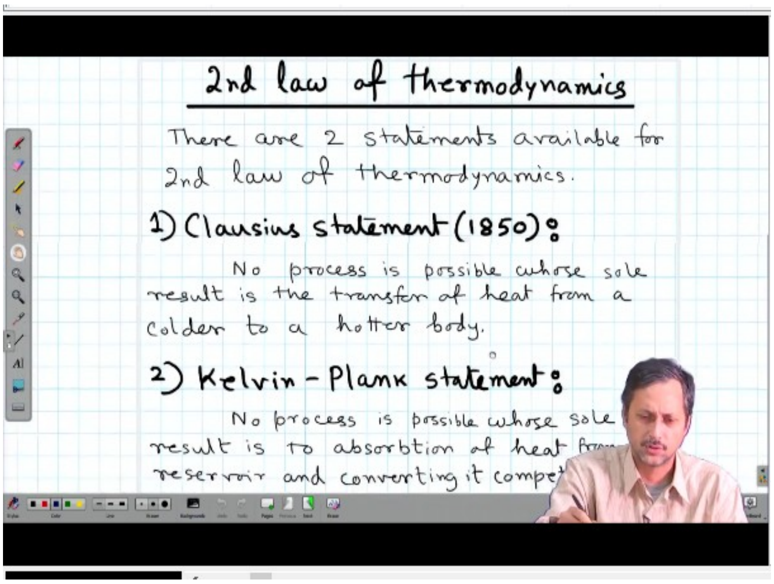
Thermal Physics
Prof. Debamalya Banerjee
Department of Physics
Indian Institute of Technology-Kharagpur

Lecture-39
Topic-2nd Law and Clausius Theorem

Hello and welcome back to another lecture on this NPTEL course of thermal physics. Now for today's lecture we will continue with 2nd law of thermodynamics. In the last lecture I have discussed two alternative statements of 2nd law of thermodynamics and today at the beginning I will show you that these two statements are actually equivalent to each other. So, once again 2nd law cannot be proved, what we can do is? We can we have to accept it in its original form whatever it is.

And as there are two statements; the best statements, best we can do is we can prove the equivalence of these two statements to begin with. Also let me tell you that today's lecture is kind of boring lecture because today we are not going to solve any problem, the discussion will be primarily theoretical in nature, but we will build on this discussion and in the next class we will do some very interesting calculation.

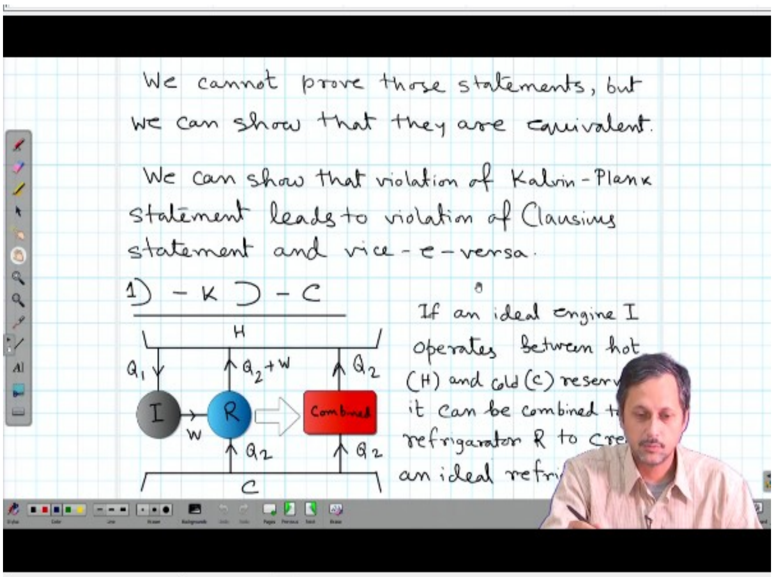
(Refer Slide Time: 01:30)



So, let us begin without any further delay. So, let me quickly review the two alternative statements of the 2nd law of thermodynamics, one is the Clausius statement which says that no Clausius is possible whose sole result is to transfer of heat from a colder to a hotter body. So, basically the Clausius statement denies the presence of an ideal refrigerator which can transform heat from the colder to a hotter body without any external power or external energy sources.

