5 Gases and the Kinetic-Molecular Theory

Key Principles
to focus on while studying this chapter

- The physical properties of gases differ significantly from those of liquids and solids because gas particles are much farther apart. ***(Section 5.1)***
- *Pressure* is a force acting on an area; the atmosphere's gases exert a pressure on Earth's surface that is measured with a *barometer.* ***(Section 5.2)***
- Four gas variables—*volume* (V), *pressure* (P), *temperature* (T), and *amount* (n)—are *interdependent*. For a hypothetical *ideal gas*, volume changes *linearly* with a change in any one of the other variables, as long as the remaining two are held constant. These behaviors are described by gas laws *(Boyle's, Charles's,* and *Avogadro's)*, which are combined into the *ideal gas law* ($PV = nRT$). Most simple gases behave ideally at ordinary pressures and temperatures. ***(Section 5.3)***
- Rearrangements of the ideal gas law are used to calculate the *density* and *molar mass* of a gas and the *partial pressure* of each gas in a gas mixture *(Dalton's law)*. We use gas variables (P, V, and T) in stoichiometry problems to find the amounts (n) of gaseous reactants or products in a reaction. ***(Section 5.4)***
- To explain the behavior of gases, the *kinetic-molecular theory* postulates that an ideal gas consists of *points of mass moving in straight lines between elastic collisions* (no loss of energy). A key result of the theory is that, at a given temperature, the particles of a gas have a range of speeds, but all gases have the same average kinetic energy. Thus, temperature is a measure of *molecular motion*, as given by the average kinetic energy of gas particles. ***(Section 5.5)***
- The theory also predicts that heavier gas particles move more slowly on average than lighter ones, and, thus, two gases *effuse* (move through a tiny hole into a vacuum) or *diffuse* (move through one another) at rates inversely proportional to the square roots of their molar masses *(Graham's law)*. ***(Section 5.5)***
- At extremely low temperature and high pressure, *real gas behavior deviates* from ideal behavior because the actual volume of the gas particles and the attractions (and repulsions) they experience during collisions become important factors. To account for real gas behavior, the ideal gas law is revised to the more accurate *van der Waals equation.* ***(Section 5.6)***

The Power of Expanding Gas At 180°C, the bit of water inside a kernel of popcorn vaporizes, and the gas pressure reaches more than nine times that of the atmosphere. The hull ruptures, and the corn's starch and proteins form an expanded foamy mass.

Outline

People have been studying the behavior of gases and the other states of matter throughout history; in fact, three of the four "elements" proposed by the ancient Greeks were air (gas), water (liquid), and earth (solid). Yet, despite millennia of observations, many questions remain. In this chapter and its companion, Chapter 12, we examine the physical states and their interrelations. Here, we highlight the gaseous state, the one we understand best. However, we'll put aside the *chemical* behavior unique to each specific gas and focus instead *on the **physical** behavior common to all gases.* For instance, although the particular gases differ, the same physical behaviors underlie the operation of a car and the baking of bread, the thrust of a rocket engine and the explosion of a kernel of popcorn, the process of breathing and the creation of thunder.

CONCEPTS & SKILLS TO REVIEW
before studying this chapter

- physical states of matter (Section 1.1)
- SI unit conversions (Section 1.4)
- amount-mass-number conversions (Section 3.1)

5.1 • AN OVERVIEW OF THE PHYSICAL STATES OF MATTER

Most substances can exist as a solid, a liquid, or a gas under appropriate conditions of pressure and temperature. In Chapter 1, we used the relative position and motion of the particles of a substance to distinguish how each state fills a container (see Figure 1.2). Recall that:

- A gas adopts the container shape and fills it, because its particles are far apart and move randomly.
- A liquid adopts the container shape to the extent of its volume and forms an upper surface because its particles are close together but free to move around each other.
- A solid has a fixed shape regardless of the container shape, because its particles are close together and held rigidly in place.

Figure 5.1 focuses on the three states of bromine.

Several other aspects of their behaviors distinguish gases from liquids and solids:

1. *Gas volume changes significantly with pressure.* When a sample of gas is confined to a container of variable volume, such as a cylinder with a piston, *increasing* the force on the piston *decreases* the gas volume. Removing the force allows the volume to

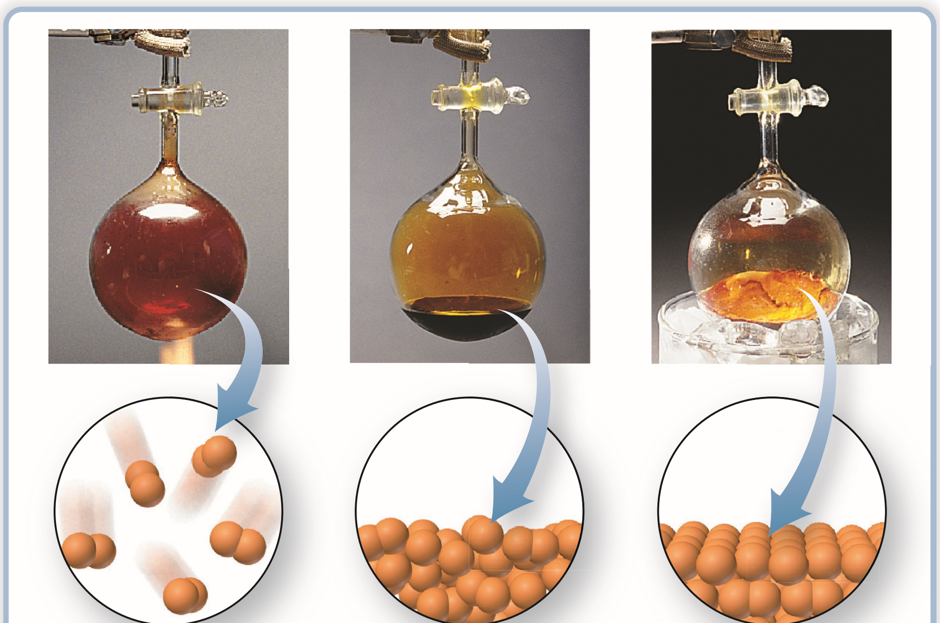


Figure 5.1 The three states of matter. Many substances, such as bromine (Br_2), can exist under appropriate conditions of pressure and temperature as a gas, liquid, or solid.

increase again. Gases under pressure can do work: compressed air in a jackhammer breaks rock and cement, and in tires it lifts the weight of a car. In contrast, the volume of a liquid or a solid does not change significantly under pressure.

2. *Gas volume changes significantly with temperature.* When a sample of gas at constant pressure is heated, it expands; when it is cooled, it shrinks. This volume change is 50 to 100 times greater for gases than for liquids or solids. The expansion that occurs when gases are rapidly heated can lift a rocket or pop corn.
3. *Gases flow very freely.* Gases flow much more freely than liquids and solids. This behavior allows gases to be transported more easily through pipes, but it also means they leak more rapidly out of small holes and cracks.
4. *Gases have relatively low densities.* Gas density is usually measured in units of grams per liter (g/L), whereas liquid and solid densities are in grams per milliliter (g/mL), about 1000 times as dense. For example, at 20°C and normal atmospheric pressure, the density of $O_2(g)$ is 1.3 g/**L,** whereas the density of $H_2O(l)$ is 1.0 g/**mL** and the density of NaCl(*s*) is 2.2 g/**mL.** When a gas cools, its density *increases* because its volume *decreases:* on cooling from 20°C to 0°C, the density of $O_2(g)$ increases from 1.3 to 1.4 g/L.
5. *Gases form a solution in any proportions.* Air is a solution of 18 gases. Two liquids, however, may or may not form a solution: water and ethanol do, but water and gasoline do not. Two solids generally do not form a solution unless they are melted, mixed, and then allowed to solidify (as when the alloy bronze is made from copper and tin).

These macroscopic properties arise because the particles in a gas are much farther apart than those in a liquid or a solid.

Summary of Section 5.1

- The volume of a gas can be altered significantly by changing the applied force or the temperature. Corresponding changes for liquids and solids are *much* smaller.
- Gases flow more freely and have much lower densities than liquids and solids.
- Gases mix in any proportions to form solutions; liquids and solids generally do not.
- Differences in the physical states are due to the greater average distance between particles in a gas than in a liquid or a solid.

5.2 • GAS PRESSURE AND ITS MEASUREMENT

You can blow up a balloon or pump up a tire because *a gas exerts pressure on the walls of its container.* **Pressure (*P*)** is defined as the force exerted per unit of surface area:

$$\text{Pressure} = \frac{\text{force}}{\text{area}}$$

Earth's gravity attracts the atmospheric gases, and they exert a force uniformly on *all* surfaces. The force, or *weight,* of these gases creates a pressure of about 14.7 pounds per square inch (lb/in^2; psi) of surface. Thus, a pressure of 14.7 lb/in^2 exists on the outside of your room (or your body), and it equals the pressure on the inside. What would happen if the pressures were *not* equal? Consider the empty can attached to a vacuum pump in Figure 5.2. With the pump off *(left)* the can maintains its shape because the pressure on the outside is equal to the pressure on the inside. With the pump on *(right),* nearly all of the air inside is removed, decreasing the internal pressure greatly, and the pressure of the atmosphere easily crushes the can. The vacuum-filtration flasks and tubing that you may have used in the lab have thick walls that withstand the enormous difference in pressure that arises as the flask is evacuated.

Measuring Atmospheric Pressure

The **barometer** is used to measure atmospheric pressure. The device is still essentially the same as it was when invented in 1643 by the Italian physicist Evangelista Torricelli: a tube about 1 m long, closed at one end, filled with mercury (Hg), and inverted into a dish containing more mercury. When the tube is inverted, some of the mercury

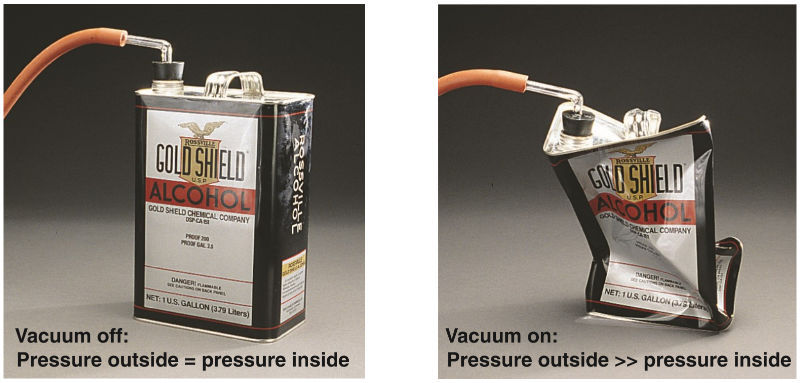


Figure 5.2 Effect of atmospheric pressure when it is exerted equally on inner and outer surfaces *(left)* and when the internal pressure is greatly decreased *(right)*.

flows out into the dish, and a vacuum forms above the mercury remaining in the tube (Figure 5.3). At sea level, under ordinary atmospheric conditions, the mercury stops flowing out when the surface of the mercury in the tube is about 760 mm above the surface of the mercury in the dish. At that height, the column of mercury exerts the same pressure (weight/area) on the mercury surface in the dish as the atmosphere does: $P_{Hg} = P_{atm}$. Likewise, if you evacuate a closed tube and invert it into a dish of mercury, the atmosphere pushes the mercury up to a height of about 760 mm.

Notice that we did not specify the diameter of the barometer tube. If the mercury in a 1-cm diameter tube rises to a height of 760 mm, the mercury in a 2-cm diameter tube will rise to that height also. The *weight* of mercury is greater in the wider tube, but so is the area; thus, the *pressure,* the *ratio* of weight to area, is the same.

Because the pressure of the mercury column is directly proportional to its height, a unit commonly used for pressure is millimeters of mercury (mmHg). We discuss other units of pressure shortly. *At sea level and 0°C, normal atmospheric pressure is 760 mmHg;* at the top of Mt. Everest (elevation 29,028 ft, or 8848 m), the atmospheric pressure is only about 270 mmHg. Thus, *pressure decreases with altitude:* the column of air above the sea is taller, so it weighs more than the column of air above Mt. Everest.

Laboratory barometers contain mercury because its high density allows these instruments to be a convenient size. If a barometer contained water instead, it would have to be more than 34 ft high, because the pressure of the atmosphere equals the pressure of a column of water about 10,300 mm (almost 34 ft) high. For a given pressure, the ratio of heights (h) of the liquid columns is inversely related to the ratio of the densities (d) of the liquids:

$$\frac{h_{H_2O}}{h_{Hg}} = \frac{d_{Hg}}{d_{H_2O}}$$

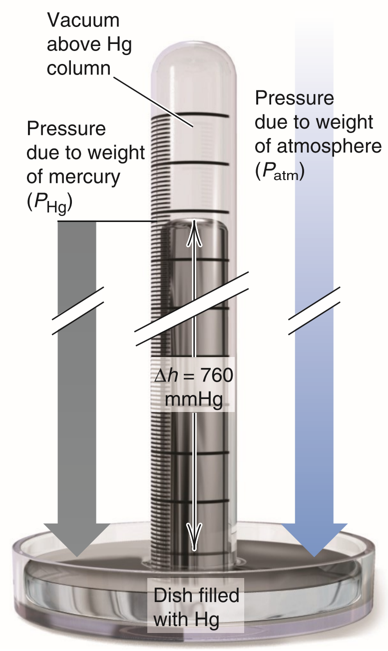


Figure 5.3 A mercury barometer. The pressure of the atmosphere, P_{atm}, balances the pressure of the mercury column, P_{Hg}.

Units of Pressure

Pressure results from a force exerted on an area. The SI unit of force is the newton (N): 1 N = 1 kg·m/s^2 (about the weight of an apple). The SI unit of pressure is the **pascal (Pa),** which equals a force of one newton exerted on an area of one square meter:

$$1 \text{ Pa} = 1 \text{ N/m}^2$$

A much larger unit is the **standard atmosphere (atm),** the average atmospheric pressure measured at sea level and 0°C. It is defined in terms of the pascal:

$$1 \text{ atm} = 101.325 \text{ kilopascals (kPa)} = 1.01325\times10^5 \text{ Pa}$$

Another common unit is the **millimeter of mercury (mmHg),** mentioned earlier; in honor of Torricelli, this unit has been renamed the **torr:**

$$1 \text{ torr} = 1 \text{ mmHg} = \frac{1}{760} \text{ atm} = \frac{101.325}{760} \text{ kPa} = 133.322 \text{ Pa}$$

The *bar* is coming into more common use in chemistry:

$$1 \text{ bar} = 1\times10^2 \text{ kPa} = 1\times10^5 \text{ Pa}$$

Table 5.1 Common Units of Pressure

Unit	Normal Atmospheric Pressure at Sea Level and 0°C
pascal (Pa); kilopascal (kPa)	1.01325×10^5 Pa; 101.325 kPa
atmosphere (atm)	1 atm*
millimeters of mercury (mmHg)	760 mmHg*
torr	760 torr*
pounds per square inch (lb/in^2 or psi)	14.7 lb/in^2
bar	1.01325 bar

*This is an exact quantity; in calculations, we use as many significant figures as necessary.

Despite a gradual change to SI units, many chemists still express pressure in torrs and atmospheres, so those units are used in this book, with reference to pascals and bars. Table 5.1 lists some important pressure units with the corresponding values for normal atmospheric pressure.

Sample Problem 5.1 Converting Units of Pressure

Problem A geochemist heats a limestone ($CaCO_3$) sample and collects the CO_2 released in an evacuated flask. After the system comes to room temperature, Δh = 291.4 mmHg. Calculate the CO_2 pressure in torrs, atmospheres, and kilopascals.

Plan The CO_2 pressure is given in units of mmHg, so we construct conversion factors from Table 5.1 to find the pressure in the other units.

Solution Converting from mmHg to torr:

$$P_{CO_2}\text{ (torr)} = 291.4\ \cancel{\text{mmHg}} \times \frac{1\text{ torr}}{1\ \cancel{\text{mmHg}}} = \boxed{291.4\text{ torr}}$$

Converting from torr to atm:

$$P_{CO_2}\text{ (atm)} = 291.4\ \cancel{\text{torr}} \times \frac{1\text{ atm}}{760\ \cancel{\text{torr}}} = \boxed{0.3834\text{ atm}}$$

Converting from atm to kPa:

$$P_{CO_2}\text{ (kPa)} = 0.3834\ \cancel{\text{atm}} \times \frac{101.325\text{ kPa}}{1\ \cancel{\text{atm}}} = \boxed{38.85\text{ kPa}}$$

Check There are 760 torr in 1 atm, so ~300 torr should be <0.5 atm. There are ~100 kPa in 1 atm, so <0.5 atm should be <50 kPa.

Comment **1.** In the conversion from torr to atm, we retained four significant figures because the conversion factor (1 atm = 760 torr) is an *exact* number and has as many significant figures as required (see the footnote on Table 5.1).
2. From here on, except in complex situations, *unit canceling will no longer be shown in equations.*

FOLLOW-UP PROBLEM 5.1 The CO_2 released from another mineral sample is collected in an evacuated flask, and the measured P_{CO_2} is 579.6 torr. What is this pressure in torrs, pascals, and lb/in^2?

Summary of Section 5.2

- Gases exert pressure (force/area) on all surfaces they contact.
- A barometer measures atmospheric pressure based on the height of a mercury column that the atmosphere can support (760 mmHg at sea level and 0°C).
- Pressure units include the atmosphere (atm), torr (identical to mmHg), and pascal (Pa, the SI unit).

5.3 • THE GAS LAWS AND THEIR EXPERIMENTAL FOUNDATIONS

The physical behavior of a sample of gas can be described completely by four variables: pressure (P), volume (V), temperature (T), and amount (number of moles, n). These variables are interdependent, which means that *any one of them can be determined by measuring the other three.* Three key relationships exist among the four gas variables—Boyle's, Charles's, and Avogadro's laws. Each of these *gas laws expresses the effect of one variable on another, with the remaining two variables held constant.* Because volume is so easy to measure, the laws are expressed as the effect on gas volume of a change in the pressure, temperature, or amount of the gas.

The individual gas laws are special cases of a unifying relationship called the *ideal gas law,* which quantitatively describes the behavior of an **ideal gas,** one that exhibits linear relationships among volume, pressure, temperature, and amount. Although *no ideal gas actually exists,* most simple gases behave nearly ideally at ordinary temperatures and pressures. We discuss the ideal gas law after the three individual laws.

The Relationship Between Volume and Pressure: Boyle's Law

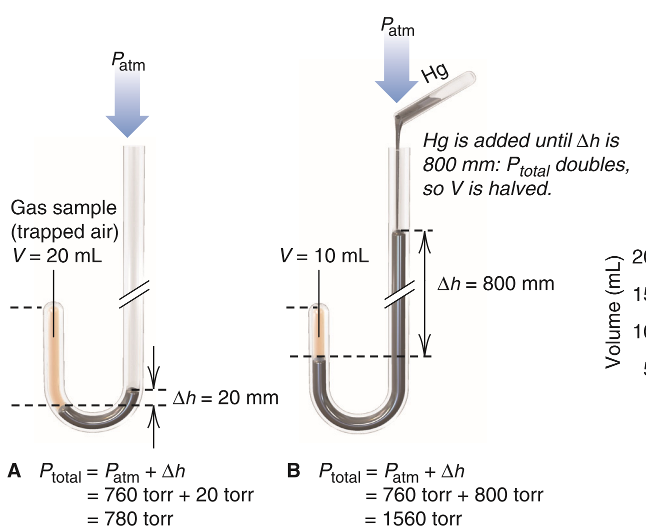
Following Torricelli's invention of the barometer, the great 17th-century English chemist Robert Boyle studied the effect of pressure on the volume of a sample of gas.

1. *The experiment.* Figure 5.4 illustrates the setup Boyle might have used in his experiments (parts A and B), the data he might have collected (part C), and graphs of the data (parts D and E). Boyle sealed the shorter leg of a J-shaped glass tube and poured mercury into the longer open leg, thereby trapping some air (the gas in the experiment) in the shorter leg. He calculated the gas volume (V_{gas}) from the height of the trapped air and the diameter of the tube. The total pressure, P_{total}, applied to the trapped gas is the pressure of the atmosphere, P_{atm} (760 mm, measured with a barometer), plus the difference in the heights of the mercury columns (Δh) in the two legs of the J tube, 20 mm (Figure 5.4A); thus, P_{total} is 780 torr. By adding mercury, Boyle increased P_{total}, and the gas volume decreased. In Figure 5.4B, more mercury has been added to the longer leg of the tube, increasing Δh to 800 mm, so P_{total} doubles to 1560 torr; note that V_{gas} is halved from 20 mL to 10 mL. In this way, by keeping the temperature and amount of gas constant, Boyle was able to measure the effect of the applied pressure on gas volume.

Note the following results in Figure 5.4:

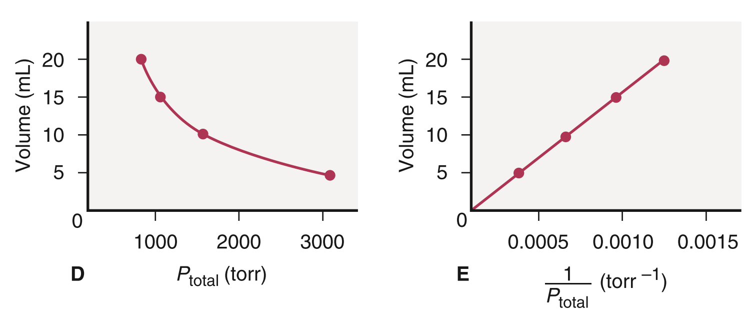
- The product of corresponding P and V values is a constant (part C, rightmost column).
- V is *inversely* proportional to P (part D).
- V is *directly* proportional to $1/P$ (part E), and a plot of V versus $1/P$ is linear. This *linear relationship between two gas variables* is a hallmark of ideal gas behavior.

Figure 5.4 Boyle's law, the relationship between the volume and pressure of a gas.



