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Module - 01 Review of Basic Thermodynamics Lecture - 03 Heat Engines and Refrigerators / Heat Pump - Second Law of Thermodynamics

Dear learners, greetings from IIT, Guwahati. We are in the course Advanced Thermodynamics and Combustions which is 1st module, that is Review of Thermodynamics.

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And in this module, we had 3 lectures, first 2 lectures we have covered and it was based on temperature and zeroth law of thermodynamics, second one was work and heat transfer that is first law of thermodynamics. Now, we are going to look at the second law of thermodynamics which is mainly based on heat engines and refrigerators or heat pumps.

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Lecture 3	
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So, in this particular lecture we are mainly concentrating on the following topics, that is conversion of heat and work, then second law of thermodynamics, then it gives the concept of reversibility and irreversibility. Then moving further, the ideal cycle for conversion of heat to work is the Carnot cycle.

We will try to explain what a Carnot cycle is all about, then in the last segment, which is the most important inference of Carnot cycle that is the interpretation of absolute temperatures. And that we can do it through analysis of thermodynamic temperature scale.



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So, let us start the first segment of this lectures that is the conversion of heat and work. So, from the first law, it says that the work and heat they can be related together by this equations, that is dQ = dU + dW, where work transfer and heat transfer are equal when this processes are taken place in a cycles. At that point of time your internal energy is equal to 0. So, what we can write for a cycle? We say dQ = dU + dW and here dQ is your heat interactions, dW is the work interactions, dU is the internal property of this system.

Now, when in a cyclic process what happens, the starting point and end point remains same so there is no change in the internal energy. So, we can write $Q_{cycle} = W_{cycle}$ and this equation also says that $W_{cycle} = Q_{cycle}$. So, these 2 equations although meaning wise they are same, but in terms of interpretation of heat and work they are little bit different.

So, what it says is that first law does not distinguish between the work and heat, but they are interpreted as a energy and when you say $W_{cycle} = Q_{cycle}$, it means that complete conversion of work to heat is possible, but in other words ideally speaking we can as well say that complete conversion of heat to work is possible.

But here the first law does not distinguish this equations. Now, here we have to make a pause saying that whether we can write this both the equations in a correct way or not. So, this turns out to be the interpretation of second law. So, in a sense that when you say heat, it is by virtue of temperature difference and when we say work, it is interpreted as the displacement under a action of force. So, many a times we view this as a rising and falling of a weight.

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So, just to make some summary of conversion of work to heat. So, in general we can say work of any kind may be done on the systems in contact with the reservoirs, causing heat to leave the systems without altering the state of the systems. So, it is apparent from the first law transformation that "work to heat" can be accomplished with 100 percent efficiency.

That is W = Q and this process can be continue can be continued indefinitely; that means, that means, as long as we have work available to us we can keep on converting it to heat. But the opposite process that is conversion of heat to work completely and indefinitely is not really true, even if the first law is satisfied.

For example, we can say in an isothermal expansion process of course, there is no change in internal energy because there is no change in the heat transfer. We can say Q = W and the process involves change of state of the gas that means, in isothermal expansion temperature remains same, the volume increases, pressure decreases.

But this continual decrease of pressure is possible till one particular point. For example, in this case the downstream atmospheric conditions restricts this expansion process; that means, pressure can be decreased continuously to the dead state atmospheric conditions. So, in other words we can say that isothermal process cannot continue indefinitely, it has to stop somewhere. So, this is the conditions that first law does not identify this concept.

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So, in a thermodynamic view point we can say that there may be series of processes through which the system can be brought to its initial state that is cycle and each process of the cycle involves the involvement of work flow and heat flow from the system and the surroundings.

So, the work interactions or heat interactions can occur between two reservoirs, which are maintained at two different temperatures one at higher temperatures, other at the lower temperature of the systems. So, this concept was told that if you want to transfer the work interactions from heat, then you have to view it as a cyclic process that should occur between two temperature limits that is at high temperature and lower temperatures.

And the absolute values of work and heat transfer is based on the type of feasibility of the formulation of power requirement. So, this gives the either concept of heat engines refrigerators or heat pumps. Now, from the second law which we will be talking later, that when you talk about conversion of heat to work, it is accomplished through a device and or you call it as a cyclic device and in our term, we call this as a engine.

So, this engine could be an internal combustion engines like petrol engines, diesel engines or any kind of external combustion engines like steam engines or we can have refrigerators or heat pumps which consume work. So, all these things we are going to explain subsequently.

