Chemical Engineering Thermodynamics
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Lecture – 07
Second Law and Entropy

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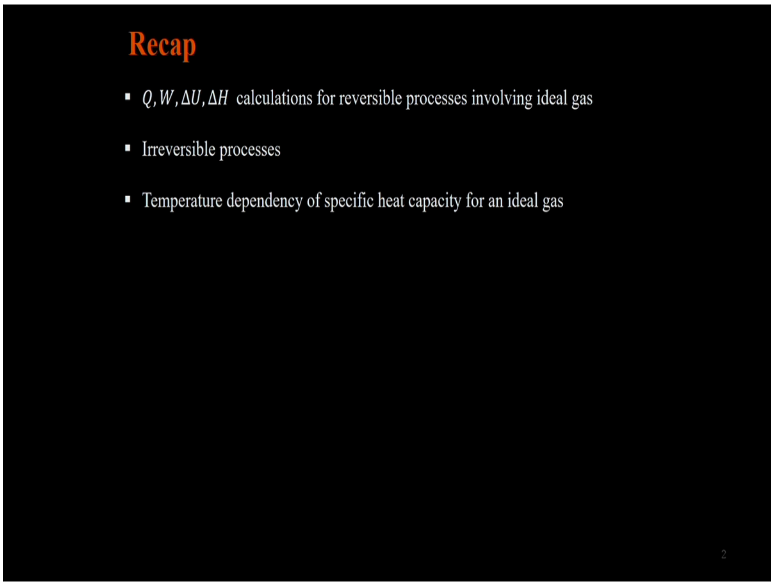

Hello and welcome back. In the previous lectures, we have looked at calculations of the heat about changes in a process, the internal energy and enthalpy changes for reversible processes involving ideal gas as well as for irreversible processes that involve ideal gas. We have also looked at how to account for the temperature dependency of the specific heat capacity. We looked at c p, but since for an ideal gas cpi g minus cbigs are essentially we can account for the temperature dependency of heat capacity for an ideal gas by integrating the appropriate equations the polynomial expressions for c p or c v.

So, far we did look at irreversible processes, but then the efficiency of a process has been given to us. This irreversibility as we discussed earlier is caused due to things like friction, the velocity gradients and other dissipations that occur during the course of a process. And, in general these inefficiencies in a process we are interested in knowing how these inefficiencies in a process can be accounted for; because ultimately that would give us how much work output comes out of a process. We would like to maximize the work output from a process or work requirement is something we would like to minimize in a process right.

So, if it is a process which involves work input then we would like to minimize that work requirement. If it is a process from which we are extracting work, then we would like to maximize the work output from the process. And, in either case we would like to know how we can maximize or minimize the work and that depends on the inefficiency or efficiency of the process right. Usually these are addressed by using a quantity known as entropy in thermodynamics. The word entropy is quite from a Greek word like by Clausius which means essentially transformation. So, it acts as a measure to transform energy into useful work. It is a difficult concept one of the most difficult concepts in thermodynamics, when we encountered it the first time to understand and appreciate.

Partly because, its influence on physical processes is very subtle and we rely on heavy mathematical expressions to be able to understand this concept. So, it sort of to the beginners it looks as an abstract concept, but its if you want to think about it is similar to thermodynamic variables such as internal energy or enthalpy which are useful tools for us to quantify what is happening in a process. Same is the case with entropy. To begin with let us start looking at the process and try to talk about what we mean by work and heat requirements for the process or how much heat is converted to work or vice versa. Let us take very simple example.

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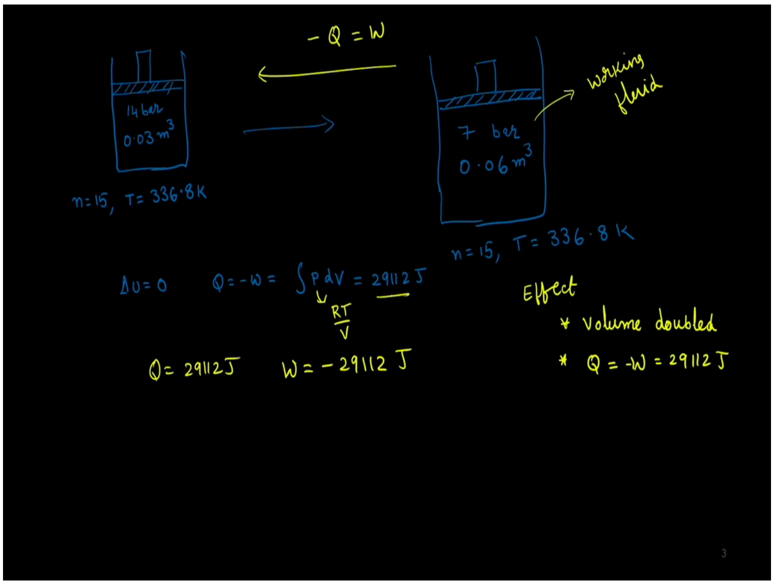

