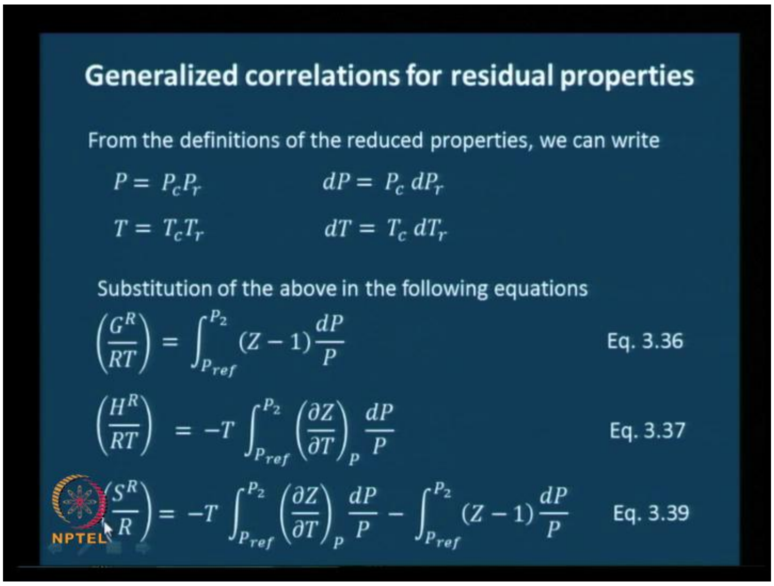
Thermodynamics (Classical) for Biological Systems
Prof. G. K. Suraishkumar
Department of Biotechnology
Indian Institute of Technology Madras

Module No. # 03
Thermodynamics of Pure Substances
Lecture No. # 16
Generalized Correlations and Residual Properties

Welcome. We are now considering residual properties. As we said earlier, the residual property is nothing but the difference between the actual quantity, and the ideal gas quantity. The advantage in using residual properties is that you can get generalized correlations. And, generalized correlations can be used in general, may be, for most gases, and you we do not have to worry about looking at particular properties for particular gases.

(Refer Slide Time: 00:46)



Generalized correlations for residual properties

From the definitions of the reduced properties, we can write

$P = P_c P_r \qquad dP = P_c\, dP_r$

$T = T_c T_r \qquad dT = T_c\, dT_r$

Substitution of the above in the following equations

$$\left(\frac{G^R}{RT}\right) = \int_{P_{ref}}^{P_2} (Z-1)\frac{dP}{P} \qquad \text{Eq. 3.36}$$

$$\left(\frac{H^R}{RT}\right) = -T\int_{P_{ref}}^{P_2} \left(\frac{\partial Z}{\partial T}\right)_P \frac{dP}{P} \qquad \text{Eq. 3.37}$$

$$\left(\frac{S^R}{R}\right) = -T\int_{P_{ref}}^{P_2} \left(\frac{\partial Z}{\partial T}\right)_P \frac{dP}{P} - \int_{P_{ref}}^{P_2} (Z-1)\frac{dP}{P} \qquad \text{Eq. 3.39}$$

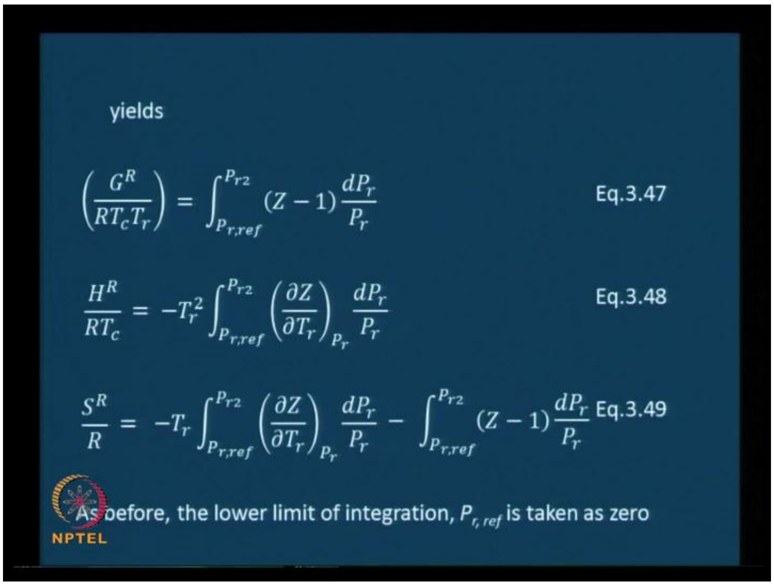
In the last class, we were somewhere here. We were in the middle of developing generalized correlations for residual properties. And, we said from the definitions of the residual properties, we could write the actual pressure as a product of critical and residual pressures and therefore, the differentials … for example, the differential d P can be written as P c, a constant, times d P r. Similar things could be done for the temperature.

