In this winter scene in Yellowstone Park, we recognize the three states of matter for water: as a liquid, as a solid (snow and ice), and as a gas (steam). In this Chapter we examine the microscopic theory of matter as atoms or molecules that are always in motion, which we call kinetic theory. We will see that the temperature of a gas is directly related to the average translational kinetic energy of its molecules. We will consider ideal gases, but we will also look at real gases and how they change phase, including evaporation, vapor pressure, and humidity.

CHAPTER 18

Kinetic Theory of Gases

CHAPTER-OPENING QUESTION—Guess now!

The typical speed of an air molecule at room temperature (20°C) is

(a) nearly at rest (<10 km/h).
(b) on the order of 10 km/h.
(c) on the order of 100 km/h.
(d) on the order of 1000 km/h.
(e) nearly the speed of light.

CONTENTS

The analysis of matter in terms of atoms in continuous random motion is called **kinetic theory**. We now investigate the properties of a gas from the point of view of kinetic theory, which is based on the laws of classical mechanics. But to apply Newton's laws to each one of the vast number of molecules in a gas ($>10^{25}/\text{m}^3$ at STP) is far beyond the capability of any present computer. Instead we take a statistical approach and determine averages of certain quantities, and these averages correspond to macroscopic variables. We will, of course, demand that our microscopic description correspond to the macroscopic properties of gases; otherwise our theory would be of little value. Most importantly, we will arrive at an important relation between the average kinetic energy of molecules in a gas and the absolute temperature.

18–1 The Ideal Gas Law and the Molecular Interpretation of Temperature

We make the following assumptions about the molecules in a gas. These assumptions reflect a simple view of a gas, but nonetheless the results they predict correspond well to the essential features of real gases that are at low pressures and far from the liquefaction point. Under these conditions real gases follow the ideal gas law quite closely, and indeed the gas we now describe is referred to as an ideal gas. The assumptions, which represent the basic postulates of the kinetic theory for an ideal gas, are

1. There are a large number of molecules, N, each of mass m, moving in random directions with a variety of speeds. This assumption is in accord with our observation that a gas fills its container and, in the case of air on Earth, is kept from escaping only by the force of gravity.
2. The molecules are, on average, far apart from one another. That is, their average separation is much greater than the diameter of each molecule.
3. The molecules are assumed to obey the laws of classical mechanics, and are assumed to interact with one another only when they collide. Although molecules exert weak attractive forces on each other between collisions, the potential energy associated with these forces is small compared to the kinetic energy, and we ignore it for now.
4. Collisions with another molecule or the wall of the vessel are assumed to be perfectly elastic, like the collisions of perfectly elastic billiard balls (Chapter 9). We assume the collisions are of very short duration compared to the time between collisions. Then we can ignore the potential energy associated with collisions in comparison to the kinetic energy between collisions.

We can see immediately how this kinetic view of a gas can explain Boyle's law (Section 17–6). The pressure exerted on a wall of a container of gas is due to the constant bombardment of molecules. If the volume is reduced by (say) half, the molecules are closer together and twice as many will be striking a given area of the wall per second. Hence we expect the pressure to be twice as great, in agreement with Boyle's law.

Now let us calculate quantitatively the pressure a gas exerts on its container as based on kinetic theory. We imagine that the molecules are inside a rectangular container (at rest) whose ends have area A and whose length is ℓ, as shown in Fig. 18–1a. The pressure exerted by the gas on the walls of its container is, according to our model, due to the collisions of the molecules with the walls. Let us focus our attention on the wall, of area A, at the left end of the container and examine what happens when one molecule strikes this wall, as shown in Fig. 18–1b. This molecule exerts a force on the wall, and according to Newton's third law the wall exerts an equal and opposite force back on the molecule. The magnitude of this force on the molecule, according to Newton's second law, is equal to the molecule's rate of change of momentum, $F = dp/dt$ (Eq. 9–2). Assuming the collision is elastic, only the x component of the molecule's momentum changes, and it changes from $-mv_x$ (if it is moving in the negative x direction) to $+mv_x$. Thus the change in the molecule's momentum, $\Delta(mv)$, which is the final momentum minus the initial momentum, is

$$\Delta(mv) = mv_x - (-mv_x) = 2mv_x$$

for one collision. This molecule will make many collisions with the wall, each separated by a time Δt, which is the time it takes the molecule to travel across the container and back again, a distance (x component) equal to 2ℓ. Thus $2\ell = v_x\,\Delta t$, or

$$\Delta t = \frac{2\ell}{v_x}.$$

The time Δt between collisions is very small, so the number of collisions per second is very large. Thus the average force—averaged over many collisions—will be equal to the momentum change during one collision divided by the time between collisions (Newton's second law):

$$F = \frac{\Delta(mv)}{\Delta t} = \frac{2mv_x}{2\ell/v_x} = \frac{mv_x^2}{\ell}. \qquad \text{[due to one molecule]}$$

During its passage back and forth across the container, the molecule may collide with the tops and sides of the container, but this does not alter its x component of momentum and thus does not alter our result. It may also collide with other molecules, which may change its v_x. However, any loss (or gain) of momentum is acquired by other molecules, and because we will eventually sum over all the molecules, this effect will be included. So our result above is not altered.

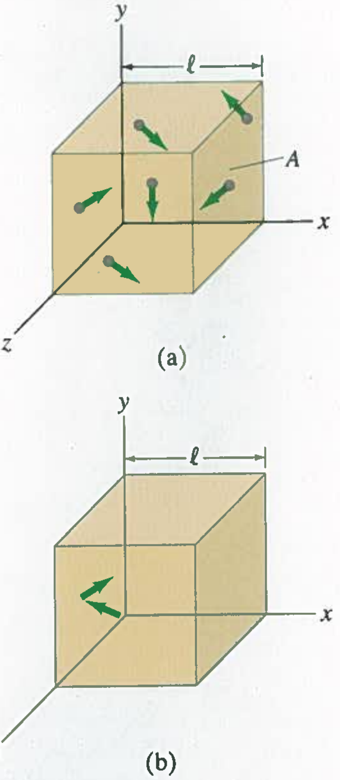


FIGURE 18–1 (a) Molecules of a gas moving about in a rectangular container. (b) Arrows indicate the momentum of one molecule as it rebounds from the end wall.

The actual force due to one molecule is intermittent, but because a large number of molecules are striking the wall per second, the force is, on average, nearly constant. To calculate the force due to *all* the molecules in the container, we have to add the contributions of each. Thus the net force on the wall is

$$F = \frac{m}{\ell}\left(v_{x1}^2 + v_{x2}^2 + \cdots + v_{xN}^2\right),$$

where v_{x1} means v_x for molecule number 1 (we arbitrarily assign each molecule a number) and the sum extends over the total number of molecules N in the container. The average value of the square of the x component of velocity is

$$\overline{v_x^2} = \frac{v_{x1}^2 + v_{x2}^2 + \cdots + v_{xN}^2}{N}, \tag{18-1}$$

where the overbar ($\overline{\ }$) means "average." Thus we can write the force as

$$F = \frac{m}{\ell} N \overline{v_x^2}.$$

We know that the square of any vector is equal to the sum of the squares of its components (theorem of Pythagoras). Thus $v^2 = v_x^2 + v_y^2 + v_z^2$ for any velocity v. Taking averages, we obtain

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

Since the velocities of the molecules in our gas are assumed to be random, there is no preference to one direction or another. Hence

$$\overline{v_x^2} = \overline{v_y^2} = \overline{v_z^2}.$$

Combining this relation with the one just above, we get

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

We substitute this into the equation for net force F:

$$F = \frac{m}{\ell} N \frac{\overline{v^2}}{3}.$$

The pressure on the wall is then

$$P = \frac{F}{A} = \frac{1}{3}\frac{Nm\overline{v^2}}{A\ell}$$

or

$$P = \frac{1}{3}\frac{Nm\overline{v^2}}{V}, \tag{18-2}$$

where $V = \ell A$ is the volume of the container. This is the result we were seeking, the pressure exerted by a gas on its container expressed in terms of molecular properties.

