Basic Thermodynamics

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Lecture - 08

Second Law and its Corollaries – III

Good morning, I welcome you to this session of thermodynamics. In the last session, we were discussing about the entropy - how the entropy was defined? We first recognized that the integral of delta Q divided by T for a reversible cycle is 0, where delta Q is an infinite small amount of heat added to a system in a process and T is the temperature at which the heat is added and the cyclic integral over a reversible cycle is 0.

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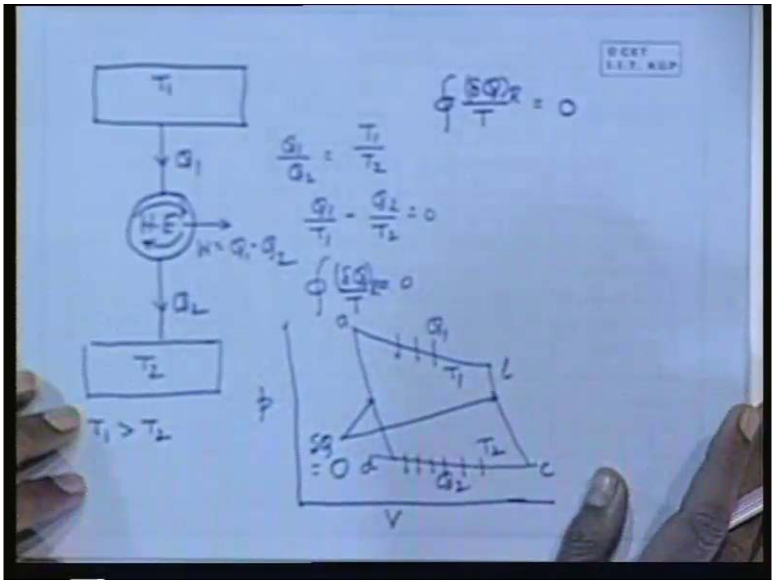

If we write this, last time there was a confusion that I used d, that is not a perfect differential that to represent an infinite small amount. Since Q is not a point function, better write delta Q which I used earlier, divided by T, over a reversible cycle. That means, either you write here or you write here R, that means over a reversible cycle is 0; cyclic integral is 0 that we recognized.

I again repeat, how did we do that? We took a reversible heat engine, HE, we did it like this, which takes heat from a thermal reservoir at temperature T_1 in absolute thermodynamic scale of temperature which takes heat Q_1. Similarly, which rejects heat Q_2 to a thermal reservoir at a temperature T_2, where T_1 is greater than T_2 - just recapitulation of the earlier thing and obviously delivering work is equal to Q_1 minus Q_2.

If it is a reversible engine, then by definition of the temperatures in absolute thermodynamic temperature scale, we can write that Q_1 by Q_2 is equal to T_1 by T_2. So that Q_1 by T_1, one can write is equal to minus Q_2 by T_2, which give this algebraic sum or cyclic integral as we tell that delta Q divided by T is equal to 0 provided this is a reversible cycle; this we proved. So this particular engine where the heat is added at a constant temperature, that means, the system which executes the cyclic process undergoes a reversible isothermal process of heat addition. Similarly, reversible isothermal processes of heat rejection which can be represented as a Carnot cycle, as I told in a pressure volume diagram like this (Refer Slide Time: 03:40 min). This block diagram of the engine can be represented as a cyclic diagram in pV coordinates like this.

These are the process abcd. In this process, heat is being added - Q_1 and substantially the temperature remains constant. So an isothermal process of heat addition and rejections, T_1 and T_2, this can be represented. These two processes are adiabatic process (Refer Slide Time: 04:09 min), where delta Q is equal to 0.

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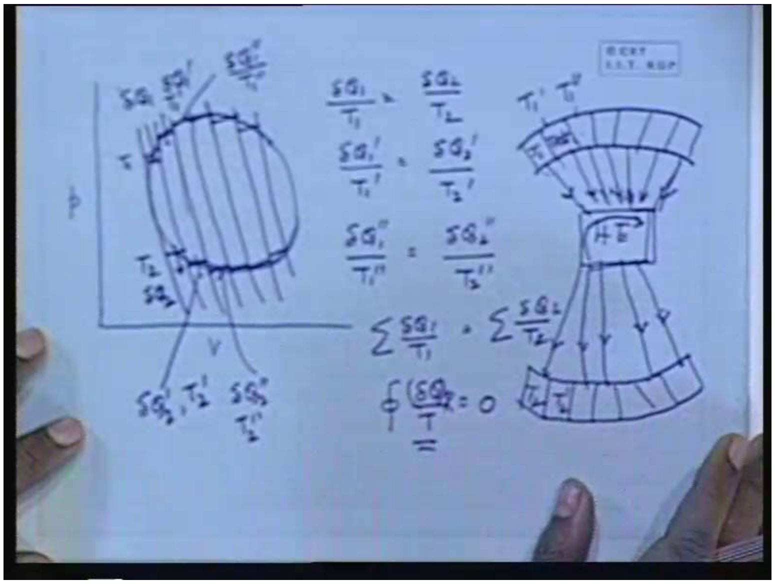

So this proof, cyclic integral of delta Q_R by T is equal to 0, can be made also, very simple logic, for an engine which is not taking heat at an isothermal condition. In other way we can tell that in any thermodynamic coordinate, let us consider pV, any closed loop we can consider as a thermodynamic cycle, where heat is being added. For example; this part of this cycle heat is being added (Refer Slide Time: 04:41 min) and some other part of the cycle, heat is being rejected.

Any arbitrary closed loop can be thought of a cycle; it is not necessarily always the temperature has to be constant in heat addition and heat rejection. So we can prove this way, this is one another very important thing that any closed cycle, reversible cycle, can be divided into a number of elementary Rankin cycle. How? We can construct a number of adiabatic processes, very closely spaced like this (Refer Slide Time: 05:14 min) and similarly number of isotherms like this. These are the isotherms (Refer Slide Time: 05:27 min). We can divide this closed loop into a number of elementary Carnot cycles by drawing number of adiabats and number of isothermals closely space, so that this becomes an elementary Carnot cycle where we can consider heat is being taken. Let the temperature of this is T_1 (Refer Slide Time: 05:47 min), this is a small part where the temperature can be considered as constant T_1; that is, the temperature at this location and let the heat taken is delta Q_1. Similarly, this temperature is T_2 and heat rejected is delta Q. Again, for this elementary Carnot cycle (Refer Slide Time: 06:12 min), let the heat taken is delta Q_1 dash and the temperature is T_1 dash. Similarly, for this one (Refer Slide Time: 06:21 min) the heat rejected is delta Q_2 dash and the temperature is T_2 dash.

Similarly, we can consider another elemental cycle here, (Refer Slide Time: 06:31 min), where the heat addition is delta Q_1 double dash and the temperature T_1 double dash. This is the temperature here (Refer Slide Time: 06:42 min). Similarly, here also the heat rejected is delta Q_2 double dash and the temperature T_2 double dash and so on; infinite number of elemental Carnot cycle. For each cycle, it is a reversible cycle, because, Carnot cycles we can write delta Q_1 by $T_{1,}$ for example: this one here, is equal to delta Q_2 by T_2, delta Q_1 dash by T_1 dash, and the next elementary cycle, is equal to delta Q_2 dash by T_2 dash.

Similarly, delta Q_1 double dash by T_1 double dash, simple logic, is equal to delta Q_2 double dash by T_2 double dash. So, if we add up, then we will get sigma of delta Q_1 divided by T_1 is equal to sigma of delta Q_2 divided by $T_{2.}$ This is reversible cycle. So, this I write by the definition of the temperature in absolute thermodynamic scale, so that cyclic integral of delta Q.

So ultimately, I can prove for any cycle, not necessarily the temperature of heat addition or rejection has to be constant, but if it is a reversible cycle the cyclic integral delta Q by T, if it is reversible, is 0; this we have proved. While, cyclic integral of any parameter is 0 that parameter can be expressed as a differential of a point function. Now before that, we can tell this can be visualized in practice by a block diagram. If this be the heat engine (Refer Slide Time: 08:18 min), I am not drawing it a circular as I did earlier. Then we can consider an infinite number of small reservoirs as I already discussed that earlier…. these are the thermal reservoirs - T_1 plus Dt_1 that is T_1 dash, that is T_1 double dash; all are infinite small difference with each other. That means number of reservoirs; the working fluid or the working media in the heat engine, in the process of heat addition has to be in contact with infinite reservoirs.

Similar is the case, when it rejects the heat we have to conceive of an infinite number of thermal reservoirs, so that the working fluid or the working system will be in contact with all the reservoirs in succession for a reversible heat rejection. Why? Because, always the heat addition or heat rejection process, that means heat transfer process, should take place under an infinite small temperature difference for a reversible heat transfer process to be accomplished.

So this is the conception (Refer Slide Time: 09:31 min). So with this concept one can draw a closed loop and can divide it into a number of elemental cycles; that means, one takes heat from this reservoir and rejects heat in this reservoir. Another one is T_1 dash T_2 dash; we can divide the engine into a number of elemental Carnot cycles and we can prove this thing. Therefore, what is our use is it is not of much importance that how you prove it, this is logic.