Let us say I have an idea of gas right in a piston and a cylinder assembly right, I have an ideal gas, this is a piston and a cylinder assembly. This ideal gas in the piston cylinder assembly at 14 bar and 0.03 meter cube is a total volume. So, because it is an ideal gas and if I know the total number of moles, I can calculate the temperature or vice versa. Let us say for example, this ideal gas has 15 moles in the in this assembly or system and the temperature turns out to be 336.8 Kelvin. Now, if I allow this ideal gas to expand in a process expand in a process such that the pressure has pressure falls down by 50 percent; the temperature it is a closed system and still 15 we are going to take an isothermal process.

So, the temperature is still going to remain the same. All I am doing is I am allowing the pressure to fall by half to 7 bar which means the volume is going to double; the total volume is going to double to 0.06 meter cube. So, we have double the volume everything else being the same, the pressure is going to reduce by half. Now, if this is the process this is an isothermal process for an ideal gas. So, as we have done earlier in the previous lectures delta U is going to be 0 because, this is an idea of gas, there is no temperature change. Q is going to be minus W it is going to be the integral of P dv. And, that turns out to be 29112 joules if you run through the calculations and get the number right the way we did it the last time essentially this is RT by V temperature is constant.

So, it will be RT l n V 2 over V 1 and then we can get the final number. So, the total work output from the process is 29112 joules right. How much is the heat, that we need to supply to get this work done: Q is also equal to 29112 joules. The system has lost work so, W is going to be negative of that this many joules. So, although it looks as if all the heat is converted to work which is true, but if we want to run a processes cyclic process out of this; we also need to note that the system conditions have changed right. So, the only effect of this process is the effect of this process or if I want to write the effects of this process; then the process has double the volume of my gas.

And, it has also produced a work equal to 29112 joules which is also same as the heat exchange. So, these are the effects of my process on the system as well as our surroundings. We have supplied this much energy from the surroundings to the system, the system has produced so, much work and at the same time the volume of the fluid inside the system which we tend to call as the working fluid has doubled. Now so, the effect heat is converted into work, but at the same time there is also another change where the volume of the fluid has doubled. Now, if I were to bring this fluid back to its original state: one of the ways to do it would be to take another isothermal process and extract heat out of the system right.

The same quantity of heat out of the system then the work would be negative of this quantity and then you will put the system back to the original state. But, the network in that scenario would be 0 because, in one direction you are extracting work in the other direction you are putting the same amount of work back on the system. So, in a fact you know there is no network produced from the whole cyclic process if the system were to go back to its original state. But, then in real life right if we were to produce work from a system continuously, we need to build a process which we call as a cyclic process right.

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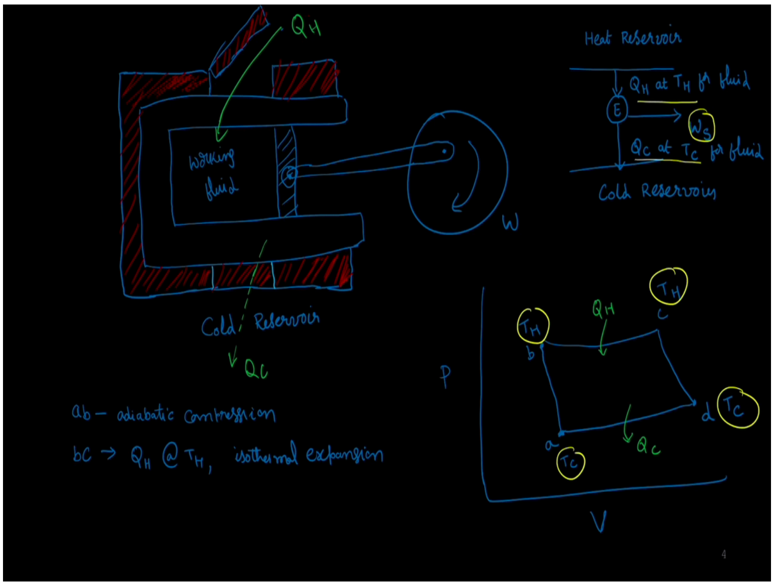

So, let us take an example and we do this by using and we call the systems which produce forecast engines right. So, were in we have a heat reservoir; reservoir essentially is the term we use which is capable of supplying large amount of heat without change in the total property of the reservoir itself. So, this E here stands for engine. So, the engine gets some amount of heat from the hot reservoir at a temperature of T H for the fluid, it then produces some work W S. And, after that point it rejects it reject some amount of work Q C at a temperature of T C for the fluid right to the cold reservoir.

