volume and that way we will get the volume here.

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**Using Compressibility Chart
(Appendix C)**

z^0, z^1

First, find critical points

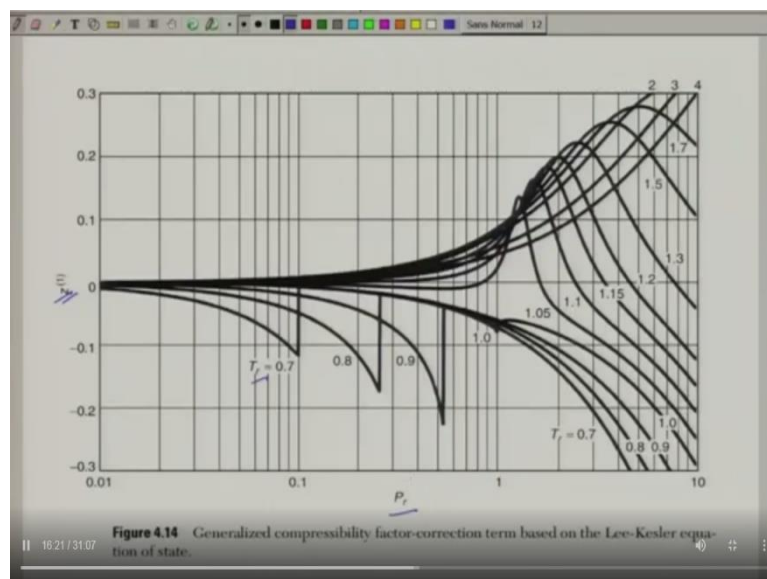
$$P_r = \frac{P}{P_c} = \frac{50 \text{ bar}}{37.9 \text{ bar}} = 1.32, \quad T_r = \frac{T}{T_c} = \frac{333.2 \text{ K}}{425.2 \text{ K}} = 0.78, \quad \text{and } \omega = 0.193$$

Table C1 and C2

T_r	z^0		z^1	
	P_r	P_r	P_r	P_r
	1.3	1.4	1.3	1.4
0.75	0.2142	0.2303	-0.0871	-0.0934
0.78 (interpolated)	0.2116	0.2274	-0.0843	-0.0903
0.80	0.2099	0.2255	-0.0825	-0.0883

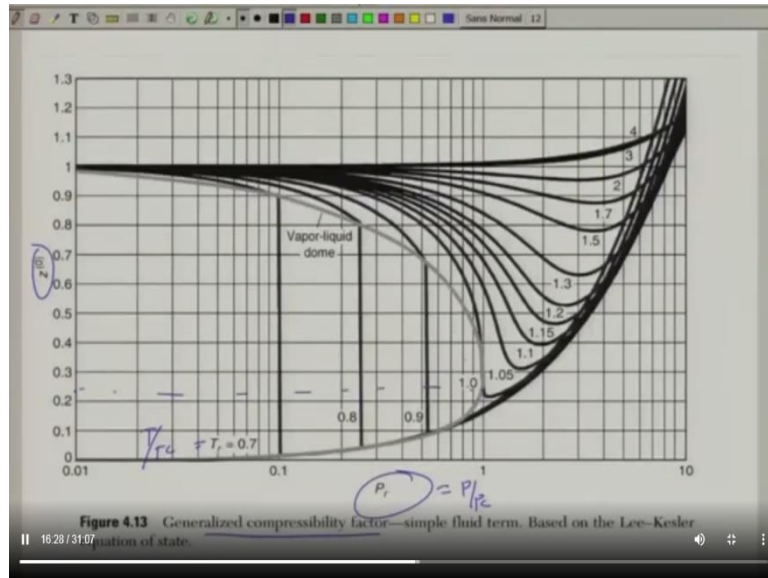
So what about the compressibility chart. So we make use of the same thing we know the P_r because we have just got the P_c so we can calculate the P_r and the T_r and since it is not a spherical molecule so there will be a ω so essentially you not only have to look at z^0 but also z^1 . Now one way of course is to look at the chart because it is a 1.32 and 0.78. So you can look at the chart here

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So, 1.32 and 78. Now if you look at it is little trickier 0.78 to be somewhere here and essentially it will be lot of errors associated with it.

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So what we have done is instead of using simple chart like this, which we can of course do as discussed earlier.

