18 THERMAL PROPERTIES OF MATTER

? The higher the temperature of a gas, the greater the average kinetic energy of its molecules. How much faster are molecules moving in the air above a frying pan (100°C) than in the surrounding kitchen air (25°C)?

The kitchen is a great place to learn about how the properties of matter depend on temperature. When you boil water in a tea kettle, the increase in temperature produces steam that whistles out of the spout at high pressure. If you forget to poke holes in a potato before baking it, the high-pressure steam produced inside the potato can cause it to explode messily. Water vapor in the air can condense into droplets of liquid on the sides of a glass of ice water; if the glass is just out of the freezer, frost will form on the sides as water vapor changes to a solid.

These examples show the relationships among the large-scale or *macroscopic* properties of a substance, such as pressure, volume, temperature, and mass. But we can also describe a substance using a *microscopic* perspective. This means investigating small-scale quantities such as the masses, speeds, kinetic energies, and momenta of the individual molecules that make up a substance.

The macroscopic and microscopic descriptions are intimately related. For example, the (microscopic) forces that occur when air molecules strike a solid surface (such as your skin) cause (macroscopic) atmospheric pressure. To produce standard atmospheric pressure of 1.01×10^5 Pa, 10^{32} molecules strike your skin every day with an average speed of over 1700 km/h (1000 mi/h)!

In this chapter we'll begin our study of the thermal properties of matter by looking at some macroscopic aspects of matter in general. We'll pay special attention to the *ideal gas,* one of the simplest types of matter to understand. Using our knowledge of momentum and kinetic energy, we'll relate the macroscopic properties of an ideal gas to the microscopic behavior of its individual molecules. We'll also use microscopic ideas to understand the heat capacities of both gases and solids. Finally, we'll take a look at the various phases of matter—gas, liquid, and solid—and the conditions under which each occurs.

18.1 **Equations of State**

The conditions in which a particular material exists are described by physical quantities such as pressure, volume, temperature, and amount of substance. For example, a tank of oxygen in a welding outfit has a pressure gauge and a label stating its volume. We could add a thermometer and place the tank on a scale to determine its mass. These variables describe the *state* of the material and are called **state variables.**

The volume V of a substance is usually determined by its pressure p, temperature T, and amount of substance, described by the mass m_{total} or number of moles n. (We are calling the total mass of a substance m_{total} because later in the chapter we will use m for the mass of one molecule.) Ordinarily, we can't change one of these variables without causing a change in another. When the tank of oxygen gets hotter, the pressure increases. If the tank gets too hot, it explodes.

In a few cases the relationship among p, V, T, and m (or n) is simple enough that we can express it as an equation called the **equation of state.** When it's too complicated for that, we can use graphs or numerical tables. Even then, the relationship among the variables still exists; we call it an equation of state even when we don't know the actual equation.

Here's a simple (though approximate) equation of state for a solid material. The temperature coefficient of volume expansion β (see Section 17.4) is the fractional volume change $\Delta V/V_0$ per unit temperature change, and the compressibility k (see Section 11.4) is the negative of the fractional volume change $\Delta V/V_0$ per unit pressure change. If a certain amount of material has volume V_0 when the pressure is p_0 and the temperature is T_0, the volume V at slightly differing pressure p and temperature T is approximately

$$V = V_0[1 + \beta(T - T_0) - k(p - p_0)] \qquad (18.1)$$

(There is a negative sign in front of the term $k(p - p_0)$ because an *increase* in pressure causes a *decrease* in volume.)

The Ideal-Gas Equation

Another simple equation of state is the one for an *ideal gas.* Figure 18.1 shows an experimental setup to study the behavior of a gas. The cylinder has a movable piston to vary the volume, the temperature can be varied by heating, and we can pump any desired amount of any gas into the cylinder. We then measure the pressure, volume, temperature, and amount of gas. Note that *pressure* refers both to the force per unit area exerted by the cylinder on the gas and to the force per unit area exerted by the gas on the cylinder; by Newton's third law, these must be equal.

It is usually easiest to describe the amount of gas in terms of the number of moles n, rather than the mass. (We did this when we defined molar heat capacity in Section 17.5.) The **molar mass** M of a compound (sometimes called *molecular weight*) is the mass per mole, and the total mass m_{total} of a given quantity of that compound is the number of moles n times the mass per mole M:

$$m_{total} = nM \qquad \text{(total mass, number of moles, and molar mass)} \quad (18.2)$$

Hence if we know the number of moles of gas in the cylinder, we can determine the mass of gas using Eq. (18.2).
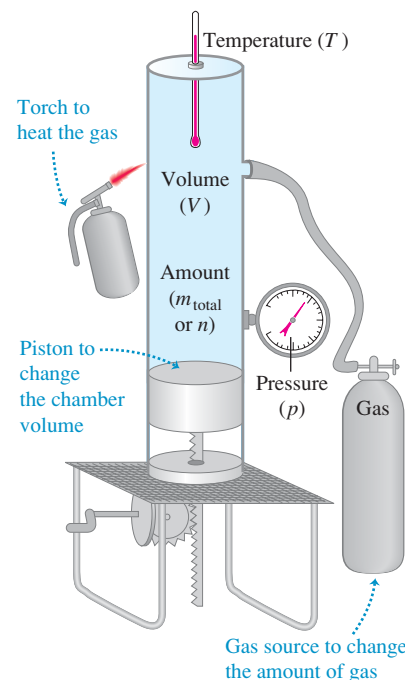
Measurements of the behavior of various gases lead to three conclusions:

1. The volume V is proportional to the number of moles n. If we double the number of moles, keeping pressure and temperature constant, the volume doubles.

18.1 A hypothetical setup for studying the behavior of gases. By heating the gas, varying the volume with a movable piston, and adding more gas, we can control the gas pressure p, volume V, temperature T, and number of moles n.

Temperature (T)

Torch to heat the gas

Volume (V)

Amount (m_{total} or n)

Piston to change the chamber volume

Pressure (p)

Gas

Gas source to change the amount of gas

2. The volume varies *inversely* with the absolute pressure p. If we double the pressure while holding the temperature T and number of moles n constant, the gas compresses to one-half of its initial volume. In other words, $pV = $ constant when n and T are constant.

3. The pressure is proportional to the *absolute* temperature. If we double the absolute temperature, keeping the volume and number of moles constant, the pressure doubles. In other words, $p = $ (constant)T when n and V are constant.

These three relationships can be combined neatly into a single equation, called the **ideal-gas equation:**

$$pV = nRT \qquad \text{(ideal-gas equation)} \qquad (18.3)$$

where R is a proportionality constant. An **ideal gas** is one for which Eq. (18.3) holds precisely for *all* pressures and temperatures. This is an idealized model; it works best at very low pressures and high temperatures, when the gas molecules are far apart and in rapid motion. It is reasonably good (within a few percent) at moderate pressures (such as a few atmospheres) and at temperatures well above those at which the gas liquefies (Fig. 18.2).

We might expect that the constant R in the ideal-gas equation would have different values for different gases, but it turns out to have the same value for *all* gases, at least at sufficiently high temperature and low pressure. It is called the **gas constant** (or *ideal-gas constant*). The numerical value of R depends on the units of p, V, and T. In SI units, in which the unit of p is Pa (1 Pa $= 1$ N/m^2) and the unit of V is m^3, the current best numerical value of R is

$$R = 8.314472(15) \text{ J/mol} \cdot \text{K}$$

or $R = 8.314$ J/mol $\cdot$ K to four significant figures. Note that the units of pressure times volume are the same as the units of work or energy (for example, N/m^2 times m^3); that's why R has units of energy per mole per unit of absolute temperature. In chemical calculations, volumes are often expressed in liters (L) and pressures in atmospheres (atm). In this system, to four significant figures,

$$R = 0.08206 \frac{\text{L} \cdot \text{atm}}{\text{mol} \cdot \text{K}}$$

We can express the ideal-gas equation, Eq. (18.3), in terms of the mass m_{total} of gas, using $m_{\text{total}} = nM$ from Eq. (18.2):

$$pV = \frac{m_{\text{total}}}{M}RT \qquad (18.4)$$

From this we can get an expression for the density $\rho = m_{\text{total}}/V$ of the gas:

$$\rho = \frac{pM}{RT} \qquad (18.5)$$

CAUTION **Density vs. pressure** When using Eq. (18.5), be certain that you distinguish between the Greek letter ρ (rho) for density and the letter p for pressure. ▌

For a *constant mass* (or constant number of moles) of an ideal gas the product nR is constant, so the quantity pV/T is also constant. If the subscripts 1 and 2 refer to any two states of the same mass of a gas, then

$$\frac{p_1V_1}{T_1} = \frac{p_2V_2}{T_2} = \text{constant} \qquad \text{(ideal gas, constant mass)} \qquad (18.6)$$

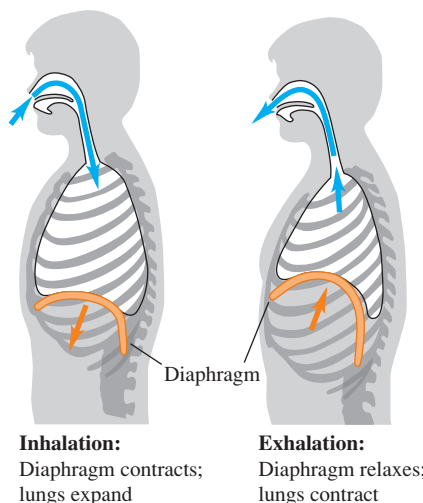Notice that you don't need the value of R to use this equation.

18.2 The ideal-gas equation $pV = nRT$ gives a good description of the air inside an inflated vehicle tire, where the pressure is about 3 atmospheres and the temperature is much too high for nitrogen or oxygen to liquefy. As the tire warms (T increases), the volume V changes only slightly but the pressure p increases.

Application **Respiration and the Ideal-Gas Equation**
To breathe, you rely on the ideal-gas equation $pV = nRT$. Contraction of the dome-shaped diaphragm muscle increases the volume V of the thoracic cavity (which encloses the lungs), decreasing its pressure p. The lowered pressure causes the lungs to expand and fill with air. (The temperature T is kept constant.) When you exhale, the diaphragm relaxes, allowing the lungs to contract and expel the air.

Inhalation: Diaphragm contracts; lungs expand

Exhalation: Diaphragm relaxes; lungs contract

We used the proportionality of pressure to absolute temperature in Chapter 17 to define a temperature scale in terms of pressure in a constant-volume gas thermometer. That may make it seem that the pressure–temperature relationship in the ideal-gas equation, Eq. (18.3), is just a result of the way we define temperature. But the equation also tells us what happens when we change the volume or the amount of substance. Also, we'll see in Chapter 20 that the gas-thermometer scale corresponds closely to a temperature scale that does *not* depend on the properties of any particular material. For now, consider Eq. (18.6) as being based on this genuinely material-independent temperature scale.

Problem-Solving Strategy 18.1   Ideal Gases

MP

IDENTIFY *the relevant concepts:* Unless the problem states otherwise, you can use the ideal-gas equation to find quantities related to the state of a gas, such as pressure p, volume V, temperature T, and/or number of moles n.

SET UP *the problem* using the following steps:
1. List the known and unknown quantities. Identify the target variables.
2. If the problem concerns only one state of the system, use Eq. (18.3), $pV = nRT$.
3. Use Eq. (18.5), $\rho = pM/RT$, as an alternative to Eq. (18.3) if the problem involves the density ρ rather than n and V.
4. In problems that concern two states (call them 1 and 2) of the same amount of gas, if all but one of the six quantities p_1, p_2, V_1, V_2, T_1, and T_2 are known, use Eq. (18.6), $p_1V_1/T_1 = p_2V_2/T_2 = $ constant. Otherwise, use Eq. (18.3) or Eq. (18.5) as appropriate.

EXECUTE *the solution* as follows:
1. Use consistent units. (SI units are entirely consistent.) The problem statement may make one system of units more con-

venient than others. Make appropriate unit conversions, such as from atmospheres to pascals or from liters to cubic meters.
2. You may have to convert between mass m_{total} and number of moles n, using $m_{total} = Mn$, where M is the molar mass. If you use Eq. (18.4), you *must* use the same mass units for m_{total} and M. So if M is in grams per mole (the usual units for molar mass), then m_{total} must also be in grams. To use m_{total} in kilograms, you must convert M to kg/mol. For example, the molar mass of oxygen is 32 g/mol or 32×10^{-3} kg/mol.
3. Remember that in the ideal-gas equations, T is always an *absolute* (Kelvin) temperature and p is always an absolute (not gauge) pressure.
4. Solve for the target variables.

EVALUATE *your answer:* Do your results make physical sense? Use benchmarks, such as the result of Example 18.1 below that a mole of an ideal gas at 1 atmosphere pressure occupies a volume of 22.4 liters.

Example 18.1   Volume of an ideal gas at STP

What is the volume of a container that holds exactly 1 mole of an ideal gas at *standard temperature and pressure* (STP), defined as $T = 0°C = 273.15$ K and $p = 1$ atm $= 1.013 \times 10^5$ Pa?

SOLUTION

IDENTIFY and SET UP: This problem involves the properties of a single state of an ideal gas, so we use Eq. (18.3). We are given the pressure p, temperature T, and number of moles n; our target variable is the corresponding volume V.

EXECUTE: From Eq. (18.3), using R in J/mol · K,

$$V = \frac{nRT}{p} = \frac{(1 \text{ mol})(8.314 \text{ J/mol} \cdot \text{K})(273.15 \text{ K})}{1.013 \times 10^5 \text{ Pa}}$$

$$= 0.0224 \text{ m}^3 = 22.4 \text{ L}$$

EVALUATE: At STP, 1 mole of an ideal gas occupies 22.4 L. This is the volume of a cube 0.282 m (11.1 in.) on a side, or of a sphere 0.350 m (13.8 in.) in diameter.

Example 18.2   Compressing gas in an automobile engine

In an automobile engine, a mixture of air and vaporized gasoline is compressed in the cylinders before being ignited. A typical engine has a compression ratio of 9.00 to 1; that is, the gas in the cylinders is compressed to $\frac{1}{9.00}$ of its original volume (Fig. 18.3). The intake

and exhaust valves are closed during the compression, so the quantity of gas is constant. What is the final temperature of the compressed gas if its initial temperature is 27°C and the initial and final pressures are 1.00 atm and 21.7 atm, respectively?

Continued

SOLUTION

IDENTIFY and SET UP: We must compare two states of the same quantity of ideal gas, so we use Eq. (18.6). In the uncompressed state, $p_1 = 1.00$ atm and $T_1 = 27°C = 300$ K. In the compressed state 2, $p_2 = 21.7$ atm. The cylinder volumes are not given, but we have $V_1 = 9.00V_2$. The temperature T_2 of the compressed gas is the target variable.

EXECUTE: We solve Eq. (18.6) for T_2:

$$T_2 = T_1 \frac{p_2 V_2}{p_1 V_1} = (300 \text{ K}) \frac{(21.7 \text{ atm}) V_2}{(1.00 \text{ atm})(9.00 V_2)} = 723 \text{ K} = 450°C$$

EVALUATE: This is the temperature of the air–gasoline mixture *before* the mixture is ignited; when burning starts, the temperature becomes higher still.

18.3 Cutaway of an automobile engine. While the air–gasoline mixture is being compressed prior to ignition, the intake and exhaust valves are both in the closed (up) position.
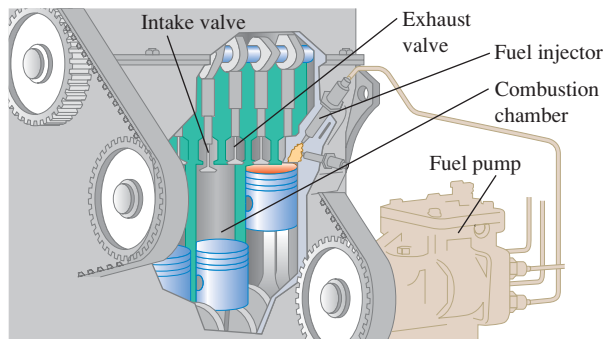
Example 18.3 Mass of air in a scuba tank

An "empty" aluminum scuba tank contains 11.0 L of air at 21°C and 1 atm. When the tank is filled rapidly from a compressor, the air temperature is 42°C and the gauge pressure is 2.10×10^7 Pa. What mass of air was added? (Air is about 78% nitrogen, 21% oxygen, and 1% miscellaneous; its average molar mass is 28.8 g/mol = 28.8×10^{-3} kg/mol.)

SOLUTION

IDENTIFY and SET UP: Our target variable is the difference $m_2 - m_1$ between the masses present at the end (state 2) and at the beginning (state 1). We are given the molar mass M of air, so we can use Eq. (18.2) to find the target variable if we know the number of moles present in states 1 and 2. We determine n_1 and n_2 by applying Eq. (18.3) to each state individually.

EXECUTE: We convert temperatures to the Kelvin scale by adding 273 and convert the pressure to absolute by adding 1.013×10^5 Pa.

The tank's volume is hardly affected by the increased temperature and pressure, so $V_2 = V_1$. From Eq. (18.3), the numbers of moles in the empty tank (n_1) and the full tank (n_2) are

$$n_1 = \frac{p_1 V_1}{RT_1} = \frac{(1.013 \times 10^5 \text{ Pa})(11.0 \times 10^{-3} \text{ m}^3)}{(8.314 \text{ J/mol} \cdot \text{K})(294 \text{ K})} = 0.46 \text{ mol}$$

$$n_2 = \frac{p_2 V_2}{RT_2} = \frac{(2.11 \times 10^7 \text{ Pa})(11.0 \times 10^{-3} \text{ m}^3)}{(8.314 \text{ J/mol} \cdot \text{K})(315 \text{ K})} = 88.6 \text{ mol}$$

We added $n_2 - n_1 = 88.6$ mol $- 0.46$ mol $= 88.1$ mol to the tank. From Eq. (18.2), the added mass is $M(n_2 - n_1) = (28.8 \times 10^{-3}$ kg/mol$)(88.1$ mol$) = 2.54$ kg.

EVALUATE: The added mass is not insubstantial: You could certainly use a scale to determine whether the tank was empty or full.

Example 18.4 Variation of atmospheric pressure with elevation

Find the variation of atmospheric pressure with elevation in the earth's atmosphere. Assume that at all elevations, $T = 0°C$ and $g = 9.80$ m/s².

SOLUTION

IDENTIFY and SET UP: As the elevation y increases, both the atmospheric pressure p and the density ρ decrease. Hence we have *two* unknown functions of y; to solve for them, we need two independent equations. One is the ideal-gas equation, Eq. (18.5), which is expressed in terms of p and ρ. The other is Eq. (12.4), the relationship that we found in Section 12.2 among p, ρ, and y in a fluid in equilibrium: $dp/dy = -\rho g$. We are told to assume that g and T are the same at all elevations; we also assume that the atmosphere has the same chemical composition, and hence the same molar mass M, at all heights. We combine the two equations and solve for $p(y)$.

