

**Thermodynamics (Classical) for Biological Systems**

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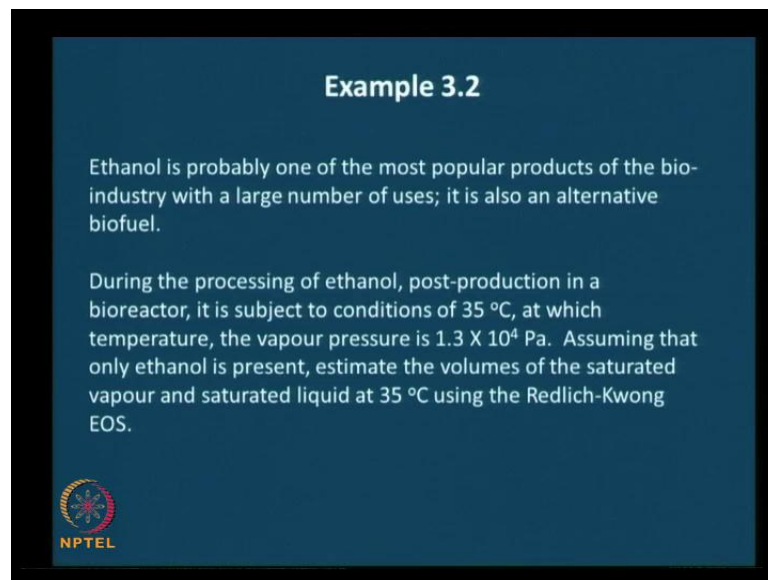
**Module No. # 03**

**Thermodynamics of pure substances**

**Lecture No. # 13**

**Volume Estimation (Continued) Generalized Correlations**


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**Example 3.2**

Ethanol is probably one of the most popular products of the bio-industry with a large number of uses; it is also an alternative biofuel.

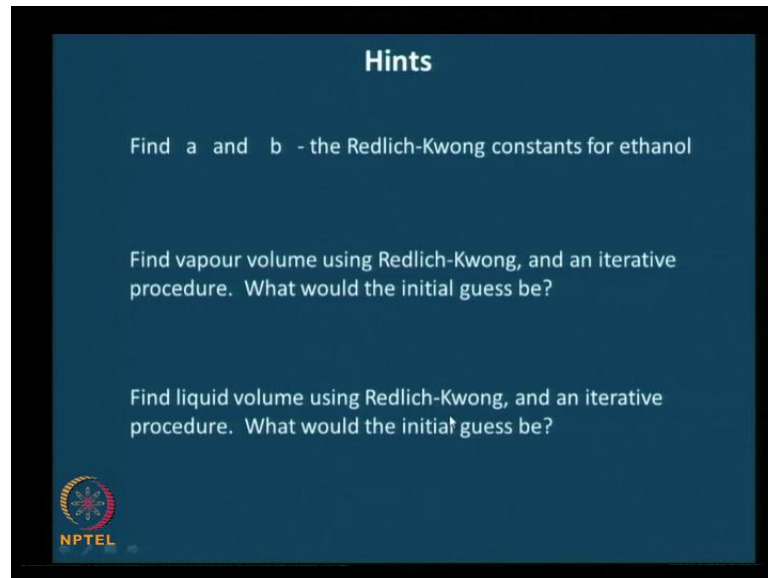
During the processing of ethanol, post-production in a bioreactor, it is subject to conditions of 35 °C, at which temperature, the vapour pressure is  $1.3 \times 10^4$  Pa. Assuming that only ethanol is present, estimate the volumes of the saturated vapour and saturated liquid at 35 °C using the Redlich-Kwong EOS.



NPTEL


Welcome back, we had started to look at this problem yesterday, example 3.2. Let me read it out again for completeness, today. Ethanol is probably one of the most popular products in the bio industry with the large number of uses. It is also an alternative bio fuel. During the processing of ethanol post production in the bioreactor, it is subject to conditions of 35 degree C, at which temperature, the vapour pressure is 1.3 into 10 power 4 pascals. Assuming that only ethanol is present, estimate the volumes of the saturated vapour and the saturated liquid at 35 degree C using the Redlich-Kwong equation of state. This was the problem or the example that was presented. And then, I had also given you some hints and time to work it out. Hopefully you had worked out the solution in full. We will any way present the solution now, after these hints.

