

Chapter 9

Gases



Figure 9.1 The hot air inside these balloons is less dense than the surrounding cool air. This results in a buoyant force that causes the balloons to rise when their guy lines are untied. (credit: modification of work by Anthony Quintano)

Chapter Outline

- 9.1 Gas Pressure
- 9.2 Relating Pressure, Volume, Amount, and Temperature: The Ideal Gas Law
- 9.3 Stoichiometry of Gaseous Substances, Mixtures, and Reactions
- 9.4 Effusion and Diffusion of Gases
- 9.5 The Kinetic-Molecular Theory
- 9.6 Non-Ideal Gas Behavior

Introduction

We are surrounded by an ocean of gas—the atmosphere—and many of the properties of gases are familiar to us from our daily activities. Heated gases expand, which can make a hot air balloon rise (**Figure 9.1**) or cause a blowout in a bicycle tire left in the sun on a hot day.

Gases have played an important part in the development of chemistry. In the seventeenth and eighteenth centuries, many scientists investigated gas behavior, providing the first mathematical descriptions of the behavior of matter.

In this chapter, we will examine the relationships between gas temperature, pressure, amount, and volume. We will study a simple theoretical model and use it to analyze the experimental behavior of gases. The results of these analyses will show us the limitations of the theory and how to improve on it.

9.1 Gas Pressure

By the end of this section, you will be able to:

- Define the property of pressure
- Define and convert among the units of pressure measurements
- Describe the operation of common tools for measuring gas pressure
- Calculate pressure from manometer data

The earth's atmosphere exerts a pressure, as does any other gas. Although we do not normally notice atmospheric pressure, we are sensitive to pressure changes—for example, when your ears “pop” during take-off and landing while flying, or when you dive underwater. Gas pressure is caused by the force exerted by gas molecules colliding with the surfaces of objects (Figure 9.2). Although the force of each collision is very small, any surface of appreciable area experiences a large number of collisions in a short time, which can result in a high pressure. In fact, normal air pressure is strong enough to crush a metal container when not balanced by equal pressure from inside the container.

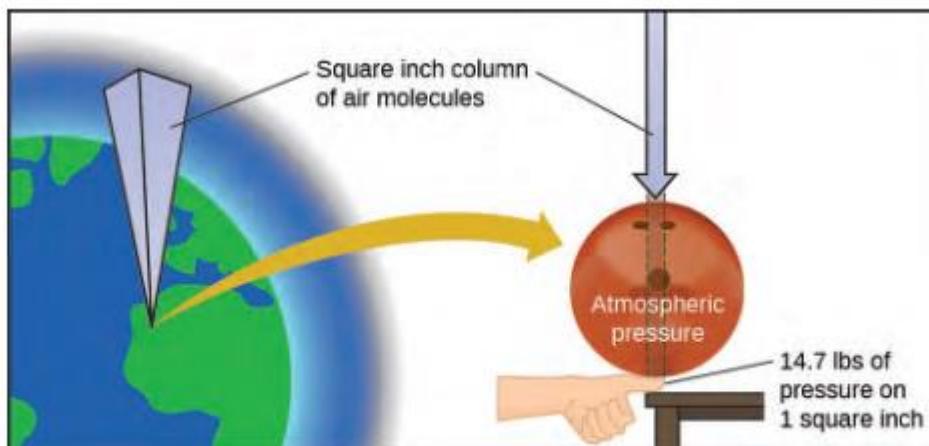


Figure 9.2 The atmosphere above us exerts a large pressure on objects at the surface of the earth, roughly equal to the weight of a bowling ball pressing on an area the size of a human thumbnail.

Atmospheric pressure is caused by the weight of the column of air molecules in the atmosphere above an object, such as the tanker car. At sea level, this pressure is roughly the same as that exerted by a full-grown African elephant standing on a doormat, or a typical bowling ball resting on your thumbnail. These may seem like huge amounts, and they are, but life on earth has evolved under such atmospheric pressure. If you actually perch a bowling ball on your thumbnail, the pressure experienced is *twice* the usual pressure, and the sensation is unpleasant.

In general, **pressure** is defined as the force exerted on a given area: $P = \frac{F}{A}$. Note that pressure is directly proportional to force and inversely proportional to area. Thus, pressure can be increased either by increasing the amount of force or by decreasing the area over which it is applied; pressure can be decreased by decreasing the force or increasing the area.

Let's apply this concept to determine which would be more likely to fall through thin ice in **Figure 9.3**—the elephant or the figure skater? A large African elephant can weigh 7 tons, supported on four feet, each with a diameter of about 1.5 ft (footprint area of 250 in^2), so the pressure exerted by each foot is about 14 lb/in^2 :

$$\text{pressure per elephant foot} = 14,000 \frac{\text{lb}}{\text{elephant}} \times \frac{1 \text{ elephant}}{4 \text{ feet}} \times \frac{1 \text{ foot}}{250 \text{ in}^2} = 14 \text{ lb/in}^2$$

The figure skater weighs about 120 lbs, supported on two skate blades, each with an area of about 2 in^2 , so the pressure exerted by each blade is about 30 lb/in^2 :

$$\text{pressure per skate blade} = 120 \frac{\text{lb}}{\text{skater}} \times \frac{1 \text{ skater}}{2 \text{ blades}} \times \frac{1 \text{ blade}}{2 \text{ in}^2} = 30 \text{ lb/in}^2$$

Even though the elephant is more than one hundred-times heavier than the skater, it exerts less than one-half of the pressure and would therefore be less likely to fall through thin ice. On the other hand, if the skater removes her skates and stands with bare feet (or regular footwear) on the ice, the larger area over which her weight is applied greatly reduces the pressure exerted:

$$\text{pressure per human foot} = 120 \frac{\text{lb}}{\text{skater}} \times \frac{1 \text{ skater}}{2 \text{ feet}} \times \frac{1 \text{ foot}}{30 \text{ in}^2} = 2 \text{ lb/in}^2$$



(a)



(b)

Figure 9.3 Although (a) an elephant's weight is large, creating a very large force on the ground, (b) the figure skater exerts a much higher pressure on the ice due to the small surface area of her skates. (credit a: modification of work by Guido da Rozze; credit b: modification of work by Ryosuke Yagi)

The SI unit of pressure is the **pascal (Pa)**, with $1 \text{ Pa} = 1 \text{ N/m}^2$, where N is the newton, a unit of force defined as 1 kg m/s^2 . One pascal is a small pressure; in many cases, it is more convenient to use units of kilopascal ($1 \text{ kPa} = 1000 \text{ Pa}$) or **bar** ($1 \text{ bar} = 100,000 \text{ Pa}$). In the United States, pressure is often measured in pounds of force on an area of one square inch—**pounds per square inch (psi)**—for example, in car tires. Pressure can also be measured using the unit **atmosphere (atm)**, which originally represented the average sea level air pressure at the approximate latitude of Paris (45°). **Table 9.1** provides some information on these and a few other common units for pressure measurements

Pressure Units	
Unit Name and Abbreviation	Definition or Relation to Other Unit
pascal (Pa)	$1 \text{ Pa} = 1 \text{ N/m}^2$ recommended IUPAC unit
kilopascal (kPa)	$1 \text{ kPa} = 1000 \text{ Pa}$
pounds per square inch (psi)	air pressure at sea level is ~14.7 psi
atmosphere (atm)	$1 \text{ atm} = 101,325 \text{ Pa}$ air pressure at sea level is ~1 atm
bar (bar, or b)	$1 \text{ bar} = 100,000 \text{ Pa}$ (exactly) commonly used in meteorology
millibar (mbar, or mb)	$1000 \text{ mbar} = 1 \text{ bar}$
inches of mercury (in. Hg)	$1 \text{ in. Hg} = 3386 \text{ Pa}$ used by aviation industry, also some weather reports
torr	$1 \text{ torr} = \frac{1}{760} \text{ atm}$ named after Evangelista Torricelli, inventor of the barometer
millimeters of mercury (mm Hg)	$1 \text{ mm Hg} \sim 1 \text{ torr}$

Table 9.1

Example 9.1

Conversion of Pressure Units

The United States National Weather Service reports pressure in both inches of Hg and millibars. Convert a pressure of 29.2 in. Hg into:

- (a) torr
- (b) atm
- (c) kPa
- (d) mbar

Solution

This is a unit conversion problem. The relationships between the various pressure units are given in **Table 9.1**.

$$(a) 29.2 \text{ in. Hg} \times \frac{760 \text{ torr}}{29.92 \text{ in. Hg}} = 742 \text{ torr}$$

$$(b) 742 \text{ torr} \times \frac{1 \text{ atm}}{760 \text{ torr}} = 0.976 \text{ atm}$$

$$(c) 742 \text{ torr} \times \frac{101,325 \text{ kPa}}{760 \text{ torr}} = 98.9 \text{ kPa}$$

$$(d) 98.9 \text{ kPa} \times \frac{1000 \text{ Pa}}{1 \text{ kPa}} \times \frac{1 \text{ bar}}{100,000 \text{ Pa}} \times \frac{1000 \text{ mbar}}{1 \text{ bar}} = 989 \text{ mbar}$$

Check Your Learning

A typical barometric pressure in Kansas City is 740 torr. What is this pressure in atmospheres, in millimeters of mercury, in kilopascals, and in bar?

Answer: 0.974 atm; 740 mm Hg; 98.7 kPa; 0.987 bar

We can measure atmospheric pressure, the force exerted by the atmosphere on the earth's surface, with a **barometer** (Figure 9.4). A barometer is a glass tube that is closed at one end, filled with a nonvolatile liquid such as mercury, and then inverted and immersed in a container of that liquid. The atmosphere exerts pressure on the liquid outside the tube, the column of liquid exerts pressure inside the tube, and the pressure at the liquid surface is the same inside and outside the tube. The height of the liquid in the tube is therefore proportional to the pressure exerted by the atmosphere.

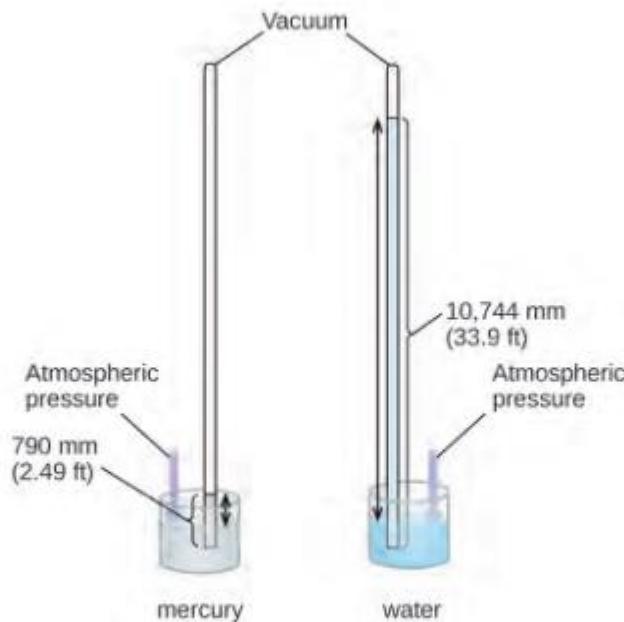


Figure 9.4 In a barometer, the height, h , of the column of liquid is used as a measurement of the air pressure. Using very dense liquid mercury (left) permits the construction of reasonably sized barometers, whereas using water (right) would require a barometer more than 30 feet tall.

If the liquid is water, normal atmospheric pressure will support a column of water over 10 meters high, which is rather inconvenient for making (and reading) a barometer. Because mercury (Hg) is about 13.6-times denser than water, a mercury barometer only needs to be $\frac{1}{13.6}$ as tall as a water barometer—a more suitable size. Standard atmospheric pressure of 1 atm at sea level (101,325 Pa) corresponds to a column of mercury that is about 760 mm (29.92 in.) high. The **torr** was originally intended to be a unit equal to one millimeter of mercury, but it no longer corresponds exactly. The pressure exerted by a fluid due to gravity is known as **hydrostatic pressure**, p :

$$p = h\rho g$$

where h is the height of the fluid, ρ is the density of the fluid, and g is acceleration due to gravity.

Example 9.2**Calculation of Barometric Pressure**

Show the calculation supporting the claim that atmospheric pressure near sea level corresponds to the pressure exerted by a column of mercury that is about 760 mm high. The density of mercury = 13.6 g/cm^3 .

Solution

The hydrostatic pressure is given by $p = h\rho g$, with $h = 760 \text{ mm}$, $\rho = 13.6 \text{ g/cm}^3$, and $g = 9.81 \text{ m/s}^2$. Plugging these values into the equation and doing the necessary unit conversions will give us the value we seek. (Note: We are expecting to find a pressure of $\sim 101,325 \text{ Pa}$:

$$\begin{aligned} 101,325 \text{ N/m}^2 &= 101,325 \frac{\text{kg}\cdot\text{m/s}^2}{\text{m}^2} = 101,325 \frac{\text{kg}}{\text{m}\cdot\text{s}^2} \\ p &= \left(760 \text{ mm} \times \frac{1 \text{ m}}{1000 \text{ mm}}\right) \times \left(\frac{13.6 \text{ g}}{1 \text{ cm}^3} \times \frac{1 \text{ kg}}{1000 \text{ g}} \times \frac{(100 \text{ cm})^3}{(1 \text{ m})^3}\right) \times \left(\frac{9.81 \text{ m}}{1 \text{ s}^2}\right) \\ &= (0.760 \text{ m})(13,600 \text{ kg/m}^3)(9.81 \text{ m/s}^2) = 1.01 \times 10^5 \text{ kg/ms}^2 = 1.01 \times 10^5 \text{ N/m}^2 \\ &= 1.01 \times 10^5 \text{ Pa} \end{aligned}$$

Check Your Learning

Calculate the height of a column of water at 25°C that corresponds to normal atmospheric pressure. The density of water at this temperature is 1.0 g/cm^3 .

Answer: 10.3 m

A **manometer** is a device similar to a barometer that can be used to measure the pressure of a gas trapped in a container. A closed-end manometer is a U-shaped tube with one closed arm, one arm that connects to the gas to be measured, and a nonvolatile liquid (usually mercury) in between. As with a barometer, the distance between the liquid levels in the two arms of the tube (h in the diagram) is proportional to the pressure of the gas in the container. An open-end manometer (Figure 9.5) is the same as a closed-end manometer, but one of its arms is open to the atmosphere. In this case, the distance between the liquid levels corresponds to the difference in pressure between the gas in the container and the atmosphere.

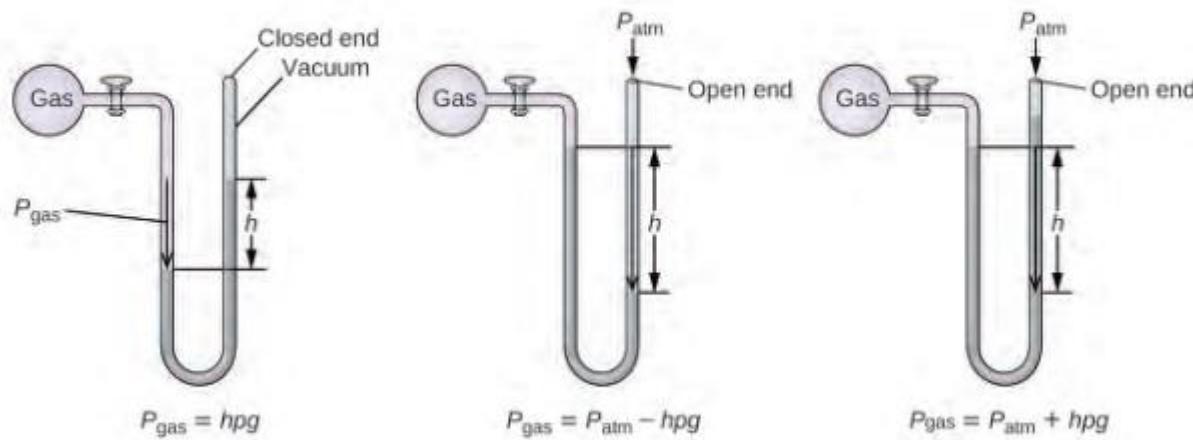
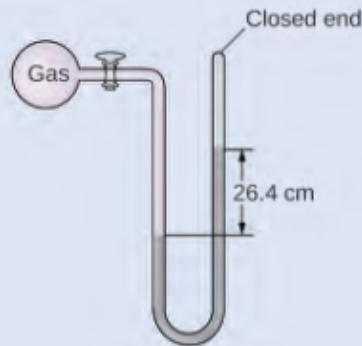


Figure 9.5 A manometer can be used to measure the pressure of a gas. The (difference in) height between the liquid levels (h) is a measure of the pressure. Mercury is usually used because of its large density.

Example 9.3**Calculation of Pressure Using a Closed-End Manometer**

The pressure of a sample of gas is measured with a closed-end manometer, as shown to the right. The liquid in the manometer is mercury. Determine the pressure of the gas in:

- (a) torr
- (b) Pa
- (c) bar

**Solution**

The pressure of the gas is equal to a column of mercury of height 26.4 cm. (The pressure at the bottom horizontal line is equal on both sides of the tube. The pressure on the left is due to the gas and the pressure on the right is due to 26.4 cm Hg, or mercury.) We could use the equation $p = h\rho g$ as in [Example 9.2](#), but it is simpler to just convert between units using [Table 9.1](#).

$$(a) 26.4 \text{ cm Hg} \times \frac{10 \text{ mm Hg}}{1 \text{ cm Hg}} \times \frac{1 \text{ torr}}{1 \text{ mm Hg}} = 264 \text{ torr}$$

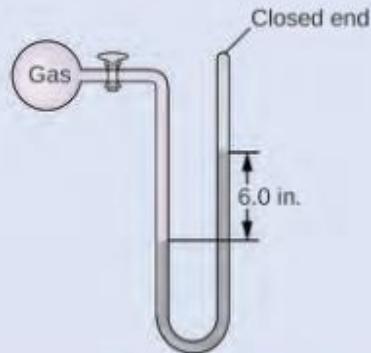
$$(b) 264 \text{ torr} \times \frac{1 \text{ atm}}{760 \text{ torr}} \times \frac{101,325 \text{ Pa}}{1 \text{ atm}} = 35,200 \text{ Pa}$$

$$(c) 35,200 \text{ Pa} \times \frac{1 \text{ bar}}{100,000 \text{ Pa}} = 0.352 \text{ bar}$$

Check Your Learning

The pressure of a sample of gas is measured with a closed-end manometer. The liquid in the manometer is mercury. Determine the pressure of the gas in:

- (a) torr
- (b) Pa
- (c) bar



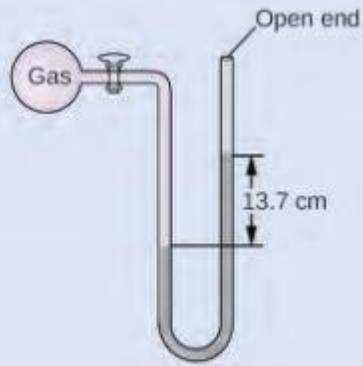
Answer: (a) ~150 torr; (b) ~20,000 Pa; (c) ~0.20 bar

Example 9.4

Calculation of Pressure Using an Open-End Manometer

The pressure of a sample of gas is measured at sea level with an open-end Hg (mercury) manometer, as shown to the right. Determine the pressure of the gas in:

- (a) mm Hg
- (b) atm
- (c) kPa



Solution

The pressure of the gas equals the hydrostatic pressure due to a column of mercury of height 13.7 cm plus the pressure of the atmosphere at sea level. (The pressure at the bottom horizontal line is equal on both sides of the tube. The pressure on the left is due to the gas and the pressure on the right is due to 13.7 cm of Hg plus atmospheric pressure.)

