Thermodynamics (Classical) for Biological Systems

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Module No. # 03

Thermodynamics of Pure Substances

Lecture No. # 11

Equations of State-Cubic Equations

In the last class, we started looking at equations of state. We started out with the ideal gas equation P V equals R T, which we realize is an equation of state. And as we said an equation of state is something that connects the pressure, specific volume, temperature of a pure substance. Then, we said that most gases are real, and therefore, we need more accurate representations of those gases than what is given by the ideal gas law, that is P V equals R T. And the first improvement that we saw was the virial equation of state, which we said could be written either in terms of a series in pressure or a series in specific volume. Then we had posed this problem to become comfortable with the use of virial equation, and I had given you some hints and an initial part of the solution.

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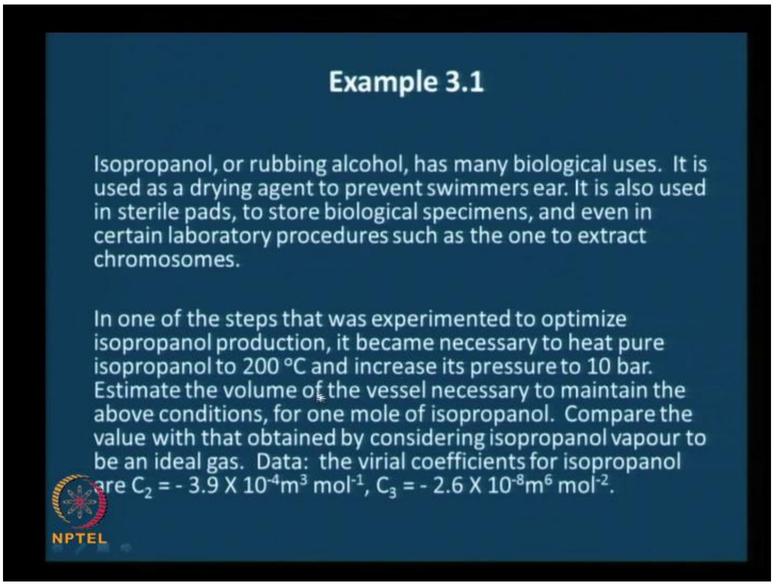

Example 3.1

Isopropanol, or rubbing alcohol, has many biological uses. It is used as a drying agent to prevent swimmers ear. It is also used in sterile pads, to store biological specimens, and even in certain laboratory procedures such as the one to extract chromosomes.

In one of the steps that was experimented to optimize isopropanol production, it became necessary to heat pure isopropanol to 200 °C and increase its pressure to 10 bar. Estimate the volume of the vessel necessary to maintain the above conditions, for one mole of isopropanol. Compare the value with that obtained by considering isopropanol vapour to be an ideal gas. Data: the virial coefficients for isopropanol are $C_2 = -3.9 \times 10^{-4} m^3 mol^{-1}$, $C_3 = -2.6 \times 10^{-8} m^6 mol^{-2}$.

So, let me present the complete solution here. This was the problem regarding isopropanol, and we said that, we are looking at an isopropanol at 200 degree C and 10 bars. And we need to estimate the volume of the vessel necessary to maintain the above conditions for one mole of isopropanol. Therefore, you have pressure … temperature here, you have pressure here. You are asked to find this specific volume of the molar volume, volume for one mole. And, the virial coefficients in terms of the volume expansion were given; C 2 and C 3 were given.

