

Basic Thermodynamics

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Lecture - 06

Second Law and its Corollaries – I

Good afternoon, I welcome you all to this session. Last class, we discussed the first law of thermodynamics. In the last two consecutive classes, we have completed the discussion on first law of thermodynamics, applied to both closed and open system. Today, we are going to start the discussion on second law of thermodynamics. The first part of the lecture, I just request you not to take any notes, you listen to it. This is the introduction to the second law.

The second law of thermodynamics is probably the most important axiom or law of nature in all branches of physical sciences. This is the law which puts a directional constraint or unidirectional characteristics of all natural processes. Well, in the beginning of this class, I told you that natural processes do not take place at random. There are certain rhythms or certain directional constraint on conditions for natural processes to occur. It is the second law of thermodynamics which imposes this directional constraint, but these directional constraints are imposed in various forms on different natural processes. That is the reason that the second law is expressed in various forms, though they originate from the same basic concept of directional constraint.

Just an example I am telling you - that if there are students from different branches, for example: there is a student of material science, there is a student of physics, there is a student of chemistry, there is a student of mechanical engineering, there is a student of chemical engineering, metallurgical engineering, energy engineering and so on. This is a common experience, practical experience, if we ask what second law of thermodynamics is, we will see that everybody is answering in different forms and all the answers are correct, which means the second law of

thermodynamics is very wide and they can be expressed in various forms, but they originate from the same principle of directional constraint on natural processes.

What is this directional constraint? We must understand **this**, before coming to some formal statements and its applications to certain aspects of engineering which is within the scope of this subject. Let me first tell you, what is this directional constraint?

Now let us start this way. We know that spontaneous natural processes always proceed towards equilibrium and take place in a particular direction. What is this? For example, liquid always or fluid always flows from a higher elevation to a lower elevation spontaneously. Heat always flows from high temperature to low temperature. Materials always diffuse from high concentration to low concentration spontaneously. Reverse of this never happens. If it has to happen, it will be with the aid of external energy or some external source. Without any source of external agency or without aided any external source, this spontaneous processes take place in this direction.

Now come to another category of processes in nature aided by external agency they also take place in one direction. Just for an example, a moving wheel can be brought to rest by the application of frictional brake and by doing so the wheel and the brake gets hot. We can explain this from physical principle that kinetic energy is converted into inter molecular energy, but the reverse of this, that means to set this wheel in motion by pulling the wheel and the brake is never possible by any external agent.

Similar is the case, that when you pass electric current through an electrical conductor or electrical wire or conducting wire, we see that the wire becomes hot. If it is insulated its temperature is raised, but attainment of electrical work by cooling this conductive resistance can never be done. There are list of such processes aided by external sources also take place in one direction, but there are number of processes which are more in number in nature which take place input the directions, the concept lies here.

For example, you heat a body from a low temperature to a high temperature. You can cool a body from high temperature to low temperature; heating and cooling both are possible. You can expand a gas from a high pressure to a low pressure and you can compress a gas from the low

pressure to high pressure. While the gas is expanded from high pressure to low pressure, work is delivered, while you compress the gas from low pressure to high pressure work is given to the gas. Similarly, we will see afterwards that a heat engine can deliver work by interacting with two temperature levels that it can take heat from a high temperature source and it can give heat to a low temperature sink. Similarly, a heat pump can be made to operate which will take heat from a low temperature sink and will pump heat to a high temperature source. So, large classes of processes in nature take place in both directions, but here, what is the directional constraint?

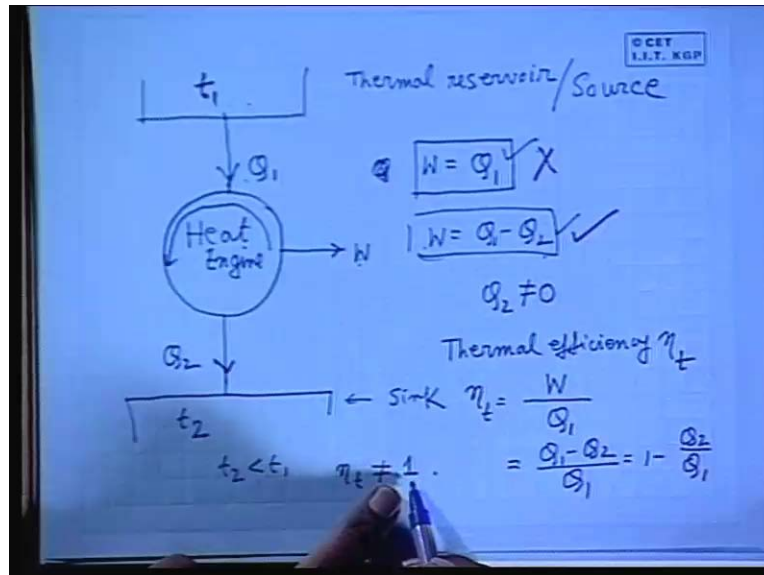
That means, these processes have a directional constraint. Like these, these processes are such, if they are executed in both the directions, then though this system comes back to the initial condition, the surrounding does not come back to an initial condition. Surrounding suffers a permanent change in a particular direction. This gives the clue to the irreversible process that I will tell you afterwards. Therefore, we see that depending upon the class of problems, the directional constraint or unidirectional characteristics are imposed in various forms.

That is why the thermodynamics second law has been evolved in various forms which ultimately possess some directional constraint on the process. Whatever may be the process, some process may not be possible in reverse direction. Some process may be possibly in both forward and reverse direction, but put a constraint on the surroundings that though the system comes back to initial state surrounding fails to attend the initial state. So, these were the directional constraints are imposed in various forms and the thermodynamics second laws are expressed in various forms.

In this class, we will be interested in understanding the second law of thermodynamics or directional constraints mainly from the engineering point of view in relation to energy conversion and specifically in relation to interchangeability between heat and work. These two types of energy in transit that heat and work, how you will start this?

Now, let us see before giving you any formal statement of second law in relation to interchangeability heat and work, let us see that few definitions are required.

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Now, what is heat engine? Let us consider a heat engine. Some definitions are important to know. Heat engine is a device where a system operates in a cyclic process so that it develops work when some heat is given to it. **Do you see? You can see.** When some heat is being given to it, let this heat is Q_1 . Heat engine is a device which operates from a thermodynamics cyclic process whose output is the mechanical work and there is an input of heat. To add heat, we have to have a system at some higher temperature. Let this temperature be t_1 . In this connection, we define the word thermal reservoir. What is the definition of thermal reservoir?

