Advanced Thermodynamics and Combustion

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Module - 02
Entropy and Exergy
Lecture - 05
Entropy Analysis (Part II)

Dear learners, welcome to this course Advanced Thermodynamics and Combustions, we are in module two that is Entropy and exergy.

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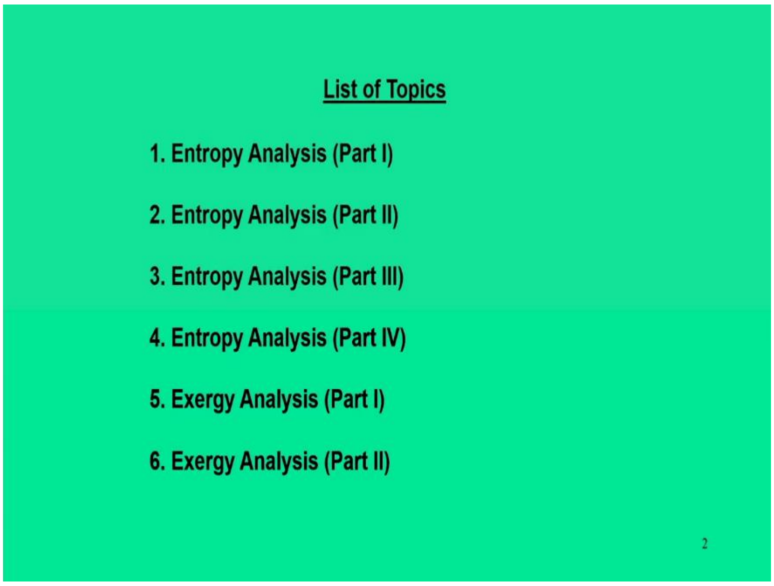

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On this module, we are in the second lecture that is entropy analysis that is part II.

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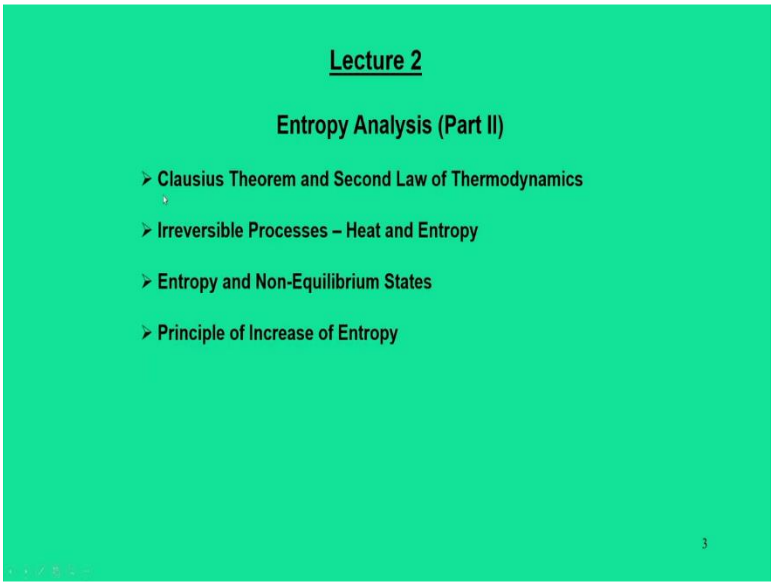

Lecture 2

Entropy Analysis (Part II)

- Clausius Theorem and Second Law of Thermodynamics
- Irreversible Processes – Heat and Entropy
- Entropy and Non-Equilibrium States
- Principle of Increase of Entropy

And in this lecture, we will discuss the following topics. So, first one is Clausius Theorem and Second Law of Thermodynamics. In fact, some of the components we have already seen in the first lecture. Then next segment will be irreversible process that is evaluation of heat and entropy; in fact, in our previous lecture we mostly concentrated on reversible processes.

And the third segment of this lecture will be entropy for non-equilibrium states; that means, normally when the entropy is evaluated, we assume that initial and final states are in equilibrium states. And if under some circumstances, if that condition is not ensured how do you calculate the entropy. And the last segment of this lecture will be principle of increase in the entropy, or we can say law of universe for entropy.

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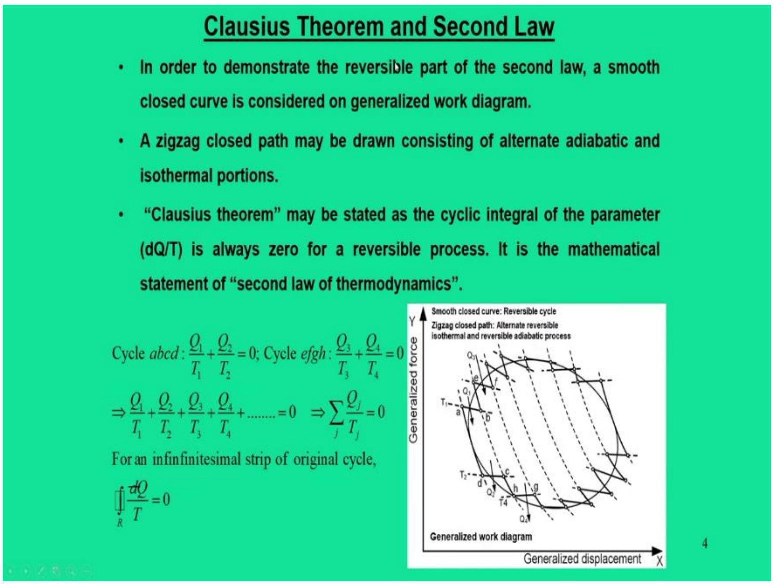

Clausius Theorem and Second Law

- In order to demonstrate the reversible part of the second law, a smooth closed curve is considered on generalized work diagram.
- A zigzag closed path may be drawn consisting of alternate adiabatic and isothermal portions.
- "Clausius theorem" may be stated as the cyclic integral of the parameter (dQ/T) is always zero for a reversible process. It is the mathematical statement of "second law of thermodynamics".

Cycle $abcd: \frac{Q_1}{T_1} + \frac{Q_2}{T_2} = 0$; Cycle $efgh: \frac{Q_3}{T_3} + \frac{Q_4}{T_4} = 0$

$\Rightarrow \frac{Q_1}{T_1} + \frac{Q_2}{T_2} + \frac{Q_3}{T_3} + \frac{Q_4}{T_4} + \ldots\ldots = 0 \quad \Rightarrow \sum_j \frac{Q_j}{T_j} = 0$

For an infinfinitesimal strip of original cycle,

$\oint_R \frac{đQ}{T} = 0$

So, let us revisit the Clausius Theorem which was stated for a reversible cycle. In the previous lecture, what it says is that, during this particular reversible cycle we consider that the entire cycle is discretized in terms of small segments or we can say the closed path of the reversible cycle is replaced with another closed but, zigzag path which consists of alternate reversible isothermal and reversible adiabatic processes and each one consist of a Carnot cycles.

So, likewise we can have many number of Carnot cycles for this closed system or the closed cycle. Now, considering this what we found is that, the cyclic integral of the parameter$\oint_R \frac{đQ}{T} = 0$. So, this was the stated as a one of the Clausius theorem for a reversible process. What it says that, Clausius theorem may be stated as the cyclic integral of the parameter $\oint_R \frac{đQ}{T} = 0$for a reversible process. In fact, it is the another form of the second law of thermodynamics.

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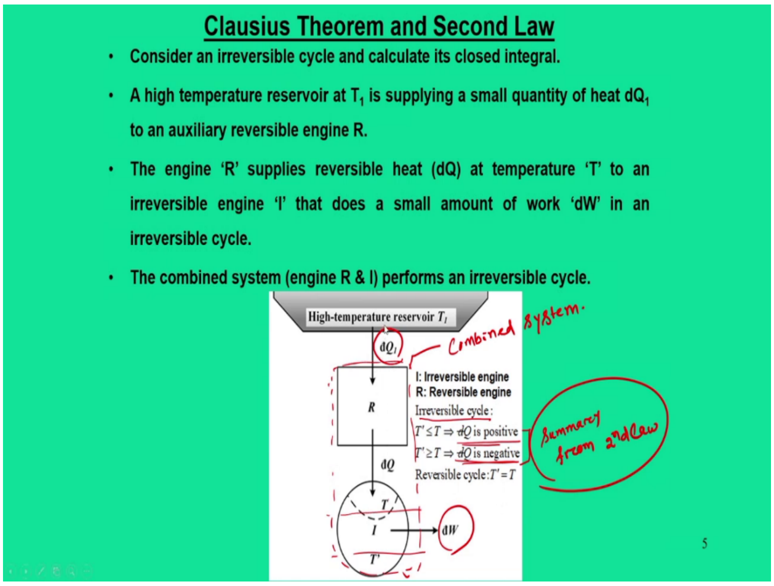

Clausius Theorem and Second Law

- Consider an irreversible cycle and calculate its closed integral.
- A high temperature reservoir at T_1 is supplying a small quantity of heat dQ_1 to an auxiliary reversible engine R.
- The engine 'R' supplies reversible heat (dQ) at temperature 'T' to an irreversible engine 'I' that does a small amount of work 'dW' in an irreversible cycle.
- The combined system (engine R & I) performs an irreversible cycle.

