

CHAPTER 12: GASES

Enhanced Introductory College Chemistry

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Chapter Contents

- 12.1 Gas Pressure
- 12.2 Relating Pressure, Volume, Amount, and Temperature: The Ideal Gas Law
- 12.3 Effusion and Diffusion of Gases
- 12.4 Stoichiometry of Gaseous Substances, Mixtures, and Reactions
- 12.5 The Kinetic-Molecular Theory
- 12.6 Non-Ideal Gas Behaviour
- Summary
- Review

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Please visit the web version of Enhanced Introductory College Chemistry (<https://ecampusontario.pressbooks.pub/enhancedchemistry/>) to access the complete book, interactive activities and ancillary resources.

In this chapter, you will learn about

- The relationships of Pressure, Temperature and Volume as they pertain to gases
- The nature of gas particle movement

To better support your learning, you should be familiar with the following concepts before starting this chapter:

- Mathematics
- Stoichiometry



Figure 12a 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: work by Elif Tütüncü, CC BY-SA 4.0)

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 12.a) 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 behaviour, providing the first mathematical descriptions of the behaviour 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 behaviour of gases. The results of these analyses will show us the limitations of the theory and how to improve on it.

Attribution & References

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(<https://openstax.org/books/chemistry/pages/1-introduction>)

12.1 GAS PRESSURE

Learning Objectives

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 12.1a). 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.

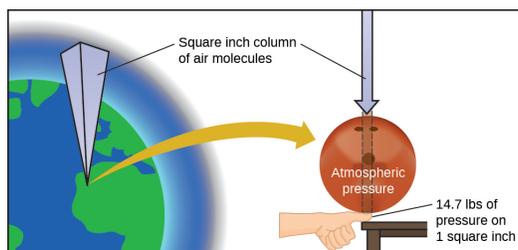


Figure 12.1a The atmosphere above us exerts a large pressure on objects at the surface of the earth, roughly equal to the weight of a bowling ball pressing on an area the size of a human thumbnail (credit: *Chemistry (OpenStax)*, CC BY 4.0).

Watch Railroad tank car vacuum implosion (1 min) (https://www.youtube.com/watch?v=Zz95_VvTxZM)

Watch Crush a 55 gallon drum with air pressure (4 mins) (https://www.youtube.com/watch?v=c5_ho2sc0fc)

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

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

Let's apply this concept to determine which would be more likely to fall through thin ice in Figure 12.1b—the elephant or the figure skater? A large African elephant can weigh 7 tons, supported on four feet, each with a diameter of about 1.5 ft (footprint area of 250 in^2), so the pressure exerted by each foot is about 14 lb/in^2 :

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

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

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

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

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



(a)



(b)

Figure 12.1b Although (a) an elephant's weight is large, creating a very large force on the ground, (b) the figure skater exerts a much higher pressure on the ice due to the small surface area of her skates. (credit a: modification of work by Guido da Rozze, CC BY 2.0; credit b: modification of work by Ryosuke Yagi, CC BY 2.0)

Watch Describing the invisible properties of gas – Brian Bennett (4 mins)

(https://www.youtube.com/watch?v=EHxdVtygP1g&feature=emb_imp_woyt)

Exercise 12.1a

Practice using the following PhET simulation: Gases Intro (https://phet.colorado.edu/sims/html/gases-intro/latest/gases-intro_en.html)

The SI unit of pressure is the **pascal (Pa)**, with $1 \text{ Pa} = 1 \text{ N/m}^2$, where N is the newton, a unit of force defined as 1 kg m/s^2 . One pascal is a small pressure; in many cases, it is more convenient to use units of kilopascal ($1 \text{ kPa} = 1000 \text{ Pa}$) or bar ($1 \text{ bar} = 100,000 \text{ Pa}$). In the United States, pressure is often measured in pounds of force on an area of one square inch—**pounds per square inch (psi)**—for example, in car tires. Pressure can also be measured using the unit **atmosphere (atm)**, which originally represented the average sea level air pressure at the approximate latitude of Paris (45°). Table 12.1a provides some information on these and a few other common units for pressure measurements

Table 12.1a Pressure Units

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	$1 \text{ torr} = \frac{1}{760} \text{ atm}$ named after Evangelista Torricelli, inventor of the barometer
millimeters of mercury (mm Hg)	1 mm Hg ~1 torr

Exercise 12.1b

Check Your Learning Exercise (Text Version)

Canadian tire pressure gauges are marked in units of kilopascals. The reading on this type of pressure gauge for 32 psi will be

Check Your Answer¹

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Example 12.1a

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:

- torr
- atm
- kPa
- mbar

Solution

This is a unit conversion problem. The relationships between the various pressure units are given in Table 12.1a.

- $29.2 \text{ in Hg} \times \frac{25.4 \text{ mm}}{1 \text{ in}} \times \frac{1 \text{ torr}}{1 \text{ mm Hg}} = 742 \text{ torr}$
- $742 \text{ torr} \times \frac{1 \text{ atm}}{760 \text{ torr}} = 0.976 \text{ atm}$
- $742 \text{ torr} \times \frac{101.325 \text{ kPa}}{760 \text{ torr}} = 98.9 \text{ kPa}$
- $98.9 \text{ kPa} \times \frac{1000 \text{ Pa}}{1 \text{ kPa}} \times \frac{1 \text{ bar}}{100,000 \text{ Pa}} \times \frac{1000 \text{ mbar}}{1 \text{ bar}} = 989 \text{ mbar}$

Exercise 12.1c

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

Check Your Answer²

We can measure atmospheric pressure, the force exerted by the atmosphere on the earth's surface, with a **barometer** (Figure 12.1d). 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.

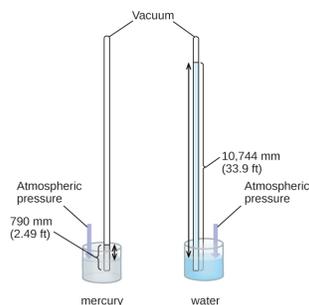


Figure 12.1d In a barometer, the height, h , of the column of liquid is used as a measurement of the air pressure. Using very dense liquid mercury (left) permits the construction of reasonably sized barometers, whereas using water (right) would require a barometer more than 30 feet tall (credit: *Chemistry (OpenStax)*, CC BY 4.0).

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

$$p = h\rho g$$

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

Exercise 12.1d

Check Your Learning Exercise (Text Version)

Why should you roll or belly-crawl rather than walk across a thinly-frozen pond?

Check Your Answer³

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Example 12.1b

Calculation of Barometric Pressure

Show the calculation supporting the claim that atmospheric pressure near sea level corresponds to the pressure exerted by a column of mercury that is about 760 mm high. The density of mercury = 13.6 g/cm³.

Solution

The hydrostatic pressure is given by $p = h\rho g$, with $h = 760$ mm, $\rho = 13.6$ g/cm³, and $g = 9.81$ m/s². Plugging these values into the equation and doing the necessary unit conversions will give us the value we seek. (Note: We are expecting to find a pressure of ~101,325 Pa:)

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

Exercise 12.1e

Calculate the height of a column of water at 25 °C that corresponds to normal atmospheric pressure. The density of water at this temperature is 1.0 g/cm³.

Check Your Answer⁴

Exercise 12.1f

Check Your Learning Exercise (Text Version)

A typical barometric pressure in Denver, Colorado, is 615 mm Hg. What is this pressure in atmospheres and kilopascals?

Check Your Answer⁵

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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 12.1e) 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.

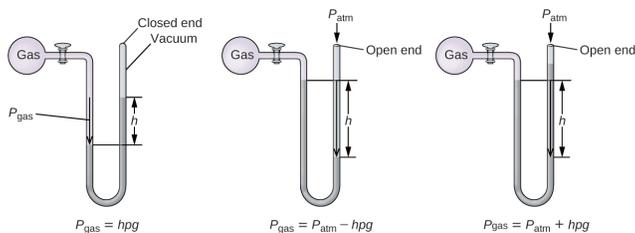


Figure 12.1e A manometer can be used to measure the pressure of a gas. The (difference in) height between the liquid levels (h) is a measure of the pressure. Mercury is usually used because of its large density (credit: *Chemistry (OpenStax)*, CC BY 4.0).

Exercise 12.1g

Check Your Learning Exercise (Text Version)

The pressure of a sample of gas is measured at sea level with an open-end mercury manometer and height (h) in open end is measured as 13.7cm below the gas height in the closed end. Assuming atmospheric pressure is 760.0 mm Hg, determine the pressure of the gas in

- mm Hg
- atm
- kPa

Check Your Answer⁶

Source: “Exercise 12.1g” is adapted from “8.1 Example 4” in *General Chemistry 1 & 2*, a derivative of *Chemistry (Open Stax)* by Paul Flowers, Klaus Theopold, Richard Langley & William R. Robinson, licensed under CC BY 4.0.

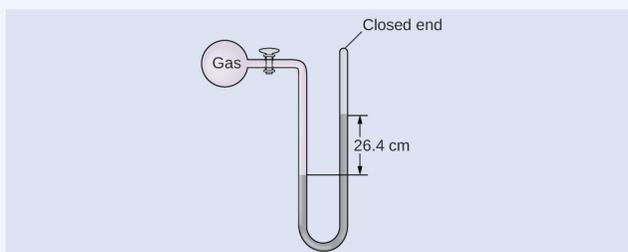
Example 12.1c

Calculation of Pressure Using a Closed-End Manometer

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

- torr

- b. Pa
c. bar



Solution

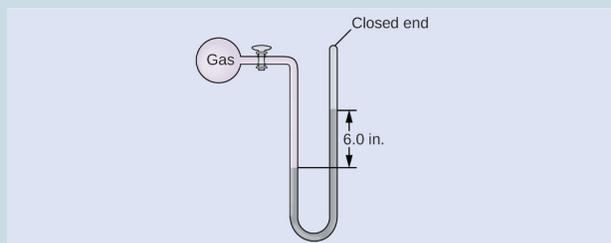
The pressure of the gas is equal to a column of mercury of height 26.4 cm. (The pressure at the bottom horizontal line is equal on both sides of the tube. The pressure on the left is due to the gas and the pressure on the right is due to 26.4 cm Hg, or mercury.) We could use the equation $p = h\rho g$ as in Example 12.1b, but it is simpler to just convert between units using Table 12.1a.

$$\begin{aligned} \text{a. } & 26.4 \text{ cm Hg} \times \frac{10 \text{ mm Hg}}{1 \text{ mm Hg}} \times \frac{1 \text{ torr}}{1 \text{ mm Hg}} = 264 \text{ torr} \\ \text{b. } & 264 \text{ torr} \times \frac{1 \text{ atm}}{760 \text{ torr}} \times \frac{101,325 \text{ Pa}}{1 \text{ atm}} = 35,200 \text{ Pa} \\ \text{c. } & 35,200 \text{ Pa} \times \frac{1 \text{ bar}}{100,000 \text{ Pa}} = 0.352 \text{ bar} \end{aligned}$$

Exercise 12.1h

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

- a. torr
b. Pa
c. bar



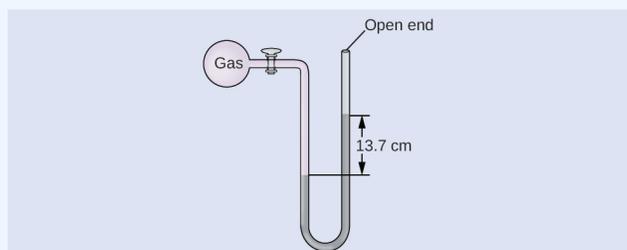
Check Your Answer⁷

Example 12.1d

Calculation of Pressure Using an Open-End Manometer

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

- mm Hg
- atm
- kPa



Solution

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

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

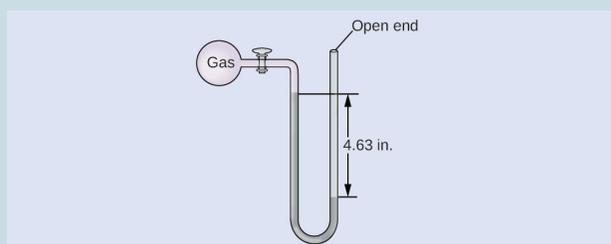
$$\text{b. } 897 \text{ mm Hg} \times \frac{1 \text{ atm}}{760 \text{ mm Hg}} = 1.18 \text{ atm}$$

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

Exercise 12.1i

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

- mm Hg
- atm
- kPa



Check Your Answer⁸

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 12.1f). 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 millimetres of mercury (mm Hg).

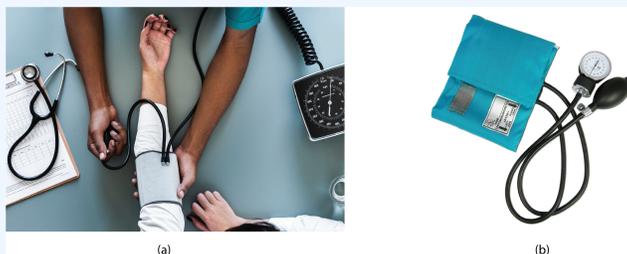


Figure 12.1f (a) A medical technician prepares to measure a patient's blood pressure with a sphygmomanometer. (b) A typical sphygmomanometer uses a valved rubber bulb to inflate the cuff and a diaphragm gauge to measure pressure. (credit a: work by rawpixel.com, CC0; credit b: work by Medisave UK, CC BY 2.0)

METEOROLOGY, CLIMATOLOGY, AND ATMOSPHERIC SCIENCE

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

Weather forecasts are the result of thousands of measurements of air pressure, temperature, and the like, which are compiled, modelled, and analyzed in weather centres worldwide.

