Thermal Engineering: Basic and Applied

Prof. Dr. Pranab K Mondal
Department of Mechanical Engineering
Indian Institute of Technology - Guwahati

Lecture – 04

Second Law of Thermodynamics: A Brief Review

I welcome you all to this session of thermal engineering and the topic of our today's discussion is a brief review of the second law of thermodynamics. In the last class, we have briefly talked upon this aspect and we have discussed that the objective of the second law in the context of thermodynamics essentially and though the subject is thermal engineering and we shall be discussing about a few cyclic systems, I mean the system's undergoing through cyclic processes, but, I wanted to have this discussion, keeping in mind that all the processes which are there in real applications are the irreversible process.

So, we have studied in thermodynamics that irreversibility leads to destruction of the performance. So, our objective should be to know about this, to quantify about this and then upon quantifying, we should take some kind of measures to reduce the degree of irreversibility is associated with any particular process. We should study about this, why? So, we know that all processes are having some degree of irreversibility and knowing that cannot we try to study what is the degree of irreversibility present in this process? In other way cannot we tell to what extent our real process is deviating from the reversible process?

And if we really know that this particular real process is deviating from these reversible process and if we can quantify the extent of deviation then that would be good for the system. So, the next objective is to quantify the extent of deviation mathematically of course, and having quantification of this particular term, we can definitely take some preventive measures, essentially to increase the performance or efficiency of the systems.

So, second law of thermodynamics is important in this context. Second Law of Thermodynamics provides us a means of quantifying the degree of irreversibility present in any process. So, before going to discuss about that part, of course, not in a greater detail, but I would like to briefly touch upon that, let us recall 2 important statements that we have studied in the context of second law. What are those? First is Kelvin Planck statement that you have studied what is this statement?

We have studied that it would be very difficult to have a device that will operate in a cycle and will produce no effect other than raising a weight while exchanging heat with a single thermal temperature reservoir. So, let me tell you again, never try to memorize rather try to understand what the statement talks about and then try to describe it in your own sentence.

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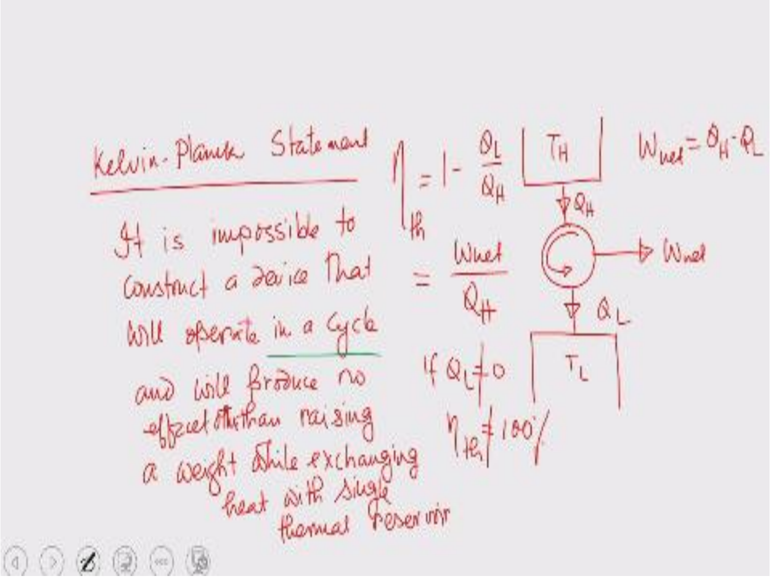

Kelvin-Planck Statement

It is impossible to construct a device that will operate in a cycle and will produce no effect other than raising a weight while exchanging heat with single thermal reservoir

$$\eta_{th} = 1 - \frac{Q_L}{Q_H} = \frac{W_{net}}{Q_H}$$

$W_{net} = Q_H - Q_L$

if $Q_L \neq 0$

$\eta_{th} \neq 100\%$

Kelvin Planck statement.

It is impossible to construct a device that will operate in a cycle; of course, a mechanical device in the context of this course, we can say thermal device that will operate in a cycle and will produce no effect then raising a weight while exchanging heat with single thermal reservoir.

So, this is the statement of second law; I mean Kelvin Planck to be precise, and we all have studied about it. What it physically tells us? It is telling that it would be very difficult to construct a device that will operate in a cycle I mean, if we do not include these words, then perhaps it would be possible. So, if you would like to have the cyclic operation, then it would be very difficult to construct a device, which will produce no effect than raising a weight while exchanging heat with single temperature thermal reservoir. So, if we try to draw schematically one device, basically these 2 statements of second law are used in the context of either heat engine or heat pump or refrigerator.

