Thermodynamics (Classical) for Biological Systems

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Module No. # 03
Thermodynamics of Pure Substances
Lecture No. # 14
Generalized Correlations (continued) Residual Properties

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 equals Z 0, Z superscript 0 plus omega, which is the acentric factor times Z superscript 1. We said … that 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. And 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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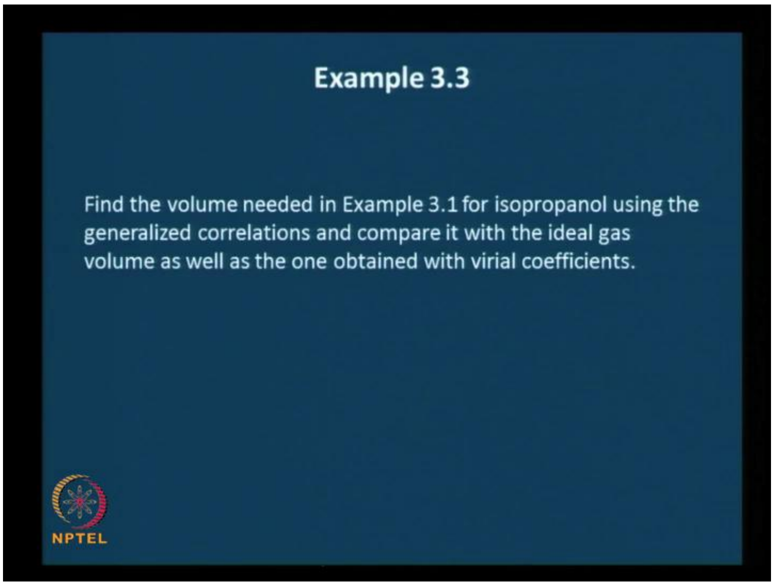

Example 3.3

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.

What I’d do is, let you think about how to go about doing it … get your bearings straight. How do you ... 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 naught, omega, and Z 1, let us take and locate the part of solution.

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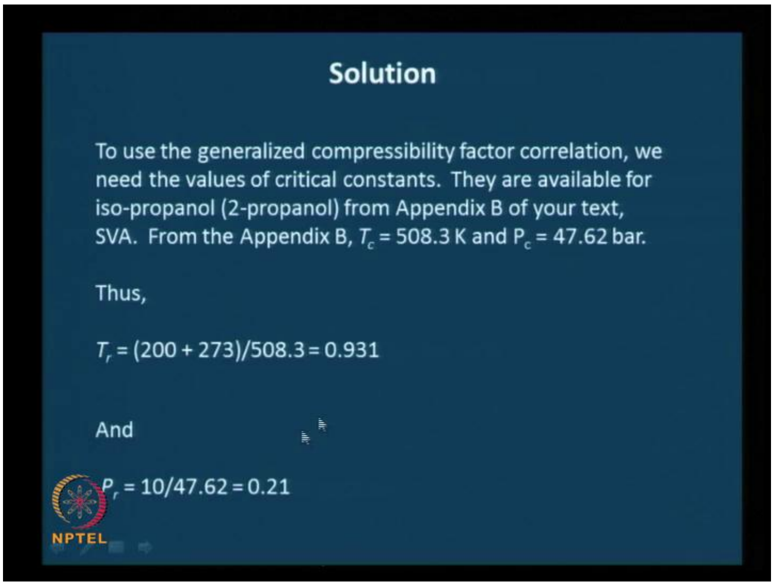

Solution

To use the generalized compressibility factor correlation, we need the values of critical constants. They are available for iso-propanol (2-propanol) from Appendix B of your text, SVA. From the Appendix B, T_c = 508.3 K and P_c = 47.62 bar.

Thus,

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

And

$P_r = 10/47.62 = 0.21$

To use the generalized compressibility factor correlation, we definitely need the values of the critical constants. You … go back and see the relationships; you would know that you would need critical constants. And the critical constants as we have already seen before are available in appendix B of your text. And 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.

