Basic Thermodynamics

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Lecture - 09

Second Law and its Corollaries-IV

Good afternoon to all of you to this session of thermodynamics. Last session, we were discussing the entropy which is one of the most important and useful concept. So, I will repeat a part of our discussion in the last session for the sake of continuity to the material of the present section. Let us start with little recapitulation of the things which we discussed earlier.

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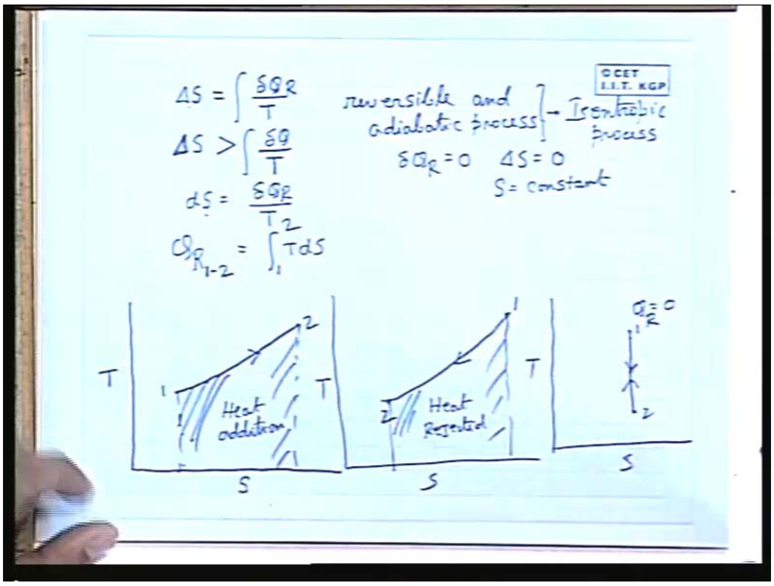

$$\Delta S = \int \frac{\delta Q_R}{T}$$

$$\Delta S > \int \frac{\delta Q}{T}$$

$$dS = \frac{\delta Q_R}{T}$$

$$Q_{R_{1-2}} = \int_1^2 T\,dS$$

reversible and adiabatic process → Isentropic process

$\delta Q_R = 0$ $\Delta S = 0$

$S =$ constant

Delta S - change in entropy - was defined as in any process as the delta Q in a reversible process, integral delta Q_R divided by T. So, this is valid for any reversible or irreversible process.

The definition for the change in entropy is valid for any process, but it is defined through this quantity delta Q_R divided by T in a reversible process.

Also, we recognize that for any other process, if the process is not reversible then how delta S relates with this quantity for the process that delta S is greater than delta Q divided by T. It is a repetition of what I have told earlier. The delta Q divided by T quantities, integral of these quantities for a process is always less than delta S which means that delta S is greater than delta Q divided by T for any process.

Then we recognize that if a process is adiabatic and reversible, delta Q is 0 and moreover the process is reversible that means delta Q_R is 0 so, delta S becomes 0.

For a reversible and adiabatic process, delta S is equal to 0 which gives S is constant which tells that in a reversible adiabatic process entropy remains constant. That is why a reversible adiabatic process is known as isentropic process, but for any reversible process, delta S is delta Q_R divided by T where there is a heat transfer. It means that any reversible, non adiabatic or diabatic process delta S is delta Q_R divided by T. So, we can write this in a differential form as dS is delta Q_R divided by T.

If we integrate this, we can tell that the heat transfer added or rejected in any process connecting the stage 1 to 2, for a reversible one, is TdS 1 2 (Refer Slide Time: 04:00 min). We are interested in this heat transfer added or rejected. In a reversible process, heat added or rejected connecting the state points 1 to 2 can be written like this. So, this is a useful relation in a sense that if we represent a reversible process in a TS diagram where T is the temperature and S is the entropy.

If the process is like this, 1 to 2 in this direction (Refer Slide Time; 04:30 min), so, when the process is this way where the entropy increases and temperature increases, it is a heating process where delta Q_R is greater than 0 and Q_R is greater than 0 for which entropy change is greater than 0. Entropy increases and temperature also increases. So, it is a reversible heating process.

In this case, the area under this curve intercepted on from S axis gives the heat addition (Refer Slide Time: 05:02 min). Similarly, if the process is a heat rejection reversible process then the direction of the process is other way that means initial point one here, two here where the entropy is decreased because delta Q is negative there by the usual sign convention. Delta S is less than 0. So, dS is less than 0.

This area represents the heat rejected which means that the area under the curve in TS plane of a reversible process represents the heat interaction quantities and if a reversible process does not interact heat that means reversible adiabatic process we know entropy remains same.

That process will be expansion or compression, 1 to 2 or 2 to 1, where temperature will increase or decrease. This is a non isentropic process, reversible adiabatic process and this does not have any heat transfer that means Q_R is equal to 0. This is the line. There is no intercepted area on this TS axis (Refer Slide Time: 06:09 min). So, these are very simple.

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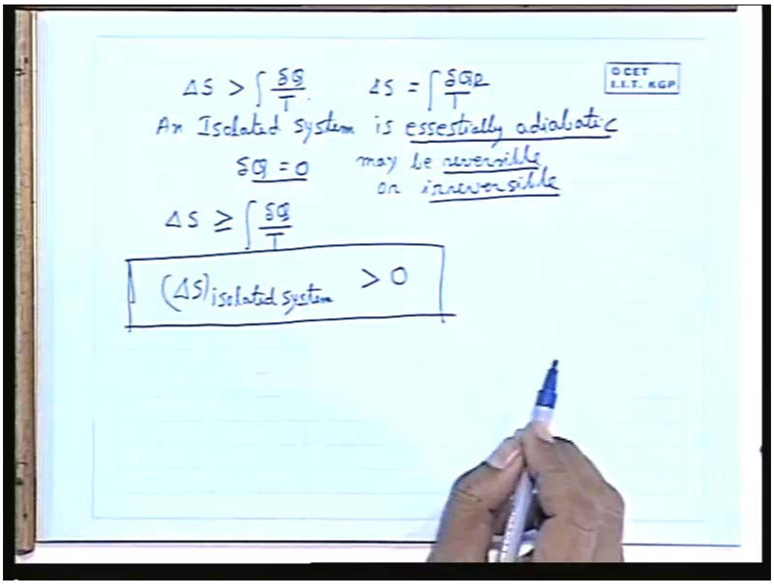

$\Delta S > \int \frac{\delta Q}{T}$ $\Delta S = \int \frac{\delta Q_R}{T}$

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An Isolated system is essestially adiabatic

$\delta Q = 0$ may be reversible or irreversible

$\Delta S \geq \int \frac{\delta Q}{T}$

$\boxed{(\Delta S)_{\text{isolated system}} > 0}$

Now, again I start repetition of the earlier thing that delta S for any process is greater than integral delta Q divided by T. Now with this, what we deduce earlier that an isolated system, what is an isolated system?

An isolated system is essentially adiabatic that means delta Q is 0. System may be reversible or irreversible that means the process within this system may be reversible or irreversible that means an isolated system where there is no heat transfer and work transfer. So, essentially adiabatic from the heat transfer point of view, if any internal processes within the system may be reversible, may be irreversible, but delta Q is 0 and we had this, delta S is greater than integral of delta Q by T that is for an irreversible process.

So, when it is reversible process, delta S is equal to delta Q_R divided by T. So, combining these two, we wrote delta S is greater than equal to integral of delta Q divided by T that means it is valid for any process. If it is reversible, equality sign holds goods, if it is irreversible, greater than sign holds good.

Now for an isolated system, this delta Q is 0. So, delta $S_{\text{isolated system}}$ is greater than 0. This is one of the very important principle that for an isolated system the change of entropy is greater than 0.

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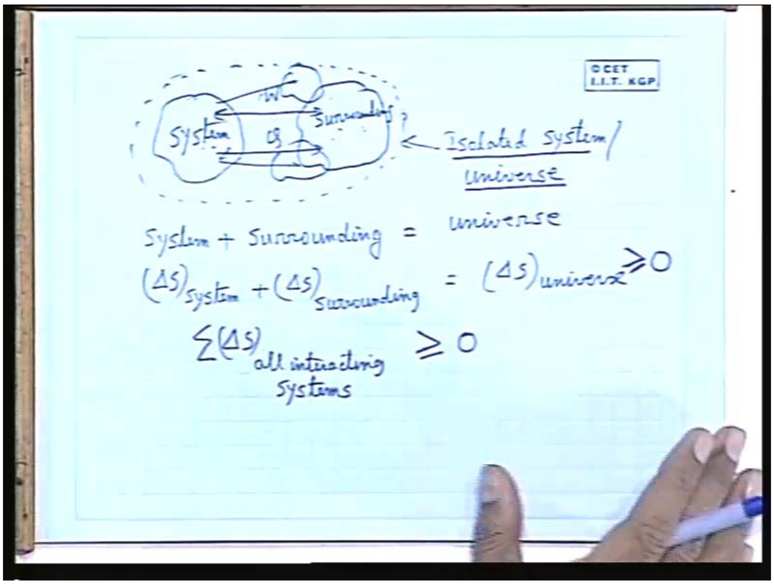

System + Surrounding = universe

$$(\Delta S)_{\text{System}} + (\Delta S)_{\text{Surrounding}} = (\Delta S)_{\text{universe}} \geq 0$$

$$\sum (\Delta S)_{\substack{\text{all interacting} \\ \text{systems}}} \geq 0$$

Then what we discussed is that if there is a system which interacts with the surrounding that means if we identify a system and its interacting surrounding that means they are interacting with each other in any directions in terms of work and heat. That is the only way by which system and surrounding can interact with each other then we can define an equivalent system consisting of the system and surrounding as an isolated system or universe (Refer Slide Time: 08:42 min). This is in a limited sense as I have told earlier. The isolated system is defined as a universe which does not have any other interactions with the rest part of the surrounding. So, this surrounding means another system which is interacting with this system.

So, there may be a number of other systems which is interacting between each other. The number of interacting systems can be considered together as an isolated or universe where the systems consisting the isolated system or constituting the isolated system do not have any interaction with the rest part of the surrounding. This represents an isolated system or universe. So, we can write system plus surrounding means interacting system to that system, so system surroundings are interchangeable.

System plus surrounding comprises an isolated system or universe. Therefore delta S that is a change of entropy of the system plus delta $S_{\text{surrounding}}$ becomes delta S of the universe or the isolated system. Just now we have seen that delta S is greater than 0. So delta S_{universe} is greater than 0 or it is equal to 0. This takes care of both the things that mean the reversible and irreversible interaction. This means that within this universe or isolated system, the interactions are going between different systems which constitutes this isolated systems or system and surrounding. If the interactions between these constituent systems are irreversible then delta S of the universe that means system plus surrounding is greater than 0.

If these interactions are reversible then delta $S_{universe}$ equals to 0. This can be written in a broader sense, delta S algebraic of all interacting systems that means if we can define an isolated system consisting of many interacting systems where the interactions taking place between the systems only nothing else, so that all of them together define an universe or an isolated system then these become greater than equal to 0 (Refer Slide Time: 11:13 min) depending upon whether these interactions are reversible or irreversible. For reversible, it equals to 0, but for an irreversible, it is greater than 0.

Now, after this I come to this concept of delta S of a system.

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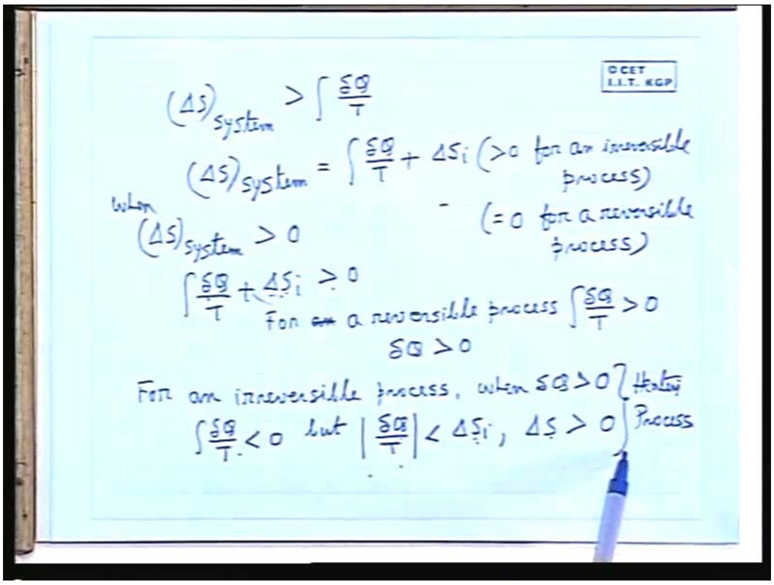

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$(\Delta S)_{system} > \int \frac{\delta Q}{T}$

$(\Delta S)_{system} = \int \frac{\delta Q}{T} + \Delta S_i$ (>0 for an irreversible process)
(=0 for a reversible process)

when

$(\Delta S)_{system} > 0$

$\int \frac{\delta Q}{T} + \Delta S_i > 0$

For ~~an~~ a reversible process $\int \frac{\delta Q}{T} > 0$

$\delta Q > 0$

For an irreversible process, when $\delta Q > 0$ } Heating Process

$\int \frac{\delta Q}{T} < 0$ but $\left| \frac{\delta Q}{T} \right| < \Delta S_i$, $\Delta S > 0$

Delta S of a system is greater than delta Q divided by T which leads us to think that delta S of a system is equal to delta Q divided by T plus delta S_i, some positive quantity which is always greater than 0 for an irreversible process. For any irreversible process, delta S_{system} is more than delta Q divided by T and which equals to 0 for a reversible process. Now here is the concept.

