1.1 INTRODUCTION

The word thermodynamics is made up of two greek words : 'Therme' means heat and 'dynamis' means motion. Hence thermodynamics means heat in motion. Thermodynamics may be defined as *the field of science dealing with energy in the form of heat and work and their conversion into each other*. This study is based upon observations of common experience which have been formulated into thermodynamic laws. The applications of the thermodynamic laws are found in all fields of energy transfer, mainly, in steam and nuclear power plants, gas turbines, internal combustion engines, air conditioning, refrigeration, gas dynamics, air compressors, chemical process plants etc.

1.2 MACROSCOPIC AND MICROSCOPIC ANALYSIS

There are two points of view by which behaviour of matter can be studied : (*i*) Macroscopic, (*ii*) Microscopic. *The description of a system using a few measurable properties is known as macroscopic analysis of the system*. In case of macroscopic study, the structure of the matter is not considered *i.e.* the behaviour of the individual particles (molecules) constituting the matter is not focused. Basically, this study concerns with the overall effect of the individual molecular interactions. *e.g.* Let us consider a petrol engine cylinder having a mixture of air and petrol vapours. The volume of this mixture at any position of piston can be easily measured. The pressure and temperature can also be measured for each position of piston in cylinder. The above mentioned properties describing the condition of system are known as macroscopic properties. The macroscopic approach is also known as classical approach. *But, if the study is made on the basis of behaviour of individual atoms and molecules of a substance, then the study is said to be microscopic study*. The microscopic approach is also termed as statistical approach. Macroscopic observations are completely independent of the assumptions regarding nature of matter. However, the results of macroscopic thermodynamics can be derived from microscopic study of matter.

1.3 THERMODYNAMIC SYSTEM, SURROUNDINGS, BOUNDARY, UNIVERSE AND STATE

A. System : A thermodynamic system is defined as *a quantity of matter or a prescribed region in space upon which attention is focused for study.*

B. Surroundings : *Everything external to the system is called as surroundings or the environment.*

C. **Boundary :** *It is kind of envelope which separates the system from surroundings.* The boundary may be real or imaginary. It may be fixed or moving. Piston moving in a cylinder containing gas is an example of moving boundary.