I: Irreversible engine
R: Reversible engine
Irreversible cycle:
$T' \leq T \Rightarrow dQ$ is positive
$T' \geq T \Rightarrow dQ$ is negative
Reversible cycle: $T' = T$

So, the story does not stop here, but what we can extend this particular theorem is to analyze this Clausius theorem for an irreversible cycle. In fact, this is the main emphasis of today's lecture where we will consider the irreversible cycle and calculates its closed integrals. So, to do that let us see this particular figure where we are basically looking irreversible engine I and this irreversible engine takes certain quantity of dQ, heat is receiving and it is producing dW amount of work.

But in one sense we can say that in doing so, only for this irreversible engine we can maybe bit of some analysis we can say that there are two temperature reservoir sources only for this irreversible engine that takes dQ amount of heat at temperature T. And this engine also has another partition which says that as if some invisible temperature source at a T' is sitting onto there, where the engine is supposed to reject the heat and it produces the dW amount of work.

But, what we can see is that when it receives the dQ amount of heat, it is nothing but a heat rejected by a reversible engines. So, essentially the entire combined systems if you look at the reversible engine R receives dQ_1 amount of heat from a high temperature source at T_1. And it rejects dQ amount of heat to the irreversible engines, and side by side it produces dW amount of work. So, in fact, if you consider this reversible and irreversible engine together, this entire things; so, you can say this is the combined system.

So, this combined system consists of the reversible engine as well as the irreversible engine. And another important point that I need to emphasize that, for this irreversible cycle, this dQ is positive when $T' \leq T$; when $T' \geq T$, dQ is negative.

In fact, this is nothing but the summary from the second law; so, this is the conclusion what we are going to make. So, in a sense that when you talk about these combined systems involving reversible engine and irreversible engine, it seems that the entire combined systems receives dQ_1 amount of heat and it produces dW amount of work.

But this is not possible, because it violates second law of thermodynamics or Kelvin Planck statements which means that there is no heat rejection systems here; that means, this combined system is interacting only a single reservoir.

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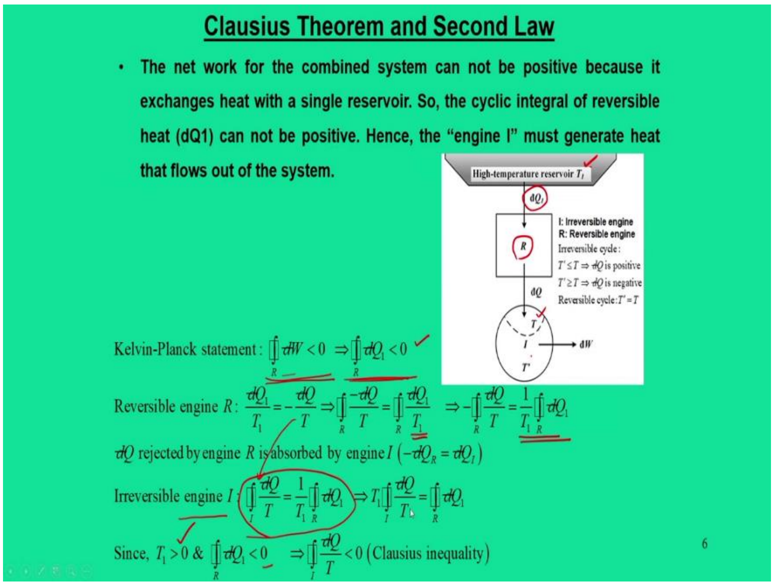

Clausius Theorem and Second Law

- The net work for the combined system can not be positive because it exchanges heat with a single reservoir. So, the cyclic integral of reversible heat (dQ1) can not be positive. Hence, the "engine I" must generate heat that flows out of the system.

Kelvin-Planck statement: $\oint_R \delta W < 0 \Rightarrow \oint_R \delta Q_1 < 0$

Reversible engine R: $\frac{\delta Q_1}{T_1} = -\frac{\delta Q}{T} \Rightarrow \oint_R \frac{-\delta Q}{T} = \oint_R \frac{\delta Q_1}{T_1} \Rightarrow -\oint_R \frac{\delta Q}{T} = \frac{1}{T_1}\oint_R \delta Q_1$

δQ rejected by engine R is absorbed by engine I $(-\delta Q_R = \delta Q_I)$

Irreversible engine I: $\oint_I \frac{\delta Q}{T} = \frac{1}{T_1}\oint_R \delta Q_1 \Rightarrow T_1 \oint_I \frac{\delta Q}{T} = \oint_R \delta Q_1$

Since, $T_1 > 0$ & $\oint_R \delta Q_1 < 0 \Rightarrow \oint_I \frac{\delta Q}{T} < 0$ (Clausius inequality)

So that means, the Kelvin Planck statement is violated. So, for that things; so, this must give us the conditions that for this reversible engine dW is less than 0 and this implies that you will also have dQ_1 for this reversible engine is also less than 0.

So, what we can say; the net work for the combined systems cannot be positive, because it exchanges heat only with a single reservoir. So, the cyclic integral of reversible heat that is dQ_1 cannot be positive hence the engine I must generate heat that flows out of the systems. So; that means, there has to be another reservoir; and in fact, this another reservoir means it is having a temperature T'. And this $T' \leq T$ then dQ is positive; when this $T' \geq T$, dQ is negative and for a reversible cycle this $T'$and T must be equal.

So, same philosophy if it is represented in a mathematical form what we can write first thing we say that based on the Kelvin Planck statements we can write $\oint_R đW < 0$. So, this means your $\oint_R đQ_1 < 0$, because this reversible engine is interacting with the high temperature source at temperature T1 by receiving dQ_1 amount of heat. And again, if you talk the temperature of reservoirs that this reversible engine interacts is nothing, but your T and T_1.

So, based on this we can write the ratios of heat to temperature that is $\frac{đQ_1}{T_1} = -\frac{đQ}{T}$. And in fact, this minus dQ sign is because this dQ with respect to reversible engine, it is negative, but this is being absorbed by the irreversible engines. So, irreversible engine if you write this negative sign goes off.

So, we can write this as $\oint_I \frac{đQ}{T}$. Now, if you simplify this equations what we land of is the fact that $\oint_I \frac{đQ}{T} = \frac{1}{T_1}\oint_R đQ_1$. Because, T_1 is a constant temperature because it is a reservoir temperature which is constant. So, it is taken out of this integral as you can see here, this T_1 is taken out of the integral here; and finally, this particular expressions is now written in terms of this important expressions $\oint_I \frac{đQ}{T} = \frac{1}{T_1}\oint_R đQ_1$. Now, from this what we can conclude is that here we can say that since T_1 is greater than 0, because it is always absolute temperature and dQ_1 is less than 0 that we have concluded from the Kelvin Planck statement. So, this means that your $\oint_I \frac{đQ}{T} < 0$ and this is what we call as Clausius inequality.