C

V (mL)	P (torr) Δh	+ P_{atm}	= P_{total}	$\frac{1}{P_{total}}$	PV (torr•mL)
20.0	20.0	760	780	0.00128	1.56×10^4
15.0	278	760	1038	0.000963	1.56×10^4
10.0	800	760	1560	0.000641	1.56×10^4
5.0	2352	760	3112	0.000321	1.56×10^4



2. *Conclusion and statement of the law*. The generalization of Boyle's observations is known as **Boyle's law:** *at constant temperature, the volume occupied by a fixed amount of gas is* ***inversely*** *proportional to the applied (external) pressure,* or

$$V \propto \frac{1}{P} \qquad [T \text{ and } n \text{ fixed}] \tag{5.1}$$

This relationship can also be expressed as

$$PV = \text{constant} \qquad \text{or} \qquad V = \frac{\text{constant}}{P} \qquad [T \text{ and } n \text{ fixed}]$$

That is, at fixed T and n,

$$P\uparrow,\ V\downarrow \qquad \text{and} \qquad P\downarrow,\ V\uparrow$$

The constant is the same for most simple gases under ordinary conditions. Thus, tripling the external pressure reduces the volume of a gas to a third of its initial value; halving the pressure doubles the volume; and so forth.

The wording of Boyle's law focuses on *external* pressure. But notice that, as mercury is added, the mercury level rises until the pressure of the trapped gas *on* the mercury increases enough to stop its rise. At that point, the pressure exerted *on* the gas equals the pressure exerted *by* the gas (P_{gas}). Thus, in general, if V_{gas} increases, P_{gas} decreases, and vice versa.

The Relationship Between Volume and Temperature: Charles's Law

Boyle's work showed that the pressure-volume relationship holds only at constant temperature, but why should that be so? It would take more than a century, until the work of French scientists J. A. C. Charles and J. L. Gay-Lussac around 1800, for the relationship between gas volume and temperature to be understood.

1. *The experiment.* Let's examine this relationship by measuring the volume at different temperatures of a fixed amount of a gas under constant pressure. A straight tube, closed at one end, traps a fixed amount of gas (air) under a small mercury plug. The tube is immersed in a water bath that is warmed with a heater or cooled with ice. After each change of temperature, we measure the length of the gas column, which is proportional to its volume. The total pressure exerted on the gas is constant because the mercury plug and the atmospheric pressure do not change (Figure 5.5, parts A and B).

Figure 5.5C shows some typical data. Consider the red line, which shows how the volume of 0.04 mol of gas at 1 atm pressure changes with temperature. Extrapolating that line to lower temperatures *(dashed portion)* shows that, in theory, the gas occupies zero volume at −273.15°C (the intercept on the temperature axis). Plots for a different amount of gas *(green)* or a different gas pressure *(blue)* have different slopes, but they all converge at this temperature, called *absolute zero* (0 K, or −273.15°C). And *this linear relation between gas volume and absolute temperature holds for most common gases over a wide temperature range.*

2. *Conclusion and statement of the law.* Note that, unlike the relationship between volume and pressure, *this linear relationship between volume and temperature is directly proportional.* This behavior is incorporated into the modern statement of the volume-temperature relationship, which is known as **Charles's law:** *at constant pressure, the volume occupied by a fixed amount of gas is* ***directly*** *proportional to its absolute (Kelvin) temperature,* or

$$V \propto T \qquad [P \text{ and } n \text{ fixed}] \tag{5.2}$$

This relationship can also be expressed as

$$\frac{V}{T} = \text{constant} \qquad \text{or} \qquad V = \text{constant} \times T \qquad [P \text{ and } n \text{ fixed}]$$

That is, at fixed P and n,

$$T\uparrow,\ V\uparrow \qquad \text{and} \qquad T\downarrow,\ V\downarrow$$

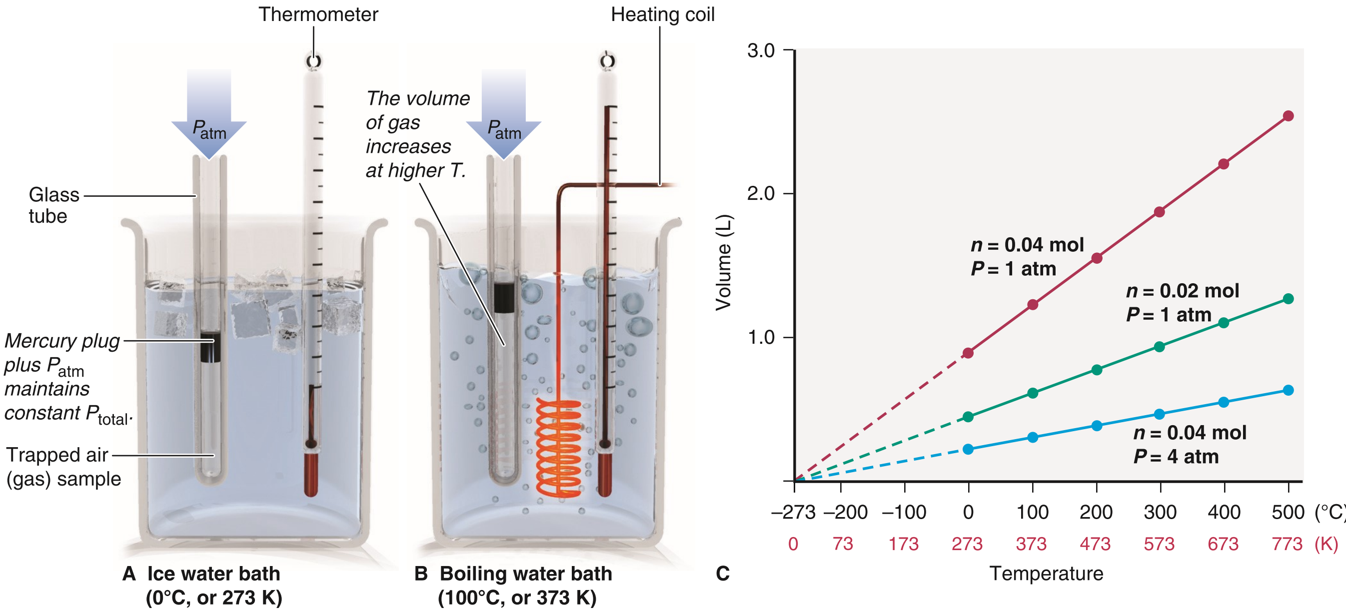


Figure 5.5 Charles's law, the relationship between the volume and temperature of a gas.

If T increases, V increases, and vice versa. Once again, for any given P and n, the constant is the same for most simple gases under ordinary conditions.

The dependence of gas volume on the *absolute* temperature means that you *must use the Kelvin scale in gas law calculations.* For instance, if the temperature changes from 200 K to 400 K, the volume of gas doubles. But, if the temperature changes from 200°C to 400°C, the volume increases by a factor of 1.42; that is,

$$\left(\frac{400°\text{C} + 273.15}{200°\text{C} + 273.15}\right) = \frac{673}{473} = 1.42$$

Other Relationships Based on Boyle's and Charles's Laws Two other important relationships arise from Boyle's and Charles's laws:

1. *The pressure-temperature relationship.* Charles's law is expressed as the effect of temperature on gas *volume* at constant pressure. But volume and pressure are interdependent, so a similar relationship can be expressed for the effect of temperature on pressure (sometimes referred to as *Amontons's law*). Measure the pressure in your car or bike tires before and after a long ride, and you'll find that it increases. Heating due to friction between the tires and the road increases the air temperature inside the tires, but since a tire's volume can't increase very much, the air pressure does. Thus, *at constant volume, the pressure exerted by a fixed amount of gas is directly proportional to the absolute temperature:*

$$P \propto T \qquad [V \text{ and } n \text{ fixed}] \tag{5.3}$$

or

$$\frac{P}{T} = \text{constant} \qquad \text{or} \qquad P = \text{constant} \times T$$

That is, at fixed V and n,

$$T\uparrow, P\uparrow \qquad \text{and} \qquad T\downarrow, P\downarrow$$

2. *The combined gas law.* Combining Boyle's and Charles's laws gives the *combined gas law,* which applies to cases when changes in *two* of the three variables (V, P, T) affect the third:

$$V \propto \frac{T}{P} \qquad \text{or} \qquad V = \text{constant} \times \frac{T}{P} \qquad \text{or} \qquad \frac{PV}{T} = \text{constant}$$

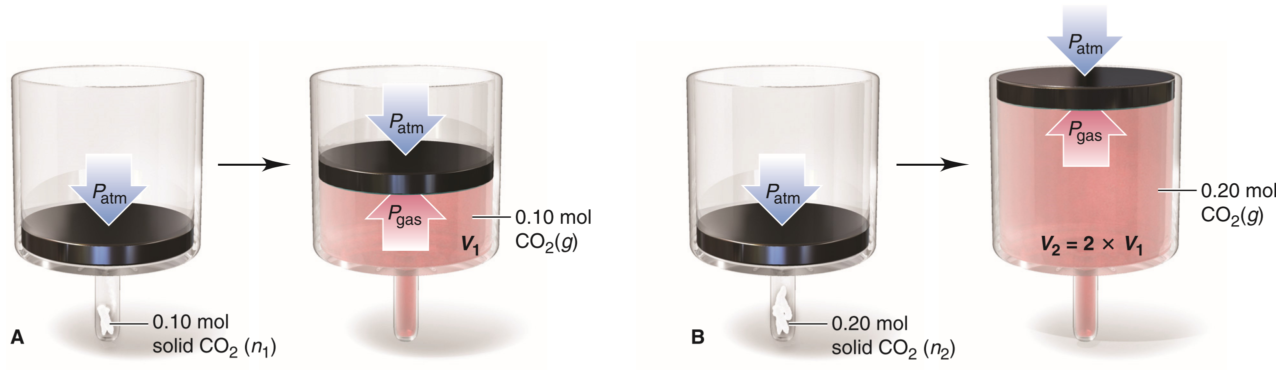


Figure 5.6 The relationship between the volume and amount of a gas.

The Relationship Between Volume and Amount: Avogadro's Law

Let's see why both Boyle's and Charles's laws specify a fixed amount of gas.

1. *The experiment.* Figure 5.6 shows an experiment that involves two small test tubes, each fitted to a much larger piston-cylinder assembly. We add 0.10 mol (4.4 g) of dry ice (solid CO_2) to the first tube (A) and 0.20 mol (8.8 g) to the second tube (B). As the solid CO_2 warms to room temperature, it changes to gaseous CO_2, and the volume increases until $P_{gas} = P_{atm}$. At constant temperature, when all the solid has changed to gas, cylinder B has twice the volume of cylinder A.

2. *Conclusion and statement of the law.* Thus, *at fixed temperature and pressure, the volume occupied by a gas is directly proportional to the amount (mol) of gas:*

$$V \propto n \qquad [P \text{ and } T \text{ fixed}] \tag{5.4}$$

That is, as n increases, V increases, and vice versa. This relationship is also expressed as

$$\frac{V}{n} = \text{constant} \qquad \text{or} \qquad V = \text{constant} \times n$$

That is, at fixed P and T,

$$n\uparrow, V\uparrow \qquad \text{and} \qquad n\downarrow, V\downarrow$$

The constant is the same for all simple gases at ordinary temperature and pressure. This relationship is another way of expressing **Avogadro's law,** which states that *at fixed temperature and pressure, equal volumes of* ***any*** *ideal gas contain equal numbers of particles (or moles).*

Familiar Applications of the Gas Laws The gas laws apply to countless familiar phenomena: gasoline burning in a car engine, dough rising and baking—even the act of breathing (Figure 5.7). When you inhale, the downward movement of your diaphragm and the expansion of your rib cage increase your lung volume, which decreases the air pressure inside, so air rushes in (Boyle's law). The greater amount of air stretches the lung tissue, which expands the volume further (Avogadro's law), and the air expands slightly as it warms to body temperature (Charles's law). When you exhale, these steps occur in reverse.

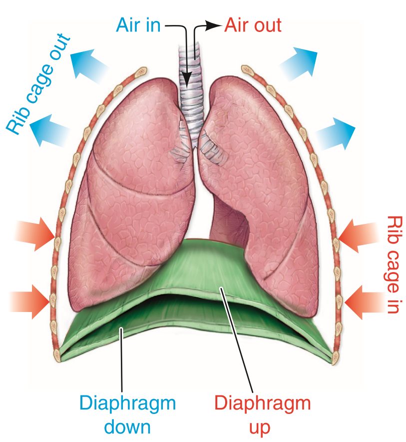


Figure 5.7 The process of breathing applies the gas laws.

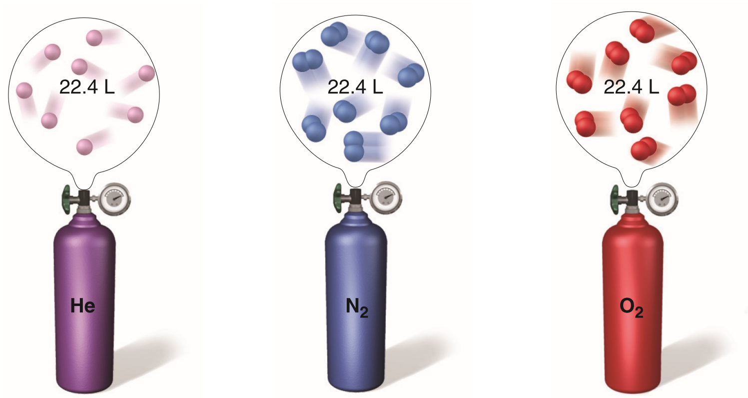
Gas Behavior at Standard Conditions

To better understand the factors that influence gas behavior, chemists have assigned a baseline set of *standard conditions* called **standard temperature and pressure (STP):**

$$\text{STP:} \quad 0°\text{C } (273.15 \text{ K}) \text{ and } 1 \text{ atm } (760 \text{ torr}) \tag{5.5}$$

Under these conditions, the volume of 1 mol of an ideal gas is called the **standard molar volume:**

$$\text{Standard molar volume} = 22.4141 \text{ L or } 22.4 \text{ L } [\text{to 3 sf}] \tag{5.6}$$



n = 1 mol	n = 1 mol	n = 1 mol
P = 1 atm (760 torr)	P = 1 atm (760 torr)	P = 1 atm (760 torr)
T = 0°C (273 K)	T = 0°C (273 K)	T = 0°C (273 K)
V = 22.4 L	V = 22.4 L	V = 22.4 L
Number of gas particles = 6.022×10^{23}	Number of gas particles = 6.022×10^{23}	Number of gas particles = 6.022×10^{23}
Mass = 4.003 g	Mass = 28.02 g	Mass = 32.00 g
d = 0.179 g/L	d = 1.25 g/L	d = 1.43 g/L

Figure 5.8 Standard molar volume. One mole of an ideal gas occupies 22.4 L at STP (0°C and 1 atm).

Figure 5.8 compares the properties of 1 mol of three simple gases—helium, nitrogen, and oxygen—at STP. Note that they differ only in terms of mass and, thus, density. Figure 5.9 compares the volumes of some familiar objects with the standard molar volume of an ideal gas.

Figure 5.9 The volumes of 1 mol (22.4 L) of an ideal gas and of some familiar objects: 1 gal of milk (3.79 L), a basketball (7.50 L), and 2.00 L of a carbonated drink.

The Ideal Gas Law

Each of the three gas laws shows how one of the three other gas variables affects gas volume:

- Boyle's law focuses on pressure ($V \propto 1/P$).
- Charles's law focuses on temperature ($V \propto T$).
- Avogadro's law focuses on amount (mol) of gas ($V \propto n$).

By combining these individual effects, we obtain the **ideal gas law** (or *ideal gas equation*):

$$V \propto \frac{nT}{P} \qquad \text{or} \qquad PV \propto nT \qquad \text{or} \qquad \frac{PV}{nT} = R$$

where R is a proportionality constant known as the **universal gas constant.** Rearranging the equation on the right above gives the most common form of the ideal gas law:

$$PV = nRT \tag{5.7}$$

We obtain a value of R by measuring the volume, temperature, and pressure of a given amount of gas and substituting the values into the ideal gas law. For example, using standard conditions for the gas variables and 1 mol of gas, we have

$$R = \frac{PV}{nT} = \frac{1\ \text{atm} \times 22.4141\ \text{L}}{1\ \text{mol} \times 273.15\ \text{K}} = 0.082058\ \frac{\text{atm·L}}{\text{mol·K}} = 0.0821\ \frac{\text{atm·L}}{\text{mol·K}}\ [\text{to 3 sf}] \tag{5.8}$$

This numerical value of R corresponds to P, V, and T expressed *in these units; R has a different numerical value when different units are used*. For example, on p. 174, R has the value 8.314 J/mol·K (J stands for joule, the SI unit of energy).

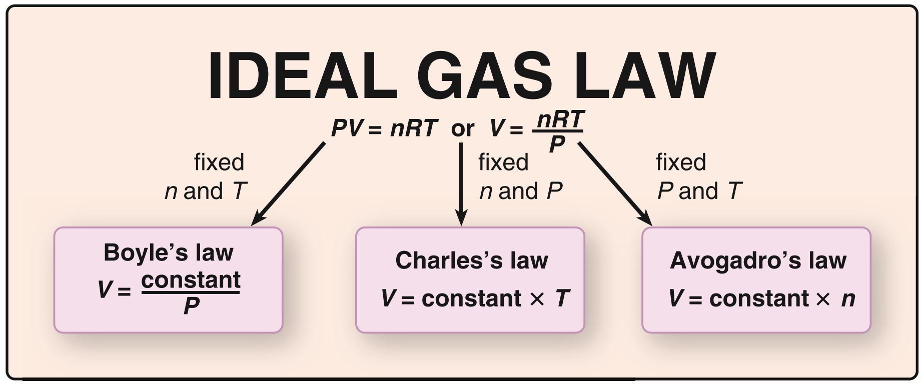


Figure 5.10 The individual gas laws as special cases of the ideal gas law.

Figure 5.10 makes a central point: the ideal gas law *becomes* one of the individual gas laws when two of the four variables are kept constant. When initial conditions (subscript 1) change to final conditions (subscript 2), we have

$$P_1V_1 = n_1RT_1 \quad \text{and} \quad P_2V_2 = n_2RT_2$$

Thus
$$\frac{P_1V_1}{n_1T_1} = R \quad \text{and} \quad \frac{P_2V_2}{n_2T_2} = R$$

so
$$\frac{P_1V_1}{n_1T_1} = \frac{P_2V_2}{n_2T_2}$$

Notice that if, for example, the two variables P and T remain constant, then $P_1 = P_2$ and $T_1 = T_2$, and we obtain an expression for Avogadro's law:

$$\frac{\cancel{P_1}V_1}{n_1\cancel{T_1}} = \frac{\cancel{P_2}V_2}{n_2\cancel{T_2}} \quad \text{or} \quad \frac{V_1}{n_1} = \frac{V_2}{n_2}$$

As you'll see next, you can use a similar approach to solve gas law problems. Thus, by keeping track of the initial and final values of the gas variables, you avoid the need to memorize the three individual gas laws.

Solving Gas Law Problems

Gas law problems are stated in many ways but are usually one of two types:

1. *A change in one of the four variables causes a change in another, while the two other variables remain constant.* In this type, the ideal gas law reduces to one of the individual gas laws, and you solve for the new value of the affected variable. Units must be consistent and T must always be in kelvins, but R is not involved. Sample Problems 5.2 to 5.4 and 5.6 are of this type. [A variation on this type involves the combined gas law (p. 156) when simultaneous changes in two of the variables cause a change in a third.]

2. *One variable is unknown, but the other three are known and no change occurs.* In this type, exemplified by Sample Problem 5.5, you apply the ideal gas law directly to find the unknown, and the units must conform to those in R.

Solving these problems requires a systematic approach:

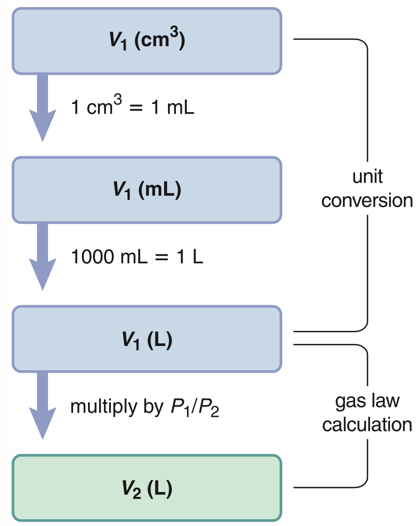
- Summarize the changing gas variables—knowns and unknown—and those held constant.
- Convert units, if necessary.
- Rearrange the ideal gas law to obtain the needed relationship of variables, and solve for the unknown.

Sample Problem 5.2 Applying the Volume-Pressure Relationship

Problem Boyle's apprentice finds that the air trapped in a J tube occupies 24.8 cm^3 at 1.12 atm. By adding mercury to the tube, he increases the pressure on the trapped air to 2.64 atm. Assuming constant temperature, what is the new volume of air (in L)?

Plan We must find the final volume (V_2) in liters, given the initial volume (V_1), initial pressure (P_1), and final pressure (P_2). The temperature and amount of gas are fixed. We convert the units of V_1 from cm^3 to mL and then to L, rearrange the ideal gas law to the appropriate form, and solve for V_2. (Note that the road map has two parts.)

Road Map



Solution Summarizing the gas variables:

$P_1 = 1.12$ atm $\qquad$ $P_2 = 2.64$ atm

$V_1 = 24.8$ cm^3 (convert to L) $\qquad$ $V_2 =$ unknown $\qquad$ T and n remain constant

Converting V_1 from cm^3 to L:

$$V_1 = 24.8\ \text{cm}^3 \times \frac{1\ \text{mL}}{1\ \text{cm}^3} \times \frac{1\ \text{L}}{1000\ \text{mL}} = 0.0248\ \text{L}$$

Rearranging the ideal gas law and solving for V_2: At fixed n and T, we have

$$\frac{P_1V_1}{\cancel{n_1T_1}} = \frac{P_2V_2}{\cancel{n_2T_2}} \quad \text{or} \quad P_1V_1 = P_2V_2$$

$$V_2 = V_1 \times \frac{P_1}{P_2} = 0.0248\ \text{L} \times \frac{1.12\ \text{atm}}{2.64\ \text{atm}} = \boxed{0.0105\ \text{L}}$$

Check The relative values of P and V can help us check the math: P more than doubled, so V_2 should be less than $\frac{1}{2}V_1$ ($0.0105/0.0248 < \frac{1}{2}$).

