Thermodynamics (Classical) for Biological Systems

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Module No. # 03

Thermodynamics of Pure Substances

Lecture No. # 15

Residual Properties (continued)

Welcome. In the last class, we ended when we were looking at G by R T. And we were looking at getting the other four functions. Remember, there were five other thermodynamic functions, which are not so easy to measure. We are trying to express that in terms of P, V and T. They are U, S, H, A, and G, and we started looking at G by R T. The reason for that will become apparent in a little while later either in this class itself or the next class.

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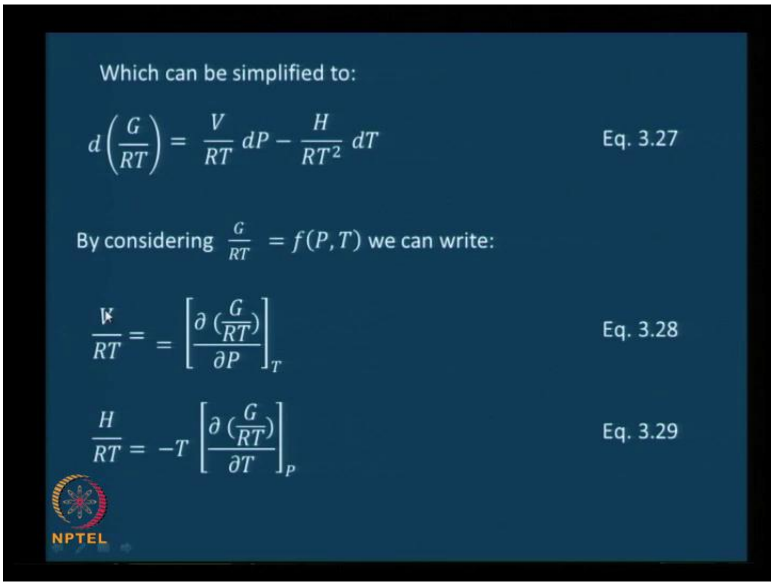

Which can be simplified to:

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

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

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

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

We started considering G by R T, and then from G by R T, we got the other four U, S, H, and A. Let us go through it once again for completeness. … We saw that by considering G by R T as a function of pressure and temperature alone, we could get this V by R T as dou of G by R T by dou P at constant T, which is what is here; and H by R T … as you know this is minus H by R T squared. And therefore, if you are going to replace this with a partial differential it would be dou G by R T by dou T at constant P and that would be minus H by R T squared. And therefore, H by R T is minus of T of the partial differential. And so, we are done with V, H … V is an additional, thing here.

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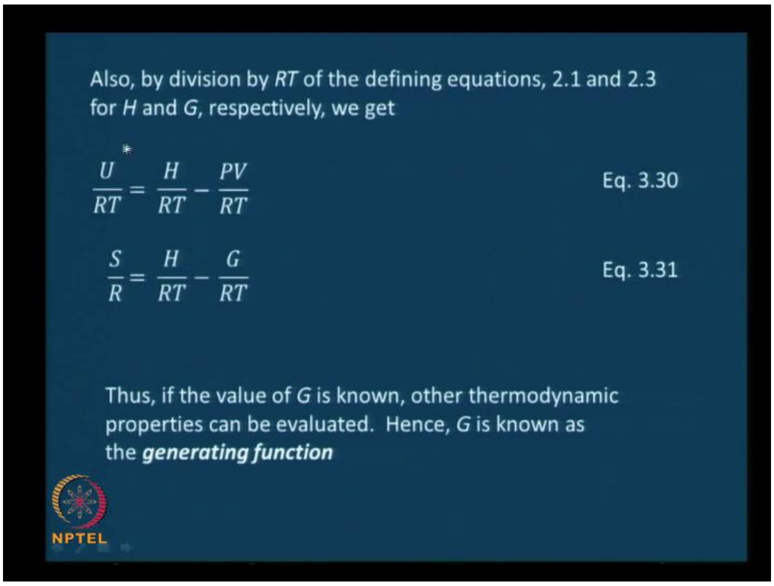

Also, by division by *RT* of the defining equations, 2.1 and 2.3 for *H* and *G*, respectively, we get

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

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

Thus, if the value of *G* is known, other thermodynamic properties can be evaluated. Hence, *G* is known as the ***generating function***

And, we also found that from the original definitions, we could write U in terms of H and P V, which in turn were it in terms of G by R T earlier. And S by R could be written in terms of H by R T and G by R T. If you look at it, we have V by R T here, H by R T here, and U by R T as well as S by R. Therefore, we have a complete set of thermodynamic variables. If you know, G by R T, and … for that reason this G is known as the regenerating function; the Gibbs free energy is known as a generating function. We use it in the form of G by R T here.

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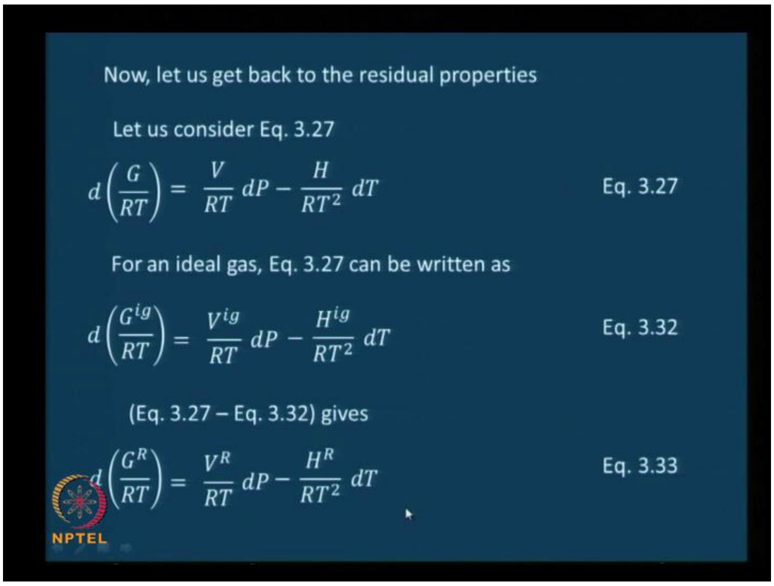

Now, let us get back to the residual properties

Let us consider Eq. 3.27

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

For an ideal gas, Eq. 3.27 can be written as

$$d\left(\frac{G^{ig}}{RT}\right) = \frac{V^{ig}}{RT}\,dP - \frac{H^{ig}}{RT^2}\,dT \qquad \text{Eq. 3.32}$$

(Eq. 3.27 – Eq. 3.32) gives

$$d\left(\frac{G^{R}}{RT}\right) = \frac{V^{R}}{RT}\,dP - \frac{H^{R}}{RT^2}\,dT \qquad \text{Eq. 3.33}$$

Let us continue and get back to right proper residual properties now. Let us consider equation 3.27. I am going to represent it here again. We do not have to go back. Now, d of G by R T equals V by R T d P minus H by R T squared d T; this was equation 3.27. If we write this for an ideal gas, then this becomes d of G ideal gas by R T equals V ideal gas by R T d P minus H of ideal gas by R T squared d T.

