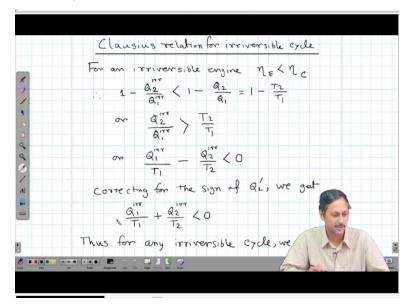
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## Lecture-40 Topic-Concept of Entropy and Mathematical Form of 2nd Law

Hello and welcome to the last lecture of week 8 of this NPTEL course on thermal physics. Now, in this week, we have defined cyclic process, we have defined heating engine, we have defined refrigerator and finally, also we have defined or we have stated the 2 alternative statements of second law of thermodynamics proved their equivalents. We have stated Carnot stated and proved Carnot theorem. And lastly, we started in the last lecture, we started discussing Clausius relations. Now, we have seen that for a reversible cycle, the overall integral dQ by T over an reversible cycle remains 0.

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Now, in today's lecture, we will start by looking at the same relation from the perspective of an irreversible cycle. Now, for an irreversible engine, let us consider an irreversible engine because irreversible engine works with operates in irreversible cycles. We have eta E is being the efficiency of the reversible engine. So, we have eta E less than eta C.. So, 1 by Q 2 by Q 1 for the reversible process is less than 1 minus Q 2 by Q 1 which is the right hand side is for a reversible process we can equate it with 1 minus T 2 by T 1.

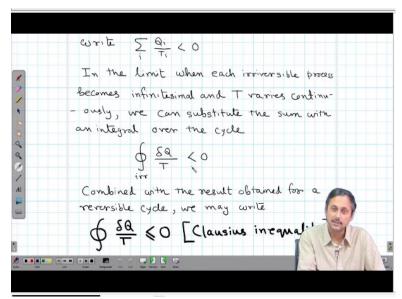
Now, if we simplify the above relation we get Q 2 irreversible divided by Q 1 irreversible is greater than T 2 by T 1 which gives you Q 1 irreversible by T 1 minus Q 2 reversible by T 2

less than 0. Now, once again we need to correct for the sign of Q 2 because in this case Q 2 is the heat going out of the system and the convention that we have decided to follow throughout the course of this lecture series that work done on the system is negative, work done by the system is positive.

Similarly, heat going into the system is positive well whereas, the heat that is coming out of the system is negative. So, going by that convention, Q 2 is negative. So, we can correct for the sign of this Q 2 and we can write Q 1 by T 1 plus Q 2 by T 2 for an irreversible process that superscript irr stands for the irreversible process is less than 0. Then this is just for a simple 2 step irreversible process. Now, as in case of a reversible cycle, we have seen that any arbitrary reversible cycle can be broken into an infinite many numbers of consecrated Carnot cycle.

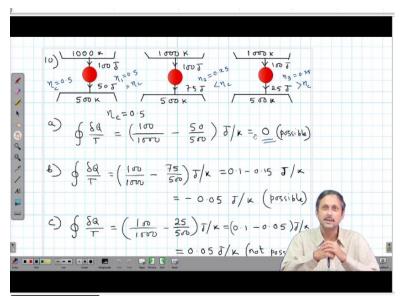
For each of those Carnot cycle the relation Q 1 by T 1 plus Q 2 by T 2 plus 0 that holds so, as a whole in a similar manner if we now divide an arbitrary irreversible cycle over a large number of such irreversible cycles working between 2 temperatures T 1 and T 2.

