Chapter 7

Gases

Figure 7.1 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

7.1 Gas Pressure

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

7.3 Stoichiometry of Gaseous Substances, Mixtures, and Reactions

7.4 The Kinetic-Molecular Theory

7.5 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 7.1**) 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.

7.1 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 7.2**). 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.

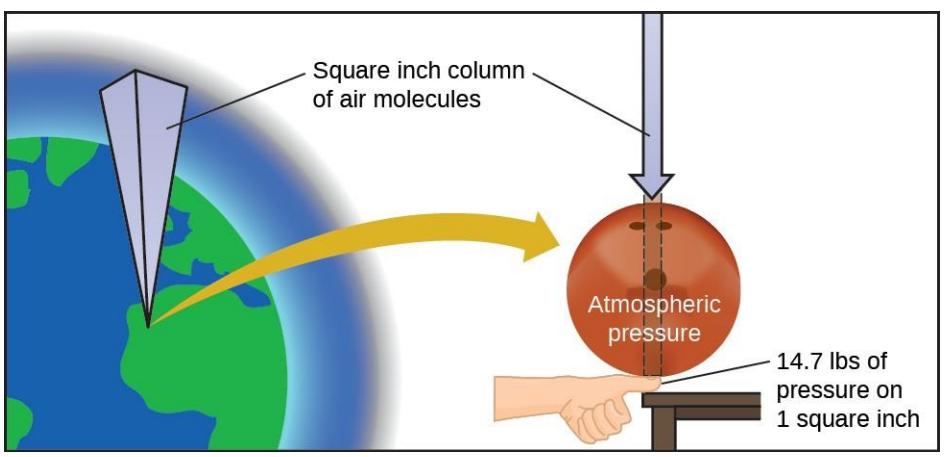


Figure 7.2 The atmosphere above us exerts a large pressure on objects at the surface of the earth, roughly equal to the weight of a bowling ball pressing on an area the size of a human thumbnail.

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.

The SI unit of pressure is the **pascal (Pa)**, with 1 Pa = 1 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 kPa = 1000 Pa) or **bar** (1 bar = 100,000 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 7.1 provides some information on these and a few other common units for pressure measurements.

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

Table 7.1: Pressure Units

Example 7.1

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 7.1**.

(a) $29.2\ in\ Hg * \frac{(25.4\ mm)}{1\ in} * \frac{(1\ torr)}{1\ mm\ Hg} = 742\ torr$

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

(c) $742\ torr * \frac{(101.325\ Kpa\ )}{760\ torr} = 98.9\ kPa$

(d) $98.9\ kPa * \frac{(1000\ Pa\ )}{1\ kPa} * \frac{1\ bar}{100{,}000\ Pa} * \frac{1000\ m\ bar}{1\ bar} = 989\ m$

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

Self-assessment 7.1:

What is the pressure reading on this gauge? In kPa? In Atm? In torr? In PSI?

Answers:

Gauge 1 is from a liquid nitrogen tank.

Step 1: The readings are 1.45 ×100 kPa (145 kPa) on the outer, black, ring, and 21 PSI on the inner, red ring.

Step 2: Convert to Atmospheres

$$\frac{(145\ kPa)}{1} \times \frac{(1\ Atm)}{101.32\ kPa} = 1.43\ Atm$$

Step 3: Convert from Atm to torr

$$\frac{(1.43\ Atm)}{1} \times \frac{(760\ torr)}{1Atm} = 1087\ torr\ or\ 1090\ torr\ to\ 3\ s.f.$$

Gauge 2 is from a gaseous nitrogen tank

Step 1: readings are 13,300 kPa (outer ring) and 1,910 PSI (inner ring)

Step 2: Convert one of the two readings to Atm

$$\frac{(13{,}300\ kPa)}{1} \times \frac{(1\ Atm)}{101.32\ kPa} = 131.3\ Atm$$

Step 3: Convert pressure in Atm to pressure in torr

$$\frac{(131.3\ Atm)}{1} \times \frac{(760\ torr)}{1\ Atm} = 99{,}760\ torr$$

Gauge 3 is from an oxygen tank attached to an instrument

Step 1: The readings are 32 Atm (inner reading) and 460 PSI (outer reading)

Step 2: Convert from Atm to kPA

$$\frac{(32\ Atm)}{1} \times \frac{(101.32\ kPa)}{1\ Atm} = 3{,}242\ kPa = 3{,}200\ kPa\ with\ 2\ s.f.$$

Step 3: Convert from Atm to torr

$$\frac{(32\ Atm)}{1} \times \frac{(760\ torr)}{1\ Atm} = 24{,}320\ torr = 24{,}000\ torr\ with\ 2\ s.f.$$

We can measure atmospheric pressure, the force exerted by the atmosphere on the earth's surface, with a **barometer** (**Figure 7.4**). 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.

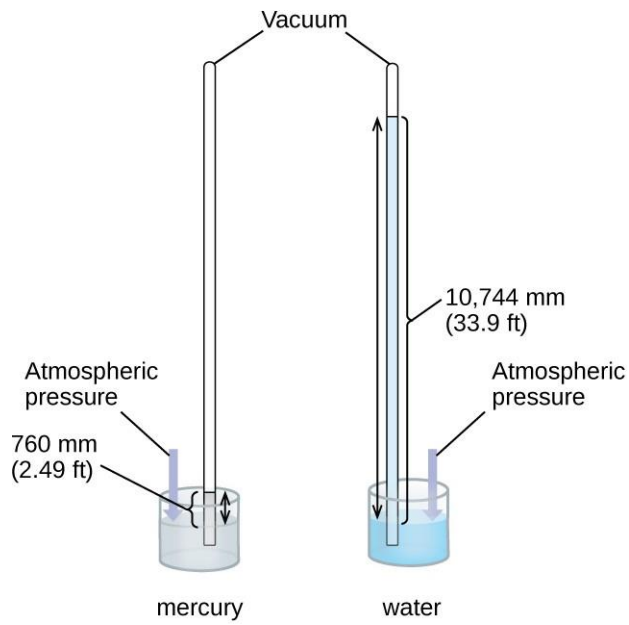


Figure 7.4 In a barometer, the height, *h*, of the column of liquid is used as a measurement of the air pressure. Using very dense liquid mercury (left) permits the construction of reasonably sized barometers, whereas using water (right) would require a barometer more than 30 feet tall.

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.

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 7.5**) 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.

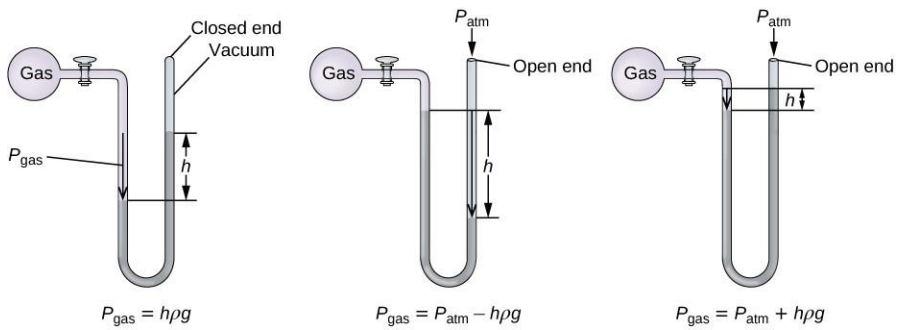


Figure 7.5 A manometer can be used to measure the pressure of a gas. The (difference in) height between the liquid levels (*h*) is a measure of the pressure. Mercury is usually used because of its large density.

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 7.6**). 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).

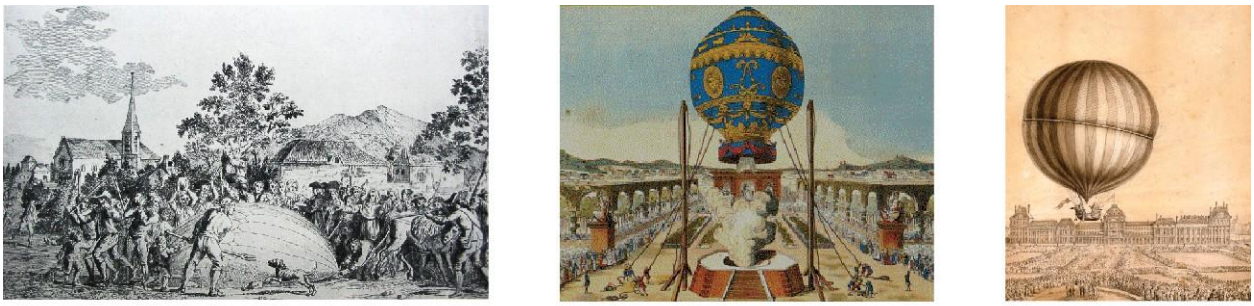
Figure 7.6 (a) A medical technician prepares to measure a patient's blood pressure with a sphygmomanometer. (b) A typical sphygmomanometer uses a valved rubber bulb to inflate the cuff and a diaphragm gauge to measure pressure. (credit a: modification of work by Master Sgt. Jeffrey Allen)

7.2 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 7.9**), 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.