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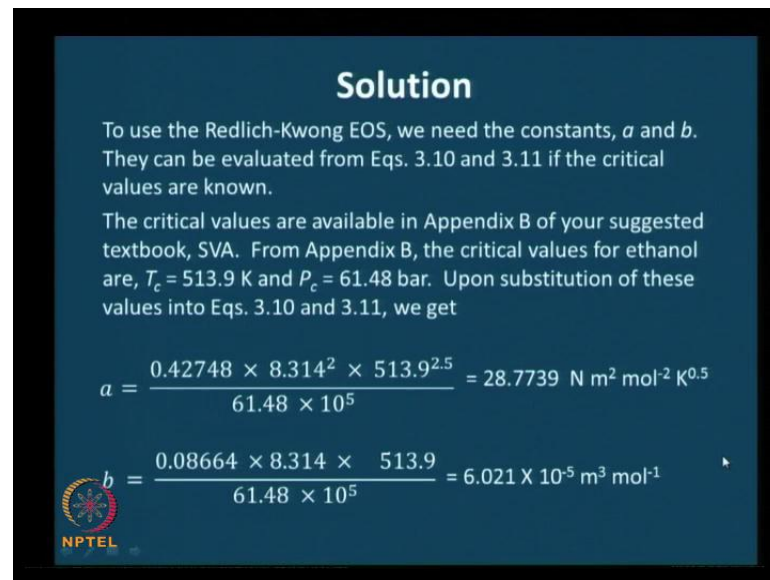
**Hints**

- Find  $a$  and  $b$  - the Redlich-Kwong constants for ethanol
- Find vapour volume using Redlich-Kwong, and an iterative procedure. What would the initial guess be?
- Find liquid volume using Redlich-Kwong, and an iterative procedure. What would the initial guess be?

 NPTEL

The hints were to use the Redlich-Kwong equation, we need to find the Redlich-Kwong constants, constants  $a$ , and  $b$  for ethanol, and I had asked you to find that out first. You had to look at the appropriate appendix. And then find the vapour volume using the Redlich-Kwong equation, and an iterative procedure. The question was what would the initial guess be? The initial guess is the ideal ... the volume that one obtains from the ideal gas equation. And then the other hint was to find out the liquid volume, which is the next part of the solution using the Redlich-Kwong equation of state and an iterative procedure. In this case, the initial **guess** was going to be the volume of the molecules as given by the constant  $b$ .

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**Solution**

To use the Redlich-Kwong EOS, we need the constants,  $a$  and  $b$ . They can be evaluated from Eqs. 3.10 and 3.11 if the critical values are known.

The critical values are available in Appendix B of your suggested textbook, SVA. From Appendix B, the critical values for ethanol are,  $T_c = 513.9$  K and  $P_c = 61.48$  bar. Upon substitution of these values into Eqs. 3.10 and 3.11, we get

$$a = \frac{0.42748 \times 8.314^2 \times 513.9^{2.5}}{61.48 \times 10^5} = 28.7739 \text{ N m}^2 \text{ mol}^{-2} \text{ K}^{0.5}$$
$$b = \frac{0.08664 \times 8.314 \times 513.9}{61.48 \times 10^5} = 6.021 \times 10^{-5} \text{ m}^3 \text{ mol}^{-1}$$



So, the solution itself in terms of numbers to for you, to verify yours. The constants  $a$ , and  $b$  can be obtained from the equations that give the constants in terms of the critical values. The critical values are available in the appendix B, this is the actual appendix ... of Smith, VanNess, and Abbott, which gives you the values of the critical parameters, critical temperature, critical pressure. And from appendix B, the critical values of ethanol are critical temperature  $T_c$  is 513.9 Kelvin and the critical pressure is 61.48 bar. It will be good to visualize, what exactly these mean in terms of your  $P-V$  diagram,  $P$  versus  $v$  diagram. The top point of the dome with under which you have the saturated region. Or in the  $P-T$  diagram it is essentially the point at the end point of the line, the vaporisation line there.

Upon substitution of these values into equation 3.10 and 3.11, which give you the expressions for  $a$ , and  $b$ . This is 0.42748 into  $R$  squared into  $T_c^{2.5}$ , 513.9  $T_c^{2.5}$ .  $R$ , of course, in the relevant units is 8.314, divided by  $P_c$ ; this is 61.48 bar. Therefore, we need it in Newton per meter square and therefore, you need to multiply it by  $10^5$ . This value turns out to be 28.7739 newton per meter squared per mole squared per Kelvin to the power of 0.5.