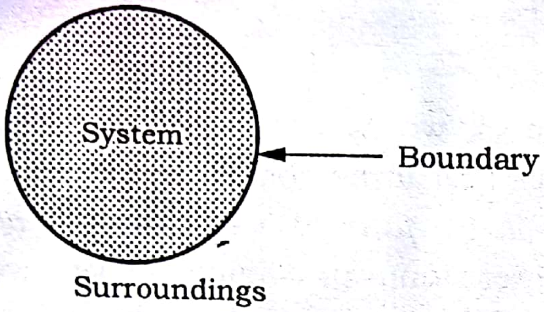

Fig. 1.1 : Thermodynamic System

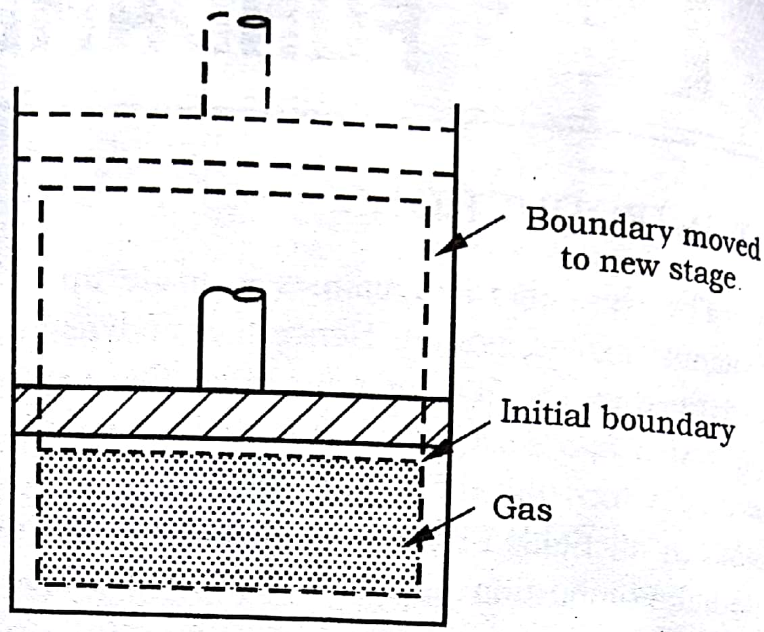

Fig. 1.2 : Moving Boundary

D. **Universe :** *A system and its surroundings together form a universe.*

E. **State :** *The condition of a system at any instant of time described by its physical properties is known as state of the system.* Let us consider a piston cylinder arrangement having gas enclosed in it. The condition of the system at any instant will be given by pressure, volume and temperature of the gas. When all such properties have a definite value, a definite state is said to exist. When piston moves downwards, the properties of the system change (Pressure and temperature increase while volume decreases). *Any such operation in which properties of system change is called a change of state.*

1.4 TYPES OF THERMODYNAMIC SYSTEMS

Thermodynamic systems can be classified into the following types :

(*a*) Closed system,

(*b*) Open system,

(*c*) Isolated system.

(*a*) **Closed System :** *If there is no transfer of mass across the system boundary (i.e. between system and surroundings), it is called closed system.* However, energy may be transferred into or out of system. Fig. 1.3 shows a piston cylinder arrangement containing a gas, which is an example of closed system. When heat is supplied to the cylinder from some external source, temperature of gas increases and the piston rises. Due to piston rise, the boundary of system will move upward. Therefore, heat and work energy transfer take place across the system boundary, whereas there is no addition or loss of mass of working substance.

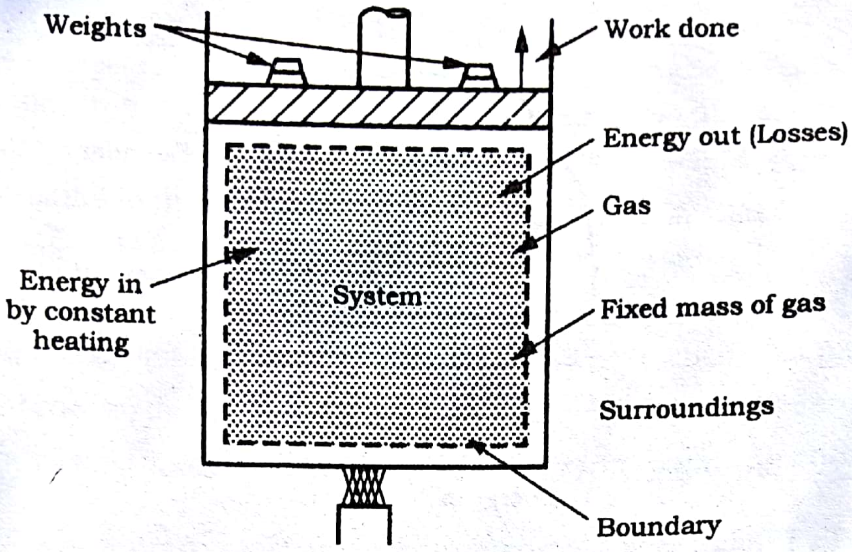

Fig. 1.3 : A Closed System

Other examples of a closed system are :

(*i*) Motor-car battery,

(*ii*) Bomb calorimeter,

(*iii*) Kitchen refrigerator etc.

(*b*) Open System : *In an open system, there is an exchange of mass across the system boundary*. There may be energy transfer also. Most of the engineering devices are generally open system. *e.g.* an air compressor. In an air compressor, air enters at low pressure and leaves at high pressure. Work input is given across the boundary through the motor and driving shaft and heat is transferred across the boundary from cylinder walls. Figs. 1.4 and 1.5 shows examples of open system.

