Advanced Thermodynamics and Combustion

Prof. Niranjan Sahoo
Department of Mechanical Engineering
Indian Institute of Technology, Guwahati

Module - 02
Entropy and Exergy
Lecture - 04
Entropy Analysis (Part I)

Dear learners, greetings from IIT Guwahati. We are in the MOOCs course that is Advanced Thermodynamics and Combustions. Today we are going to start the second module and title of this module is Entropy and Exergy.

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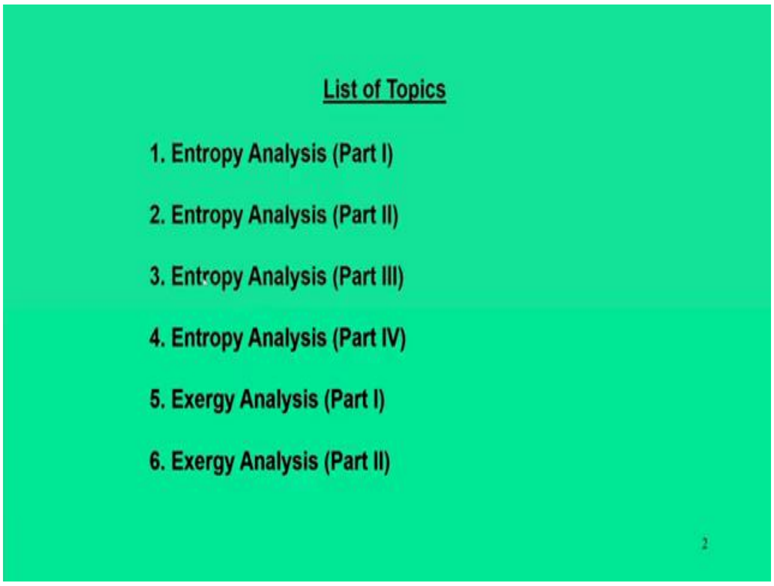

List of Topics

1. Entropy Analysis (Part I)
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6. Exergy Analysis (Part II)

So, the list of topics under this module will be covered mainly will be focusing on entropy which is one of the consequence or you can say the statement from the second law. Other option is that we are going to discuss something on exergy; that means, this is the another form of representation of energy that is exergy which says what is the maximum amount of exergy what a system can have considering the potential of the systems.

So, on this module there will be 6 lectures. So, let us start the first lecture today that is Entropy Analysis Part I.

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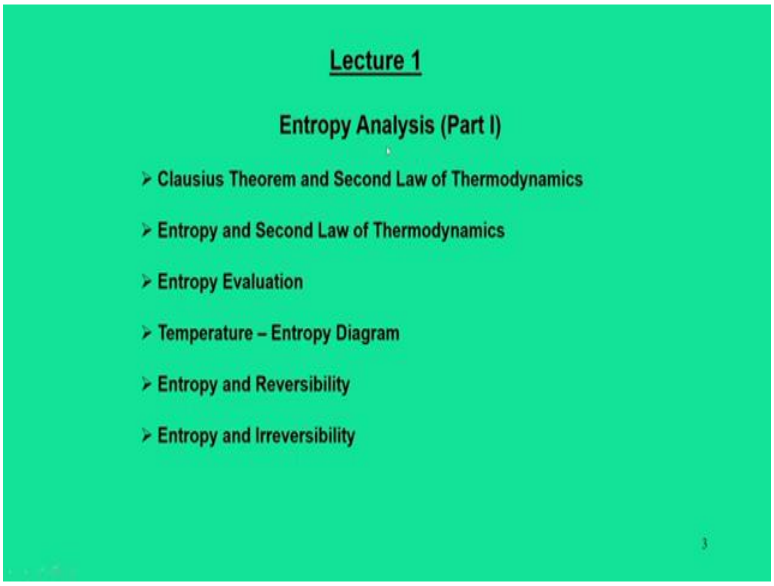

Lecture 1

Entropy Analysis (Part I)

- Clausius Theorem and Second Law of Thermodynamics
- Entropy and Second Law of Thermodynamics
- Entropy Evaluation
- Temperature – Entropy Diagram
- Entropy and Reversibility
- Entropy and Irreversibility

So, in this entropy analysis we are going to discuss the following topics that is, Clausius theorem and second law of thermodynamics. Prior to this we have already discussed exhaustively about the zeroth law, first law and second law. And here we will be giving specific emphasis to second law just to define the property which is known as entropy. Then we are going to discuss about the entropy and second law where is the what is the link in between and since this is entropy then we must evaluate this entropy.

So, what are the possible methods what we have to calculate the entropy of a system? Now, one of the fundamental diagrams based on the entropy is the temperature entropy diagram. This is similar to the very basic concept when you dealt with the first law, we talk about work and this work transfer was expressed in terms of pressure volume diagram or PV diagram.

And this PV diagram is used for work transfer and since the second law talks about heat, so, we must include that what diagram will talk about the heat transfer from a systems. So, that is nothing but your temperature entropy diagram. And in the second law it also introduce the concept of inequality; that means entropy or work transfer can increase or decrease. So, it is not possible to have complete conversion of heat to work.

So, in order to make it equal then we need to introduce some topics or some restrictions and those restrictions will be covered in the name of reversibility and irreversibility and both reversibility and the irreversibility have definite bearing for the parameter entropy.

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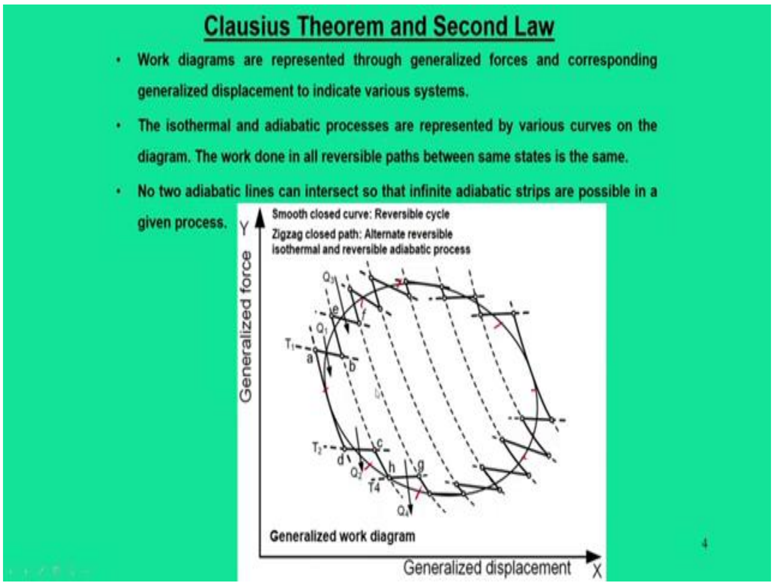

Clausius Theorem and Second Law

- Work diagrams are represented through generalized forces and corresponding generalized displacement to indicate various systems.
- The isothermal and adiabatic processes are represented by various curves on the diagram. The work done in all reversible paths between same states is the same.
- No two adiabatic lines can intersect so that infinite adiabatic strips are possible in a given process.

So, let us start the first segment of this today’s lecture that is Clausius theorem and second law. Prior to this we have discussed about the second law in two forms; one is Kelvin-Planck statement and Clausius statement. And another consequence of the second law is nothing but the Clausius theorem.

What does that Clausius theorem is all about we are going to explain. To start with first thing, first we can introduce that when you talk about this work diagram it is normally represented in terms of generalized force versus generalized displacements. So, if you look at this particular figure you can see that there is a circle or you can say we can find out many points on this circle.

And thermodynamically we can represent it as a closed cycle; that means, a system can undergo in a closed cycle or in other words we can talk of a cyclic systems. So, here the smooth closed curve we call this as a reversible cycles; that means, we can choose any direction any path and find out all the properties based on the this diagram; that is based on the force and the displacements we can represent this work diagram and one interesting thing is that mathematically we can view this entire curve or this closed curve in a multiple number of zigzag paths.

So, this zigzag path can be represented as you can see here one particular path can be a-b-c-d, other path can be e-f-g-h and side by side you can have multiple number of zigzag path or rather you can say infinite number of zigzag path. And these zigzag paths we can construct with a concept of Carnot cycle.

What does this mean that we can imagine this particular reversible cycle with multiple or infinite number of reversible processes that involves alternate reversible isothermal process and reversible adiabatic process which means this is nothing but the processes that are involved in a Carnot cycles.

So, for example, one can split this entire closed curve in a cycle like a-b-c-d. So, a-b-c-d is one particular Carnot cycle, e-f-g-h is another cycle and in each cycle we can say that there are some heat is getting added, some heat is getting rejected and so on. So, this is nothing but your work diagrams and we will find its significance in the subsequent slides. What we will talk about what is the relation between this Q_1 and T_1.

Maybe when you talk about Q_1 it is happening at constant temperature process, now when you are talking about b-c process it is nothing but a reversible adiabatic process. So, to summarize this what we can say that these isothermal and adiabatic processes are represented by various diagrams and the work done in all reversible paths between the same states is the same that is the consequence that we derived earlier.

And moreover another important point that to be noted is that; no two adiabatic lines can intersect so that infinite adiabatic strips is possible. That means, this adiabatic strips, at any point of time they cannot intersect and so we can have any adiabatic strips. So, likewise the complete process on this work diagram can be represented by infinite number of Carnot cycles.

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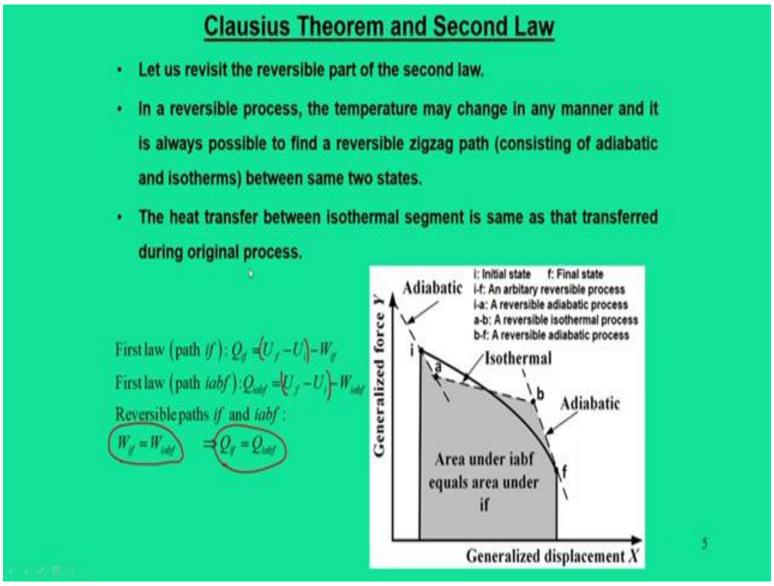

Clausius Theorem and Second Law

- Let us revisit the reversible part of the second law.
- In a reversible process, the temperature may change in any manner and it is always possible to find a reversible zigzag path (consisting of adiabatic and isotherms) between same two states.
- The heat transfer between isothermal segment is same as that transferred during original process.

First law (path if): $Q_{if} = (U_f - U_i) - W_{if}$

First law (path $iabf$): $Q_{iabf} = (U_f - U_i) - W_{iabf}$

Reversible paths if and $iabf$:

$W_{if} = W_{iabf} \Rightarrow Q_{if} = Q_{iabf}$

This is one part. Now, let us talk about one particular segment of this closed curve. So, what I can say? If you take one particular segment in which a system undergoes a change of state from its initial state ‘i’ to a final state ‘f’ and this is nothing but a reversible process.

