Thermodynamics (Classical) for Biological Systems

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Module No # 02

Additional Thermodynamic Functions

Lecture No # 05

Inter-Relationships between Thermodynamic Variables

In the last class, we ended by posing this question, mainly as practice exercise, for using the various relationships to get difficult to measure thermodynamic variables in terms of easy-to-measure thermodynamic variables. I hope you had … had time to work this out. I will give you the solution to begin with, so that it will help you understand the ways of looking at such manipulations a little better. Essentially, we are using some, few principles in mathematics … theorems in mathematics to come up with this relationship between the thermodynamic variables, to relate, in this particular case, difficult to measure thermodynamic variables to easy-to-measure thermodynamic variables.

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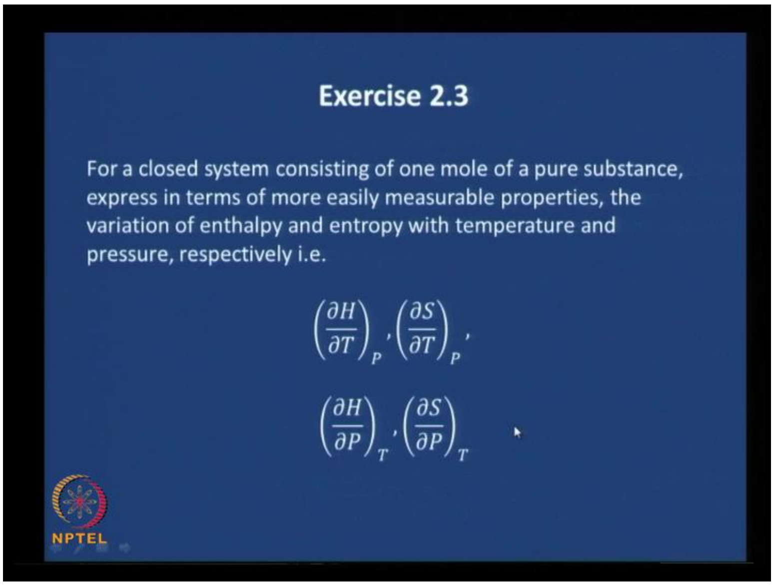

Exercise 2.3

For a closed system consisting of one mole of a pure substance, express in terms of more easily measurable properties, the variation of enthalpy and entropy with temperature and pressure, respectively i.e.

$$\left(\frac{\partial H}{\partial T}\right)_P, \left(\frac{\partial S}{\partial T}\right)_P,$$

$$\left(\frac{\partial H}{\partial P}\right)_T, \left(\frac{\partial S}{\partial P}\right)_T$$

This exercise was for a closed system consisting of 1 mole of a pure substance, express in terms of more easily measurable properties, the variation of enthalpy and entropy with temperature and pressure, respectively. In other words, dow H dow T at constant P, dow S dow T at constant P, and just the flip with P and T, dow H dow P at constant T, dow S dow P at constant T.

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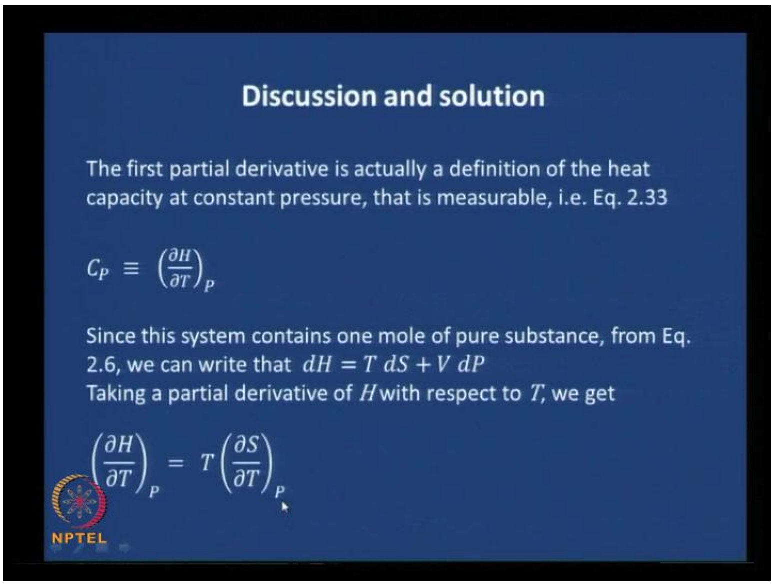