And, if we substitute these values in the three equations that we had developed for the thermodynamic properties in terms of … for the thermodynamic properties such as G R by R T, H R by R T, and S R by R. We had developed these expressions in terms of the easier to measure compressibility factor, pressure, and so on … and temperature.

So, we said that if we could substitute the values in terms of the residual properties, we could get generalized correlations in terms of residual properties, and the usage of them would become a lot simpler in terms of need for data. And towards the end of the class, I had said that if we can substitute these expressions into equation 3.36, 3.37 and 3.39 and develop the correlations, it will be better. You would understand where it comes from.

For example, to give you an idea if you had not already done, for T, here you put in T c T r, for P here … rather d P here, you could put P c d P r and P would be P c P r. And the P c, P c would cancel out here. And, … when you are integrating with respect to the variable P r or the reduce pressure, it makes sense to have the limits of integration in terms of the reduced pressure. Therefore, these would automatically change and we could get expressions in terms of the reduced properties.

(Refer Slide Time: 03:11)



yields

$$\left(\frac{G^R}{RT_cT_r}\right) = \int_{P_{r,ref}}^{P_{r2}} (Z-1)\frac{dP_r}{P_r} \qquad \text{Eq.3.47}$$

$$\frac{H^R}{RT_c} = -T_r^2 \int_{P_{r,ref}}^{P_{r2}} \left(\frac{\partial Z}{\partial T_r}\right)_{P_r} \frac{dP_r}{P_r} \qquad \text{Eq.3.48}$$

$$\frac{S^R}{R} = -T_r \int_{P_{r,ref}}^{P_{r2}} \left(\frac{\partial Z}{\partial T_r}\right)_{P_r} \frac{dP_r}{P_r} - \int_{P_{r,ref}}^{P_{r2}} (Z-1)\frac{dP_r}{P_r} \qquad \text{Eq.3.49}$$

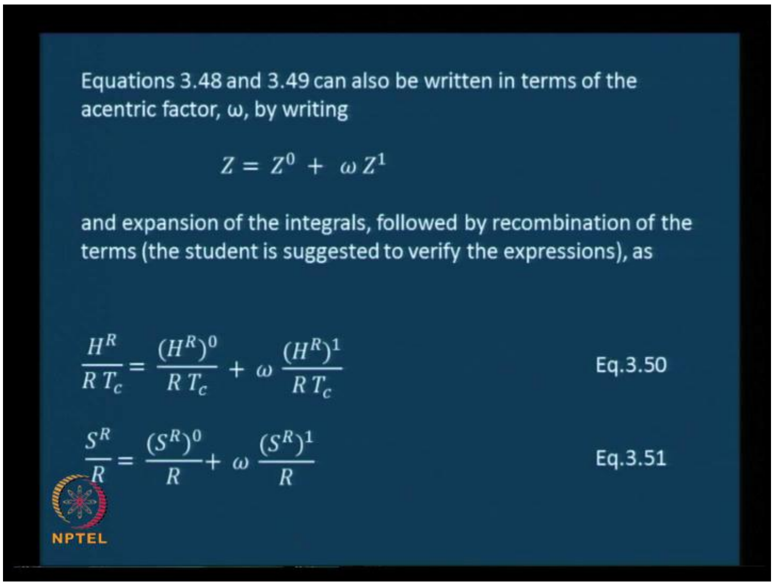
As before, the lower limit of integration, $P_{r,\,ref}$ is taken as zero

Hopefully, you would have got an expression such as this: G R by R T c T r … you know, when, we substituted T in terms of T c and T r equals integral from P r reference to P r 2 of Z minus 1 d P r by P r. P c, P c will cancel out here and so, we would get this. We will call this equation 3.47, and similar substitutions would yield us H R by R T c equals minus T r squared integral P r reference to P r 2, dou dou T r of Z at constant P r d P r by P r. We call this equation 3.48. And S R by R would turn out to be minus T r integral of P r reference to P r 2 dou Z dou T r at constant P r d P r by P r minus integral from P r reference to P r 2 Z minus 1 by P r d P r.