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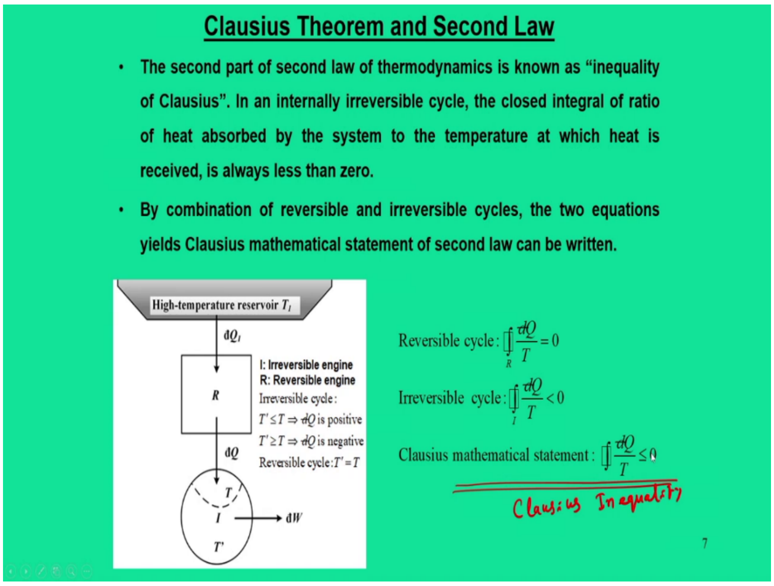

Clausius Theorem and Second Law

- The second part of second law of thermodynamics is known as "inequality of Clausius". In an internally irreversible cycle, the closed integral of ratio of heat absorbed by the system to the temperature at which heat is received, is always less than zero.
- By combination of reversible and irreversible cycles, the two equations yields Clausius mathematical statement of second law can be written.

I: Irreversible engine
R: Reversible engine
Irreversible cycle:
$T' \le T \Rightarrow đQ$ is positive
$T' \ge T \Rightarrow đQ$ is negative
Reversible cycle: $T' = T$

Reversible cycle: $\oint_R \frac{đQ}{T} = 0$

Irreversible cycle: $\oint_I \frac{đQ}{T} < 0$

Clausius mathematical statement: $\oint \frac{đQ}{T} \le 0$

Clausius Inequality

Now, there are two options we have the Clausius equality sign for a reversible cycle. Now, we have proved the Clausius inequality situations for an irreversible cycle. So, for a reversible cycle $\oint_R \frac{đQ}{T} = 0$ and for irreversible cycle $\oint_I \frac{đQ}{T} < 0$. By combining them together, we can frame this Clausius mathematical statement of second law and sometimes we call this as a Clausius inequality. So, it says that $\oint \frac{đQ}{T} \le 0$.

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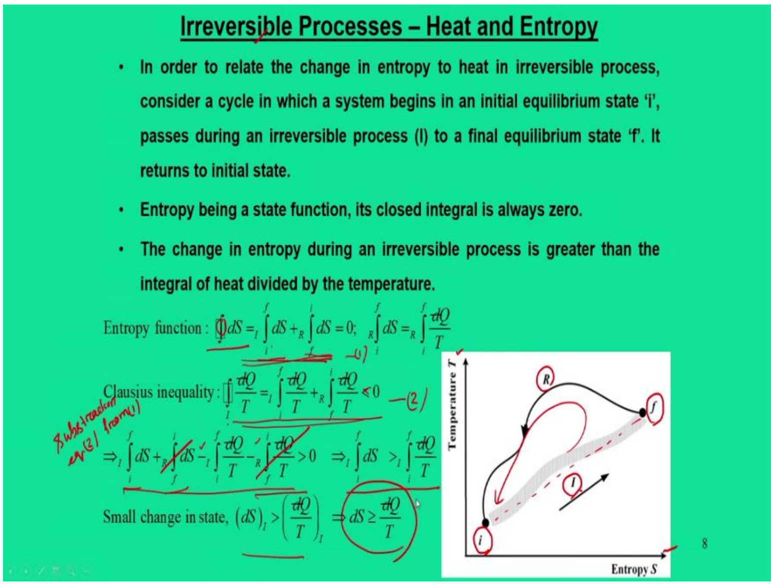

Irreversible Processes – Heat and Entropy

- In order to relate the change in entropy to heat in irreversible process, consider a cycle in which a system begins in an initial equilibrium state 'i', passes during an irreversible process (I) to a final equilibrium state 'f'. It returns to initial state.
- Entropy being a state function, its closed integral is always zero.
- The change in entropy during an irreversible process is greater than the integral of heat divided by the temperature.

Entropy function: $\oint dS = {}_I\int_i^f dS + {}_R\int_f^i dS = 0; \quad {}_R\int_i^f dS = {}_R\int_i^f \frac{đQ}{T}$ —(1)

Clausius inequality: $\oint \frac{đQ}{T} = {}_I\int_i^f \frac{đQ}{T} + {}_R\int_f^i \frac{đQ}{T} < 0$ —(2)

Substraction eq(2) from(1)

$\Rightarrow {}_I\int_i^f dS + \cancel{{}_R\int_f^i dS} - {}_I\int_i^f \frac{đQ}{T} - \cancel{{}_R\int_f^i \frac{đQ}{T}} > 0 \quad \Rightarrow {}_I\int_i^f dS > {}_I\int_i^f \frac{đQ}{T}$

Small change in state, $(dS)_I > \left(\frac{đQ}{T}\right)_I \Rightarrow \boxed{dS \ge \frac{đQ}{T}}$

So, the next segment we have is that we have to elaborate more with respect to irreversible process and to elaborate more we need to see the evaluation of heat and entropy and their correlations. So, in order to relate the change in entropy of heat for an irreversible process, we are now considering a cycle in which the system begins from an initial state i and passes during an irreversible process I to the final state f. So, then it returns to the initial state.

So, what we say here that to analyse this relation for heat and entropy for an reversible process, we are considering this temperature entropy diagram. So, in this temperature and entropy diagram we are fixing this initial state i first, then system is supposed to go to the final state f. And since your analysis is focused on irreversible process; so, we assume that there is some kind of irreversible process which is denoted by this dotted line and it is proceeding in these directions.

Now, while in return this final stage takes a reversible path; so, this is a reversible path and this is an irreversible path. Now, what we are trying to say that what happens to entropy and heat for these reversible and irreversible paths. So, remember one thing, heat is a path function, but entropy is a point functions.

So, it depends on the point to point; that means, entropy is independent of the path. So, we must know that what is the difference in the entropy between the final and initial states. Second part we need to emphasize that during this reversible path and irreversible path what is the magnitude of heat that is going to change or going into the path that if it is a reversible and if it is not a reversible.

So, first thing to analyse this heat and entropy separately. So, let us first consider this entropy function that is $\oint dS$, when it is evaluated? It is evaluated for the cycle; that means, for the cycle it goes in this way and comes back in this path. So, this consist of two paths, the entropy for this irreversible path i and entropy change for this reversible path r.

So, if the system goes from i to f; so, $\oint dS =_I \int_i^f dS +_R \int_f^i dS$. So, this is what for what you write for entropy and what you can write with respect to Clausius inequality from this equations. That means, we can replace $\oint_R dS = \oint_R \frac{\text{đ}Q}{T}$.

So, we can write these two equations, but this $\oint_I \frac{\text{đ}Q}{T} < 0$. And; in fact, when you if you have put this equation as 1 and this equation as 2; so, on subtraction of 2 from 1; we can write that dS this is first term sits here.

Second term of the first equation it is also here then since you are subtracting there is a negative sign here and negative sign for this equation 2 and this must be greater than 0. Because, in this case it is less than 0; in this case it is greater than 0, because from 1 to 2 when you subtract this will take a other trend; so, it will be greater than 0. $\Rightarrow {}_I\int_i^f dS + {}_R\int_f^i dS - {}_I\int_i^f \frac{\text{đ}Q}{T} - {}_R\int_f^i \frac{\text{đ}Q}{T} > 0$

But interestingly if you look at this particular equations and try to find out by definition of entropy what it means to us is $\oint_R dS = \oint_R \frac{\text{đ}Q}{T}$. So, this reversible term will get cancelled and irreversible term will remain. So, when you only look for this irreversible process, we end up in having this expressions that ${}_I\int_i^f dS >{}_I \int_i^f \frac{\text{đ}Q}{T}$.

That means, entropy is greater than the cyclic integral value and for the very small changes; that means, we can remove this integral. So, we can represent in terms of differential form that is $(dS)_I > \left(\frac{\text{đ}Q}{T}\right)_I$. Or in other words in a general sense that for any process we can write this particular expression by putting an inequality and equality signs where it says $dS \geq \frac{\text{đ}Q}{T}$.

