2.1 INTRODUCTION

Thermodynamics is the branch of science that deals with energy possesed by gases and vapours. In other words, it is the science which deals with the energy transformation from one form to another and the relationship between the properties of the working substance. These transformations are governed by the various 'Laws of Thermodynamics'. The working substance or the working fluid, which may be in gaseous or liquid form, convey energy from one point to another. If the working fluid remains in gaseous state and obeys certain 'Law of Gases' throughout the energy transformation then we refer it as a 'Perfect Gas'.

Generally, thermodynamics is concerned with two forms of energy i.e. Heat and Work.

The science of thermodynamics is based on the four laws of thermodynamics known as Zeroth, First, Second and Third laws.

The application of thermodynamics is extremely wide. Its principles are used in the designing of energy converting devices such as Steam engines, Internal Combustion engines, steam and gas turbines, fuel cells etc. It also used in refrigerators, airconditioners, etc.

2.2 WORKING SUBSTANCE

The working substance in most work producing and absorbing devices is gas or vapour, or vapour and liquid in equilibrium. In order to understand their working, it is essential to know the behaviour and properties of the working substance. The concept of pure substance is useful in the determination of the properties of the working substance at variours conditions of pressure and temperature.

A material of single or homogeneous chemical structure is known as pure substance.

Water is an example of pure substance. Air may be considered as a pure substance in the gaseous state. However, when it is in equilibrium with the liquid phase, it cannot be called a pure substance. For example, steam power generating plants use water vapour and ice plants use ammonia or freon as the working substance.

2.3 THERMODYNAMIC SYSTEM

The term system is defined as a prescribed region of space or finite quantity of matter, whose behaviour is to be studied is known as a Thermodynamic System.

2.3.1 Boundary

An envelope enclosing the system is known as Boundary of the system.

The boundary may be a real physical surface, such as the walls of a vessel, Internal Combustion engine cylinder, etc. or it may be an imaginary surface enclosing some matter such as steam, gas vapour etc.

The boundary may be fixed or it may be moving, as when a system containing a gas is compressed or expanded. So, we can say that, the system is defined as a specified region wherein changes due to transfer of mass or energy are both to be studied.

In a system, it is not necessary that the volume or shape should remain fixed.

2.3.2 Surrounding

Everything outside the system boundary is called the Surrounding.

2.3.3 Universe

A system and its surrounding when put together, is called Universe. A piston cylinder arrangement shown in the Fig. 1 in which system, boundary and surrounding are described.

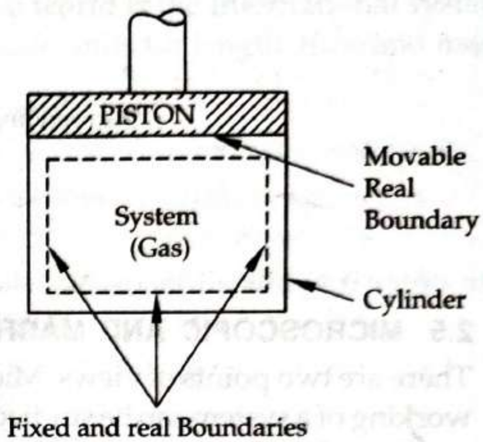

Fig. 1 Representation of System, Boundary and Surrounding

2.4 TYPES OF SYSTEM

There are three types of systems:

1. Closed 2. Open and 3. Isolated System

1. Closed System: A system is called a closed system in which the mass within the boundary of the system remains constant, so that no mass enters or leaves the system, and only the energy (heat and work) may transfer across its boundary e.g., Piston cylinder.

Such a closed system is shown in Fig. 2 in which the gas is confined between the piston and the cylinder. The mass of the gas is constant within the system even though the gas may be expanded or compressed because it is closed from all the sides. A variation in the volume of the gas may occur. But the transfer of heat and work energy are taking place in the closed system.

2. Open System: A system is called an open system in which the mass and energy of the system are transfer across its boundaries.

Such as open system is shown in Fig. 3 in which the gas is entering and coming out of the system while transfer of heat and work energy is also taking place. The net amount of mass within the system may also vary with time e.g. Turbine.