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Now, how this conversion of heat to work is possible? So, here we have explained about the concept of heat engines, then we have refrigerator, then we have heat pump. So, the first figure says that there is a high temperature reservoir at T_H , there is a low temperature reservoir at T_L and we have a heat engines in order to have a net effect of work transfer from heat to work.

Then we must introduce an cyclic device and this cyclic device we call this as a heat engine, it must takes Q_h amount of heat and reject Q_l amount of heat to the low temperature reservoir. So, in the process, if you can just look into its first law analysis then we can say net work is nothing but difference in the Q_h and Q_l and from this we can also derive the expressions for efficiency of this heat engines that is nothing but ratio of Q_{net} by Q_h .

So, this turns out to be efficiency of this heat engine is $1 - \frac{Q_l}{Q_h}$. So, this is one concept where we call this as a power producing device, where work comes out of the systems. That means, a work is done by the system. Now, in other two situations what we have is that work is being fed into the systems and side by side if you do this then this particular cycle, heat engine cycle can be reversed.

One is; that means, heat can be taken from the cold space and it can be rejected to warm environment. So, in other situations also similar concept is there, but in both the cases we have the required input is W_{net} , but the desired output is different. If you are concentrating on the desired output as Q_h , then such a philosophy we will we call this as a heat pump.

If Q_l is the essence of your requirement and so we call this as a refrigerators. So, based on this we derive the expressions for coefficient of performance, that is $\frac{Q_l}{W_{net}}$. So, same expression we can use in a different form; that means, $Q_h - Q_l$ is nothing, but your W_{net} , net amount of work which is done on to this systems.

Other concept we can use it COP as $Q_h/(Q_h - Q_l)$. So, this is the three situations where we have demonstrated that how conversion of heat to work is possible.



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And these concepts leads to the fact that is called as second law of thermodynamics. So, when you talk about the second law of thermodynamics, there are two possibilities or two important statements. One is Kelvin-Planck statements other is Clausius statements.

So, let us talk about the first statement which is Kelvin-Planck statement and it is based on the concept of heat engines. So essentially, we have a high temperature reservoir, we have a low temperature reservoir. So, if a heat engine has to operate in a cyclic manner, then we can say the heat engine takes Q_H amount of heat and rejects Q_L amount of heat to the low temperature reservoir.

And side by side we get W amount of work. Now, one of the interesting feature is that, when you say that the process has to occur in a very in slow manner, then we can view this particular things as a reversible processes. So, what we can have is that when you take this Q_H amount of heat, we assume that temperature of hot reservoirs should not drop.

That means this particular temperature T_H of the hot reservoir remains as it is and the process has to take place in an isothermal manner. Similarly, when we reject the heat to the low temperature reservoir that is T_L , then the temperature of this low temperature reservoir should not change, all these processes has to occur in a isothermal manner.

So, that is what we say there is some processes or series of processes during which heat is absorbed from the external reservoir at higher temperatures, there are some series of processes that occurs for which the heat rejection takes place to the external reservoir at lower temperatures. Now, in this process what we can say based on the first law, we can say cyclic heat transfer $Q_{cycle} = W_{cycle}$.

And one of the important thing is that, I will try to say that if there is no change in the internal energy, then we can say that the first law is satisfied; that means, $Q_{cycle} = W_{cycle}$, but what imposes the second law is it possible that all the $Q_{cycle} = W_{cycle}$, here the second law imposes the conditions that $W_{cycle} \leq 0$.

So, if W_{cycle} less than 0 means that some part of heat must be rejected to the low temperature reservoir. So, with this condition of impositions, we can write the second law of statement in a negative form that is it is impossible to construct a heat engines that operates in a cycle and will produce no effect other than the extraction of heat from a reservoir to perform an equivalent amount of work.

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Now, again this second law of thermodynamics can also be interpreted in another way and we call this as a Clausius statements. So, in a Clausius statement, if you recall our concept of refrigerators or heat pump we say that the Q_l amount of heat is taken by the refrigerator or heat pump from the low temperature sink.

And this refrigerator or heat pump rejects Q_h amount of heat to the heated space or warmer environment. So, to do this we must provide some of the net work input into this cyclic device. So, that is W_{net} . Now if you say this is the actual concept of converting heat to work or taking heat from low temperature sink to the high temperature source.

Which means that it must take some W_{net} amount of heat to perform this change; that means, to reject this Q_h amount of heat to the warm environment.

