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DEPARTMENT OF CHEMISTRY

A Project work on

"THERMODYNAMICS"

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THERMODYNAMICS

Definition :- The scientific study of the relations between heat and other forms of energy

- Thermodynamics is a greek word which means flow of heat in physical and chemical reactions
- Thermodynamics is a branch of science which deals with the study of different forms of energy and their interconversions
- It deals with energy changes in physical and chemical processes

Thermodynamics was introduced by

Pierre Perrot claims that the term thermodynamics was coined by James Joule in 1858 to designate the science of relations between heat and power, however, Joule never used that term, but used instead the term perfect thermo-dynamic engine in reference to Thomson's 1849 phraseology

Father of Thermodynamics

Nicolas Léonard Sadi Carnot is often described as the "Father of Thermodynamics."

History:-

Historically, thermodynamics developed out of a desire to increase the efficiency of early steam engines, particularly through the work of French physicist Nicolas Léonard Sadi Carnot (1824) who believed that engine efficiency was the key that could help France win the Napoleonic Wars.[1] Scots-Irish physicist Lord Kelvin was the first to formulate a concise definition of thermodynamics in 1854[2] which stated, "Thermo-dynamics is the subject of the relation of heat to forces acting between contiguous parts of bodies, and the relation of heat to electrical agency."

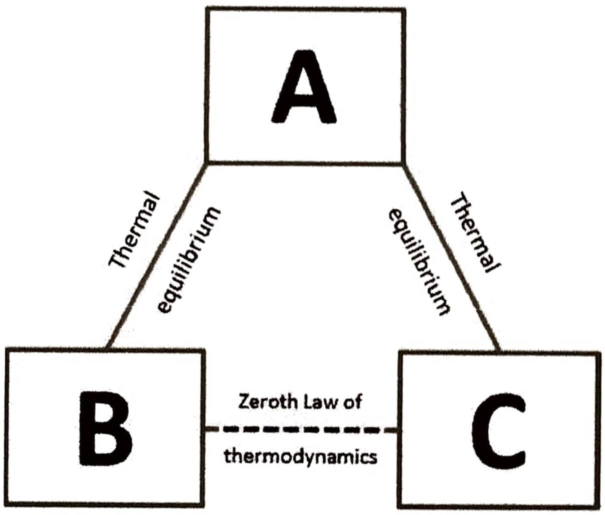
The initial application of thermodynamics to mechanical heat engines was quickly extended to the study of chemical compounds and chemical reactions. Chemical thermodynamics studies the nature of the role of entropy in the process of chemical reactions and has provided the bulk of expansion and knowledge of the field. Other formulations of thermodynamics emerged. Statistical thermodynamics, or statistical mechanics, concerns itself with statistical predictions of the collective motion of particles from their microscopic behavior. In 1909, Constantin Carathéodory presented a purely mathematical approach in an axiomatic formulation, a description often referred to as geometrical thermodynamics.

Laws of Thermodynamics :-

The laws of thermodynamics define a group of physical quantities, such as temperature, energy, and entropy, that characterize thermodynamic systems in thermodynamic equilibrium. The laws also use various parameters for thermodynamic processes, such as thermodynamic work and heat, and establish relationships between them

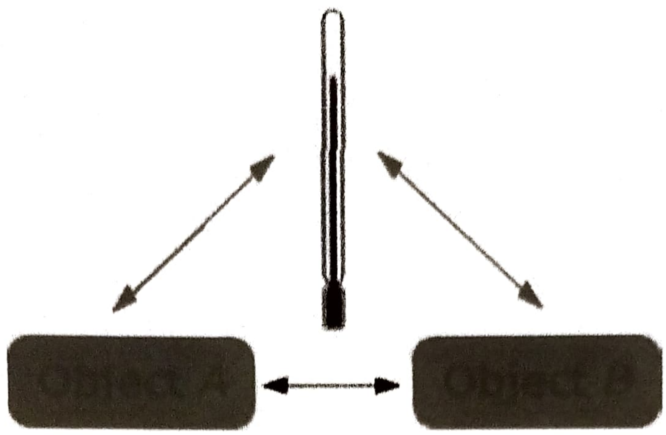
- *zeroth law of thermodynamics:-*

The zeroth law of thermodynamics defines thermal equilibrium and forms a basis for the definition of temperature: If two systems are each in thermal equilibrium with a third system, then they are in thermal equilibrium with each other.



Applications:-

When a thermometer is used to measure our body temperature the glass wall attains thermal equilibrium with our body. ... Using the zeroth law of thermodynamics we can say that our body and mercury are in thermal equilibrium i.e. in same temperature. This is how mercury thermometer measures the temperature.



