## 2.1 MACROSCOPIC AND MICROSCOPIC POINTS OF VIEW

- **Thermodynamic studies are undertaken by the following two different approaches.**

**1.Macroscopic approach (Macro mean big or total)**

**2. Microscopic approach (Micro means small)**

| S.No | **Macroscopic approach** | **Microscopic approach** |
|---|---|---|
| 1 | In this approach a certain **quantity of material** is considered **without taking into account the events occurring at molecular level**. In other words, this approach to thermodynamics is concerned with gross or overall behaviour. This is known as classical thermodynamics. | The approach considers that the system is made up of a very large number of **discrete particles known as molecules**. These molecules have different velocities and energies. The values of these energies are constantly changing with time. This approach to thermodynamics which is concerned directly with the **structure of the material(particles)** is known as statistical thermodynamics. |
| 2 | **The analysis of macroscopic system requires simple mathematical formulae.** | **The behaviour of the system is found by using statistical methods as the number of molecules is very large.** So advanced statistical and mathe-matical methods are needed to explain the changes in the system. |
| 3 | The values of the properties of the system are their average values. | **The properties like velocity, momentum, impulse, kinetic energy, force of impa**ct etc. |

| | | |
|---|---|---|
| | For example, consider a sample of a gas in a closed container. The pressure of the gas is the average value of the pressur.**These properties like pressure and temperature can be measured very easily**. The changes in properties can be felt by our senses. | which describe the molecule cannot be easily measured by instruments. Our senses cannot feel them. |
| 4 | **In order to describe a system only a few properties are needed.** | **Large number of variables are needed to describe a system.** So the approach is complicated. |

## 2.2 PURE SUBSTANCE

A pure substance is one that has a homogeneous and invariable chemical composition even though there is a change of phase. In other words, it is a system which is **(a) homogeneous in composition, (b) homogeneous in chemical aggregation**. **Examples: Liquid, water, mixture of liquid water and steam**, mixture of ice and water. The mixture of liquid air and gaseous air is not a pure substance.

## 2.3 PROPERTIES OF SYSTEMS

**A property of a system is a characteristic of the system which depends upon its state**, but not upon how the state is reached. There are two sorts of property:

**1. Intensive properties. These properties do not depend on the mass of the system. Examples: Temperature and pressure.**
**2.Extensive properties. These properties depend on the mass of the system. Example Volume.** Extensive properties are often divided by mass associated with them to obtain the intensive properties. For example, if the volume of a system of mass m is V, then the specific volume of matter within the system is

$$\frac{\mathrm{V}}{m} = \square \text{ which is an intensive property.}$$

## 2.4 STATE

**State is the condition of the system at an instant of time** as described or measured by its properties. Or each unique condition of a system is called a **state.**

It follows from the definition of state that each property has a single value at each state. Stated differently, all properties are state or point functions. Therefore, all properties are identical for identical states.

On the basis of the above discussion, we can determine if a given variable is property or not by applying the following tests:

**-A variable is a property, if and only if, it has a single value** at each equilibrium state.

-**A variable is a property, if and only if, the change in its value between any two pre-scribed equilibrium states is single-valued**

Therefore, any variable whose change is fixed by the end states is a property.

## 2.5 PROCESS

A process occurs when the system undergoes **a change in a state of material** or an energy transfer at a steady state. A process may be non-flow in which a fixed mass within the defined boundary is undergoing a change of state. Example: A substance which is being heated in a closed cylinder undergoes a non-flow process (Fig. 3). **Closed systems undergo non-flow processes.** A process may be a flow process in which mass is entering and leaving through the boundary of an **open system. In a steady flow process** (Fig. 4) mass is crossing the boundary from surroundings at entry, and an equal mass is crossing the boundary at the exit so that the total mass of the system remains constant. In an open system it is necessary to take account of the work delivered from the surroundings to the system at entry to cause the mass to enter, and also of the work delivered from the system at surroundings to cause the mass to leave, as well as any heat or work crossing the boundary of the system.

Quasi-static process. Quasi means 'almost'. A quasi-static process is also called a replayed process. This process is a succession of equilibrium states and infinite slowness is its characteristic feature.

