

(SECTION - C)  
"STATISTICAL INTERPRETATION OF ENTROPY AND  
 CARNOT'S CYCLE"

Statistical Definition of Entropy  $\rightarrow$  Any macrostate of system is characterised by a definite value of thermodynamic probability ( $W$ ). The thermodynamic probability depends on volume ( $V$ ), energy ( $U$ ) and the no. of particles ( $n$ ) of the system. Since the value of  $W$  is very large, so it is convenient to deal with  $\log_e W$  rather than  $W$ , because  $\log_e W$  is very small quantity. In order to describe the natural tendency of the system to attain the most probable macrostate concept of entropy has been introduced.

i.e.  $S \propto \log W$

or  $S = k \log_e W$  ——— ①

The new parameter  $S$  is called Entropy.

$k = 1.38 \times 10^{-23} \text{ JK}^{-1}$  is Boltzmann's constant. Since  $\log_e W$  is dimensionless quantity, so the unit of entropy is same as that of Boltzmann's constant.

Thus unit of entropy is  $\text{JK}^{-1}$  or  $\text{Cal K}^{-1}$

For a system which is in state of equilibrium,  $W = W_{\text{max}}$ , therefore, the entropy of system which is in equilibrium is given by

$$S = k \log_e W_{\text{max}} \text{ ——— ②}$$

Here  $S = S(P, V, T)$

Change of Entropy due to change of state  $\rightarrow$  We know that the entropy of one mole of perfect gas of volume  $V$  at temperature  $T$  is given by

$$S = \frac{3}{2}R + R \ln(\beta V T^{3/2}) \quad \left[ \beta = \frac{1}{kT} \right] \text{ ——— ①}$$

Diff. both sides to obtain

$$dS = 0 + \frac{R}{\beta V T^{3/2}} \left[ \beta V \frac{3}{2} T^{1/2} dT + \beta T^{3/2} dV \right]$$

$$dS = R \left[ \frac{3}{2} \frac{dT}{T} + \frac{dV}{V} \right]$$

$$dS = \frac{3}{2}R \frac{dT}{T} + \frac{RdV}{V} \text{ ——— ②}$$

The eqn. of state for one mole of perfect gas is

$$PV = RT \quad \Rightarrow \quad V = \frac{RT}{P} \text{ ——— ③}$$

Substitute this value of  $V$  in eqn. (2) to obtain

$$dS = \frac{3}{2}R \frac{dT}{T} + \frac{PdV}{T} \quad \text{--- (4)}$$

The molar specific heat at constant volume for a perfect gas is given by

$$C_v = \frac{3}{2}R \quad \text{--- (5)}$$

Using this result in eqn. (4) we obtain

$$dS = C_v \frac{dT}{T} + \frac{PdV}{T} \quad \text{--- (6)}$$

The molar specific heat at constant volume is given by

$$C_v = \left( \frac{\partial U}{\partial T} \right)_V \quad \text{--- (7)}$$

The internal energy of a perfect gas depends only on temperature. Therefore

$$\left( \frac{\partial U}{\partial T} \right)_V = \frac{dU}{dT} \quad \text{--- (8)}$$

Thus eqn. (7) becomes

$$C_v = \frac{dU}{dT}$$

$$dU = C_v dT \quad \text{--- (9)}$$

Substitute this result in eqn. (6) to obtain

$$dS = \frac{dU}{T} + \frac{PdV}{T} = \frac{dU + PdV}{T} \quad \text{--- (10)}$$

Suppose  $dQ$  is the amount of heat given to the system to bring about infinitesimal small change of entropy  $dS$ . The acc. to first law of thermodynamics

$$dQ = dU + PdV \quad \text{--- (11)}$$

Using this result in eqn. (10) we obtain

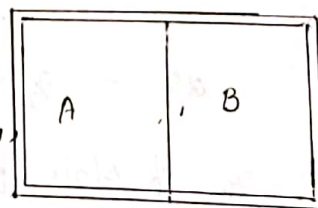
$$dS = \frac{dQ}{T} \quad \text{--- (12)}$$

Additive nature of Entropy :→ Consider a system in equilibrium is divided into two parts A and B as shown in fig

let  $W$  and  $S$  be thermodynamic probability and entropy of the whole system.