Discussion and solution

The first partial derivative is actually a definition of the heat capacity at constant pressure, that is measurable, i.e. Eq. 2.33

$$C_P \equiv \left(\frac{\partial H}{\partial T}\right)_P$$

Since this system contains one mole of pure substance, from Eq. 2.6, we can write that $dH = T\,dS + V\,dP$
Taking a partial derivative of H with respect to T, we get

$$\left(\frac{\partial H}{\partial T}\right)_P = T\left(\frac{\partial S}{\partial T}\right)_P$$

The way to go about this would be as follows. The 1st partial derivative was dow H dow T at constant P. If you go back into your notes or into the earlier slides of this lecture, you would actually find, that this is the definition of C P, which is a measured quantity, which is … the data of which is available. So, we do not have to do anything further, dow H dow T at constant P is itself a measured quantity.

Since the system consists of 1 mole of pure substance, if you look at the equation 2.6, that we had written earlier, we can write the same equation 2.6 given here, d H equals T dS plus V dP; it is for a closed system consisting of 1 mole of a pure substance.

Now, if we take the partial derivative of H with respect to T at constant P, dow H dow T at constant P, the 1st term will be T dow S dow T at constant P and the 2nd term is going to vanish here because we are forcing P to remain constant. Therefore, d P will go to 0 and this term would vanish. Therefore, dow H dow T at constant P equals T dow S dow T at constant P.

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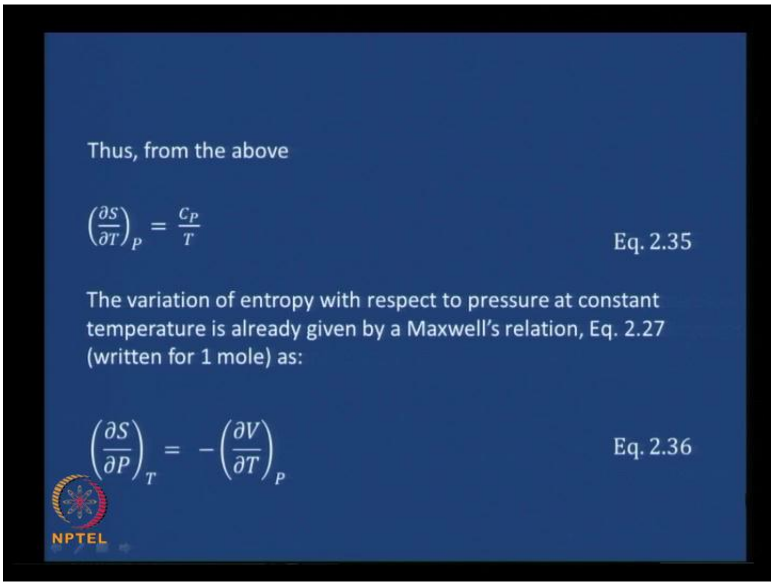

Thus, from the above

$$\left(\frac{\partial S}{\partial T}\right)_P = \frac{C_P}{T} \qquad \text{Eq. 2.35}$$

The variation of entropy with respect to pressure at constant temperature is already given by a Maxwell's relation, Eq. 2.27 (written for 1 mole) as:

$$\left(\frac{\partial S}{\partial P}\right)_T = -\left(\frac{\partial V}{\partial T}\right)_P \qquad \text{Eq. 2.36}$$

Proceeding further, dow S dow T at constant P equals C P by T. This, you get by comparing the previous equations. Let us go back a little bit, this is dow H dow T at constant P equals C P. dow H dow T at constant P … we had gotten this as T dow S dow

T at constant P, you equate this to this, C P is easily measurable, and therefore, we get dow S dow T at constant P equals C P by T. So, we have handled this also. We will call this equation 2.35.

So, we have some more remaining. The variation of entropy S with respect to pressure at constant temperature, dow S dow P with T remaining constant, is actually given by Maxwell's relation. You go back to your … we had written all four equations for 1 mole of a pure substance; you can go back and look at that. Actually, equation 2.27, written for 1 mole was dow S dow P at constant T equals minus dow V dow T at constant P. Let us call this as equation 2.36 here; and therefore, that takes care of three different parts of the question.