Thermal reservoir is a system of infinite capacity such that when heat transfer takes place either heat is taken from that reservoir or heat is given to the reservoir, its temperature remains invariant. That means it is a constant temperature, infinite heat capacity system that is known as thermal reservoir. When the thermal reservoir is at a high temperature from where heat is being **((no audio)) ((00:09:49 min to 00:11:18 min))**

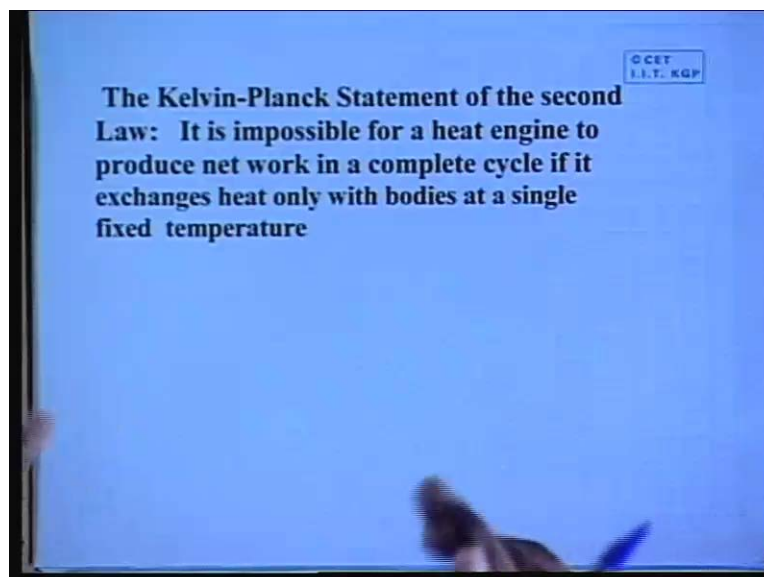
or that rejection you have to have an another thermal reservoir at a temperature t_2 where t_2 is less than t_1 another thermal reservoir known as sink, where heat is **((no audio)) ((00:11:31 min to 00:11:56 min))**

This is also true, but second law tells no this is not true (Refer Slide Time: 12:00 min). This is the only solution, that means second law tells that we have only this, W is equal to Q_1 minus Q_2 as the solution that means Q_2 is not equal to 0 ((no audio)) ((00:12:08 min to 00:12:33 min)) thermal efficiency.

What is the definition of thermal efficiency? η_t . This is related to the heat engine. Thermal efficiency of a heat engine determines its effectiveness in converting heat into work. That means work W is its output and this input heat Q_1 . From the first law of thermodynamics from the energy balance, we can write this Q_1 minus Q_2 by Q_1 , which becomes equal to 1 minus Q_2 by Q_1 .

So, second law tells, Q_2 cannot be 0, even if the process is ideal. In absence of all thick friction, all dissipative effect, everything is ideal; even in that case, Q_2 cannot be equal to 0. That means the efficiency η_t can never become equal to 1. That means a heat engine can never run even in an idealized condition with an efficiency equal to 1 or 100 percent. That means there has to be a rejection of heat. You cannot continuously convert the heat into an equal amount of work. This is precisely the first law of thermodynamics as expressed in terms of a heat engine as far as inter-conversion of heat into work. This was first told by Kelvin and the original statement actually came in a little different way as I explained.

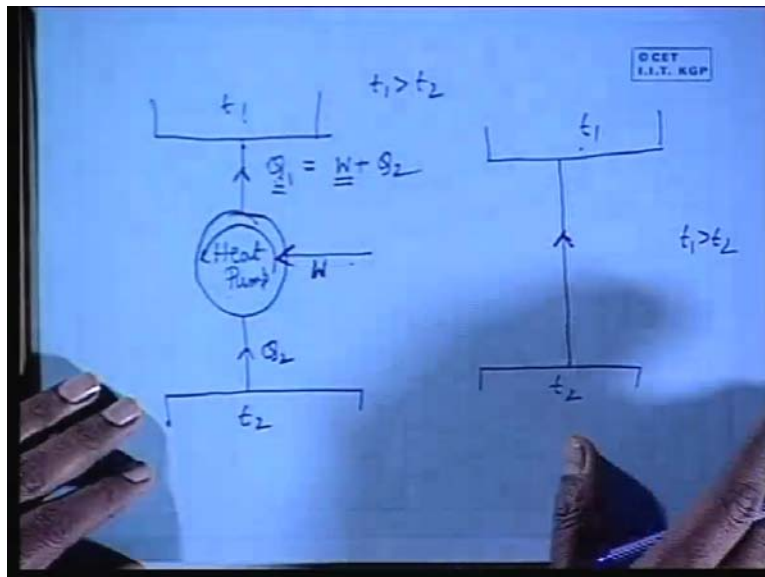
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Because this is the easier way to understand the thing rather than first following the Kelvin-Planck statement like that. Now, you can appreciate this statement, the Kelvin-Planck statement of the second law: It is impossible for a heat engine to produce net work in a complete cycle if it exchanges heat only with bodies at a single fixed temperature. That means, it has to take heat and it has to reject heat. For doing so, we must have at least two temperature reservoirs, two distinct different temperature reservoirs, because from temperature reservoirs of a single fixed temperature you cannot perform these two processes. That means you can take heat, but you cannot reject heat.

So, therefore Kelvin-Planck first put the statement in this fashion, that if it exchanges heat only with bodies at a single fixed temperature. **Clear?** Now, you will come to the next definition.

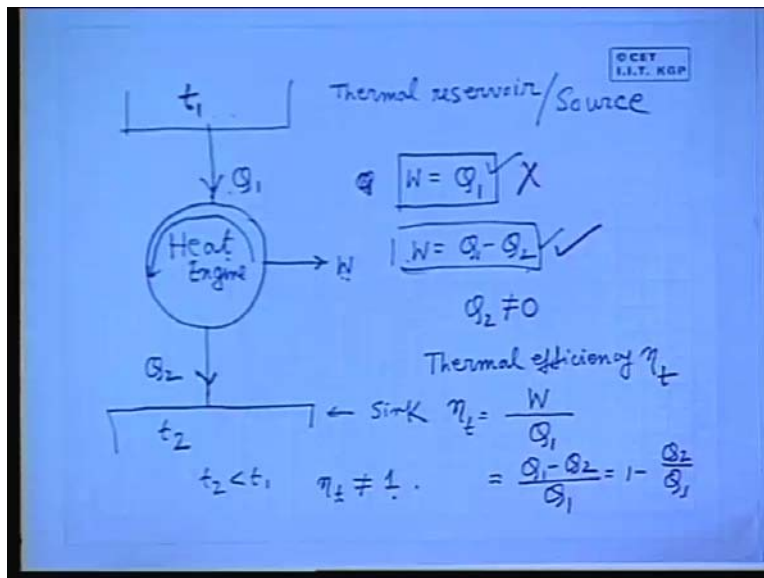
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Let us consider another system, another form of this statement. You consider another cyclic device known as heat pump. What is this? Its function is like that. Before that, we should tell that, if there is a temperature t_2 and there is a temperature t_1 and if t_1 is greater than t_2 , we know the spontaneous as I told that heat cannot flow from lower to high temperature. This is a law of nature that we have found in nature. So, this is another form of second law that heat cannot continuously flow from lower temperature to higher temperature.

This is not a spontaneous process but, we can make a device which operates on a cyclic process such that it can take heat from low temperature and absorb work from surroundings and can deliver heat to the higher temperature. That means, t_1 is greater than t_2 same thing. That means, pumping heat from lower to higher temperature is possible, not spontaneously, but we have to make some external arrangement for which we have to operate a heat pump which will absorb work from surroundings. In this case, we can write from the first law of thermodynamics, conservation of energy Q_1 is equal to W plus Q_2 that means this work is being converted into heat and by an equal amount. Here you see that heat is being pumped, but what is the underlying concept? That continuously this work form of energy transfer is now appearing in the form of it. That means this Q_1 heat which is being pumped to higher temperature, some part of it equals to the amount of work W , which means that work can be continuously converted into heat. Therefore, I can write this thing now to tell you in a more clear way.