By doing this so, if I were to just absorb heat from the hot reservoir and do some amount of work, there is a change like we have seen in the earlier example in the conditions of the working fluid. And, if I were to bring this working fluid back to its original state so, that it can accept another batch of heat from the hot reservoir and then I can make a cyclic process out of it. It has to discard some amount of heat to the cold reservoir. Let us say this amount of heat it discards to the cold reservoir elevated a different temperature Q S T C will be equal to Q C. Then essentially what the engine will do is absorb heat at a temperature of Q H from the hot reservoir and discard heat at a temperature T C to the cold reservoir.

And, in the process it also does a 4 equal to W S on the surroundings. So, this is something we call as a heat engine right. Now, it is a if I go to build a cyclic process using this heat engine it is pretty straightforward; all we need to do is imagine a nice system which can do this job for us right. So, let us see if we can draw that system which can do this job. I am going to have both a piston and a cylinder assembly right. So, this is my cylinder and then I am going to put a piston in this ok. And, this piston is connected to some sort of device that is turbine or something like that which is going to rotate when it moves and produce work right. So, this piston movement of the piston is going to transfer into work. And, now these are the walls of the cylinder; if I do not insulate them they are going to continuously exchange heat with the surroundings.

We do not want to do that, we want to do that only at when we desire to do it. We want to do it at some high temperature T H; we want to exchange or absorb heat from the hot reservoir and its some cold temperature T C we want to discard heat to the cold reservoir. So, let us say I have my cold reservoir on this side. This is a simple scenario which makes it easy for us to understand right and a hot reservoir it on this side. And, we would also this is a pictorial representation and it is nicely illustrated in a textbook by Professor Elliot from University of Akron and Professor Leader from Michigan state. So, I would recommend you guys look at this representation for more details, but to quickly summarize this type of device this is what we have.

So, what am drawing around it this let us say this thing is an insulation. So, whenever you insulate this guy right, it is also put a break here; we are going to insulate the walls of the cylinder right. So, it looks something like this. A movable insulation which can be open and closed as well, one for the hot reservoir side and another for the cold reservoir side. So, when I open this then you are exposing the wall and then it can absorb heat let us take that out, let us use a different color there just to make it easy for us. So, when this insulation is open right or maybe I should just open it a little bit more. So, that it is easy to appreciate right.

So, it looks something like that right and when this is open, this heat is transferred. When we want to isolate it, not exchange that heat we are going to close that flap. And, similarly we can have one on the cold reservoir side; when need be this flap at the bottom can be opened or closed. So, this way we have a piston and a cylinder assembly and inside is my working fluid right. And, now let us say initially we start at a condition this is easily represented on a plot a P versus V plot right. The initial state of the system is at a point a and then a to b is going to be an adiabatic compression that is my point b. This is my point a; a to b is adiabatic compression and at b we open the flap at the bottom at the top. So, that it can exchange heat with the hot reservoir a temperature T H.

So, let us write this down a to b is adiabatic compression right; a to b is adiabatic compression and b to c is expansion Q H at T H. It exchanges that heat isothermally and expands. So, because it expands the volume is going to increase and we have something like that; this is b to c right and this happens isothermally. So, the pressure is going to change slightly and the volume is going to increase manifold. And, then we have c to d where we have an adiabatic expansion again to a temperature of T C and then d to a is isothermal compression back to its original state. So, a to b is adiabatic compression from T C to T H, b to c is isothermal expansion, c to d is adiabatic expansion and again it comes back to T C and d to a is at the same temperature T C.

So, this way am going to highlight the temperatures at each of these states right. So, and when these are isothermal conditions in one scenario we are going to reject heat to the cold reservoir, in the other scenario it is going to accept heat from the hot reservoir. So, this is how my whole process looks like and then it becomes a cyclic process. By building a process using this piston and cylinder assembly, I can continuously produce some amount of work. We can very quickly do a first law balance on this process right.

