Thermodynamics for Biological Systems: Classical and Statistical Aspects

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Lecture – 11
Some Useful Mathematical Manipulations

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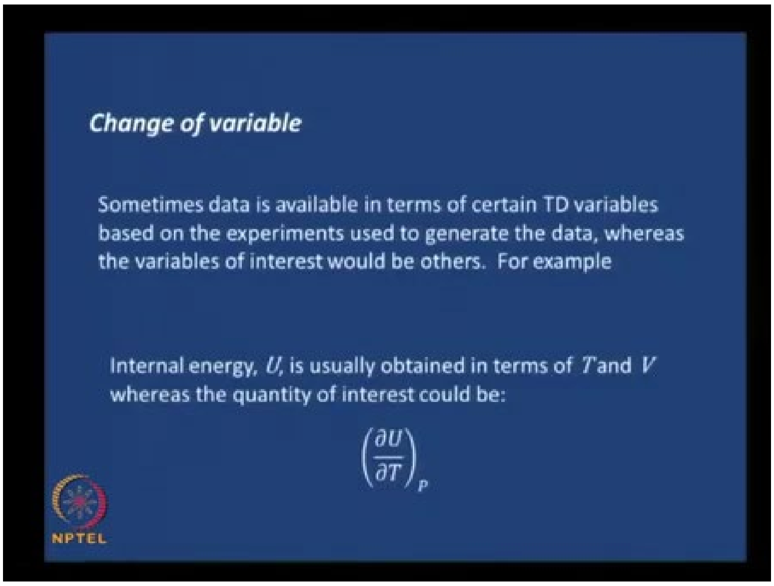

Welcome!

In the last class, we ended when we started looking at some useful mathematical manipulations.

We introduced the change of variable manipulation. We said that sometimes we would have data in terms of variables, and what is needed, the quantity that is needed, could be in terms of other variables. Whether we could use mathematical manipulations to represent data that is available in one way, in terms of what we need is whatever we are going to look at.

The example that we started out with was internal energy. We said, it was usually obtained in terms of its variation with temperature at constant volume, whereas the quantity of interest could be internal energy variation with temperature at constant pressure.

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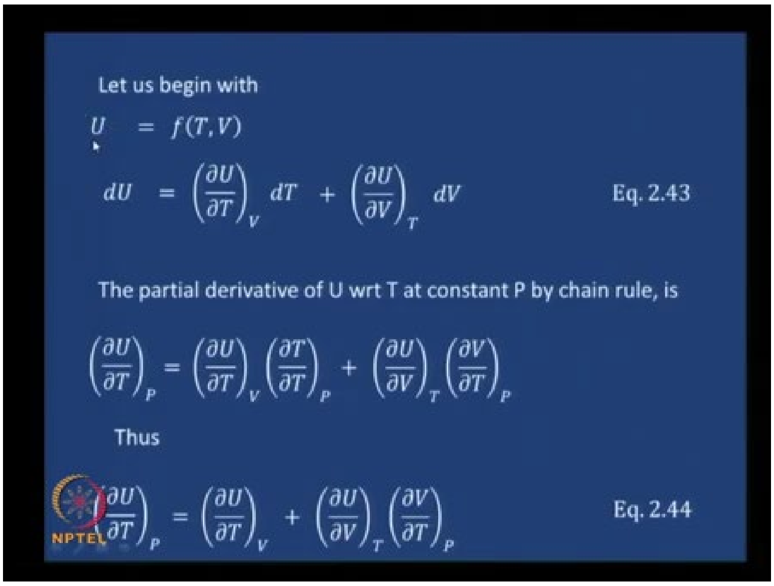


To look at that, let us begin with internal energy as a function of temperature and volume, this is how we have our data. The total differential dU, as you all know, can be written as

$$dU = \left(\frac{\partial U}{\partial T}\right)_V dT + \left(\frac{\partial U}{\partial V}\right)_T dV$$

We will call this equation 2.43.