(a) (b) (c)

Figure 7.9 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 – Gay-Lussac'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 7.10**) and the pressure increases.

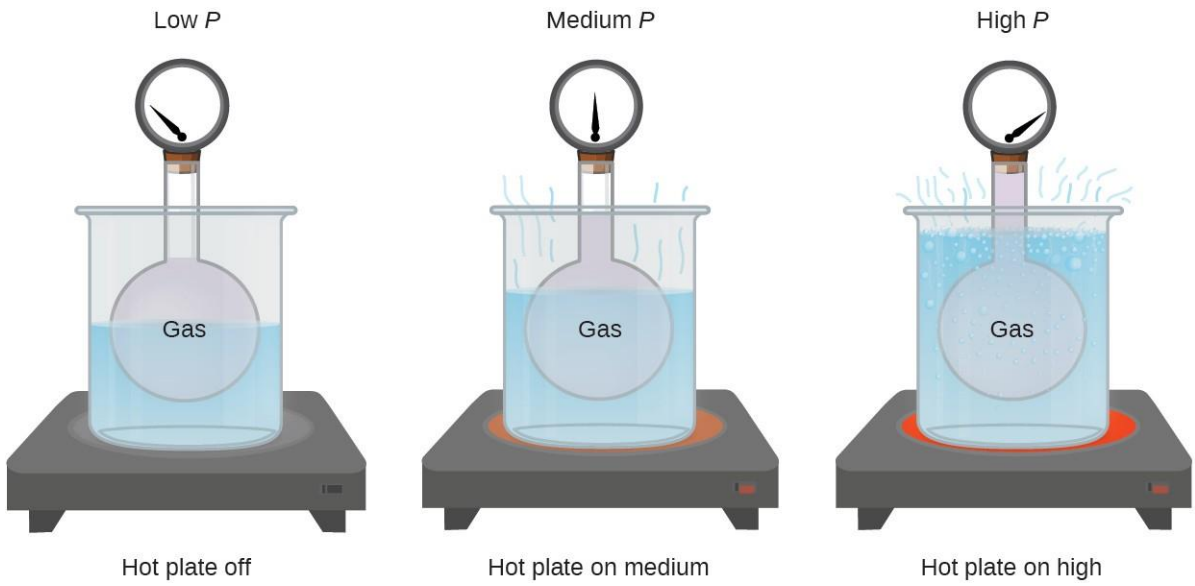


Figure 7.10 The effect of temperature on gas pressure: When the hot plate is off, the pressure of the gas in the sphere is relatively low. As the gas is heated, the pressure of the gas in the sphere increases.

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 7.11** We find that temperature and pressure are linearly related, and if the temperature is on the kelvin scale, then *P* and 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

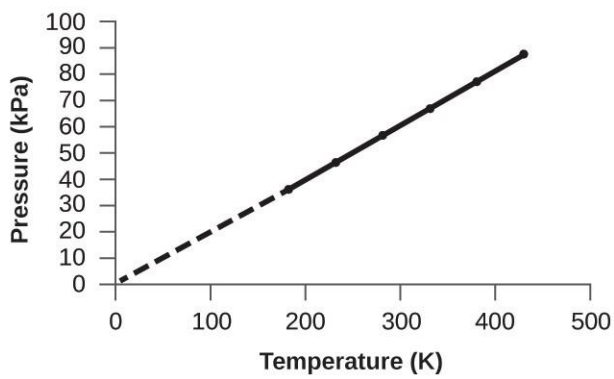


Figure 9.11 For a constant volume and amount of air, the pressure and temperature are directly proportional, provided the temperature is in kelvin. (Measurements cannot be made at lower temperatures because of the condensation of the gas.) When this line is extrapolated to lower pressures, it reaches 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:

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

where ∝ 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 $\left(i.e., \frac{P}{T} = K\right)$. 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 $\frac{P_1}{T_1} = k \text{ and } \frac{P_2}{T_2} = k$, 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 7.2

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 °C to K, we have:

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

Rearranging and solving gives: $P_2 = \frac{(360\ kPa * 330k)}{297\ K} = 390\ kPa$

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

Self-assessment 7.2:

Type D cylinders are 4.3 inches in diameter and 16.5 inches tall. The internal pressure is 2,015 PSI. You can hold 14.6 cubic feet (413.4 L) of oxygen in these tanks. If the temperature in a storage room raises from 72 °F (22.2 °C) to 100 °F (37.8 °C), what is the new pressure? If the tank will rupture at 4,000 psi (272 Atm), is this safe? What temperature will cause a rupture of the tank?

Answer:

Key Equation:

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

Knowns: P_1 = 2,015 PSI, T_1 = 22.2 °C, T_2 = 37.8 °C

Strategy: Convert pressure in PSI to Atm and Temperatures in °F to Kelvin. Rearrange Guy-Lussac's Law to solve for P_2, t hen compares the new pressure to the rupture pressure.

Step 1: Convert P_1 to Atm

$$\frac{(2{,}015\ PSI)}{1} \times \frac{\frac{1\ Atm}{14.70\ PSI}}{14.70\ PSI} = 137.07\ Atm$$

Step 2: Convert T_1 and T_2 from Fahrenheit to Kelvin

$$T_1 = 22.2 + 273 = 295\ K$$

$$T_2 = 37.8 + 273 = 310\ K$$

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

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

$$P_2 = P_1 \left(\frac{T_2}{T_1}\right)$$

$$V_2 = 137.07\ Atm * \frac{310\ K}{295\ K}$$

$$V_2 = 144\ Atm.$$

Step 3: Compare the new pressure to the rupture pressure

$144\ Atm < 272\ Atm$ therefore, there is no danger of the tank exploding.

Step 4: Set a new P_2 to be the rupture temperature and rearrange Guy-Lussac's Law to solve for the unknown temperature.

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

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

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

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

$$T_2 = T_1 \times \left(\frac{P_2}{P_1}\right)$$

$$T_2 = 295\ K\ \left(\frac{272\ Atm}{137.07\ Atm}\right)$$

$$T_2 = 585.4\ K, or\ 312\ °C$$

The room would need to be above boiling point of water before the tank would explode.

Self-assessment 7.3:

Bacteria and viruses are destroyed by temperatures above 135 °C in an autoclave. If an autoclave initially generates steam at 100 °C and 1 Atm (the conditions under which water boil), to get steam to reach 135 °C, what minimum pressure will need to be reached?

Answer: First let's convert temperatures from Celsius to Kelvin, then rearrange Guy-Lussac's Law to solve for the new temperature.

Knowns: T_1 = 100 °C, T_2 = 135 °C, P_1 = 1 Atm

Key Equation:

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

Step 1: Convert Celsius to Kelvin.

$$T_1 = 100 + 273 = 373\ K$$

$$T_2 = 135 + 273 = 408\ K$$

Step 2: Rearrange to solve for P_2

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

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

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

$$P_2 = P_1 \times \frac{(T_2\ )}{T_1}$$

$$P_2 = 1\ Atm \left(\frac{408\ K}{373\ K}\right)$$

$$P_2 = 1.09\ Atm$$

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.

Link to Learning

This **video (http://openstaxcollege.org/l/16CharlesLaw)** shows how cooling and heating a gas causes its volume to decrease or increase, respectively.

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

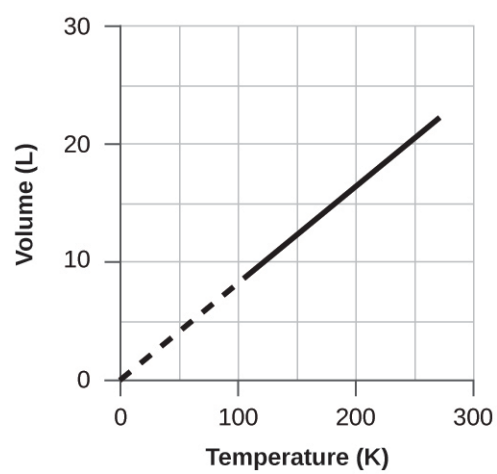


Figure 9.12 The volume and temperature are linearly related for 1 mole of methane gas at a constant pressure of 1 atm. If the temperature is in kelvin, volume and temperature are directly proportional. The line stops at 111 K because methane liquefies at this temperature; when extrapolated, it intersects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

$$V \ \alpha \ \ T \ or \ V = constant * T \ or \ V = K * T \ or \ \frac{V_1}{T_1} = \frac{V_2}{T_2}$$

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 *P-T* relationship, this lead to another form of Charles's law:

$$\frac{V_1}{T_1} = \frac{V_2}{T_2}$$

Example 7.3

Predicting Change in Volume with Temperature: A sample of carbon dioxide, CO_2, 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 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:

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

Rearranging and solving gives:

$$V_2 = \frac{(0.300\ L\ * 303\ K\ )}{283\ K} = 0.321\ L$$

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 7.4

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 cm^3 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 cm^3. 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 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:

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

Rearrangement gives

$$T_2 = \frac{131.7\ cm^{\ 3} * 273.15\ k}{150.0\ cm^3} = 239.8\ k$$

Subtracting 273.15 from 239.8 K, 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

Self-assessment 7.4:

Helium gas is used to inflate the abdomen during laparoscopic surgery. If 1.0 L of gas initially at 22 °C is delivered into a patent with a body temperature of 37 °C, what is the volume of the gas when it warms up?