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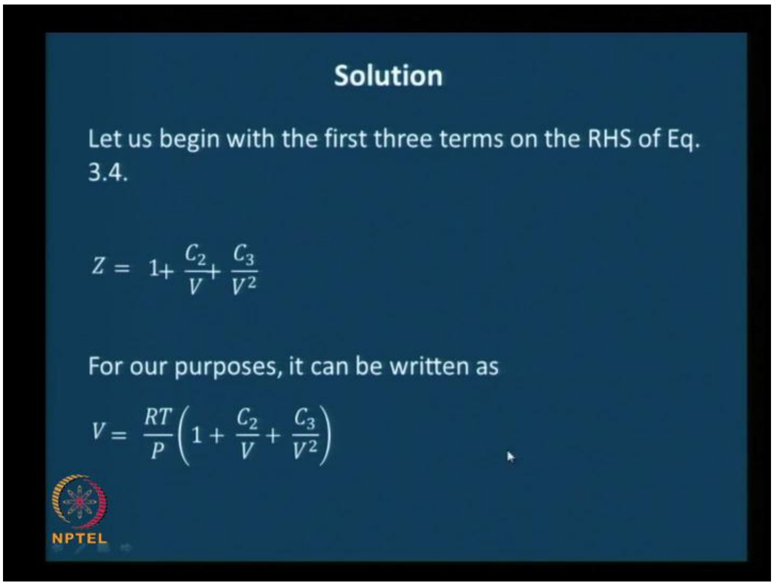

Solution

Let us begin with the first three terms on the RHS of Eq. 3.4.

$$Z = 1 + \frac{C_2}{V} + \frac{C_3}{V^2}$$

For our purposes, it can be written as

$$V = \frac{RT}{P}\left(1 + \frac{C_2}{V} + \frac{C_3}{V^2}\right)$$

Then, after a couple of hints, we went ahead with the solution…, mentioned that we could start out with just three terms, in the virial expansion for specific volume, Z equals 1 plus C 2 by V plus C 3 by V squared; this should work in most cases except when the pressures are high and so on. For our purposes we said, we could write this as this Z equals P V by R T, and therefore, multiplying by R T by P on both sides, we have V in terms of V, an implicit equation, which would be good for iterations and this requires an iterative solution.

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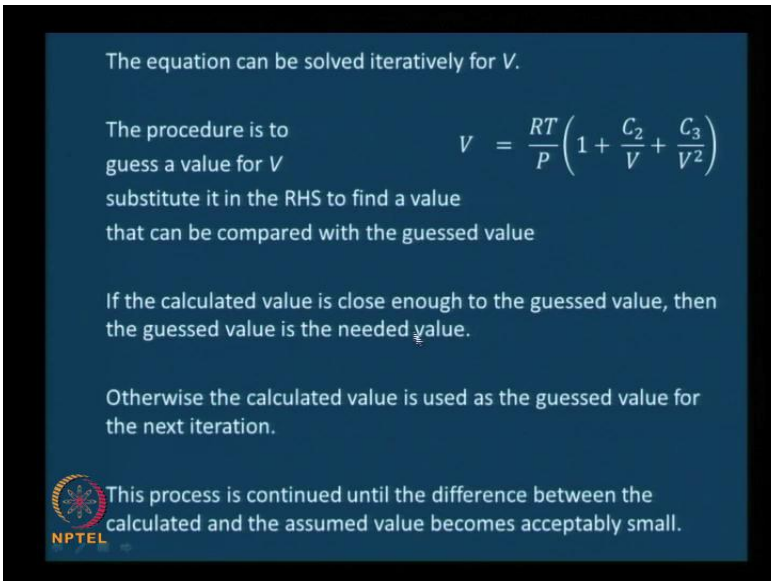

The equation can be solved iteratively for V.

The procedure is to
guess a value for V
substitute it in the RHS to find a value
that can be compared with the guessed value

$$V = \frac{RT}{P}\left(1 + \frac{C_2}{V} + \frac{C_3}{V^2}\right)$$

If the calculated value is close enough to the guessed value, then the guessed value is the needed value.

Otherwise the calculated value is used as the guessed value for the next iteration.

This process is continued until the difference between the calculated and the assumed value becomes acceptably small.

And, I had given you the procedure for iteration and asked you to work things out. What I will do now is to present a few more steps, and again ask you to work things out, because you need to get a little more comfortable with an iteration process. I am not very sure, how many of you have solved problems that had iterative solutions.