Now, if we take the partial derivative of U with respect to T at constant P, then by using the chain rule, we have

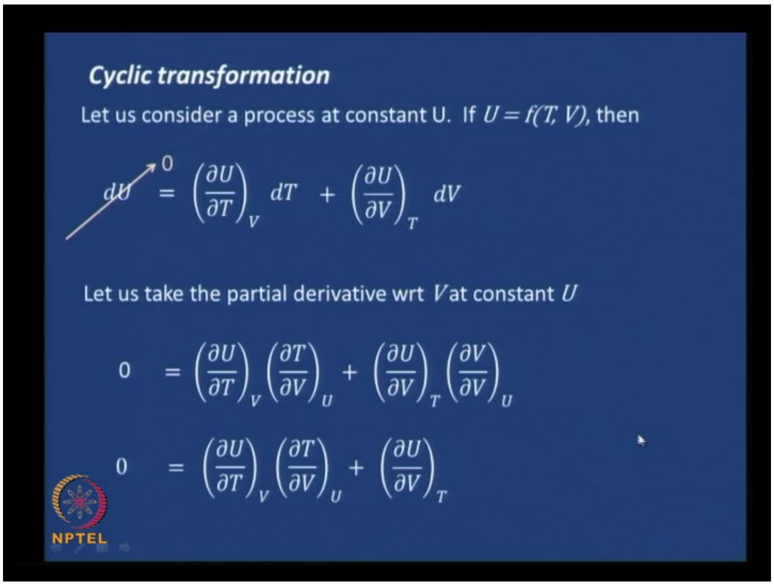
$$\left(\frac{\partial U}{\partial T}\right)_P = \left(\frac{\partial U}{\partial T}\right)_V \left(\frac{\partial T}{\partial T}\right)_P + \left(\frac{\partial U}{\partial V}\right)_T \left(\frac{\partial V}{\partial T}\right)_P$$

You can all see, that $\left(\frac{\partial T}{\partial T}\right)_P$ goes to 1, therefore

$$\left(\frac{\partial U}{\partial T}\right)_P = \left(\frac{\partial U}{\partial T}\right)_V + \left(\frac{\partial U}{\partial V}\right)_T \left(\frac{\partial V}{\partial T}\right)_P$$

equation 2.44.

And now, we the variation of U with temperature at constant pressure, which is what we need, starting with data, that gave us a U as a variation of temperature with constant volume.



The next mathematical manipulation that we are going to look at, which will again, turn out to be very useful, is called cyclic transformation. To know what cyclic transformation is, to get an idea what cyclic transformation is, let us consider a process at constant internal energy. And, if we write U, internal energy, as a function of T and V, then we are all very familiar with this expansion now. The total differential dU, when it is a function of T and V,

$$dU = \left(\frac{\partial U}{\partial T}\right)_V dT + \left(\frac{\partial U}{\partial V}\right)_T dV$$

Note that this is a process at constant U and therefore, the total differential is going to go to 0. Let us just consider that for the time being for our manipulations. Now, if we take the partial derivative of V … with respect to V at constant U, then

$$0 = \left(\frac{\partial U}{\partial T}\right)_V \left(\frac{\partial T}{\partial V}\right)_U + \left(\frac{\partial U}{\partial V}\right)_T \left(\frac{\partial V}{\partial V}\right)_U$$

Note, that we are taking the derivative with respect to V at constant U. Plus dow U dow V at constant T dow V dow V at constant U. This of course, goes to 1. So that can be written as

$$0 = \left(\frac{\partial U}{\partial T}\right)_V \left(\frac{\partial T}{\partial V}\right)_U + \left(\frac{\partial U}{\partial V}\right)_T$$