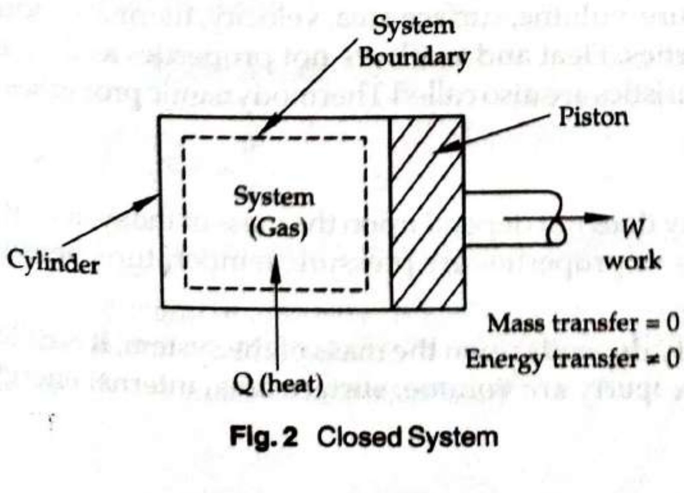

Fig. 2 Closed System

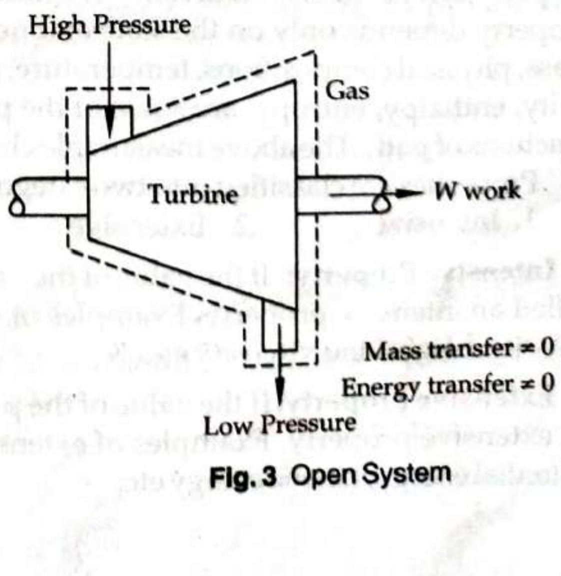

Fig. 3 Open System

3. **Isolated System:** A system is called an isolated system in which mass and energy both of the system are not allowed to cross the boundary of the system e.g. gas enclosed in a perfectly insulated closed vessel (Thermos flask). Shown in Fig. 4.

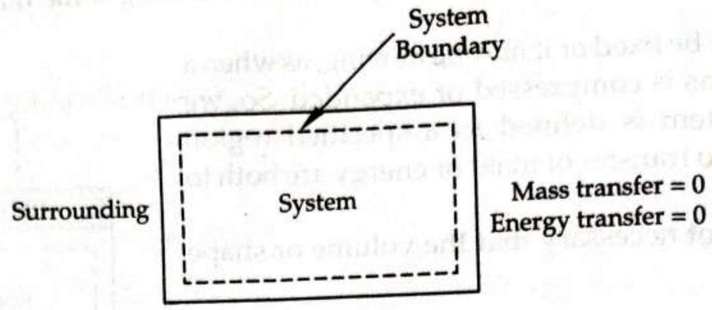

Fig. 4 Isolated System

2.5 MICROSCOPIC AND MACROSCOPIC POINT OF VIEW

There are two points of views, Microscopic and Macroscopic, from which the behaviour of matter or working of a system can be studied.

From Microscopic point of view, it is considered that the matter is not continuous, but it is made up of a large number of identical particles called Molecules.

For Example, consider a gas in a cylinder as system. Then this gas is made up of a number of molecules. Each molecules of a gas, at a given instant has certain position, energy, etc. and for each molecule these changes rapidly because of the collisions (striking). The behaviour of the gas is described by summing up the behaviour of the molecules. For summing up the behaviour of molecules statistical methods are employed and hence it is also called as Statistical Thermodynamics.

In Macroscopic point of view a certain quantity of matter is considered and the events that are taking place at the molecular level are not taken into account.

