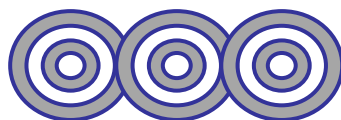




Chemistry, The Central Science, 11th edition
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Chapter 10

Gases

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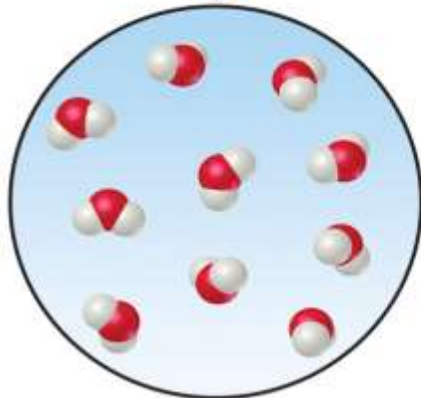
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Classification of matter according to its physical state

Gas

has no fixed volume or shape, it conforms to the volume and shape of its containers, It can be compressed or expand
It molecule far apart

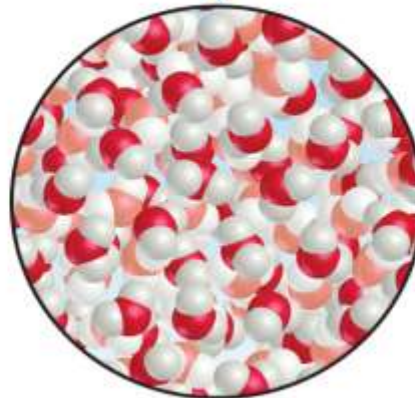


Gas



Liquid

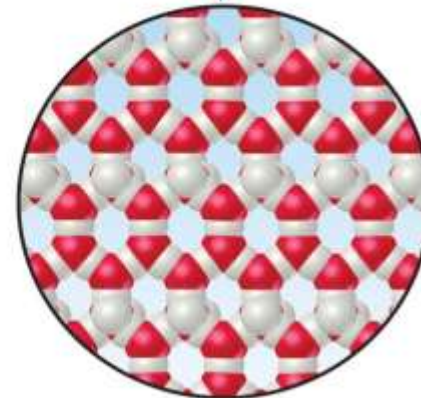
has distinct volume but has no specific shape



Liquid

Solid

has both definite shape and volume

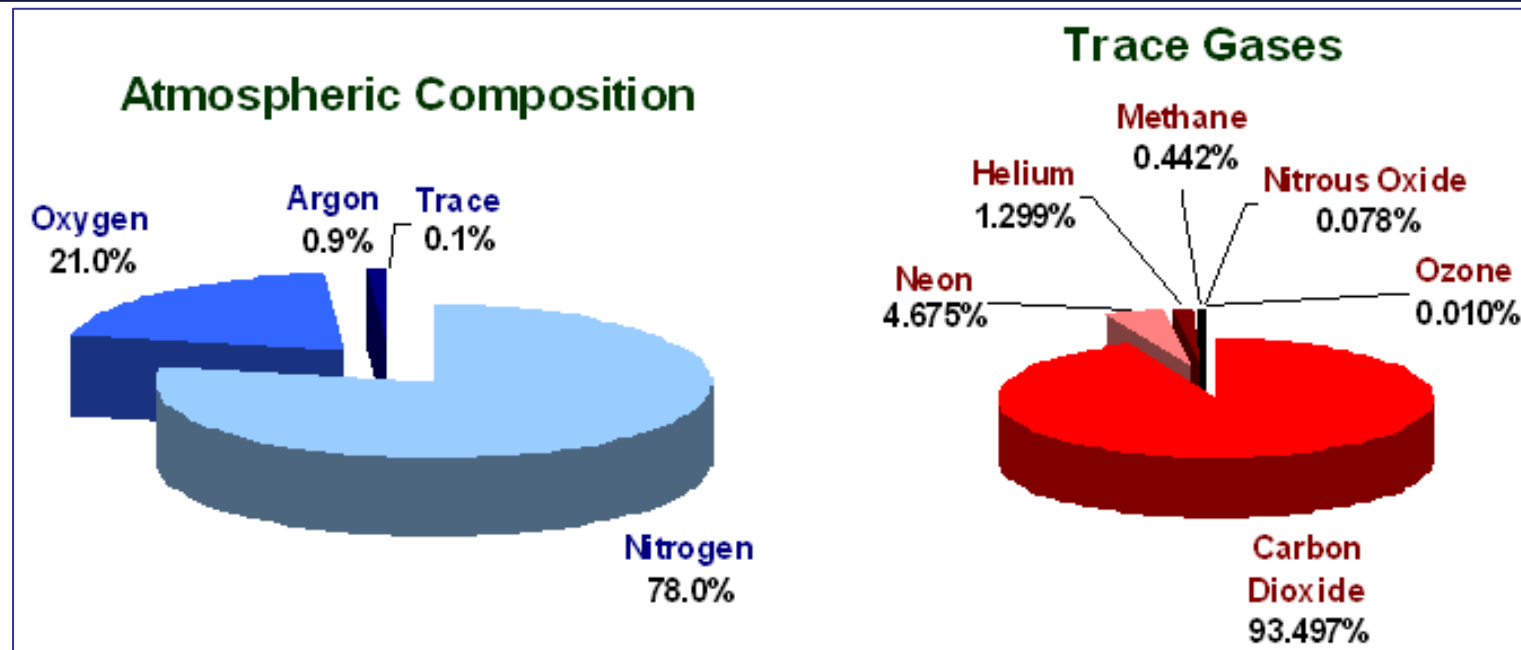


Solid

10.1

Characteristics of Gases

Characteristics of Gases



- Air is a complex mixture of several substances.
- Although N_2 has very different chemical properties from O_2 , Air mixture behaves physically as one gaseous material.
- Only few elements exist as gases under ordinary conditions of temperature and pressure.
- The noble gases (**He, Ne, Ar, Kr and Xe**) are all monoatomic gases, whereas H_2 , N_2 , O_2 , F_2 and Cl_2 are diatomic gases.

Many molecular compounds are also gases (all these gases are composed entirely of nonmetallic elements, all have **simple molecular formulas** and therefore **low molar masses**).

TABLE 10.1 ■ Some Common Compounds That Are Gases at Room Temperature

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

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

Unlike liquids and solids, gases

- Expand spontaneously to fill their containers.
- The volume of gas equals the volume of the containers in which its held.
- Are highly compressible; when pressure is applied to a gas, its volume readily decreases.
- Have extremely low densities.
- Have relatively low molar masses.

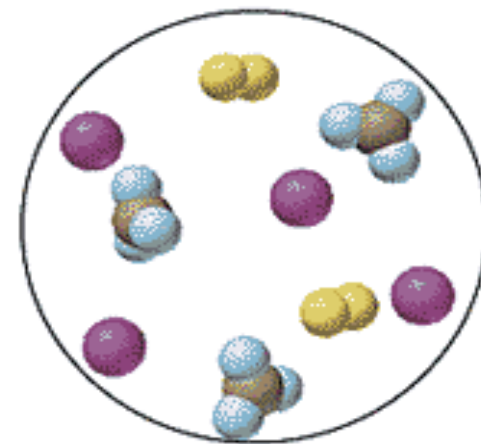
Gases form homogeneous mixtures with each other regardless of the identities or relative proportions of the component gases. The atmosphere serves as an excellent example (N_2 and O_2).

As a further example, when water and gasoline are mixed, the two liquids remain as separate layers. In contrast, the water vapor and gasoline vapors above the liquids form a homogeneous gas mixture.

What is the major reason that physical properties do not differ much from one gaseous substance to another ???

The characteristic properties of gases arise because the individual molecules are relatively far apart. In the air we breathe, for example, the molecules take up only about 0.1% of the total volume, with the rest being empty space. Thus, each molecule behaves largely as though the others were not present.

As a result, different gases behave similarly, even though they are made up of different molecules. In contrast, the individual molecules in a liquid are close together and occupy perhaps 70% of the total space. The **attractive forces** among the molecules keep the liquid together.