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If you convert heat in a cyclic process like this work, you always get work less than Q , but if you convert work in a cyclic process to get heat, work can be continuously converted. That means, W is always less than Q but, Q is equal to W . Try to understand. Not always it is the case, but you can never do it under ideal conditions. But here, you can do it under ideal conditions that all the work can be continuously converted into heat where all the heat cannot be continuously converted into work. Now, here I tell you one very important thing which many people even

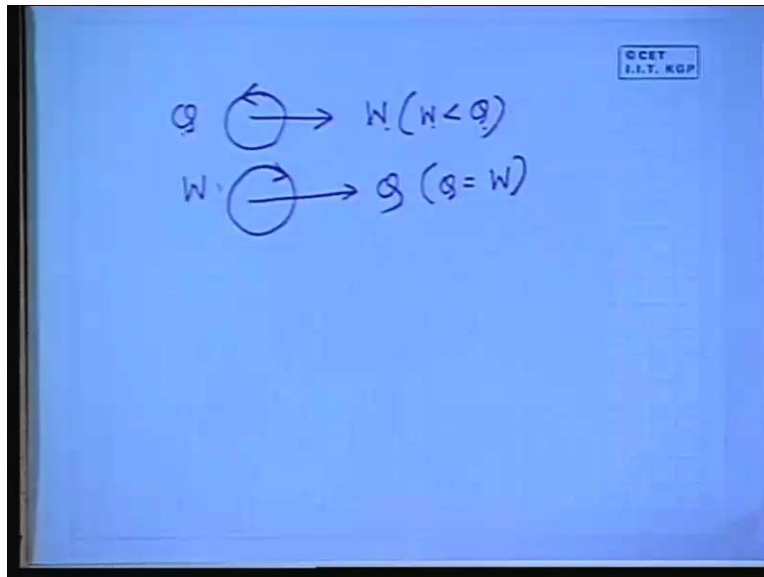
after reading thermodynamics many times fail to understand that this interchangeability heat into work that a heat engine has to reject a heat.

For example, this thing I tell you again, this is a very important concept that a heat engine has to reject a heat even in the ideal case. That means its efficiency can never become one. This is a restriction from the physical law that even an ideal machine cannot do, not from the practical constraints.

For example, electrical motor can attend hundred 100 percent efficiency. A mechanical transmission system, a fluid transmission system, or a generator, they can all attend 100 percent efficiency without **burying** any physical law, but they cannot attain because of practical constraint. We cannot get rid of dissipative effects, electrical resistivity, magnetic hysteresis, fluid friction, and mechanical friction; they prevent them from attaining 100 percent efficiency, but we can conceive our frictionless fluid transmission or mechanical transmission system. We can consider a motor without any current loss and having 100% efficiency. From the viewpoint of physics, this is permissible, but in case of heat engines, even an ideal heat engine in absence of friction or any dissipative effect, they can never attain 100 percent efficiency.

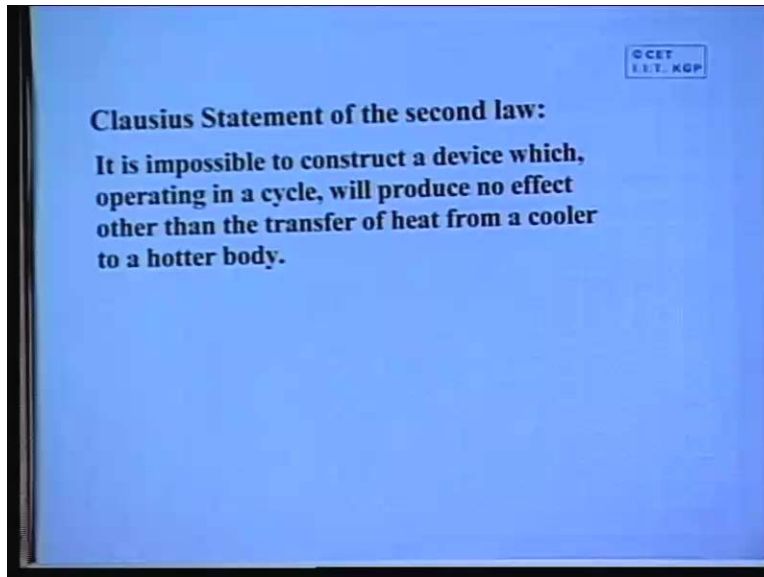
That means, this constraint or restriction of un-attainability of 100 percent efficiency is even on the ideal case. That means this is the law of physics. This constraint is there on the law of physics. It is not because of natural constraint because of dissipative effect, even if the ideal case it does not happen. This is an axiom this is the second law as for as the interchangeability heat and work is concerned.

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Again, we see that continuous convertibility heat into work (Refer Slide Time: 19:55 min), work is always less than heat. Some heat has to be always rejected in converting heat into work, but if we want to convert work into heat, we do not have to reject work. All work can equally be converted into heat and this (Refer Slide Time: 20:07 min) is the base by which we define heat as low-grade energy and work as a high grade energy, that I will come afterwards. Before that, we go through another statement of second law which is the Clausius statement.

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This statement tells that it is impossible to construct a device which operating in a cycle will produce no effect other than the transfer of heat from a cooler or to a hotter body. That means continuously heat cannot be transferred from a cooler body to hotter body without producing any other effect. That means it can be done by a heat pump if it takes work from the surrounding. That means there is an effect in the surrounding, that surrounding losing some work surrounding has to give that work.

This is another statement, it is not very important to memorize this statement; just to know how this statement was first described by the scientist Clausius by the scientist Kelvin and Planck, but their implacability, but how they are used that is more important.

Now after this, I come to the definition of reversible process which is very important. What is the reversible process? We know by information, we have told so many times that all natural processes are irreversible processes. Then what is a reversible process?

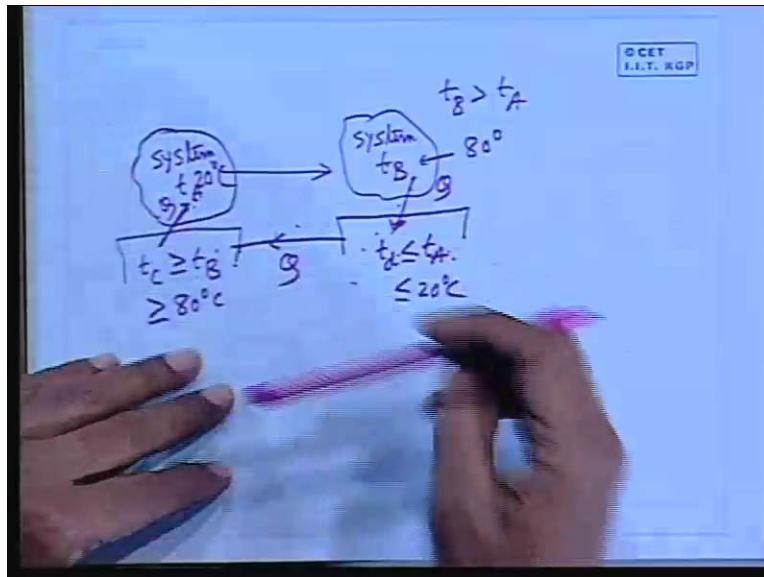
All processes are irreversible process that is the directional law. That is also a second law. I told that all process natural process have a unidirectional characteristic, have a directional constraint. What is that constraint? It is that all processes are irreversible. Very apparently, it seems that irreversible process means, the process cannot be reverse back and it is true for some processes

which cannot be reverse back. I told you that conversion of mechanical energy to intermolecular energy, it cannot be reversed back. Heating of an electrical wire by applying electrical work transfer cannot be reversed back. That means, I cannot cool the wire and get the electrical work back, these are very easily understood, but large classes of practical problem can be made to occur in both the directions. Then where is the definition of reversible process?

A process is reversible is not that the process cannot be reverse back, but the definition is that, if a process has to be reversible that after the conclusion of the process, if by any means the system can be made to the original state without affecting the surrounding then the process is reversible. That means, if after the conclusion of the process, by any means, we can restore both the system and the surrounding at the initial conditions then the process is reversible which we cannot do for any natural processes. This is expressed in various ways we can tell the language may be different that after the conclusion of the process if the system and surrounding is made to come back to the initial stage without any change in the rest of the universe the process is known as reversible, otherwise it is irreversible.