(a) In mm Hg, this is: $137 \text{ mm Hg} + 760 \text{ mm Hg} = 897 \text{ mm Hg}$

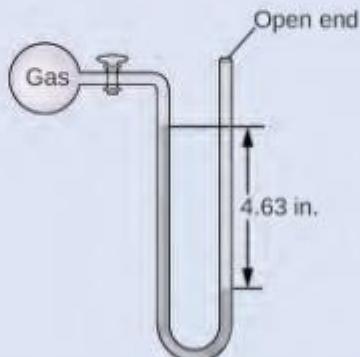
$$(b) 897 \frac{\text{mm Hg}}{760 \frac{\text{mm Hg}}{1 \text{ atm}}} = 1.18 \text{ atm}$$

$$(c) 1.18 \frac{\text{atm}}{1 \frac{\text{atm}}{101.325 \text{ kPa}}} = 1.20 \times 10^2 \text{ kPa}$$

Check Your Learning

The pressure of a sample of gas is measured at sea level with an open-end Hg manometer, as shown to the right. Determine the pressure of the gas in:

- (a) mm Hg
- (b) atm
- (c) kPa



Answer: (a) 642 mm Hg; (b) 0.845 atm; (c) 85.6 kPa

Chemistry in Everyday Life

Measuring Blood Pressure

Blood pressure is measured using a device called a sphygmomanometer (Greek *sphygmos* = "pulse"). It consists of an inflatable cuff to restrict blood flow, a manometer to measure the pressure, and a method of determining when blood flow begins and when it becomes impeded (Figure 9.6). Since its invention in 1881, it has been an essential medical device. There are many types of sphygmomanometers: manual ones that require a stethoscope and are used by medical professionals; mercury ones, used when the most accuracy is required; less accurate mechanical ones; and digital ones that can be used with little training but that have limitations. When using a sphygmomanometer, the cuff is placed around the upper arm and inflated until blood flow is completely blocked, then slowly released. As the heart beats, blood forced through the arteries causes a rise in pressure. This rise in pressure at which blood flow begins is the *systolic pressure*—the peak pressure in the cardiac cycle. When the cuff's pressure equals the arterial systolic pressure, blood flows past the cuff, creating audible sounds that can be heard using a stethoscope. This is followed by a decrease in pressure as the heart's ventricles prepare for another beat. As cuff pressure continues to decrease, eventually sound is no longer heard; this is the *diastolic pressure*—the lowest pressure (resting phase) in the cardiac cycle. Blood pressure units from a sphygmomanometer are in terms of millimeters of mercury (mm Hg).



(a)



(b)

Figure 9.6 (a) A medical technician prepares to measure a patient's blood pressure with a sphygmomanometer. (b) A typical sphygmomanometer uses a valved rubber bulb to inflate the cuff and a diaphragm gauge to measure pressure. (credit a: modification of work by Master Sgt. Jeffrey Allen)

How Sciences Interconnect

Meteorology, Climatology, and Atmospheric Science

Throughout the ages, people have observed clouds, winds, and precipitation, trying to discern patterns and make predictions: when it is best to plant and harvest; whether it is safe to set out on a sea voyage; and much more. We now face complex weather and atmosphere-related challenges that will have a major impact on our civilization and the ecosystem. Several different scientific disciplines use chemical principles to help us better understand weather, the atmosphere, and climate. These are meteorology, climatology, and atmospheric science. Meteorology is the study of the atmosphere, atmospheric phenomena, and atmospheric effects on earth's weather. Meteorologists seek to understand and predict the weather in the short term, which can save lives and benefit the economy. Weather forecasts (Figure 9.7) are the result of thousands of measurements of air pressure, temperature, and the like, which are compiled, modeled, and analyzed in weather centers worldwide.

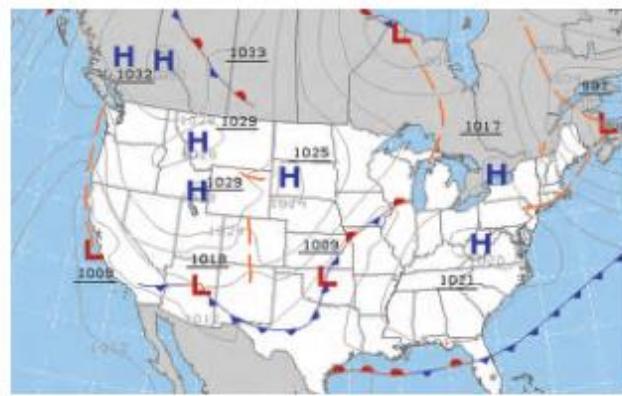


Figure 9.7 Meteorologists use weather maps to describe and predict weather. Regions of high (H) and low (L) pressure have large effects on weather conditions. The gray lines represent locations of constant pressure known as isobars. (credit: modification of work by National Oceanic and Atmospheric Administration)

In terms of weather, low-pressure systems occur when the earth's surface atmospheric pressure is lower than the surrounding environment: Moist air rises and condenses, producing clouds. Movement of moisture and air within various weather fronts instigates most weather events.

The atmosphere is the gaseous layer that surrounds a planet. Earth's atmosphere, which is roughly 100–125 km thick, consists of roughly 78.1% nitrogen and 21.0% oxygen, and can be subdivided further into the regions shown in Figure 9.8: the exosphere (furthest from earth, > 700 km above sea level), the thermosphere (80–700 km), the mesosphere (50–80 km), the stratosphere (second lowest level of our atmosphere, 12–50 km above sea level), and the troposphere (up to 12 km above sea level, roughly 80% of the earth's atmosphere by mass and the layer where most weather events originate). As you go higher in the troposphere, air density and temperature both decrease.

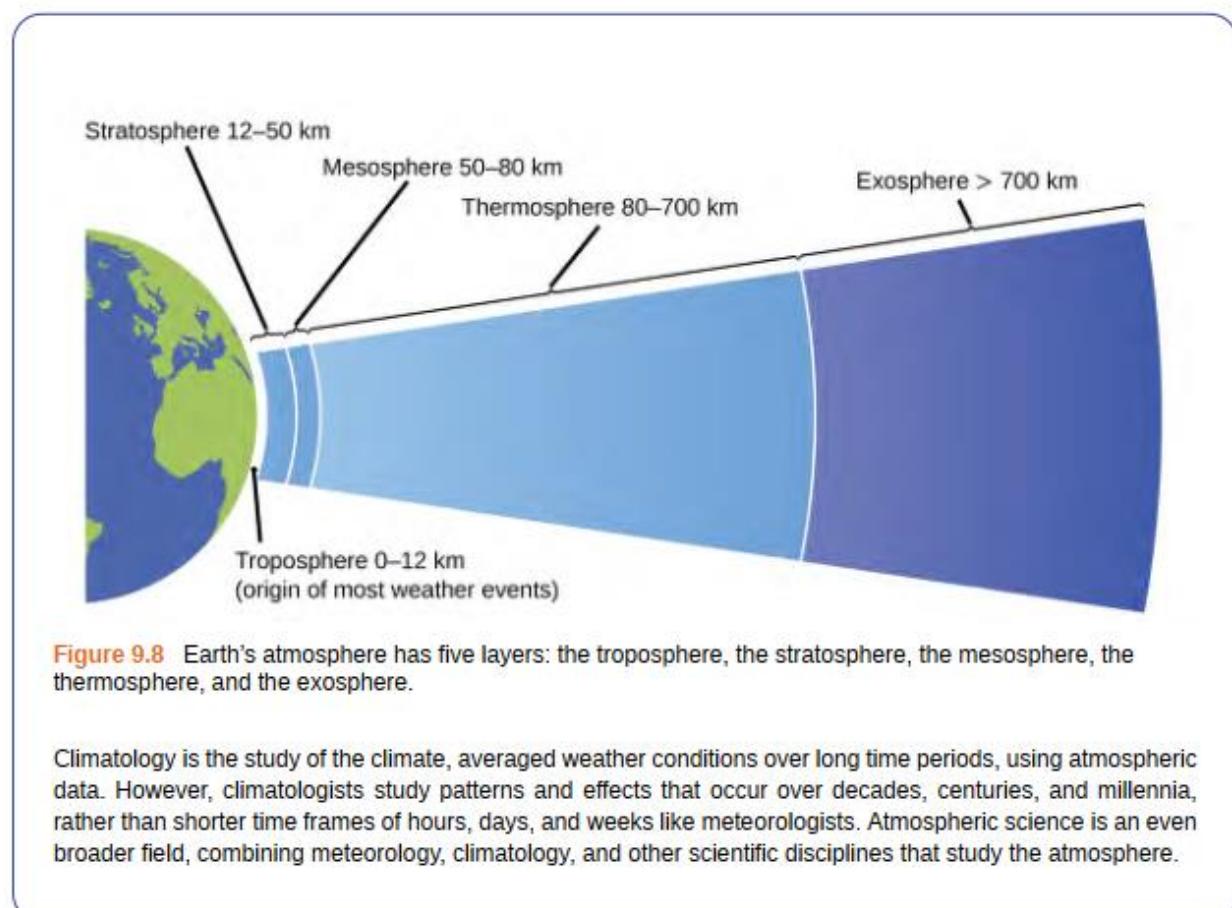


Figure 9.8 Earth's atmosphere has five layers: the troposphere, the stratosphere, the mesosphere, the thermosphere, and the exosphere.

Climatology is the study of the climate, averaged weather conditions over long time periods, using atmospheric data. However, climatologists study patterns and effects that occur over decades, centuries, and millennia, rather than shorter time frames of hours, days, and weeks like meteorologists. Atmospheric science is an even broader field, combining meteorology, climatology, and other scientific disciplines that study the atmosphere.

9.2 Relating Pressure, Volume, Amount, and Temperature: The Ideal Gas Law

By the end of this section, you will be able to:

- Identify the mathematical relationships between the various properties of gases
- Use the ideal gas law, and related gas laws, to compute the values of various gas properties under specified conditions

During the seventeenth and especially eighteenth centuries, driven both by a desire to understand nature and a quest to make balloons in which they could fly (**Figure 9.9**), a number of scientists established the relationships between the macroscopic physical properties of gases, that is, pressure, volume, temperature, and amount of gas. Although their measurements were not precise by today's standards, they were able to determine the mathematical relationships between pairs of these variables (e.g., pressure and temperature, pressure and volume) that hold for an *ideal gas*—a hypothetical construct that real gases approximate under certain conditions. Eventually, these individual laws were combined into a single equation—the *ideal gas law*—that relates gas quantities for gases and is quite accurate for low pressures and moderate temperatures. We will consider the key developments in individual relationships (for pedagogical reasons not quite in historical order), then put them together in the ideal gas law.

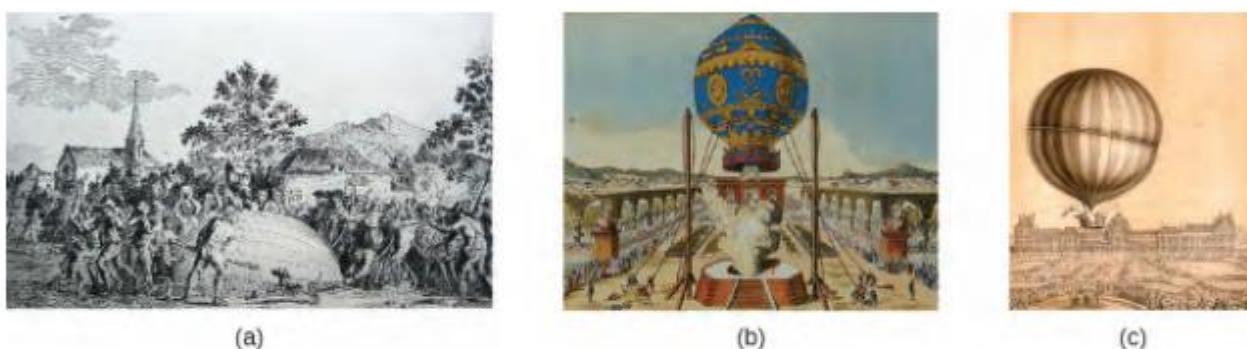


Figure 9.9 In 1783, the first (a) hydrogen-filled balloon flight, (b) manned hot air balloon flight, and (c) manned hydrogen-filled balloon flight occurred. When the hydrogen-filled balloon depicted in (a) landed, the frightened villagers of Gonesse reportedly destroyed it with pitchforks and knives. The launch of the latter was reportedly viewed by 400,000 people in Paris.

Pressure and Temperature: Amontons's Law

Imagine filling a rigid container attached to a pressure gauge with gas and then sealing the container so that no gas may escape. If the container is cooled, the gas inside likewise gets colder and its pressure is observed to decrease. Since the container is rigid and tightly sealed, both the volume and number of moles of gas remain constant. If we heat the sphere, the gas inside gets hotter (Figure 9.10) and the pressure increases.

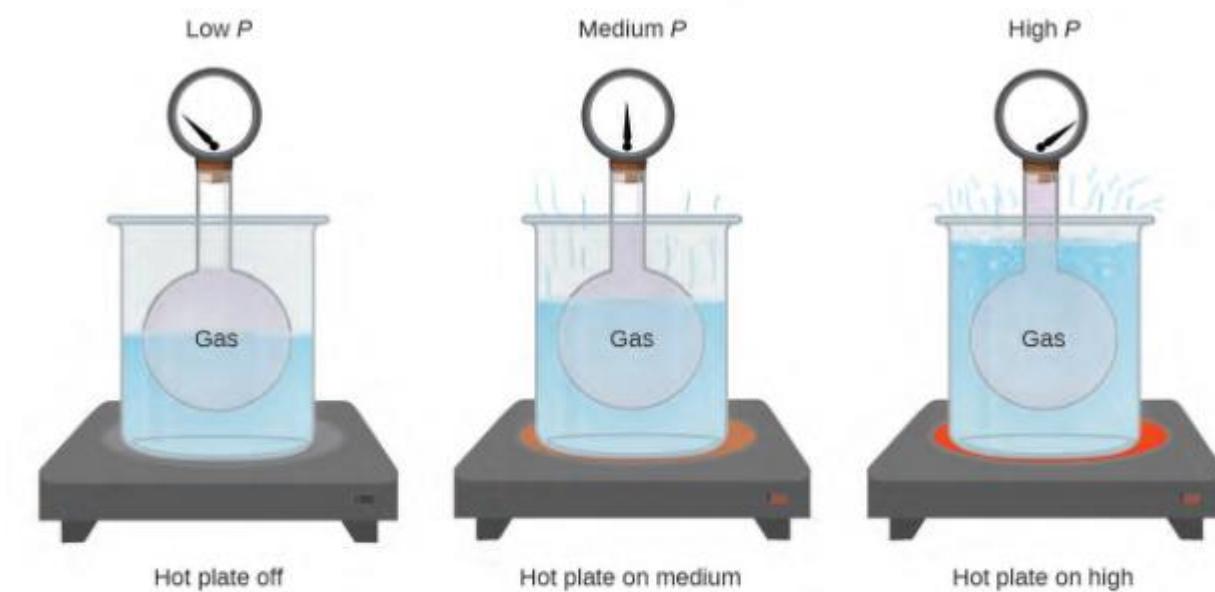


Figure 9.10 The effect of temperature on gas pressure: When the hot plate is off, the pressure of the gas in the sphere is relatively low. As the gas is heated, the pressure of the gas in the sphere increases.

This relationship between temperature and pressure is observed for any sample of gas confined to a constant volume. An example of experimental pressure-temperature data is shown for a sample of air under these conditions in Figure 9.11. We find that temperature and pressure are linearly related, and if the temperature is on the kelvin scale, then P and T are directly proportional (again, when *volume and moles of gas are held constant*); if the temperature on the kelvin scale increases by a certain factor, the gas pressure increases by the same factor.

Temperature (°C)	Temperature (K)	Pressure (kPa)
-150	173	36.0
-100	223	46.4
-50	273	56.7
0	323	67.1
50	373	77.5
100	423	88.0

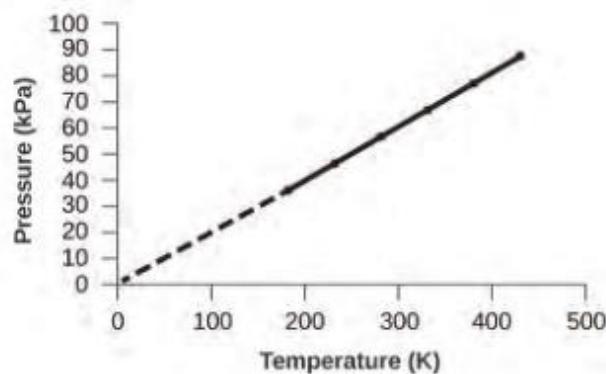


Figure 9.11 For a constant volume and amount of air, the pressure and temperature are directly proportional, provided the temperature is in kelvin. (Measurements cannot be made at lower temperatures because of the condensation of the gas.) When this line is extrapolated to lower pressures, it reaches a pressure of 0 at -273°C , which is 0 on the kelvin scale and the lowest possible temperature, called absolute zero.

Guillaume Amontons was the first to empirically establish the relationship between the pressure and the temperature of a gas (~1700), and Joseph Louis Gay-Lussac determined the relationship more precisely (~1800). Because of this, the *P-T* relationship for gases is known as either **Amontons's law** or **Gay-Lussac's law**. Under either name, it states that *the pressure of a given amount of gas is directly proportional to its temperature on the kelvin scale when the volume is held constant*. Mathematically, this can be written:

$$P \propto T \text{ or } P = \text{constant} \times T \text{ or } P = k \times T$$

where \propto means “is proportional to,” and k is a proportionality constant that depends on the identity, amount, and volume of the gas.

For a confined, constant volume of gas, the ratio $\frac{P}{T}$ is therefore constant (i.e., $\frac{P}{T} = k$). If the gas is initially in “Condition 1” (with $P = P_1$ and $T = T_1$), and then changes to “Condition 2” (with $P = P_2$ and $T = T_2$), we have that $\frac{P_1}{T_1} = k$ and $\frac{P_2}{T_2} = k$, which reduces to $\frac{P_1}{T_1} = \frac{P_2}{T_2}$. This equation is useful for pressure-temperature calculations for a confined gas at constant volume. Note that temperatures must be on the kelvin scale for any gas law calculations (0 on the kelvin scale and the lowest possible temperature is called **absolute zero**). (Also note that there are at least three ways we can describe how the pressure of a gas changes as its temperature changes: We can use a table of values, a graph, or a mathematical equation.)

Example 9.5

Predicting Change in Pressure with Temperature

A can of hair spray is used until it is empty except for the propellant, isobutane gas.

- (a) On the can is the warning “Store only at temperatures below 120°F (48.8°C). Do not incinerate.” Why?
- (b) The gas in the can is initially at 24°C and 360 kPa, and the can has a volume of 350 mL. If the can is left in a car that reaches 50°C on a hot day, what is the new pressure in the can?

Solution

- (a) The can contains an amount of isobutane gas at a constant volume, so if the temperature is increased by heating, the pressure will increase proportionately. High temperature could lead to high pressure, causing the can to burst. (Also, isobutane is combustible, so incineration could cause the can to explode.)

(b) We are looking for a pressure change due to a temperature change at constant volume, so we will use Amontons's/Gay-Lussac's law. Taking P_1 and T_1 as the initial values, T_2 as the temperature where the pressure is unknown and P_2 as the unknown pressure, and converting $^{\circ}\text{C}$ to K, we have:

$$\frac{P_1}{T_1} = \frac{P_2}{T_2} \text{ which means that } \frac{360 \text{ kPa}}{297 \text{ K}} = \frac{P_2}{323 \text{ K}}$$

$$\text{Rearranging and solving gives: } P_2 = \frac{360 \text{ kPa} \times 323 \text{ K}}{297 \text{ K}} = 390 \text{ kPa}$$

Check Your Learning

A sample of nitrogen, N_2 , occupies 45.0 mL at 27°C and 600 torr. What pressure will it have if cooled to -73°C while the volume remains constant?

Answer: 400 torr

Volume and Temperature: Charles's Law

If we fill a balloon with air and seal it, the balloon contains a specific amount of air at atmospheric pressure, let's say 1 atm. If we put the balloon in a refrigerator, the gas inside gets cold and the balloon shrinks (although both the amount of gas and its pressure remain constant). If we make the balloon very cold, it will shrink a great deal, and it expands again when it warms up.

These examples of the effect of temperature on the volume of a given amount of a confined gas at constant pressure are true in general: The volume increases as the temperature increases, and decreases as the temperature decreases. Volume-temperature data for a 1-mole sample of methane gas at 1 atm are listed and graphed in [Figure 9.12](#).