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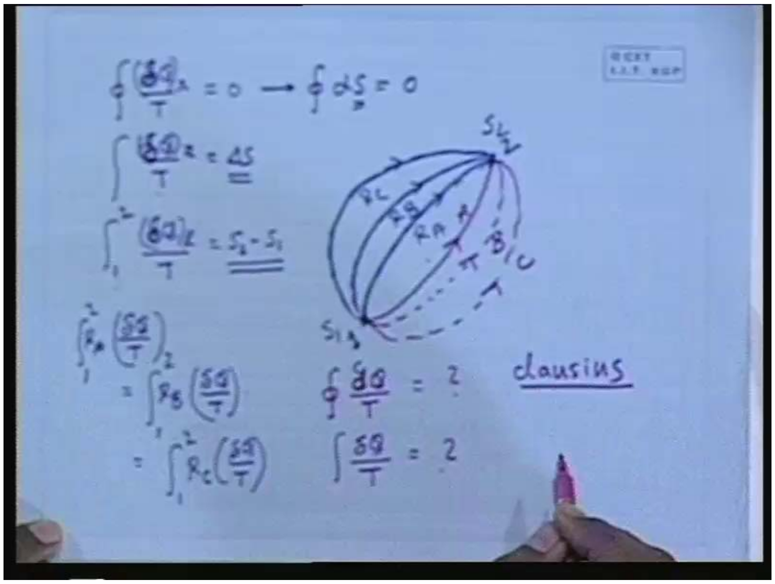

$$\oint \left(\frac{\delta Q}{T}\right)_R = 0 \longrightarrow \oint dS = 0$$

$$\int \left(\frac{\delta Q}{T}\right)_R = \underline{\underline{\Delta S}}$$

$$\int_1^2 \left(\frac{\delta Q}{T}\right)_R = \underline{\underline{S_2 - S_1}}$$

$$\int_1^2 R_A \left(\frac{\delta Q}{T}\right) = \int_1^2 R_B \left(\frac{\delta Q}{T}\right) = \int_1^2 R_C \left(\frac{\delta Q}{T}\right)$$

$$\oint \frac{\delta Q}{T} = ? \qquad \int \frac{\delta Q}{T} = ?$$

The most important thing is the information that means the cyclic integral of delta Q by T in a reversible process is 0; which means that the integral of delta Q by T in a reversible process is a point function; this is equal to delta S (Refer Slide Time: 10:17 min).

We can write this as cyclic integral of delta Q_R by T is 0, as cyclic integral of dS is equal to 0, d is of differential of point function and S, is entropy... So that if we define two states which it is connected by a reversible process then that becomes is equal to S_2 minus S_1. The integral of delta Q by T, in any reversible process connecting two fixed states are dependent on state points - S_2 minus S_1. It does not depend on the type of the reversible processes or the nature of the reversible processes, which we can show it like this - if there are two states, for example, 1 and another is 2. (Refer Slide Time: 11:08 min) If we connect them - 1 and 2 by – by different reversible processes, let the first one is R_A, let the second one is reversible process R_B and the third, reversible process R_C. All are accomplished like that. Then what is the information we get? delta Q_R by T is the change of a point function; through 1 and 2, it is S_2, S_1. S_2 is fixed with this point; it is the state variables S_1. One can write this 1 to 2 via R_A. here dQ or delta Q. I am writing delta Q, better you follow delta Q. So that delta Q divided by T is equal to integration of 1 to 2 via the process R_B delta Q divided by T, all reversible process. I am not writing R again, is equal to 1 to 2 R_C delta Q divided by T.

The integration of delta Q divided by T, if it is performed through a reversible process, it does not depend upon the type of the reversible process, because, it is a point function, but process has to reversible. If there are a number of reversible processes connecting between the same state points, then the integral delta Q divided by T via the reversible process, by any of the reversible process, will remain same and that is defined as the change of entropy between the two states. (Refer Slide Time: 12:50 min)

Now the question is if I concede number of irreversible processes on the other hand, then what happens? For example, if we consider a number of irreversible processes, reversible processes I can show by firm line (Refer Slide Time: 13:09 min); number of irreversible processes which should be shown as dotted line. First one, I draw like that does not matter.

This red one is the irreversible processes A, B and C, these are the irreversible paths; in that case, the question comes, how do you define entropy? Entropy definition is [ ] that is this equates the delta Q divided by T by a reversible process; this does not equate the change of entropy via the quantity delta Q divided by T by an irreversible process; that is number one concept. Only this integral delta Q divided by T via a reversible process is a point function. Therefore, the entropy change between two points is defined in terms of the heat quantity and the temperature in this manner via only a reversible process. This is because for all reversible processes this quantity remains constant (Refer Slide Time: 14:03 min) and this gives the definition of entropy. Is this clear?

Now the question comes: what is the value of cyclic integral of delta Q by T for an irreversible process? I am not writing R that means for an irreversible process. [I am writing delta Q by T, for an irreversible process.] Now the question comes that, what is this value of a cyclic process for an irreversible cycle? Before going to prove, I must first tell you the information; the answer to this question was given by Clausius and is known as Clausius inequality.

What is the value of the counterpart quantity delta Q divided by T over an irreversible cycle? And next, what is the value of this counterpart delta Q divided by T in an irreversible process, not a cycle? What are those things? Are they equal to the counterpart in irreversible process? Or even if they are not equal then what happens? Are they less or greater than the counterpart?

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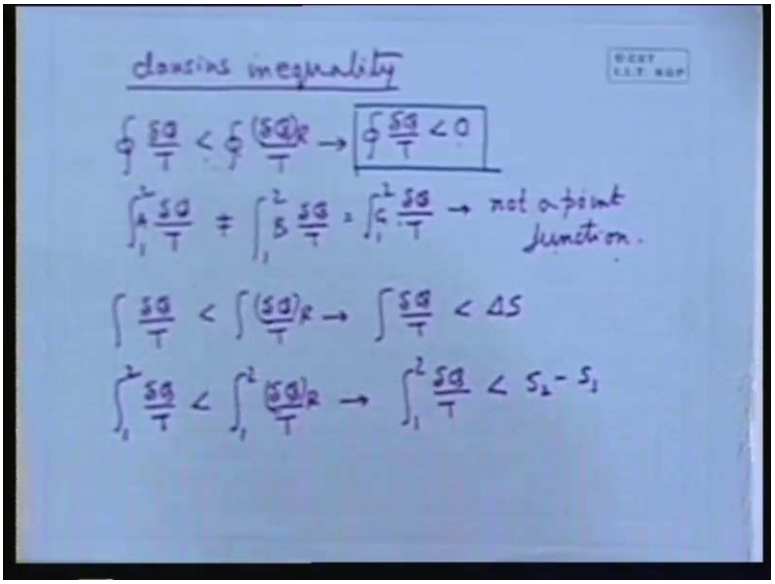

clausius inequality

$$\oint \frac{\delta Q}{T} < \oint \frac{(\delta Q)_R}{T} \rightarrow \boxed{\oint \frac{\delta Q}{T} < 0}$$

$$\int_{1,A}^{2} \frac{\delta Q}{T} \neq \int_{1,B}^{2} \frac{\delta Q}{T} \neq \int_{1,C}^{2} \frac{\delta Q}{T} \rightarrow \text{not a point function.}$$

$$\int \frac{\delta Q}{T} < \int \frac{(\delta Q)_R}{T} \rightarrow \int \frac{\delta Q}{T} < \Delta S$$

$$\int_1^2 \frac{\delta Q}{T} < \int_1^2 \frac{(\delta Q)_R}{T} \rightarrow \int_1^2 \frac{\delta Q}{T} < S_2 - S_1$$

The query to this question was answered by Clausius and is known as Clausius inequality. This Clausius inequality tells that cyclic integral of delta Q divided by T, for an irreversible process, is less than its counterpart for a reversible process; this is the information. First, you take the information, very important - less than cyclic integral - that means, what this leads because this is 0.

So I can write that cyclic integral delta Q divided by T, for any irreversible cycle, for a natural cyclic process, must be less than 0; because this is the cyclic integral of delta Q divided by T for an irreversible process, is 0. Less than 0 means next is that obviously delta Q divided by T for any process it is less than 0; that means it is not equal to 0. This is not a point function, which means that 1 to 2 by process A not equal to 1 to 2 by process B not equal to 1 to 2 by process C.

When it is not 0 either greater or less, it cannot be a point function. This integral is not a point function; integral delta Q divided by T is not a point function, in case of an irreversible process that means it varies from process to process.

In case of a reversible process, this was 0; so this became the point function (Refer Slide Time: 17:18 min). Then, obviously, when this is less than its counterpart, similarly, for a process also delta Q divided by T is less than its counterpart delta Q divided by T in a reversible process, which means that delta Q divided by T - this quantity (Refer Slide Time: 17:38 min) - in any process is less than the delta S, because, this is defined as delta S. For a process connecting points 1 and 2 delta Q divided by T is less than the counterpart of this, for the process connecting the state points 1 and 2, which means, that 1 to 2 delta Q divided by T is less than equal to S_2 minus S_1.

If there are two state points, delta Q divided by T varies from process to process, if they are irreversible process. If they are reversible processes this quantity (Refer Slide Time: 18:17 min) remains the same and that is the definition of entropy change between the two state points.

What is the value of delta Q divided by T for any reversible path? That is less than equal to the change in entropy, that means, less than equal to the corresponding value between the same state points by a reversible path. So this information was furnished by Clausius and it is known as Clausius inequality. I again repeat it that integral delta Q divided by T in an irreversible cycle is less than its counterpart quantity for a reversible cycle. Integral delta Q divided by T for an irreversible cycle is less than its counterpart for a reversible cycle. Therefore, this is less than equal to 0, because, this is integral delta Q by T in a reversible cycle is 0. Therefore, cyclic integral delta Q divided by T for any natural cycle is less than 0. It is very important.

If it is so, then obviously one can prove that delta Q divided by T, for any natural process is less than its counterpart in a reversible process. This means, since this is the definition of change in entropy, delta Q divided by T in an irreversible process is less than the change of entropy. It is more easily visualized if we connect the two state points; then 1 to 2 delta Q divided by T for a natural process or an irreversible process is less than its counterpart by an ideal or reversible process which is nothing but the change in the entropy between the state point. At the same time, automatically, it is a byproduct that these natural processes, this quantity (Refer Slide Time: 19:43 min) varies from process to process or path to path; they are not constant, not a point function. Is it clear?