Answer:

Key Equation:

$$\frac{V_1}{T_1} = \frac{V_2}{T_2}$$

Knowns: V_1 = 1.0 L, T_1= 22 °C, T_2= 37 °C

Strategy: Convert temperatures in Celsius into Kelvin. Use Charles' Law to solve for the new volume.

Step 1:

$$T_1 = 22 + 273 = 295\ K$$

$$T_2 = 37 + 273 = 310\ K$$

Step 2: Rearrange Charles' Law to solve for V_2

$$\frac{V_1}{T_1} = \frac{V_2}{T_2}$$

$$T_2 \times \frac{V_1}{T_1} = \frac{\frac{V_2}{T_2}}{T_2} \times T_2$$

$$V_2 = V_1\left(\frac{T_2}{T_1}\right)$$

$$V_2 = 1.0\ L\left(\frac{310\ K}{295\ K}\right)$$

$$V_2 = 1.05\ L$$

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 7.13**.

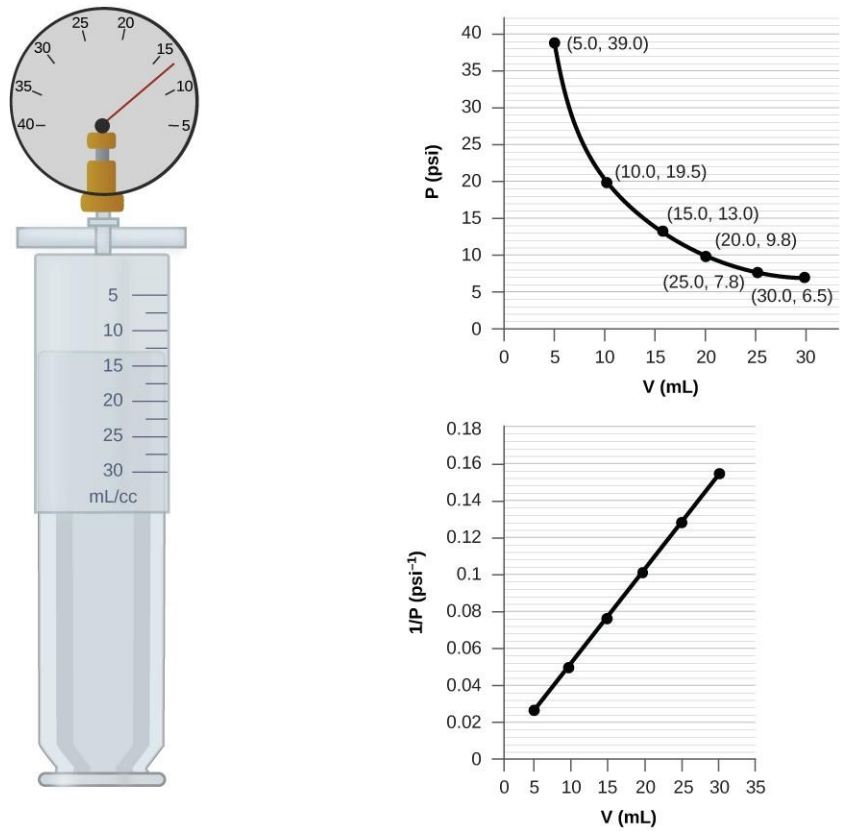


Figure 7.13 When a gas occupies a smaller volume, it exerts a higher pressure; when it occupies a larger volume, it exerts a lower pressure (assuming the amount of gas and the temperature do not change). Since P and V are inversely proportional, a graph of $\frac{1}{P}\ vs\ V$ is linear.

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:

$$p\ \alpha\ \frac{1}{V}\ \ or\ P = \frac{K*1}{V}\ \ or\ \ P_1V_1 = P_2\,V_2$$

with k being a constant.

If we plot P versus V, we obtain a hyperbola (see **Figure 7.14**)

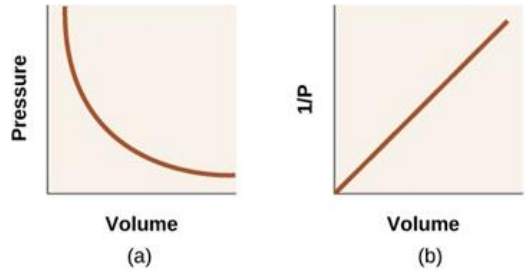


Figure 7.14 The relationship between pressure and volume is inversely proportional. (a) The graph of P vs. V is a hyperbola, whereas (b) the graph of $\left(\frac{1}{P}\right)$ $vs\ V$ is linear.

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 7.5

Volume of a Gas Sample: The sample of gas in **Figure 7.13** 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 7.13**

(b) the $\left(\frac{1}{P}\right)$ vs V graph in **Figure 7.13**

(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 $\left(\frac{1}{P}\right)$ $vs\ V$ 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 13.0 psi and 15.0 mL, P_2 as the pressure at which the volume is unknown, and V_2 as the unknown volume, we have:

$$P_2 = \frac{13.0\ Psi * 15.0\ ml}{7.5\ mL} = 26\ psi$$

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 7.13** 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 psi, using:

(a) the P-V graph in **Figure 7.13**

(b) the $\frac{1}{P}$ $vs. V$ graph in **Figure 7.13**

(c) the Boyles'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

Self-assessment 7.5:

A patient receives oxygen as part of an asthma treatment, and the initial gauge reading on 12-L tank is 3,800 mmHg. What volume of gas is available for patent use at 1 Atm? (Assuming no change in T or *n*).

Answer:

Strategy: Convert knowns to appropriate units, then use Boyles Law (the relation between Pressure and Temperature), solve for the unknown volume.

Key equation $P_1V_1 = P_2V_2$

Knowns: P_1 = 3,800 mmHg, V_1= 12 liters, P_2 = 1 Atm.

Step 1: Convert P_1 from mmHg to Atm

$$\frac{3{,}800\ mmHg}{1} \times \frac{1\ Atm}{760\ torr} = 5.00\ Atm$$

Step 2: Rearrange Boyle's Law to solve for new volume V_2.

$$P_1V_1 = P_2V_2$$

$$\frac{P_1V_1}{P_2} = \frac{P_2V_2}{P_2}$$

$$V_2 = V_1\left(\frac{P_1}{P_2}\right)$$

$$V_2 = 12\ L\left(\frac{5.00\ Atm}{1.00\ Atm}\right)$$

$$V_2 = 60\ L\ of\ oxygen\ are\ available$$

Self-assessment 7.6:

The current "free diving" record is 214 meters (702 feet) (held by Herbert Nitsch). Average lung capacity for men is 4.5 Liters. Assuming a pressure of 327 PSI of overbearing sea water, what is the volume of the lungs at depth? What percent of the original volume is that? 1 atm = 14.70 PSI

Strategy: Covert the pressure in PSI to units of Atm. Use Boyle's Law to determine the new volume. Finally, find the percentage of the two volumes.

Answer:

Key equation

$$P_1V_1 = P_2V_2$$

Knowns: P_1 =1 Atm, V_1= 4.5 liters, P_2 = 327 PSI.

Step 1: Convert PSI to Atm

$$\frac{327\ PSI}{1} \times \frac{1\ Atm}{14.70\ PSI} = 22.2\ Atm$$

Step 2: Rearrange Boyle's Law to solve for the new volume

$$P_1V_1 = P_2V_2$$

$$\frac{P_1V_1}{P_2} = \frac{P_2V_2}{P_2}$$

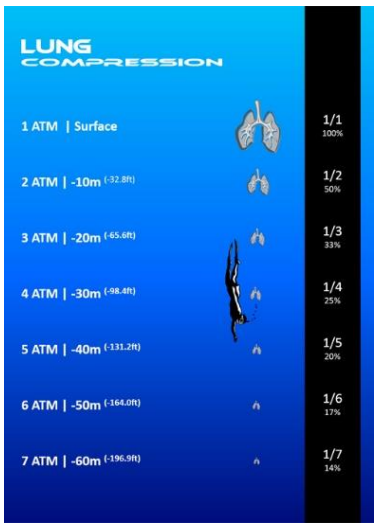
$$V_2 = V_1\left(\frac{P_1}{P_2}\right)$$

$$V_2 = 4.5\ L\left(\frac{1.00\ Atm}{22.2\ Atm}\right)$$

$$V_2 = 0.203\ Liters$$

Step 3: Divide the V_2 by V_1 to determine the compression ratio.

$$\frac{V_2}{V_1} \times 100 = \frac{0.203\ L}{4.5\ L} \times 100 = 4.50\ \%\ of\ the\ orginal\ volume$$



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 7.15**).

