MODULE 3

Reversibility: Definitions of a reversible process, reversible heat engine, importance and superiority of a reversible heat engine and irreversible processes; factors that make a process irreversible, reversible heat engines. Unresisted expansion, remarks on Carnot's engine, internal and external reversibility, Definition of the thermodynamic temperature scale. Problems
Entropy: Clasius inequality, Statement- proof, Entropy- definition, a property, change of entropy, entropy as a quantitative test for irreversibility, principle of increase in entropy, entropy as a coordinate

REVERSIBILITY

OBJECTIVE:

- **Concept of reversible process and condition for a system to be reversible**

STRUCTURE:

3.1 Reversible process:

3.2 Factors that make process irreversible:

3.3 Free expansion process or Unresisted expansion:

3.4 Remarks on carnot Engine:

3.5 Externally Reversible Processes

3.6 Internally Reversible Processes

3.7 Carnot Theorem

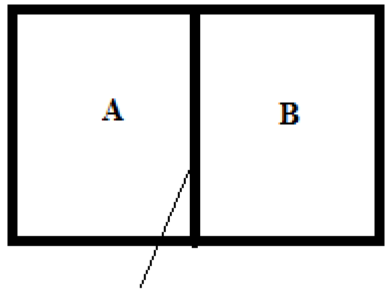
3.1 Reversible process:

A Reversible or ideal process is one in which both the systems and surroundings can be restored to their respective initial states by reversing the direction of process.

3.2 Factors that make process irreversible:

1. Friction
2. Electrical resistance
3. In elastic solid deformation.
4. Free expansion (Unrestrained expansion)
5. Transfer of energy in the form of heat through a finite temperature difference
6. Lack of equilibrium during the process.

3.3 Free expansion process or Unresisted expansion: Consider an adiabatic vessel separated by a partition wall as shown in the figure. If the partition wall is suddenly removed, the air will fill the entire volume of the vessel instantaneously, and this process is not quasi-static and the air is not interacting with surroundings.



To restore original state of the system, the air is to be compressed by an imaginary piston and heat transfer also occurs. These work and heat interactions cause a change in the surroundings and the surroundings are not restored to their initial states. This indicates that, freee expansion is an irreversible process.

3.4 Remarks on carnot Engine:

1. The efficiency of carnot engine depends only on source and sink temperatures and sink temperature and is independent of working fluid. The efficiency becomes maximum when sink temperature T2 = 0 , but this is impossible and it violates Kelvin Planck statement of second law.
2. As the temperature difference between source and sink increases, efficiency also increases and is directly proportional to T1 –T2.
3. The efficiency can be increased either by increasing source temperature or by decreasing sink temperature.

The Carnot Engine is a hypothetical device because:

1. All 4 processes are reversible. For this to happen there should not be any inernal friction between particles of working fluid and no friction exists between the piston and cylinder walls.
2. The heat absorption and rejection have to take place with infinitesimal temperature differences.
3. The piston has to move very slowly to achieve isothermal compression or expansion. In the meantime, piston movement must be very fast to achieve adiabatic compression or expansion . It is impossible to achieve different speeds of the piston during different processes.

3.5 Externally Reversible Processes

- No irreversibilities exist in the surroundings.
- Heat transfer can occur between the system and the surroundings, but only with an infinitesimal temperature difference.
- There may be irreversibilities within the system.

3.6 Internally Reversible Processes

- No irreversibilities exist within the system.
- The system moves slowly and without friction through a series of equilibrium states.

- Irreversibilities may exist in the surroundings, usually due to heat transfer through a finite temperature difference.

3.7 CARNOT THEOREM

Define Carnot Theorem and also give its proof.

Carnot theorem states that no heat engine working in a cycle between two constant temperature reservoirs can be more efficient than a reversible engine working between the same reservoirs. In other words it means that all the engines operating between a given constant temperature source and a given constant temperature sink, none, has a higher efficiency than a reversible engine.

Proof:

Suppose there are two engines E_A and E_B operating between the given source at temperature T_1 and the given sink at temperature T_2.

Let E_A be any irreversible heat engine and E_B be any reversible heat engine. We have to prove that efficiency of heat engine E_B is more than that of heat engine E_A.

Suppose both the heat engines receive same quantity of heat Q from the source at temperature T1. Let W_A and W_B be the work output from the engines and their corresponding heat rejections be $(Q – W_A)$ and $(Q – W_B)$ respectively.

Assume that the efficiency of the irreversible engine be more than the reversible engine i.e. $\eta_A > \eta_B$. Hence,

$W_A /Q > W_B /Q$

I.e. $W_A > W_B$

Now let us couple both the engines and E_B is reversed which will act as a heat pump. It receives $(Q – W_B)$ from sink and W_A from irreversible engine E_A and pumps heat Q to the source at temperature T_1. The net result is that heat $(W_A – W_B)$ is taken from sink and equal amount of work is produce. This violates second law of thermodynamics. Hence the assumption we made that irreversible engine having higher efficiency than the reversible engine is wrong.

