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Course
on
Laws of Thermodynamics

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Lecture 13: Second Law and its Corollaries (Part II)

Good afternoon and I welcome you all to this lecture section of the course laws of thermodynamics, now last class we discussed the Kelvin plant statement and Corollaries statement to formal statement of second law of thermodynamics, from the prospective of mechanical engineering and we show that the equivalence of the two statement that means the one statement is invalid then other statement is automatically invalid.

The we shown this in the case that Kelvin plant statement is invalid if we consider then we have seen that the collision statement is also invalid and vice versa the other one left to you as an exercise or you see in any book, now today we will start a very important concept which is known as reversible process.

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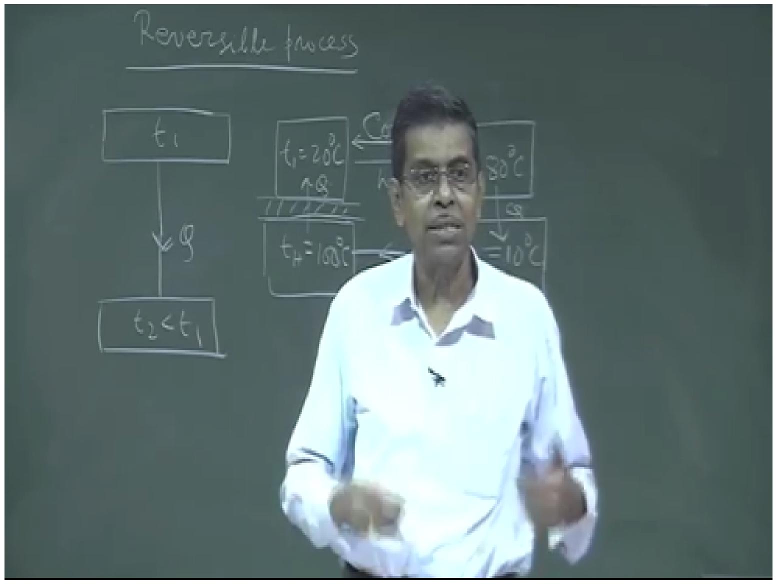

What is a reversible process by definition initially told you the directional constant that some process are unidirectional in nature they cannot be brought back in the other way, they cannot be made to occur in another way other way that means it occurs only in one way not the reverse one, the reverse one takes place apparently it means those process switch by it is just definition in this mean is reversible.

That means the process which can be which can take place in both the ways and the process which cannot take place in both the ways that means it take place in one way or one direction that is irreversible process no that is not the correct I told you earlier that there is some permanent change in the surroundings when a process takes place a system from initial state to final state and the back the reveres of the process that means from the final state to initial state there is some change in the permanent change in the surrounding and that gives rise to the concept of a revisable process you understand.

So therefore revisable process by it is formal statement you can tell like that a revisable process is that process if at the conclusion of the process are formed by a system going from 1 state initial state to the another final state the process is reverse back okay so that this system is brought back to it is initial state the surrounding cannot come to the initial state or the initial state surrounding cannot come to the initial state this is for all natural process if we can consider a process which after it is conclusion from 1 state to other state is brought back in the reverse way.

To comer to the initial position and surroundings also comes to initial position that process is known as reversible process that means we can restore both the system and surrounding at their initial condition or initial state by occurring the process by making the process to occur in direction form 1 state to other state and reverse back from the final state to initial state in such a way that surrounding does not suffer any permanent change that means surrounding also comes to it is initial state.

That process is known as reversible process but unfortunately all process in nature are reversible they are all irreversible process now I tell you one example which told earlier that with respect to heat transfer process you see that if we consider heat transfer natural case heat transfer t1 to t2 where t2 is ≤t1 heat transfer takes place but the reverse is not possible that means this the natural process which occurs in one direction this way it is reversible but if we consider this one that a body let us consider at a temperature t1 that 20^0 C.

For better understanding is heated finite body to a temperature of 80^0 C this heating and if it is clod again cooling from 80^0C to 20^0C system come back to initial state that mean this process of heating is not a unidirectional process the cooling is also possible but how does system surrounding gets a formulate surrounding cannot come to the initial state let us consider this that to heat it from 200 to 800C we have to put it, keep it in contact with the hot body th whose temperature should be either 800C or > than 800C if you keep it at 800C then heat transfer at the end will be very slow with the temperature will be close to 800C the rate of interest for will be so.