Equation 18–2 can be rewritten in a clearer form by multiplying both sides by V and rearranging the right-hand side:

$$PV = \tfrac{2}{3}N\left(\tfrac{1}{2}m\overline{v^2}\right). \tag{18-3}$$

The quantity $\frac{1}{2}m\overline{v^2}$ is the average translational kinetic energy $\overline{K}$ of the molecules in the gas. If we compare Eq. 18–3 with Eq. 17–4, the ideal gas law $PV = NkT$, we see that the two agree if

$$\tfrac{2}{3}\left(\tfrac{1}{2}m\overline{v^2}\right) = kT,$$

TEMPERATURE RELATED TO AVERAGE KINETIC ENERGY OF MOLECULES

or

$$\overline{K} = \tfrac{1}{2}m\overline{v^2} = \tfrac{3}{2}kT. \qquad \text{[ideal gas]} \tag{18-4}$$

This equation tells us that

> **the average translational kinetic energy of molecules in random motion in an ideal gas is directly proportional to the absolute temperature of the gas.**

The higher the temperature, according to kinetic theory, the faster the molecules are moving on the average. This relation is one of the triumphs of the kinetic theory.

EXAMPLE 18–1 **Molecular kinetic energy.** What is the average translational kinetic energy of molecules in an ideal gas at 37°C?

APPROACH We use the absolute temperature in Eq. 18–4.

SOLUTION We change 37°C to 310 K and insert into Eq. 18–4:

$$\overline{K} = \tfrac{3}{2}kT = \tfrac{3}{2}(1.38 \times 10^{-23}\,\mathrm{J/K})(310\,\mathrm{K}) = 6.42 \times 10^{-21}\,\mathrm{J}.$$

NOTE A mole of molecules would have a total translational kinetic energy equal to $(6.42 \times 10^{-21}\,\mathrm{J})(6.02 \times 10^{23}) = 3860\,\mathrm{J}$, which equals the kinetic energy of a 1-kg stone traveling almost 90 m/s.

EXERCISE A In a mixture of the gases oxygen and helium, which statement is valid: (*a*) the helium molecules will be moving faster than the oxygen molecules, on average; (*b*) both kinds of molecules will be moving at the same speed; (*c*) the oxygen molecules will, on average, be moving more rapidly than the helium molecules; (*d*) the kinetic energy of the helium will exceed that of the oxygen; (*e*) none of the above.

Equation 18–4 holds not only for gases, but also applies reasonably accurately to liquids and solids. Thus the result of Example 18–1 would apply to molecules within living cells at body temperature (37°C).

We can use Eq. 18–4 to calculate how fast molecules are moving on the average. Notice that the average in Eqs. 18–1 through 18–4 is over the *square* of the speed. The square root of $\overline{v^2}$ is called the **root-mean-square** speed, v_{rms} (since we are taking the square *root* of the *mean* of the *square* of the speed):

$$v_{\mathrm{rms}} = \sqrt{\overline{v^2}} = \sqrt{\frac{3kT}{m}}. \tag{18-5}$$

EXAMPLE 18–2 **Speeds of air molecules.** What is the rms speed of air molecules (O_2 and N_2) at room temperature (20°C)?

APPROACH To obtain v_{rms}, we need the masses of O_2 and N_2 molecules and then apply Eq. 18–5 to oxygen and nitrogen separately, since they have different masses.

SOLUTION The masses of one molecule of O_2 (molecular mass = 32 u) and N_2 (molecular mass = 28 u) are (where 1 u = 1.66×10^{-27} kg)

$$m(O_2) = (32)(1.66 \times 10^{-27}\,\mathrm{kg}) = 5.3 \times 10^{-26}\,\mathrm{kg},$$
$$m(N_2) = (28)(1.66 \times 10^{-27}\,\mathrm{kg}) = 4.6 \times 10^{-26}\,\mathrm{kg}.$$

Thus for oxygen

$$v_{\mathrm{rms}} = \sqrt{\frac{3kT}{m}} = \sqrt{\frac{(3)(1.38 \times 10^{-23}\,\mathrm{J/K})(293\,\mathrm{K})}{(5.3 \times 10^{-26}\,\mathrm{kg})}} = 480\,\mathrm{m/s},$$

and for nitrogen the result is $v_{\mathrm{rms}} = 510\,\mathrm{m/s}$. These speeds are more than 1700 km/h or 1000 mi/h, and are greater than the speed of sound ≈340 m/s at 20°C (Chapter 16).

NOTE The speed v_{rms} is a magnitude only. The *velocity* of molecules averages to zero: the velocity has direction, and as many molecules move to the right as to the left, as many up as down, as many inward as outward.

EXERCISE B Now you can return to the Chapter-Opening Question, page 476, and answer it correctly. Try to explain why you may have answered differently the first time.

EXERCISE C If you double the volume of a gas while keeping the pressure and number of moles constant, the average (rms) speed of the molecules (*a*) doubles, (*b*) quadruples, (*c*) increases by $\sqrt{2}$, (*d*) is half, (*e*) is $\frac{1}{4}$.

EXERCISE D By what factor must the absolute temperature change to double v_{rms}? (*a*) $\sqrt{2}$; (*b*) 2; (*c*) $2\sqrt{2}$; (*d*) 4; (*e*) 16.

CONCEPTUAL EXAMPLE 18–3 **Less gas in the tank.** A tank of helium is used to fill balloons. As each balloon is filled, the number of helium atoms remaining in the tank decreases. How does this affect the rms speed of molecules remaining in the tank?

RESPONSE The rms speed is given by Eq. 18–5: $v_{\mathrm{rms}} = \sqrt{3kT/m}$. So only the temperature matters, not pressure P or number of moles n. If the tank remains at a constant (ambient) temperature, then the rms speed remains constant even though the pressure of helium in the tank decreases.

In a collection of molecules, the **average speed**, $\bar{v}$, is the average of the magnitudes of the speeds themselves; $\bar{v}$ is generally not equal to v_{rms}. To see the difference between the average speed and the rms speed, consider the following Example.

EXAMPLE 18–4 **Average speed and rms speed.** Eight particles have the following speeds, given in m/s: 1.0, 6.0, 4.0, 2.0, 6.0, 3.0, 2.0, 5.0. Calculate (*a*) the average speed and (*b*) the rms speed.

APPROACH In (*a*) we sum the speeds and divide by $N = 8$. In (*b*) we square each speed, sum the squares, divide by $N = 8$, and take the square root.

SOLUTION (*a*) The average speed is

$$\bar{v} = \frac{1.0 + 6.0 + 4.0 + 2.0 + 6.0 + 3.0 + 2.0 + 5.0}{8} = 3.6\,\mathrm{m/s}.$$

(*b*) The rms speed is (Eq. 18–1):

$$v_{\mathrm{rms}} = \sqrt{\frac{(1.0)^2 + (6.0)^2 + (4.0)^2 + (2.0)^2 + (6.0)^2 + (3.0)^2 + (2.0)^2 + (5.0)^2}{8}}\,\mathrm{m/s}$$
$$= 4.0\,\mathrm{m/s}.$$

We see in this Example that $\bar{v}$ and v_{rms} are not necessarily equal. In fact, for an ideal gas they differ by about 8%. We will see in the next Section how to calculate $\bar{v}$ for an ideal gas. We already have the tool to calculate v_{rms} (Eq. 18–5).

*Kinetic Energy Near Absolute Zero

Equation 18–4, $\overline{K} = \frac{3}{2}kT$, implies that as the temperature approaches absolute zero, the kinetic energy of molecules approaches zero. Modern quantum theory, however, tells us this is not quite so. Instead, as absolute zero is approached, the kinetic energy approaches a very small nonzero minimum value. Even though all real gases become liquid or solid near 0 K, molecular motion does not cease, even at absolute zero.

