Thermodynamics of Fluid Phase Equilibria
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Lecture – 08
Review of the second law of thermodynamics

Welcome back. In this lecture, we will be reviewing the second law of thermodynamics.

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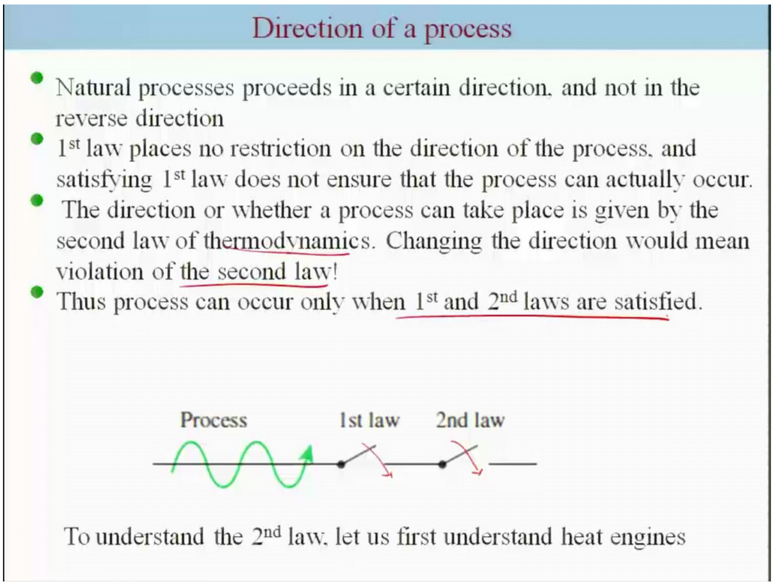

As we know that many processes are natural processes and some processes by default will not occur unless we make use of external devices. So, there is a certain direction of the process and this is basically governed by the laws of thermodynamics.

So, in order to have some processes to occur we need to make sure that the first law and the second law satisfies. So, in other word the direction of a process can take place is given by the second law of thermodynamics ok, the first law of thermodynamics do not put any restriction on the direction of the process.

So, it cannot ensure the with process can actually occur and changing the direction or the direction itself is controlled by the second law of thermodynamics hence changing the direction would mean quality in the second law. So, as I said a process can occur only when the first and second law are satisfied. So, let us just take an example which is well known to us.

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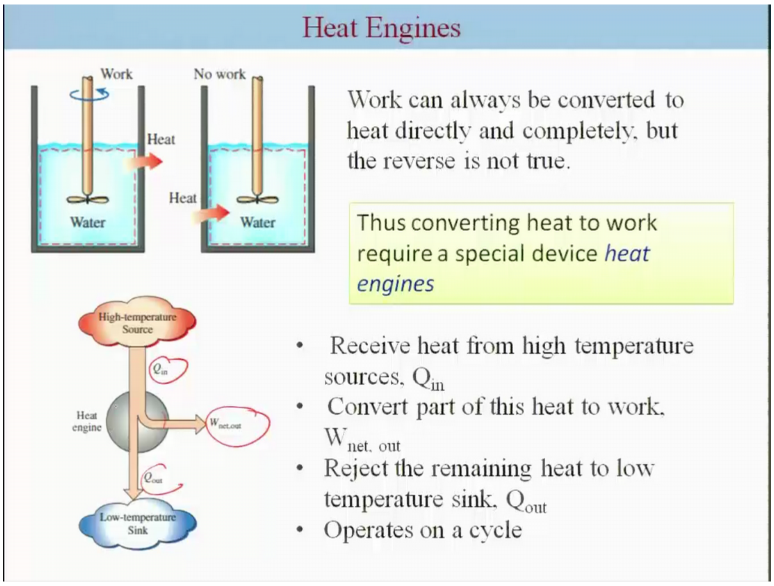

For example you have a stirrer in a container having water and while we rotate this shaft which means that we are doing certain work because of that there is a heat being generated. That means, the work is getting converted into heat on the other hand if you apply heat you cannot rotate the shaft or this will not rotate and thus the process of heat directly to work is not spontaneous. So, there is a direction to the process, the first where the work automatically gets converted into heat whereas, the opposite process is not feasible; that means, the reverse is not true.

So, in order to convert heat to work a special device is being developed that is which we call it heat engine. So, let me just summarize what let me just quickly go through the heat engine concept. So, heat engine basically consists of many devices, here within this circle and it operates on a cycle. It receives heat from a high temperature source Q in converts certain part of that as w net out and reject certain amount to a low temperature sink in other in order to have a complete cycle.