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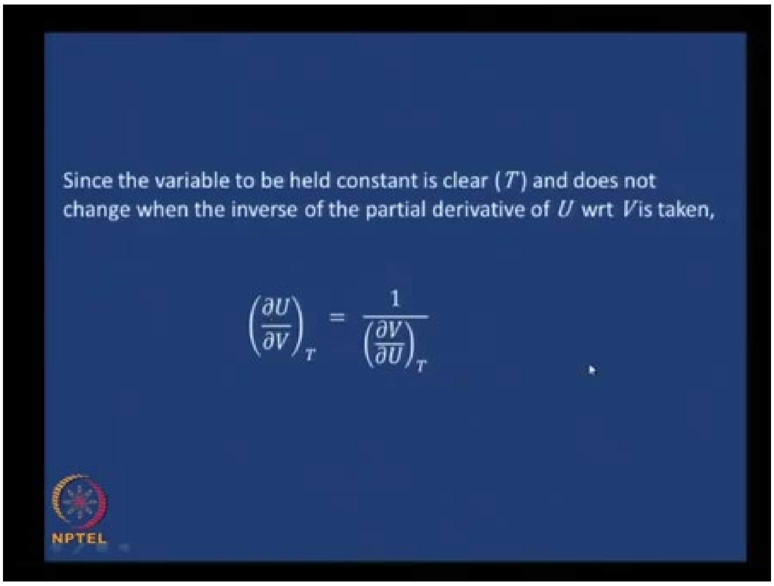

Now, note this. This is a partial derivative and when you take a partial derivative, some other variables are retained constant. When the variable to be retained constant is very clear and it does not change when you take the inverse, then you can write,

$$\left(\frac{\partial U}{\partial V}\right)_T = \frac{1}{\left(\frac{\partial V}{\partial U}\right)_T}$$

Note, that this is not always true in calculus. This is true only in the special case when we are very clear, that the variable to be held constant remains the same, whether we consider this or the inverse dow V dow U at constant T – not exactly an inverse, it is the variation of the function with respect to a certain variable – that is the way to look at it; just happens to resemble an inverse.

Now, that we have noted this, we will replace the left hand side. To tell you a little more clearly, this was the 2nd term on the right hand side to begin with, of the expression that we gave earlier. Now, this is the term that we are considering now. If you subtract the same term from both sides, we will get minus dow U dow V at constant T here and it will vanish from here.

$$\frac{-1}{\left(\frac{\partial V}{\partial U}\right)_T} = \left(\frac{\partial U}{\partial T}\right)_V \left(\frac{\partial T}{\partial V}\right)_U$$

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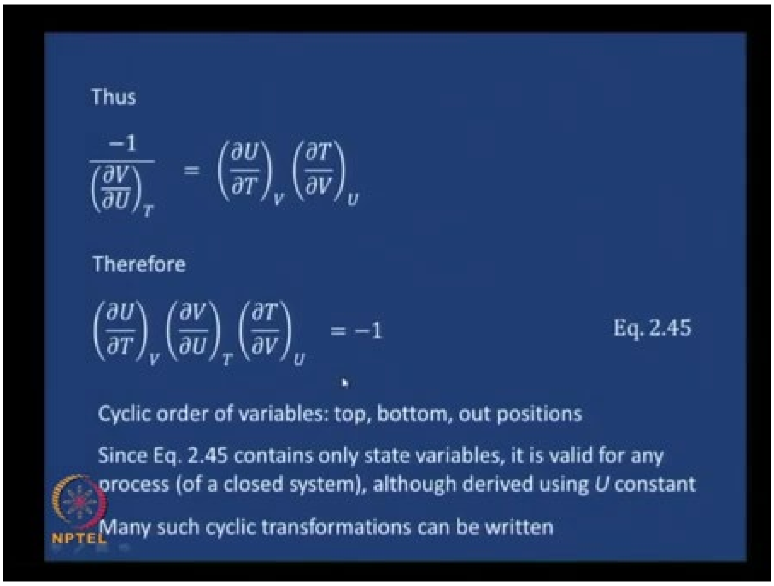

And, if we substitute the inverse,

$$\left(\frac{\partial U}{\partial T}\right)_V \left(\frac{\partial V}{\partial U}\right)_T \left(\frac{\partial T}{\partial V}\right)_U = -1$$

