Applied Thermodynamics for Engineers

Dipankar N. Basu
Department of Mechanical Engineering
Indian Institute of Technology – Guwahati

Lecture - 03
Concept of Entropy and Entropy Generation

Hello friends. Welcome back for the third lecture of this particular week where we are reviewing our principles of basic thermodynamics, with the focus of setting up for the concept which we may have to use in the subsequent weeks. Now, in the first and second lectures, we have discussed about some very fundamental aspects like the concept of thermodynamic system, property, state, equilibrium. Then, we discussed about the different laws of thermodynamics like in the first week or in the first lecture, I mentioned about the zeroth law of thermodynamics which gave us the concept of the property named temperature and in the previous lecture, I mentioned about both first and second law of thermodynamics. Now, from the first law of thermodynamics, we got the concept of internal energy or total energy of a system is a property. we have also seen how to apply the first law principle for both closed and open system analysis. The second law was also introduced where generally we talk about two different statements, the Kelvin-Planck statement, which is the suitable one for heat engines whereas the Clausius statement which is a suitable one for heat pumps and refrigerators or in one word the reverse heat engines.

Now, while the analysis of a system following the first law of thermodynamics is quite straightforward i.e., we just have to go for the balance of energies which are either coming to the system or going out of the system. Or in a way, we can say that whatever energy interactions are taking place within the system and surrounding, we just have to take a balance of that and that should give you an idea about the change in the total energy content of the system.

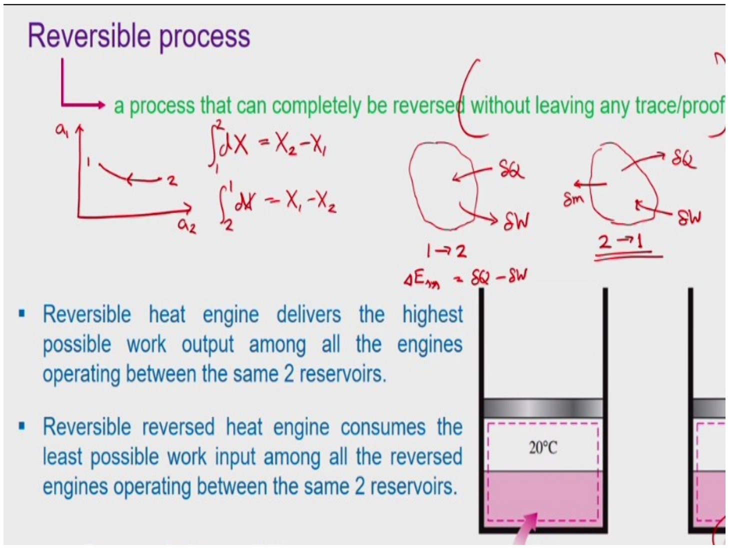
However, for second law of thermodynamics, we do not have such straightforward approach. We generally have two kinds of approach to choose from, one based upon the property called entropy, other based on the concept called exergy. So, in today's lecture, I am going to talk about entropy, introduce the property entropy to you and see how we can calculate entropy for a system.

And in the next lecture, which is going to fourth and last one for this week, I shall be introducing the property exergy and then we shall be seeing how to analyze a thermodynamic system following the second law of thermodynamics based upon the exergy approach.

So, let us start with our discussion on entropy. Now, in the previous lectures, we have seen that there are two different statements of thermodynamics and depending on what kind of system we are talking about, we can choose any one of them. And we know that though the statements look quite different, they are actually equivalent to each other i.e., any violation of the Kelvin-Planck statement leads to violation of the Clausius statement or vice-versa. If you are not sure about how to prove that, you can refer to any standard thermodynamics book.

Now, the first term that I would like to introduce today which comes straight as a corollary or a consequence of the second law of thermodynamics is the reversible process.

(Refer Slide Time: 03:28)



Reversible process

a process that can completely be reversed without leaving any trace/proof

$$\int_1^2 dX = X_2 - X_1$$

$$\int_2^1 dX = X_1 - X_2$$

$$\Delta E_{sys} = \delta Q - \delta W$$

- Reversible heat engine delivers the highest possible work output among all the engines operating between the same 2 reservoirs.
- Reversible reversed heat engine consumes the least possible work input among all the reversed engines operating between the same 2 reservoirs.

Now, the reversible process refers to a process that can completely be reversed without leaving any trace of proof on the surrounding. It means we are talking about changing the direction of a process without keeping any mark on the surrounding.

If we draw a very basic property diagram, let us say I draw a property diagram where we are using some properties a_1 and a_2 based upon which we are plotting. This a_1 and a_2 can be any properties of our choice like pressure and specific volume, pressure and temperature or maybe something else. Let us say this is our initial point 1 and this is state point 2. So, this is our state point 1 and state point 2. So, we are having a process somewhat like this which has taken place. So, during the process, all properties are changing, if we talk about any standard extensive property say *X*, then the change in this extensive property during the process will be:

$$\int_1^2 dX = X_2 - X_1$$

And also, certain interactions are taking place between system and surrounding during this process. Let us say this is our system, so during this forward process, the system receives this amount of heat (δQ) from the surrounding and gives this much of work output (δW). So, this is the scenario during this process 1 to 2. Now, if this process 1 to 2 is a reversible one, then we can reverse its direction thereby moving from this so-called final state back to the initial state without leaving any mark on the surrounding. That we say now we are talking about while the points remain the same 1 to 2, we shall be following exactly the same path. but now the direction will be opposite going back from 2 to 1.

Now, what about the change in the properties? Properties are point functions i.e., whatever maybe the nature of the process, the final change in the property will always remain the same. In the second process, the change in same property X will be from, will be again:

$$\int_2^1 dX = X_1 - X_2$$

properties being point functions we do not need to bother about them.

But we are talking about without leaving any trace of proof on the surrounding or mark on the surrounding that will be coming in terms of whatever interactions that are taking place. That is, if the process has to be completely reversed without giving any mark on the surrounding, then it would be the same process. Then, in the first case we have moved from 1 to 2. Now, we are going back from 2 to 1 and to make this process perfectly reversible, then during the second process the system should reject exactly same amount of heat (δQ) to the surrounding and receives exactly same amount of work (δW) from the surrounding. Then only, whatever energy interactions that has taken place during the forward process 1 to 2, we can completely reverse all those energy interactions during the backward process and thereby getting both system and surrounding back to its initial condition.

If there is any mass transfer involved, let us say δm amount of mass also moved in during the forward process. Then, during the reverse process, exactly the same amount i.e., δm, amount of mass must move back from the system to the surrounding. So, when we are performing the reverse process that is going back from 2 to 1, the system is always restored. Because we are back to the initial point, so all the system properties will go back to its initial value. However, the surrounding may not be restored if the process is not a reversible one. Because just think about during the forward process, if we neglect that mass transfer for the moment, then how much is the net energy that system has received? So, δE for the system is expressed as:

$$\Delta E_{sys} = \delta Q - \delta W$$

where
δQ is the amount of heat received
δW amount of work given

Now, δE for the surrounding, how much is that? If we consider to have just two systems, one is that so-called system, other is the surrounding. Then, for the surrounding how much is energy interaction? It can be expressed as follows:

$$\Delta E_{sur} = \delta W - \delta Q$$

So, once we are performing this reverse process, the system is coming back to its initial state. So, all system properties are restored. However, to restore the surrounding also back to its initial condition, we must take away this amount of heat from the surrounding so that during the reverse process, the energy interaction corresponding to the surrounding is:

$$\Delta E_{sur} = \delta Q - \delta W$$

thereby restoring the surrounding as well. So, we can identify system to be reversible only when during the reverse process both the system and the surrounding has been restored back to its initial condition. Otherwise, it is not a reversible one. The most common situation is the system gets restored to the initial situation but the surrounding does not and thereby the process is not a reversible one what we call is an irreversible process. Truly speaking, all practical processes are irreversible in nature because this particular condition that is without leaving any mark or trace or proof on the surrounding that is extremely difficult to achieve.