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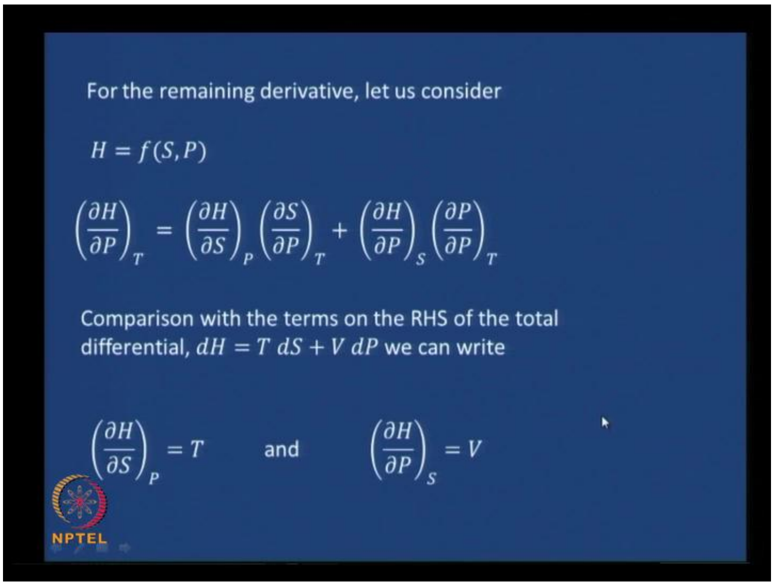

For the remaining derivative, let us consider

$H = f(S,P)$

$$\left(\frac{\partial H}{\partial P}\right)_T = \left(\frac{\partial H}{\partial S}\right)_P \left(\frac{\partial S}{\partial P}\right)_T + \left(\frac{\partial H}{\partial P}\right)_S \left(\frac{\partial P}{\partial P}\right)_T$$

Comparison with the terms on the RHS of the total differential, $dH = T\,dS + V\,dP$ we can write

$$\left(\frac{\partial H}{\partial S}\right)_P = T \qquad \text{and} \qquad \left(\frac{\partial H}{\partial P}\right)_S = V$$

There is one more part that is remaining. For that, let us consider H as a function of S and P you can consider, whatever as function of the relevant variables. In this case, let us consider enthalpy as a function of entropy and pressure. If you do this, dH, you know, can be written as dow H dow S at constant P dS, dow H dow P at constant S dP.

Now, if you take the partial of that … with respect to P at constant temperature, dow H dow P at constant T, this is the quantity that we need … dow H dow S at constant P, which is a 1st term, that came from the previous total differential writing and of course, dow S dow P at constant T, and this again comes from the partial differential writing, the total differential expansion dow H dow P at constant S. And here, dP would be there, you take the partial derivative dow P dow P at constant T; very easy to see that this goes to 1.

Now, comparison with the terms on the right hand side of the total differential, dH equals T dS plus V dP this is the total differential of dH. We can write, that dow H dow S at constant P equals T, and dow H dow P at constant S equals V.

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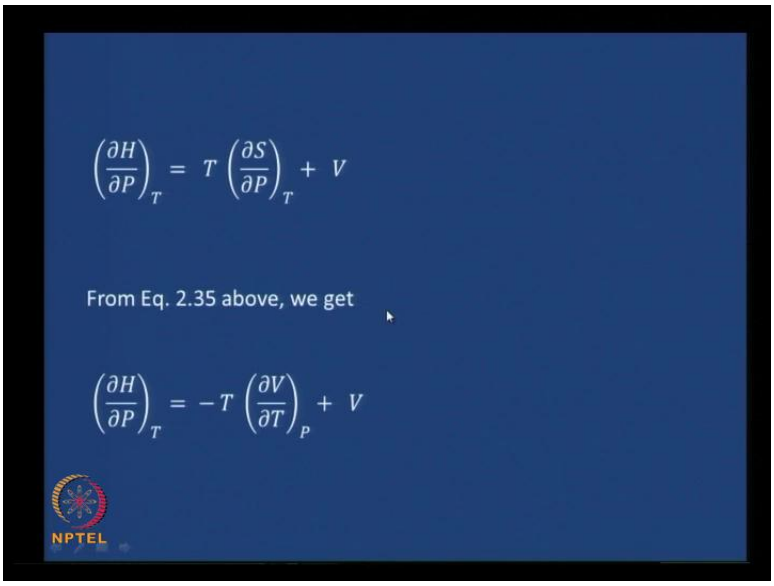

$$\left(\frac{\partial H}{\partial P}\right)_T = T\left(\frac{\partial S}{\partial P}\right)_T + V$$

