

WHAT'S AHEAD

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10

GASES

10.1 | Characteristics of Gases



In this chapter, we examine the physical properties of gases—what is atmospheric pressure, how do gases respond to changes in pressure and temperature, and what does temperature measure at the molecular level? Because gases are the simplest state of matter, they serve as an excellent starting point for probing the behavior of large collections of atoms or molecules. Indeed, it is fairly straightforward to formulate a simple model for gases that explains their behavior under most common conditions. We gain further insight by then comparing how real gases differ from this ideal model as conditions change.

Thus, while we start with a description that treats all gases the same regardless of their chemical identity, we end by gaining an understanding of important aspects of the physical behavior of molecules.

By the end of this section, you should be able to

- Appreciate the fundamental differences between a gas and the condensed phases (liquid and solid) of a molecular compound.

Of the few elements that exist as gases at ordinary temperatures and pressures, He, Ne, Ar, Kr, and Xe are monatomic and H₂, N₂, O₂, F₂, and Cl₂ are diatomic. Many molecular compounds are gases, and **Table 10.1** lists a few of them. Notice that all of these gases are composed entirely of nonmetallic elements. Furthermore, all have simple molecular formulas and, therefore, low molar masses.

Substances that are liquids or solids under ordinary conditions can also exist in the gaseous state, where they are often referred to as **vapors**. The substance H₂O, for example, can exist as liquid water, solid ice, or water vapor.

Even though different gaseous substances may have very different *chemical* properties, they behave quite similarly as far as their *physical* properties are concerned. For example, the N₂ and O₂ that account for approximately 99% of our atmosphere have very different chemical properties—O₂ supports human life but N₂ does not, to name just one difference—but these two components of air behave physically as one gaseous material because their physical properties are essentially identical.

The physical properties of gases differ significantly from those of solids and liquids. For example, a gas expands spontaneously to fill its container. Consequently, the volume of a gas equals the volume of its container. Gases also are highly compressible: When pressure is applied to a gas, its volume readily decreases. Solids and liquids, on the other hand, do not expand to fill their containers and are not readily compressible.

Two or more gases form a homogeneous mixture regardless of the identities or relative proportions of the gases; the atmosphere serves as an excellent example. Two or more liquids or two or more solids may or may not form homogeneous mixtures, depending on their chemical nature. For example, when water and gasoline are mixed, the two liquids remain as separate layers. In contrast, the water vapor and gasoline vapors above the liquids form a homogeneous gas mixture.

The characteristic properties of gases—expanding to fill a container, being highly compressible, forming homogeneous mixtures—arise because the molecules are relatively far apart. In any given volume of air, for example, the molecules take up only about 0.1% of the total volume with the rest being empty space. Thus, each molecule behaves largely as though the others were not present. As a result, different gases behave similarly even though they are made up of different molecules.

TABLE 10.1 Some Common Compounds That Are Gases at Room Temperature

Formula	Name	Characteristics
HCN	Hydrogen cyanide	Very toxic, slight odor of bitter almonds
H ₂ S	Hydrogen sulfide	Very toxic, odor of rotten eggs
CO	Carbon monoxide	Toxic, colorless, odorless
CO ₂	Carbon dioxide	Colorless, odorless
CH ₄	Methane	Colorless, odorless, flammable
C ₂ H ₄	Ethene (Ethylene)	Colorless, ripens fruit
C ₃ H ₈	Propane	Colorless, odorless, bottled gas
N ₂ O	Nitrous oxide	Colorless, sweet odor, laughing gas
NO ₂	Nitrogen dioxide	Toxic, red-brown, irritating odor
NH ₃	Ammonia	Colorless, pungent odor
SO ₂	Sulfur dioxide	Colorless, irritating odor

Self-Assessment Exercise

10.1 True or false: All gases condense at the same temperature.

(a) True

(b) False

Exercises

10.2 Which of the following statements is false?

(a) Gases are far less dense than liquids.

(b) Gases are far more compressible than liquids.

(c) Because liquid water and liquid carbon tetrachloride do not mix, neither do their vapors.

(d) The volume occupied by a gas is determined by the volume of its container.

10.1 (b)

Answers to Self-Assessment Exercises



10.2 | Pressure



What is the weather going to be like today or this week? Such knowledge not only helps us choose the clothing we wear during the day, but it also assists the farmer in planting and harvesting and the sailor in charting a course. The gases in our atmosphere, primarily N₂ and O₂ molecules, are heated by the Sun and moved here and there by pressure differences that create wind.

It is the behavior of gases that creates our weather—the gentle breezes, the violent storms, the humidity, and the rain. Tornadoes, like the one shown here, form when moist, warm air at lower elevations converges with cooler, dry air above. The resultant air flows produce winds that can approach speeds up to 500 km/hr.

By the end of this section, you should be able to

- Understand the molecular basis of pressure.

The molecules of a gas move chaotically, colliding with each other and with the walls of their container. The impacts with the container walls exert a force—an outward push against the walls. The **pressure**, *P*, that a gas exerts is defined as the force, *F*, divided by the area, *A*, of the surface on which the force is acting:

$$P = \frac{F}{A} \quad [10.1]$$

Gases exert a pressure on any surface with which they are in contact. The gas in an inflated balloon, for example, exerts a pressure on the inside surface of the balloon.

Atmospheric Pressure and the Barometer

People, coconuts, and nitrogen molecules all experience an attractive gravitational force that pulls them toward the center of the Earth. When a coconut comes loose from a tree, for example, this force causes the coconut to be accelerated toward Earth, its speed increasing as its potential energy is converted into kinetic energy. The gas atoms and molecules of the atmosphere also experience a gravitational acceleration. Because these particles have such tiny masses, however, their thermal energies of motion (their kinetic energies) override the gravitational forces, so the particles that make up the atmosphere don't pile up at the Earth's surface. Nevertheless, the gravitational force does operate, and it causes the atmosphere as a whole to press down on the Earth's surface, creating *atmospheric pressure*, defined as the force exerted by the atmosphere on a given surface area.

You can demonstrate the existence of atmospheric pressure with an empty plastic water bottle. If you suck on the mouth of the empty bottle, chances are you can cause the bottle to partially cave in. When you break the partial vacuum you have created, the bottle pops out to its original shape. The bottle caves in because, once you've sucked out some of the air molecules, the air molecules in the atmosphere exert a force on the outside of the bottle that is greater than the force exerted by the lesser number of air molecules inside the bottle.

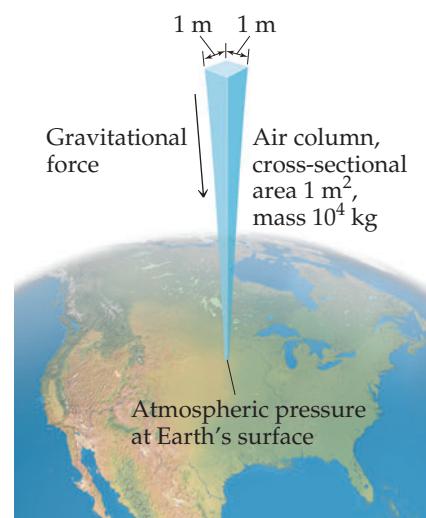
We can calculate the magnitude of the atmospheric pressure using Equation 10.1. The force, *F*, exerted by any object is the product of its mass, *m*, and its acceleration, *a*: *F* = *ma*. When applied to our atmosphere, the force is the gravitational force, which is also commonly called weight. The acceleration is that due to gravity, *g* = 9.8 m/s². Thus, the gravitational force of the atmosphere on the Earth's surface (the weight of the atmosphere) is given by *F* = *mg*.

Now imagine a column of air, 1 m² in cross section, extending through the entire atmosphere (Figure 10.1). That column has a mass of roughly 10,000 kg. The downward gravitational force exerted on this column is

$$F = (10,000 \text{ kg})(9.8 \text{ m/s}^2) = 1 \times 10^5 \text{ kg m/s}^2 = 1 \times 10^5 \text{ N}$$

where N is the abbreviation for *newton*, the SI unit for force: 1 N = 1 kg m/s².

The pressure exerted by the column is this force divided by the cross-sectional area, *A*, over which the force is applied. Because our air column has a cross-sectional area of 1 m², we have for the magnitude of atmospheric pressure at sea level



▲ Figure 10.1 Calculating atmospheric pressure.

$$P = \frac{F}{A} = \frac{1 \times 10^5 \text{ N}}{1 \text{ m}^2} = 1 \times 10^5 \text{ N/m}^2 = 1 \times 10^5 \text{ Pa} = 1 \times 10^2 \text{ kPa}$$

The SI unit of pressure is the **pascal** (Pa), named for Blaise Pascal (1623–1662), a French scientist who studied pressure: $1 \text{ Pa} = 1 \text{ N/m}^2$. A related pressure unit is the **bar**: $1 \text{ bar} = 10^5 \text{ Pa} = 10^5 \text{ N/m}^2$. Thus, the atmospheric pressure at sea level we just calculated, 100 kPa, can be reported as 1 bar. (The actual atmospheric pressure at any location depends on weather conditions and altitude.) Another pressure unit is pounds per square inch (psi, lbs/in.²). At sea level, atmospheric pressure is 14.7 psi.

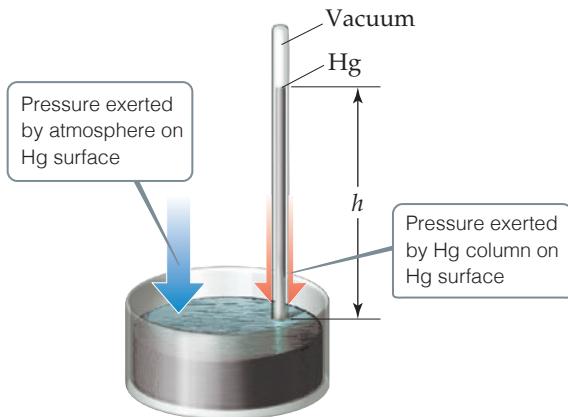
In the seventeenth century, many scientists and philosophers believed that the atmosphere had no weight. Evangelista Torricelli (1608–1647), a student of Galileo's, proved this untrue. He invented the *barometer* (Figure 10.2), which is made from a glass tube more than 760 mm long that is closed at one end, completely filled with mercury, and inverted into a dish of mercury. (Care must be taken so that no air gets into the tube.) When the tube is inverted into the dish, some of the mercury flows out of the tube, but a column of mercury remains in the tube. Torricelli argued that the mercury surface in the dish experiences the full force of Earth's atmosphere, which pushes the mercury up the tube until the pressure exerted by the mercury column downward, due to gravity, equals the atmospheric pressure at the base of the tube. Therefore *the height, h, of the mercury column is a measure of atmospheric pressure and changes as atmospheric pressure changes*.

Standard atmospheric pressure, which corresponds to the typical pressure at sea level, is the pressure sufficient to support a column of mercury 760 mm high. In SI units, this pressure is $1.01325 \times 10^5 \text{ Pa}$. Standard atmospheric pressure defines some common non-SI units used to express gas pressure, such as the **atmosphere** (atm) and the **millimeter of mercury** (mm Hg). The latter unit is also called the **torr**, after Torricelli: $1 \text{ torr} = 1 \text{ mm Hg}$. Thus, we have

$$1 \text{ atm} = 760. \text{ mm Hg} = 760. \text{ torr} = 1.01325 \times 10^5 \text{ Pa} = 101.325 \text{ kPa} = 1.01325 \text{ bar}$$

Go Figure

What happens to *h*, the height of the mercury column, if the atmospheric pressure increases?



▲ Figure 10.2 A mercury barometer.

We use various devices to measure the pressures of enclosed gases. Tire gauges, for example, measure the pressure of air in car and bicycle tires. In laboratories, we sometimes use a *manometer*, which operates on a principle similar to that of a barometer, as shown in Sample Exercise 10.2.

Sample Exercise 10.1

Calculating Pressure

What is the pressure, in kilopascals, on the body of a diver if she is 31.0 m below the surface of the water when the atmospheric pressure on the surface is 98 kPa? Assume that the density of the water is $1.00 \text{ g/cm}^3 = 1.00 \times 10^3 \text{ kg/m}^3$. The gravitational constant is 9.81 m/s^2 , and $1 \text{ Pa} = 1 \text{ kg m s}^{-2}$.

SOLUTION

Analyze We are asked to calculate the pressure on the diver given the atmospheric pressure (98 kPa) and the depth of the water (31.0 m).

Plan The total pressure on the diver equals that of the atmosphere plus that of the water. The pressure of the water can be calculated starting with Equation 10.1, $P = F/A$. The force, F , due to the water above the diver is given by its mass times the acceleration due to gravity, $F = mg$, where $g = 9.81 \text{ m/s}^2$.

Solve The pressure caused by the water is

$$P = \frac{F}{A} = \frac{mg}{A}$$

The mass of the water is related to its density ($d = m/V$, so $m = d \times V$). We can treat the water as a column whose volume equals its cross-sectional area times its height: $V = A \times h$. When we make these substitutions for mass ($m = d \times V$) and volume ($V = A \times h$), we have

$$P = \frac{mg}{A} = \frac{dVg}{A} = \frac{d(\cancel{A}h)g}{\cancel{A}} = dhg$$

Inserting SI quantities, we have

$$\begin{aligned} P &= dhg = (1.00 \times 10^3 \text{ kg/m}^3)(31.0 \text{ m})(9.81 \text{ m/s}^2) \\ &= 3.00 \times 10^5 \frac{\text{kg}}{\text{m s}^2} = 3.00 \times 10^5 \text{ Pa} \end{aligned}$$

Thus, the total pressure on the diver is

$$P_{\text{total}} = 98 \text{ kPa} + 300 \text{ kPa} = 398 \text{ kPa}$$

► Practice Exercise

What would be the height of the column in a barometer if the external pressure was 101 kPa and water ($d = 1.00 \text{ g/cm}^3$) was used in place of mercury?

- (a) 0.0558 m (b) 0.760 m (c) $1.03 \times 10^4 \text{ m}$
 (d) 10.3 m (e) 0.103 m

Sample Exercise 10.2

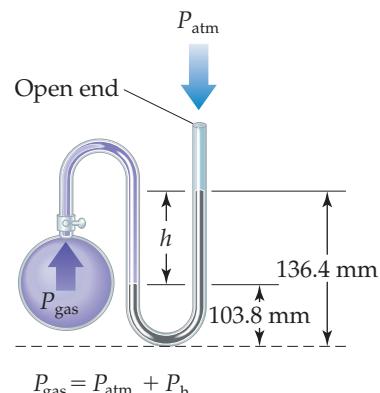
Using a Manometer to Measure Gas Pressure

On a certain day, a laboratory barometer indicates that the atmospheric pressure is 764.7 torr. A sample of gas is placed in a flask attached to an open-end mercury manometer (Figure 10.3), and a meter stick is used to measure the height of the mercury in the two arms of the U tube. The height of the mercury in the open-ended arm is 136.4 mm, and the height in the arm in contact with the gas in the flask is 103.8 mm. What is the pressure of the gas in the flask (a) in atmospheres, (b) in kilopascals?

SOLUTION

Analyze We are given the atmospheric pressure (764.7 torr) and the mercury heights in the two arms of the manometer and asked to determine the gas pressure in the flask. Recall that millimeters of mercury is a pressure unit. We know that the gas pressure from the flask must be greater than atmospheric pressure because the mercury level in the arm on the flask side (103.8 mm) is lower than the level in the arm open to the atmosphere (136.4 mm). Therefore, the gas from the flask is pushing mercury from the arm in contact with the flask into the arm open to the atmosphere.

Plan We will use the difference in height between the two arms (h in Figure 10.3) to obtain the amount by which the pressure of the gas exceeds atmospheric pressure. Because an open-end



▲ Figure 10.3 A mercury manometer.

mercury manometer is used, the height difference directly measures the pressure difference in mm Hg or torr between the gas and the atmosphere.

Solve

(a) The pressure of the gas equals the atmospheric pressure plus h :

$$\begin{aligned} P_{\text{gas}} &= P_{\text{atm}} + h \\ &= 764.7 \text{ torr} + (136.4 \text{ torr} - 103.8 \text{ torr}) \\ &= 797.3 \text{ torr} \end{aligned}$$

We convert the pressure of the gas to atmospheres:

$$P_{\text{gas}} = (797.3 \text{ torr}) \left(\frac{1 \text{ atm}}{760 \text{ torr}} \right) = 1.049 \text{ atm}$$

- (b) To calculate the pressure in kPa, we employ the conversion factor between atmospheres and kPa:

$$1.049 \text{ atm} \left(\frac{101.3 \text{ kPa}}{1 \text{ atm}} \right) = 106.3 \text{ kPa}$$

Check The calculated pressure is a bit more than 1 atm, which is about 101 kPa. This makes sense because we anticipated that the pressure in the flask would be greater than the atmospheric pressure (764.7 torr = 1.01 atm) acting on the manometer.

► Practice Exercise

If the pressure of the gas inside the flask were increased and the height of the column in the open-ended arm went up by 5.0 mm, what would be the new pressure of the gas in the flask, in kilopascals?

CHEMISTRY AND LIFE Blood Pressure

The human heart pumps blood to the parts of the body through arteries, and the blood returns to the heart through veins. When your blood pressure is measured, two values are reported, such as 120/80 (120 over 80), which is a normal reading. The first measurement is the *systolic pressure*, the maximum pressure when the heart is pumping. The second is the *diastolic pressure*, the pressure when the heart is in the resting part of its pumping cycle. The units associated with these pressure measurements are torr.

Blood pressure is measured using a pressure gauge attached to a closed, air-filled jacket or cuff that is applied like a tourniquet to the arm (Figure 10.4). The pressure gauge may be a mercury manometer or some other device. The air pressure in the cuff is increased using a small pump until it is above the systolic pressure and prevents the flow of blood. The air pressure inside the cuff is then slowly reduced until blood just begins to pulse through the artery, as detected by the use of a stethoscope. At this point the pressure in the cuff equals the pressure that the blood exerts inside the arteries. Reading the gauge gives the systolic pressure. The pressure in the cuff is then reduced further until the blood flows freely. The pressure at this point is the diastolic pressure.

Hypertension is the presence of abnormally high blood pressure. The usual criterion for hypertension is a blood pressure greater than



▲ Figure 10.4 Measuring blood pressure.

140/90, although recent studies suggest that health risks increase for systolic readings above 120. Hypertension significantly increases the workload on the heart and also places a stress on the walls of the blood vessels throughout the body. These effects increase the risk of aneurysms, heart attacks, and strokes.

Self-Assessment exercise

- 10.3** An altimeter is an instrument used to measure the altitude of an aircraft and gives a reading in feet above a datum (usually ground level). It detects the atmospheric pressure outside the aircraft. As the reading on the altimeter increases, does the atmospheric pressure outside the aircraft:

- (a) Increase
(b) Decrease

Exercises

- 10.4** A set of bookshelves rests on a hard floor surface on four legs, each having a cross-sectional dimension of $4.0 \times 5.0 \text{ cm}$ in contact with the floor. The total mass of the shelves plus the books stacked on them is 200 kg. Calculate the pressure in atmospheres exerted by the shelf footings on the surface.
- 10.5** (a) The compound 1-iodododecane is a nonvolatile liquid with a density of 1.20 g/mL . The density of mercury is 13.6 g/mL . What do you predict for the height of a barometer column based on 1-iodododecane, when the atmospheric

pressure is 749 torr? (b) What is the pressure, in atmospheres, on the body of a diver if he is 21 ft below the surface of the water when the atmospheric pressure is 742 torr?

- 10.6** Perform the following conversions: (a) 0.912 atm to torr, (b) 0.685 bar to kilopascals, (c) 655 mm Hg to atmospheres, (d) $1.323 \times 10^5 \text{ Pa}$ to atmospheres, (e) 2.50 atm to psi.
- 10.7** Hurricane Wilma of 2005 is the most intense hurricane on record in the Atlantic basin, with a low-pressure reading of 882 mbar (millibars). Convert this reading into (a) atmospheres, (b) torr, and (c) inches of Hg.

- 10.8** An open-end manometer containing mercury is connected to a container of gas, as depicted in Sample Exercise 10.2. What is the pressure of the enclosed gas in torr in each of the following situations? (a) The mercury in the arm attached to

the gas is 15.4 mm higher than in the one open to the atmosphere; atmospheric pressure is 0.985 atm. (b) The mercury in the arm attached to the gas is 12.3 mm lower than in the one open to the atmosphere; atmospheric pressure is 0.99 atm.

10.3 (b)

Answers to Self-Assessment Exercises



10.3 | The Gas Laws



It is said that Joseph Montgolfier first got the idea of a hot air balloon when he observed how laundry, drying over a fire, occasionally trapped air and billowed upwards. With the help of his brother Etienne, he built and tested an unmanned balloon using smoldering wool and hay as a heat source. This proved so successful that the balloon rose out of their control and crashed some 2 km away. On 19 September 1783, the brothers demonstrated their invention in front of King Louis XVI of France and Queen Marie Antoinette. The balloon had a basket attached to it carrying a sheep, a duck, and a rooster. All three animals survived the 3 km flight in which the balloon reached an estimated 1500 feet. Seeing this, the king sanctioned the first human flight in a hot air balloon. This was undertaken by Etienne in a tethered balloon with the first untethered flight being made in November of the same year.

