# Thermodynamics for Biological Systems:
# Classical and Statistical Aspects

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## Lecture - 10
## Inter-Relationships Between Thermodynamic Variables

Welcome!

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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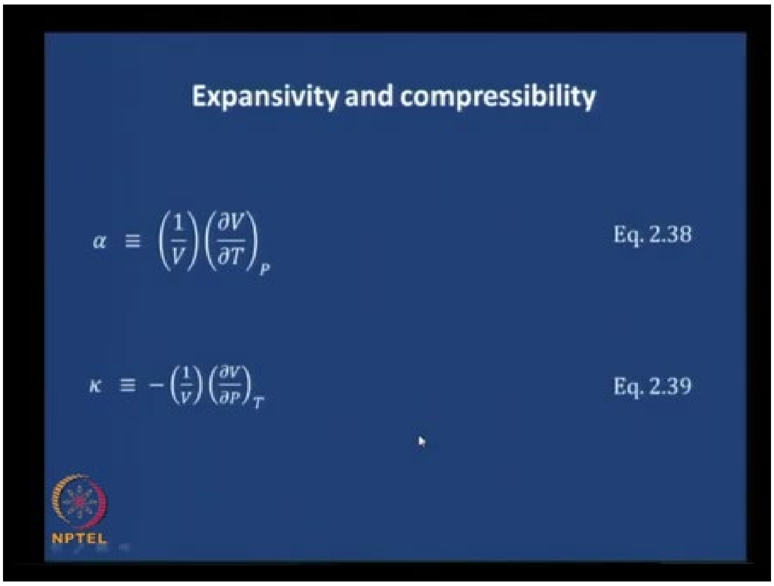

Expansivity and compressibility

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

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

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

$$\alpha \equiv \left(\frac{1}{V}\right)\left(\frac{\partial V}{\partial T}\right)_P$$

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

$$\kappa \equiv -\left(\frac{1}{V}\right)\left(\frac{\partial V}{\partial P}\right)_T$$

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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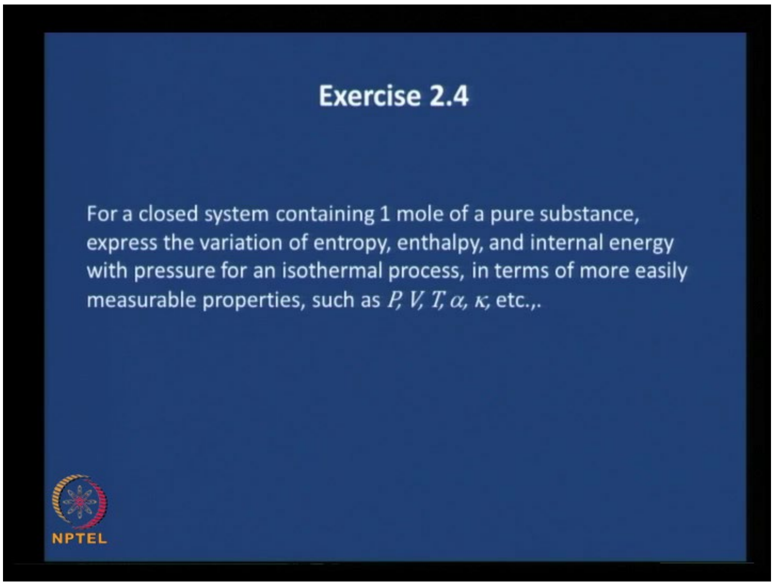

### Exercise 2.4

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 $P$, $V$, $T$, $\alpha$, $\kappa$, 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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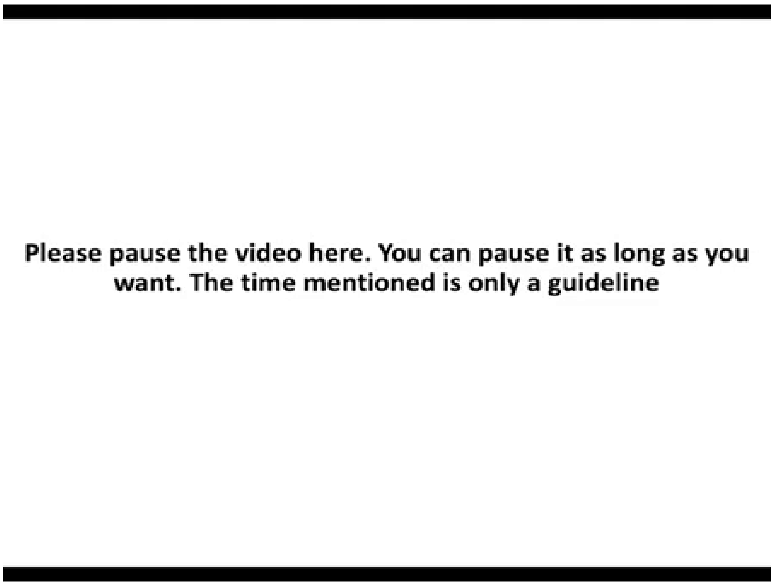

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Let us look at the part of the solution now. We have already seen – if you go back and look at equation 2.36,