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

The atmosphere is the gaseous layer that surrounds a planet. Earth's atmosphere, which is roughly 100–125 km thick, consists of roughly 78.1% nitrogen and 21.0% oxygen, and can be subdivided further into the regions shown in Figure 12.1h: the exosphere (furthest from earth, > 700 km above sea level), the thermosphere (80–700 km), the mesosphere (50–80 km), the stratosphere (second lowest level of our atmosphere, 12–50 km above sea level), and the troposphere (up to 12 km above sea level, roughly 80% of the earth's atmosphere by mass and the layer where most weather events originate). As you go higher in the troposphere, air density and temperature both decrease.

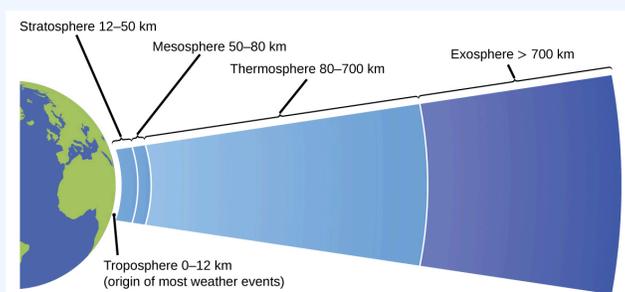


Figure 12.1g Earth's atmosphere has five layers: the troposphere, the stratosphere, the mesosphere, the thermosphere, and the exosphere.

Climatology is the study of the climate, averaged weather conditions over long time periods, using atmospheric data. However, climatologists study patterns and effects that occur over decades, centuries, and millennia, rather than shorter time frames of hours, days, and weeks like meteorologists. Atmospheric science is an even broader field, combining meteorology, climatology, and other scientific disciplines that study the atmosphere (credit: *Chemistry (OpenStax)*, CC BY 4.0).

Links to Interactive Learning Tools

Explore Pressure Concepts (<https://www.physicsclassroom.com/Concept-Builders/Chemistry/Pressure-Concepts>) from the Physics Classroom. (<https://www.physicsclassroom.com/>)

Key Equations

- $P = \frac{F}{A}$
- $p = h\rho g$

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Notes

1. 2.2×10^2 kPa
2. 0.974 atm; 740 mm Hg; 98.7 kPa; 0.987 bar
3. Lying down distributes your weight over a larger surface area, exerting less pressure on the ice compared to standing up. If you exert less pressure, you are less likely to break through thin ice.
4. 10.3 m
5. 0.809 atm and 82.0 kPa
6. (a) 623 mm Hg; (b) 0.820 atm; (c) 83.1 kPa
7. (a) ~150 torr; (b) ~20,000 Pa; (c) ~0.20 bar
8. (a) 642 mm Hg; (b) 0.845 atm; (c) 85.6 kPa

12.2 RELATING PRESSURE, VOLUME, AMOUNT, AND TEMPERATURE: THE IDEAL GAS LAW

Learning Objectives

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 12.2a), a number of scientists established the relationships between the macroscopic physical properties of gases, that is, pressure, volume, temperature, and amount of gas. Although their measurements were not precise by today's standards, they were able to determine the mathematical relationships between pairs of these variables (e.g., pressure and temperature, pressure and volume) that hold for an *ideal gas*—a hypothetical construct that real gases approximate under certain conditions. Eventually, these individual laws were combined into a single equation—the *ideal gas law*—that relates gas quantities for gases and is quite accurate for low pressures and moderate temperatures. We will consider the key developments in individual relationships (for pedagogical reasons not quite in historical order), then put them together in the ideal gas law.

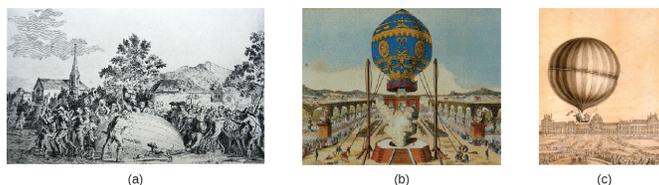


Figure 12.2a In 1783, the first (a) hydrogen-filled balloon flight, (b) manned hot air balloon flight, and (c) manned hydrogen-filled balloon flight occurred. When the hydrogen-filled balloon depicted in (a) landed, the frightened villagers of Gonesse reportedly destroyed it with pitchforks and knives. The launch of the latter was reportedly viewed by 400,000 people in Paris. (credit: a) work by unknown, PD; b) work by Claude Louis Desrais, PD; c) work by unknown, digitally enhanced by RawPixel, CC BY-SA 4.0)

Pressure and Temperature: 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 12.2b) and the pressure increases.

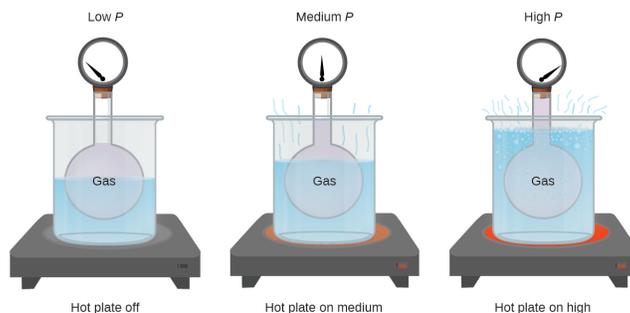


Figure 12.2b The effect of temperature on gas pressure: When the hot plate is off, the pressure of the gas in the sphere is relatively low. As the gas is heated, the pressure of the gas in the sphere increases (credit: Chemistry (OpenStax), CC BY 4.0).

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 12.2c. We find that temperature and pressure are linearly related, and if the temperature is on the kelvin scale, then P and T are directly proportional (again, when *volume and moles of gas are held constant*); if the temperature on the kelvin scale increases by a certain factor, the gas pressure increases by the same factor.

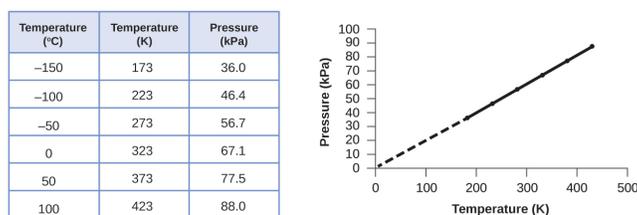


Figure 12.2c For a constant volume and amount of air, the pressure and temperature are directly proportional, provided the temperature is in kelvin. (Measurements cannot be made at lower temperatures because of the condensation of the gas.) When this line is extrapolated to lower pressures, it reaches a pressure of 0 at $-273\text{ }^{\circ}\text{C}$, which is 0 on the kelvin scale and the lowest possible temperature, called absolute zero (credit: *Chemistry (OpenStax)*, CC BY 4.0).

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' law** or **Gay-Lussac's law**. Under either name, it states that *the pressure of a given amount of gas is directly proportional to its temperature on the kelvin scale when the volume is held constant*. Mathematically, this can be written:

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

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

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

Example 12.2a

Predicting Change in Pressure with Temperature

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

- On the can is the warning “Store only at temperatures below $120\text{ }^{\circ}\text{F}$ ($48.8\text{ }^{\circ}\text{C}$). 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 can of hair spray is used until it is empty except for the propellant, isobutane gas.

- 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'/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:

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

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

Exercise 12.2a

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?

Check Your Answer¹

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.

Watch Liquid Nitrogen Experiments: The Balloon (3 mins) (<https://www.youtube.com/watch?v=ZgT'TUuJZAFs>)

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 .

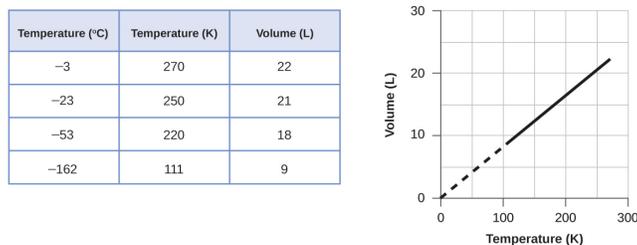


Figure 12.2d The volume and temperature are linearly related for 1 mole of methane gas at a constant pressure of 1 atm. If the temperature is in kelvin, volume and temperature are directly proportional. The line stops at 111 K because methane liquefies at this temperature; when extrapolated, it intersects the graph's origin, representing a temperature of absolute zero (credit: *Chemistry (OpenStax)*, CC BY 4.0).

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

Mathematically, this can be written as:

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

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

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

Example 12.2b

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 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 $^{\circ}\text{C}$ into K we have:

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

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

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

Exercise 12.2b

A sample of oxygen, O_2 , occupies 32.2 mL at 30°C and 452 torr. What volume will it occupy at -70°C and the same pressure?

Check Your Answer²

Example 12.2c

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:

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

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

Subtracting 273.15 from 239.8 K, we find that the temperature of the boiling ammonia on the Celsius scale is $-33.4 \text{ }^\circ\text{C}$.

Exercise 12.2c

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?

Check Your Answer³

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 $25 \text{ }^\circ\text{C}$. 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

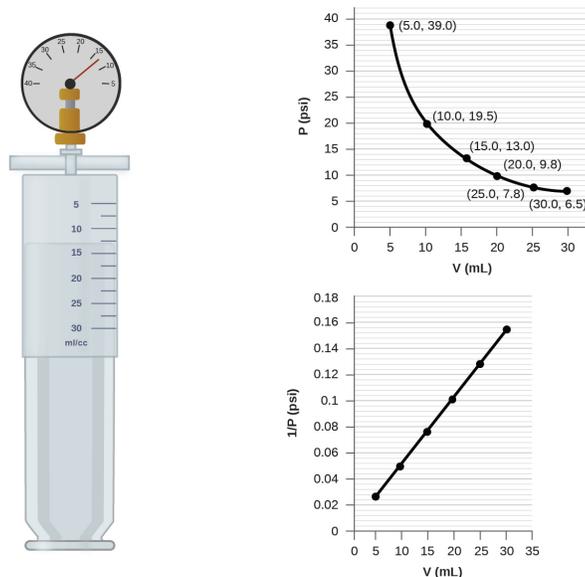


Figure 12.2e. When a gas occupies a smaller volume, it exerts a higher pressure; when it occupies a larger volume, it exerts a lower pressure (assuming the amount of gas and the temperature do not change). Since P and V are inversely proportional, a graph of $1/P$ vs. V is linear (credit: *Chemistry (OpenStax)*, CC BY 4.0).

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

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

with k being a constant. Graphically, this relationship is shown by the straight line that results when plotting the inverse of the pressure ($\frac{1}{P}$) versus the volume (V), or the inverse of volume ($\frac{1}{V}$) versus the pressure (P).

Graphs with curved lines are difficult to read accurately at low or high values of the variables, and they are more difficult to use in fitting theoretical equations and parameters to experimental data. For those reasons, scientists often try to find a way to “linearize” their data. If we plot P versus V , we obtain a hyperbola (see Figure 12.2f).

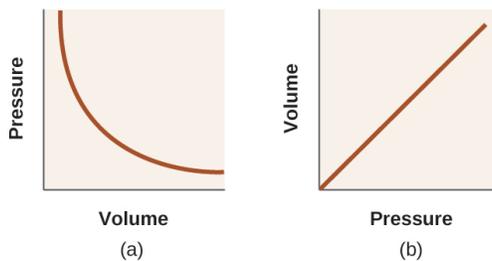


Figure 12.2f The relationship between pressure and volume is inversely proportional. (a) The graph of P vs. V is a hyperbola, whereas (b) the graph of $(1/P)$ vs. V is linear (credit: *Chemistry (OpenStax)*, CC BY 4.0).

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 12.2d

Volume of a Gas Sample

The sample of gas in Figure 12.2e 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:

- the P - V graph in Figure 12.2e
- the $\frac{1}{P}$ vs. V graph in Figure 12.2e
- the Boyle's law equation

Comment on the likely accuracy of each method.

Solution

- Estimating from the P - V graph gives a value for P somewhere around 27 psi.
- Estimating from the $\frac{1}{P}$ versus V graph give a value of about 26 psi.
- 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:

$P_1V_1 = P_2V_2$ or $13.0 \text{ psi} \times 15.0 \text{ mL} = P_2 \times 7.5 \text{ mL}$ Solving:

$$P_2 = \frac{13.0 \text{ psi} \times 15.0 \text{ mL}}{7.5 \text{ mL}} = 26 \text{ psi}$$

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.

Exercise 12.2d

The sample of gas in Figure 12.2e 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:

- the P - V graph in Figure 12.2e
- the $\frac{1}{P}$ vs. V graph in Figure 12.2e
- the Boyle's law equation

Comment on the likely accuracy of each method.

Check Your Answer⁴

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 12.2g).

