Module I
Thermodynamics

1.1. Introduction.

An excellent definition of thermodynamics is that it is the science of energy, entropy and equilibrium. Since we have not defined the terms energy, entropy and equilibrium, we can define thermodynamics as the science that deals with heat and work. The study of thermodynamics is of special importance to the engineers since it finds applications in almost all power producing as well as power absorbing devices. For an efficient utilization of energy a deep knowledge of the subject is essential.

Macroscopic and microscopic approach

A thermodynamic analysis can be carried out either by considering the gross behavior of matter or by considering the behavior of individual molecules of the matter. The former is called macroscopic approach and the latter is called microscopic approach. Macroscopic approach is concerned with the effect of many molecules together. These effects can be perceived by human senses and can be measured directly. In microscopic approach the matter is considered to be composed of molecules and the analysis is carried out by considering the position, velocity and energy of each molecule at a given instant, ie, in microscopic approach we are concerned with the events happening at the molecular level. The microscopic approach is not essential for solving many of the engineering problems and we can obtain excellent solutions using the simple macroscopic approach.

1.2. Thermodynamic systems.

System

A system is any prescribed and identifiable collection of matter. It can be any object, any quantity of matter, any region of space etc, selected for study. The matter or region outside the system is termed as surroundings. The real or imaginary envelope which encloses a system and separate it from its surroundings is called boundary of the system. A boundary which does not permit matter to pass through it is called impermeable boundary. A boundary which resists any normal or shear forces without changing

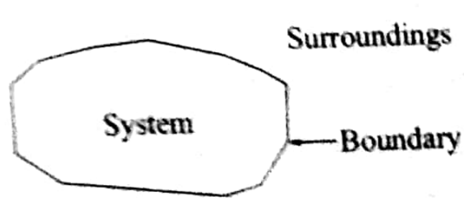

Fig. 1.1 Representation of system, boundary and surroundings.

shape or size is called rigid boundary. A boundary which does not permit matter and energy to pass through it is called isolating boundary. Fig. 1.1 shows the usual representation of system, boundary and surroundings.

Thermodynamic systems are classified into three groups.

i) Closed system (ii) Open system and (iii) Isolated system

Closed system

If there is no transfer of mass across the boundary of a system and if the boundary permits transfer of energy across it, then such a system is known as closed system. A gas heated in a cylinder fitted with a piston, as shown in fig. 1.2 is an example of a closed system.

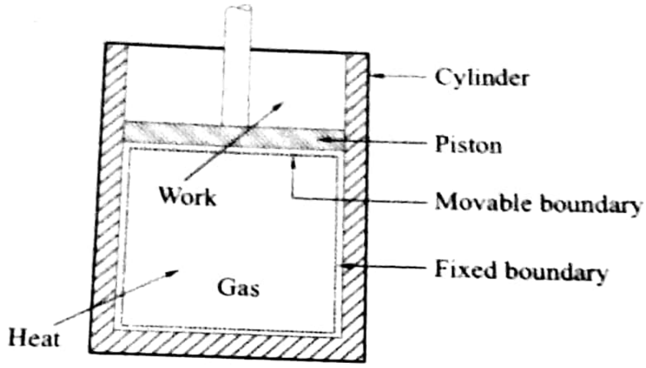

Fig. 1.2 Closed system

In this case energy (heat and work) crosses the boundary of the system but the mass does not cross the boundary. It should be noted that the boundary of a closed system may or may not move and change the position.

Open system

An open system is one with transfer of mass and energy across its boundary. Steam turbines, pumps etc, are examples of open system. In the case of a steam turbine, mass (steam) as well as energy crosses the boundary of the system as shown in fig 1.3.

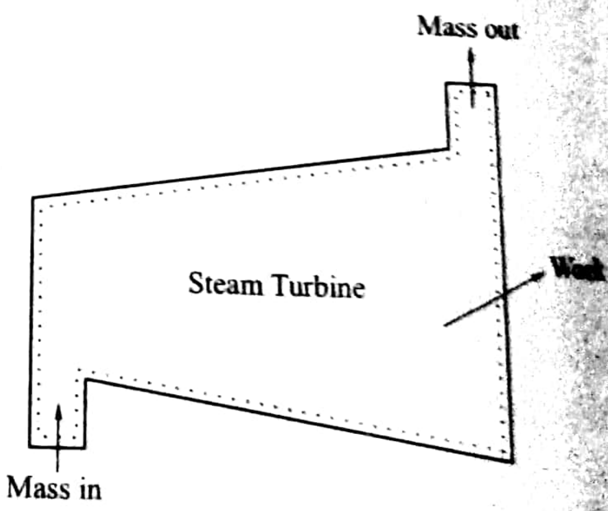

Fig 1.3 Open System

Isolated system

It is a system enclosed by an isolating boundary. It is not influenced by the surroundings. Since the system is bounded by an isolating boundary, there is no flow of mass or energy across the boundary of the system.