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

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

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

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,

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

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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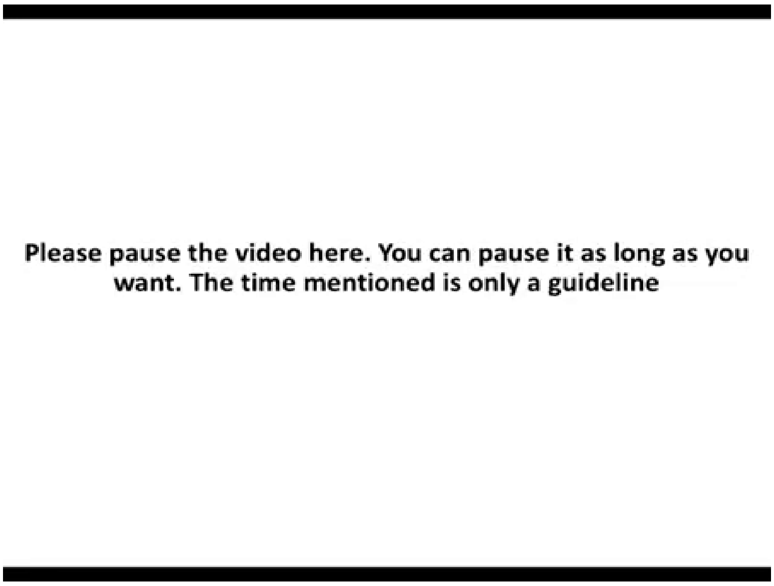

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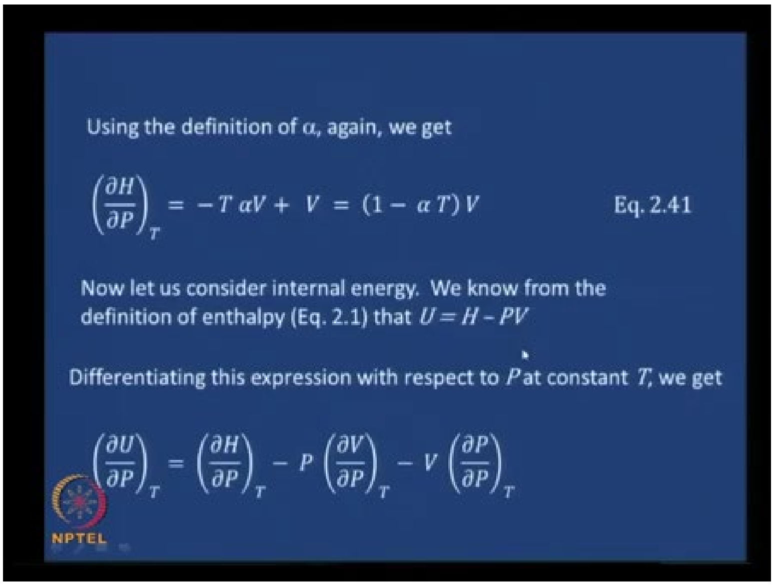

Using the definition of $\alpha$, again, we get

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

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

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

Let us call this equation 2.41.

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

$U = H - PV$

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.

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

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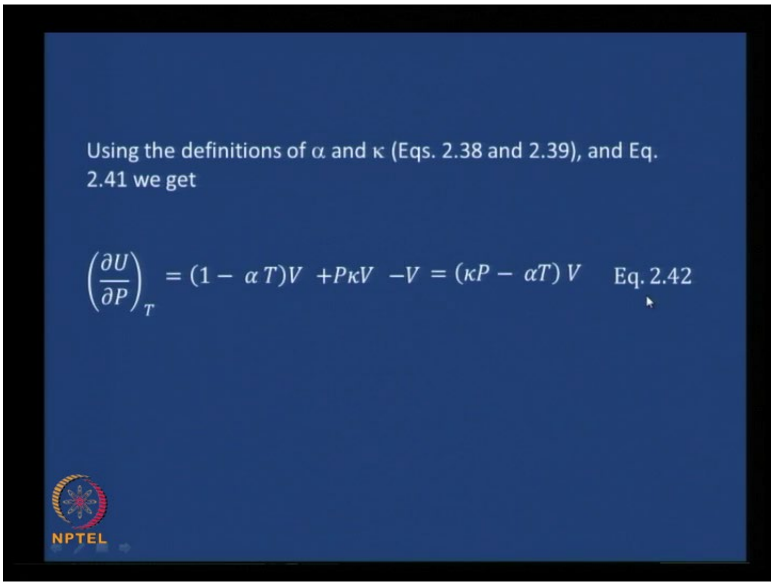

Using the definitions of $\alpha$ and $\kappa$ (Eqs. 2.38 and 2.39), and Eq. 2.41 we get

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

Now, if you use definitions of alpha and kappa, we can write

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

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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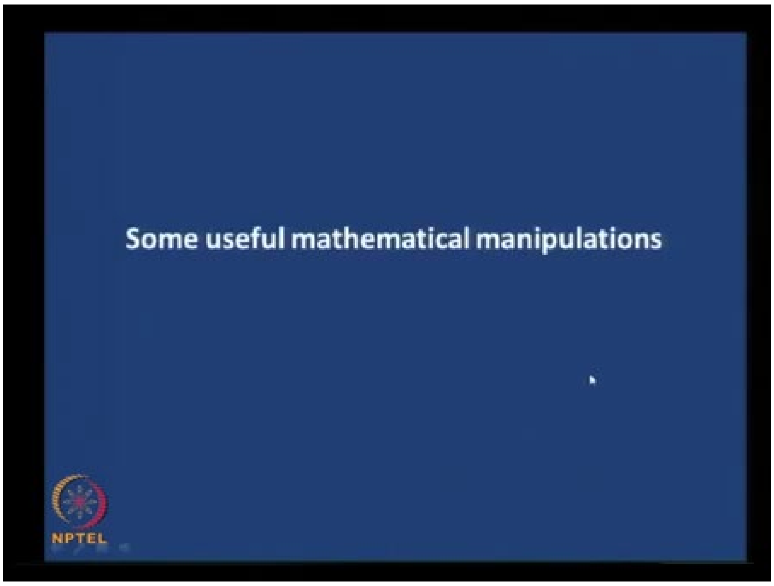

Some useful mathematical manipulations

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.