Statistical Mechanics

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Lecture – 03
Second Law of Thermodynamics and Heat Engines

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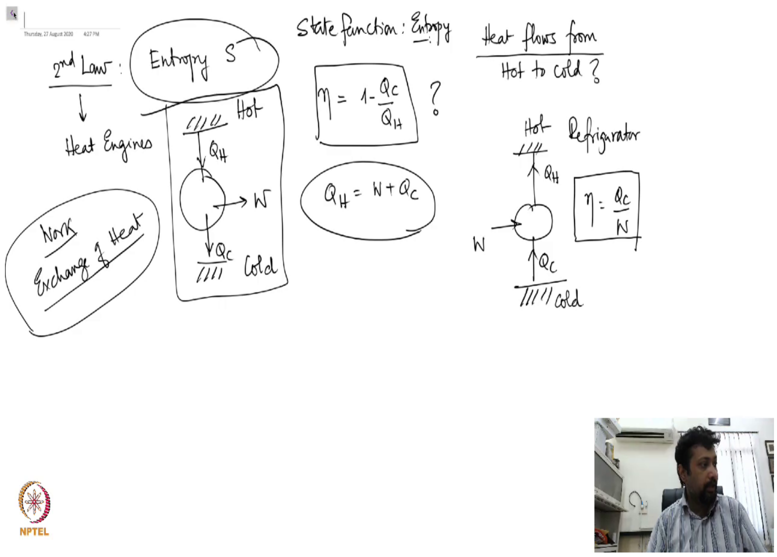

Now comes the second law, the second law is slightly different in the sense that the second law gives you introduces an important quantity which is the Entropy S. Now historically the second law was formulated with the beginning of the Heat Engines right and what is the heat engine you realize the heat engine is basically an engine which takes a certain amount of heat from a hot reservoir does an amount of work W and dump some amount of work QC to the cold reservoir.

So, this is my hot reservoir and this is my cold reservoir and clearly I mean here if you have designed an engine, then you want to know; what is the efficiency of that engine. The efficiency of the engine is defined as QC of QH 1 minus that this is how you define the efficiency of the engine.

So, historically the origin of the second law lies in the development of heat engines people developed diesel engines and all these things were developed historically. And people wanted to know what is how do I calculate the efficiency I mean they are not violative and there has to be a method of calculating the efficiency and therein came in the second law.

So, once I have a heat engine you can see that there is a work involved in this, there is also an exchange of heat that is involved over here. And the efficiency of this heat engine is given by 1 minus QC over QH clearly if I want to apply the conservation of energy then I have QH is equal to W plus QC and this machine does not seem to violate the conservation of energy. Therefore, it does not violate the first law.

So, it is in principle allowed, but then I want to know is there any upper bound of the in the efficiency can I have a 100 percent efficient engine. So, that is precisely where second law steps in. But on top of it remember that the second law also introduces the concept of entropy which is a state function ok. You also realize that in this particular diagram that we have drawn for the heat engine there is a flow of heat that has been indicated that it flows from the hot to the cold.

But why is that? Here in also the answer comes from the second law. Now just for completeness the opposite the reverse of a heat engine is a refrigerator. So, a refrigerator is essentially a heat engine which is worked in a opposite cycle. So, you take an amount of heat QC and you essentially do an amount of work W and you dump an amount of heat QH to the cold reservoir to the hot reservoir.

Now, if you recall if we have seen the old refrigerators at home, then you would have seen that there is a wire mesh that is fixed at the back of the refrigerator, that wire mesh essentially dissipates this QH heat in the environment. So, that backside of this is hot that is why also the external units of air conditions are very hot.

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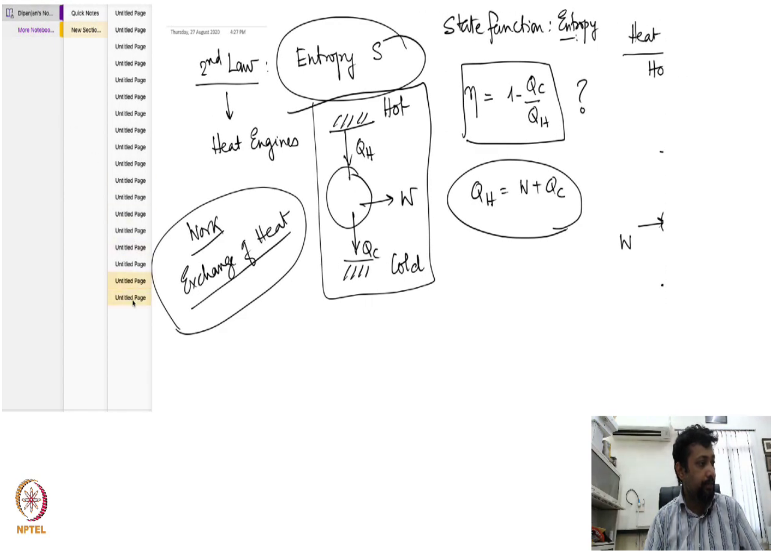

