Thermodynamics for Biological Systems:
Classical and Statistical Aspects

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Lecture – 19
Generalized Correlations

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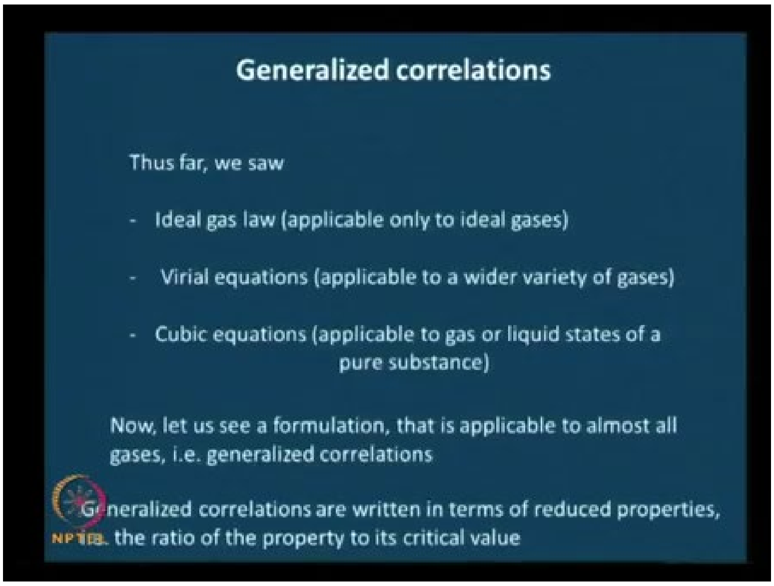

Generalized correlations

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, i.e. the ratio of the property to its critical value

Welcome!

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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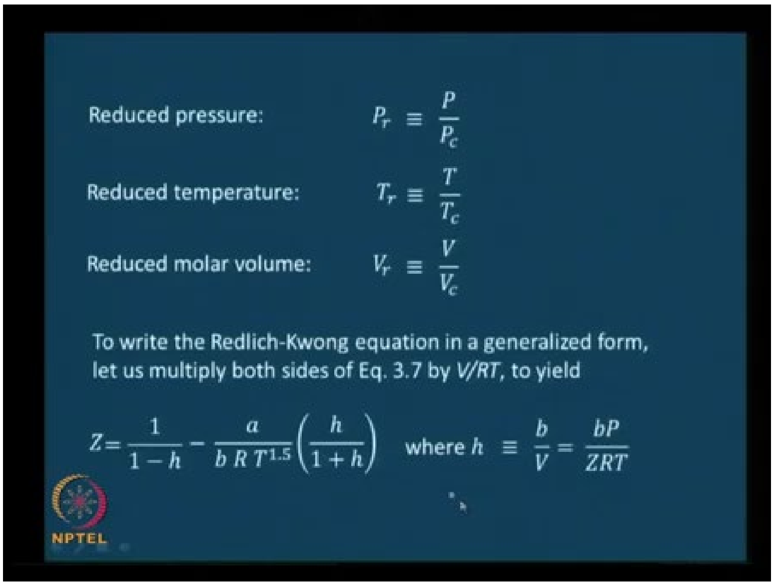

Reduced pressure: $P_r \equiv \frac{P}{P_c}$

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

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

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.

$$P_r \equiv \frac{P}{P_c}$$

Reduced temperature we already saw; T r is defined as the actual temperature to the critical temperature,

$$T_r \equiv \frac{T}{T_c}$$

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

$$V_r \equiv \frac{V}{V_c}$$

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 R T 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

