Engineering Thermodynamics

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Lecture - 17

Laws of Thermodynamics:
Entropy. Entropy change for a system.

Now, we will look at Entropy. And go to the same sort of set of arguments which we did yesterday, in looking at energy into energy for that mole.

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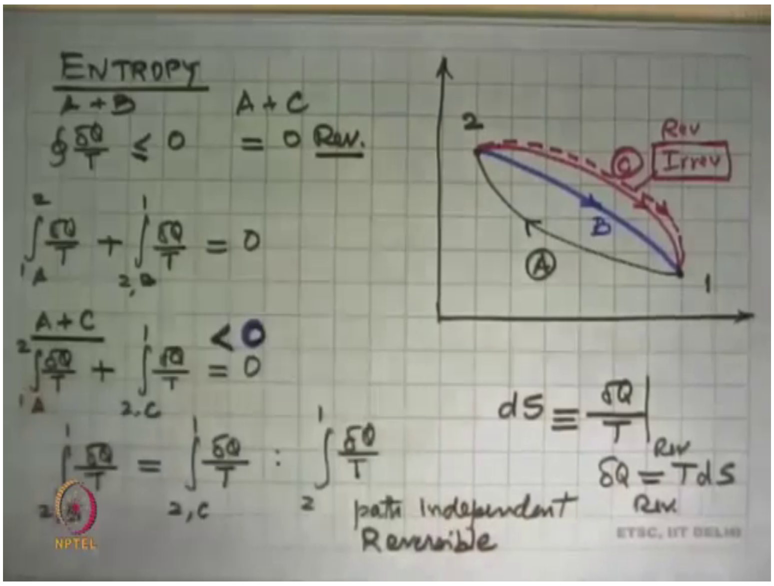

ENTROPY

A + B   A + C

$\oint \frac{\delta Q}{T} \le 0 \qquad = 0$ Rev.

$\int_{1,A}^{2} \frac{\delta Q}{T} + \int_{2,B}^{1} \frac{\delta Q}{T} = 0$

A + C

$\int_{1,A}^{2} \frac{\delta Q}{T} + \int_{2,C}^{1} \frac{\delta Q}{T} \overset{< 0}{= 0}$

$\int_{2}^{1} \frac{\delta Q}{T} = \int_{2,C}^{1} \frac{\delta Q}{T} : \int_{2}^{1} \frac{\delta Q}{T}$

path Independent
Reversible

$dS \equiv \left.\frac{\delta Q}{T}\right|_{Rev}$

$\delta Q = T\,dS$
Rev

Here any two properties against which we have plotting here. And like yesterday we say that we have two state points 1 and 2. And a process takes the system from state 1 to state 2 along path A. During this time there is some work transfer and heat transfer with this system. And then we complete the cycle by saying that there is one path which is B with (Refer Time: 01:17) and we also define yet another path by with which we complete the cycle, this is C.

And yesterday we applied to we looked at two cycles now here, A plus B is one cycle and A plus C this is the other cycle. Yesterday we looked at cyclic integral of heat equal to cyclic integral of work for this. Today we will look at cyclic integral of delta Q by T. So, first we evaluate this and we know that from Clausius inequality this is less than or equal to 0. And for to begin with we will assume that equal to sign is applicable for reversible cycles.

So, we will consider that A plus C, A plus B is a reversible process. And A plus C is also a reversible cycle. So, that two cycles both are reversible. So, cyclic integral of this for A plus B becomes integral 1 to 2 along path A integral delta Q by T plus integral 2 to 1 along path B, delta Q by T and this we say is 0. That is a reversible cycle, we are assuming that all process are reversible.

We get the same sort of statement for A plus C cycle now. So, this becomes integral 1 to 2 delta Q by T upon along path A to a integral 2 to 1 along path C delta Q by T, this is 0. And we subtract these two and what we get is integral 2 to 1 along path B delta Q by T is equal to integral 2 to 1 along path C delta Q by T. And what it is this tells us is that integral delta Q by T from 2 to 1 is path independent.