Comment Predicting the direction of the change provides another check on the problem setup: Since P increases, V will decrease; thus, V_2 should be less than V_1. To make $V_2 < V_1$, we must multiply V_1 by a number *less than* 1. This means the ratio of pressures must be *less than* 1, so the larger pressure (P_2) must be in the denominator, or P_1/P_2.

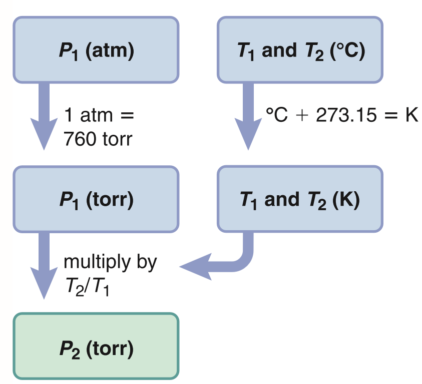
FOLLOW-UP PROBLEM 5.2 A sample of argon gas occupies 105 mL at 0.871 atm. If the temperature remains constant, what is the volume (in L) at 26.3 kPa?

Sample Problem 5.3 Applying the Pressure-Temperature Relationship

Problem A steel tank used for fuel delivery is fitted with a safety valve that opens if the internal pressure exceeds 1.00×10^3 torr. It is filled with methane at 23°C and 0.991 atm and placed in boiling water 100.°C. Will the safety valve open?

Plan The question "Will the safety valve open?" translates to "Is P_2 greater than 1.00×10^3 torr at T_2?" Thus, P_2 is the unknown, and T_1, T_2, and P_1 are given, with V (steel tank) and n fixed. We convert both T values to kelvins and P_1 to torrs in order to compare P_2 with the safety-limit pressure. We rearrange the ideal gas law and solve for P_2.

Road Map



Solution Summarizing the gas variables:

$P_1 = 0.991$ atm (convert to torr) $\qquad$ $P_2 =$ unknown

$T_1 = 23$°C (convert to K) $\qquad$ $T_2 = 100.$°C (convert to K)

V and n remain constant

Converting T from °C to K:

$$T_1\ (\text{K}) = 23°\text{C} + 273.15 = 296\ \text{K} \qquad T_2\ (\text{K}) = 100.°\text{C} + 273.15 = 373\ \text{K}$$

Converting P from atm to torr:

$$P_1\ (\text{torr}) = 0.991\ \text{atm} \times \frac{760\ \text{torr}}{1\ \text{atm}} = 753\ \text{torr}$$

Rearranging the ideal gas law and solving for P_2: At fixed n and V, we have

$$\frac{P_1\cancel{V_1}}{\cancel{n_1}T_1} = \frac{P_2\cancel{V_2}}{\cancel{n_2}T_2} \quad \text{or} \quad \frac{P_1}{T_1} = \frac{P_2}{T_2}$$

$$P_2 = P_1 \times \frac{T_2}{T_1} = 753 \text{ torr} \times \frac{373 \text{ K}}{296 \text{ K}} = 949 \text{ torr}$$

P_2 is less than 1.00×10^3 torr, so the valve will *not* open.

Check Let's predict the change to check the math: Because $T_2 > T_1$, we expect $P_2 > P_1$. Thus, the temperature ratio should be >1 (T_2 in the numerator). The T ratio is about 1.25 (373/296), so the P ratio should also be about 1.25 ($950/750 \approx 1.25$).

FOLLOW-UP PROBLEM 5.3 An engineer pumps air at 0°C into a newly designed piston-cylinder assembly. The volume measures 6.83 cm^3. At what temperature (in K) will the volume be 9.75 cm^3?

Sample Problem 5.4 Applying the Volume-Amount Relationship

Problem A scale model of a blimp rises when it is filled with helium to a volume of 55.0 dm^3. When 1.10 mol of He is added to the blimp, the volume is 26.2 dm^3. How many more grams of He must be added to make it rise? Assume constant T and P.

Plan We are given the initial amount of helium (n_1), the initial volume of the blimp (V_1), and the volume needed for it to rise (V_2), and we need the additional mass of helium to make it rise. So we first need to find n_2. We rearrange the ideal gas law to the appropriate form, solve for n_2, subtract n_1 to find the additional amount ($n_{\text{add'l}}$), and then convert moles to grams.

Road Map

n_1 (mol) of He

↓ multiply by V_2/V_1

n_2 (mol) of He

↓ subtract n_1

$n_{\text{add'l}}$ (mol) of He

↓ multiply by $\mathcal{M}$ (g/mol)

Mass (g) of He

Solution Summarizing the gas variables:

$$n_1 = 1.10 \text{ mol} \qquad n_2 = \text{unknown (find, and then subtract } n_1)$$
$$V_1 = 26.2 \text{ dm}^3 \qquad V_2 = 55.0 \text{ dm}^3$$

P and T remain constant

Rearranging the ideal gas law and solving for n_2: At fixed P and T, we have

$$\frac{\cancel{P_1}V_1}{n_1\cancel{T_1}} = \frac{\cancel{P_2}V_2}{n_2\cancel{T_2}} \quad \text{or} \quad \frac{V_1}{n_1} = \frac{V_2}{n_2}$$

$$n_2 = n_1 \times \frac{V_2}{V_1} = 1.10 \text{ mol He} \times \frac{55.0 \text{ dm}^3}{26.2 \text{ dm}^3} = 2.31 \text{ mol He}$$

Finding the additional amount of He:

$$n_{\text{add'l}} = n_2 - n_1 = 2.31 \text{ mol He} - 1.10 \text{ mol He} = 1.21 \text{ mol He}$$

Converting amount (mol) of He to mass (g):

$$\text{Mass (g) of He} = 1.21 \text{ mol He} \times \frac{4.003 \text{ g He}}{1 \text{ mol He}} = 4.84 \text{ g He}$$

Check We predict that $n_2 > n_1$ because $V_2 > V_1$: since V_2 is about twice V_1 ($55/26 \approx 2$), n_2 should be about twice n_1 ($2.3/1.1 \approx 2$). Since $n_2 > n_1$, we were right to multiply n_1 by a number >1 (that is, V_2/V_1). About 1.2 mol $\times$ 4 g/mol $\approx$ 4.8 g.

Comment **1.** A different sequence of steps will give the same answer: first find the additional volume ($V_{\text{add'l}} = V_2 - V_1$), and then solve directly for $n_{\text{add'l}}$. Try it yourself.
2. You saw that Charles's law ($V \propto T$ at fixed P and n) becomes a similar relationship between P and T at fixed V and n. The follow-up problem demonstrates that Avogadro's law ($V \propto n$ at fixed P and T) becomes a similar relationship at fixed V and T.

FOLLOW-UP PROBLEM 5.4 A rigid plastic container holds 35.0 g of ethylene gas (C_2H_4) at a pressure of 793 torr. What is the pressure if 5.0 g of ethylene is removed at constant temperature?

Sample Problem 5.5 Solving for an Unknown Gas Variable at Fixed Conditions

Problem A steel tank has a volume of 438 L and is filled with 0.885 kg of O_2. Calculate the pressure of O_2 at 21°C.

Plan We are given V, T, and the mass of O_2, and we must find P. Since conditions are not changing, we apply the ideal gas law without rearranging it. We use the given V in liters, convert T to kelvins and mass (kg) of O_2 to amount (mol), and solve for P.

Solution Summarizing the gas variables:

$V = 438$ L $\qquad T = 21°$C (convert to K)
$n = 0.885$ kg O_2 (convert to mol) $\qquad P =$ unknown

Converting T from °C to K:

$$T\ (\mathrm{K}) = 21°\mathrm{C} + 273.15 = 294\ \mathrm{K}$$

Converting from mass (g) of O_2 to amount (mol):

$$n = \text{mol of } O_2 = 0.885\ \text{kg } O_2 \times \frac{1000\ \text{g}}{1\ \text{kg}} \times \frac{1\ \text{mol } O_2}{32.00\ \text{g } O_2} = 27.7\ \text{mol } O_2$$

Solving for P (note the unit canceling here):

$$P = \frac{nRT}{V} = \frac{27.7\ \cancel{\text{mol}} \times 0.0821\ \dfrac{\text{atm}\cdot\cancel{\text{L}}}{\cancel{\text{mol}}\cdot\cancel{\text{K}}} \times 294\ \cancel{\text{K}}}{438\ \cancel{\text{L}}}$$
$$= \boxed{1.53\ \text{atm}}$$

Check The amount of O_2 seems correct: ~900 g/(30 g/mol) = 30 mol. To check the approximate size of the final calculation, round off the values, including that for R:

$$P = \frac{30\ \text{mol } O_2 \times 0.1\ \dfrac{\text{atm}\cdot\text{L}}{\text{mol}\cdot\text{K}} \times 300\ \text{K}}{450\ \text{L}} = 2\ \text{atm}$$

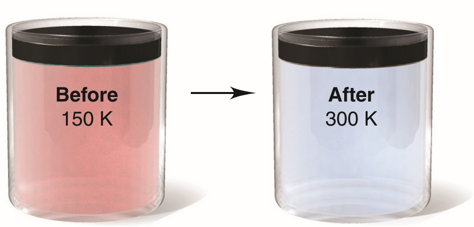
which is reasonably close to 1.53 atm.

FOLLOW-UP PROBLEM 5.5 The steel tank in the sample problem develops a slow leak that is discovered and sealed. A pressure gauge fitted on the tank shows the new pressure is 1.37 atm. How many grams of O_2 remain?

Finally, in a picture problem, we apply the gas laws to determine the balanced equation for a gaseous reaction.

Sample Problem 5.6 Using Gas Laws to Determine a Balanced Equation

Problem The piston-cylinder below is depicted before and after a gaseous reaction that is carried out in it at constant pressure: the temperature is 150 K before and 300 K after the reaction. (Assume the cylinder is insulated.)



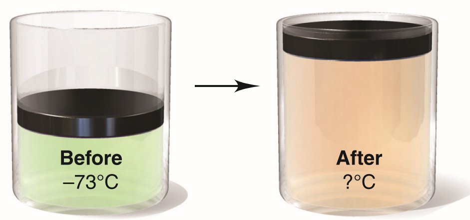
Which of the following balanced equations describes the reaction?
(1) $A_2(g) + B_2(g) \longrightarrow 2AB(g)$
(2) $2AB(g) + B_2(g) \longrightarrow 2AB_2(g)$
(3) $A(g) + B_2(g) \longrightarrow AB_2(g)$
(4) $2AB_2(g) \longrightarrow A_2(g) + 2B_2(g)$

Plan We are shown a depiction of the volume and temperature of a gas mixture before and after a reaction and must deduce the balanced equation. The problem says that P is constant, and the picture shows that, when T doubles, V stays the same. If n were also constant, Charles's law tells us that V should double when T doubles. But, since V does not change, n cannot be constant. From Avogadro's law, the only way to maintain V constant, with P constant and T doubling, is for n to be halved. So we examine the four balanced equations and count the number of moles on each side to see in which equation n is halved.

Solution In equation (1), n does not change, so doubling T would double V.
In equation (2), n decreases from 3 mol to 2 mol, so doubling T would increase V by one-third.
In equation (3), n decreases from 2 mol to 1 mol. Doubling T would exactly balance the decrease from halving n, so V would stay the same.
In equation (4), n increases, so doubling T would more than double V.
Therefore, equation (3) is correct:

$$A(g) + B_2(g) \longrightarrow AB_2(g)$$

FOLLOW-UP PROBLEM 5.6 The piston-cylinder below shows the volumes of a gaseous reaction mixture before and after a reaction that takes place at constant pressure and an initial temperature of $-73°C$.



If the *unbalanced* equation is $CD(g) \longrightarrow C_2(g) + D_2(g)$, what is the final temperature (in °C)?

Summary of Section 5.3

- Four interdependent variables define the physical behavior of an ideal gas: volume (V), pressure (P), temperature (T), and amount (number of moles, n).
- Most simple gases display nearly ideal behavior at ordinary temperatures and pressures.
- Boyle's, Charles's, and Avogadro's laws refer to the linear relationships between the volume of a gas and the pressure, temperature, and amount of gas, respectively.
- At STP (0°C and 1 atm), 1 mol of an ideal gas occupies 22.4 L.
- The ideal gas law incorporates the individual gas laws into one equation: $PV = nRT$, where R is the universal gas constant.

5.4 • REARRANGEMENTS OF THE IDEAL GAS LAW

In this section, we mathematically rearrange the ideal gas law to find gas density, molar mass, the partial pressure of each gas in a mixture, and the amount of gaseous reactant or product in a reaction.

The Density of a Gas

One mole of any gas behaving ideally occupies the same volume at a given temperature and pressure, so differences in gas density ($d = m/V$) depend on differences in molar mass (see Figure 5.8). For example, at STP, 1 mol of O_2 occupies the same volume as 1 mol of N_2; however, O_2 is denser because each O_2 molecule has a greater mass (32.00 amu) than each N_2 molecule (28.02 amu). Thus, d of O_2 is $\frac{32.00}{28.02} \times d$ of N_2.

We can rearrange the ideal gas law to calculate the density of a gas from its molar mass. Recall that the number of moles (n) is the mass (m) divided by the molar mass ($\mathcal{M}$), $n = m/\mathcal{M}$. Substituting for n in the ideal gas law gives

$$PV = \frac{m}{\mathcal{M}}RT$$

Rearranging to isolate m/V gives

$$\frac{m}{V} = d = \frac{\mathcal{M} \times P}{RT} \tag{5.9}$$

Two important ideas are expressed by Equation 5.9:

- *The density of a gas is directly proportional to its molar mass.* The volume of a given amount of a heavier gas equals the volume of the same amount of a lighter gas (Avogadro's law), so the density of the heavier gas is higher (as you just saw for O_2 and N_2).
- *The density of a gas is inversely proportional to the temperature.* As the volume of a gas increases with temperature (Charles's law), the same mass occupies more space, so the density of the gas is lower.

We use Equation 5.9 to find the density of a gas at any temperature and pressure near standard conditions.

Sample Problem 5.7 Calculating Gas Density

Problem A chemical engineer uses waste CO_2 from a manufacturing process, instead of chlorofluorocarbons, as a "blowing agent" in the production of polystyrene. Find the density (in g/L) of CO_2 and the number of molecules per liter **(a)** at STP (0°C and 1 atm) and **(b)** at room conditions (20.°C and 1.00 atm).

Plan We must find the density (d) and the number of molecules of CO_2, given two sets of P and T data. We find $\mathcal{M}$, convert T to kelvins, and calculate d with Equation 5.9. Then we convert the mass per liter to molecules per liter with Avogadro's number.

Solution **(a)** Density and molecules per liter of CO_2 at STP. Summary of gas properties:

$$T = 0°\text{C} + 273.15 = 273\ \text{K} \qquad P = 1\ \text{atm} \qquad \mathcal{M}\text{ of } CO_2 = 44.01\ \text{g/mol}$$

Calculating density (note the unit canceling here):

$$d = \frac{\mathcal{M} \times P}{RT} = \frac{44.01\ \text{g}/\cancel{\text{mol}} \times 1.00\ \cancel{\text{atm}}}{0.0821\ \dfrac{\cancel{\text{atm}}\cdot\text{L}}{\cancel{\text{mol}}\cdot\cancel{\text{K}}} \times 273\ \cancel{\text{K}}} = \boxed{1.96\ \text{g/L}}$$

Converting from mass/L to molecules/L:

$$\text{Molecules } CO_2/\text{L} = \frac{1.96\ \text{g } CO_2}{1\ \text{L}} \times \frac{1\ \text{mol } CO_2}{44.01\ \text{g } CO_2} \times \frac{6.022\times10^{23}\ \text{molecules } CO_2}{1\ \text{mol } CO_2}$$

$$= \boxed{2.68\times10^{22}\ \text{molecules } CO_2/\text{L}}$$

(b) Density and molecules of CO_2 per liter at room conditions. Summary of gas properties:

$$T = 20.°\text{C} + 273.15 = 293\ \text{K} \qquad P = 1.00\ \text{atm} \qquad \mathcal{M}\text{ of } CO_2 = 44.01\ \text{g/mol}$$

Calculating density:

$$d = \frac{\mathcal{M} \times P}{RT} = \frac{44.01\ \text{g/mol} \times 1.00\ \text{atm}}{0.0821\ \dfrac{\text{atm}\cdot\text{L}}{\text{mol}\cdot\text{K}} \times 293\ \text{K}} = \boxed{1.83\ \text{g/L}}$$

Converting from mass/L to molecules/L:

$$\text{Molecules } CO_2/\text{L} = \frac{1.83\ \text{g } CO_2}{1\ \text{L}} \times \frac{1\ \text{mol } CO_2}{44.01\ \text{g } CO_2} \times \frac{6.022\times10^{23}\ \text{molecules } CO_2}{1\ \text{mol } CO_2}$$

$$= \boxed{2.50\times10^{22}\ \text{molecules } CO_2/\text{L}}$$

Check Round off to check the density values; for example, in (a), at STP:

$$\frac{50 \text{ g/mol} \times 1 \text{ atm}}{0.1 \frac{\text{atm·L}}{\text{mol·K}} \times 250 \text{ K}} = 2 \text{ g/L} \approx 1.96 \text{ g/L}$$

At the higher temperature in (b), the density should decrease, which can happen only if there are fewer molecules per liter, so the answer is reasonable.

Comment **1.** An *alternative approach* for finding the density of most simple gases, but *at STP only,* is to divide the molar mass by the standard molar volume, 22.4 L:

$$d = \frac{\mathcal{M}}{V} = \frac{44.01 \text{ g/mol}}{22.4 \text{ L/mol}} = 1.96 \text{ g/L}$$

Then, once you know the density at one temperature (0°C), you can find it at any other temperature with the following relationship: $d_1/d_2 = T_2/T_1$.

2. Note that we have different numbers of significant figures for the pressure values. In (a), "1 atm" is part of the definition of STP, so it is an exact number. In (b), "1.00 atm" is specified to allow three significant figures in the answer.

FOLLOW-UP PROBLEM 5.7 Compare the density of CO_2 at 0°C and 380. torr with its density at STP.

The Molar Mass of a Gas

Through another rearrangement of the ideal gas law, we can determine the molar mass of an unknown gas or a volatile liquid (one that is easily vaporized):

$$n = \frac{m}{\mathcal{M}} = \frac{PV}{RT} \quad \text{so} \quad \mathcal{M} = \frac{mRT}{PV} \tag{5.10}$$

Notice that this equation is just a rearrangement of Equation 5.9.

Sample Problem 5.8 Finding the Molar Mass of a Volatile Liquid

Problem An organic chemist isolates a colorless liquid from a petroleum sample. She places the liquid in a preweighed flask and puts the flask in boiling water, which vaporizes the liquid and fills the flask with gas. She closes the flask and reweighs it. She obtains the following data:

Volume (V) of flask = 213 mL T = 100.0°C P = 754 torr
Mass of flask + gas = 78.416 g Mass of flask = 77.834 g

Calculate the molar mass of the liquid.

Plan We are given V, T, P, and mass data and must find the molar mass ($\mathcal{M}$) of the liquid. We convert V to liters, T to kelvins, and P to atmospheres, find the mass of gas by subtracting the mass of the flask from the mass of the flask plus gas, and use Equation 5.10 to calculate $\mathcal{M}$.

Solution Summarizing and converting the gas variables:

$$V \text{ (L)} = 213 \text{ mL} \times \frac{1 \text{ L}}{1000 \text{ mL}} = 0.213 \text{ L} \qquad T \text{ (K)} = 100.0°\text{C} + 273.15 = 373.2 \text{ K}$$

$$P \text{ (atm)} = 754 \text{ torr} \times \frac{1 \text{ atm}}{760 \text{ torr}} = 0.992 \text{ atm} \qquad m = 78.416 \text{ g} - 77.834 \text{ g} = 0.582 \text{ g}$$

Calculating $\mathcal{M}$:

$$\mathcal{M} = \frac{mRT}{PV} = \frac{0.582 \text{ g} \times 0.0821 \frac{\text{atm·L}}{\text{mol·K}} \times 373.2 \text{ K}}{0.992 \text{ atm} \times 0.213 \text{ L}} = 84.4 \text{ g/mol}$$

Check Rounding to check the arithmetic, we have

$$\frac{0.6 \text{ g} \times 0.08 \frac{\text{atm·L}}{\text{mol·K}} \times 375 \text{ K}}{1 \text{ atm} \times 0.2 \text{ L}} = 90 \text{ g/mol} \qquad \text{(which is close to 84.4 g/mol)}$$

FOLLOW-UP PROBLEM 5.8 An empty 149-mL flask weighs 68.322 g before a sample of volatile liquid is added. The flask is then placed in a hot (95.0°C) water bath; the barometric pressure is 740. torr. The liquid vaporizes and the gas fills the flask. After cooling, flask and condensed liquid together weigh 68.697 g. What is the molar mass of the liquid?

The Partial Pressure of Each Gas in a Mixture of Gases

The gas behaviors we've discussed so far were observed in experiments with air, which is a mixture of gases; thus, the ideal gas law holds for virtually any simple gas at ordinary conditions, whether pure or a mixture, because

- Gases mix homogeneously (form a solution) in any proportions.
- Each gas in a mixture behaves as if it were the only gas present (assuming no chemical interactions).