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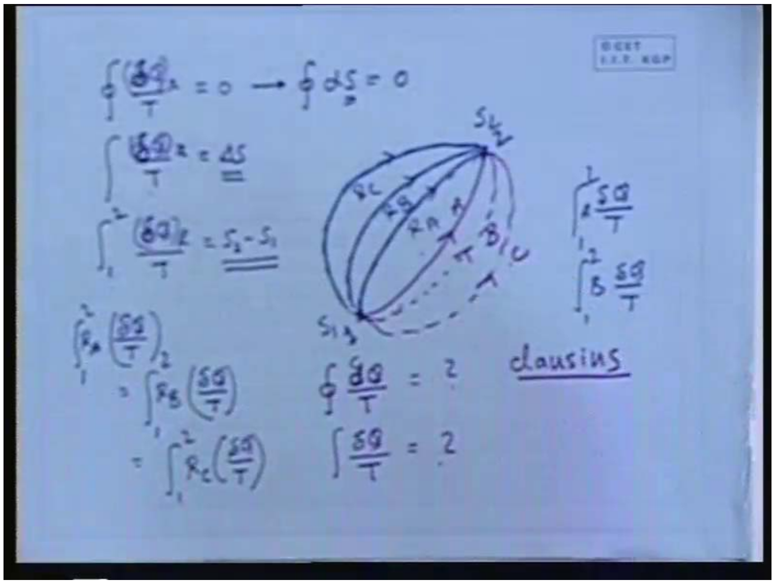

Now I can again come to this. Therefore, if we can consider two classes of process one is a reversible process R_A, R_B, R_C. There are number of reversible process, one category of processes. Another is natural or irreversible processes. Now the quantity delta Q divided by T connecting these two, for path B these are all different. But given the maximum value amongst all these natural processes conceivable should be less than the unique value rendered by all reversible processes connecting the two states; this is defined as the change in entropy that is uniquely specified by all reversible processes.

Whereas the integral delta Q divided by T connecting two state points are varying from process to process, if the processes are natural. The maximum one is still less than the unique value specified by all reversible processes connecting these two state points. Therefore the change of entropy does not depend upon whether the process is reversible or irreversible, or even the process is reversible, what type of reversible process? Because all reversible processes, given the same value of delta Q divided by T and that equals to its change in entropy.

So change in entropy relates heat and temperature only for a reversible process, but not for irreversible process. In irreversible process, only an inequality relationship is known that this quantity, delta Q by T, for any irreversible or natural process is less than the change in entropy of the process connecting the two state points.

Now, next I will go the Clausius inequality proof. Now, how do you prove this Clausius inequality? Again, very simple.

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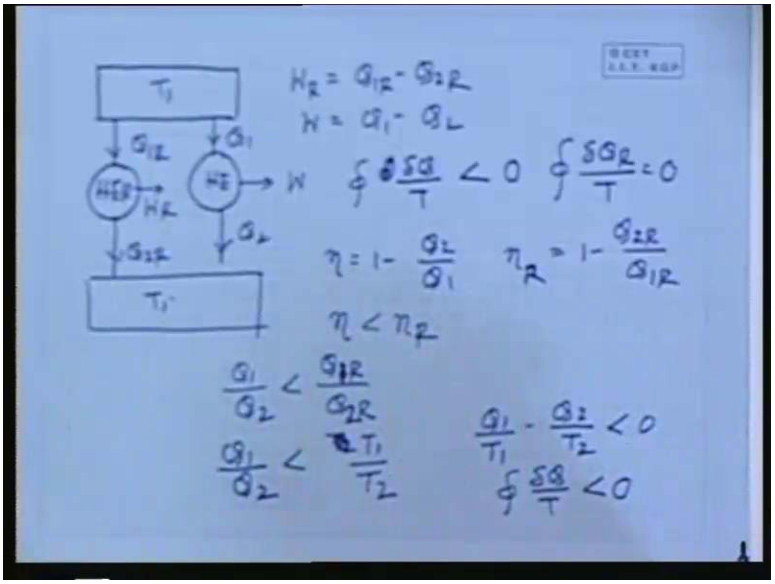

If we take, in the similar way, two heat engines and one is a reversible, HE$_R$ and another one is irreversible, natural, HE and working between the same temperatures. Again, I take the constant temperature. Now the reversible engine, I take Q_{1R} and Q_{2R}; for irreversible engine Q_1 and Q_2. Q_1 may be equal to Q_{1R} or may not be; here, for these two it is not always necessary.

This [developed] W_R which is the difference between Q_{1R} minus Q_{2R} and the irreversible engine is W which is difference between Q_1 minus Q_2. W_R, this always we should write, so that always the first law is being brushed up, is equal to Q_{1R} minus Q_{2R}. It is a good habit of writing everything even if it is not required. W is equal to Q_1 minus Q_2.

So how can I prove here the cyclic integral of delta Q divided by T for this irreversible cycle is less than its counterpart. That means less than 0 because, already I know this has been proved that cyclic integral of delta Q_R by T is 0; it is already proved. So what philosophy or what statement of the second law will I utilize here?

[(Conversation between Student and the Professor Not audible ((00:23:07 min))]

What?

[Conversation between Student and Professor – Not audible ((00:23:09 min))]

Efficiency, Very Good.

So, efficiency of an irreversible engine is less than that of a reversible engine. Very good. So, what is the efficiency of this engine, HE? Efficiency of this engine is 1 minus Q_2 by Q_1, where efficiency of a reversible engine eta$_R$ is what? 1 minus Q_{2R} divided by Q_{1R}. We know that efficiency of this natural engine, HE, is less than eta. So Carnot's theorem, that means eta will be greater than eta$_R$, if we make the reciprocal - Q_1 by Q_2 again will be less than Q_{1R} by Q_{2R}. These are very simple. By the definition of T_1, T_2 in the absolute thermodynamic scale, this is nothing but T_1 by T_2. This Q_{1R} /Q_{2R} (Refer Slide Time: 24:06 min). So, Q_1 by T_1 minus Q_2 by T_2 is less than 0. So, cyclic integral delta Q divided by T is less than 0; very simple proof.

Any question please? What happened?

[Conversation between Student and Professor – Not audible ((00:24:26 min))]

Oh! For this correction, I am sorry for this correction yes.

Q_1 by Q_2, etaR is less than eta that means this quantity, 1 minus Q_2 by Q_1 is greater than this quantity, 1 minus Q_{2R} by Q_{1R}. Again I make the reciprocal so that Q_1 by Q_2 is less than Q_{1R} by Q_{2R}. So Q_{1R} by Q_{2R} are by the definition of the absolute thermodynamic scale of temperature is T_1 by T_2; so that one can prove it. This proof also can be done via the elementary cycles.

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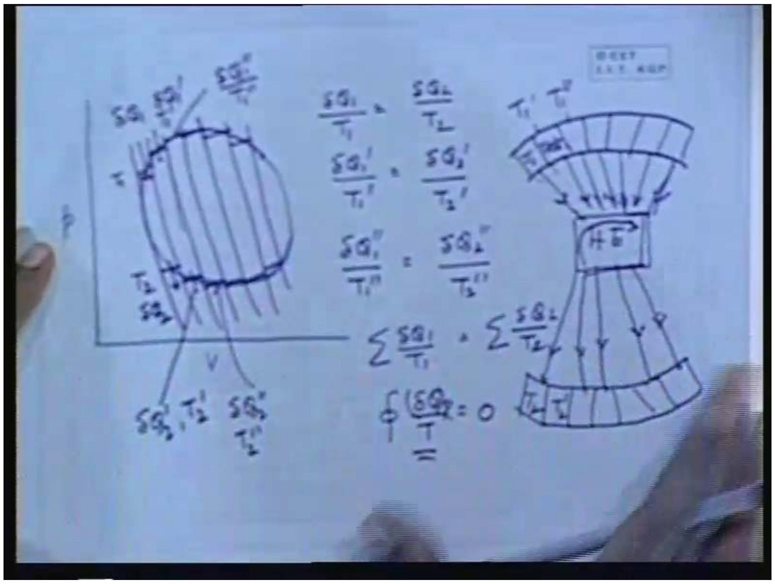

That means via the elementary cycle also we can prove. If we consider this cycle in general where the heat is not being transferred at constant temperatures neither the heat addition nor the heat rejection process. Then we can write for an irreversible cycle that delta Q_1 divided by T_1 is not equal to delta Q_2 divided by T_2. Comparing the reversible and irreversible cycles and then we can add up.

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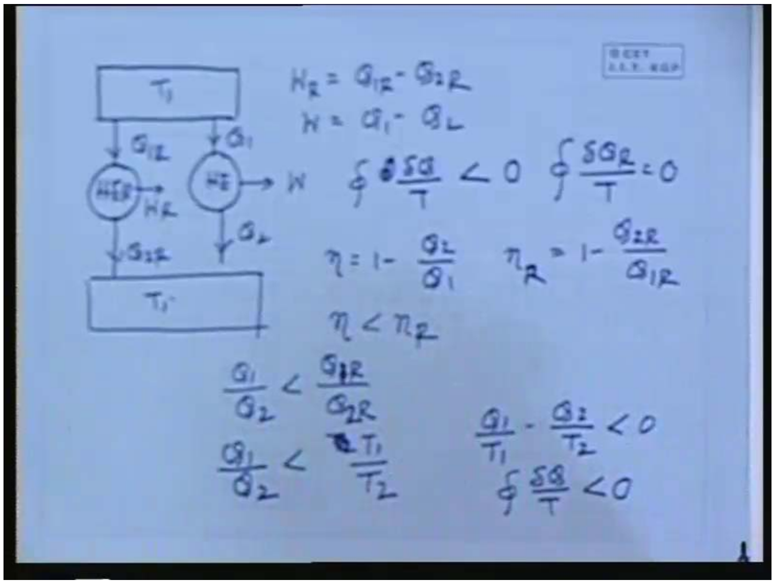

$$W_R = Q_{1R} - Q_{2R}$$

$$W = Q_1 - Q_2$$

$$\oint \frac{\delta Q}{T} < 0 \qquad \oint \frac{\delta Q_R}{T} = 0$$

$$\eta = 1 - \frac{Q_2}{Q_1} \qquad \eta_R = 1 - \frac{Q_{2R}}{Q_{1R}}$$

$$\eta < \eta_R$$

$$\frac{Q_1}{Q_2} < \frac{Q_{1R}}{Q_{2R}}$$

$$\frac{Q_1}{Q_2} < \frac{T_1}{T_2} \qquad \frac{Q_1}{T_1} - \frac{Q_2}{T_2} < 0$$

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

In the similar fashion, we can prove that the efficiency of delta Q divided by T for a cyclic integral for an irreversible cycle is less than 0.

