Thermal Physics
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Lecture-45
Topic-Entropy and Available Energy

Hello and welcome back to the last lecture of week 9 of this NPTL lecture series on thermal physics. Now, for last two lectures, we have been talking about the application of thermodynamic cycles. So, namely the petrol engine, the auto cycle and the diesel cycle. And in the last class we have also discussed about certain technical details of main differences between these two types of engine. So, for the last lecture of this week, we will go back to the basics and we will be discussing some of the fundamental aspects of entropy.

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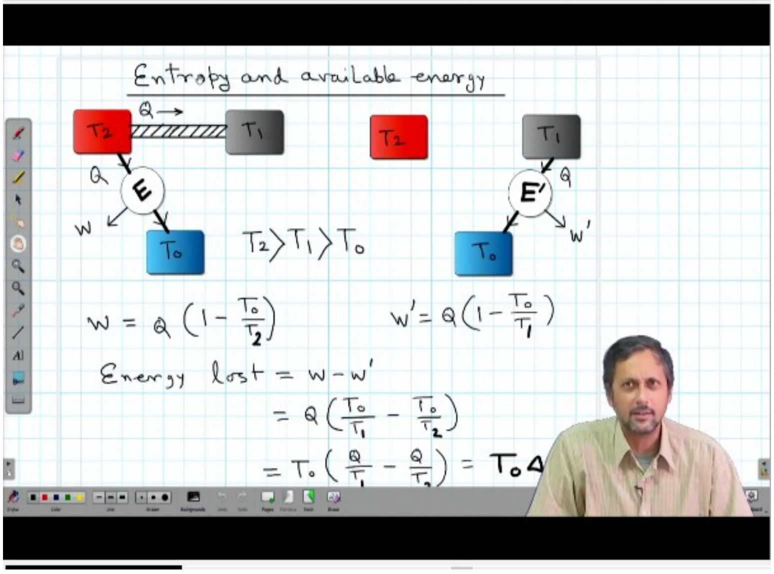

Entropy and available energy

$T_2 > T_1 > T_0$

$W = Q\left(1 - \frac{T_0}{T_2}\right)$

$W' = Q\left(1 - \frac{T_0}{T_1}\right)$

Energy lost $= W - W'$

$= Q\left(\frac{T_0}{T_1} - \frac{T_0}{T_2}\right)$

$= T_0\left(\frac{Q}{T_1} - \frac{Q}{T_2}\right) = T_0\Delta$

So, let us start by defining or not defining rather demonstrating that entropy and there is a relation between entropy and available energy. Now, let us understand the situation. Let us assume that there are 2 heat deservers; one at temperature T 2 and one at temperature T 1 and there is a cold reservoir at hand. So, that T 2 is greater than T 1 greater than T 0, T 0 being the temperature of the coldest possible reservoir in hand. So, it could be some reference point.

So, T 0 is fixed, T 1, T 2 are arbitrary, only criteria is T 2 and T 1. T 2 has to be greater than T 1. Now, let us assume we are operating an engine; let us name this as some engine E that is being operated between 2 reservoirs at temperature T 2 and T 0. Now, it will extract some heat Q from this hot reservoir, will reject something in the cold reservoir and will produce some work W.

So, in terms of efficiency basically we can write eta is equal to 1 minus W by Q which once again assuming that this engine is a reversible engine. This is nothing but 1 minus T 0 by T 2 and now, let us assume that we connect a conducting rod which is between these 2 reservoirs; one at temperature T 2, one at temperature T 1. Now, because T 2 is greater than T 1 what is going to happen? There is certain amount of heat that will get transferred from T 2 to T 1 and as their reservoirs and we assume that reservoirs have an infinite heat capacity.

So, a small amount of heat Q if it is exchanged between the reservoirs or it goes from the hot to one reserve to the other the temperature does not change. Now, as we have seen that from the efficiency expression given that this E is a reversible engine, we can write W is equal to Q 1 minus T 0 by T 2. Now, after that let us assume that we are putting another reversible engine maybe the same engine once again between the reservoir T 1 and T 0.

Now, for the same extracted heat Q from the reservoir at temperature T 1. Now, the work produced will be W prime, where W prime is given by Q times 1 minus T 0 by T 2 and it is not very difficult to compute. So, for that fact we do not have to assume that these are the same 2 engine we call it E and E prime here. That makes more sense, but the only criteria is E and E prime both are reversible engine.

So, these are all hypothetical by the way it is always possible to get an reversible engine which will extract exact same Q amount of heat from both the first reservoir and the second reservoir. But please remember both are hot reservoirs here. Now, what we see here is W prime is equal to Q times 1 minus T 0 by T 2 and as T 2 is greater than T 1, we can say that, this quantity T 0 by T 2 is smaller in magnitude as compared to this quantity T 0 by T 1. So, W is greater than W prime. So, that means, when we are extracting a same amount of heat Q from a reservoir at a higher temperature we are getting more work.