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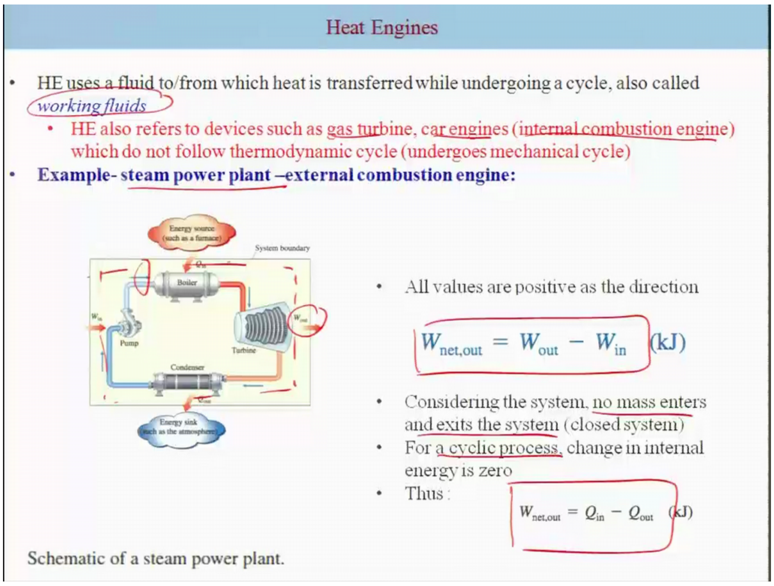

And that the fluid which is used as a part of the heat engine is some we call it working fluid.

So, it could be water for example, in steam power plant water is used or it could be gas that would be the case of let us say a gas turbine or car engine which is a part of a internal combustion engine, which do not follow precisely the thermodynamic cycle, but it follows a mechanical cycle.

So, considering the heat engine here as you can see it consists of a 4 basic unit, the boiler turbine condenser and pump and this is the direction ok. It goes in this way, it takes a heat hits up the fluid which is in this case water for the steam power plant to a very high pressure expands in the turbine to a low pressure and because of expansion it can it rotate the shaft getting the work out.

At low pressure it rejects heat from the vapor it gets condensed to the liquid, liquid gets pumped back to the pressure of the boiler and this continues in a cycle.

So, if you do a simple balance here you have you have this work out which is a w out minus w in and then this must be equated to the net heat in also. So, that means, from based on the first law of thermodynamics w net out should be equal to Q in minus Q out and this is closed system; that means, there is no mass enters and exist the system and there are other thing which we have assumed because delta u of the cycle is 0 because it is a cyclic process ok.

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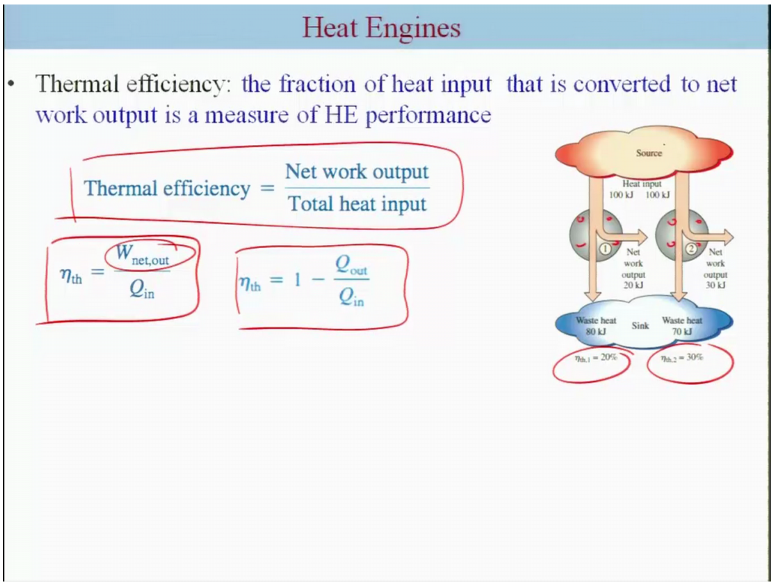

So, how do you define efficiency of a heat engine, as I said that not all a part of the heat gets converted to the work, certain amount of the Q in gets converted into the work and the rest are rejected as Q out?

So, we defined that efficiency of the heat engine in terms of net work out divided by total heat in, in other word eta is w net out divided by Q in or you can write it in this form. So, which essentially means that you may have the source and saying for 2 different engines same, but it may have different efficiency because that may depends on internal part of the or internal part of this the heat engine device heat engine overall. That means, there are 4 pa 4 devices for a generic heat engine and it may depend on the efficiency of individual devices ok, but the eta in clearly depends on w net out and hence you can work on the devices in order to increase the efficiency for a given source and sink.

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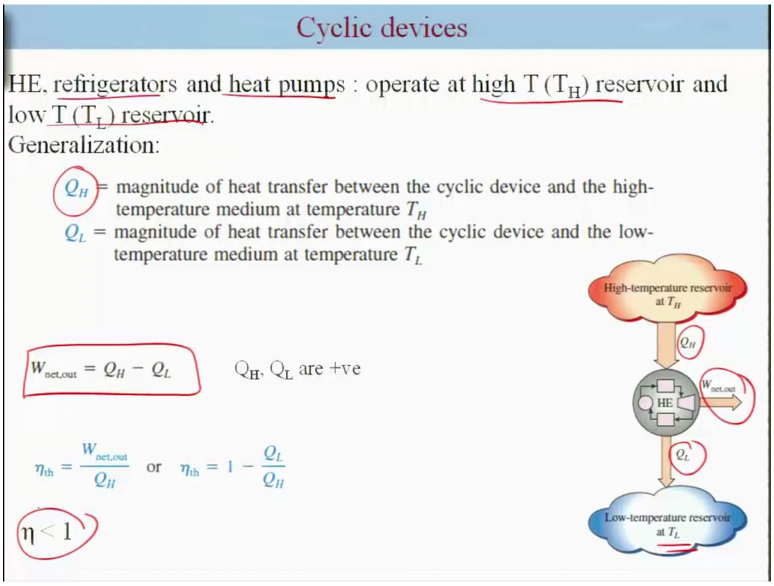

