Chapter 21

The Kinetic Theory of Gases

▲ Dogs do not have sweat glands like humans. In hot weather, dogs pant to promote evaporation from the tongue. In this chapter, we show that evaporation is a cooling process based on the removal of molecules with high kinetic energy from a liquid. (Frank Oberle/Getty Images)

In Chapter 19 we discussed the properties of an ideal gas, using such macroscopic variables as pressure, volume, and temperature. We shall now show that such large-scale properties can be related to a description on a microscopic scale, where matter is treated as a collection of molecules. Newton's laws of motion applied in a statistical manner to a collection of particles provide a reasonable description of thermodynamic processes. To keep the mathematics relatively simple, we shall consider primarily the behavior of gases, because in gases the interactions between molecules are much weaker than they are in liquids or solids. In our model of gas behavior, called **kinetic theory**, gas molecules move about in a random fashion, colliding with the walls of their container and with each other. Kinetic theory provides us with a physical basis for our understanding of the concept of temperature.

## 21.1 Molecular Model of an Ideal Gas

We begin this chapter by developing a microscopic model of an ideal gas. The model shows that the pressure that a gas exerts on the walls of its container is a consequence of the collisions of the gas molecules with the walls and is consistent with the macroscopic description of Chapter 19. In developing this model, we make the following assumptions:

1. **The number of molecules in the gas is large, and the average separation between them is large compared with their dimensions.** This means that the molecules occupy a negligible volume in the container. This is consistent with the ideal gas model, in which we imagine the molecules to be point-like.

2. **The molecules obey Newton's laws of motion, but as a whole they move randomly.** By "randomly" we mean that any molecule can move in any direction with any speed. At any given moment, a certain percentage of molecules move at high speeds, and a certain percentage move at low speeds.

3. **The molecules interact only by short-range forces during elastic collisions.** This is consistent with the ideal gas model, in which the molecules exert no long-range forces on each other.

4. **The molecules make elastic collisions with the walls.**

5. **The gas under consideration is a pure substance; that is, all molecules are identical.**

Although we often picture an ideal gas as consisting of single atoms, we can assume that the behavior of molecular gases approximates that of ideal gases rather well at low pressures. Molecular rotations or vibrations have no effect, on the average, on the motions that we consider here.

For our first application of kinetic theory, let us derive an expression for the pressure of N molecules of an ideal gas in a container of volume V in terms of microscopic quantities. The container is a cube with edges of length d (Fig. 21.1). We shall first

Assumptions of the molecular model of an ideal gas
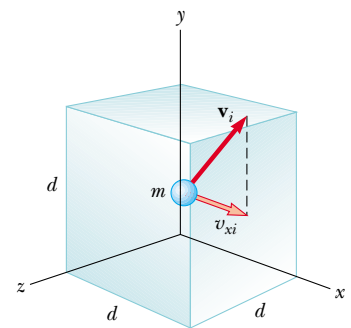
Figure 21.1 A cubical box with sides of length d containing an ideal gas. The molecule shown moves with velocity $\mathbf{v}_i$.
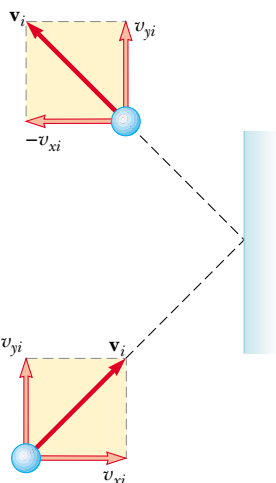
Active Figure 21.2 A molecule makes an elastic collision with the wall of the container. Its x component of momentum is reversed, while its y component remains unchanged. In this construction, we assume that the molecule moves in the xy plane.

At the Active Figures link at http://www.pse6.com, *you can observe molecules within a container making collisions with the walls of the container and with each other.*

focus our attention on one of these molecules of mass m, and assume that it is moving so that its component of velocity in the x direction is v_{xi} as in Figure 21.2. (The subscript i here refers to the ith molecule, not to an initial value. We will combine the effects of all of the molecules shortly.) As the molecule collides elastically with any wall (assumption 4), its velocity component perpendicular to the wall is reversed because the mass of the wall is far greater than the mass of the molecule. Because the momentum component p_{xi} of the molecule is mv_{xi} before the collision and $-mv_{xi}$ after the collision, the change in the x component of the momentum of the molecule is

$$\Delta p_{xi} = -mv_{xi} - (mv_{xi}) = -2mv_{xi}$$

Because the molecules obey Newton's laws (assumption 2), we can apply the impulse-momentum theorem (Eq. 9.8) to the molecule to give us

$$\bar{F}_{i,\text{on molecule}} \Delta t_{\text{collision}} = \Delta p_{xi} = -2mv_{xi}$$

where $\bar{F}_{i,\text{on molecule}}$ is the x component of the average force that the wall exerts on the molecule during the collision and $\Delta t_{\text{collision}}$ is the duration of the collision. In order for the molecule to make another collision with the same wall after this first collision, it must travel a distance of $2d$ in the x direction (across the container and back). Therefore, the time interval between two collisions with the same wall is

$$\Delta t = \frac{2d}{v_{xi}}$$

The force that causes the change in momentum of the molecule in the collision with the wall occurs only during the collision. However, we can average the force over the time interval for the molecule to move across the cube and back. Sometime during this time interval, the collision occurs, so that the change in momentum for this time interval is the same as that for the short duration of the collision. Thus, we can rewrite the impulse-momentum theorem as

$$\bar{F}_i \Delta t = -2mv_{xi}$$

where $\bar{F}_i$ is the average force component over the time for the molecule to move across the cube and back. Because exactly one collision occurs for each such time interval, this is also the long-term average force on the molecule, over long time intervals containing any number of multiples of Δt.

This equation and the preceding one enable us to express the x component of the long-term average force exerted by the wall on the molecule as

$$\bar{F}_i = \frac{-2mv_{xi}}{\Delta t} = \frac{-2mv_{xi}^2}{2d} = \frac{-mv_{xi}^2}{d}$$

Now, by Newton's third law, the average x component of the force exerted by the molecule on the wall is equal in magnitude and opposite in direction:

$$\bar{F}_{i,\text{on wall}} = -\bar{F}_i = -\left(\frac{-mv_{xi}^2}{d}\right) = \frac{mv_{xi}^2}{d}$$

The total average force $\bar{F}$ exerted by the gas on the wall is found by adding the average forces exerted by the individual molecules. We add terms such as that above for all molecules:

$$\bar{F} = \sum_{i=1}^{N} \frac{mv_{xi}^2}{d} = \frac{m}{d} \sum_{i=1}^{N} v_{xi}^2$$

where we have factored out the length of the box and the mass m, because assumption 5 tells us that all of the molecules are the same. We now impose assumption 1, that the number of molecules is large. For a small number of molecules, the actual force on the

wall would vary with time. It would be nonzero during the short interval of a collision of a molecule with the wall and zero when no molecule happens to be hitting the wall. For a very large number of molecules, however, such as Avogadro's number, these variations in force are smoothed out, so that the average force given above is the same over *any* time interval. Thus, the *constant* force F on the wall due to the molecular collisions is

$$F = \frac{m}{d} \sum_{i=1}^{N} v_{xi}^2$$

To proceed further, let us consider how to express the average value of the square of the x component of the velocity for N molecules. The traditional average of a set of values is the sum of the values over the number of values:

$$\overline{v_x^2} = \frac{\sum_{i=1}^{N} v_{xi}^2}{N}$$

The numerator of this expression is contained in the right-hand side of the preceding equation. Thus, combining the two expressions, the total force on the wall can be written

$$F = \frac{m}{d} N\overline{v_x^2} \tag{21.1}$$

Now let us focus again on one molecule with velocity components v_{xi}, v_{yi}, and v_{zi}. The Pythagorean theorem relates the square of the speed of the molecule to the squares of the velocity components:

$$v_i^2 = v_{xi}^2 + v_{yi}^2 + v_{zi}^2$$

Hence, the average value of v^2 for all the molecules in the container is related to the average values of $\overline{v_x^2}$, $\overline{v_y^2}$, and $\overline{v_z^2}$ according to the expression

$$\overline{v^2} = \overline{v_x^2} + \overline{v_y^2} + \overline{v_z^2}$$

Because the motion is completely random (assumption 2), the average values $\overline{v_x^2}$, $\overline{v_y^2}$, and $\overline{v_z^2}$ are equal to each other. Using this fact and the preceding equation, we find that

$$\overline{v^2} = 3\overline{v_x^2}$$

Thus, from Equation 21.1, the total force exerted on the wall is

$$F = \frac{N}{3}\left(\frac{m\overline{v^2}}{d}\right)$$

Using this expression, we can find the total pressure exerted on the wall:

$$P = \frac{F}{A} = \frac{F}{d^2} = \tfrac{1}{3}\left(\frac{N}{d^3}\, m\overline{v^2}\right) = \tfrac{1}{3}\left(\frac{N}{V}\right) m\overline{v^2}$$

$$P = \tfrac{2}{3}\left(\frac{N}{V}\right)\left(\tfrac{1}{2}m\overline{v^2}\right) \tag{21.2}$$

Relationship between pressure and molecular kinetic energy

This result indicates that **the pressure of a gas is proportional to the number of molecules per unit volume and to the average translational kinetic energy of the molecules, $\tfrac{1}{2}m\overline{v^2}$.** In analyzing this simplified model of an ideal gas, we obtain an important result that relates the macroscopic quantity of pressure to a microscopic quantity—the average value of the square of the molecular speed. Thus, we have established a key link between the molecular world and the large-scale world.

You should note that Equation 21.2 verifies some features of pressure with which you are probably familiar. One way to increase the pressure inside a container is to increase the number of molecules per unit volume N/V in the container. This is what you do when you add air to a tire. The pressure in the tire can also be increased by increasing the average translational kinetic energy of the air molecules in the tire.

This can be accomplished by increasing the temperature of that air, as we shall soon show mathematically. This is why the pressure inside a tire increases as the tire warms up during long trips. The continuous flexing of the tire as it moves along the road surface results in work done as parts of the tire distort, causing an increase in internal energy of the rubber. The increased temperature of the rubber results in the transfer of energy by heat into the air inside the tire. This transfer increases the air's temperature, and this increase in temperature in turn produces an increase in pressure.

Molecular Interpretation of Temperature

We can gain some insight into the meaning of temperature by first writing Equation 21.2 in the form

$$PV = \tfrac{2}{3}N(\tfrac{1}{2}m\overline{v^2})$$

Let us now compare this with the equation of state for an ideal gas (Eq. 19.10):

$$PV = Nk_{\mathrm{B}}T$$

Recall that the equation of state is based on experimental facts concerning the macroscopic behavior of gases. Equating the right sides of these expressions, we find that

Temperature is proportional to average kinetic energy

$$T = \frac{2}{3k_{\mathrm{B}}}\,(\tfrac{1}{2}m\overline{v^2}) \qquad (21.3)$$

This result tells us that temperature is a direct measure of average molecular kinetic energy. By rearranging Equation 21.3, we can relate the translational molecular kinetic energy to the temperature:

Average kinetic energy per molecule

$$\tfrac{1}{2}m\overline{v^2} = \tfrac{3}{2}k_{\mathrm{B}}T \qquad (21.4)$$

That is, the average translational kinetic energy per molecule is $\tfrac{3}{2}k_{\mathrm{B}}T$. Because $\overline{v_x^2} = \tfrac{1}{3}\overline{v^2}$, it follows that

$$\tfrac{1}{2}m\overline{v_x^2} = \tfrac{1}{2}k_{\mathrm{B}}T \qquad (21.5)$$

In a similar manner, it follows that the motions in the y and z directions give us

$$\tfrac{1}{2}m\overline{v_y^2} = \tfrac{1}{2}k_{\mathrm{B}}T \qquad \text{and} \qquad \tfrac{1}{2}m\overline{v_z^2} = \tfrac{1}{2}k_{\mathrm{B}}T$$

Thus, each translational degree of freedom contributes an equal amount of energy, $\tfrac{1}{2}k_{\mathrm{B}}T$, to the gas. (In general, a "degree of freedom" refers to an independent means by which a molecule can possess energy.) A generalization of this result, known as the **theorem of equipartition of energy**, states that

Theorem of equipartition of energy

each degree of freedom contributes $\tfrac{1}{2}k_{\mathrm{B}}T$ to the energy of a system, where possible degrees of freedom in addition to those associated with translation arise from rotation and vibration of molecules.

The total translational kinetic energy of N molecules of gas is simply N times the average energy per molecule, which is given by Equation 21.4:

Total translational kinetic energy of N molecules

$$K_{\text{tot trans}} = N(\tfrac{1}{2}m\overline{v^2}) = \tfrac{3}{2}Nk_{\mathrm{B}}T = \tfrac{3}{2}nRT \qquad (21.6)$$

where we have used $k_{\mathrm{B}} = R/N_{\mathrm{A}}$ for Boltzmann's constant and $n = N/N_{\mathrm{A}}$ for the number of moles of gas. If we consider a gas in which molecules possess only translational kinetic energy, Equation 21.6 represents the internal energy of the gas. This result implies that **the internal energy of an ideal gas depends only on the temperature.** We will follow up on this point in Section 21.2.

