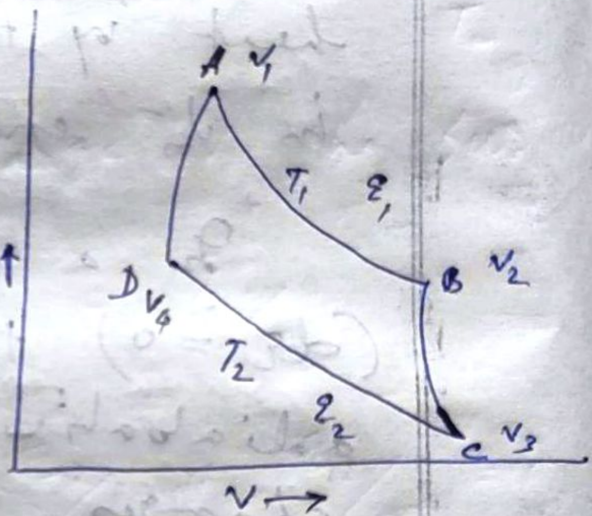
* Entropy changes in Reversible and Irreversible Process :-

(i) Entropy changes in Reversible cyclic Process –

In a carnot cycle, we have

$$\frac{dq_1}{T_1} = \frac{dq_2}{T_2}$$

$$\Rightarrow \frac{dq_1}{T_1} + \left(-\frac{dq_2}{T_2}\right) = 0$$



where dq_1 is the heat received from source and dq_2 is the heat given up to the sink. hence $-dq_2$ means heat absorbed, so we may write,

$$\frac{dq_1}{T_1} + \frac{dq_2}{T_2} = 0$$

Along the adiabatic steps BC and DA, heat changes is nil. so for entire carnot cycle,

$$\oint \frac{dQ}{T} = \frac{dQ_1}{T_1} + \frac{dQ_2}{T_2} = 0$$

But, $\oint ds = \oint \frac{dQ}{T}$

$\therefore$ for a carnot cycle, $\oint ds = 0$

In any reversible cyclic process, the net increase in entropy of the system is zero. #

(ii) Entropy changes of the Universe —

In estimating the entropy change of a cyclic process, we have considered only the working system but the entropy changes of the source and the sink or surrounding have not been taken into account. When heat transfer takes place the surrounding also gain or lose heat and so their entropies also change. The total entropy change which would cover the entropy change in the working system as also the surrounding is named entropy change of the Universe. Hence,

$$\Delta S_{Uni} = \Delta S_{sys.} + \Delta S_{surr.}$$

Considering the carnot cycle, we know

$$\Delta S_{sys} = 0$$

and loss of entropy of the source $= \frac{q_1}{T_1}$

gain of entropy of the sink $= \frac{q_2}{T_2}$

Hence the entropy change of the surrounding,

$$\Delta S_{surr.} = q_1/T_1 + q_2/T_2$$

already we have, $q_1/T_1 + q_2/T_2 = 0$

hence, $\Delta S_{surr} = 0$

$$\therefore \Delta S_{Uni} = \Delta S_{sys.} + \Delta S_{surr.}$$

$$= 0$$

ie. The net entropy change in a reversible process is zero.

(iii) Entropy changes in Irreversible Process :-

Since entropy is a state function, the entropy of a system from a given state I to a given state II is always the same and independent on the path.

If the path is reversible, the entropy is given by,

$$\Delta S = S_{II} - S_{I} = \int_{I}^{II} \frac{dq_r}{T}$$

Hence, in order to compute the entropy change of a system in a irreversible process, we may conceive of taking the system from state I to state II along any reversible path and then devide the heat absorbed at each point by the tempr. and sum up them.

It may be stated that in any irreversible process there would be a net increase in entropy. Some simple processes would illustrate this.

(a) Irreversible flow of heat :-

Suppose a heat reservoir at temp. T_1 is brought in contact with a second reservoir at a lower temp. T_2. Let a small quantity of heat q flow from T_1 to T_2, thus

the decrease in entropy of $A = \frac{q}{T_1}$

the increase in entropy of $B = \frac{q}{T_2}$

$\therefore$ net entropy change $= \frac{q}{T_2} - \frac{q}{T_1}$

$$= q\,\frac{T_1 - T_2}{T_1 T_2}$$

$\because T_1 > T_2$, $\quad = +ve$ quantity

$\therefore$ hence irreversible flows of heat leads to an increase in entropy.

