

**NPTEL**

**NPTEL ONLINE CERTIFICATION COURSE**

**Course  
on  
Laws of Thermodynamics**

**by  
Prof. Sankar Kumar Som  
Department of Mechanical Engineering  
Indian Institute of Technology Kharagpur**

**Lecture 12: Second Law and its Corollaries (Part I)**

Good afternoon and I welcome you all to this lecture session of the course laws of thermodynamics last class we discussed few problems in relation to the application of first law that is the conservation of energy to an open system, so today we will discuss another problem another interesting problem and then after that we will start the second law of thermodynamics.

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**Problem 4:** A mass-loaded piston/cylinder, containing air, is at 300 kPa, 17°C with a volume of 0.25 m<sup>3</sup>, while at the stops  $V = 1 \text{ m}^3$ . An air line, 500 kPa, 600 K, is connected by a valve that is then opened until a final inside pressure of 400 kPa is reached, at which point  $T = 350 \text{ K}$ . Find the air mass that enters, the work, and the heat transfer.

So let us now concentrate on the problem which we will discuss today this problem 4, 3 problems were solved last class a mass loaded piston cylinder containing air is at 300 kPa and 17°C with a volume of 0.25m<sup>3</sup> while at the stops  $v$  is equal to 1 m<sup>3</sup> an airline 500 kPa 600 K is

connected by a valve that is then opened until a final inside pressure of 400 kilo Pascal is reached at which point  $t = 350\text{ K}$  find the air mass that enters the work and the heat transfer.

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$p_2 = 400\text{ kPa}$   
 $T_2 = 350\text{ K}$   
 $V_2 = 1\text{ m}^3$   
 $R = 0.287\text{ kJ/kgK}$   
 $p_1 = 500\text{ kPa}$   
 $T_1 = 600\text{ K}$   
 $c_v$   
 $c_p$   
 $h_i = c_p T_i$   
 $u_i = c_v T_i$   
 $u_2 = c_v T_2$   
 $u_1 = c_v T_1$   
 $m_2 u_2 - m_1 u_1 = m_1 h_i + Q - W$   
 $W = 225\text{ kJ}$   
 $Q = -819\text{ kJ}$   
 $W = \int p dV$   
 $W = p_1 (V_2 - V_1)$

Now let us say this in the boat now the problem is like this there is a piston and air whose initial state 1 which is given by  $P_1 =$  in the problem which is given by  $P_1 = 300\text{ kPa}$   $T_1$  is  $17^\circ\text{ C}$  that means  $290\text{ K}$  and the volume  $V_1$  is  $0.25\text{ m}^3$  okay this is the state on now what is the problem is this air flows through this when the valve is open the air in the line this is the line flows through this cylinder.

So line pressure  $P_1$  that is the line pressure this is the I state I the line pressure  $P_1$  is  $500\text{ kPa}$  the line temperature is given by  $P_1$   $600\text{ Kelvin}$  it is given now the problem is that as soon as the air enters the pistol the mass loaded pistol goes up and it hits the stop, now the question tells that at state 2 that final state let us consider the piston hits the top before the final state this is the final state of the before the final state is reached that means here the condition the state point is two this is the final state we consider the piston reaches the stop before the final state is achieved I will tell how do you know.

It but at this final state  $P_2 =$  that  $P_2$  is given by  $400\text{ kPa}$   $400\text{ kPa}$   $t_2$  is given by  $T_2$  is given as  $350\text{ K}$  and the volume that is at stop it is written the volume at stops is  $1\text{ m}^3$  when the piston reaches the stops the volume is  $1\text{ m}^3$  now this type of problem is like this you have to understand when the air goes in this mass loaded piston it pushes the piston and piston goes up there is a

displacement of the piston and as it goes up the work is done by the system, now this case this type of problems when mass loaded piston is there then it is pushed by air it is always going with or expanding with constant pressure.

