Applied Thermodynamics for Marine Systems

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Lecture -5
Second Law & Carnot Principle

Given the classical statements for second law of thermodynamics, from those statements we have seen that it is impossible to construct a heat engine which will have cent percent efficiency or that it is impossible to construct a refrigeration cycle which will have infinite COP or coefficient of performance. Then, it becomes the logical question that, what could be the maximum possible efficiency of a heat engine, or how we can construct a heat engine which will have maximum possible efficiency. In that regard I told that, if the heat engine cycle is a reversible cycle then, we will have highest efficiency possible for a heat engine and for a reversible cycle we need all the processes of the cycle to be reversible. We started identifying what are the reversible process and irreversible processes?

In that regard I said that, if there is a change of state by a particular process and if we can reverse the process in such a manner so that, both the system and surrounding can be brought to the initial state without leaving any change either in the system or in the surrounding then the process can be called a reversible process. All the natural processes are irreversible processes but with all the processes different degrees of irreversibilities are associated. There are some reasons which increase the irreversibility of the processes and we started identifying different reasons for irreversibility. We were making a list of the causes of irreversibility.

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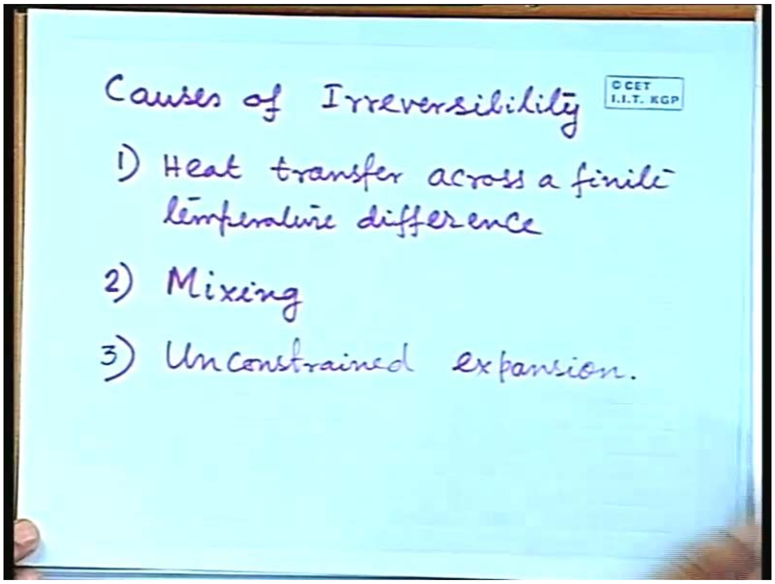

I said that, the heat transfer across a finite temperature difference causes irreversibility; mixing of two materials causes irreversibility and third we can name the unconstrained expansion. This also causes irreversibility. Let me explain the last item.

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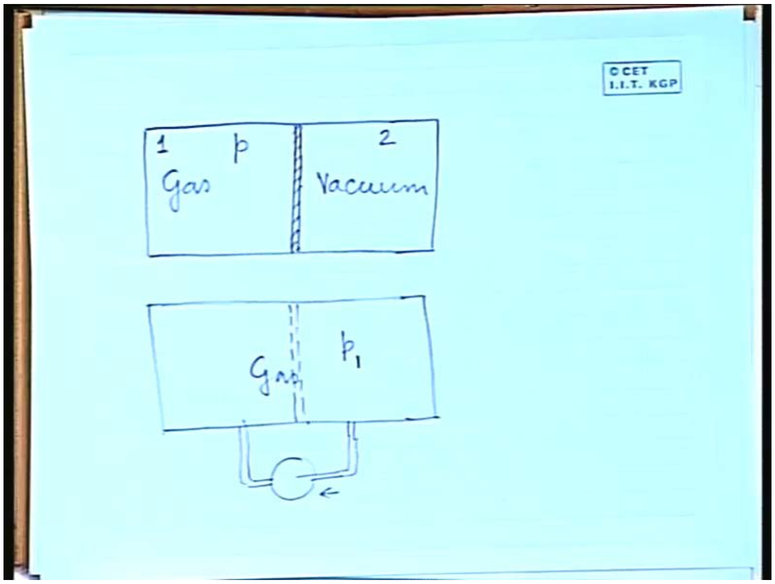

Let us say that, we have got a compartment like this. In this compartment there is a partition. Basically in this compartment, we are having two chambers. In the first chamber we are having a gas with a certain pressure. Let us say the pressure is p. In the second chamber it is a vacuum. If somehow this partition is removed, then what we will find is that, the gas of the first compartment will occupy the entire space and it will have a different temperature. Let us say p_1. This process is a highly irreversible process because, if we want to come back to the initial condition we have to put some partition here and then we should have some sort of a pumping device which will pump back all the gases from this chamber to the other chamber till the pressure in this chamber becomes p. We have to do a certain amount of additional work. Not only that, while we are compressing the gas in this chamber, the gas temperature will rise and probably we have to cool the gas. We can see that from the surrounding we have to put some more effort or there will be certain changes in the surrounding.

