Chemical Thermodynamics (II)

The Second law of Thermodynamics:-

(i) Kelvin statement — It is impossible by an inanimate material agency (an engine) to derive mechanical effect (work) from any portion of matter by cooling it below the temp.r of the coldest of the surrounding

(ii) Planck's statement — It is impossible to construct an engine, working in a cycle, which would produce no effect except the raising of a weight and the cooling of a heat reservoir.

(iii) Ostwald statement — It is impossible to construct a perpetual motion machine of the second kind.

Thus, it is true that, heat obtained from a supplier at the same or lower temp.r than that of the engine can't be transformed into work in a cyclic process. But when heat flows from a reservoir at higher temp (called the source) to a reservoir at lower temp. (called the sink), it can be transformed into work with the intervention of an engine. The engine would pick-up Q calories from source transform only a portion of it into work, W and return the rest of the heat Q' to the sink.

According to the Ist law, $W = Q - Q'$

The amount of work to be obtained from a given amount of heat will depend on the nature of the engine and the temp. of the source and sink, we can define the efficiency of an engine,

$$\eta = \frac{\text{work performed}}{\text{heat supplied}} = \frac{W}{Q}$$

$$= \frac{Q - Q'}{Q} = 1 - \frac{Q'}{Q}$$

* Carnot Cycle :
* The mathematical expression of 2nd law :
* The efficiency of a heat engine :

The efficiency of an engine can be realised by considering a cyclic Process. The most ideal of such cyclic processes would be the Carnot's Cycle.

Sadi Carnot (1824) one brilliant French engineer, who explained clearly how and to what extent work is obtainable from heat. Carnot started with two essential pre-requisities. Firstly, to estimate the work obtained from heat during its passage from a higher to a lower temp. the external agency (the engine) must come back to its original state so as to exclude any work involved in its own change. That is the engine must operate in complete cycles.

Secondly, to obtain max^m work in a cycle of operations, every step should be carried out in a reversible fashion.

The typical Carnot cycle consists of four successive operations using one gm. mole of perfect gas as the working substance: we take the gas enclosed in a cylinder fitted with a frictionless piston. To start with, the cylinder containing the gas is kept in a large thermostate at the higher temp^r (source) and suppose the vol^m. of the gas be V_1

