Chemical Principles II

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Module 04
Lecture 26

Carnot Cycle and Entropy

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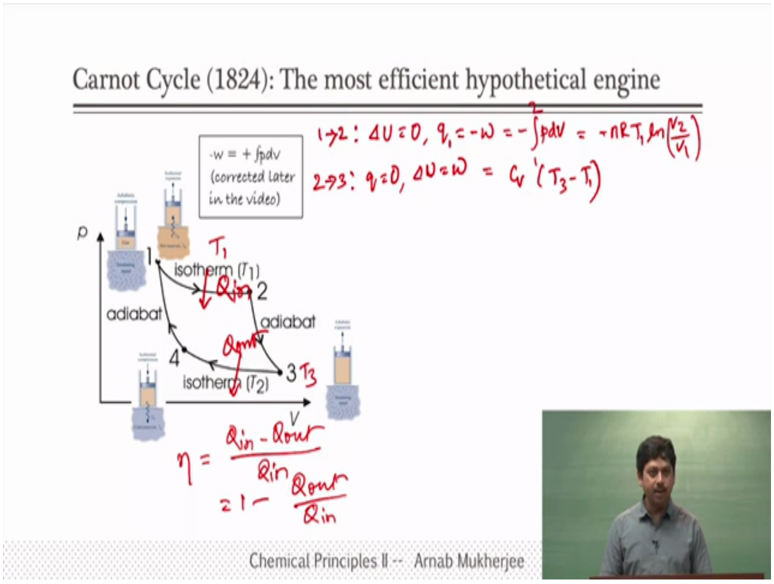

We are going to talk about the most efficient engines called Carnot Engine. So notice that timeline 1824, so we talked about in the history of thermodynamics and all. In that we discussed about steam engine coming around 1796 and all that, right? Many other things but even we talked about Papa's Engine around 1600 some time, I do not remember exactly. So Papa's Engine was, they digested was something where digested where was getting heated up, it is like a pressure cooker, heat and then it was cooling down. Like the two-step process, heating and cooling.

However during the industrial revolution time people were trying to make more efficient engines and they did not have the idea of any of the laws of thermodynamics, not even the first law, not even zeroth law, not the second law either. People were only concerned about designing efficient engine. I will talk about that by then two types of engines were already known, one is steam engine, maybe many more but majorly important engines are like steam engine by James Watt and the second one was Stirling engine.

Stirling engine came around 8 years before this time, we will talk about that. So steam engine and stirling engines are both called external combustion engine. Our cars are internal combustion engine, you put the fuel inside the car, combustion happens inside and that heat drives the car. However for steam engine your combustion happens outside, you generate the heat outside and that pushes the engine and piston and then it moves. Stirling engine is also an external combustion engine and that can we show as an example.

However this Carnot engine were not any real engine, it is a hypothetical engine. Carnot showed that this engine will have the maximum efficiency and we are going to see that in how, meaning what is the construction of that engine. It came even after the stirling engine. So what Carnot did is that, he said okay, I have to create a cyclic process, so he created a cyclic process, no laws of thermodynamics right now is there. He created a cyclic process in which just like Papa's engine but little bit more complicated not just heating and cooling but the process is done in such a way that first step will be an isothermal expansion process from 1 to 2.

So this is the diagram that every step what happens. And this isothermal expansion process means it must be connected to a reservoir having the temperature T1 and expansion happens. Remember isothermal expansion, you know that in isothermal expansion temperature does not change. If temperature does not change means internal energy does not change which means that, but 1 to 2 there is some work done, which means heat must be getting input to the system. So the heat comes in during this step, that is followed by an adiabatic process from 2 to 3. Since it is an adiabatic process there is no heat going in or coming out which means the internal energy of the system is getting converted to the work.

Now you know that in internal energy when it changes, temperature changes. So the temperature drops from 2 to 3, let us call that as T3 temperature and that temperature now again an isothermal compression is done. Now in isothermal compression what happens is that again your internal energy is 0, change is 0, therefore heat is proportional to the work, it is equal to the work. And since now work is, it is now work done on the system and therefore the heat must be going out of the system. So let us call that as Q out and lets us call that as Q in. And then from 4 to 1 is just exactly the opposite of 2 to 3 and no heat exchange happens.

