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(3)

and chemical equilibrium are not satisfied because a natural process does not take place quasi-statically, and

(2) Dissipative effects, such as friction, viscosity, inelasticity, electric resistance are always present. Spontaneous expansion of a gas into an evacuated space, transfer of electricity through a resistor are the the examples of irreversible process.

Quasistatic process:-

Any change in force, temperature or chemical activity of the system in thermodynamic equilibrium leads it to a non-equilibrium state. But if the external forces are varied only slightly so that unbalanced force is infinitesimal, the process is quasi-static. In this process the deviation from ~~infinitesimal~~ thermodynamic equilibrium is infinitesimal and all the states through which the system passes during a quasistatic process can be considered as equilibrium states. A quasistatic process is an ideal concept which can never be satisfied rigorously in practice.

surroundings. The boundary of the system means that the matter (enclosed gas) in the system [illegible] remains constant. Walls of the cylinder are made up of a good conducting material.

(iii) **Isolated System** — If a system can not exchange matter and energy of any kind with the surroundings, is called isolated system. In such case the cylinder is made up of bad conducting material i.e. insulator.

Thermodynamic variables — The thermodynamic state or macroscopic state of a system is determined by four observable properties. These properties are the composition, pressure, volume and temperature and these are called the variables of state. These are also called thermodynamic co-ordinates. For a homogeneous system, having single substance, the composition is fixed, the density remains constant throughout. So, here the state of the system is determined by the three variables, i.e. Pressure (P), Volume (V) and temperature T).

The variables defining a thermodynamic system are essentially of two types.

(1) the *extensive variables* like volume (V), internal energy (U), which are proportional to the mass (or number of molecules present) and

(2) the *intensive variables* like pressure (P), temperature (T), which are independent of mass.

Thermodynamics - It is the branch of physics which deals with the transformation of heat into mechanical work; i.e it is the mathematical science that describes the relationship of heat and mechanical energy with the passage of time. The scope of thermodynamics has embraced a variety of phenomena in all branches of physics as well as chemistry and engineering. Thermodynamics makes no hypothesis about the structure of matter. Here we only deal with macroscopic (large scale) properties and do not go into detailed structure. In thermodynamics, we are concerned with the study of the interior of a system but describe it in terms of macroscopic quantities, which have a bearing on its internal scale. These macroscopic quantities are called the thermodynamics co-ordinates, or state variables.

Thermodynamic System -

~~Assy~~ A system may be defined as a definite quantity of matter i.e. solid, liquid and gas bounded by some closed surface. The simplest example of a thermodynamic system is a gas contained

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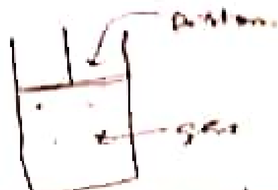
in a cylinder with a movable piston



The terms frequently encountered in thermodynamics are –

Homogeneous system – when a system is completely uniform throughout such as gas or mixture of gases is called homogeneous system. In other words, A homogeneous system is that, whose intensive properties like density and pressure are continuous function of position.

Heterogeneous or inhomogeneous System

If the intensive properties of the system are discontinuous, the system is called heterogeneous. A heterogeneous system may be considered to be composed of a number of homogeneous ones separated from one another by surfaces of discontinuity, each separate portion being called a phase. e.g. a solution of water and oil. Liquid and its vapour i.e. two immiscible or partially miscible liquids.

Surroundings – Anything outside the system which can exchange energy with it is called surroundings. A system may be separated from its surroundings by a real or imaginary boundary through which heat or mechanical energy may pass.

Universe - The combination of a system and its surroundings is called an universe.

A system may be classified as—

① Open system - The system which can exchange matter and energy with its surroundings, is called open system. e.g. Air Compressor: Air at low pressure enters and air at high pressure leaves the system, this shows the exchange of matter and energy with the surroundings

② Closed system - A system which can exchange only energy but not matter with the surroundings is called a closed system. e.g. If a gas enclosed in cylinder expands when heated and drives the piston

(7)

Process:- ~~Process~~ any change in thermodynamic co-ordinates of a system is called a process.

Reversible ~~Process~~ Process-

If a process is carried out in such a way that at every instant the pressure, temperature and density of each homogeneous portion of a system remains essentially uniform, the process is called reversible. Thus the reversible process can be defined as a succession of equilibrium states or states that depart only infinitesimally from equilibrium. Such process must be take place slowly in a controlled ~~manner~~ manner. It can be ~~retraced~~ be traced in opposite direction by changing external conditions infinitesimally.

Irreversible process- It may be defined as a process, which produces a permanent change in thermodynamic state of the system and can be retraced in the opposite order. In nature all changes are irreversible, because of the following reasons.

① The conditions for thermodynamic equilibrium i.e. mechanical, thermal

Equation of state – For a system, there is an equation of state,

$f(P, V, T) = 0$.

Therefore, P, V and T are not independent variables. The thermodynamic state of a homogeneous system is completely determined by knowing two out of three variables.

For example, the equation of state for an ideal gas is,

$PV = RT$.

where, R is universal gas constant.

For a van der waal's gas, the equation of state is,

$$\left(P + \frac{a}{V^2}\right)(V - b) = RT.$$

Here, a and b are van der waal's constant.

Thermodynamic Equillibrium –

Let us first know, mechanical equillibrium, thermal equillibrium and chemical equillibrium –

Mechanical Equillibrium – when there is no unbalanced force between the system and the surroundings and none exists between different parts of the system itself, i.e. there should be no macroscopic movement within the system, the system is said to be in a state of mechanical equilibrium.

Thermal Equilibrium - If the temperature of all parts of the system is uniform and is the same, as that of the surroundings, the system is said to be in thermal equilibrium.

Chemical Equilibrium :- If the chemical composition of the system is the same throughout, means there is no chemical reaction within the system and no movement of any chemical constituent from one part of the system to the other; the system is said to be in chemical equilibrium.

A system which is in mechanical, thermal, and chemical equilibrium is called to be in thermodynamic equilibrium. The state of a system in thermodynamic equilibrium can be represented by specifying its pressure (P), volume (V) and temperature (T)