And 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 kelvin 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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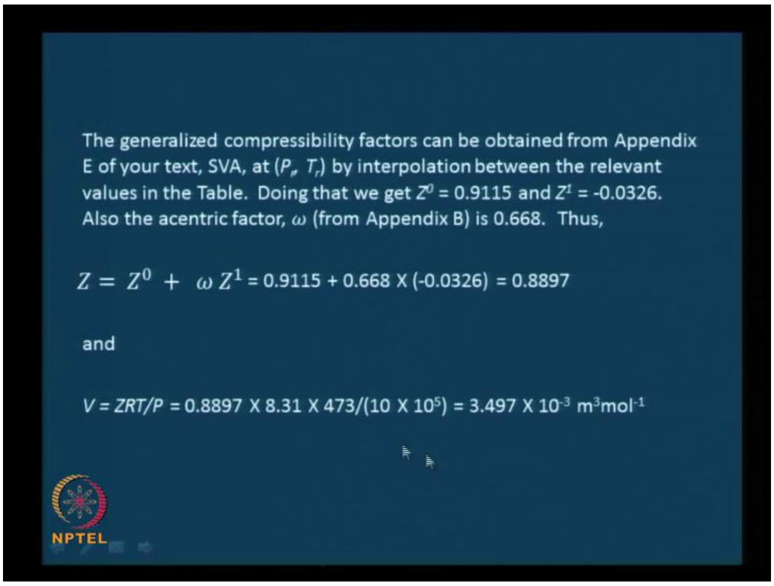

The generalized compressibility factors can be obtained from Appendix E of your text, SVA, at (P_r, T_r) by interpolation between the relevant values in the Table. Doing that we get $Z^0 = 0.9115$ and $Z^1 = -0.0326$. Also the acentric factor, ω (from Appendix B) is 0.668. Thus,

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

and

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

Now, this is the generalized … correlation, and the values of Z naught Z 1 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 P r and T r 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 P r and T r 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 naught, 0.9115 plus acentric factor 0.668 times Z 1, 0.0326. Do the calculations you will get 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.

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Let us continue. V in this calculation, equals Z RT by P. Z is P V by RT. So, transposition gives V equals Z RT by P, the molar volume. Z, we have found as 0.8897 R of course, is 8.31 t is 473. That is 200 degree C is 473 Kelvin and 10 bar is 10 power 6 Newton per meter squared – 10 into 10 power 5. And the if you do the calculations it will turn out be 3.497 into 10 power minus 3 meter cubed per mole. So, that is the molar volume.

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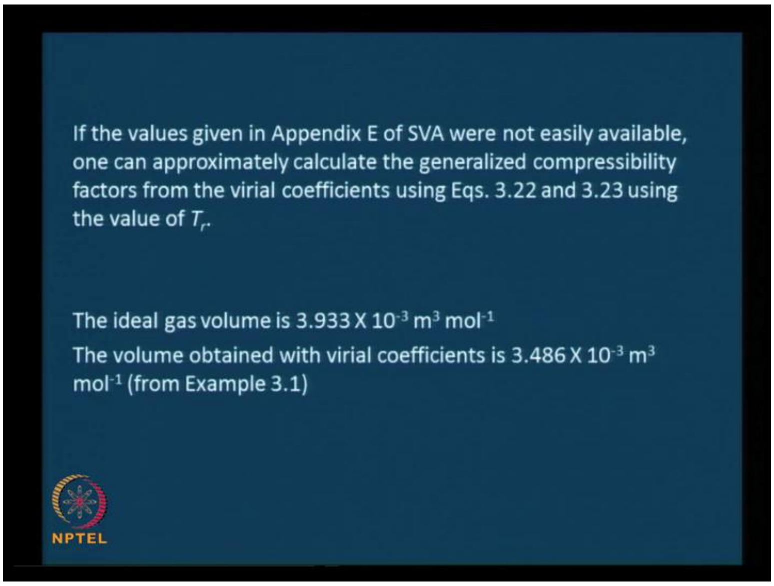

If the values given in Appendix E of SVA were not easily available, one can approximately calculate the generalized compressibility factors from the virial coefficients using Eqs. 3.22 and 3.23 using the value of T_r.