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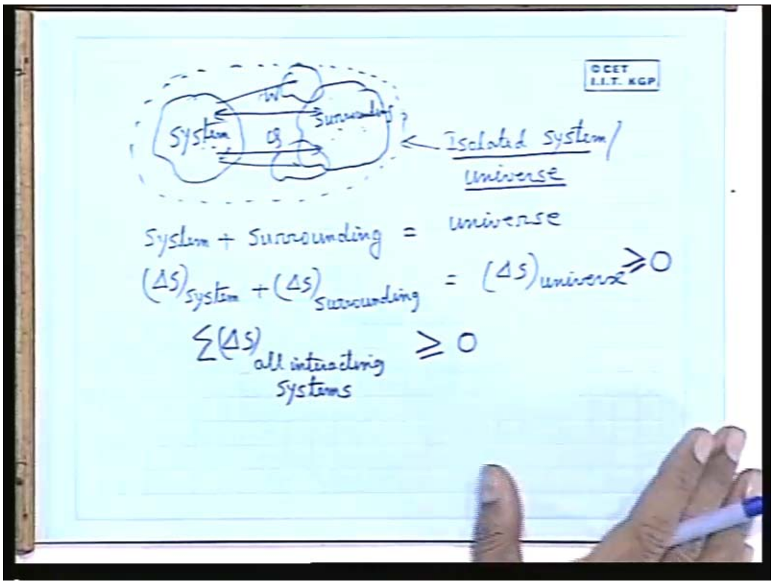

← Isolated system / universe

System + Surrounding = universe

$$(\Delta S)_{system} + (\Delta S)_{surrounding} = (\Delta S)_{universe} \geqslant 0$$

$$\sum (\Delta S)_{\substack{\text{all interacting}\\ \text{systems}}} \geqslant 0$$

This definition that delta S$_{universe}$ that means algebraic sum of the change of entropy of the system plus surrounding or change of entropy of all interacting systems, algebraic sum is greater than is equal to 0 that means it can never become less than 0. This is known as principle of increase of entropy (Refer Slide Time; 13:02 min) and it is one of the very useful concept or corollary of the second law of thermodynamics that delta S of the universe that is system plus surrounding can never be less than 0. It is always greater than 0 for a natural universe or for a natural isolated system where the interacting processes are irreversible and in an ideal case, it is equal to 0.

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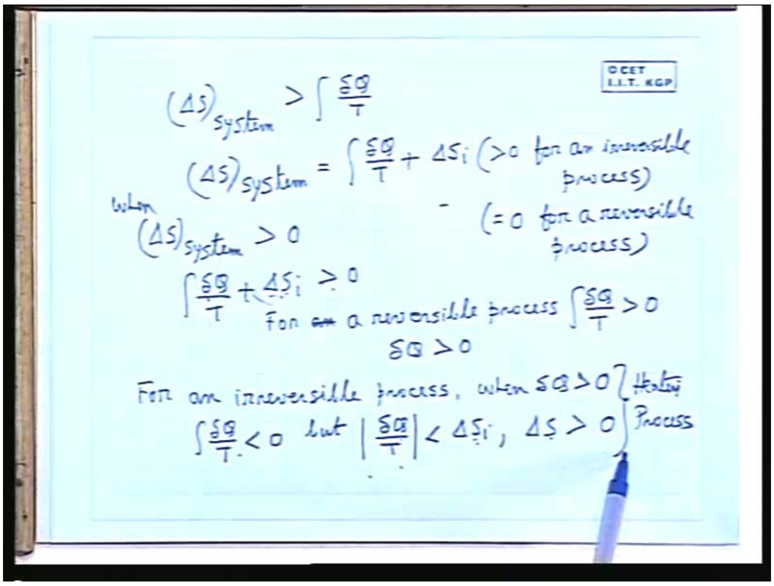

$$(\Delta S)_{system} > \int \frac{\delta Q}{T}$$

$$(\Delta S)_{system} = \int \frac{\delta Q}{T} + \Delta S_i \quad \begin{array}{l}(>0 \text{ for an irreversible process})\\ (=0 \text{ for a reversible process})\end{array}$$

when $(\Delta S)_{system} > 0$

$$\int \frac{\delta Q}{T} + \Delta S_i > 0$$

For ~~an~~ a reversible process $\int \frac{\delta Q}{T} > 0$

$$\delta Q > 0$$

For an irreversible process, when $\delta Q > 0$

$\int \frac{\delta Q}{T} < 0$ but $\left|\frac{\delta Q}{T}\right| < \Delta S_i$, $\Delta S > 0$

Heating Process

But for a system as we define the change of entropy which may be greater than 0 may be less than 0. So, now I see when delta S_{system} is greater than 0. What is that? Integral delta Q divided by T plus delta S_i has to be greater than 0. Now, for a reversible process, this delta S_i is 0, so integral delta Q by T has to be 0. For an irreversible process, delta S_i is greater than 0, so integral delta Q by T may be or may not be greater than 0. So, for a reversible process, delta S to be 0 because delta S_i is 0, delta Q divided by T has to be greater than 0 which means delta Q has to be greater than 0. It has to be added to the process.

It is sometimes asked in many interviews very important concept usually we may not get in all books.

For an irreversible process, now if delta Q is greater than 0 that means if heat is added obviously delta S is 0 that means when delta Q is 0 that means if we add heat to a process in an irreversible manner and there are also internal irreversibility then obviously delta S_i is greater than 0 and this integral delta Q by T is also greater than 0. So, delta S_{system} has to be greater than 0 because delta S_{system} is integral delta Q by T plus delta S_i.

But for an irreversible process, there are cases when delta Q divided by T less than 0, even it may happen. Usually this is like this, delta Q is greater than 0, This is a heating process. But even if the delta Q is taken out, but in an irreversible case, delta Q by T, if this thing is less than delta S_i the absolute value, then this (Refer Slide Time: 15:40 min) will be always greater than 0. Delta S is always greater than 0. Have you understood this? If delta Q divided by T is negative, but it cannot counter with the positive contribution of delta S_i then delta S is greater than 0 that means in case of an irreversible process even we extract the heat, entropy may increase, but in both the cases temperature increase, so heating process, I have to explain.

For an irreversible process, if you add heat plus the internal irreversibility so, obviously temperature will increase then it is a heating process and entropy will increase. But here, even if we take the heat (Refer Slide Time: 16:23 min), but if delta S_i is more than this absolute magnitude of delta Q divided by T, this sum, integral delta Q by T plus delta S_i is greater than 0. This also a heating process, here temperature increases, but heat is taken out so, entropy is increasing. These are rare situations.

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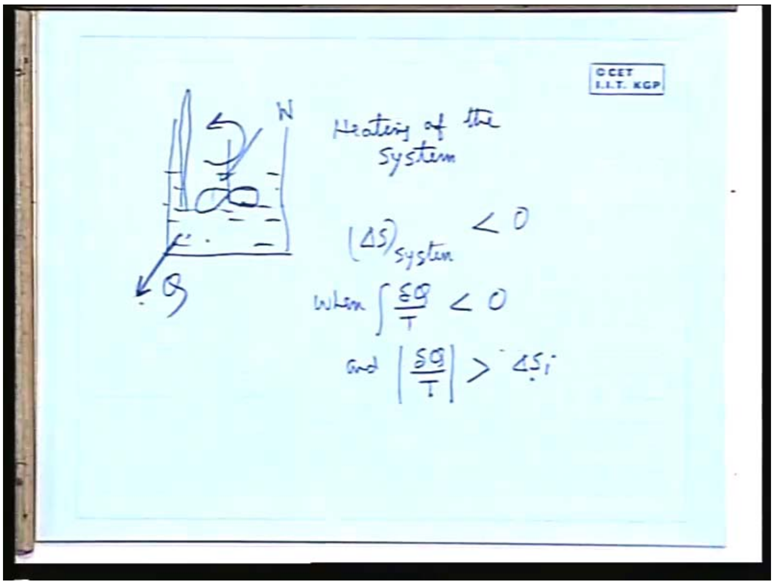

Heating of the System

$(\Delta S)_{system} < 0$

when $\int \frac{\delta Q}{T} < 0$

and $\left|\frac{\delta Q}{T}\right| > \Delta S_i$

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I just give you an example. So that in interviews if it is asked by somebody [ ]. Let us consider a mass of water. It is very important. You may not get in many books also. You stir the water, you make a paddle wheel work input and at the same time you take heat out. Now, it may so happen that if put a thermometer that depending upon the rate of heat extraction from it and the rate of work done or the internal irreversibility. It does not depend only on the work, but the dissipation that means the fluid viscosity is such that dissipation is more that the fluid is heated.

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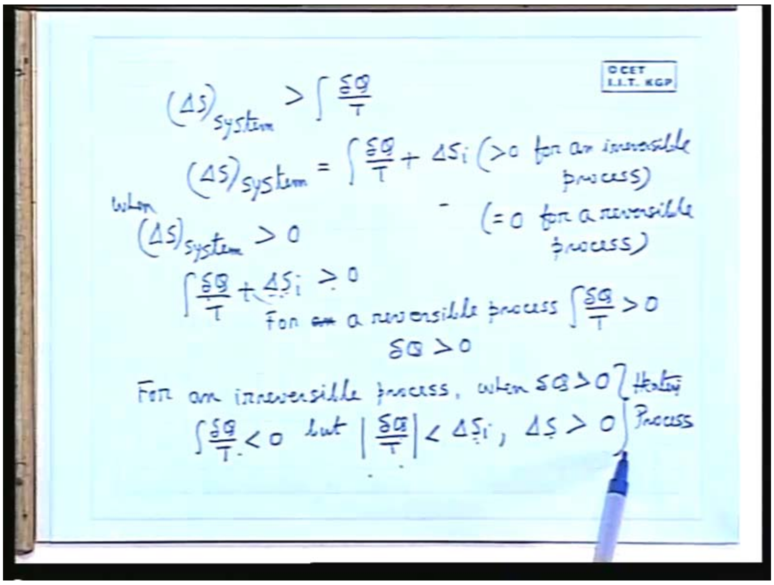

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For ~~an~~ a reversible process $\int \frac{\delta Q}{T} > 0$

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For an irreversible process, when $\delta Q > 0$ Heating Process

$\int \frac{\delta Q}{T} < 0$ but $\left|\frac{\delta Q}{T}\right| < \Delta S_i$, $\Delta S > 0$

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When this exists that means internal entropy change due to internal irreversibility are more than the magnitude of delta Q by T .

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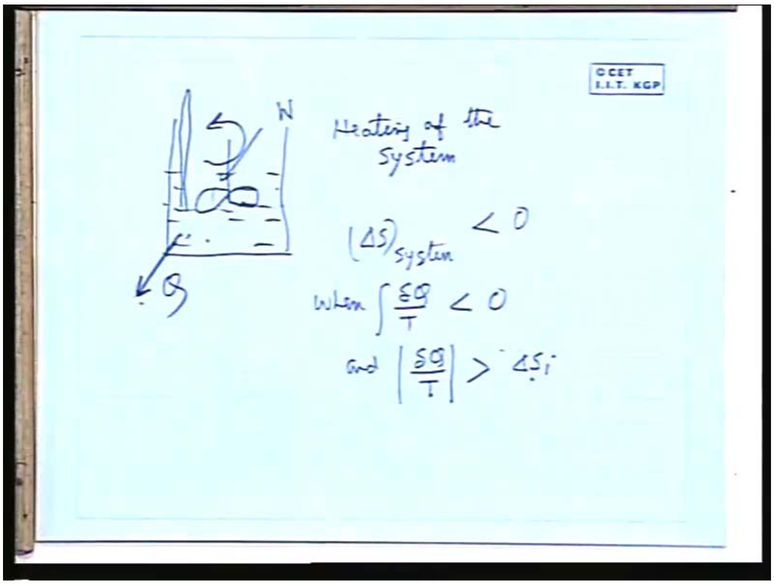

Heating of the System

$$(\Delta S)_{system} < 0$$

when $\int \frac{\delta Q}{T} < 0$

and $\left|\frac{\delta Q}{T}\right| > \Delta S_i$

Then ultimate effect is the heating of the system though the heat is taken out. It is heated because of this irreversibility. So, some of the work is being dissipated through mechanical irreversibility into inter molecular energy which rises the temperature.

Whenever the system temperature is raised, we tell it is heated, so whether heat is supplied or not, due to frictional heat we will tell due to friction, the system is heated. No heat was supplied. It is some form of mechanical energy is being dissipated which is known as degraded that I will come afterwards according to second law of thermodynamics. This dissipation is termed as degraded; some form of mechanical energy is being degraded in terms of heat or intermolecular energy where temperature is increasing. So, in this case, entropy still increases. Sometimes it is asked can we give an example where heat is being taken out of a system till its temperature, till its entropy increases.