Though by some effort we can bring the system to its original condition to state 1, there will be certain changes laid in the surrounding. In other words, we can see that, the pressurized gas is having certain potential for doing work. If we allow it to expand freely, the unconstrained expansion is also termed as free expansion. If we allow the gas to expand freely, it is losing its potential of work because it is going through an irreversible process. We can have different dissipative processes. What are the dissipative processes? There are different processes which are known as dissipative processes. Some of the examples are like this; there is friction. In ideal cases, we do not consider friction. But in actual case we know that there is certain amount of friction associated between two solid surfaces. When we like to have a relative motion between two solid surfaces, there will be friction and due that friction some amount of energy will be dissipated, some amount of energy will be converted in some form which cannot be recovered easily or which cannot be recovered at all.

This is a highly irreversible process. One can take different example where friction or dissipation due to friction is there. One can find a similar phenomenon in fluid flow. In fluid flow we know that viscosity puts some resistance to the fluid motion and there will be some amount of dissipation of energy in the fluid due to the presence of viscosity. One can take the example of flow of current through some resistor. As the current is flowing through the resistor there will be ohmic heating and this is also a dissipative process. Some amount of energy will be lost due to this dissipation.

These are all examples of irreversible processes. There are some other irreversible processes. In fact there are number of other irreversible processes, but we are not going to list them one by one. Now we have some idea regarding what the irreversible processes are and while designing a heat engine for its maximum performance, one should try to avoid these irreversible processes or one should select the processes where the irreversibility will be minimum. Based on this, logic Sadi Carnot has postulated one heat engine cycle which is a reversible cycle made up of reversible processes and which can perform at its maximum limit. Let us see how the Carnot engine or Carnot cycle is constituted.

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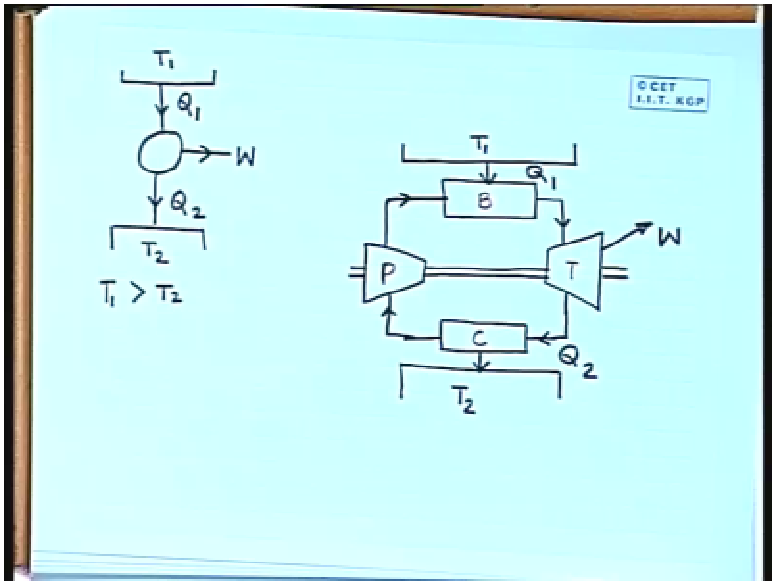

Let me draw a heat engine cycle schematically. It will be like this. There is a high temperature source at T_1, there is a low temperature sink at T_2, where T_1 is greater than T_2. Heat flows from the high temperature source. Let us say this is Q_1; to the low temperature source Q_2 amount of heat is rejected and W amount of work is done. From the first law, we know Q_1 minus Q_2 is W. In our heat engine cycle there should be one heat source and one heat sink. In Carnot cycle also there is one heat source and one heat sink. Let us say this is our heat source and this is the heat sink. Energy will be supplied from the heat source to this engine or to the Carnot cycle. We know that heat transfer across a finite temperature difference is an irreversible process. If heat transfer is inevitable for a heat engine cycle or for one process of the heat engine, we have to select a process where there is no temperature difference. There is no temperature difference but flow of heat is there. One can select a process if there is a phase change process.

Let us say the process of boiling. If the fluid is at its saturation temperature it needs latent heat for the transformation of phase but there is no change of temperature. One can ideally think of a process like this by which there will be heat transfer from the heat source to the Carnot engine. That is what I have written here. Let us say it is a boiler. It is an ideal boiler where there is heat transfer from a high temperature source and fluid is at its saturation condition. It is only picking up the latent heat and a transformation is taking place from the liquid phase to vapor phase. After that, there is an expansion of the fluid and it is doing a certain amount of work. Basically, the next component which I am drawing represents a turbine. It is doing certain amount of work and in this process the fluid temperature is also falling. As there is a change in temperature in this process, there should not be any sort of heat transfer. Along with the temperature change if we have heat transfer then the process will become an irreversible process. Basically, this is some adiabatic expansion of the fluid.