So, if it is a device which is operating in a cyclic process and while exchanging heat with single temperature thermal reservoir; say temperatures are T_H & T_L. So, thermal reservoirs are very large, so, we can maintain the constant temperature T_H and upon receiving heat Q_H, it is telling something about raising a weight, so, it has to do some work W_{net} and that is what you have studied in thermodynamics.

So, while exchanging heat with single temperature thermal reservoir and exchanging it will not be possible in a cyclic manner. So, that means, upon receiving Q_H heat from this temperature reservoir, if you would like to get W_{net}, it will not be possible. So, that means, some amount of heat Q_L must be rejected by this device to another reservoir. You know that we have studied about this thermal efficiency, η_{th}

$$\eta_{th} = 1 - \frac{Q_L}{Q_H}$$

So, here if we assume all the processes are reversible process, we can write

$$W_{net} = Q_H - Q_L$$

So this, just we can write from first law of thermodynamics, if the processes are reversible process.

$$\text{Now,} \eta_{th} = \frac{W_{net}}{Q_H}$$

So, Kelvin plank statement tells us that this $Q_L \neq 0$, if $Q_L = 0$ efficiency will be 100%. But, Kelvin Planck statement tells us that if you would like to run this device in a cyclic process, then efficiency cannot be 100%. So, efficiency cannot be 100% and Q_L should not be equal to 0. So, that means, some amount of heat must be rejected to another thermal reservoir to operate this device in a cyclic manner. So, this is what the statement talks about.

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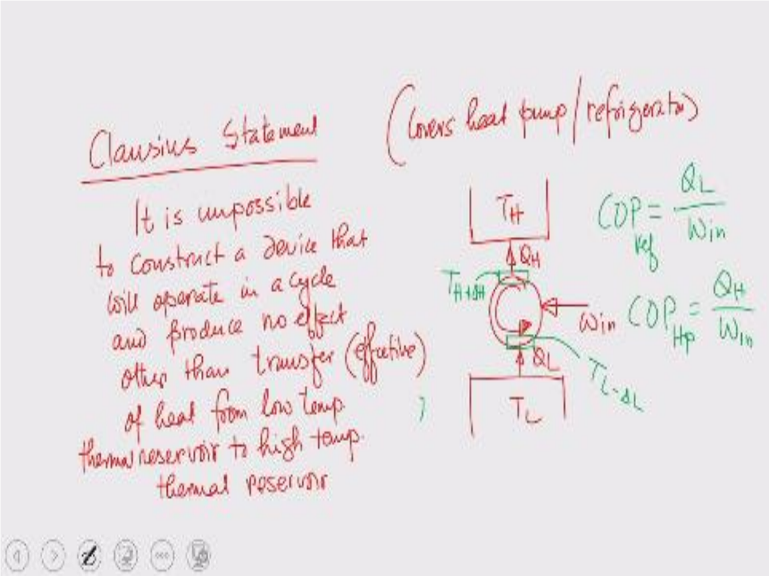

Clausius Statement (Covers heat pump / refrigerator)

It is impossible
to construct a device that
will operate in a cycle
and produce no effect
other than transfer (effective)
of heat from low temp
thermal reservoir to high temp.
thermal reservoir

$COP_{ref} = \frac{Q_L}{W_{in}}$

$COP_{Hp} = \frac{Q_H}{W_{in}}$

Let’s go to another statement that is Clausius statement. It is impossible to construct a device that will operate in a cycle and produce no effect other than effective transfer of heat from low temperature thermal reservoir to high temperature thermal reservoir. I would like to use one word that is effective, effective transfer of heat. So, this statement is again important as this statement is used to cover heat pump or refrigerator.

You know that if we again draw a device and if we assume this is low temperature thermal reservoir and this is high temperature thermal reservoir and this is drawing heat from this low temperature reservoir and supplying heat to the high temperature reservoir. So, the effective transfer of heat using this device only possible if you would like to run this device in a cyclic manner.

So, essentially if you would like to transport heat from this reservoir to that reservoir, this is very important and this transport of heat is mediated by this device and it is not possible if the device is running in a cyclic manner. So, if you would like to have it, we must have work input to the device, basically by supplying work into this device. So, this arrangement is such that, it is now transferring heat from this low temperature thermal reservoir to high temperature thermal reservoir.