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So, based on that we can also imagine in a similar way, what it says is that we have a refrigerator or heat pump that takes W amount of work input. And while doing so, then it can take Q_l amount of heat from the low temperature reservoir and it can reject the Q_h amount of heat to the high temperature reservoirs.

The high temperature reservoir is maintained at T_H and low temperature reservoir is maintained at T_L . And of course, in a similar sense we can also view that process has to occur in a very quasi static manner and mostly it should be in isothermal process so that the temperature of the reservoirs do not change.

And since there is no change in internal energy so that heat rejected to the high temperature reservoir is always larger than the heat extracted from the low temperature reservoir by an amount of work done onto the systems. So, this frames the basics of the negative statement of second law and that is commonly known as Clausius statement.

So, what it says is that it is impossible to construct a refrigerator that operates in a cycle and it will produce no effect other than the transfer of heat from the low temperature reservoir to a high temperature reservoir. I need to emphasize here the fact that the Kelvin-Planck and Clausius statements are negative statements and they has to be written in this particular manner.

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And whatever may be the interpretations of Kelvin-Planck or statement or Clausius statement of second law, one thing is ensured that both of them are the statements of second law and they are equivalent to each other. That means, if some system violates a Kelvin-Planck statement, then it must also violate Clausius statements.

And if some system violates Clausius statements, it also should violate Kelvin-Planck statements. Here I have demonstrated the fact that how a refrigerator and heat engine that acts together they violate the Kelvin-Planck statements. What I can say here that as if we can think about a refrigerator that takes Q_l amount of heat and also it rejects Q_l amount of heat to the high temperature reservoir.

And in this process, there is no work done in the systems. So, this violates Clausius statements. Now, side by side we can also construct another heat engines that takes, that takes Q_h amount of heat and rejects Q_l amount of heat. So, in this process it does the W amount of work which is nothing but the difference between Q_h and Q_l . Now, if you take together both heat engine and refrigerator and they operate in this manner.

It can be viewed that a system takes some Q_h amount of heat and gives a W amount of work, but; that means, this will violate the Kelvin-Planck statements. Similar logic also can be applied for a situation where heat engine and refrigerator they act together and they violate Clausius statements.

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Now, after this let me talk about some of the inferences that are dealt from the second law of thermodynamics. So, this second law of thermodynamics deductions is not a deduction from the first law, rather it stands itself as a separate law of nature. So, it puts the upper limit of any kind of devices that takes some amount of heat to convert into work. So, it means all the heat cannot be converted to work completely and indefinitely.

And in a Layman sense we can say that the first law denies the possibility of creating and destroying the energy, while the second law denies the utilization of energy in a particular manner. So, any device or machines that violates first law is known as perpetual motion machine of first kind, any machine that violates the second law of thermodynamics we call this as a perpetual motion machine of second kind.

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	Reversibility and Irreversibility	
•	A reversible process is the one that is performed in such a way that both system	
	and the local surroundings may be restored to their initial states without producing	
	changes in the rest of the universe. The process that does not fulfil the stringent	
	requirement is said to be irreversible.	
•	All natural spontaneous processes are irreversible: Nointernal reversibility ($W_{rever} < 9$ Nointernal reversibility ($W_{rever} < 9$)	
	> One of conditions of mechanical, thermal or chemical equilibrium (or	
	thermodynamic equilibrium) are not satisfied.	
	\succ Dissipative effects (friction, viscosity, inelasticity, electrical resistance and	
	magnetic hysteresis) are present.	
•	Some of the classical thermodynamic examples are as follows:	
	Isothermal and adiabatic transformation of work into internal energy	
	Ideal gas rushing to vacuum (Free expansion – Joule expansion)	
	> Throttling process (Joule – Thomson expansion)	
	All chemical reactions and phase change processes	
	> Diffusion of gases, mixing of different phases of matter 13	

Now, we will go to the next segment that is reversibility and irreversibility. One thing we can derive from the Kelvin-Planck statements that cyclic work is always less than or equal to 0. Now, here there are two possibilities in this equations, if you say that there is some internal irreversibility, then the cyclic work is always less than 0, but if there is no internal irreversibility the cyclic work is equal to 0.

So, this particular Kelvin-Planck statement that the cyclic work can either be less than equal to 0 or equal to 0, it depends on the concept of reversibility and irreversibilities. So, here we define this reversible process based on the second law in such a way that one can view this reversible process is to be performed in such a way that both system and local surroundings may be restored to the initial states without producing changes in the rest of the universe.

This process does not fulfil the stringent requirement and if the process does not full this stringent requirement, then it is called as an irreversible process. Of course, all natural spontaneous processes are irreversible.