Though such a system has no practical interest, it is a useful concept in the study of thermodynamics. If the universe itself is taken as a system then it will be an isolated system.

1.3. State of a system

The condition of physical existence of a system at any instant is called its state. The state of a system is its condition or configuration described in sufficient details such that one state may be distinguished from all other states. The state of a thermodynamic system is described by specifying its thermodynamic co-ordinates. Pressure, temperature, volume, density etc are typical examples of thermodynamic co-ordinates. Thus the state of a thermodynamic system is its condition or configuration which can be well defined by the above said thermodynamic co-ordinates.

1.4. Property of a system

Property can be defined as any quantity that depends on the state of the system and is independent of how the system is arrived at that state. The thermodynamic co-ordinates such as temperature, pressure, volume, density etc, which are used to identify or describe the state of a system are called properties. Since properties are functions of states only, these are called point functions or state functions.

Intensive and extensive properties

If the value of a property is independent of mass of the system, it is called an intensive property. It is a property whose value remains the same whether we refer to the whole system or a portion of the system. Pressure, temperature, velocity, specific volume etc, are examples of intensive properties.

If the value of a property is proportional to the mass of the system, it is called an extensive property. Volume, energy etc are examples of extensive properties.

If a quantity of matter in a given state is divided into two equal parts, each part will have the same value of intensive properties as the original value whereas the value of extensive property of each part will be only half of the original value.

1.5. Path

If a thermodynamic system passes through a series of states, it is said to describe a path. If the value of thermodynamic variable depends upon the path followed in going from one state to another, then the variable is a path function.

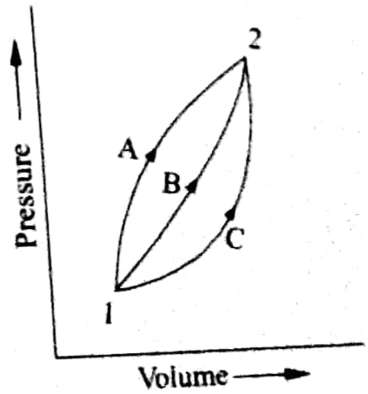

Fig. 1.4.

Consider the change of state of a system from state 1 defined by pressure p_1, volume V_1 and temperature T_1 to state 2 defined by pressure p_2 volume V_2 and temperature T_2. It is possible to go from state 1 to state 2 along different paths such as 1-A-2, 1-B-2 or 1-C-2 as shown in fig. 1.4. At state 2 the values of pressure, volume and temperature will be the same whether the state 2 is arrived along the path 1-A-2, 1-B-2 or 1-C-2. ie., the value of pressure, volume and temperature at state 2 is independent of the path followed and depends only on the state 2. Hence these quantities are state functions or point functions. A state function or point function is a property of the system.

M is a property of a system, then $\int_1^2 dM = M_2 - M_1$, ie., the change in the value of a property during a process depends only on the end states and is independent of the path followed.

A variable whose value depends on the path folllowed during a change of state, is a path function. If M is a variable whose change in the value during a process depends on the path followed, then $\int_1^2 dM \neq M_2 - M_1$. The value of $\int_1^2 dM$ can be determined only if the path followed is known. A path function is not a property of the system. Work and heat interactions during a process are examples of path functions.