So immediately you see the efficiency of this engine will be the work done by heat input which is work done will be Q in minus Q out by heat input is Q in, so it will be 1 minus Q out by Q in. So this is exactly that kind of engine that we are talking about, is not it? Just now with the cyclic process. The circle that I was drawing is to denote a cyclic process. And how to achieve a cyclic process is through this combination of isothermal and adiabatic processes.

Now let us work out the efficiency of this particular engine and step by step. And all the required formulations are already done in the first law of thermodynamics part. So let us do that. So for 1 to 2 it is an expansion process. And you know that delta U is equal to 0, therefore Q will be, or Q1, so Q1 equal to minus w and minus w you know as pdv, this we already know going from 1 to 2. And you already know that what is the value of this one, right? P is nRT by V, so minus nRT1 ln V2 by V1.

We have already derived the work done for an isothermal process. Expansion and contraction we do not have to worry, isothermal process final value to initial value, minus nRT ln. Second step, 2 to 3, 2 to 3 Q is 0 or we can say, okay, Q is 0. So work done is equal to change in internal energy and which means it is equal to Cv d T, so T3 minus T1, is it understandable? Cv d T is the work done. We are not using the complicated adiabatic PV work, it is just very simple by using Cv d T formula. We can do that. And another thing we know that, since 2 to 3 is an adiabatic process, in adiabatic process there are this formula, right?

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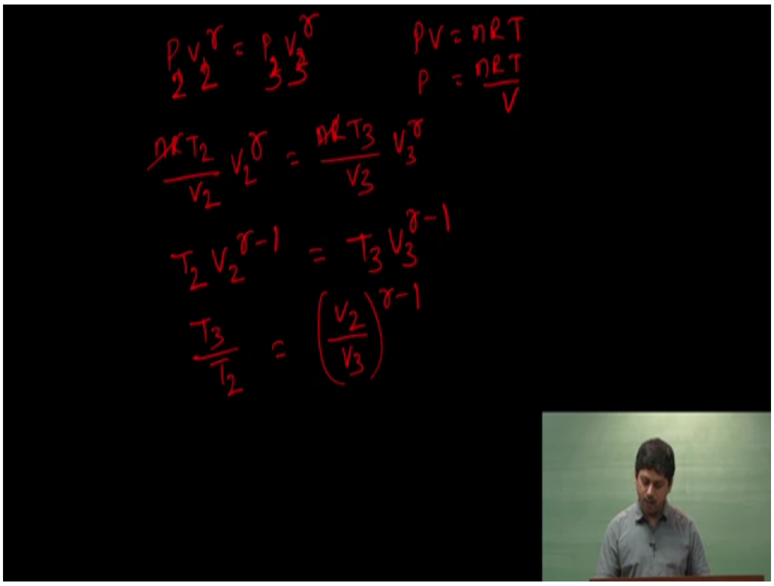

We know that in adiabatic process P1V1 to the power gamma is equal to P2V2 to the power gamma, right? And since it is 2 to 3 process let us call it 2 2 3 3. At the same time we know that PV equal to nRT, that also we know. Now if we know that, then we can always replace P by nRT by V. So let us replace that, nRT2 by V2 into V2 to the power gamma equal to nRT3 by V3. I am just substituting the P, V3 to the power gamma. nR, nR cancels. So T2 V2 to the power gamma minus 1 is equal to T3 V3 to the power gamma minus 1.

There is another formula of an adiabatic process which means that if I take the ratios of the temperature, into adiabatic processes, T3 by T2 will be V2 by V3 to the power gamma minus 1, correct? This we are going to use, so therefore I have just derived this one. So remember T3 by T2 is V2 by V3, just the opposite of that, to the power gamma minus 1. Now let us go back to that.