One can say that when a process is not reversible, the conditions that has to be satisfied is that the system and surroundings must be in the complete thermodynamic equilibrium. By thermodynamic equilibrium we mean that conditions of mechanical, thermal and chemical equilibrium is satisfied. Other option of irreversibility is that there are some dissipative effects and which are not recoverable. So, such dissipative effects include friction, viscosity, inelasticity, electric resistance all other things. Now, we are going to talk about some of the classical thermodynamic examples how the process is irreversible in nature.

Some processes are like isothermal and adiabatic transformation of work to internal energy. So, this is a situation where work is converted to internal energy, in one case, process is isothermal, other case process is adiabatic.

So, in these processes we can say the they are irreversible processes and when ideal gas rushes to vacuum; that means, as if you can imagine that there are two gases, they are separated by complete partitions. And entire system is insulated and if you remove the partition the gas which is at higher pressure will rush into the gas which is at low pressures.

So, this pressure process we call as a free expansion process; that means, one can say that as if you can view this gas rushing to a vacuum, there is a tremendous pressure difference between them through a partitions. Other type of processes like throttling process which is an irreversible process, all chemical reactions, phase change process are considered as a reversible process, diffusion of gases mixing of different phases of matter are also considered as a irreversible process.

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Carnot Cycle	
 An engine is said to operate between two reservoirs for which heat is extracted from higher temperature reservoir (source) and some portion of heat is rejected to low temperature reservoir (sink). Some of the important question marks are as follows: Maximum thermal efficiency of the engine for fixed operating temperatures of source and sink 	
 Characteristics features of such engines Effects of nature of working substance. 	
 Thus, carnot cycle is proposed consisting or a set or processes that can be performed by any thermodynamic systems (hydrostatic, chemical, electrical, magnetic etc.) 	
The system or the working system is imagined first to be in thermal equilibrium with reservoir at low temperature.	14
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After complete understanding of reversible process and irreversible process, concept of work and heat, now we are in a positions to define a heat engine. Now, this heat engine is based on the fundamental cycles and what we call is as a Carnot cycles. So, this Carnot cycle when it is introduced to give the concept of engines which means that the conversion of heat to work has to be done through a device which is called as heat engines.

And this conversion has to take place between two temperatures reservoirs, one at high temperature which is called as source, other is at low temperature which is the sink. But here there are some important question mark that remains, that what is the maximum thermal efficiency of the engines for a fixed operating temperatures between source and sink, what is the characteristics features of the engine, what is the effect of nature of working substance. Because we say that there is a cyclic device which converts heat to work.

So, these questions needs to be answered and this answer is possible by drawing a Carnot cycle. So, a Carnot cycle is proposed consisting of set of processes that are performed by the thermodynamic systems, by this we mean it is either a hydrostatic system, chemical system, electrical systems or magnetic systems. The system and the working medium is imagined to be the thermal equilibrium with the reservoir at low temperatures. So, this is the another assumption that we make.

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	Carnot Cycle	
• т	here are four processes in a Carnot cycle in the following order:	
1	. A reversible adiabatic process in a direction to rise the temperature to that of high temperature reservoir $(T_{\rm H})$	
1	I. The working substance is maintained in contact with the reservoir T_{μ} , and a reversible isothermal process is performed in such a direction so that the a fixed amount heat (Q_{μ}) is absorbed from the reservoir	
I	II. A reversible adiabatic process is performed in the opposite direction (step I) and the temperature drops to the low temperature reservoir (T _L)	
1	V. The working substance is maintained in contact with the low temperature reservoir T_L , and a reversible isothermal process is performed in the opposite direction step II until the working substance and the surroundings are in their initial state. During this process, a fixed amount heat (Q_L) is rejected to the low temperature reservoir.	
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Now, when you say that a Carnot cycle, we say there are four processes that occur in the Carnot cycle, the first one is a reversible adiabatic process that occurs in a direction to rise the temperature to high temperature reservoir; that means, there is a reservoir which is at high temperatures and the process has to proceed in a directions to reach this temperature T_H .

The working substance is maintained in contact with that reservoir T_H and reversible isothermal process is performed in such a direction so that fixed amount of heat Q_H is absorbed from the reservoir. The third process is a reversible adiabatic process which is performed in the opposite direction of step 1; that means, this process should proceed towards the low temperature reservoir so that temperature drops.

