

# THE KINETIC THEORY OF GASES

## 19-1 WHAT IS PHYSICS?

One of the main subjects in thermodynamics is the physics of gases. A gas consists of atoms (either individually or bound together as molecules) that fill their container's volume and exert pressure on the container's walls. We can usually assign a temperature to such a contained gas. These three variables associated with a gas—volume, pressure, and temperature—are all a consequence of the motion of the atoms. The volume is a result of the freedom the atoms have to spread throughout the container, the pressure is a result of the collisions of the atoms with the container's walls, and the temperature has to do with the kinetic energy of the atoms. The **kinetic theory of gases**, the focus of this chapter, relates the motion of the atoms to the volume, pressure, and temperature of the gas.

Applications of the kinetic theory of gases are countless. Automobile engineers are concerned with the combustion of vaporized fuel (a gas) in the automobile engines. Food engineers are concerned with the production rate of the fermentation gas that causes bread to rise as it bakes. Beverage engineers are concerned with how gas can produce the head in a glass of beer or shoot a cork from a champagne bottle. Medical engineers and physiologists are concerned with calculating how long a scuba diver must pause during ascent to eliminate nitrogen gas from the bloodstream (to avoid the *bends*). Environmental scientists are concerned with how heat exchanges between the oceans and the atmosphere can affect weather conditions.

The first step in our discussion of the kinetic theory of gases deals with measuring the amount of a gas present in a sample, for which we use Avogadro's number.

## 19-2 Avogadro's Number

When our thinking is slanted toward atoms and molecules, it makes sense to measure the sizes of our samples in moles. If we do so, we can be certain that we are comparing samples that contain the same number of atoms or molecules. The *mole* is one of the seven SI base units and is defined as follows:



One mole is the number of atoms in a 12 g sample of carbon-12.

The obvious question now is: “How many atoms or molecules are there in a mole?” The answer is determined experimentally and, as you saw in Chapter 18, is

$$N_A = 6.02 \times 10^{23} \text{ mol}^{-1} \quad (\text{Avogadro's number}), \quad (19-1)$$

where  $\text{mol}^{-1}$  represents the inverse mole or “per mole,” and mol is the abbreviation for mole. The number  $N_A$  is called **Avogadro's number** after Italian scientist Amedeo Avogadro (1776–1856), who suggested that all gases occupying the same volume under the same conditions of temperature and pressure contain the same number of atoms or molecules.

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

$$n = \frac{N}{N_A}. \quad (19-2)$$

(*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 find the number of moles  $n$  in a sample from the mass  $M_{\text{sam}}$  of the sample and either the *molar mass*  $M$  (the mass of 1 mol) or the *molecular mass*  $m$  (the mass of one molecule):

$$n = \frac{M_{\text{sam}}}{M} = \frac{M_{\text{sam}}}{mN_A}. \quad (19-3)$$

In Eq. 19-3, we used the fact that the mass  $M$  of 1 mol is the product of the mass  $m$  of one molecule and the number of molecules  $N_A$  in 1 mol:

$$M = mN_A. \quad (19-4)$$

### 19-3 Ideal Gases

Our goal in this chapter is to explain the macroscopic properties of a gas—such as its pressure and its temperature—in terms of the behavior of the molecules that make it up. However, there is an immediate problem: which gas? Should it be hydrogen, oxygen, or methane, or perhaps uranium hexafluoride? They are all different. Experimenters have found, though, that if we confine 1 mol samples of various gases in boxes of identical volume and hold the gases at the same temperature, then their measured pressures are almost the same, and at lower densities the differences tend to disappear. Further experiments show that, at low enough densities, all real gases tend to obey the relation

$$pV = nRT \quad (\text{ideal gas law}), \quad (19-5)$$

in which  $p$  is the absolute (not gauge) pressure,  $n$  is the number of moles of gas present, and  $T$  is the temperature in kelvins. The symbol  $R$  is a constant called the **gas constant** that has the same value for all gases—namely,

$$R = 8.31 \text{ J/mol} \cdot \text{K}. \quad (19-6)$$

Equation 19-5 is called the **ideal gas law**. Provided the gas density is low, this law 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.)

We can rewrite Eq. 19-5 in an alternative form, in terms of a constant called the **Boltzmann constant**  $k$ , which is defined as

$$k = \frac{R}{N_A} = \frac{8.31 \text{ J/mol} \cdot \text{K}}{6.02 \times 10^{23} \text{ mol}^{-1}} = 1.38 \times 10^{-23} \text{ J/K}. \quad (19-7)$$

This allows us to write  $R = kN_A$ . Then, with Eq. 19-2 ( $n = N/N_A$ ), we see that

$$nR = Nk. \quad (19-8)$$

Substituting this into Eq. 19-5 gives a second expression for the ideal gas law:

$$pV = NkT \quad (\text{ideal gas law}). \quad (19-9)$$

(*Caution:* Note the difference between the two expressions for the ideal gas law—Eq. 19-5 involves the number of moles  $n$ , and Eq. 19-9 involves the number of molecules  $N$ .)

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. 19-5 and 19-9) that governs its macroscopic properties. Using this law—as you will see—we can deduce many properties of the ideal gas in a simple way. Although there is no such thing in nature as a truly ideal gas, *all real* 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. Thus, the ideal gas concept allows us to gain useful insights into the limiting behavior of real gases.

The interior of the railroad tank car in Fig. 19-1 was being cleaned with steam by a crew late one afternoon. When they left for the night, they sealed the car. When they returned the next morning, they discovered that something had crushed the car in spite of its extremely strong steel walls, as if some giant creature from a grade B science fiction movie had stepped on it during a rampage that night.

With Eq. 19-9, we can explain what actually crushed the railroad tank car. When the car was being cleaned, its interior was filled with very hot steam, which is a gas of water molecules. The cleaning crew left the steam inside the car when they closed all the valves on the car at the end of their work shift. At that point the pressure of the gas in the car was equal to atmospheric pressure because the valves had been opened to the atmosphere during the cleaning. As the car cooled during the night, the steam cooled and much of it condensed, which means that the number  $N$  of gas molecules and the temperature  $T$  of the gas both decreased. Thus, the right side of Eq. 19-9 decreased, and because volume  $V$  was constant, the gas pressure  $p$  on the left side also decreased. At some point during the night, the gas pressure inside the car reached such a low value that the external atmospheric pressure was able to crush the car’s steel walls. The cleaning crew could have prevented this accident by leaving the valves open, so that air could enter the car to keep the internal pressure equal to the external atmospheric pressure.



**Fig. 19-1** A railroad tank car crushed overnight. (Photo courtesy [www.Houston.RailFan.net](http://www.Houston.RailFan.net))

## Work Done by an Ideal Gas at Constant Temperature

Suppose we put an ideal gas in a piston–cylinder arrangement like those in Chapter 18. 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

$$p = nRT \frac{1}{V} = (\text{a constant}) \frac{1}{V}. \quad (19-10)$$

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.

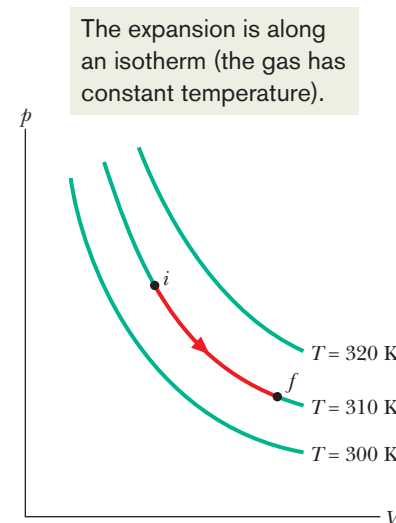
To find the work done by an ideal gas during an isothermal expansion, we start with Eq. 18-25,

$$W = \int_{V_i}^{V_f} p \, dV. \quad (19-11)$$

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. 19-5 ( $pV = nRT$ ) to substitute for  $p$ , obtaining

$$W = \int_{V_i}^{V_f} \frac{nRT}{V} \, dV. \quad (19-12)$$

Because we are considering an isothermal expansion,  $T$  is constant, so we can



**Fig. 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—that is, an isothermal compression.

move it in front of the integral sign to write

$$W = nRT \int_{V_i}^{V_f} \frac{dV}{V} = nRT \left[ \ln V \right]_{V_i}^{V_f}. \quad (19-13)$$

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

$$W = nRT \ln \frac{V_f}{V_i} \quad (\text{ideal gas, isothermal process}). \quad (19-14)$$

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

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 always go back to Eq. 19-11 to find the work  $W$  done by an ideal gas (or any other gas) during any process, such as a constant-volume process and a constant-pressure process. If the volume of the gas is constant, then Eq. 19-11 yields

$$W = 0 \quad (\text{constant-volume process}). \quad (19-15)$$

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

$$W = p(V_f - V_i) = p \Delta V \quad (\text{constant-pressure process}). \quad (19-16)$$



#### CHECKPOINT 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

### Sample Problem

#### Ideal gas and changes of temperature, volume, and 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.

#### KEY IDEA

Because the gas is ideal, we can use the ideal gas law to relate its parameters, both in the initial state  $i$  and in the final state  $f$ .

**Calculations:** From Eq. 19-5 we can write

$$p_i V_i = nRT_i \quad \text{and} \quad p_f V_f = nRT_f.$$

Dividing the second equation by the first equation and solving for  $p_f$  yields

$$p_f = \frac{p_i T_f V_i}{T_i V_f}. \quad (19-17)$$

Note here that if we converted the given initial and final volumes from liters to the proper units of cubic meters, the multiplying conversion factors would cancel out of Eq. 19-17. The same would be true for conversion factors that convert the pressures from atmospheres to the proper 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

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

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

Inserting the given data into Eq. 19-17 then yields

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

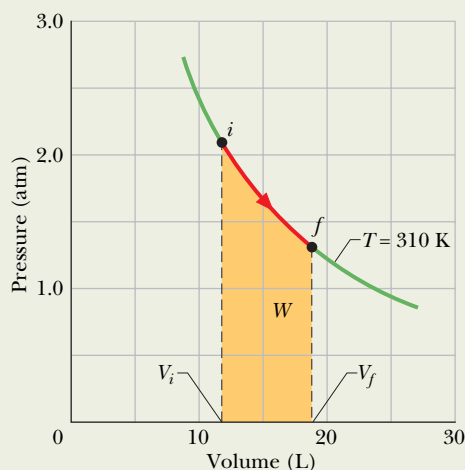


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## Sample Problem

## Work by an ideal gas

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?



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

## KEY IDEA

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.

**Calculation:** Therefore, we can write

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

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  $if$ .

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.



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## 19-4 Pressure, Temperature, and RMS Speed

Here is our first kinetic theory problem. Let  $n$  moles of an ideal gas be confined in a cubical box of volume  $V$ , as in Fig. 19-4. The walls of the box are held at temperature  $T$ . What is the connection between the pressure  $p$  exerted by the gas on the walls and the speeds of the molecules?

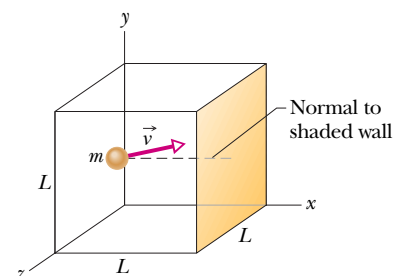
The molecules of gas in the box are moving in all directions and with various speeds, bumping into one another and bouncing from the walls of the box like balls in a racquetball court. We ignore (for the time being) collisions of the molecules with one another and consider only elastic collisions with the walls.

Figure 19-4 shows a typical gas molecule, of mass  $m$  and velocity  $\vec{v}$ , that 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 is the  $x$  component, and that component is reversed. This means that the only change in the particle's momentum is along the  $x$  axis, and that change is

$$\Delta p_x = (-mv_x) - (mv_x) = -2mv_x.$$

Hence, the momentum  $\Delta p_x$  delivered to the wall by the molecule during the collision is  $+2mv_x$ . (Because in this book the symbol  $p$  represents both momentum and pressure, we must be careful to note that here  $p$  represents momentum and is a vector quantity.)

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  $2L$ ) 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



**Fig. 19-4** A cubical box of edge length  $L$ , containing  $n$  moles of an ideal gas. A molecule of mass  $m$  and velocity  $\vec{v}$  is about to collide with the shaded wall of area  $L^2$ . A normal to that wall is shown.



rate at which momentum is delivered to the shaded wall by this single molecule is

$$\frac{\Delta p_x}{\Delta t} = \frac{2mv_x}{2L/v_x} = \frac{mv_x^2}{L}.$$

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 the molecules that strike the wall, allowing for the possibility that they all have different speeds. Dividing the magnitude of the total force  $F_x$  by the area of the wall ( $= L^2$ ) then gives the pressure  $p$  on that wall, where now and in the rest of this discussion,  $p$  represents pressure. Thus, using the expression for  $\Delta p_x/\Delta t$ , we can write this pressure as

$$p = \frac{F_x}{L^2} = \frac{mv_{x1}^2/L + mv_{x2}^2/L + \cdots + mv_{xN}^2/L}{L^2} \\ = \left(\frac{m}{L^3}\right)(v_{x1}^2 + v_{x2}^2 + \cdots + v_{xN}^2), \quad (19-18)$$

where  $N$  is the number of molecules in the box.