Let us understand how it happens in some natural processes as I have described which can be cause to occur in both the direction. Consider heating of a body and cooling of a body, very simple example. It will always tell us why it is not irreversible process. I can heat a body from some temperature to a higher temperature, I can cool it. Yes, I will start with that.

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Let us consider a system, which is at a temperature t_A . Now, let us heat it to a temperature t_B , a same system, heat it to a temperature t_B . Now t_B is greater than t_A . What we should do? Tell me? We should keep a hot body with a diathermic wall which will transfer heat Q whose temperature t_C which will be greater than equal to t_B , otherwise it cannot be heated up to t_B . If we make equal to t_B , then ultimately it will be a very slow process at the end and slowly asymptotically it will reach the temperature t_B , but in practice what happens? This t_C is much higher even than t_B , within a small time it is heated from t_A to t_B (Refer Slide Time: 24:27 min). If we cool it back again from t_B to t_A it is permissible. We can do it, what we have to do in that case?

We will have to extract the heat and where the heat will be rejected? That means we will have to consider another body from the surrounding with a diathermic wall so that heat can transfer whose temperature t_d has to be less than equal to t_A . Now, you see the system comes back to its initial state, but surrounding suffers a permanent change. Surrounding does not accept it. Why? Because we have taken Q from a high temperature body of the surrounding and we are giving back the same Q to a low temperature body of this surrounding. That means if you want to make the surrounding to come back to the initial state that means you will have to return this to this (Refer Slide Time: 25:16 min). For an example, let this t_A is 20 degree Celsius, just a numeric, t_B is 80 degree Celsius. That means this temperature will be 80 degree Celsius or more than that and this temperature will be less than 20 degree Celsius.

Therefore, we will have to give back the heat from 20 degree Celsius to 80 degree Celsius. It is not possible spontaneously. Then we have to make a use a heat pump which will again take work from the surrounding. That means without any change in the surrounding we cannot give it back, because this process is not spontaneous. There is a permanent change in the surrounding. Heat is lost from one part of the surrounding it is gained in the other part of the surrounding. That means if I take money from you and give it back to him, I think as I am concerned I come to the initial state. I did not have money I took the money, I have given back the money, but this class room has not come to the initial state, because money has come from him and has gone to him, he has to give back the money to him. This way we have to understand that heating process or a cooling process is an irreversible process.

Consider the expansion and compression of a gas. Can you tell me why it is irreversible? Because I can expand a gas from certain pressure and temperature in a piston cylinder arrangement, for example, to some pressure and temperature, lower pressure and temperature. I can again compress back the gas to reach initial pressure and temperature in which way the surroundings suffers a permanent change, can you tell in doing so?

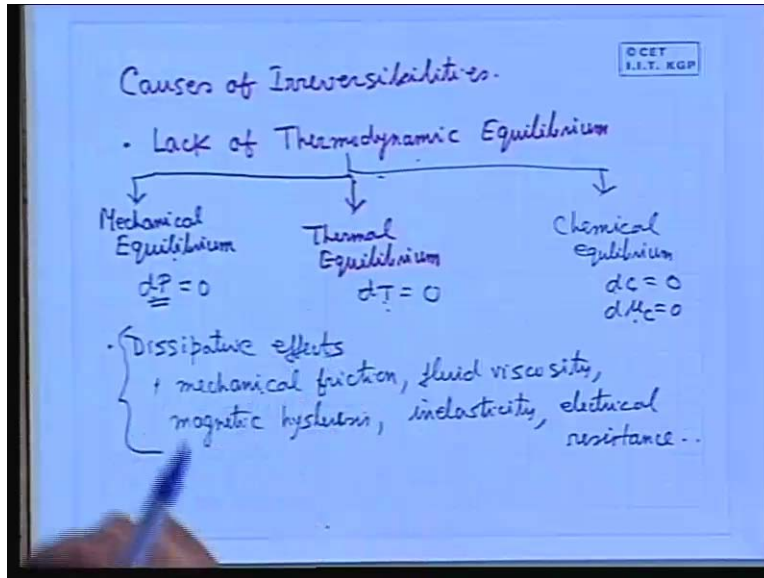
[Conversation between Student and Professor – Not audible ((00:26:50 min))]

No heat exchange, I consider an adiabatic system. Adiabatic system take some gas we expand it, you understand that temperature falls down. Then we compress the gas to a high temperature no heat interactions. I restrict the heat interactions if he tells heat interactions, he can explain through that. But if we restrict the heat interactions, I can keep make some gas within a cylinder and piston. Everything is insulated. I can expand from high temperature and pressure to a low temperature and pressure and I can again compress. The work done in these two processes will not be the same. That means work obtained in one process will not be the same. If we measure the work, if we calculate theoretically through an ideal system or reversible process, they will be the same $p dV$ work which is not the actual work.

The actual work requirement in compression is not the same as actual work obtained in the expansion process because of what? Because of the hysteresis, due to mechanical dissipative effect friction. These are the examples by which you can see that all natural processes which can be reversed back occurred in such a way that this surrounding suffers a permanent change. The

surroundings cannot come back to the initial stage before the occurrence of the process. This is the basic definition of reversible and irreversible process.

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With this in mind, Now, I write that; what are the causes of irreversible? All natural processes are irreversible processes. There are two causes; one is lack of thermodynamic equilibrium. Thermodynamic equilibrium consists of three equilibriums, one is mechanical equilibrium, another one is thermal equilibrium, and another one is chemical equilibrium.

Lack of any of these - equilibrium, mechanical equilibrium is associated with dp , thermal equilibrium is associated with dT , and chemical equilibrium is associated with concentration or chemical potential that is dc or $d\mu_c$, this is of course beyond the scope of your subject. Whenever a process occurs there is always a lack of equilibrium. What transfer has to take place? There will be a lack of pressure. That means mechanical equilibrium lack of pressure equilibrium, there is a lack of temperature equilibrium that is thermal equilibrium there has to be a temperature difference for heat transfer to take place.

Similarly, there has to be a concentration difference for a mass transfer process to take place and there has to be a chemical potential difference for a chemical reaction to take place, but when all these equilibrium that means all these things dp is 0, dT is 0, and dc is 0 that means all the

equilibrium are established and there is perfect thermodynamic equilibrium and no process will occur. Whenever there is a natural process, there is a lack of thermodynamic equilibrium, because lack of thermodynamic equilibrium initiates the natural process. This is one of the prime causes of irreversibility.

Another cause of irreversibility are dissipative effects. You know what are dissipative effects? There are different kinds of dissipative effects. Dissipative effects are always associated with all natural processes. What are those dissipative effects? Please tell me one of you.

[Conversation between Student and Professor – Not audible ((00:31:18 min))]

Mechanical friction. Very good

Please tell few other.

[Conversation between Student and Professor – Not audible ((00:31:27 min))]

Fluid viscosity, very good tell please fluid viscosity I am happy please tell.

[Conversation between Student and Professor – Not audible ((00:31:34 min))]

Magnetic hysteresis, then inelasticity, electrical resistance and so on. There are large numbers of dissipative effects associated with natural processes. They are also causes of irreversibility which means if there is no lack of thermodynamic equilibrium and there is no dissipative effect, the process will be reversible, but for all natural processes, there have to be lack of thermodynamic equilibrium and there have to be dissipative effects. Therefore, we can conclude that all natural processes are irreversible. This is because the basic requirements of the natural processes are the causes of irreversibility. Other way, the causes of irreversibilities lie in the basic requirement of natural processes. Therefore, a perfect reversible process means there is no process. We can only think of a limiting reversible process. Reversible process in limit you can think this way.