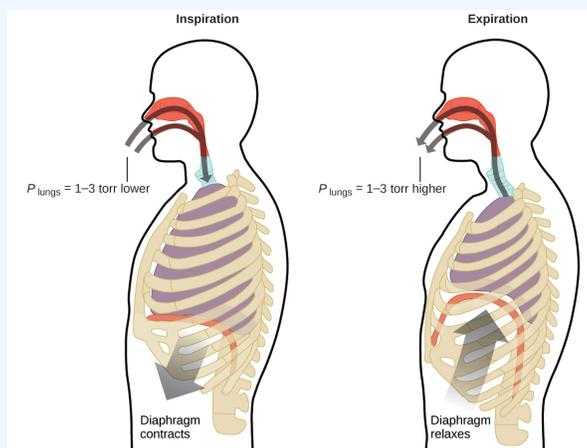


Figure 12.2g Breathing occurs because expanding and contracting lung volume creates small pressure differences between your lungs and your surroundings, causing air to be drawn into and forced out of your lungs (credit: Chemistry (OpenStax), CC BY 4.0).

Moles of Gas and Volume: Avogadro's Law

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

In equation form, this is written as:

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

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

Exercise 12.2e

Practice using the following PhET simulation: Gas Properties (https://phet.colorado.edu/sims/html/gas-properties/latest/gas-properties_en.html)

The Ideal Gas Law

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

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

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

$$PV = nRT$$

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

Gases whose properties of P , V , and T are accurately described by the ideal gas law (or the other gas laws) are said to exhibit *ideal behaviour* 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 behaviour, 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* behaviour observed for many gases at relatively high pressures and low temperatures.

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

Example 12.2e

Using the Ideal Gas Law

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

Solution

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

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

Converting into the “right” units:

$$n = 655 \text{ g } \text{CH}_4 \times \frac{1 \text{ mol}}{16.043 \text{ g } \text{CH}_4} = 40.8 \text{ mol}$$

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

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

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

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

Exercise 12.2f

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.

Check Your Answer⁵

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

Example 12.2f

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 12.2h). If the water temperature is 27 °C, how many litres 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 12.2h Scuba divers use compressed air to breathe while underwater (credit: work by Subro89, CC BY-SA 4.0).

Solution

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

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

Solving for V_2 :

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

(Note: Be advised that this particular example is one in which the assumption of ideal gas behaviour 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.)

Exercise 12.2g

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.

Check Your Answer⁶

The Interdependence between Ocean Depth and Pressure in Scuba Diving

Whether scuba diving at the Great Barrier Reef in Australia (shown in Figure 12.2i) or in the Caribbean, divers must understand how pressure affects a number of issues related to their comfort and safety.



Figure 12.2i 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: work by Kyle Taylor, CC BY 2.0)

Pressure increases with ocean depth, and the pressure changes most rapidly as divers reach the surface. The pressure a diver experiences is the sum of all pressures above the diver (from the water and the air). Most pressure measurements are given in units of atmospheres, expressed as “atmospheres absolute” or ATA in the diving community: Every 33 feet of salt water represents 1 ATA of pressure in addition to 1 ATA of pressure from the atmosphere at sea level. As a diver descends, the increase in pressure causes the body’s air pockets in the ears and lungs to compress; on the ascent, the decrease in pressure causes these air pockets to expand, potentially rupturing eardrums or bursting the lungs. Divers must therefore undergo equalization by adding air to body airspaces on the descent by

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

Watch The ABC's of gas: Avogadro, Boyle, Charles – Brian Bennett (<https://www.youtube.com/watch?v=BY9VGS2eXas>)

Standard Conditions of Temperature and Pressure

We have seen that the volume of a given quantity of gas and the number of molecules (moles) in a given volume of gas vary with changes in pressure and temperature. Chemists sometimes make comparisons against a **standard temperature and pressure (STP)** for reporting properties of gases: 273.15 K and 1 atm (101.325 kPa). At STP, an ideal gas has a volume of about 22.4 L—this is referred to as the **standard molar volume** (Figure 12.2j).

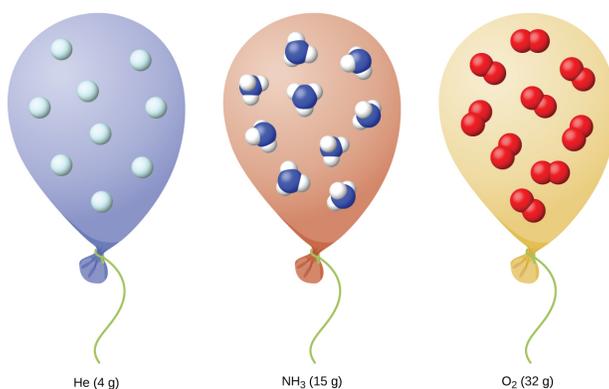


Figure 12.2j Since the number of moles in a given volume of gas varies with pressure and temperature changes, chemists use standard temperature and pressure (273.15 K and 1 atm or 101.325 kPa) to report properties of gases (credit: *Chemistry (OpenStax)*, CC BY 4.0).

Exercise 12.2h

Check Your Learning Exercise (Text Version)

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 ($T = 475\text{ °C}$), what will be the pressure in the hot can?

Check Your Answer⁷

Source: “Exercise 12.2h” is adapted from “Exercise 8.2-10” in General Chemistry 1 & 2, a derivative of Chemistry (Open Stax) by Paul Flowers, Klaus Theopold, Richard Langley & William R. Robinson, licensed under CC BY 4.0.

Links to Interactive Learning Tools

Explore Volume-Temperature Gas Law (<https://www.physicsclassroom.com/Concept-Builders/Chemistry/Volume-Temperature>) from the Physics Classroom (<https://www.physicsclassroom.com/>).

Explore Pressure-Volume Gas Law (<https://www.physicsclassroom.com/Concept-Builders/Chemistry/Pressure-Volume>) from the Physics Classroom (<https://www.physicsclassroom.com/>).

Explore Pressure-Temperature Gas Law (<https://www.physicsclassroom.com/Concept-Builders/Chemistry/Pressure-Temperature>) from the Physics Classroom (<https://www.physicsclassroom.com/>).

Key Equations

- $PV = nRT$

Attribution & References

Except where otherwise noted, this page is adapted by JR van Haarlem from “9.2 Relating Pressure, Volume,

Amount, and Temperature: The Ideal Gas Law” In *General Chemistry 1 & 2* by Rice University, a derivative of *Chemistry (Open Stax)* by Paul Flowers, Klaus Theopold, Richard Langley & William R. Robinson and is licensed under CC BY 4.0. Access for free at *Chemistry (OpenStax)* (<https://openstax.org/books/chemistry/pages/1-introduction>)

Notes

1. 400 torr
2. 21.6 mL
3. 635 mL
4. (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
5. 350 bar
6. 0.193 L
7. 3.4×10^3 torr

12.3 EFFUSION AND DIFFUSION OF GASES

Learning Objectives

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

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

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

In general, we know that when a sample of gas is introduced to one part of a closed container, its molecules very quickly disperse throughout the container; this process by which molecules disperse in space in response to differences in concentration is called **diffusion** (shown in Figure 12.3a). The gaseous atoms or molecules are, of course, unaware of any concentration gradient, they simply move randomly—regions of higher concentration have more particles than regions of lower concentrations, and so a net movement of species from high to low concentration areas takes place. In a closed environment, diffusion will ultimately result in equal concentrations of gas throughout, as depicted in Figure 12.3a. The gaseous atoms and molecules continue to move, but since their concentrations are the same in both bulbs, the rates of transfer between the bulbs are equal (no *net* transfer of molecules occurs).

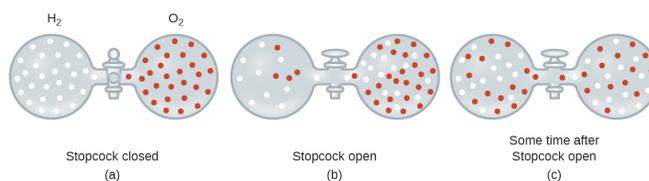


Figure 12.3a (a) Two gases, H_2 and O_2 , are initially separated. (b) When the stopcock is opened, they mix together. The lighter gas, H_2 , passes through the opening faster than O_2 , so just after the stopcock is opened, more H_2 molecules move to the O_2 side than O_2 molecules move to the H_2 side. (c) After a short time, both the slower-moving O_2 molecules and the faster-moving H_2 molecules have distributed themselves evenly on both sides of the vessel (credit: *Chemistry (OpenStax)*, CC BY 4.0).

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

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

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

A process involving movement of gaseous species similar to diffusion is **effusion**, the escape of gas molecules through a tiny hole such as a pinhole in a balloon into a vacuum (Figure 12.3b). Although diffusion and effusion rates both depend on the molar mass of the gas involved, their rates are not equal; however, the ratios of their rates are the same.

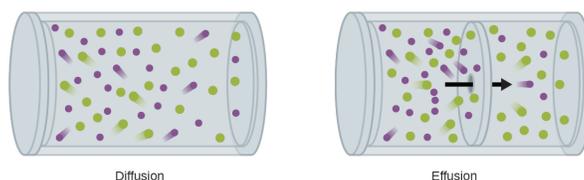


Figure 12.3b Diffusion occurs when gas molecules disperse throughout a container. Effusion occurs when a gas passes through an opening that is smaller than the mean free path of the particles, that is, the average distance traveled between collisions. Effectively, this means that only one particle passes through at a time (credit: *Chemistry (OpenStax)*, CC BY 4.0).

If a mixture of gases is placed in a container with porous walls, the gases effuse through the small openings in the walls. The lighter gases pass through the small openings more rapidly (at a higher rate) than the heavier ones (Figure 12.3c). In 1832, Thomas Graham studied the rates of effusion of different gases and formulated **Graham's law of effusion**: *The rate of effusion of a gas is inversely proportional to the square root of the mass of its particles*:

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

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

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



Figure 12.3c A balloon filled with air (the blue one) remains full overnight. A balloon filled with helium (the green one) partially deflates because the smaller, light helium atoms effuse through small holes in the rubber much more readily than the heavier molecules of nitrogen and oxygen found in air. (credit: modification of work by Mark Ott in *Chemistry (OpenStax)*, CC BY 4.0.)

Example 12.3a

Applying Graham's Law to Rates of Effusion

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

Solution

From Graham's law, we have:

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

Using molar masses:

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

Hydrogen effuses four times as rapidly as oxygen.

Exercise 12.3a

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

Check Your Answer¹

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

Example 12.3b

Effusion Time Calculations

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

Solution

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

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

and combine it with Graham's law:

$$\frac{\text{rate of effusion of gas Xe}}{\text{rate of effusion of gas Ne}} = \frac{\sqrt{\mathcal{M}_{\text{Ne}}}}{\sqrt{\mathcal{M}_{\text{Xe}}}}$$

To get:

$$\frac{\frac{\text{amount of Xe transferred}}{\text{time for Xe}}}{\frac{\text{amount of Ne transferred}}{\text{time for Ne}}} = \frac{\sqrt{\mathcal{M}_{\text{Ne}}}}{\sqrt{\mathcal{M}_{\text{Xe}}}}$$

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

$$\frac{\frac{\text{amount of Xe}}{\text{time for Xe}}}{\frac{\text{amount of Ne}}{\text{time for Ne}}} = \frac{\text{time for Ne}}{\text{time for Xe}} = \frac{\sqrt{\mathcal{M}_{\text{Ne}}}}{\sqrt{\mathcal{M}_{\text{Xe}}}} = \frac{\sqrt{\mathcal{M}_{\text{Ne}}}}{\sqrt{\mathcal{M}_{\text{Xe}}}}$$

and substitute values:

$$\frac{\text{time for Ne}}{243 \text{ s}} = \sqrt{\frac{20.2 \text{ g mol}^{-1}}{131.3 \text{ g mol}^{-1}}} = 0.392$$

Finally, solve for the desired quantity:

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

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

Exercise 12.3b

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

Check Your Answer²

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

Example 12.3c

Determining Molar Mass Using Graham's Law

An unknown gas effuses 1.66 times more rapidly than CO_2 . What is the molar mass of the unknown gas? Can you make a reasonable guess as to its identity?

Solution

From Graham's law, we have:

$$\frac{\text{rate of effusion of Unknown}}{\text{rate of effusion of CO}_2} = \frac{\sqrt{\mathcal{M}_{\text{CO}_2}}}{\sqrt{\mathcal{M}_{\text{Unknown}}}}$$

Plug in known data:

$$\frac{1.66}{1} = \frac{\sqrt{44.0 \text{ g/mol}}}{\sqrt{\mathcal{M}_{\text{Unknown}}}}$$

Solve:

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

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

Exercise 12.3c

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

Check Your Answer³

Use of Diffusion for Nuclear Energy Applications: Uranium Enrichment

Gaseous diffusion has been used to produce enriched uranium for use in nuclear power plants and weapons. Naturally occurring uranium contains only 0.72% of ²³⁵U, the kind of uranium that is “fissile,” that is, capable of sustaining a nuclear fission chain reaction. Nuclear reactors require fuel that is 2–5% ²³⁵U, and nuclear bombs need even higher concentrations. One way to enrich uranium to the desired levels is to take advantage of Graham’s law. In a gaseous diffusion enrichment plant, uranium hexafluoride (UF₆, the only uranium compound that is volatile enough to work) is slowly pumped through large cylindrical vessels called diffusers, which contain porous barriers with microscopic openings. The process is one of diffusion because the other side of the barrier is not evacuated. The ²³⁵UF₆ molecules have a higher average speed and diffuse through the barrier a little faster than the heavier ²³⁸UF₆ molecules. The gas that has passed through the barrier is slightly enriched in ²³⁵UF₆.

and the residual gas is slightly depleted. The small difference in molecular weights between $^{235}\text{UF}_6$ and $^{238}\text{UF}_6$ only about 0.4% enrichment, is achieved in one diffuser (Figure 12.3d). But by connecting many diffusers in a sequence of stages (called a cascade), the desired level of enrichment can be attained.