Let us call this equation 3.32. To be in line 3.27 came a little earlier. Equation 3.32 is the next number in sequence. Now, if we subtract 3.32 from 3.27 – note this is the actual value, this is the ideal value, and therefore, actual value minus the ideal value must give us the residual value. Therefore, d of G R the residual by R T equals V residual by R T d P minus of H residual by R T squared d T. Let us call this equation 3.33. Earlier, we considered G or rather, G by R T as a function of P and T and derived the other thermodynamic functions.

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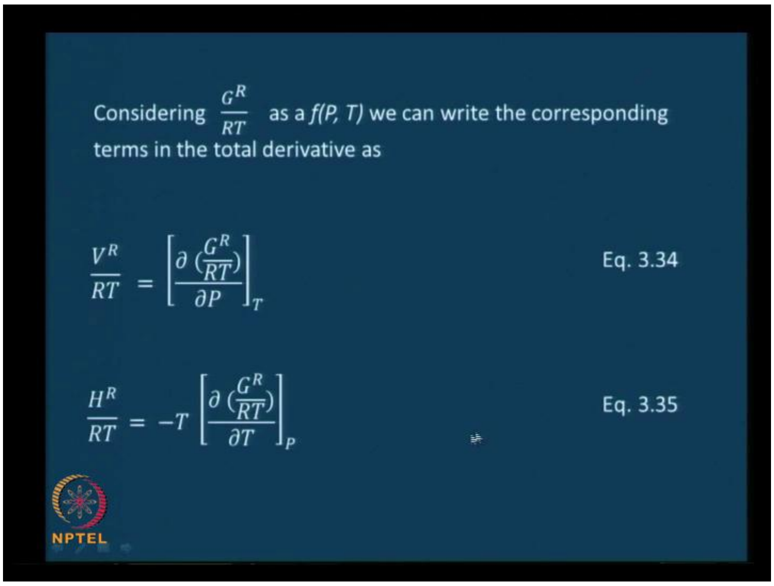

Considering $\frac{G^R}{RT}$ as a *f(P, T)* we can write the corresponding terms in the total derivative as

$$\frac{V^R}{RT} = \left[\frac{\partial\left(\frac{G^R}{RT}\right)}{\partial P}\right]_T \qquad \text{Eq. 3.34}$$

$$\frac{H^R}{RT} = -T\left[\frac{\partial\left(\frac{G^R}{RT}\right)}{\partial T}\right]_P \qquad \text{Eq. 3.35}$$

Now, let us consider G R by R T as a function of P and T and let us write the corresponding terms. What I would like you to do is take … may be about 5 minutes and do this exercise. Consider … G R by R T as a function of P and T. Consider the total derivative in terms of the partial derivatives and therefore, write the functionalities of the partial derivatives in terms of the thermodynamic variables that we need. And thus establish that you could use G R by R T to generate the other thermodynamic functions. Go ahead. May be you want to take about 10 minutes. Since, we are looking at this for the first time, take about 10 minutes and do it. Go ahead please.

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Let us continue. This was in the same vein as earlier for G by R T. You know instead of the actual values, we have the residual values here. Therefore, the same argument holds. See whether you got this. If you did not get this go back again and look at how we obtain the relationships for the actual values.

V R by R T equals dou G R by R T dou P at constant T; let us call this equation 3.34. And H R by R T equals minus T dou G R by R T dou T at constant P. Essentially this comes from just expressing the total derivative in terms of the partial derivatives for an exact differential and writing the partial derivatives as equivalent to the thermodynamic functions. The last equation let us call that as equation 3.35.

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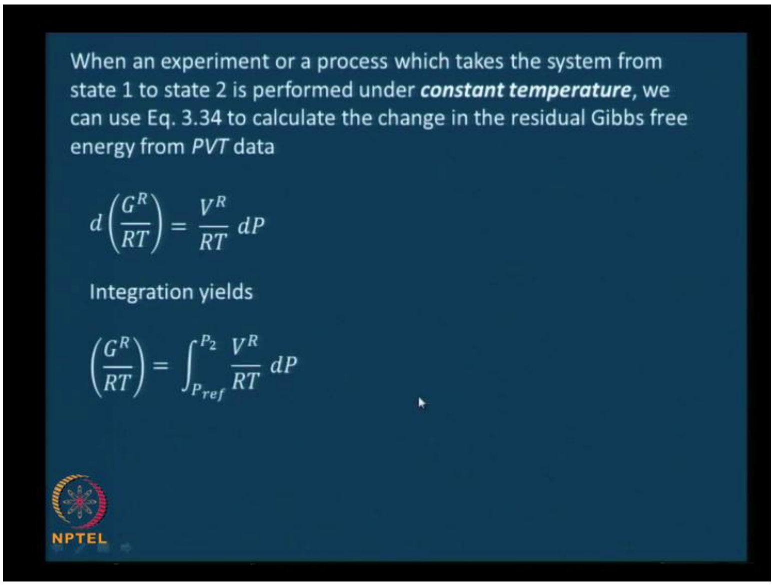

When an experiment or a process which takes the system from state 1 to state 2 is performed under ***constant temperature***, we can use Eq. 3.34 to calculate the change in the residual Gibbs free energy from *PVT* data

$$d\left(\frac{G^R}{RT}\right) = \frac{V^R}{RT}\,dP$$

Integration yields

$$\left(\frac{G^R}{RT}\right) = \int_{P_{ref}}^{P_2} \frac{V^R}{RT}\,dP$$

Now, when an experiment or a process takes the system, lets say from state 1 to state 2 and let us say that this is performed under constant temperature. We are imposing the condition of constant temperature for this process. In such a case, we can use the equation 3.34, which is essentially an equation where the partial derivative is taken and the temperature is held constant. Let us take look at that 3.34 here, V R by R T equals dou dou P of G R by R T at constant temperature.