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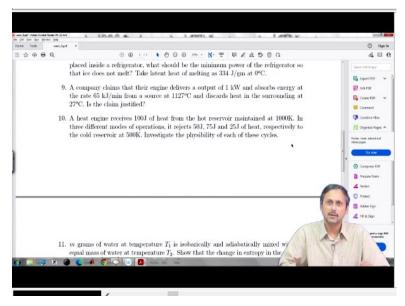
Then finally, we can write Q i by T i less than 0 for any number of such irreversible cycles. Now, in the limit when each of these processes are infinitesimal and the temperatures of interest temperature T is are really close to each other. So, it is like an almost uniform variation, continuous variation of temperature in that limit, we can write over an irreversible cycle the integral dQ by T is less than 0. Now, in the previously we have got that for a reversible cycle dQ by T is equal to 0. So we can combine these 2 results and we can write in general for any cyclic process, the integral dQ by T is less than or equal to 0 where the equal sign holds for reversible cycle. Whereas when it is a non reversible cycle, the inequality side holds. And this relation is the famous Clausius theorem or sometimes referred as the Clausius inequality as well. Now, so far we have been discussing the general nature of the cyclic processes, we have got two relations which are combined into 1 relation in here for case of general cyclic process.

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Now, we will take 1 step forward and we will define, so, we will just do a quick problem on this and then we will go on from there.

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So, let us look at problem number 10. A heat engine receives 100 Joules of heat from the hot reservoir maintained at 1000 Kelvin in 3 different modes of operation, it rejects 50 Joules, 75 Joules and 25 Joules of heat respectively, to the cold reservoir kept at 500 Kelvin. Investigate the feasibility of these cycles. Now, of course, we can do one thing we can check whether what are the efficiencies of each of these three of the engine in these three modes of operation. And we can compare that with an ideal reversible engine operating between these two temperatures that is 1000 Kelvin and 500 Kelvin.

And we can say whether this process is feasible or not, but we can do the same thing using this Clausius relation here, because according to the Clausius relation, dQ by T will be equal to 0 for a reversible cycle has to be less than 0 for any other irreversible cycle. So, you see, for the first case, we have 3 cases A, B and C, in all 3 cases the temperatures 1000 and 500, 1500, 100 Joules is the input in 3 cases, output is 50, 75 and 25.

Now, if we compute for the same two temperatures, if we compute the efficiency of an ideal reversible Carnot engine, it should be 1 minus T 2 by T 1 that is 1 minus 500 by 1000 that means, 1 minus half that is 0.5. So, of course, we can do it in both ways. So, we will just to demonstrate that both are actually equivalent techniques, what we are going to do is we are going to write eta is equal to or eta C is equal to 0.5. This is for all 3 cases I mean eta C is irrespective of whether we have an reversible engine or not eta C is the idealized case.

Now, for the first case, what do we get, what is the efficiency here? 100 Joules taken 50 Joules rejected. So, 1 minus Q 2 by Q 1 that is 1 minus 50 by 100 once again is 0.5. So, eta 1 is equal to once again 0.5. So, this is an ideal case. So, it is theoretically possible physically might not be possible, but we do not care at this point because we are just verifying whether this inequality holds or not.

And without surprise, we see dQ by T if we compute for this process, this will be 100 by 1000 - 50 by 100, which will be equal to 0 because this is a reversible process, the efficiency of this engine is exactly equal to the Carnot engine. Now, for the second process, 75 Joules is being rejected and 100 Joules being absorbed. So, 1 minus Q 2 by Q 1 is equal to 1 minus 75 by 100. So, 1 minus 3 by 4, which is 4 minus 3 by 4 that is 1 by 4.

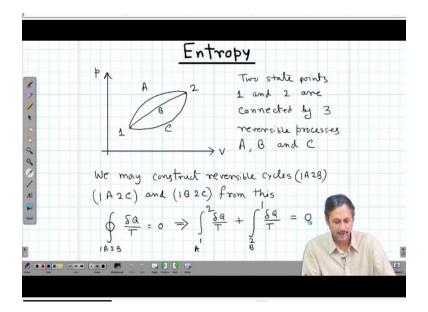
So, eta 2 I will just write it here, eta 2 will be 0.25. Of course, this is less than eta C. So, in this case this is equal eta C, in this case it is less than eta C and this process is possible. So, any engine that has an efficiency less than the Carnot engine is allowed. And of course, once we calculate dQ by T it is 100 by 1000 minus 75 by 500, computing this we get sorry there should be a minus sign here I missed it. So, it is 0.1 minus 0.15, so it is -0.05 Joules per Kelvin.