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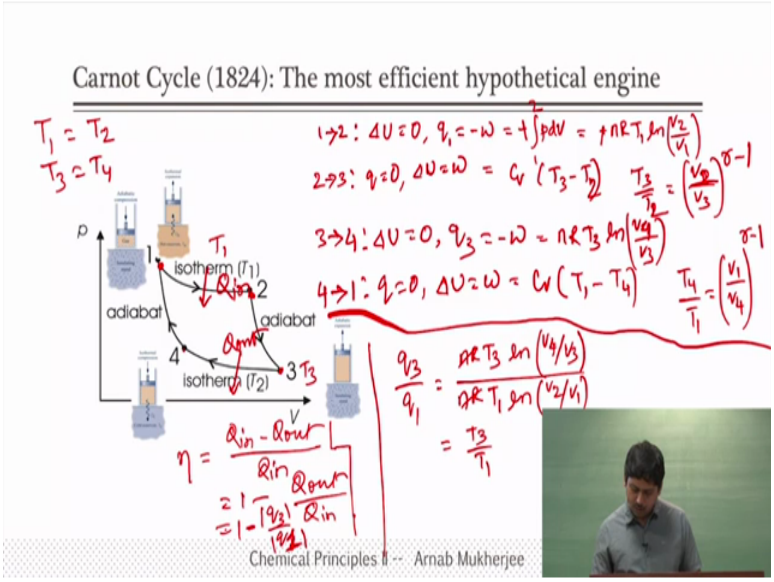

So which means we are going to talk about 3 and 2, so T3 by T1 is going to be V1 by V3 to the power gamma minus 1. 3 to 4, same as 1 to 2 but just the opposite, so delta U equal to 0, let us call that Q3 because that is the step where Q changes, equal to minus w again. See, I am not changing the sign or anything because automatically it will become positive or negative based on this one. Minus w is plus PDV, I am sorry, it should have been, minus w is always plus PDV, so it is plus nRT not minus.

Okay, w is by definition is minus PDV, so minus w is plus PDV. So it is plus nRT. Minus w, so here it will be nRT3 ln is going from 3 to 4, so V4 by V3. Third step is done. Fourth step, just opposite of 2 to 3, Q equal to 0, delta U equal to w, equal to Cv T1 minus T4. Another thing is that in the second step 2 to 3, it will be T3 minus T2. Of course, we know that T1 is equal to T2 and T3 is equal to T4, that we know because they are isothermal processes. So the temperature in 1 and temperature in 2 is the same, temperature in 3 and temperature in 4 is same because they are isothermal processes, we know that.

And we know the relation between temperature of T3 and T2 and T4 and T1. For example, here we can write that, T4 by, so in the second step instead of it will be T2 not T1 because we are talking about 2 and 3, that is why. So that I have corrected now. So now T4 by T1 is equal to V1 by V4 to the power gamma minus 1. We have done all the steps of the Carnot Cycle. So now if we have to calculate the efficiency, we know that this efficiency will be 1 minus Q3 by Q2, correct? Let us put it mod. Why? Q out is Q3 and Q in is Q1.

So we have to calculate Q3 by Q1 then. So let us calculate that. Q3 by Q1 is equal to, what is our Q3? We have it somewhere, it is nRT3 ln V4 by V3. And Q1 is nRT1 ln V2 by V1. nR cancels, so equal to T3 by T1. Now what is the relation between V4 and V3, that we have to see.

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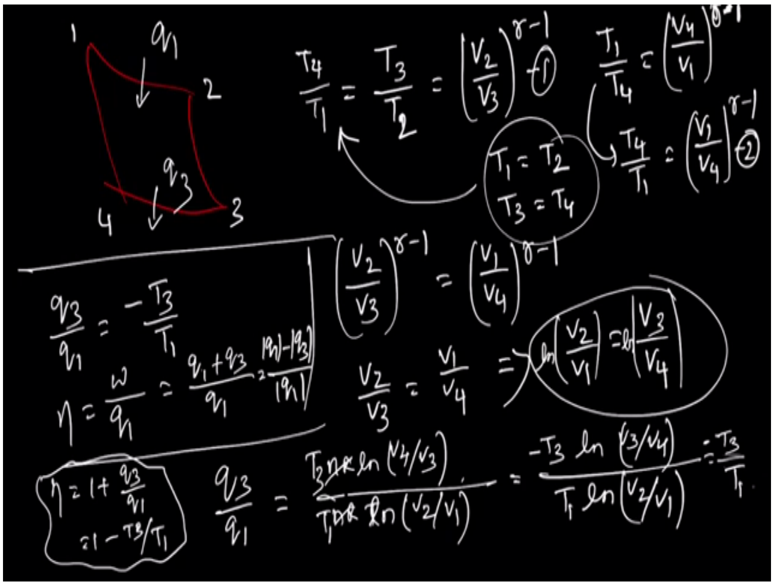