EXECUTE: We substitute $\rho = pM/RT$ into $dp/dy = -\rho g$, separate variables, and integrate, letting p_1 be the pressure at elevation y_1 and p_2 be the pressure at y_2:

$$\frac{dp}{dy} = -\frac{pM}{RT} g$$

$$\int_{p_1}^{p_2} \frac{dp}{p} = -\frac{Mg}{RT} \int_{y_1}^{y_2} dy$$

$$\ln\frac{p_2}{p_1} = -\frac{Mg}{RT}(y_2 - y_1)$$

$$\frac{p_2}{p_1} = e^{-Mg(y_2 - y_1)/RT}$$

Now let $y_1 = 0$ be at sea level and let the pressure at that point be $p_0 = 1.013 \times 10^5$ Pa. Then the pressure p at any height y is

$$p = p_0 e^{-Mgy/RT}$$

EVALUATE: According to our calculation, the pressure decreases exponentially with elevation. The graph in Fig. 18.4 shows that the slope dp/dy becomes less negative with greater elevation. That result makes sense, since $dp/dy = -\rho g$ and the density also

18.4 The variation of atmospheric pressure p with elevation y, assuming a constant temperature T.
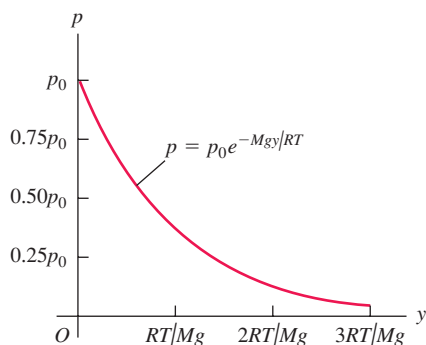
decreases with elevation. At the summit of Mount Everest, where $y = 8863$ m,

$$\frac{Mgy}{RT} = \frac{(28.8 \times 10^{-3}\ \text{kg/mol})(9.80\ \text{m/s}^2)(8863\ \text{m})}{(8.314\ \text{J/mol} \cdot \text{K})(273\ \text{K})} = 1.10$$

$$p = (1.013 \times 10^5\ \text{Pa})e^{-1.10} = 0.337 \times 10^5\ \text{Pa} = 0.33\ \text{atm}$$

The assumption of constant temperature isn't realistic, and g decreases a little with increasing elevation (see Challenge Problem 18.92). Even so, this example shows why mountaineers need to carry oxygen on Mount Everest. It also shows why jet airliners, which typically fly at altitudes of 8000 to 12,000 m, *must* have pressurized cabins for passenger comfort and health.
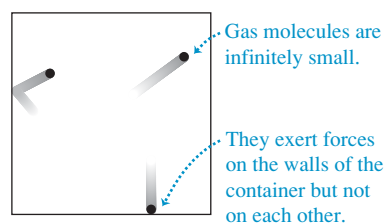
The van der Waals Equation

The ideal-gas equation, Eq. (18.3), can be obtained from a simple molecular model that ignores the volumes of the molecules themselves and the attractive forces between them (Fig. 18.5a). We'll examine that model in Section 18.3. Meanwhile, we mention another equation of state, the **van der Waals equation,** that makes approximate corrections for these two omissions (Fig. 18.5b). This equation was developed by the 19th-century Dutch physicist J. D. van der Waals; the interaction between atoms that we discussed in Section 14.4 was named the *van der Waals interaction* after him. The van der Waals equation is

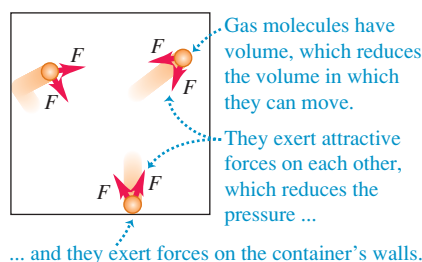$$\left(p + \frac{an^2}{V^2}\right)(V - nb) = nRT \tag{18.7}$$

The constants a and b are empirical constants, different for different gases. Roughly speaking, b represents the volume of a mole of molecules; the total volume of the molecules is then nb, and the volume remaining in which the molecules can move is $V - nb$. The constant a depends on the attractive intermolecular forces, which reduce the pressure of the gas for given values of n, V, and T by *pulling* the molecules together as they *push* on the walls of the container. The decrease in pressure is proportional to the number of molecules per unit volume in a layer near the wall (which are exerting the pressure on the wall) and is also proportional to the number per unit volume in the next layer beyond the wall (which are doing the attracting). Hence the decrease in pressure due to intermolecular forces is proportional to n^2/V^2.

When n/V is small (that is, when the gas is *dilute*), the average distance between molecules is large, the corrections in the van der Waals equation become insignificant, and Eq. (18.7) reduces to the ideal-gas equation. As an example, for carbon dioxide gas (CO_2) the constants in the van der Waals equation are $a = 0.364\ \text{J} \cdot \text{m}^3/\text{mol}^2$ and $b = 4.27 \times 10^{-5}\ \text{m}^3/\text{mol}$. We found in Example 18.1 that 1 mole of an ideal gas at $T = 0°C = 273.15$ K and $p = 1$ atm $= 1.013 \times 10^5$ Pa occupies a volume $V = 0.0224\ \text{m}^3$; according to Eq. (18.7),

(a) An idealized model of a gas

Gas molecules are infinitely small.

They exert forces on the walls of the container but not on each other.

(b) A more realistic model of a gas

Gas molecules have volume, which reduces the volume in which they can move.

They exert attractive forces on each other, which reduces the pressure ...

... and they exert forces on the container's walls.

18.5 A gas as modeled by (a) the ideal-gas equation and (b) the van der Waals equation.

1 mole of CO_2 occupying this volume at this temperature would be at a pressure 532 Pa less than 1 atm, a difference of only 0.5% from the ideal-gas value.

pV-Diagrams

We could in principle represent the *p-V-T* relationship graphically as a *surface* in a three-dimensional space with coordinates *p*, *V*, and *T*. This representation sometimes helps us grasp the overall behavior of the substance, but ordinary two-dimensional graphs are usually more convenient. One of the most useful of these is a set of graphs of pressure as a function of volume, each for a particular constant temperature. Such a diagram is called a *pV*-**diagram.** Each curve, representing behavior at a specific temperature, is called an **isotherm,** or a *pV-isotherm.*

Figure 18.6 shows *pV*-isotherms for a constant amount of an ideal gas. Since $p = nRT/V$ from Eq. (18.3), along an isotherm (constant *T*) the pressure *p* is inversely proportional to the volume *V* and the isotherms are hyperbolic curves.

Figure 18.7 shows a *pV*-diagram for a material that *does not* obey the ideal-gas equation. At temperatures below T_c the isotherms develop flat regions in which we can compress the material (that is, reduce the volume *V*) without increasing the pressure *p*. Observation shows that the gas is *condensing* from the vapor (gas) to the liquid phase. The flat parts of the isotherms in the shaded area of Fig. 18.7 represent conditions of liquid-vapor *phase equilibrium.* As the volume decreases, more and more material goes from vapor to liquid, but the pressure does not change. (To keep the temperature constant during condensation, we have to remove the heat of vaporization, discussed in Section 17.6.)

When we compress such a gas at a constant temperature T_2 in Fig. 18.7, it is vapor until point *a* is reached. Then it begins to liquefy; as the volume decreases further, more material liquefies, and *both* the pressure and the temperature remain constant. At point *b*, all the material is in the liquid state. After this, any further compression requires a very rapid rise of pressure, because liquids are in general much less compressible than gases. At a lower constant temperature T_1, similar behavior occurs, but the condensation begins at lower pressure and greater volume than at the constant temperature T_2. At temperatures greater than T_c, *no* phase transition occurs as the material is compressed; at the highest temperatures, such as T_4, the curves resemble the ideal-gas curves of Fig. 18.6. We call T_c the *critical temperature* for this material. In Section 18.6 we'll discuss what happens to the phase of the gas above the critical temperature.

We will use *pV*-diagrams often in the next two chapters. We will show that the *area* under a *pV*-curve (whether or not it is an isotherm) represents the *work* done by the system during a volume change. This work, in turn, is directly related to heat transfer and changes in the *internal energy* of the system.

18.6 Isotherms, or constant-temperature curves, for a constant amount of an ideal gas. The highest temperature is T_4; the lowest is T_1. This is a graphical representation of the ideal-gas equation of state.

Each curve represents pressure as a function of volume for an ideal gas at a single temperature.

For each curve, *pV* is constant and is directly proportional to *T* (Boyle's law).

$T_4 > T_3 > T_2 > T_1$
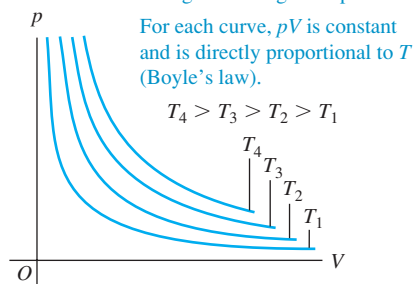
18.7 A *pV*-diagram for a nonideal gas, showing isotherms for temperatures above and below the critical temperature T_c. The liquid–vapor equilibrium region is shown as a green shaded area. At still lower temperatures the material might undergo phase transitions from liquid to solid or from gas to solid; these are not shown in this diagram.

$T_4 > T_3 > T_c > T_2 > T_1$

Above the critical temperature T_c there is no liquid–vapor phase transition.

Below T_c, the material condenses to liquid as it is compressed.

Liquid

Vapor

Liquid–vapor phase equilibrium region

Test Your Understanding of Section 18.1 Rank the following ideal gases in order from highest to lowest number of moles: (i) pressure 1 atm, volume 1 L, and temperature 300 K; (ii) pressure 2 atm, volume 1 L, and temperature 300 K; (iii) pressure 1 atm, volume 2 L, and temperature 300 K; (iv) pressure 1 atm, volume 1 L, and temperature 600 K; (v) pressure 2 atm, volume 1 L, and temperature 600 K. ❙
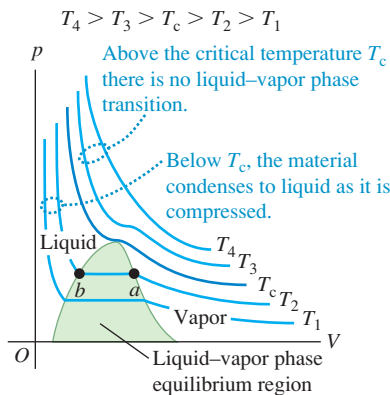
18.2 Molecular Properties of Matter

We have studied several properties of matter in bulk, including elasticity, density, surface tension, heat capacities, and equations of state. Now we want to look in more detail at the relationship of bulk behavior to *molecular* structure. We begin with a general discussion of the molecular structure of matter. Then in the next two sections we develop the kinetic-molecular model of an ideal gas, obtaining from this molecular model the equation of state and an expression for heat capacity.

Molecules and Intermolecular Forces

Any specific chemical compound is made up of identical **molecules.** The smallest molecules contain one atom each and are of the order of 10^{-10} m in size; the largest contain many atoms and are at least 10,000 times larger. In gases the molecules move nearly independently; in liquids and solids they are held together by intermolecular forces. These forces arise from interactions among the electrically charged particles that make up the molecules. Gravitational forces between molecules are negligible in comparison with electrical forces.

The interaction of two *point* electric charges is described by a force (repulsive for like charges, attractive for unlike charges) with a magnitude proportional to $1/r^2$, where r is the distance between the points. We will study this relationship, called *Coulomb's law,* in Chapter 21. Molecules are *not* point charges but complex structures containing both positive and negative charge, and their interactions are more complex. The force between molecules in a gas varies with the distance r between molecules somewhat as shown in Fig. 18.8, where a positive F_r corresponds to a repulsive force and a negative F_r to an attractive force. When molecules are far apart, the intermolecular forces are very small and usually attractive. As a gas is compressed and its molecules are brought closer together, the attractive forces increase. The intermolecular force becomes zero at an equilibrium spacing r_0, corresponding roughly to the spacing between molecules in the liquid and solid states. In liquids and solids, relatively large pressures are needed to compress the substance appreciably. This shows that at molecular distances slightly *less* than the equilibrium spacing, the forces become *repulsive* and relatively large.

Figure 18.8 also shows the potential energy as a function of r. This function has a *minimum* at r_0, where the force is zero. The two curves are related by $F_r(r) = -dU/dr$, as we showed in Section 7.4. Such a potential-energy function is often called a **potential well.** A molecule at rest at a distance r_0 from a second molecule would need an additional energy $|U_0|$, the "depth" of the potential well, to "escape" to an indefinitely large value of r.

Molecules are always in motion; their kinetic energies usually increase with temperature. At very low temperatures the average kinetic energy of a molecule may be much *less* than the depth of the potential well. The molecules then condense into the liquid or solid phase with average intermolecular spacings of about r_0. But at higher temperatures the average kinetic energy becomes larger than the depth $|U_0|$ of the potential well. Molecules can then escape the intermolecular force and become free to move independently, as in the gaseous phase of matter.
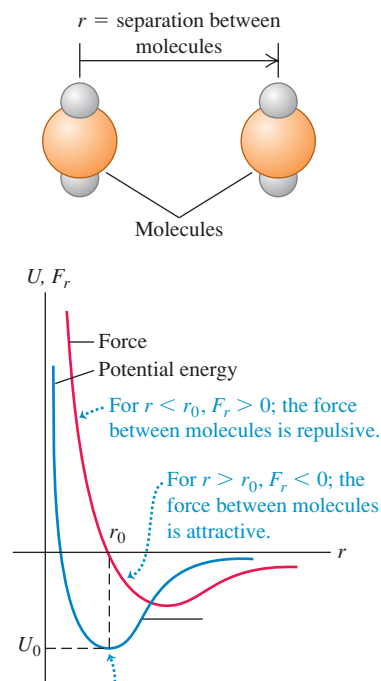
In *solids,* molecules vibrate about more or less fixed points. In a crystalline solid these points are arranged in a *crystal lattice.* Figure 18.9 shows the cubic crystal structure of sodium chloride, and Fig. 18.10 shows a scanning tunneling microscope image of individual silicon atoms on the surface of a crystal.

The vibration of molecules in a solid about their equilibrium positions may be nearly simple harmonic if the potential well is approximately parabolic in shape at distances close to r_0. (We discussed this kind of simple harmonic motion in Section 14.4.) But if the potential-energy curve rises more gradually for $r > r_0$ than for $r < r_0$, as in Fig. 18.8, the average position shifts to larger r with increasing amplitude. As we pointed out in Section 17.4, this is the basis of thermal expansion.

In a *liquid,* the intermolecular distances are usually only slightly greater than in the solid phase of the same substance, but the molecules have much greater freedom of movement. Liquids show regularity of structure only in the immediate neighborhood of a few molecules.

The molecules of a *gas* are usually widely separated and so have only very small attractive forces. A gas molecule moves in a straight line until it collides with another molecule or with a wall of the container. In molecular terms, an *ideal gas* is a gas whose molecules exert *no* attractive forces on each other (see Fig. 18.5a) and therefore have no *potential* energy.

18.8 How the force between molecules and their potential energy of interaction depend on their separation r.

r = separation between molecules

Molecules

U, F_r

Force

Potential energy

For $r < r_0$, $F_r > 0$; the force between molecules is repulsive.

For $r > r_0$, $F_r < 0$; the force between molecules is attractive.

r_0

r

U_0

At a separation $r = r_0$, the potential energy of the two molecules is minimum and the force between the molecules is zero.

18.9 Schematic representation of the cubic crystal structure of sodium chloride (ordinary salt).

Chloride ions

Sodium ions
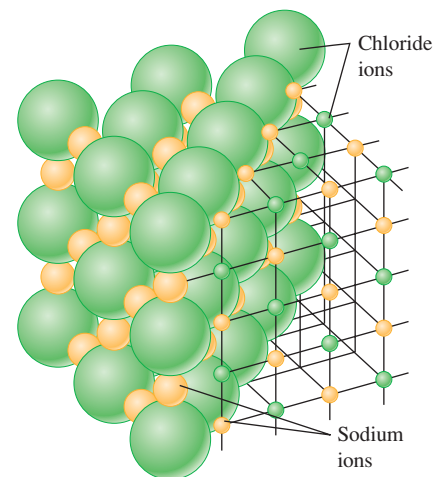
18.10 A scanning tunneling microscope image of the surface of a silicon crystal. The area shown is only 9.0 nm $(9.0 \times 10^{-9}$ m$)$ across. Each blue "bead" is an individual silicon atom; you can clearly see how these atoms are arranged in a (nearly) perfect array of hexagons.
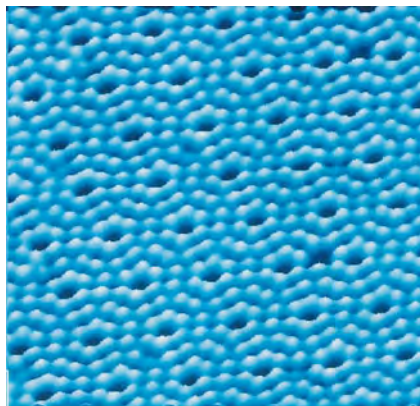
At low temperatures, most common substances are in the solid phase. As the temperature rises, a substance melts and then vaporizes. From a molecular point of view, these transitions are in the direction of increasing molecular kinetic energy. Thus temperature and molecular kinetic energy are closely related.

Moles and Avogadro's Number

We have used the mole as a measure of quantity of substance. One **mole** of any pure chemical element or compound contains a definite number of molecules, the same number for all elements and compounds. The official SI definition is:

> **One mole is the amount of substance that contains as many elementary entities as there are atoms in 0.012 kilogram of carbon-12.**

In our discussion, the "elementary entities" are molecules. (In a monatomic substance such as carbon or helium, each molecule is a single atom.) Atoms of a given element may occur in any of several isotopes, which are chemically identical but have different atomic masses; "carbon-12" is a specific isotope of carbon.

The number of molecules in a mole is called **Avogadro's number,** denoted by N_A. The current best numerical value of N_A is

$$N_A = 6.02214179(30) \times 10^{23} \text{ molecules/mol (Avogadro's number)}$$

The *molar mass M* of a compound is the mass of 1 mole. It is equal to the mass m of a single molecule multiplied by Avogadro's number:

$$M = N_A m \qquad \text{(molar mass, Avogadro's number, and mass of a molecule)} \qquad (18.8)$$

When the molecule consists of a single atom, the term *atomic mass* is often used instead of molar mass or molecular weight.

Example 18.5 | Atomic and molecular mass

Find the mass of a single hydrogen atom and of a single oxygen molecule.

SOLUTION

IDENTIFY and SET UP: This problem involves the relationship between the mass of a molecule or atom (our target variable) and the corresponding molar mass M. We use Eq. (18.8) in the form $m = M/N_A$ and the values of the atomic masses from the periodic table of the elements (see Appendix D).

EXECUTE: For atomic hydrogen the atomic mass (molar mass) is $M_H = 1.008$ g/mol, so the mass m_H of a single hydrogen atom is

$$m_H = \frac{1.008 \text{ g/mol}}{6.022 \times 10^{23} \text{ atoms/mol}} = 1.674 \times 10^{-24} \text{ g/atom}$$

For oxygen the atomic mass is 16.0 g/mol, so for the diatomic (two-atom) oxygen molecule the molar mass is 32.0 g/mol. Then the mass of a single oxygen molecule is

$$m_{O_2} = \frac{32.0 \text{ g/mol}}{6.022 \times 10^{23} \text{ molecules/mol}} = 53.1 \times 10^{-24} \text{ g/molecule}$$

EVALUATE: We note that the values in Appendix D are for the *average* atomic masses of a natural sample of each element. Such a sample may contain several *isotopes* of the element, each with a different atomic mass. Natural samples of hydrogen and oxygen are almost entirely made up of just one isotope.

Test Your Understanding of Section 18.2 Suppose you could adjust the value of r_0 for the molecules of a certain chemical compound (Fig. 18.8) by turning a dial. If you doubled the value of r_0, the density of the solid form of this compound would become (i) twice as great; (ii) four times as great; (iii) eight times as great; (iv) $\frac{1}{2}$ as great; (v) $\frac{1}{4}$ as great; (vi) $\frac{1}{8}$ as great.

18.3 Kinetic-Molecular Model of an Ideal Gas

The goal of any molecular theory of matter is to understand the *macroscopic* properties of matter in terms of its atomic or molecular structure and behavior. Once we have this understanding, we can design materials to have specific desired properties. Theories have led to the development of high-strength steels, semiconductor materials for electronic devices, and countless other materials essential to contemporary technology.

In this and the following sections we will consider a simple molecular model of an ideal gas. This *kinetic-molecular model* represents the gas as a large number of particles bouncing around in a closed container. In this section we use the kinetic-molecular model to understand how the ideal-gas equation of state, Eq. (18.3), is related to Newton's laws. In the following section we use the kinetic-molecular model to predict the molar heat capacity of an ideal gas. We'll go on to elaborate the model to include "particles" that are not points but have a finite size.

Our discussion of the kinetic-molecular model has several steps, and you may need to go over them several times. Don't get discouraged!

Here are the assumptions of our model:

1. A container with volume V contains a very large number N of identical molecules, each with mass m.
2. The molecules behave as point particles that are small compared to the size of the container and to the average distance between molecules.
3. The molecules are in constant motion. Each molecule collides occasionally with a wall of the container. These collisions are perfectly elastic.
4. The container walls are rigid and infinitely massive and do not move.