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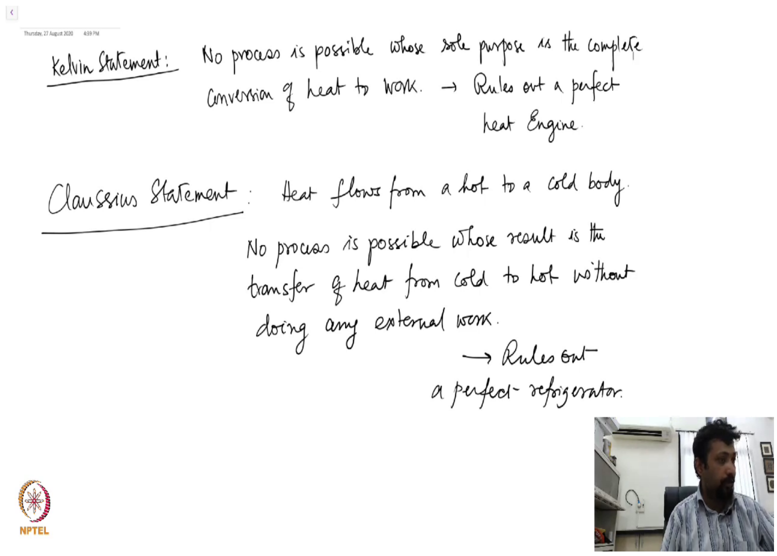

Now let us just quickly go to the next page. There are 2 statements of second law the first statement is essentially a Kelvin statement, that tells you that no process is possible whose sole result is the conversion of this is a complete conversion of heat to work is to convert heat completely to work that you do not get.

So, let us just reformulate this to write down that whose sole purpose is the complete conversion of heat to work. Now this essentially rules out a perfect heat engine right, because this essentially tells you that the efficiency of a heat engine must be less than 1.

The alternative statement is Clausius statement and that tells you that heat essentially flows from a hot to a cold body. In other words that you cannot have no process is possible, where let us say this result is the transfer of heat from cold to hot without doing any external work and this essentially rules out a perfect refrigerator. Now, we want to have the proof of equivalence for this. So, let us just come over here and we want to have the proof of equivalence.

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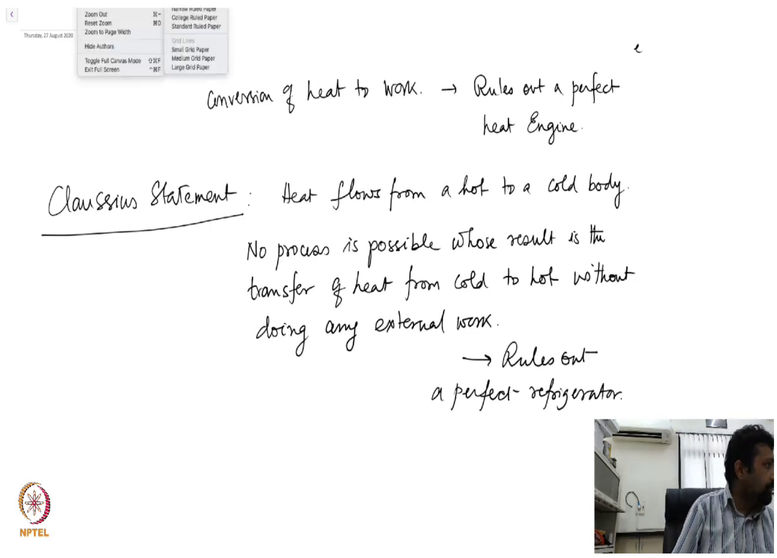