When the same amount of heat is extracted from a reservoir which is at a lower temperature with reference to the same cold reservoir that is important. So, that T 0 has to be identical in both cases the cold reservoir. So, we see the work done we get is less, now what is the difference, what I should not call it exactly energy lost, but it is rather the work loss actually work loss is W minus W prime which is Q times T 0 by T 2 minus T 0 by T 1 which is once again T 0 times Q by T 2 minus Q by T 1.

And if you remember, in one of the earlier classes I think lecture 42 or maybe 41 I do not remember exactly, one of the earlier classes we have calculated the entropy change when an irreversible process occurs between 2 reservoirs and that is exactly Q by T 2 minus Q by T 1 where T 2 and T 1 are the respective colder and hotter reservoir. So, heat goes from temperature T 2 to temperature T 1. So, this is the expression for entropy change and let me just quickly look into it, it should be T 1 minus T 2.

So, it should be W minus W prime. So, Q times 1 minus T 0 by T 2. So, this will be T 1, this will be T 2, this will be T 1, this will be T 2. Of course, because T 2 is greater, so, this quantity will be smaller. So, the final answer is correct in my notes, I had to make some corrections sorry. So, the final energy loss or work loss whatever you might call it is exactly T 0 times delta S, where delta S is the entropy that is changed entropy of the universe that has been changed when a reversible heat transfer between the reservoir of T 2 and reservoir on T 1 takes place.

Now, what is the implication of this result? This implies that any irreversible process will lose certain amount of energy I mean unit of work is also energy. So, basically this the same amount of heat Q when it is extracted at a higher temperature, it gives a work output which is more as compared to when it is extracted from a lower temperature and the energy difference is given by this expression.

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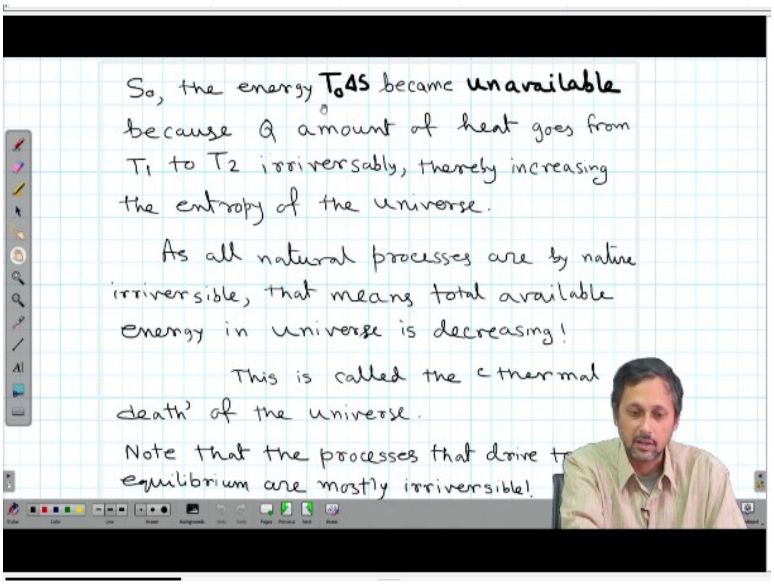

So, the energy $T_0 \Delta S$ became **unavailable** because Q amount of heat goes from T_1 to T_2 irriversably, thereby increasing the entropy of the universe.

As all natural processes are by nature irriversible, that means total available energy in universe is decreasing!

This is called the 'thermal death' of the universe.

Note that the processes that drive t
equilibrium are mostly irriversible!

So, this the amount T 0 delta S of energy becomes unavailable as the entropy of the universe changes by delta S and this is because we have taken a combination of an reversible process with an irreversible process. So, we can always break down any natural process into a series of reversible and irreversible processes and this relation is in general true.

So, that means, in other words, as the entropy of the universe is increasing the available energy of the universe is decreasing. So, these in terms of theoretical jargon it is called the thermal death of the universe. So, and this is exactly what we talk about when we say that there is an energy crisis what do you mean by that energy crisis means, we are extracting or we are actually exhausting all our resources, all our natural resources and world is driven towards a thermal equilibrium, which is also the state of a thermal equilibrium on the universe, which is also a state of maximum entropy.

Take an example you take we have to talk about diffusion when we mix two types of liquid, even if we do not stir them, if we stir them the mixing will be almost instantaneous, but even if we do not stir them, this slowly diffused into each other and after some time, we have a homogeneous mixture of two liquids. Given that the mix there are certain liquids, for example, oil and water they do not mix, that is a different story altogether. This aggregate is separate, but in general, if we put salt in water and if we wait for 15, 20 minutes, even if we do not stir the solution, it will be all salt.