We have to assume that this process is such that this is a constant pressure process we have already you have already come to know what is meant by quasi-static process that means it is almost a very slow process quasi-static process which passes through number of equilibrium state expands in such a way that the width of the piston is always balanced by the pressure within the gas or within the air that pressure force within the air.

So pressure is balanced by view it so at every instant pressure is same until analyst it hits the stop that is the pivotal concept of this problem, so piston expands under a constant pressure then when it hits the stop if then air still flows then the pressure increases, so therefore we need just detach the stop pressure is same as the initial pressure 300 kPa when we know the final state pressure is 400 kPa that means the piston has reached the stop after that air still flows, so that the pressure increases and that case we pressure is balanced by the piston weight plus the reaction at the stops.

So that is the problem, so therefore this problem is very simple now when you understand the problem this way and we can write the mass conservation from the mass conservation we can write that  $m_2 - m_1$  that is initial final mass – initial mass is the mass that has entered through the line.

Now  $m_2$  is found out by what  $m_2$  is  $P_2 V_2 / RT_2$  and  $m_1$  is  $P_1 V_1 / RT_1$  so  $P_1 P_2 V_2 T_2$  is given  $P_2 V_2 T_2$ , similarly  $P_1 V_1 P_1$  is given so  $m_2$  and  $m_1$  can be found out, so therefore we can find out the value of  $m_i$ . now this value if you calculate use R for aR 0.287kJ/ kg k, so it is there so you get the value of  $m_i$ . which comes out to be if you calculate the answer I am giving 3.082 to 3.082kg.

Now I write the energy equation for this finite process energy equation is also very simple that changing the internal energy of the control volume, we have considered this as the control volume we have considered this as the control volume and here the control volume does work so control volume does work W and also heat transfer is there because in the problem it is told the

mass of air that enters work and heat transfer and ill-considered first the heat added to the control volume  $Q$  and this is the positive.

If the result comes negative then heat will come out let us see how you will do now the change of energy  $e_2$  is the specific energy  $m_2 e_2$  the change of energy in this the control volume equals to what  $m_2 e_2 - m_1 e_1$  or rather you can do this search okay, this is the change in energy in the control volume equals to the inflow of energy that means  $m_1$  into the energy which is coming through this with the flow which is the flow energy which is nothing but the  $h$  enthalpy this we have told that  $Q + P_v$  so this is enthalpies there's flow work is added.

So in that case we can from the beginning write this is the within this cylinder air is at rest so therefore this is only the intermolecular energy, so that you can understand so this is the energy which is coming and at the same time it has received heat and it has delivered one so this is simply the conservation of energy which you can get by integrating the as I told earlier the general energy equation in the rate form, integrating with respect to time but it is not required all the time to remember that equation.

You can state right from the concept of conservation of energy this is the rise in the internal energy of the control volume, that means the internal energy of the tank then this equals to the mass which has entered  $m_1$  associated with its energy which is enthalpy because internal energy plus the flow up and we neglect the kinetic energy and potential energy plus the heat required heat received and the work done. Now here you see we know  $m$  – now  $U_2$  is  $C_v$  which we have told  $C_v T_2$  and  $E_1$  is  $C_v T_1$ , so therefore if we substitute this we know you to anyone with value of  $C_v$  for air =  $0.717 \text{ kJ/kg K}$ , okay so therefore left hand side everything is known for an ideal gas  $U_2$  is  $C_v T_2$   $e_1$  is  $C_v T_1$  now here  $m_1$  is known  $m_2 - m_1$  already we have found that and  $h_1$  you substitute as  $C_p T_1$ .

And the value of  $C_p$  for air is  $1.00 \text{ kJ/kg K}$  you take this value  $kg$  key so to unknown is there  $Q$  and  $W$  so to find out any one of them from this equation you have to know other one from an independent equation what is that, that is the work done. This work I have told the piston is moving slowly that at all stage stages is mass is balanced by the pressure and since this mass or weight is balanced by the pressure force of the pressure means that the pressure remains constant at  $300 \text{ kilo Pascal's}$ .

