# Limitations of the First law. Need for the Second law.

1. The First law establishes definite relationship between 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, for example, 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 a lower to a higher temperature is not possible without expenditure of energy, *i.e.*, without doing some external work. It is known, on the other hand, 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 amount of work. There is thus need for another law, *viz.*, the Second law of thermodynamics.

The Second law helps us to determine the direction in which energy can be transferred. It also helps us to predict whether a given process or a chemical reaction can occur spontaneously. It introduces a new concept of entropy. It also helps us to know 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 cannot 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 an isolated system.

# Spontaneous or Irreversible processes

1. Water flows downhill spontaneously. We cannot reverse the direction of flow without some external aid.

2. If a bar of metal is hot at one end and cold at the other end, heat flows spontaneously from the hot end to the cold end until the temperature of the rod becomes uniform throughout, *i.e.*, until equilibrium is attained. This process, evidently, cannot be reversed. Our experience does not show that a metal bar having uniform temperature can become hot at one end and cold at the other end spontaneously.

3. The diffusion of a solute from a more concentrated solution to a less concentrated solution when these are brought into contact proceeds spontaneously till the concentration becomes uniformly the same, *i.e.*, till the equilibrium is attained. This process also cannot be reversed because once the concentration becomes uniform, it is not possible to make spontaneously one part of the solution more concentrated than any other part.

4. Heat flows spontaneously from a hot reservoir to a cold reservoir. For the reverse process, *i.e.*, for the transfer of heat from a cold reservoir to a hot reservoir, as in a refrigerator, energy has to be supplied from outside the system.

5. Electricity flows spontaneously from a point at a higher potential to a point at a lower. potential. The direction of flow of current can be reversed only by applying an external field in the opposite direction,

6. A gas expands spontaneously from a region of high pressure to a region of low pressure or in vacuum.