Thermodynamics for Biological Systems:
Classical and Statistical Aspects
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Lecture - 5
State and Path Variable

Welcome!

Let us first consider a single component system, which is also in a single phase. For simplicity. Let us … go step by step. Single component for example, H_2O, and let us say that it is completely in the liquid phase; the temperature pressure combinations are such that it is completely in the liquid phase. And that is an example of a single component, single phase system.

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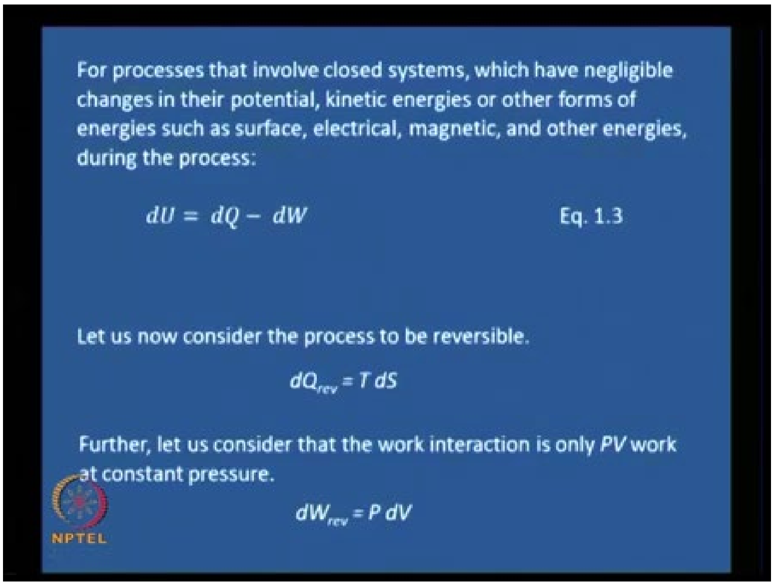

For processes that involve closed systems, which have negligible changes in their potential, kinetic energies or other forms of energies such as surface, electrical, magnetic, and other energies, during the process:

$$dU = dQ - dW \qquad \text{Eq. 1.3}$$

Let us now consider the process to be reversible.

$$dQ_{rev} = T\,dS$$

Further, let us consider that the work interaction is only *PV* work at constant pressure.

$$dW_{rev} = P\,dV$$

For processes that involve closed systems, which have negligible changes in the other types of energies such as potential energy, kinetic energy, surface energy, electrical energy, magnetic energy and many other types of energies. Or in other words, there is only … some types of energies that are relevant here; the other things are not relevant. During such a process,

$$dU = dQ - dW$$

from first law. Recall the first law for a closed system. And this is nothing but the differential form of the first law: the total differential of U equals the total differential of Q minus the total differential of W. Recall that dQ …Q is nothing but the heat interaction across the system boundary, W is the work interaction across a system boundary.

Now let us consider the process to be reversible. We all know what the concept of reversible process is. If the process is reversible, from the second law, we know that

$$dQ_{rev} = T\,dS$$

Recall that dS equals $dQ_{\text{reversible}}$ by T; from that we get dQ equals T dS … $dQ_{\text{reversible}}$ equals T dS. Now, let us further consider that the work interaction is only PV work at constant pressure. Earlier we said that there are no other kinds of energies that are relevant, and then we considered the process reversible, and then now we are looking at only PV work. If it is only PV work we know from earlier classes that dW, the work term $dW_{\text{reversible}}$ is

$$dW_{rev} = P\,dV$$

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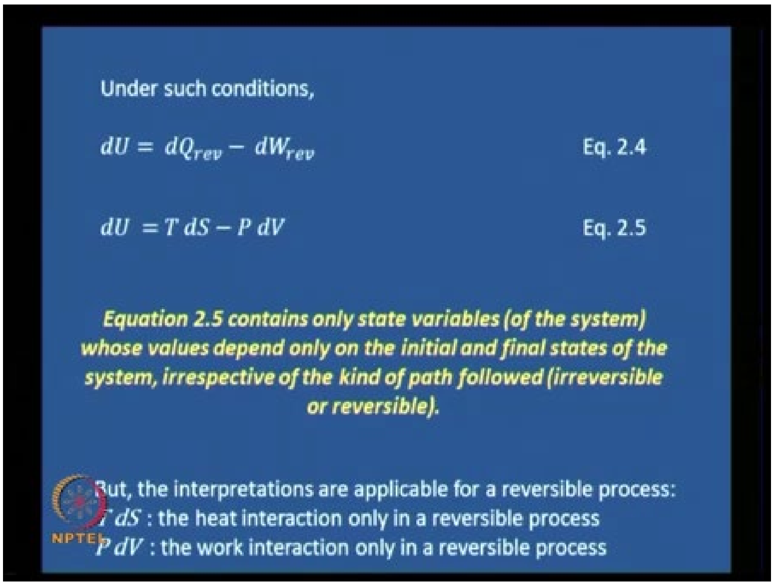

Under such conditions,

$$dU = dQ_{rev} - dW_{rev} \qquad \text{Eq. 2.4}$$

$$dU = T\,dS - P\,dV \qquad \text{Eq. 2.5}$$

Equation 2.5 contains only state variables (of the system) whose values depend only on the initial and final states of the system, irrespective of the kind of path followed (irreversible or reversible).

