

# 1

## Introduction

Thermodynamics is the science of energy transfer and its effect on the physical properties of substances. It is based upon observations of common experience which have been formulated into thermodynamic laws. These laws govern the principles of energy conversion. The applications of the thermodynamic laws and principles are found in all fields of energy technology, notably in steam and nuclear power plants, internal combustion engines, gas turbines, air conditioning, refrigeration, gas dynamics, jet propulsion, compressors, chemical process plants, and direct energy conversion devices.

### 1.1 Macroscopic Vs Microscopic Viewpoint

There are two points of view from which the behaviour of matter can be studied: the macroscopic and the microscopic. In the macroscopic approach, a certain quantity of matter is considered, without the events occurring at the molecular level being taken into account. From the microscopic point of view, matter is composed of myriads of molecules. If it is a gas, each molecule at a given instant has a certain position, velocity, and energy, and for each molecule these change very frequently as a result of collisions. The behaviour of the gas is described by summing up the behaviour of each molecule. Such a study is made in *microscopic or statistical thermodynamics*. *Macroscopic thermodynamics* is only concerned with the effects of the action of many molecules, and these effects can be perceived by human senses. For example, the macroscopic quantity, pressure, is the average rate of change of momentum due to all the molecular collisions made on a unit area. The effects of pressure can be felt. The macroscopic point of view is not concerned with the action of individual molecules, and the force on a given unit area can be measured by using, e.g., a pressure gauge. These macroscopic observations are completely independent of the assumptions regarding the nature

of matter. All the results of classical or macroscopic thermodynamics can, however, be derived from the microscopic and statistical study of matter.

## 1.2 Thermodynamic System and Control Volume

A thermodynamic *system* is defined as a quantity of matter or a region in space upon which attention is concentrated in the analysis of a problem. Everything external to the system is called the *surroundings* or the *environment*. The system is separated from the surroundings by the system boundary (Fig. 1.1). The boundary may be either *fixed* or *moving*. A system and its surroundings together comprise a *universe*.

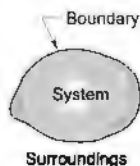


Fig. 1.1 A thermodynamic system

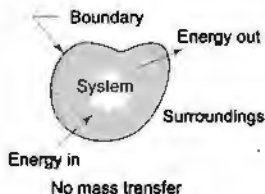


Fig. 1.2 A closed system

There are three classes of systems: (a) closed system, (b) open system and (c) isolated system. The *closed system* (Fig. 1.2) is a system of fixed mass. There is no mass transfer across the system boundary. There may be energy transfer into or out of the system. A certain quantity of fluid in a cylinder bounded by a piston constitutes a closed system. The *open system* (Fig. 1.3) is one in which matter crosses the boundary of the system. There may be energy transfer also. Most of the engineering devices are generally open systems, e.g., an air compressor in which air enters at low pressure and leaves at high pressure and there are energy transfers across the system boundary. The *isolated system* (Fig. 1.4) is one in which there is no interaction between the system and the surrounding. It is of fixed mass and energy, and there is no mass or energy transfer across the system boundary.

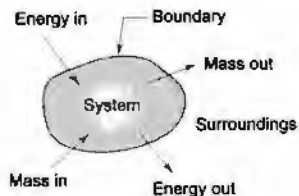


Fig. 1.3 An open system

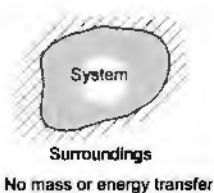


Fig. 1.4 An isolated system

If a system is defined as a certain quantity of matter, then the system contains the same matter and there can be no transfer of mass across its boundary.

However, if a system is defined as a region of space within a prescribed boundary, then matter can cross the system boundary. While the former is called a closed system, the latter is an open system.

For thermodynamic analysis of an open system, such as an air compressor (Fig. 1.5), attention is focussed on a certain volume in space surrounding the compressor, known as the *control volume*, bounded by a surface called the *control surface*. Matter as well as energy crosses the control surface.