$$S = k \log W \quad \text{--- (1)}$$

If  $W_1$  and  $W_2$  be thermodynamic probability,  $S_1$  and  $S_2$  be the entropies of sub systems A and B respectively.



$$\therefore S_1 = k \log W_1 \quad \text{--- (2)}$$

$$\text{and } S_2 = k \log W_2 \quad \text{--- (3)}$$

We know, if probabilities of occurrence of two independent events are  $W_1$  and  $W_2$ , then the entropies of sub-systems A and B respectively. Probabilities of occurrence of two events simultaneously is given by

$$W = W_1 W_2$$

Taking natural logarithms, we get

$$\log W = \log W_1 + \log W_2$$

Multiplying both sides by  $k$ , we have

$$k \log W = k \log W_1 + k \log W_2$$

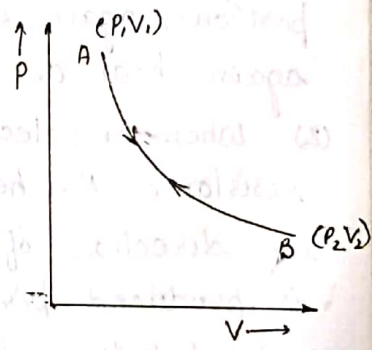
Using eqn. (1) to (3), we get

$$S = S_1 + S_2 \quad \text{--- (4)}$$

Thus entropy of the system as a whole is given by the sum of entropies of two parts. In general, the entropy of system is given by summation of entropies of all the sub-systems of the system.

i.e. 
$$S = \sum_{i=1}^k S_i \quad \text{--- (5)}$$

Reversible Process  $\rightarrow$  A process in which a system can be retraced to its initial state by reversing the controlling factors is called reversible process.



For example, when a spring is slowly stretched, the work is done on it. Now, if the same spring is allowed to contract slowly to the original length, the same amount of work is done by the spring against the stretching force. However, it must be remembered that the extension or contraction must be done very slowly. In other words, the reversible process is quasi-static process.

In terms of statistics, a reversible process is one in which the change in entropy is zero

i.e. 
$$\Delta S = 0$$

Conditions for Reversibility  $\rightarrow$  The basic requirements for a process to be reversible are:

- ① The substance undergoing a reversible change must not lose heat in overcoming friction or through conduction, convection or radiation.

## TEMPERATURE - ENTROPY (T-S) DIAGRAM →

According to second law of thermodynamics

$$dS = \frac{dQ}{T} \text{ or } dQ = TdS \text{ ——— ①}$$

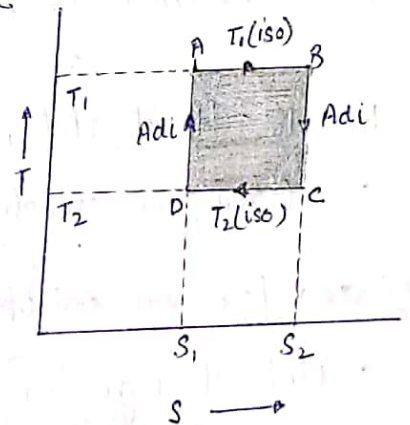
which is infinitesimal amount of change in heat in a reversible process.

Therefore, total amount of heat transferred in a reversible process is given by

$$\int dQ = \int_i^f TdS \text{ or } Q = \int_i^f TdS \text{ ——— ②}$$

The R.H.S. can be interpreted graphically as the area under a curve on a diagram in which  $S$  is plotted along X-axis and  $T$  is plotted along y-axis. Such a diagram is called T-S diagram

An isothermal process, in which temperature remains constant, is obviously represented by straight line parallel to S-axis.



