The total of all these forms of energy for the system of interest is given the symbol U and is called the **internal energy**.

The **first law of thermodynamics** is based on our experience that energy can be neither created nor destroyed, if both the system and the surroundings are taken into account. This law can be formulated in a number of equivalent forms. Our initial formulation of this law is stated as follows:

The internal energy, U, of an isolated system is constant.

This form of the first law looks uninteresting, because it suggests that nothing happens in an isolated system. How can the first law tell us anything about thermodynamic processes such as chemical reactions? When changes in U occur in a system in contact with its surroundings, ΔU_{total} is given by

$$\Delta U_{total} = \Delta U_{system} + \Delta U_{surroundings} = 0 \tag{2.1}$$

Therefore, the first law becomes

$$\Delta U_{system} = -\Delta U_{surroundings} \tag{2.2}$$

For any decrease of U_{system}, $U_{surroundings}$ must increase by exactly the same amount. For example, if a gas (the system) is cooled, the temperature of the surroundings must increase.

How can the energy of a system be changed? There are many ways to alter U, several of which are discussed in this chapter. Experience has shown that all changes in a closed system in which no chemical reactions or phase changes occur can be classified only as heat, work, or a combination of both. Therefore, the internal energy of such a system can only be changed by the flow of heat or work across the boundary between the system and surroundings. For example, U for a gas can be increased by heating it in a flame or by doing compression work on it. This important recognition leads to a second and more useful formulation of the first law:

$$\Delta U = q + w \tag{2.3}$$

where q and w designate heat and work, respectively. We use ΔU without a subscript to indicate the change in internal energy of the system. What do we mean by heat and work? In the following two sections, we define these important concepts and discuss how they differ.

The symbol Δ is used to indicate a change that occurs as a result of an arbitrary process. The simplest processes are those in which only one of P, V, or T changes. A constant temperature process is referred to as **isothermal**, and the corresponding terms for constants P and V are **isobaric** and **isochoric**, respectively.

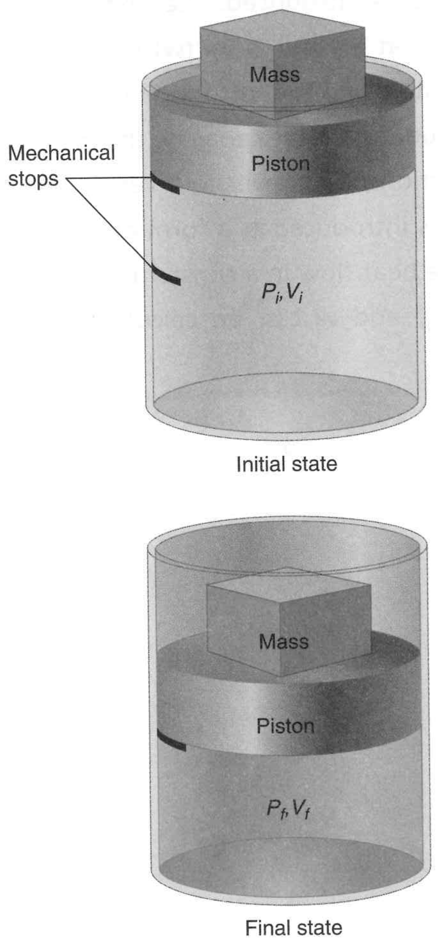

FIGURE 2.1
A system is shown in which compression work is being done on a gas. The walls are adiabatic.

2.2 WORK

In this and the next section, we discuss the two ways in which the internal energy of a system can be changed. **Work** in thermodynamics is defined as any quantity of energy that "flows" across the boundary between the system and surroundings that can be used to change the height of a mass in the surroundings. An example is shown in Figure 2.1. We define the system as the gas inside the adiabatic cylinder and piston. Everything else shown in the figure is in the surroundings. As the gas is compressed, the height of the mass in the surroundings is lowered and the initial and final volumes are defined by the mechanical stops indicated in the figure.