Temperature (°C)	Temperature (K)	Volume (L)
-3	270	22
-23	250	21
-53	220	18
-162	111	9

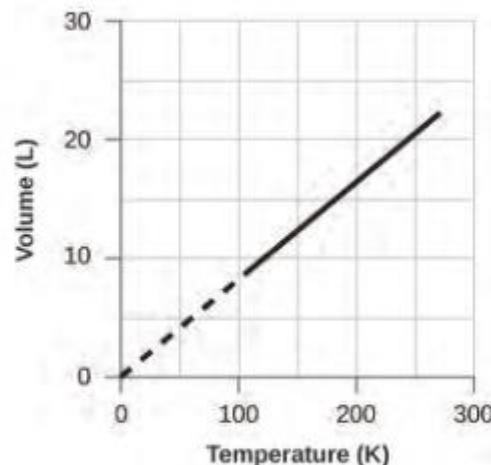


Figure 9.12 The volume and temperature are linearly related for 1 mole of methane gas at a constant pressure of 1 atm. If the temperature is in kelvin, volume and temperature are directly proportional. The line stops at 111 K because methane liquefies at this temperature; when extrapolated, it intersects the graph's origin, representing a temperature of absolute zero.

The relationship between the volume and temperature of a given amount of gas at constant pressure is known as Charles's law in recognition of the French scientist and balloon flight pioneer Jacques Alexandre César Charles. **Charles's law** states that *the volume of a given amount of gas is directly proportional to its temperature on the kelvin scale when the pressure is held constant*.

Mathematically, this can be written as:

$$V \propto T \text{ or } V = \text{constant} \cdot T \text{ or } V = k \cdot T \text{ or } V_1/T_1 = V_2/T_2$$

with k being a proportionality constant that depends on the amount and pressure of the gas.

For a confined, constant pressure gas sample, $\frac{V}{T}$ is constant (i.e., the ratio = k), and as seen with the V - T relationship, this leads to another form of Charles's law: $\frac{V_1}{T_1} = \frac{V_2}{T_2}$.

Example 9.6

Predicting Change in Volume with Temperature

A sample of carbon dioxide, CO₂, occupies 0.300 L at 10 °C and 750 torr. What volume will the gas have at 30 °C and 750 torr?

Solution

Because we are looking for the volume change caused by a temperature change at constant pressure, this is a job for Charles's law. Taking V_1 and T_1 as the initial values, T_2 as the temperature at which the volume is unknown and V_2 as the unknown volume, and converting °C into K we have:

$$\frac{V_1}{T_1} = \frac{V_2}{T_2} \text{ which means that } \frac{0.300 \text{ L}}{283 \text{ K}} = \frac{V_2}{303 \text{ K}}$$

$$\text{Rearranging and solving gives: } V_2 = \frac{0.300 \text{ L} \times 303 \text{ K}}{283 \text{ K}} = 0.321 \text{ L}$$

This answer supports our expectation from Charles's law, namely, that raising the gas temperature (from 283 K to 303 K) at a constant pressure will yield an increase in its volume (from 0.300 L to 0.321 L).

Check Your Learning

A sample of oxygen, O₂, occupies 32.2 mL at 30 °C and 452 torr. What volume will it occupy at -70 °C and the same pressure?

Answer: 21.6 mL

Example 9.7

Measuring Temperature with a Volume Change

Temperature is sometimes measured with a gas thermometer by observing the change in the volume of the gas as the temperature changes at constant pressure. The hydrogen in a particular hydrogen gas thermometer has a volume of 150.0 cm³ when immersed in a mixture of ice and water (0.00 °C). When immersed in boiling liquid ammonia, the volume of the hydrogen, at the same pressure, is 131.7 cm³. Find the temperature of boiling ammonia on the kelvin and Celsius scales.

Solution

A volume change caused by a temperature change at constant pressure means we should use Charles's law. Taking V₁ and T₁ as the initial values, T₂ as the temperature at which the volume is unknown and V₂ as the unknown volume, and converting °C into K we have:

$$\frac{V_1}{T_1} = \frac{V_2}{T_2} \text{ which means that } \frac{150.0 \text{ cm}^3}{273.15 \text{ K}} = \frac{131.7 \text{ cm}^3}{T_2}$$

$$\text{Rearrangement gives } T_2 = \frac{131.7 \text{ cm}^3 \times 273.15 \text{ K}}{150.0 \text{ cm}^3} = 239.8 \text{ K}$$

Subtracting 273.15 from 239.8 K, we find that the temperature of the boiling ammonia on the Celsius scale is -33.4 °C.

Check Your Learning

What is the volume of a sample of ethane at 467 K and 1.1 atm if it occupies 405 mL at 298 K and 1.1 atm?

Answer: 635 mL

Volume and Pressure: Boyle's Law

If we partially fill an airtight syringe with air, the syringe contains a specific amount of air at constant temperature, say 25 °C. If we slowly push in the plunger while keeping temperature constant, the gas in the syringe is compressed into a smaller volume and its pressure increases; if we pull out the plunger, the volume increases and the pressure decreases. This example of the effect of volume on the pressure of a given amount of a confined gas is true in general. Decreasing the volume of a contained gas will increase its pressure, and increasing its volume will decrease its pressure. In fact, if the volume increases by a certain factor, the pressure decreases by the same factor, and vice versa. Volume-pressure data for an air sample at room temperature are graphed in **Figure 9.13**.

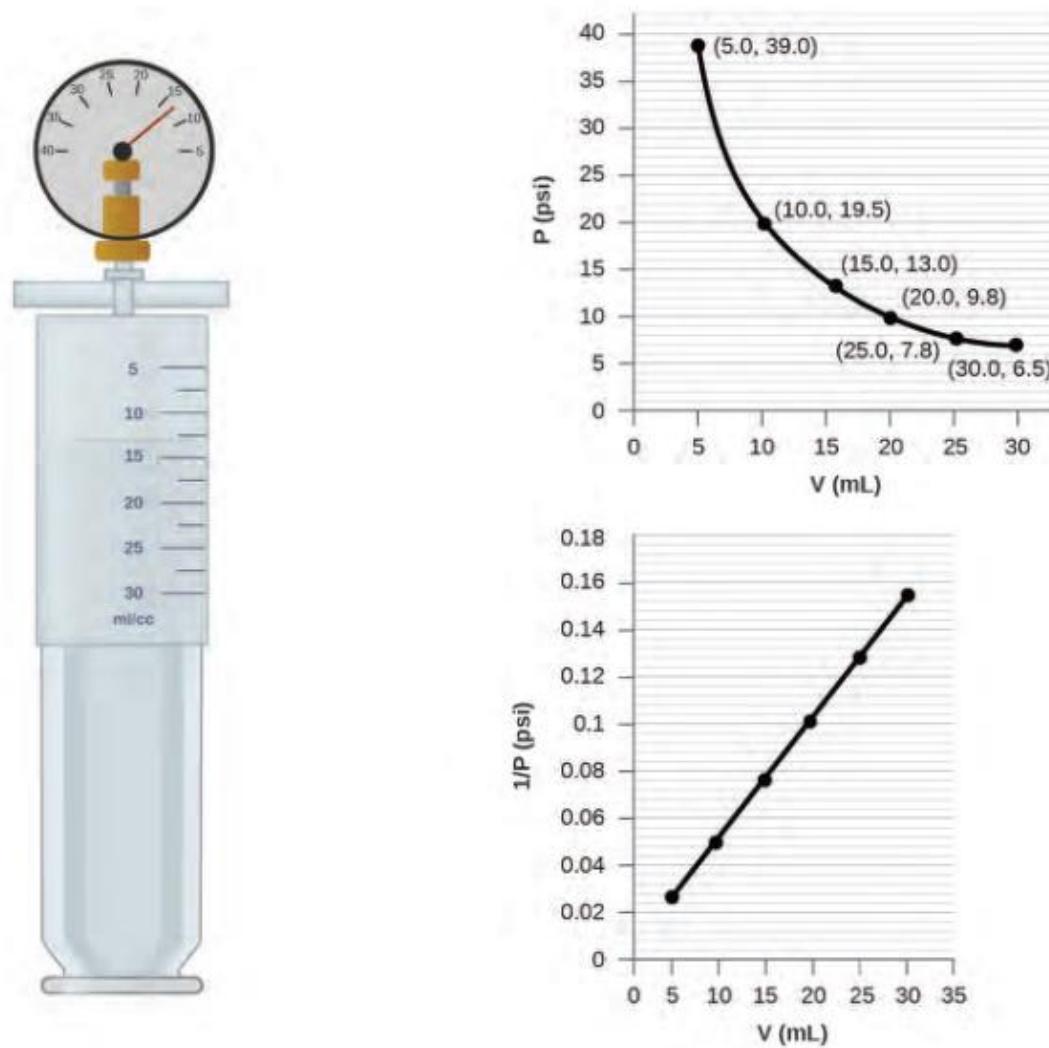


Figure 9.13 When a gas occupies a smaller volume, it exerts a higher pressure; when it occupies a larger volume, it exerts a lower pressure (assuming the amount of gas and the temperature do not change). Since P and V are inversely proportional, a graph of $\frac{1}{P}$ vs. V is linear.

Unlike the $P-T$ and $V-T$ relationships, pressure and volume are not directly proportional to each other. Instead, P and V exhibit inverse proportionality: Increasing the pressure results in a decrease of the volume of the gas. Mathematically this can be written:

$$P \propto 1/V \text{ or } P = k \cdot 1/V \text{ or } P \cdot V = k \text{ or } P_1 V_1 = P_2 V_2$$

with k being a constant. Graphically, this relationship is shown by the straight line that results when plotting the inverse of the pressure ($\frac{1}{P}$) versus the volume (V), or the inverse of volume ($\frac{1}{V}$) versus the pressure (P). Graphs with curved lines are difficult to read accurately at low or high values of the variables, and they are more difficult to use in fitting theoretical equations and parameters to experimental data. For those reasons, scientists often try to find a way to “linearize” their data. If we plot P versus V , we obtain a hyperbola (see [Figure 9.14](#)).

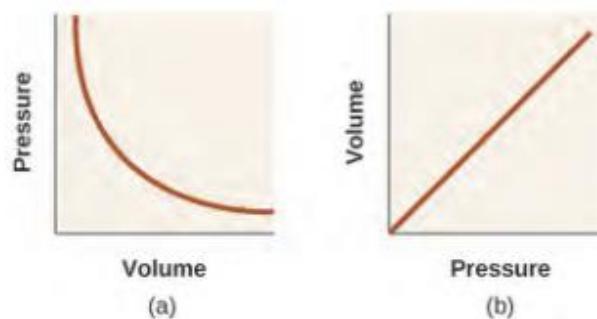


Figure 9.14 The relationship between pressure and volume is inversely proportional. (a) The graph of P vs. V is a parabola, whereas (b) the graph of $(\frac{1}{P})$ vs. V is linear.

The relationship between the volume and pressure of a given amount of gas at constant temperature was first published by the English natural philosopher Robert Boyle over 300 years ago. It is summarized in the statement now known as **Boyle's law**: *The volume of a given amount of gas held at constant temperature is inversely proportional to the pressure under which it is measured.*

Example 9.8

Volume of a Gas Sample

The sample of gas in [Figure 9.13](#) has a volume of 15.0 mL at a pressure of 13.0 psi. Determine the pressure of the gas at a volume of 7.5 mL, using:

- (a) the P - V graph in [Figure 9.13](#)
- (b) the $\frac{1}{P}$ vs. V graph in [Figure 9.13](#)
- (c) the Boyle's law equation

Comment on the likely accuracy of each method.

Solution

(a) Estimating from the P - V graph gives a value for P somewhere around 27 psi.

(b) Estimating from the $\frac{1}{P}$ versus V graph give a value of about 26 psi.

(c) From Boyle's law, we know that the product of pressure and volume (PV) for a given sample of gas at a constant temperature is always equal to the same value. Therefore we have $P_1V_1 = k$ and $P_2V_2 = k$ which means that $P_1V_1 = P_2V_2$.

Using P_1 and V_1 as the known values 0.993 atm and 2.40 mL, P_2 as the pressure at which the volume is unknown, and V_2 as the unknown volume, we have:

$$P_1 V_1 = P_2 V_2 \text{ or } 13.0 \text{ psi} \times 15.0 \text{ mL} = P_2 \times 7.5 \text{ mL}$$

Solving:

$$V_2 = \frac{13.0 \text{ psi} \times 15.0 \text{ mL}}{7.5 \text{ mL}} = 26 \text{ mL}$$

It was more difficult to estimate well from the P - V graph, so (a) is likely more inaccurate than (b) or (c). The calculation will be as accurate as the equation and measurements allow.

Check Your Learning

The sample of gas in [Figure 9.13](#) has a volume of 30.0 mL at a pressure of 6.5 psi. Determine the volume of the gas at a pressure of 11.0 mL, using:

- (a) the P - V graph in [Figure 9.13](#)
- (b) the $\frac{1}{P}$ vs. V graph in [Figure 9.13](#)
- (c) the Boyle's law equation

Comment on the likely accuracy of each method.

Answer: (a) about 17–18 mL; (b) ~18 mL; (c) 17.7 mL; it was more difficult to estimate well from the P - V graph, so (a) is likely more inaccurate than (b); the calculation will be as accurate as the equation and measurements allow

Chemistry in Everyday Life

Breathing and Boyle's Law

What do you do about 20 times per minute for your whole life, without break, and often without even being aware of it? The answer, of course, is respiration, or breathing. How does it work? It turns out that the gas laws apply here. Your lungs take in gas that your body needs (oxygen) and get rid of waste gas (carbon dioxide). Lungs are made of spongy, stretchy tissue that expands and contracts while you breathe. When you inhale, your diaphragm and intercostal muscles (the muscles between your ribs) contract, expanding your chest cavity and making your lung volume larger. The increase in volume leads to a decrease in pressure (Boyle's law). This causes air to flow into the lungs (from high pressure to low pressure). When you exhale, the process reverses: Your diaphragm and rib muscles relax, your chest cavity contracts, and your lung volume decreases, causing the pressure to increase (Boyle's law again), and air flows out of the lungs (from high pressure to low pressure). You then breathe in and out again, and again, repeating this Boyle's law cycle for the rest of your life ([Figure 9.15](#)).

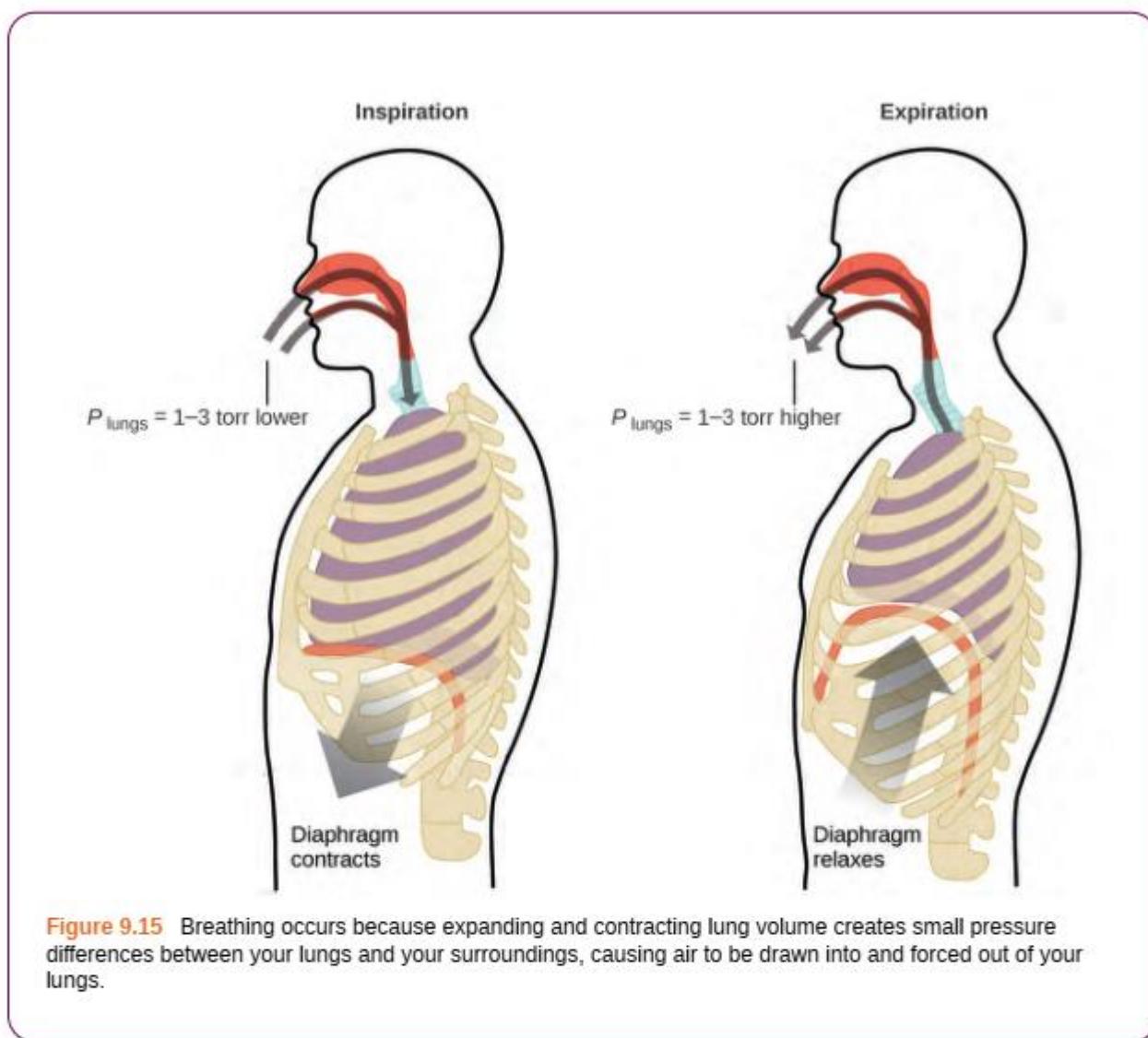


Figure 9.15 Breathing occurs because expanding and contracting lung volume creates small pressure differences between your lungs and your surroundings, causing air to be drawn into and forced out of your lungs.

Moles of Gas and Volume: Avogadro's Law

The Italian scientist Amedeo Avogadro advanced a hypothesis in 1811 to account for the behavior of gases, stating that equal volumes of all gases, measured under the same conditions of temperature and pressure, contain the same number of molecules. Over time, this relationship was supported by many experimental observations as expressed by **Avogadro's law**: *For a confined gas, the volume (V) and number of moles (n) are directly proportional if the pressure and temperature both remain constant.*

In equation form, this is written as:

$$V \propto n \text{ or } V = k \times n \text{ or } \frac{V_1}{n_1} = \frac{V_2}{n_2}$$

Mathematical relationships can also be determined for the other variable pairs, such as P versus n , and n versus T .

Link to Learning



Visit this [interactive PhET simulation](http://openstaxcollege.org/II_16IdealGasLaw) (http://openstaxcollege.org/II_16IdealGasLaw) to investigate the relationships between pressure, volume, temperature, and amount of gas. Use the simulation to examine the effect of changing one parameter on another while holding the other parameters constant (as described in the preceding sections on the various gas laws).

The Ideal Gas Law

To this point, four separate laws have been discussed that relate pressure, volume, temperature, and the number of moles of the gas:

- Boyle's law: $PV = \text{constant}$ at constant T and n
- Amontons's law: $\frac{P}{T} = \text{constant}$ at constant V and n
- Charles's law: $\frac{V}{T} = \text{constant}$ at constant P and n
- Avogadro's law: $\frac{V}{n} = \text{constant}$ at constant P and T

Combining these four laws yields the **ideal gas law**, a relation between the pressure, volume, temperature, and number of moles of a gas:

$$PV = nRT$$

where P is the pressure of a gas, V is its volume, n is the number of moles of the gas, T is its temperature on the kelvin scale, and R is a constant called the **ideal gas constant** or the universal gas constant. The units used to express pressure, volume, and temperature will determine the proper form of the gas constant as required by dimensional analysis, the most commonly encountered values being $0.08206 \text{ L atm mol}^{-1} \text{ K}^{-1}$ and $8.314 \text{ kPa L mol}^{-1} \text{ K}^{-1}$.