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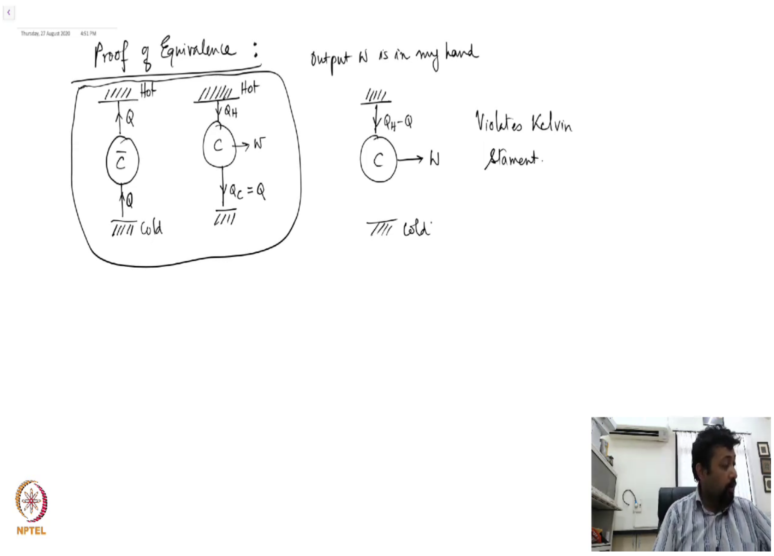

Let us just remove this; so what does this mean what do I mean by proof of equivalence I want to show that if I have, if I violate the Clausius statement I also simultaneously violate Kelvin statement. Similarly if I violate Kelvin's statement I also simultaneously violate Clausius statement.

So, suppose now I have an engine which I shall denote with the bar because it violates Clausius statement and here I have an amount of heat QC that goes in over here and right. So, by definition by conservation of energy this is exactly this. So, I do not have to worry about anything.

Now, what can I do? So, this machine clearly violates Clausius statement because I can see that the heat has been extracted from the cold reservoir. So, this is the hot reservoir and this is the cold reservoir, when heat has been extracted from the cold reservoir and has been dumped into the hot reservoir.

So, in principle what I will do here is I will operate another machine which is a regular Carnot engine that extracts an amount of heat QH does an amount of work W and dumps an amount of work QC to the cold reservoir up to this is fine.

But remember that this output, output W is in my hand. So, I can clearly regulate this, I regulate it in such a way that it dumps amount of heat Q to the cold reservoir. Therefore, if you look at this whole machine together what do you get you get Q, if you look at it carefully then you will get an amount of heat which is QH minus Q which is drawn from the hot reservoir and an amount of W which is converted to 1. So, this machine clearly violates Kelvin statement.

So, the first proof of equivalence essentially tells you that if I have a machine that violates Clausius statement, that is equivalent . If you violate Clausius statement that is equivalent to violating Kelvin's statement right. What about the other way round the other way around is when you violate Kelvin's statement.

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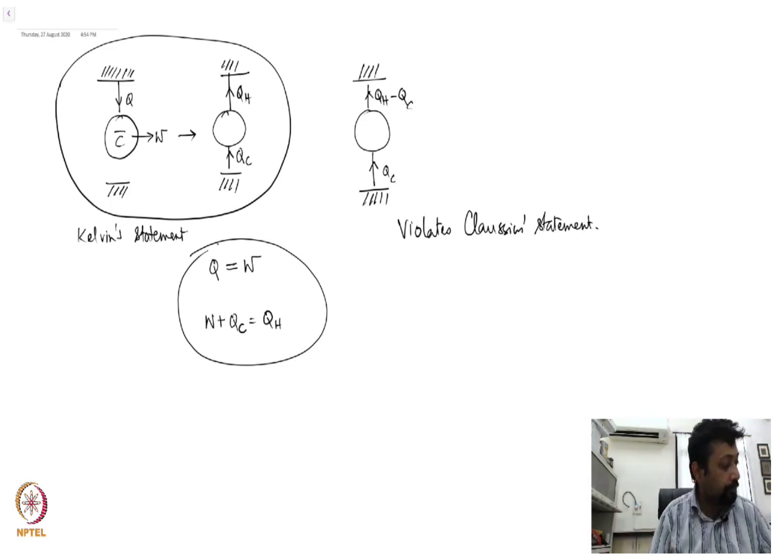

So, if I let us violate Kelvin's I mean by purpose so I have a machine with which I denote by bar, because again it is violating a statement it draws an amount of heat Q from the hot reservoir and does an amount of heat W completely converting this heat into W.

So, when you complete because this then violates Kelvin statement now this work I can use to drive a refrigerator. A refrigerator would take up a heat QC and would dump a heat QH. So, this one violates Kelvin's statement. Now let us look at this whole thing together if I look at this whole thing together.

Then you realize that I have QH minus Q so I have a machine which essentially is in which there is a flow of heat from the cold reservoir to the hot reservoir without any external work that has been done. So, this now violates Clausius's statement right.