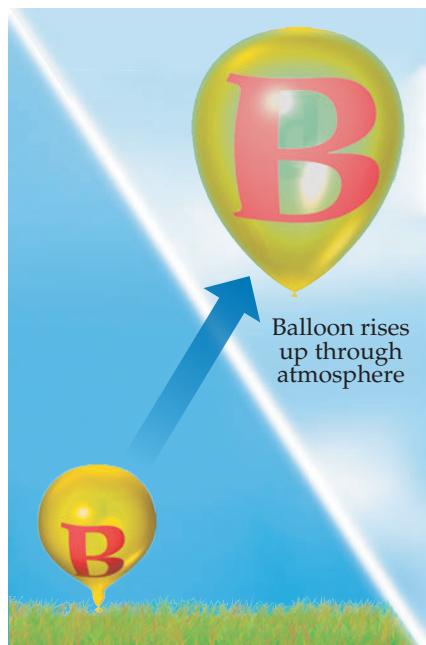
The bright colors of a hot air balloon can sometimes be seen in the still air of the early morning. In this section, we study some fundamental physical properties of gases. By the end of the section, you should be able to

- Understand the relationship between volume, temperature, and pressure of a gas.

Four variables are needed to define the physical condition, or *state*, of a gas: temperature, pressure, volume, and amount of gas, usually expressed as number of moles. The equations that express the relationships among these four variables are known as the *gas laws*. Because volume is easily measured, the first gas laws to be studied expressed the effect of one of the variables on volume, with the remaining two variables held constant.

**Go Figure**

Does atmospheric pressure increase or decrease as altitude increases? (Neglect changes in temperature.)



▲ Figure 10.5 As a balloon rises in the atmosphere, its volume increases.

The Pressure–Volume Relationship: Boyle's Law

Gas volume increases as the pressure exerted on the gas decreases. Thus, an inflated weather balloon released at the Earth's surface expands as it rises (**Figure 10.5**) because the pressure of the atmosphere decreases with increasing elevation.

The British chemist Robert Boyle (1627–1691) was the first person to investigate the quantitative relationship between the pressure of a gas and its volume. He found, for example, that decreasing the pressure of a gas to half its original value causes the volume to double. Conversely, doubling the pressure causes the volume to decrease to half its original value.

Boyle's law, which summarizes these observations, states that:

The volume of a fixed quantity of gas maintained at constant temperature is inversely proportional to the pressure.

When two measurements are inversely proportional, one gets smaller as the other gets larger. Boyle's law can be expressed mathematically as

$$V = \text{constant} \times \frac{1}{P} \quad \text{or} \quad PV = \text{constant} \quad [10.2]$$

The value of the constant depends on temperature and on the amount of gas in the sample.

The graph of V versus P in **Figure 10.6** shows the curve obtained for a given quantity of gas at a fixed temperature. A linear relationship is obtained when V is plotted versus $1/P$ as shown on the right in Figure 10.6.

Boyle's law occupies a special place in the history of science because Boyle was the first to carry out experiments in which one variable was systematically changed to determine the effect on another variable. The data from the experiments were then employed to establish an empirical relationship—a “law.”

We apply Boyle's law every time we breathe. The rib cage, which can expand and contract, and the diaphragm, a muscle beneath the lungs, govern the volume of the lungs. Inhalation occurs when the rib cage expands and the diaphragm moves downward. Both actions increase the volume of the lungs, thus decreasing the gas pressure inside the lungs. Atmospheric pressure then forces air into the lungs until the pressure in the lungs equals atmospheric pressure. Exhalation reverses the process—the rib cage contracts and the diaphragm moves up, decreasing the volume of the lungs. Air is forced out of the lungs by the resulting increase in pressure.

The Temperature–Volume Relationship: Charles's Law

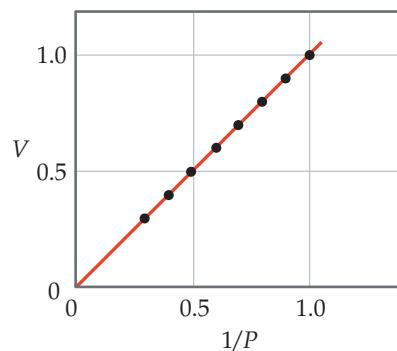
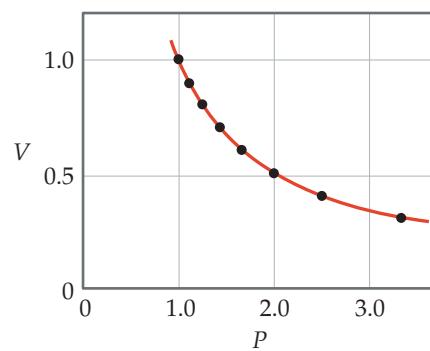
As **Figure 10.7** illustrates, the volume of an inflated balloon increases when the temperature of the gas inside the balloon increases and decreases when the temperature of the gas decreases. This relationship between gas volume and temperature was discovered in 1787 by French



▲ Figure 10.7 The effect of temperature on volume.

Go Figure

What would a plot of P versus $1/V$ look like for a fixed quantity of gas at a fixed temperature?



▲ Figure 10.6 Boyle's Law. For a fixed quantity of gas at constant temperature, the volume of the gas is inversely proportional to its pressure.

scientist Jacques Charles (1746–1823). Some typical volume–temperature data are shown in **Figure 10.8**. Notice that the extrapolated (dashed) line passes through -273°C . Note also that the gas is predicted to have zero volume at this temperature. This condition is never realized, however, because all gases liquefy or solidify before reaching this temperature.

In 1848, William Thomson (1824–1907), a British physicist whose title was Lord Kelvin, proposed an absolute-temperature scale, now known as the Kelvin scale. On this scale, 0 K, called *absolute zero*, equals -273.15°C . In terms of the Kelvin scale, **Charles's law** states:

The volume of a fixed amount of gas maintained at constant pressure is directly proportional to its absolute temperature.

Thus, doubling the absolute temperature causes the gas volume to double. Mathematically, Charles's law takes the form

$$V = \text{constant} \times T \quad \text{or} \quad \frac{V}{T} = \text{constant} \quad [10.3]$$

with the value of the constant depending on the pressure and on the amount of gas.

The Quantity–Volume Relationship: Avogadro's Law

The relationship between the quantity of a gas and its volume follows from the work of Joseph Louis Gay-Lussac (1778–1823) and Amedeo Avogadro (1776–1856).

Gay-Lussac was one of those extraordinary figures in the history of science who could truly be called an adventurer. In 1804, he ascended to 7000 m in a hot air balloon—an exploit that held the altitude record for several decades. To better control the balloon, Gay-Lussac studied the properties of gases. In 1808, he observed the *law of combining volumes*: At a given pressure and temperature, the volumes of gases that react with one another are in the ratios of small whole numbers. For example, two volumes of hydrogen gas react with one volume of oxygen gas to form two volumes of water vapor.

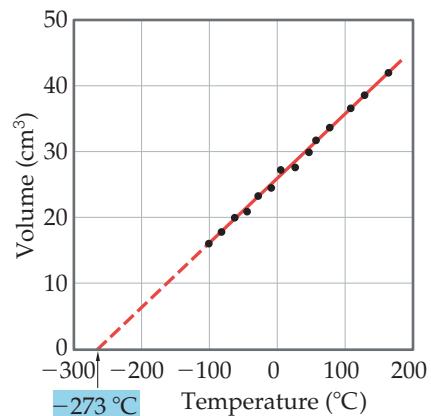
Three years later, Amedeo Avogadro interpreted Gay-Lussac's observation by proposing what is now known as **Avogadro's hypothesis**:

Equal volumes of gases at the same temperature and pressure contain equal numbers of molecules.

For example, 22.4 L of any gas at 0°C and 101.3 kPa contain 6.02×10^{23} gas molecules (that is, 1 mol), as depicted in **Figure 10.9**.

Avogadro's law follows from Avogadro's hypothesis:

The volume of a gas maintained at constant temperature and pressure is directly proportional to the number of moles of the gas.



▲ **Figure 10.8 Charles's Law.** For a fixed quantity of gas at constant pressure, the volume of the gas is proportional to its temperature.

Go Figure How many moles of gas are in each vessel?



Volume	22.4 L	22.4 L	22.4 L
Pressure	101.3 kPa	101.3 kPa	101.3 kPa
Temperature	0°C	0°C	0°C
Mass of gas	4.00 g	28.0 g	16.0 g
Number of gas molecules	6.02×10^{23}	6.02×10^{23}	6.02×10^{23}

▲ **Figure 10.9 Avogadro's hypothesis.** At the same volume, pressure, and temperature, samples of different gases have the same number of molecules but different masses.

That is,

$$V = \text{constant} \times n \quad \text{or} \quad \frac{V}{n} = \text{constant} \quad [10.4]$$

where n is number of moles. Thus, for instance, doubling the number of moles of gas causes the volume to double if T and P remain constant.



Sample Exercise 10.3

Evaluating the Effects of Changes in P , V , n , and T on a Gas



Suppose we have a gas confined to a cylinder with a movable piston that is sealed so there are no leaks. How will each of the following changes affect (i) the pressure of the gas, (ii) the number of moles of gas in the cylinder, (iii) the average distance between molecules: (a) Heating the gas while maintaining a constant pressure; (b) Reducing the volume while maintaining a constant temperature; (c) Injecting additional gas while keeping the temperature and volume constant.

SOLUTION

Analyze We need to think how each change affects (1) the pressure of the gas, (2) the number of moles of gas in the cylinder, and (3) the average distance between molecules.

Plan We can use the gas laws to evaluate the changes in pressure. The number of moles of gas in the cylinder will not change unless gas is either added or removed. Assessing the average distance between molecules is not quite as straightforward. For a given number of gas molecules, the average distance between molecules increases as the volume increases. Conversely, for constant volume, the average distance between molecules decreases as the number of moles increases. Thus, the average distance between molecules will be proportional to V/n .

Solve

- (a) Because it is stipulated that the pressure remains constant, pressure is not a variable in this problem, and the total number of moles of gas will also remain constant. We know from Charles's law, however, that heating the gas while maintaining constant pressure will cause the piston to move and the volume to increase. Thus, the distance between molecules will increase.
- (b) The reduction in volume causes the pressure to increase (Boyle's law). Compressing the gas into a smaller volume does not change the total number of gas molecules; thus, the total number of moles remains the same. The average distance between molecules, however, must decrease because of the smaller volume.

(c) Injecting more gas into the cylinder means that more molecules are present and there will be an increase in the number of moles of gas in the cylinder. Because we have added more molecules while keeping the volume constant, the average distance between molecules must decrease. Avogadro's law tells us that the volume of the cylinder should have increased when we added more gas, provided the pressure and temperature were held constant. Here the volume is held constant, as is the temperature, which means the pressure must change. Knowing from Boyle's law that there is an inverse relationship between volume and pressure ($PV = \text{constant}$), we conclude that if the volume does not increase on injecting more gas the pressure must increase.

► Practice Exercise

An oxygen cylinder used in a hospital contains 35.4 L of oxygen gas at a pressure of 15.16 GPa. How much volume would the oxygen occupy if it were transferred to a container that maintained a pressure of 101.3 kPa if the temperature remains constant?

Self-Assessment Exercise

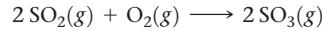
- 10.9** What happens to the pressure of a gas in a closed container if you double its volume while its temperature is held constant?

- (a) The pressure is halved
- (b) The pressure remains the same
- (c) The pressure is doubled

Exercises

- 10.10** You have a gas at 25 °C confined to a cylinder with a movable piston. Which of the following actions would double the gas pressure? (a) Lifting up on the piston to double the volume while keeping the temperature constant; (b) Heating the gas so that its temperature rises from 25 °C to 50 °C, while keeping the volume constant; (c) Pushing down on the piston to halve the volume while keeping the temperature constant.

- 10.11** In the contact process, sulfur dioxide and oxygen gas react to form sulfur trioxide as follows:

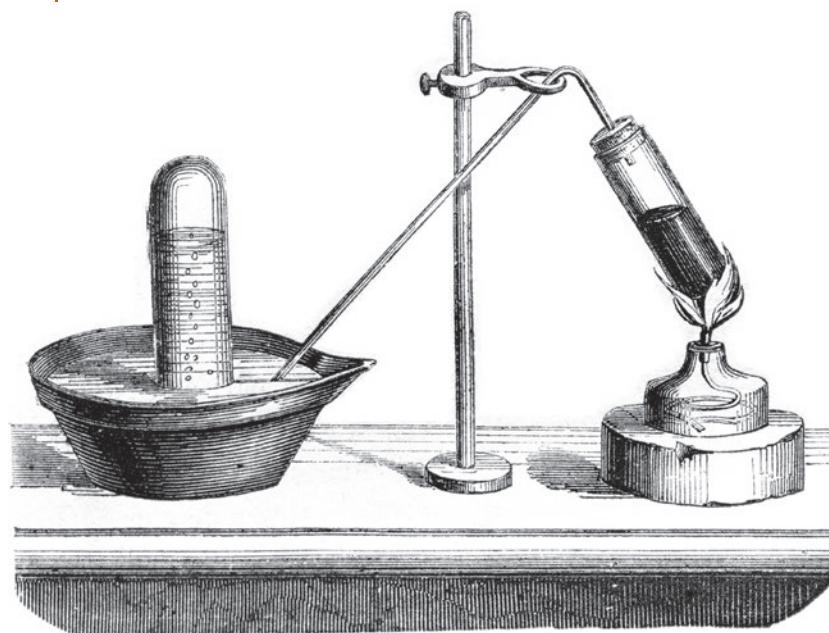


At a certain temperature and pressure, 50 L of SO_2 reacts with 25 L of O_2 . If all the SO_2 and O_2 are consumed, what volume of SO_3 , at the same temperature and pressure, will be produced?

10.9 (a)



10.4 | The Ideal Gas Equation



Early work on gases assumed that they were composed of individual atoms. This made them appealing to study as the interaction between atoms could be put on one side and the physical properties of the gas studied as a window onto the atomic world. There were some confusing observations, however. For example, the French chemist Gay-Lussac noticed that some reactions between gasses produced twice the volume of product than he expected. This was later explained by Amedeo Avogadro, a physics professor at the University of Turin in Italy, who suggested that gases were made of clusters of atoms; what we now call molecules. This breakthrough led to a new dawn of understanding of matter and chemical bonding.

By the end of this section, you should be able to

- Use the ideal gas equation to relate the amount of gas to its volume, pressure, and temperature.
- Calculate the molar mass of a gas from its density.

All three laws we just examined were obtained by holding two of the four variables P , V , T , and n constant and seeing how the remaining two variables affect each other. We can express each law as a proportionality relationship. Using the symbol \propto for “is proportional to,” we have

$$\text{Boyle's law: } V \propto \frac{1}{P} \quad (\text{constant } n, T)$$

$$\text{Charles's law: } V \propto T \quad (\text{constant } n, P)$$

$$\text{Avogadro's law: } V \propto n \quad (\text{constant } P, T)$$

We can combine these relationships into a general gas law:

$$V \propto \frac{nT}{P}$$

If we call the proportionality constant R , we obtain an equality:

$$V = R\left(\frac{nT}{P}\right)$$

which we can rearrange to

$$PV = nRT \quad [10.5]$$

TABLE 10.2 Numerical Values of the Gas Constant R in Various Units

Units	Numerical Value
L atm/mol K	0.08206
J/mol K*	8.314
m ³ Pa/mol K*	8.314
L torr/mol K	62.36
L kPa/mol K	8.314

*SI unit

which is the **ideal gas equation** (also called the **ideal gas law**). An **ideal gas** is a hypothetical gas whose pressure, volume, and temperature relationships are described completely by the ideal gas equation.

In deriving the ideal gas equation, we make two assumptions:

- the molecules of an ideal gas do not interact with one another,
- the combined volume of the molecules is much smaller than the volume the gas occupies.

For these reasons, we consider the molecules as taking up no space in the container. In many cases, the small error introduced by these assumptions is acceptable. If more accurate calculations are needed, we can correct for the assumptions if we know something about the attraction molecules have for one another and the size of the molecules.

The term *R* in the ideal gas equation is the **gas constant**. The value and units of *R* depend on the units of *P*, *V*, *n*, and *T*. The value for *T* in the ideal gas equation must *always* be the absolute temperature (in kelvins instead of degrees Celsius). The quantity of gas, *n*, is normally expressed in moles. The units chosen for pressure are most often atmospheres or Pascals and the units of volume in liters. **Table 10.2** shows the numerical value for *R* in various units. In working with the ideal gas equation, you must choose the form of *R* in which the units agree with the units of *P*, *V*, *n*, and *T* given in the problem.

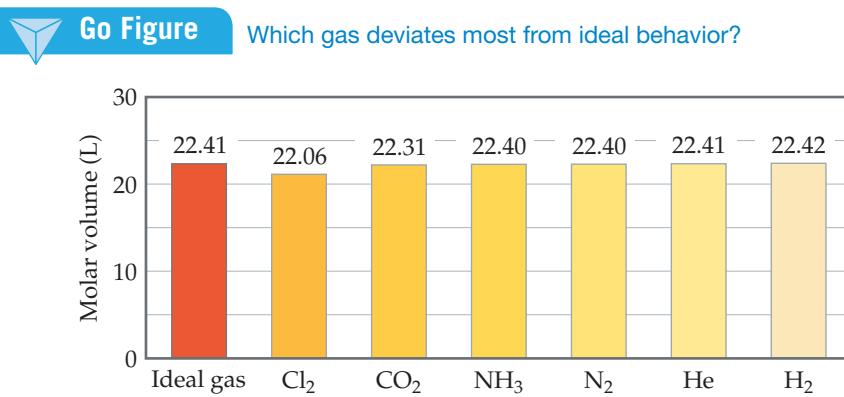
Suppose we have 1.000 mol of an ideal gas at 101.325 kPa and 0.00 °C (273.15 K). According to the ideal gas equation, the volume of the gas is

$$V = \frac{nRT}{P}$$

$$= \frac{(1.000 \text{ mol})(8.314 \text{ m}^3 \text{ Pa/mol K})(273.15 \text{ K})}{101.325 \times 10^3 \text{ Pa}} = 22.41 \text{ L}$$

The conditions 0 °C and 101.325 kPa are referred to as **standard temperature and pressure (STP)**. The volume occupied by 1 mol of ideal gas at STP, 22.41 L, is known as the **molar volume** of an ideal gas at STP.

The ideal gas equation accounts adequately for the properties of most gases under a variety of circumstances. The equation is not exactly correct, however, for any real gas. Thus, the measured volume for given values of *P*, *n*, and *T* might differ from the volume calculated from *PV = nRT* (**Figure 10.10**). Although real gases do not always behave ideally, their behavior differs so little from ideal behavior that we can ignore any deviations for all but the most accurate work.



▲ **Figure 10.10** Comparison of molar volumes at STP.



Sample Exercise 10.4

Using the Ideal Gas Equation



Calcium carbonate, $\text{CaCO}_3(s)$, the principal compound in limestone, decomposes upon heating to $\text{CaO}(s)$ and $\text{CO}_2(g)$. A sample of CaCO_3 is decomposed, and the carbon dioxide is collected in a 250 mL flask. After decomposition is complete, the gas has a pressure of 131.72 kPa at a temperature of 31 °C. How many moles of CO_2 gas were generated?

SOLUTION

Analyze We are given the volume (250 mL), pressure (131.72 kPa), and temperature (31 °C) of a sample of CO_2 gas and asked to calculate the number of moles of CO_2 in the sample.

Plan Because we are given V , P , and T , we can solve the ideal gas equation for the unknown quantity, n .

Solve In analyzing and solving gas law problems, it is helpful to tabulate the information given in the problems and then to convert the values to units that are consistent with those for R (8.314 m³ Pa/mol K). In this case, the given values are

$$V = 250 \text{ mL} = 0.250 \text{ L} = 2.5 \times 10^{-4} \text{ m}^3$$

$$P = 131.72 \text{ kPa} = 131.72 \times 10^3 \text{ Pa}$$

$$T = 31^\circ\text{C} = (31 + 273) \text{ K} = 304 \text{ K}$$

Remember: *Absolute temperature must always be used when the ideal gas equation is solved.*

We now rearrange the ideal gas equation (Equation 10.5) to solve for n

$$n = \frac{PV}{RT}$$

$$\begin{aligned} n &= \frac{(131.72 \times 10^3 \text{ Pa})(2.5 \times 10^{-4} \text{ m}^3)}{(8.314 \text{ m}^3 \text{ Pa/mol K})(304 \text{ K})} \\ &= 0.013 \text{ mol CO}_2 \end{aligned}$$

Check Appropriate units cancel, thus ensuring that we have properly rearranged the ideal gas equation and have converted to the correct units.

► Practice Exercise

Tennis balls are usually filled with either air or N_2 gas to a pressure above atmospheric pressure to increase their bounce. If a tennis ball has a volume of 144 cm³ and contains 0.33 g of N_2 gas, what is the pressure inside the ball at 24 °C?

STRATEGIES FOR SUCCESS**Calculations Involving Many Variables**

In this chapter, we encounter a variety of problems based on the ideal gas equation, which contains four variables— P , V , n , and T —and one constant, R . Depending on the type of problem, we might need to solve for any of the four variables.

To extract the necessary information from problems involving more than one variable, we suggest the following steps:

- 1. Tabulate information.** Read the problems carefully to determine which variable is the unknown and which variables have numeric values given. Every time you encounter a numerical value, jot it down. In many cases, constructing a table of the given information will be useful.
- 2. Convert to consistent units.** Make certain that quantities are converted to the proper units. In using the ideal gas equation, for example, we usually use the value of R that has units of m³ Pa/mol K.
- 3. If a single equation relates the variables, solve the equation for the unknown.** For the ideal gas equation, these algebraic rearrangements will all be used at one time or another:

$$P = \frac{nRT}{V}, \quad V = \frac{nRT}{P}, \quad n = \frac{PV}{RT}, \quad T = \frac{PV}{nR}$$

- 4. Use dimensional analysis.** Carry the units through your calculation. Using dimensional analysis enables you to check that you have solved an equation correctly. If the units in the equation cancel to give the units of the desired variable, you have probably used the equation correctly.