1.6. Process

When a thermodynamic system changes from one state to another it is said to have undergone a process. The state of a system can be represented by a point located on a diagram using two properties as co-ordinates. When a system changes its state in such a way that at any instant during the process the state point can be located on the diagram, the

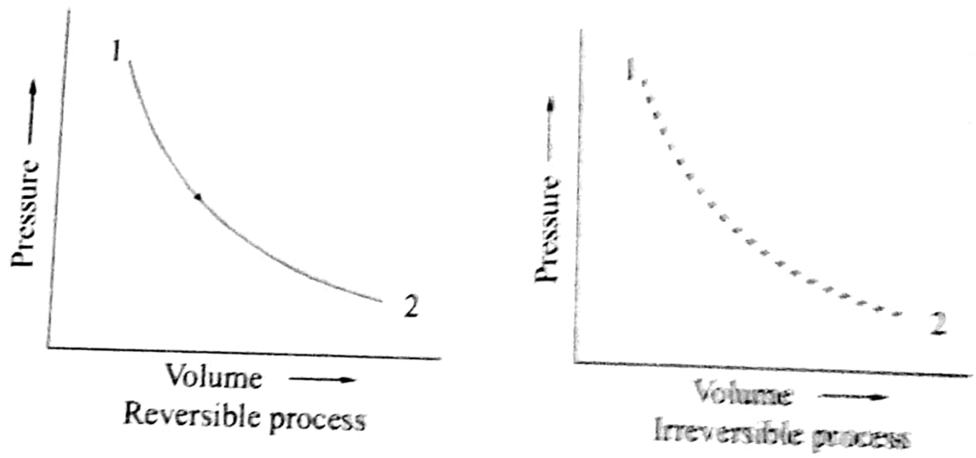

Fig. 1.5. Representation of reversible and irreversible processes.

process is said to be reversible. Thus a reversible process between two states can be shown by a continuous line on any diagram of properties. In a real process the intermediate states points cannot be located on the property diagrams. Such a real process is called irreversible process. An irreversible process is usually represented by a dotted line joining the end states to indicate that the intermediate states are indeterminate. Fig. 1.5 shows the usual representation of reversible and irreversible processes.

When a system undergoes a reversible process both the system and its surroundings can always be restored to their original state by reversing the process.

1.7. Cycle

When a thermodynamic system changes from one state to another, it is said to have undergone a process. At the end of the last process if the system returns to its original state, it is said to have completed one thermodynamic cycle. When these processes are plotted on a property diagram, they form a closed contour as shown in fig. 1.6. The net change in any property of the system is zero for a cycle $\oint dx = 0$ where x is any property and the symbol $\oint$ represents integration around a cycle.

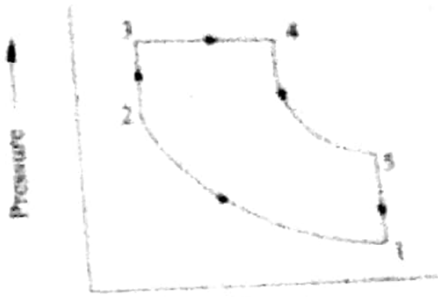

Fig. 1.6

1.8. Zeroth law of thermodynamics

Zeroth law of thermodynamics gives the basis for measuring temperature. It was recognised as a separate fundamental law relatively late and after the formulation of the first law of thermodynamics. Because of its basic importance in thermodynamics, it was listed before the first law. Zeroth law of thermodynamics states that,

" If two systems are in thermal equilibrium with a third system, separately, then they are also in thermal equilibrium with each other".

Consider three systems A, B and C. If the systems A and B are separately in thermal equilibrium with the system C, then the systems A and B are in thermal equilibrium.

Using Zeroth law of thermodynamics the equality of temperature of two systems can be

1.12. Work

In mechanics work is defined as the product of force and distance moved in the direction of force. It is denoted by W and the unit of work is N - m. 1 Nm = 1 J. In thermodynamics, the energy transfer across the boundary of a system on account of reasons other than temperature difference is called work. Work is said to be done by a system if the sole effect external to the system can be reduced to the lifting of a weight.

Consider a storage electric battery as a system, which is connected to a resistor by means of a switch as shown in Fig. 1.11. When the switch is closed, current flows through the resistor and the resistor becomes warmer. According to the definition of work in mechanics, no work is done. The sole effect external to the system, ie., warming of resistor can be reduced to the lifting of weight, if the resistor is replaced by a motor and a load as shown in Fig. 1.12. When the switch is closed, motor shaft rotates and the load is lifted. Hence when the switch is closed, the system interacts with its surroundings and the sole effect could be reduced to the lifting of a weight. Therefore, the system (battery) does work when the switch is closed.

Like heat, work is also energy in transit. A system does not contain work, upon entering the system it is converted into stored energy. Work is a path function and hence it is not a property of the system $\int_1^2 dW \neq W_2 - W_1$. $\int_1^2 dW = {}_1W_2$. ${}_1W_2$ is the amount of work transferred during a process 1 - 2.