Since  $N = nN_A$ , there are  $nN_A$  terms in the second set of parentheses of Eq. 19-18. We can replace that quantity by  $nN_A(v_x^2)_{\text{avg}}$ , where  $(v_x^2)_{\text{avg}}$  is the average value of the square of the  $x$  components of all the molecular speeds. Equation 19-18 then becomes

$$p = \frac{nmN_A}{L^3}(v_x^2)_{\text{avg}}.$$

However,  $mN_A$  is the molar mass  $M$  of the gas (that is, the mass of 1 mol of the gas). Also,  $L^3$  is the volume of the box, so

$$p = \frac{nM(v_x^2)_{\text{avg}}}{V}. \quad (19-19)$$

For any molecule,  $v^2 = v_x^2 + v_y^2 + v_z^2$ . Because there are many molecules and because they are all moving in random directions, the average values of the squares of their velocity components are equal, so that  $v_x^2 = \frac{1}{3}v^2$ . Thus, Eq. 19-19 becomes

$$p = \frac{nM(v^2)_{\text{avg}}}{3V}. \quad (19-20)$$

The square root of  $(v^2)_{\text{avg}}$  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  $\sqrt{(v^2)_{\text{avg}}} = v_{\text{rms}}$ , we can then write Eq. 19-20 as

$$p = \frac{nMv_{\text{rms}}^2}{3V}. \quad (19-21)$$

This 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. 19-21 around and use it to calculate  $v_{\text{rms}}$ . Combining Eq. 19-21 with the ideal gas law ( $pV = nRT$ ) leads to

$$v_{\text{rms}} = \sqrt{\frac{3RT}{M}}. \quad (19-22)$$

Table 19-1 shows some rms speeds calculated from Eq. 19-22. 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! On the surface of the Sun, where the temperature is  $2 \times 10^6$  K, the rms speed of hydrogen

Table 19-1

Some RMS Speeds at Room Temperature ( $T = 300$  K)<sup>a</sup>

Gas	Molar Mass ( $10^{-3}$ kg/mol)	$v_{\text{rms}}$ (m/s)
Hydrogen (H <sub>2</sub> )	2.02	1920
Helium (He)	4.0	1370
Water vapor (H <sub>2</sub> O)	18.0	645
Nitrogen (N <sub>2</sub> )	28.0	517
Oxygen (O <sub>2</sub> )	32.0	483
Carbon dioxide (CO <sub>2</sub> )	44.0	412
Sulfur dioxide (SO <sub>2</sub> )	64.1	342

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

molecules would be 82 times greater than at room temperature were it not for the fact that at such high speeds, the molecules cannot survive collisions among themselves. Remember too that the rms speed is only a kind of average speed; many molecules move much faster than this, and some much slower.

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.

A question often arises: 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? The answer is that, as we shall discuss in Section 19-6, each perfume molecule may have a high speed but it 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.

### Sample Problem

#### Average and rms values

Here are five numbers: 5, 11, 32, 67, and 89.

(a) What is the average value  $n_{\text{avg}}$  of these numbers?

**Calculation:** We find this from

$$n_{\text{avg}} = \frac{5 + 11 + 32 + 67 + 89}{5} = 40.8. \quad (\text{Answer})$$

(b) What is the rms value  $n_{\text{rms}}$  of these numbers?

**Calculation:** We find this from

$$n_{\text{rms}} = \sqrt{\frac{5^2 + 11^2 + 32^2 + 67^2 + 89^2}{5}} = 52.1. \quad (\text{Answer})$$

The rms value is greater than the average value because the larger numbers—being squared—are relatively more important in forming the rms value.



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## 19-5 Translational Kinetic Energy

We 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

$$K_{\text{avg}} = (\tfrac{1}{2}mv^2)_{\text{avg}} = \tfrac{1}{2}m(v^2)_{\text{avg}} = \tfrac{1}{2}mv_{\text{rms}}^2, \quad (19-23)$$

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 time. (Provided the total energy of the gas is not changing and provided we observe our molecule for long enough, this assumption is appropriate.) Substituting for  $v_{\text{rms}}$  from Eq. 19-22 leads to

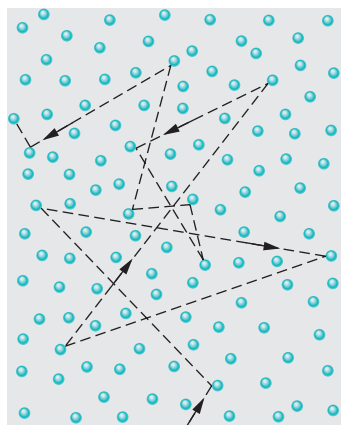
$$K_{\text{avg}} = (\tfrac{1}{2}m) \frac{3RT}{M}.$$

However,  $M/m$ , the molar mass divided by the mass of a molecule, is simply Avogadro's number. Thus,

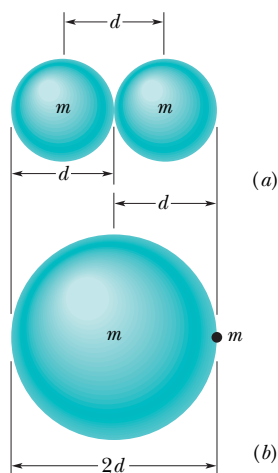
$$K_{\text{avg}} = \frac{3RT}{2N_A}.$$

### CHECKPOINT 2

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.



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



**Fig. 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 as having a radius  $d$  and all other molecules as being points. The condition for a collision is unchanged.

Using Eq. 19-7 ( $k = R/N_A$ ), we can then write

$$K_{\text{avg}} = \frac{3}{2}kT. \quad (19-24)$$

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,  $\frac{3}{2}kT$ . When we measure the temperature of a gas, we are also measuring the average translational kinetic energy of its molecules.

## 19-6 Mean Free Path

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, the molecule moves in a straight line at constant speed. Although the figure shows the other molecules as stationary, they are (of course) also moving.

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 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—with their diameter  $d$ , say. (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.

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

$$\lambda = \frac{1}{\sqrt{2}\pi d^2 N/V} \quad (\text{mean free path}). \quad (19-25)$$

To justify Eq. 19-25, 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 two molecules come within a distance  $d$  of each other, as in Fig. 19-6a. 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. 19-6b. 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 interval  $\Delta t$ , 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.

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



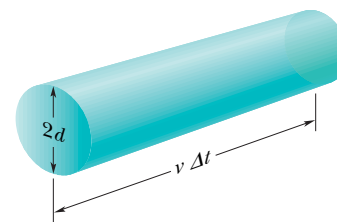
of the cylinder) divided by this number:

$$\begin{aligned}\lambda &= \frac{\text{length of path during } \Delta t}{\text{number of collisions in } \Delta t} \approx \frac{v \Delta t}{\pi d^2 v \Delta t N/V} \\ &= \frac{1}{\pi d^2 N/V}.\end{aligned}\quad (19-26)$$

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. 19-25 results. Note that it differs from the (approximate) Eq. 19-26 only by a factor of  $1/\sqrt{2}$ .

The approximation in Eq. 19-26 involves the two  $v$  symbols we canceled. The  $v$  in the numerator is  $v_{\text{avg}}$ , the mean speed of the molecules *relative to the container*. The  $v$  in the denominator is  $v_{\text{rel}}$ , 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  $v_{\text{rel}} = \sqrt{2}v_{\text{avg}}$  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 (of Freon, carbon dioxide, and ozone) that simulate upper atmospheric conditions.



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



### CHECKPOINT 3

One mole of gas *A*, with molecular diameter  $2d_0$  and average molecular speed  $v_0$ , is placed inside a certain container. One mole of gas *B*, with molecular diameter  $d_0$  and average molecular speed  $2v_0$  (the molecules of *B* are smaller but faster), is placed in an identical container. Which gas has the greater average collision rate within its container?

## Sample Problem

### Mean free path, average speed, collision frequency

(a) What is the mean free path  $\lambda$  for oxygen molecules at temperature  $T = 300 \text{ K}$  and pressure  $p = 1.0 \text{ atm}$ ? Assume that the molecular diameter is  $d = 290 \text{ pm}$  and the gas is ideal.

#### KEY IDEA

Each oxygen molecule moves among other *moving* oxygen molecules in a zigzag path due to the resulting collisions. Thus, we use Eq. 19-25 for the mean free path.

**Calculation:** We first 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. 19-9 ( $pV = NkT$ ) to write  $N/V = p/kT$ . Substituting this into Eq. 19-25, we find

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

This is about 380 molecular diameters.

(b) Assume the average speed of the oxygen molecules is  $v = 450 \text{ m/s}$ . What is the average time  $t$  between successive

collisions for any given molecule? At what rate does the molecule collide; that is, what is the frequency  $f$  of its collisions?

#### KEY IDEAS

(1) Between collisions, the molecule travels, on average, the mean free path  $\lambda$  at speed  $v$ . (2) The average rate or frequency at which the collisions occur is the inverse of the time  $t$  between collisions.

**Calculations:** From the first key idea, the average time between collisions is

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

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

From the second key idea, the collision frequency is

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

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



Additional examples, video, and practice available at WileyPLUS

## 19-7 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? What fraction have speeds 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  $T = 80 \text{ K}$ .

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

$$P(v) = 4\pi \left( \frac{M}{2\pi RT} \right)^{3/2} v^2 e^{-Mv^2/2RT}. \quad (19-27)$$

Here  $M$  is the molar mass of the gas,  $R$  is the gas constant,  $T$  is the gas temperature, and  $v$  is the molecular speed. It is this equation that is plotted in Fig. 19-8a, b. The quantity  $P(v)$  in Eq. 19-27 and Fig. 19-8 is a *probability distribution function*: For any speed  $v$ , the product  $P(v) dv$  (a dimensionless quantity) is the fraction of molecules with speeds in the interval  $dv$  centered on speed  $v$ .

As Fig. 19-8a shows, this fraction is equal to the area of a strip with height  $P(v)$  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,

$$\int_0^\infty P(v) dv = 1. \quad (19-28)$$

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

$$\text{frac} = \int_{v_1}^{v_2} P(v) dv. \quad (19-29)$$

### Average, RMS, and Most Probable Speeds

In principle, we can find the **average speed**  $v_{\text{avg}}$  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  $P(v) dv$  of molecules with speeds in a differential interval  $dv$  centered on  $v$ . Then we add up all these values of  $v P(v) dv$ . The result is  $v_{\text{avg}}$ . In practice, we do all this by evaluating

$$v_{\text{avg}} = \int_0^\infty v P(v) dv. \quad (19-30)$$

Substituting for  $P(v)$  from Eq. 19-27 and using generic integral 20 from the list of integrals in Appendix E, we find

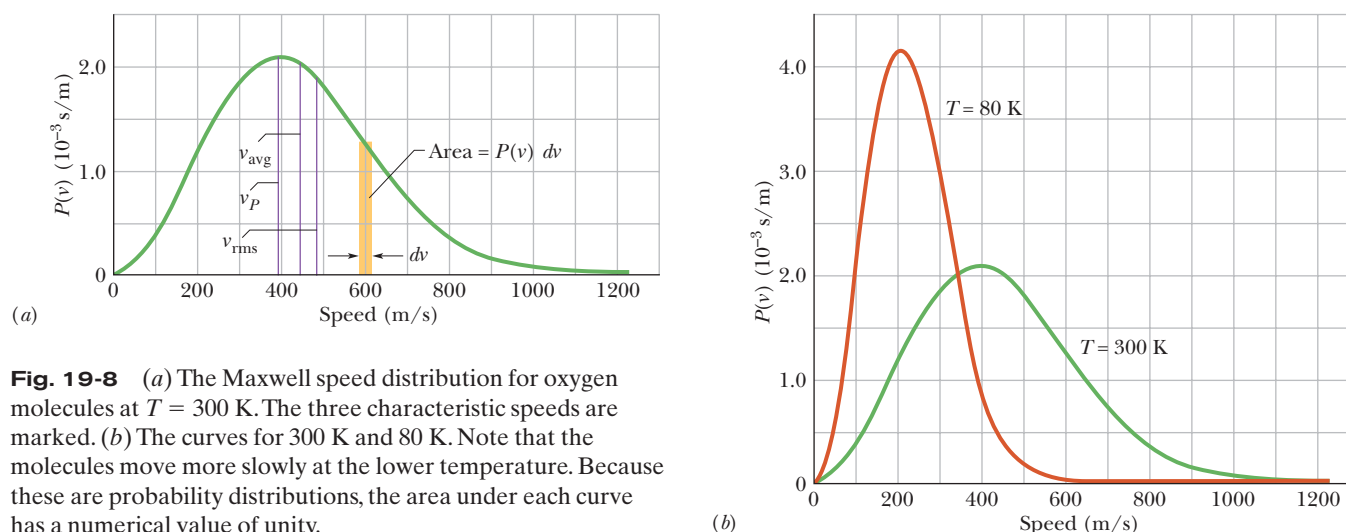
$$v_{\text{avg}} = \sqrt{\frac{8RT}{\pi M}} \quad (\text{average speed}). \quad (19-31)$$

Similarly, we can find the average of the square of the speeds  $(v^2)_{\text{avg}}$  with

$$(v^2)_{\text{avg}} = \int_0^\infty v^2 P(v) dv. \quad (19-32)$$

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

$$(v^2)_{\text{avg}} = \frac{3RT}{M}. \quad (19-33)$$



**Fig. 19-8** (a) The Maxwell speed distribution for oxygen molecules at  $T = 300$  K. The three characteristic speeds are marked. (b) The curves for 300 K and 80 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.