Let us take an example. Let us take a cup of tea. So, we have taken a cup of tea, let us say we have a paper cup which is filled with some tea and now I have dropped that cup to the floor. So, as I drop the cup to the floor then what will happen, the tea or the liquid that I had in the cup gets splashed everywhere i.e., poured on the floor and there may be scattered drops also all around. So, if we want to now reverse that process, then what should happen, that tea which is now scattered everywhere that should come back to the cup and that cup filled with tea should come back to my hand. Now, that is practically looking quite impossible and that is why reversible process, the term is only an idealization, all real processes are irreversible in nature.

Despite mentioning that no real processes are reversible, then why you are so much interested with this term? Because it can we proved that and you must have learnt that in your basic thermodynamics that whenever a heat engine is undergoing a reversible process, then it is expected to produce the highest possible work output among all the engines operating between the two same reservoirs.

Similarly, when we are talking about energy absorbing device like a compressor or a pump. If a reversible reversed heat engine consumes work. When we are working on a reversible process, it will consume the least possible work input among all the reversed engines operating between again the same two reservoirs. So, once we fix up the two reservoirs that is the upper and lower temperature limits of the operation, then, for a reversible heat engine you are going to get the maximum possible work output and from a reversible heat pump or refrigerator, we need to provide the minimum possible work input. So, that is the most ideal process that we would always like to achieve. That is why we are very much interested in a reversible process because reversible process sets up the upper limit of operation both in case of heat engines and reversed heat engines.

But practically there are several hindrances because of which a process can move away from the reversible nature. The most common causes are friction, because friction is a kind of irreversible effect. Like, suppose, I move my right hand over my left one, then what will happen? As I am moving forward there is some kind of rubbing of friction action that is taking place and because of which some energy is being lost. So, if I want to reverse this action completely, then what should happen? Whatever amount of energy that I have lost because of friction which eventually gets converted to heat that should come back to my hand thereby enabling my hand to move back into the original position. But that is never possible because you know that whenever hand is moving in this direction, friction is acting opposite to motion. Similarly, when I am moving the hand back into the original position, again friction is opposing the motion. It is always acting opposite to the motion and immediately converting that corresponding mechanical energy or lost mechanical energy to thermal energy thereby making it possible to recover that lost energy. So, friction is the biggest source of irreversibility.

Under certain situation, we may have unrestrained or uncompressed or I should say unrestricted expansion of certain gases, in very specific situation you may get that. But the third one is a very common source again, heat transfer through a finite temperature difference. From the Clausius statement of the second law of thermodynamics, we know that heat can move only from a high temperature body to a low temperature body.

And to have any kind of heat transfer, we need to have a certain amount of temperature difference between the two bodies. If both the bodies are at the same temperature, then we can never have any kind of heat transfer because heat transfer requires the temperature difference as its driving potential. If the temperatures are same, there is no driving potential so there will be no heat transfer.

However, as heat can flow only from high temperature body to a low temperature body and the reverse is impossible therefore that is also a kind of irreversibility. Now, the first two friction and unrestrained expansion or primarily friction are generally referred as the reasons for internal irreversibility. That means if the system is frictionless and there is no unrestrained expansion, then we can call the system to be internally reversible.

Similarly, when there is no heat transfer through a finite temperature difference, then we call the system to be externally reversible. It is possible for a system to be internally reversible but externally irreversible and similarly a system can be internally irreversible because of the presence of friction but maybe externally reversible.

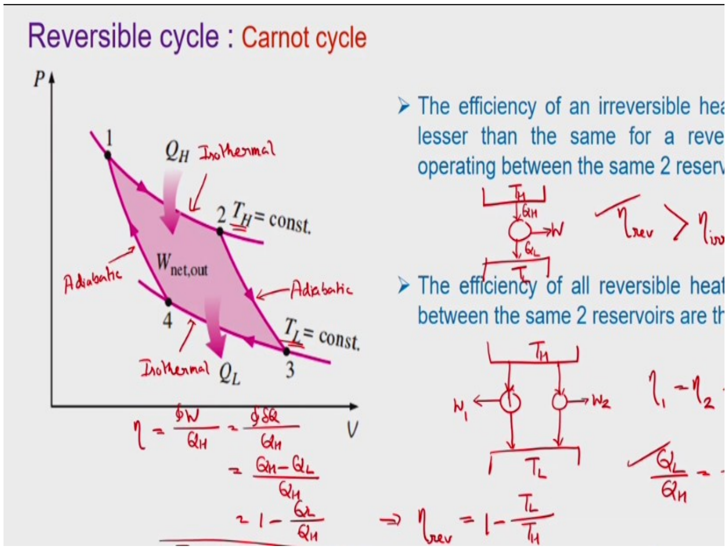
Let us take this example here. So, here I have got a system which is kept at 20 ºC. Now, if I want to transfer some heat from the surrounding to the system following a reversible manner, then the surrounding has to be at the same temperature but if it is at the same temperature then there will be no heat transfer. So, we can assume that surrounding is at an infinitesimally small temperature difference higher than the system thereby facilitating this heat transfer. So, here the heat transfer is taking place because of an infinitesimally small temperature difference between system and surrounding. So, it is a totally reversible process, of course assuming there is no friction, it is externally reversible.

Now, look at the second example where the surroundings at a much higher temperature, there is a distinct temperature difference existing between system and surroundings. However, inside the system temperature is same everywhere i.e., system itself is in thermal equilibrium. This is the situation of internally reversible but externally irreversible process because there is a heat transfer taking place with finite temperature difference 30 ºC on one side, 20 ºC on the other side, there is a finite temperature difference of 10 ºC and this heat transfer is taking place because of the finite temperature difference, so the system is externally irreversible but internally reversible.

We can also have the other example when a system is internally irreversible because of the presence of friction, but externally reversible. Externally reversible is possible when this heat transfer is taking place because of extremely small temperature difference or if there is no heat transfer at all. If there is no heat transfer at all, then this point never comes into picture. So, there also the system can be externally reversible.

Therefore, for a system to be externally reversible, we need to have either an adiabatic process i.e., no heat transfer or an isothermal heat transfer process during which system and surrounding are at the same temperature, that takes us to the concept of a reversible cycle.

(Refer Slide Time: 16:07)



Reversible cycle : Carnot cycle

- The efficiency of an irreversible hea
lesser than the same for a reve
operating between the same 2 reserv

$\eta_{rev} > \eta_{i}$

- The efficiency of all reversible heat
between the same 2 reservoirs are th

$\eta_1 = \eta_2$

$\frac{Q_L}{Q_H} =$

$$\eta = \frac{\oint W}{Q_H} = \frac{\oint \delta Q}{Q_H}$$
$$= \frac{Q_H - Q_L}{Q_H}$$
$$= 1 - \frac{Q_L}{Q_H}$$

$$\Rightarrow \eta_{rev} = 1 - \frac{T_L}{T_H}$$

Practically, all power producing or power consuming systems has to work on certain cycle, so that they can keep on repeating the same action over a long period of time. And as we are going to get the largest possible work output from a reversible process, so a cycle which works only using reversible processes is expected to give the largest possible work output and that is the interest of talking about a reversible cycle.