Because of infinite small temperature difference so therefore for a natural process to occur to within a infinite time , we take this th > 80^0 that 10^0C and they are put into contact thermal contact by a the thermic one then if takes it okay and goes to 800 oh in this 800C body is cool that means the reversible process to reveled back to 200C we take a body, let take this tl lower temperature body which is equal to 100C and it gives takes heat from the body and cool it to 200C then you see though this system at the initial state.

But surrounding what is happen, the surrounding as given heat from his source at 100^0C that means from a thermal deserver that 1000C and he has got the heat back to his thermal reserve and 10^0C and this one is surrounding is not at the identical condition which it had initially no it has they will heat from one part of this surrounding one reserves and taken it in another preserver so if you want to make this surrounding to the initial state, that mean to restore this surrounding to its initial state then we have to get back these heat.

Where from it was given this all this surrounding and this is another part of the surrounding we together differ this surroundings that if we can get this heat to this body, then surrounding will come to the initial state but this is not possible this is the cross statement without any other external line we cannot do it. We can do it by the help of a heat pump or refrigerator that we have to take one that is surroundings of final will change, so therefore these so surroundings offers a permanent change.

Similar way I tell you that if you have cylinder in piston then if you compress the air and forms some pressure and temperature to a high pressure and temperature and then expanding and if you come back to the initial state, after compression then expansion then the compression process is any reversible process why or other way if first expansion then compression, so that expansion followed by compression or compression followed by expansion so that the initial state is less to but in that case also surroundings offers in permanent change that in actual case the work delivered in case of expansion and.

Work required or given in case of compression this is because of mechanical histories due to friction and other deceptive effects, so therefore this way all natural process is when they come back when the natural process is in a system changes from 1 state to other state is made to occur in the river so it for the system to restore the initial position, initial state rather then this surroundings offers say permanently change the surroundings state is permanently change, so this way we define that all the natural process is the irreversible.

If we can make the process reversible then this is possible because the definition of reversible process is that after the conclusion of a process if it is reversed back.

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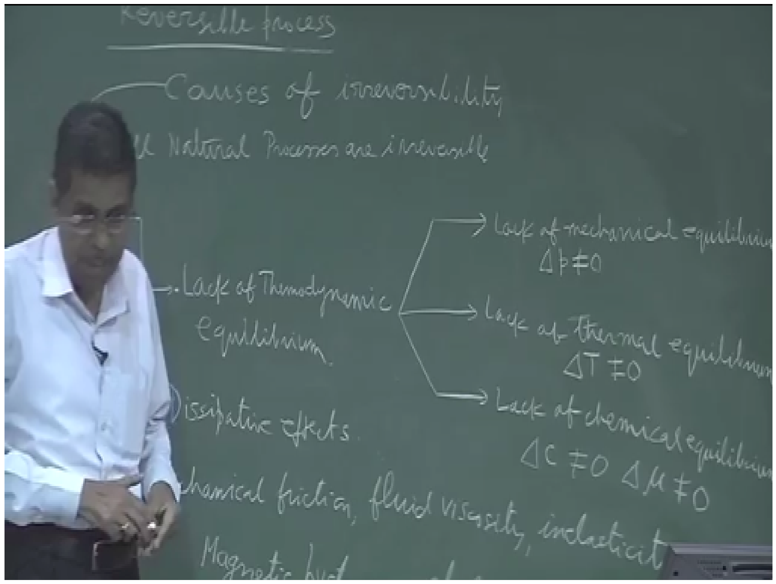

Both the system and surrounding can be raised to its initial state but this may ever happens that I will show you that causes now why it does not happen causes so therefore we must know causes of reverse all natural process are irreversible process irreversibility causes of irreversibility now causes of irreversibility all natural irreversible process are irreversible process, process are irreversible now this causes of irreversibility here is the lack of thermodynamic equilibrium you have already come to know what is thermodynamic equilibrium lack of thermodynamic equilibrium and this thermodynamic equilibrium consists of mechanical equilibrium so therefore lack of mechanical equilibrium, lack of thermal equilibrium 3 equilibrium consists the thermodynamic equilibrium.

That you have already read we have discuss it earlier and lack of chemical equilibrium, now lack of mechanical equilibrium happens when ΔP not equal to 0, in case of mechanical equilibrium ΔP is 0 there is no pressure difference between the system and the surroundings and the mechanical work is delivered in that way that there is no dis-balance force acting on this system so ΔP has to be 0 for mechanical equilibrium to be achieved.