So, the salt is evenly mixed and all these processes are irreversible, even if we keep this mixture of 2 liquids forever, at the same room temperature it will never get separated once again. So, the entropy this is as totally irreversible process in which entropy has gone up. So, that way all the natural processes, we have certain, different bodies, different objects at different temperature inside a room. And after a while, we will find that if they have all have come to a uniform temperature.

That means, mutual energy transfer has been taken place between those bodies, mostly through convection, if they are in touch through conduction, even slight amount will be transmitted through radiation. So, this is the natural process in which that drives everything towards equilibrium. And we see from this very simple thought experiment, the exact same process also leads to increase in available energy of the entire universe.

So, we have just taken two reservoirs. But, so, basically our universe is this small we have three reservoirs and one engine. But that itself, I think it gives you a general idea that what I am talking about. So, this is one thing when we say that we are driven towards equilibrium that means most of the time we are going towards higher entropy steps or we are increasing the entropy of the process in effect, we are reducing the available energy.

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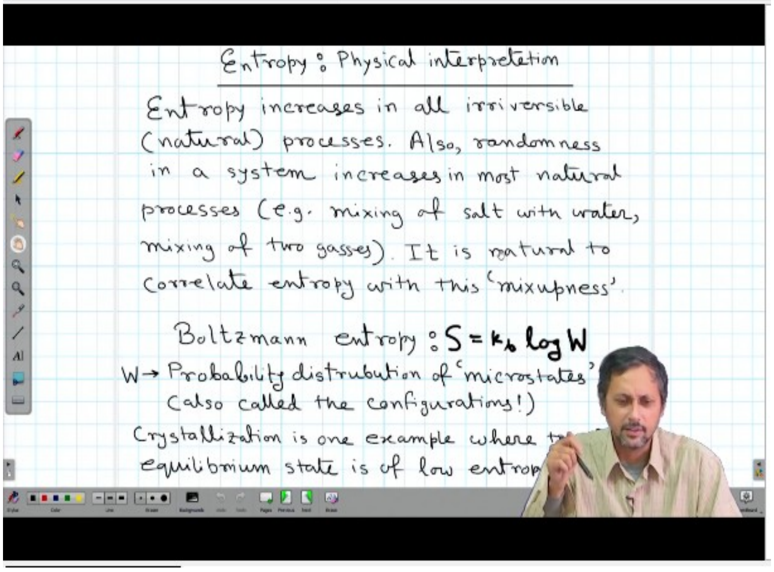

Entropy : Physical interpretetion

Entropy increases in all irriversible (natural) processes. Also, randomness in a system increases in most natural processes (e.g. mixing of salt with water, mixing of two gasses). It is natural to correlate entropy with this 'mixupness'.

Boltzmann entropy : $S = k_b \log W$

W → Probability distrubution of 'microstates' (also called the configurations!)

Crystallization is one example where
equilibrium state is of low entrop

Next is we try to discuss in very brief, what is the physical interpretation of entropy. Now, as we have said that most of the natural processes or almost all of the natural processes are irreversible, it also means that the randomness of the system increases. Take the example of two liquids mixing up. So, initially when we had two phases, we just have, let us say, two compartment containers, we have two liquids and there is a partition in between.

So, for each set of molecules, let us call it molecule A and B, only a part of this total volume was available with them. So, their maximum displacement was confined within that volume. Now, when we remove the partition, we allow these two liquids to mix together for each molecule or each particle available volume becomes more. So, that means the randomness of the system increases, same goes for salt and water.

Water molecules already had the access to the entire space. But once the salt gets dissolved, the salt crystals were tiny crystals. So, whatever the sodium, potassium ions were confined, they were confined within their equilibrium position, maybe some thermal vibration were allowed, but now, after this salt get mixed into water, what happens the sodium, potassium ions can actually sample the entire volume I mean they can move around this entire volume. So, the randomness increases.

So, what do we see? We see that entropy increases in any E reversible natural process. Similarly, the randomness or mixupness, what you might call it also increases. Now, Boltzmann was first to put this into perspective and I mean, he used this kinetic theory of gas model to come up with a very simple equation which is S = k B log W, where W is actually the probability distribution of the microstates also called the configuration of the underlying gas molecules.

So, I am not going into the details of this, because this is entirely in the domain of statistical mechanics, how to define the problem, what is probability probably know a little bit but how to define a microstate or what is the configuration exactly, but let me tell you, as in the first example, that I have discussed in today's lecture when 2 liquids mix the number of microstates available to each of these molecules, they also increase.

So, that means, when they mix S becomes more, W increases S becomes more. Now one exception you might ask that okay what happens during crystallization, now crystallization is probably one process naturally occurring sometime because we retrieve crystals from underwater or inside certain body parts of such certain organism or maybe inside mines also we get crystalline forms of diamond.

Diamond is a crystalline form of carbon for example, so, this crystallization also occurs, getting salt from seawater itself is crystallization. So, there are many ways we can get crystallized phase and crystallized phase is probably one of the better examples of a low entropy phase, which is ordered why it is low entropy because it is ordered. So, W becomes very small for a crystalline phase.

