Chemical Engineering Thermodynamics
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Lecture – 17
Thermodynamic Property Calculations using Cubic EoS Pitzer Correlations and Thermodynamic Tables

Hello and welcome back. In the previous lectures we were looking at thermodynamic property calculations or changes in thermodynamic properties for over a process.

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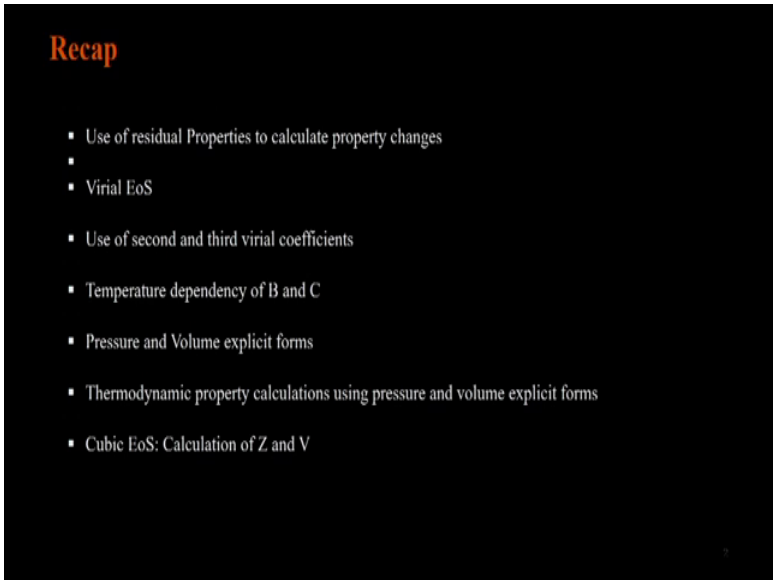

And we looked at calculation of these changes for ideal gases. And then we introduced the concept of residual properties which are corrections over the ideal gas. And we have looked at how to calculate these residual properties like residual enthalpy, residual entropy, residual Gibbs free energy using virial equation of state. We have looked at how to calculate them using second and third virial coefficients; one of them is going to be explicit in pressure, the other one is going to be in explicit in volume. We have looked at both versions for calculation or for residual properties. We also looked at the temperature dependency of B and c; the second and third virial coefficients and how that effects or how that is introduced into these calculations.

And finally, we have introduced the cubic equation of state. And using cubic equation of state we have calculated the compressibility factor and the molar volume of a fluid. What

we will do in this lecture today is extend these ideas and concepts to calculate other thermodynamic variables such as residual Gibbs, free energy residual enthalpy, residual entropy etcetera using the cubic equation of state. Later on in this video we are also going to talk about using what are known as Pitzer correlations, and one of the more famous Pitzer correlations are Lee-Kesler tables.

So, we are going a look at Lee-Kesler tables and how they are used in calculation of various thermodynamic variables.

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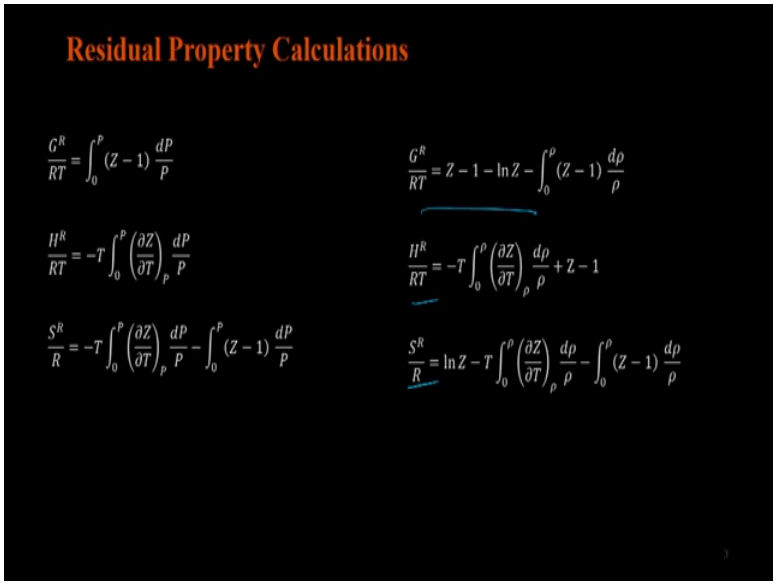

To begin with let us quickly summarize what we did earlier in terms of some mathematical expressions. We looked at expressions for the Gibbs free energy and we said we are going to use Gibbs free energy as the generating function. We have looked at expressions for residual Gibbs free energy in both the pressure and volume explicit forms. One of them applicable for the cubic equation of state, more applicable for the cubic equation of state is going to be this one it is easier to handle these expressions. And based on this generating function we have also derived the enthalpy and entropy.

So, if you look at the right-hand side there is the compressibility factor and then integrals in terms of density.

