

Basic Thermodynamics

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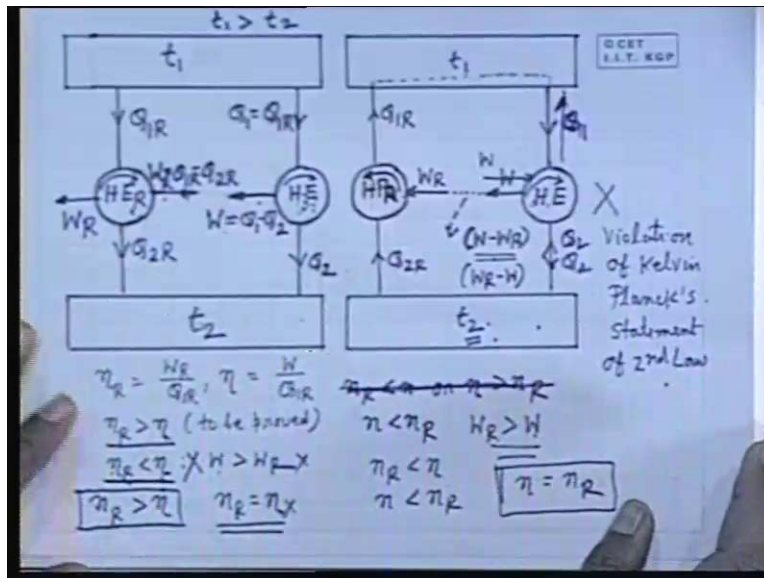
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Lecture - 07

Second Law and its Corollaries – II

I welcome you to this session of thermodynamics. In the last session, we discussed that if two engines operate between the same temperature limits, one is the temperature for heat addition and another is the temperature for heat rejection. If one is a reversible engine, its efficiency is higher than that of an irreversible engine. The corollary to it is that all reversible engines operating between the same temperature limits have the same efficiency. So these things we discussed and proved logically, but I think there was little confusion in its understanding through logic, that is why I will repeat this thing again, this proof.

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You see that, let there are two thermal reservoirs one is at temperature t_1 another is at temperature t_2 ; t_1 is greater than t_2 and we know that the two temperature reservoirs are essential for a heat engine to operate to develop work in a continuous cycle.

Let us consider one reversible heat engine, HE_R , which takes heat Q_{1R} , this subscript R is used for reversible engine from this high temperature reservoir, source t_1 , and it has to reject according to thermodynamics second law, the amount Q_{2R} to the thermal reservoir t_2 . While doing so, it develops a work W_R . Here also it is written W_R which is equal to, from the first law of thermodynamics that is energy balance Q_{1R} minus Q_{2R} . Second law tells that Q_{2R} cannot be 0, there has to be Q_{2R} that is the only restriction, but first law is always valid like this. We consider another heat engine, HE, working in a continuous cycle which is not a reversible heat engine, which draws an amount of heat Q_1 which we said deliberately for the proof equals to that of the heat taken by the reversible engine, that means Q_{1R} .

Obviously, since HE is an irreversible engine, it will reject an amount of heat Q_2 which is different from that (Refer Slide Time: 03:11 min). If the heat addition and rejections are same, the work quantity will be same by the first law. Out of these three quantities - heat addition, heat rejection, and work - two are independent and one is dependent by the conservation of energy. So, they cannot be same for a reversible engine. When it is an irreversible engine, they have to be different. That is the very first logic.

Let us consider that HE rejects Q_2 which is different from Q_{2R} and while doing so it develops a work W which equals to Q_1 minus Q_2 . Now we have to prove that, now what is eta, first of all? Definition of eta is what? Work for reversible engine, work developed by the heat added, η_R is equal to W_R by Q_{1R} . What is eta for this irreversible engine which is a natural engine? W by Q_{1R} . For both it is Q_{1R} since Q_1 has been set Q_{1R} . Now, we have to prove that η_R is greater than eta. To prove this, we first assume that η_R is less than eta. We first assume that and then we prove that this is not possible. How? If η_R is less than eta, then what we get? W_R is less than W , η_R is less than eta, Q_{1R} is same, so W_R is less than W , or we can write other way W is greater than W_R .

Now what we can do? Just see here. That is the most important thing (Refer Slide Time: 05:01 min). If HE_R is a reversible heat engine, all the processes can be reversed. Reversible heat engine means, that all the processes are reversible processes, so all processes can be reversed without any other change in the surrounding. According to the requirement of a reversible process or characteristic feature of a reversible process, that means, if we reverse all the processes of this heat engine it will act as a reversible heat pump, HP_R . If this reversible heat pump HP_R is allowed to operate then it will give the same amount of heat Q_{1R} in t_1 which we use to take while

acting as an engine. It will draw the same amount of heat Q_{2R} from the reservoir t_2 and it will demand the same amount of work which it delivered W_R to the surrounding in case of an engine. That means, this work and heat quantities interactions are equal in magnitude, but opposite in direction (Refer Slide Time: 06:07). That is the characteristic feature of the reversible heat engine. But if we reverse the heat engine, HE, it will work as a heat pump. Do not consider that as it is an irreversible heat engine, it cannot be made to operate as a heat pump. In that case, the directions of the heating directions will be opposite, definitely, the working directions will be opposite. It will draw work, it will give heat; in that case, the quantities will not be same. If it has to elevate heat or pump heat Q_1 to the temperature t_1 , it may not draw the work W from the surrounding, it may not draw or it may not take the heat Q_2 from this t_2 . That is the difference between a reversible and irreversible engine.

Therefore it is always useful for us to prove W is greater than W_R to make this reversible heat engine to operate in a reverse direction as a reversible heat pump, so that the quantities reveal the same magnitude, but in the opposite direction. Now, we have assumed that η_R , the efficiency of the reversible heat engine, is less than η , which means the work developed W by the irreversible heat engine is more than that of the work developed by the reversible engine W_R . Therefore in this case what we can do? We can couple these two, HP_R and HE so that the work developed from the heat engine can be utilized to drive the heat pump and in spite of that, we get a net amount of work W minus W_R as the work output.

Since these two heat quantities, Q_{1R} and Q_1 , are same, they can be joined by a diathermic wall (Refer Slide Time: 07:40 min). This reservoir t_1 is redundant. The working fluid of this heat pump HP_R will act as the thermal reservoir for the heat engine HE, and the working fluid of this engine will act as the thermal reservoir of this heat pump HP_R . The heat rejected by this heat pump will be delivered to this heat engine as the additional thing. Therefore, the entire system corresponds to a machine which interacts with only one thermal reservoir (Refer Slide Time: 08:09 min), a thermal reservoir of a single fixed temperature and developing a network which is not possible and violation of Kelvin Planck's statement. This is violation of Kelvin Planck's statement of second law.

