

## 19 The Kinetic Theory of Gases



When a container of cold champagne, soda pop, or any other carbonated drink is opened, a slight fog forms around the opening and some of the liquid sprays outward. (In the photograph, the fog is the white cloud that surrounds the stopper, and the spray has formed streaks within the cloud.)

**What causes the fog?**

---

*The answer is in this chapter.*

## 19-1 Molecules and Thermal Gas Behavior

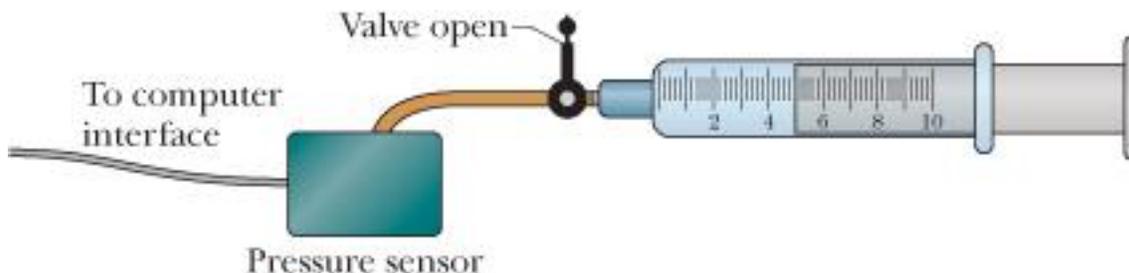
In our studies of mechanics and thermodynamics we have found a number of strange and interesting results. In mechanics, we saw that moving objects tend to run down and come to a stop. We attributed this to the inevitable presence of friction and drag forces. Without these nonconservative forces mechanical energy would be conserved and perpetual motion would be possible. In thermodynamics, we discovered that ordinary objects, by virtue of their temperature, contain huge quantities of internal energy. This is where the “lost” energy resulting from friction forces is hidden. In this chapter, we will learn about some ways that matter can store internal energy. What you are about to learn may be counterintuitive. Instead of finding that the “natural state” of a system is to lose energy, you will find considerable evidence that the “natural state” of a system is quite the opposite. It is one in which its fundamental parts (atoms and molecules) are traveling every which way—in a state of perpetual motion.

Classical thermodynamics—the subject of the previous chapter—has nothing to say about atoms or molecules. Its laws are concerned only with such macroscopic variables as pressure, volume, and temperature. In this chapter we begin an exploration of the atomic and molecular basis of thermodynamics. As is usual in the development of new theories in physics, we start with a simple model. The fact that gases are fluid and compressible is evidence that their molecules are quite small relative to the average spacing between them. If so, we expect that gas molecules are relatively free and independent of one another. For this reason, we believe that the thermal behavior of gases will be easier to understand than that of liquids and solids. Thus, we begin an exploration of the atomic and molecular basis of thermodynamics by developing the kinetic theory of gases—a simplified model of gas behavior based on the laws of classical mechanics.

We start with a discussion of how the ideal gas law characterizes the macroscopic behavior of simple gases. This macroscopic law relates the amount of gas and its pressure, temperature, and volume to each other. Next we consider how kinetic theory, which provides us with a molecular (or microscopic) model of gas behavior, can be used to explain observed macroscopic relationships between gas pressure, volume, and temperature. We then move on to using kinetic theory as an underlying model of the characteristics of an ideal gas. The basic ideas of kinetic theory are that: (1) an ideal gas at a given temperature consists of a collection of tiny particles (atoms or molecules) that are in perpetual motion—colliding with each other and the walls of their container; and (2) the hidden internal energy of an ideal gas is directly proportional to the kinetic energy of its particles.

## 19-2 The Macroscopic Behavior of Gases

Any gas can be described by its macroscopic variables volume  $V$ , pressure  $P$ , and temperature  $T$ . Simple experiments were performed on low density gases in the 17th and 18th centuries to relate these variables. Robert Boyle (b. 1627) determined that at a constant temperature the product of pressure and volume remains constant. (See Fig. 19-1.)



**FIGURE 19-1** A contemporary setup for determining the relationship between gas pressure and volume using an inexpensive medical syringe and an electronic pressure sensor attached to a computer data acquisition system. The volume is changed when the plunger is pushed or pulled. When temperature is held constant,  $P$  and  $V$  turn out to be inversely proportional to each other so that  $PV$  is constant.

French scientists Jacques Charles (b. 1746) and Joseph Gay-Lussac (b. 1778) found that as the Kelvin temperature of a fixed volume of gas is raised its pressure increases proportionally. (See Fig. 19-16.) Similarly, Charles, who was a hot-air balloonist, discovered that for a constant pressure (such as atmospheric pressure) the volume of a gas is proportional to its temperature. (See Fig. 19-15.) By combining the results of all three of these experiments we must conclude that there is a proportionality between  $PV$  and  $T$ :

$$PV \propto T.$$

## The Molecular Form of the Ideal Gas Law

If we can find a constant of proportionality between  $PV$  and  $T$  for a relatively low density gas, then we will have formulated a gas law. An examination of the student-generated  $P$  vs.  $T$  data shown in Fig. 19-17 indicates that the constant of proportionality between the product  $PV$  and the variable  $T$  (determined by the slopes) of the graphs decreases as the mass of gas confined to the same volume decreases. Similar experiments have shown that the slope of a  $P$  vs.  $T$  graph will change if the same volume and mass of a different kind of gas is used. This suggests that the constant of proportionality we are looking for must be a function of *both* the mass and type of gas. It was puzzling to early investigators that the slopes of their  $P$  vs.  $T$  and  $V$  vs.  $T$  graphs were not just proportional to the mass of the different gases used in the experiments.

The key to finding a constant of proportionality that embodies both gas type and mass was a hypothesis developed in the early 19th century by the Italian scientist Amadeo Avogadro (1776–1856). In 1811, Avogadro proposed that equal volumes of any kind of gas at the same pressure would have the same number of molecules and occupy the same volume. Eventually it was discovered that the constant of proportionality needed for the fledgling gas law was one that is directly proportional to the number of molecules of a gas rather than its mass, so that

$$PV = Nk_bT \quad (\text{molecular ideal gas law}), \quad (20-1)$$

where  $N$  is the number of molecules of confined gas and  $k_B$  is a proportionality constant needed to shift from kelvins to joules, the SI units for the product  $PV$ . The experimentally determined value of  $k_B$  is known historically as the Boltzmann constant. Its measured value is

$$k_B = 1.38 \times 10^{-23} \text{ J/K} \quad (\text{Boltzmann constant}). \quad (20-2)$$

It turns out that common gases such as  $\text{O}_2$ ,  $\text{N}_2$ , and Ar behave like ideal gases at relatively low pressure ( $< 10$  atm) when their temperatures are well above their boiling points. For example, air near room temperature and 1 atm of pressure behaves like an ideal gas.

## Avogadro's Number and the Mole

The problem with the molecular form of the ideal gas law we just presented is that it is hard to count molecules. It is much easier to measure the mass of a sample of gas or its volume at a standard pressure. In this subsection we will define two new quantities—*mole* and *molar mass*. Although these quantities are related to the number of molecules in a gas, they can be measured macroscopically, so it is useful to reformulate the ideal gas law in terms of moles.

Let's start our reformulation of the ideal gas law with definitions of mole and molar mass. In Section 1-7, we presented the SI definition of the *atomic mass unit* in terms of the mass of a carbon-12 atom. In particular, carbon-12 is assigned an atomic mass of exactly 12 u. Here the atomic mass unit u represents grams per mole (g/mol). In a related fashion, the SI definition of the *mole* (or *mol* for short) relates the number of particles in a substance to its macroscopic mass.

A **mole** is defined as the amount of any substance that contains the same number of atoms or molecules as there are in *exactly* 12 g of carbon-12.

The results of many different types of experiments, including x-ray diffraction studies in crystals, have revealed that there are a very large number of atoms in 12 g of carbon-12. The number of atoms is known as Avogadro's number and is denoted as  $N_A$ .

$$N_A = 6.022137 \times 10^{23} \text{ mol}^{-1} \quad (\text{Avogadro's number}). \quad (20-3)$$

Here the symbol  $\text{mol}^{-1}$  represents the inverse mole or "per mole." Usually we round off the value to three significant figures so that  $N_A = 6.02 \times 10^{23} \text{ mol}^{-1}$ .

The number of moles  $n$  contained in a sample of any substance is equal to the ratio of the number of atoms or molecules  $N$  in the sample to the number of atoms or molecules  $N_A$  in 1 mole of the same substance:

$$n = \frac{N}{N_A}. \quad (20-4)$$

(*Caution:* The three symbols in this equation can easily be confused with one another, so you should sort them with their meanings now, before you end in “N-confusion.”)

We can easily calculate the mass of one mole of atoms or molecules in any sample, defined as the **molar mass** (denoted as  $M$ ), by looking in a table of atomic or molecular masses.

Note that if we refer to Appendix F to find the molar mass,  $M$ , in grams of a sample of matter, we can determine the number of moles in the sample by determining its mass  $M_{\text{sam}}$  and using the equation

$$n = \frac{M_{\text{sam}}}{M}. \quad (20-5)$$

For atoms, the molar mass is just the atomic mass so that molar mass also has the unit g/mol, which is often denoted as u.

It is puzzling to note that the atomic mass of carbon that is listed in Appendix F is given as 12.01115 u rather than 12.00000 u. This is because a natural sample of carbon does not consist of only carbon-12. Instead it contains a relatively small percentage of carbon-13, which has an extra neutron in its nucleus. Nevertheless, by definition, a mole of pure carbon-12 and a mole of a naturally occurring mixture of carbon-12 and carbon-13 both contain Avogadro’s number of atoms.

## The Molar Form of the Ideal Gas Law

We can rewrite the molecular ideal gas law expressed in Eq. 19-1 in an alternative form by using Eq. 19-4, so that

$$PV = Nk_B T = nN_A k_B T.$$

Since both Avogadro’s number and the Boltzmann constant are constants, we can replace their product with a new constant  $R$ , which is called the **universal gas constant** because it has the same value for all ideal gases—namely,

$$R = N_A k_B = 6.02 \times 10^{23} \text{ mol}^{-1} (1.38 \times 10^{-23} \text{ J/K}) = 8.31 \text{ J/mol} \cdot \text{K}. \quad (20-6)$$

This allows us to write

$$nR = Nk_B. \quad (20-7)$$

Substituting this into Eq. 19-1 gives a second expression for the **ideal gas law**:

$$PV = nRT \quad (\text{molar ideal gas law}), \quad (20-8)$$

in which  $P$  is the absolute (not gauge) pressure,  $V$  is the volume,  $n$  is the number of moles of gas present, and  $T$  is the temperature in Kelvin. Provided the gas density is low, the ideal gas law as represented in either Eq. 19-1 or Eq. 19-8 holds for any single gas or for any mixture of different gases. (For a mixture,  $n$  is the total number of moles in the mixture.)

Note the difference between the two expressions for the ideal gas law—Eq. 19-8 involves the number of moles  $n$  and Eq. 19-1 involves the number of atoms  $N$ . That is, the Boltzmann constant  $k_B$  tells us about individual atomic particles, whereas the gas constant  $R$  tells us about moles of particles. Recall that moles are defined via macroscopic measurements that are easily done in the lab—such as 1 mol of carbon has a mass of 12 g. As a result,  $R$  is easily measured in the lab. On the other hand, since  $k_B$  is about individual atoms, to get to it from a lab measurement we have to count the number of molecules in a mole. This is a decidedly nontrivial task.

You may well ask, “What is an *ideal gas* and what is so ‘ideal’ about it?” The answer lies in the simplicity of the law (Eqs. 19-1 and 19-8) that describes the macroscopic properties of a gas. Using this law—as you will see—we can deduce many properties of the ideal gas in a simple way. There is no such thing in nature as a truly ideal gas. But *all* gases approach the ideal state at low enough densities—that is, under conditions in which their molecules are far enough apart that they do not interact with one another as much as they do with the walls of their containers. Thus, the two equivalent ideal gas equations allow us to gain useful insights into the behavior of most real gases at low densities.

---

#### TOUCHSTONE EXAMPLE 19-1: Final Pressure

---

A cylinder contains 12 L of oxygen at 20°C and 15 atm. The temperature is raised to 35°C, and the volume is reduced to 8.5 L. What is the final pressure of the gas in atmospheres? Assume that the gas is ideal.

**SOLUTION** The **Key Idea** here is that, because the gas is ideal, its pressure, volume, temperature, and number of moles are related by the ideal gas law, both in the initial state  $i$  and in the final state  $f$  (after the changes). Thus, from Eq. 19-8 we can write  $P_i V_i = nRT_i$  and  $P_f V_f = nRT_f$ . Dividing the second equation by the first equation and solving for  $P_f$  yields

$$P_f = \frac{P_i T_f V_i}{T_i V_f}. \quad (20-9)$$

Note here that if we converted the given initial and final volumes from liters to SI units of cubic meters, the multiplying conversion factors would cancel out of Eq. 19-9. The same would be true for conversion factors that convert the pressures from atmospheres to the more accepted SI unit of pascals. However, to convert the given temperatures to kelvins requires the addition of an amount that would not cancel and thus must be included. Hence, we must write

$$T_i = (273 + 20) \text{ K} = 293 \text{ K}$$

and

$$T_f = (273 + 35) \text{ K} = 308 \text{ K}.$$

Inserting the given data into Eq. 19-9 then yields

$$P_f = \frac{(15 \text{ atm})(308 \text{ K})(12 \text{ L})}{(293 \text{ K})(8.5 \text{ L})} = 22 \text{ atm.} \quad (\text{Answer})$$

---

## 19-3 Work Done by Ideal Gases

Heat engines are devices that can absorb thermal energy and do useful work on their surroundings. As you will see in the next chapter, air, which is typically used as a working medium in heat engines, behaves like an ideal gas in some circumstances. For this reason engineers are interested in knowing how to calculate the work done by ideal gases. Before we turn our attention to how the action of molecules that make up an ideal gas can be used to explain the ideal gas law, we first consider how to calculate the work done by ideal gases under various conditions. We restrict ourselves to expansions that occur slowly enough that the gas is very close to thermal equilibrium throughout its volume.

### Work Done by an Ideal Gas at Constant Temperature

Suppose we put an ideal gas in a piston–cylinder arrangement like those in Chapter 19. Suppose also that we allow the gas to expand from an initial volume  $V_i$  to a final volume  $V_f$  while we keep the temperature  $T$  of the gas constant. Such a process, at *constant temperature*, is called an **isothermal expansion** (and the reverse is called an **isothermal compression**).

On a  $P$ - $V$  diagram, an *isotherm* is a curve that connects points that have the same temperature. Thus, it is a graph of pressure versus volume for a gas whose temperature  $T$  is held constant. For  $n$  moles of an ideal gas, it is a graph of the equation

$$P = nRT \frac{1}{V} = (\text{a constant}) \frac{1}{V}. \quad (20-10)$$

Figure 19-2 shows three isotherms, each corresponding to a different (constant) value of  $T$ . (Note that the values of  $T$  for the isotherms increase upward to the right.)

Superimposed on the middle isotherm is the path followed by a gas during an isothermal expansion from state  $i$  to state  $f$  at a constant temperature of 310 K.

To find the work done by an ideal gas during an isothermal expansion, we start with Eq. 19-16,

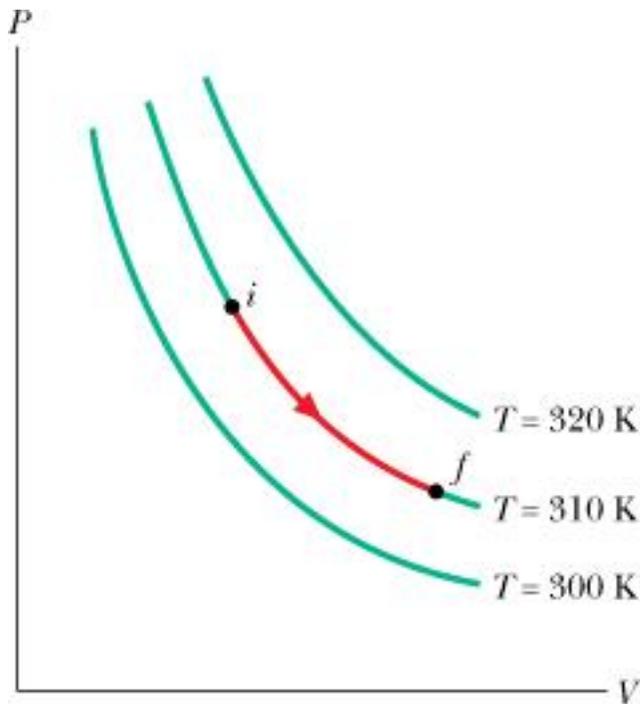
$$W = \int_{V_i}^{V_f} P dV. \quad (20-11)$$

This is a general expression for the work done during any change in volume of any gas. For an ideal gas, we can use Eq. 19-8 to substitute for  $P$ , obtaining

$$W = \int_{V_i}^{V_f} \frac{nRT}{V} dV. \quad (20-12)$$

Because we are considering an isothermal expansion,  $T$  is constant and we can move it in front of the integral sign to write

$$W = nRT \int_{V_i}^{V_f} \frac{dV}{V} = nRT [\ln V]_{V_i}^{V_f}. \quad (20-13)$$



**FIGURE 19-2** Three isotherms on a  $P$ - $V$  diagram. The path shown along the middle isotherm represents an isothermal expansion of a gas from an initial state  $i$  to a final state  $f$ . The path from  $f$  to  $i$  along the isotherm would represent the reverse process, an isothermal compression.