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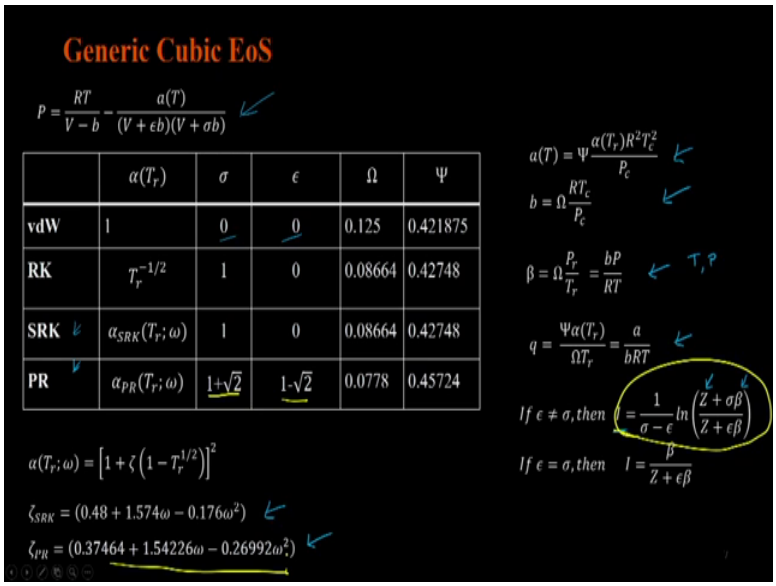

	$\alpha(T_r)$	σ	ϵ	Ω	Ψ
vdW	1	0	0	0.125	0.421875
RK	$T_r^{-1/2}$	1	0	0.08664	0.42748
SRK	$\alpha_{SRK}(T_r;\omega)$	1	0	0.08664	0.42748
PR	$\alpha_{PR}(T_r;\omega)$	$1+\sqrt{2}$	$1-\sqrt{2}$	0.0778	0.45724

In the generic form if you recall we have expressed the cubic equation of state we have this expression. This is a general cubic equation of state. The expression for a epsilon and sigma determine; what type of cubic equation of state we have we looked at four different a cubic equations, early earlier right.

So, we are going to these definitions for a and b is something we looked at earlier. In addition we derive a few other parameters: beta which is going to be dependent on both temperature and pressure in addition to B and q which will depend on a temperature pressure and the parameter a itself. Once we have beta and q we calculate I which essentially corresponds to the integral we were doing earlier as in case of van der Waals we were integrating it with respect to density. So, that I stands for the integral value.

And it is different depending on what values of sigma and epsilon we have. And if you look at the table in certain scenarios sigma and epsilon are same, in certain scenario sigma and epsilon are different. Therefore, each case we have different expression for I, right. It is given in terms of the compressibility factor Z and beta in addition to sigma and epsilon.

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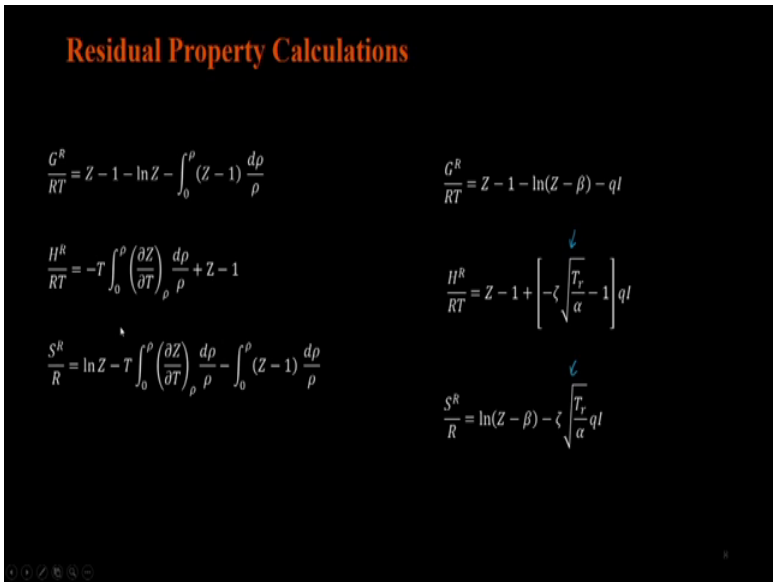

Once we calculate all of this right, then we can go back and use these variables we have calculated to write the expressions out for various residual properties. In particular for G R over RT; we have already calculated the compressibility factor the term beta q and I. So, I can plug those in there to get G R over RT.

Similarly for H R over RT and S R over RT there is a derivative term of the compressibility factor with respect to temperature and the derivative with respect to temperature brings in this additional term square root of T r over alpha. And if you look at the previous slide this alpha right when we take the derivative for van der Waals a was not a function of temperature, but for other equations of state like these two it will be a function of temperature. And for these equations of state we take the derivative when we do the integration after taking that derivative we end up with these terms square root of T r over alpha and zeta; which again is given in the expressions here, right. For SRK and Peng-Robinson equation of state for others of course. We do not have the value for zeta, it they are not dependent on temperature.

