INTRODUCTION AND BASIC CONCEPTS

THERMODYNAMICS:

Thermodynamics is the science of energy transfer and its effect on the physical properties of substances.

System: A specific region or mass in space on which attention is concentrated in the analysis of problem.

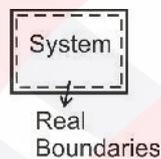**Surrounding:** Everything apart from the system is called surrounding.

Boundary: Which separates the system from the surrounding is called boundary.
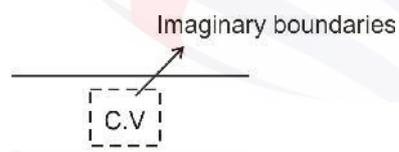
CLASSIFICATION OF BOUNDRIES

- Boundaries can be classified in to:

  (i)   Real Boundaries   (ii)   Imaginary Boundaries

1)   Real Boundaries

2)   Imaginary Boundaries

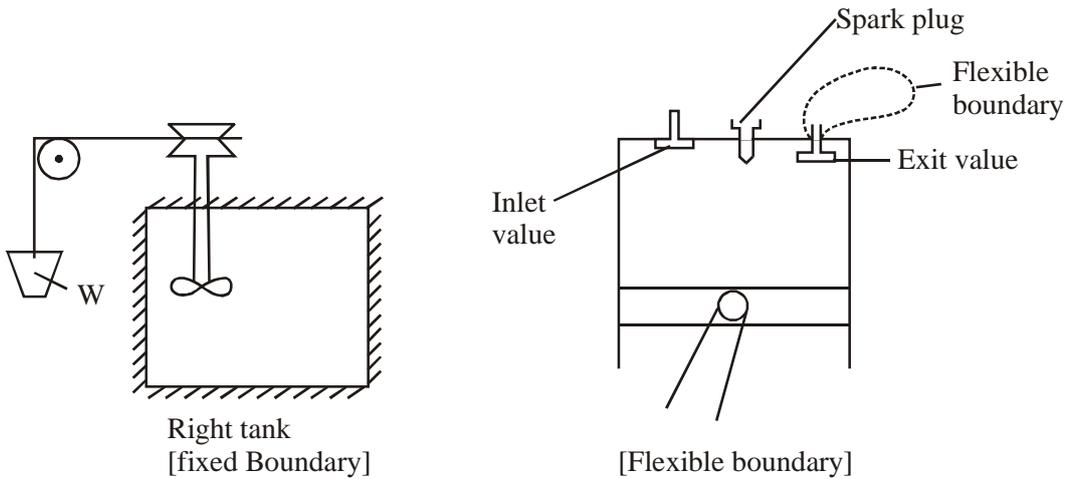- Boundaries can also i.e. classified in to:

  (i)   Rigid Boundaries   (ii)   Flexible Boundaries

Note: Flexible boundaries are not fixed, its keep on changing.

Example:

Right tank
[fixed Boundary]   [Flexible boundary]

CLASSIFICATION OF SYSTEM

There are 3 types of system

1) Closed system
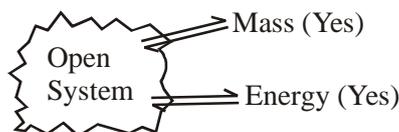
2) Open system

3) Isolated system

1) **CLOSED SYSETM:-** It is a system in which there is no mass transfer between system and surroundings and there is energy transfers in closed system.

  Example: (*i*) Piston cylinder arrangement without any valve.

Energy transfer is in the form of mechanical work
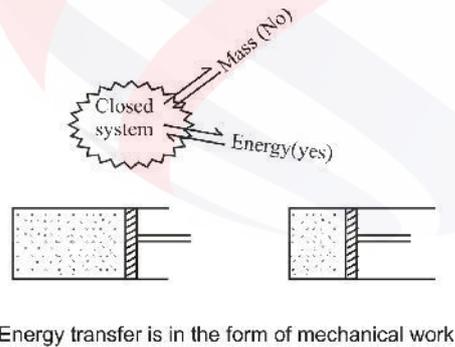
  Ñ This system is also called control mass system.

2) **OPEN SYSTEM:-** It is a system in which both mass and energy cross the boundary of the system.

  Example: (*i*) Piston cylinder arrangement without any valve.