And the 2nd one is the Kelvin-Planck statement which denies the presence of an ideal engine, so it says no process is possible whose sole result is to absorb heat from a reservoir and convert it completely to work. So, from the 2nd law we understand that every heat engine has to reject some heat to another cold reservoir or another reservoir that is available. So, in no case the 100% absorbed heat can be converted into work.

(Refer Slide Time: 02:51)



Now let us first start with the equivalence of these two laws, so what we can show that the violation of one leads to the violation of the other statement. So, interestingly I have discovered very recently that in this software open board which I am using it also has this nice shape features which I was not aware of, so now onwards I will be using some of these shapes there. So, first we start with the violation of the Clausius or Kelvin-Planck statement I am just putting it as K and we will show that the violation of Kelvin-Planck statement will lead to the violation of Clausius statement.

So, mathematically minus K implements minus C. So, let us start, so what is the Kelvin-Planck statement? Kelvin-Planck's statement denies the presence of an ideal engine but let us assume that there is an ideal engine I and it is working between what the effect of this is to absorb Q 1 amount of heat from the hot reservoir and converting it completely into what W. So, this W is equivalent to Q 1. So, let us assume that there is a refrigerator R need not be an ideal reversible refrigerator any refrigerator R.

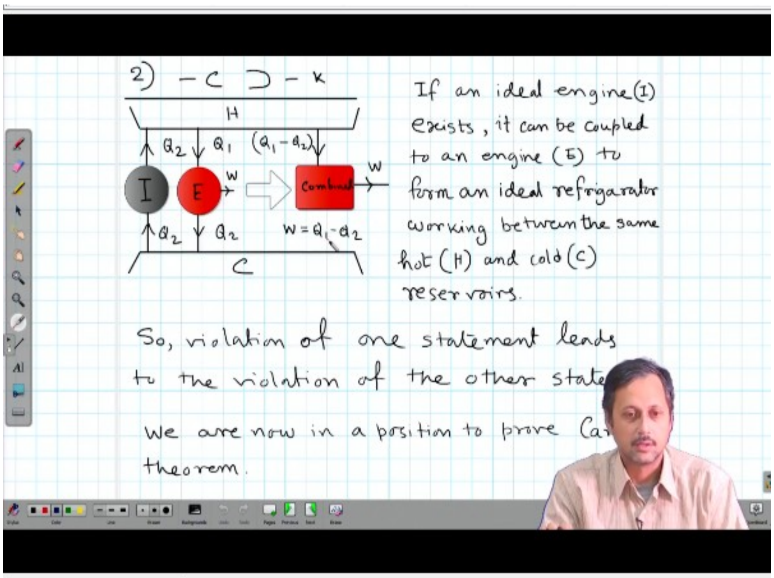
So, only criteria is for this, this is kind of a thought experiment. So, for this thought experiment we have to assume that the heat rejected by this well actually it is, so we can take any refrigerator, so only assumption is this refrigerator will need this exact W amount of work. So, that it can take Q 2 amount of heat from a cold reservoir C which is available and reject Q 2 plus W amount of heat in the hot reservoir, the same hot reservoir between from which the ideal engine I is taking its heat.

So, now if we combine these 2 into 1 system that is absolutely possible because output of this ideal engine is working as the power input to this refrigerator. So, if the combined system if we look at it carefully the engine takes Q 1 amount of heat the refrigerator rejects Q 2 plus W, W is equivalent to Q 1, please remember. So, it rejects Q 2 plus Q 1 amount of heat to the hot reservoir.

So, in effect what it does is actually the combined system gives Q 2 amount of net heat to the hot reservoir and the ideal engine does not reject anything into the cold reservoir. So, this there is no heat that is being rejected. So, only heat that is taken away from the cold reservoir is this Q 2 amount of heat which is taken by this refrigerator. So, this combined system does not need any external work and it gives away this Q 2 amount of it completely into the hot reservoir which is a violation of the Clausius statement.

Because Clausius statement says no process is possible whose sole result is the transfer of heat from a colder to a hotter body? So, we see that if we start with the assumption that the Kelvin-Planck statement is violated by an ideal engine then we end up with a ideal refrigerator the combined system in this case which transforms Q 2 amount of it from a colder to a hotter body without need of any external work.