Think of it I mean you have a glass of water molecules are totally they can have really random movement, I will not call it totally random because still some microstructure exist inside that liquid water. That is fill by itself the local microstructure, local structures and all, we are not going into the detail, just you have to trust me that there is certain microstructure exists.

Now, when we start cooling it down, it crystallizes, ice is also a natural form of crystal that is naturally occurring, but, please keep in mind that most of the ice or snow what we see these are amorphous in nature, but some parts inside that there are microcrystals also, so crystallization do occur. Now, when that happens, a molecule is confined to its particular location and maybe certain thermal vibrations is allowed, we have talked about degrees of freedom of crystalline system or that solid. So, that means, certain degree of freedom is allowed.

So, there is I mean W is not exactly 1, so that S is 0, it is not exactly that, but it is very low as compared to in a liquid state. So, that is probably one example, where the final equilibrium state is a low entropy phase. But, otherwise almost all other natural processes like dissolving of the crystal inside liquid melting except freezing or crystallization, everything probably is driving towards a high entropy state or rather the entropy of the universe as a work increases. So, that is where we stopped this theoretical discussion. For the rest of the class we discuss two more problems from the classroom problems.

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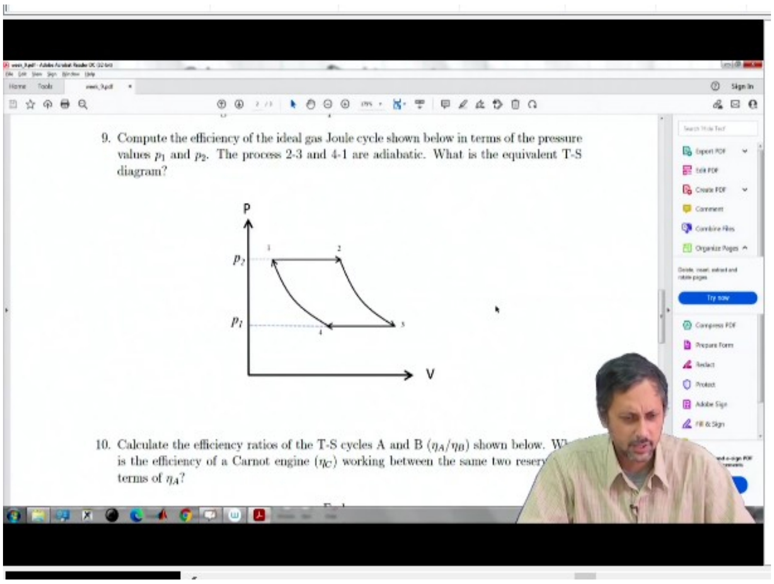

9. Compute the efficiency of the ideal gas Joule cycle shown below in terms of the pressure values p_1 and p_2. The process 2-3 and 4-1 are adiabatic. What is the equivalent T-S diagram?

10. Calculate the efficiency ratios of the T-S cycles A and B (η_A/η_B) shown below. W
is the efficiency of a Carnot engine (η_C) working between the same two reserv
terms of η_A?

So, we have already discussed a problem 8 of this particular problem we said, we have two more problems to discuss 9 and 10. So, let us do that. So, in problem 9 we have compute the efficiency of the ideal gas Joule cycle shown below in terms of the pressure values P 1 and P 2, the process 2 to 3 and 4 to 1 are adiabatic. What is the equivalent T-S diagram? So, we have a ideal Joule cycle and we have to find out the efficiency of this and also we have to find out what is the equivalent T-S diagram.

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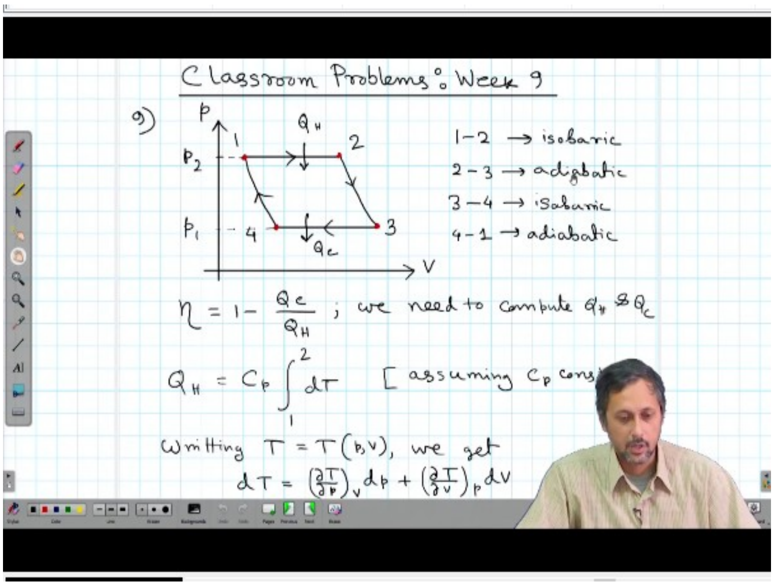