And the fourth process is the working substance is maintained in contact with the low temperature reservoir and the reversible isothermal process is performed in opposite direction of step 2, until the working substance and the surroundings are at their initial states. So, during this process the fixed amount of heat Q_l is rejected to the low temperature reservoir. So, these are the statement of all the four processes in a Carnot cycle.



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Now let us see how these four processes are represented in a graphical form. Here there are two figures which are shown here, from the first one we say that Carnot cycle is drawn for a real gas. So, what we draw is that process 1-2 which is a reversible adiabatic

compression process, process 2-3 is reversible isothermal expansion. Process 3-4 reversible adiabatic expansion and process 4-1 reversible isothermal compressions.

And of course, all the processes are quasistatic in natures. So, this is done for a real gas. Now, you can think about a Carnot cycle which is operated for a mixture of liquid and vapour. So, when I say liquid and vapour we draw two limits; that means, we draw one vertical line L_A and L_B .

So; that means, in this region this state of the system is completely liquid and there is a region beyond V_A and V_B . So, in this region, the state of the system is completely vapour and we are operating the Carnot cycle between these two lines and. In fact, this is nothing but the concept of Rankine cycle where the cycle is operated between two lines, saturated liquid line and saturated vapour line.

So, that is a different segment, but here if you want to draw this particular processes what we call this that process 1-2 is a reversible adiabatic compression, 2 to 3 reversible isothermal and this process 2 to 3 since it is a phase change process, we say it is isothermal as well as isobaric process and this process is known as vaporization, process 3-4 is a reversible adiabatic expansion.

And then 4-1 is again isothermal condensations and this isothermal condensation process is also in isobaric nature, because these two processes that is 2-3 and 4-1 they occur at same temperature and pressure.

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Then having said this, now we are going to come back again to Carnot refrigerating systems; that means, how that similar concept of Carnot engine is going to be extended for a situations, if it is a refrigerators. So, when you say cannot engines, it produces W amount of heat and will say Carnot refrigerator it takes W amount of heat to transfer heat from the low temperature reservoir to high temperature reservoir.

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In	<u>Carnot Cycle</u>	
•	Carnot theorem states that no heat engines operating between two reservoirs can be more efficient than a Carnot engine operating between the same two reservoirs.	
•	A corollary to Carnot theorem may be stated as, all Carnot engines operating between the same two reservoirs have same efficiency.	
•	The maximum thermal efficiency that can be achieved by a heat engine operating between two heat reservoirs at different temperatures is the efficiency of the Carnot engine operating with same temperature limits.	
•	The essential characteristics of a Carnot engine is that it is reversible and operates between two reservoirs. The superiority in the efficiency is due to its absorbing all heat at highest temperature and rejecting all heat at the lowest temperature.	
•	A Carnot engine is independent of the working substance of the system.	1

Now, from this entire Carnot cycle analysis we can frame some inferences. First one is Carnot theorem it states that no heat engines operating between two reservoirs can be more efficient than a Carnot engines operating between same two reservoirs.

So, we will prove this that what it means is that if a Carnot engine is operating between two reservoirs, that is temperature T_H and T_L , then any other heat engines can not have efficiency more than this Carnot engine. A corollary to this Carnot theorem is that all Carnot engines operating between two reservoirs have same efficiency that is quite obvious.

The maximum thermal efficiency that can be achieved by heat engine operating between two reservoirs at different temperatures is the efficiency of the Carnot engines with same temperature limit. The essential characteristics of the Carnot engine is that it is reversible and operates between two reservoir, the superiority in the efficiency is mainly due to the fact it absorbs all the heat at higher temperatures.

That means we imagine this absorption of heat to occur in a very quasi static manner or in this case in an isothermal manner so that temperature does not change. That mean and all the heat gets absorbed by the engine and in similar sense it also rejects that rejects all the heat at low temperatures. And moreover we are going to prove that the Carnot engine is independent of working substance of the system.



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So, now we will try to move to next segment and which is called as thermodynamic temperature scales. Now, to prove this things; that means, we always say that there is a high temperature reservoir, there is a low temperature reservoir and some heat is taken from high temperature reservoir and rejected to low temperature reservoir.

So, what is the correlation between this heat and the temperatures and that to whether it is reservoir dependent or not, whether it is working fluid substance dependent or not. So, to bring this ambiguity we are now going to define a scale and what we call as a thermodynamic temperature scales. So, to prove this we consider a Carnot engines, that absorbs Q_H amount of heat from a reservoir at temperature T_H and rejects Q_L unit of heat to the low temperature T_L . And of course, it has an efficiency which is independent of working substance this we are going to prove. So, to consider this, let us view this particular explanation in this manner. So, we can say that we have a high temperature reservoir and which is maintained at T_H and there is a low temperature reservoir which is at T_L .