Therefore, we have all these in terms of the reduced properties and since the reduced properties are applicable over a large variety of gases, you could apply these equations without the need for particular data for particular gases. Let us move forward. Before that it is good to note that as earlier the lower limit for integration, the P r reference is usually taken to be 0. You can choose that as anything. It is usually taken to be 0 so that, we do not have to worry about values there.

Now, these equations 3.48 and 3.49 which are here, H R by R T c equals minus T r squared integral of dou Z by dou Z dou T r d P r P r, and S R by r equals minus T r integral P r reference to P r 2 dou Z dou T r at constant P r d P r by P r minus of integral P reference to P r 2 Z minus 1 d P r by P r. These are expressions, where H R by R T c and S R by R, let us concentrate on these two.

(Refer Slide Time: 05:45)



Equations 3.48 and 3.49 can also be written in terms of the acentric factor, ω, by writing

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

and expansion of the integrals, followed by recombination of the terms (the student is suggested to verify the expressions), as

$$\frac{H^R}{R\,T_c} = \frac{(H^R)^0}{R\,T_c} + \omega\,\frac{(H^R)^1}{R\,T_c} \qquad \text{Eq.3.50}$$

$$\frac{S^R}{R} = \frac{(S^R)^0}{R} + \omega\,\frac{(S^R)^1}{R} \qquad \text{Eq.3.51}$$

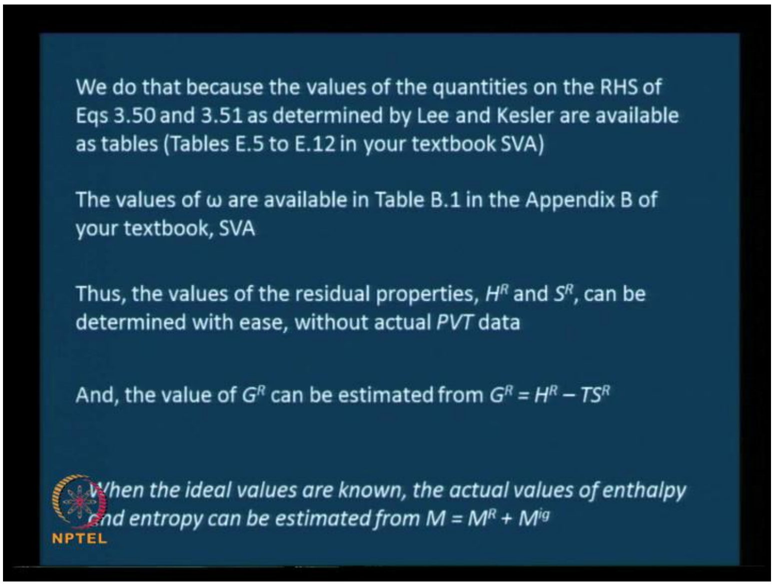
These two equations can be written in terms of Z 0 and Z 1 by using the acentric factor. The earlier expressions were only in terms of Z, and we could write those expressions in terms of some terms containing Z 0 and the other terms containing Z 1. If we substitute the Z there as Z 0 plus omega times Z 1. What I would like you to do is, substitute Z equals Z 0 plus omega times Z 1 in the previous equations 3.48 and 3.49, and group the terms appropriately in the integrals, and get at the actual expressions. It is good for you to do that, because I am not going to give the complete derivation here. It is good for you to do that and convince yourself that whatever I am going to present next is what you are actually getting; that improves confidence significantly. So, take about 15 minutes even if you are … if you will take your time in doing that, please take about 15 minutes and then we will come back. 15 minutes please.

(No audio from 06:56 to 20:05).

Let us continue. If we do that, that is substitute Z in the previous expressions in terms of Z 0 plus omega times Z 1, H R by R T c can be written as H R 0 by R T c plus omega H R 1 by R T c. I hope you would have already gotten some integral and so on and so forth, which can be written in terms of H R 0. You have an expression for H R by R T c earlier. So, a similar expression would have resulted for H R 0, and a similar expression for H R 1. Therefore, you could combine them both with the acentric factor when the Z was replaced with Z 0 plus omega times Z 1.

