Thermodynamics for Biological Systems: Classical and Statistical Aspects
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Lecture – 20
Generalized Correlations (Contd.,)

Welcome!

In the last class, we saw the generalized correlation, which is applicable to a wide variety of may be, gases. We said that it can be written of the form

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

omega is the acentric factor. We could write this, because the values of Z^0 and Z^1 are available in tables along with the values of the acentric factor omega for different pure substances. Even if the tables are not available, we said that there are analytical expressions, which work reasonably well. What we will start doing in today's class is to get a little more comfortable with the generalized correlations, generalized relationships. To do that, we will work out an example or an exercise. So, this is example 3.3.

Find the volume needed in example 3.1 for isopropanol using the generalized correlations, and compare it with the ideal gas volume as well as the one obtained with virial coefficients. This is going to be the question. As I said isopropanol is going to be one of our favourite compounds, it has a lot of biological applications.

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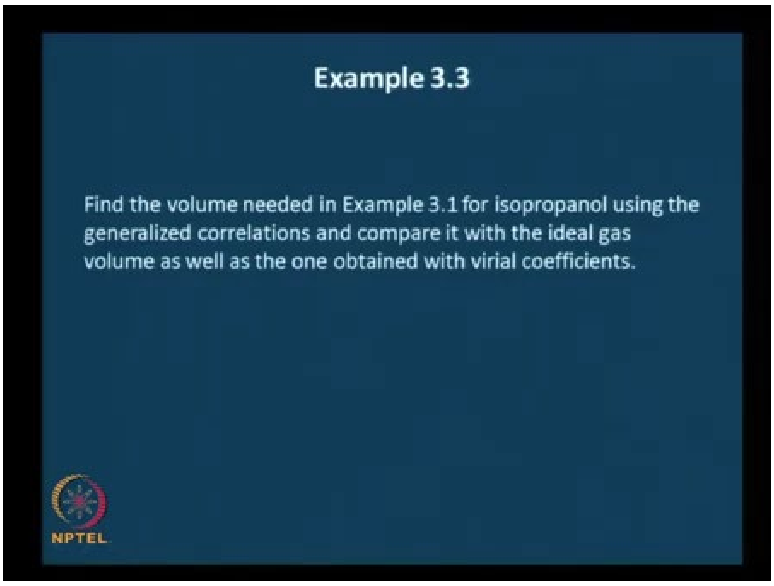

What I'd do is, let you think about how to go about doing it … get your bearings straight. What we need is the volume, the same as example 3.1 for isopropanol under the same conditions. But this time we are asked to use the generalized correlations. And of course, compare it with the ideal gas volume as well as one obtained with the virial coefficients. These two we already have from the previous examples. So, can you take a few minutes may be 5 minutes to see how you would go about doing it, and then I will present a part of the solution; go ahead please.

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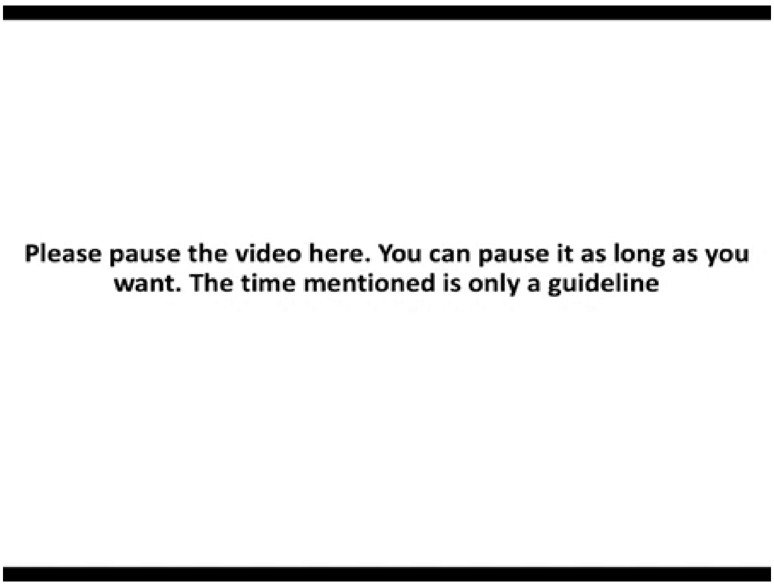

Now that you have familiarized yourself with what the generalized correlation is, and where you could get the values for isopropanol of $Z^0, \omega,\ and\ Z^1$, let us take and locate the part of solution.