What I would like you to note … Of course, this is equal to minus 1, the other side, and we will call this equation 2.45. What I would like you to note is the ordering here, it is a cyclic order in terms of top, bottom and out. Whatever was in the top comes to the bottom in the next. Whatever was in the bottom, comes out. And whatever was out goes to the top. U, T, V – V goes to the top here; V, U comes to the bottom here; U, T goes out. T. And compared to this, if you look at this U, … sorry, … T goes to the top here, U comes out and V comes below. So, there is a cyclic order here of variables, top, bottom … in the top, bottom and out positions. And you can, … more importantly you should note, that all these are state variables.

Now, I would like you to recall our earlier analogy of a mountainous region. The difference in heights between the places, irrespective of the path taken, the difference in heights is going to be the same since height is a state variable and so on. Recall that and apply that thought here. Why I would like you to apply that thought? Because we started deriving this equation by assuming a constant U process, but we ended up with an expression or an equation in terms of only the state variables U, T and V. And since this equation is in terms of only the state variables, this is applicable to whatever process, that the system undergoes. And therefore, this can be taken as a generalized equation. Formally said here: since 2.45 contains only state variables, it is valid for any process of a closed system; we are considering only closed systems now, although derived using U to be constant.

And this is not the only cyclic transformation that can be written. We can write cyclic transformations for many different sets of variables. It can be easily proved, … as you will do yourself in the example that is going to follow.

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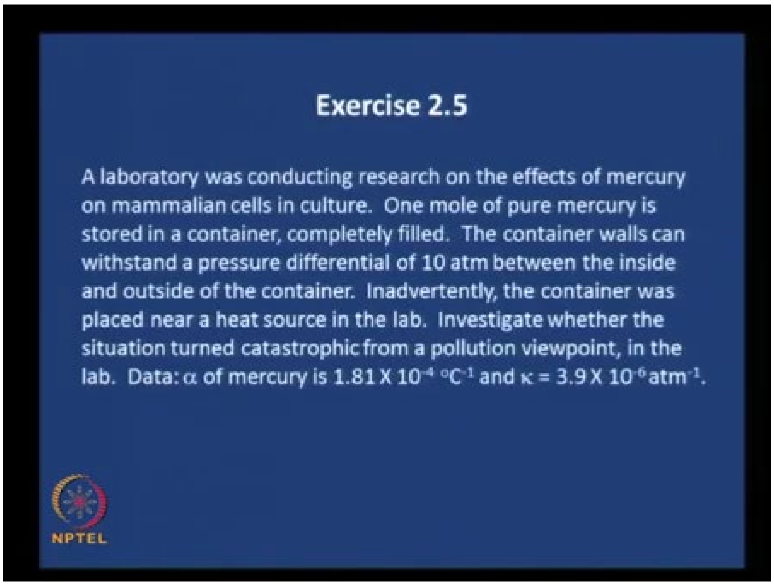

The example or the exercise is exercise 2.5. As I mentioned, as we have been doing in this course, I will present the exercise, then I will give you time to work that out. Then I will present you a part of the solution and then give you more time to work it out, and then present the complete solution.

The exercise is this - a laboratory was conducting a research on the effects of mercury on mammalian cells in culture, a very typical experiment. One mole of pure mercury is stored in a container, completely filled. The container walls can withstand a pressure differential of 10 atmospheres between the inside and the outside of the container. Inadvertently, the container was placed near the heat source in the lab, which happens often in the lab – you should be careful. Investigate whether the situation turned catastrophic from a pollution view point in the lab. What is meant by this is … when mercury spills out, that is … that can cause big pollution, and … catastrophic pollution.

