$$f(p,\ V,\ T) = 0, \tag{3.2}$$

where V, p, and T are the volume, pressure, and temperature of the system at a given condition.

In principle, this equation of state exists for any thermodynamic system but is not always readily available. The forms of $f(p,\ V,\ T) = 0$ for many materials have been determined either experimentally or theoretically. In the preceding chapter, we saw an example of an equation of state for an ideal gas, $f(p,\ V,\ T) = pV - nRT = 0.$

We have so far introduced several physical properties that are relevant to the thermodynamics of a thermodynamic system, such as its volume, pressure, and temperature. We can separate these quantities into two generic categories. The quantity associated with an amount of matter is an **extensive variable**, such as the volume and the number of moles. The other properties of a system are **intensive variables**, such as the pressure and temperature. An extensive variable doubles its value if the amount of matter in the system doubles, provided all the intensive variables remain the same. For example, the volume or total energy of the system doubles if we double the amount of matter in the system while holding the temperature and pressure of the system unchanged.

3.2 | Work, Heat, and Internal Energy

Learning Objectives

By the end of this section, you will be able to:

- Describe the work done by a system, heat transfer between objects, and internal energy change of a system
- Calculate the work, heat transfer, and internal energy change in a simple process

We discussed the concepts of work and energy earlier in mechanics. Examples and related issues of heat transfer between different objects have also been discussed in the preceding chapters. Here, we want to expand these concepts to a thermodynamic system and its environment. Specifically, we elaborated on the concepts of heat and heat transfer in the previous two chapters. Here, we want to understand how work is done by or to a thermodynamic system; how heat is transferred between a system and its environment; and how the total energy of the system changes under the influence of the work done and heat transfer.

Work Done by a System

A force created from any source can do work by moving an object through a displacement. Then how does a thermodynamic system do work? **Figure 3.4** shows a gas confined to a cylinder that has a movable piston at one end. If the gas expands against the piston, it exerts a force through a distance and does work on the piston. If the piston compresses the gas as it is moved inward, work is also done—in this case, on the gas. The work associated with such volume changes can be determined as follows: Let the gas pressure on the piston face be p. Then the force on the piston due to the gas is pA, where A is the area of the face. When the piston is pushed outward an infinitesimal distance dx, the magnitude of the work done by the gas is

$$dW = F\,dx = pA\,dx.$$

Since the change in volume of the gas is $dV = A\,dx,$ this becomes

$$dW = pdV. \tag{3.3}$$

For a finite change in volume from V_1 to $V_2,$ we can integrate this equation from V_1 to V_2 to find the net work:

$$W = \int_{V_1}^{V_2} pdV. \tag{3.4}$$

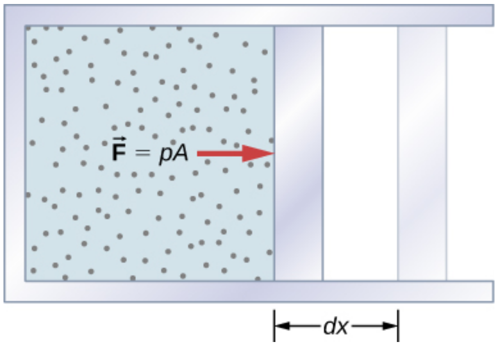

Figure 3.4 The work done by a confined gas in moving a piston a distance dx is given by $dW = Fdx = pdV$.

This integral is only meaningful for a **quasi-static process**, which means a process that takes place in infinitesimally small steps, keeping the system at thermal equilibrium. (We examine this idea in more detail later in this chapter.) Only then does a well-defined mathematical relationship (the equation of state) exist between the pressure and volume. This relationship can be plotted on a pV diagram of pressure versus volume, where the curve is the change of state. We can approximate such a process as one that occurs slowly, through a series of equilibrium states. The integral is interpreted graphically as the area under the pV curve (the shaded area of **Figure 3.5**). Work done by the gas is positive for expansion and negative for compression.

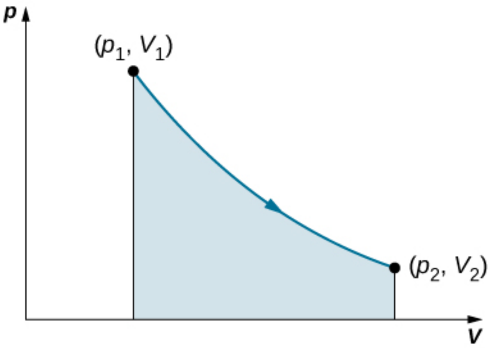

Figure 3.5 When a gas expands slowly from V_1 to V_2, the work done by the system is represented by the shaded area under the pV curve.