So this does PDB 1 and this PDB 1 get constant pressure amongst to be pressure  $p_1$  that is the constant into  $v_2 - v_1$  because PDB 1  $W$  is integral this PDB 1 because the piston is moving very slowly and always there is a balance between piston weight and the pressure of the air so if pressure is constant it comes out  $v \times (v_2 - v_1)$  we know  $V_2$  we know  $V_1$  we know  $P_1$  so therefore independently we can find the work done that is the PBR 1 at constant pressure.

So we can find out  $Q$  and the value of work and  $Q$  comes out to be I tell you the value of work is mine 225 kilo joule 225 this is positive means this is done by the system and  $Q$  comes out to be - 819 kilo joule this minus sign indicates that heat has come out of the system that means heat finally is not going in which we have taken and written this equation but finally it has come out so this is the problem, clear? Okay.

So here we see the difference between the with the earlier problem is that where there was a turbine work instead that there is a piston expansion that PDB1 here more important concept through this problem is there that even in an open system we have PDB 1 that PDB work is not only for a closed system this is an open system where there is a inflow but this is an unsteady open system there is no outflow but this air pushes the piston to go up.

So therefore we can have PDB work even in a in an open system but this one requires a quasi-static process or a reversible process which we will discuss afterwards very slow process that always there will be thermodynamic equilibrium of the system okay . Then this is the problem. Now we will discuss the second law of thermodynamics, the second law of thermodynamics is very conceptual regime or rather we can tell is a very conceptual area.

Now first law we have seen it is a conservation of energy principle or law of conservation of energy, second law as I told earlier in the introductory class is an independent law which puts the directional constraint on all natural processes or a unidirectional characteristics of natural processes, it apparently means that all natural processes takes place in one direction but it is not like that it is not so rather we can understand it better in this way that yes there are natural processes which always takes place in one direction.

For example the fluid flows from high energy level to low energy level the water runs down it there is a statement like that that means if water is there at the top of the hill it spontaneously comes down because the potential energy is high at the top and low at the bottom, similarly the

heat is always transferred from high temperature to low temperature not from low temperature to high temperature.

Similarly the electric current flows from high voltage to low voltage the mass transfer of a species takes place from high concentration to low concentration okay, so these are the examples of natural processes which takes place spontaneously takes occurs in one direction there are another class of problems which are not spontaneous process but which can be made by man they also in take place in one direction, what are those process some example I am giving you.

That consider a rotating wheel now we stop it by applying a brake then what happens is that mechanical break for example then what happens that will comes to rest and the breakthrough and the will gets heated that means its temperature rises and let us consider the entire system is insulated no heat transfer is the surrounding this process from first law of thermodynamics we can tell that the kinetic energy is converted into intermolecular energy, so total energy within this system remain same but the kinetic energy is transferred in the form of the energy is transferred from the, in the form of from the form of kinetic energy to the intermolecular energy for which this has become hot that means temperature is increased.

But there is no way by decreasing the temperature of the will and the break to set the wheel in motion, so this is the one directional process. Similar is the case if you take liquid in a container and if we start the liquid then you will see the liquid temperature increases and in that case also we tell that the stirring for stirring the liquid some mechanical work is done on the system if we consider liquid as a system the mass of the liquid the mechanical work which is transferred into this liquid has increased this intermolecular energy for which there is an increasing temperature.

But there is no process by which temperature is brought down and we get back the motion of this star this is not possible, these are known as adiabatic transformation of kinetic energy into intermolecular energy or mechanical energy into intermolecular energy afterwards we will see these are known as dissipation of energy and this type of processes are one directional or unidirectional.