You would have heard of the Minamata bay disorder … Minamata bay disaster and so on and so forth, where fishes in Japan were poisoned with mercury. So, this is, from that angle you need to check whether there was a spill of mercury. In other words, whether the container exploded. To do that, some data that may be helpful, if at all you take that root, is that the expansivity alpha is the thermal expansivity of mercury, is 1.81 into 10 to the power minus 4 atmospheres, and compressibility kappa is 3.9 into 10 to the power minus 6 degree C. Please go ahead and work it out, please take about 10 minutes to begin with before I present the solution

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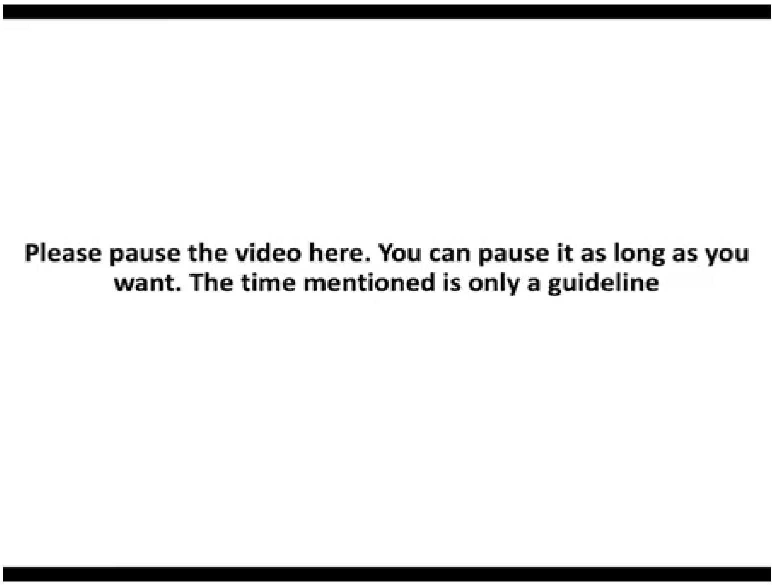

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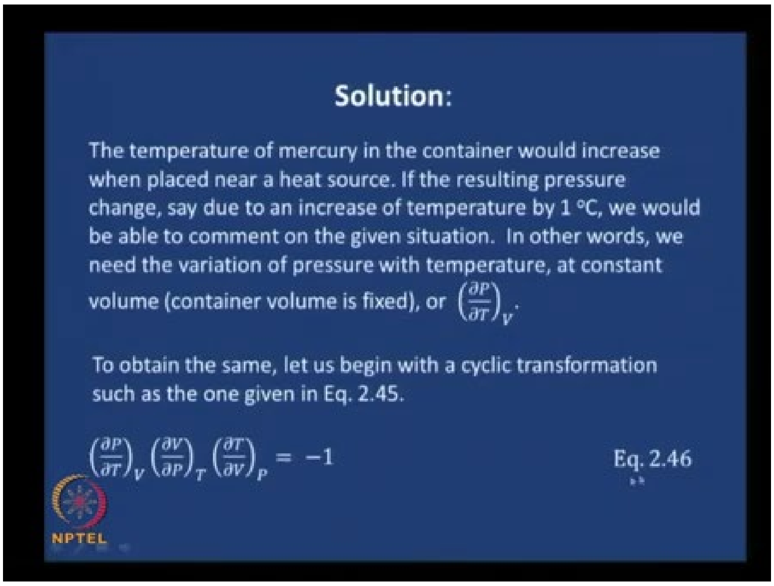

Let me present a part of the solution. This is the thinking that was partly mentioned in the exercise itself. The temperature of mercury in the container would increase when placed near a heat source. If the resulting pressure change, say, due to an increase in temperature by 1 degree C … we would be able to comment on the given situation. If we know about that – if the pressure is going to exceed the pressure that the vessel can withstand, there is going to be an explosion, or there is going to be disruption of the vessel and therefore, spillage of mercury into the lab.

In other words, look at this, this is what we need. We need the variation of pressure with temperature. We said we would like to know the pressure change … resulting pressure change due to an increase of temperature by 1 degree C. And, in terms of mathematics, we need to know the variation of pressure with temperature at constant volume

$$\left(\frac{\partial P}{\partial T}\right)_V$$

This is the first thing you need to recognize.

