Thermodynamics:

Thermodynamics is a branch of science which deals with the energy changes accompanying physical and chemical transformation. It is not concerned with the total energy of a body but with energy changes accompanying a given process or transformations. Since thermodynamics is concerned with energy it is applicable to all phenomenons in nature.

Terminology of Thermodynamics:

1. System, boundary and surroundings:

A thermodynamic system may be defined as any specified portion of matter in the universe which is under study. A system may consist of one or more substances.

The rest of the universe which might be in a position to exchange energy and matter with the system is called the surroundings. Thus the system is separated from the surroundings by a boundary which may be real or imaginary.

Isolated system:

A system can exchange neither energy nor matter with its surroundings is called an isolated system.

Closed system:

A system which can exchange energy but not matter with its surroundings is called a closed system.

Open system:

A system which can exchange matter as well as energy with its surroundings is said be an open system.

The environment of living organisms is absolutely essential to them, not only as a source of free energy but also as a source of raw materials. In the language of thermodynamics, living organisms are open systems because they exchange both energy and matter with their environment and, in so doing, transform it. It is characteristic of open systems that they are not in equilibrium with their environment.

Although living organisms may appear to be in equilibrium, because they may not change visibly as we observe them over a period of time, actually they usually exist in a steady state, that condition of an open system in which the rate of transfer of matter and energy from the environment into the system is exactly balanced by the rate of transfer of matter and energy out of the system.

Homogeneous and Heterogeneous System:

A system is said to be homogeneous when it is completely uniform throughout, as, for example a pure solid or all liquid or a solution or a mixture of gases. In other words, a homogeneous system consists of only one phase.

A phase is defined as a homogeneous and physically distinct part of a system which is bounded by a surface and is mechanically separable from other parts of the system.

A system is said to be heterogeneous when it is not uniform throughout. In other words, a heterogeneous system is one which consists of two or more phases. Thus, a system consisting of two or more immiscible liquids, or a solid in contact with a liquid in which it does not dissolve, is a heteroge-neous system.

Thermodynamic Equilibrium:

A system in which the macroscopic properties do not undergo any change with time is said to be in thermodynamic equilibrium, suppose a system is heteroge-neous, i.e. it consists of more than one phase. Then, if it is in equilibrium, the macroscopic properties in the various phases remain unaltered with time.

In fact, the term thermodynamic equilibrium implies the existence of three kinds of equilibria in the system. These are (i) thermal equilibrium (ii) mechanical equilibrium and (iii) chemical equilibrium.

A system is said to be in thermal equilibrium if there is no flow of heat from one portion of the system to another. This is possible if the temperature remains the same throughout in all parts of the system.

A system is said to be in mechanical equilibrium if no mechanical work is done by one part of the system on another part of the system. This is possible if the pressure remains the same throughout in all parts of the system.

A system is said to be in chemical equilibrium if the composition of the various phases in the system remains the same throughout.

Processes and Their Types:

The operation by which a system changes from one state to another is called a process. Whenever a system changes from one state to another it is accompanied by change in energy. In the case of open systems, there may be change of matter as well.

The following types of processes are known:

Isothermal Process:

A process is said to be isothermal if the temperature of the system remains constant during each stage of the process.

Adiabatic Process:

A process is said to be adiabatic if no heat enters or leaves the system during any step of the process.

Isobaric Process:

A process is said to be isobaric if the pressure of the system remains constant during each step of the process.

Reversible and Irreversible Processes:

A process carried out infinitesimally slowly so that the driving force is only infinitesimally greater than the opposing force, is called a reversible process.

Any process which does not take place in the above manner, i.e., a process which does not take place infinitesimally slowly, is said to be an Irreversible process.

A reversible process cannot be realised in practice because it would require infinite time for its completion. Hence, almost all processes occurring in nature or laboratory are irreversible. A reversible process, therefore, remains imaginary and theoretical.

The First Law of Thermodynamics:

The First Law of Thermodynamics states that energy can be converted from one form to another with the interaction of heat, work and internal energy, but it cannot be created nor destroyed, under any circumstances. Mathematically, this is represented as

 $\Delta U=q+w$

Where,

 ΔU is the total change in internal energy of a system, q is the heat exchanged between a system and its surroundings, and w is the work done by or on the system.