Let me tell you, it is next to impossible to transfer heat from low to high temperature thermal reservoir. So, that means, there is a special arrangement, where we are having surface boundary and at these 2 surfaces here temperature is $T_{L-\Delta L}$ and here temperature is $T_{H+\Delta H}$. So, the temperature at the surface must be higher than T_H and temperature at the surface must be lower than temperature $T_L$as shown in slide. And it is because of this arrangement, it would be possible to transfer heat continuously from this low temperature reservoir to the high temperature reservoir. So, if you would like to have it we need to have this special arrangement and as if you know this arrangement.

So, basically the transport of heat that is from lower reservoir to higher reservoir is mediated by the arrangement and to run this device we need to supply continuously energy by work that is W_{in}. So, this covers pump and refrigerator and I am telling that for this particular case, we need to define something called coefficient of performance, COP. So, this device can be used to refrigerant the refrigerator also heat pump.

$$COP_{ref} = \frac{Q_l}{W_{in}}$$

So, essentially at the cost of this input energy by work, how much energy in terms of heat we can transport, so that this space can be refrigerated and that is how this whole COP is defined. Now question is why it is COP? Because our objective should be to reduce more amount of Q L to refrigerated space. So, basically $COP_{ref} > 1$ because Q_L is higher than W_{in}.

So, basically unity; so, basically if you would like to define it as efficiency, it looks odd to have efficiency higher than 1. So, we have studied about efficiency in the context of hydraulic machines in different paradigms. So, basically efficiency we know that it cannot be more than 100% that is what we have seen in the last slide. So, if we define it as the efficiency it looks odd, so, to avoid that the coefficient of performance is coming into the picture. So, basically this quantity is greater than one and to make it different from the efficiency this coefficient of performance is coming into the picture.

So, the coefficient of performance for the heat pump

$$COP_{Hp} = \frac{Q_H}{W_{in}}$$

So, basically I would like to supply heat or I need to pump heat so, that is why heat pump is coming. And it you would like to pump heat, this device will run and we need to supply energy to the device.

Why I am discussing about these 2 statements again; because these are very trivial and you have studied about all these in the context of basic thermodynamics course.

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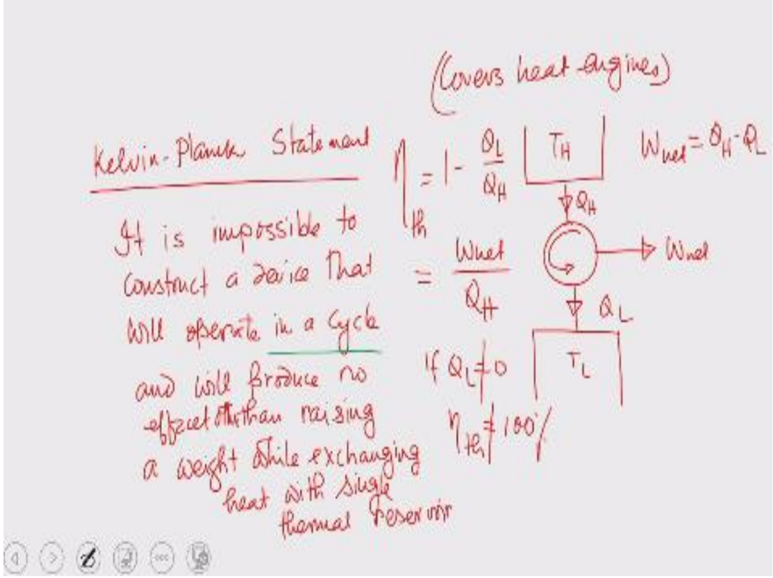

(Covers heat engines)

Kelvin-Planck Statement

It is impossible to construct a device that will operate in a cycle and will produce no effect other than raising a weight while exchanging heat with single thermal reservoir

$$\eta_{th} = 1 - \frac{Q_L}{Q_H} = \frac{W_{net}}{Q_H}$$

$$W_{net} = Q_H - Q_L$$

$$\text{If } Q_L \neq 0$$

$$\eta_{th} \neq 100\%$$

But if you go back to my previous slide, what I have written over here is that this is used to covers heat engine. Now, why I am telling it because, very soon we will start discussing about the steam power cycle. And you would like to get continuous supply of electricity from the power plant that means, it is a continuous process. So, maybe just for example, to get electricity either in a thermal power plant or a hydro power plant, we need to have continuous supply of energy. So, basically in a thermal power plant, by burning coal energy is given to a place where in water gets converted into steam. And that steam is taken to another device, wherein it does work on the rotating part of the machine and we are getting electricity.