So, a cycle is called a reversible if all the constituent processes are reversible in nature i.e., they are frictionless and none of the processes involved heat transfer with finite temperature difference. The most common cycle that we talk about as a reversible one is a Carnot cycle, which is again an idealization but it is possible to have any other kind of reversible cycles also. In a Carnot cycle, we generally consider four processes to constitute the cycle.

Process number 1, which is from this process or point 4 to 1, this is an adiabatic process and also frictionless adiabatic process. So, during this process, it is frictionless so internally reversible and also adiabatic so externally reversible. Therefore, this 4 to 1 is a perfectly reversible process or totally reversible process.

Next process 1 to 2, 1 to 2 refers to an isothermal heat addition process, so Q_H amount of heat gets added to the system during which its temperature remains constant at T_H, 2 to 3 is again an adiabatic process during which the temperature reduces from this high temperature T_H to low temperature T_L and 3 to 4 another isothermal heat rejection process. So, the first process is an adiabatic one, it is a frictionless adiabatic.

Similarly, third one, this is also a frictionless adiabatic process. This second process 1 to 2 is an isothermal process performed at the temperature T_H. Similarly, this fourth process 3 to 4 is another isothermal process performed at the temperature T_L during which Q_L amount of heat is rejected to the surrounding. So, this is how we talk about the Carnot cycle.

Now in a Carnot cycle then how can we calculate the efficiency of the cycle? So, you know that efficiency for any heat engine can be written as:

$$\eta = \frac{\oint W}{Q_H} = \frac{\oint \delta Q}{Q_H} = \frac{Q_H - Q_L}{Q_H} = 1 - \frac{Q_L}{Q_H}$$

where

Q_H is the amount of heat added to the system
Q_L is the amount of heat rejected
This expression is true for any heat engines.

Now, somehow you have to establish a relation between this 'Q_L/Q_H' to this 'T_L/T_H' and then only we can represent the efficiency of this Carnot cycle in terms of temperatures only and in this context, couple of Carnot principles comes into picture.

The first Carnot principle says that the efficiency of an irreversible heat engine is always less than the same for a reversible heat engine operating between the same two reservoirs. It means suppose if we decide two reservoirs one at temperature T_H and another at temperature T_L and heat engine operating between the two getting suppose Q_H amount of heat from the high temperature body rejecting Q_L to the low temperature body and producing W amount of work. Then, it is saying that once we have fixed up these two reservoirs, then whatever may be the nature of this heat engine, whatever may be the magnitude of Q_H, W and Q_L, the efficiency of any reversible heat engine working between these two reservoirs will always be greater than any irreversible heat engine i.e., a reversible heat engine is going to give the maximum possible efficiency.

$$\eta_{rev} > \eta_{irr}$$

Second Carnot principle talks about the efficiency of all reversible heat engines operating between the same two reservoirs are the same, means again we are fixing up two reservoirs, one at temperature T_H, other at temperature T_L. Now, you are talking about two engines, both are reversible in nature. So, engine 1 is giving you W amount of work output, engine 2 is giving W_2 amount of work output. Both 1 and 2 are reversible nature but they are having different kinds of heat interaction producing different amount of work. Now, the second Carnot principle says that efficiency of 1 and efficiency of 2 has to be equal and this whatever may be the nature of the reversible cycle as long as that is reversible that efficiency will be always the same. What does it indicate?

So, once we specify the two end temperatures, the efficiency does not change, whatever may be the magnitude of heat drawn by the system or whatever may be the working fluid, you will always get the same efficiency. That means this has to be a function of these two temperatures T_H and T_L.

$$\eta_1 = \eta_2 = f(T_H, T_L)$$

Once you fix up these two temperatures, the efficiency of any reversible heat engine is fixed. From there, we get the concept of a thermodynamic temperature scale and using the Joule postulate, it can be shown that:

$$\frac{Q_L}{Q_H} = \frac{T_L}{T_H}$$

i.e., the ratio of heat transfer can be directly equal to the ratio of corresponding temperatures. And accordingly, we get efficiency for any reversible heat engine, Carnot cycle, or any other kind of reversible heat engine, it is:

$$\eta_{rev} = 1 - \frac{T_L}{T_H}$$

So, once you know these two temperatures, you can calculate the efficiency of any reversible heat engine. The same principle is also applicable to reversed heat engines. So, like COP for a reversible heat pump, we know COP for any heat pump is:

$$COP_{HP,rev} = \frac{Q_H}{Q_H - Q_L} = \frac{T_H}{T_H - T_L}$$

Similarly, COP for a reversible refrigerator is:

$$COP_{R,rev} = \frac{Q_L}{Q_H - Q_L} = \frac{T_L}{T_H - T_L}$$

Say for example, if we consider a situation of a heat engine which is operating between the temperatures where T_H=1000 K and T_L=300 K. Then, without knowing anything else we can say that the efficiency of this reversible heat engine or the maximum possible efficiency following this principle once we have fix up these two temperatures, the maximum possible efficiency any heat engine can be given as:

$$\eta_{rev} = 1 - \frac{300}{1000} = 0.7$$

So, that is the maximum possible efficiency a heat engine operating between these two temperatures can give you. If the engine is a reversible one, you are going to get the 70% efficiency. If the engine is an irreversible one, your efficiency will be much lesser and how much less it will be? That depends upon the level of irreversibility is present in the system.

Similarly, if we talk about the example of a refrigerator, so I give you refrigerator which is operating between the temperatures.

$T_L = 280$ K

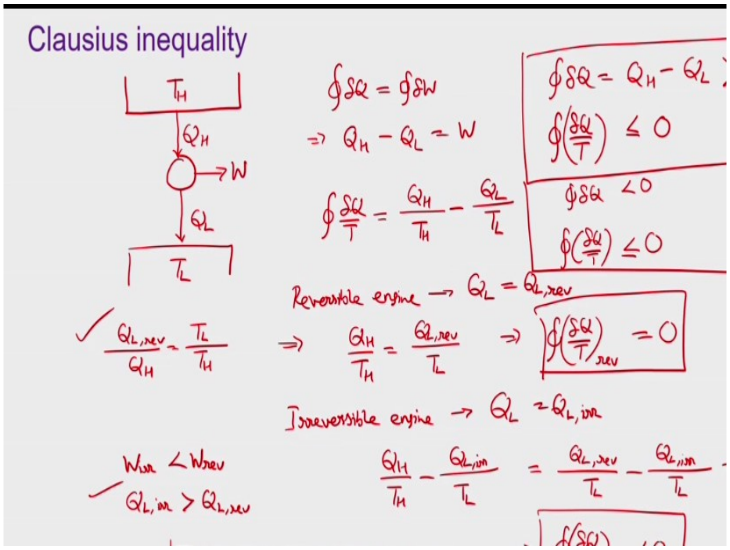
$T_H = 300$ K

Then, the maximum possible COP this refrigerator can have is the one corresponding to its reversible version which is:

$$COP_{R,rev} = \frac{280}{300-280} = \frac{280}{20} = 14$$

So, this way we can calculate the upper limit of efficiency or COP for a heat engine or reversed heat engine respectively once the two temperature limits are given.