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Using Compressibility Chart (Appendix C)

z^0, z^1

First, find critical points

$$P_r = \frac{P}{P_c} = \frac{50 \text{ bar}}{37.9 \text{ bar}} = 1.32, \quad T_r = \frac{T}{T_c} = \frac{333.2 \text{ K}}{425.2 \text{ K}} = 0.78, \quad \text{and } \omega = 0.193$$

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0.80	0.2099	0.2255	-0.0825	-0.0883

We can also make use of the table C1 and C2 which simplifies this. Now here the data point are given in this way. So for 0.75 and 1.3 this is the value. For 0.75 1.4 this is a value because since our P_r is 1.32 it lies between 1.3 and 1.4. So we have now used this we have just written this part, in order for us to do interpolation. The other one is since also T_r is 0.78 so I which and the data point which is given in table C1 and C2 is 0.75 and 0.80. So we also write this in order to have the complete table.

Now we can do interpolations, for 0.78. Corresponding to 0.78 and then the corresponding P_r we can calculate that will be this and similarly for 0.78 corresponding P_r at 1.4 so corresponding Z_0 at 1.4 P_r . So, essentially this interpolation is to get the Z_0 . So again how it started that from the table we got 0.75 the Z_0 value given here. These are the two values which are for 1.3 and 1.4 correspondingly and similarly for 0.80 Z_0 value are 0.2098 at 1.3 and 0.2255 at 1.4 P_r and this we can evaluate from interpolation.

Now similarly I have to do that for Z_1 . So I have to find out this and this at 0.78 from this information. So once we have done this exercise then I can get again Z_0 .

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$$z^{(0)} = 0.2116 + \frac{0.02}{0.1}(0.2274 - 0.2116) = 0.2148$$

$$z^{(1)} = -0.0843 + \frac{0.02}{0.1}(-0.0903 - (-0.0843)) = -0.0855$$

$$z = z^{(0)} + \omega z^{(1)} = 0.198$$

Low value indicate liquid

$$v = \frac{zRT}{P} = \frac{0.198 \times 8.314 \times 333.15}{50 \times 10^5} = 1.1 \times 10^{-4} \left[\frac{\text{m}^3}{\text{mol}} \right]$$

$$V = \frac{m}{MW} \times v = \frac{10}{.05812} \times 1.1 \times 10^{-4} = 0.019 \text{ [m}^3\text{]}$$

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Using Compressibility Chart (Appendix C)

$z^0, z^{(1)}$

First, find critical points

$P_r = \frac{P}{P_c} = \frac{50 \text{ bar}}{37.9 \text{ bar}} = 1.32$, $T_r = \frac{T}{T_c} = \frac{333.2\text{K}}{425.2\text{K}} = 0.78$ and $\omega = 0.193$

Table C1 and C2

T_r	z^0		z^1	
	P_r	P_r	P_r	P_r
0.75	1.3	1.4	1.3	1.4
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0.78 (interpolated)	0.2116	0.2274	-0.0843	-0.0903
0.80	0.2099	0.2255	-0.0825	-0.0883

So Z^0 we need to find out Z^0 as 1.32 and 0.75 78. So since we have calculated the interpolation for we did that for 1.3 at 0.78. So, similarly 1.4 P_r at 0.78. Now the next question is that given this information that we have 1.78 we do have now. Now what about 1.32 so we have to do again a second interpolation between these two. So keeping the 0.78 fix and that is exactly what we are doing here.

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$$z^{(0)} = 0.2116 + \frac{0.02}{0.1}(0.2274 - 0.2116) = 0.2148$$

$$z^{(1)} = -0.0843 + \frac{0.02}{0.1}(-0.0903 - (-0.0843)) = -0.0855$$

$$z = z^{(0)} + \omega z^{(1)} = 0.198$$
Low value indicate liquid

$$v = \frac{zRT}{P} = \frac{0.198 \times 8.314 \times 333.15}{50 \times 10^5} = 1.1 \times 10^{-4} \left[\frac{\text{m}^3}{\text{mol}} \right]$$

$$V = \frac{m}{MW} \times v = \frac{10}{.05812} \times 1.1 \times 10^{-4} = 0.019 \text{ [m}^3\text{]}$$

. So this is the difference 0.03 is nothing but more than 1.3 and this is a difference between 1.3 and 1.4.

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$$z^{(0)} = 0.2116 + \frac{0.02}{0.1}(0.2274 - 0.2116) = 0.2148 \quad \checkmark$$

$$z^{(1)} = -0.0843 + \frac{0.02}{0.1}(-0.0903 - (-0.0843)) = -0.0855$$

$$z = z^{(0)} + \omega z^{(1)} = 0.198$$
Low value indicate liquid

$$v = \frac{zRT}{P} = \frac{0.198 \times 8.314 \times 333.15}{50 \times 10^5} = 1.1 \times 10^{-4} \left[\frac{\text{m}^3}{\text{mol}} \right]$$

$$V = \frac{m}{MW} \times v = \frac{10}{.05812} \times 1.1 \times 10^{-4} = 0.019 \text{ [m}^3\text{]}$$

And this is the value the difference here 0.2274 minus 0.22 plus the initial Z 0 Value at 1.32, so that way we have now into this is the second interpolation which gives us Z 0 2.48.