And we see both this Clausius inequality also holds the Carnot theorem also holds, we do not have any problem. Now, for the last case, we have 100 Joules being absorbed, 25 joules being rejected that means 75 Joules is in use for work. So, the efficiency is 1 minus 25 by 100 that is 1 minus 1 by 4 that is 3 by 4 that is 0.75. Now, eta 3, which is 0.75 is greater than eta C which is not possible by Carnac theorem.

Now, if we look at the Clausius inequality, you see, integral dQ by T is 100 by 1000 minus 25 by 100 this is 0.1 minus 0.05. So, 0.05 Joules per K, which is not in agreement with the Clausius inequality. And this is without surprise we see when the Clausius inequality does not hold the Carnot theorem is also being violated. So, this third case is not possible both by Clausius inequality and by Carnot theorem whichever way you want to call it.

And this is not surprising, because both are alternative statements of or both are the direct consequence of the second law of thermodynamics. And actually Clausius inequality has been derived, keeping the Carnot theorem in mind that an irreversible engine has an efficiency less than any reversible engine. So, there is no contradiction here. And we see this is Clausius inequality as of now gives us only another way of verifying whether an engine is following the second law of thermodynamics or not.

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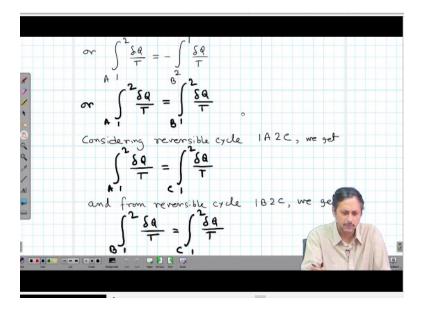


But we can take it 1 step forward from here or actually, it is a huge step forward, when we are going to define something called the entropy and we will use this Clausius inequality in order to find out some very interesting and very universal properties of this quantity entropy. Now, let us just consider 2 states; 1 and 2 in this PV indicator diagram. And, between these 2 states, we are free to choose, free to construct any number of reversible paths, I mean, it is a night I mean again a point choice of **1** the state 1 and 2 are arbitrary and choices of A, B and C, these 3 reversible paths are also arbitrary.

Now, what we can do is we can construct 3 different cycles using this actually 1, 2, 3, we can do more than that, but let us consider these 3 cycles, 1 is 1 A, 2 B 1. So, that means, this cycle, the second 1 is 1 A, 2 C 1 that is this cycle and the third one is 1 B 2 C 1 that was this cycle. So, of course, we can also consider another cycle here A, B. So, we have considered this, we have considered this and we have considered this. I think these are the 3 possibilities we have of course, the reverse cycle and the forward cycle is identical.

Now, from the first cycle, which is 1 A 2 B, please remember all these three are reversible cycles. So, going by the Clausius inequality or Clausius theorem, this equality sign will hold here and in all three cases the close integral dQ by T has to be equal to 0. Now, if we apply this theorem on 1 A the first cycle 1 A 2 B. That means, this cycle here, we get integration 1 to 2 allow A dQ by T + integration 2 to 1 along B dQ by T is equal to 0.

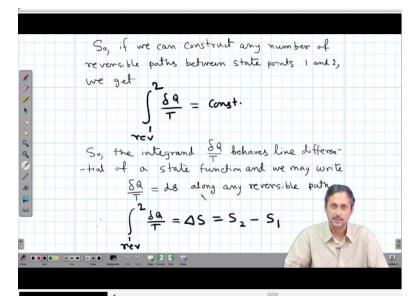
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And what we can do is we can simply take this one to this side with a negative sign because in a definite integral, if the limits are i to f and if we put a minus sign the limits will interchange and we will have f to i. So, we can do that and simple manipulation will give you integration 1 to 2 over A dQ by T is equal to integration 1 2 over B dQ by T. Now considering reversible cycle, 1 A 2 C. Now if we consider this cycle over here, we can construct in a similar manner integration 1 to 2 along A dQ by T is equal to integration 1 to 2 along C dQ by T.

