Thermodynamics for Biological Systems:
Classical and Statistical Aspects

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Lecture – 21
Residual Properties

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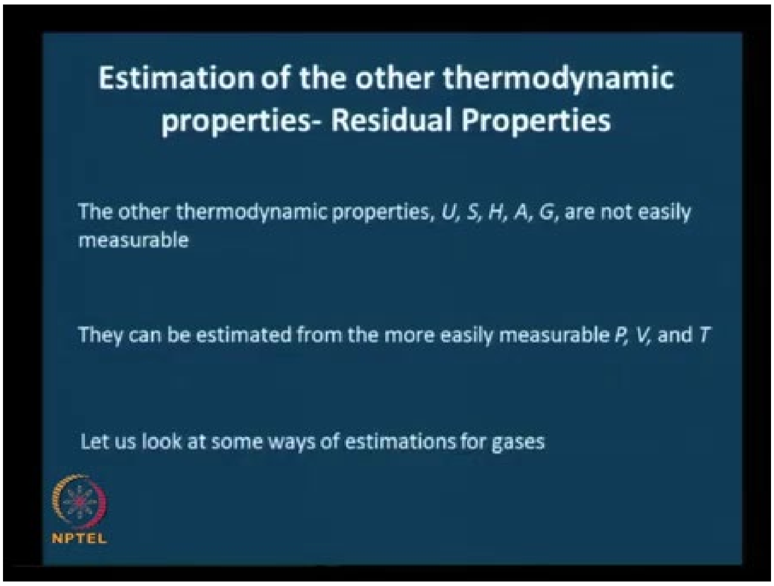

Estimation of the other thermodynamic properties- Residual Properties

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

Welcome!

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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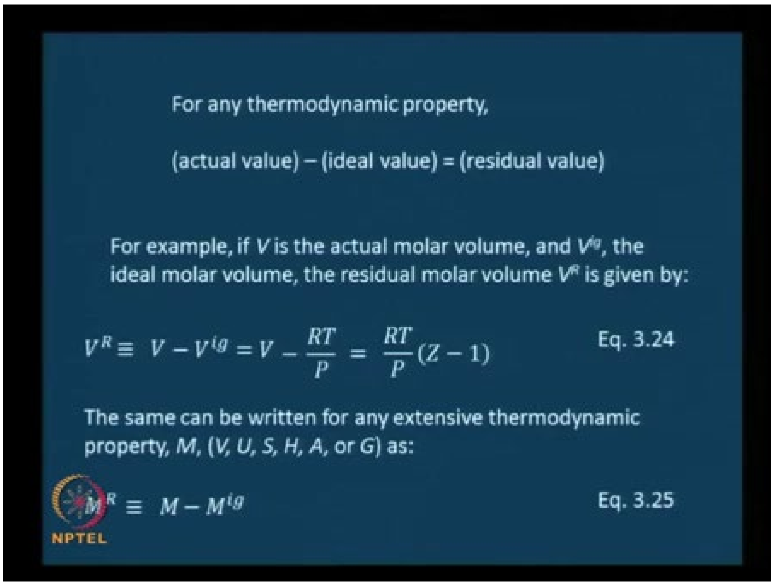

For any thermodynamic property,

(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.

$$V^R \equiv V - V^{ig} = V - \frac{RT}{P} = \frac{RT}{P}(Z-1)$$

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.

$$M^R \equiv M - M^{ig}$$

We will call that equation 3.25.

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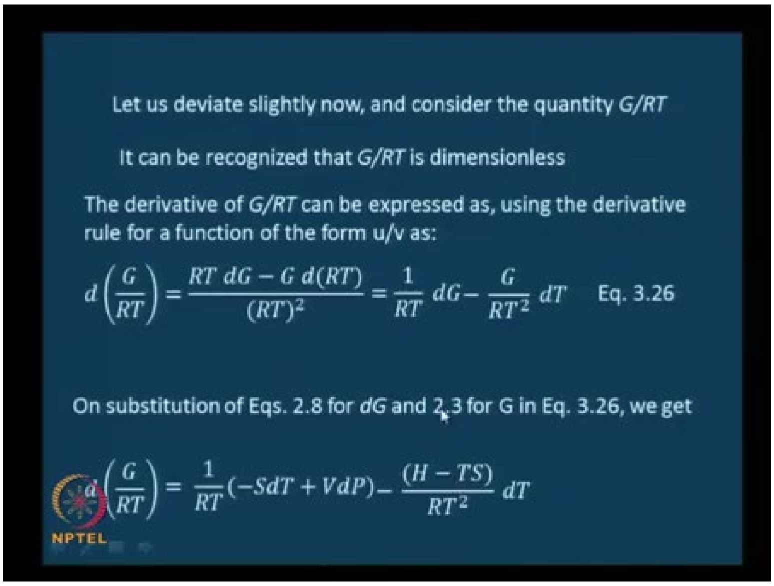