Sometimes you will not be given explicit values for several variables, making it look like a problem that cannot be solved. In these cases, however, you should look for information that can be used to determine the needed variables. For example, suppose you are using the ideal gas equation to calculate a pressure in a problem that gives a value for T but not for n or V . However, the problem states that “the sample contains 0.15 mol of gas per liter.” You can turn this statement into the expression

$$\frac{n}{V} = 0.15 \text{ mol/L}$$

Solving the ideal gas equation for pressure yields

$$P = \frac{nRT}{V}$$

which we can rewrite as follows:

$$P = \left(\frac{n}{V} \right) RT$$

Thus, we can solve the equation even though we are not given values for n and V .

As we have continuously stressed, the most important thing you can do to become proficient at solving chemistry problems is to do the practice exercises, the end-of-section exercises and end-of-chapter exercises. By using systematic procedures, such as those described here, you should be able to minimize difficulties in solving problems involving many variables.

Relating the Ideal Gas Equation and the Gas Laws

The gas laws we discussed in Section 10.3 are special cases of the ideal gas equation. For example, when n and T are held constant, the product nRT contains three constants and so must itself be a constant:

$$PV = nRT = \text{constant} \quad \text{or} \quad PV = \text{constant} \quad [10.6]$$

Note that this rearrangement gives Boyle's law. We see that if n and T are constant, the values of P and V can change, but the product PV must remain constant.

We can use Boyle's law to determine how the volume of a gas changes when its pressure changes. For example, if a cylinder fitted with a movable piston holds 50.0 L of O₂ gas at 1.875 MPa and 21 °C, what volume will the gas occupy if the temperature is maintained at 21 °C while the pressure is reduced to 101.3 kPa? Because the product PV is a constant when a gas is held at constant n and T , we know that

$$P_1 V_1 = P_2 V_2 \quad [10.7]$$

where P_1 and V_1 are initial values and P_2 and V_2 are final values. Dividing both sides of this equation by P_2 gives the final volume, V_2 :

$$V_2 = V_1 \times \frac{P_1}{P_2} = (50.0 \text{ L}) \left(\frac{1.875 \text{ MPa}}{101.3 \text{ kPa}} \right) = 925 \text{ L}$$

The answer is reasonable because a gas expands as its pressure decreases.

In a similar way, we can start with the ideal gas equation and derive relationships between any other two variables, V and T (Charles's law), n and V (Avogadro's law), or P and T .

We are often faced with the situation in which P , V , and T all change for a fixed number of moles of gas. Because n is constant in this situation, the ideal gas equation gives

$$\frac{PV}{T} = nR = \text{constant}$$



Sample Exercise 10.5

Calculating the Effect of Temperature Changes on Pressure

The gas pressure in an aerosol can is 152 kPa at 25 °C. Assuming that the gas obeys the ideal gas equation, what is the pressure when the can is heated to 450 °C?

SOLUTION

Analyze We are given the initial pressure (152 kPa) and temperature (25 °C) of the gas and asked for the pressure at a higher temperature (450 °C).

Plan The volume and number of moles of gas do not change, so we must use a relationship connecting pressure and temperature. Converting temperature to the Kelvin scale and tabulating the given information, we have

	<i>P</i>	<i>T</i>
Initial	152 kPa	298 K
Final	P_2	723 K

Solve To determine how P and T are related, we start with the ideal gas equation and isolate the quantities that do not change (n , V , and R) on one side and the variables (P and T) on the other side.

$$\frac{P}{T} = \frac{nR}{V} = \text{constant}$$

Because the quotient P/T is a constant, we can write

$$\frac{P_1}{T_1} = \frac{P_2}{T_2}$$

(where the subscripts 1 and 2 represent the initial and final states, respectively). Rearranging to solve for P_2 and substituting the given data give

$$P_2 = (152 \text{ kPa}) \left(\frac{723 \text{ K}}{298 \text{ K}} \right) = 368.8 \text{ kPa}$$

Check This answer is intuitively reasonable—increasing the temperature of a gas increases its pressure.

Comment It is evident from this example why aerosol cans carry a warning not to incinerate.

► Practice Exercise

The pressure in a natural-gas tank is maintained at 222.9 kPa. On a day when the temperature is –15 °C, the volume of gas in the tank is $3.25 \times 10^3 \text{ m}^3$. What is the volume of the same quantity of gas on a day when the temperature is 31 °C?



Sample Exercise 10.6

Using the Combined Gas Law

An inflated balloon has a volume of 6.0 L at sea level (101.3 kPa) and is allowed to ascend until the pressure is 45.6 kPa. During ascent, the temperature of the gas falls from 22 °C to –21 °C. Calculate the volume of the balloon at its final altitude.

SOLUTION

Analyze We need to determine a new volume for a gas sample when both pressure and temperature change.

Plan Let's again proceed by converting temperatures to kelvins and tabulating our information.

	P	V	T
Initial	101.3 kPa	6.0 L	295 K
Final	45.6 kPa	V_2	252 K

Because n is constant, we can use Equation 10.8.

Solve Rearranging Equation 10.8 to solve for V_2 gives

$$\begin{aligned} V_2 &= V_1 \times \frac{P_1}{P_2} \times \frac{T_2}{T_1} \\ &= (6.0 \text{ L}) \left(\frac{101.3 \text{ kPa}}{45.6 \text{ kPa}} \right) \left(\frac{252 \text{ K}}{295 \text{ K}} \right) = 11 \text{ L} \end{aligned}$$

Check The result appears reasonable. Notice that the calculation involves multiplying the initial volume by a ratio of pressures and a ratio of temperatures. Intuitively, we expect decreasing pressure to cause the volume to increase, while decreasing the temperature should have the opposite effect. Because the change in pressure is more dramatic than the change in temperature, we expect the effect of the pressure change to predominate in determining the final volume, as it does.

► Practice Exercise

A 0.50-mol sample of oxygen gas is confined at 0 °C and 101.3 kPa in a cylinder with a movable piston. The piston compresses the gas so that the final volume is half the initial volume and the final pressure is 222.9 kPa. What is the final temperature of the gas in degrees Celsius?

If we represent the initial and final conditions by subscripts 1 and 2, respectively, we can write an equation that is often called the *combined gas law*:

$$\frac{P_1 V_1}{T_1} = \frac{P_2 V_2}{T_2} \quad [10.8]$$

We now use the ideal gas equation first to define the relationship between the density of a gas and its molar mass and then to calculate the volumes of gases formed or consumed in chemical reactions.

Gas Densities and Molar Mass

Recall that density has units of mass per unit volume ($d = m/V$). We can arrange the ideal gas equation to obtain similar units of moles per unit volume:

$$\frac{n}{V} = \frac{P}{RT}$$

If we multiply both sides of this equation by the molar mass, \mathcal{M} , which is the number of grams in 1 mol of a substance, we obtain

$$\frac{n\mathcal{M}}{V} = \frac{PM}{RT} \quad [10.9]$$

The term on the left equals the density in grams per liter:

$$\frac{\text{moles}}{\text{liter}} \times \frac{\text{grams}}{\text{mole}} = \frac{\text{grams}}{\text{liter}}$$

Thus, the density of the gas is also given by the expression on the right in Equation 10.9:

$$d = \frac{n\mathcal{M}}{V} = \frac{PM}{RT} \quad [10.10]$$



Sample Exercise 10.7

Calculating Gas Density

What is the density of tetrachloromethane (CCl_4) vapor at 95.19 kPa and 125 °C?

SOLUTION

Analyze We are asked to calculate the density of a gas given its name, its pressure, and its temperature.

Plan We can use Equation 10.10 to calculate the density. Before we can do that, however, we must convert the given quantities to the appropriate units, degrees Celsius to kelvins. We must also calculate the molar mass of CCl_4 .

Solve The absolute temperature is $125 + 273 = 398$ K.

The pressure is 95.19 kPa. The molar mass of CCl_4 is $12.01 + (4)(35.45) = 153.8$ g/mol. Therefore,

$$d = \frac{PM}{RT} = \frac{(95.19 \times 10^3 \text{ Pa})(153.8 \text{ g/mol})}{(8.314 \text{ m}^3 \text{ Pa} \cdot \text{mol K})(398 \text{ K})} = 4424 \text{ g/m}^3 = 4.42 \text{ g/L}$$

Check If we divide molar mass (g/mol) by density (g/L), we end up with L/mol. The numerical value is roughly $154/4.4 = 35$, which is in the right ballpark for the molar volume of a gas heated to 125 °C at near atmospheric pressure. We may thus conclude our answer is reasonable.

► Practice Exercise

The mean molar mass of the atmosphere at the surface of Titan, Saturn's largest moon, is 28.6 g/mol. The surface temperature is 95 K, and the pressure is 162 kPa. Assuming ideal behavior, calculate the density of Titan's atmosphere.



▲ **Figure 10.11** Carbon dioxide gas flows downward because it is denser than air.

This equation tells us that the density of a gas depends on its pressure, molar mass, and temperature. The higher the molar mass and pressure, the denser the gas. The higher the temperature, the less dense the gas. Although gases form homogeneous mixtures, a less dense gas will lie above a denser gas in the absence of mixing. For example, CO_2 has a higher molar mass than N_2 or O_2 and is therefore denser than air. For this reason, CO_2 released from a CO_2 fire extinguisher blankets a fire, preventing O_2 from reaching the combustible material. "Dry ice," which is solid CO_2 , converts directly to CO_2 gas at room temperature, and the resulting "fog" (which is actually condensed water droplets cooled by the CO_2) is carried downward by the heavier, but colorless, CO_2 (Figure 10.11).

When we have equal molar masses of two gases at the same pressure but different temperatures, the hotter gas is less dense than the cooler one, so the hotter gas rises. The difference between the densities of hot and cold air is responsible for the lift of hot air balloons. It is also responsible for many phenomena in weather, such as the formation of large thunderheads during thunderstorms.

Equation 10.10 can be rearranged to solve for the molar mass of a gas:

$$\mathcal{M} = \frac{dRT}{P} \quad [10.11]$$

Thus, we can use the experimentally measured density of a gas to determine the molar mass of the gas molecules, as shown in Sample Exercise 10.8.



Sample Exercise 10.8

Calculating the Molar Mass of a Gas

A large evacuated flask initially has a mass of 134.567 g. When the flask is filled with a gas of unknown molar mass to a pressure of 97.99 kPa at 31 °C, its mass is 137.456 g. When the flask is evacuated again and then filled with water at 31 °C, its mass is 1067.9 g. (The density of water at this temperature is 0.997 g/mL.) Assuming the ideal gas equation applies, calculate the molar mass of the gas.

SOLUTION

Analyze We are given the temperature (31°C) and pressure (97.99 kPa) for a gas, together with information to determine its volume and mass, and we are asked to calculate its molar mass.

Plan The data obtained when the flask is filled with water can be used to calculate the volume of the container. The mass of the empty flask and of the flask when filled with gas can be used to calculate the mass of the gas. From these quantities we calculate the gas density and then apply Equation 10.11 to calculate the molar mass of the gas.

Solve The gas volume equals the volume of water the flask can hold, calculated from the mass and density of the water. The mass of the water is the difference between the masses of the full and evacuated flask:

$$1067.9 \text{ g} - 134.567 \text{ g} = 933.3 \text{ g}$$

Rearranging the equation for density ($d = m/V$), we have

$$V = \frac{m}{d} = \frac{(933.3 \text{ g})}{(0.997 \text{ g/mL})} = 936 \text{ mL} = 0.936 \text{ L}$$

The gas mass is the difference between the mass of the flask filled with gas and the mass of the evacuated flask:

$$137.456 \text{ g} - 134.567 \text{ g} = 2.889 \text{ g}$$

Knowing the mass of the gas (2.889 g) and its volume (0.936 L), we can calculate the density of the gas:

$$d = 2.889 \text{ g}/0.936 \text{ L} = 3.09 \text{ g/L} = 3.09 \times 10^3 \text{ g/m}^3$$

After converting temperature to kelvins, we can use Equation 10.11 to calculate the molar mass:

$$\begin{aligned} M &= \frac{dRT}{P} \\ &= \frac{(3.09 \times 10^3 \text{ g/m}^3)(8.314 \text{ m}^3 \text{ Pa/mol K})(304 \text{ K})}{(97.99 \times 10^3 \text{ Pa})} \\ &= 79.7 \text{ g/mol} \end{aligned}$$

Check The units work out appropriately, and the value of molar mass obtained is reasonable for a substance that is gaseous near room temperature.

► Practice Exercise

What is the molar mass of an unknown hydrocarbon whose density is measured to be 1.97 g/L at STP?

- (a) 4.04 g/mol (b) 30.7 g/mol (c) 44.1 g/mol
(d) 48.2 g/mol

Volumes of Gases in Chemical Reactions

We are often concerned with knowing the identity and/or quantity of a gas involved in a chemical reaction. Thus, it is useful to be able to calculate the volumes of gases consumed or produced in reactions. Such calculations are based on the mole concept and balanced chemical equations. The coefficients in a balanced chemical equation tell us the relative amounts (in moles) of reactants and products in a reaction. The ideal gas equation relates the number of moles of a gas to P , V , and T .



Sample Exercise 10.9

Relating Gas Variables and Reaction Stoichiometry

Automobile air bags are inflated by nitrogen gas generated by the rapid decomposition of sodium azide, NaN_3 :



If an air bag has a volume of 36 L and is to be filled with nitrogen gas at 116.5 kPa and 26°C , how many grams of NaN_3 must be decomposed?

SOLUTION

Analyze This is a multistep problem. We are given the volume, pressure, and temperature of the N_2 gas and the chemical equation for the reaction by which the N_2 is generated. We must use this information to calculate the number of grams of NaN_3 needed to obtain the necessary N_2 .

Plan We need to use the gas data (P , V , and T) and the ideal gas equation to calculate the number of moles of N_2 gas that should be formed for the air bag to operate correctly. We can then use the balanced equation to determine the number of moles of NaN_3 needed. Finally, we can convert moles of NaN_3 to grams.

Solve

The conversion sequence is:



The number of moles of N₂ is determined using the ideal gas equation:

$$n = \frac{PV}{RT} = \frac{(116.5 \times 10^3 \text{ Pa})(0.036 \text{ m}^3)}{(8.314 \text{ m}^3 \text{ Pa/mol K})(299 \text{ K})}$$

$$= 1.7 \text{ mol N}_2$$

We use the coefficients in the balanced equation to calculate the number of moles of NaN₃:

$$(1.7 \text{ mol N}_2) \left(\frac{2 \text{ mol NaN}_3}{3 \text{ mol N}_2} \right) = 1.1 \text{ mol NaN}_3$$

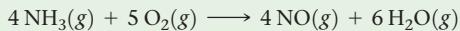
Finally, using the molar mass of NaN₃, we convert moles of NaN₃ to grams:

$$(1.1 \text{ mol NaN}_3) \left(\frac{65.0 \text{ g NaN}_3}{1 \text{ mol NaN}_3} \right) = 72 \text{ g NaN}_3$$

Check The units cancel properly at each step in the calculation, leaving us with the correct units in the answer, g NaN₃.

► Practice Exercise

In the first step of the industrial process for making nitric acid, ammonia reacts with oxygen in the presence of a suitable catalyst to form nitric oxide and water vapor:



How many liters of NH₃(g) at 850 °C and 506.6 kPa are required to react with 1.00 mol of O₂(g) in this reaction?

Self-Assessment Exercises

- 10.12** The Goodyear blimps frequently fly over sporting events. One such blimp holds approximately 4955 m³ helium. If the gas is at 23 °C and 101.33 kPa, what mass of helium is in a blimp?
(a) 816 g
(b) 2.63 kg
(c) 816 kg
(d) 2630 kg
- 10.13** Calculate the density of dinitrogen tetroxide gas (N₂O₄) at 111.5 kPa and 0 °C.
(a) 0.0491 g/L
(b) 4.52 g/L
(c) 472 g/L
- 10.14** Calculate the molar mass of a gas if 2.70 g occupies 0.97 L at 134.7 kPa and 100 °C.
(a) 8.27 g/mol
(b) 17.2 g/mol
(c) 64.1 g/mol

Exercises

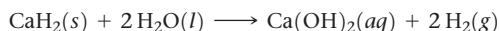
- 10.15** Suppose you are given two flasks at the same temperature, one of volume 2 L and the other of volume 3 L. The 2 L flask contains 4.8 g of gas, and the gas pressure is x kPa. The 3 L flask contains 0.36 g of gas, and the gas pressure is 0.1x. Do the two gases have the same molar mass? If not, which contains the gas of higher molar mass?
- 10.16** Calculate each of the following quantities for an ideal gas:
(a) the volume of the gas, in liters, if 1.50 mol has a pressure of 126.7 kPa at a temperature of -6 °C;
(b) the absolute temperature of the gas at which 3.33 × 10⁻³ mol occupies 478 mL at 99.99 kPa;
(c) the pressure, in pascals, if 0.00245 mol occupies 413 mL at 138 °C;
(d) the quantity of gas, in moles, if 126.5 L at 54 °C has a pressure of 11.25 kPa.
- 10.17** A neon sign is made of glass tubing whose inside diameter is 3.0 cm and length is 10.0 m. If the sign contains neon at a pressure of 265 Pa at 30 °C, how many grams of neon are in the sign? (The volume of a cylinder is $\pi r^2 h$.)
- 10.18** Many gases are shipped in high-pressure containers. Consider a steel tank whose volume is 210.0 L that contains O₂ gas at a pressure of 16,500 kPa at 23 °C. **(a)** What mass of O₂ does the tank contain? **(b)** What volume would the gas occupy at STP? **(c)** At what temperature would the pressure in the tank equal 15.2 MPa? **(d)** What would be the pressure of the gas, in kPa, if it were transferred to a container at 24 °C whose volume is 55.0 L?
- 10.19** The physical fitness of athletes is measured by "V_{O₂} max," which is the maximum volume of oxygen consumed by an individual during incremental exercise (for example, on a treadmill). An average male has a V_{O₂} max of 45 mL O₂/kg body mass/min, but a world-class male athlete can have a V_{O₂} max reading of 88.0 mL O₂/kg body mass/min. **(a)** Calculate the volume of oxygen, in mL, consumed in 1 hr by an average man who weighs 85 kg and has a V_{O₂} max reading of 47.5 mL O₂/kg body mass/min. **(b)** If this man lost 10 kg, exercised,

and increased his V_{O_2} max to 65.0 mL O₂/kg body mass/min, how many mL of oxygen would he consume in 1 hr?

10.20 Rank the following gases and vapors from least dense to most dense at 101.33 kPa and 298 K: water vapor (H₂O(g)), nitrogen (N₂), hydrogen sulfide (H₂S).

10.21 (a) Calculate the density of sulfur hexafluoride gas at 94.26 kPa and 21 °C. (b) Calculate the molar mass of a vapor that has a density of 7.135 g/L at 12 °C and 99.06 kPa.

10.22 Calcium hydride, CaH₂, reacts with water to form hydrogen gas:



This reaction is sometimes used to inflate life rafts, weather balloons, and the like, when a simple, compact means of

generating H₂ is desired. How many grams of CaH₂ are needed to generate 145 L of H₂ gas if the pressure of H₂ is 110 kPa at 21 °C?

10.23 Both Jacques Charles and Joseph Louis Guy-Lussac were avid balloonists. In his original flight in 1783, Jacques Charles used a balloon that contained approximately 31,150 L of H₂. Charles generated the H₂ using the reaction between iron and hydrochloric acid:



How many kilograms of iron were needed to produce this volume of H₂ if the temperature was 22 °C?

10.12 (c) 10.13 (b) 10.14 (c)

Answers to Self-Assessment Exercises

10.5 | Gas Mixtures and Partial Pressures



Humphry Davy coined the term ‘laughing gas’ for nitrous oxide (N₂O) after observing that inhaling the gas provided a sense of euphoria. Laughing gas parties became popular among the British wealthy around 1800, but the gas also had a serious use as an anesthetic. It is still commonly used in dentistry, where it is administered as a 2:1 ratio with oxygen. Controlling the proportion of the two gases breathed in by the patient is important to ensure pain relief while allowing sufficient oxygen to be present to allow normal respiration.

Other uses of nitrous oxide include its use as a rocket fuel, as a booster to fuel use in racing cars, and as the propellant in aerosol food stuffs such as cooking oil and whipped cream. N₂O dissolves well in fat and can provide a foam of twice the volume attainable by using air while not having the undesirable effect of making the fats go rancid.

By the end of this section, you should be able to

- Understand and use partial pressures and mole fractions

Thus far we have considered mainly pure gases—those that consist of only one substance in the gaseous state. How do we deal with mixtures of two or more different gases? While studying the properties of air, John Dalton made an important observation:

The total pressure of a mixture of gases equals the sum of the pressures that each would exert if it were present alone.

The pressure exerted by a particular component of a mixture of gases is called the **partial pressure** of that component. Dalton's observation is known as **Dalton's law of partial pressures**.