Gases whose properties of P , V , and T are accurately described by the ideal gas law (or the other gas laws) are said to exhibit *ideal behavior* or to approximate the traits of an **ideal gas**. An ideal gas is a hypothetical construct that may be used along with *kinetic molecular theory* to effectively explain the gas laws as will be described in a later module of this chapter. Although all the calculations presented in this module assume ideal behavior, this assumption is only reasonable for gases under conditions of relatively low pressure and high temperature. In the final module of this chapter, a modified gas law will be introduced that accounts for the *non-ideal* behavior observed for many gases at relatively high pressures and low temperatures.

The ideal gas equation contains five terms, the gas constant R and the variable properties P , V , n , and T . Specifying any four of these terms will permit use of the ideal gas law to calculate the fifth term as demonstrated in the following example exercises.

Example 9.9

Using the Ideal Gas Law

Methane, CH_4 , is being considered for use as an alternative automotive fuel to replace gasoline. One gallon of gasoline could be replaced by 655 g of CH_4 . What is the volume of this much methane at 25°C and 745 torr?

Solution

We must rearrange $PV = nRT$ to solve for V : $V = \frac{nRT}{P}$

If we choose to use $R = 0.08206 \text{ L atm mol}^{-1} \text{ K}^{-1}$, then the amount must be in moles, temperature must be in kelvin, and pressure must be in atm.

Converting into the “right” units:

$$n = 6.55 \frac{\text{g CH}_4}{\text{mol}} \times \frac{1 \text{ mol}}{16.043 \frac{\text{g CH}_4}{\text{mol}}} = 0.408 \text{ mol}$$

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

$$P = 745 \frac{\text{torr}}{\text{atm}} \times \frac{1 \text{ atm}}{760 \frac{\text{torr}}{\text{atm}}} = 0.980 \text{ atm}$$

$$V = \frac{nRT}{P} = \frac{(0.408 \text{ mol})(0.08206 \text{ L atm mol}^{-1} \text{ K}^{-1})(298 \text{ K})}{0.980 \text{ atm}} = 1.02 \times 10^3 \text{ L}$$

It would require 1020 L (269 gal) of gaseous methane at about 1 atm of pressure to replace 1 gal of gasoline. It requires a large container to hold enough methane at 1 atm to replace several gallons of gasoline.

Check Your Learning

Calculate the pressure in bar of 2520 moles of hydrogen gas stored at 27 °C in the 180-L storage tank of a modern hydrogen-powered car.

Answer: 350 bar

If the number of moles of an ideal gas are kept constant under two different sets of conditions, a useful mathematical relationship called the combined gas law is obtained: $\frac{P_1 V_1}{T_1} = \frac{P_2 V_2}{T_2}$ using units of atm, L, and K. Both sets of conditions are equal to the product of $n \times R$ (where n = the number of moles of the gas and R is the ideal gas law constant).

Example 9.10

Using the Combined Gas Law

When filled with air, a typical scuba tank with a volume of 13.2 L has a pressure of 153 atm (Figure 9.16). If the water temperature is 27 °C, how many liters of air will such a tank provide to a diver’s lungs at a depth of approximately 70 feet in the ocean where the pressure is 3.13 atm?



Figure 9.16 Scuba divers use compressed air to breathe while underwater. (credit: modification of work by Mark Goodchild)

Letting 1 represent the air in the scuba tank and 2 represent the air in the lungs, and noting that body temperature (the temperature the air will be in the lungs) is 37 °C, we have:

$$\frac{P_1 V_1}{T_1} = \frac{P_2 V_2}{T_2} \rightarrow \frac{(153 \text{ atm})(13.2 \text{ L})}{(300 \text{ K})} = \frac{(3.13 \text{ atm})(V_2)}{(310 \text{ K})}$$

Solving for V_2 :

$$V_2 = \frac{(153 \text{ atm})(13.2 \text{ L})(310 \text{ K})}{(300 \text{ K})(3.13 \text{ atm})} = 667 \text{ L}$$

(Note: Be advised that this particular example is one in which the assumption of ideal gas behavior is not very reasonable, since it involves gases at relatively high pressures and low temperatures. Despite this limitation, the calculated volume can be viewed as a good "ballpark" estimate.)

Check Your Learning

A sample of ammonia is found to occupy 0.250 L under laboratory conditions of 27 °C and 0.850 atm. Find the volume of this sample at 0 °C and 1.00 atm.

Answer: 0.538 L

Chemistry in Everyday Life

The Interdependence between Ocean Depth and Pressure in Scuba Diving

Whether scuba diving at the Great Barrier Reef in Australia (shown in Figure 9.17) or in the Caribbean, divers must understand how pressure affects a number of issues related to their comfort and safety.



Figure 9.17 Scuba divers, whether at the Great Barrier Reef or in the Caribbean, must be aware of buoyancy, pressure equalization, and the amount of time they spend underwater, to avoid the risks associated with pressurized gases in the body. (credit: Kyle Taylor)

Pressure increases with ocean depth, and the pressure changes most rapidly as divers reach the surface. The pressure a diver experiences is the sum of all pressures above the diver (from the water and the air). Most pressure measurements are given in units of atmospheres, expressed as "atmospheres absolute" or ATA in the diving community: Every 33 feet of salt water represents 1 ATA of pressure in addition to 1 ATA of pressure

from the atmosphere at sea level. As a diver descends, the increase in pressure causes the body's air pockets in the ears and lungs to compress; on the ascent, the decrease in pressure causes these air pockets to expand, potentially rupturing eardrums or bursting the lungs. Divers must therefore undergo equalization by adding air to body airspaces on the descent by breathing normally and adding air to the mask by breathing out of the nose or adding air to the ears and sinuses by equalization techniques; the corollary is also true on ascent, divers must release air from the body to maintain equalization. Buoyancy, or the ability to control whether a diver sinks or floats, is controlled by the buoyancy compensator (BCD). If a diver is ascending, the air in his BCD expands because of lower pressure according to Boyle's law (decreasing the pressure of gases increases the volume). The expanding air increases the buoyancy of the diver, and she or he begins to ascend. The diver must vent air from the BCD or risk an uncontrolled ascent that could rupture the lungs. In descending, the increased pressure causes the air in the BCD to compress and the diver sinks much more quickly; the diver must add air to the BCD or risk an uncontrolled descent, facing much higher pressures near the ocean floor. The pressure also impacts how long a diver can stay underwater before ascending. The deeper a diver dives, the more compressed the air that is breathed because of increased pressure: If a diver dives 33 feet, the pressure is 2 ATA and the air would be compressed to one-half of its original volume. The diver uses up available air twice as fast as at the surface.

Standard Conditions of Temperature and Pressure

We have seen that the volume of a given quantity of gas and the number of molecules (moles) in a given volume of gas vary with changes in pressure and temperature. Chemists sometimes make comparisons against a **standard temperature and pressure (STP)** for reporting properties of gases: 273.15 K and 1 atm (101.325 kPa). At STP, an ideal gas has a volume of about 22.4 L—this is referred to as the **standard molar volume** (Figure 9.18).

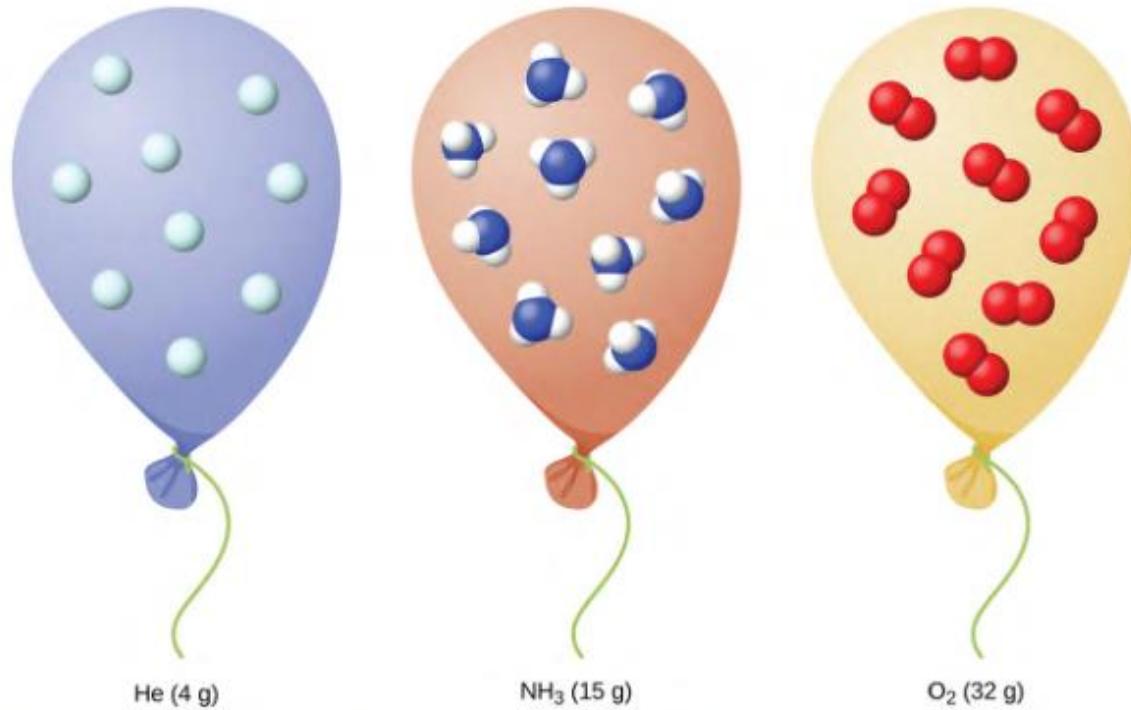


Figure 9.18 Since the number of moles in a given volume of gas varies with pressure and temperature changes, chemists use standard temperature and pressure (273.15 K and 1 atm or 101.325 kPa) to report properties of gases.

9.3 Stoichiometry of Gaseous Substances, Mixtures, and Reactions

By the end of this section, you will be able to:

- Use the ideal gas law to compute gas densities and molar masses
- Perform stoichiometric calculations involving gaseous substances
- State Dalton's law of partial pressures and use it in calculations involving gaseous mixtures

The study of the chemical behavior of gases was part of the basis of perhaps the most fundamental chemical revolution in history. French nobleman Antoine Lavoisier, widely regarded as the “father of modern chemistry,” changed chemistry from a qualitative to a quantitative science through his work with gases. He discovered the law of conservation of matter, discovered the role of oxygen in combustion reactions, determined the composition of air, explained respiration in terms of chemical reactions, and more. He was a casualty of the French Revolution, guillotined in 1794. Of his death, mathematician and astronomer Joseph-Louis Lagrange said, “It took the mob only a moment to remove his head; a century will not suffice to reproduce it.”^[1]

As described in an earlier chapter of this text, we can turn to chemical stoichiometry for answers to many of the questions that ask “How much?” We can answer the question with masses of substances or volumes of solutions. However, we can also answer this question another way: with volumes of gases. We can use the ideal gas equation to relate the pressure, volume, temperature, and number of moles of a gas. Here we will combine the ideal gas equation with other equations to find gas density and molar mass. We will deal with mixtures of different gases, and calculate amounts of substances in reactions involving gases. This section will not introduce any new material or ideas, but will provide examples of applications and ways to integrate concepts we have already discussed.

Density of a Gas

Recall that the density of a gas is its mass to volume ratio, $\rho = \frac{m}{V}$. Therefore, if we can determine the mass of some volume of a gas, we will get its density. The density of an unknown gas can be used to determine its molar mass and thereby assist in its identification. The ideal gas law, $PV = nRT$, provides us with a means of deriving such a mathematical formula to relate the density of a gas to its volume in the proof shown in [Example 9.11](#).

Example 9.11

Derivation of a Density Formula from the Ideal Gas Law

Use $PV = nRT$ to derive a formula for the density of gas in g/L

Solution

Step 1. $PV = nRT$

Step 2. Rearrange to get (mol/L): $\frac{n}{V} = \frac{P}{RT}$

Step 3. Multiply each side of the equation by the molar mass, M . When moles are multiplied by M in g/mol, g are obtained:

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

Step 4. $g/L = \rho = \frac{PM}{RT}$

Check Your Learning

1. “Quotations by Joseph-Louis Lagrange,” last modified February 2006, accessed February 10, 2015, <http://www-history.mcs.st-andrews.ac.uk/Quotations/Lagrange.html>

A gas was found to have a density of 0.0847 g/L at 17.0 °C and a pressure of 760 torr. What is its molar mass? What is the gas?

$$\text{Answer: } \rho = \frac{PM}{RT}$$

$$0.0847 \text{ g/L} = 760 \text{ torr} \times \frac{1 \text{ atm}}{760 \text{ torr}} \times \frac{M}{0.0821 \text{ L atm/mol K}} \times 290 \text{ K}$$

$$M = 2.02 \text{ g/mol}; \text{ therefore, the gas must be hydrogen (H}_2\text{, 2.02 g/mol)}$$

We must specify both the temperature and the pressure of a gas when calculating its density because the number of moles of a gas (and thus the mass of the gas) in a liter changes with temperature or pressure. Gas densities are often reported at STP.

Example 9.12

Empirical/Molecular Formula Problems Using the Ideal Gas Law and Density of a Gas

Cyclopropane, a gas once used with oxygen as a general anesthetic, is composed of 85.7% carbon and 14.3% hydrogen by mass. Find the empirical formula. If 1.56 g of cyclopropane occupies a volume of 1.00 L at 0.984 atm and 50 °C, what is the molecular formula for cyclopropane?

Solution

Strategy: First solve the empirical formula problem using methods discussed earlier. Assume 100 g and convert the percentage of each element into grams. Determine the number of moles of carbon and hydrogen in the 100-g sample of cyclopropane. Divide by the smallest number of moles to relate the number of moles of carbon to the number of moles of hydrogen. In the last step, realize that the smallest whole number ratio is the empirical formula:

$$85.7 \text{ g C} \times \frac{1 \text{ mol C}}{12.01 \text{ g C}} = 7.136 \text{ mol C} \quad \frac{7.136}{7.136} = 1.00 \text{ mol C}$$

$$14.3 \text{ g H} \times \frac{1 \text{ mol H}}{1.01 \text{ g H}} = 14.158 \text{ mol H} \quad \frac{14.158}{7.136} = 1.98 \text{ mol H}$$

Empirical formula is CH₂ [empirical mass (EM) of 14.03 g/empirical unit].

Next, use the density equation related to the ideal gas law to determine the molar mass:

$$d = \frac{PM}{RT} \quad \frac{1.56 \text{ g}}{1.00 \text{ L}} = 0.984 \text{ atm} \times \frac{M}{0.0821 \text{ L atm/mol K}} \times 323 \text{ K}$$

$$M = 42.0 \text{ g/mol}, \quad \frac{M}{EM} = \frac{42.0}{14.03} = 2.99, \quad \text{so } (3)(\text{CH}_2) = \text{C}_3\text{H}_6 \text{ (molecular formula)}$$

Check Your Learning

Acetylene, a fuel used welding torches, is comprised of 92.3% C and 7.7% H by mass. Find the empirical formula. If g of acetylene occupies of volume of 1.00 L at 1.15 atm and 59.5 °C, what is the molecular formula for acetylene?

Answer: Empirical formula, CH; Molecular formula, C₂H₂

Molar Mass of a Gas

Another useful application of the ideal gas law involves the determination of molar mass. By definition, the molar mass of a substance is the ratio of its mass in grams, *m*, to its amount in moles, *n*:

$$\mathcal{M} = \frac{\text{grams of substance}}{\text{moles of substance}} = \frac{m}{n}$$

The ideal gas equation can be rearranged to isolate n :

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

and then combined with the molar mass equation to yield:

$$\mathcal{M} = \frac{mRT}{PV}$$

This equation can be used to derive the molar mass of a gas from measurements of its pressure, volume, temperature, and mass.

Example 9.13

Determining the Molar Mass of a Volatile Liquid

The approximate molar mass of a volatile liquid can be determined by:

1. Heating a sample of the liquid in a flask with a tiny hole at the top, which converts the liquid into gas that may escape through the hole
2. Removing the flask from heat at the instant when the last bit of liquid becomes gas, at which time the flask will be filled with only gaseous sample at ambient pressure
3. Sealing the flask and permitting the gaseous sample to condense to liquid, and then weighing the flask to determine the sample's mass (see [Figure 9.19](#))

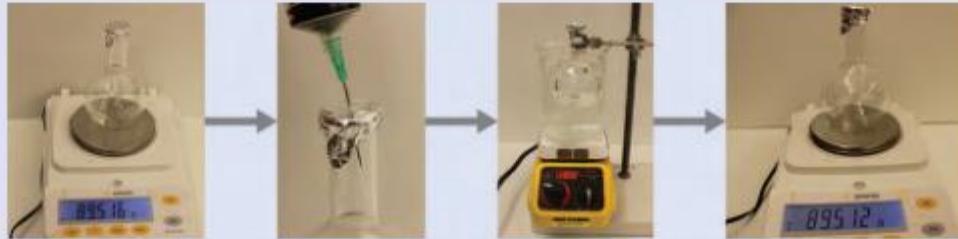


Figure 9.19 When the volatile liquid in the flask is heated past its boiling point, it becomes gas and drives air out of the flask. At $t_f \rightarrow g$, the flask is filled with volatile liquid gas at the same pressure as the atmosphere. If the flask is then cooled to room temperature, the gas condenses and the mass of the gas that filled the flask, and is now liquid, can be measured. (credit: modification of work by Mark Ott)

Using this procedure, a sample of chloroform gas weighing 0.494 g is collected in a flask with a volume of 129 cm^3 at 99.6°C when the atmospheric pressure is 742.1 mm Hg. What is the approximate molar mass of chloroform?

Solution

Since $\mathcal{M} = \frac{m}{n}$ and $n = \frac{PV}{RT}$, substituting and rearranging gives $\mathcal{M} = \frac{mRT}{PV}$,

then

$$\mathcal{M} = \frac{mRT}{PV} = \frac{(0.494 \text{ g}) \times 0.08206 \text{ L-atm/mol K} \times 372.8 \text{ K}}{0.976 \text{ atm} \times 0.129 \text{ L}} = 120 \text{ g/mol.}$$

Check Your Learning

A sample of phosphorus that weighs 3.243×10^{-2} g exerts a pressure of 31.89 kPa in a 56.0-mL bulb at 550 °C. What are the molar mass and molecular formula of phosphorus vapor?

Answer: 124 g/mol P₄

The Pressure of a Mixture of Gases: Dalton's Law

Unless they chemically react with each other, the individual gases in a mixture of gases do not affect each other's pressure. Each individual gas in a mixture exerts the same pressure that it would exert if it present alone in the container (Figure 9.20). The pressure exerted by each individual gas in a mixture is called its **partial pressure**. This observation is summarized by **Dalton's law of partial pressures**: *The total pressure of a mixture of ideal gases is equal to the sum of the partial pressures of the component gases*:

$$P_{Total} = P_A + P_B + P_C + \dots = \sum_i P_i$$

In the equation P_{Total} is the total pressure of a mixture of gases, P_A is the partial pressure of gas A; P_B is the partial pressure of gas B; P_C is the partial pressure of gas C; and so on.



Figure 9.20 If equal-volume cylinders containing gas A at a pressure of 300 kPa, gas B at a pressure of 600 kPa, and gas C at a pressure of 450 kPa are all combined in the same-size cylinder, the total pressure of the mixture is 1350 kPa.

The partial pressure of gas A is related to the total pressure of the gas mixture via its **mole fraction** (X), a unit of concentration defined as the number of moles of a component of a solution divided by the total number of moles of all components):

$$P_A = X_A \times P_{Total} \quad \text{where} \quad X_A = \frac{n_A}{n_{Total}}$$

where P_A , X_A , and n_A are the partial pressure, mole fraction, and number of moles of gas A, respectively, and n_{Total} is the number of moles of all components in the mixture.

Example 9.14

The Pressure of a Mixture of Gases

A 10.0-L vessel contains 2.50×10^{-3} mol of H₂, 1.00×10^{-3} mol of He, and 3.00×10^{-4} mol of Ne at 35 °C.