In the next step we will have another component where the heat has to be rejected to the low temperature sink. Here also this heat rejection process should take place at constant temperature or isothermally. This can be done through a condensation process. The next component we can denote as a condenser, so here we are having a condenser. Now what happens is, after the boiler we had the vapor phase. The vapor phase has expanded through the turbine adiabatically. After expansion, its pressure is low but still it is in the vapor phase. Then it has condensed so it is in the liquid phase. But, its pressure is low so now we need its pressure to be raised so that it comes back to its initial condition. So we need another component here where pressure rise will take place. This component could be equivalent to a pump or a compressor; so, let me put this to be P. This arrow mark shows the direction of fluid movement. Here in the turbine it produces some external work. Now this work should be sufficient to run the pump also and the extra amount of work could be given to the surrounding. From the boiler Q_1 amount of heat will come and in the condenser Q_2 amount of heat will be rejected. Again in the pump we will have adiabatic compression of the fluid. Basically, we can see that the Carnot cycle, the way Carnot has postulated it, it is made up of four different processes. We can write down like this.

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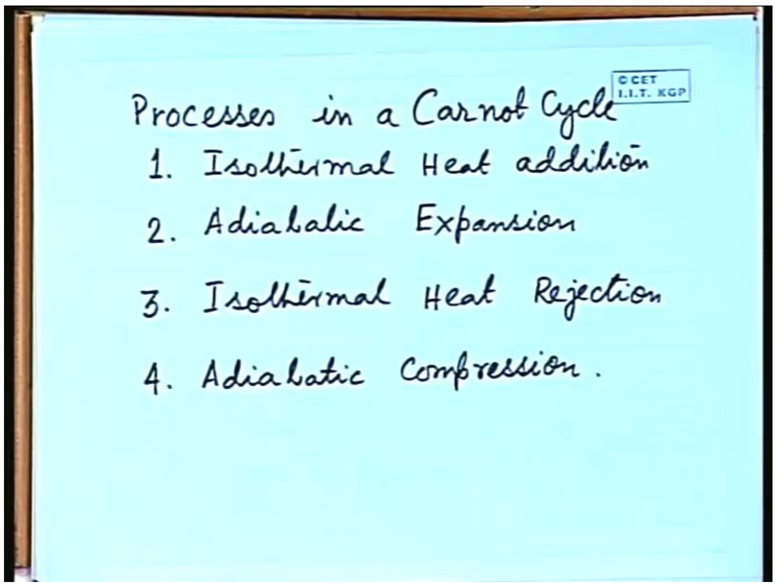

Processes in a Carnot cycle: 1 is isothermal heat addition, second one is adiabatic expansion, third one is isothermal heat rejection and finally adiabatic compression. So these are the four processes by which a Carnot cycle is constituted. The example which I have selected here or the block diagram which I have shown here, it shows a flow process. It has four components which to some extent is similar to our conventional steam power plant. We have got a component like boiler, we have got a turbine, a condenser and then a feed pump. It is interesting to note that as all the processes are reversible processes, so they can be reversible. The direction of fluid flow that also can be reversed theoretically and we can get another cycle which will be either a refrigeration cycle or a heat pump cycle.

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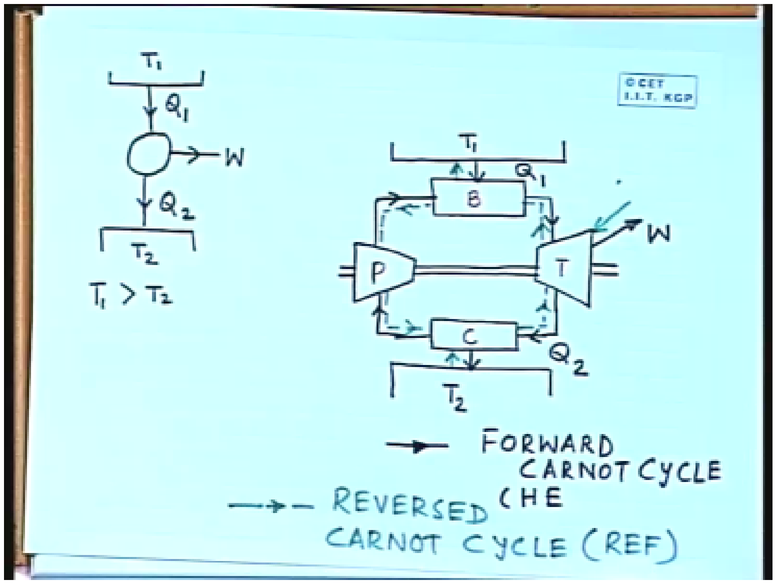

We can have something like this. There could be a net heat transfer from the outside and we can have the direction of fluid flow reversed like this. We can write this. This arrow indicates forward Carnot cycle or a heat engine cycle and this arrow indicates a reversed Carnot cycle or a refrigeration cycle. It should also be noted that, this is not the only configuration of a Carnot cycle. One can have a compressible fluid inside a piston cylinder arrangement and can have this Carnot cycle, where these four basic processes like isothermal heat addition, adiabatic expansion, isothermal heat rejection and adiabatic compression are present.