So, you can say path i-f is a reversible process. But if you want to represent this particular path in terms of Carnot cycles, so, what I can draw? At point ‘i’ can draw a adiabatic line and point ‘f’ also I can draw another adiabatic line and at one particular point that is on this adiabatic line which passes through the initial point we can also draw another path a-b which is nothing but an isothermal path.

So, in other words what I can say that the initial state when the system undergoes a change of states from its initial state ‘i’ to ‘f’ then what happens? We can as well say that this is a path process i-f, but side by side we can construct like i-a-b-f. So, what does this mean? In a such a way that area under the path i-f is also equal to area under the path i-a-b-f.

So, in a sense we have represented this particular any reversible path with respect to a Carnot cycle. So, if these two are these two areas are equal then we can frame this relations like for we can use the first law for the process i-f. So, you can write $Q_{if} = U_f - U_i - W_{if}$ that is change in the internal energy minus work transfer during this path.

Now, same equation we are going to use for the path i-a-b-f which means that I can write it as $Q_{iabf} = U_f - U_i - W_{iabf}$. $U_f - U_i$ is nothing but the internal energy change at the final and initial state and it will remain same. So, this factor always will remain same because this is change in internal energy and it is a point functions.

So, from these two equations we can say that if you have reversible paths like one in a Carnot cycle other is like any reversible path. So, we can say $W_{if} = W_{iabf}$ or similarly we can say $Q_{if} = Q_{iabf}$. So, it is a very important consequence that says that work transfer and heat transfer among all reversible paths are same.

So, in a reversible process the temperature may change in any manner, but it is always possible to find a reversible zigzag path consisting of adiabatic and isotherms, but the heat transfer between isothermal segment is same as that of original process.

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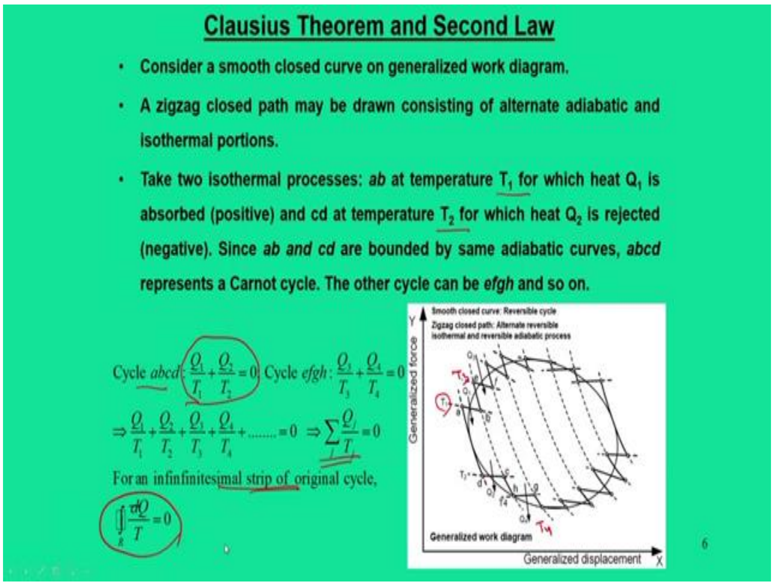

Clausius Theorem and Second Law

- Consider a smooth closed curve on generalized work diagram.
- A zigzag closed path may be drawn consisting of alternate adiabatic and isothermal portions.
- Take two isothermal processes: *ab* at temperature T_1 for which heat Q_1 is absorbed (positive) and cd at temperature T_2 for which heat Q_2 is rejected (negative). Since *ab and cd* are bounded by same adiabatic curves, *abcd* represents a Carnot cycle. The other cycle can be *efgh* and so on.

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

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

For an infinfinitesimal strip of original cycle,

$\oint_R \frac{đQ}{T}=0$

So, now that particular consequence again we are going to revisit the work diagram and we try to see another type of relations and in fact this will talk about nothing but your Clausius theorem. So, what has been found by the Clausius is that we are choosing two isothermal processes that is one is a-b at temperature T_1 and we can find out another isothermal process that is c-d at temperature to T_1 and T_2.

So, basically we are talking about a cycle a-b-c-d in which Q_1 amount of heat is being transferred through the process a-b at temperature T_1 and this process is isothermal and Q_2 heat is rejected at temperature T_2. And for this particular cycle a particular relation always holds good that is for the cycle a-b-c-d. We can found that $\frac{Q_1}{T_1} + \frac{Q_2}{T_2} = 0$.

Now, you repeat the same thing for all subsequent cycles. Like we can think about a cycle e-f-g-h in which Q_3 is added at temperature T_3 and Q_4 is rejected at temperature T_4. So, for this process we can write also another expression $\frac{Q_3}{T_3} + \frac{Q_4}{T_4} = 0$.

So, likewise we can think about multiple number of segments consisting of alternate reversible isotherms and adiabats and frame an equations such that it can be written as $\frac{Q_1}{T_1} + \frac{Q_2}{T_2} + \frac{Q_3}{T_3} + \frac{Q_4}{T_4} + \cdots \ldots \ldots = 0$. So, this entire expression may be summarized in terms of summations, that is $\sum_j \frac{Q_j}{T_j} = 0$.

Now, we have expressed this path in a discrete manner and if it has to happen in a continuous manner; that means, if these strips are very close. So, these steps can be represented in terms of integrations. So, this integration; that means, a parameter which is defined that is dQ and this dQ is nothing but this very small reversible heat transfer by T is equal to 0 $\oint_R \frac{đQ}{T} = 0$.

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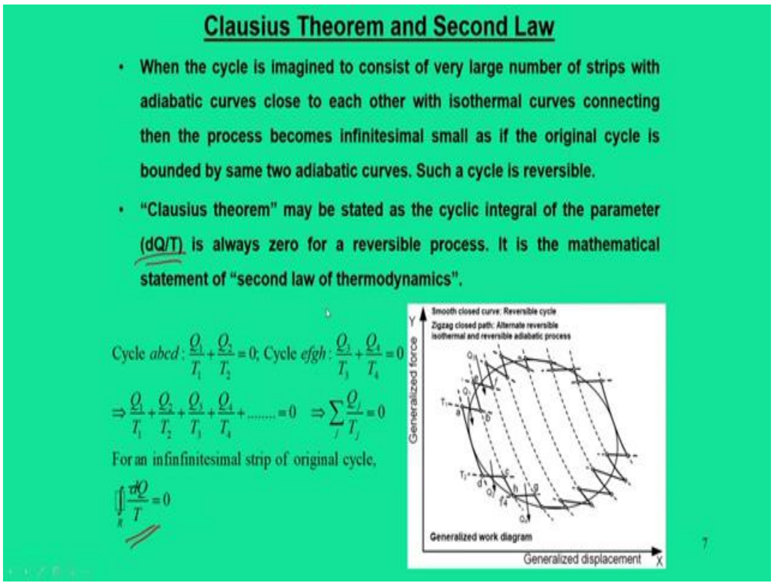

Clausius Theorem and Second Law

- When the cycle is imagined to consist of very large number of strips with adiabatic curves close to each other with isothermal curves connecting then the process becomes infinitesimal small as if the original cycle is bounded by same two adiabatic curves. Such a cycle is reversible.
- "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*: $\frac{Q_3}{T_3} + \frac{Q_4}{T_4} = 0$

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

For an infinfinitesimal strip of original cycle,

$\oint_R \frac{đQ}{T} = 0$

So, what we can summarize that when a cycle is imagined to be consist of large number of strips with adiabatic curves close to each other with isothermal curves connecting them, the process becomes infinitesimally small as if the original cycle is bounded by two adiabatic curves and such a cycle is reversible and based on this logic Clausius framed a theorem which called as Clausius theorem.

It states that the cyclic integral of the parameter $\oint_R \frac{\text{đ}Q}{T}$, this is nothing but this integral term is 0 for a reversible process. So, this is another consequence and another mathematical statement for the second law of thermodynamics.

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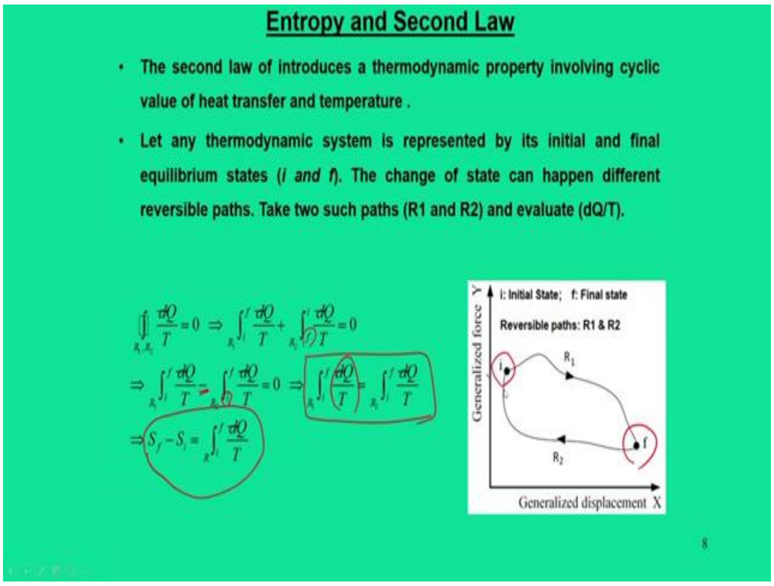

Entropy and Second Law

- The second law of introduces a thermodynamic property involving cyclic value of heat transfer and temperature .
- Let any thermodynamic system is represented by its initial and final equilibrium states (*i and f*). The change of state can happen different reversible paths. Take two such paths (R1 and R2) and evaluate (dQ/T).

$$\oint_{R_1,R_2} \frac{\text{đ}Q}{T} = 0 \Rightarrow {}_{R_1}\int_i^f \frac{\text{đ}Q}{T} + {}_{R_2}\int_f^i \frac{\text{đ}Q}{T} = 0$$

$$\Rightarrow {}_{R_1}\int_i^f \frac{\text{đ}Q}{T} - {}_{R_2}\int_i^f \frac{\text{đ}Q}{T} = 0 \Rightarrow \boxed{{}_{R_1}\int_i^f \frac{\text{đ}Q}{T} = {}_{R_2}\int_i^f \frac{\text{đ}Q}{T}}$$

$$\Rightarrow S_f - S_i = {}_{R}\int_i^f \frac{\text{đ}Q}{T}$$

Now, let us find more details on what is this $\frac{\text{đ}Q}{T}$. So, if you again generalize this in another view point like we have another figure that talks about; for example, there may be any thermodynamic processes. So, you have some initial states i and some final states f; that means these are the state points or thermodynamic coordinates on a general work diagram.

Now, what we are going to talk about is that we are going from initial state to final state in any one reversible path. So, R_1 is one such reversible path, but we are not returning again same path, but we are returning in another reversible path. So, R_1, R_2 is nothing but the reversible paths.

So from the Clausius theorem we can write that cyclic integral for the path R_1 and R_2 must be equal to 0. So, you can split this since from system initial state i we are going to go to the final state f. So, for which the reversible heat transfer is ${}_{R_1}\int_i^f \frac{\text{đ}Q}{T}$.