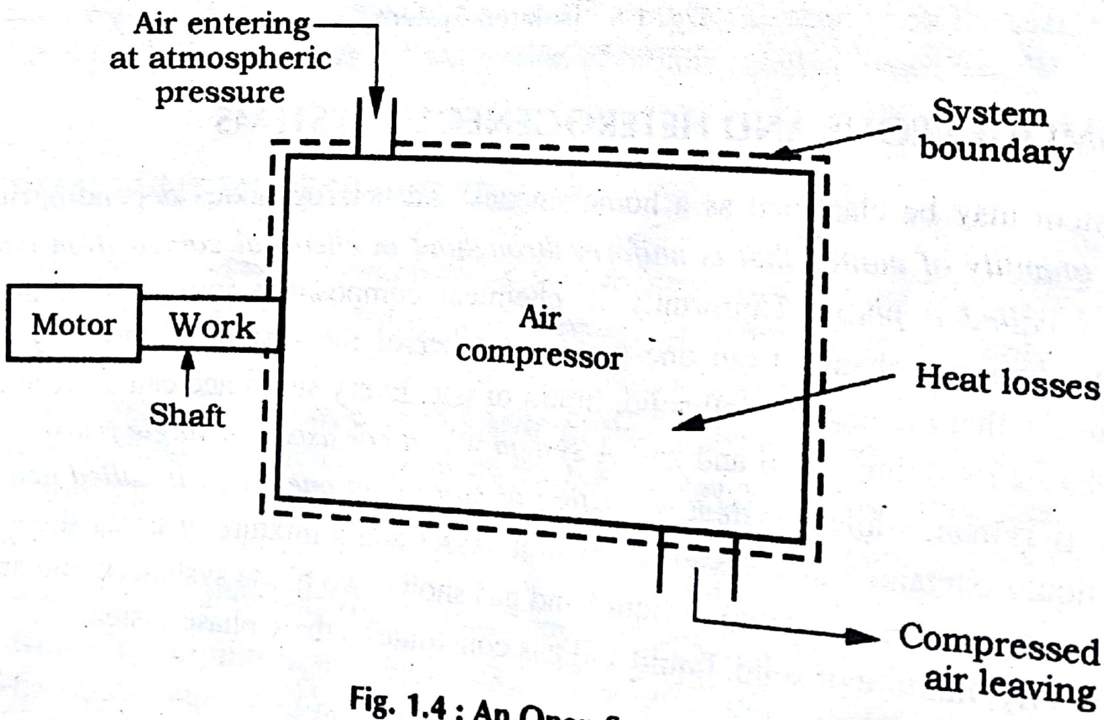

Fig. 1.4 : An Open System

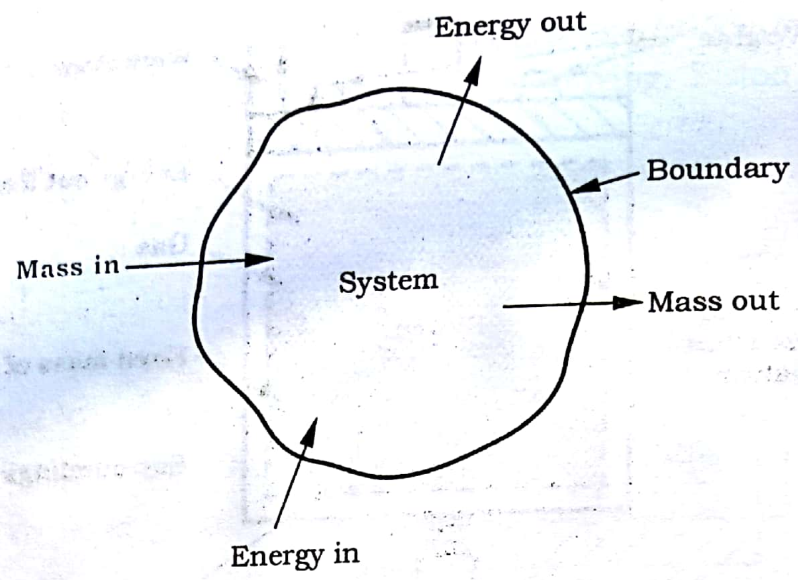

Fig. 1.5 : An Open System

(c) **Isolated System :** Fig. 1.6 shows an isolated system. *In an isolated system, there is no transfer of mass and energy to and from the system.* It is a system of fixed mass and no heat or work energy can cross the system boundary.