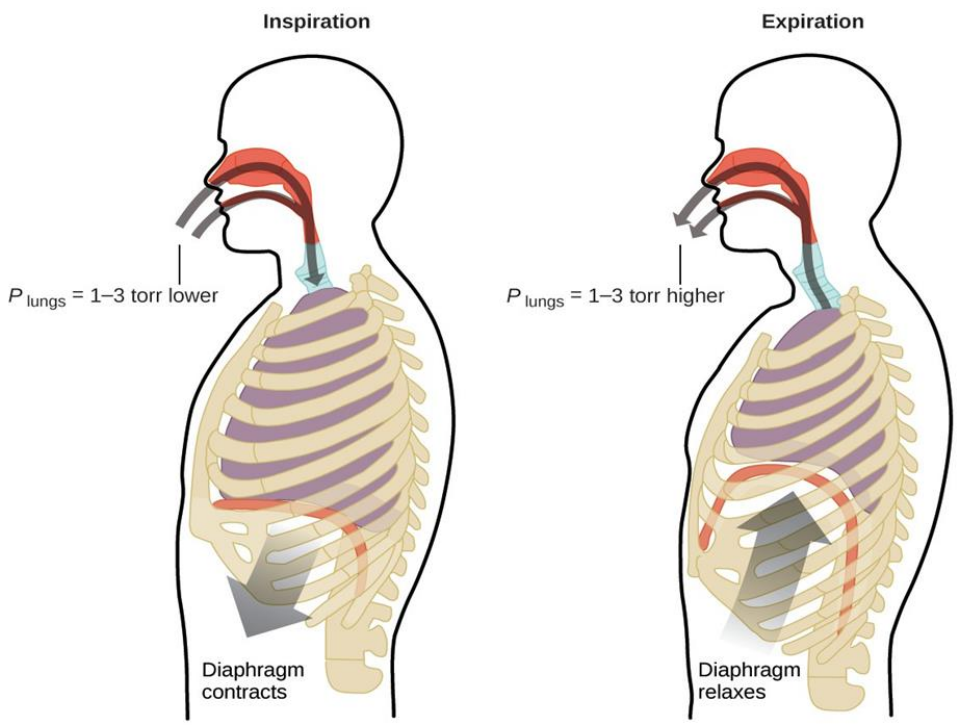


Figure 7.15: Moles of Gas and Volume: Avogadro's Law

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:

$$V \propto n \text{ or } V = K * n \text{ or } \frac{V_1}{n_1} = \frac{V_2}{n_2}$$

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/l/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).

Self-assessment 7.7:

An EMT blows air into a patient's lungs during CPR. The unconscious persons lung volume went from 3.0-L to 5.8-L. If three liters of air contain 0.123 moles of gas, how many moles of air were added into the patient's lung by the EMT (assuming no change in temperature or pressure).

Key Equation

$$\frac{V_1}{n_1} = \frac{V_2}{n_2}$$

<u>Answer</u>: Use Avogadro's Law to solve for new total number of moles. Subtract the initial number of moles from the new total to find the number of additional moles.

Knowns: V_1 = 3.0 L, V_2 = 5.8 L, n_1 = 0.123 moles, n_2 = ?

Step 1: Rearrange and solve for n_2

$$\frac{V_1}{n_1} = \frac{V_2}{n_2}$$

$$n_2 \times \frac{V_1}{n_1} = \frac{V_2}{n_2} \times n_2$$

$$\frac{n_1}{V_1} \times \frac{n_2 V_1}{n_1} = V_2 \times \frac{n_1}{V_1}$$

$$n_2 = n_1 \times \left(\frac{V_2}{V_1}\right)$$

$$n_2 = 0.123\ moles \times \left(\frac{5.8\ L}{3.0\ L}\right)$$

$$n_2 = 0.238\ moles$$

Step 2: Determine the number of additional moles by subtraction.

$$Total\ moles = Inital\ moles + Added\ moles$$

$$0.238\ moles = 0.123\ moles + Added\ moles$$

$$Added\ moles = 0.238\ moles - 0.132\ moles = 0.115\ moles\ added$$

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 = constant at constant T and n
- Amonton's law: $\frac{P}{T}$ = constant at constant V and n
- Charle's law: $\frac{V}{T}$ = constant at constant P and n
- Avogadro's law $\frac{V}{n}$ = 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 L atm mol^{-1} K^{-1} and 8.314 kPa L mol^{-1} 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 7.6

Using the Ideal Gas Law: Methane, CH4, is being considered for use as an alternative automotive fuel to replace gasoline. One gallon of gasoline could be replaced by 655 g of CH4. 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 L atm mol–1 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:

$$n = 6.55 gCH_4 * \frac{1\ mol}{16.043\ g\ CH_4} = 40.8\ mol$$

$$T = 25\ °C + 273 = 298\ K$$

$$p = 745\ torr * \frac{1\ atm}{760\ torr} = 0.980\ atm$$

$$V = \frac{nRT}{P} = \frac{(40.8\ mol)(0.08206\ L\ atm\ mol^{-1}K^{-1})(298K)}{0.980\ atm} = 1.02 * 10^3 L$$

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 bars

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).

Self-assessment 7.8:

Chlorine gas is used to purify water. If 0.240 moles of Cl_2 are held in a 6.00 Liter tank at 25.0 °C, what is the pressure of the gas inside the tank?

Answer**:** Convert temperature from Celsius to Kelvin, then use the Ideal Gas Law to calculate the Pressure.

Key Equation

$$PV = nRT$$

Knowns: V = 6.00 L, n = 0.240 moles, $R = 0.821\ \frac{L*Atm}{mol*K}$, T = 25.0 °C, P = ?

Step 1: Convert temperature to Kelvin

$$T = 25.0 + 273 = 298\ K$$

Step 2: Rearrange the Ideal Gas Law to solve for P

$$PV = nRT$$

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

$$P = \frac{(0.240\ mol)\left(0.0821\frac{L \times Atm}{mol \times K}\right)(298\ K)}{6.00\ L}$$

Or

$$P = \frac{0.240\ mol}{1} \times \frac{0.0821\ L \times Atm}{mol\ \times K} \times \frac{298\ K}{1} \times \frac{1}{6\ L}$$

$$P = 0.978\ L$$

Example 7.7

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 7.16**). 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 7.16 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:

$$\frac{P_{1V_1}}{T_1} = \frac{P_2V_2}{T_2} \rightarrow \frac{(153\ atm)(13.2L)}{(300\ k)} = \frac{(3.13\ atm)}{(310K)}$$

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

(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: 0.193 L

Chemistry in Everyday Life: Scuba Diving

Whether scuba diving at the Great Barrier Reef in Australia (shown in **Figure 7.17**) or in the Caribbean, divers must understand how pressure affects a number of issues related to their comfort and safety.

Figure 7.17 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 saltwater 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, one mole of an ideal gas has a volume of about 22.4 L—this is referred to as the **standard molar volume** (**Figure 7.18**).

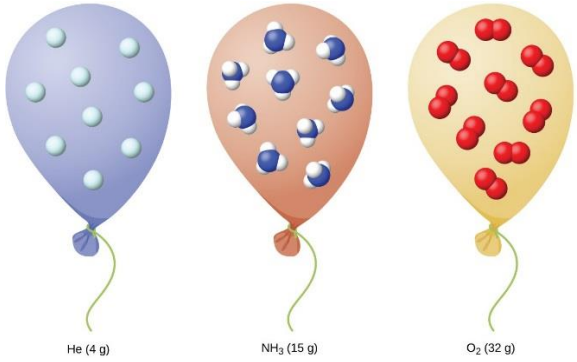


Figure 7.18 Since the number of moles in a given volume of gas varies with pressure and temperature changes,

chemists use standard temperature and pressure (273.15 K and 1 atm or 101.325 kPa) to report properties of gases.

7.2 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.

Answer: Empirical formula, CH; Molecular formula, C_2H_2

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*:

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

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 7.8

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 7.19**)

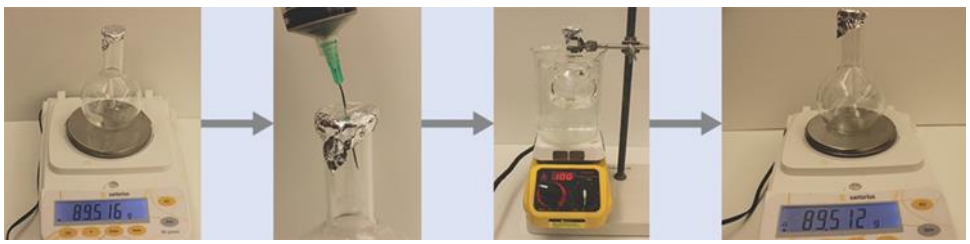


Figure 7.19 When the volatile liquid in the flask is heated past its boiling point, it becomes gas and drives air out of the flask. At $^{t}l \longrightarrow g$, the flask is filled with volatile liquid gas at the same pressure as the atmosphere. If the flask is then cooled to room temperature, the gas 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

$$M = \frac{mRT}{PV} = \frac{(0.494\ g) * 0.08206 \frac{L * atm}{mol * K} * 372.8\ K}{0.976\ atm * 0.129\ L} = 120 \frac{g}{mol}$$

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, P_4

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 were present alone in the container (**Figure 7.20**). 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*:

$$P_{Total} = P_A + P_B + P_C + \cdots = \Sigma_i P_i$$

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.