Dalton's Law of Partial Pressures The second point above was discovered by John Dalton. During a nearly lifelong study of humidity, he observed that when water vapor is added to dry air, the total air pressure increases by the pressure of the water vapor:

$$P_{\text{humid air}} = P_{\text{dry air}} + P_{\text{added water vapor}}$$

He concluded that each gas in the mixture exerts a **partial pressure** equal to the pressure it would exert *by itself.* Stated as **Dalton's law of partial pressures,** his discovery was that *in a mixture of unreacting gases, the total pressure is the sum of the partial pressures of the individual gases:*

$$P_{\text{total}} = P_1 + P_2 + P_3 + \cdots \qquad (5.11)$$

As an example, suppose we have a tank of fixed volume that contains nitrogen gas at a certain pressure, and we introduce a sample of hydrogen gas into the tank. Each gas behaves independently, so we can write an ideal gas law expression for each:

$$P_{N_2} = \frac{n_{N_2}RT}{V} \qquad \text{and} \qquad P_{H_2} = \frac{n_{H_2}RT}{V}$$

Because each gas occupies the same total volume and is at the same temperature, the pressure of each gas depends only on its amount, n. Thus, the total pressure is

$$P_{\text{total}} = P_{N_2} + P_{H_2} = \frac{n_{N_2}RT}{V} + \frac{n_{H_2}RT}{V} = \frac{(n_{N_2} + n_{H_2})RT}{V} = \frac{n_{\text{total}}RT}{V}$$

where $n_{\text{total}} = n_{N_2} + n_{H_2}$.

Each component in a mixture contributes a fraction of the total number of moles in the mixture; this portion is the **mole fraction (X)** of that component. Multiplying X by 100 gives the mole percent. The sum of the mole fractions of all components must be 1, and the sum of the mole percents must be 100%. For N_2 in our mixture, the mole fraction is

$$X_{N_2} = \frac{n_{N_2}}{n_{\text{total}}} = \frac{n_{N_2}}{n_{N_2} + n_{H_2}}$$

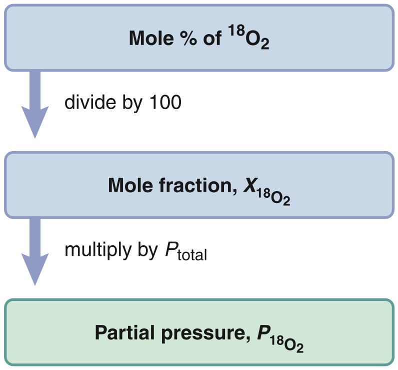
If the total pressure is due to the total number of moles, the partial pressure of gas A is the total pressure multiplied by the mole fraction of A, X_A:

$$P_A = X_A \times P_{\text{total}} \qquad (5.12)$$

Equation 5.12 is a very useful result. To see that it is valid for the mixture of N_2 and H_2, we recall that $X_{N_2} + X_{H_2} = 1$; then we obtain

$$P_{\text{total}} = P_{N_2} + P_{H_2} = (X_{N_2} \times P_{\text{total}}) + (X_{H_2} \times P_{\text{total}}) = (X_{N_2} + X_{H_2})P_{\text{total}} = 1 \times P_{\text{total}}$$

Road Map



Sample Problem 5.9 Applying Dalton's Law of Partial Pressures

Problem To study O_2 uptake by muscle at high altitude, a physiologist prepares an atmosphere consisting of 79 mole % N_2, 17 mole % $^{16}O_2$, and 4.0 mole % $^{18}O_2$. (The isotope ^{18}O will be measured to determine O_2 uptake.) The total pressure is 0.75 atm to simulate high altitude. Find the mole fraction and partial pressure of $^{18}O_2$ in the mixture.

Plan We must find $X_{^{18}O_2}$ and $P_{^{18}O_2}$ from P_{total} (0.75 atm) and the mole % of $^{18}O_2$ (4.0). Dividing the mole % by 100 gives the mole fraction, $X_{^{18}O_2}$. Then, using Equation 5.12, we multiply $X_{^{18}O_2}$ by P_{total} to find $P_{^{18}O_2}$.

Solution Calculating the mole fraction of $^{18}O_2$:

$$X_{^{18}O_2} = \frac{4.0 \text{ mol \% } ^{18}O_2}{100} = \boxed{0.040}$$

Solving for the partial pressure of $^{18}O_2$:

$$P_{^{18}O_2} = X_{^{18}O_2} \times P_{total} = 0.040 \times 0.75 \text{ atm} = \boxed{0.030 \text{ atm}}$$

Check $X_{^{18}O_2}$ is small because the mole % is small, so $P_{^{18}O_2}$ should be small also.

Comment At high altitudes, specialized brain cells that are sensitive to O_2 and CO_2 levels in the blood trigger an increase in rate and depth of breathing for several days, until a person becomes acclimated.

FOLLOW-UP PROBLEM 5.9 To prevent the presence of air, noble gases are placed over highly reactive chemicals to act as inert "blanketing" gases. A chemical engineer puts a mixture of noble gases consisting of 5.50 g of He, 15.0 g of Ne, and 35.0 g of Kr in a piston-cylinder assembly at STP. Calculate the partial pressure of each gas.

Table 5.2 Vapor Pressure of Water (P_{H_2O}) at Different T

T (°C)	P_{H_2O} (torr)	T (°C)	P_{H_2O} (torr)
0	4.6	40	55.3
5	6.5	45	71.9
10	9.2	50	92.5
12	10.5	55	118.0
14	12.0	60	149.4
16	13.6	65	187.5
18	15.5	70	233.7
20	17.5	75	289.1
22	19.8	80	355.1
24	22.4	85	433.6
26	25.2	90	525.8
28	28.3	95	633.9
30	31.8	100	760.0
35	42.2		

Collecting a Gas over Water Whenever a gas is in contact with water, some of the water vaporizes into the gas. The water vapor that mixes with the gas contributes the *vapor pressure,* a portion of the total pressure that depends only on the water temperature (Table 5.2). A common use of the law of partial pressures is to determine the yield of a water-insoluble gas formed in a reaction: the gaseous product bubbles through water, some water vaporizes into the bubbles, and the mixture of product gas and water vapor is collected into an inverted container (Figure 5.11).

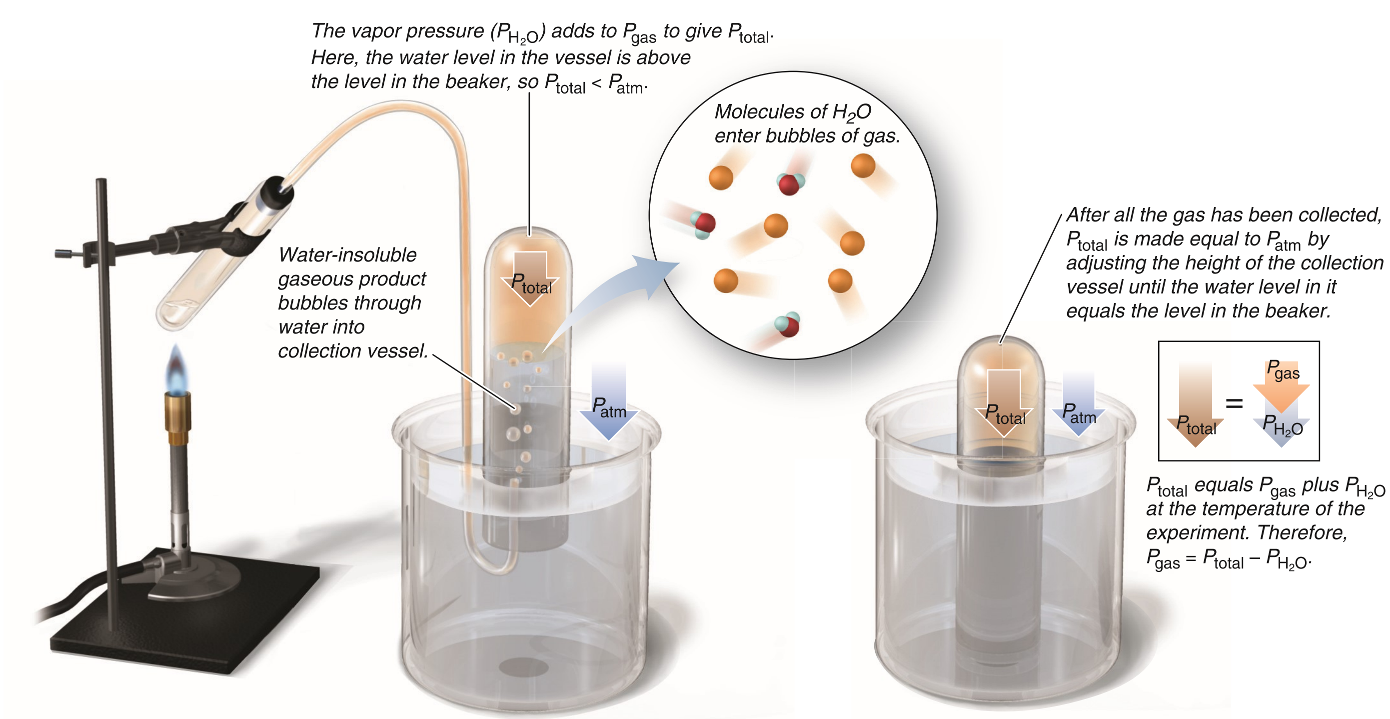


Figure 5.11 Collecting a water-insoluble gaseous product and determining its pressure.

To determine the yield, we look up the vapor pressure (P_{H_2O}) at the temperature of the experiment in Table 5.2 and subtract it from the total gas pressure (P_{total}, corrected for barometric pressure) to get the partial pressure of the gaseous product (P_{gas}). With V and T known, we can calculate the amount of product.

Sample Problem 5.10 Calculating the Amount of Gas Collected over Water

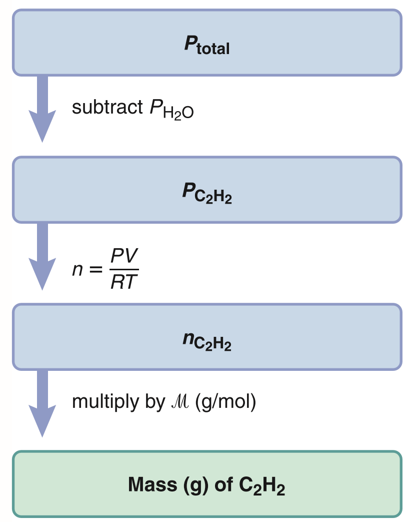
Problem Acetylene (C_2H_2), an important fuel in welding, is produced in the laboratory when calcium carbide (CaC_2) reacts with water:

$$CaC_2(s) + 2H_2O(l) \longrightarrow C_2H_2(g) + Ca(OH)_2(aq)$$

For a sample of acetylene collected over water, total gas pressure (adjusted to barometric pressure) is 738 torr and the volume is 523 mL. At the temperature of the gas (23°C), the vapor pressure of water is 21 torr. How many grams of acetylene are collected?

Plan In order to find the mass of C_2H_2, we first need to find the number of moles of C_2H_2, $n_{C_2H_2}$, which we can obtain from the ideal gas law by calculating $P_{C_2H_2}$. The barometer reading gives us P_{total}, which is the sum of $P_{C_2H_2}$ and P_{H_2O}, and we are given P_{H_2O}, so we subtract to find $P_{C_2H_2}$. We are also given V and T, so we convert to consistent units, and find $n_{C_2H_2}$ from the ideal gas law. Then we convert moles to grams using the molar mass from the formula, as shown in the road map.

Road Map



Solution Summarizing and converting the gas variables:

$$P_{C_2H_2}\ (\text{torr}) = P_{total} - P_{H_2O} = 738\ \text{torr} - 21\ \text{torr} = 717\ \text{torr}$$

$$P_{C_2H_2}\ (\text{atm}) = 717\ \text{torr} \times \frac{1\ \text{atm}}{760\ \text{torr}} = 0.943\ \text{atm}$$

$$V\ (\text{L}) = 523\ \text{mL} \times \frac{1\ \text{L}}{1000\ \text{mL}} = 0.523\ \text{L}$$

$$T\ (\text{K}) = 23°\text{C} + 273.15 = 296\ \text{K}$$

$$n_{C_2H_2} = \text{unknown}$$

Solving for $n_{C_2H_2}$:

$$n_{C_2H_2} = \frac{PV}{RT} = \frac{0.943\ \text{atm} \times 0.523\ \text{L}}{0.0821\ \frac{\text{atm·L}}{\text{mol·K}} \times 296\ \text{K}} = 0.0203\ \text{mol}$$

Converting $n_{C_2H_2}$ to mass (g):

$$\text{Mass (g) of } C_2H_2 = 0.0203\ \text{mol}\ C_2H_2 \times \frac{26.04\ \text{g}\ C_2H_2}{1\ \text{mol}\ C_2H_2} = \boxed{0.529\ \text{g}\ C_2H_2}$$

Check Rounding to one significant figure and doing a quick arithmetic check for n gives

$$n \approx \frac{1\ \text{atm} \times 0.5\ \text{L}}{0.08\ \frac{\text{atm·L}}{\text{mol·K}} \times 300\ \text{K}} = 0.02\ \text{mol} \approx 0.0203\ \text{mol}$$

Comment The C_2^{2-} ion (called the *carbide,* or *acetylide, ion*) is $^-C{\equiv}C^-$, which acts as a base in water, removing an H^+ ion from two H_2O molecules to form acetylene, $H{-}C{\equiv}C{-}H$.

FOLLOW-UP PROBLEM 5.10 A small piece of zinc reacts with dilute HCl to form H_2, which is collected over water at 16°C into a large flask. The total pressure is adjusted to barometric pressure (752 torr), and the volume is 1495 mL. Use Table 5.2 to help calculate the partial pressure and mass of H_2.

The Ideal Gas Law and Reaction Stoichiometry

As you saw in Chapters 3 and 4, and in the preceding discussion of collecting a gas over water, many reactions involve gases as reactants or products. From the balanced equation for such a reaction, you can calculate the amounts (mol) of reactants and products and convert these quantities into masses or numbers of molecules. Figure 5.12 *(next page)* shows how you use the ideal gas law to convert between gas variables (P, T, and V) and amounts (mol) of gaseous reactants and products. In effect, you combine a gas law problem with a stoichiometry problem, as you'll see in Sample Problems 5.11 and 5.12.

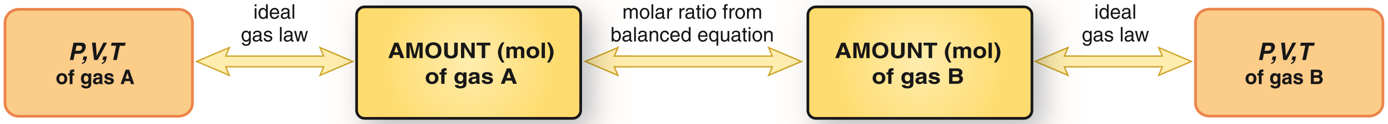


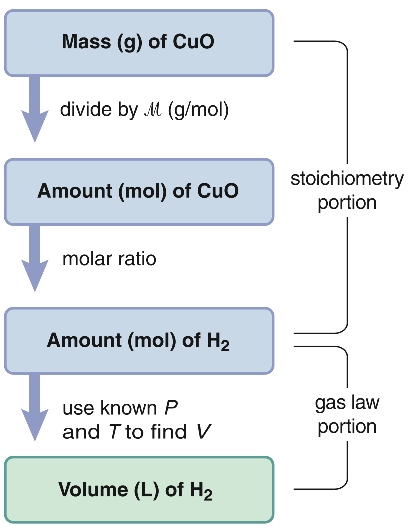
Figure 5.12 The relationships among the amount (mol, n) of gaseous reactant (or product) and the gas pressure (P), volume (V), and temperature (T).

Sample Problem 5.11 Using Gas Variables to Find Amounts of Reactants or Products I

Problem Copper reacts with any oxygen present as an impurity in the ethylene used to make polyethylene. The copper is regenerated when hot H_2 reduces the copper(II) oxide, forming the pure metal and H_2O. What volume of H_2 at 765 torr and 225°C is needed to reduce 35.5 g of copper(II) oxide?

Plan This is a stoichiometry *and* gas law problem. To find V_{H_2}, we first need n_{H_2}. We write and balance the equation. Next, we convert the given mass (35.5 g) of copper(II) oxide, CuO, to amount (mol) and use the molar ratio to find amount (mol) of H_2 needed (stoichiometry portion). Then, we use the ideal gas law to convert moles of H_2 to liters (gas law portion). A road map is shown, but you are familiar with all the steps.

Road Map



Solution Writing the balanced equation:

$$CuO(s) + H_2(g) \longrightarrow Cu(s) + H_2O(g)$$

Calculating n_{H_2}:

$$n_{H_2} = 35.5 \text{ g CuO} \times \frac{1 \text{ mol CuO}}{79.55 \text{ g CuO}} \times \frac{1 \text{ mol } H_2}{1 \text{ mol CuO}} = 0.446 \text{ mol } H_2$$

Summarizing and converting other gas variables:

$$V = \text{unknown} \qquad P\,(\text{atm}) = 765 \text{ torr} \times \frac{1 \text{ atm}}{760 \text{ torr}} = 1.01 \text{ atm}$$

$$T\,(\text{K}) = 225°\text{C} + 273.15 = 498 \text{ K}$$

Solving for V_{H_2}:

$$V = \frac{nRT}{P} = \frac{0.446 \text{ mol} \times 0.0821 \frac{\text{atm·L}}{\text{mol·K}} \times 498 \text{ K}}{1.01 \text{ atm}} = \boxed{18.1 \text{ L}}$$

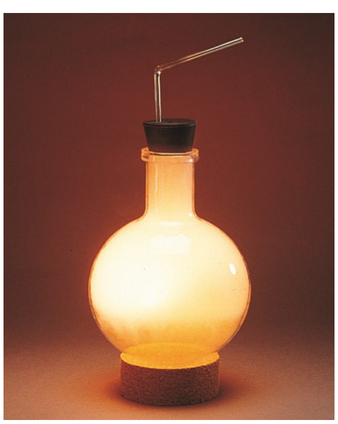
Check One way to check the answer is to compare it with the molar volume of an ideal gas at STP (22.4 L at 273.15 K and 1 atm). One mole of H_2 at STP occupies about 22 L, so less than 0.5 mol occupies less than 11 L. T is less than twice 273 K, so V should be less than twice 11 L.

Comment The main point here is that the stoichiometry provides one gas variable (n), two more are given, and the ideal gas law is used to find the fourth.

FOLLOW-UP PROBLEM 5.11 Sulfuric acid reacts with sodium chloride to form aqueous sodium sulfate and hydrogen chloride gas. How many milliliters of gas form at STP when 0.117 kg of sodium chloride reacts with excess sulfuric acid?

Sample Problem 5.12 Using Gas Variables to Find Amounts of Reactants or Products II

Problem The alkali metals [Group 1A(1)] react with the halogens [Group 7A(17)] to form ionic metal halides. What mass of potassium chloride forms when 5.25 L of chlorine gas at 0.950 atm and 293 K reacts with 17.0 g of potassium *(see photo)*?



Chlorine gas reacting with potassium.

Plan The amounts of two reactants are given, so this is a limiting-reactant problem. The only difference between this and previous limiting-reactant problems (see Sample

Problem 3.19, p. 96) is that here we use the ideal gas law to find the amount (n) of gaseous reactant from the known V, P, and T. We first write the balanced equation and then use it to find the limiting reactant and the amount and mass of product.

Solution Writing the balanced equation:

$$2K(s) + Cl_2(g) \longrightarrow 2KCl(s)$$

Summarizing the gas variables:

$$P = 0.950 \text{ atm} \qquad V = 5.25 \text{ L}$$
$$T = 293 \text{ K} \qquad n = \text{unknown}$$

Solving for n_{Cl_2}:

$$n_{Cl_2} = \frac{PV}{RT} = \frac{0.950 \text{ atm} \times 5.25 \text{ L}}{0.0821 \frac{\text{atm}\cdot\text{L}}{\text{mol}\cdot\text{K}} \times 293 \text{ K}} = 0.207 \text{ mol}$$

Converting from mass (g) of potassium (K) to amount (mol):

$$\text{Amount (mol) of K} = 17.0 \text{ g K} \times \frac{1 \text{ mol K}}{39.10 \text{ g K}} = 0.435 \text{ mol K}$$

Determining the limiting reactant: If Cl_2 is limiting,

$$\text{Amount (mol) of KCl} = 0.207 \text{ mol } Cl_2 \times \frac{2 \text{ mol KCl}}{1 \text{ mol } Cl_2} = 0.414 \text{ mol KCl}$$

If K is limiting,

$$\text{Amount (mol) of KCl} = 0.435 \text{ mol K} \times \frac{2 \text{ mol KCl}}{2 \text{ mol K}} = 0.435 \text{ mol KCl}$$

Cl_2 is the limiting reactant because it forms less KCl.
Converting from amount (mol) of KCl to mass (g):

$$\text{Mass (g) of KCl} = 0.414 \text{ mol KCl} \times \frac{74.55 \text{ g KCl}}{1 \text{ mol KCl}} = 30.9 \text{ g KCl}$$

Check The gas law calculation seems correct. At STP, 22 L of Cl_2 gas contains about 1 mol, so a 5-L volume will contain a bit less than 0.25 mol of Cl_2. Moreover, since P (in numerator) is slightly lower than STP, and T (in denominator) is slightly higher than STP, these values should lower the calculated n further below the ideal value. The mass of KCl seems correct: less than 0.5 mol of KCl gives $<0.5 \text{ mol} \times \mathcal{M}$ (~75 g/mol), and $30.9 \text{ g} < 0.5 \text{ mol} \times 75$ g/mol.

FOLLOW-UP PROBLEM 5.12 Ammonia and hydrogen chloride gases react to form solid ammonium chloride. A 10.0-L reaction flask contains ammonia at 0.452 atm and 22°C, and 155 mL of hydrogen chloride gas at 7.50 atm and 271 K is introduced. After the reaction occurs and the temperature returns to 22°C, what is the pressure inside the flask? (Neglect the volume of the solid product.)