- (a) What are the partial pressures of each of the gases?
- (b) What is the total pressure in atmospheres?

Solution

The gases behave independently, so the partial pressure of each gas can be determined from the ideal gas equation, using $P = \frac{nRT}{V}$:

$$P_{H_2} = \frac{(2.50 \times 10^{-3} \text{ mol})(0.08206 \text{ L atm mol}^{-1} \text{ K}^{-1})(308 \text{ K})}{10.0 \text{ L}} = 6.32 \times 10^{-3} \text{ atm}$$

$$P_{He} = \frac{(1.00 \times 10^{-3} \text{ mol})(0.08206 \text{ L atm mol}^{-1} \text{ K}^{-1})(308 \text{ K})}{10.0 \text{ L}} = 2.53 \times 10^{-3} \text{ atm}$$

$$P_{Ne} = \frac{(3.00 \times 10^{-4} \text{ mol})(0.08206 \text{ L atm mol}^{-1} \text{ K}^{-1})(308 \text{ K})}{10.0 \text{ L}} = 7.58 \times 10^{-4} \text{ atm}$$

The total pressure is given by the sum of the partial pressures:

$$P_T = P_{H_2} + P_{He} + P_{Ne} = (0.00632 + 0.00253 + 0.00076) \text{ atm} = 9.61 \times 10^{-3} \text{ atm}$$

Check Your Learning

A 5.73-L flask at 25 °C contains 0.0388 mol of N₂, 0.147 mol of CO, and 0.0803 mol of H₂. What is the total pressure in the flask in atmospheres?

Answer: 1.137 atm

Here is another example of this concept, but dealing with mole fraction calculations.

Example 9.15

The Pressure of a Mixture of Gases

A gas mixture used for anesthesia contains 2.83 mol oxygen, O₂, and 8.41 mol nitrous oxide, N₂O. The total pressure of the mixture is 192 kPa.

- (a) What are the mole fractions of O₂ and N₂O?
- (b) What are the partial pressures of O₂ and N₂O?

Solution

The mole fraction is given by $X_A = \frac{n_A}{n_{Total}}$ and the partial pressure is $P_A = X_A \times P_{Total}$.

For O₂,

$$X_{O_2} = \frac{n_{O_2}}{n_{Total}} = \frac{2.83 \text{ mol}}{(2.83 + 8.41) \text{ mol}} = 0.252$$

$$\text{and } P_{O_2} = X_{O_2} \times P_{Total} = 0.252 \times 192 \text{ kPa} = 48.4 \text{ kPa}$$

For N_2O ,

$$X_{\text{O}_2} = \frac{n_{\text{O}_2}}{n_{\text{Total}}} = \frac{2.83 \text{ mol}}{(2.83 + 8.41) \text{ mol}} = 0.252$$

and

$$P_{\text{O}_2} = X_{\text{O}_2} \times P_{\text{Total}} = (0.252) \times 192 \text{ kPa}$$

$$P_{\text{O}_2} = X_{\text{O}_2} \times P_{\text{Total}} = 0.252 \times 192 \text{ kPa} = 48.4 \text{ kPa}$$

Check Your Learning

What is the pressure of a mixture of 0.200 g of H_2 , 1.00 g of N_2 , and 0.820 g of Ar in a container with a volume of 2.00 L at 20 °C?

Answer: 1.87 atm

Collection of Gases over Water

A simple way to collect gases that do not react with water is to capture them in a bottle that has been filled with water and inverted into a dish filled with water. The pressure of the gas inside the bottle can be made equal to the air pressure outside by raising or lowering the bottle. When the water level is the same both inside and outside the bottle (Figure 9.21), the pressure of the gas is equal to the atmospheric pressure, which can be measured with a barometer.

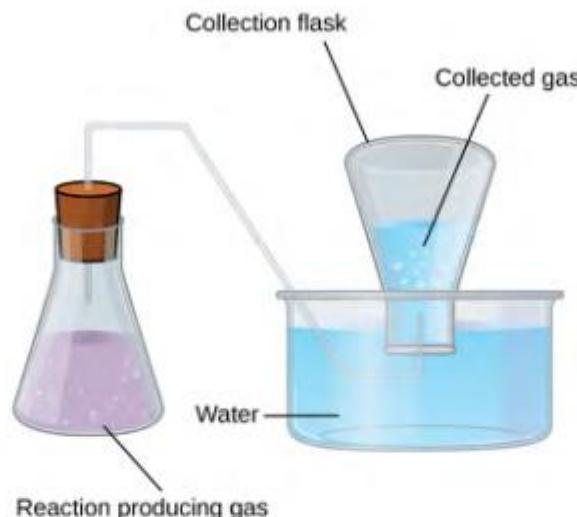


Figure 9.21 When a reaction produces a gas that is collected above water, the trapped gas is a mixture of the gas produced by the reaction and water vapor. If the collection flask is appropriately positioned to equalize the water levels both within and outside the flask, the pressure of the trapped gas mixture will equal the atmospheric pressure outside the flask (see the earlier discussion of manometers).

However, there is another factor we must consider when we measure the pressure of the gas by this method. Water evaporates and there is always gaseous water (water vapor) above a sample of liquid water. As a gas is collected over water, it becomes saturated with water vapor and the total pressure of the mixture equals the partial pressure of the gas plus the partial pressure of the water vapor. The pressure of the pure gas is therefore equal to the total pressure minus the pressure of the water vapor—this is referred to as the “dry” gas pressure, that is, the pressure of the gas only, without water vapor. The **vapor pressure of water**, which is the pressure exerted by water vapor in equilibrium with liquid water in a closed container, depends on the temperature (Figure 9.22); more detailed information on the

temperature dependence of water vapor can be found in **Table 9.2**, and vapor pressure will be discussed in more detail in the next chapter on liquids.

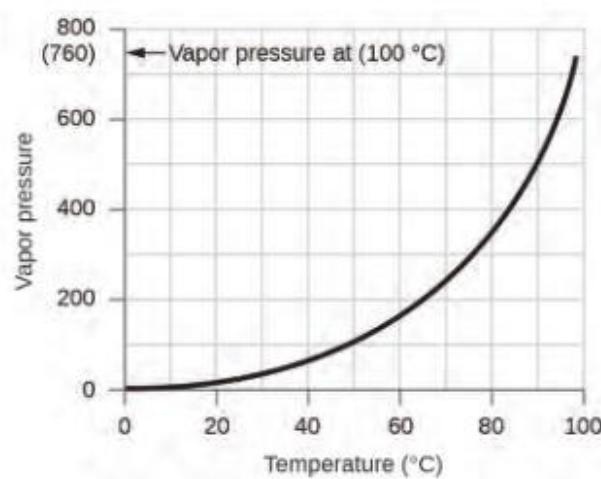


Figure 9.22 This graph shows the vapor pressure of water at sea level as a function of temperature.

Vapor Pressure of Ice and Water in Various Temperatures at Sea Level

Temperature (°C)	Pressure (torr)	Temperature (°C)	Pressure (torr)	Temperature (°C)	Pressure (torr)
-10	1.95	18	15.5	30	31.8
-5	3.0	19	16.5	35	42.2
-2	3.9	20	17.5	40	55.3
0	4.6	21	18.7	50	92.5
2	5.3	22	19.8	60	149.4
4	6.1	23	21.1	70	233.7
6	7.0	24	22.4	80	355.1
8	8.0	25	23.8	90	525.8
10	9.2	26	25.2	95	633.9
12	10.5	27	26.7	99	733.2
14	12.0	28	28.3	100.0	760.0
16	13.6	29	30.0	101.0	787.6

Table 9.2

Example 9.16

Pressure of a Gas Collected Over Water

If 0.200 L of argon is collected over water at a temperature of 26 °C and a pressure of 750 torr in a system like that shown in [Figure 9.21](#), what is the partial pressure of argon?

Solution

According to Dalton's law, the total pressure in the bottle (750 torr) is the sum of the partial pressure of argon and the partial pressure of gaseous water:

$$P_T = P_{\text{Ar}} + P_{\text{H}_2\text{O}}$$

Rearranging this equation to solve for the pressure of argon gives:

$$P_{\text{Ar}} = P_T - P_{\text{H}_2\text{O}}$$

The pressure of water vapor above a sample of liquid water at 26 °C is 25.2 torr ([Appendix E](#)), so:

$$P_{\text{Ar}} = 750 \text{ torr} - 25.2 \text{ torr} = 725 \text{ torr}$$

Check Your Learning

A sample of oxygen collected over water at a temperature of 29.0 °C and a pressure of 764 torr has a volume of 0.560 L. What volume would the dry oxygen have under the same conditions of temperature and pressure?

Answer: 734 torr

Chemical Stoichiometry and Gases

Chemical stoichiometry describes the quantitative relationships between reactants and products in chemical reactions.

We have previously measured quantities of reactants and products using masses for solids and volumes in conjunction with the molarity for solutions; now we can also use gas volumes to indicate quantities. If we know the volume, pressure, and temperature of a gas, we can use the ideal gas equation to calculate how many moles of the gas are present. If we know how many moles of a gas are involved, we can calculate the volume of a gas at any temperature and pressure.

Avogadro's Law Revisited

Sometimes we can take advantage of a simplifying feature of the stoichiometry of gases that solids and solutions do not exhibit: All gases that show ideal behavior contain the same number of molecules in the same volume (at the same temperature and pressure). Thus, the ratios of volumes of gases involved in a chemical reaction are given by the coefficients in the equation for the reaction, provided that the gas volumes are measured at the same temperature and pressure.

We can extend Avogadro's law (that the volume of a gas is directly proportional to the number of moles of the gas) to chemical reactions with gases: Gases combine, or react, in definite and simple proportions by volume, provided that all gas volumes are measured at the same temperature and pressure. For example, since nitrogen and hydrogen gases react to produce ammonia gas according to $\text{N}_2(g) + 3\text{H}_2(g) \longrightarrow 2\text{NH}_3(g)$, a given volume of nitrogen gas reacts with three times that volume of hydrogen gas to produce two times that volume of ammonia gas, if pressure and temperature remain constant.

The explanation for this is illustrated in [Figure 9.23](#). According to Avogadro's law, equal volumes of gaseous N_2 , H_2 , and NH_3 , at the same temperature and pressure, contain the same number of molecules. Because one molecule of N_2 reacts with three molecules of H_2 to produce two molecules of NH_3 , the volume of H_2 required is three times the volume of N_2 , and the volume of NH_3 produced is two times the volume of N_2 .

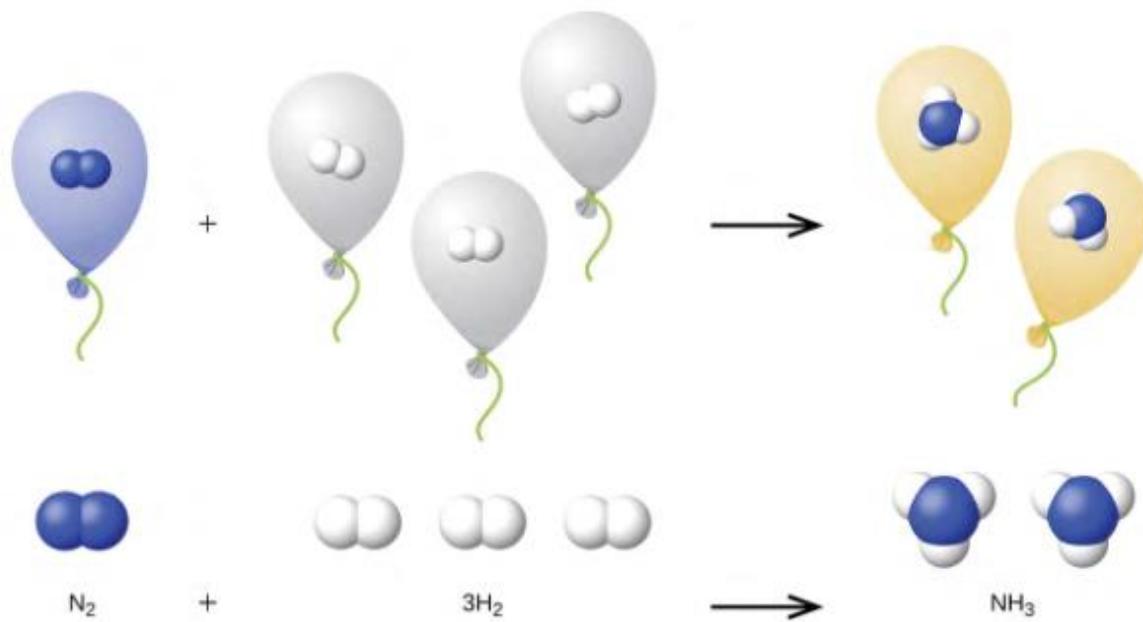


Figure 9.23 One volume of N_2 combines with three volumes of H_2 to form two volumes of NH_3 .

Example 9.17

Reaction of Gases

Propane, $\text{C}_3\text{H}_8(g)$, is used in gas grills to provide the heat for cooking. What volume of $\text{O}_2(g)$ measured at 25°C and 760 torr is required to react with 2.7 L of propane measured under the same conditions of temperature and pressure? Assume that the propane undergoes complete combustion.

Solution

The ratio of the volumes of C_3H_8 and O_2 will be equal to the ratio of their coefficients in the balanced equation for the reaction:



From the equation, we see that one volume of C_3H_8 will react with five volumes of O_2 :

$$2.7 \text{ L C}_3\text{H}_8 \times \frac{5 \text{ L O}_2}{1 \text{ L C}_3\text{H}_8} = 13.5 \text{ L O}_2$$

A volume of 13.5 L of O_2 will be required to react with 2.7 L of C_3H_8 .

Check Your Learning

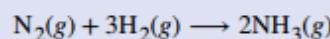
An acetylene tank for an oxyacetylene welding torch provides 9340 L of acetylene gas, C_2H_2 , at 0°C and 1 atm. How many tanks of oxygen, each providing 7.00×10^3 L of O_2 at 0°C and 1 atm, will be required to burn the acetylene?



Answer: 3.34 tanks (2.34×10^4 L)

Example 9.18**Volumes of Reacting Gases**

Ammonia is an important fertilizer and industrial chemical. Suppose that a volume of 683 billion cubic feet of gaseous ammonia, measured at 25 °C and 1 atm, was manufactured. What volume of H₂(g), measured under the same conditions, was required to prepare this amount of ammonia by reaction with N₂?

**Solution**

Because equal volumes of H₂ and NH₃ contain equal numbers of molecules and each three molecules of H₂ that react produce two molecules of NH₃, the ratio of the volumes of H₂ and NH₃ will be equal to 3:2. Two volumes of NH₃, in this case in units of billion ft³, will be formed from three volumes of H₂:

$$683 \frac{\text{billion ft}^3}{\text{NH}_3} \times \frac{3 \text{ billion ft}^3 \text{ H}_2}{2 \text{ billion ft}^3 \text{ NH}_3} = 1.02 \times 10^3 \text{ billion ft}^3 \text{ H}_2$$

The manufacture of 683 billion ft³ of NH₃ required 1020 billion ft³ of H₂. (At 25 °C and 1 atm, this is the volume of a cube with an edge length of approximately 1.9 miles.)

Check Your Learning

What volume of O₂(g) measured at 25 °C and 760 torr is required to react with 17.0 L of ethylene, C₂H₄(g), measured under the same conditions of temperature and pressure? The products are CO₂ and water vapor.

Answer: 51.0 L

Example 9.19**Volume of Gaseous Product**

What volume of hydrogen at 27 °C and 723 torr may be prepared by the reaction of 8.88 g of gallium with an excess of hydrochloric acid?

**Solution**

To convert from the mass of gallium to the volume of H₂(g), we need to do something like this:



The first two conversions are:

$$8.88 \frac{\text{g Ga}}{} \times \frac{1 \text{ mol Ga}}{69.723 \text{ g Ga}} \times \frac{3 \text{ mol H}_2}{2 \text{ mol Ga}} = 0.191 \text{ mol H}_2$$

Finally, we can use the ideal gas law:

$$V_{\text{H}_2} = \left(\frac{nRT}{P}\right)_{\text{H}_2} = \frac{0.191 \text{ mol} \times 0.08206 \text{ L atm mol}^{-1} \text{ K}^{-1} \times 300 \text{ K}}{0.951 \text{ atm}} = 4.94 \text{ L}$$

Check Your Learning

Sulfur dioxide is an intermediate in the preparation of sulfuric acid. What volume of SO_2 at $343\text{ }^{\circ}\text{C}$ and 1.21 atm is produced by burning 1.00 kg of sulfur in oxygen?

Answer: $1.30 \times 10^3\text{ L}$

How Sciences Interconnect

Greenhouse Gases and Climate Change

The thin skin of our atmosphere keeps the earth from being an ice planet and makes it habitable. In fact, this is due to less than 0.5% of the air molecules. Of the energy from the sun that reaches the earth, almost $\frac{1}{3}$ is reflected back into space, with the rest absorbed by the atmosphere and the surface of the earth. Some of the energy that the earth absorbs is re-emitted as infrared (IR) radiation, a portion of which passes back out through the atmosphere into space. However, most of this IR radiation is absorbed by certain substances in the atmosphere, known as greenhouse gases, which re-emit this energy in all directions, trapping some of the heat. This maintains favorable living conditions—without atmosphere, the average global average temperature of $14\text{ }^{\circ}\text{C}$ ($57\text{ }^{\circ}\text{F}$) would be about $-19\text{ }^{\circ}\text{C}$ ($-2\text{ }^{\circ}\text{F}$). The major greenhouse gases (GHGs) are water vapor, carbon dioxide, methane, and ozone. Since the Industrial Revolution, human activity has been increasing the concentrations of GHGs, which have changed the energy balance and are significantly altering the earth's climate (Figure 9.24).

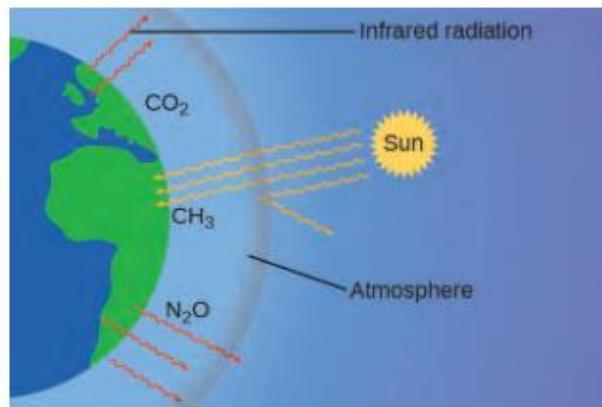


Figure 9.24 Greenhouse gases trap enough of the sun's energy to make the planet habitable—this is known as the greenhouse effect. Human activities are increasing greenhouse gas levels, warming the planet and causing more extreme weather events.

There is strong evidence from multiple sources that higher atmospheric levels of CO_2 are caused by human activity, with fossil fuel burning accounting for about $\frac{3}{4}$ of the recent increase in CO_2 . Reliable data from ice cores reveals that CO_2 concentration in the atmosphere is at the highest level in the past 800,000 years; other evidence indicates that it may be at its highest level in 20 million years. In recent years, the CO_2 concentration has increased from historical levels of below 300 ppm to almost 400 ppm today (Figure 9.25).

