Chemical Engineering Thermodynamics

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Lecture 13

The Second Law of the Thermodynamics Review

Welcome back. In the last set of few lectures we have covered the first law and its applications. Today and next few lectures we will be focusing on the second law of Thermodynamics, reversibility, irreversibility and basically the heat engine concepts. So, some of you must have gone through this earlier but we will be trying to recap the fundamentals and some applications we will do in order to complete the concept.

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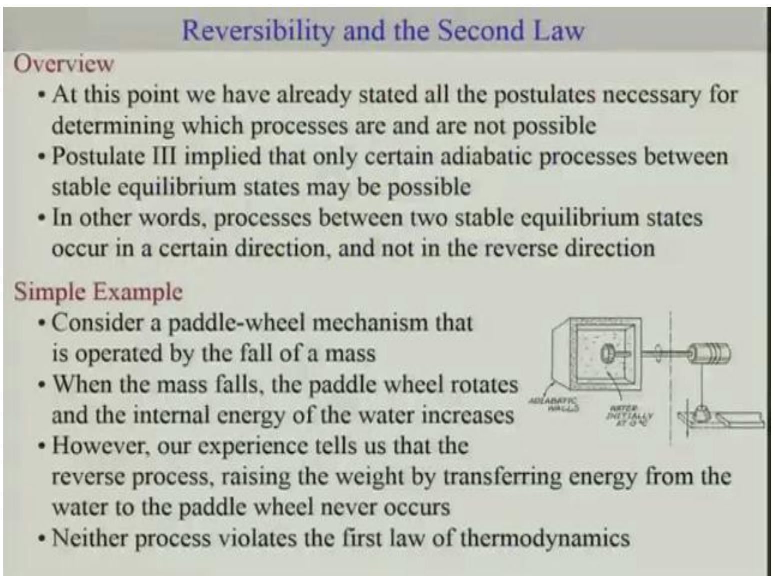

So, we just to revise or review what we have learnt we have introduced certain postulates earlier and that is something which we know that particularly postulate 3 which we have gone through last few lectures implies that only certain adiabatic processes between stable equilibrium states may be possible. In other words, processes between two stable equilibrium state occur in a certain direction, and not in the reverse direction. So, you cannot come up with a specific adiabatic process for the reverse direction and something which we have shown in some form but may not be very clear when we are trying to articulate here. But let us take the same concept through some examples.

So, consider a simple example which is the paddle-wheel mechanism as shown here. So, when the weight falls here, essentially what we are doing is we are doing a work and then we are changing the internal energy of water which increases. The reverse cannot be done. You cannot raise the same weight by transferring energy from water to paddle. So, transferring energy from water to paddle will never occur. So, there is a specific direction of the process. Though from the first law of concept the energy still will be balanced but the process will never occur. So, the first law still does not violate if its infectious way of doing something like this cannot be feasible, but it does not occur. Unless we take some help.

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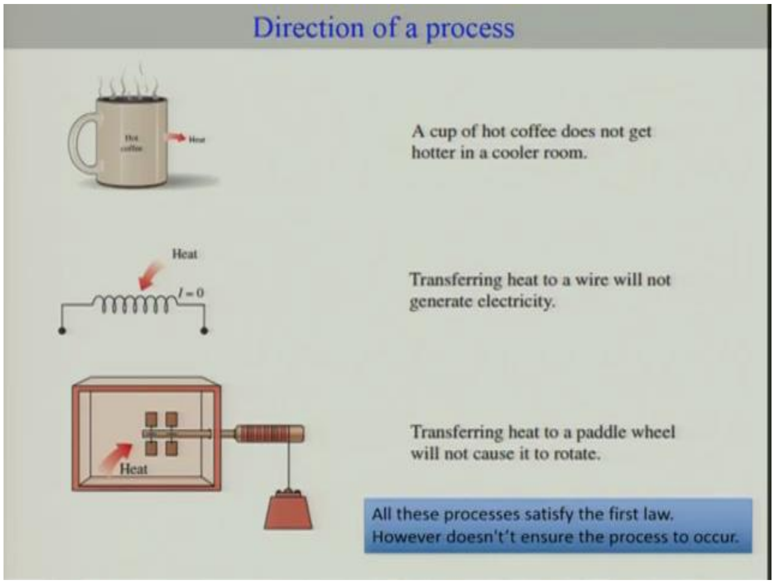

There are many other examples which we know from our day to daily life. So, one of the examples is that a cup of hot coffee does not get hotter in a cooler room. So always there is a transfer of heat from a high temperature to the low temperature.

This never occurs the other way round. Though the first law of the thermodynamics will not be violated if there is heat transfer from a low temperature to high temperature, but it never occurs. Similarly, transferring heat to wire will not generate electricity. So, while you generate electricity if heat is dissipated but the other way round it does not occur. So, transferring heat as we already discussed this part in the previous one so I will skip that part.

So, this tells you that all of the process which we have discussed satisfy the first law of thermodynamics. The reverse of the process does not occur. So even if the, fictitious reverse process satisfy the first law of thermodynamics that does not guarantee whether the process will occur.

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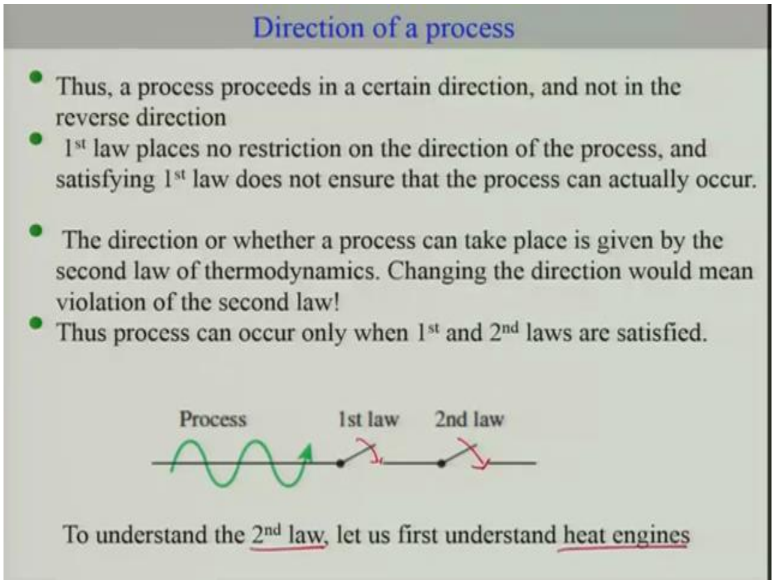

So, that means the process spontaneously proceeds to a certain direction and not in the reverse direction. First law places no restriction on the direction of the process and satisfying first law does not ensure that the process can actually occur. That it is extremely important for us to understand. The direction of whether a process can take place is given by what we are going to introduce a second law of thermodynamics changing the direction means violation of the second law. So, the process does not occur these that the second law is also valid. But the reverse process does not occur which means the second law will be violated if we try to bring in something like that. Though the first law is still is valid.