Now, in addition to the heat engine you have other cyclic devices and this these are refrigerant and heat pumps, particularly heat refrigerant heat pumps they operate at a high temperature reservoir and low temperature reservoir. So, in addition to heat engine refrigerators and heat pumps they are also part of the cyclic devices which operates at high temperature reservoir and low temperature reservoir.

So, in general we can generalize that Q H is the magnitude of a heat transfer between the sa cyclic device and high temperature medium at temperature t h and similarly Q L is the magnitude of heat transfer between the cyclic device and a low temperature reservoir and w net out would be simply Q H minus Q L both are positive ok. So, this is a generic definition as far as the reservoir is concerned for all these cyclic devices and eta will be always less than 1.

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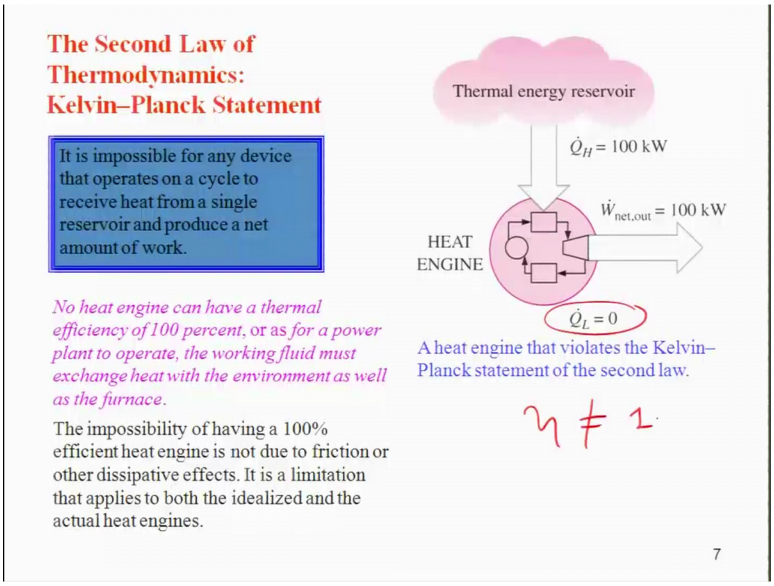

So, this brings to the second law of thermodynamic statements. So, for heat engine we make use of a Kelvin Planck statement, which says that it is impossible for any device that operates on a cycle to receive heat from a single reservoir and produce a net amount of work this is equivalent of saying that Q L would be 0, which would mean that it will violate this second law or violet the Kelvin Planck statement of the second law. So, in other word eta can never be 1 ok.

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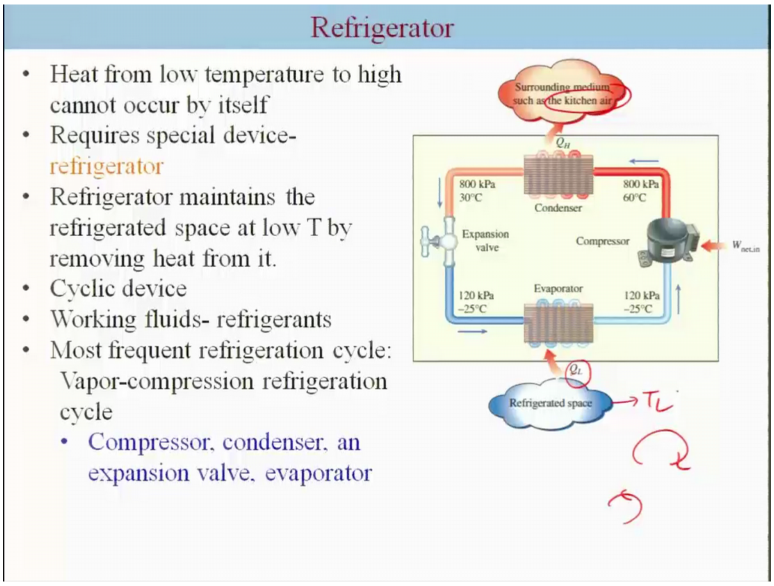

Now, in addition to heat engine if you want to transfer heat from a low temperature to the high temperature which is not a natural process you need to use a different device which we call it refrigerator ok. A refrigerator basically also have many components in it this is example of vapor compression refrigeration where you have condenser compressor evaporated in exponential wall and its purpose is to maintain the refrigerated space at a certain temperature, let u say t l this works also in cyclic device and the fluid which is used in this device is called refrigerants. So, this is the typical 1. So, instead of the path for heat engines which is in this direction, this is anti-clockwise for the case of refrigerant cycles or for the case of this cycle.