Yes, so we can tell that entropy will increase if we giving heat to either a reversible process or an irreversible process. For an irreversible process, this part, delta S_i is 0. So for a reversible process, if we give heat, entropy will increase; if we take heat, entropy will decrease. There is no other way out. So it is directly related to the heat quantity, but for an irreversible process, if we add heat to a system, definitely it will increase the entropy because delta Q by T plus delta S_i, but if we take out heat entropy may still increase depending upon the relative magnitude of delta Q by T is less than delta S_i.

In a similar fashion, I can tell that the entropy of this system, a mass of water, will decrease, delta S system is less than 0 when delta Q divided by T, that means there has to be a rejection of heat and at the same time, this magnitude, delta Q by T should be greater than delta S_i.

Therefore, we arrive at the conclusion that the entropy of a system may decrease, may increase.

A simple example is that you heat a body, its temperature will increase and entropy will increase. You cool a body, its temperature will decrease and entropy will decrease and that depends upon the relative magnitude of the delta Q divided by T and the delta S_i so that both increase in entropy and decrease in entropy is possible for a system, but when we add together, the entropy change of the surroundings.

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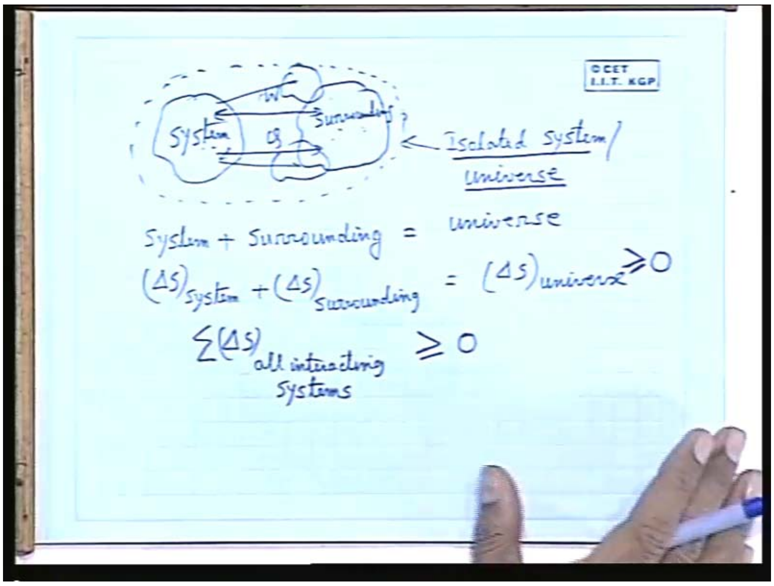

System + Surrounding = universe

$$(\Delta S)_{system} + (\Delta S)_{surrounding} = (\Delta S)_{universe} \geq 0$$

$$\sum (\Delta S)_{\text{all interacting systems}} \geq 0$$

If we add up this two, delta S system and delta S surrounding and find the delta S is universe, it can never decrease that it can never less than 0. It will be either greater than 0 or is equal to 0. Next, I will tell you that how we can just find some examples. Now let us see one thing that is also very important. You may not get I am telling you again and again in many books.

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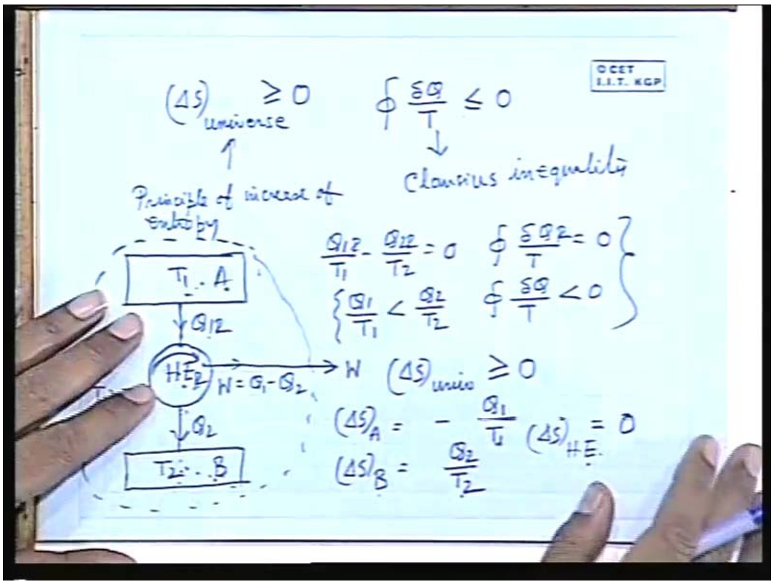

So far, delta $S_{universe}$, now I know what universe is or what it means in thermodynamics, is greater than is equal to 0, taking care of both irreversible and reversible. At the same time, we know cyclic integral of delta Q divided by T, taking care of both reversible and irreversible cycles, is less than equal to 0. Delta $S_{universe}$ is greater than equal to 0 is known as principle of increase of entropy and cyclic integral of delta Q by T is less than equal to 0 is known as Clausius inequality. Now these two are same that means one is a consequence of the other with a negative sign.

Let us understand this to make our concept very clear. Let us consider a reversible heat engine HE. Let us consider a thermal reservoir at high temperature T_1 and takes heat Q_1 and it rejects heat continuously by the amount Q_2 to a thermal reservoir T_2. T_1 is greater than T_2 and that maintains respects all first law and second law W is equal to Q_1 minus Q_2.

Now, we know that by this Clausius inequality Q_1 by T_1 minus Q_2 by T_2 is equal to 0. Clausius inequality is a straightforward consequence of the definition of absolute thermodynamics temperature scales. When we recapitulate everything, the step by step, all the corollaries are being recapitulated. We know the definitions of absolute thermodynamics temperature skills are Q_1 by Q_2 is T_1 by T_2. If we represent the temperature of the thermal reservoirs in absolute thermodynamic temperature skill, then Q_1 by T_1 minus Q_2 by T_2 is equal to 0 which is nothing, but the cyclic integral delta Q divided by T, is equal to 0, for a reversible engine is 0, but if it is an irreversible engine then Q_1 by T_1 is less than Q_2 by T_2 and cyclic integral of delta Q divided by T is less than 0. This we have already studied. This is because the efficiency of an irreversible engine and this Q_1 by T_1 is less than Q_2 by T_2 is in case of an irreversible engine.

Let us consider R by giving R as the reversible law (Refer Slide Time: 23:16 min). So and this is the efficiency of an irreversible engine is less than this. Now I apply the delta $S_{universe}$. Let us find out what is the change of entropy of the universe. Consider a reversible engine then considering these three (Refer Slide Time: 23:37 min), I can consider these as an isolated system.

Yes, you can argue. Sir, why this is an isolated system? Work is coming out. Yes.

Work is coming out, but at least we can consider it as an adiabatic system, so with respect to heat interactions, it follows the same principle as that of an isolated system because work coming out to the surrounding does not do anything with the entropy. So, if we do that way then I can tell that delta S of this entire universe consisting of this thermal reservoir at T_1 and thermal reservoir at T_2 and the heat engine must be greater than equal to 0 by this principle, equal when reversible and greater than is when irreversible.

What is the delta S of the thermal reservoir? Let this $T_1$is A, this T_2 is B. So delta S_A is minus Q_1 by T_1. If it is a reversible, then Q_{1R}, now here I am not writing Q_{1R} or $Q_{2R,}$ let us consider it may be a reversible or it may be an irreversible. So, what is delta $S_{B?}$ It is Q_2 by T_2. Let us consider for the irreversible case without R suffix. What is delta S of heat engine? Please tell me. It loses heat. So, its entropy change is Q_1 by $T_{1.}$ Delta Q divided by T. T is constant at constant temperature minus Q_1 by T_1. It exceed at a constant temperature $T_{2,}$ so delta S_B is Q_2 by T_2.

What is delta $S_{heat\ engine}$? That is system operating on the heat engine is 0. Why? This is operating on a cycle. So, a system operating on a cycle continuously, its change of entropy will be 0. It is a point function, so change of entropy in any cyclic process is 0. What are the systems? All interacting systems taken together constitute an isolated system. We are interacting systems at reservoir A, heat engine HE, reservoir B. Reservoir A undergoes a process, reservoir B undergoes a process. This Q_{1R} is a heat rejection process.

Reservoir B undergoes a heat addition process and heat engine fluid takes heat from the reservoir A, gives heat to the reservoir B, but it operates a cyclic process. There are other processes also that means in a total cyclic process, the entropy change of the heat engine is 0. Therefore, this delta $S_{heat\ engine}$ is 0.

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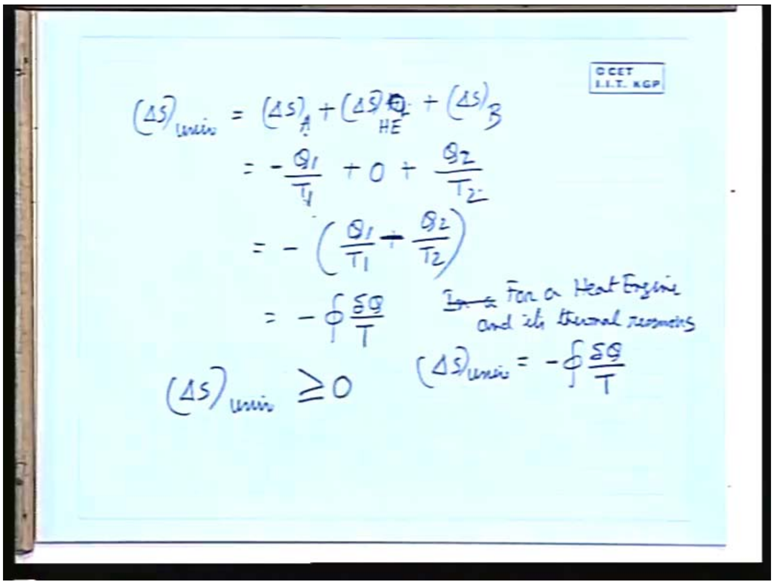

$$(\Delta S)_{univ} = (\Delta S)_A + (\Delta S)_{HE} + (\Delta S)_B$$
$$= -\frac{Q_1}{T_1} + 0 + \frac{Q_2}{T_2}$$
$$= -\left(\frac{Q_1}{T_1} + \frac{Q_2}{T_2}\right)$$
$$= -\oint \frac{\delta Q}{T}$$

~~In a~~ For a Heat Engine and its thermal reservoirs

$$(\Delta S)_{univ} = -\oint \frac{\delta Q}{T}$$

$$(\Delta S)_{univ} \geq 0$$

So, with this thing, we can write therefore delta $S_{universe}$ is equal to delta S_A plus delta S_{HE} heat engine plus delta $S_{B.}$

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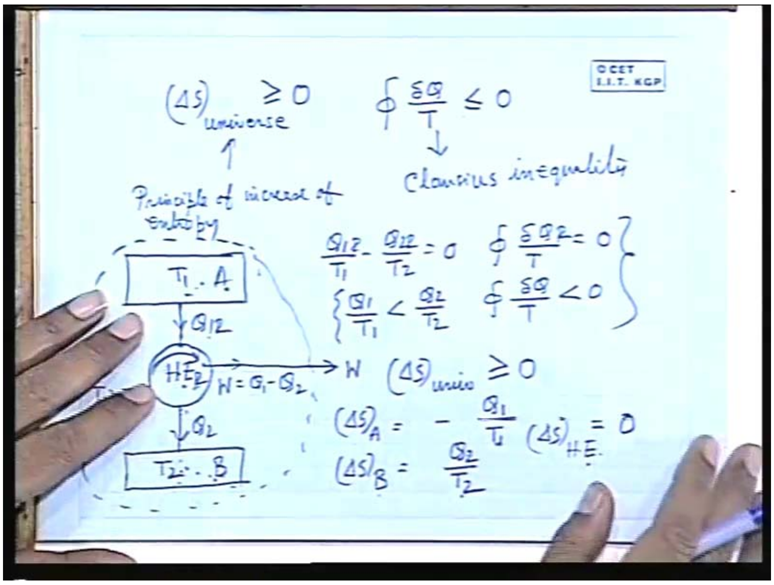

$$(\Delta S)_{universe} \geq 0 \qquad \oint \frac{\delta Q}{T} \leq 0$$

Principle of increase of entropy

Clausius inequality

$$\frac{Q_{12}}{T_1} - \frac{Q_{12}}{T_2} = 0 \qquad \oint \frac{\delta Q_R}{T} = 0$$
$$\frac{Q_1}{T_1} < \frac{Q_2}{T_2} \qquad \oint \frac{\delta Q}{T} < 0$$

$$(\Delta S)_{univ} \geq 0$$
$$(\Delta S)_A = -\frac{Q_1}{T_1} \qquad (\Delta S)_{HE} = 0$$
$$(\Delta S)_B = \frac{Q_2}{T_2}$$

Now delta S_A is minus Q_1 by T_1, delta S_B is Q_2 by T_2 and delta $S_{heat\ engine}$ is 0.