By evaluating the expression in brackets at the limits and then using the relationship  $\ln a - \ln b = \ln (a/b)$ , we find that

$$W = nRT \ln \frac{V_f}{V_i} = Nk_B \ln \frac{V_f}{V_i} \quad (\text{ideal gas, isothermal process}). \quad (20-14)$$

Recall that the symbol  $\ln$  specifies a *natural* logarithm, which has base  $e$ .

As we often do in science and engineering we have derived a mathematical relationship. Before using this relationship it's a good idea to check our equation to see whether it makes sense. Unless a gas is undergoing a free expansion into a vacuum, we know that an expanding gas does work on its surroundings. If the gas contracts we expect that the surroundings have done work on the gas instead. Is this what Eq. 19-14 tells us? For an expansion,  $V_f$  is greater than  $V_i$ , so the ratio  $V_f/V_i$  in Eq. 19-14 is greater than unity. The natural logarithm of a quantity greater than unity is positive, and so the work  $W$  done by an ideal gas during an isothermal expansion is positive, as we expect. For a compression,  $V_f$  is less than  $V_i$ , so the ratio of volumes in Eq. 19-14 is less than unity. The natural logarithm in that equation—hence the work  $W$ —is negative, again as we expect.

## Work Done at Constant Volume and at Constant Pressure

Equation 19-14 does not give the work  $W$  done by an ideal gas during *every* thermodynamic process. Instead, it gives the work only for a process in which the temperature is held constant. If the temperature varies, then the symbol  $T$  in Eq. 19-12 cannot be moved in front of the integral symbol as in Eq. 19-13, and thus we do not end up with Eq. 19-14.

However, we can go back to Eq. 19-11 to find the work  $W$  done by an ideal gas (or any other gas) during two more processes—a constant-volume process and a constant-pressure process. If the volume of the gas is constant, then Eq. 19-11 yields

$$W = 0 \quad (\text{constant-volume process}). \quad (20-15)$$

If, instead, the volume changes while the pressure  $P$  of the gas is held constant, then Eq. 19-11 becomes

$$W = P(V_f - V_i) = P\Delta V \quad (\text{constant-pressure process}). \quad (20-16)$$

**READING EXERCISE 19-1:** An ideal gas has an initial pressure of 3 pressure units and an initial volume of 4 volume units. The table gives the final pressure and volume of the gas (in those same units) in five processes. Which processes start and end on the same isotherm?

	<i>a</i>	<i>b</i>	<i>c</i>	<i>d</i>	<i>e</i>
<i>P</i>	12	6	5	4	1
<i>V</i>	1	2	7	3	12

---

**TOUCHSTONE EXAMPLE 19-2:** Work Done by Expansion

---

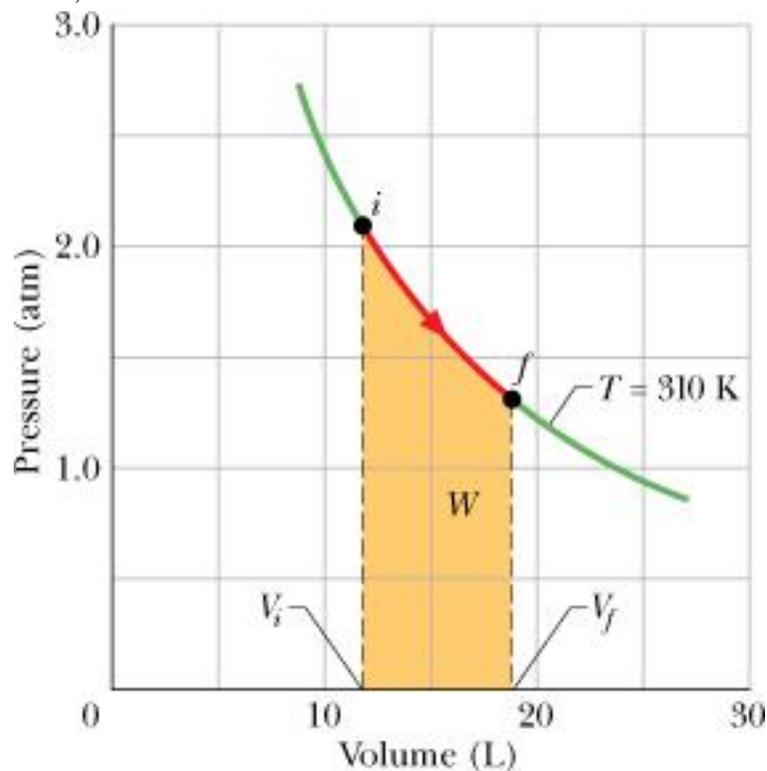
One mole of oxygen (assume it to be an ideal gas) expands at a constant temperature  $T$  of 310 K from an initial volume  $V_i$  of 12 L to a final volume  $V_f$  of 19 L. How much work is done by the gas during the expansion?

**SOLUTION** The **Key Idea** is this: Generally we find the work by integrating the gas pressure with respect to the gas volume, using Eq. 19-11. However, because the gas here is ideal and the expansion is isothermal, that integration leads to Eq. 19-14. Therefore, we can write

$$\begin{aligned} W &= nRT \ln \frac{V_f}{V_i} \\ &= (1 \text{ mol})(8.31 \text{ J/mol} \cdot \text{K})(310 \text{ K}) \ln \left( \frac{19 \text{ L}}{12 \text{ L}} \right) \\ &= 1180 \text{ J.} \end{aligned} \quad \text{(Answer)}$$

The expansion is graphed in the  $P$ - $V$  diagram of Fig. 19-3. The work done by the gas during the expansion is represented by the area beneath the curve between  $i$  and  $f$ .

You can show that if the expansion is now reversed, with the gas undergoing an isothermal compression from 19 L to 12 L, the work done by the gas will be  $-1180 \text{ J}$ . Thus, an external force would have to do 1180 J of work on the gas to compress it.



---

**FIGURE 19-3** The shaded area represents the work done by 1 mol of oxygen in expanding from  $V_i$  to  $V_f$  at a constant temperature  $T$  of 310 K.

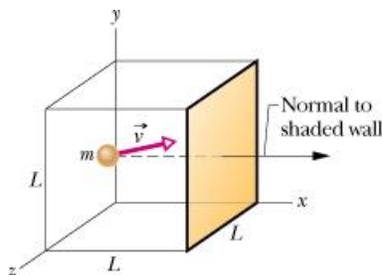
---

## 19-4 Pressure, Temperature, and Molecular Kinetic Energy

In terms of our everyday experiences, molecules and atoms are invisible. Only in the past 40 years or so have scientists been able to “see” molecules using electron microscopes and field ion microscopes. But long before atoms and molecules could be “seen,” 19th-century scientists such as James Clerk Maxwell and Ludwig Boltzmann in Europe and Josiah Willard Gibbs in the United States constructed models that made the description and prediction of the *macroscopic* (visible to the naked eye) behavior of thermodynamic systems possible. Their models were based on the yet unseen *microscopic* atoms and molecules.

Is it possible to describe the behavior of an ideal gas that obeys the first law of thermodynamics microscopically as a collection of moving molecules? To answer this question, let’s observe the pressure exerted by a hypothetical molecule undergoing perfectly elastic collisions with the walls of a cubical box. By using the laws of mechanics we can derive a mathematical expression for the pressure exerted by just one of the molecules as a function of the volume of the box. Next we can extend our “ideal gas” so it is a low-density collection of molecules all having the same mass. By low density we mean that the volume occupied by the molecules is negligible compared to the volume of their container. This means that the molecules are far enough apart on the average that attractive interactions between molecules are also negligible. For this reason an ideal gas has internal energy related to its configuration. If we then define temperature as being related to the average kinetic energy of the molecules in an ideal gas, we can show that kinetic theory is a powerful construct for explaining both the ideal gas law and the first law of thermodynamics.

We start developing our idealized kinetic theory model by considering  $N$  molecules of an ideal gas that are confined in a cubical box of volume  $V$ , as in Fig. 19-4. The walls of the box are held at temperature  $T$ . How is the pressure  $P$  exerted by the gas on the walls related to the speeds of the molecules? Remember from our discussions of fluids in Chapter 15 that pressure is a scalar defined as the ratio of the magnitude of force (exerted normal to a surface) and the area of the surface. In the example at hand, a gas confined to a box, the pressure results from the motion of molecules in all directions resulting in elastic collisions between gas molecules and the walls of the box. We ignore (for the time being) collisions of the molecules with one another and consider only elastic collisions with the walls.



**FIGURE 19-4** We assume a cubical box of edge  $L$  contains  $N$  ideal gas molecules (not shown) that move around perpetually without losing energy. One of the molecules of mass  $m$  and velocity  $\vec{v}$  is shown heading for a collision with the shaded wall of area  $L^2$ . The normal to the shaded wall points in the positive  $x$  direction.

Figure 19-4 shows a typical gas molecule, of mass  $m$  and velocity  $\vec{v}$ , which is about to collide with the shaded wall. Because we assume that any collision of a molecule with a wall is elastic, when this molecule collides with the shaded wall, the only component of its velocity that is changed by the collision is its  $x$ -component. That  $x$ -component has the same magnitude after collision but its sign is reversed. This means that the only change in the particle's momentum is along the  $x$  axis, so

$$(\Delta p_x)_{\text{molecule}} = p_{fx} - p_{ix} = (-m|v_x|) - (+m|v_x|) = -2m|v_x|.$$

But the law of conservation of momentum tells us that the momentum change  $(\Delta p_x)_{\text{wall}}$  that the wall experiences after a molecule collides with it is  $+2m|v_x|$ . Remember that in this book  $\vec{p}$ ,  $p_x$ ,  $p_y$ , and  $p_z$  denote momentum vectors or vector components and capital  $P$  represents pressure. *Be careful not to confuse them.*

The molecule of Fig. 19-4 will hit the shaded wall repeatedly. The time  $\Delta t$  between collisions is the time the molecule takes to travel to the opposite wall and back again (a distance of  $2L$ ) at speed  $|v_x|$ . Thus,  $\Delta t$  is equal to  $2L/|v_x|$ . (Note that this result holds even if the molecule bounces off any of the other walls along the way, because those walls are parallel to  $x$  and so cannot change  $|v_x|$ .) Therefore, the average rate at which momentum is delivered to the shaded wall by this single molecule is

$$\frac{(\Delta p_x)_{\text{wall}}}{\Delta t} = \frac{+2m|v_x|}{2L/|v_x|} = \frac{mv_x^2}{L}.$$

From Newton's Second Law ( $\vec{F} = d\vec{p}/dt$ ), the rate at which momentum is delivered to the wall is the force acting on that wall. To find the total force, we must add up the contributions of all of the  $N$  molecules that strike the wall during a short time interval  $\Delta t$ . We will allow for the possibility that all the molecules have different velocities. Then we can divide the magnitude of the total force acting normal to the shaded wall  $|F_x|$  by the area of the wall ( $L^2$ ) to determine the pressure  $P$  on that wall. Thus,

$$\begin{aligned} P &= \frac{|F_x|}{L^2} = \frac{mv_{x1}^2/L + mv_{x2}^2/L + \cdots + mv_{xN}^2/L}{L^2} \\ &= \left(\frac{m}{L^3}\right)(v_{x1}^2 + v_{x2}^2 + \cdots + v_{xN}^2). \end{aligned} \quad (20-17)$$

Since by definition  $\langle v_x^2 \rangle = (v_{x1}^2 + v_{x2}^2 + \dots + v_{xN}^2) / N$  we can replace the sum of squares of the velocities in the second parentheses of Eq. 19-17 by  $N \langle v_x^2 \rangle$ , where  $\langle v_x^2 \rangle$  is the average value of the square of the  $x$ -components of all the speeds. Equation 19-17 for the pressure on the container wall then reduces to

$$P = \frac{Nm}{L^3} \langle v_x^2 \rangle = \frac{Nm}{V} \langle v_x^2 \rangle, \quad (20-18)$$

since the volume  $V$  of the cubical box is just  $L^3$ .

It is reasonable to assume that molecules are moving at random in three dimensions rather than just in the  $x$  direction that we considered initially, so that  $\langle v_x^2 \rangle = \langle v_y^2 \rangle = \langle v_z^2 \rangle$  and

$$\langle v^2 \rangle = \langle v_x^2 + v_y^2 + v_z^2 \rangle = \langle v_x^2 \rangle + \langle v_y^2 \rangle + \langle v_z^2 \rangle = 3 \langle v_x^2 \rangle,$$

or

$$\langle v_x^2 \rangle = \langle v^2 \rangle / 3.$$

Thus, we can rewrite the expression above as

$$P = \frac{Nm \langle v^2 \rangle}{3V}. \quad (20-19)$$

The square root of  $\langle v^2 \rangle$  is a kind of average speed, called the **root-mean-square speed** of the molecules and symbolized by  $v^{\text{rms}}$ . Its name describes it rather well: You *square* each speed, you find the *mean* (that is, the average) of all these squared speeds, and then you take the square *root* of that mean. With  $\sqrt{\langle v^2 \rangle} = v^{\text{rms}}$ , we can then write Eq. 19-19 as

$$P = \frac{Nm(v^{\text{rms}})^2}{3V}. \quad (20-20)$$

Equation 19-20 is very much in the spirit of kinetic theory. It tells us how the pressure of the gas (a purely macroscopic quantity) depends on the speed of the molecules (a purely microscopic quantity). We can turn Eq. 19-20 around and use it to calculate  $v^{\text{rms}}$  as

$$v^{\text{rms}} = \sqrt{\frac{3PV}{Nm}}.$$

Combining this with the molecular form of the ideal gas law in Eq. 19-1 ( $PV = Nk_B T$ ) gives us

$$v^{\text{rms}} = \sqrt{\frac{3k_B T}{m}} \quad (\text{ideal gas}), \quad (20-21)$$

where  $m$  is the mass of a single molecule in kilograms.

Table 19-1 shows some rms speeds calculated from Eq. 19-21. The speeds are surprisingly high. For hydrogen molecules at room temperature (300 K), the rms speed is 1920 m/s or 4300 mi/h—faster than a speeding bullet! Remember too that the rms speed is only a kind of average speed; some molecules move much faster than this, and some much slower.

**TABLE 19-1**  
Some Molecular Speeds at Room Temperature ( $T = 300 \text{ K}$ )<sup>a</sup>

Gas	Molar Mass $M = mN_A$ ( $10^{-3} \text{ kg/mol}$ )	$v^{\text{rms}}$ (m/s)
Hydrogen ( $\text{H}_2$ )	2.02	1920
Helium (He)	4.0	1370
Water vapor ( $\text{H}_2\text{O}$ )	18.0	645
Nitrogen ( $\text{N}_2$ )	28.0	517
Oxygen ( $\text{O}_2$ )	32.0	483
Carbon dioxide ( $\text{CO}_2$ )	44.0	412
Sulfur dioxide ( $\text{SO}_2$ )	64.1	342

<sup>a</sup>For convenience, we often set room temperature at 300 K even though (at 27°C or 81°F) that represents a fairly warm room.

The speed of sound in a gas is closely related to the rms speed of the molecules of that gas. In a sound wave, the disturbance is passed on from molecule to molecule by means of collisions. The wave cannot move any faster than the “average” speed of the molecules. In fact, the speed of sound must be somewhat less than this “average” molecular speed because not all molecules are moving in exactly the same direction as the wave. As examples, at room temperature, the rms speeds of hydrogen and nitrogen molecules are 1920 m/s and 517 m/s, respectively. The speeds of sound in these two gases at this temperature are 1350 m/s and 350 m/s, respectively.

## Translational Kinetic Energy

Let's again consider a single molecule of an ideal gas as it moves around in the box of Fig. 19-4, but we now assume that its speed changes when it collides with other molecules. Its translational kinetic energy at any instant is  $\frac{1}{2}mv^2$ . Its *average* translational kinetic energy over the time that we watch it is

$$\langle K \rangle = \frac{1}{2} \langle mv^2 \rangle = \frac{1}{2} m \langle v^2 \rangle = \frac{1}{2} m (v^{\text{rms}})^2, \quad (20-22)$$

in which we make the assumption that the average speed of the molecule during our observation is the same as the average speed of all the molecules at any given instant. (Provided the total energy of the gas is not changing and we observe our molecule for long enough, this assumption is appropriate.) Substituting for  $v^{\text{rms}}$  from Eq. 19-21 leads to

$$\langle K \rangle = \left(\frac{1}{2}m\right) \frac{3k_B T}{m}$$

so that 
$$\langle K \rangle = \frac{3}{2} k_B T \quad (\text{one ideal gas molecule}). \quad (20-23)$$

This equation tells us something unexpected:

At a given temperature  $T$ , all ideal gas molecules—no matter what their mass—have the same average translational kinetic energy—namely,  $(\frac{3}{2})k_B T$ . When we measure the temperature of a gas, we are also measuring the average translational kinetic energy of its molecules.