CAUTION **Molecules vs. moles** Make sure you don't confuse N, the number of *molecules* in the gas, with n, the number of *moles*. The number of molecules is equal to the number of moles multiplied by Avogadro's number: $N = nN_A$. ▌

Collisions and Gas Pressure

During collisions the molecules exert *forces* on the walls of the container; this is the origin of the *pressure* that the gas exerts. In a typical collision (Fig. 18.11) the velocity component parallel to the wall is unchanged, and the component perpendicular to the wall reverses direction but does not change in magnitude.

Our program is first to determine the *number* of collisions that occur per unit time for a certain area A of wall. Then we find the total momentum change associated with these collisions and the force needed to cause this momentum change. From this we can determine the pressure, which is force per unit area, and compare the result to the ideal-gas equation. We'll find a direct connection between the temperature of the gas and the kinetic energy of the gas molecules.

To begin, we will assume that all molecules in the gas have the same *magnitude* of x-velocity, $|v_x|$. This isn't right, but making this temporary assumption helps to clarify the basic ideas. We will show later that this assumption isn't really necessary.

As shown in Fig. 18.11, for each collision the x-component of velocity changes from $-|v_x|$ to $+|v_x|$. So the x-component of momentum changes from $-m|v_x|$ to $+m|v_x|$, and the *change* in the x-component of momentum is $m|v_x| - (-m|v_x|) = 2m|v_x|$.

If a molecule is going to collide with a given wall area A during a small time interval dt, then at the beginning of dt it must be within a distance $|v_x|\, dt$ from the wall (Fig. 18.12) and it must be headed toward the wall. So the number of molecules that collide with A during dt is equal to the number of molecules within a cylinder with base area A and length $|v_x|\, dt$ that have their x-velocity aimed
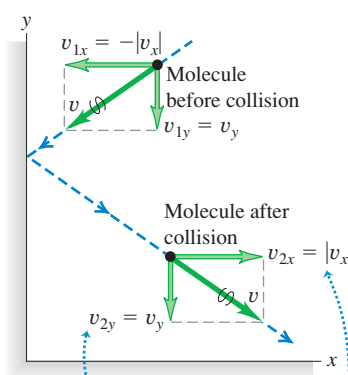
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18.11 Elastic collision of a molecule with an idealized container wall.

- Velocity component parallel to the wall (y-component) does not change.
- Velocity component perpendicular to the wall (x-component) reverses direction.
- Speed v does not change.

18.12 For a molecule to strike the wall in area A during a time interval dt, the molecule must be headed for the wall and be within the shaded cylinder of length $|v_x|\, dt$ at the beginning of the interval.
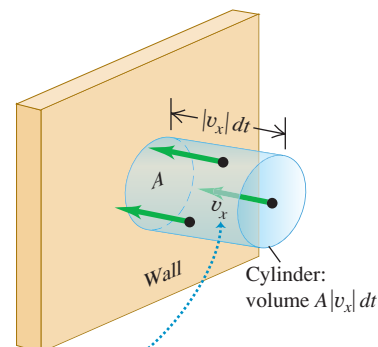
All molecules are assumed to have the same magnitude $|v_x|$ of x-velocity.

toward the wall. The volume of such a cylinder is $A|v_x|\, dt$. Assuming that the number of molecules per unit volume (N/V) is uniform, the *number* of molecules in this cylinder is $(N/V)(A|v_x|\, dt)$. On the average, half of these molecules are moving toward the wall and half are moving away from it. So the number of collisions with A during dt is

$$\tfrac{1}{2}\left(\frac{N}{V}\right)(A|v_x|\, dt)$$

For the system of all molecules in the gas, the total momentum change dP_x during dt is the *number* of collisions multiplied by $2m|v_x|$:

$$dP_x = \tfrac{1}{2}\left(\frac{N}{V}\right)(A|v_x|\, dt)(2m|v_x|) = \frac{NAmv_x^2\, dt}{V} \qquad (18.9)$$

(We are using capital P for total momentum and small p for pressure. Be careful!) We wrote v_x^2 rather than $|v_x|^2$ in the final expression because the square of the absolute value of a number is equal to the square of that number. The *rate* of change of momentum component P_x is

$$\frac{dP_x}{dt} = \frac{NAmv_x^2}{V} \qquad (18.10)$$

According to Newton's second law, this rate of change of momentum equals the force exerted by the wall area A on the gas molecules. From Newton's *third* law this is equal and opposite to the force exerted *on* the wall *by* the molecules. Pressure p is the magnitude of the force exerted on the wall per unit area, and we obtain

$$p = \frac{F}{A} = \frac{Nmv_x^2}{V} \qquad (18.11)$$

The pressure exerted by the gas depends on the number of molecules per volume (N/V), the mass m per molecule, and the speed of the molecules.

Pressure and Molecular Kinetic Energies

We mentioned that $|v_x|$ is really *not* the same for all the molecules. But we could have sorted the molecules into groups having the same $|v_x|$ within each group, then added up the resulting contributions to the pressure. The net effect of all this is just to replace v_x^2 in Eq. (18.11) by the *average* value of v_x^2, which we denote by $(v_x^2)_{av}$. We can relate $(v_x^2)_{av}$ to the *speeds* of the molecules. The speed v of a molecule is related to the velocity components v_x, v_y, and v_z by

$$v^2 = v_x^2 + v_y^2 + v_z^2$$

We can average this relation over all molecules:

$$(v^2)_{av} = (v_x^2)_{av} + (v_y^2)_{av} + (v_z^2)_{av}$$

But there is no real difference in our model between the x-, y-, and z-directions. (Molecular speeds are very fast in a typical gas, so the effects of gravity are negligibly small.) It follows that $(v_x^2)_{av}$, $(v_y^2)_{av}$, and $(v_z^2)_{av}$ must all be *equal*. Hence $(v^2)_{av}$ is equal to $3(v_x^2)_{av}$ and

$$(v_x^2)_{av} = \tfrac{1}{3}(v^2)_{av}$$

so Eq. (18.11) becomes

$$pV = \tfrac{1}{3}Nm(v^2)_{av} = \tfrac{1}{3}N\left[\tfrac{1}{2}m(v^2)_{av}\right] \qquad (18.12)$$

We notice that $\tfrac{1}{2}m(v^2)_{av}$ is the average translational kinetic energy of a single molecule. The product of this and the total number of molecules N equals the

total random kinetic energy K_{tr} of translational motion of all the molecules. (The notation K_{tr} reminds us that this is the energy of *translational* motion. There may also be energies associated with molecular rotation and vibration.) The product pV equals two-thirds of the total translational kinetic energy:

$$pV = \tfrac{2}{3}K_{tr} \qquad (18.13)$$

Now we compare this with the ideal-gas equation,

$$pV = nRT$$

which is based on experimental studies of gas behavior. For the two equations to agree, we must have

$$K_{tr} = \tfrac{3}{2}nRT \qquad \begin{array}{l}\text{(average translational kinetic}\\ \text{energy of } n \text{ moles of ideal gas)}\end{array} \qquad (18.14)$$

This remarkably simple result shows that K_{tr} is *directly proportional* to the absolute temperature T (Fig. 18.13).

The average translational kinetic energy of a single molecule is the total translational kinetic energy K_{tr} of all molecules divided by the number of molecules, N:

$$\frac{K_{tr}}{N} = \tfrac{1}{2}m(v^2)_{av} = \frac{3nRT}{2N}$$

Also, the total number of molecules N is the number of moles n multiplied by Avogadro's number N_A, so

$$N = nN_A \qquad \frac{n}{N} = \frac{1}{N_A}$$

and

$$\frac{K_{tr}}{N} = \tfrac{1}{2}m(v^2)_{av} = \tfrac{3}{2}\left(\frac{R}{N_A}\right)T \qquad (18.15)$$

The ratio R/N_A occurs frequently in molecular theory. It is called the **Boltzmann constant,** k:

$$k = \frac{R}{N_A} = \frac{8.314 \text{ J/mol} \cdot \text{K}}{6.022 \times 10^{23} \text{ molecules/mol}}$$

$$= 1.381 \times 10^{-23} \text{ J/molecule} \cdot \text{K}$$

(The current best numerical value of k is $1.3806504(24) \times 10^{-23}$ J/molecule $\cdot$ K). In terms of k we can rewrite Eq. (18.15) as

$$\tfrac{1}{2}m(v^2)_{av} = \tfrac{3}{2}kT \qquad \begin{array}{l}\text{(average translational kinetic}\\ \text{energy of a gas molecule)}\end{array} \qquad (18.16)$$

This shows that the average translational kinetic energy *per molecule* depends only on the temperature, not on the pressure, volume, or kind of molecule. We can obtain the average translational kinetic energy *per mole* by multiplying Eq. (18.16) by Avogadro's number and using the relation $M = N_Am$:

$$N_A\tfrac{1}{2}m(v^2)_{av} = \tfrac{1}{2}M(v^2)_{av} = \tfrac{3}{2}RT \qquad \begin{array}{l}\text{(average translational kinetic}\\ \text{energy per mole of gas)}\end{array} \qquad (18.17)$$

The translational kinetic energy of a mole of an ideal gas depends only on T.

18.13 Summer air (top) is warmer than winter air (bottom); that is, the average translational kinetic energy of air molecules is greater in summer.

Finally, it is sometimes convenient to rewrite the ideal-gas equation on a molecular basis. We use $N = N_A n$ and $R = N_A k$ to obtain this alternative form:

$$pV = NkT \qquad (18.18)$$

This shows that we can think of the Boltzmann constant k as a gas constant on a "per-molecule" basis instead of the usual "per-mole" basis for R.

Molecular Speeds

From Eqs. (18.16) and (18.17) we can obtain expressions for the square root of $(v^2)_{av}$, called the **root-mean-square speed** (or **rms speed**) v_{rms}:

$$v_{rms} = \sqrt{(v^2)_{av}} = \sqrt{\frac{3kT}{m}} = \sqrt{\frac{3RT}{M}} \quad \begin{array}{l}\text{(root-mean-square speed}\\\text{of a gas molecule)}\end{array} \qquad (18.19)$$

It might seem more natural to characterize molecular speeds by their *average* value rather than by v_{rms}, but we see that v_{rms} follows more directly from Eqs. (18.16) and (18.17). To compute the rms speed, we square each molecular speed, add, divide by the number of molecules, and take the square root; v_{rms} is the *root* of the *mean* of the *squares*. Example 18.7 illustrates this procedure.

Equations (18.16) and (18.19) show that at a given temperature T, gas molecules of different mass m have the same average kinetic energy but different root-mean-square speeds. On average, the nitrogen molecules $(M = 28 \text{ g/mol})$ in the air around you are moving faster than are the oxygen molecules $(M = 32 \text{ g/mol})$. Hydrogen molecules $(M = 2 \text{ g/mol})$ are fastest of all; this is why there is hardly any hydrogen in the earth's atmosphere, despite its being the most common element in the universe (Fig. 18.14). A sizable fraction of any H_2 molecules in the atmosphere would have speeds greater than the earth's escape speed of 1.12×10^4 m/s (calculated in Example 13.5 in Section 13.3) and would escape into space. The heavier, slower-moving gases cannot escape so easily, which is why they predominate in our atmosphere.

The assumption that individual molecules undergo perfectly elastic collisions with the container wall is actually a little too simple. More detailed investigation has shown that in most cases, molecules actually adhere to the wall for a short time and then leave again with speeds that are characteristic of the temperature *of the wall*. However, the gas and the wall are ordinarily in thermal equilibrium and have the same temperature. So there is no net energy transfer between gas and wall, and this discovery does not alter the validity of our conclusions.

18.14 While hydrogen is a desirable fuel for vehicles, it is only a trace constituent of our atmosphere (0.00005% by volume). Hence hydrogen fuel has to be generated by electrolysis of water, which is itself an energy-intensive process.

| **Problem-Solving Strategy 18.2** | **Kinetic-Molecular Theory** | (MP) |

IDENTIFY *the relevant concepts:* Use the results of the kinetic-molecular model to relate the macroscopic properties of a gas, such as temperature and pressure, to microscopic properties, such as molecular speeds.

SET UP *the problem* using the following steps:
1. List knowns and unknowns; identify the target variables.
2. Choose appropriate equation(s) from among Eqs. (18.14), (18.16), and (18.19).

EXECUTE *the solution* as follows: Maintain consistency in units. Note especially the following:
1. The usual units for molar mass M are grams per mole; these units are often omitted in tables. In equations such as Eq. (18.19), when you use SI units you must express M in kilograms per

mole. For example, for oxygen $M_{O_2} = 32$ g/mol $= 32 \times 10^{-3}$ kg/mol.
2. Are you working on a "per-molecule" basis (with m, N, and k) or a "per-mole" basis (with M, n, and R)? To check units, think of N as having units of "molecules"; then m has units of mass per molecule, and k has units of joules per molecule per kelvin. Similarly, n has units of moles; then M has units of mass per mole and R has units of joules per mole per kelvin.
3. Remember that T is always *absolute* (Kelvin) temperature.

EVALUATE *your answer:* Are your answers reasonable? Here's a benchmark: Typical molecular speeds at room temperature are several hundred meters per second.

Example 18.6 Molecular kinetic energy and v_{rms}

(a) What is the average translational kinetic energy of an ideal-gas molecule at 27°C? (b) What is the total random translational kinetic energy of the molecules in 1 mole of this gas? (c) What is the root-mean-square speed of oxygen molecules at this temperature?

SOLUTION

IDENTIFY and SET UP: This problem involves the translational kinetic energy of an ideal gas on a per-molecule and per-mole basis, as well as the root-mean-square molecular speed v_{rms}. We are given $T = 27°C = 300$ K and $n = 1$ mol; we use the molecular mass m for oxygen. We use Eq. (18.16) to determine the average kinetic energy of a molecule, Eq. (18.14) to find the total molecular kinetic energy K_{tr} of 1 mole, and Eq. (18.19) to find v_{rms}.

EXECUTE: (a) From Eq. (18.16),

$$\tfrac{1}{2}m(v^2)_{av} = \tfrac{3}{2}kT = \tfrac{3}{2}(1.38 \times 10^{-23} \text{ J/K})(300 \text{ K})$$
$$= 6.21 \times 10^{-21} \text{ J}$$

(b) From Eq. (18.14), the kinetic energy of one mole is

$$K_{tr} = \tfrac{3}{2}nRT = \tfrac{3}{2}(1 \text{ mol})(8.314 \text{ J/mol} \cdot \text{K})(300 \text{ K}) = 3740 \text{ J}$$

(c) We found the mass per molecule m and molar mass M of molecular oxygen in Example 18.5. Using Eq. (18.19), we can calculate v_{rms} in two ways:

$$v_{rms} = \sqrt{\frac{3kT}{m}} = \sqrt{\frac{3(1.38 \times 10^{-23} \text{ J/K})(300 \text{ K})}{5.31 \times 10^{-26} \text{ kg}}}$$
$$= 484 \text{ m/s} = 1740 \text{ km/h} = 1080 \text{ mi/h}$$

$$v_{rms} = \sqrt{\frac{3RT}{M}} = \sqrt{\frac{3(8.314 \text{ J/mol} \cdot \text{K})(300 \text{ K})}{32.0 \times 10^{-3} \text{ kg/mol}}} = 484 \text{ m/s}$$

EVALUATE: The answer in part (a) does not depend on the mass of the molecule. We can check our result in part (b) by noting that the translational kinetic energy per mole must be equal to the product of the average translational kinetic energy per molecule from part (a) and Avogadro's number N_A: $K_{tr} = (6.022 \times 10^{23} \text{ molecules})$ $(6.21 \times 10^{-21} \text{ J/molecule}) = 3740 \text{ J}$.

Example 18.7 Calculating rms and average speeds

Five gas molecules chosen at random are found to have speeds of 500, 600, 700, 800, and 900 m/s. What is the rms speed? What is the *average* speed?

SOLUTION

IDENTIFY and SET UP: We use the definitions of the root mean square and the average of a collection of numbers. To find v_{rms}, we square each speed, find the average (mean) of the squares, and take the square root of the result. We find v_{av} as usual.

EXECUTE: The average value of v^2 and the resulting v_{rms} for the five molecules are

$$(v^2)_{av} = \frac{500^2 + 600^2 + 700^2 + 800^2 + 900^2}{5} \text{ m}^2/\text{s}^2$$
$$= 5.10 \times 10^5 \text{ m}^2/\text{s}^2$$

$$v_{rms} = \sqrt{(v^2)_{av}} = 714 \text{ m/s}$$

The average speed v_{av} is

$$v_{av} = \frac{500 + 600 + 700 + 800 + 900}{5} \text{ m/s} = 700 \text{ m/s}$$

EVALUATE: In general v_{rms} and v_{av} are *not* the same. Roughly speaking, v_{rms} gives greater weight to the higher speeds than does v_{av}.

Collisions Between Molecules

We have ignored the possibility that two gas molecules might collide. If they are really points, they *never* collide. But consider a more realistic model in which the molecules are rigid spheres with radius r. How often do they collide with other molecules? How far do they travel, on average, between collisions? We can get approximate answers from the following rather primitive model.

Consider N spherical molecules with radius r in a volume V. Suppose only one molecule is moving. When it collides with another molecule, the distance between centers is $2r$. Suppose we draw a cylinder with radius $2r$, with its axis parallel to the velocity of the molecule (Fig. 18.15). The moving molecule collides with any other molecule whose center is inside this cylinder. In a short time dt a molecule with speed v travels a distance $v\,dt$; during this time it collides with any molecule that is in the cylindrical volume of radius $2r$ and length $v\,dt$. The volume of the cylinder is $4\pi r^2 v\,dt$. There are N/V molecules per unit volume, so the number dN with centers in this cylinder is

$$dN = 4\pi r^2 v\,dt\,N/V$$

18.15 In a time dt a molecule with radius r will collide with any other molecule within a cylindrical volume of radius $2r$ and length $v\,dt$.
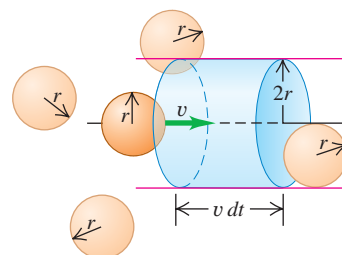
Thus the number of collisions *per unit time* is

$$\frac{dN}{dt} = \frac{4\pi r^2 v N}{V}$$

This result assumes that only one molecule is moving. The analysis is quite a bit more involved when all the molecules move at once. It turns out that in this case the collisions are more frequent, and the above equation has to be multiplied by a factor of $\sqrt{2}$:

$$\frac{dN}{dt} = \frac{4\pi \sqrt{2} r^2 v N}{V}$$

The average time t_{mean} between collisions, called the *mean free time,* is the reciprocal of this expression:

$$t_{mean} = \frac{V}{4\pi \sqrt{2} r^2 v N} \qquad (18.20)$$

The average distance traveled between collisions is called the **mean free path,** denoted by λ (the Greek letter lambda). In our simple model, this is just the molecule's speed v multiplied by t_{mean}:

18.16 If you try to walk through a crowd, your mean free path—the distance you can travel on average without running into another person—depends on how large the people are and how closely they are spaced.

$$\lambda = vt_{mean} = \frac{V}{4\pi \sqrt{2} r^2 N} \qquad \text{(mean free path of a gas molecule)} \qquad (18.21)$$

The mean free path is inversely proportional to the number of molecules per unit volume (N/V) and inversely proportional to the cross-sectional area πr^2 of a molecule; the more molecules there are and the larger the molecule, the shorter the mean distance between collisions (Fig. 18.16). Note that the mean free path *does not* depend on the speed of the molecule.

We can express Eq. (18.21) in terms of macroscopic properties of the gas, using the ideal-gas equation in the form of Eq. (18.18), $pV = NkT$. We find

$$\lambda = \frac{kT}{4\pi \sqrt{2} r^2 p} \qquad (18.22)$$

If the temperature is increased at constant pressure, the gas expands, the average distance between molecules increases, and λ increases. If the pressure is increased at constant temperature, the gas compresses and λ decreases.

Example 18.8 Calculating mean free path

(a) Estimate the mean free path of a molecule of air at 27°C and 1 atm. Model the molecules as spheres with radius $r = 2.0 \times 10^{-10}$ m. (b) Estimate the mean free time of an oxygen molecule with $v = v_{rms}$ at 27°C and 1 atm.