(Refer Slide Time: 24:26)



Clausius inequality

$\oint \delta Q = \oint \delta W$

$\Rightarrow Q_H - Q_L = W$

$\oint \frac{\delta Q}{T} = \frac{Q_H}{T_H} - \frac{Q_L}{T_L}$

$\oint \delta Q = Q_H - Q_L$

$\oint \left(\frac{\delta Q}{T}\right) \leq 0$

$\oint \delta Q < 0$

$\oint \left(\frac{\delta Q}{T}\right) \leq 0$

Reversible engine $\rightarrow Q_L = Q_{L,rev}$

✓ $\frac{Q_{L,rev}}{Q_H} = \frac{T_L}{T_H}$ $\Rightarrow \frac{Q_H}{T_H} = \frac{Q_{L,rev}}{T_L} \Rightarrow \boxed{\oint \left(\frac{\delta Q}{T}\right)_{rev} = 0}$

Irreversible engine $\rightarrow Q_L = Q_{L,irr}$

$W_{irr} < W_{rev}$

✓ $Q_{L,irr} > Q_{L,rev}$

$\frac{Q_H}{T_H} - \frac{Q_{L,irr}}{T_L} = \frac{Q_{L,rev}}{T_L} - \frac{Q_{L,irr}}{T_L}$

Now, let us use this concept to derive another important principle known as the Clausius inequality, for which we consider a heat engine. This T_H and T_L are the two temperatures, we have the heat engine which is drawing Q_H amount of heat rejecting Q_L amount of heat and producing W amount of work. This heat engine can be reversible, can be irreversible, we do not care.

Now, if we apply the first law of thermodynamics on this over cycle, we know that

$$\oint \delta Q = \oint \delta W$$

Now, amount of heat it is taking is

$$Q_H - Q_L = W$$

Q_H definitely is higher than Q_L; otherwise there will be no W. So,

$$\oint \delta Q = Q_H - Q_L > 0$$

Now, we take the quantity,

$$\oint \frac{\delta Q}{T} = \frac{Q_H}{T_H} - \frac{Q_L}{T_L}$$

where T is the absolute temperature so that is always a positive quantity. So, the symbol of this one will depend upon the symbol of Q, so you have *'Q_H/T_H-Q_L/T_L'* because Q_L is negative.

Now, we have just seen that following the Carnot principle, for a reversible one, we can say that:

$$\frac{Q_{L,rev}}{Q_H} = \frac{T_L}{T_H}$$

So, if we use that for first, we consider the reversible heat engine. So, reversible means we are indicating Q_L as $Q_{L,rev}$. Then, using this particular principle, we can write that by rearranging them, we can write:

$$\frac{Q_H}{T_H} = \frac{Q_{L,rev}}{T_L} \rightarrow \oint \left(\frac{\delta Q}{T}_{rev}\right) = 0$$

Now, we take an irreversible heat engine where Q_L=$Q_{L,\ irr}$.

Now, this we know that work output from the Carnot principle, the work output in this case will be lesser than the reversible one i.e.,

$$W_{irr} < W_{rev}$$

If Q_H remains the same that means:

$$Q_{L,irr} > Q_{L,rev}$$

i.e., larger fraction of heat will be rejected, only lesser fraction will be converted to work. So, if we take now:

$$\frac{Q_H}{T_H} - \frac{Q_{L,irr}}{T_L} = \frac{Q_{L,rev}}{T_L} - \frac{Q_{L,irr}}{T_L} = \frac{1}{T_L}\left(Q_{L,rev} - Q_{L,irr}\right) < 0$$

That means

$$\oint\left(\frac{\delta Q}{T}\right)_{irr} < 0$$

So, if we combine this particular one for reversible one and this particular one for an irreversible one, then together we can write:

$$\oint\left(\frac{\delta Q}{T}\right)_{irr} \leq 0$$

where the equality holds for a reversible one which is the limiting case. It is possible to prove the same thing for a heat pump cycle also. Only for a heat pump, you are going to get, if this particular situation we have derived for heat engine, if we do the same thing for heat pump, you are going to get:

$$\oint\left(\frac{\delta Q}{T}\right) < 0$$

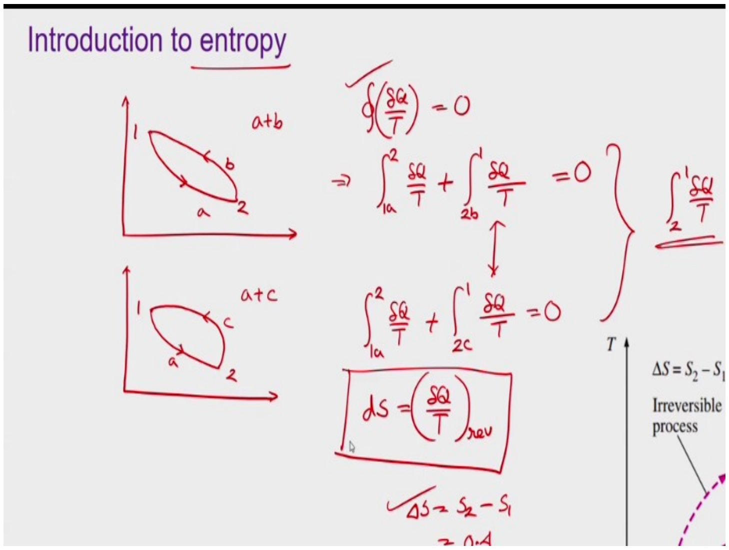
However,

Therefore, we can conclude that for any kind of system, heat engines or reversed heat engines, reversible or irreversible; we can always write:

$$\oint\left(\frac{\delta Q}{T}\right) \leq 0$$

This is called the Clausius inequality which sets up with us with the concept of entropy.

(Refer Slide Time: 29:54)



Introduction to entropy

$$\oint\left(\frac{\delta Q}{T}\right) = 0$$

$$\Rightarrow \int_{1a}^{2}\frac{\delta Q}{T} + \int_{2b}^{1}\frac{\delta Q}{T} = 0$$

$$\int_{1a}^{2}\frac{\delta Q}{T} + \int_{2c}^{1}\frac{\delta Q}{T} = 0$$

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

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

$$\Delta S = S_2 - S_1$$

$$= 0.4$$

So, to discuss the concept of entropy, let us briefly consider again a property diagram where we move from a point 1 to 2 following this particular process ‘a’, and then we go back from 2 to 1 following the process ‘b’. Let us say this is a reversible cycle that is both ‘a’ and ‘b’ are reversible processes. Then, following Clausius inequality we have just derived that

$$\oint \left(\frac{\delta Q}{T}\right) = 0$$

That means:

$$\oint_{1a}^{2} \frac{\delta Q}{T} + \oint_{2b}^{1} \frac{\delta Q}{T} = 0$$

Now, if we consider another cycle which is quite similar, again we have the same two endpoints 1 and 2 and the same process ‘a’, i.e., from 1 to 2 we are going following the same process a. However, during return we are taking a different route something like this a ‘c’ which is again a reversible process. So, in the first case, we had reversible cycle comprising of ‘a’ and ‘b’, in the second case, we had reversible cycle comprising of ‘a’ and ‘c’. So, in this case also we can use the Clausius inequality and accordingly we can write:

$$\oint_{1a}^{2} \frac{\delta Q}{T} + \oint_{2c}^{1} \frac{\delta Q}{T} = 0$$

So, if we compare these two, then we can say that for both the situations $\oint_{2}^{1} \frac{\delta Q}{T}$ is the same.