The ideal gas volume is 3.933×10^{-3} m^3 mol^{-1}

The volume obtained with virial coefficients is 3.486×10^{-3} m^3 mol^{-1} (from Example 3.1)

So, we have gotten whatever we need from the generalized correlations. And of course, 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. And 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.

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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.

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Let us continue. Some of the solutions to earlier things are given here for comparison. You would have already seen that.

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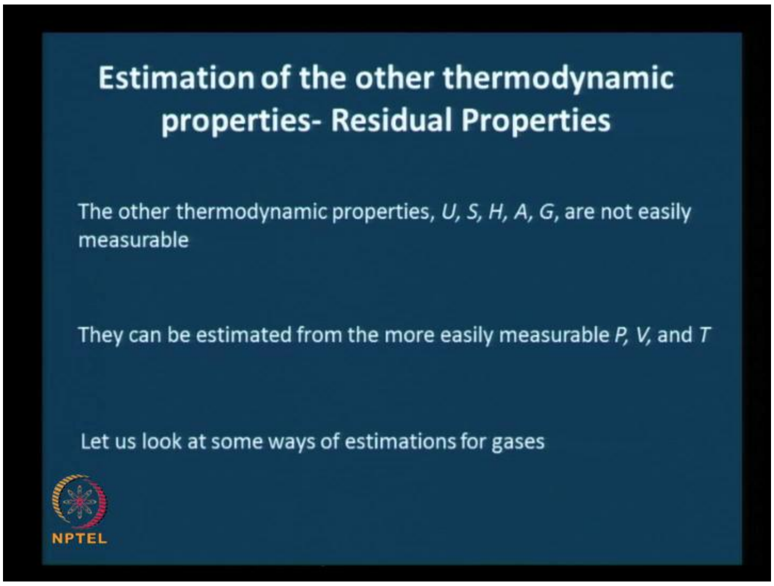

Estimation of the other thermodynamic properties- Residual Properties

The other thermodynamic properties, *U, S, H, A, G*, are not easily measurable

They can be estimated from the more easily measurable *P, V,* and *T*

Let us look at some ways of estimations for gases

Now, let us start looking at a totally different aspect, or the next aspect. Earlier it was all in terms of getting the equations or state or considering different equations of state to improve the generality of application. As you know the equation of state is something that relates the P, V and T of a pure substance. Now we are going to use that information P, V and T to estimate the other thermodynamic properties. And the way we are going to do that is use something called residual properties.

If you use this formulation it becomes possible to estimate the other thermodynamic properties. Remember that U, S, H, A and G … we could estimate the other properties using P, V, T. So, let us take a look at how to go about doing that. The motivation … as we all know by now is that U, S, H, A and G are not easily measurable. They are of course, estimated they can be estimated by the more easily measurable P, V and T.