But there are number of processes which are not unidirectional, for example you can heat a body from a lower temperature of  $T_1$  to a higher temperature of  $T_2$ , but at the same time you can pull the body from this higher temperature  $T_2$  to the lower temperature  $T_1$ , so in that case the process

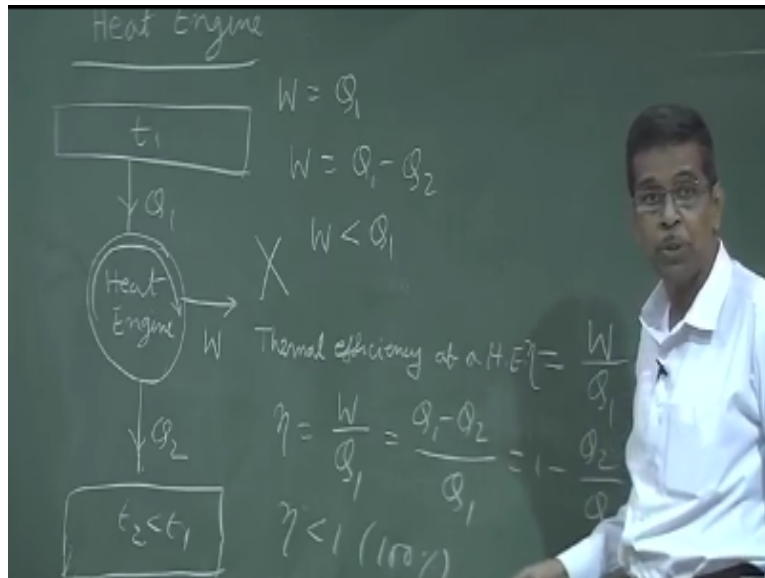
can be reversed what is the directional constraint. For example you can compress a gas from a lower pressure and temperature to a higher pressure and temperature in a piston cylinder arrangement and you can expand the gas from the same lower, higher pressure and temperature to the lower pressure and temperature so the process can be reversed back.

So many such processes in nature can be made to occur in both the direction, but these processes when they occur in both the direction they make some permanent changes in the surrounding which I will come later on and they have to follow a particular principle because of the change in the surrounding so when they go in one direction and they come back in other direction we make the process to occur in both direction there is some permanent change in the surrounding for all natural processes and that change in the surrounding is expressed in the form of some principle okay, and that principle has to be followed by any natural processes.

And that principle or that law that is basically the second law is expressed in various forms in it will working indifferent a different area they use for example people in material science, people in mechanical engineering, people in electrical engineering, people of physics so they people in chemical engineering working in different area this directional constant which is imposed because of the occurrence of the process in both the directions as a permanent change in the surrounding is expressed in different forms but the genesis is same that this imposes a directional constraint.

Now this will be explained further afterwards but now from the viewpoint of mechanical engineering there are two classical statements for the second law of thermodynamics one is Kelvin-Planck statement another is known as Clausius statement, but before coming to this statement I will tell you that certain definition.

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So definition of first I will tell you the definitions of thermal reservoir thermal reservoir, thermal reservoir is considered to be a body with very high capacity heat capacity so that if it supplies heat or receives it supplies heat to somebody some system or receives heat from some system its temperature does not change this thermal capacity is very high compared to this it transfer this is known as thermal reservoir when it supplies it then it is known as source the reservoir is known as source when it receives it the reservoir is known as sink, so this is known as thermal reservoir this is the concept of thermal reservoir. Now with this concept we now go to the concept of heat engine.

What is the heat engine? Now heat engine is defined like this basic definition of heat engine is like that it is a device let us write this heat engine afterwards I will use  $H_e$  only heat engine where a working system operates on a thermodynamic cycle you know what is the thermodynamic cycle that means thermodynamic cycle consists of a number of processes executed by the system such that the system.

Come back to its initial state after the last process the final state and initial state becomes in the final state is the initial state it operates heat engine on a thermodynamic cycle the working system operates in thermodynamic cycle and it receives some heat that means it as a heat input from a thermal reservoir let us consider a temperature  $T_1$  and it has an work out put  $W$  so this is the basic definition of heat engine that which has an heat input  $q_1$  and to gave an heat input it has



to have a thermal source  $t_1$  and come that it has a work output that means it converts heat into work.