Classroom Problems: Week 9

9)

1 – 2 → isobaric
2 – 3 → adiabatic
3 – 4 → isobaric
4 – 1 → adiabatic

$\eta = 1 - \frac{Q_c}{Q_H}$; we need to compute Q_H & Q_c

$Q_H = C_p \int_1^2 dT$ [assuming C_p cons

Writting $T = T(p, V)$, we get

$dT = \left(\frac{\partial T}{\partial p}\right)_V dp + \left(\frac{\partial T}{\partial V}\right)_p dV$

So, of course, we although it is not given in the question here, but it is obvious that heat can enter only in this adiabatic, it is isobaric, isobaric expansion phase and heat may go out of the system only in this isobaric compression phase. So, typically that happens inside a cycle that during the expansion, heat comes in, during the compression heat goes out and of course, these 2 processes are adiabatic. So, there is no heat exchange.

So, we just named them 1, 2, 3 and 4 and pressure corresponding to one point 1 and 2 is p 1 responding to p 2 and point 3 and 4 is p 1. So, the efficiency eta will be given by this relation 1 minus Q C by Q H. So, we need to compute the expression for Q C and Q H. Now, as the process 1 to 2 and 3 to 4, they are isobaric. So, we just take Q H, Q H will be C p integration 1 to 2 dT. Now, of course, we cannot really integrate dT directly. So, what we have to do is we have to use this relation that T can be written as T of p and v.

So, dT will be del T del p v dp plus del T del v p dV and in isobaric process, dp is equal to 0. So, this term goes to 0. So, dT for this particular process will be del T del v p dv. Now, this is an ideal gas cycle. So, we have the ideal gas relation pv = nRT where n is the number of moles. So, del T del v p is equal to p by nRT. So, we have here p by nR and we have Q H is equal to C p integration 1 to 2 dT. So, finally, dT is nothing but p by nR dv. So, and we assume that C p stays constant during the process. So, we can take C p out of the integration.

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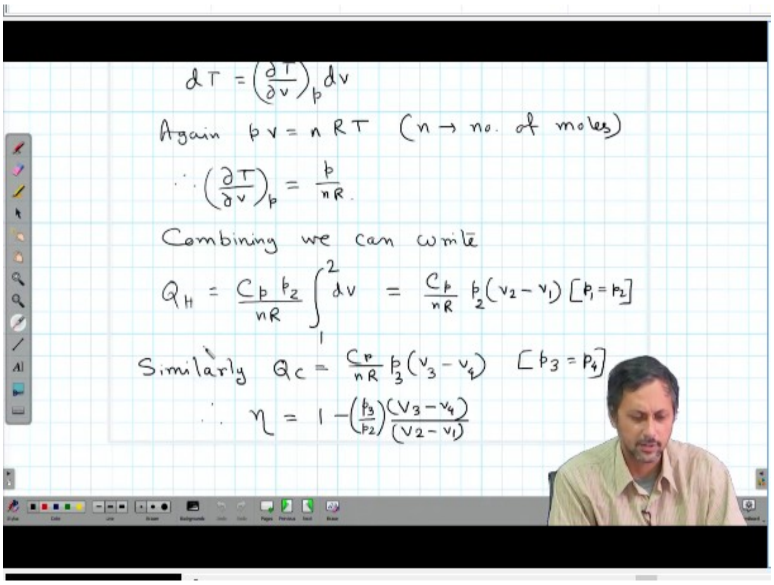

$$dT = \left(\frac{\partial T}{\partial v}\right)_p dv$$

Again $pv = nRT$ ($n \rightarrow$ no. of moles)

$$\therefore \left(\frac{\partial T}{\partial v}\right)_p = \frac{p}{nR}.$$

Combining we can write

$$Q_H = \frac{C_p \, p_2}{nR}\int_1^2 dv = \frac{C_p}{nR} p_2 (v_2 - v_1) \; [p_1 = p_2]$$

Similarly $Q_C = \frac{C_p}{nR} p_3 (v_3 - v_4) \quad [p_3 = p_4]$

$$\therefore \eta = 1 - \left(\frac{p_3}{p_2}\right)\frac{(V_3 - v_4)}{(V_2 - v_1)}$$

So, we can write C p p 2 by nR dv. Now, corresponding to p 1 and p 2 it is the same pressure p 2 we just take it out and put p 2 here. So, it is given as p 2 in the problem. So, we just write p 2 here. So, finally, we get C p nR p 2 v 2 minus v 1. Next, similarly, for Q C what we can do is we can compute Q C as C p divided by nR, this will be 1 I just wrote this as p 3, but I think you understand that, so, let us call it p 3 for now. So, p 3 and p 4 like working on the problem, I just followed the nomenclature of the cyclic process that corresponding to point 1 the pressure is p 1, point 2 pressure is p 2, p 3 and p 4 with that, but I hope you understand.