So I am not going to prove that it is very simple; so this is the way one can prove. So the information again is that the Clausius inequality delta Q divided by T for an irreversible cycle is less than 0.

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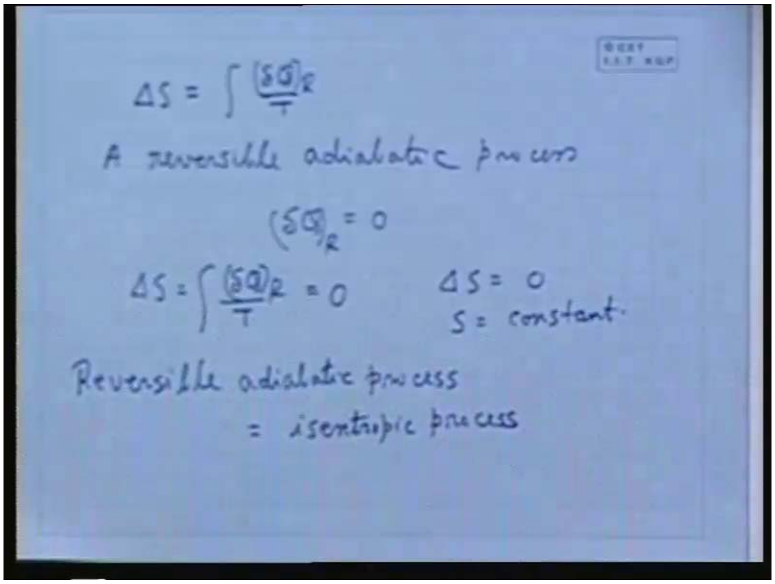

$$\Delta S = \int \frac{(\delta Q)_R}{T}$$

A reversible adiabatic process

$$(\delta Q)_R = 0$$

$$\Delta S = \int \frac{(\delta Q)_R}{T} = 0 \qquad \Delta S = 0$$

S = constant.

Reversible adiabatic process

= isentropic process

Therefore, we get that delta S is equal to integral of delta Q divided by T in a reversible process. All right? Now the question is that an irreversible process does not interact with the surrounding in terms of heat transfer; that means, there is an irreversible process, for example, adiabatic process.

What is an adiabatic process? No heat transfer, but whether it is reversible or irreversible we do not know; it is simply told that it, is an adiabatic process; may be a reversible adiabatic process also. Then we cannot equate that delta is equal to 0. If the process is reversible, then only we can tell that delta is equal to 0; that means we consider a reversible adiabatic process. What is reversible adiabatic process? What is an adiabatic process? Delta Q is 0. The process is reversible that means delta Q_R is equal to 0. This delta Q, I can equate with the entropy. So therefore this becomes is equal to delta Q; delta S is equal to 0; S is constant.

If you have any query please ask me please. Do you have any question?

[Conversation between Student and Professor – Not audible ((00:27:18 min))]

What you thought you ask me?

So a reversible adiabatic process is a constant entropy process which is known as isentropic process. It is clear that a reversible adiabatic process is an isentropic process.

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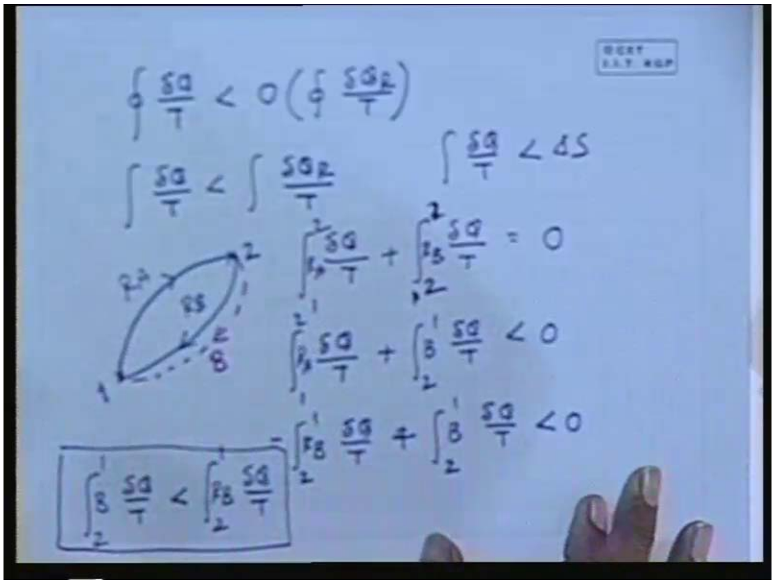

$\oint \frac{\delta Q}{T} < 0 \left(\oint \frac{\delta Q_R}{T}\right)$

$\int \frac{\delta Q}{T} < \int \frac{\delta Q_R}{T}$

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

$\int_{1,R_A}^{2} \frac{\delta Q}{T} + \int_{2,R_S}^{1} \frac{\delta Q}{T} = 0$

$\int_{1,R_A}^{2} \frac{\delta Q}{T} + \int_{2,B}^{1} \frac{\delta Q}{T} < 0$

$-\int_{2,R_S}^{1} \frac{\delta Q}{T} + \int_{2,B}^{1} \frac{\delta Q}{T} < 0$

$\boxed{\int_{2,B}^{1} \frac{\delta Q}{T} < \int_{2,R_S}^{1} \frac{\delta Q}{T}}$

But what is it for an irreversible adiabatic process? Before that again I come back to this initial thing that we have already proved that cyclic integral of delta Q divided by T is less than 0 that means the counterpart, 0 is what? That is counterpart in a reversible cycle, which I have proved.

But it is also simple to prove that with this information that delta Q divided by T, in any process, is less than their counterpart in reversible process. How to prove it?

This proof is also simple, when this is proved, this delta Q by T is less than 0, this counterpart. Then this proof is very simple. You take two state points, join one reversible path R_A going from 1 to 2. While it is comes back let us consider another reversible path R_B and join it by another irreversible path, natural path, that is simply B. Now this R_A and R_B constitute a reversible cycle.

So that delta Q divided by T in path R_A that means, we can write $1R_A$ 2 plus delta Q by T $2R_B1$ is 0. Very simple proof, but I have to do it.

[Conversation between Student and Professor – Not audible ((00:29:39 min))]

2 R_B1. But, I have already proved this. For an irreversible cycle, what will it be? Now R_A and B is an irreversible cycle. Why? Because for a reversible cycle, all processes have to be reversible, if any one process is irreversible, cycle is irreversible. Therefore, this cycle consisting of one reversible process R_A and this back process or the reverse process, irreversible B constitutes an irreversible cycle.

So this cycle will be 1 root 2 R_A plus 2 B 1 delta Q divided by T is less than 0. Now from here I can replace this (Refer Slide Time: 30:35 min), 1 to 2 means minus 2 to 1. minus 2 R_B 1 delta Q divided by T is equal to or plus, first you write this, 2 $_B$ 1 delta Q divided by T is less than 0. So, that means the integral 2 to 1 via the natural process or irreversible process is less than the counterpart via the reversible process. So, now I proved this statement. I am in a position to prove. This is very simple which means that this delta Q by T is less than delta Q_R by T, is proved, for a given process or a path this value, delta Q by T over an irreversible path is less than its counterpart. Counterpart is a defined as delta S, so that integral of delta Q divided by T is less than delta S.

Again and again I am telling because the confusion is here only. All right? This proof is all right.

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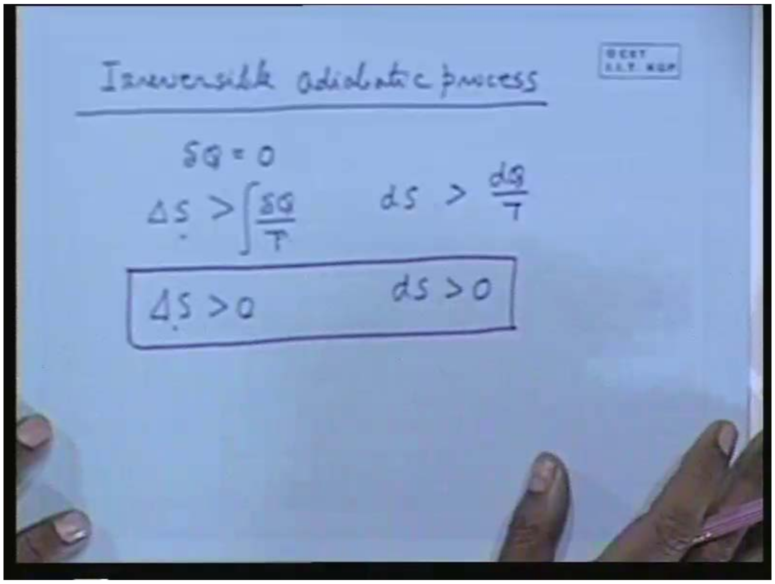

Irreversible adiabatic process

$\delta Q = 0$

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

$\boxed{\Delta S > 0 \qquad dS > 0}$

Now question is that, if it is an irreversible adiabatic process. All the natural adiabatic processes are irreversible. So, it is very easy to conceive irreversible adiabatic process. For example, there is a mass of gas, high temperature and pressure within a piston and cylinder; totally insulate the piston and cylinder. No heat transfer will take place. If we expand the piston fast; not at an extremely slow rate, that is impossible to approach to a quasi equilibrium or quasi static process. Normal processes are fast that means there will be friction, there will be a mechanical dissipation, the process is irreversible, but adiabatic.

Another simple example, you take a mass of fluid in a container, fully insulated, static mass of fluid. You stir the fluid; that means, you make a work transfer; that is known as paddle wheel one. By virtue of friction, the work transfer will take place and it will cause the temperature of the fluid to rise. But no heat will be allowed to flow, because, of the insulation; that means it is an adiabatic process, but irreversible adiabatic process.