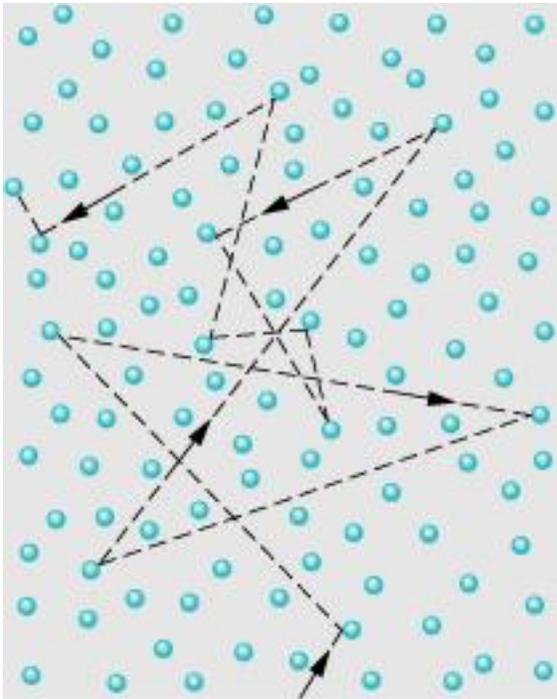
**READING EXERCISE 19-2:** What happens to the average translational kinetic energy of each molecule in a gas when its temperature in kelvin: (a) doubles and (b) is reduced to zero?

**READING EXERCISE 19-3:** A gas mixture consists of molecules of types 1, 2, and 3, with molecular masses  $m_1 > m_2 > m_3$ . Rank the three types according to (a) average kinetic energy and (b) rms speed, greatest first.

## 19-5 Mean Free Path

In considering the motion of molecules, a question often arises: If molecules move so fast (hundreds of meters per second), why does it take as long as a minute or so before you can smell perfume when someone opens a bottle across a room (only a few meters away)? To answer this question, we continue to examine the motion of molecules in an ideal gas. Figure 19-5 shows the path of a typical molecule as it moves through the gas, changing both speed and direction abruptly as it collides elastically with other molecules. Between collisions, our typical molecule moves in a straight line at constant speed. Although the figure shows all the other molecules as stationary, they too are moving similarly.

One useful parameter to describe this random motion is the **mean free path**  $\lambda$  of the molecules. As its name implies,  $\lambda$  is the average distance traversed by a molecule between collisions. We expect  $\lambda$  to vary inversely with  $N/V$ , the number of molecules per unit volume (or “number density” of molecules). The larger  $N/V$  is, the more collisions there should be and the smaller the mean free path. We also expect  $\lambda$  to vary inversely with the size of the molecules, say, with their diameter  $d$ . (If the molecules were points, as we have assumed them to be, they would never collide and the mean free path would be infinite.) Thus, the larger the molecules are, the smaller the mean free path. We can even predict that  $\lambda$  should vary (inversely) as the *square* of the molecular diameter because the cross section of a molecule—not its diameter—determines its effective target area.



**FIGURE 19-5** A molecule traveling through a gas, colliding with other gas molecules in its path. Although the other molecules are shown as stationary, we believe they are also moving in a similar fashion.

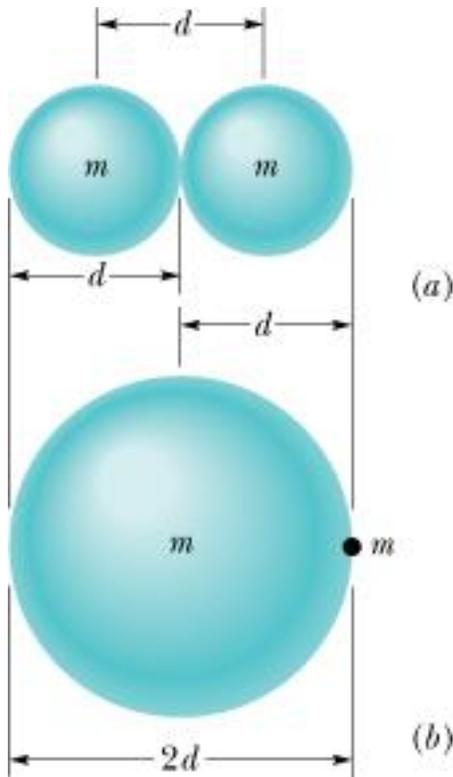
The expression for the mean free path does, in fact, turn out to be

$$\lambda = \frac{1}{\sqrt{2}\pi d^2 N/V} \quad (\text{ideal gas mean free path}). \quad (20-24)$$

To justify Eq. 19-24, we focus attention on a single molecule and assume—as Fig. 19-5 suggests—that our molecule is traveling with a constant speed  $v$  and that all the other molecules are at rest. Later, we shall relax this assumption.

We assume further that the molecules are spheres of diameter  $d$ . A collision will then take place if the centers of the molecules come within a distance  $d$  of each other, as in Fig. 19-6*a*. Another, more helpful way to look at the situation is to consider our single molecule to have a *radius* of  $d$  and all the other molecules to be *points*, as in Fig. 19-6*b*. This does not change our criterion for a collision.

As our single molecule zigzags through the gas, it sweeps out a short cylinder of cross-sectional area  $\pi d^2$  between successive collisions. If we watch this molecule for a time interval  $\Delta t$ , it moves a distance  $v\Delta t$ , where  $v$  is its assumed speed. Thus, if we align all the short cylinders swept out in  $\Delta t$ , we form a composite cylinder (Fig. 19-7) of length  $v\Delta t$  and volume  $(\pi d^2)(v\Delta t)$ . The number of collisions that occur in time  $\Delta t$  is then equal to the number of (point) molecules that lie within this cylinder.



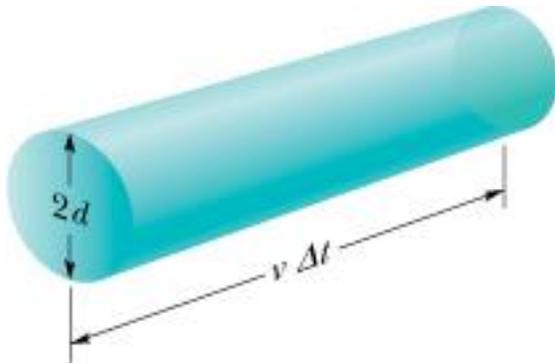
**FIGURE 19-6** (a) A collision occurs when the centers of two molecules come within a distance  $d$  of each other,  $d$  being the molecular diameter. (b) An equivalent but more convenient representation is to think of

the moving molecule of interest as having a *radius*  $d$  and all other molecules as being points. The condition for a collision is unchanged.

Since  $N/V$  is the number of molecules per unit volume, the number of molecules in the cylinder is  $N/V$  times the volume of the cylinder, or  $(N/V)(\pi d^2 v \Delta t)$ . This is also the number of collisions in time  $\Delta t$ . The mean free path is the length of the path (and of the cylinder) divided by this number:

$$\begin{aligned} \lambda &= \frac{\text{length of path}}{\text{number of collisions}} \approx \frac{v \Delta t}{\pi d^2 v \Delta t N/V} \\ &= \frac{1}{\pi d^2 N/V}. \end{aligned} \tag{20-25}$$

This equation is only approximate because it is based on the assumption that all the molecules except one are at rest. In fact, *all* the molecules are moving; when this is taken properly into account, Eq. 19-24 results. Note that it differs from the (approximate) Eq. 19-25 only by a factor of  $1/\sqrt{2}$ .



**FIGURE 19-7** In time  $\Delta t$  the moving molecule effectively sweeps out a cylinder of length  $v \Delta t$  and radius  $d$ .

We can even get a glimpse of what is “approximate” about Eq. 19-25. The  $v$  in the numerator and that in the denominator are—strictly—not the same. The  $v$  in the numerator is  $\langle v \rangle$ , the mean speed of the molecule *relative to the container*. The  $v$  in the denominator is  $\langle v^{\text{rel}} \rangle$ , the mean speed of our single molecule *relative to the other molecules*, which are moving. It is this latter average speed that determines the number of collisions. A detailed calculation, taking into account the actual speed distribution of the molecules, gives  $\langle v^{\text{rel}} \rangle = \sqrt{2} \langle v \rangle$  and thus the factor  $\sqrt{2}$ .

The mean free path of air molecules at sea level is about  $0.1 \mu\text{m}$ . At an altitude of 100 km, the density of air has dropped to such an extent that the mean free path rises to about 16 cm. At 300 km, the mean free path is about 20 km. A problem faced by those who would study the physics and chemistry of the upper atmosphere in the laboratory is the unavailability of containers large enough to hold gas samples that simulate upper

atmospheric conditions. Yet studies of the concentrations of freon, carbon dioxide, and ozone in the upper atmosphere are of vital public concern.

Recall the question that began this section: If molecules move so fast, why does it take as long as a minute or so before you can smell perfume when someone opens a bottle across a room? We now know part of the answer. In still air, each perfume molecule moves away from the bottle only very slowly because its repeated collisions with other molecules prevent it from moving directly across the room to you.

---

**TOUCHSTONE EXAMPLE 19-3: Mean Free Path**

---

(a) What is the mean free path  $\lambda$  for oxygen molecules at temperature  $T = 300$  K and pressure  $P = 1.00$  atm? Assume that the molecular diameter is  $d = 290$  pm and the gas is ideal.

**SOLUTION** The **Key Idea** here is that each oxygen molecule moves among other *moving* oxygen molecules in a zigzag path due to the resulting collisions. Thus, we use Eq. 19-24 for the mean free path, for which we need the number of molecules per unit volume,  $N/V$ . Because we assume the gas is ideal, we can use the ideal gas law of Eq. 19-1 ( $PV = Nk_B T$ ) to write  $N/V = P/k_B T$ . Substituting this into Eq. 19-24, we find

$$\begin{aligned}\lambda &= \frac{1}{\sqrt{2}\pi d^2 N/V} = \frac{k_B T}{\sqrt{2}\pi d^2 P} \\ &= \frac{(1.38 \times 10^{-23} \text{ J/K})(300 \text{ K})}{\sqrt{2}\pi (2.9 \times 10^{-10} \text{ m})^2 (1.01 \times 10^5 \text{ Pa})} && \text{(Answer)} \\ &= 1.1 \times 10^{-7} \text{ m}.\end{aligned}$$

This is about 380 molecular diameters.

(b) Assume the average speed of the oxygen molecules is  $\langle v \rangle = 450$  m/s. What is the average time interval  $\Delta t$  between successive collisions for any given molecule? At what rate does the molecule collide; that is, what is the frequency  $f$  of its collisions?

**SOLUTION** To find the time interval  $\Delta t$  between collisions, we use this **Key Idea**: Between collisions, the molecule travels, on average, the mean free path  $\lambda$  at average speed  $\langle v \rangle$ . Thus, the average time between collisions is

$$\begin{aligned}\langle vt \rangle &= \frac{\text{(distance)}}{\text{(average speed)}} = \frac{\lambda}{\langle v \rangle} = \frac{1.1 \times 10^{-7} \text{ m}}{450 \text{ m/s}} && \text{(Answer)} \\ &= 2.44 \times 10^{-10} \text{ s} \approx 0.24 \text{ ns}.\end{aligned}$$

This tells us that, on average, any given oxygen molecule has less than a nanosecond between collisions.

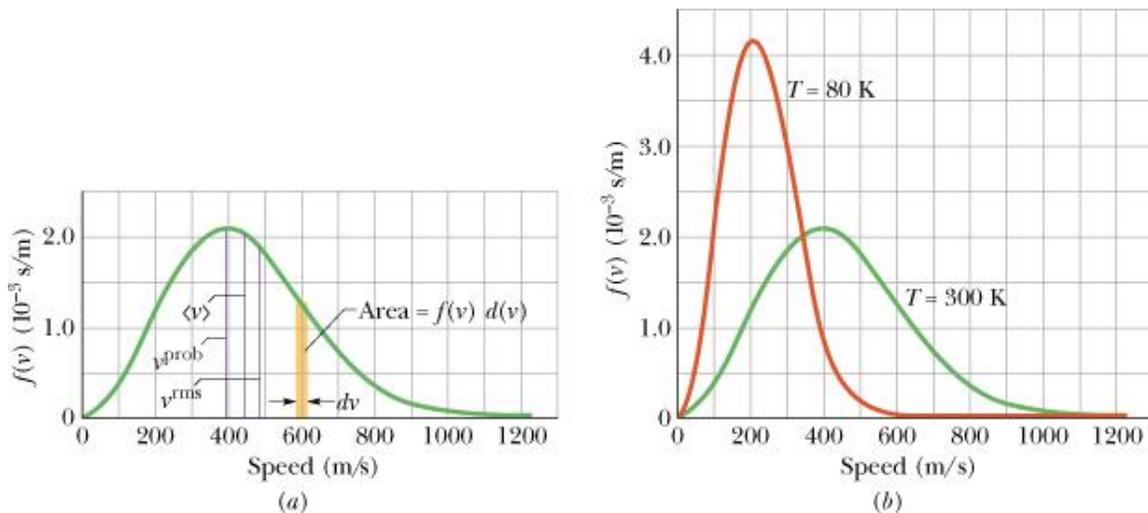
To find the frequency  $f$  of the collisions, we use this **Key Idea**: The average rate or frequency at which the collisions occur is the inverse of the average time  $\langle \Delta t \rangle$  between collisions. Thus,

$$f = \frac{1}{2.44 \times 10^{-10} \text{ s}} = 4.1 \times 10^9 \text{ s}^{-1}. \quad (\text{Answer})$$

This tells us that, on average, any given oxygen molecule makes about 4 billion collisions per second.

## 19-6 The Distribution of Molecular Speeds

The root-mean-square speed  $v^{\text{rms}}$  gives us a general idea of molecular speeds in a gas at a given temperature. We often want to know more. For example, what fraction of the molecules have speeds greater than the rms value? Greater than twice the rms value? To answer such questions, we need to know how the possible values of speed are distributed among the molecules. Figure 19-8a shows this distribution for oxygen molecules at room temperature ( $T = 300 \text{ K}$ ); Fig. 19-8b compares it with the distribution at  $T = 80 \text{ K}$ .



**FIGURE 19-8** (a) The Maxwell speed distribution for oxygen molecules at  $T = 300 \text{ K}$ . The three characteristic speeds are marked. (b) The curves for  $300 \text{ K}$  and  $80 \text{ K}$ . Note that the molecules move more slowly at the lower temperature. Because these are probability distributions, the area under each curve has a numerical value of unity.

In 1852, Scottish physicist James Clerk Maxwell first solved the problem of finding the speed distribution of gas molecules. His result, known as **Maxwell's speed distribution law**, is

$$f(v) = 4\pi \left( \frac{m}{2\pi k_B T} \right)^{3/2} v^2 e^{-mv^2/2k_B T}. \quad (20-26)$$

Here  $v$  is the molecular speed,  $T$  is the gas temperature,  $m$  is the mass of a single gas molecule, and  $k_B$  is Boltzmann's constant. It is this equation that is plotted in Fig. 19-8a, b. The quantity  $f(v)$  in Eq. 19-26 and Fig. 19-8 is a *probability distribution function*: For

any speed  $v$ , the product  $f(v)dv$  (a dimensionless quantity) is the fraction of molecules whose speeds lie in the interval of width  $dv$  centered on speed  $v$ .

As Fig. 19-8a shows, this fraction is equal to the area of a strip with height  $f(v)$  and width  $dv$ . The total area under the distribution curve corresponds to the fraction of the molecules whose speeds lie between zero and infinity. All molecules fall into this category, so the value of this total area is unity; that is,

$$\int_0^{\infty} f(v)dv = 1. \quad (20-27)$$

The fraction of molecules with speeds in an interval of, say,  $v_1$  to  $v_2$  is then

$$\text{fraction} = \int_{v_1}^{v_2} f(v)dv. \quad (20-28)$$

## Average, RMS, and Most Probable Speeds

In principle, we can find the **average speed**  $\langle v \rangle$  of the molecules in a gas with the following procedure: We *weight* each value of  $v$  in the distribution; that is, we multiply it by the fraction  $f(v) dv$  of molecules with speeds in a differential interval  $dv$  centered on  $v$ . Then we add up all these values of  $vf(v)dv$ . The result is  $\langle v \rangle$ . In practice, we do all this by evaluating

$$\langle v \rangle = \int_0^{\infty} v f(v) dv. \quad (20-29)$$

Substituting for  $f(v)$  from Eq. 19-26 and using definite integral 20 from the list of integrals in Appendix E, we find

$$\langle v \rangle = \sqrt{\frac{8k_B T}{\pi m}} \quad (\text{average speed}). \quad (20-30)$$

Similarly, we can find the average of the square of the speeds  $\langle v^2 \rangle$  with

$$\langle v^2 \rangle = \int_0^{\infty} v^2 f(v)dv. \quad (20-31)$$

Substituting for  $f(v)$  from Eq. 19-27 and using generic integral 16 from the list of integrals in Appendix E, we find

$$\langle v^2 \rangle = \frac{3k_B T}{m}. \quad (20-32)$$

The square root of  $\langle v^2 \rangle$  is the **root-mean-square speed**  $v^{\text{rms}}$ . Thus,

$$v^{\text{rms}} = \sqrt{\frac{3k_B T}{m}} \quad (\text{rms speed}). \quad (20-33)$$

which agrees with Eq. 19-21.