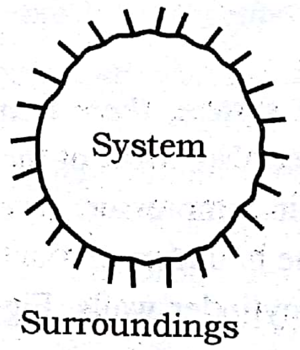

Fig. 1.6 : Isolated System

1.5 HOMOGENEOUS AND HETEROGENEOUS SYSTEMS

A system may be classified as a homogeneous and heterogeneous depending upon phase change. *A quantity of matter that is uniform throughout in chemical composition and physical structure is called a phase.* Uniformity in chemical composition implies that the chemical composition does not change from one part to another of the system. Uniformity in physical structure means that the matter is all solid, liquid or gas. Every substance can exist in any one of the three phases *i.e.* solid, liquid and gas. *A system which consists of a single phase in known as homogeneous system*, while *a system consisting of more than one phase is called heterogeneous system.* A liquid contained in a vessel, a gas in a vessel and a mixture of gases show one phase system. A system having a mixture of liquid and gas shows two phase system (liquid and gaseous phase). Similarly, mixture of solid, liquid and gas constitutes a three phase system.

equilibrium. The system and surroundings will undergo a change of state, if an unbalance force exists. This will continue till a new mechanical equilibrium is attained.

(*b*) **Chemical Equilibrium :** *If there is no chemical reaction or transfer of matter with in system or between the system and surroundings, the system is said to be in a state of chemical equilibrium.*

(*c*) **Thermal Equilibrium :** *It is the condition or state in which the temperature of the system is uniform is called as thermal equilibrium.* Let us take an example of vessel containing hot fluid. Let this system be under mechanical and chemical equilibrium. Heat will flow from hot fluid to atmosphere till both attain the same temperature and then the heat transfer will cease. Such a state will be called as thermal equilibrium.

1.8 THERMODYNAMIC PROCESS

When a system changes its state from one equilibrium state to another equilibrium state, then the path of successive states through which system passes is known as thermodynamic process. In fig. 1.7, 1 – 2 shows a process.

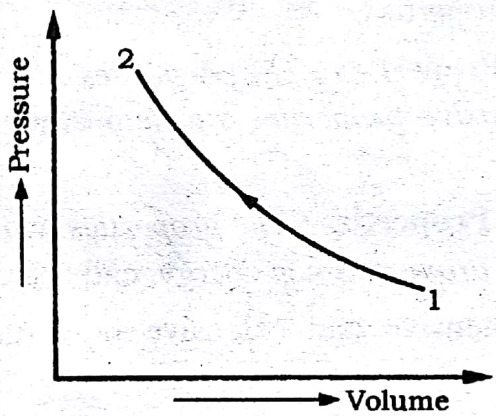

Fig. 1.7 : Thermodynamic Process

1.9 REVERSIBLE AND IRREVERSIBLE PROCESSES

A process which can be reversed in direction and the system retraces the same path and the same equilibrium states is known as reversible process. Fig. 1.8 shows a reversible process.

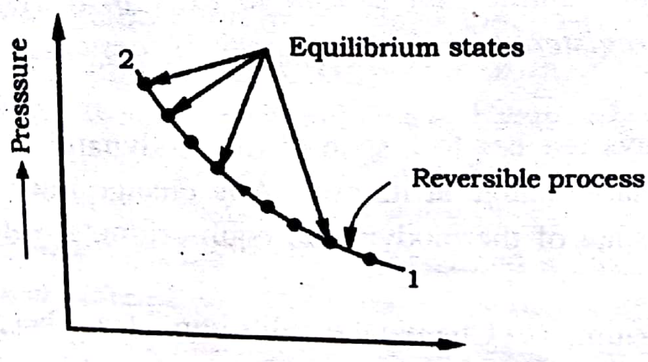

Fig. 1.8 : Reversible Process

Initially, the path is 1 – 2. If the process is reversed, path 2 – 1 will be followed and the system will restore to its respective initial states. Followings are the conditions which should be satisfied for the process to be reversible :

(*i*) Process should be frictionless.