So, in order to have a process to occur, you need something like this. You need to have first law to be valid, as well as the second law to be valid, as far as the process direction occurs. So, to understand the second law we need to first understand the heat engine concepts.

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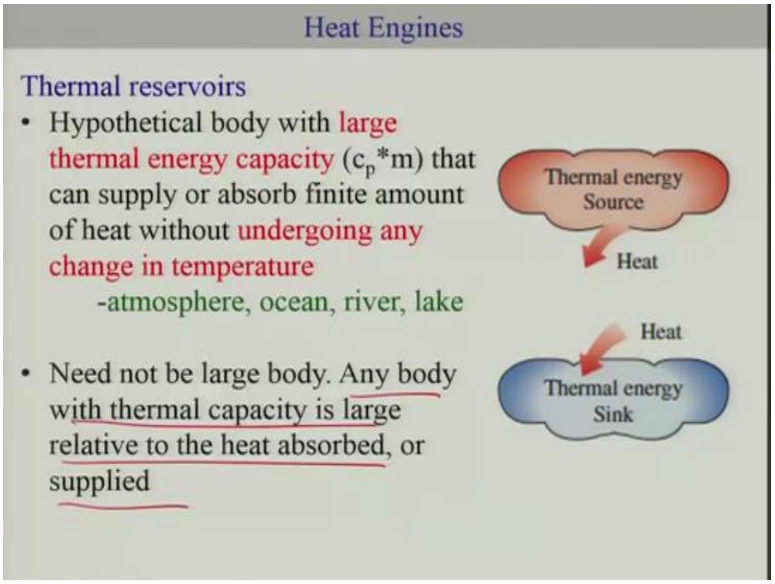

And for that we define few things, so one of the things which we must understand or rather we often use is called thermal reservoirs. So, thermal reservoirs are basically a hypothetical body with a large thermal energy capacity, that can supply or absorb finite amount of heat without undergoing any change in the atmosphere.

So, examples would be atmosphere, ocean, river, lake so that is something which can consider that there is constant temperature of the such a reservoir. Now, usually it need not be the large body such about what we are talking about ocean, river but, any body with a thermal capacity is large related to the heat absorbed or supplied. So, you can have a body where the amount of heat does not affect the property of the thermal reservoir is good enough for considering to be a thermal reservoir.

So, any body can be considered if the heat interaction or heat transfer does not change the property as such in terms of the temperature. So, it could be a differential change but that can be ignored, if that is the case, then we can consider that with thermal reservoir. But, usually, in all of our problems when we consider we will be using something like atmosphere, ocean and things like that as a thermal energy source. So, the thermal energy source will be the one which will provide the heat and thermal energy sink will be the one which will absorb the heat.

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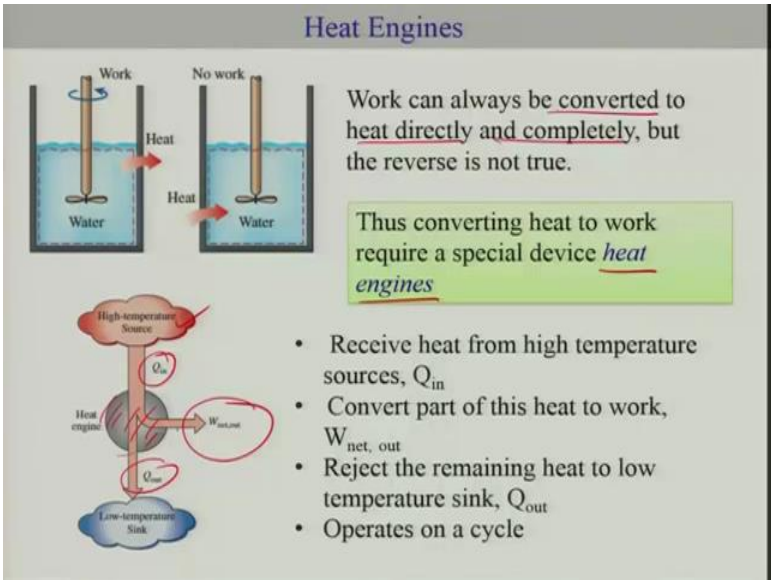

So, let us now come to the point where we can introduce heat engine, so let us go back to the question of direction of the process. So, if you consider this stirrer, a rotation of this paddle, would provide would increase the internal energy and then it can be dissipated out of it if this is not adiabatic, not insulated. Now, if you provide the heat you know that this will not rotate, there would be no transfer of heat to the work just like that. You need something a specific device which does this activity. So, work can always be converted to heat directly and completely but the reverse is not true.

Thus, converting the heat to work requires a specific or a special device which we are calling as heat engines. So, heat engines are the one which converts heat to our work and that is something the holy grail of thermodynamic in the earlier days where the whole idea of this development was to convert heat to work. So, let me just describe the schematic of the heat engine.

Heat engine consist of many devices but we are just representing by these circles here. So, heat engine takes the heat from Qin which receives the heat from the high temperature reservoir and throws out some amount of heat to the low temperature reservoir and the rest comes out as something we call work net out. So that is the work which is can be converted to the Qin and so this operates in a cycle, so this whole thing operates in a cycle

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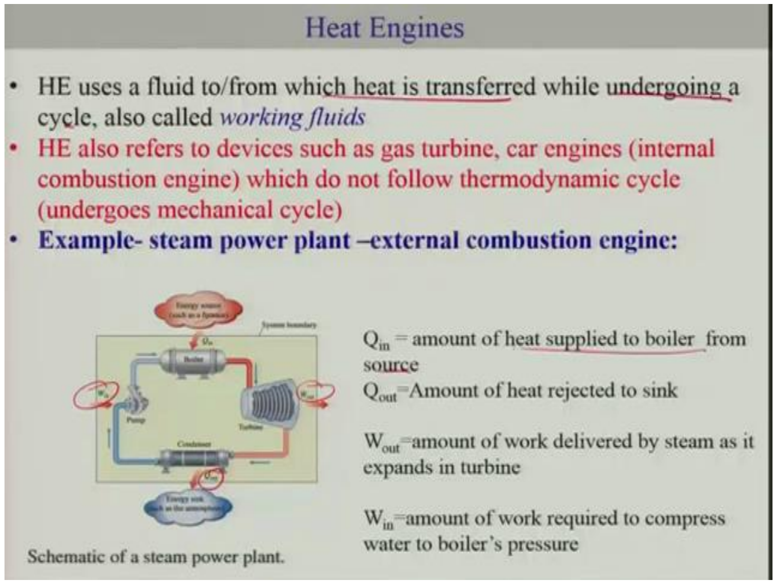

And it uses certain fluid which is used to and from which heat is transferred while undergoing the cycles. So, heat engine uses a fluid which heat you know using that we are trying to make use of the heat transfer from the reservoir, the sink, while undergoing this cycle and so often called work in fluid. So, for the case of steam turbine, the steam itself is your water is working fluid for the case of refrigerant. You have these refrigerant fluids which are called working fluid. Now heat engine also refers to devices such as gas turbine, car engines. Car engine is an internal combustion engine which is not truly thermodynamic cycle but it undergoes some mechanical cycle.