    Ñ   Control volume:- It is a open system where the volume remains constant.

    Ñ   All open systems are not control volume but control volumes are open system.

    Ñ   Boundaries of control volumes are called control surface. In control volume, boundaries are fixed (rigid or hypothetical).

3)   **ISOLATED SYSTEM**: It is a system in which neither mass transfer nor energy cross the boundary of the system. E.g. Thermoflask

- Thermodynamics universe is an isolated system
- 100% heat insulation is not possible – Ideal condition
- For thermodynamic analysis of an open system, for example an air compressor as shown in figure, attention is focused on a certain volume in space surrounding the compressor, it is called control volume, bounded by a surface called the control surface.
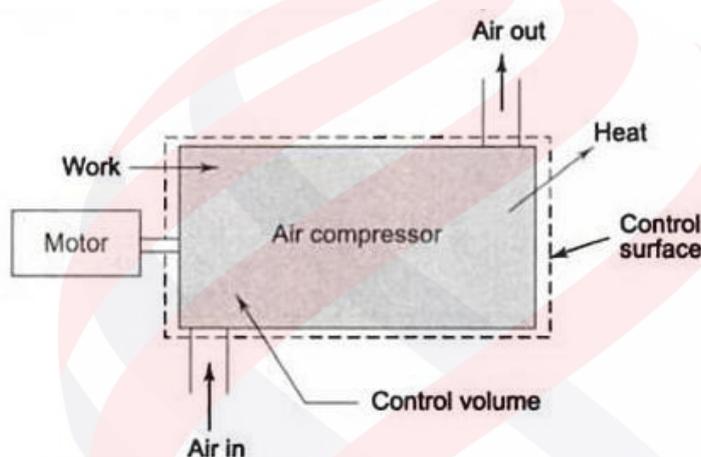
PROPERTIES

Every system has certain characteristics by which its physical condition may be described.

For e.g. : Temperature, pressure, mass, kinetic energy, volume, potential energy, internal etc.

➢   Properties are point function.

➢   Properties are exact differentials.

Classification of properties:

1)   **Intensive property:** It is a property which will not depend upon the mass of the system. For eg.

- Temperature, Pressure, density, specific internal energy.
➢   Extensive properties per unit mass, such as specific volume, is intensive properties.
➢   An intensive property is independent of the size of system

2)   **Extensive property:** It is a property which will depend upon the mass (extent) of the system.

    e.g. Mass, volume, internal energy, enthalpy, entropy

➢   The value of an extensive property varies directly with the mass

➢ Difference between Extensive property and intensive property

Extensive property	Intensive property
1.Its value depends on how large a portion of system has been considered.	1. Its value remains constant whether we consider the whole system or a part of it.
2. It depends on mass of system.	2. It is independent of mass of system.
3. Energy, enthalpy, entropy, volume, area, hear etc. are its examples.	3. Pressure, temperature, density, thermal conductivity and viscosity are its examples.

➢ If 'p' is any parameter of the system & 'dp' is an exact differential, then we can say 'p' is an property of the system.
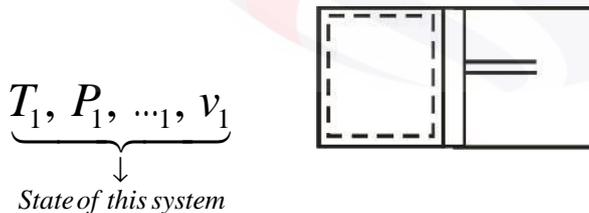
$$\int_{1}^{2} dp = p_2 - p_1$$
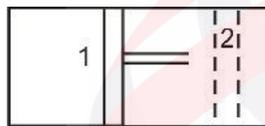
Work is not a property of this system because

$$\int_{1}^{2} dw \neq w_2 - w_1$$

But pressure is a property of this system

$$\int_{1}^{2} dp = p_2 - p_1$$

➢ State of a system: it is the condition of its existence

$$\underbrace{T_1, P_1, \cdots_1, v_1}_{\downarrow}$$
*State of this system*

Thermodynamic Equilibrium:

A system will be in a state of thermodynamics equilibrium, if the conditions for the following three types of equilibrium are satisfied.

i) **Mechanical Equilibrium:-** A system is said to be in mechanical equilibrium if there is no unbalanced force within the system if system is isolated from the surroundings.

ii)   **Thermal Equilibrium:-** A system is said to be in thermal equilibrium if there is no heat transfer within the system if system is isolated from the surroundings.