So, keeping these in mind we essentially we do not have to use these expressions, you can start out from the equation of state derive like we have done for van der Waals equation of state we will. Still end up with the same result, but it is convenient to have handy expressions such as these as long as we remember where they came from. And

once we have these expressions it is pretty straightforward to use them in our calculations.

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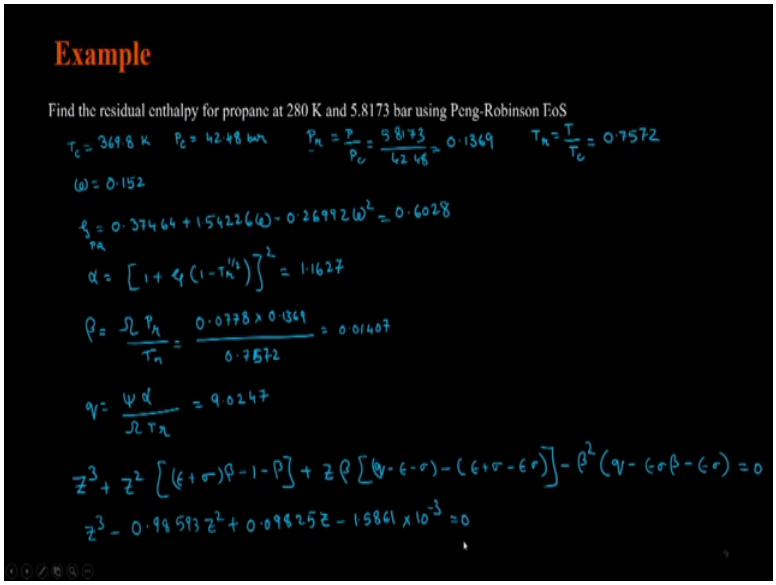

So, what we want to do is: now let us look at an example Going to find the residual enthalpy of propane at 280 Kelvin and 5.8 bar using Peng-Robinson equation of state. If you look at this, if you want to find the residual enthalpy I need to calculate the compressibility factor Z alpha T r q I etcetera.

So, let us first go back to what Peng-Robinson equation of state is, this is at right. And then for Peng-Robinson I am interested in sigma and epsilon values, they are not same. So if I when I am calculating I i am going to use this expression for I because sigma and epsilon are not same and other equations are they are same for all equations of state. And of course, for calculating alpha I want a value for zeta which will come from here; in case of Peng-Robinson.

In these scheme of things the first thing then I want to find our P c and T c. So, I am going to look up a data handbook or your textbook for propane the critical temperature is 369.8 Kelvin critical pressure is 42.48 bar. And hence we calculate the reduced temperature and reduce pressure P over P c which in this case turns out to be 5.8173 over 42.48 which is 0.1369. And similarly T r is T over T c which turns out to be 0.7572.

Once I have these two values and also the value of omega the eccentric factor for propane from the tables in this case its 0.152. Once I have these values I can calculate zeta which is for Peng-Robinson it is 0.37464 plus 1.54226 omega minus 0.26992 omega square. And this value turns out to be 0.6028.

And once I have omega I can calculate alpha which is 1 plus zeta 1 minus T r to the power half whole squared.

So, I know zeta I know the reduced temperature, so I can plug the numbers in to get the value for alpha; in this case this value turns out to be 1.1627 right. I have alpha, I have zeta, the other things I need for in this calculation are beta which is omega it is omega P r over T r or B P over RT whichever one is convenient depending on what we have. In this case let us just go with omega P r over T r both are equivalent expressions P r over T r. And for P Peng-Robinson omega is 0.0778, P r is 0.136 and T r is 0. 7572.

So, this beta; then turns out to be 0.01407. Similarly q is psi alpha by omega T r. And I have all the numbers I need if I plug these numbers n I will end up with a numerical value of 9.02. I have beta and q. The next thing to find is the actual value of the compressibility factor itself. And in one of the previous lectures when we looked at using cubic equations of state for finding the compressibility factor or the molar volume, we have written the expression in terms of a cubic polynomial in a Z.

So, let us write that down again. Its Z cube plus Z squared epsilon plus sigma times beta minus 1 minus beta plus Z times beta q minus epsilon minus sigma minus epsilon plus sigma minus epsilon sigma. And finally, the constant term which is beta square q minus epsilon sigma beta minus epsilon sigma is equals 0.

Now I have everything I need to get the coefficients of this polynomial in Z, I can put these terms here and turns out that the polynomial I am going to end up with is 0. 98593 Z square plus 0.09825 Z minus 1.5861 10 power negative 3, this equal 0.