But, in general, we prefer these devices where the heat is transferred to work, device which is referred to as heat engine. But even the mechanical cycle part is also included in the list of the heat engines. So, let us look at a specific example here, the example of a steam power plant which is external combustion engine and so just to illustrate how this cycle has been devised or this itself is a heat engine concept here.

So this is a steam power plant where what we are doing is we are taking a heat from some source such as furnace, this could be like coal you're burning and from there the heat is being transferred to the boiler at a constant temperature and also we do not usually worry about this part unless we are interested to understand some aspects from second law. But what we are interested at this point is the amount of Q in which basically constant transfer, amount of heat supplied to the boiler from the source.

So and from here it goes to the turbine it expands and thus it does some work and the low pressure fluid comes to the condenser and finally condenses, then there is a phase transition here and the latent heat is transferred as Q out then the liquid here because it is condensed liquid is pumped here back into the high pressure, off pressure equivalent to the boiler and is further up and creating a steam out of it.

So, this is the process which keeps going on. In the process of pumping steam in order to raise the pressure you are bringing these Win in addition work is done. So, the net work is nothing but W out minus Win. Net heat supplied is nothing but Qin minus Q out.

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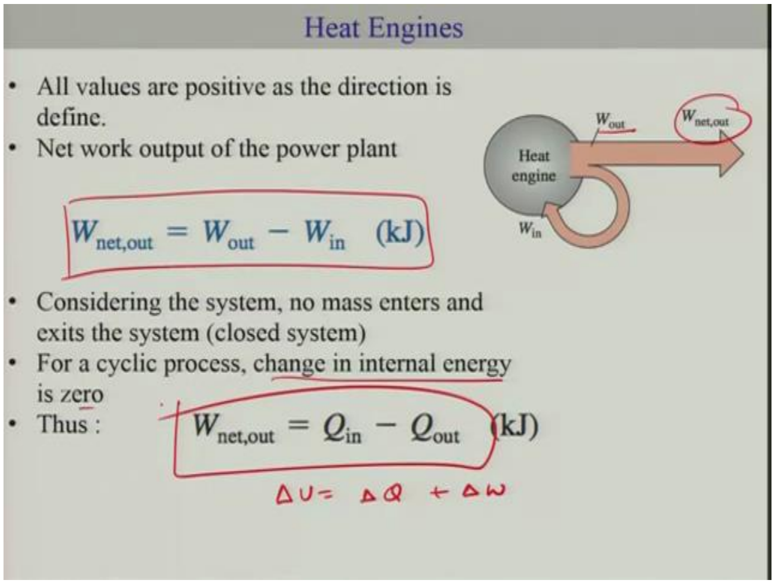

So this is what we are saying this is a net work. So, heat engine is a cycle here and effectively W out some part of W out can be considered as the part of the W in which is used by the pump.

So effectively this is the W net,out. So, by doing a simple energy balance ok for a cycle the change in the internal energy should be 0, right. But if you just look at the energy balance so it is going to be del u is going to be your Q del Q plus del W. Right and if you consider the whole cycle so essentially you can show that the W net, out is nothing but should be equal to Q in minus Q out. So that is based on the simple energy balance.

$$W_{net,out} = W_{out} - W_{in} \quad (kJ)$$

$$W_{net,out} = Q_{in} - Q_{out} \quad (kJ)$$

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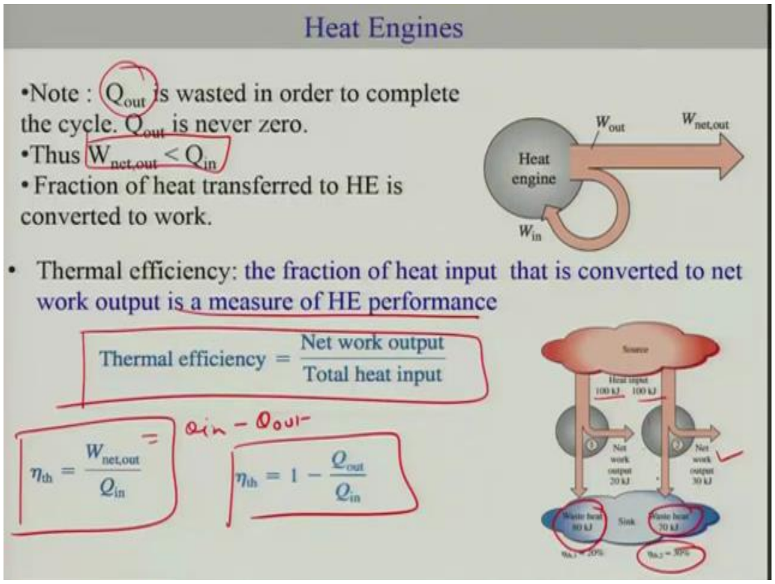

Now if you note that we Q out is always there is wasted in order to complete the cycles. Q out apparently is never 0. So if that is the case that means the Q in is much greater than W net,out that is indeed the case where we rather the constraint for us and that means fraction of heat that transfers to the heat engine is converted to work. So, in order to identify the amount of transfer of heat to the work we define something called efficiency. We called it thermal efficiency which is the fraction of heat input that is converted to net work output and is a measure of a heat engines performance.

So, you can have heat engines of relatively different performance and that is what we are going to make use of this kind of efficiency to identify which is a good or better heat engine. So formally thermal efficiency is nothing but is ratio of net work output divided by total heat input. So that is a case it is nothing but W net,out divided by Q in. Now W net,out is nothing but Q in minus Q out. So, if you done this it can be written in this form.

