Indian Institute of Technology Madras

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CHEMICAL ENGINEERING THERMODYNAMICS

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Lecture 3
Sadi Carnot and the second law

Carnot introduced several important ideas. First he introduced the idea of a reservoir. He did not use these words. Many of these words come to us. A reservoir is simply a system that is so large that addition of taking subtraction of heat from the reservoir does no t make a difference to its temperature. So he introduced the concept of reservoir. He assumed that there was a TH, a high temperature and a low temperature reservoir. You can use T as t if you like, to indicate, you still do not know what absolute temperature is. Carnot introduced the idea of absolute temperature.

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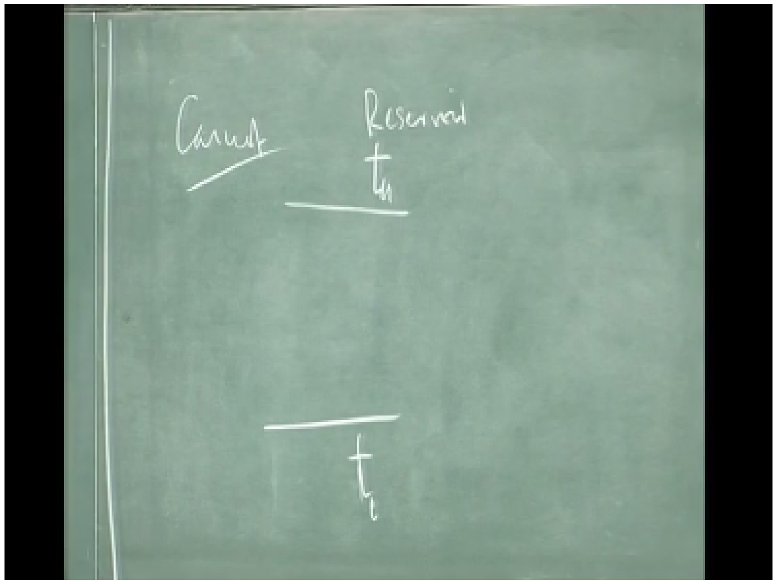

Although the idea of ideal gas absolute temperature had been introduced by Gay Lusac earlier he showed how to go back and say here, if you measure the volume of gases and your temperature by any empirical temperature t, Gay Lusac showed that the volume can be expressed in this fashion and he showed and α turned out to be 1/273 .15 or whatever.

So the numerical value if t was measured in degree C and this is experimentally measured and so Gay Lusac, essentially the conclusion was that if you went to -273.25 degrees, there will be no volume and therefore there cannot be temperatures below that. So the empirical temperature scale had already been introduced, T ideal gas was simply t+273.15. This was known.

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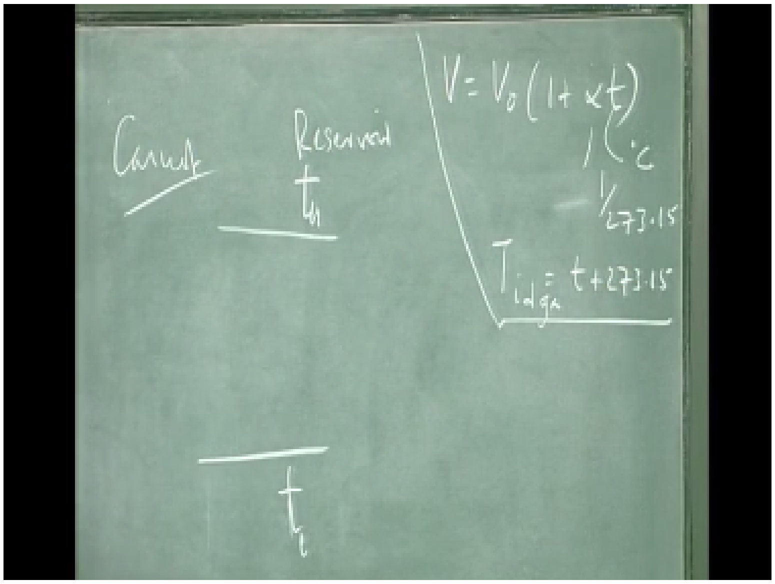

But the ideal gas temperature is not the same as the absolute temperature that Carnot came up with. You can show that the two have to be proportional. Luckily for you, the proportional P constant was chosen as 1. So you can completely confuse yourself about the ideal gas, thermodynamic absolute temperature and the ideal gas absolute temperature and make no mistake in which they have chosen some 1.23 then we would have had one more question in the exam to trick you.

If you use 1.21 then we can give you a -2 or do something like that. But luckily you have been spared that. So what Carnot said was that he is going to take heat from the higher temperature. Reject heat to a body at lower temperature and perform a certain amount of work δ W.

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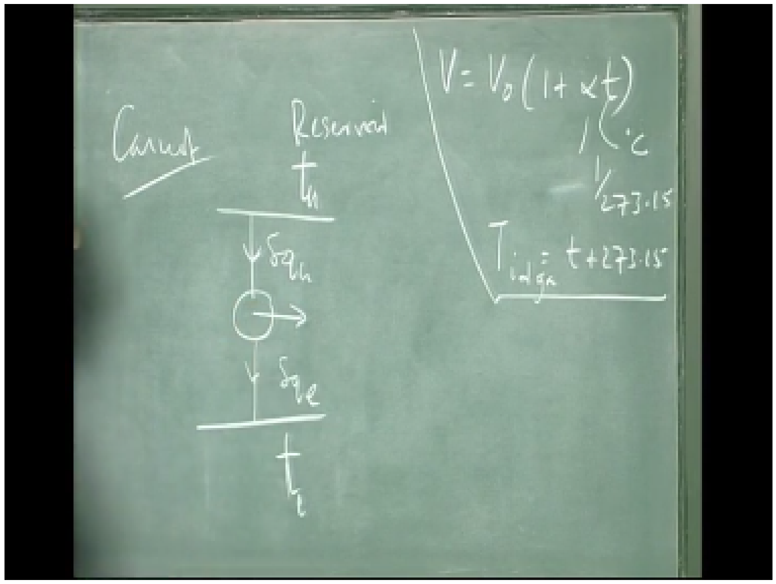

He said this engine could in principle he called this a reversible engine. He simply assumed that an engine could be run backwards. So he takes another engine which is also a reversible engine. We can take here, a certain amount of heat say δ QL ` from the lower temperature reject heat, $\delta$ QH ` to a higher temperature in putting work δ W `.

The key idea was reversible. Earlier at this is around the time when everybody was working in various engines, you had diesel engines, you had internal combustion engine was there everybody was making a slightly more efficient engine every other week. So or at least claim that it was a more efficient engine, and Carnot asked the theoretical question, is there a limit to all this madness, can I tell them when to stop and he assumed one thing.

He made a universal law which is still the law, said you cannot take a body, you cannot take heat from a body and convert it completely to work without rejecting some heat to a body at a lower temperature. This is an assumption he made because of the nature he found, I mean people knew that frictional heat generation was there when you did work. You could convert work to heat but converting heat to work had never been achieved with a single body.