Let me go a little further before you can work things out or … you take time to work things out. This is what we need, dow P dow T at constant V, and to obtain this we would like to begin with the cyclic transformation, such as one given in 2.45, that was a slightly different cyclic transformation. The one that is needed to get this would be different.

Let us start with this.

$$\left(\frac{\partial P}{\partial T}\right)_V \left(\frac{\partial V}{\partial P}\right)_T \left(\frac{\partial T}{\partial V}\right)_P = -1$$

We will call this equation 2.46, but I do not want you to take this on face value as I give you here.

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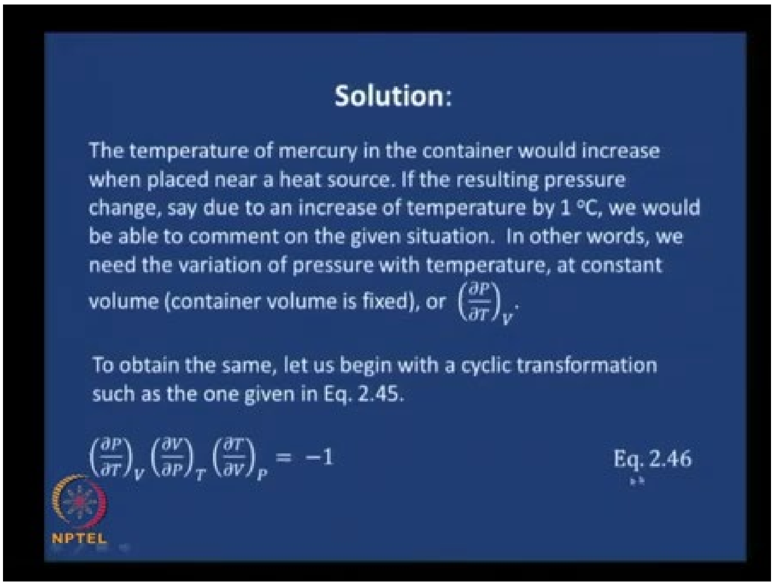

I am going to give you some extra time to go on the side of this problem. You know this equation 2.46, that we mentioned here can be obtained in the same way as equation 2.45, by starting with pressure as a function of temperature and volume considering a constant pressure process and taking the partial derivative with respect to V.

What I am going to do now is … although I say here as a separate exercise, you take time now and work things out; it will be good to have a complete package there. So, I am going to give you another 10 minutes. Before you can go on the side, I would like you to get or derive this expression 2.46,

$$\left(\frac{\partial P}{\partial T}\right)_V \left(\frac{\partial V}{\partial P}\right)_T \left(\frac{\partial T}{\partial V}\right)_P = -1$$

Please go ahead and do this please take about 10 minutes for this.

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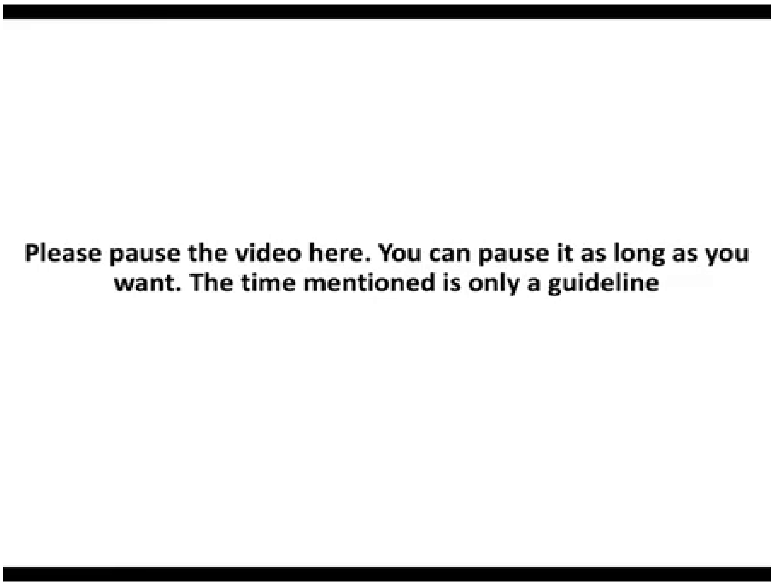

