surrounded by adiabatic walls, the heat gained by one system is equal to the heat lost by the other system. ...(iv)

4.4 Thermodynamic Equilibrium

Any state of homogeneous system in which any two of the three variables P, V and T remain constant, as long as the external conditions remain unchanged is said to be in thermodynamic equilibrium.

A system in thermodynamic equilibrium must satisfy the following requirements strictly :

(i) Mechanical Equilibrium. For a system to be in mechanical equilibrium, there should be no macroscopic movement within the system (*i.e.* no unbalanced forces acting) or of the system with respect to its surroundings.

(ii) Thermal Equilibrium. For a system to be in thermal equilibrium, there should be no temperature difference between the parts of the system or between the system and the surroundings.

(iii) Chemical Equilibrium. For a system to be in chemical equilibrium, there should be no chemical reaction within the system and also no movement of any chemical constituent from one part of the system to the other.

Quasistatic Process

A finite unbalanced force may cause the system to pass through *non-equilibrium* states. A quasistatic process is defined as the process in which the deviation from thermodynamic equilibrium is infinitesimal and all the states through which the system passes during a quasistatic process can be considered as equilibrium states.

A quasistatic process is an ideal concept which can never be satisfied rigorously in practice. However, in actual practice, many processes closely approach a quasistatic process with no significant error.

4.5 Work: A path dependent function

A system can be taken from state A to state B by many ways as shown in fig. 4.2. Let the coordinates of state A and B be $A\ (P_1\ V_1)$ and $B\ (P_2,\ V_2)$ respectively, where P_1 and V_1 represents pressure and volume of state A and P_2 and V_2 that of state B.

1. Starting from point A, the pressure is continuously decreased from P_1 to P_2 along the curve AB so that volume increases from V_1 to V_2. The work done by the system is given by

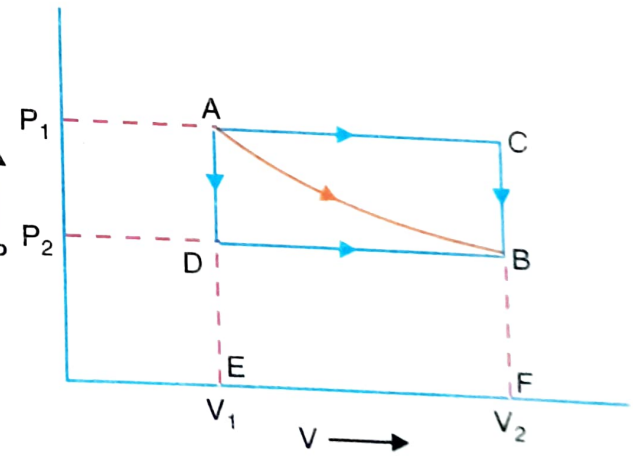


Fig. 4.2

$$W_1 = \int_{V_1}^{V_2} PdV = \text{area } ABFE$$

2. Starting from point A the volume V_1 is kept constant in going from A to D, the pressure decreases from P_1 to P_2 and then P_2 is kept constant from D to B. The work done in this process *i.e.* along ADB path given by

$$W_2 = P_2 (V_2 - V_1) = \text{area } DBFE$$

3. Again starting from point A, the pressure P_1 is kept constant in going from A to C and then the volume V_2 is kept constant from C to B. The work done in this process *i.e.* along path ACB is given by

$$W_3 = P_1 (V_2 - V_1) = \text{area } ACFE$$

$$\therefore \quad W_1 \neq W_2 \neq W_3$$

Thus, the work done depends on the path of the process when the system goes from one thermodynamic state to another.

4.6 Internal Energy (U)

The energy content of a system is called its internal energy. It is the sum of following forms of energy of the system:

(*i*) kinetic energy due to translational, rotational and vibrational motion of the molecules, all of which depend only on the temperature,

(*ii*) potential energy due to intermolecular forces, which depends on the separation between the molecules, and

(*iii*) the energy of electrons and nuclei.

In practice, it is not possible to measure the total internal energy of a system in any given state. Only change in its value can be measured.

If the state of the system is changed from an initial state 1 to a final state 2, by supplying heat Q to the system and if W is the work done by the system during the change, then increase in the internal energy of the system is given by

$$(U_2 - U_1) = Q - W \qquad \ldots(4.1)$$

where U_1 is the internal energy in state 1, and U_2 the internal energy in state 2.

Internal Energy of a Real gas and Ideal gas

The internal energy of a perfect (or ideal) gas is only dependent upon temperature where as that of a real gas, it is a function of both temperature and volume.

For a perfect gas, the internal energy is only kinetic energy of its molecules. It is proportional to kT and hence only depends upon temperature (T), k being Boltzmann's constant. The internal energy of a perfect gas is independent of its volume.