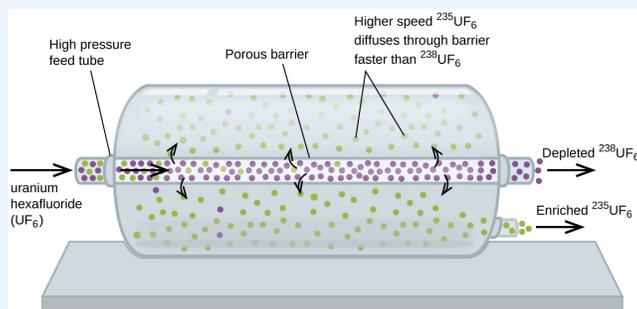


Figure 12.3d In a diffuser, gaseous UF_6 is pumped through a porous barrier, which partially separates $^{235}\text{UF}_6$ from $^{238}\text{UF}_6$. The UF_6 must pass through many large diffuser units to achieve sufficient enrichment in ^{235}U . (credit: Chemistry (OpenStax), CC BY 4.0).

The large scale separation of gaseous $^{235}\text{UF}_6$ from $^{238}\text{UF}_6$ was first done during the World War II, at the atomic energy installation in Oak Ridge, Tennessee, as part of the Manhattan Project (the development of the first atomic bomb). Although the theory is simple, this required surmounting many daunting technical challenges to make it work in practice. The barrier must have tiny, uniform holes (about 10^{-6} cm in diameter) and be porous enough to produce high flow rates. All materials (the barrier, tubing, surface coatings, lubricants, and gaskets) need to be able to contain, but not react with, the highly reactive and corrosive UF_6 .

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

Key Equations

- rate of diffusion = $\frac{\text{amount of gas passing through an area}}{\text{unit of time}}$
- $\frac{\text{rate of effusion of gas A}}{\text{rate of effusion of gas B}} = \frac{\sqrt{m_B}}{\sqrt{m_A}} = \frac{\sqrt{\mathcal{M}_B}}{\sqrt{\mathcal{M}_A}}$

Attribution & References

Except where otherwise noted, this page is adapted by JR van Haarlem from “8.4 Effusion and Diffusion of Gases” In *General Chemistry 1 & 2* by Rice University, a derivative of *Chemistry (Open Stax)* by Paul Flowers, Klaus Theopold, Richard Langley & William R. Robinson and is licensed under CC BY 4.0. Access for free at *Chemistry (OpenStax)* (<https://openstax.org/books/chemistry/pages/1-introduction>)

Notes

1. 52 mL/s
2. 32 h
3. 163 g/mol

12.4 STOICHIOMETRY OF GASEOUS SUBSTANCES, MIXTURES, AND REACTIONS

Learning Objectives

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

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

Density of a Gas

Recall that the density of a gas is its mass to volume ratio, $\rho = \frac{m}{V}$. Therefore, if we can determine the mass of some volume of a gas, we will get its density. The density of an unknown gas can be used to determine its molar mass and thereby assist in its identification. The ideal gas law, $PV = nRT$, provides us with a means of deriving such a mathematical formula to relate the density of a gas to its volume in the proof shown in Example 1.

Example 12.4a

Derivation of a Density Formula from the Ideal Gas Law

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

Solution

1. $PV = nRT$
2. Rearrange to get (mol/L): $\frac{n}{v} = \frac{P}{RT}$
3. Multiply each side of the equation by the molar mass, \mathcal{M} . When moles are multiplied by \mathcal{M} in g/mol, g are obtained:

$$(\mathcal{M})\left(\frac{n}{V}\right) = \left(\frac{P}{RT}\right)(\mathcal{M})$$
4. $g/L = \rho = \frac{P\mathcal{M}}{RT}$

Exercise 12.4a

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

Check Your Answer²

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

Example 12.4b

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

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

Solution

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

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

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

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

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

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

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

Exercise 12.4b

Acetylene, a fuel used welding torches, is comprised of 92.3% C and 7.7% H by mass. Find the empirical formula. If 1.10 g of acetylene occupies a volume of 1.00 L at 1.15 atm and 59.5 °C, what is the molecular formula for acetylene?

Check Your Answer³

Molar Mass of a Gas

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

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

The ideal gas equation can be rearranged to isolate n :

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

and then combined with the molar mass equation to yield:

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

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

Example 12.4c

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 12.4a)

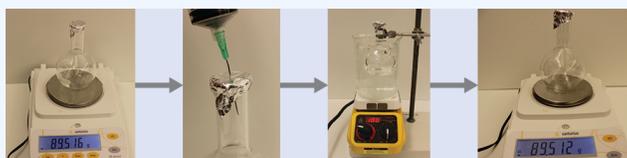


Figure 12.4a When the volatile liquid in the flask is heated past its boiling point, it becomes gas and drives air out of the flask. At $t_{l \rightarrow g}$, the flask is filled with volatile liquid gas at the same pressure as the atmosphere. If the flask is then cooled to room temperature, the gas condenses and the mass of the gas that filled the flask, and is now liquid, can be measured. (credit: modification of work by Mark Ott in *Chemistry (OpenStax)*, CC BY 4.0).

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 $99.6 \text{ }^\circ\text{C}$ when the atmospheric pressure is 742.1 mm Hg. What is the approximate molar mass of chloroform?

Solution

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

then

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

Exercise 12.4c

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 vapour?

Check Your Answer⁴

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 12.4b). 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*:

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

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

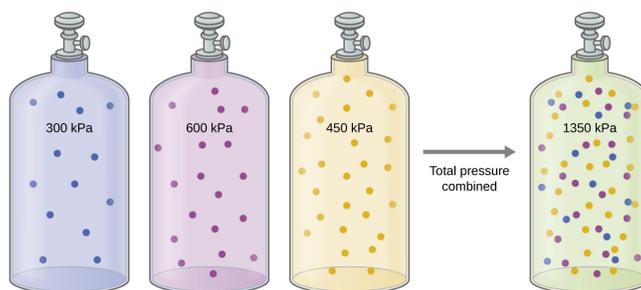


Figure 12.4b If equal-volume cylinders containing gas A at a pressure of 300 kPa, gas B at a pressure of 600 kPa, and gas C at a pressure of 450 kPa are all combined in the same-size cylinder, the total pressure of the mixture is 1350 kPa (credit: *Chemistry (OpenStax)*, CC BY 4.0).

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

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

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

Example 12.4d

The Pressure of a Mixture of Gases

A 10.0-L vessel contains 2.50×10^{-3} mol of H_2 , 1.00×10^{-3} mol of He, and 3.00×10^{-4} mol of Ne at 35 °C.

- What are the partial pressures of each of the gases?
- 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 $P = \frac{nRT}{V}$:

$$P_{\text{H}_2} = \frac{(2.50 \times 10^{-3} \text{ mol})(0.08206 \text{ L atm mol}^{-1}\text{K}^{-1})(308 \text{ K})}{10.0 \text{ L}} = 6.32 \times 10^{-3} \text{ atm}$$

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

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

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

$$P_T = P_{\text{H}_2} + P_{\text{He}} + P_{\text{Ne}} = (0.00632 + 0.00253 + 0.00076) \text{ atm} = 9.61 \times 10^{-3} \text{ atm}$$

Exercise 12.4d

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

Check Your Answer⁵

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

Example 12.4e

The Pressure of a Mixture of Gases

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

- What are the mole fractions of O₂ and N₂O?
- What are the partial pressures of O₂ and N₂O?

Solution

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

For O₂,

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

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

For N₂O,

$$X_{N_2O} = \frac{n_{N_2O}}{n_{Total}} = \frac{8.41 \text{ mol}}{(2.83 + 8.41) \text{ mol}} = 0.748$$

and

$$P_{N_2O} = X_{N_2O} \times P_{Total} = 0.748 \times 192 \text{ kPa} = 143.6 \text{ kPa}$$

Exercise 12.4e

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?

Check Your Answer⁶

Collection of Gases over Water

A simple way to collect gases that do not react with water is to capture them in a bottle that has been filled with water and inverted into a dish filled with water. The pressure of the gas inside the bottle can be made equal to the air pressure outside by raising or lowering the bottle. When the water level is the same both inside and outside the bottle (Figure 12.4c), the pressure of the gas is equal to the atmospheric pressure, which can be measured with a barometer.



Figure 12.4c When a reaction produces a gas that is collected above water, the trapped gas is a mixture of the gas produced by the reaction and water vapour. If the collection flask is appropriately positioned to equalize the water levels both within and outside the flask, the pressure of the trapped gas mixture will equal the atmospheric pressure outside the flask (see the earlier discussion of manometers) (credit: *Chemistry (OpenStax)*, CC BY 4.0).

However, there is another factor we must consider when we measure the pressure of the gas by this method. Water evaporates and there is always gaseous water (water vapour) above a sample of liquid water. As a gas is collected over water, it becomes saturated with water vapour and the total pressure of the mixture equals the partial pressure of the gas plus the partial pressure of the water vapour. The pressure of the pure gas is

therefore equal to the total pressure minus the pressure of the water vapour—this is referred to as the “dry” gas pressure, that is, the pressure of the gas only, without water vapour. The **vapour pressure of water**, which is the pressure exerted by water vapour in equilibrium with liquid water in a closed container, depends on the temperature (Figure 12.4d); more detailed information on the temperature dependence of water vapour can be found in Table 12.4a, and vapour pressure will be discussed in more detail in the next chapter on liquids.

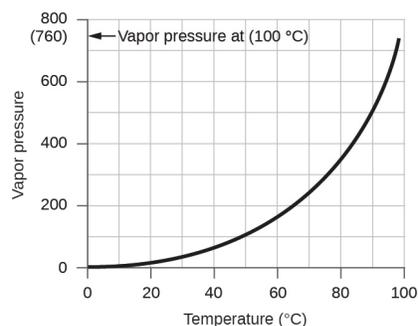


Figure 12.4d This graph shows the vapour pressure of water at sea level as a function of temperature (credit: *Chemistry (OpenStax)*, CC BY 4.0).

Table 12.4a Vapour Pressure of Ice and Water in Various Temperatures at Sea Level

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

Example 12.4f

Pressure of a Gas Collected Over Water

If 0.200 L of argon is collected over water at a temperature of 26 °C and a pressure of 750 torr in a system like that shown in Figure 3, what is the partial pressure of argon?

Solution

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

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

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

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

The pressure of water vapour above a sample of liquid water at 26 °C is 25.2 torr (Appendix F), so:

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

Exercise 12.4f

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

Check Your Answer⁷

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 behaviour 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 according to $\text{N}_2(g) + 3\text{H}_2(g) \longrightarrow 2\text{NH}_3(g)$, a given volume of nitrogen gas reacts with three times that volume of hydrogen gas to produce two times that volume of ammonia gas, if pressure and temperature remain constant.

The explanation for this is illustrated in Figure 12.4e. 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 .

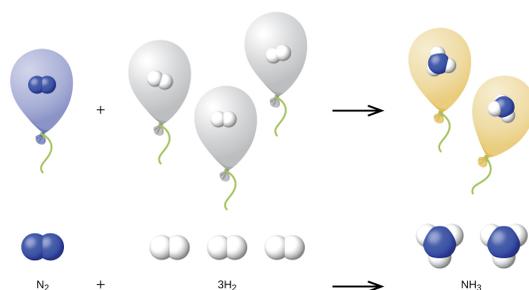


Figure 12.4e One volume of N_2 combines with three volumes of H_2 to form two volumes of NH_3 (credit: *Chemistry (OpenStax)*, CC BY 4.0).

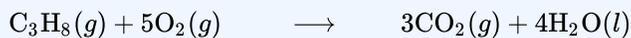
Example 12.4g

Reaction of Gases

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

Solution

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



1 volume + 5 volumes 3 volumes + 4 volumes

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

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

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

Exercise 12.4g

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?

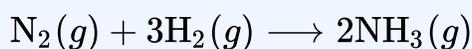


Check Your Answer⁸

Example 12.4h

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 $\text{H}_2(g)$, measured under the same conditions, was required to prepare this amount of ammonia by reaction with N_2 ?



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 :

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

The manufacture of 683 billion 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.)

Exercise 12.4h

What volume of $O_2(g)$ measured at $25\text{ }^\circ\text{C}$ 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 vapour.