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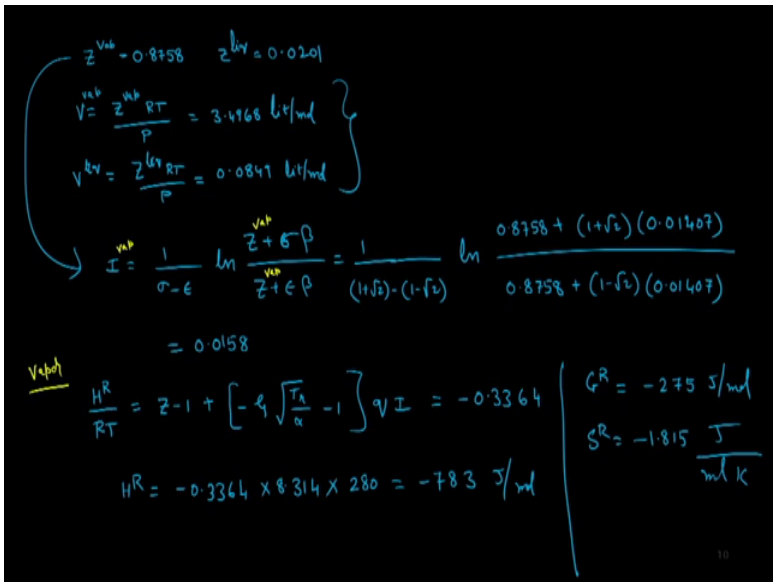

These are the coefficients for the polynomial. I can solve this polynomial and it turns out this polynomial we will give me three roots a vapor root which is 0.8758 and a liquid root which is 0.0201. These are the vapor and the liquid roots I have for this particular polynomial. Based on these roots I can calculate the molar volume, for the vapor it is going to be Z for the vapor RT over P. Now recall that RT over P is the molar volume for the ideal gas so this is the vapor molar volume right.

And this number turns out to be 3.4968 liters per mole. And the liquid molar volume is going to be Z liquid RT over P which is 0.849 liters per mole. These compare well with the experimental values. But for this particular problem what we are interested in is actually the integral I and then calculating H R over RT. We in fact, do not have to calculate the liquid and vapor molar volumes I have just calculated them to refresh your memory on how we have use these to calculate molar volumes. But, what we can do is actually take that and now calculate I.

The question is which value of the compressibility factor do I use. The expression for I is 1 by sigma minus epsilon l ln Z plus sigma beta Z plus epsilon beta. So, which value of Z will I use to calculate I. Turns out that we can use the vapor value to calculate the residual enthalpy for the vapor phase and the liquid value to calculate residual enthalpy for the liquid phase. So, what we will do then is let us say we want to calculate the residual enthalpy for the vapor phase.

So, we will use the expression for I and replace Z with Z for the vapor. So, that what we end up is calculating I for the vapor phase which in turn will be used in calculating the residual enthalpy for the vapor. So, I am going to plug in this value of Z for the vapor phase epsilon sigma epsilon and beta to calculate I. If you recall this was 1 plus square root of 2 minus 1 minus square root of 2 right ln of 0.8758 that was the vapor Z plus 1 plus square root of 2 beta 0.01407 over 0.8758 plus 1 minus square root of 2 0.01407 again for beta. Now if I simplify this numerical expression: what I end up is a value for I vapor in this case it is 0.0158.

And once I have I vapor, I can go back and calculate H R by RT remembering that this is the calculation for the vapor phase. If I want it for the liquid phase I can do a similar exercise, but involve the liquid compressibility factor. H R by RT is Z minus 1 plus negative of zeta square root of T r over alpha minus 1 times qi. And if I plug in all the numbers I have what I end up with is negative 0.3364. This is H R over RT, I can use it to calculate H R I just have to multiply this number with R in Joules per mole per Kelvin if that is the units I will be using times T the temperature I have is 280 Kelvin. So, what I will end up is in Joules per mole 783 Joules per mole.

I can do a similar exercise use the expressions for G R over RT right. As in this slide, I can use the expressions for G R over RT or S R over R and then calculate the other thermodynamic residual values if need be, but this would be the general procedure. Just for your reference the values I have for G R are negative 275 Joules per mole and S R is negative 1.815 Joules per mole Kelvin right.

So, this is how I will use a cubic equation of state and calculate various residual properties. We have looked at how we can derive the expressions given a cubic equation of state or use the generic expression the one that is readily available for the four different cubic equations we looked so far.

So, this ends our discussion on using cubic equation of state for residual property calculations. What we will do next is look at what are known as Pitzer correlations. If you recall, when we introduced the cubic equations of state we said two parameter theorem of corresponding states does not hold well for fluids that are not simple; simple fluids be spiracle, non-polar etcetera. But we used a quantity called as eccentric factor and included it in our cubic equation of state and we said.