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Process	Perfectly Reversible	Reversible in the limit
Mechanical Work transfer	$\Delta P = 0$	$\Delta P \rightarrow 0$ (dP)
Heat Transfer Process	$\Delta T = 0$	$\Delta T \rightarrow 0$ (dT)
Mass Transfer	$\Delta C = 0$	$\Delta C \rightarrow 0$ (dC)
Chemical reaction	$\Delta \mu_c = 0$	$\Delta \mu_c \rightarrow 0$ ($d\mu_c$)

No dissipative Effect

That is the process perfectly reversible or ideally reversible and reversible in the limit. What it will be? If it is a mechanical work transfer process for a perfectly reversible dP is 0. There is no pressure varying. I will not write like that I will write ΔP is 0. In a reversible unit dP is very small or ΔP tending to 0.

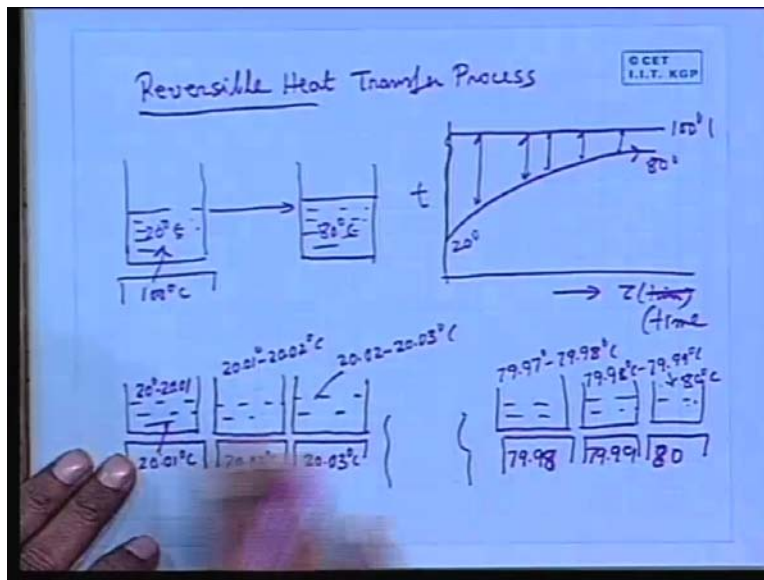
Similarly, for heat transfer process ΔT has to be 0. That is no process, perfectly reversible means no process because without a temperature difference heat cannot be transferred, but in the limiting case, when ΔT tends to 0 that is a reversible heat transfer process in the limit.

Mass transfer process, you see that ΔC is 0, there should not be any concentration gradient, but ironically without concentration gradient mass transfer is not possible. Therefore, we think of a limiting reversible mass transfer process when the mass transfer takes place and infinite small concentration gradient. This means the infinite small gradients are there that means dP , dT that means work transfer is taking place with an infinite small difference of pressure dP . Heat transfer is taking place with an infinite small difference in temperature dT . Similarly, mass transfer is taking place with an infinite small concentration difference dC (Refer Slide Time: 34:54 min). Similarly, chemical reaction $\Delta \mu_c$ is equal to 0, this of course you do not know. $\Delta \mu_c$ that is chemical potential which causes the reaction to take place that means there will be an infinite small chemical potential (Refer Slide Time: 35:16 min).

Therefore, for a reversible process, these have to be 0 and in the limit this has to be, but for all of these one thing is obviously valid, no dissipative effect. That means on the top of it, there should not be any dissipative effect plus all these equilibrium should be established (Refer Slide Time: 35: 43 min). That means no process, but in practice if you said this infinite small usually this in turn related dissipative effects also will be 0. Dissipative effects will be less because if there is a work transfer with a small pressure difference, the process will be so slow that mechanical dissipative effects, the mechanical hysteresis will be less. Similarly, if you pass current against infinites small voltage difference, the electrical hysteresis and electrical dissipation will be less. This is the conclusion for the reversible process.

Now let us take a very interesting one which will be important afterwards a reversible heat transfer process. Example of reversible heat transfer process. **How do you conceive it?**

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Let us consider a mass of water in a beaker, simple, at 20 degree Celsius and we want to heat it to 80 degree Celsius. Just like give an example with numerical figure, I heat it by placing it with 100 degree Celsius body. Let us take an arbitrary temperature 100 degree Celsius, which is higher than this 80 degree Celsius so that in some finite time, I get this result 80 degree Celsius. Then what is happening? Is this a reversible or irreversible heat transfer?

[Conversation between Student and Professor – Not audible ((00:37:24 min))]

This is irreversible, because there is always the temperature gradient. If I take it at 80 degree Celsius, for example, if I draw the temperature versus time, τ , τ is the time here. This is the source temperature remaining constant 100 degree Celsius, let us consider this body is of infinite capacity whose temperature does not change (Refer Slide Time: 37:50 min). That means it is going like this. So initially, 20 degree Celsius, it is 80 degree Celsius, it is Δt . That means the degree of irreversibility ultimately is reduced at the end of the heating process. This is the Δt . This causes the reversibility.

This is a purely reversible heat transfer. As you want to make this process faster and faster, you have to make a more and more temperature gradient so that process becomes more and more irreversible. Fastness of the process in that way is directly related to the irreversibility. The more is the process fast, more is the irreversibility. But how do you conceive a reversible heat transfer? Same thing can be done if I consider it this way, that if I consider number of reservoirs. One reservoir is 20.01 degree Celsius these may be still smaller resolution, just I gave an example.

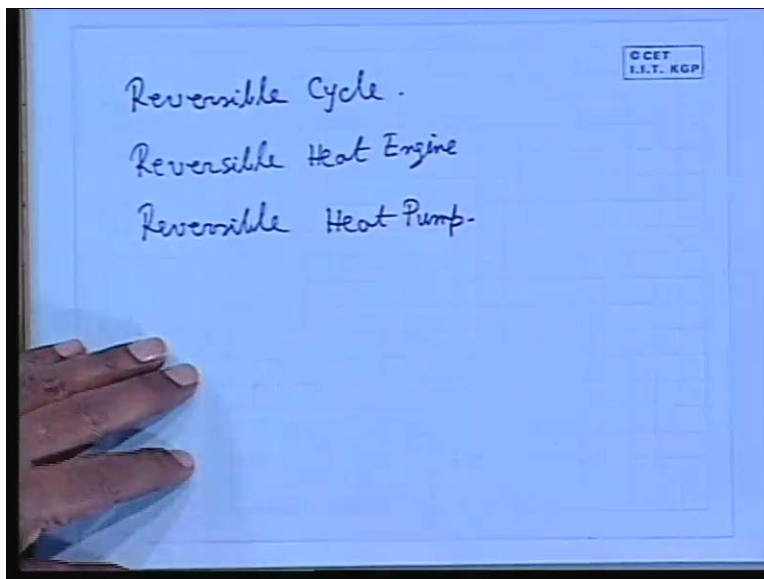
Instead of placing it directly to a reservoir of 100 degree Celsius, I do like that 20.03 degree Celsius and this way I go and ultimately I have also 3 reservoirs in this way (Refer Slide Time: 39:11 min). These are 79.98 degree Celsius, 79.99 degree Celsius, and 80 degree Celsius and what we do if we keep this system water here and we heat it from 20 degree Celsius to 20.01 degree Celsius, with an infinite small temperature difference of 0.1 degree Celsius, it will take infinite time, but this heat transfer is in the limit reversible. Then will place this, where we heat this from 20.01 degree Celsius to 20.02 degree Celsius. Again, we keep it here. These are extremely slow process until its temperature 20.02 degree Celsius to 20.03 degree Celsius (Refer Slide Time: 40:01 min).