I am giving you 4 digits here, because this is the calculation, 4 is reasonably fine. When you are working with experimental values you need to be a little careful with the number of digits that you get here. Although your calculations would give you a large number of

digits, your calculator would give you a large number of digits, they usually do not make much sense given the accuracy with which the measurements can themselves be made.


The confidence with which measurements can be made is probably limited to 1 or 2 decimal places after this and therefore, it may not make sense to give experimental values in terms of a large number of decimal places. Whenever, it becomes relevant I will mention it again. But, in this case it is OK. 'a' turns out to be 28.7739 ... Newton meter squared per mole squared Kelvin to the power of 0.5. Similarly, b in terms of the critical values is 0.08664, this was the constant in the equation times R, 8.314, times T c, which is 513.9, divided by V c, which turns out to be 6.021 into 10 power minus 5 meter cubed per mole. This is the volume of the molecules.

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Through the use of Eq. 3.12, we can find the vapour volume, the convergence in this case happens in one step when we use the ideal gas volume obtained from  $RT/P$ , as the first guess,  $V_0 = 0.197 \text{ m}^3 \text{ mol}^{-1}$ , in

$$V_{n+1} = \frac{RT}{P} + b - \frac{a(V_n - b)}{T^{0.5} P V_n (V_n + b)}$$

The value converges well with  $V_2$ , which turns out to be  $0.1964 \text{ m}^3 \text{ mol}^{-1}$ , the volume of the saturated vapour.

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Now, that we have this, the second part is to find out the gas volumes and that can be ... or the vapour volume, and that can be done through the equation of 3.12. You can go back and check it is essentially an equation that is set up to find out volumes for a gas. The convergence in this case for this iterative solution happens in one step or in two steps.

When we use the ideal gas volume, ... if we look at  $RT$  by  $P$  as the initial guess  $V_0$ , which is the initial guess turns out to be 0.197 meter cubed per mole. And this is the equation that we considered for the iteration. And  $V_2$ , which is after two iterations turns out to be 0.1964 meter cube per mole; and since the difference between this and the  $V_1$


value is less than certain acceptable percent in this case very less, this can be taken as the volume of the saturated vapour. This is nice – it just turned out that the solution was close to the initial guess. So, we did not have to do too many iterations. Sometimes we may have to do a large number of iterations, in which case it is best to feed this into a computer that does it or write a program, computer program, that does it in terms of excel and so on so forth ... MS excel. Or, write a program to do it in terms of any of these standard programming languages.

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The liquid volume can be found, as mentioned earlier through iterations using Eq. 3.14

$$V_{n+1} = \left( b^2 + \frac{bRT}{P} - \frac{a}{P T^{0.5}} \right)^{-1} \left( V_n^3 - \frac{RT}{P} V_n^2 - \frac{ab}{P T^{0.5}} \right)$$

If the initial guess is  $b = 6.021 \times 10^{-5} \text{ m}^3 \text{ mol}^{-1}$ , the convergence happens in about 5 or 6 iterations to yield  $V_5 = 7.655 \times 10^{-5} \text{ m}^3 \text{ mol}^{-1}$  as the volume of the saturated liquid.



So, this is the second part. The third part was to find out the liquid volume. This ... again ... the liquid volume, we needed to use another formulation to avoid the dropping of the second term, because you had a V minus V term earlier, if you recall that. You can go back and check why we had used a different polynomial formulation for this iterations ... this set of iterations.  $V_{n+1}$  equals  $b^2 + \frac{bRT}{P} - \frac{a}{P T^{0.5}}$ , the inverse of this into  $V_n^3 - \frac{RT}{P} V_n^2 - \frac{ab}{P T^{0.5}}$ .

If we do the iterations here with an initial guess, as b t,he volume of the molecules 6.01 into 10 power minus 5 meter cube per mole, the convergence happens in about 6 iterations to give you a value of 7.655 into 10 power minus 5 meter cubed per mole as the volume of the saturated liquid.

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**Generalized correlations**

Thus far, we saw

- Ideal gas law (applicable only to ideal gases)
- Virial equations (applicable to a wider variety of gases)
- Cubic equations (applicable to gas or liquid states of a pure substance)

Now, let us see a formulation, that is applicable to almost all gases, i.e. generalized correlations

Generalized correlations are written in terms of reduced properties, the ratio of the property to its critical value

 NPTEL

So, that is the numerical solution. Please check it. If you have any doubts, any clarifications that are needed you can always get back.

