Limitation of first law of thermodynamics

The first law states about Conversion of energy i.e different form of energy is Interconvertible. It means One form of energy disappears then equivalent amount of another form of energy appears.

First law does not tell whether the change will atall occur and if occurs to what extent. It does not tell about the direction of change, extent of change and feasibility of the change.

Spontaneous or Irreversible Processes-

Changes which occur without the aid or help of any external agency are called Spontaneous processes.

The following examples can illustrate spontaneous processes.

When a hotter body is connected to a colder body then heat flows from the hotter body to the colder body till temperature of both is same and, and equilibrium is attained.

The heat will not flow from colder to the hotter body so the process in irreversible. Now we can say that the spontaneous process is an irreversible, because its process is one directional or such process occurs in one direction. In order to revert the spontaneous change there is a outsider agency required to revert it.

No useful work is done in irreversible process, but using a suitable mechanism, useful work can be acheived. It means the work obtained in irreversible process is much less than the work obtained in reversible manner i.e In a "reversible" process work obtained is maximum.

Cyclic Process: — When a system, after completing a series of changes, returns to original state, is said to have completed a cycle. The entire process is know as cyclic process.
In a cyclic process, net change in internal energy is zero.
i.e $\Delta U = 0$, Then from 1st law $\Delta U = q + w$

$$\text{or } 0 = q + w, \quad \text{Or } q = -W$$

2nd Law of thermodynamics: — The law which specifies the condition in which transformation of heat into work can take place is called the 2nd Law of thermodynamics

Clausius or Kelvin statement: — It is impossible to construct heat engine which is contineously abstract heat from a single body and convert whole of it into work without leaving any change in working system.

Plank's statement of 2nd Law: — It is impossible to construct a machine operating in cycles that will convert heat into work without producing any other changes in the surrounding.

Thomson's statement: — All natural and spontaneous process tends to go to a state of equilibrium.

Carnot Theorem

These two deductions may be dedue on the basis of the validity of the 2nd Law. According to this theorem working between the same temperature limit-

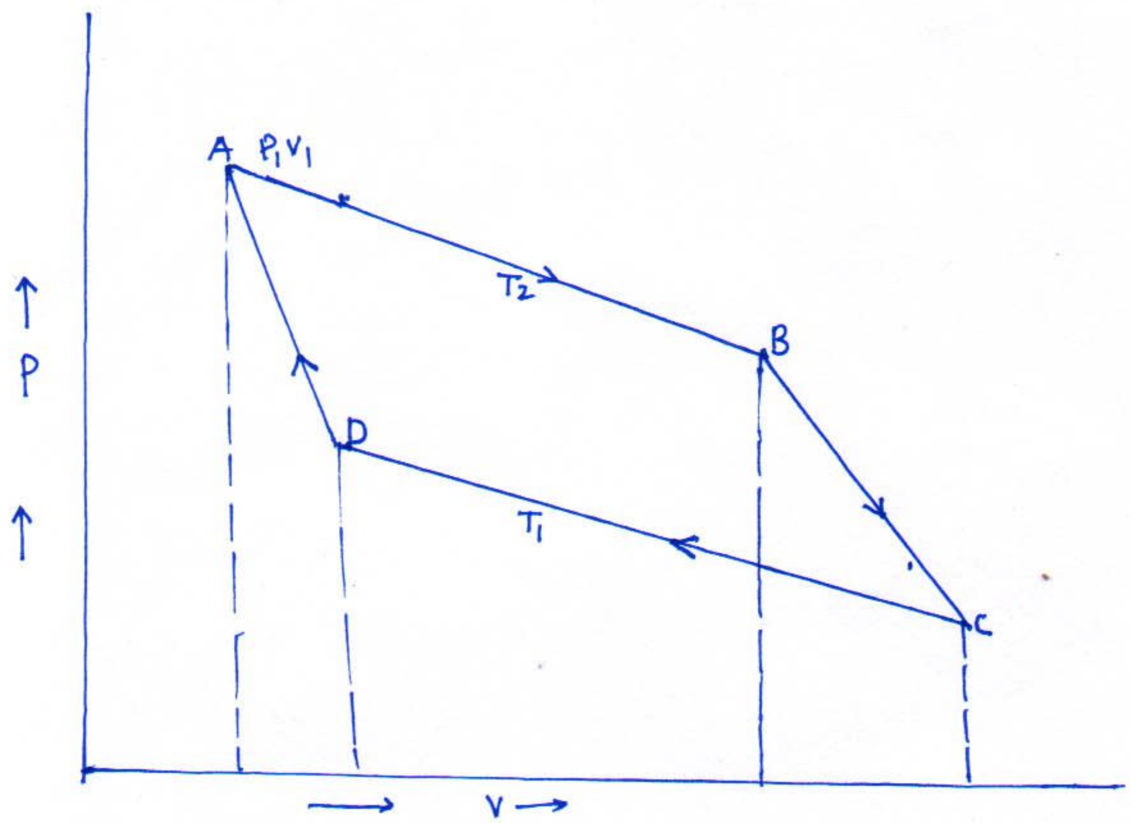
(a) A reversible engine is more efficient than an irreversible.

(b) All reversible engines are equally efficient.

Or "All Periodic machines working reversibly between the same two temperature have the same efficiency" This statement is known as Carnot theorem.