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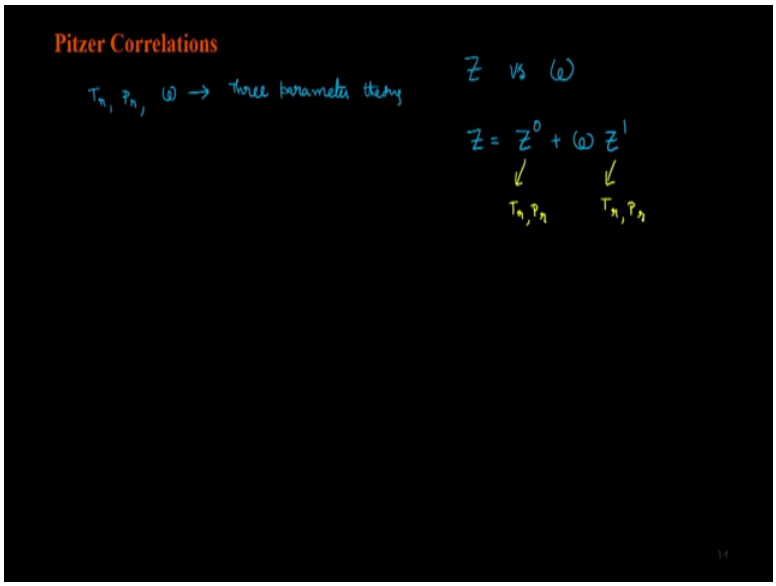

Fluids that are at the same reduced temperature, reduced pressure and have the same value of eccentric factor behaved similarly. And we call this as the three parameter theory of corresponding states right.

So, Pitzer has taken this idea, and what he has done is looked at the behavior of the compressibility factor Z versus the eccentric factor omega. And it turns out in most cases Z is fairly linear function of omega. So, what fits our proposed is Z can be expressed as a linear function of omega Z is Z naught plus omega Z 1. And these two parameters is Z naught and Z 1 are going to be functions of the reduced conditions both T r and P r.

So, in this sense omega Z will be a linear function of omega, whereas T r and P r will affect both the values of Z naught and Z 1. That is how all the three parameters contribute to the total compressibility factor Z.

One of the famous tables that have been proposed based on this concept are known as Lee-Kesler tables.

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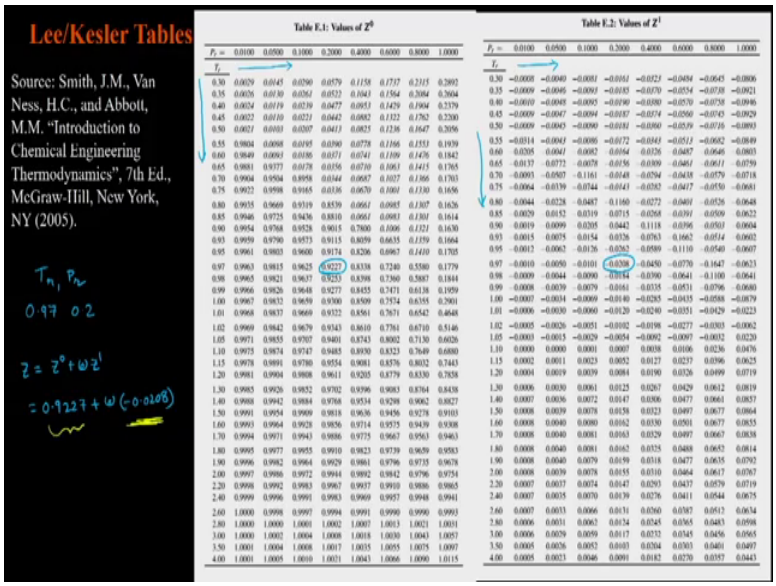

Taken this from one of your textbooks, I have taken this table from one of your textbooks. And if you see at these tables the values of both to Z naught we talked about and Z 1 are listed as a function of pressure; the reduced pressure I should say. It changes horizontally like that and the reduced temperature changes vertically like that. Similarly both Z 1; sorry Z 1 also is expressed as a function of reduced temperature and reduced pressure. These are tables for Z naught and Z 1 right.

So, given a reduced condition T r and P r right for example, T r is 0.97, P r is 0.2 I can locate what the value of Z naught is going to be at 0.97 and 0.2. Similarly I can locate what the value of Z 1 is going to be at the same reduced conditions. Once I have these two numbers then it turns out Z is going to be Z naught plus omega Z 1. So, if I have omega I can readily calculate 27 plus omega times negative 0.0208 that will be the value of Z.

And if you look at this expression for Z a majority of the contribution still comes from Z naught, which is the case for a simple fluid omega is 0 this is Z naught comes from the simple fluid contribution. And Z 1 is a correction over the simple fluid contribution its much smaller than this value omega is usually around 0.1 0.2 at most. So, the contribution of the second term is pretty small compared to that of the first term nevertheless it is a correction over the simple fluid correlation. That is how it is corrected using the three parameters T r P r and omega.

Now these like I said are known as Lee-Kesler tables what we will do is quickly learn to use these tables for two different scenarios and then we will look at calculation of other thermodynamic properties using these Lee-Kesler tables. What we want to do is calculate the molar volume of propane vapor at 280 Kelvin and 4 bar right. At 280 Kelvin and 4 bar remember we have to use the reduced conditions.