And this way, we can choose any process to go back from 2 to 1, as long as that is reversible, the magnitude of this $\oint_{2}^{1} \frac{\delta Q}{T}$ will remain the same. Therefore what does that indicate? That definitely indicates that the change or rather the magnitude of this quantity is independent of the process path that has been followed that is whatever may be the process path we are following between 2 to 1 as long as that is reversible, this quantity remain the same and therefore that has to be some property.

Also, cyclic integral of some quantity to be 0 does mean that that has to be a property and that property is called entropy, which is generally denoted by the symbol S.
So it has to denote change in property as S_1-S_2.
So, the change in any property dS is defined as:

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

following a reversible path.

As long as you are following a reversible path, just this δQ/T this quantity is going to give you the change in property.

However, one thing you have to be careful, here we are going from one state point to another state point that is from 1 to 2 or 2 to 1. So, regardless of you are following a reversible path or irreversible path, the change in entropy will always remain the same because you are talking about a property.

However, the magnitude of that change in entropy, magnitude of that property can be calculated using the heat transfer value only if you are following a reversible path. Like take this example, where we have plotted two processes between point 1 and 2. Now, during 1 to 2, the change in entropy is from point 3 to point 7. So, the ΔS, the change in entropy is

$$\Delta S = S_2 - S_1 = 0.4 \text{ kJ/K}$$

Now, if we follow an irreversible process, even in that case also, the change in entropy will remain the same because again you are going away from the same initial state back to the same final state. So, the change in entropy which is there also will remain to be 0.4 kJ/K. However, in the first case, as we are following a reversible path, so the change in entropy in this case will be:

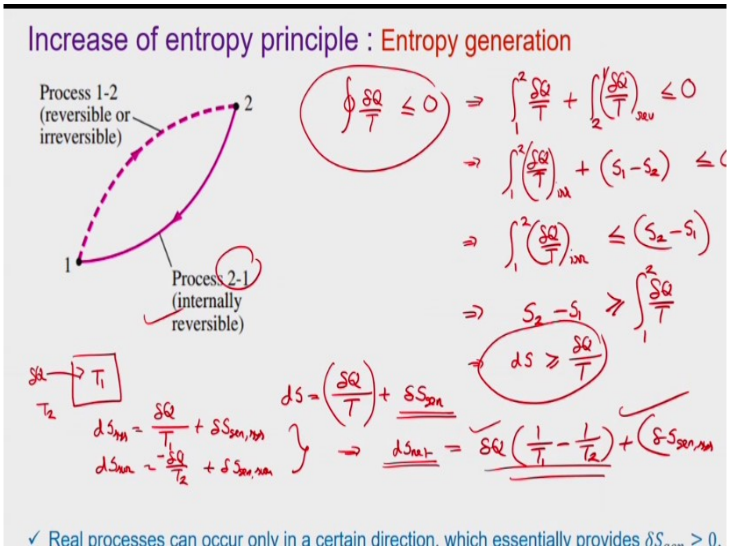
$$dS = \frac{\delta Q}{T}$$

However, in this case,

$$dS \neq \frac{\delta Q}{T}$$

So, if we are following a reversible path and we are plotting that on a TS diagram using temperature and entropy as the two axes, then the area under this particular curve that is this shaded portion will be giving you the amount of heat transfer involved with this. However, that is not true for the irreversible path. So, entropy can be defined as the property which satisfies this particular relation that is the magnitude of this '*δQ/T*' following a reversible path.

(Refer Slide Time: 34:53)


Increase of entropy principle : Entropy generation

$$\oint \frac{\delta Q}{T} \le 0 \Rightarrow \int_1^2 \frac{\delta Q}{T} + \int_2^1 \left(\frac{\delta Q}{T}\right)_{rev} \le 0$$

$$\Rightarrow \int_1^2 \left(\frac{\delta Q}{T}\right)_{irr} + (S_1 - S_2) \le 0$$

$$\Rightarrow \int_1^2 \left(\frac{\delta Q}{T}\right)_{irr} \le (S_2 - S_1)$$

$$\Rightarrow S_2 - S_1 \geq \int_1^2 \frac{\delta Q}{T}$$

$$\Rightarrow dS \geq \frac{\delta Q}{T}$$

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

$$\left.\begin{aligned} dS_{sys} &= \frac{\delta Q}{T_1} + \delta S_{gen,sys} \\ dS_{sur} &= \frac{-\delta Q}{T_2} + \delta S_{gen,sur} \end{aligned}\right\} \Rightarrow dS_{net} = \delta Q\left(\frac{1}{T_1} - \frac{1}{T_2}\right) + (\delta S_{gen,sys}$$

✓ Real processes can occur only in a certain direction, which essentially provides $\delta S_{gen} > 0$.

Now, we consider another cycle which is actually an irreversible cycle. It comprises of one irreversible and a reversible process. So, process 1 to 2 is irreversible, in fact that can be reversible as well but process 2 to 1 is internally reversible. Now, we are applying the Clausius inequality on this.

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

If 1 to 2 is reversible, then the equality will hold, otherwise it will be that less than zero. So, if we write this now, break this:

$$\int_1^2 \frac{\delta Q}{T} + \int_2^1 \left(\frac{\delta Q}{T}\right)_{rev} \le 0$$

$$\int_1^2 \left(\frac{\delta Q}{T}\right)_{irr} + (S_1 - S_2) \le 0$$

$$\int_1^2 \left(\frac{\delta Q}{T}\right)_{irr} \le (S_1 - S_2)$$

Or, if we write formally then

$$(S_1 - S_2) \geq \int_1^2 \left(\frac{\delta Q}{T}\right)$$

As long as we are following a reversible path then the equality will hold and the change in entropy can directly be related to this *'δQ/T'* quantity. However, if we are following an irreversible path, then *'δQ/T'* alone is not sufficient rather, we need some other contribution. That is in differential if we write:

$$dS \geq \frac{\delta Q}{T}$$

So, informally if we want to avoid this inequality sign, we can write this:

$$dS = \frac{\delta Q}{T} + \delta S_{gen}$$

which relates to the entropy generation. So, during the irreversible process, we can see that entropy change cannot be related fully to this term but there will be some additional contribution coming from the entropy generation which actually is a result of all the irreversibilities that are present inside the system.

For a reversible process, we do not need to bother about this particular part i.e., δS_{gen}. However, when we are following an irreversible process, then this entropy generation will always be there and that itself a very important principle known as the increase in entropy principle. So, even if we are talking about a reversible process, then there is no entropy generation. However, entropy generation is always a positive term. At the limiting case of a reversible process, it can be 0 and therefore during any real process the entropy of the system or entropy of the system surrounding combination will always keep on increasing.

Let us take an example. So, this is our system, outside we have the surrounding and during this δQ amount of heat moves from system to the surrounding. So, if suppose T_1 is the system temperature, T_2 is the surrounding temperature. Then, how much will be the entropy change for the system? It will be equal to:

$$dS_{sys} = \frac{\delta Q}{T_1} + \delta S_{gen,sys}$$

And entropy change for the surrounding will be:

$$dS_{surr} = \frac{-\delta Q}{T_2} + \delta S_{gen,surr}$$

Here δQ is positive for the system because it is receiving heat but it is negative for the surrounding. Now, if the limiting case of $T_1 + T_2$ or rather $T_1 = T_2$, how much is the net entropy generation? If we combine these two, dS_{net}, the net entropy generation or net entropy exchange here is:

$$dS_{net} = \delta Q \left(\frac{1}{T_1} - \frac{1}{T_2}\right) + (\delta S_{gen,sys} + \delta S_{gen,surr})$$

Now, as heat is being transferred from surrounding to system, T_2 has to be greater than T_1 thereby getting this quantity to be positive.