So, we said that the procedure was to guess a value for V, and substitute it into the right hand side and find the value of the right hand side. And this can be compared with a guessed value. One way of comparing is to take the difference between the calculated value and the guessed value. And if the calculated value on the right hand side is close enough to the guessed value, then the guessed value is a needed a value. We said close enough, we need to be little careful.

Otherwise, the calculated value is used as the guessed value for the next iteration. And then you use that volume here, substitute that volume here to find out the right hand side, and then compare again. And the process is continued until the difference between the calculated, and the assumed value becomes acceptably small. This is where we left off last time; I hope you would have worked things out. If you had some difficulty, please pay attention to what follows.

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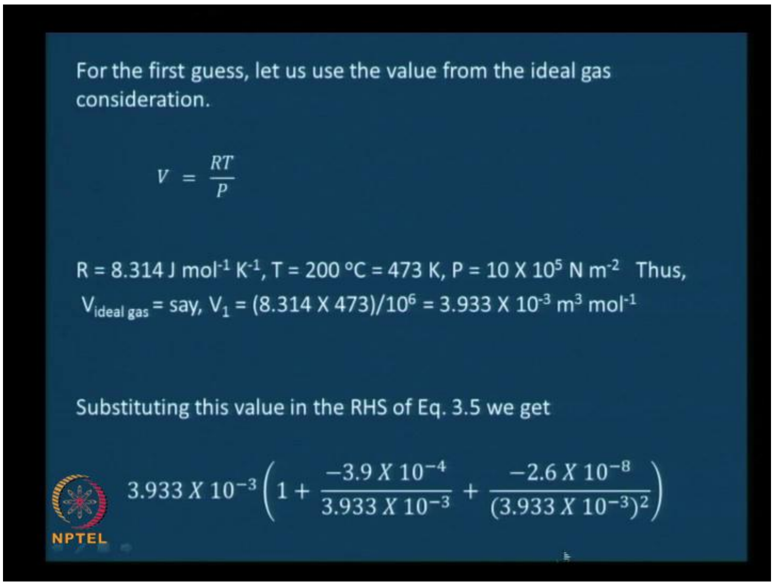

For the first guess, let us use the value from the ideal gas consideration.

$$V = \frac{RT}{P}$$

R = 8.314 J mol^{-1} K^{-1}, T = 200 °C = 473 K, P = 10 X 10^{5} N m^{-2} Thus, $V_{\text{ideal gas}}$ = say, V_1 = (8.314 X 473)/10^{6} = 3.933 X 10^{-3} m^{3} mol^{-1}

Substituting this value in the RHS of Eq. 3.5 we get

$$3.933\,X\,10^{-3}\left(1+\frac{-3.9\,X\,10^{-4}}{3.933\,X\,10^{-3}}+\frac{-2.6\,X\,10^{-8}}{(3.933\,X\,10^{-3})^{2}}\right)$$

For the first guess … we need to start with the first guess, and where do we get that first guess from? If it is a gas, this equation is valid for a gas; we could use the ideal gas value – whatever, we get from P V equals R T as the first guess; we would not be way off. Therefore, V equals R T by P from the ideal gas equation. And if we substitute the values in this particular case, in this particular exercise, R as we all know as 8.314 joules per mole per Kelvin, T was 200 degree C, but we know that, we need to use T in Kelvin. So, add a 273 to it to get 473 Kelvin, and pressure was 10 atmospheres.

We need it in a consistent set of units therefore, we multiplied by 10 of 5 Newton per meter squared. And if we substitute R T by P here, the numbers for that we get the ideal gas, let us say V 1 in terms of our iterative solution as 3.933 into 10 power minus 3, you know 8.314 into 473 divided by this is 10 power 6.

So, 3.933 into 10 power minus 3 meter cubed per mole. Hopefully, you got this if you knew where to look for. Substituting this value in to the right hand side of the earlier equation, you know we had set of the iterative volume equation there. … 3.933 into 10 power minus 3, V, plus into 1 plus C 2 by V, plus C 3 by V squared. C 2 was minus 3.9 into 10 power minus 4, V is 3.933 into 10 power minus 3 C 3 was minus 2.6 into 10 power minus 8 and V squared is this.