For example, let us consider a system of an I.C. engine, consisting of a charge in the engine cylinder. At any instant the system has a certain volume depending upon the position of the piston, this volume is easily measurable. Another quantity to describe the system is the pressure of the gas inside the cylinder. A pressure gauge can be used to measure the same. Similarly, temperature, chemical composition etc. may be described. Thus, in macroscopic point of view the system will be described by large scale properties. It is also called "Classical Thermodynamics".

2.6 PROPERTY

The quantities which characterise the given state of the system are called properties or parameters. A property can be measured directly or indirectly while the system is in equilibrium. The value of the property depends only on the state and not on the process or path by which the state is achieved. Mass, physical compositions, temperature, pressure, volume, surface area, velocity, thermal conductivity, enthalpy, entropy are some of the properties. Heat and work are not properties as they are functions of path. The above measurable characteristics are also called Thermodynamic properties.

Properties are classified into two categories:

1. Intensive 2. Extensive

1. **Intensive Property:** If the value of the property does not depend upon the mass of the system, it is called an intensive property. Examples of intensive properties are pressure, temperature, density, velocity, height, and viscosity etc.

2. **Extensive property:** If the value of the property depends upon the mass of the system, it is called an extensive property. Examples of extensive property are volume, surface area, internal energy, potential energy, kinetic energy etc.

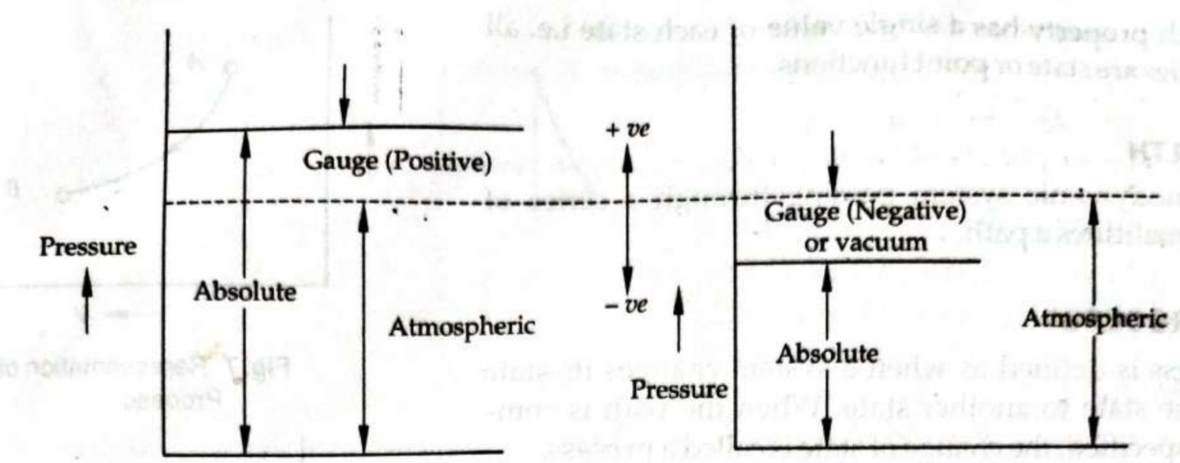

Fig. 5 Pressure Measurement

The other units are:

1 bar = 10^5 N/m^2 = 10^5 Pa = 0.1MPa

1 atm = 101325 Pa = 760 mm of Hg = 14.696 lbf/in^2 or Psi

1 kgf/cm^2 = 0.980665 bar.

1 torr = 1 mm Hg.

1 micron = 1 μ = 10^{-6} m Hg = 10^{-3} mm Hg

1 mm of Hg = 133.3 N/m^2 = 0.13332 kPa = 0.0013332 bar.

1 N/mm^2 = 10^6 N/m^2

2.14 THERMODYNAMIC EQUILIBRIUM

A system is said to be in thermodynamic equilibrium if the value of the property is the same at all the the points in the system.

Thermodynamic equilibrium is a complete equilibrium if it satisfies the following three equilibrium:

1. Mechanical Equilibrium (no unbalancing)
2. Chemical Equilibrium (no reaction)
3. Thermal Equilibrium (no temperature gradient)

Mechanical Equilibrium: A system is said to be in mechanical equilibrium when there is no unbalanced forces acting on any part of the system or system as a whole.