But ΔP not 0 is the lack of mechanical equilibrium departure from mechanical equilibrium, similarly the thermal equilibrium demands ΔT should be 0 but ΔT not 0 is the lack of thermal equilibrium by virtue of which the system transfer heat to the surrounding by virtue of which system transfers work that means interacts work with the surrounding interacts in terms of heat transfer with the surrounding.

Similarly lack of chemical equilibrium is concentration difference is not 0 or chemical potential which is responsible for chemical reaction this is responsible for mass transfer they are not 0 but if all ΔP, ΔT, ΔC, $\Delta\mu$ as 0 the system is in thermo dynamic equilibrium does it interact with the surrounding in terms of either work transfer, heat transfer, mass transfer or chemical reaction.

So therefore for a reversible process this has to be 0 so these are the causes of irreversibility with it departs from the 0 value there has to be some pressure difference there has to be some temperature difference there has to be some ΔC $\Delta\mu$ for irreversibility to be there for the existence of the irreversibility. So one is lack of thermo dynamic equilibrium another is the dissipative effects.

Dissipative effects are like this under this heading dissipative effects we have mechanical friction we have mechanical friction you know these are the dissipative effect fluid viscosity these are innovative lymph practice fluid viscosity inelasticity then magnetic hysteresis, electrical resistance all these things are dissipative effect then in any process for example in mechanical movement of piston and cylinder.

This is there is mechanical friction fluid viscosity appears inelasticity if you stretch aware magnetic hysteresis in magnetic work transpose in electric resistance electric one work transpose and the effect this all dissipative effects basic purpose is same what they do they convert the mechanical energy or the work mechanical work electric work all constitutes the work in thermodynamics into inter molecular energy.
By which the system becomes hot so therefore this is known as dissipative effect they dissipate the energy and why the term dissipation is there I will tell you afterwards that mechanical energy or work they are organized form of work and energy from the molecular point of view where the inter molecular energy is disorganized form of energy, and these are called as low grade energy that is high grade energy, and already we have seen earlier that heat cannot be converted completely into the work.

But work can be converted completely into the heat in a heat compound refrigerator, so that is another we define high grade and low grade energy that means work or mechanical energy is high grade energy which is being transferred to the intermolecular energy by all this agents they are the agents and they are always present in any process and they are known as dissipative effects.

So this way we see that the thermodynamic equilibrium is distorted and the dissipative effects all together calls make the system the, possess irreversible. Now what happen that means irreversibility if we have to have a reversible process, P1 is reversible then this has to be 0 ΔP is 0, ΔT is 0, ΔC is 0 Δμ is 0 that means there is no process at all, because they are the motive forces for the process and obviously there will be no dissipative effect that means if you occur any, even a process is occurred if you make to occur any process then automatically there will be thermodynamic lack of thermodynamic equilibrium.

Therefore, this statement is very important the irreversibility of any natural process lies in it is basic requirement for the process to occur, so therefore without any if there is no process without any lack of equilibrium that means for complete thermodynamic equilibrium system is at rest and there will be no dissipative effects, so therefore Po reversible process actual reversible process pure reversible process can never occur.

But we can think of some process which is close to reversible process what are those let me see, close to reversible process so from this concept we can think of process close to reversible process why if we have the process where thermodynamic equilibrium departure is infinite small, that means for process.

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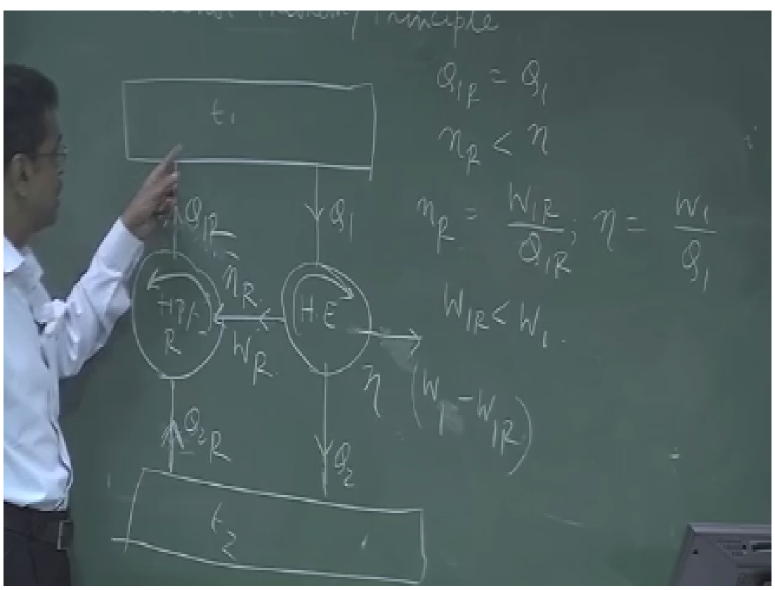