Now of course, this is more tedious job, but what we are trying to do is do a more thorough more correct information graphically, you can obtain of course, but the others may be very large given the nature of the scale of the graph. Similar to this Z 0 we would be also doing the

same exercise for Z 1. So once we have Z 0 and Z 1 we can get our Z, which is 0.198. So, looking at it here.

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$$z^{(0)} = 0.2116 + \frac{0.02}{0.1}(0.2274 - 0.2116) = 0.2148$$

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$$z = z^{(0)} + \omega z^{(1)} = 0.198$$

Low value indicate liquid

$$v = \frac{zRT}{P} = \frac{0.198 \times 8.314 \times 333.15}{50 \times 10^5} = 1.1 \times 10^{-4} \left[\frac{\text{m}^3}{\text{mol}} \right]$$

$$V = \frac{m}{MW} \times v = \frac{10}{58.12} \times 1.1 \times 10^{-4} = 0.019 \text{ [m}^3\text{]}$$

So once we have now our Z here, we calculate our V. So V is 1.1 into 10 to the minus 4 now, this is something we can compare.

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Example

Calculate the volume occupied by 10 kg of butane at 50 bar and 60°C using the Redlich-Kwong equation and the generalized compressibility charts.

$$P = \frac{RT}{v-b} \frac{a}{T^{1/2}v(v+b)}$$

We first find the Redlich-Kwong parameters a and b using critical properties:

$$a = \frac{0.42748R^2T_c^{2.5}}{P_c} = 29.08 \left[\frac{\text{J}^{1/2}\text{m}^3}{\text{mol}^2} \right] \text{ and } b = \frac{0.08664RT_c}{P_c} = 8.09 \times 10^{-5} \left[\frac{\text{m}^3}{\text{mol}} \right]$$

$$v = 1.2 \times 10^{-4} \text{ [m}^3\text{/mol]}$$

By Trial and Error

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$$z^{(0)} = 0.2116 + \frac{0.02}{0.1}(0.2274 - 0.2116) = 0.2148$$

$$z^{(1)} = -0.0843 + \frac{0.02}{0.1}(-0.0903 - (-0.0843)) = -0.0855$$

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$$V = \frac{m}{MW} \times v = \frac{10}{0.05812} \times 1.1 \times 10^{-4} = 0.019 \left[\text{m}^3 \right]$$

Low value indicate liquid

This was 1.2 into 10 to power minus 4 this is 1.1, that means the equation of state was giving me a bit more molar volume and corresponding volume turns out to be 0.019 meter cube, which is slightly lower than 0.021 meter cube value which came from the RK equation.

(Refer Slide Time: 20:37).

Example

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$$v = 1.2 \times 10^{-4} \left[\text{m}^3/\text{mol} \right] \quad \text{By Trial and Error}$$

. So from this RK equation turns out to be very good.

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Using Compressibility Chart (Appendix C)

z^0, z^1

First, find critical points

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Compared to the chart which was turned out to be more rigorous exercise. But otherwise it gives you the similar numbers.

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EOS for liquids

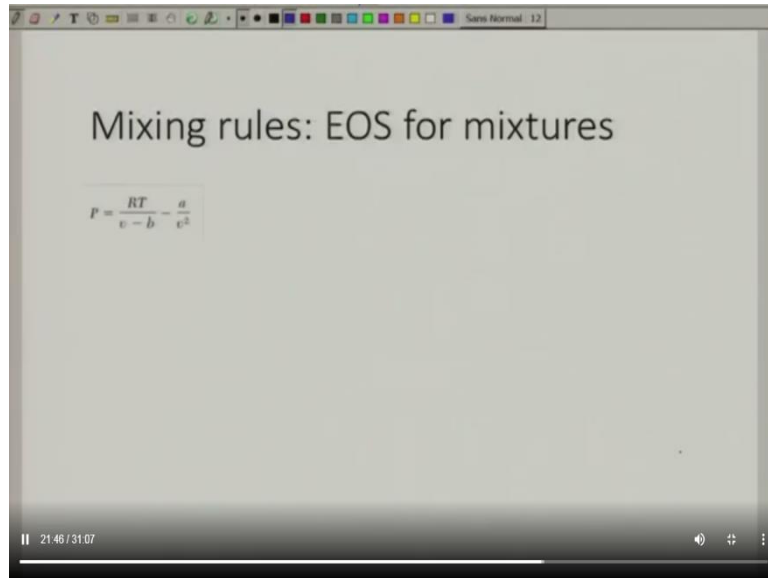
- Some EOS are applicable to liquids as well as gases.
 - Benedict-Webb-Rubin equation of state provides reasonable estimates for most hydrocarbons.
- The generalized compressibility charts
 - can be used for both gas and liquid phases.
- Alternatively, correlations have been developed explicitly for the liquid phase.
 - For example, the liquid volume at saturation is given by the Rackett equation:

$$v^L_{sat} = \frac{RT_c}{P_c} (0.29056 - 0.08775\omega)^{1 + (1 - Z_c)^2}$$

These exercises were for the gases the equation of state which we are used for example, RK and others where the used for the gases, but there are equation of state which are applicable for liquid as well. For example, this equation of state provides reasonable estimates for most hydrocarbons, and in fact generalized compressibility chart can also be used but often not done there are correlations which are developed for the liquid phase. For example, the liquid volume at saturation is given by this Rackett equation, which is nothing but a molar volume liquid

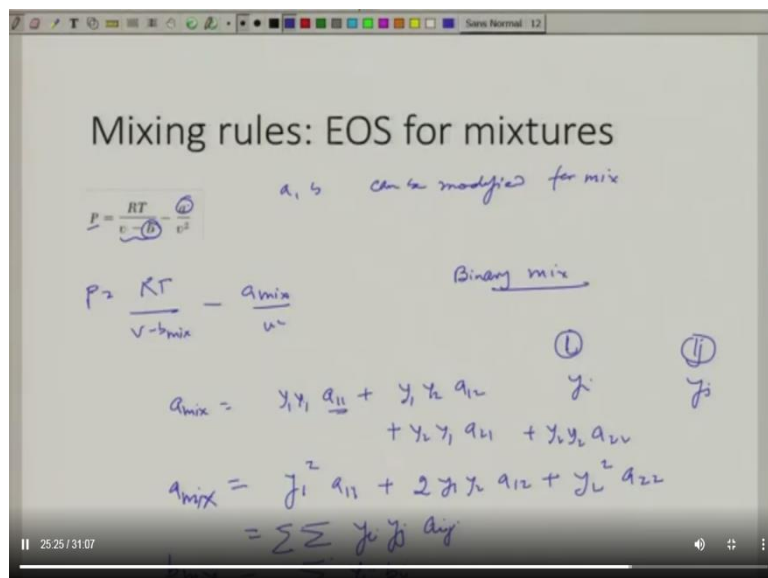
saturation and it depends on the T C P C and W and as well as TR. So this kind of correlation has been also developed.

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Now we have talked about the pure fluids till date. Now let us try to see how this equation of state can be extended to the mixtures.

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So in this case if you look at a simple VanDer Waal's equation of state you have pressure which is related to this term, which is a modified equation, modified ideal gas where the expected volume is there and then the attracted term.

So here the A and B are the parameters which can be modified for your equation for the mixtures. So A and B can be modified for mixtures.

$$P = \frac{RT}{V - b_{mix}} - \frac{a_{mix}}{V^2}$$

Now a mix if you have let us say a binary mixture, so I can write a because a if you think about it, a is nothing but the interaction between two particles with basically nothing but the two body particle. So if it is one here and one here is just talking about the interaction between this.

$$a_{mix} = y_1 y_1 a_{11} + y_1 y_2 a_{12} + y_2 y_1 a_{21} + y_2 y_2 a_{22}$$

$$a_{mix} = y_1^2 a_{11} + 2y_1 y_2 a_{12} + y_2^2 a_{22} = \sum \sum y_i y_j a_{ij}$$

So this gives you a mixture here. So we can generalize this by saying summation, this is something we can generalize. What about b excluded volumes, so excluded volume would be simply the weighted average. So I can write here b mix is summation y i b i. So this will be nothing but weighted average of the excluded volume in a given system. So with this kind of mixing rule, I can easily apply to any binary, ternary mixtures. So that becomes much easier for me for the application.

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Mixing rules: EOS for mixtures

a, b can be modified for mix

$$P = \frac{RT}{v-b} - \frac{a}{v^2}$$

Binary mix

$$P = \frac{RT}{v-b_{mix}} - \frac{a_{mix}}{v^2}$$

$$a_{mix} = y_1 y_1 a_{11} + y_1 y_2 a_{12} + y_2 y_1 a_{21} + y_2 y_2 a_{22}$$

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

Now in the similar line I can also come up with the mixing rule for virial equation state. So again, let us look at virial equation state.