Now, this, η_R is less than η , is not possible. Therefore there are two possibilities, η_R is greater than η or η_R is equal to η . Now the logic is that η_R cannot be equal to η , because an irreversible engine and reversible engine are different, so their heating interactions and

working interactions are different. So that when we reverse an irreversible engine, it will not reveal the same magnitude. It has to be a different engine than that of the reversible one, so we cut this logic, these two, η_{R} and η , cannot be equal either this will be greater or less than this. That means, these two engines will be different. So with this logic, we can prove that the only go is that η_{R} is greater than η . It is clear

Now the next step is that if both of them, HE_{R} and HE are reversible then they are of equal efficiencies. The next corollary to this theorem is that if there are number of reversible engines operating between the two fixed temperatures their efficiencies will be same, they cannot be different. How to prove it? Now the same thing, I am not going to a different drawing. Consider both the engines are now reversible. I am not giving this subscript 2_{R} W_{R} then it will be more congested, because then R_1, R_2 . Let us consider this Q_2 (Refer Slide Time: 10:02 min) is the heat rejected by another reversible engine. W is the work developed by another reversible engine. We consider two different reversible engines and we consider similar way that η_{R} is greater than η , that means efficiency of the reversible engine HE_{R} is greater than the HE .

Now in this case, I consider this machine, HE , also as a reversible, η is the efficiency of a reversible engine that is the engine at the right, right to me (Refer Slide Time: 10:27 min). Now, in this case, as I have shown, I can reverse the HE_{R} and prove that η_{R} is less than η is not possible. Now since HE is a reversible engine, in the next step, I can reverse this one and can get these quantities exactly in the same magnitude (Refer Slide Time: 10:45 min), because which I could not do in the earlier case, but now I can do it, it is also reversible. That means Q_1 and Q_2 .

Now when I assume this, η_{R} is greater than η , I reverse the one, HE_{R} . When I assume that, η_{R} is less than η or η is greater than η_{R} , then I reverse HE . If I reverse this one when η_{R} is greater than η then, what happened? to be proved? η_{R} is less than η , then W is greater than W_{R} .

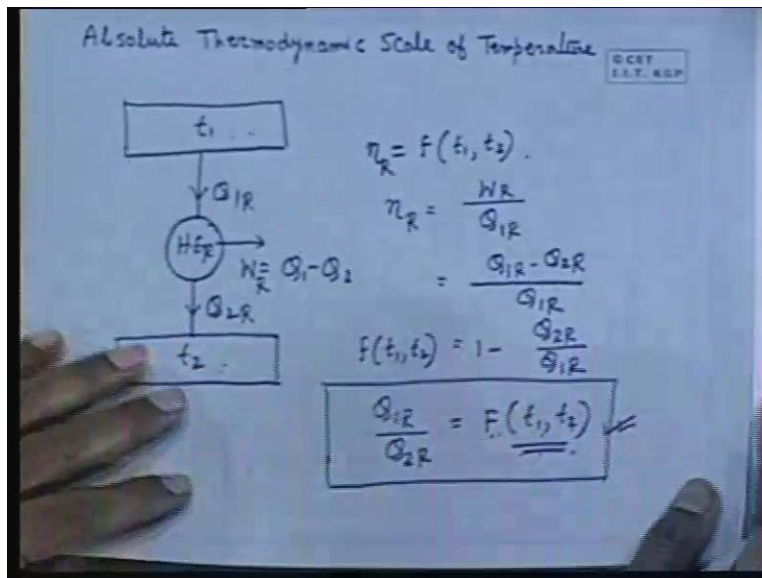
In that case, I will reverse HE_{R} . Now I will take η less than η_{R} , that means, W_{R} is greater than W . In that case, I will reverse the HE . First, I considered η_{R} is less than η that means W is more than W_{R} . So, I reverse the HE_{R} and we proved that η_{R} is less than η is not possible. Now I consider η less than η_{R} and I reverse, when we consider η less than η_{R} , means W_{R} greater than W , I reverse HE . Now here since, it is also a reversible engine at the beginning we have considered here the both are reversible. Then I can reverse it.

In the similar manner, I can prove there is a work because W_R is a more than W . Network W_R minus W coming out of these two, HP_R and HE . We can couple these two HP_R and HE and HE_R will remain as a heat engine. In that case, we can couple these two, HE_R and HE and we get the work, W_R is greater than W , which is violation of Kelvin Planck's statement. We proved neither η_R is less than η nor η is less than η_R . The only possibility is the η is equal to η_R . Try to understand the logic, so that if two of the reversible engines, then if I assume that. One of these engines for example, η_R is less than this, then I reverse this engine, HE_R and prove that this is a violation of Kelvin Planck's statement. In another case, if I consider HE is less than the engine HE_R , the efficiency of the engine, HE is less than HE_R then I reverse HE and I can prove that the equivalent one is a machine which interacts with a thermal reservoir at a single fixed temperature and developing a network violation of Kelvin Planck's statement. So, only opportunity is η is equal to η_R . So, I think logic is convincing, but it is not at all essential to memorize this thing, because nobody will ask us for this how did you prove it.

It is extremely important to know this theorem throughout the course of thermodynamics wherever you go even at the higher level. What is this theorem? If there are two thermal reservoirs at different temperatures t_1 and t_2 a heat engine will operate, it will take heat from the higher temperature reservoir, it will reject heat at the lower temperature reservoir and will operate in a continuous cyclic process and will develop work which according to first law of thermodynamics, will be the difference between the heat added and the heat rejected. This is number one.

Number two, if there is a reversible engine operating between the same temperature limits its efficiency is the highest among all other irreversible engines. Next is, all reversible engines have the same efficiency if they operate under the same temperature limits. The efficiency of reversible engine is unique when the temperature limits are prescribed. This acts as the maximum performance criterion or the ideal value for any natural engine. That means the efficiency of any natural engine, so at the same time you can think that is true that all natural engines will be having different efficiencies, operating between the same temperature limits. Even the maximum of these efficiencies is lower than the efficiency of a reversible heat engine operating between the same temperature limits.

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So with this, I will go to a very interesting thing that concept of absolute thermodynamic scale of temperature. Now, so far what you have read, if we have a thermal reservoir at any temperature t_1 , at any conventional scale. Let us consider Celsius scale and if there is a heat engine which is a reversible one H_{ER} . If there is a reversible heat engine and it takes Q_1 amount of heat. Now this is the block diagram of any heat engine. Now, we know that the efficiency of a reversible heat engine is fixed when the two temperatures are fixed. When the two temperatures are fixed the efficiency of a reversible engine is uniquely fixed. All reversible engines have the same efficiencies.