Similarly, another expression you can say write from final state to initial state we are going to for the path 2 ${}_{R_2}\int_f^i \frac{\text{đ}Q}{T}$; So, ${}_{R_1}\int_i^f \frac{\text{đ}Q}{T} + {}_{R_2}\int_f^i \frac{\text{đ}Q}{T} = 0$. Now, from these equations we can rewrite; that means, initial and final states are now reversed. So, the minus sign comes here. ${}_{R_1}\int_i^f \frac{\text{đ}Q}{T} - {}_{R_2}\int_i^f \frac{\text{đ}Q}{T} = 0$

Now, when you do this one interesting thing again we can frame out that now if you just differentiate what happens in two different reversible path. What you can see that one of the cyclic integral is ${}_{R_1}\int_i^f \frac{\text{đ}Q}{T}$ and the cyclic integral ${}_{R_2}\int_i^f \frac{\text{đ}Q}{T}$ is in another reversible path is R$_2$ and likewise we can keep on writing infinite number of reversible path.

So, one interesting thing is that integral of that parameter $\frac{\text{đ}Q}{T}$ remains constant. And since it is constant and what is remains fixed that we have fixed our initial state and final state. Now when a such a parameter is dependent on the state points, then we call this as a property and this property what we call this as a entropy change that is $S_f - S_i$.

And this is a point function or it is not path dependent. It depends on the initial state and the final state.

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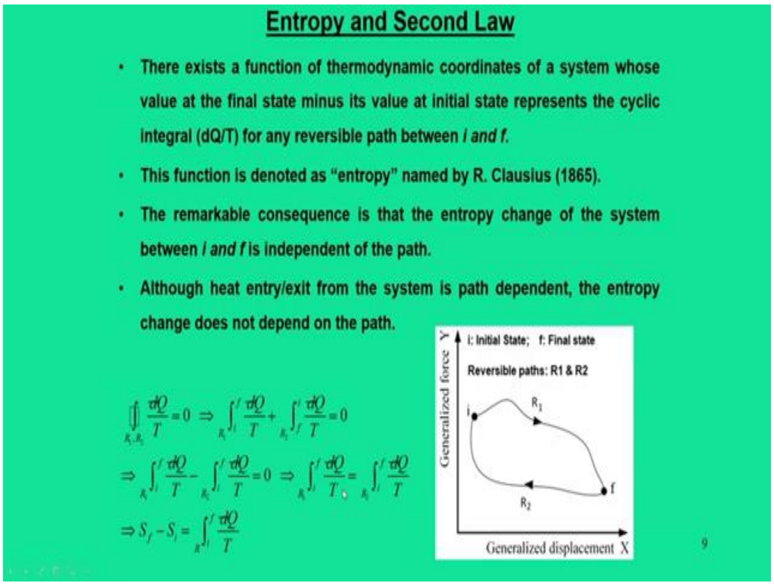

Entropy and Second Law

- There exists a function of thermodynamic coordinates of a system whose value at the final state minus its value at initial state represents the cyclic integral (dQ/T) for any reversible path between *i and f.*
- This function is denoted as “entropy” named by R. Clausius (1865).
- The remarkable consequence is that the entropy change of the system between *i and f* is independent of the path.
- Although heat entry/exit from the system is path dependent, the entropy change does not depend on the path.

$$\oint_{R_1 - R_2} \frac{\text{đ}Q}{T} = 0 \Rightarrow {}_{R_1}\int_i^f \frac{\text{đ}Q}{T} + {}_{R_2}\int_f^i \frac{\text{đ}Q}{T} = 0$$

$$\Rightarrow {}_{R_1}\int_i^f \frac{\text{đ}Q}{T} - {}_{R_2}\int_i^f \frac{\text{đ}Q}{T} = 0 \Rightarrow {}_{R_1}\int_i^f \frac{\text{đ}Q}{T} = {}_{R_2}\int_i^f \frac{\text{đ}Q}{T}$$

$$\Rightarrow S_f - S_i = {}_{R}\int_i^f \frac{\text{đ}Q}{T}$$

Now, let us have a more clear understanding of this. What the Clausius said is that there exist a function of thermodynamic coordinates of the system whose value at the final state minus its value at the initial states represents the cyclic integral $\frac{\text{đ}Q}{T}$ for any reversible path between i and f.

And this function is denoted as entropy and this concept of entropy is demonstrated by Clausius in 1865, but one of the remarkable consequence what you can see here is that entropy change of the system is independent of the path rather it depends on the point i and f. But although there can be a heat transfer; that means, heat can come out of the system or heat can be entered into the system, they are path dependent, but the entropy change does not depend on the path.

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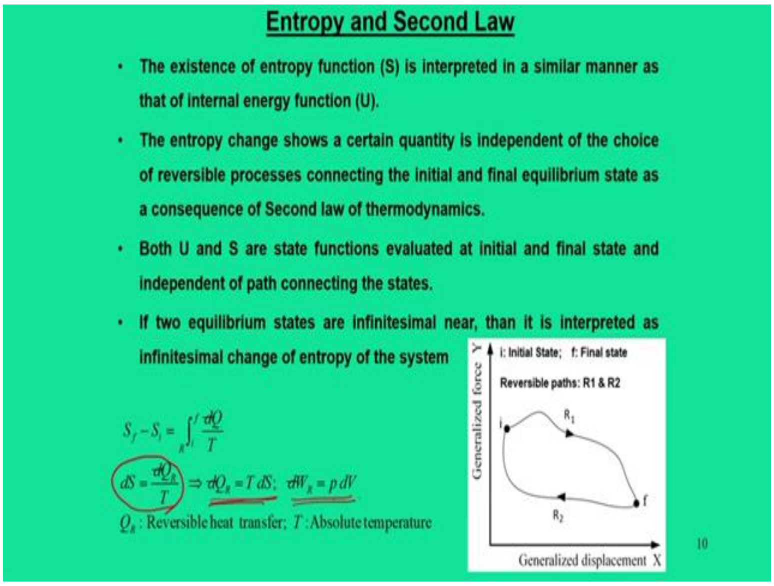

Entropy and Second Law

- The existence of entropy function (S) is interpreted in a similar manner as that of internal energy function (U).
- The entropy change shows a certain quantity is independent of the choice of reversible processes connecting the initial and final equilibrium state as a consequence of Second law of thermodynamics.
- Both U and S are state functions evaluated at initial and final state and independent of path connecting the states.
- If two equilibrium states are infinitesimal near, than it is interpreted as infinitesimal change of entropy of the system

$$S_f - S_i = \int_{R\,i}^{f} \frac{đQ}{T}$$

$$\boxed{dS = \frac{đQ_R}{T}} \Rightarrow \underline{đQ_R = T\,dS}; \quad \underline{đW_R = p\,dV}$$

Q_R : Reversible heat transfer; T : Absolute temperature

So, the concept of this existence of entropy is interpreted in a similar manner as that of internal energy functions. So, First law introduced the concept of internal energy function in a similar sense we can also define the function which is entropy functions. This entropy change shows certain quantity is independent of the choice of the reversible processes connecting the initial and final equilibrium state as a consequence of second law of thermodynamics.

Since both U and S are state functions they are evaluated from the initial and final states. And they are independent on path connecting between the states. Now that change in the entropy if the state points are very near, so that they are infinitesimally near then we can $S_f - S_i$ we can write it as a dS. So, basically we are representing this entropy change in a very infinitesimally small process that is $dS = \frac{đQ_R}{T}$.

Here I have denoted R because this Q_R is nothing but it is a reversible heat transfer. And in fact, and it is a consequence that this T has to be represented in terms of absolute temperatures and this is again the corollary of the Carnot theorem. So, one thing we can see is that when you talk about $\text{đ}Q_R = TdS$. So, this is another important significance which has close relevance with respect to work transfers.

So, when you say reversible work transfer we write it as a pdV. When you say reversible heat transfer you write it as a TdS. So, these two things makes us our understanding simple to talk about heat and work transfer in a particular process.

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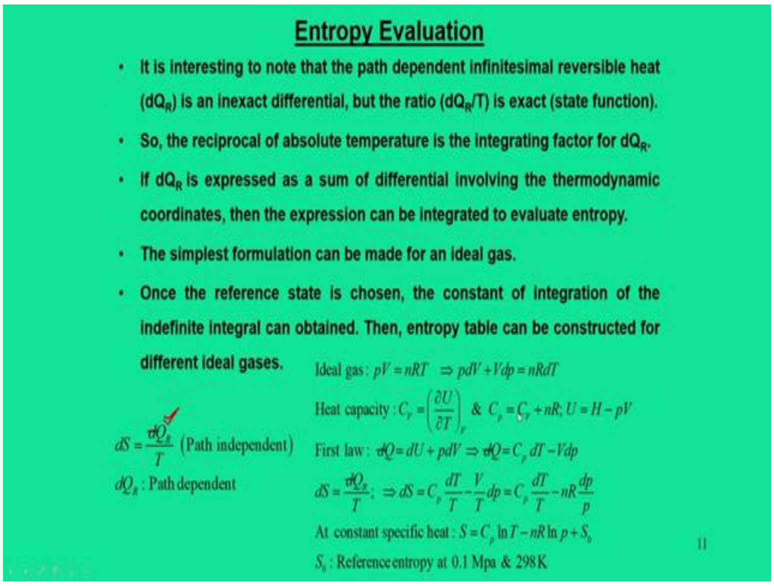

Entropy Evaluation

- It is interesting to note that the path dependent infinitesimal reversible heat (dQ_R) is an inexact differential, but the ratio (dQ_R/T) is exact (state function).
- So, the reciprocal of absolute temperature is the integrating factor for dQ_R.
- If dQ_R is expressed as a sum of differential involving the thermodynamic coordinates, then the expression can be integrated to evaluate entropy.
- The simplest formulation can be made for an ideal gas.
- Once the reference state is chosen, the constant of integration of the indefinite integral can obtained. Then, entropy table can be constructed for different ideal gases.

$dS = \frac{\text{đ}Q_R}{T}$ (Path independent)

$\text{đ}Q_R$: Path dependent

Ideal gas : $pV = nRT \Rightarrow pdV + Vdp = nRdT$

Heat capacity : $C_v = \left(\frac{\partial U}{\partial T}\right)_v$ & $C_p = C_v + nR; U = H - pV$

First law : $\text{đ}Q = dU + pdV \Rightarrow \text{đ}Q = C_p dT - Vdp$

$dS = \frac{\text{đ}Q_R}{T}; \Rightarrow dS = C_p \frac{dT}{T} - \frac{V}{T} dp = C_p \frac{dT}{T} - nR \frac{dp}{p}$

At constant specific heat : $S = C_p \ln T - nR \ln p + S_0$

S_0 : Reference entropy at 0.1 Mpa & 298 K

So, I mentioned earlier that we talk about entropy, but next question is that how you are going to evaluate the entropy and we already mentioned that the entropy is a state functions and it is independent of the path. And one thing you can say that if you recall this particular equation $dS = \frac{\text{đ}Q_R}{T}$, here this $\text{đ}Q_R$ is a in exact differential.

So, this is an in exact differential. Whereas, that in exact differential when divided by absolute temperature, it gives an exact differential. So, this is a one of the mathematical consequence that how it happens and that is the reason that one case $\text{đ}Q_R$ is a path dependent, but whereas, dS is a path independent.

So, with this logic, so instead of looking at Q_R alone we can also talk about the property entropy for a any thermodynamic systems. Likewise for any systems we evaluate the thermodynamic properties based on states, in a similar way we have to explore that how we can find the property that is entropy for any thermodynamic processes. So, one simplest formulation that can be made is for ideal gas.