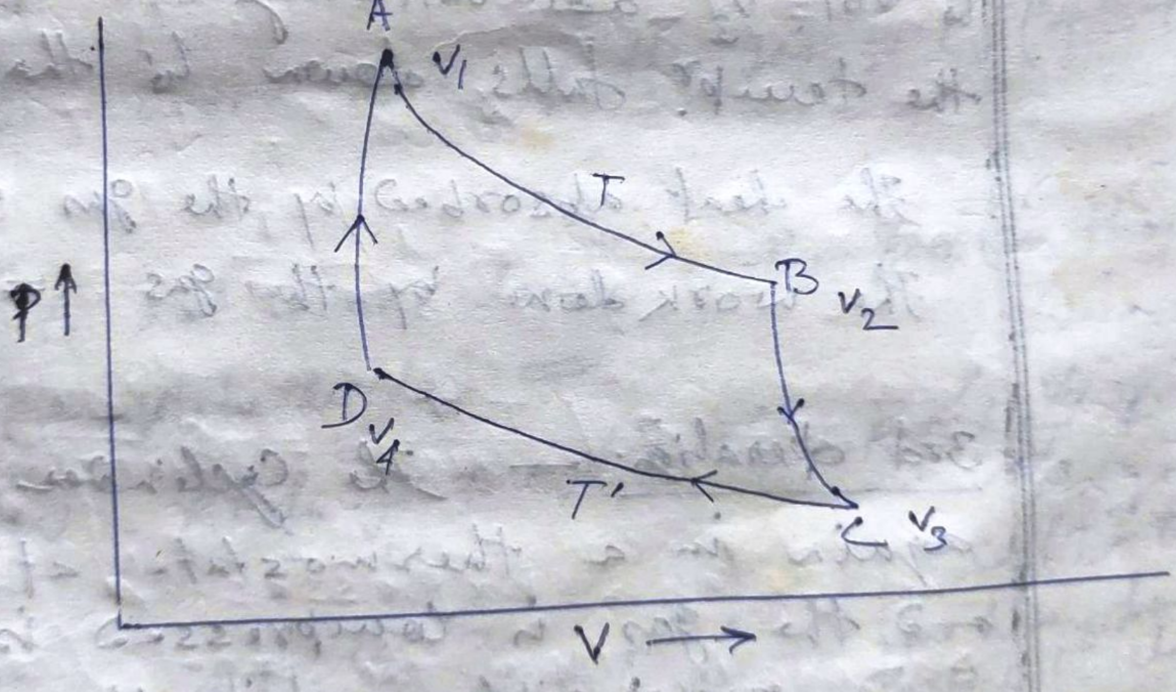

fig. carnot cycle.

Ist operation — The gas is allowed to expand isothermally and reversibly from the vol^m. V_1 to V_2.

The heat absorbed by the gas $= Q$

The work done by the gas $= RT \ln \frac{V_2}{V_1}$

$\because$ the gas is ideal, we know $Q = RT \ln \frac{V_2}{V_1}$

2nd operation — The cylinder is next taken out of the thermostate and kept in a thermally insulated enclosure. The gas is allowed to expand further from vol^n. V_2 to vol^m. V_3 adiabatically and reversibly until the temp^r. falls down to that of sink, T'.

The heat absorbed by the gas $= 0$

The work done by the gas $= C_v(T - T')$

3rd operation — The cylinder is then placed again in a thermostate at temp^r. T' (sink) and the gas is compressed isothermally and reversibly until the vol^m changes to V_4 from V_3

The heat given out by the gas $= Q'$

The work done by the gas $= RT' \ln \frac{V_4}{V_3}$

4th operation :— The cylinder is now thermally isolated as in operation 2nd. Now the gas is compressed adiabatically and reversibly to its initial volm. V_1 from V_4 and its original temp. T is attained. Thus the gas come back to its initial state. Hence the cycle is complete.

The heat absorbed by the gas = 0

The work done by the gas = $C_v(T'-T)$

∴ The net work done by the gas (in the complete cycle) =

$$W = RT \ln \frac{V_2}{V_1} + C_v(T-T') + RT' \ln \frac{V_4}{V_3} + C_v(T'-T)$$

$$= RT \ln \frac{V_2}{V_1} + RT' \ln \frac{V_4}{V_3}$$

$$= RT \ln \frac{V_2}{V_1} - RT' \ln \frac{V_3}{V_4}$$

$$= RT \ln \frac{V_2}{V_1} - RT' \ln \frac{V_2}{V_1}$$

$$\therefore W = R(T-T') \ln \frac{V_2}{V_1}$$

We have, from 2 adiabatic changes

$TV_2^{\gamma-1} = T'V_3^{\gamma-1}$

$TV_1^{\gamma-1} = T'V_4^{\gamma-1}$

$\therefore V_2/V_1 = V_3/V_4$

∴ The efficiency of the Process is given by,

$$\eta = \frac{W}{Q}$$

$$= \frac{R(T-T')\ln\frac{V_2}{V_1}}{RT\ln\frac{V_2}{V_1}}$$

$$\eta = \frac{T-T'}{T}$$

$$\eta = 1 - \frac{T'}{T}$$

$$\text{or } \eta = \frac{W}{Q} = 1 - \frac{T'}{T}$$

$$\therefore W = Q\cdot\left(\frac{T-T'}{T}\right) = Q\frac{\Delta T}{T}$$

This relation expresses the max. work obtainable from the heat flowing from T to T'.

This is the mathematical form of the 2nd law of thermodynamics.

This is the expression of efficiency of a heat engine