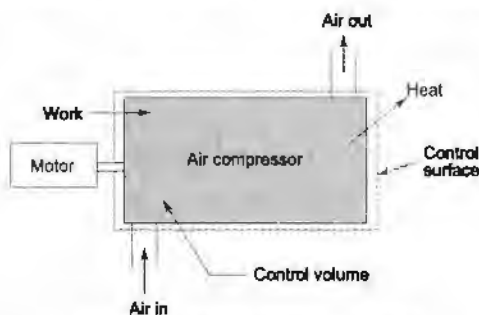


Fig. 1.5 Control volume and control surface

A closed system is a system closed to matter flow, though its volume can change against a flexible boundary. When there is matter flow, then the system is considered to be a volume of fixed identity, the control volume. There is thus no difference between an open system and a control volume.

### 1.3 Thermodynamic Properties, Processes and Cycles

Every system has certain characteristics by which its physical condition may be described, e.g., volume, temperature, pressure, etc. Such characteristics are called *properties* of the system. These are all *macroscopic* in nature. When all the properties of a system have definite values, the system is said to exist at a definite *state*. Properties are the coordinates to describe the state of a system. They are the state variables of the system. Any operation in which one or more of the properties of a system changes is called a *change of state*. The succession of states passed through during a change of state is called the *path* of the change of state. When the path is completely specified, the change of state is called a *process*, e.g., a constant pressure process. A thermodynamic *cycle* is defined as a series of state changes such that the final state is identical with the initial state (Fig. 1.6)

Properties may be of two types. *Intensive properties* are independent of the mass in the system, e.g., pressure, temperature, etc. *Extensive properties* are related to mass, e.g., volume, energy, etc. If mass is increased, the values of the extensive properties also increase. Specific extensive properties, i.e., extensive

properties per unit mass, are intensive properties, e.g., specific volume, specific energy, density, etc.

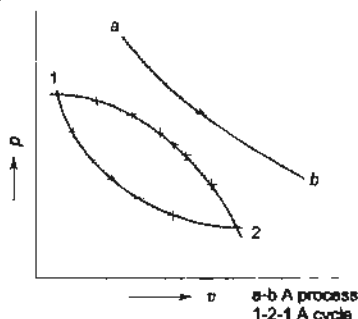


Fig. 1.6 A process and a cycle

## 1.4 Homogeneous and Heterogeneous Systems

A quantity of matter homogeneous throughout in chemical composition and physical structure is called a *phase*. Every substance can exist in any one of the three phases, viz., solid, liquid and gas. A system consisting of a single phase is called a *homogeneous system*, while a system consisting of more than one phase is known as a *heterogeneous system*.

## 1.5 Thermodynamic Equilibrium

A system is said to exist in a state of *thermodynamic equilibrium* when no change in any macroscopic property is registered, if the system is isolated from its surroundings.

An isolated system always reaches in course of time a state of thermodynamic equilibrium and *can never depart from it spontaneously*.

Therefore, there can be no *spontaneous change in any macroscopic property* if the system exists in an equilibrium state. Thermodynamics studies mainly the properties of physical systems that are found in equilibrium states.

A system will be in a state of thermodynamic equilibrium, if the conditions for the following three types of equilibrium are satisfied:

- (a) Mechanical equilibrium
- (b) Chemical equilibrium
- (c) Thermal equilibrium

In the absence of any unbalanced force within the system itself and also between the system and the surroundings, the system is said to be in a state of *mechanical equilibrium*. If an unbalanced force exists, either the system alone or both the system and the surroundings will undergo a change of state till mechanical equilibrium is attained.

If there is no chemical reaction or transfer of matter from one part of the system to another, such as diffusion or solution, the system is said to exist in a state of *chemical equilibrium*.

When a system existing in mechanical and chemical equilibrium is separated from its surroundings by a diathermic wall (diathermic means 'which allows heat to flow') and if there is no spontaneous change in any property of the system, the system is said to exist in a state of *thermal equilibrium*. When this is not satisfied, the system will undergo a change of state till thermal equilibrium is restored.