So, the fluid gets evaporated further compressed and the condensed and basically expansion evolve is used to expand and the heat has been rejected to the kitchen air and the heat is being extracted from the refrigerant space to maintain a certain temperature t l ok.

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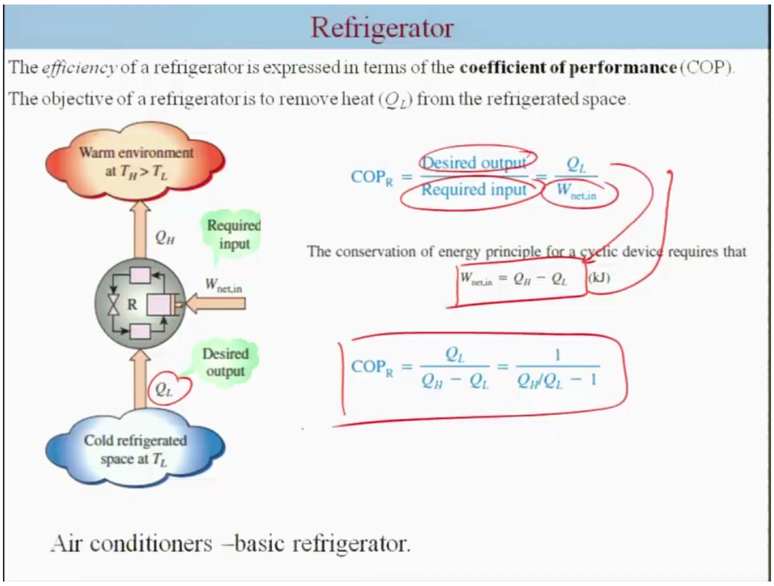

To define efficiency we use the coefficient of performance which is nothing, but is a ratio of the desired output and the required input for the case of a refrigerator what is the desired output. It is the amount of the heat which is being released from the cold space in order to maintain the temperature. So, Q L becomes the desired output and divided by the required input is the w net in.

Now, for the case of a heat pump the purpose is to maintain the environment of the room at a certain temperature t h and thus for the case of the heat pump the desired output is going to be Q h. So, the case of the heat pump the coefficient of performance would be Q H divided by w net in. So, this is a generic idea behind this cyclic devices and one can also rewrite this in this form because we know that on the first law analysis the w net in is Q H minus Q L you can plug in in this equation and you can get c o p in this form ok.

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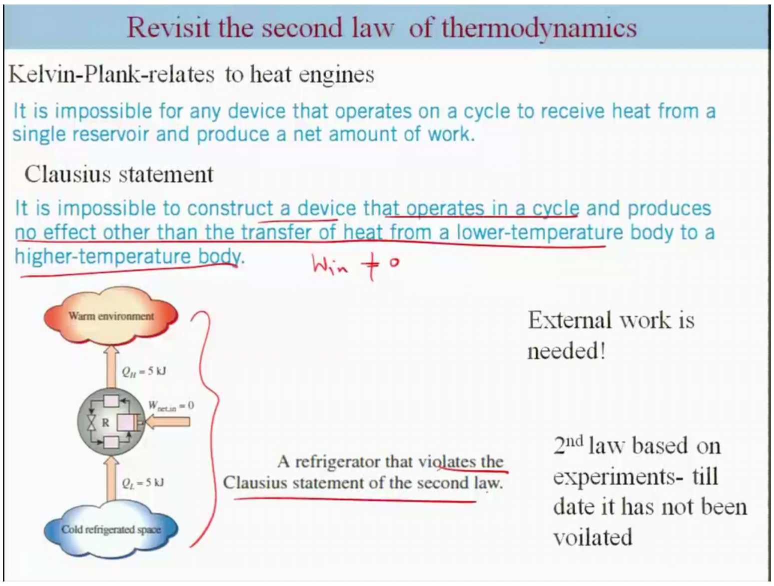

Now, as we also mention about the law statements of the second law of thermodynamics can be Planck's clearly statement relates to the heat engine whereas, for the case of refrigerant we are refrigeration since devices we make use of Clausius statement which is basically that it is impossible to construct a device that operates in a cycle and produces no effect other than transfer of heat from a lower temperature body to a high temperature body.

So, it simply means that w in cannot be 0 for the case of refrigerator. So, such scenario violates the Clausius statement of the second law ok, all right now though having briefly reviewed this expects of the second law.