Internal Energy U:

Every substance is associated with a definite amount of energy which depends upon its chemi-cal nature as well as upon its temperature, pressure and volume. This energy is known as internal energy. The internal energy of a substance or a system is a definite quantity and it is a function only of the state (i.e., chemical nature, composition, temperature, pressure and volume) of the

system at the given moment, irrespective of the manner in which the state has been brought about. The actual value of internal energy cannot be determined but the change in internal energy accompanying a chemical or physical process is a measurable quantity.

Enthalpy

The sum of the internal energy and the product of the pressure and volume of a thermodynamic system. Enthalpy is an energy-like property or state function—it has the dimensions of energy (and is thus measured in units of joules or ergs), and its value is determined entirely by the temperature, pressure, and composition of the system and not by its history.

In symbols, the enthalpy, H, equals the sum of the internal energy, E, and the product of the pressure, P, and volume, V, of the system:

$$\mathbf{H} = \mathbf{E} + \mathbf{PV}.$$

According to the law of energy conservation, the change in internal energy is equal to the heat transferred to, less the work done by, the system. If the only work done is a change of volume at constant pressure, the enthalpy change is exactly equal to the heat transferred to the system. When energy needs to be added to a material to change its phase from a liquid to a gas, that amount of energy is called the enthalpy (or latent heat) of vaporization and is expressed in units of joules per mole. Other phase transitions have similar associated enthalpy changes, such as the enthalpy (or latent heat) of fusion for changes from a solid to a liquid. As with other energy functions, it is neither convenient nor necessary to determine absolute values of enthalpy. For each substance, the zero-enthalpy state can be some convenient reference state.

When a process occurs at constant pressure, the heat evolved (either released or absorbed) is equal to the change in enthalpy. Enthalpy (H) is the sum of the internal energy (U) and the product of pressure and volume (PV) given by the equation:

H=U+PV(1)

When a process occurs at constant pressure, the heat evolved (either released or absorbed) is equal to the change in enthalpy. Enthalpy is a state function which depends entirely on the state functions T, P and U. Enthalpy is usually expressed as the change in enthalpy (ΔH) for a process between initial and final states:

$\Delta H = \Delta U + \Delta PV(2)$

If temperature and pressure remain constant through the process and the work is limited to pressure-volume work, then the enthalpy change is given by the equation:

$\Delta H = \Delta U + P \Delta V(3)$

Also at constant pressure the heat flow (q) for the process is equal to the change in enthalpy defined by the equation:

$\Delta H=q(4)$

By looking at whether q is exothermic or endothermic we can determine a relationship between ΔH and q. If the reaction absorbs heat it is endothermic meaning the reaction consumes heat

from the surroundings so q>0 (positive). Therefore, at constant temperature and pressure, by the equation above, if q is positive then ΔH is also positive. And the same goes for if the reaction releases heat, then it is exothermic, meaning the system gives off heat to its surroundings, so q<0 (negative). If q is negative, then ΔH will also be negative.

What Is the Importance of Enthalpy?

- Measuring the change in enthalpy allows us to determine whether a reaction was endothermic (absorbed heat, positive change in enthalpy) or exothermic (released heat, a negative change in enthalpy.)
- It is used to calculate the heat of reaction of a chemical process.
- Change in enthalpy is used to measure heat flow in calorimetry.
- It is measured to evaluate a throttling process or Joule-Thomson expansion.
- Enthalpy is used to calculate minimum power for a compressor.
- Enthalpy change occurs during a change in the state of matter.
- There are many other applications of enthalpy in thermal engineering.

Second Law of Thermodynamics:

The second law of thermodynamics state that, whenever a spontaneous process takes place, it is accompanied by an increase in the total energy of the universe.

More specifically, the term universe means the system and the surrounding, thus

 ΔS univ = ΔS system + ΔS surrounding

The second law as stated above tells us that when an irreversible spontaneous process occurs, the entropy of the system and the surroundings increases. In other words, ASuniv> O (zero), when reversible process occurs, the entropy of the system is constant ASsurr. = O. Since the entire universe is undergoing spontaneous change, the second law cannot be most generally and concisely stated as the entropy of the system is constantly increasing.

The Concept of Entropy:

Entropy (S) is a quantitative expression for the randomness or disorder in a system. When the products of a reaction are less complex and more disordered than the reactants, the reaction is said to proceed with a gain in entropy.