Here we are only using the reversible property of the cycles and nothing else and of course, we are using Clausius theorem and nothing else. Similarly, for the cycle 1 B 2 C that means, this cycle over here, we can construct a similar we follow the similar construction and get 1 by 2 along B dQ by T is 1 by 2 along C dQ by T. So, what do we see? We see dQ over here it is written with a d that means it is an imperfect integral. So, it depends on the path; that we have discussed in details why and why it is depend on the path and all.

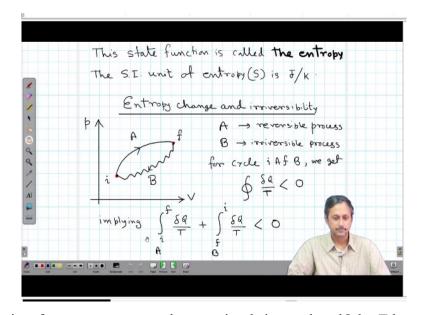
But once we divide this quantity by the temperature and integrate this via strike a perfect differential, because you see the primary property of perfect differential is it does not depend on the path of integral. So, basically this quantity dQ by T behaves like a state function. (Refer Slide Time: 16:13)



So, what we see is we can actually construct any number of reversible path and we can take construct any number of such reversible cycles of course, if we just take 2 step cycles between 1 to 2 and 2 to 1. We can take arbitrarily any number of such cycles and we can prove that for any reversible path connecting between 1 and 2 the integration 1 to 2 dQ by T remains constant. So, that means, this integrant dQ by T behaves like a state function, we have like a differential of a state function and we can write this as dQ by T is equal to ds along any reversible path.

So, finally, we can write integration 1 to 2 dQ by T, which is actually integration 1 to 2 ds is equal to delta S that is S 2 minus S 1 along any reversible path. This quantity f is called the entropy. Now, typically it is you know you say that okay I will write E for entropy, but unfortunately E has been taken by energy already before this concept of entropy has come into picture. So, the letter S has been chosen and this is also the primary work of one of the fundamental works of Clausius to describe entropy and to determine the few characteristic properties of entropy.

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Now, the SI units of entropy as we see the quantity ds is equal to dQ by T here, so the SI unit will be Joules per Kelvin. Now, let us consider entropy. So, far the definition of entropy is on a reversible process. So, ds is equal to dQ by T, please remember ds is equal to dQ by T only along a reversible path, the integration can be computed only along a reversible path; being a state function we can connect any number of such, we can construct any number of paths or any arbitrary reversible path, it does not matter the integration dQ by T between the first state point 1 to 2 will be equal to delta s.

So, it is not a path dependent function anywhere. All we have to do is we have to find a suitable path along which we can compute the integration and so, basically what I meant to say is if we know the initial state and the final state, all we have to do is we have to connect those with a reversible path along which we can compute the integration. So, it does not matter whether the actual processes followed that path or not.

As long as the initial and the final states are known, we can always perform this integration along any non reversible path. We will come to that once again when we will be discussing examples. At present it is just a theoretical concept, we will build on that very soon. Now, let us consider what happens in an irreversible cycle. Now, let us as you once again 1, two state points let us call it i and f, in this case, initial and final.

And we take a cycle this is a reversible cycle and by construction there are two parts. So, the cycle is i, A, f, B i. The path A is a reversible path, whereas the path B is an irreversible path which is given by this saw-tooth type of structure. Now, as this is part of the cycle is

irreversible, let it be a very tiny part, but once there is an irreversible portion in this cycle, the Clausius inequality holds and we can write the close integration of dQ by T over this particular path particular cycle has to be less than 0, which implies i to f along A dQ by T plus f to i along B dQ by T is less than or or less than 0.