In a reversible adiabatic process  $dQ=0$ , hence from eqn. (1), we have  $dS=0$  i.e.,  $S$  remains constant i.e. the system undergoes an isentropic process. Thus reversible adiabatic process on a T-S diagram is obviously a vertical line parallel to T-axis. Hence the top isothermal and two adiabatic processes which go to make up the Carnot cycle form a rectangle on a T-S diagram, no matter what the working substance is

The amount of heat  $Q_1$  absorbed in isothermal expansion AB at Temperature  $T_1$  is given by area  $ABS_1S_2$ . In a similar way the amount of heat  $Q_2$  rejected in isothermal compression CD at temperature  $T_2$  is given by area  $DCS_1S_2$

$$\text{Here, total heat absorbed } Q_1 = T_1(S_2 - S_1) = \text{area } ABS_2S_1$$

$$\text{Total heat rejected, } Q_2 = T_2(S_2 - S_1) = \text{area } DCS_2S_1$$

$$\therefore \text{Heat converted into work, } W = Q_1 - Q_2 = (T_1 - T_2)(S_2 - S_1) = \text{shaded area } ABCD$$

$$\text{Efficiency } \eta = \frac{W}{Q_1} = \frac{(T_1 - T_2)(S_2 - S_1)}{T_1(S_2 - S_1)}$$

or

$$\eta = \frac{T_1 - T_2}{T_1} = 1 - \frac{T_2}{T_1}$$

rest :

The efficiency expression is same as we have obtained by the usual treatment on P-V diagram of a Carnot cycle. Hence efficiency expression obtained on T-S diagram is much simpler as compared to P-V indicator diagram.

Entropy Change in Carnot's Cycle  $\rightarrow$  let us consider the system as a whole which consists of source, sink and working substance. In the first step of Carnot cycle, the working substance absorbs heat  $Q_1$  at  $T_1$  from the source

$$\therefore \text{Gain in entropy of working substance} = +Q_1/T_1$$
$$\text{and loss in entropy of source} = -Q_1/T_1$$

$\therefore$  Net change in entropy of whole system in this step is

$$\Delta S = \frac{Q_1}{T_1} - \frac{Q_1}{T_1} = 0$$

In the second step of the cycle, which is adiabatic, no heat is either absorbed or rejected. Therefore change in entropy,

$$\Delta S = dQ/T = 0$$

In the third step, gas rejects heat  $Q_2$  at temp.  $T_2$  to the sink.

$$\therefore \text{Gain in entropy of sink} = +Q_2/T_2$$

$$\text{and loss in entropy of working substance} = -Q_2/T_2$$

$\therefore$  Net change in entropy of whole system is =  ~~$Q_2/T_2$~~

$$\Delta S = \frac{Q_2}{T_2} - \frac{Q_2}{T_2} = 0$$

In the fourth step, which is again adiabatic, no heat is either absorbed or rejected. Therefore, change in entropy of system is zero.

Hence total change in entropy of whole system in a Carnot's cycle is zero.

Entropy change of working substance  $\rightarrow$

let us calculate the change in entropy of working substance only in Carnot's cycle.

In the 1st step, the working substance absorbs heat  $Q_1$  at temperature  $T_1$ .

$$\therefore \text{change in entropy of working substance, } \Delta S = Q_1/T_1$$

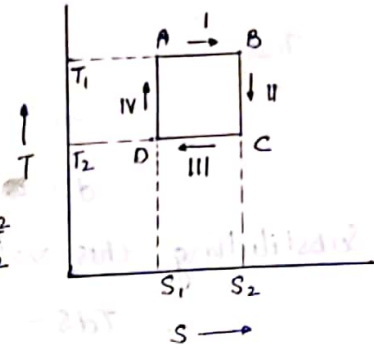
and  $\dots$  respectively.

In the 1<sup>st</sup> step, there is no absorption or rejection of heat by the working substance.

∴ change in entropy of working substance,  $\Delta S = 0$

In the 3<sup>rd</sup> step, working substance reject heat  $Q_2$  at temperature  $T_2$

∴ change in entropy of working substance,  $\Delta S = \frac{-Q_2}{T_2}$



In IV<sup>th</sup> step, the change in entropy = 0

This can be demonstrated with help of T-S diagram.