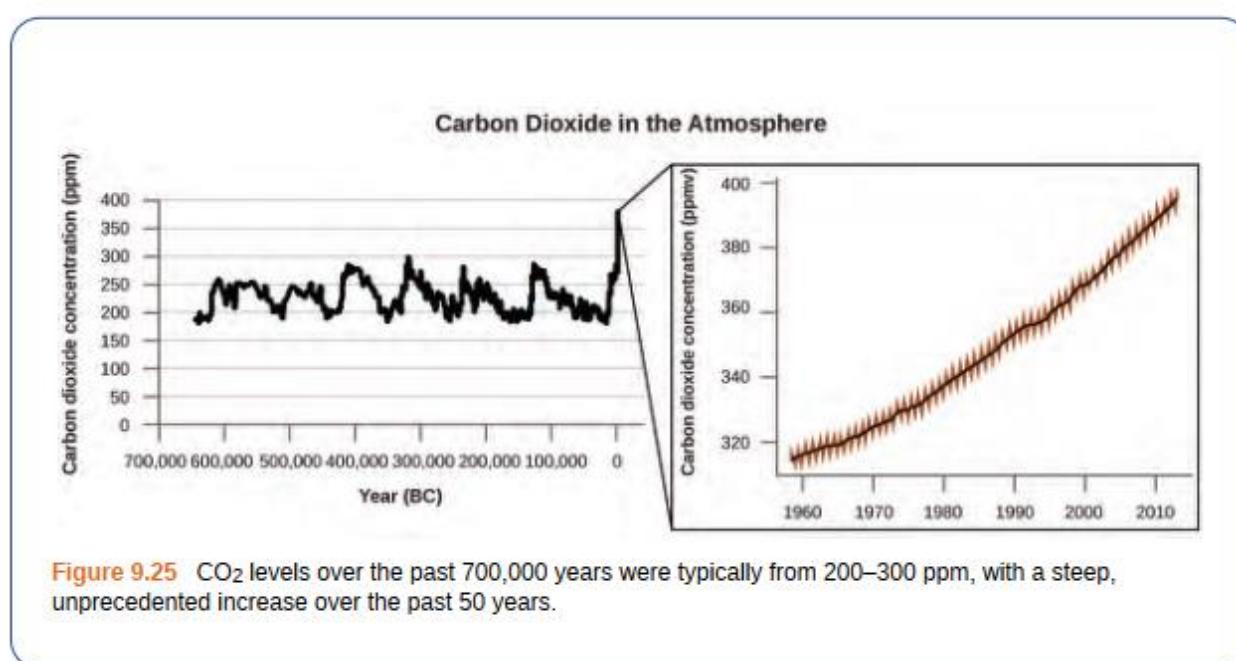


Figure 9.25 CO₂ levels over the past 700,000 years were typically from 200–300 ppm, with a steep, unprecedented increase over the past 50 years.

Portrait of a Chemist

Susan Solomon

Atmospheric and climate scientist Susan Solomon (Figure 9.26) is the author of one of *The New York Times* books of the year (*The Coldest March*, 2001), one of Time magazine's 100 most influential people in the world (2008), and a working group leader of the Intergovernmental Panel on Climate Change (IPCC), which was the recipient of the 2007 Nobel Peace Prize. She helped determine and explain the cause of the formation of the ozone hole over Antarctica, and has authored many important papers on climate change. She has been awarded the top scientific honors in the US and France (the National Medal of Science and the Grande Médaille, respectively), and is a member of the National Academy of Sciences, the Royal Society, the French Academy of Sciences, and the European Academy of Sciences. Formerly a professor at the University of Colorado, she is now at MIT, and continues to work at NOAA.

For more information, watch this video (<http://openstaxcollege.org/l/16SusanSolomon>) about Susan Solomon.



Figure 9.26 Susan Solomon's research focuses on climate change and has been instrumental in determining the cause of the ozone hole over Antarctica. (credit: National Oceanic and Atmospheric Administration)

9.4 Effusion and Diffusion of Gases

By the end of this section, you will be able to:

- Define and explain effusion and diffusion
- State Graham's law and use it to compute relevant gas properties

If you have ever been in a room when a piping hot pizza was delivered, you have been made aware of the fact that gaseous molecules can quickly spread throughout a room, as evidenced by the pleasant aroma that soon reaches your nose. Although gaseous molecules travel at tremendous speeds (hundreds of meters per second), they collide with other gaseous molecules and travel in many different directions before reaching the desired target. At room temperature, a gaseous molecule will experience billions of collisions per second. The **mean free path** is the average distance a molecule travels between collisions. The mean free path increases with decreasing pressure; in general, the mean free path for a gaseous molecule will be hundreds of times the diameter of the molecule.

In general, we know that when a sample of gas is introduced to one part of a closed container, its molecules very quickly disperse throughout the container; this process by which molecules disperse in space in response to differences in concentration is called **diffusion** (shown in **Figure 9.27**). The gaseous atoms or molecules are, of course, unaware of any concentration gradient, they simply move randomly—regions of higher concentration have more particles than regions of lower concentrations, and so a net movement of species from high to low concentration areas takes place. In a closed environment, diffusion will ultimately result in equal concentrations of gas throughout, as depicted in **Figure 9.27**. The gaseous atoms and molecules continue to move, but since their concentrations are the same in both bulbs, the rates of transfer between the bulbs are equal (no net transfer of molecules occurs).

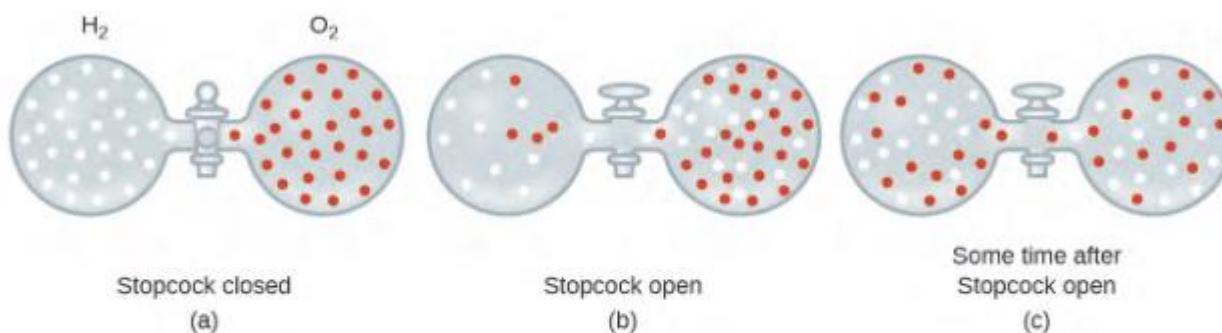


Figure 9.27 (a) Two gases, H_2 and O_2 , are initially separated. (b) When the stopcock is opened, they mix together. The lighter gas, H_2 , passes through the opening faster than O_2 , so just after the stopcock is opened, more H_2 molecules move to the O_2 side than O_2 molecules move to the H_2 side. (c) After a short time, both the slower-moving O_2 molecules and the faster-moving H_2 molecules have distributed themselves evenly on both sides of the vessel.

We are often interested in the **rate of diffusion**, the amount of gas passing through some area per unit time:

$$\text{rate of diffusion} = \frac{\text{amount of gas passing through an area}}{\text{unit of time}}$$

The diffusion rate depends on several factors: the concentration gradient (the increase or decrease in concentration from one point to another); the amount of surface area available for diffusion; and the distance the gas particles must travel. Note also that the time required for diffusion to occur is inversely proportional to the rate of diffusion, as shown in the rate of diffusion equation.

A process involving movement of gaseous species similar to diffusion is **effusion**, the escape of gas molecules through a tiny hole such as a pinhole in a balloon into a vacuum (Figure 9.28). Although diffusion and effusion rates both depend on the molar mass of the gas involved, their rates are not equal; however, the ratios of their rates are the same.

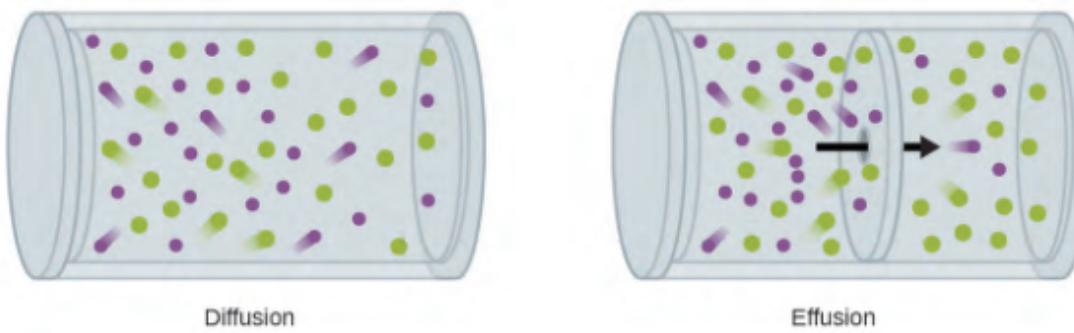


Figure 9.28 Diffusion occurs when gas molecules disperse throughout a container. Effusion occurs when a gas passes through an opening that is smaller than the mean free path of the particles, that is, the average distance traveled between collisions. Effectively, this means that only one particle passes through at a time.

If a mixture of gases is placed in a container with porous walls, the gases effuse through the small openings in the walls. The lighter gases pass through the small openings more rapidly (at a higher rate) than the heavier ones (Figure 9.29). In 1832, Thomas Graham studied the rates of effusion of different gases and formulated **Graham's law of effusion**: *The rate of effusion of a gas is inversely proportional to the square root of the mass of its particles*:

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

This means that if two gases A and B are at the same temperature and pressure, the ratio of their effusion rates is inversely proportional to the ratio of the square roots of the masses of their particles:

$$\frac{\text{rate of effusion of } A}{\text{rate of effusion of } B} = \frac{\sqrt{M_B}}{\sqrt{M_A}}$$

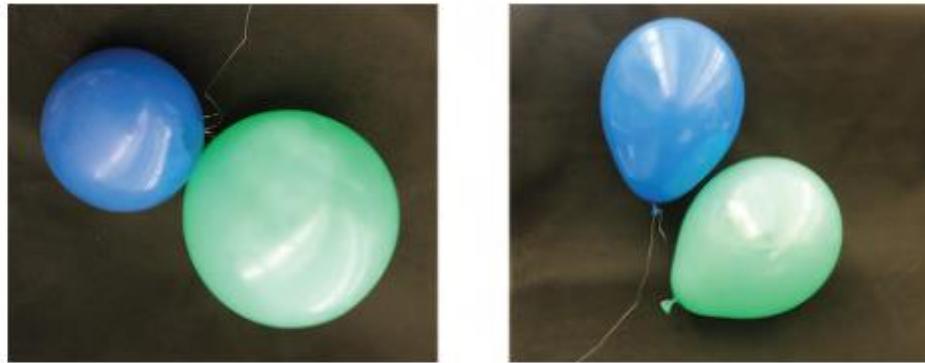


Figure 9.29 A balloon filled with air (the blue one) remains full overnight. A balloon filled with helium (the green one) partially deflates because the smaller, light helium atoms effuse through small holes in the rubber much more readily than the heavier molecules of nitrogen and oxygen found in air. (credit: modification of work by Mark Ott)

Example 9.20

Applying Graham's Law to Rates of Effusion

Calculate the ratio of the rate of effusion of hydrogen to the rate of effusion of oxygen.

Solution

From Graham's law, we have:

$$\frac{\text{rate of effusion of hydrogen}}{\text{rate of effusion of oxygen}} = \frac{\sqrt{1.43 \text{ g L}^{-1}}}{\sqrt{0.0899 \text{ g L}^{-1}}} = \frac{1.20}{0.300} = \frac{4}{1}$$

Using molar masses:

$$\frac{\text{rate of effusion of hydrogen}}{\text{rate of effusion of oxygen}} = \frac{\sqrt{32 \text{ g mol}^{-1}}}{\sqrt{2 \text{ g mol}^{-1}}} = \frac{\sqrt{16}}{\sqrt{1}} = \frac{4}{1}$$

Hydrogen effuses four times as rapidly as oxygen.

Check Your Learning

At a particular pressure and temperature, nitrogen gas effuses at the rate of 79 mL/s. Using the same apparatus at the same temperature and pressure, at what rate will sulfur dioxide effuse?

Answer: 52 mL/s

Here's another example, making the point about how determining times differs from determining rates.

Example 9.21

Effusion Time Calculations

It takes 243 s for 4.46×10^{-5} mol Xe to effuse through a tiny hole. Under the same conditions, how long will it take 4.46×10^{-5} mol Ne to effuse?

Solution

It is important to resist the temptation to use the times directly, and to remember how rate relates to time as well as how it relates to mass. Recall the definition of rate of effusion:

$$\text{rate of effusion} = \frac{\text{amount of gas transferred}}{\text{time}}$$

and combine it with Graham's law:

$$\frac{\text{rate of effusion of Xe}}{\text{rate of effusion of Ne}} = \frac{\sqrt{M_{Ne}}}{\sqrt{M_{Xe}}}$$

To get:

$$\frac{\frac{\text{amount of Xe transferred}}{\text{time for Xe}}}{\frac{\text{amount of Ne transferred}}{\text{time for Ne}}} = \frac{\sqrt{M_{Ne}}}{\sqrt{M_{Xe}}}$$

Noting that *amount of A* = *amount of B*, and solving for *time for Ne*:

$$\frac{\frac{\text{amount of Xe}}{\text{time for Xe}}}{\frac{\text{amount of Ne}}{\text{time for Ne}}} = \frac{\text{time for Ne}}{\text{time for Xe}} = \frac{\sqrt{M_{Ne}}}{\sqrt{M_{Xe}}} = \frac{\sqrt{M_{Ne}}}{\sqrt{M_{Xe}}}$$

and substitute values:

$$\frac{\text{time for Ne}}{243 \text{ s}} = \sqrt{\frac{20.2 \text{ g/mol}}{131.3 \text{ g/mol}}} = 0.392$$

Finally, solve for the desired quantity:

$$\text{time for Ne} = 0.392 \times 243 \text{ s} = 95.3 \text{ s}$$

Note that this answer is reasonable: Since Ne is lighter than Xe, the effusion rate for Ne will be larger than that for Xe, which means the time of effusion for Ne will be smaller than that for Xe.

Check Your Learning

A party balloon filled with helium deflates to $\frac{2}{3}$ of its original volume in 8.0 hours. How long will it take an identical balloon filled with the same number of moles of air ($M = 28.2 \text{ g/mol}$) to deflate to $\frac{1}{2}$ of its original volume?

Answer: 32 h

Finally, here is one more example showing how to calculate molar mass from effusion rate data.

Example 9.22

Determining Molar Mass Using Graham's Law

An unknown gas effuses 1.66 times more rapidly than CO₂. What is the molar mass of the unknown gas? Can you make a reasonable guess as to its identity?

Solution

From Graham's law, we have:

$$\frac{\text{rate of effusion of unknown}}{\text{rate of effusion of O}_2} = \frac{\sqrt{M_{CO_2}}}{\sqrt{M_{Unknown}}}$$

Plug in known data:

$$\frac{1.66}{1} = \frac{\sqrt{44.0 \text{ g/mol}}}{\sqrt{M_{Unknown}}}$$

Solve:

$$M_{Unknown} = \frac{44.0 \text{ g/mol}}{(1.66)^2} = 16.0 \text{ g/mol}$$

The gas could well be CH₄, the only gas with this molar mass.

Check Your Learning

Hydrogen gas effuses through a porous container 8.97-times faster than an unknown gas. Estimate the molar mass of the unknown gas.

Answer: 163 g/mol

How Sciences Interconnect

Use of Diffusion for Nuclear Energy Applications: Uranium Enrichment

Gaseous diffusion has been used to produce enriched uranium for use in nuclear power plants and weapons. Naturally occurring uranium contains only 0.72% of ²³⁵U, the kind of uranium that is "fissile," that is, capable of sustaining a nuclear fission chain reaction. Nuclear reactors require fuel that is 2–5% ²³⁵U, and nuclear bombs need even higher concentrations. One way to enrich uranium to the desired levels is to take advantage of Graham's law. In a gaseous diffusion enrichment plant, uranium hexafluoride (UF₆, the only uranium compound that is volatile enough to work) is slowly pumped through large cylindrical vessels called diffusers, which contain porous barriers with microscopic openings. The process is one of diffusion because the other side of the barrier is not evacuated. The ²³⁵UF₆ molecules have a higher average speed and diffuse through the barrier a little faster than the heavier ²³⁸UF₆ molecules. The gas that has passed through the barrier is slightly enriched in ²³⁵UF₆ and the residual gas is slightly depleted. The small difference in molecular weights between ²³⁵UF₆ and ²³⁸UF₆ only about 0.4% enrichment, is achieved in one diffuser (Figure 9.30). But by connecting many diffusers in a sequence of stages (called a cascade), the desired level of enrichment can be attained.

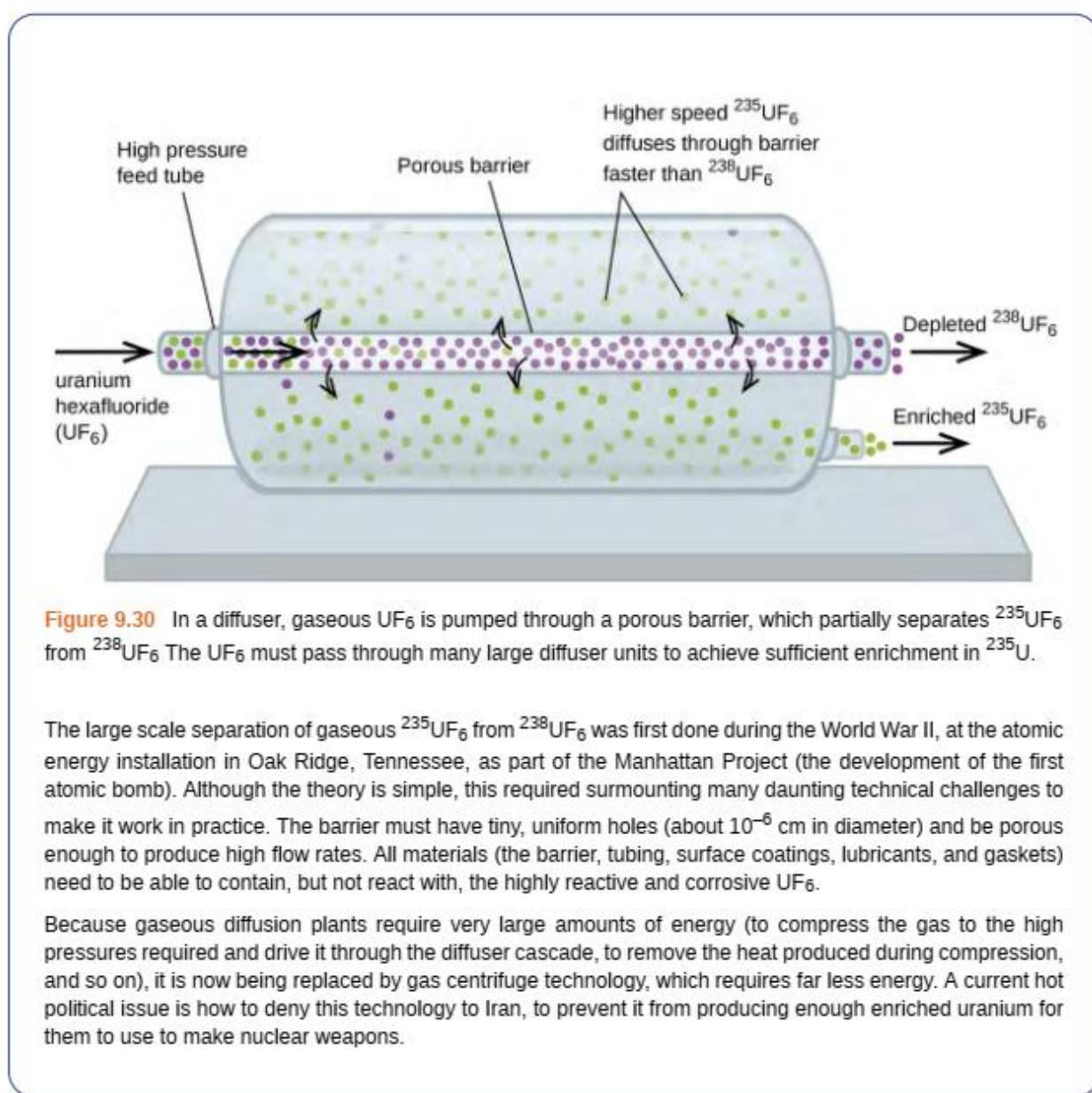


Figure 9.30 In a diffuser, gaseous UF₆ is pumped through a porous barrier, which partially separates ²³⁵UF₆ from ²³⁸UF₆. The UF₆ must pass through many large diffuser units to achieve sufficient enrichment in ²³⁵U.

