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CARNOT THEOREM

- Efficiency of a machine working reversibly depends only on the temperature of the source and the sink.
- It is independent of the nature of the substance used for operations.
- **"All periodic machines working reversibly between the same two temperature have the same efficiency." This statement is known as the CARNOT THEOREM.**
- First law tells that when one form of the energy is converted into another, the amount of energy that disappears is exactly equal to the amount of energy that is produced.
- It doesn't tell about the extent to which such conversion can occur.
- The second law tells about this point. It tells us that all other forms of energy can be completely converted into heat, but the complete conversion of heat into any other form of energy cannot take place without leaving some lasting change in the system. This leads to second law of thermodynamics.
- "It is impossible to convert heat into work without compensation."

ENTROPY

- It is the measure of the randomness or disorder of the system.
- The greater the randomness, the greater the entropy.
- Entropy of a crystalline substance is minimum in the solid state and maximum in the gaseous state.
- Entropy is represented by S
- It depends on temperature and increase with increase in temperature.
- The change in entropy is equal to heat absorbed isothermally and reversibly during a process divides by absolute temperature at which heat is absorbed.

$$\therefore \quad \Delta S = q\ rev/T$$

- For Carnot cycle;

$$\frac{W}{Q2} = \frac{Q2+Q1}{Q2} = \frac{T2-T1}{T2}$$

OR

$$\frac{Q1}{T1} + \frac{Q2}{T2} = 0$$

- Unit of entropy (e.u.) : **"calories per degree per mole"**

OR

"calories per degree per gram"

ENTROPY: A NEW STATE FUNCTION

$$\therefore \quad \frac{Q1}{T1} + \frac{Q2}{T2} = 0$$

- Thus, when the isothermal and adiabatic processes in a Carnot cycle are carried out slowly, the summation of $\frac{q}{T}$ terms is equal to zero.
- Any cyclic process can be considered as a series of carnot cycles, if it is carried out reversibly.
- Consider a cyclic process in which the change from state A to state B and back to the state A is carried out reversibly.
- Let us consider the path ABA is made up of a number of small Carnot cycles.
- The horizontal lines are isothermals and vertical lines are adiabatic of the small carnot cycles.

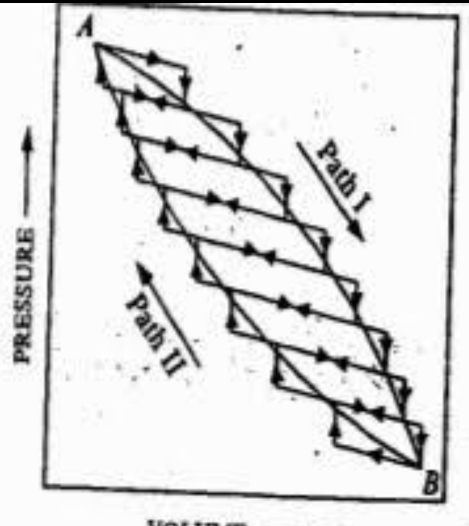

Fig. 2. Entropy change in a reversible cyclic process.

- For each carnot cycle $\frac{Q1}{T1} + \frac{Q2}{T2} = 0$, so for reversible cycle ABA;

$$\Sigma \frac{q}{T} = 0 \qquad \_\_\_\_\_\_\_\_\_\_\_\_(1)$$

- The changes are very small, so

$$\Sigma \frac{dq}{T} = 0 \qquad \_\_\_\_\_\_\_\_\_\_\_\_(2)$$

- The cycle is performed in two steps;

$$\Sigma \frac{dq}{T} = \int_A^B \frac{dq}{T} + \int_B^A \frac{dq}{T} = 0 \qquad \_\_\_\_\_\_\_\_\_\_\_\_(3)$$

- The integral $\int_A^B \frac{dq}{T}$ is the sum of all the $\frac{dq}{T}$ terms when the system changes from A to B, along path I.
- The integral $\int_B^A \frac{dq}{T}$ is the sum of all the $\frac{dq}{T}$ terms when the system returns from state B to the original state A .
- From equation (3);

$$\int_A^B \frac{dq}{T} = -\int_B^A \frac{dq}{T}$$

$$\therefore \int_A^B \frac{dq}{T} \text{ (path I)} = \int_A^B \frac{dq}{T} \text{ (path II)} \qquad \_\_\_\_\_\_\_\_\_\_(4)$$