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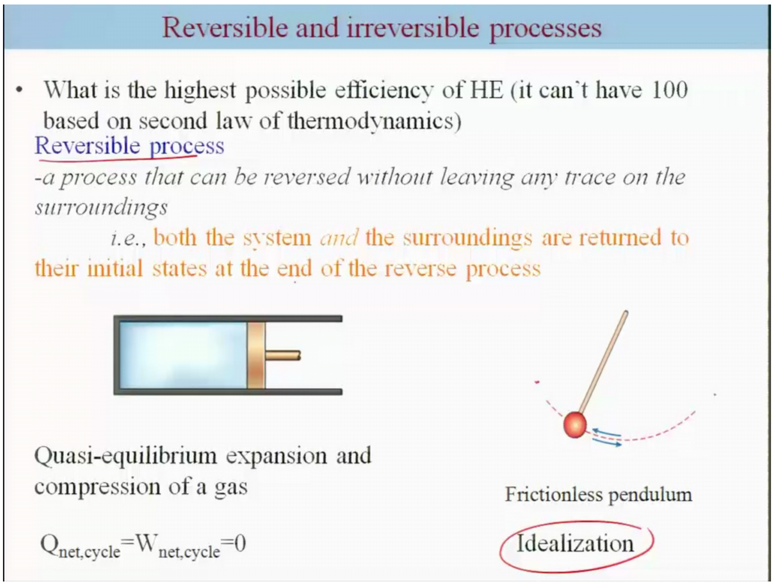

We will also talk about the reversible and irreversible process. Now, what is the highest efficiency for a heat engine and as we know that eta can never be 1 or it can we can never achieve 100 percent efficiency, but then still the question is that we would like to theoretically attain a highest efficiency in order to consider that as a yardstick for our designs. So, what would be the case for highest efficiency that would be when this the device operates on a reversible process or paths are considered to be reversible?

So, let first review the reversible process it is basically a process that can be reversed without leaving any trace on the surrounding which essentially means that you can bring back the system the, the processes is such that that you once the process occurred in such a way that you can bring back the system to the original state and similarly you can also bring back the surrounding to the original state without affecting overall any trace changes or. That means, you are bringing the server system and surrounding back to the original states, now this is difficult to imagine though ah, but we can consider a case of a expansion and compression of a system where we operate in such a fashion that it is.

So, slow that external and internal is all the time at its equilibrium with a very small change in pressure for example, and thus the forward and the reverse process do not affect the overall systems after it returns back to the original state or similarly you can also consider let us say frictionless pendulum from going to this point to this point and coming back do not affect the surrounding as well as the system here. So, this is basically nothing, but idealization.

So, let me again summarize refer reversible process, it is a process that can be reversed without leaving any trace on the surrounding; that means, both the system and the surrounding are returned to the initial state at the end of the reverse process.

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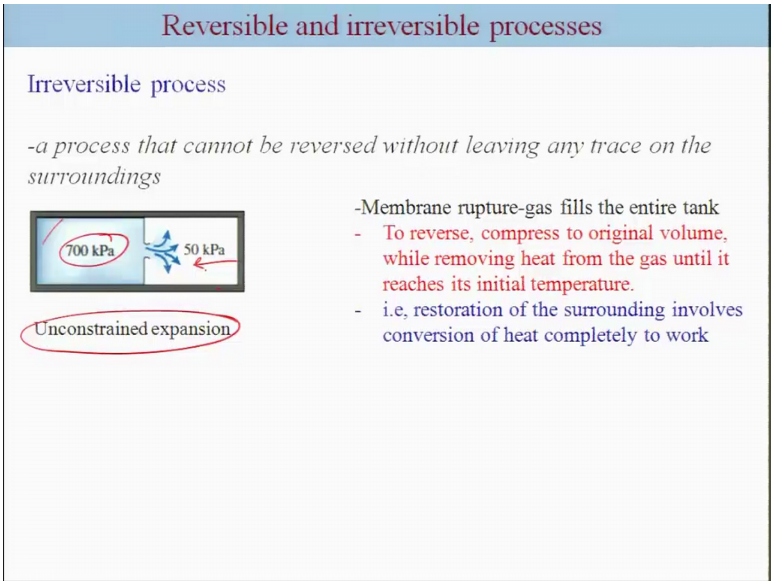

However irreversible process are of course, widespread and example of such a process could be considered in unconstraint expansion. So, you have a container containing gas at very high pressure separated from this low pressure system, subsystem with by a membrane which gets ruptured and upon ruptured the gas via force from this part to this part and fills the entire volume.

Now, if you would like to return this back to the original state we must try to push this gas from here onward using some kind of a piston. Now, while we push back the pressure will increase and leading to increase in the temperature, but if you want to return that to the original temperature you have to take it out the heat. So, you are doing a work and as well as you have to remove the heat, in order to make sure that the system plus surrounding returns back to the original state you have to convert all the heat which you have taken out to the work which essentially means you are trying to wall it the second law and that is not feasible in this case ok. So, this kind of a case would be in a reversible process.