SOLUTION

IDENTIFY and SET UP: This problem uses the concepts of mean free path and mean free time (our target variables). We use Eq. (18.22) to determine the mean free path λ. We then use the basic relationship $\lambda = vt_{mean}$ in Eq. (18.21), with $v = v_{rms}$, to find the mean free time t_{mean}.

EXECUTE: (a) From Eq. (18.22),

$$\lambda = \frac{kT}{4\pi \sqrt{2} r^2 p} = \frac{(1.38 \times 10^{-23} \text{ J/K})(300 \text{ K})}{4\pi \sqrt{2}(2.0 \times 10^{-10} \text{ m})^2(1.01 \times 10^5 \text{ Pa})}$$

$$= 5.8 \times 10^{-8} \text{ m}$$

(b) From Example 18.6, for oxygen at 27°C the root-mean-square speed is $v_{rms} = 484$ m/s, so the mean free time for a molecule with this speed is

$$t_{mean} = \frac{\lambda}{v} = \frac{5.8 \times 10^{-8} \text{ m}}{484 \text{ m/s}} = 1.2 \times 10^{-10} \text{ s}$$

This molecule undergoes about 10^{10} collisions per second!

EVALUATE: Note that from Eqs. (18.21) and (18.22) the mean free *path* doesn't depend on the molecule's speed, but the mean free *time* does. Slower molecules have a longer average time interval t_{mean} between collisions than do fast ones, but the average *distance* λ between collisions is the same no matter what the molecule's speed. Our answer to part (a) says that the molecule doesn't go far between collisions, but the mean free path is still several hundred times the molecular radius r.

Test Your Understanding of Section 18.3   Rank the following gases in order from (a) highest to lowest rms speed of molecules and (b) highest to lowest average translational kinetic energy of a molecule: (i) oxygen ($M = 32.0$ g/mol) at 300 K; (ii) nitrogen ($M = 28.0$ g/mol) at 300 K; (iii) oxygen at 330 K; (iv) nitrogen at 330 K.

18.4 **Heat Capacities**

When we introduced the concept of heat capacity in Section 17.5, we talked about ways to *measure* the specific heat or molar heat capacity of a particular material. Now we'll see how to *predict* these on theoretical grounds.

Heat Capacities of Gases

The basis of our analysis is that heat is *energy* in transit. When we add heat to a substance, we are increasing its molecular energy. In this discussion the volume of the gas will remain constant so that we don't have to worry about energy transfer through mechanical work. If we were to let the gas expand, it would do work by pushing on moving walls of its container, and this additional energy transfer would have to be included in our calculations. We'll return to this more general case in Chapter 19. For now, with the volume held constant, we are concerned with C_V, the molar heat capacity *at constant volume*.

In the simple kinetic-molecular model of Section 18.3 the molecular energy consists only of the translational kinetic energy K_{tr} of the pointlike molecules. This energy is directly proportional to the absolute temperature T, as shown by Eq. (18.14), $K_{tr} = \frac{3}{2}nRT$. When the temperature changes by a small amount dT, the corresponding change in kinetic energy is

$$dK_{tr} = \tfrac{3}{2}\,nR\,dT \qquad (18.23)$$

From the definition of molar heat capacity at constant volume, C_V (see Section 17.5), we also have

$$dQ = nC_V\,dT \qquad (18.24)$$

where dQ is the heat input needed for a temperature change dT. Now if K_{tr} represents the total molecular energy, as we have assumed, then dQ and dK_{tr} must be *equal* (Fig. 18.17). From Eqs. (18.23) and (18.24), this says

$$nC_V\,dT = \tfrac{3}{2}\,nR\,dT$$

$$C_V = \tfrac{3}{2}R \qquad \text{(ideal gas of point particles)} \qquad (18.25)$$

This surprisingly simple result says that the molar heat capacity at constant volume is $3R/2$ for *any* gas whose molecules can be represented as points.

Does Eq. (18.25) agree with measured values of molar heat capacities? In SI units, Eq. (18.25) gives

$$C_V = \tfrac{3}{2}(8.314\ \text{J/mol} \cdot \text{K}) = 12.47\ \text{J/mol} \cdot \text{K}$$

For comparison, Table 18.1 gives measured values of C_V for several gases. We see that for *monatomic* gases our prediction is right on the money, but that it is way off for diatomic and polyatomic gases.

This comparison tells us that our point-molecule model is good enough for monatomic gases but that for diatomic and polyatomic molecules we need something more sophisticated. For example, we can picture a diatomic molecule as

18.17 (a) A fixed volume V of a monatomic ideal gas. (b) When an amount of heat dQ is added to the gas, the total translational kinetic energy increases by $dK_{tr} = dQ$ and the temperature increases by $dT = dQ/nC_V$.
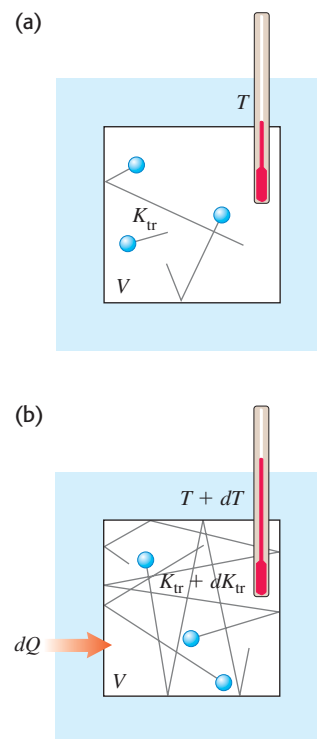
(a)

(b)

Table 18.1 Molar Heat Capacities of Gases

| Type of Gas	Gas	C_V (J/mol $\cdot$ K)
Monatomic	He	12.47
	Ar	12.47
Diatomic	H_2	20.42
	N_2	20.76
	O_2	20.85
	CO	20.85
Polyatomic	CO_2	28.46
	SO_2	31.39
	H_2S	25.95

18.18 Motions of a diatomic molecule.

(a) **Translational motion.** The molecule moves as a whole; its velocity may be described as the *x*-, *y*-, and *z*-velocity components of its center of mass.

We can treat each atom's mass as being located at its nucleus.
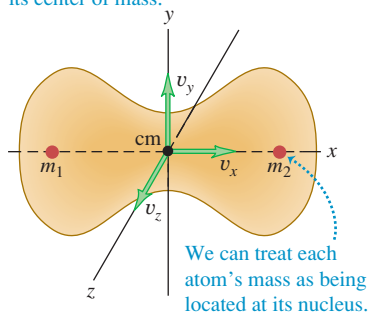
(b) **Rotational motion.** The molecule rotates about its center of mass. This molecule has two independent axes of rotation.
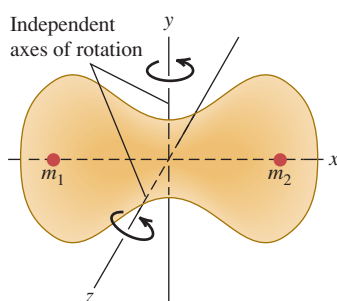
(c) **Vibrational motion.** The molecule oscillates as though the nuclei were connected by a spring.
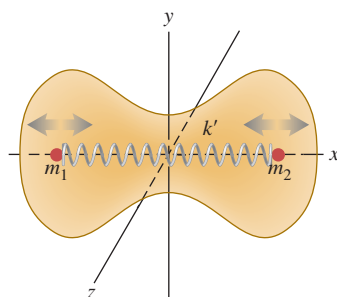
two point masses, like a little elastic dumbbell, with an interaction force between the atoms of the kind shown in Fig. 18.8. Such a molecule can have additional kinetic energy associated with *rotation* about axes through its center of mass. The atoms may also have *vibrating* motion along the line joining them, with additional kinetic and potential energies. Figure 18.18 shows these possibilities.

When heat flows into a *monatomic* gas at constant volume, *all* of the added energy goes into an increase in random *translational* molecular kinetic energy. Equation (18.23) shows that this gives rise to an increase in temperature. But when the temperature is increased by the same amount in a *diatomic* or *polyatomic* gas, additional heat is needed to supply the increased rotational and vibrational energies. Thus polyatomic gases have *larger* molar heat capacities than monatomic gases, as Table 18.1 shows.

But how do we know how much energy is associated with each additional kind of motion of a complex molecule, compared to the translational kinetic energy? The new principle that we need is called the principle of **equipartition of energy.** It can be derived from sophisticated statistical-mechanics considerations; that derivation is beyond our scope, and we will treat the principle as an axiom.

The principle of equipartition of energy states that each velocity component (either linear or angular) has, on average, an associated kinetic energy per molecule of $\frac{1}{2}kT$, or one-half the product of the Boltzmann constant and the absolute temperature. The number of velocity components needed to describe the motion of a molecule completely is called the number of **degrees of freedom.** For a monatomic gas, there are three degrees of freedom (for the velocity components v_x, v_y, and v_z); this gives a total average kinetic energy per molecule of $3(\frac{1}{2}kT)$, consistent with Eq. (18.16).

For a *diatomic* molecule there are two possible axes of rotation, perpendicular to each other and to the molecule's axis. (We don't include rotation about the molecule's own axis because in ordinary collisions there is no way for this rotational motion to change.) If we assign five degrees of freedom to a diatomic molecule, the average total kinetic energy per molecule is $\frac{5}{2}kT$ instead of $\frac{3}{2}kT$. The total kinetic energy of n moles is $K_{total} = nN_A(\frac{5}{2}kT) = \frac{5}{2}n(kN_A)T = \frac{5}{2}nRT$, and the molar heat capacity (at constant volume) is

$$C_V = \frac{5}{2}R \qquad \text{(diatomic gas, including rotation)} \qquad (18.26)$$

In SI units,

$$C_V = \frac{5}{2}(8.314 \text{ J/mol} \cdot \text{K}) = 20.79 \text{ J/mol} \cdot \text{K}$$

This agrees within a few percent with the measured values for diatomic gases given in Table 18.1.

Vibrational motion can also contribute to the heat capacities of gases. Molecular bonds are not rigid; they can stretch and bend, and the resulting vibrations lead to additional degrees of freedom and additional energies. For most diatomic gases, however, vibrational motion does *not* contribute appreciably to heat capacity. The reason for this is a little subtle and involves some concepts of quantum mechanics. Briefly, vibrational energy can change only in finite steps. If the energy change of the first step is much larger than the energy possessed by most molecules, then nearly all the molecules remain in the minimum-energy state of motion. In that case, changing the temperature does not change their average vibrational energy appreciably, and the vibrational degrees of freedom are said to be "frozen out." In more complex molecules the gaps between permitted energy levels are sometimes much smaller, and then vibration *does* contribute to heat capacity. The rotational energy of a molecule also changes by finite steps, but they are usually much
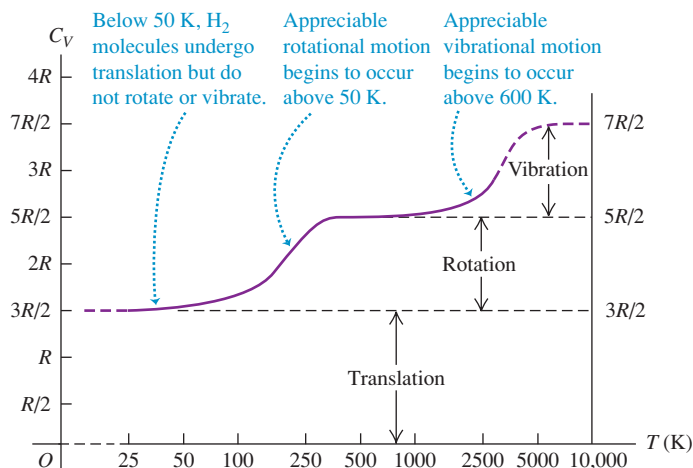
18.19 Experimental values of C_V, the molar heat capacity at constant volume, for hydrogen gas (H_2). The temperature is plotted on a logarithmic scale.

smaller; the "freezing out" of rotational degrees of freedom occurs only in rare instances, such as for the hydrogen molecule below about 100 K.

In Table 18.1 the large values of C_V for some polyatomic molecules show the contributions of vibrational energy. In addition, a molecule with three or more atoms that are not in a straight line has three, not two, rotational degrees of freedom.

From this discussion we expect heat capacities to be temperature-dependent, generally increasing with increasing temperature. Figure 18.19 is a graph of the temperature dependence of C_V for hydrogen gas (H_2), showing the temperatures at which the rotational and vibrational energies begin to contribute.

Heat Capacities of Solids

We can carry out a similar heat-capacity analysis for a crystalline solid. Consider a crystal consisting of N identical atoms (a *monatomic solid*). Each atom is bound to an equilibrium position by interatomic forces. The elasticity of solid materials shows us that these forces must permit stretching and bending of the bonds. We can think of a crystal as an array of atoms connected by little springs (Fig. 18.20). Each atom can *vibrate* about its equilibrium position.

Each atom has three degrees of freedom, corresponding to its three components of velocity. According to the equipartition principle, each atom has an average kinetic energy of $\frac{1}{2}kT$ for each degree of freedom. In addition, each atom has *potential* energy associated with the elastic deformation. For a simple harmonic oscillator (discussed in Chapter 14) it is not hard to show that the average kinetic energy of an atom is *equal* to its average potential energy. In our model of a crystal, each atom is essentially a three-dimensional harmonic oscillator; it can be shown that the equality of average kinetic and potential energies also holds here, provided that the "spring" forces obey Hooke's law.

Thus we expect each atom to have an average kinetic energy $\frac{3}{2}kT$ and an average potential energy $\frac{3}{2}kT$, or an average total energy $3kT$ per atom. If the crystal contains N atoms or n moles, its total energy is

$$E_{\text{total}} = 3NkT = 3nRT \qquad (18.27)$$
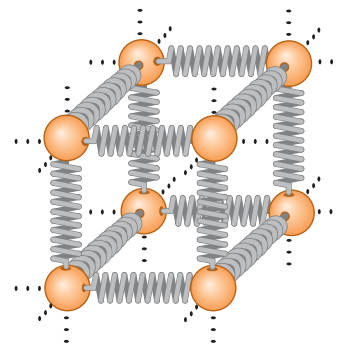
From this we conclude that the molar heat capacity of a crystal should be

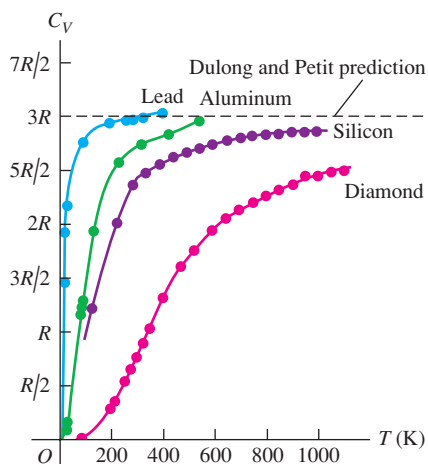$$C_V = 3R \qquad \text{(ideal monatomic solid)} \qquad (18.28)$$

In SI units,

$$C_V = (3)(8.314 \text{ J/mol} \cdot \text{K}) = 24.9 \text{ J/mol} \cdot \text{K}$$

18.20 To visualize the forces between neighboring atoms in a crystal, envision every atom as being attached to its neighbors by springs.

This is the **rule of Dulong and Petit,** which we encountered as an *empirical* finding in Section 17.5: Elemental solids all have molar heat capacities of about 25 J/mol · K. Now we have *derived* this rule from kinetic theory. The agreement is only approximate, to be sure, but considering the very simple nature of our model, it is quite significant.

At low temperatures, the heat capacities of most solids *decrease* with decreasing temperature (Fig. 18.21) for the same reason that vibrational degrees of freedom of molecules are frozen out at low temperatures. At very low temperatures the quantity kT is much *smaller* than the smallest energy step the vibrating atoms can take. Hence most of the atoms remain in their lowest energy states because the next higher energy level is out of reach. The average vibrational energy per atom is then *less* than $3kT$, and the heat capacity per molecule is *less* than $3k$. At higher temperatures when kT is *large* in comparison to the minimum energy step, the equipartition principle holds, and the total heat capacity is $3k$ per molecule or $3R$ per mole as the Dulong and Petit rule predicts. Quantitative understanding of the temperature variation of heat capacities was one of the triumphs of quantum mechanics during its initial development in the 1920s.

18.21 Experimental values of C_V for lead, aluminum, silicon, and diamond. At high temperatures, C_V for each solid approaches about $3R$, in agreement with the rule of Dulong and Petit. At low temperatures, C_V is much less than $3R$.

Test Your Understanding of Section 18.4 A cylinder with a fixed volume contains hydrogen gas (H_2) at 25 K. You then add heat to the gas at a constant rate until its temperature reaches 500 K. Does the temperature of the gas increase at a constant rate? Why or why not? If not, does the temperature increase most rapidly near the beginning or near the end of this process? ∎

18.5 Molecular Speeds

As we mentioned in Section 18.3, the molecules in a gas don't all have the same speed. Figure 18.22 shows one experimental scheme for measuring the distribution of molecular speeds. A substance is vaporized in a hot oven; molecules of the vapor escape through an aperture in the oven wall and into a vacuum chamber. A series of slits blocks all molecules except those in a narrow beam, which is aimed at a pair of rotating disks. A molecule passing through the slit in the first disk is blocked by the second disk unless it arrives just as the slit in the second disk is lined up with the beam. The disks function as a speed selector that passes only molecules within a certain narrow speed range. This range can be varied by changing the disk rotation speed, and we can measure how many molecules lie within each of various speed ranges.

To describe the results of such measurements, we define a function $f(v)$ called a *distribution function.* If we observe a total of N molecules, the number dN having speeds in the range between v and $v + dv$ is given by

$$dN = Nf(v)\,dv \qquad (18.29)$$

18.22 A molecule with a speed v passes through the slit in the first rotating disk. When the molecule reaches the second rotating disk, the disks have rotated through the offset angle θ. If $v = \omega x/\theta$, the molecule passes through the slit in the second rotating disk and reaches the detector.
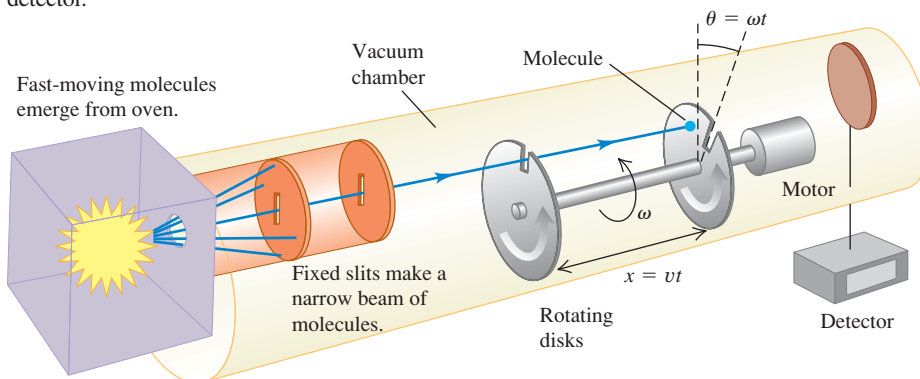
We can also say that the *probability* that a randomly chosen molecule will have a speed in the interval v to $v + dv$ is $f(v) \, dv$. Hence $f(v)$ is the probability per unit speed *interval;* it is *not* equal to the probability that a molecule has speed exactly equal to v. Since a probability is a pure number, $f(v)$ has units of reciprocal speed (s/m).

Figure 18.23a shows distribution functions for three different temperatures. At each temperature the height of the curve for any value of v is proportional to the number of molecules with speeds near v. The peak of the curve represents the *most probable speed* v_{mp} for the corresponding temperature. As the temperature increases, the average molecular kinetic energy increases, and so the peak of $f(v)$ shifts to higher and higher speeds.

Figure 18.23b shows that the area under a curve between any two values of v represents the fraction of all the molecules having speeds in that range. Every molecule must have *some* value of v, so the integral of $f(v)$ over all v must be unity for any T.