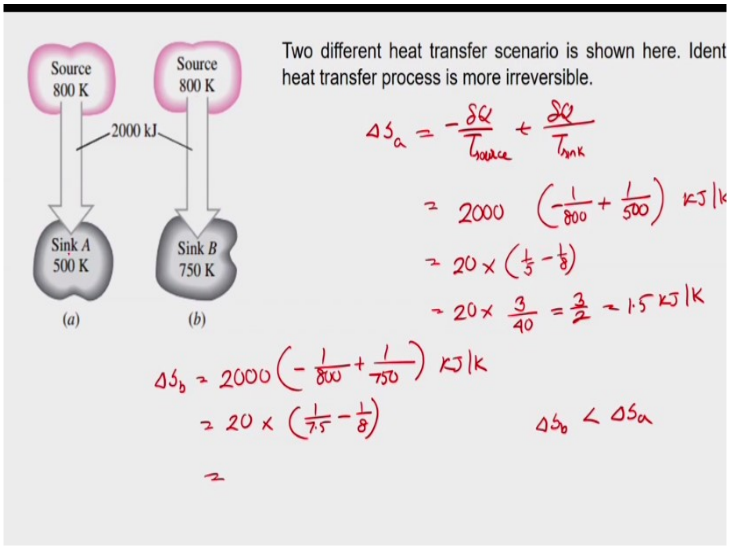
In the limiting case, when T_1 and T_2 are equal that is we are talking about an isothermal heat transfer, the first quantity goes to 0. However, this entire quantity is always positive and thereby this net change in entropy is greater than 0. This is what we call the increase in entropy principle i.e., the entropy of the system surrounding combination or entropy of the universe is what we say in formal thermodynamics term, this always increasing.

However, for the system, entropy can always decrease but we are here talking not only about the system, not only about the surrounding, we are talking about the system surrounding combination which we refer as a universe. So, entropy of the universe is always increasing because of this entropy generation.

So, with this we can have a few important conclusions.

1. First, real processes can occur only in a certain direction, which gives to a positive entropy generation or in the limiting case zero entropy generation for a reversible process. Negative entropy generation is never possible and therefore any hypothetical thermodynamic process if that indicates negative entropy generation that is impossible.
2. Secondly, entropy is a non-conserved property because of the presence of these inequalities and also the presence of this inequality here. So, entropy is a non-conserved property, so there is nothing like conservation of entropy. We talk about conservation of mass, momentum, energy but not conservation of entropy. We can only write an entropy balance equation where we incorporate this entropy generation term. But conservation of entropy is never possible.
3. And third, presence of irreversibilities degrade the performance of engineering systems and this entropy generation gives us an idea to measure such irreversibilities. More about this third point means how to calculate the irreversibilities using the concept of entropy generation we shall be discussing in the next lecture where we talk about exergy.

(Refer Slide Time: 41:47)



Two different heat transfer scenario is shown here. Ident
heat transfer process is more irreversible.

$\Delta S_a = -\frac{\delta Q}{T_{source}} + \frac{\delta Q}{T_{sink}}$

$= 2000 \left(-\frac{1}{800} + \frac{1}{500}\right)$ kJ/K

$= 20 \times \left(\frac{1}{5} - \frac{1}{8}\right)$

$= 20 \times \frac{3}{40} = \frac{3}{2} = 1.5$ kJ/K

$\Delta S_b = 2000 \left(-\frac{1}{800} + \frac{1}{750}\right)$ kJ/K

$= 20 \times \left(\frac{1}{7.5} - \frac{1}{8}\right)$

$=$

$\Delta S_b < \Delta S_a$

Let us quickly do one calculation. Here, I am presenting you with two situations; in situation ‘a’ you have a source at temperature 800 K and sink at temperature 500 K and exchanging 2000 kJ of heat. Then, how much is the entropy transfer in case number ‘a’? So, in case number ‘a’ entropy transfer associated with the heat transfer will be:

$$\Delta S_a = \frac{-\delta Q}{T_{source}} + \frac{\delta Q}{T_{sink}}$$

So, if you take δQ common which is the same as:

$$= 2000\left(-\frac{1}{800} + \frac{1}{500}\right) kJ/K$$

So, I have not calculated the numbers but you can try to simplify this if I neglect the 0s. So, I have 20. I should put the unit at the end, which is kilo joule per Kelvin. So, it is:

$$= 20\left(-\frac{1}{8} + \frac{1}{5}\right) = 20 \times \frac{3}{40} = \frac{3}{2} = 1.5 kJ/K$$

Now, in case ‘b’,

$$\Delta S_b = 2000\left(-\frac{1}{800} + \frac{1}{750}\right) kJ/K$$

So, taking it common if I write this way, so it is

$$= 20\left(-\frac{1}{7.5} + \frac{1}{8}\right) = ?$$

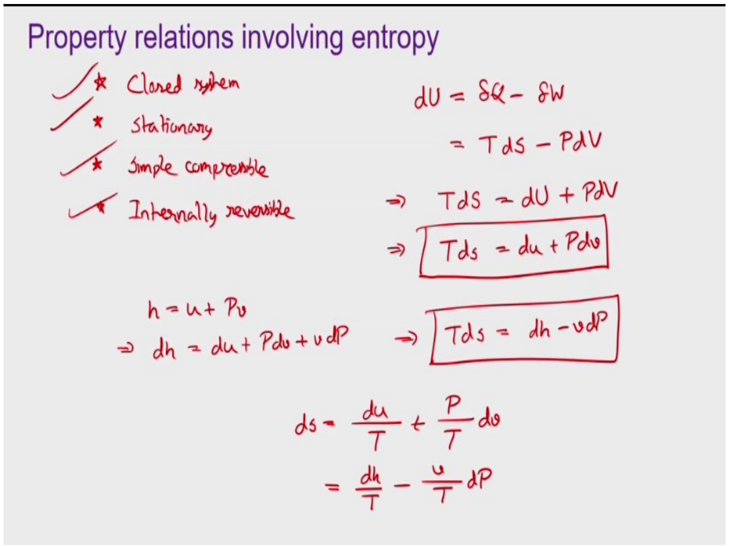
So, you please calculate this, as I do not have a calculator with me now. But you please calculate this one and surely, we say that in this situation the value will be coming lesser than the previous case that is you are going to get:

$$\Delta S_b < \Delta S_a$$

So, definitely the second situation is more irreversible because here the, this is more irreversible because the temperature difference involved here is of 300 K whereas here it is only 50 K, so much lesser temperature difference and hence much lesser level of external irreversibility.

In the first case, we are having heat transfer over 300 K temperature difference; there is only 50 K in the second case. Therefore, despite this amount of heat transfer remaining the same, we are having lesser amount of irreversibility in the second case. So, quickly we shall be checking out if your property relations involving entropy which we have to make use of in the following lectures in the next week itself.