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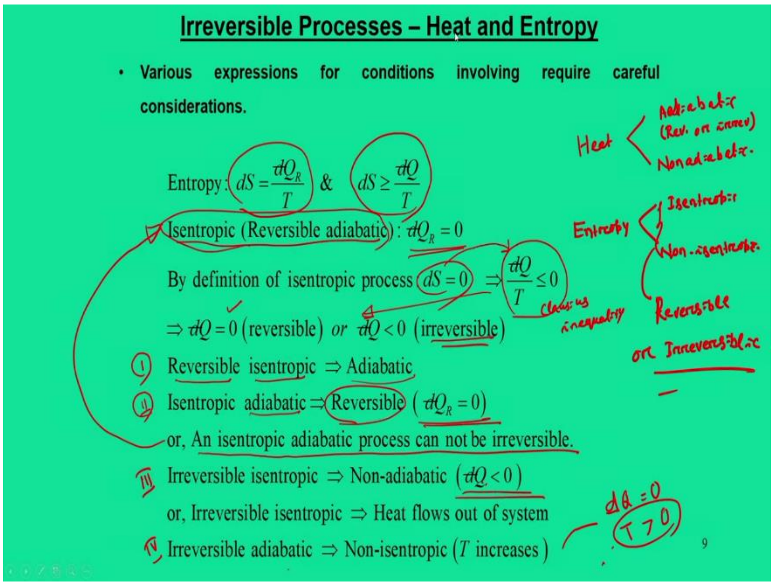

Irreversible Processes – Heat and Entropy

- Various expressions for conditions involving require careful considerations.

Entropy: $dS = \frac{\text{đ}Q_R}{T}$ & $dS \geq \frac{\text{đ}Q}{T}$

Isentropic (Reversible adiabatic): $\text{đ}Q_R = 0$

By definition of isentropic process $(dS = 0) \Rightarrow \frac{\text{đ}Q}{T} \leq 0$

$\Rightarrow \text{đ}Q = 0$ (reversible) *or* $\text{đ}Q < 0$ (irreversible)

(i) Reversible isentropic ⇒ Adiabatic

(ii) Isentropic adiabatic ⇒ Reversible $(\text{đ}Q_R = 0)$

or, An isentropic adiabatic process can not be irreversible.

(iii) Irreversible isentropic ⇒ Non-adiabatic $(\text{đ}Q < 0)$

or, Irreversible isentropic ⇒ Heat flows out of system

(iv) Irreversible adiabatic ⇒ Non-isentropic (T increases)

Now, having said this we now have many inferences or consequences from our analysis. So, let us club them together that to find what are the possible sequences. Since we have heat, we have entropy; so, the processes that can have is, for heat we can think of the process can be adiabatic or the process can be non-adiabatic.

And when you have this adiabatic and non adiabatic, we may have reversible or irreversible. And similarly for entropy, we can say it is an isentropic process; that means, entropy does not change and it is a non-isentropic process. And these things can be applied for a reversible process or irreversible process; so, this is the basics of this particular analysis.

So, we are trying to evaluate mathematically what are the different consequences we are going to see. So, first thing we say by definition of entropy we say $dS = \frac{đQ_R}{T}$ and this for a irreversible process $dS \geq \frac{đQ}{T}$. So, here Q_R stands for, the heat transfer that happens in a reversible process.

So, as you all know at this stage that always we use the word isentropic as reversible adiabatic which means $đQ_R = 0$. So, this is the truth, but there are other possibilities and finally, with those possibilities we can analyze that this is the only truth that is possible which means always a reversible adiabatic path means isentropic.

Now, let us evaluate one by one. So, first by definition when you say isentropic process we say $dS = 0$; so, this means $\frac{đQ}{T} \leq 0$; this is from Clausius inequality. But; however, when this equality sign will hold good if the process is reversible.

So, what are the consequence of isentropic process means, because isentropic process does not talk about heat transfer. And from this analysis we can say that if dQ is equal to 0 which means process is reversible or dQ is less than 0 means process is irreversible. That means, from this expressions we have two possibilities, either dQ is equal to 0 or dQ less than 0.

Now, let us see the consequence one by one. So, first one if a process is reversible, but isentropic. So, means your dQ is equal to 0 and isentropic and dS is equal to 0. So, dQ is equal to 0 and dS is equal to 0; means, this process has to be adiabatic because, dQ is 0.

Now, second consequence if the process is isentropic and adiabatic, process is isentropic and adiabatic; isentropic means, your dS is 0 adiabatic means is dQ is equal to 0.

So, then it has to be a reversible one which means $đQ_R = 0$. Or in other words we can write this statement that an isentropic adiabatic process cannot be irreversible. So, in a very simple sense we normally refer the same consequence as isentropic process which is nothing but a reversible adiabatic process. Now, let us move towards the irreversible situations; so, the case three.

Irreversible isentropic means your dS is equal to 0, but your dQ is less than 0 because this will come from the Clausius inequality. So, when I say process is irreversible, but isentropic it is of course, a non adiabatic process, but dQ is less than 0.

So, which means in an irreversible isentropic process heat always flows out of the systems; so, dQ is always negative is less than 0. And fourth category, if the process is irreversible and adiabatic; so, by irreversible I mean, we are looking into Clausius inequality and by adiabatic I mean dQ is equal to 0.

So, if you put this things equation, you will see that dQ is equal to 0 and process is irreversible then we can say your T must be always greater than 0; that means, temperature always increases. So, in a sense that in a non isentropic process temperature always increases. So, this is the some of the summary that has come out from our analysis of irreversible process in the name of heat and entropy.

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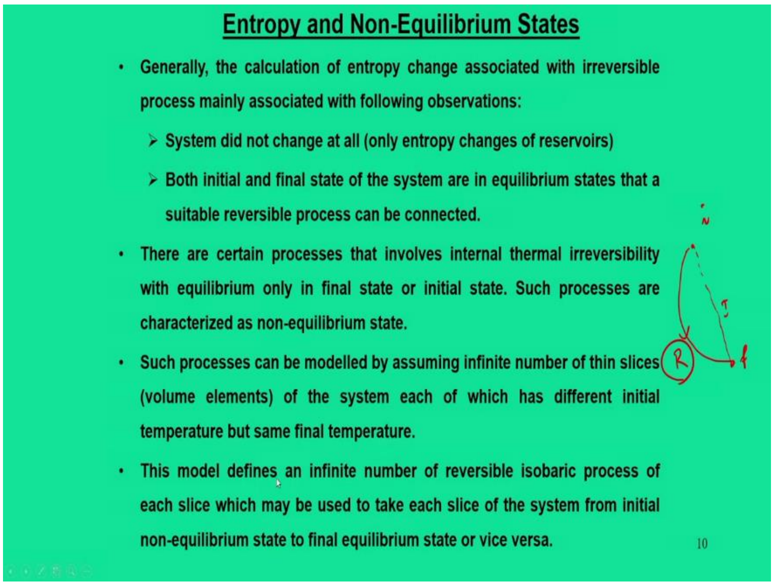

Entropy and Non-Equilibrium States

- Generally, the calculation of entropy change associated with irreversible process mainly associated with following observations:
  - System did not change at all (only entropy changes of reservoirs)
  - Both initial and final state of the system are in equilibrium states that a suitable reversible process can be connected.
- There are certain processes that involves internal thermal irreversibility with equilibrium only in final state or initial state. Such processes are characterized as non-equilibrium state.
- Such processes can be modelled by assuming infinite number of thin slices (volume elements) of the system each of which has different initial temperature but same final temperature.
- This model defines an infinite number of reversible isobaric process of each slice which may be used to take each slice of the system from initial non-equilibrium state to final equilibrium state or vice versa.

Now, till this point of time whatever we have evaluated it is about the initial state, final state, entropy, heat and we are mainly focused on the equilibrium state. That means, always we say initial state and final state are in thermodynamic equilibrium. That means, it is when we say thermodynamic equilibrium all unbalanced force are 0, temperature is 0, no chemical reactions, all these things are satisfied.

But what happens in some situations if it is unable to achieve the equilibrium states, then what is going to happen? So, there are some circumstances in the nature, it is not possible to achieve the equilibrium states. So, generally the calculation of entropy change is associated with the irreversible processes are with following observations.

That means system did not change at all only entropy changes for the reservoirs. In fact, for all our previous analysis in terms of reversible processes, we have seen either system did not change at all, but only entropy change that happens in the reservoirs. Both initial and final states of the systems are in equilibrium states which are suitable for which a reversible process can be connected.

That means if your initial and final states are equilibrium then we can say that actual process is irreversible, but we can connect this actual processes with a reversible one. So, if this is possible then still then also process is treated as irreversible and we can evaluate the properties from the initial and final point through this data of the reversible process.

