Chapter 12
Thermodynamics

12.1 Introduction

***Thermodynamics** is the study of the connection between heat and work and the conversion of one into the other.* The name "Thermodynamics" implies that it is connected with both "thermal and mechanical" (dynamic) concepts.

The principles of thermodynamics are used by engineers to design the various heat engines, nuclear power stations, missiles, aircrafts, refrigerators and air conditioning system. Thermodynamics is used in chemistry in chemical equilibrium and for the explanation of certain biological processes.

12.2 Thermal Equilibrium

The state of a thermodynamic system is decided by certain parameters called ***thermo dynamic variables***. These quantities may vary in a thermal process. eg., pressure, volume, temperature, composition and mass. If these quantities do not change with time, the system is said to be in equilibrium.

Thermal equilibrium is the central concept of thermodynamics. To make the concept of thermal equilibrium clear, let us consider two systems A and B separated by an insulating wall, known as adiabatic wall. Now keep a thermoscope in contact with A and B separately and the thermoscope displays two different thermal levels (say).

Now A and B are separated by a diathermic wall, a conducting wall, which enables the heat flow. Again, the thermoscope is kept in contact with A and B separately. It displays the same reading in the two systems. Now A and B are said to be in thermal equilibrium.

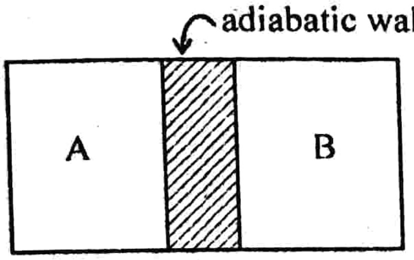

Fig. 1

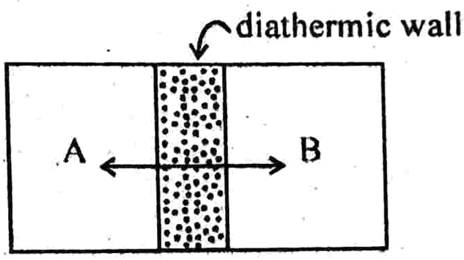

Fig. 2

Thus it is clear that, the thermal equilibrium describes the unique state, i.e., the two systems A and B are at the same temperature.

12.3 ZEROTH LAW OF THERMODYNAMICS

The above said experimental fact can be summed up and stated as Zeroth law of thermodynamics. This law came only in 1930's, a long time after the three main laws in thermodynamics had been introduced. But at the same time it takes the first place in its concept, hence the name. The Zeroth law makes it clear that when two systems are in thermal equilibrium, at least there is one thermal property common to them. This common property is called temperature.

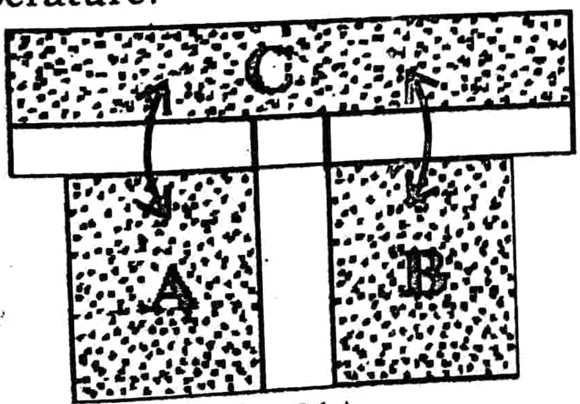

Fig. 3(a)

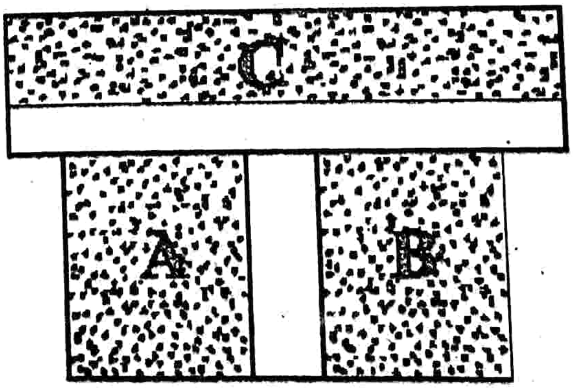

Fig. 3(b)

***The Zeroth law** can be stated as "when two bodies A and B are separately in thermal equilibrium with a third body C, then A and B are also in thermal equilibrium.*

The Zeroth law defines the concept of *temperature.*

12.4 Heat, Internal Energy and Work

***Heat** is a form of energy which produces a sensation of warmth.* Heat is the total thermal energy of a body which is the sum of kinetic energies of all the individual molecules of the body due to translational, vibrational and rotational motion of the molecules. *The energy associated with configuration and random motion of the atoms or molecules is called **internal energy** of the body. Energy due to molecular motion is called **internal kinetic energy** (U_k) and the energy due to the configuration of molecules is called **internal potential energy** (U_p).* Then internal energy U of the system is

$$U = U_k + U_p$$

Heat energy is a part of the internal energy which is transferred from one body to another due to a difference in temperature between the two bodies. Hence we can say that heat energy is the internal energy of a body in transit. Let us have a system with temperature θ and surroundings with temperature θ_s. If $\theta \neq \theta_s$, then there is a transfer of energy from the system to the surroundings (or viceversa) till both attains equal temperature and then thermal equilibrium is reached. This transferred energy is called heat and is represented as Q. If $\theta_s < \theta$, Q is positive and if $\theta_s > \theta$, Q is negative. Q is positive, means energy is transferred from the system to the surroundings and Q is negative, means energy is transferred from the surroundings to the system. If $\theta = \theta_s$, then Q = 0. In this case, heat is neither released nor absorbed.

Before the introduction of heat as energy in transit, scientists measured it in the unit calorie, based on caloric theory. But now heat, as in the case of other forms of energy, is also measured in joule.

$$1\,\text{cal} = 4.1860\,\text{J} \approx 4.2\,\text{J}$$

12.5 First Law of Thermodynamics

The first law of thermodynamics is a generalization of the energy conservation principle. The first law also provides the link between the microscopic and macroscopic properties. The energy transfer takes place between a system and its surroundings in two ways.

i. Work done by or on the system $\rightarrow$ measures changes in the macroscopic variables.

ii. Heat transfer $\rightarrow$ takes place in the microscopic level.

Both work (W) and heat (Q) depend on the nature of process. Experimentally it is found that Q – W is same for all processes. This shows that the quantity Q – W is path independent and it depends only on the initial and final stages. Hence the quantity Q – W is an intrisnic property of the system, is known as the internal energy 'U' of the system and is represented as U = Q – W. This is the first law of thermodynamics.

If a thermodynamic system undergoes a differentiable change, the first law can be represented as

$\Delta U = \Delta Q - \Delta W$. This can be called the differential form of I[st] law of thermodynamics.

Thus the ***first law of thermodynamics*** *is stated that the energy transferred to or from a system must be conserved.*

Conventionally work done by a system is positive and work done on the system is negative.

The above expression can also be written as, $\boxed{\Delta Q = \Delta U + \Delta W}$

Hence the ***first law of thermodynamics*** *can also be stated as the energy supplied to a system is the sum of increase in the internal energy of the system and the work done.*