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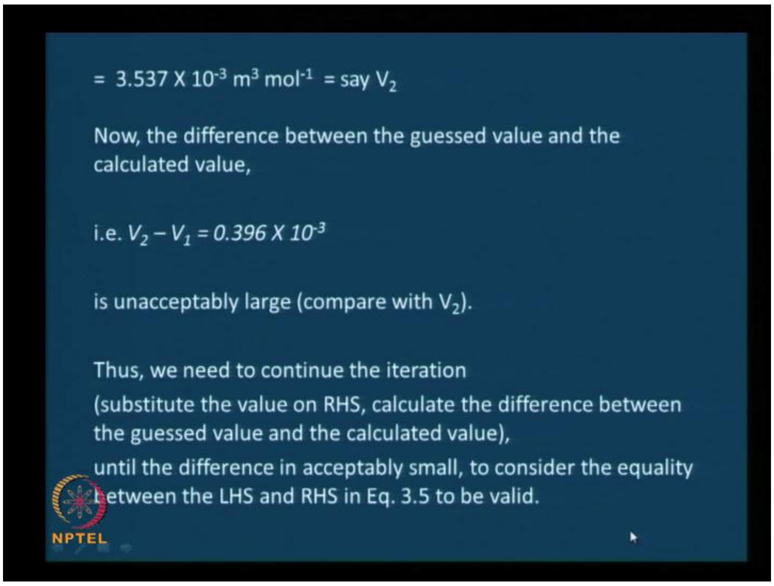

$= 3.537 \times 10^{-3}\ m^3\ mol^{-1}$ = say V_2

Now, the difference between the guessed value and the calculated value,

i.e. $V_2 - V_1 = 0.396 \times 10^{-3}$

is unacceptably large (compare with V_2).

Thus, we need to continue the iteration
(substitute the value on RHS, calculate the difference between the guessed value and the calculated value),
until the difference in acceptably small, to consider the equality between the LHS and RHS in Eq. 3.5 to be valid.

So, if we substitute the values her,e we end up with 3.573 into 10 power minus 3 meter cubed per mole. This is V 2, which is the calculated value, starting with V 1 the ideal gas value. On the face of it these seems small, but, let us consider this further. We need to take the difference between the guessed value, which was the ideal gas value and the calculated value, which is this 3.537 to 10 power minus 3. In other words, the difference between V 2 and V 1 in this case. Which turns out to be 0.396 in to 10 power minus 3. You know this is 3.96 into 10 power minus 4, which is almost 11 to 12 percent of this value.

That is not acceptable, that is very high. 11 to 12 percent is very high, is unacceptably large and therefore, we need to continue the iteration. In other words, we substitute V 2 into the R H S. Calculate the value and … calculate the value of the R H S that is, and then calculate the difference between the guessed value and the calculated value, till the difference is acceptably small.

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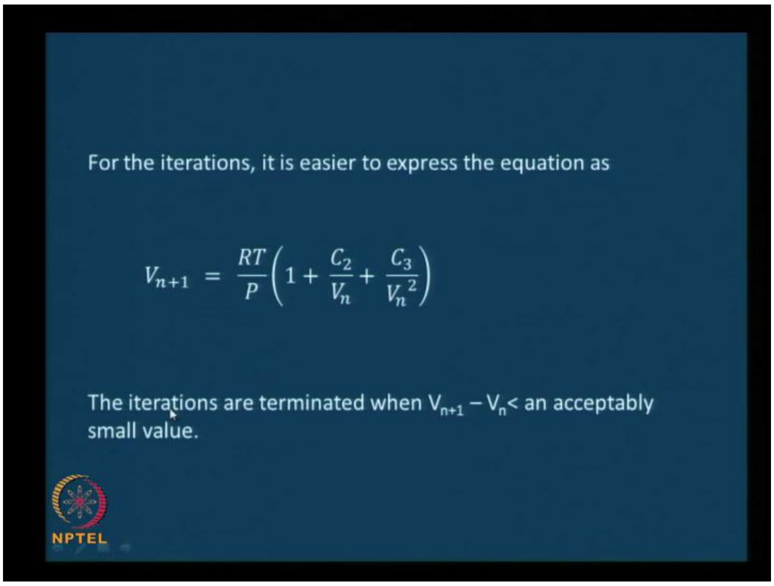