When the conditions for any one of the three types of equilibrium are not satisfied, a system is said to be in a *nonequilibrium state*. If the nonequilibrium of the state is due to an unbalanced force in the interior of a system or between the system and the surrounding, the pressure varies from one part of the system to another. There is no single pressure that refers to the system as a whole. Similarly, if the nonequilibrium is because of the temperature of the system being different from that of its surroundings, there is a nonuniform temperature distribution set up within the system and there is no single temperature that stands for the system as a whole. It can thus be inferred that when the conditions for thermodynamic equilibrium are not satisfied, the states passed through by a system cannot be described by thermodynamic properties which represent the system as a whole.

Thermodynamic properties are the macroscopic coordinates defined for, and significant to, only thermodynamic equilibrium states. Both classical and statistical thermodynamics study mainly the equilibrium states of a system.

## 1.6 Quasi-Static Process

Let us consider a system of gas contained in a cylinder (Fig. 1.7). The system initially is in equilibrium state, represented by the properties  $p_1$ ,  $v_1$ ,  $t_1$ . The weight on the piston just balances the upward force exerted by the gas. If the weight is removed, there will be an unbalanced force between the system and the surroundings, and under gas pressure, the piston will move up till it hits the stops.

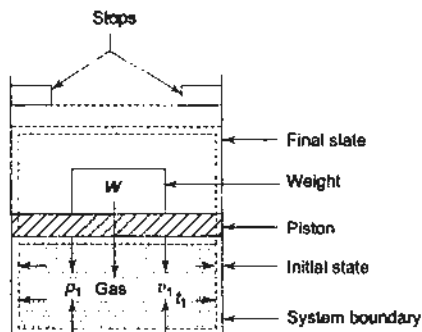


Fig. 1.7 Transition between two equilibrium states by an unbalanced force

consideration, and  $\delta F_n$  is the component of force normal to  $\delta A$  (Fig. 1.13), the pressure  $p$  at a point on the wall is defined as

$$p = \lim_{\delta A \rightarrow \delta A'} \frac{\delta F_n}{\delta A}$$

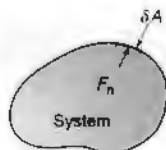


Fig. 1.13 Definition of pressure

The pressure  $p$  at a point in a fluid in equilibrium is the same in all directions.

The unit for pressure in the SI system is the *pascal* (Pa), which is the force of one newton acting on an area of  $1 \text{ m}^2$ .

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

The unit of pascal is very small. Very often kilo-pascal (kPa) or mega-pascal (MPa) is used.

Two other units, not within the SI system of units, continue to be widely used. These are the *bar*, where

$$1 \text{ bar} = 10^5 \text{ Pa} = 100 \text{ kPa} = 0.1 \text{ MPa}$$

and the standard atmosphere, where

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

Most instruments indicate pressure relative to the atmospheric pressure, whereas the pressure of a system is its pressure above zero, or relative to a perfect vacuum. The pressure relative to the atmosphere is called *gauge pressure*. The pressure relative to a perfect vacuum is called *absolute pressure*.

$$\text{Absolute pressure} = \text{Gauge pressure} + \text{Atmospheric pressure}$$

When the pressure in a system is less than atmospheric pressure, the gauge pressure becomes negative, but is frequently designated by a positive number and called *vacuum*. For example, 16 cm vacuum will be

$$\frac{76 - 16}{76} \times 1.013 = 0.08 \text{ bar}$$

Figure 1.14 shows a few pressure measuring devices. Figure (a) shows the Bourdon gauge which measures the difference between the system pressure inside the tube and atmospheric pressure. It relies on the deformation of a bent hollow tube of suitable material which, when subjected to the pressure to be measured on the inside (and atmospheric pressure on the outside), tends to unbend. This moves a pointer through a suitable gear-and-lever mechanism against a calibrated scale. Figure (b) shows an open U-tube indicating gauge pressure, and Fig. (c) shows an open U-tube indicating vacuum. Figure (d) shows a closed U-tube indicating