From Eq. 2.35 above, we get

$$\left(\frac{\partial H}{\partial P}\right)_T = -T\left(\frac{\partial V}{\partial T}\right)_P + V$$

Therefore, dow H dow P at constant T, which is the one that we require – it is nothing but T dow S dow P at constant T plus V. So, we have gotten all four quantities, that we were required to get. If you look at it, it is essentially, manipulation, appropriate manipulation of the mathematical relationships to get whatever we needed. This is still in terms of dow S dow P at constant T and this is not completely in terms of easily measurable variables, but using the relationship between dow S dow P at constant T, that we had given in equation 2.35 earlier. You can look at equation 2.35, we have numbered that … yeah, dow S dow T at constant P as CP by T. We can write dow H dow P at constant T equals minus T dow V dow T at constant P plus V. This is the other relationship, which brings dow S dow P at constant T in terms of V, T and P. We will call this equation 2.37. That completes the solution.

Now, let us look at some of the other variables, which are somewhat easily measurable and more importantly, for which data is available in terms of tables and figures in various sources, including the appendices of your textbook Smith, VanNesss and Abbott.

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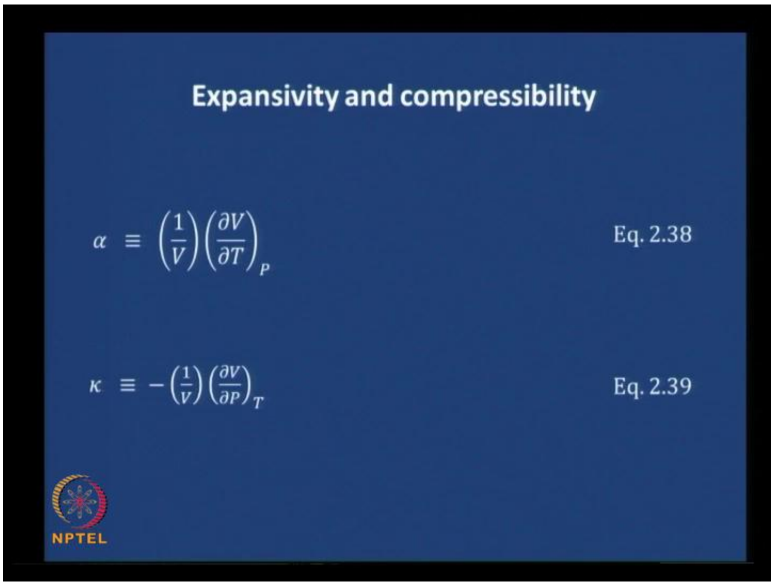

Expansivity and compressibility

$$\alpha \equiv \left(\frac{1}{V}\right)\left(\frac{\partial V}{\partial T}\right)_P \qquad \text{Eq. 2.38}$$

$$\kappa \equiv -\left(\frac{1}{V}\right)\left(\frac{\partial V}{\partial P}\right)_T \qquad \text{Eq. 2.39}$$

We are going to look at two things, expansivity and compressibility. Once we have some values associated with these, that gives us an easier way of relating things to unknown aspects. Expansivity is defined as 1 by V dow V dow T at constant P, … that is the definition of alpha, the variation of volume with time or specific volume with time at constant pressure … which is normalized with respect to the volume itself … the specific volume itself. Let us call that equation 2.38.

And compressibility, which is given the symbol kappa, is defined as dow V dow P at constant T, the variation of specific volume with pressure when the temperature is held constant and that again normalized with respect to specific volume – the negative of it. Let us call this equation 2.39.