$$Z = \frac{1}{1-h} - \frac{a}{b\,R\,T^{1.5}}\left(\frac{h}{1+h}\right)$$

where $h \equiv \frac{b}{V} = \frac{bP}{ZRT}$

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 R T 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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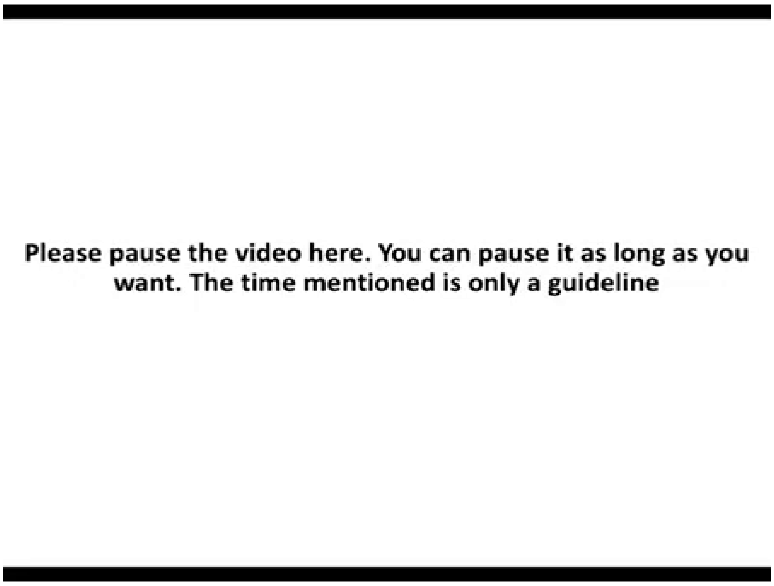

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Hopefully, you would have arrived at this expression here, which is by mere substitution and grouping b by V as h, and some transposition may be required … may be more of grouping of terms is required to get this expression.

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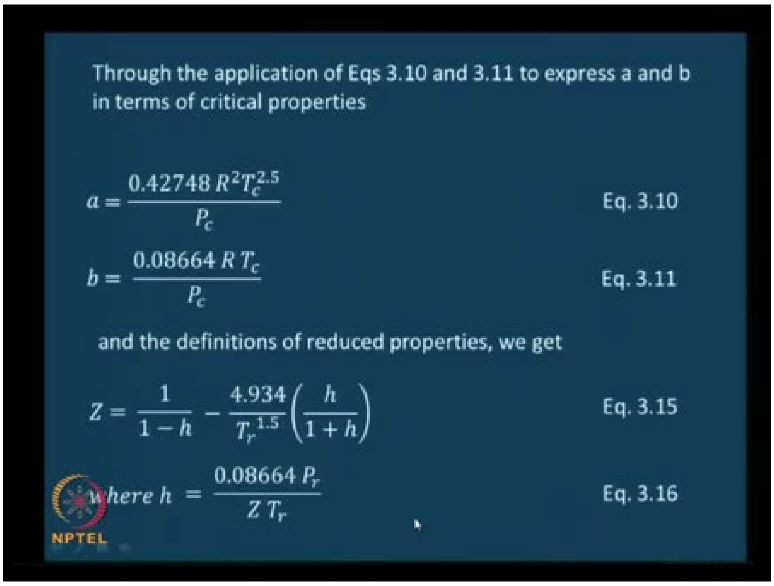

Through the application of Eqs 3.10 and 3.11 to express a and b in terms of critical properties

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

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

and the definitions of reduced properties, we get

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

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

We have already seen that a, and b can be expressed in terms of critical properties. 3.10 and 3.11,

$$a = \frac{0.42748\, R^2 T_c^{2.5}}{P_c}$$

$$b = \frac{0.08664\, R\, T_c}{P_c}$$

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.

$$Z = \frac{1}{1-h} - \frac{4.934}{T_r^{\,1.5}}\left(\frac{h}{1+h}\right)$$

We will call this equation 3.15.

$$h = \frac{0.08664\, P_r}{Z\, T_r}$$

We will call this equation 3 16.

