factor of 1000, and the density decreases by a factor of 1000.

13.4 Kinetic Theory: Atomic and Molecular Explanation of Pressure and Temperature

We have developed macroscopic definitions of pressure and temperature. Pressure is the force divided by the area on which the force is exerted, and temperature is measured with a thermometer. We gain a better understanding of pressure and temperature from the kinetic theory of gases, which assumes that atoms and molecules are in continuous random motion.

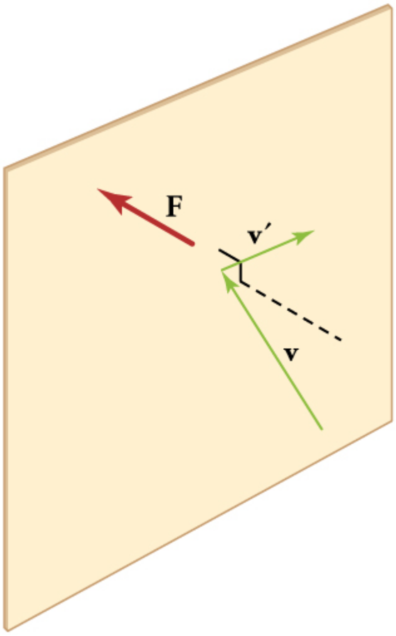

Figure 13.20 When a molecule collides with a rigid wall, the component of its momentum perpendicular to the wall is reversed. A force is thus exerted on the wall, creating pressure.

Figure 13.20 shows an elastic collision of a gas molecule with the wall of a container, so that it exerts a force on the wall (by Newton's third law). Because a huge number of molecules will collide with the wall in a short time, we observe an average force per unit area. These collisions are the source of pressure in a gas. As the number of molecules increases, the number of collisions and thus the pressure increase. Similarly, the gas pressure is higher if the average velocity of molecules is higher. The actual relationship is derived in the Things Great and Small feature below. The following relationship is found:

$$PV = \frac{1}{3}Nm\overline{v^2}, \tag{13.42}$$

where P is the pressure (average force per unit area), V is the volume of gas in the container, N is the number of molecules in the container, m is the mass of a molecule, and $\overline{v^2}$ is the average of the molecular speed squared.

What can we learn from this atomic and molecular version of the ideal gas law? We can derive a relationship between temperature and the average translational kinetic energy of molecules in a gas. Recall the previous expression of the ideal gas law:

$$PV = NkT. \tag{13.43}$$

Equating the right-hand side of this equation with the right-hand side of $PV = \frac{1}{3}Nm\overline{v^2}$ gives

$$\frac{1}{3}Nm\overline{v^2} = NkT. \tag{13.44}$$

Making Connections: Things Great and Small—Atomic and Molecular Origin of Pressure in a Gas

Figure 13.21 shows a box filled with a gas. We know from our previous discussions that putting more gas into the box produces greater pressure, and that increasing the temperature of the gas also produces a greater pressure. But why should increasing the temperature of the gas increase the pressure in the box? A look at the atomic and molecular scale gives us some answers, and an alternative expression for the ideal gas law.

The figure shows an expanded view of an elastic collision of a gas molecule with the wall of a container. Calculating the average force exerted by such molecules will lead us to the ideal gas law, and to the connection between temperature and molecular kinetic energy. We assume that a molecule is small compared with the separation of molecules in the gas, and that its interaction with other molecules can be ignored. We also assume the wall is rigid and that the molecule's direction changes, but that its speed remains constant (and hence its kinetic energy and the magnitude of its momentum remain constant as well). This assumption is not always valid, but the same result is obtained with a more detailed description of the molecule's exchange of energy and momentum with the wall.