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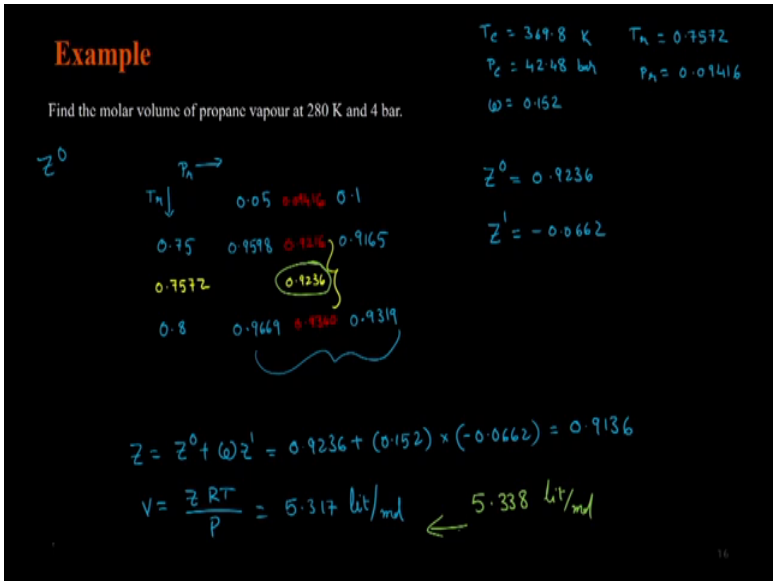

So, the first thing we will be needing is T c P c and omega. For propane omega is 0.152, P c is 42.48 bar, and T c is 369.8 Kelvin. Once I have these values I can calculate T r and P r : T r in this case turns out to be 0.7572, this is t over T c and P r is 0.09416; this is P over P c. Once I have T r P r and omega I can actually go back to the tables and look for the value I am after.

So, 0.7572 is my T r and if I look at this table let us pick that 0.7572.

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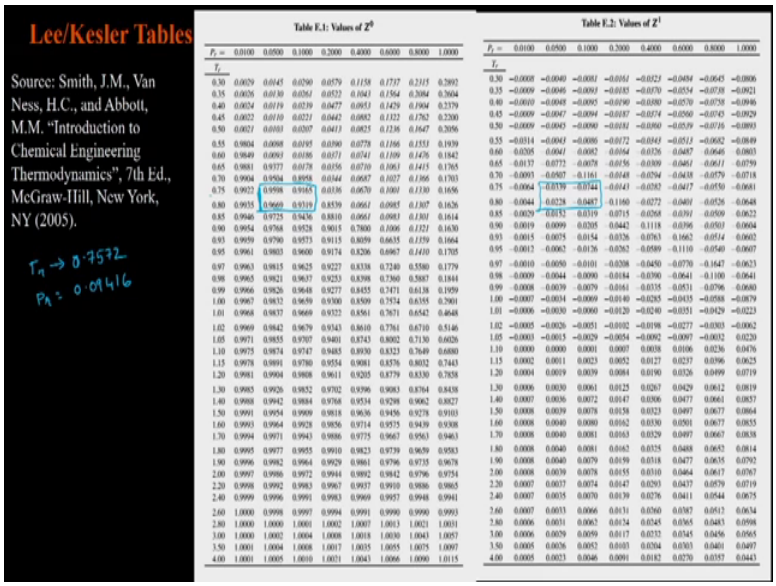

So, it's going to be this is 0.75; this is 0.8, so it is going to be in between these two rows. And the T r value we calculated, maybe I should just write those T r and P r from there here it might just be easier to work with, but anyway. And the T r for this problem we have is 0.7572 and P r is 0.09416. So, it is going to be in between these two values here on the vertical and between 0.05 for P r and 0.1 for P r right. So, it is going to be between these four numbers somewhere in between them, right.

So, I have to do a linear interpolation. And in this case I do not have the numbers for the exact T r or for P r. So, what I will end up doing is what we call as a double linear interpolation. So, we are going to do a linear interpolation on the pressures first and then on the temperatures or we can do it vice versa right.

So, what we will do is write these numbers T r is going like this 0.75 and 0.8; I have it at 0.75 and 0.8 I am interested in 0.7572. I have it at a pressure of 0.05 I also have it at a pressure of 0.1, but what I am interested in is at a pressure of 0.09416, right. So, let us first fill in the details we have at the four conditions. 0.75 and 0.05 I have it as 0.9598; these are values for Z naught and for 0.1 it is 0.9165. At 0.8 and 0.05 this value is 0.9669 and this value here is 0.9319. What we will do is; do a linear interpolation between 0.05 and 0.01 to get at 0.8, but then at this P r; T r is still point 8, but at this P r which means I just need to do a regular linear interpolation between these two values and that gives me a value of 0.9360.