If we let P_t be the total pressure of a mixture of gases and P_1, P_2, P_3 , and so forth be the partial pressures of the individual gases, we can write Dalton's law of partial pressures as

$$P_t = P_1 + P_2 + P_3 + \dots \quad [10.12]$$

This equation implies that each gas behaves independently of the others, as we can see by the following analysis. Let n_1, n_2, n_3 , and so forth be the number of moles of each of the gases in the mixture and n_t be the total number of moles of gas. If each gas obeys the ideal gas equation, we can write

$$P_1 = n_1 \left(\frac{RT}{V} \right); \quad P_2 = n_2 \left(\frac{RT}{V} \right); \quad P_3 = n_3 \left(\frac{RT}{V} \right); \quad \text{and so forth}$$

All of the gases in a container must occupy the same volume and will come to the same temperature in a relatively short period of time. Using these facts to simplify Equation 10.12, we obtain

$$P_t = (n_1 + n_2 + n_3 + \dots) \left(\frac{RT}{V} \right) = n_t \left(\frac{RT}{V} \right) \quad [10.13]$$

That is, at constant temperature and constant volume the total pressure of a gas sample is determined by the total number of moles of gas present, whether that total represents just one gas or a mixture of gases.



Sample Exercise 10.10

Applying Dalton's Law of Partial Pressures

A mixture of 6.00 g of $O_2(g)$ and 9.00 g of $CH_4(g)$ is placed in a 15.0 L vessel at 0 °C. What is the partial pressure of each gas, and what is the total pressure in the vessel?

SOLUTION

Analyze We need to calculate the pressure for two gases in the same volume and at the same temperature.

Plan Because each gas behaves independently, we can use the ideal gas equation to calculate the pressure each would exert if the other were not present. From Dalton's law, the total pressure is the sum of these two partial pressures.

Solve We first convert the mass of each gas to moles:

$$n_{O_2} = (6.00 \text{ g } O_2) \left(\frac{1 \text{ mol } O_2}{32.0 \text{ g } O_2} \right) = 0.188 \text{ mol } O_2$$

$$n_{CH_4} = (9.00 \text{ g } CH_4) \left(\frac{1 \text{ mol } CH_4}{16.0 \text{ g } CH_4} \right) = 0.563 \text{ mol } CH_4$$

We use the ideal gas equation to calculate the partial pressure of each gas:

$$\begin{aligned} P_{O_2} &= \frac{n_{O_2}RT}{V} = \frac{(0.188 \text{ mol})(8.314 \text{ m}^3 \text{ Pa/mol K})(273 \text{ K})}{0.015 \text{ m}^3} \\ &= 28.45 \text{ kPa} \end{aligned}$$

$$\begin{aligned} P_{CH_4} &= \frac{n_{CH_4}RT}{V} = \frac{(0.563 \text{ mol})(8.314 \text{ m}^3 \text{ Pa/mol K})(273 \text{ K})}{0.015 \text{ m}^3} \\ &= 85.19 \text{ kPa} \end{aligned}$$

According to Dalton's law of partial pressures (Equation 10.12), the total pressure in the vessel is the sum of the partial pressures:

$$\begin{aligned} P_t &= P_{O_2} + P_{CH_4} \\ &= 28.45 \text{ kPa} + 85.19 \text{ kPa} = 113.64 \text{ kPa} \end{aligned}$$

Check A pressure of around 101.3 kPa seems right for a mixture of about 0.2 mol O_2 and a bit more than 0.5 mol CH_4 , together in a 15-L volume, because 1 mol of an ideal gas at 1 atm pressure and 0 °C occupies about 22 L.

► Practice Exercise

What is the total pressure exerted by a mixture of 2.00 g of $H_2(g)$ and 8.00 g of $N_2(g)$ at 273 K in a 10.0-L vessel?

Partial Pressures and Mole Fractions

Because each gas in a mixture behaves independently, we can relate the amount of a given gas in a mixture to its partial pressure. For an ideal gas, we can write

$$\frac{P_1}{P_t} = \frac{n_1 RT/V}{n_t RT/V} = \frac{n_1}{n_t} \quad [10.14]$$

The ratio n_1/n_t is called the *mole fraction of gas 1*, which we denote X_1 . The **mole fraction**, X , is a dimensionless number that expresses the ratio of the number of moles of one component in a mixture to the total number of moles in the mixture. Thus, for gas 1 we have

$$X_1 = \frac{\text{Moles of compound 1}}{\text{Total moles}} = \frac{n_1}{n_t} \quad [10.15]$$

We can combine Equations 10.14 and 10.15 to give

$$P_1 = \left(\frac{n_1}{n_t}\right)P_t = X_1 P_t \quad [10.16]$$

The mole fraction of N₂ in air is 0.78—that is, 78% of the molecules in air are N₂. This means that if the barometric pressure is 101.3 kPa, the partial pressure of N₂ is

$$P_{N_2} = (0.78)(101.3 \text{ kPa}) = 79.04 \text{ kPa}$$

This result makes intuitive sense: Because N₂ makes up 78% of the mixture, it contributes 78% of the total pressure.



Sample Exercise 10.11

Relating Mole Fractions and Partial Pressures

A study of the effects of certain gases on plant growth requires a synthetic atmosphere composed of 1.5 mol % CO₂, 18.0 mol % O₂ and 80.5 mol % Ar. (a) Calculate the partial pressure of O₂ in the mixture if the total pressure of the atmosphere is to be 99.33 kPa. (b) If this atmosphere is to be held in a 121 L space at 295 K, how many moles of O₂ are needed?

SOLUTION

Analyze For (a) we need to calculate the partial pressure of O₂ given its mole percent and the total pressure of the mixture. For (b) we need to calculate the number of moles of O₂ in the mixture given its volume (121 L), temperature (295 K), and partial pressure from part (a).

Solve

- (a) The mole percent is the mole fraction times 100. Therefore, the mole fraction of O₂ is 0.180. Equation 10.16 gives:
- (b) Tabulating the given variables and converting to appropriate units, we have:

Plan We calculate the partial pressures using Equation 10.16, and then use P_{O_2} , V , and T in the ideal gas equation to calculate the number of moles of O₂.

$$P_{O_2} = (0.180)(99.33 \text{ kPa}) = 17.88 \text{ kPa}$$

$$P_{O_2} = 17.88 \text{ kPa}$$

$$V = 121 \text{ L} = 0.121 \text{ m}^3$$

$$n_{O_2} = ?$$

$$R = 8.314 \text{ m}^3 \text{ Pa/mol K}$$

$$T = 295 \text{ K}$$

Solving the ideal gas equation for n_{O_2} , we have:

$$n_{O_2} = P_{O_2} \left(\frac{V}{RT} \right)$$

$$= 17.88 \text{ kPa} \frac{0.121 \text{ m}^3}{(8.314 \text{ m}^3 \text{ Pa/mol K})(295 \text{ K})} = 0.882 \text{ mol}$$

Check The units check out, and the answer seems to be the right order of magnitude.

► Practice Exercise

A 4.0-L vessel containing N₂ at STP and a 2.0-L vessel containing H₂ at STP are connected by a valve. If the valve is opened allowing the two gases to mix, what is the mole fraction of hydrogen in the mixture? (a) 0.034 (b) 0.33 (c) 0.50 (d) 0.67 (e) 0.96

Self-Assessment Exercise

- 10.24** At an underwater depth of 100 m, the pressure is 1.11 MPa. What should the partial pressure of oxygen be in the diving gas for the mole fraction of oxygen in the mixture to be 0.21, the same as in air?

- (a) $P_{O_2} = 210 \text{ kPa}$
 (b) $P_{O_2} = 233 \text{ kPa}$
 (c) $P_{O_2} = 5.29 \text{ MPa}$

Exercises

- 10.25** Consider a mixture of two gases, A and B, confined in a closed vessel. A quantity of a third gas, C, is added to the same vessel at the same temperature. How does the addition of gas C affect the following: (a) the partial pressure of gas A, (b) the total pressure in the vessel, (c) the mole fraction of gas B?
- 10.26** A deep-sea diver uses a gas cylinder with a volume of 10.0 L and a content of 51.2 g of O₂ and 32.6 g of He. Calculate the partial pressure of each gas and the total pressure if the temperature of the gas is 19 °C.
- 10.27** The atmospheric concentration of CO₂ gas is presently 407 ppm (parts per million, by volume; that is, 407 L of every 10⁶ L of the atmosphere are CO₂). What is the mole fraction of CO₂ in the atmosphere?
- 10.28** A sample of 5.00 mL of diethylether (C₂H₅OC₂H₅, density = 0.7134 g/mL) is introduced into a 6.00-L vessel

that already contains a mixture of N₂ and O₂, whose partial pressures are $P_{N_2} = 21.08 \text{ kPa}$ and $P_{O_2} = 76.1 \text{ kPa}$. The temperature is held at 35.0 °C, and the diethylether totally evaporates. (a) Calculate the partial pressure of the diethylether. (b) Calculate the total pressure in the container.

- 10.29** A rigid vessel containing a 3:1 mol ratio of carbon dioxide and water vapor is held at 200 °C where it has a total pressure of 202.7 kPa. If the vessel is cooled to 10 °C so that all of the water vapor condenses, what is the pressure of carbon dioxide? Neglect the volume of the liquid water that forms on cooling.
- 10.30** (a) What are the mole fractions of each component in a mixture of 15.08 g of O₂, 8.17 g of N₂, and 2.64 g of H₂? (b) What is the partial pressure in atm of each component of this mixture if it is held in a 15.50 L vessel at 15 °C?

10.24 (b)

Answers to Self-Assessment Exercises

10.6 | The Kinetic-Molecular Theory of Gases



The Roman philosopher Lucretius wrote:

Observe what happens when sunbeams are admitted into a building and shed light on its shadowy places. You will see a multitude of tiny particles...dancing.

In 1827, some 1900 years later, the Scottish botanist Robert Brown observed the movement of microscopic particles while studying pollen grains suspended in water. At first, he thought the movement was due to some living motion but showed it also occurred with inanimate particles such as those found in smoke. It became known as Brownian motion. Both Lucretius and Brown concluded the random motion was due to the particles being constantly bombarded by even smaller bodies—atoms and molecules. Einstein, in a 1905 publication, presented the mathematics behind the observed random movement and used it as indirect evidence of the existence of atoms and molecules.

By the end of this section, you should be able to

- Use the kinetic-molecular theory of gases to explain the gas laws and rates of effusion and diffusion

The ideal gas equation describes *how* gases behave but not *why* they behave as they do. Why does a gas expand when heated at constant pressure? Or why does its pressure increase when the gas is compressed at constant temperature? To understand the physical properties of gases, we need a model that helps us picture what happens to gas particles when conditions such as pressure or temperature change. Such a model, known as the **kinetic-molecular theory of gases**, was developed over a period of about 100 years, culminating in 1857 when Rudolf Clausius (1822–1888) published a complete and satisfactory form of the theory.

The kinetic-molecular theory (the theory of moving molecules) is summarized by the following statements:

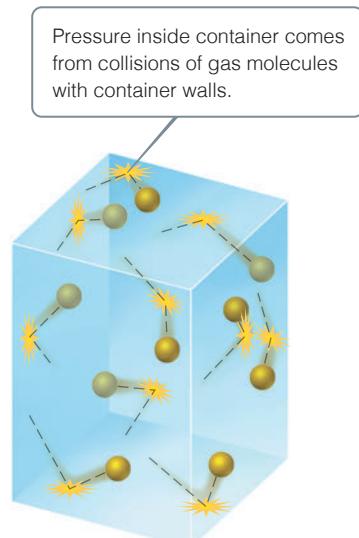
- 1. Random motion** Gases consist of large numbers of molecules that are in continuous, random motion. (The word *molecule* is used here to designate the smallest particle of any gas even though some gases, such as the noble gases, consist of individual atoms. All we learn about gas behavior from the kinetic-molecular theory applies equally to atomic gases.)
- 2. Negligible molecular volume** The combined volume of all the molecules of the gas is negligible relative to the total volume in which the gas is contained.
- 3. Negligible forces** Attractive and repulsive forces between gas molecules are negligible.
- 4. Constant average kinetic energy** Energy can be transferred between molecules during collisions but, as long as temperature remains constant, the *average* kinetic energy of the molecules does not change with time.
- 5. Average kinetic energy proportional to temperature** The average kinetic energy of the molecules is proportional to the absolute temperature. At any given temperature, the molecules of all gases have the same average kinetic energy.

The kinetic-molecular theory explains both pressure and temperature at the molecular level. The pressure of a gas is caused by collisions of the molecules with the walls of the container (**Figure 10.12**). The magnitude of the pressure is determined by how often and how forcefully the molecules strike the walls.

The absolute temperature of a gas is a measure of the *average* kinetic energy of its molecules. If two gases are at the same temperature, their molecules have the same average kinetic energy (statement 5 of the kinetic-molecular theory). If the absolute temperature of a gas is doubled, the average kinetic energy of its molecules doubles. Thus, molecular motion increases with increasing temperature.

Distributions of Molecular Speed

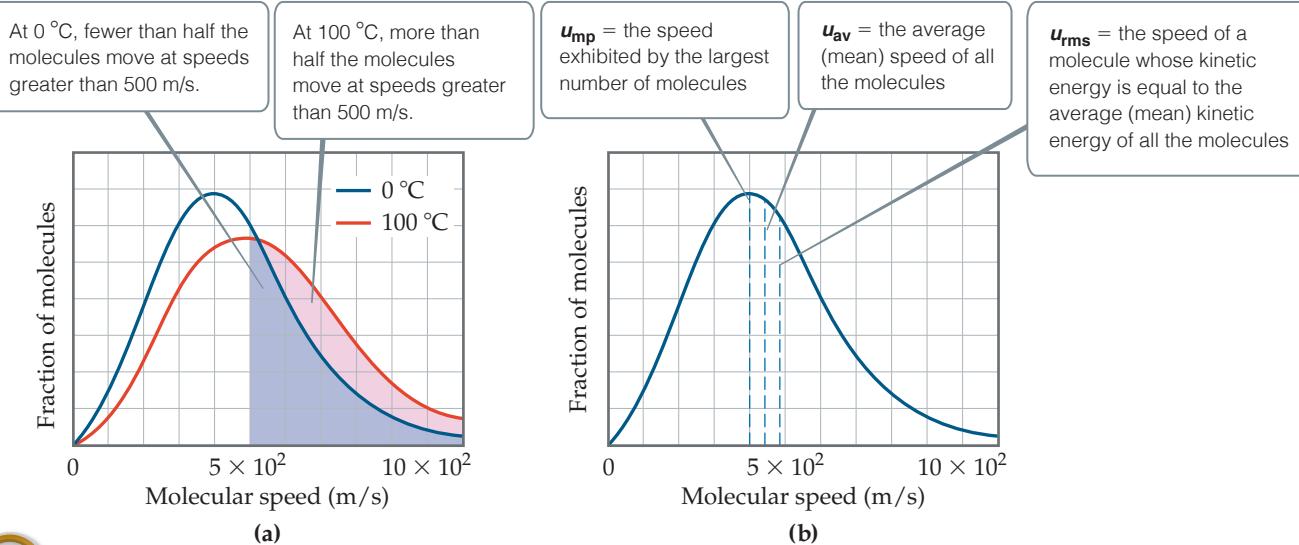
Although collectively the molecules in a sample of gas have an *average* kinetic energy and hence an average speed, the individual molecules are moving at different speeds. Each molecule collides frequently with other molecules. Momentum is conserved in each collision, but one of the colliding molecules might be deflected off at high speed while the other is nearly stopped. The result is that, at any instant, the molecules in the sample have a wide range of speeds. In **Figure 10.13(a)**, which shows the distribution of



▲ **Figure 10.12** The molecular origin of gas pressure.

**Go Figure**

Estimate the fraction of molecules at 100 °C with speeds less than 300 m/s.



▲ **Figure 10.13** Distribution of molecular speeds for nitrogen gas. (a) The effect of temperature on molecular speed. The relative area under the curve for a range of speeds gives the relative fraction of molecules that have those speeds. (b) Position of most probable (u_{mp}), average (u_{av}), and root-mean-square (u_{rms}) speeds of gas molecules. The data shown here are for nitrogen gas at 0 °C.

molecular speeds for nitrogen gas at 0 °C and 100 °C, we see that a larger fraction of the 100 °C molecules moves at the higher speeds. This means that the 100 °C sample has the higher average kinetic energy.

In any graph of the distribution of molecular speeds in a gas sample, the peak of the curve represents the most probable speed, u_{mp} [Figure 10.13(b)]. The most probable speeds in Figure 10.13(a), for instance, are 4×10^2 m/s for the 0 °C sample and 5×10^2 m/s for the 100 °C sample. Figure 10.13(b) also shows the **root-mean-square (rms) speed**, u_{rms} , of the molecules. This is the speed of a molecule possessing a kinetic energy identical to the average kinetic energy of the sample. The rms speed is not quite the same as the average (mean) speed, u_{av} . The difference between the two is small, however. In Figure 10.13(b), for example, the root-mean-square speed is about 4.9×10^2 m/s and the average speed is about 4.5×10^2 m/s.

If you calculate the rms speeds (as we will in Section 10.7), you will find that the rms speed is almost 6×10^2 m/s for the 100 °C sample but slightly less than 5×10^2 m/s for the 0 °C sample. Notice that the distribution curve broadens as we go to a higher temperature, which tells us that the range of molecular speeds increases with temperature.

The rms speed is important because the average kinetic energy of the gas molecules in a sample is equal to $\frac{1}{2}m(u_{rms})^2$. Because mass does not change with temperature, the increase in the average kinetic energy $\frac{1}{2}m(u_{rms})^2$ as the temperature increases implies that the rms speed of the molecules (as well as u_{av} and u_{mp}) increases as temperature increases.

Application of Kinetic-Molecular Theory to the Gas Laws

The empirical observations of gas properties as expressed by the various gas laws are readily understood in terms of the kinetic-molecular theory. The following examples illustrate this point:

- 1. An increase in volume at constant temperature causes pressure to decrease.** A constant temperature means that the average kinetic energy of the gas molecules remains unchanged. This means that the rms speed of the molecules remains unchanged. When the volume is increased, the molecules must move a longer distance between collisions. Consequently, there are fewer collisions per unit time

with the container walls, which means the pressure decreases. Thus, kinetic-molecular theory explains Boyle's law.

2. A temperature increase at constant volume causes pressure to increase.

increase. An increase in temperature means an increase in the average kinetic energy of the molecules and in u_{rms} . Because there is no change in volume, the temperature increase causes more collisions with the walls per unit time because the molecules are all moving faster. Furthermore, the momentum in each collision increases (the molecules strike the walls more forcefully). A greater number of more forceful collisions means the pressure increases, and the theory explains this increase.

A CLOSER LOOK The Ideal Gas Equation

The ideal gas equation can be derived from the five statements given in the text for the kinetic-molecular theory. Rather than perform the derivation, however, let's consider in qualitative terms how the ideal gas equation might follow from these statements. The total force of the molecular collisions on the walls and hence the pressure (force per unit area, Section 10.2) produced by these collisions depend both on how strongly the molecules strike the walls (impulse imparted per collision) and on the rate at which the collisions occur:

$$P \propto \text{impulse imparted per collision} \times \text{collision rate}$$

For a molecule traveling at the rms speed, the impulse imparted by a collision with a wall depends on the momentum of the molecule; that is, it depends on the product of the molecule's mass and speed: mu_{rms} . The collision rate is proportional to the number of molecules per unit volume, n/V , and to their speed, which is u_{rms}

because we are talking about only molecules traveling at this speed. Thus, we have

$$P \propto mu_{\text{rms}} \times \frac{n}{V} \times u_{\text{rms}} \propto \frac{nm(u_{\text{rms}})^2}{V} \quad [10.17]$$

Because the average kinetic energy, $\frac{1}{2}m(u_{\text{rms}})^2$, is proportional to temperature, we have $m(u_{\text{rms}})^2 \propto T$. Making this substitution in Equation 10.17 gives

$$P \propto \frac{nm(u_{\text{rms}})^2}{V} \propto \frac{nT}{V} \quad [10.18]$$

If we put in a proportionality constant, calling it R , the gas constant, you can see that we obtain the ideal gas equation:

$$P = \frac{nRT}{V} \quad [10.19]$$

Related Exercises: 10.32, 10.91



Sample Exercise 10.12

Applying the Kinetic-Molecular Theory

A sample of O₂ gas initially at STP is compressed to a smaller volume at constant temperature. What effect does this change have on (a) the average kinetic energy of the molecules, (b) their average speed, (c) the number of collisions they make with the container walls per unit time, (d) the number of collisions they make with a unit area of container wall per unit time, (e) the pressure?

SOLUTION

Analyze We need to apply the concepts of the kinetic-molecular theory of gases to a gas compressed at constant temperature.

Plan We will determine how each of the quantities in (a)–(e) is affected by the change in volume at constant temperature.

Solve (a) Because the average kinetic energy of the O₂ molecules is determined only by temperature, this energy is unchanged by the compression. (b) Because the average kinetic energy of the molecules does not change, their average speed remains constant. (c) The number of collisions with the walls per unit time increases because the molecules are moving in a smaller volume but with the same average speed as before. Under these conditions they will strike the walls of the container more frequently. (d) The number of collisions with a unit area of wall per unit time increases because the total number of collisions with the walls per unit time increases and the area of the walls decreases. (e) Although the average force with which the molecules collide with the walls remains constant, the pressure increases because there are more collisions per unit area of wall per unit time.

Check In a conceptual exercise of this kind, there is no numerical answer to check. All we can check in such cases is our reasoning in the course of solving the problem. The increase in pressure seen in part (e) is consistent with Boyle's law.