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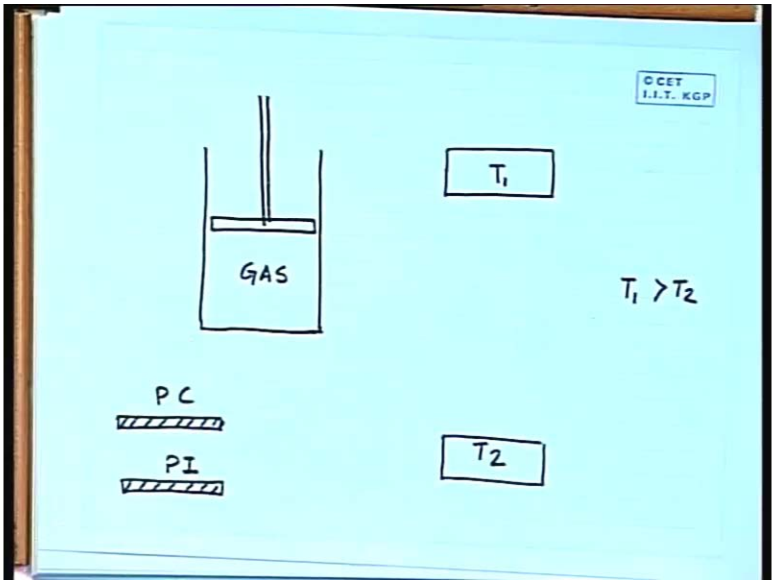

This is a piston cylinder arrangement. Inside this piston cylinder arrangement, certain compressible fluid or gas is there. One can think of an ideal cycle where, you are having two reservoirs; one reservoir is at temperature T_1, another reservoir is at temperature T_2 and T_1 is greater than T_2. This is the cylinder and you have got two cylinder heads. One head is perfect conductor of heat and another head is a perfect insulator of the heat. To start the cycle, let us say that isothermal heat addition is our first process of the cycle. In that case perfect conductor will be fitted to the cylinder as the cylinder head and it will communicate with the thermal source at temperature T_1. Isothermal heat addition will take place. Then at next moment I will remove this perfect conductor and put this perfect insulator here. Now, as the gas will expand, it will expand adiabatically. Then again in the next moment, I will remove the perfect insulator and put the perfect conductor as the cylinder head and make a communication with another thermal source at temperature T_2. The isothermal heat rejection will take place. Then finally I will remove the conductor, put the insulator so that there is adiabatic compression.

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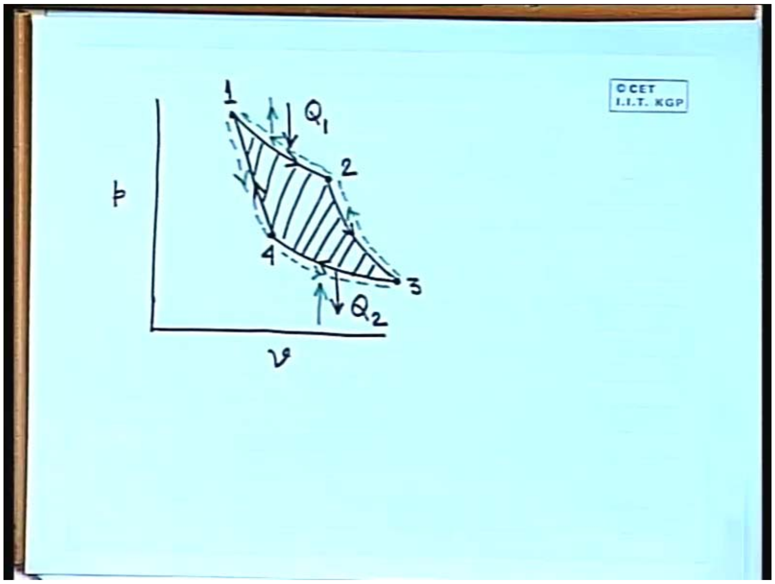

For this piston cylinder arrangement if I draw the pv diagram, pressure volume diagram, I will get something like this. Let us say this is 1, this is 2, this is 3 and this is 4. 1 to 2 is the isothermal heat addition and 2 to 3 is the adiabatic expansion; 3 to 4 is isothermal heat rejection and 4 to 1 is adiabatic compression. What we can get here is, this is Q_1 heat addition, Q_2 heat rejection and in the pv diagram the area of this particular cycle becomes the work done during the cycle. This much amount of work will be done by the Carnot cycle. In this case also, one can reverse the direction of heat addition and work transfer. If we do this we will get a heat pump or a refrigeration cycle. The cycle with this green dot indicates a reverse Carnot cycle which is not a heat engine cycle, but a heat pump or a refrigeration cycle. The direction of heat flow will also be different or reversed. This gives us a good idea about the Carnot cycle, which Sadi Carnot has proposed as an ideal heat engine cycle. Along with the proposition of this cycle, he has also given a few attributes or characteristics, qualities of these cycles. Two of them are very important.