So 1, 2, 3, 4, So T3 by T2 is V2 by V3 to the power gamma minus 1. And T1 by T4 is V4 by V1 to the power gamma minus 1. This I know. Now we also know that T1 equal to T2 and T3 equal to T4. So therefore we can write same for this one, T4 by T1. So you see T4 by T1 is coming out to be V2 by V3 to the power gamma minus 1. And T1 by T4 is just the opposite, so from here we can get T4 by T1 is just V1 by V4 to the power gamma minus 1. So from here we get this and from this relation we get that.

Now we are equating then, we can equate equation 1 and equation 2 to get V2 by V3 to the power gamma minus 1 is equal to V1 by V4 to the power gamma minus 1. Are you following? Gamma minus 1 cancels, so V2 by V3 is equal to V1 by V4 or V2 by V1 is equal to V3 by V4. This result we are going to use. So what was the Q3 by Q1? So here this Q1 and this is Q3, right? We remember that what was the Q, Q was the work done, so what was nRT1 ln V2 by V1, and no sorry, it was V4 by V3, I will just, can I use this?

You can use this, good. Q3 by Q1 we are going to write, so what is Q3? nR ln V4 by V3. What is Q1? nR ln V2 by V1. nR cancels, oh, and nRT, we have T3 here and we have T1 here. So you see that it is T3 ln V4 by V3, so I can write minus T3 ln V3 by V4 and I can write T1 ln V2 by V1. Now you see since V2 by V1 is same as V3 by V4, ln of that also will be same which means that ln V3 by V4 is equal to ln V2 by V1 which is giving us minus T3 by T1. So what you got finally? I can write here. We got Q3 by Q1 is equal to minus T3 by T1.

Now what is the significance of this? One thing I just would like to tell you, when we calculated Q3 and Q1 and all, we did not care about the sign. We just simply calculated based on initial point to final point, so which means when you calculate the efficiency of engine eta, efficiency says that work done by heat input. Our heat input is Q1, work done is what? Heat input minus heat output. But heat output is minus only when we take the heat to be positive quantity or modulus of the heat. If we do not take the modulus of the heat, it is simply the overall change in the heat.

Since we did not care about the sign at all, it will be Q1 plus Q3 by Q1. People we have confusion at this stage. I would like to tell you that the above one, the numerator is such that the overall heat will be less than Q1 because Q3 is a negative number. So we are going to check the overall change in the heat. So change in the heat when you calculate it, we calculate just the heat the way we normally do and it turns out to be something minus something.

So you can say that it is actually Q1, modulus of Q1 minus modulus of Q3 by modulus of Q1. So the point that I would like to tell you is that is overall change in the heat divided by heat input. And now we know that since it is Q1 plus Q3 by Q1, which is that means our eta is 1 plus Q3 by Q1 which is 1 minus T3 by T1. And this is the most important result of the Carnot Cycle, that the efficiency of the engine is 1 minus T3 by T1. So I will go back and write that.

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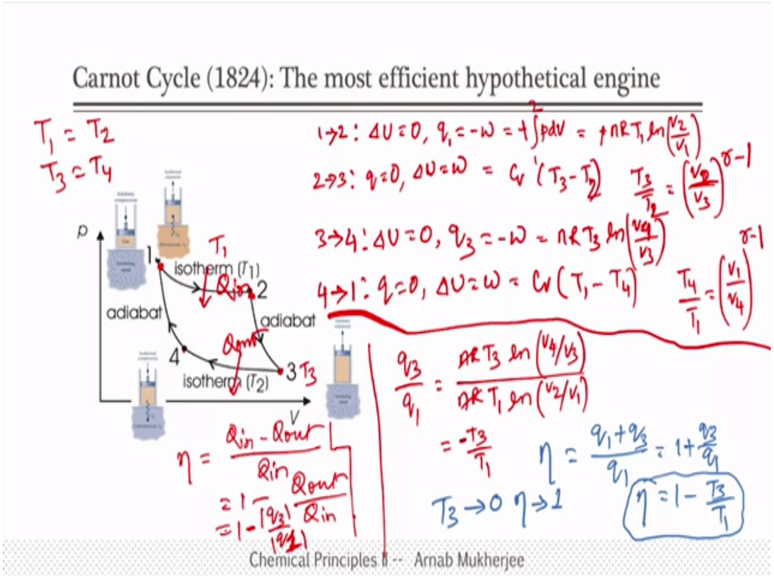