Here all BCD or anything else did not matter. The only restriction we have took so far were that these are reversible processes. So, we define, so this has to be a property. So, we define the new property now entropy dS S delta Q by T means some these argument is come out from a reversible process and also tells us that delta Q for a reversible process is TdS ok. So, if we integrate this equation now.

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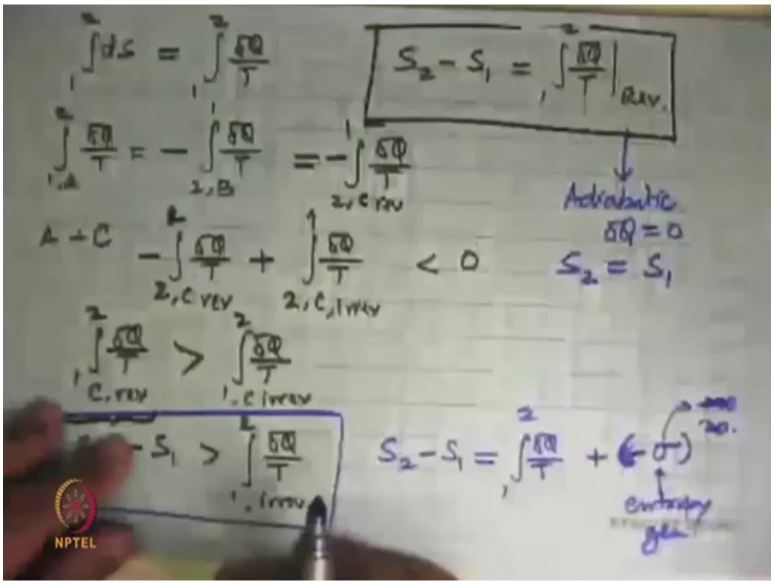

$$\int_1^2 dS = \int_1^2 \frac{\delta Q}{T}$$

$$\boxed{S_2 - S_1 = \int_1^2 \frac{\delta Q}{T}\Big|_{\text{Rev.}}}$$

$$\int_{1,A}^{2} \frac{\delta Q}{T} = -\int_{2,B}^{1} \frac{\delta Q}{T} = -\int_{2,C\,\text{rev}}^{1} \frac{\delta Q}{T}$$

Adiabatic

$\delta Q = 0$

$S_2 = S_1$

A + C $\quad -\int_{2,C\,\text{rev}}^{1} \frac{\delta Q}{T} + \int_{2,C,\,\text{Irrev}}^{1} \frac{\delta Q}{T} < 0$

$$\int_{1,\,C,\,\text{rev}}^{2} \frac{\delta Q}{T} > \int_{1,\,C\,\text{Irrev}}^{2} \frac{\delta Q}{T}$$

$$- S_1 > \int_{1,\,\text{Irrev}}^{2} \frac{\delta Q}{T}$$

$$S_2 - S_1 = \int_1^2 \frac{\delta Q}{T} + (\sigma)$$

entropy gen

So, we have integrate dS is 1 to 2 is equal to integral sorry I am just splitting on the steps delta Q by T. Then left side becomes S 2 minus S 1 is equal to integral 1 2 delta Q by T for a reversible process. So, that is a important relation we have got that tells us what is the entropy change during a process. But what if the process were irreversible?

Hey, so now we will read what we have done there going back. Now we say that C, earlier we took this as reversible now we take this irreversible; and irreversible means that at every intermediate state is not defined. So, this line should not technically be shown as a dotted line. So, that is process C which is now irreversible. As we develop the same things here and what we get is A plus B remains unchanged.

But A plus C is now an irreversible cycle and so Clausius inequality tells us is that A plus C is the B equal to 0 is now less than 0 here is. So, what happens now from the first equation? This is equal to 0 because that is a reversible cycle. So, we get integral 1 to 2 A delta Q by T is equal to minus integral 2 to 1 by path B delta Q by T. And you know this is a reversible process so yes we can say that is C over a reversible process 2 to 1 C reversible then I can put this way.