From fig:

Increase in entropy in 1<sup>st</sup> step is given by

$$S_2 - S_1 = \frac{Q_1}{T_1} \quad \text{or} \quad Q_1 = T_1 (S_2 - S_1)$$

Decrease in entropy in 3<sup>rd</sup> step is given by

$$S_1 - S_2 = \frac{-Q_2}{T_2} = Q_2 = T_2 (S_2 - S_1)$$

In steps, 1<sup>st</sup> and 3<sup>rd</sup> change in entropy is zero.

$$\begin{aligned} \therefore W &= Q_1 - Q_2 = (T_1 - T_2) \times (S_2 - S_1) \\ &= \text{Area ABCD in T-S diagram.} \end{aligned}$$

Entropy of a Perfect Gas → Consider one mole of a perfect gas at temperature  $T$ . Let  $P$  and  $V$  be pressure and volume of gas at temperature  $T$ . Suppose an infinitesimal small amount of heat  $dQ$  is supplied to gas. Then acc. to first law of thermodynamics.

$$dQ = dU + dW \quad \text{--- (1)}$$

The increase in entropy of gas due to heat  $dQ$  is

$$dS = \frac{dQ}{T}$$

$$\therefore dQ = T dS \quad \text{--- (2)}$$

Substitute this value of  $dQ$  in eqn. (1) to obtain

$$T dS = dU + dW \quad \text{--- (3)}$$

We know that the specific heat at constant volume  $C_v$  is

given by  $C_v = \left( \frac{\partial U}{\partial T} \right)_V \quad \text{--- (4)}$

Since the internal energy of an ideal gas depends only on temperature  $T$ , therefore

$$\left(\frac{\partial U}{\partial T}\right)_V = \frac{dU}{dT} \quad \text{--- (3)}$$

Thus

$$C_V = \frac{dU}{dT}$$

$$dU = C_V dt \quad \text{--- (6)}$$

Substituting this value of  $dU$  in eqn (3) we obtain

$$Tds = C_V dT + dW \quad \text{--- (7)}$$

The amount of work done by gas during volume change  $dV$  is

$$dW = PdV \quad \text{--- (8)}$$

Thus eqn. (7) reduces to

$$Tds = C_V dT + PdV$$

$$ds = C_V \frac{dT}{T} + \frac{P}{T} dV \quad \text{--- (9)}$$

The eqn. of state for one mole of perfect gas is

$$PV = RT$$

$$P = \frac{RT}{V} \quad \text{--- (10)}$$

Substituting this value of  $P$  in eqn. (9) we obtain

$$ds = C_V \frac{dT}{T} + R \frac{dV}{V} \quad \text{--- (11)}$$

Suppose the gas is taken from state A ( $P_1, V_1, T_1$ ) to state B ( $P_2, V_2, T_2$ ) by a reversible process. Then the total change in entropy of ideal gas is

$$\int_A^B ds = C_V \int_A^B \frac{dT}{T} + R \int_A^B \frac{dV}{V}$$

$$S_B - S_A = C_V \ln\left(\frac{T_B}{T_A}\right) + R \ln\left(\frac{V_B}{V_A}\right) \quad \text{--- (12)}$$

where  $S_B$  and  $S_A$  are entropies of the gas in states B and A respectively.

Eqn. (12) gives the change in entropy for 1 mole of perfect gas. To determine the entropy of the gas in a state, we arbitrarily assign a value to the entropy of some chosen state say state A.

A and B respectively.

cal cases

Suppose the gas is heated at constant volume. Then

$$V_A = V_B \quad \text{--- (13)}$$

Eqn. (12) takes the form

$$S_B - S_A = C_v \ln \left( \frac{T_B}{T_A} \right) + R \ln 1 \quad \text{--- (14)}$$

Since  $\ln 1 = 0$  we obtain

$$S_2 - S_1 = C_v \ln \left( \frac{T_B}{T_A} \right) \quad \text{--- (15)}$$

(ii) Suppose the gas is heated at constant temperature. Then

$$T_A = T_B \quad \text{--- (16)}$$

Eqn. (12) becomes

$$S_B - S_A = C_v \ln 1 + R \ln \left( \frac{V_B}{V_A} \right)$$

$$S_B - S_A = R \ln \left( \frac{V_B}{V_A} \right) \quad \text{--- (17)}$$

(iii) Suppose the gas is heated at constant pressure. Then

$$P_A = P_B \quad \text{--- (18)}$$

The gas equation

$$\frac{P_A V_A}{T_A} = \frac{P_B V_B}{T_B}$$

becomes

$$\frac{P_A V_A}{T_A} = \frac{P_A V_B}{T_B}$$

$$\frac{V_A}{T_A} = \frac{V_B}{T_B}$$

$$\frac{T_B}{T_A} = \frac{V_B}{V_A} \quad \text{--- (19)}$$

Substitute the value in eqn. (12) to obtain

$$S_B - S_A = C_v \ln \left( \frac{V_B}{V_A} \right) + R \ln \left( \frac{V_B}{V_A} \right)$$

$$S_B - S_A = (C_v + R) \ln \left( \frac{V_B}{V_A} \right) \quad \text{--- (20)}$$