For the iterations, it is easier to express the equation as

$$V_{n+1} = \frac{RT}{P}\left(1+\frac{C_2}{V_n}+\frac{C_3}{V_n^{\,2}}\right)$$

The iterations are terminated when $V_{n+1} - V_n <$ an acceptably small value.

For the iterations, it is easier to express the equation in the form of n and n plus 1. In other words, you know we said V 2 was … we get in terms of V 1, and so on. So, we can generalize that and say V n plus 1 R T by P into 1 plus C 2 by V n plus C 3 by V n squared. If we do this it gives us a nice way of looking at the … iterations. As well as to write a program to let a computing device do the iterations for us. We do not have to do it manually. And the iterations can be terminated, when V n plus 1 minus V n, the difference between V n plus 1 and the guessed value V n, is less than an acceptably small value, may be about 1 percent or 2 percent of the actual value.

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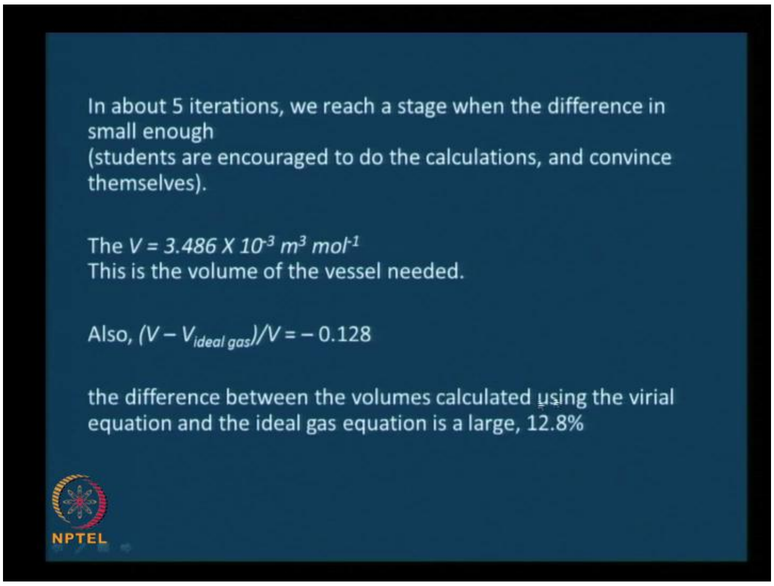

In about 5 iterations, we reach a stage when the difference in small enough
(students are encouraged to do the calculations, and convince themselves).

The $V = 3.486 \times 10^{-3}\ m^3\ mol^{-1}$
This is the volume of the vessel needed.

Also, $(V - V_{ideal\ gas})/V = -0.128$

the difference between the volumes calculated using the virial equation and the ideal gas equation is a large, 12.8%

What I would like you to do is … this is this will converge in about 5 iterations. So, I would like you take another 10 to 15 minutes. And actually work out the iterations. It is going to take some time, because you are going to substitute numbers and so on. But, it is good to get comfortable with the procedure. If you have already done it as a part of the home work given yesterday. Go forward … by about 10 to 15 minutes to the next part of the solution and the lecture, but, otherwise please take the time now. Take about 15 minutes and do the iterations. Please go ahead.

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You would have had enough time, to do the calculations. See whether you got this value at the end of about 5 iterations, 3.486 in to 10 power minus 3 meter cubed for mole. This is when the right hand side value is different from the left hand side value, or the guessed value, only by a small amount – an acceptably small amount. And thus we have reached the volume of the vessel, that was needed, which was actually what we started out looking for in the exercise.

Also, there was another part to the exercise. That was to find out the variation between the value given by the virial equation, the volume given by the virial equation and the volume given by the ideal gas. In other words, to find out the percentage difference.