Hence it is concluded that reversible engine working between same temperature limits is more efficient than irreversible engine thereby proving Carnot's theorem.

Thermodynamic Temperature scale:

A temperature scale which is independent of the property of thermometric substance is known as Thermodynamic temperature scale.

OUTCOMES: Explain the concept of reversible and irreversible process and factors affecting it.

IMPORTANT THEORY QUESTIONS:

1. List the factors that renders a system reversible.
2. What is thermodynamic temperature scale and deduce the relation between Q and T as proposed by Lord Kelvin.
3. Why it is impossible to carry out the Carnot cycle in real engines.

FURTHER READING:

- Basic Engineering Thermodynamics, A.Venkatesh, Universities Press, 2008
- Basic and Applied Thermodynamics, P.K.Nag, 2nd Ed., Tata McGraw Hill Pub.
- http://www.nptel.ac.in/courses/112104113/4#

ENTROPY

OBJECTIVES:

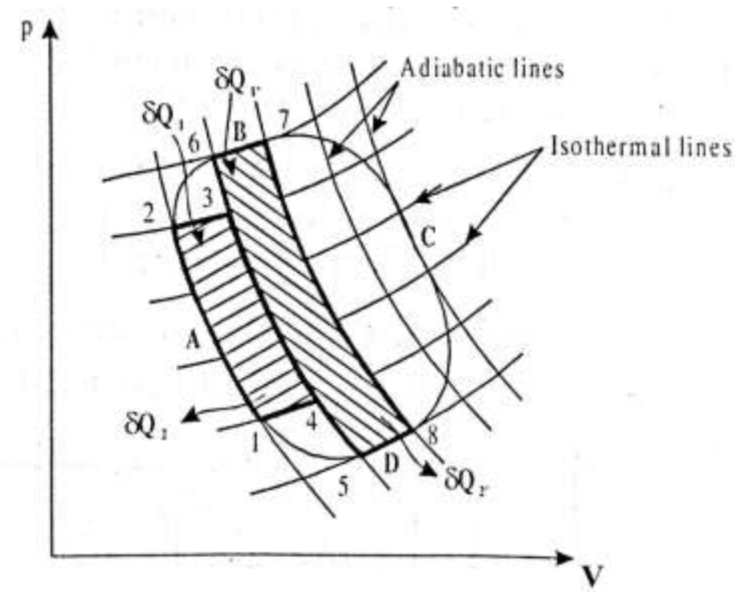
1. Clausius theorem and concept of entropy
2. Entropy as a state property
3. Entropy principle

STRUCTURE:

3.2.8 Entropy
3.2.9 Clausius theorem
3.2.10 Clausius Inequality
3.2.11 Entropy is a property

3.2.8 Entropy: The measure of a system's thermal energy per unit temperature that is unavailable for doing useful work.

3.2.9 Clausius theorem:



- Consider a system undergoing a cycle A-B-C-D as shown in the figure in the p-V diagram.
- This cycle is broken into a large number of sall carnot cycles by a family of reversible adiabatic and eversible isothermal lines on the p-V diagram.
- Thus the whole cycle is represented by a small numbe of carnot cycles 1-2-3-4 , 5-6-7-8 etc.
- Now consider carnot cycles 1-2-3-4 and 5-6-7-8. In these two cycles 3-4 and 5-6 represent adiabatic expansion and adiabatic compression respectively in which heat rejection and heat addition takes place.Thus process 3-4 is cancelled out as far as energy transfer with process 5-6 is concerned.
- Also the adiabatics have no contribution to the heat added. Furtherr, if the number of carnot cycles is very large and the adiabatic lines are close to one another, in the limiting case all these small carnot cycles coincide with the given reversible cycle A-B-C-D.
- Let Q_1 , $Q_{1'}$ …. be the amount of heat exchanged during heat absorption and let Q_2 ,$Q_{2'}$ …. be the amount of heat exchanged during rejection.
- Then for small Carnot cycle 1-2-3-4 we may write

  we know that for a reversible process $\oint \frac{\delta Q}{T} = 0$

  Then we can write $\frac{\delta Q_1}{T_1} + \frac{\delta Q_2}{T_2} = 0$ ……. 1

Similarly for cycle 5-6-7-8

$$\frac{\delta Q_{1'}}{T_{1'}} + \frac{\delta Q_{2'}}{T_{2'}} = 0 \text{……..2}$$

Adding the equation 1 and 2 we get

$$\frac{\delta Q_1}{T_1} + \frac{\delta Q_2}{T_2} + \frac{\delta Q_{1'}}{T_{1'}} + \frac{\delta Q_{2'}}{T_{2'}} = \sum \frac{\delta Q}{T} = 0$$