So, please note that the conservation of energy should give you Q is equal to W and W plus QC is equal to QH right. So, essentially yeah so these 2 should give you ok. So, this violates

Clausius statement. So, essentially if you violate one statement you violate the other statement right.

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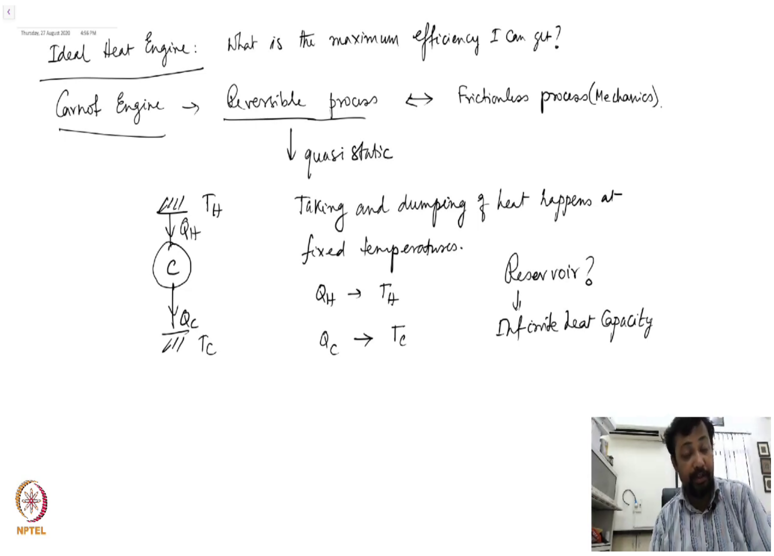

So, now we want to look at what is an Ideal Heat Engine and this is like coming back to the question what is the maximum efficiency I can get. What is the maximum efficiency I can get, because clearly there is involvement of heat and work in this machines right.

And the answer lies in what is called a Carnot engine, in Carnot engines all the processes that are involved are reversible. Well a reversible process you can imagine they in analogy with mechanics they are essentially frictionless processes, which means there is no dissipation process in mechanics. This is the analogy that you have with mechanics and if you reverse the time you can reverse the inputs and the outputs in a reversible process. So, the equivalent of that in mechanics is a frictionless process.

Since essentially there is the reversibility implies an equilibrium this necessarily means that this process has to be a quasi static process. All reversible processes are quasi static process, but the reverse is not generally true. Now what is a Carnot engine well a Carnot engine is the one so I have a Carnot engine it takes up a heat QH and it dumps a heat QC and essentially in a Carnot engine the taking up of the heat and the dumping of the heat. So, in a Carnot engine and the dumping of the heat happens at fixed temperatures.

So, QH is taken up by the system at a temperature TC sorry TH and QC is come to the cold reservoir at a temperature TC. In no other in all the other processes that may be involved in this Carnot engine, there is no heat exchange with either of the reservoirs.

So, here a very short note what is the reservoir, a reservoir is the one which has an infinite heat capacity. And that essentially means even if you dump if you take away certain amount of heat or you dump certain amount of heat to the reservoir its temperature remains fixed.

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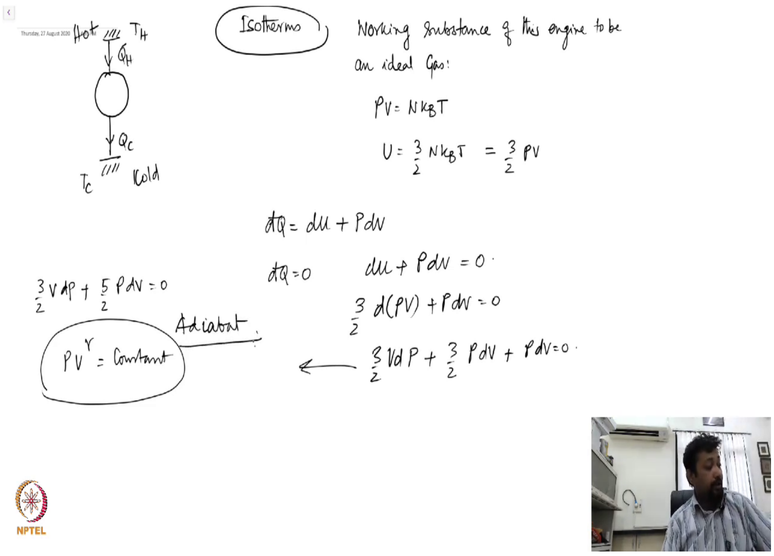

So, let us go ahead with this happens at t h and this happens at TC. The dumping of the heat happens at TC. So, once again this is my hot reservoir and this is my cold reservoir now TH and TC are therefore so isotherms and hear in my zeroth law comes in to rescue me. Zeroth law tells me that how I can pick isotherms right. But it remains because the rest of the processes must be adiabatic I do not know because no heat exchanges are allowed. So, I have to figure it out how adiabatic process (Refer Time: 15:36).