So, if you would like to have continuous work output from this particular cycle, there must be a place where in some amount of energy should be rejected. So, keep this in mind & again I will be discussing this part relating to this particular statement, when we shall be discussing about steam power cycle.

So, now very important aspect I am going to discuss. We have talked about Kelvin Planck statement and also the Clausius statement. Again, I am coming back to that particular point that we really would like to know, the extent of deviation of all the processes from the reversible one. We have assume that all these processes are reversible. But, in reality, it is very difficult to achieve a reversible process. So, all processes are irreversible. Now, keeping that in mind our objective should be to find out to define or to quantify the degree of irreversibility present in a process and that is done using this second law.

In the context of thermodynamics, you have studied that one most classical inequality that is the Clausius inequality.

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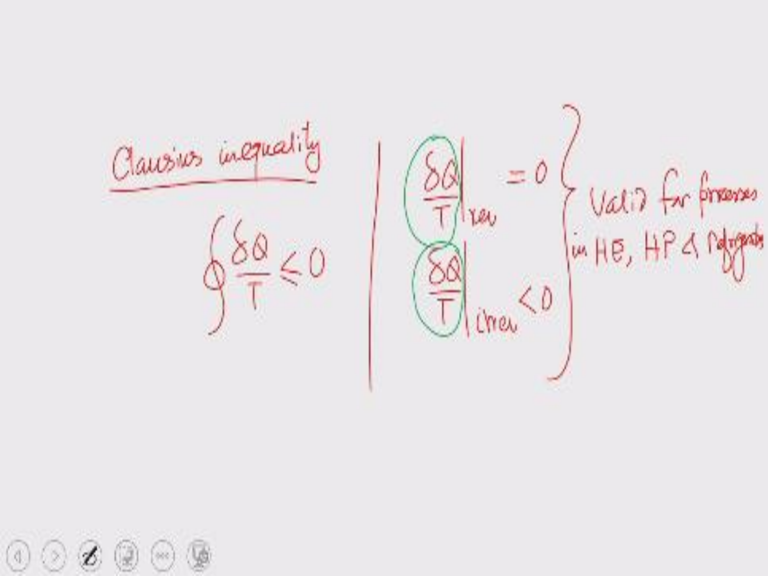

Clausius inequality

$$\oint \frac{\delta Q}{T} \le 0$$

$$\left.\frac{\delta Q}{T}\right|_{rev} = 0$$

$$\left.\frac{\delta Q}{T}\right|_{irrev} < 0$$

Valid for processes in HE, HP & Refrigerator

So, I am trying to discuss about the Clausius inequality. So, what is this? So, this is one of the most classical inequalities, which is studied in thermodynamics.

$$\oint \frac{\delta Q}{T} \le 0\,; \left(\frac{\delta Q}{T}\right)_{rev} = 0 \;\&\; \left(\frac{\delta Q}{T}\right)_{irrev} < 0$$

So, now, we have discussed about heat pump or heat engine now, if it is all the processes are reversible. This can be established through some mathematical analysis, I am not going to do it because that is available in textbook. So if we calculate $\frac{\delta Q}{T}$ for the reversible processes, the processes are getting executed following the reversible path then it is equal to 0. While $\frac{\delta Q}{T}$ for irreversible processes is always less than equal to 0, no matter whether the process is getting executed in heat pump or refrigerator or heat engine. So, this is valid for processes in heat engines heat pumps and refrigerators. So, we can say that this quantity is something special. And we are getting a clue that somehow if we can calculate this, it is for reversal path equal to 0 and it is for reversal path less than 0. So, now, say I would like to calculate this for different reversible path. I am not telling that whether this quantity will give us a mean of quantifying the degree of irreversibility present in the processes, but as if this quantity is giving some indication. So, basically if you try to calculate this quantity for any process, which is getting executed via reversible path, it is equal to 0, and for the irreversible path, it is then less than equal to 0. So, now, let us try to find out this quantity for different reversible processes or paths.