For 1 mole of perfect gas

$$C_p = C_v + R \quad \text{--- (21)}$$

Using this result in eqn. (20) we obtain

$$S_B - S_A = C_p \ln \left( \frac{V_B}{V_A} \right) \quad \text{--- (22)}$$



## Equation of State of Perfect Gas from Statistical Considerations

Acc. to statistical definition of entropy, the entropy of sys. is given by

$$S = k \ln W \quad \text{--- (23)}$$

where  $k$  is Boltzmann constant and  $W$  is the thermodynamic probability of system

Consider  $n$  moles of ideal gas at a pressure  $P$ , Volume  $V$  and temperature  $T$ . We know that molecules of a perfect gas obey Maxwell-Boltzmann statistics. The thermodynamic probability of macrostate  $(N_1, N_2, \dots, N_k)$  is given by

$$W = N! \prod_{i=1}^k \frac{(g_i)^{N_i}}{N_i!} \quad \text{--- (24)}$$

where  $k$  is Boltzmann constant and  $W$  is the thermodynamic probability of the system.

Consider  $n$  moles of an ideal gas at a pressure  $P$ , Volume  $V$  and temperature  $T$ . We know that molecules of a perfect gas obey Maxwell-Boltzmann statistics. The thermodynamic probability of macrostate  $(N_1, N_2, \dots, N_k)$

where  $N$  is total no. of molecules in the gas and  $g_i$  is the no. of cells in compartment  $i$

$$W = N! \prod_{i=1}^k \frac{(g_i)^{N_i}}{N_i!} V^N \quad [\text{Here } g_i = \alpha V]$$

$$W = C V^N \quad \text{--- (25)}$$

where  $C$  stands for

$$C = N! \prod_{i=1}^k \frac{(g_i)^{N_i}}{N_i!} \quad \text{--- (26)}$$

Using eqn. (25) in eqn. (23) we obtain

$$S = k \ln (C V^N)$$

$$S = k \ln C + k \ln V^N$$

$$S = k \ln C + Nk \ln V \quad \text{--- (27)}$$

Suppose an infinitesimal small amount of heat  $dQ$  is given to the perfect gas. Then according to first law of thermodynamics,

$$dQ = dU + PdV \quad \text{--- (28)}$$

Since the gas remains in equilibrium during infinitesimal change, the total internal energy  $U$  remains constant. Therefore  $A$  and  $B$  respectively.

$$dU = 0 \quad \text{--- (29)}$$

Eqn. (28) becomes

$$dQ = PdV \quad \text{--- (30)}$$

The change in entropy of gas during infinitesimal change is

$$dS = \frac{dQ}{T}$$

$$dQ = TdS \quad \text{--- (31)}$$

Substitute this value of  $dQ$  in eqn. (30) to obtain

$$TdS = PdV$$

$$\text{or} \quad \left(\frac{\partial S}{\partial V}\right)_U = \frac{P}{T} \quad \text{--- (32)}$$

Differentiate eq. (27) partially w.r.t.  $V$  keeping  $U$  constant

This gives

$$\left(\frac{\partial S}{\partial V}\right)_U = 0 + \frac{Nk}{V} = \frac{Nk}{V} \quad \text{--- (33)}$$

Comparing eqs. (32) and (33) we obtain

$$\frac{P}{T} = \frac{Nk}{V}$$

$$PV = NkT \quad \text{--- (34)}$$

If  $N_0$  is Avogadro number, then no. of molecules  $N$  in  $n$  moles of perfect gas

$$N = N_0 n \quad \text{--- (35)}$$

Substituting this value in eqn. (34) we obtain

$$PV = N_0 n k T$$

But

$$N_0 k = R = \text{universal gas constant}$$

Thus

$$PV = nRT \quad \text{--- (36)}$$

This is equation of state for an ideal gas of  $n$  moles.