CHAPTER

21

The Kinetic Theory of Gases

21.1 Molecular Model of an Ideal Gas

21.2 Molar Specific Heat of an Ideal Gas

21.3 The Equipartition of Energy

21.4 Adiabatic Processes for an Ideal Gas

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A boy inflates his bicycle tire with a hand-operated pump. Kinetic theory helps to describe the details of the air in the pump. *(© Cengage Learning/ George Semple)*

In Chapter 19, we discussed the properties of an ideal gas by using such macroscopic variables as pressure, volume, and temperature. Such large-scale properties can be related to a description on a microscopic scale, where matter is treated as a collection of molecules. Applying Newton's laws of motion in a statistical manner to a collection of particles provides 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.

We shall begin by relating pressure and temperature directly to the details of molecular motion in a sample of gas. Based on these results, we will make predictions of molar specific heats of gases. Some of these predictions will be correct and some will not. We will extend our model to explain those values that are not predicted correctly by the simpler model. Finally, we discuss the distribution of molecular speeds in a gas.

21.1 Molecular Model of an Ideal Gas

In this chapter, we will investigate a *structural model* for an ideal gas. A **structural model** is a theoretical construct designed to represent a system that cannot be observed directly because it is too large or too small. For example, we can only observe the solar system from the inside; we cannot travel outside the solar system and look back to see how it works. This restricted vantage point has led to different historical structural models of the solar system: the g*eocentric model,* with the Earth at the center, and the *heliocentric model,* with the Sun at the center. Of course, the latter has been shown to be correct. An example of a system too small to observe directly is the hydrogen atom. Various structural models of this system have been developed, including the *Bohr model* (Section 42.3) and the *quantum model* (Section 42.4). Once a structural model is developed, various predictions are made for experimental observations. For example, the geocentric model of the solar system makes predictions of how the movement of Mars should appear from the Earth. It turns out that those predictions do not match the actual observations. When that occurs with a structural model, the model must be modified or replaced with another model.

The structural model that we will develop for an ideal gas is called **kinetic theory.** This model treats an ideal gas as a collection of molecules with the following properties:

1. *Physical components:*
   The gas consists of a number of identical molecules within a cubic container of side length d. The number of molecules in the gas is large, and the average separation between them is large compared with their dimensions. Therefore, the molecules occupy a negligible volume in the container. This assumption is consistent with the ideal gas model, in which we imagine the molecules to be point-like.
2. *Behavior of the components:*
   (a) The molecules obey Newton's laws of motion, but as a whole their motion is isotropic: any molecule can move in any direction with any speed.
   (b) The molecules interact only by short-range forces during elastic collisions. This assumption is consistent with the ideal gas model, in which the molecules exert no long-range forces on one another.
   (c) The molecules make elastic collisions with the walls.

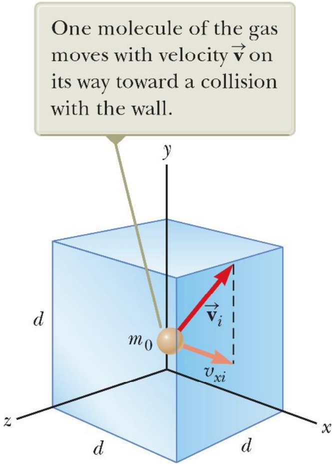

Figure 21.1 A cubical box with sides of length d containing an ideal gas.

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

For our first application of kinetic theory, let us relate the macroscope variable of pressure P to microscopic quantities. Consider a collection of N molecules of an ideal gas in a container of volume V. As indicated above, the container is a cube with edges of length d (Fig. 21.1). We shall first focus our attention on one of these molecules of mass m_0 and assume 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 in the collection, not to an initial value. We will combine the effects of all the molecules shortly.) As the molecule collides elastically with any wall (property 2(c) above), its velocity component perpendicular to the wall is reversed because the mass of the wall is far greater than the mass of the molecule. The molecule is modeled as a nonisolated system for which the impulse from the wall causes a change in the molecule's momentum. Because the momentum component p_{xi} of the molecule is m_0v_{xi} before the collision and $-m_0v_{xi}$ after the collision, the change in the x component of the momentum of the molecule is

$$\Delta p_{xi} = -m_0v_{xi} - (m_0v_{xi}) = -2m_0v_{xi} \quad (21.1)$$

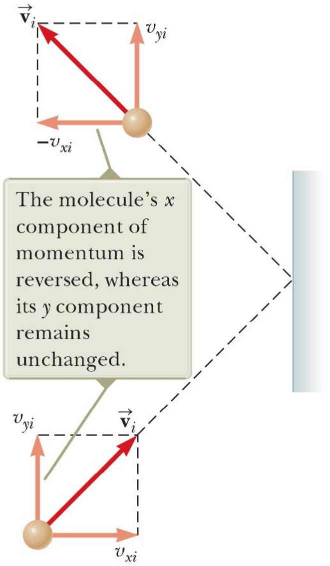

Figure 21.2 A molecule makes an elastic collision with the wall of the container. In this construction, we assume the molecule moves in the xy plane.

From the nonisolated system model for momentum, we can apply the impulse-momentum theorem (Eqs. 9.11 and 9.13) to the molecule to give

$$\overline{F}_{i,\text{on molecule}}\,\Delta t_{\text{collision}} = \Delta p_{xi} = -2m_0 v_{xi} \tag{21.2}$$

where $\overline{F}_{i,\text{on molecule}}$ is the x component of the average force[1] the wall exerts on the molecule during the collision and $\Delta t_{\text{collision}}$ is the duration of the collision. 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 cube and back). Therefore, the time interval between two collisions with the same wall is

$$\Delta t = \frac{2d}{v_{xi}} \tag{21.3}$$

The force that causes the change in momentum of the molecule in the collision with the wall occurs only during the collision. We can, however, find the long-term average force for many back-and-forth trips across the cube by averaging the force in Equation 21.2 over the time interval for the molecule to move across the cube and back once, Equation 21.3. The average change in momentum per trip for the time interval for many trips is the same as that for the short duration of the collision. Therefore, we can rewrite Equation 21.2 as

$$\overline{F}_i\,\Delta t = -2m_0 v_{xi} \tag{21.4}$$

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

Equation 21.3 and 21.4 enable us to express the x component of the long-term average force exerted by the wall on the molecule as

$$\overline{F}_i = -\frac{2m_0 v_{xi}}{\Delta t} = -\frac{2m_0 v_{xi}^2}{2d} = -\frac{m_0 v_{xi}^2}{d} \tag{21.5}$$

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

$$\overline{F}_{i,\text{on wall}} = -\overline{F}_i = -\left(-\frac{m_0 v_{xi}^2}{d}\right) = \frac{m_0 v_{xi}^2}{d} \tag{21.6}$$

The total average force $\overline{F}$ exerted by the gas on the wall is found by adding the average forces exerted by the individual molecules. Adding terms such as those in Equation 21.6 for all molecules gives

$$\overline{F} = \sum_{i=1}^{N} \frac{m_0 v_{xi}^2}{d} = \frac{m_0}{d}\sum_{i=1}^{N} v_{xi}^2 \tag{21.7}$$

where we have factored out the length of the box and the mass m_0 because property 1 tells us that all the molecules are the same. We now impose an additional feature from property 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 such as Avogadro's number, however, these variations in force are smoothed out so that the average force given above is the same over *any* time interval. Therefore, the *constant* force F on the wall due to the molecular collisions is

$$F = \frac{m_0}{d}\sum_{i=1}^{N} v_{xi}^2 \tag{21.8}$$

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[1] For this discussion, we use a bar over a variable to represent the average value of the variable, such as $\overline{F}$ for the average force, rather than the subscript "avg" that we have used before. This notation is to save confusion because we already have a number of subscripts on variables.

To proceed further, let's 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:

$$\overline{v_x^{\,2}} = \frac{\sum_{i=1}^{N} v_{xi}^{\,2}}{N} \rightarrow \sum_{i=1}^{N} v_{xi}^{\,2} = N\overline{v_x^{\,2}} \tag{21.9}$$

Using Equation 21.9 to substitute for the sum in Equation 21.8 gives

$$F = \frac{m_0}{d} N\overline{v_x^{\,2}} \tag{21.10}$$

Now let's 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:

$$v_i^2 = v_{xi}^{\,2} + v_{yi}^{\,2} + v_{zi}^{\,2} \tag{21.11}$$

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

$$\overline{v^2} = \overline{v_x^{\,2}} + \overline{v_y^{\,2}} + \overline{v_z^{\,2}} \tag{21.12}$$

Because the motion is isotropic (property 2(a) above), the average values $\overline{v_x^{\,2}}$, $\overline{v_y^{\,2}}$, and $\overline{v_z^{\,2}}$ are equal to one another. Using this fact and Equation 21.12, we find that

$$\overline{v^2} = 3\overline{v_x^{\,2}} \tag{21.13}$$

Therefore, from Equation 21.10, the total force exerted on the wall is

$$F = \tfrac{1}{3}N\frac{m_0\overline{v^2}}{d} \tag{21.14}$$

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

$$P = \frac{F}{A} = \frac{F}{d^2} = \tfrac{1}{3}N\frac{m_0\overline{v^2}}{d^3} = \tfrac{1}{3}\left(\frac{N}{V}\right)m_0\overline{v^2}$$

$$P = \tfrac{2}{3}\left(\frac{N}{V}\right)\left(\tfrac{1}{2}m_0\overline{v^2}\right) \tag{21.15}$$

Relationship between pressure and molecular kinetic energy

where we have recognized the volume V of the cube as d^3.