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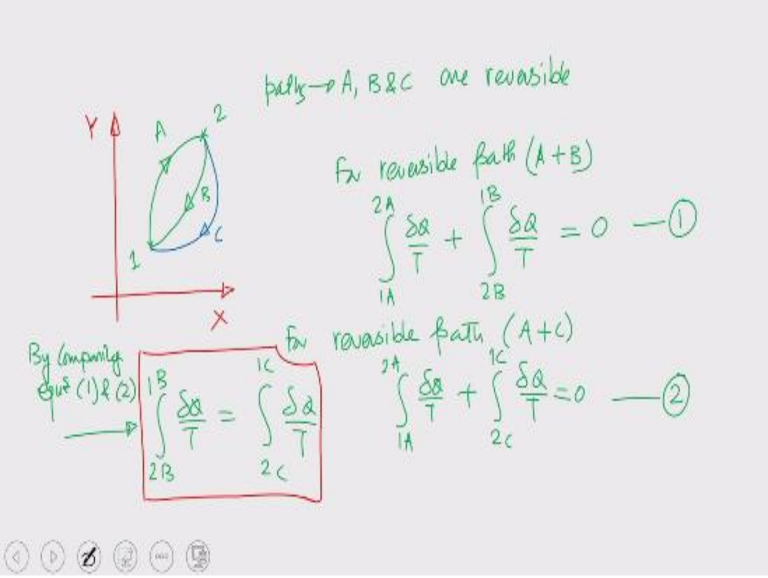

paths → A, B & C are reversible

For reversible path (A + B)

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

For reversible path (A + C)

$$\int_{1A}^{2A} \frac{\delta Q}{T} + \int_{2C}^{1C} \frac{\delta Q}{T} = 0 \quad \text{—} ②$$

By comparing eqn (1) & (2)

$$\boxed{\int_{2B}^{1B} \frac{\delta Q}{T} = \int_{2C}^{1C} \frac{\delta Q}{T}}$$

So, I would like to represent any process in this thermodynamics coordinate diagram. So, X may be volume, Y may be pressure or it may be entropy or temperature. So, I would like to represent a particular process which is changing its state from state 1 to state 2 in this coordinate diagram. So, this is state point 1 and this is state point 2. So, what we are trying to do? We are trying to calculate this particular quantity $\frac{\delta Q}{T}$ for different reversible paths.

So, one path is like from 1-2 and that is path A. This is a cyclic process, because there is cyclic integral $\frac{\delta Q}{T}$. So, this is an inequality. So, basically system is coming back to its original position via path B.

$$\text{For reversible path (A + B)} \rightarrow \int_{1A}^{2A} \frac{\delta Q}{T} + \int_{2B}^{1B} \frac{\delta Q}{T} = 0 ------(1)$$

Now, a system is undergoing a cyclic process and by virtue of this process it changes state from 1 to 2 and it is again coming back to original state. So, that is a cyclic process.

$$\text{For reversible path (A + C)} \rightarrow \int_{1A}^{2A} \frac{\delta Q}{T} + \int_{2C}^{1C} \frac{\delta Q}{T} = 0 ------(2)$$

So, basically there are 3 different paths A B and C and these paths are reversible path.

So, basically we try to quantify $\frac{\delta Q}{T}$ for different reversible process, & here the system is changing its state from 1 to 2 and it is again coming back to its original state, but following different reversible path. If we try to look at these 2 equations 1 and 2, then by comparing these 2 equations we can write

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

So, here perhaps, we are getting an important clue. So, try to understand in previous slide, I did not write that this $\frac{\delta Q}{T}$ less than equal to 0, but, I am telling you, you will find it in all textbooks that this $\frac{\delta Q}{T}$ for reversible process is equal to 0 but for irreversible process is less than equal to 0. It does not matter whether you are calculating this quantity for reversible or irreversible processes, occurring either in heat engine or heat pump or refrigerator. So, we have also discussed that this quantity is giving us a clue that probably we can measure the degree of irreversibility present in the system. So, from this very trivial exercise, we could write the above equation regarding path B & C. And mind it that path B and path C are reversible.

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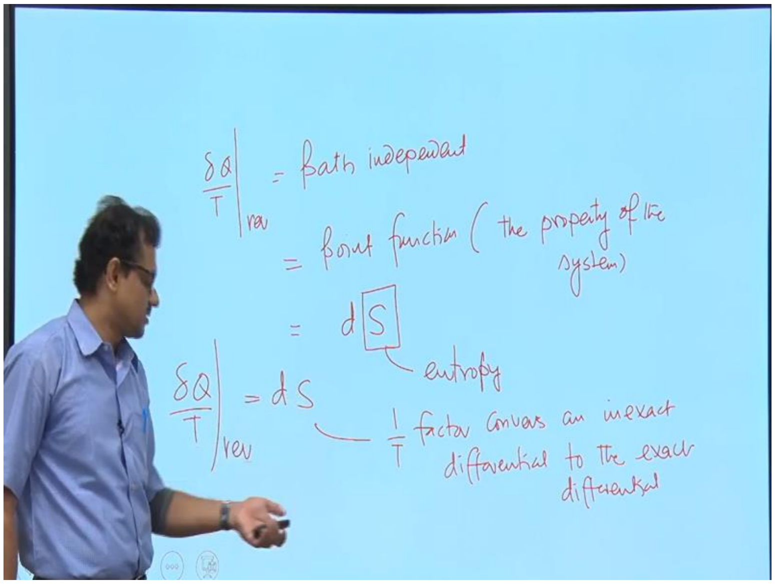