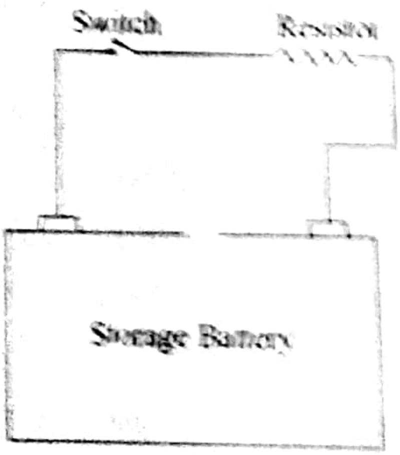

Fig. 1.11

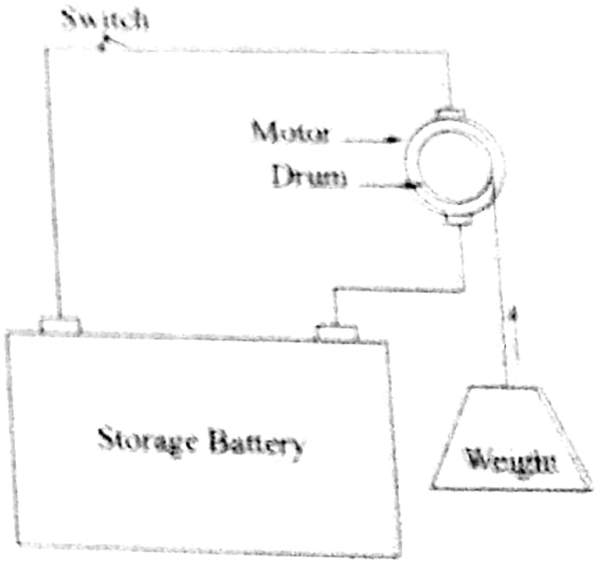

Fig. 1.12

Consider the expansion of a gas inside a cylinder fitted with a piston. Refer Fig. 1.13. Let the pressure and volume of the gas at state 1 be p_1 and V_1 respectively. This gas is expanded section of the piston. Let the piston moves through a small distance dx, the work done is $p \times a \times dx$. But $a \times dx$ is the change in volume of gas when the piston moves through the small distance dx. Hence work done is equal to $p \times dV$, the shaded area in the p - V diagram. Therefore the area under the curve 1 - 2, $\int_1^2 p\,dV$ will give the work done when the gas changes its volume from V_1 to V_2 or when the gas expands from state 1 to state 2. Work done during the process 1 - 2, $W_{1-2} = \int_1^2 p\,dV$. Work is taken as positive when it is done by the system and negative when it is done on the system. The unit of work is Joule (N m).

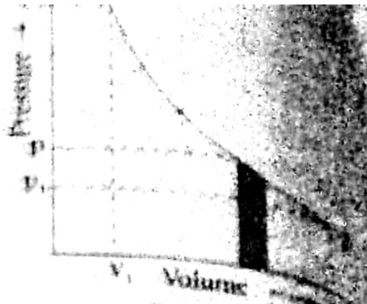

Fig. 1.13

The conditions under which expression $W = \int p\,dV$ holds are :

(i) The system is closed.

(ii) The process is quasi static.

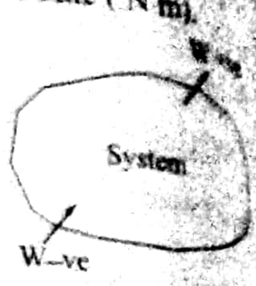

Fig 1.14

1.13. First law of thermodynamics.

The study of thermodynamics is based on two general laws of nature, the first law of thermodynamics and the second law of thermodynamics. These laws are based on physical observations and hence cannot be proved mathematically. However no violation of these laws has ever been noticed. Moreover various experiments have proved the validity of these laws.

The first law is a theorem of conservation of energy. It makes no distinction between the various modes of energy and declares that all forms of energy are equivalent. The second law states that all forms of energy are not equivalent in their ability to do work. It declares that certain processes are impossible to perform even though these processes do not violate the first law.

The first law of thermodynamics can be stated as, “For a system operating in a cycle, the net heat transfer is equal to the net work transfer”.

$$\text{ie.,} \oint dQ = \oint dW$$

$\therefore \oint (dQ - dW) = 0$, where $\oint$ stands for the summation over the cyclic process or cyclic integral.