10.2

Pressure

Pressure

Among the most readily measured properties of a gas are its **temperature**, **volume**, and **pressure**.

Many early studies of gases focused on relationships among these properties.

Pressure is the amount of force applied to an area (ratio of force to the area over which that force is distributed).

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

Pressure is force per unit area applied in a direction perpendicular to the surface of an object.

Atmospheric pressure is the weight of air per unit of area.

The force F exerted by any object is the product of its mass m times its acceleration a that is,

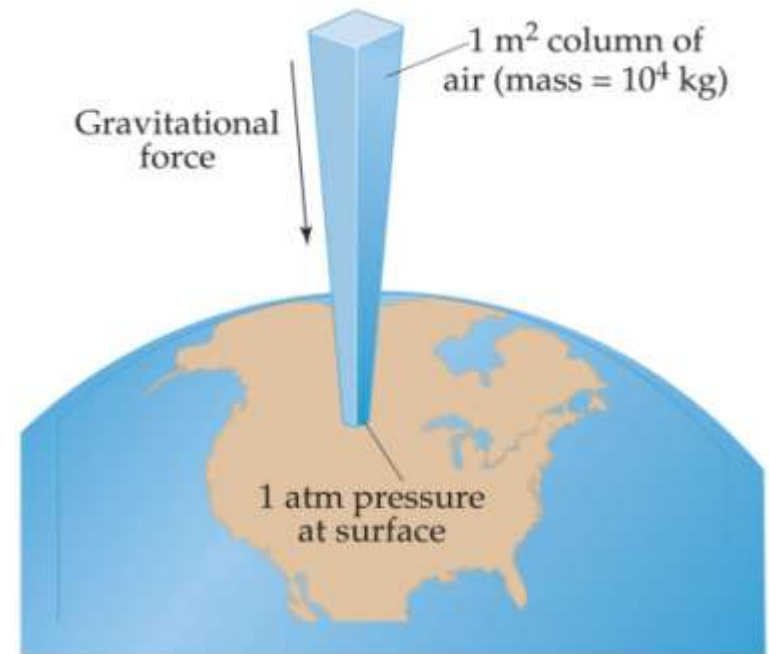
$$\mathbf{F = ma}$$

The acceleration by Earth's gravity to any object located near Earth's surface is 9.8 m/s^2 .

The **SI** unit for force is kg.m/s^2 and is called the newton (N): $1 \text{ N} = 1 \text{ kg.m/s}^2$.

The pressure exerted by the column is the force divided by the cross-sectional area A over which the force is applied.

The **SI** unit of pressure is N/m^2 . it is given the name pascal (Pa).



$$F = (10000 \text{ kg}) (9.8 \text{ m/s}^2) = 1 \times 10^5 \text{ kg.m/s}^2 = 1 \times 10^5 \text{ N}$$

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

Standard Atmospheric Pressure

Normal atmospheric pressure at sea level is referred to as **standard pressure**

It is equal to 1.00 atm,
760 torr, 760 mmHg or 100 kPa or 1 bar.

The actual atmospheric pressure at any location depends on weather conditions and altitude.

Standard atmospheric pressure is the pressure sufficient to support a column of mercury 760 mm high (equal 1.01325×10^5 Pa).

Non-SI units may also be used, such as **atmosphere (atm)** or **millimeter of mercury (mm Hg)** which equal **Torricelli (torr)**.

Units of Pressure

Pressure Units						
	pascal (Pa)	bar (bar)	atmosphere (atm)	torr (torr)	pound-force per square inch (psi)	kilogram-force per square centimeter (kgf/cm ²)
1 Pa	$\equiv 1 \text{ N/m}^2$	10^{-5}	9.8692×10^{-6}	7.5006×10^{-3}	145.04×10^{-6}	1.01972×10^{-5}
1 bar	100,000	$\equiv 10^6 \text{ dyn/cm}^2$	0.98692	750.06	14.504	1.01972
1 atm	101,325	1.01325	$\equiv 1 \text{ atm}$	760	14.696	1.03323
1 torr	133.322	1.3332×10^{-3}	1.3158×10^{-3}	$\equiv 1 \text{ torr}$ $\approx 1 \text{ mmHg}$	19.337×10^{-3}	1.35951×10^{-3}
1 psi	6,894.76	68.948×10^{-3}	68.046×10^{-3}	51.715	$\equiv 1 \text{ lbf/in}^2$	7.03059×10^{-2}
1 kgf/cm²	98,066.5	0.980665	0.967838	735.5576	14.22357	$\equiv 1 \text{ kgf/cm}^2$
Example reading: $1 \text{ Pa} = 1 \text{ N/m}^2 = 10^{-5} \text{ bar} = 9.8692 \times 10^{-6} \text{ atm} = 7.5006 \times 10^{-3} \text{ torr}$, etc. Note: mmHg is an abbreviation for millimetre of mercury						

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

Barometer

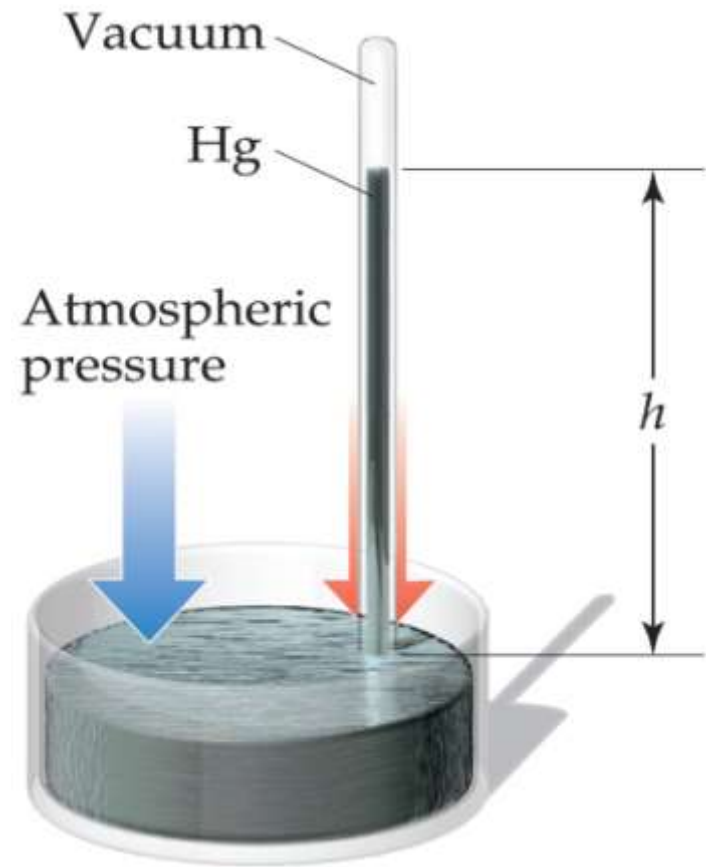
Is the atmosphere has weight?

Torricelli invented the barometer, which is made from a glass tube more than 760 mm long that is closed at one end, completely filled with mercury, and inverted into a dish that contains additional mercury (care must be taken so that no air gets into the tube).

When the mercury-filled tube is inverted into the dish of mercury, some of the mercury flows out of the tube, but a column of mercury remains inside.

The mercury surface in the dish experiences the full force, or weight, of Earth's atmosphere, which pushes the mercury up the tube until the pressure at the base of the tube. So the height, h , of the mercury column is a measure of the atmosphere's pressure, and it changes as the atmospheric pressure changes.

As the barometer ascended, the height of the mercury column diminished, because the amount of atmosphere pressing down on the surface decreases as one moves higher.