Now in this respect we have to know that for a continuous conversion of heat to work the cyclic operation is required a cyclic operation is required for continuous conversion of heat to work and that is why the system has to operate on a thermodynamic cycle. So this is the basic definition of heat engine takes a heat input and delivers or now from thermodynamics first law we can write that this work equals to  $Q_1$ .

So as far as the basic definitions of heat engine and first law of thermodynamic the conservation of energy I am write up to this point but the second law which is formulated again I tell you from the basic observations in nature tells no this is never possible you can never convert the entire heat into work continuously in a cyclic process, so what then you can do? Thermodynamic second law tells first know this you cannot do so what you have to do if you want to convert work from heat  $q_1$  then you have to reject some amount of heat for which you require another thermal reservoir that is sink this is source  $t_2$  which is less than  $Q_1$  and in that case  $W$  will be  $q_1 - q_2$ .

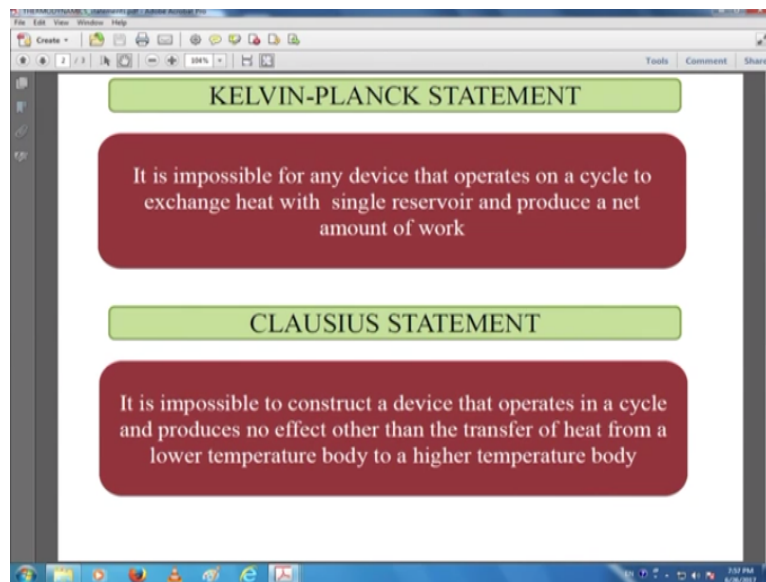
So which means  $W$  is always less than  $Q$  so the entire  $Q$  heat which you receive from the source cannot be converted into what continuously in acyclic operation by a heat engine, so this is the concept now in this context we define thermal efficiency thermal efficiency of a heat engine as the desired output  $W$  divided by heat input  $q_1$ , this is given by  $\eta$ . So therefore  $\eta$  is  $w / q_1$  or one can write  $q_1 - q_2 / q_1$  that is equal to  $1 - Q$  by second law  $W$  is always less than  $G_1$  that means  $q_2$  can never become zero  $q_2$  has to be greater than 0 and  $W$  has to be less than  $q_1$  which means each other is less than 100%.

That means a heat engine can never reach a hundred percent efficiency but here one very important point is there that this heat engine can never reach 100% efficiency that is even the heat engine is an ideal one and it consists of all ideal processes that means reversible processes which I will come afterwards even in the most ideal case that in absence of all dissipative effects and everything then also this cannot achieve 100% efficiency here is a very strong concept that sometimes we tell a generator cannot attain 100% efficiency electrical motor cannot attain 100% efficiency and the mechanical transmission system cannot attain 100% efficiency this is because

of practical things dissipative effects friction hysteresis all these things come into picture electrical hysteresis magnetic hysteresis.