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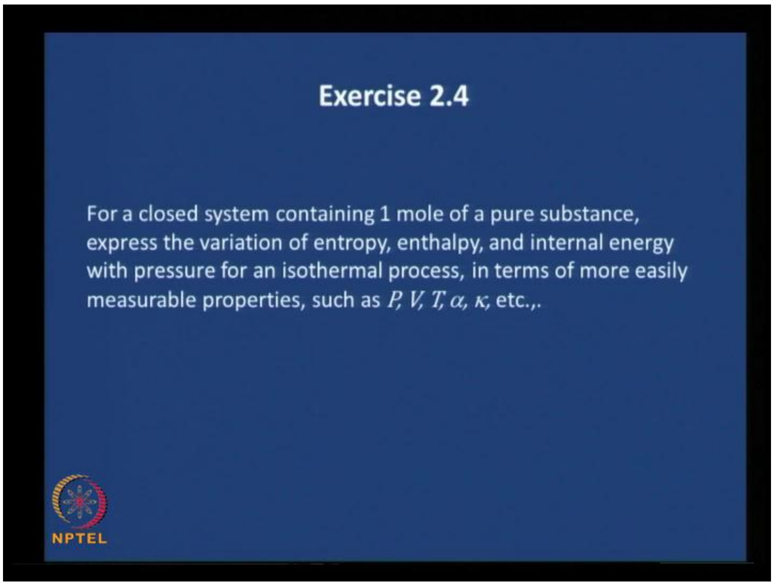

Exercise 2.4

For a closed system containing 1 mole of a pure substance, express the variation of entropy, enthalpy, and internal energy with pressure for an isothermal process, in terms of more easily measurable properties, such as P, V, T, α, κ, etc.,.

So, with these two definitions it is much easier to get a feel of these … of the use of these definitions, alpha and kappa, … expansivity and compressibility. If we work out an example or an exercise, that is exercise 2.4 here: For a closed system containing 1 mole of a pure substance, express the variation of entropy, enthalpy and internal energy – these three are somewhat more difficult to measure – the variation of these with pressure, for an isothermal process, in terms of more easily measurable properties, such as, pressure, volume, temperature, alpha, kappa – expansivity, compressibility, etcetera. Note, that this is an isothermal process and therefore, the temperature is held constant there. This will take some thinking, so take about 15 to 20 minutes or so to work out this problem and probably, after about 10 minutes, I will give you a part of the solution to help you in further solution; go ahead.

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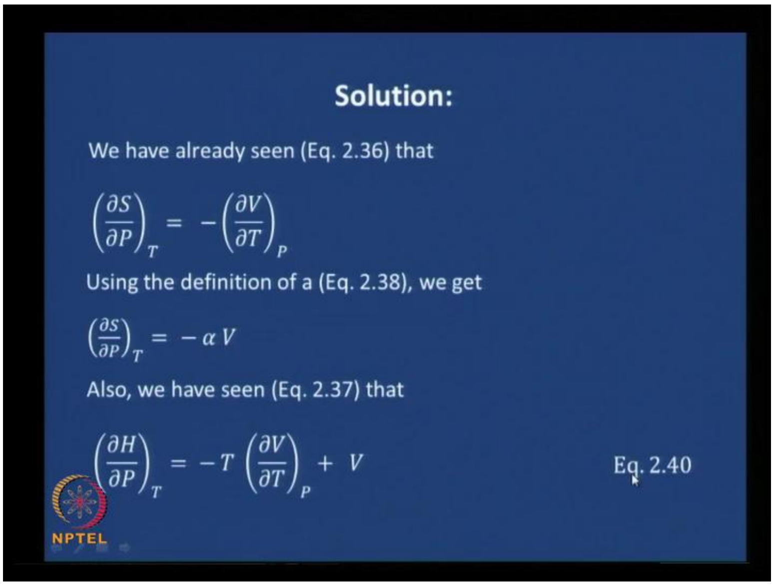

Solution:

We have already seen (Eq. 2.36) that

$$\left(\frac{\partial S}{\partial P}\right)_T = -\left(\frac{\partial V}{\partial T}\right)_P$$