If we know $f(v)$, we can calculate the most probable speed v_{mp}, the average speed v_{av}, and the rms speed v_{rms}. To find v_{mp}, we simply find the point where $df/dv = 0$; this gives the value of the speed where the curve has its peak. To find v_{av}, we take the number $Nf(v) \, dv$ having speeds in each interval dv, multiply each number by the corresponding speed v, add all these products (by integrating over all v from zero to infinity), and finally divide by N. That is,

$$v_{av} = \int_0^\infty v f(v) \, dv \qquad (18.30)$$

The rms speed is obtained similarly; the average of v^2 is given by

$$(v^2)_{av} = \int_0^\infty v^2 f(v) \, dv \qquad (18.31)$$

and v_{rms} is the square root of this.

The Maxwell–Boltzmann Distribution

The function $f(v)$ describing the actual distribution of molecular speeds is called the **Maxwell–Boltzmann distribution.** It can be derived from statistical-mechanics considerations, but that derivation is beyond our scope. Here is the result:

$$f(v) = 4\pi \left(\frac{m}{2\pi kT} \right)^{3/2} v^2 e^{-mv^2/2kT} \qquad \text{(Maxwell–Boltzmann distribution)} \qquad (18.32)$$

We can also express this function in terms of the translational kinetic energy of a molecule, which we denote by ϵ; that is, $\epsilon = \frac{1}{2}mv^2$. We invite you to verify that when this is substituted into Eq. (18.32), the result is

$$f(v) = \frac{8\pi}{m} \left(\frac{m}{2\pi kT} \right)^{3/2} \epsilon e^{-\epsilon/kT} \qquad (18.33)$$
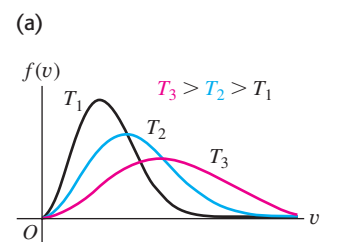
This form shows that the exponent in the Maxwell–Boltzmann distribution function is $-\epsilon/kT$ and that the shape of the curve is determined by the relative magnitude of ϵ and kT at any point. We leave it to you (see Exercise 18.48) to prove that the *peak* of each curve occurs where $\epsilon = kT$, corresponding to a most probable speed v_{mp} given by

$$v_{mp} = \sqrt{\frac{2kT}{m}} \qquad (18.34)$$

To find the average speed, we substitute Eq. (18.32) into Eq. (18.30) and carry out the integration, making a change of variable $v^2 = x$ and then integrating by parts. The result is

$$v_{av} = \sqrt{\frac{8kT}{\pi m}} \qquad (18.35)$$

18.23 (a) Curves of the Maxwell–Boltzmann distribution function $f(v)$ for three temperatures. (b) The shaded areas under the curve represent the fractions of molecules within certain speed ranges. The most probable speed v_{mp} for a given temperature is at the peak of the curve.

(a)

As temperature increases:
• the curve flattens.
• the maximum shifts to higher speeds.

(b)

Fraction of molecules with speeds from v_1 to v_2

Fraction of molecules with speeds greater than v_A
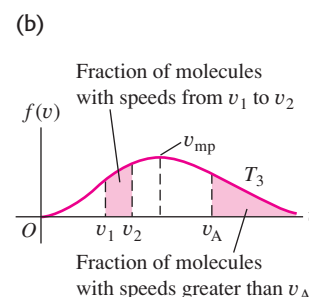
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ActivPhysics 8.2: Maxwell-Boltzmann Distribution—Conceptual Analysis
ActivPhysics 8.3: Maxwell-Boltzmann Distribution—Quantitative Analysis

Finally, to find the rms speed, we substitute Eq. (18.32) into Eq. (18.31). Evaluating the resulting integral takes some mathematical acrobatics, but we can find it in a table of integrals. The result is

$$v_{rms} = \sqrt{\frac{3kT}{m}} \tag{18.36}$$

This result agrees with Eq. (18.19); it *must* agree if the Maxwell–Boltzmann distribution is to be consistent with the equipartition principle and our other kinetic-theory calculations.

Table 18.2 shows the fraction of all the molecules in an ideal gas that have speeds *less than* various multiples of v_{rms}. These numbers were obtained by numerical integration; they are the same for all ideal gases.

The distribution of molecular speeds in liquids is similar, although not identical, to that for gases. We can understand the vapor pressure of a liquid and the phenomenon of boiling on this basis. Suppose a molecule must have a speed at least as great as v_A in Fig. 18.23b to escape from the surface of a liquid into the adjacent vapor. The number of such molecules, represented by the area under the "tail" of each curve (to the right of v_A), increases rapidly with temperature. Thus the rate at which molecules can escape is strongly temperature-dependent. This process is balanced by another one in which molecules in the vapor phase collide inelastically with the surface and are trapped back into the liquid phase. The number of molecules suffering this fate per unit time is proportional to the pressure in the vapor phase. Phase equilibrium between liquid and vapor occurs when these two competing processes proceed at exactly the same rate. So if the molecular speed distributions are known for various temperatures, we can make a theoretical prediction of vapor pressure as a function of temperature. When liquid evaporates, it's the high-speed molecules that escape from the surface. The ones that are left have less energy on average; this gives us a molecular view of evaporative cooling.

Rates of chemical reactions are often strongly temperature-dependent, and the reason is contained in the Maxwell–Boltzmann distribution. When two reacting molecules collide, the reaction can occur only when the molecules are close enough for the electric-charge distributions of their electrons to interact strongly. This requires a minimum energy, called the *activation energy,* and thus a certain minimum molecular speed. Figure 18.23a shows that the number of molecules in the high-speed tail of the curve increases rapidly with temperature. Thus we expect the rate of any reaction that depends on an activation energy to increase rapidly with temperature.

Table 18.2 Fractions of Molecules in an Ideal Gas with Speeds Less than Various Multiples of v/v_{rms}

v/v_{rms}	Fraction
0.20	0.011
0.40	0.077
0.60	0.218
0.80	0.411
1.00	0.608
1.20	0.771
1.40	0.882
1.60	0.947
1.80	0.979
2.00	0.993

Application **Activation Energy and Moth Activity**
This hawkmoth of genus *Manduca* cannot fly if the temperature of its muscles is below 29°C. The reason is that the enzyme-catalyzed reactions that power aerobic metabolism and enable muscle action require a minimum molecular energy (activation energy). Just like the molecules in an ideal gas, at low temperatures very few of the molecules involved in these reactions have high energy. As the temperature increases, more molecules have the required minimum energy and the reactions take place at a greater rate. Above 29°C, enough power is generated to allow the hawkmoth to fly.
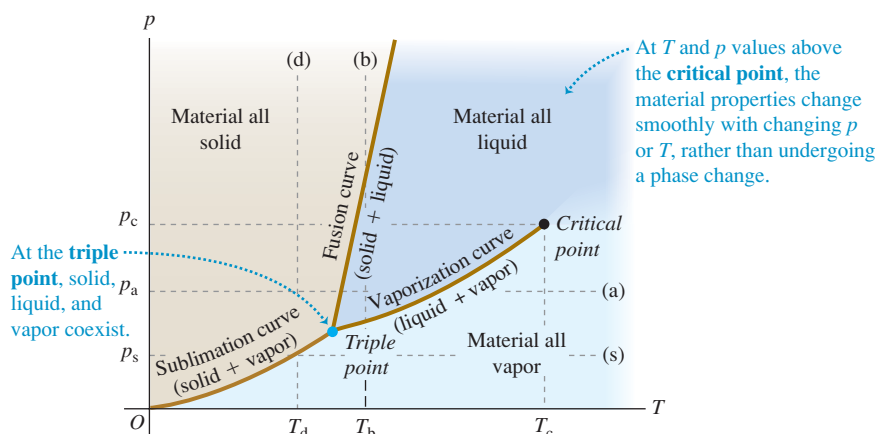
Test Your Understanding of Section 18.5 A quantity of gas containing N molecules has a speed distribution function $f(v)$. How many molecules have speeds between v_1 and $v_2 > v_1$? (i) $\int_0^{v_2} f(v)\, dv - \int_0^{v_1} f(v)\, dv$; (ii) $N[\int_0^{v_2} f(v)\, dv - \int_0^{v_1} f(v)\, dv]$; (iii) $\int_0^{v_1} f(v)\, dv - \int_0^{v_2} f(v)\, dv$; (iv) $N[\int_0^{v_1} f(v)\, dv - \int_0^{v_2} f(v)\, dv]$; (v) none of these.

18.6 Phases of Matter

An ideal gas is the simplest system to analyze from a molecular viewpoint because we ignore the interactions between molecules. But those interactions are the very thing that makes matter condense into the liquid and solid phases under some conditions. So it's not surprising that theoretical analysis of liquid and solid structure and behavior is a lot more complicated than that for gases. We won't try to go far here with a microscopic picture, but we can talk in general about phases of matter, phase equilibrium, and phase transitions.

18.24 A typical pT phase diagram, showing regions of temperature and pressure at which the various phases exist and where phase changes occur.

In Section 17.6 we learned that each phase is stable only in certain ranges of temperature and pressure. A transition from one phase to another ordinarily requires **phase equilibrium** between the two phases, and for a given pressure this occurs at only one specific temperature. We can represent these conditions on a graph with axes p and T, called a **phase diagram;** Fig. 18.24 shows an example. Each point on the diagram represents a pair of values of p and T.

Only a single phase can exist at each point in Fig. 18.24, except for points on the solid lines, where two phases can coexist in phase equilibrium. The fusion curve separates the solid and liquid areas and represents possible conditions of solid-liquid phase equilibrium. The vaporization curve separates the liquid and vapor areas, and the sublimation curve separates the solid and vapor areas. All three curves meet at the **triple point,** the only condition under which all three phases can coexist (Fig. 18.25). In Section 17.3 we used the triple-point temperature of water to define the Kelvin temperature scale. Table 18.3 gives triple-point data for several substances.

If we add heat to a substance at a constant pressure p_a, it goes through a series of states represented by the horizontal line (a) in Fig. 18.24. The melting and boiling temperatures at this pressure are the temperatures at which the line intersects the fusion and vaporization curves, respectively. When the pressure is p_s, constant-pressure heating transforms a substance from solid directly to vapor. This process is called *sublimation;* the intersection of line (s) with the sublimation curve gives the temperature T_s at which it occurs for a pressure p_s. At any pressure less than the triple-point pressure, no liquid phase is possible. The triple-point pressure for carbon dioxide is 5.1 atm. At normal atmospheric pressure, solid carbon dioxide ("dry ice") undergoes sublimation; there is no liquid phase at this pressure.

Line (b) in Fig. 18.24 represents compression at a constant temperature T_b. The material passes from vapor to liquid and then to solid at the points where line (b) crosses the vaporization curve and fusion curve, respectively. Line (d) shows constant-temperature compression at a lower temperature T_d; the material passes from vapor to solid at the point where line (d) crosses the sublimation curve.

We saw in the pV-diagram of Fig. 18.7 that a liquid-vapor phase transition occurs only when the temperature and pressure are less than those at the point lying at the top of the green shaded area labeled "Liquid-vapor phase equilibrium region." This point corresponds to the endpoint at the top of the vaporization curve in Fig. 18.24. It is called the **critical point,** and the corresponding values of p and T are called the critical pressure and temperature, p_c and T_c. A gas at a pressure *above* the critical pressure does not separate into two phases when it is cooled at constant pressure (along a horizontal line above the critical point in Fig. 18.24). Instead, its properties change gradually and continuously from those we ordinarily associate with a gas (low density, large compressibility) to those of a liquid (high density, small compressibility) *without a phase transition*.

18.25 Atmospheric pressure on earth is higher than the triple-point pressure of water (see line (a) in Fig. 18.24). Depending on the temperature, water can exist as a vapor (in the atmosphere), as a liquid (in the ocean), or as a solid (like the iceberg shown here).

Table 18.3 Triple-Point Data

Substance	Temperature (K)	Pressure (Pa)
Hydrogen	13.80	0.0704×10^5
Deuterium	18.63	0.171×10^5
Neon	24.56	0.432×10^5
Nitrogen	63.18	0.125×10^5
Oxygen	54.36	0.00152×10^5
Ammonia	195.40	0.0607×10^5
Carbon dioxide	216.55	5.17×10^5
Sulfur dioxide	197.68	0.00167×10^5
Water	273.16	0.00610×10^5

You can understand this by thinking about liquid-phase transitions at successively higher points on the vaporization curve. As we approach the critical point, the *differences* in physical properties (such as density and compressibility) between the liquid and vapor phases become smaller. Exactly *at* the critical point they all become zero, and at this point the distinction between liquid and vapor disappears. The heat of vaporization also grows smaller as we approach the critical point, and it too becomes zero at the critical point.

For nearly all familiar materials the critical pressures are much greater than atmospheric pressure, so we don't observe this behavior in everyday life. For example, the critical point for water is at 647.4 K and 221.2×10^5 Pa (about 218 atm or 3210 psi). But high-pressure steam boilers in electric generating plants regularly run at pressures and temperatures well above the critical point.

Many substances can exist in more than one solid phase. A familiar example is carbon, which exists as noncrystalline soot and crystalline graphite and diamond. Water is another example; at least eight types of ice, differing in crystal structure and physical properties, have been observed at very high pressures.
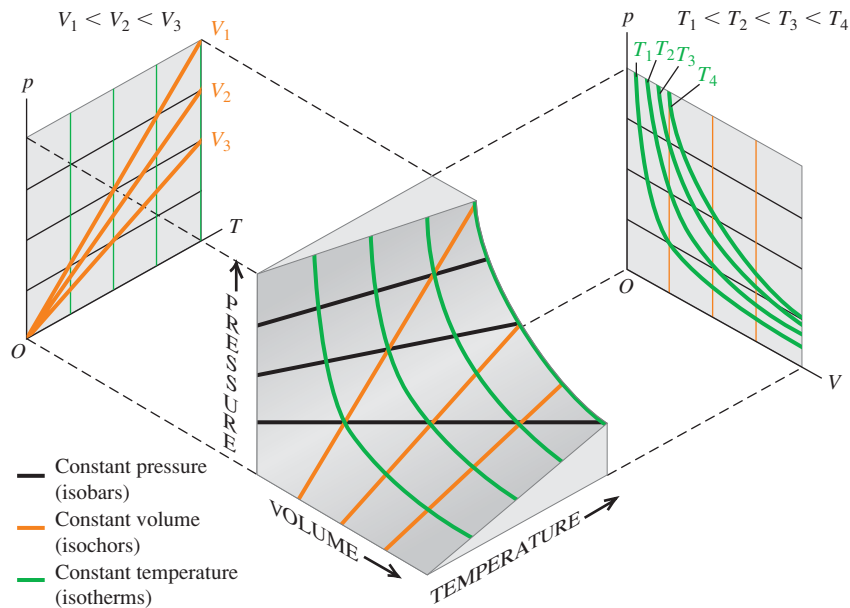
pVT-Surfaces

We remarked in Section 18.1 that the equation of state of any material can be represented graphically as a surface in a three-dimensional space with coordinates *p*, *V*, and *T*. Visualizing such a surface can add to our understanding of the behavior of materials at various temperatures and pressures. Figure 18.26 shows a typical *pVT*-surface. The light lines represent *pV*-isotherms; projecting them onto the *pV*-plane gives a diagram similar to Fig. 18.7. The *pV*-isotherms represent contour lines on the *pVT*-surface, just as contour lines on a topographic map represent the elevation (the third dimension) at each point. The projections of the edges of the surface onto the *pT*-plane give the *pT* phase diagram of Fig. 18.24.

Line *abcdef* in Fig. 18.26 represents constant-pressure heating, with melting along *bc* and vaporization along *de*. Note the volume changes that occur as *T* increases along this line. Line *ghjklm* corresponds to an isothermal (constant temperature) compression, with liquefaction along *hj* and solidification along *kl*. Between these, segments *gh* and *jk* represent isothermal compression with increase in pressure; the pressure increases are much greater in the liquid region

18.26 A *pVT*-surface for a substance that expands on melting. Projections of the boundaries on the surface onto the *pT*- and *pV*-planes are also shown.
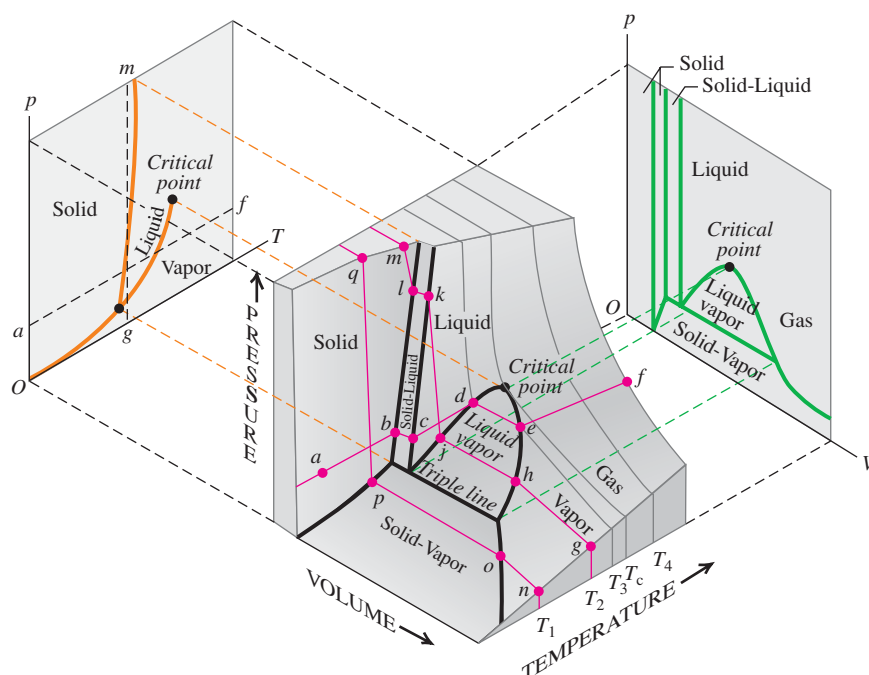
18.27 A pVT-surface for an ideal gas. At the left, each red line corresponds to a certain constant volume; at the right, each green line corresponds to a certain constant temperature.

jk and the solid region lm than in the vapor region gh. Finally, line $nopq$ represents isothermal solidification directly from vapor, as in the formation of snowflakes or frost.

Figure 18.27 shows the much simpler pVT-surface for a substance that obeys the ideal-gas equation of state under all conditions. The projections of the constant-temperature curves onto the pV-plane correspond to the curves of Fig. 18.6, and the projections of the constant-volume curves onto the pT-plane show that pressure is directly proportional to absolute temperature.