$$\left.\frac{\delta Q}{T}\right|_{rev} = \text{path independent}$$

$$= \text{point function (the property of the system)}$$

$$= d\boxed{S}$$

entropy

$$\left.\frac{\delta Q}{T}\right|_{rev} = dS$$

$\frac{1}{T}$ factor converts an inexact differential to the exact differential

So, what we can say that, this $\frac{\delta Q}{T}$ for the reversible path is path independent. So, if we try to calculate only for the reversible processes or the processes getting executed via reversible paths, then we can write that $\left(\frac{\delta Q}{T}\right)_{rev}$ is path independent. So, this is very important clue. And now, if $\frac{\delta Q}{T}$ is path independent then going back to this ordinate diagram what we can tell?

So, if we try to calculate $\frac{\delta Q}{T}$ for the reversible processes or the processes getting executed following or through the reversible paths, it does not depend on the path. So, basically, it is just the difference between these 2 state points. So, if it is path independent, we have seen from thermodynamics that heat and work are path functions, these are the inexact differential. So, if $\frac{\delta Q}{T}$ is path independent that means it is point function, & it is the property of the system. So, this quantity does not depend on the path, it will depend on the 2 state points of the system. I mean the system is getting changed from state point 1 to state point 2; no matter whether the system is changing its state from 1 to 2 following path B or C as long as paths are reversible, this $\frac{\delta Q}{T}$ is independent of path and naturally it is then point function from our knowledge in thermodynamics that we have learnt.

If it is point function then it is a property of the system & we can write it in the form of exact differential.

$$\left(\frac{\delta Q}{T}\right)_{rev} = \text{Path independent} = \text{Point function} = ds$$

So, basically S is called the entropy of the system. Starting from the Clausius inequality, we could observe that $\left(\frac{\delta Q}{T}\right)_{rev}$ is independent of the path and this is nothing but the point function. And this is the property of the system so we can write it in this exact differential form. So, basically we can write this $\frac{\delta Q}{T}$ via reversible path is the property of the system that is entropy. Very interesting to note that the right hand side of this equation is exact differential while if we look at the left hand side it is inexact differential. So, I mean something is trying to convert this inexact differential to the exact differential & what is that; this 1 / T is basically just an integrating factors & this 1 / T factor converts an inexact differential to the exact differential. So, that is very important that if we take several processes, and can ensure that the processes are reversible processes & then measure δQ for the reversible processes to calculate $\frac{\delta Q}{T}$ over the reversible path & integrate then we will be getting this new property that is called entropy dS. So, this is very important that $\left(\frac{\delta Q}{T}\right)_{rev} = ds$. So, this is entropy.

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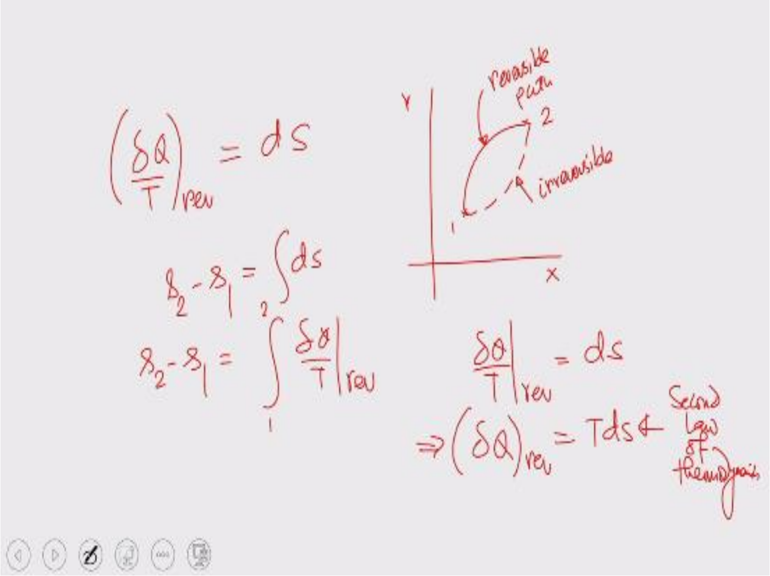

$$\left(\frac{\delta Q}{T}\right)_{rev} = ds$$

$$S_2 - S_1 = \int_1^2 ds$$

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

$$\frac{\delta Q}{T}\Big|_{rev} = ds$$

$$\Rightarrow (\delta Q)_{rev} = Tds \leftarrow$$ Second law of thermodynamics

So, this property is written in the differential form. So, this equation does not talk about what entropy is physically. So, it does not talk about what is entropy itself physically rather it gives us a clue about the change in entropy.