So, for an ideal gas we can write the basic equations $pV = nRT$, where n stands for number of moles and these equations can be rewritten in a differential part $pdV + Vdp = nRdT$. Then from our previous understandings we can recall this definition that is heat capacity, specific heat at constant volume $C_V = \left(\frac{\partial U}{\partial T}\right)_V$. We also know that $C_p = C_V + nR$. Then we also know $U = H - pV$.

So, these equations can be used in the first law to evaluate the property entropy. How? So, first thing is that we can replace this dQ in terms of dS and then we can replace dU in terms of dH then pdV will get cancelled. So, ultimately we get an expression $dS = C_p \frac{dT}{T} - \frac{V}{T} dp$. Or in other words that is also in terms of pressure we can write in terms of $C_p \frac{dT}{T} - nR \frac{dp}{p}$.

So, this particular equation can be integrated to find the absolute entropy and since it is any arbitrary integral, so, there is a term S_0 and that term S_0 in terms of integration we call this as a constant. In our thermodynamic view point we call this as a reference entropy.

So, for any kind of systems when you always evaluate the change, we have to see this change or reference value with respect to a with respect to certain pressure and temperatures. And in our case it is the atmospheric conditions that is close to 0.1 MPa and 298 K; entropy of any gas is calculated.

So, $S - S_0 = C_p \ln T - nR \ln p$. Now, when you look at this change of entropy and this change of entropy between one particular state to another state; obviously, this S_0 is going to be eliminated.

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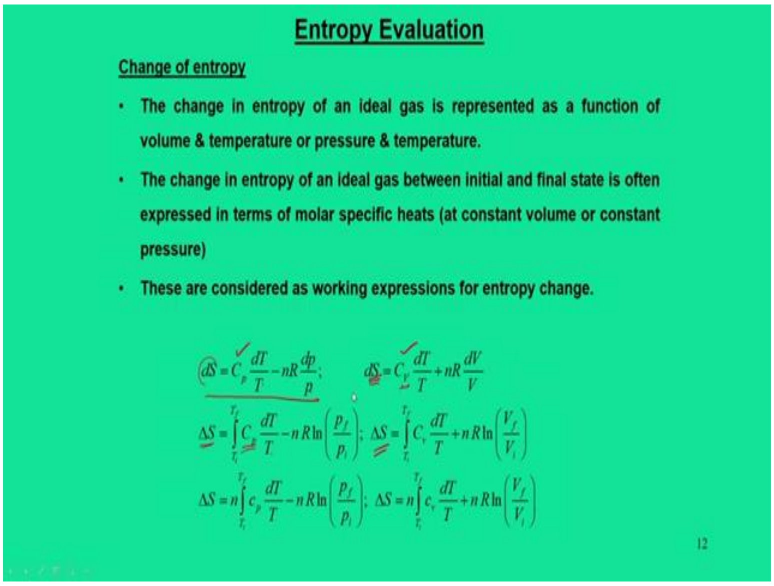

Entropy Evaluation

Change of entropy

- The change in entropy of an ideal gas is represented as a function of volume & temperature or pressure & temperature.
- The change in entropy of an ideal gas between initial and final state is often expressed in terms of molar specific heats (at constant volume or constant pressure)
- These are considered as working expressions for entropy change.

$$dS = C_p \frac{dT}{T} - nR\frac{dp}{p}; \qquad dS = C_v \frac{dT}{T} + nR\frac{dV}{V}$$

$$\Delta S = \int_{T_i}^{T_f} C_p \frac{dT}{T} - nR\ln\left(\frac{p_f}{p_i}\right); \quad \Delta S = \int_{T_i}^{T_f} C_v \frac{dT}{T} + nR\ln\left(\frac{V_f}{V_i}\right)$$

$$\Delta S = n\int_{T_i}^{T_f} c_p \frac{dT}{T} - nR\ln\left(\frac{p_f}{p_i}\right); \quad \Delta S = n\int_{T_i}^{T_f} c_v \frac{dT}{T} + nR\ln\left(\frac{V_f}{V_i}\right)$$

Now, let us see how we can talk about this entropy evaluation or change of entropy in another workable expressions. So, let us recall that the entropy change can be represented in two expressions; one is in terms of C_p other in term is in terms of C_V. $dS = C_p \frac{dT}{T} - nR\frac{dp}{p}$.

And if you remove this change with respect to finite change that is $\Delta S = \int_{T_i}^{T_f} C_p \frac{dT}{T} - nR\ln\left(\frac{p_f}{p_i}\right)$, so, you can integrate this equations from T_i to T_f and of course, from p_i to p_f and of course, here if the Cp is not a function of temperature, then it this has to be within the integral, if not then we can take out these integrals.

Similarly, another way of representing this entropy change in terms of C_V. So, here it is $\Delta S = \int_{T_i}^{T_f} C_v \frac{dT}{T} + nR\ln\left(\frac{V_f}{V_i}\right)$. So, in a similar way dS can be replaced with ΔS. So, these two expressions gives us the workable model or workable expressions to calculate the entropy change. So, by workable model I mean we know the thermodynamic coordinates and in our case either it is a pressure-temperature or it is a temperature-volume.

So, in both the way if you know any two parameters then we can also find out the entropy change.

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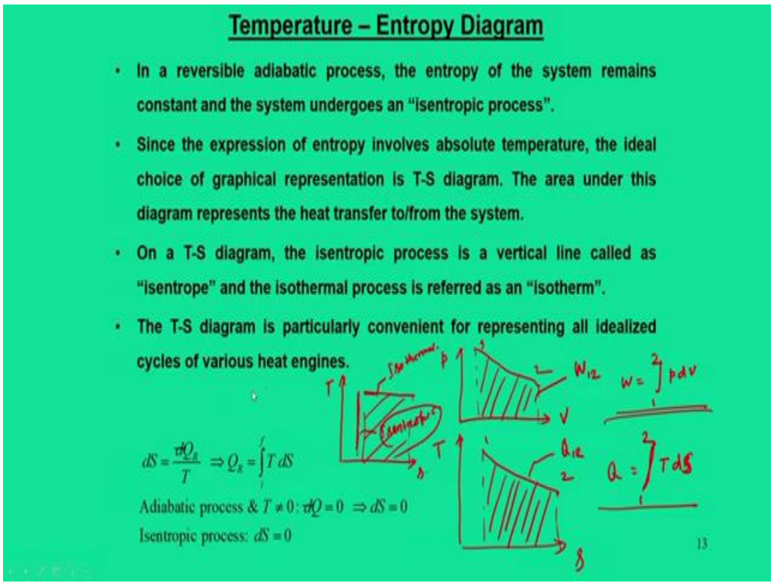

Temperature – Entropy Diagram

- In a reversible adiabatic process, the entropy of the system remains constant and the system undergoes an "isentropic process".
- Since the expression of entropy involves absolute temperature, the ideal choice of graphical representation is T-S diagram. The area under this diagram represents the heat transfer to/from the system.
- On a T-S diagram, the isentropic process is a vertical line called as "isentrope" and the isothermal process is referred as an "isotherm".
- The T-S diagram is particularly convenient for representing all idealized cycles of various heat engines.

$dS = \frac{đQ_R}{T} \Rightarrow Q_R = \int_i^f T\,dS$

Adiabatic process & $T \neq 0$: $đQ = 0 \Rightarrow dS = 0$

Isentropic process: $dS = 0$

$W = \int_1^2 p\,dV$

$Q = \int_1^2 T\,dS$

Then after this entropy evaluation we are now going to talk about something on temperature-entropy diagrams. So, I mentioned that when you talk about work transfer in a pV diagram. So, any process goes from 1 to 2 and we say if you drop normal, so, we can say area under this curve is nothing but work transfer. In the same logic we are going to say because $W = \int_1^2 pdV$.

In the same logic we can represent the temperature diagram and for same process 1 to 2 and our expression shows that this $Q_R = \int_i^f TdS$, so, it means that area under the temperature entropy diagram represent the heat transfer, area under pV diagram which represents the work transfer.

Now, here we are going to introduce some terms like if you have this temperature-entropy diagrams we may have a situations where for an isentropic process in a vertical line, other may be an isothermal process in a horizontal line. So, such a process and if you talk about this, this is nothing but your isentropic. As you can clearly see there is no area. So, it means that in isentropic process Q is equal to 0 and when you go for isothermal process this diagram will be a rectangle.

So, it is a isothermal process and the area under the diagram will be a rectangle. So, to summarize this, what you can say? Area under the diagram represent the heat transfer to or from the systems. In a $T - S$ diagram, an isentropic process is nothing but a vertical line and we call this as isentrope and this isothermal process is referred as a isotherm. And why it is important? Because it is particularly convenient for representing all idealized cycles of heat engines.

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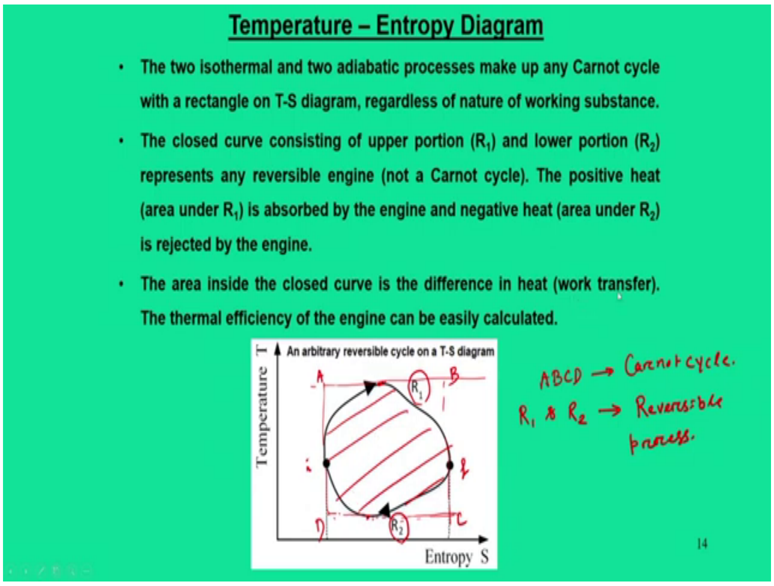

Temperature – Entropy Diagram

- The two isothermal and two adiabatic processes make up any Carnot cycle with a rectangle on T-S diagram, regardless of nature of working substance.
- The closed curve consisting of upper portion (R_1) and lower portion (R_2) represents any reversible engine (not a Carnot cycle). The positive heat (area under R_1) is absorbed by the engine and negative heat (area under R_2) is rejected by the engine.
- The area inside the closed curve is the difference in heat (work transfer). The thermal efficiency of the engine can be easily calculated.

ABCD → Carnot cycle.
R_1 & R_2 → Reversible process.

Now, moving further there are some other viewpoints like how this temperature-entropy diagram is again linked with the Carnot cycles. So, for example, if you have some initial state i to f and you are going this in a one of the reversible path R_1 and another reversible path R_2, there may be infinite number of reversible path possibilities, and as you can say the net heat transfer during this process will be the area under the closed curve. Now, one of the important thing is that we can talk about Carnot cycle like talking about the two upper limits and we can draw a rectangle. So, the upper limit of temperature is this. So, I can say AB line we can draw a isotherm. Another line which is DC which is the lowest point on this curve, so, I can talk about another line. So, ABCD is nothing but a Carnot cycle consisting of two reversible isothermal processes and two reversible adiabatic process.

However, we have this R_1 and R_2 they are nothing but the reversible path or reversible processes. So, once you know the heat transfer from this $T - S$ diagram we can easily calculate the work transfers. Then thermal efficiency for the engine can be evaluated.

