

Class \Rightarrow B.Sc. Part II (Hons.)
 Subject \Rightarrow Chemistry
 Chapter \Rightarrow Thermodynamics
 Topic \Rightarrow statements, cyclic process,
 Heat engine, Efficiency of a
 heat engine.

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Second Law of Thermodynamics Statements

Whenever a spontaneous process takes place, it is accompanied by an increase in the total energy of the universe.

We take the term 'universe' to mean the system and the surroundings. Thus,

$$\Delta S_{\text{univ.}} = \Delta S_{\text{syst.}} + \Delta S_{\text{surrr.}}$$

When an irreversible spontaneous process occurs, the entropy of the system and the surroundings increases, i.e., $\Delta S_{\text{univ.}} > 0$.

When a reversible process occurs, the entropy of the system remains constant, i.e.,

$$\Delta S_{\text{univ.}} = 0$$

Since, the entire universe is undergoing spontaneous change.

Thus second law of thermodynamics stated as -

"The entropy of the system is constantly increasing."

According to Kelvin

It is impossible to take heat from a hotter reservoir and convert it completely into work by a cyclic process without transferring a part of heat to a cooler reservoir.

According to Clausius

It is impossible for a cyclic process to transfer heat from a body at a lower temperature to one at higher temperature without at the same time converting some work to heat.

steam tube

cyclic process

When a system undergoes a series of changes and in the end returns to its original state, it is said to have completed a cycle. The entire process is called a cyclic process.

Since, the internal energy of a system depends only upon its state, it follows that in a cyclic process, the net change of internal energy is zero.

$$\therefore \Delta E = 0$$

∴ According to first law of thermodynamics

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

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

If the series of changes in a cycle are conducted at constant temperature, the cycle is called an Isothermal cycle.

If the cycle is said to be, changes are carried out reversibly, the cycle is called reversible cycle.

Heat engines

A machine which can do work by using heat that flows out spontaneously from a high-temperature source to a low-temperature sink is called a heat engine.

A heat engine running on a periodic cyclic process can yield work continuously.

Efficiency of a Heat Engine

The ratio of the work obtained in a cyclic process (w) to the heat taken from the high-temperature reservoir (q) is called the efficiency of a heat engine.

Efficiency of a heat engine is given by

$$\eta = \frac{w}{q}$$

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