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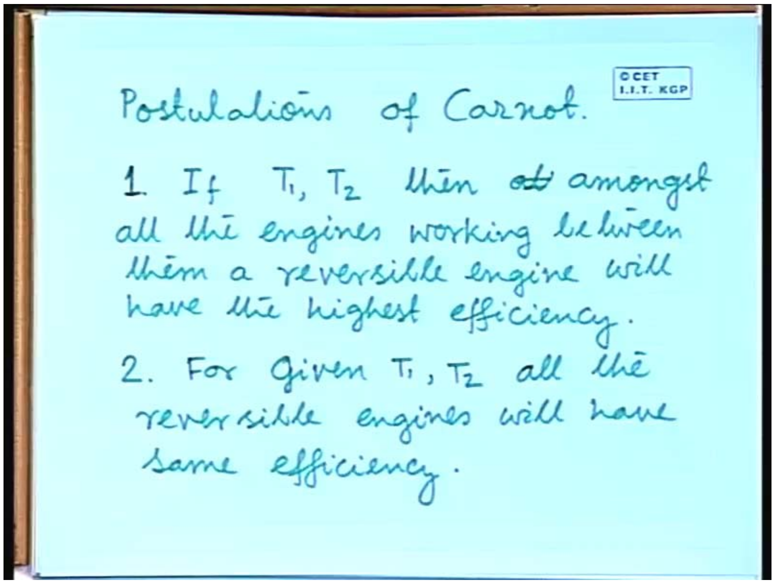

These are known as postulations of Carnot. The first one says that, if two temperature limits or two thermal reservoirs are given; if T_1 T_2, these two are the temperatures of two thermal reservoirs if these are given then, amongst all the engines working between them a reversible engine will have the highest efficiency. Let us say we have got two thermal reservoirs. The thermal reservoir which is a source that has a temperature T_1 and the other thermal reservoir which is acting as a sink have a temperature T_2, where T_1 is greater than T_2. Then, we know that we can run a heat engine between these two thermal reservoirs. If we have a number of heat engines in between these two thermal reservoirs then a reversible heat engine will have the highest efficiency.

One can prove this, though I am not going to do it in this class; it is available in any thermodynamics book. If we assume that an irreversible engine is having higher efficiency compared to a reversible engine we will see that it will amount to violation of the second law. As the second law is a fundamental law of nature it is never violated. So it is not possible for an irreversible engine to have higher efficiency compared to a reversible engine working between same temperature limit. That is very important. Always, one should try to build engines or cycles which are closer to reversible cycles and reversible engines. The second point is also important. It says that for a given T_1 and T_2, all the reversible engines will have the same efficiency. This is also very important. If

T_1 and T_2 are given, if two thermal reservoirs are fixed, then the numbers of reversible heat engines are working between them, all of them will have same efficiency. What does it mean?

It means that, the efficiency of the reversible heat engine does not depend on the working fluid or the working medium which we have selected. It does not depend on the physical size of the cycle or engine that we have selected. It depends only on one parameter that is, the temperatures of the thermal reservoirs T_1 and T_2. If these two things are fixed, then its efficiency is also fixed. This is a very important observation which Carnot made. Let us start from this point that, efficiency of reversible heat engines depends only on the temperatures of the thermal reservoirs.

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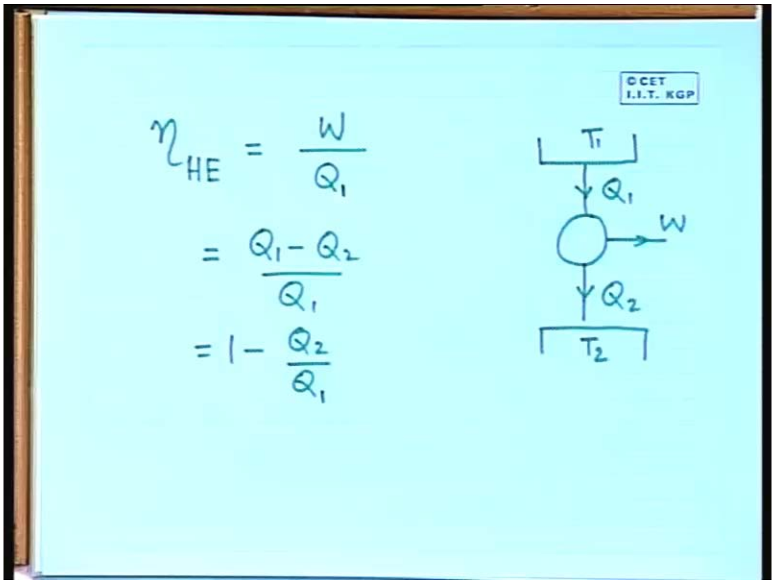

The efficiency of a heat engine is W by Q_1. Side by side let me draw our old figure. This is W, this is Q_1, this is Q_2; T_1 and T_2 these two are the temperatures. That means, we can write Q_1 minus Q_2 by Q_1 or we can write 1 minus Q_2 by Q_1. This is the efficiency of a heat engine and then this expression is valid both for reversible and irreversible heat engines. For all heat engines, this particular expression is valid. Then, Carnot postulated that for a reversible heat engine, this efficiency depends only on temperatures of the two thermal reservoirs.