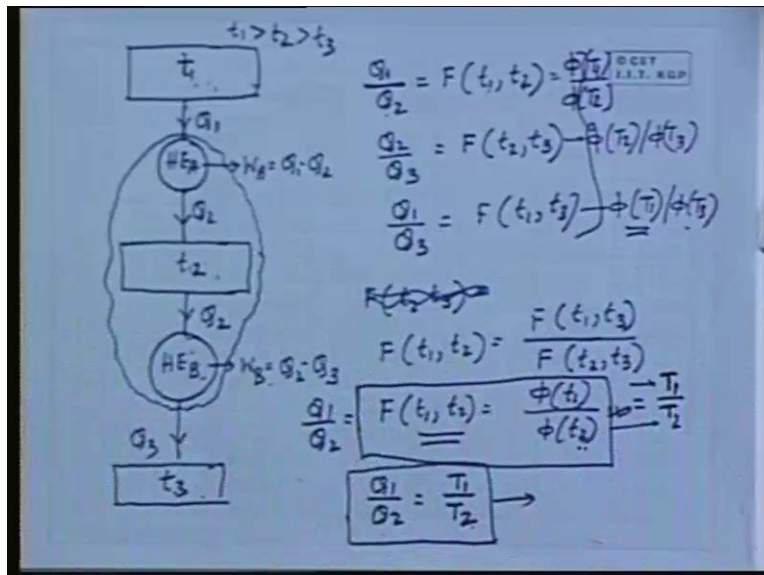
The second part of the Carnot's theorem which can be expressed mathematically that efficiency of reversible engine, I can give this η_{R} is therefore a function of these two temperatures, η_{R} is equal to function of temperatures t_1 and t_2 . Now, how do we define the efficiency? Now in all cases the efficiency is defined by the unique manner that is work done by heat added. Now I am not using the subscript R. Let us use the subscript R for your understanding, for a reversible engine.

Now the efficiency is same for reversible or irreversible engine. It is the work divided by the heat added. Similarly, the work is the difference between the two heat quantities, it is also same for both the engines, because it is the law of conservation of energy. There is no restrictions for friction and other conditions that irreversibility. Therefore, it is valid; you have to remember that. In this case, Q_{1R} minus Q_{2R} by Q_{1R} , so we can write 1 minus Q_{2R} by Q_{1R} . We see that, η_{R} is a

function of temperature t_1 and t_2 from which we can tell this is a very important conclusion. That the ratio of the heat interactions, **I write in this fashion it looks nice**, that heat added to heat rejected is some function of two temperatures. It is a very important conclusion that the ratio of heat added to heat rejected is a function of two temperatures (Refer Slide Time: 18:25 min), the ratio of the heat interactions Q_{2R} or Q_{1R} also. That means the ratio of the two heat quantities of interactions by the reversible heat engine are a function of temperatures only. This is valid only for a reversible engine. For irreversible engine, it is not so. This is because, for irreversible engines if t_1 t_2 are fixed, different irreversible engines will depict different efficiencies. It is because of the fact that all reversible engines have the same efficiency when t_1 and t_2 are fixed. The efficiency of a reversible engine is a function of the two temperatures only.

Now we will exploit this definition to define thermodynamic scale of temperature. At this moment, we do not know anything about this functional relationship of t_1 and t_2 . We can only express in an implicit form like this (Refer Slide Time: 19:11 min) that some function of t_1 and t_2 , unknown function, but let us utilize the concept of heat engine to go one step further to give some particular form of the function. What is that? We remember this definition and then we construct this.

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Let us consider a reversible engine, there are three temperatures. One, now here all reversible engines, I am not using subscript R, so one reversible engine is heat engine, HE_A which takes heat Q_1 from a thermal reservoir t_1 and rejects heat Q_2 to a thermal reservoir t_2 . t_1 small t_1 you give

because, now it is a conventional scale and let us consider a Celsius scale. Therefore, t_1 has to be greater than t_2 and HE_A develops a work W_A which must be equal to Q_1 minus Q_2 . Now we consider another heat engine, HE_B , which takes this heat Q_2 from this thermal reservoir, t_2 . This thermal reservoir, t_2 , is in contact with both the engines. So, this heat engine B takes this heat Q_2 from the thermal reservoir t_2 and delivers or rejects heat Q_3 at another thermal reservoir t_3 , where t_3 is less than t_2 obviously, and it develops a work W_B which is equal to Q_2 minus Q_3 .

Now, according to this relation that the ratios of heat interactions are the functions of the temperatures, we can write for the heat engine HE_A , Q_1 by Q_2 , all are reversible engines. So I am not writing the subscript R any more, is equal to what? Same, function of t_1 t_2 . Q_1 by Q_2 is equal to the functions of t_1 and t_2 . For the reversible engine HE_B , what it will be? Q_2 by Q_3 and it will be equal to the same function with the argument change, because here the temperatures are t_2 , t_3 . Same function F. If we consider these two heats, the heat rejected by the heat engine A and the heat taken by the heat engine B, now we can remove this reservoir, t_2 , because, we can make these two heat engines, A and B, connected. So that heat rejected by this heat engine A will be taken by this heat engine B. That means the working fluid of heat engine A will be the source or thermal reservoir for the working fluid of heat engine B and the vice versa.

So that we can get rid of this t_2 and we can connect this heat engines A and B. **I am not drawing this separate figure.** In that case, the combination of A and B (Refer Slide Time: 22:14 min), these are known as heat engines in series, will be an equivalent heat engine developing a work of W_A plus W_B and interacting with thermal reservoirs t_1 and t_3 . They are taking heat that means equivalent engine is taking heat Q_1 from t_1 and rejecting heat Q_3 to t_3 . For that equivalent engine also one can write Q_1 by Q_3 is the same function t_1 , t_3 .

Now this gives a further clue (Refer Slide Time: 22:44 min) to the type of this function. We may not know this function explicitly, but at least a type of the function is known the particular type how we can write this? If we see the left hand side, we can write this function of t_2 , t_3 , Q_2 by Q_3 . **is what? How to write it? I think it will be better if we write this way** Function of t_1 , t_2 that will be better becomes is equal to Q_1 by Q_2 , means what? Q_1 by Q_2 means Q_1 by Q_3 divided by Q_2 by Q_3 that means function of, **anyway we can write, there are various ways we can write this, is now very simple** t_2 , t_3 (Refer Slide Time: 23:36 min). That means, Q_1 by Q_2 is equal to Q_1 by Q_3 divided by Q_3 by Q_2 . Anyway we can write, Q_2 by Q_3 also the similar way this into this (Refer Slide Time: 23:47 min). So, if we write this way, then we see that the function should be such

that the function of t_1, t_2 must come out as the quotient of the two functions one is t_1, t_3 and other is the function t_2, t_3 . So, what is the alternative?