The square root of $\overline{v^2}$ is called the *root-mean-square* (rms) *speed* of the molecules. From Equation 21.4 we find that the rms speed is

$$v_{\text{rms}} = \sqrt{\overline{v^2}} = \sqrt{\frac{3k_{\text{B}}T}{m}} = \sqrt{\frac{3RT}{M}} \tag{21.7}$$

Root-mean-square speed

where M is the molar mass in kilograms per mole and is equal to mN_{A}. This expression shows that, at a given temperature, lighter molecules move faster, on the average, than do heavier molecules. For example, at a given temperature, hydrogen molecules, whose molar mass is 2.02×10^{-3} kg/mol, have an average speed approximately four times that of oxygen molecules, whose molar mass is 32.0×10^{-3} kg/mol. Table 21.1 lists the rms speeds for various molecules at 20°C.

Table 21.1

Some rms Speeds		
Gas	**Molar mass (g/mol)**	**v_{rms} at 20°C (m/s)**
H_2	2.02	1 902
He	4.00	1 352
H_2O	18.0	637
Ne	20.2	602
N_2 or CO	28.0	511
NO	30.0	494
O_2	32.0	478
CO_2	44.0	408
SO_2	64.1	338

▲ **PITFALL PREVENTION**

21.1   The Square Root of the Square?

Notice that taking the square root of $\overline{v^2}$ does not "undo" the square because we have taken an average *between* squaring and taking the square root. While the square root of $(\overline{v})^2$ is $\overline{v}$ because the squaring is done after the averaging, the square root of $\overline{v^2}$ is *not* $\overline{v}$, but rather v_{rms}.

Example 21.1   A Tank of Helium

A tank used for filling helium balloons has a volume of 0.300 m³ and contains 2.00 mol of helium gas at 20.0°C. Assume that the helium behaves like an ideal gas.

(A) What is the total translational kinetic energy of the gas molecules?

Solution Using Equation 21.6 with $n = 2.00$ mol and $T = 293$ K, we find that

$$K_{\text{tot trans}} = \tfrac{3}{2}nRT = \tfrac{3}{2}(2.00 \text{ mol})(8.31 \text{ J/mol·K})(293 \text{ K})$$

$$= \boxed{7.30 \times 10^3 \text{ J}}$$

(B) What is the average kinetic energy per molecule?

Solution Using Equation 21.4, we find that the average kinetic energy per molecule is

$$\tfrac{1}{2}m\overline{v^2} = \tfrac{3}{2}k_{\text{B}}T = \tfrac{3}{2}(1.38 \times 10^{-23} \text{ J/K})(293 \text{ K})$$

$$= \boxed{6.07 \times 10^{-21} \text{ J}}$$

What If? What if the temperature is raised from 20.0°C to 40.0°C? Because 40.0 is twice as large as 20.0, is the total translational energy of the molecules of the gas twice as large at the higher temperature?

Answer The expression for the total translational energy depends on the temperature, and the value for the temperature must be expressed in kelvins, not in degrees Celsius. Thus, the ratio of 40.0 to 20.0 is *not* the appropriate ratio. Converting the Celsius temperatures to kelvins, 20.0°C is 293 K and 40.0°C is 313 K. Thus, the total translational energy increases by a factor of 313 K/293 K = 1.07.

Quick Quiz 21.1   Two containers hold an ideal gas at the same temperature and pressure. Both containers hold the same type of gas but container B has twice the volume of container A. The average translational kinetic energy per molecule in container B is (a) twice that for container A (b) the same as that for container A (c) half that for container A (d) impossible to determine.

> **Quick Quiz 21.2** Consider again the situation in Quick Quiz 21.1. The internal energy of the gas in container B is (a) twice that for container A (b) the same as that for container A (c) half that for container A (d) impossible to determine.

> **Quick Quiz 21.3** Consider again the situation in Quick Quiz 21.1. The rms speed of the gas molecules in container B is (a) twice that for container A (b) the same as that for container A (c) half that for container A (d) impossible to determine.
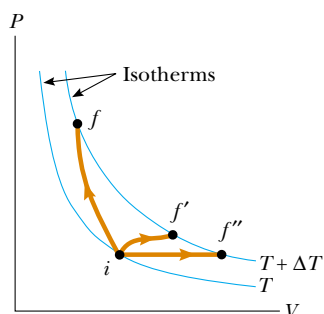
Figure 21.3 An ideal gas is taken from one isotherm at temperature T to another at temperature $T + \Delta T$ along three different paths.

21.2 Molar Specific Heat of an Ideal Gas

Consider an ideal gas undergoing several processes such that the change in temperature is $\Delta T = T_f - T_i$ for all processes. The temperature change can be achieved by taking a variety of paths from one isotherm to another, as shown in Figure 21.3. Because ΔT is the same for each path, the change in internal energy ΔE_{int} is the same for all paths. However, we know from the first law, $Q = \Delta E_{int} - W$, that the heat Q is different for each path because W (the negative of the area under the curves) is different for each path. Thus, the heat associated with a given change in temperature does *not* have a unique value.

We can address this difficulty by defining specific heats for two processes that frequently occur: changes at constant volume and changes at constant pressure. Because the number of moles is a convenient measure of the amount of gas, we define the **molar specific heats** associated with these processes with the following equations:

$$Q = nC_V \Delta T \qquad \text{(constant volume)} \tag{21.8}$$

$$Q = nC_P \Delta T \qquad \text{(constant pressure)} \tag{21.9}$$

where C_V is the **molar specific heat at constant volume** and C_P is the **molar specific heat at constant pressure.** When we add energy to a gas by heat at constant pressure, not only does the internal energy of the gas increase, but work is done on the gas because of the change in volume. Therefore, the heat $Q_{\text{constant } P}$ must account for both the increase in internal energy and the transfer of energy out of the system by work. For this reason, $Q_{\text{constant } P}$ is greater than $Q_{\text{constant } V}$ for given values of n and ΔT. Thus, C_P is greater than C_V.

In the previous section, we found that the temperature of a gas is a measure of the average translational kinetic energy of the gas molecules. This kinetic energy is associated with the motion of the center of mass of each molecule. It does not include the energy associated with the internal motion of the molecule—namely, vibrations and rotations about the center of mass. This should not be surprising because the simple kinetic theory model assumes a structureless molecule.

In view of this, let us first consider the simplest case of an ideal monatomic gas, that is, a gas containing one atom per molecule, such as helium, neon, or argon. When energy is added to a monatomic gas in a container of fixed volume, all of the added energy goes into increasing the translational kinetic energy of the atoms. There is no other way to store the energy in a monatomic gas. Therefore, from Equation 21.6, we see that the internal energy E_{int} of N molecules (or n mol) of an ideal monatomic gas is

Internal energy of an ideal monatomic gas

$$E_{int} = K_{\text{tot trans}} = \tfrac{3}{2}Nk_B T = \tfrac{3}{2}nRT \tag{21.10}$$

Note that for a monatomic ideal gas, E_{int} is a function of T only, and the functional relationship is given by Equation 21.10. In general, the internal energy of an ideal gas is a function of T only, and the exact relationship depends on the type of gas.

If energy is transferred by heat to a system at *constant volume*, then no work is done on the system. That is, $W = -\int P\,dV = 0$ for a constant-volume process. Hence, from the first law of thermodynamics, we see that

$$Q = \Delta E_{int} \tag{21.11}$$

In other words, all of the energy transferred by heat goes into increasing the internal energy of the system. A constant-volume process from i to f for an ideal gas is described in Figure 21.4, where ΔT is the temperature difference between the two isotherms. Substituting the expression for Q given by Equation 21.8 into Equation 21.11, we obtain

$$\Delta E_{int} = nC_V\,\Delta T \tag{21.12}$$

If the molar specific heat is constant, we can express the internal energy of a gas as

$$E_{int} = nC_VT$$

This equation applies to all ideal gases—to gases having more than one atom per molecule as well as to monatomic ideal gases. In the limit of infinitesimal changes, we can use Equation 21.12 to express the molar specific heat at constant volume as

$$C_V = \frac{1}{n}\frac{dE_{int}}{dT} \tag{21.13}$$

Let us now apply the results of this discussion to the monatomic gas that we have been studying. Substituting the internal energy from Equation 21.10 into Equation 21.13, we find that

$$C_V = \tfrac{3}{2}R \tag{21.14}$$

This expression predicts a value of $C_V = \tfrac{3}{2}R = 12.5\,\text{J/mol·K}$ for *all* monatomic gases. This prediction is in excellent agreement with measured values of molar specific heats for such gases as helium, neon, argon, and xenon over a wide range of temperatures (Table 21.2). Small variations in Table 21.2 from the predicted values are due to the
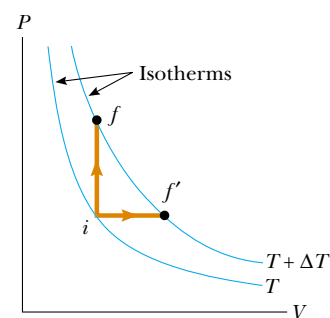
Active Figure 21.4 Energy is transferred by heat to an ideal gas in two ways. For the constant-volume path $i \rightarrow f$, all the energy goes into increasing the internal energy of the gas because no work is done. Along the constant-pressure path $i \rightarrow f'$, part of the energy transferred in by heat is transferred out by work.

At the Active Figures link at http://www.pse6.com, you can choose initial and final temperatures for one mole of an ideal gas undergoing constant-volume and constant pressure processes and measure Q, W, ΔE_{int}, C_V, and C_P.

Table 21.2

Molar Specific Heats of Various Gases			
Molar Specific Heat (J/mol · K)[a]			
Gas	**C_P**	**C_V**	**$C_P - C_V$**	**$\gamma = C_P/C_V$**
Monatomic Gases				
He	20.8	12.5	8.33	1.67
Ar	20.8	12.5	8.33	1.67
Ne	20.8	12.7	8.12	1.64
Kr	20.8	12.3	8.49	1.69
Diatomic Gases				
H_2	28.8	20.4	8.33	1.41
N_2	29.1	20.8	8.33	1.40
O_2	29.4	21.1	8.33	1.40
CO	29.3	21.0	8.33	1.40
Cl_2	34.7	25.7	8.96	1.35
Polyatomic Gases				
CO_2	37.0	28.5	8.50	1.30
SO_2	40.4	31.4	9.00	1.29
H_2O	35.4	27.0	8.37	1.30
CH_4	35.5	27.1	8.41	1.31

[a]   All values except that for water were obtained at 300 K.

fact that real gases are not ideal gases. In real gases, weak intermolecular interactions occur, which are not addressed in our ideal gas model.

Now suppose that the gas is taken along the constant-pressure path $i \to f'$ shown in Figure 21.4. Along this path, the temperature again increases by ΔT. The energy that must be transferred by heat to the gas in this process is $Q = nC_P \Delta T$. Because the volume changes in this process, the work done on the gas is $W = -P \Delta V$ where P is the constant pressure at which the process occurs. Applying the first law of thermodynamics to this process, we have

$$\Delta E_{int} = Q + W = nC_P \Delta T + (-P \Delta V) \tag{21.15}$$

In this case, the energy added to the gas by heat is channeled as follows: Part of it leaves the system by work (that is, the gas moves a piston through a displacement), and the remainder appears as an increase in the internal energy of the gas. But the change in internal energy for the process $i \to f'$ is equal to that for the process $i \to f$ because E_{int} depends only on temperature for an ideal gas and because ΔT is the same for both processes. In addition, because $PV = nRT$, we note that for a constant-pressure process, $P \Delta V = nR \Delta T$. Substituting this value for $P \Delta V$ into Equation 21.15 with $\Delta E_{int} = nC_V \Delta T$ (Eq. 21.12) gives

$$nC_V \Delta T = nC_P \Delta T - nR \Delta T$$

$$C_P - C_V = R \tag{21.16}$$

This expression applies to *any* ideal gas. It predicts that the molar specific heat of an ideal gas at constant pressure is greater than the molar specific heat at constant volume by an amount R, the universal gas constant (which has the value 8.31 J/mol·K). This expression is applicable to real gases, as the data in Table 21.2 show.