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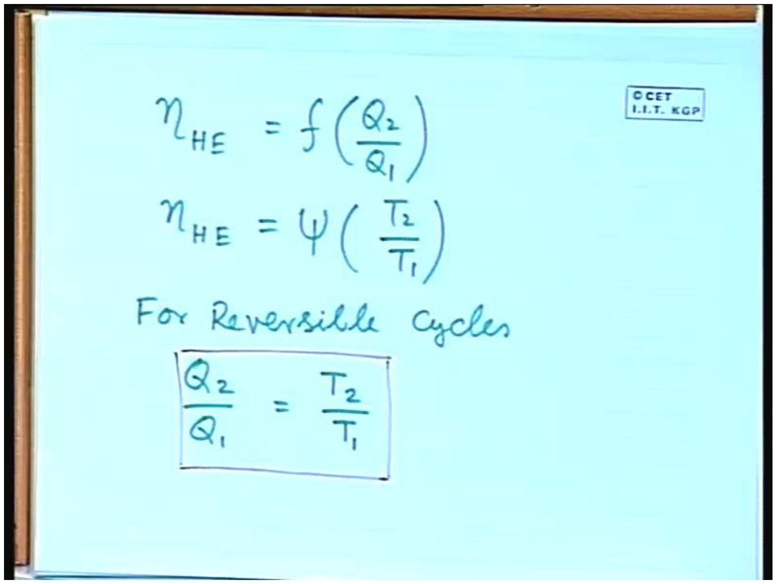

Basically, what we can see is that eta heat engine is a function of let us say Q_2 by Q_1. Again from Carnot's postulation, we can see that this is another function of T_2 T_1. Some sort of logical reasoning can be given for selecting this type of a functional relationship, but it can be shown that the heat engine efficiency if it is depending on the temperatures T_2 and T_1, one can write it like this. There is a direct relationship between Q_2 by Q_1 and T_2 by T_1 for a reversible heat engine cycle. With some amount of logical reasoning and with the selection of a proper temperature scale, one can show for reversible cycles that Q_2 by Q_1 is equal to T_2 by T_1. This is for reversible cycles. This is a very important observation. Based on this, one can define a thermodynamic scale of temperature.

We know that all the scales of temperature which are made earlier are dependent on some material property. Let us say the expansion of a liquid could be one property by which a temperature scale can be generated. But, here, without taking any material property a scale of temperature has been developed based on thermodynamic logic only; that is known as thermodynamic scale of temperature. Sometimes, this is called the absolute scale of temperature also and this temperature is referred to as the absolute temperature. We are already familiar with this absolute temperature from the knowledge of our physics. That is why I do not want to elaborate much regarding this absolute scale of temperature. But, the relationship to which I will draw your attention which is very important is this: Q_2 by Q_1 is equal to T_2 by T_1 for reversible cycle. If we extend this further then we get something like this.

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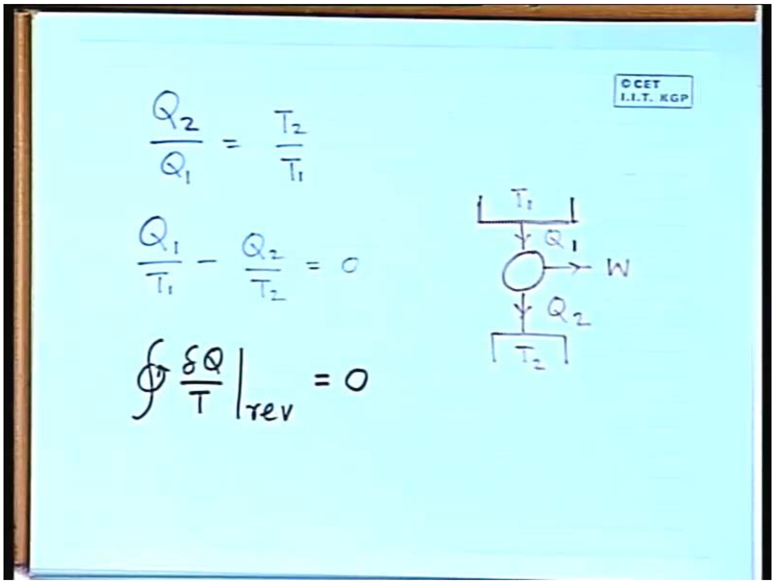

Q_2 by Q_1 is equal to T_2 by T_1 or Q_1 by T_1 minus Q_2 by T_2 that is equal to 0. Or if we take this example of the Carnot cycle where there is reversible heat transfer and reversible work transfer, this is Q_1, this is Q_2, this is T_1, this is T_2 and this is W. We can write the cyclic integral of dQ by T reversible is equal to 0. This Q_1 by T_1 minus Q_2 by T_2 is nothing but cyclic integral of dQ by T if we consider these two figures side by side this figure and this expression side by side. If we take dQ by T, what it becomes for a cycle? This becomes Q_1 by T_1, because this is the heat addition and then, heat rejection is Q_2 that is taking place at temperature T_2. As it is heat rejection a negative sign will come and it becomes Q_2 by T_2. Then if we put the entire thing, it is equal to 0 which amounts to the cyclic integral of dQ by T reversible and that is equal to 0.