But there are certain processes that involves internal thermal irreversibility with equilibrium only in the final state or initial state, such processes are characterized as non equilibrium states. And when such a processes are modelled, we are talking about infinite number of thin slice of volume element of each systems for which we have different initial temperature, but same final temperature. And when you do this particular analysis, it will talk about infinite number of reversible isobaric processes of each slice which may be used to take the system from the initial non equilibrium state to final equilibrium state and vice versa.

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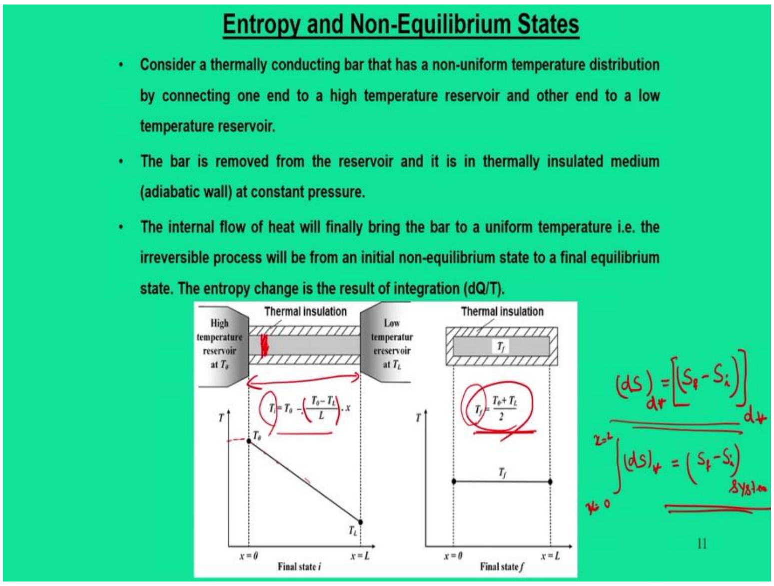

Entropy and Non-Equilibrium States

- Consider a thermally conducting bar that has a non-uniform temperature distribution by connecting one end to a high temperature reservoir and other end to a low temperature reservoir.
- The bar is removed from the reservoir and it is in thermally insulated medium (adiabatic wall) at constant pressure.
- The internal flow of heat will finally bring the bar to a uniform temperature i.e. the irreversible process will be from an initial non-equilibrium state to a final equilibrium state. The entropy change is the result of integration (dQ/T).

$$(ds)_{dv} = \left[(S_f - S_i)\right]_{dv}$$

$$\int_{x=0}^{x=L} (ds)_v = (S_f - S_i)_{system}$$

Now, one such example I can give here. So, whatever we have talked about in the previous slides, if you can simplify our thought process it goes like this. For example, we have a metallic bar which is connected between a high temperature reservoir and low temperature reservoir that is T_0 and T_L. Of course, the bar is thermally insulated; that means, only heat can be conducted through the bar.

So; obviously, what happens is that, as long as the heat getting conducted, temperature distribution along the bar can be drawn in a linear fashion. By recalling Fourier law we can find out the linear relations of temperature that is from initial to final temperature with respect to x, x means the length of the bar.

Now, your length of the bar is L. So, assuming a in linear distribution of temperatures we can write this equations $T_i = T_0 - \frac{T_0 - T_L}{L}x$. So, basically from this equations we can find out all the intermediate points that joins T_0 and T_L. And in fact, from this slope of the line we can find out temperature distribution at any location of the bar.

And ultimately another way of modelling this is that same bar is now kept in thermal insulations. But only difference is that now they are not connected with the reservoirs. If this happens the; obviously, since heat cannot come out from the bar, we will have a final equilibrium temperature T_f and that is nothing but $\frac{T_0+T_L}{2}$. So, this can be drawn as the final equilibrium temperatures.

Now, the same problem we are looking as if it we have a gross bar, but what we can view is that we can take small volume element from this bar. And for this volume element we can actually evaluate the same equilibrium to initial temperature and final temperatures and try to see the entropy.

Now; that means, for the small element we write $dS_{dV} = \left(S_f - S_I\right)_{dV}$ final entropy minus in initial entropy and this we say this is only for small volume element dv. First, we have to evaluate this, then we can integrate, $\int_{x=0}^{x=L} dS_V = \left(S_f - S_I\right)_{system}$ to find entropy change of the system. So, this is the analysis which we are going to do in one of the problems where we can evaluate the entropy change in which the system goes from initial non equilibrium state to the final equilibrium state and that is for an irreversible process.

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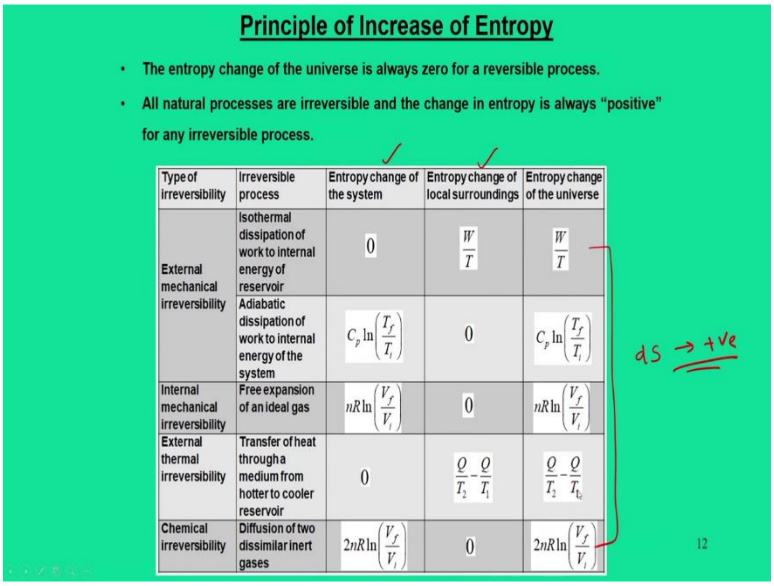

Principle of Increase of Entropy

- The entropy change of the universe is always zero for a reversible process.
- All natural processes are irreversible and the change in entropy is always “positive” for any irreversible process.

Type of irreversibility	Irreversible process	Entropy change of the system ✓	Entropy change of local surroundings ✓	Entropy change of the universe
External mechanical irreversibility	Isothermal dissipation of work to internal energy of reservoir	0	$\frac{W}{T}$	$\frac{W}{T}$
	Adiabatic dissipation of work to internal energy of the system	$C_p \ln\left(\frac{T_f}{T_i}\right)$	0	$C_p \ln\left(\frac{T_f}{T_i}\right)$
Internal mechanical irreversibility	Free expansion of an ideal gas	$nR \ln\left(\frac{V_f}{V_i}\right)$	0	$nR \ln\left(\frac{V_f}{V_i}\right)$
External thermal irreversibility	Transfer of heat through a medium from hotter to cooler reservoir	0	$\frac{Q}{T_2} - \frac{Q}{T_1}$	$\frac{Q}{T_2} - \frac{Q}{T_1}$
Chemical irreversibility	Diffusion of two dissimilar inert gases	$2nR \ln\left(\frac{V_f}{V_i}\right)$	0	$2nR \ln\left(\frac{V_f}{V_i}\right)$

$ds \rightarrow \underline{\underline{+ve}}$

So, after talking exhaustively about reversible and irreversible processes, we are now trying to frame the principle of increase in the entropy. So, in our previous lecture we discussed that entropy change for the universe is always 0 for a reversible processes, and all natural processes are irreversible, but the change in the entropy is always positive.

And what are the natural processes which are actually irreversible, but we have modelled as if a reversible process can connect between them, they involve external mechanical irreversibility, internal mechanical irreversibility, external thermal irreversibility, and chemical irreversibility. And for all these cases we calculated entropy change of the system, entropy change of the surroundings and all these values we say that dS is always positive. And in fact, this expression will talk about that the terms dS of the universe is always positive.