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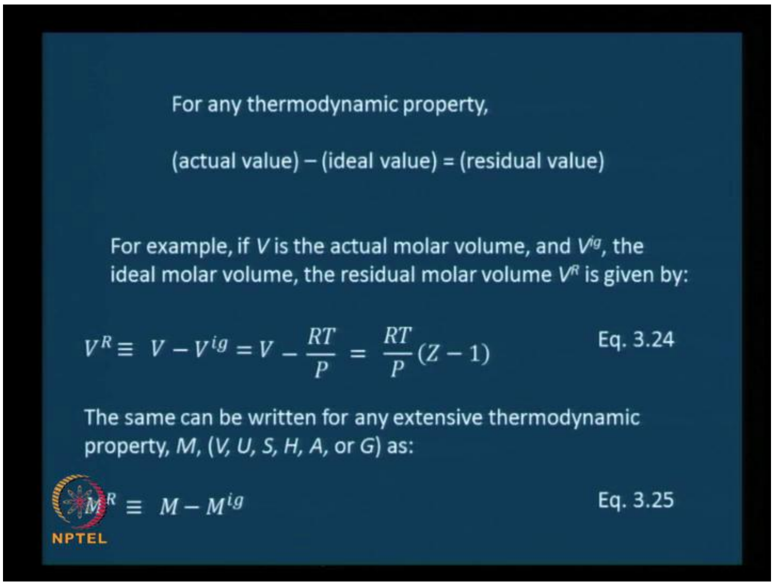

For any thermodynamic property,

(actual value) – (ideal value) = (residual value)

For example, if V is the actual molar volume, and V^{ig}, the ideal molar volume, the residual molar volume V^R is given by:

$$V^R \equiv V - V^{ig} = V - \frac{RT}{P} = \frac{RT}{P}(Z-1) \qquad \text{Eq. 3.24}$$

The same can be written for any extensive thermodynamic property, M, (V, U, S, H, A, or G) as:

$$M^R \equiv M - M^{ig} \qquad \text{Eq. 3.25}$$

And we are going to limit ourselves to gases to begin with. Pay a little bit of attention to this. For any thermodynamic property, for the 5 that we are looking it now, you can write this for any thermodynamic property or even combinations of any thermodynamic properties. The actual value minus the ideal value or the difference between the actual value and the ideal value is actually called … or it is called the residual value. Now to give you an example, if V is the actual molar volume of a substance and V ideal gas, V i g is the ideal gas molar volume then the residual molar volume, represented as V R, is given as the difference between the actual value V and the ideal value V i g.

Let us take this a little further. This is the basic definition of a residual property now given in terms of molar volumes. And since this is the molar volume let us try to take this a little further. This is nothing but, V minus V ideal gases RT by P. And we know that P V by RT is Z, and therefore, we can write this as P V by RT. And therefore, if you take this out you are going to get RT by P into Z minus 1. Rather we are writing V in terms of Z which is Z RT by P and therefore, RT by P common out Z minus 1.

We will call this equation 3.24. And since we can write this for any thermodynamic property, we could … of course, we will give you a formal expression for that. If M is any extensive thermodynamic property such as U, S, H, A, G or V, the residual property of that M is nothing, but, M minus M ideal gas. We will call that equation 3.25.

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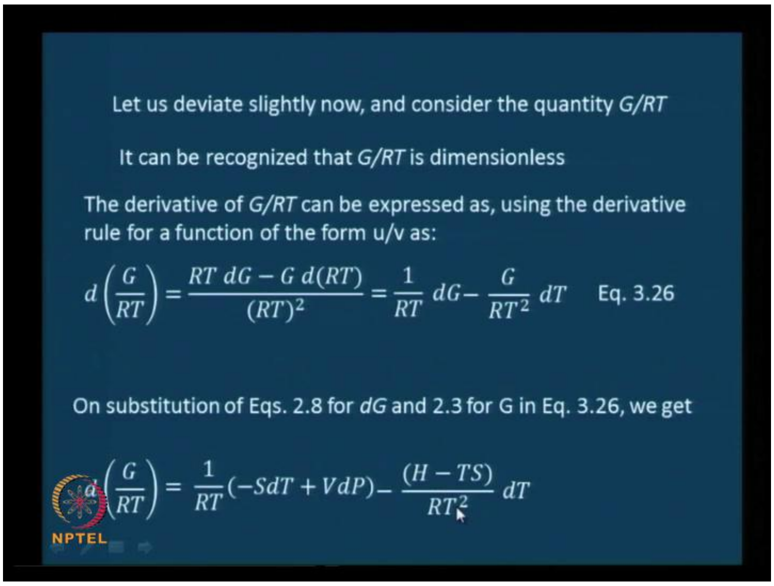