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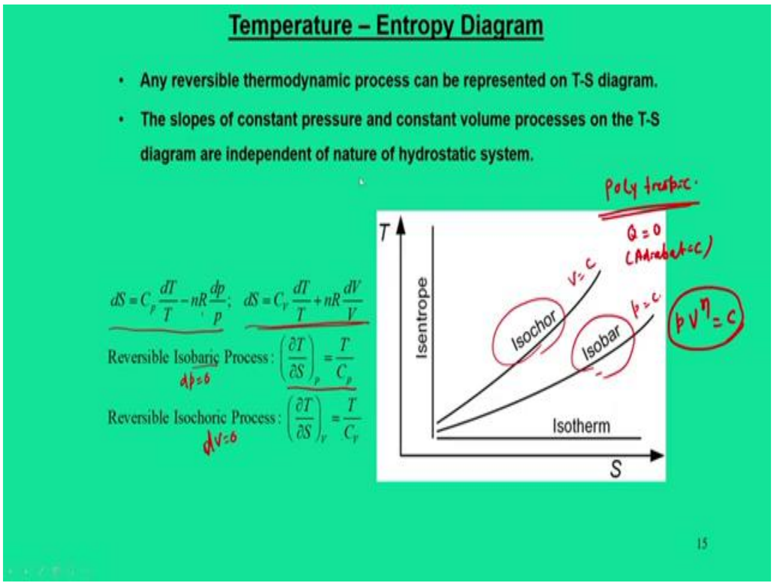

Temperature – Entropy Diagram

- Any reversible thermodynamic process can be represented on T-S diagram.
- The slopes of constant pressure and constant volume processes on the T-S diagram are independent of nature of hydrostatic system.

$dS = C_p \frac{dT}{T} - nR\frac{dp}{p}$; $dS = C_V \frac{dT}{T} + nR\frac{dV}{V}$

Reversible Isobaric Process: $\left(\frac{\partial T}{\partial S}\right)_p = \frac{T}{C_p}$

$dp=0$

Reversible Isochoric Process: $\left(\frac{\partial T}{\partial S}\right)_V = \frac{T}{C_V}$

$dV=0$

Again moving further some important significance for entropy diagram we can draw. So, I have already demonstrated what is an isentrope constant entropy line in a T-S diagram, what is an isotherm which is a constant temperature line in a T-S diagram and there are other processes like we can have a isochoric process. So, your volume is equal to constant. So, this curves goes in this manner. There are isobaric where curves are remains constant.

We can also talk about an adiabatic process where $Q = 0$. We can also talk about polytropic process. All these processes can be talked about by giving the definition $pV^n = C$.

So, this part I have already mentioned based on the exponent n, this path can be specified. But one more important thing is that if you recall our expressions of entropy in terms of C_P and in terms of C_V specifically for isochoric process and isobaric process, one important consequence it gives that for an isobaric process we say $dp = 0$. So, this particular expression now becomes $\left(\frac{\partial T}{\partial S}\right)_p = \frac{T}{C_p}$.

And similarly, for an isochoric process when $dV = 0$, so, $\left(\frac{\partial T}{\partial S}\right)_V = \frac{T}{C_V}$. So, what it says is that $\frac{\partial T}{\partial S}$ is nothing but the slope of this diagram. So, if it is a constant pressure process or whether it is a constant volume process.

So, the slope of the constant pressure and constant volume process on a T-S diagram is independent on the nature of the systems. So, here you can say T is your absolute temperature, C_V is your property, the specific heat capacity of the medium. So, these are independent on any other nature of the hydrostatic systems.

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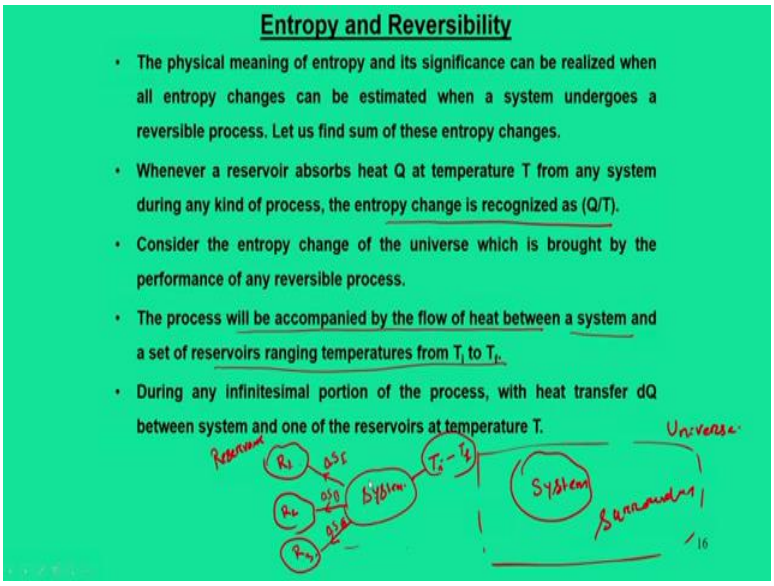

Entropy and Reversibility

- The physical meaning of entropy and its significance can be realized when all entropy changes can be estimated when a system undergoes a reversible process. Let us find sum of these entropy changes.
- Whenever a reservoir absorbs heat Q at temperature T from any system during any kind of process, the entropy change is recognized as (Q/T).
- Consider the entropy change of the universe which is brought by the performance of any reversible process.
- The process will be accompanied by the flow of heat between a system and a set of reservoirs ranging temperatures from T_i to T_f.
- During any infinitesimal portion of the process, with heat transfer dQ between system and one of the reservoirs at temperature T.

Now, let us talk some something on entropy which has relation with respect to irreversibility. So, we have mentioned here that there may be infinite number of reversible processes that we can view and in each process we can calculate the entropy change.

What important significance is that we are talking about entropy of two things; one is entropy change for the systems and entropy change of the surroundings. And change of entropy of system and surrounding will give us the change in the entropy of for the universe.

So, this is exactly what we are going to find out that what is the meaning of the sum of these entropy changes or in other words we are going to say that physical meaning of entropy and significance of all entropy changes can be estimated. So, for example, if you consider a reservoir that absorbs Q amount of heat at temperature T from many systems, so, we can say that entropy change is recognized as $\frac{Q}{T}$. We can also say that what happens to entropy change of the universe.

So, if you have a system and we have the surroundings, so, both constitutes this universe. So, what we are looking at that for example, we are considering a process which is accompanied by flow of heat between a system and a set of reservoirs consisting from T_i to T_f. So, we can say that as if we have a system and there are some reservoirs R_1, R_2, R_3 and so on and all the reservoirs are within the surroundings.

So, what we do is that system undergoes a change of state from T_i to T_f. Now, the final stage happens in a multiple number of steps; that means, first the system interacts with reservoir 1, next it interacts with reservoir 2 and next it interacts with reservoir 3 and in this process it has $\Delta S_1,\ \Delta S_2,\ \Delta S_3$. So, all these things are entropy change when the system is undergoes reservoir 1, 2, 3 and there may be many number of reservoirs like this. And through the process what change has happened?

The system undergoes from T_i to T_f, through this process there are also change in the entropy for reservoir 1, 2, 3. So, summing of all these things will talk about the total change in the entropy of the inverse. So, we will now calculate how we are going to evaluate it.

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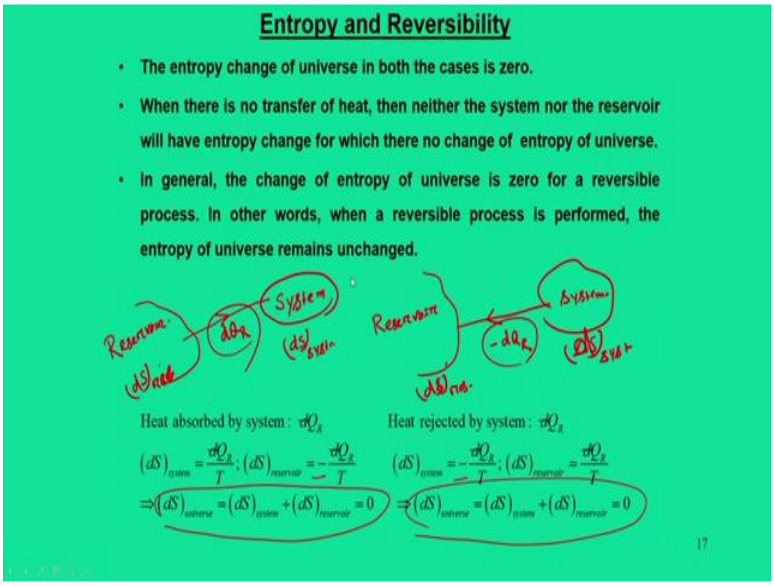

Entropy and Reversibility

- The entropy change of universe in both the cases is zero.
- When there is no transfer of heat, then neither the system nor the reservoir will have entropy change for which there no change of entropy of universe.
- In general, the change of entropy of universe is zero for a reversible process. In other words, when a reversible process is performed, the entropy of universe remains unchanged.

Heat absorbed by system : $đQ_R$

$(dS)_{system} = \frac{đQ_R}{T};\ (dS)_{reservoir} = -\frac{đQ_R}{T}$

$\Rightarrow \boxed{(dS)_{universe} = (dS)_{system} + (dS)_{reservoir} = 0}$

Heat rejected by system : $đQ_R$

$(dS)_{system} = -\frac{đQ_R}{T};\ (dS)_{reservoir} = \frac{đQ_R}{T}$

$\Rightarrow \boxed{(dS)_{universe} = (dS)_{system} + (dS)_{reservoir} = 0}$

So, for that we are talking about two situations like in one case system and there is a reservoir. So, we will consider only one reservoir in this case. So, here heat is absorbed by the system; that means I am taking heat from the reservoir. So, heat is absorbed by this system. So, you say dQ_R.

In another situations we can have a reservoir and we have system. So, here heat is rejected from the systems. So, we say it is a $-dQ_R$. So, from this what we can say? This is nothing but $(ds)_{system}$ and this is nothing but $(ds)_{reservoir}$.

So, one case it is negative. So, in this case when heat is rejected by the system is negative, when heat is enters into the system it is positive. So, based on that one can have appropriately use the positive and negative signs and finally, we can calculate entropy change of the universe in both the cases and it happens to be 0 because all are reversible path and it entropy change of the universe is 0.

So, in a reversible process the change in the entropy is always 0. So, this is the consequence that we can make that when a reversible process is performed the entropy of the universe remains unchanged.

