Thermodynamics for Biological Systems:
Classical and Statistical Aspects
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Lecture – 13
Maximum Work

Welcome!

In this class, let us begin by considering maximum work as well as lost work. When we are considering a process, we would like to know, what is the maximum amount of work that can be expected from that process, for various reasons. It could be for designing the process or it could be for … may be evaluating the claims made by others toward the maximum work that is possible from a particular process. In the same vein, we would also like to know the amount of work that is lost. In other words, in comparison to the maximum work or the ideal work, what is the actual work that you are getting out of the system and in the process how much work is being lost compared to the maximum of work.

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To do that, let us start here. We have already seen that the change in entropy of the system plus the change in entropy of the surroundings is a positive quantity – let us call that d epsilon – way back in equation 1.6.

$$dS_{system} + dS_{surroundings} = d\epsilon$$

We also said that the entropy of the universe can only increase – that was one of the statements of the second law. Now let us consider these surroundings as a heat sink, as it is called, at a constant temperature T 0. This heat sink is a very useful concept; it actually refers to the bodies whose temperatures do not change despite the interactions with the systems that they are in contact with. For example, there are many things that can be considered as sinks or approximated as sinks; some of them are given here. We can consider the earth's atmosphere as a sink … it remains at a constant temperature for a certain period of time. Or, the earth's surface could also be considered as a suitable sink especially for biological systems of relevance.

Let me also state this; it may not be completely clear right now, but it will become clear may be after the fifth module or so. The heat sink is also supposed to be in a condition of internal equilibrium with no irreversible changes occurring inside it. This needs to be stated as one of the conditions of the heat sink. Let me state it again and leave it at that, and let us wait till the fifth chapter or fifth module to make a little better sense of it: The heat sink is supposed to be at a condition of internal equilibrium with no irreversible changes occurring inside it.

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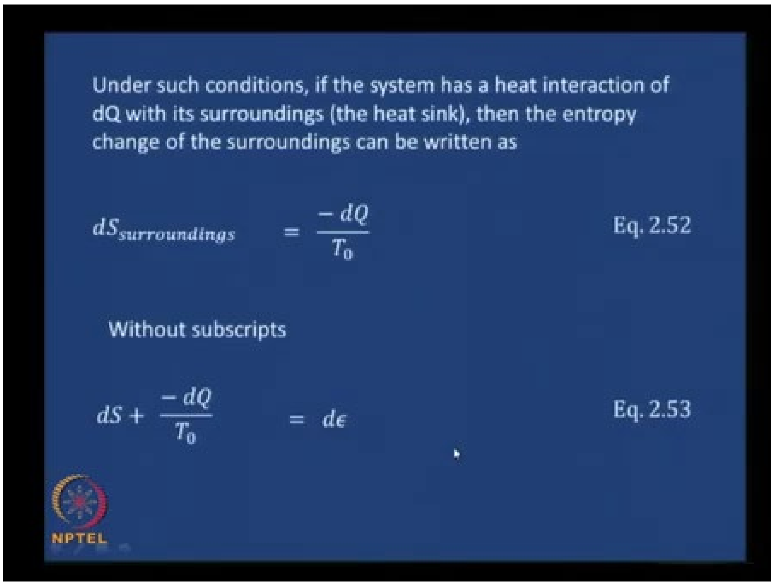

Under such conditions, if the system … has a heat interaction of dQ, a differential Q, with its surroundings, which is the heat sink in this case. The entropy change or the surroundings can be written as – remember the second law that we looked at earlier

$$dS_{surroundings} = \frac{-dQ}{T_0}$$

Minus because of the convention, the direction with which this negative is associated. Remember we are writing this for the surroundings; so, minus dQ by T 0. Let us call this equation 2.52. Since we have already identified dS surroundings as minus d q by T 0, we will drop the subscripts now just for convenience and d S will, as usual, correspond to the system. d S system plus d S surroundings, which is being replaced by minus d q by T 0 … is the same d epsilon;

$$dS + \frac{-dQ}{T_0} = d\epsilon$$

Let us call this equation 2.53.