The **most probable speed**  $v^{\text{prob}}$  is the speed at which  $f(v)$  is maximum (see Fig. 19-8a). To calculate  $v^{\text{prob}}$ , we set  $df/dv = 0$  (the slope of the curve in Fig. 19-8a is zero at the maximum of the curve) and then solve for  $v$ . Doing so, we find

$$v^{\text{prob}} = \sqrt{\frac{2k_B T}{m}} \quad (\text{most probable speed}). \quad (20-34)$$

What is the relationship between the most probable speed, the average speed, and the rms speed of a molecule? The relationship is fixed.

The most probable speed  $v^{\text{prob}}$  is always less than the average speed  $\langle v \rangle$  which in turn is less than the rms speed  $v^{\text{rms}}$ . More specifically,  $v^{\text{prob}} = 0.82 v^{\text{rms}}$  and  $\langle v \rangle = 0.92 v^{\text{rms}}$ .

This is consistent with the idea that a molecule is more likely to have speed  $v^{\text{prob}}$  than any other speed, but some molecules will have speeds that are many times  $v^{\text{prob}}$ . These molecules lie in the *high-speed tail* of a distribution curve like that in Fig. 19-8a. We should be thankful for these few, higher speed molecules because they make possible both rain and sunshine (without which we could not exist). We next see why.

**Rain:** The speed distribution of water molecules in, say, a pond at summertime temperatures can be represented by a curve similar to that of Fig. 19-8a. Most of the molecules do not have nearly enough kinetic energy to escape from the water through its surface. However, small numbers of very fast molecules with speeds far out in the tail of the curve can do so. It is these water molecules that evaporate, making clouds and rain a possibility.

As the fast water molecules leave the surface, carrying energy with them, the temperature of the remaining water is maintained by thermal energy transfer from the surroundings. Other fast molecules—produced in particularly favorable collisions—quickly take the place of those that have left, and the speed distribution is maintained.

**Sunshine:** Let the distribution curve of Fig. 19-8a now refer to protons in the core of the Sun. The Sun's energy is supplied by a nuclear fusion process that starts with the merging of two protons. However, protons repel each other because of their electrical charges, and protons of average speed do not have enough kinetic energy to overcome the repulsion

and get close enough to merge. Very fast protons with speeds in the tail of the distribution curve can do so, however, and thus the Sun can shine.

## 19-7 The Molar Specific Heats of an Ideal Gas

Up to now, we have taken the specific heat of a substance as a quantity to be measured. But now, with the kinetic theory of gases, we know something about the structure of matter and where its energy is stored. With this additional information, we can actually calculate and make predictions about what we expect the specific heats of different kinds of gases to be. If we compare our predictions based on kinetic theory to experimental measurements, we get some good agreement and also some surprises. The surprises are among the first hints that the laws of matter at the atomic level are not just Newton's laws scaled down. In other words, we begin to notice that atoms aren't just little billiard balls but something different from any macroscopic object with which we have experience.

To explore this idea, we derive here (from molecular considerations) an expression for the internal energy  $E^{\text{int}}$  of an ideal gas. In other words, we find an expression for the energy associated with the random motions of the atoms or molecules in the gas. We shall then use that expression to derive the molar specific heats of an ideal gas.

### Internal Energy $E^{\text{int}}$

Let us first assume that our ideal gas is a *monatomic gas* (which has individual atoms rather than molecules), such as helium, neon, or argon. Let us also assume that the internal energy  $E^{\text{int}}$  of our ideal gas is simply the sum of the translational kinetic energies of its atoms.

The average translational kinetic energy of a single atom depends only on the gas temperature and is given by Eq. 19-23 as  $\langle K \rangle = \frac{3}{2} k_B T$ . A sample of  $n$  moles of such a gas contains  $nN_A$  atoms. The internal energy  $E^{\text{int}}$  of the sample is then

$$E^{\text{int}} = (nN_A) \langle K \rangle = (nN_A) \left( \frac{3}{2} k_B T \right). \quad (20-35)$$

Using Eq. 19-6 ( $k_B = R/N_A$ ), we can rewrite this as

$$E^{\text{int}} = \frac{3}{2} N k_B T = \frac{3}{2} nRT \quad (\text{monatomic ideal gas}). \quad (20-36)$$

Thus,

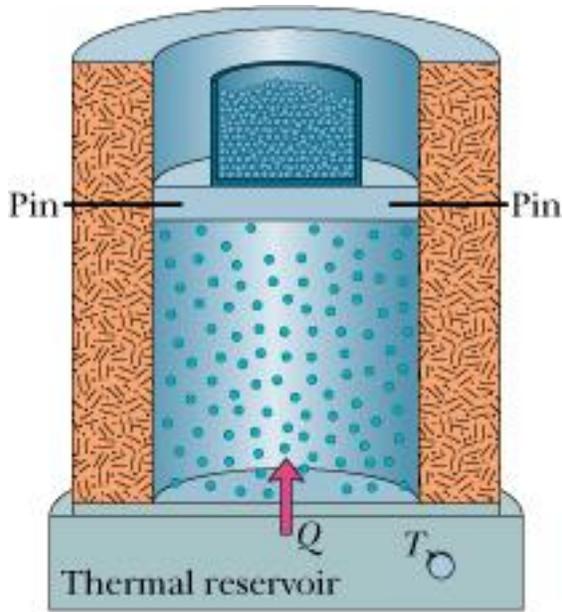
The internal energy  $E^{\text{int}}$  of an ideal gas is a function of the gas temperature *only*; it does not depend on any other variable.

With Eq. 19-36 in hand, we are now able to derive an expression for the molar specific heat of an ideal gas. Actually, we shall derive two expressions. One is for the

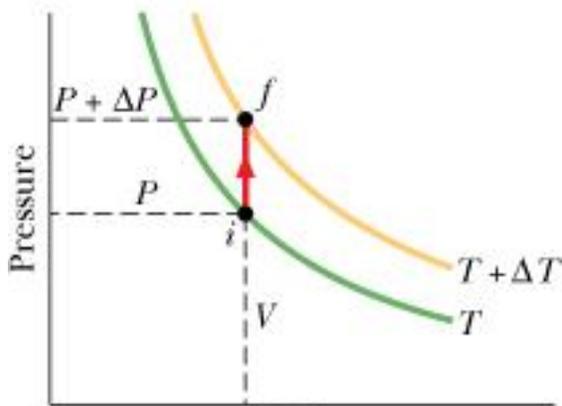
case in which the volume of the gas remains constant as thermal energy is transferred to or from it. The other is for the case in which the pressure of the gas remains constant as thermal energy is transferred to or from it. The symbols for these two molar specific heats are  $C_V$  and  $C_P$ , respectively. (By convention, the capital letter  $C$  is used in both cases, even though  $C_V$  and  $C_P$  represent types of specific heat and not heat capacities.)

## Molar Specific Heat at Constant Volume

Figure 19-9a shows  $n$  moles of an ideal gas at pressure  $P$  and temperature  $T$ , confined to a cylinder of fixed volume  $V$ . This *initial state*  $i$  of the gas is marked on the  $P$ - $V$  diagram of Fig. 19-9b. Suppose that you add a small amount of thermal energy  $Q$  to the gas by slowly turning up the temperature of the thermal reservoir. The gas temperature rises a small amount to  $T + \Delta T$ , and its pressure rises to  $P + \Delta P$ , bringing the gas to *final state*  $f$ .



(a)



(b)

**FIGURE 19-9** (a) The temperature of an ideal gas is raised from  $T$  to  $T + \Delta T$  in a constant-volume process. Thermal energy is added, but no work is done. (b) The process on a  $P$ - $V$  diagram. (The system's insulated lid is not shown.)

In such experiments, we would find that the thermal energy transferred  $Q$  is related to the temperature change  $\Delta T$  by

$$Q = nC_V\Delta T \quad (\text{constant volume}), \quad (20-37)$$

where  $C_V$  is a constant called the **molar specific at constant volume**. Substituting this expression for  $Q$  into the first law of thermodynamics as given by Eq. 19-17 ( $\Delta E^{\text{int}} = Q - W$ ) yields

$$\Delta E^{\text{int}} = nC_v\Delta T - W. \quad (20-38)$$

With the volume held constant, the gas cannot expand and thus cannot do any work. Therefore,  $W = 0$ , and Eq. 19-38 gives us

$$C_v = \frac{\Delta E^{\text{int}}}{n\Delta T}. \quad (20-39)$$

From Eq. 19-36 we know that  $E^{\text{int}} = \frac{3}{2}nRT$ , so the change in internal energy must be

$$\Delta E^{\text{int}} = \frac{3}{2}nR\Delta T. \quad (20-40)$$

Substituting this result into Eq. 19-39 yields

$$C_v = \frac{3}{2}R = 12.5 \text{ J/mol} \cdot \text{K} \quad (\text{monatomic gas}). \quad (20-41)$$

As Table 19-2 shows, this prediction that  $C_v = \frac{3}{2}R$  based on ideal gas kinetic theory agrees very well with experiment for the real monatomic gases (the case that we have assumed). The experimental values of  $C_v$  for *diatomic gases* and *polyatomic gases* (which have molecules with more than two atoms) are greater than the predicted value of  $\frac{3}{2}R$ . Reasons for this will be discussed in Section 19-8.

**TABLE 19-2**  
**Molar Specific Heats**

Molecule		Example	$C_v$ (J/mol · K)
	Ideal		$\frac{3}{2}R = 12.5$
Monatomic (1 atom)	Real	He	12.5
	Real	Ar	12.6
	Ideal		$\frac{5}{2}R = 20.8^*$
Diatomic (2 atoms)	Real	N <sub>2</sub>	20.7
	Real	O <sub>2</sub>	20.8
	Ideal		$3R = 24.9^*$
Polyatomic (> 2 atoms)	Real	NH <sub>4</sub>	29.0
	Real	CO <sub>2</sub>	29.7

\*The presentation of the  $\frac{5}{2}R$  and  $3R$  will be explained in the next section.

We can now generalize Eq. 19-36 for the internal energy of any ideal gas by substituting  $C_V$  for  $\frac{3}{2}R$ ; we get

$$E^{\text{int}} = nC_V T \quad (\text{any ideal gas}). \quad (20-42)$$

This equation applies not only to an ideal monatomic gas but also to diatomic and polyatomic ideal gases, provided the experimentally determined value of  $C_V$  is used. Just as with Eq. 19-37, we see that the internal energy of a gas depends on the temperature of the gas but not on its pressure or density.

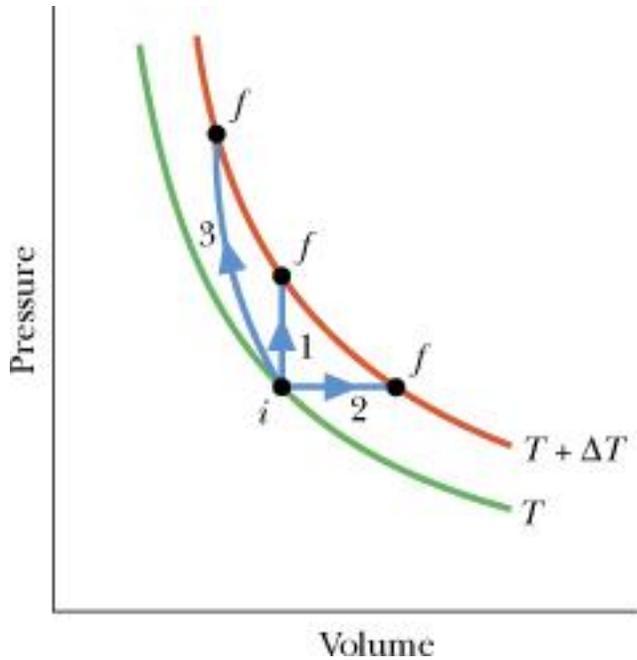
When an ideal gas that is confined to a container undergoes a temperature change  $\Delta T$ , then from either Eq. 19-39 or Eq. 19-42 we can write the resulting change in its internal energy as

$$\Delta E^{\text{int}} = nC_V \Delta T \quad (\text{any ideal gas, any process}). \quad (20-43)$$

This equation tells us:

A change in the internal energy  $E^{\text{int}}$  of a confined ideal gas depends on the change in the gas temperature only; it does *not* depend on what type of process produces the change in the temperature.

As examples, consider the three paths between the two isotherms in the  $P$ - $V$  diagram of Fig. 19-10. Path 1 represents a constant-volume process. Path 2 represents a constant-pressure process (that we are about to examine). Path 3 represents a process in which no thermal energy is exchanged with the system's environment (we discuss this in Section 19-11). Although the values of  $Q$  and work  $W$  associated with these three paths differ, as do  $P_f$  and  $V_f$ , the values of  $\Delta E^{\text{int}}$  associated with the three paths are identical and are all given by Eq. 19-43, because they all involve the same temperature change  $\Delta T$ . Therefore, no matter what path is actually taken between  $T$  and  $T + \Delta T$ , we can *always* use path 1 and Eq. 19-43 to compute  $\Delta E^{\text{int}}$  easily.



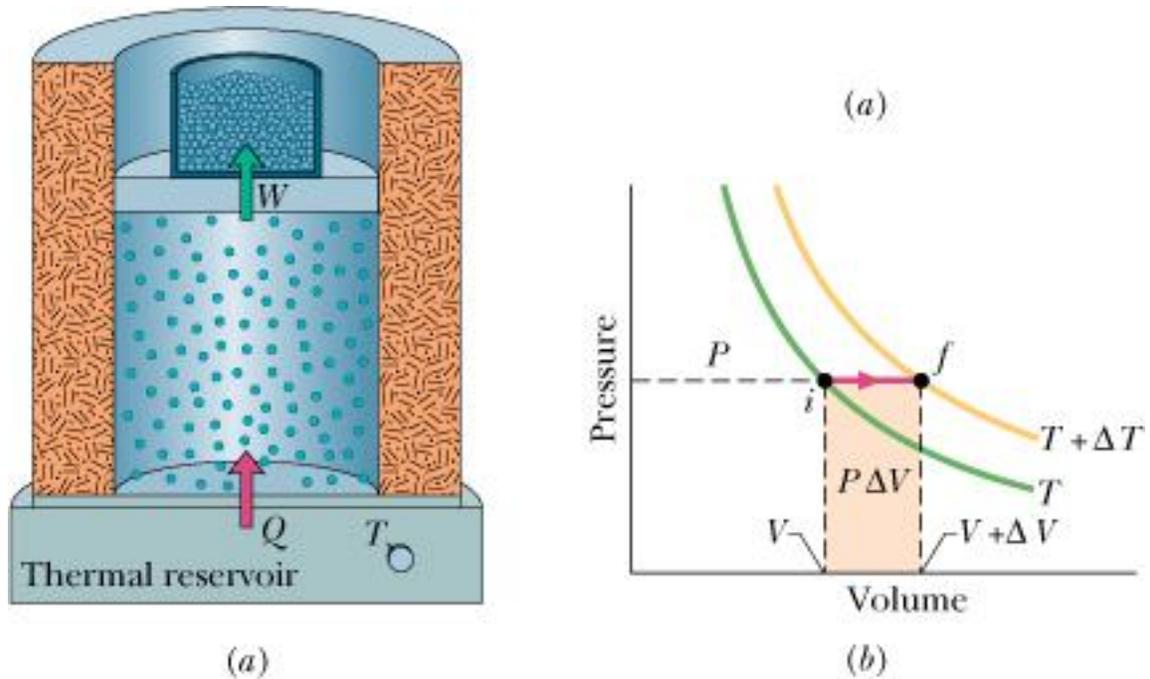
**FIGURE 19-10** Three paths representing three different processes that take an ideal gas from an initial state  $i$  at temperature  $T$  to some final state  $f$  at temperature  $T + \Delta T$ . The change  $\Delta E^{\text{int}}$  in the internal energy of the gas is the same for these three processes and for any others that result in the same change of temperature.

## Molar Specific Heat at Constant Pressure

We now assume that the temperature of the ideal gas is increased by the same small amount  $\Delta T$  as previously, but that the necessary thermal energy ( $Q$ ) is added with the gas under constant pressure. An experiment for doing this is shown in Fig. 19-11*a*; the  $P$ - $V$  diagram for the process is plotted in Fig. 19-11*b*. From such experiments we find that the transferred thermal energy  $Q$  is related to the temperature change  $\Delta T$  by

$$Q = nC_p\Delta T \quad (\text{constant pressure}), \quad (20-44)$$

where  $C_p$  is a constant called the **molar specific heat at constant pressure**. This  $C_p$  is *greater* than the molar specific heat at constant volume  $C_v$ , because energy must now be supplied not only to raise the temperature of the gas but also for the gas to do work—that is, to lift the weighted piston of Fig. 19-11*a*.