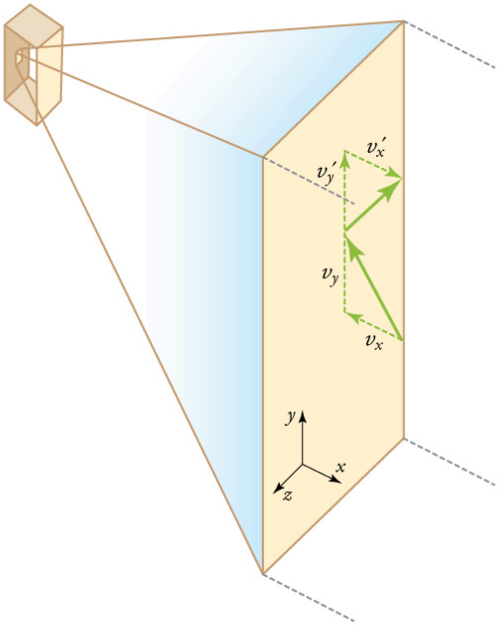

Figure 13.21 Gas in a box exerts an outward pressure on its walls. A molecule colliding with a rigid wall has the direction of its velocity and momentum in the x-direction reversed. This direction is perpendicular to the wall. The components of its velocity momentum in the y- and z-directions are not changed, which means there is no force parallel to the wall.

If the molecule's velocity changes in the x-direction, its momentum changes from $-mv_x$ to $+mv_x$. Thus, its change in momentum is $\Delta mv = +mv_x - (-mv_x) = 2mv_x$. The force exerted on the molecule is given by

$$F = \frac{\Delta p}{\Delta t} = \frac{2mv_x}{\Delta t}. \tag{13.45}$$

There is no force between the wall and the molecule until the molecule hits the wall. During the short time of the collision, the force between the molecule and wall is relatively large. We are looking for an average force; we take Δt to be the average time between collisions of the molecule with this wall. It is the time it would take the molecule to go across the box and back (a distance $2l$) at a speed of v_x. Thus $\Delta t = 2l/v_x$, and the expression for the force becomes

$$F = \frac{2mv_x}{2l/v_x} = \frac{mv_x^2}{l}. \tag{13.46}$$

This force is due to *one* molecule. We multiply by the number of molecules N and use their average squared velocity to find the force

$$F = N\frac{m\overline{v_x^2}}{l}, \tag{13.47}$$

where the bar over a quantity means its average value. We would like to have the force in terms of the speed v, rather than the x-component of the velocity. We note that the total velocity squared is the sum of the squares of its components, so that

$$\overline{v^2} = \overline{v_x^2} + \overline{v_y^2} + \overline{v_z^2}. \tag{13.48}$$

Because the velocities are random, their average components in all directions are the same:

$$\overline{v_x^2} = \overline{v_y^2} = \overline{v_z^2}. \tag{13.49}$$

Thus,

$$\overline{v^2} = 3\overline{v_x^2}, \tag{13.50}$$

or

$$\overline{v_x^2} = \frac{1}{3}\overline{v^2}. \tag{13.51}$$

Substituting $\frac{1}{3}\overline{v^2}$ into the expression for F gives

$$F = N\frac{m\overline{v^2}}{3l}. \tag{13.52}$$

The pressure is F/A, so that we obtain

$$P = \frac{F}{A} = N\frac{m\overline{v^2}}{3Al} = \frac{1}{3}\frac{Nm\overline{v^2}}{V}, \tag{13.53}$$

where we used $V = Al$ for the volume. This gives the important result.

$$PV = \frac{1}{3}Nm\overline{v^2} \tag{13.54}$$

This equation is another expression of the ideal gas law.

We can get the average kinetic energy of a molecule, $\frac{1}{2}m\overline{v^2}$, from the right-hand side of the equation by canceling N and multiplying by 3/2. This calculation produces the result that the average kinetic energy of a molecule is directly related to absolute temperature.

$$\overline{\mathrm{KE}} = \frac{1}{2}m\overline{v^2} = \frac{3}{2}kT \tag{13.55}$$

The average translational kinetic energy of a molecule, $\overline{\mathrm{KE}}$, is called **thermal energy.** The equation $\overline{\mathrm{KE}} = \frac{1}{2}m\overline{v^2} = \frac{3}{2}kT$ is a molecular interpretation of temperature, and it has been found to be valid for gases and reasonably accurate in liquids and solids. It is another definition of temperature based on an expression of the molecular energy.