The square root of  $(v^2)_{\text{avg}}$  is the root-mean-square speed  $v_{\text{rms}}$ . Thus,

$$v_{\text{rms}} = \sqrt{\frac{3RT}{M}} \quad (\text{rms speed}), \quad (19-34)$$

which agrees with Eq. 19-22.

The **most probable speed**  $v_P$  is the speed at which  $P(v)$  is maximum (see Fig. 19-8a). To calculate  $v_P$ , we set  $dP/dv = 0$  (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

$$v_P = \sqrt{\frac{2RT}{M}} \quad (\text{most probable speed}). \quad (19-35)$$

A molecule is more likely to have speed  $v_P$  than any other speed, but some molecules will have speeds that are many times  $v_P$ . These molecules lie in the *high-speed tail* of a distribution curve like that in Fig. 19-8a. Such higher speed molecules make possible both rain and sunshine (without which we could not exist):

**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 high-speed 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 heat 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 high-speed tail of the distribution curve can do so, however, and for that reason the Sun can shine.

## Sample Problem

## Speed distribution in a gas

A container is filled with oxygen gas maintained at room temperature (300 K). What fraction of the molecules have speeds in the interval 599 to 601 m/s? The molar mass  $M$  of oxygen is 0.0320 kg/mol.

## KEY IDEAS

1. The speeds of the molecules are distributed over a wide range of values, with the distribution  $P(v)$  of Eq. 19-27.
2. The fraction of molecules with speeds in a differential interval  $dv$  is  $P(v) dv$ .
3. For a larger interval, the fraction is found by integrating  $P(v)$  over the interval.
4. However, the interval  $\Delta v = 2$  m/s here is small compared to the speed  $v = 600$  m/s on which it is centered.

**Calculations:** Because  $\Delta v$  is small, we can avoid the integration by approximating the fraction as

$$\text{frac} = P(v) \Delta v = 4\pi \left( \frac{M}{2\pi RT} \right)^{3/2} v^2 e^{-Mv^2/2RT} \Delta v.$$

The function  $P(v)$  is plotted in Fig. 19-8a. The total area between the curve and the horizontal axis represents the to-

tal fraction of molecules (unity). The area of the thin gold strip represents the fraction we seek.

To evaluate  $\text{frac}$  in parts, we can write

$$\text{frac} = (4\pi)(A)(v^2)(e^B)(\Delta v), \quad (19-36)$$

where

$$\begin{aligned} A &= \left( \frac{M}{2\pi RT} \right)^{3/2} = \left( \frac{0.0320 \text{ kg/mol}}{(2\pi)(8.31 \text{ J/mol} \cdot \text{K})(300 \text{ K})} \right)^{3/2} \\ &= 2.92 \times 10^{-9} \text{ s}^3/\text{m}^3 \\ \text{and } B &= -\frac{Mv^2}{2RT} = -\frac{(0.0320 \text{ kg/mol})(600 \text{ m/s})^2}{(2)(8.31 \text{ J/mol} \cdot \text{K})(300 \text{ K})} \\ &= -2.31. \end{aligned}$$

Substituting  $A$  and  $B$  into Eq. 19-36 yields

$$\begin{aligned} \text{frac} &= (4\pi)(A)(v^2)(e^B)(\Delta v) \\ &= (4\pi)(2.92 \times 10^{-9} \text{ s}^3/\text{m}^3)(600 \text{ m/s})^2(e^{-2.31})(2 \text{ m/s}) \\ &= 2.62 \times 10^{-3}. \end{aligned} \quad (\text{Answer})$$

Thus, at room temperature, 0.262% of the oxygen molecules will have speeds that lie in the narrow range between 599 and 601 m/s. If the gold strip of Fig. 19-8a were drawn to the scale of this problem, it would be a very thin strip indeed.

## Sample Problem

## Average speed, rms speed, most probable speed

The molar mass  $M$  of oxygen is 0.0320 kg/mol.

- (a) What is the average speed  $v_{\text{avg}}$  of oxygen gas molecules at  $T = 300$  K?

## KEY IDEA

To find the average speed, we must weight speed  $v$  with the distribution function  $P(v)$  of Eq. 19-27 and then integrate the resulting expression over the range of possible speeds (from zero to the limit of an infinite speed).

**Calculation:** We end up with Eq. 19-31, which gives us

$$\begin{aligned} v_{\text{avg}} &= \sqrt{\frac{8RT}{\pi M}} \\ &= \sqrt{\frac{8(8.31 \text{ J/mol} \cdot \text{K})(300 \text{ K})}{\pi(0.0320 \text{ kg/mol})}} \\ &= 445 \text{ m/s}. \end{aligned} \quad (\text{Answer})$$

This result is plotted in Fig. 19-8a.

- (b) What is the root-mean-square speed  $v_{\text{rms}}$  at 300 K?

## KEY IDEA

To find  $v_{\text{rms}}$ , we must first find  $(v^2)_{\text{avg}}$  by weighting  $v^2$  with the distribution function  $P(v)$  of Eq. 19-27 and then integrating the expression over the range of possible speeds. Then we must take the square root of the result.

**Calculation:** We end up with Eq. 19-34, which gives us

$$\begin{aligned} v_{\text{rms}} &= \sqrt{\frac{3RT}{M}} \\ &= \sqrt{\frac{3(8.31 \text{ J/mol} \cdot \text{K})(300 \text{ K})}{0.0320 \text{ kg/mol}}} \\ &= 483 \text{ m/s}. \end{aligned} \quad (\text{Answer})$$

This result, plotted in Fig. 19-8a, is greater than  $v_{\text{avg}}$  because the greater speed values influence the calculation more when we integrate the  $v^2$  values than when we integrate the  $v$  values.

(c) What is the most probable speed  $v_P$  at 300 K?

### KEY IDEA

Speed  $v_P$  corresponds to the maximum of the distribution function  $P(v)$ , which we obtain by setting the derivative  $dP/dv = 0$  and solving the result for  $v$ .

**Calculation:** We end up with Eq. 19-35, which gives us

$$\begin{aligned} v_P &= \sqrt{\frac{2RT}{M}} \\ &= \sqrt{\frac{2(8.31 \text{ J/mol} \cdot \text{K})(300 \text{ K})}{0.0320 \text{ kg/mol}}} \\ &= 395 \text{ m/s.} \end{aligned}$$

(Answer)

This result is also plotted in Fig. 19-8a.



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## 19-8 The Molar Specific Heats of an Ideal Gas

In this section, we want to derive from molecular considerations an expression for the internal energy  $E_{\text{int}}$  of an ideal gas. In other words, we want 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. (As explained by quantum theory, individual atoms do not have rotational kinetic energy.)

The average translational kinetic energy of a single atom depends only on the gas temperature and is given by Eq. 19-24 as  $K_{\text{avg}} = \frac{3}{2}kT$ . A sample of  $n$  moles of such a gas contains  $nN_A$  atoms. The internal energy  $E_{\text{int}}$  of the sample is then

$$E_{\text{int}} = (nN_A)K_{\text{avg}} = (nN_A)\left(\frac{3}{2}kT\right). \quad (19-37)$$

Using Eq. 19-7 ( $k = R/N_A$ ), we can rewrite this as

$$E_{\text{int}} = \frac{3}{2}nRT \quad (\text{monatomic ideal gas}). \quad (19-38)$$

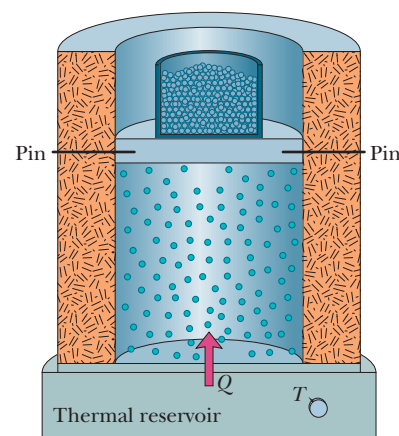


The internal energy  $E_{\text{int}}$  of an ideal gas is a function of the gas temperature *only*; it does not depend on any other variable.

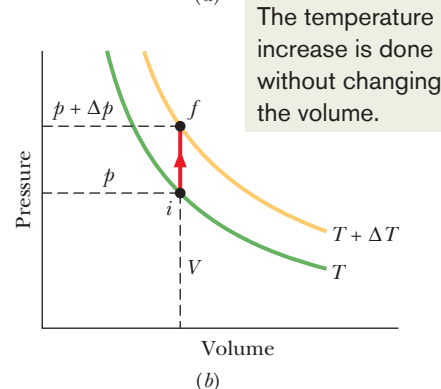
With Eq. 19-38 in hand, we are now able to derive an expression for the molar specific heat of an ideal gas. Actually, we shall derive two expressions. One is for the case in which the volume of the gas remains constant as energy is transferred to or from it as heat. The other is for the case in which the pressure of the gas remains constant as energy is transferred to or from it as heat. 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 now that you add a small amount of



(a)



(b)

**Fig. 19-9** (a) The temperature of an ideal gas is raised from  $T$  to  $T + \Delta T$  in a constant-volume process. Heat is added, but no work is done. (b) The process on a  $p$ - $V$  diagram.



**Table 19-2**  
Molar Specific Heats at  
Constant Volume

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

energy to the gas as heat  $Q$  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*  $f$ . In such experiments, we would find that the heat  $Q$  is related to the temperature change  $\Delta T$  by

$$Q = nC_V \Delta T \quad (\text{constant volume}), \quad (19-39)$$

where  $C_V$  is a constant called the **molar specific heat at constant volume**. Substituting this expression for  $Q$  into the first law of thermodynamics as given by Eq. 18-26 ( $\Delta E_{\text{int}} = Q - W$ ) yields

$$\Delta E_{\text{int}} = nC_V \Delta T - W. \quad (19-40)$$

With the volume held constant, the gas cannot expand and thus cannot do any work. Therefore,  $W = 0$ , and Eq. 19-40 gives us

$$C_V = \frac{\Delta E_{\text{int}}}{n \Delta T}. \quad (19-41)$$

From Eq. 19-38, the change in internal energy must be

$$\Delta E_{\text{int}} = \frac{3}{2}nR \Delta T. \quad (19-42)$$

Substituting this result into Eq. 19-41 yields

$$C_V = \frac{3}{2}R = 12.5 \text{ J/mol} \cdot \text{K} \quad (\text{monatomic gas}). \quad (19-43)$$

As Table 19-2 shows, this prediction of the kinetic theory (for ideal gases) agrees very well with experiment for real monatomic gases, the case that we have assumed. The (predicted and) experimental values of  $C_V$  for *diatomic gases* (which have molecules with two atoms) and *polyatomic gases* (which have molecules with more than two atoms) are greater than those for monatomic gases for reasons that will be suggested in Section 19-9.

We can now generalize Eq. 19-38 for the internal energy of any ideal gas by substituting  $C_V$  for  $\frac{3}{2}R$ ; we get


$$E_{\text{int}} = nC_V T \quad (\text{any ideal gas}). \quad (19-44)$$

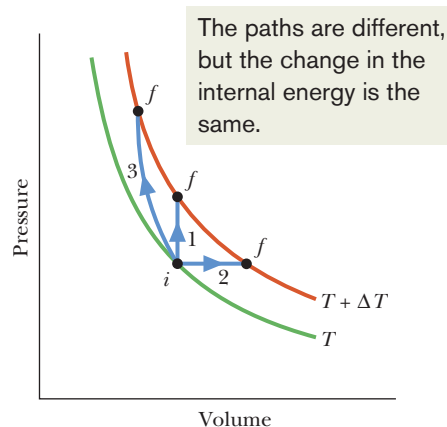
This equation applies not only to an ideal monatomic gas but also to diatomic and polyatomic ideal gases, provided the appropriate value of  $C_V$  is used. Just as with Eq. 19-38, we see that the internal energy of a gas depends on the temperature of the gas but not on its pressure or density.