18–2 Distribution of Molecular Speeds

The Maxwell Distribution

The molecules in a gas are assumed to be in random motion, which means that many molecules have speeds less than the average speed and others have speeds greater than the average. In 1859, James Clerk Maxwell (1831–1879) worked out a formula for the most probable distribution of speeds in a gas containing N molecules. We will not give a derivation here but merely quote his result:

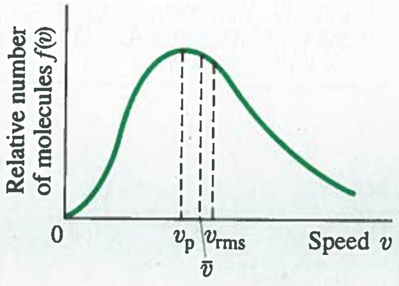
$$f(v) = 4\pi N\left(\frac{m}{2\pi kT}\right)^{\frac{3}{2}} v^2 e^{-\frac{1}{2}\frac{mv^2}{kT}} \tag{18–6}$$

where $f(v)$ is called the **Maxwell distribution of speeds**, and is plotted in Fig. 18–2. The quantity $f(v)\,dv$ represents the number of molecules that have speed between v and $v + dv$. Notice that $f(v)$ does not give the number of molecules with speed v; $f(v)$ must be multiplied by dv to give the number of molecules (the number of molecules depends on the "width" or "range" of velocities included, dv). In the formula for $f(v)$, m is the mass of a single molecule, T is the absolute temperature, and k is the Boltzmann constant. Since N is the total number of molecules in the gas, when we sum over all the molecules in the gas we must get N; thus we must have

$$\int_0^\infty f(v)\,dv = N.$$

(Problem 22 is an exercise to show that this is true.)

FIGURE 18–2 Distribution of speeds of molecules in an ideal gas. Note that $\bar{v}$ and v_{rms} are not at the peak of the curve. This is because the curve is skewed to the right: it is not symmetrical. The speed at the peak of the curve is the "most probable speed," v_{p}.



Experiments to determine the distribution of speeds in real gases, starting in the 1920s, confirmed with considerable accuracy the Maxwell distribution (for gases at not too high a pressure) and the direct proportion between average kinetic energy and absolute temperature, Eq. 18–4.

The Maxwell distribution for a given gas depends only on the absolute temperature. Figure 18–3 shows the distributions for two different temperatures. Just as v_{rms} increases with temperature, so the whole distribution curve shifts to the right at higher temperatures.

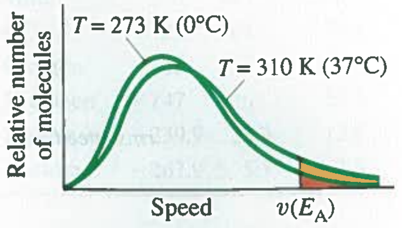


FIGURE 18–3 Distribution of molecular speeds for two different temperatures.

PHYSICS APPLIED
How chemical reactions depend on temperature

Figure 18–3 illustrates how kinetic theory can be used to explain why many chemical reactions, including those in biological cells, take place more rapidly as the temperature increases. Most chemical reactions take place in a liquid solution, and the molecules in a liquid have a distribution of speeds close to the Maxwell distribution. Two molecules may chemically react only if their kinetic energy is great enough so that when they collide, they partially penetrate into each other. The minimum energy required is called the *activation energy*, E_{A}, and it has a specific value for each chemical reaction. The molecular speed corresponding to a kinetic energy of E_{A} for a particular reaction is indicated in Fig. 18–3. The relative number of molecules with energy greater than this value is given by the area under the curve to the right of $v(E_{\mathrm{A}})$, shown in Fig. 18–3 by the two different shadings. We see that the number of molecules that have kinetic energies in excess of E_{A} increases greatly for only a small increase in temperature. The rate at which a chemical reaction occurs is proportional to the number of molecules with energy greater than E_{A}, and thus we see why reaction rates increase rapidly with increased temperature.

*Calculations Using the Maxwell Distribution

Let us see how the Maxwell distribution can be used to obtain some interesting results.

EXAMPLE 18–5 **Determining $\bar{v}$ and v_{p}.** Determine formulas for (*a*) the average speed, $\bar{v}$, and (*b*) the most probable speed, v_{p}, of molecules in an ideal gas at temperature T.

APPROACH (*a*) The average value of any quantity is found by multiplying each possible value of the quantity (here, speed) by the number of molecules that have that value, and then summing all these numbers and dividing by N (the total number). For (*b*), we want to find where the curve of Fig. 18–2 has zero slope; so we set $df/dv = 0$.

SOLUTION (*a*) We are given a continuous distribution of speeds (Eq. 18–6), so the sum over the speeds becomes an integral over the product of v and the number $f(v)\,dv$ that have speed v:

$$\bar{v} = \frac{\int_0^\infty v\,f(v)\,dv}{N} = 4\pi\left(\frac{m}{2\pi kT}\right)^{\frac{3}{2}}\int_0^\infty v^3 e^{-\frac{1}{2}\frac{mv^2}{kT}}\,dv.$$

We can integrate by parts or look up the definite integral in a Table, and obtain

$$\bar{v} = 4\pi\left(\frac{m}{2\pi kT}\right)^{\frac{3}{2}}\left(\frac{2k^2T^2}{m^2}\right) = \sqrt{\frac{8}{\pi}\frac{kT}{m}} \approx 1.60\sqrt{\frac{kT}{m}}.$$

(*b*) The *most probable speed* is that speed which occurs more than any others, and thus is that speed where $f(v)$ has its maximum value. At the maximum of the curve, the slope is zero: $df(v)/dv = 0$. Taking the derivative of Eq. 18–6 gives

$$\frac{df(v)}{dv} = 4\pi N\left(\frac{m}{2\pi kT}\right)^{\frac{3}{2}}\left(2ve^{-\frac{mv^2}{2kT}} - \frac{2mv^3}{2kT}e^{-\frac{mv^2}{2kT}}\right) = 0.$$

Solving for v, we find

$$v_{\mathrm{p}} = \sqrt{\frac{2kT}{m}} \approx 1.41\sqrt{\frac{kT}{m}}.$$

(Another solution is $v = 0$, but this corresponds to a minimum, not a maximum.)

In summary,

Most probable speed, v_p

$$v_p = \sqrt{2\frac{kT}{m}} \approx 1.41\sqrt{\frac{kT}{m}} \qquad (18\text{–}7a)$$

Average speed, $\bar{v}$

$$\bar{v} = \sqrt{\frac{8}{\pi}\frac{kT}{m}} \approx 1.60\sqrt{\frac{kT}{m}} \qquad (18\text{–}7b)$$

and from Eq. 18–5

rms speed, v_{rms}

$$v_{rms} = \sqrt{3\frac{kT}{m}} \approx 1.73\sqrt{\frac{kT}{m}}.$$

These are all indicated in Fig. 18–2. From Eq. 18–6 and Fig. 18–2, it is clear that the speeds of molecules in a gas vary from zero up to many times the average speed, but as can be seen from the graph, most molecules have speeds that are not far from the average. Less than 1% of the molecules exceed four times v_{rms}.

18–3 Real Gases and Changes of Phase

The ideal gas law

$$PV = NkT$$

is an accurate description of the behavior of a real gas as long as the pressure is not too high and as long as the temperature is far from the liquefaction point. But what happens when these two criteria are not satisfied? First we discuss real gas behavior, and then we examine how kinetic theory can help us understand this behavior.

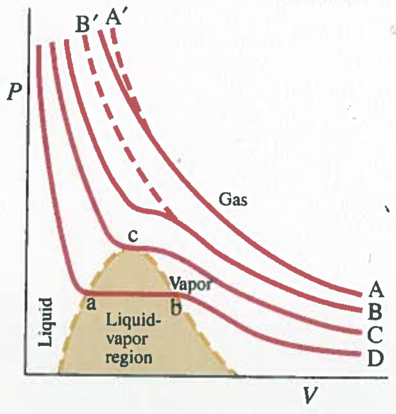


FIGURE 18–4 *PV* diagram for a real substance. Curves A, B, C, and D represent the same substance at different temperatures ($T_A > T_B > T_C > T_D$).

