



## THERMODYNAMICS

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### 11.1 INTRODUCTION

In previous chapter we have studied thermal properties of matter. In this chapter we shall study laws that govern thermal energy. We shall study the processes where work is converted into heat and vice versa. In winter, when we rub our palms together, we feel warmer; here work done in rubbing produces the 'heat'. Conversely, in a steam engine, the 'heat' of the steam is used to do useful work in moving the pistons, which in turn rotate the wheels of the train.

In physics, we need to define the notions of heat, temperature, work, etc. more carefully. Historically, it took a long time to arrive at the proper concept of 'heat'. Before the modern picture, heat was regarded as a fine invisible fluid filling in the pores of a substance. On contact between a hot body and a cold body, the fluid (called caloric) flowed from the colder to the hotter body ! This is similar to what happens when a horizontal pipe connects two tanks containing water up to different heights. The flow continues until the levels of water in the two tanks are the same. Likewise, in the 'caloric' picture of heat, heat flows until the 'caloric levels' (i.e., the temperatures) equalise.

In time, the picture of heat as a fluid was discarded in favour of the modern concept of heat as a form of energy. An important experiment in this connection was due to Benjamin Thomson (also known as Count Rumford) in 1798. He observed that boring of a brass cannon generated a lot of heat, indeed enough to boil water. More significantly, the amount of heat produced depended on the work done (by the horses employed for turning the drill) but not on the sharpness of the drill. In the caloric picture, a sharper drill would scoop out more heat fluid from the pores; but this was not observed. A most natural explanation of the observations was that heat was a form of energy and the experiment demonstrated conversion of energy from one form to another—from work to heat.

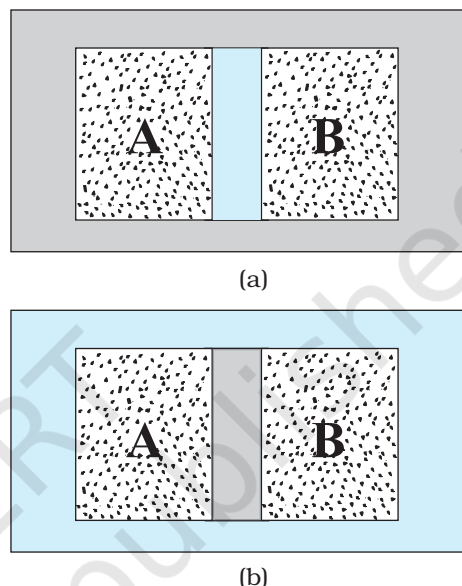
Thermodynamics is the branch of physics that deals with the concepts of heat and temperature and the inter-conversion of heat and other forms of energy. Thermodynamics is a macroscopic science. It deals with bulk systems and does not go into the molecular constitution of matter. In fact, its concepts and laws were formulated in the nineteenth century before the molecular picture of matter was firmly established. Thermodynamic description involves relatively few macroscopic variables of the system, which are suggested by common sense and can be usually measured directly. A microscopic description of a gas, for example, would involve specifying the co-ordinates and velocities of the huge number of molecules constituting the gas. The description in kinetic theory of gases is not so detailed but it does involve molecular distribution of velocities. Thermodynamic description of a gas, on the other hand, avoids the molecular description altogether. Instead, the state of a gas in thermodynamics is specified by macroscopic variables such as pressure, volume, temperature, mass and composition that are felt by our sense perceptions and are measurable\*.

The distinction between mechanics and thermodynamics is worth bearing in mind. In mechanics, our interest is in the motion of particles or bodies under the action of forces and torques. Thermodynamics is not concerned with the motion of the system as a whole. It is concerned with the internal macroscopic state of the body. When a bullet is fired from a gun, what changes is the mechanical state of the bullet (its kinetic energy, in particular), not its temperature. When the bullet pierces a wood and stops, the kinetic energy of the bullet gets converted into heat, changing the temperature of the bullet and the surrounding layers of wood. Temperature is related to the energy of the internal (disordered) motion of the bullet, not to the motion of the bullet as a whole.

## 11.2 THERMAL EQUILIBRIUM

Equilibrium in mechanics means that the net external force and torque on a system are zero. The term 'equilibrium' in thermodynamics appears

in a different context : we say the state of a system is an equilibrium state if the macroscopic variables that characterise the system do not change in time. For example, a gas inside a closed rigid container, completely insulated from its surroundings, with fixed values of pressure, volume, temperature, mass and composition that do not change with time, is in a state of thermodynamic equilibrium.



**Fig. 11.1** (a) Systems A and B (two gases) separated by an adiabatic wall – an insulating wall that does not allow flow of heat. (b) The same systems A and B separated by a diathermic wall – a conducting wall that allows heat to flow from one to another. In this case, thermal equilibrium is attained in due course.

In general, whether or not a system is in a state of equilibrium depends on the surroundings and the nature of the wall that separates the system from the surroundings. Consider two gases A and B occupying two different containers. We know experimentally that pressure and volume of a given mass of gas can be chosen to be its two independent variables. Let the pressure and volume of the gases be  $(P_A, V_A)$  and  $(P_B, V_B)$  respectively. Suppose first that the two systems are put in proximity but are separated by an

\* Thermodynamics may also involve other variables that are not so obvious to our senses e.g. entropy, enthalpy, etc., and they are all macroscopic variables. However, a thermodynamic state is specified by five state variables viz., pressure, volume, temperature, internal energy and entropy. Entropy is a measure of disorderliness in the system. Enthalpy is a measure of total heat content of the system.