So, taking an example of the fact that heat engine can have some different possible efficiency even though the source could be same. For example, in this case heat input is given to the same amount of heat is given to two different devices 1 and 2 and in the first case the waste heat is 80 kilo joules and second is 70 kilo joules leading to better efficiency for the second one. So, it all depends on how it does design your heat engine.

$$Thermal\ Efficiency = \frac{Net\ work\ output}{Total\ heat\ input}$$

$$\eta_{th} = \frac{W_{net,out}}{Q_{in}} \qquad \eta_{th} = 1 - \frac{Q_{out}}{Q_{in}}$$

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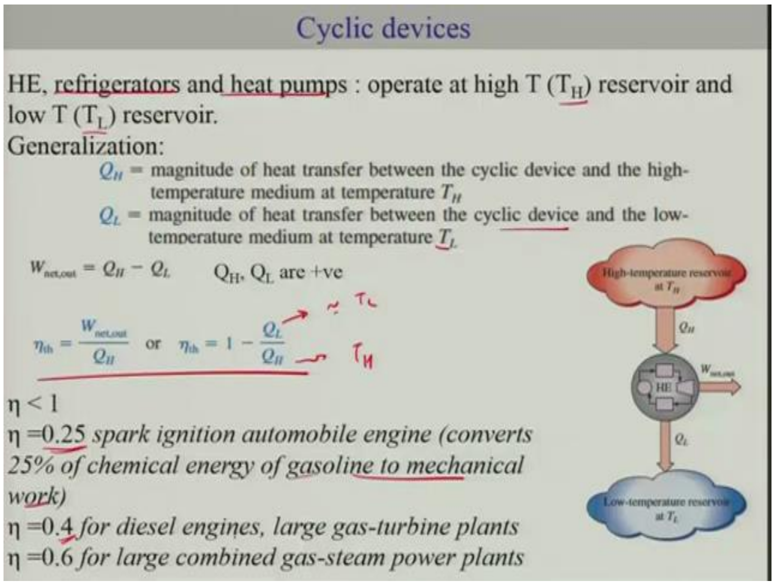

Along with heat engine you have refrigerators and heat pumps which we are going to describe a bit later. This operates at a temperature high temperature reservoir and low temperature reservoir for the case of heat engine, for the case of refrigerator and heat pumps. It also is the same thing but of course the cycle is little opposite compared to heat engine, will describe that part.

But to generalize that any high temperature we are going to define as TH and low temperature reservoir we are going to define as TL and QH is the magnitude of the heat transferred between the cycle and the high temperature medium in QL will be the heat transfer between the cycle device and the low temperature. So, you can have Q in also Q out but you can also assign this as Q H and Q L cross point to the T L and T H.

So, you can also have this same set of expressions, so instead of saying Q out by Q in you are saying Q L by Q H because this corresponds to that of T L this corresponds to that of T H. So many textbooks be using this kind of terminology also. So, as I said that Q out cannot be 0 that means eta is always less than 1. In case of spark ignition automobile engines eta is 25 percent which essentially means that 25 percent of the chemical energy of gasoline, because gasoline is the one which reacts and provides the heat that is your Q in. Q L which converts to the mechanical work so only 25 percent. In case of diesel engine 40 percent is used. Particularly for large gas-turbine plants. For the case of gas and steam power plant combined one is 60 percent. So that is the maximum as of now.

$$\eta_{th} = \frac{W_{net,out}}{Q_H} \quad or \quad \eta_{th} = 1 - \frac{Q_L}{Q_H}$$

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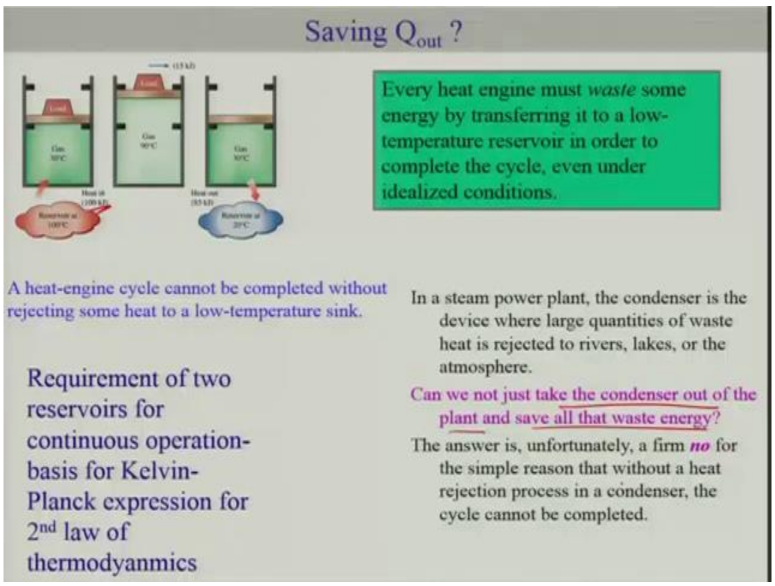

So you might ask the question why we cannot make Q out to be 0, we must just using this illustration we can clearly see that we must try to throw on the Q out into the reservoir in order to complete the cycle so as this since this is the cycle device the Q out has to be non-zero there will be some amount of Q out, of course you can have a co-generation, you can make use of what the Q which you lose to do some other work do some other activities that can be done but as far as the heat engine cycle is concerned for the case of the cyclic device we must have some amount of Q out.

So, some energy will be wasted. So, example is that if we consider reservoir under 100 degree Celsius and this is a heat in let us say 100 kilo joules, there is a gas and there is a load as you provide the heat this load is elevated and there is work which is done. So, it goes to 90 degrees Celsius some amount of work is taken to take off the load.

Now if you want to bring in back, in order to get the same temperature, the heat out would be something 85 kilo joules to a lower temperature. Remember that the to a lower temperature so we have, we cannot go back to the same state 90 to 30 without transferring the heat from this temperature to a lower temperature. So, in order to have a proper heat transfer which we know only from a high temperature to low temperature that means essentially, we must lose temperature in order to bring this temperature to 30 degree Celsius. While anyways this is something which we wanted to talk here as far as saving this Q out is concerned.

So, the question is can we not just take the condenser out of the plant and save all the waste energy? The answer is unfortunately no, for the simple reason without heat rejection process in the condenser the cycle cannot be completed as we have seen here. So, this we cannot get rid of that in order to get back to the same point here we need to lose it, in order to get something which is part of our understanding. So that means one thing is very clear that there is a requirement for two reservoirs for continuous operation for such devices and this becomes a part of Kelvin Planck expression for the second law of thermodynamics.

