The Second Law of Thermodynamics

Limitations of first law. Need for the second law:-

The First law of thermodynamics, has following limitations:-

1) The first law establishes definite relationship b/w the heat absorbed and the work performed by a system in a given process. But it puts no restriction on the direction of flow of heat.
According to the first law, it is not impossible to extract heat from ice by cooling it to a low temperature and then use it for warming water. But it is known from experience that such a transfer of heat from lower to a higher temperature is not possible without expenditure of energy, i.e. without doing some external work. It is known that heat flows spontaneously i.e. of its own accord, from a higher to a lower temperature.

2) According to the First law, the energy of an isolated system remains constant during a specified change of state. But it does not tell whether a specified change or a process including a chemical reaction can occur spontaneously, i.e., whether it is feasible.

3) The first law, states that energy of one form can be converted into an equivalent amount of energy of another form. But it does not tell that heat energy cannot be completely converted into an equivalent of work.

These point proves that there is need of second Law of thermodynamics.

The second law helps us to determine the direction in which energy can be transferred. It is helping us to predict whether a given process or a chemical reaction can occur spontaneously.

It introduces new concept of entropy and find the equilibrium conditions.

It is known from experience that although various forms of energy can be completely transformed into one another, yet heat is a typical form of energy which can not be completely transformed into work.

The second Law helps us to calculate the maximum fraction of heat that can be converted into work in a given process.

* Entropy can be thought of as arising from the dispersal or degradation of the total energy of the isolated system.

Spontaneous or Irreversible Processes :-

Natural processes are spontaneous and irreversible. A few examples are given below :-

1. Water flows downhill spontaneously.

2) Flow of heat from one end to the another cold end.

3) The diffusion of solute from a more concentrated solution to a less concentrated solution when these come into contact proceeds spontaneously till the concentration becomes uniformly the same, until attainment of equilibrium.

4) A gas expands spontaneously from a region of high pressure to a region of low pressure in a vacuum.

Cyclic Processes :-

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 processes.

The internal energy of a system depends only upon its state, it follows that in a cyclic processes the change of internal energy is zero, i.e. $\Delta U = 0$.
According to First law,

$$\Delta U = 0 = q + w$$

$$\text{or} \quad q = -w$$

If the series of changes in a cycle are conducted at constant temperature, the cycle is said to be a reversible cycle.