THERMODYNAMICS

THERMODYNAMIC TERMS

INTRODUCTION

Thermodynamics is the branch of chemistry that deals with energy changes occurring during various physical & chemical processes. It also deals with the transformation between different forms of energy.

Basic Terms Used in Thermodynamics

System: The part of universe under thermodynamics investigation is called system.

Surrounding: Anything outside the system is called surrounding.

$$\text{Universe} = \text{System} + \text{Surroundings}$$

TYPES OF SYSTEM

Depending on Exchange of Energy Between System and Surroundings System can be Classified as:

(i) **Open System**: A system which can exchange both energy and matter with surrounding.

(ii) **Closed System:** A system which can exchange only energy with surrounding.

(iii) **Isolated System**: A system which cannot exchange matter or energy with surrounding.

Depending on the Components of System Involved it can also be Classified as:

Homogeneous System: System consisting of single phase. e.g., Pure solid, a pure liquid a solution, or a mixture of gases (gases always form homogeneous mixture)

Heterogenous System: A system consisting of more than one phase.

Ex. System of two immiscible liquids, two or more solids, a liquid in contact with its vapour etc. are example of heterogenous system.

Boundary: Anything which separates system and surrounding is called boundary. Across boundary energy and mass are transferred between system and surrounding.

A boundary can be real or hypothetical.

Types of Walls or Boundary

Rigid Wall: The wall is immovable.

Non-Rigid Wall: The wall is movable.

Adiabatic Wall: No heat exchange across the wall i.e., $q = 0$.

Diathermic Wall: The heat can be exchanged across the wall i.e., $q \neq 0$.

State Variables & State of a System

State Variables: To define a thermodynamics state of a system, we have to specify the values of certain measurable quantities. These are called thermodynamic variable or state variable. A system can be completely defined by four variables namely pressure, temperature, volume

and composition. A system is said to be in a certain definite state when all of its properties have definite value.

State of System: We specify the state of a system - say, a sample of material - by specifying the values of all the variables describing the system.

If the system is a sample of a pure substance this would mean specifying the values of the Temperature(T), Pressure(P), Volume(V)and the number of moles of the substance(n).

"When the values of state variables change the state of system also changes i.e., state of a system depends on the value of state variables and if their value changes the state of system also changes"

Example Based on Basic Definition

Ex. When no heat and matter is allowed to enter or leave the system, it is called: -

(A) open system **(B)** closed system

(C) isolated system **(D)** may be open or close

Ans. **(C)**

Ex. A well stoppered thermos flask contains some ice cubes. This is an example of a :-

(A) closed system **(B)** open system

(C) isolated system **(D)** non-thermodynamics system

Ans. **(C)**

STATE FUNCTIONS

"These are the thermodynamic functions whose value depends only on the state of system and is independent of the path followed to change the state of system."

- Both state function and state variables are same.
- Change in value of state function (ΔA) = A_{final} - $A_{initial}$
- Differential of a state function integrated over a cyclic path returns zero. In other words, overall change in state function in a cyclic process is equal to zero.

  if $\Rightarrow X \quad \oint dX = 0$ is a state function (property of state function)

Ex. Enthalpy(H), Internal Energy(E), Entropy(S), Gibbs free Energy(G) etc.

PATH FUNCTIONS

These are the thermodynamic functions whose value depend on the path connecting two states. There can be infinite values of path function between two states depending upon path or process.

Path functions are also called indefinite quantities since between two fixed state the value of path function is not fixed. Heat and Work are two important path dependent quantities with which we deal in this chapter.

EXTENSIVE AND INTENSIVE PROPERTIES

Extensive: The Properties of system which depend on the amount of the substance (or substances) present in the system and size of system are called extensive properties. e.g., Mass, volume, heat capacity, internal energy, entropy, Gibb's free energy (G), surface area etc.