➤   Temperature at every point should remain the same in thermal equilibrium, but in mechanical equilibrium, pressure at every point within the system should remain the same is not a necessary condition.

iii)   **Chemical Equilibrium:** A system is said to be in chemical equilibrium if there is no any chemical reaction within the system when the system is isolated from the surroundings.

➤   Phase of a system: A quantity of matter homogeneous in physical structure and chemical composition is called a phase. E.g.: Ice is phase {homogeneity in physical structure and chemical composition}

Oil in water is not a single phase system, but it is two phase system.

➤   Homogeneous system: A system which has got only one phase is called homogenous system. E.g.:- Ice, water, air

➤   Within the thermodynamics range of temperature, air is treated as homogenous   system.

➤   Heterogeneous system: A system which has got more than one phase is called   heterogeneous system.

  e.g.: Boiling water

Pure substance:

➤   Pure substance is homogeneous and invariable in chemical composition throughout its mass.

➤   A mixture of two or more phases of a pure substance is still a pure substance as long as the chemical composition of all phase is the same.

Example: Mixture of water and water vapour, mixture of water and alcohol, air etc.

➤   **Process:** When the path is completely specified, the change of state is called process eg. Constant pressure process.

➤   **Cycle:** It is defined as a series of state changes such that the final state is identical with the initial state as shown in fig.
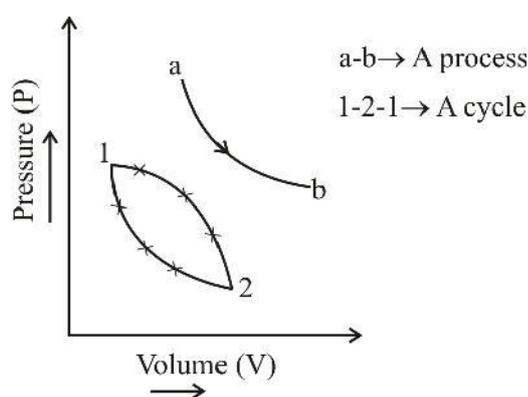
A process and a cycle

QUASI-STATIC PROCESS:

➢ **Quasistatic process** is a thermodynamic process that happens infinitely slowly and no real process is quasistatic. Hence in practice, such processes can only be approximated by performing them infinitesimally slowly.

➢ Infinite slowness is the characteristic feature of quasi-static process

➢ A quasi-static process is thus a succession of equilibrium states

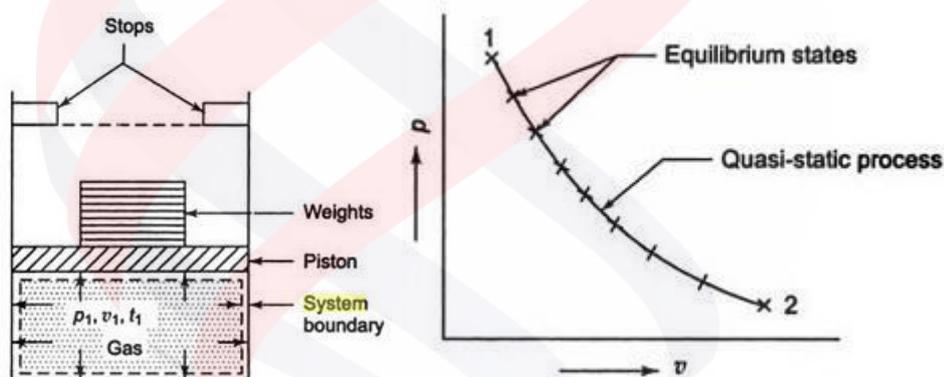➢ All reversible process must be quasi-static but all quasi-static process

Figure: Infinitely slow transition of a system by infinitesimal force

Figure: A quasi-static process.

REVERSIBLE PROCESS/ IDEAL PROCESS:

A reversible process is one which is performed in such a way that at the conclusion of the process, both system and surrounding may be restored to their initial states, without producing any changes in the rest of universe.

➢ A reversible process is carried out infinitely slowly with an infinitesimal gradient, so that every state passed through by the system is an equilibrium state.