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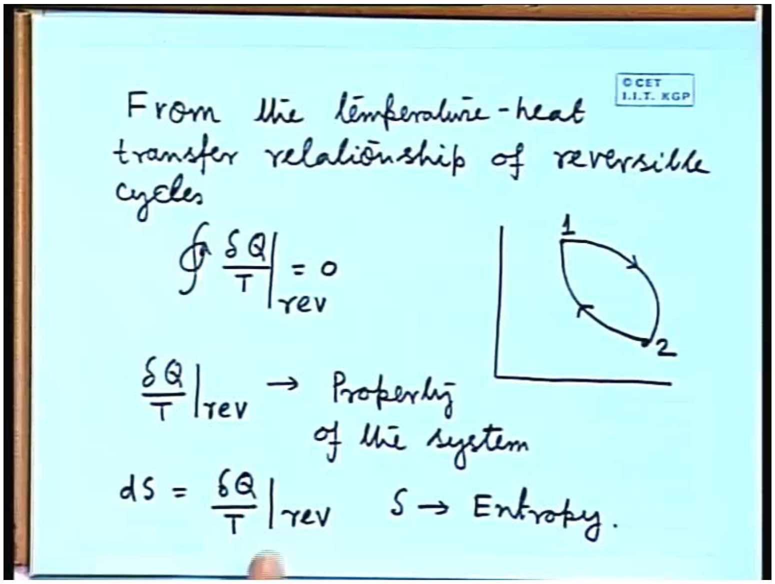

From the temperature- heat transfer relationship of reversible cycle, we get the cyclic integral of dQ by T is equal to 0. If the cyclic integral of dQ by T becomes 0, It has to be qualified that it is for reversible process. We have got similar situation earlier in our first law. What can we conclude from it? Let us say there is a cyclic process like this. We have taken two arbitrary processes, any two arbitrary processes; 1 to 2 is one process and then 2 to 1, that completes the cycle. If we have to take cyclic integral of dQ by T, we have to compute dQ by T from 1 to 2 and then we have to compute dQ by T from 2 to 1. We have to add this quantity and we have to add this quantity.

If we do the addition we get 0. It means that dQ by T, whatever path we may take is not dependent on the path. It is dependent only on the end state and it becomes a property of the system. It is not a path function but it is the function of the state point; then it becomes a property of the system. It is very interesting to note dQ heat; Time and again I have told and we know also that heat transfer is a path function. It depends on the type of process or type of path taken by the thermodynamic system. If we have a constant volume process, we will have some amount of heat transfer. If we have some constant pressure process we will have some different amount of heat transfer. But, dQ by T becomes a property. It does not depend on the path. If the end states are fixed then, the change in dQ by T, that is also fixed. We can write down now dQ by T; we have to put this for reversible. This is a property of the system and this new property is termed as entropy. We can write dS is equal to dQ by T, where S is entropy. We are getting a similar situation as we have seen in case of first law.

From the discussion of the first law, we could identify a new property which is internal energy or stored energy. Here also, we are identifying a new property which is entropy. In that case, two path functions were involved dQ and dW. Here, only one path function is involved and that is dQ. We should not forget to put reversible because, this dQ by T which is for reversible process, that only gives the property entropy. As it is a function of state point we can do the integration easily.

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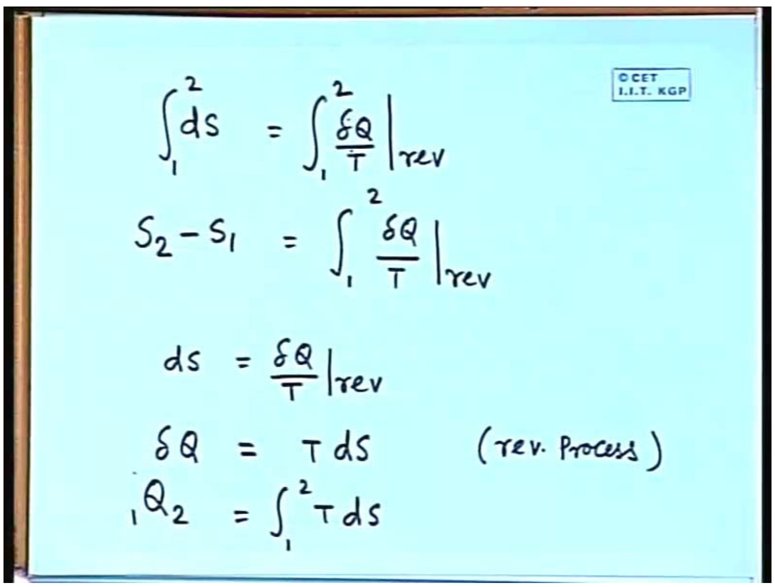

dS let us say 1 to 2 is equal to dQ by T 1 to 2 and we can write in the next step S_2 minus S_1 is equal to 1 to 2 dQ by T reversible. The integration on the right hand side can be done if the relationship between Q and T are known. If this relationship is known then we can do the integration. This is how we can calculate the change in the property, entropy. Again, this particular relationship is also expressed in a different way. The basic relationship is dS is equal to dQ by T, one can again write, for reversible process. So, dQ is equal to Tds and again it is for the reversible process. From here, if we do the integration, ${}_1Q_2$ that is 1 to 2 Tds, if the relationship between T and S temperature and entropy are known then, one can have what is the reversible heat transfer during this process? This we have to keep in mind, the reversible heat transfer. If the process is reversible, then the heat transfer is also reversible and one can get it by this particular expression.