Let us deviate slightly now, and consider the quantity G/RT

It can be recognized that G/RT is dimensionless

The derivative of G/RT can be expressed as, using the derivative rule for a function of the form u/v as:

$$d\left(\frac{G}{RT}\right) = \frac{RT\,dG - G\,d(RT)}{(RT)^2} = \frac{1}{RT}\,dG - \frac{G}{RT^2}\,dT \qquad \text{Eq. 3.26}$$

On substitution of Eqs. 2.8 for dG and 2.3 for G in Eq. 3.26, we get

$$d\left(\frac{G}{RT}\right) = \frac{1}{RT}(-SdT + VdP) - \frac{(H - TS)}{RT^2}\,dT$$

Now let us kind of deviate slightly … it is still very related but, this becomes essential to develop a means of relating the excess properties to P, V, and T. Therefore, let us kind of deviate slightly and consider the quantity G by RT. The residuals of this could also be written as you will see. We will consider … we will start considering G by RT. Please work out the dimensions of G by R T. If you need you can back to your notes find out what the dimensions of G are, R are, T are, and then work out the dimensions. Take about 3 minutes to do it, and convince yourself that it is dimensionless.

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You should have gotten no dimensions for G by RT. If not please check after the class. Now let us consider the derivative, the total derivative of G by RT. You know that this is of a u by v form. R of course, is a constant but, G and T are variables. And it is of the u by v form. And therefore, the total derivative of G by RT is nothing but, you know, denominator function into derivative of the numerator function minus the numerator function into derivative of the denominator function divided by the denominator function squared.

So, in other words denominator function RT into derivative of the numerator function d G minus numerator function G times derivative of the denominator function RT divided by RT squared. Which can of course, be … you know … you take the common terms out 1 by RT d G minus G by RT squared. One of the RT will get cancelled. G by RT squared times d T. Now … we will call this equation 3.26.

Now let us express d G and G in terms of the expressions that we already know. In other words we are going to use equation 2.8 for d G and 2.3 for G. You do not have to go back and check … these equations will come back to you when I substitute them. If you use these two equations in 3.26, d G by RT equals 1 by RT. From here d G is nothing but for a closed system minus S d T plus V d P. So, that comes in here, minus G, by definition, is H minus T S. So, H minus T S. That is equation 2.3 by RT squared d T.

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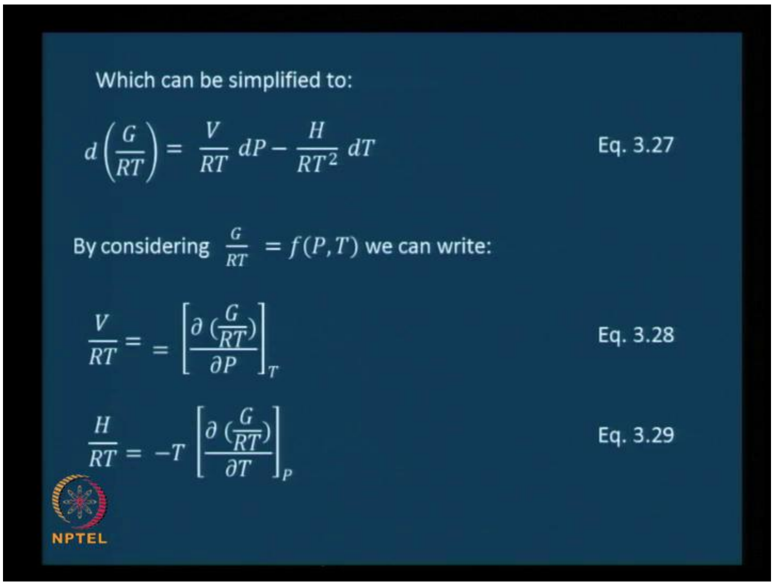