- *First law of Thermodynamics :-*

The first law of thermodynamics is a version of the law of conservation of energy, adapted for thermodynamic processes, distinguishing two kinds of transfer of energy, as heat and as thermodynamic work, and relating them to a function of a body's state, called internal energy.

The law of conservation of energy states that the total energy of an isolated system is constant; energy can be transformed from one form to another, but can be neither created nor destroyed.

For a thermodynamic process without transfer of matter, the first law is often formulated

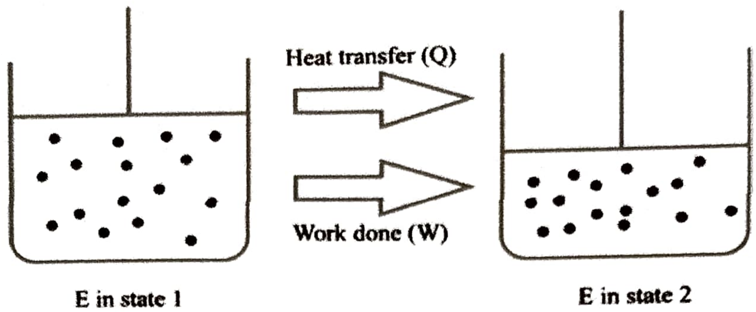
$$\Delta U = Q - W.$$

- where ΔU denotes the change in the internal energy of a closed system,
- Q denotes the quantity of energy supplied to the system as heat, and
- W denotes the amount of thermodynamic work done by the system on its surroundings. An equivalent statement is that perpetual motion machines of the first kind are impossible.

For processes that include transfer of matter, a further statement is needed: 'With due account of the respective reference states of the systems, when two systems, which may be of different chemical compositions, initially separated only by an impermeable wall, and otherwise isolated, are combined into a new system by the thermodynamic operation of removal of the wall, then

$$U_0 = U_1 + U_2$$

- where U_0 denotes the internal energy of the combined system,
- U_1 and U_2 denote the internal energies of the respective separated systems.



$\Delta U = E_2 - E_1 = Q - W$

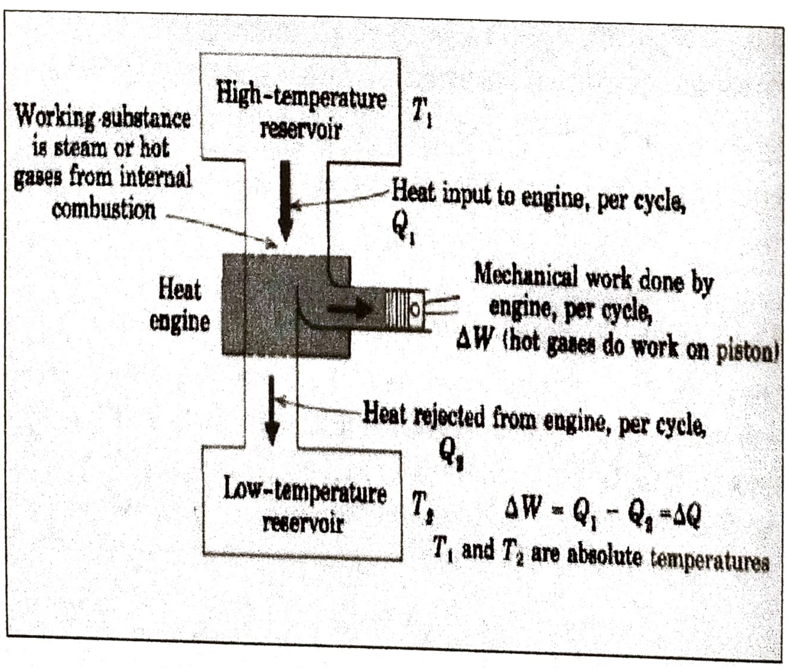
Representation of the first law of thermodynamics

Applications :-

The most common practical application of the First Law is the heat engine. Heat engines convert thermal energy into mechanical energy and vice versa. ... The water is converted to steam, and the pressure is then used to drive a piston that converts heat energy to mechanical energy.

Heat engine working based on the first law of thermodynamics

Steam engines operate in a cyclic fashion, with the piston moving up and down once for each cycle. ... Since the engine returns to its initial state, its internal energy U does not change ($\Delta U = 0$). Thus, by the first law of thermodynamics, the work done for each complete cycle must be $W = Q1 - Q2$.