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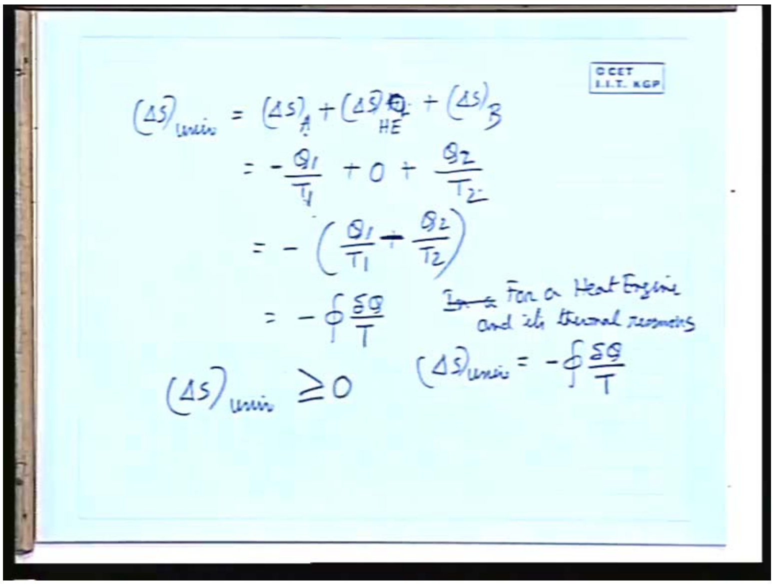

$$(\Delta S)_{univ} = (\Delta S)_A + (\Delta S)_{HE} + (\Delta S)_B$$

$$= -\frac{Q_1}{T_1} + 0 + \frac{Q_2}{T_2}$$

$$= -\left(\frac{Q_1}{T_1} - \frac{Q_2}{T_2}\right)$$

$$= -\oint \frac{\delta Q}{T}$$

~~In a~~ For a Heat Engine and its thermal reservoirs

$$(\Delta S)_{univ} = -\oint \frac{\delta Q}{T}$$

$$(\Delta S)_{univ} \geq 0$$

So that is minus Q_1 by T_1 plus 0 plus Q_2 by T_2. Then what it is? minus (Q_1 by T_1 minus Q_2 by T_2.

What is this? Our very old known things.

[Conversation between Student and Professor – Not audible ((00:27:26 min))]

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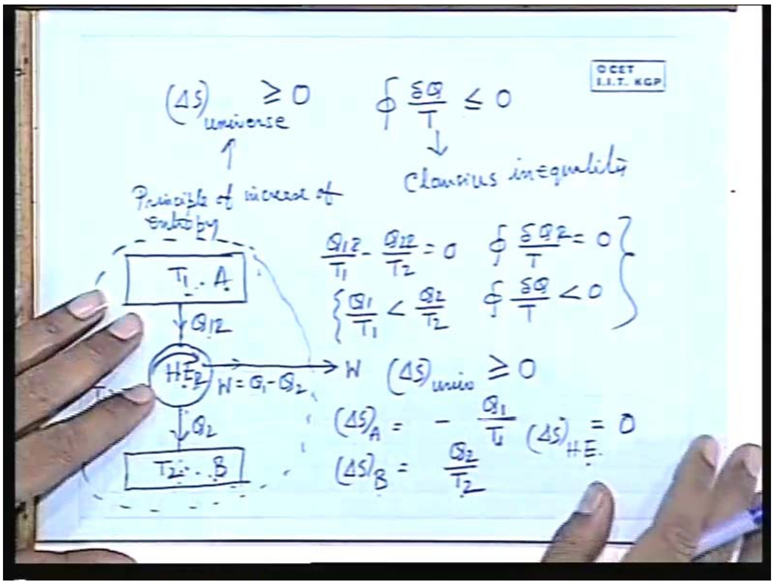


$$(\Delta S)_{universe} \geq 0$$

Principle of increase of entropy

$$\oint \frac{\delta Q}{T} \leq 0$$

Clausius inequality

$$\frac{Q_{1R}}{T_1} - \frac{Q_{2R}}{T_2} = 0 \qquad \oint \frac{\delta Q_R}{T} = 0$$

$$\frac{Q_1}{T_1} < \frac{Q_2}{T_2} \qquad \oint \frac{\delta Q}{T} < 0$$

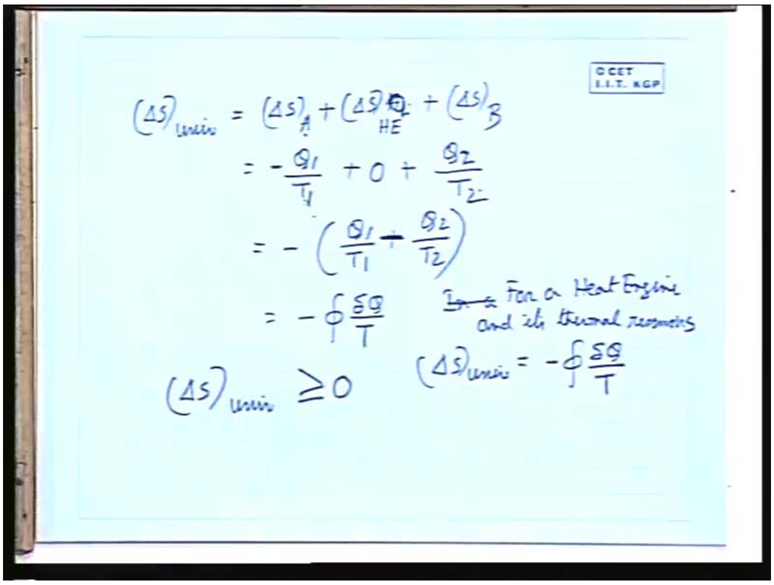
$$(\Delta S)_{univ} \geq 0$$

$$(\Delta S)_A = -\frac{Q_1}{T_1} \qquad (\Delta S)_{HE} = 0$$

$$(\Delta S)_B = \frac{Q_2}{T_2}$$

Again, we are getting confused. Change of entropy of A is minus Q_1 by T_1, change of entropy of B is Q_2 by /T_2. Because the entropy of A is decreased, entropy of B is increased.

(Refer Slide Time: 27:43)



OCET
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$$(\Delta S)_{univ} = (\Delta S)_A + (\Delta S)_{HE} + (\Delta S)_B$$

$$= -\frac{Q_1}{T_1} + 0 + \frac{Q_2}{T_2}$$

$$= -\left(\frac{Q_1}{T_1} - \frac{Q_2}{T_2}\right)$$

$$= -\oint \frac{\delta Q}{T}$$

~~In a~~ For a Heat Engine and its thermal reservoirs

$$(\Delta S)_{univ} = -\oint \frac{\delta Q}{T}$$

$$(\Delta S)_{univ} \geq 0$$

Okay! So this is alright.

Sir, there is a minus [ ]

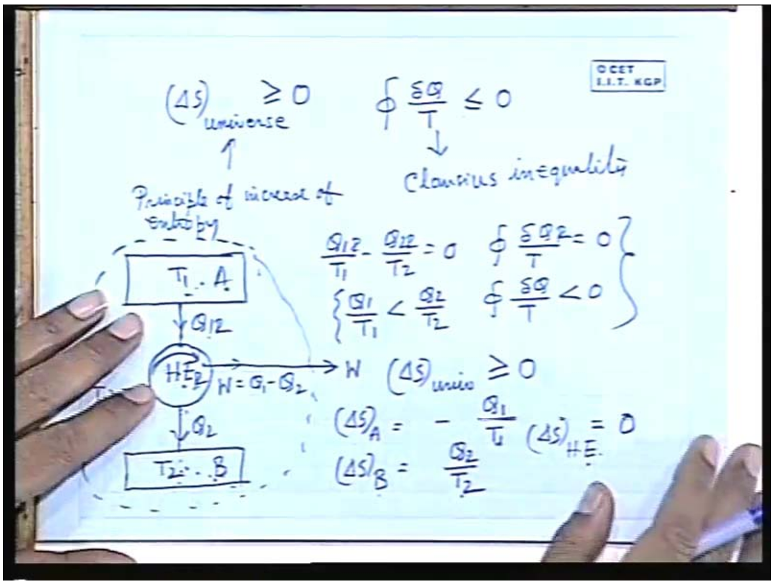
[Conversation between the Student and Professor – Not audible ((00:27:46 min))] Where?

$-[(Q_1/T_1)-(Q_2/T_2)]$ (Refer Slide Time: 27:52 min).

Then what is this cyclic integral of delta Q divided by T, and cyclic of integral of delta Q divided by T is always less than 0 for an irreversible process, is equal to 0 for a reversible process which means delta $S_{universe}$ is greater than equal to 0. That means what I want to say now is this delta $S_{universe}$ for a heat engine and its thermal reservoirs, delta $S_{universe}$ is nothing, but minus of cyclic integral of delta Q divided by T (Refer Slide Time: 28:51 min). So these are synonymous thing with change in the sign. When I tell minus Q_1 by T_1, it denotes the entropy change of the reservoir A that is the source where I tell plus Q_1 by T_1, it depends upon the Q divided by T quantity in the heating process of the working system in the engine.

Similarly, when I tell plus Q_2 by T_2, it represents the change of entropy of the thermal reservoir at T_2, but when I tell minus Q_2 by T_2, it represents the Q divided by T quantities during the heat rejection process of the system executing the heat engine cycle. Therefore the Clausius inequality delta Q divided by T and delta $S_{universe}$.

(Refer Slide Time: 29:36)

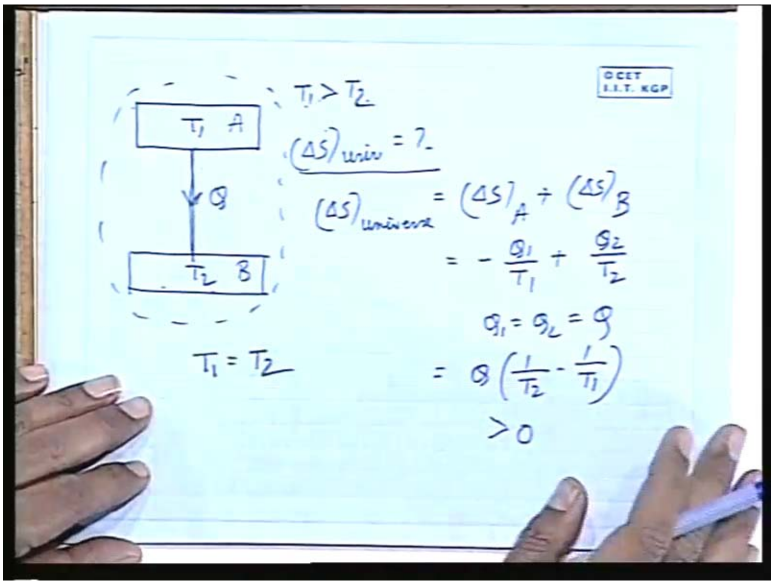


They are what I started here, Clausius inequality and principle of the increase of entropy, they are almost same that means with a negative quantity. So this is a direct consequence of delta Q divided by T that means starting from the basic second law, the Carnot's theorem, the deficiency of a reversible engine is the maximum one when operating between the same temperature limits and for all reversible engines, this is an unique value when they operating between the same temperature limits. This gives the thing that Q_1 by Q_2 is equal to T_1 by T_2 or Q_1 by T_1 is equal to Q_2 by T_2.

This gives rise to the fact that cyclic integral delta Q divided by T will be 0. Then Clausius inequality counts that cyclic integral delta Q divided by T for an irreversible cycle is less than 0. The principle of increase of entropy also gives in the same way because the birth of entropy takes place through this origin that cyclic integral delta Q divided by T for a reversible cycle is 0, for which integral delta Q divided by T for a reversible process is a point function and that becomes equal to the change in the property entropy.

Therefore delta $S_{universe}$, which we have proved independently, has to be greater than or is equal to 0, can never become less than 0 which is known as principle of increase in entropy. It is almost synonymous with a negative quantity that Clausius inequality, cyclic integral of delta Q divided by T will be other way less than equal to 0 can never become greater than 0 because it is a difference with the sign. So delta Q divided by T for a natural engine is less than 0. For a reversible engine equals to 0, can never become greater than 0.

(Refer Slide Time: 31:21)



Now, we should have some other examples. Let us consider the spontaneous heat transfer between two bodies at T_1 and T_2. If they are made contact with a conducting material or through a diathermic wall, then heat comes through it. Now let us first consider these two bodies of infinite heat capacities. It is the concept of infinite thermal reservoirs, sourcing that means their temperature remains same, but T_1 greater than T_2 because this is a spontaneous process, feasible process (Refer Slide Time: 31:52 min).

T_1 is higher than T_2 then spontaneously heat will flow from T_1 to T_2 then if I find out then, let this $T_1$is A and this $T_2$is B, then what is delta $S_{universe}$? How to find out universe? I can define these two systems (Refer Slide Time: 32:10 min) as a universe and what is this value? We can find out delta $S_{universe}$ so universe comprises the system A and system B, delta S_A plus delta S_B.