Let us look at a graph of pressure plotted against volume for a given amount of gas. On such a "*PV* diagram," Fig. 18–4, each point represents an equilibrium state of the given substance. The various curves (labeled A, B, C, and D) show how the pressure varies, as the volume is changed at constant temperature, for several different values of the temperature. The dashed curve A′ represents the behavior of a gas as predicted by the ideal gas law; that is, PV = constant. The solid curve A represents the behavior of a real gas at the same temperature. Notice that at high pressure, the volume of a real gas is less than that predicted by the ideal gas law. The curves B and C in Fig. 18–4 represent the gas at successively lower temperatures, and we see that the behavior deviates even more from the curves predicted by the ideal gas law (for example, B′), and the deviation is greater the closer the gas is to liquefying.

To explain this, we note that at higher pressure we expect the molecules to be closer together. And, particularly at lower temperatures, the potential energy associated with the attractive forces between the molecules (which we ignored before) is no longer negligible compared to the now reduced kinetic energy of the molecules. These attractive forces tend to pull the molecules closer together so that at a given pressure, the volume is less than expected from the ideal gas law, as in Fig. 18–4. At still lower temperatures, these forces cause liquefaction, and the molecules become very close together. Section 18–5 discusses in more detail the effect of these attractive molecular forces, as well as the effect of the volume which the molecules themselves occupy.

Curve D represents the situation when liquefaction occurs. At low pressure on curve D (on the right in Fig. 18–4), the substance is a gas and occupies a large volume. As the pressure is increased, the volume decreases until point b is reached. Beyond b the volume decreases with no change in pressure; the substance is gradually changing from the gas to the liquid phase. At point a, all of the substance has changed to liquid. Further increase in pressure reduces the volume only slightly—liquids are nearly incompressible—so on the left the curve is very steep as shown. The colored area under the dashed line represents the region where the gas and liquid phases exist together in equilibrium.

Curve C in Fig. 18–4 represents the behavior of the substance at its **critical temperature**; the point c (the one point where curve C is horizontal) is called the **critical point**. At temperatures less than the critical temperature (and this is the definition of the term), a gas will change to the liquid phase if sufficient pressure is applied. Above the critical temperature, no amount of pressure can cause a gas to change phase and become a liquid. The critical temperatures for various gases are given in Table 18–1. Scientists tried for many years to liquefy oxygen without success. Only after the discovery of the behavior of substances associated with the critical point was it realized that oxygen can be liquefied only if first cooled below its critical temperature of −118°C.

Often a distinction is made between the terms "gas" and "vapor": a substance below its critical temperature in the gaseous state is called a **vapor**; above the critical temperature, it is called a **gas**.

The behavior of a substance can be diagrammed not only on a *PV* diagram but also on a *PT* diagram. A *PT* diagram, often called a **phase diagram**, is particularly convenient for comparing the different phases of a substance. Figure 18–5 is the phase diagram for water. The curve labeled ℓ-v represents those points where the liquid and vapor phases are in equilibrium—it is thus a graph of the boiling point versus pressure. Note that the curve correctly shows that at a pressure of 1 atm the boiling point is 100°C and that the boiling point is lowered for a decreased pressure. The curve s-ℓ represents points where solid and liquid exist in equilibrium and thus is a graph of the freezing point versus pressure. At 1 atm, the freezing point of water is 0°C, as shown. Notice also in Fig. 18–5 that at a pressure of 1 atm, the substance is in the liquid phase if the temperature is between 0°C and 100°C, but is in the solid or vapor phase if the temperature is below 0°C or above 100°C. The curve labeled s-v is the *sublimation point* versus pressure curve. **Sublimation** refers to the process whereby at low pressures a solid changes directly into the vapor phase without passing through the liquid phase. For water, sublimation occurs if the pressure of the water vapor is less than 0.0060 atm. Carbon dioxide, which in the solid phase is called dry ice, sublimates even at atmospheric pressure (Fig. 18–6).

The intersection of the three curves (in Fig. 18–5) is the **triple point**. For water this occurs at $T = 273.16\,\text{K}$ and $P = 6.03 \times 10^{-3}\,\text{atm}$. It is only at the triple point that the three phases can exist together in equilibrium. Because the triple point corresponds to a unique value of temperature and pressure, it is precisely reproducible and is often used as a point of reference. For example, the standard of temperature is usually specified as exactly 273.16 K at the triple point of water, rather than 273.15 K at the freezing point of water at 1 atm.

Notice that the solid liquid (s-ℓ) curve for water slopes upward to the left. This is true only of substances that *expand* upon freezing: at a higher pressure, a lower temperature is needed to cause the liquid to freeze. More commonly, substances contract upon freezing and the s-ℓ curve slopes upward to the right, as shown for carbon dioxide (CO_2) in Fig. 18–6.

The phase transitions we have been discussing are the common ones. Some substances, however, can exist in several forms in the solid phase. A transition from one phase to another occurs at a particular temperature and pressure, just like ordinary phase changes. For example, ice has been observed in at least eight forms at very high pressure. Ordinary helium has two distinct liquid phases, called helium I and II. They exist only at temperatures within a few degrees of absolute zero. Helium II exhibits very unusual properties referred to as **superfluidity**. It has essentially zero viscosity and exhibits strange properties such as climbing up the sides of an open container. Also interesting are **liquid crystals** (used for TV and computer monitors, Section 35–11) which can be considered to be in a phase between liquid and solid.

TABLE 18–1 Critical Temperatures and Pressures

Substance	Critical Temperature °C	Critical Temperature K	Critical Pressure (atm)
Water	374	647	218
CO_2	31	304	72.8
Oxygen	−118	155	50
Nitrogen	−147	126	33.5
Hydrogen	−239.9	33.3	12.8
Helium	−267.9	5.3	2.3

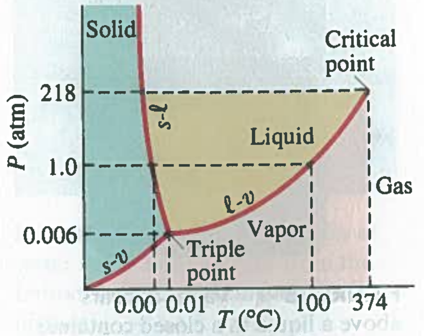
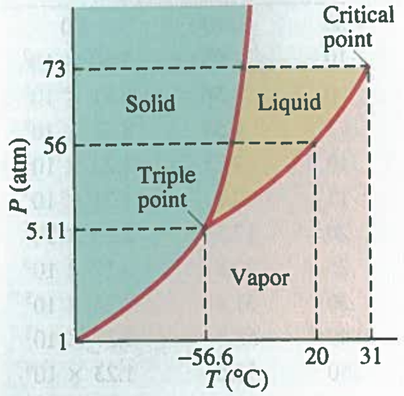


FIGURE 18–5 Phase diagram for water (note that the scales are not linear).

FIGURE 18–6 Phase diagram for carbon dioxide.



PHYSICS APPLIED
Liquid crystals

18–4 Vapor Pressure and Humidity

Evaporation

PHYSICS APPLIED
Evaporation cools

If a glass of water is left out overnight, the water level will have dropped by morning. We say the water has evaporated, meaning that some of the water has changed to the vapor or gas phase.

This process of **evaporation** can be explained on the basis of kinetic theory. The molecules in a liquid move past one another with a variety of speeds that follow, approximately, the Maxwell distribution. There are strong attractive forces between these molecules, which is what keeps them close together in the liquid phase. A molecule near the surface of the liquid may, because of its speed, leave the liquid momentarily. But just as a rock thrown into the air returns to the Earth, so the attractive forces of the other molecules can pull the vagabond molecule back to the liquid surface—that is, if its velocity is not too large. A molecule with a high enough velocity, however, will escape the liquid entirely (like an object leaving Earth with a high enough speed, Section 8–7), and become part of the gas phase. Only those molecules that have kinetic energy above a particular value can escape to the gas phase. We have already seen that kinetic theory predicts that the relative number of molecules with kinetic energy above a particular value (such as E_A in Fig. 18–3) increases with temperature. This is in accord with the well-known observation that the evaporation rate is greater at higher temperatures.

Because it is the fastest molecules that escape from the surface, the average speed of those remaining is less. When the average speed is less, the absolute temperature is less. Thus kinetic theory predicts that *evaporation is a cooling process*. You have no doubt noticed this effect when you stepped out of a warm shower and felt cold as the water on your body began to evaporate; and after working up a sweat on a hot day, even a slight breeze makes you feel cool through evaporation.