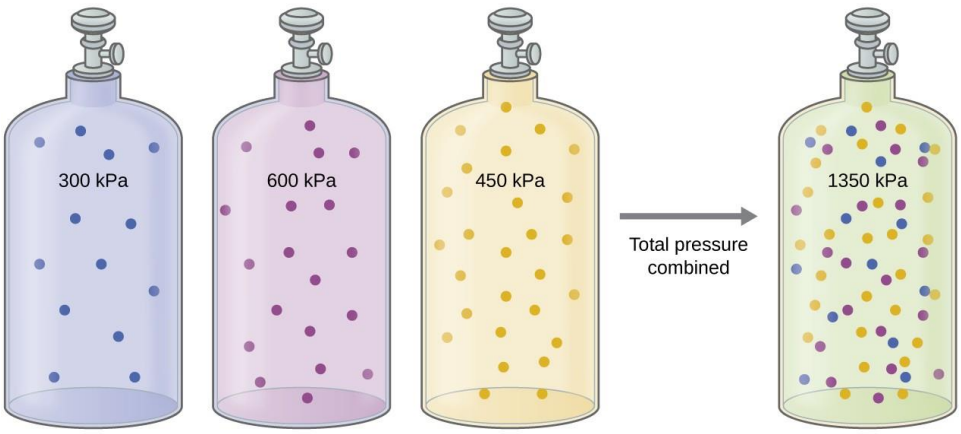


Figure 7.20 If equal-volume cylinders containing gas A at a pressure of 300 kPa, gas B at a pressure of 600 kPa, and gas C at a pressure of 450 kPa are all combined in the same-size cylinder, the total pressure of the mixture is 1350 kPa.

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:

$$P_A = X_A * P_{Total} \;\; where\; X_A = \frac{n_A}{n_{Total}}$$

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 7.9

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

$$p = \frac{nRT}{V}.$$

$$P_{H_2} = \frac{(2.50 * 10^{-3}\ mol)\left(0.08206\ \frac{L * atm}{mol * K}\right)(308\ K)}{10.0\ L} = 6.32 * 10^{-3}\ atm$$

$$P_{He} = \frac{(1.00 * 10^{-3} mol)\left(0.08206\ \frac{L * atm}{mol * K}\right)(308K)}{10.0\ L} = 2.53 * 10^{-3} atm$$

$$P_{Ne} = \frac{(3.00 * 10^{-4} mol)\left(0.08206\ \frac{L * atm}{mol * k}\right)(308\ k)}{10.0\ l} = 7.58 * 10^{-4}\ atm$$

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

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

Check Your Learning

A 5.73-L flask at 25 °C contains 0.0388 mol of N_2, 0.147 mol of CO, and 0.0803 mol of H_2. 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 7.10

The Pressure of a Mixture of Gases: A gas mixture used for anesthesia contains 2.83 mol oxygen, O_2, and 8.41 mol nitrous oxide, N_2O. The total pressure of the mixture is 192 kPa.

(a) What are the mole fractions of O_2 and N_2O?

(b) What are the partial pressures of O_2 and N_2O?

Solution:

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

For O_2,

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

And

$$P_{O_2} = X_{O_2} * P_{Total} = 0.252 * 192\ kPa = 48.4\ kPa$$

For N_2O,

$$X_{N_2} = \frac{n_{N_2}}{n_{Total}} = \frac{8.41\ mol}{(2.83 + 8.41\ )} = 0.748$$

And

$$P_{N_2} = X_{N_2} * P_{Total} = 0.748 * 192\ kPa = 143.6\ kPa$$

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

Self-assessment 7.9:

Dental nitrous oxide (N_2O) is delivered in a ratio of 1:1 with oxygen (O_2). If the partial pressure of oxygen in a tank is 29 Atm, what is the total pressure in the tank in Atm?

Strategy: Find the partial pressures of oxygen and nitrous oxide. Use Henry's Law to determine the total Pressure from the Partial Pressures.

Answer:

Key Equation:

$$P_{total} = P_A + P_B + P_C \ldots$$

Step 1: Find the partial pressure of the nitrous oxide.

The pressure of the oxygen and nitrous oxide are the same.

$$P_{O_2} = P_{N_2O} = 29\ Atm$$

Step 2: Find the total pressure in the system

$$P_{total} = P_{O_2} + P_{N_2O}$$

$$P_{total} = 29\ Atm + 29\ Atm$$

$$P_{total} = 58\ Atm$$

Self-assessment 7.10:

Nitrous oxide anesthetic can come premixed with oxygen in a ratio 30% oxygen to 70% N_2O. If the total pressure in a tank is 45 Atm, what is the partial pressure of the oxygen?

Answer:

Strategy: Use Henry's Law to and mol fractions determine the partial pressure of oxygen.

Key Equation:

$$P_{total} = X_A P_{total} + X_B P_{total} + X_c P_{total} \ldots$$

and

$$P_A = X_A P_{total}$$

Knowns: P_{total} = 45 Atm, X_{O2} = 0.30

Because the two gasses ratios are known, the mole fraction of each is just the decimal version of the percent.

For Oxygen, $P_{O_2} = X_{O_2} P_{total}$

$$P_{O_2} = (0.30) \times (45\ Atm)$$

$$P_{O_2} = 13.5\ Atm$$

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 $N_2(g) + 3H_2(g) \longrightarrow 2NH_3(g)$, 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, see **Figure 7.23**. 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.

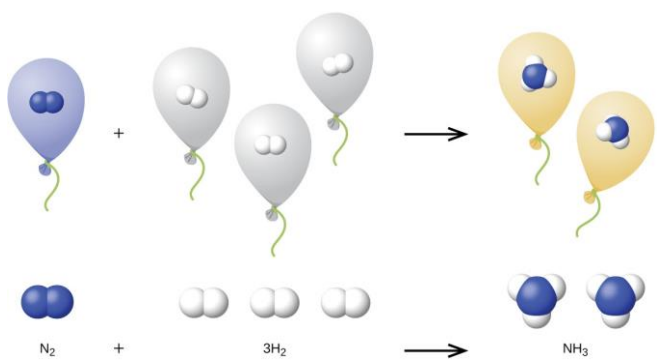


Figure 7.23 One volume of N_2 combines with three volumes of H_2 to form two volumes of NH_3.

Example 7.11

Reaction of Gases: Propane, $C_3H_8(g)$, is used in gas grills to provide the heat for cooking. What volume of $O_2(g)$ 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:

$$C_3H_8\ (g) + 5O_2(g) \rightarrow\ 3CO_2(g) + 4H_2O(l)$$
$$1\,\text{volume} + 5\,\text{volumes} \qquad 3\,\text{volumes} + 4\,\text{volumes}$$

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

$$2.7\ l\ C_3H_8 * \frac{5\ L\ O_2}{1\ L\ C_3H_8} = 13.5\ L\ O_2$$

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?

$$2C_2H_2\ +\ 5O_2\ \longrightarrow\ 4CO_2\ +\ 2H_2O$$

Answer: 3.34 tanks (2.34×10^4 L)

Example 7.12

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 $H_2(g)$, measured under the same conditions, was required to prepare this amount of ammonia by reaction with N_2?

$$\boldsymbol{N_2(g) + 3H_2(g)\ \rightarrow 2\ NH_3(g)}$$

Solution:

Because equal volumes of H_2 and NH_3 contain equal numbers of molecules and each three molecules of H_2 that react produce two molecules of NH_3, the ratio of the volumes of H_2 and NH_3 will be equal to 3:2. Two volumes of NH_3, in this case in units of billion ft^3, will be formed from three volumes of H_2:

$$683\ billion\ ft^3\ NH_3\ * \frac{3\ billion\ ft^3\ H_2}{2\ billion\ ft^3\ NH_3} = 1.02 *\ 10^3\ billion\ ft^3\ H_2$$

The manufacture of 683 billion ft^3 of NH_3 required 1020 billion ft^3 of H_2. (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 $O_2(g)$ measured at 25 °C and 760 torr is required to react with 17.0 L of ethylene, $C_2H_4(g)$, measured under the same conditions of temperature and pressure? The products are CO_2 and water vapor.

Answer: 51.0 L

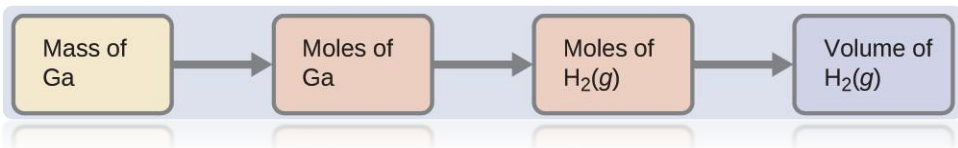
Example 7.13

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?

$$\mathbf{2\ Ga(s) + 6\ HCl\ (aq) \rightarrow 2GaCl_3(aq) + 3H_2(g)}$$

Solution:

To convert from the mass of gallium to the volume of $H_2(g)$, we need to do something like this:



The first two conversions are:

$$8.88\ Ga * \frac{1\ mol\ Ga}{69.723\ g\ Ga} * \frac{3\ mol\ H_2}{2\ mol\ Ga}\ m = 0.191\ mol\ H_2$$

Finally, we can use the ideal gas law:

$$V_2 = \frac{nRT}{P_2} = \frac{0.191\ mol * \ 0.08206\ \frac{L * atm}{mol\ K} * 300\ k}{0.951\ Atm} = \ 4.94\ L$$

Check Your Learning

Sulfur dioxide is an intermediate in the preparation of sulfuric acid. What volume of SO_2 at 343 °C and 1.21 atm is produced by burning l.00 kg of sulfur in oxygen?