Equation 21.15 indicates that the pressure of a gas is proportional to (1) the number of molecules per unit volume and (2) the average translational kinetic energy of the molecules, $\tfrac{1}{2}m_0\overline{v^2}$. In analyzing this structural 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. Therefore, a key link between the molecular world and the large-scale world has been established.

Notice that Equation 21.15 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. That is what you do when you add air to a tire. The pressure in the tire can also be raised by increasing the average translational kinetic energy of the air molecules in the tire. That can be accomplished by increasing the temperature of that air, which is why the pressure inside a tire increases as the tire warms up during long road trips. The continuous flexing of the tire as it moves along the road surface results in work done on the rubber 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

Let's now consider another macroscopic variable, the temperature T of the gas. We can gain some insight into the meaning of temperature by first writing Equation 21.15 in the form

$$PV = \tfrac{2}{3}N\left(\tfrac{1}{2}m_0\overline{v^2}\right) \qquad \textbf{(21.16)}$$

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

$$PV = Nk_BT \qquad \textbf{(21.17)}$$

Equating the right sides of Equations 21.16 and 21.17 and solving for T gives

Relationship between temperature and molecular kinetic energy

$$T = \frac{2}{3k_B}\left(\tfrac{1}{2}m_0\overline{v^2}\right) \qquad \textbf{(21.18)}$$

This result tells us that temperature is a direct measure of average molecular kinetic energy. By rearranging Equation 21.18, we can relate the translational molecular kinetic energy to the temperature:

Average kinetic energy per molecule

$$\boxed{\tfrac{1}{2}m_0\overline{v^2} = \tfrac{3}{2}k_BT} \qquad \textbf{(21.19)}$$

That is, the average translational kinetic energy per molecule is $\frac{3}{2}k_BT$. Because $\overline{v_x^{\,2}} = \frac{1}{3}\overline{v^2}$ (Eq. 21.13), it follows that

$$\tfrac{1}{2}m_0\overline{v_x^{\,2}} = \tfrac{1}{2}k_BT \qquad \textbf{(21.20)}$$

In a similar manner, for the y and z directions,

$$\tfrac{1}{2}m_0\overline{v_y^{\,2}} = \tfrac{1}{2}k_BT \quad \text{and} \quad \tfrac{1}{2}m_0\overline{v_z^{\,2}} = \tfrac{1}{2}k_BT$$

Therefore, each translational degree of freedom contributes an equal amount of energy, $\frac{1}{2}k_BT$, 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,** is as follows:

Theorem of equipartition of energy

> Each degree of freedom contributes $\frac{1}{2}k_BT$ to the energy of a system, where possible degrees of freedom are those associated with translation, 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 21.19:

Total translational kinetic energy of *N* molecules

$$\boxed{K_{\text{tot trans}} = N\left(\tfrac{1}{2}m_0\overline{v^2}\right) = \tfrac{3}{2}Nk_BT = \tfrac{3}{2}nRT} \qquad \textbf{(21.21)}$$

where we have used $k_B = R/N_A$ for Boltzmann's constant and $n = N/N_A$ for the number of moles of gas. If the gas molecules possess only translational kinetic energy, Equation 21.21 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 21.19, we find that the rms speed is

Root-mean-square speed

$$v_{\text{rms}} = \sqrt{\overline{v^2}} = \sqrt{\frac{3k_BT}{m_0}} = \sqrt{\frac{3RT}{M}} \qquad \textbf{(21.22)}$$

where M is the molar mass in kilograms per mole and is equal to m_0N_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 Root-Mean-Square (rms) Speeds**

Gas	Molar Mass (g/mol)	v_{rms} at 20°C (m/s)	Gas	Molar Mass (g/mol)	v_{rms} at 20°C (m/s)
H_2	2.02	1902	NO	30.0	494
He	4.00	1352	O_2	32.0	478
H_2O	18.0	637	CO_2	44.0	408
Ne	20.2	602	SO_2	64.1	338
N_2 or CO	28.0	511			

Pitfall Prevention 21.1

The Square Root of the Square? 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. Although the square root of $(\overline{v})^2$ is $\overline{v} = v_{\text{avg}}$ because the squaring is done after the averaging, the square root of $\overline{v^2}$ is *not* v_{avg}, but rather v_{rms}.

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. **(i)** What is the average translational kinetic energy per molecule in container B? (a) twice that of container A (b) the same as that of container A (c) half that of container A (d) impossible to determine **(ii)** From the same choices, describe the internal energy of the gas in container B.

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 the helium behaves like an ideal gas.

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

SOLUTION

Conceptualize Imagine a microscopic model of a gas in which you can watch the molecules move about the container more rapidly as the temperature increases. Because the gas is monatomic, the total translational kinetic energy of the molecules is the internal energy of the gas.

Categorize We evaluate parameters with equations developed in the preceding discussion, so this example is a substitution problem.

Use Equation 21.21 with $n = 2.00$ mol and $T = 293$ K:

$$E_{\text{int}} = \tfrac{3}{2}nRT = \tfrac{3}{2}(2.00 \text{ mol})(8.31 \text{ J/mol}\cdot\text{K})(293 \text{ K})$$

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

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

SOLUTION

Use Equation 21.19:

$$\tfrac{1}{2}m_0\overline{v^2} = \tfrac{3}{2}k_BT = \tfrac{3}{2}(1.38 \times 10^{-23} \text{ J/K})(293 \text{ K})$$

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

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. Therefore, 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. Therefore, the total translational energy increases by a factor of only 313 K/293 K = 1.07.

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

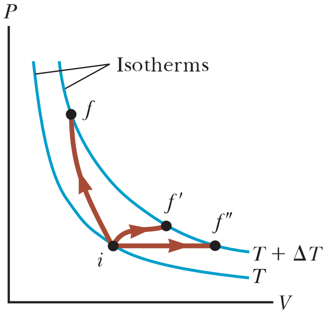


Figure 21.3 An ideal gas is taken from one isotherm at temperature T to another at temperature $T + \Delta T$ along three different paths.

by taking a variety of paths from one isotherm to another as shown in Figure 21.3. Because ΔT is the same for all paths, the change in internal energy ΔE_{int} is the same for all paths. The work W done on the gas (the negative of the area under the curves), however, is different for each path. Therefore, from the first law of thermodynamics, we can argue that the heat $Q = \Delta E_{\text{int}} - W$ associated with a given change in temperature does *not* have a unique value as discussed in Section 20.4.

We can address this difficulty by defining specific heats for two special processes that we have studied: isovolumetric and isobaric. Because the number of moles n is a convenient measure of the amount of gas, we define the **molar specific heats** associated with these processes as follows:

$$Q = nC_V\,\Delta T \quad \text{(constant volume)} \tag{21.23}$$

$$Q = nC_P\,\Delta T \quad \text{(constant pressure)} \tag{21.24}$$

where C_V is the **molar specific heat at constant volume** and C_P is the **molar specific heat at constant pressure.** When energy is added to a gas by heat at constant pressure, not only does the internal energy of the gas increase, but (negative) work is done on the gas because of the change in volume required to keep the pressure constant. Therefore, the heat Q in Equation 21.24 must account for both the increase in internal energy and the transfer of energy out of the system by work. For this reason, Q is greater in Equation 21.24 than in Equation 21.23 for given values of n and ΔT. Therefore, 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. That should not be surprising because the simple kinetic theory model assumes a structureless molecule.

So, let's 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 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 21.21, 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 ▶

$$E_{\text{int}} = K_{\text{tot trans}} = \tfrac{3}{2}Nk_{\text{B}}T = \tfrac{3}{2}nRT \tag{21.25}$$

For a monatomic ideal gas, E_{int} is a function of T only and the functional relationship is given by Equation 21.25. In general, the internal energy of any 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, 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,

$$Q = \Delta E_{\text{int}} \tag{21.26}$$

In other words, all 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 21.23 into Equation 21.26, we obtain

$$\Delta E_{\text{int}} = nC_V\,\Delta T \tag{21.27}$$

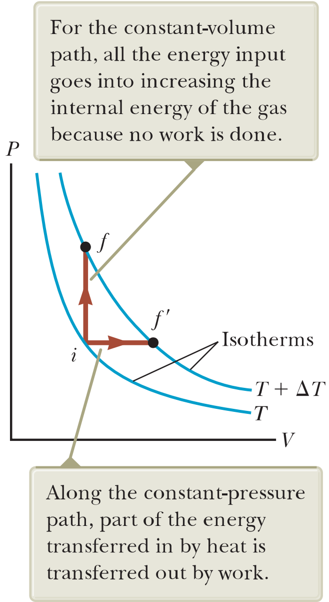
This equation applies to all ideal gases, those gases having more than one atom per molecule as well as monatomic ideal gases.

In the limit of infinitesimal changes, we can use Equation 21.27 to express the molar specific heat at constant volume as

$$C_V = \frac{1}{n}\frac{dE_{\text{int}}}{dT} \tag{21.28}$$

Let's now apply the results of this discussion to a monatomic gas. Substituting the internal energy from Equation 21.25 into Equation 21.28 gives

$$C_V = \tfrac{3}{2}R = 12.5\ \mathrm{J/mol \cdot K} \qquad \textbf{(21.29)}$$



For the constant-volume path, all the energy input goes into increasing the internal energy of the gas because no work is done.

Along the constant-pressure path, part of the energy transferred in by heat is transferred out by work.

Figure 21.4 Energy is transferred by heat to an ideal gas in two ways.