Therefore, if we perform an experiment under constant temperature conditions you can use this equation directly to get this from this. And we can use that to calculate the residual Gibbs free energy from the P V T data. Let us take a look at that right now. d G R by R T equals V R by R T d P at constant temperature. The other derivative at constant temperature goes away because that goes to 0 rather the d T terms goes to 0. And therefore, the other term drops out. Under these conditions, integration of this equation you know … integral of d G R by R T is nothing but G R by R T and if we integrate this side, let us say from P reference to a certain pressure P 2, V R by R T d P.

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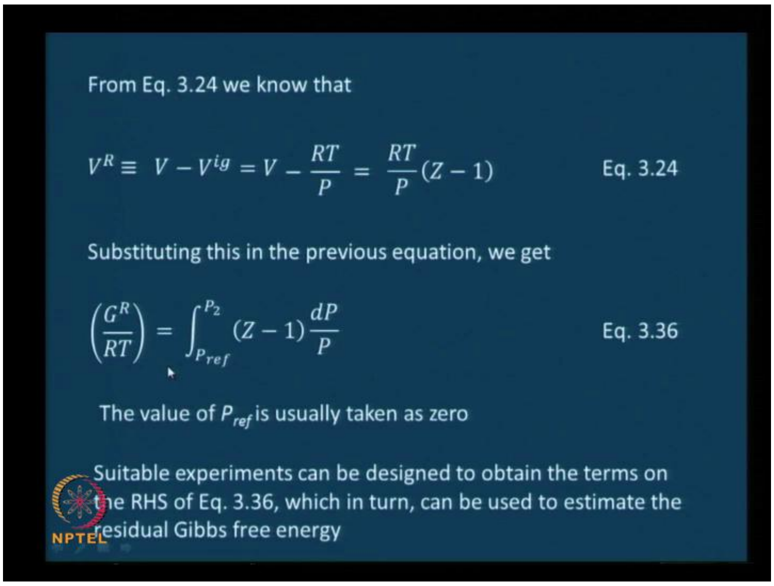

From Eq. 3.24 we know that

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

Substituting this in the previous equation, we get

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

The value of P_{ref} is usually taken as zero

Suitable experiments can be designed to obtain the terms on the RHS of Eq. 3.36, which in turn, can be used to estimate the residual Gibbs free energy

From an earlier equation 3.24, we know that V R it is essentially the residual property of V, the molar volume. The actual volume minus ideal gas volume, which we said was equal to V minus R T by P, because ideal gas molar volume is R T by P, which when expressed in terms of the compressibility factor becomes R T by P Z minus 1. This we saw in equation 3.24 itself. If we substitute this in the previous equation for V R we get G R by R T equals integral from P reference to P 2, Z minus 1 d P by P. We will call that 3.36 … equation.

And the value of P reference is usually taken to be 0, which is fine. And if that is a case then you can design suitable experiments to obtain the terms on the right hand side of this equation 3.36, which can in turn be used to calculate G R by R T the residual Gibbs free energy. And from the earlier equations, we can relate the Gibbs free energy, the generating function, to get the other thermodynamic variables U R, S R, H R and A R; and from the residuals you can get the actual quantities.

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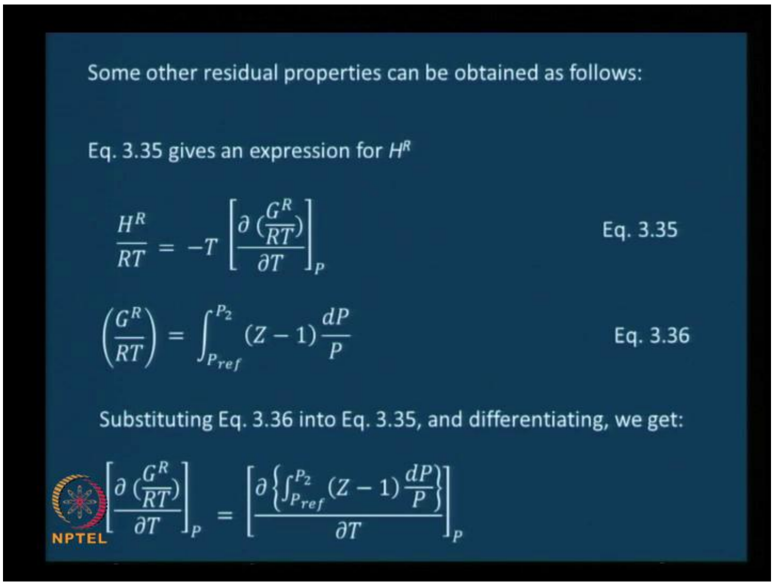

Some other residual properties can be obtained as follows:

Eq. 3.35 gives an expression for H^R

$$\frac{H^R}{RT} = -T\left[\frac{\partial\left(\frac{G^R}{RT}\right)}{\partial T}\right]_P \qquad \text{Eq. 3.35}$$

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

Substituting Eq. 3.36 into Eq. 3.35, and differentiating, we get:

$$\left[\frac{\partial\left(\frac{G^R}{RT}\right)}{\partial T}\right]_P = \left[\frac{\partial\left\{\int_{P_{ref}}^{P_2} (Z-1)\frac{dP}{P}\right\}}{\partial T}\right]_P$$

Some other residual properties can be obtained as follows. … I am going to explain whatever I said in brief earlier. Equation 3.35 directly gives an expression for H R, the residual enthalpy. H R by R T equals minus T dou dou T of G R by R T times P. Therefore, once we know G R by R T we can get H R by R T from this expression. Let us call that equation … rather we already called it 3.35. G R by R T, we have already seen, is P reference to P 2 integrated, of Z minus 1 by P d P. And if we substitute equation 3.36 for G R by R T into equation 3.35 to get H R by R T, we get it into this situation. dou G R by R T dou T at constant P equals dou dou T of P reference to P 2, … Z minus 1 by P d P.

I would like you to ponder over the right hand idea of this. Have you seen such expressions earlier? What is so special about that take a couple of minutes to, you know, ponder about , and then I will come back and tell you how to handle this.

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Hopefully you would have seen that it is a derivative, a partial derivative, of an integral.