So it turns out to be minus and I am going to use a different color to show that eta is basically Q1 plus Q3 by Q1, equal to 1 plus Q3 by Q1 equal to 1 minus T3 by T1. And so what it says? This is extremely result of the second law of thermodynamics. Again second law of thermodynamics formally has not come yet. However Carnot finds that, and we are talking about ideal engine, ideal gas engine which means that we are not talking about all the frictional loss, any other because of friction, because of other things, because of design, any losses.

We are not talking about anything. We are talking about the most perfect ideal engine possible and that too for an ideal gas system. Even in that, what Carnot finds is that you are not going to get efficiency 1 because in order to get efficiency 1 what you have to do? Can you tell me? This is the formula that you get, 1 minus T3 by T1, now how do you get efficiency 1 in this?

Student is answering: T3.

Correct, if T3 goes to 0, then your efficiency will go to 1, is not it? Since your efficiency cannot go to 1, T3 will not be able to go to 0. So you get one more version of second law of thermodynamics, that one cannot attain absolute zero temperature. Because if you could, you could have made an engine having efficiency 1 which would have violated the second law of thermodynamics, Kelvin-Planck Statement, which would have violated the Clausius Statement that heat would transfer from low temperature to high temperature spontaneously.

You see how well they are connected. So this remarkable engine however is still a hypothetical engine, ideal which is possible, achievable. So given, so what it says is that given two temperature reservoirs the maximum efficiency of an engine, why we are saying maximum? Because we are considering an ideal engine, a reversible engine and reversible engine and ideal and reversible engine. These are the two things we are using it because of which we are getting maximum efficiency.

So efficiency can be just lower than that when the temperature differences are the same. In these two temperature differences the efficiency cannot be higher than this one minus (()) (21:03). That is what Carnot got. Here again we did not come to the second law of thermodynamics as of yet because what we have done is just, and Kelvin-Planck Statement did not come because in 1824 Kelvin was just born. And Clausius was born just two years before, 1822. So Kelvin-Planck Statement did not come. Kelvin just talked about the efficiency. Sorry, Carnot just talked about the efficiency of the engine.

Kelvin-Planck Statement did not come because this can be used in Kelvin Statement because this gives you the idea that efficiency cannot be 1 but it did not come. Clausius formulated what we formally known as entropy and the second law of thermodynamics, again from the Carnot Cycle itself. So from the Carnot Cycle we can observe one particular thing and that is that you saw what was happening. There were four steps in the cycle. It is a cyclic process.

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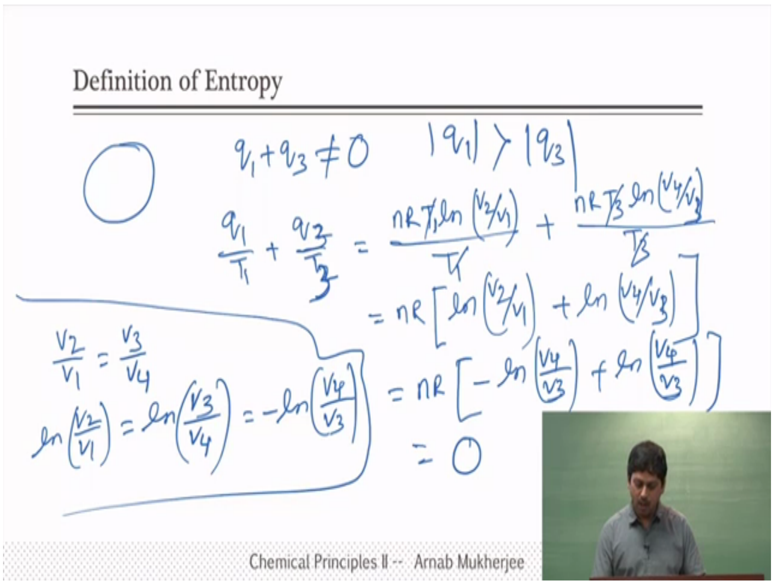