(*ii*) The process should proceed at infinitely slow speed (quasti-static).

(*iii*) The heat exchange, if any, should be only through infinitely small temperature difference.

A process is said to be irreversible if a system passes through a sequence of non-equilibrium states. An irreversible process cannot come back to the original state, if made to proceed in reverse direction. Fig. 1.9 shows an irreversible process with dotted lines (because properties are definite only at initial and final states.)

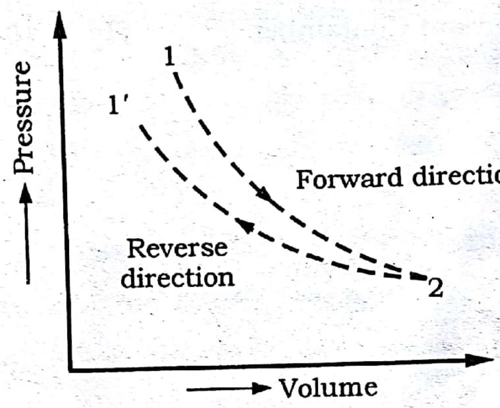

Fig. 1.9 : Irreversible Process

1.10 QUASI-STATIC PROCESS

When the process is carried out in such a manner that at every instant, the system deviation from the thermodynamic equilibrium is very small, then the process is known as quasti-static process. A quasi-static process is also called a reversible process. Let us take an example of a system (gas) enclosed in a cylinder and piston arrangement shown in fig. 1.10(*a*). The system initially is in equilibrium state, given by properties P_1, V_1 and T_1. In equilibrium position, the upward forces exerted by the gas just balance the weights on the piston. If weight is removed, there will be an unbalanced force between the system and surroundings, and the piston will move up due to gas pressure till it hits the stop at point 2. The system again comes to an equilibrium state with the new properties P_2, V_2, and T_2. The intermediate states passed by the system are non equilibrium states which cannot be described by thermodynamic coordinates. The line joining points 1 to 2 is a dotted line as shown in Fig. 1.10 (*b*). Now suppose, the single weight is made up of a number of very small weights as shown in fig. 1.10(*a*) and the weights are removed one by one very slowly from the top of piston. In this case, at any instant of upward movement of piston, the deviation of the state from thermodynamic equilibrium will be infinitesimally small. So every state passed through by the system will be an equilibrium state. Such a process which consists of all these equilibrium states is known as quasi static process. Fig. 1.11 shows the quasi static process.