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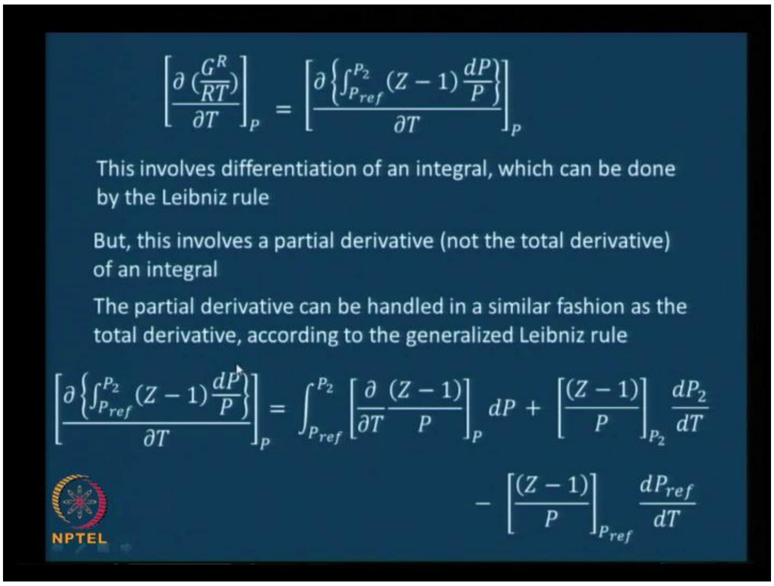

$$\left[\frac{\partial\left(\frac{G^R}{RT}\right)}{\partial T}\right]_P = \left[\frac{\partial\left\{\int_{P_{ref}}^{P_2}(Z-1)\frac{dP}{P}\right\}}{\partial T}\right]_P$$

This involves differentiation of an integral, which can be done by the Leibniz rule

But, this involves a partial derivative (not the total derivative) of an integral

The partial derivative can be handled in a similar fashion as the total derivative, according to the generalized Leibniz rule

$$\left[\frac{\partial\left\{\int_{P_{ref}}^{P_2}(Z-1)\frac{dP}{P}\right\}}{\partial T}\right]_P = \int_{P_{ref}}^{P_2}\left[\frac{\partial}{\partial T}\frac{(Z-1)}{P}\right]_P dP + \left[\frac{(Z-1)}{P}\right]_{P_2}\frac{dP_2}{dT} - \left[\frac{(Z-1)}{P}\right]_{P_{ref}}\frac{dP_{ref}}{dT}$$

… That we have here, how you do that? There is something called a Leibniz rule, which you would have encountered in your first or second course in mathematics in your first year, which allows us to differentiate an integral. Nevertheless, that Leibniz rule would have been written for a total derivative, and what we have here is a partial derivative.

If it had been the total derivative whatever you had learnt from the first year course would have sufficed to do this. You might forgotten that … you might want to go back and verify how to do a differentiation of an integral. But that does not matter. Here, you have a partial derivative and therefore, you need to consider it further, and there is something called generalized Leibniz rule. And what it says is that you can look through this and probably some specialized books in mathematics. What it says is that the partial derivative can be handled in a similar fashion to the total derivative according to the generalized Leibniz rule.

Therefore, whatever you did for the total derivative of an integral can be done for the partial derivative of the integral too, is what this says. Therefore, dou dou T of integral P reference to P 2, Z minus 1 by P d P at constant pressure can be written as … you know … recall the Leibniz rule. This was integral between the same two limits. You take the derivative inside the integral dou dou T of Z minus 1 by P at constant P d P. This is the first term, plus the function evaluated at the upper limit times the derivative of the upper limit with respect to d T which is the function here with which it is differentiated.

Therefore, d d T of P 2 minus the value of the function evaluated at the lower limit times the derivative with respect to T with respect to this variable of the lower limit which is P reference. So, this is exactly the same form that you would have learnt in your earlier mathematics class.

Now, take a look at this. This is fine; we will come back to this a little later. This is d d T of P 2; P 2 is a particular pressure value. Similarly, P reference is a particular pressure value. In this case it happens to be 0. Therefore, we are actually doing the differentiation of a constant. Therefore; these two terms go to 0. And therefore, these two, the second and third terms on the right hand side are actually 0.

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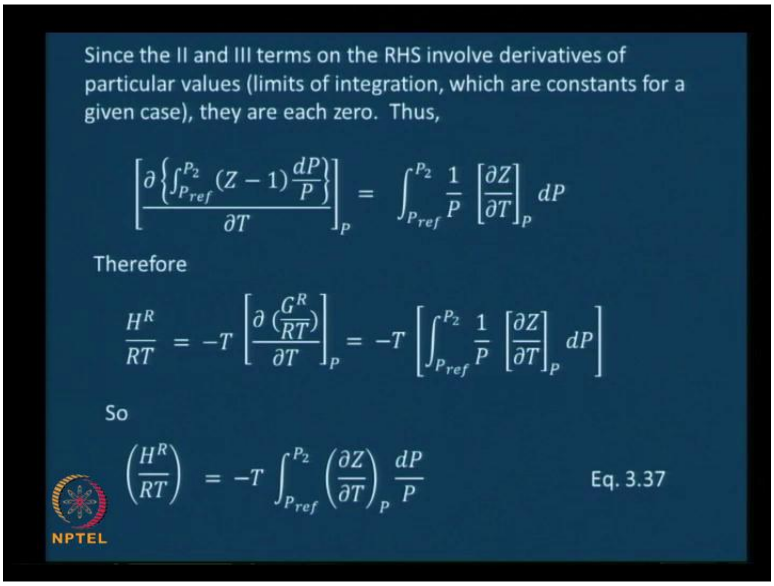

Since the II and III terms on the RHS involve derivatives of particular values (limits of integration, which are constants for a given case), they are each zero. Thus,

$$\left[\frac{\partial\left\{\int_{P_{ref}}^{P_2}(Z-1)\frac{dP}{P}\right\}}{\partial T}\right]_P = \int_{P_{ref}}^{P_2}\frac{1}{P}\left[\frac{\partial Z}{\partial T}\right]_P dP$$

Therefore

$$\frac{H^R}{RT} = -T\left[\frac{\partial\left(\frac{G^R}{RT}\right)}{\partial T}\right]_P = -T\left[\int_{P_{ref}}^{P_2}\frac{1}{P}\left[\frac{\partial Z}{\partial T}\right]_P dP\right]$$

So

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

Eq. 3.37

Therefore, dou dou T of P reference to P 2, Z minus 1 by P d P at constant pressure reduces to integral of P reference to P 2, 1 by P dou Z dou T at constant P, which is what this one reduces to. … If you take the derivative here at constant P, that reduces to this. Please verify this. I am not going to give you extra here but you can go back after the class and verify this; P integral of P reference to P 2 1 by P dou Z dou T at constant P d P.