Summary of Section 5.4

- Gas density is inversely related to temperature: higher T causes lower d, and vice versa. At the same P and T, gases with larger $\mathcal{M}$ have higher d.
- In a mixture of gases, each component contributes its partial pressure to the total pressure (Dalton's law of partial pressures). The mole fraction of each component is the ratio of its partial pressure to the total pressure.
- When a gaseous reaction product is collected by bubbling it through water, the total pressure is the sum of the gas pressure and the vapor pressure of water at the given temperature.
- By converting the variables P, V, and T for a gaseous reactant (or product) to amount (n, mol), we can solve stoichiometry problems for gaseous reactions.

5.5 • THE KINETIC-MOLECULAR THEORY: A MODEL FOR GAS BEHAVIOR

So far we have discussed behaviors of various gas samples under different conditions: decreasing cylinder volume, increasing tank pressure, and so forth. This section presents the central model that explains macroscopic gas behavior at the level of individul particles: the **kinetic-molecular theory.** The theory draws quantitative conclusions based on a few postulates (assumptions), but our discussion will be largely qualitative.

How the Kinetic-Molecular Theory Explains the Gas Laws

Let's address some questions the theory must answer, state the postulates, and then draw conclusions that explain the gas laws and related phenomena.

Questions Concerning Gas Behavior Observing gas behavior at the macroscopic level, we must derive a molecular model that explains it:

1. *Origin of pressure.* Pressure is a measure of the force a gas exerts on a surface. How do individual gas particles create this force?
2. *Boyle's law ($V \propto 1/P$).* A change in gas pressure in one direction causes a change in gas volume in the other. What happens to the particles when external pressure compresses the gas volume? And why aren't liquids and solids compressible?
3. *Dalton's law ($P_{total} = P_1 + P_2 + P_3 + \cdots$).* The pressure of a gas mixture is the sum of the pressures of the individual gases. Why does each gas contribute to the total pressure in proportion to its number of particles?
4. *Charles's law ($V \propto T$).* A change in temperature causes a corresponding change in volume. What effect does higher temperature have on gas particles that increases gas volume? This question raises a more fundamental one: what does temperature measure on the molecular scale?
5. *Avogadro's law ($V \propto n$).* Gas volume depends on the number of moles present, not on the chemical nature of the gas. But shouldn't 1 mol of heavier particles exert more pressure, and thus take up more space, than 1 mol of lighter ones?

Postulates of the Kinetic-Molecular Theory The theory is based on three postulates:

Postulate 1. *Particle volume.* A gas consists of a large collection of individual particles with empty space between them. The volume of each particle is so small compared with the volume of the whole sample that it is assumed to be zero; each particle is essentially a point of mass.

Postulate 2. *Particle motion.* The particles are in constant, random, straight-line motion, except when they collide with the container walls or with each other.

Postulate 3. *Particle collisions.* The collisions are *elastic,* which means that, like minute billiard balls, the colliding particles exchange energy but do not lose any energy through friction. Thus, *their total kinetic energy (E_k) is constant.* Between collisions, the particles do not influence each other by attractive or repulsive forces.

Gas behavior that conforms to these postulates is called *ideal*. (As you'll see in Section 5.6, most real gases behave almost ideally at ordinary temperatures and pressures.)

Imagine what a sample of gas in a container looks like. Countless minute particles move in every direction, smashing into the container walls and each other. Any given particle changes its speed often—at one moment standing still from a head-on collision and the next moment zooming away from a smash on the side.

In the sample as a whole, *each particle has a molecular speed* (u); *most are moving near the most probable speed, but some are much faster and others much slower.* Figure 5.13 depicts this distribution of molecular speeds for N_2 gas at three temperatures.

Note that the curves flatten and spread at higher temperatures and that the *most probable speed (the peak of each curve) increases as the temperature increases.* This

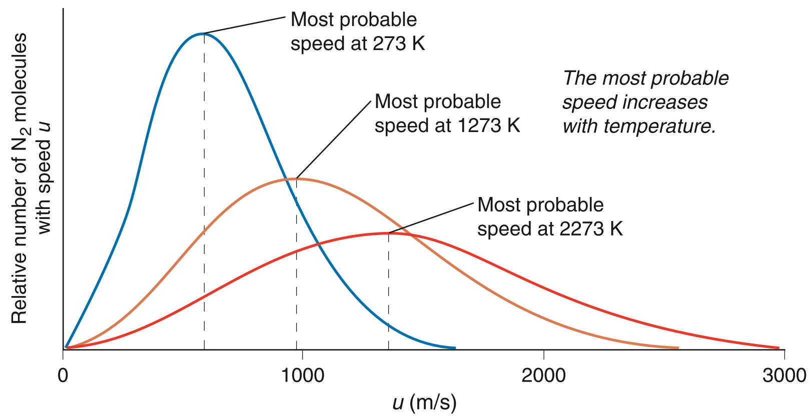


Figure 5.13 Distribution of molecular speeds for N_2 at three temperatures.

increase occurs because the average kinetic energy of the molecules, which is related to the most probable speed, is proportional to the absolute temperature: $\overline{E_k} \propto T$, or $\overline{E_k} = cT$, where $\overline{E_k}$ is the average kinetic energy of the molecules (an overbar indicates the average value of a quantity) and c is a constant that is the same for any gas. (We'll return to this equation shortly.) Thus, a major conclusion based on the distribution of speeds, which arises directly from postulate 3, is that *at a given temperature, all gases have the same average kinetic energy.*

A Molecular View of the Gas Laws Let's keep visualizing gas particles in a container to see how the theory explains the macroscopic behavior of gases and answers the questions we posed above:

1. *Origin of pressure* (Figure 5.14). From postulates 1 and 2, each gas particle (point of mass) colliding with the container walls (and bottom of piston) exerts a force. Countless collisions over the inner surface of the container result in a pressure. The greater the number of particles, the more frequently they collide with the container, and so the greater the pressure.

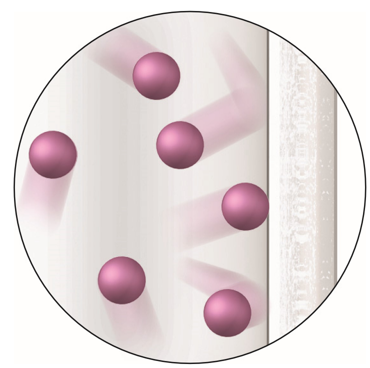


Figure 5.14 Pressure arises from countless collisions between gas particles and walls.

2. *Boyle's law* ($V \propto 1/P$) (Figure 5.15). The particles in a gas are points of mass with empty space between them (postulate 1). Before any change in pressure, the pressure exerted *by* the gas (P_{gas}) equals the pressure exerted *on* the gas (P_{ext}), and there is some average distance (d_1) between the particles and the container walls. As P_{ext} increases at constant temperature, the average distance (d_2) between the particles and the walls decreases (that is, $d_2 < d_1$), and so the sample volume decreases. Collisions of the particles with the walls become more frequent over the shorter average distance, which causes P_{gas} to increase until it again equals P_{ext}. The fact that liquids and solids cannot be compressed implies there is little, if any, free space between their particles.

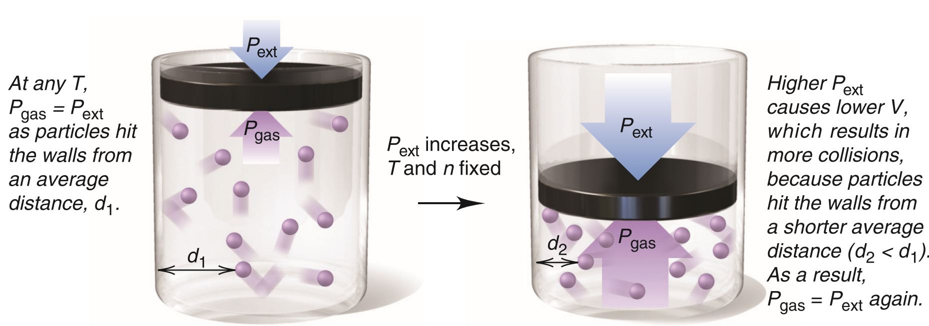


Figure 5.15 A molecular view of Boyle's law.

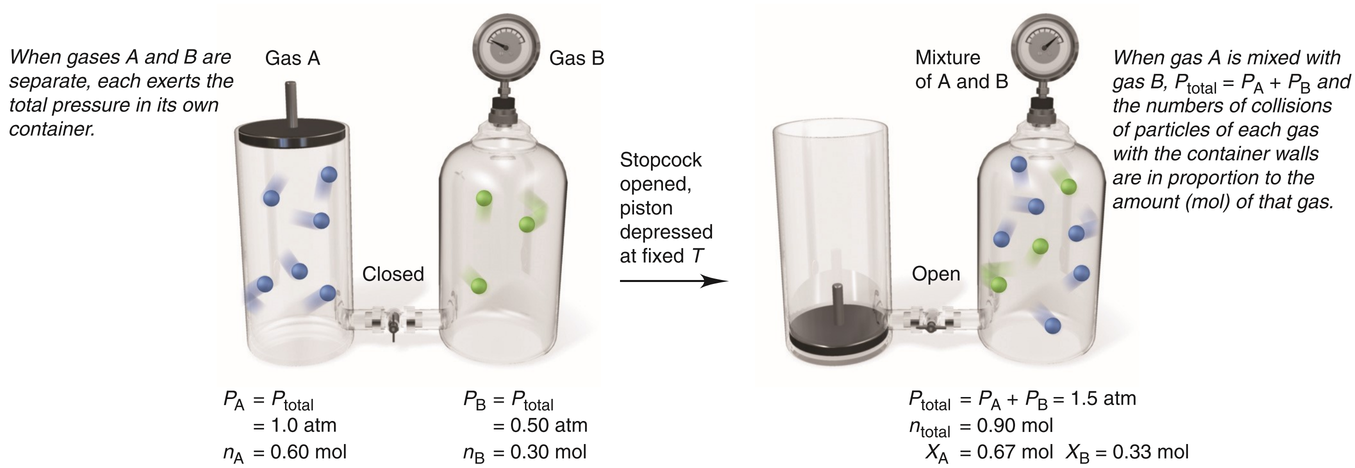
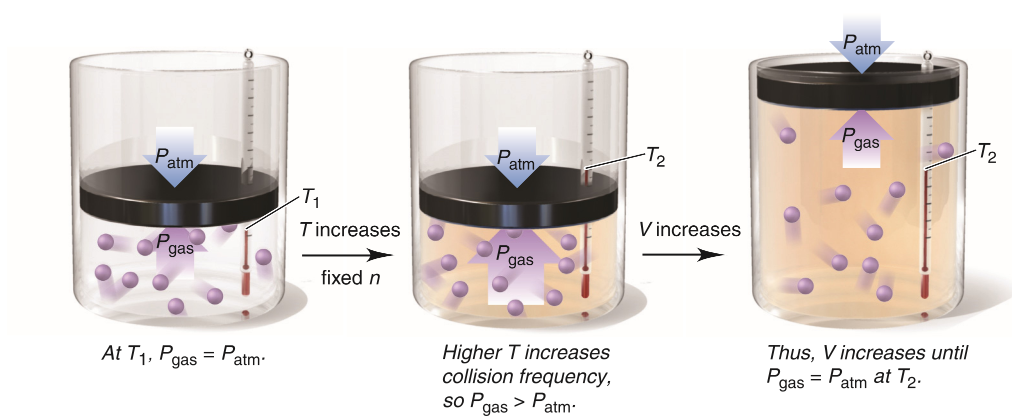


Figure 5.16 A molecular view of Dalton's law.

3. *Dalton's law of partial pressures* ($P_{total} = P_A + P_B$) (Figure 5.16). Adding a given amount (mol) of gas A to a given amount of gas B causes an increase in the total number of particles, in proportion to the particles of A added. This increase causes a corresponding increase in the total number of collisions with the walls per second (postulate 2), which causes a corresponding increase in the total pressure of the gas mixture (P_{total}). Each gas exerts a fraction of P_{total} in proportion to its fraction of the total number of particles (or equivalently, its fraction of the total number of moles, that is, the mole fraction).

4. *Charles's law* ($V \propto T$) (Figure 5.17). At some starting temperature, T_1, the external (atmospheric) pressure (P_{atm}) equals the pressure of the gas (P_{gas}). When the gas is heated and the temperature increases to T_2, the most probable molecular speed and the average kinetic energy increase (postulate 3). Thus, the particles hit the walls more frequently *and* more energetically. This change temporarily increases P_{gas}. As a result, the piston moves up, which increases the volume and lowers the collision frequency until P_{atm} and P_{gas} are again equal.

Figure 5.17 A molecular view of Charles's law.



5. *Avogadro's law* ($V \propto n$) (Figure 5.18). At some starting amount, n_1, of gas, P_{atm} equals P_{gas}. When more gas is added from the attached tank, the amount increases to n_2. Thus, more particles hit the walls more frequently, which temporarily increases P_{gas}. As a result, the piston moves up, which increases the volume and lowers the collision frequency until P_{atm} and P_{gas} are again equal.

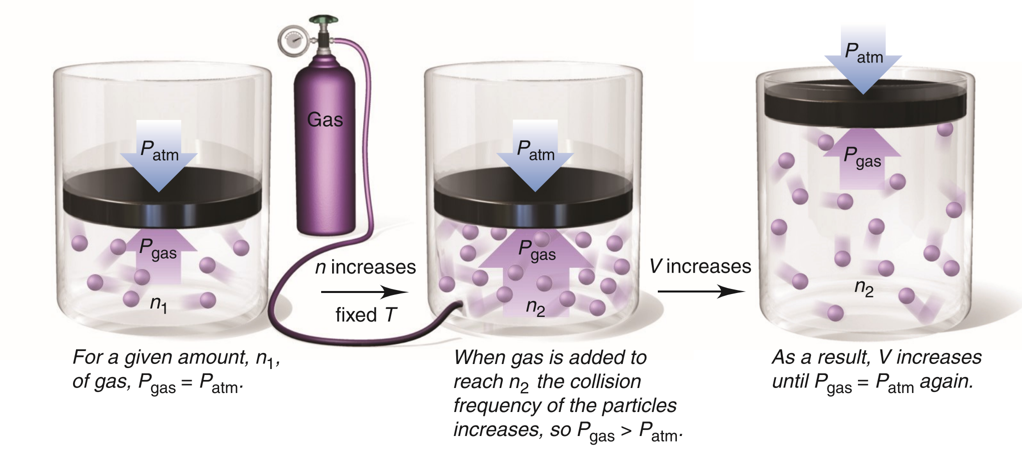


Figure 5.18 A molecular view of Avogadro's law.

The Central Importance of Kinetic Energy Recall from Chapter 1 that the kinetic energy of an object is the energy associated with its motion. It is key to explaining some implications of Avogadro's law and, most importantly, the meaning of temperature.

1. *Implications of Avogadro's law*. As we just saw, Avogadro's law says that, at any given T and P, the volume of a gas depends only on the number of moles—that is, number of particles—in the sample. The law doesn't mention the chemical nature of the gas, so equal numbers of particles of any two gases, say O_2 and H_2, should occupy the same volume. But, why don't the heavier O_2 molecules exert more pressure on the container walls, and thus take up more volume, than the lighter H_2 molecules? To answer this, we'll show one way to express kinetic energy mathematically:

$$E_k = \frac{1}{2}\text{mass} \times \text{speed}^2$$

This equation says that, for a given E_k, an object's mass and speed are inversely related, which means that *a heavier object moving slower can have the same kinetic energy as a lighter object moving faster.* Figure 5.19 shows that, for several gases, *the most probable speed (top of each curve) increases as the molar mass (number in parentheses) decreases*.

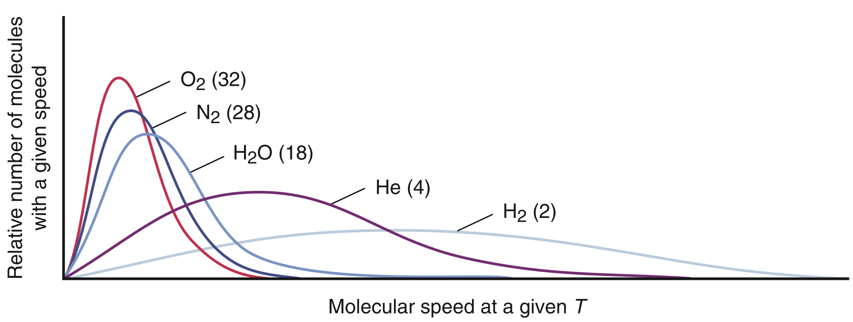


Figure 5.19 The relationship between molar mass and molecular speed. At a given temperature, gases with lower molar masses (numbers in parentheses) have higher most probable speeds (peak of each curve).

As we saw earlier, postulate 3 of the kinetic-molecular theory directly implies that, at a given T, all gases have the same average kinetic energy. From Figure 5.19, we see that O_2 molecules move more slowly, on average, than H_2 molecules. With their higher most probable speed, H_2 molecules collide with the walls of a container more often than O_2 molecules do, but their lower mass means that each collision has less force. Therefore, at a given T, equimolar samples of H_2 and O_2 (or any other gas) exert the same pressure and, thus, occupy the same volume because, on average, *their molecules hit the walls with the same kinetic energy*.

2. *The meaning of temperature.* Closely related to these ideas is the central relation between kinetic energy and temperature. Earlier we said that the average kinetic energy of the particles ($\overline{E_k}$) equals the absolute temperature times a constant; that is, $\overline{E_k} = cT$. Using definitions of velocity, momentum, force, and pressure, we can express this relationship by an equation that reveals the constant c:

$$\overline{E_k} = \tfrac{3}{2}\left(\frac{R}{N_A}\right)T$$

where R is the gas constant and N_A is the symbol for Avogadro's number. This equation makes the essential point that *temperature is a* ***measure*** *of the average kinetic energy of the particles:* as T increases, $\overline{E_k}$ increases, and vice versa. Temperature is an intensive property (Section 1.4), so it is not related to the *total* energy of motion of the particles, which depends on the size of the sample, but to the *average* energy.

Thus, for example, in the macroscopic world, we heat a beaker of water over a flame and see the mercury rise inside a thermometer we put in the beaker. We see this because, in the molecular world, kinetic energy transfers from higher energy gas particles in the flame, in turn, to lower energy particles in the beaker glass, the water molecules, the particles in the thermometer glass, and the atoms of mercury.

Root-Mean-Square Speed Finally, let's derive an expression for the speed of a gas particle that has the average kinetic energy of the particles in a sample. From the general expression for kinetic energy of an object,

$$E_k = \tfrac{1}{2}\text{mass} \times \text{speed}^2$$

the average kinetic energy of each particle in a large population is

$$\overline{E_k} = \tfrac{1}{2}m\overline{u^2}$$

where m is the particle's mass (atomic or molecular) and $\overline{u^2}$ is the average of the squares of the molecular speeds. Setting these two expressions for average kinetic energy equal to each other gives

$$\tfrac{1}{2}m\overline{u^2} = \tfrac{3}{2}\left(\frac{R}{N_A}\right)T$$

Multiplying through by Avogadro's number, N_A, gives the average kinetic energy for a mole of gas particles:

$$\tfrac{1}{2}N_A\, m\overline{u^2} = \tfrac{3}{2}RT$$

Avogadro's number times the molecular mass, $N_A \times m$, is the molar mass, $\mathcal{M}$, and solving for $\overline{u^2}$, we have

$$\overline{u^2} = \frac{2}{\mathcal{M}} \times \frac{3}{2}RT = \frac{3RT}{\mathcal{M}}$$

The square root of $\overline{u^2}$ is the root-mean-square speed, or **rms speed (u_{rms}):** *a particle moving at this speed has the average kinetic energy*. Taking the square root of both sides of the previous equation gives

$$\boxed{u_{rms} = \sqrt{\frac{3RT}{\mathcal{M}}}} \quad \textbf{(5.13)}$$

where R is the gas constant, T is the absolute temperature, and $\mathcal{M}$ is the molar mass. (Because we want u in m/s and R includes the joule, which has units of kg·m²/s², we use the value 8.314 J/mol·K for R and express $\mathcal{M}$ in kg/mol.)

Thus, as an example, the root-mean-square speed of an O_2 molecule ($\mathcal{M}$ = 3.200×10^{-2} kg/mol) at room temperature (20°C, or 293 K) in the air you're breathing right now is

$$u_{rms} = \sqrt{\frac{3RT}{\mathcal{M}}} = \sqrt{\frac{3(8.314\ \text{J/mol·K})(293\ \text{K})}{3.200\times10^{-2}\ \text{kg/mol}}} = \sqrt{\frac{3(8.314\ \cancel{\text{kg}}\cdot\text{m}^2/\text{s}^2/\cancel{\text{mol}}\cdot\cancel{\text{K}})(293\ \cancel{\text{K}})}{3.200\times10^{-2}\ \cancel{\text{kg}}/\cancel{\text{mol}}}}$$

$$= 478\ \text{m/s (about 1070 mi/hr)}$$

Effusion and Diffusion

The movement of a gas into a vacuum and the movement of gases through one another are phenomena with some vital applications.

The Process of Effusion One of the early triumphs of the kinetic-molecular theory was an explanation of **effusion,** the process by which a gas escapes through a tiny hole in its container into an evacuated space. In 1846, Thomas Graham studied the effusion rate of a gas, the number of molecules escaping per unit time, and found that it was inversely proportional to the square root of the gas density. But, density is directly related to molar mass, so **Graham's law of effusion** is stated as follows: *the rate of effusion of a gas is inversely proportional to the square root of its molar mass,* or

$$\text{Rate of effusion} \propto \frac{1}{\sqrt{\mathcal{M}}}$$

Argon (Ar) is lighter than krypton (Kr), so it effuses faster, assuming equal pressures of the two gases (Figure 5.20). Thus, the ratio of the rates is

$$\frac{\text{Rate}_{\text{Ar}}}{\text{Rate}_{\text{Kr}}} = \frac{\sqrt{\mathcal{M}_{\text{Kr}}}}{\sqrt{\mathcal{M}_{\text{Ar}}}} \quad \text{or, in general,} \quad \frac{\text{Rate}_{\text{A}}}{\text{Rate}_{\text{B}}} = \frac{\sqrt{\mathcal{M}_{\text{B}}}}{\sqrt{\mathcal{M}_{\text{A}}}} = \sqrt{\frac{\mathcal{M}_{\text{B}}}{\mathcal{M}_{\text{A}}}} \qquad (5.14)$$

The kinetic-molecular theory explains that, at a given temperature and pressure, *the gas with the lower molar mass effuses faster because the rms speed of its molecules is higher; therefore, more molecules collide with the hole and escape per unit time.*

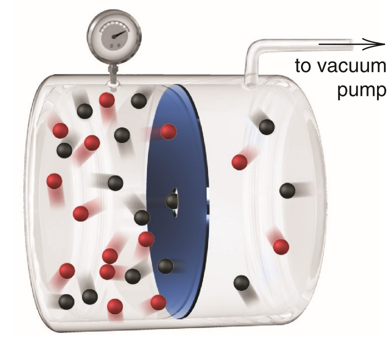


Figure 5.20 Effusion. Lighter *(black)* particles effuse faster than heavier *(red)* particles.