Which can be simplified to:

$$d\left(\frac{G}{RT}\right) = \frac{V}{RT}dP - \frac{H}{RT^2}dT \qquad \text{Eq. 3.27}$$

By considering $\frac{G}{RT} = f(P,T)$ we can write:

$$\frac{V}{RT} = = \left[\frac{\partial\left(\frac{G}{RT}\right)}{\partial P}\right]_T \qquad \text{Eq. 3.28}$$

$$\frac{H}{RT} = -T\left[\frac{\partial\left(\frac{G}{RT}\right)}{\partial T}\right]_P \qquad \text{Eq. 3.29}$$

This can of course, be simplified to V by RT d P minus H by RT squared d T. I am sure you can see this here, equation 3.27. Now this is the total differential. You know that total differential of a exact differential can be written as a partial differential times, you know, dou G by RT dou P dP … plus dou G by RT dou T d T. Therefore, this should be equal to let us let us take one step at a time. By considering G by RT as a function of P and T we can write V by RT as dou G by RT dou P … this term at constant temperature here. We will call this equation 3.28.

And H by RT equals minus T because H by RT squared will turn out to be the partial derivative here with respect to temperature at constant pressure. And therefore, H by RT is minus T dou G by RT dou T at constant P. We will call this equation 3.29.

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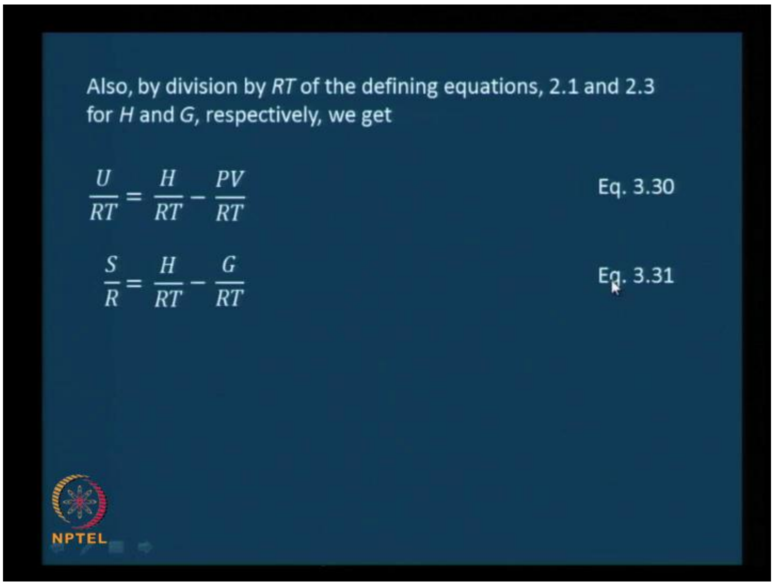

Also, by division by *RT* of the defining equations, 2.1 and 2.3 for *H* and *G*, respectively, we get

$$\frac{U}{RT} = \frac{H}{RT} - \frac{PV}{RT} \qquad \text{Eq. 3.30}$$

$$\frac{S}{R} = \frac{H}{RT} - \frac{G}{RT} \qquad \text{Eq. 3.31}$$

By dividing equations 2.1 and 2.3 by RT … this will come back to you straightaway. You do not go, do not need to go back. U was nothing but H minus P V or H equals U plus P V therefore U equals H minus PV. And you divide throughout by RT, U by RT is going to be H by RT minus PV by RT; equation 3.30. And … S by R equals H by RT minus G by RT though it is TS. You know G equals H minus TS, and from that we get S by R equals H by RT minus G by RT. What we will do now is, we will stop here with this equation 3.31, because the further development … we would like it be a little more continuous, and we will continue with this in the next class.