This way, if we keep this we will see, that means here 79.97 degree Celsius (Refer Slide Time: 40:11 min) because earlier reservoir it was to 79.97 degree Celsius to 79.98 degree Celsius. Here also 79.98 degree Celsius to 79.99 degree Celsius and finally here it will attain 79.99 degree Celsius to 80 degree Celsius. So that, this way if we think of an infinite number of reservoirs with small temperature differences and we always keep the system with all reservoirs for an infinite small amount of temperature rise, then we can conceive of a heat transfer process which

is infinitely slow, but with an infinite small temperature gradient. So, that is in the limit a reversible heat transfer which is very important afterwards in the analysis of cycle it will come. How we can conceive a reversible heat transfer when the temperature of the system varying?

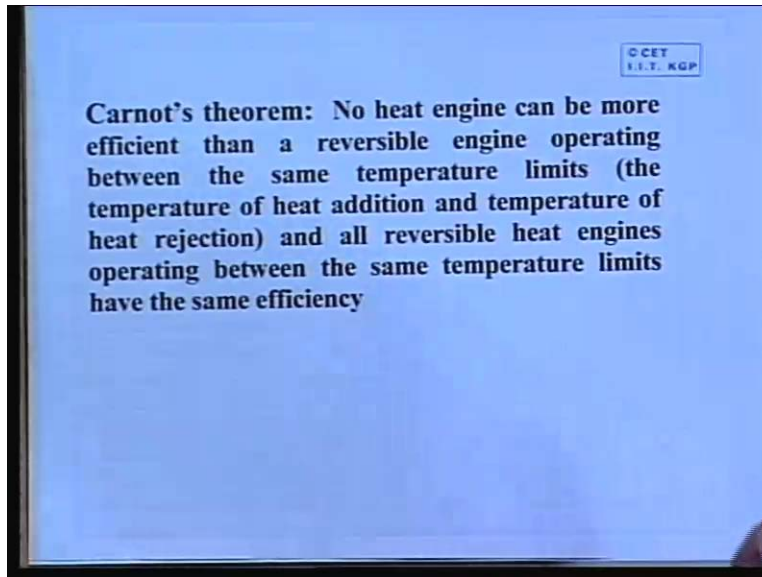
So, with this, I can conclude this understanding of reversible process. What are the causes of irreversibilities? And under what condition a reversible process can be conceived? Actually, that condition leads us that there should not be any process, but in the limit we can have a reversible process when the equilibrium is very small. That means a very infinite small departure from the equilibrium - thermodynamic equilibrium - and at the same time dissipative effects are small. After this, I will come to a very important statement of Carnot's. Before that, I will tell what is a reversible heat engine, which is very important.

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A reversible heat engine and reversible cycle, obviously, by common sense, one can define reversible cycle. Cycle means series of processes so that initial state and final states are same. A reversible cycle is a cycle, where all the processes are reversible. That means if any one of the processes becomes irreversible, the cycle is irreversible. A heat engine or a heat pump both operating on a reversible cycle are called reversible heat engine or reversible heat pump. **So simple.** With this in mind, we will go to a very important theorem or corollary of the second law. This is probably the most important corollary of the second law.

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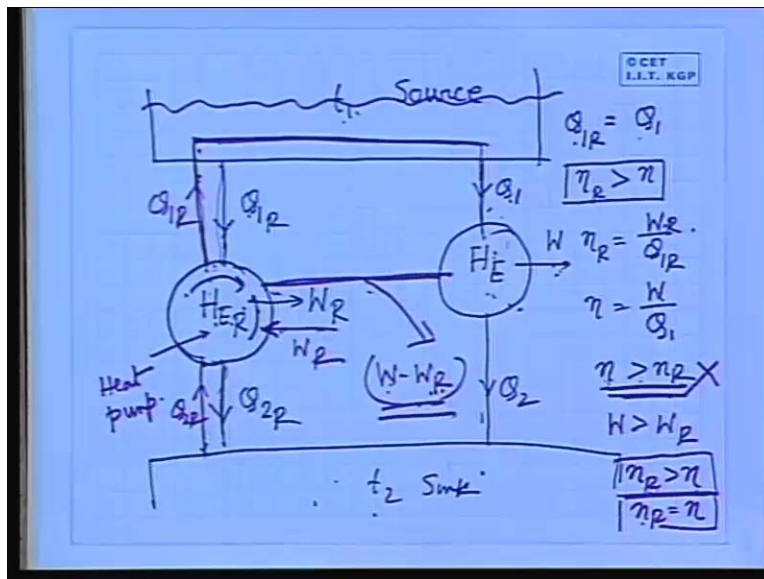


After that, the entropy will come, that is known as Carnot's theorem. He is the man who is the inventor of the second law. Carnot's theorem: No heat engine can be more efficient than a reversible engine operating between the same temperature limits. It may appear very simple, common sense, but it is not, so it has to be proved logically. He was the first man who proved it logically. Between the same temperature limits, what do you mean by temperature limits? That is temperature of heat addition and temperature of heat rejection. That means, if you make the temperature of heat addition and temperature of heat rejection same, then if you operate a reversible engine and irreversible engine, the reversible engine will always be having the higher efficiency than an irreversible or a natural engine.

All natural engines are irreversible engines because all natural processes are irreversible processes. At the same time, the second part of it and all reversible heat engines operating between the same temperature limits have the same efficiency. What does it mean? That means if the two temperatures are fixed and we operate different engines, but all reversible, their design is different, their fluid is different, the system is different, working fluid or working system, but all are reversible heat engine. Then they yield a unique efficiency when the two temperature labels are fixed. All reversible heat engines yield a unique efficiency, but on the other hand, if you fix these same two temperatures limits and operate number of irreversible or natural heat engines they will yield different efficiencies. That is the beauty. They will not yield same efficiency, but

even the maximum of these efficiencies is lower than the efficiency given by all reversible heat engines. Do you understand? That means efficiency of all reversible heat engines will be the same and that will impose a maximum value on the efficiency of all the irreversible engines. That, all irreversible engines can never attain these values. Their values will be different, but their maximum also will not be equal to the efficiency of a reversible engine. This is the basic understanding of this Carnot's theorem. Let us prove this Carnot's theorem.

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Let us consider a source t_1 , source you know thermal reservoir at high temperature which is fixed if you take heat of infinite capacity. Afterwards, for our convenience, we take a constant temperature source. Afterwards we will think that even if this temperature may vary that means, heat engine may interact with the bodies of finite capacities. That means heat is extracted the temperature of the bodies that source also changes. That will come afterwards; in that case, the mean temperature of heat addition and rejection will come. But now, we will assume that temperature of heat addition and rejection remains the same. That means the source and sink there by their literal meaning their source that means, even if they transfer heat, the temperature remains the same, even if they take heat, the temperature remains the same.

We consider a heat engine. One is a reversible heat engine, H_{ER} . t_2 is the sink and another one we consider is an irreversible heat engine. I just designate at H_E and for this analyses, what we do?

We just set the heat addition by the reversible engine, Q_{1R} , and heat addition or heat taken by the irreversible engine, Q_1 is same. That means we put first this for this proof we first use the equation Q_{1R} is equal to Q_1 . That means, as if they are taking the same heat, there is no problem in it. Because we know, that work delivered, heat added and heat rejected out of these three (Refer Slide Time: 47:24 min), two are independent, one is automatically fixed. Do you understand?