## 2.6 CYCLE

**Any process or series of processes** whose end states are identical is termed a cycle. The processes through which the system has passed can be shown on a state diagram, but a complete section of the path requires in addition a statement of the heat and work crossing the boundary of the system. Fig. 5 shows-such a cycle in which a system commencing at condition changes in pressure and volume through a path 123 and returns 'to its initial condition

Fig.5 cycle

## 2.7 POINT FUNCTION

When two properties locate a point on the graph (co-ordinate axes) then those properties are called as point function

**Examples. Pressure, temperature, volume etc**

$$\int_{\mathbf{1}}^{\mathbf{2}} \boldsymbol{dv} = \mathbf{V}_2 - \mathbf{V}_1 \ (\textbf{an exact differential})$$

## 2.8 PATH FUNCTION

There are certain quantities which cannot be located on a graph by a point but are given by the area or so, on that graph. In that case, the area on the graph, pertaining to the particular process,

is a function of the path of the process. Such quantities are called path functions.

**Examples. Heat, work etc**

Heat and work are inexact differentials. Their change cannot be written as difference between their end states**.**

$$\int_{\mathbf{1}}^{\mathbf{2}} \boldsymbol{\delta Q}. \neq \boldsymbol{Q2} - \mathbf{Q1} \boldsymbol{and\ is\ shown\ 1Q2\ OR\ Q1} - \mathbf{2}$$

**Similar**

$$\int_1^2 \delta W. \neq W2 - \mathrm{W1} and\ is\ shown\ 1W2\ OR\ W1 - 2$$

## 2.9 Equilibrium

It's a universal observation that any real system, if left alone for enough time, reaches a state where the macroscopic properties stop changing. If a ball is dropped onto the floor, it will bounce for a while but eventually it will sit motionless. If a drop of dye is placed in a glass of water, the dye will slowly diffuse away until the dye concentration is the same everywhere in the glass, after which no further change is observed. If a fluid is stirred and then left alone, the motion will eventually cease, due to viscosity. We call the motionless, **unchanging state a physical system approaches at long times the equilibrium state**.

**The word equilibrium is defined as "a state of balance between opposing forces or actions."** When a physical system is in an equilibrium state, every part of it is in balance (equilibrium) with every other part. There is no net transfer of matter or energy between any two parts of the system. The balance is dynamic, since molecules may leave one region and enter another (in a liquid or gas), but the same number must be going the opposite direction, since otherwise of molecules.

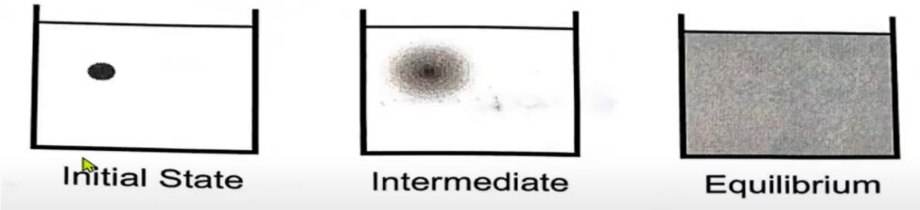

**Figure 6: Diffusion of a drop of dye in water**

A general characteristic of equilibrium states is that they are much simpler to describe than non-equilibrium states. For example, to describe the stateate Windows shortly after a drop of dye has been introduced into a glass of water requires.

### 2.9.1Mechanical Equilibrium

Suppose a cylinder is divided in two parts (A and B) by a piston, which can move back and forth (Fig. 7). The piston is initially locked rigidly in place and some gas is added to each side of the cylinder. The piston is now unlocked, and oscillates back and forth a while. Eventually, friction or viscous forces damp out the piston motion, and it will stop, though perhaps not at its initial position. Once it has stopped, we say A and B are in mechanical equilibrium with each other.

If the piston is stationary, the force must be the same on both sides. Therefore, **PA = PB if A and B are in mechanical equilibrium.** Pressure is seen to be the property which tells us if two adjacent parts of a system are in mechanical equilibrium with one another.