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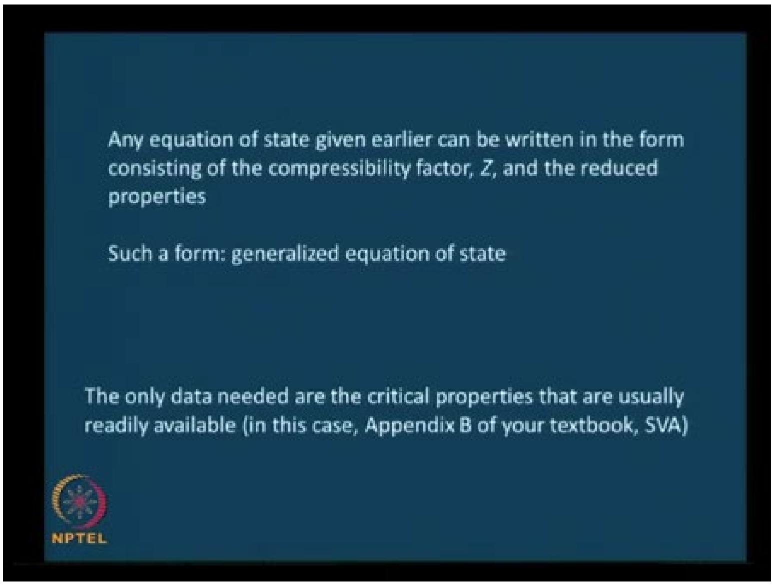

Any equation of state given earlier can be written in the form consisting of the compressibility factor, *Z*, and the reduced properties

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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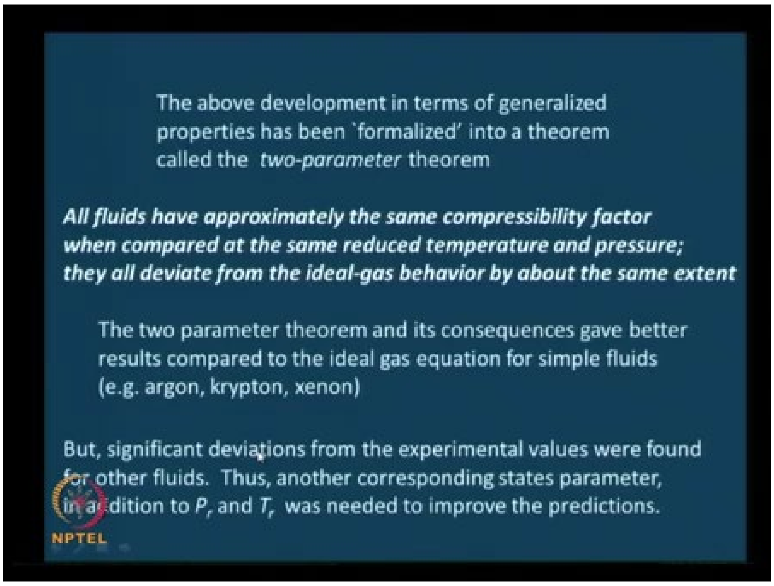

The above development in terms of generalized properties has been 'formalized' into a theorem called the *two-parameter* theorem

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 it is 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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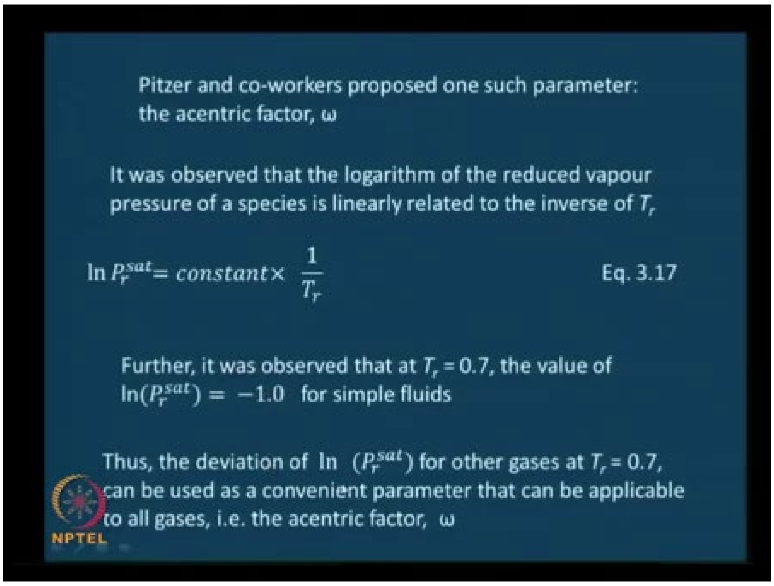