Now, we imagine that one engine which is nothing but a reversible engine that is R_A , which operates between T_H and T_L and let us say it takes Q_1 amount of heat and rejects Q_2 amount of heat. And thereby it does W_A amount of work. Now, within the same temperature limit, we can also have multiple number of Carnot engines.

That means one can think of another reservoir which operates in between. So, let us put this T_H will represent as T_1 and this T_L represent as T_2 and in between you have another reservoir T_3 and we can frame another heat engine which takes Q_1 amount of heat and rejects Q_3 amount of heat and thereby it does W_B amount of work.

Now, between the reservoir T_3 and T_2 we can have another reversible heat engine R_C that delivers W_C amount of work while taking Q_3 amount of heat and rejecting Q_2 amount of heat to the temperature T_C . So, this is the explanation that we gave that, in other words we can say there may be infinite number of reversible engines that can be operated between the temperature T_1 and T_2 .

So, here we make a conditions that for a three temperature reservoir $T_1 > T_3 > T_2$, what we can write that efficiency of the reversible engine is $1 - \frac{Q_L}{Q_H}$. So, in other words we can represent this particular equations as efficiency in a functional form that is $\phi(T_H, T_L)$.

Now, from this equation we can find another expressions that is $\frac{Q_H}{Q_L} = \frac{1}{1 - \phi(T_H, T_L)} = f(T_H, T_L)$. So, basically what you are writing this particular equation is in a functional form. Now, here we will try to impose the situation that a Carnot engine operating between three reservoirs $T_1 > T_3 > T_2$.

We can think that there is engine R_A, which of which is operating between T₁ and T₂. So, we can write $\frac{Q_1}{Q_2} = f(T_1, T_2)$, another engine that operates between T₁ and T₃. So, $\frac{Q_1}{Q_3} = f(T_1, T_3)$, for engine C this $\frac{Q_3}{Q_2} = f(T_3, T_2)$. So, if you take this ratio what it turns out to be is that the functional form $f(T_1, T_2) = \frac{f(T_1, T_3)}{f(T_3, T_2)}$.

So, here you can see that we have a equation and in the left hand of side of the equation there is no term T_3 , but in the right hand side term that is there is a term T_3 . So, we can say that these relations exist in such a way that the T_3 vanishes while taking this ratio and that means, since this functional relation are arbitrarily chosen. So, T_3 should vanish.

So, in other words we can write $f(T_1, T_2) = \frac{\psi(T_1)}{\psi(T_2)}$. So, by this concept we can now write this particular equation in this manner, where would say $\frac{Q_1}{Q_2} = \frac{\psi(T_1)}{\psi(T_2)}$. And here if you choose the functional relation in such a way that simplest one will be linear relations.

So, if I can say that we choose the relation in such a way that the $\frac{Q_1}{Q_2} = \frac{T_1}{T_2}$ and such a situation we call this as a ratio of thermodynamic temperatures.

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Now, let us see what is its significance. Now, when we say this $\frac{Q_1}{Q_2} = \frac{\psi(T_1)}{\psi(T_2)}$, it means that we are now correlated that we have temperature T_1 and there is a engine, there is a low temperature T_2 . So, it is a source and it is sink and we have Q_1 amount of heat and it is goes as Q_2 amount of heat by virtue of this work, that is going out as W. Now, we have now framed this equation Q_1 and Q_2 , this ratio and Q_2 / T_2 and this functional relations becomes a linear relations that is $\frac{T_1}{T_2}$ with certain conditions.

And that conditions we are going to establish such a way that the one of the important relation will remain that it has to be $\frac{Q_1}{Q_2} = \frac{T_1}{T_2}$; under what circumstances this relation is valid. So, this we are going to prove. So, for that what has been chosen is that we take some kind of temperatures and this state temperature has to be a T₂.

We can bring it to a temperature which is nothing but the triple point of water, for which we know what is the value of heat transfer when the heat is rejected at a temperature which is nothing but the triple point of water. And that point of time what is the amount of Q_1 . So, this will give you the basic definition of another temperature for the which is called as absolute temperatures.

At that absolute temperatures when you say triple point of water, there we can say that all the three matters coexist; that means, if you take a water at maybe 273 K we can say that solid, liquid and vapor all the three phase coexist. At that point the choice of working substance becomes now independents. So, this is the essential concept of definition of an absolute scale.