Because $C_V = \frac{3}{2}R$ for a monatomic ideal gas, Equation 21.16 predicts a value $C_P = \frac{5}{2}R = 20.8$ J/mol·K for the molar specific heat of a monatomic gas at constant pressure. The ratio of these molar specific heats is a dimensionless quantity γ (Greek gamma):

$$\gamma = \frac{C_P}{C_V} = \frac{5R/2}{3R/2} = \frac{5}{3} = 1.67 \tag{21.17}$$

Theoretical values of C_V, C_P and γ are in excellent agreement with experimental values obtained for monatomic gases, but they are in serious disagreement with the values for the more complex gases (see Table 21.2). This is not surprising because the value $C_V = \frac{3}{2}R$ was derived for a monatomic ideal gas and we expect some additional contribution to the molar specific heat from the internal structure of the more complex molecules. In Section 21.4, we describe the effect of molecular structure on the molar specific heat of a gas. The internal energy—and, hence, the molar specific heat—of a complex gas must include contributions from the rotational and the vibrational motions of the molecule.

In the case of solids and liquids heated at constant pressure, very little work is done because the thermal expansion is small. Consequently, C_P and C_V are approximately equal for solids and liquids.

Quick Quiz 21.4   How does the internal energy of an ideal gas change as it follows path $i \to f$ in Figure 21.4? (a) E_{int} increases. (b) E_{int} decreases. (c) E_{int} stays the same. (d) There is not enough information to determine how E_{int} changes.

Quick Quiz 21.5   How does the internal energy of an ideal gas change as it follows path $f \to f'$ along the isotherm labeled $T + \Delta T$ in Figure 21.4? (a) E_{int} increases. (b) E_{int} decreases. (c) E_{int} stays the same. (d) There is not enough information to determine how E_{int} changes.

Example 21.2   Heating a Cylinder of Helium

A cylinder contains 3.00 mol of helium gas at a temperature of 300 K.

(A) If the gas is heated at constant volume, how much energy must be transferred by heat to the gas for its temperature to increase to 500 K?

Solution For the constant-volume process, we have

$$Q_1 = nC_V \Delta T$$

Because $C_V = 12.5$ J/mol · K for helium and $\Delta T = 200$ K, we obtain

$$Q_1 = (3.00 \text{ mol})(12.5 \text{ J/mol} \cdot \text{K})(200 \text{ K})$$

$$= \boxed{7.50 \times 10^3 \text{ J}}$$

(B) How much energy must be transferred by heat to the gas at constant pressure to raise the temperature to 500 K?

Solution Making use of Table 21.2, we obtain

$$Q_2 = nC_P \Delta T$$

$$= (3.00 \text{ mol})(20.8 \text{ J/mol} \cdot \text{K})(200 \text{ K})$$

$$= \boxed{12.5 \times 10^3 \text{ J}}$$

Note that this is larger than Q_1, due to the transfer of energy out of the gas by work in the constant pressure process.

21.3   Adiabatic Processes for an Ideal Gas

As we noted in Section 20.6, an **adiabatic process** is one in which no energy is transferred by heat between a system and its surroundings. For example, if a gas is compressed (or expanded) very rapidly, very little energy is transferred out of (or into) the system by heat, and so the process is nearly adiabatic. Such processes occur in the cycle of a gasoline engine, which we discuss in detail in the next chapter. Another example of an adiabatic process is the very slow expansion of a gas that is thermally insulated from its surroundings.

Suppose that an ideal gas undergoes an adiabatic expansion. At any time during the process, we assume that the gas is in an equilibrium state, so that the equation of state $PV = nRT$ is valid. As we show below, the pressure and volume of an ideal gas at any time during an adiabatic process are related by the expression

$$PV^\gamma = \text{constant} \qquad (21.18)$$

◄ Relationship between *P* and *V* for an adiabatic process involving an ideal gas

where $\gamma = C_P/C_V$ is assumed to be constant during the process. Thus, we see that all three variables in the ideal gas law—*P*, *V*, and *T*—change during an adiabatic process.

Proof That *PV*$^\gamma$ = Constant for an Adiabatic Process

When a gas is compressed adiabatically in a thermally insulated cylinder, no energy is transferred by heat between the gas and its surroundings; thus, $Q = 0$. Let us imagine an infinitesimal change in volume dV and an accompanying infinitesimal change in temperature dT. The work done on the gas is $-P \, dV$. Because the internal energy of an ideal gas depends only on temperature, the change in the internal energy in an adiabatic process is the same as that for an isovolumetric process between the same temperatures, $dE_{\text{int}} = nC_V \, dT$ (Eq. 21.12). Hence, the first law of thermodynamics, $\Delta E_{\text{int}} = Q + W$, with $Q = 0$ becomes
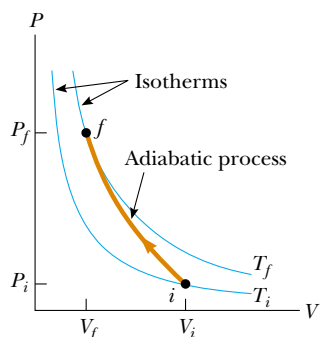
$$dE_{\text{int}} = nC_V \, dT = -P \, dV$$

Taking the total differential of the equation of state of an ideal gas, $PV = nRT$, we see that

$$P \, dV + V \, dP = nR \, dT$$

Eliminating dT from these two equations, we find that

$$P \, dV + V \, dP = -\frac{R}{C_V} P \, dV$$

Figure 21.5 The *PV* diagram for an adiabatic compression. Note that $T_f > T_i$ in this process, so the temperature of the gas increases.

Relationship between *T* and *V* for an adiabatic process involving an ideal gas

Substituting $R = C_P - C_V$ and dividing by PV, we obtain

$$\frac{dV}{V} + \frac{dP}{P} = -\left(\frac{C_P - C_V}{C_V}\right)\frac{dV}{V} = (1 - \gamma)\frac{dV}{V}$$

$$\frac{dP}{P} + \gamma\frac{dV}{V} = 0$$

Integrating this expression, we have

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

which is equivalent to Equation 21.18:

$$PV^\gamma = \text{constant}$$

The *PV* diagram for an adiabatic compression is shown in Figure 21.5. Because $\gamma > 1$, the *PV* curve is steeper than it would be for an isothermal compression. By the definition of an adiabatic process, no energy is transferred by heat into or out of the system. Hence, from the first law, we see that ΔE_{int} is positive (work is done on the gas, so its internal energy increases) and so ΔT also is positive. Thus, the temperature of the gas increases ($T_f > T_i$) during an adiabatic compression. Conversely, the temperature decreases if the gas expands adiabatically.[1] Applying Equation 21.18 to the initial and final states, we see that

$$P_iV_i{}^\gamma = P_fV_f{}^\gamma \tag{21.19}$$

Using the ideal gas law, we can express Equation 21.19 as

$$T_iV_i{}^{\gamma-1} = T_fV_f{}^{\gamma-1} \tag{21.20}$$

Example 21.3 A Diesel Engine Cylinder

Air at 20.0°C in the cylinder of a diesel engine is compressed from an initial pressure of 1.00 atm and volume of 800.0 cm³ to a volume of 60.0 cm³. Assume that air behaves as an ideal gas with $\gamma = 1.40$ and that the compression is adiabatic. Find the final pressure and temperature of the air.

Solution Conceptualize by imagining what happens if we compress a gas into a smaller volume. Our discussion above and Figure 21.5 tell us that the pressure and temperature both increase. We categorize this as a problem involving an adiabatic compression. To analyze the problem, we use Equation 21.19 to find the final pressure:

$$P_f = P_i\left(\frac{V_i}{V_f}\right)^\gamma = (1.00 \text{ atm})\left(\frac{800.0 \text{ cm}^3}{60.0 \text{ cm}^3}\right)^{1.40}$$

$$= \boxed{37.6 \text{ atm}}$$

Because $PV = nRT$ is valid throughout an ideal gas process and because no gas escapes from the cylinder,

$$\frac{P_iV_i}{T_i} = \frac{P_fV_f}{T_f}$$

$$T_f = \frac{P_fV_f}{P_iV_i}T_i = \frac{(37.6 \text{ atm})(60.0 \text{ cm}^3)}{(1.00 \text{ atm})(800.0 \text{ cm}^3)}(293 \text{ K})$$

$$= 826 \text{ K} = \boxed{553°C}$$

To finalize the problem, note that the temperature of the gas has increased by a factor of 2.82. The high compression in a diesel engine raises the temperature of the fuel enough to cause its combustion without the use of spark plugs.

21.4 The Equipartition of Energy

We have found that predictions based on our model for molar specific heat agree quite well with the behavior of monatomic gases but not with the behavior of complex gases (see Table 21.2). The value predicted by the model for the quantity $C_P - C_V = R$, however, is the same for all gases. This is not surprising because this difference is the result of the work done on the gas, which is independent of its molecular structure.

---

[1] In the adiabatic free expansion discussed in Section 20.6, the temperature remains constant. This is a special process in which no work is done because the gas expands into a vacuum. In general, the temperature decreases in an adiabatic expansion in which work is done.

To clarify the variations in C_V and C_P in gases more complex than monatomic gases, let us explore further the origin of molar specific heat. So far, we have assumed that the sole contribution to the internal energy of a gas is the translational kinetic energy of the molecules. However, the internal energy of a gas includes contributions from the translational, vibrational, and rotational motion of the molecules. The rotational and vibrational motions of molecules can be activated by collisions and therefore are "coupled" to the translational motion of the molecules. The branch of physics known as *statistical mechanics* has shown that, for a large number of particles obeying the laws of Newtonian mechanics, the available energy is, on the average, shared equally by each independent degree of freedom. Recall from Section 21.1 that the equipartition theorem states that, at equilibrium, each degree of freedom contributes $\frac{1}{2}k_B T$ of energy per molecule.

Let us consider a diatomic gas whose molecules have the shape of a dumbbell (Fig. 21.6). In this model, the center of mass of the molecule can translate in the x, y, and z directions (Fig. 21.6a). In addition, the molecule can rotate about three mutually perpendicular axes (Fig. 21.6b). We can neglect the rotation about the y axis because the molecule's moment of inertia I_y and its rotational energy $\frac{1}{2}I_y\omega^2$ about this axis are negligible compared with those associated with the x and z axes. (If the two atoms are taken to be point masses, then I_y is identically zero.) Thus, there are five degrees of freedom for translation and rotation: three associated with the translational motion and two associated with the rotational motion. Because each degree of freedom contributes, on the average, $\frac{1}{2}k_B T$ of energy per molecule, the internal energy for a system of N molecules, ignoring vibration for now, is

$$E_{int} = 3N(\tfrac{1}{2}k_B T) + 2N(\tfrac{1}{2}k_B T) = \tfrac{5}{2}Nk_B T = \tfrac{5}{2}nRT$$

We can use this result and Equation 21.13 to find the molar specific heat at constant volume:

$$C_V = \frac{1}{n}\frac{dE_{int}}{dT} = \frac{1}{n}\frac{d}{dT}(\tfrac{5}{2}nRT) = \tfrac{5}{2}R \qquad (21.21)$$

From Equations 21.16 and 21.17, we find that

$$C_P = C_V + R = \tfrac{7}{2}R$$

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

These results agree quite well with most of the data for diatomic molecules given in Table 21.2. This is rather surprising because we have not yet accounted for the possible vibrations of the molecule.

In the model for vibration, the two atoms are joined by an imaginary spring (see Fig. 21.6c). The vibrational motion adds two more degrees of freedom, which correspond to the kinetic energy and the potential energy associated with vibrations along the length of the molecule. Hence, classical physics and the equipartition theorem in a model that includes all three types of motion predict a total internal energy of

$$E_{int} = 3N(\tfrac{1}{2}k_B T) + 2N(\tfrac{1}{2}k_B T) + 2N(\tfrac{1}{2}k_B T) = \tfrac{7}{2}Nk_B T = \tfrac{7}{2}nRT$$

and a molar specific heat at constant volume of

$$C_V = \frac{1}{n}\frac{dE_{int}}{dT} = \frac{1}{n}\frac{d}{dT}(\tfrac{7}{2}nRT) = \tfrac{7}{2}R \qquad (21.22)$$

This value is inconsistent with experimental data for molecules such as H_2 and N_2 (see Table 21.2) and suggests a breakdown of our model based on classical physics.