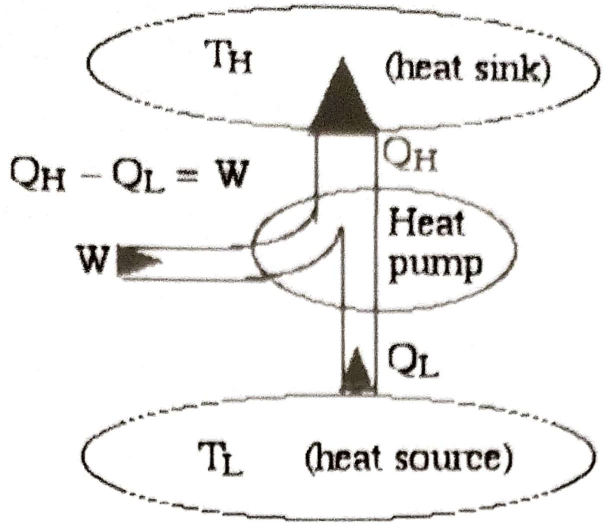


- *Second law of thermodynamics:-*

The second law of thermodynamics establishes the concept of entropy as a physical property of a thermodynamic system. Entropy predicts the direction of spontaneous processes, and determines whether they are irreversible or impossible despite obeying the requirement of conservation of energy as expressed in the first law of thermodynamics. The second law may be formulated by the observation that the entropy of isolated systems left to spontaneous evolution cannot decrease, as they always arrive at a state of thermodynamic equilibrium, where the entropy is highest. If all processes in the system are reversible, the entropy is constant.An increase in entropy accounts for the irreversibility of natural processes, often referred to in the concept of the arrow of time.

Historically, the second law was an empirical finding that was accepted as an axiom of thermodynamic theory. Statistical mechanics provides a microscopic explanation of the law in terms of probability distributions of the states of large assemblies of atoms or molecules. The second law has been expressed in many ways. Its first formulation, which preceded the proper definition of entropy and was based on caloric theory, is Carnot's theorem, credited to the French scientist Sadi Carnot, who in 1824 showed that the efficiency of conversion of heat to work in a heat engine has an upper limit. The first rigorous definition of the second law based on the concept of entropy came from German scientist Rudolph Clausius in the 1850s including his statement that heat can never pass from a colder to a warmer body without some other change, connected therewith, occurring at the same time.

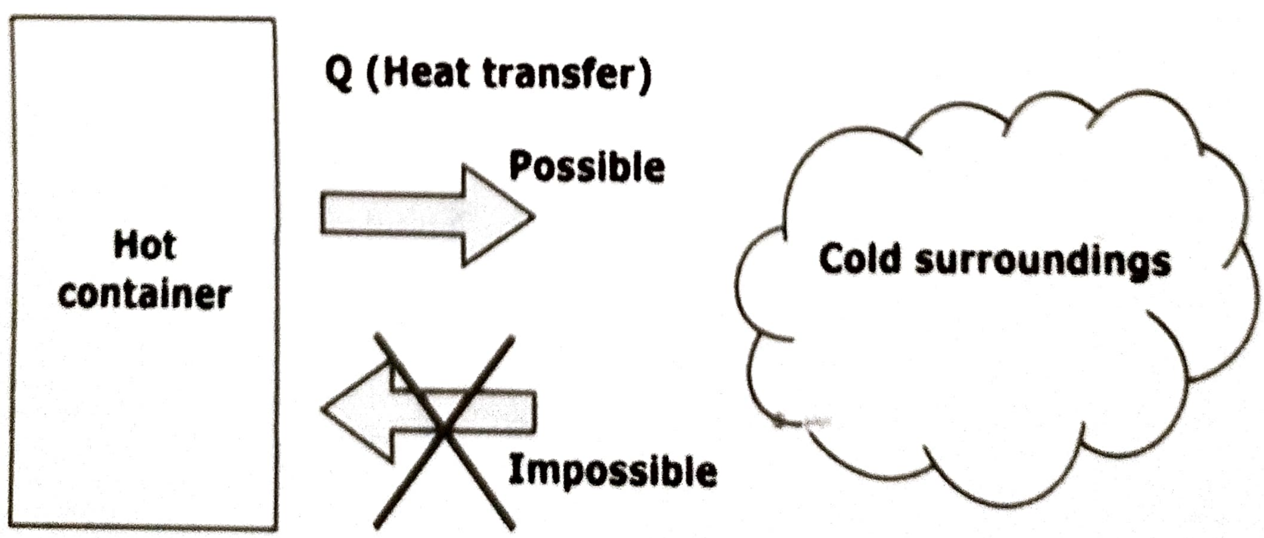
The second law of thermodynamics can also be used to define the concept of thermodynamic temperature, but this is usually delegated to the zeroth law of thermodynamics.