Check Your Answer⁹

Example 12.4i

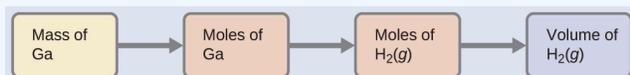
Volume of Gaseous Product

What volume of hydrogen at $27\text{ }^\circ\text{C}$ and 723 torr may be prepared by the reaction of 8.88 g of gallium with an excess of hydrochloric acid?



Solution

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



The first two conversions are:

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

Finally, we can use the ideal gas law:

$$V_{H_2} = \left(\frac{nRT}{P}\right)_{H_2} = \frac{0.191\text{ mol} \times 0.08206\text{ L atm mol}^{-1}\text{K}^{-1} \times 300\text{ K}}{0.951\text{ atm}} = 4.94\text{ L}$$

Exercise 12.4i

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

Check Your Answer¹⁰

Greenhouse Gases and Climate Change

The thin skin of our atmosphere keeps the earth from being an ice planet and makes it habitable. In fact, this is due to less than 0.5% of the air molecules. Of the energy from the sun that reaches the earth, almost $\frac{1}{3}$ is reflected back into space, with the rest absorbed by the atmosphere and the surface of the earth. Some of the energy that the earth absorbs is re-emitted as infrared (IR) radiation, a portion of which passes back out through the atmosphere into space. However, most of this IR radiation is absorbed by certain substances in the atmosphere, known as greenhouse gases, which re-emit this energy in all directions, trapping some of the heat. This maintains favourable living conditions—without atmosphere, the average global average temperature of $14\text{ }^\circ\text{C}$ ($57\text{ }^\circ\text{F}$) would be about $-19\text{ }^\circ\text{C}$ ($-2\text{ }^\circ\text{F}$). The major greenhouse gases (GHGs) are water vapor, carbon dioxide, methane, and ozone. Since the Industrial Revolution, human activity has been increasing the concentrations of GHGs, which have changed the energy balance and are significantly altering the earth's climate (Figure 12.4f).

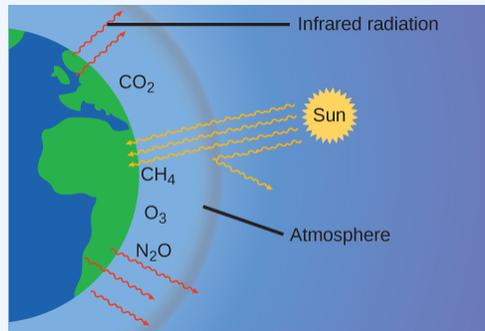


Figure 12.4f Greenhouse gases trap enough of the sun's energy to make the planet habitable—this is known as the greenhouse effect. Human activities are increasing greenhouse gas levels, warming the planet and causing more extreme weather events (credit: *Chemistry (OpenStax)*, CC BY 4.0).

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

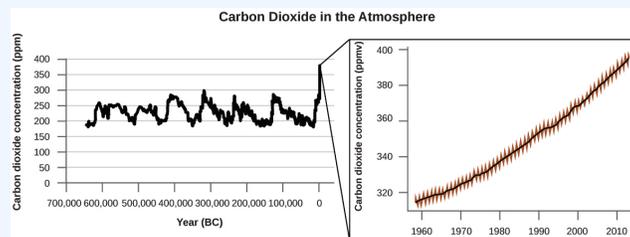


Figure 12.4g CO_2 levels over the past 700,000 years were typically from 200–300 ppm, with a steep, unprecedented increase over the past 50 years (credit: *Chemistry (OpenStax)*, CC BY 4.0).

Watch The Greenhouse Effect (2 mins) (<https://www.youtube.com/watch?v=VYMjSule0Bw>)

Scientists in Action: Dr. Susan Solomon

Atmospheric and climate scientist Dr. Susan Solomon (Figure 12.4h) 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.



Figure 12.4h Atmospheric and climate scientist Susan Solomon (credit: work by Bengt Nyman, CC BY 2.0)

She has been awarded the top scientific honours 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 *Introducing: Atmospheric Chemist – Prof. Susan Solomon* [New Tab] (<https://youtu.be/tx3BCP7fmtM>)

Key Equations

- $P_{Total} = P_A + P_B + P_C + \dots = \sum_i P_i$
- $P_A = X_A P_{Total}$
- $X_A = \frac{n_A}{n_{Total}}$

Attribution & References

Except where otherwise noted, this page is adapted by JR van Haarlem from “9.3 Stoichiometry of Gaseous Substances, Mixtures, and Reactions” In *Chemistry 2e (OpenStax)* by Paul Flowers, Klaus Theopold, Richard Langley, & William R. Robinson, licensed under CC BY 4.0. Access for free at *Chemistry 2e (OpenStax)*.

Notes

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

2.
$$\rho = \frac{P\mathcal{M}}{RT}$$

$$0.0847 \text{ g/L} = 760 \text{ torr} \times \frac{1 \text{ atm}}{760 \text{ torr}} \times \frac{\mathcal{M}}{0.0821 \text{ L atm/mol K}} \times 290 \text{ K} \quad \mathcal{M} = 2.02 \text{ g/mol}; \text{ therefore, the gas must be hydrogen (H}_2\text{, 2.02 g/mol)}$$

3. Empirical formula, CH; Molecular formula, C₂H₂
4. 124 g/mol P₄
5. 1.137 atm
6. 1.87 atm
7. 0.583 L
8. 3.34 tanks (2.34 × 10⁴ L)
9. 51.0 L
10. 1.30 × 10³ L

12.5 THE KINETIC-MOLECULAR THEORY

Learning Objectives

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

- 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 behaviour 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 behaviour 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', 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 Behaviour 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 behaviour of a gas as follows:

- *Amontons' 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 12.5a.a).
- *Charles' 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 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 12.5a.b).
- *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 12.5a.c).
- *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.

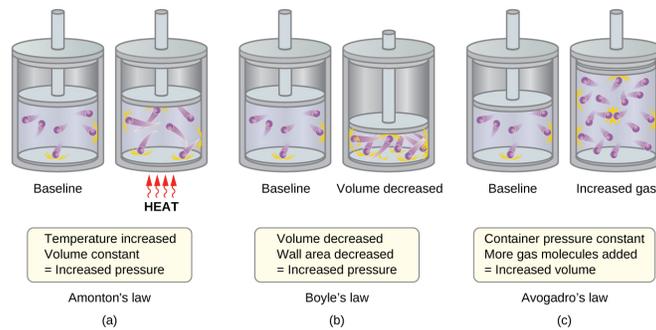


Figure 12.5a (a) When gas temperature increases, gas pressure increases due to increased force and frequency of molecular collisions. (b) When volume decreases, gas pressure increases due to increased frequency of molecular collisions. (c) When the amount of gas increases at a constant pressure, volume increases to yield a constant number of collisions per unit wall area per unit time (credit: *Chemistry (OpenStax)*, CC BY 4.0).

Molecular Velocities and Kinetic Energy

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

In a gas sample, individual molecules have widely varying speeds; however, because of the *vast* number of molecules and collisions involved, the molecular speed distribution and average speed are constant. This molecular speed distribution is known as a Maxwell-Boltzmann distribution, and it depicts the relative numbers of molecules in a bulk sample of gas that possesses a given speed (Figure 12.5b).

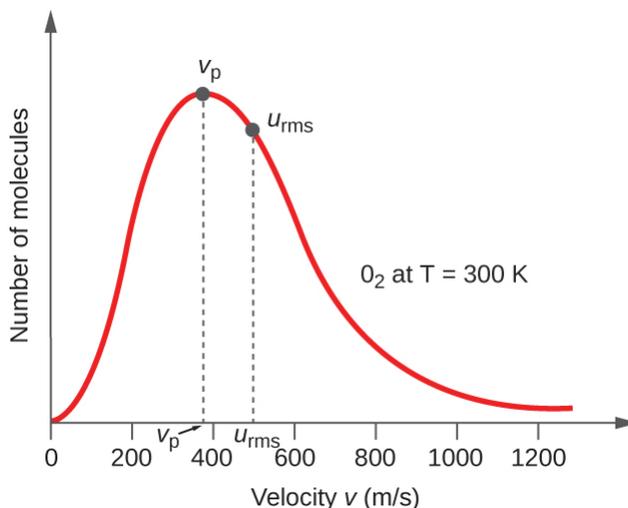


Figure 12.5b The molecular speed distribution for oxygen gas at 300 K is shown here. Very few molecules move at either very low or very high speeds. The number of molecules with intermediate speeds increases rapidly up to a maximum, which is the most probable speed, then drops off rapidly. Note that the most probable speed, v_p , is a little less than 400 m/s, while the root mean square speed, u_{rms} , is closer to 500 m/s (credit: *Chemistry (OpenStax)*, CC BY 4.0).

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

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

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

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

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

$$\text{KE}_{\text{avg}} = \frac{1}{2}mu_{\text{rms}}^2$$

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

$$\text{KE}_{\text{avg}} = \frac{3}{2}RT$$

where R is the gas constant and T is the kelvin temperature. When used in this equation, the appropriate

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

$$\frac{1}{2} m u_{\text{rms}}^2 = \frac{3}{2} RT$$

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

Example 12.5a

Calculation of u_{rms}

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

Solution

Convert the temperature into Kelvin:

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

Determine the mass of a nitrogen molecule in kilograms:

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

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

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

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

Exercise 12.5a

Calculate the root-mean-square velocity for an oxygen molecule at $-23\text{ }^{\circ}\text{C}$.

Check Your Answer¹

If the temperature of a gas increases, its KE_{avg} increases, more molecules have higher speeds and fewer molecules have lower speeds, and the distribution shifts toward higher speeds overall, that is, to the right. If temperature decreases, KE_{avg} decreases, more molecules have lower speeds and fewer molecules have higher speeds, and the distribution shifts toward lower speeds overall, that is, to the left. This behaviour is illustrated for nitrogen gas in Figure 12.5c.

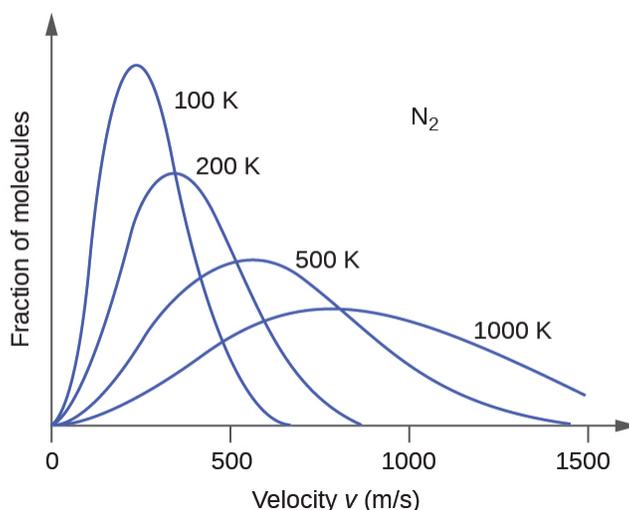


Figure 12.5c The molecular speed distribution for nitrogen gas (N_2) shifts to the right and flattens as the temperature increases; it shifts to the left and heightens as the temperature decreases (credit: *Chemistry (OpenStax)*, CC BY 4.0).

At a given temperature, all gases have the same KE_{avg} for their molecules. Gases composed of lighter molecules have more high-speed particles and a higher u_{rms} , with a speed distribution that peaks at relatively higher velocities. Gases consisting of heavier molecules have more low-speed particles, a lower u_{rms} , and a speed distribution that peaks at relatively lower velocities. This trend is demonstrated by the data for a series of noble gases shown in Figure 12.5d.

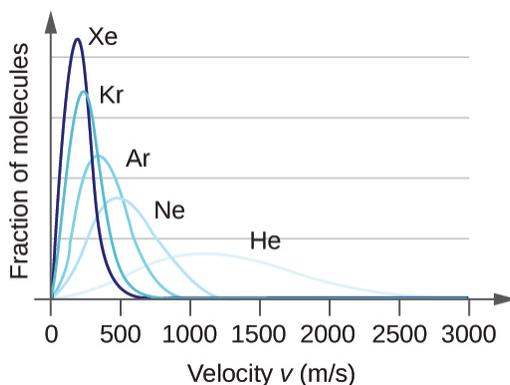


Figure 12.5d The molecular speed distribution for nitrogen gas (N_2) shifts to the right and flattens as the temperature increases; it shifts to the left and heightens as the temperature decreases (credit: *Chemistry (OpenStax)*, CC BY 4.0).

The simulator in Exercise 12.5b may be used to examine the effect of temperature on molecular velocities. Examine the simulator’s “energy histograms” (molecular speed distributions) and “species information” (which gives average speed values) for molecules of different masses at various temperatures.