This expression predicts a value of $C_V = \frac{3}{2}R$ 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 because real gases are not ideal gases. In real gases, weak intermolecular interactions occur, which are not addressed in our ideal gas model.

Now suppose the gas is taken along the constant-pressure path $i \rightarrow f'$ 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

$$\Delta E_{\text{int}} = Q + W = nC_P\,\Delta T + (-P\,\Delta V) \qquad \textbf{(21.30)}$$

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. The change in internal energy for the process $i \rightarrow f'$, however, is equal to that for the process $i \rightarrow f$ because E_{int} depends only on temperature for an ideal gas and ΔT is the same for both processes. In addition, because $PV = nRT$, note that for a constant-pressure process, $P\,\Delta V = nR\,\Delta T$. Substituting this value for $P\,\Delta V$ into Equation 21.30 with $\Delta E_{\text{int}} = nC_V\,\Delta T$ (Eq. 21.27) gives

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

$$C_P - C_V = R \qquad \textbf{(21.31)}$$

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.

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.

Because $C_V = \frac{3}{2}R$ for a monatomic ideal gas, Equation 21.31 predicts a value $C_P = \frac{5}{2}R = 20.8\ \mathrm{J/mol \cdot K}$ 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 letter gamma):

Ratio of molar specific heats for a monatomic ideal gas

$$\gamma = \frac{C_P}{C_V} = \frac{5R/2}{3R/2} = \frac{5}{3} = 1.67 \qquad \textbf{(21.32)}$$

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). That is not surprising; 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 21.3, 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 during such a process because the thermal expansion is small. Consequently, C_P and C_V are approximately equal for solids and liquids.

Quick Quiz 21.2 **(i)** How does the internal energy of an ideal gas change as it follows path $i \rightarrow f$ 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. **(ii)** From the same choices, how does the internal energy of an ideal gas change as it follows path $f \rightarrow f'$ along the isotherm labeled $T + \Delta T$ in Figure 21.4?

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

Conceptualize Run the process in your mind with the help of the piston–cylinder arrangement in Figure 19.12. Imagine that the piston is clamped in position to maintain the constant volume of the gas.

Categorize We evaluate parameters with equations developed in the preceding discussion, so this example is a substitution problem.

Use Equation 21.23 to find the energy transfer:

$$Q_1 = nC_V\,\Delta T$$

Substitute the given values:

$$Q_1 = (3.00\ \mathrm{mol})(12.5\ \mathrm{J/mol \cdot K})(500\ \mathrm{K} - 300\ \mathrm{K}) = \boxed{7.50 \times 10^3\ \mathrm{J}}$$

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

SOLUTION

Use Equation 21.24 to find the energy transfer:

$$Q_2 = nC_P\,\Delta T$$

Substitute the given values:

$$Q_2 = (3.00\ \mathrm{mol})(20.8\ \mathrm{J/mol \cdot K})(500\ \mathrm{K} - 300\ \mathrm{K}) = \boxed{12.5 \times 10^3\ \mathrm{J}}$$

This value is larger than Q_1 because of the transfer of energy out of the gas by work to raise the piston in the constant pressure process.

21.3 The Equipartition of Energy

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 similarity is not surprising because this difference is the result of the work done on the gas, which is independent of its molecular structure.

To clarify the variations in C_V and C_P in gases more complex than monatomic gases, let's explore further the origin of molar specific heat. So far, we have assumed the sole contribution to the internal energy of a gas is the translational kinetic energy of the molecules. The internal energy of a gas, however, 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 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 $\frac{1}{2}k_BT$ of energy per molecule.

Let's consider a diatomic gas whose molecules have the shape of a dumbbell (Fig. 21.5). In this model, the center of mass of the molecule can translate in the x, y, and z directions (Fig. 21.5a). In addition, the molecule can rotate about three mutually perpendicular axes (Fig. 21.5b). The rotation about the y axis can be neglected 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 modeled as particles, then I_y is identically zero.) Therefore, 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 average, $\frac{1}{2}k_BT$ of energy per molecule, the internal energy for a system of N molecules, ignoring vibration for now, is

$$E_{\text{int}} = 3N(\tfrac{1}{2}k_BT) + 2N(\tfrac{1}{2}k_BT) = \tfrac{5}{2}Nk_BT = \tfrac{5}{2}nRT$$

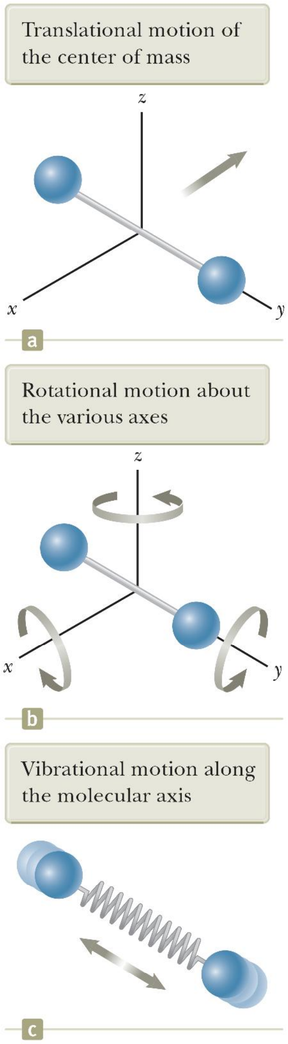


Figure 21.5 Possible motions of a diatomic molecule.

We can use this result and Equation 21.28 to find the molar specific heat at constant volume:

$$C_V = \frac{1}{n}\frac{dE_{\text{int}}}{dT} = \frac{1}{n}\frac{d}{dT}(\tfrac{5}{2}nRT) = \tfrac{5}{2}R = 20.8\ \text{J/mol}\cdot\text{K} \qquad \textbf{(21.33)}$$

From Equations 21.31 and 21.32, we find that

$$C_P = C_V + R = \tfrac{7}{2}R = 29.1\ \text{J/mol}\cdot\text{K}$$

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

These results agree quite well with most of the data for diatomic molecules given in Table 21.2. That 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. 21.5c). 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, a model that includes all three types of motion predicts a total internal energy of

$$E_{\text{int}} = 3N(\tfrac{1}{2}k_BT) + 2N(\tfrac{1}{2}k_BT) + 2N(\tfrac{1}{2}k_BT) = \tfrac{7}{2}Nk_BT = \tfrac{7}{2}nRT$$

and a molar specific heat at constant volume of

$$C_V = \frac{1}{n}\frac{dE_{\text{int}}}{dT} = \frac{1}{n}\frac{d}{dT}(\tfrac{7}{2}nRT) = \tfrac{7}{2}R = 29.1\ \text{J/mol}\cdot\text{K} \qquad \textbf{(21.34)}$$

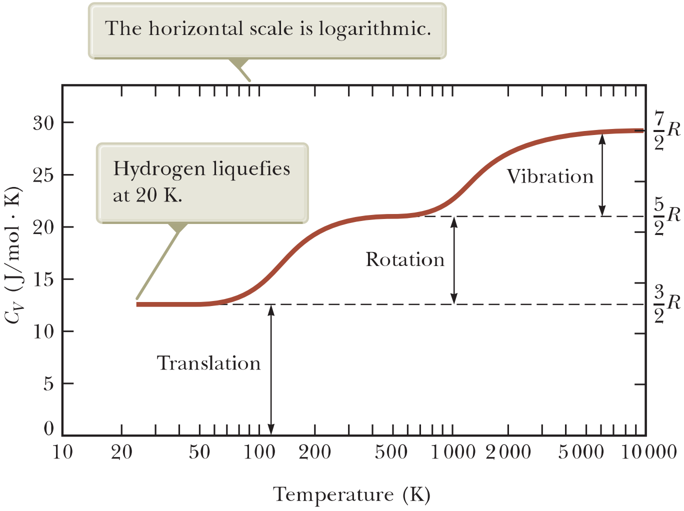


Figure 21.6 The molar specific heat of hydrogen as a function of temperature.

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 single temperature that gives us the values in Table 21.2. Figure 21.6 shows the molar specific heat of hydrogen as a function of temperature. The remarkable feature about the three plateaus in the graph's curve is that they are at the values of the molar specific heat predicted by Equations 21.29, 21.33, and 21.34! 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's make some brief remarks about polyatomic gases. For molecules with more than two atoms, three axes of rotation are available. The vibrations are more complex than for diatomic molecules. Therefore, the number of degrees of freedom is even larger. The result is an even higher predicted molar specific heat, which is in qualitative agreement with experiment. The molar specific heats for the polyatomic gases in Table 21.2 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 21.6, only agrees with experimental measurements made at high temperatures. To explain why this value is only true at high temperatures and why the plateaus in Figure 21.6 exist, 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; only certain frequencies of standing waves can exist. That is a natural result whenever waves are subject to boundary conditions.

Quantum physics (Chapters 40 through 43) shows that atoms and molecules can be described by the waves under boundary conditions analysis model. 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 21.7 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.** The black lines show the energies allowed for the molecule. Notice that allowed vibrational states are separated by larger energy gaps than are rotational states.

At low temperatures, the energy 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. Therefore, even though rotation and vibration are allowed according to classical physics, they do not occur in reality at low temperatures. All molecules are in the ground state for rotation and vibration. The only contribution to the molecules' average energy is from translation, and the specific heat is that predicted by Equation 21.29.

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 21.6, 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 21.33.

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, which happens in Figure 21.6 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 21.34.

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 21.6.