So, hopefully you would have gotten this, if not you could go back and check and see how to get this. We will call this equation 3.50. And, S R by R can be grouped into S R 0 by R plus omega times S R one by R we will call this equation 3.51. Why did we go through all this trouble of something that was … of converting something that was given in terms of Z to something in terms of a certain Z 0 and a certain Z 1, and therefore, in terms of a certain H R 0 and H R 1 or S R 0 and S R 1 would become apparent now.

(Refer Slide Time: 21:46)



We do that because the values of the quantities on the RHS of Eqs 3.50 and 3.51 as determined by Lee and Kesler are available as tables (Tables E.5 to E.12 in your textbook SVA)

The values of ω are available in Table B.1 in the Appendix B of your textbook, SVA

Thus, the values of the residual properties, H^R and S^R, can be determined with ease, without actual *PVT* data

And, the value of G^R can be estimated from $G^R = H^R - TS^R$

When the ideal values are known, the actual values of enthalpy and entropy can be estimated from $M = M^R + M^{ig}$

We essentially did this because the quantities on the right hand side, you know, something in terms of H R 0 by R T c and H R 1 by R T c and so on; these values are actually available to us. So, in order to use these values we have formulated something for our quantities in terms of the available values. These were determined by Lee and Kessler; these are available as tables. In fact, these are available as tables in the appendix E.5 to E.12 in your text book of Smith VanNess and Abbott.

What I would like you to do now is not to take this on base value. Please take up your text book. Take up your text book, go to tables E 5 and E 12, and just get a feel. See what is listed there? What are the functions that are listed there? What are the kinds of values that are listed there from tables E 5 to E 12? I will give you about 5 minutes to do that, essentially we are getting familiar with the tables E 5 to E 12. Go ahead, please. 5 minutes.

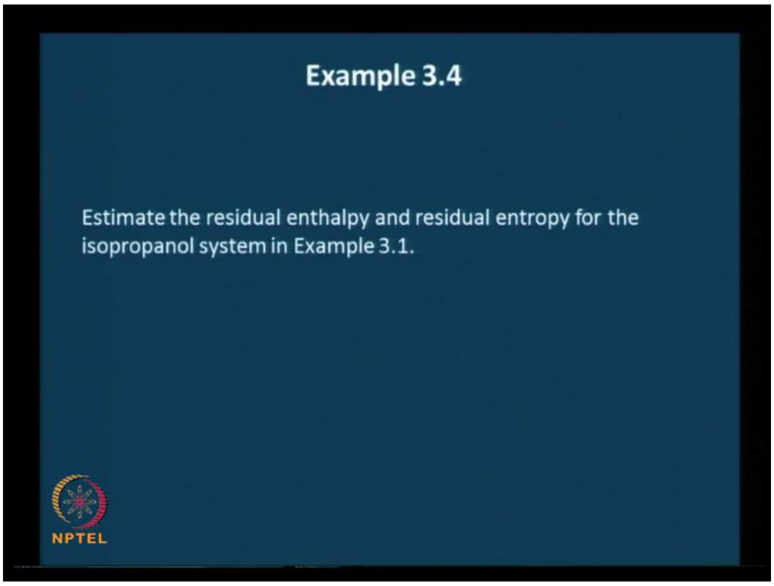
(No audio from 23:03 to 28:01).

Let us continue. You would have seen how the tables for H R 0 by R T c, H R 1 by R T c and S R 0 by R and S R 1 by R look like, and how you could use those tables at a particular … in a particular situation. When you know the values of the functions … which determine the values of the quantities H R 0, H R 1 and so on and so forth. The values of omega as we have already seen are available in table B 1 in the appendix B of your text book.

You have already seen this, we do not have to go back and see it. Now, you know, just to recall, omega is one of the values that is given in the table along with many other constants for those pure substances. Therefore, the values of the residual properties H R and S R can be determined even without the need for the actual P V T data for each pure substance separately. So, that is the power of writing something in terms of residual properties and getting … and using the generalized correlations that result from the generalized properties or residual properties.

And, we started concentrating on H R and S R or H R by R T c and S R by R. From that you could get H R and S R. And from H R and S R we know that G or G R … G, to begin with, is defined as H minus T S and therefore, G R is defined as H R minus T S R. Once we have these values, we can substitute these here to also get the value of G R. And, once the ideal values are known, you know, we have already seen how to get the ideal values in terms of P V T, and so on. The actual values of enthalpy and entropy can be estimated from the definition of the residual property. Residual property was actual minus the ideal; and therefore, the actual is residual plus the ideal property … ideal gas property.