**FIGURE 19-11** (a) The temperature of an ideal gas is raised from  $T$  to  $T + \Delta T$  in a constant-pressure process. Thermal energy is added and work is done in lifting the loaded piston. (b) The process on a  $P$ - $V$  diagram. The work  $P\Delta V$  is given by the shaded area.

To relate molar specific heats  $C_p$  and  $C_v$ , we start with the first law of thermodynamics (Eq. 19-17):

$$\Delta E^{\text{int}} = Q - W. \quad (20-45)$$

We next replace each term in Eq. 19-45. For  $\Delta E^{\text{int}}$ , we substitute from Eq. 19-43. For  $Q$ , we substitute from Eq. 19-44. To replace  $W$ , we first note that since the pressure remains constant, Eq. 19-16 tells us that  $W = P\Delta V$ . Then we note that, using the ideal gas equation ( $PV = nRT$ ), we can write

$$W = P\Delta V = nR\Delta T. \quad (20-46)$$

Making these substitutions in Eq. 19-45, we find

$$nC_v\Delta T = nC_p\Delta T - nR\Delta T$$

and then dividing through by  $n \Delta T$ ,

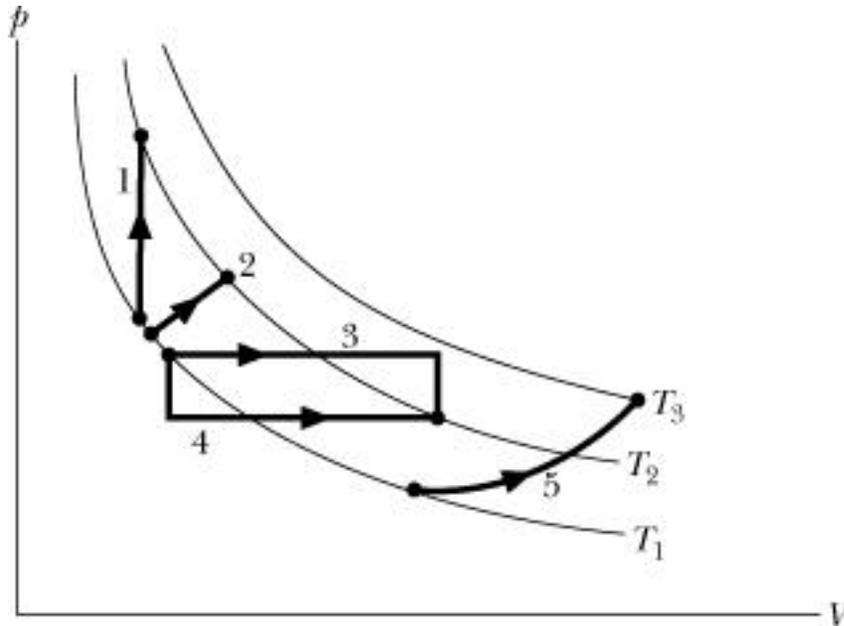
$$C_v = C_p - R,$$

so

$$C_p = C_v + R \quad (\text{any ideal gas}). \quad (20-47)$$

This relationship between  $C_P$  and  $C_V$  predicted by kinetic theory agrees well with experiment, not only for monatomic gases but for gases in general, as long as their density is low enough so that we may treat them as ideal. As we discuss in Section 19-5, there is very little difference between  $C_P$  and  $C_V$  for liquids and solids because of their relative incompressibility.

**READING EXERCISE 19-4:** The figure here shows five paths traversed by a gas on a  $P$ - $V$  diagram. Rank the paths according to the change in internal energy of the gas, greatest first.




---

**TOUCHSTONE EXAMPLE 19-4:** Helium Bubble

---

A bubble of 5.00 mol of helium is submerged at a certain depth in liquid water when the water (and thus the helium) undergoes a temperature increase  $\Delta T$  of 20.0 C° at constant pressure. As a result, the bubble expands. The helium is monatomic and ideal.

(a) How much thermal energy is added to the helium during the increase and expansion?

**SOLUTION** One **Key Idea** here is that the thermal energy transferred  $Q$  is related to the temperature change  $\Delta T$  by the molar specific heat of the gas. Because the pressure  $P$  is held constant during the addition of energy, we use the molar specific heat at constant pressure  $C_P$  and Eq. 19-44,

$$Q = nC_P\Delta T, \quad (20-48)$$

to find  $Q$ . To evaluate  $C_P$  we go to Eq. 19-47, which tells us that for any ideal gas,  $C_P = C_V + R$ . Then from Eq. 19-41, we know that for any *monatomic* gas (like helium),  $C_V = \frac{3}{2}R$ . Thus, Eq. 19-48 gives us

$$\begin{aligned}
Q &= n(C_v + R)\Delta T = n\left(\frac{3}{2}R + R\right)\Delta T = n\left(\frac{5}{2}R\right)\Delta T \\
&= (5.00 \text{ mol})(2.5)(8.31 \text{ J/mol}\cdot\text{K})(20.0 \text{ C}^\circ) && \text{(Answer)} \\
&= 2077.5 \text{ J} \approx 2080 \text{ J}.
\end{aligned}$$

(b) What is the change  $\Delta E^{\text{int}}$  in the internal energy of the helium during the temperature increase?

**SOLUTION** Because the bubble expands, this is not a constant-volume process. However, the helium is nonetheless confined (to the bubble). Thus, a **Key Idea** here is that the change  $\Delta E^{\text{int}}$  is the same as *would occur* in a constant-volume process with the same temperature change  $\Delta T$ . We can easily find the constant-volume change  $\Delta E^{\text{int}}$  with Eq. 19-43:

$$\begin{aligned}
\Delta E^{\text{int}} &= nC_v\Delta T = n\left(\frac{3}{2}R\right)\Delta T \\
&= (5.00 \text{ mol})(1.5)(8.31 \text{ J/mol}\cdot\text{K})(20.0 \text{ C}^\circ) && \text{(Answer)} \\
&= 1246.5 \text{ J} \approx 1250 \text{ J}.
\end{aligned}$$

(c) How much work  $W$  is done by the helium as it expands against the pressure of the surrounding water during the temperature increase?

**SOLUTION** One **Key Idea** here is that the work done by *any* gas expanding against the pressure from its environment is given by Eq. 19-11, which tells us to integrate  $P dV$ . When the pressure is constant (as here), we can simplify that to  $W = P \Delta V$ . When the gas is *ideal* (as here), we can use the ideal gas law (Eq. 19-8) to write  $P \Delta V = nR \Delta T$ . We end up with

$$\begin{aligned}
W &= nR\Delta T \\
&= (5.00 \text{ mol})(8.31 \text{ J/mol}\cdot\text{K})(20.0 \text{ C}^\circ) && \text{(Answer)} \\
&= 831 \text{ J}.
\end{aligned}$$

Because we happen to know  $Q$  and  $\Delta E^{\text{int}}$ , we can work this problem another way. The **Key Idea** now is that we can account for the energy changes of the gas with the first law of thermodynamics, writing

$$\begin{aligned}
W &= Q - \Delta E^{\text{int}} = 2077.5 \text{ J} - 1246.5 \text{ J} && \text{(Answer)} \\
&= 831 \text{ J}.
\end{aligned}$$

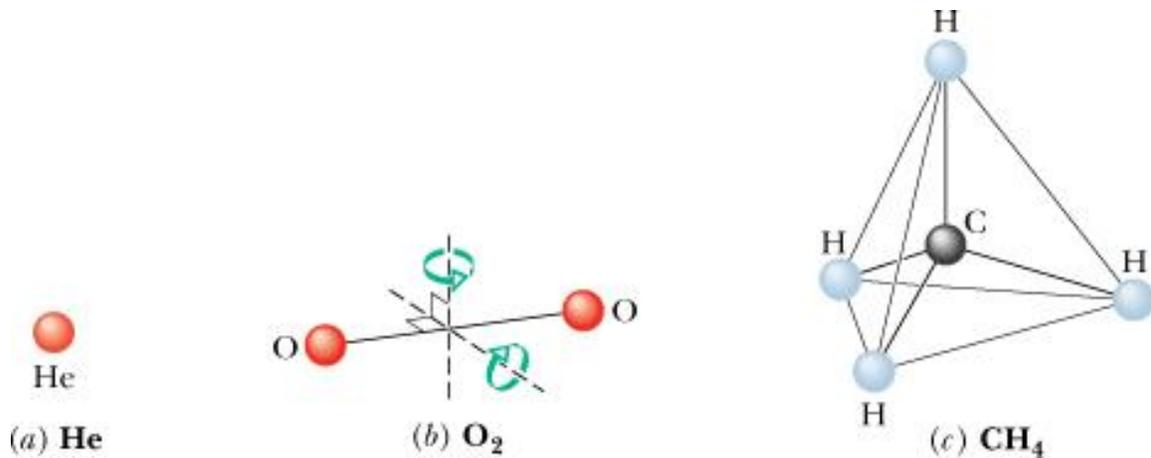
Note that during the temperature increase, only a portion (1250 J) of the thermal energy (2080 J) that is transferred to the helium goes to increasing the internal energy of the helium and thus the temperature of the helium. The rest (831 J) is transferred out of the helium as work that the helium does during the expansion. If the water were frozen, it would not allow that expansion. Then the same temperature increase of 20.0 C° would require only 1250 J of energy, because no work would be done by the helium.

---

## 19-8 Degrees of Freedom and Molar Specific Heats

As Table 19-2 shows, the prediction that  $C_V = \frac{3}{2}R$  agrees with experiment for monatomic gases. But it fails for diatomic and polyatomic gases. Let us try to explain the discrepancy by considering the possibility that molecules with more than one atom can store internal energy in forms other than *translational* kinetic energy.

Figure 19-12 shows common models of helium (a *monatomic* molecule, containing a single atom), oxygen (a *diatomic* molecule, containing two atoms), and methane (a *polyatomic* molecule). From such models, we would assume that all three types of molecules can have translational motions (say, moving left-right and up-down) and rotational motions (spinning about an axis like a top). However, due to their highly symmetric nature, rotational motions in a monatomic molecule need special consideration. We will return to this point shortly. In addition, we would assume that the diatomic and polyatomic molecules can have oscillatory motions, with the atoms oscillating slightly toward and away from one another, as if attached to opposite ends of a spring.



**FIGURE 19-12** Models of molecules as used in kinetic theory: (a) helium, a typical monatomic molecule; (b) oxygen, a typical diatomic molecule; and (c) methane, a typical polyatomic molecule. The spheres represent atoms, and the lines between them represent bonds. Two rotation axes are shown for the oxygen molecule.

To keep account of the various ways in which energy can be stored in a gas, James Clerk Maxwell introduced the theorem of the **equipartition of energy**:

Every kind of molecule has a certain number  $f$  of **degrees of freedom**, which are independent ways in which the molecule can store energy. Each such degree of freedom has associated with it—on average—an energy of  $\frac{1}{2}k_B T$  per molecule (or  $\frac{1}{2}RT$  per mole).

Let us apply the theorem to the translational and rotational motions of the molecules in Fig. 19-12. (We discuss oscillatory motion in the next section.) For the translational motion, superimpose an  $xyz$  coordinate system on any gas. The molecules will, in general, have velocity components along all three axes. Thus, gas molecules of all types have three degrees of translational freedom (three ways to move in translation) and, on average, an associated energy of  $3(\frac{1}{2}k_B T)$  per molecule.

For the rotational motion, imagine the origin of our  $xyz$  coordinate system at the center of each molecule in Fig. 19-12. In a gas, each molecule should be able to rotate with an angular velocity component along each of the three axes, so each gas should have three degrees of rotational freedom and, on average, an additional energy of  $3(\frac{1}{2}k_B T)$  per molecule. *However*, experiment shows this is true only for the polyatomic molecules.

A possible solution to this dilemma is that rotations about an axis of symmetry don't count as a degree of freedom. For example, as seen in Fig. 19-12, a single-atom molecule is symmetric about all three (mutually perpendicular) axes through the molecule. Hence, according to our proposed solution, these rotations are not additional degrees of freedom. A diatomic molecule is symmetric about only one axis (the axis through the center of both atoms). Accordingly, a diatomic molecule would have two rather than three degrees of freedom associated with rotation of the molecule.

It appears that modifying our theory in this manner brings us more in alignment with the experimental results. However, one should ask what reasoning (other than experimental evidence) supports this modification of the theory. One thing is clear. If a molecule were rotating about an axis of symmetry, it would be impossible to tell. Unlike a baseball (which has stitches or other marks) molecules have no characteristics that allow us to sense the rotation. Although classical physics gives us no real foundation for ignoring the motion simply because it is indistinguishable from no motion at all, this is what quantum theory would suggest.

So, according to our new model, a monatomic molecule has zero degrees of freedom associated with rotation because any rotation would be about an axis of symmetry. A diatomic molecule has two degrees of freedom associated with rotations about the two axes perpendicular to the line connecting the atoms (the axes are shown in Fig. 19-12*b*) but no degree of freedom for rotation about that line itself. Therefore, a diatomic molecule can have a rotational energy of only  $2(\frac{1}{2}k_B T)$  per molecule. A polyatomic molecule has a full three degrees of freedom associated with rotational motion.

To extend our analysis of molar specific heats ( $C_P$  and  $C_V$ , in Section 19-7) to ideal diatomic and polyatomic gases, it is necessary to retrace the derivations of that analysis in detail. First, we replace Eq. 19-36 with  $(E^{\text{int}} = \frac{3}{2}nRT)$  with  $E^{\text{int}} = (f/2)nRT$ , where  $f$  is the number of degrees of freedom listed in Table 19-3. Doing so leads to the prediction

$$C_V = \left(\frac{f}{2}\right)R = 4.16f \text{ J/mol} \cdot \text{K}, \quad (20-49)$$

which agrees—as it must—with Eq. 19-41 for monatomic gases ( $f = 3$ ). As Table 19-3 shows, this prediction also agrees with experiment for diatomic gases ( $f = 5$ ), but it is too low for polyatomic gases. *Note:* The symbol  $f$  used here to denote degrees of freedom should not be confused with  $f(v)$  used to describe the velocity distribution function for molecules.

**TABLE 19-3**  
**Degrees of Freedom for Various Molecules**

Molecule	Example	Degrees of Freedom			Predicted Molar Specific heats	
		Translational	Rotational	Total ( $f$ )	$C_V$ (Eq. 19-47)	$C_P = C_V + R$
Monatomic	He	3	0	3	$\frac{3}{2}R$	$\frac{5}{2}R$
Diatomic	O <sub>2</sub>	3	2	5	$\frac{5}{2}R$	$\frac{7}{2}R$
Polyatomic	CH <sub>4</sub>	3	3	6	$3R$	$4R$

**TOUCHSTONE EXAMPLE 19-5: Internal Energy Change**

A cabin of volume  $V$  is filled with air (which we consider to be an ideal diatomic gas) at an initial low temperature  $T_1$ . After you light a wood stove, the air temperature increases to  $T_2$ . What is the resulting change  $\Delta E^{\text{int}}$  in the internal energy of the air in the cabin?

**SOLUTION** As the air temperature increases, the air pressure  $P$  cannot change but must always be equal to the air pressure outside the room. The reason is that, because the room is not airtight, the air is not confined. As the temperature increases, air molecules leave through various openings and thus the number of moles  $n$  of air in the room decreases. Thus, one **Key Idea** here is that we *cannot* use Eq. 19-43 ( $\Delta E^{\text{int}} = nC_V \Delta T$ ) to find  $\Delta E^{\text{int}}$ , because it requires constant  $n$ .

A second **Key Idea** is that we *can* relate the internal energy  $E^{\text{int}}$  at any instant to  $n$  and the temperature  $T$  with Eq. 19-42 ( $E^{\text{int}} = nC_V T$ ). From that equation we can then write

$$\Delta E^{\text{int}} = \Delta(nC_V T) = C_V \Delta(nT).$$

Next, using Eq. 19-8 ( $PV = nRT$ ), we can replace  $nT$  with  $PV/R$ , obtaining

$$\Delta E^{\text{int}} = C_V \Delta \left( \frac{PV}{R} \right). \quad (20-50)$$

Now, because  $P$ ,  $V$ , and  $R$  are all constants, Eq. 19-50 yields

$$\Delta E^{\text{int}} = 0, \quad (\text{Answer})$$

even though the temperature changes.