So these are the examples that are irreversible adiabatic processes which are the natural processes. In that case what happens that is true, for the process is delta Q is equal to 0, but the process is irreversible; so I cannot equate delta S of the process. I know the Clausius inequality that delta S of the process will be greater than integral delta Q divided by T, because, this is the Clausius inequality. In the differential form, we can write dS is greater than dQ by T, because Clausius inequality delta Q by T is is less than delta S. I am writing other way delta S is greater.

The change in entropy is like this and for an adiabatic process this is 0. So delta s is greater than 0 or a dS in a differential form is greater than 0. If the process is adiabatic process, but not reversible one, heat entropy must increase, that means, delta S always greater than 0. delta S is defined as the change in entropy, which is the delta Q divided by T in a reversible process.

Physically it tells that if you cause an irreversible adiabatic process when a process changes from one system to other system, if we could have thought of this change between these two states by a reversible process which could have definitely taken heat. Do you understand?

That is the physical concept. This is a very simple conclusion - that delta S for a reversible adiabatic process is always greater than 0, because, delta Q divided by T is less than delta S from the Clausius inequality. So, delta S is always greater than 0 because integral delta Q by T is 0 for an irreversible adiabatic process; which means, that connecting the two state points for an irreversible adiabatic process if we could have conceived a reversible process that could not be adiabatic. Rather that could be a process which could have demanded heat from the surroundings for which the entropy has increased.

You stir a mass of water in an insulated bath, the temperature will rise. This is an irreversible process. You cannot stir; you cannot perform the work until and unless there is a friction. The friction dissipation is there, but the similar rise in temperature, you could have done by a reversible process. Then, you could have slowly transferred heat into the system. Therefore, that is a rise in entropy. So, that is the physical concept and this comes directly as the mathematical consequence that the irreversible adiabatic process delta S is greater than 0.

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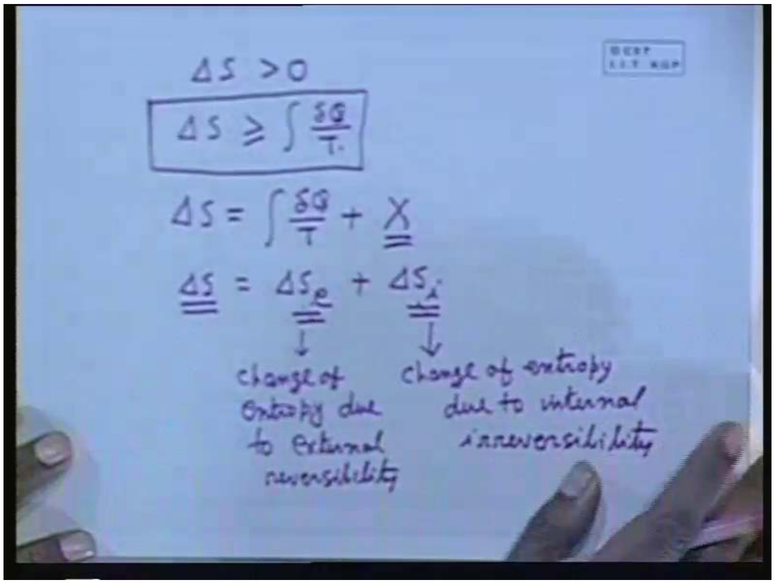

$$\Delta S > 0$$

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

$$\Delta S = \int \frac{\delta Q}{T} + \underline{\underline{X}}$$

$$\underline{\underline{\Delta S}} = \underline{\underline{\Delta S_e}} + \underline{\underline{\Delta S_i}}$$

↓ change of entropy due to external reversibility

↓ change of entropy due to internal irreversibility

Now, a very interesting thing that if delta S is greater than 0 for an irreversible adiabatic process, I can write then delta S is greater than integral of delta Q divided by T. What does this mean? That is same as the Clausius inequality. That means, delta S is greater than delta Q divided by T. Again, I am coming to Clausius inequality; delta S, for any process, is greater than delta Q divided by T or equals to. We can tell that if it is a reversible process, then it is equal or delta S is always greater than… that means for any process entropy change, now I can combine the definition of entropy and the Clausius inequality for a process as delta S is greater than is equal to delta Q divided by T.

When this will be a reversible process then equality sign will holds good, if it is an irreversible process then greater than sign. I can write this as delta S is equal to del Q by T plus some positive quantity X because delta S is greater than delta Q by T. So, I can write like this. This is actually represented like delta S_e plus delta S_i. In irreversible thermodynamics, this is expressed in this fashion that change of entropy of a system is composed of change of entropy due to heat transfer plus a change of entropy due to internal irreversibility. This part, delta S_i, is internal irreversibility. This is because of the heat transfer. For any process, the delta Q divided by T for an irreversible process has not been given the status of entropy change, because, it is not a point function.

So it is always less than the entropy change or entropy change is always greater than the quantity integral delta Q by T. If I make an equality by number X which is greater than 0 and then I give a definition to the quantity, integral delta Q by T, for an irreversible process, delta Q divided by T a name that is the entropy change due to external irreversibility; this is nothing but the counterpart of delta Q divided by T in a natural processes. That means natural process there is a heat transfer, I can tell the integral delta Q divided by T as the entropy change due to externally irreversibility. But that may not be the sole entropy change, then, the entire definition will collapse. This (Refer Slide Time: 37:55 min) has to be added with some other positive quantity to satisfy the Clausius inequality. This delta S_i is defined as the change of entropy due to internal reversibility. So I must write this thing. This delta S_e is known as change of entropy due to external irreversibility. Why I write this word external irreversibility?

This is because of the heat transfer through a finite temperature difference and this delta S_i is the change of entropy due to internal irreversibility. This is another fashion of writing this from irreversible thermodynamics point of view.

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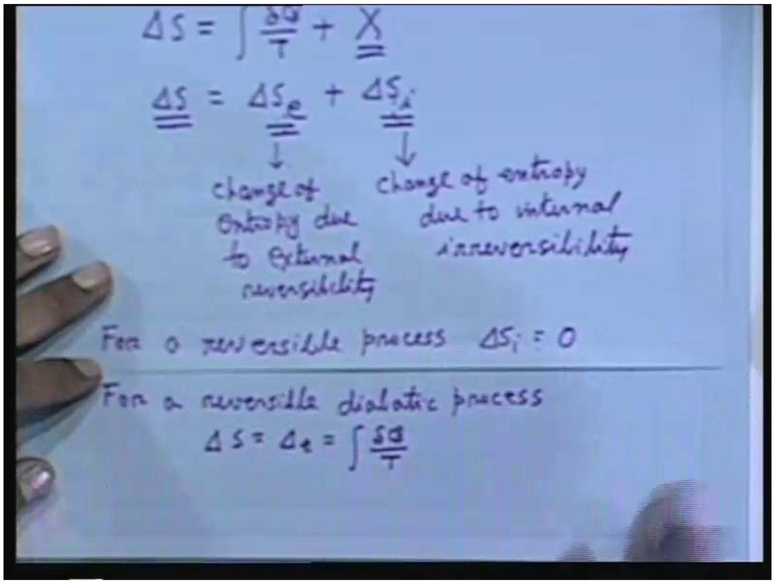

$$\Delta S = \int \frac{\delta Q}{T} + \underline{\underline{X}}$$

$$\underline{\underline{\Delta S}} = \underbrace{\Delta S_e}_{\text{change of entropy due to external reversibility}} + \underbrace{\Delta S_i}_{\text{change of entropy due to internal irreversibility}}$$

For a reversible process $\Delta S_i = 0$

For a reversible diabatic process

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

Now, for a reversible process, delta S_i is 0; this change of entropy due to internal irreversibility, there is no irreversibility. But, if a reversible process there is a heat transfer. that means process is diabatic - a diabatic reversible process. A reversible process with heat interaction then entropy change exactly equal to delta s_e that means delta Q; this defines the entropy as this definition came into picture, but it is a reversible process that is 0.

On the other hand, if it is an adiabatic process, then this part, delta S_e is 0 . Therefore, for a reversible diabatic process delta S is equal to delta e that means equal to delta Q divided by T. Diabatic means what? That means with heat transfer.

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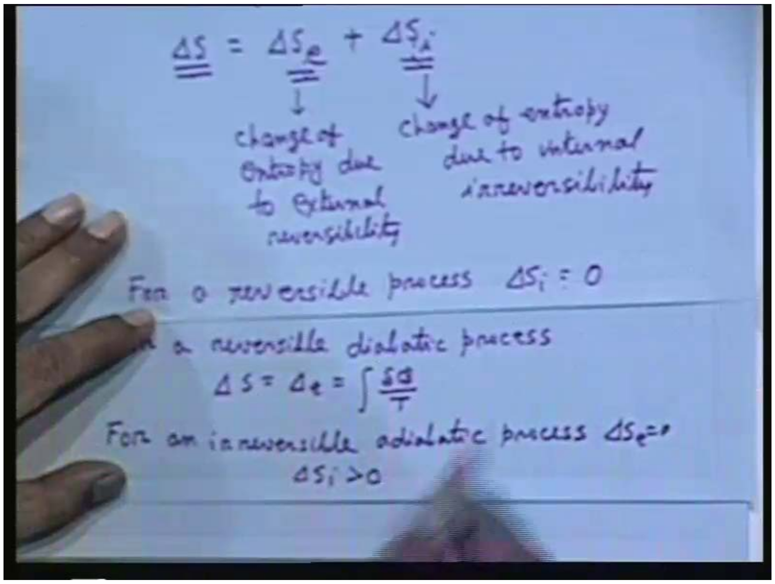

$$\underline{\underline{\Delta S}} = \underline{\underline{\Delta S_e}} + \underline{\underline{\Delta S_i}}$$

change of entropy due to external reversibility

change of entropy due to internal irreversibility

For a reversible process $\Delta S_i = 0$

a reversible diabatic process

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

For an irreversible adiabatic process $\Delta S_e = 0$

$\Delta S_i > 0$

Now all right you can see, no you cannot, saying you can see this step.