Pitzer and co-workers proposed one such parameter: the acentric factor, ω

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

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

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, ω

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 by T r. It is linearly related to the inverse of the reduced temperature.

$$\ln P_r^{sat} = constant \times \frac{1}{T_r}$$

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.

$$\ln(P_r^{sat}) = -1.0$$

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 equals 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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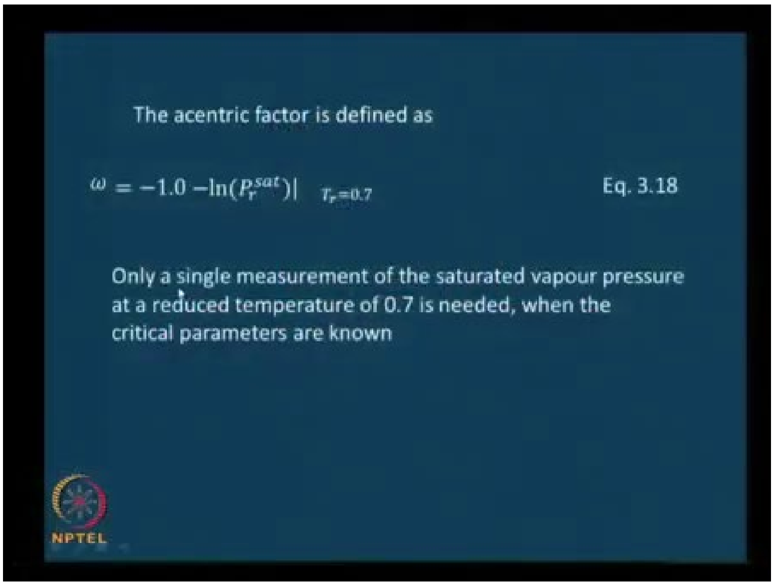

The acentric factor is defined as

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

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

And therefore, the acentric factor was defined as

$$\omega = -1.0 - ln(P_r^{sat})|_{T_r=0.7}$$

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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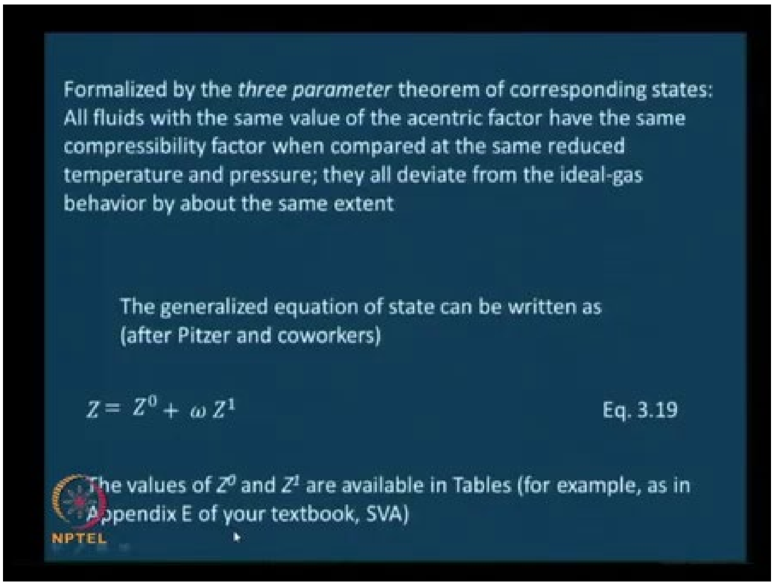

Formalized by the *three parameter* theorem of corresponding states: All fluids with the same value of the acentric factor have the same compressibility factor when compared at the same reduced temperature and pressure; they all deviate from the ideal-gas behavior by about the same extent

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

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

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

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.