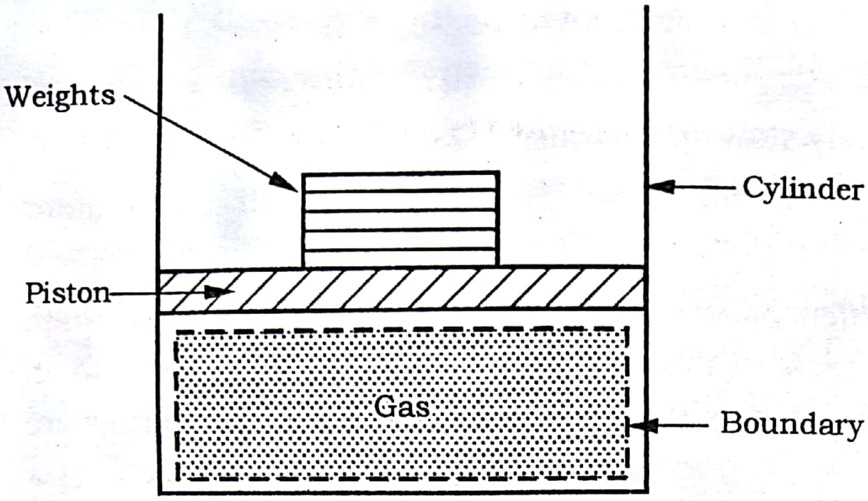

Fig. 1.10(a) Piston Cylinder Arrangement Containing Weights

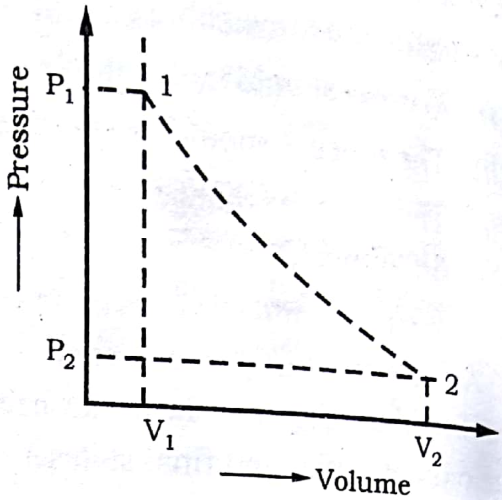

Fig. 1.10(b) P–V Diagram for Non-equilibrium Process 1-2

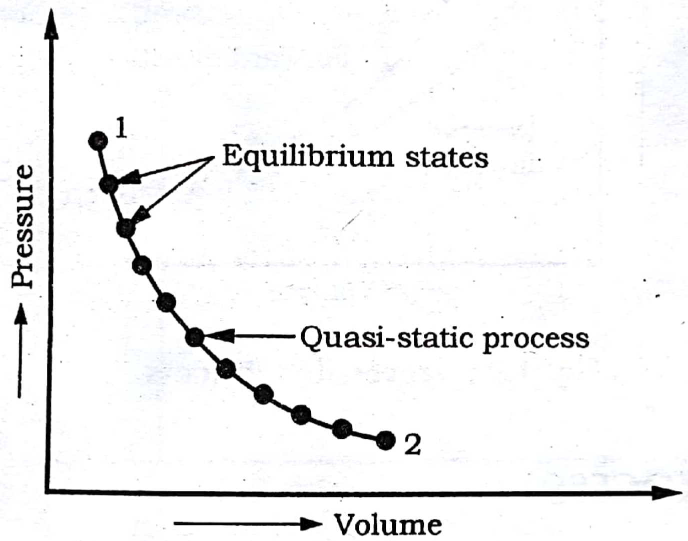

Fig. 1.11 : P–V Diagram for Quasi-static Process

1.11 PRESSURE

Pressure may be defined as *the normal force exerted by a system against unit area of the surface.*

$$\text{Pressure, P} = \frac{F}{A} \qquad \text{...(1.1)}$$

where F is the normal force and A is the area on which force is exerted.

The S.I. unit of pressure is N/m^2. Other units are N/mm^2, kN/m^2, MN/m^2 etc. Sometimes, a bigger unit is also used. *i.e.*,

$$1 \text{ bar} = 1 \times 10^5 \text{ N/m}^2 = 0.1 \text{ MN/m}^2$$

Another unit of pressure is Pa (Pascal) which is given by

$$1 \text{ Pa} = 1\text{N/m}^2$$

Also $$1 \text{ atm.} = 101.325 \text{ kPa} = 1.01325 \text{ bar}$$

The following terms are generally used for the measurement of pressure :

(*a*) **Atmospheric Pressure (P_{atm}) :** *It is the pressure exerted by the air on the surface of earth*. The standard value of pressure at the sea level is 760 mm of Hg or 1.01325 bar. It is also equivalent to 10.336 metre of water column or 101.325 kPa.

(*b*) **Absolute Pressure (P_{abs}) :** Absolute pressure is defined as *the pressure acting on a surface due to the interaction of fluid particles amongst themselves*. An absolute zero pressure occurs when molecular momentum is zero. Such a condition occurs at perfect vacuum. *Pressure measured with respect to vacuum or zero pressure is known as absolute pressure.*

(*c*) **Gauge Pressure (P_g) :** *The pressure measured by a pressure gauge will be called as gauge pressure*. All the pressure gauges read the difference between the actual pressure in any system and the atmospheric pressure. *When the unknown pressure is more than the atmospheric pressure, the pressure measured is known as gauge pressure or positive pressure. If the unknown pressure is less than atmospheric pressure, then pressure is known as vacuum or negative pressure.*

i.e. Absolute pressure = Atmospheric pressure + Gauge pressure ...(1.2)

and Absolute pressure = Atmospheric pressure – Vacuum pressure ...(1.3)

Fig. 1.12 is shows the relationship among these pressure.