It is sometimes useful to rearrange $\overline{\mathrm{KE}} = \frac{1}{2}m\overline{v^2} = \frac{3}{2}kT$, and solve for the average speed of molecules in a gas in terms of temperature,

$$\sqrt{\overline{v^2}} = v_{\mathrm{rms}} = \sqrt{\frac{3kT}{m}}, \tag{13.56}$$

where v_{rms} stands for root-mean-square (rms) speed.

EXAMPLE 13.10

Calculating Kinetic Energy and Speed of a Gas Molecule

(a) What is the average kinetic energy of a gas molecule at $20.0^\circ\mathrm{C}$ (room temperature)? (b) Find the rms speed of a nitrogen molecule (N_2) at this temperature.

Strategy for (a)

The known in the equation for the average kinetic energy is the temperature.

$$\overline{\text{KE}} = \frac{1}{2}m\overline{v^2} = \frac{3}{2}kT \tag{13.57}$$

Before substituting values into this equation, we must convert the given temperature to kelvins. This conversion gives $T = (20.0 + 273)\text{ K} = 293\text{ K}.$

Solution for (a)

The temperature alone is sufficient to find the average translational kinetic energy. Substituting the temperature into the translational kinetic energy equation gives

$$\overline{\text{KE}} = \frac{3}{2}kT = \frac{3}{2}\left(1.38 \times 10^{-23}\text{ J/K}\right)(293\text{ K}) = 6.07 \times 10^{-21}\text{ J.} \tag{13.58}$$

Strategy for (b)

Finding the rms speed of a nitrogen molecule involves a straightforward calculation using the equation

$$\sqrt{\overline{v^2}} = v_{\text{rms}} = \sqrt{\frac{3kT}{m}}, \tag{13.59}$$

but we must first find the mass of a nitrogen molecule. Using the molecular mass of nitrogen N_2 from the periodic table,

$$m = \frac{2\,(14.0067) \times 10^{-3}\text{ kg/mol}}{6.02 \times 10^{23}\text{ mol}^{-1}} = 4.65 \times 10^{-26}\text{ kg.} \tag{13.60}$$

Solution for (b)

Substituting this mass and the value for k into the equation for v_{rms} yields

$$v_{\text{rms}} = \sqrt{\frac{3kT}{m}} = \sqrt{\frac{3\left(1.38 \times 10^{-23}\text{ J/K}\right)(293\text{ K})}{4.65 \times 10^{-26}\text{ kg}}} = 511\text{ m/s.} \tag{13.61}$$

Discussion

Note that the average kinetic energy of the molecule is independent of the type of molecule. The average translational kinetic energy depends only on absolute temperature. The kinetic energy is very small compared to macroscopic energies, so that we do not feel when an air molecule is hitting our skin. The rms velocity of the nitrogen molecule is surprisingly large. These large molecular velocities do not yield macroscopic movement of air, since the molecules move in all directions with equal likelihood. The *mean free path* (the distance a molecule can move on average between collisions) of molecules in air is very small, and so the molecules move rapidly but do not get very far in a second. The high value for rms speed is reflected in the speed of sound, however, which is about 340 m/s at room temperature. The faster the rms speed of air molecules, the faster that sound vibrations can be transferred through the air. The speed of sound increases with temperature and is greater in gases with small molecular masses, such as helium. (See Figure 13.22.)