FIGURE 18–7 Vapor appears above a liquid in a closed container.

TABLE 18–2 Saturated Vapor Pressure of Water

Temperature (°C)	Saturated Vapor Pressure torr (= mm-Hg)	Pa (= N/m²)
−50	0.030	4.0
−10	1.95	2.60×10^2
0	4.58	6.11×10^2
5	6.54	8.72×10^2
10	9.21	1.23×10^3
15	12.8	1.71×10^3
20	17.5	2.33×10^3
25	23.8	3.17×10^3
30	31.8	4.24×10^3
40	55.3	7.37×10^3
50	92.5	1.23×10^4
60	149	1.99×10^4
70†	234	3.12×10^4
80	355	4.73×10^4
90	526	7.01×10^4
100‡	760	1.01×10^5
120	1489	1.99×10^5
150	3570	4.76×10^5

† Boiling point on summit of Mt. Everest.
‡ Boiling point at sea level.

Vapor Pressure

Air normally contains water vapor (water in the gas phase), and it comes mainly from evaporation. To look at this process in a little more detail, consider a closed container that is partially filled with water (or another liquid) and from which the air has been removed (Fig. 18–7). The fastest moving molecules quickly evaporate into the empty space above the liquid's surface. As they move about, some of these molecules strike the liquid surface and again become part of the liquid phase: this is called **condensation**. The number of molecules in the vapor increases until a point is reached when the number of molecules returning to the liquid equals the number leaving in the same time interval. Equilibrium then exists, and the space above the liquid surface is said to be *saturated*. The pressure of the vapor when it is saturated is called the **saturated vapor pressure** (or sometimes simply the vapor pressure).

The saturated vapor pressure does not depend on the volume of the container. If the volume above the liquid were reduced suddenly, the density of molecules in the vapor phase would be increased temporarily. More molecules would then be striking the liquid surface per second. There would be a net flow of molecules back to the liquid phase until equilibrium was again reached, and this would occur at the same value of the saturated vapor pressure, as long as the temperature had not changed.

The saturated vapor pressure of any substance depends on the temperature. At higher temperatures, more molecules have sufficient kinetic energy to break from the liquid surface into the vapor phase. Hence equilibrium will be reached at a higher pressure. The saturated vapor pressure of water at various temperatures is given in Table 18–2. Notice that even solids—for example, ice—have a measurable saturated vapor pressure.

In everyday situations, evaporation from a liquid takes place into the air above it rather than into a vacuum. This does not materially alter the discussion above relating to Fig. 18–7. Equilibrium will still be reached when there are sufficient molecules in the gas phase that the number reentering the liquid equals the number leaving. The concentration of particular molecules (such as water) in the gas phase is not affected by the presence of air, although collisions with air molecules may lengthen the time needed to reach equilibrium. Thus equilibrium occurs at the same value of the saturated vapor pressure as if air were not there.

If the container is large or is not closed, all the liquid may evaporate before saturation is reached. And if the container is not sealed—as, for example, a room in your house—it is not likely that the air will become saturated with water vapor (unless it is raining outside).

Boiling

The saturated vapor pressure of a liquid increases with temperature. When the temperature is raised to the point where the saturated vapor pressure at that temperature equals the external pressure, **boiling** occurs (Fig. 18–8). As the boiling point is approached, tiny bubbles tend to form in the liquid, which indicate a change from the liquid to the gas phase. However, if the vapor pressure inside the bubbles is less than the external pressure, the bubbles immediately are crushed. As the temperature is increased, the saturated vapor pressure inside a bubble eventually becomes equal to or exceeds the external pressure. The bubble will then not collapse but can rise to the surface. Boiling has then begun. *A liquid boils when its saturated vapor pressure equals the external pressure*. This occurs for water at a pressure of 1 atm (760 torr) at 100°C, as can be seen from Table 18–2.

The boiling point of a liquid clearly depends on the external pressure. At high elevations, the boiling point of water is somewhat less than at sea level since the air pressure is less up there. For example, on the summit of Mt. Everest (8850 m) the air pressure is about one-third of what it is at sea level, and from Table 18–2 we can see that water will boil at about 70°C. Cooking food by boiling takes longer at high elevations, since the temperature is less. Pressure cookers, however, reduce cooking time, because they build up a pressure as high as 2 atm, allowing higher boiling temperatures to be attained.

FIGURE 18–8 Boiling: bubbles of water vapor float upward from the bottom (where the temperature is highest).

Partial Pressure and Humidity

When we refer to the weather as being dry or humid, we are referring to the water vapor content of the air. In a gas such as air, which is a mixture of several types of gases, the total pressure is the sum of the *partial pressures* of each gas present.† By **partial pressure**, we mean the pressure each gas would exert if it alone were present. The partial pressure of water in the air can be as low as zero and can vary up to a maximum equal to the saturated vapor pressure of water at the given temperature. Thus, at 20°C, the partial pressure of water cannot exceed 17.5 torr (see Table 18–2). The **relative humidity** is defined as the ratio of the partial pressure of water vapor to the saturated vapor pressure at a given temperature. It is usually expressed as a percentage:

$$\text{Relative humidity} = \frac{\text{partial pressure of } H_2O}{\text{saturated vapor pressure of } H_2O} \times 100\%.$$

Thus, when the humidity is close to 100%, the air holds nearly all the water vapor it can.

EXAMPLE 18–6 **Relative humidity.** On a particular hot day, the temperature is 30°C and the partial pressure of water vapor in the air is 21.0 torr. What is the relative humidity?

APPROACH From Table 18–2, we see that the saturated vapor pressure of water at 30°C is 31.8 torr.

SOLUTION The relative humidity is thus

$$\frac{21.0\text{ torr}}{31.8\text{ torr}} \times 100\% = 66\%.$$

[†] For example, 78% (by volume) of air molecules are nitrogen and 21% oxygen, with much smaller amounts of water vapor, argon, and other gases. At an air pressure of 1 atm, oxygen exerts a partial pressure of 0.21 atm and nitrogen 0.78 atm.

PHYSICS APPLIED
Humidity and comfort

Humans are sensitive to humidity. A relative humidity of 40–50% is generally optimum for both health and comfort. High humidity, particularly on a hot day, reduces the evaporation of moisture from the skin, which is one of the body's vital mechanisms for regulating body temperature. Very low humidity, on the other hand, can dry the skin and mucous membranes.

PHYSICS APPLIED
Weather

Air is saturated with water vapor when the partial pressure of water in the air is equal to the saturated vapor pressure at that temperature. If the partial pressure of water exceeds the saturated vapor pressure, the air is said to be **supersaturated**. This situation can occur when a temperature decrease occurs. For example, suppose the temperature is 30°C and the partial pressure of water is 21 torr, which represents a humidity of 66% as we saw in Example 18–6. Suppose now that the temperature falls to, say, 20°C, as might happen at nightfall. From Table 18–2 we see that the saturated vapor pressure of water at 20°C is 17.5 torr. Hence the relative humidity would be greater than 100%, and the supersaturated air cannot hold this much water. The excess water may condense and appear as dew, or as fog or rain (Fig. 18–9).

FIGURE 18–9 Fog or mist settling around a castle where the temperature has dropped below the dew point.

When air containing a given amount of water is cooled, a temperature is reached where the partial pressure of water equals the saturated vapor pressure. This is called the **dew point**. Measurement of the dew point is the most accurate means of determining the relative humidity. One method uses a polished metal surface in contact with air, which is gradually cooled down. The temperature at which moisture begins to appear on the surface is the dew point, and the partial pressure of water can then be obtained from saturated vapor pressure Tables. If, for example, on a given day the temperature is 20°C and the dew point is 5°C, then the partial pressure of water (Table 18–2) in the 20°C air is 6.54 torr, whereas its saturated vapor pressure is 17.5 torr; hence the relative humidity is 6.54/17.5 = 37%.

EXERCISE E As the air warms up in the afternoon, how would the relative humidity change if there were no further evaporation? It would (*a*) increase, (*b*) decrease, (*c*) stay the same.