Sample Problem 5.13 Applying Graham's Law of Effusion

Problem A mixture of helium (He) and methane (CH_4) is placed in an effusion apparatus. Calculate the ratio of their effusion rates.

Plan The effusion rate is inversely proportional to $\sqrt{\mathcal{M}}$, so we find the molar mass of each substance from the formula and take its square root. The inverse of the ratio of the square roots is the ratio of the effusion rates.

Solution $\mathcal{M}$ of CH_4 = 16.04 g/mol $\mathcal{M}$ of He = 4.003 g/mol

Calculating the ratio of the effusion rates:

$$\frac{\text{Rate}_{\text{He}}}{\text{Rate}_{\text{CH}_4}} = \sqrt{\frac{\mathcal{M}_{\text{CH}_4}}{\mathcal{M}_{\text{He}}}} = \sqrt{\frac{16.04 \text{ g/mol}}{4.003 \text{ g/mol}}} = \sqrt{4.007} = 2.002$$

Check A ratio >1 makes sense because the lighter He should effuse faster than the heavier CH_4. Because the molar mass of CH_4 is about four times the molar mass of He, He should effuse about twice as fast as CH_4 ($\sqrt{4}$).

FOLLOW-UP PROBLEM 5.13 If it takes 1.25 min for 0.010 mol of He to effuse, how long will it take for the same amount of ethane (C_2H_6) to effuse?

Applications of Effusion The process of effusion has two important uses.

1. *Determination of molar mass.* We can also use Graham's law to *determine the molar mass of an unknown gas.* By comparing the effusion rate of gas X with that of a known gas, such as He, we can solve for the molar mass of X:

$$\frac{\text{Rate}_{\text{X}}}{\text{Rate}_{\text{He}}} = \sqrt{\frac{\mathcal{M}_{\text{He}}}{\mathcal{M}_{\text{X}}}}$$

Squaring both sides and solving for the molar mass of X gives

$$\mathcal{M}_{\text{X}} = \mathcal{M}_{\text{He}} \times \left(\frac{\text{rate}_{\text{He}}}{\text{rate}_{\text{X}}}\right)^2$$

2. *Preparation of nuclear fuel.* By far the most important application of Graham's law is in the preparation of fuel for nuclear energy reactors. The process of *isotope enrichment* increases the proportion of fissionable, but rarer, ^{235}U (only 0.7% by mass of naturally occurring uranium) to the nonfissionable, more abundant ^{238}U (99.3% by mass). Because the two isotopes have identical chemical properties, they are extremely difficult to separate chemically. But, one way to separate them takes advantage of a difference in a physical property—the effusion rate of their gaseous compounds. Uranium ore is treated with fluorine to yield a gaseous mixture of $^{238}UF_6$ and $^{235}UF_6$ that is pumped through a series of chambers separated by porous barriers. Molecules of $^{235}UF_6$ are slightly lighter ($\mathcal{M} = 349.03$) than molecules of $^{238}UF_6$ ($\mathcal{M} = 352.04$), so they move slightly faster and effuse through each barrier 1.0043 times faster. Many passes must be made, each one increasing the fraction of $^{235}UF_6$, until the mixture obtained is 3–5% by mass $^{235}UF_6$. This process was developed during the latter years of World War II and produced enough ^{235}U for two of the world's first atomic bombs.

The Process of Diffusion Closely related to effusion is the process of gaseous **diffusion,** the movement of one gas through another. Diffusion rates are also described generally by Graham's law:

$$\text{Rate of diffusion} \propto \frac{1}{\sqrt{\mathcal{M}}}$$

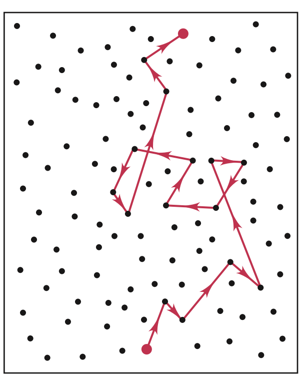
For two gases at equal pressures, such as NH_3 and HCl, moving through another gas or a mixture of gases, such as air, we find

$$\frac{\text{Rate}_{NH_3}}{\text{Rate}_{HCl}} = \sqrt{\frac{\mathcal{M}_{HCl}}{\mathcal{M}_{NH_3}}}$$

The reason for this dependence on molar mass is the same as for effusion rates: *lighter molecules have higher average speeds than heavier molecules, so they move farther in a given time.*

THINK OF IT THIS WAY

A Bizarre (and Dangerous) Molecular Highway



Why don't you smell perfume until a few seconds after the bottle has been opened? One reason is that a molecule of the scent doesn't travel very far before it collides with another molecule in the air. Look at the tortuous path of the red "odor" molecule, and imagine how much faster you could walk through an empty room than through a room full of moving people. Behavior in the molecular world is almost inconceivable in everyday life: to match the number of collisions per second of an N_2 molecule in room air, a bumper car in an enormous amusement-park ride would travel at 2.8 billion mi/s (4.5 billion km/s, much faster than the speed of light!) and would smash into another car every 700 yd (640 m).

Diffusion also occurs when a gas enters a liquid (and to a small extent in a solid). However, the average distances between molecules are so much shorter in a liquid that collisions are much more frequent; thus, diffusion of a gas through a liquid is *much* slower than through a gas. Nevertheless, this type of diffusion is vital in organisms, for example, in the movement of O_2 from lungs to blood.

Summary of Section 5.5

- The kinetic-molecular theory postulates that gas particles have no volume, move in straight-line paths between elastic (energy-conserving) collisions, and have average kinetic energies proportional to the absolute temperature of the gas.
- This theory explains the gas laws in terms of changes in distances between particles and the container walls, changes in molecular speed, and the energy of collisions.
- Temperature is a measure of the average kinetic energy of the particles.
- Molecular motion is characterized by a temperature-dependent, most probable speed (within a range of speeds).
- Effusion and diffusion rates are *inversely* proportional to the square root of the molar mass (Graham's law) because they are *directly* proportional to molecular speed.

5.6 • REAL GASES: DEVIATIONS FROM IDEAL BEHAVIOR

A fundamental principle of science is that simpler models are more useful than complex ones, as long as they explain the data. With only a few postulates, the kinetic-molecular theory explains the behavior of most gases under ordinary conditions. But two of the postulates are useful approximations that do not reflect reality:

1. *Gas particles are **not** points of mass* but have volumes determined by the sizes of their atoms and the lengths and directions of their bonds.
2. *Attractive and repulsive forces **do** exist among gas particles* because atoms contain charged subatomic particles and many bonds are polar. (As you'll see in Chapter 12, such forces lead to changes of physical state.)

These two features cause deviations from ideal behavior under *extreme conditions of low temperature and high pressure.* These deviations mean that we must alter the simple model and the ideal gas law to predict the behavior of real gases.

Effects of Extreme Conditions on Gas Behavior

At ordinary conditions—relatively high temperatures and low pressures—most real gases exhibit nearly ideal behavior. Yet, even at STP (0°C and 1 atm), gases deviate *slightly* from ideal behavior. Table 5.3 shows that the standard molar volumes of several gases, when measured to five significant figures, do not equal the ideal value. Note that the deviations increase as the boiling point rises.

The phenomena that cause slight deviations under standard conditions exert more influence as the temperature decreases and pressure increases. Figure 5.21 shows a plot of PV/RT versus external pressure (P_{ext}) for 1 mol of several real gases and an ideal gas. The values on the horizontal axis are the external pressures at which the PV/RT ratios were calculated. The PV/RT values range from normal (at $P_{ext} = 1$ atm, $PV/RT = 1$) to very high (at $P_{ext} \approx 1000$ atm, $PV/RT \approx 1.6$ to 2.3). For the *ideal* gas, PV/RT is 1 at any P_{ext}.

The PV/RT curve for methane (CH_4) is typical of most gases: it decreases *below* the ideal value at moderately high P_{ext} and then rises *above* the ideal value as P_{ext} increases to very high values. This shape arises from two overlapping effects:

- At moderately high P_{ext}, PV/RT values are lower than ideal values (less than 1) because of *interparticle attractions.*
- At very high P_{ext}, PV/RT values are greater than ideal values (more than 1) because of *particle volume.*

Table 5.3 Molar Volume of Some Common Gases at STP (0°C and 1 atm)

Gas	Molar Volume (L/mol)	Boiling Point (°C)
He	22.435	−268.9
H_2	22.432	−252.8
Ne	22.422	−246.1
Ideal gas	**22.414**	—
Ar	22.397	−185.9
N_2	22.396	−195.8
O_2	22.390	−183.0
CO	22.388	−191.5
Cl_2	22.184	−34.0
NH_3	22.079	−33.4

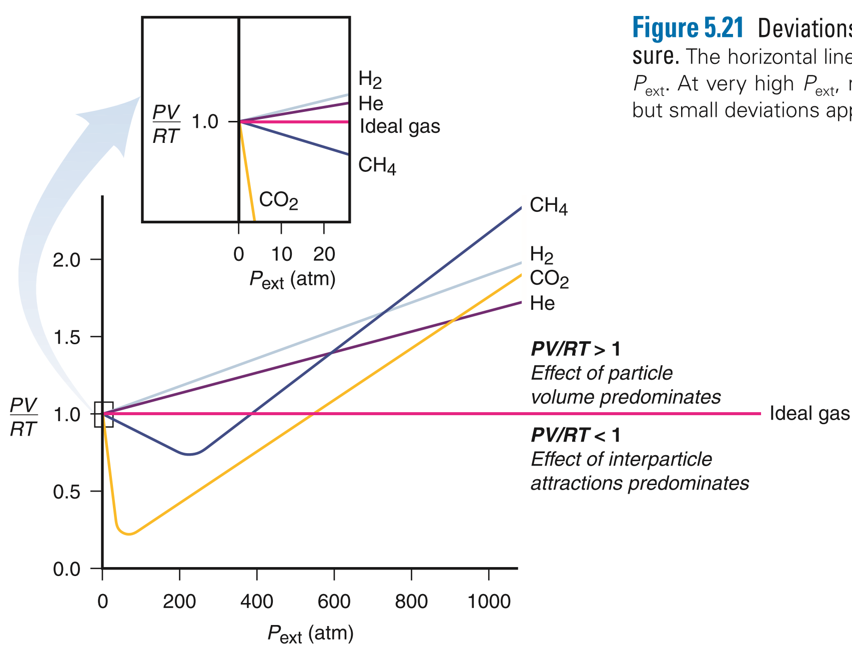


Figure 5.21 Deviations from ideal behavior with increasing external pressure. The horizontal line shows that, for 1 mol of ideal gas, $PV/RT = 1$ at all P_{ext}. At very high P_{ext}, real gases deviate significantly from ideal behavior, but small deviations appear even at ordinary pressures (expanded portion).

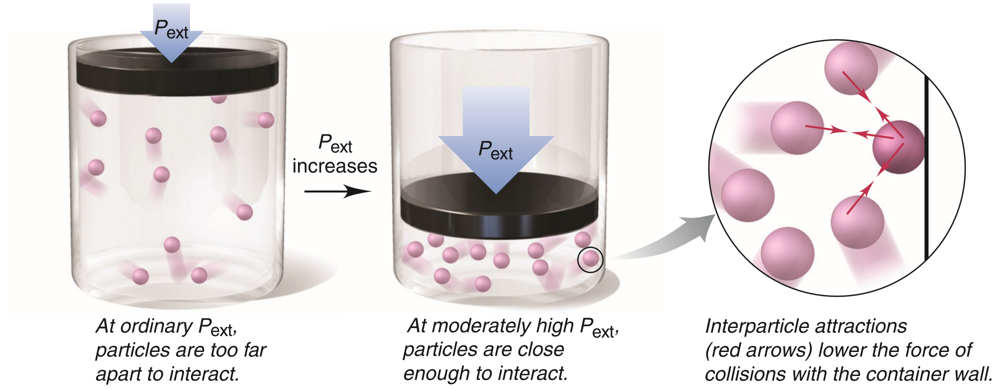


Figure 5.22 The effect of interparticle attractions on measured gas pressure.

Let's examine these effects on the molecular level:

1. *Effect of interparticle attractions.* Interparticle attractions occur between separate atoms or molecules and are caused by imbalances in electron distributions. They are important only over *very* short distances and are *much* weaker than the covalent bonding forces that hold a molecule together. At normal P_{ext}, the spaces between the particles are so large that attractions are negligible and the gas behaves nearly ideally. As P_{ext} rises, the volume of the sample decreases and the particles get closer together, so interparticle attractions have a greater effect. As a particle approaches the container wall under these higher pressures, nearby particles attract it, which lessens the force of its impact (Figure 5.22). *Repeated throughout the sample, this effect results in decreased gas pressure and, thus, a smaller numerator in PV/RT.* Similarly, lowering the temperature slows the particles, so they attract each other for a longer time.

2. *Effect of particle volume.* At normal P_{ext}, the space between particles (free volume) is enormous compared with the volume of the particles *themselves* (particle volume); thus, the free volume is essentially equal to V, the container volume in PV/RT. At *moderately* high P_{ext} and as free volume decreases, the particle volume makes up an increasing proportion of the container volume. At *extremely* high pressures, the particle volume makes the free volume significantly *less* than the container volume (Figure 5.23). But, we continue to use the container volume for V in PV/RT. Thus, the numerator *and* the ratio become artificially high. This particle volume effect increases as P_{ext} increases, eventually outweighing the effect of interparticle attractions and causing PV/RT to rise above the ideal value.

In Figure 5.21, note that the H_2 and He curves do not show the typical dip at moderate pressures. These gases consist of particles with such weak interparticle attractions that the particle volume effect predominates at all pressures.

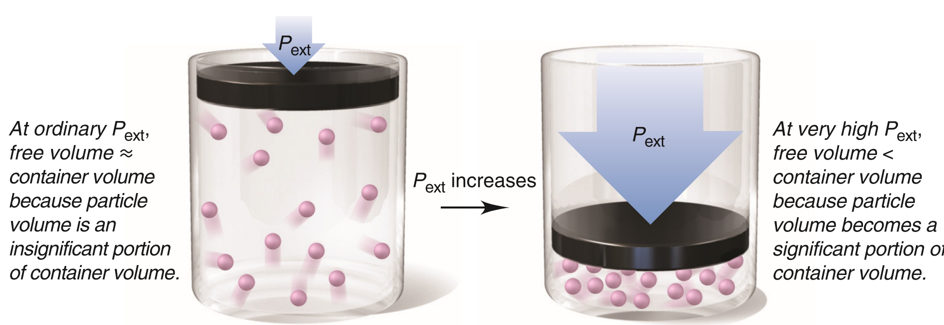


Figure 5.23 The effect of particle volume on measured gas volume.

The van der Waals Equation: Adjusting the Ideal Gas Law

To describe real gas behavior more accurately, we need to adjust the ideal gas equation in two ways:

1. Adjust P *up* by adding a factor that accounts for interparticle attractions.
2. Adjust V *down* by subtracting a factor that accounts for particle volume.

In 1873, Johannes van der Waals revised the ideal gas equation to account for the behavior of real gases. The **van der Waals equation** for n moles of a real gas is

$$\underbrace{\left(P + \frac{n^2a}{V^2}\right)}_{\text{adjusts } P \text{ up}}\underbrace{(V - nb)}_{\text{adjusts } V \text{ down}} = nRT \tag{5.15}$$

where P is the measured pressure, V is the known container volume, n and T have their usual meanings, and a and b are **van der Waals constants,** experimentally determined and specific for a given gas (Table 5.4). The constant a depends on the number and distribution of electrons, which relate to the complexity of a particle and the strength of its interparticle attractions. The constant b relates to particle volume. For instance, CO_2 is both more complex and larger than H_2, and the values of their constants reflect this.

Here is a typical application of the van der Waals equation. A 1.98-L vessel contains 215 g (4.89 mol) of dry ice. After standing at 26°C (299 K), the $CO_2(s)$ changes to $CO_2(g)$. The pressure is measured (P_{real}) and then calculated by the ideal gas law (P_{IGL}) and, using the appropriate values of a and b, by the van der Waals equation (P_{VDW}). The results are revealing:

$$P_{real} = 44.8 \text{ atm} \qquad P_{IGL} = 60.6 \text{ atm} \qquad P_{VDW} = 45.9 \text{ atm}$$

Comparing the real value with each calculated value shows that P_{IGL} is 35.3% greater than P_{real}, but P_{VDW} is only 2.5% greater than P_{real}. At these conditions, CO_2 deviates so much from ideal behavior that the ideal gas law is not very useful.

Table 5.4 Van der Waals Constants for Some Common Gases

Gas	$a\left(\frac{atm \cdot L^2}{mol^2}\right)$	$b\left(\frac{L}{mol}\right)$
He	0.034	0.0237
Ne	0.211	0.0171
Ar	1.35	0.0322
Kr	2.32	0.0398
Xe	4.19	0.0511
H_2	0.244	0.0266
N_2	1.39	0.0391
O_2	1.36	0.0318
Cl_2	6.49	0.0562
CH_4	2.25	0.0428
CO	1.45	0.0395
CO_2	3.59	0.0427
NH_3	4.17	0.0371
H_2O	5.46	0.0305

Summary of Section 5.6

- At very high P or low T, all gases deviate significantly from ideal behavior.
- As external pressure increases, most real gases exhibit first a lower and then a higher PV/RT; for 1 mol of an ideal gas, this ratio remains constant at 1.
- The deviations from ideal behavior are due to (1) attractions between particles, which lower the pressure (and decrease PV/RT), and (2) the volume of the particles themselves, which takes up an increasingly larger fraction of the container volume (and increases PV/RT).
- The van der Waals equation includes constants specific for a given gas to correct for deviations from ideal behavior.

CHAPTER REVIEW GUIDE

The following sections provide many aids to help you study this chapter. (Numbers in parentheses refer to pages, unless noted otherwise.)

Learning Objectives

These are concepts and skills to review after studying this chapter.

Related section (§), sample problem (SP), and end-of-chapter problem (EP) numbers are listed in parentheses.

1. Explain how gases differ from liquids and solids (§5.1) (EPs 5.1, 5.2)
2. Understand how a barometer works and interconvert units of pressure (§5.2) (SP 5.1) (EPs 5.3–5.9)
3. Describe Boyle's, Charles's, and Avogadro's laws, understand how they relate to the ideal gas law, and apply them in calculations (§5.3) (SPs 5.2–5.6) (EPs 5.10–5.24)
4. Apply the ideal gas law to determine the density of a gas at different temperatures, the molar mass of a gas, and the partial pressure (or mole fraction) of each gas in a mixture (Dalton's law) (§5.4) (SPs 5.7–5.10) (EPs 5.25–5.37, 5.44–5.47)
5. Use stoichiometry and the gas laws to calculate amounts of reactants and products (§5.4) (SPs 5.11, 5.12) (EPs 5.38–5.43, 5.48–5.51)
6. Understand the kinetic-molecular theory and how it explains the gas laws, average molecular speed and kinetic energy, and the processes of effusion and diffusion (§5.5) (SP 5.13) (EPs 5.52–5.63)
7. Explain why interparticle attractions and particle volume cause real gases to deviate from ideal behavior and how the van der Waals equation corrects for the deviations (§5.6) (EPs 5.64–5.67)

Key Terms

These important terms appear in boldface in the chapter and are defined again in the Glossary.

Section 5.2
pressure (P) (150)
barometer (150)
pascal (Pa) (151)
standard atmosphere (atm) (151)
millimeter of mercury (mmHg) (151)
torr (151)

Section 5.3
ideal gas (153)
Boyle's law (154)
Charles's law (154)
Avogadro's law (156)
standard temperature and pressure (STP) (156)
standard molar volume (156)
ideal gas law (157)
universal gas constant (R) (157)

Section 5.4
partial pressure (165)
Dalton's law of partial pressures (165)
mole fraction (X) (165)

Section 5.5
kinetic-molecular theory (170)
rms speed (u_{rms}) (174)
effusion (175)
Graham's law of effusion (175)
diffusion (176)

Section 5.6
van der Waals equation (179)
van der Waals constants (179)

Key Equations and Relationships

Numbered and screened concepts are listed for you to refer to or memorize.