Chemical Equilibrium: A system is said to be in chemical equilibrium when there is no chemical reaction within the system and also there is no movement of any chemical constituent from one part of the system to the other.

Thermal Equilibrium: A system is said to be in thermal equilibrium where there is no temperature difference between the parts of the system or between the system and the surroundings.

2.15 STATE

The instantaneous condition of a thermodynamic system is called its state. In other words, state is the condition of a system at a particular time. The state of the system is described by its properties such as pressure, temperature, density etc. This is shown on pressure-volume diagram as state 1 and 2.

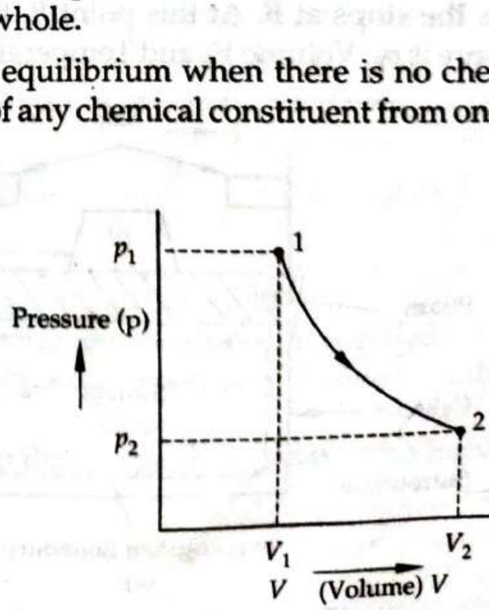

Fig. 6 State of a System

Each property has a single value of each state i.e. all properties are state or point functions.

2.16 PATH

A thermodynamic system passing through a series of states constitutes a path.

2.17 PROCESS

A process is defined as when a system changes its state from one state to another state. When the path is completely specified, the change of state is called a process.

In Fig. 7 state A is the initial state of the system. Then due to expansion of the system, the final state is *B*. The line *AB* is the process that has taken place.

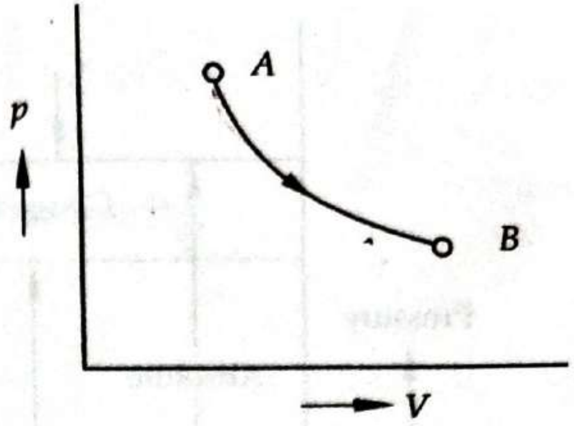

Fig. 7 Representation of Process

2.18 CYCLIC PROCESS

When a process or processes are performed on a system in such a way that the final state is identical with the initial state. It is then known as cyclic process.

A cyclic process may be represented on *p-V* diagram as shown in Fig. 8 if the various state and paths are known.

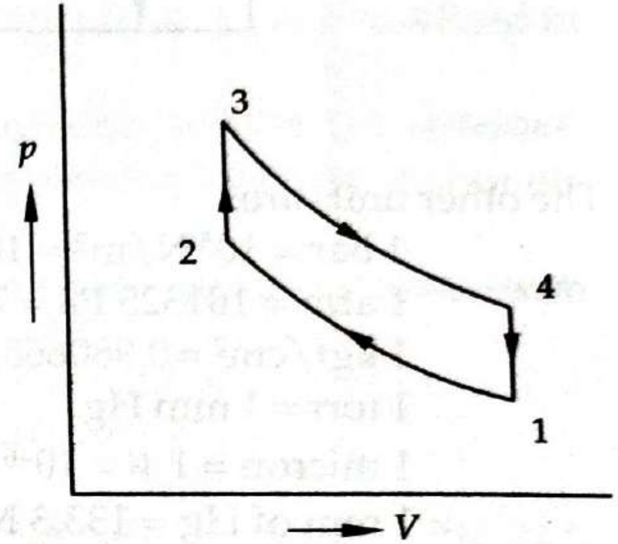

Fig. 8 Cyclic Process

2.20 REVERSIBLE AND IRREVERSIBLE PROCESSES

If a system passes through a continuous series of equilibrium states, the states can be easily identified by the statement of their properties.