(Refer Slide Time: 30:48)



Example 3.4

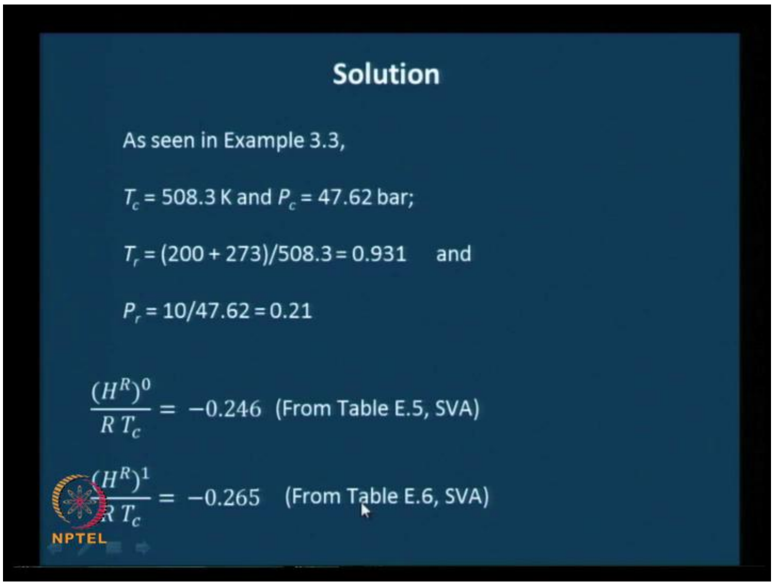
Estimate the residual enthalpy and residual entropy for the isopropanol system in Example 3.1.

To get a little more familiar with the use of generalized correlations, let us work out the example 3.4 here. We are going to continue with our favorite model system, isopropanol. The question here is: Estimate the residual enthalpy and residual entropy for the isopropanol system, with the same conditions as given in example 3.1. Please go ahead and do it. It is a straight forward thing. So, I do not think, I will give you many hints here. If at all you need I can give you the hint right now and give you some extra time also.

This is the residual enthalpy and residual entropy. We have expressions for residual enthalpy and residual entropy in terms of H R 0 and H R 1. And you know where those H R 0 and H R 1 values can be found – tables E 5 to E 12 of your text book. So, go ahead and do these, 15 minutes please.

(No audio 31:47 to 44:47).

(Refer Slide Time: 45:00)



Solution

As seen in Example 3.3,

T_c = 508.3 K and P_c = 47.62 bar;

T_r = (200 + 273)/508.3 = 0.931 and

P_r = 10/47.62 = 0.21

$$\frac{(H^R)^0}{R\,T_c} = -0.246$$ (From Table E.5, SVA)

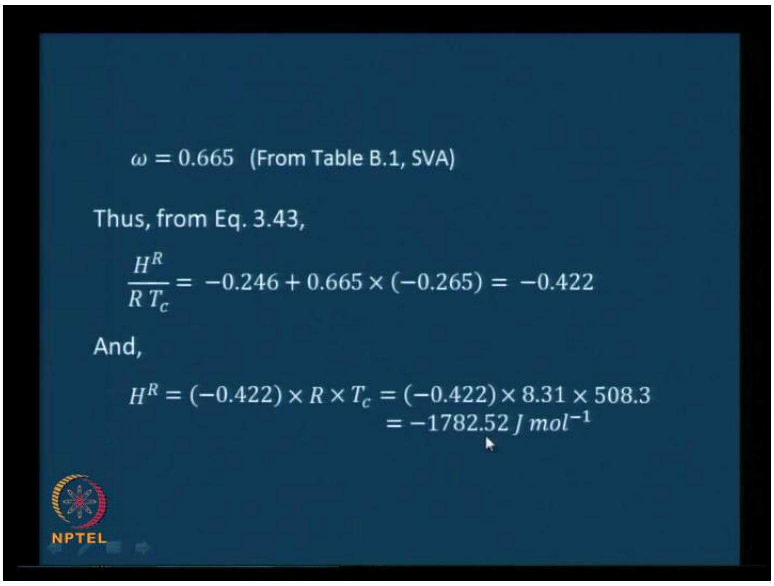
$$\frac{(H^R)^1}{R\,T_c} = -0.265$$ (From Table E.6, SVA)

Hopefully, you would have found the values of residual entropy and residual enthalpy. Let me quickly show you the solution. You can check whether you got the same. Our T c P c values are known, 508.3 Kelvin and 47.62 bar. And therefore, for the conditions of temperature and pressure in the problem, which is 200 degree C and 10 atmospheres, if I remember correctly. The residual temperature will turn out to be 0.931. This is 200 degree C plus 273. So, 473 Kelvin divided by the … T c value 508.3. That turns out to be 0.931.