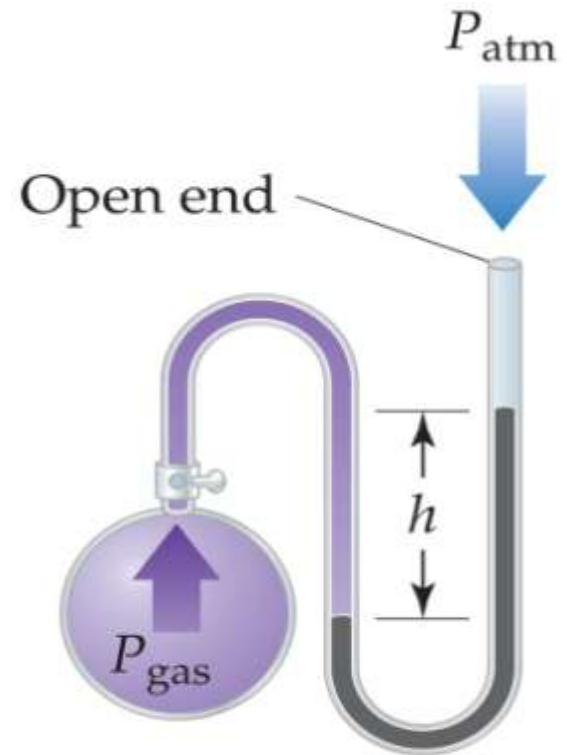
Manometer

Various devices used to measure the pressures of enclosed gases.

e.g., Tire gauges, measure the pressure of air in automobile and bicycle tires.

This device is used to measure the difference in pressure between atmospheric pressure and that of a gas in a vessel.

Manometer operates on a principle similar to that of a barometer.



$$P_{\text{gas}} = P_{\text{atm}} + P_h$$

Sample Exercise 10.1 Converting Units of Pressure

(a) Convert 0.357 atm to torr. (b) Convert 6.6×10^{-2} torr to atm. (c) Convert 147.2 kPa to torr.

Solution

(a) To convert atmospheres to torr, we use the relationship $760 \text{ torr} = 1 \text{ atm}$:

$$(0.357 \text{ atm}) \left(\frac{760 \text{ torr}}{1 \text{ atm}} \right) = 271 \text{ torr}$$

Note that the units cancel in the required manner.

(b) We use the same relationship as in part (a). To get the appropriate units to cancel, we must use the conversion factor as follows:

$$(6.6 \times 10^{-2} \text{ torr}) \left(\frac{1 \text{ atm}}{760 \text{ torr}} \right) = 8.7 \times 10^{-5} \text{ atm}$$

(c) The relationship $760 \text{ torr} = 101.325 \text{ kPa}$ allows us to write an appropriate conversion factor for this problem:

$$(147.2 \text{ kPa}) \left(\frac{760 \text{ torr}}{101.325 \text{ kPa}} \right) = 1104 \text{ torr}$$

Practice Exercise

(a) In countries that use the metric system, such as Canada, atmospheric pressure in weather reports is given in units of kPa. Convert a pressure of 745 torr to kPa. (b) An English unit of pressure sometimes used in engineering is pounds per square inch (lb/in^2), or psi: $1 \text{ atm} = 14.7 \text{ lb}/\text{in}^2$. If a pressure is reported as 91.5 psi, express the measurement in atmospheres.

Answer: (a) 99.3 kPa, (b) 6.22 atm

Sample Exercise 10.2 Using a Manometer to Measure Gas Pressure

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

Solution

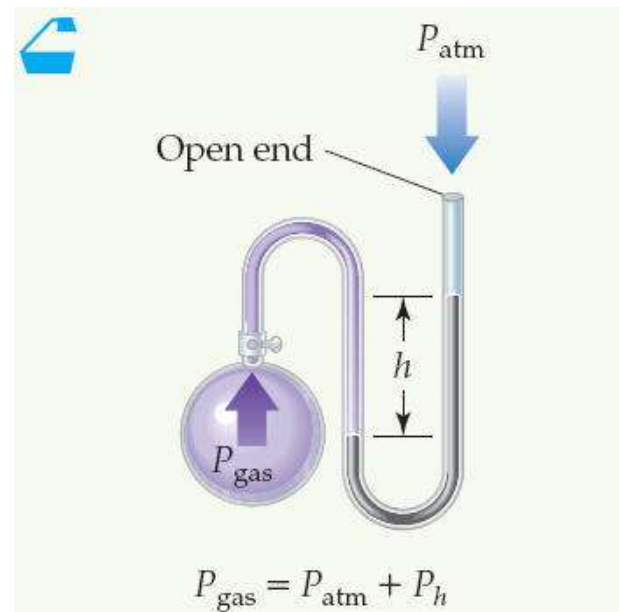
(a) The pressure of the gas equals the atmospheric pressure plus h . We convert the pressure of the gas to atmospheres:

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

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

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

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



▲ **Figure 10.3 A mercury manometer.** This device is sometimes employed in the laboratory to measure gas pressures near atmospheric pressure.

Practice Exercise

Convert a pressure of 0.975 atm into Pa and kPa.

Answer: 9.88×10^4 Pa and 98.8 kPa

10.3

The Gas Laws

The Gas Laws

Experiments with a large number of gases reveal that four variables are needed to define the physical condition, or state of a gas:

- Temperature (**T**)
- Pressure (**P**)
- Volume (**V**)
- Amount of gas, usually expressed as the number of moles (**n**).

The equations that express the relationships among **T**, **P**, **V**, and **n** are known as the **gas laws**.

Boyle's Law (the V-P relationship)

Boyle's Law: "The volume of a fixed quantity of gas at constant temperature is inversely proportional to the pressure".

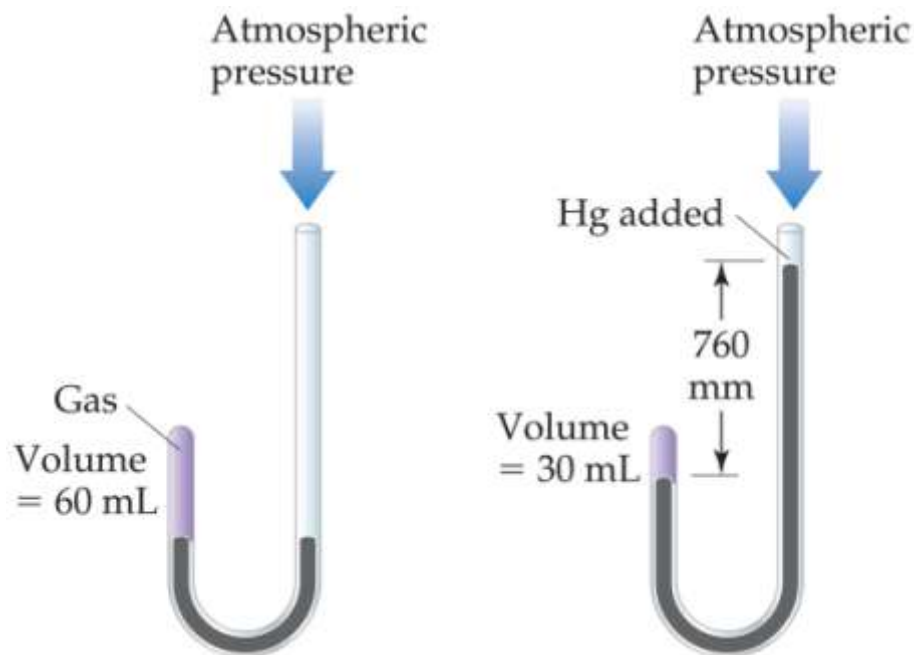
$$V \propto 1/P$$

Boyles experiment

Boyle used J-shaped tube, in the tube on the left, a quantity of gas is trapped above a column of mercury. Boyle changed the pressure on the gas by adding mercury to the tube.

He found that the volume of the gas decreased as the pressure increased.

e.g., doubling the pressure caused the gas volume to decrease to half its original value.