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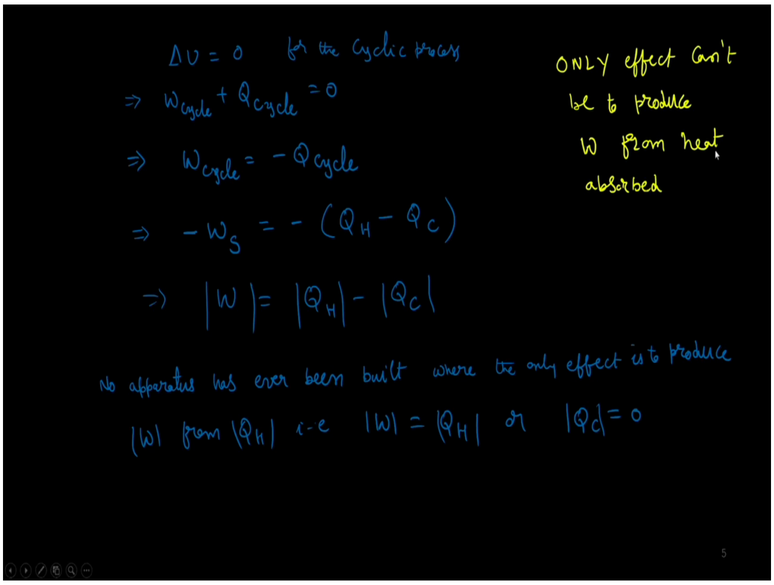

And come up with the total net amount of work that is produced because, it is a cyclic process delta U for the whole cycle is 0 right which means W for the cycle plus Q for the cycle is 0. Or, this means W for the cycle is going to be negative of Q for the cycle right. W for the cycle is negative W S that is the total amount of work it is producing because, the system is doing work on the surroundings you get the negative sign. And, on this side it is negative of its gaining and energy of Q H and T H and losing Q C to T C. Or, W S is going to be Q H minus Q C to avoid the confusion of the signs we usually put an absolute value on Q H and Q C. So, that we get the signs we need on or we get the correct sign convention on these quantities right. And in fact, on this side as well we can remove the shaft or for now let us just call it as W for the process itself.

So, W for the process is going to be Q H minus Q C. This is a total amount of work done by the process. Now, we go come to the first statement of the second law. It turns out that no apparatus right or no heat engine has ever been built where, the only effect is to produce W from Q H right; that is where W is only equal to Q H or where Q C equals 0. We can now, that it has never been built this is an engineering of observation no operators has ever been built where the Q C can be equal to 0. So, that all the work produced or the work produced is equal to the total heat absorbed from the hot reservoir which is Q H. So, this is the basis for the first statement of the second law right which says that it is not possible that the only effect of any process cannot be to produce work from heat absorb. In addition the process will all there will always be some change either in the system or the surroundings. And, because of that we lose some amount of work or heat that we have exchanged with the system right. Now, another way of defining the same thing is through what we call as efficiency of the process.

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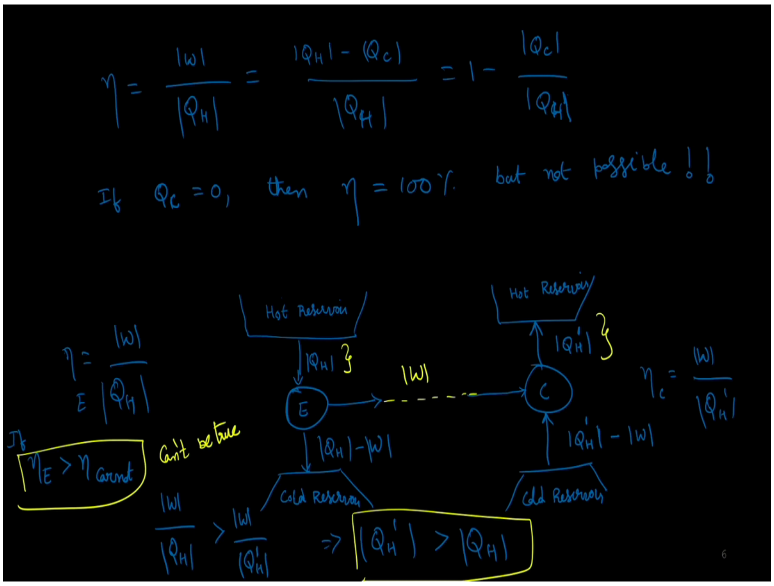

The thermal efficiency of such a heat engine is defined as the total amount of work we can produce over the total heat we have exchanged with the engine and at the hot reservoir. The efficiency is W by Q H right and because by virtue of the first law W we said is Q H minus Q C the efficiency is going to be equal to 1 minus of Q C over to Q H. Notice what happens, if Q C equals 0 then efficiency will be equal to 100 percent, but we said it is not possible to have any process or any engine where Q C can be 0; that is violation of the first statement of the second law. So, there can be no process where the thermal efficiency can be 100 percent or we can produce work, we can convert all the heat into work.