Using the definition of a (Eq. 2.38), we get

$$\left(\frac{\partial S}{\partial P}\right)_T = -\alpha V$$

Also, we have seen (Eq. 2.37) that

$$\left(\frac{\partial H}{\partial P}\right)_T = -T\left(\frac{\partial V}{\partial T}\right)_P + V \qquad \text{Eq. 2.40}$$

Let us look at the part of the solution now. We have already seen – if you go back and look at equation 2.36, that dow S dow P at constant T is minus dow V dow T at constant P. And using the definition of alpha, which was given in equation 2.38, alpha, 1 by V dow V dow T at constant P, we get dow S dow P at constant T, the left hand side, is nothing but alpha times V, this is dow V dow T at constant P. And we saw what alpha was. So, this right hand side becomes alpha times V with the minus sign from here.

Also, we have seen from that equation 2.37, dow H dow P at constant T equals minus T dow V dow T at constant P plus V. Let me call this equation 2.40. I have started you on this process. So, take some more time to see, whether you can build up on this, develop on this and get the internal energy, enthalpy and entropy in terms of easily measurable or variables for which data is available, such as, P, V, T, alpha and kappa. Go ahead please.

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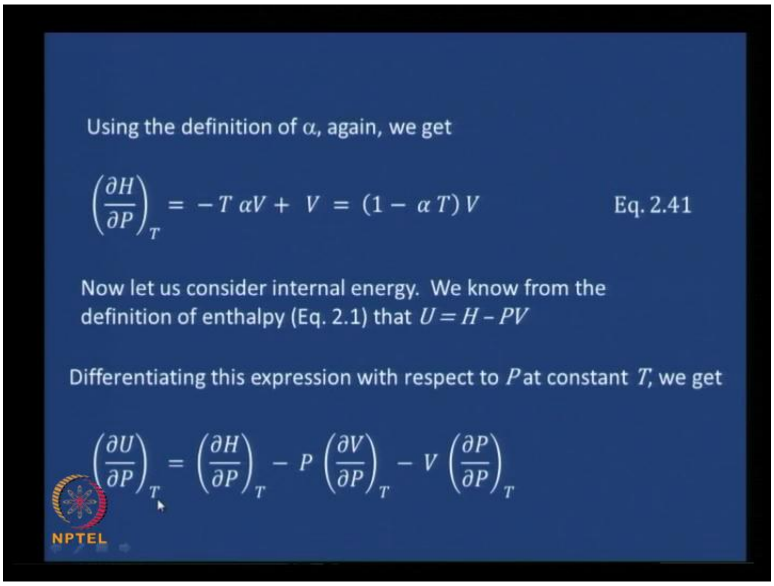

Using the definition of α, again, we get

$$\left(\frac{\partial H}{\partial P}\right)_T = -T\,\alpha V + V = (1-\alpha T)\,V \qquad \text{Eq. 2.41}$$

Now let us consider internal energy. We know from the definition of enthalpy (Eq. 2.1) that $U = H - PV$

Differentiating this expression with respect to P at constant T, we get

$$\left(\frac{\partial U}{\partial P}\right)_T = \left(\frac{\partial H}{\partial P}\right)_T - P\left(\frac{\partial V}{\partial P}\right)_T - V\left(\frac{\partial P}{\partial P}\right)_T$$

Let us look at the remainder of the solution. Using the definition of alpha again by 1 by V dow V dow T at constant P, we can write the dow H dow P at constant T in the previous equation as minus T alpha V plus V. You can see this here, minus T alpha V plus V. And if you factorize a V out, you can write this as 1 minus alpha T the whole into V. Let us call this equation 2.41. So, this takes care of the variation of enthalpy with respect to pressure in an isothermal process, the constant temperature process in terms of alpha, T and V, very nicely.

Now, let us consider internal energy. We all know, that definition of enthalpy, which is internal energy plus PV, you can write U, internal energy, equals H, enthalpy, minus PV. And now, if you differentiate this expression with respect to P at constant T – note that we are looking for dow U dow P at constant T, and that is what we get by doing this. dow U dow P at constant T equals dow H dow P at … constant T minus, this is by chain rule, P dow V dow P at constant T minus V dow P dow P at constant T, 1st function into the derivative of the 2nd function plus the 2nd function into derivative of the 1st function. Of course, there is a minus here. All this done at constant T.