The temperature is an intensive property of the system and entropy is an extensive property of the system. One can define specific entropy, entropy per unit mass; then it becomes some derived intensive property. But these two are independent properties and they can be used as two ordinates of a thermodynamic plane and we can represent thermodynamic processes on TS plane. We are familiar with the thermodynamic plane where p and v are used. Either we can use the volume or we can use specific volume as two axes of this particular plane.

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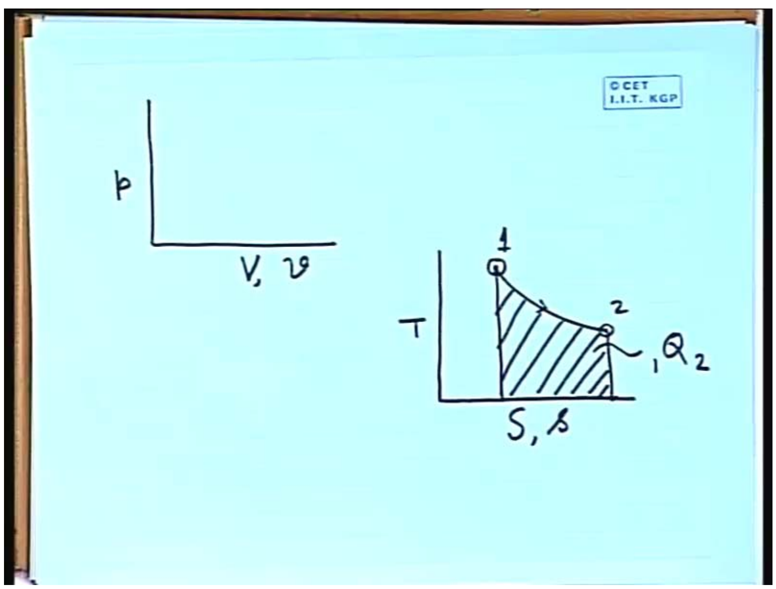

Similarly, one can have a TS diagram, where T and either entropy or the specific entropy can be used as another ordinate. The thermodynamic processes can be represented on the pv plane and on the TS plane also. If we represent it in the TS plane, then, let us say there is a process like this. The process is represented by the curve 1 2. The area under this curve becomes the heat transfer during this process. This will be $_1Q_2$. We can see that once we have got the property entropy, with that we can have thermodynamic representation of the process and area under the TS curve becomes your heat transfer during a particular process.

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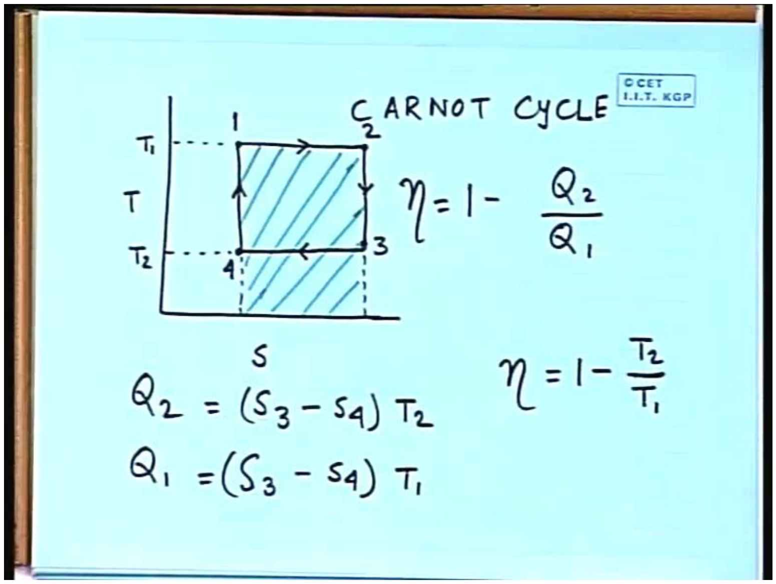

The Carnot cycle which I have represented in pv diagram, can be represented in TS diagram also. We know that there are two isothermal processes, one at high temperature let us say T_1. So, 1 2 and then there is an adiabatic process and reversible adiabatic process. So, the reversible adiabatic process becomes an isentropic process. So, 3 then there is one isothermal heat rejection process at temperature T_2 and then there is one adiabatic compression process. This becomes the representation of Carnot cycle in TS plane and very easily I can get the efficiency of the cycle from here. The cycle efficiency we are trying to determine from our classical expression of the first law, which is 1 minus Q_2 by Q_1; that is your efficiency. What is Q_2? Q_2 is the heat rejected and if we call this point 4 then Q_2 is equal to area of this particular portion and that will be given by S_3 minus S_4 multiplied by T_2. Similarly, Q_1 will be given by S_3 minus S_4 multiplied by T_1. If I substitute these values then efficiency will be 1 minus T_2 by T_1, which we have got from the first relation of Carnot.

I think we will stop here today and next day we will try to see some more implications or some more significance of entropy. Thank you.