So, we know that there is some amount of heat that would not be possible to be converted into work we can only convert so, much. Then we ask the next question, if that be the case what are the limits on the amount of work I can produce; it is fairly straightforward question to answer. But, before we go there let us talk about something known as a Carnot engine. A Carnot engine is something where all the processes occur irreversibly. So, if you look at the previous slide right if you look at this slide we had 4 steps in the whole cyclic process, each of these steps has to occur at a reversible condition. Because, reversibility will reduce the inefficiencies in the process the idea is that the Carnot engine will have the maximum possible thermal efficiency ok; that can be proved by taking a Carnot engine and a Carnot refrigerator together right.

So, let us look at how we prove that a Carnot engine is the engine that will have the maximum efficiency. So, let us take a hot reservoir and let us build an engine which will accept Q H from the hot reservoir at the temperature of T H and then reject Q C to the cold reservoir at the temperature of T C. And, let us say this produces a work of W by virtue of first law Q H minus Q C is W we are more interested in W. So, let us just write this guy as Q H minus W right, it is the same thing we just got rid of one variable instead of using the first law every time. Now, an opposite of this Carnot engine is what we call as a Carnot refrigerator. In a Carnot refrigerator we actually reject heat to the hot reservoir right and accept heat from the cold reservoir; we call this as a Carnot refrigerator.

To be able to do that instead of producing work we have to actually do work on the refrigerator ok, we have to do work on this refrigerator. So, let us say it needs a work of W again and we can make these quantities different; this is Q H prime and by virtue of the first law this will be Q H prime for the refrigerator it will be Q H prime right minus definitely. So, you add this to quantities it will be Q H right. So, this is how it looks like this is a Carnot refrigerator. Now, let us say I have a Carnot engine and a Carnot refrigerator. In the engine mode the efficiency is going to be W over Q H right. What we can do is we can actually combine these together such that the work coming out of the engine can be used to drive the refrigerator because, it is the same amount of work.

If we try to do that imagine that we can use this work to drive the refrigerator because, both these works are W's right; they are the same quantities. So, I can combine them and make it look like this right. So, if you now look at it right there is no external work that we are doing on the engine and refrigerator combination. There is no external work on this engine refrigerator combination right and in this case it will be W or Q H prime. Now for a minute so, we can combine this engine and refrigerator together such that the W of the work produced by the engine can drive the refrigerator right. So, in one case the efficiency is W by Q H for the engine and in the other case for the refrigerator it is W by Q H prime. The question is can any engine have a efficiency that is greater than the Carnot engine right. To answer that question we can simply like I said combine these two engine and refrigerator combinations. And, let us say that the efficiency of this heat engine we are considering here is greater than that of the Carnot engine.

If that be the case, if that be the case then what it means is that W because, it is simply the sign that is different in these two; engine and reservoir what this means is W over Q H is going to be greater than W over Q H prime right or this implies Q H prime is greater than Q H. So, if the if I have any engine whose efficiency is greater than that of the Carnot engine what it will do is that, it will make Q H prime which is the heat that is rejected at the hot reservoir greater than Q H. It is the same amount of work right, if you look at the overall scenario what it is doing then is that there is no external work on this engine and refrigerator combination. But, then we are only driving or drawing some heat from the cold reservoir and rejecting it to the hot reservoir without actually doing any external work which is again a violation of the second law statement, that is not possible which means this cannot be true.

So, there can be no engine which whose efficiency is going to be greater than that of a Carnot engine. So, the maximum possible efficiency thermal efficiency we can get is going to be that for a Carnot engine.

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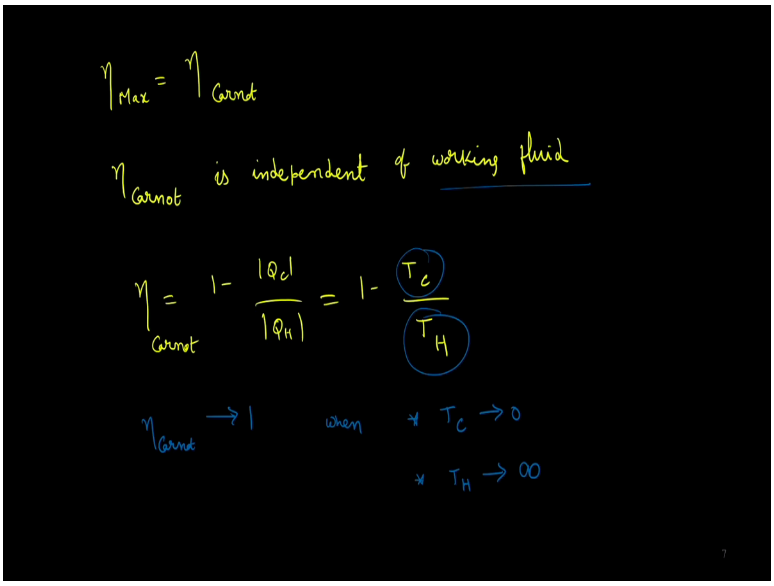

So, if the maximum efficiency is always going to be the efficiency of a Carnot engine otherwise we can build a device which does not require any work, but will be able to draw heat from a cold reservoir and rejected to the hot reservoir which is not possible.