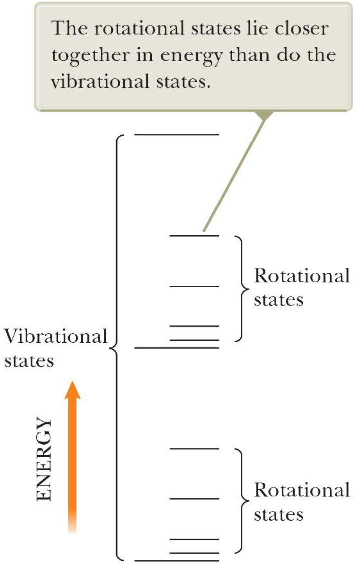


Figure 21.7 An energy-level diagram for vibrational and rotational states of a diatomic molecule.

Quick Quiz 21.3 The molar specific heat of a diatomic gas is measured at constant volume and found to be 29.1 J/mol · K. What are the types of energy that are contributing to the molar specific heat? **(a)** translation only **(b)** translation and rotation only **(c)** translation and vibration only **(d)** translation, rotation, and vibration

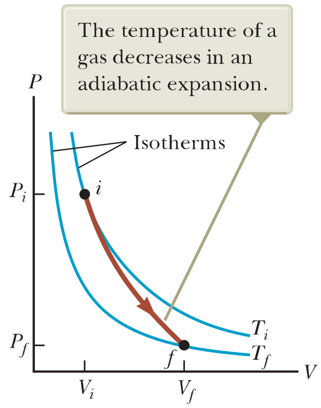
Quick Quiz 21.4 The molar specific heat of a gas is measured at constant volume and found to be $11R/2$. Is the gas most likely to be **(a)** monatomic, **(b)** diatomic, or **(c)** polyatomic?

21.4 Adiabatic Processes for an Ideal Gas

As 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) rapidly, very little energy is transferred out of (or into) the system by heat, so the process is nearly adiabatic. Such processes occur in the cycle of a gasoline engine, which is discussed in detail in Chapter 22. Another example of an adiabatic process is the slow expansion of a gas that is thermally insulated from its surroundings. All three variables in the ideal gas law—P, V, and T—change during an adiabatic process.

Let's imagine an adiabatic gas process involving 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. 21.27). Hence, the first law of thermodynamics, $\Delta E_{\text{int}} = Q + W$, with $Q = 0$, becomes the infinitesimal form

$$dE_{\text{int}} = nC_V\,dT = -P\,dV \qquad \textbf{(21.35)}$$



The temperature of a gas decreases in an adiabatic expansion.

Figure 21.8 The *PV* diagram for an adiabatic expansion of an ideal gas.

Taking the total differential of the equation of state of an ideal gas, $PV = nRT$, gives

$$P\,dV + V\,dP = nR\,dT \tag{21.36}$$

Eliminating dT from Equations 21.35 and 21.36, we find that

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

Substituting $R = C_P - C_V$ and dividing by PV gives

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

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

Integrating this expression, we have

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

which is equivalent to

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

$$PV^{\gamma} = \text{constant} \tag{21.37}$$

The *PV* diagram for an adiabatic expansion is shown in Figure 21.8. Because $\gamma > 1$, the *PV* curve is steeper than it would be for an isothermal expansion, for which $PV =$ constant. 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 negative (work is done *by* the gas, so its internal energy decreases) and so ΔT also is negative. Therefore, the temperature of the gas decreases ($T_f < T_i$) during an adiabatic expansion.[2] Conversely, the temperature increases if the gas is compressed adiabatically. Applying Equation 21.37 to the initial and final states, we see that

$$P_iV_i^{\gamma} = P_fV_f^{\gamma} \tag{21.38}$$

Using the ideal gas law, we can express Equation 21.37 as

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

$$TV^{\gamma-1} = \text{constant} \tag{21.39}$$

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 cm^3 to a volume of 60.0 cm^3. Assume air behaves as an ideal gas with $\gamma = 1.40$ and the compression is adiabatic. Find the final pressure and temperature of the air.

SOLUTION

Conceptualize Imagine what happens if a gas is compressed into a smaller volume. Our discussion above and Figure 21.8 tell us that the pressure and temperature both increase.

Categorize We categorize this example as a problem involving an adiabatic process.

Analyze Use Equation 21.38 to find the final pressure:

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

$$= 37.6\text{ atm}$$

---

[2] In the adiabatic free expansion discussed in Section 20.6, the temperature remains constant. In this unique process, 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.

21.3 continued

Use the ideal gas law to find the final temperature:

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

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

$$= 826 \text{ K} = \boxed{553°\text{C}}$$

Finalize The temperature of the gas increases by a factor of 826 K/293 K = 2.82. The high compression in a diesel engine raises the temperature of the gas enough to cause the combustion of fuel without the use of spark plugs.

21.5 Distribution of Molecular Speeds

Thus far, we have considered only average values of the energies of all the molecules in a gas and have not addressed the distribution of energies among individual molecules. The motion of the molecules is extremely chaotic. Any individual molecule collides 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 21.22 shows that rms molecular speeds increase with increasing temperature. At a given time, 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 $E + dE$. (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, the number density is found from statistical mechanics to be

$$n_V(E) = n_0 e^{-E/k_BT} \qquad \textbf{(21.40)}$$

◀ **Boltzmann distribution law**

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_BT. 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.

Pitfall Prevention 21.2

The Distribution Function

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.

Example 21.4 Thermal Excitation of Atomic Energy Levels

As 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. 21.9). Determine the ratio of the number of atoms in the higher energy level to the number in the lower energy level.

SOLUTION

Conceptualize In your mental representation of this example, remember that only two possible states are allowed for the system of the atom. Figure 21.9 helps you visualize the two states on an energy-level diagram. In this case, the atom has two possible energies, E_1 and E_2, where $E_1 < E_2$.

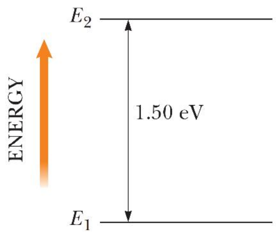


Figure 21.9 (Example 21.4) Energy-level diagram for a gas whose atoms can occupy two energy states.

continued

21.4 continued

Categorize We categorize this example as one in which we focus on particles in a two-state quantized system. We will apply the Boltzmann distribution law to this system.

Analyze Set up the ratio of the number of atoms in the higher energy level to the number in the lower energy level and use Equation 21.40 to express each number:

$$(1)\quad \frac{n_V(E_2)}{n_V(E_1)} = \frac{n_0 e^{-E_2/k_BT}}{n_0 e^{-E_1/k_BT}} = e^{-(E_2-E_1)/k_BT}$$

Evaluate k_BT in the exponent:

$$k_BT = (1.38 \times 10^{-23}\ \text{J/K})(2\,500\ \text{K})\left(\frac{1\ \text{eV}}{1.60 \times 10^{-19}\ \text{J}}\right) = 0.216\ \text{eV}$$

Substitute this value into Equation (1):

$$\frac{n_V(E_2)}{n_V(E_1)} = e^{-1.50\ \text{eV}/0.216\ \text{eV}} = e^{-6.96} = \boxed{9.52 \times 10^{-4}}$$

Finalize 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 21.9 were closer together in energy? Would that increase or decrease the fraction of the atoms in the upper energy level?

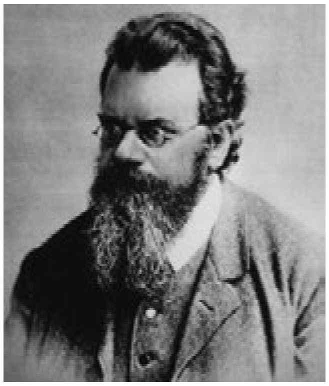
Answer If the excited level is lower in energy than that in Figure 21.9, it would be easier for thermal agitation to excite atoms to this level and the fraction of atoms in this energy level would be larger, which we can see mathematically by expressing Equation (1) as

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

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

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

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

Now that we have discussed the distribution of energies among molecules in a gas, let's think about the 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. About 60 years later, however, experiments were devised that confirmed Maxwell's predictions.

Let's 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 401 m/s. Intuitively, we expect the speed distribution to depend on temperature. Furthermore, we expect the distribution to peak 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 21.10. The quantity N_v, called the **Maxwell–Boltzmann speed distribution function,** is defined as follows. If N is the total number of molecules, 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 21.10. 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

$$N_v = 4\pi N\left(\frac{m_0}{2\pi k_B T}\right)^{3/2} v^2 e^{-m_0 v^2/2k_B T} \tag{21.41}$$

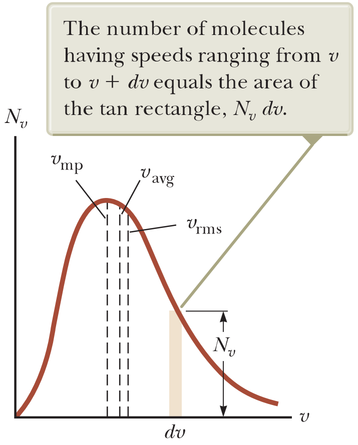
where m_0 is the mass of a gas molecule, k_B is Boltzmann's constant, and T is the absolute temperature.[3] Observe the appearance of the Boltzmann factor $e^{-E/k_B T}$ with $E = \frac{1}{2}m_0 v^2$.

As indicated in Figure 21.10, 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 21.41, we find that

$$v_{rms} = \sqrt{\overline{v^2}} = \sqrt{\frac{3k_B T}{m_0}} = 1.73\sqrt{\frac{k_B T}{m_0}} \tag{21.42}$$

$$v_{avg} = \sqrt{\frac{8k_B T}{\pi m_0}} = 1.60\sqrt{\frac{k_B T}{m_0}} \tag{21.43}$$

$$v_{mp} = \sqrt{\frac{2k_B T}{m_0}} = 1.41\sqrt{\frac{k_B T}{m_0}} \tag{21.44}$$



The number of molecules having speeds ranging from v to $v + dv$ equals the area of the tan rectangle, $N_v\,dv$.