It will therefore, become easy to mark these states on a diagram of appropriate properties such as *P-V* diagram shown in Fig. 10.

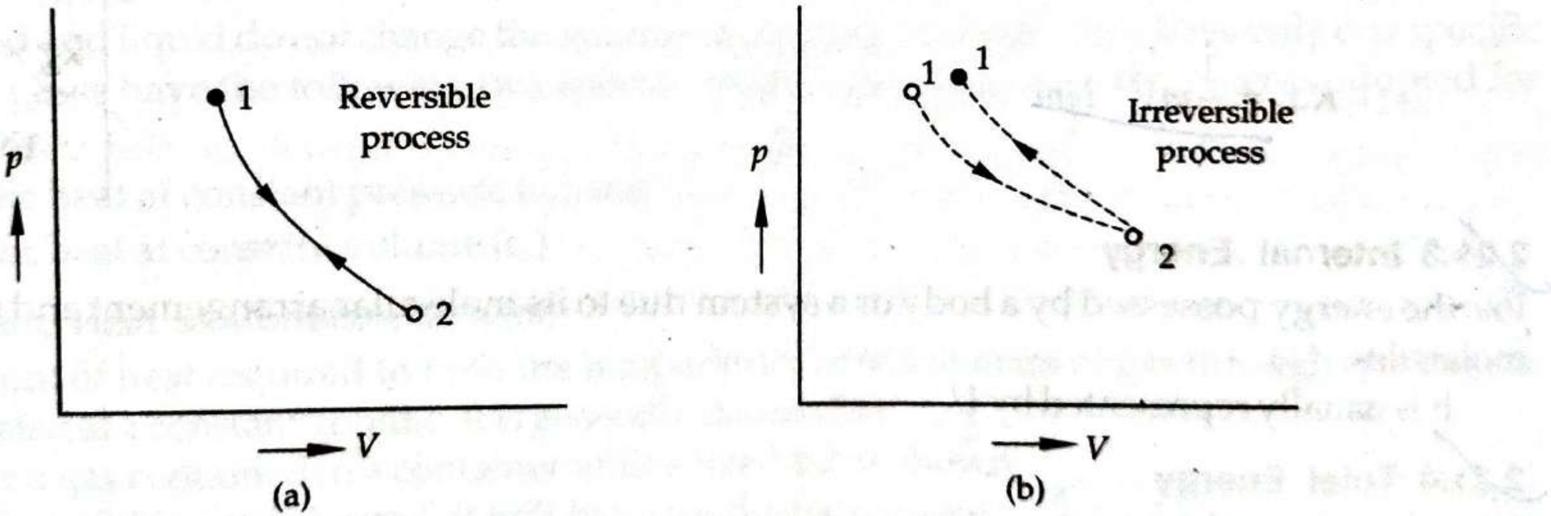

Fig. 10

A line representing the path of process can be drawn through all the points.

A thermodynamic process which can be operated in the reverse direction is called reversible process. On the other hand, if a system passes through a sequence of non-equilibrium state during a process, these states cannot be identified.

A thermodynamic process which cannot be operated in the reverse direction is called Irreversible process.

2.21 ENERGY

It is the capacity to do work. In other words, a system is said to possess energy when it is capable of doing some work.

The energy possessed by a system is of the following two types:

1. Stored energy 2. Transit energy

1. *Stored energy:* This is the energy which is contained within the system boundaries. Examples of stored energy are potential energy, kinetic energy and internal energy etc.

2. *Transit energy:* This is the energy which crosses the system boundaries. Examples of transit energy are heat, work and electric energy.

2.21.1 Potential Energy

It is the energy, possessed by a body because of its height above the earth surface (ground level) e.g. a body raised to some height above the ground level possesses potential energy because it can do some work by falling on earth's surface.