Hey, so what I have done is we taken this first equation taken this term to a right side and that gave us this equation. And now we argue that is to the B if this was C and C were reversible then it will be equal because this is path independent we just shown that ok. So, that is what we done and now we will go back and put it in our this equation A plus C. So, now, we will go back and see what happens to A plus C.

So, A here integral 1 to 2 A is now replaced by this one 2 to 1 C reversible process. So, a minus there plus integral 2 to 1 C which is now we are looking at the irreversible one is less than 0. So, what it tells us if we change things and flip little bit of things there a integral 1 to 2 delta Q by T C reversible is greater than 1 to 2 delta Q by T C irreversible. And the left side we just derived that for a reversible process integral of delta Q by T over two states which is here is S 2 minus S 1 this will be greater than integral delta Q by T then the process is irreversible.

And that is one important inequality that has come about. And to make it equal what is we can do is say that S 2 minus S 1 I want to make it equal. So, this terms stays where it is 1 to 2 delta Q by T plus a minus sigma which is entropy generation. Why? On plus minus sigma we will come up little later when we do some more analysis. But its implication is the same thing that when Clausius inequality says that be less than 0 sigma should be a positive number.

So, this sigma itself is a positive number, then things fall place sorry this is sigma the entropy generation the cycle to remind us sorry. Now let us go back and look at these equations, say if it is a reversible process and in a reversible process we say it is adiabatic which means that delta Q is equal to 0 then S 2 is equal to S 1.

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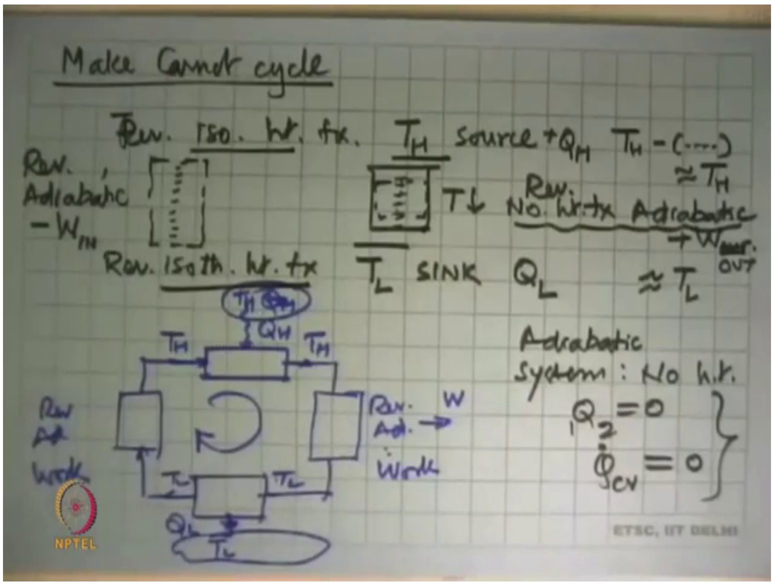

And this becomes nice for us because that is what we were talking of an; the question that how can I make a Carnot cycle. And what we are seen here is that the two isothermal heat transfer processes.

Then, the reversible adiabatic process a reversible adiabatic process and we just saw that if it is reversible and if it is adiabatic then S 2 is equal to S 1; that means, during the process there is no entropy change.