This is simply human experience. You will be able to see it and generalize it takes a genius. When we are discussing the Carnot cycle, the key concept in it what you take for granted is the concept of a reversible engine. There is a reservoir, there are several concepts. The word reservoir has been used or source and sink and the word sink is now used so widely, for example they will say research is a sink.

This is from the finance secretary. He says that you take up a any amount of money and nothing comes out of it and no change in state as far as he is concerned. So these words have become common parlance now. So when you talk of a machine, that takes heat δ Q lets say thus the amount of work δ W and rejects heat, this is δ QH or lower temperature to a sink at a lower temperature. Both the sink and the source are reservoirs.

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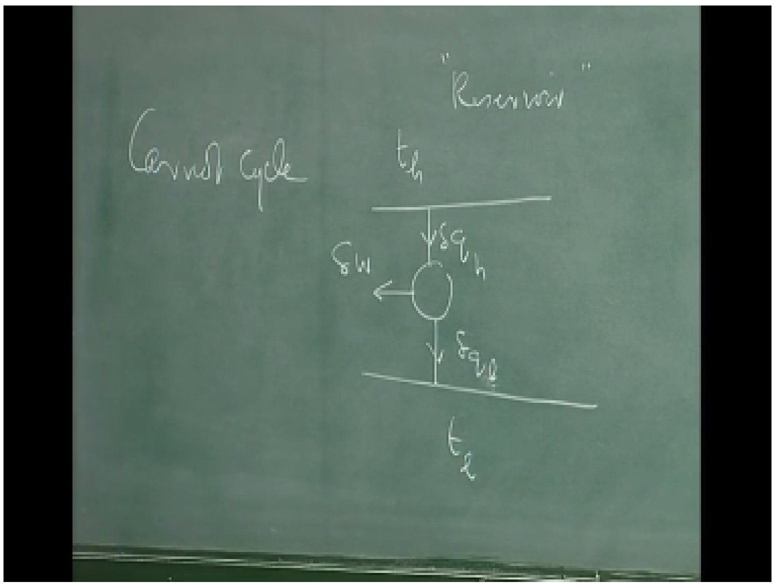

Carnot argued that any useful engine has to work in a cycle because it will have to come back to a same state and then go around cyclical change so that you can repeat it and get reasonable amount of work. If it is a one a shot affair, it is no use. The second thing he said was he introduced the concept of a reversible engine. This engine works forwards. This was known you could convert heat to work by that time, auto diesel he demonstrated it and showed that you could take heat reject heat and convert the balance into work.

This was also essentially washable they had already had the refrigeration kind of cycles in the receded form you could take heat from a lower source, put in work and to get heat at a higher temperature. This is what possible. This is what you do in refrigeration. So the point is he looked at an engine and said I am going to setup an engine and its reverse and ask what is the most efficient way of converting heat to work he made a statement that you have to make a hypothesis all the time. This is sink this is source.

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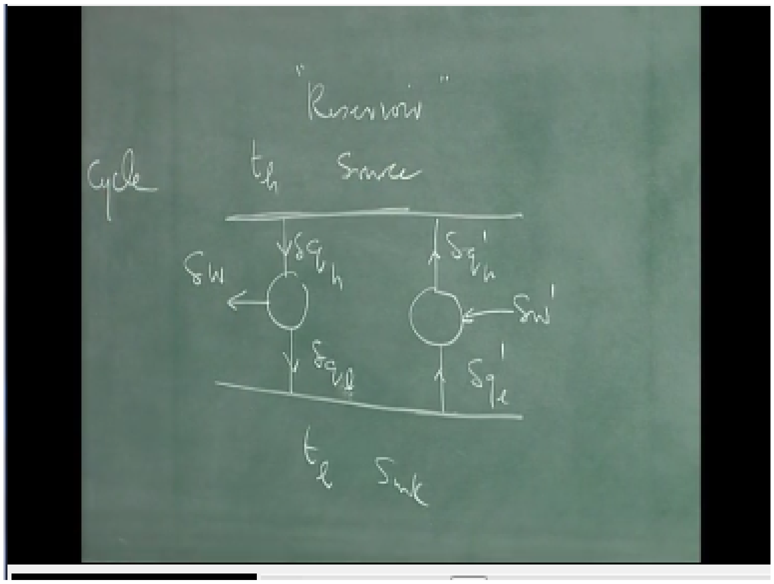

He made a statement that it is impossible on the basis of just experience, he said this is impossible to take heat from a source, go through a process and return the heat to the same source that may take a net heat, keep on less heat. This net heat cannot be completely converted to work and vice-versa. Actually vice-versa he did not make the statement, he made the statement only one way. Vice-versa is actually possible.

He said you cannot take, that is you cannot leave the state of the universe the same, go through a cyclic process take heat convert it to work completely. So that is the assumption. With that assumption he is going to give you a proof and the proof is prevail, let us say you have δ QH taken up, so net heat, if these both work in cycles, okay let us say this works over N cycles, that is you operate this engine over N cycles and this engine over N ` cycles.

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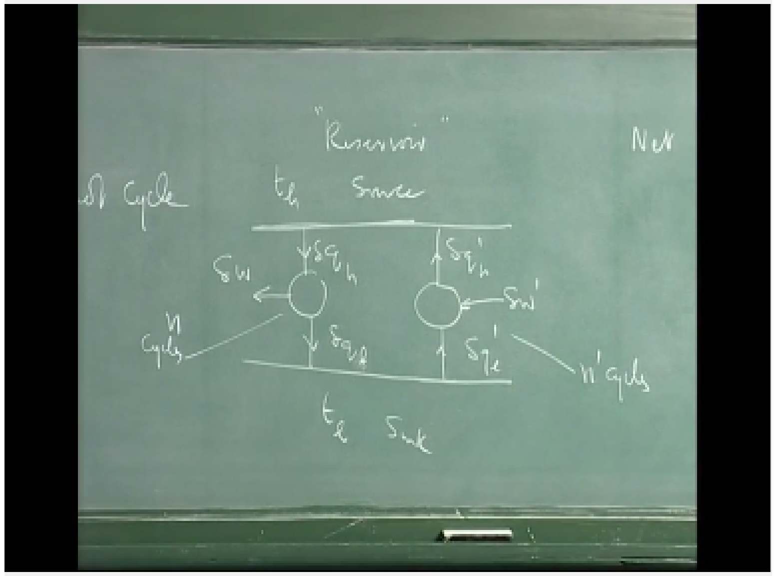

N and N` are integers but you can choose integers large enough so that the ratio of N/N ` can be any number I mean reasonable. But net heat taken from the source is n times δ qh – n times δ qh`. Net heat rejected to sink is $\delta$ qh n times $\delta$ qn – n times $\delta$ qn. Then net work is work done by the first engine is N times $\delta$ w – n` δ w`. When you finish an integral number of cycles this is left unchanged.

And the remarkable thing about Carnot is he refused to be drawn into details of what the engine was. It is not as if people did not pester him. People said what engine are you talking about and already there were local advertising campaigns. Otto said are you talking about mine, Diesel said are you talking about mine and so on. He said I am completely contentious of the type of engine which is first thing you have to do.