So, let me tell you again, from this equation, we are getting that there exists a property that is entropy, but this equation does not provide any means to calculate the entropy or it does not provide the absolute sense of entropy in a quantitative manner, but it talks about the change in entropy that is ds. So, this is very important.

Now, if we consider say one process and the state point changes from 1 to 2. So, this is the reversible process. And the irreversible processes are shown by this dotted line. So, for the reversible process, what we need to do, we need to calculate δQ, and then we need to integrate $\left(\frac{\delta Q}{T}\right)_{rev}$. So, basically we can say process 1-2 is a reversible path. So, we can calculate δQ for the reversible process, if we integrate this quantity for this reversible path, then we can write

$$s_2 - s_1 = ds$$

$$s_2 - s_1 = \left(\frac{\delta Q}{T}\right)_{rev}$$

$$\left(\frac{\delta Q}{T}\right)_{rev} = ds \;\; \Rightarrow (\delta Q)_{rev} = Tds$$

So, this is the equation that we are getting from the second law of thermodynamics. Again, I am telling, I am not going to discuss in detail about several issues related to this, but just to recapitulate whatever you have learned from basic thermodynamics course and I would like to discuss only those parts which will be useful to understand the remaining content of this course.

Now time has come to discuss about the combined first and second law. I mean, I would like to discuss about our framed equations by making use of first and second law of thermodynamics.

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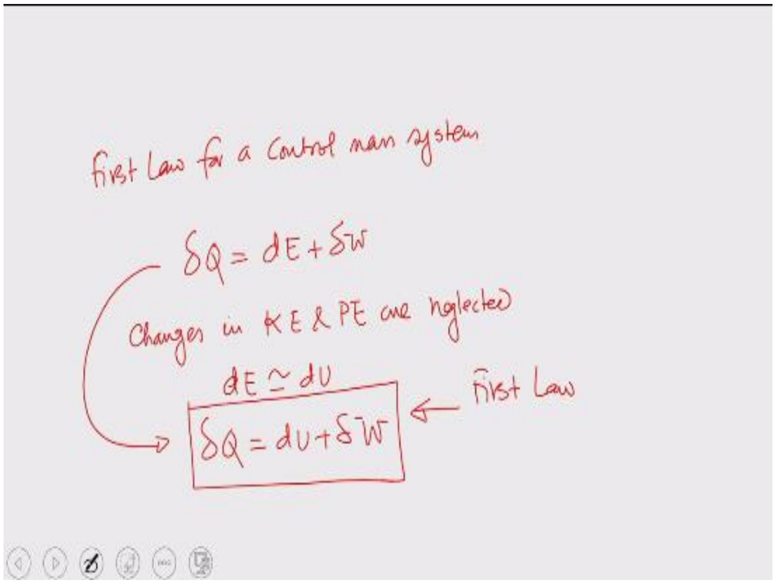

First Law for a Control mass system

$$\delta Q = dE + \delta W$$

Changes in KE & PE are neglected

$$dE \simeq dU$$

$$\boxed{\delta Q = dU + \delta W}$$

First Law

$$\text{First law for a control mass system} \rightarrow \delta Q = dE + \delta W$$

$$\text{Second law of Thermodynamics} \rightarrow (\delta Q)_{rev} = Tds$$

Now if we consider that changes in kinetic energy and potential energy are neglected then we can write $dE \approx dU$.

$$\text{First law for a control mass system} \rightarrow \delta Q = dU + \delta W$$