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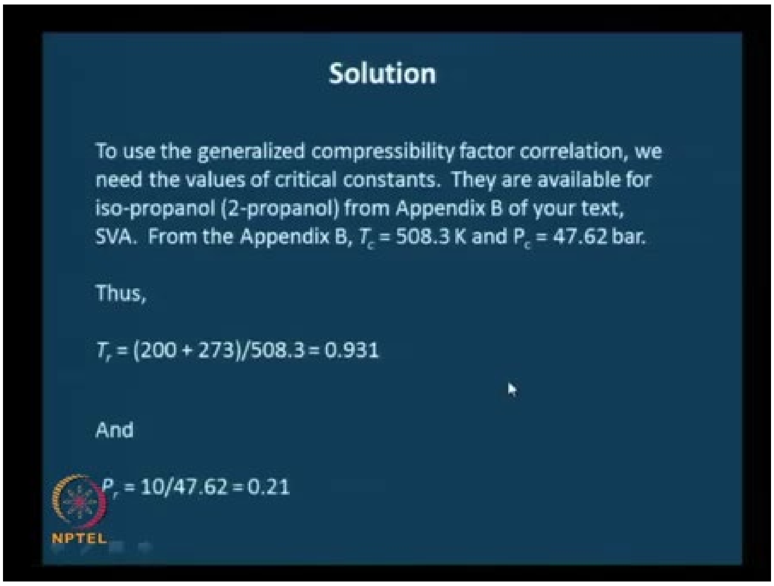

To use the generalized compressibility factor correlation, we definitely need the values of the critical constants. If you go back and see the relationships, you would know that you would need critical constants. The critical constants, as we have already seen befor,e are available in appendix B of your text. The compound that we are looking at the pure substance that we are looking at is isopropanol. I think it is listed under 2 propanol in your appendix of Smith VanNess and Abbott.

If you take a look at that … you may have already done that in the time that was given, you would find that the critical temperature is 508.3 K and critical pressure are 47.62 bar. You have already seen this in the earlier examples. You needed it in the earlier examples also. Therefore, the reduced temperature this is essentially why we were looking at the critical constants so that we could calculate the reduced temperatures. Therefore, we could use the generalized correlation.

For the reduced temperature, you need the temperature in Kelvin therefore; you add 273 to the temperature given in degree C. This is the critical temperature 508.3. 200 was given in the earlier example 3.1, 200 plus 273 to get in Kelvin and critical temperature 508.3. Therefore, the reduced temperatures turns out be 0.931. And similarly, the reduced pressure the 10 bar – 10 bar and 200 degree C were the conditions – 10 by the critical pressure 47.62 bar turns out to be 0.21.

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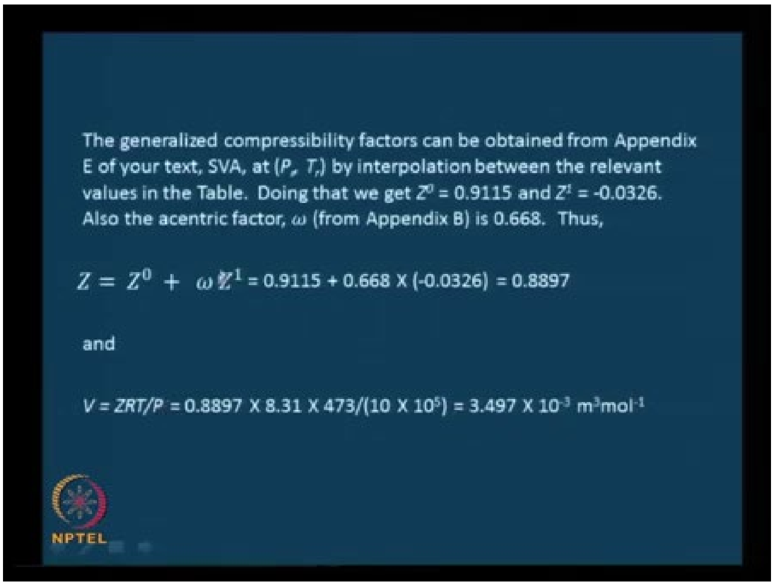