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Virial EOS

$$Z = 1 + \frac{B}{V} + \frac{C}{V^2} + \frac{D}{V^3} + \dots$$

pure fluid

$$Z_{mix} = 1 + \frac{B_{mix}}{V} + \frac{C_{mix}}{V^2} + \frac{D_{mix}}{V^3} + \dots$$

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

$$C_{mix} = \sum_i \sum_j \sum_k y_i y_j y_k C_{ijk}$$

So you have Z is equal to 1 plus B 1 by V plus C V square plus D So the question is, this is for the pure fluid. What about if we consider mixture? So B will become B mix/V similarly C will become mix and similarly D will become D mix. So got to be B mix, so we will be using the similar concept as we have done that for Van der Waal equation of state to active parameter a we can also come up with a similar kind of concept here where this would be your again y i y j B i j. So this is something which will can be written here. Now similarly for C mix this will

be Triple this y i j k because they are three particles remember that D is for two body interactions C is for three body interactions.

$$Z = 1 + \frac{B}{V} + \frac{C}{V^2} + \frac{D}{V^3} + \dots$$

$$B_{mix} = \sum \sum y_i y_j B_{ij}$$

$$C_{mix} = \sum \sum \sum y_i y_j y_k C_{ijk}$$

So, C mix will become for C i j k. So you are trying to weight it by three mole fractions of different components, and so forth. Now, most of the time we often use only for the binary mixtures. And in that case, of course, it will become c 1 1 2 or 1 2 2 and so forth. So I am not doing any example for this particular aspect but I think you probably can get the idea that how this can be extended further for the binary mixtures all the equation of state by considering some mixing rule. So mixing rule is certainly is approximation.

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Mixing rules: EOS for mixtures

a, b can be modified for mix

$$P = \frac{RT}{v - b} - \frac{a}{v^2}$$

$$P = \frac{RT}{v - b_{mix}} - \frac{a_{mix}}{v^2}$$

Binary mix

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

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

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For example, if you look at the mixing rule here you may ask this question. Well, we may know this a 1 1 and a 2 2 because a 1 1 can be simply a 1, that means that attractive term for a given fluid for the pure phase and similarly a 2 2 could be simply a 2, what about a 1 2 so we a 1 2 can be considered simply as a square root of a 1 1 a 1 or a 2. So this is the geometric mean of this attractive terms or parameters of pure fluid a and 2 in order to get the binary interaction parameter for a 1 and a 2.

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Mixing rules: EOS for mixtures

a, b can be modified for mix

$$P = \frac{RT}{v - b} - \frac{a}{v^2}$$

$$P = \frac{RT}{v - b_{mix}} - \frac{a_{mix}}{v^2}$$

Binary mix

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

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

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That means a 1 2 but this is one of the approximation, you know, there could be other approximation such that we can add this and because it may not actually may not give the right kind of interactions and there has been some correction term which people have used such as 1 minus Alpha 1 2. So this 1 2 becomes a cross correlation parameter and that is also used sometimes in the Peng-Robinson equation.

So this mixing rule becomes an important element in order to address the correct behavior of a binary, ternary and so forth mixtures and this corrections is basically is usually driven by the non agreement with the experiment and hence people come with these kind of concepts here. Now, for the case of Alpha, of course, the variety of different systems have been... people have come with this kind of terms. I will not be going into details of that.

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Mixing rules: EOS for mixtures

a, b can be modified for mix

$$P = \frac{RT}{v-b} - \frac{a}{v^2}$$

Binary mix $\frac{1}{\sqrt{a_1 a_2}} (1 - x_{12})$

$$a_{mix} = y_1^2 a_{11} + y_1 y_2 a_{12} + y_2 y_1 a_{21} + y_2^2 a_{22}$$

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

$$= \sum_i \sum_j y_i y_j a_{ij}$$

The text book does give some examples and it is also recommended that you look at it we will also try to have a set of examples, set of questions in the as a part of the assignments, to give a flavor of this kind of mixing rule.

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Mixing rules: EOS for mixtures

a, b can be modified for mix

$$P = \frac{RT}{v-b} - \frac{a}{v^2}$$

Binary mix $\frac{1}{\sqrt{a_1 a_2}} (1 - x_{12})$

$$a_{mix} = y_1^2 a_{11} + y_1 y_2 a_{12} + y_2 y_1 a_{21} + y_2^2 a_{22}$$

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

$$= \sum_i \sum_j y_i y_j a_{ij}$$

So with this we will end today's lecture and in the next lecture will start a new topic, topic on the fugacity and subsequently we will look into the mixtures more in details. So I will see you in the next lecture.