As **P** and **V** are inversely proportional;

$$V \propto 1/P$$

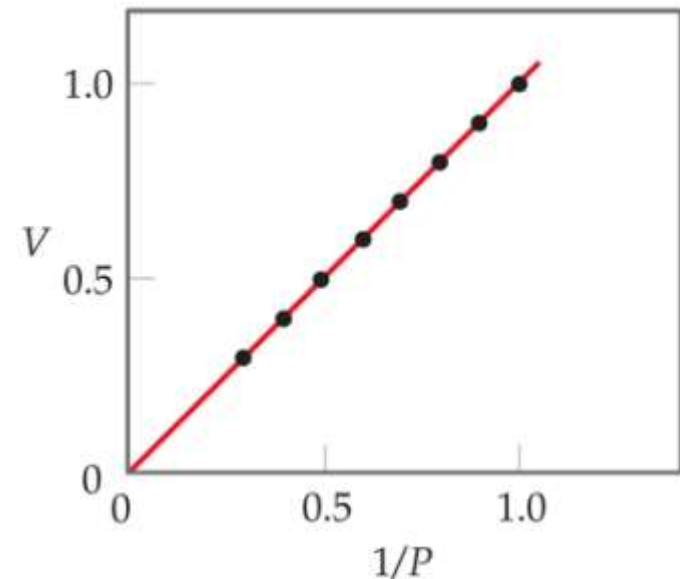
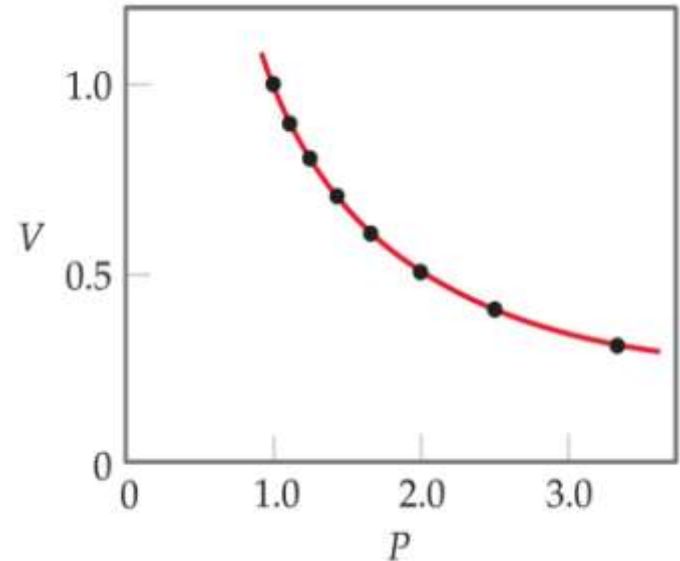
A plot of **V** versus **P** results in a curve.

Since **$PV = k$**

$$V = k(1/P)$$

This means a plot of **V** versus **1/P** will be a straight line.

The value of the constant depends on the **T** and **n**.



Charles's Law (the V-T relationship)

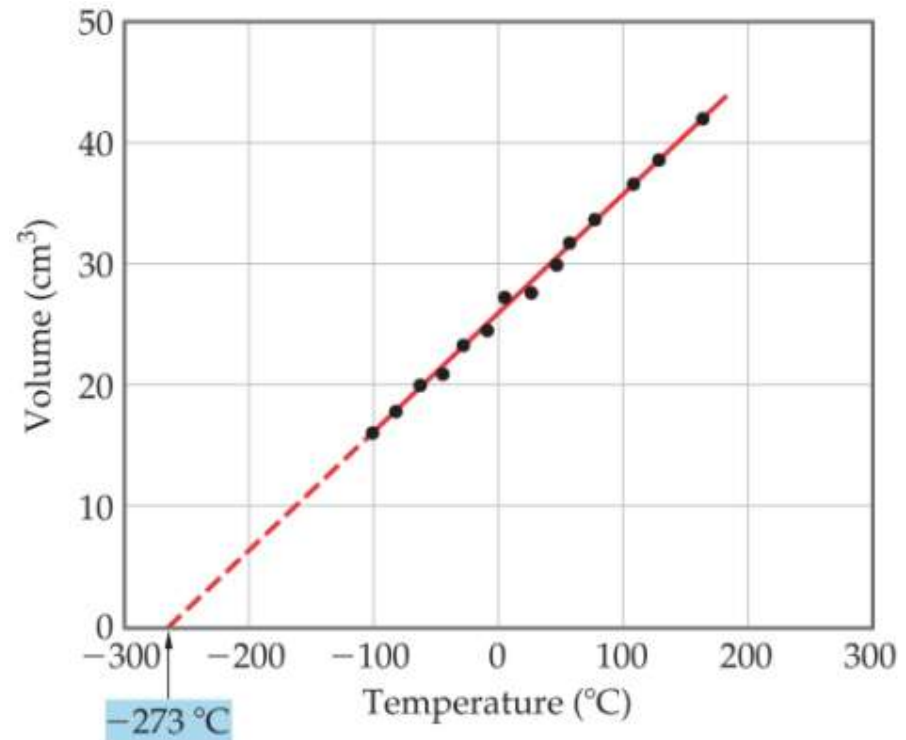
Charles's Law: "The volume of a fixed amount of gas at constant pressure is directly proportional to its absolute temperature".

$$V \propto T$$

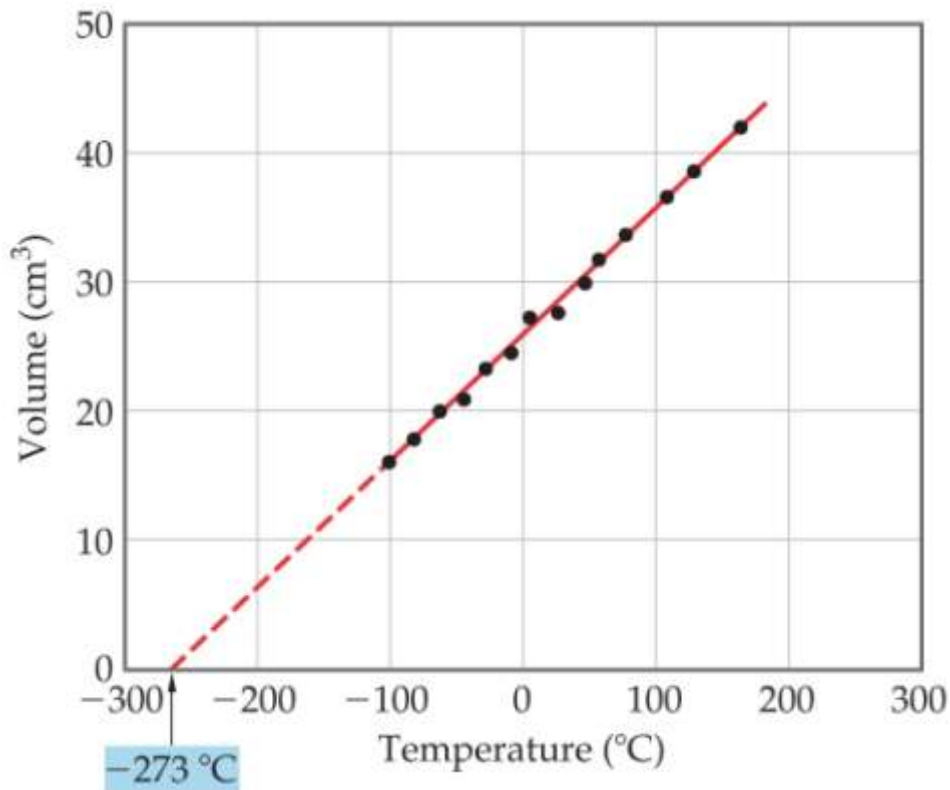
- i.e., $\frac{V}{T} = k$

A plot of **V** versus **T** will be a straight line.

The value of the constant depends on the **P** and **n**.