So, if we try to write this equation for the reversible process or if we assume that the control mass system is undergoing a process which is reversible one, then

$$(\delta Q)_{rev} = dU + (\delta W)_{rev}$$

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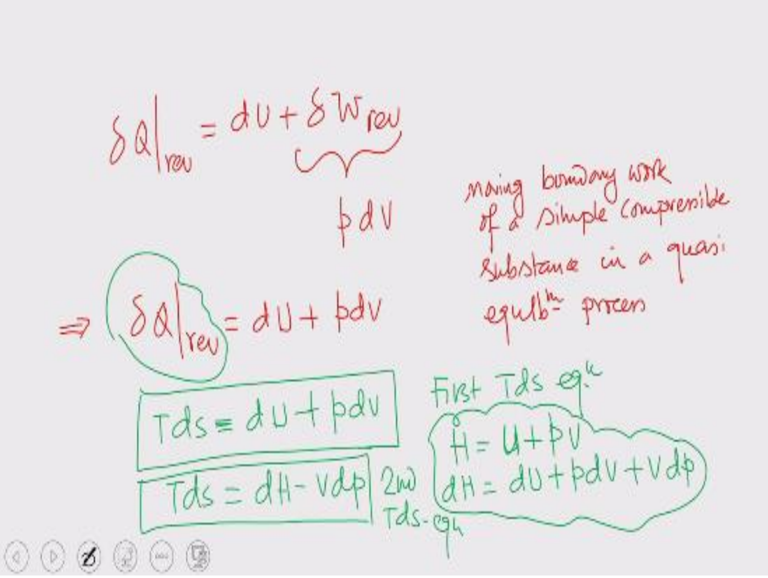

$$\delta Q|_{rev} = dU + \underbrace{\delta W_{rev}}_{pdV}$$

moving boundary work of a simple compressible substance in a quasi equlb^m process

$$\Rightarrow \delta Q|_{rev} = dU + pdV$$

$$\boxed{Tds = dU + pdV}$$

First Tds eq^n

$$H = U + pV$$

$$dH = dU + pdV + Vdp$$

$$\boxed{Tds = dH - Vdp}$$

2nd Tds-eq^n

This is very important to know that $(\delta W)_{rev} = pdV$. So, you have studied that $(\delta W)_{rev}$ is the moving boundary work of a simple compressible substance in a quasi-equilibrium process. So, if system change its state from state 1 to state 2 and because of this change in states, the work done is pdV that means, if it is simple compressible substance only then you can write this is pdV work and moving boundary work. We are excluding the other effects like electrical effect, magnetic effect. So, we can write

$$(\delta Q)_{rev} = dU + pdV$$

You know that all reversible processes are quasi equilibrium processes. So this for the quasi static or quasi-equilibrium processes. So, the process is occurring following another quasistatically or almost statically. So here this is a reversible process. All reversible processes are quasi static process, but reverse is not true. That is all quasi static processes are not the reversible processes. Quasi static processes need not to be reversible processes because they might be externally irreversible. So, this is not our issue. I telling this because we can write $(\delta W)_{rev} = pdV$, when the process is quasi static process. So, all reversible processes are quasi static process, but all quasi static processes are not reversible process because external irreversibility might be here.

$$(\delta Q)_{rev} = dU + pdV$$

$$\text{From second law}, (\delta Q)_{rev} = Tds$$

$$\Rightarrow Tds = dU + pdV$$

Probably this is very common equation that you have learned and this is known as first TdS equation in the context of thermodynamics. We also can write it in terms of entropy, internal energy in specific form that is $TdS = dU + p\,dv$.

So, that is only the matter of writing whether you would like to write in total form or specific form. So, this is the first Tds equation, we have derived. We also need to write the second Tds equation. This is very simple because

$$H = U + pV$$

$$\Rightarrow dH = dU + pdV + Vdp$$

$$\Rightarrow dU = dH - pdV - Vdp$$

Now replacing the dU in the first Tds equation

$$Tds = dH - Vdp$$

So, this is known as second TdS equation. So, basically we are using this property relationship to get the second TdS equation. So, now if you would like to summarize then these two Tds equations are obtained from the combination of first and second law. And the first TdS equation is valid for every processes, but, conceptually it is very important to note that before applying this equation for any processes, we need to integrate it over the reversible path and then only the result of integration can be applied to any processes. So, this is the conceptual part. This equation is valid or applicable to any processes, but, the conceptual thing is that we need to integrate this equation over the reversible path and then the results of integration can be applied to any processes.

So, to summarize today's class, starting from the brief description of the second law of thermodynamics, we could arrive at an equation and that equation defining a new property that is entropy, that is the property or point function of the system and using that particular equation and invoking the first law of thermodynamics for the control mass system, we could establish these 2 important property relations and these 2 important relations will be useful to several processes that we shall discuss in the several modules of this course.

So, with this I stop here today and from the next class onwards, we shall try to discuss about several processes by applying these 2 equations and also by calling our conceptual understanding whatever you have learned from the first and second laws of thermodynamics. With this I stop here today. Thank you.