5.1 Expressing the volume-pressure relationship (Boyle's law) (154):

$$V \propto \frac{1}{P} \quad \text{or} \quad PV = \text{constant} \quad [T \text{ and } n \text{ fixed}]$$

5.2 Expressing the volume-temperature relationship (Charles's law) (154):

$$V \propto T \quad \text{or} \quad \frac{V}{T} = \text{constant} \quad [P \text{ and } n \text{ fixed}]$$

5.3 Expressing the pressure-temperature relationship (Amontons's law) (155):

$$P \propto T \quad \text{or} \quad \frac{P}{T} = \text{constant} \quad [V \text{ and } n \text{ fixed}]$$

5.4 Expressing the volume-amount relationship (Avogadro's law) (156):

$$V \propto n \quad \text{or} \quad \frac{V}{n} = \text{constant} \quad [P \text{ and } T \text{ fixed}]$$

5.5 Defining standard temperature and pressure (156):

STP: 0°C (273.15 K) and 1 atm (760 torr)

5.6 Stating the volume of 1 mol of an ideal gas at STP (156):

Standard molar volume = 22.4141 L = 22.4 L [3 sf]

5.7 Relating volume to pressure, temperature, and amount (ideal gas law) (157):

$$PV = nRT \quad \text{and} \quad \frac{P_1V_1}{n_1T_1} = \frac{P_2V_2}{n_2T_2}$$

5.8 Calculating the value of R (157):

$$R = \frac{PV}{nT} = \frac{1\text{ atm} \times 22.4141\text{ L}}{1\text{ mol} \times 273.15\text{ K}}$$

$$= 0.082058\,\frac{\text{atm}\cdot\text{L}}{\text{mol}\cdot\text{K}} = 0.0821\,\frac{\text{atm}\cdot\text{L}}{\text{mol}\cdot\text{K}} \quad [3\text{ sf}]$$

5.9 Rearranging the ideal gas law to find gas density (163):

$$PV = \frac{m}{\mathcal{M}}RT$$

so

$$\frac{m}{V} = d = \frac{\mathcal{M} \times P}{RT}$$

5.10 Rearranging the ideal gas law to find molar mass (164):

$$n = \frac{m}{\mathcal{M}} = \frac{PV}{RT} \quad \text{so} \quad \mathcal{M} = \frac{mRT}{PV}$$

5.11 Relating the total pressure of a gas mixture to the partial pressures of the components (Dalton's law of partial pressures) (165):

$$P_{\text{total}} = P_1 + P_2 + P_3 + \cdots$$

5.12 Relating partial pressure to mole fraction (165):

$$P_A = X_A \times P_{\text{total}}$$

5.13 Defining rms speed as a function of molar mass and temperature (174):

$$u_{\text{rms}} = \sqrt{\frac{3RT}{\mathcal{M}}}$$

5.14 Applying Graham's law of effusion (175):

$$\frac{\text{Rate}_A}{\text{Rate}_B} = \frac{\sqrt{\mathcal{M}_B}}{\sqrt{\mathcal{M}_A}} = \sqrt{\frac{\mathcal{M}_B}{\mathcal{M}_A}}$$

5.15 Applying the van der Waals equation to find the pressure or volume of a gas under extreme conditions (179):

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

BRIEF SOLUTIONS TO FOLLOW-UP PROBLEMS

Compare your own solutions to these calculation steps and answers.

5.1 $$P_{CO_2}\,(\text{torr}) = (753.6\text{ mmHg} - 174.0\text{ mmHg}) \times \frac{1\text{ torr}}{1\text{ mmHg}} = 579.6\text{ torr}$$

$$P_{CO_2}\,(\text{Pa}) = 579.6\text{ torr} \times \frac{1\text{ atm}}{760\text{ torr}} \times \frac{1.01325\times10^5\text{ Pa}}{1\text{ atm}} = 7.727\times10^4\text{ Pa}$$

$$P_{CO_2}\,(\text{lb/in}^2) = 579.6\text{ torr} \times \frac{1\text{ atm}}{760\text{ torr}} \times \frac{14.7\text{ lb/in}^2}{1\text{ atm}} = 11.2\text{ lb/in}^2$$

5.2 $$P_2\,(\text{atm}) = 26.3\text{ kPa} \times \frac{1\text{ atm}}{101.325\text{ kPa}} = 0.260\text{ atm}$$

$$V_2\,(\text{L}) = 105\text{ mL} \times \frac{1\text{ L}}{1000\text{ mL}} \times \frac{0.871\text{ atm}}{0.260\text{ atm}} = 0.352\text{ L}$$

5.3 $$T_2\,(\text{K}) = 273\text{ K} \times \frac{9.75\text{ cm}^3}{6.83\text{ cm}^3} = 390.\text{ K}$$

5.4 $$P_2\,(\text{torr}) = 793\text{ torr} \times \frac{35.0\text{ g} - 5.0\text{ g}}{35.0\text{ g}} = 680.\text{ torr}$$

(There is no need to convert mass to moles because the ratio of masses equals the ratio of moles.)

5.5 $$n = \frac{PV}{RT} = \frac{1.37\text{ atm} \times 438\text{ L}}{0.0821\,\frac{\text{atm·L}}{\text{mol·K}} \times 294\text{ K}} = 24.9\text{ mol } O_2$$

$$\text{Mass (g) of } O_2 = 24.9\text{ mol } O_2 \times \frac{32.00\text{ g } O_2}{1\text{ mol } O_2} = 7.97\times10^2\text{ g } O_2$$

5.6 The balanced equation is $2CD(g) \longrightarrow C_2(g) + D_2(g)$, so n does not change. Therefore, given constant P, the temperature, T, must double: $T_1 = -73°C + 273.15 = 200$ K; so $T_2 = 400$ K, or $400\text{ K} - 273.15 = 127°C$.

5.7 $$d\,(\text{at } 0°\text{C and } 380\text{ torr}) = \frac{44.01\text{ g/mol} \times \frac{380\text{ torr}}{760\text{ torr/atm}}}{0.0821\,\frac{\text{atm·L}}{\text{mol·K}} \times 273\text{ K}} = 0.982\text{ g/L}$$

The density is lower at the smaller P because V is larger. In this case, d is lowered by one-half because P is one-half as much.

5.8 $$\mathcal{M} = \frac{(68.697\text{ g} - 68.322\text{ g}) \times 0.0821\,\frac{\text{atm·L}}{\text{mol·K}} \times (273.15 + 95.0)\text{ K}}{\frac{740.\text{ torr}}{760\text{ torr/atm}} \times \frac{149\text{ mL}}{1000\text{ mL/L}}} = 78.1\text{ g/mol}$$

5.9 $$n_{\text{total}} = \left(5.50\text{ g He} \times \frac{1\text{ mol He}}{4.003\text{ g He}}\right) + \left(15.0\text{ g Ne} \times \frac{1\text{ mol Ne}}{20.18\text{ g Ne}}\right) + \left(35.0\text{ g Kr} \times \frac{1\text{ mol Kr}}{83.80\text{ g Kr}}\right) = 2.53\text{ mol}$$

$$P_{He} = \left(\frac{5.50\text{ g He} \times \frac{1\text{ mol He}}{4.003\text{ g He}}}{2.53\text{ mol}}\right) \times 1\text{ atm} = 0.543\text{ atm}$$

$P_{Ne} = 0.294$ atm $P_{Kr} = 0.165$ atm

5.10 $$P_{H_2} = 752\text{ torr} - 13.6\text{ torr} = 738\text{ torr}$$

$$\text{Mass (g) of } H_2 = \left(\frac{\frac{738\text{ torr}}{760\text{ torr/atm}} \times 1.495\text{ L}}{0.0821\,\frac{\text{atm·L}}{\text{mol·K}} \times 289\text{ K}}\right) \times \frac{2.016\text{ g } H_2}{1\text{ mol } H_2} = 0.123\text{ g } H_2$$

5.11 $$H_2SO_4(aq) + 2NaCl(s) \longrightarrow Na_2SO_4(aq) + 2HCl(g)$$

$$n_{HCl} = 0.117\text{ kg NaCl} \times \frac{10^3\text{ g}}{1\text{ kg}} \times \frac{1\text{ mol NaCl}}{58.44\text{ g NaCl}} \times \frac{2\text{ mol HCl}}{2\text{ mol NaCl}} = 2.00\text{ mol HCl}$$

$$\text{At STP, } V\,(\text{mL}) = 2.00\text{ mol} \times \frac{22.4\text{ L}}{1\text{ mol}} \times \frac{10^3\text{ mL}}{1\text{ L}} = 4.48\times10^4\text{ mL}$$

5.12 $NH_3(g) + HCl(g) \longrightarrow NH_4Cl(s)$

$n_{NH_3} = 0.187$ mol and $n_{HCl} = 0.0522$ mol; thus, HCl is the limiting reactant.

$$n_{NH_3}\text{ after reaction} = 0.187\text{ mol } NH_3 - \left(0.0522\text{ mol HCl} \times \frac{1\text{ mol } NH_3}{1\text{ mol HCl}}\right) = 0.135\text{ mol } NH_3$$

$$P = \frac{0.135\text{ mol} \times 0.0821\,\frac{\text{atm·L}}{\text{mol·K}} \times 295\text{ K}}{10.0\text{ L}} = 0.327\text{ atm}$$

5.13 $$\frac{\text{Rate of He}}{\text{Rate of } C_2H_6} = \sqrt{\frac{30.07\text{ g/mol}}{4.003\text{ g/mol}}} = 2.741$$

Time for C_2H_6 to effuse $= 1.25\text{ min} \times 2.741 = 3.43$ min

PROBLEMS

Problems with **colored** numbers are answered in Appendix E. Sections match the text and provide the numbers of relevant sample problems. Bracketed problems are grouped in pairs (indicated by a short rule) that cover the same concept. Comprehensive Problems are based on material from any section or previous chapter.

An Overview of the Physical States of Matter

5.1 How does a sample of gas differ in its behavior from a sample of liquid in each of the following situations?
(a) The sample is transferred from one container to a larger one.
(b) The sample is heated in an expandable container, but no change of state occurs.
(c) The sample is placed in a cylinder with a piston, and an external force is applied.

5.2 Are the particles in a gas farther apart or closer together than the particles in a liquid? Use your answer to explain each of the following general observations:
(a) Gases are more compressible than liquids.
(b) Gases flow much more freely than liquids.
(c) After thorough stirring, all gas mixtures are solutions.
(d) The density of a substance in the gas state is lower than in the liquid state.

Gas Pressure and Its Measurement

(Sample Problem 5.1)

5.3 How does a barometer work? Is the column of mercury in a barometer shorter when it is on a mountaintop or at sea level? Explain.

5.4 On a cool, rainy day, the barometric pressure is 730 mmHg. Calculate the barometric pressure in centimeters of water (cmH_2O) (d of Hg = 13.5 g/mL; d of H_2O = 1.00 g/mL).

5.5 A long glass tube, sealed at one end, has an inner diameter of 10.0 mm. The tube is filled with water and inverted into a pail of water. If the atmospheric pressure is 755 mmHg, how high (in mmH_2O) is the column of water in the tube (d of Hg = 13.5 g/mL; d of H_2O = 1.00 g/mL)?

5.6 Convert the following:
(a) 0.745 atm to mmHg (b) 992 torr to bar
(c) 365 kPa to atm (d) 804 mmHg to kPa

5.7 Convert the following:
(a) 76.8 cmHg to atm (b) 27.5 atm to kPa
(c) 6.50 atm to bar (d) 0.937 kPa to torr

5.8 Convert each of the pressures described below to atm:
(a) At the peak of Mt. Everest, atmospheric pressure is only 2.75×10^2 mmHg.
(b) A cyclist fills her bike tires to 86 psi.
(c) The surface of Venus has an atmospheric pressure of 9.15×10^6 Pa.
(d) At 100 ft below sea level, a scuba diver experiences a pressure of 2.54×10^4 torr.

5.9 The gravitational force exerted by Earth on an object is given by $F = mg$, where F is the force in newtons, m is the mass in kilograms, and g is the acceleration due to gravity (9.81 m/s^2).
(a) Use the definition of the pascal to calculate the mass (in kg) of the atmosphere above 1 m^2 of ocean.
(b) Osmium ($Z = 76$) is a transition metal in Group 8B(8) and has the highest density of any element (22.6 g/mL). If an osmium column is 1 m^2 in area, how high must it be for its pressure to equal atmospheric pressure? [Use the answer from part (a) in your calculation.]

The Gas Laws and Their Experimental Foundations

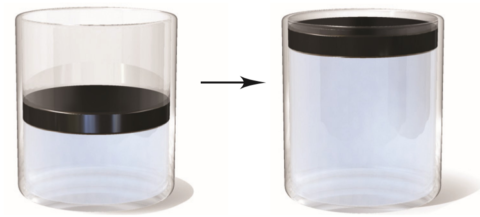
(Sample Problems 5.2 to 5.6)

5.10 A student states Boyle's law as follows: "The volume of a gas is inversely proportional to its pressure." How is this statement incomplete? Give a correct statement of Boyle's law.

5.11 In the following relationships, which quantities are variables and which are fixed: (a) Charles's law; (b) Avogadro's law; (c) Amontons's law?

5.12 Boyle's law relates gas volume to pressure, and Avogadro's law relates gas volume to amount (mol). State a relationship between gas pressure and amount (mol).

5.13 Each of the following processes caused the gas volume to double, as shown. For each process, tell how the remaining gas variable changed or state that it remained fixed:
(a) T doubles at fixed P.
(b) T and n are fixed.
(c) At fixed T, the reaction is $CD_2(g) \longrightarrow C(g) + D_2(g)$.
(d) At fixed P, the reaction is $A_2(g) + B_2(g) \longrightarrow 2AB(g)$.



5.14 What is the effect of the following on the volume of 1 mol of an ideal gas?
(a) The pressure is tripled (at constant T).
(b) The absolute temperature is increased by a factor of 3.0 (at constant P).
(c) Three more moles of the gas are added (at constant P and T).

5.15 What is the effect of the following on the volume of 1 mol of an ideal gas?
(a) The pressure is reduced by a factor of 4 (at constant T).
(b) The pressure changes from 760 torr to 202 kPa, and the temperature changes from 37°C to 155 K.
(c) The temperature changes from 305 K to 32°C, and the pressure changes from 2 atm to 101 kPa.

5.16 A sample of sulfur hexafluoride gas occupies 9.10 L at 198°C. Assuming that the pressure remains constant, what temperature (in °C) is needed to reduce the volume to 2.50 L?

5.17 A 93-L sample of dry air cools from 145°C to −22°C while the pressure is maintained at 2.85 atm. What is the final volume?

5.18 A sample of Freon-12 (CF_2Cl_2) occupies 25.5 L at 298 K and 153.3 kPa. Find its volume at STP.

5.19 A sample of carbon monoxide occupies 3.65 L at 298 K and 745 torr. Find its volume at −14°C and 367 torr.

5.20 A sample of chlorine gas is confined in a 5.0-L container at 328 torr and 37°C. How many moles of gas are in the sample?

5.21 If 1.47×10^{-3} mol of argon occupies a 75.0-mL container at 26°C, what is the pressure (in torr)?

5.22 You have 357 mL of chlorine trifluoride gas at 699 mmHg and 45°C. What is the mass (in g) of the sample?

5.23 A 75.0-g sample of dinitrogen monoxide is confined in a 3.1-L vessel. What is the pressure (in atm) at 115°C?

5.24 In preparation for a demonstration, your professor brings a 1.5-L bottle of sulfur dioxide into the lecture hall before class to allow the gas to reach room temperature. If the pressure gauge reads 85 psi and the temperature in the hall is 23°C, how many moles of sulfur dioxide are in the bottle? (*Hint:* The gauge reads zero when 14.7 psi of gas remains.)

Rearrangements of the Ideal Gas Law

(Sample Problems 5.7 to 5.12)

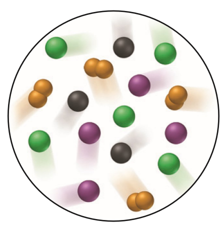
5.25 Why is moist air less dense than dry air?

5.26 To collect a beaker of H_2 gas by displacing the air already in the beaker, would you hold the beaker upright or inverted? Why? How would you hold the beaker to collect CO_2?

5.27 Why can we use a gas mixture, such as air, to study the general behavior of an ideal gas under ordinary conditions?

5.28 How does the partial pressure of gas A in a mixture compare to its mole fraction in the mixture? Explain.

5.29 The scene at right represents a portion of a mixture of four gases A *(purple)*, B *(black)*, C *(green)*, and D_2 *(orange)*.
(a) Which has the highest partial pressure?
(b) Which has the lowest partial pressure?
(c) If the total pressure is 0.75 atm, what is the partial pressure of D_2?



5.30 What is the density of Xe gas at STP?

5.31 Find the density of Freon-11 ($CFCl_3$) at 120°C and 1.5 atm.

5.32 How many moles of gaseous arsine (AsH_3) occupy 0.0400 L at STP? What is the density of gaseous arsine?

5.33 The density of a noble gas is 2.71 g/L at 3.00 atm and 0°C. Identify the gas.

5.34 Calculate the molar mass of a gas at 388 torr and 45°C if 206 ng occupies 0.206 μL.

5.35 When an evacuated 63.8-mL glass bulb is filled with a gas at 22°C and 747 mmHg, the bulb gains 0.103 g in mass. Is the gas N_2, Ne, or Ar?

5.36 After 0.600 L of Ar at 1.20 atm and 227°C is mixed with 0.200 L of O_2 at 501 torr and 127°C in a 400-mL flask at 27°C, what is the pressure in the flask?

5.37 A 355-mL container holds 0.146 g of Ne and an unknown amount of Ar at 35°C and a total pressure of 626 mmHg. Calculate the number of moles of Ar present.

5.38 How many grams of phosphorus react with 35.5 L of O_2 at STP to form tetraphosphorus decaoxide?

$$P_4(s) + 5O_2(g) \longrightarrow P_4O_{10}(s)$$

5.39 How many grams of potassium chlorate decompose to potassium chloride and 638 mL of O_2 at 128°C and 752 torr?

$$2KClO_3(s) \longrightarrow 2KCl(s) + 3O_2(g)$$

5.40 How many grams of phosphine (PH_3) can form when 37.5 g of phosphorus and 83.0 L of hydrogen gas react at STP?

$$P_4(s) + H_2(g) \longrightarrow PH_3(g) \quad [\text{unbalanced}]$$

5.41 When 35.6 L of ammonia and 40.5 L of oxygen gas at STP burn, nitrogen monoxide and water form. After the products return to STP, how many grams of nitrogen monoxide are present?

$$NH_3(g) + O_2(g) \longrightarrow NO(g) + H_2O(l) \quad [\text{unbalanced}]$$

5.42 Aluminum reacts with excess hydrochloric acid to form aqueous aluminum chloride and 35.8 mL of hydrogen gas over water at 27°C and 751 mmHg. How many grams of aluminum reacted?

5.43 How many liters of hydrogen gas are collected over water at 18°C and 725 mmHg when 0.84 g of lithium reacts with water? Aqueous lithium hydroxide also forms.

5.44 The air in a hot-air balloon at 744 torr is heated from 17°C to 60.0°C. Assuming that the amount (mol) of air and the pressure remain constant, what is the density of the air at each temperature? (The average molar mass of air is 28.8 g/mol.)

5.45 A sample of a liquid hydrocarbon known to consist of molecules with five carbon atoms is vaporized in a 0.204-L flask by immersion in a water bath at 101°C. The barometric pressure is 767 torr, and the remaining gas weighs 0.482 g. What is the molecular formula of the hydrocarbon?

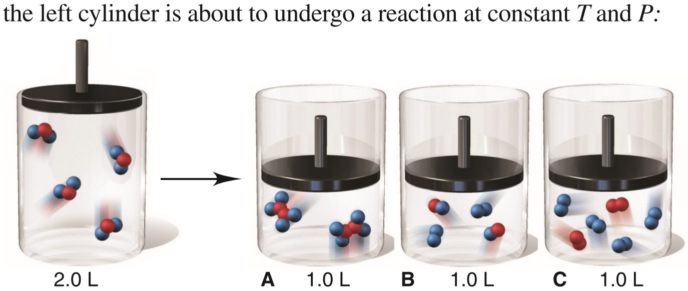
5.46 A sample of air contains 78.08% nitrogen, 20.94% oxygen, 0.05% carbon dioxide, and 0.93% argon, by volume. How many molecules of each gas are present in 1.00 L of the sample at 25°C and 1.00 atm?

5.47 An environmental chemist sampling industrial exhaust gases from a coal-burning plant collects a CO_2-SO_2-H_2O mixture in a 21-L steel tank until the pressure reaches 850. torr at 45°C.
(a) How many moles of gas are collected?
(b) If the SO_2 concentration in the mixture is 7.95×10^3 parts per million by volume (ppmv), what is its partial pressure? [*Hint:* ppmv = (volume of component/volume of mixture) $\times 10^6$.]

5.48 "Strike anywhere" matches contain the compound tetraphosphorus trisulfide, which burns to form tetraphosphorus decoxide and sulfur dioxide gas. How many milliliters of sulfur dioxide, measured at 725 torr and 32°C, can be produced from burning 0.800 g of tetraphosphorus trisulfide?

5.49 Xenon hexafluoride was one of the first noble gas compounds synthesized. The solid reacts rapidly with the silicon dioxide in glass or quartz containers to form liquid $XeOF_4$ and gaseous silicon tetrafluoride. What is the pressure in a 1.00-L container at 25°C after 2.00 g of xenon hexafluoride reacts? (Assume that silicon tetrafluoride is the only gas present and that it occupies the entire volume.)

5.50 In the four piston-cylinder assemblies below, the reactant in the left cylinder is about to undergo a reaction at constant *T* and *P*:



Which of the other three depictions best represents the products of the reaction?

5.51 Roasting galena [lead(II) sulfide] is a step in the industrial isolation of lead. How many liters of sulfur dioxide, measured at STP, are produced by the reaction of 3.75 kg of galena with 228 L of oxygen gas at 220°C and 2.0 atm? Lead(II) oxide also forms.

The Kinetic-Molecular Theory: A Model for Gas Behavior

(Sample Problem 5.13)

5.52 Use the kinetic-molecular theory to explain the change in gas pressure that results from warming a sample of gas.

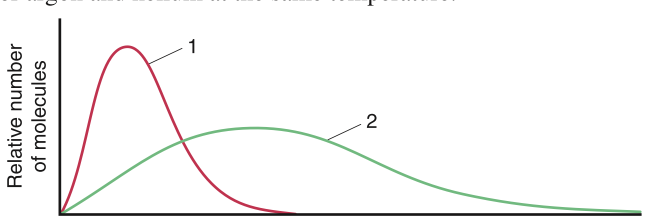
5.53 How does the kinetic-molecular theory explain why 1 mol of krypton and 1 mol of helium have the same volume at STP?