When a confined ideal gas undergoes temperature change  $\Delta T$ , then from either Eq. 19-41 or Eq. 19-44 the resulting change in its internal energy is

$$\Delta E_{\text{int}} = nC_V \Delta T \quad (\text{ideal gas, any process}). \quad (19-45)$$

This equation tells us:

 A change in the internal energy  $E_{\text{int}}$  of a confined ideal gas depends on only the change in the temperature, *not* on what type of process produces the change.



**Fig. 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.

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 heat is exchanged with the system's environment (we discuss this in Section 19-11). Although the values of heat  $Q$  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. 19-45, 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. 19-45 to compute  $\Delta E_{\text{int}}$  easily.

## Molar Specific Heat at Constant Pressure

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

$$Q = nC_p \Delta T \quad (\text{constant pressure}), \quad (19-46)$$

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. 19-11a.

To relate molar specific heats  $C_p$  and  $C_v$ , we start with the first law of thermodynamics (Eq. 18-26):

$$\Delta E_{\text{int}} = Q - W. \quad (19-47)$$

We next replace each term in Eq. 19-47. For  $\Delta E_{\text{int}}$ , we substitute from Eq. 19-45. For  $Q$ , we substitute from Eq. 19-46. 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

$$W = p \Delta V = nR \Delta T. \quad (19-48)$$

Making these substitutions in Eq. 19-47 and then dividing through by  $n \Delta T$ , we find

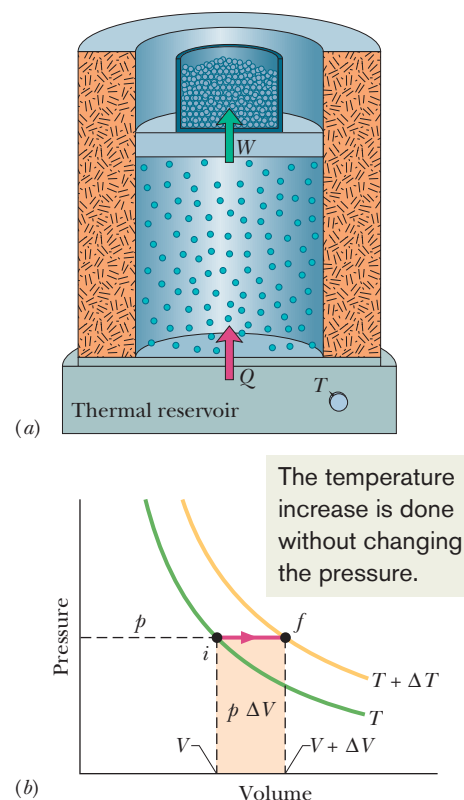
$$C_v = C_p - R$$

and then

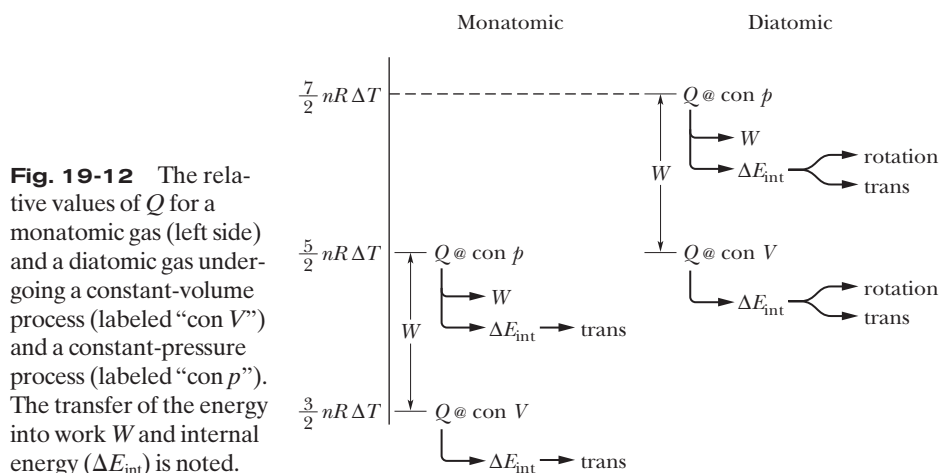
$$C_p = C_v + R. \quad (19-49)$$

This prediction of kinetic theory agrees well with experiment, not only for monatomic gases but also for gases in general, as long as their density is low enough so that we may treat them as ideal.

The left side of Fig. 19-12 shows the relative values of  $Q$  for a monatomic gas undergoing either a constant-volume process ( $Q = \frac{3}{2}nR \Delta T$ ) or a constant-pressure process ( $Q = \frac{5}{2}nR \Delta T$ ). Note that for the latter, the value of  $Q$  is higher by the amount  $W$ , the work done by the gas in the expansion. Note also that for the constant-volume process, the energy added as  $Q$  goes entirely into the change in internal energy  $\Delta E_{\text{int}}$  and for the constant-pressure process, the energy added as  $Q$  goes into both  $\Delta E_{\text{int}}$  and the work  $W$ .



**Fig. 19-11** (a) The temperature of an ideal gas is raised from  $T$  to  $T + \Delta T$  in a constant-pressure process. Heat 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.

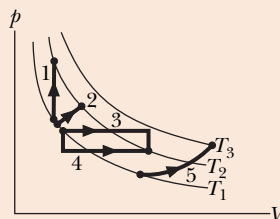


**Fig. 19-12** The relative values of  $Q$  for a monatomic gas (left side) and a diatomic gas undergoing a constant-volume process (labeled “con  $V$ ”) and a constant-pressure process (labeled “con  $p$ ”). The transfer of the energy into work  $W$  and internal energy ( $\Delta E_{\text{int}}$ ) is noted.



## CHECKPOINT 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.



## Sample Problem

## Monatomic gas, heat, internal energy, and work

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 energy is added to the helium as heat during the increase and expansion?

## KEY IDEA

Heat  $Q$  is related to the temperature change  $\Delta T$  by a molar specific heat of the gas.

**Calculations:** 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. 19-46,

$$Q = nC_p \Delta T, \quad (19-50)$$

to find  $Q$ . To evaluate  $C_p$  we go to Eq. 19-49, which tells us that for any ideal gas,  $C_p = C_v + R$ . Then from Eq. 19-43, we know that for any *monatomic* gas (like the helium here),  $C_v = \frac{3}{2}R$ . Thus, Eq. 19-50 gives us

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

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

## KEY IDEA

Because the bubble expands, this is not a constant-volume process. However, the helium is nonetheless confined (to the bubble). Thus, the change  $\Delta E_{\text{int}}$  is the same as *would occur* in a constant-volume process with the same temperature change  $\Delta T$ .

**Calculation:** We can now easily find the constant-volume change  $\Delta E_{\text{int}}$  with Eq. 19-45:

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

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

## KEY IDEAS

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. 19-5) to write  $p \Delta V = nR \Delta T$ .

**Calculation:** We end up with

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

**Another way:** Because we happen to know  $Q$  and  $\Delta E_{\text{int}}$ , we can work this problem another way: We can account for the energy changes of the gas with the first law of thermodynamics, writing

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

**The transfers:** Let's follow the energy. Of the 2077.5 J transferred to the helium as heat  $Q$ , 831 J goes into the work  $W$  required for the expansion and 1246.5 J goes into the internal energy  $E_{\text{int}}$ , which, for a monatomic gas, is entirely the kinetic energy of the atoms in their translational motion. These several results are suggested on the left side of Fig. 19-12.



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## 19-9 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 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 19-13 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). 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.

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  $\frac{1}{2}kT$  per molecule (or  $\frac{1}{2}RT$  per mole).

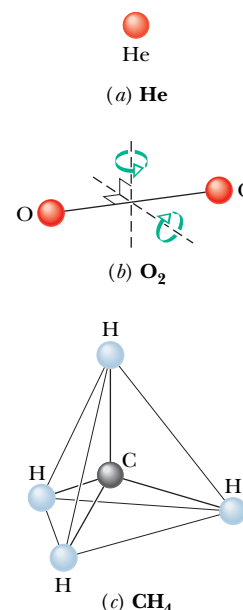
Let us apply the theorem to the translational and rotational motions of the molecules in Fig. 19-13. (We discuss oscillatory motion in the next section.) For the translational motion, superimpose an  $xyz$  coordinate system on any gas. The molecules will, in general, have velocity components along all 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  $3(\frac{1}{2}kT)$  per molecule.

For the rotational motion, imagine the origin of our  $xyz$  coordinate system at the center of each molecule in Fig. 19-13. 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  $3(\frac{1}{2}kT)$  per molecule. *However*, experiment shows this is true only for the polyatomic molecules. According to *quantum theory*, the physics dealing with the allowed motions and energies of molecules and atoms, a monatomic gas molecule does not rotate and so has no rotational energy (a single atom cannot rotate like a top). A diatomic molecule can rotate like a top only about axes perpendicular to the line connecting the atoms (the axes are shown in Fig. 19-13*b*) and not about that line itself. Therefore, a diatomic molecule can have only two degrees of rotational freedom and a rotational energy of only  $2(\frac{1}{2}kT)$  per molecule.

To extend our analysis of molar specific heats ( $C_p$  and  $C_V$ , in Section 19-8) to ideal diatomic and polyatomic gases, it is necessary to retrace the derivations of that analysis in detail. First, we replace Eq. 19-38 ( $E_{\text{int}} = \frac{3}{2}nRT$ ) 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

$$C_V = \left(\frac{f}{2}\right)R = 4.16f \text{ J/mol} \cdot \text{K}, \quad (19-51)$$

which agrees—as it must—with Eq. 19-43 for monatomic gases ( $f = 3$ ). As Table 19-2 shows, this prediction also agrees with experiment for diatomic gases ( $f = 5$ ), but it is too low for polyatomic gases ( $f = 6$  for molecules comparable to  $\text{CH}_4$ ).



**Fig. 19-13** 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.

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. 19-51)	$C_p = C_V + R$
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	$3R$	$4R$

## Sample Problem

## Diatomic gas, heat, temperature, internal energy

We transfer 1000 J as heat  $Q$  to a diatomic gas, allowing the gas to expand with the pressure held constant. The gas molecules each rotate around an internal axis but do not oscillate. How much of the 1000 J goes into the increase of the gas's internal energy? Of that amount, how much goes into  $\Delta K_{\text{tran}}$  (the kinetic energy of the translational motion of the molecules) and  $\Delta K_{\text{rot}}$  (the kinetic energy of their rotational motion)?

## KEY IDEAS

1. The transfer of energy as heat  $Q$  to a gas under constant pressure is related to the resulting temperature increase  $\Delta T$  via Eq. 19-46 ( $Q = nC_p \Delta T$ ).
2. Because the gas is diatomic with molecules undergoing rotation but not oscillation, the molar specific heat is, from Fig. 19-12 and Table 19-3,  $C_p = \frac{7}{2}R$ .
3. The increase  $\Delta E_{\text{int}}$  in the internal energy is the same as would occur with a constant-volume process resulting in the same  $\Delta T$ . Thus, from Eq. 19-45,  $\Delta E_{\text{int}} = nC_V \Delta T$ . From Fig. 19-12 and Table 19-3, we see that  $C_V = \frac{5}{2}R$ .
4. For the same  $n$  and  $\Delta T$ ,  $\Delta E_{\text{int}}$  is greater for a diatomic gas than a monatomic gas because additional energy is required for rotation.

**Increase in  $E_{\text{int}}$ :** Let's first get the temperature change  $\Delta T$  due to the transfer of energy as heat. From Eq. 19-46, substituting  $\frac{7}{2}R$  for  $C_p$ , we have

$$\Delta T = \frac{Q}{\frac{7}{2}nR}. \quad (19-52)$$

We next find  $\Delta E_{\text{int}}$  from Eq. 19-45, substituting the molar specific heat  $C_V (= \frac{5}{2}R)$  for a constant-volume process and using the same  $\Delta T$ . Because we are dealing with a di-

atomic gas, let's call this change  $\Delta E_{\text{int,dia}}$ . Equation 19-45 gives us

$$\begin{aligned} \Delta E_{\text{int,dia}} &= nC_V \Delta T = n\left(\frac{5}{2}R\right)\left(\frac{Q}{\frac{7}{2}nR}\right) = \frac{5}{7}Q \\ &= 0.71428Q = 714.3 \text{ J}. \end{aligned} \quad (\text{Answer})$$

In words, about 71% of the energy transferred to the gas goes into the internal energy. The rest goes into the work required to increase the volume of the gas, as the gas pushes the walls of its container outward.