Similarly I will interpolate between these two values to get at a condition of 0.7 for T r and 0.09416 for P r. And if I do that linear interpolation between these two numbers what I will get is 0.9216. So now, I have it at a pressure at the required desired reduced pressure, but at two different T r. So, I need to do a regular linear interpolation between these two numbers again to get it at the T r I am interested in 0.7572. And if I do that between these two numbers to get it at this condition, it turns out to be 0.9236 right. So, this is the number I am after 0.9236. So, what we have done is a double linear interpolation to get this number, right.

So, that is how we do a double linear interpolation if I have a table to get it at the condition I am interested in at T r and P r of these two values, right. Similarly I can do a double linear interpolation for Z 1 between the pressures that are in the table. If we go back to the table for Z 1 again, it is the same reduced temperatures and reduced pressure. So, I am looking at a double linear interpolation between these four quantities between those four quantities.

And if I do the double linear interpolation for the desired reduced temperature and pressure what I have is a value of negative 0.0662. And once I have Z naught and Z 1 from the Lee-Kesler tables I can calculate Z it is Z naught plus omega Z 1. So, its going to be 0.9236 plus 0.152 times 0.066 to negative of that. And that will give me 0.9136. And if I were to calculate V using this it will be Z RT over P again remember RT over P is the ideal gas value, Z is the compressibility factor and if I simplify what I have is 5.317 liters per mole. And it turns out experimentally measured value for these conditions is 5.338 liters per mole.

So, pretty close comparison using the tables right. So, that is how I am going to use Lee-Kesler table to calculate molar volume and compressibility factor.

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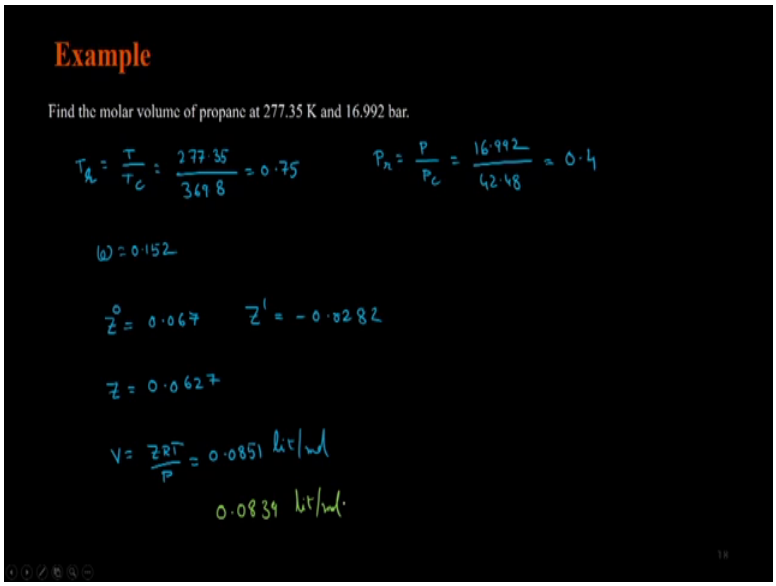

Let us look at another example. Find the molar volume of propane at 277.35 Kelvin and 16.992 bar. We still want to use the Lee-Kesler tables. We will do a similar exercise as we have done earlier and quickly calculate T r which is T over T c. And in this case it is 277.35 over 369.8 turns out to be 0.75. Luckily we do not have to do a linear interpolation in this case at least it looks like so far. This is P over P c which is 16.992 over P c is 42.48. So, I have a value of 0.4.

Now remember omega for propane is 0.152.

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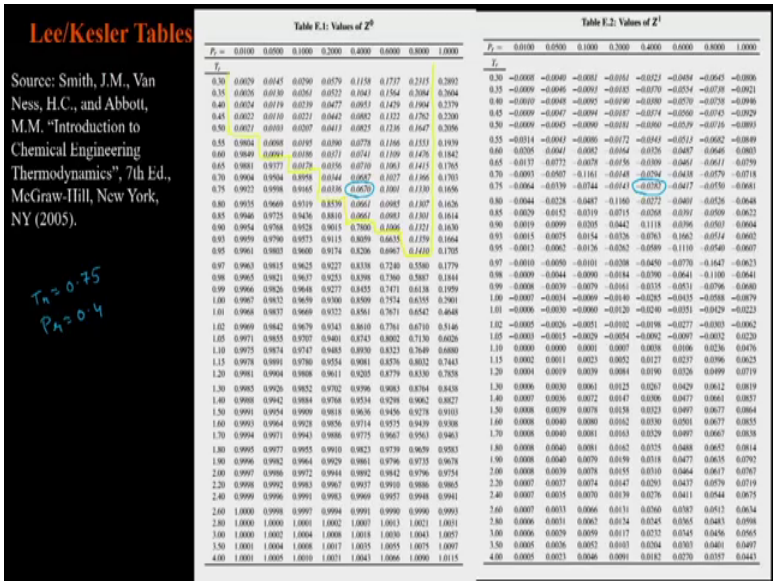

So, let us look at the table 0.75; the value is we listed or 0.75 for reduced temperature and 0.44 reduced pressure. Let me see where I can find these numbers. 0.75 for reduced temperature and 0.44 reduced pressure; 0.75 and 0.44.