► Practice Exercise

Consider two gas cylinders of the same volume and temperature, one containing 1.0 mol of propane, C₃H₈, and the other 2.0 mol of methane, CH₄. Which of the following statements is true? (a) The C₃H₈ and CH₄ molecules have the same u_{rms} (b) The C₃H₈ and CH₄ molecules have the same average kinetic energy (c) The rate at which the molecules collide with the cylinder walls is the same for both cylinders (d) The gas pressure is the same in both cylinders

Self-Assessment Exercise

10.31 Consider three gases, all at 298 K: Kr, N₂, and NH₃. List the gases in order of increasing average speed of the molecules (or atoms).

- (a) Kr < N₂ < NH₃
- (b) Kr < NH₃ < N₂
- (c) NH₃ < N₂ < Kr
- (d) N₂ < NH₃ < Kr

Exercises

10.32 Indicate which of the following statements regarding the kinetic-molecular theory of gases are correct. (a) The average kinetic energy of a collection of gas molecules at a given temperature is proportional to $m^{1/2}$. (b) The gas molecules are assumed to exert no forces on each other. (c) All the molecules of a gas at a given temperature have the same kinetic energy. (d) The volume of the gas molecules is negligible in comparison to the total volume in which the gas is contained. (e) All gas molecules move with the same speed if they are at the same temperature.

10.33 Radon (Rn) is the heaviest (and only radioactive) member of the noble gases. How much slower is the root-mean-square speed of Rn than He at 300 K?

10.34 (a) Place the following gases in order of increasing average molecular speed at 300 K: CO, SF₆, H₂S, Cl₂, HBr. (b) Calculate the rms speeds of CO and Cl₂ molecules at 300 K. (c) Calculate the most probable speeds of CO and Cl₂ molecules at 300 K.

10.31 (a)

Answers to Self-Assessment Exercises



10.7 | Molecular Effusion and Diffusion



Natural gas is a convenient, efficient fuel source and is transported by pipes, pressurized tankers and in gas bottles. It is colorless and odorless, making the detection of leaks difficult. This is problematic as a buildup of gas in an enclosed space might go undetected and result in an explosion. To guard against this, an additive, usually ethanethiol (CH₃CH₂SH), which has an unpleasant smell that can alert people to the possibility of a leak, is used. This compound has the advantages that very small amounts are detected by the human nose (of the order of a few parts per billion), the compound has long term

stability when added to a gas supply and does not interfere with the combustion of the gas. It is sometimes referred to as ‘stench gas’ and in some countries is used to release into the ventilation system of underground mines to alert the miners in the case of an emergency.

By the end of this section, you should be able to

- Distinguish between effusion and diffusion and relate them to the molar mass of the gas.

According to the kinetic-molecular theory of gases, the average kinetic energy of *any* collection of gas molecules, $\frac{1}{2}m(u_{\text{rms}})^2$, has a specific value at a given temperature. Thus, for two gases at the same temperature a gas composed of low-mass particles, such as He, has the same average kinetic energy as one composed of more massive particles, such as Xe. The mass of the particles in the He sample is smaller than that in the Xe sample. Consequently, the He particles must have a higher rms speed than the Xe particles. The equation that expresses this fact quantitatively is

$$u_{\text{rms}} = \sqrt{\frac{3RT}{M}} \quad [10.20]$$

where M is the molar mass of the particles, which can be derived from the kinetic-molecular theory. Because M appears in the denominator, the less massive the gas particles, the higher their rms speed.

Figure 10.14 shows the distribution of molecular speeds for several gases at 25 °C. Notice how the distributions are shifted toward higher speeds for gases of lower molar masses.

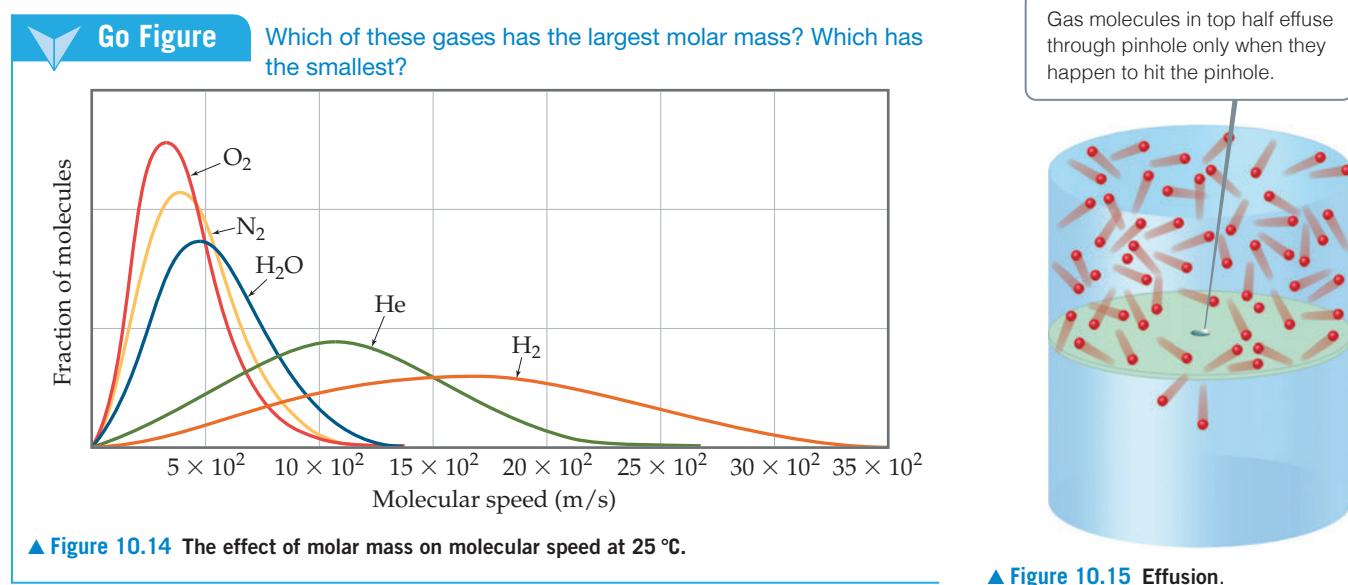
The most probable speed of a gas molecule can also be derived:

$$u_{\text{mp}} = \sqrt{\frac{2RT}{M}} \quad [10.21]$$

The dependence of molecular speed on mass has two interesting consequences. The first is **effusion**, which is the escape of gas molecules through a tiny hole (**Figure 10.15**). The second is **diffusion**, which is the spread of one substance throughout a space or throughout a second substance. For example, the molecules of a perfume diffuse throughout a room.

Graham's Law of Effusion

In 1846, Thomas Graham (1805–1869) discovered that the effusion rate of a gas is inversely proportional to the square root of its molar mass. Assume we have two gases at the same temperature and pressure in two containers with identical pinholes. If the rates





Sample Exercise 10.13

Calculating a Root-Mean-Square Speed

Calculate the rms speed of the molecules in a sample of N₂ gas at 25 °C.

SOLUTION

Analyze We are given the identity of a gas and the temperature, the two quantities we need to calculate the rms speed.

Plan We calculate the rms speed using Equation 10.20.

Solve We must convert each quantity in our equation to SI units. We will also use R in units of J/mol K (Table 10.2) to make the units cancel correctly.

$$T = 25 + 273 = 298 \text{ K}$$

$$\mathcal{M} = 28.0 \text{ g/mol} = 28.0 \times 10^{-3} \text{ kg/mol}$$

$$R = 8.314 \text{ J/mol K} = 8.314 \text{ kg m}^2/\text{s}^2 \text{ mol K} (\text{Since } 1 \text{ J} = 1 \text{ kg m}^2/\text{s}^2)$$

$$\begin{aligned} u_{\text{rms}} &= \sqrt{\frac{3RT}{\mathcal{M}}} \\ &= \sqrt{\frac{3(8.314 \text{ kg m}^2/\text{s}^2 \text{ mol K})(298 \text{ K})}{28.0 \times 10^{-3} \text{ kg/mol}}} = 5.15 \times 10^2 \text{ m/s} \end{aligned}$$

Comment This corresponds to a speed of 1854 km/hr. Because the average molecular weight of air molecules is slightly greater than that of N₂, the rms speed of air molecules is a little smaller than that for N₂.

► Practice Exercise

Fill in the blanks for the following statement: The rms speed of the molecules in a sample of H₂ gas at 300 K will be _____ times larger than the rms speed of O₂ molecules at the same temperature, and the ratio $u_{\text{rms}}(\text{H}_2)/u_{\text{rms}}(\text{O}_2)$ _____ with increasing temperature.

- (a) four, will not change (b) four, will increase (c) sixteen, will not change (d) sixteen, will decrease (e) Not enough information is given to answer this question.

of effusion of the two gases are r_1 and r_2 and their molar masses are \mathcal{M}_1 and \mathcal{M}_2 , **Graham's law** states that

$$\frac{r_1}{r_2} = \sqrt{\frac{\mathcal{M}_2}{\mathcal{M}_1}} \quad [10.22]$$

a relationship that indicates that the lighter gas has the higher effusion rate.

The only way for a molecule to escape from its container is for it to “hit” the hole in the partitioning wall of Figure 10.15. The faster the molecules are moving, the more often they hit the partition wall and the greater the likelihood that a molecule will hit the hole and effuse. This implies that the rate of effusion is directly proportional to the rms speed of the molecules. Because R and T are constant, we have, from Equation 10.22

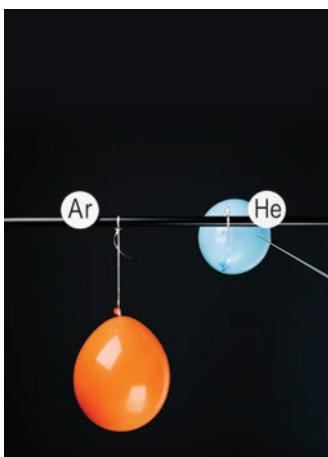
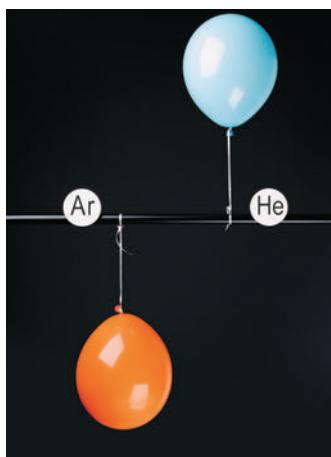
$$\frac{r_1}{r_2} = \frac{u_{\text{rms}1}}{u_{\text{rms}2}} = \sqrt{\frac{3RT/\mathcal{M}_1}{3RT/\mathcal{M}_2}} = \sqrt{\frac{\mathcal{M}_2}{\mathcal{M}_1}} \quad [10.23]$$

As expected from Graham's law, helium escapes from containers through tiny pinhole leaks more rapidly than other gases of higher molecular weight (Figure 10.16).



Go Figure

Because pressure and temperature are constant in this figure but volume changes, which other quantity in the ideal gas equation must also change?



Both gases effuse through pores in balloon, but lighter helium gas effuses faster than heavier argon gas.

▲ Figure 10.16 An illustration of Graham's law of effusion.



Sample Exercise 10.14

Applying Graham's Law

An unknown gas composed of homonuclear diatomic molecules effuses at a rate that is 0.355 times the rate at which O₂ gas effuses at the same temperature. Calculate the molar mass of the unknown and identify it.

SOLUTION

Analyze We are given the rate of effusion of an unknown gas relative to that of O₂ and asked to find the molar mass and identity of the unknown. Thus, we need to connect relative rates of effusion to relative molar masses.

Plan We use Equation 10.22 to determine the molar mass of the unknown gas. If we let r_x and M_x represent the rate of effusion and molar mass of the gas, we can write

$$\frac{r_x}{r_{O_2}} = \sqrt{\frac{M_{O_2}}{M_x}}$$

Solve From the information given,

$$r_x = 0.355 \times r_{O_2}$$

Thus,

$$\frac{r_x}{r_{O_2}} = 0.355 = \sqrt{\frac{32.0 \text{ g/mol}}{M_x}}$$

$$\frac{32.0 \text{ g/mol}}{M_x} = (0.355)^2 = 0.126$$

$$M_x = \frac{32.0 \text{ g/mol}}{0.126} = 254 \text{ g/mol}$$

Because we are told that the unknown gas is composed of homonuclear diatomic molecules, it must be an element. The molar mass must represent twice the atomic weight of the atoms in the unknown gas. We conclude that the unknown gas must have an atomic weight of 127 g/mol and therefore is I₂.

► Calculate the ratio of the effusion rates of N₂ gas and O₂ gas.

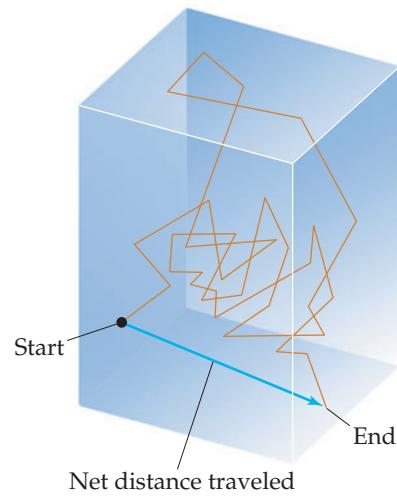
Diffusion and Mean Free Path

Although diffusion, like effusion, is faster for lower-mass molecules than for higher-mass ones, molecular collisions make diffusion more complicated than effusion.

Graham's law, Equation 10.22, approximates the ratio of the diffusion rates of two gases under identical conditions. We can see from the horizontal axis in Figure 10.15 that the speeds of molecules are quite high. For example, the rms speed of molecules of N₂ gas at room temperature is 515 m/s. In spite of this high speed, if someone opens a vial of perfume at one end of a room, some time elapses—perhaps a few minutes—before the scent is detected at the other end of the room. This tells us that the diffusion rate of gases throughout a volume of space is much slower than molecular speeds.* This difference is due to molecular collisions, which occur frequently for a gas at atmospheric pressure—about 10¹⁰ times per second for each molecule. Collisions occur because real gas molecules have finite volumes.

Because of molecular collisions, the direction of motion of a gas molecule is constantly changing. Therefore, the diffusion of a molecule from one point to another consists of many short, straight-line segments as collisions buffet it around in random directions (Figure 10.17).

The average distance traveled by a molecule between collisions, called the molecule's **mean free path**, varies with pressure as the following analogy illustrates. Imagine



*The rate at which the perfume moves across the room also depends on how well stirred the air is from temperature gradients and the movement of people. Nevertheless, even with the aid of these factors, it still takes much longer for the molecules to traverse the room than one would expect from their rms speed.

▲ **Figure 10.17** Diffusion of a gas molecule. For clarity, no other gas molecules in the container are shown.

CHEMISTRY PUT TO WORK Gas Separations

The fact that lighter molecules move at higher average speeds than more massive ones has many interesting applications. For example, developing the atomic bomb during World War II required scientists to separate the relatively low-abundance uranium isotope ^{235}U (0.7%) from the much more abundant ^{238}U (99.3%). This separation was accomplished by converting the uranium into a volatile compound, UF_6 , that was then allowed to pass through a porous barrier (Figure 10.18). Because of the pore diameters, this process is not simple effusion. Nevertheless, the way in which rate of passing through the pores depends on molar mass is essentially the same as that in effusion. The slight difference in molar mass between $^{235}\text{UF}_6$ and $^{238}\text{UF}_6$ caused the molecules to move at slightly different rates:

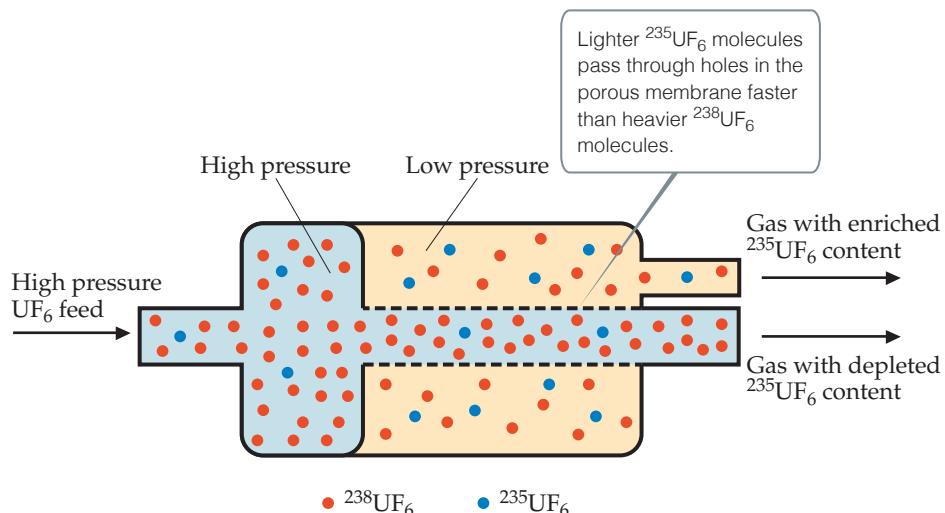
$$\frac{r_{235}}{r_{238}} = \sqrt{\frac{352.04}{349.03}} = 1.0043$$

Thus, the gas initially appearing on the opposite side of the barrier is very slightly enriched in ^{235}U . The process is repeated thousands

of times, leading to a nearly complete separation of the two isotopes. Because of the large number of steps needed to adequately separate the isotopes, gaseous diffusion facilities are large-scale structures.

An increasingly popular method of separating uranium isotopes is by a technique that uses centrifuges. In this procedure, cylindrical rotors containing UF_6 vapor spin at high speed inside an evacuated casing. Molecules of $^{238}\text{UF}_6$ move closer to the spinning walls, whereas molecules of $^{235}\text{UF}_6$ remain in the middle of the cylinders. A stream of gas moves the $^{235}\text{UF}_6$ from the center of one centrifuge into another. Plants that use centrifuges consume less energy than those that use effusion and can be constructed in a more compact, modular fashion.

Related Exercises: 10.37, 10.97



▲ **Figure 10.18 Uranium enrichment by gaseous diffusion.** The lighter $^{235}\text{UF}_6$ effuses through a porous barrier at a slightly faster rate than $^{238}\text{UF}_6$. The pressure difference across the membrane drives the effusion. The enrichment shown here for a single step is exaggerated for illustrative purposes.

walking through a shopping mall. When the mall is crowded (high pressure), the average distance you can walk before bumping into someone is short (short mean free path). When the mall is empty (low pressure), you can walk a long way (long mean free path) before bumping into someone. The mean free path for air molecules at sea level is about 60 nm. At about 100 km in altitude, where the air pressure is much lower, the mean free path is about 10 cm, over 1 million times longer than at the Earth's surface.

Self-Assessment Exercise

- 10.35** One of worst smelling compounds known is thioacetone ($\text{C}_3\text{H}_6\text{S}$). If a sample of thioacetone and ethanethiol ($\text{C}_2\text{H}_6\text{S}$) were released into a laboratory, which compound would travel farther in one minute?

(a) $\text{C}_2\text{H}_6\text{S}$

(b) $\text{C}_3\text{H}_6\text{S}$

Exercises

10.36 Which one or more of the following statements are true?

- (a) O₂ will effuse faster than Cl₂.
- (b) Effusion and diffusion are different names for the same process.
- (c) Perfume molecules travel to your nose by the process of effusion.
- (d) The higher the density of a gas, the shorter the mean free path.

10.37 As discussed in the “Chemistry Put to Work” box in Section 10.7, enriched uranium can be produced by effusion of gaseous UF₆ across a porous membrane. Suppose a process

were developed to allow effusion of gaseous uranium atoms, U(g). Calculate the ratio of effusion rates for ²³⁵U and ²³⁸U, and compare it to the ratio for UF₆ given in the essay.

10.38 A gas of unknown molecular mass was allowed to effuse through a small opening under constant-pressure conditions. It required 105 s for 1.0 L of the gas to effuse. Under identical experimental conditions it required 31 s for 1.0 L of O₂ gas to effuse. Calculate the molar mass of the unknown gas. (Remember that the faster the rate of effusion, the shorter the time required for effusion of 1.0 L; in other words, rate is the amount that diffuses over the time it takes to diffuse.)

10.35 (a)

Answers to Self-Assessment Exercises



10.8 | Real Gases: Deviations from Ideal Behavior



Many people are unaware of the vast network of underground pipelines that undergirds the developed world and that is used to move vast quantities of liquids and gases over considerable distances. The pipeline system consists of large diameter (120 cm) trunk lines at high pressure, with branch lines of small diameter (35 cm) at lower pressure for local transport to and from the trunk lines. Methane-rich natural gas is processed to remove particulates, water, and various gas impurities, such as hydrogen sulfide and carbon dioxide. The gas is then compressed to pressure of between 3.5 MPa and 10 MPa depending on the diameter of the pipe. The pressure is maintained by compressor stations along the pipeline at roughly 100 km intervals. The high pressures mean that chemical engineers can no longer rely on the ideal gas equation but employ more accurate equations to describe the behavior of the gas.