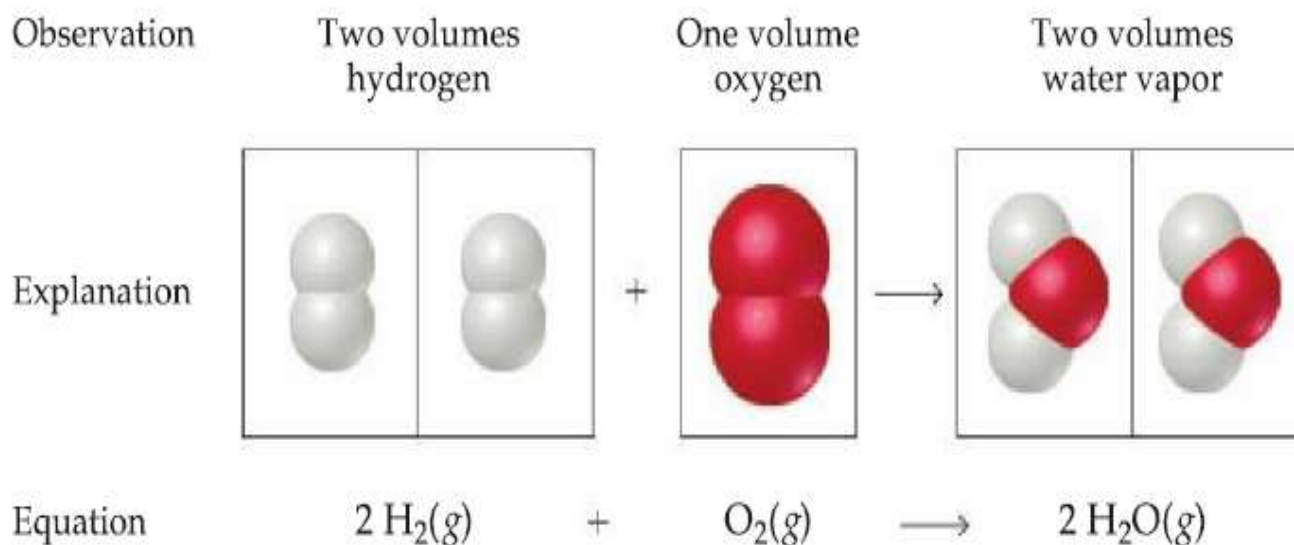
The extrapolated (extended) line (which is dashed) passes through -273°C . Note also that the gas is predicted to have zero volume at this temperature. This condition is never realized, however, because all gases liquefy or solidify before reaching this temperature. This is called **absolute zero** ($0\text{ K} = -273.15^{\circ}\text{C}$).



The dashed line is an extrapolation to temperature at which the substance is no longer a gas.

Avogadro's Law (the V-n relationship)

The relationship between the quantity of a gas and its volume follows from the work of Joseph Gay-Lussac and Amedeo Avogadro.



Law of combining volumes




At a given pressure and temperature, the volumes of gases that react with one another are in the ratios of small whole numbers.

e.g., two volumes of hydrogen gas react with one volume of oxygen gas to form two volumes of water vapor.

Avogadro's law: "The volume of a gas at constant temperature and pressure is directly proportional to the number of moles of the gas".

$$V \propto n$$

Mathematically, this means $V = k n$

			
Volume	22.4 L	22.4 L	22.4 L
Pressure	1 atm	1 atm	1 atm
Temperature	0 °C	0 °C	0 °C
Mass of gas	4.00 g	28.0 g	16.0 g
Number of gas molecules	6.02×10^{23}	6.02×10^{23}	6.02×10^{23}

A comparison illustrating Avogadro's hypothesis. Each gas has the same **V**, **T** and **P** and thus contains the same number of molecules.

Because a molecule of one substance differs in mass from a molecule of another, the masses of gas in the three containers differ.

Sample Exercise 10.3 Evaluating the Effects of Changes in P , V , n and T on a Gas

Suppose we have a gas confined to a cylinder as shown in the figure below. Consider the following changes: **(a)** Heat the gas from 298 K to 360 K, while maintaining the piston in the position shown in the drawing. **(b)** Move the piston to reduce the volume of gas from 1 L to 0.5 L. **(c)** Inject additional gas through the gas inlet valve. Indicate how each of these changes will affect the average distance between molecules, the pressure of the gas, and the number of moles of gas present in the cylinder

Solution

(a) Heating the gas while maintaining the position of the piston will cause no change in the number of molecules per unit volume. Thus, the distance between molecules and the total moles of gas remain the same. The increase in temperature, however, will cause the pressure to increase (**Charles's law**).

(b) Moving the piston compresses the same quantity of gas into a smaller volume. The total number of molecules of gas, and thus the total number of moles, remains the same. The average distance between molecules, however, must decrease because of the smaller volume in which the gas is confined. The reduction in volume causes the pressure to increase (**Boyle's law**).

(c) Injecting more gas into the cylinder while keeping the volume and temperature the same will result in more molecules and thus a greater number of moles of gas. The average distance between atoms must decrease because their number per unit volume increases. Correspondingly, the pressure increases (**Avogadro's law**).



Cylinder with piston and gas inlet valve.

Practice Exercise

What happens to the density of a gas as **(a)** the gas is heated in a constant-volume container; **(b)** the gas is compressed at constant temperature; **(c)** additional gas is added to a constant-volume container?

Answer: **(a)** no change, **(b)** increase, **(c)** increase

10.4

The Ideal Gas Equation

Ideal-Gas Equation

- Gas laws ...

$V \propto 1/P$ (Boyle's law)

$V \propto T$ (Charles's law)

$V \propto n$ (Avogadro's law)

- Combining these laws ...

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

- Then becomes ...

$$V = R \frac{nT}{P} \quad \text{or} \quad PV = nRT$$

$$PV = nRT$$

This equation is known as the **ideal gas equation**.

An ideal gas is a hypothetical gas whose pressure, volume and temperature behavior are described completely by the ideal gas equation.

The constant of proportionality is known as **R**, the gas constant.

$$R = \frac{PV}{nT}$$

Units	Numerical Value
L-atm/mol-K	0.08206
J/mol-K*	8.314
cal/mol-K	1.987
m ³ -Pa/mol-K*	8.314
L-torr/mol-K	62.36

*SI unit

In working problems with the ideal gas equation, the units of **P**, **T**, **n** and **V** must agree with the unit in the gas constant

Suppose you have 1.00 mol of an ideal gas at 1.00 atm and 0.00 °C (273.15 K). According to the ideal gas equation, the volume of the gas is:

$$V = \frac{nRT}{P} = \frac{(1.000 \text{ mol})(0.08206 \text{ L-atm/mol-K})(273.15 \text{ K})}{1.000 \text{ atm}} = 22.41 \text{ L}$$

The conditions **0 °C** and **1 atm** are referred to as the standard temperature and pressure (**STP**).

The volume occupied by one mole of ideal gas at **STP** (22.41 L) is known as the **molar volume** of an ideal gas at **STP**.

How many molecules are in 22.41 L of an ideal gas at **STP** ?

Answer: 6.02×10^{23} molecules

Sample Exercise 10.4 Using the Ideal-Gas equation

Calcium carbonate, $\text{CaCO}_3(s)$, decomposes upon heating to give $\text{CaO}(s)$ and $\text{CO}_2(g)$. A sample of CaCO_3 is decomposed, and the carbon dioxide is collected in a 250-mL flask. After the decomposition is complete, the gas has a pressure of 1.3 atm at a temperature of 31 °C. How many moles of CO_2 gas were generated?

Solution

In analyzing and solving gas-law problems, it is helpful to tabulate the information given in the problems and then to convert the values to units that are consistent with those for R (0.0821 L-atm/mol-K). In this case the given values are

$$V = 250 \text{ mL} = 0.250 \text{ L}$$

$$P = 1.3 \text{ atm}$$

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

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

We now rearrange the ideal-gas equation to solve for n

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

$$n = \frac{(1.3 \text{ atm})(0.250 \text{ L})}{(0.0821 \text{ L-atm/mol-K})(304 \text{ K})} = 0.013 \text{ mol CO}_2$$

Practice Exercise

Tennis balls are usually filled with air or N_2 gas to a pressure above atmospheric pressure to increase their “bounce.” If a particular tennis ball has a volume of 144 cm^3 and contains 0.33 g of N_2 gas, what is the pressure inside the ball at 24 °C?

Answer: 2.0 atm

Relating the Ideal Gas Equation and the Gas Laws

Boyle's law is special case of the ideal gas equation. e.g., when **n** and **T** are held constant. Therefore, the product **nRT** is the product of three constants and must itself be a constant.

$$PV = nRT = \text{constant} \quad \text{or} \quad PV = \text{constant}$$

Thus, we have Boyle's law. We see that if **n** and **T** are constant, the individual values of **P** and **V** can change, but the product **PV** must remain constant.

$$P_1V_1 = P_2V_2$$

In a similar way, we can derive the relationships for Charle's (**V** and **T**) and Avogadro's (**n** and **V**) or (**P** and **T**) Laws.