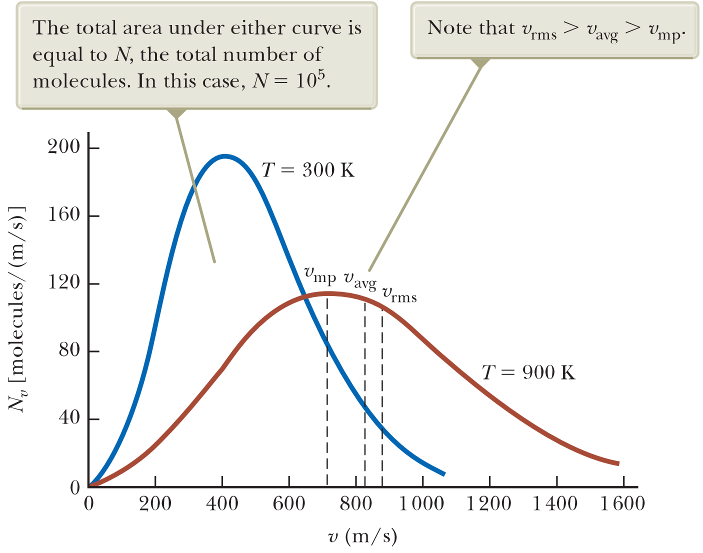
Figure 21.10 The speed distribution of gas molecules at some temperature. The function N_v approaches zero as v approaches infinity.

Equation 21.42 has previously appeared as Equation 21.22. The details of the derivations of these equations from Equation 21.41 are left for the end-of-chapter problems (see Problems 42 and 69). From these equations, we see that

$$v_{rms} > v_{avg} > v_{mp}$$

Figure 21.11 represents speed distribution curves for nitrogen, N_2. The curves were obtained by using Equation 21.41 to evaluate the distribution function at various speeds and at two temperatures. Notice that the peak in each curve shifts to the right as T increases, indicating that the average speed increases with increasing temperature, as expected. Because the lowest speed possible is zero and the upper classical limit of the speed is infinity, the curves are asymmetrical. (In Chapter 39, we show that the actual upper limit is the speed of light.)

Equation 21.41 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. Hence,



The total area under either curve is equal to N, the total number of molecules. In this case, $N = 10^5$.

Note that $v_{rms} > v_{avg} > v_{mp}$.

Figure 21.11 The speed distribution function for 10^5 nitrogen molecules at 300 K and 900 K.

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[3] For the derivation of this expression, see an advanced textbook on thermodynamics.

lighter molecules such as H_2 and He escape into space 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 21.11. We can understand the phenomenon of evaporation of a liquid from this distribution in speeds, given that some molecules in the liquid are more energetic than others. Some of the faster-moving molecules in the liquid penetrate the surface and even leave the liquid 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 can be placed on a feverish head to cool and comfort a patient.

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

Conceptualize Imagine a small number of particles moving in random directions with the few speeds listed. This situation is not representative of the large number of molecules in a gas, so we should not expect the results to be consistent with those from statistical mechanics.

Categorize Because we are dealing with a small number of particles, we can calculate the average speed directly.

Analyze Find the average speed of the particles by dividing the sum of the speeds by the total number of particles:

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

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

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

SOLUTION

Find the average speed squared of the particles by dividing the sum of the speeds squared by the total number of particles:

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

$$= 178\text{ m}^2/\text{s}^2$$

Find the rms speed of the particles by taking the square root:

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

(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 four have different speeds. Hence, the most probable speed v_{mp} is 12.0 m/s.

Finalize Compare this example, in which the number of particles is small and we know the individual particle speeds, with the next example.

Example 21.6 Molecular Speeds in a Hydrogen Gas

A 0.500-mol sample of hydrogen gas is at 300 K.

(A) Find the average speed, the rms speed, and the most probable speed of the hydrogen molecules.

SOLUTION

Conceptualize Imagine a huge number of particles in a real gas, all moving in random directions with different speeds.

Categorize We cannot calculate the averages as was done in Example 21.5 because the individual speeds of the particles are not known. We are dealing with a very large number of particles, however, so we can use the Maxwell-Boltzmann speed distribution function.

Analyze Use Equation 21.43 to find the average speed:

$$v_{\text{avg}} = 1.60\sqrt{\frac{k_BT}{m_0}} = 1.60\sqrt{\frac{(1.38\times10^{-23}\text{ J/K})(300\text{ K})}{2(1.67\times10^{-27}\text{ kg})}}$$

$$= \boxed{1.78\times10^3\text{ m/s}}$$

Use Equation 21.42 to find the rms speed:

$$v_{\text{rms}} = 1.73\sqrt{\frac{k_BT}{m_0}} = 1.73\sqrt{\frac{(1.38\times10^{-23}\text{ J/K})(300\text{ K})}{2(1.67\times10^{-27}\text{ kg})}}$$

$$= \boxed{1.93\times10^3\text{ m/s}}$$

Use Equation 21.44 to find the most probable speed:

$$v_{\text{mp}} = 1.41\sqrt{\frac{k_BT}{m_0}} = 1.41\sqrt{\frac{(1.38\times10^{-23}\text{ J/K})(300\text{ K})}{2(1.67\times10^{-27}\text{ kg})}}$$

$$= \boxed{1.57\times10^3\text{ m/s}}$$

(B) Find the number of molecules with speeds between 400 m/s and 401 m/s.

SOLUTION

Use Equation 21.41 to evaluate the number of molecules in a narrow speed range between v and $v + dv$:

$$(1)\quad N_v\,dv = 4\pi N\left(\frac{m_0}{2\pi k_BT}\right)^{3/2} v^2 e^{-m_0v^2/2k_BT}\,dv$$

Evaluate the constant in front of v^2:

$$4\pi N\left(\frac{m_0}{2\pi k_BT}\right)^{3/2} = 4\pi nN_A\left(\frac{m_0}{2\pi k_BT}\right)^{3/2}$$

$$= 4\pi(0.500\text{ mol})(6.02\times10^{23}\text{ mol}^{-1})\left[\frac{2(1.67\times10^{-27}\text{ kg})}{2\pi(1.38\times10^{-23}\text{ J/K})(300\text{ K})}\right]^{3/2}$$

$$= 1.74\times10^{14}\text{ s}^3/\text{m}^3$$

Evaluate the exponent of e that appears in Equation (1):

$$-\frac{m_0v^2}{2k_BT} = -\frac{2(1.67\times10^{-27}\text{ kg})(400\text{ m/s})^2}{2(1.38\times10^{-23}\text{ J/K})(300\text{ K})} = -0.064\,5$$

Evaluate $N_v\,dv$ using these values in Equation (1):

$$N_v\,dv = (1.74\times10^{14}\text{ s}^3/\text{m}^3)(400\text{ m/s})^2e^{-0.064\,5}(1\text{ m/s})$$

$$= \boxed{2.61\times10^{19}\text{ molecules}}$$

Finalize In this evaluation, we could calculate the result without integration because $dv = 1$ m/s is much smaller than $v = 400$ m/s. Had we sought the number of particles between, say, 400 m/s and 500 m/s, we would need to integrate Equation (1) between these speed limits.

Summary

Concepts and Principles

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

$$P = \tfrac{2}{3}\left(\frac{N}{V}\right)\left(\tfrac{1}{2}m_0\overline{v^2}\right) \qquad \textbf{(21.15)}$$

The average translational kinetic energy per molecule of a gas, $\frac{1}{2}m_0\overline{v^2}$, is related to the temperature T of the gas through the expression

$$\tfrac{1}{2}m_0\overline{v^2} = \tfrac{3}{2}k_BT \qquad \textbf{(21.19)}$$

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

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

$$E_{\text{int}} = \tfrac{3}{2}Nk_BT = \tfrac{3}{2}nRT \qquad \textbf{(21.25)}$$

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

$$\Delta E_{\text{int}} = nC_V\,\Delta T \qquad \textbf{(21.27)}$$

where C_V is the **molar specific heat at constant volume.**

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

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

$$PV^{\gamma} = \text{constant} \qquad \textbf{(21.37)}$$

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

$$n_V(E) = n_0e^{-E/k_BT} \qquad \textbf{(21.40)}$$

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

$$N_v = 4\pi N\left(\frac{m_0}{2\pi k_BT}\right)^{3/2} v^2e^{-m_0v^2/2k_BT} \qquad \textbf{(21.41)}$$

Equation 21.41 enables us to calculate the **root-mean-square speed,** the **average speed,** and the **most probable speed** of molecules in a gas:

$$v_{\text{rms}} = \sqrt{\overline{v^2}} = \sqrt{\frac{3k_BT}{m_0}} = 1.73\sqrt{\frac{k_BT}{m_0}} \qquad \textbf{(21.42)}$$

$$v_{\text{avg}} = \sqrt{\frac{8k_BT}{\pi m_0}} = 1.60\sqrt{\frac{k_BT}{m_0}} \qquad \textbf{(21.43)}$$

$$v_{\text{mp}} = \sqrt{\frac{2k_BT}{m_0}} = 1.41\sqrt{\frac{k_BT}{m_0}} \qquad \textbf{(21.44)}$$

Objective Questions

$\boxed{1.}$ denotes answer available in *Student Solutions Manual/Study Guide*

1. Cylinder A contains oxygen (O_2) gas, and cylinder B contains nitrogen (N_2) gas. If the molecules in the two cylinders have the same rms speeds, which of the following statements is *false*? (a) The two gases have different temperatures. (b) The temperature of cylinder B is less than the temperature of cylinder A. (c) The temperature of cylinder B is greater than the temperature of cylinder A. (d) The average kinetic energy of the nitrogen molecules is less than the average kinetic energy of the oxygen molecules.