By the end of this section, you should be able to

- Describe why a real gas does not conform to the ideal gas equation

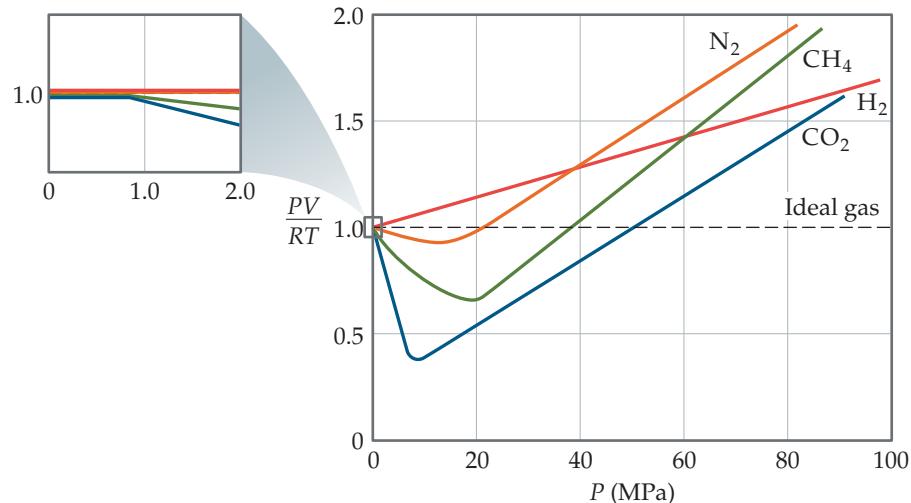
The extent to which a real gas departs from ideal behavior can be seen by rearranging the ideal gas equation to solve for n :

$$\frac{PV}{RT} = n \quad [10.24]$$

This form of the equation tells us that for 1 mol of ideal gas, the quantity PV/RT equals 1 at all pressures. In **Figure 10.19**, PV/RT is plotted as a function of P for 1 mol of several real gases. At high pressures (generally above 1.013 MPa), the deviation from ideal behavior ($PV/RT = 1$) is large and different for each gas. *Real gases, in other words, do not behave ideally at high pressure.* At lower pressures (usually below 1.013 MPa), however, the deviation from ideal behavior is small, and we can use the ideal gas equation without generating serious error.

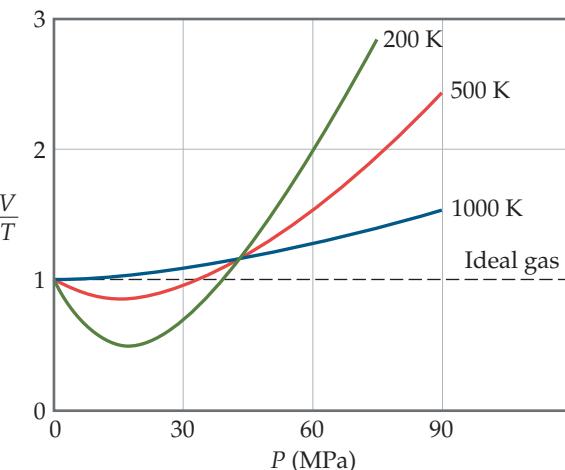
Deviation from ideal behavior also depends on temperature. As temperature increases, the behavior of a real gas more nearly approaches that of the ideal gas (**Figure 10.20**). In general, *the deviation from ideal behavior increases as temperature decreases*, becoming significant near the temperature at which the gas liquefies.

► **Figure 10.19** The effect of pressure on the behavior of several real gases. Data for 1 mol of gas in all cases. Data for N₂, CH₄, and H₂ are at 300 K; for CO₂ data are at 313 K because under high pressure CO₂ liquefies at 300 K.



Go Figure

True or false: Nitrogen gas behaves more like an ideal gas as the temperature increases.



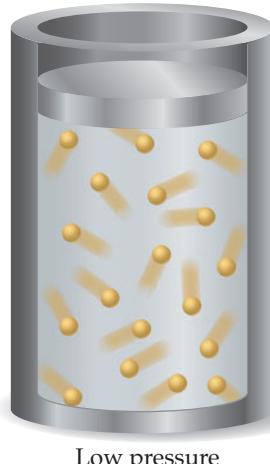
▲ **Figure 10.20** The effect of temperature and pressure on the behavior of nitrogen gas.

The basic assumptions of the kinetic-molecular theory of gases give us insight into why real gases deviate from ideal behavior. The molecules of an ideal gas are assumed to occupy no space and have no attraction for one another. *Real molecules, however, do have finite volumes and do attract one another.* As Figure 10.21 shows, the unoccupied space in which real molecules can move is less than the container volume. At low pressures, the combined volume of the gas molecules is negligible relative to the container volume. Thus, the unoccupied volume available to the molecules is essentially the container volume. At high pressures, the combined volume of the gas molecules is *not* negligible relative to the container volume. Now the unoccupied volume available to the molecules is less than the container volume. At high pressures, therefore, gas volumes tend to be slightly greater than those predicted by the ideal gas equation.

Another reason for nonideal behavior at high pressures is that the attractive forces between molecules come into play at the short intermolecular distances found when molecules are crowded together at high pressures. Because of these attractive forces, the impact of a given molecule with the container wall is lessened. If we could stop the motion in a gas, as illustrated in Figure 10.22, we would see that a molecule about to collide with the wall experiences the attractive forces of nearby molecules. These attractions lessen the force with which the molecule hits the wall. As a result, the gas pressure is less than that of an ideal gas. This effect decreases PV/RT to below its ideal value, as seen at the lower pressures in Figures 10.20 and 10.21. When the pressure is sufficiently high, however, the volume effects dominate and PV/RT increases to above the ideal value.

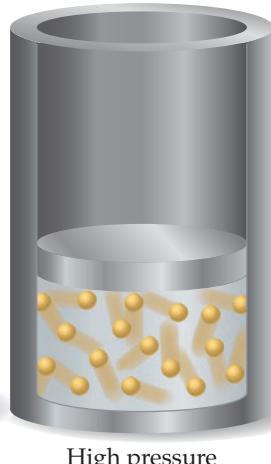
Temperature determines how effective attractive forces between gas molecules are in causing deviations from ideal behavior at lower pressures. Figure 10.21 shows that, at pressures below about 40 MPa, cooling increases the extent to which a gas deviates from ideal behavior. As the gas cools, the average kinetic energy of the molecules decreases. This drop in kinetic energy means the molecules do not have the energy needed to overcome intermolecular attraction, and the molecules will be more likely to stick to each other than bounce off each other.

Gas molecules occupy a small fraction of the total volume.



Low pressure

Gas molecules occupy a larger fraction of the total volume.



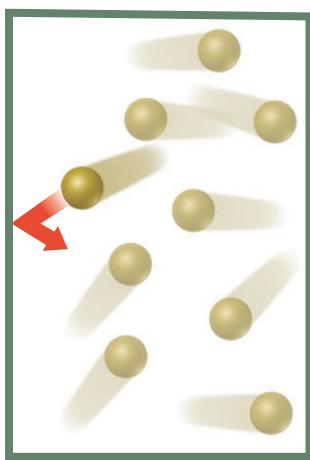
High pressure

▲ Figure 10.21 Gases behave more ideally at low pressure than at high pressure.

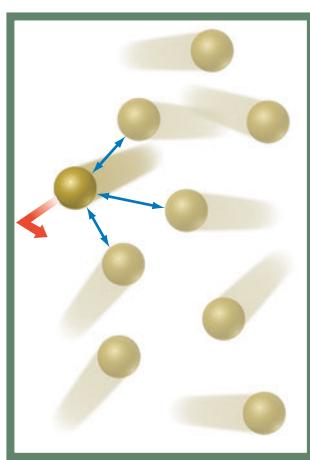


Go Figure

How would you expect the pressure of a gas to change if suddenly the intermolecular forces were repulsive rather than attractive?



Ideal gas



Real gas

▲ Figure 10.22 In any real gas, attractive intermolecular forces reduce pressure to values lower than in an ideal gas.

As the temperature of a gas increases—as, say, from 200 to 1000 K in Figure 10.21—the negative deviation of PV/RT from the ideal value of 1 disappears. As noted earlier, the deviations seen at high temperatures stem mainly from the effect of the finite volumes of the molecules.

The van der Waals Equation

Engineers and scientists who work with gases at high pressures often cannot use the ideal gas equation because departures from ideal behavior are too large. One useful equation developed to predict the behavior of real gases was proposed by the Dutch scientist Johannes van der Waals (1837–1923).

As we have seen, a real gas has a lower pressure due to intermolecular forces, and a larger volume due to the finite volume of the molecules, relative to an ideal gas. Van der Waals recognized that it would be possible to retain the form of the ideal gas equation, $PV = nRT$, if corrections were made to the pressure and the volume. He introduced two constants for these corrections: a , a measure of how strongly the gas molecules attract one another, and b , a measure of the finite volume occupied by the molecules. His description of gas behavior is known as the **van der Waals equation**:

$$\left(P + \frac{n^2a}{V^2} \right) (V - nb) = nRT \quad [10.25]$$

The term n^2a/V^2 accounts for the attractive forces. The equation adjusts the pressure upward by adding n^2a/V^2 because attractive forces between molecules tend to reduce the pressure (Figure 10.22). The added term has the form n^2a/V^2 because the attractive force between pairs of molecules increases as the square of the number of molecules per unit volume, $(n/V)^2$.

The term nb accounts for the small but finite volume occupied by the gas molecules (Figure 10.22). The van der Waals equation subtracts nb to adjust the volume downward to give the volume that would be available to the molecules in the ideal case. The constants a and b , called *van der Waals constants*, are experimentally determined positive quantities that differ from one gas to another. Notice in Table 10.3 that a and b generally increase with increasing molecular mass. Larger, more massive molecules have larger volumes and tend to have greater intermolecular attractive forces.

TABLE 10.3 Van der Waals Constants for Gas Molecules

Substance	a (L ² kPa/mol ²)	b (L/mol)
He	3.46	0.02370
Ne	21.4	0.0171
Ar	135	0.0322
Kr	235	0.0398
Xe	425	0.0510
H ₂	24.7	0.0266
N ₂	141	0.0391
O ₂	138	0.0318
F ₂	107	0.0290
Cl ₂	658	0.0562
H ₂ O	553	0.0305
NH ₃	423	0.0371
CH ₄	228	0.0428
CO ₂	364	0.0427
CCl ₄	2067	0.1383



Sample Exercise 10.15

Using the van der Waals Equation

If 10.00 mol of an ideal gas were confined to 22.41 L at 0.0 °C, it would exert a pressure of 1.013 MPa. Use the van der Waals equation and Table 10.3 to estimate the pressure exerted by 10.00 mol of Cl₂(g) in 22.41 L at 0.0 °C.

SOLUTION

Analyze We need to determine a pressure. Because we will use the van der Waals equation, we must identify the appropriate values for the constants in the equation.

Plan Rearrange Equation 10.25 to isolate P .

Solve Substituting $n = 10.00 \text{ mol}$, $R = 8.314 \text{ m}^3 \text{ Pa/mol K}$, $T = 273.2 \text{ K}$, $V = 22.41 \text{ L} = 2.241 \times 10^{-2} \text{ m}^3$, $a = 658 \text{ L}^2 \text{ kPa/mol}^2$, and $b = 0.0562 \text{ L/mol}$:

$$\begin{aligned} P &= \frac{(10.00 \text{ mol})(8.314 \text{ m}^3 \text{ Pa/mol K})(273.2 \text{ K})}{2.241 \times 10^{-2} \text{ m}^3 - (10.00 \text{ mol})(5.62 \times 10^{-5} \text{ m}^3/\text{mol})} \\ &\quad - \frac{(10.00 \text{ mol})^2(658 \text{ L}^2 \text{ kPa/mol}^2)}{(22.41 \text{ L})^2} \\ &= 1039.6 \text{ kPa} - 130.7 \text{ kPa} = 908.9 \text{ kPa} \end{aligned}$$

Comment Notice that the term 1039.6 kPa is the pressure corrected for molecular volume. This value is higher than the ideal value, 1.013 MPa, because the volume in which the molecules are free to move is smaller than the container volume, 22.41 L. Thus, the molecules collide more frequently with the container walls and the pressure is higher than that of a real gas. The term 130.7 kPa makes a correction in the opposite direction for intermolecular forces. The correction for intermolecular forces is the larger of the two, and thus the pressure 908.9 kPa is smaller than would be observed for an ideal gas.

► Practice Exercise

A sample of 1.000 mol of CO₂(g) is confined to a 3.000-L container at 0.000 °C. Calculate the pressure of the gas using **(a)** the ideal gas equation and **(b)** the van der Waals equation.



Sample Integrative Exercise

Putting Concepts Together

Cyanogen, a highly toxic gas, is 46.2% C and 53.8% N by mass. At 25 °C and 100.1 kPa, 1.05 g of cyanogen occupies 0.500 L.

(a) What is the molecular formula of cyanogen? Predict **(b)** its molecular structure and **(c)** its polarity.

SOLUTION

Analyze We need to determine the molecular formula of a gas from elemental analysis data and data on its properties. Then we need to predict the structure of the molecule and from that, its polarity.

(a) Plan We can use the percentage composition of the compound to calculate its empirical formula. Then we can determine the molecular formula by comparing the mass of the empirical formula with the molar mass.

Solve To determine the empirical formula, we assume we have a 100-g sample and calculate the number of moles of each element in the sample:

$$\text{Moles C} = (46.2 \text{ g C}) \left(\frac{1 \text{ mol C}}{12.01 \text{ g C}} \right) = 3.85 \text{ mol C}$$

$$\text{Moles N} = (53.8 \text{ g N}) \left(\frac{1 \text{ mol N}}{14.01 \text{ g N}} \right) = 3.84 \text{ mol N}$$

Because the ratio of the moles of the two elements is essentially 1:1, the empirical formula is CN. To determine the molar mass, we use Equation 10.11.

$$\begin{aligned} M &= \frac{dRT}{P} = \frac{(1.05 \text{ g}/0.500 \text{ L})(10^3 \text{ m}^3/\text{L})(8.314 \text{ m}^3 \text{ Pa/mol K})(298 \text{ K})}{100.1 \times 10^3 \text{ Pa}} \\ &= 52.0 \text{ g/mol} \end{aligned}$$

The molar mass associated with the empirical formula CN is $12.0 + 14.0 = 26.0 \text{ g/mol}$. Dividing the molar mass by that of its

empirical formula gives $(52.0 \text{ g/mol})/(26.0 \text{ g/mol}) = 2.00$. Thus, the molecule has twice as many atoms of each element as the empirical formula, giving the molecular formula C₂N₂.

(b) Plan To determine the molecular structure, we must determine the Lewis structure. We can then use the VSEPR model to predict the structure.

Solve The molecule has $2(4) + 2(5) = 18$ valence-shell electrons. By trial and error, we seek a Lewis structure with 18 valence electrons in which each atom has an octet and the formal charges are as low as possible. The structure



meets these criteria. (This structure has zero formal charge on each atom.)

The Lewis structure shows that each atom has two electron domains. (Each nitrogen has a nonbonding pair of electrons and a triple bond, whereas each carbon has a triple bond and a single bond.) Thus, the electron-domain geometry around each atom is linear, causing the overall molecule to be linear.

(c) Plan To determine the polarity of the molecule, we must examine the polarity of the individual bonds and the overall geometry of the molecule.

Solve Because the molecule is linear, we expect the two dipoles created by the polarity in the carbon–nitrogen bond to cancel each other, leaving the molecule with no dipole moment.

Self-Assessment Exercise

10.39 Under which conditions do you expect H₂ gas to deviate most from ideal behavior?

- (a) 70 K and 101.3 kPa
- (b) 70 K and 506.6 kPa
- (c) 350 K and 202.7 kPa

Exercises

10.40 (a) List two experimental conditions under which gases deviate from ideal behavior. (b) List two reasons why the gases deviate from ideal behavior.

10.41 Based on their respective van der Waals constants (Table 10.3), is Ar or CO₂ expected to behave more nearly like an ideal gas at high pressures?

10.42 Calculate the pressure that CCl₄ will exert at 80 °C if 1.00 mol occupies 33.3 L, assuming that (a) CCl₄ obeys the ideal gas equation; (b) CCl₄ obeys the van der Waals equation. (Values for the van der Waals constants are given in

Table 10.3.) (c) Which would you expect to deviate more from ideal behavior under these conditions, Cl₂ or CCl₄? Explain.

10.43 Table 10.3 shows that the van der Waals *b* parameter has units of L/mol. This means that we can calculate the sizes of atoms or molecules from the *b* parameter. Refer back to the discussion in Section 7.3. Is the van der Waals radius we calculate from the *b* parameter of Table 10.3 more closely associated with the bonding or nonbonding atomic radius discussed there? Explain.

10.39 (b)

Answers to Self-Assessment Exercises



Chapter Summary and Key Terms

CHARACTERISTICS OF GASES (SECTION 10.1) Substances that are gases at room temperature tend to be molecular substances with low molar masses. Air, a mixture composed mainly of N₂ and O₂, is the most common gas we encounter. Some liquids and solids can also exist in the gaseous state, where they are known as **vapors**. Gases are compressible; they mix in all proportions because their component molecules are far apart from each other.

PRESSURE (SECTION 10.2) To describe the state or condition of a gas, we must specify four variables: pressure (*P*), volume (*V*), temperature (*T*), and quantity (*n*). Volume is usually measured in liters, temperature in kelvins, and quantity of gas in moles. **Pressure** is the force per unit area and is expressed in SI units as **pascals**, Pa (1 Pa = 1 N/m²). A related unit, the **bar**, equals 10⁵ Pa. In chemistry, **standard atmospheric pressure** is used to define the **atmosphere** (atm) and the **torr** (also called the millimeter of mercury). One atmosphere of pressure equals 101.325 kPa, or 760 torr. A barometer is often used to measure the atmospheric pressure. A manometer can be used to measure the pressure of enclosed gases.

THE GAS LAWS (SECTION 10.3) Studies have revealed several simple gas laws: For a constant quantity of gas at constant temperature, the volume of the gas is inversely proportional to the pressure (**Boyle's law**). For a fixed quantity of gas at constant pressure, the volume is directly proportional to its absolute temperature (**Charles's law**). Equal volumes of gases at the same temperature and pressure contain equal numbers of molecules (**Avogadro's hypothesis**). For a gas at constant temperature and pressure, the volume of the gas is directly proportional to the number of moles of gas (**Avogadro's law**). Each of these gas laws is a special case of the ideal gas equation.

THE IDEAL GAS EQUATION (SECTIONS 10.4) The **ideal gas equation**, $PV = nRT$, is the equation of state for an **ideal gas**.

The term *R* in this equation is the **gas constant**. We can use the ideal gas equation to calculate variations in one variable when one or more of the others are changed. Most gases at pressures less than 10 atm and temperatures near 273 K and above obey the ideal gas equation reasonably well. The conditions of 273 K (0 °C) and 1 atm are known as the **standard temperature and pressure (STP)**. In all applications of the ideal gas equation, we must remember to convert temperatures to the absolute-temperature scale (the kelvin scale).

Using the ideal gas equation, we can relate the density of a gas to its molar mass: $\mathcal{M} = dRT/P$. We can also use the ideal gas equation to solve problems involving gases as reactants or products in chemical reactions.

GAS MIXTURES AND PARTIAL PRESSURES (SECTION 10.5) In gas mixtures, the total pressure is the sum of the **partial pressures** that each gas would exert if it were present alone under the same conditions (**Dalton's law of partial pressures**). The partial pressure of a component of a mixture is equal to its mole fraction times the total pressure: $P_i = X_i P_t$. The **mole fraction** *X* is the ratio of the moles of one component of a mixture to the total moles of all components.

THE KINETIC-MOLECULAR THEORY OF GASES (SECTION 10.6) The **kinetic-molecular theory of gases** accounts for the properties of an ideal gas in terms of a set of statements about the nature of gases. Briefly, these statements are as follows: Molecules are in continuous chaotic motion. The volume of gas molecules is negligible compared to the volume of their container. The gas molecules neither attract nor repel each other. The average kinetic energy of the gas molecules is proportional to the absolute temperature and does not change if the temperature remains constant.

The individual molecules of a gas do not all have the same kinetic energy at a given instant. Their speeds are distributed over a

wide range; the distribution varies with the molar mass of the gas and with temperature. The **root-mean-square (rms) speed**, u_{rms} , varies in proportion to the square root of the absolute temperature and inversely with the square root of the molar mass: $u_{\text{rms}} = \sqrt{3RT/M}$. The most probable speed of a gas molecule is given by $u_{\text{mp}} = \sqrt{2RT/M}$.

MOLECULAR EFFUSION AND DIFFUSION (SECTION 10.7) It follows from kinetic-molecular theory that the rate at which a gas undergoes **effusion** (escapes through a tiny hole) is inversely proportional to the square root of its molar mass (**Graham's law**). The **diffusion** of one gas through the space occupied by a second gas is another phenomenon related to the speeds at which molecules move. Because moving molecules undergo frequent collisions with one another, the **mean free path**—the

mean distance traveled between collisions—is short. Collisions between molecules limit the rate at which a gas molecule can diffuse.

REAL GASES: DEVIATIONS FROM IDEAL BEHAVIOR (SECTION 10.8)

Departures from ideal behavior increase in magnitude as pressure increases and as temperature decreases. Real gases depart from ideal behavior because (1) the molecules possess finite volume and (2) the molecules experience attractive forces for one another. These two effects make the volumes of real gases larger and their pressures smaller than those of an ideal gas. The **van der Waals equation** is an equation of state for gases, which modifies the ideal gas equation to account for intrinsic molecular volume and intermolecular forces.