There are other corollaries to it, we can also show that the Carnot engine or the efficiency of the Carnot engine is independent of the working fluid. So, you can have any working fluid inside; it does not matter the Carnot engine is always going to have the same efficiency right. That again can be derived from the fact that you can combine an engine and refrigerator working with two different fluids.

And, if they have different efficiencies then it will violate the second law right. Because, it is independent of the working fluid right. I can also use an ideal gas as a working fluid and the moment I use an ideal gases as a working fluid, it turns out that the efficiency can be rewritten in terms of temperatures and pressures. And, you can relate it to the temperature of the fluid at the cold reservoir or temperature of the fluid when the heat is rejected to a cold reservoir which is T C and temperature where, it accepts the heat from the hot reservoir which is T H. So, the efficiency of the Carnot engine is then going to be simply equal to 1 minus T C over T H.

If the working fluid is ideal gas you can derive this equation for an ideal gas, but then because we are claiming that it is going to be independent of the working fluid this relation then is going to work for any fluid irrespective of the work employed. Although, the derivation itself is based on ideal gas at the end of the day Carnot engine efficiency is always going to be 1 minus T C by T H and it will be independent of the working fluid. And finally, this is the efficiency of Carnot engine for an irreversible process this is the maximum efficiency we can achieve in any engine for processes or engines which are irreversible the efficiency is going to be even lower.

So, this is the maximum limit we are imposing on the thermal efficiency for a particular process right and when will this efficiency be 1. So, the efficiency of a Carnot engine is going to approach 1 when T C is going to be 0; when we can reject the heat to the cold reservoir almost at 0 Kelvin or when T H approaches infinity. In either of these two cases when we have a very high temperature or a very low temperature we approach a thermal efficiency that is equal to 1 otherwise it is going to be limited by this expression here which is 1 minus T C over T H. So, this is a summary of second law a Carnot engine and then the thermal efficiency for a Carnot engine.

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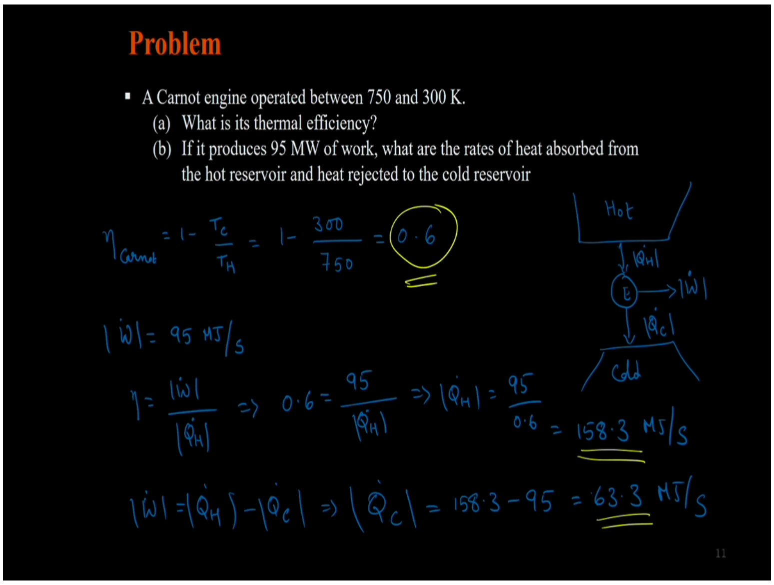

Let us quickly look at one example problem based on these ideas right. We have a Carnot engine that is operated between 750 and 300 Kelvin. First question is what is its thermal efficiency and if it produces 95 megawatts of work what are the rates of heat absorbed from the hot reservoir and heat rejected to the cold reservoir ok. Let us see if we can answer this question; it is a pretty straightforward question once we understand the concepts we discussed a minute ago. Like we said the thermal efficiency of a Carnot engine is going to be 1 minus T C over T H right. In this case what you are seeing work these are rates of work. So, let us use a dot there, this is Q H dot, this is W dot and this is Q C dot. And, we are rejecting heat to the cold reservoir; we are accepting heat from the hot reservoir. The efficiency is 1 minus T C by T H. So, this is 1 minus the cold reservoir is at 300 Kelvin, the hot reservoir is at 750 Kelvin. So, the efficiency is going to be 0.6. So, when we operate a engine between 300 and 750 Kelvin the Carnot efficiency is 0.6.

