Define entropy and discuss how entropy changes in reversible and irreversible processes.

Entropy :- If a substance takes in an amount of heat Q in a reversible process at a constant temperature T, then Q/T is called the "increase in entropy" of the substance. Similarly, if the substance gives up an amount of heat Q at constant temperature T, then Q/T is called the "decrease in entropy" of the substance. The change in entropy is denoted by ΔS. Thus

$$\Delta S = \frac{Q}{T}.$$

If the temperature of the substance does not remain constant during the process, we may consider the heat to be taken in or given up in successive small elements dQ such that the temperature remains sensibly constant for each element. The change in entropy will then be

$$\Delta S = \int \frac{dQ}{T}.$$

Change in entropy in reversible cycle (Clausius Theorem) :- The Clausius theorem states that "in any reversible cycle the net change in entropy is zero", that is,

$$\oint \frac{dQ}{T} = 0 .$$

Let us first prove it for a (reversible) Carnot cycle as shown in fig - (1).
Let us start with working substance in the state A. During the isothermal expansion AB, the working substance takes in an amount of heat Q_1 from the source at the constant temp T_1 of the source. Its entropy therefore increases by Q_1/T_1.

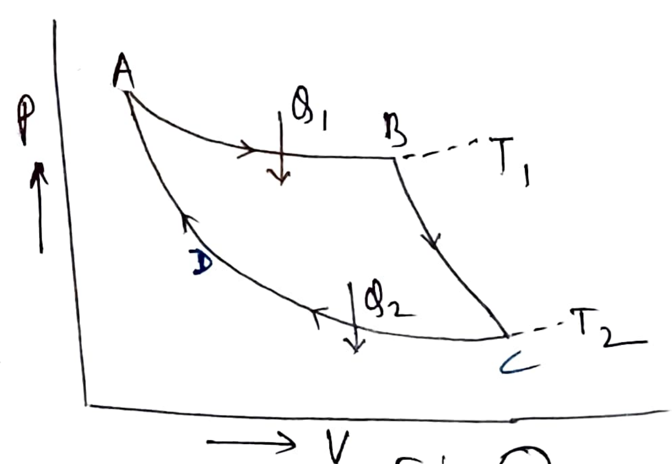


Fig - (1).

This is also the decrease in the entropy of the source. During the adiabatic expansion BC no heat is taken in or given up, so the entropy remains unchanged. During the isothermal compression CD, the working substance gives up an amount of heat Q_2 to the sink at constant temp T_2. Its entropy therefore decreases by Q_2/T_2. This is also the increase in the entropy of the sink. During the adiabatic compression DA there is again no change in entropy. Thus, for the whole cycle, the net increase in the entropy of the working substance is

$$\Delta S = \frac{Q_1}{T_1} - \frac{Q_2}{T_2}.$$

This is also the net decrease in the entropy of the source - sink system.

But, the definition of Kelvin's scale of temperature, $\frac{Q_1}{T_1} = \frac{Q_2}{T_2}$. Therefore

$$\Delta S = \frac{Q_1}{T_1} - \frac{Q_2}{T_2} = 0.$$

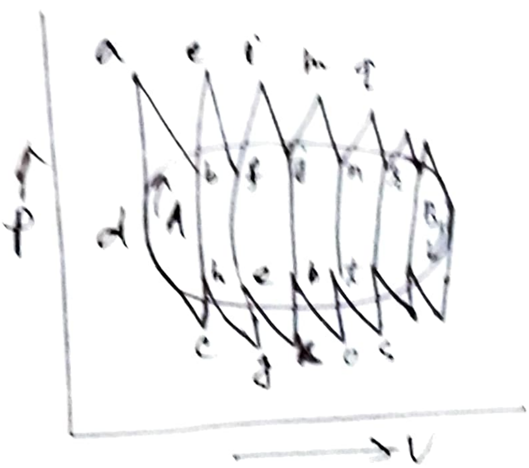
Thus, the net change in entropy of the working substance, and also of the surroundings during a complete Carnot cycle is zero.

If we regard the heat taken in by the substance as positive and heat given up as negative, then Q_1 will be positive and Q_2 will be negative. The above eqn then becomes

$$\Delta S = \frac{Q_1}{T_1} + \frac{Q_2}{T_2} = 0 \qquad (1)$$

This eqn indicates that the sum of the quantities Q/T is zero for a Carnot cycle.

Let us now consider the general case of any reversible cycle, indicated by the curve A → B → A as shown in fig (2).



We may consider this cycle fig (2) to be made up of a large number of elementary Carnot cycles abcd, efgh, ijkl, etc. Let us imagine that the substance, instead of tracing the smooth curve A → B → A, traces successively the cycles abcd, efgh, ijkl, ... In following these cycles the portions bh, fl, jp, nt and so on, are traversed twice in the reverse order, and their effects are thus cancelled out. The net effect of the whole process is that the substance goes along the closed zigzag path abefi ... ghcda.

Now for each elementary Carnot cycle the above relation (i) holds and may be written in the form

$$\delta s = \frac{\delta Q_1}{T_1} + \frac{\delta Q_2}{T_2} = 0$$

Taking the sum of such results for all the cycles we conclude that for the closed zigzag path abefi, ... ghcda, we have,

$$\Delta s = \sum \frac{\delta Q}{T} = 0 .$$

If the adiabatics of the elementary Carnot cycles be infinitesimally close together, they will be connected with infinitesimally small isothermals. Then the zigzag path will coincide with the smooth curve $A \to B \to A$, and we may write

$$\Delta s = \oint \frac{dQ}{T} = 0$$

The symbol $\oint$ denotes the integration over the whole cycle. Thus, in any reversible cycle the net change in entropy is zero. This is Clausius theorem.