And the dimension of entropy is given as Joules per Kelvin. Now, so far we have discussed about reversible paths. Now, let us talk about irreversible, what happens in an entropy change during an irreversible cycle. So, let us consider two state points 1 and 2 and let us say there is a reversible path A between these two points and another reversible path B between these two points. Now, the cycle 1 A 2 B 1 this actually is irreversible cycle because of this irreversible path D which is given as a saw-tooth here.

Now, for this irreversible cycle we can write close integral dQ by T is less than 0, because even if we have a tiny bit irreversible part in a cycle this makes the entire cycle irreversible. So, we have integration dQ by T less than 0. Implying we can break it into 2 parts along A we can write 1 to 2 dQ Q reversible by T plus along B 2 to 1 Q reversible by 2. Now Q reversible by T is precisely the entropy difference and instead of A we can choose any arbitrary reversible path that is okay, that is absolutely okay. But finally, this gives you the entropy difference between point 2 and point 1.

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 $\int_{T}^{L} \frac{\delta q_{T} v_{T}}{T} = \Delta S = S_2 - S_1 \implies S_2 - S_1 + S_2 = S_2 - S_1 \implies S_2 - S_1 + S_1 = S_2$  re-arranging, we get  $S_1 - S_2$ As points 1 and 2 are ambitary, we worte 5 8Q. [could sign for any for any 2 states i and f. Now, to generalize we may choose them very close and get roid of the integral sign. This is another from of Clausius inequality ---....

So, we can write this as S 2 minus S 1 plus dQ reversible by T from 2 to 1 integrated along B and this whole thing is less than 0. Now, if we rearrange this we can take S 1 to this side, S 2 to this side and we get this relation is S 1 minus S 2 is greater than integration 2 to 1

irreversible divided by T. So, and as the choice of point 1 and 2 are pretty arbitrary, we can get similar relations for example, in the reverse pathway also if we instead of going from 1 to 2 first.

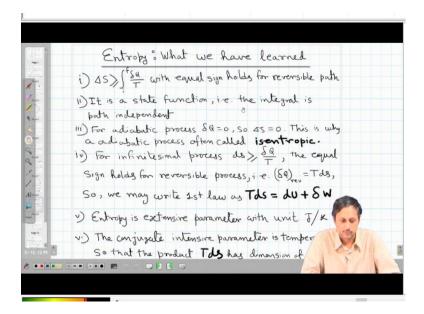
If we decide to go from 1 to 2 through this irreversible path and come back to this reversible path, we get a similar relation that will be like S 2 minus S 1 is integration 1 to 2 Q reversible by T. Please do not try to put in a negative sign on both sides and say that okay. So, if this is true, then what we can do is we can multiply it with negative sign and write S 2 minus S 1 will be integration will be less than integration 1 to 2 reversible by T.

Do not do that, because we do not know which way the heat flows, but every time you do it on a complete cycle without manipulating the sign, we will get a relation of this form, what is important is if we have S 1 here, we should have 1 in the upper limit of this integral, if we have S 2 here, we should have 2 in the lower limit of this of the right hand side integrals. So, instead of writing 1 2 etcetera if we simply write i and f for my initial and the final state, then the general relation which will come out of this type of closed cycle integration will be S f minus S i is greater than equal to integration i to f dQ by T, where this equality sign holds strictly for a reversible path connecting i f and or i and f.

Now, also please keep in mind that the choice of i and f has been totally arbitrary, we have demonstrated here using this diagram, we could take any two state point we can take any reversible path connecting those we can take any reversible path connecting those. So, also we can take them infinite close to each other. In that case, the integration becomes irrelevant. So, we do not even have to write the integration.

So, the most general relation that we can think of from this type of mathematical construction is dS is greater than equal to dQ by T. Now, the 2 relations that we have derived here, these are 2 alternative statements of Clausius theorem or Clausius inequality as of now, we do not have a physical significance of this relations, but very soon actually precisely in the next lecture, we will go in more details about entropy change and we will see that these relations actually help us defining the entropic principle.