You have to when you do generalizations you have to take out all the non essentials. So he said I do not care what the engine is, it works in a cycle. That means when once the cycle is over it comes back to its original state. These two of course are by definitions sinks and sources, so they do not change at all. Nothing happens to them. If you add a bit of heat it does not matter as long as it is finite. So this is the net process and the process tells you that this should be equal to this minus this so n δ w – n ` $\delta$ w ` -. Now he said first of all choose N, N ` such that n $\delta$ ql = n ` δ ql`.

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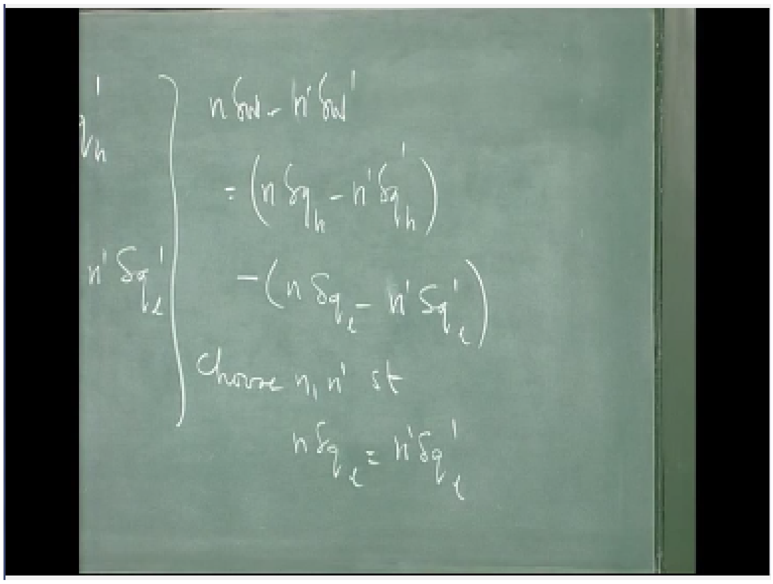

You know always do that, you just running this N times this N ` times, you have control over it and you simply decide to choose this N and N ` such that these two are equal. So this term will vanish. If there is a reversible engine, and if there is, so you have the engine and the reversible engine, you know the two operate, this has to be satisfied and if this has to be satisfied and this is zero then you got a conversion of certain amount of heat into work completely with no change in state of any body.

So this is impossible unless EC is zero. It is a bit tricky. This is why the thermodynamics is difficult but it sort of it looks like total logy but the point is this, I cannot take heat let us say completely from the reservoir, net amount of heat and convert it completely to work. That is the principle. But that is what is happening here because I have chosen the key concept was the reversible engine. It cannot run backwards and the reversible engine can be chosen so that at this stage I have not said anything about the efficiency of a, engines.

So I have got efficiency, by efficiency is meant δ w by δ qh, the fraction of heat that is converted to work if you like. I have not said anything about it. Right now this can set to zero. If I set this to zero, I get a contradiction if this term is positive. If this term is negative, I will simply reverse both in ends so that this term is positive, that is I will run this engine forwards and this engine backwards. So that is a second part of it.

But it is possible for me to choose this to be positive and this to be zero. If I do that I have conversion of heat to work without change in state of anything in the universe and this is impossible. The first law tells you that this quantity has to be equal to these two together that is all the first law tells you. It does not say anything about whether you can convert heat completely to work or not. The second law tells you, not only cannot you do that, each has to be equal to zero by hypothesis if you like and hypothesis becomes a law.

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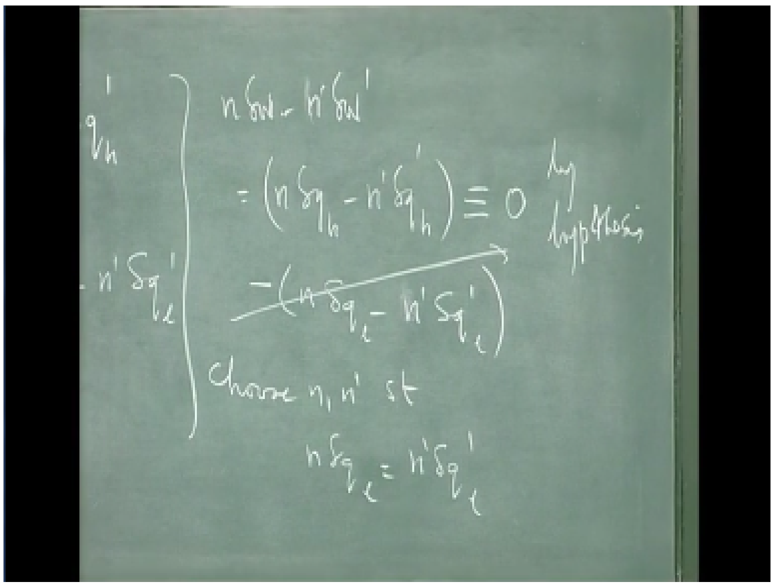

The hypothesis says that you cannot take heat from a body, convert it completely to work without leaving the rest of the universe unchanged. That is all. The argument was a beautiful argument therefore if this has to be equal to zero, one possibility is you can re-arrange this equation and ask this is possible. That is, this implies δ w by δ qh = δ w ` by $\delta$ qh `, because I can say these two equal and these two equal. That is one way of satisfying it.

Of course if this is actually zero, then you are not doing anything. Right you are taking any heat out of the system, out of the reservoir source, then you are not doing anything therefore you cannot say anything. That is the trivial case. The non-trivial case is when this term, this you are taking net heat out but this is equal to this and this is equal to this. Right these two are equal or this by this is equal to this by this. So the non-trivial case implies in the non-trivial case or δ, this is one, δ w is δ qh – δ q kal by δ qh= δ qh ` – $\delta$ ql ` by δ qh `.

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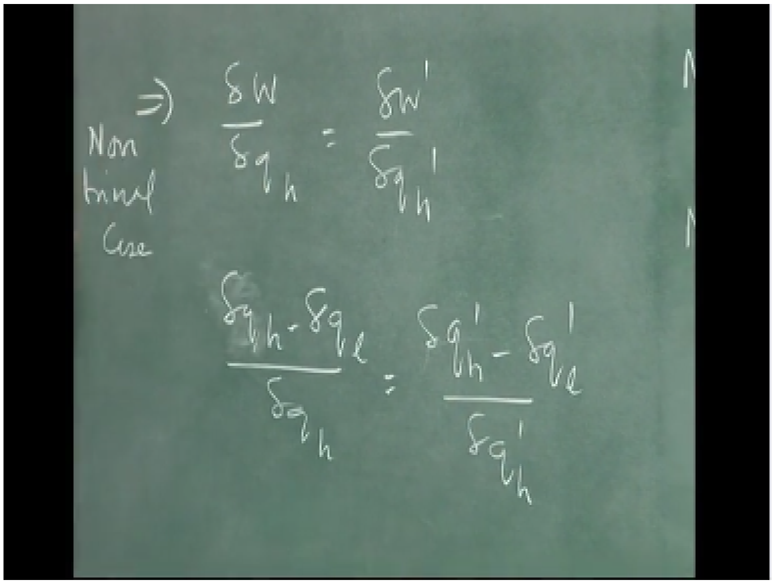