2. An ideal gas is maintained at constant pressure. If the temperature of the gas is increased from 200 K to 600 K, what happens to the rms speed of the molecules? (a) It increases by a factor of 3. (b) It remains the same. (c) It is one-third the original speed. (d) It is $\sqrt{3}$ times the original speed. (e) It increases by a factor of 6.

3. Two samples of the same ideal gas have the same pressure and density. Sample B has twice the volume of sample A. What is the rms speed of the molecules in sample B? (a) twice that in sample A (b) equal to that in sample A (c) half that in sample A (d) impossible to determine

$\boxed{4.}$ A helium-filled latex balloon initially at room temperature is placed in a freezer. The latex remains flexible. **(i)** Does the balloon's volume (a) increase, (b) decrease, or (c) remain the same? **(ii)** Does the pressure of the helium gas (a) increase significantly, (b) decrease significantly, or (c) remain approximately the same?

5. A gas is at 200 K. If we wish to double the rms speed of the molecules of the gas, to what value must we raise its temperature? (a) 283 K (b) 400 K (c) 566 K (d) 800 K (e) 1130 K

6. Rank the following from largest to smallest, noting any cases of equality. (a) the average speed of molecules in a particular sample of ideal gas (b) the most probable speed (c) the root-mean-square speed (d) the average vector velocity of the molecules

7. A sample of gas with a thermometer immersed in the gas is held over a hot plate. A student is asked to give a step-by-step account of what makes our observation of the temperature of the gas increase. His response includes the following steps. (a) The molecules speed up. (b) Then the molecules collide with one another more often. (c) Internal friction makes the collisions inelastic. (d) Heat is produced in the collisions. (e) The molecules of the gas transfer more energy to the thermometer when they strike it, so we observe that the temperature has gone up. (f) The same process can take place without the use of a hot plate if you quickly push in the piston in an insulated cylinder containing the gas. **(i)** Which of the parts (a) through (f) of this account are correct statements necessary for a clear and complete explanation? **(ii)** Which are correct statements that are not necessary to account for the higher thermometer reading? **(iii)** Which are incorrect statements?

8. An ideal gas is contained in a vessel at 300 K. The temperature of the gas is then increased to 900 K. **(i)** By what factor does the average kinetic energy of the molecules change, (a) a factor of 9, (b) a factor of 3, (c) a factor of $\sqrt{3}$, (d) a factor of 1, or (e) a factor of $\frac{1}{3}$? Using the same choices as in part (i), by what factor does each of the following change: **(ii)** the rms molecular speed of the molecules, **(iii)** the average momentum change that one molecule undergoes in a collision with one particular wall, **(iv)** the rate of collisions of molecules with walls, and **(v)** the pressure of the gas.

9. Which of the assumptions below is *not* made in the kinetic theory of gases? (a) The number of molecules is very large. (b) The molecules obey Newton's laws of motion. (c) The forces between molecules are long range. (d) The gas is a pure substance. (e) The average separation between molecules is large compared to their dimensions.

Conceptual Questions

$\boxed{1.}$ denotes answer available in *Student Solutions Manual/Study Guide*

1. Hot air rises, so why does it generally become cooler as you climb a mountain? *Note:* Air has low thermal conductivity.

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

$\boxed{3.}$ When alcohol is rubbed on your body, it lowers your skin temperature. Explain this effect.

$\boxed{4.}$ What happens to a helium-filled latex balloon released into the air? Does it expand or contract? Does it stop rising at some height?

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

6. One container is filled with helium gas and another with argon gas. Both containers are at the same temperature. Which molecules have the higher rms speed? Explain.

7. Dalton's law of partial pressures states that the total pressure of a mixture of gases is equal to the sum of the pressures that each gas in the mixture would exert if it were alone in the container. Give a convincing argument for this law based on the kinetic theory of gases.

Problems

ENHANCED WebAssign The problems found in this chapter may be assigned online in Enhanced WebAssign

1. straightforward; **2.** intermediate; **3.** challenging

$\boxed{1.}$ full solution available in the *Student Solutions Manual/Study Guide*

AMT Analysis Model tutorial available in Enhanced WebAssign

GP Guided Problem

M Master It tutorial available in Enhanced WebAssign

W Watch It video solution available in Enhanced WebAssign

Section 21.1 Molecular Model of an Ideal Gas

Problem 30 in Chapter 19 can be assigned with this section.

$\boxed{1.}$ M (a) How many atoms of helium gas fill a spherical balloon of diameter 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 rms speed of the helium atoms?

$\boxed{2.}$ M 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 rms speed of each type of molecule?

3. W 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 a speed of 8.00 m/s. Assuming the collisions are elastic, find (a) the average force and (b) the average pressure on the window during this interval.

4. In an ultrahigh vacuum system (with typical pressures lower than 10^{-7} pascal), the pressure is measured to be 1.00×10^{-10} torr (where 1 torr = 133 Pa). Assuming the temperature is 300 K, find the number of molecules in a volume of 1.00 m^3.

5. M A spherical balloon of volume 4.00×10^3 cm^3 contains helium at a 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. A spherical balloon of volume V contains helium at a pressure P. How many moles of helium are in the balloon if the average kinetic energy of the helium atoms is $\overline{K}$?

7. W 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 the oxygen molecules under these conditions.

8. Oxygen, modeled as an ideal gas, is in a container and has a temperature of 77.0°C. What is the rms-average magnitude of the momentum of the gas molecules in the container?

9. Calculate the mass of an atom of (a) helium, (b) iron, and (c) lead. Give your answers in kilograms. The atomic masses of these atoms are 4.00 u, 55.9 u, and 207 u, respectively.

10. The rms speed of an oxygen molecule (O_2) in a container of oxygen gas is 625 m/s. What is the temperature of the gas?

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

12. A 7.00-L vessel contains 3.50 moles of gas at a pressure of 1.60×10^6 Pa. Find (a) the temperature of the gas and (b) the average kinetic energy of the gas molecules in the vessel. (c) What additional information would you need if you were asked to find the average speed of the gas molecules?

13. M W In a period of 1.00 s, 5.00×10^{23} nitrogen molecules strike a wall with an area of 8.00 cm^2. Assume 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? *Note:* The mass of one N_2 molecule is 4.65×10^{-26} kg.

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 $C_V = \frac{3}{2}R$ and $C_P = \frac{5}{2}R$, and a "diatomic ideal gas" to have $C_V = \frac{5}{2}R$ and $C_P = \frac{7}{2}R$.

14. W 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 work done on the gas, (b) the increase in internal energy of the gas, and (c) its final temperature.

15. A sample of a diatomic ideal gas has pressure P and volume V. When the gas is warmed, its pressure triples and its volume doubles. This warming 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.

16. **Review.** 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 all 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. M 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.

18. A vertical cylinder with a heavy piston contains air at 300 K. The initial pressure is 2.00×10^5 Pa, and the initial volume is 0.350 m^3. Take the molar mass of air as 28.9 g/mol and assume $C_V = \frac{5}{2}R$. (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 assume the heavy piston is free to move. Find the energy input required to raise the temperature to 700 K.

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

20. A 1.00-L insulated bottle is full of tea at 90.0°C. You pour out one cup of tea and immediately screw the stopper back on the bottle. Make an order-of-magnitude estimate of the change in temperature of the tea remaining in the bottle 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.

21. **Review.** This problem is a continuation of Problem 39 in Chapter 19. A hot-air balloon consists of an envelope of constant volume 400 m^3. Not including the air inside, the balloon and cargo have mass 200 kg. The air outside and originally inside is a diatomic ideal gas at 10.0°C and 101 kPa, with density 1.25 kg/m^3. A propane burner at the center of the spherical envelope injects energy into the air inside. The air inside stays at constant pressure. Hot air, at just the temperature required to make the balloon lift off, starts to fill the envelope at its closed top, rapidly enough so that negligible energy flows by heat to the cool air below it or out through the wall of the balloon. Air at 10°C leaves through an opening at the bottom of the envelope until the whole balloon is filled with hot air at uniform temperature. Then the burner is shut off and the balloon rises from the ground. (a) Evaluate the quantity of energy the burner must transfer to the air in the balloon. (b) The "heat value" of propane—the internal energy released by burning each kilogram—is 50.3 MJ/kg. What mass of propane must be burned?

Section 21.3 The Equipartition of Energy

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

23. In a crude model (Fig. P21.23) of a rotating diatomic chlorine molecule (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?

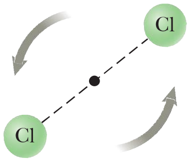

Figure P21.23

24. *Why is the following situation impossible?* A team of researchers discovers a new gas, which has a value of $\gamma = C_P/C_V$ of 1.75.

25. M The relationship between the heat capacity of a sample and the specific heat of the sample material is discussed in Section 20.2. Consider a sample containing 2.00 mol of an ideal diatomic gas. Assuming the molecules rotate but do not vibrate, find (a) the total heat capacity of the sample at constant volume and (b) the total heat capacity at constant pressure. (c) **What If?** Repeat parts (a) and (b), assuming the molecules both rotate and vibrate.