Consider the two processes involving an ideal gas that are represented by paths AC and ABC in **Figure 3.6**. The first process is an isothermal expansion, with the volume of the gas changing its volume from V_1 to V_2. This isothermal process is represented by the curve between points A and C. The gas is kept at a constant temperature T by keeping it in thermal equilibrium with a heat reservoir at that temperature. From **Equation 3.4** and the ideal gas law,

$$W = \int_{V_1}^{V_2} pdV = \int_{V_1}^{V_2} \left(\frac{nRT}{V}\right) dV.$$

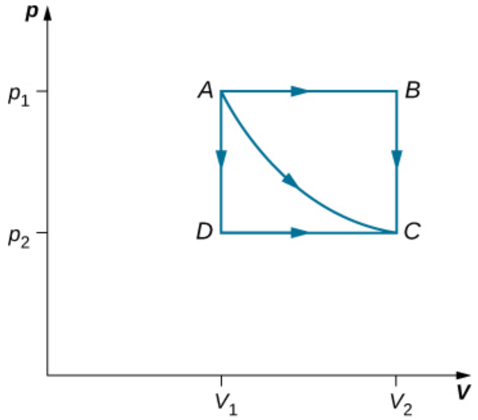

Figure 3.6 The paths *ABC*, *AC*, and *ADC* represent three different quasi-static transitions between the equilibrium states *A* and *C*.

The expansion is isothermal, so *T* remains constant over the entire process. Since *n* and *R* are also constant, the only variable in the integrand is *V*, so the work done by an ideal gas in an isothermal process is

$$W = nRT\int_{V_1}^{V_2}\frac{dV}{V} = nRT\ln\frac{V_2}{V_1}.$$

Notice that if $V_2 > V_1$ (expansion), *W* is positive, as expected.

The straight lines from *A* to *B* and then from *B* to *C* represent a different process. Here, a gas at a pressure p_1 first expands isobarically (constant pressure) and quasi-statically from V_1 to V_2, after which it cools quasi-statically at the constant volume V_2 until its pressure drops to p_2. From *A* to *B*, the pressure is constant at *p*, so the work over this part of the path is

$$W = \int_{V_1}^{V_2} p dV = p_1\int_{V_1}^{V_2} dV = p_1(V_2 - V_1).$$

From *B* to *C*, there is no change in volume and therefore no work is done. The net work over the path *ABC* is then

$$W = p_1(V_2 - V_1) + 0 = p_1(V_2 - V_1).$$

A comparison of the expressions for the work done by the gas in the two processes of **Figure 3.6** shows that they are quite different. This illustrates a very important property of thermodynamic work: It is *path dependent*. We cannot determine the work done by a system as it goes from one equilibrium state to another unless we know its thermodynamic path. Different values of the work are associated with different paths.

Example 3.1

Isothermal Expansion of a van der Waals Gas

Studies of a van der Waals gas require an adjustment to the ideal gas law that takes into consideration that gas molecules have a definite volume (see **The Kinetic Theory of Gases**). One mole of a van der Waals gas has an equation of state

$$\left(p + \frac{a}{V^2}\right)(V - b) = RT,$$

where *a* and *b* are two parameters for a specific gas. Suppose the gas expands isothermally and quasi-statically from volume V_1 to volume V_2. How much work is done by the gas during the expansion?

Strategy

Because the equation of state is given, we can use **Equation 3.4** to express the pressure in terms of V and T. Furthermore, temperature T is a constant under the isothermal condition, so V becomes the only changing variable under the integral.

Solution

To evaluate this integral, we must express p as a function of V. From the given equation of state, the gas pressure is

$$p = \frac{RT}{V - b} - \frac{a}{V^2}.$$

Because T is constant under the isothermal condition, the work done by 1 mol of a van der Waals gas in expanding from a volume V_1 to a volume V_2 is thus

$$\begin{aligned} W &= \int_{V_1}^{V_2} \left(\frac{RT}{V - b} - \frac{a}{V^2} \right) = \left| RT \ln(V - b) + \frac{a}{V} \right|_{V_1}^{V_2} \\ &= RT \ln\left(\frac{V_2 - b}{V_1 - b} \right) + a\left(\frac{1}{V_2} - \frac{1}{V_1} \right). \end{aligned}$$

Significance

By taking into account the volume of molecules, the expression for work is much more complex. If, however, we set $a = 0$ and $b = 0$, we see that the expression for work matches exactly the work done by an isothermal process for one mole of an ideal gas.