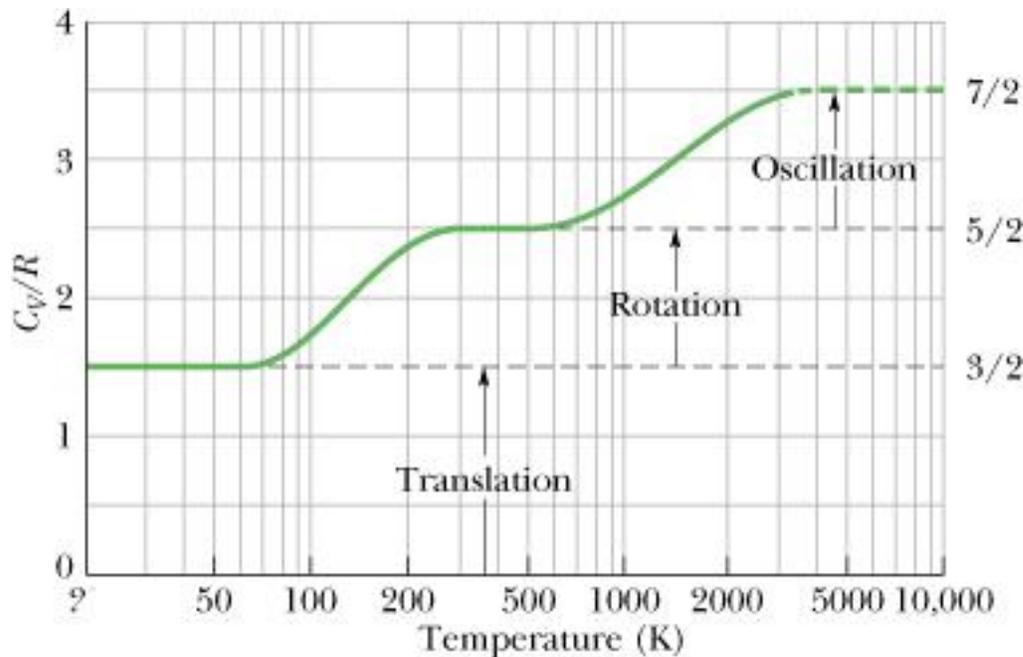
Why does the cabin feel more comfortable at the higher temperature? There are at least two factors involved: (1) You exchange electromagnetic radiation (thermal

radiation) with surfaces inside the room, and (2) you exchange energy with air molecules that collide with you. When the room temperature is increased, (1) the amount of thermal radiation emitted by the surfaces and absorbed by you is increased, and (2) the amount of energy you gain through the collisions of air molecules with you is increased.

## 19-9 A Hint of Quantum Theory

We can improve the agreement of kinetic theory with experiment by including the oscillations of the atoms in a gas of diatomic or polyatomic molecules. For example, the two atoms in the  $O_2$  molecule of Fig. 19-12*b* can oscillate toward and away from each other, with the interconnecting bond acting like a spring. However, experiment shows that such oscillations occur only at relatively high temperatures of the gas—the motion is “turned on” only when the gas molecules have relatively large energies. Rotational motion is also subject to such “turning on,” but at a lower temperature.

Figure 19-13 is of help in seeing this turning on of rotational motion and oscillatory motion. The ratio  $C_V/R$  for diatomic hydrogen gas ( $H_2$ ) is plotted there against temperature, with the temperature scale logarithmic to cover several orders of magnitude. Below about 80 K, we find that  $C_V/R = 1.5$ . This result implies that only the three translational degrees of freedom of hydrogen are involved in the specific heat.



**FIGURE 19-13** A plot of  $C_V/R$  versus temperature for (diatomic) hydrogen gas. Because rotational and oscillatory motions begin at certain energies, only translation is possible at very low temperatures. As the temperature increases, rotational motion can begin. At still higher temperatures, oscillatory motion can begin.

As the temperature increases, the value of  $C_V/R$  gradually increases to 2.5, implying that two additional degrees of freedom have become involved. Quantum theory shows that these two degrees of freedom are associated with the rotational motion of the hydrogen molecules and that this motion requires a certain minimum amount of energy. At very low temperatures (below 80 K), the molecules do not have enough energy to rotate. As the temperature increases from 80 K, first a few molecules and then more and more obtain enough energy to rotate, and  $C_V/R$  increases, until all of them are rotating and  $C_V/R = 2.5$ .

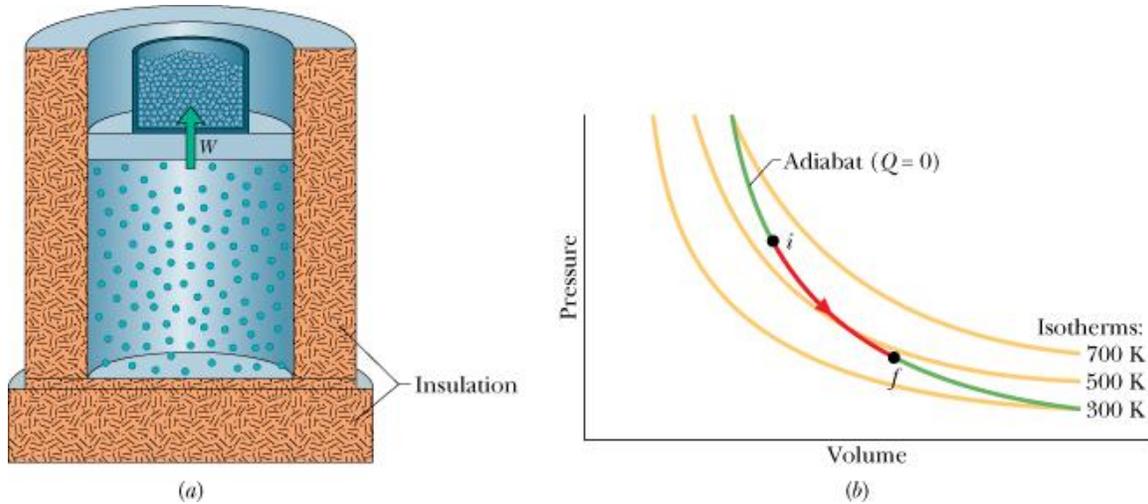
Similarly, quantum theory shows that oscillatory motion of the molecules requires a certain (higher) minimum amount of energy. This minimum amount is not met until the molecules reach a temperature of about 1000 K, as shown in Fig. 19-13. As the temperature increases beyond 1000 K, the number of molecules with enough energy to oscillate increases, and  $C_V/R$  increases, until all of them are oscillating and  $C_V/R = 3.5$ . (In Fig. 19-13, the plotted curve stops at 3190 K because at that temperature, the atoms of a hydrogen molecule oscillate so much that they overwhelm their bond, and the molecule then *dissociates* into two separate atoms.)

The observed fact that rotational degrees of freedom are not excited until sufficiently high temperatures are reached implies that rotational kinetic energy is not a continuous function of angular velocity. Instead, a discrete, quantized energy level must be attained before rotation is excited. This discreteness of energy levels is a hallmark of quantum mechanical behavior. It is interesting to note that some of the issues discussed in this chapter are the first examples (with many more to come) that macroscopic properties of matter, which are easily measured in the laboratory, depend critically on (and provide strong evidence for) the quantum theory we will develop later.

The compatibility between microscopic theory and macroscopic observations when coupled with quantum theory and other phenomena in physics and chemistry provided additional support for the theory that matter is composed of atoms and molecules.

## 19-10 The Adiabatic Expansion of an Ideal Gas

We saw in Section 18-2 that sound waves are propagated through air and other gases as a series of compressions and expansions; these variations in the transmission medium take place so rapidly that there is no time for thermal energy to be transferred from one part of the medium to another. As we saw in Section 19-8, a process for which  $Q = 0$  is an *adiabatic process*. We can ensure that  $Q = 0$  either by carrying out the process very quickly (as in sound waves) or by doing it (at any rate) in a well-insulated container. Let us see what the kinetic theory has to say about adiabatic processes.



**FIGURE 19-14** (a) The volume of an ideal gas is increased by removing weight from the piston. The process is adiabatic ( $Q = 0$ ). (b) The process proceeds from  $i$  to  $f$  along an adiabat on a  $P$ - $V$  diagram.

Figure 19-14a shows our usual insulated cylinder. Its insulating lid is not shown. It now contains an ideal gas and rests on an insulating stand. By removing mass from the piston, we can allow the gas to expand adiabatically (in a slow process rather than a free expansion). As the volume increases, both the pressure and the temperature drop. We shall prove next that the relation between the pressure and the volume during such an adiabatic process is

$$PV^\gamma = \text{a constant} \quad (\text{ideal gas adiabatic process}), \quad (20-51)$$

in which  $\gamma = C_p/C_v$ , the ratio of the molar specific heats for the gas. On a  $P$ - $V$  diagram such as that in Fig. 19-14b, the process occurs along a line (called an *adiabat*) that has the equation  $P = (\text{a constant})/V^\gamma$ . Since the gas goes from an initial state  $i$  to a final state  $f$ , we can rewrite Eq. 19-51 as

$$P_i V_i^\gamma = P_f V_f^\gamma \quad (\text{ideal gas adiabatic process}). \quad (20-52)$$

We can also write an equation for an adiabatic process in terms of  $T$  and  $V$ . To do so, we use the ideal gas equation ( $PV = nRT$ ) to eliminate  $P$  from Eq. 19-51, finding

$$\left( \frac{nRT}{V} \right) V^\gamma = \text{a constant}.$$

Because  $n$  and  $R$  are constants, we can rewrite this in the alternative form

$$TV^{\gamma-1} = \text{a constant} \quad (\text{ideal gas adiabatic process}). \quad (20-53)$$

in which the constant is different from that in Eq. 19-51. When the gas goes from an initial state  $i$  to a final state  $f$ , we can rewrite Eq. 19-53 as

$$T_i V_i^{\gamma-1} = T_f V_f^{\gamma-1} \quad (\text{adiabatic process}). \quad (20-54)$$

We can now answer the question that opens this chapter. At the top of an unopened carbonated drink, there is a gas of carbon dioxide and water vapor. Because the pressure of the gas is greater than atmospheric pressure, the gas expands out into the atmosphere when the container is opened. Thus, the gas increases its volume, but that means it must do work to push against the atmosphere. Because the expansion is so rapid, it is adiabatic and the only source of energy for the work is the internal energy of the gas. Because the internal energy decreases, the temperature of the gas must also decrease, which can cause the water vapor in the gas to condense into tiny drops, forming the fog. (Note that Eq. 19-54 also tells us that the temperature must decrease during an adiabatic expansion: Since  $V_f$  is greater than  $V_i$ , then  $T_f$  must be less than  $T_i$ .)

### Proof of Eq. 19-51

Suppose that you remove some shot from the piston of Fig. 19-14a, allowing the ideal gas to push the piston and the remaining shot upward and thus to increase the volume by a differential amount  $dV$ . Since the volume change is tiny, we may assume that the pressure  $P$  of the gas on the piston is constant during the change. This assumption allows us to say that the work  $dW$  done by the gas during the volume increase is equal to  $P dV$ . From Eq. 19-18, the first law of thermodynamics can then be written as

$$dE^{\text{int}} = Q - P dV. \quad (20-55)$$

Since the gas is thermally insulated (and thus the expansion is adiabatic), we substitute 0 for  $Q$ . Then we use Eq. 19-43 to substitute  $nC_V dT$  for  $dE^{\text{int}}$ . With these substitutions, and after some rearranging, we have

$$n dT = - \left( \frac{P}{C_V} \right) dV. \quad (20-56)$$

Now using the ideal gas law ( $PV = nRT$ ) and derivative rule 3 in Appendix E we have

$$P dV + V dP = nR dT. \quad (20-57)$$

Replacing  $R$  with its equal,  $C_P - C_V$ , in Eq. 19-57 yields

$$n dT = \frac{P dV + V dP}{C_P - C_V}. \quad (20-58)$$

Equating Eqs. 19-56 and 19-58 and rearranging them give

$$\frac{dP}{P} + \left( \frac{C_p}{C_v} \right) \frac{dV}{V} = 0.$$

Replacing the ratio of the molar specific heats with  $\gamma$  and integrating (see integral 5 in Appendix E) yield

$$\ln P + \gamma \ln V = \text{a constant.}$$

Rewriting the left side as  $\ln PV^\gamma$  and then taking the antilog of both sides, we find

$$PV^\gamma = \text{a constant,} \quad (20-59)$$

which is what we set out to prove.

## Free Expansions

Recall from Section 19-8 that a free expansion of a gas is an adiabatic process that involves no work done on or by the gas, and no change in the internal energy of the gas. A free expansion is thus quite different from the type of adiabatic process described by Eqs. 19-51 through 19-59, in which work is done and the internal energy changes. Those equations then do *not* apply to a free expansion, even though such an expansion is adiabatic.

Also recall that in a free expansion, a gas is in equilibrium only at its initial and final points; thus, we can plot only those points, but not the expansion itself, on a  $P$ - $V$  diagram. In addition, because  $\Delta E^{\text{int}} = 0$ , the temperature of the final state must be that of the initial state. Thus, the initial and final points on a  $P$ - $V$  diagram must be on the same isotherm, and instead of Eq. 19-54 we have

$$T_i = T_f \quad (\text{free expansion}). \quad (20-60)$$

If we next assume that the gas is ideal (so that  $PV = nRT$ ), because there is no change in temperature, there can be no change in the product  $PV$ . Thus, instead of Eq. 19-51 a free expansion involves the relation

$$P_i V_i = P_f V_f \quad (\text{free expansion}). \quad (20-61)$$

---

**TOUCHSTONE EXAMPLE 19-6: Final Temperature**

---

In Touchstone Example 19-2, 1 mol of oxygen (assumed to be an ideal gas) expands isothermally (at 310 K) from an initial volume of 12 L to a final volume of 19 L.

(a) What would be the final temperature if the gas had expanded adiabatically to this same final volume? Oxygen ( $O_2$ ) is diatomic and here has rotation but not oscillation.

**SOLUTION** The **Key Ideas** here are as follows:

1. When a gas expands against the pressure of its environment, it must do work.
2. When the process is adiabatic (no thermal energy is transferred as heat), then the energy required for the work can come only from the internal energy of the gas.
3. Because the internal energy decreases, the temperature  $T$  must also decrease.

We can relate the initial and final temperatures and volumes with Eq. 19-54:

$$T_i V_i^{\gamma-1} = T_f V_f^{\gamma-1}. \quad (20-62)$$

Because the molecules are diatomic and have rotation but not oscillation, we can take the molar specific heats from Table 19-3. Thus,

$$\gamma = \frac{C_P}{C_V} = \frac{\frac{7}{2}R}{\frac{5}{2}R} = 1.40.$$

Solving Eq. 19-62 for  $T_f$  and inserting known data then yield

$$\begin{aligned} T_f &= \frac{T_i V_i^{\gamma-1}}{V_f^{\gamma-1}} = \frac{(310 \text{ K})(12 \text{ L})^{1.40-1}}{(19 \text{ L})^{1.40-1}} && \text{(Answer)} \\ &= (310 \text{ K})\left(\frac{12}{19}\right)^{0.40} = 258 \text{ K}. \end{aligned}$$

(b) What would be the final temperature and pressure if, instead, the gas had expanded freely to the new volume, from an initial pressure of 2.0 Pa?

**SOLUTION** Here the **Key Idea** is that the temperature does not change in a free expansion:

$$T_f = T_i = 310 \text{ K}. \quad \text{(Answer)}$$

We find the new pressure using Eq. 19-61, which gives us

$$P_f = P_i \frac{V_i}{V_f} = (2.0 \text{ Pa}) \frac{12 \text{ L}}{19 \text{ L}} = 1.3 \text{ Pa}. \quad \text{(Answer)}$$

## Conceptual Questions

- 1 For four situations for an ideal gas, the table gives the energy transferred to or from the gas as heat  $Q$  and either the work  $W$  done by the gas or the work  $W_{\text{on}}$  done on the gas, all in joules. Rank the four situations in terms of the temperature change of the gas, most positive first.

	$a$	$b$	$c$	$d$
$Q$	-50	+35	-15	+20
$W$	-50	+35		
$W_{\text{on}}$			-40	+40

- 2 In the  $p$ - $V$  diagram of Fig. 19-17, the gas does 5 J of work when taken along isotherm  $ab$  and 4 J when taken along adiabat  $bc$ . What is the change in the internal energy of the gas when it is taken along the straight path from  $a$  to  $c$ ?

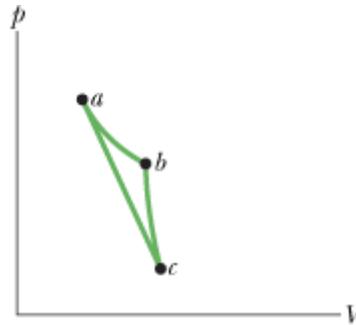


Figure 19-17 Question 2.

- 3 For a temperature increase of  $\Delta T_1$ , a certain amount of an ideal gas requires 30 J when heated at \_\_\_\_\_ and 50 J when heated at constant pressure. How much work is done by the gas \_\_\_\_\_ in the second situation?
- 4 The dot in Fig. 19-18a represents the initial state of a gas, and the vertical line through the dot divides the  $p$ - $V$  diagram into regions 1 and 2. For the following processes, determine whether the work  $W$  done by the gas is positive, negative, or zero: (a) the gas moves up along the vertical line, (b) it moves down along the vertical line, (c) it moves to anywhere in region 1, and (d) it moves to anywhere in region 2.