So, to find out the percentage difference, we take the difference divided by the actual volume, and actually we need to multiply it by 100. We will do that in a little while, for now V minus V ideal gas the whole divided by the volume will turn out to be minus 0.128. Therefore, the difference between the volumes calculated using the virial equation and the ideal gas equation is large. It is about 13 percent … 12.8 percent. This you should keep in mind.

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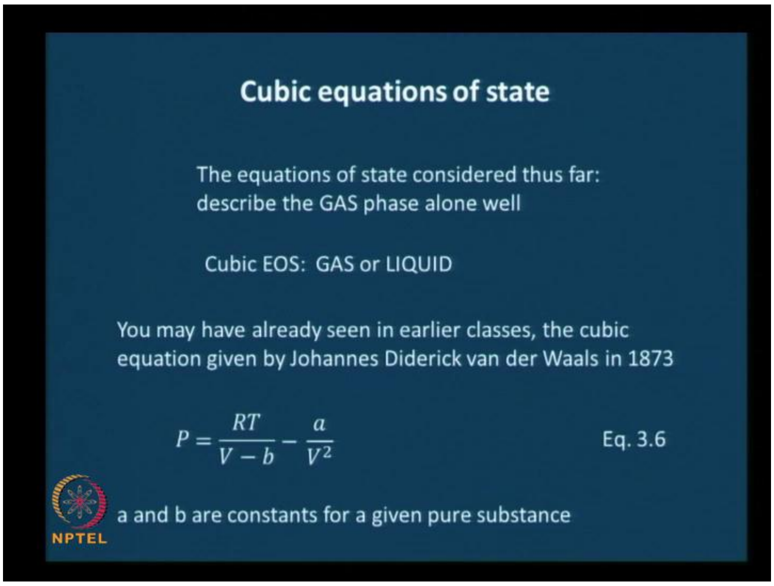

Cubic equations of state

The equations of state considered thus far:
describe the GAS phase alone well

Cubic EOS: GAS or LIQUID

You may have already seen in earlier classes, the cubic equation given by Johannes Diderick van der Waals in 1873

$$P = \frac{RT}{V-b} - \frac{a}{V^2} \qquad \text{Eq. 3.6}$$

a and b are constants for a given pure substance

The next equation of state that we are going to consider in this course is called the cubic equation of state. There are many cubic equations; we will probably see 1 or 2. The equations of state that we have considered thus far, which we reviewed in the beginning of this class which was the ideal gas equation and the virial equation. These equations described only the gas phase, which is reasonable general for a pure substance, but, they look only at the gas phase.

Whereas, cubic equations of state, have an ability to describe either the gas phase or the liquid phase with equal ease. Or, they can describe … I would not get in to the ease of description. They can describe the ... both the gas phase and the liquid phase. In other words, the combination of P V T, if know P and T, how do you get V? Or if you know P and V, how do you get T? It is good in predictions for both the gas and the liquid phase and it is close to experimental values, somewhat close.

And what might be surprising, it is that you have already seen one of the cubic equations in your earlier classes. I am sure you would have seen the VanderWaals equation. Which is actually given by VanderWaals, the full name is Johannes Diderick VanderWaals. He gave it way back in 1873 and even if you do not remember the name you may remember the equation, this is P equals R T by V minus b, minus a by V squared.

Let us call this equation 3.6. You know this cubic equation has the ability to describe the liquid phase because, the interactions between molecules are considered in the cubic equations, a little better. And, a and b, as you already know, in the Vander Waals equation are constants for a given pure substance. Therefore, you would have a table that lists a, and b for various different pure substances. There is one that lists at the end your text book itself.