Now, let us look at something called generalized correlations. To see this in the context of whatever we have already seen, we have already seen ideal gas law which is applicable only to ideal gases, very few gases. Virial equations which is applicable to a wider variety of gases, and the cubic equations - the VanderWaals and the Redlich-Kwong are the examples of cubic equations of state that we saw. These are applicable to a gas or a liquid state of a pure substance.

Now, we are going to see a formulation that is applicable to almost all gases. Baring a very few, these generalized correlations are applicable to almost all gases, and that is our interest in such a formulation. These generalized correlations are usually written in terms of what are called reduced properties. Reduced property is nothing but, you take a value let us say if you are talking of reduced temperature you take the actual temperature. Take the ratio of the actual temperature to the critical temperature of that pure substance. Then you get reduced temperature. As we go along the generality of this particular use will become very apparent.


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Reduced pressure:  $P_r \equiv \frac{P}{P_c}$

Reduced temperature:  $T_r \equiv \frac{T}{T_c}$

Reduced molar volume:  $V_r \equiv \frac{V}{V_c}$

To write the Redlich-Kwong equation in a generalized form, let us multiply both sides of Eq. 3.7 by  $V/RT$ , to yield

$$Z = \frac{1}{1-h} - \frac{a}{bRT^{1.5}} \left( \frac{h}{1+h} \right) \quad \text{where } h \equiv \frac{b}{V} = \frac{bP}{ZRT}$$


But, let us start with the definitions themselves. Reduced pressure is nothing but ... which is represented as  $P_r$ , is defined as the actual pressure to the critical pressure. Reduced temperature we already saw;  $T_r$  is defined as the actual temperature to the critical temperature, and reduced molar volume which is represented as  $V_r$  is defined as  $V$  which is the actual molar volume divided by the critical molar volume.

Usually, we start out with one of these equations; in this case we will start with the Redlich-Kwong equation of state and write it in a generalized form. To do that, what we will do is multiply both sides of equation 3.7. You can go back and check; equation 3.7 is nothing but, the Redlich-Kwong equation of state. If you multiply that by,  $V$  by  $RT$  you will get ... in fact, I would like you to do this right now, let me first present the equation ...  $Z$  the compressibility factor is  $1$  by  $1 - h$  minus  $a$  by  $bRT^{0.5}$  into  $h$  by  $1 + h$ , where  $h$  that we have defined, which we have introduced here is nothing but,  $b$  by the molar volume or in terms of the compressibility factor it is  $bP$  by  $ZRT$ . Now  $V$  can be written as  $ZRT$  by  $P$  and therefore, you get  $bP$  by  $ZRT$ . What I would like you to do is just do not take this on face value. There are some, which we may have to do because of the scope of this course itself.

But, in this case its straight forward substitution, and substitution in terms of critical properties and finding out this particular expression. I would like you to take the next 10 minutes to start out with the Redlich-Kwong equation, multiply both sides by  $V$  by  $RT$

and bring it to this form. Please go ahead and do this and convince yourself that this is indeed the correct expression. Go ahead please 10 minutes.

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Hopefully, you would have arrived at this expression here, which is by mere substitution and grouping b by V as h, and some transposition may be required ... may be more of grouping of terms is required to get this expression.

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Through the application of Eqs 3.10 and 3.11 to express a and b in terms of critical properties

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

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

and the definitions of reduced properties, we get

$$Z = \frac{1}{1-h} - \frac{4.934}{T_r^{1.5}} \left( \frac{h}{1+h} \right) \quad \text{Eq. 3.15}$$