Let W = Weight of the body

m = Mass of the body

z = Distance through which the body falls, and

g = Acceleration due to gravity = 9.81 m/s²

$\therefore$ Potential energy, $P.E = Wz\ Nm$

or $P.E = mgz\ Nm$ $\left[\begin{array}{l} \text{kg} \times \dfrac{m}{s^2} \times m = N - m \\ \because\ 1N = \dfrac{1\text{kg} - m}{s^2} \end{array}\right]$

2.21.2 Kinetic Energy

It is the energy possessed by a body by virtue of its mass and velocity of motion.

Let m = Mass of the body, and

V = Velocity of the body

Kinetic Energy,

$$K.E = \frac{1}{2} mV^2\ Nm \qquad \left[\begin{array}{l} \text{kg} \times \dfrac{m^2}{s^2} = Nm \\ \because\ 1N = \dfrac{1\text{kg} - m}{s^2} \end{array}\right]$$

2.21.3 Internal Energy

It is the energy possessed by a body or a system due to its molecular arrangement and motion of the molecules.

It is usually represented by U.

2.21.4 Total Energy

It is sum of potential, kinetic and internal energy.

$$E = P.E + K.E + U = mgz + \frac{1}{2}mV^2 + U$$

2.21.5 Law of Conservation of Energy

It states that the energy can neither be created nor destroyed. This means that the total energy possessed by a body remains constant. Energy can be changed from one form to another form as explained in the following two Examples.

(i) Water flows from a tank through a vertical pipe — Potential energy is converted into Kinetic energy.

(ii) Brake is applied in an automobile — Kinetic energy of the wheel is converted into heat energy due to friction.

2.21.6 Law of Conservation of Mass

This law states that the mass can neither be created nor destroyed but can only be changed from one form to another form.

A substance can be changed from solid to liquid and liquid to gas or vice-versa.

2.22 HEAT

Heat is defined as the energy that is transfered across the boundary of a system due to the temperature difference between the two systems and in the direction of higher temperature system to lower temperature system.

It is usually represented by Q and is expressed in Joule (J) or Kilo Joule (kJ) in english system, its unit is calorie.

Heat transferred to a system is considered positive and heat transferred from a system is considered negative. It is a path function.

The heat can be transferred in three ways i.e. conduction, convection and radiation. The transfer of heat through solids take place by conduction, while the transfer of heat through fluids is by convection. The radiation is an electromagnetic wave phenomenon in which energy can be transported through transparent substances and even through a vaccum.

2.23 SPECIFIC HEAT

The specific heat of a substance is defined as the amount of heat required to raise the temperature of a unit mass of any substance through one degree.

It is generally denoted by c. In S.I. system of units, the unit of specific heat is taken as kJ/Kg K. If m kg of a substance of specific heat, c is required to raise the temperature from an initial temperature T_1, to a final temperature of T_2, then

$$\text{Heat required} = m\,c\,(T_2 - T_1)\ \text{KJ}$$

where T_1 and T_2 may be either in °C or in K.

Since solid and liquid do not change the volume on heating, therefore they have only one specific heat. But the gases have the following two specific heats depending upon the process adopted for heating the gas.

1. Specific heat at constant pressure (c_p) and
2. Specific heat at constant volume (c_v)

2.23.1 Specific Heat at Constant Volume

It is the amount of heat required to raise the temperature of a unit mass of gas through one degree when it is heated at a constant volume. It is generally denoted by c_v.

Consider a gas contained in a container with a fixed lid as shown in Fig. 11. Now, if this gas is heated, it will increase the temperature and pressure of the gas in the container. Since the lid of the container is fixed, therefore the volume of gas remains unchanged.

Let m = Mass of the gas

T_1 = Initial temperature of the gas and

T_2 = Final temperature of the gas

∴ Total heat supplied to the gas at constant volume

Q = Mass × Specific heat at a constant volume × Rise in temperature

$$= m\,c_v\,(T_2 - T_1)$$

It may be noted that whenever a gas is heated at constant volume, no work is done by the gas.