Answer: 1.30×10^3 L

Self-assessment 7.11:

A stomach contains between 20 and 100 mL of hydrochloric acid at a pH of 1.5 to 3.5 (0.032 *M* to 3.16×10^{-4} *M*). If a stressed out nursing student treats his heart burn with an OTC antacid which contains 500 mg of calcium carbonate ($CaCO_3$) as the active ingredient. The chemical reaction is as follows:

$$CaCO_3(s) + 2\ HCl\ (aq) \rightarrow CO_2(g) + H_2O(l) + CaCl2\ (aq)$$

What volume of gas will need to exit the student? Assuming 75 mL of stomach acid at 0.032 *M*, temperature of 25 C, and 1 atm pressure.

Answer:

This is a limiting reactant type of problem, where the final answer is to be given in volume of gas. Strategy: Convert values to moles, then use the mole-mole ratio between the limiting reactant and H_2 to find moles of H_2. Use the ideal gas law to determine the volume of hydrogen.

Step one: Convert grams of $CaCO_3$ to moles using the molar mass

$$\frac{500\ mg\ CaCO_3}{1} \times \frac{1\ g}{1{,}000\ mg} \times \frac{1\ mol}{100.1\ g\ CaCO_3} = 4.995\ \times 10^{-3} mol\ CaCO_3$$

Step two: determine the moles of available HCl from volume and concentration.

$$moles = Volume \times Concentration$$

$$\frac{75\ mL\ HCl}{1} \times \frac{1\ L}{1{,}000\ mL} \times \frac{0.032\ mol\ HCl}{1\ L\ HCl} = 2.4\ \times 10^{-3} mol\ HCl$$

Step three: determine the limiting reactant, and limited number of moles of product using stoichiometric coefficients the balanced chemical equation.

$$\frac{4.995\ \times 10^{-3} mol\ CaCO_3}{1} \times \frac{1\ mol\ CO_2}{1\ mol\ CaCO_3} = 4.995\ \times 10^{-3} mol\ CO_2$$

$$\frac{2.4\ \times 10^{-3} mol\ HCl}{1} \times \frac{1\ mol\ CO_2}{2\ mol\ HCl} = 1.2\ \times 10^{-3} mol\ CO_2$$

Because the given amount of HCl produces fewer moles of product, it is the limiting reactant. The maximum number of moles of gas that that can be produced is therefore 1.2×10^{-3} mol of CO_2.

Step four: Use the ideal gas law to determine the volume of gas.

Key Equation:

$$PV = nRT$$

Knowns: P = 1 Atm, n = , R = 0.821 L*Atm/mol*k, T = 25.0 °C → 298 K

$$PV = nRT$$

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

$$V = \frac{(1.2\ \times 10^{-3} mol\ CO_2)\left(0.0821 \frac{L \times Atm}{mol \times K}\right)(298\ K)}{1\ Atm}$$

OR

$$V = \frac{1.2\ \times 10^{-3} mol\ CO_2}{1} \times \frac{0.0821\ L \times Atm}{mol\ \times K} \times \frac{298\ K}{1} \times \frac{1}{1\ Atm}$$

$$V = 0.0294\ L \quad or\ 29.4\ mL\ of\ CO_2$$

Portrait of a Chemist

Susan Solomon: Atmospheric and climate scientist Susan Solomon (**Figure 7.26**) 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 Medaille, 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 7.26 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)

7.4 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 7.31**).

- *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 balance the effect of increased collision forces due to the greater kinetic energy at the higher temperature.

- *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 7.31**).

- *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 7.31**).

- *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.

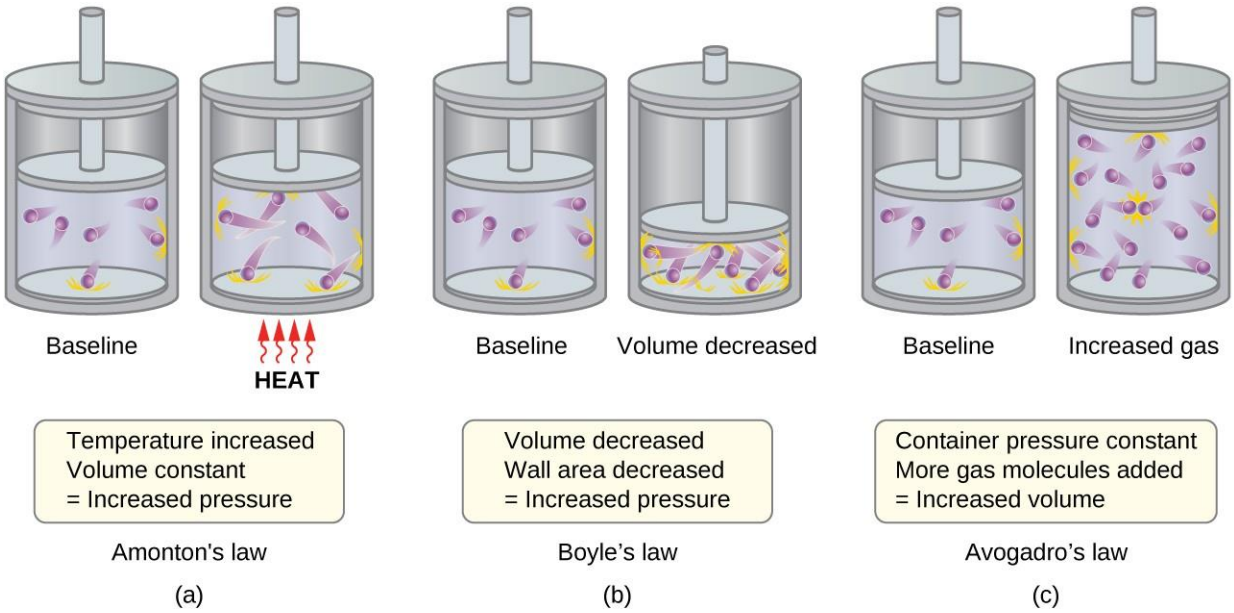


Figure 7.31 (a) When gas temperature increases, gas pressure increases due to increased force and frequency of molecular collisions. (b) When volume decreases, gas pressure increases due to increased frequency of molecular collisions. (c) When the amount of gas increases at a constant pressure, volume increases to yield a constant number of collisions per unit wall area per unit time.

7.5 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

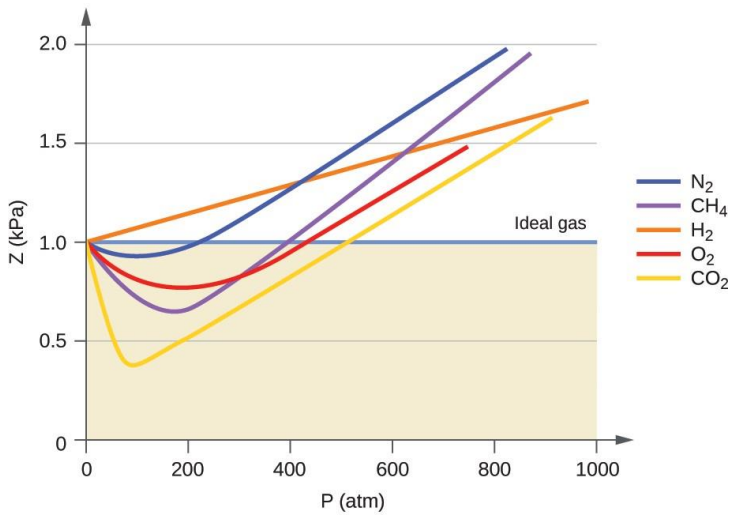
Thus far, the ideal gas law, $PV = nRT$, has been applied to a variety of different types of problems, ranging from reaction stoichiometry and empirical and molecular formula problems to determining the density and molar mass of a gas. As mentioned in the previous modules of this chapter, however, the 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:

$$Z = \frac{molar\ volume\ of\ gas\ at\ same\ T\ and\ P}{molar\ volume\ of\ ideal\ gas\ at\ same\ T\ and\ P} = \frac{PV_m}{RT}$$

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 7.35** shows plots of Z over a large pressure range for several common gases.

Figure 7.35 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 7.35**, 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 7.36**). 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.

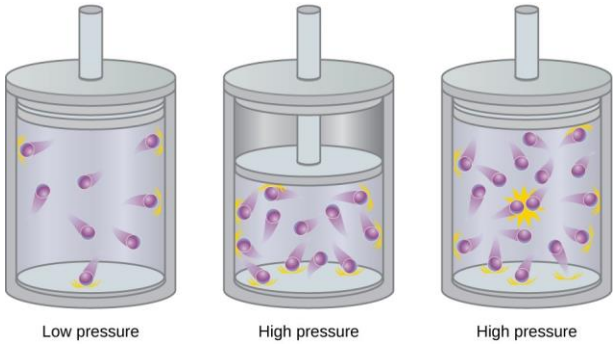


Figure 7.36 Raising the pressure of a gas increases the fraction of its volume that is occupied by the gas molecules and makes the gas less compressible.