So, the alternative is this, it can only happen if and only if this function can be expressed as a function of t_1 and t_2 , like this, in terms of quotients (Refer Slide Time: 24:22 min). So that it cancels out, so this is very important. Where it comes from? That if this, function of t_1, t_2 is equal to function of t_1, t_3 by function of t_2, t_3 has to be true, this is only possible if this function and relationship, function of t_1, t_2 , is of this form, function of t_1 by function of t_2 . If it can be expressed by this, only we can get this relationship. Any of these combinations, Q_2 by Q_3 is equal to function of t_2, t_3 or Q_1 by Q_3 is equal to function of t_1, t_3 , will give like this provided, this becomes a function of t_1 by function of t_2 . Clear? Okay, very good.

Now this function of t_1 divided by t_2 is the base, first we started with that the heat interactions by a reversible engine between the two thermal reservoirs is a function of two temperatures. Then we came to a conclusion using two reversible heat engines in series that this function will have a shape like this, function of t_1 by function of t_2 , in terms of quotients. The type of function will be like these that functions of t_1, t_2 should be a function of t_1 divided by another function of t_2 , same function.

This function, T_1 by T_2 , is ultimately declared as the absolute thermodynamic temperature scale (Refer Slide Time: 25:40 min). This function itself, this is the function of temperature only, is defined to be the absolute thermodynamic temperature scale. Therefore, the absolute thermodynamic temperature scales are defined. So what is F_{t_1, t_2} ? It is Q_1 by Q_2 . Therefore, what we get? Q_1 by Q_2 is T_1 by T_2 . Now, we see all these functions are defined as the quotient, Q_1 by Q_2 is ϕT_1 by ϕT_2 . Similarly, Q_2 by Q_3 function will be ϕT_2 by ϕT_3 . So, this function, Q_1 by Q_3 will be a function of T_1 by function of T_3 . So, these functions are defined as the absolute thermodynamic temperature scale. The absolute thermodynamic temperature scale is declared to be that function of the temperature, this may be in any conventional scale which means, the basic definition of absolute thermodynamic temperature scale or absolute thermodynamic scale of temperature is this one, Q_1 by Q_2 is equal to T_1 by T_2 . It is such the ratio of these two temperatures is equal to the ratio of the heat interactions by a reversible heat engine.

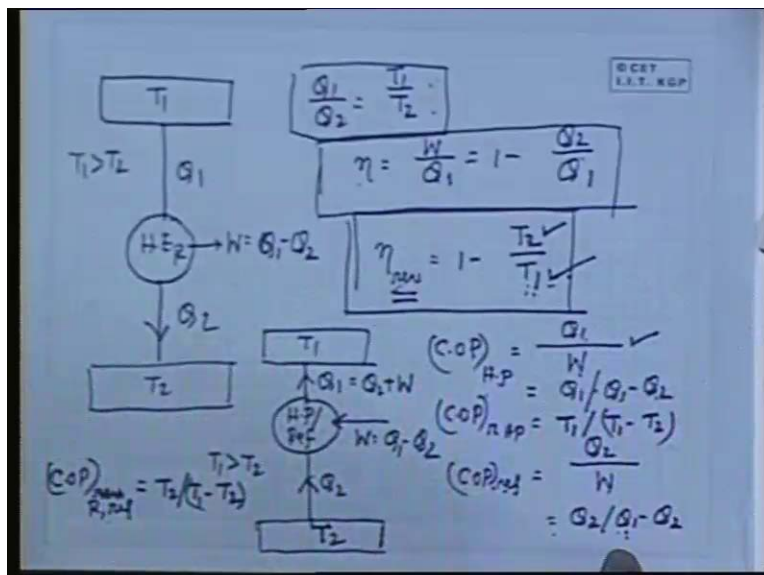
So immediate question comes, then how do we fix this temperature? How do we determine this temperature? We cannot have any reversible engine in practice, this is an ideal abstraction. Yes, its basic definition is like this, but afterwards we will see that the heat interactions, the ratio of

heat interactions by ideal heat engines can be expressed in terms of other properties, other measurable properties through which we can ultimately determine in practice the absolute thermodynamic temperature scale.

Afterwards, it will be shown that this absolute thermodynamic temperature scale which we are now defining following the second law of thermodynamics is exactly same to the ideal gas temperature scale which we have already read. Ideal gas temperature scale, they are identical. That will be proved afterwards, but now we learned that absolute thermodynamic temperature scale or absolute temperature on an absolute thermodynamic scale is such that their ratios equals to the ratio of the heat interactions by a reversible heat engine connected between these two temperatures. If a heat engine is connected between two reservoirs and if we want to designate the temperature of the reservoirs by absolute thermodynamic temperature scale as t_1 and t_2 then the ratio of t_1 and t_2 will be the ratio of Q_1 by Q_2 by the heat engine.

So, here also you see, like your internal energy, internal energy definition came through its difference, not the absolute value. The difference of internal energy is the heat and work interactions, net heat and work interactions by a system in a process. Similarly, the definition of absolute thermodynamic temperature scale has also come through its ratio t_1 by t_2 .

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Now, with this you can write that if there is a reversible engine, again the same thing, It will be a little boring at this moment, I denote the temperatures as the absolute thermodynamic and you consider a reversible engine, HE_R , and giving heat T_2 . We can write Q_1 by Q_2 is T_1 by T_2 . What

is the efficiency? W is Q_1 minus Q_2 . Its efficiency η is W by Q_1 is 1 minus Q_2 by Q_1 (Refer Slide Time: 29:34 min). This is valid for all engines. There is no restriction. It is the definition of efficiency and then this part, W by Q_1 is the definition of efficiency and this part, Q_2 by Q_1 , is the first law thermodynamics. But for a reversible engine, we can write it as 1 minus T_2 by T_1 which means that, the efficiency of a reversible engine working between two temperature limits T_1 and T_2 , where T_1 is the temperature of heat addition and T_2 is the temperature of the thermal reservoirs where heat is being rejected, is given by 1 minus T_2 by T_1 . This is the efficiency of all reversible engines which operate between the two temperature limits (Refer Slide Time: 30:22 min), T_2 as the temperature of heat rejection, T_1 as the temperature of the heat addition. Here, one question comes which will be cleared later on that in case the temperature is not constant during the heat addition and heat rejection process. A reversible engine not necessarily always has to take heat at a constant temperature. There may be a variation in temperature while heat is added and while heat is rejected. In that case this, T_2 by T_1 will be treated as mean temperature of heat addition that means 1 minus mean temperature of heat rejection by mean temperature of heat addition. This will be cleared afterwards.