Learning Outcomes After studying this chapter, you should be able to:

- Calculate pressure and convert between pressure units with an emphasis on torr and atmospheres. (Section 10.2)
Related Exercises: 10.57, 10.58, 10.59
- Calculate P , V , n , or T using the ideal gas equation. (Section 10.4)
Related Exercises: 10.66, 10.69, 10.73
- Explain how the gas laws relate to the ideal gas equation and apply the gas laws in calculations. (Sections 10.3 and 10.4)
Related Exercises: 10.10, 10.69, 10.71
- Calculate the density or molecular weight of a gas. (Section 10.4)
Related Exercises: 10.13, 10.75, 10.78
- Calculate the volume of gas consumed or formed in a chemical reaction. (Section 10.4) *Related Exercises: 10.80, 10.83*
- Calculate the total pressure of a gas mixture given its partial pressures or given information for calculating partial pressures. (Section 10.5) *Related Exercises: 10.50, 10.84, 10.85*
- Describe the kinetic-molecular theory of gases and how it explains the pressure and temperature of a gas, the gas laws, and the rates of effusion and diffusion. (Sections 10.6 and 10.7)
Related Exercises: 10.52, 10.91, 10.93, 10.97
- Explain why intermolecular attractions and molecular volumes cause real gases to deviate from ideal behavior at high pressure or low temperature. (Section 10.8)
Related Exercises: 10.40, 10.100, 10.120

Key Equations

- $PV = nRT$ [10.5] Ideal gas equation
- $\frac{P_1V_1}{T_1} = \frac{P_2V_2}{T_2}$ [10.8] The combined gas law, showing how P , V , and T are related for a constant n
- $d = \frac{PM}{RT}$ [10.10] Density or molar mass of a gas
- $P_t = P_1 + P_2 + P_3 + \dots$ [10.12] Relating the total pressure of a gas mixture to the partial pressures of its components (Dalton's law of partial pressures)
- $P_1 = \left(\frac{n_1}{n_t}\right)P_t = X_1P_t$ [10.16] Relating partial pressure to mole fraction
- $u_{\text{rms}} = \sqrt{\frac{3RT}{M}}$ [10.20] Definition of the root-mean-square (rms) speed of gas molecules
- $\frac{r_1}{r_2} = \sqrt{\frac{M_2}{M_1}}$ [10.22] Relating the relative rates of effusion of two gases to their molar masses
- $\left(P + \frac{n^2a}{V^2}\right)(V - nb) = nRT$ [10.25] The van der Waals equation

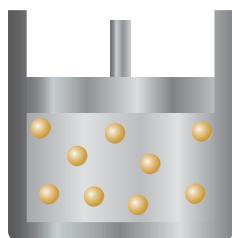
Exercises

Visualizing Concepts

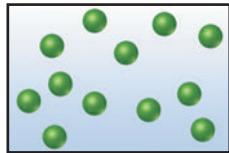
10.44 Mars has an average atmospheric pressure of 709 Pa. Would it be easier or harder to drink from a straw on Mars than on Earth? Explain. [Section 10.2]

10.45 You have a sample of gas in a container with a movable piston, such as the one in the drawing. (a) Redraw the container to show what it might look like if the temperature of the gas is increased from 300 to 500 K while the pressure is kept constant. (b) Redraw the container to show what it might look

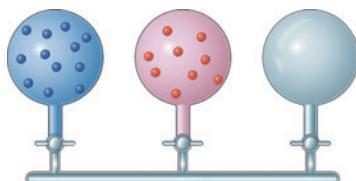
like if the external pressure on the piston is increased from 101.3 kPa to 202.7 kPa while the temperature is kept constant. (c) Redraw the container to show what it might look like if the temperature of the gas decreases from 300 to 200 K while the pressure is kept constant (assume the gas does not liquefy). [Section 10.3]



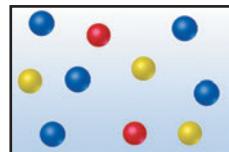
- 10.46** Consider the sample of gas depicted here. What would the drawing look like if the volume and temperature remained constant while you removed enough of the gas to decrease the pressure by a factor of 2? [Section 10.3]
- It would contain the same number of molecules.
 - It would contain half as many molecules.
 - It would contain twice as many molecules.
 - There is insufficient data to say.



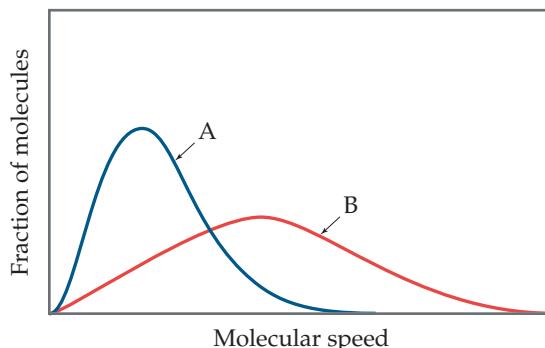
- 10.47** Imagine that the reaction $2 \text{CO}(g) + \text{O}_2(g) \longrightarrow 2 \text{CO}_2(g)$ occurs in a container that has a piston that moves to maintain a constant pressure when the reaction occurs at constant temperature. Which of the following statements describes how the volume of the container changes due to the reaction: (a) the volume increases by 50%, (b) the volume increases by 33%, (c) the volume remains constant, (d) the volume decreases by 33%, (e) the volume decreases by 50%. [Sections 10.3 and 10.4]
- 10.48** Suppose you have a fixed amount of an ideal gas at a constant volume. If the pressure of the gas is doubled while the volume is held constant, what happens to its temperature? [Section 10.4]
- 10.49** The apparatus shown here has two gas-filled containers and one empty container, all attached to a hollow horizontal tube. When the valves are opened and the gases are allowed to mix at constant temperature, what is the distribution of atoms in each container? Assume that the containers are of equal volume and ignore the volume of the connecting tube. Which gas has the greater partial pressure after the valves are opened? [Section 10.6]



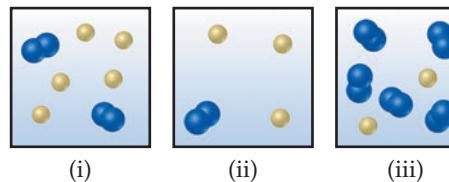
- 10.50** The accompanying drawing represents a mixture of three different gases. (a) Rank the three components in order of increasing partial pressure. (b) If the total pressure of the mixture is 141.9 kPa, calculate the partial pressure of each gas. [Section 10.6]



- 10.51** On a single plot, qualitatively sketch the distribution of molecular speeds for (a) $\text{Kr}(g)$ at -50°C , (b) $\text{Kr}(g)$ at 0°C , (c) $\text{Ar}(g)$ at 0°C . [Section 10.6]
- 10.52** Consider the following graph. (a) If curves A and B refer to two different gases, He and O_2 , at the same temperature, which curve corresponds to He? (b) If A and B refer to the same gas at two different temperatures, which represents the higher temperature? (c) For each curve, which speed is highest: the most probable speed, the root-mean-square speed, or the average speed? [Section 10.6]



- 10.53** Consider the following samples of gases:

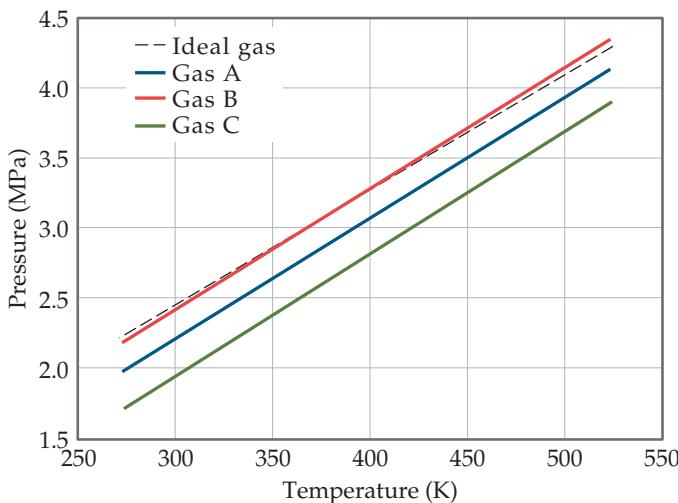


● = He
●● = N_2

If the three samples are all at the same temperature, rank them with respect to (a) total pressure, (b) partial pressure of helium, (c) density, (d) average kinetic energy of particles. [Sections 10.5 and 10.6]

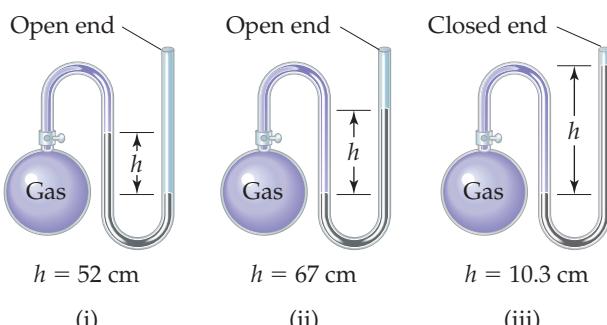
- 10.54** A thin glass tube 1 m long is filled with Ar gas at 101.3 kPa, and the ends are stoppered with cotton plugs as shown. HCl gas is introduced at one end of the tube, and simultaneously NH_3 gas is introduced at the other end. When the two gases diffuse through the cotton plugs down the tube and meet, a white ring appears due to the formation of $\text{NH}_4\text{Cl}(s)$. At which location—*a*, *b*, or *c*—do you expect the ring to form? [Section 10.7]

- 10.55** This shows the change in pressure as the temperature increases for a 1-mol sample of a gas confined to a 1-L container. The four plots correspond to an ideal gas and three real gases: CO₂, N₂, and Cl₂. **(a)** At room temperature, all three real gases have a pressure less than the ideal gas. Which van der Waals constant, *a* or *b*, accounts for the influence intermolecular forces have in lowering the pressure of a real gas? **(b)** Use the van der Waals constants in Table 10.3 to match the labels in the plot (A, B, and C) with the respective gases (CO₂, N₂, and Cl₂). [Section 10.8]



Gas Characteristics; Pressure (Sections 10.1 and 10.2)

- 10.56** **(a)** Are you more likely to see the density of a gas reported in g/mL, g/L, or kg/cm³? **(b)** Which units are appropriate for expressing atmospheric pressures, N, Pa, atm, kg/m²? **(c)** Which is most likely to be a gas at room temperature and ordinary atmospheric pressure, F₂, Br₂, K₂O.
- 10.57** A person weighing 75 kg is standing on a three-legged stool. The stool momentarily tilts so that the entire weight is on one foot. If the contact area of each foot is 5.0 cm², calculate the pressure exerted on the underlying surface in **(a)** bars, **(b)** atmospheres, and **(c)** pounds per square inch.
- 10.58** **(a)** How high in meters must a column of ethanol be to exert a pressure equal to that of a 100-mm column of mercury? The density of ethanol is 0.79 g/mL, whereas that of mercury is 13.6 g/mL. **(b)** What pressure, in atmospheres, is exerted on the body of a diver if she is 10 m below the surface of the water when the atmospheric pressure is 100 kPa? Assume that the density of the water is 1.00 = 1.00 × 10³ kg/m³. The gravitational constant is 9.81 m/s², and 1 Pa = 1 kg/ms².
- 10.59** The highest barometric pressure ever recorded was 823.7 torr at Agata in Siberia, Russia on December 31, 1968. Convert this pressure to **(a)** atm, **(b)** mm Hg, **(c)** pascals, **(d)** bars, **(e)** psi.
- 10.60** If the atmospheric pressure is 0.995 atm, what is the pressure of the enclosed gas in each of the three cases depicted in the drawing? Assume that the gray liquid is mercury.



The Gas Laws (Section 10.3)

- 10.61** A fixed quantity of gas at 25 °C exhibits a pressure of 99 kPa and occupies a volume of 4.00 L. **(a)** Calculate the volume the gas will occupy if the pressure is increased to 202.6 kPa while the temperature is held constant. **(b)** Calculate the volume the gas will occupy if the temperature is increased to 100 °C while the pressure is held constant.
- 10.62** **(a)** Amonton's law expresses the relationship between pressure and temperature. Use Charles's law and Boyle's law to derive the proportionality relationship between *P* and *T*. **(b)** If a car tire is filled to a pressure of 220.6 kPa measured at 24 °C, what will be the tire pressure if the tires heat up to 49 °C during driving?
- 10.63** **(a)** What conditions are represented by the abbreviation STP? **(b)** What is the molar volume of an ideal gas at STP? **(c)** Room temperature is often assumed to be 25 °C. Calculate the molar volume of an ideal gas at 25 °C and 101.3 kPa pressure. **(d)** If you measure pressure in bars instead of atmospheres, calculate the corresponding value of *R* in L bar/mol K.
- 10.64** To derive the ideal-gas equation, we assume that the volume of a gas's atoms/molecules can be neglected. Given that the atomic radius of argon is 0.097 nm, and knowing that a sphere has a volume of $4\pi r^3/3$, calculate the fraction of space that Ar atoms occupy in a sample of argon at STP.
- 10.65** Suppose you are given two 2-L flasks and told that one contains a gas of molar mass 28, the other a gas of molar mass 56, both at the same temperature and pressure. The mass of gas in the flask A is 1.0 g and the mass of gas in the flask B is 2.0 g. Which flask contains the gas of molar mass 28, and which contains the gas of molar mass 56?
- 10.66** Complete the following table for an ideal gas:
- | <i>P</i> | <i>V</i> | <i>n</i> | <i>T</i> |
|------------|----------|-----------|----------|
| 303.98 kPa | 3.00 L | 1.500 mol | ? K |
| 50.663 kPa | 0.750 L | ? mol | 300 K |
| 101.33 kPa | ? L | 3.333 mol | 300 K |
| ? kPa | .750 L | 0.750 mol | 298 K |
- 10.67** **(a)** Calculate the number of molecules in a deep breath of air whose volume is 2.25 L at body temperature, 37 °C, and a pressure of 97.99 kPa. **(b)** The adult blue whale has a lung capacity of 5.0×10^3 L. Calculate the mass of air (assume an average molar mass of 28.98 g/mol) contained in an adult blue whale's lungs at 0.0 °C and 101.33 kPa, assuming the air behaves ideally.
- 10.68** **(a)** If the pressure exerted by ozone, O₃, in the stratosphere is 304 Pa and the temperature is 250 K, how many ozone molecules are in a liter? **(b)** Carbon dioxide makes up approximately 0.04% of Earth's atmosphere. If you collect a 2.0-L sample from the atmosphere at sea level (101.33 kPa) on a warm day (27 °C), how many CO₂ molecules are in your sample?
- 10.69** A scuba diver's tank contains 2.50 kg of O₂ compressed into a volume of 11.0 L. **(a)** Calculate the gas pressure inside the tank at 10 °C. **(b)** What volume would this oxygen occupy at 25 °C and 101.33 kPa?
- 10.70** An aerosol spray can with a volume of 125 mL contains 1.30 g of propane gas (C₃H₈) as a propellant. **(a)** If the can is at 25 °C, what is the pressure in the can? **(b)** What volume would the butane occupy at STP? **(c)** The can's label says that exposure to temperatures above 50 °C may cause the can to burst. What is the pressure in the can at this temperature?

10.71 A 50.0 g sample of solid CO₂ (dry ice) is added at -100 °C to an evacuated (all of the gas removed) container with a volume of 5.0 L. If the container is sealed and then allowed to warm to room temperature (25 °C) so that the entire solid CO₂ is converted to a gas, what is the pressure inside the container?

10.72 A 334-mL cylinder for use in chemistry lectures contains 5.225 g of helium at 23 °C. How many grams of helium must be released to reduce the pressure to 7.60 MPa assuming ideal gas behavior?

10.73 Chlorine is widely used to purify municipal water supplies and to treat swimming pool waters. Suppose that the volume of a particular sample of Cl₂ gas is 8.70 L at 119.3 kPa and 24 °C. **(a)** How many grams of Cl₂ are in the sample? **(b)** What volume will the Cl₂ occupy at STP? **(c)** At what temperature will the volume be 15.00 L if the pressure is 116.8 kPa? **(d)** At what pressure will the volume equal 5.00 L if the temperature is 58 °C?

10.74 In an experiment reported in the scientific literature, male cockroaches were made to run at different speeds on a miniature treadmill while their oxygen consumption was measured. In 30 minutes, the average cockroach (running at 0.08 km/h) consumed 1.0 mL of O₂ at 101.33 kPa pressure and 20 °C per gram of insect mass. **(a)** How many moles of O₂ would be consumed in 1 day by a 6.3-g cockroach moving at this speed? **(b)** This same cockroach is caught by a child and placed in a 2.0 L fruit jar with a tight lid. Assuming the same level of continuous activity as in the research, how much of the available O₂ will the cockroach consume in 1 day? (Air is 21 mol % O₂.)

10.75 Rank the following gases from least dense to most dense at 101.33 kPa and 298 K: O₂, Ar, NH₃, HCl.

10.76 Which of the following statements best explains why a closed balloon filled with helium gas rises in air?

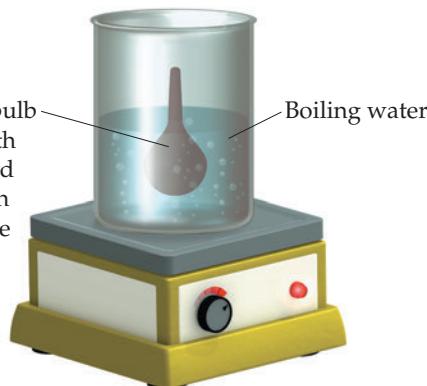
- (a)** Helium is a monatomic gas, whereas nearly all the molecules that make up air, such as nitrogen and oxygen, are diatomic.
- (b)** The average speed of helium atoms is greater than the average speed of air molecules, and the greater speed of collisions with the balloon walls propels the balloon upward.
- (c)** Because the helium atoms are of lower mass than the average air molecule, the helium gas is less dense than air. The mass of the balloon is thus less than the mass of the air displaced by its volume.
- (d)** Because helium has a lower molar mass than the average air molecule, the helium atoms are in faster motion. This means that the temperature of the helium is greater than the air temperature. Hot gases tend to rise.

10.77 Which of the following statements best explains why nitrogen gas at STP is less dense than Xe gas at STP?

- (a)** Because Xe is a noble gas, there is less tendency for the Xe atoms to repel one another, so they pack more densely in the gaseous state.
- (b)** Xe atoms have a higher mass than N₂ molecules. Because both gases at STP have the same number of molecules per unit volume, the Xe gas must be denser.
- (c)** The Xe atoms are larger than N₂ molecules and thus take up a larger fraction of the space occupied by the gas.
- (d)** Because the Xe atoms are much more massive than the N₂ molecules, they move more slowly and thus exert less upward force on the gas container and make the gas appear denser.

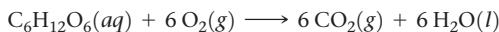
10.78 In the Dumas-bulb technique for determining the molar mass of an unknown liquid, you vaporize the sample of a liquid that boils below 100 °C in a boiling-water bath and determine the mass of vapor required to fill the bulb. From the following data, calculate the molar mass of the unknown

liquid: mass of unknown vapor, 1.012 g; volume of bulb, 354 cm³; pressure, 98.93 kPa; temperature, 99 °C.



10.79 The molar mass of a volatile substance was determined by the Dumas-bulb method described in Exercise 10.78. The unknown vapor had a mass of 2.55 g; the volume of the bulb was 500 mL, pressure 101.33 kPa, and temperature 37 °C. Calculate the molar mass of the unknown vapor.

10.80 The metabolic oxidation of glucose, C₆H₁₂O₆, in our bodies produces CO₂, which is expelled from our lungs as a gas:



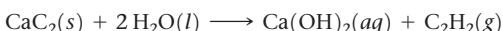
(a) Calculate the volume of dry CO₂ produced at normal body temperature, 37 °C, and 101.33 kPa when 10.0 g of glucose is consumed in this reaction. **(b)** Calculate the volume of oxygen you would need, at 100 kPa and 298 K, to completely oxidize 15.0 g of glucose.

10.81 In a "Kipp generator", hydrogen gas is produced when zinc flakes react with hydrochloric acid:



If 30.0 mL of wet H₂ is collected over water at 20 °C and a barometric pressure of 101.33 kPa, how many grams of Zn have been consumed? (The vapor pressure of water is tabulated in Appendix B.)

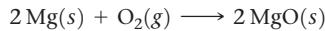
10.82 Acetylene gas, C₂H₂(g), can be prepared by the reaction of calcium carbide with water:



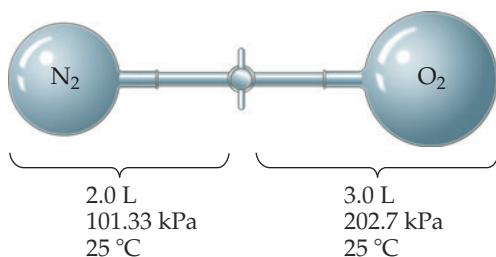
Calculate the volume of C₂H₂ that is collected over water at 23 °C by reaction of 1.524 g of CaC₂ if the total pressure of the gas is 100.4 kPa. (The vapor pressure of water is tabulated in Appendix B.)

Partial Pressures (Section 10.5)

10.83 Magnesium can be used as a "getter" in evacuated enclosures to react with the last traces of oxygen. (The magnesium is usually heated by passing an electric current through a wire or ribbon of the metal.) If an enclosure of 5.67 L has a partial pressure of O₂ of 7.066 mPa at 30 °C, what mass of magnesium will react according to the following equation?



10.84 Consider the apparatus shown in the following drawing. **(a)** When the valve between the two containers is opened and the gases are allowed to mix, how does the volume occupied by the N₂ gas change? What is the partial pressure of N₂ after mixing? **(b)** How does the volume of the O₂ gas change when the gases mix? What is the partial pressure of O₂ in the mixture? **(c)** What is the total pressure in the container after the gases mix?