This implies again that δ ql by δ qh

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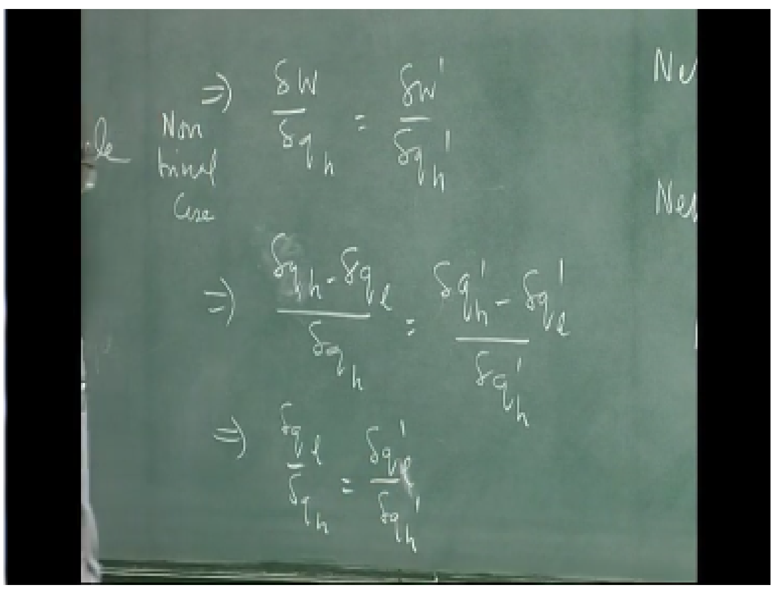

Then comes the beauty of his assumption, he said I do not care what the engines are I do not care how they work. I mean you can think of any kind of engine because it is independent to the type of engines and depends only on QL and QH, L and H. Therefore it must depend only on the temperatures of the source and the sink because the only characteristic of the source and the sink, the only characteristic of each is its temperature, is its degree of hotness.

So this is equal to function of TH, TL. I do not know the form of the function yet. This is 1780's, feel a little humble you know, when you know anything know, that 1780 years a guy equipped with practically nothing, even the first law was not stated in explicit form. We had an intuitive feel for it. Then he goes through a whole book called Reflexiums. He just, he is reflecting on the nature of heat and work.

To able to just sit in a corner and think about heat and work for one hour, he must be given a prize. Here is the guy thinking about just heat and work two years, he is supposed to be an army guy. It is amazing.

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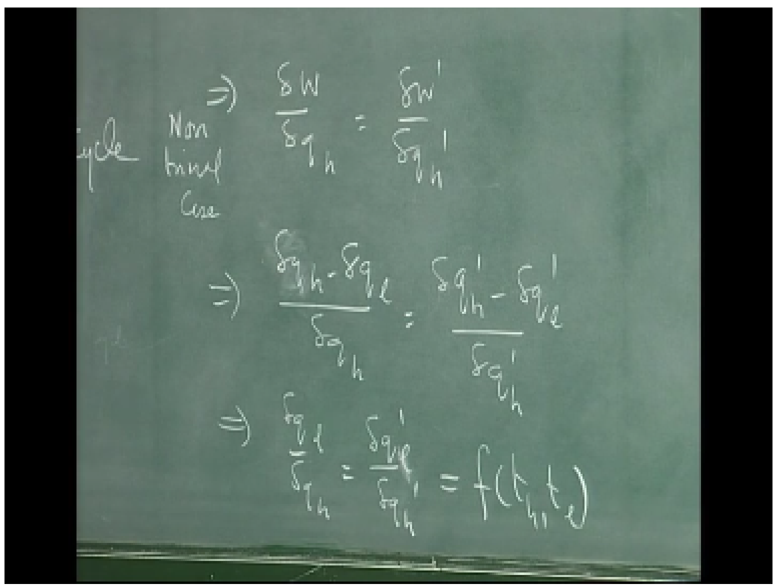

So having said this he did not stop here. He said no, not only his, this is a function of TH divided by the same function of TL, its not only this form, its not an arbitrary function of t_h and t_l its also actually a ratio of a function of TH divided by the same function of TL and to know that he did another clever thing.

I am very bad at drawing which is one of the reasons I took to thermodynamics because here you have to only draw circles, lines and something, nothing else. So let us say I have a T1 for convenience then I have a reservoir at T2. So it is great fun to draw, now if you have let us say I take δ Q1 reject δ Q2.

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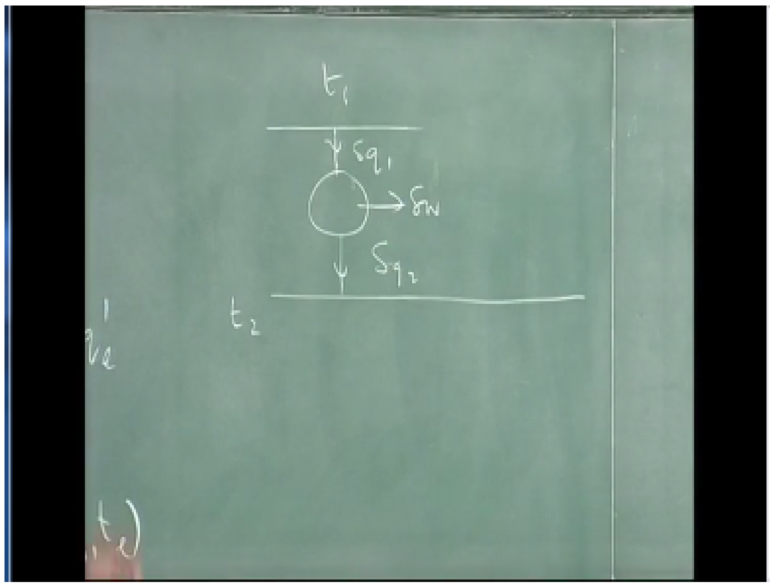

And then from this, we will call this δ W12 between 1 and 2. This is between 2 and 3 and I do some work. I reject heat δ Q3.

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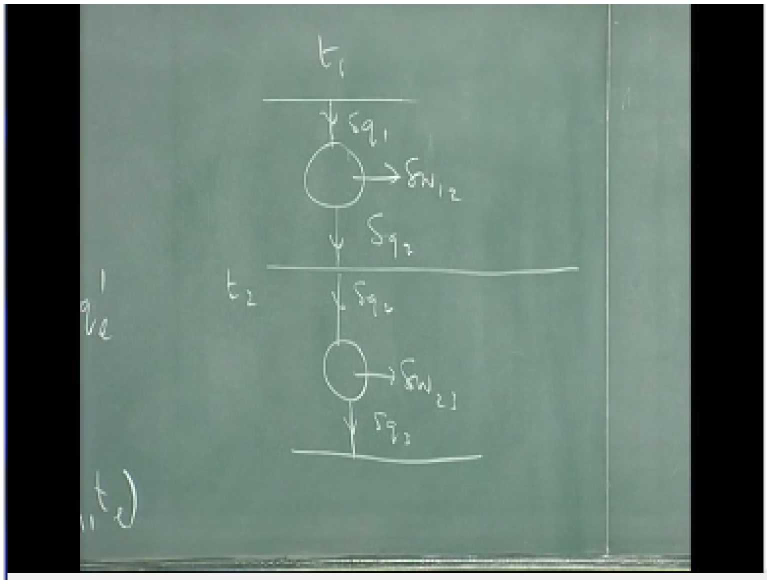

So I have now three reservoirs since it was great fun playing with two reservoirs now you play with three. I mean you can try playing with four you will not get any new result. So it takes wisdom to stop with number. Carnot had the wisdom to decide it this worth only playing with three. Then he said why not work between these two. So he had an engine or put an engine work here δ W13. So here you are rejecting heat here to T1. Again you can put`s if you like.