But at the present moment we learn through a very simple case that, let us consider the temperature of heat addition is constant that means isothermal heat addition process, isothermal heat rejection process. This is the reversible heat engine therefore efficiency is 1 minus temperature of heat rejection by temperature of heat addition. But this is not true for an irreversible engine (Refer Slide Time: 31:21 min). We cannot write. We can write only this, because this relationship, Q_1 by Q_2 is equal to T_1 by T_2 , is not valid for an irreversible engine. For a heat pump or refrigerator, H_P or refrigerator, **I am not writing the full**, it is other way, it is giving heat, elevating heat to a higher temperature. Here, in the case of an irreversible heat engine, what happens? T_1 is greater than T_2 here also, in the case of heat pump or refrigerator, the same thing, T_1 is greater than T_2 . It draws work from the surrounding, in doing so which again according to first law W will be Q_1 minus Q_2 or Q_1 is equal to Q_2 plus W , it is written in this fashion so that this is manifested that work is being converted into heat. We write Q_1 is Q_2 plus W , it is a convention. Here we do not try W is Q_1 minus Q_2 , same thing we can write because it is the conservation of energy. So, this is the way as a heat pump or refrigerator works. So, COP of a heat pump is defined for any engine reversible or irreversible, as its performance that is how much heat is being elevated at high temperature divided by how much work it takes.

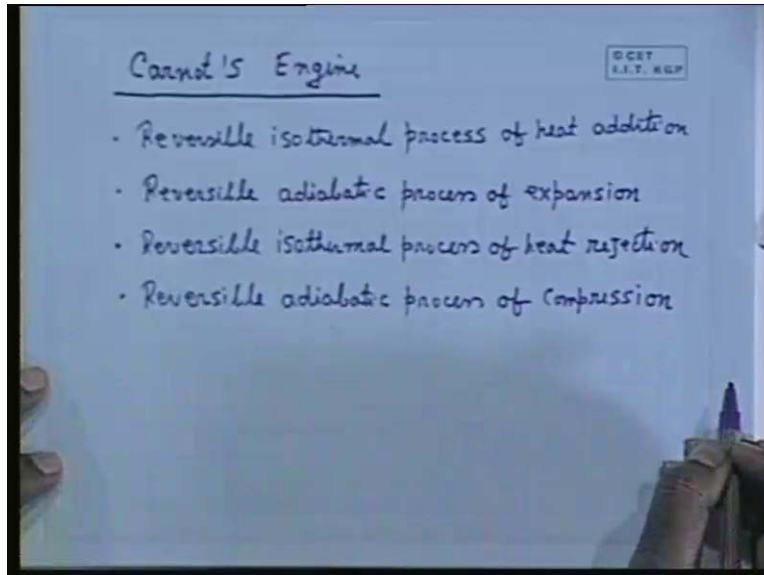
Similarly, COP of a refrigerator is, the denominator is the same numerator is changed because this is the heat, how much heat is being taken from the lower temperature divided by this, that is Q_2 by W . These two are the definitions. From first law we can write this, Q_1 by W is Q_1 divided by Q_1 minus Q_2 . Similarly, Q_2 by W is Q_2 divided by Q_1 minus Q_2 and one important relationship comes from this that COP of a H_p is one plus COP of a refrigerator. That is a very simple thing, I am not doing that because this is so simple because this is the definition (Refer Slide Time: 33:27 min) I already told earlier that COP of a heat pump is Q_1 by W , COP of a refrigerator is Q_2 by W . With reference to this figure, Q_1 is the heat elevator to higher temperature, Q_2 is the heat rejected taken from this lower temperature T_2 , lower temperature. So, a same machine works both as a heat pump also as a refrigerator. When our attention is here, at Q_1 , it is heat pump, when our desired objective is this one Q_2 taking heat from a lower temperature, it is refrigerator. COP of a heat pump is defined like this, then by the principle of first law of thermodynamics Q_1 by W is Q_1 divided by Q_1 minus Q_2 . So, these are the definitions.

COP of a heat pump will be 1 plus COP of a refrigerator. That means, COP of a heat pump minus COP of a refrigerator will be 1, because if we subtract Q_1 by Q_1 minus Q_2 from Q_2 by Q_1 minus Q_2 you will get 1, but now I come to a case of COP of a reversible heat pump, This will be T_1 by T_1 minus T_2 these Q values may be replaced by T values, because Q_1 by Q_2 is T_1 by T_2 . Similarly, COP of a reversible refrigerator is equal to T_2 by T_1 minus T_2 . That means, this definition of COP in terms of the temperatures are valid for reversible machine. That means reversible heat pump and reversible refrigerator like the reversible engines. This means that ratios of Q 's can be substituted in the ratios of the temperatures that are as simple as this.

Now, little bit of conceptual thing I will discuss that so many things we have learnt through a reversible engine, but how to conceive a reversible engine? First, Carnot's gave an idea that how we can achieve a reversible. **You know, things came like that.** So, many things were developed by physicists about the reversible engines and ideal performance and everybody knows that reversible process is the ideal process where the dissipation is nil. So a reversible cycle has the highest efficiency amongst all irreversible cycles. After knowing all these things then an engineer started thinking how to achieve an engine very close to a reversible engine. You know the reversible engine or reversible cycle is our ideal performance criterion. Therefore the thought process started evolving that how one can go very close to a reversible process. So, it was Sadi Carnot, he was basically an engineer and physicist, of course who first developed a concept by

which one can visualize in practice a reversible engine and that engine was named as Carnot's engine.

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Let us consider the Carnot's engine. This was the first concept of a reversible engine given by Sadi Carnot. He was a French, he was an engineer, a mechanical engineer and then converted in to a physicist. Carnot's engine consists of 4 processes. **Just to write first the processes.** One is reversible isothermal process of heat addition. He conceived a reversible isothermal process, because it is very simple to us to conceive. What is the criterion of a reversible heat transfer addition or rejection? That the temperature difference between the two system interacting heat will be 0, but this is not possible. Earlier also I told that a reversible process means there cannot be any process. Therefore, in a limit a reversible process can be thought if the temperature difference can be maintained infinite small.