So, out of these two, I can set one Q_1 for both the cases, heat addition to be same. In that case, what will happen? H_{ER} will be W_R and H_E will be ordinary W . Heat rejected will be different, because they are different engines. If we keep this one (Refer Slide Time: 47:49 min), the efficiency will be different. So that heat rejected is Q_{2R} for reversible engine and Q_2 for ordinary engine. Now, what we have to prove? We have to prove the thermal efficiency of this is greater than what? This we have to prove. What is the definition of η_R ? That is W_R by Q_{1R} . What is the definition for η_E ? The same definition, what is the expression? η is equal to W by Q_1 . Well, so I have to prove that W_R is greater than W .

[Conversation between Students and Professor – Not audible ((00:48:21 min))]

We assume the reverse, that η is greater than η_R . We assume this first. Now we see the concept lies here. We reverse the reversible heat engine. It is very important concept. We can reverse the irreversible heat engine also and it will operate. Because I told you, reverse direction a cycle can operate a process can operate, but what is the difference? If it is a reversible process, if it is reverse the surrounding will be the same. That means it will produce the exactly identical opposite effect to the surrounding. Similar is the case for the cycle also. That means if I reverse this one, H_{ER} , then what will happen? Just let this is acting as a heat pump. Now I reverse this. That means this is the cycle, I reverse the cycle use it to act as a heat pump (Refer Slide Time: 49:25 min). What it will do? In that case, take the same heat Q_{2R} and will give this same heat Q_{1R} and it will demand the same W_R , why?

Because it is a reversible cycle, reversible heat engine, so that surrounding coming to the same condition. That means the identically opposite effect it will give to the surrounding. Just I told, if the expansion and compression any of the processes could have been reversible, in that case what will happen? Work given and work taken will be the same similar is the case. That means if we

make this reversible heat engine to operate in a reverse direction as a heat pump, it will take W_R , and Q_{2R} and it will deliver Q_{1R} . That means we can tell this way that for the same W_R input and same Q_{2R} taken from here it will deliver the same Q_{1R} .

Now, if this Q_{1R} I can give to heat (Refer Slide Time: 50:32 min), because this heat engine, H_E once Q_1 which is equal to Q_{1R} , So, this source, t_1 , is redundant, is not required. That means the system here, H_{ER} will act as a source for H_E that means I can link these. Because, this Q_{1R} which is elevated from H_{ER} , that will be given to this heat engine, H_E . That means the system of this heat engine, H_E , will act as a source to the H_{ER} , where the heat to high temperature reservoir heat will be given. Since I have assumed this, η greater than η_R means W is greater than W_R . That means I am getting a work which is more than this requirement that means I can link this H_E and H_{ER} and I get an additional amount of work W minus W_R .

[Conversation between Student and Professor – Not audible ((00:51:21 min))]

Again, I am telling if I reverse this H_{ER} back, then it will take W_R amount of work to take Q_{2R} from the sink, t_2 , and to deliver Q_{1R} to this t_1 temperature, t_2 to t_1 . It requires the Q_1 is equal to Q_{1R} that means, I can link H_{ER} to H_E , this heat, Q_{1R} is given to the heat engine, H_E .

When W is more than W_R a part of W can be given to H_{ER} to drive this heat pump. Till then we are getting some work W minus W_R . That means the equivalent system is a system which delivers continues work by operating with a single fixed temperature which is the violation of Kelvin-Planck statement, therefore it is not correct that means this assumption, η is greater than η_R , is wrong.

[Conversation between Student and Professor – Not audible ((00:52:18 min))]

What is the last part?

[Conversation between Student and Professor – Not audible ((00:52:21 min))]

Because W is more than W_R because we have assumed η is greater than η_R , which means W is greater than W_R . That means some part of the W can be used to drive H_{ER} , try to understand logically, that means, still W minus W_R amount of work is available. The equivalent system is a system which develops work W minus W_R by exchanging heat with only bodies at single fixed

temperature (Refer Slide Time: 52:44 min). That means the η cannot be greater than η_R , what are the options? η_R is greater than η or η_R is equal to η .

Now, η_R cannot be equal to η , if η_R is equal to η , that means what happens these two engines, H_{E_R} and H_E , are identical. That means H_E will be also a reversible engine, which start with the proposition that H_E is not same as H_{E_R} . This has to be different, there is the logic. So that mathematically only this solution, η_R is greater than η , is correct. Therefore, the efficiency of a reversible engine is more than that of an irreversible engine.

Any difficulty in understanding? Please tell me. Final logic is that, η_R is greater than η . That means, the efficiency of a reversible engine is more than that of an irreversible engine, if they are working under the same temperature limits.

[Conversation between Student and Professor – Not audible ((00:53:44 min))]

Because these are the two same engine if η_R is equal to η that means Q_{1R} , Q_{2R} , Q_1 , and Q_2 they give the same work, so interchangeability of heat and work are the same, then they are the identical machines.

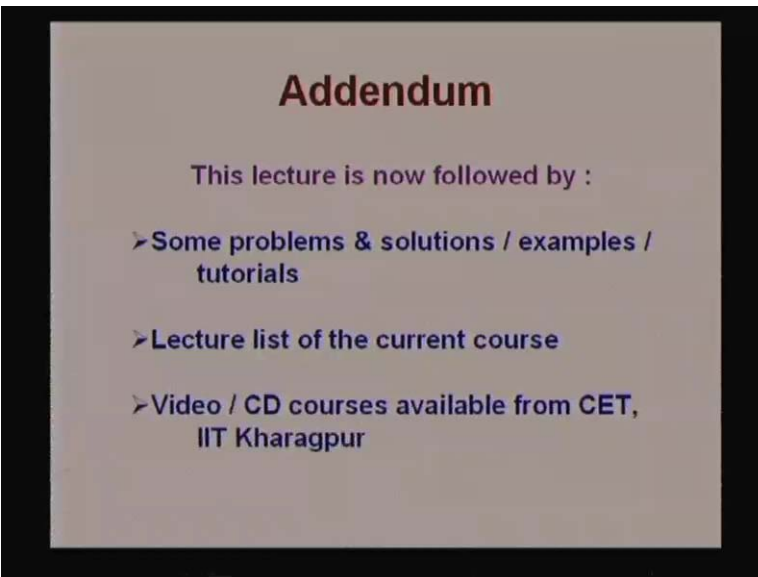
[Conversation between Student and Professor – Not audible ((00:53:57 min))]

The reversible engines and irreversible engines are different. Do you understand? That if an engine gives the same work with the same addition of heat and accordingly the same rejection of heat that means that the two engines are identical. That means one is the reversible, other one also has to be a reversible. Do you understand? This is the logic that two cannot be equal that means this has to be different. Otherwise, they are same. When we will prove the next class the same logic, I will give that the two reversible engines have the same efficiency. That if you reverse the one this cannot be greater than this, you reverse another one this cannot be greater than that. Is it clear? It cannot be equal, this is a good question I understand if they two equal there is no proof that means we start with the identical engines which take same heat, develop the same one their efficiencies are same. The basic assumption is that an irreversible engine and reversible engines are different engines means that their thermal efficiencies are different.

Only two possibilities are there, either greater than or less than. If they are equal that means they are same. That means they are either irreversible engines or reversible engines. In case of two irreversible engines, they are identical engines giving the same efficiency.

Thank you.