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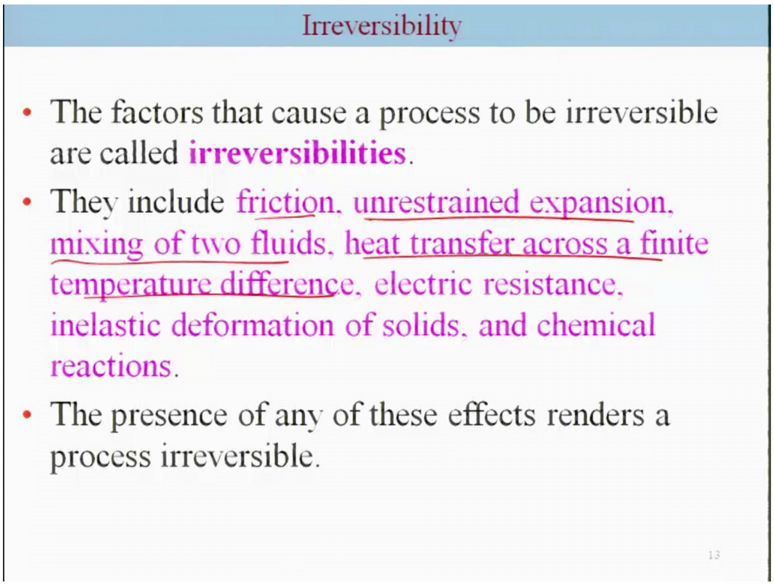

So, what is the cause for the irreversibility, these are the friction unrestrained expansion mixing of 2 fluids heat transfer across a finite temperature difference and electrical resistance. Now, for example, heat transfer across the finite temperature difference means the heat transfer will be very fast, on the other hand when the delta t between the system and surrounding is very very small then the system is very slow in transferring the heat and that is what we assume as far as the reversal process is concerned ok, beside this in a reversible process.

So, the one which we have talked about is basically total reversible process here in addition we also consider when the system is internally reversible in such case what we assume that system can be brought to the original state; however, the surrounding may contain all the irreversibility's in that those kind of cases we will call as internally reversible where the surrounding may have from the system to surrounding may have finite temperature difference, but within the system we will consider that everything is reversible.

So, those are the systems or those cases particularly internal reversible are the ones which we are going to consider most of the time when we discuss the problem ok.

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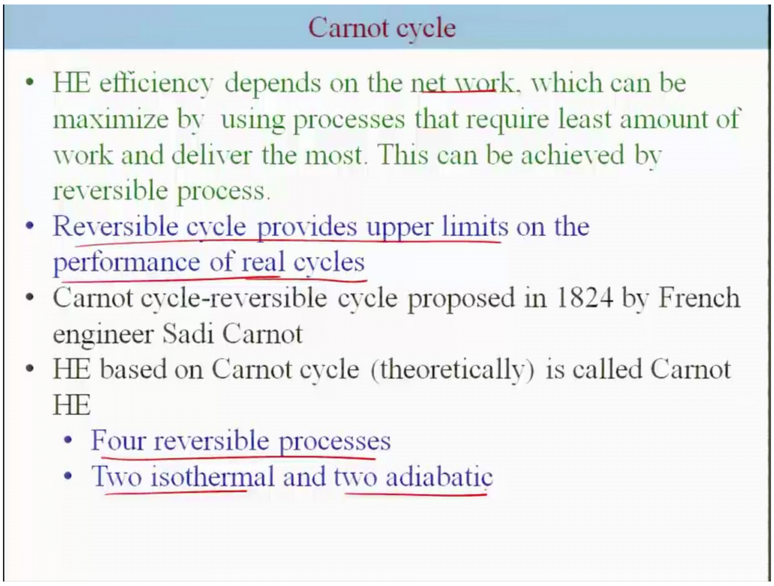

So, now I move on to a particular case where we make use of a Carnot cycle ok, now heat engine as I said depends on the network as far as the efficiency is concerned and we would like to increase the efficiency of the heat engine and that can be done when we maximize the network. So, maximum work can be achieved when the process is reversible ok. So, reversible cycle provide upper limits on the performance of the real cycle now this is something which becomes a yardstick for our design.

So, one of the reversible cycle propose was proposed by Sadi Carnot ok, it consists of 4 reversible processes and 2 of them isothermal and 2 of them are adiabatic.

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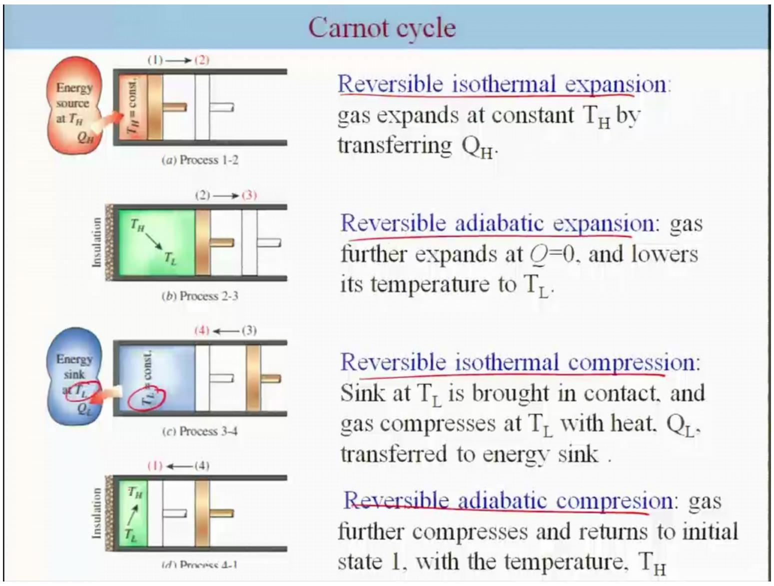

So, it is considered a gas in which the first let is say the first state to second state is been considered where this is a reversible isothermal expansion, heat is being transferred from the source at a constant temperature, the piston expand very very slowly or quasi static expansion and this is also the or reversibly reversible expansion at a constant temperature. Upon expansion from 1 to 2 the system is insulated and continues to expand while it continues to expand the temperature reduces from T H to T L ok.