Test Your Understanding of Section 18.6 The average atmospheric pressure on Mars is 6.0×10^2 Pa. Could there be lakes or rivers of liquid water on Mars today? What about in the past, when the atmospheric pressure is thought to have been substantially greater than today? ∎

Equations of state: The pressure p, volume V, and absolute temperature T of a given quantity of a substance are related by an equation of state. This relationship applies only for equilibrium states, in which p and T are uniform throughout the system. The ideal-gas equation of state, Eq. (18.3), involves the number of moles n and a constant R that is the same for all gases. (See Examples 18.1–18.4.)
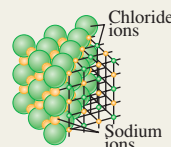
$$pV = nRT \qquad (18.3)$$
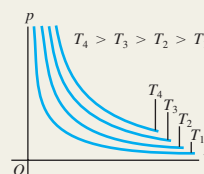
Molecular properties of matter: The molar mass M of a pure substance is the mass per mole. The mass m_{total} of a quantity of substance equals M multiplied by the number of moles n. Avogadro's number N_A is the number of molecules in a mole. The mass m of an individual molecule is M divided by N_A. (See Example 18.5.)

$$m_{total} = nM \qquad (18.2)$$

$$M = N_A m \qquad (18.8)$$

Kinetic-molecular model of an ideal gas: In an ideal gas, the total translational kinetic energy of the gas as a whole (K_{tr}) and the average translational kinetic energy per molecule $\left[\frac{1}{2}m(v^2)_{av}\right]$ are proportional to the absolute temperature T, and the root-mean-square speed of molecules is proportional to the square root of T. These expressions involve the Boltzmann constant $k = R/N_A$. (See Examples 18.6 and 18.7.)
The mean free path λ of molecules in an ideal gas depends on the number of molecules per volume (N/V) and the molecular radius r. (See Example 18.8.)

$$K_{tr} = \tfrac{3}{2}nRT \qquad (18.14)$$

$$\tfrac{1}{2}m(v^2)_{av} = \tfrac{3}{2}kT \qquad (18.16)$$

$$v_{rms} = \sqrt{(v^2)_{av}} = \sqrt{\frac{3kT}{m}} \qquad (18.19)$$

$$\lambda = vt_{mean} = \frac{V}{4\pi\sqrt{2}\,r^2 N} \qquad (18.21)$$
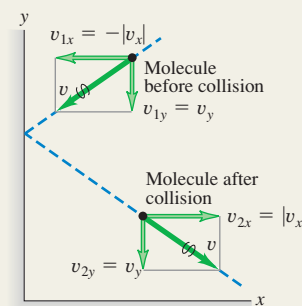
Heat capacities: The molar heat capacity at constant volume C_V is a simple multiple of the gas constant R for certain idealized cases: an ideal monatomic gas [Eq. (18.25)]; an ideal diatomic gas including rotational energy [Eq. (18.26)]; and an ideal monatomic solid [Eq. (18.28)]. Many real systems are approximated well by these idealizations.

$$C_V = \tfrac{3}{2}R \quad \text{(monatomic gas)} \qquad (18.25)$$

$$C_V = \tfrac{5}{2}R \quad \text{(diatomic gas)} \qquad (18.26)$$

$$C_V = 3R \quad \text{(monatomic solid)} \qquad (18.28)$$
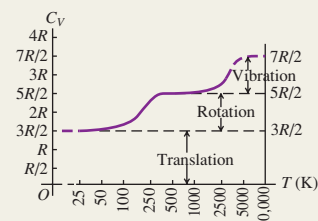
Molecular speeds: The speeds of molecules in an ideal gas are distributed according to the Maxwell–Boltzmann distribution $f(v)$. The quantity $f(v)\,dv$ describes what fraction of the molecules have speeds between v and $v + dv$.

$$f(v) = 4\pi\left(\frac{m}{2\pi kT}\right)^{3/2} v^2 e^{-mv^2/2kT} \qquad (18.32)$$
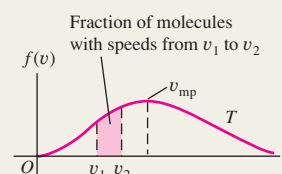
Phases of matter: Ordinary matter exists in the solid, liquid, and gas phases. A phase diagram shows conditions under which two phases can coexist in phase equilibrium. All three phases can coexist at the triple point. The vaporization curve ends at the critical point, above which the distinction between the liquid and gas phases disappears.
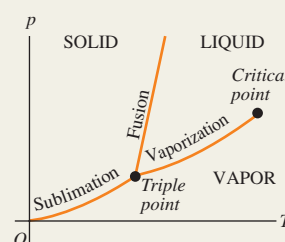
An astronaut visiting Jupiter's satellite Europa leaves a canister of 1.20 mol of nitrogen gas (28.0 g/mol) at 25.0°C on the satellite's surface. Europa has no significant atmosphere, and the acceleration due to gravity at its surface is 1.30 m/s^2. The canister springs a leak, allowing molecules to escape from a small hole. (a) What is the maximum height (in km) above Europa's surface that is reached by a nitrogen molecule whose speed equals the rms speed? Assume that the molecule is shot straight up out of the hole in the canister, and ignore the variation in g with altitude. (b) The escape speed from Europa is 2025 m/s. Can any of the nitrogen molecules escape from Europa and into space?

SOLUTION GUIDE

See MasteringPhysics® study area for a Video Tutor solution. (MP)

IDENTIFY and SET UP

1. Draw a sketch of the situation, showing all relevant dimensions.
2. Make a list of the unknown quantities, and decide which are the target variables.

3. How will you find the rms speed of the nitrogen molecules? What principle will you use to find the maximum height that a molecule with this speed can reach?
4. Does the rms speed of molecules in an ideal gas represent the maximum speed of the molecules? If not, what is the maximum speed?

EXECUTE

5. Solve for the rms speed. Use this to calculate the maximum height that a molecule with this speed can reach.
6. Use your result from step 5 to answer the question in part (b).

EVALUATE

7. Do your results depend on the amount of gas in the container? Why or why not?
8. How would your results from steps 5 and 6 be affected if the gas cylinder were instead left on Jupiter's satellite Ganymede, which has higher surface gravity than Europa and a higher escape speed? Like Europa, Ganymede has no significant atmosphere.

Problems   For instructor-assigned homework, go to www.masteringphysics.com (MP)

•, ••, •••: Problems of increasing difficulty. **CP**: Cumulative problems incorporating material from earlier chapters. **CALC**: Problems requiring calculus. **BIO**: Biosciences problems.

DISCUSSION QUESTIONS

Q18.1 Section 18.1 states that ordinarily, pressure, volume, and temperature cannot change individually without one affecting the others. Yet when a liquid evaporates, its volume changes, even though its pressure and temperature are constant. Is this inconsistent? Why or why not?

Q18.2 In the ideal-gas equation, could an equivalent Celsius temperature be used instead of the Kelvin one if an appropriate numerical value of the constant R is used? Why or why not?

Q18.3 On a chilly morning you can "see your breath." Can you really? What are you actually seeing? Does this phenomenon depend on the temperature of the air, the humidity, or both? Explain.

Q18.4 When a car is driven some distance, the air pressure in the tires increases. Why? Should you let out some air to reduce the pressure? Why or why not?

Q18.5 The coolant in an automobile radiator is kept at a pressure higher than atmospheric pressure. Why is this desirable? The radiator cap will release coolant when the gauge pressure of the coolant reaches a certain value, typically 15 lb/in.^{2} or so. Why not just seal the system completely?

Q18.6 Unwrapped food placed in a freezer experiences dehydration, known as "freezer burn." Why?

Q18.7 "Freeze-drying" food involves the same process as "freezer burn," referred to in Discussion Question Q18.6. For freeze-drying, the food is usually frozen first, and then placed in a vacuum chamber and irradiated with infrared radiation. What is the purpose of the vacuum? The radiation? What advantages might freeze-drying have in comparison to ordinary drying?

Q18.8 A group of students drove from their university (near sea level) up into the mountains for a skiing weekend. Upon arriving at the slopes, they discovered that the bags of potato chips they had brought for snacks had all burst open. What caused this to happen?

Q18.9 How does evaporation of perspiration from your skin cool your body?

Q18.10 A rigid, perfectly insulated container has a membrane dividing its volume in half. One side contains a gas at an absolute temperature T_0 and pressure p_0, while the other half is completely empty. Suddenly a small hole develops in the membrane, allowing the gas to leak out into the other half until it eventually occupies twice its original volume. In terms of T_0 and p_0, what will be the new temperature and pressure of the gas when it is distributed equally in both halves of the container? Explain your reasoning.

Q18.11 (a) Which has more atoms: a kilogram of hydrogen or a kilogram of lead? Which has more mass? (b) Which has more atoms: a mole of hydrogen or a mole of lead? Which has more mass? Explain your reasoning.

Q18.12 Use the concepts of the kinetic-molecular model to explain: (a) why the pressure of a gas in a rigid container increases as heat is added to the gas and (b) why the pressure of a gas increases as we compress it, even if we do not change its temperature.

Q18.13 The proportions of various gases in the earth's atmosphere change somewhat with altitude. Would you expect the proportion of oxygen at high altitude to be greater or less than at sea level compared to the proportion of nitrogen? Why?

Q18.14 Comment on the following statement: *When two gases are mixed, if they are to be in thermal equilibrium, they must have the*

same average molecular speed. Is the statement correct? Why or why not?

Q18.15 The kinetic-molecular model contains a hidden assumption about the temperature of the container walls. What is this assumption? What would happen if this assumption were not valid?

Q18.16 The temperature of an ideal gas is directly proportional to the average kinetic energy of its molecules. If a container of ideal gas is moving past you at 2000 m/s, is the temperature of the gas higher than if the container was at rest? Explain your reasoning.

Q18.17 If the pressure of an ideal monatomic gas is increased while the number of moles is kept constant, what happens to the average translational kinetic energy of one atom of the gas? Is it possible to change *both* the volume and the pressure of an ideal gas and keep the average translational kinetic energy of the atoms constant? Explain.

Q18.18 In deriving the ideal-gas equation from the kinetic-molecular model, we ignored potential energy due to the earth's gravity. Is this omission justified? Why or why not?

Q18.19 The derivation of the ideal-gas equation included the assumption that the number of molecules is very large, so that we could compute the average force due to many collisions. However, the ideal-gas equation holds accurately only at low pressures, where the molecules are few and far between. Is this inconsistent? Why or why not?

Q18.20 A gas storage tank has a small leak. The pressure in the tank drops more quickly if the gas is hydrogen or helium than if it is oxygen. Why?

Q18.21 Consider two specimens of ideal gas at the same temperature. Specimen A has the same total mass as specimen B, but the molecules in specimen A have greater molar mass than they do in specimen B. In which specimen is the total kinetic energy of the gas greater? Does your answer depend on the molecular structure of the gases? Why or why not?

Q18.22 The temperature of an ideal monatomic gas is increased from 25°C to 50°C. Does the average translational kinetic energy of each gas atom double? Explain. If your answer is no, what would the final temperature be if the average translational kinetic energy was doubled?

Q18.23 If the root-mean-square speed of the atoms of an ideal gas is to be doubled, by what factor must the Kelvin temperature of the gas be increased? Explain.

Q18.24 (a) If you apply the same amount of heat to 1.00 mol of an ideal monatomic gas and 1.00 mol of an ideal diatomic gas, which one (if any) will increase more in temperature? (b) Physically, *why* do diatomic gases have a greater molar heat capacity than monatomic gases?

Q18.25 The discussion in Section 18.4 concluded that all ideal diatomic gases have the same heat capacity C_V. Does this mean that it takes the same amount of heat to raise the temperature of 1.0 g of each one by 1.0 K? Explain your reasoning.

Q18.26 In a gas that contains N molecules, is it accurate to say that the number of molecules with speed v is equal to $f(v)$? Is it accurate to say that this number is given by $Nf(v)$? Explain your answers.

Q18.27 Imagine a special air filter placed in a window of a house. The tiny holes in the filter allow only air molecules moving faster than a certain speed to exit the house, and allow only air molecules moving slower than that speed to enter the house from outside. What effect would this filter have on the temperature inside the house? (It turns out that the second law of thermodynamics—which we will discuss in Chapter 20—tells us that such a wonderful air filter would be impossible to make.)

Q18.28 A beaker of water at room temperature is placed in an enclosure, and the air pressure in the enclosure is slowly reduced. When the air pressure is reduced sufficiently, the water begins to boil. The temperature of the water does not rise when it boils; in fact, the temperature *drops* slightly. Explain these phenomena.

Q18.29 Ice is slippery to walk on, and especially slippery if you wear ice skates. What does this tell you about how the melting temperature of ice depends on pressure? Explain.

Q18.30 Hydrothermal vents are openings in the ocean floor that discharge very hot water. The water emerging from one such vent off the Oregon coast, 2400 m below the surface, has a temperature of 279°C. Despite its high temperature, the water doesn't boil. Why not?

Q18.31 The dark areas on the moon's surface are called *maria,* Latin for "seas," and were once thought to be bodies of water. In fact, the maria are not "seas" at all, but plains of solidified lava. Given that there is no atmosphere on the moon, how can you explain the absence of liquid water on the moon's surface?

Q18.32 In addition to the normal cooking directions printed on the back of a box of rice, there are also "high-altitude directions." The only difference is that the "high-altitude directions" suggest increasing the cooking time and using a greater volume of boiling water in which to cook the rice. Why should the directions depend on the altitude in this way?

EXERCISES

Section 18.1 Equations of State

18.1 • A 20.0-L tank contains 4.86×10^{-4} kg of helium at 18.0°C. The molar mass of helium is 4.00 g/mol. (a) How many moles of helium are in the tank? (b) What is the pressure in the tank, in pascals and in atmospheres?

18.2 •• Helium gas with a volume of 2.60 L, under a pressure of 0.180 atm and at a temperature of 41.0°C, is warmed until both pressure and volume are doubled. (a) What is the final temperature? (b) How many grams of helium are there? The molar mass of helium is 4.00 g/mol.

18.3 • A cylindrical tank has a tight-fitting piston that allows the volume of the tank to be changed. The tank originally contains 0.110 m³ of air at a pressure of 0.355 atm. The piston is slowly pulled out until the volume of the gas is increased to 0.390 m³. If the temperature remains constant, what is the final value of the pressure?

18.4 • A 3.00-L tank contains air at 3.00 atm and 20.0°C. The tank is sealed and cooled until the pressure is 1.00 atm. (a) What is the temperature then in degrees Celsius? Assume that the volume of the tank is constant. (b) If the temperature is kept at the value found in part (a) and the gas is compressed, what is the volume when the pressure again becomes 3.00 atm?

18.5 • **Planetary Atmospheres.** (a) Calculate the density of the atmosphere at the surface of Mars (where the pressure is 650 Pa and the temperature is typically 253 K, with a CO_2 atmosphere), Venus (with an average temperature of 730 K and pressure of 92 atm, with a CO_2 atmosphere), and Saturn's moon Titan (where the pressure is 1.5 atm and the temperature is −178°C, with a N_2 atmosphere). (b) Compare each of these densities with that of the earth's atmosphere, which is 1.20 kg/m³. Consult the periodic chart in Appendix D to determine molar masses.

18.6 •• You have several identical balloons. You experimentally determine that a balloon will break if its volume exceeds 0.900 L. The pressure of the gas inside the balloon equals air pressure (1.00 atm). (a) If the air inside the balloon is at a constant temperature of

22.0°C and behaves as an ideal gas, what mass of air can you blow into one of the balloons before it bursts? (b) Repeat part (a) if the gas is helium rather than air.

18.7 •• A Jaguar XK8 convertible has an eight-cylinder engine. At the beginning of its compression stroke, one of the cylinders contains 499 cm³ of air at atmospheric pressure (1.01×10^5 Pa) and a temperature of 27.0°C. At the end of the stroke, the air has been compressed to a volume of 46.2 cm³ and the gauge pressure has increased to 2.72×10^6 Pa. Compute the final temperature.

18.8 •• A welder using a tank of volume 0.0750 m³ fills it with oxygen (molar mass 32.0 g/mol) at a gauge pressure of 3.00×10^5 Pa and temperature of 37.0°C. The tank has a small leak, and in time some of the oxygen leaks out. On a day when the temperature is 22.0°C, the gauge pressure of the oxygen in the tank is 1.80×10^5 Pa. Find (a) the initial mass of oxygen and (b) the mass of oxygen that has leaked out.

18.9 •• A large cylindrical tank contains 0.750 m³ of nitrogen gas at 27°C and 7.50×10^3 Pa (absolute pressure). The tank has a tight-fitting piston that allows the volume to be changed. What will be the pressure if the volume is decreased to 0.480 m³ and the temperature is increased to 157°C?

18.10 • An empty cylindrical canister 1.50 m long and 90.0 cm in diameter is to be filled with pure oxygen at 22.0°C to store in a space station. To hold as much gas as possible, the absolute pressure of the oxygen will be 21.0 atm. The molar mass of oxygen is 32.0 g/mol. (a) How many moles of oxygen does this canister hold? (b) For someone lifting this canister, by how many kilograms does this gas increase the mass to be lifted?

18.11 • The gas inside a balloon will always have a pressure nearly equal to atmospheric pressure, since that is the pressure applied to the outside of the balloon. You fill a balloon with helium (a nearly ideal gas) to a volume of 0.600 L at a temperature of 19.0°C. What is the volume of the balloon if you cool it to the boiling point of liquid nitrogen (77.3 K)?

18.12 • **Deviations from the Ideal-Gas Equation.** For carbon dioxide gas (CO_2), the constants in the van der Waals equation are $a = 0.364$ J·m³/mol² and $b = 4.27 \times 10^{-5}$ m³/mol. (a) If 1.00 mol of CO_2 gas at 350 K is confined to a volume of 400 cm³, find the pressure of the gas using the ideal-gas equation and the van der Waals equation. (b) Which equation gives a lower pressure? Why? What is the percentage difference of the van der Waals equation result from the ideal-gas equation result? (c) The gas is kept at the same temperature as it expands to a volume of 4000 cm³. Repeat the calculations of parts (a) and (b). (d) Explain how your calculations show that the van der Waals equation is equivalent to the ideal-gas equation if n/V is small.

18.13 •• If a certain amount of ideal gas occupies a volume V at STP on earth, what would be its volume (in terms of V) on Venus, where the temperature is 1003°C and the pressure is 92 atm?

18.14 • A diver observes a bubble of air rising from the bottom of a lake (where the absolute pressure is 3.50 atm) to the surface (where the pressure is 1.00 atm). The temperature at the bottom is 4.0°C, and the temperature at the surface is 23.0°C. (a) What is the ratio of the volume of the bubble as it reaches the surface to its volume at the bottom? (b) Would it be safe for the diver to hold his breath while ascending from the bottom of the lake to the surface? Why or why not?

18.15 • A metal tank with volume 3.10 L will burst if the absolute pressure of the gas it contains exceeds 100 atm. (a) If 11.0 mol of an ideal gas is put into the tank at a temperature of 23.0°C, to what temperature can the gas be warmed before the tank ruptures? You can ignore the thermal expansion of the tank. (b) Based on your

answer to part (a), is it reasonable to ignore the thermal expansion of the tank? Explain.

18.16 • Three moles of an ideal gas are in a rigid cubical box with sides of length 0.200 m. (a) What is the force that the gas exerts on each of the six sides of the box when the gas temperature is 20.0°C? (b) What is the force when the temperature of the gas is increased to 100.0°C?

18.17 • With the assumptions of Example 18.4 (Section 18.1), at what altitude above sea level is air pressure 90% of the pressure at sea level?

18.18 • Make the same assumptions as in Example 18.4 (Section 18.1). How does the percentage decrease in air pressure in going from sea level to an altitude of 100 m compare to that when going from sea level to an altitude of 1000 m? If your second answer is not 10 times your first answer, explain why.

18.19 •• (a) Calculate the mass of nitrogen present in a volume of 3000 cm³ if the temperature of the gas is 22.0°C and the absolute pressure of 2.00×10^{-13} atm is a partial vacuum easily obtained in laboratories. (b) What is the density (in kg/m³) of the N_2?

18.20 •• With the assumption that the air temperature is a uniform 0.0°C (as in Example 18.4), what is the density of the air at an altitude of 1.00 km as a percentage of the density at the surface?

18.21 • At an altitude of 11,000 m (a typical cruising altitude for a jet airliner), the air temperature is -56.5°C and the air density is 0.364 kg/m³. What is the pressure of the atmosphere at that altitude? (*Note:* The temperature at this altitude is not the same as at the surface of the earth, so the calculation of Example 18.4 in Section 18.1 doesn't apply.)

Section 18.2 Molecular Properties of Matter

18.22 • A large organic molecule has a mass of 1.41×10^{-21} kg. What is the molar mass of this compound?

18.23 •• Suppose you inherit 3.00 mol of gold from your uncle (an eccentric chemist) at a time when this metal is selling for $14.75 per gram. Consult the periodic table in Appendix D and Table 12.1. (a) To the nearest dollar, what is this gold worth? (b) If you have your gold formed into a spherical nugget, what is its diameter?

18.24 •• Modern vacuum pumps make it easy to attain pressures of the order of 10^{-13} atm in the laboratory. Consider a volume of air and treat the air as an ideal gas. (a) At a pressure of 9.00×10^{-14} atm and an ordinary temperature of 300.0 K, how many molecules are present in a volume of 1.00 cm³? (b) How many molecules would be present at the same temperature but at 1.00 atm instead?

18.25 •• The Lagoon Nebula (Fig. E18.25) is a cloud of hydrogen gas located 3900 light-years from the earth. The cloud is about 45 light-years in diameter and glows because of its high temperature of 7500 K. (The gas is raised to this temperature by the stars that

Figure **E18.25**

lie within the nebula.) The cloud is also very thin; there are only 80 molecules per cubic centimeter. (a) Find the gas pressure (in atmospheres) in the Lagoon Nebula. Compare it to the laboratory pressure referred to in Exercise 18.24. (b) Science-fiction films sometimes show starships being buffeted by turbulence as they fly through gas clouds such as the Lagoon Nebula. Does this seem realistic? Why or why not?