➢ Reversible process coincides with a quasi-state process.

Examples

1. Evaporation.
2. Frictionless adiabatic expansion and compression process.
3. Electrolysis.
4. Frictionless relative motion

IRREVERSIBLE PROCESS / NATURAL PROCESS:

A process is said to be irreversible, if the system passes through sequence of non-equilibrium states

Any natural process carried out with finite gradient is an irreversible process.

The causes of irreversibility:

1. Unrestricted friction.
2. Mechanical and fluid friction.
3. Heat transfer with finite temperature difference.
4. Involvement of dissipative effects.
5. Lack of equilibrium during the process

Examples:

1. Relative motion with friction.
2. Diffusion of gases.
3. Dissolving of sugar or salt in H_2O.
4. Plastic deformation.
5. Heat transfer by convection

➤ **Adiabatic wall:**   Which does not permit the flow of heat
➤ **Diathermic Wall:**   Which permit the flow of heat

MACROSCOPIC AND MICROSCOPIC VIEWPOINT

There are two approaches to study the thermodynamics:

(i)   Macroscopic Approach {classical Thermodynamics}

(ii)   Microscopic Approach {Statistical Thermodynamics}

In Macroscopic approach, the behavior of the gas is described by the net effect of action of all the molecules, which can be perceived by human senses.

➤ The structure of matter is not considered
➤ Only a few variables are used to describe the state of matter.

The values of these variables can be measured.

In Microscopic approach, the behavior of the gas is described by the summing up the behavior of each molecule.

> ➢ A knowledge of the structure of matter is essential
> ➢ A large number of variables are needed to describe the state of matter.

ZEROTH LAW OF THERMODYNAMICS:

If anybody A is in thermal equilibrium with body B and C separately then B and C will be in thermal equilibrium.

> ➢ It is the basis of temperature measurement.
> ➢ In order to obtain a quantitative measure of temperature, a reference body is used, and a certain physical characteristic of this body which changes with temperature is selected. The changes in the selected characteristic may be taken as an indication of change in temperature. The selected characteristic is called the thermometric property, and the reference body which is used in the determination of temperature is called the thermometer.
> ➢ There are five different kinds of thermometer, each with its own thermometric property, as shown in table.

Thermometer	Thermometric Property	Symbol
Constant volume gas thermometer	Pressure	P
Constant pressure gas thermometer	Volume	V
Electric resistance thermometer	Resistance	R
Thermo couple	EMF	e
Mercury in glass thermometer	Length	L

> ➢ Conversion of temperature unit:-

$$\frac{^{o}C}{5} = \frac{F-32}{9} = \frac{T-273.15}{5}$$

> ➢ The advantage of a thermocouple is that it comes to thermal equilibrium with the system, whose temperature is to be measured, quite rapidly because its mass is small.
> ➢ Thermocouple circuit is made up from joining two wires 'A' and 'B' made of dis similar metals. Due to seebeck effect, a net emf is generated in the circuit which depends on the difference in temperature between the hot and cold junctions. This emf is measure by a micro volt meter to a high degree of accuracy.
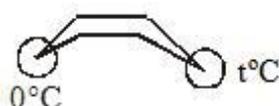
➢ Reverse effect of see back effect is peltier effect. Cooling and heating of two junctions of dissimilar materials when direct current is passed through then, the heat transfer rate being proportional to the current.

➢ Before 1954, two fixed points, the ice point and steam point, were used to quantify the temperature of a system. After 1954, only one fixed point, the triple point of water 273.16 K is used and it is the standard fixed point of thermometer.

➢ Choice of metals depends largely on the temperature range to be investigated.

➢ Time-constant is the amount of time required for a thermo couple to indicate 63.2% of step change in temperature of a surrounding media.

Gibbs Phase Rule:

$$P + F = C + 2$$

P - Number of Phases

F – Degree of freedom

C – Number of components

DOF is the minimum number of independent intensive variable required to fix the state.

Ideal gas:

Assumptions:

1. Intermolecular forces are negligible

2. The volume occupied by molecular are negligible as compared to volume of container

It has been established from experimental observation that the p-v-T behavior of gases at a low pressure is closely given by the following relation

$$p\bar{v} = \bar{R}T$$