For any process where ΔP tends to 0 is very small, ΔT tends to 0 very small, ΔC tends to 0, Δμ tends to 0 and dissipative effect if it is tends to 0, now when this we will tend to 0 the process will be extremely slow heat transfer under infinite small temperature differences is extremely slow, what transfer under any infinite work pressure difference, mass transfer under the infinite small concentration differ, chemical reaction under infinite small chemical potential difference are extremely slow and obviously dissipative effects will tend to 0.

This process is known as Quasi reversible or Quasi static process and another condition is that when this process will take place and that very small that means with the process takes place in such a way that there is an infinite small thermodynamic potential, thermodynamic equilibrium or if there is a infinite small departures from thermodynamic equilibrium and process is extremely small and each and every state the process is in thermodynamic equilibrium, that means for example if we expand the gash with a very small ΔP from a high pressure to low pressure, first you expand from a high pressure to a very small ΔP difference, very close to the high pressure then we keep the gash at rest for some time.

Well, so that the it comes to thermal equilibrium then again we expand to another lower pressure which is very close to the initial pressure, very slowly and then at rest for some time so that it attends a thermodynamic equilibrium, that means the process should pass through all thermodynamic equilibrium states and it is extremely slow and takes place under infinite small potential difference either ΔP, ΔT, ΔC, Δμ this is like that. If I walk like that it is an irreversible process, but if I walk like this that is slowly and take rest for some time thermodynamic equilibrium exist within me, thermodynamic equilibrium exist so this is a reversible process.

But reversible process is extremely slow so that from one state to other state reaching the one state to other state reaching one state to other state exist some state in finite time so this is known as quasi reversible process now this can be explained in terms of the heat transfer let us explain that there are there is a t1 temperature if you have to make it is a thermal reservoir source if you have to make a reversible heat transfer to a body then this body temperature should be t1 – dt, small difference where dt is extremely small that means infinite small temperature difference heat transfer is the reversible heat transfer.

Or you can take that some t2 t2 + other way you can show that heat is transfer from a body at t2 to t2 + dt that means the heat has to be transfer when infinite small temperature difference. Now we earlier consider that 20^0 C body was heated to 80^0 C and what do we did we first took it a body of 100^0 which is more than 80^0 to $20^{0,}$ so that in a finite time heated it is heated to 80^0 C that is heating process.

And similarly if you cool replace a body at 10^0 C and allow the heat to flow from here and it will come in your finite time 20^0 this is irreversible process we are seen because the surrounding does not come its initial state after cooling but now if w make a reversible heat transfer this is the reversible heat transfer but here the body is are at same temperature t1, t1 – dt t2 there the thermal reversible source and sink finite its capacity infinite it capacity but her the body is a finite heat capacity heating process that 20 to 80 in that case we can achieve the reversible heat transfer if we consider in number of reservoirs with the very small difference 0.01^0 C20 20.01 20.02 20.03 like that in infinite number of reservoirs like 79.01 difference 99 then last two is like that 80^0 C.

So if you consider this infinite number of reservoirs with 0.01^0 C differences then we just take arbitrarily and finally to 80^0 and you first make this system to come to this contact so that it will be heated extremely slowly with the temperature difference of 0.01^0 C that means which is a limiting reversible process or quasi reversible process they leave it in case quasi static process because the process is extremely slow when it reaches 20.01.

Then you wait for sometime so that entire system assumes a uniform temperature of 20.01then you keep it in contact to it 20.02 reservoir it is heated that means I am doing full wrong so it is heat is going so that it is heated top 20.02 then you bring this here 20.when it reaches 20.02 we bring it here so that always what we do 20 to 20.01 take some time so that it reaches uniform temperature then with the reservoir at 20.02 then we reaches 20.02 with the reservoir at 20.03 so that it guess 20.03 and finally it gets 80^0 form this 79.9 then 80^0 okay that means here the body you will attend 79.9^0 C then it is 80^0 C.