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 7.37**). 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.

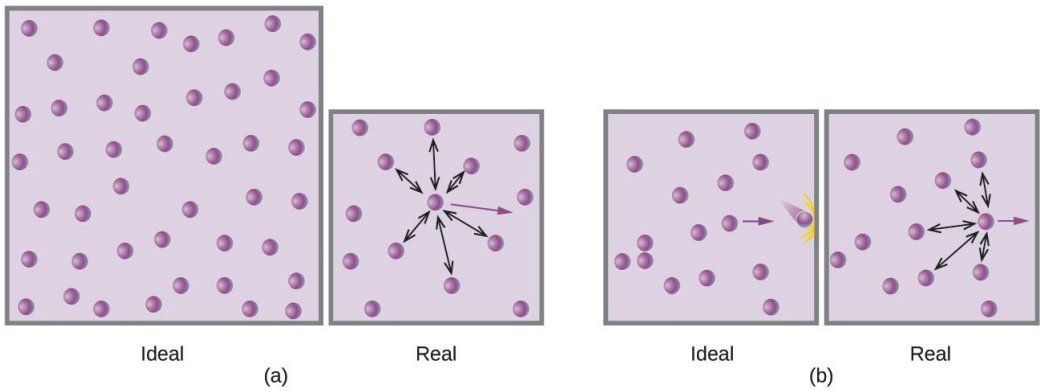


Figure 7.37 (a) Attractions between gas molecules serve to decrease the gas volume at constant pressure compared to an ideal gas whose molecules experience no attractive forces. (b) These attractive forces will decrease the force of collisions between the molecules and container walls, therefore reducing 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.

$$PV = nRT \longrightarrow \underbrace{\left(P + \frac{an^2}{V^2}\right)}_{\text{Correction for molecular attraction}} \underbrace{(V - nb)}_{\text{Correction for volume of molecules}} = nRT$$

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 7.3**.

Gas	*a* (L^2 atm/mol^2)	*b* (L/mol)
N_2	1.39	0.0391
O_2	1.36	0.0318
CO_2	3.59	0.0427
H_2O	5.46	0.0305
He	0.0342	0.0237
CCl_4	20.4	0.1383

Table 7.3 Values of van der Waals Constants for Some Common Gases

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.

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.

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 = 0.08206 L atm mol^{-1} K^{-1} or 8.314 L kPa mol^{-1} 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

partial pressure pressure exerted by an individual gas in a mixture

pascal (Pa) SI unit of pressure; 1 Pa = 1 N/m^2

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

pressure force exerted per unit area

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 atm is equivalent to 760 torr

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

- $PV = nRT$
- $P_{Total} = P_A + P_B + P_C + \ldots = \Sigma_i P_i$

Summary

7.1 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.

7.2 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.

7.3 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.

7.4 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.

7.5 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 these conditions.

Exercises

7.1 **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. Hg, 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?

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

13. Sometimes leaving a bicycle in the sun on a hot day will cause a blowout. Why?

14. Explain how the volume of the bubbles exhausted by a scuba diver (**Figure 7.16**) change as they rise to the surface, assuming that they remain intact.

15. One way to state Boyle's law is "All other things being equal, the pressure of a gas is inversely proportional to its volume." (a) What is the meaning of the term "inversely proportional?" (b) What are the "other things" that must

be equal?

16. An alternate way to state Avogadro's law is "All other things being equal, the number of molecules in a gas is directly proportional to the volume of the gas." (a) What is the meaning of the term "directly proportional?" (b) What are the "other things" that must be equal?

17. A spray can is used until it is empty except for the propellant gas, which has a pressure of 1344 torr at 23 °C. If the can is thrown into a fire (T = 475 °C), what will be the pressure in the hot can?

18. What is the temperature of an 11.2-L sample of carbon monoxide, CO, at 744 torr if it occupies 13.3 L at 55 °C and 744 torr?

19. A 2.50-L volume of hydrogen measured at –196 °C is warmed to 100 °C. Calculate the volume of the gas at the higher temperature, assuming no change in pressure.

20. A balloon inflated with three breaths of air has a volume of 1.7 L. At the same temperature and pressure, what is the volume of the balloon if five more same-sized breaths are added to the balloon?

21. A weather balloon contains 8.80 moles of helium at a pressure of 0.992 atm and a temperature of 25 °C at ground level. What is the volume of the balloon under these conditions?

22. The volume of an automobile air bag was 66.8 L when inflated at 25 °C with 77.8 g of nitrogen gas. What was the pressure in the bag in kPa?

23. How many moles of gaseous boron trifluoride, BF_3, are contained in a 4.3410-L bulb at 788.0 K if the pressure is 1.220 atm? How many grams of BF_3?

24. Iodine, I_2, is a solid at room temperature but sublimes (converts from a solid into a gas) when warmed. What is the temperature in a 73.3-mL bulb that contains 0.292 g of I_2 vapor at a pressure of 0.462 atm?

25. How many grams of gas are present in each of the following cases?

(a) 0.100 L of CO_2 at 307 torr and 26 °C

(b) 8.75 L of C_2H_4, at 378.3 kPa and 483 K

(c) 221 mL of Ar at 0.23 torr and –54 °C

26. A high altitude balloon is filled with 1.41×10^4 L of hydrogen at a temperature of 21 °C and a pressure of 745 torr. What is the volume of the balloon at a height of 20 km, where the temperature is –48 °C and the pressure is

63.1 torr?

27. A cylinder of medical oxygen has a volume of 35.4 L, and contains O_2 at a pressure of 151 atm and a temperature of 25 °C. What volume of O_2 does this correspond to at normal body conditions, that is, 1 atm and 37 °C?

28. A large scuba tank (**Figure 7.16**) with a volume of 18 L is rated for a pressure of 220 bar. The tank is filled at 20 °C and contains enough air to supply 1860 L of air to a diver at a pressure of 2.37 atm (a depth of 45 feet). Was the tank filled to capacity at 20 °C?

29. A 20.0-L cylinder containing 11.34 kg of butane, C_4H_{10}, was opened to the atmosphere. Calculate the mass of the gas remaining in the cylinder if it were opened and the gas escaped until the pressure in the cylinder was equal to the atmospheric pressure, 0.983 atm, and a temperature of 27 °C.

30. While resting, the average 70-kg human male consumes 14 L of pure O_2 per hour at 25 °C and 100 kPa. How many moles of O_2 are consumed by a 70 kg man while resting for 1.0 h?

31. A liter of methane gas, CH_4, at STP contains more atoms of hydrogen than does a liter of pure hydrogen gas, H_2, at STP. Using Avogadro's law as a starting point, explain why.

32. The effect of chlorofluorocarbons (such as CCl_2F_2) on the depletion of the ozone layer is well known. The use of substitutes, such as $CH_3CH_2F(g)$, for the chlorofluorocarbons, has largely corrected the problem. Calculate the volume occupied by 10.0 g of each of these compounds at STP:

(a) $CCl_2F_2(g)$

(b) $CH_3CH_2F(g)$

33. As 1 g of the radioactive element radium decays over 1 year, it produces 1.16×10^{18} alpha particles (helium nuclei). Each alpha particle becomes an atom of helium gas. What is the pressure in pascal of the helium gas produced if it occupies a volume of 125 mL at a temperature of 25 °C?

34. A balloon that is 100.21 L at 21 °C and 0.981 atm is released and just barely clears the top of Mount Crumpet in British Columbia. If the final volume of the balloon is 144.53 L at a temperature of 5.24 °C, what is the pressure experienced by the balloon as it clears Mount Crumpet?

35. If the temperature of a fixed amount of a gas is doubled at constant volume, what happens to the pressure?

36. If the volume of a fixed amount of a gas is tripled at constant temperature, what happens to the pressure?

7.3 Stoichiometry of Gaseous Substances, Mixtures, and Reactions

37. What is the density of laughing gas, dinitrogen monoxide, N_2O, at a temperature of 325 K and a pressure of 113.0 kPa?

38. Calculate the density of Freon 12, CF_2Cl_2, at 30.0 °C and 0.954 atm.

39. Which is denser at the same temperature and pressure, dry air or air saturated with water vapor? Explain.

40. A cylinder of $O_2(g)$ used in breathing by emphysema patients has a volume of 3.00 L at a pressure of 10.0 atm. If the temperature of the cylinder is 28.0 °C, what mass of oxygen is in the cylinder?

41. What is the molar mass of a gas if 0.0494 g of the gas occupies a volume of 0.100 L at a temperature 26 °C and a pressure of 307 torr?

42. What is the molar mass of a gas if 0.281 g of the gas occupies a volume of 125 mL at a temperature 126 °C and a pressure of 777 torr?

43. How could you show experimentally that the molecular formula of propene is C_3H_6, not CH_2?

44. The density of a certain gaseous fluoride of phosphorus is 3.93 g/L at STP. Calculate the molar mass of this fluoride and determine its molecular formula.