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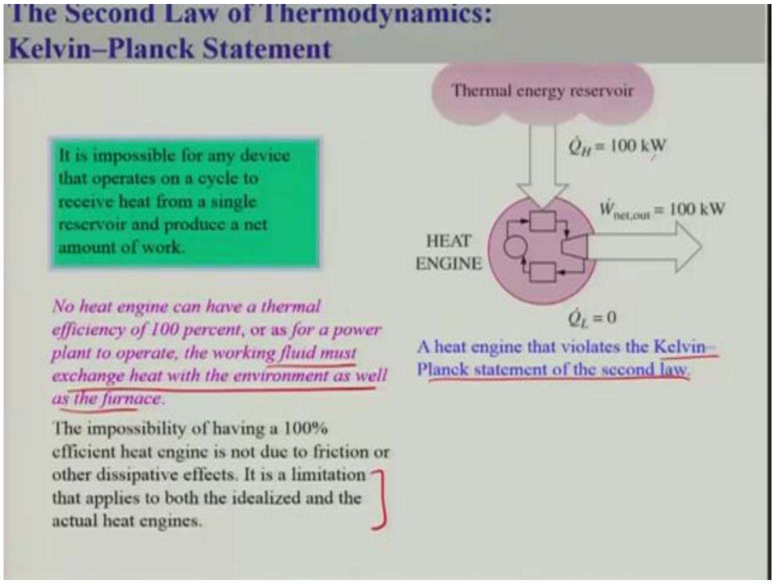

So, it says that it is impossible for any device that operates on a cycle to receive heat from a single reservoir and produce a net amount of work. So, if you take out the second reservoir you are saying that well it is 0 and you can convert this heat which comes of a high temperature reservoir directly to work, that is not possible that will violate the Kelvin Planck statement of the second law. So that is the statement we are talking about. So, no heat engine can have 100 percent efficiency and their working fluid must exchange heat with the environment as well as the furnace.

So, the impossibility of having 100 percent is not because of the friction or other dissipative effects. It is a limitation that applies to both the idealized and the actual heat engine. So, this is something which we must understand. It is not because of the loses its the limitations of the process, it's the limitation of the idealized actual heat engine because of the necessity for the completion of the cycles and in that some amount of heat must be to be a lower temperature. Now of course you can make those that heat whatever it is use for some other application and reduce the overall loss by some percentage, but that anyway we have to do.

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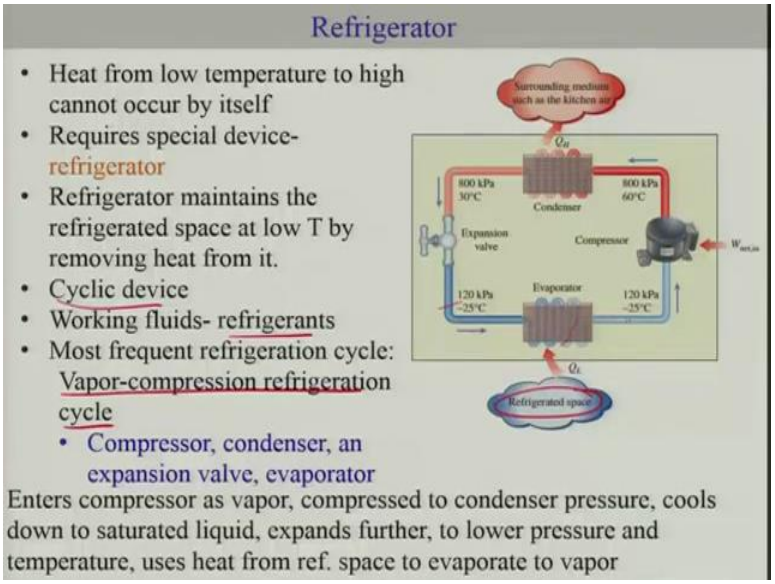

So, let us quickly go through the refrigerator which is a little different from the heat engines but it also have follows the same cycle though. Similarly cycles, so refrigerator is nothing but is it takes the heat from the low temperature. So, this refrigerator space is nothing but the fridge within the refrigerator the space which you would like to maintain at certain temperature.

So, it continuously takes out the heat so that you can maintain it let us say at 5 degrees,1 degree Celsius. So that is done through this heat is taken here and then there is a evaporator which so this heat is taken and this evaporates this, so there is a change in a phase here and then it goes to compressor and there work is done on a compressor increasing the pressure and temperature, led then there is condenser brings down to the saturated liquid condition and then there is expansion wall creating this saturated vapor condition here, or saturated liquid condition here.

So, what we are doing is this, this basically is saturated liquid, this is a saturated vapor, this is kind of a super-heated and then you have a condenser and then its expansion. So well so the idea is you are using this heat and basically trying to do make the same cycle in the process what you have done is you have maintained the temperature here. In order to do that you have to bring you have to do some work here. So that is a compressor work. So, this is called refrigerator cycle and this indeed is a special device, because what you are doing is you are taking the heat from a low temperature to high. So, it is a cyclic device working, fluid is refrigerant.

Most frequent example is what we have shown here, or discussed is something called vapor-compression cycle. So that is the vapor is been compressed here. So, it enters compressor as vapor, compressed to condenser pressure, cools down to saturated liquid, expands further to a lower pressure and temperature uses heat from refrigerator space to evaporate to vapor. So that is the complete cycle.

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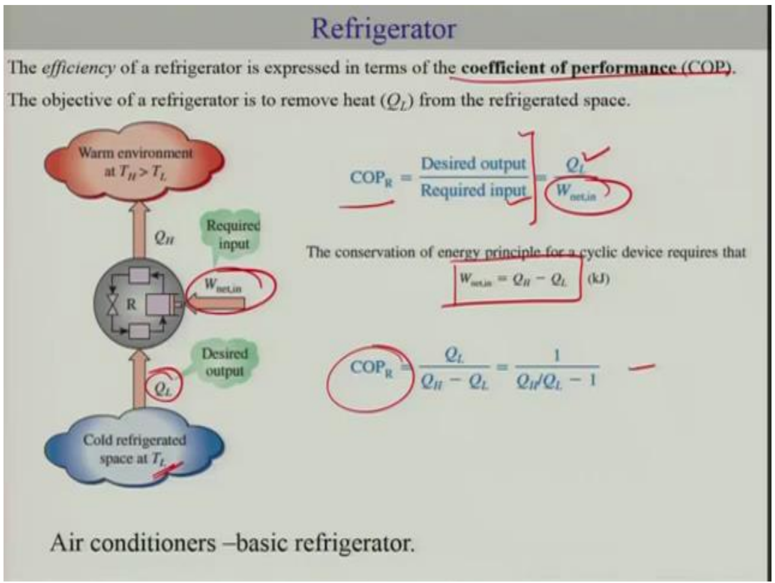

Now for the case of refrigerator we can also define efficiency. Now efficiency in case of refrigerator is defined little differently. By default, efficiency is nothing but the ratio of the desired output by divided by ratio of desired output and required input which is what it is. But in the case of a refrigerator what is the desired output? It is not QH, it is the amount of heat which you extract from the cool refrigerator to maintain the space at that particular temperature which make our T L. So desired output is Q L, required input is the W net,in.