(Refer Slide Time: 07:02)



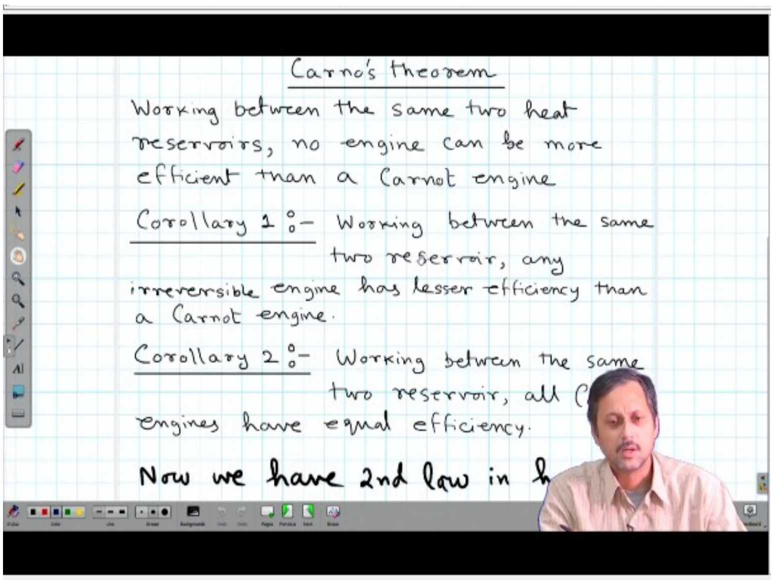
So, that is the proof that the 2 statements at least in its negative form is equivalent. Now let us do it in the other way round. So, let us assume that the Clausius statement is false. So, that means there exist an ideal refrigerator once again I denote it with I here, which takes Q 2 amount of heat from the colder body and transforms it entirely into a hotter reservoir without the need of any external work. So, Q 2 in and Q 2 out.

Now let us assume that there is a engine working between the same 2 reservoir, it takes Q 1 amount of heat, performs W amount of work and rejects Q 2 amount of heat to the cold reservoir. So, only criteria is we have to choose the engine such that the heat rejected by it is equal to the heat taken by the ideal refrigerator. Once again if we look at the combined system you see the cold reservoir gives away Q 2 amount of heat to the ideal engine and receives Q 2 amount of heat to the ideal refrigerator and receives Q 2 amount of heat from the ordinary engine.

So, the combined system does not accept any heat from the cold reservoir or reject any heat to the cold reservoir, what it does is it takes away Q 1 minus Q 2 amount of heat from the hot reservoir and converts it completely into work W which is equal to Q 1 minus Q 2. So, once again it gives the combined system behaves like an ideal engine which is not possible by Kelvin-Planck statement. So, we start off once again we start off with the violation of Clausius statement and we see that this eventually leads to a violation of the Kelvin-Planck statement.

So, both these proves the negative proofs in a sense that we cannot really prove that if one holds the other also holds, but we can show you that if one is violated the other is violated in both cases, both ways. So, that actually proves the equivalence of these two statements of the 2nd law of thermodynamics. Now as we have these two statements and of course we have to accept the 2nd law in one of its forms, once we do that we are also in a position to prove the Carnot theorem. Now what is Carnot theorem?

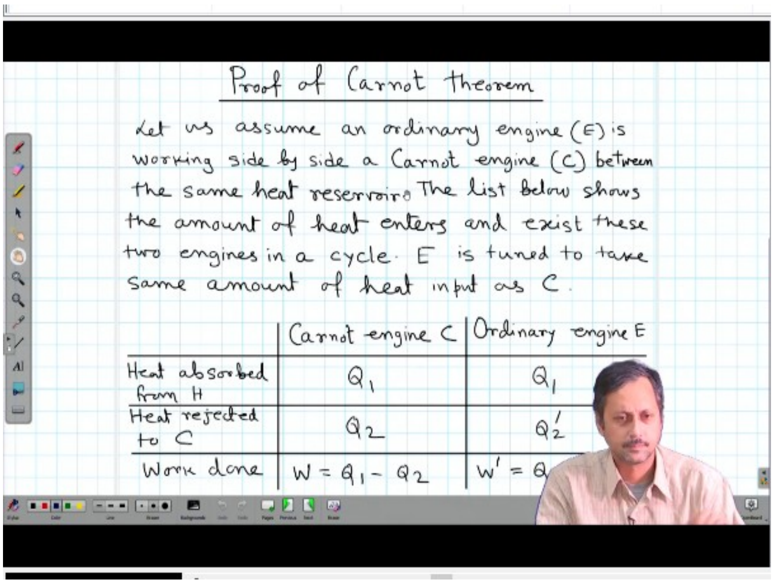
(Refer Slide Time: 09:49)