Therefore, H R by R T, which is what we started looking at, and we went in to all this Leibniz rule business because we wanted to differentiate an integral to get H R by R T from G R by R T. And this is, as we know, from the expression earlier minus T dou dou T of G R by R T at constant P. And, if we substitute this we would get minus T from here times P reference to P 2, 1 by P dou Z dou T at constant P times d P. Therefore, H R by R T can be evaluated from minus T integral of P reference to P 2, dou Z dou T at constant P … into 1 by P d P. So, we have gotten H R by T, or H R in terms of easily measurable properties. Let us call this equation 3.37.

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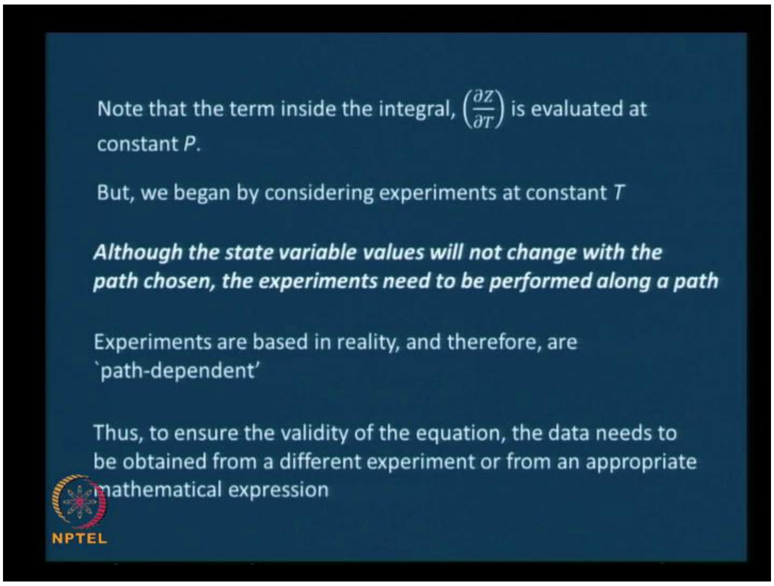

Note that the term inside the integral, $\left(\frac{\partial Z}{\partial T}\right)$ is evaluated at constant *P*.

But, we began by considering experiments at constant *T*

Although the state variable values will not change with the path chosen, the experiments need to be performed along a path

Experiments are based in reality, and therefore, are `path-dependent'

Thus, to ensure the validity of the equation, the data needs to be obtained from a different experiment or from an appropriate mathematical expression

Now, the term inside the integral here dou Z dou T is actually evaluated at constant pressure. But, we began by considering experiments it constant temperature. But the second term went off when we considered the process at constant temperature. Therefore, d T went to 0, and so on.

We began by considering experiments at constant temperature but this is still valid, you know, by using one of her usual arguments. The state … although the state variables will not change along the … will not change with the path chosen, the experiments need to be performed along a path. Experiments are based in reality, and therefore, are path-dependent. Therefore, to ensure the validity of the equation, … the data needs to be obtained from a different experiment, or from an appropriate mathematical expression.

So, the dou Z dou T at constant P data needs to be obtained from a different set of experiment not the same constant temperature experiment; that will not be valid here. … I think, I should mention this again. This is a slightly different way of presenting the same basic argument.

Here, we are in the realm of experiments which are grounded in reality. We are looking at ways to get dou Z dou T at constant P. Whereas, we started the derivation by looking at a constant temperature process. And since, the experiments are path-dependent, we need to obtain dou Z dou T at constant P from a different set of experiments, where the P is held constant.

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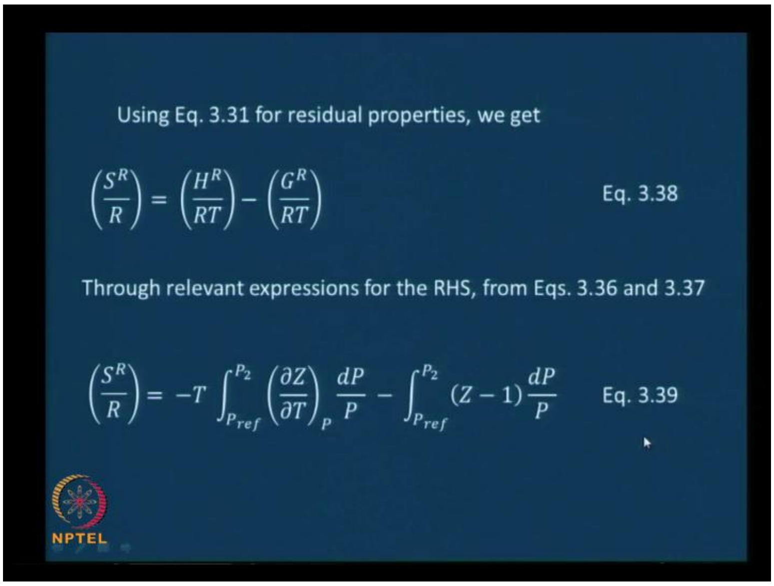

Using Eq. 3.31 for residual properties, we get

$$\left(\frac{S^R}{R}\right) = \left(\frac{H^R}{RT}\right) - \left(\frac{G^R}{RT}\right) \qquad \text{Eq. 3.38}$$

Through relevant expressions for the RHS, from Eqs. 3.36 and 3.37

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

Now, you seeing equation 3.31 for residual properties, we can get the other variables S R by R equals H R by R minus G R … sorry … H R by R T minus G R by R T. This we have already seen earlier. And we have an expression for H R by R T, which we just derived by going through the differentiation of integral, and so on. We also have an expression for G R by R T in terms of the measurable properties. Therefore, if we substitute both of them here, we have S R by R equals … H R by R is minus T integral of P reference to P 2, dou Z dou T at constant P into 1 by P d P, minus G R by R T that we have already seen earlier; … integral from P reference to P 2, Z minus 1 by P d P. Therefore, we have S R in terms of T, P, Z, and so on. We will call this equation 3.39.