Well if you take the working substance of this engine of this engine to be an ideal gas, then I know for the ideal gas PV is equal to NKBT right. And the internal energy of the ideal gas is 3 by 2 NKBT, if you are I mean if you want to be you can take this factor to be more generally depending on the type of ideal. So, you will consider the ideal gas to be mono atomic or made up of mono atomic particles.

So, once I have this then I know that d cut Q is equal to d u plus PdV remember in the last lecture we have discussed this that the generalized pressure I mean the force for hydrostatic system is minus P and therefore this is what it becomes. Now since I am not allowing any heat exchange it follows d cut Q is equal to 0.

So, d u plus P d V must be equal to 0. So, d u is 3 by 2 let us just write this over here as PV 3 by 2 PdV well let us be d of PV plus PdV is equal to 0. So, 3 by 2 d P plus 3 by 2 P d V plus P d V must be equal to 0.

So, this means 3 by 2 VdP plus 5 by 2 PdV is equal to 0 and you can clearly see PV to the power gamma is constant. So, this is an equation of an adiabat provided your working substance is an ideal gas.

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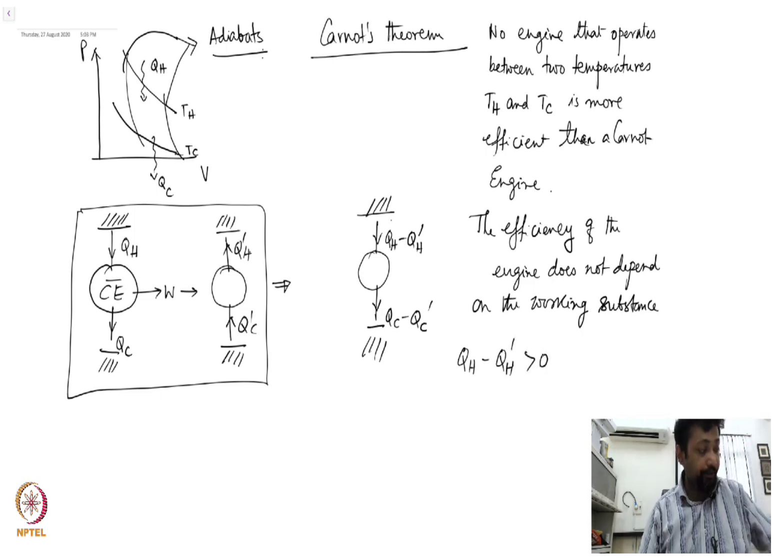

So, if I want to look at the PV diagram then I have the isotherms and I have the adiabats right. So, the isotherms is where the heat is taken this is TH and this is TC and the adiabat is and the second one is where the heat is dumped the isotherm corresponding to TC. These 2 are adiabats and therefore there is no heat exchange that is allowed. So, this is the simplest form of a Carnot engine.

Now, Carnot's theorem tells you that the following no engine that operates between 2 temperatures TH and TC is more efficient than a Carnot engine. Remember what is so special about a Carnot engine because all my processes are reversible number 1, the efficiency of the engine does not depend on the working substance.

So, you might as well do it with a magnetic substance instead of working with a ideal gas, essentially what you will have is the same efficiency if your temperatures TH and TC remain the same.

So, once I have that so let us see if I can prove it. So, what I will do over here is I will take a non Carnot engine which means which is standard in the sense it extracts an amount of QH amount of heat dumps a QC amount of heat and does a work W. This is your hot and this is your cold and that work is used to run a refrigerator which extracts an amount of heat Q prime and dumps an amount of heat Q prime h to the hot reservoir.

If I now look at the combined system together then put them in a box and just look at what this thing is doing this equivalence is that I extract an amount of heat QC minus QC prime, the orders has to be different . So, essentially I will do it in the following way I will write it down like QH minus QH prime or Q prime H and QC minus Q prime C right. Let us see now I have done it is in the following because, if this the arrows were reverse then it violates Clausius's theorem statement of the second law.