The large scale separation of gaseous ²³⁵UF₆ from ²³⁸UF₆ was first done during the World War II, at the atomic energy installation in Oak Ridge, Tennessee, as part of the Manhattan Project (the development of the first atomic bomb). Although the theory is simple, this required surmounting many daunting technical challenges to make it work in practice. The barrier must have tiny, uniform holes (about 10^{-6} cm in diameter) and be porous enough to produce high flow rates. All materials (the barrier, tubing, surface coatings, lubricants, and gaskets) need to be able to contain, but not react with, the highly reactive and corrosive UF₆.

Because gaseous diffusion plants require very large amounts of energy (to compress the gas to the high pressures required and drive it through the diffuser cascade, to remove the heat produced during compression, and so on), it is now being replaced by gas centrifuge technology, which requires far less energy. A current hot political issue is how to deny this technology to Iran, to prevent it from producing enough enriched uranium for them to use to make nuclear weapons.

9.5 The Kinetic-Molecular Theory

- State the postulates of the kinetic-molecular theory
- Use this theory's postulates to explain the gas laws

The gas laws that we have seen to this point, as well as the ideal gas equation, are empirical, that is, they have been derived from experimental observations. The mathematical forms of these laws closely describe the macroscopic behavior of most gases at pressures less than about 1 or 2 atm. Although the gas laws describe relationships that have been verified by many experiments, they do not tell us why gases follow these relationships.

The **kinetic molecular theory** (KMT) is a simple microscopic model that effectively explains the gas laws described in previous modules of this chapter. This theory is based on the following five postulates described here. (Note: The term "molecule" will be used to refer to the individual chemical species that compose the gas, although some gases are composed of atomic species, for example, the noble gases.)

1. Gases are composed of molecules that are in continuous motion, travelling in straight lines and changing direction only when they collide with other molecules or with the walls of a container.
2. The molecules composing the gas are negligibly small compared to the distances between them.
3. The pressure exerted by a gas in a container results from collisions between the gas molecules and the container walls.
4. Gas molecules exert no attractive or repulsive forces on each other or the container walls; therefore, their collisions are *elastic* (do not involve a loss of energy).
5. The average kinetic energy of the gas molecules is proportional to the kelvin temperature of the gas.

The test of the KMT and its postulates is its ability to explain and describe the behavior of a gas. The various gas laws can be derived from the assumptions of the KMT, which have led chemists to believe that the assumptions of the theory accurately represent the properties of gas molecules. We will first look at the individual gas laws (Boyle's, Charles's, Amontons's, Avogadro's, and Dalton's laws) conceptually to see how the KMT explains them. Then, we will more carefully consider the relationships between molecular masses, speeds, and kinetic energies with temperature, and explain Graham's law.

The Kinetic-Molecular Theory Explains the Behavior of Gases, Part I

Recalling that gas pressure is exerted by rapidly moving gas molecules and depends directly on the number of molecules hitting a unit area of the wall per unit of time, we see that the KMT conceptually explains the behavior of a gas as follows:

- *Amontons's law.* If the temperature is increased, the average speed and kinetic energy of the gas molecules increase. If the volume is held constant, the increased speed of the gas molecules results in more frequent and more forceful collisions with the walls of the container, therefore increasing the pressure ([Figure 9.31](#)).
- *Charles's law.* If the temperature of a gas is increased, a constant pressure may be maintained only if the volume occupied by the gas increases. This will result in greater average distances traveled by the molecules to reach the container walls, as well as increased wall surface area. These conditions will decrease the both the frequency of molecule-wall collisions and the number of collisions per unit area, the combined effects of which outweigh those of increased collision forces due to the greater kinetic energy at the higher temperature. The net result is a decrease in gas pressure.
- *Boyle's law.* If the gas volume is decreased, the container wall area decreases and the molecule-wall collision frequency increases, both of which increase the pressure exerted by the gas ([Figure 9.31](#)).
- *Avogadro's law.* At constant pressure and temperature, the frequency and force of molecule-wall collisions are constant. Under such conditions, increasing the number of gaseous molecules will require a proportional increase in the container volume in order to yield a decrease in the number of collisions per unit area to compensate for the increased frequency of collisions ([Figure 9.31](#)).
- *Dalton's Law.* Because of the large distances between them, the molecules of one gas in a mixture bombard the container walls with the same frequency whether other gases are present or not, and the total pressure of a gas mixture equals the sum of the (partial) pressures of the individual gases.

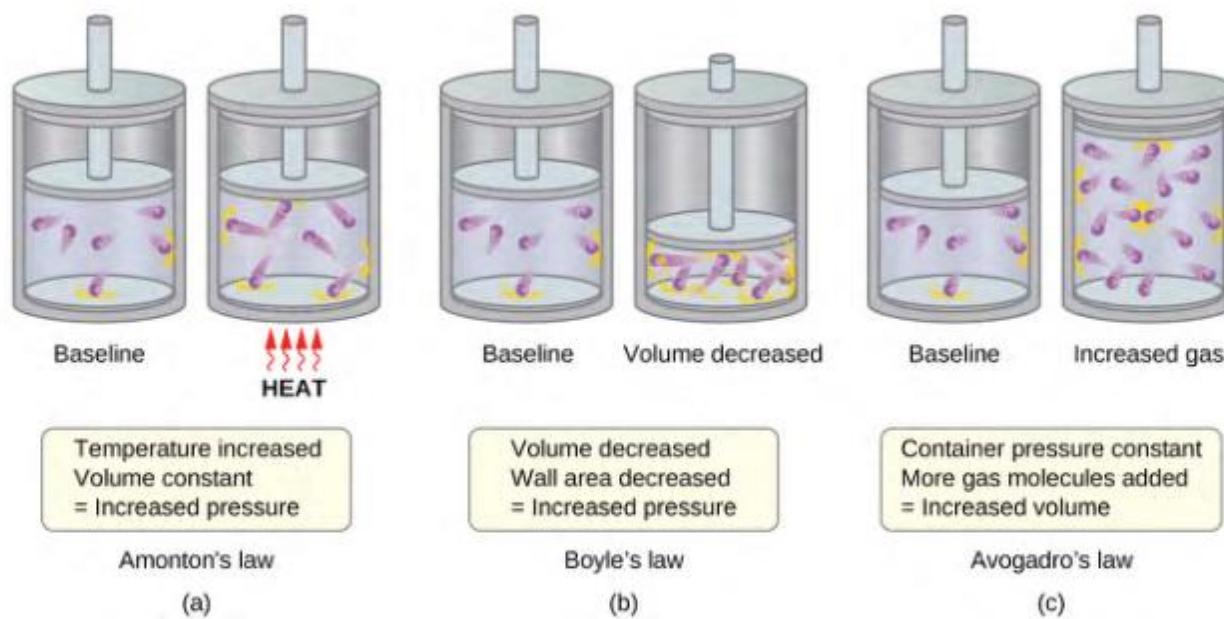


Figure 9.31 (a) When gas temperature increases, gas pressure increases due to increased force and frequency of molecular collisions. (b) When volume decreases, gas pressure increases due to reduced frequency of molecular collisions. (c) When the amount of gas increases at a constant pressure, volume increases to yield a constant number of collisions per unit wall area.

Molecular Velocities and Kinetic Energy

The previous discussion showed that the KMT qualitatively explains the behaviors described by the various gas laws. The postulates of this theory may be applied in a more quantitative fashion to derive these individual laws. To do this, we must first look at velocities and kinetic energies of gas molecules, and the temperature of a gas sample.

In a gas sample, individual molecules have widely varying speeds; however, because of the vast number of molecules and collisions involved, the molecular speed distribution and average speed are constant. This molecular speed distribution is known as a Maxwell-Boltzmann distribution, and it depicts the relative numbers of molecules in a bulk sample of gas that possesses a given speed (**Figure 9.32**).

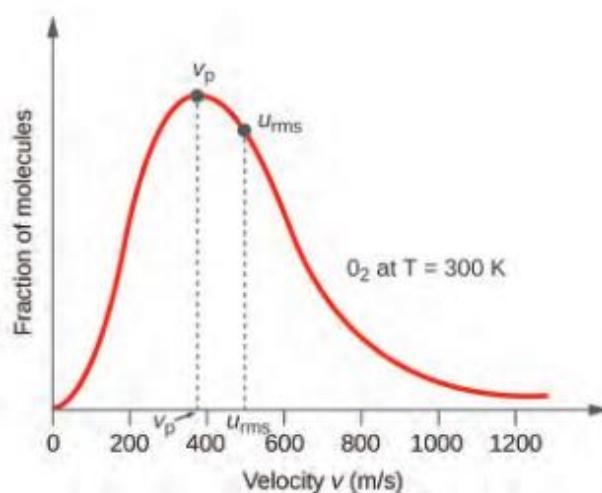


Figure 9.32 The molecular speed distribution for oxygen gas at 300 K is shown here. Very few molecules move at either very low or very high speeds. The number of molecules with intermediate speeds increases rapidly up to a maximum, which is the most probable speed, then drops off rapidly. Note that the most probable speed, v_p , is a little less than 400 m/s, while the root mean square speed, u_{rms} , is closer to 500 m/s.

The kinetic energy (KE) of a particle of mass (m) and speed (u) is given by:

$$KE = \frac{1}{2}mu^2$$

Expressing mass in kilograms and speed in meters per second will yield energy values in units of joules ($J = \text{kg m}^2\text{s}^{-2}$). To deal with a large number of gas molecules, we use averages for both speed and kinetic energy. In the KMT, the **root mean square velocity** of a particle, u_{rms} , is defined as the square root of the average of the squares of the velocities with n = the number of particles:

$$u_{rms} = \sqrt{\bar{u^2}} = \sqrt{\frac{u_1^2 + u_2^2 + u_3^2 + u_4^2 + \dots}{n}}$$

The average kinetic energy, KE_{avg} , is then equal to:

$$KE_{avg} = \frac{1}{2}mu_{rms}^2$$

The KE_{avg} of a collection of gas molecules is also directly proportional to the temperature of the gas and may be described by the equation:

$$KE_{avg} = \frac{3}{2}RT$$

where R is the gas constant and T is the kelvin temperature. When used in this equation, the appropriate form of the gas constant is 8.314 J/K (8.314 $\text{kg m}^2\text{s}^{-2}\text{K}^{-1}$). These two separate equations for KE_{avg} may be combined and rearranged to yield a relation between molecular speed and temperature:

$$\begin{aligned} \frac{1}{2}mu_{rms}^2 &= \frac{3}{2}RT \\ u_{rms} &= \sqrt{\frac{3RT}{m}} \end{aligned}$$

Example 9.23

Calculation of u_{rms}

Calculate the root-mean-square velocity for a nitrogen molecule at 30 °C.

Solution

Convert the temperature into Kelvin:

$$30 \text{ }^{\circ}\text{C} + 273 = 303 \text{ K}$$

Determine the mass of a nitrogen molecule in kilograms:

$$\frac{28.0 \text{ g}}{1 \text{ mol}} \times \frac{1 \text{ kg}}{1000 \text{ g}} = 0.028 \text{ kg/mol}$$

Replace the variables and constants in the root-mean-square velocity equation, replacing Joules with the equivalent $\text{kg m}^2 \text{s}^{-2}$:

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

$$u_{\text{rms}} = \sqrt{\frac{3(8.314 \text{ J/mol K})(303 \text{ K})}{(0.028 \text{ kg/mol})}} = \sqrt{2.70 \times 10^5 \text{ m}^2 \text{ s}^{-2}} = 519 \text{ m/s}$$

Check Your Learning

Calculate the root-mean-square velocity for an oxygen molecule at -23 °C.

Answer: 441 m/s

If the temperature of a gas increases, its KE_{avg} increases, more molecules have higher speeds and fewer molecules have lower speeds, and the distribution shifts toward higher speeds overall, that is, to the right. If temperature decreases, KE_{avg} decreases, more molecules have lower speeds and fewer molecules have higher speeds, and the distribution shifts toward lower speeds overall, that is, to the left. This behavior is illustrated for nitrogen gas in **Figure 9.33**.

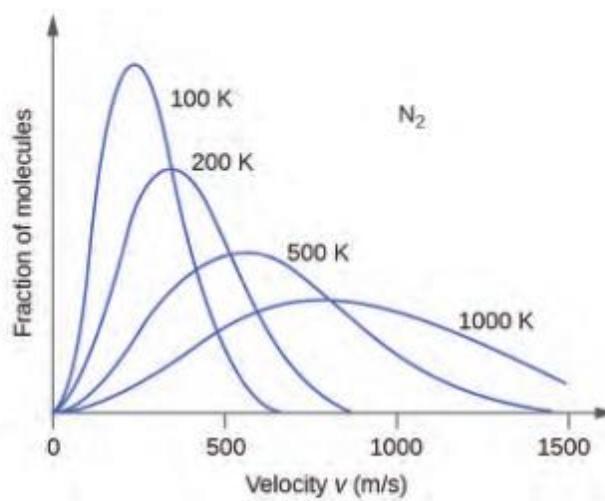


Figure 9.33 The molecular speed distribution for nitrogen gas (N₂) shifts to the right and flattens as the temperature increases; it shifts to the left and heightens as the temperature decreases.

At a given temperature, all gases have the same KE_{avg} for their molecules. Gases composed of lighter molecules have more high-speed particles and a higher u_{rms} , with a speed distribution that peaks at relatively higher velocities. Gases

consisting of heavier molecules have more low-speed particles, a lower u_{rms} , and a speed distribution that peaks at relatively lower velocities. This trend is demonstrated by the data for a series of noble gases shown in [Figure 9.34](#).

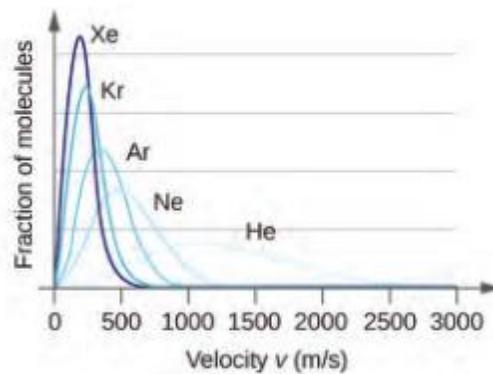


Figure 9.34 Molecular velocity is directly related to molecular mass. At a given temperature, lighter molecules move faster on average than heavier molecules.

The Kinetic-Molecular Theory Explains the Behavior of Gases, Part II

According to Graham's law, the molecules of a gas are in rapid motion and the molecules themselves are small. The average distance between the molecules of a gas is large compared to the size of the molecules. As a consequence, gas molecules can move past each other easily and diffuse at relatively fast rates.

The rate of effusion of a gas depends directly on the (average) speed of its molecules:

$$\text{effusion rate} \propto u_{\text{rms}}$$

Using this relation, and the equation relating molecular speed to mass, Graham's law may be easily derived as shown here:

$$\begin{aligned} u_{\text{rms}} &= \sqrt{\frac{3RT}{m}} \\ m &= \frac{3RT}{u_{\text{rms}}^2} = \frac{3RT}{u^2} \\ \frac{\text{effusion rate A}}{\text{effusion rate B}} &= \frac{u_{\text{rms A}}}{u_{\text{rms B}}} = \frac{\sqrt{\frac{3RT}{m_A}}}{\sqrt{\frac{3RT}{m_B}}} = \sqrt{\frac{m_B}{m_A}} \end{aligned}$$

The ratio of the rates of effusion is thus derived to be inversely proportional to the ratio of the square roots of their masses. This is the same relation observed experimentally and expressed as Graham's law.

9.6 Non-Ideal Gas Behavior

By the end of this section, you will be able to:

- Describe the physical factors that lead to deviations from ideal gas behavior
- Explain how these factors are represented in the van der Waals equation
- Define compressibility (Z) and describe how its variation with pressure reflects non-ideal behavior
- Quantify non-ideal behavior by comparing computations of gas properties using the ideal gas law and the van der Waals equation

Thus far, the ideal gas law, $PV = nRT$, has been applied to a variety of different types of problems, ranging from reaction stoichiometry and empirical and molecular formula problems to determining the density and molar mass of a gas. As mentioned in the previous modules of this chapter, however, the behavior of a gas is often non-ideal, meaning that the observed relationships between its pressure, volume, and temperature are not accurately described by the gas laws. In this section, the reasons for these deviations from ideal gas behavior are considered.

One way in which the accuracy of $PV = nRT$ can be judged is by comparing the actual volume of 1 mole of gas (its molar volume, V_m) to the molar volume of an ideal gas at the same temperature and pressure. This ratio is called the **compressibility factor (Z)** with:

$$Z = \frac{\text{molar volume of gas at same } T \text{ and } P}{\text{molar volume of ideal gas at same } T \text{ and } P} = \left(\frac{PV_m}{RT} \right)_{\text{measured}}$$

Ideal gas behavior is therefore indicated when this ratio is equal to 1, and any deviation from 1 is an indication of non-ideal behavior. **Figure 9.35** shows plots of Z over a large pressure range for several common gases.

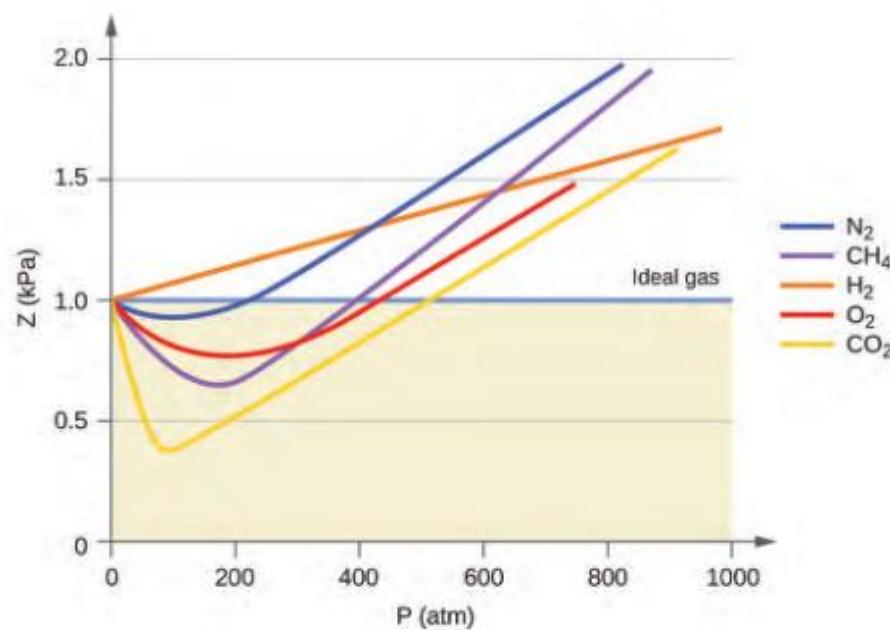


Figure 9.35 A graph of the compressibility factor (Z) vs. pressure shows that gases can exhibit significant deviations from the behavior predicted by the ideal gas law.

As is apparent from **Figure 9.35**, the ideal gas law does not describe gas behavior well at relatively high pressures. To determine why this is, consider the differences between real gas properties and what is expected of a hypothetical ideal gas.

Particles of a hypothetical ideal gas have no significant volume and do not attract or repel each other. In general, real gases approximate this behavior at relatively low pressures and high temperatures. However, at high pressures, the molecules of a gas are crowded closer together, and the amount of empty space between the molecules is reduced. At these higher pressures, the volume of the gas molecules themselves becomes appreciable relative to the total volume occupied by the gas (Figure 9.36). The gas therefore becomes less compressible at these high pressures, and although its volume continues to decrease with increasing pressure, this decrease is not *proportional* as predicted by Boyle's law.

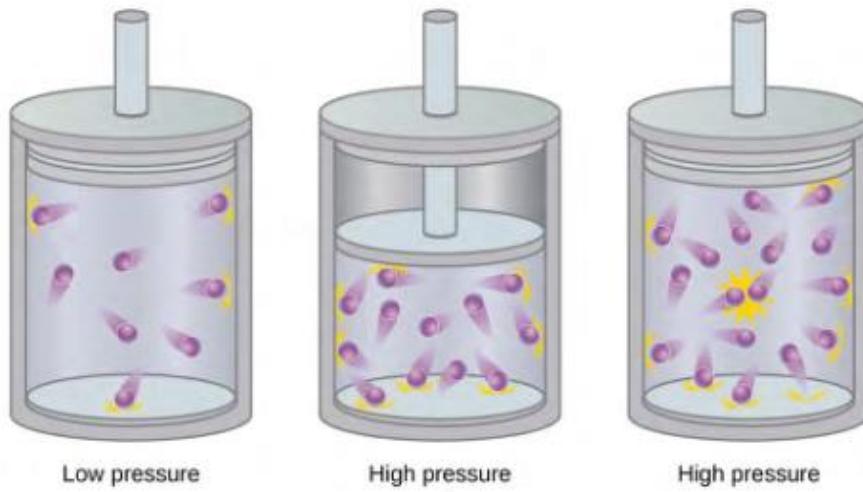


Figure 9.36 Raising the pressure of a gas increases the fraction of its volume that is occupied by the gas molecules and makes the gas less compressible.