Let us deviate slightly now, and consider the quantity *G/RT*

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 start by 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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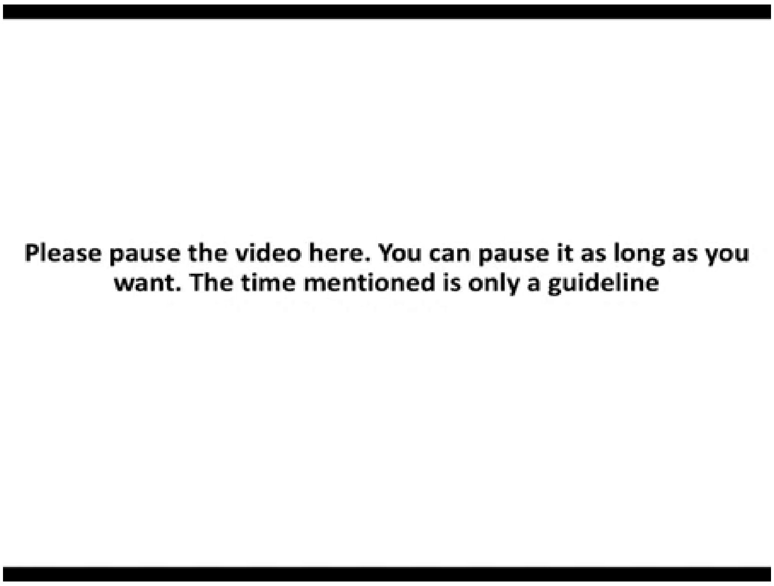

Please pause the video here. You can pause it as long as you want. The time mentioned is only a guideline

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.

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

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.

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

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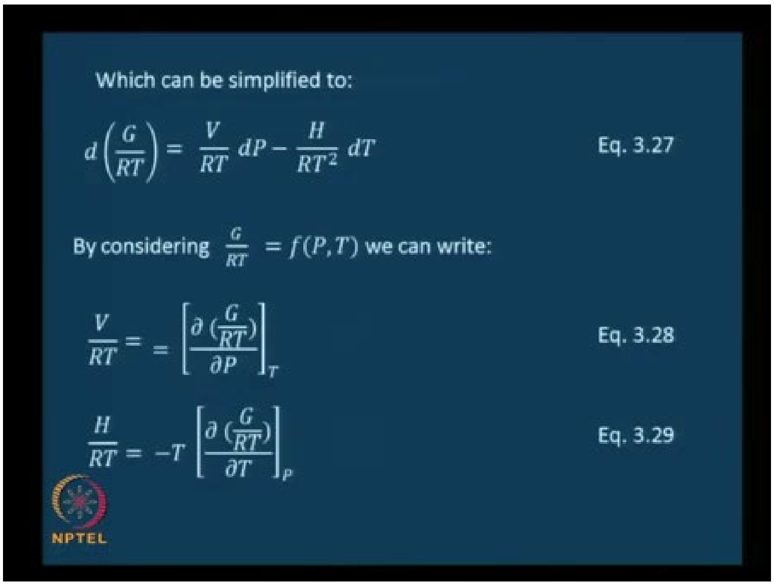

Which can be simplified to:

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

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

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

I am sure you can see this here, equation 3.27. Now this is the total differential. You know that total differential of an 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

$$\frac{G}{RT} = f(P,T)$$

we can write V by RT as dou G by RT dou P … this term at constant temperature here.

$$\frac{V}{RT} = \left[\frac{\partial\left(\frac{G}{RT}\right)}{\partial P}\right]_T$$

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,

$$\frac{H}{RT} = -T\left[\frac{\partial\left(\frac{G}{RT}\right)}{\partial T}\right]_P$$

We will call this equation 3.29.

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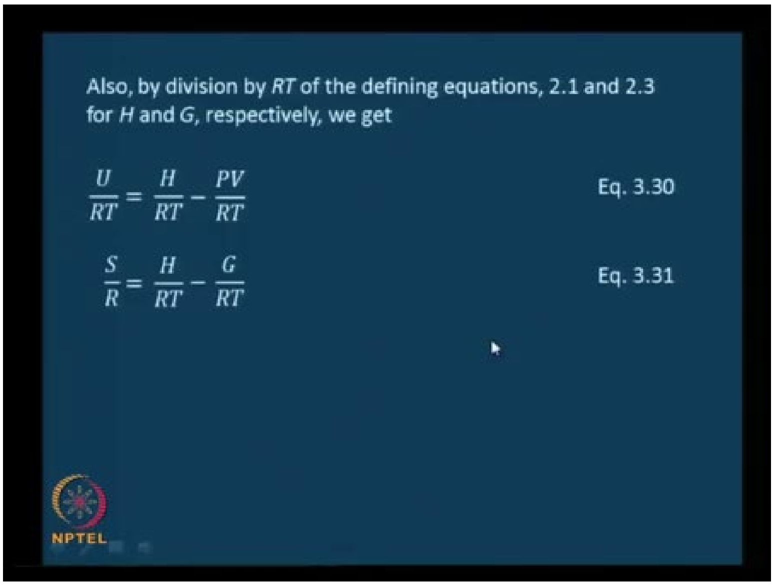

Also, by division by RT of the defining equations, 2.1 and 2.3 for H and G, respectively, we get

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

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

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,

$$\frac{U}{RT} = \frac{H}{RT} - \frac{PV}{RT}$$

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

$$\frac{S}{R} = \frac{H}{RT} - \frac{G}{RT}$$

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.