It is always easy to conceive that both the system and its surrounding maintain the same dT throughout and to do it both the system and the surrounding has to be at constant temperature. Therefore, it is always better to conceive an isothermal process of heat transfer to be a reversible heat transfer process. Otherwise, what will happen? If you consider the process to vary with the temperature which happens with a finite body when it gives heats or loses heats its temperature varies then always we will think of an infinite number of reservoirs as I explained earlier for reversible heat transfer process. Therefore, always system and surroundings will have to be in contact with each other through an infinite small temperature difference. That is the reason for

which in isothermal process of heat interactions heat addition or rejections had been thought of as a reversible heat transfer process. Nevertheless, the process where the temperature varies is not a reversible heat addition heat rejection process. Many students or even not students many people have these confusions that always think that for a heat addition process to be reversible or heat rejection process to be reversible it has to be isothermal. No, this is because of this fact that it is easy to conceive. Carnot initially thought that the process of heat addition should be isothermal and reversal. Isothermal process also does not be in reversible. These are the concepts I am telling in thermodynamics, because all these things are written in the book. That for example two systems are there heat is being transferred from one to other and they are maintaining same temperature. System temperature is T_1 and the surrounding temperature is T_2 and while receiving heat, system is at constant temperature T_1 surrounding is at constant temperature T_2 , but there is a finite gap, T_1 minus T_2 , it is not a reversible heat transfer process.

Requirement of a reversible heat transfer process is ΔT between the system and this surrounding should be as small as possible. Whether the system remains isothermal or not, that is not the criteria. But if system remains isothermal, surrounding has to remain isothermal. Otherwise ΔT , small ΔT will not be maintained. This is a very useful concept. Next process is a reversible adiabatic process of expansion. When I will come to different cycle, then I will explain how the reversible heat addition through varying temperatures is possible. What is adiabatic? Do you know this terminology adiabatic?

Sir, no heat interaction.

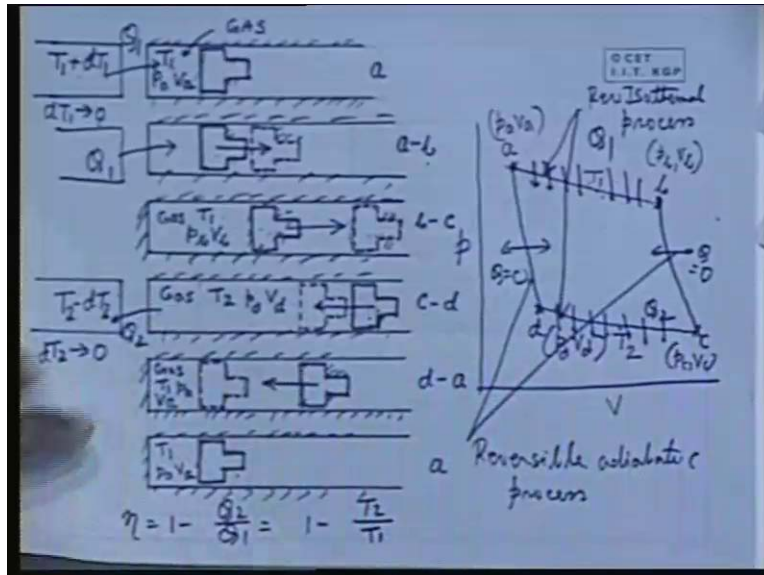
Adiabatic process is a process during which there is no heat interaction between the system and the surrounding that means the entire boundary of the system is made insulated. Then reversible isothermal process of heat rejection. According to second law thermodynamics there should be a process of heat because only adding heat one cannot get work in a continuous cyclic process. All the heats cannot be converted into work in a continuous cyclic process. What is the next one?

[Conversation between student and professor - Not audible (00:41:28)]

Reversible adiabatic process of compression. Therefore, we see that Carnot's engine comprises 4 reversible processes. It is a reversible engine; one is reversible isothermal process of heat addition, reversible adiabatic process of expansion, reversible isothermal process of heat rejection and reversible adiabatic process of compression (Refer Slide Time: 42:02 min).

Expansion means, where pressure is reduced volume is increased, compression means, where pressure is increased and volume is reduced. So, 4 processes

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Now, this is conceived in practice like this (Refer Slide Time: 42:19 min). Let us consider stages like that, a piston and cylinder which is easy to conceive in practice which contains a gas inside it at a temperature T_1 and a pressure $P_a V_a$ which refers to a state 'a'. Temperature T_1 , I have not given the suffix 'a' deliberately $T_1 P_a V_a$ these are the properties there may other many properties you know number of independent properties are fixed other properties will be fixed. P, V, T are three fundamental properties always. That is why, people represent with these three properties. These are the three fundamental measurable properties at a state 'a'.

What we do at this stage? We take a body or external heat source whose temperature is, it should be theoretically T_1 for a reversible heat addition. First process is isothermal reversible heat addition, but it cannot be made. We take a very small dT_1 , where dT_1 tending to 0.

What we do? We insulate the entire lateral surface of the piston and we just make it close contact through a diathermic wall with its (()) (00:43:34) external heat source. So that, some amount of heat, let Q_1 flow to it. Now, thing is that, if we want to make an isothermal heat addition whenever heat will be added the temperature will go on increasing. To make this temperature T_1 constant, an infinite small temperature difference always exists for a reversible heat transfer; we have to slowly push the piston so that the gas expands. That means, as if heat is added temperature is going to rise, and at the same time, if we expand the gas slowly, the temperature

will fall. That means it can make an adjustment of constant temperature process. Afterwards, we will see for an ideal gas internal energy is the function of temperature. That means the amount of heat added is coming out as the amount of work done, so that the change in internal energy remains same and the temperature remains same. But at this movement, I think it is not proper to say that because we are not sure that when that internal energy will remain same, temperature will remain same or not.

But you can say that, if you expand the gas in an adjusted manner you can make it possible an isothermal process of heat addition. So that a stage 'b' comes where the piston moves a little distance in this side (Refer Slide Time: 44:48 min) and some amount of heat by that time is added to this at a constant temperature T_1 . This is the process a to b. Therefore what happens at this stage b here, the gas is at a T_1 . Now I disconnect this heat source and at different pressure P_b and V_b , because the gas has expanded, but during this time some amount of heat has been added. This is the state b, at this position the gas is at state b (Refer Slide Time: 45:21 min). I have not written that. This is the process a to b where the heat has been transferred. During this process isothermal heat addition, Q_1 has taken place. That means in this process, I should have drawn this also, the body is there at T_1 plus dT_1 .