At relatively low pressures, gas molecules have practically no attraction for one another because they are (on average) so far apart, and they behave almost like particles of an ideal gas. At higher pressures, however, the force of attraction is also no longer insignificant. This force pulls the molecules a little closer together, slightly decreasing the pressure (if the volume is constant) or decreasing the volume (at constant pressure) (Figure 9.37). This change is more pronounced at low temperatures because the molecules have lower KE relative to the attractive forces, and so they are less effective in overcoming these attractions after colliding with one another.

Particles of a hypothetical ideal gas have no significant volume and do not attract or repel each other. In general, real gases approximate this behavior at relatively low pressures and high temperatures. However, at high pressures, the molecules of a gas are crowded closer together, and the amount of empty space between the molecules is reduced. At these higher pressures, the volume of the gas molecules themselves becomes appreciable relative to the total volume occupied by the gas (Figure 9.36). The gas therefore becomes less compressible at these high pressures, and although its volume continues to decrease with increasing pressure, this decrease is not *proportional* as predicted by Boyle's law.

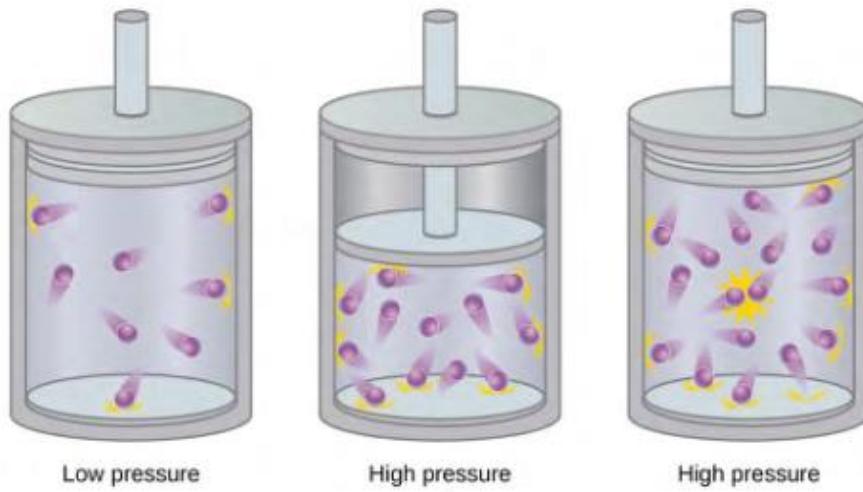


Figure 9.36 Raising the pressure of a gas increases the fraction of its volume that is occupied by the gas molecules and makes the gas less compressible.

At relatively low pressures, gas molecules have practically no attraction for one another because they are (on average) so far apart, and they behave almost like particles of an ideal gas. At higher pressures, however, the force of attraction is also no longer insignificant. This force pulls the molecules a little closer together, slightly decreasing the pressure (if the volume is constant) or decreasing the volume (at constant pressure) (Figure 9.37). This change is more pronounced at low temperatures because the molecules have lower KE relative to the attractive forces, and so they are less effective in overcoming these attractions after colliding with one another.

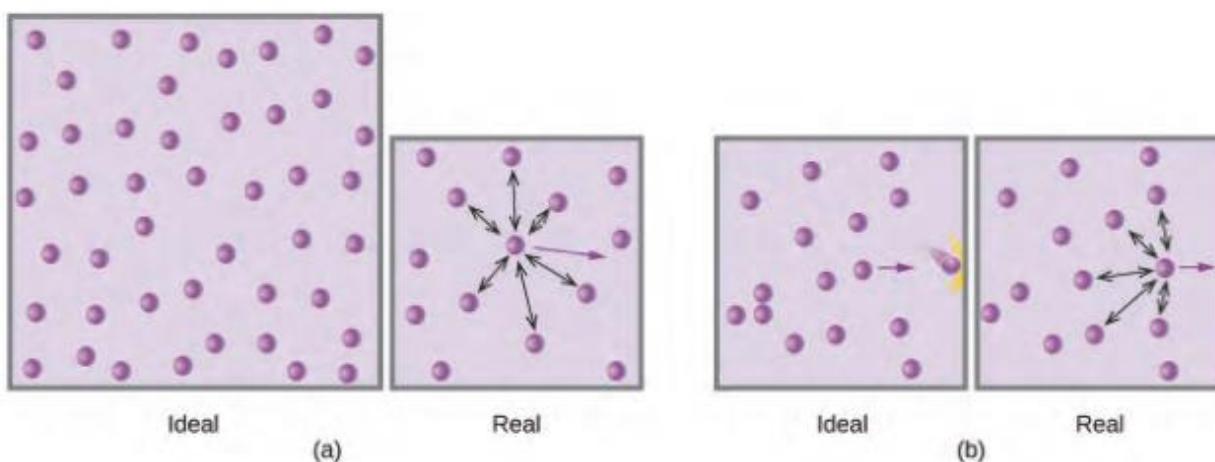


Figure 9.37 (a) Attractions between gas molecules serve to decrease the gas volume at constant pressure compared to an ideal gas whose molecules experience no attractive forces. (b) These attractive forces will decrease the force of collisions between the molecules and container walls, therefore reducing the pressure exerted compared to an ideal gas.

There are several different equations that better approximate gas behavior than does the ideal gas law. The first, and simplest, of these was developed by the Dutch scientist Johannes van der Waals in 1879. The **van der Waals equation** improves upon the ideal gas law by adding two terms: one to account for the volume of the gas molecules and another for the attractive forces between them.

$$PV = nRT \longrightarrow \left(P + \frac{an^2}{V^2} \right) (V - nb) = nRT$$

Correction for molecular attraction Correction for volume of molecules

The constant a corresponds to the strength of the attraction between molecules of a particular gas, and the constant b corresponds to the size of the molecules of a particular gas. The “correction” to the pressure term in the ideal gas law is $\frac{n^2a}{V^2}$, and the “correction” to the volume is nb . Note that when V is relatively large and n is relatively small,

both of these correction terms become negligible, and the van der Waals equation reduces to the ideal gas law, $PV = nRT$. Such a condition corresponds to a gas in which a relatively low number of molecules is occupying a relatively large volume, that is, a gas at a relatively low pressure. Experimental values for the van der Waals constants of some common gases are given in **Table 9.3**.

Values of van der Waals Constants for Some Common Gases

Gas	a ($\text{L}^2 \text{ atm/mol}^2$)	b (L/mol)
N_2	1.39	0.0391
O_2	1.36	0.0318
CO_2	3.59	0.0427

Table 9.3

Values of van der Waals Constants for Some Common Gases

Gas	a ($\text{L}^2 \text{ atm/mol}^2$)	b (L/mol)
H_2O	5.46	0.0305
He	0.0342	0.0237
CCl_4	20.4	0.1383

Table 9.3

At low pressures, the correction for intermolecular attraction, a , is more important than the one for molecular volume, b . At high pressures and small volumes, the correction for the volume of the molecules becomes important because the molecules themselves are incompressible and constitute an appreciable fraction of the total volume. At some intermediate pressure, the two corrections have opposing influences and the gas appears to follow the relationship given by $PV = nRT$ over a small range of pressures. This behavior is reflected by the “dips” in several of the compressibility curves shown in Figure 9.35. The attractive force between molecules initially makes the gas more compressible than an ideal gas, as pressure is raised (Z decreases with increasing P). At very high pressures, the gas becomes less compressible (Z increases with P), as the gas molecules begin to occupy an increasingly significant fraction of the total gas volume.

Strictly speaking, the ideal gas equation functions well when intermolecular attractions between gas molecules are negligible and the gas molecules themselves do not occupy an appreciable part of the whole volume. These criteria are satisfied under conditions of *low pressure and high temperature*. Under such conditions, the gas is said to behave ideally, and deviations from the gas laws are small enough that they may be disregarded—this is, however, very often not the case.

Example 9.24

Comparison of Ideal Gas Law and van der Waals Equation

A 4.25-L flask contains 3.46 mol CO_2 at 229 °C. Calculate the pressure of this sample of CO_2 :

- (a) from the ideal gas law
- (b) from the van der Waals equation
- (c) Explain the reason(s) for the difference.

Solution

(a) From the ideal gas law:

$$P = \frac{nRT}{V} = \frac{3.46 \text{ mol} \times 0.08206 \text{ L atm mol}^{-1} \text{ K}^{-1} \times 502 \text{ K}}{4.25 \text{ L}} = 33.5 \text{ atm}$$

(b) From the van der Waals equation:

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

$$P = \frac{3.46 \text{ mol} \times 0.08206 \text{ L atm mol}^{-1} \text{ K}^{-1} \times 502 \text{ K}}{(4.25 \text{ L} - 3.46 \text{ mol} \times 0.0427 \text{ L mol}^{-1})} - \frac{(3.46 \text{ mol})^2 \times 3.59 \text{ L}^2 \text{ atm mol}^2}{(4.25 \text{ L})^2}$$

This finally yields $P = 32.4 \text{ atm}$.

(c) This is not very different from the value from the ideal gas law because the pressure is not very high and the temperature is not very low. The value is somewhat different because CO₂ molecules do have some volume and attractions between molecules, and the ideal gas law assumes they do not have volume or attractions.

Check your Learning

A 560-mL flask contains 21.3 g N₂ at 145 °C. Calculate the pressure of N₂:

- (a) from the ideal gas law
- (b) from the van der Waals equation
- (c) Explain the reason(s) for the difference.

Answer: (a) 46.562 atm; (b) 46.594 atm; (c) The van der Waals equation takes into account the volume of the gas molecules themselves as well as intermolecular attractions.

Key Terms

absolute zero temperature at which the volume of a gas would be zero according to Charles's law.

Amontons's law (also, Gay-Lussac's law) pressure of a given number of moles of gas is directly proportional to its kelvin temperature when the volume is held constant

atmosphere (atm) unit of pressure; 1 atm = 101,325 Pa

Avogadro's law volume of a gas at constant temperature and pressure is proportional to the number of gas molecules

bar (bar or b) unit of pressure; 1 bar = 100,000 Pa

barometer device used to measure atmospheric pressure

Boyle's law volume of a given number of moles of gas held at constant temperature is inversely proportional to the pressure under which it is measured

Charles's law volume of a given number of moles of gas is directly proportional to its kelvin temperature when the pressure is held constant

compressibility factor (Z) ratio of the experimentally measured molar volume for a gas to its molar volume as computed from the ideal gas equation

Dalton's law of partial pressures total pressure of a mixture of ideal gases is equal to the sum of the partial pressures of the component gases.

diffusion movement of an atom or molecule from a region of relatively high concentration to one of relatively low concentration (discussed in this chapter with regard to gaseous species, but applicable to species in any phase)

effusion transfer of gaseous atoms or molecules from a container to a vacuum through very small openings

Graham's law of effusion rates of diffusion and effusion of gases are inversely proportional to the square roots of their molecular masses

hydrostatic pressure pressure exerted by a fluid due to gravity

ideal gas hypothetical gas whose physical properties are perfectly described by the gas laws

ideal gas constant (R) constant derived from the ideal gas equation $R = 0.08226 \text{ L atm mol}^{-1} \text{ K}^{-1}$ or $8.314 \text{ L kPa mol}^{-1} \text{ K}^{-1}$

ideal gas law relation between the pressure, volume, amount, and temperature of a gas under conditions derived by combination of the simple gas laws

kinetic molecular theory theory based on simple principles and assumptions that effectively explains ideal gas behavior

manometer device used to measure the pressure of a gas trapped in a container

mean free path average distance a molecule travels between collisions

mole fraction (X) concentration unit defined as the ratio of the molar amount of a mixture component to the total number of moles of all mixture components

partial pressure pressure exerted by an individual gas in a mixture

pascal (Pa) SI unit of pressure; $1 \text{ Pa} = 1 \text{ N/m}^2$

pounds per square inch (psi) unit of pressure common in the US

pressure force exerted per unit area

rate of diffusion amount of gas diffusing through a given area over a given time

root mean square velocity (u_{rms}) measure of average velocity for a group of particles calculated as the square root of the average squared velocity

standard conditions of temperature and pressure (STP) 273.15 K (0°C) and 1 atm (101.325 kPa)

standard molar volume volume of 1 mole of gas at STP, approximately 22.4 L for gases behaving ideally

torr unit of pressure; $1 \text{ torr} = \frac{1}{760} \text{ atm}$

van der Waals equation modified version of the ideal gas equation containing additional terms to account for non-ideal gas behavior

vapor pressure of water pressure exerted by water vapor in equilibrium with liquid water in a closed container at a specific temperature

Key Equations

- $P = \frac{F}{A}$
- $p = h\rho g$
- $PV = nRT$
- $P_{\text{Total}} = P_A + P_B + P_C + \dots = \sum_i P_i$
- $P_A = X_A P_{\text{Total}}$
- $X_A = \frac{n_A}{n_{\text{Total}}}$
- rate of diffusion = $\frac{\text{amount of gas passing through an area}}{\text{unit of time}}$
- $\frac{\text{rate of effusion of A as A}}{\text{rate of effusion of B as B}} = \frac{\sqrt{m_B}}{\sqrt{m_A}} = \frac{\sqrt{\mathcal{M}_B}}{\sqrt{\mathcal{M}_A}}$
- $u_{\text{rms}} = \sqrt{\bar{u^2}} = \sqrt{\frac{u_1^2 + u_2^2 + u_3^2 + u_4^2 + \dots}{n}}$
- $\text{KE}_{\text{avg}} = \frac{3}{2}RT$
- $u_{\text{rms}} = \sqrt{\frac{3RT}{m}}$
- $Z = \frac{\text{molar volume of gas at same } T \text{ and } P}{\text{molar volume of ideal gas at same } T \text{ and } P} = \left(\frac{P \times V_m}{R \times T} \right)_{\text{measured}}$
- $\left(P + \frac{n^2 a}{V^2} \right) \times (V - nb) = nRT$

Summary

9.1 Gas Pressure

Gases exert pressure, which is force per unit area. The pressure of a gas may be expressed in the SI unit of pascal or kilopascal, as well as in many other units including torr, atmosphere, and bar. Atmospheric pressure is measured using a barometer; other gas pressures can be measured using one of several types of manometers.

9.2 Relating Pressure, Volume, Amount, and Temperature: The Ideal Gas Law

The behavior of gases can be described by several laws based on experimental observations of their properties. The pressure of a given amount of gas is directly proportional to its absolute temperature, provided that the volume does not change (Amontons's law). The volume of a given gas sample is directly proportional to its absolute temperature at constant pressure (Charles's law). The volume of a given amount of gas is inversely proportional to its pressure when temperature is held constant (Boyle's law). Under the same conditions of temperature and pressure, equal volumes of all gases contain the same number of molecules (Avogadro's law).

The equations describing these laws are special cases of the ideal gas law, $PV = nRT$, where P is the pressure of the gas, V is its volume, n is the number of moles of the gas, T is its kelvin temperature, and R is the ideal (universal) gas constant.

9.3 Stoichiometry of Gaseous Substances, Mixtures, and Reactions

The ideal gas law can be used to derive a number of convenient equations relating directly measured quantities to properties of interest for gaseous substances and mixtures. Appropriate rearrangement of the ideal gas equation may be made to permit the calculation of gas densities and molar masses. Dalton's law of partial pressures may be used to relate measured gas pressures for gaseous mixtures to their compositions. Avogadro's law may be used in stoichiometric computations for chemical reactions involving gaseous reactants or products.

9.4 Effusion and Diffusion of Gases

Gaseous atoms and molecules move freely and randomly through space. Diffusion is the process whereby gaseous atoms and molecules are transferred from regions of relatively high concentration to regions of relatively low concentration. Effusion is a similar process in which gaseous species pass from a container to a vacuum through very small orifices. The rates of effusion of gases are inversely proportional to the square roots of their densities or to the square roots of their atoms/molecules' masses (Graham's law).

9.5 The Kinetic-Molecular Theory

The kinetic molecular theory is a simple but very effective model that effectively explains ideal gas behavior. The theory assumes that gases consist of widely separated molecules of negligible volume that are in constant motion, colliding elastically with one another and the walls of their container with average velocities determined by their absolute temperatures. The individual molecules of a gas exhibit a range of velocities, the distribution of these velocities being dependent on the temperature of the gas and the mass of its molecules.

9.6 Non-Ideal Gas Behavior

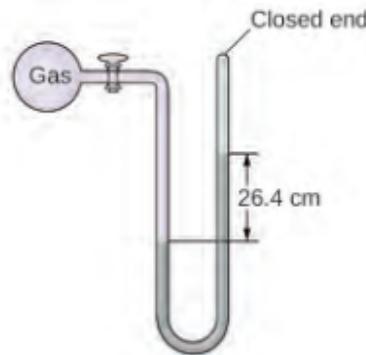
Gas molecules possess a finite volume and experience forces of attraction for one another. Consequently, gas behavior is not necessarily described well by the ideal gas law. Under conditions of low pressure and high temperature, these factors are negligible, the ideal gas equation is an accurate description of gas behavior, and the gas is said to exhibit ideal behavior. However, at lower temperatures and higher pressures, corrections for molecular volume and molecular attractions are required to account for finite molecular size and attractive forces. The van der Waals equation is a modified version of the ideal gas law that can be used to account for the non-ideal behavior of gases under conditions.

Exercises

9.1 Gas Pressure

1. Why are sharp knives more effective than dull knives (Hint: think about the definition of pressure)?

2. Why do some small bridges have weight limits that depend on how many wheels or axles the crossing vehicle has?
3. Why should you roll or belly-crawl rather than walk across a thinly-frozen pond?
4. A typical barometric pressure in Redding, California, is about 750 mm Hg. Calculate this pressure in atm and kPa.
5. A typical barometric pressure in Denver, Colorado, is 615 mm Hg. What is this pressure in atmospheres and kilopascals?
6. A typical barometric pressure in Kansas City is 740 torr. What is this pressure in atmospheres, in millimeters of mercury, and in kilopascals?
7. Canadian tire pressure gauges are marked in units of kilopascals. What reading on such a gauge corresponds to 32 psi?
8. During the Viking landings on Mars, the atmospheric pressure was determined to be on the average about 6.50 millibars (1 bar = 0.987 atm). What is that pressure in torr and kPa?
9. The pressure of the atmosphere on the surface of the planet Venus is about 88.8 atm. Compare that pressure in psi to the normal pressure on earth at sea level in psi.
10. A medical laboratory catalog describes the pressure in a cylinder of a gas as 14.82 MPa. What is the pressure of this gas in atmospheres and torr?
11. Consider this scenario and answer the following questions: On a mid-August day in the northeastern United States, the following information appeared in the local newspaper: atmospheric pressure at sea level 29.97 in., 1013.9 mbar.
 - (a) What was the pressure in kPa?
 - (b) The pressure near the seacoast in the northeastern United States is usually reported near 30.0 in. Hg. During a hurricane, the pressure may fall to near 28.0 in. Hg. Calculate the drop in pressure in torr.
12. Why is it necessary to use a nonvolatile liquid in a barometer or manometer?
13. The pressure of a sample of gas is measured at sea level with a closed-end manometer. The liquid in the manometer is mercury. Determine the pressure of the gas in:
 - (a) torr
 - (b) Pa
 - (c) bar



14. The pressure of a sample of gas is measured with an open-end manometer, partially shown to the right. The liquid in the manometer is mercury. Assuming atmospheric pressure is 29.92 in. Hg, determine the pressure of the gas in:
 - (a) torr
 - (b) Pa
 - (c) bar