And there were four steps in the cycle, two isothermal and two adiabatic steps. Now if you see that, your overall change in the heat was Q1 plus Q3 and that is not equal to 0 because obviously Q1, modulus of Q1 is larger than modulus of Q3. Because some work is being done. However when you do Q1 by T1 and Q2 by T2, what you get? Do you remember that? So let us calculate that Q1 plus, so what is Q1? Again I remind you Q1 is nRT1 ln V2 by V1 by T1. And Q2 by T2 is nRT3 ln, it was 1, 2, 3, 4, so V4 by V1 by T3, nR.

But we already showed that V2 by V1, sorry V3 it will be because we are going from 3 to 4, and this will be 3, right? So it is just simply the way we define it. But I just remind you that V2 by V1 was V3 by V4. Ln of V2 by V1 is ln of V3 by V4 or minus ln of V4 by V3, which means I can just substitute this equation here, minus ln of V4 by V3 plus ln of V4 by V3 and we are going to get a zero.

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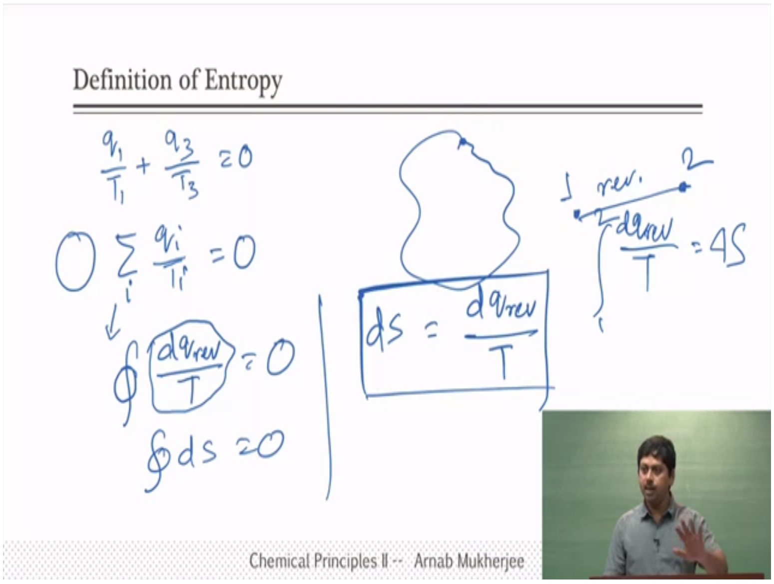

So you see that for a cyclic process, when you do Q1 by T1, so now in general for a cyclic process, here we have like two steps only, Q1 by T1 plus Q3 by T3 is equal to zero. So in general, for cyclic process having more number of such steps, one can write that Qi by Ti, however condition is that for reversible processes, right? Because Carnot Cycle is all about reversible processes. Remember we have not discussed any irreversible processes as of yet, so all the work done in isothermal or adiabatic or wherever we only talked about reversible processes.

For a reversible process, when we calculate Q1 by T1 and sum over for whole the cyclic steps like this i should be such that it makes a cycle, then it is turning out to be 0. Now which means that if we extend it to infinitesimal small small steps, then sum becomes integration and since we are talking about a cyclic process, we denote by a cycle and we write d Q reversible by T is going to be 0. So now what we saw here is that and what are the properties that in a cycle become 0, we discussed about that last time, which quantities if you go in a cycle and come back to the same point will be equal to 0, do you remember?

Student is answering: Internal energy.

Internal energy of course, but what are those class of quantities, class of variables? We said in a particular name for that, right? State function. So state function are those which does not depend on the path, so whatever you do if you come back to the same point, it will have the same value. And therefore when you integrate over that and come back to the same point, you will get zero. So now we see that a new state function has emerged. Clausius saw that a new state function has emerge, dQ by T. So it must be very special because state functions are special because they are invariant to all those changes.