The combined gas law:

$$\frac{PV}{nT} = R$$

$$\frac{P_1V_1}{T_1} = \frac{P_2V_2}{T_2}$$

Sample Exercise 10.5 Calculating the Effect of Temperature Changes on Pressure

The gas pressure in an aerosol can is 1.5 atm at 25 °C. Assuming that the gas inside obeys the ideal-gas equation, what would the pressure be if the can were heated to 450 °C?

Solution

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

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

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

	P	T
INITIAL	1.5 atm	298 K
FINAL	P_2	723 K

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

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

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

$$P_2 = (1.5 \text{ atm}) \left(\frac{723 \text{ K}}{298 \text{ K}} \right) = 3.6 \text{ atm}$$

Practice Exercise

A large natural-gas storage tank is arranged so that the pressure is maintained at 2.20 atm. On a cold day in December when the temperature is -15 °C (4 °F), the volume of gas in the tank is $3.25 \times 10^3 \text{ m}^3$. What is the volume of the same quantity of gas on a warm July day when the temperature is 31 °C (88 °F)?

Answer: $3.83 \times 10^3 \text{ m}^3$

Sample Exercise 10.6 Calculating the Effect of Changing P and T on the Volume of a Gas

An inflated balloon has a volume of 6.0 L at sea level (1.0 atm) and is allowed to ascend in altitude until the pressure is 0.45 atm. During ascent the temperature of the gas falls from 22 °C to −21 °C. Calculate the volume of the balloon at its final altitude.

Solution

Let's again proceed by converting temperature to the Kelvin scale and tabulating the given information.

	P	V	T
INITIAL	1.0 atm	6.0 L	295 K
FINAL	0.45 atm	V_2	252 K

Because n is constant, we can use Equation 10.8.

Solve: Rearranging Equation 10.8 to solve for V_2 gives

$$V_2 = V_1 \times \frac{P_1}{P_2} \times \frac{T_2}{T_1} = (6.0 \text{ L}) \left(\frac{1.0 \text{ atm}}{0.45 \text{ atm}} \right) \left(\frac{252 \text{ K}}{295 \text{ K}} \right) = 11 \text{ L}$$

Practice Exercise

A 0.50-mol sample of oxygen gas is confined at 0 °C in a cylinder with a movable piston, such as that shown in Figure 10.12. The gas has an initial pressure of 1.0 atm. The piston then compresses the gas so that its final volume is half the initial volume. The final pressure of the gas is 2.2 atm. What is the final temperature of the gas in degrees Celsius?

Answer: 27 °C

10.5

Further Applications of the Ideal Gas Equation

Gas Densities and Molar Mass

The diagram illustrates the derivation of gas density from the ideal gas law. It starts with the ideal gas law $PV = nRT$ on the left. Two arrows branch from this equation. The upper arrow points to the equation $\frac{n}{V} = \frac{P}{RT}$. Above this equation is the definition of molar mass: $M = \frac{n \text{ (mol)}}{V \text{ (L)}}$. A thick arrow then points from $\frac{n}{V}$ to the final equation $M = \frac{P}{RT}$. The lower arrow points to the equation $n = \frac{m}{\mathcal{M}}$. To its right is the definition of density: $d = \frac{m}{V}$. A thick arrow then points from these two equations to the final equation $d = \frac{P \mathcal{M}}{RT}$. All final equations are in red.

$$PV = nRT$$
$$\frac{n}{V} = \frac{P}{RT} \quad M = \frac{n \text{ (mol)}}{V \text{ (L)}} \quad \rightarrow \quad M = \frac{P}{RT}$$
$$n = \frac{m}{\mathcal{M}} \quad d = \frac{m}{V} \quad \rightarrow \quad d = \frac{P \mathcal{M}}{RT}$$

The density of a gas depends on its pressure, molar mass and temperature. The higher the molar mass and pressure, the more dense the gas. The higher the temperature, the less dense the gas.

Although gases form homogeneous mixtures regardless of their identities, a less dense gas will lie above a more dense gas in the absence of mixing. e.g., CO_2 has a higher molar mass than N_2 or O_2 and is therefore more dense than air. When CO_2 is released from a CO_2 fire extinguisher, it blankets a fire, preventing O_2 from reaching the combustible material.



The fact that a hotter gas is less dense than a cooler one explains why hot air rises. The difference between the densities of hot and cold air is responsible for lift of hot air balloons. It is also responsible for many phenomena in weather, such as the formation of large thunderhead clouds during thunderstorms.

Sample Exercise 10.7 Calculating Gas Density

What is the density of carbon tetrachloride vapor at 714 torr and 125 °C?

Solution

The temperature on the Kelvin scale is $125 + 273 = 398$ K.

The pressure in atmospheres is $(714 \text{ torr})(1 \text{ atm}/760 \text{ torr}) = 0.939 \text{ atm}$.

The molar mass of CCl_4 is $12.0 + (4)(35.5) = 154.0 \text{ g/mol}$.

Using these quantities along with Equation 10.10, we have

$$d = \frac{(0.939 \text{ atm})(154.0 \text{ g/mol})}{(0.0821 \text{ L-atm/mol-K})(398 \text{ K})} = 4.43 \text{ g/L}$$

Practice Exercise

The mean molar mass of the atmosphere at the surface of Titan, Saturn's largest moon, is 28.6 g/mol. The surface temperature is 95 K, and the pressure is 1.6 atm. Assuming ideal behavior, calculate the density of Titan's atmosphere.

Answer: 5.9 g/L

Sample Exercise 10.8 Calculating the Molar Mass of a Gas

A series of measurements are made to determine the molar mass of an unknown gas. First, a large flask is evacuated and found to weigh 134.567 g. It is then filled with the gas to a pressure of 735 torr at 31 °C and reweighed. Its mass is now 137.456 g. Finally, the flask is filled with water at 31 °C and found to weigh 1067.9 g. (The density of the water at this temperature is 0.997 g/mL.) Assume that the ideal-gas equation applies, and calculate the molar mass of the unknown gas.

Solution

The mass of the gas is the difference between the mass of the flask filled with gas and that of the empty (evacuated) flask:

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

The volume of the gas equals the volume of water that the flask can hold. The volume of water is calculated from its mass and density. The mass of the water is the difference between the masses of the full and empty flask:

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

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

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

Knowing the mass of the gas (2.889 g) and its volume (936 mL), we can calculate the density of the gas:

$$2.889 \text{ g} / 0.936 \text{ L} = 3.09 \text{ g/L}$$

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

$$\begin{aligned} \mathcal{M} &= \frac{dRT}{P} \\ &= \frac{(3.09 \text{ g/L})(0.0821 \text{ L}\cdot\text{atm/mol}\cdot\text{K})(304 \text{ K})}{(735/760) \text{ atm}} \\ &= 79.7 \text{ g/mol} \end{aligned}$$

Practice Exercise

Calculate the average molar mass of dry air if it has a density of 1.17 g/L at 21 °C and 740.0 torr.

Answer: 29.0 g/mol.

Volumes of Gases in Chemical Reactions

In the chemical reactions, mole concept together with balanced chemical equations are used for these types of calculations.

The coefficients in balanced chemical equations tell us the relative amounts (in moles) of reactants and products in a reaction.

The ideal gas equation relates the number of moles of a gas, to **P**, **V** and **T**.

Sample Exercise 10.9 Relating the Volume of a Gas to the Amount of Another Substance in a Reaction

The safety air bags in automobiles are inflated by nitrogen gas generated by the rapid decomposition of sodium azide, NaN_3 :



If an air bag has a volume of 36 L and is to be filled with nitrogen gas at a pressure of 1.15 atm at a temperature of 26.0 °C, how many grams of NaN_3 must be decomposed?

Solution

The number of moles of N_2 is determined using the ideal-gas equation:

$$n = \frac{PV}{RT} = \frac{(1.15 \text{ atm})(36 \text{ L})}{(0.0821 \text{ L-atm/mol-K})(299 \text{ K})} = 1.7 \text{ mol N}_2$$

From here we use the coefficients in the balanced equation to calculate the number of moles of NaN_3 .