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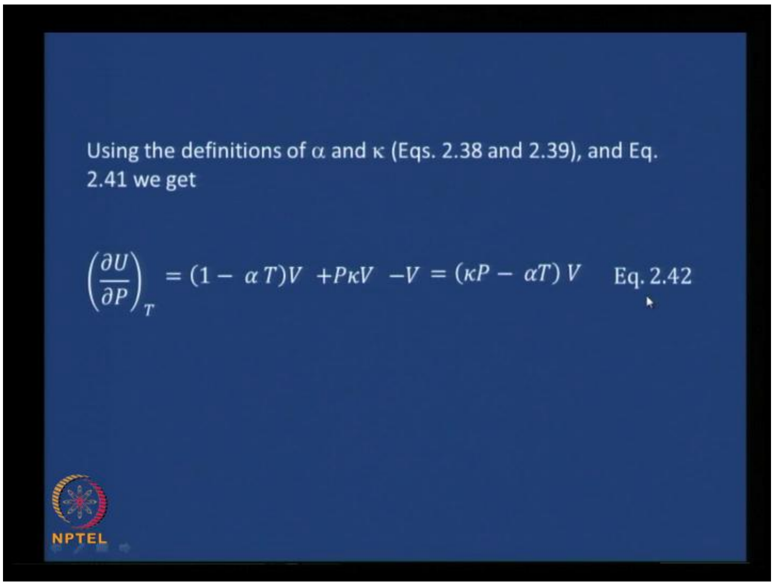

Using the definitions of α and κ (Eqs. 2.38 and 2.39), and Eq. 2.41 we get

$$\left(\frac{\partial U}{\partial P}\right)_T = (1-\alpha T)V + P\kappa V - V = (\kappa P - \alpha T)V \quad \text{Eq. 2.42}$$

Now, if you use definitions of alpha and kappa, we can write dow U dow P at constant T; and we have already seen what the 1st one was, 1 minus alpha T into V. This dow H dow P at constant T is 1 minus alpha T into V. And, this P dow V dow P at constant T is nothing but related to the definition of kappa and this of course, is 1. So, we do not have to worry too much about that, therefore you get dow U dow P at constant T is 1 minus alpha T into V plus P kappa V minus V. And V common out, you get kappa P minus alpha T into V. So, all this is in terms of kappa, P, alpha, T, and the specific volume – all of which are measurable. Let us call this equation 2.42.

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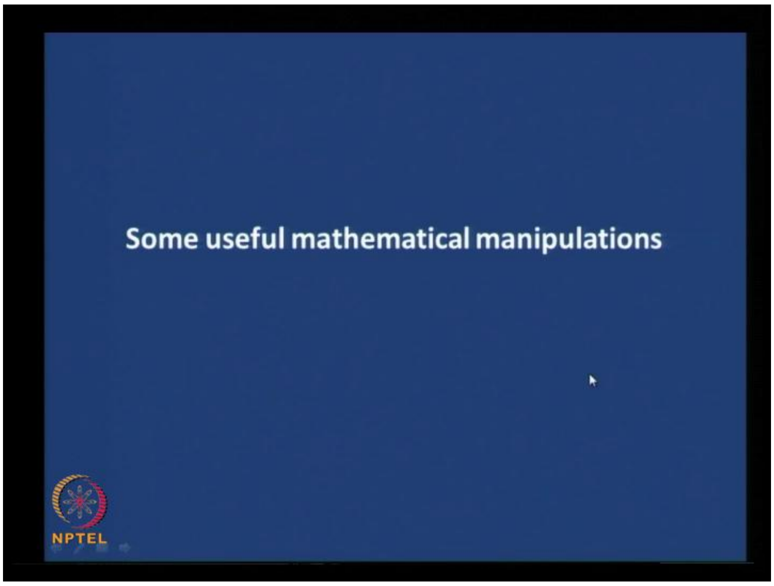

Some useful mathematical manipulations

So, that completes the relationships, that we had needed in the previous problem and what we are going to see next is some more useful mathematical manipulations from the point of view of a classical thermodynamics applied to biological systems. There are of course many, I have chosen probably, the most used ones to give you a flavor, so that you will feel comfortable whenever there is a need to apply these mathematical relationships. We will continue in the next class.