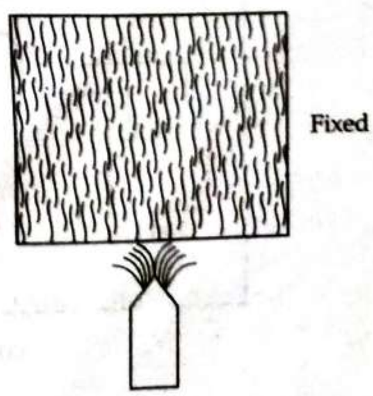

Fig. 11 Heat being supplied at constant volume

We know that,

work done, $W = pdV = p(V_2 - V_1)$

where p = Pressure of the gas

dV = Change in volume = $V_2 - V_1$

When there is no change in volume, then

$$dV = 0$$

Therefore $W = 0$

2.23.2 Specific Heat at Constant Pressure

It is the amount of heat required to raise the temperature of a unit mass of a gas through one degree, when it is heated at constant pressure. It is generally denoted by c_p.

Consider a gas contained in a container with a movable lid as shown in Fig. 12. Now, if this gas is heated, it will increase the temperature and pressure of the gas in the container. Since the lid of the container is movable, therefore it will move upwards, in order to counterbalance the tendency for pressure to rise.

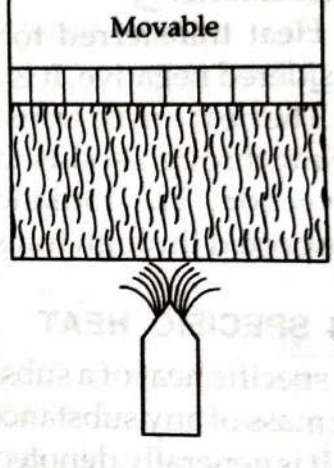

Fig. 12 Heat being supplied at constant pressure

Let m = Mass of the gas

T_1 = Initial temperature of the gas

T_2 = Final temperature of the gas

v_1 = Initial volume of the gas

v_2 = Final volume of the gas

$\therefore$ Total heat supplied to the gas, at constant pressure

Q = Mass × Specific heat at constant pressure × Rise in temperature

$= m\,c_p\,(T_2 - T_1)$

2.24 WORK

Work is an energy interaction between a system and its surroundings. Energy can cross the boundary of a closed system in the form of heat or work. In fact, heat and work are the only two mechanisms by which the energy of a closed system can be changed. Therefore, if the energy crossing the boundary is not heat, it must be work. We can say simply that, an energy interaction which is not caused by a temperature difference between the system and its surroundings is work.