Carnot theorem I have just discussed in one of the previous lectures. That says working between any two reservoirs Carnot engine is the most efficient engine, yes and it has two corollary, one is working between the same two reservoirs an ordinary engine or a irreversible engine has to have lesser efficiency as compared to a idealized or Carnot engine or reversible engine.

Whereas and the second corollary says working between the same two reservoir all Carnot engine have equal efficiency. Now what we are going to do is? We are going to use the 2nd law of thermodynamics and we will try to prove this Carnot theorem.

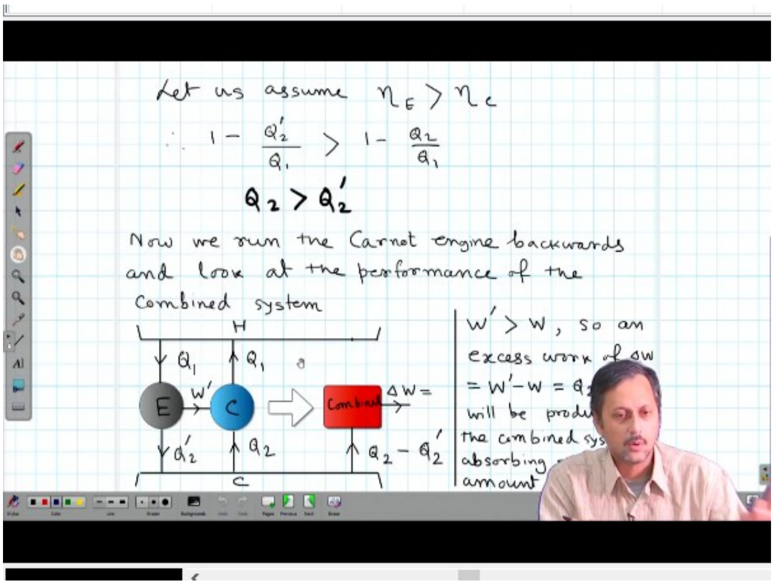
(Refer Slide Time: 10:35)



So, let us assume that an ordinary engine E is working side by side with the Carnot engine C. And it is working between the same 2 heat reservoirs; let us call it H and C hot and cold. So, what we do here we first list the amount of heat that is been accepted by both this engine. Let us assume they accept the absorbed same amount of heat Q 1 from the hot reservoir, of course they have different efficiency.

So, the rejected heat and the work done will be different. So, the Carnot engine rejects Q 2 amount of heat performs Q 1 minus Q 2 amount of work, but whereas the ordinary engine E rejects Q 2 prime amount of heat and performs Q 1 minus Q 2 prime amount of work, which I write with W prime and this one Q 1 minus Q 2 is given as W.

(Refer Slide Time: 11:34)



Now so once again it will be a negative proof like we first assume that the Carnot theorem is false and we will see what happens. So, let us first assume that the ordinary engine has more efficiency as compared to the Carnot engine. When this is the case 1 minus Q 2 prime by Q 1, so if eta E is greater than eta C we can write 1 minus Q 2 prime by Q 1 is greater than 1 minus Q 2 by Q 1 which essentially means Q 2 by Q 1 is greater than Q 2 prime by Q 1.

And then we can write Q 2 is greater than Q 2 prime and this is also obvious because the engine which is more efficient if we accept this, this is very easy to understand the engine that is more efficient in this case the ordinary engine will give lesser heat to the cold reservoir as compared to the another engine, which is less efficient. So, Q 2 has to be more than Q 2 prime.

Now a beauty of Carnot engine is Carnot engine can be it is a reversible engine, so Carnot engine can be reversed, the operation can just be reversed and we can use it as a refrigerator. So, if a Carnot engine accepts Q 1 amount of heat and performs the Q 1 minus Q 2 amount of work and rejects Q 2 amount of heat if we invert it, it will accept Q 2 from the cold reservoir and if we apply Q1 minus Q 2 amount of work on it, it will just give away Q 1 amount of it to the hot reservoir.