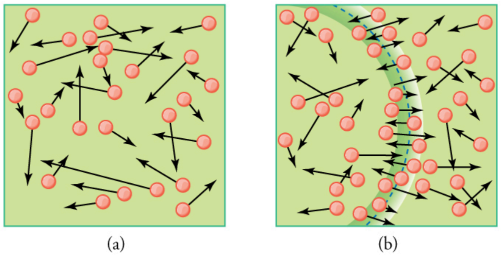

Figure 13.22 (a) There are many molecules moving so fast in an ordinary gas that they collide a billion times every second. (b) Individual

molecules do not move very far in a small amount of time, but disturbances like sound waves are transmitted at speeds related to the molecular speeds.

Making Connections: Historical Note—Kinetic Theory of Gases

The kinetic theory of gases was developed by Daniel Bernoulli (1700–1782), who is best known in physics for his work on fluid flow (hydrodynamics). Bernoulli's work predates the atomistic view of matter established by Dalton.

Distribution of Molecular Speeds

The motion of molecules in a gas is random in magnitude and direction for individual molecules, but a gas of many molecules has a predictable distribution of molecular speeds. This distribution is called the *Maxwell-Boltzmann distribution*, after its originators, who calculated it based on kinetic theory, and has since been confirmed experimentally. (See Figure 13.23.) The distribution has a long tail, because a few molecules may go several times the rms speed. The most probable speed v_p is less than the rms speed v_{rms}. Figure 13.24 shows that the curve is shifted to higher speeds at higher temperatures, with a broader range of speeds.

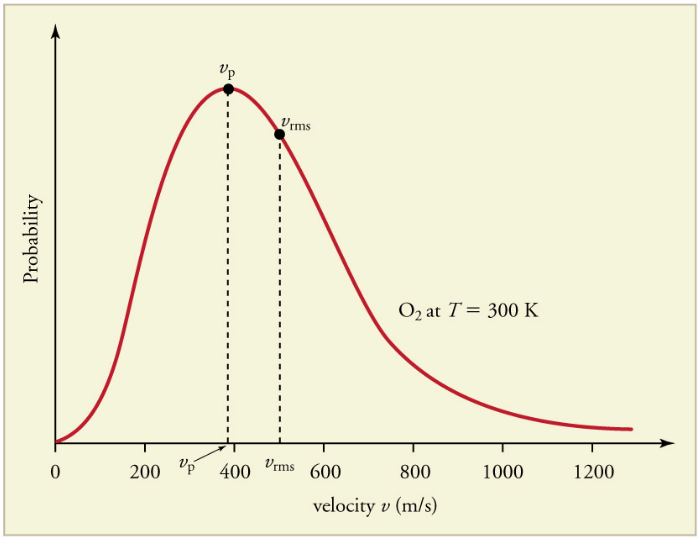

Figure 13.23 The Maxwell-Boltzmann distribution of molecular speeds in an ideal gas. The most likely speed v_p is less than the rms speed v_{rms}. Although very high speeds are possible, only a tiny fraction of the molecules have speeds that are an order of magnitude greater than v_{rms}.

The distribution of thermal speeds depends strongly on temperature. As temperature increases, the speeds are shifted to higher values and the distribution is broadened.

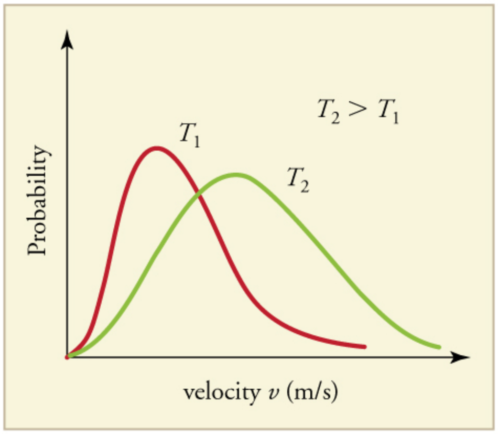

Figure 13.24 The Maxwell-Boltzmann distribution is shifted to higher speeds and is broadened at higher temperatures.

What is the implication of the change in distribution with temperature shown in Figure 13.24 for humans? All other things being equal, if a person has a fever, he or she is likely to lose more water molecules, particularly from linings along moist cavities such as the lungs and mouth, creating a dry sensation in the mouth.