Section 21.4 Adiabatic Processes for an Ideal Gas

26. M 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? Find (c) Q, (d) ΔE_{int}, and (e) W for the gas during this process.

27. W 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 air–fuel mixture behaves as a diatomic ideal gas, (a) by what factor does the volume change and (b) by what factor does the temperature change? Assuming the compression starts with 0.016 0 mol of gas at 27.0°C, find the values of (c) Q, (d) ΔE_{int}, and (e) W that characterize the process.

28. W 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) **What If?** How much work is required to produce the same compression in an adiabatic process? (c) What is the final pressure in part (a)? (d) What is the final pressure in part (b)?

29. M 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?

30. *Why is the following situation impossible?* A new diesel engine that increases fuel economy over previous models is designed. Automobiles fitted with this design become incredible best sellers. Two design features are responsible for the increased fuel economy: (1) the engine is made entirely of aluminum to reduce the weight of the automobile, and (2) the exhaust of the engine is used to prewarm the air to 50°C before it enters the cylinder to increase the final temperature of the compressed gas. The engine has a *compression ratio*—that is, the ratio of the initial volume of the air to its final volume after compression—of 14.5. The compression process is adiabatic, and the air behaves as a diatomic ideal gas with $\gamma = 1.40$.

31. 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. Assume (1) the engine is running at 2 500 cycles/min; (2) the gauge pressure immediately before the expansion is 20.0 atm; (3) the volumes of the mixture immediately before and after the expansion are 50.0 cm^3 and 400 cm^3, respectively (Fig. P21.31); (4) the time interval for 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 power stroke.

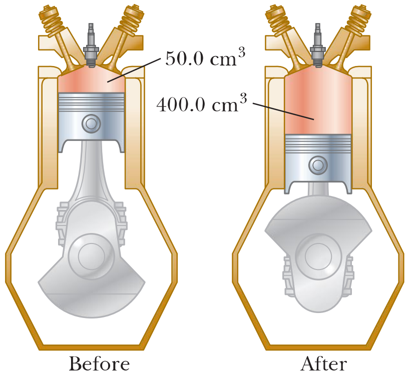

Figure P21.31

32. GP Air (a diatomic ideal gas) at 27.0°C and atmospheric pressure is drawn into a bicycle pump (see the chapter-opening photo on page 626) that has a cylinder with an inner diameter of 2.50 cm and length 50.0 cm. The downstroke adiabatically compresses the air, which reaches a gauge pressure of 8.00×10^5 Pa before entering the tire. We wish to investigate the temperature increase of the pump. (a) What is the initial volume of the air in the pump? (b) What is the number of moles of air in the pump? (c) What is the absolute pressure of the compressed air? (d) What is the volume of the compressed air? (e) What is the temperature of the compressed air? (f) What is the increase in internal energy of the gas during the compression? **What If?** The pump is made of steel that is 2.00 mm thick. Assume 4.00 cm of the cylinder's length is allowed to come to thermal equilibrium with the air. (g) What is the volume of steel in this 4.00-cm length? (h) What is the mass of steel in this 4.00-cm length? (i) Assume the pump is compressed once. After the adiabatic expansion, conduction results in the energy increase in part (f) being shared between the gas and the 4.00-cm length of steel. What will be the increase in temperature of the steel after one compression?

33. 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 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?

34. An ideal gas with specific heat ratio γ 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?

Section 21.5 Distribution of Molecular Speeds

35. 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.

36. M 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.

37. W One cubic meter of atomic hydrogen at 0°C at 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 that of the lowest state, called the ground state. Use the Boltzmann factor to find the number of atoms in the first excited state (a) at 0°C and at (b) (1.00×10^4)°C.

38. Two gases in a mixture diffuse through a filter at rates proportional to their 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. **Review.** At what temperature would the average speed of helium atoms equal (a) the escape speed from the Earth, 1.12×10^4 m/s, and (b) the escape speed from the Moon, 2.37×10^3 m/s? *Note:* The mass of a helium atom is 6.64×10^{-27} kg.

40. Consider a container of nitrogen gas molecules at 900 K. Calculate (a) the most probable speed, (b) the average speed, and (c) the rms speed for the molecules. (d) State how your results compare with the values displayed in Figure 21.11.

41. Assume the Earth's atmosphere has a uniform temperature of 20.0°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 y above sea level according to

$$n_V(y) = n_0 e^{-m_0 g y / k_B T}$$

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.

42. From the Maxwell–Boltzmann speed distribution, show that the most probable speed of a gas molecule is given by Equation 21.44. *Note:* The most probable speed corresponds to the point at which the slope of the speed distribution curve dN_v/dv is zero.

43. The law of atmospheres states that the number density of molecules in the atmosphere depends on height y above sea level according to

$$n_V(y) = n_0 e^{-m_0 g y / k_B T}$$

where n_0 is the number density at sea level (where $y = 0$). The average height of a molecule in the Earth's atmosphere is given by

$$y_{\text{avg}} = \frac{\displaystyle\int_0^\infty y n_V(y)\, dy}{\displaystyle\int_0^\infty n_V(y)\, dy} = \frac{\displaystyle\int_0^\infty y e^{-m_0 g y / k_B T}\, dy}{\displaystyle\int_0^\infty e^{-m_0 g y / k_B T}\, dy}$$

(a) Prove that this average height is equal to $k_B T / m_0 g$. (b) Evaluate the average height, assuming the temperature is 10.0°C and the molecular mass is 28.9 u, both uniform throughout the atmosphere.

Additional Problems

44. Eight molecules have speeds of 3.00 km/s, 4.00 km/s, 5.80 km/s, 2.50 km/s, 3.60 km/s, 1.90 km/s, 3.80 km/s, and 6.60 km/s. Find (a) the average speed of the molecules and (b) the rms speed of the molecules.

45. A small oxygen tank at a gauge pressure of 125 atm has a volume of 6.88 L at 21.0°C. (a) If an athlete breathes oxygen from this tank at the rate of 8.50 L/min when measured at atmospheric pressure and the temperature remains at 21.0°C, how long will the tank last before it is empty? (b) At a particular moment during this process, what is the ratio of the rms speed of the molecules remaining in the tank to the rms speed of those being released at atmospheric pressure?

46. The dimensions of a classroom are 4.20 m × 3.00 m × 2.50 m. (a) Find the number of molecules of air in the classroom at atmospheric pressure and 20.0°C. (b) Find the mass of this air, assuming the air consists of diatomic molecules with molar mass 28.9 g/mol. (c) Find the average kinetic energy of the molecules. (d) Find the rms molecular speed. (e) **What If?** Assume the molar specific heat of the air is independent of temperature. Find the change in internal energy of the air in the room as the temperature is raised to 25.0°C. (f) Explain how you could convince a fellow student that your answer to part (e) is correct, even though it sounds surprising.

47. The Earth's atmosphere consists primarily of oxygen (21%) and nitrogen (78%). The rms speed of oxygen molecules (O_2) in the atmosphere at a certain location is 535 m/s. (a) What is the temperature of the atmosphere at this location? (b) Would the rms speed of nitrogen molecules (N_2) at this location be higher, equal to, or lower than 535 m/s? Explain. (c) Determine the rms speed of N_2 at his location.

48. AMT The *mean free path* ℓ of a molecule is the average distance that a molecule travels before colliding with another molecule. It is given by

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

where d is the diameter of the molecule and N_V is the number of molecules per unit volume. The number of collisions that a molecule makes with other molecules per unit time, or *collision frequency* f, is given by

$$f = \frac{v_{\text{avg}}}{\ell}$$

(a) If the diameter of an oxygen molecule is 2.00×10^{-10} m, find the mean free path of the molecules in a scuba tank that has a volume of 12.0 L and is filled with oxygen at a gauge pressure of 100 atm at a temperature of 25.0°C. (b) What is the average time interval between molecular collisions for a molecule of this gas?

49. AMT 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 the rifle starts with 12.0 cm^3 of compressed air, which behaves as an ideal gas with $\gamma = 1.40$. The expanding air pushes a 1.10-g pellet as a piston with cross-sectional area 0.030 0 cm^2 along the 50.0-cm-long gun barrel. What initial pressure is required to eject the pellet with a muzzle speed of 120 m/s? Ignore the effects of the air in front of the bullet and friction with the inside walls of the barrel.

50. In a sample of a solid metal, each atom is free to vibrate about some equilibrium position. The atom's energy consists of kinetic energy for motion in the x, y, and z directions plus elastic potential energy associated with the Hooke's law forces exerted by neighboring atoms on it in the x, y, and z directions. According to the theorem of equipartition of energy, assume the average energy of each atom is $\frac{1}{2}k_BT$ for each degree of freedom. (a) Prove that the molar specific heat of the solid is $3R$. The *Dulong–Petit law* states that this result generally describes pure solids at sufficiently high temperatures. (You may ignore the difference between the specific heat at constant pressure and the specific heat at constant volume.) (b) Evaluate the specific heat c of iron. Explain how it compares with the value listed in Table 20.1. (c) Repeat the evaluation and comparison for gold.

51. A certain ideal gas has a molar specific heat of $C_V = \frac{7}{2}R$. A 2.00-mol sample of the gas always starts at pressure 1.00×10^5 Pa and temperature 300 K. For each of the following processes, determine (a) the final pressure, (b) the final volume, (c) the final temperature, (d) the change in internal energy of the gas, (e) the energy added to the gas by heat, and (f) the work done on the gas. **(i)** The gas is heated at constant pressure to 400 K. **(ii)** The gas is heated at constant volume to 400 K. **(iii)** The gas is compressed at constant temperature to 1.20×10^5 Pa. **(iv)** The gas is compressed adiabatically to 1.20×10^5 Pa.