It might seem that our model is a failure for predicting molar specific heats for diatomic gases. We can claim some success for our model, however, if measurements of molar specific heat are made over a wide temperature range, rather than at the
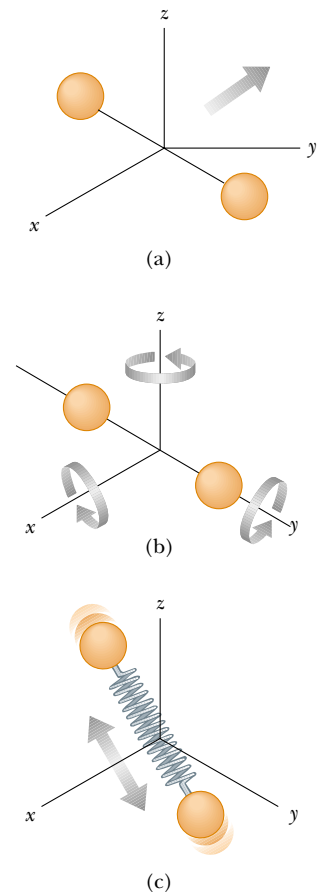
Figure 21.6 Possible motions of a diatomic molecule: (a) translational motion of the center of mass, (b) rotational motion about the various axes, and (c) vibrational motion along the molecular axis.
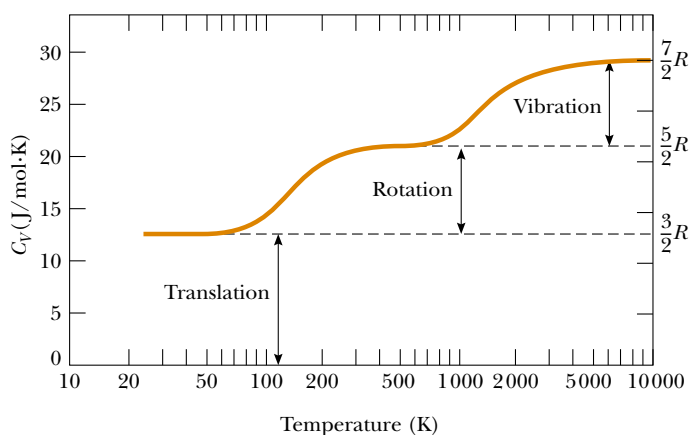
Figure 21.7 The molar specific heat of hydrogen as a function of temperature. The horizontal scale is logarithmic. Note that hydrogen liquefies at 20 K.

single temperature that gives us the values in Table 21.2. Figure 21.7 shows the molar specific heat of hydrogen as a function of temperature. There are three plateaus in the curve. The remarkable feature of these plateaus is that they are at the values of the molar specific heat predicted by Equations 21.14, 21.21, and 21.22! For low temperatures, the diatomic hydrogen gas behaves like a monatomic gas. As the temperature rises to room temperature, its molar specific heat rises to a value for a diatomic gas, consistent with the inclusion of rotation but not vibration. For high temperatures, the molar specific heat is consistent with a model including all types of motion.

Before addressing the reason for this mysterious behavior, let us make a brief remark about polyatomic gases. For molecules with more than two atoms, the vibrations are more complex than for diatomic molecules and the number of degrees of freedom is even larger. This results in an even higher predicted molar specific heat, which is in qualitative agreement with experiment. For the polyatomic gases shown in Table 21.2 we see that the molar specific heats are higher than those for diatomic gases. The more degrees of freedom available to a molecule, the more "ways" there are to store energy, resulting in a higher molar specific heat.

A Hint of Energy Quantization

Our model for molar specific heats has been based so far on purely classical notions. It predicts a value of the specific heat for a diatomic gas that, according to Figure 21.7, only agrees with experimental measurements made at high temperatures. In order to explain why this value is only true at high temperatures and why the plateaus exist in Figure 21.7, we must go beyond classical physics and introduce some quantum physics into the model. In Chapter 18, we discussed quantization of frequency for vibrating strings and air columns. This is a natural result whenever waves are subject to boundary conditions.

Quantum physics (Chapters 40 to 43) shows that atoms and molecules can be described by the physics of waves under boundary conditions. Consequently, these waves have quantized frequencies. Furthermore, in quantum physics, the energy of a system is proportional to the frequency of the wave representing the system. Hence, **the energies of atoms and molecules are quantized.**

For a molecule, quantum physics tells us that the rotational and vibrational energies are quantized. Figure 21.8 shows an **energy-level diagram** for the rotational and vibrational quantum states of a diatomic molecule. The lowest allowed state is called the **ground state**. Notice that vibrational states are separated by larger energy gaps than are rotational states.
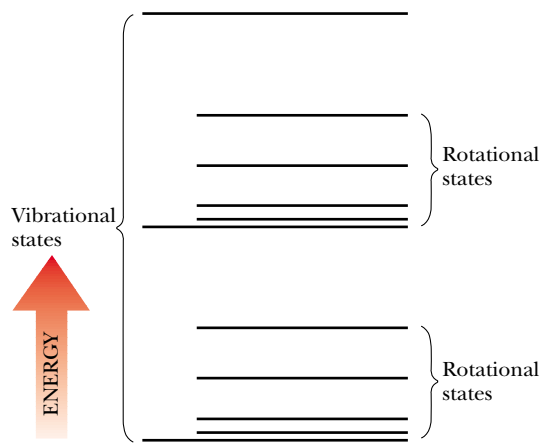
Figure 21.8 An energy-level diagram for vibrational and rotational states of a diatomic molecule. Note that the rotational states lie closer together in energy than the vibrational states.

At low temperatures, the energy that a molecule gains in collisions with its neighbors is generally not large enough to raise it to the first excited state of either rotation or vibration. Thus, even though rotation and vibration are classically allowed, they do not occur at low temperatures. All molecules are in the ground state for rotation and vibration. Thus, the only contribution to the molecules' average energy is from translation, and the specific heat is that predicted by Equation 21.14.

As the temperature is raised, the average energy of the molecules increases. In some collisions, a molecule may have enough energy transferred to it from another molecule to excite the first rotational state. As the temperature is raised further, more molecules can be excited to this state. The result is that rotation begins to contribute to the internal energy and the molar specific heat rises. At about room temperature in Figure 21.7, the second plateau has been reached and rotation contributes fully to the molar specific heat. The molar specific heat is now equal to the value predicted by Equation 21.21.

There is no contribution at room temperature from vibration, because the molecules are still in the ground vibrational state. The temperature must be raised even further to excite the first vibrational state. This happens in Figure 21.7 between 1 000 K and 10 000 K. At 10 000 K on the right side of the figure, vibration is contributing fully to the internal energy and the molar specific heat has the value predicted by Equation 21.22.

The predictions of this model are supportive of the theorem of equipartition of energy. In addition, the inclusion in the model of energy quantization from quantum physics allows a full understanding of Figure 21.7.

> **Quick Quiz 21.6** The molar specific heat of a diatomic gas is measured at constant volume and found to be 29.1 J/mol·K. The types of energy that are contributing to the molar specific heat are (a) translation only (b) translation and rotation only (c) translation and vibration only (d) translation, rotation, and vibration.
>
> **Quick Quiz 21.7** The molar specific heat of a gas is measured at constant volume and found to be $11R/2$. The gas is most likely to be (a) monatomic (b) diatomic   (c) polyatomic.

The Molar Specific Heat of Solids

The molar specific heats of solids also demonstrate a marked temperature dependence. Solids have molar specific heats that generally decrease in a nonlinear manner with decreasing temperature and approach zero as the temperature approaches
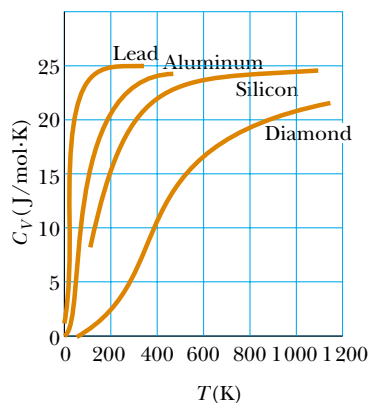
Figure 21.9 Molar specific heat of four solids. As T approaches zero, the molar specific heat also approaches zero.

absolute zero. At high temperatures (usually above 300 K), the molar specific heats approach the value of $3R \approx 25$ J/mol·K, a result known as the *DuLong–Petit law*. The typical data shown in Figure 21.9 demonstrate the temperature dependence of the molar specific heats for several solids.

We can explain the molar specific heat of a solid at high temperatures using the equipartition theorem. For small displacements of an atom from its equilibrium position, each atom executes simple harmonic motion in the x, y, and z directions. The energy associated with vibrational motion in the x direction is

$$E = \tfrac{1}{2}mv_x^2 + \tfrac{1}{2}kx^2$$

The expressions for vibrational motions in the y and z directions are analogous. Therefore, each atom of the solid has six degrees of freedom. According to the equipartition theorem, this corresponds to an average vibrational energy of $6(\tfrac{1}{2}k_B T) = 3k_B T$ per atom. Therefore, the internal energy of a solid consisting of N atoms is

Total internal energy of a solid

$$E_{int} = 3Nk_B T = 3nRT \tag{21.23}$$

From this result, we find that the molar specific heat of a solid at constant volume is

Molar specific heat of a solid at constant volume

$$C_V = \frac{1}{n}\frac{dE_{int}}{dT} = 3R \tag{21.24}$$

This result is in agreement with the empirical DuLong–Petit law. The discrepancies between this model and the experimental data at low temperatures are again due to the inadequacy of classical physics in describing the world at the atomic level.

21.5 The Boltzmann Distribution Law

Thus far we have considered only average values of the energies of molecules in a gas and have not addressed the distribution of energies among molecules. In reality, the motion of the molecules is extremely chaotic. Any individual molecule is colliding with others at an enormous rate—typically, a billion times per second. Each collision results in a change in the speed and direction of motion of each of the participant molecules. Equation 21.7 shows that rms molecular speeds increase with increasing temperature. What is the relative number of molecules that possess some characteristic, such as energy within a certain range?

We shall address this question by considering the **number density** $n_V(E)$. This quantity, called a *distribution function*, is defined so that $n_V(E)\ dE$ is the number of molecules per unit volume with energy between E and $E + dE$. (Note that the ratio of the number of molecules that have the desired characteristic to the total number of molecules is the probability that a particular molecule has that characteristic.) In general,

▲ **PITFALL PREVENTION**

21.2 The Distribution Function

Notice that the distribution function $n_V(E)$ is defined in terms of the number of molecules with energy in the range E to $E + dE$ rather than in terms of the number of molecules with energy E. Because the number of molecules is finite and the number of possible values of the energy is infinite, the number of molecules with an *exact* energy E may be zero.

the number density is found from statistical mechanics to be

$$n_V(E) = n_0 e^{-E/k_B T} \qquad (21.25)$$

where n_0 is defined such that $n_0 \, dE$ is the number of molecules per unit volume having energy between $E = 0$ and $E = dE$. This equation, known as the **Boltzmann distribution law,** is important in describing the statistical mechanics of a large number of molecules. It states that **the probability of finding the molecules in a particular energy state varies exponentially as the negative of the energy divided by $k_B T$.** All the molecules would fall into the lowest energy level if the thermal agitation at a temperature T did not excite the molecules to higher energy levels.

### Example 21.4   Thermal Excitation of Atomic Energy Levels   `Interactive`

As we discussed in Section 21.4, atoms can occupy only certain discrete energy levels. Consider a gas at a temperature of 2 500 K whose atoms can occupy only two energy levels separated by 1.50 eV, where 1 eV (electron volt) is an energy unit equal to 1.60×10^{-19} J (Fig. 21.10). Determine the ratio of the number of atoms in the higher energy level to the number in the lower energy level.

Solution Equation 21.25 gives the relative number of atoms in a given energy level. In this case, the atom has two possible energies, E_1 and E_2, where E_1 is the lower energy level. Hence, the ratio of the number of atoms in the higher energy level to the number in the lower energy level is

$$(1) \qquad \frac{n_V(E_2)}{n_V(E_1)} = \frac{n_0 e^{-E_2/k_B T}}{n_0 e^{-E_1/k_B T}} = e^{-(E_2 - E_1)/k_B T}$$

In this problem, $E_2 - E_1 = 1.50$ eV, and the denominator of the exponent is

$$k_B T = (1.38 \times 10^{-23} \text{ J/K})(2\,500 \text{ K})\left(\frac{1 \text{ eV}}{1.60 \times 10^{-19} \text{ J}}\right)$$

$$= 0.216 \text{ eV}$$
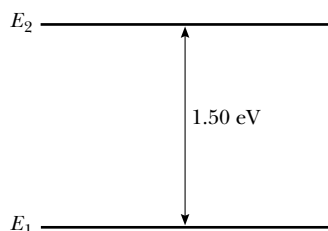
Figure 21.10 (Example 21.4) Energy-level diagram for a gas whose atoms can occupy two energy states.

Therefore, the required ratio is

$$\frac{n_V(E_2)}{n_V(E_1)} = e^{-1.50 \text{ eV}/0.216 \text{ eV}} = e^{-6.94}$$

$$= \boxed{9.64 \times 10^{-4}}$$

This result indicates that at $T = 2\,500$ K, only a small fraction of the atoms are in the higher energy level. In fact, for every atom in the higher energy level, there are about 1 000 atoms in the lower level. The number of atoms in the higher level increases at even higher temperatures, but the distribution law specifies that at equilibrium there are always more atoms in the lower level than in the higher level.

What If? What if the energy levels in Figure 21.10 were closer together in energy? Would this increase or decrease the fraction of the atoms in the upper energy level?