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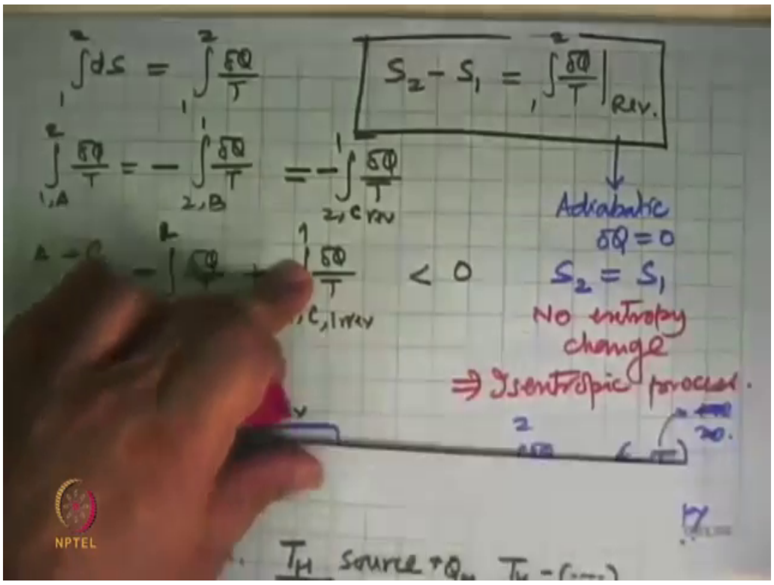

$$\int_1^2 dS = \int_1^2 \frac{\delta Q}{T}$$

$$\boxed{S_2 - S_1 = \int_1^2 \frac{\delta Q}{T}\Big|_{Rev.}}$$

$$\int_{1,A}^{2} \frac{\delta Q}{T} = -\int_{2,B}^{1} \frac{\delta Q}{T} = -\int_{2,C\,rev}^{1} \frac{\delta Q}{T}$$

A → C $\quad -\int^{2} \frac{\delta Q}{T} + \int_{2,C,Irrev}^{1} \frac{\delta Q}{T} < 0$

Adiabatic

$\delta Q = 0$

$S_2 = S_1$

No entropy change

⇒ Isentropic process.

T_H source

So, this is an isentropic process.

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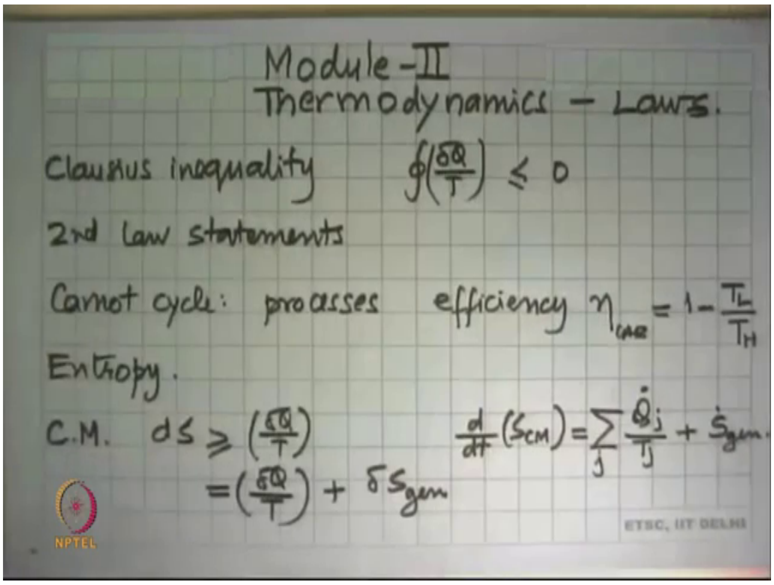

Module-II

Thermodynamics – Laws.

Clausius inequality $\oint\left(\frac{\delta Q}{T}\right) \le 0$

2nd law statements

Carnot cycle: processes efficiency $\eta_{CAR} = 1 - \frac{T_L}{T_H}$

Entropy.

C.M. $dS \ge \left(\frac{\delta Q}{T}\right)$

$= \left(\frac{\delta Q}{T}\right) + \delta S_{gen}$

$\frac{d}{dt}(S_{CM}) = \sum_j \frac{\dot{Q}_j}{T_j} + \dot{S}_{gen}$

We looked at the second law statements the Clausius Inequality which told us that cyclic integral of delta Q by T is less than or equal to 0. We looked at two statements of the second law, the Kelvin Planck statement and the Clausius statement. Both of this told us that certain thing certain cycles are not possible. We can looked at how what would it take to make such as objective possible.