Any concept, any confusion, you can ask me.

What is delta S_A? minus Q_1 by T_1.

[Conversation between Student and the Professor – Not audible ((00:32:32 min))].

What is delta S_B? Q_2 by T_2.

[Conversation between Student and Professor – Not audible ((00:32:36 min))]

Q_1 is equal to Q_2 is equal to Q.

Yes, I by mistake wrote Q_1, Q_2. So I rectified it by writing again Q_1 is equal to Q_2 is equal to Q, in examination also if you do like that you write this again.

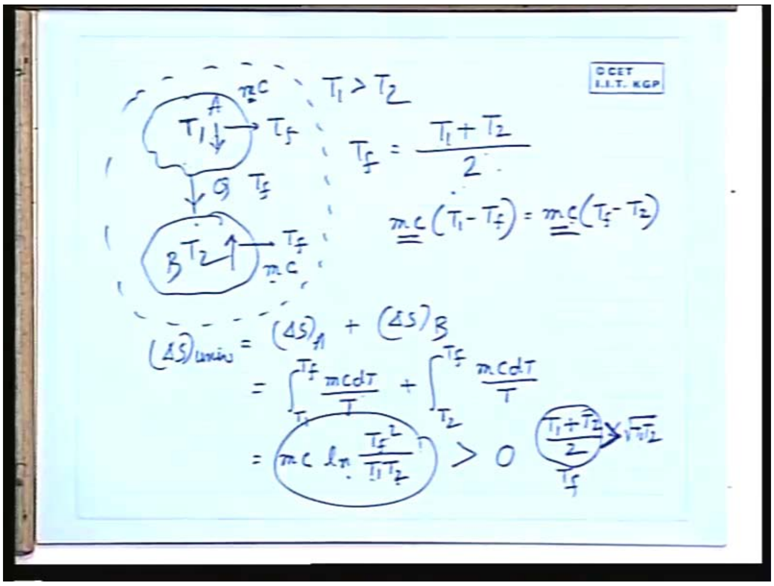
So it will be Q into (1 by T_2) minus (1byT_1). For a spontaneous heat transfer from one reservoir to other reservoir without any other effect in the surrounding, as I have told T_1 has to be more than T_2.; so, this delta S is greater than 0, but if it is a reversible heat transfer, what is the condition?

T_1 has to be T2.

[Conversation between Student and the Professor – Not audible ((00:33:15 min))]

Therefore, this is 0 which cannot be made (Refer Slide Time: 33:20 min). Therefore we see this thing that the entropy change is irreversible.

(Refer Slide Time: 33:30)



$T_1 > T_2$

$$T_f = \frac{T_1 + T_2}{2}$$

$$\underline{\underline{mc}}(T_1 - T_f) = \underline{\underline{mc}}(T_f - T_2)$$

$$(\Delta S)_{univ} = (\Delta S)_A + (\Delta S)_B$$

$$= \int_{T_1}^{T_f} \frac{mc\,dT}{T} + \int_{T_2}^{T_f} \frac{mc\,dT}{T}$$

$$= mc \ln \frac{T_f^2}{T_1 T_2} > 0 \qquad \underbrace{\frac{T_1 + T_2}{2}}_{T_f} > \sqrt{T_1 T_2}$$

Now we come to another case that when there are two finite systems T_1 and T_2 and make a simplification initially of same capacities that means same mass m, same specific heat c at constant pressure or volume. I am not just distinguishing it now. So some specific heat c, which is multiplied by mass, gives the heat capacity (Refer Slide Time: 33:52 min).

This is defined in a sense this can be equated with the change in temperature. So now if these two finite systems now connected so, heat will flow. Since these are finite systems that mean systems with finite capacities, if we start with T_1 greater than T_2 then only heat will flow in this direction. When it happens, this temperature T_1 will decrease and the temperature T_2will increase and ultimately they will come to a common temperature T_f.

T_1 will go to this T_f and T_2 will go to T_f (Refer Slide Time: 34:27 min) when the temperature equalization will be there, there will be no heat transfer. So let us consider just as the earlier case, the natural spontaneous heat transfer between two constant temperature reservoirs, now I consider two very simple case that is most natural case that two finite systems, finite capacities. So what is this T_f? If the heat capacities are same, you will know from your primary school level thing that T_1 plus T_2 devided by 2 that means it is the arithmetic mean. We make the energy balance mc (T_1 minus T_f), that is the heat given by the finite system T_1 is equal to mc (T_f minus T_2), this is heat taken. So, the specific heats are defined that way. So it may be constant volume, constant pressure depending among the constants at which heat has been taken. We are not much bothered for that now.

So any specific heat would define and if the heat capacities are same for the two bodies then the algebraic sum is that. What is this universe? (Refer Slide Time: 35:24 min)Universe consisting of this, let this body $T_1$is A, let this body T_2 is B then, delta Suniverse is equal to delta S_A plus delta S_B.

How to find out delta S_A?

Now tell me.

[Conversation between Student and Professor – Not audible ((00:35:48 min))]

Integral T_1 to $T_{f,}$ how to write delta Q? It is mcdT by T. Now here is the concept. When I write it while doing problems I am okay, I can make 100% correct, all the problems do well in the exams, get marks, but after completing the exam and getting an excellent grade now the confusion comes to me, but this is an irreversible heat transfer then how do I write this as a change in entropy because when the heat is transferred between a finite temperature difference from this body T_1 to this body T_2.

So, how do you calculate the rate of heat transfer by delta Q divided by T because we know that delta S for a reversible process can be equated as delta Q divided by T but for an irreversible process, it is equals to delta Q divided by T plus delta S_i. So, delta Q divided by T integral of that is never equals to delta Q. It is less than delta S. So delta S is greater than integral delta Q divided by T, but why then I am doing integral delta Q divided by T here to find out the entropy change.

Any answer

[Conversation between Student and Professor - Not audible ((00:36:56 min))]

This expression we write for a reversible problem that means that mcdT by T is the heat transferred through a reversible process and when we write this and finally we come up to an expression which only contains the state variables that the two points or two ends states that means it equals to the delta S. I told at the beginning that actual process may be the reversible, but if we can connect this two end states by a reversible process and can find out the delta Q divided by T for that reversible process that defines the change in entropy for any process.

So, mcdT that is the question, so this will be from T_2 to T_f, mcdT by T, so they give mc ln T_f^2 by T_1T_2 (Refer Slide Time: 37:57 min).

[Conversation between Student and Professor – Not audible ((00:37:59 min))]

mc ln T_f byT_1 another line, T_1 to T_f mcdt by T will be mc ln T_f byT_1, T_2 to T_f, mcdT by T will be mc ln T_f by$T_{2.}$ So, this ln T_f by T_1 plus ln T_f by $T_{2,}$ mc is common, constant so ln this into this that means ln T_f^2 by $T_1T_{2.}$ So this is an irreversible heat transfer.

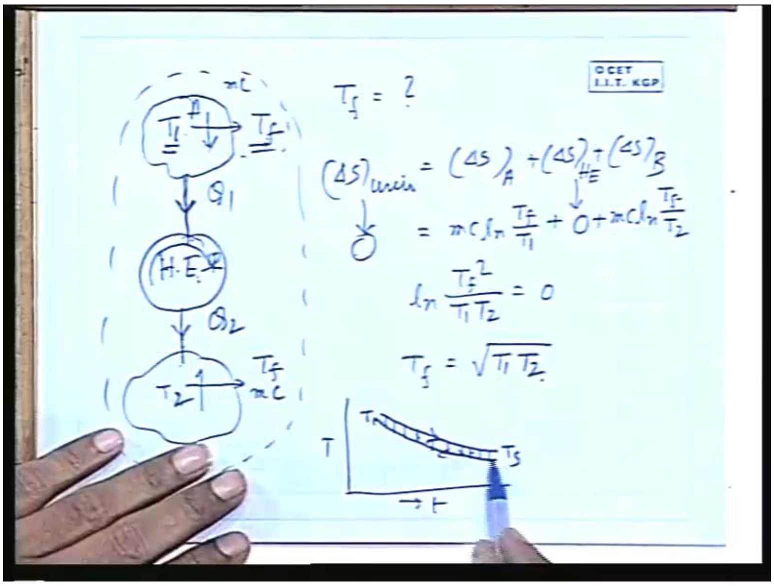
T_1 is greater than $T_{2.}$ So this has to be greater than 0 and this mc ln T_f^2 by T_1T_2 is greater than 0 (Refer Slide Time: 38:27 min) because T_f^2 is greater than T_1 plus T_2. T_f is arithmetic mean and T_1, T_2 is the [Conversation between Student and Professor – Not audible ((00:38:38 min))] square root of the geometric mean.

So always T_1 plus T_2 by2 is greater than root over T_1T_2, geometric mean is [Conversation between Student and Professor – Not audible ((00:38:51 min))] greater than other way around. Arithmetic mean is greater than this.

This T_1 plus T_2 by 2 is T_f, other way around. So this Tf minus square root of T_1 T_2 is greater than 0.

Now after this, I will do another problem that these are the classical examples.

(Refer Slide Time: 39:15)



$T_f = ?$

$(\Delta S)_{univ} = (\Delta S)_A + (\Delta S)_{HE} + (\Delta S)_B$

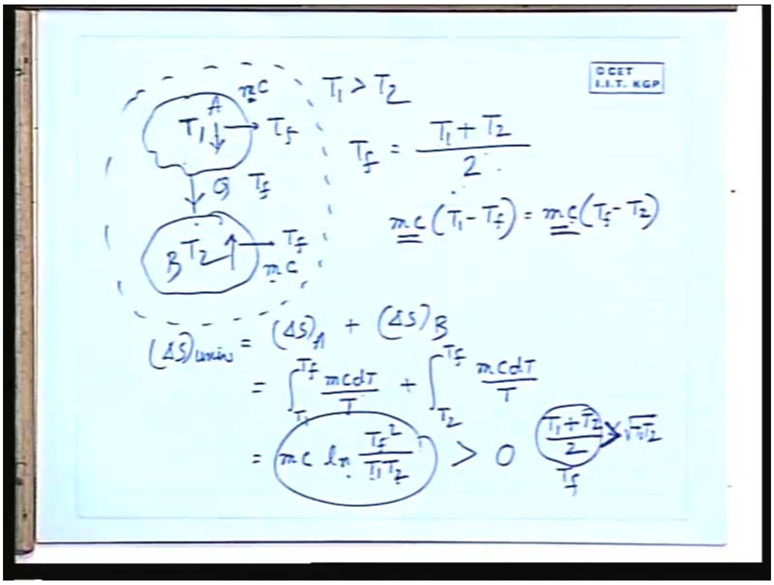
$= mC\ln\frac{T_f}{T_1} + 0 + mC\ln\frac{T_f}{T_2}$

$\ln\frac{T_f^2}{T_1T_2} = 0$

$T_f = \sqrt{T_1T_2}$

Now, if we have a finite system at a temperature T_1 and another finite system at a temperature T_2 and let their capacities are same. This is just a continuation of the earlier thing. If we connect this by a diathermic wall or a conducting rod, this is the expression.

(Refer Slide Time: 39:33)



That they attend a finite temperature, a final temperature depending upon their heat capacities. If they are same, arithmetic mean and we can find out the entropy change of the universe consisting of this two.

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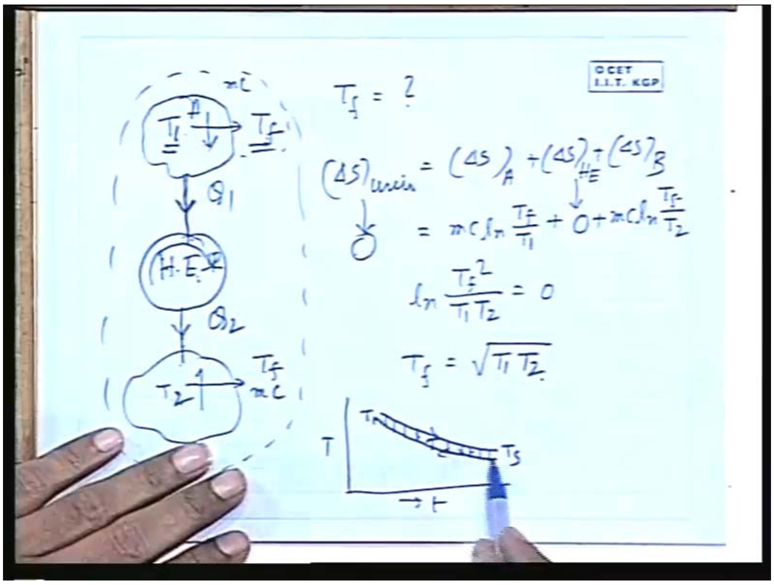

But if they are connected by a heat engine and this heat engine is reversible heat engine, then what happens?