Answer If the excited level is lower in energy than that in Figure 21.10, it would be easier for thermal agitation to excite atoms to this level, and the fraction of atoms in this energy level would be larger. Let us see this mathematically by expressing Equation (1) as

$$r_2 = e^{-(E_2 - E_1)/k_B T}$$

where r_2 is the ratio of atoms having energy E_2 to those with energy E_1. Differentiating with respect to E_2, we find

$$\frac{dr_2}{dE_2} = \frac{d}{dE_2}\left(e^{-(E_2 - E_1)/k_B T}\right) = -\frac{1}{k_B T} e^{-(E_2 - E_1)/k_B T} < 0$$

Because the derivative has a negative value, we see that as E_2 decreases, r_2 increases.

*At the Interactive Worked Example link at **http://www.pse6.com,** you can investigate the effects of changing the temperature and the energy difference between the states.*

21.6 Distribution of Molecular Speeds

In 1860 James Clerk Maxwell (1831–1879) derived an expression that describes the distribution of molecular speeds in a very definite manner. His work and subsequent developments by other scientists were highly controversial because direct detection of molecules could not be achieved experimentally at that time. However, about 60 years later, experiments were devised that confirmed Maxwell's predictions.
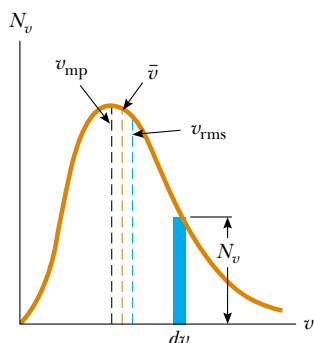
Active Figure 21.11 The speed distribution of gas molecules at some temperature. The number of molecules having speeds in the range v to $v + dv$ is equal to the area of the shaded rectangle, $N_v dv$. The function N_v approaches zero as v approaches infinity.

At the Active Figures link at http://www.pse6.com, *you can move the blue triangle and measure the number of molecules with speeds within a small range.*

Ludwig Boltzmann
Austrian physicist (1844–1906)

Boltzmann made many important contributions to the development of the kinetic theory of gases, electromagnetism, and thermodynamics. His pioneering work in the field of kinetic theory led to the branch of physics known as statistical mechanics. *(Courtesy of AIP Niels Bohr Library, Lande Collection)*

Let us consider a container of gas whose molecules have some distribution of speeds. Suppose we want to determine how many gas molecules have a speed in the range from, for example, 400 to 410 m/s. Intuitively, we expect that the speed distribution depends on temperature. Furthermore, we expect that the distribution peaks in the vicinity of v_{rms}. That is, few molecules are expected to have speeds much less than or much greater than v_{rms} because these extreme speeds result only from an unlikely chain of collisions.

The observed speed distribution of gas molecules in thermal equilibrium is shown in Figure 21.11. The quantity N_v, called the **Maxwell–Boltzmann speed distribution function,** is defined as follows. If N is the total number of molecules, then the number of molecules with speeds between v and $v + dv$ is $dN = N_v\, dv$. This number is also equal to the area of the shaded rectangle in Figure 21.11. Furthermore, the fraction of molecules with speeds between v and $v + dv$ is $(N_v\, dv)/N$. This fraction is also equal to the probability that a molecule has a speed in the range v to $v + dv$.

The fundamental expression that describes the distribution of speeds of N gas molecules is

$$N_v = 4\pi N \left(\frac{m}{2\pi k_B T} \right)^{3/2} v^2 e^{-mv^2/2k_B T} \tag{21.26}$$

where m is the mass of a gas molecule, k_B is Boltzmann's constant, and T is the absolute temperature.[2] Observe the appearance of the Boltzmann factor $e^{-E/k_B T}$ with $E = \frac{1}{2}mv^2$.

As indicated in Figure 21.11, the average speed is somewhat lower than the rms speed. The *most probable speed* v_{mp} is the speed at which the distribution curve reaches a peak. Using Equation 21.26, one finds that

$$v_{rms} = \sqrt{\overline{v^2}} = \sqrt{\frac{3k_B T}{m}} = 1.73 \sqrt{\frac{k_B T}{m}} \tag{21.27}$$

$$\overline{v} = \sqrt{\frac{8k_B T}{\pi m}} = 1.60 \sqrt{\frac{k_B T}{m}} \tag{21.28}$$

$$v_{mp} = \sqrt{\frac{2k_B T}{m}} = 1.41 \sqrt{\frac{k_B T}{m}} \tag{21.29}$$
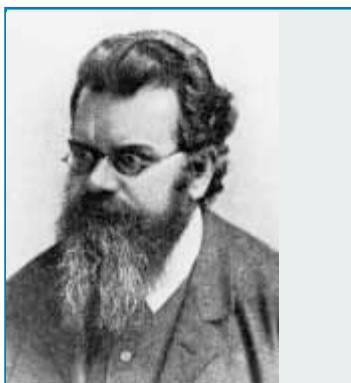
Equation 21.27 has previously appeared as Equation 21.7. The details of the derivations of these equations from Equation 21.26 are left for the student (see Problems 39 and 65). From these equations, we see that

$$v_{rms} > \overline{v} > v_{mp}$$

Figure 21.12 represents speed distribution curves for nitrogen, N_2. The curves were obtained by using Equation 21.26 to evaluate the distribution function at various speeds and at two temperatures. Note that the peak in the curve shifts to the right as T increases, indicating that the average speed increases with increasing temperature, as expected. The asymmetric shape of the curves is due to the fact that the lowest speed possible is zero while the upper classical limit of the speed is infinity. (In Chapter 39, we will show that the actual upper limit is the speed of light.)

Equation 21.26 shows that the distribution of molecular speeds in a gas depends both on mass and on temperature. At a given temperature, the fraction of molecules with speeds exceeding a fixed value increases as the mass decreases. This explains why lighter molecules, such as H_2 and He, escape more readily from the Earth's atmosphere than do heavier molecules, such as N_2 and O_2. (See the discussion of escape speed in Chapter 13. Gas molecules escape even more readily from the Moon's surface than from the Earth's because the escape speed on the Moon is lower than that on the Earth.)

The speed distribution curves for molecules in a liquid are similar to those shown in Figure 21.12. We can understand the phenomenon of evaporation of a liquid from this distribution in speeds, using the fact that some molecules in the liquid are more
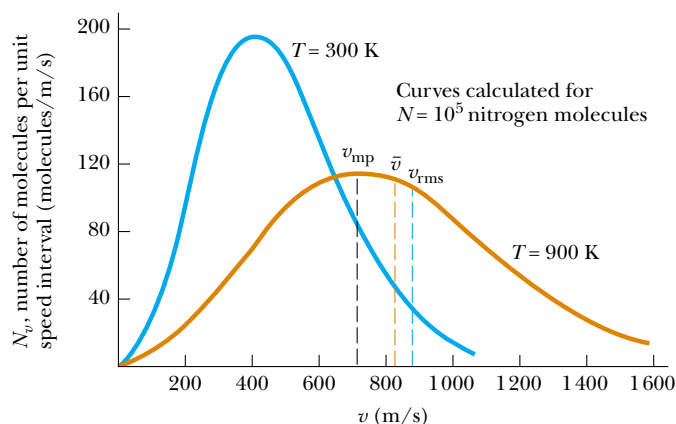
---

[2] For the derivation of this expression, see an advanced textbook on thermodynamics, such as that by R. P. Bauman, *Modern Thermodynamics with Statistical Mechanics*, New York, Macmillan Publishing Co., 1992.

Active Figure 21.12 The speed distribution function for 10^5 nitrogen molecules at 300 K and 900 K. The total area under either curve is equal to the total number of molecules, which in this case equals 10^5. Note that $v_{rms} > \bar{v} > v_{mp}$.

energetic than others. Some of the faster-moving molecules in the liquid penetrate the surface and leave the liquid even at temperatures well below the boiling point. The molecules that escape the liquid by evaporation are those that have sufficient energy to overcome the attractive forces of the molecules in the liquid phase. Consequently, the molecules left behind in the liquid phase have a lower average kinetic energy; as a result, the temperature of the liquid decreases. Hence, evaporation is a cooling process. For example, an alcohol-soaked cloth often is placed on a feverish head to cool and comfort a patient.

Quick Quiz 21.8 Consider the qualitative shapes of the two curves in Figure 21.12, without regard for the numerical values or labels in the graph. Suppose you have two containers of gas *at the same temperature.* Container A has 10^5 nitrogen molecules and container B has 10^5 hydrogen molecules. The correct qualitative matching between the containers and the two curves in Figure 21.12 is (a) container A corresponds to the blue curve and container B to the brown curve (b) container B corresponds to the blue curve and container A to the brown curve (c) both containers correspond to the same curve.

Example 21.5   A System of Nine Particles

Nine particles have speeds of 5.00, 8.00, 12.0, 12.0, 12.0, 14.0, 14.0, 17.0, and 20.0 m/s.

(A) Find the particles' average speed.

Solution The average speed of the particles is the sum of the speeds divided by the total number of particles:

$$\bar{v} = \frac{(5.00 + 8.00 + 12.0 + 12.0 + 12.0 + 14.0 + 14.0 + 17.0 + 20.0) \text{ m/s}}{9}$$

$$= \boxed{12.7 \text{ m/s}}$$

(B) What is the rms speed of the particles?

Solution The average value of the square of the speed is

$$\overline{v^2} = \frac{(5.00^2 + 8.00^2 + 12.0^2 + 12.0^2 + 12.0^2 + 14.0^2 + 14.0^2 + 17.0^2 + 20.0^2) \text{ m}^2/\text{s}^2}{9}$$

$$= 178 \text{ m}^2/\text{s}^2$$
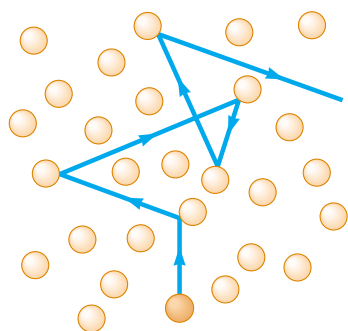
Hence, the rms speed of the particles is

$$v_{rms} = \sqrt{\overline{v^2}} = \sqrt{178 \text{ m}^2/\text{s}^2} = \boxed{13.3 \text{ m/s}}$$

(C) What is the most probable speed of the particles?

Solution Three of the particles have a speed of 12.0 m/s, two have a speed of 14.0 m/s, and the remaining have different speeds. Hence, we see that the most probable speed v_{mp} is $\boxed{12.0 \text{ m/s.}}$

Figure 21.13 A molecule moving through a gas collides with other molecules in a random fashion. This behavior is sometimes referred to as a *random-walk process*. The mean free path increases as the number of molecules per unit volume decreases. Note that the motion is not limited to the plane of the paper.

21.7 Mean Free Path

Most of us are familiar with the fact that the strong odor associated with a gas such as ammonia may take a fraction of a minute to diffuse throughout a room. However, because average molecular speeds are typically several hundred meters per second at room temperature, we might expect a diffusion time of much less than one second. The reason for this difference is that molecules collide with one other because they are not geometrical points. Therefore, they do not travel from one side of a room to the other in a straight line. Between collisions, the molecules move with constant speed along straight lines. The average distance between collisions is called the **mean free path**. The path of an individual molecule is random and resembles that shown in Figure 21.13. As we would expect from this description, the mean free path is related to the diameter of the molecules and the density of the gas.

We now describe how to estimate the mean free path for a gas molecule. For this calculation, we assume that the molecules are spheres of diameter d. We see from Figure 21.14a that no two molecules collide unless their paths, assumed perpendicular to the page in Figure 21.14a are less than a distance d apart as the molecules approach each other. An equivalent way to describe the collisions is to imagine that one of the molecules has a diameter $2d$ and that the rest are geometrical points (Fig. 21.14b). Let us choose the large molecule to be one moving with the average speed $\overline{v}$. In a time interval Δt, this molecule travels a distance $\overline{v}\,\Delta t$. In this time interval, the molecule sweeps out a cylinder having a cross-sectional area πd^2 and a length $\overline{v}\,\Delta t$ (Fig. 21.15). Hence, the volume of the cylinder is $\pi d^2\overline{v}\,\Delta t$. If n_V is the number of molecules per unit volume, then the number of point-size molecules in the cylinder is $(\pi d^2\overline{v}\,\Delta t)\,n_V$. The molecule of equivalent diameter $2d$ collides with every molecule in this cylinder in the time interval Δt. Hence, the number of collisions in the time interval Δt is equal to the number of molecules in the cylinder, $(\pi d^2\overline{v}\,\Delta t)\,n_V$.