And came up with the fact that it must have heat exchanged with two reservoirs and have work input or output work output will be a heat engine work input will be a refrigerator. And then we went on to look at what is most ideal cycle that we have. And that is where we came up with the idea of a Carnot cycle where we said that every process is internally reversible and externally reversible.

We saw that it consist of four process; two isothermal heat transfer process and two adiabatic work transfer process all of which are reversible. That gave us the idea that we can; so, the cycle that is going to be the best cycle or it given TH and TL. And for that we calculated the efficiency that the maximum efficiency which is the Carnot cycle efficiency will be 1 minus TL upon TH. TL is the temperature of the low temperature a reservoir which is the sink; TH is the temperature of the source from where we draw energy.

So, this gives us the upper limit on how good a cycle we can make. Irrespective of what type of a cycle it is what source we have easy. And we put some numbers last time on it that if I have a (Refer Time: 14:07) power plant what do I get if it is solar thermal ocean thermal. We looked may easy and set to be the type of efficiency we get there all listed in 1. And the real world the actual efficiency we get are even much lower than that. But that is the motivating factor why we need to do from the development and research and come up with new technology is to try to increase that efficiency of real cycle.

Knowing that the most ideal case will be the Carnot cycle which have been never achieve. But the clever I get back the better it is. And the (Refer Time: 14:43) for doing it these days is that when you make the cycle more efficient of the same output your energy input goes down which means that your carbon foot print has gone down it will become more in coefficient. So, whether it is an aircraft engine or a coal filed power plant everyone is looking to go in that direction.

So, this was very simple, but, but our statement or a fact of very far which consequences which makes everything move in some directions. We then went on to look at we defined entropy. And we said that how what is entropy we for control mass we got a relation dS greater than or equal to dQ del Q by T. Or to make it an equal to sign we said that we have generated entropy which means that that was some irreversibility in the system.

Because of that irreversibility this entropy got generated and our objective would be in a process or in a cycle can we minimize the generation of entropy. Basically we are saying the same thing that we can be increase the efficiency of this. So, we got this equation for a control mass, the rate of change of entropy of the control mass d dT S CM equal to entropy associated with all the heat transverse which is the summation for every heat transfer that is happening to the control mass which is Q dot j by T j, j is individual heat transfer terms plus the rate of generation of entropy. So, this is just the term for a process this is a rate term d by d t, but this is for a control mass. So, that is one equation we have and we left it at that point.

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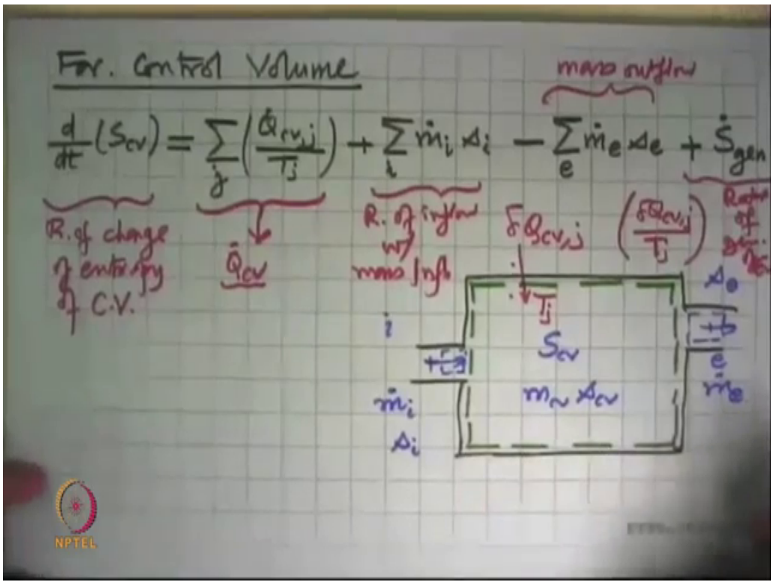