**Increases in  $K$ :** If we were to increase the temperature of a *monatomic* gas (with the same value of  $n$ ) by the amount given in Eq. 19-52, the internal energy would change by a smaller amount, call it  $\Delta E_{\text{int,mon}}$ , because rotational motion is not involved. To calculate that smaller amount, we still use Eq. 19-45 but now we substitute the value of  $C_V$  for a monatomic gas—namely,  $C_V = \frac{3}{2}R$ . So,

$$\Delta E_{\text{int,mon}} = n\left(\frac{3}{2}R\right)\Delta T.$$

Substituting for  $\Delta T$  from Eq. 19-52 leads us to

$$\begin{aligned} \Delta E_{\text{int,mon}} &= n\left(\frac{3}{2}R\right)\left(\frac{Q}{\frac{7}{2}nR}\right) = \frac{3}{7}Q \\ &= 0.42857Q = 428.6 \text{ J}. \end{aligned}$$

For the monatomic gas, all this energy would go into the kinetic energy of the translational motion of the atoms. The important point here is that for a diatomic gas with the same values of  $n$  and  $\Delta T$ , the same amount of energy goes into the kinetic energy of the translational motion of the molecules. The rest of  $\Delta E_{\text{int,dia}}$  (that is, the additional 285.7 J) goes into the rotational motion of the molecules. Thus, for the diatomic gas,

$$\Delta K_{\text{trans}} = 428.6 \text{ J} \quad \text{and} \quad \Delta K_{\text{rot}} = 285.7 \text{ J}. \quad (\text{Answer})$$



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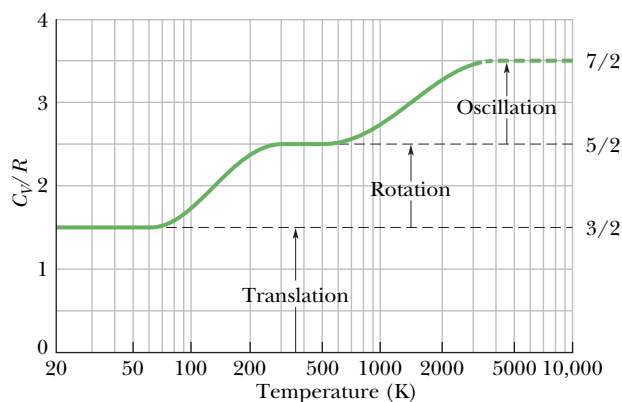
## 19-10 A Hint of Quantum Theory

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  $\text{O}_2$  molecule of Fig. 19-13*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 19-14 is of help in seeing this turning on of rotational motion and oscillatory motion. The ratio  $C_V/R$  for diatomic hydrogen gas ( $\text{H}_2$ ) 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.

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 of them obtain enough energy to rotate, and the value of  $C_V/R$  increases, until all of the molecules 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. 19-14. As the temperature increases beyond 1000 K, more and more molecules have enough energy to oscillate and the value of  $C_V/R$  increases, until all of the molecules are oscillating and  $C_V/R = 3.5$ . (In Fig. 19-14, the plotted curve stops at 3200 K because there the atoms of a hydrogen molecule oscillate so much that they overwhelm their bond, and the molecule then *dissociates* into two separate atoms.)



**Fig. 19-14**  $C_V/R$  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.

## 19-11 The Adiabatic Expansion of an Ideal Gas

We saw in Section 17-4 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 energy to be transferred from one part of the medium to another as heat. As we saw in Section 18-11, 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.

Figure 19-15*a* shows our usual insulated cylinder, now containing an ideal gas and resting on an insulating stand. By removing mass from the piston, we can allow the gas to expand adiabatically. 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

$$pV^\gamma = \text{a constant} \quad (\text{adiabatic process}), \quad (19-53)$$

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. 19-15*b*, 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. 19-53 as

$$p_i V_i^\gamma = p_f V_f^\gamma \quad (\text{adiabatic process}). \quad (19-54)$$

To write an equation for an adiabatic process in terms of  $T$  and  $V$ , we use the ideal gas equation ( $pV = nRT$ ) to eliminate  $p$  from Eq. 19-53, finding

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

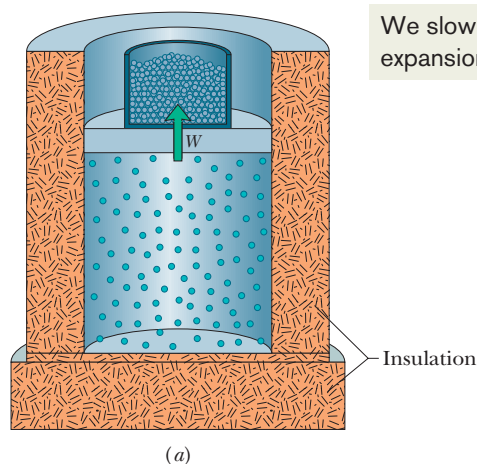
Because  $n$  and  $R$  are constants, we can rewrite this in the alternative form

$$TV^{\gamma-1} = \text{a constant} \quad (\text{adiabatic process}), \quad (19-55)$$

in which the constant is different from that in Eq. 19-53. When the gas goes from an initial state  $i$  to a final state  $f$ , we can rewrite Eq. 19-55 as

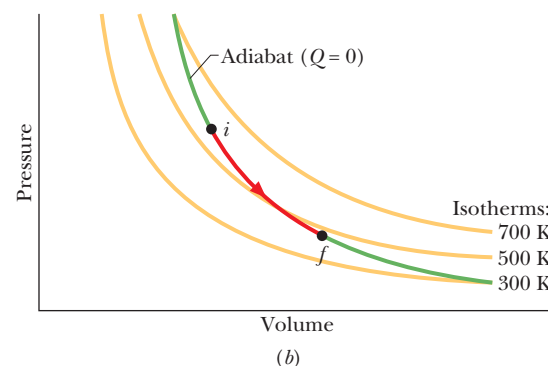
$$T_i V_i^{\gamma-1} = T_f V_f^{\gamma-1} \quad (\text{adiabatic process}). \quad (19-56)$$

Understanding adiabatic processes allows you to understand why popping the cork on a cold bottle of champagne or the tab on a cold can of soda causes a slight fog to form at the opening of the container. At the top of any unopened carbonated drink sits a gas of carbon dioxide and water vapor. Because the gas pressure is greater than atmospheric pressure, the gas expands out into the atmosphere



**Fig. 19-15** (a) The volume of an ideal gas is increased by removing mass 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.

We slowly remove lead shot, allowing an expansion without any heat transfer.



when the container is opened. Thus, the gas volume increases, but that means the gas must do work pushing against the atmosphere. Because the expansion is 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 also decreases, which causes the water vapor in the gas to condense into tiny drops of fog.

### Proof of Eq. 19-53

Suppose that you remove some shot from the piston of Fig. 19-15a, 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. 18-27, the first law of thermodynamics can then be written as

$$dE_{\text{int}} = Q - p dV. \quad (19-57)$$

Since the gas is thermally insulated (and thus the expansion is adiabatic), we substitute 0 for  $Q$ . Then we use Eq. 19-45 to substitute  $nC_V dT$  for  $dE_{\text{int}}$ . With these substitutions, and after some rearranging, we have

$$n dT = -\left(\frac{p}{C_V}\right) dV. \quad (19-58)$$

Now from the ideal gas law ( $pV = nRT$ ) we have

$$p dV + V dp = nR dT. \quad (19-59)$$

Replacing  $R$  with its equal,  $C_p - C_V$ , in Eq. 19-59 yields

$$n dT = \frac{p dV + V dp}{C_p - C_V}. \quad (19-60)$$

Equating Eqs. 19-58 and 19-60 and rearranging then 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

$$pV^\gamma = \text{a constant}. \quad (19-61)$$

### Free Expansions

Recall from Section 18-11 that a free expansion of a gas is an adiabatic process with *no* work or change in internal energy. Thus, a free expansion differs from the adiabatic process described by Eqs. 19-53 through 19-61, 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. 19-56 we have

$$T_i = T_f \quad (\text{free expansion}). \quad (19-62)$$

If we next assume that the gas is ideal (so that  $pV = nRT$ ), then because there is no change in temperature, there can be no change in the product  $pV$ . Thus, instead of Eq. 19-53 a free expansion involves the relation

$$p_i V_i = p_f V_f \quad (\text{free expansion}). \quad (19-63)$$

## Sample Problem

## Adiabatic expansion, free expansion

Initially, 1 mol of oxygen (assumed to be an ideal gas) has temperature 310 K and volume 12 L. We will allow it to expand to volume 19 L.

(a) What would be the final temperature if the gas expands adiabatically? Oxygen ( $O_2$ ) is diatomic and here has rotation but not oscillation.

## KEY IDEAS

1. When a gas expands against the pressure of its environment, it must do work.
2. When the process is adiabatic (no 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.

**Calculations:** We can relate the initial and final temperatures and volumes with Eq. 19-56:

$$T_i V_i^{\gamma-1} = T_f V_f^{\gamma-1}. \quad (19-64)$$

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. 19-64 for  $T_f$  and inserting known data then yield

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

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

## KEY IDEA

The temperature does not change in a free expansion because there is nothing to change the kinetic energy of the molecules.

**Calculation:** Thus, the temperature is

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

We find the new pressure using Eq. 19-63, which gives us

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

## Problem-Solving Tactics

## A Graphical Summary of Four Gas Processes

In this chapter we have discussed four special processes that an ideal gas can undergo. An example of each (for a monatomic ideal gas) is shown in Fig. 19-16, and some associated characteristics are given in Table 19-4, including two process names (isobaric and isochoric) that we have not used but that you might see in other courses.

## CHECKPOINT 5

Rank paths 1, 2, and 3 in Fig. 19-16 according to the energy transfer to the gas as heat, greatest first.

**Fig. 19-16** A  $p$ - $V$  diagram representing four special processes for an ideal monatomic gas.

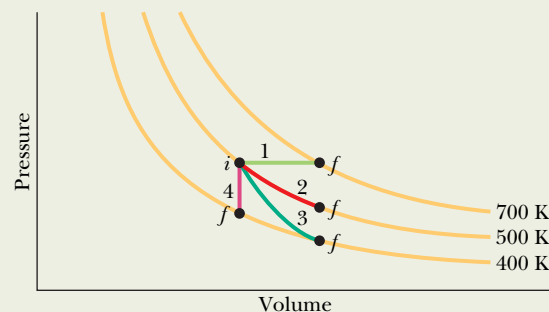


Table 19-4

## Four Special Processes

Path in Fig. 19-16	Constant Quantity	Process Type	Some Special Results
			$(\Delta E_{\text{int}} = Q - W \text{ and } \Delta E_{\text{int}} = nC_V \Delta T \text{ for all paths})$
1	$p$	Isobaric	$Q = nC_p \Delta T; W = p \Delta V$
2	$T$	Isothermal	$Q = W = nRT \ln(V_f/V_i); \Delta E_{\text{int}} = 0$
3	$pV^\gamma, TV^{\gamma-1}$	Adiabatic	$Q = 0; W = -\Delta E_{\text{int}}$
4	$V$	Isochoric	$Q = \Delta E_{\text{int}} = nC_V \Delta T; W = 0$



Additional examples, video, and practice available at WileyPLUS

## REVIEW &amp; SUMMARY

**Kinetic Theory of Gases** The *kinetic theory of gases* relates the *macroscopic* properties of gases (for example, pressure and temperature) to the *microscopic* properties of gas molecules (for example, speed and kinetic energy).

**Avogadro's Number** One mole of a substance contains  $N_A$  (*Avogadro's number*) elementary units (usually atoms or molecules), where  $N_A$  is found experimentally to be

$$N_A = 6.02 \times 10^{23} \text{ mol}^{-1} \quad (\text{Avogadro's number}). \quad (19-1)$$

One molar mass  $M$  of any substance is the mass of one mole of the substance. It is related to the mass  $m$  of the individual molecules of the substance by

$$M = mN_A. \quad (19-4)$$

The number of moles  $n$  contained in a sample of mass  $M_{\text{sam}}$ , consisting of  $N$  molecules, is given by

$$n = \frac{N}{N_A} = \frac{M_{\text{sam}}}{M} = \frac{M_{\text{sam}}}{mN_A}. \quad (19-2, 19-3)$$

**Ideal Gas** An *ideal gas* is one for which the pressure  $p$ , volume  $V$ , and temperature  $T$  are related by

$$pV = nRT \quad (\text{ideal gas law}). \quad (19-5)$$

Here  $n$  is the number of moles of the gas present and  $R$  is a constant ( $8.31 \text{ J/mol} \cdot \text{K}$ ) called the **gas constant**. The ideal gas law can also be written as

$$pV = NkT, \quad (19-9)$$

where the **Boltzmann constant**  $k$  is

$$k = \frac{R}{N_A} = 1.38 \times 10^{-23} \text{ J/K}. \quad (19-7)$$

**Work in an Isothermal Volume Change** The work done by an ideal gas during an **isothermal** (constant-temperature) change from volume  $V_i$  to volume  $V_f$  is

$$W = nRT \ln \frac{V_f}{V_i} \quad (\text{ideal gas, isothermal process}). \quad (19-14)$$

**Pressure, Temperature, and Molecular Speed** The pressure exerted by  $n$  moles of an ideal gas, in terms of the speed of its molecules, is

$$p = \frac{nMv_{\text{rms}}^2}{3V}, \quad (19-21)$$

where  $v_{\text{rms}} = \sqrt{(v^2)_{\text{avg}}}$  is the **root-mean-square speed** of the molecules of the gas. With Eq. 19-5 this gives

$$v_{\text{rms}} = \sqrt{\frac{3RT}{M}}. \quad (19-22)$$

**Temperature and Kinetic Energy** The average translational kinetic energy  $K_{\text{avg}}$  per molecule of an ideal gas is

$$K_{\text{avg}} = \frac{3}{2}kT. \quad (19-24)$$

**Mean Free Path** The *mean free path*  $\lambda$  of a gas molecule is its average path length between collisions and is given by

$$\lambda = \frac{1}{\sqrt{2}\pi d^2 N/V}, \quad (19-25)$$

where  $N/V$  is the number of molecules per unit volume and  $d$  is the molecular diameter.

