of an isolated system remains constant or increases according as the process is reversible or irreversible i.e., $dS \geq 0$.

CLAUSIUS INEQUALITY : PRINCIPLES OF INCREASE OF ENTROPY :

A system passes through a cyclic process which consists of a set of states and finally comes to the initial state to start with. As shown in the figure, the original cyclic process represented as AKPH may be supposed to consist of large number of small steps represented by *ab, bc, cd, de, ef* etc, these isothermals are at temperatures T_1, T_2, T_3, ... T_n and larger is the number of steps, better will be the simulation of the original cycle with a set of states on isotherms. Let Q_1, Q_2, Q_3, etc be the heat absorbed by the system at these temperatures. Let there be a reservoir at temperature T_0 higher than the highest of T_1, T_2, T_3.....T_n. We will consider n number of Carnot engines between reservoir at T_0 and heat reservoirs at T_1, T_2, T_3.....T_n. These Carnot engines absorb heat Q_1^0, Q_2^0, Q_3^0.....Q_n^0 from the reservior at T_0 and reject Q_1, Q_2, Q_3,.......Q_n at the heat reserviors at temperatures T_1, T_2, ...T_n.

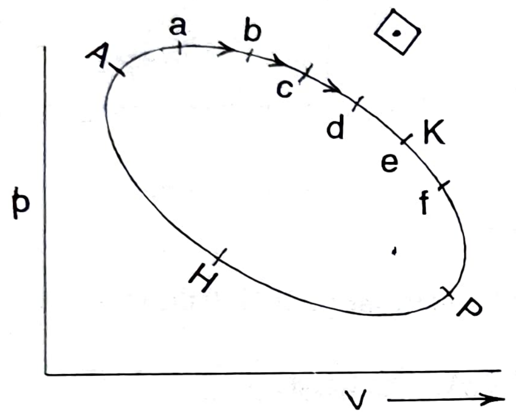

Fig. 10.6

Now, during a cyclic process the amount of work performed is equal to the amount of heat absorbed. Due to operations of the Carnot's engines, the heat reservoirs at T_1, T_2, T_3, ...T_n do not lose or gain heat, the total heat absorbed from T_0 would be completely converted into work.

Now, $Q_0 = Q_1^0 + Q_2^0 + Q_3^0 + \ldots\ldots\ldots\ldots + Q_n^0$.

Because of Carnot operations, we have,

$$\frac{Q_1^0}{T_0} = \frac{Q_1}{T_1} \Rightarrow Q_1^0 = T_0\left(\frac{Q_1}{T_1}\right)$$

So for all the Carnot engines, we get,

$$Q_o = T_o\left(\frac{Q_1}{T_1} + \frac{Q_2}{T_2} + \ldots\ldots\ldots\ldots\ldots + \frac{Q_n}{T_n}\right)$$

$$= T_o \sum \frac{Q_i}{T_i}$$

and this is to be completely converted into work. But this is not possible in accordance with Second law. It means that heat Q_1^0, Q_2^0, etc cannot enter the system.

$$Q_o = T_o \sum \frac{Q_i}{T_i} \leq 0$$

$$\Rightarrow \sum_{i=1}^{n} \frac{Q_i}{T_i} \leq 0$$

If n is very large, then the above inequality can be written as

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

$$\Rightarrow \oint \frac{dQ}{T} \leq 0.$$

This is called **CLAUSIUS INEQUALITY.**

Let us consider an irreversible cycle, the transformation ABC is an irreversible path and the back transformation from C to A through a reversible process R,

From Clausius Inequality,

$$\int_A^C \left(\frac{dQ}{T}\right)_I + \int_C^A \left(\frac{dQ}{T}\right)_R \leq 0.$$

$$\Rightarrow \int_A^C \left(\frac{dQ}{T}\right)_I + (S_A - S_C) \leq 0$$

$$\Rightarrow \left[\int_A^C \left(\frac{dQ}{T}\right)_I - (S_C - S_A)\right] \leq 0.$$

$$\Rightarrow (S_C - S_A) \geq \int_A^C \left(\frac{dQ}{T}\right)_I$$

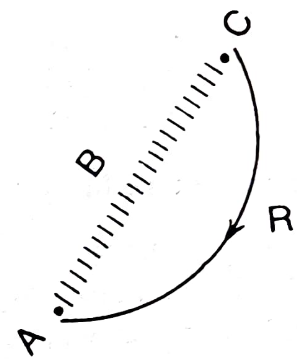

Fig. 10·7

If the system under consideration is isolated (adiabatic), $dQ = 0$, so

$$(S_C - S_A) = \Delta S \geq 0$$

$$\Rightarrow S_c \geq S_A$$

Thus for any transformation occurring in an isolated system, ***the final entropy is greater than that of the initial state.*** The entropy of an isolated system cannot decrease. This fact leads to establish the Principle of increase of entropy as enunciated earlier.

Calculation of entropy change in different irreverible process :

To calculate the entropy change in an irreversible process we have to replace the process by an equivalent reversible process by which we reach from a given initial state to a given final state. This is because

$$dQ_r = du + pdv \text{ and } dQ_{irr} = du + dw$$

Where dQ_r denotes heat change in reversible process and dQ_{irr} denotes heat change in irreversible process.

Now, for identical state changes.

$$(du)_{irr} = (du)_r$$

$$\therefore dQ_r = dQ_{irr} + pdv - dw$$

$$\text{or, } \frac{dQ_r}{T} = \frac{dQ_{irr}}{T} + \frac{pdv - dw}{T}$$

In case of reversible process, the second term on the right vanishes because $dw = pdv$ and therefore,

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

So we are to replace the irreversible process by an equivalent reversible path.