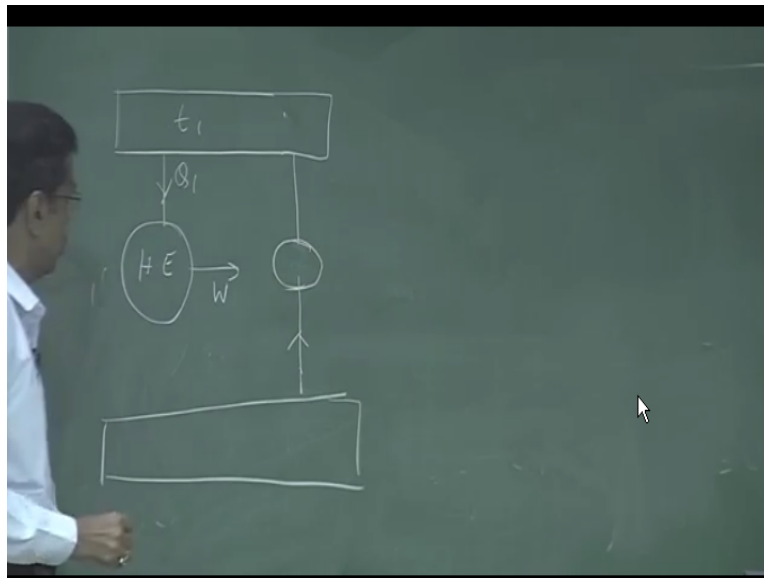
But in an ideal case we can conceive of such systems with 100% efficiency but yes we cannot conceive of an ideal heat engine in absence of all frictional and all dissipative effects to attain the 100% then this imposition by the second law is imposition even on the ideal system so this is the this is the heat engine definition okay.

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Now I will tell you the Kelvin plank statement and the this is the Kelvin-plank statement which says it is impossible for any device that operates on a cycle to exchange heat with single reservoir and produce a net amount of water that I have described and Clausius statement tells it is impossible to construct a device that operates in a cycle and produces no effect other than the transfer of heat from a lower temperature body to a higher temperature body that fountain spontaneously heat cannot be transferred from lower temperature body to higher temperature body.

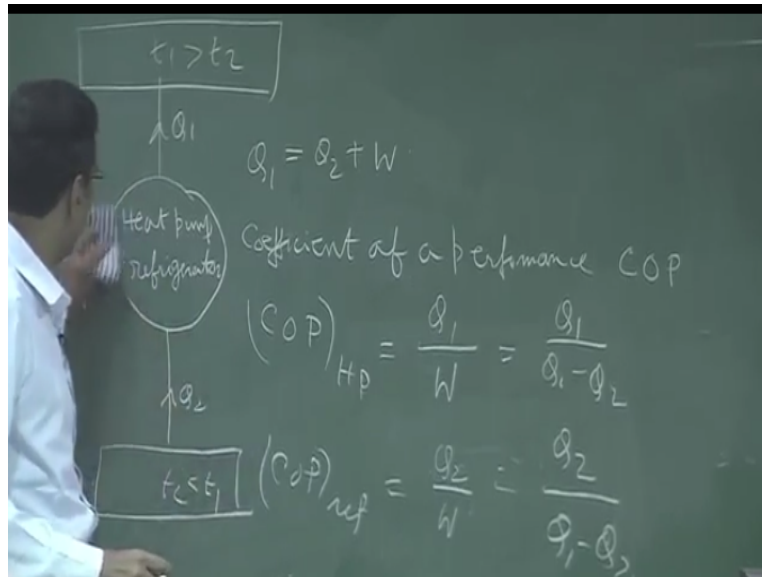
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These are two statements so now these two statements are equivalent that means if Clausius statement is invalid then Kelvin statement is invalid if Kelvin statement is invalid Clausius statement is invalid now let me prove that let us consider the Kelvin-plank statement is invalid that means there is a temperature  $t_1$  and let us consider a sheet engine operating violating the Kelvin-plank statement by exchanging heat let this is  $Q_1$  with this  $t_1$  temperature and develop work.

And let us consider that a system that X so this is the Kelvin that is the violation of Kelvin-plank statement  $t_1$  and we consider that this there is a heat pump of course we have to tell the heat pump before that you have to know the heat pump otherwise it will be difficult for you to know let us see that we'll go back to the definition of hit pump then we will put this sorry otherwise.