So, p 3 is it will be p 3 times v 3 minus v 4. So, efficiency eta will be equal to **C** C p by nR will cancel out from numerator and denominator. So, we have p 3 by p 2 v 3 minus v 4 divided by v 2 minus v 1. Now, all we have to do is we need to find out this. So, the final answer should be in terms of the pressure. So, I have written p 3 by p 2 which actually means**,** so, basically means p 2 by p 1, we will correct it at the end. So, we have to express v 3, v 4, v 2, v 1, this in terms of pressure.

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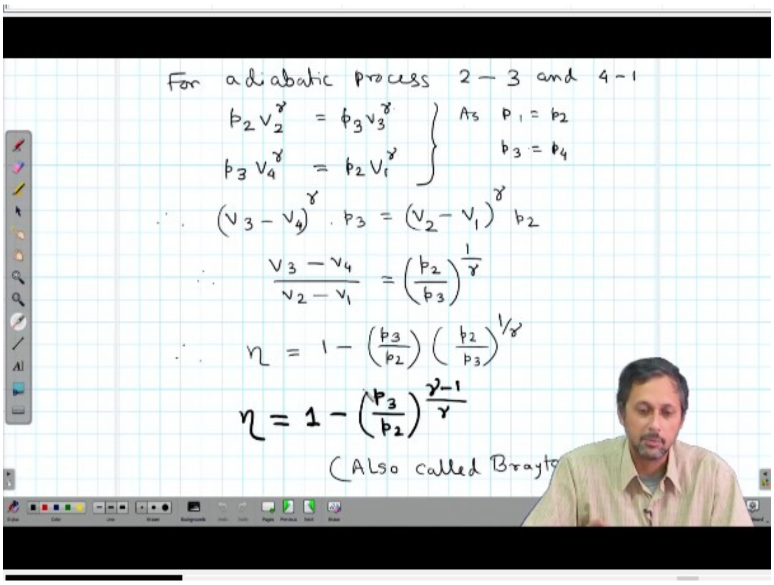

For adiabatic process 2 – 3 and 4 – 1

$$\left.\begin{aligned} p_2 V_2^{\gamma} &= p_3 V_3^{\gamma} \\ p_3 V_4^{\gamma} &= p_2 V_1^{\gamma} \end{aligned}\right\} \quad \begin{aligned} \text{As } & p_1 = p_2 \\ & p_3 = p_4 \end{aligned}$$

$$\therefore (V_3 - V_4)^{\gamma} \cdot p_3 = (V_2 - V_1)^{\gamma} p_2$$

$$\therefore \frac{V_3 - V_4}{V_2 - V_1} = \left(\frac{p_2}{p_3}\right)^{\frac{1}{\gamma}}$$

$$\therefore \eta = 1 - \left(\frac{p_3}{p_2}\right)\left(\frac{p_2}{p_3}\right)^{1/\gamma}$$

$$\eta = 1 - \left(\frac{p_3}{p_2}\right)^{\frac{\gamma-1}{\gamma}}$$

(Also called Brayt

And we can do that by means of this 2 adiabatic process 2 to 3 and 4 to 1. Once again the nomenclature is what we have already discussed in the class; it does not match with the problem that is my mistake once again but I hope you understand. So, p 2 v 2 to the power gamma is p 3 v 3 to the power gamma, p 3 v 4 to the power gamma is equal to p 2 v 1 to the power gamma, once again p 2 and p 3 we can understand, p 4 v 4, because p 3 = p 4 and **v 1** p 1 and p 2 are equal.

So, we can write p 3 v 4 to the power gamma is equal to p 2 v 1 gamma instead of writing p 4 v 4 to the power gamma is equal to p 1 v 1 to the power gamma. So, from this two we can get v 3 minus v 4 to the power gamma is equal to times p 3 is equal to v 2 minus v 1 to the power gamma times p 2. So, this expression v 3 minus v 4 by v 2 minus v 1 is equal to p 2 by p 3 divided by 1 over gamma and substituting we get eta is equal to 1 minus p 3 by p 2 times p 2 by p 3 whole to the power 1 over gamma.

So, we see there is a p 3 here or p 3 here and p 2 here and p 2 here. So, it will be finally, 1 minus 1 over gamma, which is gamma minus 1 by gamma. So, eta is equal to 1 minus p 3 by p 2 gamma minus 1 to the power gamma, see this expression in terms of the original problem will be p 2 by T 1 not p 3 is p 1. So, it will be actually p 1 by p 2 whole to the power gamma – 1 by gamma. So, I think you can do the correction yourself, I will just keep it like this only. And this cycle by the way is also called the Brayton cycle, because it was co-invented by both Joule and Brayton together.