So, this is a reversible adiabatic expansion gas this is a reversible adiabatic expansion the first is reversible isothermal expansion. Now, from three to 4 we have reversible isothermal compression which rejects heat at a constant temperature note that this is also T L and this is also T L. So, there is a no finite temperature difference in principle, this will be slightly higher than then the T L in order to heat transfer ok. So, this is a reversible isothermal compression and followed by insulation ah; that means, a reversible adiabatic compression which further heats up the temperature T L to T H.

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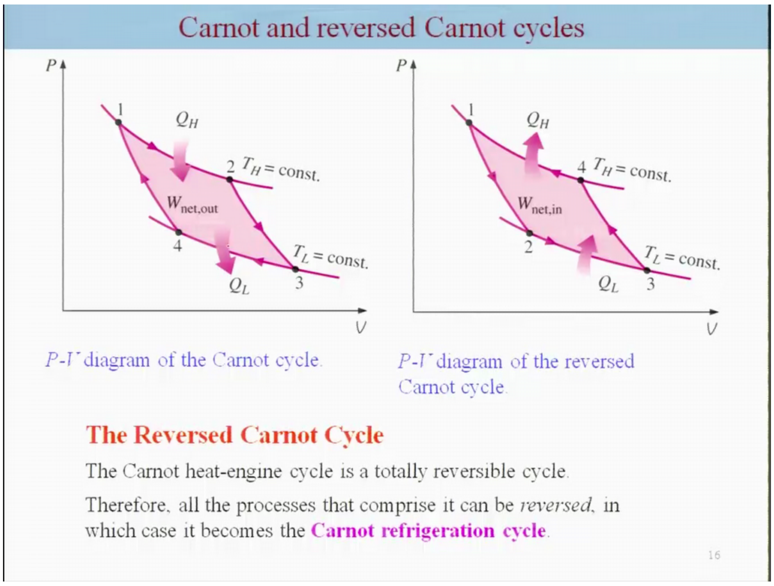

So, this force cycles for 4 powers complete the cycle and this can be pictorially represented in this form from 1 to 2 isothermal expansion, 2 to 3 adiabatic expansion, 3 to 4 isothermal compression adiabatic compression 4 to 1 and of course the area under this curves are nothing, but area under the curve is nothing, but w net out and if you reverse the cycle you get basically nothing, but refrigeration cycle Carnot refrigeration cycle this is a Carnot heat engine cycle the gases can be considered to be idle gas in order to do all the analysis ok.

This is something which you must have done that in your undergraduate thermodynamics ok.

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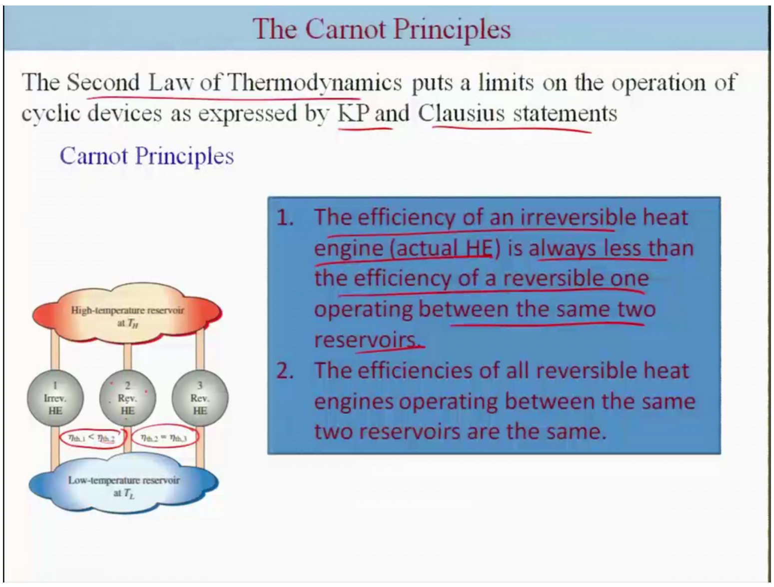

So, what is the principle of a Carnot based on this analysis ok. So, making use of the second law of thermodynamics and the statements of a Kelvin Planck and Clausius statements ah, the Carnot principle says that the efficiency of an irreversible heat engine or actual heat engine is always less than the efficiency of a reversible one operating between the same 2 reservoir. Which means that this let us assume this is a heat engine which is irreversible and this is a heat engine which is reversible which essentially means the part of the devices which we use here works in a way which is very very ah, works in a reversible path on the other hand there is a irreversibility associated with the processes here.