So, if you try to correlate with temperature what we have studied while talking about zeroth law of thermodynamics, we said that there is a temperature scales which depends on the specific working substance. For example, when you say gas thermometer, when you say mercury thermometer. So, all these things are essentially dependent on the working substance, whether it is a mercury or it is a gas or any other substance.

So, zeroth law of thermodynamics when it gives the concept of temperature, it always relates with the nature of the working substance. But here, when you deal with the Carnot cycle and the thermodynamic temperature scale, we are going to choose a temperature scale in such a way that relation between Q_1 and Q_2 are linear at the same time the choice of working substance is independent.

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And under such circumstances we say that we write this $\frac{Q_1}{Q_2}$ relations in a form, that if you take the triple point of water which is nothing but 273.16 K where the choice of working substance becomes independent. That point $T = 273.16K\left(\frac{Q}{Q_{TP}}\right)$. And now in this equations if $Q = Q_{TP}$, then this will imply T = 273.16 K and this is nothing but your absolute temperatures.

So, definition of absolute temperature can be written like this and this definition we got it from the Carnot cycle informations. So, what does it say that when a system undergoes a reversible isothermal process without transfer of heat, then the temperature at which it takes place is called as absolute temperature. Now, at this point there is no concept of I am isothermal or adiabatic all are identical. And here the choice of unit which can be either "Kelvin or Rankine."

So, many times the standard practice that we are using the SI system of unit and that is kelvin and if you go for the British systems it is referred as Rankine.

<u>Intermodynamic Temperature Scale</u> <u>Samo efficiency</u> • A Carnot engine absorbing Q_H amount of heat from hot reservoir T_H and rejecting Q_L amount of heat to cooler reservoir T_L, will have an efficiency as a function of temperature ratio. • It is clear that a Carnot engine will have 100% efficient when T_L reaches "absolute zero". It is possible only when all heat is converted to work. • The nature does not provide reservoir with absolute zero temperature i.e. a heat engine with 100% efficiency is a practical impossibility. • The definition of "absolute zero" holds good for all substances and therefore independent the specific properties of any arbitrary chosen substances. • The thermodynamic temperature is numerically equal to the ideal gas temperature. It can be measured with a gas thermometer in proper range. $\eta_{\kappa} = 1 - \frac{Q_{L}}{Q_{\mu}} : \frac{Q_{L}}{Q_{\mu}} = \frac{T_{L}}{T_{\mu}} = \eta_{\kappa} = 1 - \frac{Q_{L}}{Q_{\mu}}}$

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Now, at this particular point, we are now able to define an efficiency what is called as Carnot efficiency. So, if you look at this particular equation again that for a reversible heat engines, we can write this expression of efficiency as $\eta_R = 1 - \frac{Q_L}{Q_H}$. Now, putting $\frac{Q_L}{Q_H} = \frac{T_L}{T_H}$, we can write for a reversible engine this efficiency comes as $1 - \frac{T_L}{T_H}$ and here the temperature has to be expressed in a absolute scale.

Now, in this equation what we can say when the T_L goes to 0, which implies efficiency of a reversible engine goes to 100 percent. And T_L goes to 0 means it is a almost impossible situations, $T_L = 0$ means we are going to absolute 0. So, it is almost an impossible situations. So, the Carnot engine can never have 100 percent efficient ; that means, in other words T_L must have a finite value, then if you go to the reverse concept then you can say

that the conversion of heat to work is possible only when there is a rejection of heat to the low temperature sink.

So, the nature does not provide any reservoir with absolute 0 temperature, that is a heat engine with 100 percent efficiency is a practical impossibility. So, the definition of absolute 0 holds good for all substance and therefore, it is independent of specific properties of any arbitrary chosen substances.

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So, with this we come to the end of this module 1. But before I conclude I will just try to give some fundamental concept which are left out in this lecture. First is prove the equivalence of Kelvin-Planck and Clausius statement of second law of thermodynamics. So, I have already mentioned that if Kelvin-Planck statement is invalid other is also invariant; that means, Clausius statement is also invalid.

So, to do that let us recall our figure which you have shown earlier, where it is said that, in the first case we have a refrigerator and other one is heat engine. So, first of all let me put k as Kelvin-Planck statement and if it is false then I will put it as a -k. Similarly, C stands for Clausius statement.

So, I will put - C as false if the Clausius statement is not satisfied. So, since the second law of thermodynamics is the negative statement. So, you try to interpret equivalence between k and C. In other words, I can say if k is true then Clausius statement is also true.

Otherwise, if negative statement of kelvin statement is false then Clausius statement is also false.