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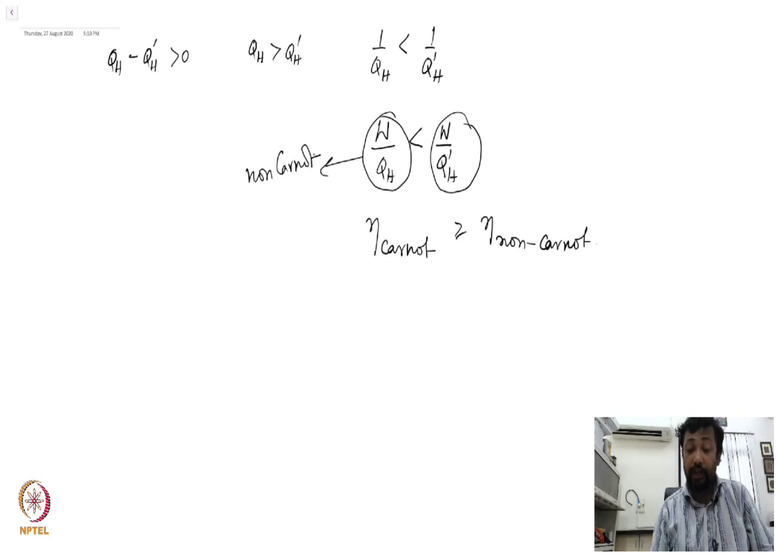

So, it follows that QH minus Q prime H must be positive. If QH that means, QH is greater than Q prime H right. So, it follows since I am multiplying this the work done is same in both cases if I am define right. Therefore, eta Carnot which is essentially W by QH must be greater than eta non Carnot remember this is your proper Carnot engine where you have taken the amount of heat Q prime H and this is the one.

This is the one which was your non Carnot engine which violates the Carnot's theorem, but it clearly tells you that if you have to design a non Carnot engine where it violates the Carnot's theorem, then essentially you also violate Clausius's theorem.

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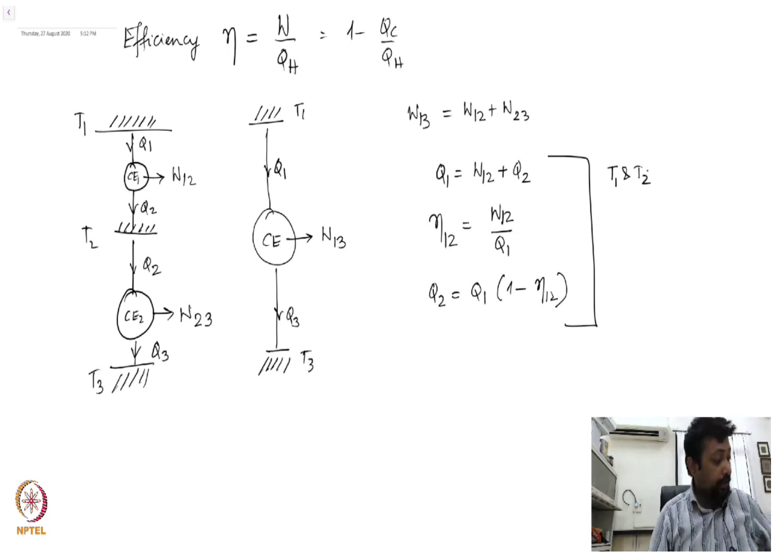

So, question now remains is what should be the efficiency eta, which is W over QH which is 1 minus QC over QH. Now for this case we will consider 2 Carnot engines one at T1. So, operating the second one T2 and yet a third one which is at T3. So, it takes an amount of heat Q1 dumps it to Q2 does an amount of work W 1 2 this one takes an amount of work Q2 as amount of heat the same amount of heat Q2 and does an work W 13 and dumps an amount of heat Q3.

So, this is what we call as Carnot engine 1 and this is what we call as Carnot engine 2. Once again if I look at the combined effect of this engine this combined effect of this engine is that I have 1 Carnot engine which is operating between the temperatures T1 and T3 and does an amount of work W 1 3 right this. So, it extracts an amount of energy Q 1 dumps an amount of heat Q 3 correct.

Now, let us see first of all W 1 3 this is wrong this has to be W 2 3, W 1 3 is W 1 2 plus W 2 3 the total work that has been extracted from the 2 heat engines and in tandem is equal to the 2 works W 1 2 W 1 3 . It also follows that Q 1 plus W 1 2 is equal to Q.

So, if I now apply the conservation of energy then this means that Q 1 is W 1 2 plus Q 2 right. But from the definition of this efficiency I can write eta 1 2 as W 1 2 divided by Q 1. So, therefore Q 2 is Q 1 1 minus eta1 2 right let us look at. So, this follows from the engine which works between T1 and T2 what happens.