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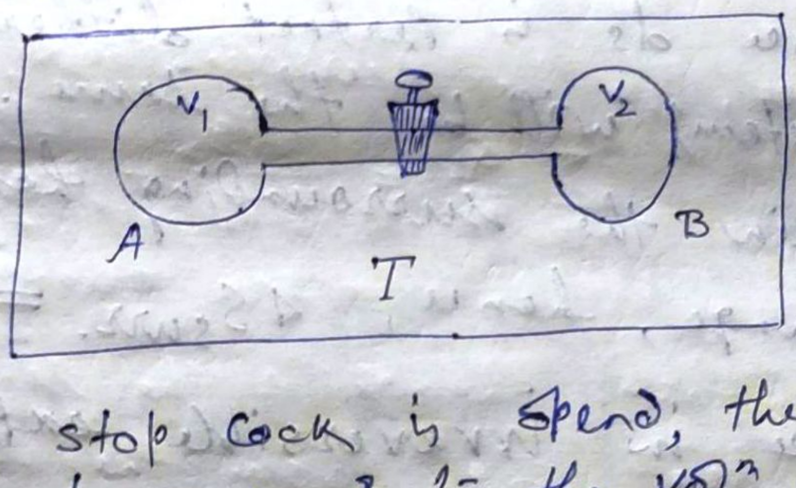
(b) Irreversible isothermal expansion of an ideal gas :–

Suppose n moles of an ideal gas is enclosed in a vessel A of vol^m. V_1. The vessel is connected through a stop cock to a completely evacuated vessel B of vol^m. V_2. Temp^r. T of the system is insulated.



When stop cock is opend, the gas is spontaneously expand to the vol^m $(V_1 + V_2)$

The work is $= 0$ (irreversible Process)

heat supplied (q) from surrounding $= 0$

$\Delta H = 0$; T is const.

$\therefore q = \Delta U + w$

$= 0$

Now if this expansion of the gas were carried out reversibly at $T°K$ from vol^m. V_1 to vol^m. $(V_1 + V_2)$, the heat absorbed,

$$q_{rev.} = \Delta U + RT \ln \frac{V_1 + V_2}{V_1}$$

$$= 0 + RT \ln \frac{V_1 + V_2}{V_1}$$

$$\therefore \Delta S_{sys.} = \frac{q_{rev.}}{T}$$

$$= R \ln \frac{V_1 + V_2}{V_1}$$

Since ds is perfect differential, ΔS_{irr} (system) will be the same.

Again the surrounding has no thermal change, hence, $\Delta S_{surr.} = 0$

Hence in irreversible expansion,

$$\Delta S_{uni} = \Delta S_{sys} + \Delta S_{sur.}$$

$$= R \ln \frac{V_1 + V_2}{V_1} + 0$$

$$= R \ln \frac{V_1 + V_2}{V_1}$$

$$= +ve \text{ quantity}$$

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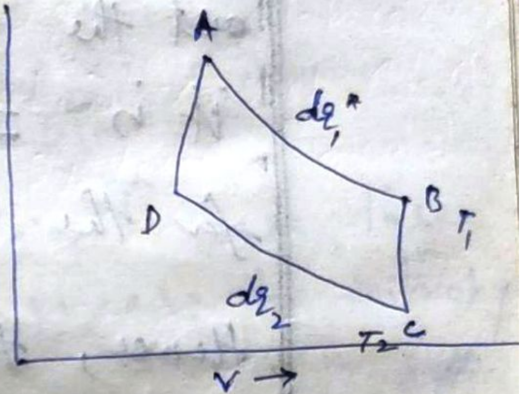
(c) Irreversible Cyclic Process :–

Considering a cyclic process, similar to that of Carnot cycle, in which one or more of its stages are performed irreversibly.



Let ABCD denote the cycle, in which AB and CD are the isothermal stages. Let us further suppose, the absorption of heat dq_1^* by the system at tempr. T_1 from the source along AB is irreversible. The rest of the stages are carried out reversibly. The heat dq_2 is given up to the sink at tempr. T_2 along CD.

This is an irreversible cycle and hence the efficiency of the engine is less than that of the carnot cycle, or

$$\frac{dq_1^* - dq_2}{dq_1^*} < \frac{T_1 - T_2}{T_1}$$

$$\Rightarrow \quad \frac{dq_2}{T_2} - \frac{dq_1^*}{T_1} > 0 \longrightarrow (1)$$

When the cycle is completed, the engine has returned to its initial state,

$$\therefore \Delta S_{sys.} = 0$$

Now considering the surroundings and find out the Q/T terms,
it is $-\frac{dQ_1^*}{T_1}$ for the source and $\frac{dQ_2}{T_2}$ for the sink.

Hence, for the surroundings,

$$\sum \frac{Q}{T} = \frac{dQ_2}{T_2} - \frac{dQ_1^*}{T_1} > 0$$

$$= +ve \text{ quantity}$$

The heat change of the sink is reversible. The heat dQ_1^* from the source was taken by the system irreversibly. The source has lost dQ_1^* and its entropy has decreased. The entropy change of the source from $A \longrightarrow B$ would be evaluated as stated earlier by supposing the loss of heat dQ_1 occurred reversibly and consequently

$$\Delta S_{source} = -\frac{dQ_1^*}{T}$$

$\Rightarrow$ We can say, $\Delta S_{sur.} = \frac{dq_2}{T_2} - \frac{dq_1}{T_1} > 0$

In this irreversible cyclic Process,

$\therefore \Delta S_{uni} = \Delta S_{sys} + \Delta S_{sur.}$

$= 0 + \Delta S_{sur} > 0$

$=$ +ve quantity

In an irreversible cyclic Process, there would occur a net increase in entropy.

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