And, our P r, residual pressure, is 10 atmospheres divided by P c, 47.62. And that will turn out to be 0.21. Going to the tables in the appendices of the text book, the value of H

R 0 by R T c will be minus 0.246 from table E 5 and the value of H R 1 by R T c would turn out to be 0.265 … minus 0.265 from table E 6.

(Refer Slide Time: 46:22)



$\omega = 0.665$ (From Table B.1, SVA)

Thus, from Eq. 3.43,

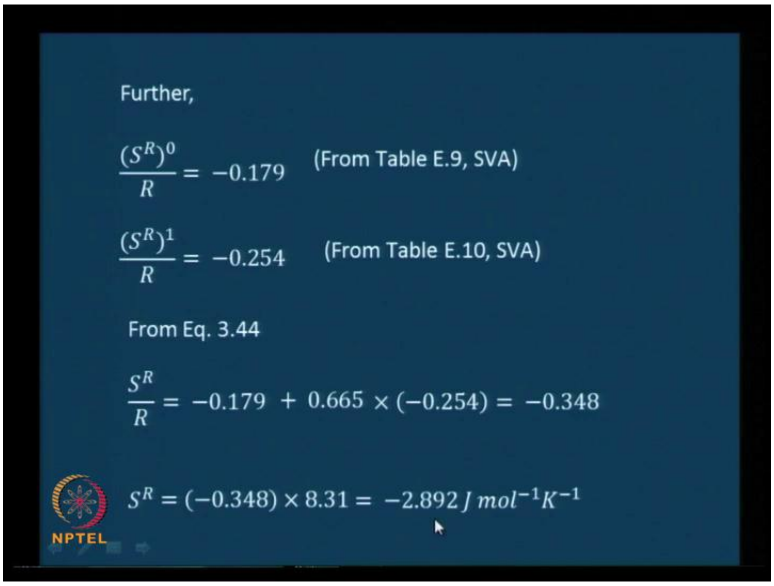
$$\frac{H^R}{R\,T_c} = -0.246 + 0.665 \times (-0.265) = -0.422$$

And,

$$H^R = (-0.422) \times R \times T_c = (-0.422) \times 8.31 \times 508.3$$
$$= -1782.52\,J\,mol^{-1}$$

Omega as we all know … you would have already seen earlier … was 0.665, from, I think, table B 1; table B 1 of the text book appendix. And therefore, from our equation 3.43 … that we had seen earlier; it will come back to you, we do not have to go back … H R by R T c is minus 0.246 plus omega 0.665 into minus 0.265, which will turn out to be minus 0.422. And … therefore, H R is minus 0.422 into R into T c, which will turn out to be minus 0.422 into 8.31 into 508.3. That is minus 1782.52 joules per mole.

(Refer Slide Time: 47:23)



Further,

$$\frac{(S^R)^0}{R} = -0.179$$ (From Table E.9, SVA)

$$\frac{(S^R)^1}{R} = -0.254$$ (From Table E.10, SVA)

From Eq. 3.44

$$\frac{S^R}{R} = -0.179 + 0.665 \times (-0.254) = -0.348$$

$$S^R = (-0.348) \times 8.31 = -2.892\, J\, mol^{-1} K^{-1}$$

Now, we have the H R value here. We still need to worry about S R. That can be obtained again from the values given in the tables S R 0 by R … will turn out to be minus 0.179, from the value given in table E 9 of your text book. And S R 1 by R is minus 0.254, from the table E 10 of your text book. And therefore, from equation 3.44, S R by R is S R naught by R plus omega times S R 1 by R, which will turn out to be minus 0.348. Therefore, the S R value is minus 0.348 into R, which is 8.31, and that is minus 2.892 joules per mole per Kelvin. So, that is what we were expected to find. Let us stop here today; and in the next class, we will start with the estimation of the fugacity coefficient.