$$COP_R = \frac{Desired\ output}{Required\ input} = \frac{Q_L}{W_{net,in}}$$

$$W_{net,in} = Q_H - Q_L\ (kJ)$$

$$COP_R = \frac{Q_L}{Q_H - Q_L} = \frac{1}{\frac{Q_H}{Q_L} - 1}$$

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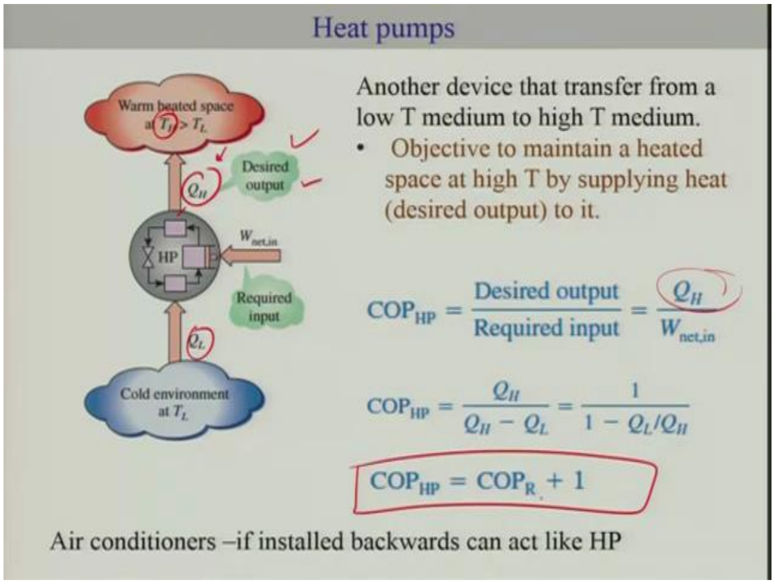

Now similarly the we do have heat pumps also which maintains the room let us say you heat up certain room and maintains the temperature of the room. So, the desired output in that case is going to be the amount of heat which must be transferred to a specific space in order to maintain a temperature. So here it is again. So, we do have the similar cycle as we have seen for the refrigerator. But the desired output is different.

So, in this case the heat is taken from the cold environment and work is been provided here for completion of the cycle. So, heat from the condenser here right goes to the space.

$$COP_{HP} = \frac{Desired\ output}{Required\ input} = \frac{Q_H}{W_{net,in}}$$

$$COP_{HP} = \frac{Q_H}{Q_H - Q_L} = \frac{1}{1 - \frac{Q_L}{Q_H}}$$

$$COP_{HP} = COP_R + 1$$

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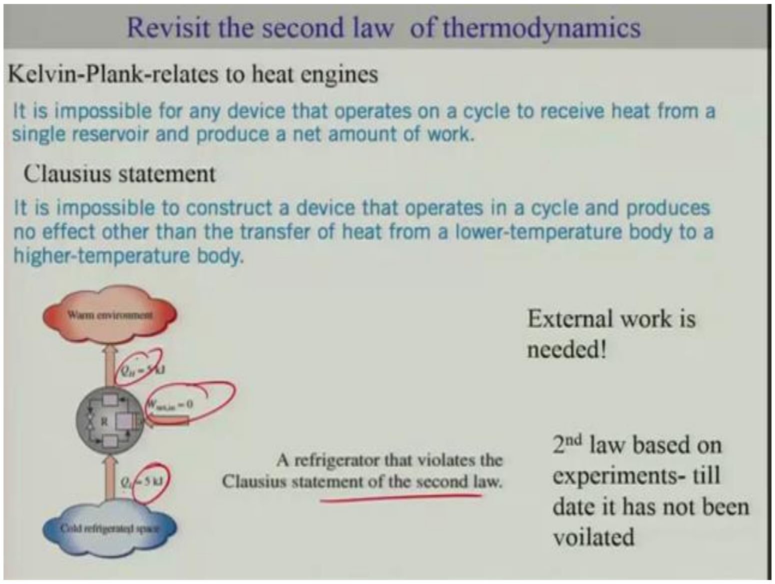

So, let us revisit the second law of thermodynamics. We have already seen a statement related to the engines that it is impossible for any device that operates on a cycle to receive heat from a single reservoir and produce a net amount of work. Now for the case of refrigerator, Clausius came up with the statement and it says that it is impossible to construct a device that operates in a cycle and produces no effect other than the transfer of heat from a low temperature body to a high temperature body.

So, it says that it will, I mean this is something that is related to the refrigerator. So that is impossible. That you can transfer just heat without affecting anything. That is what he says that. So, this is a statement which says that well, you cannot simply transfer, so you have this you need to bring in something Win. You cannot transfer this heat directly to heat. So, this is impossible that is the example of violating the second law that is based on the Clausius statement.

It says that the external work is indeed needed and many experiments have been tried to come up with the to prove this one can come up with such kind of device, without having any additional work but of course till date this has not been shown.

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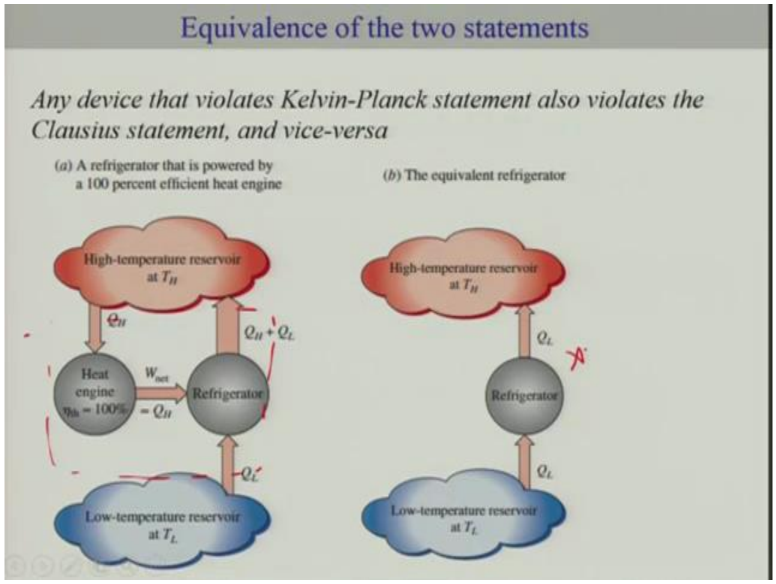

So, these two statements one related to heat engine other related to refrigerator are equivalent. So, in order to show that you can consider a simple example here which is this, that you have the same high temperature reservoir TH and the other one is low temperature reservoir TL, you have a heat engine which is 100 percent efficient, you have heat engine and as well as refrigerator. Now let us assume that there is a violation in the Kelvin-Planck statement which says that you cannot have this kind of process which transfers the heat completed to work that means the efficiency of 100 percent. So, assume that the particular work is done, our work W net is produced by heat engine and using this simple balance W net has to be equal to Q H.