Then for an irreversible adiabatic process, which one will be 0? delta S_e is 0, this delta Q divided by T is 0. delta s_e is 0, but delta S_i is greater than 0. That means there is a change of entropy due to irreversibility. If we stir a liquid, totally insulated, entropy increases. If you expand a gas at fast rate or compress the gas in a piston cylinder or in any expansion compression device with fully insulated, then there is an increase of entropy, because of this delta S_i. That means this portion - change of entropy due to internal irreversibility. Now, if the process is both reversible and adiabatic, then both these terms, delta S_e and delta S_i will be 0 and delta S will be 0. All right?

[Conversation between Student and Professor – Sir, can you define entropy for an irreversible process then… Not audible ((00:41:29 min))]

Definition of entropy? That is the basic question so far what I have told. Definition of entropy is through a reversible process, but is defined for any process. Do not have this confusion that definition of entropy is for a reversible process. Again and again I am telling so. What example I gave you - that if there is an irreversible process, the entropy change is defined by delta Q divided by T for a reversible process.

If the same state points could have been connected by a reversible process what could have been the value of this - that is the entropy change. The entropy change between the two state points is defined and to define that we always take a reversible path, that is by definition - through a reversible path. Try to understand, that is very simple. This example I gave you so that all confusions will go; if change of entropy is between two points, is not for a process, change of internal energy is between two state points, it is not for a process. So, any process is performed between these two state points the change of entropy will remain same. But, if we have to find out the value of this entropy change from the heat transfer quantities, then we will have to conceive a reversible process. Then, we can find out the integral of delta Q divided by T for that reversible process and then you can tell this is the entropy change - whether it is a reversible or irreversible.

Just very simple example I gave, that there is a mass of liquid. You stir the liquid, its state point is changed; its temperature is increased. So, there is a change in entropy, but how do you measure this entropy? If want to equate this entropy with the heat interactions of the process then you are at an erroneous result, then heat interaction is 0 in this process, only work is transferred that is a paddle wheel work. But entropy is changed, entropy is increased. From the Clausius inequality also we get there is an increase in entropy, because, there will be a heat transfer, if this state can be changed by a reversible process. Then you have to apply heat.

To calculate the entropy we have to connect the two state points via a reversible process and then only we can find out the integral delta Q divided by T, which is ascribed as the change in the entropy between the two state points, whatever may be the process. Change of a point function is never defined for a process that definition of entropy change for a process is [ ] statement.

Change in internal energy is a point function; change in potential energy is never defined by a process or by a path. [ ], change in potential energy in any conservative force is defined from point to point. Change in potential energy between this point and that point in a conservative force field.

Nobody tells via the path.

[Conversation between Student and Professor – Not audible ((00:44:09 min))]

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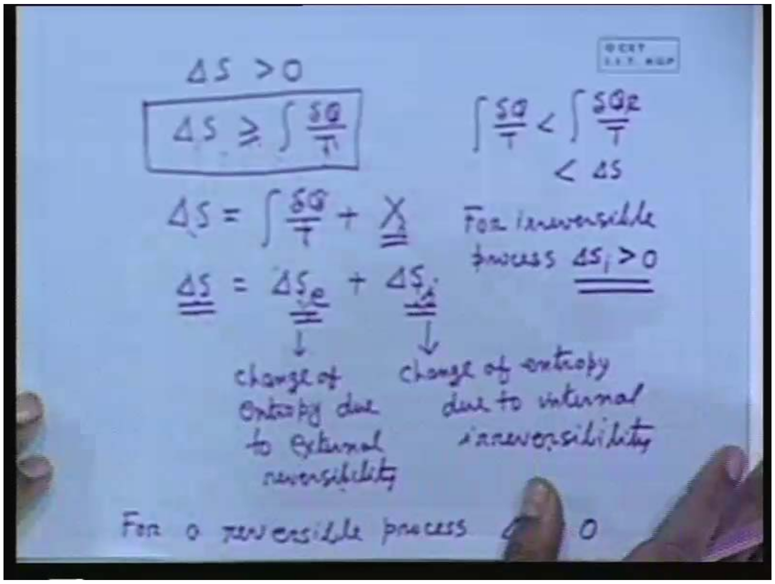

$\Delta S > 0$

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

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

$$\Delta S = \int \frac{\delta Q}{T} + X$$

$$\Delta S = \Delta S_e + \Delta S_i$$

ΔS_e: change of entropy due to external reversibility

ΔS_i: change of entropy due to internal irreversibility

For irreversible process $\Delta S_i > 0$

For a reversible process [illegible] 0

Concept of externally irreversibility and internal irreversibility, I shall explain it again.

We know that delta S, the change of entropy of any process is greater than delta Q divided by T, in general. Greater than and is equal to; because, Clausius inequality tells that integral of delta Q divided by T for any process is less than the counter part for a reversible process which is a point function, which is the delta S.

Therefore delta S is greater than integral of delta Q_R by T, this is for any process. If I combine these for both reversible and irreversible process, I can write this - delta S is greater than and equal to integral delta Q by T. If the process is reversible delta S exactly equals to integral delta Q divided by T. If the process is irreversible then delta S is greater than this integral delta Q by T. So, in general, if I consider the process may be irreversible and reversible. I can write this, delta S is equals to integral delta Q by T plus some positive quantity, which is 0 in case of a reversible process, when this equality will hold good.

Otherwise, this positive quantity X will take care of this inequality. So this positive quantity is defined as entropy change due to internal irreversibility. When there is a reversible process this becomes 0 for a reversible process. So, delta S is equal to delta S_e, but for an irreversible process this component, delta S_i comes into picture.

So there are three cases, one is an adiabatic process, there is no heat transfer, so del S_e, change of entropy due to external irreversibility is 0. This part, delta S_e, equates the heat transfer for any process whether reversible or irreversible. In adiabatic process heat transfer part is 0, so delta s_e

is 0. In that case, only delta S_i is there because for irreversible process delta S_i is 0. So, two things are very important. For irreversible process delta S_i is greater than 0. Therefore, the change in entropy due to an irreversible adiabatic process is contributed by the delta S_i.

Now, next, what we can discuss is that the isentropic process.

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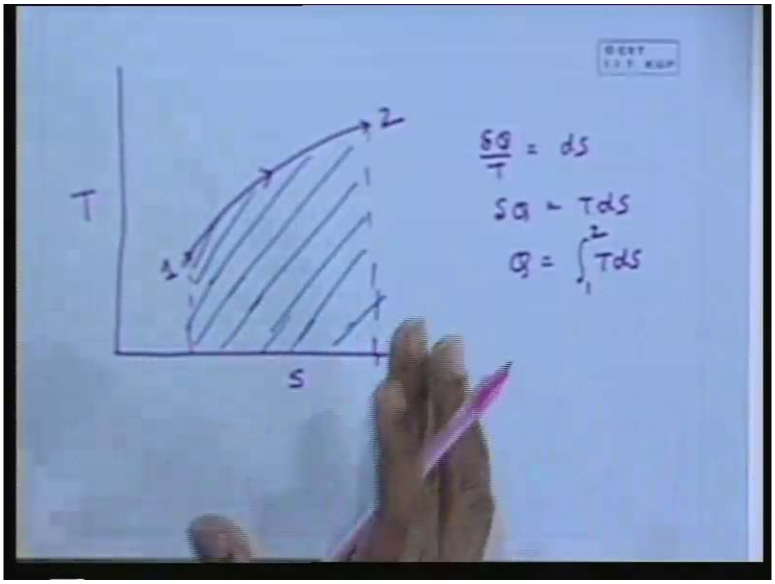

Now we have seen that entropy is a very useful concept, an isentropic process is a process which is reversible and adiabatic. Now if I draw a curve in TS plane.

Please please listen to me what I am teaching.

Let us consider a process 1 to 2. If I represent the process, a reversible process in TS diagram, then TS diagram is useful that if it is a reversible process, then we know that delta Q divided by T is equal to ds. Therefore, delta Q is Tds. Therefore, Q is integral of Tds from 1 to 2. The area under this curve (Refer Slide Time: 47:36 min) 1 to 2 represents the heat interaction, this area. The way pdV curve is important because the area under the pdV curve gives us the work interaction. Similarly, area under the TS curve gives us the heat interaction. Therefore, a TS plot is very important - the temperature entropy plot. So that it gives the impression or gives a qualitative idea about the heat interaction processes. So, next I will say that how we can define the change of entropy.

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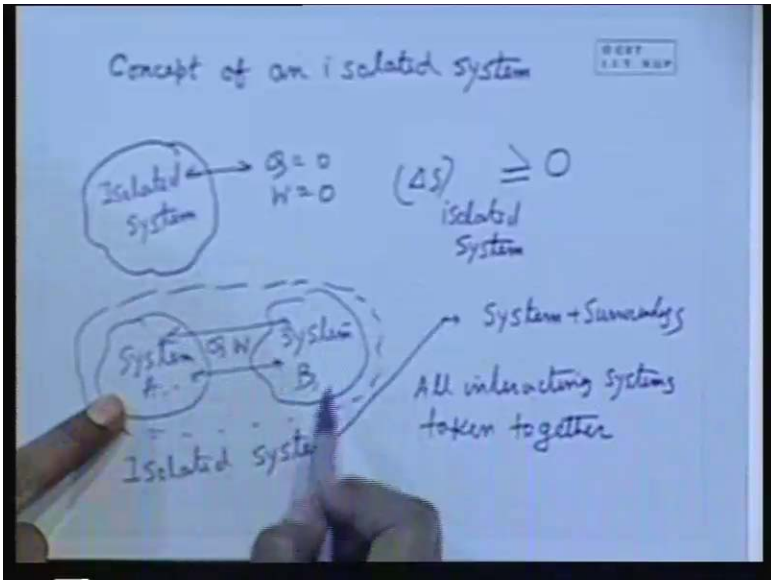

Now we see the concept of an isolated system. What is an isolated system?

Any question? Yes, please. Can we absolutely find out the value of entropy sir? I will come afterwards .This is a very relevant question I told you at the beginning.