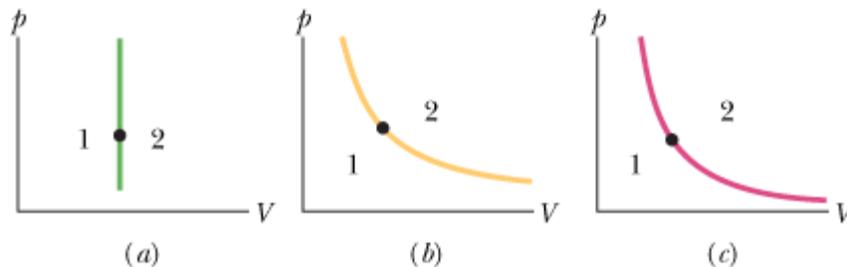


Figure 19-18 Questions 4, 6, and 8.

- 5 A certain amount of energy is to be transferred as heat to 1 mol of a monatomic gas (a) at constant pressure and (b) at constant volume, and to 1 mol of a diatomic gas (c) at constant pressure and (d) at constant volume. Figure 19-19 shows four paths from an initial point to four final points on a  $p$ - $V$  diagram. Which path goes with which process? (e) Are the molecules of the diatomic gas rotating?

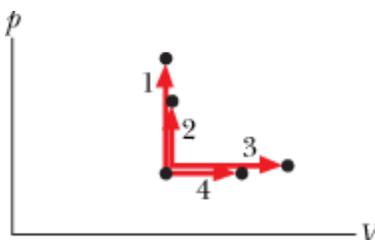


Figure 19-19 Question 5.

- 6 The dot in Fig. 19-18*b* represents the initial state of a gas, and the isotherm through the dot divides the  $p$ - $V$  diagram into regions 1 and 2. For the following processes, determine whether the change  $\Delta E_{\text{int}}$  in the internal energy of the gas is positive, negative, or zero: (a) the gas moves up along the isotherm, (b) it moves down along the isotherm, (c) it moves to anywhere in region 1, and (d) it moves to anywhere in region 2.
- 7 (a) Rank the four paths of Fig. 19-16 according to the work done by the gas, greatest first. (b) Rank paths 1, 2, and 3 according to the change in the internal energy of the gas, most positive first and most negative last.
- 8 The dot in Fig. 19-18*c* represents the initial state of a gas, and the adiabat through the dot divides the  $p$ - $V$  diagram into regions 1 and 2. For the following processes, determine whether the corresponding heat  $Q$  is positive, negative, or zero: (a) the gas moves up along the adiabat, (b) it moves down along the adiabat, (c) it moves to anywhere in region 1, and (d) it moves to anywhere in region 2.
- 9 An ideal diatomic gas, with molecular rotation but not oscillation, loses energy as heat  $Q$ . Is the resulting decrease in the internal energy of the gas greater if the loss occurs in a constant-volume process or in a constant-pressure process?
- 10 Does the temperature of an ideal gas increase, decrease, or stay the same during (a) an isothermal expansion, (b) an expansion at constant pressure, (c) an adiabatic expansion, and (d) an increase in pressure at constant volume?

## Problems

### SEC. 19-2 THE MACROSCOPIC BEHAVIOR OF GASES

1. **Arsenic** Find the mass in kilograms of  $7.50 \times 10^{24}$  atoms of arsenic, which has a molar mass of 74.9 g/mol.
2. **Gold** Gold has a molar mass of 197 g/mol. (a) How many moles of gold are in a 2.50 g sample of pure gold? (b) How many atoms are in the sample?
3. **Water** If the water molecules in 1.00 g of water were distributed uniformly over the surface of Earth, how many such molecules would there be on  $1.00 \text{ cm}^2$  of the surface?
4. **It Is Written** A distinguished scientist has written: "There are enough molecules in the ink that makes one letter of this sentence to provide not only one for every inhabitant of Earth, but one for every creature if each star of our galaxy had a planet as populous as Earth." Check this statement. Assume the ink sample (molar mass = 18 g/mol) to have a mass of  $1 \mu\text{g}$ , the population of Earth to be  $5 \times 10^9$ , and the number of stars in our galaxy to be  $10^{11}$ .

**5. Compute** Compute (a) the number of moles and (b) the number of molecules in  $1.00 \text{ cm}^3$  of an ideal gas at a pressure of  $100 \text{ Pa}$  and a temperature of  $220 \text{ K}$ .

**6. Best Vacuum** The best laboratory vacuum has a pressure of about  $1.00 \times 10^{-18} \text{ atm}$ , or  $1.01 \times 10^{-13} \text{ Pa}$ . How many gas molecules are there per cubic centimeter in such a vacuum at  $293 \text{ K}$ ?

**7. Oxygen Gas** Oxygen gas having a volume of  $1000 \text{ cm}^3$  at  $40.0^\circ\text{C}$  and  $1.01 \times 10^5 \text{ Pa}$  expands until its volume is  $1500 \text{ cm}^3$  and its pressure is  $1.06 \times 10^5 \text{ Pa}$ . Find (a) the number of moles of oxygen present and (b) the final temperature of the sample.

**8. Tire** An automobile tire has a volume of  $1.64 \times 10^{-2} \text{ m}^3$  and contains air at a gauge pressure (pressure above atmospheric pressure) of  $165 \text{ kPa}$  when the temperature is  $0.00^\circ\text{C}$ . What is the gauge pressure of the air in the tires when its temperature rises to  $27.0^\circ\text{C}$  and its volume increases to  $1.67 \times 10^{-2} \text{ m}^3$ ? Assume atmospheric pressure is  $1.00 \times 10^5 \text{ Pa}$ .

**9. A Quantity of Ideal Gas** A quantity of ideal gas at  $10.0^\circ\text{C}$  and  $100 \text{ kPa}$  occupies a volume of  $2.50 \text{ m}^3$ . (a) How many moles of the gas are present? (b) If the pressure is now raised to  $300 \text{ kPa}$  and the temperature is raised to  $30.0^\circ\text{C}$ , how much volume does the gas occupy? Assume no leaks.

### SEC. 19-3 WORK DONE BY IDEAL GASES

**10. Work Done by External Agent** Calculate the work done by an external agent during an isothermal compression of  $1.00 \text{ mol}$  of oxygen from a volume of  $22.4 \text{ L}$  at  $0^\circ\text{C}$  and  $1.00 \text{ atm}$  pressure to  $16.8 \text{ L}$ .

**11.  $P$ ,  $V$ ,  $T$**  Pressure  $P$ , volume  $V$ , and temperature  $T$  for a certain non-ideal material are related by

$$P = \frac{AT - BT^2}{V},$$

where  $A$  and  $B$  are constants. Find an expression for the work done by the material if the temperature changes from  $T_1$  to  $T_2$  while the pressure remains constant.

**12. A Container Encloses** A container encloses two ideal gases. Two moles of the first gas are present, with molar mass  $M_1$ . The second gas has molar mass  $M_2 = 3M_1$ , and  $0.5 \text{ mol}$  of this gas is present. What fraction of the total pressure on the container wall is attributable to the second gas? (The kinetic theory explanation of pressure leads to the experimentally discovered law of partial pressures for a mixture of gases that do not react chemically: *The total pressure exerted by the mixture is equal to the sum of the pressures that the several gases would exert separately if each were to occupy the vessel alone.*)

**13. Air Initially Occupies** Air that initially occupies  $0.14 \text{ m}^3$  at a gauge pressure of  $103.0 \text{ kPa}$  is expanded isothermally to a pressure of  $101.3 \text{ kPa}$  and then cooled at constant pressure until it reaches its initial volume. Compute the work done by the air. (Gauge pressure is the difference between the actual pressure and atmospheric pressure.)

**14. A Sample** A sample of an ideal gas is taken through the cyclic process  $abca$  shown in Fig. 19-15; at point  $a$ ,  $T = 200 \text{ K}$ . (a) How many moles of gas are in the sample? What are (b) the temperature of the gas at point  $b$ , (c) the temperature of the gas at point  $c$ , and (d) the net thermal energy transferred to the gas during the cycle?

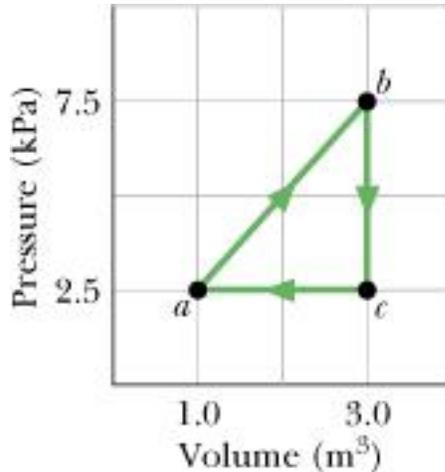


FIGURE 19-15 Problem 14.

**15. Air Bubble** An air bubble of  $20 \text{ cm}^3$  volume is at the bottom of a lake  $40 \text{ m}$  deep where the temperature is  $4.0^\circ\text{C}$ . The bubble rises to the surface, which is at a temperature of  $20^\circ\text{C}$ . Take the temperature of the bubble's air to be the same as that of the surrounding water. Just as the bubble reaches the surface, what is its volume?

**16. Pipe of Length  $L$**  A pipe of length  $L = 25.0 \text{ m}$  that is open at one end contains air at atmospheric pressure. It is thrust vertically into a freshwater lake until the water rises halfway up in the pipe, as shown in Fig. 19-16. What is the depth  $h$  of the lower end of the pipe? Assume that the temperature is the same everywhere and does not change.

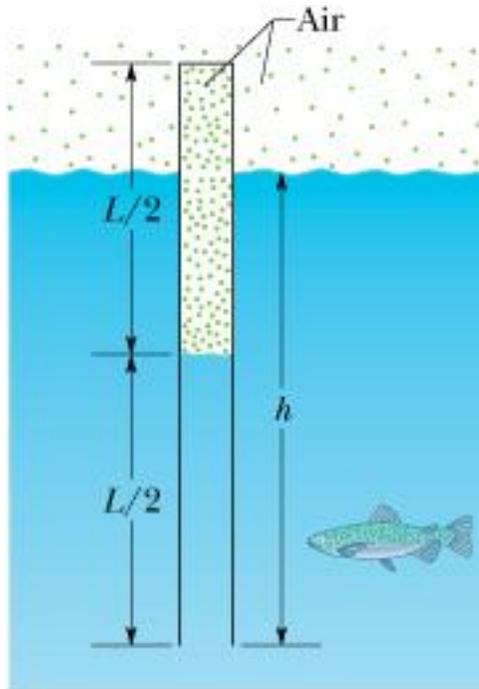


FIGURE 19-16 Problem 16.

**17. Container A** Container A in Fig. 19-17 holds an ideal gas at a pressure of  $5.0 \times 10^5$  Pa and a temperature of 300 K. It is connected by a thin tube (and a closed valve) to container B, with four times the volume of A. Container B holds the same ideal gas at a pressure of  $1.0 \times 10^5$  Pa and a temperature of 400 K. The valve is opened to allow the pressures to equalize, but the temperature of each container is kept constant at its initial value. What then is the pressure in the two containers?

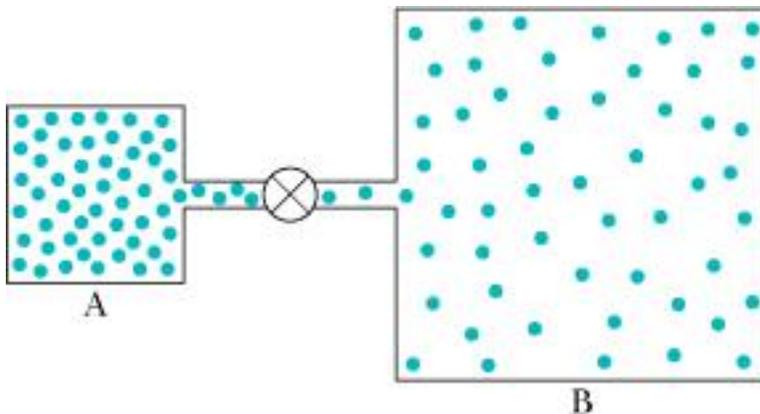


FIGURE 19-17 Problem 17.

#### SEC. 19-4 PRESSURE, TEMPERATURE, AND MOLECULAR KINETIC ENERGY

**18. Helium Atoms** Calculate the rms speed of helium atoms at 1000 K. See Appendix F for the molar mass of helium atoms.

- 19. Lowest Possible** The lowest possible temperature in outer space is 2.7 K. What is the root-mean-square speed of hydrogen molecules at this temperature? (The molar mass of hydrogen molecules ( $\text{H}_2$ ) is given in Table 19-1)
- 20. Speed of Argon** Find the rms speed of argon atoms at 313 K. See Appendix F for the molar mass of argon atoms.
- 21. Sun's Atmosphere** The temperature and pressure in the Sun's atmosphere are  $2.00 \times 10^6$  K and 0.0300 Pa. Calculate the rms speed of free electrons (mass =  $9.11 \times 10^{-31}$  kg) there, assuming they are an ideal gas.
- 22. Nitrogen Molecule** (a) Compute the root-mean-square speed of a nitrogen molecule at  $20.0^\circ\text{C}$ . The molar mass of nitrogen molecules ( $\text{N}_2$ ) is given in Table 20-1. At what temperatures will the root-mean-square speed be (b) half that value and (c) twice that value?
- 23. Hydrogen Molecules** A beam of hydrogen molecules ( $\text{H}_2$ ) is directed toward a wall, at an angle of  $55^\circ$  with the normal to the wall. Each molecule in the beam has a speed of 1.0 km/s and a mass of  $3.3 \times 10^{-24}$  g. The beam strikes the wall over an area of  $2.0 \text{ cm}^2$ , at the rate of  $10^{23}$  molecules per second. What is the beam's pressure on the wall?
- 24. Density of Gas** At 273 K and  $1.00 \times 10^{-2}$  atm, the density of a gas is  $1.24 \times 10^{-5}$  g/cm<sup>3</sup>. (a) Find  $v^{\text{rms}}$  for the gas molecules. (b) Find the molar mass of the gas and identify the gas. (*Hint:* The gas is listed in Table 19-1.)
- 25. Translational Kinetic Energy** What is the average translational kinetic energy of nitrogen molecules at 1600 K?
- 26. Average Value** Determine the average value of the translational kinetic energy of the molecules of an ideal gas at (a)  $0.00^\circ\text{C}$  and (b)  $100^\circ\text{C}$ . What is the translational kinetic energy per mole of an ideal gas at (c)  $0.00^\circ\text{C}$  and (d)  $100^\circ\text{C}$ ?
- 27. Evaporating Water** Water standing in the open at  $32.0^\circ\text{C}$  evaporates because of the escape of some of the surface molecules. The heat of vaporization (539 cal/g) is approximately equal to  $\epsilon n$ , where  $\epsilon$  is the average energy of the escaping molecules and  $n$  is the number of molecules per gram. (a) Find  $\epsilon$ . (b) What is the ratio of  $\epsilon$  to the average kinetic energy of  $\text{H}_2\text{O}$  molecules, assuming the latter is related to temperature in the same way as it is for gases?
- 28. Alternative Form** Show that the ideal gas equation, Eq. 19-8, can be written in the alternative form  $P = \rho RT/M$ , where  $\rho$  is the mass density of the gas and  $M$  is the molar mass.
- 29. Avogadro's Law** Avogadro's law states that under the same conditions of temperature and pressure, equal volumes of gas contain equal numbers of molecules. Is this law equivalent to the ideal gas law? Explain.

### SEC. 19-5 MEAN FREE PATH

**30. Nitrogen Molecules** The mean free path of nitrogen molecules at  $0.0^\circ\text{C}$  and  $1.0\text{ atm}$  is  $0.80 \times 10^{-5}\text{ cm}$ . At this temperature and pressure there are  $2.7 \times 10^{19}\text{ molecules/cm}^3$ . What is the molecular diameter?

**31. Earth's Surface** At  $2500\text{ km}$  above Earth's surface, the number density of the atmosphere is about  $1\text{ molecule/cm}^3$ . (a) What mean free path is predicted by Eq. 19-24 and (b) what is its significance under these conditions? Assume a molecular diameter of  $2.0 \times 10^{-8}\text{ cm}$ .

**32. What Frequency** At what frequency would the wavelength of sound in air be equal to the mean free path of oxygen molecules at  $1.0\text{ atm}$  pressure and  $0.00^\circ\text{C}$ ? Take the diameter of an oxygen molecule to be  $3.0 \times 10^{-8}\text{ cm}$ .

**33. Mean Free Path of Jelly Beans** Assuming that jelly beans in a bag could behave like ideal gas particles, what is the mean free path for 15 spherical jelly beans in a bag that is vigorously shaken? The volume of the bag is  $1.0\text{ L}$ , and the diameter of a jelly bean is  $1.0\text{ cm}$ . (Consider bean-bean collisions, not bean-bag collisions.)

**34. Mean Free Path for Argon** At  $20^\circ\text{C}$  and  $750\text{ torr}$  pressure, the mean free paths for argon gas (Ar) and nitrogen gas ( $\text{N}_2$ ) are  $\lambda_{\text{Ar}} = 9.9 \times 10^{-6}\text{ cm}$  and  $\lambda_{\text{N}_2} = 27.5 \times 10^{-6}\text{ cm}$ . (a) Find the ratio of the effective diameter of argon to that of nitrogen. What is the mean free path of argon at (b)  $20^\circ\text{C}$  and  $150\text{ torr}$ , and (c)  $-40^\circ\text{C}$  and  $750\text{ torr}$ ?