This net if you applied to provide to the refrigerator then you have a situation where the Q L is this, this is the net heat and this would be your Q H plus Q L based on simple energy balance right. So if that is the case, so this is the refrigerator that is 100 percent efficiency of heat engine, now what you can do is you can consider this as a system here and since Q H is which is being provided from high thermal reservoir, the same Q H is brought back here so actually this cancels. So, what you have effectively is a system where Q L is 100 percent transfer to the from the lower temperature to high temperature which is indicates that if this example in which violates Kelvin-Planck statement then this also implies that this effectively violates the also the Clausis statement as clearly seen. So, this is of course not possible.

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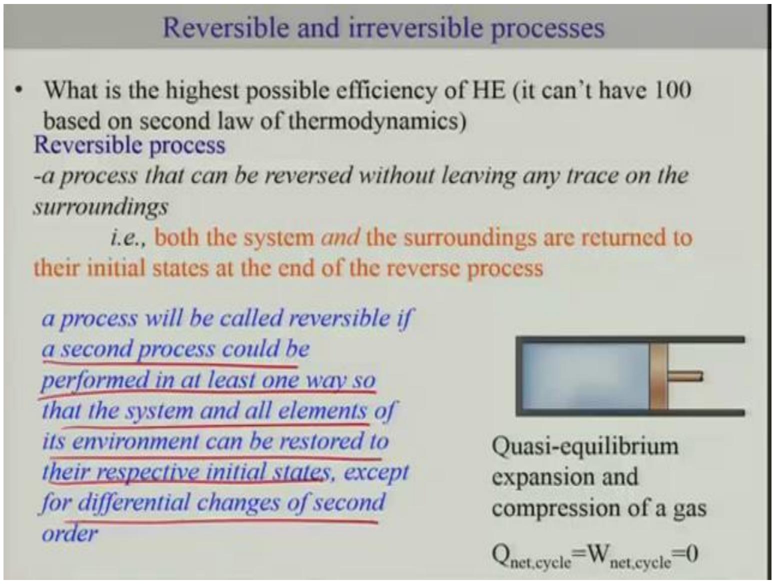

So that is all about this now we will quickly look at some aspects of reversible and irreversible process. The reason why we are interested to have this heat engine is the purpose is to convert the heat to work but then it also limits the efficiency also limits the utility of the heat engine. Hence it becomes the holy grill to figure it out to find out the best possible engine with maximum efficiency, but this is also limited by the second law of thermodynamics which we are going to discuss in the later part but let us first understand what are the issues related to the efficiency, so efficiency gets reduced only when there are some aspects of process design or if there are irreversibly associated with the processes.

So, in order to have understanding let us first make the statement here. The reversible process and the irreversible process. So, what are the reversible process? A process that can be reversed without leaving any trace on the surrounding both the system and the surrounding are return to their initial states and the end of reverse process which essentially means that it is extremely slow process so causing equilibrium expansion and compression of a system, so that means that there is differential properties or variations in the system which is extremely negligible.

So, a process will be called reversible if a second process could be performed in at least one way or the other so that the system in all elements of it environment can be restored to the respective initial state except for differential changes of second order.

So this is what we are trying to say if we can expand using if there is expansion and then you bring it use some other external force but you do it in a way which does not affect the external environment even in the second order form changes.

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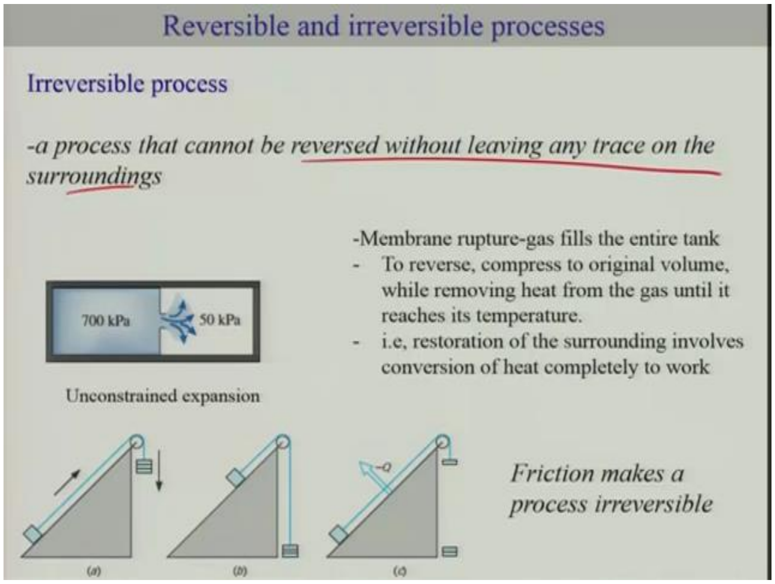

So, what are the irreversible process? A process that cannot be reversed without leaving any trace on the surrounding. So example could be unconstrained expansion, membrane rupture, so this is a simple example to reverse and compress original volume while removing heat from the gas until it reaches temperature to that means you have to restore the surrounding involve conversion of heat completed to work so in order to restore back essentially you have to do additional work and that would affect the surrounding. So, this is something which is easy to understand when the other thing is that the friction makes the process irreversible. So, you are losing heat and there is no way you can come with that.

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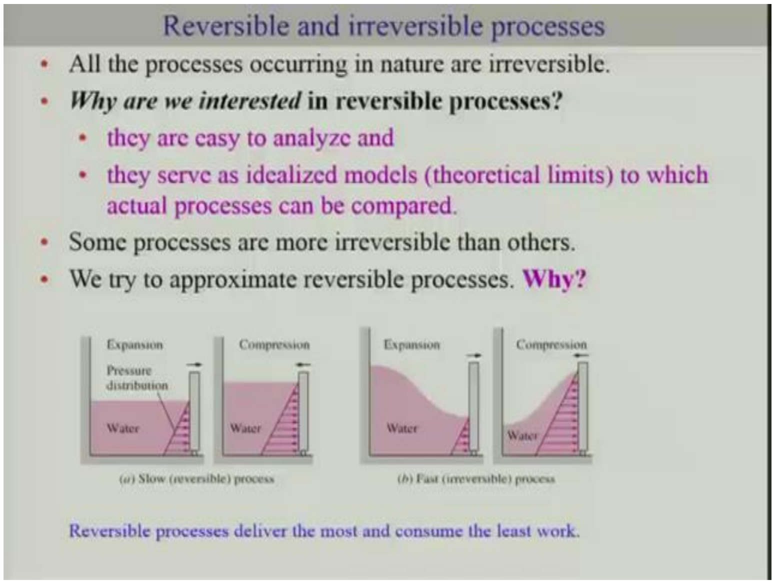

So, all the processes are occurring in nature are actually irreversible, they are mostly spontaneous they have a specific direction, so if you have to bring in you have to do some work essentially means that the work is going to be irreversible. Then, in that case why are we using this irreversible process? Because it is easy to analyze and they serve as an idealized model to which the actual process can be compared. That means that they become a yardstick for us to achieve.