Exercise 12.5b

Practice using the following PhET simulation: Gas Properties (https://phet.colorado.edu/sims/html/gas-properties/latest/gas-properties_en.html)

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

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

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

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

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

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

$$m = \frac{3RT}{u_{\text{rms}}^2} = \frac{3RT}{\bar{u}^2}$$

$$\frac{\text{effusion rate of A}}{\text{effusion rate of B}} = \frac{u_{\text{rms A}}}{u_{\text{rms B}}} = \frac{\sqrt{\frac{3RT}{m_A}}}{\sqrt{\frac{3RT}{m_B}}} = \sqrt{\frac{m_B}{m_A}}$$

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

Key Equations

- $u_{\text{rms}} = \sqrt{\overline{u^2}} = \sqrt{\frac{u_1^2 + u_2^2 + u_3^2 + u_4^2 + \dots}{n}}$
- $\text{KE}_{\text{avg}} = \frac{3}{2}RT$
- $u_{\text{rms}} = \sqrt{\frac{3RT}{m}}$

Attribution & References

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Notes

1. 441 m/s

12.6 NON-IDEAL GAS BEHAVIOUR

Learning Objectives

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

- Describe the physical factors that lead to deviations from ideal gas behaviour
- 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 behaviour
- Quantify non-ideal behaviour 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 behaviour 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 behaviour are considered.

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

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

Ideal gas behaviour is therefore indicated when this ratio is equal to 1, and any deviation from 1 is an indication of non-ideal behaviour. Figure 12.6a shows plots of Z over a large pressure range for several common gases.

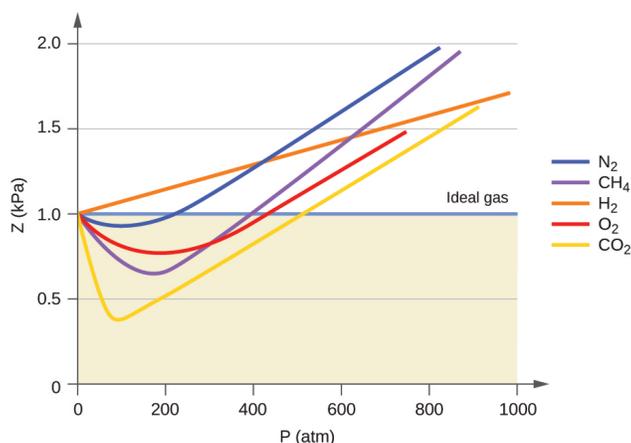


Figure 12.6a A graph of the compressibility factor (Z) vs. pressure shows that gases can exhibit significant deviations from the behaviour predicted by the ideal gas law (credit: *Chemistry (OpenStax)*, CC BY 4.0).

As is apparent from Figure 12.6a, the ideal gas law does not describe gas behaviour 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 behaviour 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 12.6b). 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.

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 12.6b). 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.

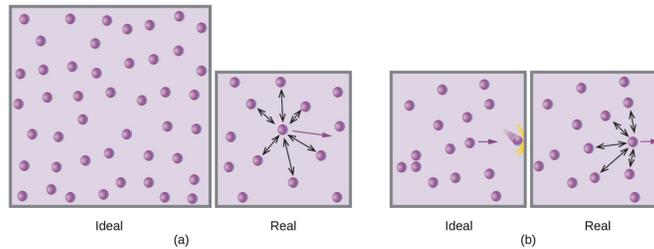


Figure 12.6b (a) Attractions between gas molecules serve to decrease the gas volume at constant pressure compared to an ideal gas whose molecules experience no attractive forces. (b) These attractive forces will decrease the force of collisions between the molecules and container walls, therefore reducing the pressure exerted compared to an ideal gas (credit: *Chemistry (OpenStax)*, CC BY 4.0).

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

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

Correction for molecular attraction
Correction for volume of molecules

Figure 12.6c The van der Waals equation derived from the ideal gas law (credit: *Chemistry (OpenStax)*, CC BY 4.0).

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 $\frac{n^2 a}{V^2}$, 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 12.6a.

Table 12.6a Values of van der Waals Constants for Some Common Gases

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 ₂ O	5.46	0.0305
He	0.0342	0.0237
CCl ₄	20.4	0.1383

At low pressures, the correction for intermolecular attraction, a , is more important than the one for molecular volume, b . At high pressures and small volumes, the correction for the volume of the molecules becomes important because the molecules themselves are incompressible and constitute an appreciable fraction of the total volume. At some intermediate pressure, the two corrections have opposing influences and the gas appears to follow the relationship given by $PV = nRT$ over a small range of pressures. This behaviour is reflected by the “dips” in several of the compressibility curves shown in Figure 12.6a. The attractive force between molecules initially makes the gas more compressible than an ideal gas, as pressure is raised (Z decreases with increasing P). At very high pressures, the gas becomes less compressible (Z increases with P), as the gas molecules begin to occupy an increasingly significant fraction of the total gas volume.

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

Example 12.6a

Comparison of Ideal Gas Law and van der Waals Equation

A 4.25-L flask contains 3.46 mol CO₂ at 229 °C. Calculate the pressure of this sample of CO₂:

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

Solution

- a. From the ideal gas law: $P = \frac{nRT}{V} = \frac{3.46 \text{ mol} \times 0.08206 \text{ L atm mol}^{-1} \text{ K}^{-1} \times 502 \text{ K}}{4.25 \text{ L}} = 33.5 \text{ atm}$
- b. From the van der Waals equation: $(P + \frac{n^2 a}{V^2}) \times (V - nb) = nRT \rightarrow P = \frac{nRT}{(V - nb)} - \frac{n^2 a}{V^2}$
 $P = \frac{3.46 \text{ mol} \times 0.08206 \text{ L atm mol}^{-1} \text{ K}^{-1} \times 502 \text{ K}}{(4.25 \text{ L} - 3.46 \text{ mol} \times 0.0427 \text{ L mol}^{-1})} - \frac{(3.46 \text{ mol})^2 \times 3.59 \text{ L}^2 \text{ atm mol}^{-2}}{(4.25 \text{ L})^2}$ This finally yields $P = 32.4 \text{ atm}$.
- c. This is not very different from the value from the ideal gas law because the pressure is not very high and the temperature is not very low. The value is somewhat different because CO₂ molecules do have some volume and attractions between molecules, and the ideal gas law assumes they do not have volume or attractions.

Exercise 12.6a

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

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

Check Your Answer

1

Key Equations

- $Z = \frac{\text{molar volume of gas at same } T \text{ and } P}{\text{molar volume of ideal gas at same } T \text{ and } P} = \left(\frac{P \times V_m}{R \times T}\right)_{\text{measured}}$
- $(P + \frac{n^2 a}{V^2}) \times (V - nb) = nRT$

Attribution & References

Except where otherwise noted, this page is adapted by JR van Haarlem from “8.6 Non-Ideal Gas Behavior (<https://boisestate.pressbooks.pub/chemistry/chapter/5-6-non-ideal-gas-behavior/>)” In *General Chemistry 1*

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Notes

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

CHAPTER 12 - SUMMARY

12.1 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.

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

The behaviour 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 (Amonton's law). The volume of a given gas sample is directly proportional to its absolute temperature at constant pressure (Charles' 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.

12.3 Effusion and Diffusion of Gases

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

12.4 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.

12.5 The Kinetic-Molecular Theory

The kinetic molecular theory is a simple but very effective model that effectively explains ideal gas behaviour. 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 speeds determined by their absolute temperatures. The individual molecules of a gas exhibit a range of speeds, the distribution of these speeds being dependent on the temperature of the gas and the mass of its molecules.

12.6 Non-Ideal Gas Behaviour

Gas molecules possess a finite volume and experience forces of attraction for one another. Consequently, gas behaviour 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 behaviour, and the gas is said to exhibit ideal behaviour. 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 behaviour of gases under these conditions.

Attribution & References

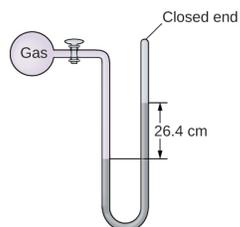
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CHAPTER 12 - REVIEW

12.1 Gas Pressure

1. Why are sharp knives more effective than dull knives (Hint: think about the definition of pressure)?
Check Answer:¹
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? **Check Answer:**²
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? **Check Answer:**³
6. A typical barometric pressure in Kansas City is 740 torr. What is this pressure in atmospheres, in millimetres 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? **Check Answer:**⁴
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. **Check Answer:**⁵
10. A medical laboratory catalog describes the pressure in a cylinder of a gas as 14.82 MPa. What is the pressure of this gas in atmospheres and torr?
11. Consider this scenario and answer the following questions: On a mid-August day in the northeastern United States, the following information appeared in the local newspaper: atmospheric pressure at sea level 29.97 in., 1013.9 mbar.
 1. What was the pressure in kPa?
 2. 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.
Check Answer:⁶
12. Why is it necessary to use a nonvolatile liquid in a barometer or manometer?
13. The pressure of a sample of gas is measured at sea level with a closed-end manometer. See figure below. The liquid in the manometer is mercury. Determine the pressure of the gas in:

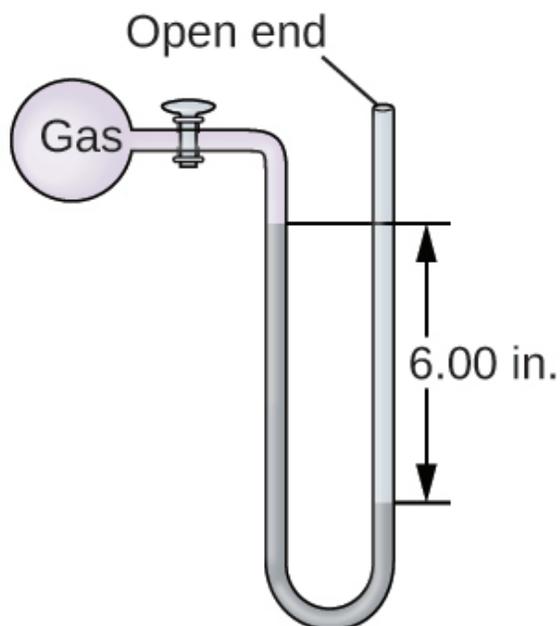
1. torr
2. Pa
3. bar



Check Answer: ⁷

14. The pressure of a sample of gas is measured with an open-end manometer. See figure below. The liquid in the manometer is mercury. Assuming atmospheric pressure is 29.92 in. Hg, determine the pressure of the gas in:

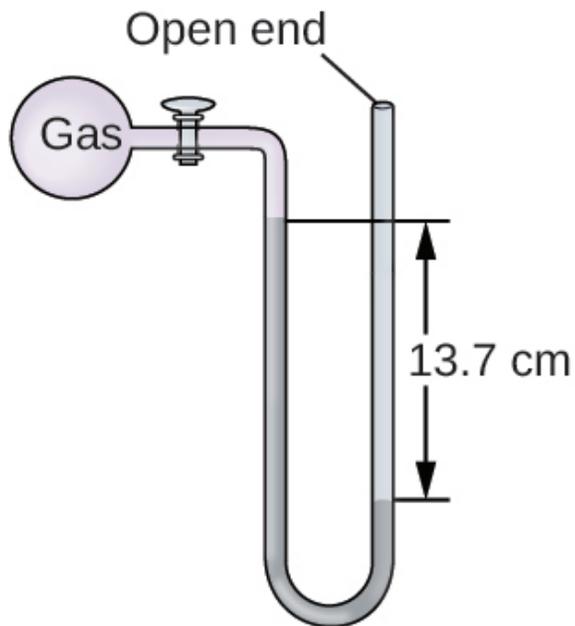
1. torr
2. Pa



3. bar

15. The pressure of a sample of gas is measured at sea level with an open-end mercury manometer. See figure below. Assuming atmospheric pressure is 760.0 mm Hg, determine the pressure of the gas in:

1. mm Hg
2. atm

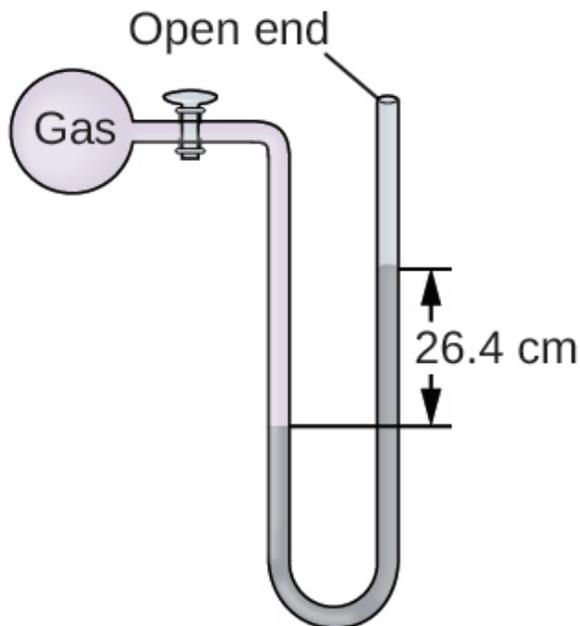


3. kPa

Check Answer:⁸

16. The pressure of a sample of gas is measured at sea level with an open-end mercury manometer. See figure below. Assuming atmospheric pressure is 760 mm Hg, determine the pressure of the gas in:

1. mm Hg
2. atm



3. kPa

17. How would the use of a volatile liquid affect the measurement of a gas using open-ended manometers vs. closed-end manometers? **Check Answer:**⁹

12.2 Relating Pressure, Volume, Amount, and Temperature:

The Ideal Gas Law

1. Sometimes leaving a bicycle in the sun on a hot day will cause a blowout. Why?
2. Explain how the volume of the bubbles exhausted by a scuba diver (Figure 12.2h) change as they rise to the surface, assuming that they remain intact. **Check Answer:**¹⁰
3. 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?
4. 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? **Check Answer:**¹¹
5. How would the graph in Figure 12.2d change if the number of moles of gas in the sample used to determine the curve were doubled?
6. How would the graph in Figure 12.2e change if the number of moles of gas in the sample used to determine the curve were doubled? **Check Answer:**¹²
7. In addition to the data found in Figure 12.2e, what other information do we need to find the mass of the sample of air used to determine the graph?
8. Determine the volume of 1 mol of CH_4 gas at 150 K and 1 atm, using Figure 12.2d **Check Answer:**¹³
9. Determine the pressure of the gas in the syringe shown in Figure 12.2e, when its volume is 12.5 mL, using:
 - a. the appropriate graph
 - b. Boyle's law
10. 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 ($T = 475\text{ °C}$), what will be the pressure in the hot can? **Check Answer:**¹⁴
11. 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?
12. 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. **Check Answer:**¹⁵
13. 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?
14. 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?