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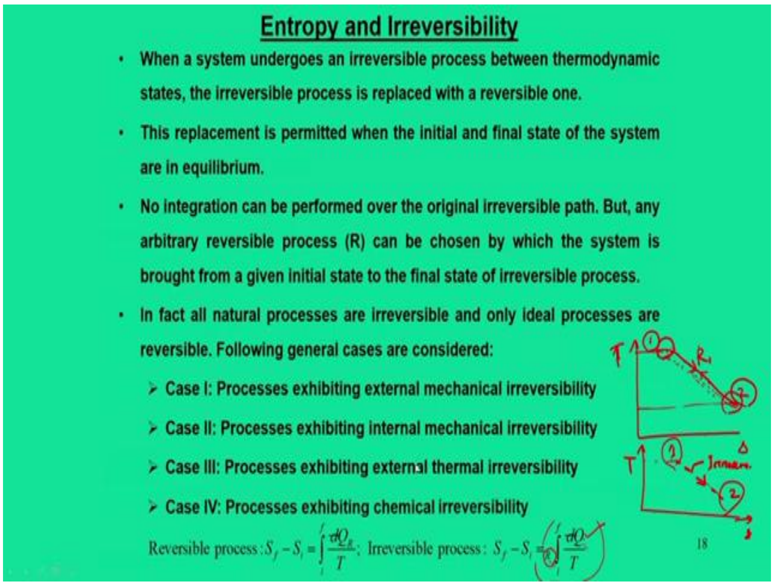

Entropy and Irreversibility

- When a system undergoes an irreversible process between thermodynamic states, the irreversible process is replaced with a reversible one.
- This replacement is permitted when the initial and final state of the system are in equilibrium.
- No integration can be performed over the original irreversible path. But, any arbitrary reversible process (R) can be chosen by which the system is brought from a given initial state to the final state of irreversible process.
- In fact all natural processes are irreversible and only ideal processes are reversible. Following general cases are considered:
  - Case I: Processes exhibiting external mechanical irreversibility
  - Case II: Processes exhibiting internal mechanical irreversibility
  - Case III: Processes exhibiting external thermal irreversibility
  - Case IV: Processes exhibiting chemical irreversibility

Reversible process: $S_f - S_i = \int_i^f \frac{dQ_R}{T}$; Irreversible process: $S_f - S_i \neq \int_i^f \frac{dQ}{T}$

Now, when you say a process undergoes a reversible path, we can say that we can calculate this entropy, but there are situations that always reversible path is not possible. So, we have to rely on all natural processes and they are mostly irreversible. So, what we can view this particular analysis is that, in order to analyze a irreversible path or in order to introduce a concept of irreversibility what has been done is that first you write the expressions for entropy change that is $S_f - S_i = \int_i^f \frac{dQ_R}{T}$ that is nothing but your reversible heat transfer. Now, same expressions can be used for irreversible path with some change like. So, when

I say a process goes from a reversible process. So, 1 to 2. Now, if same process if I want to have it maintaining initial state and final state same, let us say it is reversible path R_1. So, in a reversible path initial state and final state are always in equilibrium, at the same time all intermediate states are also in thermodynamic equilibrium.

But what happens? If it is an irreversible path, we can only assume that initial state and final state are in equilibrium. So, this continuous curve we normally represented in a dotted line. So, that we can say that in a process 1 to 2 we can take either from 1 to 2 and also from 2 to 1 we can travel. So, in both way the process can occur, but whereas, in a irreversible path the process can occur only in one direction.

So, if same states I represent 1 and 2, I normally represent in a dotted line and this is nothing but your irreversible path. So, it means that process can occur only from 1 to 2 not from 2 to 1. So, this is the basic difference, but in terms of end results what we are assuming as if this initial states and final states are in equilibrium and what we do is here we can calculate the heat transfer from 1 to 2.

So, we can write it as a dQ, but this is not a reversibility transfers, but the path is as if we are calculating this for a reversible process. So, R we are putting it here as if this value is calculated for an reversible process. So, already we proved that entropy change for the universe is 0 for all the reversible process. Now, we are going to calculate what happens for irreversible processes.

Now these irreversible processes are nothing but your natural processes and they can be categorized in four segments. 1: Processes exhibiting external mechanical irreversibility. Case 2: Processes that exhibit internal mechanical irreversibility that means external means outside of the system or surrounding gets affected.

Processes that exhibit internal mechanical irreversibility; that means only internal structure of the system or internal change of the system happens. Processes that exhibit external thermal irreversibility. So, this is a thermal that means, outside only thermal change has happened and last one is processes that exhibit chemical irreversibility. So, all these processes we are now going to discuss.

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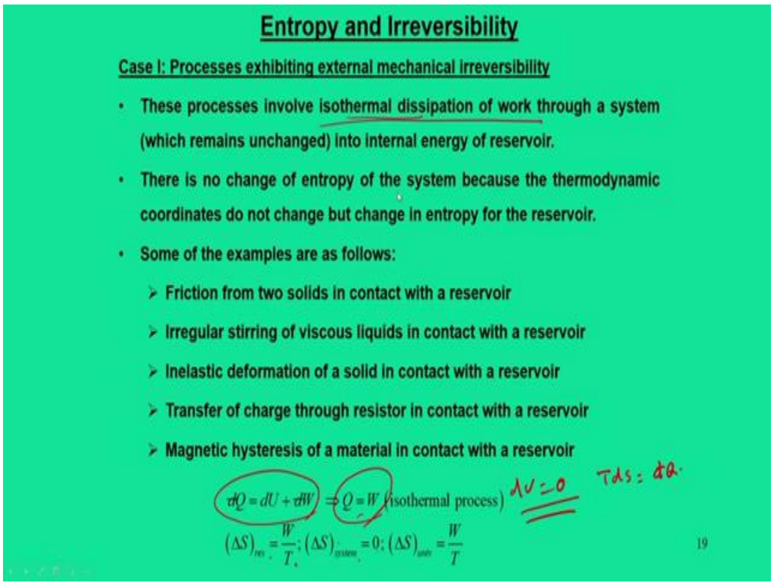

Entropy and Irreversibility

Case I: Processes exhibiting external mechanical irreversibility

- These processes involve isothermal dissipation of work through a system (which remains unchanged) into internal energy of reservoir.
- There is no change of entropy of the system because the thermodynamic coordinates do not change but change in entropy for the reservoir.
- Some of the examples are as follows:
  - Friction from two solids in contact with a reservoir
  - Irregular stirring of viscous liquids in contact with a reservoir
  - Inelastic deformation of a solid in contact with a reservoir
  - Transfer of charge through resistor in contact with a reservoir
  - Magnetic hysteresis of a material in contact with a reservoir

$\text{đ}Q = dU + \text{đ}W \Rightarrow Q = W$ (isothermal process) $dU = 0$ $Tds = \text{đ}Q$

$(\Delta S)_{res} = \frac{W}{T}; (\Delta S)_{system} = 0; (\Delta S)_{univ} = \frac{W}{T}$

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So, first one is processes that exhibit external mechanical irreversibility. So, there are there are two categories of the process. One is isothermal dissipation of work a through a system in which the work which remains unchanged that changes into internal change of the reservoir. So, here there is no change in the entropy of the systems, because the thermodynamic coordinates do not change, but change of entropy for the reservoir.

So, if you look at this first law, you start with a first law, $\text{đ}Q = dU + \text{đ}W$ and we say it is a isothermal process. So, $Q = W$ because $dU = 0$ and when $Q = 0$ we can write $dQ = Tds$.

So, we can write $(\Delta S)_{res} = \frac{W}{T}$ and $(\Delta S)_{system} = 0$ because there is no change in the internal change of the system because thermodynamic coordinates do not change. So, that $(\Delta S)_{univ} = \frac{W}{T}$.

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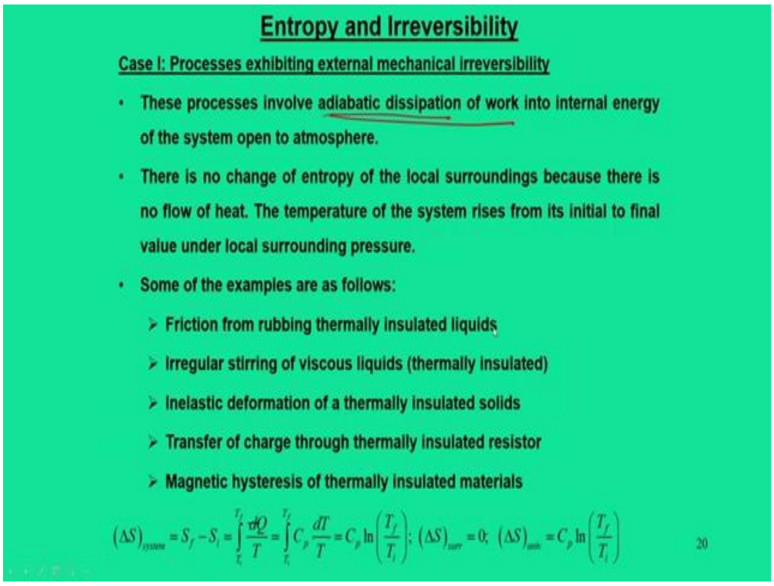

Entropy and Irreversibility

Case I: Processes exhibiting external mechanical irreversibility

- These processes involve adiabatic dissipation of work into internal energy of the system open to atmosphere.
- There is no change of entropy of the local surroundings because there is no flow of heat. The temperature of the system rises from its initial to final value under local surrounding pressure.
- Some of the examples are as follows:
  - Friction from rubbing thermally insulated liquids
  - Irregular stirring of viscous liquids (thermally insulated)
  - Inelastic deformation of a thermally insulated solids
  - Transfer of charge through thermally insulated resistor
  - Magnetic hysteresis of thermally insulated materials

$$(\Delta S)_{system} = S_f - S_i = \int_{T_i}^{T_f} \frac{\bar{d}Q}{T} = \int_{T_i}^{T_f} C_p \frac{dT}{T} = C_p \ln\left(\frac{T_f}{T_i}\right);\ (\Delta S)_{surr} = 0;\ (\Delta S)_{univ} = C_p \ln\left(\frac{T_f}{T_i}\right)$$

In another case same change of state happens, and we call this as external mechanical irreversibility, but the process involves adiabatic dissipation of work. So, the same equation can be used, but with a viewpoint that we can calculate because the system undergoes an adiabatic change from final states to initial states.

So, we can calculate this $(\Delta S)_{system} = C_p \ln\left(\frac{T_f}{T_i}\right)$. And the $(\Delta S)_{surr} = 0$ because since the process is adiabatic, there is no flow of heat to the surroundings. So, from this we can calculate $(\Delta S)_{univ} = C_p \ln\left(\frac{T_f}{T_i}\right)$.

So, typical examples that involved the friction from the rubbing of insulated liquids, inelastic deformations, irregular stirring of viscous liquids there are multiple examples in this category.

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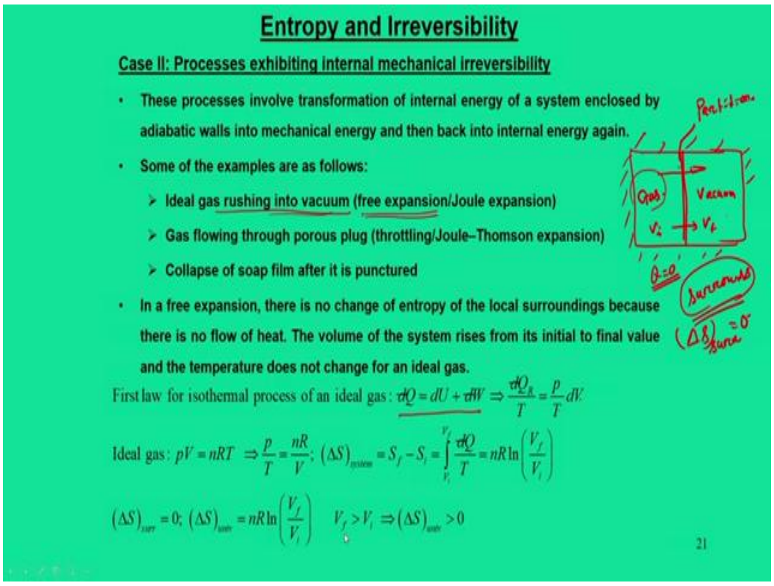

Entropy and Irreversibility

Case II: Processes exhibiting internal mechanical irreversibility

- These processes involve transformation of internal energy of a system enclosed by adiabatic walls into mechanical energy and then back into internal energy again.
- Some of the examples are as follows:
  - Ideal gas rushing into vacuum (free expansion/Joule expansion)
  - Gas flowing through porous plug (throttling/Joule–Thomson expansion)
  - Collapse of soap film after it is punctured
- In a free expansion, there is no change of entropy of the local surroundings because there is no flow of heat. The volume of the system rises from its initial to final value and the temperature does not change for an ideal gas.