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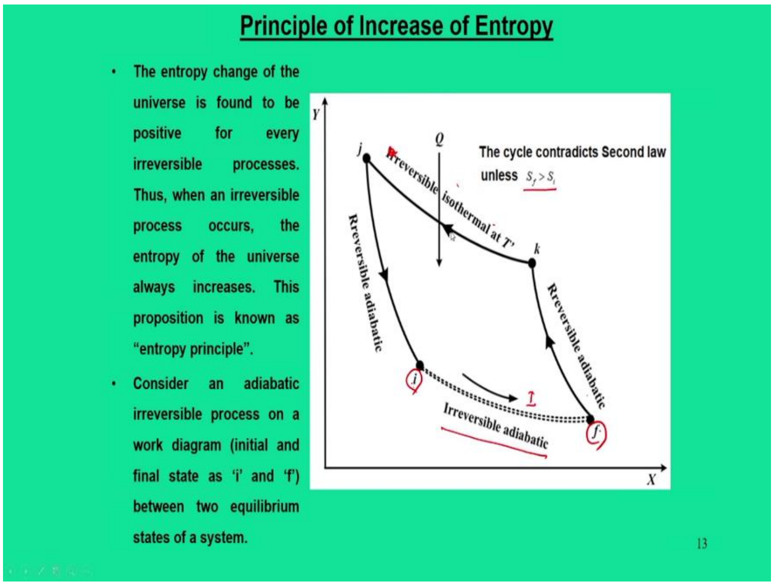

Principle of Increase of Entropy

- The entropy change of the universe is found to be positive for every irreversible processes. Thus, when an irreversible process occurs, the entropy of the universe always increases. This proposition is known as "entropy principle".
- Consider an adiabatic irreversible process on a work diagram (initial and final state as 'i' and 'f') between two equilibrium states of a system.

The cycle contradicts Second law unless $S_f > S_i$

Now, with this idea and with the Clausius inequality we are going to talk about the entropy principle. So, what does this mean that the entropy change of the universe it is found to be positive for every irreversible process, thus when an irreversible process occurs the entropy of the inverse always increases. And this is called as preposition of entropy principle which means entropy of the universe always increases.

Now, to prove it in a more elaborate way we can say that another way of looking at the fact that we can actually prove this is that entropy by assuming the second law of thermodynamic thermodynamics is correct. For which the entropy of the final state is always greater than the initial states, this has to be true.

So, for that reason we want to ensure that we have some initial state i and we have from final state f, the process goes in an irreversible adiabatic manner that is the irreversible process is conducted between i and f. But, through this irreversible process we can connect the final state to initial state through a reversible adiabatic process, irreversible isothermal process, and reversible adiabatic process; so, this is reversible.

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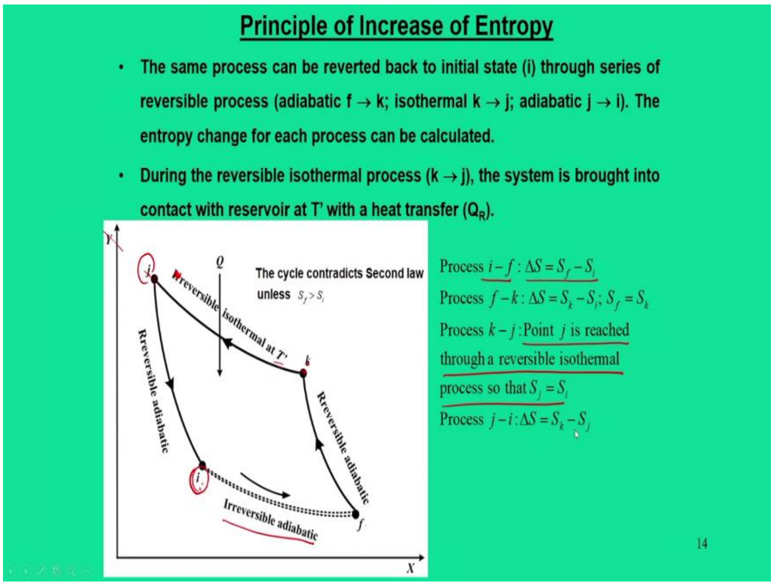

Principle of Increase of Entropy

- **The same process can be reverted back to initial state (i) through series of reversible process (adiabatic f → k; isothermal k → j; adiabatic j → i). The entropy change for each process can be calculated.**
- **During the reversible isothermal process (k → j), the system is brought into contact with reservoir at T' with a heat transfer (Q_R).**

The cycle contradicts Second law unless $S_f > S_i$

Process $i-f: \Delta S = S_f - S_i$

Process $f-k: \Delta S = S_k - S_i; S_f = S_k$

Process $k-j$: Point j is reached through a reversible isothermal process so that $S_j = S_i$

Process $j-i: \Delta S = S_k - S_j$

The reversible isothermal process when you do it, we can show that the second law has to be satisfied. And for that reasons let us evaluate the work diagram which is represented as a x and y in this case which says which can be written in this manner that the process which is i f and when you say i f we say irreversible adiabatic. So, we can write $\Delta S = S_f - S_i$.

Now, you are assuming to connect this final state to initial state in a reversible manner which says goes from f to k, k to j and j to i; so, let us see one by one. So, process f to k the entropy change will be $S_k - S_i$, and since, since this process is reversible adiabatic. So, we can say $S_f = S_k$. And for the process k to j now when we are from this process we reach here.

Now, k to j we can join in and we get the point j such that it is achieved through a reversible isothermal process. That means, from to k to j you draw a isothermal curve proceeding in this directions and finally, whatever this entropy at i and j are equal $S_j = S_i$. So, wherever they cut it the point j is located; that means, for the process j-I, we can write $\Delta S = S_k - S_j$.

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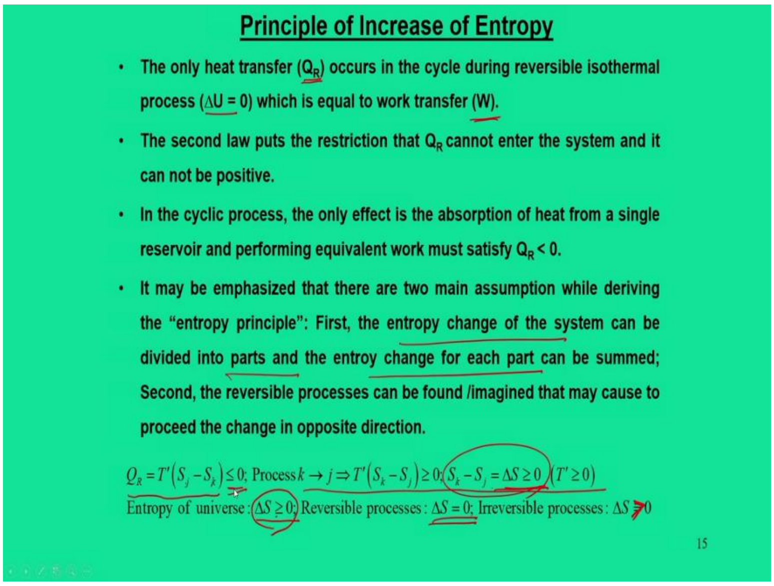

Principle of Increase of Entropy

- The only heat transfer (Q_R) occurs in the cycle during reversible isothermal process ($\Delta U = 0$) which is equal to work transfer (W).
- The second law puts the restriction that Q_R cannot enter the system and it can not be positive.
- In the cyclic process, the only effect is the absorption of heat from a single reservoir and performing equivalent work must satisfy $Q_R < 0$.
- It may be emphasized that there are two main assumption while deriving the "entropy principle": First, the entropy change of the system can be divided into parts and the entroy change for each part can be summed; Second, the reversible processes can be found /imagined that may cause to proceed the change in opposite direction.

$Q_R = T'(S_j - S_k) \leq 0$; Process $k \rightarrow j \Rightarrow T'(S_k - S_j) \geq 0$; $S_k - S_j = \Delta S \geq 0$ $(T' \geq 0)$

Entropy of universe : $\Delta S \geq 0$; Reversible processes : $\Delta S = 0$; Irreversible processes : $\Delta S > 0$

Now, from this we can now conclude the fact that in this entire cyclic process we see that only heat transfer that happens is during this reversible isothermal process that is at temperature some temperature T'. And all other processes does not involve any heat transfer, because the processes are adiabatic. So, considering this we can say the only heat transfer Q_R occurs in the cycle and I have written Q_R, because that particular process is reversible one.

Reversible isothermal process for which we have $\Delta U = 0$ which means this Q_R is nothing but your work transfer W. But, the second law puts the restriction that Q_R cannot enter the system, it cannot be positive. Because, it is interacting with only one reservoir, there is no second reservoir in which because heat interaction takes place at Q_R at temperature T', there is no heat rejections. So, this Q_R cannot enter the systems; means it cannot be positive.