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It is very difficult to understand Rascal equality of the two a heat pump or a refrigerator heat pump or a refrigerators just the reverse of the heat engine that means what it does it takes heat from a low temperature body and pumps heat to a high temperature body but it is not possible according to cross via statement but it takes work from outside so giving work from outside one can take heat from a low temperature  $t_2$  is less than  $t_1$  or  $t_1$  is greater than  $t_2$  to a high temperature body in this case it is possible it takes 1 not spontaneously without any effect in the surrounding in this respect if you write the conservation of energy  $Q_1$  becomes is equal to  $Q_2+W$ .

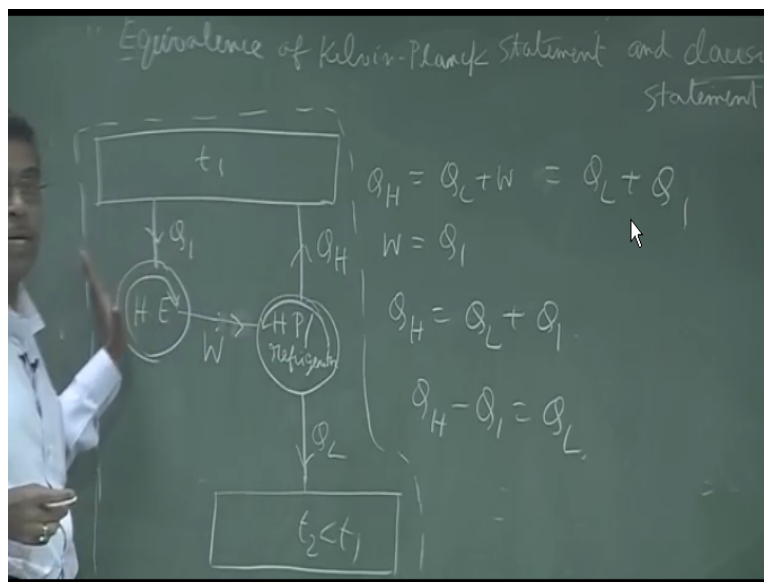
So  $t_1$  is equal to this  $t_1$  giving equal to  $Q_2 +W$  so this  $W$  taken this is just the reverse of heat engine in this context two things are define coefficient of performance just like thermal efficiency of a heat engine we define coefficient of performance COP now when our desired objective is to pump heat to higher temperature then we call it as a heat pump when a desired objective is to take heat from a lower temperature you call it as a refrigerator, a refrigerator and heat pump is the same devices.

We will see in your house that if you stand the size of the refrigerator it will be hot it is exchanging heat to the surrounding so if you think in that terms I get shipped from the refrigerator outside that is a heat pump and if the inside of the refrigerator what is the evaporator

box that is the deep freeze so they are the cold space is there where the heat is being taken so if the desired objective is  $Q_2$  that taken heat from the low temperatures refrigerator and the desire then it is equal.

So therefore COP of a heat pump is given by the desire of the  $Q_1/W$  & COP of a refrigerator is  $Q_2/W$  and from the first law we can write that  $W$  is nothing but  $Q_1 - Q_2$  so therefore  $Q_2/Q_1$  so with this definition of heat pump or refrigerator now we can prove the equivalence of cross here statement and the Kelvin plank statement okay Kelvin-plank statement.

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And cross he escape Kelvin-plank and Kelvin-plank statement and cross your statement and close your statement now you see the equivalents of Kelvin plank and let us consider that means equivalence mean if Kelvin-plank statement is not valid then Clausius statement will also not be valid similarly the Clausius statement is not valid Kelvin plus statement will not be valid let us consider the Clausius kelvin-planck statement is invalid that means there is a heat engine which takes heat  $Q_1$  from a source  $t_1$  and develops what?  $W$  and develops work  $W$  here I write, there is no other deserve one that means, the entire  $Q_1$  is converted to  $W$  high lighting the Kelvin - Planck statement it operates with single fixed server. Now we consider a heat pump or are refrigerator, a heat pump or a refrigerator.