EXAMPLE 13.11

Calculating Temperature: Escape Velocity of Helium Atoms

In order to escape Earth's gravity, an object near the top of the atmosphere (at an altitude of 100 km) must travel away from Earth at 11.1 km/s. This speed is called the *escape velocity*. At what temperature would helium atoms have an rms speed equal to the escape velocity?

Strategy

Identify the knowns and unknowns and determine which equations to use to solve the problem.

Solution

1. Identify the knowns: v is the escape velocity, 11.1 km/s.

2. Identify the unknowns: We need to solve for temperature, T. We also need to solve for the mass m of the helium atom.

3. Determine which equations are needed.

- To solve for mass m of the helium atom, we can use information from the periodic table:

$$m = \frac{\text{molar mass}}{\text{number of atoms per mole}}. \tag{13.62}$$

- To solve for temperature T, we can rearrange either

$$\overline{\text{KE}} = \frac{1}{2}m\overline{v^2} = \frac{3}{2}kT \tag{13.63}$$

  or

$$\sqrt{\overline{v^2}} = v_{\text{rms}} = \sqrt{\frac{3kT}{m}} \tag{13.64}$$

  to yield

$$T = \frac{m\overline{v^2}}{3k}, \tag{13.65}$$

  where k is the Boltzmann constant and m is the mass of a helium atom.

4. Plug the known values into the equations and solve for the unknowns.

$$m = \frac{\text{molar mass}}{\text{number of atoms per mole}} = \frac{4.0026 \times 10^{-3}\ \text{kg/mol}}{6.02 \times 10^{23}\ \text{mol}} = 6.65 \times 10^{-27}\ \text{kg} \tag{13.66}$$

$$T = \frac{\left(6.65 \times 10^{-27}\ \text{kg}\right)\left(11.1 \times 10^{3}\ \text{m/s}\right)^2}{3\left(1.38 \times 10^{-23}\ \text{J/K}\right)} = 1.98 \times 10^{4}\ \text{K} \tag{13.67}$$

Discussion

This temperature is much higher than atmospheric temperature, which is approximately 250 K (–25ºC or –10ºF) at high altitude. Very few helium atoms are left in the atmosphere, but there were many when the atmosphere was formed. The reason for the loss of helium atoms is that there are a small number of helium atoms with speeds higher than Earth's escape velocity even at normal temperatures. The speed of a helium atom changes from one instant to the next, so that at any instant, there is a small, but nonzero chance that the speed is greater than the escape speed and the molecule escapes from Earth's gravitational pull. Heavier molecules, such as oxygen, nitrogen, and water (very little of which reach a very high altitude), have smaller rms speeds, and so it is much less likely that any of them will have speeds greater than the escape velocity. In fact, so few have speeds above the escape velocity that billions of years are required to lose significant amounts of the atmosphere. Figure 13.25 shows the impact of a lack of an atmosphere on the Moon. Because the gravitational pull of the Moon is much weaker, it has lost almost its entire atmosphere. The comparison between Earth and the Moon is discussed in this chapter's Problems and Exercises.

Figure 13.25 This photograph of Apollo 17 Commander Eugene Cernan driving the lunar rover on the Moon in 1972 looks as though it was taken at night with a large spotlight. In fact, the light is coming from the Sun. Because the acceleration due to gravity on the Moon is so low (about 1/6 that of Earth), the Moon's escape velocity is much smaller. As a result, gas molecules escape very easily from the Moon, leaving it with virtually no atmosphere. Even during the daytime, the sky is black because there is no gas to scatter sunlight. (credit: Harrison H. Schmitt/NASA)

CHECK YOUR UNDERSTANDING

If you consider a very small object such as a grain of pollen, in a gas, then the number of atoms and molecules striking its surface would also be relatively small. Would the grain of pollen experience any fluctuations in pressure due to statistical fluctuations in the number of gas atoms and molecules striking it in a given amount of time?