where  $h = \frac{0.08664 P_r}{Z T_r}$  Eq. 3.16

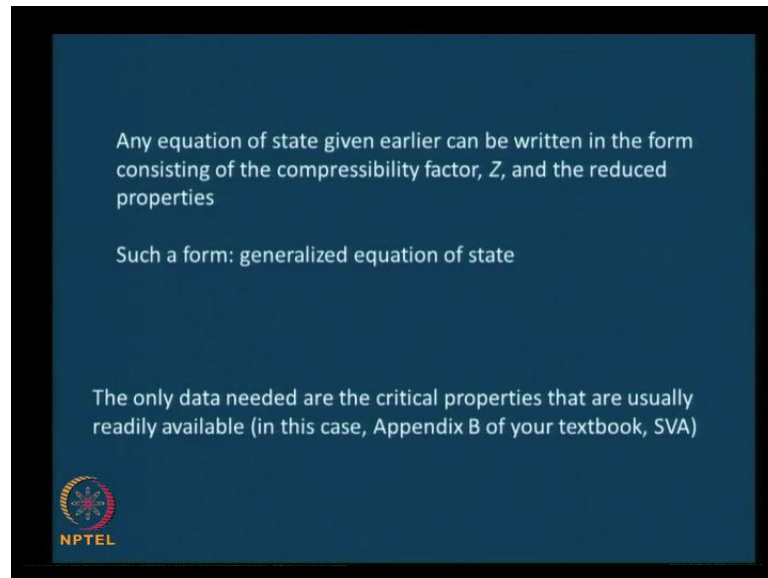
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We have already seen that a, and b can be expressed in terms of critical properties. 3.10 and 3.11, and this T c can be written in terms of the reduced properties. You know T r is nothing but, T by T c therefore; ... T c is nothing but, T by T r. If we do that and substitute these expressions for a and b in the earlier formulation which is this. Z equals 1 by 1 minus h minus a by b R T power 1.5 into h by 1 minus h. We do that here you have a and b here we are going to substitute here. We will get Z equals 1 by 1 minus h minus combine all those constants together you get 4.934 divided by T r power 1.5 into h by 1 plus h, we will call this equation 3.15.

And, h we said was b by V and that can be written in terms of, the combination of 0.08664 P r by Z T r, we will call this equation 3 16.




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Any equation of state given earlier can be written in the form consisting of the compressibility factor,  $Z$ , and the reduced properties

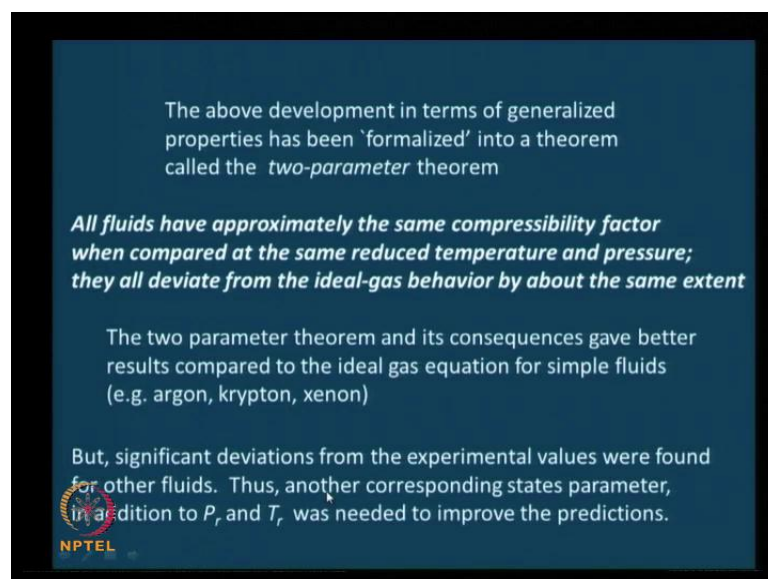
Such a form: generalized equation of state

The only data needed are the critical properties that are usually readily available (in this case, Appendix B of your textbook, SVA)



It so happens, that any equation of state can be written in terms of the compressibility factor and reduced properties. If it is written in that way or written in that form, it is called the generalized equation of state. And in such a case the advantage, the big advantage is, the only data that one requires to use that equation ... are the critical properties that are usually found in tables such as the one that is available in your textbook.

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The above development in terms of generalized properties has been 'formalized' into a theorem called the *two-parameter* theorem

***All fluids have approximately the same compressibility factor when compared at the same reduced temperature and pressure; they all deviate from the ideal-gas behavior by about the same extent***

The two parameter theorem and its consequences gave better results compared to the ideal gas equation for simple fluids (e.g. argon, krypton, xenon)

But, significant deviations from the experimental values were found for other fluids. Thus, another corresponding states parameter, in addition to  $P_r$  and  $T_r$ , was needed to improve the predictions.



Whatever, we have said just now has already been formalized. You know when something is formalized, then there is a significant confidence in that formalism to use it in general. Whatever we have said so far in the generalized equations of state has actually been formalized into a theorem called the two-parameter theorem, which essentially states, that all fluids have approximately the same compressibility factor when compared at the same reduced temperature and reduced pressure. Or, in other words they all deviate from the ideal gas behaviour by about the same extent. This is essentially saying the same thing that we have mentioned earlier but, this brings in another prospective.