Consider the system and surroundings before and after the process shown in Figure 2.1, and note that the height of the mass in the surroundings has changed. It is this change that distinguishes work from heat. Work has several important characteristics:

- Work is transitory in that it only appears during a change in state of the system and surroundings. Only energy, and not work, is associated with the initial and final states of the systems.
- The net effect of work is to change U of the system and surroundings in accordance with the first law. If the only change in the surroundings is that a mass has been raised or lowered, work has flowed between the system and the surroundings.
- The quantity of work can be calculated from the change in potential energy of the mass, $\Delta E_{potential} = mgh$, where g is the gravitational acceleration and h is the change in the height of the mass, m.
- The sign convention for work is as follows. If the height of the mass in the surroundings is lowered, w is positive; if the height is raised, w is negative. In short, $w > 0$ if $\Delta U > 0$. It is common usage to say that if w is positive, work is done on the system by the surroundings. If w is negative, work is done by the system on the surroundings.

How much work is done in the process shown in Figure 2.1? Using a definition from physics, work is done when an object subject to a force, **F**, is moved through a distance, d**l**, given by

$$w = \int \mathbf{F} \cdot d\mathbf{l} \tag{2.4}$$

Using the definition of pressure as the force per unit area, the work done in moving the mass is given by

$$w = \int \mathbf{F} \cdot d\mathbf{l} = -\int P_{external}\, dV \tag{2.5}$$

The minus sign appears because of our sign convention for work. Note that the pressure that appears in this expression is the external pressure, $P_{external}$, which need not equal the system pressure, P.

An example of another important kind of work, namely, electrical work, is shown in Figure 2.2 in which the content of the cylinder is the system. Electrical current flows through a conductive aqueous solution and water undergoes electrolysis to produce H_2 and O_2 gas. The current is produced by a generator, like that used to power a light on a bicycle through the mechanical work of pedaling. As current flows, the mass that drives the generator is lowered. In this case, the surroundings do the electrical work on the system. As a result, some of the liquid water is transformed to H_2 and O_2. From electrostatics, the work done in transporting a charge, Q, through an electrical potential difference, ϕ, is

$$w_{electrical} = Q\phi \tag{2.6}$$

For a constant current, I, that flows for a time, t, $Q = It$. Therefore,

$$w_{electrical} = I\phi t \tag{2.7}$$

The system also does work on the surroundings through the increase in the volume of the gas phase at constant external pressure. The total work done is

$$w = w_{P-V} + w_{electrical} = I\phi t - \int P_{external}\, dV$$

$$= I\phi t - P_{external}\int dV = I\phi t - P_{external}(V_f - V_i) \tag{2.8}$$

Other forms of work include the work of expanding a surface, such as a soap bubble, against the surface tension. Table 2.1 shows the expressions for work for four different cases. Each of these different types of work poses a requirement on the walls separating the system and surroundings. To be able to carry out the first three types of work, the walls must be movable, whereas for electrical work, they must be conductive. Several examples of work calculations are given in Example Problem 2.1.

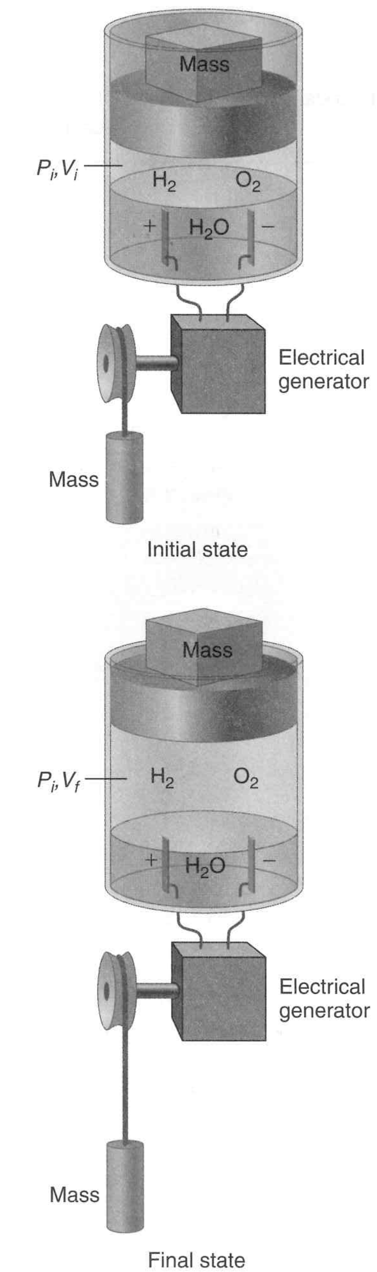

FIGURE 2.2
Current produced by a generator is used to electrolyze water and thereby do work on the system as shown by the lowered mass linked to the generator. The gas produced in this process does P–V work on the surroundings, as shown by the raised mass on the piston.