

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 at all 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 is irreversible. We can say that the spontaneous process is an irreversibility 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 achieved. 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, it is said to have completed a cycle. The entire process is known as cyclic process. In a cyclic process, net change in internal energy is zero.
i.e. $\Delta U = 0$, Then from 1st law $\Delta U = q + w$
or $0 = q + w$, 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 continuously abstract heat from a single body and convert whole of it into work without leaving any change in working system.

Planck'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 deduced 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 engine.

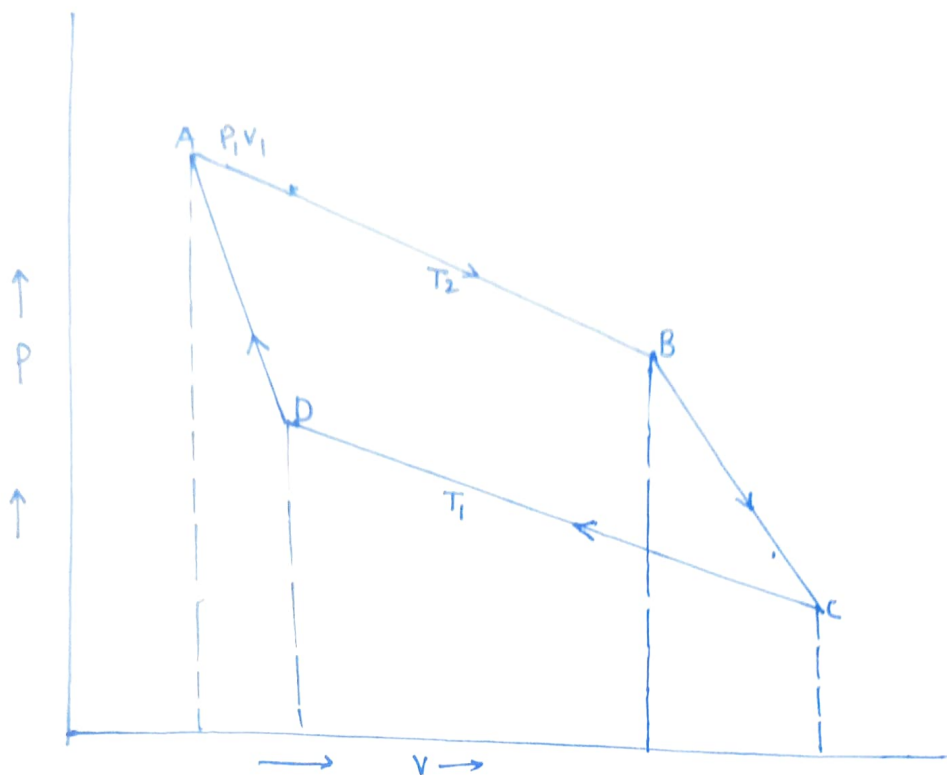
(b) All reversible engines are equally efficient.

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 strokes.



Stroke I: - Isothermal expansion:-

Isothermally expansion of a gas in reversible manner at temperature (Max) T_2 .
Now expansion of gas from point A having volume V_1 to

Point B, volume V_2 at temperature T_2 .

$$\text{From 1st law } \Delta U = q + w$$

$$q = -w$$

\therefore Process is isothermal so temp is constant so $\Delta U = 0$

Let q_2 is heat absorbed by the system at temp. T_2 and w_1 is the work done by the system on surrounding.

$$\text{then, } q_2 = -w_1$$

$$= -(-RT_2 \ln \frac{V_2}{V_1})$$

$$= +RT_2 \ln \frac{V_2}{V_1}$$

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

Stroke II: - Adiabatic expansion of a gas from V_2 to V_3 .

(i) Heat absorbed = 0

$$\text{(ii) Work done by the gas } (-w_2) = -C_v (T_2 - T_1) \quad \text{--- (2)}$$

where C_v is heat capacity at constant volume.

Stroke 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

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