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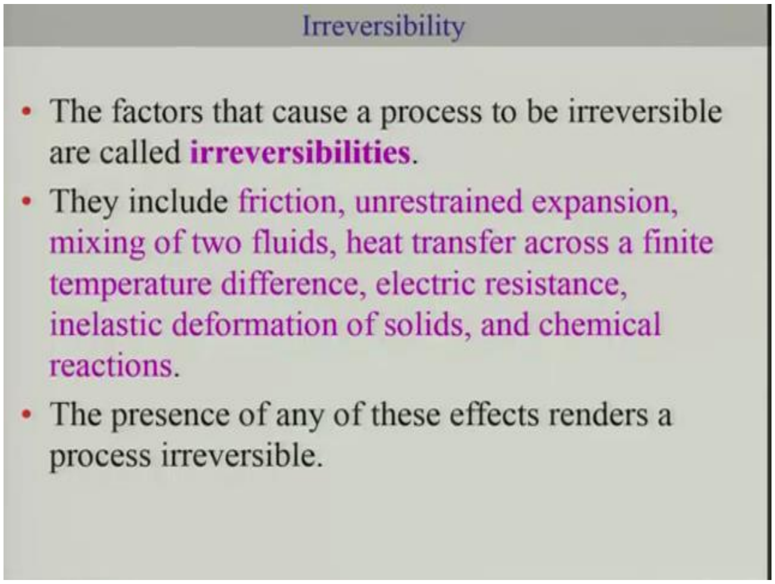

So as I said the factors which causes the process to be irreversible is a friction, anything is unrestrained expansion, mixing, heat transfer across a finite temperature difference, electrical resistance, inelastic deformations ,chemical reactions so these are the things which will probably render the process irreversible, so that is something this example.

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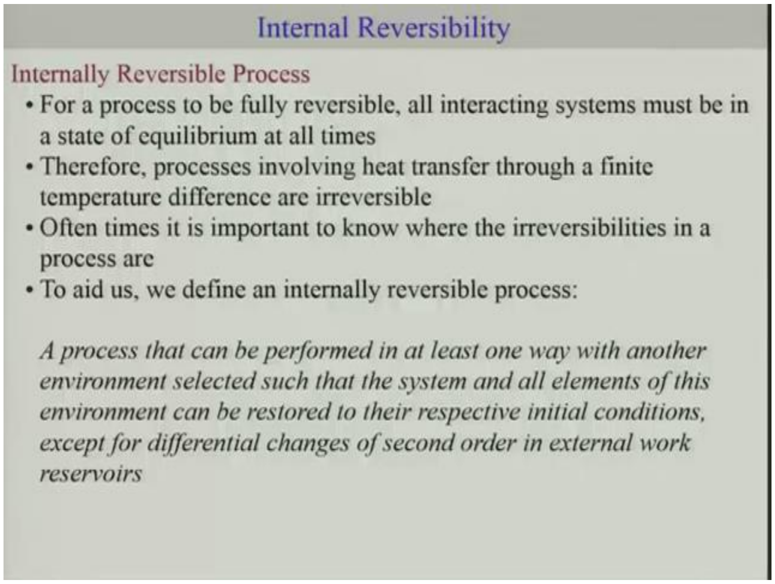

So, the many a times we make use of the fact that some processes or some process we can consider to be internally irreversible, some we can say totally irreversible, these are the processes or these are the assumptions which we can use to solve problems. So, for process to be fully reversible all interactive systems must be in the state of equilibrium at all time. So, whatever the changes are so slow that at any moment they are equilibrium that is what a fully reversible process will be. Therefore, process involving heat transferred through a finite temperature difference, are irreversible.

So, if there is a heat transfer occurring from outside the temperature here and here need to be extremely I mean, they should be equal to the something like 6th decimal point or so forth. So, difference will be absolutely can be negligible but still there is transfer of heat. In that case actually there would be small difference but can be extremely small.

Often time it is important to know where the reversibility in the process are, so in order to define we can we can define in order to aid we can define this internal reversible process which is that a process that can be performed in at least one way with another environment, selected such that the system and all elements of this environment can be restored to their respective initial condition except for differential changes in second order in external work reservoir. So, this is something which we have already mentioned.

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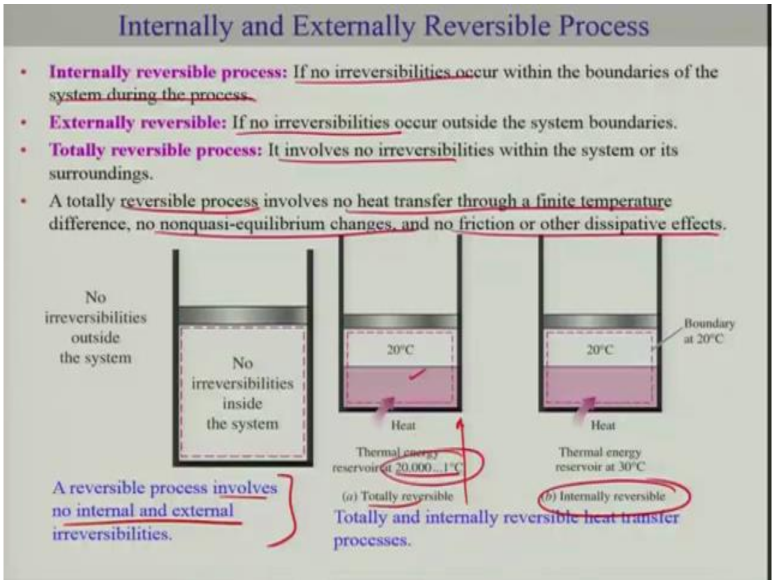

So, let me just summarize this, so if internally reversible processes are then if no irreversibility occurs within the boundaries of the system doing the process which means there is no final difference, there is no change in the pressure, everything is more like a homogenous. So then we can say that it is internally reversible process. External reversible process is if there is no irreversibility which occurs outside the system boundary and totally reversible process, it involves no irreversibility within the system or its surrounding.

So that means totally reversible process involves no heat transfer through a finite temperature difference, no nonquasi changes, no friction or other dissipated effects. So examples of these things here is total reversible process where the temperature here is extremely small difference and they are almost similar to what is in the system but the difference is there still and in this case this is going to be internal reversible where the properties here is all homogeneous but the but the outside temperature is much larger.

There is a finite difference and finally let me just conclude that a reversible process involves no internal and external reversibility. So in this lecture I wanted to cover the basic concept of the second law of thermodynamics and particularly related to heat engine and refrigerators, so in the next few lectures we are going to do some applications so hopefully we will be covering the concept with some applications, I think that would be the end of today's class. I will see you in the next class.