**Maxwell Speed Distribution** The *Maxwell speed distribution*  $P(v)$  is a function such that  $P(v) dv$  gives the *fraction* of molecules with speeds in the interval  $dv$  at speed  $v$ :

$$P(v) = 4\pi \left( \frac{M}{2\pi RT} \right)^{3/2} v^2 e^{-Mv^2/2RT}. \quad (19-27)$$

Three measures of the distribution of speeds among the molecules of a gas are

$$v_{\text{avg}} = \sqrt{\frac{8RT}{\pi M}} \quad (\text{average speed}), \quad (19-31)$$

$$v_p = \sqrt{\frac{2RT}{M}} \quad (\text{most probable speed}), \quad (19-35)$$

and the rms speed defined above in Eq. 19-22.

**Molar Specific Heats** The molar specific heat  $C_V$  of a gas at constant volume is defined as

$$C_V = \frac{Q}{n \Delta T} = \frac{\Delta E_{\text{int}}}{n \Delta T}, \quad (19-39, 19-41)$$

in which  $Q$  is the energy transferred as heat to or from a sample of  $n$  moles of the gas,  $\Delta T$  is the resulting temperature change of the gas, and  $\Delta E_{\text{int}}$  is the resulting change in the internal energy of the gas. For an ideal monatomic gas,

$$C_V = \frac{3}{2}R = 12.5 \text{ J/mol} \cdot \text{K}. \quad (19-43)$$

The molar specific heat  $C_p$  of a gas at constant pressure is defined to be

$$C_p = \frac{Q}{n \Delta T}, \quad (19-46)$$

in which  $Q$ ,  $n$ , and  $\Delta T$  are defined as above.  $C_p$  is also given by

$$C_p = C_V + R. \quad (19-49)$$

For  $n$  moles of an ideal gas,

$$E_{\text{int}} = nC_V T \quad (\text{ideal gas}). \quad (19-44)$$

If  $n$  moles of a confined ideal gas undergo a temperature change  $\Delta T$  due to *any* process, the change in the internal energy of the gas is

$$\Delta E_{\text{int}} = nC_V \Delta T \quad (\text{ideal gas, any process}). \quad (19-45)$$

**Degrees of Freedom and  $C_V$**  We find  $C_V$  by using the *equipartition of energy* theorem, which states that every *degree of freedom* of a molecule (that is, every independent way it can store energy) has associated with it—on average—an energy  $\frac{1}{2}kT$  per molecule ( $= \frac{1}{2}RT$  per mole). If  $f$  is the number of degrees of freedom, then  $E_{\text{int}} = (f/2)nRT$  and

$$C_V = \left( \frac{f}{2} \right) R = 4.16f \text{ J/mol} \cdot \text{K}. \quad (19-51)$$

For monatomic gases  $f = 3$  (three translational degrees); for diatomic gases  $f = 5$  (three translational and two rotational degrees).

**Adiabatic Process** When an ideal gas undergoes a slow adiabatic volume change (a change for which  $Q = 0$ ),

$$pV^\gamma = \text{a constant} \quad (\text{adiabatic process}), \quad (19-53)$$

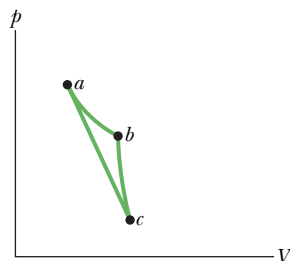
in which  $\gamma (= C_p/C_V)$  is the ratio of molar specific heats for the gas. For a free expansion, however,  $pV = \text{a constant}$ .



**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

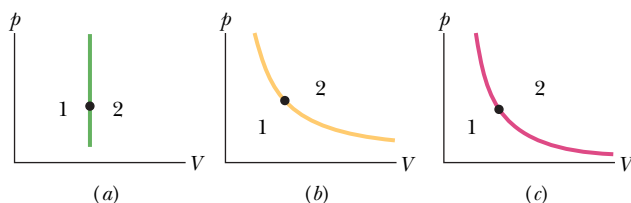
**2** In the  $p$ - $V$  diagram of Fig. 19-17, the gas does 5 J of work when taken along isotherm  $ab$  and 4 J when taken along adiabat  $bc$ . What is the change in the internal energy of the gas when it is taken along the straight path from  $a$  to  $c$ ?



**Fig. 19-17** Question 2.

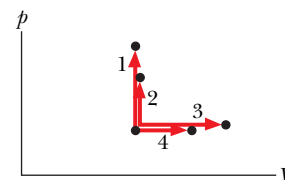
**3** For a temperature increase of  $\Delta T_1$ , a certain amount of an ideal gas requires 30 J when heated at constant volume and 50 J when heated at constant pressure. How much work is done by the gas in the second situation?

**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.



**Fig. 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?



**Fig. 19-19** Question 5.

**6** The dot in Fig. 19-18b 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. 19-18c 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



Tutoring problem available (at instructor's discretion) in WileyPLUS and WebAssign



Worked-out solution available in Student Solutions Manual

WWW Worked-out solution is at



Number of dots indicates level of problem difficulty

ILW Interactive solution is at

<http://www.wiley.com/college/halliday>



Additional information available in *The Flying Circus of Physics* and at [flyingcircusofphysics.com](http://flyingcircusofphysics.com)

### sec. 19-2 Avogadro's Number

**•1** 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 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?


### sec. 19-3 Ideal Gases

**•3 SSM** Oxygen gas having a volume of 1000 cm<sup>3</sup> at 40.0°C and  $1.01 \times 10^5$  Pa expands until its volume is 1500 cm<sup>3</sup> and its pressure is

$1.06 \times 10^5$  Pa. Find (a) the number of moles of oxygen present and (b) the final temperature of the sample.

**•4** A quantity of ideal gas at 10.0°C and 100 kPa occupies a volume of 2.50 m<sup>3</sup>. (a) How many moles of the gas are present? (b) If the pressure is now raised to 300 kPa and the temperature is raised to 30.0°C, how much volume does the gas occupy? Assume no leaks.

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

•6  **Water bottle in a hot car.** In the American Southwest, the temperature in a closed car parked in sunlight during the summer can be high enough to burn flesh. Suppose a bottle of water at a refrigerator temperature of  $5.00^\circ\text{C}$  is opened, then closed, and then left in a closed car with an internal temperature of  $75.0^\circ\text{C}$ . Neglecting the thermal expansion of the water and the bottle, find the pressure in the air pocket trapped in the bottle. (The pressure can be enough to push the bottle cap past the threads that are intended to keep the bottle closed.)


•7 Suppose  $1.80\text{ mol}$  of an ideal gas is taken from a volume of  $3.00\text{ m}^3$  to a volume of  $1.50\text{ m}^3$  via an isothermal compression at  $30^\circ\text{C}$ . (a) How much energy is transferred as heat during the compression, and (b) is the transfer *to* or *from* the gas?


•8 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  $220\text{ K}$ .

•9 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  $1.01 \times 10^5\text{ Pa}$ .

•10 A container encloses  $2\text{ mol}$  of an ideal gas that has molar mass  $M_1$  and  $0.5\text{ mol}$  of a second ideal gas that has molar mass  $M_2 = 3M_1$ . 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.*)

•11 **SSM ILW WWW** Air that initially occupies  $0.140\text{ m}^3$  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.)

•12  **Submarine rescue.** When the U. S. submarine *Squalus* became disabled at a depth of  $80\text{ m}$ , a cylindrical chamber was lowered from a ship to rescue the crew. The chamber had a radius of  $1.00\text{ m}$  and a height of  $4.00\text{ m}$ , was open at the bottom, and held two rescuers. It slid along a guide cable that a diver had attached to a hatch on the submarine. Once the chamber reached the hatch and clamped to the hull, the crew could escape into the chamber. During the descent, air was released from tanks to prevent water from flooding the chamber. Assume that the interior air pressure matched the water pressure at depth  $h$  as given by  $p_0 + \rho gh$ , where  $p_0 = 1.000\text{ atm}$  is the surface pressure and  $\rho = 1024\text{ kg/m}^3$  is the density of seawater. Assume a surface temperature of  $20.0^\circ\text{C}$  and a submerged water temperature of  $-30.0^\circ\text{C}$ . (a) What is the air volume in the chamber at the surface? (b) If air had not been released from the tanks, what would have been the air volume in the chamber at depth  $h = 80.0\text{ m}$ ? (c) How many moles of air were needed to be released to maintain the original air volume in the chamber?

•13  A sample of an ideal gas is taken through the cyclic process *abca* shown in Fig. 19-20. The scale of the vertical axis is set

by  $p_b = 7.5\text{ kPa}$  and  $p_{ac} = 2.5\text{ kPa}$ . 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 energy added to the gas as heat during the cycle?

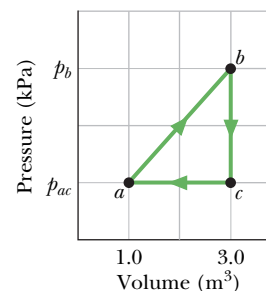


Fig. 19-20 Problem 13.

•14 In the temperature range  $310\text{ K}$  to  $330\text{ K}$ , the pressure  $p$  of a certain nonideal gas is related to volume  $V$  and temperature  $T$  by

$$p = (24.9\text{ J/K}) \frac{T}{V} - (0.00662\text{ J/K}^2) \frac{T^2}{V}.$$

How much work is done by the gas if its temperature is raised from  $315\text{ K}$  to  $325\text{ K}$  while the pressure is held constant?

•15 Suppose  $0.825\text{ mol}$  of an ideal gas undergoes an isothermal expansion as energy is added to it as heat  $Q$ . If Fig. 19-21 shows the final volume  $V_f$  versus  $Q$ , what is the gas temperature? The scale of the vertical axis is set by  $V_{fs} = 0.30\text{ m}^3$ , and the scale of the horizontal axis is set by  $Q_s = 1200\text{ J}$ .

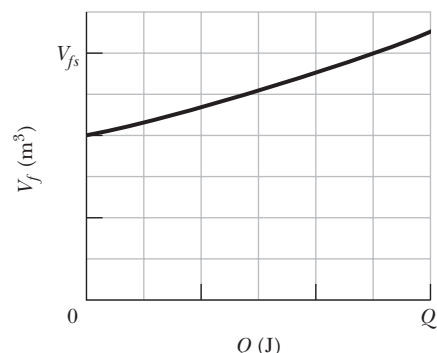



Fig. 19-21 Problem 15.

•16 An air bubble of volume  $20\text{ cm}^3$  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?

•17  Container A in Fig. 19-22 holds an ideal gas at a pressure of  $5.0 \times 10^5\text{ Pa}$  and a temperature of  $300\text{ K}$ . 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  $1.0 \times 10^5\text{ Pa}$  and a temperature of  $400\text{ K}$ . The valve is opened to allow the pressures to equalize, but the temperature of each container is maintained. What then is the pressure?

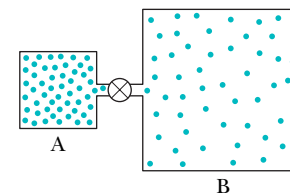


Fig. 19-22 Problem 17.

#### sec. 19-4 Pressure, Temperature, and RMS Speed

•18 The temperature and pressure in the Sun's atmosphere are  $2.00 \times 10^6\text{ K}$  and  $0.0300\text{ Pa}$ . Calculate the rms speed of free electrons (mass  $9.11 \times 10^{-31}\text{ kg}$ ) there, assuming they are an ideal gas.

•19 (a) Compute the rms speed of a nitrogen molecule at 20.0°C. The molar mass of nitrogen molecules ( $N_2$ ) is given in Table 19-1. At what temperatures will the rms speed be (b) half that value and (c) twice that value?

•20 Calculate the rms speed of helium atoms at 1000 K. See Appendix F for the molar mass of helium atoms.

•21 **SSM** The lowest possible temperature in outer space is 2.7 K. What is the rms speed of hydrogen molecules at this temperature? (The molar mass is given in Table 19-1.)

•22 Find the rms speed of argon atoms at 313 K. See Appendix F for the molar mass of argon atoms.