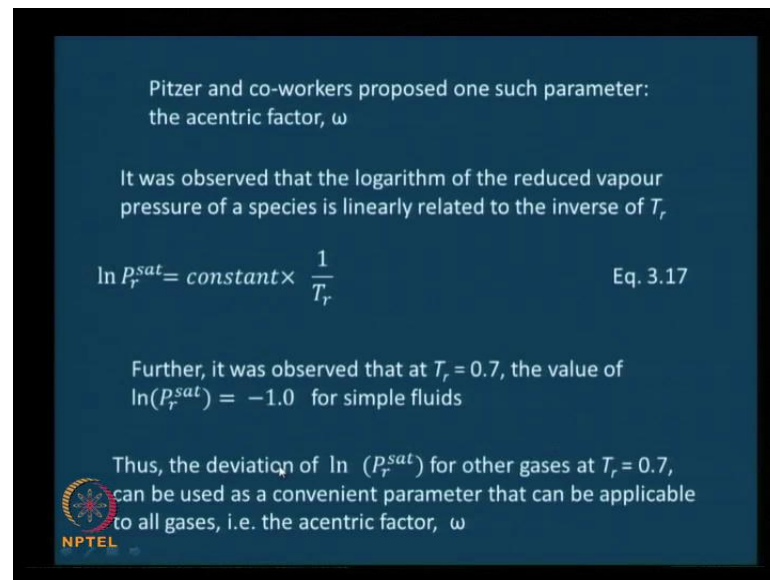
Let us read the first sentence again to understand this prospective. All fluids have approximately the same compressibility factor, when compared at the same reduced temperature and reduced pressure. And from this just, by using the reduced temperature and reduced pressure appropriately, and using the compressibility factor we have information about a large variety of gases. That is the advantage here.

The theorem that we just mentioned, the two-parameter theorem and its consequences gave results that were better compared to the ... ideal gas equation for some simple fluids such as argon, krypton, xenon.

So, there was some level of generalization there but, not the level that was acceptable. Therefore, ... or significant deviations from the experimental values were found for other fluids apart from these so called simple fluids such as argon, krypton, xenon.

And the way to handle that was to bring in another corresponding states parameter, in addition to this reduced pressure and reduced temperature. Now, we can see why this is called the corresponding states parameter. Compare this state ... this word corresponding states parameter (this phrase) with the theorem here: all fluids have approximately the same compressibility factor when compared at the same reduced temperature and reduced pressure. You would understand why we are calling this a corresponding states parameter.

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Pitzer and co-workers proposed one such parameter: the acentric factor,  $\omega$

It was observed that the logarithm of the reduced vapour pressure of a species is linearly related to the inverse of  $T_r$

$$\ln P_r^{sat} = \text{constant} \times \frac{1}{T_r} \quad \text{Eq. 3.17}$$

Further, it was observed that at  $T_r = 0.7$ , the value of  $\ln(P_r^{sat}) = -1.0$  for simple fluids

Thus, the deviation of  $\ln(P_r^{sat})$  for other gases at  $T_r = 0.7$ , can be used as a convenient parameter that can be applicable to all gases, i.e. the acentric factor,  $\omega$



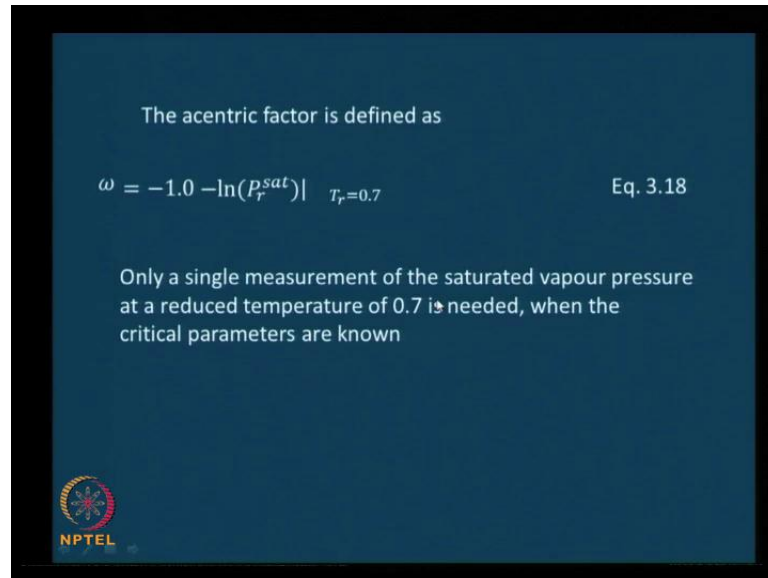
And ... when the third parameter was looked into to improve the predictions, Pitzer and co-workers came up with a parameter called the Acentric factor, which we will represent by this letter omega here. What they found was – this was experimentally found by analysing a large amount of data. They observed that the logarithm of the reduced vapour pressure of a species or of a pure substance is linearly related to the inverse of the reduced temperature. This was a powerful kind of information that was gathered from a large amount of data. Or, in other words, the logarithm of the reduced vapour pressure,  $P_r^{sat}$  – saturated pressure is the vapour pressure that we are talking about – is a constant times  $1/T_r$ . It is linearly related to the inverse of the reduced temperature. We will call this equation 3.17.