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Perpetual motion machine of first kind (PMM - 1)

PMM - 1 is any device, which operates in a cycle without receiving energy from any source, but delivers work to the surroundings. Such a device would create work from nothing. This is clearly a violation of the first law of thermodynamics and hence a perpetual motion machine of the first kind is impossible.

1.14. Application of first law to closed system

There exists a property of a closed system such that change in its value is equal to the difference between the heat supplied and the work done during any process. This property is called energy and is denoted by E.

ie., Change in energy during any process 1 - 2, $(E_2 - E_1) = \Delta E = {}_1Q_2 - {}_1W_2$, where ${}_1Q_2$ is the heat supplied during the process 1 - 2 and ${}_1W_2$ is the work done during the process 1 - 2.

Consider a system, which changes its states from 1to 2, along a path A. Let the system return to its original state 1 either along path B or along path C as shown in the p-V diagram.

Applying the first law of thermodynamics to the closed cycle 1 - A - 2 - B - 1,

$$\oint (dQ - dW) = 0$$

$$\int_{1-A}^{2} (dQ - dW) + \int_{2-B}^{1} (dQ - dW) = 0 ....(1)$$

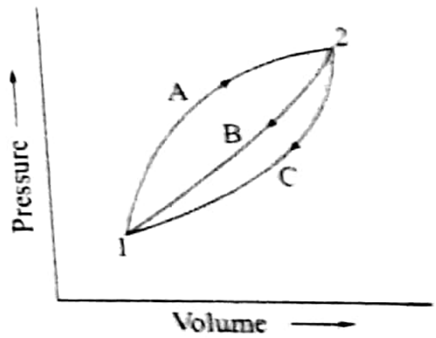

Fig. 1.15

For the closed cycle 1-A-2-C-1, $\oint (dQ - dW) = 0$

$$\int_{1-A}^{2} (dQ - dW) + \int_{2-C}^{1} (dQ - dW) = 0 ....(2)$$

From the equations (1) and (2),

$$\int_{2-B}^{1} (dQ - dW) = \int_{2-C}^{1} (dQ - dW)$$

i.e., whether the process takes the path B or C, the quantity (dQ - dW) is the same. The value of (dQ - dW) depends only on the end states and hence it is a property of the system. This property is called energy.

Internal Energy

Internal energy of a substance may be defined as the algebric sum of internal kinetic energy and internal potential energy of its molecules and is denoted by U. It is very difficult to determine the absolute value of internal energy possessed by a substance. In most of the thermodynamic applications we are mainly interested only in the changes in the internal energy of a system. The total energy of a system is the sum of potential energy, kinetic energy, internal energy and other energies due to electricity, magnetism etc. In engineering thermodynamics the concern is with the first three types of energies and electrical energy, magnetic energy etc, can be neglected.

$$\therefore E = PE + KE + U$$

Change in energy, $\Delta E = \Delta PE + \Delta KE + \Delta U$

For a stationary closed system undergoing a process 1 - 2,

$$\Delta PE = 0,\ \Delta KE = 0$$

$$\Delta E = \Delta U = {}_1Q_2 - {}_1W_2$$

$${}_1Q_2 = {}_1W_2 + \Delta U$$

When heat is supplied to a closed system, a portion of it is converted into work and the remaining portion is used to increase the internal energy of the system.

Problem 1.3.

5 kg of gas is contained in a cylinder fitted with a piston. 160 kJ of heat is transferred to the gas and simultaneously the piston is forced to compress the gas with an expenditure of work equivalent to 120 kJ. Determine the change in specific internal energy of the gas.

Solution:

Given: $m = 5$ kg, $W = -120$ kJ, $Q = 160$ kJ

To find: $\frac{\Delta U}{m}$

Using the relation,

$$\Delta U = {}_1Q_2 - {}_1W_2$$

$$\Delta U = 160 - (-120) = 280 \text{ kJ}$$

$$\therefore \frac{\Delta U}{m} = \frac{280}{5} = 56 \text{ kJ/kg}$$

Problem 1.4

A tank containing a fluid is stirred by a stirrer. The power input to the stirrer is 3 kW. Heat is transferred from the tank at the rate of 6000 kJ/hour. Considering the tank and the fluid as a system, determine the change in internal energy of the system in one hour.