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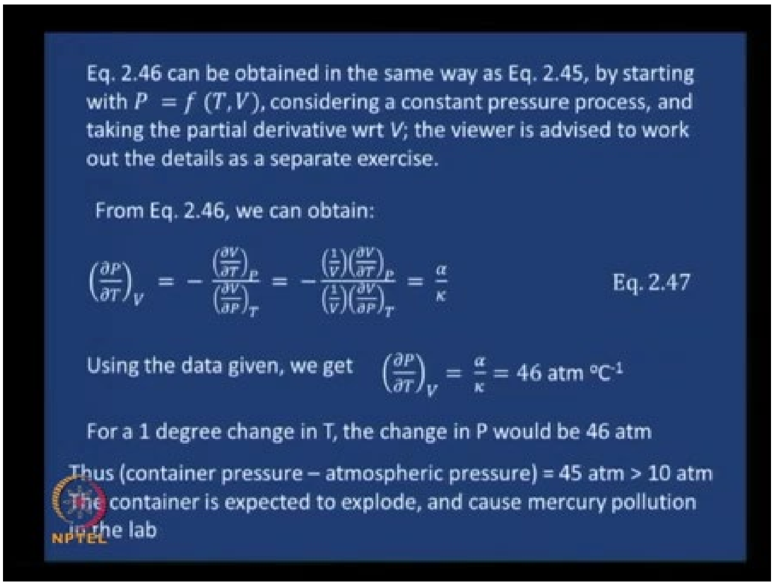

Now, you would have derived this expression. If you are unable to derive you can, of course, ask for help. Now, that we have this expression, we can write this, you know …, starting with

$$\left(\frac{\partial P}{\partial T}\right)_V \left(\frac{\partial V}{\partial P}\right)_T \left(\frac{\partial T}{\partial V}\right)_P = -1$$

What we need is this, which is the first term. This can be written as … this can be represented by transposing this particular equation in terms of these three quantities, and if we do that, we will have

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

In this case we have taken the inverse because we know the variable that is held constant.

If you want you can go back to equation 2.46 in the previous slide and see how this thing comes about in some detail.

Now, can you substitute the values in, let us say, in 2 minutes and see what value of $\left(\frac{\partial P}{\partial T}\right)_V$ you get and how would you interpret it. Take about 2 minutes and then I will present the solution and that, with that we will end this class.

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You have had time to work things out. Alpha and kappa are already given in the problem statement; the data is already given. If we substitute here,

$$\left(\frac{\partial P}{\partial T}\right)_V = \frac{\alpha}{\kappa} = 46 \text{ atm } {}^{o}C^{-1}$$

Now what is this? Dow P dow T at constant V. In other words, with this we have a change in pressure for a unit change in temperature. So, if the change in temperature is 1 degree, then the change in pressure would be 46 atmospheres. And what the container can withstand is only 10 atmospheres. Or the container pressure minus atmospheric pressure is 46 minus 1, that is, 45; atmospheric pressure is 1 atmosphere. That is 45 atmospheres. It is much greater than the 10 atmospheres that the container can withstand. And therefore, the container can be expected to explode and cause mercury pollution in the lab.

I would like you to go back and see the thinking. There was a real life situation, that was given. And we converted that into some sort of a mathematical model, if you will; in terms of mathematical expressions and then, we could use the data that was available to come up with some useful or relevant information. We would know the dangers that are posed by keeping the container of mercury near a heat source. And if you know this, probably we would not do that.

We will continue in the next class.