The mean free path ℓ equals the average distance $\overline{v}\,\Delta t$ traveled in a time interval Δt divided by the number of collisions that occur in that time interval:

$$\ell = \frac{\overline{v}\,\Delta t}{(\pi d^2\,\overline{v}\,\Delta t)\,n_V} = \frac{1}{\pi d^2 n_V}$$

Because the number of collisions in a time interval Δt is $(\pi d^2\overline{v}\,\Delta t)\,n_V$, the number of collisions per unit time interval, or **collision frequency f,** is

$$f = \pi d^2\overline{v} n_V$$

The inverse of the collision frequency is the average time interval between collisions, known as the **mean free time.**
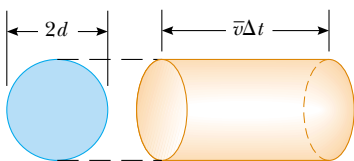
Our analysis has assumed that molecules in the cylinder are stationary. When the motion of these molecules is included in the calculation, the correct results are

Mean free path
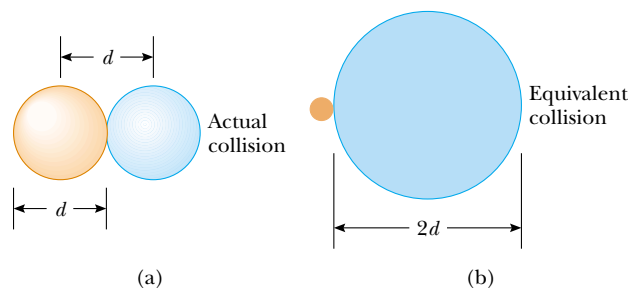
$$\ell = \frac{1}{\sqrt{2}\,\pi d^2 n_V} \tag{21.30}$$

Collision frequency

$$f = \sqrt{2}\,\pi d^2\overline{v} n_V = \frac{\overline{v}}{\ell} \tag{21.31}$$

Figure 21.15 In a time interval Δt, a molecule of effective diameter $2d$ and moving to the right sweeps out a cylinder of length $\overline{v}\Delta t$ where $\overline{v}$ is its average speed. In this time interval, it collides with every point molecule within this cylinder.

Figure 21.14 (a) Two spherical molecules, each of diameter d and moving along paths perpendicular to the page, collide if their paths are within a distance d of each other. (b) The collision between the two molecules is equivalent to a point molecule colliding with a molecule having an effective diameter of $2d$.

Example 21.6   **Bouncing Around in the Air**

Approximate the air around you as a collection of nitrogen molecules, each having a diameter of 2.00×10^{-10} m.

(A) How far does a typical molecule move before it collides with another molecule?

Solution Assuming that the gas is ideal, we can use the equation $PV = Nk_BT$ to obtain the number of molecules per unit volume under typical room conditions:

$$n_V = \frac{N}{V} = \frac{P}{k_BT} = \frac{1.01 \times 10^5 \text{ N/m}^2}{(1.38 \times 10^{-23} \text{ J/K})(293 \text{ K})}$$

$$= 2.50 \times 10^{25} \text{ molecules/m}^3$$

Hence, the mean free path is

$$\ell = \frac{1}{\sqrt{2}\pi d^2 n_V}$$

$$= \frac{1}{\sqrt{2}\pi(2.00 \times 10^{-10} \text{ m})^2(2.50 \times 10^{25} \text{ molecules/m}^3)}$$

$$= \boxed{2.25 \times 10^{-7} \text{ m}}$$

This value is about 10^3 times greater than the molecular diameter.

(B) On average, how frequently does one molecule collide with another?

Solution Because the rms speed of a nitrogen molecule at 20.0°C is 511 m/s (see Table 21.1), we know from Equations 21.27 and 21.28 that $\bar{v} = (1.60/1.73)(511 \text{ m/s}) = 473$ m/s. Therefore, the collision frequency is

$$f = \frac{\bar{v}}{\ell} = \frac{473 \text{ m/s}}{2.25 \times 10^{-7} \text{ m}} = \boxed{2.10 \times 10^9/\text{s}}$$

The molecule collides with other molecules at the average rate of about two billion times each second!

The mean free path ℓ is *not* the same as the average separation between particles. In fact, the average separation d between particles is approximately $n_V^{-1/3}$. In this example, the average molecular separation is

$$d = \frac{1}{n_V^{1/3}} = \frac{1}{(2.5 \times 10^{25})^{1/3}} = 3.4 \times 10^{-9} \text{ m}$$

SUMMARY

The pressure of N molecules of an ideal gas contained in a volume V is

$$P = \tfrac{2}{3}\frac{N}{V}(\tfrac{1}{2}m\overline{v^2}) \tag{21.2}$$

The average translational kinetic energy per molecule of a gas, $\tfrac{1}{2}m\overline{v^2}$, is related to the temperature T of the gas through the expression

$$\tfrac{1}{2}m\overline{v^2} = \tfrac{3}{2}k_BT \tag{21.4}$$

where k_B is Boltzmann's constant. Each translational degree of freedom (x, y, or z) has $\tfrac{1}{2}k_BT$ of energy associated with it.

The **theorem of equipartition of energy** states that the energy of a system in thermal equilibrium is equally divided among all degrees of freedom.

The internal energy of N molecules (or n mol) of an ideal monatomic gas is

$$E_{\text{int}} = \tfrac{3}{2}Nk_BT = \tfrac{3}{2}nRT \tag{21.10}$$

The change in internal energy for n mol of any ideal gas that undergoes a change in temperature ΔT is

$$\Delta E_{\text{int}} = nC_V\Delta T \tag{21.12}$$

where C_V is the molar specific heat at constant volume.

The molar specific heat of an ideal monatomic gas at constant volume is $C_V = \tfrac{3}{2}R$; the molar specific heat at constant pressure is $C_P = \tfrac{5}{2}R$. The ratio of specific heats is given by $\gamma = C_P/C_V = \tfrac{5}{3}$.

If an ideal gas undergoes an adiabatic expansion or compression, the first law of thermodynamics, together with the equation of state, shows that

$$PV^\gamma = \text{constant} \tag{21.18}$$

Take a practice test for this chapter by clicking on the Practice Test link at http://www.pse6.com.

The **Boltzmann distribution law** describes the distribution of particles among available energy states. The relative number of particles having energy between E and $E + dE$ is $n_V(E) \, dE$, where

$$n_V(E) = n_0 e^{-E/k_B T} \tag{21.25}$$

The **Maxwell–Boltzmann speed distribution function** describes the distribution of speeds of molecules in a gas:

$$N_v = 4\pi N \left(\frac{m}{2\pi k_B T} \right)^{3/2} v^2 e^{-mv^2/2k_B T} \tag{21.26}$$

This expression enables us to calculate the **root-mean-square speed,** the **average speed,** and **the most probable speed:**

$$v_{\text{rms}} = \sqrt{\overline{v^2}} = \sqrt{\frac{3k_B T}{m}} = 1.73 \sqrt{\frac{k_B T}{m}} \tag{21.27}$$

$$\overline{v} = \sqrt{\frac{8k_B T}{\pi m}} = 1.60 \sqrt{\frac{k_B T}{m}} \tag{21.28}$$

$$v_{\text{mp}} = \sqrt{\frac{2k_B T}{m}} = 1.41 \sqrt{\frac{k_B T}{m}} \tag{21.29}$$

QUESTIONS

1. Dalton's law of partial pressures states that the total pressure of a mixture of gases is equal to the sum of the partial pressures of gases making up the mixture. Give a convincing argument for this law based on the kinetic theory of gases.

2. One container is filled with helium gas and another with argon gas. If both containers are at the same temperature, which molecules have the higher rms speed? Explain.

3. A gas consists of a mixture of He and N_2 molecules. Do the lighter He molecules travel faster than the N_2 molecules? Explain.

4. Although the average speed of gas molecules in thermal equilibrium at some temperature is greater than zero, the average velocity is zero. Explain why this statement must be true.

5. When alcohol is rubbed on your body, it lowers your skin temperature. Explain this effect.

6. A liquid partially fills a container. Explain why the temperature of the liquid decreases if the container is then partially evacuated. (Using this technique, it is possible to freeze water at temperatures above 0°C.)

7. A vessel containing a fixed volume of gas is cooled. Does the mean free path of the molecules increase, decrease, or remain constant in the cooling process? What about the collision frequency?

8. A gas is compressed at a constant temperature. What happens to the mean free path of the molecules in this process?

9. If a helium-filled balloon initially at room temperature is placed in a freezer, will its volume increase, decrease, or remain the same?

10. Which is denser, dry air or air saturated with water vapor? Explain.

11. What happens to a helium-filled balloon released into the air? Will it expand or contract? Will it stop rising at some height?

12. Why does a diatomic gas have a greater energy content per mole than a monatomic gas at the same temperature?

13. An ideal gas is contained in a vessel at 300 K. If the temperature is increased to 900 K, by what factor does each one of the following change? (a) The average kinetic energy of the molecules. (b) The rms molecular speed. (c) The average momentum change of one molecule in a collision with a wall. (d) The rate of collisions of molecules with walls. (e) The pressure of the gas.

14. A vessel is filled with gas at some equilibrium pressure and temperature. Can all gas molecules in the vessel have the same speed?

15. In our model of the kinetic theory of gases, molecules were viewed as hard spheres colliding elastically with the walls of the container. Is this model realistic?

16. In view of the fact that hot air rises, why does it generally become cooler as you climb a mountain? (Note that air has low thermal conductivity.)

17. Inspecting the magnitudes of C_V and C_P for the diatomic and polyatomic gases in Table 21.2, we find that the values increase with increasing molecular mass. Give a qualitative explanation of this observation.

PROBLEMS

1, **2**, **3** = straightforward, intermediate, challenging   ☐ = full solution available in the *Student Solutions Manual and Study Guide*

🌐 = coached solution with hints available at http://www.pse6.com   🖳 = computer useful in solving problem

▨ = paired numerical and symbolic problems

Section 21.1 Molecular Model of an Ideal Gas

1. In a 30.0-s interval, 500 hailstones strike a glass window of area 0.600 m^2 at an angle of 45.0° to the window surface. Each hailstone has a mass of 5.00 g and moves with a speed of 8.00 m/s. Assuming the collisions are elastic, find the average force and pressure on the window.

2. In a period of 1.00 s, 5.00×10^{23} nitrogen molecules strike a wall with an area of 8.00 cm^2. If the molecules move with a speed of 300 m/s and strike the wall head-on in elastic collisions, what is the pressure exerted on the wall? (The mass of one N$_2$ molecule is 4.68×10^{-26} kg.)

3. A sealed cubical container 20.0 cm on a side contains three times Avogadro's number of molecules at a temperature of 20.0°C. Find the force exerted by the gas on one of the walls of the container.

4. A 2.00-mol sample of oxygen gas is confined to a 5.00-L vessel at a pressure of 8.00 atm. Find the average translational kinetic energy of an oxygen molecule under these conditions.

5. A spherical balloon of volume 4 000 cm^3 contains helium at an (inside) pressure of 1.20×10^5 Pa. How many moles of helium are in the balloon if the average kinetic energy of the helium atoms is 3.60×10^{-22} J?

6. Use the definition of Avogadro's number to find the mass of a helium atom.

7. (a) How many atoms of helium gas fill a balloon having a diameter of 30.0 cm at 20.0°C and 1.00 atm? (b) What is the average kinetic energy of the helium atoms? (c) What is the root-mean-square speed of the helium atoms?

8. Given that the rms speed of a helium atom at a certain temperature is 1 350 m/s, find by proportion the rms speed of an oxygen (O$_2$) molecule at this temperature. The molar mass of O$_2$ is 32.0 g/mol, and the molar mass of He is 4.00 g/mol.

9. 🌐 A cylinder contains a mixture of helium and argon gas in equilibrium at 150°C. (a) What is the average kinetic energy for each type of gas molecule? (b) What is the root-mean-square speed of each type of molecule?

10. A 5.00-L vessel contains nitrogen gas at 27.0°C and a pressure of 3.00 atm. Find (a) the total translational kinetic energy of the gas molecules and (b) the average kinetic energy per molecule.

11. (a) Show that 1 Pa = 1 J/m^3. (b) Show that the density in space of the translational kinetic energy of an ideal gas is $3P/2$.

Section 21.2 Molar Specific Heat of an Ideal Gas

Note: You may use data in Table 21.2 about particular gases. Here we define a "monatomic ideal gas" to have molar specific heats $C_V = 3R/2$ and $C_P = 5R/2$, and a "diatomic ideal gas" to have $C_V = 5R/2$ and $C_P = 7R/2$.

12. Calculate the change in internal energy of 3.00 mol of helium gas when its temperature is increased by 2.00 K.

13. 🌐 A 1.00-mol sample of hydrogen gas is heated at constant pressure from 300 K to 420 K. Calculate (a) the energy transferred to the gas by heat, (b) the increase in its internal energy, and (c) the work done on the gas.

14. A 1.00-mol sample of air (a diatomic ideal gas) at 300 K, confined in a cylinder under a heavy piston, occupies a volume of 5.00 L. Determine the final volume of the gas after 4.40 kJ of energy is transferred to the air by heat.

15. In a constant-volume process, 209 J of energy is transferred by heat to 1.00 mol of an ideal monatomic gas initially at 300 K. Find (a) the increase in internal energy of the gas, (b) the work done on it, and (c) its final temperature.