**35. Particle Accelerator** In a certain particle accelerator, protons travel around a circular path of diameter  $23.0\text{ m}$  in an evacuated chamber, whose residual gas is at  $295\text{ K}$  and  $1.00 \times 10^{-6}\text{ torr}$  pressure, (a) Calculate the number of gas molecules per cubic centimeter at this pressure. (b) What is the mean free path of the gas molecules if the molecular diameter is  $2.00 \times 10^{-8}\text{ cm}$ ?

### SEC. 19-6 THE DISTRIBUTION OF MOLECULAR SPEEDS

**36. Twenty-Two Particles** Twenty-two particles have speeds as follows ( $N_i$  represents the number of particles that have speed  $v_i$ ):

$N_i$	2	4	6	8	2
$v_i(\text{cm/s})$	1.0	2.0	3.0	4.0	5.0

(a) Compute their average speed  $\langle v \rangle$ . (b) Compute their root-mean-square speed  $v^{\text{rms}}$ . (c) Of the five speeds shown, which is the most probable speed  $v^{\text{prob}}$ ?

**37. Ten Molecules** The speeds of 10 molecules are  $2.0, 3.0, 4.0 \dots, 11\text{ km/s}$ . (a) What is their average speed? (b) What is their root-mean-square speed?

**38. Ten Particles** (a) Ten particles are moving with the following speeds: four at 200 m/s, two at 500 m/s, and four at 600 m/s. Calculate their average and root-mean-square speeds. Is  $v^{\text{rms}} > \langle v \rangle$ ? (b) Make up your own speed distribution for the 10 particles and show that  $v^{\text{rms}} \geq \langle v \rangle$  for your distribution. (c) Under what condition (if any) does  $v^{\text{rms}} = \langle v \rangle$ ?

**39. Compute Temperature** (a) Compute the temperatures at which the rms speed for (a) molecular hydrogen and (b) molecular oxygen is equal to the speed of escape from Earth. (c) Do the same for the speed of escape from the Moon, assuming the local gravitational constant on its surface to be 0.16g. (d) The temperature high in Earth's upper atmosphere (in the thermosphere) is about 1000 K. Would you expect to find much hydrogen there? Much oxygen? Explain.

**40. Most Probable Speed** It is found that the most probable speed of molecules in a gas when it has (uniform) temperature  $T_2$  is the same as the rms speed of the molecules in this gas when it has (uniform) temperature  $T_1$ . Calculate  $T_2/T_1$ .

**41. Hydrogen Molecule** A molecule of hydrogen (diameter  $1.0 \times 10^{-8}$  cm), traveling with the rms speed, escapes from a furnace ( $T = 4000$  K) into a chamber containing atoms of *cold* argon (diameter  $3.0 \times 10^{-8}$  cm) at a number density of  $4.0 \times 10^{19}$  atoms/cm<sup>3</sup>. (a) What is the speed of the hydrogen molecule? (b) If the H<sub>2</sub> molecule collides with an argon atom, what is the closest their centers can be, considering each as spherical? (c) What is the initial number of collisions per second experienced by the hydrogen molecule? (*Hint*: Assume that the cold argon atoms are stationary. Then the mean free path of the hydrogen molecule is given by Eq. 19-25, and not Eq. 19-24.)

**42. Two Containers—Same Temperature** Two containers are at the same temperature. The first contains gas with pressure  $P_1$ , molecular mass  $m_1$ , and root-mean-square speed  $v_1^{\text{rms}}$ . The second contains gas with pressure  $2P_1$ , molecular mass  $m_2$ , and average speed  $\langle v_2 \rangle = 2v_1^{\text{rms}}$ . Find the mass ratio  $m_1/m_2$ .

**43. Hypothetical Speeds** Figure 19-18 shows a hypothetical speed distribution for a sample of  $N$  gas particles (note that  $f(v) = 0$  for  $v > 2v_0$ ). (a) Express  $a$  in terms of  $N$  and  $v_0$ . (b) How many of the particles have speeds between  $1.5v_0$  and  $2.0v_0$ ? (c) Express the average speed of the particles in terms of  $v_0$ . (d) Find  $v^{\text{rms}}$ .

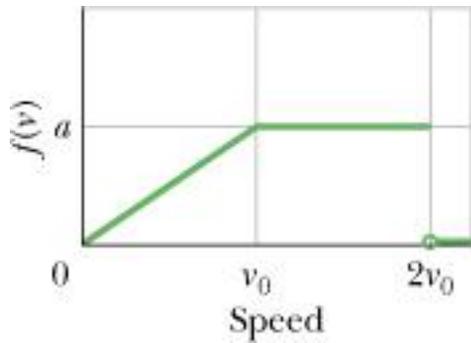


FIGURE 19-18 Problem 43.

### SEC. 19-7 THE MOLAR SPECIFIC HEATS OF AN IDEAL GAS

**44. Internal Energy** What is the internal energy of 1.0 mol of an ideal monatomic gas at 273 K?

**45. Isothermal Expansion** One mole of an ideal gas undergoes an isothermal expansion. Find the thermal energy  $Q$  added to the gas in terms of the initial and final volumes and the temperature. (*Hint:* Use the first law of thermodynamics.)

**46. Added as Heat** When 20.9 J of thermal energy was added to a particular ideal gas, the volume of the gas changed from  $50.0 \text{ cm}^3$  to  $100 \text{ cm}^3$  while the pressure remained constant at 1.00 atm. (a) By how much did the internal energy of the gas change? If the quantity of gas present is  $2.00 \times 10^{-3} \text{ mol}$ , find the molar specific heat of the gas at (b) constant pressure and (c) constant volume.

**47. Three Nonreacting Gases** A container holds a mixture of three nonreacting gases:  $n_1$  moles of the first gas with molar specific heat at constant volume  $C_1$ , and so on. Find the molar specific heat at constant volume of the mixture, in terms of the molar specific heats and quantities of the separate gases.

**48. Ideal Diatomic Gas** One mole of an ideal diatomic gas goes from  $a$  to  $c$  along the diagonal path in Fig. 19-19. During the transition, (a) what is the change in internal energy of the gas, and (b) how much thermal energy is added to the gas? (c) How much thermal energy is required if the gas goes from  $a$  to  $c$  along the indirect path  $abc$ ?

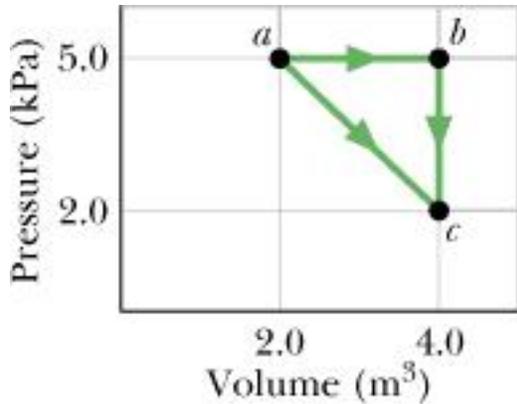


FIGURE 19-19 Problem 48.

**49. Gas Molecule** The mass of a gas molecule can be computed from its specific heat at constant volume  $C_V$ . Take  $C_V = 0.075 \text{ cal/g} \cdot \text{C}^\circ$  for argon and calculate (a) the mass of an argon atom and (b) the molar mass of argon.

#### SEC. 19-8 DEGREES OF FREEDOM AND MOLAR SPECIFIC HEATS

**50. Heating a Diatomic Gas** We give 70 J of thermal energy to a diatomic gas, which then expands at constant pressure. The gas molecules rotate but do not oscillate. By how much does the internal energy of the gas increase?

**51. One Mole of Oxygen** One mole of oxygen ( $\text{O}_2$ ) is heated at constant pressure starting at  $0^\circ\text{C}$ . How much energy  $Q$  must be added to the gas to double its volume? (The molecules rotate but do not oscillate.)

**52. Oxygen Heating** Suppose 12.0 g of oxygen ( $\text{O}_2$ ) is heated at constant atmospheric pressure from  $25.0^\circ\text{C}$  to  $125^\circ\text{C}$ . (a) How many moles of oxygen are present? (See Table 19-1 for the molar mass.) (b) How much thermal energy is transferred to the oxygen? (The molecules rotate but do not oscillate.) (c) What fraction of the thermal energy absorbed by the oxygen is used to raise the internal energy of the oxygen?

**53. Molecular Rotation** Suppose 4.00 mol of an ideal diatomic gas, with molecular rotation but not oscillation, experienced a temperature increase of 60.0 K under constant-pressure conditions. (a) How much thermal energy was transferred to the gas? (b) How much did the internal energy of the gas increase? (c) How much work was done by the gas? (d) How much did the translational kinetic energy of the gas increase?

#### SEC. 19-10 THE ADIABATIC EXPANSION OF AN IDEAL GAS

**54. Liter of Gas** (a) One liter of a gas with  $\gamma = 1.3$  is at 273 K and 1.0 atm pressure. It is suddenly compressed adiabatically to half its original volume. Find its final pressure and temperature. (b) The gas is now cooled back to 273 K at constant pressure. What is its final volume?

**55. A Certain Gas** A certain gas occupies a volume of 4.3 L at a pressure of 1.2 atm and a temperature of 310 K. It is compressed adiabatically to a volume of 0.76 L. Determine (a) the final pressure and (b) the final temperature, assuming the gas to be an ideal gas for which  $\gamma = 1.4$ .

**56. Adiabatic Process** We know that for an adiabatic process  $PV^\gamma = \text{a constant}$ . Evaluate the constant for an adiabatic process involving exactly 2.0 mol of an ideal gas passing through the state having exactly  $P = 1.0$  atm and  $T = 300$  K. Assume a diatomic gas whose molecules have rotation but not oscillation.

**57. Let  $n$  Moles** Let  $n$  moles of an ideal gas expand adiabatically from an initial temperature  $T_1$  to a final temperature  $T_2$ . Prove that the work done by the gas is  $nC_V(T_1 - T_2)$ , where  $C_V$  is the molar specific heat at constant volume. (*Hint:* Use the first law of thermodynamics.)

**58. Bulk Modulus** For adiabatic processes in an ideal gas, show that (a) the bulk modulus is given by

$$B = -V \frac{dP}{dV} = \gamma P,$$

and therefore (b) the speed of sound in the gas is

$$v_{\text{wave}} = \sqrt{\frac{\gamma P}{\rho}} = \sqrt{\frac{\gamma RT}{M}}.$$

See Eqs. 18-1 and 18-2. Here  $M$  is the molar mass and the total mass of the gas is  $m = nM$ .

**59. Molar Specific Heats** Air at 0.000°C and 1.00 atm pressure has a density of  $1.29 \times 10^{-3}$  g/cm<sup>3</sup>, and the speed of sound in air is 331 m/s at that temperature. Use those data to compute the ratio  $\gamma$  of the molar specific heats of air. (*Hint:* See Problem 58.)

**60. Free Expansion** (a) An ideal gas initially at pressure  $P_0$  undergoes a free expansion until its volume is 3.00 times its initial volume. What then is its pressure? (b) The gas is next slowly and adiabatically compressed back to its original volume. The pressure after compression is  $(3.00)^{1/3} P_0$ . Is the gas monatomic, diatomic, or polyatomic? (c) How does the average kinetic energy per molecule in this final state compare with that in the initial state?

**61. The Cycle** One mole of an ideal monatomic gas traverses the cycle of Fig. 19-20. Process 1  $\rightarrow$  2 occurs at constant volume, process 2  $\rightarrow$  3 is adiabatic, and process 3  $\rightarrow$  1 occurs at constant pressure. (a) Compute the thermal energy  $Q$  absorbed by the gas, the change in its internal energy  $\Delta E^{\text{int}}$ , and the work done by the gas  $W$ , for each of the three processes and for the cycle as a whole. (b) The initial pressure at point 1 is 1.00 atm. Find

the pressure and the volume at points 2 and 3. Use  $1.00 \text{ atm} = 1.013 \times 10^5 \text{ Pa}$  and  $R = 8.314 \text{ J/mol} \cdot \text{K}$ .

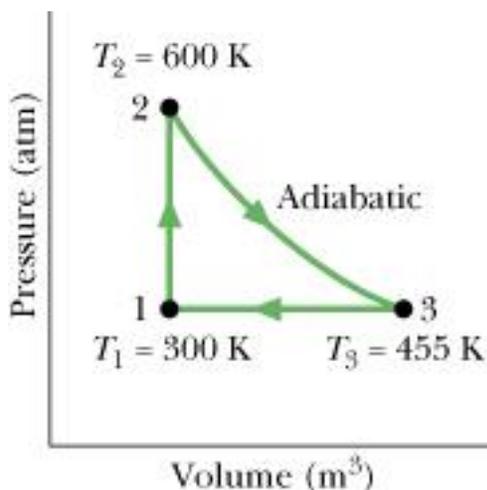


FIGURE 19-20 Problem 61.

## Additional Problems

**62. Extensive vs. Intensive** An intensive variable is one that can be defined locally within a system. Its magnitude does not depend on whether we select the whole system or a part of the system. An extensive variable is one that is defined for the system as a whole; its magnitude does depend on how much of the system we choose to select. Which of the following variables are intensive and which are extensive? Explain your reasoning in each case.

(a) density, (b) pressure, (c) volume, (d) temperature, (e) mass, (f) internal energy, (g) number of moles, and (h) molecular weight.

**63. Changes in Gas Molecules** An ideal gas is contained in an airtight box. Complete each of the following five statements below to show the quantitative change that will occur. For example, if you want to say that the volume, initially equal to  $V$ , quadruples, complete the statement with “ $4V$ ”.

(a) If the absolute temperature of the gas is halved, the average speed of a gas molecule,  $\langle v \rangle$ , becomes\_\_\_\_\_.

(b) If the average speed of a gas molecule doubles, the pressure,  $P$ , on a the wall of the box becomes\_\_\_\_\_.

(c) If the absolute temperature of the gas is halved, the pressure,  $P$ , on a wall of the box becomes\_\_\_\_\_.

(d) If the absolute temperature of the gas is increased by 25%, the total internal energy of the gas,  $E^{\text{int}}$ , becomes\_\_\_\_\_.

(e) If the number of gas molecules inside the box is doubled, but the temperature is kept the same, the pressure,  $P$ , on a wall of the box becomes\_\_\_\_\_.

**64. Scales in a Gas** The actual diameter of an atom is about 1 angstrom ( $10^{-10}$  m). In order to develop some intuition for the molecular scale of a gas, assume that you are considering a liter of air (mostly  $\text{N}_2$  and  $\text{O}_2$ ) at room temperature and a pressure of  $10^5$  Pa. (a) Calculate the number of molecules in the sample of gas. (b) Estimate the average spacing between the molecules. (c) Estimate the average speed of a molecule using the Maxwell-Boltzmann distribution, (d) Suppose that the gas were rescaled upward so that each atom was the size of a tennis ball (but we don't change the time scale). What would be the average spacing between molecules and the average speed of the molecules in miles/hour?

**65. Is the M-B Distribution Wrong?** A good student makes the following observation. "If I try to accelerate a small sphere through air, it will be resisted by air drag. If I drop an object, it will eventually reach a terminal velocity where the air is resisting as much as gravity is trying to accelerate (Eq. 6-25). The smaller the ball, the slower is the terminal velocity. But you tell me the Maxwell distribution says that the molecules of air move very rapidly. I estimate that this is much faster than the molecule's terminal velocity, so it can't move that fast. The Maxwell distribution must be wrong." (a) The Newton drag law for a sphere moving through air is calculated by a molecular model to be  $D = \rho\pi R^2 v^2$ , where  $D$  is the magnitude of the drag force,  $R$  is the radius of the sphere,  $\rho$  is the density of the air, and  $v$  is the velocity of the object through the air. Calculate the terminal velocity for a sphere the size and mass of an air molecule falling through a fluid the density of air ( $\rho = 1 \text{ kg/m}^3$ ). (b) From your estimate in part (a), is this speed greater or less than the average speed the molecule should have given the M-B distribution? What is wrong with the student's argument?

**66. Avogadro's Hypothesis** Why does Avogadro's hypothesis (that a given volume of gas at a given temperature and pressure has the same number of molecules no matter what kind of gas it is) not hold for liquids and solids?

**67. Boiling Molecules** When a molecule of a liquid approaches the surface, it experiences a force barrier that tries to keep it in the liquid. Thus it has to do work to escape and loses some of its kinetic energy when it leaves.

(a) Assume that a water molecule can evaporate from the liquid if it hits the surface from the inside with a kinetic energy greater than the thermal energy corresponding to the temperature of boiling water,  $100^\circ\text{C}$ . Use this to estimate the numerical value of the work  $W$  required to remove a water molecule from the liquid.

**(b)** Even though the average speed of a molecule in water below the boiling point corresponds to a kinetic energy less than  $W$ , some molecules leave anyway and the water evaporates. Explain why this happens.