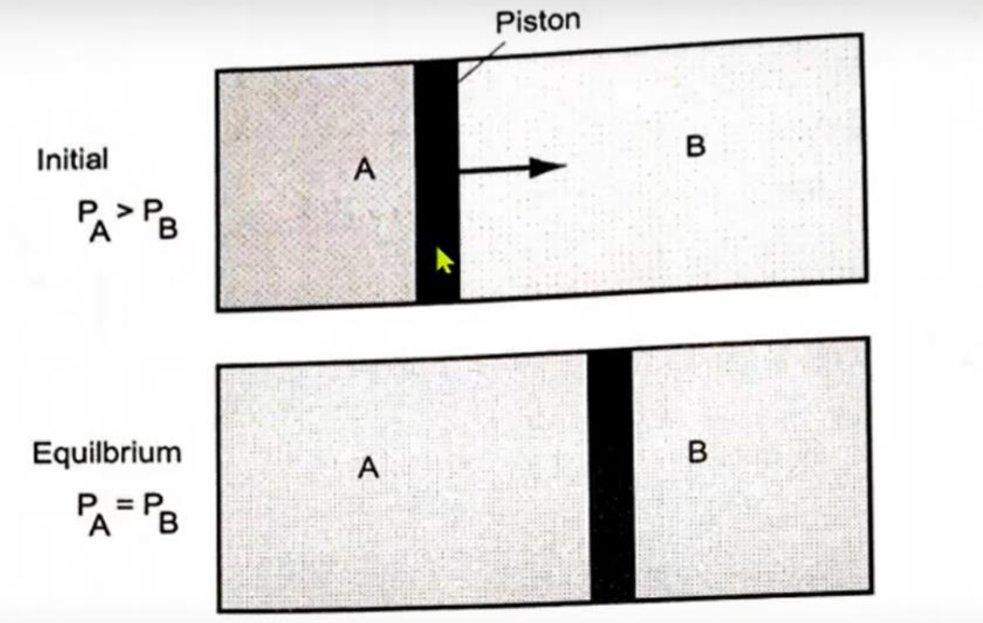

Fig. 7: Mechanical equilibrium: the piston moves until PA = PB.

## 2.9.2Thermal Equilibrium

Consider now two systems connected by a rigid wall which can conduct heat (Fig. 8). (We say they are in "thermal contact.") When they are placed in thermal contact, energy may transfer through the wall as heat, but eventually no net energy transfer will occur. When this condition is reached, the two systems are in thermal equilibrium.

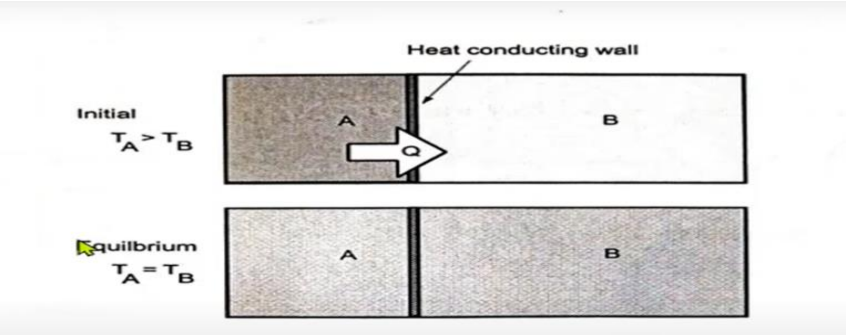

Figure 8: Thermal equilibrium: heat flows until $T_A$ $T_B$

not the energy, since the two systems may have very different compositions and sizes, and so will have different energies even at thermal equilibrium.

### 2.9.3 Diffusive Equilibrium

If a dye drop is added to a glass of water, we know that at equilibrium the dye will diffuse throughout the glass. This type of equilibrium is known as diffusive equilibrium. We would like to define some property of the water/dye system we could calculate for various regions in the water, to test if they are in diffusive equilibrium.

### 2.9.4 Phase Equilibrium

If a substance is placed in a sealed container, under some conditions it segregates into separate regions with distinct properties (**for example, solid and liquid, or liquid and vapor**). We call each region with homogeneous properties a phase. **When the amount of each phase is constant, the substance is in phase equilibrium .**

**The chemical potential of any given phase of a pure substance is some function of T and P**.

## 2.9.5 Chemical Equilibrium

**If multiple chemical species are mixed together, they might chemically react. If they do, the concentration of each reactant will decrease, and the concentrations of the products of the reaction will build up.** The products may react with one another, too, "reversing" the reaction and re-forming the reactants. Eventually, the concentrations of all species will settle at values such that the forward reaction rate just balances the reverse one. **When this happens, the concentrations will no longer change, and we say the system is in chemical equilibrium. As we'll see later, the chemical potential is again the relevant property to determine when a system is in chemical equilibrium**, although the analysis is more complicated than for diffusive or phase equilibrium.

## 2.9.6 Thermodynamic Equilibrium

**When all parts of a system are equilibrated in all ways (mechanical, thermal, diffusive, phase, chemical), we say the system is in thermodynamic equilibrium**. The temperature, pressure, and chemical potential will be the same in all parts of a system in thermodynamic equilibrium, and the concentrations of every chemical species will be constant in time.

## 2.9.7 Restricted Equilibrium

Sometimes a system is kept from attaining one type of equilibrium, although it is equilibrated in other ways. For example, a rigid, heat-conducting partition dividing a system in

two parts will allow thermal, but not mechanical, equilibrium to be attained. In other cases, there is no partition but one type of equilibrium is attained very slowly compared to other types. **When a system is equilibrated in some ways but not others, we say it is in restricted equilibrium.**