First law for isothermal process of an ideal gas: $\underline{đQ = dU + đW} \Rightarrow \frac{đQ_R}{T} = \frac{p}{T}dV$

Ideal gas: $pV = nRT \Rightarrow \frac{p}{T} = \frac{nR}{V}$; $(\Delta S)_{system} = S_f - S_i = \int_{V_i}^{V_f} \frac{đQ}{T} = nR\ln\left(\frac{V_f}{V_i}\right)$

$(\Delta S)_{surr} = 0$; $(\Delta S)_{univ} = nR\ln\left(\frac{V_f}{V_i}\right)$ $\quad V_f > V_i \Rightarrow (\Delta S)_{univ} > 0$

In another case that involved the transformation of internal energy of the systems in adiabatic wall into mechanical energy and then back to the internal energy again. So, this is another example where the processes that occur exhibit internal mechanical irreversibility. Other case was the external mechanical irreversibility and this case was internal mechanical irreversibility.

So, they are characterized by the fact that the transformation of internal energy of the system is done which are enclosed by closed adiabatic wall. What it means is that, now, let us talk about one particular example. Ideal gas rushing to the vacuum and such a process we call this as a free expansion. What we have is that we can have an adiabatic enclosure one side and there are there is a partition and one side we have vacuum and we have other side we have some gas.

So, what happens here that, when partition is removed the gas suddenly rushes into the vacuum. So, what happens here? The volume of the gas changes from initial volume V_i to final volume V_f, but in this process what happens to the surroundings; since it is an adiabatic enclosure. So, there is no change in the entropy for universe because Q = 0.

And because of this reason what happens? We can revisit our basic equations $đQ = dU + đW$ and $\frac{đQ_R}{T} = \frac{p}{T}dV$ because dU is also 0 here. Now, from these equations we can use this ideal gas equations and to frame out the entropy change of the systems, then we have entropy change of the surrounding is 0 and finally, we can calculate summing it of entropy change of the system and surroundings.

$$\text{Idealgas}: pV = nRT \Rightarrow \frac{p}{T} = \frac{nR}{V}; (\Delta S)_{system} = S_f - S_i = \int_{V_i}^{V_f} \frac{đQ}{T}$$

$$= nR\ln\left(\frac{V_f}{V_i}\right);\ \ (\Delta S)_{surr} = 0; (\Delta S)_{univ} = nR\ln\left(\frac{V_f}{V_i}\right)$$

So, from this equation we can say that $V_f > V_i$. So, $(\Delta S)_{univ} > 0$.

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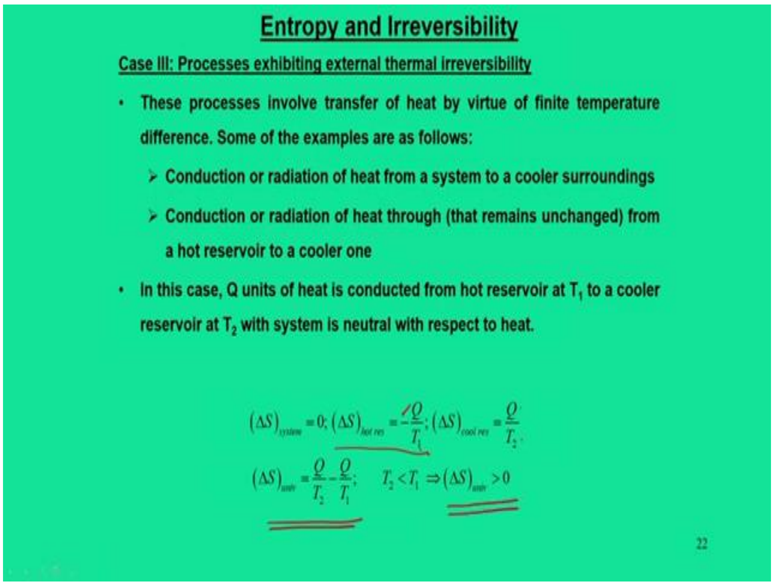

Entropy and Irreversibility

Case III: Processes exhibiting external thermal irreversibility

- These processes involve transfer of heat by virtue of finite temperature difference. Some of the examples are as follows:
  - ➢ Conduction or radiation of heat from a system to a cooler surroundings
  - ➢ Conduction or radiation of heat through (that remains unchanged) from a hot reservoir to a cooler one
- In this case, Q units of heat is conducted from hot reservoir at T_1 to a cooler reservoir at T_2 with system is neutral with respect to heat.

$$(\Delta S)_{system} = 0; \underline{(\Delta S)_{hot\ res} = -\frac{Q}{T_1}}; (\Delta S)_{cool\ res} = \frac{Q}{T_2};$$

$$\underline{\underline{(\Delta S)_{univ} = \frac{Q}{T_2} - \frac{Q}{T_1}}}; \quad T_2 < T_1 \Rightarrow \underline{\underline{(\Delta S)_{univ} > 0}}$$

The third case, which is nothing but the processes that exhibit external thermal irreversibility. So, these processes involve the transfer of heat by virtue of finite temperature difference. So, typical example is that conduction or radiation of heat from the system to a cooler surroundings or conduction or radiation of heat that remain from a hot reservoir to a cooler one.

So, in this case what happens? If you take a particular examples, we have some Q units of heat which is conducted from hot reservoir at T_1 to a cooler reservoir at T_2. So, from this case for hot reservoirs, the heat transfer takes place as heat rejection. So, it is $-\frac{Q}{T_1}$ because hot reservoir is at temperature T_1.

And similarly for cold reservoir we can write heat is absorbing; so, it is $\frac{Q}{T_2}$ and from this we can find out the entropy change of the universe. So, here obviously, we can say it is $(\Delta S)_{univ} = \frac{Q}{T_2} - \frac{Q}{T_1}$. Since $T_2 < T_1 \Rightarrow (\Delta S)_{univ} > 0$.

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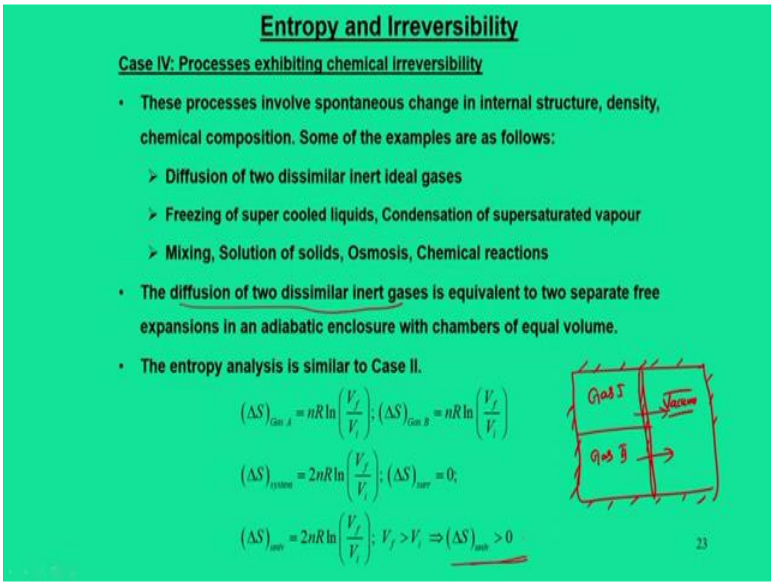

Entropy and Irreversibility

Case IV: Processes exhibiting chemical irreversibility

- These processes involve spontaneous change in internal structure, density, chemical composition. Some of the examples are as follows:
  - Diffusion of two dissimilar inert ideal gases
  - Freezing of super cooled liquids, Condensation of supersaturated vapour
  - Mixing, Solution of solids, Osmosis, Chemical reactions
- The diffusion of two dissimilar inert gases is equivalent to two separate free expansions in an adiabatic enclosure with chambers of equal volume.
- The entropy analysis is similar to Case II.

$$(\Delta S)_{Gas\ A} = nR\ln\left(\frac{V_f}{V_i}\right);\ (\Delta S)_{Gas\ B} = nR\ln\left(\frac{V_f}{V_i}\right)$$

$$(\Delta S)_{system} = 2nR\ln\left(\frac{V_f}{V_i}\right);\ (\Delta S)_{surr} = 0;$$

$$(\Delta S)_{univ} = 2nR\ln\left(\frac{V_f}{V_i}\right);\ V_f > V_i \Rightarrow \underline{(\Delta S)_{univ} > 0}$$

And last one is a processes which exhibit chemical irreversibility. So, what happens? Now you are moving into entropy change in a chemical process that could be a diffusion process that could be a freezing or condensation process that could be a mixing or solutions or osmosis process or any chemical reactions.

And one typical example we can say that diffusion of two dissimilar metals. So, this is just a situation for the entropy analysis for case 2 where we said that there is a gas. Now, here I can put it as a gas I gas II; there are many gases like this and there is a partition here and it is adiabatically closed; that means there is no heat transfer.

And this side is also vacuum and some chemical reactions has happened because of it pressure has changed and all these gases rushes into this. So, that particular things case 1, which can be visualize as if it is a multiple number of expansions and that expansion happens in an adiabatic enclosure with chambers of equal volume.

So, likewise we can find out for gas A what happens to entropy change, for gas B what happens to the entropy change. So, this is the for total change of the systems, then total change of the surrounding is 0 because there is no Q or Q = 0. Then we can find out the entropy change of the universe and here also entropy change of the universe it has been found there it is always greater than 0.

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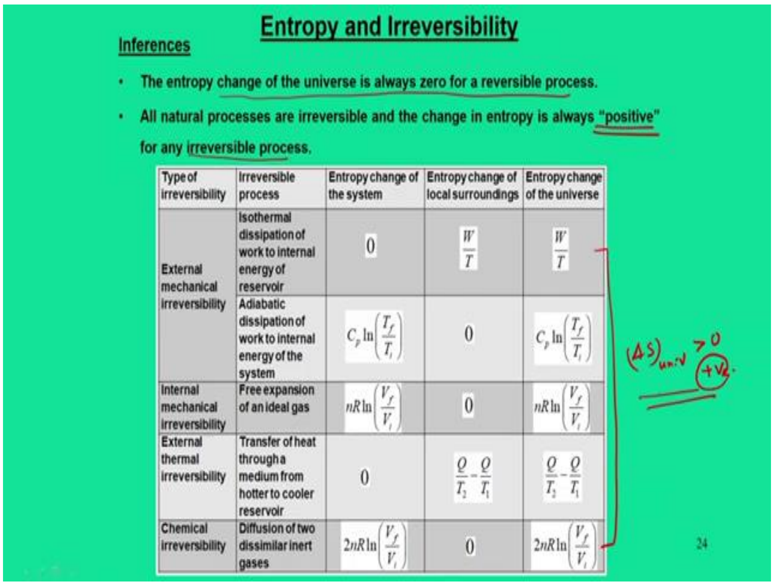

Entropy and Irreversibility

Inferences

- 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	$2nR\ln\left(\frac{V_f}{V_i}\right)$

$(\Delta S)_{univ} > 0$ $\boxed{+ve}$.