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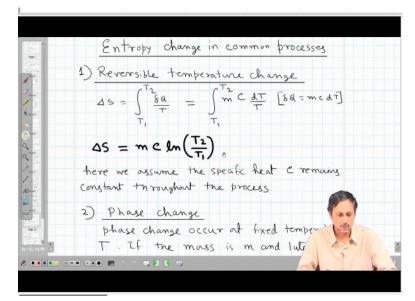
So, now, let us summarize on what have we learned about entropy so far. First of all ds delta s is equal to integration are greater than equal to integration i to f dQ by T which we have just proved where the equality holds for the reversible path. Secondly, it is a static function that is the integral is path independent. Now, thirdly for adiabatic process dQ is equal to 0. So, obviously ds which is dQ by T is equal to 0. So, I should have written ds because DS it means the same thing, but, basically it means S is equal to constant, delta is equal to 0 that means, ds is equal to 0 means S = constant.

And that is why an adiabatic process is often called an isentropic process. Now, for infinity symbol process ds is greater than equal to dQ by T. Once again the equality holds only for the reversible path. So, we can use this relation and for a reversible process we can write dQ reversible or delta Q reversible is equal to Tds. So, the first law of thermodynamics takes the mathematical form Tds = du + dw, where the process is along a reversible path.

And also please keep in mind that entropy that we have defined is extensive parameter because if we divide the system let us say the total entropy of the system, of course, total entropy cannot be measured which we will discuss once again. But, we can measure the entropy change like internal energy we can see measured the change in internal energy, but not the total internal energy of the system except for ideal gases maybe. But, once again if we divide the system into 2 the entropy will also be divided among 2 half.

So, it is an extensive property of the system with and for each expensive parameter there has to be an intensive parameter to combination of which will have the dimension of energy as entropy has an units of Joules per Kelvin. Temperature is the intensity parameter of interest and the product TDS has the dimension of energy. So, we see here this Tds here, this has the dimension of tendency. Tds also has other significance, we will very soon encounter or next week we will be discussing about Tds equations, there we will have more discussion on this particular parameter.

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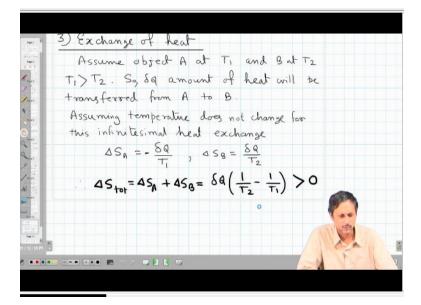


So, now, let us compute entropy change in some common processes. For example, a reversible temperature change for an object of mass m and specific heat capacity C, if we write delta s, if the temperature changes from T 1 to T 2, the entropy change is simply dQ by T integration from T 1 to T 2 and writing dQ as mC dT, what we can do is we can write this as mC dT by T T 1 T 2.

Now mass is the constant and as long as the heat capacity C does not change with temperature, we can integrate this, we can take this out of the integration and we can get delta s is equal to mC ln T 2 by T 1. Once again keeping this constant over a very wide range of temperature is not a good assumption; we have already seen that for solid the specific heat especially at low temperature specific heat varies with the temperature, but even for a limited temperature range it is probably okay.

Now, next comes the another simple process of phase change. Now, what is phase change? Phase change is when an object goes from solid to liquid or liquid to gas or vice versa. So, that is called a phase change. And each phase transition given pressure takes place at a constant temperature.

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And there is always a latent heat L associated with each phase change which gives us the entropy change delta s is equal to mL divided by T, where L is the latent heat per unit mass, m is the mass and T is the temperature of the phase transition. Now, exchange of exchange of heat with ease in this case, we have taken 2 deservers A and B at temperature T 1 and T 2 respectively. And let us assume we are being heat reservoir taking or giving or going small amount of heat dQ does not affect the temperature of this object.