So this special function, this new quantity is defined as entropy. So the definition of entropy is dS, change in entropy is dQ reversible, do not forget any of this particular thing that I am saying, dQ reversible by T. It is not dQ by T, it is dQ reversible by T. So when you go from one step 1 to 2 along a reversible path, whatever changes of Q will happen, divide by the temperature and integrate to 1 to 2, you are going to get the change in entropy. Tropy is transformation.

So he introduced the term as transformation, so remember the definition of entropy came from Carnot Cycle but Clausius gave that definition of entropy. So we have seen that, like somehow the Q was path function, see Q is not a state function. But by dividing by T is called sometimes the integration factor also. So sometimes integrating factor, sometimes you have done some integration with some integrating factor, that makes it easier, it gives you a differential that is easy to integrate. So the T works as an integrating factor.

So somehow this quantity came out to be something very unique and it was called as entropy. So now that is there, so we have now defined the entropy definition. So it is something that says that okay, change in the heat in reversible manner divided by T is the change in entropy.

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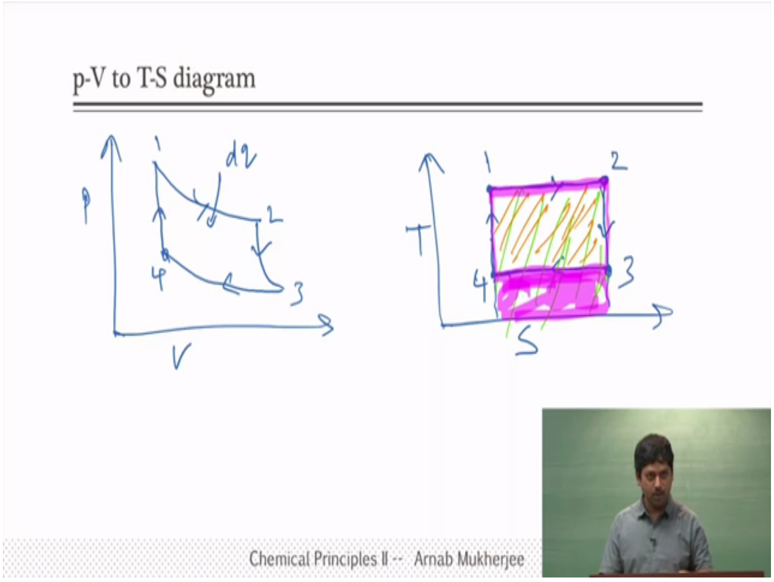

And easy way to understand this conversion of heat to work and all by using TS diagram rather than a PV diagram, so that is very simple at least for the Carnot process. So what we saw in the Carnot Cycle is that first step is an isothermal, then adiabatic expansion, then an isothermal compression, then adiabatic compression. Now what will happen if we do convert the same thing in a TS diagram? You will find that the TS diagram is very easy to get the change in the heat and other things and work done out of that and all.

So in 1 to 2 step, temperature does not change because it is isothermal process. However heat comes in, so Q changes and it is positive or negative it comes to the system. So therefore must be positive. So temperature remains the same but entropy increases. Second to third step, reversible heat change is zero, so entropy is 0 but temperature goes down. Third step is exactly the reverse, entropy decreases but by the same amount and entropy comes to the same, it has to come to the same value and then there is no entropy change and it comes back.

So you see the amount of heat is different between 1 to 2 and 3 to 4, however entropy change is the same because the T balances. So this is a typical TS diagram and from the TS diagram you can actually get the full overall heat is the area under the curve of 1-2 line. I will just denote that by some green color. And the work done is what is enclosed within the rectangle. So this much work only you are getting out of the whole thing and this is the loss, this part which I am going to show in this color. This is the loss because we are not getting that.

The input, loss in the efficiency, for example we are not getting the entire, you asked the question, right? Why we are not getting? What prevents us to get the entire amount of heat to work? This is the heat that is lost, this heat it is not being able to convert to work because we took the whole area under this line. However, we are only getting this much which means the other things is lost, loss to the environment. So we will come back to that again, and we see the total change of entropy of the system remains zero.