- 10.85** A mixture containing 0.50 mol $\text{H}_2(g)$, 1.00 mol $\text{O}_2(g)$, and 3.50 mol $\text{N}_2(g)$ is confined in a 25.0-L vessel at 25 °C. **(a)** Calculate the total pressure of the mixture. **(b)** Calculate the partial pressure of each of the gases in the mixture.
- 10.86** A plasma-screen TV contains thousands of tiny cells filled with a mixture of Xe, Ne, and He gases that emits light of specific wavelengths when a voltage is applied. A particular plasma cell, 0.900 mm × 0.300 mm × 10.0 mm, contains 4% Xe in a 1:1 Ne:He mixture at a total pressure of 66.66 kPa. Calculate the number of Xe, Ne, and He atoms in the cell and state the assumptions you need to make in your calculation.
- 10.87** A piece of dry ice (solid carbon dioxide) with a mass of 20.0 g is placed in a 25.0-L vessel that already contains air at 50.66 kPa and 25 °C. After the carbon dioxide has totally sublimed, what is the partial pressure of the resultant CO_2 gas, and the total pressure in the container at 25 °C?
- 10.88** If 5.15 g of Ag_2O is sealed in a 75.0-mL tube filled with 101.3 kPa of N_2 gas at 32 °C, and the tube is heated to 320 °C, the Ag_2O decomposes to form oxygen and silver. What is the total pressure inside the tube assuming the volume of the tube remains constant?
- 10.89** A quantity of N_2 gas originally held at 531.96 kPa pressure in a 1.00-L container at 26 °C is transferred to a 12.5-L container at 20 °C. A quantity of O_2 gas originally at 531.96 kPa and 26 °C in a 5.00 L container is transferred to this same container. What is the total pressure in the new container?
- 10.90** A sample of 3.00 g of $\text{SO}_2(g)$ originally in a 5.00 L vessel at 21 °C is transferred to a 10.0 L vessel at 26 °C. A sample of 2.35 g of $\text{N}_2(g)$ originally in a 2.50 L vessel at 20 °C is transferred to this same 10.0 L vessel. **(a)** What is the partial pressure of $\text{SO}_2(g)$ in the larger container? **(b)** What is the partial pressure of $\text{N}_2(g)$ in this vessel? **(c)** What is the total pressure in the vessel?
- Kinetic-Molecular Theory of Gases; Effusion and Diffusion (Sections 10.6 and 10.7)**
- 10.91** Determine whether each of the following changes will increase, decrease, or not affect the rate with which gas molecules collide with the walls of their container: **(a)** increasing the volume of the container, **(b)** increasing the temperature, **(c)** increasing the molar mass of the gas.
- 10.92** You have an evacuated container of fixed volume and known mass and introduce a known mass of a gas sample. Measuring the pressure at constant temperature over time, you are surprised to see it slowly dropping. You measure the mass of the gas-filled container and find that the mass is what it should be—gas plus container—and the mass does not change over time, so you do not have a leak. Suggest an explanation for your observations.
- 10.93** The temperature of a 5.00-L container of N_2 gas is increased from 20 °C to 250 °C. If the volume is held constant, predict qualitatively how this change affects the following: **(a)** the average kinetic energy of the molecules; **(b)** the root-mean-square speed of the molecules; **(c)** the strength of the

impact of an average molecule with the container walls; **(d)** the total number of collisions of molecules with walls per second.

- 10.94** Suppose you have two 1 L flasks, one containing N_2 at STP, the other containing CH_4 at STP. How do these systems compare with respect to **(a)** number of molecules, **(b)** density, **(c)** average kinetic energy of the molecules, **(d)** rate of effusion through a pinhole leak?
- 10.95** **(a)** Place the following gases in order of increasing average molecular speed at 25 °C: O_2 , Ar, CO, HCl, CH_4 . **(b)** Calculate the rms speed of CO molecules at 25 °C. **(c)** Calculate the most probable speed of an argon atom in the stratosphere, where the temperature is 0 °C.
- 10.96** At constant pressure, the mean free path (λ) of a gas molecule is directly proportional to temperature. At constant temperature, λ is inversely proportional to pressure. If you compare two different gas molecules at the same temperature and pressure, λ is inversely proportional to the square of the diameter of the gas molecules. Put these facts together to create a formula for the mean free path of a gas molecule with a proportionality constant (call it R_{mfp} , like the ideal gas constant) and define units for R_{mfp} .
- 10.97** Hydrogen has two naturally occurring isotopes, ^1H and ^2H . Chlorine also has two naturally occurring isotopes, ^{35}Cl and ^{37}Cl . Thus, hydrogen chloride gas consists of four distinct types of molecules: $^1\text{H}^{35}\text{Cl}$, $^1\text{H}^{37}\text{Cl}$, $^2\text{H}^{35}\text{Cl}$, and $^2\text{H}^{37}\text{Cl}$. Place these four molecules in order of increasing rate of effusion.
- 10.98** Arsenic(III) sulfide sublimes readily, even below its melting point of 320 °C. The molecules of the vapor phase are found to effuse through a tiny hole at 0.52 times the rate of effusion of Xe atoms under the same conditions of temperature and pressure. What is the molecular formula of arsenic(III) sulfide in the gas phase?

Nonideal Gas Behavior (Section 10.8)

- 10.99** The planet Jupiter has a surface temperature of 140 K and a mass 318 times that of Earth. Mercury (the planet) has a surface temperature between 600 K and 700 K and a mass 0.05 times that of Earth. On which planet is the atmosphere more likely to obey the ideal gas law? Explain.
- 10.100** Which statement concerning the van der Waals constants a and b is true?
- (a)** The magnitude of a relates to molecular volume, whereas b relates to attractions between molecules.
 - (b)** The magnitude of a relates to attractions between molecules, whereas b relates to molecular volume.
 - (c)** The magnitudes of a and b depend on pressure.
 - (d)** The magnitudes of a and b depend on temperature.
- 10.101** In Sample Exercise 10.15, we found that ten mole of Cl_2 confined to 22.41 L at 0 °C deviated slightly from ideal behavior. Calculate the pressure exerted by 1.00 mol Cl_2 confined to a smaller volume, 5.00 L, at 25 °C. **(a)** First use the ideal gas equation and **(b)** then use the van der Waals equation for your calculation. (Values for the van der Waals constants are given in Table 10.3.) **(c)** Why is the difference between the result for an ideal gas and that calculated using the van der Waals equation greater when the gas is confined to 5.00 L compared to 22.4 L?
- 10.102** Table 10.3 shows that the van der Waals b parameter has units of L/mol . This implies that we can calculate the size of atoms or molecules from b . Using the value of b for Xe, calculate the radius of a Xe atom and compare it to the value found in Figure 7.7, that is, 140 pm. Recall that the volume of a sphere is $(4/3)\pi r^3$.

Additional Exercises

10.103 Torricelli, who invented the barometer, used mercury in its construction because mercury has a very high density, which makes it possible to make a more compact barometer than one based on a less dense fluid. Calculate the density of mercury using the observation that the column of mercury is 760 mm high when the atmospheric pressure is 1.01×10^5 Pa. Assume the tube containing the mercury is a cylinder with a constant cross-sectional area.

10.104 Consider a lake that is about 40 m deep. A gas bubble with a diameter of 1.0 mm originates at the bottom of a lake where the pressure is 405.3 kPa. Calculate its volume when the bubble reaches the surface of the lake where the pressure is 98 kPa, assuming that the temperature does not change.

10.105 A 6.0 L tank is filled with helium gas at a pressure of 2 MPa. How many balloons (each 2.00 L) can be inflated to a pressure of 101.3 kPa, assuming that the temperature remains constant and that the tank cannot be emptied below 101.3 kPa?

10.106 A 500 mL incandescent light bulb is filled with 1.5×10^{-5} mol of xenon to minimize the rate of evaporation of the tungsten filament. What is the pressure of xenon in the light bulb at 25 °C?

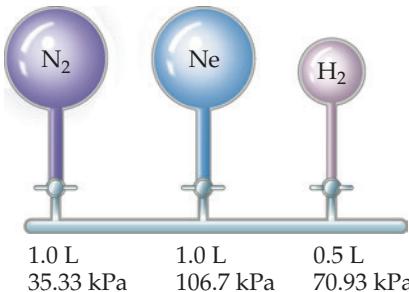
10.107 Carbon dioxide, which is recognized as the major contributor to global warming as a “greenhouse gas,” is formed when fossil fuels are combusted, as in electrical power plants fueled by coal, oil, or natural gas. One potential way to reduce the amount of CO₂ added to the atmosphere is to store it as a compressed gas in underground formations. Consider a 1000 megawatt coal-fired power plant that produces about 6×10^6 tons of CO₂ per year. (a) Assuming ideal gas behavior, 101.3 kPa, and 27 °C, calculate the volume of CO₂ produced by this power plant. (b) If the CO₂ is stored underground as a liquid at 10 °C and 12.16 MPa and a density of 1.2 g/cm³, what volume does it possess? (c) If it is stored underground as a gas at 30 °C and 7.09 MPa, what volume does it occupy?

10.108 Propane, C₃H₈, liquefies under modest pressure, allowing a large amount to be stored in a container. (a) Calculate the number of moles of propane gas in a 20 L container at 709.3 kPa and 25 °C. (b) Calculate the number of moles of liquid propane that can be stored in the same volume if the density of the liquid is 0.590 g/mL. (c) Calculate the ratio of the number of moles of liquid to moles of gas. Discuss this ratio in light of the kinetic-molecular theory of gases.

10.109 Nickel carbonyl, Ni(CO)₄, is one of the most toxic substances known. The present maximum allowable concentration in laboratory air during an 8 hr workday is 1 ppb (parts per billion) by volume, which means that there is one mole of Ni(CO)₄ for every 10^9 moles of gas. Assume 24 °C and 101.3 kPa pressure. What mass of Ni(CO)₄ is allowable in a laboratory room that is 3.5 m × 6.0 m × 2.5 m?

10.110 When a large evacuated flask is filled with argon gas, its mass increases by 3.224 g. When the same flask is again evacuated and then filled with a gas of unknown molar mass, the mass increase is 8.102 g. (a) Based on the molar mass of argon, estimate the molar mass of the unknown gas. (b) What assumptions did you make in arriving at your answer?

10.111 Consider the arrangement of bulbs shown in the drawing. Each of the bulbs contains a gas at the pressure shown. What is the pressure of the system when all the stopcocks are opened, assuming that the temperature remains constant? (We can neglect the volume of the capillary tubing connecting the bulbs.)

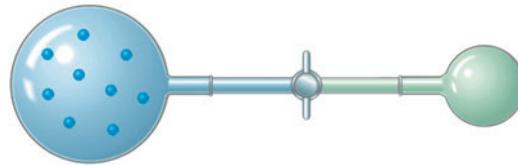


10.112 Assume that a single cylinder of an automobile engine has a volume of 524 cm³. (a) If the cylinder is full of air at 74 °C and 99.3 kPa, how many moles of O₂ are present? (The mole fraction of O₂ in dry air is 0.2095.) (b) How many grams of C₈H₁₈ could be combusted by this quantity of O₂, assuming complete combustion with formation of CO₂ and H₂O?

10.113 Assume that an exhaled breath of air consists of 74.8% N₂, 15.3% O₂, 3.7% CO₂, and 6.2% water vapor. (a) If the total pressure of the gases is 99.8 kPa, calculate the partial pressure of each component of the mixture. (b) If the volume of the exhaled gas is 455 mL and its temperature is 37 °C, calculate the number of moles of CO₂ exhaled. (c) How many grams of glucose (C₆H₁₂O₆) would need to be metabolized to produce this quantity of CO₂? (The chemical reaction is the same as that for combustion of C₆H₁₂O₆. See Section 3.2 and Exercise 10.80.)

10.114 An 8.40 g sample of argon and an unknown mass of H₂ are mixed in a flask at room temperature. The partial pressure of the argon is 44.0 kPa, and that of the hydrogen is 57.33 kPa. What is the mass of the hydrogen?

10.115 An ideal gas at a pressure of 152 kPa is contained in a bulb of unknown volume. A stopcock is used to connect this bulb with a previously evacuated bulb that has a volume of 0.800 L as shown here. When the stopcock is opened, the gas expands into the empty bulb. If the temperature is held constant during this process and the final pressure is 92.66 kPa, what is the volume of the bulb that was originally filled with gas?



10.116 The density of a gas of unknown molar mass was measured as a function of pressure at 0 °C, as in the table that follows. (a) Determine a precise molar mass for the gas. [Hint: Graph d/P versus P.] (b) Why is d/P not a constant as a function of pressure?

Pressure (kPa)	101.3	67.48	50.66	33.74	25.33
Density (g/L)	2.3074	1.5263	1.1401	0.7571	0.5660

10.117 A glass vessel fitted with a stopcock valve has a mass of 337.428 g when evacuated. When filled with Ar, it has a mass of 339.854 g. When evacuated and refilled with a mixture of Ne and Ar, under the same conditions of temperature and pressure, it has a mass of 339.076 g. What is the mole percent of Ne in the gas mixture?

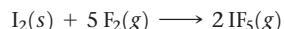
- 10.118** You have a sample of gas at 0 °C. You wish to increase the rms speed by a factor of 3. To what temperature should the gas be heated?
- 10.119** Consider the following gases, all at STP: Ne, SF₆, N₂, CH₄. **(a)** Which gas is most likely to depart from the assumption of the kinetic-molecular theory that says there are no attractive or repulsive forces between molecules? **(b)** Which one is closest to an ideal gas in its behavior? **(c)** Which one has the highest root-mean-square molecular speed at a given temperature? **(d)** Which one has the highest total molecular volume relative to the space occupied by the gas? **(e)** Which has the highest average kinetic-molecular energy? **(f)** Which one would effuse more rapidly than N₂? **(g)** Which one would have the largest van der Waals *b* parameter?
- 10.120** Does the effect of intermolecular attraction on the properties of a gas become more significant or less significant if **(a)** the gas is compressed to a smaller volume at constant temperature; **(b)** the temperature of the gas is increased at constant volume?

Integrative Exercises

- 10.124** Cyclopropane, a gas used with oxygen as a general anesthetic, is composed of 85.7% C and 14.3% H by mass. **(a)** If 1.56 g of cyclopropane has a volume of 1.00 L at 99.7 kPa and 50.0 °C, what is the molecular formula of cyclopropane? **(b)** Judging from its molecular formula, would you expect cyclopropane to deviate more or less than Ar from ideal gas behavior at moderately high pressures and room temperature? Explain. **(c)** Would cyclopropane effuse through a pinhole faster or more slowly than methane, CH₄?
- 10.125** Consider the combustion reaction between 1.00 L of liquid methanol (density = 0.850 g/mL) and 500 L of oxygen gas measured at STP. The products of the reaction are CO₂(g) and H₂O(g). Calculate the volume of liquid H₂O formed if the reaction goes to completion and you condense the water vapor.
- 10.126** An herbicide is found to contain only C, H, N, and Cl. The complete combustion of a 100.0-mg sample of the herbicide in excess oxygen produces 83.16 mL of CO₂ and 73.30 mL of H₂O vapor expressed at STP. A separate analysis shows that the sample also contains 16.44 mg of Cl. **(a)** Determine the percentage of the composition of the substance. **(b)** Calculate its empirical formula. **(c)** What other information would you need to know about this compound to calculate its true molecular formula?
- 10.127** A 4.00 g sample of a mixture of CaO and BaO is placed in a 1.00-L vessel containing CO₂ gas at a pressure of 97.33 kPa and a temperature of 25 °C. The CO₂ reacts with the CaO and BaO, forming CaCO₃ and BaCO₃. When the reaction is complete, the pressure of the remaining CO₂ is 20.0 kPa. **(a)** Calculate the number of moles of CO₂ that have reacted. **(b)** Calculate the mass percentage of CaO in the mixture.
- 10.128** Ammonia and hydrogen chloride react to form solid ammonium chloride:
- $$\text{NH}_3(\text{g}) + \text{HCl}(\text{g}) \longrightarrow \text{NH}_4\text{Cl}(\text{s})$$
- Two 2.00 L flasks at 25 °C are connected by a valve, as shown in the drawing. One flask contains 5.00 g of NH₃(g), and the other contains 5.00 g of HCl(g). When the valve is opened, the gases react until one is completely consumed. **(a)** Which gas will remain in the system after the reaction is complete? **(b)** What will be the final pressure of the system after the reaction is complete? (Neglect
- 10.121** Which of the noble gases other than radon would you expect to depart most readily from ideal behavior? Use the density data in Table 7.8 to show evidence in support of your answer.
- 10.122** It turns out that the van der Waals constant *b* equals four times the total volume actually occupied by the molecules of a mole of gas. Using this figure, calculate the fraction of the volume in a container actually occupied by Ar atoms **(a)** at STP, **(b)** at 20.27 MPa pressure and 0 °C. (Assume for simplicity that the ideal gas equation still holds.)
- 10.123** Large amounts of nitrogen gas are used in the manufacture of ammonia, principally for use in fertilizers. Suppose 120.00 kg of N₂(g) is stored in a 1100.0-L metal cylinder at 280 °C. **(a)** Calculate the pressure of the gas, assuming ideal gas behavior. **(b)** By using the data in Table 10.3, calculate the pressure of the gas according to the van der Waals equation. **(c)** Under the conditions of this problem, which correction dominates, the one for finite volume of gas molecules or the one for attractive interactions?
- the volume of the ammonium chloride formed.) **(c)** What mass of ammonium chloride will be formed?
- | | | |
|---------------------|--|--------|
| NH ₃ (g) | | HCl(g) |
| 5.00 g | | 5.00 g |
| 2.00 L | | 2.00 L |
| 25 °C | | 25 °C |
- 10.129** Gas pipelines are used to deliver natural gas (methane, CH₄) to the various regions of the United States. The total volume of natural gas that is delivered is on the order of 2.7×10^{12} L per day, measured at STP. Calculate the total enthalpy change for combustion of this quantity of methane. (Note: Less than this amount of methane is actually combusted daily. Some of the delivered gas is passed through to other regions.)
- 10.130** Chlorine dioxide gas (ClO₂) is used as a commercial bleaching agent. It bleaches materials by oxidizing them. In the course of these reactions, the ClO₂ is itself reduced. **(a)** What is the Lewis structure for ClO₂? **(b)** Why do you think that ClO₂ is reduced so readily? **(c)** When a ClO₂ molecule gains an electron, the chlorite ion, ClO₂⁻, forms. Draw the Lewis structure for ClO₂⁻. **(d)** Predict the O—Cl—O bond angle in the ClO₂⁻ ion. **(e)** One method of preparing ClO₂ is by the reaction of chlorine and sodium chlorite:
- $$\text{Cl}_2(\text{g}) + 2 \text{NaClO}_2(\text{s}) \longrightarrow 2 \text{ClO}_2(\text{g}) + 2 \text{NaCl}(\text{s})$$
- If you allow 15.0 g of NaClO₂ to react with 2.00 L of chlorine gas at a pressure of 152.0 kPa at 21 °C, how many grams of ClO₂ can be prepared?
- 10.131** Natural gas is very abundant in many Middle Eastern oil fields. However, the costs of shipping the gas to markets in other parts of the world are high because it is necessary to liquefy the gas, which is mainly methane and has a boiling point at atmospheric pressure of -164 °C. One possible strategy is to oxidize the methane to methanol, CH₃OH, which has a boiling point of 65 °C and can therefore be shipped more readily. Suppose that $3.03 \times 10^8 \text{ m}^3$ of methane at atmospheric pressure and 25 °C is oxidized to

methanol. (a) What volume of methanol is formed if the density of CH_3OH is 0.791 g/mL? (b) Write balanced chemical equations for the oxidations of methane and methanol to $\text{CO}_2(g)$ and $\text{H}_2\text{O}(l)$. Calculate the total enthalpy change for complete combustion of the $3.03 \times 10^8 \text{ m}^3$ of methane just described and for complete combustion of the equivalent amount of methanol, as calculated in part (a). (c) Methane, when liquefied, has a density of 0.466 g/mL; the density of methanol at 25 °C is 0.791 g/mL. Compare the enthalpy change upon combustion of a unit volume of liquid methane and liquid methanol. From the standpoint of energy production, which substance has the higher enthalpy of combustion per unit volume?

- 10.132** Gaseous iodine pentafluoride, IF_5 , can be prepared by the reaction of solid iodine and gaseous fluorine:



A 5.00-L flask containing 10.0 g of I_2 is charged with 10.0 g of F_2 , and the reaction proceeds until one of

the reagents is completely consumed. After the reaction is complete, the temperature in the flask is 125 °C. (a) What is the partial pressure of IF_5 in the flask? (b) What is the mole fraction of IF_5 in the flask (c) Draw the Lewis structure of IF_5 . (d) What is the total mass of reactants and products in the flask?

- 10.133** A 6.53-g sample of a mixture of magnesium carbonate and calcium carbonate is treated with excess hydrochloric acid. The resulting reaction produces 1.72 L of carbon dioxide gas at 28 °C and 99.06 kPa pressure. (a) Write balanced chemical equations for the reactions that occur between hydrochloric acid and each component of the mixture. (b) Calculate the total number of moles of carbon dioxide that forms from these reactions. (c) Assuming that the reactions are complete, calculate the percentage by mass of magnesium carbonate in the mixture.

Design an Experiment

You are given a cylinder of an unknown, nonradioactive, noble gas and tasked to determine its molar mass and use that value to identify the gas. The tools available to you are several empty mylar balloons that are about the size of a grapefruit when inflated (gases diffuse through mylar much more slowly than conventional latex balloons), an analytical balance, and three graduated glass beakers of different sizes (100 mL, 500 mL, and 2 L). (a) To how many significant figures would you need to determine the molar mass

to identify the gas? (b) Propose an experiment or series of experiments that would allow you to determine the molar mass of the unknown gas. Describe the tools, calculations, and assumptions you would need to use. (c) If you had access to a broader range of analytical instruments, describe an alternative way you could identify the gas using any experimental methods that you have learned about in the earlier chapters.