16. A house has well-insulated walls. It contains a volume of 100 m^3 of air at 300 K. (a) Calculate the energy required to increase the temperature of this diatomic ideal gas by 1.00°C. (b) **What If?** If this energy could be used to lift an object of mass m through a height of 2.00 m, what is the value of m?

17. An incandescent lightbulb contains a volume V of argon at pressure P_i. The bulb is switched on and constant power $\mathcal{P}$ is transferred to the argon for a time interval Δt. (a) Show that the pressure P_f in the bulb at the end of this process is $P_f = P_i[1 + (\mathcal{P}\Delta tR)/(P_iVC_V)]$. (b) Find the pressure in a spherical light bulb 10.0 cm in diameter 4.00 s after it is switched on, given that it has initial pressure 1.00 atm and that 3.60 W of power is transferred to the gas.

18. A vertical cylinder with a heavy piston contains air at a temperature of 300 K. The initial pressure is 200 kPa, and the initial volume is 0.350 m^3. Take the molar mass of air as 28.9 g/mol and assume that $C_V = 5R/2$. (a) Find the specific heat of air at constant volume in units of J/kg·°C. (b) Calculate the mass of the air in the cylinder. (c) Suppose the piston is held fixed. Find the energy input required to raise the temperature of the air to 700 K. (d) **What If?** Assume again the conditions of the initial state and that the heavy piston is free to move. Find the energy input required to raise the temperature to 700 K.

19. A 1-L Thermos bottle is full of tea at 90°C. You pour out one cup and immediately screw the stopper back on. Make an order-of-magnitude estimate of the change in temperature of the tea remaining in the flask that results from the admission of air at room temperature. State the quantities you take as data and the values you measure or estimate for them.

20. A 1.00-mol sample of a diatomic ideal gas has pressure P and volume V. When the gas is heated, its pressure triples and its volume doubles. This heating process includes two steps, the first at constant pressure and the second at constant volume. Determine the amount of energy transferred to the gas by heat.

21. A 1.00-mol sample of an ideal monatomic gas is at an initial temperature of 300 K. The gas undergoes an isovolumetric process acquiring 500 J of energy by heat. It then undergoes an isobaric process losing this same amount of energy by heat. Determine (a) the new temperature of the gas and (b) the work done on the gas.

22. A vertical cylinder with a movable piston contains 1.00 mol of a diatomic ideal gas. The volume of the gas is V_i, and its temperature is T_i. Then the cylinder is set on a stove and additional weights are piled onto the piston as it moves up, in such a way that the pressure is proportional to the volume and the final volume is $2V_i$. (a) What is the final temperature? (b) How much energy is transferred to the gas by heat?

23. A container has a mixture of two gases: n_1 mol of gas 1 having molar specific heat C_1 and n_2 mol of gas 2 of molar specific heat C_2. (a) Find the molar specific heat of the mixture. (b) **What If?** What is the molar specific heat if the mixture has m gases in the amounts n_1, n_2, n_3, . . . , n_m, with molar specific heats C_1, C_2, C_3, . . . , C_m, respectively?

Section 21.3 Adiabatic Processes for an Ideal Gas

24. During the compression stroke of a certain gasoline engine, the pressure increases from 1.00 atm to 20.0 atm. If the process is adiabatic and the fuel–air mixture behaves as a diatomic ideal gas, (a) by what factor does the volume change and (b) by what factor does the temperature change? (c) Assuming that the compression starts with 0.016 0 mol of gas at 27.0°C, find the values of Q, W, and ΔE_{int} that characterize the process.

25. A 2.00-mol sample of a diatomic ideal gas expands slowly and adiabatically from a pressure of 5.00 atm and a volume of 12.0 L to a final volume of 30.0 L. (a) What is the final pressure of the gas? (b) What are the initial and final temperatures? (c) Find Q, W, and ΔE_{int}.

26. Air (a diatomic ideal gas) at 27.0°C and atmospheric pressure is drawn into a bicycle pump that has a cylinder with an inner diameter of 2.50 cm and length 50.0 cm. The down stroke adiabatically compresses the air, which reaches a gauge pressure of 800 kPa before entering the tire (Fig. P21.26). Determine (a) the volume of the compressed air and (b) the temperature of the compressed air. (c) **What If?** The pump is made of steel and has an inner wall that is 2.00 mm thick. Assume that 4.00 cm of the cylinder's length is allowed to come to thermal equilibrium with the air. What will be the increase in wall temperature?

27. Air in a thundercloud expands as it rises. If its initial temperature is 300 K and no energy is lost by thermal conduction on expansion, what is its temperature when the initial volume has doubled?

28. The largest bottle ever made by blowing glass has a volume of about 0.720 m³. Imagine that this bottle is filled with air that behaves as an ideal diatomic gas. The bottle is held with its opening at the bottom and rapidly submerged into the ocean. No air escapes or mixes with the water. No energy is exchanged with the ocean by heat. (a) If the final volume of the air is 0.240 m³, by what factor does the internal energy of the air increase? (b) If the bottle is submerged so that the air temperature doubles, how much volume is occupied by air?

Figure P21.26

29. A 4.00-L sample of a diatomic ideal gas with specific heat ratio 1.40, confined to a cylinder, is carried through a closed cycle. The gas is initially at 1.00 atm and at 300 K. First, its pressure is tripled under constant volume. Then, it expands adiabatically to its original pressure. Finally, the gas is compressed isobarically to its original volume. (a) Draw a PV diagram of this cycle. (b) Determine the volume of the gas at the end of the adiabatic expansion. (c) Find the temperature of the gas at the start of the adiabatic expansion. (d) Find the temperature at the end of the cycle. (e) What was the net work done on the gas for this cycle?

30. A diatomic ideal gas ($\gamma = 1.40$) confined to a cylinder is put through a closed cycle. Initially the gas is at P_i, V_i, and T_i. First, its pressure is tripled under constant volume. It then expands adiabatically to its original pressure and finally is compressed isobarically to its original volume. (a) Draw a PV diagram of this cycle. (b) Determine the volume at the end of the adiabatic expansion. Find (c) the temperature of the gas at the start of the adiabatic expansion and (d) the temperature at the end of the cycle. (e) What was the net work done on the gas for this cycle?

31. How much work is required to compress 5.00 mol of air at 20.0°C and 1.00 atm to one tenth of the original volume (a) by an isothermal process? (b) by an adiabatic process? (c) What is the final pressure in each of these two cases?

32. During the power stroke in a four-stroke automobile engine, the piston is forced down as the mixture of combustion products and air undergoes an adiabatic expansion (Fig. P21.32). Assume that (1) the engine is running at 2 500 cycles/min, (2) the gauge pressure right before the expansion is 20.0 atm, (3) the volumes of the mixture right before and after the expansion are 50.0 and 400 cm^3, respectively, (4) the time involved in the expansion is one-fourth that of the total cycle, and (5) the mixture behaves like an ideal gas with specific heat ratio 1.40. Find the average power generated during the expansion.
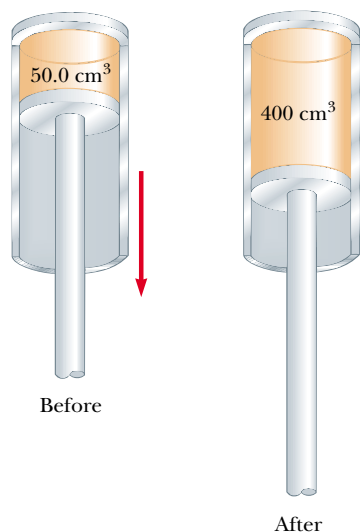

Figure P21.32

Section 21.4   The Equipartition of Energy

33. Consider 2.00 mol of an ideal diatomic gas. (a) Find the total heat capacity of the gas at constant volume and at constant pressure assuming the molecules rotate but do not vibrate. (b) **What If?** Repeat, assuming the molecules both rotate and vibrate.

34. A certain molecule has f degrees of freedom. Show that an ideal gas consisting of such molecules has the following properties: (1) its total internal energy is $fnRT/2$; (2) its molar specific heat at constant volume is $fR/2$; (3) its molar specific heat at constant pressure is $(f + 2)R/2$; (4) its specific heat ratio is $\gamma = C_P/C_V = (f + 2)/f$.

35. In a crude model (Fig. P21.35) of a rotating diatomic molecule of chlorine (Cl$_2$), the two Cl atoms are 2.00×10^{-10} m apart and rotate about their center of mass with angular speed $\omega = 2.00 \times 10^{12}$ rad/s. What is the rotational kinetic energy of one molecule of Cl$_2$, which has a molar mass of 70.0 g/mol?
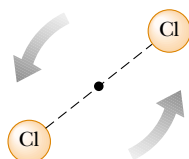

Figure P21.35

Section 21.5   The Boltzmann Distribution Law
Section 21.6   Distribution of Molecular Speeds

36. One cubic meter of atomic hydrogen at 0°C and atmospheric pressure contains approximately 2.70×10^{25} atoms. The first excited state of the hydrogen atom has an energy of 10.2 eV above the lowest energy level, called the ground state. Use the Boltzmann factor to find the number of atoms in the first excited state at 0°C and at 10 000°C.

37. Fifteen identical particles have various speeds: one has a speed of 2.00 m/s; two have speeds of 3.00 m/s; three have speeds of 5.00 m/s; four have speeds of 7.00 m/s; three have speeds of 9.00 m/s; and two have speeds of 12.0 m/s. Find (a) the average speed, (b) the rms speed, and (c) the most probable speed of these particles.

38. Two gases in a mixture diffuse through a filter at rates proportional to the gases' rms speeds. (a) Find the ratio of speeds for the two isotopes of chlorine, ^{35}Cl and ^{37}Cl, as they diffuse through the air. (b) Which isotope moves faster?

39. From the Maxwell–Boltzmann speed distribution, show that the most probable speed of a gas molecule is given by Equation 21.29. Note that the most probable speed corresponds to the point at which the slope of the speed distribution curve dN_v/dv is zero.

40. Helium gas is in thermal equilibrium with liquid helium at 4.20 K. Even though it is on the point of condensation, model the gas as ideal and determine the most probable speed of a helium atom (mass = 6.64×10^{-27} kg) in it.

41. **Review problem**. At what temperature would the average speed of helium atoms equal (a) the escape speed from Earth, 1.12×10^4 m/s and (b) the escape speed from the Moon, 2.37×10^3 m/s? (See Chapter 13 for a discussion of escape speed, and note that the mass of a helium atom is 6.64×10^{-27} kg.)

42. A gas is at 0°C. If we wish to double the rms speed of its molecules, to what temperature must the gas be brought?

43. Assume that the Earth's atmosphere has a uniform temperature of 20°C and uniform composition, with an effective molar mass of 28.9 g/mol. (a) Show that the number density of molecules depends on height according to

$$n_V(y) = n_0 e^{-mgy/k_B T}$$

where n_0 is the number density at sea level, where $y = 0$. This result is called the *law of atmospheres.* (b) Commercial jetliners typically cruise at an altitude of 11.0 km. Find the ratio of the atmospheric density there to the density at sea level.

44. *If you can't walk to outer space, can you at least walk halfway?* Using the law of atmospheres from Problem 43, we find that the average height of a molecule in the Earth's atmosphere is given by

$$\bar{y} = \frac{\displaystyle\int_0^\infty y n_V(y)\, dy}{\displaystyle\int_0^\infty n_V(y)\, dy} = \frac{\displaystyle\int_0^\infty y e^{-mgy/k_B T}\, dy}{\displaystyle\int_0^\infty e^{-mgy/k_B T}\, dy}$$

(a) Prove that this average height is equal to $k_B T/mg$. (b) Evaluate the average height, assuming the temperature is 10°C and the molecular mass is 28.9 u.

Section 21.7 Mean Free Path

45. In an ultra-high-vacuum system, the pressure is measured to be 1.00×10^{-10} torr (where 1 torr = 133 Pa). Assuming the molecular diameter is 3.00×10^{-10} m, the average molecular speed is 500 m/s, and the temperature is 300 K, find (a) the number of molecules in a volume of 1.00 m^3, (b) the mean free path of the molecules, and (c) the collision frequency.

46. In deep space the number density of particles can be one particle per cubic meter. Using the average temperature of 3.00 K and assuming the particle is H_2 with a diameter of 0.200 nm, (a) determine the mean free path of the particle and the average time between collisions. (b) **What If?** Repeat part (a) assuming a density of one particle per cubic centimeter.

47. Show that the mean free path for the molecules of an ideal gas is

$$\ell = \frac{k_B T}{\sqrt{2}\pi d^2 P}$$

where d is the molecular diameter.

48. In a tank full of oxygen, how many molecular diameters d (on average) does an oxygen molecule travel (at 1.00 atm and 20.0°C) before colliding with another O_2 molecule? (The diameter of the O_2 molecule is approximately 3.60×10^{-10} m.)