(credit: work by U.S. Department of Agriculture, CC BY 2.0)

Check Answer: ¹⁶

15. 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?
16. How many moles of gaseous boron trifluoride, BF₃, are contained in a 4.3410-L bulb at 788.0 K if the pressure is 1.220 atm? How many grams of BF₃? **Check Answer:** ¹⁷
17. Iodine, I₂, is a solid at room temperature but sublimates (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 I₂ vapour at a pressure of 0.462 atm?
18. How many grams of gas are present in each of the following cases?
 - a. 0.100 L of CO₂ at 307 torr and 26 °C
 - b. 8.75 L of C₂H₄, at 378.3 kPa and 483 K
 - c. 221 mL of Ar at 0.23 torr and -54 °C

Check Answer: ¹⁸

19. 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?
20. A cylinder of medical oxygen has a volume of 35.4 L, and contains O₂ at a pressure of 151 atm and a temperature of 25 °C. What volume of O₂ does this correspond to at normal body conditions, that is, 1 atm and 37 °C? **Check Answer:** ¹⁹
21. A large scuba tank (Figure 12.2h) 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?
22. A 20.0-L cylinder containing 11.34 kg of butane, C₄H₁₀, 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. **Check Answer:**
20

23. While resting, the average 70-kg human male consumes 14 L of pure O₂ per hour at 25 °C and 100 kPa. How many moles of O₂ are consumed by a 70 kg man while resting for 1.0 h?

24. For a given amount of gas showing ideal behaviour, draw labeled graphs of:

- the variation of P with V
- the variation of V with T
- the variation of P with T
- the variation of $\frac{1}{P}$ with V

Check Answer:²¹

25. A litre of methane gas, CH₄, at STP contains more atoms of hydrogen than does a litre of pure hydrogen gas, H₂, at STP. Using Avogadro's law as a starting point, explain why.

26. The effect of chlorofluorocarbons (such as CCl₂F₂) on the depletion of the ozone layer is well known.

The use of substitutes, such as CH₃CH₂F(*g*), for the chlorofluorocarbons, has largely corrected the problem. Calculate the volume occupied by 10.0 g of each of these compounds at STP:

- CCl₂F₂(*g*)
- CH₃CH₂F(*g*)

Check Answer:

27. 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?

28. 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?

Check Answer:²²

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

30. If the volume of a fixed amount of a gas is tripled at constant temperature, what happens to the pressure? **Check Answer:**²³

12.3 Effusion and Diffusion of Gases

- A balloon filled with helium gas is found to take 6 hours to deflate to 50% of its original volume. How long will it take for an identical balloon filled with the same volume of hydrogen gas (instead of helium) to decrease its volume by 50%? **Check Answer:**²⁴

- Explain why the numbers of molecules are not identical in the left- and right-hand bulbs shown in the centre illustration of Figure 12.3a.
- Starting with the definition of rate of effusion and Graham's finding relating rate and molar mass, show how to derive the Graham's law equation, relating the relative rates of effusion for two gases to their molecular masses. **Check Answer:**²⁵
- Heavy water, D₂O (molar mass = 20.03 g mol⁻¹), can be separated from ordinary water, H₂O (molar mass = 18.01), as a result of the difference in the relative rates of diffusion of the molecules in the gas phase. Calculate the relative rates of diffusion of H₂O and D₂O.
- Which of the following gases diffuse more slowly than oxygen? F₂, Ne, N₂O, C₂H₂, NO, Cl₂, H₂S
Check Answer:²⁶
- During the discussion of gaseous diffusion for enriching uranium, it was claimed that ²³⁵UF₆ diffuses 0.4% faster than ²³⁸UF₆. Show the calculation that supports this value. The molar mass of ²³⁵UF₆ = 235.043930 + 6 × 18.998403 = 349.034348 g/mol, and the molar mass of ²³⁸UF₆ = 238.050788 + 6 × 18.998403 = 352.041206 g/mol.
- Calculate the relative rate of diffusion of ¹H₂ (molar mass 2.0 g/mol) compared to that of ²H₂ (molar mass 4.0 g/mol) and the relative rate of diffusion of O₂ (molar mass 32 g/mol) compared to that of O₃ (molar mass 48 g/mol). **Check Answer:**²⁷
- A gas of unknown identity diffuses at a rate of 83.3 mL/s in a diffusion apparatus in which carbon dioxide diffuses at the rate of 102 mL/s. Calculate the molecular mass of the unknown gas.
- When two cotton plugs, one moistened with ammonia and the other with hydrochloric acid, are simultaneously inserted into opposite ends of a glass tube that is 87.0 cm long, a white ring of NH₄Cl forms where gaseous NH₃ and gaseous HCl first come into contact. (Hint: Calculate the rates of diffusion for both NH₃ and HCl, and find out how much faster NH₃ diffuses than HCl.)

$$\text{NH}_3(g) + \text{HCl}(g) \longrightarrow \text{NH}_4\text{Cl}(s)$$

At approximately what distance from the ammonia moistened plug does this occur?
Check Answer:²⁸

12.4 Stoichiometry of Gaseous Substances, Mixtures, and Reactions

- What is the density of laughing gas, dinitrogen monoxide, N₂O, at a temperature of 325 K and a pressure of 113.0 kPa?
- Calculate the density of Freon 12, CF₂Cl₂, at 30.0 °C and 0.954 atm. **Check Answer:**²⁹
- Which is denser at the same temperature and pressure, dry air or air saturated with water vapour? Explain.
- A cylinder of O₂(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? **Check**

Answer: ³⁰

5. 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?
6. 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? **Check Answer:** ³¹
7. How could you show experimentally that the molecular formula of propene is C₃H₆, not CH₂?
8. 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. **Check Answer:** ³²
9. 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 125 mL with a pressure of 99.5 kPa at 22 °C?
 - a. Outline the steps necessary to answer the question.
 - b. Answer the question.
10. A 36.0-L cylinder of a gas used for calibration of blood gas analyzers in medical laboratories contains 350 g CO₂, 805 g O₂, and 4,880 g N₂. At 25 degrees C, what is the pressure in the cylinder in atmospheres? **Check Answer:** ³³
11. A cylinder of a gas mixture used for calibration of blood gas analyzers in medical laboratories contains 5.0% CO₂, 12.0% O₂, and the remainder N₂ 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.)
12. A sample of gas isolated from unrefined petroleum contains 90.0% CH₄, 8.9% C₂H₆, and 1.1% C₃H₈ 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.) **Check Answer:** ³⁴
13. A mixture of 0.200 g of H₂, 1.00 g of N₂, 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 behaviour.
14. Most mixtures of hydrogen gas with oxygen gas are explosive. However, a mixture that contains less than 3.0 % O₂ is not. If enough O₂ is added to a cylinder of H₂ at 33.2 atm to bring the total pressure to 34.5 atm, is the mixture explosive? **Check Answer:** ³⁵
15. A commercial mercury vapour 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?
16. 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 12.4a for the vapour pressure of water.) **Check Answer:** ³⁶
17. 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?

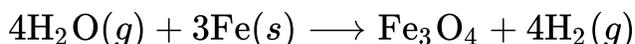
18. Joseph Priestley first prepared pure oxygen by heating mercuric oxide, HgO:



- Outline the steps necessary to answer the following question: What volume of O₂ at 23 °C and 0.975 atm is produced by the decomposition of 5.36 g of HgO?
- Answer the question.

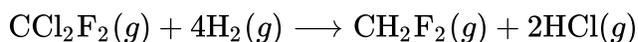
Check Answer: ³⁷

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



- Outline the steps necessary to answer the following question: What volume of H₂ at a pressure of 745 torr and a temperature of 20 °C can be prepared from the reaction of 15.0 g of H₂O?
- Answer the question.

20. The chlorofluorocarbon CCl₂F₂ can be recycled into a different compound by reaction with hydrogen to produce CH₂F₂(g), a compound useful in chemical manufacturing:



- 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 × 10³ kg) of CCl₂F₂?
- Answer the question.

Check Answer: ³⁸

21. Automobile air bags are inflated with nitrogen gas, which is formed by the decomposition of solid sodium azide (NaN₃). 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.

22. Lime, CaO, is produced by heating calcium carbonate, CaCO₃; carbon dioxide is the other product.
- Outline the steps necessary to answer the following question: What volume of carbon dioxide at 875° and 0.966 atm is produced by the decomposition of 1 ton (1.000 × 10³ kg) of calcium carbonate?

- Answer the question.

Check Answer: ³⁹

23. Before small batteries were available, carbide lamps were used for bicycle lights. Acetylene gas, C₂H₂, and solid calcium hydroxide were formed by the reaction of calcium carbide, CaC₂, 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.

- Outline the steps necessary to answer the following question: What volume of C₂H₂ at 1.005 atm and 12.2 °C is formed by the reaction of 15.48 g of CaC₂ with water?
- Answer the question.

24. Calculate the volume of oxygen required to burn 12.00 L of ethane gas, C₂H₆, to produce carbon dioxide and water, if the volumes of C₂H₆ and O₂ are measured under the same conditions of

temperature and pressure. **Check Answer:**⁴⁰

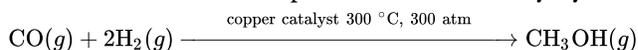
25. What volume of O_2 at STP is required to oxidize 8.0 L of NO at STP to NO_2 ? What volume of NO_2 is produced at STP?

26. Consider the following questions:

a. What is the total volume of the $CO_2(g)$ and $H_2O(g)$ at $600^\circ C$ 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? **Check Answer:**⁴¹

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

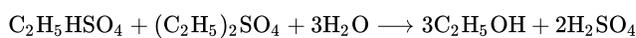


Assuming that the gases behave as ideal gases, find the ratio of the total volume of the reactants to the final volume.

28. 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 ? **Check Answer:**⁴²

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

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



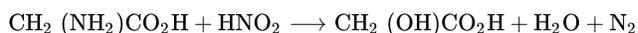
What volume of ethylene at STP is required to produce 1.000 metric ton (1000 kg) of ethanol if the overall yield of ethanol is 90.1%? **Check Answer:**⁴³

31. 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 ($37^\circ C$) and a pressure of 743 torr, what is the molar mass of hemoglobin?

32. 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.)

Check Answer:⁴⁴

33. One method of analyzing amino acids is the van Slyke method. The characteristic amino groups ($-NH_2$) in protein material are allowed to react with nitrous acid, HNO_2 , to form N_2 gas. From the volume of the gas, the amount of amino acid can be determined. A 0.0604-g sample of a biological sample containing glycine, $CH_2(NH_2)COOH$, was analyzed by the van Slyke method and yielded 3.70 mL of N_2 collected over water at a pressure of 735 torr and $29^\circ C$. What was the percentage of glycine in the sample?



12.5 The Kinetic-Molecular Theory

- Using the postulates of the kinetic molecular theory, explain why a gas uniformly fills a container of any shape.
- Can the speed of a given molecule in a gas double at constant temperature? Explain your answer. **Check Answer:**⁴⁵
- Describe what happens to the average kinetic energy of ideal gas molecules when the conditions are changed as follows:
 - The pressure of the gas is increased by reducing the volume at constant temperature.
 - The pressure of the gas is increased by increasing the temperature at constant volume.
 - The average velocity of the molecules is increased by a factor of 2.
- The distribution of molecular velocities in a sample of helium is shown in Figure 12.5d. If the sample is cooled, will the distribution of velocities look more like that of H₂ or of H₂O? Explain your answer. **Check Answer:**⁴⁶
- What is the ratio of the average kinetic energy of a SO₂ molecule to that of an O₂ molecule in a mixture of two gases? What is the ratio of the root mean square speeds, u_{rms} , of the two gases?
- A 1-L sample of CO initially at STP is heated to 546 °C, and its volume is increased to 2 L.
 - What effect do these changes have on the number of collisions of the molecules of the gas per unit area of the container wall?
 - What is the effect on the average kinetic energy of the molecules?
 - What is the effect on the root mean square speed of the molecules?**Check Answer:**⁴⁷
- The root mean square speed of H₂ molecules at 25 °C is about 1.6 km/s. What is the root mean square speed of a N₂ molecule at 25 °C?
- Answer the following questions:
 - 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?
 - 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?
 - At a pressure of 1 atm and a temperature of 20 °C, dry air has a density of 1.2256 g/L. What is the (average) molar mass of dry air?
 - The average temperature of the gas in a hot air balloon is 1.30×10^2 °F. Calculate its density, assuming the molar mass equals that of dry air.
 - The lifting capacity of a hot air balloon is equal to the difference in the mass of the cool air displaced by the balloon and the mass of the gas in the balloon. What is the difference in the mass of 1.00 L of the cool air in part (c) and the hot air in part (d)?
 - An average balloon has a diameter of 60 feet and a volume of 1.1×10^5 ft³. What is the lifting

power of such a balloon? If the weight of the balloon and its rigging is 500 pounds, what is its capacity for carrying passengers and cargo?