(Refer Slide Time: 45:01)



Property relations involving entropy

- ✓ * Closed system
- ✓ * Stationary
- ✓ * Simple compressible
- ✓ * Internally reversible

$$dU = \delta Q - \delta W$$
$$= TdS - PdV$$
$$\Rightarrow TdS = dU + PdV$$
$$\Rightarrow \boxed{Tds = du + Pdv}$$

$$h = u + Pv$$
$$\Rightarrow dh = du + Pdv + vdP \quad \Rightarrow \boxed{Tds = dh - vdP}$$

$$ds = \frac{du}{T} + \frac{P}{T}dv$$
$$= \frac{dh}{T} - \frac{v}{T}dP$$

So, here we are talking about a closed system, then we consider it to be stationary, then we consider a simple compressible system so that there is no additional effect like gravity, magnetism, electricity, etc and also, we consider an internally reversible process. So, now if you write the first law of thermodynamics for this, we can write dU because it is a stationary system. So, dU can be written as:

$$du = \delta Q - \delta W$$

Now, from the definition of entropy as we are dealing with an internally reversible process, so δQ can be written as TdS and as we are talking about the simple compressible substance so δW can be written as PdV that is we can write:

$$TdS = dU + PdV$$

or dividing everything by mass, we can write:

$$T\mathrm{d}s = \mathrm{d}u + P\mathrm{d}v$$

This is called the first TdS equation or the Gibbs equation. Again, we know that

$$h = u + Pv$$

or

$$\mathrm{d}h = \mathrm{d}u + P\mathrm{d}v + v\mathrm{d}P$$

So, if we make use of that in the previous $T\mathrm{d}S$ equation, we can write

$$T\mathrm{d}S = \mathrm{d}u + P\mathrm{d}v$$

Here $\mathrm{d}u + P\mathrm{d}v$ is replaced with $\mathrm{d}h - v\mathrm{d}P$, so the equation becomes:

$$T\mathrm{d}S = \mathrm{d}h - v\mathrm{d}P$$

So, this is the second $T\mathrm{d}S$ equation or second Gibbs equation.

These two are very important equations, remember the conditions for which you have done. We have considered closed stationary system, a simple compressible one and internally reversible. In that case, we can relate the properties, internal energy or enthalpy with entropy following this way thereby providing as a way of measuring the entropy because like if we take the first equation, we can write it as:

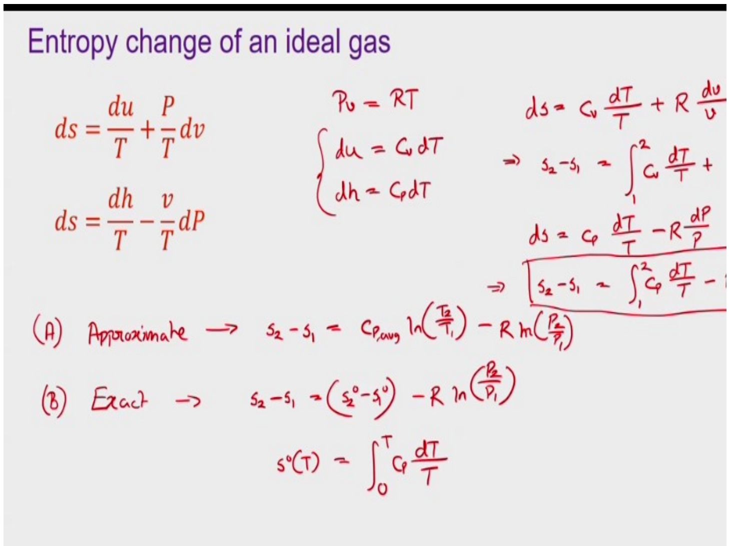
$$ds = \frac{du}{T} + \frac{P}{T}dv$$

And from the second one, we can write it as:

$$ds = \frac{dh}{T} + \frac{v}{T}dP$$

So, if we know the PVT relationship between the substances that we are talking about and also somehow if we can relate the u or h which temperature, we can calculate the change in entropy. Let us take the example of an ideal gas.

(Refer Slide Time: 48:09)



Entropy change of an ideal gas

$$ds = \frac{du}{T} + \frac{P}{T}dv$$

$$ds = \frac{dh}{T} - \frac{v}{T}dP$$

$$Pv = RT$$

$$\begin{cases} du = C_v dT \\ dh = C_p dT \end{cases}$$

$$ds = C_v \frac{dT}{T} + R\frac{dv}{v}$$

$$\Rightarrow s_2 - s_1 = \int_1^2 C_v \frac{dT}{T} +$$

$$ds = C_p \frac{dT}{T} - R\frac{dP}{P}$$

$$\Rightarrow \boxed{s_2 - s_1 = \int_1^2 C_p \frac{dT}{T} -}$$

(A) Approximate $\longrightarrow$ $s_2 - s_1 = C_{p,avg} \ln\left(\frac{T_2}{T_1}\right) - R\ln\left(\frac{P_2}{P_1}\right)$

(B) Exact $\rightarrow$ $s_2 - s_1 = \left(s_2^\circ - s_1^\circ\right) - R\ln\left(\frac{P_2}{P_1}\right)$

$$s^\circ(T) = \int_0^T C_p \frac{dT}{T}$$

So, this is the equation that we have just written. So, for ideal gas what you know? We know

$$Pv = RT$$

and also for ideal gas, we can write:

$$du = C_v\, dT$$

and

$$dh = C\, dT$$

You may have already used this relation, but in next week when we talk about the thermodynamic property relations, this one I shall be developing again. For the moment, you just take this one for granted. So, if you put this in the first equation, then we have:

$$ds = C_v \frac{dT}{T} + \frac{P}{T}$$

Here 'P/T' can be replaced with 'R/v', so '$R\, dv/v$'.

$$ds = C_v \frac{dT}{T} + R\frac{dv}{v}$$

That means

$$s_2 - s_1 = \int_1^2 C_v \frac{dT}{T} + R\int_1^2 \frac{dv}{v} \qquad (1)$$

Similarly, from the second equation, we can write

$$ds = C_p \frac{dT}{T} - R\frac{dP}{P}$$

Here 'v/T' was replaced by 'dp/P' which gives us the second equation which is as follows:

$$s_2 - s_1 = \int_1^2 C_p \frac{dT}{T} - R\int_1^2 \frac{dP}{P} \qquad (2)$$

So, this is our equation number 1, this is equation number 2 and depending upon what kind of information available to you, if you know the change in pressure and information about C_p then we use second one. If we know the change in volume and information about the C_v then we use the first one.

There are generally two kinds of approaches because C_p and C_v generally functions of temperature. So, there are two approaches, the first one is called approximate approach. In approximate approach, we consider an average value of C_p and C_v and proceed accordingly. So, if we take the second one, there we shall be having according to the approximate approach:

$$s_2 - s_1 = C_{p,avg}\, ln\left(\frac{T_1}{T_2}\right) - Rln\left(\frac{P_2}{P_1}\right)$$

following this particular equation.

