1st law of Thermodynamics

Themodynamics, as the name indicates, is concerned with the flow of heat and it deals with the relationship between heat and work. But in science of thermodynamics indeed covers a much wider field. It is now applied in studying the energy changes associated with all physical and chemical processes, and also in the mutual transformation of different kinds of energy. It acquires a great significance in the study of chemical reactions, for all chemical processes are accompanied with changes in energy.

In themodynamics, a system is defined as an object or a quantity i.e a part of the universe, chosen, for observation, separately from the rest of the universe. The system is enclosed by a boundary which separates it from the rest of the universe.

A system is said to be an isolated system, when it is incapable of exchanging either energy or matter with the surroundings.

A closed system is one in which energy-exchange with the surroundings is possible but no mass transfer across the boundary is permitted.

In an open system, the transfer of both mass and energy across the boundary is possible.

The properties of system fall into two classes: some of the properties such as volume, surface area, energy etc are depedent upon the mass of the system. These are called extensive properties. On the other hand, properties like temperature, pressure, density refractive index etc are independent of the mass of the system. These are called intensive properties.

A system is said to be in a state of equilibrium when (i) its composition remains fixed and definite (ii) the temperature at all parts of the system is the same and also identical with that of the surroundings and (iii) ther is no unbalanced force between different parts of the system or between the system and the surroundings. Therefore a system at equilibrium must have a definite pressure, temperature and composition.

Internal Energy: The internal energy is an extensive property. Five moles of a substance in a specified state have five times the internal energy possessed by one mole of the same.

When a system changes from a thermodynamic state A to a thermodynamic state B, its internal energy will also change. If U_A and U_B denote internal energies in the two states, then the change in internal energy, $\Delta U = U_B - U_A$ will be governed by the magnitudes of the variables in the final and in the initial states. ΔU will thus be independent of the process or path along which the transformation has been carried out.

Such a function, like U, whose magnitude is governed only by the state of the system and nothing else, is called a state function or a characteristic function. The change in the value of the state function for a specified transformation of the system is independent of the path of the transformation. Internal energy, U, is a state function.

The relation between heat and work, which is the origin of the first law, may be enunciated as "if or whenever, heat is obtained from work, the amount of heat produced is proportional to the work spent, or conversely, if heat is transformed into work, there is proportionality between the work obtained and the heat disappeared"

Enthalpy: The pressure (p) and volume (v) of a system are thermodynamic variables and their product PV is expressed as energy. The sum of the two energy terms associated with the system ,namely the internal energy U and the PV energy, is universely represented by H and is called the enthalpy or heat-content of the system

$$\mathbf{H} = \mathbf{U} + \mathbf{PV},$$

the quantities U,P and V are properties of the state of the system , hence H is a state function. The change in enthalpy ΔH is therefore a perfect differential like ΔU and is independent of the path of transformation of the system. The function enthalpy is such that its change is equal to the heat absorbed by the system subject to the restriction of constant pressure.

Reversible Process: In a reversible process, the change of the system is allowed to happen slowly in minute quantities until the whole of the specified change is achieved.

Irreversible Process: An irreversible process is one which occurs suddenly or spontaneously without the restriction of occurring in successive stages of infinitesimal quantities. All natural processes are irreversible process.

Heat capacity: The amount of heat required to raise the temperature of one gm of a substance by 1^{0} K is called its specific heat. The heat input required to raise by 1^{0} K the temperature of one mole of the substance is called its molar heat capacity or simply Heat capacity. It is denoted by C and

$$C = dq/dT$$

But dq is path function and its value depends on the actual process followed.

Kirchhoff's equation: If a system undergoes a change from a given state to another given state, boyh the internal energy and heat content would alter. We may write

$$U_f - U_i = \Delta U$$

 H_{f} - H_{i} = ΔH

The suffixes f and i denote final and initial states.

$$\Delta U_{\rm T} = \Delta U_0 + \int \Delta C_{\rm v} \Delta T$$
$$\Delta H_{\rm T} = \Delta H_0 + \int \Delta C_{\rm P} \Delta T$$

 ΔU_0 , ΔH_0 are integration constants and denote the corresponding internal energy and enthalpy changes at 0^0 K.

These are called Kirchhoff's equation.

Law of Lavoisier and Laplace: This law states that the heat change accompanying a chemical process in one direction is equal in magnitude but opposite in sign, to that accompanying the same reaction in the reverse direction.

$$H_2(g) + 1/2 O_2(g) = H_2O(l) \qquad \Delta H = -68.3 \text{ Kcal}$$

$$H_2O(l) = H_2(g) + 1/2 O_2(g) \qquad \Delta H = +68.3 \text{ Kcal}$$

Hess's law of constant heat summation: This law states that for a given chemical process, the net heat change $(q_p \text{ or } q_v)$ will be the same whether the process occurs in one or in several stages.

Heat of Formation: The enthalpy change occurring when a gm-molecule of a substance is formed from its constituent elements is called its heat of formation.

Heat of combustion : The heat change accompanying the complete combustion of a gm-mole of the substance at a given temperature under normal pressure is called its heat of combustion.

Heat of Neutralization: The amount of heat liberated when one gm-equvalent of an acid is neutralized by a gm equivalent of base is called the heat of neutralization. It is observed that the heat of neutralization of any strong acid by any strong base in dilute solution is always the same and is equal to 13.7 Kcal.

 $H^{\scriptscriptstyle +} + OH^{\scriptscriptstyle -} = H_2 O \qquad \qquad \Delta H = -q$

Thermodynamics does not make any hypothesis as to the structure of matter. It deals with macroscopic observable properties of matter without assumption of its atomic nature.