Which means that allow is the heat transfer take place with any finite small temperature difference is not that initially I put 100^0C huge temperature difference initially temperature difference very large irreversible is very high, finally it goes down but still when it goes to 80° still there is an irreversible because the heat transfer takes place with the temperature differences of 20° but here always heat transfer takes place with varying infinite small temperature. If you can reduce it into 0.001 differences then more number of irreversible are there that you can conceive the infinite number of reservoirs it very small resolution with the temperature difference and always keep the body to contact to reservoirs successively.

So that hit transfers takes place under infinite small temperature difference these way you can get reversible hit transfer okay reversible hitting process because if you cool this thing similarly you will pass through this infinite number of reservoir successive from another direction so that the surroundings will get the hit back from where it get the hit and from which reservoir it get the hit so it will get back.

So therefore you think over it and you will see that we concentrate reversible hit transfer process similarly a reversible expansion and compression process mechanical what done I have told that already so this is precisely the concept of reversible process which can never be achieved in practice theoretical reversible process but it can be achieve in the limiting case that is quasi reversible process or quasi-static process when the departure can come into a equilibrium its extremely small and the process is excessive slow process to the number of equilibrium states.

Now we will come to very important theorem known as Carnot theorem but sometimes people tell this is probably the most important we have in second law and from which the other deductions take place to give bath to other corollaries so this is what let us see here the Carnot's theorem or Carnot principle.

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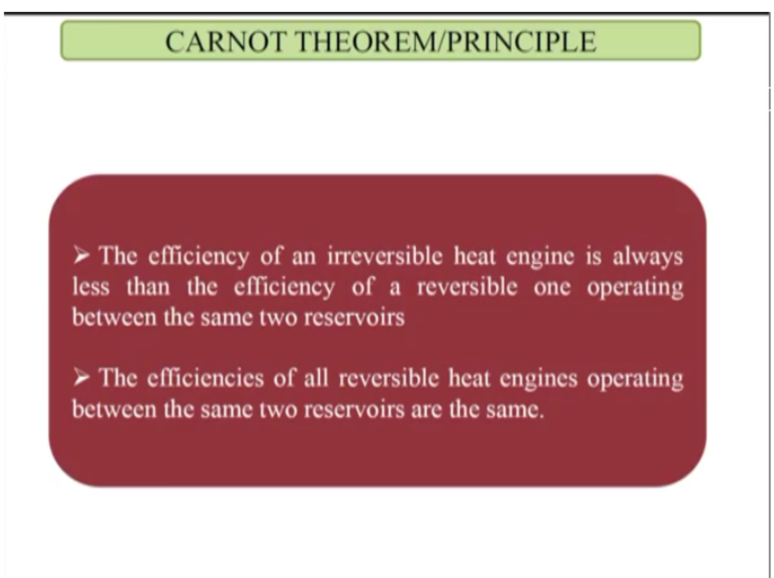

There are two statements say for it the Carnot's theorem or principle the efficiency of an irreversible het engine is always less than the efficiency of reversible one that means reversible heat engine operating between the same two reservoirs similarly the efficiencies of all reversible heat engines operating between the same two reservoirs are the same.

Again I m telling the efficiency of an irreversible het engine is always less than the efficiency of reversible one that means reversible heat engine operating between the same two reservoirs and another one is that the efficiencies of all reversible heat engines operating between the same two reservoirs are the same.

Now let me proof this one okay let me prove this one let us consider a heat source at temperature t_1 one is a reversible heat engine and another it takes heat let us consider Q_1 and rejects $Q2_R$ to a sink t_2 let us have a sink t_2 and develops W_R then we consider we have another heat engine which is not reversible it takes heat Q_1 and Q_2 they are all different.

Now by reversible het engine we mean that heating in the working system operates in thermodynamics cycle now thermodynamics cycle is composed of number of process such that the initial study equal to final state and then all the process are reversible processes that constitute reversible cycle and heat engine which operates on a reversible cycle is known as reversibility engine.

And if any process of the thermodynamics cycle is irreversible so this is an irreversibility engine now let us first consider that Q_{1R} to prove that Q_1 why because this Q_{1R} minus Q_2 are W_R for conservation of energy so here also Q_1-Q_2 is W that means that is minus rejected in work done in this equation two are independent one is dependent that means Q_1 and Q_2 are fixed.