Applications :-

Some of the prominent applications of the second law of thermodynamics are as follows:

- *The second law of thermodynamics states that heat always flows from a body at a higher temperature to a body at a lower temperature. This principle is applicable to all the heat engine cycles. This law led to the development of modern-day vehicles.*
- *Another prominent application of this lies in the working of refrigerators and air conditioners. Both the appliances work on the principle of reverse Carnot cycle. In the reverse Carnot cycle, the heat is transferred from the low-temperature reservoir to a higher temperature reservoir.*



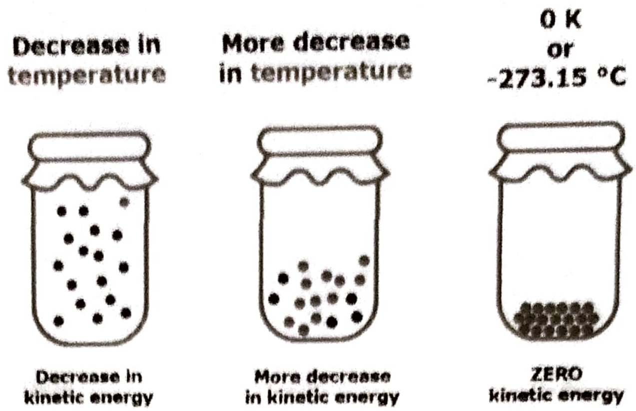
- *Third law of thermodynamics:-*

The third law of thermodynamics states as follows, regarding the properties of closed systems in thermodynamic equilibrium:
The entropy of a system approaches a constant value as its temperature approaches absolute zero.

This constant value cannot depend on any other parameters characterizing the closed system, such as pressure or applied magnetic field. At absolute zero (zero kelvins) the system must be in a state with the minimum possible energy. Entropy is related to the number of accessible microstates, and there is typically one unique state (called the ground state) with minimum energy.In such a case, the entropy at absolute zero will be exactly zero. If the system does not have a well-defined order (if its order is glassy, for example), then there may remain some finite entropy as the system is brought to very low temperatures, either because the system becomes locked into a configuration with non-minimal energy or because the minimum energy state is non-unique. The constant value is called the residual entropy of the system. The entropy is essentially a state-function meaning the inherent value of different atoms, molecules, and other configurations of particles including subatomic or atomic material is defined by entropy, which can be discovered near 0 K. The Nernst–Simon statement of the third law of thermodynamics concerns thermodynamic processes at a fixed, low temperature:
The entropy change associated with any condensed system undergoing a reversible isothermal process approaches zero as the temperature at which it is performed approaches 0 K.

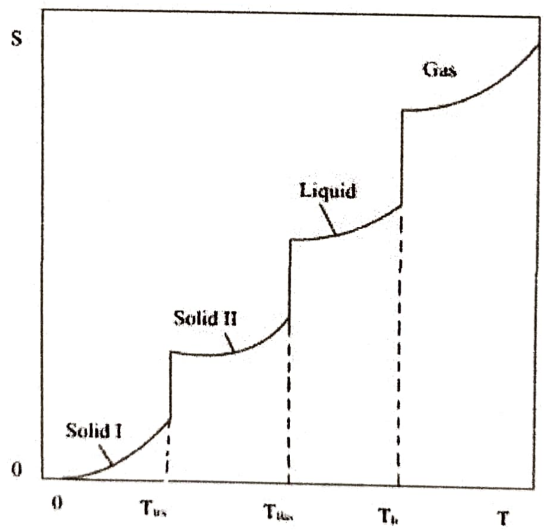
Here a condensed system refers to liquids and solids. A classical formulation by Nernst (actually a consequence of the Third Law) is:
It is impossible for any process, no matter how idealized, to reduce the entropy of a system to its absolute-zero value in a finite number of operations.

There also exists a formulation of the third law which approaches the subject by postulating a specific energy behavior:
If the composite of two thermodynamic systems constitutes an isolated system, then any energy exchange in any form between those two systems is bounded.



Applications:-

The third law of thermodynamics has two important consequences: it defines the sign of the entropy of any substance at temperatures above absolute zero as positive, and it provides a fixed reference point that allows us to measure the absolute entropy of any substance at any temperature.



Conclusion:-

The Thermodynamic Laws