- These properties will change with change in the amount of matter present in the system.
- It is important to note that the total value of an extensive property of a system is equal to the sum of the values of different parts into which the system is divided.

Intensive: Properties which are independent of the amount of substance (or substances) present in the system and size of system are called intensive properties, e.g., pressure, density, temperature, viscosity, surface tension, refractive index, emf, chemical potential, sp. heat etc. These are intensive properties.

Following are some important characteristics of Intensive & Extensive Properties

- If A & B are two extensive properties than will be $\frac{A}{B} \& \frac{dA}{dB}$ Intensive.

- If an extensive property is represented as per unit mass or mole or volume it will become an intensive property.

  Ex. Concentration = mole / volume

  Density = mass / volume

  sp. heat capacity = heat capacity / mass

  While mole, mass, heat capacity are extensive properties, concentration, density and specific heat capacity are intensive properties.

Extensive Properties	Intensive Properties
Volume	Molar Volume
Number of moles	Density
Mass	Refractive Index
Free Energy **(G)**	Surface Tension
Entropy **(S)**	Viscosity
Enthalpy **(H)**	Free Energy per mole
Internal Energy **(E & U)**	Specific Heat
Heat Capacity	Pressure
	Temperature
	Boiling Point, Freezing Point

THERMODYNAMIC EQUILIBRIUM

Thermodynamic generally deals the equilibrium state of the system in which the state variable is uniform and constant throughout the whole system.

For a system to be in thermodynamic equilibrium all the following three types of equilibrium must co-exist.

(i) **Mechanical Equilibrium**

When there is no macroscopic movement within the system itself or of the system with respect to surroundings, the system is said to be in a state of mechanical equilibrium.

(ii) **Chemical Equilibrium**

When the system consists of more than one substance and the composition of the system does not vary with time, the system is said to be in chemical equilibrium. The chemical composition of a system at equilibrium must be uniform and there should be no **net** chemical reaction taking place.

(iii) **Thermal Equilibrium**

When the temperature throughout the entire system is the same as that of the surroundings then the system is said to be in thermal equilibrium.

Ex. Which is the intensive property: -

(A) temperature **(B)** viscosity

(C) density **(D)** all

Ans. **(D)**

Ex. A thermodynamic state function is: -

(A) one which obeys all the law of thermodynamics

(B) a quantity which is used in measuring thermal changes

(C) one which is used in thermos chemistry

(D) a quantity whose value depends only on the state of system

Ans. **(D)**

Ex. A system is changed from state A to state B by one path and from B to A by another path. If DE_1 and DE_2 are the corresponding changes in internal energy, then: -

(A) $DE_2 + E_2 = +ve$ **(B)** $DE_1 + DE_2 = -ve$

(C) $DE_1 + DE_2 = 0$ **(D)** none of the above

Ans. **(C)**

THERMODYNAMIC PROCESS

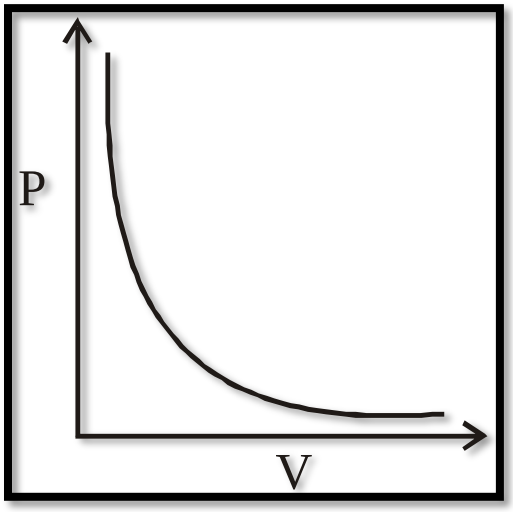
The path followed to change the state of a system is called a process.