For. Control Volume

$$\underbrace{\frac{d}{dt}(S_{cv})}_{\text{R. of change of entropy of C.V.}} = \underbrace{\sum_j \left(\frac{\dot{Q}_{cv,j}}{T_j}\right)}_{\dot{Q}_{cv}} + \underbrace{\sum_i \dot{m}_i s_i}_{\text{R. of inflow w/ mass inflow}} - \overbrace{\sum_e \dot{m}_e s_e}^{\text{mass outflow}} + \dot{S}_{gen}$$

I will take one more little time to put up this equation which is entropy generation or entropy equation for a control volume. Then the derivation will go very much the same way that we did for the mass conservation or energy conservation. Whereas, instead of energy we are now looking at entropy and the difference is that across the system boundary we now are looking at where the heat transfer is taking place.

So, this way that was the system, then our control volume like before it closes all the mass that is inside the control volume. And the way entropy first we will say then what was the inflow and outflow this is just like what we had before. This is one and this could be called inlet i. This was exit e and there was a mass flow rate associated with this m dot i.

And like that for everyone of the inflows and for here there was a out flow m dot e. And we say that which we are considered last time it carried mass then it carried energy. Now, it is carrying its specific entropy s i and this element that got out after sometime this carried it is entropy s e. And this is the control volumes so this will have S CV which is the entropy of this which we can write as m of the control volume multiplied by s of the control volume the specific entropy.

The entropy is associated with irreversibilities that will come and also with every time there is a heat transfer to the system there will be an entropy transfer in to the system. So, if at this point there was a heat transfer then the system temperature there was T j. And the heat transfer input here was q delta Q CV, j then this cost an entropy inflow of delta Q CV j upon T j. So, that is what is doing that every place where there is a heat transfer into the system there is a entropy transfer associated with that.

And then we can go about the same way that we did last time. And in the equation that comes out will be that the rate of change of entropy of the control volume rate of change of entropy of the CV. This has got the rate of outflow minus rate of inflow it on the other side of the equation state will looking like that.

That what it telling us that if that this is rate of inflow with mass rate of inflow with mass flow mass inflow this is rate of change with mass outflow. And this term this is rate of change of entropy transferred to the control volume across the system boundary due to heat associated with Q dot CV. And in the end we have this term S dot gen; this is the rate of generation of entropy. So, that is the equation that we have been looking for and it differs from the other two equations very slightly.

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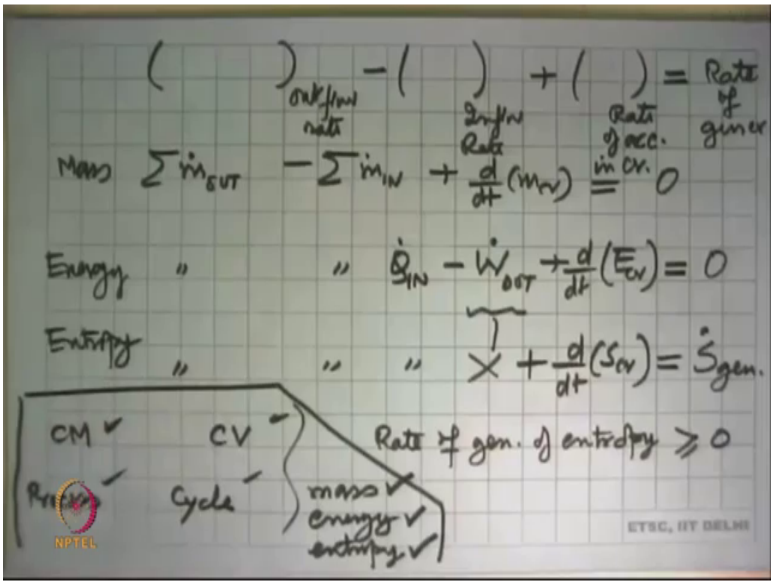