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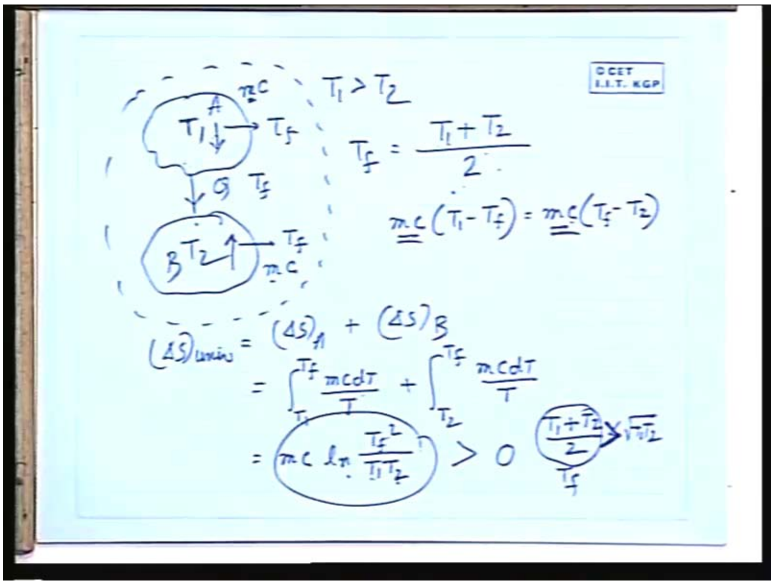
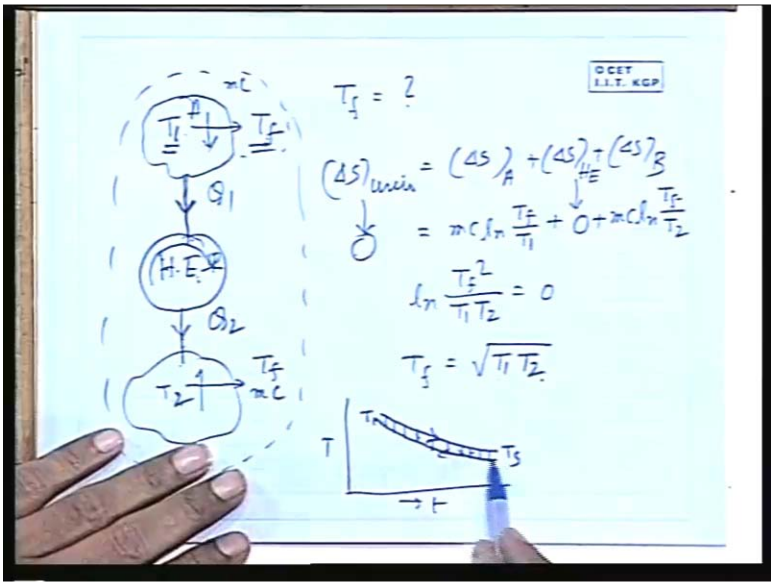


So, the concept is that two finite bodies at different temperatures connected by a diathermic wall that is an irreversible connection that means the transport process that means the heat transfer will take place. It is an irreversible process.

(Refer Slide Time: 40:14)



But these two bodies can exchange heat via some third body not directly in a reversible manner that means they can be connected in a reversible manner via a third body that is a reversible heat engine which takes heat from this T_1. Let Q_1 is the heat taken and Q_2 is the heat rejected. Now what is $Q_{1,}$ it is not constant because T_1 is changing its temperature that means when heat will be taken from this system, it goes to a temperature T_f.

Automatically T_1 temperature is going down, similarly this temperature T_2 is going up and engine will automatically stop when a common temperature, there will be an opportunity when temperature will be same then engine will be stopped, because, engine cannot operate according to the second law of thermodynamics, because, until and unless there is a temperature difference, a heat engine cannot operate. Heat engine cannot deliver work, taking heat from reservoir of single fixed temperature.

Therefore, there will be a common temperature where it is stopped and this variation of temperature from T_1 to T_f by a finite body does not tell that the reversible heat transfer will not be there. Then we can consume a reversible heat transfer with a varying temperature as I have told earlier. So, we can consume up with a reversible heat transfer to the heat engine, the heat addition and heat rejection, in spite of the fact the system is finite where the temperatures are changing.

Now question comes, what is the value of this final temperature T_f? This can be found out from the entropy principle that means the same principle as I have discussed that means let us consider this as the universe that means delta $S_{universe}$, let this T_1 is A, so delta S_A plus delta $S_{heat\ engine}$ plus delta $S_{B.}$

Similar way, we can find out delta S_A is mc ln T_f by T_1 plus this delta $S_{heat\ engine}$ is as usual 0 and this delta $S_B$is mc ln T_f by T_2 and if delta $S_{universe}$ is a reversible engine, it is 0, otherwise, it is very difficult to find out. If it is a reversible engine, it is 0 so which gives ln T_f^2 by T_1T_2 is 0. T_f is equal to square root of T_1 T_2 (Refer Slide Time: 42:42 min).Then we see an important conclusion that when they are connected by a reversible heat engine their common temperature where the process naturally stops is the geometric mean of the two provided their heat capacities are same.

[Conversation between Student and Professor- Not audible ((00:42:56 min))]

Engine reversible, the heat addition processes everything is reversible because this is a concept of infinite reservoirs. As we consider this is changing from T_1 to T_f, the working fluid or the working system also undergoes that way that always there is an infinite small temperature difference from which the heat is transferred. That I discussed many times. So, that can be considered always, that it is not that a finite system changes its temperature as it gives heat and at the same time the working fluid of the heat engine changes, its temperature as it takes heat means an irreversible process. It is a very useful concept. I am telling you.

So it is not that always for a reversible heat addition, there has to be a thermal reservoir at fixed temperature and working fluid, we also have a fixed temperature and they are equal in exact ideal case or in an limited case, their infinite small difference that is not correct.

For our initial understanding, we do like that. It may so happen that the reservoir is the finite system whose temperature is changing, at the same time, the working system in a heat engine also a finite system where the temperature is changing so that both heat addition and heat rejection process by the working system, the temperature of the working system changes and also the temperature of the thermal reservoir changes, but also we can conceive reversible heat transfer by considering infinite type of reverses.

I will explain that for example, in this case if we want to know that when T_1 to T_f that means its temperature T_1 comes to T_f (Refer Slide Time: 44:31 min). So, this is the way the temperature changes with time, for example, for this finite system and the heat engine system also temperature changes like that. That heat always takes heat with infinite small temperature differences and heat changes T_1 to T_f and heat also T_f to T_1 (Refer Slide Time: 44:56 min). So, there is a change like that.

It is always in contact with a reservoir or that body when its temperature is infinite small difference from the temperature of the working system.

So this way we can conceive. These are the concept because thermodynamics does not contain big differential equations. It is very small algebraic steps, but while doing so, we have to have the concept clear then only we get the full satisfaction otherwise we may come up to a answer which is correct, but this is the concept.

Very good, I am happy that you have asked this how it can be measured.

So this is an irreversible. So in that case, I can put delta $S_{universe}$ 0 and I get this very useful relation T_f is equal to square root of T_1 T_2that when the two bodies of same heat capacities are in contact with each other at different temperatures, they come to equilibrium temperature which is arithmetic mean but if they are connected by a reversible heat engine, they come to equilibrium temperature which is the geometric mean of these 2.

Please.

[Conversation between Student and Professor - Not audible ((00:45:57 min))

The working fluid inside the reversible heat engine is changing its temperature [ ]]

That is in one process, but it undergoes different processes and comes to the same end point. So, it is a continuous process.

[After completion of one process does not come to the same point? Conversation between Student and Professor - Not audible ((00:46:15 min))]

Same, exactly, that is the thing heat engine operates and it stops, it has to complete a cycle. It cannot complete in between. Do not unnecessarily complicate it. You are correct that heat engine naturally stops when the heat engine stops means it has completed certain number of thermodynamic cycles. Not like that, it stops like mechanical machines. That will be again clear afterwards, just at any point that is stopped and it is not completed cycle, there is a net displacement laid, it is not like that mechanics thing. So it is always executing a thermodynamic cycle. So long work will be there, it has to undergo a thermodynamic cycle. So there has to be a thermodynamic cycle always so that delta S_{HE} is 0.

Good, I appreciate your questions.

Then it is alright. Please.

[Conversation between Student and Professor - Not audible ((00:47:03 min))]

Please sit down and ask

[Conversation between Student and Professor - Not audible ((00:47:04 min))]

What is the heat capacities are not equal, how do you prove [ ]? So, then you can prove that is a little complicated algebraic step that is left as an exercise to you. Very good.

Heat capacities are not equal for both the cases that are left as an exercise. You show it to me in the next class. You do it. There is no thermodynamics any. Thermodynamics is over that is more algebraic steps so only some algebraic manipulations then the rearrangements are there. So, there is little bit algebraic, not thermodynamics that you do it, but in the simple case, I am proving it to clear the concepts. Next, what I like to do is that two very important property relations. Here also confusion is there with many people I think it will not be there for you.

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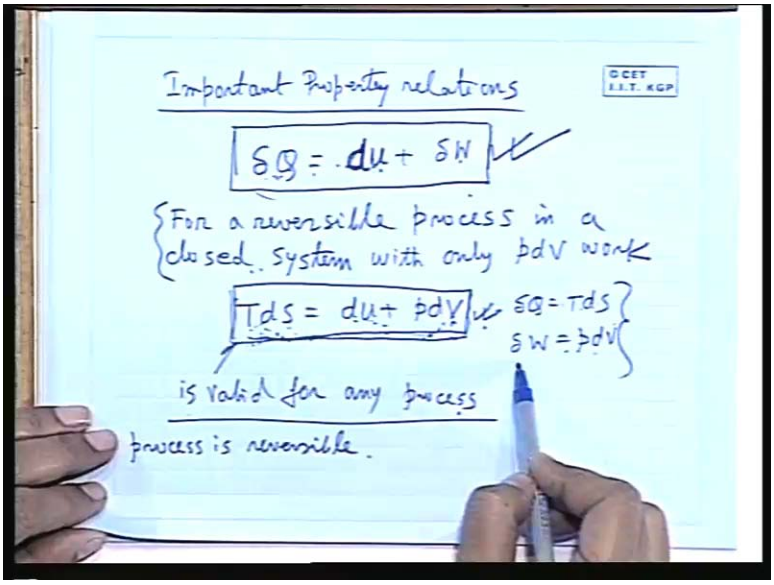

Important Property relations

OCET I.I.T. KGP

$$\boxed{\delta Q = du + \delta W}$$

For a reversible process in a closed system with only pdV work

$$\boxed{Tds = du + pdV} \quad \left.\begin{matrix}\delta Q = Tds \\ \delta W = pdV\end{matrix}\right\}$$

is valid for any process

process is reversible.

Now recall the first law of thermodynamics, let us recall delta Q is equal to delta u or du plus delta W for a closed stationery system, u is the internal energy that is the intermolecular energy. So there is no restriction so far in this first law of thermodynamics as far as reversibility and irreversibility are concerned.

There may be irreversibility and at the same time there is no such condition imposed what should be this work transfer. This may be many types of work transfer. There may be displacement work which may be irreversible displacement work even not pdV work. There may be magnetic work, there may be paddle wheel work which is highly irreversible work. There may be electric work. So, there may be number of work transfers. Heat transfer, of course, is only one type. Heat transfer is defined as it is that energy transferred because of the temperature difference and du is the change in internal energy. So this is the first law that is nothing, but the law of conservation of energy.

Now, if I write this law for a reversible process in a closed system, this is already there in a closed or stationary system where there is no other movement so that change in internal energy is only intermolecular energy, there is no change in kinetic energy or potential energy, in a closed system with only pdV work that means only displacement work under the reversible conditions. Then what is the expression? The expression is Tds is equal to du plus pdV because delta Q is Tds and delta W is pdV. Now we see that this delta Q is equal to du plus delta W is the first law where these two, delta Q and delta W, are path functions, their difference is the point function that is the precise outcome of the first law. But for a reversible process, when I write this, Tds is equal to du plus pdV then this entire equation relates only the properties, state variables. So, this relationship is now treated as property relations or we can treat these equations as important property relation equations for any process. This equation is valid for any process because this equates only the properties that mean the change of state variables, but where is the concept?

Sometimes we are confused that this was defined with respect to a reversible process. A reversible process was used as a tool to define this from the first law of thermodynamics, but when we define this (Refer Slide Time: 51:24 min) then we delete this two that means we do not use these two lines tell that this is valid as a property relation for any process.

The concept is that when the process is reversible and the work done is pdV work, these two are synonymous, they are not independent equations. These two equations are synonymous that means we can tell the Tds is equal to du plus pdV is another version of the first law.

If I ask that Tds is du plus pdV, under what condition this is a first law of thermodynamics? It has to be a closed system, a reversible heat transfer and pdV work. In that case, there is no difference between these two equations, but for any other process which is not a reversible process, these two equations are independent because for any other process is Tds. They have no relationship with delta Q.

So pdV is pdV, pressure times dV. So it has got no relationship with delta W. Therefore, it will remain as it is that means it relates Tds, du, pdV that means Tds is du plus pdV. So, these two are not same and this is the first law of thermodynamics.

Therefore, Tds is du plus pdV is a property relation valid for any process and delta Q is du plus delta W is a first law of thermodynamics. So, under reversible process these two equations are same. They are not independent, but for an irreversible process these two equations are independent. This delta Q is du plus delta W is precisely the first law and in that case for an irreversible process, this Tds is du plus pdV is the property relation. Tds not equals to delta Q. pdV not equal to delta W, for an irreversible process.