Path of a Process

The exact sequence of steps through which system changes state is called path of a process. reversible or irreversible path

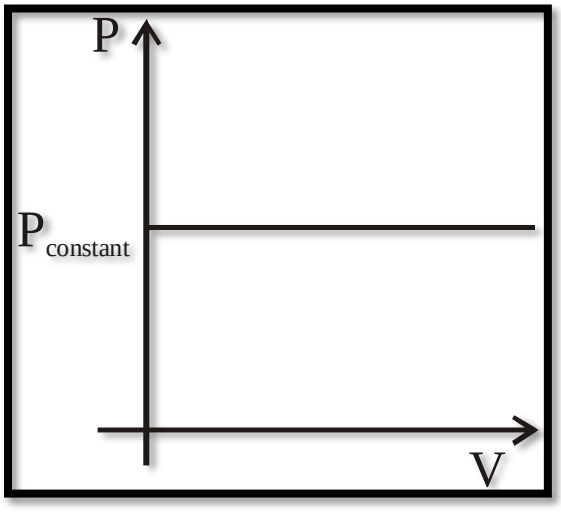
Some Thermodynamic Processes

(1) **Isothermal Process:** A process in which temperature of the system remains constant is called isothermal process

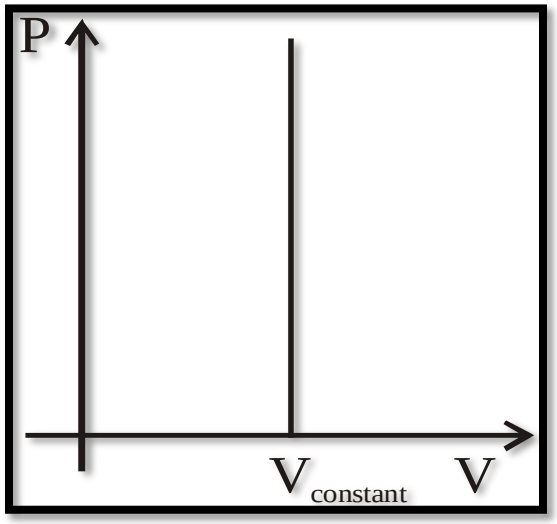


(2) **Isobaric Process:** A process in which pressure of the system remains constant is called isobaric process. Temperature and volume of the system may change.

Ex. All the reactions or processes taking place in open vessel like boiling of water in open vessel, burning of charcoal, melting of wax take place at constant pressure (1 atm.)

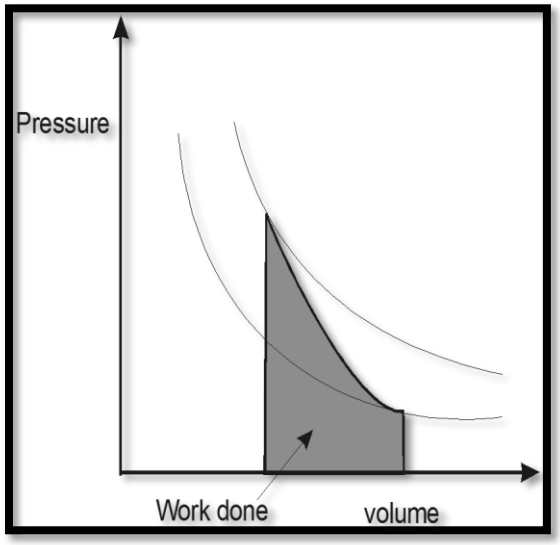


(3) **Isochoric Process:** The process for which volume of the system remains constant is called isochoric process i.e., Heating of gas in closed vessel.



(4) **Adiabatic Process**: A process in which no heat exchange takes place is called adiabatic process. Adriatic process occurs in isolated systems.

i.e., $q = 0$



(5) **Cyclic Process:** If a system after completing a series of different process returns to its initial state, then overall process is called cyclic process.

"The overall change in value of a state function during the complete cycle is zero"

Ex. $\Delta H = 0, \Delta E = 0, \Delta P.E. = 0$