So, all these things should also hold good. So, this is true statement and this is false statements and this has to be proved which we call as equivalence between Kelvin-Planck and Clausius statements. So, first thing we consider a refrigerator that takes Q_L amount of heat and also rejects Q_L amount of heat to the high temperature reservoir and in this process it does no work; that means, we can say we are now violating Clausius statement.

So, I will put it as -C. Then in the same concept between same high temperature and low temperature reservoir, we are putting an heat engine that takes Q_H amount of heat and rejects Q_L amount of heat so; that means, rejects Q_L amount of heat to the low temperature reservoir.

And as a situation we say operation of heat engine which is true. Now, but globally if you see if you take both refrigerator and heat engine together what you view is that combined machine takes $Q_H - Q_L$ amount of heat and produces W amount of that is nothing but $Q_H - Q_L$ amount of work. But by doing so it does not reject heat. So, this means it is a violation of k, that is -k.

So, in other words it says that violation of Clausius statement also is the violation of Kelvin-Planck statements. In a similar logic we will put in a reverse way that is let us see that we have a heat engine, that takes Q_H amount of heat, but no heat is rejected. So, for this no heat rejection means violation of Kelvin-Planck statement. So, I will put it as -k.

Now, while doing so we can also think about another refrigerator which takes Q_L amount of heat and rejects $Q_H + Q_L$ amount of heat to the high temperature reservoirs. Now, in this process if you join both heat engine and refrigerators. So, we say that then we have operation of refrigerator, then for combined system it takes Q_L heat, does W work and reject $Q_H + Q_L$.

So, this will imply violation of Clausius statement. From this we can say we started with violation of Kelvin-Planck statement we proved that violation of Clausius statements. So, in other words these two possibilities is never possible, when this negative statement is proved in other words there is a equivalence between Kelvin-Planck and Clausius statement, k is equivalent to C.

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Now, in another similar problem one of the corollary of Carnot cycle is that always reversible cycle is more efficient than irreversible cycle, when they operate between same two reservoirs. Now, to prove that we can say we assume that there is a hot reservoir which is at temperature T_H and there is a cold reservoir which is at temperature T_L and in between we can imagine that there is a reversible engine R and there is irreversible engine I.

Now, when I say reversible engines, the heat transfer is Q_H and heat rejection is Q_C and heat transfer from hot reservoir is Q_H and heat transfer from the to the low temperature reserve is Q_L . And the both the process is possible either we can give W_R amount of work to this reversible engine take heat Q_C from here and reject Q_H to here, otherwise in heat engine mode.

The engine can operate with W_R amount of work while taking Q_H amount of heat from the source and Q_C amount of heat to the sink. So, this is how a reversible engine operates, but in irreversible engines both this system is not possible. So, I can say it only gives in one mode that is we get W_I amount of work while taking Q_H amount of heat and rejecting Q_H ` amount of heat to this sink.

So, since these are reversible and heat reversible engines. So, to prove this fact that reversible cycle is more efficient then we have to recall Kelvin-Planck statement. So, this Kelvin-Planck statement in a mathematical form, we write that $W_{cycle} \leq 0$. Now, when

you apply this particular concept for a combined system, which includes this reversible engine and irreversible engines.

We can view this through a dotted line of this combined systems. We can write $W_I - W_R < 0$, because entire dotted line systems is nothing but is irreversible. So, we can write $W_I - W_R < 0$. So, in other words work transfer in an irreversible engine is always less than work transfer in the reversible engines.

So, this is the proof. But what we have asked for? Efficiency. So, you can rewrite this expressions $\eta_R = \frac{W_R}{Q_H}$; $\eta_I = \frac{W_I}{Q_H}$ and Q_H is same for both the cases and $W_I < W_R$. So, which means reversible engine has higher efficiency than irreversible engines.

Another concept that is first statement, second concept would be that when we say reversible and irreversible engines, if both are reversible engines then we can say $W_{R1} = W_{R2}$. So, assume that I is replaced with W_{R2} and R is reversible engines is replaced by W_{R1} . What we are trying to prove is that if the both the engines are reversible, then the efficiency of reversible engine R_1 is also equal to efficiency of the reversible engine R_2 .

Which means all the reversible engines operating between same two temperature limits have same efficiency, that is the second statement. First statement was reversible engine has always higher efficiency than the irreversible engines. So, these two statements are nothing but corollary of second law of thermodynamics or we can say Carnot theorem. So, with this I conclude this lecture for today.

Thank you for your attention.