CONCEPTUAL EXAMPLE 18–7 **Dryness in winter.** Why does the air inside heated buildings seem very dry on a cold winter day?

RESPONSE Suppose the relative humidity outside on a −10°C day is 50%. Table 18–2 tells us the partial pressure of water in the air is about 1.0 torr. If this air is brought indoors and heated to +20°C, the relative humidity is (1.0 torr)/(17.5 torr) = 5.7%. Even if the outside air were saturated at a partial pressure of 1.95 torr, the inside relative humidity would be at a low 11%.

*18–5 Van der Waals Equation of State

In Section 18–3, we discussed how real gases deviate from ideal gas behavior, particularly at high densities or when near condensing to a liquid. We would like to understand these deviations using a microscopic (molecular) point of view. J. D. van der Waals (1837–1923) analyzed this problem and in 1873 arrived at an equation of state which fits real gases more accurately than the ideal gas law. His analysis is based on kinetic theory but takes into account: (1) the finite size of molecules (we previously neglected the actual volume of the molecules themselves, compared to the total volume of the container, and this assumption becomes poorer as the density increases and molecules become closer together); (2) the range of the forces between molecules may be greater than the size of the molecules (we previously assumed that intermolecular forces act only during collisions, when the molecules are "in contact"). Let us now look at this analysis and derive the van der Waals equation of state.

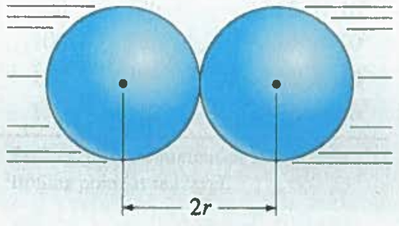


FIGURE 18–10 Molecules, of radius r, colliding.

Assume the molecules in a gas are spherical with radius r. If we assume these molecules behave like hard spheres, then two molecules collide and bounce off one another if the distance between their centers (Fig. 18–10) gets as small as $2r$. Thus the actual volume in which the molecules can move about is somewhat less than the volume V of the container holding the gas. The amount of "unavailable volume" depends on the number of molecules and on their size. Let b represent the "unavailable volume per mole" of gas. Then in the ideal gas law we replace V by $(V - nb)$, where n is the number of moles, and we obtain

$$P(V - nb) = nRT.$$

If we divide through by n, we have

$$P\left(\frac{V}{n} - b\right) = RT. \tag{18–8}$$

This relation (sometimes called the **Clausius equation of state**) predicts that for a given temperature T and volume V, the pressure P will be greater than for an ideal gas. This makes sense since the reduced "available" volume means the number of collisions with the walls is increased.

Next we consider the effects of attractive forces between molecules, which are responsible for holding molecules in the liquid and solid states at lower temperatures. These forces are electrical in nature and although they act even when molecules are not touching, we assume their range is small—that is, they act mainly between nearest neighbors. Molecules at the edge of the gas, headed toward a wall of the container, are slowed down by a net force pulling them back into the gas. Thus these molecules will exert less force and less pressure on the wall than if there were no attractive forces. The reduced pressure will be proportional to the density of molecules in the layer of gas at the surface, and also to the density in the next layer, which exerts the inward force.[†] Therefore we expect the pressure to be reduced by a factor proportional to the density squared $(n/V)^2$, here written as moles per volume. If the pressure P is given by Eq. 18–8, then we should reduce this by an amount $a(n/V)^2$ where a is a proportionality constant. Thus we have

$$P = \frac{RT}{(V/n) - b} - \frac{a}{(V/n)^2}$$

or

$$\left(P + \frac{a}{(V/n)^2}\right)\left(\frac{V}{n} - b\right) = RT, \tag{18–9}$$

which is the **van der Waals equation of state.**

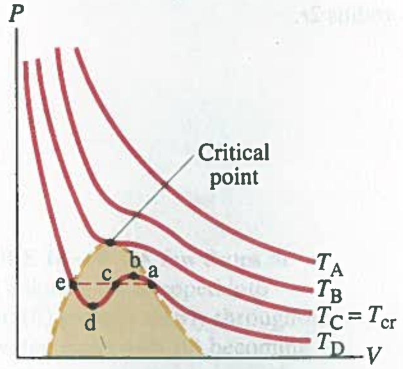


FIGURE 18–11 *PV* diagram for a van der Waals gas, shown for four different temperatures. For T_A, T_B, and T_C (T_C is chosen equal to the critical temperature), the curves fit experimental data very well for most gases. The curve labeled T_D, a temperature below the critical point, passes through the liquid–vapor region. The maximum (point b) and minimum (point d) would seem to be artifacts, since we usually see constant pressure, as indicated by the horizontal dashed line (and Fig. 18–4). However, for very pure supersaturated vapors or supercooled liquids, the sections ab and ed, respectively, have been observed. (The section bd would be unstable and has not been observed.)

The constants a and b in the van der Waals equation are different for different gases and are determined by fitting to experimental data for each gas. For CO_2 gas, the best fit is obtained for $a = 0.36\,\mathrm{N \cdot m^4/mol^2}$ and $b = 4.3 \times 10^{-5}\,\mathrm{m^3/mol}$. Figure 18–11 shows a typical *PV* diagram for Eq. 18–9 (a "van der Waals gas") for four different temperatures, with detailed caption, and it should be compared to Fig. 18–4 for real gases.

Neither the van der Waals equation of state nor the many other equations of state that have been proposed are accurate for all gases under all conditions. Yet Eq. 18–9 is a very useful relation. And because it is quite accurate for many situations, its derivation gives us further insight into the nature of gases at the microscopic level. Note that at low densities, $a/(V/n)^2 \ll P$ and $b \ll V/n$, so that the van der Waals equation reduces to the equation of state for an ideal gas, $PV = nRT$.

*18–6 Mean Free Path

If gas molecules were truly point particles, they would have zero cross-section and never collide with one another. If you opened a perfume bottle, you would be able to smell it almost instantaneously across the room, since molecules travel hundreds of meters per second. In reality, it takes time before you detect an odor and, according to kinetic theory, this must be due to collisions between molecules of nonzero size.

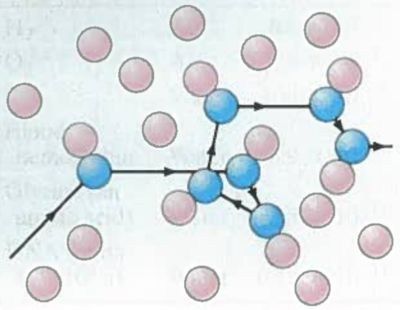


FIGURE 18–12 Zigzag path of a molecule colliding with other molecules.

If we were to follow the path of a particular molecule, we would expect to see it follow a zigzag path as shown in Fig. 18–12. Between each collision the molecule would move in a straight-line path. (Not quite true if we take account of the small intermolecular forces that act between collisions.) An important parameter for a given situation is the **mean free path**, which is defined as the average distance a molecule travels between collisions. We would expect that the greater the gas density, and the larger the molecules, the shorter the mean free path would be. We now determine the nature of this relationship for an ideal gas.

[†] This is similar to the gravitational force in which the force on mass m_1 due to mass m_2 is proportional to the product of their masses (Newton's law of universal gravitation, Chapter 6).

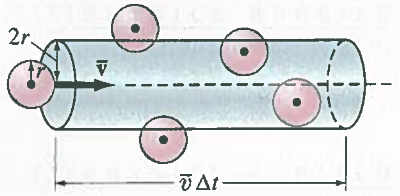


FIGURE 18–13 Molecule at left moves to the right with speed $\bar{v}$. It collides with any molecule whose center is within the cylinder of radius $2r$.