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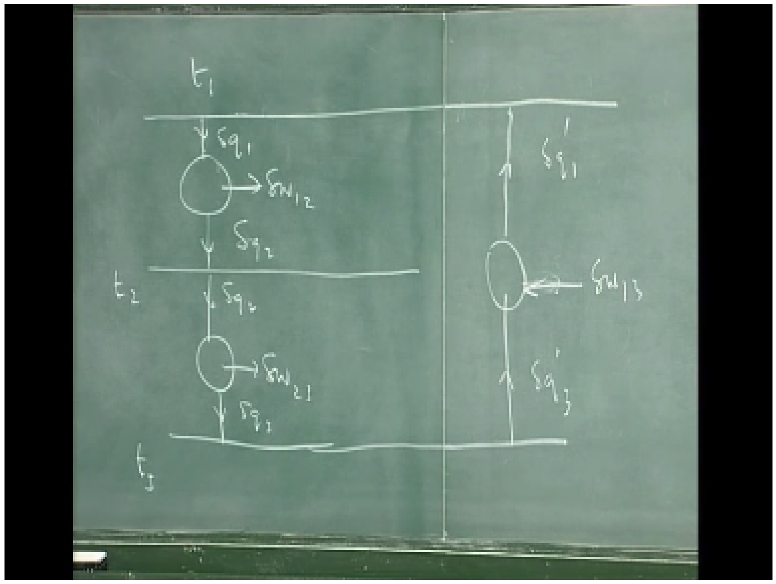

The argument can be written mathematically but you have to try and say the words yourself in order to get this right. What Carnot said was simply this, δ q 1 by δ q 2, mathematically it is just this. This is sort of clear when just write it multiply and divide it by q2 but this according to Carnot is f of t1 and t3 and this is f of t1 and t2 this is f of t2 t3. Remember as long as I have reversible engines this ratio has to be the same function because this has to be equal to this, the ` engine has to be same as the non` engine as long as both are reversible.

And both have to be reversible because otherwise I would have just taken work converted to heat which is possible. I cant covert heat to work therefore I have to be able to run it in reverse, run both in reverse, so this is the result and this from mathematics once you have function of t1 and t2 etcetera and although words state variable was defined at the time Carnot recognized that temperature itself is a state variable.

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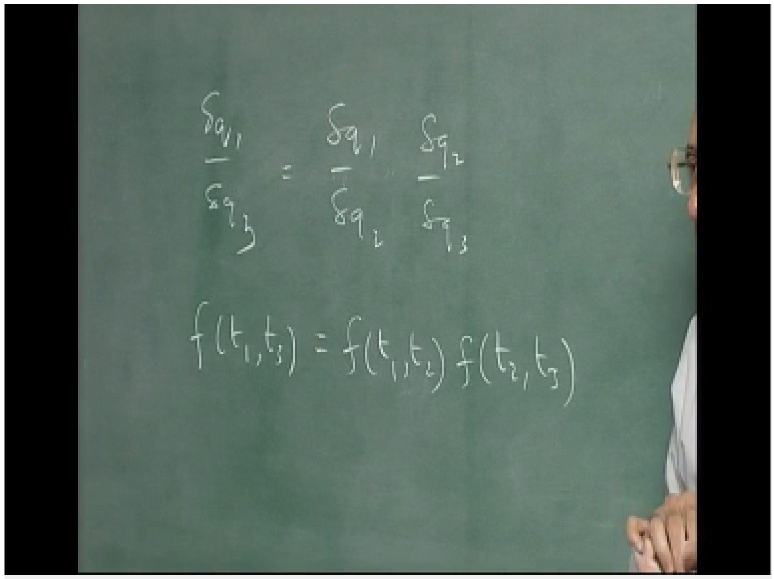

So here I have this and he said what is the form of f, now you take logarithms, log of f of t1 t3, is equal to log of f t1 t2 plus log of f t2 t3, all I do is take this.

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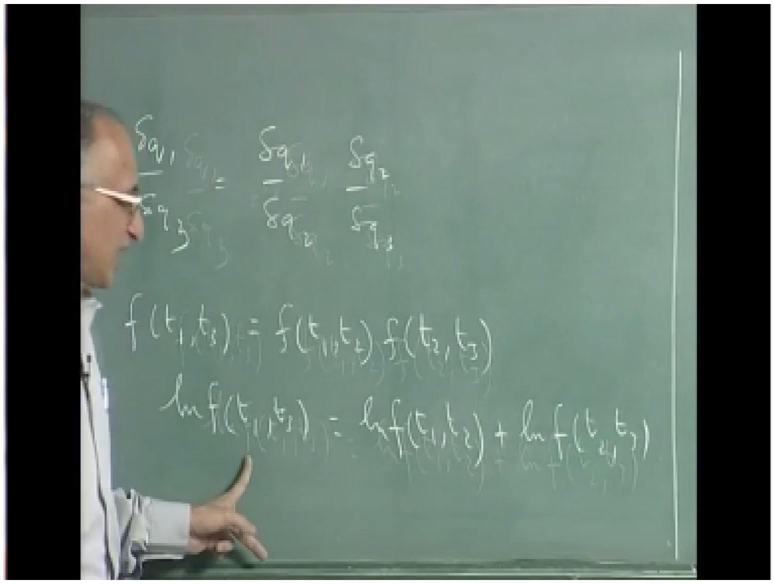

And differentiate with is respect to t1, so you get δ log f, I call this f13 okay, we call, we symbolize this by f13, that means f of t1 t3 t1, t3 with respect to t1 δ log f of 12 with respect to t1.

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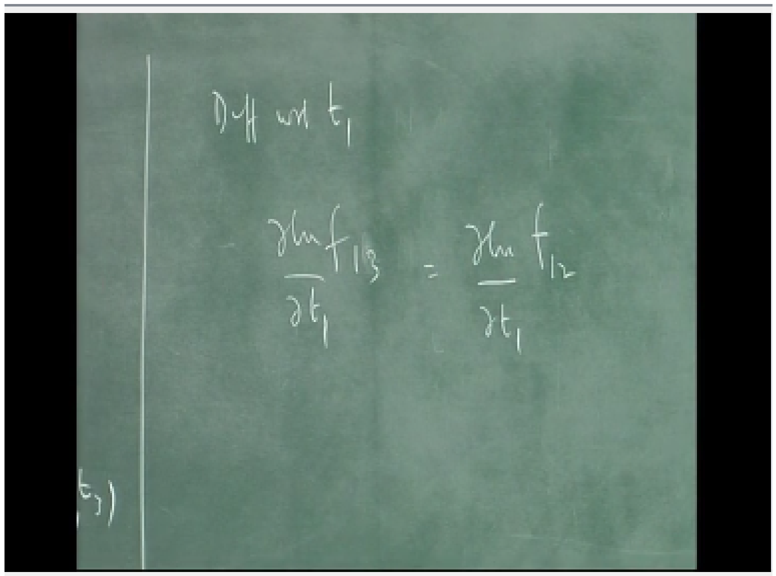

See this is the function of t1 and t3 right after I differentiate this is the function t1 and t2 and if the differential, these two have to be equal, each has be a function only of t1, it cannot be a function of t2 because then this is will be invalid, it cannot be function of t3 but this is will be invalid so this is equal, and I say function of t1 t3, this is function of t1 t2 so each can be equal to only a function of, we will call it to g of t1, best it can be is function of t1.