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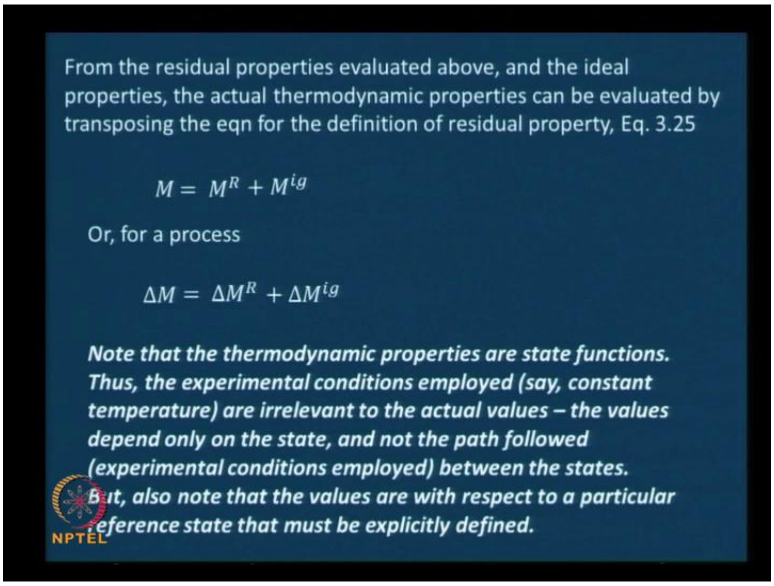

From the residual properties evaluated above, and the ideal properties, the actual thermodynamic properties can be evaluated by transposing the eqn for the definition of residual property, Eq. 3.25

$$M = M^R + M^{ig}$$

Or, for a process

$$\Delta M = \Delta M^R + \Delta M^{ig}$$

Note that the thermodynamic properties are state functions. Thus, the experimental conditions employed (say, constant temperature) are irrelevant to the actual values – the values depend only on the state, and not the path followed (experimental conditions employed) between the states. But, also note that the values are with respect to a particular reference state that must be explicitly defined.

Now, we have residual properties starting with G R by R T, and hopefully, we would have generated the other residual properties. And we know that the actual property minus the ideal gas ideal property or ideal gas property is the residual property.

And therefore, if you have expressions for the ideal gas values, then we can get the actual values from the residual values. Therefore, let us see the obvious thing; the actual property is nothing but the residual property plus the ideal gas property. Or for a process, you know, between states 1 and 2 delta M or M 2 minus M 1 is nothing delta M R plus delta M of an ideal gas. Note that the thermodynamic properties are state functions. This is repeating the earlier argument, but in the context of this process.

Thus the experimental conditions employed, say constant temperature are irrelevant to the actual process. Actual values … the values depend on only on the state and not the path followed. For example, the experimental conditions employed between the states. But also note that the values are with respect to a particular reference state which must be explicitly defined. That we know right from the beginning, but it is good to remind ourselves from time to time so that we do not forget it when we actually need to use it.

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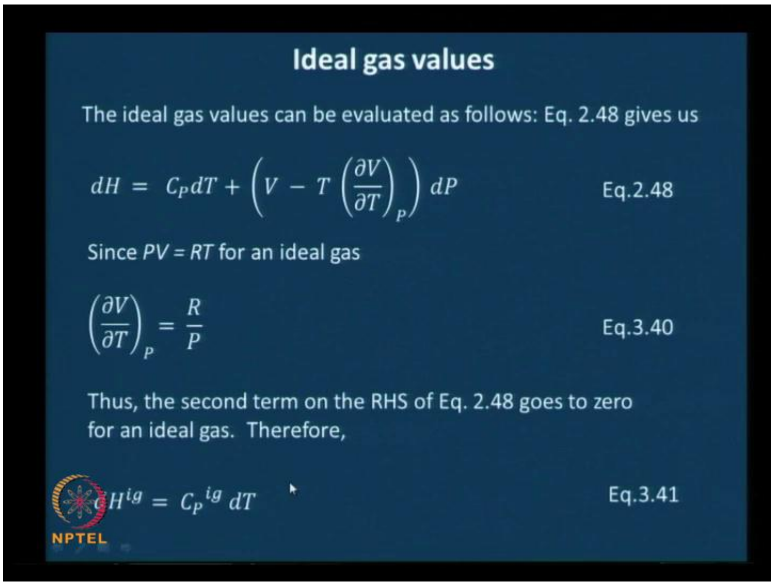

Ideal gas values

The ideal gas values can be evaluated as follows: Eq. 2.48 gives us

$$dH = C_P dT + \left(V - T\left(\frac{\partial V}{\partial T}\right)_P\right) dP \qquad \text{Eq.2.48}$$

Since $PV = RT$ for an ideal gas

$$\left(\frac{\partial V}{\partial T}\right)_P = \frac{R}{P} \qquad \text{Eq.3.40}$$

Thus, the second term on the RHS of Eq. 2.48 goes to zero for an ideal gas. Therefore,

$$dH^{ig} = C_p^{ig}\, dT \qquad \text{Eq.3.41}$$

So, let us look at the second part now, we had the residual properties evaluation in terms of P, V, T, Z, and so on. Now, let us look at how to get the ideal gas values in terms of the easily measurable quantities. The ideal gas values can be evaluated as follows: Equation 2.48 gave us d H equals C P d T plus V minus T dou V dou T at constant pressure, the whole d P; this we have already seen.

Now, since we are looking at ideal gas, we can use the relationship P V equals R T. Therefore, dou V dou T at constant P, from here, becomes R by P. You can see how to go about doing it at constant pressure you can take pressure out constant, and dou V dou T at constant pressure would turn out to be R by P, directly from this equation. Let us call that equation 3.40.

Now, the second term on the right hand side of 2.48 will go to 0 for an ideal gas. Therefore, d H ideal gas is C P ideal gas d T alone. You do not have this for an ideal gas. Why? Because, you know, you have this V minus T and you substitute R by P here you get T R by P. And T R by P is nothing but V. V minus V goes to 0. Therefore, you end up with d H ideal gases C P ideal gas d T – equation 3.41.