Suppose our gas is made up of molecules which are hard spheres of radius r. A collision will occur whenever the centers of two molecules come within a distance $2r$ of one another. Let us follow a molecule as it traces a straight-line path. In Fig. 18–13, the dashed line represents the path of our particle if it makes no collisions. Also shown is a cylinder of radius $2r$. If the center of another molecule lies within this cylinder, a collision will occur. (Of course, when a collision occurs the particle's path would change direction, as would our imagined cylinder, but our result won't be altered by unbending a zigzag cylinder into a straight one for purposes of calculation.) Assume our molecule is an average one, moving at the mean speed $\bar{v}$ in the gas. For the moment, let us assume that the other molecules are not moving, and that the concentration of molecules (number per unit volume) is N/V. Then the number of molecules whose centers lie within the cylinder of Fig. 18–13 is N/V times the volume of this cylinder, and this also represents the number of collisions that will occur. In a time Δt, our molecule travels a distance $\bar{v}\,\Delta t$, so the length of the cylinder is $\bar{v}\,\Delta t$ and its volume is $\pi(2r)^2\bar{v}\,\Delta t$. Hence the number of collisions that occur in a time Δt is $(N/V)\pi(2r)^2\bar{v}\,\Delta t$. We define the **mean free path**, ℓ_M, as the average distance between collisions. This distance is equal to the distance traveled $(\bar{v}\,\Delta t)$ in a time Δt divided by the number of collisions made in time Δt:

$$\ell_M = \frac{\bar{v}\,\Delta t}{(N/V)\pi(2r)^2\bar{v}\,\Delta t} = \frac{1}{4\pi r^2(N/V)}. \qquad (18\text{–}10a)$$

Thus we see that ℓ_M is inversely proportional to the cross-sectional area $(=\pi r^2)$ of the molecules and to their concentration (number/volume), N/V. However, Eq. 18–10a is not fully correct since we assumed the other molecules are all at rest. In fact, they are moving, and the number of collisions in a time Δt must depend on the *relative* speed of the colliding molecules, rather than on $\bar{v}$. Hence the number of collisions per second is $(N/V)\pi(2r)^2 v_{\text{rel}}\,\Delta t$ (rather than $(N/V)\pi(2r)^2\bar{v}\,\Delta t$), where v_{rel} is the average relative speed of colliding molecules. A careful calculation shows that for a Maxwellian distribution of speeds $v_{\text{rel}} = \sqrt{2}\bar{v}$. Hence the mean free path is

Mean free path

$$\ell_M = \frac{1}{4\pi\sqrt{2}r^2(N/V)}. \qquad (18\text{–}10b)$$

EXAMPLE 18–8 ESTIMATE Mean free path of air molecules at STP Estimate the mean free path of air molecules at STP, standard temperature and pressure (0°C, 1 atm). The diameter of O_2 and N_2 molecules is about 3×10^{-10} m.

APPROACH We saw in Example 17–10 that 1 mol of an ideal gas occupies a volume of $22.4 \times 10^{-3}\,\text{m}^3$ at STP. We can thus determine N/V and apply Eq. 18–10b.

SOLUTION

$$\frac{N}{V} = \frac{6.02 \times 10^{23}\ \text{molecules}}{22.4 \times 10^{-3}\,\text{m}^3} = 2.69 \times 10^{25}\ \text{molecules/m}^3.$$

Then

$$\ell_M = \frac{1}{4\pi\sqrt{2}(1.5 \times 10^{-10}\,\text{m})^2(2.7 \times 10^{25}\,\text{m}^{-3})} \approx 9 \times 10^{-8}\,\text{m}.$$

NOTE This is about 300 times the diameter of an air molecule.

At very low densities, such as in an evacuated vessel, the concept of mean free path loses meaning since collisions with the container walls may occur more frequently than collisions with other molecules. For example, in a cubical box that is (say) 20 cm on a side containing air at 10^{-7} torr ($\approx 10^{-10}$ atm), the mean free path would be about 900 m, which means many more collisions are made with the walls than with other molecules. (Note, nonetheless, that the box contains about 10^{12} molecules.) If the concept of mean free path included also collision with the walls, it would be closer to 0.2 m than to the 900 m calculated from Eq. 18–10b.

*18–7 Diffusion

If you carefully place a few drops of food coloring in a container of water as in Fig. 18–14, you will find that the color spreads throughout the water. The process may take some time (assuming you do not shake the glass), but eventually the color will become uniform. This mixing, known as **diffusion**, takes place because of the random movement of the molecules. Diffusion occurs in gases too. Common examples include perfume or smoke (or the odor of something cooking on the stove) diffusing in air, although convection (moving air currents) often plays a greater role in spreading odors than does diffusion. Diffusion depends on concentration, by which we mean the number of molecules or moles per unit volume. In general, *the diffusing substance moves from a region where its concentration is high to one where its concentration is low.*

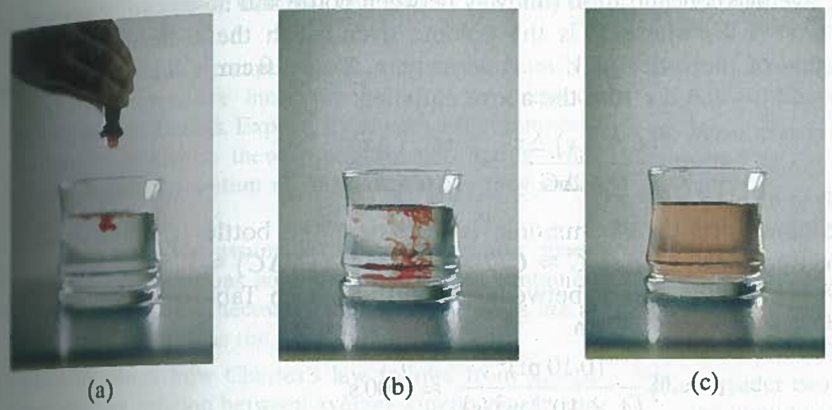

(a) (b) (c)

FIGURE 18–14 A few drops of food coloring (a) dropped into water, (b) spreads slowly throughout the water, eventually (c) becoming uniform.

Diffusion can be readily understood on the basis of kinetic theory and the random motion of molecules. Consider a tube of cross-sectional area A containing molecules in a higher concentration on the left than on the right, Fig. 18–15. We assume the molecules are in random motion. Yet there will be a net flow of molecules to the right. To see why this is true, let us consider the small section of tube of length Δx as shown. Molecules from both regions 1 and 2 cross into this central section as a result of their random motion. The more molecules there are in a region, the more will strike a given area or cross a boundary. Since there is a greater concentration of molecules in region 1 than in region 2, more molecules cross into the central section from region 1 than from region 2. There is, then, a net flow of molecules from left to right, from high concentration toward low concentration. The net flow becomes zero only when the concentrations become equal.

You might expect that the greater the difference in concentration, the greater the flow rate. Indeed, the rate of diffusion, J (number of molecules or moles or kg per second), is directly proportional to the difference in concentration per unit distance, $(C_1 - C_2)/\Delta x$ (which is called the **concentration gradient**), and to the cross-sectional area A (see Fig. 18–15):

$$J = DA\frac{C_1 - C_2}{\Delta x},$$

or, in terms of derivatives,

$$J = DA\frac{dC}{dx}. \qquad (18\text{–}11)$$

D is a constant of proportionality called the **diffusion constant**. Equation 18–11 is known as the **diffusion equation**, or **Fick's law**. If the concentrations are given in mol/m³, then J is the number of moles passing a given point per second. If the concentrations are given in kg/m³, then J is the mass movement per second (kg/s). The length Δx is given in meters. The values of D for a variety of substances are given in Table 18–3.

FIGURE 18–15 Diffusion occurs from a region of high concentration to one of lower concentration (only one type of molecule is shown).

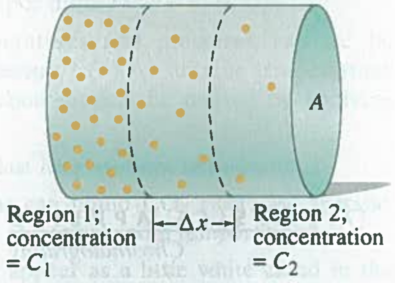


TABLE 18–3 Diffusion Constants, D (20°C, 1 atm)

Diffusing Molecules	Medium	D (m²/s)
H_2	Air	6.3×10^{-5}
O_2	Air	1.8×10^{-5}
O_2	Water	100×10^{-11}
Blood hemoglobin	Water	6.9×10^{-11}
Glycine (an amino acid)	Water	95×10^{-11}
DNA (mass 6×10^6 u)	Water	0.13×10^{-11}

PHYSICS APPLIED
Diffusion time

EXAMPLE 18–9 ESTIMATE **Diffusion of ammonia in air.** To get an idea of the time required for diffusion, estimate how long it might take for ammonia (NH_3) to be detected 10 cm from a bottle after it is opened, assuming only diffusion is occurring.