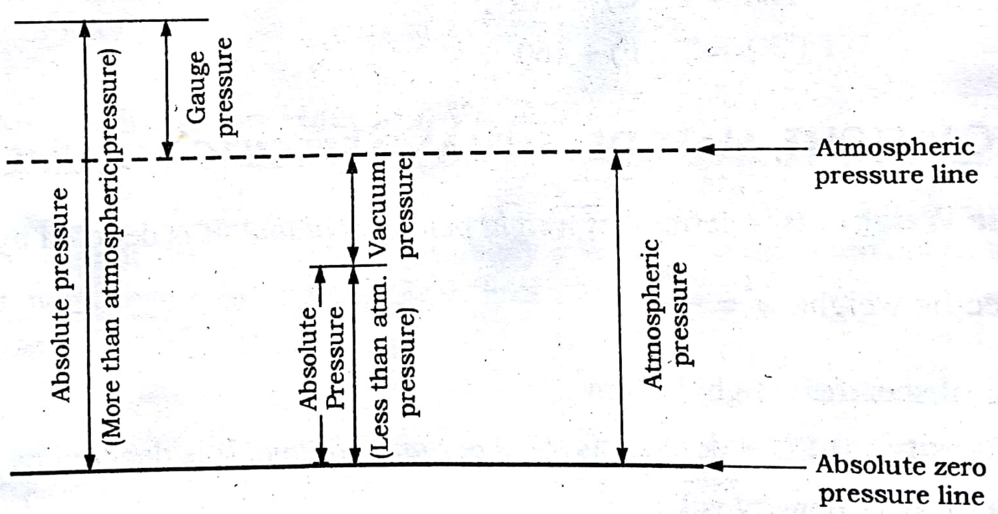

Fig. 1.12 : Relationship Between Absolute Gauge and Atmospheric Pressure

1.12 TEMPERATURE

Temperature is an intensive property which determines the degree of hotness or the level of heat intensity of a body. The temperature of a body is measured with the help of an instrument known as thermometer which looks like a glass tube containing mercury. For the measurement of temperature of body, following types of scales are used :

1. **Centigrade or Celsius Scale (°C) :** In this scale, the freezing point of water is marked as zero and the boiling point of water as 100. The space between these two points is divided into 100 equal divisions, and each division shows one degree Celsius. Most engineers and scientists use this scale.

2. **Fahrenheit Scale (°F) :** In this scale, the freezing point of water is marked as 32 and boiling point of water as 212. The scale between these two points is divided into 180 equal divisions and each division shows one degree Fahrenheit. The relationship between centigrade and Fahrenheit scales is given by

$$\frac{C}{100} = \frac{F-32}{180} \quad \text{...(1.4)}$$

3. **Absolute Temperature :** The zero readings of Celsius and Fahrenheit scales are chosen arbitrarily for the purpose of simplicity. It helps us in our calculations, when changes of temperature in a process are known. Now if the temperature in the above scales was below freezing point of water then, a need was felt to find a scale whose reference point is true zero or absolute zero. Absolute zero temperature is defined as *the temperature below which the temperature of any substance cannot fall.* For all calculations, the absolute zero temperature is taken as – 273°C in case of Celsius scale and –460°F in case of Fahrenheit scale. The absolute temperature in Celsius scale is called degree Kelvin (K) and in Fahrenheit scale is called degree Rankine (°R).

$$T\,(K) = T\,(°C) + 273 \quad \text{...(1.5)}$$

$$T\,(°R) = T\,(°F) + 460 \quad \text{...(1.6)}$$

1.13 SPECIFIC WEIGHT, MASS DENSITY AND SPECIFIC VOLUME

(*i*) **Specific Weight :** It is defined *as weight per unit volume.* It is denoted by *w*.

$$\text{Specific weight, } w = \frac{W}{V} \quad \text{...(1.7)}$$

S.I. unit of specific weight is N/m^3.

(*ii*) **Mass Density (ρ) :** It is defined as *mass per unit volume.* It is denoted by ρ.