The entropy of a system is a real physical quantity and is a definite function of the state of the body like pressure, volume, temperature or internal energy. It is difficult to define the actual entropy of a system. It is more convenient to define the change of entropy during a change of state.

Thus, change of entropy of a system may be defined as the summation of all the terms each involving heat exchanged (q) divided by the absolute temperature (T) during each infinitesimally small change of the process carried out reversibly. Thus, the entropy change for a finite change of a state of a system at constant temperature is given by

 $\Delta S = qrev/T$

The value ΔS , is a definite quantity and depends only on the initial and final states of the system. It is independent of the path or the manner by which the change has been brought about. The value will remain the same even if the change from the initial to the final state has been brought about reversibly or irreversibly.

Units of entropy:

Since entropy change is expressed by a heat term divided by the absolute temperature, entropy is expressed in terms of calories per degree i.e., cal deg-1. This is known as entropy unit, e.u. In S.I. units, the entropy is expressed as joules per degree Kelvin (JK-1).

(I) Entropy Change in Isothermal Expansion of an Ideal gas:

In isothermal expansion of an ideal gas carried out reversibly, there will be no change of internal energy i.e., AU=0 and hence from the first law equation (viz, $\Delta U=q+w$)

qrev = -w

In such a case, the work done in the expansion of n moles of a gas from volume V1 to V2, at constant temperature T, is given by

-w = nRT In (V2/V1)

 $\Delta S = R \ln (V2/V1)$

(II) Entropy Changes in Reversible (Spontaneous Process):

The total increase in entropy of the system and its surroundings during the spontaneous process of expansion involving one mole of the gas would be

A S = R In (V2/V1)

Since V2>V1, it is obvious that the spontaneous (irreversible) isothermal expansion of a gas is accompanied by an increase in the entropy of the system and its surroundings considered together. Thus we may conclude that:

A thermodynamically irreversible process is always accompanied by an increase in the entropy of the system and its surroundings taken together. Entropy changes in irreversible (spontaneous) process is zero, i.e. $\Delta S = O$. Or in other words, in a thermodynamically reversible process, the entropy of the system and its surroundings taken together remains unaltered.

Since all the process in nature occurs spontaneously, i.e., irreversibly, it follows that the entropy of the universe is increasing continuously. This is another statement of the second law.

Physical Significance of Entropy:

1. Spontaneous processes are accompanied by increase in entropy as well as increase in the disorder of the system. Therefore, entropy is regarded as a measure of the disorder of a system.

2. A spontaneous change invariably takes place from a less probable to a more probable state, thus entropy and thermodynamic probability are closely related.

Gibbs free energy

It is a measure of the potential for reversible or maximum work that may be done by a system at constant temperature and pressure. It is a thermodynamic property that was defined in 1876 by Josiah Willard Gibbs to predict whether a process will occur spontaneously at constant temperature and pressure. Gibbs free energy G is defined as

G = H - TS

where H, T, and S are the enthalpy, temperature, and entropy. The SI unit for Gibbs energy is the kilojoule.

Changes in the Gibbs free energy G correspond to changes in free energy for processes at constant temperature and pressure. The change in Gibbs free energy change is the maximum non-expansion work obtainable under these conditions in a closed system; ΔG is negative for spontaneous processes, positive for nonspontaneous processes, and zero for processes at equilibrium.

Gibbs free energy is also known as (G), Gibbs' free energy, Gibbs energy, or Gibbs function. Sometimes the term "free enthalpy" is used to distinguish it from Helmholtz free energy.

Gibbs free energy, denoted G, combines enthalpy and entropy into a single value. The change in free energy, ΔG , is equal to the sum of the enthalpy plus the product of the temperature and entropy of the system. ΔG can predict the direction of the chemical reaction under two conditions:

- constant temperature
- constant pressure.

If ΔG is positive, then the reaction is nonspontaneous (i.e., an the input of external energy is necessary for the reaction to occur) and if it is negative, then it is spontaneous (occurs without external energy input).

Standard energy change

The standard Gibbs free energy of formation of a compound is the change of Gibbs free energy that accompanies the formation of 1 mole of that substance from its component elements, at their standard states (the most stable form of the element at 25 °C and 100 kPa). Its symbol is ΔG° .

The standard Gibbs free energy of the reaction can also be determined according to:

 $\Delta G_{\circ}(reaction) = \Sigma \Delta G_{\circ}(products) - \Sigma \Delta G_{\circ}(reactants)$