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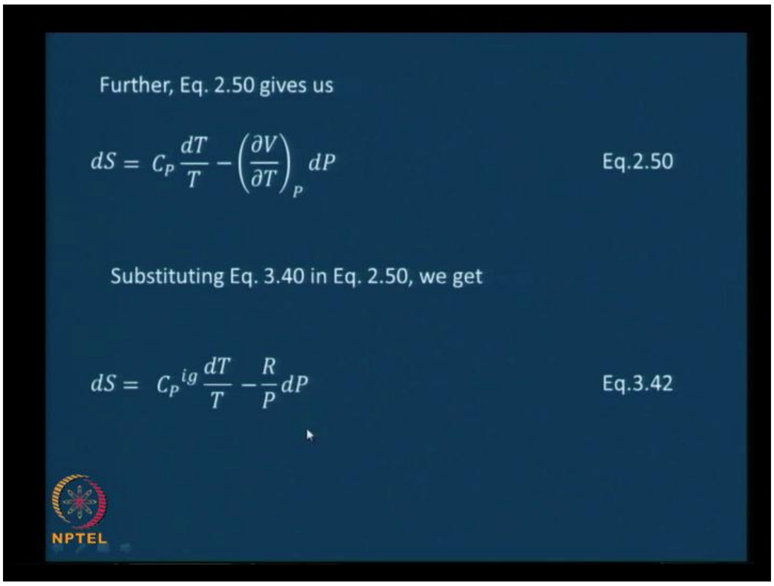

Further, Eq. 2.50 gives us

$$dS = C_P \frac{dT}{T} - \left(\frac{\partial V}{\partial T}\right)_P dP \qquad \text{Eq.2.50}$$

Substituting Eq. 3.40 in Eq. 2.50, we get

$$dS = C_P{}^{ig} \frac{dT}{T} - \frac{R}{P} dP \qquad \text{Eq.3.42}$$

And equation 2.50 from the earlier module – it gives us d S equals C P d T by T minus dou V dou T at constant pressure d P. You can go back and check if you want; this is essentially what 2.50 give us. And substituting equation 3.40 in 2.50 in terms of dou V dou T at constant P, and so on, we get d S equals C P ideal gas d T by T, minus you know we have already shown that dou V dou T at constant P was R by P. So, we substitute that here, R by P d P. We will call that equation 3.42. And therefore, we have, d S for an ideal gas in terms of easily measurable quantities.

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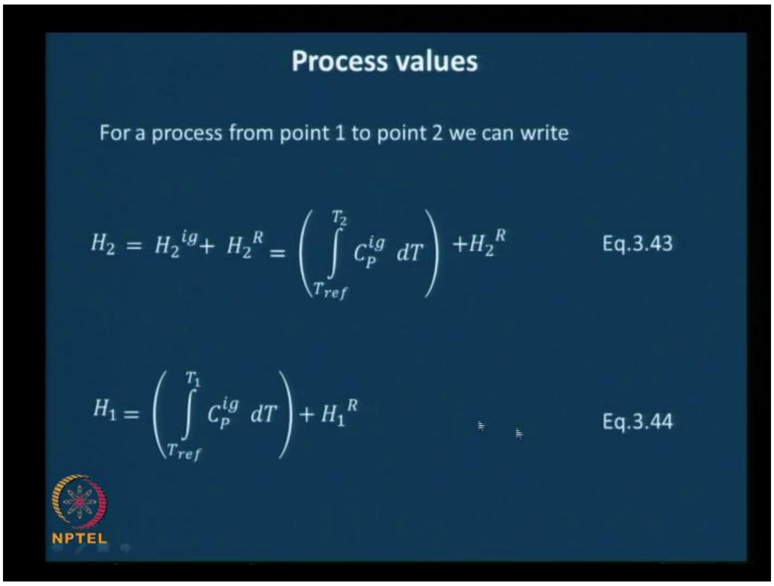

Process values

For a process from point 1 to point 2 we can write

$$H_2 = H_2{}^{ig} + H_2{}^{R} = \left(\int_{T_{ref}}^{T_2} C_P^{ig}\, dT\right) + H_2{}^{R} \qquad \text{Eq.3.43}$$

$$H_1 = \left(\int_{T_{ref}}^{T_1} C_P^{ig}\, dT\right) + H_1{}^{R} \qquad \text{Eq.3.44}$$

Now, let us look at some process values between 0.1 to 0.2 that the system takes during a process. … H 2 equals H 2 ideal gas plus H 2 R. That is from the definition. And H 2 ideal gas, we have seen, is nothing but integral of T reference to T 2, C P ideal gas d T. You know this directly comes from the definition of C P, plus H 2 R. We will call that equation 3.43. And H 1, similarly, can be written as T reference to T 1, C P ideal gas d T plus H 1 R. You know where we are going … we are going to take the difference now 3.43, 3.44.

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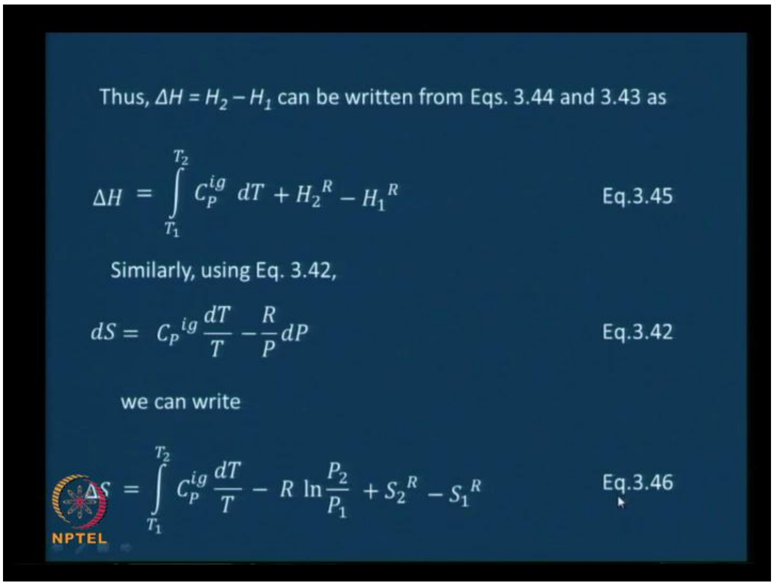

Thus, $\Delta H = H_2 - H_1$ can be written from Eqs. 3.44 and 3.43 as

$$\Delta H = \int_{T_1}^{T_2} C_P^{ig}\, dT + H_2^R - H_1^R \qquad \text{Eq.3.45}$$

Similarly, using Eq. 3.42,

$$dS = C_P{}^{ig} \frac{dT}{T} - \frac{R}{P} dP \qquad \text{Eq.3.42}$$

we can write

$$\Delta S = \int_{T_1}^{T_2} C_P^{ig} \frac{dT}{T} - R \ln \frac{P_2}{P_1} + S_2{}^R - S_1{}^R \qquad \text{Eq.3.46}$$

And delta H which is H 2 minus H 1 can be written as C P ideal gas d T integrated between T 1 and T 2. Note one was from T reference to T 2 the other one was from T reference to T 1. Subtract the two – effectively subtracting the areas. Therefore, the limits change for T 1 to T 2 plus, of course, H 2 R minus H 1 R. Let us call that equation 3.45.