18.26 •• In a gas at standard conditions, what is the length of the side of a cube that contains a number of molecules equal to the population of the earth (about 6×10^9 people)?

18.27 • How many moles are in a 1.00-kg bottle of water? How many molecules? The molar mass of water is 18.0 g/mol.

18.28 •• **How Close Together Are Gas Molecules?** Consider an ideal gas at 27°C and 1.00 atm pressure. To get some idea how close these molecules are to each other, on the average, imagine them to be uniformly spaced, with each molecule at the center of a small cube. (a) What is the length of an edge of each cube if adjacent cubes touch but do not overlap? (b) How does this distance compare with the diameter of a typical molecule? (c) How does their separation compare with the spacing of atoms in solids, which typically are about 0.3 nm apart?

18.29 •• Consider 5.00 mol of liquid water. (a) What volume is occupied by this amount of water? The molar mass of water is 18.0 g/mol. (b) Imagine the molecules to be, on average, uniformly spaced, with each molecule at the center of a small cube. What is the length of an edge of each small cube if adjacent cubes touch but don't overlap? (c) How does this distance compare with the diameter of a molecule?

Section 18.3 Kinetic-Molecular Model of an Ideal Gas

18.30 • A flask contains a mixture of neon (Ne), krypton (Kr), and radon (Rn) gases. Compare (a) the average kinetic energies of the three types of atoms and (b) the root-mean-square speeds. (*Hint:* The periodic table in Appendix D shows the molar mass (in g/mol) of each element under the chemical symbol for that element.)

18.31 • **Gaseous Diffusion of Uranium.** (a) A process called *gaseous diffusion* is often used to separate isotopes of uranium— that is, atoms of the elements that have different masses, such as ^{235}U and ^{238}U. The only gaseous compound of uranium at ordinary temperatures is uranium hexafluoride, UF_6. Speculate on how $^{235}UF_6$ and $^{238}UF_6$ molecules might be separated by diffusion. (b) The molar masses for $^{235}UF_6$ and $^{238}UF_6$ molecules are 0.349 kg/mol and 0.352 kg/mol, respectively. If uranium hexafluoride acts as an ideal gas, what is the ratio of the root-mean-square speed of $^{235}UF_6$ molecules to that of $^{238}UF_6$ molecules if the temperature is uniform?

18.32 • The ideas of average and root-mean-square value can be applied to any distribution. A class of 150 students had the following scores on a 100-point quiz:

Score	Number of Students
10	11
20	12
30	24
40	15
50	19
60	10
70	12
80	20
90	17
100	10

(a) Find the average score for the class. (b) Find the root-mean-square score for the class.

18.33 • We have two equal-size boxes, A and B. Each box contains gas that behaves as an ideal gas. We insert a thermometer into each box and find that the gas in box A is at a temperature of 50°C while the gas in box B is at 10°C. This is all we know about the gas in the boxes. Which of the following statements *must* be true? Which *could* be true? (a) The pressure in A is higher than in B. (b) There are more molecules in A than in B. (c) A and B do not contain the same type of gas. (d) The molecules in A have more average kinetic energy per molecule than those in B. (e) The molecules in A are moving faster than those in B. Explain the reasoning behind your answers.

18.34 • A container with volume 1.48 L is initially evacuated. Then it is filled with 0.226 g of N_2. Assume that the pressure of the gas is low enough for the gas to obey the ideal-gas law to a high degree of accuracy. If the root-mean-square speed of the gas molecules is 182 m/s, what is the pressure of the gas?

18.35 •• (a) A deuteron, ^2_1H, is the nucleus of a hydrogen isotope and consists of one proton and one neutron. The plasma of deuterons in a nuclear fusion reactor must be heated to about 300 million K. What is the rms speed of the deuterons? Is this a significant fraction of the speed of light ($c = 3.0 \times 10^8$ m/s)? (b) What would the temperature of the plasma be if the deuterons had an rms speed equal to $0.10c$?

18.36 • **Martian Climate.** The atmosphere of Mars is mostly CO_2 (molar mass 44.0 g/mol) under a pressure of 650 Pa, which we shall assume remains constant. In many places the temperature varies from 0.0°C in summer to −100°C in winter. Over the course of a Martian year, what are the ranges of (a) the rms speeds of the CO_2 molecules and (b) the density (in mol/m³) of the atmosphere?

18.37 •• (a) Oxygen (O_2) has a molar mass of 32.0 g/mol. What is the average translational kinetic energy of an oxygen molecule at a temperature of 300 K? (b) What is the average value of the square of its speed? (c) What is the root-mean-square speed? (d) What is the momentum of an oxygen molecule traveling at this speed? (e) Suppose an oxygen molecule traveling at this speed bounces back and forth between opposite sides of a cubical vessel 0.10 m on a side. What is the average force the molecule exerts on one of the walls of the container? (Assume that the molecule's velocity is perpendicular to the two sides that it strikes.) (f) What is the average force per unit area? (g) How many oxygen molecules traveling at this speed are necessary to produce an average pressure of 1 atm? (h) Compute the number of oxygen molecules that are actually contained in a vessel of this size at 300 K and atmospheric pressure. (i) Your answer for part (h) should be three times as large as the answer for part (g). Where does this discrepancy arise?

18.38 •• Calculate the mean free path of air molecules at a pressure of 3.50×10^{-13} atm and a temperature of 300 K. (This pressure is readily attainable in the laboratory; see Exercise 18.24.) As in Example 18.8, model the air molecules as spheres of radius 2.0×10^{-10} m.

18.39 •• At what temperature is the root-mean-square speed of nitrogen molecules equal to the root-mean-square speed of hydrogen molecules at 20.0°C? (*Hint:* The periodic table in Appendix D shows the molar mass (in g/mol) of each element under the chemical symbol for that element. The molar mass of H_2 is twice the molar mass of hydrogen atoms, and similarly for N_2.)

18.40 • Smoke particles in the air typically have masses of the order of 10^{-16} kg. The Brownian motion (rapid, irregular movement) of these particles, resulting from collisions with air molecules, can

be observed with a microscope. (a) Find the root-mean-square speed of Brownian motion for a particle with a mass of 3.00×10^{-16} kg in air at 300 K. (b) Would the root-mean-square speed be different if the particle were in hydrogen gas at the same temperature? Explain.

Section 18.4 Heat Capacities

18.41 • (a) How much heat does it take to increase the temperature of 2.50 mol of a diatomic ideal gas by 50.0 K near room temperature if the gas is held at constant volume? (b) What is the answer to the question in part (a) if the gas is monatomic rather than diatomic?

18.42 •• Perfectly rigid containers each hold n moles of ideal gas, one being hydrogen (H_2) and other being neon (Ne). If it takes 300 J of heat to increase the temperature of the hydrogen by $2.50°C$, by how many degrees will the same amount of heat raise the temperature of the neon?

18.43 •• (a) Compute the specific heat at constant volume of nitrogen (N_2) gas, and compare it with the specific heat of liquid water. The molar mass of N_2 is 28.0 g/mol. (b) You warm 1.00 kg of water at a constant volume of 1.00 L from $20.0°C$ to $30.0°C$ in a kettle. For the same amount of heat, how many kilograms of $20.0°C$ air would you be able to warm to $30.0°C$? What volume (in liters) would this air occupy at $20.0°C$ and a pressure of 1.00 atm? Make the simplifying assumption that air is 100% N_2.

18.44 •• (a) Calculate the specific heat at constant volume of water vapor, assuming the nonlinear triatomic molecule has three translational and three rotational degrees of freedom and that vibrational motion does not contribute. The molar mass of water is 18.0 g/mol. (b) The actual specific heat of water vapor at low pressures is about 2000 J/kg · K. Compare this with your calculation and comment on the actual role of vibrational motion.

18.45 •• (a) Use Eq. 18.28 to calculate the specific heat at constant volume of aluminum in units of J/kg · K. Consult the periodic table in Appendix D. (b) Compare the answer in part (a) with the value given in Table 17.3. Try to explain any disagreement between these two values.

Section 18.5 Molecular Speeds

18.46 • For a gas of nitrogen molecules (N_2), what must the temperature be if 94.7% of all the molecules have speeds less than (a) 1500 m/s; (b) 1000 m/s; (c) 500 m/s? Use Table 18.2. The molar mass of N_2 is 28.0 g/mol.

18.47 • For diatomic carbon dioxide gas $(CO_2$, molar mass 44.0 g/mol) at $T = 300$ K, calculate (a) the most probable speed v_{mp}; (b) the average speed v_{av}; (c) the root-mean-square speed v_{rms}.

18.48 • **CALC** Prove that $f(v)$ as given by Eq. (18.33) is maximum for $\epsilon = kT$. Use this result to obtain Eq. (18.34).

Section 18.6 Phases of Matter

18.49 • Solid water (ice) is slowly warmed from a very low temperature. (a) What minimum external pressure p_1 must be applied to the solid if a melting phase transition is to be observed? Describe the sequence of phase transitions that occur if the applied pressure p is such that $p < p_1$. (b) Above a certain maximum pressure p_2, no boiling transition is observed. What is this pressure? Describe the sequence of phase transitions that occur if $p_1 < p < p_2$.

18.50 • Puffy cumulus clouds, which are made of water droplets, occur at lower altitudes in the atmosphere. Wispy cirrus clouds, which are made of ice crystals, occur only at higher altitudes. Find the altitude y (measured from sea level) above which only cirrus clouds can occur. On a typical day and at altitudes less than 11 km, the temperature at an altitude y is given by $T = T_0 - \alpha y$, where $T_0 = 15.0°C$ and $\alpha = 6.0$ C°/1000 m.

18.51 • The atmosphere of the planet Mars is 95.3% carbon dioxide (CO_2) and about 0.03% water vapor. The atmospheric pressure is only about 600 Pa, and the surface temperature varies from $-30°C$ to $-100°C$. The polar ice caps contain both CO_2 ice and water ice. Could there be *liquid* CO_2 on the surface of Mars? Could there be liquid water? Why or why not?

18.52 • A physics lecture room has a volume of 216 m^3. (a) For a pressure of 1.00 atm and a temperature of $27.0°C$, use the ideal-gas law to estimate the number of air molecules in the room. Assume all the air is N_2. (b) Calculate the particle density—that is, the number of N_2 molecules per cubic centimeter. (c) Calculate the mass of the air in the room.

PROBLEMS

18.53 •• **CP** **BIO** **The Effect of Altitude on the Lungs.** (a) Calculate the *change* in air pressure you will experience if you climb a 1000-m mountain, assuming that the temperature and air density do not change over this distance and that they were $22°C$ and 1.2 kg/m^3, respectively, at the bottom of the mountain. (Note that the result of Example 18.4 doesn't apply, since the expression derived in that example accounts for the variation of air density with altitude and we are told to ignore that in this problem.) (b) If you took a 0.50-L breath at the foot of the mountain and managed to hold it until you reached the top, what would be the volume of this breath when you exhaled it there?

18.54 •• **CP** **BIO** **The Bends.** If deep-sea divers rise to the surface too quickly, nitrogen bubbles in their blood can expand and prove fatal. This phenomenon is known as the *bends*. If a scuba diver rises quickly from a depth of 25 m in Lake Michigan (which is fresh water), what will be the volume at the surface of an N_2 bubble that occupied 1.0 mm^3 in his blood at the lower depth? Does it seem that this difference is large enough to be a problem? (Assume that the pressure difference is due only to the changing water pressure, not to any temperature difference, an assumption that is reasonable, since we are warm-blooded creatures.)

18.55 ••• **CP** A hot-air balloon stays aloft because hot air at atmospheric pressure is less dense than cooler air at the same pressure. If the volume of the balloon is 500.0 m^3 and the surrounding air is at $15.0°C$, what must the temperature of the air in the balloon be for it to lift a total load of 290 kg (in addition to the mass of the hot air)? The density of air at $15.0°C$ and atmospheric pressure is 1.23 kg/m^3.

18.56 •• (a) Use Eq. (18.1) to estimate the change in the volume of a solid steel sphere of volume 11 L when the temperature and pressure increase from $21°C$ and 1.013×10^5 Pa to $42°C$ and 2.10×10^7 Pa. (*Hint:* Consult Chapters 11 and 17 to determine the values of β and k.) (b) In Example 18.3 the change in volume of an 11-L steel scuba tank was ignored. Was this a good approximation? Explain.

18.57 ••• A cylinder 1.00 m tall with inside diameter 0.120 m is used to hold propane gas (molar mass 44.1 g/mol) for use in a barbecue. It is initially filled with gas until the gauge pressure is 1.30×10^6 Pa and the temperature is $22.0°C$. The temperature of the gas remains constant as it is partially emptied out of the tank, until the gauge pressure is 2.50×10^5 Pa. Calculate the mass of propane that has been used.

18.58 • **CP** During a test dive in 1939, prior to being accepted by the U.S. Navy, the submarine *Squalus* sank at a point where the depth of water was 73.0 m. The temperature at the surface was 27.0°C, and at the bottom it was 7.0°C. The density of seawater is 1030 kg/m³. (a) A diving bell was used to rescue 33 trapped crewmen from the *Squalus*. The diving bell was in the form of a circular cylinder 2.30 m high, open at the bottom and closed at the top. When the diving bell was lowered to the bottom of the sea, to what height did water rise within the diving bell? (*Hint:* You may ignore the relatively small variation in water pressure between the bottom of the bell and the surface of the water within the bell.) (b) At what gauge pressure must compressed air have been supplied to the bell while on the bottom to expel all the water from it?

18.59 • **Atmosphere of Titan.** Titan, the largest satellite of Saturn, has a thick nitrogen atmosphere. At its surface, the pressure is 1.5 earth-atmospheres and the temperature is 94 K. (a) What is the surface temperature in °C? (b) Calculate the surface density in Titan's atmosphere in molecules per cubic meter. (c) Compare the density of Titan's surface atmosphere to the density of earth's atmosphere at 22°C. Which body has denser atmosphere?

18.60 • **Pressure on Venus.** At the surface of Venus the average temperature is a balmy 460°C due to the greenhouse effect (global warming!), the pressure is 92 earth-atmospheres, and the acceleration due to gravity is $0.894g_{earth}$. The atmosphere is nearly all CO_2 (molar mass 44.0 g/mol) and the temperature remains remarkably constant. We shall assume that the temperature does not change at all with altitude. (a) What is the atmospheric pressure 1.00 km above the surface of Venus? Express your answer in Venus-atmospheres and earth-atmospheres. (b) What is the root-mean-square speed of the CO_2 molecules at the surface of Venus and at an altitude of 1.00 km?

18.61 •• An automobile tire has a volume of 0.0150 m³ on a cold day when the temperature of the air in the tire is 5.0°C and atmospheric pressure is 1.02 atm. Under these conditions the gauge pressure is measured to be 1.70 atm (about 25 lb/in.²). After the car is driven on the highway for 30 min, the temperature of the air in the tires has risen to 45.0°C and the volume has risen to 0.0159 m³. What then is the gauge pressure?

18.62 •• A flask with a volume of 1.50 L, provided with a stopcock, contains ethane gas (C_2H_6) at 300 K and atmospheric pressure (1.013×10^5 Pa). The molar mass of ethane is 30.1 g/mol. The system is warmed to a temperature of 490 K, with the stopcock open to the atmosphere. The stopcock is then closed, and the flask is cooled to its original temperature. (a) What is the final pressure of the ethane in the flask? (b) How many grams of ethane remain in the flask?
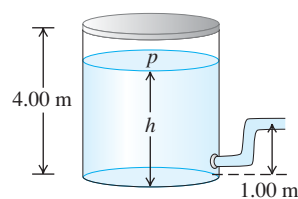
18.63 •• **CP** A balloon whose volume is 750 m³ is to be filled with hydrogen at atmospheric pressure (1.01×10^5 Pa). (a) If the hydrogen is stored in cylinders with volumes of 1.90 m³ at a gauge pressure of 1.20×10^6 Pa, how many cylinders are required? Assume that the temperature of the hydrogen remains constant. (b) What is the total weight (in addition to the weight of the gas) that can be supported by the balloon if the gas in the balloon and the surrounding air are both at 15.0°C? The molar mass of hydrogen (H_2) is 2.02 g/mol. The density of air at 15.0°C and atmospheric pressure is 1.23 kg/m³. See Chapter 12 for a discussion of buoyancy. (c) What weight could be supported if the balloon were filled with helium (molar mass 4.00 g/mol) instead of hydrogen, again at 15.0°C?

18.64 •• A vertical cylindrical tank contains 1.80 mol of an ideal gas under a pressure of 0.500 atm at 20.0°C. The round part of the tank has a radius of 10.0 cm, and the gas is supporting a piston that can move up and down in the cylinder without friction. There is a vacuum above the piston. (a) What is the mass of this piston? (b) How tall is the column of gas that is supporting the piston?

18.65 •• **CP** A large tank of water has a hose connected to it, as shown in Fig. P18.65. The tank is sealed at the top and has compressed air between the water surface and the top. When the water height h has the value 3.50 m, the absolute pressure p of the compressed air is 4.20×10^5 Pa. Assume that the air above the water expands at constant temperature, and take the atmospheric pressure to be 1.00×10^5 Pa. (a) What is the speed with which water flows out of the hose when $h = 3.50$ m? (b) As water flows out of the tank, h decreases. Calculate the speed of flow for $h = 3.00$ m and for $h = 2.00$ m. (c) At what value of h does the flow stop?

Figure **P18.65**

18.66 •• **BIO** A person at rest inhales 0.50 L of air with each breath at a pressure of 1.00 atm and a temperature of 20.0°C. The inhaled air is 21.0% oxygen. (a) How many oxygen molecules does this person inhale with each breath? (b) Suppose this person is now resting at an elevation of 2000 m but the temperature is still 20.0°C. Assuming that the oxygen percentage and volume per inhalation are the same as stated above, how many oxygen molecules does this person now inhale with each breath? (c) Given that the body still requires the same number of oxygen molecules per second as at sea level to maintain its functions, explain why some people report "shortness of breath" at high elevations.

18.67 •• **BIO** **How Many Atoms Are You?** Estimate the number of atoms in the body of a 50-kg physics student. Note that the human body is mostly water, which has molar mass 18.0 g/mol, and that each water molecule contains three atoms.

18.68 • The size of an oxygen molecule is about 2.0×10^{-10} m. Make a rough estimate of the pressure at which the finite volume of the molecules should cause noticeable deviations from ideal-gas behavior at ordinary temperatures ($T = 300$ K).

18.69 •• You have two identical containers, one containing gas A and the other gas B. The masses of these molecules are $m_A = 3.34 \times 10^{-27}$ kg and $m_B = 5.34 \times 10^{-26}$ kg. Both gases are under the same pressure and are at 10.0°C. (a) Which molecules (A or B) have greater translational kinetic energy per molecule and rms speeds? (b) Now you want to raise the temperature of only one of these containers so that both gases will have the same rms speed. For which gas should you raise the temperature? (c) At what temperature will you accomplish your goal? (d) Once you have accomplished your goal, which molecules (A or B) now have greater average translational kinetic energy per molecule?

18.70 • **Insect Collisions.** A cubical cage 1.25 m on each side contains 2500 angry bees, each flying randomly at 1.10 m/s. We can model these insects as spheres 1.50 cm in diameter. On the average, (a) how far does a typical bee travel between collisions, (b) what is the average time between collisions, and (c) how many collisions per second does a bee make?

18.71 •• You blow up a spherical balloon to a diameter of 50.0 cm until the absolute pressure inside is 1.25 atm and the temperature is 22.0°C. Assume that all the gas is N_2, of molar mass 28.0 g/mol. (a) Find the mass of a single N_2 molecule. (b) How much translational kinetic energy does an average N_2 molecule have? (c) How many N_2 molecules are in this balloon? (d) What is the *total* translational kinetic energy of all the molecules in the balloon?

18.72 • **CP** (a) Compute the increase in gravitational potential energy for a nitrogen molecule (molar mass 28.0 g/mol) for an increase in elevation of 400 m near the earth's surface. (b) At what temperature is this equal to the average kinetic energy of a nitrogen molecule? (c) Is it possible that a nitrogen molecule near sea level where $T = 15.0°C$ could rise to an altitude of 400 m? Is it likely that it could do so without hitting any other molecules along the way? Explain.