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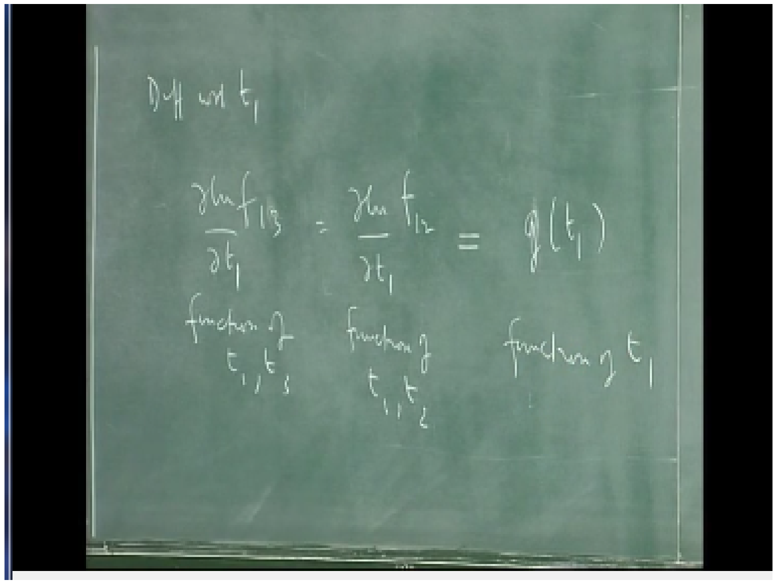

Because t1 t2 t3 are completely independent temperatures, I can choose them exactly as I please. For arbitrary temperatures if a function of t1 t3 has to be equal to a function of t1 t2 each can at best be a function of t1 alone. Now this is typical of Calculus, you differentiate then you integrate and you do not get the same result, it is slightly different because I have put in an argument that this g f t1, if I now integrate this partial equation this implies that f13 or log f13 if you like is g of t dt1 integral at constant t3, this is the constant t3, right, so if I integrate I get integral gft1 dt1 right last because t3 is constant plus some function of t3.

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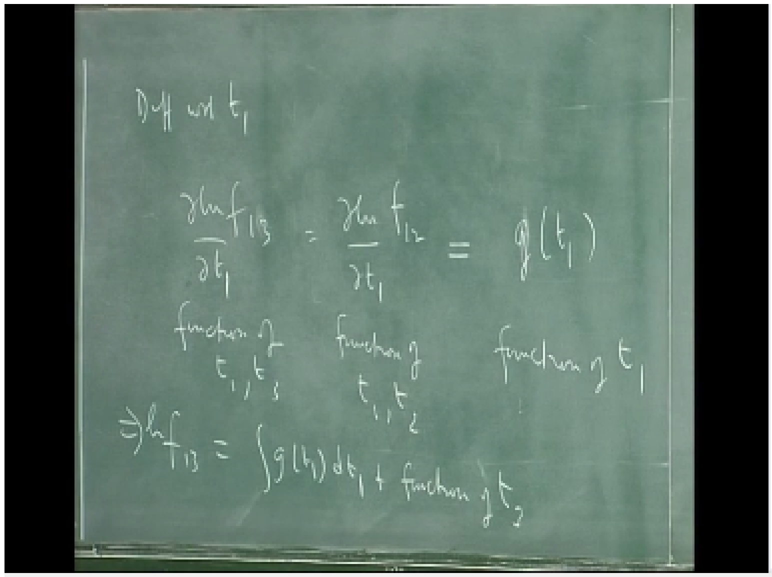

It also implies, this equation also implies f12 is equal to again integral of g of t1 dt1 plus function of t2, so I get ln f13 lets call this integral h integral g of t dt is h of t, okay this three lines means definition okay if I put three lines there instead of = sign it is definition. So I get h of t1 plus some function of t3 lets call it, since it is an, integration constant what shall we call it? Capital F, surprising how we are considering the notation, ln f12 is again h of t1 plus f of t2.

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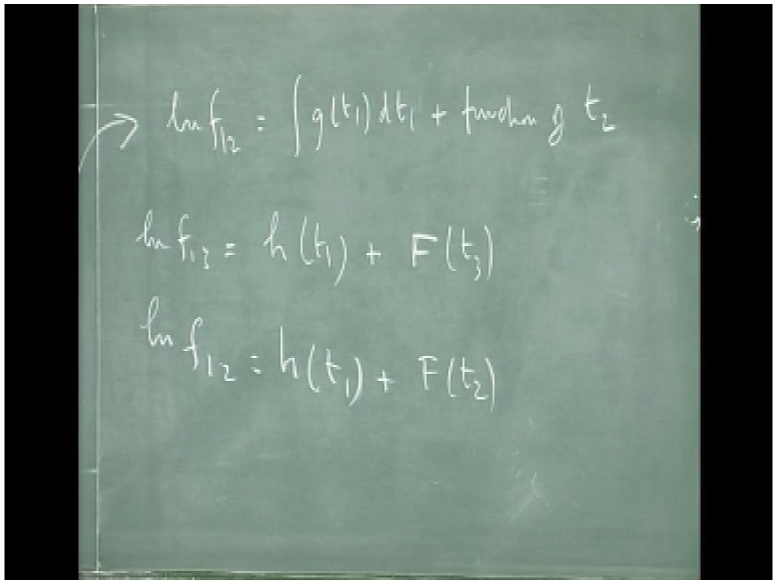

Notice if I had differentiated this equation instead of differentiating with respect to t1, suppose I differentiated with respect to t3 then I would have got this term f1 2 ft23, it would have been equal to a function of t3 which I would have integrated, I would have got h of t3. The point is that this Capital F has to be the same as this really in or suppose if it is a logarithm so it could be + or – this because the integration constant can be of different times too. Exponential of this f12 is equal to exponential of this.