APPROACH This will be an order-of-magnitude calculation. The rate of diffusion J can be set equal to the number of molecules N diffusing across area A in a time t: $J = N/t$. Then the time $t = N/J$, where J is given by Eq. 18–11. We will have to make some assumptions and rough approximations about concentrations to use Eq. 18–11.

SOLUTION Using Eq. 18–11, we find

$$t = \frac{N}{J} = \frac{N}{DA}\frac{\Delta x}{\Delta C}.$$

The average concentration (midway between bottle and nose) can be approximated by $\overline{C} \approx N/V$, where V is the volume over which the molecules move and is roughly of the order of $V \approx A\,\Delta x$, where Δx is $10\text{ cm} = 0.10\text{ m}$. We substitute $N = \overline{C}V = \overline{C}A\,\Delta x$ into the above equation:

$$t \approx \frac{(\overline{C}A\,\Delta x)\,\Delta x}{DA\,\Delta C} = \frac{\overline{C}}{\Delta C}\frac{(\Delta x)^2}{D}.$$

The concentration of ammonia is high near the bottle (C) and low near the detecting nose (≈ 0), so $\overline{C} \approx C/2 \approx \Delta C/2$, or $(\overline{C}/\Delta C) \approx \frac{1}{2}$. Since NH_3 molecules have a size somewhere between H_2 and O_2, from Table 18–3 we can estimate $D \approx 4 \times 10^{-5}\text{ m}^2/\text{s}$. Then

$$t \approx \frac{1}{2}\frac{(0.10\text{ m})^2}{(4 \times 10^{-5}\text{ m}^2/\text{s})} \approx 100\text{ s},$$

or about a minute or two.

NOTE This result seems rather long from experience, suggesting that air currents (convection) are more important than diffusion for transmitting odors.

PHYSICS APPLIED
Chromatography

CONCEPTUAL EXAMPLE 18–10 **Colored rings on a paper towel.** A child colors a small spot on a wet paper towel with a brown marker. Later, she discovers that instead of a brown spot, there are concentric colored rings around the marker spot. What happened?

RESPONSE The ink in a brown marker is composed of several different inks that mix to make brown. These inks each diffuse at different rates through the wet paper towel. After a period of time the inks have diffused far enough that the differences in distances traveled is sufficient to separate the different colors. Chemists and biochemists use a similar technique, called *chromatography*, to separate substances based on their diffusion rates through a medium.

Summary

According to the **kinetic theory** of gases, which is based on the idea that a gas is made up of molecules that are moving rapidly and at random, the average translational kinetic energy of the molecules is proportional to the Kelvin temperature T:

$$\overline{K} = \tfrac{1}{2}m\overline{v^2} = \tfrac{3}{2}kT \qquad \textbf{(18–4)}$$

where k is Boltzmann's constant.

At any moment, there exists a wide distribution of molecular speeds within a gas. The **Maxwell distribution of speeds** is derived from simple kinetic theory assumptions, and is in good accord with experiment for gases at not too high a pressure.

The behavior of real gases at high pressure, and/or when near their liquefaction point, deviates from the ideal gas law due to the finite size of molecules and to the attractive forces between molecules.

Below the **critical temperature**, a gas can change to a liquid if sufficient pressure is applied; but if the temperature is higher than the critical temperature, no amount of pressure will cause a liquid surface to form.

The **triple point** of a substance is that unique temperature and pressure at which all three phases—solid, liquid, and gas—can coexist in equilibrium. Because of its precise reproducibility, the triple point of water is often taken as a standard reference point.

Evaporation of a liquid is the result of the fastest moving molecules escaping from the surface. Because the average molecular velocity is less after the fastest molecules escape, the temperature decreases when evaporation takes place.

Saturated vapor pressure refers to the pressure of the vapor above a liquid when the two phases are in equilibrium. The vapor pressure of a substance (such as water) depends strongly on temperature and is equal to atmospheric pressure at the boiling point.

Relative humidity of air at a given place is the ratio of the partial pressure of water vapor in the air to the saturated vapor pressure at that temperature; it is usually expressed as a percentage.

[*The **van der Waals equation of state** takes into account the finite volume of molecules, and the attractive forces between molecules, to better approximate the behavior of real gases.]

[*The **mean free path** is the average distance a molecule moves between collisions with other molecules.]

[*__Diffusion__ is the process whereby molecules of a substance move (on average) from one area to another because of a difference in that substance's concentration.]

Questions

1. Why doesn't the size of different molecules enter into the ideal gas law?
2. When a gas is rapidly compressed (say, by pushing down a piston) its temperature increases. When a gas expands against a piston, it cools. Explain these changes in temperature using the kinetic theory, in particular noting what happens to the momentum of molecules when they strike the moving piston.
3. In Section 18–1 we assumed the gas molecules made perfectly elastic collisions with the walls of the container. This assumption is not necessary as long as the walls are at the same temperature as the gas. Why?
4. Explain in words how Charles's law follows from kinetic theory and the relation between average kinetic energy and the absolute temperature.
5. Explain in words how Gay-Lussac's law follows from kinetic theory.
6. As you go higher in the Earth's atmosphere, the ratio of N_2 molecules to O_2 molecules increases. Why?
7. Can you determine the temperature of a vacuum?
8. Is temperature a macroscopic or microscopic variable?
9. Explain why the peak of the curve for 310 K in Fig. 18–3 is not as high as for 273 K. (Assume the total number of molecules is the same for both.)
10. Escape velocity for the Earth refers to the minimum speed an object must have to leave the Earth and never return. (*a*) The escape velocity for the Moon is about one-fifth what it is for the Earth due to the Moon's smaller mass; explain why the Moon has practically no atmosphere. (*b*) If hydrogen was once in the Earth's atmosphere, why would it have probably escaped?
11. If a container of gas is at rest, the average velocity of molecules must be zero. Yet the average speed is not zero. Explain.
12. If the pressure in a gas is doubled while its volume is held constant, by what factor do (*a*) v_{rms} and (*b*) $\overline{v}$ change?
13. What everyday observation would tell you that not all molecules in a material have the same speed?
14. We saw that the saturated vapor pressure of a liquid (say, water) does not depend on the external pressure. Yet the temperature of boiling does depend on the external pressure. Is there a contradiction? Explain.
15. Alcohol evaporates more quickly than water at room temperature. What can you infer about the molecular properties of one relative to the other?
16. Explain why a hot humid day is far more uncomfortable than a hot dry day at the same temperature.
17. Is it possible to boil water at room temperature (20°C) without heating it? Explain.
18. What exactly does it mean when we say that oxygen boils at −183°C?
19. A length of thin wire is placed over a block of ice (or an ice cube) at 0°C and weights are hung from the ends of the wire. It is found that the wire cuts its way through the ice cube, but leaves a solid block of ice behind it. This process is called *regelation*. Explain how this happens by inferring how the freezing point of water depends on pressure.
20. Consider two days when the air temperature is the same but the humidity is different. Which is more dense, the dry air or the humid air at the same T? Explain.
21. (*a*) Why does food cook faster in a pressure cooker? (*b*) Why does pasta or rice need to boil longer at high altitudes? (*c*) Is it harder to boil water at high altitudes?
22. How do a gas and a vapor differ?
23. (*a*) At suitable temperatures and pressures, can ice be melted by applying pressure? (*b*) At suitable temperatures and pressures, can carbon dioxide be melted by applying pressure?
24. Why does dry ice not last long at room temperature?
25. Under what conditions can liquid CO_2 exist? Be specific. Can it exist as a liquid at normal room temperature?
26. Why does exhaled air appear as a little white cloud in the winter (Fig. 18–16)?

FIGURE 18–16
Question 26.

*27. Discuss why sound waves can travel in a gas only if their wavelength is somewhat larger than the mean free path.

*28. Name several ways to reduce the mean free path in a gas.