And further it was observed that at a reduced temperature of 0.7, the value of the logarithm of these saturated reduced pressures was minus one for simple fluids. So, what it did was, it lead to an interpretation that the deviation of the log of  $P_r^{sat}$  for other gases at reduced temperature of 0.7 is a single measurement that you need to differentiate between ... the simple fluids that follow the two-parameter theorem and all other fluids.

And most importantly it is just one measurement. The deviation of log of  $P_r^{sat}$  at  $T_r = 0.7$  can be used as a convenient parameter that is applicable to all gases. That is, in other words, this acentric factor can be used as a convenient parameter. The Acentric factor therefore, you know right from this thing here that at  $T_r = 0.7$  log of  $P_r^{sat}$  was

minus one for simple fluids. And therefore, the difference between this and this or the deviation here would come in as a factor that would represent something apart from the simple fluids that was the thinking.

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The acentric factor is defined as

$$\omega = -1.0 - \ln(P_r^{sat}) \Big|_{T_r=0.7} \quad \text{Eq. 3.18}$$

Only a single measurement of the saturated vapour pressure at a reduced temperature of 0.7 is needed, when the critical parameters are known

NPTEL

And therefore, the acentric factor was defined as minus 1 minus log, the natural log of  $P_r^{sat}$  at a reduced temperature of 0.7.

Let me repeat this once again for completeness. The two-parameter theorem said that at the same reduced temperature and reduced pressure all gases have the same compressibility factor. And then they found that that theorem was only applicable only to simple fluids and not to all fluids ... not to all gases. And therefore, the way of improving the two-parameter theorem was to bring in a third parameter. And search for the third parameter led to something called an Acentric factor by Pitzer and co-workers. This came about from the observation that the logarithm of  $P_r^{sat}$  for a large number of gases is directly proportional to the inverse of the reduced temperature. ... That was one aspect.

The other aspect was, at a  $T_r$  of 0.7, at a reduced temperature of 0.7, the value of log of  $P_r^{sat}$  was minus 1 for simple fluids. And therefore, the deviation from minus 1 ... of the log  $P_r^{sat}$  value at a  $T_r$  of 0.7 would possibly give us a parameter that we are looking for – that was the thinking. And that was actually defined as the acentric factor, minus 1 minus the natural log of  $P_r^{sat}$  at  $T_r$  equals 0.7. We will call this equation 3.18.

As mentioned earlier ... when I had presented this. I mentioned this ... but, let me mention this again. Only a single measurement of the saturated vapour pressure at a reduced temperature of 0.7 is needed when the critical parameters are known. Therefore, we have brought down the measurements to just one additional value to describe a large variety of gases.

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Formalized by the *three parameter* theorem of corresponding states: All fluids with the same value of the acentric factor have the same compressibility factor when compared at the same reduced temperature and pressure; they all deviate from the ideal-gas behavior by about the same extent

The generalized equation of state can be written as (after Pitzer and coworkers)

$$Z = Z^0 + \omega Z^1 \quad \text{Eq. 3.19}$$

The values of  $Z^0$  and  $Z^1$  are available in Tables (for example, as in Appendix E of your textbook, SVA)

NPTEL

This was actually formalized by the three parameter theorem of corresponding states: All fluids with the same value of acentric factor have the same compressibility factor when compared at the same reduced temperature and reduced pressure. That is the theorem. Or, in other words, they all deviate from the ideal gas behaviour by about the same extent.