The second approach is exact approach where we consider the temperature dependence of C_p while performing the integration and in that case, we represent this:

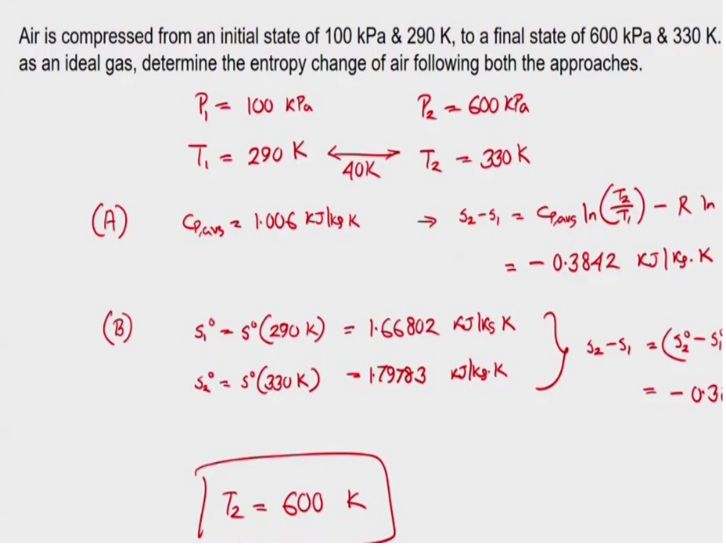
$$s_2 - s_1 = (s_2^0 - s_1^0) - Rln\left(\frac{P_2}{P_1}\right)$$

where this s^0 at any particular temperature is defined as:

$$s^0(T) = \int_0^T C_p \frac{dT}{T}$$

So, once you know C_p as a function of T, maybe a polynomial equation, maybe some other form you can perform this integration and integrated from 0 to T to get the value of s_1^0 and s_2^0. Thankfully, standard values of this s^0 are available for different temperature levels in any standard textbooks, you can refer to the appendix of your textbooks, the book of Cengel and Boles or the book of Sonntag you will have the table of this s^0.

(Refer Slide Time: 52:05)



Air is compressed from an initial state of 100 kPa & 290 K, to a final state of 600 kPa & 330 K.
as an ideal gas, determine the entropy change of air following both the approaches.

$P_1 = 100$ kPa $\qquad P_2 = 600$ kPa

$T_1 = 290\ K \underset{40K}{\longleftrightarrow} T_2 = 330\ K$

(A) $\quad C_{p,avg} = 1.006$ KJ/kg K $\quad \rightarrow s_2 - s_1 = C_{p,avg} \ln\left(\frac{T_2}{T_1}\right) - R \ln$

$= -0.3842$ KJ/kg.K

(B) $\quad s_1^\circ = s^\circ(290\ K) = 1.66802$ KJ/kg K

$s_2^\circ = s^\circ(330\ K) = 1.79783$ KJ/kg.K

$\Big\}\ s_2 - s_1 = (s_2^\circ - s_1^\circ$

$= -0.3$

$\boxed{T_2 = 600\ K}$

So, to round up the day, we shall be checking one case where we make use of this entropy calculation following both exact and approximate approach. So, our situation is air is compressed from an initial state to a final state. So, we are given with $P_1 = 100$ kPa, $T_1 = 290$ K. It is compressed to a final pressure P_2 of 600 kPa and T_2 of 330 K. Actually, it is a quite small temperature range that we are talking about.

So, we have to calculate the entropy change of air assuming to ideal gas. So, if you follow the approximate approach, say case (A) then we have to choose an average value of C_p. Let us take C_p average for air to be=1.006 kJ/kgK. In that case,

$$s_2 - s_1 = C_{p,avg}\, ln\left(\frac{T_1}{T_2}\right) - R ln\left(\frac{P_2}{P_1}\right)$$

you can put the numbers here and according the value that you are going to get is equal to

= -0.3842 kJ/kgK

You can see, here it is negative means entropy of the system is decreasing.

Now, if we follow the exact approach, say case (B) then we need the value of s^0. So, s^0 here $s_1{}^0$ means s^0 corresponding to that 290 K. Let me write it in a better way, so:

$$s_1^0 = s^0(290\ K) = 1.66802\ kJ/kgK$$

$$s_2^0 = s^0(330\ K) = 1.79783\ kJ/kgK$$

I have taken the value from that table; I will provide you the table later on. So, s^0 corresponding to that 290 K is 1.66802 kJ/kgK and s^0 corresponding to 330 K which is 1.79783 kJ/kgK.

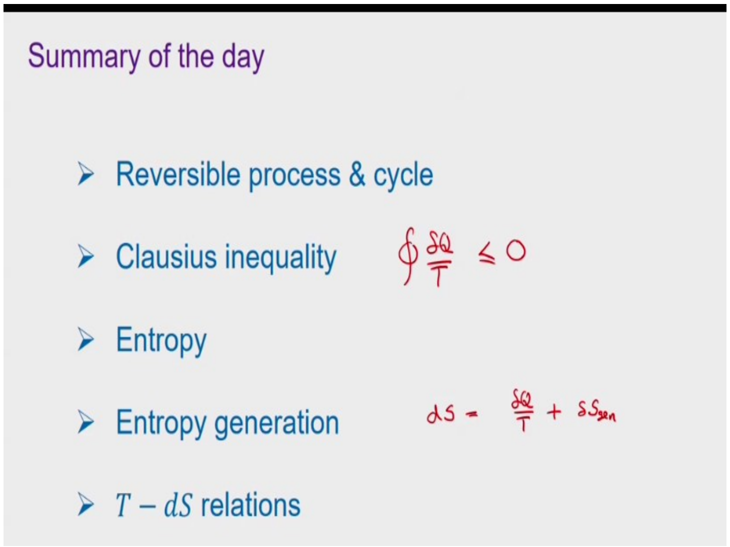
So, if you take both these two into account, then:

$$s_2 - s_1 = (s_2^0 - s_1^0) - R ln\left(\frac{P_2}{P_1}\right) = -0.3884$$

So, in this particular case, you can see that the derivation is extremely small because actually we are talking about only a 40 K temperature difference. However, you can try to solve the same problem assuming the final temperature T_2 to be something like say 600 K.

Try to solve the same problem using this and you will find that approximate approach and exact approach are giving widely different results. And that shows when to apply which approach that is when you are talking about a quite small change in temperature, we generally go for the approximate approach assuming an average value of the specific heat. However, like in several kinds of gas turbine or IC engine applications, the temperature variation can be very significant. Then, we have to consider the exact variation is specific heat and so we have to go for the exact approach. But as long as the temperature difference involved is limited to something less than 100 K, approximate approach you can easily go for.

(Refer Slide Time: 56:11)



Summary of the day

- Reversible process & cycle
- Clausius inequality $\oint \frac{\delta Q}{T} \leq 0$
- Entropy
- Entropy generation $dS = \frac{\delta Q}{T} + \delta S_{gen}$
- $T - dS$ relations

So, that takes us to the end of today's lecture where we have talked about the reversible process and irreversibilities, then the reversible cycle with Carnot cycle as the example of a reversible cycle. Then we derived the Clausius inequality which is formally given as

$$\oint \left(\frac{\delta Q}{T}\right) \leq 0$$

for any kind of system. The equality holds for the limiting case of a reversible process.

Then, we introduced the concept of entropy and entropy generation. So, we have seen that during any process, the change in entropy can be written as:

$$dS = \frac{\delta Q}{T} + \delta S_{gen}$$

For a reversible situation, the entropy generation is not there, then the change in entropy can directly be related to $\delta Q/T$ and finally we talked about the TdS relations, how to calculate entropy using the TdS relations and discussed the specific case of ideal gases.

So, that is it for the day. In the final lecture of this week, I shall be talking about the concept of exergy and available work, where we shall be using this concept of entropy calculation, TdS relations probably and also the irreversibility calculations to get a complete second law analysis of both closed and open systems. Till then, you revise this lecture and if you have any query please write back to me. Thank you.