So, what we have demonstrated in this figure below here is the reversed version of the Carnot engine which as I have said takes Q 2 amount of heat and let us say it rejects Q 1 amount of because the efficiency is fixed. So, if it takes Q 2 amount of heat and if it accepts sufficient work let us assume W prime is sufficient for its functionality. So, it will reject Q 1 amount of heat to the hot reservoir.

So, the ordinary engine which has let us say in this case more efficiency than the Carnot engine takes Q 1 amount of heat from the hot reservoir and now we look into the combined system and gives W prime amount of work to the cold reservoir. Now what is W prime? W prime is Q 1 minus Q 2 prime. Now and as the ordinary engine is assumed to be more efficient if we go back here you see W prime has to be greater than W.

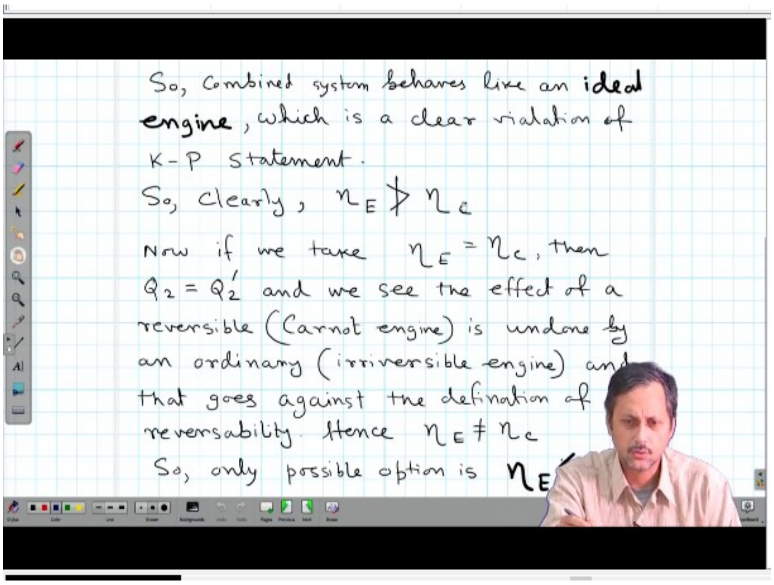
So, for the refrigerator or in this case the reversed Carnot engine there will be an excess of work which will be coming in which it cannot be will not be using. So, what happens is it will have an excess of delta W amount of work which is W prime - W and if you simplify if you just compute this from this table W prime minus W is Q 1 minus Q 2 prime minus Q 1 plus Q 2 prime. So, which is Q 2 minus Q 2 prime and as Q 2 is greater than Q 2 prime Q 2 minus Q 1 prime is a positive quantity.

So, this excess work Q 2 minus Q 2 prime will be performed by the combined system. So, now if we look at the combined system it accepts Q 2 minus Q 2 prime amount of heat from the cold reservoir and converts it completely into the delta W which is Q 2 minus Q 2 prime, this equal to sign is not needed because I have already mentioned delta W which is equal to Q 2 minus Q 2 prime in here. So, basically the combined system works as a perfect engine.

In this case it is accepting heat from the coal reservoir it does not matter, because if we go back to the original Kelvin-Planck statement it says that no process is possible whose sole result is to absorb the heat from a reservoir and converting it completely to work. Typically when we have hot and cold reservoir we think of hot reservoir from where the engine will accept the heat.

But in this case what we see is it is accepting Q 2 minus Q prime amount of heat from the cold reservoir and converting it completely into delta W of the same amount of work. So, this is a clear violation of the 2nd law of thermodynamics. So, the primary assumption that eta E is greater than eta C is not a valid assumption. So, the second possibility is if we have eta E = eta C once again that might be a possibility. So, we cannot rule that out.