But, the interpretations are applicable for a reversible process:

$T\,dS$: the heat interaction only in a reversible process

$P\,dV$: the work interaction only in a reversible process

Now let us put this all together, we can write under such conditions

$$dU = dQ_{rev} - dW_{rev}$$

by just substituting the terms into the first law. Looking at whatever we did earlier $dQ_{\text{reversible}}$ was nothing but T dS, and $dW_{\text{reversible}}$ in our particular case right now is nothing but P dV. Therefore, dU equals T dS minus P dV. And, please play a little bit of attention to this; this is the very important and a useful idea/concept … whatever you want to call it. If you look at equation 2.5,

$$dU = T\,dS - P\,dV$$

It contains all state variables. What does it contain? It contains internal energy, which is a state variable temperature is of course, a state variable; entropy is a state variable; pressure is a state variable; and specific volume is a state variable.

We know that the values of the state variable depend only on the initial and final states of the system in a process. The value of a state variable depends only on the state; and when the system undergoes the process the value of the … of such thermodynamic variables are dependent only on the initial state and final state of the system, irrespective of the path that was followed to traverse the path between points 1 and 2 or states 1 and 2. Therefore, whether it was a reversible process or not, does not matter as long as the applicability of this equation 2.5 goes. Or, irrespective of the kind of path that is followed, whether it is an irreversible path or a reversible path, this equation 2.5 is valid.

I will strengthen this thought a little bit further, because this is a concept that we use again and again; and this is the very powerful kind of a concept to come up with useful relationships.

Nevertheless the interpretations of the various terms, you know that T dS as a heat interaction, and P dV as the work interaction, these are all applicable only for the kind of process, because these are path functions. T dS is the heat interaction only in a reversible process and P dV is the work interaction only in a reversible process. Whereas, this equation 2.5, dU equals T dS minus P dV is applicable irrespective of the type of process that the system undergoes.

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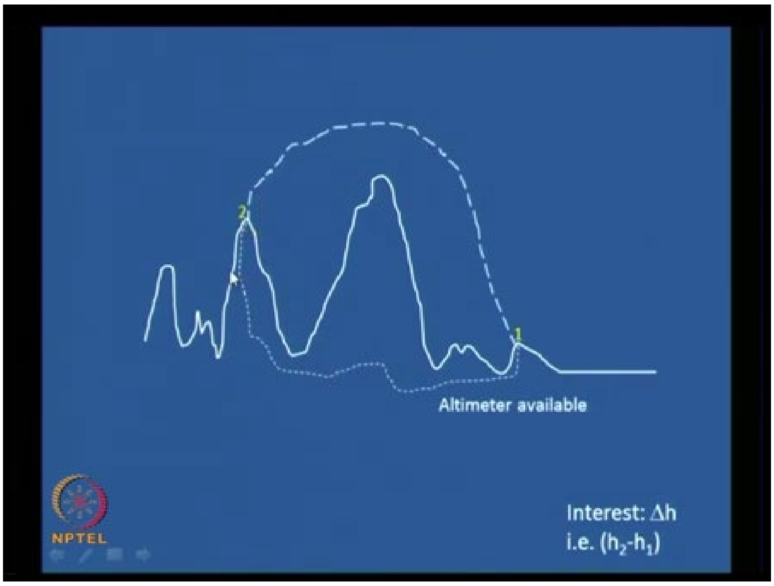

Interest: Δh
i.e. $(h_2 - h_1)$

To understand this a little further, let us consider a mountainous region; for example, let us consider the north eastern part of India, which is huge, which is a huge place, and highly mountainous. Let us say that … I have represented the mountainous region by this. Let us say that we are interested in a place given … denoted by point 1 here, and another place denoted by point 2 here. The way to get from point 1 to point 2 or place 1 to place 2 could be very many different ways. I can take the road that leads nicely, may be a well paved road between point 1 and point 2. I can take a hilly path somewhere here, which is not indicated to go from point 1 to point 2. I can even take a helicopter and fly or a plane and fly from point 1 to point 2; and there could be many other ways.

But let us say only in this particular way, shown by this dotted line here, we have an altimeter that is available to us. Let us say that there is an altimeter shop right at the beginning of that path, and that is not available; let us assume … not very realistic, but let us assume that the altimeter is not available in any of the other paths. If our interest is in finding out the difference in heights between point 1 and point 2, which is indicated by delta h, h_2 minus h_1. We know that an altimeter gives us heights. So, all we need to do is measure the heights here with the altimeter. Go through the path, and measure the height here.

Irrespective of the path in which an altimeter is available, whether that is taken or not or whether the other parts are taken or not, the difference in heights is going to remain the same. It is just that this particular path gives us an easy measure of the difference in heights. This is what one needs to understand, to understand the concept of getting things in terms of state variables. Once we get things in terms of the difference in heights, it does not really matter, which path we follow

– that would always remain the same. So, going back irrespective of the path that is followed as long as the relationship is in terms of the state variables, it does not really matter what path is experimentally taken to measure the various variables. As long as they are state variables, they would be valid.

See you in the next class.