For a real gas, say a gas obeying Van der Waals' equation, the internal energy is the sum of the kinetic and potential energies of molecules due to their mutual forces of attraction. The force of attraction between the molecules depends upon the intermolecular distance and is thus a function of volume. Hence, for a real gas, internal energy is a function of both, the temperature and volume.

Equation (4.1) is the mathematical statement of the first law of thermodynamics. In a convenient form, the law is stated below.

4.7 First Law of Thermodynamics

Statement: When a certain amount of heat Q is supplied to a system which does external work W in passing from state 1 to state 2, the amount of heat is equal to sum of the increase in the internal energy of the system and the external work done by the system. In symbols, the law is expressed as

$$Q = (U_2 - U_1) + W \qquad \ldots(4.2)$$

For a very small change in the state of the system, the law is expressed in the differential form as

$$\delta Q = dU + \delta W \quad \ldots(4.3)$$

where δQ and δW are not perfect differentials but dU is a perfect differential because U is a function of the state of the system.

It should be remembered that all the quantities in equation (4.2) or (4.3) must be expressed in unit of energy. The amount of heat Q or δQ is taken positive if heat is supplied to the system, and negative if heat is removed from it. Similarly, the work W or δW is positive when the external work is done by the system in expansion and negative if the work is done on it in compression.

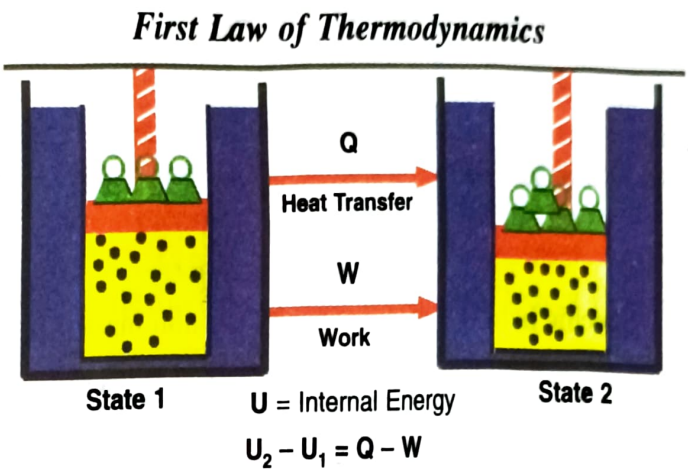
Significance of the First Law:

The first law of thermodynamics is important because

(*i*) it is applicable to any process by which a system undergoes a physical or chemical change.

(*ii*) it introduces the concept of the internal energy, and

(*iii*) it provides method for determining the change in the internal energy.



Any thermodynamic system in an equillbrium state possesses state variable called the internal energy (U). Between any two equilibrium states, the change in internal energy is equal to the difference of the heat transfer into the system and work done by the system.

Limitations of the First Law:

The first law of thermodynamics is based on the principle of conservation of energy of a system. Though it is applicable to every process in nature between the equilibrium states, it does not specify the condition under which a system can use its heat energy to produce a supply of mechanical work. It also does not say how much of the heat energy can be converted into work.

4.8 Internal Energy as a State Function

Suppose Q is the heat supplied to a working substance forming a system and W is the work done by it in taking the system from state 1 to state 2, then the increase in the internal energy of the system is given by first law of thermodynamics as

$$(U_2 - U_1) = Q - W$$

where U_1 is the initial internal energy of the system in state 1 and U_2 the final internal energy in state 2 along path A as shown in fig. 4.3.

If the state of the system is changed from the same initial state 1 to the same final state 2 by different paths, say B or C, it is found experimentally that the difference $(Q - W)$ is the same for all paths between the states 1 and 2. Hence we conclude:

When a system changes from one state to another, the change of internal energy of the system has a definite value, independent of the paths between the two states. Hence, internal energy is called as state function or point

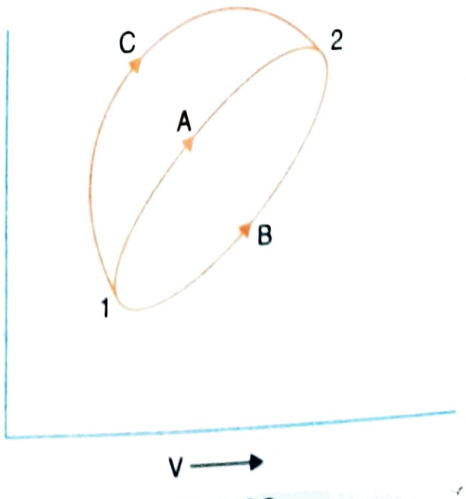


Fig. 4.3