•23 A beam of hydrogen molecules ( $H_2$ ) is directed toward a wall, at an angle of 55° 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 cm<sup>2</sup>, at the rate of  $10^{23}$  molecules per second. What is the beam's pressure on the wall?

•24 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  $v_{rms}$  for the gas molecules. (b) Find the molar mass of the gas and (c) identify the gas. (*Hint:* The gas is listed in Table 19-1.)

### sec. 19-5 Translational Kinetic Energy

•25 Determine the average value of the translational kinetic energy of the molecules of an ideal gas at (a) 0.00°C and (b) 100°C. What is the translational kinetic energy per mole of an ideal gas at (c) 0.00°C and (d) 100°C?

•26 What is the average translational kinetic energy of nitrogen molecules at 1600 K?

•27 Water standing in the open at 32.0°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  $H_2O$  molecules, assuming the latter is related to temperature in the same way as it is for gases?

### sec. 19-6 Mean Free Path

•28 At what frequency would the wavelength of sound in air be equal to the mean free path of oxygen molecules at 1.0 atm pressure and 0.00°C? The molecular diameter is  $3.0 \times 10^{-8}$  cm.

•29 **SSM** The atmospheric density at an altitude of 2500 km is about 1 molecule/cm<sup>3</sup>. (a) Assuming the molecular diameter of  $2.0 \times 10^{-8}$  cm, find the mean free path predicted by Eq. 19-25. (b) Explain whether the predicted value is meaningful.

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

•31 In a certain particle accelerator, protons travel around a circular path of diameter 23.0 m in an evacuated chamber, whose residual gas is at 295 K and  $1.00 \times 10^{-6}$  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  $2.00 \times 10^{-8}$  m?

•32 At 20°C and 750 torr pressure, the mean free paths for argon gas (Ar) and nitrogen gas ( $N_2$ ) are  $\lambda_{Ar} = 9.9 \times 10^{-6}$  cm and  $\lambda_{N_2} = 27.5 \times 10^{-6}$  cm. (a) Find the ratio of the diameter of an Ar atom to that of an  $N_2$  molecule. What is the mean free path of argon at (b) 20°C and 150 torr, and (c) -40°C and 750 torr?

### sec. 19-7 The Distribution of Molecular Speeds

•33 **SSM** The speeds of 10 molecules are 2.0, 3.0, 4.0, ..., 11 km/s. What are their (a) average speed and (b) rms speed?

•34 The speeds of 22 particles are as follows ( $N_i$  represents the number of particles that have speed  $v_i$ ):

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

What are (a)  $v_{avg}$ , (b)  $v_{rms}$ , and (c)  $v_p$ ?

•35 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 (a) average and (b) rms speeds. (c) Is  $v_{rms} > v_{avg}$ ?

•36 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  $T_2/T_1$ .

•37 **SSM WWW** Figure 19-23 shows a hypothetical speed distribution for a sample of  $N$  gas particles (note that  $P(v) = 0$  for speed  $v > 2v_0$ ). What are the values of (a)  $av_0$ , (b)  $v_{avg}/v_0$ , and (c)  $v_{rms}/v_0$ ? (d) What fraction of the particles has a speed between  $1.5v_0$  and  $2.0v_0$ ?

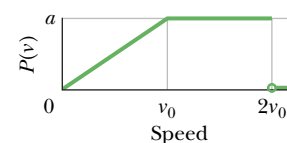


Fig. 19-23 Problem 37.

•38 Figure 19-24 gives the probability distribution for nitrogen gas. The scale of the horizontal axis is set by  $v_s = 1200$  m/s. What are the (a) gas temperature and (b) rms speed of the molecules?

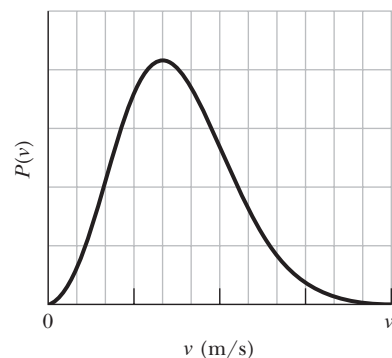


Fig. 19-24 Problem 38.

•39 At what temperature does the rms speed of (a)  $H_2$  (molecular hydrogen) and (b)  $O_2$  (molecular oxygen) equal the escape speed from Earth (Table 13-2)? At what temperature does the rms speed of (c)  $H_2$  and (d)  $O_2$  equal the escape speed from the Moon (where the gravitational acceleration at the surface has magnitude 0.16g)? Considering the answers to parts (a) and (b), should there be much (e) hydrogen and (f) oxygen high in Earth's upper atmosphere, where the temperature is about 1000 K?

•40 Two containers are at the same temperature. The first contains gas with pressure  $p_1$ , molecular mass  $m_1$ , and rms speed  $v_{rms1}$ . The second contains gas with pressure  $2.0p_1$ , molecular mass  $m_2$ , and average speed  $v_{avg2} = 2.0v_{rms1}$ . Find the mass ratio  $m_1/m_2$ .

•41 A hydrogen molecule (diameter  $1.0 \times 10^{-8}$  cm), traveling at the rms speed, escapes from a 4000 K furnace into a chamber contain-



ing cold argon atoms (diameter  $3.0 \times 10^{-8}$  cm) at a density of  $4.0 \times 10^{19}$  atoms/cm<sup>3</sup>. (a) What is the speed of the hydrogen molecule? (b) If it 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 argon atoms are stationary. Then the mean free path of the hydrogen molecule is given by Eq. 19-26 and not Eq. 19-25.)

### sec. 19-8 The Molar Specific Heats of an Ideal Gas

•42 What is the internal energy of 1.0 mol of an ideal monatomic gas at 273 K?

•43 The temperature of 3.00 mol of an ideal diatomic gas is increased by  $40.0^\circ\text{C}$  without the pressure of the gas changing. The molecules in the gas rotate but do not oscillate. (a) How much energy is transferred to the gas as heat? (b) What is the change in the internal energy of the gas? (c) How much work is done by the gas? (d) By how much does the rotational kinetic energy of the gas increase?

•44 One mole of an ideal diatomic gas goes from *a* to *c* along the diagonal path in Fig. 19-25. The scale of the vertical axis is set by  $p_{ab} = 5.0$  kPa and  $p_c = 2.0$  kPa, and the scale of the horizontal axis is set by  $V_{bc} = 4.0$  m<sup>3</sup> and  $V_a = 2.0$  m<sup>3</sup>. During the transition, (a) what is the change in internal energy of the gas, and (b) how much energy is added to the gas as heat? (c) How much heat is required if the gas goes from *a* to *c* along the indirect path *abc*?

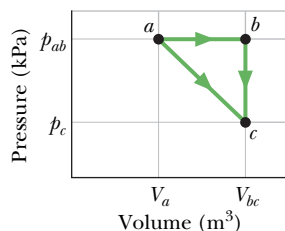


Fig. 19-25 Problem 44.

•45 The mass of a gas molecule can be computed from its specific heat at constant volume  $c_V$ . (Note that this is not  $C_V$ .) Take  $c_V = 0.075$  cal/g  $\cdot^\circ\text{C}$  for argon and calculate (a) the mass of an argon atom and (b) the molar mass of argon.

•46 Under constant pressure, the temperature of 2.00 mol of an ideal monatomic gas is raised  $15.0$  K. What are (a) the work  $W$  done by the gas, (b) the energy transferred as heat  $Q$ , (c) the change  $\Delta E_{\text{int}}$  in the internal energy of the gas, and (d) the change  $\Delta K$  in the average kinetic energy per atom?

•47 The temperature of 2.00 mol of an ideal monatomic gas is raised  $15.0$  K at constant volume. What are (a) the work  $W$  done by the gas, (b) the energy transferred as heat  $Q$ , (c) the change  $\Delta E_{\text{int}}$  in the internal energy of the gas, and (d) the change  $\Delta K$  in the average kinetic energy per atom?

•48 When  $20.9$  J was added as heat to a particular ideal gas, the volume of the gas changed from  $50.0$  cm<sup>3</sup> to  $100$  cm<sup>3</sup> while the pressure remained at  $1.00$  atm. (a) By how much did the internal energy of the gas change? If the quantity of gas present was  $2.00 \times 10^{-3}$  mol, find (b)  $C_p$  and (c)  $C_V$ .

•49 A container holds a mixture of three nonreacting gases: 2.40 mol of gas 1 with  $C_{V1} = 12.0$  J/mol  $\cdot^\circ\text{K}$ , 1.50 mol of gas 2 with  $C_{V2} = 12.8$  J/mol  $\cdot^\circ\text{K}$ , and 3.20 mol of gas 3 with  $C_{V3} = 20.0$  J/mol  $\cdot^\circ\text{K}$ . What is  $C_V$  of the mixture?

### sec. 19-9 Degrees of Freedom and Molar Specific Heats

•50 We give  $70$  J as heat 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 When  $1.0$  mol of oxygen ( $\text{O}_2$ ) gas is heated at constant pressure starting at  $0^\circ\text{C}$ , how much energy must be added to the gas as heat to double its volume? (The molecules rotate but do not oscillate.)

•52 Suppose  $12.0$  g of oxygen ( $\text{O}_2$ ) gas 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 energy is transferred to the oxygen as heat? (The molecules rotate but do not oscillate.) (c) What fraction of the heat is used to raise the internal energy of the oxygen?

•53 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. What are (a) the energy transferred as heat  $Q$ , (b) the change  $\Delta E_{\text{int}}$  in internal energy of the gas, (c) the work  $W$  done by the gas, and (d) the change  $\Delta K$  in the total translational kinetic energy of the gas?

### sec. 19-11 The Adiabatic Expansion of an Ideal Gas

•54 We know that for an adiabatic process  $pV^\gamma = \text{a constant}$ . Evaluate “a 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 rotate but do not oscillate.

•55 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 Suppose  $1.00$  L of a gas with  $\gamma = 1.30$ , initially at  $273$  K and  $1.00$  atm, is suddenly compressed adiabatically to half its initial volume. Find its final (a) pressure and (b) temperature. (c) If the gas is then cooled to  $273$  K at constant pressure, what is its final volume?

•57 The volume of an ideal gas is adiabatically reduced from  $200$  L to  $74.3$  L. The initial pressure and temperature are  $1.00$  atm and  $300$  K. The final pressure is  $4.00$  atm. (a) Is the gas monatomic, diatomic, or polyatomic? (b) What is the final temperature? (c) How many moles are in the gas?

•58 *Opening champagne.* In a bottle of champagne, the pocket of gas (primarily carbon dioxide) between the liquid and the cork is at pressure of  $p_i = 5.00$  atm. When the cork is pulled from the bottle, the gas undergoes an adiabatic expansion until its pressure matches the ambient air pressure of  $1.00$  atm. Assume that the ratio of the molar specific heats is  $\gamma = \frac{4}{3}$ . If the gas has initial temperature  $T_i = 5.00^\circ\text{C}$ , what is its temperature at the end of the adiabatic expansion?

•59 Figure 19-26 shows two paths that may be taken by a gas from an initial point *i* to a final point *f*. Path 1 consists of an isothermal expansion (work is  $50$  J in magnitude), an adiabatic expansion

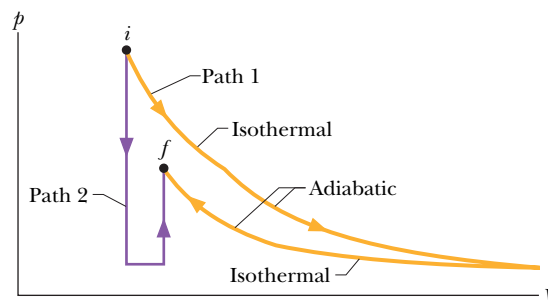





Fig. 19-26 Problem 59.

(work is 40 J in magnitude), an isothermal compression (work is 30 J in magnitude), and then an adiabatic compression (work is 25 J in magnitude). What is the change in the internal energy of the gas if the gas goes from point  $i$  to point  $f$  along path 2?

**••60**  **Adiabatic wind.** The normal airflow over the Rocky Mountains is west to east. The air loses much of its moisture content and is chilled as it climbs the western side of the mountains. When it descends on the eastern side, the increase in pressure toward lower altitudes causes the temperature to increase. The flow, then called a chinook wind, can rapidly raise the air temperature at the base of the mountains. Assume that the air pressure  $p$  depends on altitude  $y$  according to  $p = p_0 \exp(-ay)$ , where  $p_0 = 1.00$  atm and  $a = 1.16 \times 10^{-4} \text{ m}^{-1}$ . Also assume that the ratio of the molar specific heats is  $\gamma = \frac{4}{3}$ . A parcel of air with an initial temperature of  $-5.00^\circ\text{C}$  descends adiabatically from  $y_1 = 4267$  m to  $y = 1567$  m. What is its temperature at the end of the descent?