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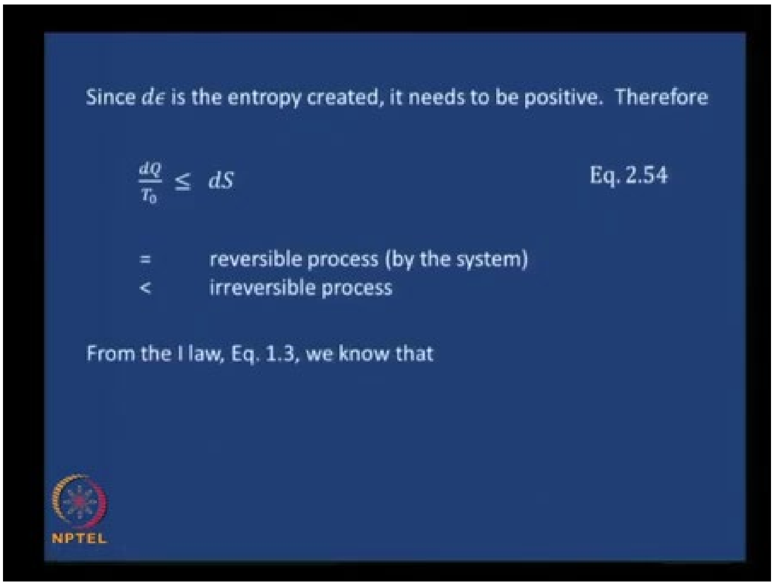

Remember, the d epsilon is the entropy that is created and according to the second law, expanding universe and so on, it definitely needs to be positive. Therefore,

$$\frac{dQ}{T_0} \leq dS$$

the d q by T 0 needs to be either less than or equal to d S. This directly follows from this equation … we are comparing this and this, this needs to be less than or equal to d S for this to be positive. We will call this equation 2.54. These are all very generic coming right from the second law. And this equals dS for a reversible process that is undergone by the system; and is less than dS for an irreversible process.

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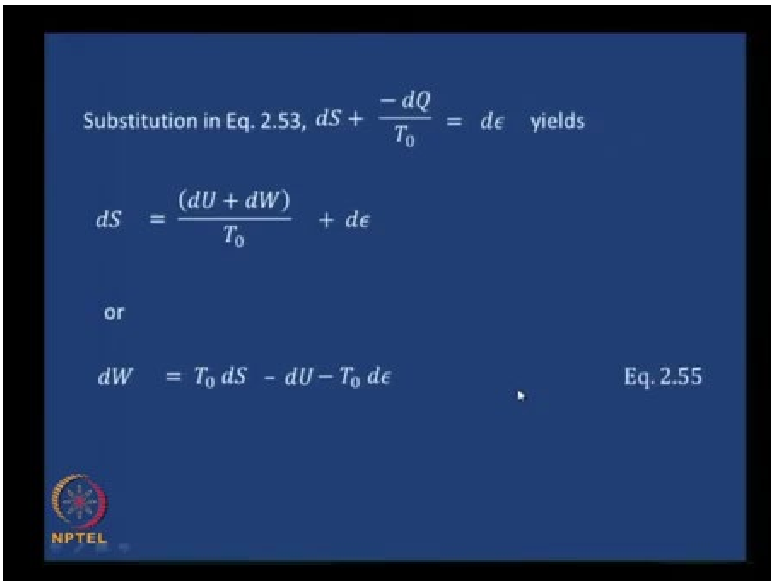

Now, let us look at the first law – some very basics again. Equation 1.3: we know that dQ – this is for a closed system –

$$dQ = dU + dW$$

If we substitute the first law … excuse me … first law of thermodynamics in this equation 2.53,

$$dS + \frac{-dQ}{T_0} = d\epsilon$$

We are going to substitute for dQ we will get

$$dS = \frac{(dU+dW)}{T_0} + d\epsilon$$

We have transposed the equation; therefore, the negative sign goes away there; or if we multiply throughout by T 0 and then transpose the equation, we will get

$$dW = T_0\,dS - dU - T_0\,d\epsilon$$

We will call this equation 2.55.