Replacing the summation by cyclic integral in the limit we can write

$$\oint \frac{\delta Q_{rev}}{T} = 0$$

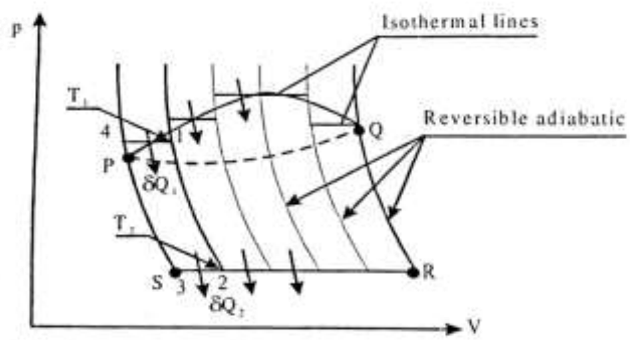
The above equation is known as **CLAUISIUS THEOREM**, Which states that the cyclic integral of $\frac{\delta Q}{T}$ for a **Reversible cycle** is equal to zero

3.2.10 Clausius Inequality:

Consider a cycle PQRS in which process PQ is either reversible or irreversible, whereas other processes QR,RS and SP are reversible as shown in the fig.

Dividing this cycle into large number of smaller cycles and considering any one of such cycles say 1-2-S-4-1, we can write thermal efficiency as

$$\eta = 1 - \left(\frac{\delta Q_2}{\delta Q_1}\right) = 1 - \frac{T_2}{T_1}$$



If the cyclic integration is applied to cyclic irreversibilities, then $\oint \frac{\delta Q}{T}$ never becomes Zero.

Thus for any small carnot cycles operating between temperature T_1 and T_2 with heat exchange δQ_1 and δQ_2 and with some irreversibility the efficiency is smaller than or equal to that of a reversible engine

Thus. $\eta_{irr} \leq \eta_{rev}$

i.e $1 - \left(\frac{\delta Q_2}{\delta Q_1}\right)_{irr} \leq 1 - \left(\frac{\delta Q_2}{\delta Q_1}\right)_{rev}$

or $\quad \frac{\delta Q_2}{\delta Q_1} \geq \left(\frac{\delta Q_2}{\delta Q_1}\right)_{rev}$

$$\frac{\delta Q_1}{\delta Q_2} \leq \left(\frac{\delta Q_1}{\delta Q_2}\right)_{rev}$$

$$But \quad \left(\frac{\delta Q_1}{\delta Q_2}\right)_{rev} \leq \frac{T_1}{T_2}$$

Substituting 2 in 1 we get

$$\frac{\delta Q_1}{\delta Q_2} \leq \frac{T_1}{T_2}$$

In general, if δQ is the heat supplied at temperature 1, then we can modify equation 3 as

$$\frac{\delta Q}{\delta Q_2} \leq \frac{T}{T_2}$$

or

$$\frac{\delta Q}{T} \leq \frac{\delta Q_2}{T_2}$$ For any process PQ reversible or irreversible

For reversible process,

$$\frac{\delta Q_{rev}}{T} = \frac{\delta Q_2}{T_2}$$

For any process PQ, $\frac{\delta Q}{T} \leq ds$

Thus for any engine working in a cycle

$$\oint \frac{\delta Q}{T} \leq \oint ds$$

Since the cyclic integral of any property is zero

$$\oint \frac{\delta \mathbf{Q}}{\mathbf{T}} \leq \mathbf{0}$$

THIS IS CLAUSIUS INEQUALITY

<u>Note:</u> If,

$\oint \frac{\delta Q}{T} = 0$ **, The cycle is reversible**

$\oint \frac{\delta Q}{T} < 0$ **, The cycle is irreversible and possible**

$\oint \frac{\delta Q}{T} > 0$ **, The cycle is impossible since it violates second law.**

3.2.11 Entropy is a property:

Consider two reversible paths A and B joining the states 1 and 2.

If path B is reverse, that is transversed from 2 to 1 , then path A and B constitute a reversible cycle.

That is

$$\oint \frac{\delta Q}{T} = \int_1^2 \frac{\delta Q}{T}_{\text{path A}} + \int_2^1 \frac{\delta Q}{T}_{\text{path B}}$$

$$\int_2^1 \frac{\delta Q}{T}_{\text{path B}} = \int_1^2 \frac{\delta Q}{T}_{\text{path A}}$$

It applies to any reversible processes joining states 1 and 2

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

Thus entropy is independent of path and therefore entropy is a property

OUTCOME:

- Explains the concept entropy and its characteristics

IMPORTANT QUESTIONS:

1. State and prove clausius inequality? What is the significance of clausius inequality
2. An adiabatic vessel contains 85kg of oil at a temperature of 27˚C. A spherical ball made of steel of 10kg AT 727˚C is immersed in oil. Determine change in entropy for the universe. Tke specific heat of oil = 3.5 kJ/kg.K, Specific heat of steel ball = 0.5kJ/kg.K
3. 0.5 Kg of air initially at 27C is heated reversibly at constant pressure until the volume is doubled and is then heated reversibly at constant volume until the pressure is doubled . For the total path , find work transfer , heat transfer and change of entrpy.
4. Explain principle of increase of entropy.
5. Prove that for a cyclic process $\int \frac{\delta Q}{T} \leq 0$, Hence define entropy

FURTHER READING:

- Basic Engineering Thermodynamics, A.Venkatesh, Universities Press, 2008