Carnot Cycle

Carnot employed a reversible Cycle to demonstrate the maximum convertibility of heat into work.
The system Consist of one mole of an ideal gas which is Subjected to a Series of four Successive Operations this is Known as four strockes.



Strocke I : - Isothermal expansion :-
Isothermal expansion of a gas in reversible manner at temperature (Maxm) T_2.
Isothermally expansion of a gas in Now expansion of gas from point A having volume V_1 to Point B, volume V_2 at temperature T_2.

From 1st law $\Delta U = q + w$ [∵ Process is isothermal so, temp is constant so $\Delta U = 0$]

$$q = -w$$

let q_2 is heat absorbed by the system at temp. T_2 and w_1 is the workdone by the system On surrounding.

then,
$$q_2 = -w_1$$
$$= -\left(-RT_2 \ln \frac{V_2}{V_1}\right)$$
$$= +RT_2 \ln \frac{V_2}{V_1}$$
$$q_2 = RT_2 \ln \frac{V_2}{V_1} \quad \text{——— (1)}$$

Strock II : - Adiabetic expansion of a gas from V_2 to V_3.

(i) Heat absorbed = 0

(ii) Workdone by the gas $(-w_2) = -C_v(T_2 - T_1)$ ——— (2)

where C_v is heat Capacity at constant volume.

Strock III : — Isothermal and reversible Compression at T_1, Volume V_3, V_4.

(i) Heat given out = q_1

(ii) Work done On the system = w_3

$$\therefore \; -q_1 = w_3 = RT_1 \ln \frac{V_4}{V_3} \quad \text{——— (3)}$$

Stroke IV :- Adiabetic Compression of gas from V_4 to V_1

(i) Heat given out = 0

(ii) Work done on the system $W_4 = C_v\,(T_2 - T_1)$

Now the net heat absorbed (q) by the ideal gas in the whole cycle is given by

$$q = (q_2) + (-q_1) = RT_2 \ln\frac{V_2}{V_1} + RT_1 \ln\frac{V_4}{V_3} \quad \text{— 3}$$

$$= RT_2 \ln\frac{V_2}{V_1} - RT_1 \ln\frac{V_3}{V_4} \quad \text{— (4)}$$

On the basis of Adiabetic expansion the following equation can be Obtained

$$C_v \ln\frac{T_2}{T_1} = R \ln\frac{V_3}{V_2} \quad (\text{For stage II})$$

$$C_v \ln\frac{T_2}{T_1} = R \ln\frac{V_4}{V_1} \quad (\text{For stage IV})$$

Or, $R \ln\frac{V_3}{V_2} = R \ln\frac{V_4}{V_1}$

or, $\frac{V_3}{V_4} = \frac{V_2}{V_1}$

Now net heat absorbed is q,

$$q = (q_2) + (-q_1) = RT_2 \ln\frac{V_2}{V_1} - RT_1 \ln\frac{V_3}{V_4}$$

$$= RT_2 \ln\frac{V_2}{V_1} - RT_1 \ln\frac{V_2}{V_1} \quad \left[\because \frac{V_3}{V_4} = \frac{V_2}{V_1}\right]$$

$$\therefore q = R(T_2 - T_1)\ln\frac{V_2}{V_1} \quad \text{— (5)}$$

Again Net work done by gas :-

$$W = (-W_1) + (-W_2) + (W_3) + (W_4)$$

On substituting the value of $-W_1$, $-W_2$, W_3 and W_4, we have.

$$W = RT_2 \ln\frac{V_2}{V_1} - \cancel{C_v(T_2 - T_1)} + RT_1 \ln\frac{V_4}{V_3} + \cancel{C_v(T_2 - T_1)}$$

$$W = RT_2 \ln\frac{V_2}{V_1} - RT_1 \ln\frac{V_3}{V_4} \quad \left[\because \frac{V_3}{V_4} = \frac{V_2}{V_1}\right]$$

$$\therefore W = RT_2 \ln\frac{V_2}{V_1} - RT_1 \ln\frac{V_2}{V_1} = R(T_2 - T_1)\ln\frac{V_2}{V_1} \quad \text{— (6)}$$

It follows from eqn (5) and (6) that $q = W$, thus essential condition for a cyclic process that the net work done is equal to the net heat absorbed is fully satisfied.

Relation between W, q_2 and higher temperature T_2 .

$$\because W = R(T_2 - T_1)\ln\frac{V_2}{V_1} \quad \text{— (6)}$$

$$\text{and } q_2 = RT_2 \ln\frac{V_2}{V_1} \quad \text{— (1)}$$

On dividing eqn (6) by eqn (1) we have

$$\frac{W}{q_2} = \frac{T_2 - T_1}{T_2}$$

$$\text{or } W = q_2\frac{(T_2 - T_1)}{T_2} \quad \text{— (7)}$$

Efficiency of a Heat engine: → The fraction of heat absorbed by an engine, that it can convert in to work gives the efficiency (η) of the engine.

$$\text{Efficiency } \eta = \frac{W}{q_2} = \frac{T_2 - T_1}{T_2}, \text{ if } T = 0, \text{ efficiency} = 1$$

The net heat absorbed by the system is q, then work $W = q_2 - q_1$ — 8

From eqn (7) and (8) $\frac{q_2 - q_1}{q_2} = \frac{T_2 - T_1}{T_2} = \eta$ (Efficiency of heat engine).