So, the maximum efficiency thermal efficiency we can get for operation between these two temperatures is 0.6. In reality if the process is irreversible, then the efficiency is going to be even lower than this value. Now, the second question we know the work produced W dot the rate of work produced is 95 megawatts or 95 mega joules per second right. And, we want to know how much heat is absorbed from the hot reservoir and how much is to be rejected to the cold reservoir. We know that the efficiency is given by the expression W amount of work we can produce by the amount of heat that is absorbed; it can also be for the rates ratio of the rates of these two quantities. So, because our efficiency is 0.6 then it is going to be 95 over Q H dot.

So, we can calculate then Q H from this expression directly because, I already know the efficiency of the Carnot engine. So, Q H dot is going to be 95 over 0.6 which turns out to be 158.3 mega joules per second. Since, by virtue of the first law W dot is going to be Q H dot minus Q C dot; we can calculate Q C to be Q H minus W or 158.3 minus 95 which happens to be 63.3 mega joules per second. So, then the 3 quantities am looking at are an efficiency of 0.6, heat accepted from the hot reservoir is 158.3 and heat rejected to the cold reservoir is 63.3. So, that 0.6 is the upper limit that is the maximum thermal efficiency I can get for any engine that operates between 300 and 750 Kelvin.

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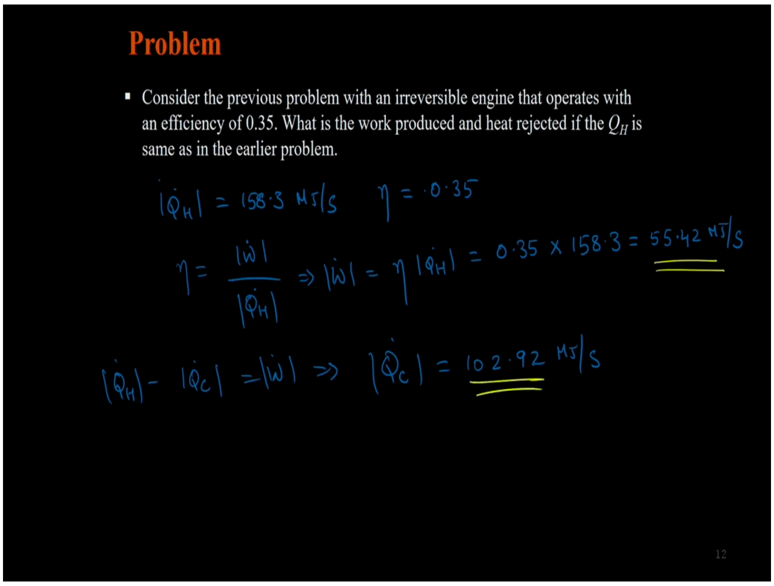

Now, let us look at another problem. We have the same scenario as earlier, but then this time the engine is irreversible; it operates with an efficiency of 0.35. Earlier we had a Carnot engine which operated with an efficiency of 0.6; this time because it is irreversible the efficiency is a little lower and is about 0.35. Now, we want to calculate the work produced and heat rejected if Q H is same as in the earlier problem right. So, we have the same scenario, but then Q H is same as an this case it is 158.3 mega joules per second. So, let us find that Q H value; since it is same as in this previous problem what we are given them is Q H is 158.3 mega joules per second. And, the efficiency this time is 0.35. If that be the case we want to calculate Q C and W, it is again a pretty straightforward application of what we have seen so far.

Efficiency as we have defined is W dot over Q H dot. So, we are interested in calculating the work produced that is W dot is going to be the efficiency multiplied with the Q H value which is 0.35 times 158.3. Or, this turns out to be 55.42 mega joules per second. Now, notice what happened to the work done the process is irreversible and the work done is only 55.42 mega joules per second. Earlier for the same amount of heat absorbed from the hot reservoir we have produced a work equal to 95 megawatts. But, now because the process is irreversible for the same amount of heat absorbed from the hot reservoir we could only produce 55.4 mega joules per second of work. And, Q C dot Q H dot is going to be equal to W dot.

So, we can rearrange the terms to calculate Q C dot to be a 102.92 mega joules per second. What essentially we are saying is, if the process has become irreversible I could produce less amount of work and end up rejecting more heat to the cold reservoir. And, absorbing the same amount of heat from the hot reservoir, but because this process is irreversible the work produced is lower and then I end up losing more heat to the cold reservoir or rejecting more heat to the cold reservoir. So, in that sense any reversible process will output less work and end up wasting more heat that I am absorbing from the hot reservoir.