So, A is giving a small amount of heat to B because T is at a higher temperature, it is a spontaneous irreversible process. Once again, we cannot really integrate this because it is an irreversible process. But, for small changes, we really do not need to integrate we can simply write delta S A is equal to minus delta Q by T 1 because dQ heat is going out of the system then it becomes negative. So, entropy change becomes negative and delta S B is equal to delta Q by T 2, where dQ heat enters the system delta B and the entropy increases.

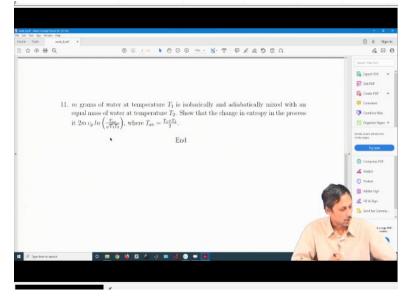
So, the total change in entropy is delta S A plus delta S B which is delta Q times 1 over T 2 minus 1 over T 1. Now as T 1 is greater than T 2, 1 over T 2 minus 1 over T 1 as well as delta Q is greater than 0, so this entire product is also greater than 0. Now this is also a very, very good example that entropy increases a irreversible process, we will have more of that in the next lecture when we will be talking about entropy principle.

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Classroom problem : week 8 11) As equal masses are mixed, the final temperature Taw = = (T1 + T2) As the process is isobarric, we get  $\Delta S_{i} = m C_{p} lm \left( \frac{T_{av}}{T_{i}} \right)$  (For initial temp  $T_{i}$ )  $\Delta S_2 = mC_p lm \left( \frac{T_{av}}{T_2} \right)$  $\Delta S = \Delta S_1 + \Delta S_2 = m C_{\text{P}} l_{\text{T}_1} \left( \frac{T_{\text{ev}}}{T_1} \right) = 2 m C_{\text{P}}$ -- -- -

But the remaining time of today's lecture let us quickly solve a problem.

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So, the last problem of today's lecture is we have m grams of water at temperature T 1; it is isobarically and adiabatically mixed with an equal mass of water at temperature T 2. Now show that the change in entropy in the process is 2m C p ln T average root over of T 1 by T 2. Where, T average is T 1 plus T 2 by 2. So, T average happens to be the final temperature of the mixture because equal amount of masses of water at different temperatures are mixed. So, that the final temperature has to be T 1 plus T 2 by 2.

We do not need even pen and paper for that we understand that this will happen. So, what we have to do is we need to compute the temperature or entropy change for each of this objects given that the temperature has changed. And of course this mixing we will see later on that

this is the totally spontaneous process and this is the totally irreversible process we cannot integrate along any reversible path.

So, what we have to do is we know the final path or we know the final state of the system final temperature of the system we have to assume that the temperature change has been reversible. So, that is why what we have to do is we simple use this relation here instead of C we replace it with C p because suppose it is isobaric and reversible change. Of course it might not be a reversible change or slightly it is not but we have to assume that.

So, delta S 1 will be m C p ln T average by T 1, delta S 2 will be m C p ln T average by T 2. And all together we have delta S is equal to delta S 1 plus delta S 2 which will be m C p ln T average by T 1 times T average by T 2 because ln A plus B is equal to ln A times d. So, this is the multiplication here. So, we have m C p ln T average square by T 1 T 2. We write the denominator as root over of T 1 T 2 whole square we take 2 in front of this ln function and the final result is 2 m C p ln T average root over of T 1 T 2.

So, that is where we stop today, that is where we finish this week's lecture and this week has been a very fruitful week for us, we have learned about cylindrical processes, we have learned about entropy, we have learned about heat engines, we have learned about Clausius theorem, we have learned about the two different statements of the second law of thermodynamics and so we will stop here and in the next week we will start from here, we will discuss something about the entropy principle and slowly and slowly we will go into other internal combustion engine and related phenomenon, till then thank you.