At this movement what we do? We remove the isothermal heat addition and we insulate the entire lateral surface of the piston as if it was there insulation (Refer Slide Time: 45:46 min). That means what we do? We additionally insulate this front portion, the head of the cylinder. That means, the total cylinder is insulated and we make the piston also insulated. Then we allow the piston to expand the large expansion process. In this way, the piston expands and comes through a stage c, for example; here this is the stage c. When it comes here, the gas is at a different volume and pressure which is P_c and V_c which has not been shown here. Then what happens? This insulation is okay then the piston is again brought in contact to a another body or thermal reservoirs whose temperature is little less than the T_2 , T_2 is the temperature at the state c whose temperature is little. So that, **some heat is**, dT_2 tending to 0. At the same time, for a heat rejection process to be isothermal we will have to slowly move the piston this side, towards the thermal reservoir, so the gas inside is compressed, so that if any cooling effect due to this rejection of V_d is being counter way and the temperature is maintained constant. So the piston is moved slowly to some distance here. This is the end of this process c-d where the piston is at point d, then this temperature remains T let T_2 , then what we do?

We just insulate the entire cylinder and remove this reservoir and again compress the gas to its initial state where it was (Refer Slide Time: 47:43 min), so the last state and the initial state is same that means the last state is T_1, P_a, V_a , this is all insulated condition. Now, this case piston is also insulated, this is all insulated condition. Piston is insulated from the beginning. Only from one side the heat addition or heat rejection was taking place. If we draw this diagram in a cyclic in a thermodynamic coordinate diagram, the cyclic process, let us consider p as the ordinate and V , we see then it will be easier to understand. In the first process, a to b the system was at some state a here. This, the situation I have explained just now, is an isothermal heat addition process. That means heat is added while temperature remains constant and to maintain so, the piston has to move outward little bit. That means gas has to expand little bit to counter way the heating effect of the gas. So, we can qualitatively draw this curve like this (Refer Slide Time: 48:50 min), there is a little expansion that is 'b' is like this. This is the condition, this is the b that means this is a, where a is $p_a V_a$ coordinate and this is b where the coordinate is $(P_b V_b)$, where P_b is less than p_a and V_b is more than V_a . Then there is a reversible adiabatic, now, what is reversible adiabatic expansion?

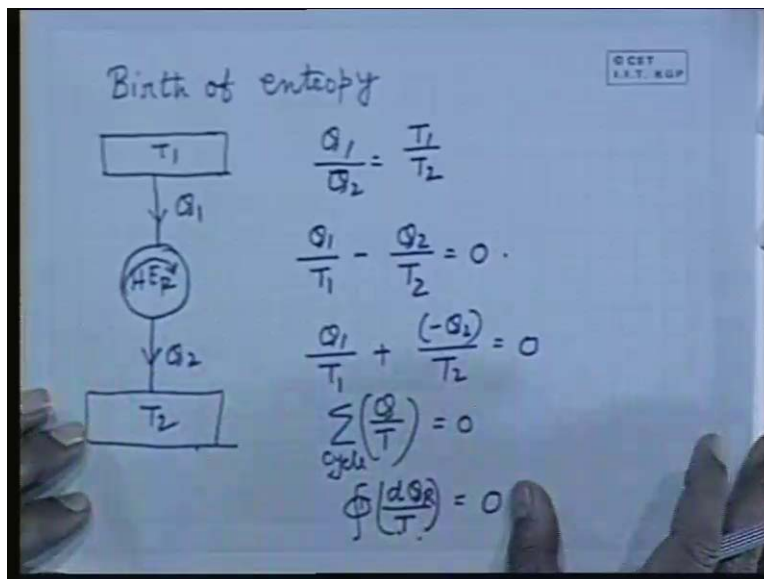
That is the piston has to move very slowly. Here, the heat transfer process is also extremely slow because (Refer Slide Time: 49:22 min) the temperature gradient is infinite small dT_1 tending to 0. When you stop this, make the entire system insulated or adiabatic, then piston has to move very slowly outwards for the expansion process because, why it is slow, to get rid of the mechanical friction as the mechanical dissipative effect, there is no heat transfer, there is no thermal dissipation, or thermal irreversibility. It is free from irreversibility. That means very slow and quasi equilibrium movement as we have given the example the piston moves as if there are number of weights there and if we slowly remove the weights in small amount, in that case what will happen? The piston will slowly move, very gradually, so that each and every intermediate steps can be conceived of a equilibrium state, the quasi equilibrium expansion.

This can be represented by a steeper graph (Refer Slide Time: 50:14 min). Here c, we do not know the exact state, we can only show the qualitative drain, because until and unless we know the equation between P and V which we can only know if we know the property relations of the gas. Otherwise, we cannot find it only qualitatively we can show. This is the process c. Then at c, what will happen? Again, there will be a heat rejection at constant temperature. To do that, piston has to move outward that means compress the gas to counter way any cooling effect of the

gas to maintain an isothermal process of heat rejection. This is a similar compression process which ends at d. Here, at d, the coordinate is $p_c V_c$, here, at c, the coordinate is $P_d V_d$, that means this is the stage here when it comes from c to d here then from d to a again, a reversible adiabatic compression (Refer Slide Time: 51:09 min). This abcd represents this reversible cycle known as Carnot's cycle in the PV diagram, which consists of two isothermal processes. This, a to b, is the isothermal process where the temperature remains T_1 , this, c to d, is the isothermal process where the temperature remains T_2 . That means temperature at a and temperature at b is same and equals to T_1 . Temperature at c and temperature at d are same and equals to T_2 .

What is the interesting thing is that? Here, these two processes there is no heat interaction, heat is only coming in this process, a to b, by an amount Q_1 (Refer Slide Time: 51:45 min) and heat is being rejected in this process, c to d, by an amount Q_2 . These two are the reversible isothermal process and there is no heat interaction Q is 0. That means these two processes are reversible adiabatic process. One is an expansion process bc another is a compression process and these two process are reversible isothermal process (Refer Slide Time: 52:24 min). In this way one can conceive of a reversible engine which was conceived first by Carnot's and it is known as Carnot's engines which consist of two isothermal reversible isothermal processes, one of heat addition another of heat rejection and two reversible adiabatic processes. Here also, eta is equal to 1 minus Q_2 by Q_1 and that is equal to 1 minus T_1 by T_2 as we know the ratio is like this.

