PI –Unit II – Chapter 3
Entropy

By

Dr Namrata Jain
Associate Professor
Department of Physics
M.D. College

Introduction

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Entropy

(1) In 1854 clausius introduces another coordinate or variable called 'entropy' alongwith pressure volume, temperature and internal en

(2) similar to internal energy the entropy is als a function of the state of system which shows direction of the process of system

(3) Physical aspect of entropy is that it remain constant during reversible process and increas during irreversible process.

(4) There is no process in which entropy decre

(5) Entropy is also a measure of the disor of the system

(6) (1) ex. — water flow by itself
(2) Electricity flow
(3) Diffusion.

4. All chemical systems under given thermodynamic condition under a reaction in a direction which leads to establishmen of equilibrium.

According to Firstlaw of thermodynamics energy can neither be destroyed nor be created
But According to second law of thermod

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entropy cannot be destroyed but can be created
According to Eddington 'entropy is time arrow'

(2) Clasius theorem of inequality:

It states that for a system s consisting of n carnot cycle performing cyclic process ~~consisting~~ and having sequence of states

$$\sum_{i=1}^{n} \frac{H_i}{T_i} \quad \text{or} \quad \sum_{i=1}^{n} \frac{\delta H_i}{T_i} \leq 0 \qquad (H = Q)$$

where H_i is the Heat absorbed or lost for i^{th} reservoir & T_i is it's temperature.

The system interact with series of reservoirs $R_1, R_2, \ldots R_N$ at temp. $T_1, T_2 \ldots T_n$ respectively & $H_1, H_2 \ldots H_n$ be heat absorbed or lost by them.

It is true ~~that~~ $\left(\sum_{i=1}^{n} \frac{H_i}{T_i} \leq 0\right)$ for reversible & irreversible process.

To. Explain Consider a system s & n carnot engine say $C_1, C_2 \ldots C_n$. working as a refrigerators or engines operating between (T_0, T_1), (T_0, T_2) . . (T_0, T_n) respectively.

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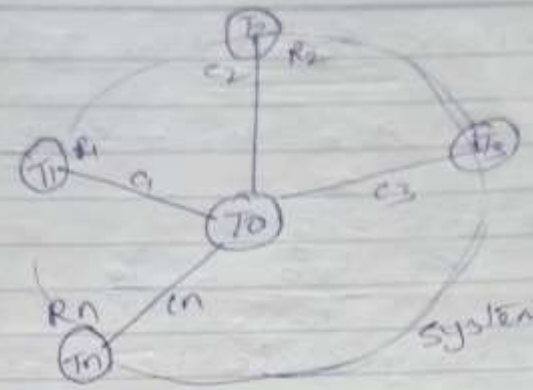

corrected

Heat absorbed at $T_1, T_2, \ldots T_n$ should be exactly equal to the quantity of heat absorbed by system-s during one cyclic transformation. In a cyclic process heat quantity of heat absorbed is equal to quantity of work performed.

There is no ~~interaction of~~ restriction on interaction of energy. Only restriction is that the changes should be consistent with first & second law of thermodynamics.

A composite cycle considered to be complex cycle consists of systems of each of Carnot cycles $C_1 \ldots C_n$.

i.e.

Complex cycle = $S_{cycle} + C_1 + C_2 \ldots C_n$ —(1)

so that system comes back to initial state, no reservoir gains or loses heat during complex cycle.

∴ net quantity of heat drawn from

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reservoir R_0 at temp. T_0 is

$$\sum_{i=1}^{n} H_{i,0} = H_0 = T_0 \sum_{i=1}^{n} \frac{H_i}{T_i} \quad \text{—(2)}$$

∴ we have a cycle

$$\frac{H_{i,0}}{H_i} = \frac{T_0}{T_i} \quad \text{—(3)}$$

i.e. In any cycle Heat absorbed equal to amount of work performed.

From above discussion, we find that for a complex cycle system returns to initial state on completion of cyclic processes & $R_1, R_2 \ldots$ donot gain or lose heat & Heat absorbed by R_0 i.e H_0 at T_0 is given by eq (3) & it should be converted into work.

Here complete Heat of reservoir i.e H_0 is converted into work which violates second law statement.

Kelvin-Planck statement

i.e $W_0 = H_0 = T_0 \sum \frac{H_i}{T_i}$

But according to second law,

$$T_0 \sum_{i=1}^{n} \frac{H_i}{T_i} \leq 0$$

This implies that

$$\sum \frac{H_i}{T_i} \leq 0$$

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for a system of no. of reservoir.

$$\frac{H_1}{T_1} + \frac{H_2}{T_2} + \cdots \frac{H_N}{T_N} \leq 0$$

$$\boxed{\oint \frac{\delta H}{T} \leq 0}$$

for infinite no of reservoir. Infinitesimal exchanged heat is given by δH.

(3) Entropy of a system

1) Entropy means 'Trope'. i.e. transformation
2) Entropy is necessary for Second law of thermodynamics
3) Entropy measures potentiality of a system for heat - work transformation
4) It is a measure of randomness or disorderliness
5) Increase in entropy means increase in disorder

To explain & get expression for entropy Consider PV indicator diagram for reversible engine. or in reversible process let the system S changes from state A to state B along path 1 & returns from B to A via path 2. Then as per clausius theorem

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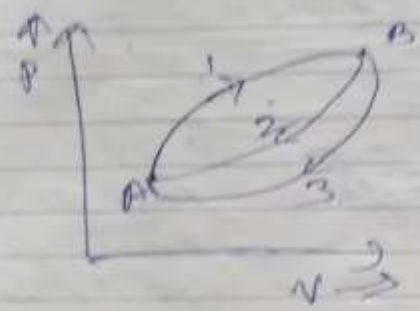

$$\oint \frac{\delta Q}{T} = 0 \quad \text{--- (1) for reversible process}$$

$$\therefore = \int_{A_1}^{B_1} \frac{\delta Q}{T} + \int_{B_2}^{A_2} \frac{\delta Q}{T} = 0 \quad \text{--- (2)}$$

δQ is heat absorbed or heat exchanged ~~with~~ by the system

$$\therefore \int_{A_1}^{B_1} \frac{\delta Q}{T} = -\int_{B_2}^{A_2} \frac{\delta Q}{T} \quad \text{--- (3)}$$

In asimilar manner if system returns from final state B to initial state A we ~~get~~ have

$$\int_{A_1}^{B_1} \frac{\delta Q}{T} + \int_{B_3}^{A_3} \frac{\delta Q}{T} = 0 \quad \text{--- (4)}$$

i.e. $$\int_{A_1}^{B_1} \frac{\delta Q}{T} = -\int_{B_3}^{A_3} \frac{\delta Q}{T} \quad \text{--- (5)}$$

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From (3) & (8) we get

$$\int_{B_2}^{A_2} \frac{\delta Q}{T} = \int_{B_3}^{A_3} \frac{\delta Q}{T}$$

hence in reversible process $\int \frac{\delta Q}{T}$ does not depend upon path it only depends upon initial state & final state.

let $ds = \frac{\delta Q}{T}$ which is small change in entropy

$$\therefore \int_A^B ds = \int_A^B \frac{\delta Q}{T}$$

$$= S_B - S_A = \int_A^B \frac{\delta Q}{T}$$

here S_B & S_A are called as entropy at B point & S_A is the entropy of A point.

hence s is called as absolute entropy

Entropy of system is extensive quantity like volume & internal energy. It is distinct from intensive quantities like pressure & temp.

SI system unit of entropy is Joule/°K & Calorie/°K.