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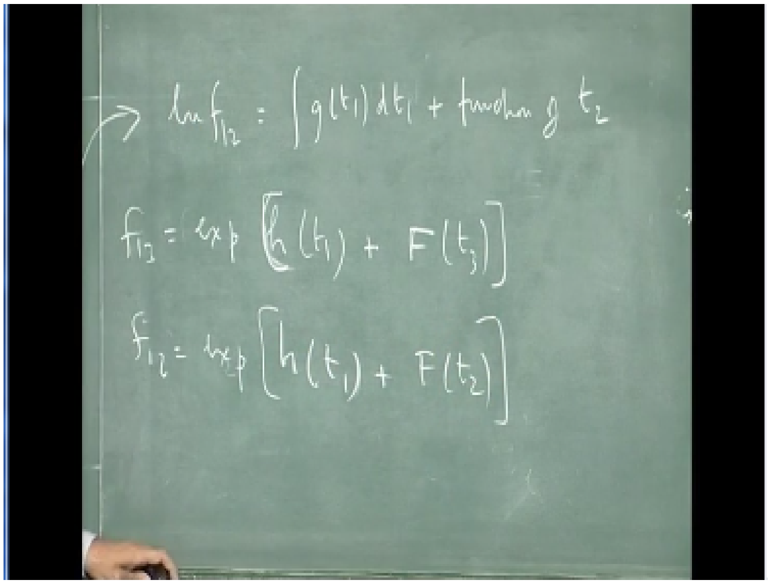

Let us find another e bar h of t1, we call it h of t1 time c bar f of t3 call this g of t3 and this is h of t1 again g of t2.

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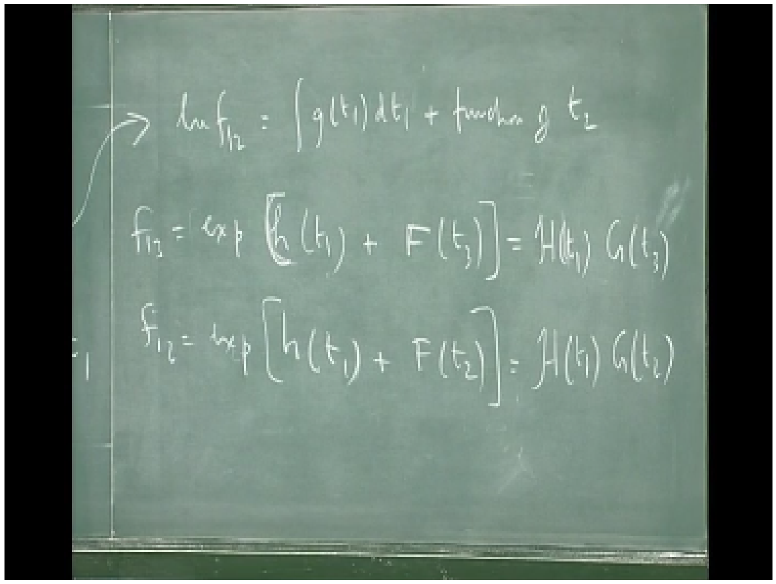

So look at this all said was only statement he made was it cant be exacted from a body and converted to work without leaving without changing the universe since by the harmless statement in would some foolish making some statement liking get by the would it from that he will put the all kind of constraints efficiency of the engine that you can drive so lets us look at this if you take is f 13 I have the expression there.

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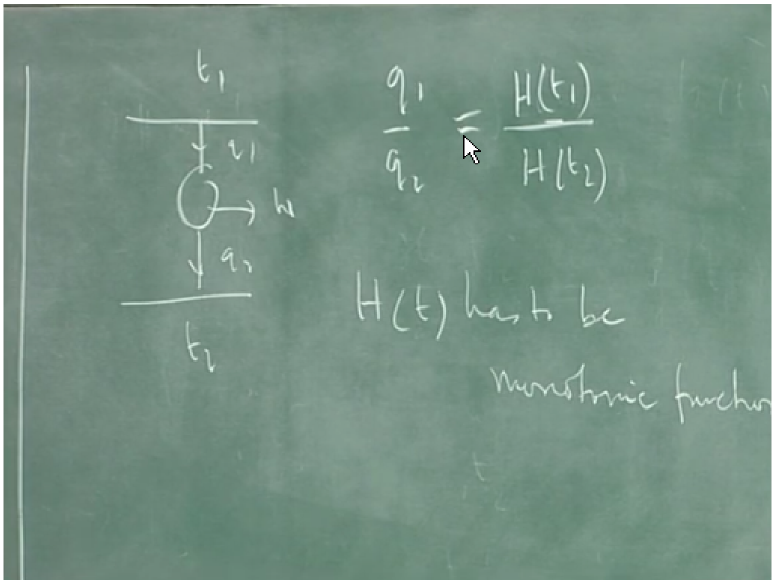

So I get h of t1 g of t3 is equal to h of t1 g of t2 then you have to h of t2 and g of t3 so clearly h of t1 g of t3 come back then you have this quantity here which therefore has to be one to get has to be one h 1/ g so finally locally step by of Carnot that it you have an engine working between T1 and T2 then Q1/ Q2 for the reversible engine is equal to G of T1 as G or H of t1 by H of t2 now I have for the arguments a show you that H of T in fact of monotonic function of t the challenge here is not a monotonic functionality.

You can go back set of this cluster of engines I am show by the rearranging engine you can convert to work without the change in rest of the universe so that I leave the words to you because any number of time I said the word to yourself so you just have to say it yourself you do not feel like fool go and front of mirror and convince yourself that is true I am going to simply say h of t has to be monotonic function of t, I think, I will have to stop here and give you five minutes for question.

So this is a crucial argument, because if it is not a monotonic function at some point HFT can switch science and so on. I will choose that interval and operate my engines in that interval. So within that interval I will produce a conflict with the first statement. You have to look at this carefully, because after this it is all everything else is detective, once you proof its monotonic function, then what function should it be.

It turns out of your play this same corner cycle to an ideal gas a particular chosen cycle it does not matter which one you choose, but if you choose an intelligent cycle then you can come to the conclusion that this HFT is actually the absolute ideal gas temperature. Its actually equal to T, if T is centigrade's then HFT will be T + 2 73.15.

Actually times any α you like, luckily for you a history chose α to be 1, I will stop there I will discuss this again next class. If you have any doubts you have to come back, but I suggest you read fimen and then put it away and say the argument for yourself because what appears obvious is not obvious when you close the book. Then you discover what is obvious says that it is obvious too that fine man understand physics, mean that to be have been obvious earlier, so its no use of that okay I will stop there.

I think Gibbs said teaching is if you tell except in those cases where it is unnecessary. And that is the same thing fine man says in his profession is original. Okay, you have questions? Yeah, Should be only a function of GFT 1, Because one is a functional 1 and 3 the other is a functional 1 and 2 the product T1, T2 since you have lot to did if you have T1 times of cos it still be only T1 as in, for example if you are FF 1, 2 is T1 x T2, then the equation $\partial/\partial t/f_{12}$ will still be the same one.

No, it will be T2 the other one will be T3, T2 cannot be equal to T3 so it cannot be of the form T1, T2 no, no if log of FF_{12} is you are saying if that is T1 times T2. I am saying it cannot be if log of FF_{12} is T1, T2 for differentiate with respective one I will get T2, but is also equal to log of FF T1, T3 with respected T1 which will give you T3.

These arguments are fairly fool proof I may make mistakes here, but if you do it carefully, incidentally I always have one line added in all, my thing. I am allowed this is called subjective silly mistakes. You does, not take away from thermodynamics. I can make mistakes, I may make a sign error and may put a one instead of two and all that, but you have to convince yourself. The basic arguments are not invalid.

These are two time, tested and if you find a fault in them be sure you will get an noble prize. I mean not a fault in what I do that may be any number of mistakes. I am talking about the subject itself in fact the famous statement of Eddie is if all the laws where to disappear where to be found wrong he will not be surprised expect he found the second law of thermodynamics.