52. 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 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 $\kappa_2 = 1/(\gamma P)$. Determine values for (d) κ_1 and (e) κ_2 for a monatomic ideal gas at a pressure of 2.00 atm.

53. **Review.** Oxygen at pressures much greater than 1 atm is toxic to lung cells. Assume 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?

54. Examine the data for polyatomic gases in Table 21.2 and give a reason why sulfur dioxide has a higher specific heat at constant volume than the other polyatomic gases at 300 K.

55. 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 2.00×10^5 Pa. Energy is transferred by heat into the system as it is permitted to expand, with the pressure rising to 4.00×10^5 Pa. Throughout the expansion, the relationship between pressure and volume is given by

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

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

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

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

where M is the molar mass. The speed of sound in a gas is given by Equation 17.8; use that equation and the definition of the bulk modulus from Section 12.4. (b) Compute the theoretical speed of sound in air at 20.0°C and state how it compares 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

$$v = \sqrt{\frac{\gamma k_B T}{m_0}}$$

where m_0 is the mass of one molecule. (d) State how the result in part (c) compares with the most probable, average, and rms molecular speeds.

57. Twenty particles, each of mass m_0 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 $6v$, and one has speed $7v$. Find (a) the average speed, (b) the rms speed, (c) the most probable speed, (d) the average pressure the particles exert on the walls of the vessel, and (e) the average kinetic energy per particle.

58. In a cylinder, a sample of an ideal gas with number of moles n undergoes an adiabatic process. (a) Starting with the expression $W = -\int P\,dV$ and using the condition PV^γ = 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, show that the work done on the gas is equal to $nC_V(T_f - T_i)$. (c) Are these two results consistent with each other? Explain.

59. As a 1.00-mol sample of a monatomic ideal gas expands adiabatically, the work done on it is -2.50×10^3 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.

60. A sample consists of an amount n in moles of a monatomic ideal gas. The gas expands adiabatically, with work W done on it. (Work W is a negative number.) The initial temperature and pressure of the gas are T_i and P_i. Calculate (a) the final temperature and (b) the final pressure.

61. When a small particle is suspended in a fluid, bombardment by molecules makes the particle jitter about at random. Robert Brown discovered this motion in 1827 while studying plant fertilization, and the motion has become known as *Brownian motion*. The particle's average kinetic energy can be taken as $\frac{3}{2}k_B T$, the same as that of a molecule in an ideal gas. Consider a spherical particle of density 1.00×10^3 kg/m^3 in water at 20.0°C. (a) For a particle of diameter d, evaluate the rms speed. (b) The particle's actual motion is a random walk, but imagine that it moves with constant velocity equal in magnitude to its rms speed. In what time interval would it move by a distance equal to its own diameter? (c) Evaluate the rms speed and the time interval for a particle of diameter 3.00 μm. (d) Evaluate the rms speed and the time interval for a sphere of mass 70.0 kg, modeling your own body.

62. A vessel contains 1.00×10^4 oxygen molecules at 500 K. (a) Make an accurate graph of the Maxwell 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.

63. AMT A pitcher throws a 0.142-kg baseball at 47.2 m/s. As it travels 16.8 m to home plate, the ball slows down to 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 $C_P = \frac{7}{2}R$ 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 16.8 m in length and 3.70 cm in radius. This air is initially at 20.0°C.

64. The latent heat of vaporization for water at room temperature is 2 430 J/g. Consider one particular molecule at the surface of a glass of liquid water, moving upward with sufficiently high speed that it will be the next molecule to join the vapor. (a) Find its translational kinetic energy. (b) Find its speed. Now consider a thin gas made only of molecules like that one. (c) What is its temperature? (d) Why are you not burned by water evaporating from a vessel at room temperature?

65. A sample of a monatomic ideal gas occupies 5.00 L at atmospheric pressure and 300 K (point A in Fig. P21.65). It is warmed 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.

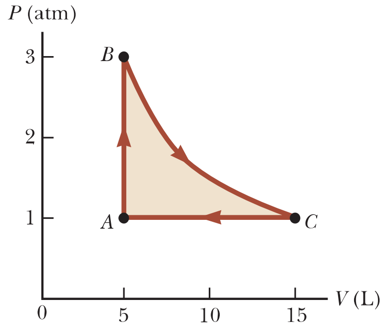

Figure P21.65

Find (b) the temperature at point B, (c) the temperature at point C, and (d) the volume at point C. (e) Now consider the processes $A \to B$, $B \to C$, and $C \to A$. Describe how to carry out each process experimentally. (f) Find Q, W, and ΔE_{int} for each of the processes. (g) For the whole cycle $A \to B \to C \to A$, find Q, W, and ΔE_{int}.

66. 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 acting on a gas molecule toward the center of the centrifuge is $m_0\omega^2 r$. (a) Discuss how a gas centrifuge can be used to separate particles of different mass. (b) Suppose the centrifuge contains a gas of particles of identical mass. Show that the density of the particles as a function of r is

$$n(r) = n_0 e^{m_0 r^2 \omega^2 / 2k_B T}$$

67. For a Maxwellian gas, use a computer or programmable calculator to find the numerical value of the ratio $N_v(v)/N_v(v_{\text{mp}})$ for the following values of v: (a) $v = (v_{\text{mp}}/50.0)$, (b) $(v_{\text{mp}}/10.0)$, (c) $(v_{\text{mp}}/2.00)$, (d) v_{mp}, (e) $2.00v_{\text{mp}}$, (f) $10.0v_{\text{mp}}$, and (g) $50.0v_{\text{mp}}$. Give your results to three significant figures.

68. A triatomic molecule can have a linear configuration, as does CO_2 (Fig. P21.68a), or it can be nonlinear, like H_2O (Fig. P21.68b). Suppose the temperature of a gas of triatomic molecules is sufficiently low that vibrational motion is negligible. What is the molar specific heat at constant volume, expressed as a multiple of the universal gas constant, (a) if the molecules are linear and (b) if the molecules are nonlinear? At high temperatures, a triatomic molecule has two modes of vibration, and each contributes $\frac{1}{2}R$ to the molar specific heat for its kinetic energy and another $\frac{1}{2}R$ for its potential energy. Identify the high-temperature molar specific heat at constant volume for a triatomic ideal gas of (c) linear molecules and (d) nonlinear molecules. (e) Explain how specific heat data can be used to determine whether a triatomic molecule is linear or nonlinear. Are the data in Table 21.2 sufficient to make this determination?

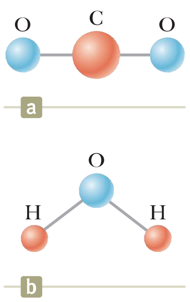

Figure P21.68

69. Using the Maxwell–Boltzmann speed distribution function, verify Equations 21.42 and 21.43 for (a) the rms speed and (b) the average speed of the molecules of a gas at a temperature T. 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 integrals B.6 in Appendix B.

70. On the PV diagram for an ideal gas, one isothermal curve and one adiabatic curve pass through each point as shown in Figure P21.70. Prove that the slope of the adiabatic curve is steeper than the slope of the isotherm at that point by the factor γ.

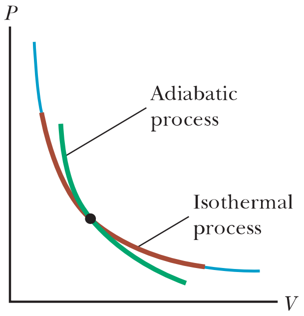

Figure P21.70

71. In 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 molar mass of water is 18.0 g/mol. (a) Find 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?

72. **Review.** (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 13.6. Using the principle of conservation of energy, show that the minimum kinetic energy needed for "escape" is $m_0 g R_E$, where m_0 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.

73. 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) Over what approximate time interval would an atom wander out of the trap region if there were no trapping action?

Challenge Problems

74. Equations 21.42 and 21.43 show that $v_{\text{rms}} > v_{\text{avg}}$ for a collection of gas particles, which turns out to be true whenever the particles have a distribution of speeds. Let us explore this inequality for a two-particle gas.

Let the speed of one particle be $v_1 = av_{\text{avg}}$ and the other particle have speed $v_2 = (2 - a)v_{\text{avg}}$. (a) Show that the average of these two speeds is v_{avg}. (b) Show that

$$v_{\text{rms}}^2 = v_{\text{avg}}^2\,(2 - 2a + a^2)$$

(c) Argue that the equation in part (b) proves that, in general, $v_{\text{rms}} > v_{\text{avg}}$. (d) Under what special condition will $v_{\text{rms}} = v_{\text{avg}}$ for the two-particle gas?

75. AMT A cylinder is closed at both ends and has insulating walls. It is divided into two compartments by an insulating piston that is perpendicular to the axis of the cylinder as shown in Figure P21.75a. Each compartment contains 1.00 mol of oxygen that behaves as an ideal gas with $\gamma = 1.40$. Initially, the two compartments have equal volumes and their temperatures are 550 K and 250 K. The piston is then allowed to move slowly parallel to the axis of the cylinder until it comes to rest at an equilibrium position (Fig. P21.75b). Find the final temperatures in the two compartments.

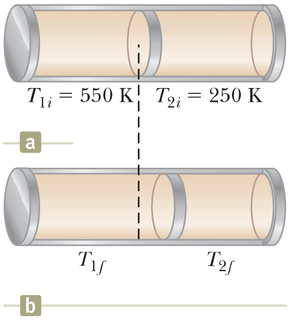

Figure P21.75