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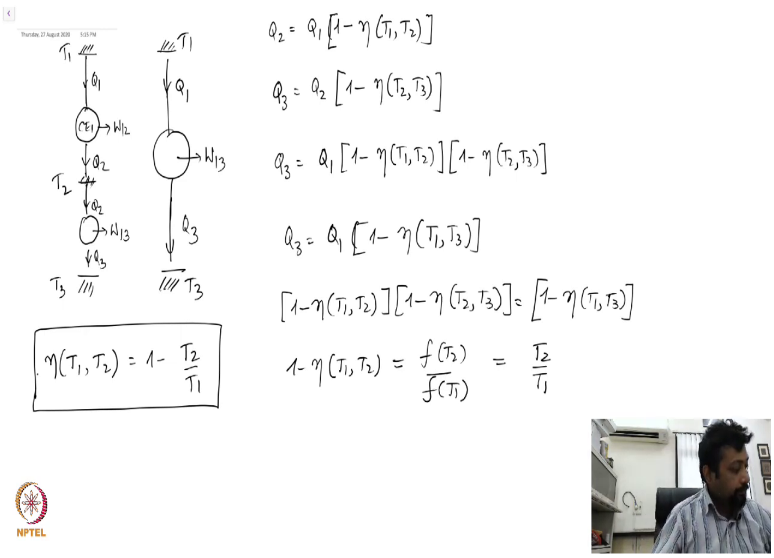

For the second engine so let us just briefly draw this again Q 1 CE 1 does the word W 1 2 Q 2 the second one again takes a heat Q 2 does the work Q 3. So, it does the work W 1 3 and dumps a heat Q 3. So, this temperature is T3 this temperature is T2 this temperature is T1 and I saw that Q 2 is Q 1 1 minus eta of we will write it down like this way.

Similarly, for the engine which operates between T2 and T3 it follows that Q 3 must be equal to Q 2 1 minus eta T2 and T3 alright. So, therefore, Q 3 is equal to Q 1 if I just substitute for Q 2 from the above equation it is 1 minus eta T1 comma T2 one minus eta T2 comma T3.

But now the combined engine does something like this and Q 3 is clearly Q 1 times 1 minus eta T1 and T3 equating these 2 equations it follows that 1 minus eta T1 comma T2 times 1 minus eta T2 comma T3 must be equal to 1 minus eta T1 comma T3 right.

Now, this equation is clearly satisfied if I have one minus eta T1 comma T2 which is equal to f T2 for f T 1. So, that there is a cancellation on the left hand side and what will be left out after the cancellation is only going to be a function of T1 and T3 and traditionally conventionally this is taken to be T2 over T1, so that the efficiency of 2 engines which operate between T1 and T2 is given by T2 over T1; this is how the Carnot efficiency look.

And you see in this form expression for the efficiency there is no material parameter involved over here, there is absolutely nothing that tells that requires or let us say like the specific heat of the system enters in the situation or the compressibility or the susceptibility that exist because there is no material parameter.

The efficiency only depends on the temperature of the 2 reservoirs, so powerful is the Carnot theory. But remember the point is that the Carnot engine is an idealized engine right and it is the maximum efficiency possible for any engine that you design which operate between 2 temperatures T1 and T2 right.

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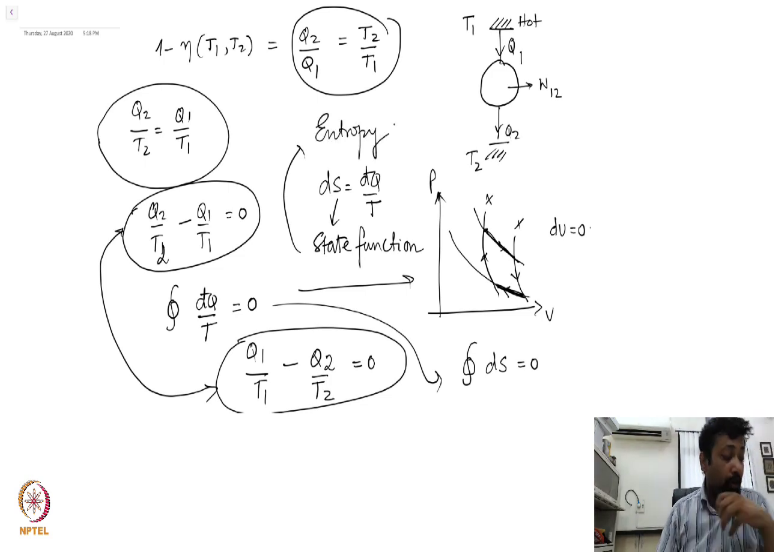

So, if I now write down one minus eta T1 comma T2 as Q 2 over Q 1 and this we saw was T2 over T1. Interestingly let us just look at this part of the equation and recast it in the following way. Now when you look at the Carnot engine which operates by taking an amount of heat Q 2 sorry an amount of heat Q 1 from the hot reservoir dumps an amount of heat Q 2 the cold reservoir does an work W 1 2.