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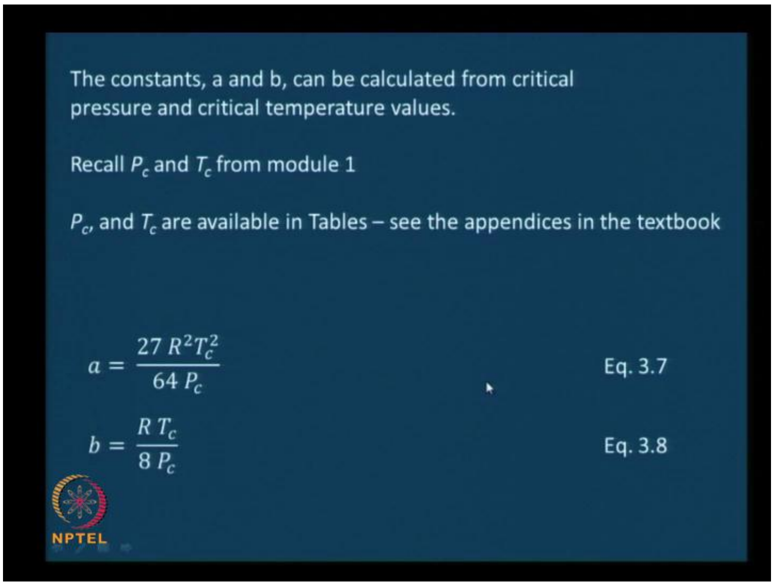

The constants, a and b, can be calculated from critical pressure and critical temperature values.

Recall P_c and T_c from module 1

P_c, and T_c are available in Tables – see the appendices in the textbook

$$a = \frac{27\, R^2 T_c^2}{64\, P_c} \qquad \text{Eq. 3.7}$$

$$b = \frac{R\, T_c}{8\, P_c} \qquad \text{Eq. 3.8}$$

The constants a, and b can be calculated from the critical pressure and the critical temperature values. I hope we can recall what P c and T c are. Remember that those are the pressure and temperature values that correspond to the critical point, you know there was it was a point in the P T diagram; and it was a point on the curve, the top part of the P V curve in a P V diagram. And that is pretty much the place where the critical phase starts. And P c and T c values are available in tables; they are available in one of the appendices in your text book also. The Smith Vanness and Abbot text book, there are values of P c and T c, the critical pressure and the critical temperature, that are given for various pure substances.

Now, let me present this first. This a in the Vander Waals equation can be written as 27 R squared; this is a gas constant - R squared, T c squared, critical temperature squared divided by 64 P c; we will call this equation 3.7. And b equals R T c by 8 P c - equation 3.8. Therefore the constants a, and b can be calculated from the critical pressure and the critical temperature values.

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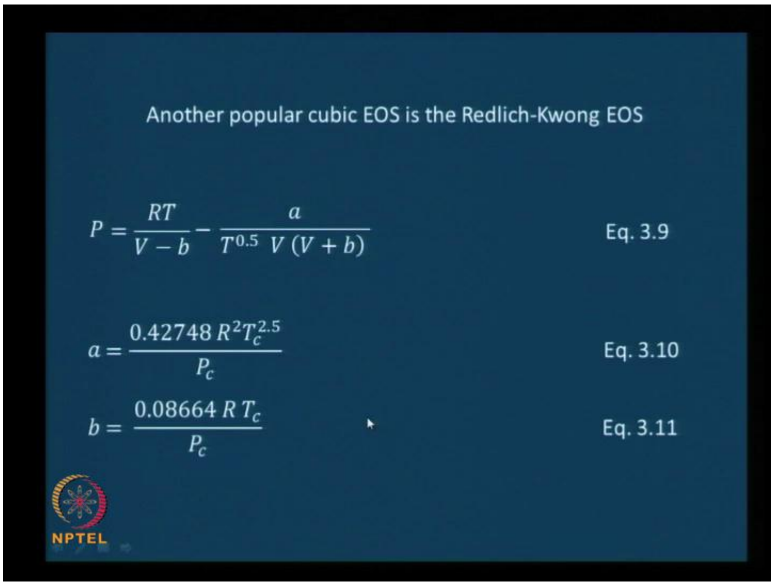

