CLASS-XI SUBJECT-CHEMISTRY

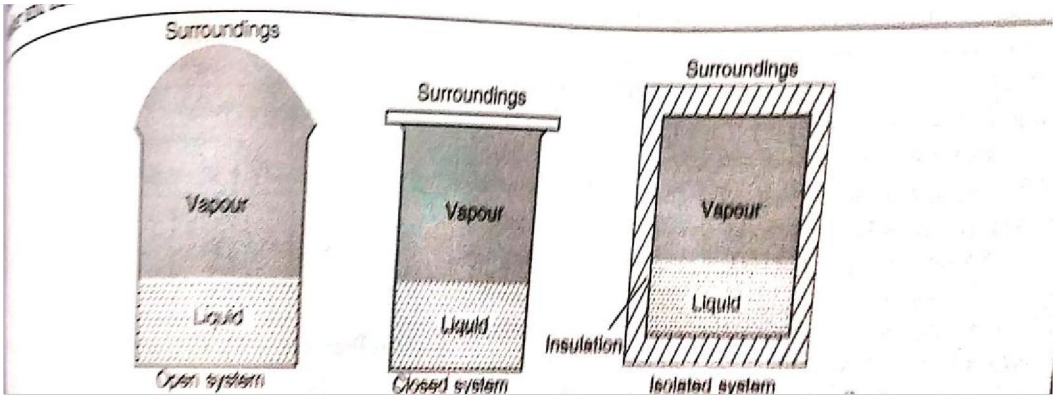
Chapter-6 THERMODYNAMICS

INTRODUCTION:

- The branch of chemistry of science which deals with study of different forms of energy and their interconversion is called thermodynamics.
- LIMITATIONS OF THERMODYNAMICS:
  (i) The laws of thermodynamics deals with the energy change taking place in macroscopic system which involves a large no. of molecules, these laws do not deal with microscopic system.
  (ii) It is based on the initial and final state of the system, does not deal with path followed by the process.
  (iii) It does not deal with the rate of the process.

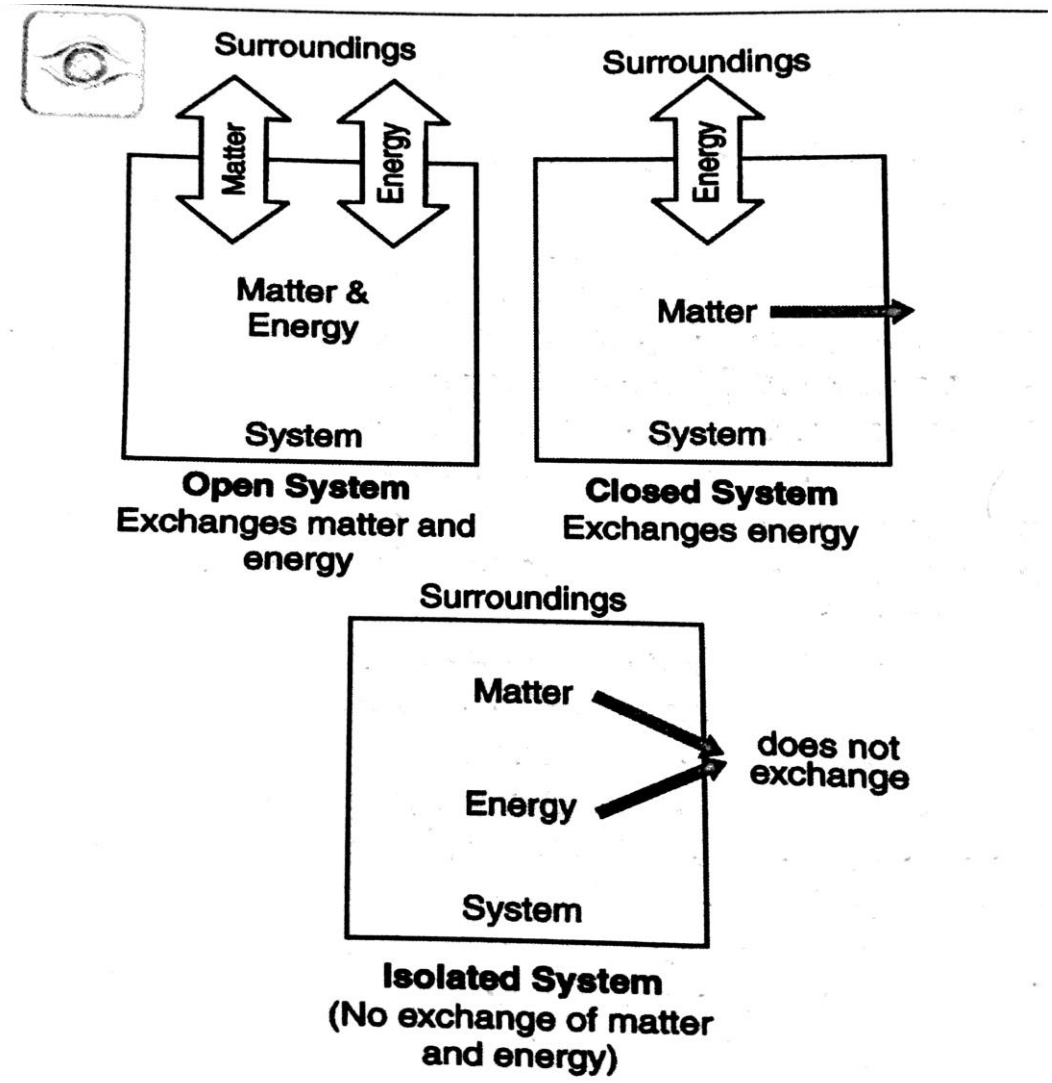
SOME BASIC CONCEPTS:

- System: The part of the universe which is under experimental study and which proper ties are being measured is called system.
  A system is called homogeneous if physical properties and chemical composition are identical throughout the system. On the other hand, a system is said to be heterogeneous if it is consists of parts (or phases) each of which has different physical and chemical properties. Thus,
  A homogeneous system consists of one phase while a heterogeneous system consists of two or more phases.
- Surroundings: The remaining portion of the universe which is not a part of the system is called the surroundings. In other words, surroundings include everything other than the system. The system and surroundings together constitute the universe.
  System + surroundings = Universe
- Boundary: The wall (real or imaginary) that separates the system from surroundings is called boundary.
- TYPES OF SYSTEM:
  Systems may be classified in to three types depending upon the movement of matter and energy in or out of the system.



- (I) Open system: A system which can exchange matter as well as energy with the surroundings is called an Open system. For example, hot coffee in an open flask is an example of open system because it can gain or loss matter as well as energy.

- (II) Closed system: A system which can exchange energy but not matter with its surroundings is called a closed system. Hot coffee in a stainless flask is an example of closed system because energy can gained or lost (through the steel walls) but not matter.
- (III) Isolated system: A system which can neither exchange matter nor energy with the surroundings is called an isolated system. There is no perfectly isolated system. However, a system which is completely sealed to prevent inflow or outflow of matter and is thermally insulated prevent flow of heat can be considered as an isolated system.



All the physical and chemical processes taking place in open in our daily life are open systems because these are continuously exchanging matter and energy with the surroundings.

- MACROSCOPIC PROPERTIES OF THE SYSTEM.

Thermodynamics deals with matter in terms of bulk (large number of chemical species i.e. atoms, molecules or ions) behavior. The properties of the system of the system which arise from the bulk behavior of matter are called macroscopic properties. The common example of macroscopic properties are pressure, volume, temperature, surface tension, viscosity, density, refractive index etc.

In thermodynamics the macroscopic properties can be sub-divided into two types:

(i) Extensive properties and

(ii) Intensive properties.

- Extensive properties: The properties of the system whose value depends upon the amount or size of substance present in the system are called extensive properties. For example mass, volume, surface area, internal energy, enthalpy, entropy, free energy, heat capacity, etc.
- Intensive energy: The property of the system whose value is independent of the amount or size of substance present in the system are called intensive properties. These properties depends only upon the nature of the substance. For example temperature, pressure, viscosity, surface tension, dielectric constant, specific heat capacity, vapour pressure, refractive index etc.
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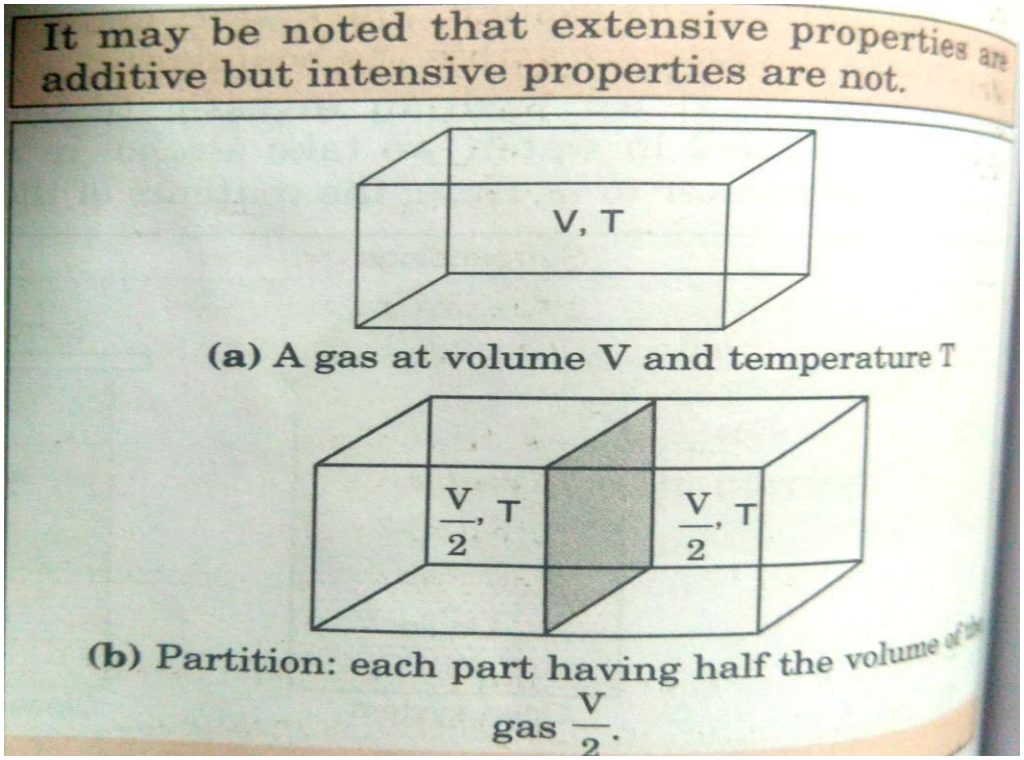