Which takes it from a low temperature body  $t_2$  which is lower than  $t_1$  here in this case you lower than  $t_1$  take some heat  $Q_L$  and this heat pump is run by this heat engine, that means the work

developed by the heat engine is given to this heat pump to run okay, this is the heat engine and this is the heat from the opposite direction cycle and then we complete rejects heat engage. Now this  $Q_H$  is what  $Q_H$  is  $Q_L + W$  and  $W$  is what?  $W = Q_H - Q_L$  again from the heat engine conservation of energy  $W$  is  $Q_H - Q_L$ . So okay  $Q_H$ , so  $Q_H$  is you will plus  $Q_L + 1$  okay.

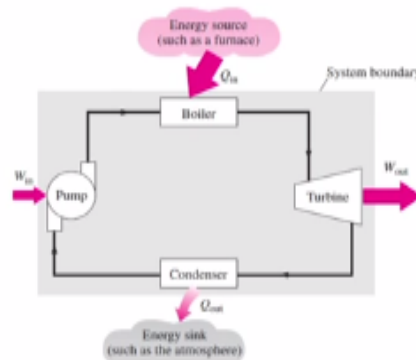
Now therefore you see that the combined system as a whole does what this takes heat  $Q_L$  from the low temperature to the high temperature because the high temperature source receives the heat it gives  $Q_H$  and takes  $Q_L$  it receives the heat,  $Q_H - Q_L$  IS  $Q_L$  that means if you see the reserved source, the high temperature reservoir it gives it  $Q_H$  receives it  $Q_H$ , so it this is the net heat  $Q_H - Q_L$  is  $Q_L$  that is what is being taken from the low temperature  $t_2$ .

So therefore the combined system spontaneously takes it from  $t_2$  and that to you on high temperature without any other affecting the surrounding because this work an internal that means this heat engine work is driving the heat pump, so combined system does not make any change in the surrounding without making any change in the surrounding lifts it from low temperature to high temperature. That means if the Kelvin Planck statement is not valid cross your statement is also not valid.

Similarly we can show that if the Clausius statement is not valid that means spontaneously heat can flow from low temperature to high temperature without any other affecting the surrounding then Clausius statement will not be valid, so this is left as an exercise to you and you can see in any thermodynamics book for this time is short, so I am not doing that, so only once I have proved that if Kelvin Planck statement is invalid Clausius statement is invalid.

So it violates the Clausius statement, similarly Clausius statement is violated Kelvin Planck statement is also violated, so after this I will show you a practical figured.  
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## SCHEMATIC OF A STEAM POWER PLANT



That this is of a typical steam power plant, you know the steam power plant from which we get electrical energy but the steam power plant layout is like that from your popular knowledge you know but I am not going into any details of that, there is a boiler where the combustion takes place of a fuel is really coal and the high-temperature gas of that after the combustion heats the water in the boiler, water is the working substance this is converted into steam and then this expands into turbine to give work.

Then after expansion the low temperature and low pressure steam is passed through a condenser where it rejects heat to the atmosphere usually the atmospheric water is a water from the atmosphere is taken as the cooling water, which takes the heat from the steam to condense then it is given to the pump where it takes work and pressure is boosted to that of the boiler pressure. So this is the thermodynamic cycle and here you so see that energy source that is the furnace where the combustion takes place and hot gas gives the heat.

That means here the working system water takes heat, so this is one reservoir and in the condenser where the steam after expansion is condensed is the sink the low temperature reservoir, that is cooling water from the atmosphere so you see that this is a heat engine where, we have two deservers that furnace of the boiler and the cooling water from the ambient or atmosphere at the condenser.

And as a result we get a network output which is the work output from the turbine the work input to the pump which is much less compared to the turbine oil, so this is one good example of a heat

engine which is a typical steam power plant in practice okay now if we close this module here next to you start the other thing thank you.