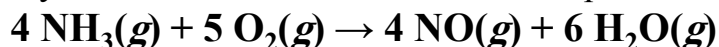
$$(1.7 \text{ mol N}_2) \left(\frac{2 \text{ mol NaN}_3}{3 \text{ mol N}_2} \right) = 1.1 \text{ mol NaN}_3$$

Finally, using the molar mass of NaN_3 , we convert moles of NaN_3 to grams:

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

Practice Exercise

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



How many liters of $\text{NH}_3(g)$ at 850 °C and 5.00 atm are required to react with 1.00 mol of $\text{O}_2(g)$ in this reaction?

Answer: 14.8 L

10.6

Gas Mixtures and Partial Pressures

Dalton's Law of Partial Pressures

We have considered mainly the behavior of pure gases, those that consist of only one substance in the gaseous state.

How do we deal with gases composed of a mixture of two or more substances ?

- **Dalton's Law of Partial Pressures**

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

In other words,

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

The pressure exerted by a particular component of a mixture of gases is called the **partial pressure** of that gas.

$$P_t = P_1 + P_2 + P_3 + \dots$$

$$**PV = nRT \qquad P = nRT/V**$$

This equation implies that each gas in the mixture behave independently of others,

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

All the gases in the mixture are at the same temperature and occupy the same volume. Therefore,

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

Sample Exercise 10.10 Applying Dalton's Law to the Partial Pressures

A gaseous mixture made from 6.00 g O₂ and 9.00 g CH₄ is placed in a 15.0-L vessel at 0 °C. What is the partial pressure of each gas, and what is the total pressure in the vessel?

Solution

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

$$n_{\text{O}_2} = (6.00 \text{ g O}_2) \left(\frac{1 \text{ mol O}_2}{32.0 \text{ g O}_2} \right) = 0.188 \text{ mol O}_2$$

$$n_{\text{CH}_4} = (9.00 \text{ g CH}_4) \left(\frac{1 \text{ mol CH}_4}{16.0 \text{ g CH}_4} \right) = 0.563 \text{ mol CH}_4$$

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

$$P_{\text{O}_2} = \frac{n_{\text{O}_2} RT}{V} = \frac{(0.188 \text{ mol})(0.0821 \text{ L-atm/mol-K})(273 \text{ K})}{15.0 \text{ L}} = 0.281 \text{ atm}$$

$$P_{\text{CH}_4} = \frac{n_{\text{CH}_4} RT}{V} = \frac{(0.563 \text{ mol})(0.0821 \text{ L-atm/mol-K})(273 \text{ K})}{15.0 \text{ L}} = 0.841 \text{ atm}$$

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

$$P_t = P_{\text{O}_2} + P_{\text{CH}_4} = 0.281 \text{ atm} + 0.841 \text{ atm} = 1.122 \text{ atm}$$

Practice Exercise

What is the total pressure exerted by a mixture of 2.00 g of H₂ and 8.00 g of N₂ at 273 K in a 10.0-L vessel?

Answer: 2.86 atm

Partial Pressures and Mole Fractions

Because each gas in a mixture behaves independently, we can relate the amount of a given gas in a mixture to its partial pressure. For an ideal gas, $P = nRT/V$ and so we can write:

$$\frac{P_1}{P_t} = \frac{n_1 RT/V}{n_t RT/V} = \frac{n_1}{n_t}$$

Where the ration n_1/n_t is called the mole fraction of gas 1, which we denote X_1 . we can rearrange the above equation to give:

$$P_1 = \left(\frac{n_1}{n_t} \right) P_t = X_1 P_t$$

Thus, the partial pressure of a gas in a mixture is its mole fraction times total pressure.

The mole fraction of N_2 in air is 0.78 (78% of the molecules in air is N_2). If the total barometric pressure is 760 torr, then the partial pressure of N_2 is;

$$P_{\text{N}_2} = (0.78) (760 \text{ torr}) = 590 \text{ torr}$$

Thus, N_2 contributes by 78% of the total pressure.

Sample Exercise 10.11 Relating Mole Fractions to Partial Pressures

A study of the effects of certain gases on plant growth requires a synthetic atmosphere composed of 1.5 mol percent CO₂, 18.0 mol percent O₂, and 80.5 mol percent Ar. **(a)** Calculate the partial pressure of O₂ in the mixture if the total pressure of the atmosphere is to be 745 torr. **(b)** If this atmosphere is to be held in a 121-L space at 295 K, how many moles of O₂ are needed?

Solution

(a) The mole percent is just the mole fraction times 100. Therefore, the mole fraction of O₂ is 0.180.

(b) Tabulating the given variables and changing them to appropriate units, we have

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

$$P_{\text{O}_2} = (0.180)(745 \text{ torr}) = 134 \text{ torr}$$

$$P_{\text{O}_2} = (134 \text{ torr}) \left(\frac{1 \text{ atm}}{760 \text{ torr}} \right) = 0.176 \text{ atm}$$

$$V = 121 \text{ L}$$

$$n_{\text{O}_2} = ?$$

$$R = 0.0821 \frac{\text{L}\cdot\text{atm}}{\text{mol}\cdot\text{K}}$$

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

$$n_{\text{O}_2} = P_{\text{O}_2} \left(\frac{V}{RT} \right)$$

$$= (0.176 \text{ atm}) \frac{121 \text{ L}}{(0.0821 \text{ L}\cdot\text{atm}/\text{mol}\cdot\text{K})(295 \text{ K})} = 0.879 \text{ mol}$$

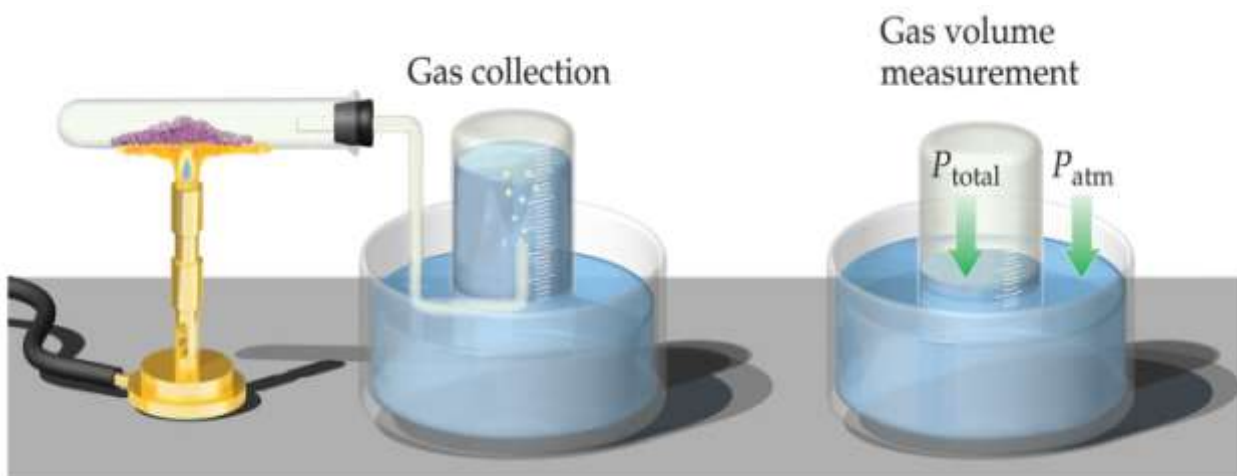
Practice Exercise

From data gathered by *Voyager 1*, scientists have estimated the composition of the atmosphere of Titan, Saturn's largest moon. The total pressure on the surface of Titan is 1220 torr. The atmosphere consists of 82 mol percent N₂, 12 mol percent Ar, and 6.0 mol percent CH₄. Calculate the partial pressure of each of these gases in Titan's atmosphere.

Answer: 1.0×10^3 torr N₂, 1.5×10^2 torr Ar, and 73 torr CH₄

Collecting Gases over Water

An experiment that is often encountered in general chemistry laboratories involves determining the number of moles of gas collected from a chemical reaction. Sometimes this gas is collected over water.