(Refer Slide Time: 16:58)

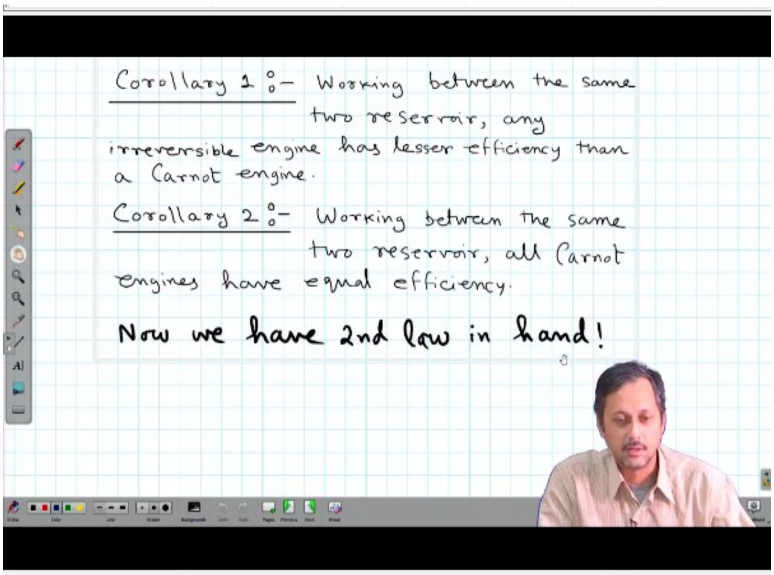


So, what happens in this case when eta E is equal to eta C then Q 2 is equal to Q 2 prime. So, in this case what happens is it will be completely 0, this Q 2 minus Q 2 prime in this both cases, so the combined system will not accept any heat from any of the reservoirs and it will not perform any work or it does not need any work external work as well. So, that eventually means an irreversible engine E is, please remember E is considered to be an irreversible ordinary engine.

So, if we accept the fact that eta E is equal to eta C that means doing of a completely reversible engine which is written as C can be undone can be completely nullified the effect of a working of a completely reversible engine C can be nullified irreversible engine E which is, so basically the effect of an ideal engine working between two reservoirs can be nullified by a non-ideal engine.

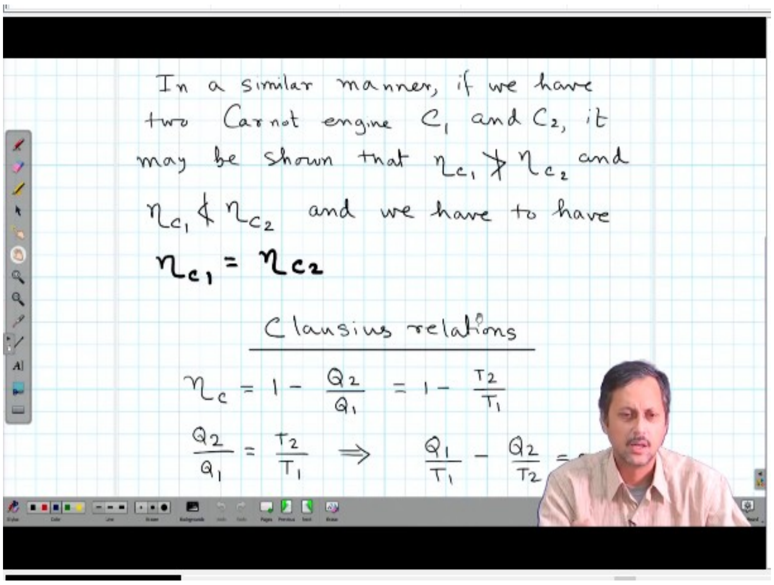
So, that clearly violates the definition of ideality. Definition of reversibility, if an irreversible process can be substituted for an reversible process that essentially means it essentially violates the definition of irreversibility. So, that is why eta E is cannot be equal to eta C. So, the only possibility that remains is eta E less than eta C. That means the ordinary engine has to have less efficiency as compared to Carnot energy.

(Refer Slide Time: 18:53)



So, which is the corollary 1 in case of Carnot theorem. Now for the second part when which says the working between same 2 reservoir all Carnot engine will have equal efficiency.