Let me give you one quick real life example of why people have started developing interest in all of these reservoirs and harder you know accepting heat from a hot reservoir, rejecting it decoders. Most of this comes from development of heat engines like I said and power cycles one of the easiest ways to appreciate the application of what we are looking at is in case of a steam power plant right.

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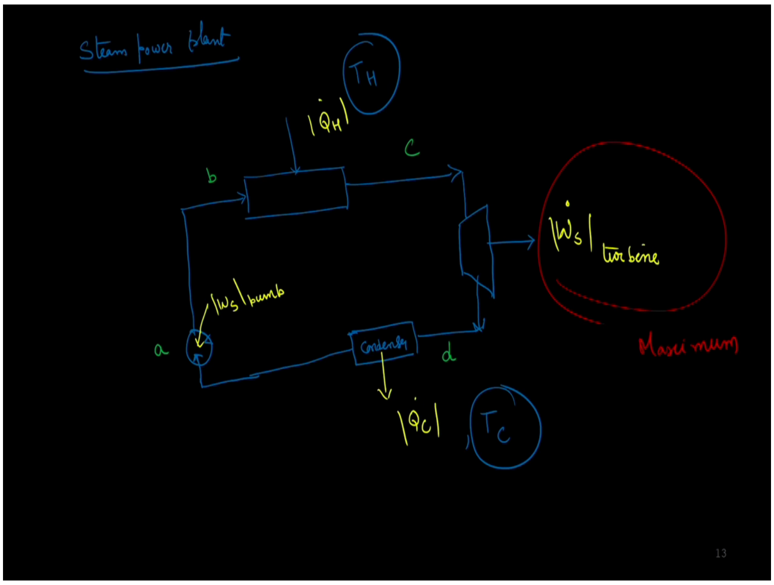

What happens in a steam power plant is we have a pump right and then we put some liquid to this pump; this is our working fluid and compress this liquid. So, to be able to compress this liquid we supply some work to this pump W S pump right and compress this liquid to a high pressure. So, we are at a condition a here and we are supplying compressing this liquid to a high pressure wherein, I am going to had heat Q H dot from the hot reservoir fine. Then it is going to accept heat from a hot reservoir you know we fire coal, we burn fuel and then that fuel is going to transfer heat at the hot reservoir to this working fluid. And, then we can let us save the work includes water then we make steam, after we add heat and then we are going to expand this hot steam; we are going to expand. And, then during this expansion we end up transferring some work to the turbine which is what we will convert eventually into electricity.

And, after the turbine we push it to a condenser right where we condense the steam coming out of the turbine or any liquid coming out of the turbine back to its original state where whatever condition we have put it into the pump to begin with right. So, that is the condition d and then we go back to the original state. So, W S pump here let us change these two different colors; so, that we can see them easily Q H dot here. W S turbine here, it is in the opposite direction the system is producing the work and then Q C here we are rejecting some heat. So, that we can condense the liquid and then we push it back to the original state. So, if you look at the conditions so, this will be at T C here and this will be at T H here right.

So, I have a liquid starting at a which is compressed to a high pressure same as that of the boiler at b and in the boiler we add heat. So, that we can mix team at high pressure T H and the temperature is going to be T H. And, we use this team to expand a turbine and produce some work whatever comes out of the turbine is going to be transferred to a condenser where, we reject heat to the surroundings. Condense the liquid, bring it back to its original state and then circulate the working fluid through the entire 4 steps; so, that we complete the cycle in this manner. So, this is how a steam power plant works and if you want to calculate the efficiency or the maximum possible thermal efficiency for the process I am burning so, much fuel. So, which means it will get this if I know the calorific value of the fuel, I know how much heat I can transfer to the working fluid.

And, for this heat I am transferring to the working fluid what would be the work I can produce out of the turbine. There is some consumption of work in terms of pumping the liquid. So, W S pump everything else is the work coming out of the turbine through the entire process. And what would be the maximum value? I can answer this question by using the ideas we learned in the Carnot engine concept right. It is going to be 1 minus T C over T H and what would be the maximum value, but because of the reversibilities in the processes and everything else that goes on the real value is going to be much lower than the maximum value. So, these are some of the applications of what we learned today in terms of the second law, the Carnot engine and thermal efficiency of a Carnot engine. When we come back in the next lecture, what we are going to do is try to extend these ideas of the Carnot engine and the maximum efficiency, thermal efficiency in a process to develop a concept known as entropy which is going to be useful in thermodynamic analysis of the processes.

Thank you.