Another popular cubic EOS is the Redlich-Kwong EOS

$$P = \frac{RT}{V-b} - \frac{a}{T^{0.5}\, V\,(V+b)} \qquad \text{Eq. 3.9}$$

$$a = \frac{0.42748\, R^2 T_c^{2.5}}{P_c} \qquad \text{Eq. 3.10}$$

$$b = \frac{0.08664\, R\, T_c}{P_c} \qquad \text{Eq. 3.11}$$

Therefore, I make some more comments on that. Let me present another popular cubic equation of state, which is called the Redlich-Kwong equation of state. The equation itself is P equals R T by V minus b, somewhat similar to the earlier cubic equation, minus a divided by T power 0.5 into V into V plus b. We will call this equation 3.9. a in this case, excuse me … is 0.42748 R squared T c power 2.5 by P c. We will call this equation 3.10. b equals 0.08664 R T c by P c. we will call this equation 3.11. Now, you might wondering, how did I really write this. I did say that you can write in terms of T c and P c. How did people get this … you know … seemingly accurate number 0.42748, and so on and so forth.

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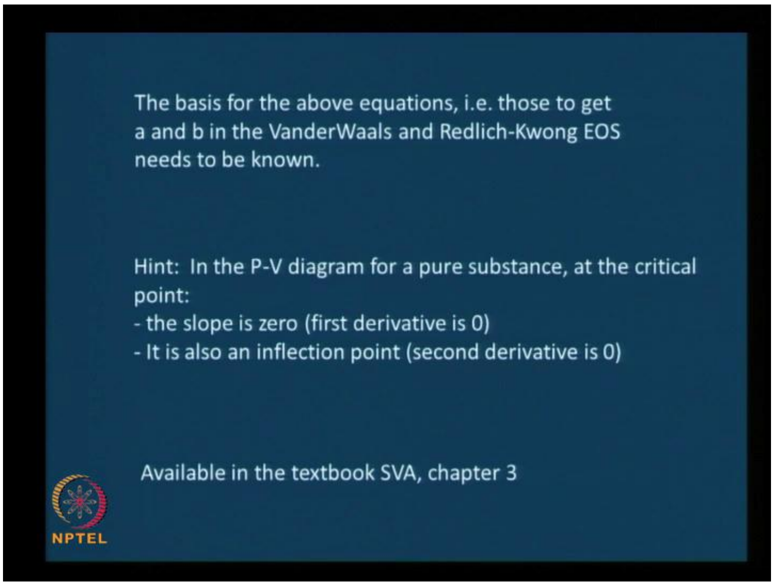

The basis for the above equations, i.e. those to get a and b in the VanderWaals and Redlich-Kwong EOS needs to be known.

Hint: In the P-V diagram for a pure substance, at the critical point:
- the slope is zero (first derivative is 0)
- It is also an inflection point (second derivative is 0)

Available in the textbook SVA, chapter 3

And that is what you are going to do as a next exercise. The basis for the above equations, that is the bases for the equations that gave you a, and b for both the Vander Waals equation and as well as the Redlich-Kwong equation. That definitely needs to be known as a part of this course. Let me give you, how to go about doing it and give you some time to do it. And then … let us see what to do.

In the, if you recall the P V diagram for a pure substance pressure versus specific volume for a pure substance, at the critical point the slope is actually 0. What is slope it is the derivative of P with respect to V. d P d V that is actually 0. Therefore, you could put d P d V equal zero and also it an inflection point these slope changes from one direction to the other exactly at that point. And that gives you another nice mathematical condition, which is d squared P by d V squared equals 0. So, you have this d P d V equals 0 and d squared P by d V squared equal 0. And you have the equations of state, which describe P V T behavior. So, please go ahead and try to get the expressions for a, and b using these conditions. Take about fifteen minutes to do it which should be till the end of this class. Please try that out. Go ahead please.

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You would have been able to work those things out, get expressions for a, and b. If you did not or even otherwise, please take a look at chapter three in your text book Smith, VanNess, Abbot. There it would have been worked out in some detail; you would need to fill in the missing steps.

We will continue the remaining in the next class.