Now, what we have discussed so far? If you can summarize that there are four particular cases; cases with external mechanical irreversibility, internal mechanical irreversibility, external thermal irreversibility and chemical irreversibility. And for all these cases we have summarized what happens to the entropy change of the systems, entropy change of the surroundings and summation of these two will give you the entropy change of the universe.

So, for all the cases one important consequence is that $(\Delta S)_{univ} > 0$ or it is always positive. So, this is the first consequence that when you calculate entropy for an irreversible process and for universe it is always a positive quantity and but when you talk about entropy change of the universe for a reversible process, it is always 0.

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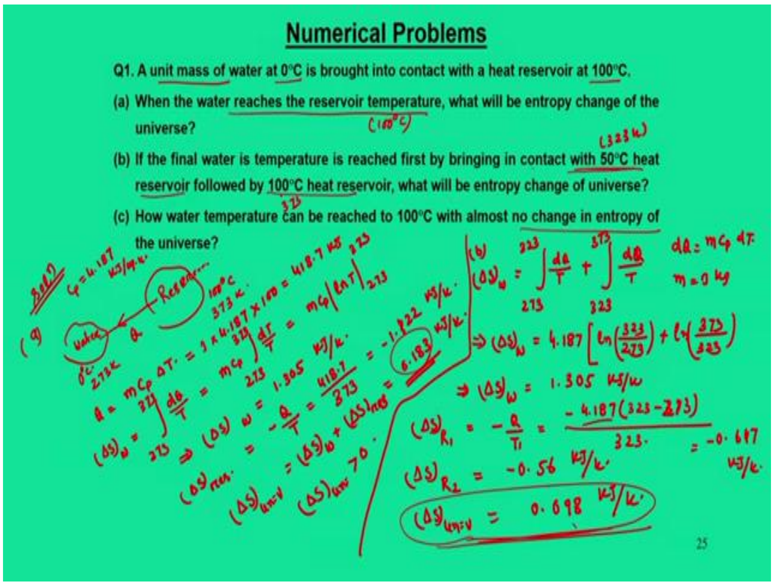

Numerical Problems

Q1. A unit mass of water at 0°C is brought into contact with a heat reservoir at 100°C.

(a) When the water reaches the reservoir temperature, what will be entropy change of the universe? (100°C)

(b) If the final water is temperature is reached first by bringing in contact with 50°C (323 K) heat reservoir followed by 100°C heat reservoir, what will be entropy change of universe?

(c) How water temperature can be reached to 100°C with almost no change in entropy of the universe?

Sol^n (a) $C_p = 4.187\ kJ/kg\text{-}K$

water 0°C 273 K ← Q ← Reservoir 100°C 373 K

$Q = mC_p\Delta T = 1 \times 4.187 \times 100 = 418.7\ kJ$

$(\Delta S)_w = \int_{273}^{373} \frac{dQ}{T} = mC_p \int_{273}^{373} \frac{dT}{T} = mC_p |\ln T|_{273}^{373}$

$\Rightarrow (\Delta S)_w = 1.305\ kJ/K$

$(\Delta S)_{res} = -\frac{Q}{T} = -\frac{418.7}{373} = -1.122\ kJ/K$

$(\Delta S)_{univ} = (\Delta S)_w + (\Delta S)_{res} = 0.183\ kJ/K$

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

(b) $(\Delta S)_w = \int_{273}^{323} \frac{dQ}{T} + \int_{323}^{373} \frac{dQ}{T}$ $\quad dQ = mC_p\, dT$, $m = 1\ kg$

$\Rightarrow (\Delta S)_w = 4.187 \left[\ln\left(\frac{323}{273}\right) + \ln\left(\frac{373}{323}\right)\right]$

$\Rightarrow (\Delta S)_w = 1.305\ kJ/K$

$(\Delta S)_{R_1} = -\frac{Q}{T_1} = \frac{-4.187(323-273)}{323} = -0.647\ kJ/K$

$(\Delta S)_{R_2} = -0.56\ kJ/K$

$\boxed{(\Delta S)_{univ} = 0.698\ kJ/K}$

So, now we are end of this particular lecture. So, I will try to solve one simple problems just to give what is our understanding. So, the first problem is about the calculation of entropy change and to visualize the concept of a reversible process, how a process can be reversibly heated. So, one typical example which is given here that there is a unit mass of water which is at 0 C, it is brought to contact with a heat reservoir at 100 C.

So, what we can see here is that we have a set of water or on this case I can say we have a unit mass of water which is available to us at 0 C. And we want to calculate the first case that when the water reaches to the reservoir temperature and this case it is 100 C, what will be the entropy change of the universe. So, basically your system will be water and there is a reservoir. So, water is at 0 C, reservoir is at 100 C.

So, we can say it is 273 K and it is 373 K. Then the water is in contact with reservoir. So obviously, heat will enter from the reservoir to water. So, you can calculate what is the heat absorbed by this. We can say $Q = mc_p\Delta T = 1 \times 4.187 \times 100 = 4187\ kJ$. Now, we have to now find out entropy change. So, first we have to find out what is ΔS_W? $\Delta S_W = \int_{273}^{373} \frac{dQ}{T} = mc_p \int_{273}^{373} \frac{dT}{T} = mc_p |\ln T|_{273}^{373} = 1.305 \frac{kJ}{K}$. Now, $\Delta S_{res} = -\frac{Q}{T} = -\frac{418.7}{373} = -1.122 \frac{kJ}{kg-K}$ because the reservoir lost the heat.

So, finally, we can say what is $\Delta S_{univ} = \Delta S_W + \Delta S_{res} = 0.183 \frac{kJ}{kg-K}$. So, you can see this $\Delta S_{univ} > 0$. So, this is the first part of the problem. Now, we can move to the second part.

So, in the second part what happens? This heating takes place in two stages; first with a 50 C heat reservoir and second with the 100 C of heat reservoir. So, these two stage of heatings will change the entropy of the water. How?

$$\Delta S_W = \int_{273}^{323} \frac{dQ}{T} + \int_{323}^{373} \frac{dQ}{T} = 4.187\left(\ln\left(\frac{323}{273}\right) + \ln\left(\frac{373}{323}\right)\right) = 1.305\,\frac{kJ}{K}$$

$$\Delta S_{res1} = -\frac{Q}{T_1} = -\frac{4.187(323-273)}{323} = -0.687\,\frac{kJ}{K}\,; \Delta S_{res2} = -\frac{Q}{T_2}$$
$$= -\frac{4.187(373-323)}{373} = -0.56\,\frac{kJ}{K}$$

$$\Delta S_{univ} = \Delta S_W + \Delta S_{res1} + \Delta S_{res2} = 0.098\,\frac{kJ}{K}$$

So, what we see is that when we do this heating in step manner that is one with 50 C then to 100 C entropy change of the universe is less; in that case it was 0.183 now it is 0.098.

So, it means if water is reversible heated almost there will not be no change in the entropy. So, the third part of the question says that how the water temperature can be reached to 100 C with almost no change in the entropy of the universe. So, that means, if you make this water to be in contact with reservoir with infinitesimally small change in the temperatures then we can say the water is reversibly heated.

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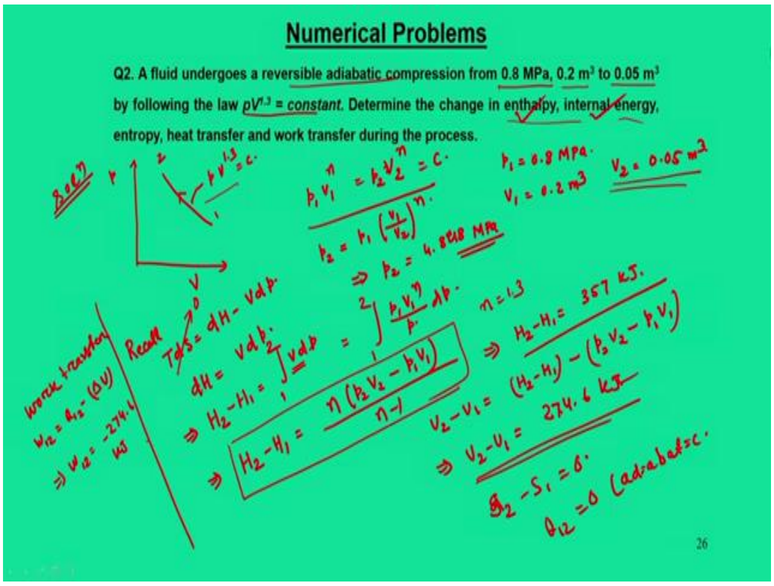

Numerical Problems

Q2. A fluid undergoes a reversible adiabatic compression from 0.8 MPa, 0.2 m³ to 0.05 m³ by following the law *pV¹·³ = constant.* Determine the change in enthalpy, internal energy, entropy, heat transfer and work transfer during the process.

Sol^n

$pV^{1.3} = c$

$p_1 V_1^n = p_2 V_2^n = C$

$p_2 = p_1 \left(\frac{V_1}{V_2}\right)^n$

$\Rightarrow p_2 = 4.8518$ MPa

$p_1 = 0.8$ MPa

$V_1 = 0.2\ m^3$

$V_2 = 0.05\ m^3$

Recall $TdS = dH - Vdp$

$dH = Vdp$

$\Rightarrow H_2 - H_1 = \int_1^2 Vdp = \int_1^2 \frac{p_1 V_1^n}{p} dp$

$\Rightarrow \boxed{H_2 - H_1 = \frac{n(p_2V_2 - p_1V_1)}{n-1}}$

$n = 1.3$

$\Rightarrow H_2 - H_1 = 357$ kJ.

$U_2 - U_1 = (H_2 - H_1) - (p_2V_2 - p_1V_1)$

$\Rightarrow U_2 - U_1 = 274.6$ kJ

$S_2 - S_1 = 0$

$Q_{12} = 0$ (adiabatic)

work transfer

$W_{12} = Q_{12} - (\Delta U)$

$\Rightarrow W_{12} = -274.6$ kJ

Now, the next problem we will talk about some definition of different thermodynamic properties for an adiabatic process. So, the problem statement goes that a fluid undergoes a reversible adiabatic compression that from initial state 0.8 MPa and initial volume 0.03 and final volume 0.05 m^3.

And it follows a laws $pv^{1.3} = C$. To do this what we can draw first is p-v diagram that talks about this path and the process goes from 1 to 2 and it is $pv^{1.3} = C$. So, we can say

$$p_1 v_1^{1.3} = p_2 v_2^{1.3} = C; p_2 = p_1 \left(\frac{v_1}{v_2}\right)^{1.3} = 4.848\ MPa$$

Then we have to recall $TdS = dH - VdP$ $(TdS = 0\ as\ reversible\ adiabatic); dH = VdP \Rightarrow H_2 - H_1 = \int_1^2 VdP = \int_1^2 \frac{(p_1 v_1^{1.3})}{p} dP = \frac{n(p_2 V_2 - p_1 V_1)}{n-1} = 357\ kJ$

$$U_2 - U_1 = H_2 - H_1 - (p_2 V_2 - p_1 V_1) = 274.6\ kJ$$

$$S_2 - S_1 = 0\ as\ reversible\ adiabatic$$

$$Q_{12} = 0\ as\ adiabatic$$

$$W_{12} = Q_{12} - \Delta U = -274.6\ kJ$$

So, from this problem this gives the basic definition for a given process how this properties value can be evaluated. So, with this I conclude this lecture for today.

Thank you for your attention.