It is the change of entropy which is defined in terms of delta Q divided by T. About the absolute entropy, I will discuss afterwards; this is not in this scope but I will tell you the concept of absolute entropy.

Can we know the TS diagram then?

So that is a reference plane. How do you ask this [ ] question? I do not understand. Whenever I told you in internal energy, it is only the , that means, to ascribe a value of entropy we will have to keep a reference data from which the entropy is defined, because, we are interested in the heat interaction. I have told you earlier also, in case of internal energy also we are interested in its change, but not in its absolute value. Here also in case of heat interaction we are interested in its change. Therefore, we always consider a reference value of entropy, reference datum, from where we find out a change by a thermodynamic process. So that equations are there we can find out a change, every datum is 0, so automatically we get an absolute value.

But this absolute value is relative to a reference datum, the way we define the potential energy. We take a datum and then we measure the potential energy from that datum. We never measure the potential energy, gravitational potential energy, from the earth's center where it is 0. But we take a reference datum and we measure the potential energy from that difference datum, so that if we know the change in potential energy reference, that time is 0, we ascribe the value. That way we ascribe the value of the entropy and we plot the entropy in TS plane.

So, we are not much interested where that entropy becomes 0, but the concept of entropy 0 comes in the third law of thermodynamics. If you are interested, I will discuss this thing afterwards or if possible at the end of this section. I will give you some idea where from you get the concept of absolute entropy which is related to the disorderliness of the molecules, molecules or atoms; it is the atomic or molecular disorderliness as we approach an absolute 0 then the absolute entropy of a system approaches 0. But that concept is beyond the scope of this class, so I do not want to discuss.

We will discuss the change of entropy here, because here we are interested in terms of heat and work interactions, like the first law we are interested in the change in the internal energy here also we are interested in the change in entropy. We have seen the definition of entropy has been evolved through its change only, not its absolute entropy. Is it clear?

Concept of an isolated system, now what is an isolated system? Isolated system does not interact with surrounding, either in terms of Q or in terms of W. That means it is a reversible process.

So what is the alternative? The change of delta S of an isolated system, what it will be please tell me. It will be 0. Just, I tell an isolated system, in general, what it will be? Q is 0, delta S of an isolated system will be greater than or is equal to 0. It equals to 0 provided the change within the isolated system is reversible otherwise, irreversible.

Now the question comes that why we talk about the change on entropy of an isolated system or change of any property of an isolated system? Isolated system does not interact with the surrounding. But still there is a change of the property which means a process is taking place within the isolated system. There is some readjustment between different parts of the isolated system. So some process is taking place within isolated system, not because of the interaction between the system and the surrounding.

If that internal processes are irreversible, then delta S is greater than 0. If they are reversible, then delta S is equal to 0. This concept of isolated system is like free body concept in mechanics which means that if there is a system A and if there is another system B, and they are interacting with each other in terms of heat and work with nothing else. The two systems are mutually interacting with one another. In that case, system B is surrounding to system A and system A is surrounding to system B. Then, as a whole, these systems A and B comprise an isolated system.

Therefore, henceforth, we will refer an isolated system as system plus surroundings. We can define all interacting systems taken together. Therefore, we see that if all interacting systems taken together as an isolated system, there may be processes interactions between the systems. All interacting systems are there between one another and as a whole, if I consider this as an isolated system, the entropy change of this isolated system will increase, if the interactions between the systems constituting the isolated systems are reversible delta S equals to 0 or delta S will be greater than 0. That means the entropy will increase, if these interactions are irreversible.

This concept is clear.

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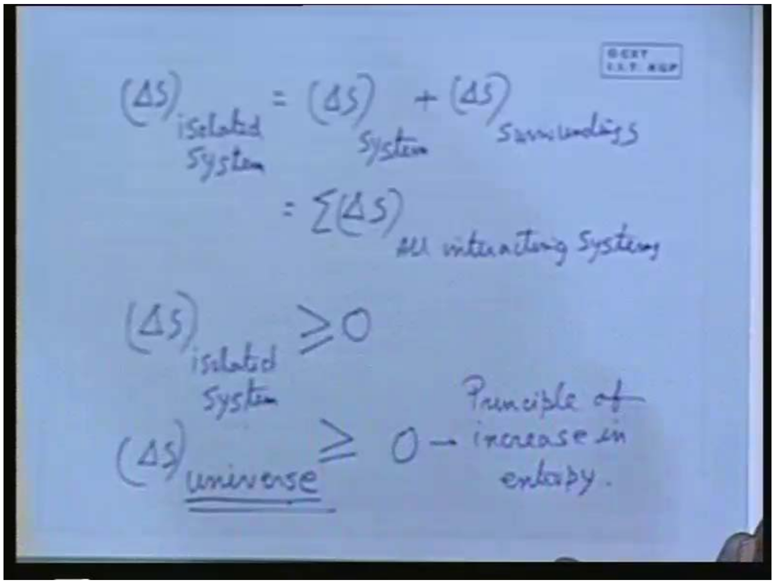

$$(\Delta S)_{\text{isolated System}} = (\Delta S)_{\text{System}} + (\Delta S)_{\text{Surroundings}}$$

$$= \sum (\Delta S)_{\text{all interacting Systems}}$$

$$(\Delta S)_{\text{isolated System}} \geq 0$$

$$(\Delta S)_{\underline{\text{universe}}} \geq 0 \rightarrow$$ Principle of increase in entropy.

Therefore for a system and surrounding, surrounding means is interacting system, one can write that delta S of an isolated system which comprises of delta S system plus delta S surroundings, or we can write, delta S, algebraic sum of delta S all interacting systems. So, we define delta S. By this concept, delta S isolated system should be either greater than 0 depending upon these interactions between the system and surrounding or all interacting systems are irreversible or not.

If it is reversible then delta S is equal to 0. If the interactions are irreversible, delta S is greater than 0 of an isolated system or delta S is equal to 0 if the interactions are reversible. In a limited sense, these isolated systems are termed in thermodynamics as universe. Because, we consider, do not ask me the questions whether, in true sense, universe is an isolated system or not. But this is the terminology in a limited sense, it is used that as if the universe is an isolated system. It does not interact with anything outside it; all interactions are within the universe. So that this is, in a limited sense used, universe, which is nothing but a synonymous term of an isolated system greater than is equal to 0 and this is known as principle of increase in entropy.

All right, concept is clear?

Thank you.

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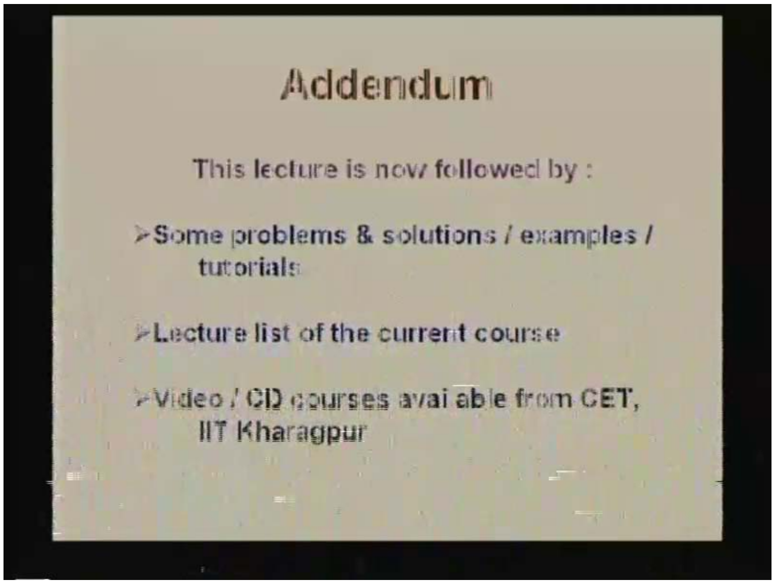

Addendum

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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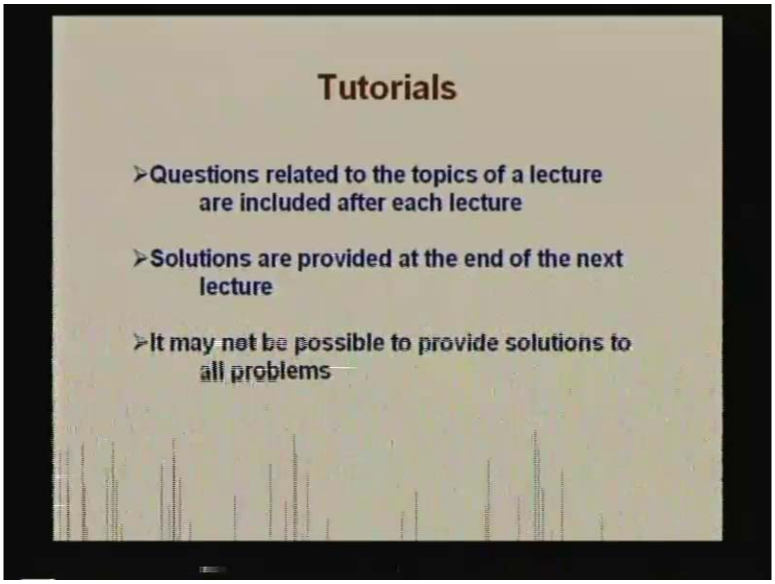

Tutorials

- 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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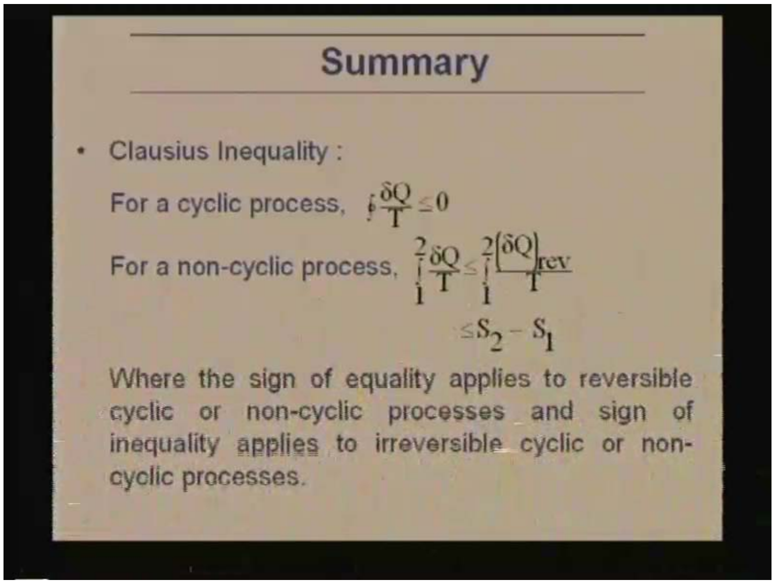

Summary

- Clausius Inequality :

  For a cyclic process, $\oint \frac{\delta Q}{T} \le 0$

  For a non-cyclic process, $\int_1^2 \frac{\delta Q}{T} \le \int_1^2 \frac{(\delta Q)_{rev}}{T}$

  $\le S_2 - S_1$

  Where the sign of equality applies to reversible cyclic or non-cyclic processes and sign of inequality applies to irreversible cyclic or non-cyclic processes.