**••61**  A gas is to be expanded from initial state  $i$  to final state  $f$  along either path 1 or path 2 on a  $p$ - $V$  diagram. Path 1 consists of three steps: an isothermal expansion (work is 40 J in magnitude), an adiabatic expansion (work is 20 J in magnitude), and another isothermal expansion (work is 30 J in magnitude). Path 2 consists of two steps: a pressure reduction at constant volume and an expansion at constant pressure. What is the change in the internal energy of the gas along path 2?

**••62**  An ideal diatomic gas, with rotation but no oscillation, undergoes an adiabatic compression. Its initial pressure and volume are 1.20 atm and  $0.200 \text{ m}^3$ . Its final pressure is 2.40 atm. How much work is done by the gas?

**••63** Figure 19-27 shows a cycle undergone by 1.00 mol of an ideal monatomic gas. The temperatures are  $T_1 = 300$  K,  $T_2 = 600$  K, and  $T_3 = 455$  K. For  $1 \rightarrow 2$ , what are (a) heat  $Q$ , (b) the change in internal energy  $\Delta E_{\text{int}}$ , and (c) the work done  $W$ ? For  $2 \rightarrow 3$ , what are (d)  $Q$ , (e)  $\Delta E_{\text{int}}$ , and (f)  $W$ ? For  $3 \rightarrow 1$ , what are (g)  $Q$ , (h)  $\Delta E_{\text{int}}$ , and (i)  $W$ ? For the full cycle, what are (j)  $Q$ , (k)  $\Delta E_{\text{int}}$ , and (l)  $W$ ? The initial pressure at point 1 is  $1.00$  atm ( $= 1.013 \times 10^5$  Pa). What are the (m) volume and (n) pressure at point 2 and the (o) volume and (p) pressure at point 3?

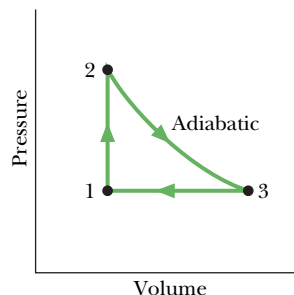


Fig. 19-27 Problem 63.

### Additional Problems

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

**65** An ideal gas undergoes an adiabatic compression from  $p = 1.0$  atm,  $V = 1.0 \times 10^6$  L,  $T = 0.0^\circ\text{C}$  to  $p = 1.0 \times 10^5$  atm,  $V = 1.0 \times 10^3$  L. (a) Is the gas monatomic, diatomic, or polyatomic? (b) What is its final temperature? (c) How many moles of gas are present? What is the total translational kinetic energy per mole (d) before and (e) after the compression? (f) What is the ratio of the squares of the rms speeds before and after the compression?

**66** An ideal gas consists of 1.50 mol of diatomic molecules that rotate but do not oscillate. The molecular diameter is 250 pm. The gas is expanded at a constant pressure of  $1.50 \times 10^5$  Pa, with a transfer of 200 J as heat. What is the change in the mean free path of the molecules?

**67** An ideal monatomic gas initially has a temperature of 330 K and a pressure of 6.00 atm. It is to expand from volume  $500 \text{ cm}^3$  to volume  $1500 \text{ cm}^3$ . If the expansion is isothermal, what are (a) the final pressure and (b) the work done by the gas? If, instead, the expansion is adiabatic, what are (c) the final pressure and (d) the work done by the gas?

**68** In an interstellar gas cloud at 50.0 K, the pressure is  $1.00 \times 10^{-8}$  Pa. Assuming that the molecular diameters of the gases in the cloud are all 20.0 nm, what is their mean free path?

**69** **SSM** The envelope and basket of a hot-air balloon have a combined weight of 2.45 kN, and the envelope has a capacity (volume) of  $2.18 \times 10^3 \text{ m}^3$ . When it is fully inflated, what should be the temperature of the enclosed air to give the balloon a *lifting capacity* (force) of 2.67 kN (in addition to the balloon's weight)? Assume that the surrounding air, at  $20.0^\circ\text{C}$ , has a weight per unit volume of  $11.9 \text{ N/m}^3$  and a molecular mass of 0.028 kg/mol, and is at a pressure of 1.0 atm.

**70** An ideal gas, at initial temperature  $T_1$  and initial volume  $2.0 \text{ m}^3$ , is expanded adiabatically to a volume of  $4.0 \text{ m}^3$ , then expanded isothermally to a volume of  $10 \text{ m}^3$ , and then compressed adiabatically back to  $T_1$ . What is its final volume?

**71** **SSM** The temperature of 2.00 mol of an ideal monatomic gas is raised 15.0 K in an adiabatic process. What are (a) the work  $W$  done by the gas, (b) the energy transferred as heat  $Q$ , (c) the change  $\Delta E_{\text{int}}$  in internal energy of the gas, and (d) the change  $\Delta K$  in the average kinetic energy per atom?

**72** At what temperature do atoms of helium gas have the same rms speed as molecules of hydrogen gas at  $20.0^\circ\text{C}$ ? (The molar masses are given in Table 19-1.)

**73** **SSM** At what frequency do molecules (diameter 290 pm) collide in (an ideal) oxygen gas ( $\text{O}_2$ ) at temperature 400 K and pressure 2.00 atm?

**74** (a) What is the number of molecules per cubic meter in air at  $20^\circ\text{C}$  and at a pressure of 1.0 atm ( $= 1.01 \times 10^5$  Pa)? (b) What is the mass of  $1.0 \text{ m}^3$  of this air? Assume that 75% of the molecules are nitrogen ( $\text{N}_2$ ) and 25% are oxygen ( $\text{O}_2$ ).

**75** The temperature of 3.00 mol of a gas with  $C_V = 6.00$  cal/mol  $\cdot$  K is to be raised 50.0 K. If the process is at *constant volume*, what are (a) the energy transferred as heat  $Q$ , (b) the work  $W$  done by the gas, (c) the change  $\Delta E_{\text{int}}$  in internal energy of the gas, and (d) the change  $\Delta K$  in the total translational kinetic energy? If the process is at *constant pressure*, what are (e)  $Q$ , (f)  $W$ , (g)  $\Delta E_{\text{int}}$ , and (h)  $\Delta K$ ? If the process is *adiabatic*, what are (i)  $Q$ , (j)  $W$ , (k)  $\Delta E_{\text{int}}$ , and (l)  $\Delta K$ ?

**76** During a compression at a constant pressure of 250 Pa, the volume of an ideal gas decreases from  $0.80 \text{ m}^3$  to  $0.20 \text{ m}^3$ . The initial temperature is 360 K, and the gas loses 210 J as heat. What are (a) the change in the internal energy of the gas and (b) the final temperature of the gas?

**77** **SSM** Figure 19-28 shows a hypothetical speed distribution

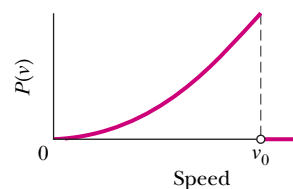


Fig. 19-28 Problem 77.



for particles of a certain gas:  $P(v) = Cv^2$  for  $0 < v \leq v_0$  and  $P(v) = 0$  for  $v > v_0$ . Find (a) an expression for  $C$  in terms of  $v_0$ , (b) the average speed of the particles, and (c) their rms speed.

**78** (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 the ratio of its pressure to  $p_0$ ? (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) What is the ratio of the average kinetic energy per molecule in this final state to that in the initial state?

**79 SSM** An ideal gas undergoes isothermal compression from an initial volume of  $4.00 \text{ m}^3$  to a final volume of  $3.00 \text{ m}^3$ . There is  $3.50 \text{ mol}$  of the gas, and its temperature is  $10.0^\circ\text{C}$ . (a) How much work is done by the gas? (b) How much energy is transferred as heat between the gas and its environment?

**80** Oxygen ( $\text{O}_2$ ) gas at  $273 \text{ K}$  and  $1.0 \text{ atm}$  is confined to a cubical container  $10 \text{ cm}$  on a side. Calculate  $\Delta U_g/K_{\text{avg}}$ , where  $\Delta U_g$  is the change in the gravitational potential energy of an oxygen molecule falling the height of the box and  $K_{\text{avg}}$  is the molecule's average translational kinetic energy.

**81** An ideal gas is taken through a complete cycle in three steps: adiabatic expansion with work equal to  $125 \text{ J}$ , isothermal contraction at  $325 \text{ K}$ , and increase in pressure at constant volume. (a) Draw a  $p$ - $V$  diagram for the three steps. (b) How much energy is transferred as heat in step 3, and (c) is it transferred *to* or *from* the gas?

**82** (a) What is the volume occupied by  $1.00 \text{ mol}$  of an ideal gas at standard conditions—that is,  $1.00 \text{ atm}$  ( $= 1.01 \times 10^5 \text{ Pa}$ ) and  $273 \text{ K}$ ? (b) Show that the number of molecules per cubic centimeter (the *Loschmidt number*) at standard conditions is  $2.69 \times 10^9$ .

**83 SSM** A sample of ideal gas expands from an initial pressure and volume of  $32 \text{ atm}$  and  $1.0 \text{ L}$  to a final volume of  $4.0 \text{ L}$ . The initial temperature is  $300 \text{ K}$ . If the gas is monatomic and the expansion isothermal, what are the (a) final pressure  $p_f$ , (b) final temperature  $T_f$ , and (c) work  $W$  done by the gas? If the gas is monatomic and the expansion adiabatic, what are (d)  $p_f$ , (e)  $T_f$ , and (f)  $W$ ? If the gas is diatomic and the expansion adiabatic, what are (g)  $p_f$ , (h)  $T_f$ , and (i)  $W$ ?

**84** An ideal gas with  $3.00 \text{ mol}$  is initially in state 1 with pressure  $p_1 = 20.0 \text{ atm}$  and volume  $V_1 = 1500 \text{ cm}^3$ . First it is taken to state 2 with pressure  $p_2 = 1.50p_1$  and volume  $V_2 = 2.00V_1$ . Then it is taken to state 3 with pressure  $p_3 = 2.00p_1$  and volume  $V_3 = 0.500V_1$ . What is the temperature of the gas in (a) state 1 and (b) state 2? (c) What is the net change in internal energy from state 1 to state 3?

**85** A steel tank contains  $300 \text{ g}$  of ammonia gas ( $\text{NH}_3$ ) at a pressure of  $1.35 \times 10^6 \text{ Pa}$  and a temperature of  $77^\circ\text{C}$ . (a) What is the volume of the tank in liters? (b) Later the temperature is  $22^\circ\text{C}$  and the pressure is  $8.7 \times 10^5 \text{ Pa}$ . How many grams of gas have leaked out of the tank?

**86** In an industrial process the volume of  $25.0 \text{ mol}$  of a monatomic ideal gas is reduced at a uniform rate from  $0.616 \text{ m}^3$  to  $0.308 \text{ m}^3$  in  $2.00 \text{ h}$  while its temperature is increased at a uniform rate from  $27.0^\circ\text{C}$  to  $450^\circ\text{C}$ . Throughout the process, the gas passes through thermodynamic equilibrium states. What are (a) the cumulative work done on the gas, (b) the cumulative energy absorbed by the gas as heat, and (c) the molar specific heat for the process? (*Hint:* To evaluate the integral for the work, you might use

$$\int \frac{a + bx}{A + Bx} dx = \frac{bx}{B} + \frac{aB - bA}{B^2} \ln(A + Bx),$$

an indefinite integral.) Suppose the process is replaced with a two-step process that reaches the same final state. In step 1, the gas volume is reduced at constant temperature, and in step 2 the temperature is increased at constant volume. For this process, what are (d) the cumulative work done on the gas, (e) the cumulative energy absorbed by the gas as heat, and (f) the molar specific heat for the process?

**87** Figure 19-29 shows a cycle consisting of five paths:  $AB$  is isothermal at  $300 \text{ K}$ ,  $BC$  is adiabatic with work  $= 5.0 \text{ J}$ ,  $CD$  is at a constant pressure of  $5 \text{ atm}$ ,  $DE$  is isothermal, and  $EA$  is adiabatic with a change in internal energy of  $8.0 \text{ J}$ . What is the change in internal energy of the gas along path  $CD$ ?

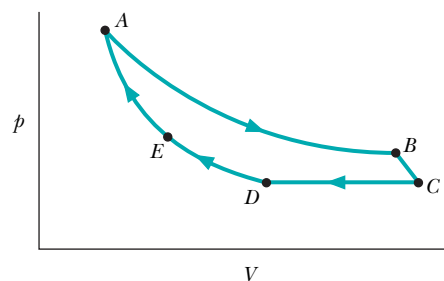


Fig. 19-29 Problem 87.

**88** An ideal gas initially at  $300 \text{ K}$  is compressed at a constant pressure of  $25 \text{ N/m}^2$  from a volume of  $3.0 \text{ m}^3$  to a volume of  $1.8 \text{ m}^3$ . In the process,  $75 \text{ J}$  is lost by the gas as heat. What are (a) the change in internal energy of the gas and (b) the final temperature of the gas?

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