- STATE OF A SYSTEM AND STATE VARIABLES:

The state of a system means the condition of existence of the system when its macroscopic properties have definite values. If any of the macroscopic properties of the system changes, the state of the system is also said to change. Thus, the state of the system is fixed by its macroscopic properties.

(i) State variables: The measurable properties required to describe the state of the system are called state variables. For example, temperature, pressure, volume, composition etc. are the state variables.

(ii) State functions: A state function is a property of the system whose value depends only upon the state of system and its independent of the path or manner by which the state is reached. The change in value depends only upon the initial and final states of the system and not on the path by which the change from initial to final state is brought about. For example pressure, volume, temperature, internal energy enthalpy entropy etc.

(iii) Thermodynamic equilibrium: A system is said to be in thermodynamic equilibrium if it's macroscopic properties (like temperature, pressure etc) do not change with time. The initial state of system corresponds to the starting state of the system in equilibrium before any type of interaction with the surroundings. In the initial state the system attains equilibrium after interaction with the surroundings. The state function gives the difference in the property of the initial state and the final state. The interaction with the surroundings means the transfer of matter or energy or both.

- TYPES OF THERMODYNAMIC PROCESSES:

A process gives a path or operation by which a system changes from one state to another.

(i) Isothermal process: remains constant. In such system, heat is either supplied to the system or removes from it.

(ii) Adiabatic process: A process in which the system does not exchange heat with the surroundings, i.e. no heat leaves or enters the system. In such a process, temperature of a system always changes. The system in which such processes occur are thermally insulated from the surroundings.

(iii) Isobaric process: A process in which the pressure of the system remains constant.

(iv) Isochoric process: A process in which volume of the system remains constant.

(v) Cyclic process: A process in which the system undergoes a series of changes and ultimately returns to its original state is called cyclic process.

(vi) Reversible process: A process in which the direction may be reversed at any stage by merely a small change in a variable like temperature, pressure, etc. therefore in a reversible process the driving force is only infinitesimally slowly. In this process, at every instant, the system remains virtually in a state of equilibrium with the surroundings.

(vii) Irreversible process: A process which is not reversible is called an irreversible process. The driving force is very different than the opening force. All natural processes are irreversible.

ENERNAL ENERGY

Energy stored within a substance or system is called its internal energy. It is a State function and depend upon mass. Internal energy of a system is made up of Energies such as chemical, mechanical, electrical, translational, vibrational and rational energy, potential energy,

The actual value of internal energy is not determined because it involves certain quantities which cannot be measured but we can measure the change in internal energy.

$$\Delta U = U_2 - U_1$$
$$\Delta U = \Sigma U_p - \Sigma U_R$$

Internal energy can be change by

- Heat is given out or heat is given to the system.
- By doing work on the system or by the system.
- Matter enters or leaves the system.

  If UR > UP, then **ΔU = -ve (extra energy is given by the system)**

  If UR< UP, then **ΔU= =ve (energy is absorbed by the system)**
- Work done in adiabatic process and sign convention:

Work done	Sign of w
By the system	-
On the system	+

- Heat changes and sign convention:

Heat (q) transferred	Sign of q
From surroundings to the system	+
From system to the surroundings	-