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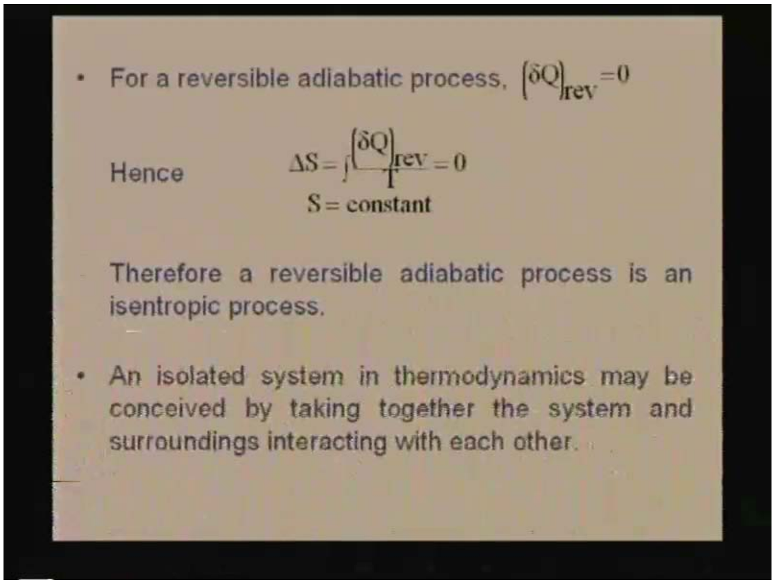

- For a reversible adiabatic process, $(\delta Q)_{rev} = 0$

  Hence $\Delta S = \int \frac{(\delta Q)_{rev}}{T} = 0$

  $S = \text{constant}$

  Therefore a reversible adiabatic process is an isentropic process.

- An isolated system in thermodynamics may be conceived by taking together the system and surroundings interacting with each other.

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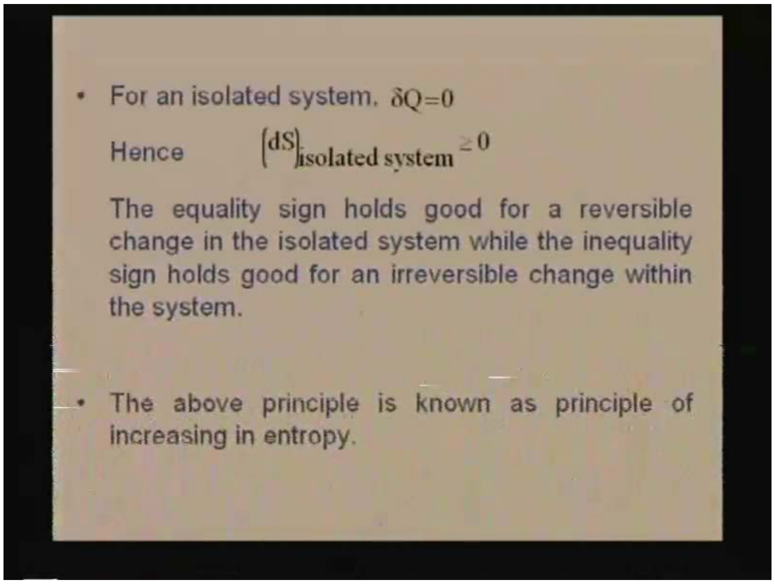

- For an isolated system, $\delta Q = 0$

  Hence $(dS)_{\text{isolated system}} \geq 0$

  The equality sign holds good for a reversible change in the isolated system while the inequality sign holds good for an irreversible change within the system.

- The above principle is known as principle of increasing in entropy.

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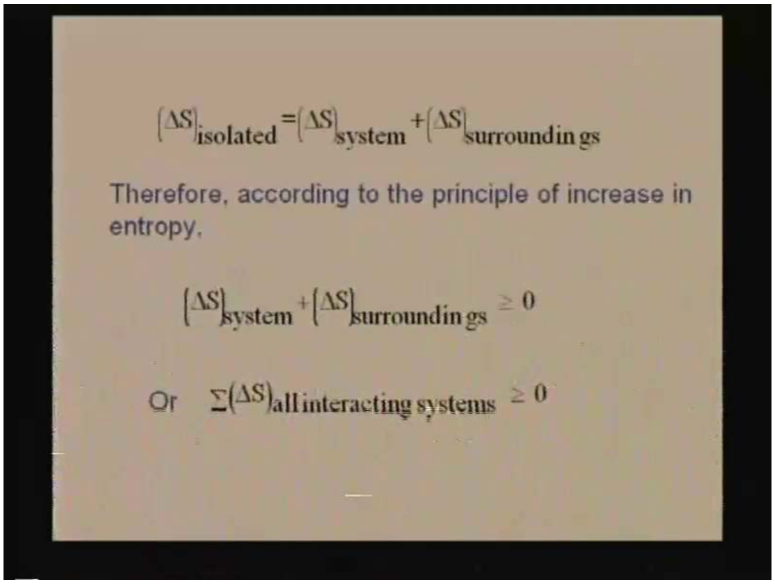

$$(\Delta S)_{\text{isolated}} = (\Delta S)_{\text{system}} + (\Delta S)_{\text{surroundings}}$$

Therefore, according to the principle of increase in entropy,

$$(\Delta S)_{\text{system}} + (\Delta S)_{\text{surroundings}} \geq 0$$

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

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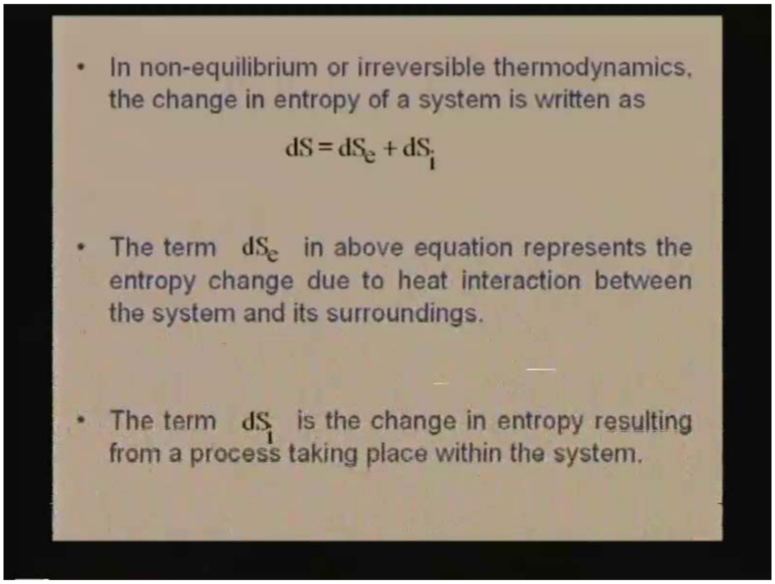

- In non-equilibrium or irreversible thermodynamics, the change in entropy of a system is written as

$$dS = dS_e + dS_i$$

- The term dS_e in above equation represents the entropy change due to heat interaction between the system and its surroundings.
- The term dS_i is the change in entropy resulting from a process taking place within the system.

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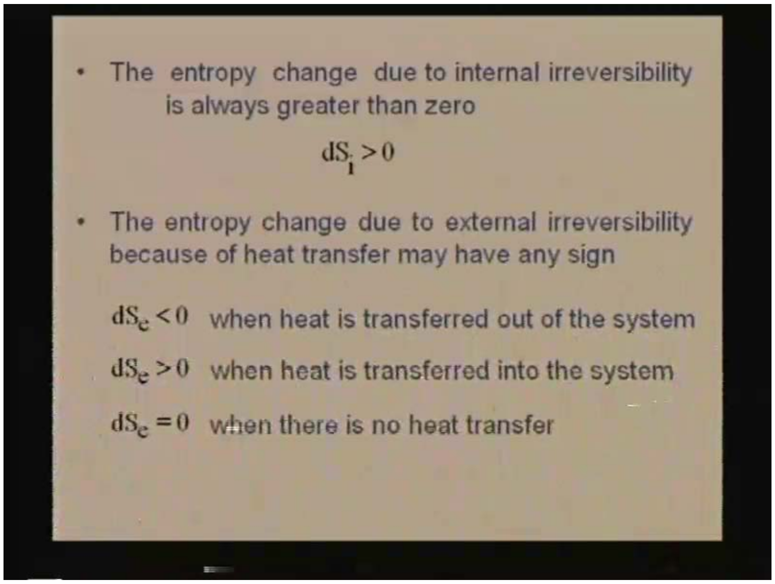

- The entropy change due to internal irreversibility is always greater than zero

$$dS_i > 0$$

- The entropy change due to external irreversibility because of heat transfer may have any sign

$dS_e < 0$ when heat is transferred out of the system

$dS_e > 0$ when heat is transferred into the system

$dS_e = 0$ when there is no heat transfer