S.I. unit of mass density is kg/m^3.

$$\rho = \frac{m}{V} \quad \text{...(1.8)}$$

(*iii*) **Specific Volume :** It is reciprocal of mass density. The specific volume of a system is *the volume occupied by the unit mass of the system.* It is denoted by v. S.I. unit of specific volume is m^3/kg.

$$v = \frac{V}{m} \quad \text{...(1.9)}$$

1.14 HEAT, WORK AND ENERGY

A. Heat : Heat is defined as *the energy transfer without transfer of mass, across the boundaries of a system due to the difference in temperature.* It is denoted by Q and its S.I. unit is Joule (J). There are three modes of heat transfer : (*i*) Conduction, (*ii*) Convection, (*iii*) Radiation.

B. Work : *Work is said to be done by a system if the sole effect of the system behaviour can be reduced to the raising of a weight.*

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

i.e. $$W = F \times x \qquad ...(1.10)$$

S.I. unit of work is Nm or J.

C. Energy

Energy is defined *as the capacity to do work.* The energy possessed by a system is of the following two types :

(*i*) Stored energy,

(*ii*) Transit energy.

(*i*) **Stored Energy :** *It is the energy possessed by a system within its boundaries. e.g.* potential energy, kinetic energy, internal energy etc.

(*ii*) **Transit energy :** *The energy which is capable of crossing system boundaries is called transmit energy. e.g.* heat, work and electrical energy.

1.14.1 Differences Between Heat and Work

Heat	Work
(*i*) Heat cannot be converted absolutely into work even in most perfect heat engine.	Work can be converted absolutely into heat.
(*ii*) It is a low grade energy.	It is a high grade energy.
(*iii*) In heat transfer, temperature difference is required.	No temperature difference is required for work flow.
(*iv*) In a stable system, there is no restriction for transfer of heat.	In a stable system, there cannot be work transfer.
(*v*) Heat supplied to system is taken as positive and heat rejected by system as negative.	The work done on system is taken as negative and by the system as positive.

1.14.2 Similarities Between Heat and Work

(*i*) Heat and work, both are path functions and are inexact differentials.

(*ii*) Both are boundary phenomenon. *i.e.* Both are observed at the boundary of the system.

(*iii*) Both are associated with a process and not with a state.

(*iv*) Heat and work, both are transient phenomenon. Heat transfer or work done can be measured when a system undergoes a change.

1.15 SPECIFIC HEAT

Specific heat of a substance may be defined as *the amount of heat required to raise the temperature of a unit mass of substance through one degree*. It is generally denoted by C. S.I unit of specific heat is J/kgK.

If the temperature of m kg of substance having specific heat C is raised from T_1 to T_2, then

Heat required $= mC\,(T_2 - T_1)$ J.

Solids and liquids have only one specific heat because volume of these do not change on heating, but gases have two specific heats depending upon the process followed :

(*i*) Specific heat at constant pressure (C_P),

(*ii*) Specific heat at constant volume (C_v).

Specific heat at constant pressure *is the quantity of heat required to raise the temperature of a unit mass of gas through one degree at constant pressure.*

Heat required at constant pressure $= mC_p\,(T_2 - T_1)$ ...(1.11)

Specific heat at constant volume *is the quantity of heat required to raise the temperature of a unit mass of gas through one degree at constant volume.*

Heat required at constant volume $= mC_v\,(T_2 - T_1)$ ...(1.12)

It should be noted that C_P is always greater than C_v. The ratio of C_P and C_v for a particular gas is constant and is given by γ.

$$\gamma = \frac{C_P}{C_v} \qquad ...(1.13)$$

For air, $C_P = 1.004$ kJ/kg K

and $C_v = 0.717$ kJ/kg K

$\therefore$ $\gamma = 1.4$

1.16 INTERNAL ENERGY AND ENTHALPY

A. Internal Energy : It is the energy stored in a body or a system due to its molecular arrangement and motion of molecules. If certain amount of heat is supplied to a gas, a part of it is converted into mechanical energy and the remaining gets stored in the gas itself. This energy is