5.54 Three 5-L flasks, fixed with pressure gauges and small valves, each contain 4 g of gas at 273 K. Flask A contains H_2, flask B contains He, and flask C contains CH_4. Rank the flask contents in terms of (a) pressure, (b) average molecular kinetic energy, (c) diffusion rate after the valve is opened, (d) total kinetic energy of the molecules, (e) density, and (f) collision frequency.

5.55 What is the ratio of effusion rates for the lightest gas, H_2, and the heaviest known gas, UF_6?

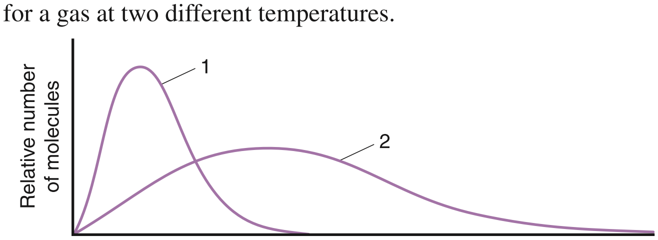
5.56 What is the ratio of effusion rates for O_2 and Kr?

5.57 The graph below shows the distribution of molecular speeds for argon and helium at the same temperature.



(a) Does curve 1 or 2 better represent the behavior of argon?
(b) Which curve represents the gas that effuses more slowly?
(c) Which curve more closely represents the behavior of fluorine gas? Explain.

5.58 The graph below shows the distribution of molecular speeds for a gas at two different temperatures.



(a) Does curve 1 or 2 better represent the behavior of the gas at the lower temperature?
(b) Which curve represents the gas when it has a higher $\overline{E}_k$?
(c) Which curve is consistent with a higher diffusion rate?

5.59 At a given pressure and temperature, it takes 4.85 min for a 1.5-L sample of He to effuse through a membrane. How long does it take for 1.5 L of F_2 to effuse under the same conditions?

5.60 A sample of an unknown gas effuses in 11.1 min. An equal volume of H_2 in the same apparatus under the same conditions effuses in 2.42 min. What is the molar mass of the unknown gas?

5.61 White phosphorus melts and then vaporizes at high temperature. The gas effuses at a rate that is 0.404 times that of neon in the same apparatus under the same conditions. How many atoms are in a molecule of gaseous white phosphorus?

5.62 Helium (He) is the lightest noble gas component of air, and xenon (Xe) is the heaviest. [For this problem, use $R = 8.314$ J/(mol·K) and $\mathcal{M}$ in kg/mol.] (a) Find the rms speed of He in winter (0.°C) and in summer (30.°C). (b) Compare the rms speed of He with that of Xe at 30.°C. (c) Find the average kinetic energy per mole of He and of Xe at 30.°C. (d) Find the average kinetic energy per molecule of He at 30.°C.

5.63 A mixture of gaseous disulfur difluoride, dinitrogen tetrafluoride, and sulfur tetrafluoride is placed in an effusion apparatus. (a) Rank the gases in order of increasing effusion rate. (b) Find the ratio of effusion rates of disulfur difluoride and dinitrogen tetrafluoride. (c) If gas X is added, and it effuses at 0.935 times the rate of sulfur tetrafluoride, find the molar mass of X.

Real Gases: Deviations from Ideal Behavior

5.64 Do interparticle attractions cause negative or positive deviations from the *PV/RT* ratio of an ideal gas? Use Table 5.3 to rank Kr, CO_2, and N_2 in order of increasing magnitude of these deviations.

5.65 Does particle volume cause negative or positive deviations from the *PV/RT* ratio of an ideal gas? Use Table 5.3 to rank Cl_2, H_2, and O_2 in order of increasing magnitude of these deviations.

5.66 Does N_2 behave more ideally at 1 atm or at 500 atm? Explain.

5.67 Does SF_6 (boiling point = 16°C at 1 atm) behave more ideally at 150°C or at 20°C? Explain.

Comprehensive Problems

5.68 Hemoglobin is the protein that transports O_2 through the blood from the lungs to the rest of the body. In doing so, each molecule of hemoglobin combines with four molecules of O_2. If 1.00 g of hemoglobin combines with 1.53 mL of O_2 at 37°C and 743 torr, what is the molar mass of hemoglobin?

5.69 A baker uses sodium hydrogen carbonate (baking soda) as the leavening agent in a banana-nut quickbread. The baking soda decomposes in either of two possible reactions:

(1) $2NaHCO_3(s) \longrightarrow Na_2CO_3(s) + H_2O(l) + CO_2(g)$

(2) $NaHCO_3(s) + H^+(aq) \longrightarrow H_2O(l) + CO_2(g) + Na^+(aq)$

Calculate the volume (in mL) of CO_2 that forms at 200.°C and 0.975 atm per gram of $NaHCO_3$ by each of the reaction processes.

5.70 Chlorine is produced from sodium chloride by the electrochemical chlor-alkali process. During the process, the chlorine is collected in a container that is isolated from the other products to prevent unwanted (and explosive) reactions. If a 15.50-L container holds 0.5950 kg of Cl_2 gas at 225°C, calculate:

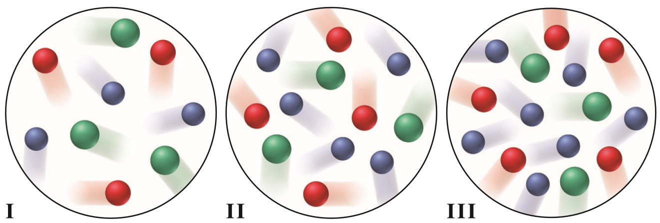
(a) P_{IGL} (b) $P_{VDW}\left(\text{use } R = 0.08206\ \dfrac{\text{atm·L}}{\text{mol·K}}\right)$

5.71 In a certain experiment, magnesium boride (Mg_3B_2) reacted with acid to form a mixture of four boron hydrides (B_xH_y), three as liquids (labeled I, II, and III) and one as a gas (IV).

(a) When a 0.1000-g sample of each liquid was transferred to an evacuated 750.0-mL container and volatilized at 70.00°C,

sample I had a pressure of 0.05951 atm; sample II, 0.07045 atm; and sample III, 0.05767 atm. What is the molar mass of each liquid? (b) Boron is 85.63% by mass in sample I, 81.10% in II, and 82.98% in III. What is the molecular formula of each sample?
(c) Sample IV was found to be 78.14% boron. Its rate of effusion was compared to that of sulfur dioxide; under identical conditions, 350.0 mL of sample IV effused in 12.00 min and 250.0 mL of sulfur dioxide effused in 13.04 min. What is the molecular formula of sample IV?

5.72 Three equal volumes of gas mixtures, all at the same *T*, are depicted below (with gas A *red,* gas B *green,* and gas C *blue*):



(a) Which sample, if any, has the highest partial pressure of A?
(b) Which sample, if any, has the lowest partial pressure of B?
(c) In which sample, if any, do the gas particles have the highest average kinetic energy?

5.73 When air is inhaled, it enters the alveoli of the lungs, and varying amounts of the component gases exchange with dissolved gases in the blood. The resulting alveolar gas mixture is quite different from the atmospheric mixture. The following table presents selected data on the composition and partial pressure of four gases in the atmosphere and in the alveoli:

	Atmosphere (sea level)		Alveoli	
Gas	Mole %	Partial Pressure (torr)	Mole %	Partial Pressure (torr)
N_2	78.6	—	—	569
O_2	20.9	—	—	104
CO_2	00.04	—	—	40
H_2O	00.46	—	—	47

If the total pressure of each gas mixture is 1.00 atm, calculate:
(a) The partial pressure (in torr) of each gas in the atmosphere
(b) The mole % of each gas in the alveoli
(c) The number of O_2 molecules in 0.50 L of alveolar air (volume of an average breath of a person at rest) at 37°C

5.74 Radon (Rn) is the heaviest, and only radioactive, member of Group 8A(18) (noble gases). It is a product of the disintegration of heavier radioactive nuclei found in minute concentrations in many common rocks used for construction. In recent years, concern has arisen about the incidence of lung cancer due to inhaled residential radon. If 1.0×10^{15} atoms of radium (Ra) produce an average of 1.373×10^{4} atoms of Rn per second, how many liters of Rn, measured at STP, are produced per day by 1.0 g of Ra?

5.75 At 1450. mmHg and 286 K, a skin diver exhales a 208-mL bubble of air that is 77% N_2, 17% O_2, and 6.0% CO_2 by volume.
(a) How many milliliters would the volume of the bubble be if it were exhaled at the surface at 1 atm and 298 K?
(b) How many moles of N_2 are in the bubble?

5.76 Nitrogen dioxide is used industrially to produce nitric acid, but it contributes to acid rain and photochemical smog. What volume (in L) of nitrogen dioxide is formed at 735 torr and 28.2°C by reacting 4.95 cm^3 of copper (d = 8.95 g/cm^3) with 230.0 mL of nitric acid (d = 1.42 g/cm^3, 68.0% HNO_3 by mass)?

$$Cu(s) + 4HNO_3(aq) \longrightarrow Cu(NO_3)_2(aq) + 2NO_2(g) + 2H_2O(l)$$

5.77 In a collision of sufficient force, automobile air bags respond by electrically triggering the explosive decomposition of sodium azide (NaN_3) to its elements. A 50.0-g sample of sodium azide was decomposed, and the nitrogen gas generated was collected over water at 26°C. The total pressure was 745.5 mmHg. How many liters of dry N_2 were generated?

5.78 An anesthetic gas contains 64.81% carbon, 13.60% hydrogen, and 21.59% oxygen, by mass. If 2.00 L of the gas at 25°C and 0.420 atm weighs 2.57 g, what is the molecular formula of the anesthetic?

5.79 Aluminum chloride is easily vaporized above 180°C. The gas escapes through a pinhole 0.122 times as fast as helium at the same conditions of temperature and pressure in the same apparatus. What is the molecular formula of aluminum chloride gas?

5.80 An atmospheric chemist studying the pollutant SO_2 places a mixture of SO_2 and O_2 in a 2.00-L container at 800. K and 1.90 atm. When the reaction occurs, gaseous SO_3 forms, and the pressure falls to 1.65 atm. How many moles of SO_3 form?

5.81 The thermal decomposition of ethylene occurs during the compound's transit in pipelines and during the formation of polyethylene. The decomposition reaction is

$$CH_2{=}CH_2(g) \longrightarrow CH_4(g) + C(\text{graphite})$$

If the decomposition begins at 10°C and 50.0 atm with a gas density of 0.215 g/mL and the temperature increases by 950 K,
(a) What is the final pressure of the confined gas (ignore the volume of graphite and use the van der Waals equation)?
(b) How does the *PV/RT* value of CH_4 compare to that in Figure 5.21? Explain.

5.82 Liquid nitrogen trichloride is heated in a 2.50-L closed reaction vessel until it decomposes completely to gaseous elements. The resulting mixture exerts a pressure of 754 mmHg at 95°C.
(a) What is the partial pressure of each gas in the container?
(b) What is the mass of the original sample?

5.83 Analysis of a newly discovered gaseous silicon-fluorine compound shows that it contains 33.01 mass % silicon. At 27°C, 2.60 g of the compound exerts a pressure of 1.50 atm in a 0.250-L vessel. What is the molecular formula of the compound?

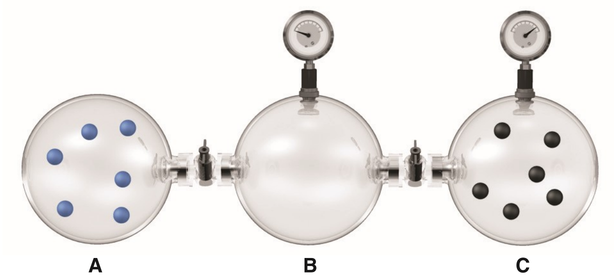
5.84 Azodicarbonamide, $NH_2CON{=}NCONH_2$, is a blowing (foaming) agent for sponge rubber and expanded plastics. Its decomposition at 195–202°C is given by

$$NH_2CON{=}NCONH_2(s) \longrightarrow NH_3(g) + CO(g) + N_2(g) + HCNO(g)$$
$$NH_3(g) + HCNO(g) \longrightarrow \text{nonvolatile polymers}(s)$$

Calculate the volume (in mL) of gas, corrected to STP, in the final mixture from decomposition of 1.00 g of azodicarbonamide.

5.85 A gaseous organic compound containing only carbon, hydrogen, and nitrogen is burned in oxygen gas, and the volume of each reactant and product is measured under the same conditions of temperature and pressure. Reaction of four volumes of the compound produces four volumes of CO_2, two volumes of N_2, and ten volumes of water vapor. (a) How many volumes of O_2 were required? (b) What is the empirical formula of the compound?

5.86 Containers A, B, and C are attached by closed stopcocks of negligible volume.



If each particle shown in the picture represents 10^6 particles,
(a) How many blue particles and black particles are in B after the stopcocks are opened and the system reaches equilibrium?
(b) How many blue particles and black particles are in A after the stopcocks are opened and the system reaches equilibrium?
(c) If the pressure in C, P_C, is 750 torr before the stopcocks are opened, what is P_C afterward? (d) What is P_B afterward?

5.87 Combustible vapor-air mixtures are flammable over a limited range of concentrations. The minimum volume % of vapor that gives a combustible mixture is called the *lower flammable limit* (LFL). Generally, the LFL is about half the stoichiometric mixture, the concentration required for complete combustion of the vapor in air. (a) If oxygen is 20.9 vol % of air, estimate the LFL for *n*-hexane, C_6H_{14}. (b) What volume (in mL) of *n*-hexane ($d = 0.660$ g/cm^3) is required to produce a flammable mixture of hexane in 1.000 m^3 of air at STP?

5.88 By what factor would a scuba diver's lungs expand if she ascended rapidly to the surface from a depth of 125 ft without inhaling or exhaling? If an expansion factor greater than 1.5 causes lung rupture, how far could she safely ascend from 125 ft without breathing? Assume constant temperature (d of seawater = 1.04 g/mL; d of Hg = 13.5 g/mL).

5.89 At a height of 300 km above Earth's surface, an astronaut finds that the atmospheric pressure is about 10^{-8} mmHg and the temperature is 500 K. How many molecules of gas are there per milliliter at this altitude?

5.90 (a) What is the rms speed of O_2 at STP? (b) If the average distance between O_2 molecules at STP is 6.33×10^{-8} m, how many collisions are there per second? [Use $R = 8.314$ J/(mol·K) and $\mathcal{M}$ in kg/mol.]

5.91 Standard conditions are based on relevant environmental conditions. If normal average surface temperature and pressure on Venus are 730. K and 90 atm, respectively, what is the standard molar volume of an ideal gas on Venus?

5.92 Each day, the Hawaiian volcano Kilauea emits an average of 1.5×10^3 m^3 of gas, when corrected to 298 K and 1.00 atm. The mixture contains gases that contribute to global warming and acid rain, and some are toxic. An atmospheric chemist analyzes a sample and finds the following mole fractions: 0.4896 CO_2, 0.0146 CO, 0.3710 H_2O, 0.1185 SO_2, 0.0003 S_2, 0.0047 H_2, 0.0008 HCl, and 0.0003 H_2S. How many metric tons (t) of each gas are emitted per year (1 t = 1000 kg)?

5.93 To study a key fuel-cell reaction, a chemical engineer has 20.0-L tanks of H_2 and of O_2 and wants to use up both tanks to form 28.0 mol of water at 23.8°C. (a) Use the ideal gas law to find the pressure needed in each tank. (b) Use the van der Waals equation to find the pressure needed in each tank. (c) Compare the results from the two equations.

5.94 How many liters of gaseous hydrogen bromide at 29°C and 0.965 atm will a chemist need if she wishes to prepare 3.50 L of 1.20 *M* hydrobromic acid?

5.95 A mixture of CO_2 and Kr weighs 35.0 g and exerts a pressure of 0.708 atm in its container. Since Kr is expensive, you wish to recover it from the mixture. After the CO_2 is completely removed by absorption with NaOH(*s*), the pressure in the container is 0.250 atm. How many grams of CO_2 were originally present? How many grams of Kr can you recover?

5.96 Aqueous sulfurous acid (H_2SO_3) was made by dissolving 0.200 L of sulfur dioxide gas at 19°C and 745 mmHg in water to yield 500.0 mL of solution. The acid solution required 10.0 mL of sodium hydroxide solution to reach the titration end point. What was the molarity of the sodium hydroxide solution?

5.97 A person inhales air richer in O_2 and exhales air richer in CO_2 and water vapor. During each hour of sleep, a person exhales a total of about 300 L of this CO_2-enriched and H_2O-enriched air. (a) If the partial pressures of CO_2 and H_2O in exhaled air are each 30.0 torr at 37.0°C, calculate the mass (g) of CO_2 and of H_2O exhaled in 1 h of sleep. (b) How many grams of body mass does the person lose in an 8-h sleep if all the CO_2 and H_2O exhaled come from the metabolism of glucose?

$$C_6H_{12}O_6(s) + 6O_2(g) \longrightarrow 6CO_2(g) + 6H_2O(g)$$

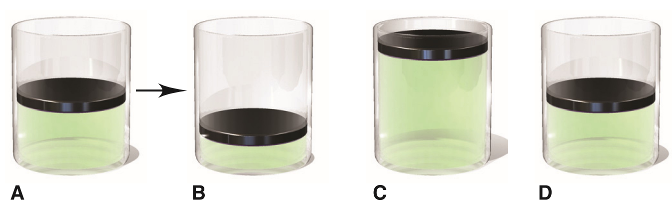
5.98 Given these relationships for average kinetic energy,

$$\overline{E_k} = \tfrac{1}{2}m\overline{u^2} \qquad \text{and} \qquad \overline{E_k} = \tfrac{3}{2}\left(\frac{R}{N_A}\right)T$$

where m is molecular mass, u is rms speed, R is the gas constant [in J/(mol·K)], N_A is Avogadro's number, and T is absolute temperature: (a) derive Equation 5.13; (b) derive Equation 5.14.

5.99 Many water treatment plants use chlorine gas to kill microorganisms before the water is released for residential use. A plant engineer has to maintain the chlorine pressure in a tank below the 85.0-atm rating and, to be safe, decides to fill the tank to 80.0% of this maximum pressure.
(a) How many moles of Cl_2 gas can be kept in an 850.-L tank at 298 K if she uses the ideal gas law in the calculation?
(b) What is the tank pressure if she uses the van der Waals equation for this amount of gas? (c) Did the engineer fill the tank to the desired pressure?

5.100 In A, the picture shows a cylinder with 0.1 mol of a gas that behaves ideally. Choose the cylinder (B, C, or D) that correctly represents the volume of the gas after each of the following changes. If none of the cylinders is correct, specify "none."
(a) P is doubled at fixed n and T.
(b) T is reduced from 400 K to 200 K at fixed n and P.
(c) T is increased from 100°C to 200°C at fixed n and P.
(d) 0.1 mol of gas is added at fixed P and T.
(e) 0.1 mol of gas is added and P is doubled at fixed T.



5.101 A 6.0-L flask contains a mixture of methane (CH_4), argon, and helium at 45°C and 1.75 atm. If the mole fractions of helium and argon are 0.25 and 0.35, respectively, how many molecules of methane are present?

5.102 A large portion of metabolic energy arises from the biological combustion of glucose:

$$C_6H_{12}O_6(s) + 6O_2(g) \longrightarrow 6CO_2(g) + 6H_2O(g)$$

(a) If this reaction is carried out in an expandable container at 37°C and 780. torr, what volume of CO_2 is produced from 20.0 g of glucose and excess O_2? (b) If the reaction is carried out at the same conditions with the stoichiometric amount of O_2, what is the partial pressure of each gas when the reaction is 50% complete (10.0 g of glucose remains)?

5.103 According to government standards, the *8-h threshold limit value* is 5000 ppmv for CO_2 and 0.1 ppmv for Br_2 (1 ppmv is 1 part by volume in 10^6 parts by volume). Exposure to either gas for 8 h above these limits is unsafe. At STP, which of the following would be unsafe for 8 h of exposure?
(a) Air with a partial pressure of 0.2 torr of Br_2
(b) Air with a partial pressure of 0.2 torr of CO_2
(c) 1000 L of air containing 0.0004 g of Br_2 gas
(d) 1000 L of air containing 2.8×10^{22} molecules of CO_2

5.104 One way to prevent emission of the pollutant NO from industrial plants is by a catalyzed reaction with NH_3:

$$4NH_3(g) + 4NO(g) + O_2(g) \xrightarrow{\text{catalyst}} 4N_2(g) + 6H_2O(g)$$

(a) If the NO has a partial pressure of 4.5×10^{-5} atm in the flue gas, how many liters of NH_3 are needed per liter of flue gas at 1.00 atm? (b) If the reaction takes place at 1.00 atm and 365°C, how many grams of NH_3 are needed per kL of flue gas?

5.105 An equimolar mixture of Ne and Xe is accidentally placed in a container that has a tiny leak. After a short while, a very small proportion of the mixture has escaped. What is the mole fraction of Ne in the effusing gas?

5.106 One way to utilize naturally occurring uranium (0.72% ^{235}U and 99.27% ^{238}U) as a nuclear fuel is to enrich it (increase its ^{235}U content) by allowing gaseous UF_6 to effuse through a porous membrane (see p. 176). From the relative rates of effusion of $^{235}UF_6$ and $^{238}UF_6$, find the number of steps needed to produce uranium that is 3.0 mole % ^{235}U, the enriched fuel used in many nuclear reactors.

5.107 In preparation for a combustion demonstration, a professor fills a balloon with equal molar amounts of H_2 and O_2, but the demonstration has to be postponed until the next day. During the night, both gases leak through pores in the balloon. If 35% of the H_2 leaks, what is the O_2/H_2 ratio in the balloon the next day?

5.108 Phosphorus trichloride is important in the manufacture of insecticides, fuel additives, and flame retardants. Phosphorus has only one naturally occurring isotope, ^{31}P, whereas chlorine has two, ^{35}Cl (75%) and ^{37}Cl (25%). (a) What different molecular masses (in amu) can be found for PCl_3? (b) Which is the most abundant? (c) What is the ratio of the effusion rates of the heaviest and the lightest PCl_3 molecules?