(Refer Slide Time: 19:08)

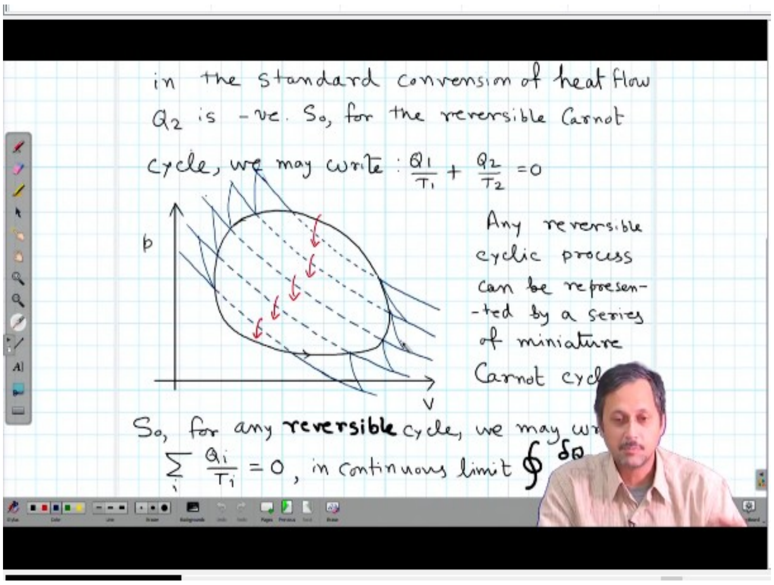


In order to prove that what we can do is we can take C1 and C2 two Carnot engine and we can prove by similar method I am not going into that because these are actually kind of tds proof and finally we know what is going to happen. If you want if you are really interested you can look into any of the standard text books and you can find the detailed proof. So, what will happen is you will see that eta C 1 cannot be greater than eta C 2 and eta C 1 cannot be greater than or less than eta C 2 either.

So, the only possibility that remains is it eta C 1 is equal to eta C 2. Only in this case all the criteria of a reversibility, all the laws of thermodynamics the first and the second law of thermodynamics will remain valid. So, that proves the corollary 2 that means working between the same 2 reservoir all Carnot engine should have equal efficiency. Next the another theoretical discussion which we are going to do is called the Clausius relations. Now for a reversible engine or a Carnot engine eta C is equal to 1 minus Q 2 by Q 1 which is also equal to 1 minus T 2 by T 1.

We have seen that, we have proven that already this part is actually for any engine we can write eta is equal to 1 minus Q 2 by Q 1, but if and only if the engine in question is reversible and that is working between 2 reservoirs at temperature T 1 and T 2 then only we can write eta C is equal to 1 minus T 2 by T 1. So, if we just consider this part we see Q 2 by Q 1 is equal to T 2 by T 1. So, that means Q 1 by T 1 minus Q 2 by T 2 is equal to 0. So, there is a minus sign between those, also you can write so basically you can rearrange this and you can write this relation.

(Refer Slide Time: 21:16)



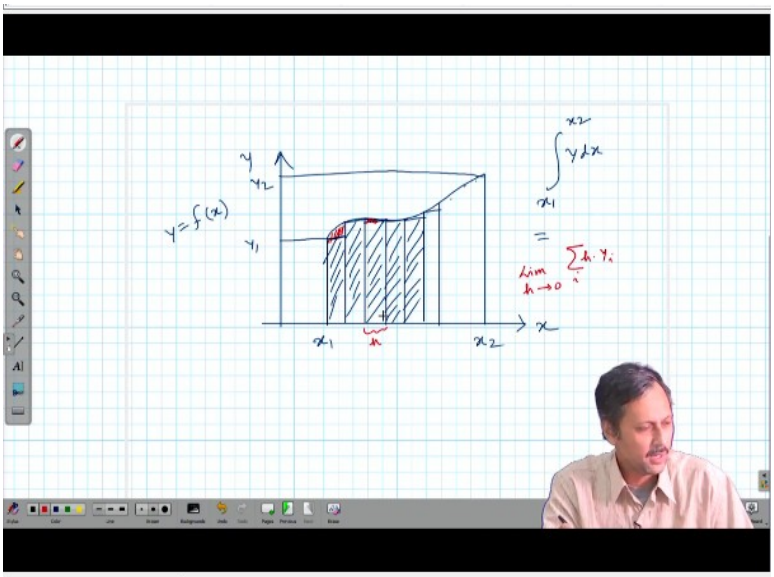
But keep in mind that the term Q 2 is actually the heat that is flowing away from the engine. Now in the standard convention which we have already discussed that work done on a system is negative, work done by a system is positive similarly heat going into a system is positive and heat coming out of the system is negative, going by that convention. This Q 2 is actually a negative quantity. So, if we put this negative value here the relation becomes Q 1 by T 1 is equal to Q 2 by T 2 is equal to 0.