So, considering this we say this $Q_R = T'(S_j - S_k) \leq 0$. That means, process k to j we can write this expressions; that means, we says $(S_k - S_j) \geq 0$. So, already we proved in some sense that for reversible and irreversible process we framed the rule $\Delta S > 0$, here also you proved it for a particular systems. And finally, it can emphasize that in terms of entropy principle which says that entropy of the system can be divided into two parts and the entropy change of each part can be summed up.

The second one is that reversible process can be found that they may cause the process to change in the opposite directions. In fact, this was actually represented in the graphically in their previous picture says that in a first thing we assume the entropy change of the systems into multiple number of parts. And for each part we can calculate this entropy that is process i to f, f to j, j to k and so on.

So, all so, for all these cases if you calculate this entropy; and finally, when you sum it up it we land of having one particular relations that is $\Delta S \geq 0$. Now; obviously, we can say now the entropy of the universe $\Delta S \geq 0$. So, this is the law of entropy or entropy of the universe.

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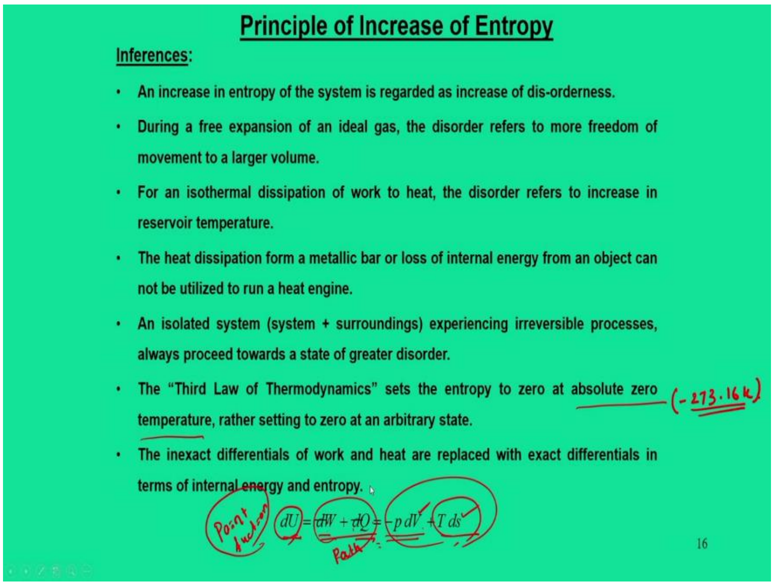

Principle of Increase of Entropy

Inferences:

- An increase in entropy of the system is regarded as increase of dis-orderness.
- During a free expansion of an ideal gas, the disorder refers to more freedom of movement to a larger volume.
- For an isothermal dissipation of work to heat, the disorder refers to increase in reservoir temperature.
- The heat dissipation form a metallic bar or loss of internal energy from an object can not be utilized to run a heat engine.
- An isolated system (system + surroundings) experiencing irreversible processes, always proceed towards a state of greater disorder.
- The "Third Law of Thermodynamics" sets the entropy to zero at absolute zero temperature, rather setting to zero at an arbitrary state. (-273.16k)
- The inexact differentials of work and heat are replaced with exact differentials in terms of internal energy and entropy.

$$dU = đW + đQ = -p\,dV + T\,ds$$

Point function

Path

So, ultimately we can summarize with following inferences an increase in the entropy of the system is regarded as the increase in the disorderness. By disorderness, we mean for a particular thermodynamic processes; for example, the disorderness during a free expansion process of an ideal gas means more freedom of movement to a larger volume. The disorderness for an isothermal dissipation of heat means increase in the reservoir temperature.

Disorderness with respect to heat dissipation from a metallic bar is nothing but the loss of internal energy from an object is not utilized to run an heat engine. For example, another kind of important thing is that heat loss from a metallic bar is viewed thermodynamically as loss of internal energy. But, this loss of internal energy cannot be utilized to run a heat engine and this goes as a irreversible loss.

And more over the isolated system that is another definition for entire universe is an isolated system which involves system and surroundings, when it experience an irreversible processes it always moves towards the state of greater disorder. Which means, entropy of the universe always increases. So, this imposes the third law of thermodynamics when entropy is zero, this is possible only at absolute zero temperature.

So, the absolute zero temperature is the basics at which the thermodynamic parameter entropy is zero and this absolute zero we say it is about - 273.16 Kelvin. And this is not an arbitrary state; that means, all of a sudden this number does not come, because at this things we say that entropy is zero.

Now, another advantage of this entropy is that, when you look at entropy it is a point functions and if you recall the first law which says $dU = \text{đ}W + \text{đ}Q$. Now, dU is a point function, but dW and dQ are their path functions; so, these are path dependent. But this point function and path dependent they cannot be correlated that is the actual assumption that we make in the beginning. But this is not true because, this path function or inexact differentials can be written in terms of point functions that is $-pdV + Tds$ and here dS stands for the entropy, V stands for the volume.

So; that means, the relation of the point function is always holds good here, even though the right hand side of the equation involving work and heat they are path function. So, it means that in exact differentials of work and heat are replaced with exact differential in terms of internal energy and entropy. So, this is another significance of the entropy; so, with this we conclude for this lecture.

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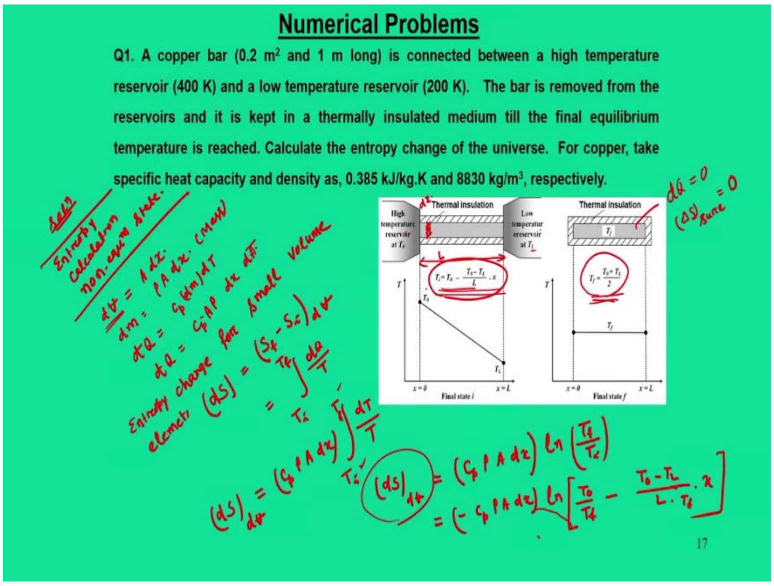

Numerical Problems

Q1. A copper bar (0.2 m^2 and 1 m long) is connected between a high temperature reservoir (400 K) and a low temperature reservoir (200 K). The bar is removed from the reservoirs and it is kept in a thermally insulated medium till the final equilibrium temperature is reached. Calculate the entropy change of the universe. For copper, take specific heat capacity and density as, 0.385 kJ/kg.K and 8830 kg/m^3, respectively.

Soln

Entropy calculation non-equi^m state.

$dV = A\,dx$

$dm = \rho A\,dx$ (mass)

$dQ = c_p(dm)dT$

$dQ = c_p A\rho\,dx\,dT$

Entropy change for small volume element $(dS) = (S_f - S_i)_{dV} = \int_{T_i}^{T_f} \frac{dQ}{T}$

$(dS)_{dV} = (c_p \rho A\,dx)\int_{T_i}^{T_f} \frac{dT}{T}$

$\boxed{(dS)_{dV}} = (c_p \rho A\,dx)\ln\left(\frac{T_f}{T_i}\right)$

$= (-c_p \rho A\,dx)\ln\left[\frac{T_0}{T_f} - \frac{T_0 - T_L}{L \cdot T_f}\cdot x\right]$

$dQ = 0$

$(\Delta S)_{surr} = 0$

Now, we will try to solve a problem which we have discussed in one of our slide which we call this as entropy calculations for non equilibrium states. Although theoretically I have explained that things. Now, there is a mathematical problem which says that we have a high temperature reservoir, we have a high temperature reservoir is at T_0, low temperature reservoir is at T_L.