Now if you look at the tables closely they are marked differently than rest of the tables. Everything in the table, right this part, this part, this part, this part, this part, this part, this part, right. Everything about this yellow line I have marked is actually in (Refer Time: 30:55) compared to rest of the table and actually that is to indicate that we are looking at the liquid phase as opposed to the vapor phase in rest of the table.

So, wherever you find these leak as flow tables you are going to find a region of T r and P r where the Z naught and Z 1 values are marked differently than rest of the table. And wherever you find this region this corresponds to the liquid phase region right. And for our particular scenario we are looking at what we marked for T r of 0.75 and P r of 0.4 we are in the liquid phase region. And we can look at the values of Z they are very small corresponding to the low liquid volumes and Z naught we have is 0.067, and Z 1 we have is negative 0.0282.

If I calculate Z here its 0.0627 and the volume is Z RT over P still its going to be 0.0851 liters per mole. And the experimentally measured value is 0.0839. Again pretty close even for the liquid phase calculations at least in this case.

So, these tables in that sense can be used in the liquid phase region also, but one needs to be careful. So, that is how I can use Lee-Kesler tables to calculate the molar volume and compressibility factor. In fact, not just for molar volume or compressibility factor Lee-Kesler tables have been developed for enthalpy, entropy, and once we have enthalpy, and entropy we can calculate all the other thermodynamic variables from there.

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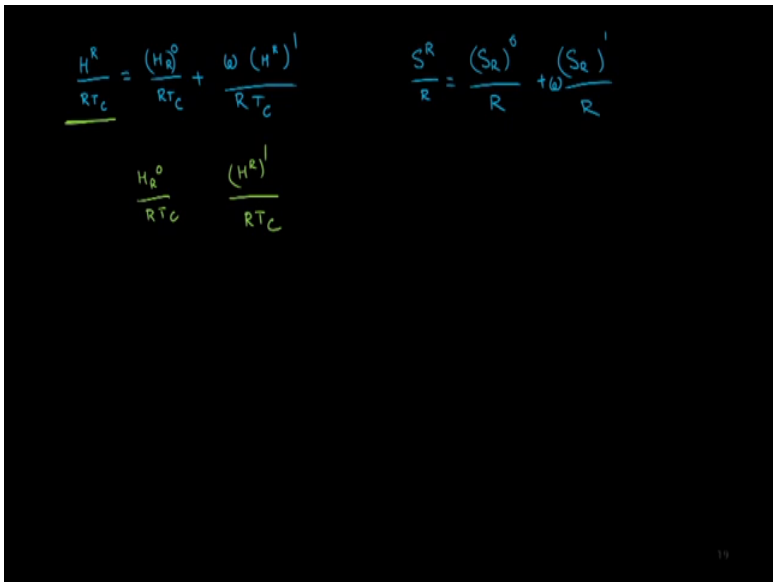

So, the expressions are a little different for entropy and enthalpy for. For example, enthalpy is written in terms of not H R, but rather H R by RT C. So, the total enthalpy residual enthalpy contribution over RT c comes from two terms: H R naught term and an H R 1 term. Still linear function of omega, but then unlike Z we have the denominator in this case which is RT C.

Similarly and the tables themselves you will find the tables for H R naught by RT C directly and the tables for H R 1 by RT C once you have the two tables you can combine them using eccentric factor and we will end up with the value of H R naught by RT C. If you are interested in H R we just need to multiply it with RT C.

Similarly for S R over R it will be S R naught over R; again you will find a table for S R naught over R; and then you will find another table for S R 1 over R multiplied with omega add them to get the value of S R over R. Once we have S R over R we can calculate S R right

So, similar to tables like the compressibility factor Lee-Kesler tables exist for residual enthalpies as well as residual entropies, they can be directly used to calculate the residual values. In that sense they are convenient. But then, we need to do a linear interpolation or a double linear interpolation as need be. Dealing with elaborate equations Lee-Kesler tables in that sense are handy. In fact, as we have seen earlier the contribution of the second term in these Lee-Kesler tables is pretty well it depends on the condition, but it is

smaller compared to that of the first term. So, for a very quick first-hand calculation one can in fact get away looking at values of Z naught or H R naught or S R naught etcetera for the simple fluids that will give a quick estimate.

So, with that we end todays lecture. We have looked at calculation of residual properties so far using a variety of methods. We looked at virial equation of state, we looked at cubic equations of state, the general cubic equation of state, we looked at thermodynamic tables thermodynamic diagrams and finally the Lee-Kesler table.

Thank you.