

**Marwari college Darbhanga**

**Subject---physics (Hons)**

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**Paper—02 ; Group –A**

**Topic--- second law of thermodynamics ( Thermal physics)**

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### **Second law of thermodynamics**

The second law of thermodynamics states that the total entropy of an isolated system can never decrease over time, and is constant if and only if all processes are reversible. Isolated systems spontaneously evolve towards thermodynamic equilibrium, the state with maximum entropy.

The second law has been expressed in many ways. Its first formulation is credited to the French scientist Sadi Carnot, who in 1824 showed that there is an upper limit to the efficiency of conversion of heat to work in a heat engine. This aspect of the second law is also known as Carnot's rule or limit.

The second law is concerned with the direction of natural processes. It asserts that a natural process runs only in one sense, and is not reversible. For example, when a path for conduction and radiation is made available, heat always flows spontaneously from a hotter to a colder body. Such phenomena are accounted for in terms of entropy.

## **Entropy**

entropy is an extensive property of a thermodynamic system. It is closely related to the number  $\Omega$  of microscopic configurations (known as microstates) that are consistent with the macroscopic quantities that characterize the system (such as its volume, pressure and temperature). Entropy expresses the number  $\Omega$  of different configurations that a system defined by macroscopic variables could assume. Under the assumption that each microstate is equally probable, the entropy  $S$  is the natural logarithm of the number of microstates, multiplied by the Boltzmann constant  $k_B$ . Formally (assuming equiprobable microstates).

$$S = k_B \ln \Omega$$

Macroscopic systems typically have a very large number  $\Omega$  of possible microscopic configurations. For example, the entropy of an ideal gas is proportional to the number of gas molecules  $N$ . The number of molecules in 22.4 liters of gas at standard temperature and pressure is roughly  $6.022 \times 10^{23}$  (the Avogadro number).

The second law of thermodynamics states that the entropy of an isolated system never decreases over time. Isolated systems spontaneously evolve towards thermodynamic equilibrium, the state with maximum entropy. Non-isolated systems, like organisms, may lose entropy, provided their environment's entropy increases by at least that amount so that the total entropy either increases or remains constant. Therefore, the entropy in a specific system can decrease as long as the total entropy of the Universe does not. Entropy is a function of the state of the system, so the change in entropy of a system is determined by its initial and final states. In the idealization that a process is reversible, the entropy does not change, while irreversible processes always increase the total entropy.

In a fictive reversible process, an infinitesimal increment in the entropy ( $dS$ ) of a system is defined to result from an infinitesimal transfer of heat ( $\delta Q$ ) to a closed system (which allows the entry or exit of energy – but not transfer of matter) divided by the common temperature ( $T$ ) of the system in equilibrium and the surroundings which supply the heat.

$$ds = \delta Q / T.$$

*(Close system, idealize fictive reversible process)*

Different notations are used for infinitesimal amounts of heat ( $\delta$ ) and infinitesimal amounts of entropy ( $d$ ) because entropy is a function of state, while heat, like work, is not. For an actually possible infinitesimal process without exchange of mass with the surroundings, the second law requires that the increment in system entropy fulfills the inequality

$$ds > \delta Q / T_{surr}$$

*(Close system, actually possible, irreversible process)*

This is because a general process for this case may include work being done on the system by its surrounding, which can have frictional or viscous effect inside the system, because a chemical reaction may be in progress, or because heat transfer actually occurs only irreversibly, driven by finite difference between the system temperature ( $T$ ) and the temperature of the surrounding  $T_{surr}$ . *Note that the equality still applies for pure heat flows,*

$$ds = \delta Q / T$$

*(Actually possible quasistatic irreversible process without composition change)*

which is the basis of the accurate determination of the absolute entropy of pure substances from measured heat capacity curves and entropy changes at phase transitions, i.e. by calorimetry.