Similarly, using 3.42 that we have shown earlier, d S equals C P ideal gas d T by T minus R by P d P by P. And therefore, for a process, delta S is integral of T 1 to T 2, C P ideal gas d T by T minus R. This is R P by 1 by P d P. The integral of that is going to be log in of P between the limits and therefore, you get minus R into ln of P 2 minus ln of P 1, which can be written as ln of P 2 by P 1; plus, of course, S 2 R minus S 1 R. You know, this is essentially the ideal gas property and we are trying to find out the delta S or

S 2 minus S 1. Therefore, you have these two terms here and let us call this equation 3.46.

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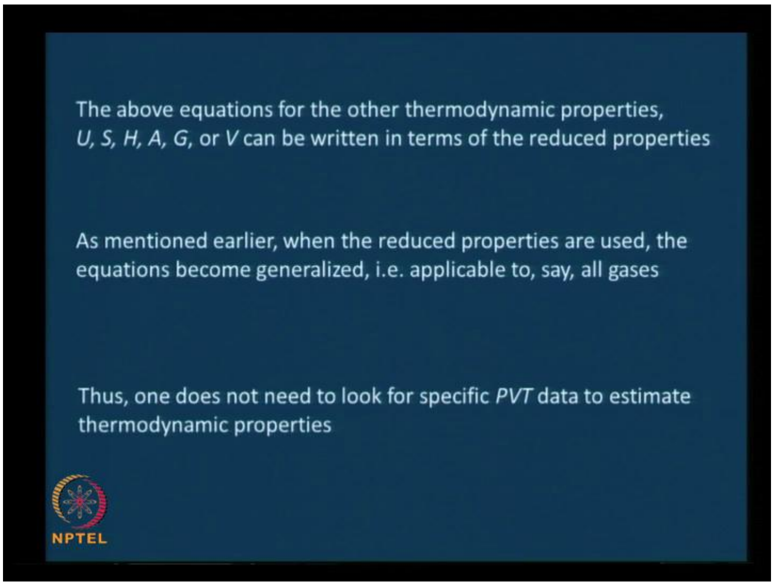

The above equations for the other thermodynamic properties, *U, S, H, A, G*, or *V* can be written in terms of the reduced properties

As mentioned earlier, when the reduced properties are used, the equations become generalized, i.e. applicable to, say, all gases

Thus, one does not need to look for specific *PVT* data to estimate thermodynamic properties

The above equations for the thermodynamic properties U, S, H, A, G or V can be written in terms of reduced properties also. And therefore, the number of measurements or the number of data points that you need from existing values becomes much less … becomes much easier to evaluate. And, as mentioned earlier, when generalized properties are used the equations become generalized. In other words, applicable to all gases. And, one therefore, does not need the P V T data for specific pure substances to estimate the thermodynamic properties.

So, essentially what we have done so far is to look at generating the not so easy to measure thermodynamic variables U, S, H, A and G from measurable … easily measurable quantities. But we focused on G begin with. We got G in terms of … in terms of the easily measurable properties. Then, we got everything else. To that we had used the residual properties formulation. And, then, we said that we are going to look at things in terms of reduced properties. And in such a case, you do not need specific P V T data. The correlations that are given would be applicable to almost all gases, in general, with a few exceptions.

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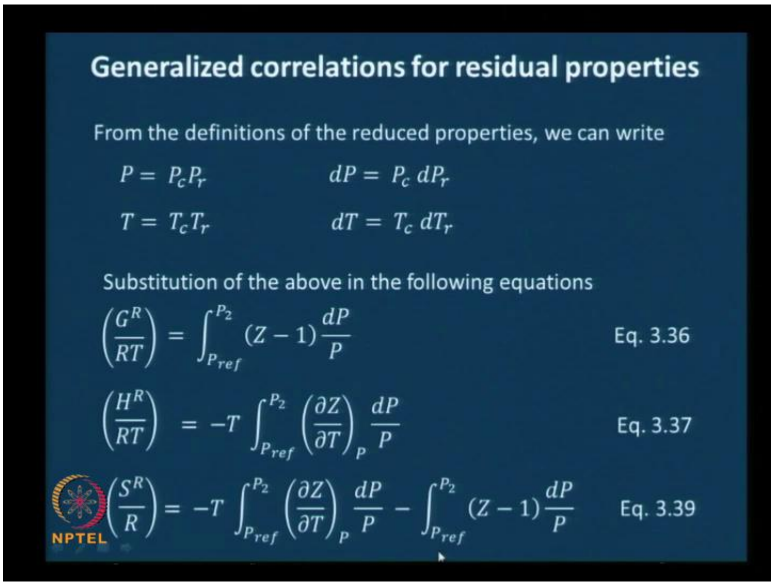

Generalized correlations for residual properties

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

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

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

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

And so, let us look at those generalized correlations to the extent possible today. From the definition of the reduced properties, we can of course, write … you know … P R, if you recall, is nothing but the ratio of P to P c, and therefore, P is nothing but P c into P R. And therefore, d P is … P c is a constant … so P c times d P r. Similarly, T is nothing but, T c T R because T by T c is the definition of T R. Therefore, d T is nothing but T c times d T r.

Now, if you substitute the above in the following equations … these were the equations that we have obtained earlier for G R by R T equals integral of P reference to P 2, Z minus 1 by P d P. This was equation 3.36 earlier. H by R T was equal to minus T into integral of P reference to P 2, dou Z dou T at constant P d P; this was equation 3.37.

And S R by R equals minus T integral of P reference to P 2, dou Z dou T at constant P d P by P minus integral P reference to P 2, Z minus 1 by P d P, equation 3.39. Why don't you go ahead and substitute in the remaining time? We have about 6 minutes left. In the remaining time, why don't you substitute P c P r wherever P occurs, T c T r wherever T occurs, and see what expressions you get in terms of the reduced quantities. Go ahead please. We will take it off from here, continue from here, when we meet next.