The machine has now operated in a cycle. So, that this has come back to its initial state, recall in the PV diagram what we had we had 2 isotherms like this way along with sheets were taken and then 2 adiabats.

So, this goes like this comes, but it comes back to this initial state, so that if it has come back to its initial state the change in internal energy is zero because internal energy is a state function right. So, it has come back to its original state, therefore the change in the internal energy is 0.

But if you just look at this equation in this whole process you can see I can again write down this equation as Q 2 T2 minus Q 1 T1 is equal to 0, but the left hand side is clearly is d cut Q over T is equal to 0. Because if I am to perform this integral over for this particular machine, if I am to apply this for this PV for the Carnot engine you see heat let us look at this integral the heat has taken place only at constant temperature.

So, it only happens over here therefore, I will have Q 2 sorry I will have Q 1 and the temperature is constant. But here heat has been dumped energy added to the system is positive, energy dumped to the from the system is negative taken out is negative.

So, it has a negative sign minus Q 2 over T2 for this part of this, no in this part there is no heat exchange in these 2 branches there is no heat exchange, therefore it follows this is equal to 0. So, this equation or equivalently this equation that we had written down is the result of this integral. Now amazingly you see that this is clearly does not depend on the path, but rather it depends on the 2 end points right.

So, therefore, I can write down this equation equivalently as d of s equal to 0. Where now d s is defined as d cut Q over T, where s is clearly is an state function. Why is it a state function? Because just like the internal energy this is a state function because just like the internal energies the system has come back to its original point this closed integral is 0. The change in this value is 0; this state function is what we call as entropy.

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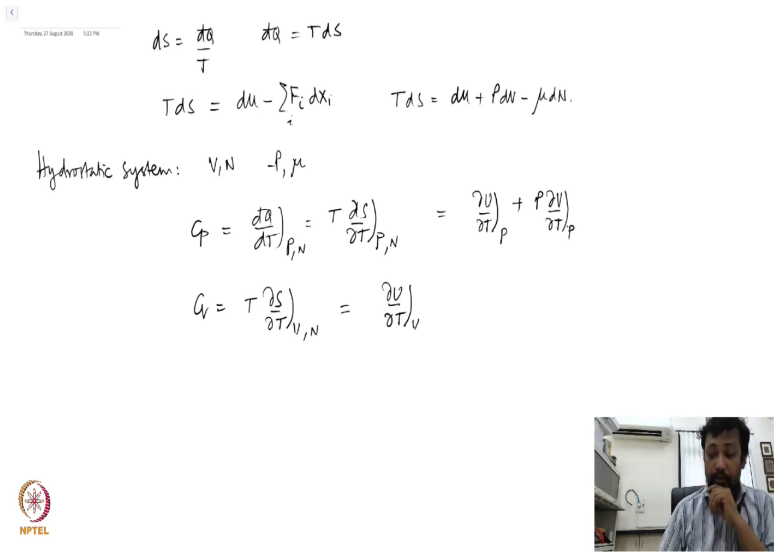

Once we have defined the entropy d s as d cut Q over T we can write down this as T d s and therefore our second first law takes the form minus f i d Xi sum over r. Remember for a hydrostatic system let us just take a very small example, for a hydrostatic system my generalized coordinates were V and U and V and N and my generalized forces were minus P and mu. And therefore your first law takes the form d u plus P d V minus mu d N right.

Once you have this of course, now the whole of thermodynamics is mostly done, now it is depends on how you apply to the system. I can determine the response function which is T del S del T at constant pressure, I can define the specific heat T del S well let us just take one step back and rewrite this as d cut Q over d T at constant pressure which is T del S del T at constant pressure and this is T similarly this becomes del S del T at constant.

So, if I now want to apply pressure is being held constant volume is being held constant. So, we will keep N fixed also over here and this is just del U del T volume constant right. Just it follows from the first law if you carefully take the derivative, this on the other hand is del U del T pressure constant del U del T pressure constant plus P del V del T pressure constant right and has been held fixed therefore this third term is 0 right.

So, this concludes our discussion on the second laws of thermodynamics.