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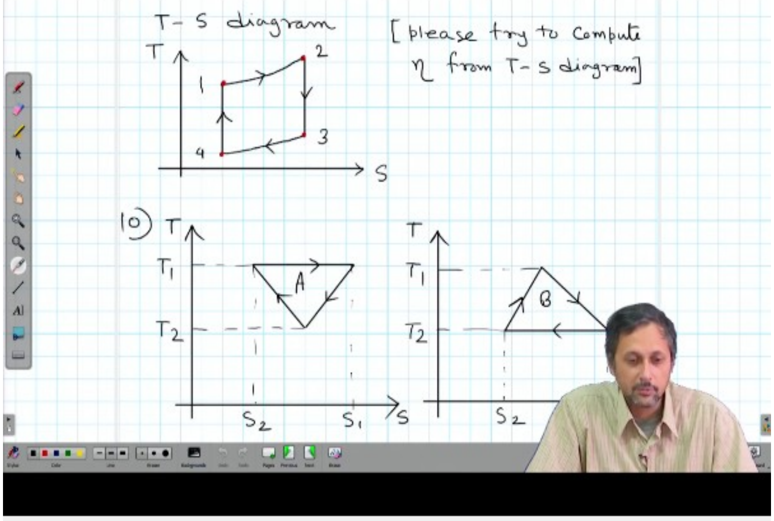

T- S diagram

[please try to compute η from T-S diagram]

Now comes the T-S diagram part. Now for the T-S diagram, it is actually very simple we have process 1 to 2 which is isobaric where the heat comes in and of course, when the heat comes in the entropy increases, the temperature increases. So, all 3 entropy volume and temperature all 3 increase, we can see air pressure remains constant, we can see volume increase from here. So, this part will be represented by a nonlinear implement of temperature and entropy.

At the same time heat Q H comes in over here, next part is 2 to 3 is the adiabatic process. So, it will be a straight arrow downwards, it is a vertical arrow 3 to 4 is a isobaric compression once again when the heat Q C leaves the cycle and finally 4 to 1 we have an adiabatic process, so it is in vertical line above. So, this is the equivalent T-S diagram. Now, I would request you to calculate the efficiency expression from the T-S diagram directly and see if you can get to the same expression; you should actually.

So, that brings us to the last problem of this week, which is problem number 10. So, it is a very simple problem. The same figure which I have drawn, so, I will not go there anyway. So, calculate the efficiency ratio of this T-S cycles A and B which is basically we need to calculate the eta A by eta B, what is the efficiency of a Carnot engine eta C working between the same 2 reservoirs in terms of eta A. So, we have two parts in this problem.

In first part we have to compute the efficiency eta A and eta B of these two cycles and then we have to express eta A in terms of eta C. So, let us do the first part eta A, once again what is the efficiency? Efficiency will be work divided by heat; work done is strictly given by the area inside the circle. So, in inside the triangle area and heat input is the total area of this rectangle here.

So, what is the height of this rectangle? It is given as T 1, what is the width it is S 1 minus S 2. So, for the cycle A the efficiency is simply T 1 times S 1 minus S 2 divided by the area of the triangle. Now, what is the area of the triangle? Half into base into height, what is the height? T 1 minus T 2, what is the base? S 1 minus S 2. So, it will be half into S 1 minus S 2 times T 1 minus T 2.

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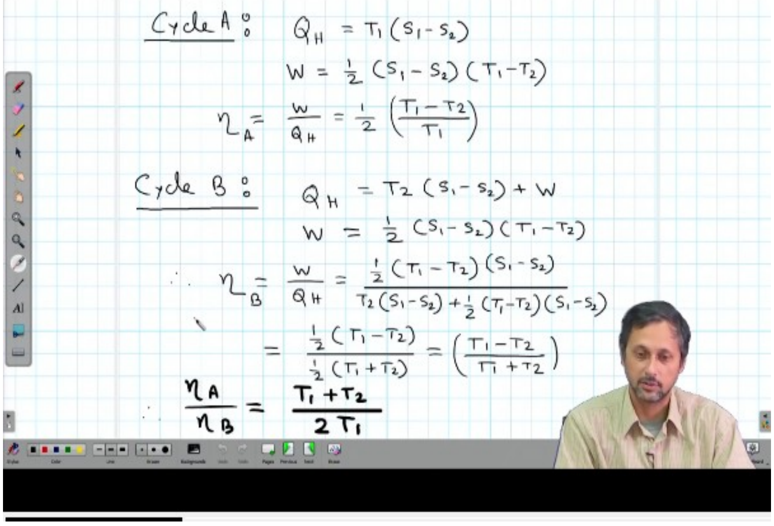