And there is a metallic bar that connects between high temperature and low temperature and there is a thermal insulation in between them. In the beginning because of this region there is a temperature change from T_0 to T_L, and this change happens in a linear fashion. Now, after sometimes the reservoirs are disconnected and this entire bar is now kept under thermal insulation.

So, that there is $dQ = 0$ for the outside; that means, so, $\Delta S_{\text{surr}} = 0$. But, what happens to the bar? Bar after certain time it assumes the equilibrium temperatures. So, what we see is that initially the system is not in equilibrium state, the final state is in equilibrium state.

So, to do that what we are going to model this that we are going to create a small element dx. And in fact, this is the length of the bar is L and we are going to calculate what is the volume element, small volume element dv. And this small volume element can be written as Adx and for the small volume element, the mass will be because we can multiply density; so, we can say $dm = \rho Adx$. For this small mass we can calculate $dQ = c_p(dm)dT = c_p.\rho.A.dx.dT$.

So, there are two integral, one is with respect to dT temperature other is with respect to x length. Now, we have already written that the final temperature is T$_f$, initial temperature is T$_i$. So, we can find out the entropy change for this small volume element.

$$dS = \left(S_f - S_i\right)_{dv} = \int_{T_i}^{T_f} \frac{dQ}{T} = \left(c_p \rho A dx\right) \int_{T_i}^{T_f} \frac{dT}{T} = \left(c_p \rho A dx\right) \ln \frac{T_f}{T_i}$$

$$= \left(-c_p \rho A dx\right) \ln\left(\frac{T_0}{T_f} - \frac{T_0 - T_L}{L T_f} x\right)$$

Now, this dv element is with respect to for small element dx.

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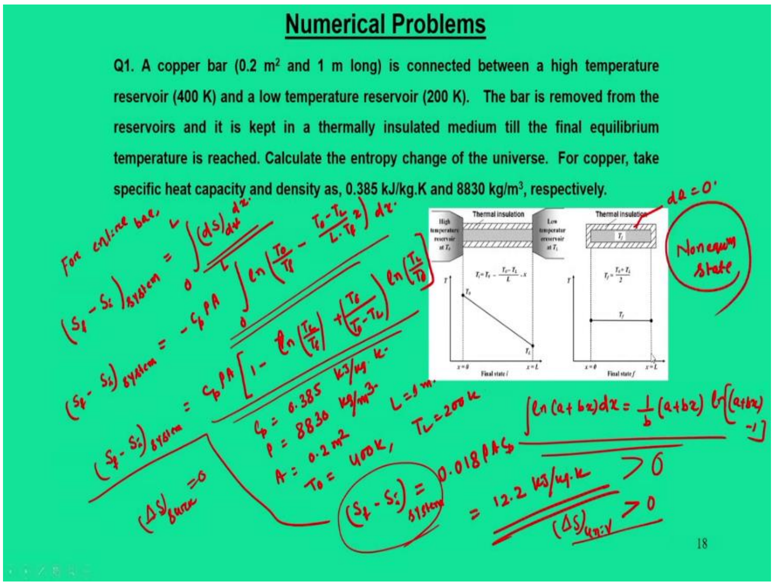

Numerical Problems

Q1. A copper bar (0.2 m^2 and 1 m long) is connected between a high temperature reservoir (400 K) and a low temperature reservoir (200 K). The bar is removed from the reservoirs and it is kept in a thermally insulated medium till the final equilibrium temperature is reached. Calculate the entropy change of the universe. For copper, take specific heat capacity and density as, 0.385 kJ/kg.K and 8830 kg/m^3, respectively.

Then this can be further integrated for the entire bar

$$\left(s_f - s_i\right)_{system} = \int_0^L (ds)_{dv} dx = \left(-c_p \rho A\right) \int_0^L \ln\left(\frac{T_0}{T_f} - \frac{T_0 - T_L}{L T_f} x\right) dx$$

$$= \left(c_p \rho A\right)\left(1 - \ln \frac{T_L}{T_f} + \frac{T_0}{T_0 - T_L} \ln \frac{T_L}{T_0}\right)$$

$$= (0.385 \times 8830 \times 0.2)\left(1 - \ln \frac{200}{300} + \frac{400}{400 - 200} \ln \frac{200}{400}\right)$$

$$= 12.2 \frac{kJ}{kg - K}$$

And. In fact, this is greater than 0 we say entropy of the universe is 0, because $\Delta S_{\text{surr}} = 0$, because this is $dQ = 0$. So, this system plus surrounding we say $\Delta S_{\text{univ}} > 0$and that is for a non equilibrium state, this is what we also prove here.

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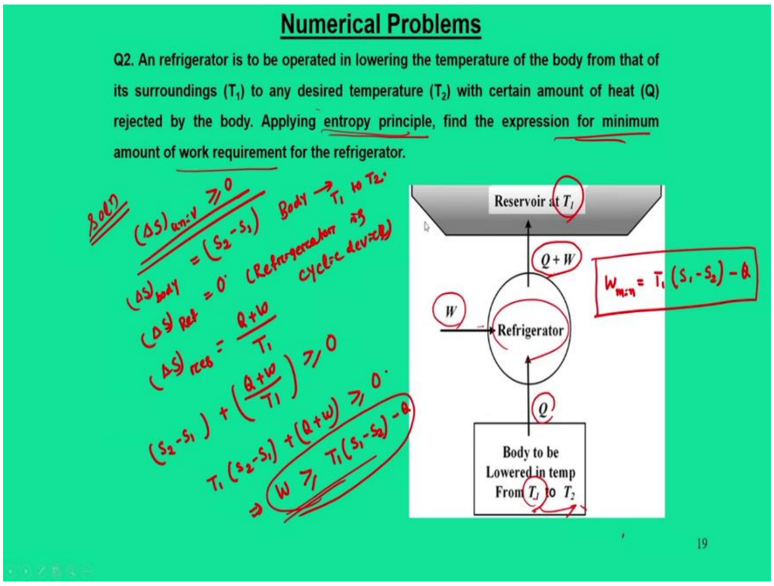

Numerical Problems

Q2. An refrigerator is to be operated in lowering the temperature of the body from that of its surroundings (T_1) to any desired temperature (T_2) with certain amount of heat (Q) rejected by the body. Applying entropy principle, find the expression for minimum amount of work requirement for the refrigerator.

Sol^n

$(\Delta S)_{univ} \geq 0$

$(\Delta S)_{body} = (S_2 - S_1)$ Body $\rightarrow$ T_1 to T_2.

$(\Delta S)_{Ref} = 0$ (Refrigerator is cyclic device)

$(\Delta S)_{res} = \frac{Q+W}{T_1}$

$(S_2 - S_1) + \left(\frac{Q+W}{T_1}\right) \geq 0$

$T_1(S_2 - S_1) + (Q+W) \geq 0$

$\Rightarrow W \geq T_1(S_1 - S_2) - Q$

$W_{min} = T_1(S_1 - S_2) - Q$

And the next problem is again in the name of entropy principle, what the problem statement is that we have a refrigerator it is to be operated in lowering the temperature of the body from that of surroundings to any desired temperature. That means, a body which is initial temperature at T_1 is to be reduced to temperature T_2. And in fact, the surrounding temperature is also T_1 and here we call this as a reservoir temperature.

So, what we can see that to talk about this entropy principle through a refrigerator think about a refrigerator that takes W as work input and to for this work input and this temperature to be lowered, it must take certain quantity of Q from this body and when the heat rejected to atmosphere again is $Q + W$.

So, by framing this we are now able to apply this entropy principle which says that $\Delta S_{\text{univ}} \geq 0$. And of course, refrigerator need some work, but we want to find out what is the minimum work.

So, for this entropy universe we have 3 parts, one is $\Delta S_{body} = S_2 - S_1$, because body goes from temperature goes from temperature T_1 to T_2. Then $\Delta S_{ref} = 0$, because refrigerator is cyclic device. Then the reservoir, we can write $\Delta S_{res} = \frac{Q+W}{T_1}$. So, by clubbing all together we can write $S_2 - S_1 + \frac{Q+W}{T_1} \geq 0;\ T_1(S_2 - S_1) + Q + W \geq 0; W \geq T_1(S_1 - S_2) - Q$. So, this is the conditions that amount of work requirement for the refrigerator.

Now, if this is the situation and the question is that minimum work. So, $W_{min} = T_1(S_1 - S_2) - Q$. So, this is the minimum work requirement for this refrigerator by applying entropy principle; so, with this I conclude this lecture today.

Thank you for your attention.