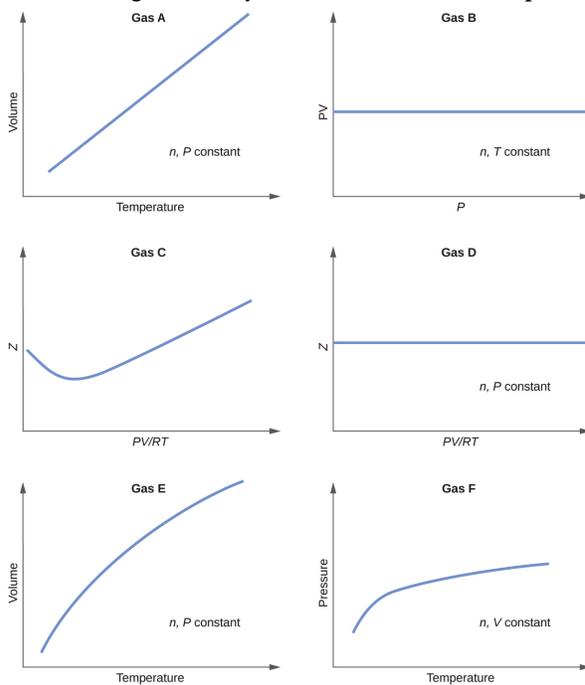
- g. A balloon carries 40.0 gallons of liquid propane (density 0.5005 g/L). What volume of CO_2 and H_2O gas is produced by the combustion of this propane?
- h. A balloon flight can last about 90 minutes. If all of the fuel is burned during this time, what is the approximate rate of heat loss (in kJ/min) from the hot air in the bag during the flight?

Check Answer:⁴⁸

9. Show that the ratio of the rate of diffusion of Gas 1 to the rate of diffusion of Gas 2, $\frac{R_1}{R_2}$, is the same at 0°C and 100°C .

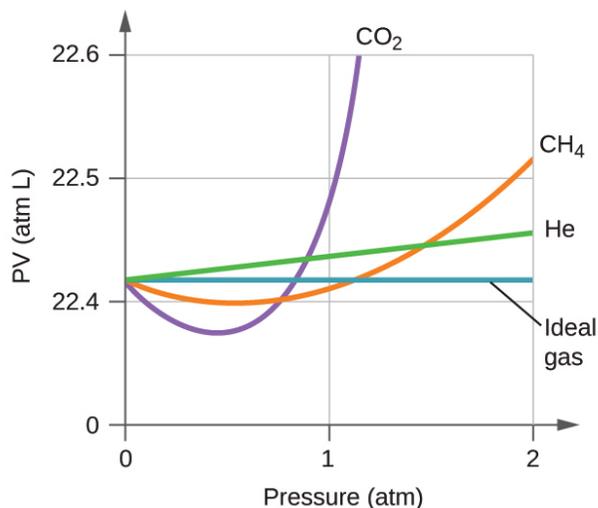
12.6 Non-Ideal Gas Behaviour

1. Graphs showing the behaviour of several different gases are below. Which of these gases exhibit behaviour significantly different from that expected for ideal gases?



Check Answer:⁴⁹

2. Explain why the plot of PV for CO_2 differs from that of an ideal gas. See figure below.



3. 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 behaviour? Explain.
1. high pressure, small volume
 2. high temperature, low pressure
 3. low temperature, high pressure
- Check Answer:** ⁵⁰
4. Describe the factors responsible for the deviation of the behaviour of real gases from that of an ideal gas.
5. For which of the following gases should the correction for the molecular volume be largest: CO, CO₂, H₂, He, NH₃, SF₆? **Check Answer:** ⁵¹
6. A 0.245-L flask contains 0.467 mol CO₂ at 159 °C. Calculate the pressure:
1. using the ideal gas law
 2. using the van der Waals equation
 3. Explain the reason for the difference.
 4. Identify which correction (that for P or V) is dominant and why.
7. Answer the following questions:
1. If XX behaved as an ideal gas, what would its graph of Z vs. P look like?
 2. For most of this chapter, we performed calculations treating gases as ideal. Was this justified?
 3. What is the effect of the volume of gas molecules on Z? Under what conditions is this effect small? When is it large? Explain using an appropriate diagram.
 4. What is the effect of intermolecular attractions on the value of Z? Under what conditions is this effect small? When is it large? Explain using an appropriate diagram.
 5. In general, under what temperature conditions would you expect Z to have the largest deviations from the Z for an ideal gas?

Check Answer: ⁵²

Attribution & References

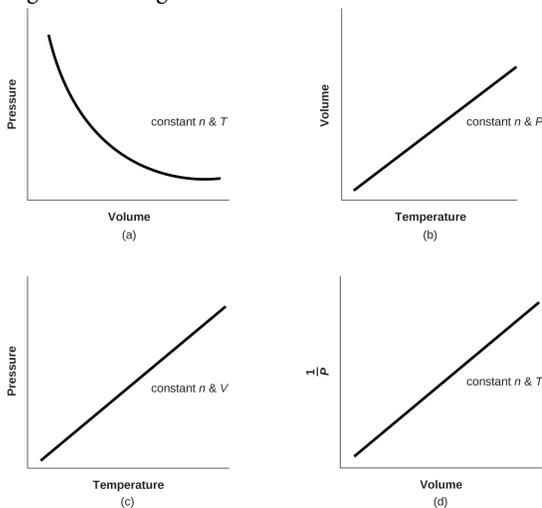
Except where otherwise noted, this page is adapted by JR van Haarlem from:

- “8.1 Gas Pressure (<https://boisestate.pressbooks.pub/chemistry/chapter/5-1-gas-pressure/>)”, “8.2 Relating Pressure, Volume, Amount, and Temperature: The Ideal Gas Law”, “8.5 The Kinetic-Molecular Theory” and “8.6 Non-Ideal Gas Behavior (<https://boisestate.pressbooks.pub/chemistry/chapter/5-6-non-ideal-gas-behavior/>)” In *General Chemistry 1 & 2* by Rice University, a derivative of *Chemistry (Open Stax)* by Paul Flowers, Klaus Theopold, Richard Langley & William R. Robinson and is licensed under CC BY 4.0. Access for free at *Chemistry (OpenStax)* (<https://openstax.org/books/chemistry/pages/1-introduction>)
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Notes

1. The cutting edge of a knife that has been sharpened has a smaller surface area than a dull knife. Since pressure is force per unit area, a sharp knife will exert a higher pressure with the same amount of force and cut through material more effectively.
2. Lying down distributes your weight over a larger surface area, exerting less pressure on the ice compared to standing up. If you exert less pressure, you are less likely to break through thin ice.
3. 0.809 atm; 82.0 kPa
4. 2.2×10^2 kPa
5. Earth: 14.7 lb in^{-2} ; Venus: $13.1 \times 10^3 \text{ lb in}^{-2}$
6. (a) 101.5 kPa; (b) 51 torr drop
7. (a) 264 torr; (b) 35,200 Pa; (c) 0.352 bar
8. (a) 623 mm Hg; (b) 0.820 atm; (c) 83.1 kPa
9. With a closed-end manometer, no change would be observed, since the vaporized liquid would contribute equal, opposing pressures in both arms of the manometer tube. However, with an open-ended manometer, a higher pressure reading of the gas would be obtained than expected, since $P_{\text{gas}} = P_{\text{atm}} + P_{\text{vol liquid}}$.
10. As the bubbles rise, the pressure decreases, so their volume increases as suggested by Boyle's law.
11. (a) The number of particles in the gas increases as the volume increases. (b) temperature, pressure
12. The curve would be farther to the right and higher up, but the same basic shape.
13. 16.3 to 16.5 L
14. 3.40×10^3 torr
15. 12.1 L
16. 217 L

17. 8.190×10^{-2} mol; 5.553 g
 18. (a) 7.24×10^{-2} g; (b) 23.1 g; (c) 1.5×10^{-4} g
 19. 5561 L
 20. 46.4 g
 21. For a gas exhibiting ideal behaviour:



22. 0.644 atm
 23. The pressure decreases by a factor of 3.
 24. 4.2 hours
 25. Effusion can be defined as the process by which a gas escapes through a pinhole into a vacuum. Graham's law states that with a mixture of two gases A and B: $\left(\frac{\text{rate A}}{\text{rate B}}\right) = \left(\frac{\text{molar mass of B}}{\text{molar mass of A}}\right)^{1/2}$. Both A and B are in the same container at the same temperature, and therefore will have the same kinetic energy:

$$\frac{v_A^2}{v_B^2} = \frac{m_B}{m_A}$$

$$\text{KE}_A = \text{KE}_B \quad \text{KE} = \frac{1}{2} m v^2 \quad \text{Therefore, } \frac{1}{2} m_A v_A^2 = \frac{1}{2} m_B v_B^2 \quad \left(\frac{v_A}{v_B}\right)^{1/2} = \left(\frac{m_B}{m_A}\right)^{1/2}$$

$$\left(\frac{v_A}{v_B}\right) = \left(\frac{m_B}{m_A}\right)^{1/2}$$

26. $\text{F}_2, \text{N}_2\text{O}, \text{Cl}_2, \text{H}_2\text{S}$
 27. 1.4; 1.2
 28. 51.7 cm
 29. 4.64 g L^{-1}
 30. 38.8 g
 31. 72.0 g mol^{-1}
 32. 88.1 g mol^{-1} ; PF_3
 33. 141 atm

34. CH_4 : 276 kPa; C_2H_6 : 27 kPa; C_3H_8 : 3.4 kPa
35. Yes
36. 740 torr
37. (a) Determine the moles of HgO that decompose; using the chemical equation, determine the moles of O_2 produced by decomposition of this amount of HgO ; and determine the volume of O_2 from the moles of O_2 , temperature, and pressure. (b) 0.308 L
38. (a) Determine the molar mass of CCl_2F_2 . From the balanced equation, calculate the moles of H_2 needed for the complete reaction. From the ideal gas law, convert moles of H_2 into volume. (b) 3.72×10^3 L
39. (a) Balance the equation. Determine the grams of CO_2 produced and the number of moles. From the ideal gas law, determine the volume of gas. (b) 7.43×10^5 L
40. 42.00 L
41. (a) 18.0 L; (b) 0.533 atm
42. 10.57 L O_2
43. 5.40×10^5 L
44. XeF_2
45. Yes. At any given instant, there are a range of values of molecular speeds in a sample of gas. Any single molecule can speed up or slow down as it collides with other molecules. The average velocity of all the molecules is constant at constant temperature.
46. H_2O . Cooling slows the velocities of the He atoms, causing them to behave as though they were heavier.
47. (a) The number of collisions per unit area of the container wall is constant. (b) The average kinetic energy doubles. (c) The root mean square speed increases to $\sqrt{2}$ times its initial value; u_{rms} is proportional to $\sqrt{\text{KE}_{\text{avg}}}$.
48. (a) equal; (b) less than; (c) 29.48 g mol^{-1} ; (d) 1.0966 g L^{-1} ; (e) 0.129 g/L; (f) 4.01×10^5 g; net lifting capacity = 384 lb; (g) 270 L; (h) 39.1 kJ min^{-1}
49. Gases C, E, and F
50. The gas behaviour most like an ideal gas will occur under the conditions in (b). Molecules have high speeds and move through greater distances between collision; they also have shorter contact times and interactions are less likely. Deviations occur with the conditions described in (a) and (c). Under conditions of (a), some gases may liquefy. Under conditions of (c), most gases will liquefy.
51. SF_6
52. (a) A straight horizontal line at 1.0; (b) When real gases are at low pressures and high temperatures they behave close enough to ideal gases that they are approximated as such, however, in some cases, we see that at a high pressure and temperature, the ideal gas approximation breaks down and is significantly different from the pressure calculated by the ideal gas equation (c) The greater the compressibility, the more the volume matters. At low pressures, the correction factor for intermolecular attractions is more significant, and the effect of the volume of the gas molecules on Z would be a small lowering compressibility. At higher pressures, the effect of the volume of the gas molecules themselves on Z would increase compressibility (see Figure 12.6a) (d) Once again, at low pressures, the effect of intermolecular attractions on Z would be more important than the correction factor for the volume of the gas molecules themselves, though perhaps still small. At higher pressures and low temperatures, the effect of intermolecular attractions would be larger. See Figure 12.6a. (e) low temperatures