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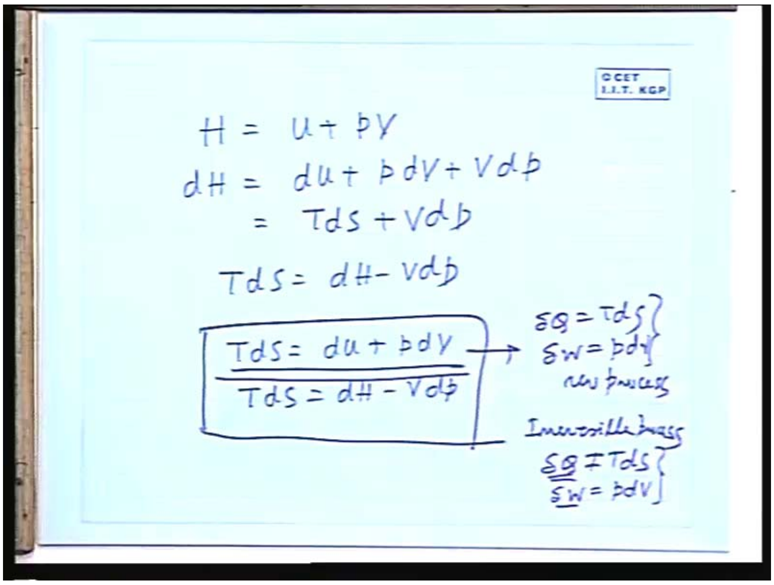

OCET I.I.T. KGP

$H = u + pV$

$dH = du + pdV + Vdp$

$= Tds + Vdp$

$Tds = dH - Vdp$

$$\boxed{\begin{array}{c} Tds = du + pdV \\ \hline Tds = dH - Vdp \end{array}}$$

$\left.\begin{array}{l}\delta Q = Tds \\ \delta W = pdV\end{array}\right\}$ rev process

Irreversible process

$\left.\begin{array}{l}\delta Q \neq Tds \\ \delta W = pdV\end{array}\right\}$

Now another important relation, H is u plus pV. We know. So, we can write dH is equal to du plus pdV plus Vdp.

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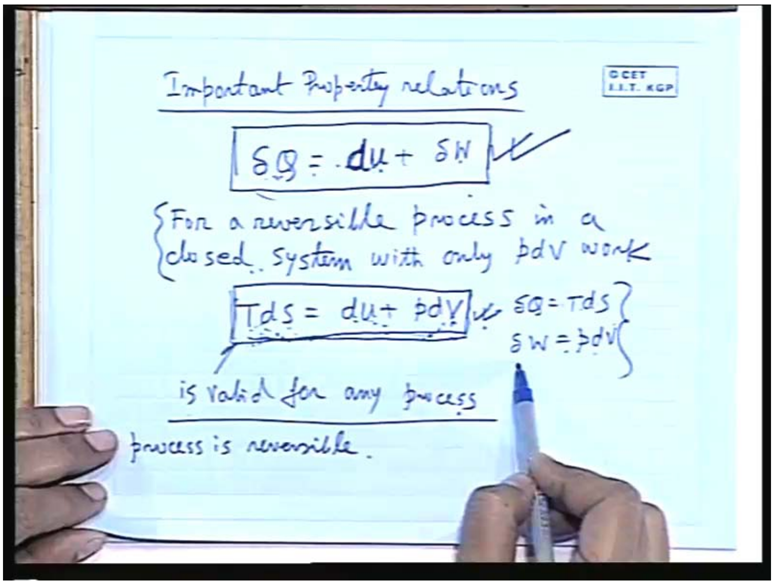

Important Property relations

OCET I.I.T. KGP

$$\boxed{\delta Q = du + \delta W}$$

For a reversible process in a closed system with only pdV work

$$\boxed{Tds = du + pdV}$$

$\left.\begin{array}{l}\delta Q = Tds \\ \delta W = pdV\end{array}\right\}$

is valid for any process

process is reversible.

Now du plus pdV for any process, as I have told, equal to Tds.

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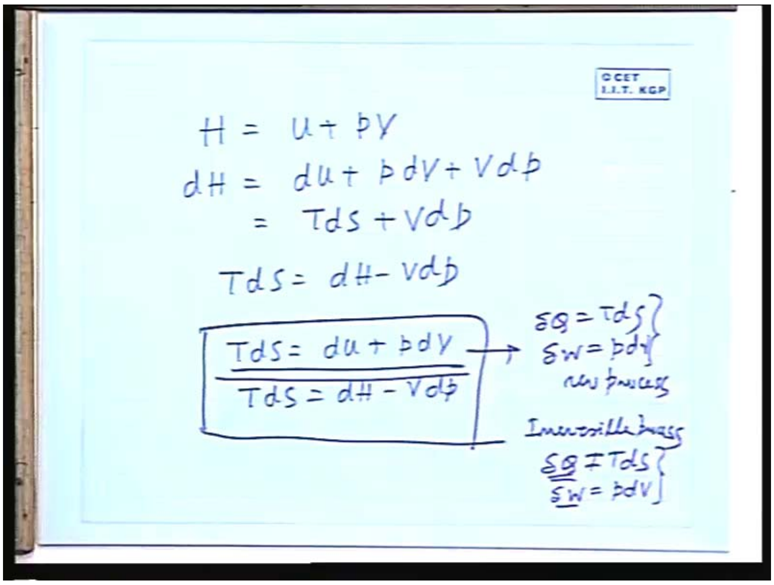

OCET
I.I.T. KGP

$$H = u + pV$$

$$dH = du + pdV + Vdp$$

$$= Tds + Vdp$$

$$Tds = dH - Vdp$$

$$\boxed{\begin{array}{c} \underline{Tds = du + pdV} \\ \hline Tds = dH - Vdp \end{array}} \rightarrow \left.\begin{array}{l} \delta Q = Tds \\ \delta W = pdV \end{array}\right\}$$

rev process

Irreversible process

$$\left.\begin{array}{l} \underline{\delta Q} \neq Tds \\ \underline{\delta W} = pdV \end{array}\right\}$$

So, I can write TdS plus Vdp. So there is another relation TdS is dH minus Vdp. Therefore I have got two relations, TdS is du plus pdV and TdS is dH minus Vdp. These two relations (Refer Slide Time: 53:50 min) are the property relations for any process, reversible or irreversible, but for the reversible process, this particular equation, Tds is equal to du plus pdV is nothing, but the first one.

Because in that case, delta Q is TdS and delta W is pdV for a reversible process, but for an irreversible process, delta Q not equals to Tds. Tds is Tds and delta W, that means Tds and pdV can never be equated with delta Q and delta W. They have no relations. Only Clausius inequality I can tell that Tds is more than delta Q, that only know and at the same time, from my understanding of reversible irreversible process also, I can tell delta W is more than pdV because in an irreversible work transferred because of the displacement is more than the pdV.

If we equate pdV work for a piston displacement and actual case if we displace the piston with the finite time and measure the work done by any dynamometer, we will see that delta W is more than pdV.

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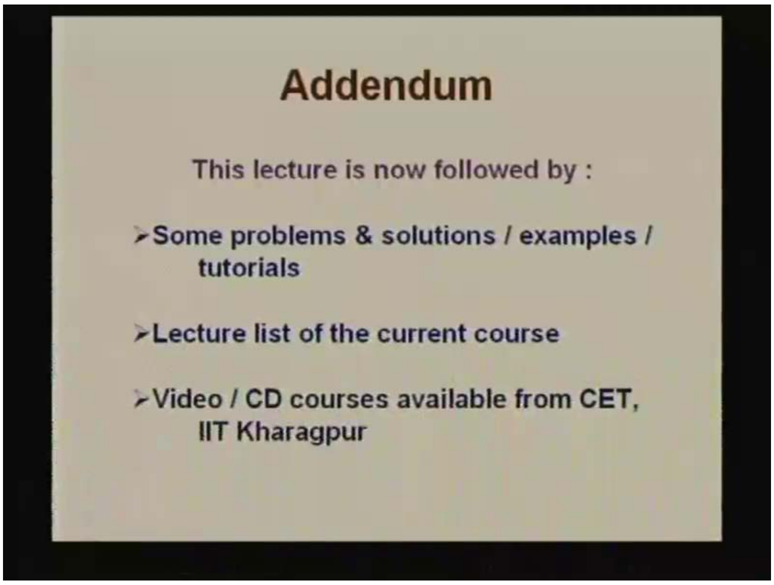

Addendum

This lecture is now followed by :

- Some problems & solutions / examples / tutorials
- Lecture list of the current course
- Video / CD courses available from CET, IIT Kharagpur

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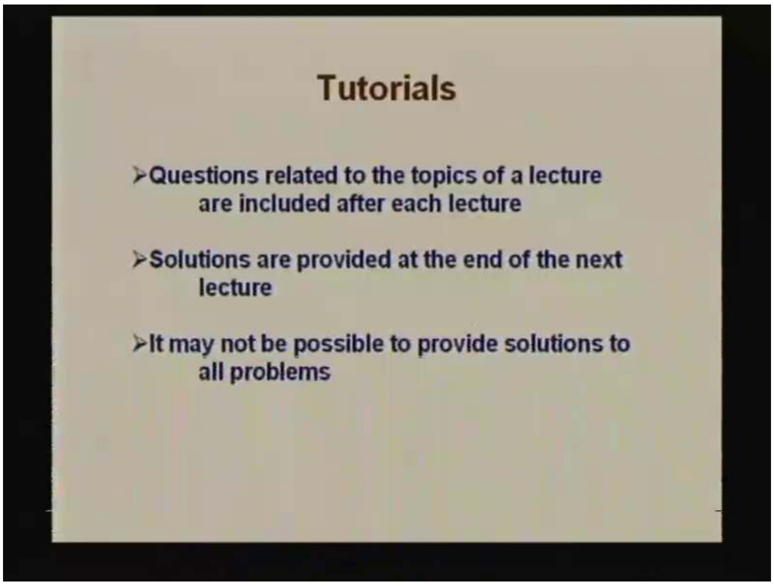

Tutorials

- Questions related to the topics of a lecture are included after each lecture
- Solutions are provided at the end of the next lecture
- It may not be possible to provide solutions to all problems

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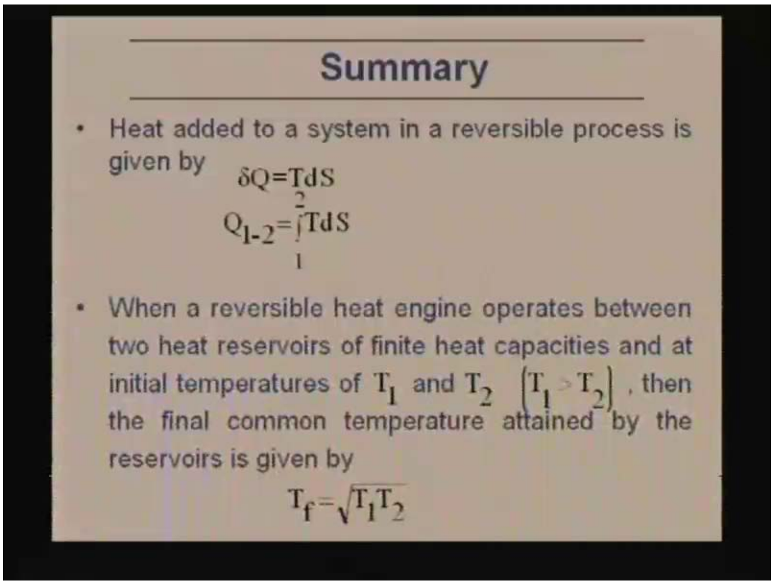

Summary

- Heat added to a system in a reversible process is given by

$$\delta Q = TdS$$

$$Q_{1-2} = \int_1^2 TdS$$

- When a reversible heat engine operates between two heat reservoirs of finite heat capacities and at initial temperatures of T_1 and T_2 $(T_1 > T_2)$, then the final common temperature attained by the reservoirs is given by

$$T_f = \sqrt{T_1 T_2}$$

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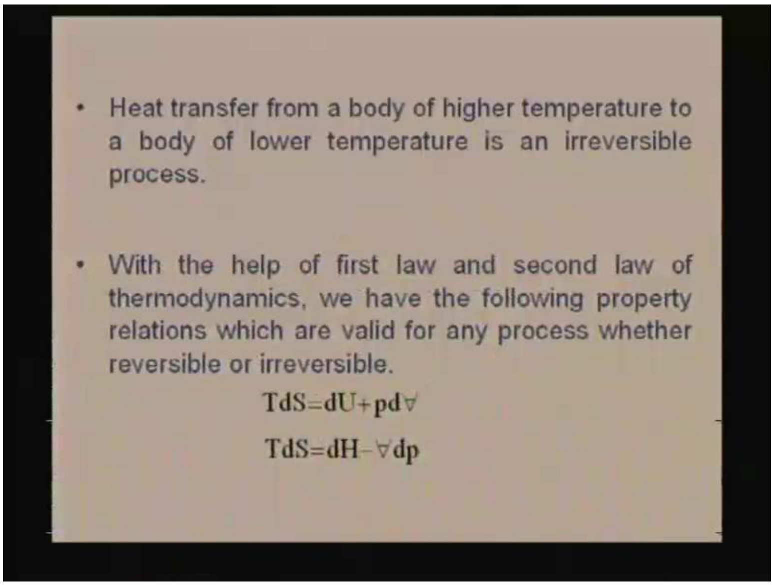

- Heat transfer from a body of higher temperature to a body of lower temperature is an irreversible process.