Solution

Yes. Such fluctuations actually occur for a body of any size in a gas, but since the numbers of atoms and molecules are immense for macroscopic bodies, the fluctuations are a tiny percentage of the number of collisions, and the averages spoken of in this section vary imperceptibly. Roughly speaking the fluctuations are proportional to the inverse square root of the number of collisions, so for small bodies they can become significant. This was actually observed in the 19th century for pollen grains in water, and is known as the Brownian effect.

Gas Properties

Pump gas molecules into a box and see what happens as you change the volume, add or remove heat, change gravity, and more. Measure the temperature and pressure, and discover how the properties of the gas vary in relation to each other. Click to open media in new browser. (https://phet.colorado.edu/en/simulation/legacy/gas-properties)

13.5 Phase Changes

Up to now, we have considered the behavior of ideal gases. Real gases are like ideal gases at high temperatures. At lower temperatures, however, the interactions between the molecules and their volumes cannot be ignored. The molecules are very close (condensation occurs) and there is a dramatic decrease in volume, as seen in Figure 13.26. The substance changes from a gas to a liquid. When a liquid is cooled to even lower temperatures, it becomes a solid. The volume never reaches zero because of the finite volume of the molecules.

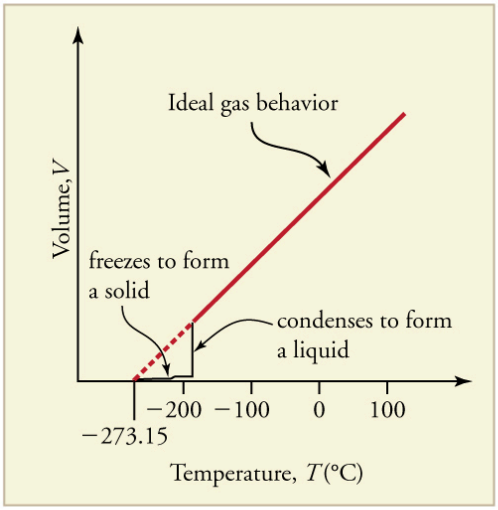

Figure 13.26 A sketch of volume versus temperature for a real gas at constant pressure. The linear (straight line) part of the graph represents ideal gas behavior—volume and temperature are directly and positively related and the line extrapolates to zero volume at -273.15°C, or absolute zero. When the gas becomes a liquid, however, the volume actually decreases precipitously at the liquefaction point. The volume decreases slightly once the substance is solid, but it never becomes zero.

High pressure may also cause a gas to change phase to a liquid. Carbon dioxide, for example, is a gas at room temperature and atmospheric pressure, but becomes a liquid under sufficiently high pressure. If the pressure is reduced, the temperature drops and the liquid carbon dioxide solidifies into a snow-like substance at the temperature -78°C. Solid CO_2 is called “dry ice.” Another example of a gas that can be in a liquid phase is liquid nitrogen (LN_2). LN_2 is made by liquefaction of atmospheric air (through compression and cooling). It boils at 77 K (-196°C) at atmospheric pressure. LN_2 is useful as a refrigerant and allows for the preservation of blood, sperm, and other biological materials. It is also used to reduce noise in electronic sensors and equipment, and to help cool down their current-carrying wires. In dermatology, LN_2 is used to freeze and painlessly remove warts and other growths from the skin.

PV Diagrams

We can examine aspects of the behavior of a substance by plotting a graph of pressure versus volume, called a ***PV* diagram**. When the substance behaves like an ideal gas, the ideal gas law describes the relationship between its pressure and volume. That is,

$$PV = NkT \text{ (ideal gas).} \tag{13.68}$$

Now, assuming the number of molecules and the temperature are fixed,

$$PV = \text{constant (ideal gas, constant temperature).} \tag{13.69}$$

For example, the volume of the gas will decrease as the pressure increases. If you plot the relationship $PV = \text{constant}$ on a PV