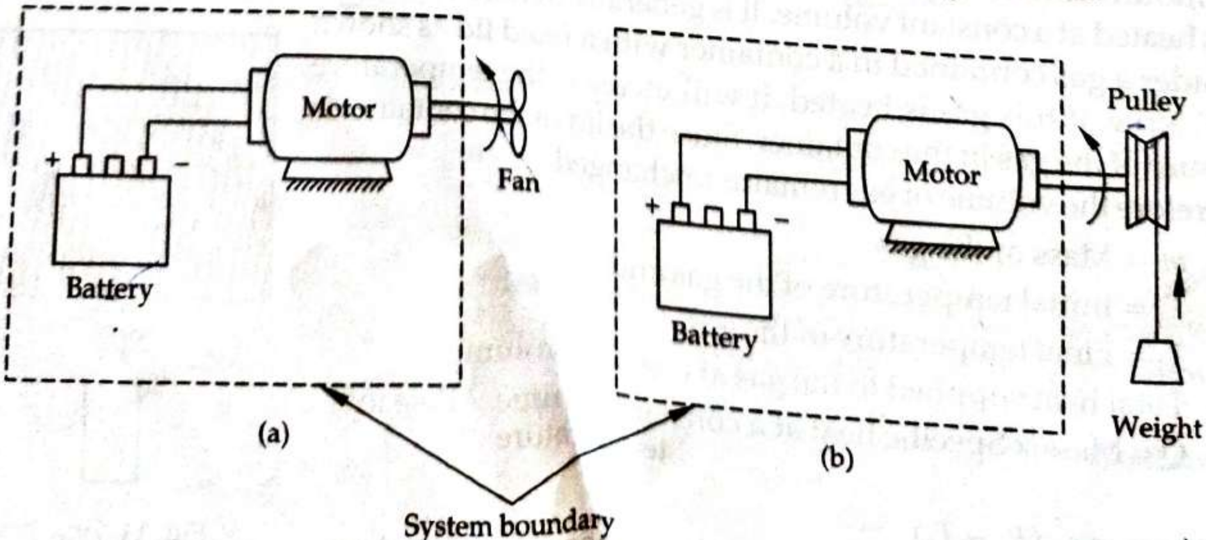

Fig. 13 Work crossing the boundary of a system

In mechanics, work is defined as the product of the force (F) and the distance moved (x) in the direction of force.

Mathematically, work done

$$W = F \cdot x$$

The unit of work depends upon the unit of force and the distance moved.

In S.I. system of unit, the practical unit of work is Newton – metre ($N-m$). The work of 1 $N-m$ is known as joule because 1 $N-m$ = 1 J.

Work is a form of energy and is done by a system if the entire effect on surroundings could be the raising of a weight.

Consider a system of battery and motor as shown in Fig. 13. The motor drives the fan in arrangement (a) The fan is replaced with the pulley and weight in arrangement (b) When the motor runs, the weight is raised. The work is crossing the boundary of the system as the sole effect external to the system is for raising of a weight.

R = Gas constant

The value of R_u is same for all gases.

In S.I. units, value of R_u is 8314 J/Kg-mol K

or 8.314 kJ/Kg-mol K.

2.28.9 Regnault's Law

This law states that the two specific heats of a gas (i.e., specific heat at constant pressure, c_p and specific heat at constant volume, c_v) do not change with the change in pressure and temperature of the gas.

2.28.10 Avogadro's Law

This law states that equal volumes of all gases, at the same temperature and pressure, contain equal number of molecules.

2.29 TEMPERATURE

A number of definitions of temperature have been proposed. In a layman's language one could define this as the degree of hotness or coldness of a body or mass.

Temperature is an intensive thermodynamic property which determines the hotness or the level of heat intensity of a body or mass.

A high temperature indicates high level of heat intensity and the body is said to be hot. Similarly, a low temperature indicates low level of heat intensity and the body is said to be cold.

The temperature of a body is measured with the help of an instrument called thermometer.

For the measurement of temperature these are two well known scales.

(1) Celsius or Centigrade Scale (2) Fahrenheit Scale

Each of these scales is based on two fixed points known as freezing point of water under atmospheric pressure or ice point and the boiling point of water or steam point.

1. **Celsius or centigrade scale:** This scale was first used by Celsius in 1742. This scale is mostly used by engineers and scientists. The freezing point of water on this scale is marked as zero, and the boiling point of water as 100. The space between these two points have 100 equal divisions, and each division represents one degree celsius (written as °C).

2. **Fahrenheit scale:** This scale was first used in 1665. In this scale, the freezing point of water is marked as 32 and the boiling point of water as 212. The space between these two points has 180 equal divisions and each division represents one degree Fahrenheit (written as °F).

The values on Fahrenheit scale can be readily converted into those on the centigrade or celcius scale and vice-versa by noting that 180 degree of the fahrenheit scale are equal to 100 degree of the centigrade or celcius scale.

The relation between celsius scale and Fahrenheit scale is

$$\frac{C}{100} = \frac{F - 32}{180}$$

or

$$\frac{C}{5} = \frac{F - 32}{9}$$

2.29.1 Absolute Temperature

The zero readings on the ordinary centigrade (celsius) and fahrenheit scale are chosen arbitarily for simplicity.

The temperature, below which the temperature of any substance can not fall, is known as absolute zero temperature.

The absolute zero temperature, for all sorts of calculations, is taken as – 273°C in case of celsius scale and – 460°F in case of Fahrenheit scale. The temperature measured from this zero are called absolute temperature. The absolute temperature in celsius scale is called degree Kelvin(K), such that K = °C + 273. Similarly, absolute temperature in Fahrenheit scale is called degree Rankine (°R) such that °R = °F + 460.