So, if I have to make a very general statement about all these conservation equations. We said that something out flow rate minus something inflow rate plus something rate of accumulation in control volume is equal to rate of production or rate of generation or rate of creation we can you use any of those term. And when we looked at this entity to be mass we said that mass outflow rates minus mass inflow rates plus rate of accumulation of mass in the control volume this we said rate of creation of mars which is 0.

There was a question on the form that also I will take up. Why are we saying 0 then there is energy associated with mass. So, I will come to that in a minute we are saying that rate of creation of mass is 0 that is why we got this 0 over here. Then we looked at energy and outflows were similar energy outflow this energy outflow. Then inflow was Q as heat, outflow was work from the system plus rate of storage of energy in the control volume.

And this equates to the fact that rate of generation of energy which it was 0 and that is how we got this equation. So, outflow rate minus inflow rate plus rate of accumulation of energy is equal to 0. For entropy things are bit different; the outflow rates inflow rates are the same there is no work no entropy associated with work transfer, plus accumulation of entropy in the control volume. This is rate of generation or the rate of creation of entropy which is always greater than 0.

Rate of generation of entropy will always be greater than or equal to 0 equal to if it the reversible process greater than otherwise. And that difference which is there we said that this is rate at which entropy is generated. So, then the difference between these two conservation equation where this a rate of creation of mass is 0 rate of creation of energy 0 entropy there is always a positive rate of creation of entropy ok. So, that is what that equation was telling us.

And now we have all the equations we have completed everything that we wanted to analyse the control mass or a control volume going either in a process or a cycle. And we now have equations for all three mass energy and entropy. So, this completes the set of governing equations of the laws of thermodynamics which each and every application must follow. There is no chance there is no probability that any of these could be violated.

The system would be impossible, or if we are solving a problem is (Refer Time: 24:53) we made a mistake. So, this is what has come out as all these discussion. And we have reached the point where we are now saying that I can analyse any system I want any machine I want any device I want. We have now the tools and we know that starting from here if we make suitable assumptions like to become bit easier. But there we will we have to make sure that all these are obeyed by that system ok. So, this is one thing we will then now look at some special cases and see how things work out and come up with some more concepts.

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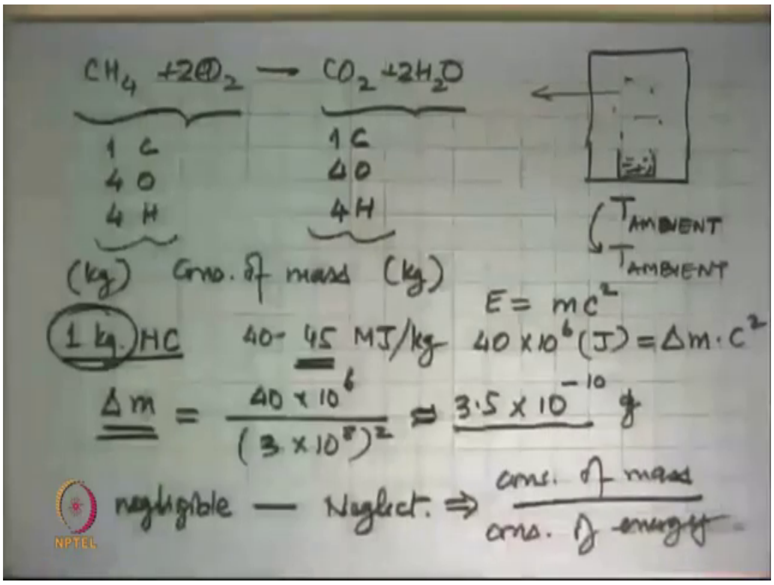

$$\underbrace{CH_4 + 2O_2}_{\substack{1\,C \\ 4\,O \\ 4\,H}} \rightarrow \underbrace{CO_2 + 2H_2O}_{\substack{1\,C \\ 4\,O \\ 4\,H}}$$