So therefore if two are independent out of this two anyone we can choose as for our choice so this is the logic for which we consider $Q1_R$ is Q_1 so according to this is heat engine and this is for reversible according to Carnot's that η R is greater than η n but who is first start to it we will show this is not possible is less than η R is W1/Q1 for this η W1/Q1 are in same then if we consider this η then W1R is less than W1.

If we consider η this Carnot's Theorem we do not accept that is W1R is less than W1 whart we consider what we do now here we just reverse this heat engine in the opposite direction and you draw another figure here that I am doing like this I have this opportunity to heat pump refrigerator reverse.

Now since this is the reversible heat engine operating on a reversible cyclic if we reverse all the process, then the surrounding will come to the initial state that means it will resemble the same magnitude of the heat transfer but in the opposite direction. That means it will take Q_2 R heat from the sink and gives Q_nR heat to the source taking WR, your requirement will be here for the heat pump the direction is changed, this will be same, the heat will be pumped to the source but not taken from the source then the magnitude will be same.

Similarly heat will be taken from the sink not rejected to the sink to the operational heat pump or refrigerator magnitude will be same because this is a reversible heat engine. This cannot be done like that, this could be made to operate in the reverse direction but these quantities will be changed. Now if we make this reversible heat engine or refrigerator has a reversible heat pump reversible heat engine to a reversible heat pump or refrigerator.

Now since W_1 are less than W_I leave this and still I get W_{1R} – sorry $W_1 - W_{1R}$ amount of work. W_1 is the work by the reversible engine, that means since this irreversible engine work is more than reversible engine work because we consider $\eta < \eta$, so therefore this less, so the part your work is taken, so that we get heat amount of work W_1. Now you see this Q_1R and this gives heat to this thermal deserver or source and from the same source Q_1 it takes heat, there is no need of t_1 this reservoir.

Why? Simply we can eliminate the reservoir and can join these two that means you are working through t_1 we will act as this same, where the heat will be given by the heat pump and the working fluid here, where from it will take heat as this source for this heat engine. So therefore since this Q_1R and they are taken from the same temperature, so they can be linked like this, so the working fluid of this will act as the source for this and the working fluid of these act as sink for this heat pump.

That means what happen? The combined assisted highlights the Kelvin plank statement, that means it interacts with single fixed reservoir and develop the net amount of $W_1 - W_{1R}$. This is not acceptable by the law of nature, the 2nd law which is Kelvin Planck statement, so therefore η_R cannot be less than η. So there are two opportunities, two possibilities η_R η or $\eta_R > \eta$. Now how to get rid of this opportunity by this condition there are two situation, two possible solution η_R cannot be > η because this Kelvin Planck statement.

So η_R cannot be < η not greater than, that this Kelvin Planck statement is highlighted, so therefore η_R is either η or $\eta_R > \eta$, so η is η then what happens all the heat transfer and work done will be same for the two engines, this is the logic only, there cannot be any analogical proof because we consider the reversible and the irreversible engine in different, in terms of their performance if $\eta = \eta$ then if we take $Q_R = Q_1R$ earlier which I took in the another figure, that both heat engines are there.

One reversible and the irreversible if η_R is η they will reject same heat and they will develop same work whatever it be, that means the performance will be identical in terms heat and work interaction that cannot happen, but this is the basic assumption or this is the basic realization that the reversible engine and irreversible engine cannot interact with the surrounding with the same heat and work interaction, so that their efficiency will be equal.

Otherwise the irreversible engine will become the reversible one, so that logic puts that logic imposition the condition that it is not valid, that means the reversible engine efficiency cannot be equal to the irreversible engine or other reversible engine efficiency cannot be equal to irreversible engine, otherwise everything will be same irreversible engine will be reversible engine because the reversible cycle is characterized by the performance.

That is efficient performance not distribution, okay so that first process with distribution cannot reveal with the same efficient, this is not accepted so therefore the only solution is that η_R that means the efficiency of the reversible engine is greater than the efficiency of the irreversible engine. So therefore the first statement is proved that the efficiency of the irreversible engine work will be to same temperature levels to the same thermal reserve source sensing, the reversible engine as the higher efficiency.

Next we have to prove that efficiency of all reversible engines operating between the same source sensing cannot be same that I will do in the next class thank you.