45. Consider this question: What is the molecular formula of a compound that contains 39% C, 45% N, and 16% H if 0.157 g of the compound occupies l25 mL with a pressure of 99.5 kPa at 22 °C?

(a) Outline the steps necessary to answer the question.

(b) Answer the question.

46. A 36.0–L cylinder of a gas used for calibration of blood gas analyzers in medical laboratories contains 350 g CO_2, 805 g O_2, and 4,880 g N_2. At 25 degrees C, what is the pressure in the cylinder in atmospheres?

47. A cylinder of a gas mixture used for calibration of blood gas analyzers in medical laboratories contains 5.0% CO_2, 12.0% O_2, and the remainder N_2 at a total pressure of 146 atm. What is the partial pressure of each component of this gas? (The percentages given indicate the percent of the total pressure that is due to each component.)

48. A sample of gas isolated from unrefined petroleum contains 90.0% CH_4, 8.9% C_2H_6, and 1.1% C_3H_8 at a total pressure of 307.2 kPa. What is the partial pressure of each component of this gas? (The percentages given indicate the percent of the total pressure that is due to each component.)

49. A mixture of 0.200 g of H_2, 1.00 g of N_2, and 0.820 g of Ar is stored in a closed container at STP. Find the volume of the container, assuming that the gases exhibit ideal behavior.

50. Most mixtures of hydrogen gas with oxygen gas are explosive. However, a mixture that contains less than 3.0
% O_2 is not. If enough O_2 is added to a cylinder of H_2 at 33.2 atm to bring the total pressure to 34.5 atm, is the mixture explosive?

51. A commercial mercury vapor analyzer can detect, in air, concentrations of gaseous Hg atoms (which are poisonous) as low as 2×10^{-6} mg/L of air. At this concentration, what is the partial pressure of gaseous mercury if the atmospheric pressure is 733 torr at 26 °C?

52. A sample of carbon monoxide was collected over water at a total pressure of 756 torr and a temperature of 18
°C. What is the pressure of the carbon monoxide? (See **Table 7.2** for the vapor pressure of water.)

53. In an experiment in a general chemistry laboratory, a student collected a sample of a gas over water. The volume of the gas was 265 mL at a pressure of 753 torr and a temperature of 27 °C. The mass of the gas was 0.472 g. What was the molar mass of the gas?

54. Joseph Priestley first prepared pure oxygen by heating mercuric oxide, HgO:

$$2HgO(s) \rightarrow 2Hg(l) + O_2(g)$$

(a) Outline the steps necessary to answer the following question: What volume of O_2 at 23 °C and 0.975 atm is produced by the decomposition of 5.36 g of HgO?

(b) Answer the question.

55. Cavendish prepared hydrogen in 1766 by the novel method of passing steam through a red-hot gun barrel:

$$4H_2O(g) + 3Fe(s) \rightarrow Fe_3O_4(s) + 4H_2(g)$$

(a) Outline the steps necessary to answer the following question: What volume of H_2 at a pressure of 745 torr and a temperature of 20 °C can be prepared from the reaction of 15.O g of H_2O?

(b) Answer the question.

56. The chlorofluorocarbon CCl_2F_2 can be recycled into a different compound by reaction with hydrogen to produce $CH_2F_2(g)$, a compound useful in chemical manufacturing:

$$CCl_2F_2(g) + 4H_2(g) \rightarrow CH_2F_2(g) + 2HCl(g)$$

(a) Outline the steps necessary to answer the following question: What volume of hydrogen at 225 atm and 35.5 °C would be required to react with 1 ton (1.000×10^3 kg) of CCl_2F_2?

(b) Answer the question.

57. Automobile air bags are inflated with nitrogen gas, which is formed by the decomposition of solid sodium azide (NaN_3). The other product is sodium metal. Calculate the volume of nitrogen gas at 27 °C and 756 torr formed by the decomposition of 125 g of sodium azide.

58. Lime, CaO, is produced by heating calcium carbonate, $CaCO_3$; carbon dioxide is the other product.

(a) Outline the steps necessary to answer the following question: What volume of carbon dioxide at 875 K and 0.966 atm is produced by the decomposition of 1 ton (1.000×10^3 kg) of calcium carbonate?

(b) Answer the question.

59. Before small batteries were available, carbide lamps were used for bicycle lights. Acetylene gas, C_2H_2, and solid calcium hydroxide were formed by the reaction of calcium carbide, CaC_2, with water. The ignition of the acetylene gas provided the light. Currently, the same lamps are used by some cavers, and calcium carbide is used to produce acetylene for carbide cannons.

(a) Outline the steps necessary to answer the following question: What volume of C_2H_2 at 1.005 atm and 12.2 °C is formed by the reaction of 15.48 g of CaC_2 with water?

(b) Answer the question.

60. Calculate the volume of oxygen required to burn 12.00 L of ethane gas, C_2H_6, to produce carbon dioxide and water, if the volumes of C_2H_6 and O_2 are measured under the same conditions of temperature and pressure.

61. What volume of O_2 at STP is required to oxidize 8.0 L of NO at STP to NO_2? What volume of NO_2 is produced at STP?

62. Consider the following questions:

(a) What is the total volume of the $CO_2(g)$ and $H_2O(g)$ at 600 °C and 0.888 atm produced by the combustion of 1.00 L of $C_2H_6(g)$ measured at STP?

(b) What is the partial pressure of H_2O in the product gases?

63. Methanol, CH_3OH, is produced industrially by the following reaction:

$$CO(g) + 2H_2(g) \xrightarrow{\text{copper catalyst, 300 °C, 300 atm}} CH_3OH(g)$$

Assuming that the gases behave as ideal gases, find the ratio of the total volume of the reactants to the final volume.

64. What volume of oxygen at 423.0 K and a pressure of 127.4 kPa is produced by the decomposition of 129.7 g of BaO_2 to BaO and O_2?

65. A 2.50-L sample of a colorless gas at STP decomposed to give 2.50 L of N_2 and 1.25 L of O_2 at STP. What is the colorless gas?

66. Ethanol, C_2H_5OH, is produced industrially from ethylene, C_2H_4, by the following sequence of reactions:

$$3C_2H_4 + 2H_2SO_4 \longrightarrow C_2H_5HSO_4 + (C_2H_5)_2SO_4$$

$$C_2H_5HSO_4 + (C_2H_5)_2SO_4 + 3H_2O \longrightarrow 3C_2H_5OH + 2H_2SO_4$$

What volume of ethylene at STP is required to produce 1.000 metric ton (1000 kg) of ethanol if the overall yield of ethanol is 90.1%?

67. One molecule of hemoglobin will combine with four molecules of oxygen. If 1.0 g of hemoglobin combines with 1.53 mL of oxygen at body temperature (37 °C) and a pressure of 743 torr, what is the molar mass of hemoglobin?

68. A sample of a compound of xenon and fluorine was confined in a bulb with a pressure of 18 torr. Hydrogen was added to the bulb until the pressure was 72 torr. Passage of an electric spark through the mixture produced Xe and HF. After the HF was removed by reaction with solid KOH, the final pressure of xenon and unreacted hydrogen in the bulb was 36 torr. What is the empirical formula of the xenon fluoride in the original sample? (Note: Xenon fluorides contain only one xenon atom per molecule.)

7.3 **The Kinetic-Molecular Theory**

69. Using the postulates of the kinetic molecular theory, explain why a gas uniformly fills a container of any shape.

70. Can the speed of a given molecule in a gas double at constant temperature? Explain your answer.

71. Describe what happens to the average kinetic energy of ideal gas molecules when the conditions are changed as follows:

(a) The pressure of the gas is increased by reducing the volume at constant temperature.

(b) The pressure of the gas is increased by increasing the temperature at constant volume.

(c) The average velocity of the molecules is increased by a factor of 2.

72. The distribution of molecular velocities in a sample of helium is shown in **Figure 7.34**. If the sample is cooled, will the distribution of velocities look more like that of H_2 or of H_2O? Explain your answer.

73. What is the ratio of the average kinetic energy of a SO_2 molecule to that of an O_2 molecule in a mixture of two gases? What is the ratio of the root mean square speeds, u_{rms}, of the two gases?

74. A 1-L sample of CO initially at STP is heated to 546 K, and its volume is increased to 2 L.

(a) What effect do these changes have on the number of collisions of the molecules of the gas per unit area of the container wall?

(b) What is the effect on the average kinetic energy of the molecules?

(c) What is the effect on the root mean square speed of the molecules?

75. The root mean square speed of H_2 molecules at 25 °C is about 1.6 km/s. What is the root mean square speed of a N_2 molecule at 25 °C?

76. Answer the following questions:

(a) Is the pressure of the gas in the hot air balloon shown at the opening of this chapter greater than, less than, or equal to that of the atmosphere outside the balloon?

(b) Is the density of the gas in the hot air balloon shown at the opening of this chapter greater than, less than, or equal to that of the atmosphere outside the balloon?

7.5 **Non-Ideal Gas Behavior**

77. Under which of the following sets of conditions does a real gas behave most like an ideal gas, and for which conditions is a real gas expected to deviate from ideal behavior? Explain.

(a) high pressure, small volume

(b) high temperature, low pressure

(c) low temperature, high pressure