$$Z = Z^0 + \omega Z^1$$

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 from 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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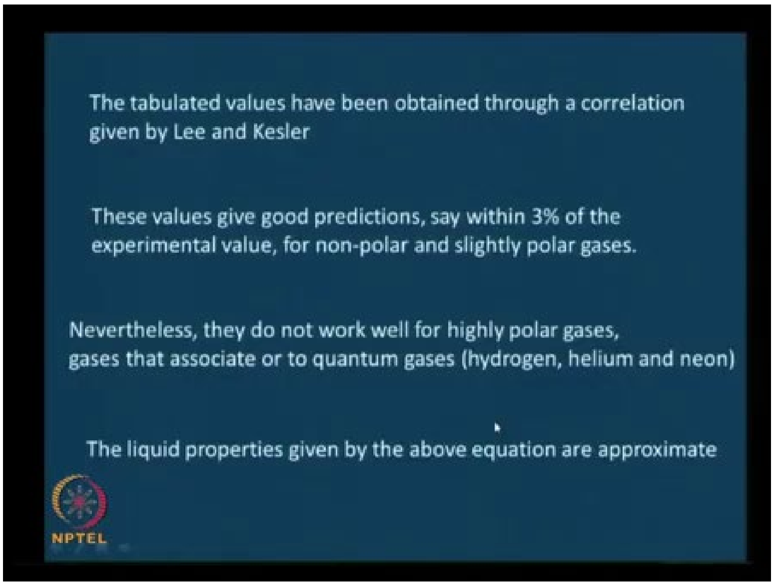

The tabulated values have been obtained through a correlation given by Lee and Kesler

These values give good predictions, say within 3% of the experimental value, for non-polar and slightly polar gases.

Nevertheless, they do not work well for highly polar gases, gases that associate or to quantum gases (hydrogen, helium and neon)

The liquid properties given by the above equation are approximate

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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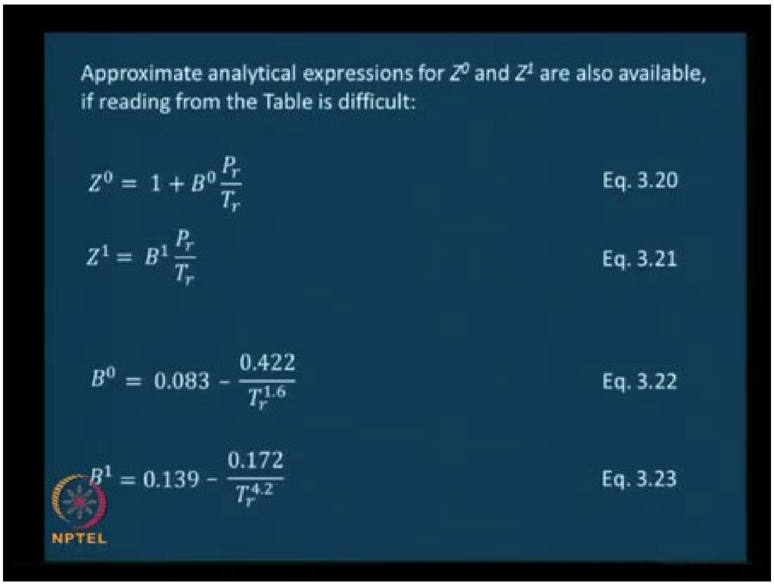

Approximate analytical expressions for Z^0 and Z^1 are also available, if reading from the Table is difficult:

$$Z^0 = 1 + B^0 \frac{P_r}{T_r} \quad \text{Eq. 3.20}$$

$$Z^1 = B^1 \frac{P_r}{T_r} \quad \text{Eq. 3.21}$$

$$B^0 = 0.083 - \frac{0.422}{T_r^{1.6}} \quad \text{Eq. 3.22}$$

$$B^1 = 0.139 - \frac{0.172}{T_r^{4.2}} \quad \text{Eq. 3.23}$$

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.

$$Z^0 = 1 + B^0 \frac{P_r}{T_r}$$

equation 3.20;

$$Z^1 = B^1 \frac{P_r}{T_r}$$

equation 3.21.

$B^0 = 0.083 - \frac{0.422}{T_r^{1.6}}$

equation 3.22;

$B^1 = 0.139 - \frac{0.172}{T_r^{4.2}}$

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.

See you in the next class.