- Thus, $\int_A^B \frac{dq}{T}$ is a definite quantity independent of the path taken for the change and depends only upon the initial and final states of the system.
- Therefore, it is a state function and known as Entropy (S).
- If S_A is the entropy in the initial state A and S_B is the entropy in the final state B.
- The change in entropy,

$$\Delta S = S_B - S_A = \int_A^B \frac{dq}{T} \qquad \text{\_\_\_\_\_\_\_\_\_\_(5)}$$

- For each infinite small change,

$$dS = \frac{dq}{T} \qquad \text{\_\_\_\_\_\_\_\_\_\_(6)}$$

- At constant temperature, for a finite change, dS becomes ΔS and dq becomes q.

$$\Delta S = \frac{q}{T} \qquad \text{\_\_\_\_\_\_\_\_\_\_(7)}$$

- Entropy is a state function, i.e. it is independent of the path. Mathematically it is written as;

$$\Delta S = \int_A^B \frac{dq}{T} \qquad \_\_\_\_\_\_\_\_\_\_(8)$$

- This equation is derived from Carnot cycle in which all the changes are reversible. Thus, the entropy change for a finite change of state of a system at constant temperature is given by;

$$\Delta S = \frac{q_{rev}}{T} \qquad \_\_\_\_\_\_\_\_\_\_\_(9)$$

- Entropy is expressed in joules per degree kelvin (JK^{-}). This is known as entropy unit, e.u.
- Entropy is an extensive property, i.e. its value depends upon the amount of the substance. Therefore, quantity of the substance must be mentioned.

ENTROPY CHANGE IN AN ISOTHERMAL EXPANSION OF AN IDEAL GAS

- If the gas is allowed to expand isothermally and reversibly, change in internal energy is zero, $\Delta U = 0$.
- From first law of thermodynamics, $q_{rev} = -w$
- The work done in the expansion of 'n' moles of a gas from volume V_1 to V_2 at constant temperature T is;

$$-w = nRT \ln (V_2/V_1)$$

$$\therefore \quad q_{rev} = -w = nRT \ln (V_2/V_1) \qquad \text{\_\_\_\_\_\_\_\_\_\_(10)}$$

$$\therefore \quad \Delta S = q_{rev}/T = nR \ln (V_2/V_1) \qquad \text{\_\_\_\_\_\_\_\_\_\_(11)}$$

ENTROPY CHANGE IN REVERSIBLE AND IRREVERSIBLE PROCESSES

- A gas is allowed to expand spontaneously at constant temperature into vacuum.
- There is no opposing force, the work done by the system will be zero.
- Process is isothermal so the change in internal energy of the system is zero, $\Delta U = 0$.
- From the first law of thermodynamics q = 0, i.e. no heat is absorbed or evolved in the process.
- The entropy of the surroundings remains unchanged.
- The volume of the gas increases, from V_1 to V_2 at constant temperature T.

$$\Delta S = R \ln (V_2/V_1)$$

- Total increase in entropy of the system and surroundings is

  R ln (V_2/V_1) + 0 = R ln (V_2/V_1).
- Now, $V_2 > V_1$ so $\Delta S > 0$. Thus, there is increase in entropy of the universe if the expansion is irreversible.
- Now consider, expansion of the ideal gas from volume V_1 to V_2 carried out reversibly at constant temperature T.
- The expansion is reversible means it is carried out very very slowly.
- The external pressure of the system is so adjusted that it remains always less than that of the system by very small amount.
- The gas does some work w = -PΔV.

- An equivalent amount of heat (q_{rev}) is absorbed by the system from the surroundings at temperature T.
- Hence, increase in the entropy of the system is q_{rev}/T.
- The heat lost by the surroundings is also q_{rev}. Hence, decrease in the entropy of the surroundings is q_{rev}/T.
- The net change of the system and the surroundings is;

$$\frac{q_{rev}}{T} - \frac{q_{rev}}{T} = 0$$

- Thus, in the reversible isothermal expansion of a gas, the total entropy change of the universe is zero.
- **For reversible process; $\Delta S_{sys} + \Delta S_{sur} = 0$ and for irreversible process; $\Delta S_{sys} + \Delta S_{sur} > 0$.**

- In a reversible process, the entropy of the universe remains constant where as in an irreversible process it increases.
- From this conclusion, we can predict whether a given process can occur spontaneous or not.
- Since all processes in nature occurs spontaneously, the entropy of the universe is increasing continuously. This is another statement of the second law.
- The first and second law was summed up by Clausius :

" The energy of the universe remains constant, the entropy of the universe tends towards a maximum"


Thank
You