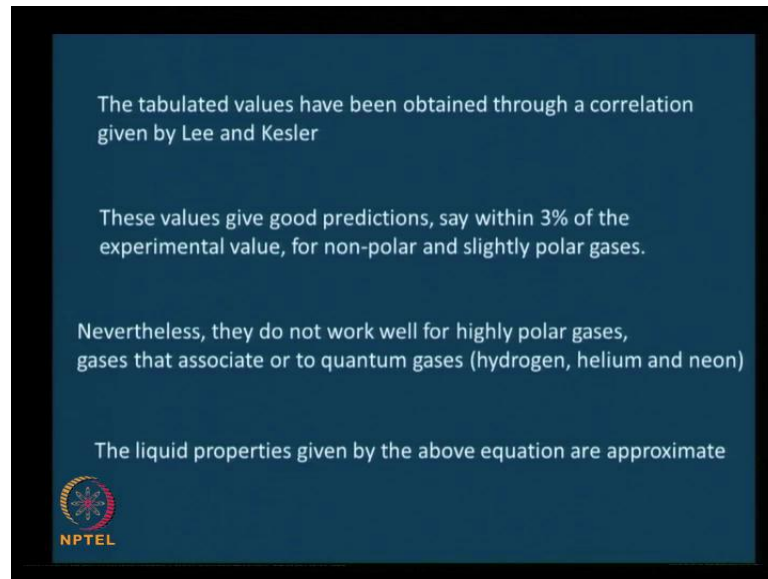
The generalized equation of state can be written as, in terms of the acentric factor, compressibility factor  $Z$  equals a certain  $Z$  naught plus the acentric factor and a certain  $Z$  1. Or, in other words the compressibility factor has been divided into two parts,  $Z$  naught part, and a  $Z$  1 part multiplied by the acentric factor. This has now become the equation of state; we will call this equation 3.19.

Why it is written in this form is that the values of  $Z$  naught and  $Z$  1 are available readily in tables. So, one can use those tables and directly calculate the compressibility factor here. One or a few such tables are given in appendix E of your textbook Smith VanNess and Abbott. What I would like you to do now is to familiarize yourself with these tables.

Please go to appendix E of your textbook Smith VanNess and Abbott and look at ... how these numbers are given there or how these values are given there,  $Z$  naught and  $Z_1$ . Take about 5 minutes please.

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Now, that you have ... familiarized yourself with the listing of  $Z$  naught and  $Z_1$  values, and the acentric values are also available in a table and the appendix, let us look at things a little further. The tabulated values actually were calculated by a correlation that was given by Lee and Kesler. And these values give very good predictions within about 3 percent of the very carefully measured experimental values, but, for non-polar and slightly polar gases. Therefore, we have generalized this, but, not completely. These gases, non-polar gases and slightly polar gases are fine, but, not the others.

They do not work for the highly polar gases and gases that associate, or quantum gases also do not work very. We need to be a little careful when we apply the generalized equation of state to these gases – for highly polar gases, gases that associate or quantum gases. Further, you can get liquid properties, or in other words, you can use those equations when you are considering the liquid state. But, the accuracy of the values is not very high.

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Approximate analytical expressions for  $Z^0$  and  $Z^1$  are also available, if reading from the Table is difficult:

$$Z^0 = 1 + B^0 \frac{P_r}{T_r} \quad \text{Eq. 3.20}$$
$$Z^1 = B^1 \frac{P_r}{T_r} \quad \text{Eq. 3.21}$$
$$B^0 = 0.083 - \frac{0.422}{T_r^{1.6}} \quad \text{Eq. 3.22}$$
$$B^1 = 0.139 - \frac{0.172}{T_r^{4.2}} \quad \text{Eq. 3.23}$$


Suppose, the table of  $Z$  naught and  $Z$  1 values are not available to you. Or the values are in a range that are not directly given in the table and reading of the table becomes difficult. In such cases, you can use the analytical expressions for  $Z$  naught and  $Z$  1. I am just going to present these analytical expressions; we are not going to get into the origins of these analytical expressions. It is useful to know this; instead of using the table, you can use this, if there is a need to use it. One should always give the first preference to use the tabulated values.

$Z$  naught is 1 plus  $B$  naught  $P_r$  by  $T_r$ , equation 3.20; and  $Z$  1 is  $B$  1  $P_r$  by  $T_r$ , equation 3.21.  $B$  naught is nothing but 0.083 minus 0.422 divided by the reduced temperature to the power of 1.6, equation 3.22; and  $B$  1 is 0.139 minus 0.172 divided by reduced temperature to the power of 4.2, equation 3.23.

What we would do next is to work out a problem to become familiar with the application of these generalized equations of state; and I think since we have almost run out of time, we will start doing that in the next class.