Now, this is the generalized … correlation, and the values of Z naught Z1 and omega need to be obtained from the tables in the appendix of your textbook. From the appendix E of your textbook you would get Z naught for the particular Pr and Tr as 0.9115 and Z 1 as minus 0.0326. Note that this is a function of P r and T r and the strength of this particular formulation is that you could get Z naught and Z 1 only as a function of Pr and Tr and use it for all pure substances. And the acentric factor which brings in the aspect of the pure substance here, as we saw in the development this is needed, from appendix B, turns out be 0.668 for isopropanol.

Therefore, if we substitute into this expression

$$Z = Z^0 + \omega Z^1 = 0.9115 + 0.668\, X\, (-0.0326) = 0.8897$$

I will give you another 10 minutes to do the calculations to get the volume as well as for the comparison. Please go ahead and do the calculations. You have enough basis … you know that Z equals P V by R T. So, please go ahead and do it.

Let us continue. V in this calculation, equals Z RT by P. Z is P V by RT.

$V = ZRT/P = 0.8897 \text{ X } 8.31 \text{ X } 473/(10 \text{ X } 10^5) = 3.497 \text{ X } 10^{-3}\ m^3mol^{-1}$

So, that is the molar volume.

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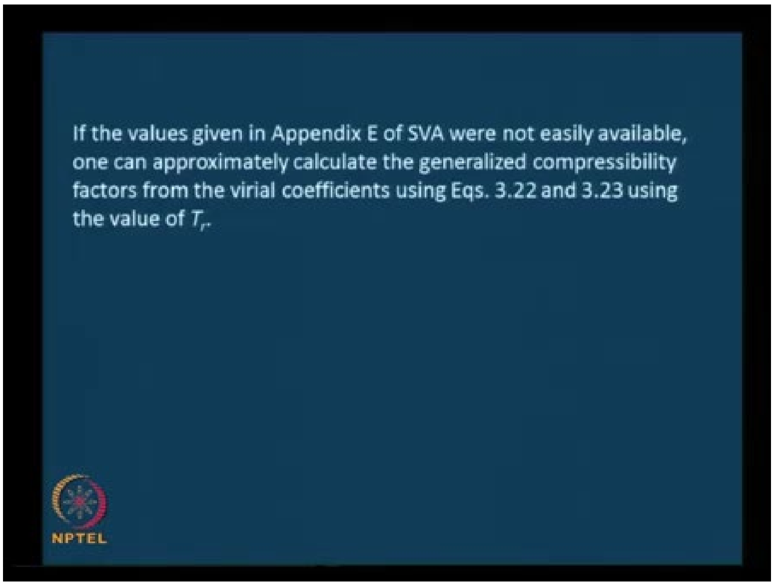

So, we have gotten whatever we need from the generalized correlations. Please go back to the earlier exercises, and see how this volume compares with the volume obtained from the ideal gas relationship, which would result in the large difference. Also the one obtained with using the virial expansion. Go ahead, and do the comparison, and take 2 minutes to do it. Why don't you go back to your exercise, and see how the values compare.

You would have found out the improvement in the level of accuracy. Hopefully, … if you compare it with the actual experimental value you will know that. But, at least, you will see the difference between the value obtained with the generalized correlation and the ideal gas volume – I definitely that would have been stark. And of course, between the generalized correlations and the virial … the one obtained with the virial coefficients will give you some idea as to what differences to expect from these two approaches.

Now, let us do a further exercise. I am just going to present it and give you time to do it. That will give you means of first deciding how to do it. That is the way to go about doing a problem. First decide how to do it, and then substitute. The extension or something likes this. Suppose the appendix was not available to you the textbook was not available to you. Or, in other words, the tables for Z naught and Z 1 were not available to you.

If the values given in appendix E of Smith VanNess and Abbott were not easily available, one can approximately calculate the generalized compressibility factors from the virial coefficients used in 3.22 and 3.23, using the value of T r. I have actually given you the way to go about this. What I would like you to do is, do the calculations and see how much of a difference you get in the values. Take about 10 minutes to do this.

See you in the next class.