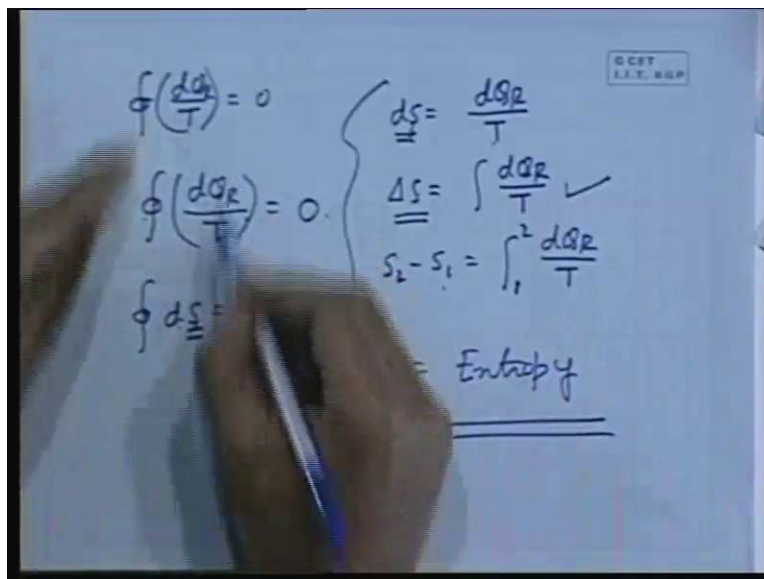
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Now, I will come to the very important concept of entropy, birth of entropy. Rather I will write like that. How do you get it? Now we know that if there are 2 reservoirs at an absolute temperature T_1 , and another at an absolute temperature T_2 and if a reversible heat engine operates between these two temperatures taking heat Q_1 and heat Q_2 , what we know? We know that, in a cycle, cyclic representation Q_1 by Q_2 is equal to T_1 by T_2 .

I will start with a very simple thing. Q_1 by Q_2 is equal to T_1 by T_2 . This we know because this is the definition of absolute thermodynamic scale of temperature. We can write this Q_1 by T_1 minus Q_2 by T_2 is 0. Then we can write Q_1 by T_1 plus (minus Q_2) by T_2 is 0. Why is this way? Because, Q_2 is the heat rejection of which the conventional sign is negative. If we take heat addition as a positive, one as a positive another as a negative. Otherwise, how I will signify or imply the sign conventions. So convention is that, this Q_1 is positive this Q_2 is negative. This can be written as sigma of quantity by T over a cycle is 0 which can be written in this form. This is the cyclic integral (Refer Slide Time; 54:47 min), always we have done this earlier. The cyclic integral of dQ by T is equal to 0. A very simple case where I consider a constant temperature thermal reservoir T_1 for heat addition, a constant temperature thermal reservoir T_2 for heat rejection and from very simple case I can immediately conclude that cyclic integral dQ by T is equal to 0. This is nothing, but the definition of absolute scale of thermodynamic temperature, or absolute thermodynamic scale of temperature. So, cyclic integral dQ by T is equal to 0.

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Now henceforth, we will have to remember one thing that if cyclic integral of any parameter is 0, here the parameter is dQ by T , if cyclic integral of any, but this cyclic integral, look, this is for a reversible engine, so we will have to give a R (Refer Slide Time: 55:38 min). This represents a reversible engine dQ_R that means cyclic integral dQ_R by T . Many book gives this R here (Refer Slide Time: 55:54 min) to represent this cyclic integral of dQ by T in a reversible cycle because, this Q_1 by Q_2 is equal to T_1 by T_2 is only valid for irreversible cycle. This equation I cannot use for any other cycle. Therefore, dQ_R by T , this quantity I prefer to give it here because, why I am telling, because I will be proving in a different way immediately, because today we do not have to prove in a very tortuous manner.

So, you know whenever we have cyclic integral of any parameter is 0, we can express that parameter as a differential of a point function. Why? Because cyclic integral of a point function is a 0, so that if I define a point function S , so that the differential of this point function, dS is dQ_R by T . Cyclic integral of any parameter is 0 means that parameter represents the differential of a point function, because differential of a point function is always 0. Cyclic integral of a differential of a point function is 0. Therefore, if I represent this dQ_R by T parameter as a differential of a point function S , then I can write dS is dQ_R by T by this analogy. Because, since cyclic integral of this dQ_R by T is 0. I know cyclic integral of any point function, differential of point function, dS is also 0. So, I can write this, so that point function can be written in this term so that differential of this point function, dS is equal to dQ_R by T , equals to the cyclic integral of dQ_R by T . This is the definition of the entropy.

If we integrate this in a finite change of S point function or this change in point function between two steps will be 1 to 2 (Refer Slide Time: 57:42 min). I will not speak of entropy, I will tell a point function S , so that it's differential equal to dQ_R by T where dQ_R is what? dQ_R is not a differentiable quantity. It is an infinite small amount of heat addition to a reversible engine and if we divide it by T , it becomes a differential way which means mathematically 1 by T is acting as an integrating factor.

[Conversion between student and professor - Not audible ((58:05 min))]

As an integrating factor. That means 1 by T into dQ_R becomes dS that is a point function. If we express the finite change in this point function, we will integrate this side, simply school level mathematic. If I want to express this point function as a difference between the two specified states 2,1. I will write the same thing with the limit 1,2. This point function S is now I declare as

entropy in my list of properties (Refer Slide Time: 58:37 min). Because any point function is a property which is a state variable of a system. This way, the birth of entropy comes into picture. So, therefore the change of entropy is the quantity dQ_R by T in a reversible process, because all are valid for a reversible process. So therefore, this is the basic definition of entropy.

Well, any problem? No problem. So, I think time is almost over so that I must stop it here.

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Summary

- The concept of absolute thermodynamic scale of temperature originates as a corollary of Carnot's theorem in relation to the thermal efficiency of a reversible heat engine.
- The absolute thermodynamic scale of temperature is defined as

$$\frac{T_1}{T_2} = \frac{Q_1}{Q_2}$$

Where T_1 and T_2 are the temperatures of two thermal reservoirs in absolute thermodynamic scale and Q_1 and Q_2 are the respective heat exchange between the reservoirs and the reversible heat engine.

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- If the temperature of two thermal reservoirs are defined in absolute thermodynamics scale as T_1 and T_2 , where $T_1 > T_2$
 - Then, the efficiency of a reversible heat engine (known as Carnot's engine) working between the two reservoirs is given as $\eta_{rev} = 1 - \frac{T_2}{T_1}$
 - The coefficient of performance of a reversible heat pump working between the reservoir is given as

$$cop_{rev \text{ heat pump}} = \frac{T_1}{T_1 - T_2}$$
 - The coefficient of performance of a reversible refrigerator working between the reservoirs is given as

$$cop_{rev \text{ refrigerator}} = \frac{T_2}{T_1 - T_2}$$

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- A direct outcome of the definition of absolute thermodynamic scale of temperature is the definition of a thermodynamic property 'entropy'.
- Entropy is defined in terms the of change in its value as

$$dS = \frac{\delta Q_{\text{rev}}}{T} \quad (\text{for an infinitesimal process})$$

$$\Delta S = S_2 - S_1 = \int \frac{\delta Q_{\text{rev}}}{T} \quad (\text{for a finite process between two states 1 and 2})$$