So, eta of 2 will be always greater than eta of 1. On the other hand, if there is another reversible heat engine which is operating between the both the same reservoir then the efficiency of this will be same as that of the another, device which is al also a reversible device. The Carnot heat engine considers the gases and you can show that that the efficiency of the Carnot heat engine is proportional to the on only depends on the temperature of the reservoir ok.

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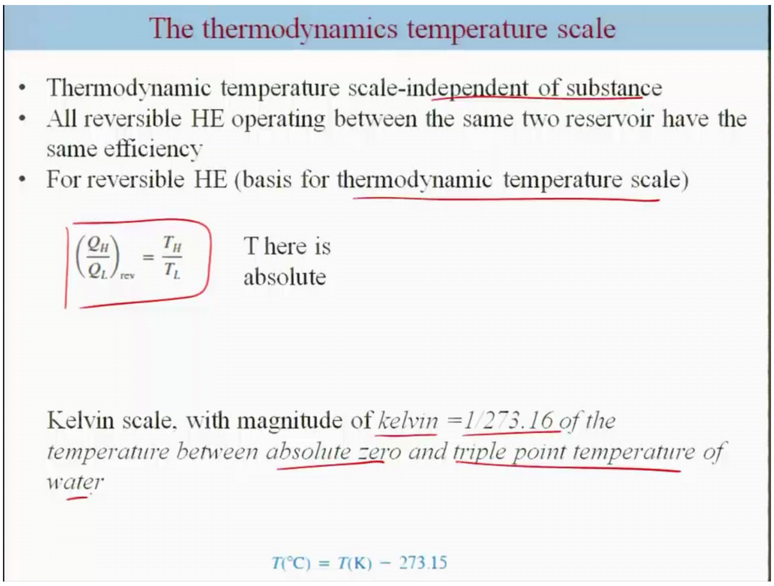

So, now this Carnot heat engine and its concept and its fundamental outcome became the basis for designing the thermodynamic temperature scale. So, based on the Carnot cycle of principle one can show that the ratio of the heats Q H and Q L is equivalent to the ratio of the temperatures where here in this case T is absolute temperature. So, thermodynamic temperature scale is basically independent of gas and that is what one can show this this is the basis for designing Kelvin scale and the Kelvin scale is based on thermodynamic temperature skill and which is basically has a magnitude of a 1 by 2 73.16 of the temperature between the absolute 0 and triple point temperature of water and of course, you know this the relation between the Celsius and the Kelvin ok.

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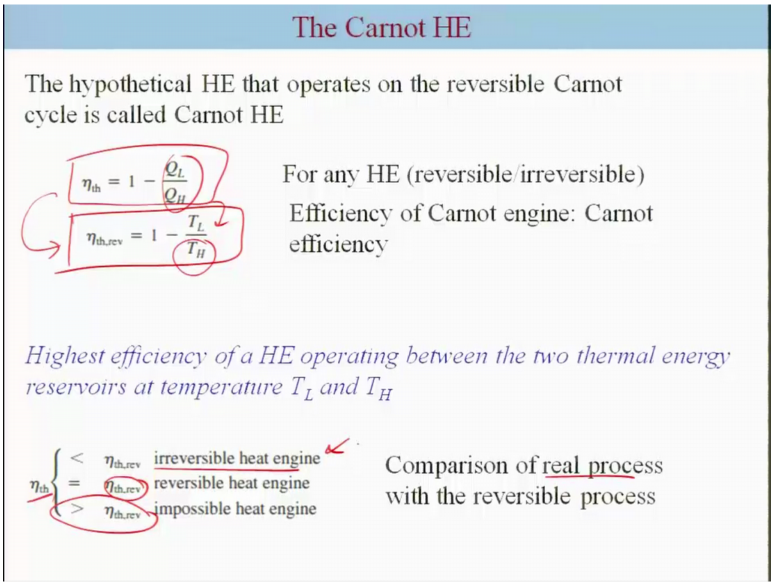

So, for Carnot heat engine as I said though is a hypothetical heat engine is valuable for using this as a yardstick in order to design the devices for any heat engine of course, whether it is reversible or irreversible the eta will be defined in this way, but for the case of a Carnot engine or reversible heat engine you can replace Q L by Q H is T L by T H, which essentially means that if you want to increase the efficiency of a heat engine, you can increase the T H or the temperature of the source or you can reduce the temperature of the sink. So, by doing that you can increase the efficiency of the heat engine and this is the indication come which comes directly from these expressions.

to summarize this Carnot heat engine based principles the we can we can since look at this eta of the real heat engine will be less than eta of the reversible heat engine for irreversible heat engine this would be the impossible case and its will be equal to the eta of reversible heat engine if it is reversible ok.

So, I think this is what I was wanted to cover at least this lecture to summarize the second law of thermodynamics, we will take up with the entropy, in the next lecture and that will be the end of our quick review of the undergraduate thermodynamics before taking up the more fundamental expect of molecular thermodynamics or solution thermodynamics. So, see you in the next lecture.