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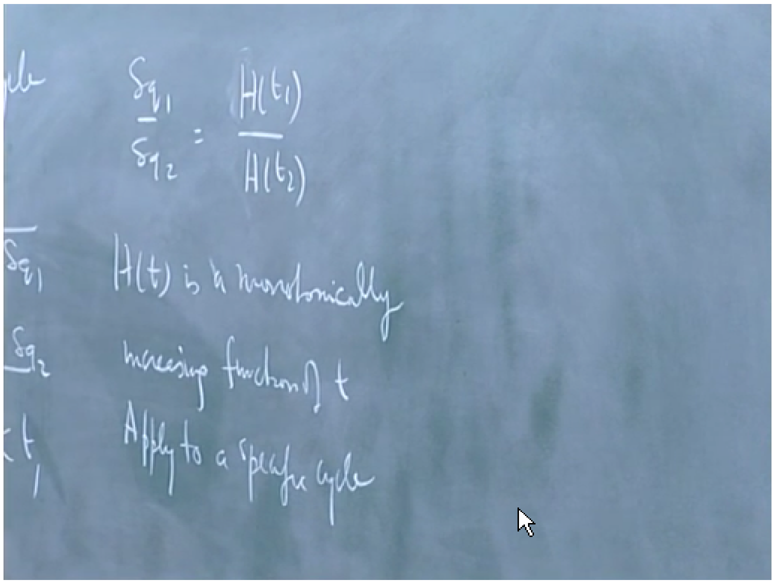

Let us start the discussing Carnot cycle we said two things first is I should have told you also an elementary another elementary concept that heat flows from higher temperature to lower temperature this is also an elementary concept simply an un contradicted experience so given that we came to this conclusion you had t_h and one is called T_1 this temperature T2 less than T1 you have heat.

We showed that Δq1/Δq2= some function and not it called at I just write as F of t1/f of t2 I said HfT is monotonically function it has to be a monotonically increasing function of T let us say obvious because it was a decreasing function then at T2 that function would be greater than a t1 so I can do this work and transfer that amount of heat back from here to here.

Then net result could have be taken out heat from body of temperature t2 converted it completely it work without any change in state of any other body, so that is not possible. So HFT has to be monotonically increasing it just detailed argument. So you just have to say do not with it and do it but you do it only once, because afterwards you take it for granted. You go through all your calculations as if everything was taken to granted, but I think you should see it once incidentally it will never come in the exam.

So for those of few were looking for equation in the exam you do not have to worry. But the real fact is that the arguments are very settle and very simple. But some of those arguments lead to performed results otherwise you could not have done the rest of thermodynamics. So fundamentally this has to be an increasing function. The suggestion was then apply this to a specific cycle.

I want to go into details of why this cycle was chosen for an ideal gas. This specific cycle was too adiabatic into isothermals. That is you go through two adiabatic and two isothermals. And you have done this before simply a matter of calculus. If you do this it turns out that HFT, this gives you the result HFT is identical with T ideal gas absolute, is equal to T +275.15 where T is degree c this it turns out this is called actually its α times T ideal gas.

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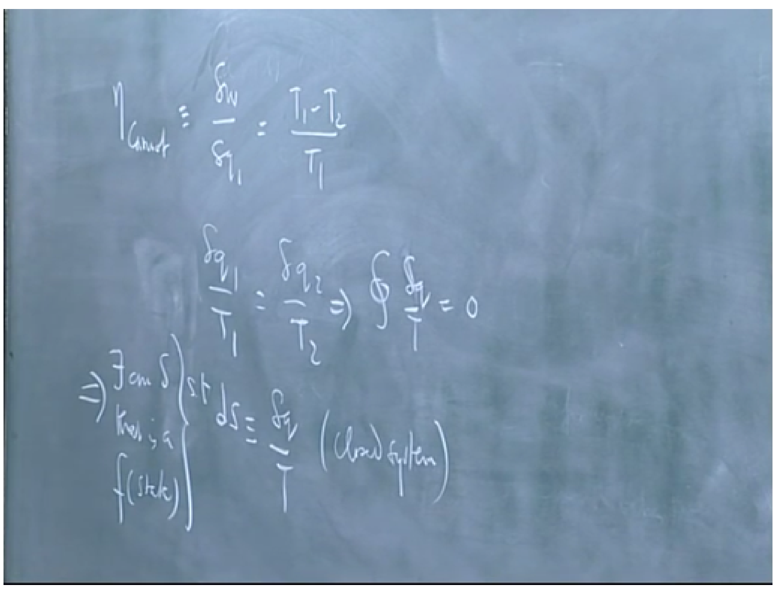

And this was chosen as α times T absolute, here after we will use capital T for absolute temperature which is the Carnot temperature, Carnot absolute temperature it is called degree Kelvin, Kelvin who really refine the whole thing I mean what classes in Kelvin did rewrite the whole thing and language that is acceptable. But this, it should say this is not α this is equal to α T, this α was chosen to be one.

What we need is a simply T absolute temperature in the ideal gas scale to be proportional to the absolute temperature thermodynamic temperature. It is just called thermodynamic temperature here after we will not make a distinction. And having said that next question was does this have other implications and classes did this. At this stage Carnot had proved this is the maximum efficiency you can get in any thermodynamic engine was simply dependent on the absolute temperatures the source and the sink in the maximum efficiency in terms of work could be simply T1 –T2 x T1.

So that is the η Carnot it was looking simply δ W x δ Q1 which was equal to T1 – T2 x T1. This has developed a point where everybody believes that so much that the patent office will reject any heat engine. If you submit a process for patent which shows the efficiency is greater than this it will simply rejective that, but more importantly what clauses is the following. This also implies the δ Q 1 \ T2 = δ Q2 \ T1 is equal to δ Q2 \ T2 rearranging the same equation.

Here was a discovery because Joule had just discovered that you have been which is whose differential DU is represented by δ Q – δ W δ Q is the function of path δ W is the function of path. But the difference is independent of the path. Similarly clauses observed that you had an other quantity that was independent of the path δ Q depends on the path, but this exactly one function which is the absolute thermodynamic temperature which can convert the differential quantity δ Q which is depend on to the path, to the quantity that is independent of the path.

And this was called DS, Ds is the δ Q \ T the integral of DS so over the whole cycle would be δ Q1 \T1 – δ Q2\T2, because when heat is observed its positive and heat is given off its negative as far as the body is concerned and over the cycle the integral is zero. This simplied that the integral cyclic integral were δ Q \T = 0. Further process you are always looking at the engine that is your body. As far as the body that is operating in a cycle is concerned δ Q\T integral cyclic integral zero which implies that there exist a DS there is exist a S such that, we have to say that this implies there exist NS which is the function of state such that DS can be defined as δ Q\T.

Because Carnot was dealing with close systems there is no mass transfer in this engine from the engine to this definition is what clauses adopted for a close system. I will say here brackets close this. Any engine could be less efficient than this which implied that the entropic of the system plus the entropic of the surrounding the net change in the entropic could be greater than 0 in that is the origin of the statement by clauses that the entropy of the universe always increases.

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