$T_{AMBIENT} \rightarrow T_{AMBIENT}$

(kg) Cons. of mass (kg)

$E = mc^2$

(1 kg) HC   40- 45 MJ/kg $40 \times 10^6 (J) = \Delta m \cdot c^2$

$$\Delta m = \frac{40 \times 10^6}{(3 \times 10^8)^2} \approx 3.5 \times 10^{-10}\ g$$

negligible — Neglect ⇒ $\frac{\text{cons. of mass}}{\text{cons. of energy}}$

Before that let me go back to what I just said that rate of creation of mass or rate of destruction of energy or creation of energy we have taken to be 0. And there the question that suppose we have a container in which we put some oxygen and we put some fuel same liquid fuel or a solid fuel and we ignite it. So, initially it is all that the ambient temperature T M. We ignited this hydrocarbon completely burns into this that everything inside the chamber becomes very hot.

And then we transfer this energy out is heat transfer across the boundary. So, that it comes back to T ambient and one more argue is well you know that energy out of the same molecules which are there conservation of mass means every atom is still there, it may be in a different form of a molecule. For example when we wrote CH 4 plus HO 2 go to CO 2 plus H 2 O when balance this 2 here and 2 there. What it tells us is that before the reaction we had one carbon atom, 4 oxygen atoms, 4 hydrogen atoms.

And after the reaction 1 carbon atom 4 oxygen atoms 4 hydrogen atoms, this in a sense of conservation of mass that at the atomic level we are saying that Bth atoms are still there their mass has not change. And so at the molecule macro level the mass is still the same the mass is conserved. So, it may this we got carbon dioxide and H 2 O, but whatever kg was there on this side is remaining as kg of CO 2 and H 2 O still there.

And so mass is conserved, the question that if we put that much energy out should not this mass be less because we have learned that E is equal to mc square and that is a very valid question. So, let us me go quick calculation and so you look how much will be the change of mass and we will do a calculation there. In this case we take 1 kg of a hydrocarbon fuel like same in methane we completely burn it and get the energy out.

And we ignore from experience that for methane or for most such hydrocarbon fuels the energy that you get out which means that you burn them and brought them back to the ambient temperature the question is how much energy came out that energy is of the order of 40 to 45 mega joules per kilogram. So, what this methane, butane, pentane, hexane, by in large it is in the same bowl path A little bit this way that way now counts are less is even less that that we will look at this particular case.

So, if we burn burnt 1 kg of a hydrocarbon fuel and say we got out 40 mega joules. So, E is 40 into 10 to the power 6 joules. The question is what was the change in the mass that took place? So, if I do this calculation the decrease in mass that we expect this will be 40 into 10 to the power 6 joules divided by C square with a speed of light 3 into 10 to the power 8 metres per second and this whole thing is square. And if we take this calculation little further this is becomes 40 upon 9.

So, we say this is about 3.5 into 10 to the power this is 16. This is 6 minus 10 grams. So, therefore, very very small amount compared to what we used of 1 kilogram. And so we are justified in classical thermodynamics are saying that whenever we talk of heat transfer the associated mass change is negligible. And so we neglect this, it is way less. So, no where we what we are looking at and so the implication is that conservation of mass is independent of conservation of energy.

This will be the case when we look at nuclear reactions where the change of mass in a reaction is substantial, then we cannot do this in this case there will be a mass term or here there will be a mass change term because of energy change and here there will be a energy loss term which that reaction produce. So, in classical thermodynamics this is ok for us. These are two independent equations they are not connected to one another. And we are justified and saying that mass change associated with energy change in classical thermodynamics is negligible ok. So, that takes care of this aspect.