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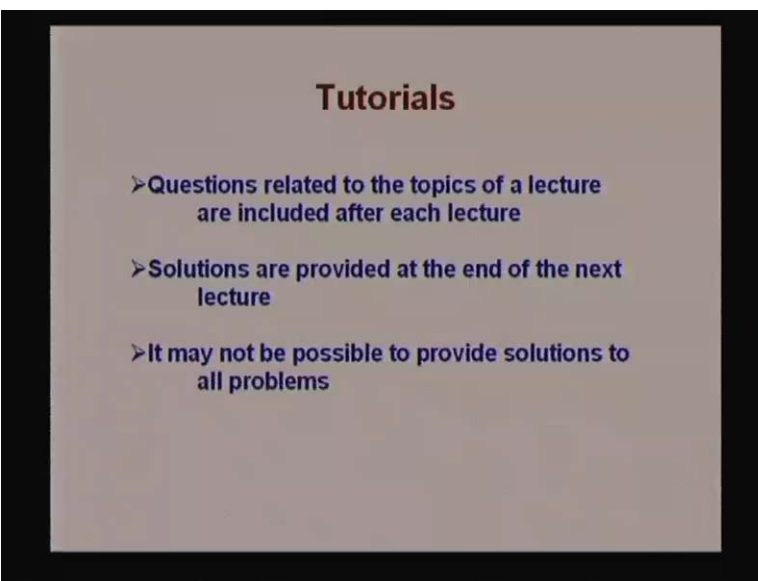


Addendum

This lecture is now followed by :

- Some problems & solutions / examples / tutorials
- Lecture list of the current course
- Video / CD courses available from CET, IIT Kharagpur

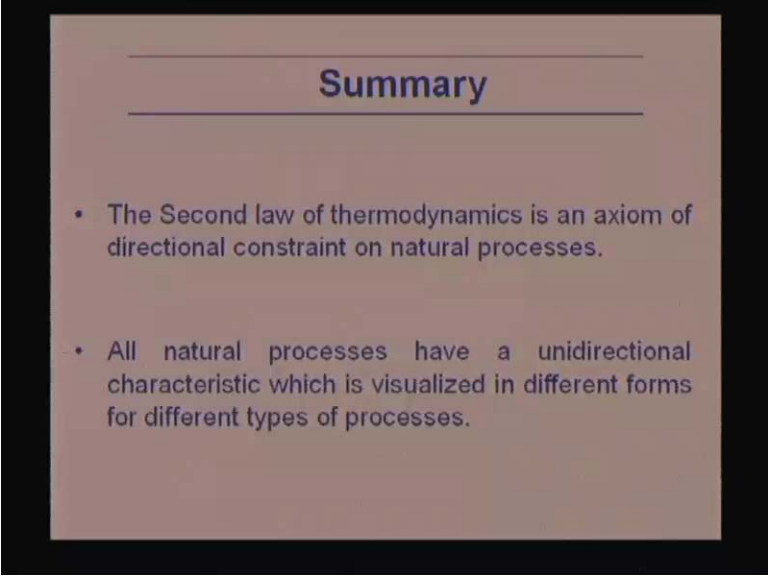
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Tutorials

- Questions related to the topics of a lecture are included after each lecture
- Solutions are provided at the end of the next lecture
- It may not be possible to provide solutions to all problems

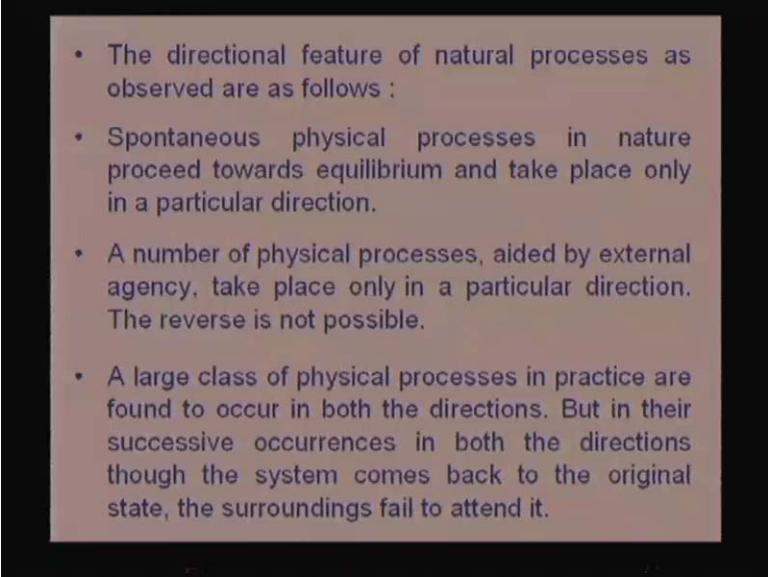
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The slide is titled "Summary" and is enclosed in a black border. It contains two bullet points:

- The Second law of thermodynamics is an axiom of directional constraint on natural processes.
- All natural processes have a unidirectional characteristic which is visualized in different forms for different types of processes.

(Refer Slide Time: 56:15)



The slide contains four bullet points:

- The directional feature of natural processes as observed are as follows :
- Spontaneous physical processes in nature proceed towards equilibrium and take place only in a particular direction.
- A number of physical processes, aided by external agency, take place only in a particular direction. The reverse is not possible.
- A large class of physical processes in practice are found to occur in both the directions. But in their successive occurrences in both the directions though the system comes back to the original state, the surroundings fail to attend it.

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- There are two classical statements of second law in relation to the interchangeability of heat and work.
- Kelvin-Planck Statement : No process is possible whose sole result is the absorption of heat from a reservoir of single fixed temperature and the conversion of this heat into work in a cyclic process.
- Clausi's Statement : It is impossible for any device to operate in a cycle so that the sole effect is the transfer of heat from one body to another body at a higher temperature.

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- A process is said to be reversible one, if it is performed in such a way that, at the conclusion of the process, both the system and the surroundings may be restored to their initial states without any change in the rest of the universe.
- All natural processes fail to fulfill the above requirement, and hence they are irreversible processes.

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- The causes of irreversibilities lie in the basic requirements for the natural processes to occur and can be divided into two main categories :
 - (i) Lack of thermodynamic equilibrium.
 - (ii) Dissipative effects.
- A reversible process is a theoretical concept.
- An extremely slow process associated with an infinitesimal departure from thermodynamic equilibrium and being almost free from any dissipative effect, approximate to a reversible process in reality. The process is known as quasi-static or quasi-equilibrium process.

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- A heat engine is a device or system which operates on a thermodynamic cycle so that there is a net heat transfer to the system and net work transfer from the system.
- A heat pump or refrigerator is a system which operates on a thermodynamic cycle so that there is a net work transfer to the system and net heat transfer from the system.

(Refer Slide Time: 58:32)

- No heat engine, operating in a thermodynamic cycle between two constant temperature heat reservoirs, can be more efficient than a reversible engine operating between the same two reservoirs. This is known as Carnot's theorem.
- A straight forward corollary of the Carnot's theorem is that the thermal efficiencies of all reversible engines operating between two fixed constant temperature heat reservoirs are equal.

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- Answers of the Review Questions given at the end of Lec. No. 5**
- (Answers to objective / short Questions are only given.
Answers to routine descriptive Questions are omitted)
-
2. When the system is in a state of thermodynamics equilibrium.
 5. (i) Two; (ii) One; (iii) Zero;
 10. The process should be (i) extremely slow with an infinitesimal departure from thermodynamic equilibrium and (ii) almost free from any dissipative effect.
 13. When there is only displacement of system boundary in a quasi-equilibrium process.

(Refer Slide Time: 56:26)

14. Irreversible work.
16. Energy.
17. Internal energy.
18. $\delta Q = dE + \delta W$: for any process
 $\delta Q = dE + p dV$: for a process executed by a closed system with only displacement work in a quasi-equilibrium path
 $\delta Q = dU + \delta W$: for a stationary closed system
21. Extensive property.
22. Not explicitly but implicitly.