- With the help of first law and second law of thermodynamics, we have the following property relations which are valid for any process whether reversible or irreversible.

$$TdS = dU + pd\forall$$

$$TdS = dH - \forall dp$$

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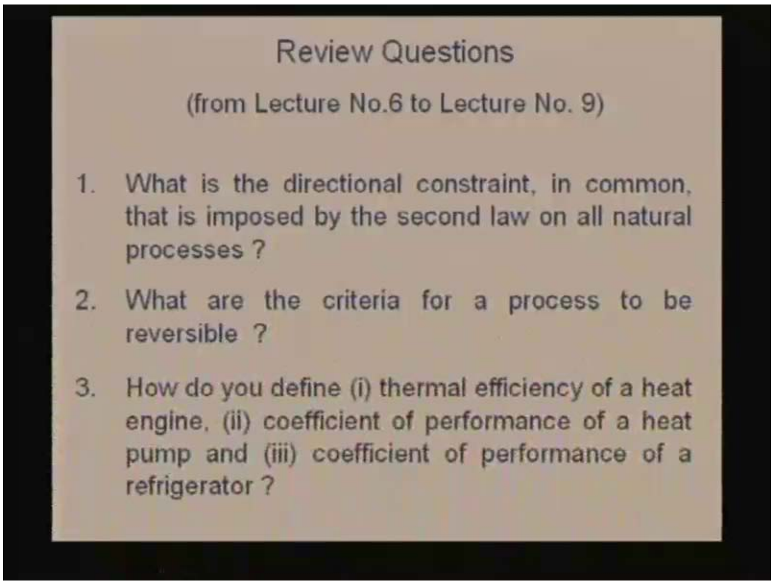

Review Questions

(from Lecture No.6 to Lecture No. 9)

1. What is the directional constraint, in common, that is imposed by the second law on all natural processes ?
2. What are the criteria for a process to be reversible ?
3. How do you define (i) thermal efficiency of a heat engine, (ii) coefficient of performance of a heat pump and (iii) coefficient of performance of a refrigerator ?

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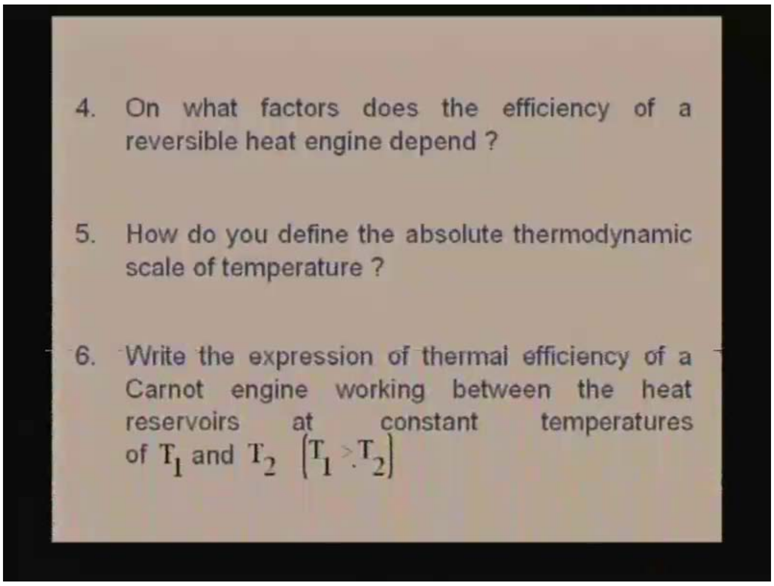

4. On what factors does the efficiency of a reversible heat engine depend ?
5. How do you define the absolute thermodynamic scale of temperature ?
6. Write the expression of thermal efficiency of a Carnot engine working between the heat reservoirs at constant temperatures of T_1 and T_2 $(T_1 > T_2)$

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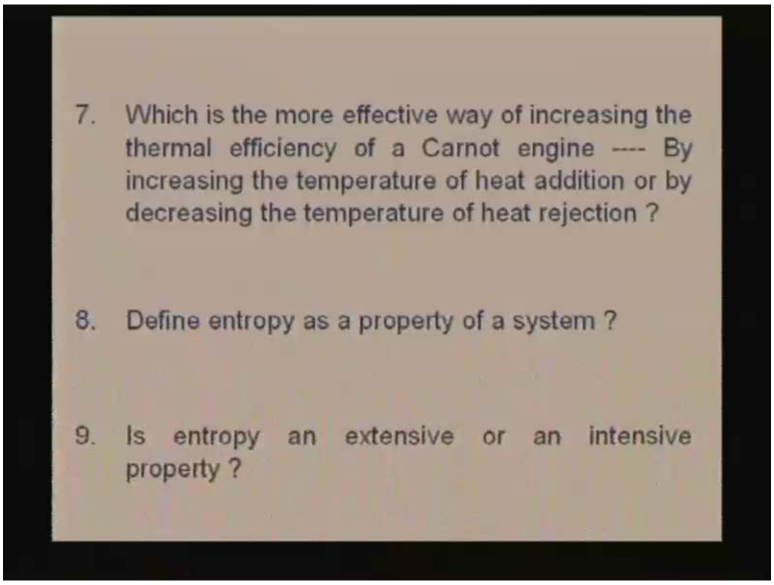

7. Which is the more effective way of increasing the thermal efficiency of a Carnot engine ---- By increasing the temperature of heat addition or by decreasing the temperature of heat rejection ?

8. Define entropy as a property of a system ?

9. Is entropy an extensive or an intensive property ?

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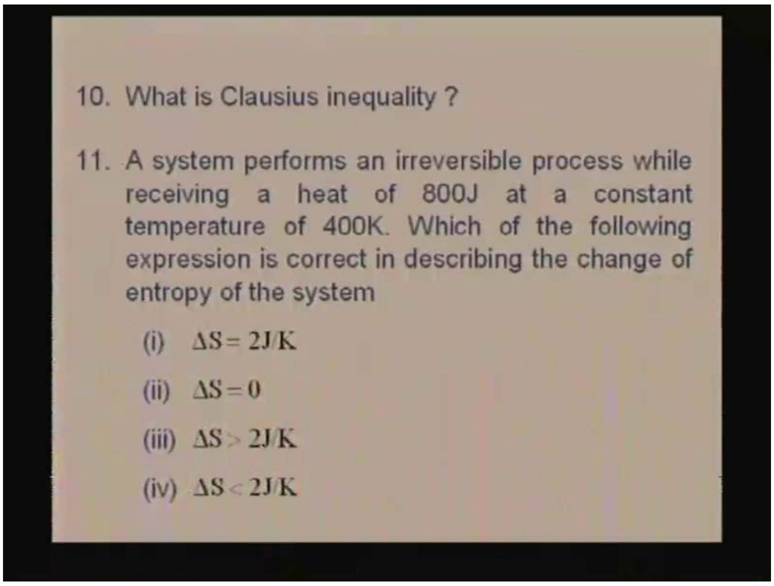

10. What is Clausius inequality ?

11. A system performs an irreversible process while receiving a heat of 800J at a constant temperature of 400K. Which of the following expression is correct in describing the change of entropy of the system
   (i) $\Delta S = 2J/K$
   (ii) $\Delta S = 0$
   (iii) $\Delta S > 2J/K$
   (iv) $\Delta S < 2J/K$

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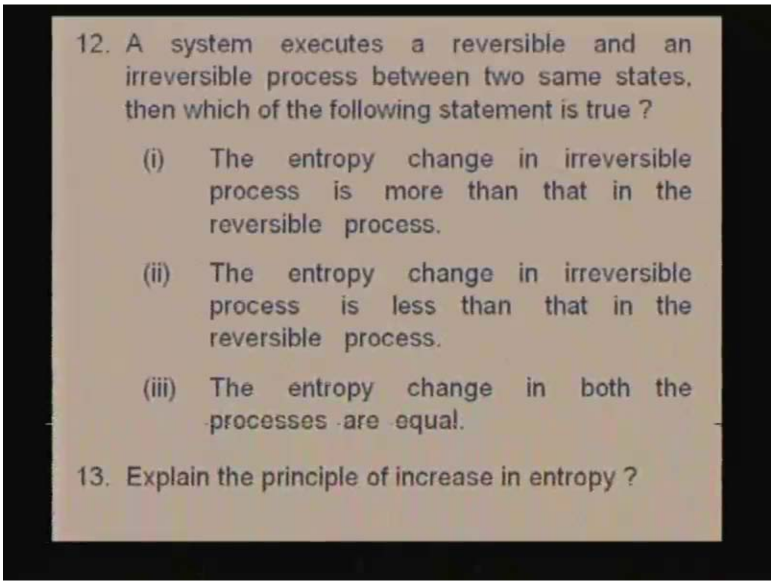

12. A system executes a reversible and an irreversible process between two same states, then which of the following statement is true ?
    - (i) The entropy change in irreversible process is more than that in the reversible process.
    - (ii) The entropy change in irreversible process is less than that in the reversible process.
    - (iii) The entropy change in both the processes are equal.

13. Explain the principle of increase in entropy ?

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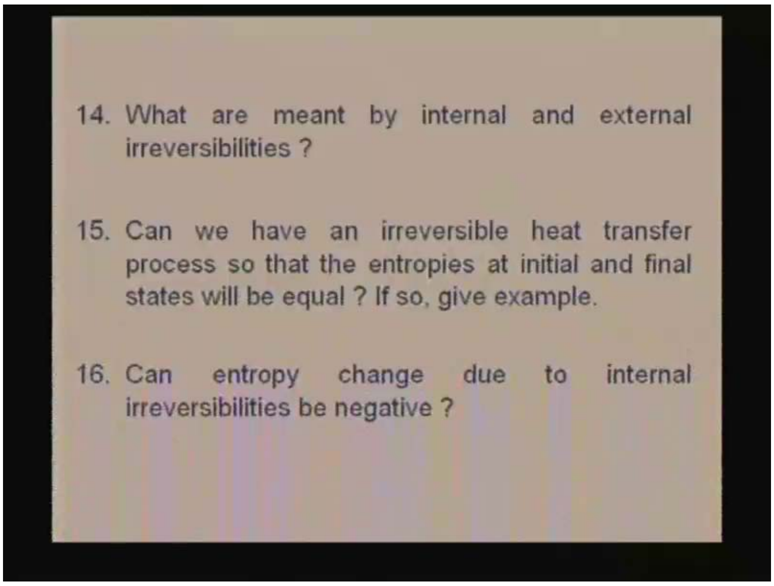

14. What are meant by internal and external irreversibilities ?

15. Can we have an irreversible heat transfer process so that the entropies at initial and final states will be equal ? If so, give example.

16. Can entropy change due to internal irreversibilities be negative ?

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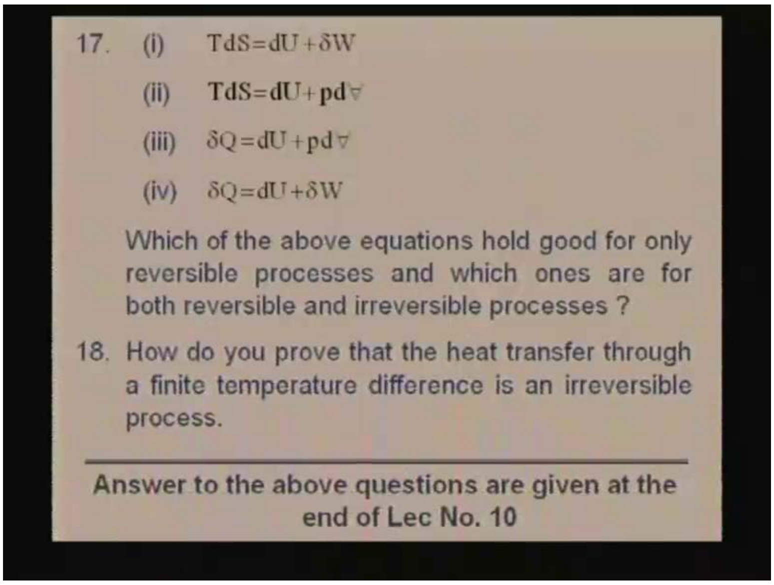

17. (i) $TdS = dU + \delta W$

(ii) $TdS = dU + pd\forall$

(iii) $\delta Q = dU + pd\forall$

(iv) $\delta Q = dU + \delta W$

Which of the above equations hold good for only reversible processes and which ones are for both reversible and irreversible processes ?

18. How do you prove that the heat transfer through a finite temperature difference is an irreversible process.

Answer to the above questions are given at the end of Lec No. 10