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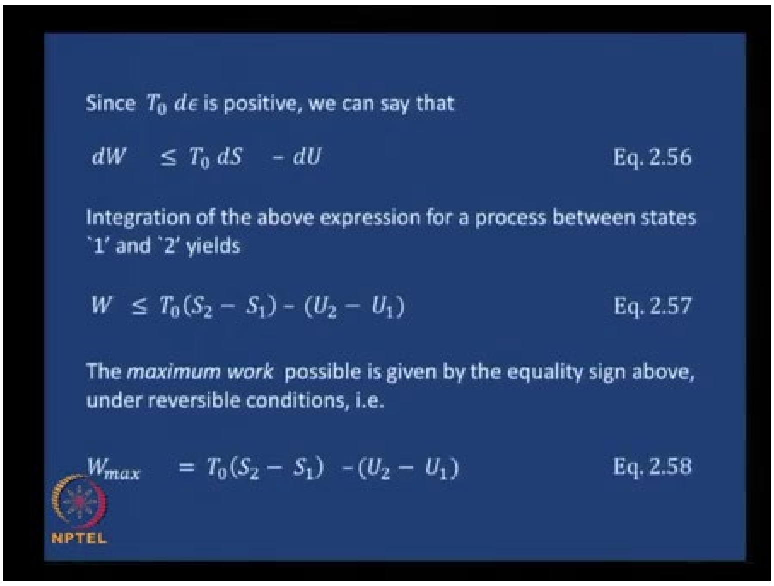

Now note that d epsilon is positive, T 0 is of course, the temperature that needs to be positive in Kelvin. Therefore, the product of those two terms T 0 d epsilon is positive, and thus

$$dW \leq T_0\, dS - dU$$

Now from here; this needs to be positive and d W needs to be less than or equal to T 0 d S minus d U; d U we do not really know what is happening here. We will call that equation 2.56. Now, if we integrate this expression, let us say between the states of 1 and 2. It's a straightforward integration: integral d W is W. This remains … this inequality remains less than or equal to T 0 d S between … integrated between 1 and 2 gives

$$W \leq T_0(S_2 - S_1) - (U_2 - U_1)$$

We will call that equation 2.57.

Now, note this equation. This is some quantity, and this is some quantity. And the maximum work possible since W is less than this, the right hand side … less than or equal to the right hand side, the maximum work that is possible is when W equals the right hand side. And therefore, the maximum work possible which happens to be under reversible conditions, if indicated by W max can be written as

$$W_{max} = T_0(S_2 - S_1) - (U_2 - U_1)$$

Therefore, we have a measure of the maximum work that is available from a process in terms of it is the state variables of the system T 0 … T 0 is of course, the temperature of the surroundings S 2, S 1, U 2, U 1 – all correspond to the state variables of the system. Let us call that equation 2.58.

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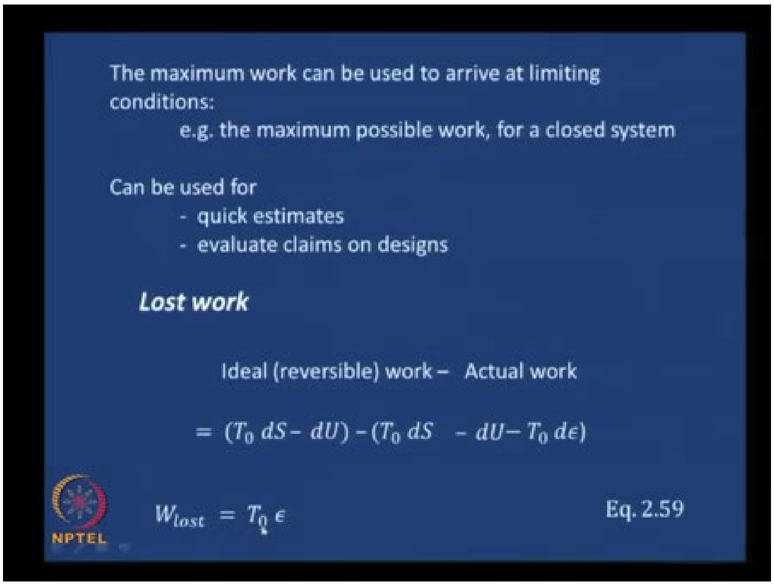

We started out by saying this; let me complete this part by reemphasizing this: the maximum work can be used to arrive at limiting conditions. For example, the maximum possible work for a closed system, which can in turn be used for quick estimates, to evaluate claims on design as well as to begin with the design itself. The lost work, as we said, is a difference between the maximum work and the actual work therefore, the ideal or the reversible work minus the actual work; the reversible work, we have an expression here T 0 d S minus d U that we got from earlier. The actual work happens to be T 0 d S minus d U minus T 0 d epsilon. Therefore, these two terms cancel, these two terms cancel we have an expression for the lost work as T 0 times epsilon. This is integrated; after integration we get work lost equals

$$W_{lost} = T_0\, \epsilon$$

in terms of the sink temperature the surroundings temperature assumed to be constant times the entropy that is created. We will call this equation 2.59.

See you in the next class.