3.1 Check Your Understanding How much work is done by the gas, as given in **Figure 3.6**, when it expands quasi-statically along the path *ADC*?

Internal Energy

The **internal energy** E_{int} of a thermodynamic system is, by definition, the sum of the mechanical energies of all the molecules or entities in the system. If the kinetic and potential energies of molecule *i* are K_i and U_i, respectively, then the internal energy of the system is the average of the total mechanical energy of all the entities:

$$E_{\text{int}} = \sum_i (\bar{K}_i + \bar{U}_i), \qquad (3.5)$$

where the summation is over all the molecules of the system, and the bars over K and U indicate average values. The kinetic energy K_i of an individual molecule includes contributions due to its rotation and vibration, as well as its translational energy $m_i v_i^2/2$, where v_i is the molecule's speed measured relative to the center of mass of the system. The potential energy U_i is associated only with the interactions between molecule *i* and the other molecules of the system. In fact, neither the system's location nor its motion is of any consequence as far as the internal energy is concerned. The internal energy of the system is not affected by moving it from the basement to the roof of a 100-story building or by placing it on a moving train.

In an ideal monatomic gas, each molecule is a single atom. Consequently, there is no rotational or vibrational kinetic energy and $K_i = m_i v_i^2/2$. Furthermore, there are no interatomic interactions (collisions notwithstanding), so $U_i = \text{constant}$, which we set to zero. The internal energy is therefore due to translational kinetic energy only and

$$E_{\text{int}} = \sum_i \bar{K}_i = \sum_i \frac{1}{2} m_i \overline{v_i^2}.$$

From the discussion in the preceding chapter, we know that the average kinetic energy of a molecule in an ideal monatomic gas is

$$\frac{1}{2} m_i \overline{v_i^2} = \frac{3}{2} k_B T,$$

where T is the Kelvin temperature of the gas. Consequently, the average mechanical energy per molecule of an ideal monatomic gas is also $3k_B T/2$, that is,

$$\overline{K_i + U_i} = \bar{K}_i = \frac{3}{2} k_B T.$$

The internal energy is just the number of molecules multiplied by the average mechanical energy per molecule. Thus for n moles of an ideal monatomic gas,

$$E_{\text{int}} = nN_A \left(\frac{3}{2} k_B T\right) = \frac{3}{2} nRT. \tag{3.6}$$

Notice that the internal energy of a given quantity of an ideal monatomic gas depends on just the temperature and is completely independent of the pressure and volume of the gas. For other systems, the internal energy cannot be expressed so simply. However, an increase in internal energy can often be associated with an increase in temperature.

We know from the zeroth law of thermodynamics that when two systems are placed in thermal contact, they eventually reach thermal equilibrium, at which point they are at the same temperature. As an example, suppose we mix two monatomic ideal gases. Now, the energy per molecule of an ideal monatomic gas is proportional to its temperature. Thus, when the two gases are mixed, the molecules of the hotter gas must lose energy and the molecules of the colder gas must gain energy. This continues until thermal equilibrium is reached, at which point, the temperature, and therefore the average translational kinetic energy per molecule, is the same for both gases. The approach to equilibrium for real systems is somewhat more complicated than for an ideal monatomic gas. Nevertheless, we can still say that energy is exchanged between the systems until their temperatures are the same.

3.3 | First Law of Thermodynamics

Learning Objectives

By the end of this section, you will be able to:

- State the first law of thermodynamics and explain how it is applied
- Explain how heat transfer, work done, and internal energy change are related in any thermodynamic process

Now that we have seen how to calculate internal energy, heat, and work done for a thermodynamic system undergoing change during some process, we can see how these quantities interact to affect the amount of change that can occur. This interaction is given by the first law of thermodynamics. British scientist and novelist C. P. Snow (1905–1980) is credited with a joke about the four laws of thermodynamics. His humorous statement of the first law of thermodynamics is stated “you can’t win,” or in other words, you cannot get more energy out of a system than you put into it. We will see in this chapter how internal energy, heat, and work all play a role in the first law of thermodynamics.

Suppose Q represents the heat exchanged between a system and the environment, and W is the work done by or on the system. The first law states that the change in internal energy of that system is given by $Q - W$. Since added heat increases the internal energy of a system, Q is positive when it is added to the system and negative when it is removed from the system.

When a gas expands, it does work and its internal energy decreases. Thus, W is positive when work is done by the system and negative when work is done on the system. This sign convention is summarized in **Table 3.1**. The **first law of**