So, this is for a reversible Carnot cycle. Now let us take any arbitrary reversible process in this PV indicator diagram. So, I have just given I mean just put a arbitrary loop I mean it could be of any shape and size, what we can do is we can draw a series of isotherms given by this blue lines, this line and this line and this line and this line. So, we can do that, we are absolutely within our limits to do that.

And the separation between these 2 lines has to be really close, they have to be very closely spaced and what we can do is, so these lines are our isotherms; this dotted part is actually within the circle. So, I have just made it dotted. So, these are our isotherms here and we can also connect closely spaced adiabatic lines. Now so I have just drawn a very coarse picture in front of you. What happens if we just keep these isotherms really close to each other like infighting similarly displaced from each other?

Then this adiabatic's kind of becomes really, really small, the adiabatic part becomes really, really small and eventually it merges with the boundary. Please remember this adiabatic process is also a reversible process in this particular case. I mean adiabatic process is also reversible process in general so and it is something like approximating if you remember for integration what do we do typically. For the fundamental numerical method of integration we have let me just quickly try to draw this.

(Refer Slide Time: 23:55)



So, we have let us say this is my arbitrary x and y axis. So, let us say this is our plot and we want to integrate or this is our function f c. So, we want to integrate between these 2 limits. So, we have x 1, x 2. So, this is my x axis, this is my y axis. Similarly we have y 1 and y 2. So, these are my limits. So, this is y 1, this is y 2. So, what do we do? This integration, so this is my function y = f x. So, integration y dx from this limit x 1 to x 2.

If we do not know the functional form what do we have to do or rather even if we know the functional form we can very much easily approximate it with the trapezoidal rule. What is trapezoidal rule? We first divide this interval into evenly spaced lines. So, we keep drawing very close lines like this and for every line we draw a trapezoidal. So, basically we take this. So, basically we draw straight lines here like this and finally some we take this area, this is our area we just take the area of each individual trapezoid or individual rectangle actually.

And then we add them. Now of course there will be error. So, this part will be not considered here. Similarly in this case we will kind of overestimate this part, this part will be underestimated and in this case if there is a convex section of the curve this will be underestimated, but in the limit when this interval h between successive points in the limit. So, this is my h, so in the limit h goes to 0, this integration will be sum over h times y.

Given that y or h times y i sum over all i. Given that y is the height of this. So, this is the simplest possible rule we have for integration. So, similarly if we go back here for this case when the separation between these 2 isotherms are approaching 0, the series of Carnot cycle we have drawn will actually coincide with this original reversible path. Now for each Carnot cycle we have shown you already that for individual Carnot cycle Q 1 by T 1 plus Q 2 by T 2 is equal to 0.

So, if we have a series of such Carnot cycle and the heat for example is coming in here that heat is rejected here. So, if you remember in the isothermal part the amount of heat that comes in the upper isotherm, in the lower isotherm that will be rejected. So, the total heat that is transformed into this reversible process can be approximated as sum over Q I T i and that has to be equal to 0.

Please remember here once again we have to take the regular convention for Q i that Q i that is entering a cycle is positive and Q i that is exiting a cycle is negative the sign. So, this will be holding this, this sum delta is sum over Q i T i is equal to 0 will hold for this particular I mean for the series of Carnot cycle and in the continuum limit when we have their Carnot cycle or the isotherms placed very close to each other the integration I mean the sum will be replaced by an integration and we can write integration delta Q by T is equal to 0.

So, this is called I mean it does not have a name actually as I mean this result is valid for a reversible cycle and it does not have a particular name as such but there will be another similar relation for irreversible cycle. Together we can call it the Clausius inequality. So, we will stop here today. I know it is already too much theory for you, but in the next lecture what we are going to do is we will start from here.

We will try to prove a similar relation, we will try to have a similar integration for a irreversible cycle and then we will combine them and we will get something called the Clausius inequality and from there we are going to define, we will be going one step ahead and define a very important parameter called the entropy. So, for this is all for today's lecture, see you once again in next lecture, bye.