49. Argon gas at atmospheric pressure and 20.0°C is confined in a 1.00-m^3 vessel. The effective hard-sphere diameter of the argon atom is 3.10×10^{-10} m. (a) Determine the mean free path ℓ. (b) Find the pressure when $\ell = 1.00$ m. (c) Find the pressure when $\ell = 3.10 \times 10^{-10}$ m.

Additional Problems

50. The dimensions of a room are 4.20 m $\times$ 3.00 m $\times$ 2.50 m. (a) Find the number of molecules of air in the room at atmospheric pressure and 20.0°C. (b) Find the mass of this air, assuming that the air consists of diatomic molecules with molar mass 28.9 g/mol. (c) Find the average kinetic energy of one molecule. (d) Find the root-mean-square molecular speed. (e) On the assumption that the molar specific heat is a constant independent of temperature, we have $E_{int} = 5nRT/2$. Find the internal energy in the air. (f) **What If?** Find the internal energy of the air in the room at 25.0°C.

51. The function $E_{int} = 3.50nRT$ describes the internal energy of a certain ideal gas. A sample comprising 2.00 mol of the gas always starts at pressure 100 kPa and temperature 300 K. For each one of the following processes, determine the final pressure, volume, and temperature; the change in internal energy of the gas; the energy added to the gas by heat; and the work done on the gas. (a) The gas is heated at constant pressure to 400 K. (b) The gas is heated at constant volume to 400 K. (c) The gas is compressed at constant temperature to 120 kPa. (d) The gas is compressed adiabatically to 120 kPa.

52. Twenty particles, each of mass m and confined to a volume V, have various speeds: two have speed v; three have speed $2v$; five have speed $3v$; four have speed $4v$; three have speed $5v$; two have speed $6v$; one has speed $7v$. Find (a) the average speed, (b) the rms speed, (c) the most probable speed, (d) the pressure the particles exert on the walls of the vessel, and (e) the average kinetic energy per particle.

53. A cylinder containing n mol of an ideal gas undergoes an adiabatic process. (a) Starting with the expression $W = -\int P dV$ and using the condition $PV^\gamma = $ constant, show that the work done on the gas is

$$W = \left(\frac{1}{\gamma - 1}\right)(P_f V_f - P_i V_i)$$

(b) Starting with the first law of thermodynamics in differential form, prove that the work done on the gas is also equal to $nC_V(T_f - T_i)$. Show that this result is consistent with the equation in part (a).

54. As a 1.00-mol sample of a monatomic ideal gas expands adiabatically, the work done on it is $-2\,500$ J. The initial temperature and pressure of the gas are 500 K and 3.60 atm. Calculate (a) the final temperature and (b) the final pressure. You may use the result of Problem 53.

55. A cylinder is closed at both ends and has insulating walls. It is divided into two compartments by a perfectly insulating partition that is perpendicular to the axis of the cylinder. Each compartment contains 1.00 mol of oxygen, which behaves as an ideal gas with $\gamma = 7/5$. Initially the two compartments have equal volumes, and their temperatures are 550 K and 250 K. The partition is then allowed to move slowly until the pressures on its two sides are equal. Find the final temperatures in the two compartments. You may use the result of Problem 53.

56. An air rifle shoots a lead pellet by allowing high-pressure air to expand, propelling the pellet down the rifle barrel. Because this process happens very quickly, no appreciable thermal conduction occurs, and the expansion is essentially adiabatic. Suppose that the rifle starts by admitting to the barrel 12.0 cm^3 of compressed air, which behaves as an ideal gas with $\gamma = 1.40$. The air expands behind a 1.10-g pellet and pushes on it as a piston with cross-sectional area 0.030 0 cm^2, as the pellet moves 50.0 cm along the gun barrel. The pellet emerges with muzzle speed 120 m/s. Use the result of problem 53 to find the initial pressure required.

57. Review problem. Oxygen at pressures much greater than 1 atm is toxic to lung cells. Assume that a deep-sea diver breathes a mixture of oxygen (O_2) and helium (He). By weight, what ratio of helium to oxygen must be used if the diver is at an ocean depth of 50.0 m?

58. A vessel contains 1.00×10^4 oxygen molecules at 500 K. (a) Make an accurate graph of the Maxwell–Boltzmann speed distribution function versus speed with points at speed intervals of 100 m/s. (b) Determine the most probable speed from this graph. (c) Calculate the average and rms speeds for the molecules and label these points on your graph. (d) From the graph, estimate the fraction of molecules with speeds in the range 300 m/s to 600 m/s.

59. The compressibility κ of a substance is defined as the fractional change in volume of that substance for a given change in pressure:

$$\kappa = -\frac{1}{V}\frac{dV}{dP}$$

(a) Explain why the negative sign in this expression ensures that κ is always positive. (b) Show that if an ideal gas is compressed isothermally, its compressibility is given by $\kappa_1 = 1/P$. (c) **What If?** Show that if an ideal gas is compressed adiabatically, its compressibility is given by $\kappa_2 = 1/\gamma P$. (d) Determine values for κ_1 and κ_2 for a monatomic ideal gas at a pressure of 2.00 atm.

60. **Review problem.** (a) Show that the speed of sound in an ideal gas is

$$v = \sqrt{\frac{\gamma RT}{M}}$$

where M is the molar mass. Use the general expression for the speed of sound in a fluid from Section 17.1, the definition of the bulk modulus from Section 12.4, and the result of Problem 59 in this chapter. As a sound wave passes through a gas, the compressions are either so rapid or so far apart that thermal conduction is prevented by a negligible time interval or by effective thickness of insulation. The compressions and rarefactions are adiabatic. (b) Compute the theoretical speed of sound in air at 20°C and compare it with the value in Table 17.1. Take $M = 28.9$ g/mol. (c) Show that the speed of sound in an ideal gas is

$$v = \sqrt{\frac{\gamma k_B T}{m}}$$

where m is the mass of one molecule. Compare it with the most probable, average, and rms molecular speeds.

61. Model air as a diatomic ideal gas with $M = 28.9$ g/mol. A cylinder with a piston contains 1.20 kg of air at 25.0°C and 200 kPa. Energy is transferred by heat into the system as it is allowed to expand, with the pressure rising to 400 kPa. Throughout the expansion, the relationship between pressure and volume is given by

$$P = CV^{1/2}$$

where C is a constant. (a) Find the initial volume. (b) Find the final volume. (c) Find the final temperature. (d) Find the work done on the air. (e) Find the energy transferred by heat.

62. *Smokin'!* A pitcher throws a 0.142-kg baseball at 47.2 m/s (Fig. P21.62). As it travels 19.4 m, the ball slows to a speed of 42.5 m/s because of air resistance. Find the change in temperature of the air through which it passes. To find the greatest possible temperature change, you may make the following assumptions: Air has a molar specific heat of $C_P = 7R/2$ and an equivalent molar mass of 28.9 g/mol. The process is so rapid that the cover of the baseball acts as thermal insulation, and the temperature of the ball itself does not change. A change in temperature happens initially only for the air in a cylinder 19.4 m in length and 3.70 cm in radius. This air is initially at 20.0°C.

63. 🖥 For a Maxwellian gas, use a computer or programmable calculator to find the numerical value of the ratio $N_v(v)/N_v(v_{mp})$ for the following values of v: $v = (v_{mp}/50)$, $(v_{mp}/10)$, $(v_{mp}/2)$, v_{mp}, $2v_{mp}$, $10v_{mp}$, and $50v_{mp}$. Give your results to three significant figures.

64. Consider the particles in a gas centrifuge, a device used to separate particles of different mass by whirling them in a circular path of radius r at angular speed ω. The force

Figure P21.62 John Lackey, the first rookie to win a World Series game 7 in 93 years, pitches for the Anaheim Angels during the final game of the 2002 World Series.

acting toward the center of the circular path on a given particle is $m\omega^2 r$. (a) Discuss how a gas centrifuge can be used to separate particles of different mass. (b) Show that the density of the particles as a function of r is

$$n(r) = n_0 e^{mr^2\omega^2/2k_B T}$$

65. Verify Equations 21.27 and 21.28 for the rms and average speed of the molecules of a gas at a temperature T. Note that the average value of v^n is

$$\overline{v^n} = \frac{1}{N}\int_0^\infty v^n N_v\, dv$$

Use the table of definite integrals in Appendix B (Table B.6).

66. On the PV diagram for an ideal gas, one isothermal curve and one adiabatic curve pass through each point. Prove that the slope of the adiabat is steeper than the slope of the isotherm by the factor γ.

67. A sample of monatomic ideal gas occupies 5.00 L at atmospheric pressure and 300 K (point A in Figure P21.67). It is heated at constant volume to 3.00 atm (point B). Then it is allowed to expand isothermally to 1.00 atm (point C) and at last compressed isobarically to its original state. (a) Find the number of moles in the sample. (b) Find the temperature at points B and C and the volume at point C. (c) Assuming that the molar specific heat does not depend on temperature, so that $E_{int} = 3nRT/2$, find the internal energy at points A, B, and C. (d) Tabulate P, V, T, and E_{int} for the states at points A, B, and C. (e) Now consider the processes $A \rightarrow B$, $B \rightarrow C$, and $C \rightarrow A$. Describe just how to carry out each process experimentally. (f) Find Q, W, and ΔE_{int} for each of the processes. (g) For the whole cycle $A \rightarrow B \rightarrow C \rightarrow A$ find Q, W, and ΔE_{int}.

68. This problem can help you to think about the size of molecules. In the city of Beijing a restaurant keeps a pot of chicken broth simmering continuously. Every morning it is topped up to contain 10.0 L of water, along with a fresh chicken, vegetables, and spices. The soup is thoroughly stirred. The molar mass of water is 18.0 g/mol. (a) Find
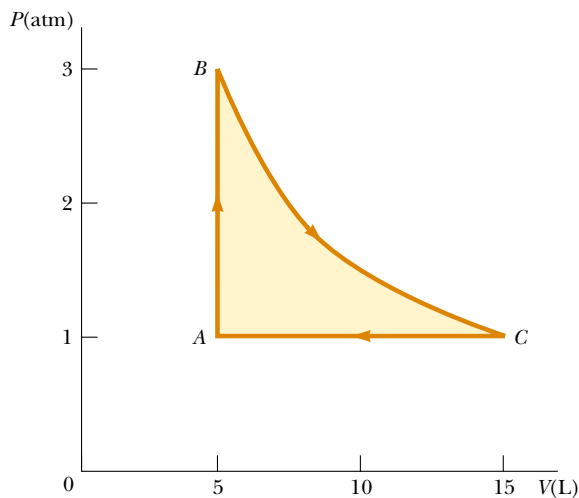
Figure P21.67

the number of molecules of water in the pot. (b) During a certain month, 90.0% of the broth was served each day to people who then emigrated immediately. Of the water molecules in the pot on the first day of the month, when was the last one likely to have been ladled out of the pot? (c) The broth has been simmering for centuries, through wars, earthquakes, and stove repairs. Suppose the water that was in the pot long ago has thoroughly mixed into the Earth's hydrosphere, of mass 1.32×10^{21} kg. How many of the water molecules originally in the pot are likely to be present in it again today?

69. **Review problem.** (a) If it has enough kinetic energy, a molecule at the surface of the Earth can "escape the Earth's gravitation," in the sense that it can continue to move away from the Earth forever, as discussed in Section 13.7. Using the principle of conservation of energy, show that the minimum kinetic energy needed for "escape" is mgR_E, where m is the mass of the molecule, g is the free-fall acceleration at the surface, and R_E is the radius of the Earth. (b) Calculate the temperature for which the minimum escape kinetic energy is ten times the average kinetic energy of an oxygen molecule.

70. Using multiple laser beams, physicists have been able to cool and trap sodium atoms in a small region. In one experiment the temperature of the atoms was reduced to 0.240 mK. (a) Determine the rms speed of the sodium atoms at this temperature. The atoms can be trapped for about 1.00 s. The trap has a linear dimension of roughly 1.00 cm. (b) Approximately how long would it take an atom to wander out of the trap region if there were no trapping action?

Answers to Quick Quizzes

21.1 (b). The average translational kinetic energy per molecule is a function only of temperature.

21.2 (a). Because there are twice as many molecules and the temperature of both containers is the same, the total energy in B is twice that in A.

21.3 (b). Because both containers hold the same type of gas, the rms speed is a function only of temperature.

21.4 (a). According to Equation 21.10, E_{int} is a function of temperature only. Because the temperature increases, the internal energy increases.

21.5 (c). Along an isotherm, T is constant by definition. Therefore, the internal energy of the gas does not change.

21.6 (d). The value of 29.1 J/mol·K is $7R/2$. According to Figure 21.7, this suggests that all three types of motion are occurring.

21.7 (c). The highest possible value of C_V for a diatomic gas is $7R/2$, so the gas must be polyatomic.

21.8 (a). Because the hydrogen atoms are lighter than the nitrogen molecules, they move with a higher average speed and the distribution curve is stretched out more along the horizontal axis. See Equation 21.26 for a mathematical statement of the dependence of N_v on m.