18.73 •• **CP, CALC** **The Lennard-Jones Potential.** A commonly used potential-energy function for the interaction of two molecules (see Fig. 18.8) is the Lennard-Jones 6-12 potential:

$$U(r) = U_0\left[\left(\frac{R_0}{r}\right)^{12} - 2\left(\frac{R_0}{r}\right)^{6}\right]$$

where r is the distance between the centers of the molecules and U_0 and R_0 are positive constants. The corresponding force $F(r)$ is given in Eq. (14.26). (a) Graph $U(r)$ and $F(r)$ versus r. (b) Let r_1 be the value of r at which $U(r) = 0$, and let r_2 be the value of r at which $F(r) = 0$. Show the locations of r_1 and r_2 on your graphs of $U(r)$ and $F(r)$. Which of these values represents the equilibrium separation between the molecules? (c) Find the values of r_1 and r_2 in terms of R_0, and find the ratio r_1/r_2. (d) If the molecules are located a distance r_2 apart [as calculated in part (c)], how much work must be done to pull them apart so that $r \to \infty$?

18.74 • (a) What is the total random translational kinetic energy of 5.00 L of hydrogen gas (molar mass 2.016 g/mol) with pressure 1.01×10^5 Pa and temperature 300 K? (Hint: Use the procedure of Problem 18.71 as a guide.) (b) If the tank containing the gas is placed on a swift jet moving at 300.0 m/s, by what percentage is the *total* kinetic energy of the gas increased? (c) Since the kinetic energy of the gas molecules is greater when it is on the jet, does this mean that its temperature has gone up? Explain.

18.75 • The speed of propagation of a sound wave in air at 27°C is about 350 m/s. Calculate, for comparison, (a) v_{rms} for nitrogen molecules and (b) the rms value of v_x at this temperature. The molar mass of nitrogen (N_2) is 28.0 g/mol.

18.76 • **Hydrogen on the Sun.** The surface of the sun has a temperature of about 5800 K and consists largely of hydrogen atoms. (a) Find the rms speed of a hydrogen atom at this temperature. (The mass of a single hydrogen atom is 1.67×10^{-27} kg.) (b) The escape speed for a particle to leave the gravitational influence of the sun is given by $(2GM/R)^{1/2}$, where M is the sun's mass, R its radius, and G the gravitational constant (see Example 13.5 of Section 13.3). Use the data in Appendix F to calculate this escape speed. (c) Can appreciable quantities of hydrogen escape from the sun? Can *any* hydrogen escape? Explain.

18.77 •• **CP** (a) Show that a projectile with mass m can "escape" from the surface of a planet if it is launched vertically upward with a kinetic energy greater than mgR_p, where g is the acceleration due to gravity at the planet's surface and R_p is the planet's radius. Ignore air resistance. (See Problem 18.76.) (b) If the planet in question is the earth, at what temperature does the average translational kinetic energy of a nitrogen molecule (molar mass 28.0 g/mol) equal that required to escape? What about a hydrogen molecule (molar mass 2.02 g/mol)? (c) Repeat part (b) for the moon, for which $g = 1.63$ m/s² and $R_p = 1740$ km. (d) While the earth and the moon have similar average surface temperatures, the moon has essentially no atmosphere. Use your results from parts (b) and (c) to explain why.

18.78 • **Planetary Atmospheres.** (a) The temperature near the top of Jupiter's multicolored cloud layer is about 140 K. The temperature at the top of the earth's troposphere, at an altitude of about 20 km, is about 220 K. Calculate the rms speed of hydrogen molecules in both these environments. Give your answers in m/s and as a fraction of the escape speed from the respective planet (see Problem 18.76). (b) Hydrogen gas (H_2) is a rare element in the earth's atmosphere. In the atmosphere of Jupiter, by contrast, 89% of all molecules are H_2. Explain why, using your results from part (a). (c) Suppose an astronomer claims to have discovered an oxygen (O_2) atmosphere on the asteroid Ceres. How likely is this? Ceres has a mass equal to 0.014 times the mass of the moon, a density of 2400 kg/m³, and a surface temperature of about 200 K.

18.79 •• (a) For what mass of molecule or particle is v_{rms} equal to 1.00 mm/s at 300 K? (b) If the particle is an ice crystal, how many molecules does it contain? The molar mass of water is 18.0 g/mol. (c) Calculate the diameter of the particle if it is a spherical piece of ice. Would it be visible to the naked eye?

18.80 •• In describing the heat capacities of solids in Section 18.4, we stated that the potential energy $U = \frac{1}{2}kx^2$ of a harmonic oscillator averaged over one period of the motion is equal to the kinetic energy $K = \frac{1}{2}mv^2$ averaged over one period. Prove this result using Eqs. (14.13) and (14.15) for the position and velocity of a simple harmonic oscillator. For simplicity, assume that the initial position and velocity make the phase angle ϕ equal to zero. (Hint: Use the trigonometric identities $\cos^2(\theta) = [1 + \cos(2\theta)]/2$ and $\sin^2(\theta) = [1 - \cos(2\theta)]/2$. What is the average value of $\cos(2\omega t)$ over one period?)

18.81 •• It is possible to make crystalline solids that are only one layer of atoms thick. Such "two-dimensional" crystals can be created by depositing atoms on a very flat surface. (a) If the atoms in such a two-dimensional crystal can move only within the plane of the crystal, what will be its molar heat capacity near room temperature? Give your answer as a multiple of R and in J/mol·K. (b) At very low temperatures, will the molar heat capacity of a two-dimensional crystal be greater than, less than, or equal to the result you found in part (a)? Explain why.

18.82 •• (a) Calculate the total *rotational* kinetic energy of the molecules in 1.00 mol of a diatomic gas at 300 K. (b) Calculate the moment of inertia of an oxygen molecule (O_2) for rotation about either the y- or z-axis shown in Fig. 18.18b. Treat the molecule as two massive points (representing the oxygen atoms) separated by a distance of 1.21×10^{-10} m. The molar mass of oxygen *atoms* is 16.0 g/mol. (c) Find the rms angular velocity of rotation of an oxygen molecule about either the y- or z-axis shown in Fig. 18.18b. How does your answer compare to the angular velocity of a typical piece of rapidly rotating machinery (10,000 rev/min)?

18.83 • For each polyatomic gas in Table 18.1, compute the value of the molar heat capacity at constant volume, C_V, on the assumption that there is no vibrational energy. Compare with the measured values in the table, and compute the fraction of the total heat capacity that is due to vibration for each of the three gases. (Note: CO_2 is linear; SO_2 and H_2S are not. Recall that a linear polyatomic molecule has two rotational degrees of freedom, and a nonlinear molecule has three.)

18.84 •• **CALC** (a) Show that $\int_0^\infty f(v)\,dv = 1$, where $f(v)$ is the Maxwell–Boltzmann distribution of Eq. (18.32). (b) In terms of the physical definition of $f(v)$, explain why the integral in part (a) *must* have this value.

18.85 •• **CALC** Calculate the integral in Eq. (18.31), $\int_0^\infty v^2 f(v)\,dv$, and compare this result to $(v^2)_{av}$ as given by Eq. (18.16). (Hint: You may use the tabulated integral

$$\int_0^\infty x^{2n} e^{-\alpha x^2}\,dx = \frac{1 \cdot 3 \cdot 5 \cdots (2n-1)}{2^{n+1}\alpha^n}\sqrt{\frac{\pi}{\alpha}}$$

where n is a positive integer and α is a positive constant.)

18.86 •• **CALC** Calculate the integral in Eq. (18.30), $\int_0^\infty v f(v)\,dv$, and compare this result to v_{av} as given by Eq. (18.35). (*Hint:* Make the change of variable $v^2 = x$ and use the tabulated integral

$$\int_0^\infty x^n e^{-\alpha x}\,dx = \frac{n!}{\alpha^{n+1}}$$

where n is a positive integer and α is a positive constant.)

18.87 •• **CALC** (a) Explain why in a gas of N molecules, the number of molecules having speeds in the *finite* interval v to $v + \Delta v$ is $\Delta N = N \int_v^{v+\Delta v} f(v)\,dv$. (b) If Δv is small, then $f(v)$ is approximately constant over the interval and $\Delta N \approx N f(v)\Delta v$. For oxygen gas ($O_2$, molar mass 32.0 g/mol) at $T = 300$ K, use this approximation to calculate the number of molecules with speeds within $\Delta v = 20$ m/s of v_{mp}. Express your answer as a multiple of N. (c) Repeat part (b) for speeds within $\Delta v = 20$ m/s of $7v_{\text{mp}}$. (d) Repeat parts (b) and (c) for a temperature of 600 K. (e) Repeat parts (b) and (c) for a temperature of 150 K. (f) What do your results tell you about the shape of the distribution as a function of temperature? Do your conclusions agree with what is shown in Fig. 18.23?

18.88 • **Meteorology.** The *vapor pressure* is the pressure of the vapor phase of a substance when it is in equilibrium with the solid or liquid phase of the substance. The *relative humidity* is the partial pressure of water vapor in the air divided by the vapor pressure of water at that same temperature, expressed as a percentage. The air is saturated when the humidity is 100%. (a) The vapor pressure of water at 20.0°C is 2.34×10^3 Pa. If the air temperature is 20.0°C and the relative humidity is 60%, what is the partial pressure of water vapor in the atmosphere (that is, the pressure due to water vapor alone)? (b) Under the conditions of part (a), what is the mass of water in 1.00 m³ of air? (The molar mass of water is 18.0 g/mol. Assume that water vapor can be treated as an ideal gas.)

18.89 • **The Dew Point.** The vapor pressure of water (see Problem 18.88) decreases as the temperature decreases. If the amount of water vapor in the air is kept constant as the air is cooled, a temperature is reached, called the *dew point,* at which the partial pressure and vapor pressure coincide and the vapor is saturated. If the air is cooled further, vapor condenses to liquid until the partial pressure again equals the vapor pressure at that temperature. The temperature in a room is 30.0°C. A meteorologist cools a metal can by gradually adding cold water. When the can temperature reaches 16.0°C, water droplets form on its outside surface. What is the relative humidity of the 30.0°C air in the room? The table lists the vapor pressure of water at various temperatures:

Temperature (°C)	Vapor Pressure (Pa)
10.0	1.23×10^3
12.0	1.40×10^3
14.0	1.60×10^3
16.0	1.81×10^3
18.0	2.06×10^3
20.0	2.34×10^3
22.0	2.65×10^3
24.0	2.99×10^3
26.0	3.36×10^3
28.0	3.78×10^3
30.0	4.25×10^3

18.90 ••• **Altitude at Which Clouds Form.** On a spring day in the midwestern United States, the air temperature at the surface is 28.0°C. Puffy cumulus clouds form at an altitude where the air temperature equals the dew point (see Problem 18.89). If the air temperature decreases with altitude at a rate of 0.6 C°/100 m, at approximately what height above the ground will clouds form if the relative humidity at the surface is 35% and 80%? (*Hint:* Use the table in Problem 18.89.)

CHALLENGE PROBLEMS

18.91 ••• **CP** **Dark Nebulae and the Interstellar Medium.** The dark area in Fig. P18.91 that appears devoid of stars is a *dark nebula,* a cold gas cloud in interstellar space that contains enough material to block out light from the stars behind it. A typical dark nebula is about 20 light-years in diameter and contains about 50 hydrogen atoms per cubic centimeter (monatomic hydrogen, *not* H_2) at a temperature of about 20 K. (A light-year is the distance light travels in vacuum in one year and is equal to 9.46×10^{15} m.) (a) Estimate the mean free path for a hydrogen atom in a dark nebula. The radius of a hydrogen atom is 5.0×10^{-11} m. (b) Estimate the rms speed of a hydrogen atom and the mean free time (the average time between collisions for a given atom). Based on this result, do you think that atomic collisions, such as those leading to H_2 molecule formation, are very important in determining the composition of the nebula? (c) Estimate the pressure inside a dark nebula. (d) Compare the rms speed of a hydrogen atom to the escape speed at the surface of the nebula (assumed spherical). If the space around the nebula were a vacuum, would such a cloud be stable or would it tend to evaporate? (e) The stability of dark nebulae is explained by the presence of the *interstellar medium* (ISM), an even thinner gas that permeates space and in which the dark nebulae are embedded. Show that for dark nebulae to be in equilibrium with the ISM, the numbers of atoms per volume (N/V) and the temperatures (T) of dark nebulae and the ISM must be related by

$$\frac{(N/V)_{\text{nebula}}}{(N/V)_{\text{ISM}}} = \frac{T_{\text{ISM}}}{T_{\text{nebula}}}$$

(f) In the vicinity of the sun, the ISM contains about 1 hydrogen atom per 200 cm³. Estimate the temperature of the ISM in the vicinity of the sun. Compare to the temperature of the sun's surface, about 5800 K. Would a spacecraft coasting through interstellar space burn up? Why or why not?

Figure **P18.91**
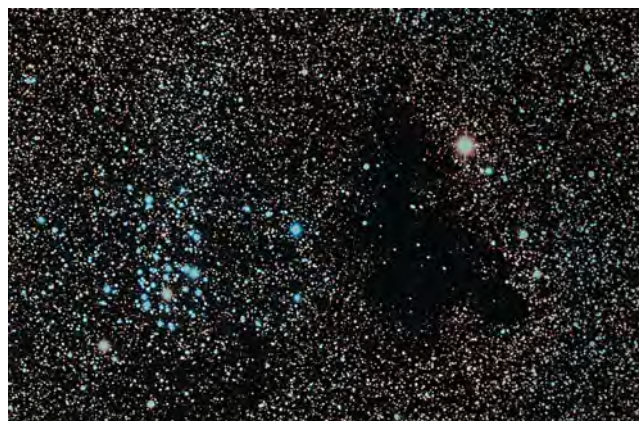
18.92 ••• **CALC** **Earth's Atmosphere.** In the *troposphere,* the part of the atmosphere that extends from earth's surface to an altitude

of about 11 km, the temperature is not uniform but decreases with increasing elevation. (a) Show that if the temperature variation is approximated by the linear relationship

$$T = T_0 - \alpha y$$

where T_0 is the temperature at the earth's surface and T is the temperature at height y, the pressure p at height y is given by

$$\ln\left(\frac{p}{p_0}\right) = \frac{Mg}{R\alpha}\ln\left(\frac{T_0 - \alpha y}{T_0}\right)$$

where p_0 is the pressure at the earth's surface and M is the molar mass for air. The coefficient α is called the lapse rate of temperature. It varies with atmospheric conditions, but an average value is about 0.6 C°/100 m. (b) Show that the above result reduces to the result of Example 18.4 (Section 18.1) in the limit that $\alpha \to 0$. (c) With $\alpha = 0.6$ C°/100 m, calculate p for $y = 8863$ m and compare your answer to the result of Example 18.4. Take $T_0 = 288$ K and $p_0 = 1.00$ atm.

18.93 ••• In Example 18.7 (Section 18.3) we saw that $v_{rms} > v_{av}$. It is not difficult to show that this is *always* the case. (The only exception is when the particles have the same speed, in which case $v_{rms} = v_{av}$.) (a) For two particles with speeds v_1 and v_2, show that $v_{rms} \geq v_{av}$, regardless of the numerical values of v_1 and v_2. Then show that $v_{rms} > v_{av}$ if $v_1 \neq v_2$. (b) Suppose that for a collection of N particles you know that $v_{rms} > v_{av}$. Another particle, with speed u, is added to the collection of particles. If the new rms and average speeds are denoted as v'_{rms} and v'_{av}, show that

$$v'_{rms} = \sqrt{\frac{Nv_{rms}^2 + u^2}{N + 1}} \quad \text{and} \quad v'_{av} = \frac{Nv_{av} + u}{N + 1}$$

(c) Use the expressions in part (b) to show that $v'_{rms} > v'_{av}$ regardless of the numerical value of u. (d) Explain why your results for (a) and (c) together show that $v_{rms} > v_{av}$ for any collection of particles if the particles do not all have the same speed.

Answers

Chapter Opening Question ?

From Eq. (18.19), the root-mean-square speed of a gas molecule is proportional to the square root of the absolute temperature T. The temperature range we're considering is from $(25 + 273.15)$ K $= 298$ K to $(100 + 273.15)$ K $= 373$ K. Hence the speeds increase by a factor of $\sqrt{(373 \text{ K})/(298 \text{ K})} = 1.12$; that is, there is a 12% increase. While 100°C feels far warmer than 25°C, the difference in molecular speeds is relatively small.

Test Your Understanding Questions

18.1 Answer: (ii) and (iii) (tie), (i) and (v) (tie), (iv) We can rewrite the ideal-gas equation, Eq. (18.3), as $n = pV/RT$. This tells us that the number of moles n is proportional to the pressure and volume and inversely proportional to the absolute temperature. Hence, compared to (i), the number of moles in each case is (ii) $(2)(1)/(1) = 2$ times as much, (iii) $(1)(2)/(1) = 2$ times as much, (iv) $(1)(1)/(2) = \frac{1}{2}$ as much, and (v) $(2)(1)/(2) = 1$ time as much (that is, equal).

18.2 Answer: (vi) The value of r_0 determines the equilibrium separation of the molecules in the solid phase, so doubling r_0 means that the separation doubles as well. Hence a solid cube of this compound might grow from 1 cm on a side to 2 cm on a side. The volume would then be $2^3 = 8$ times larger, and the density (mass divided by volume) would be $\frac{1}{8}$ as great.

18.3 Answers: (a) (iv), (ii), (iii), (i); (b) (iii) and (iv) (tie), (i) and (ii) (tie) (a) Equation (18.19) tells us that $v_{rms} = \sqrt{3RT/M}$, so the rms speed is proportional to the square root of the ratio of absolute temperature T to molar mass M. Compared to (i) oxygen at 300 K, v_{rms} in the other cases is (ii) $\sqrt{(32.0 \text{ g/mol})/(28.0 \text{ g/mol})} = 1.07$ times faster, (iii) $\sqrt{(330 \text{ K})/(300 \text{ K})} = 1.05$ times faster, and (iv) $\sqrt{(330 \text{ K})(32.0 \text{ g/mol})/(300 \text{ K})(28.0 \text{ g/mol})} = 1.12$ times faster. (b) From Eq. (18.16), the average translational kinetic energy per molecule is $\frac{1}{2}m(v^2)_{av} = \frac{3}{2}kT$, which is directly proportional to T and independent of M. We have $T = 300$ K for cases (i) and (ii) and $T = 330$ K for cases (iii) and (iv), so $\frac{1}{2}m(v^2)_{av}$ has equal values for cases (iii) and (iv) and equal (but smaller) values for cases (i) and (ii).

18.4 Answers: no, near the beginning Adding a small amount of heat dQ to the gas changes the temperature by dT, where $dQ = nC_V \, dT$ from Eq. (18.24). Figure 18.19 shows that C_V for H_2 varies with temperature between 25 K and 500 K, so a given amount of heat gives rise to different amounts of temperature change during the process. Hence the temperature will *not* increase at a constant rate. The temperature change $dT = dQ/nC_V$ is inversely proportional to C_V, so the temperature increases most rapidly at the beginning of the process when the temperature is lowest and C_V is smallest (see Fig. 18.19).

18.5 Answer: (ii) Figure 18.23b shows that the *fraction* of molecules with speeds between v_1 and v_2 equals the area under the curve of $f(v)$ versus v from $v = v_1$ to $v = v_2$. This is equal to the integral $\int_{v_1}^{v_2} f(v) \, dv$, which in turn is equal to the difference between the integrals $\int_0^{v_2} f(v) \, dv$ (the fraction of molecules with speeds from 0 to v_2) and $\int_0^{v_1} f(v) \, dv$ (the fraction of molecules with speeds from 0 to the slower speed v_1). The *number* of molecules with speeds from v_1 to v_2 equals the fraction of molecules in this speed range multiplied by N, the total number of molecules.

18.6 Answers: no, yes The triple-point pressure of water from Table 18.3 is 6.10×10^2 Pa. The present-day pressure on Mars is just less than this value, corresponding to the line labeled p_s in Fig. 18.24. Hence liquid water cannot exist on the present-day Martian surface, and there are no rivers or lakes. Planetary scientists conclude that liquid water could have and almost certainly did exist on Mars in the past, when the atmosphere was thicker.

Bridging Problem

Answers: **(a)** 102 km **(b)** yes