Cycle A:

$$Q_H = T_1(S_1 - S_2)$$

$$W = \frac{1}{2}(S_1 - S_2)(T_1 - T_2)$$

$$\eta_A = \frac{W}{Q_H} = \frac{1}{2}\left(\frac{T_1 - T_2}{T_1}\right)$$

Cycle B:

$$Q_H = T_2(S_1 - S_2) + W$$

$$W = \frac{1}{2}(S_1 - S_2)(T_1 - T_2)$$

$$\therefore \eta_B = \frac{W}{Q_H} = \frac{\frac{1}{2}(T_1 - T_2)(S_1 - S_2)}{T_2(S_1 - S_2) + \frac{1}{2}(T_1 - T_2)(S_1 - S_2)}$$

$$= \frac{\frac{1}{2}(T_1 - T_2)}{\frac{1}{2}(T_1 + T_2)} = \left(\frac{T_1 - T_2}{T_1 + T_2}\right)$$

$$\therefore \frac{\eta_A}{\eta_B} = \frac{T_1 + T_2}{2T_1}$$

So, that is exactly what we have written here. And the efficiency is equal to W by Q H is half T 1 minus T 2 divided by T 1. Now, for cycle 2 the same rule applies. Here also the work done is exactly the same because it is just the inverted triangle, but with same height and same base. So, even if we invert a triangle, it does not change the total area of the triangle. So, the formula the relation for work done remains exactly the same. Q H is this area which is the combination of this rectangle which has a width of T 2 times S 1 minus S 2 plus this triangle, which is W once again.

So Q H is T 2 times S 1 minus S 2 plus W and W is equal to half S 1 minus S 2 minus times T 1 minus T 2. So, eta B is equal to W by Q H, we write this expression fully simplify and we get this is equal to T 1 minus T 2 divided by T 1 plus T 2. So, we have eta A, which is half T 1 minus T 2 by T 1, we have eta B, which is T 1 minus T 2 by T 1 plus T 2. So, the ratio is simply eta A by eta B is equal to T 1 plus T 2 divided by 2 T 1.

Now, comes the efficiency of this Carnot engine, now, what are the temperatures T 1 and T 2 here? So, T 1 is the temperature of the hot reservoir, T 2 is the temperature of the cold reservoir. So, the Carnot engine will have an efficiency eta is equal to 1 minus T 2 by T 1 which is T 1 minus T 2 divided by T 1 and if we compare it with eta A which is just half of this T 1 minus T 2 by T 1.

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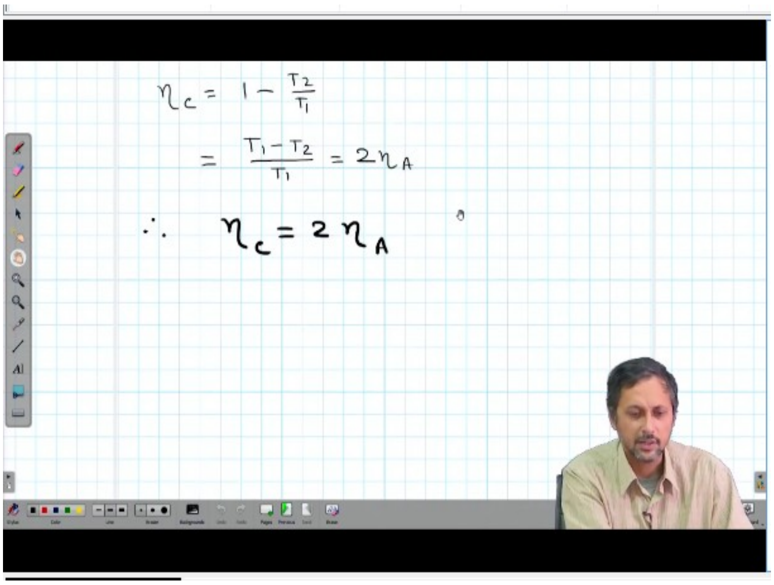

$$\eta_c = 1 - \frac{T_2}{T_1}$$

$$= \frac{T_1 - T_2}{T_1} = 2\eta_A$$

$$\therefore \quad \eta_c = 2\,\eta_A$$

So, obviously, eta C is equal to 2 times eta A. So, this is our final relation. So, that ends the discussion of this week's content. There are certain corrections which have to be made in the note in the final version. I will probably leave this unchanged for this particular question problem 9, but in the first page itself there are certain corrections to be made which I will do while before final upload.

So, what we have learnt in this week? We have learnt about entropy the physical meaning of entropy, physical interpretation of entropy that is in the last class. But before that we have learnt about many exiting and important properties of entropy the mathematical formulation of second law of thermodynamics. For example Clausius inequalities, one useful mathematical form for second law of thermodynamics and also we have learnt about the working principle at basic principle of internal composition NCC.

So, next week onwards we will be focusing more into thermodynamic relations, we will go into little more complicated relations than what we have discussed so far and then slowly and slowly we will drive towards free energies we will define free energies and we will see the usefulness of this free energy function, but that is for next week, for now it is time to say good bye.