A solid is heated, releasing a gas, which bubbled through water into a collection bottle. the bottle is then raised or lowered so that the water levels inside and outside the bottle are equal. The total pressure of the gases inside and outside the bottle is then equal to the atmospheric pressure.

When one collects a gas over water, there is water vapor mixed in with the gas.

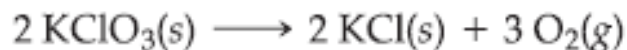
- To find only the pressure of the desired gas, one must subtract the vapor pressure of water from the total pressure.

$$P_{\text{total}} = P_{\text{gas}} + P_{\text{H}_2\text{O}}$$

Sample Exercise 10.12 Calculating the Amount of Gas Collected over Water

A sample of KClO_3 is partially decomposed, producing O_2 gas that is collected over water. The volume of gas collected is 0.250 L at 26 °C and 765 torr total pressure. **(a)** How many moles of O_2 are collected? **(b)** How many grams of KClO_3 were decomposed?

Solution



(a) The partial pressure of the O_2 gas is the difference between the total pressure, 765 torr, and the pressure of the water vapor at 26 °C, 25 torr (Appendix B):

$$P_{\text{O}_2} = 765 \text{ torr} - 25 \text{ torr} = 740 \text{ torr}$$

We can use the ideal-gas equation to calculate the number of moles of O_2 :

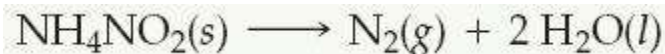
$$n_{\text{O}_2} = \frac{P_{\text{O}_2} V}{RT} = \frac{(740 \text{ torr})(1 \text{ atm}/760 \text{ torr})(0.250 \text{ L})}{(0.0821 \text{ L}\cdot\text{atm}/\text{mol}\cdot\text{K})(299 \text{ K})} = 9.92 \times 10^{-3} \text{ mol O}_2$$

(b) From Equation 10.16, we have $2 \text{ mol KClO}_3 \approx 3 \text{ mol O}_2$. The molar mass of KClO_3 is 122.6 g/mol. Thus, we can convert the moles of O_2 that we found in part (a) to moles of KClO_3 and then to grams of KClO_3

$$(9.92 \times 10^{-3} \text{ mol O}_2) \left(\frac{2 \text{ mol KClO}_3}{3 \text{ mol O}_2} \right) \left(\frac{122.6 \text{ g KClO}_3}{1 \text{ mol KClO}_3} \right) = 0.811 \text{ g KClO}_3$$

Practice Exercise

Ammonium nitrite, NH_4NO_2 , decomposes upon heating to form N_2 gas:



When a sample of NH_4NO_2 is decomposed in a test tube, as in Figure 10.16, 511 mL of N_2 gas is collected over water at 26 °C and 745 torr total pressure. How many grams of NH_4NO_2 were decomposed?

Answer: 1.26 g

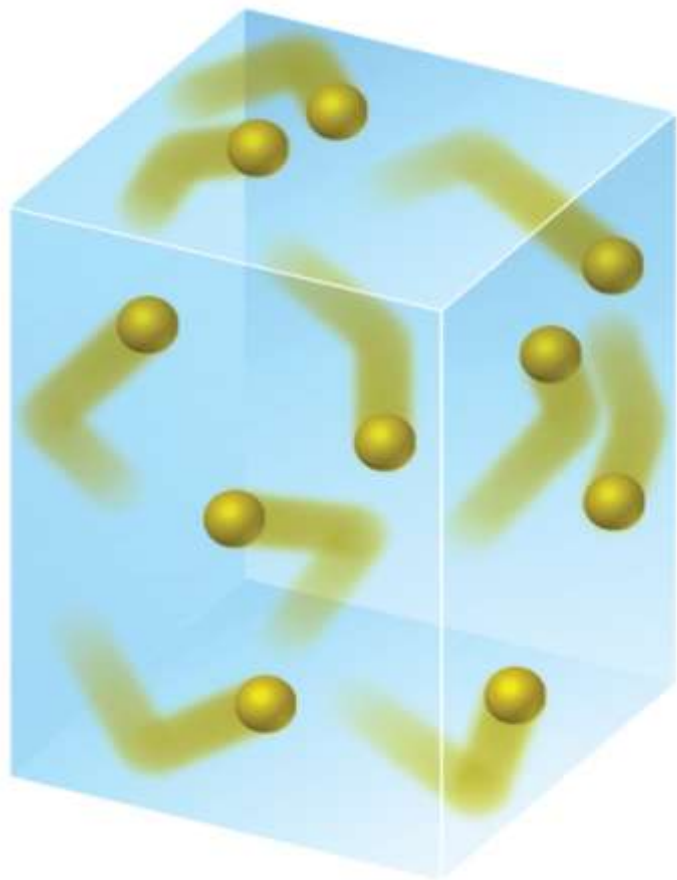
10.7

Kinetic Molecular Theory

The ideal gas equation describes how gases behave, but it does not explain why they behave as they do. Why does a gas expand when heated at constant pressure, or why does its pressure increase when the gas is compressed at constant temperature. The **kinetic molecular model** helps to understand the physical properties of gases. And what happens to gas particles as environmental conditions change.

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

- Gases consist of large numbers of molecules that are in continuous, random motion.
- The combined volume of all the molecules of the gas is negligible relative to the total volume in which the gas is contained.
- Attractive and repulsive forces between gas molecules are negligible.
- Energy can be transferred between molecules during collisions, but the average kinetic energy of the molecules does not change with time, as long as the temperature of the gas remains constant. In other words, the collisions are perfectly elastic (elastic collision, collisions in which kinetic energy is conserved).
- The average kinetic energy of the molecules is proportional to the absolute temperature. At any given temperature the molecules of all gases have the same average kinetic energy.



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

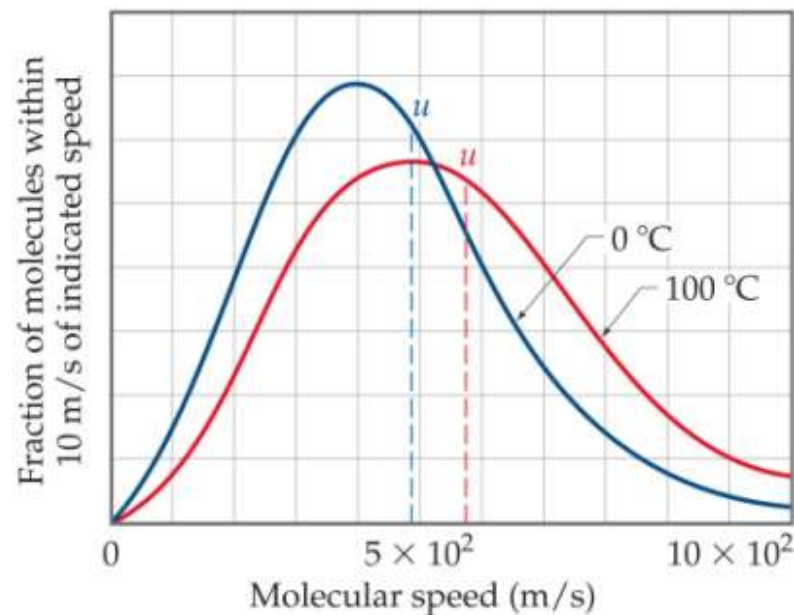
The absolute temperature of a gas is a measure of the average kinetic energy of its molecules. If two different gases are at the same temperature, their molecules have the same average kinetic energy (statement 5 of the kinetic-molecular theory). If the absolute temperature of a gas is doubled, the average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

Distributions of Molecular Speed

Although the molecules in a sample of gas have an average kinetic energy and hence an average speed, the individual molecules move at varying speeds.

The moving molecules collide frequently with other molecules. Momentum (mass and velocity of an object) is conserved in each collision, but one of the colliding molecules might be deflected off at high speed while the other is nearly stopped.

The result is that the molecules at any instant have a wide range of speeds.



The effect of temperature on molecular speed. Distribution of molecular speeds for N_2 at 0 and 100 °C. Increasing temperature increases both the most probable speed (curve maximum) and rms speed, u , (vertical dashed line.).

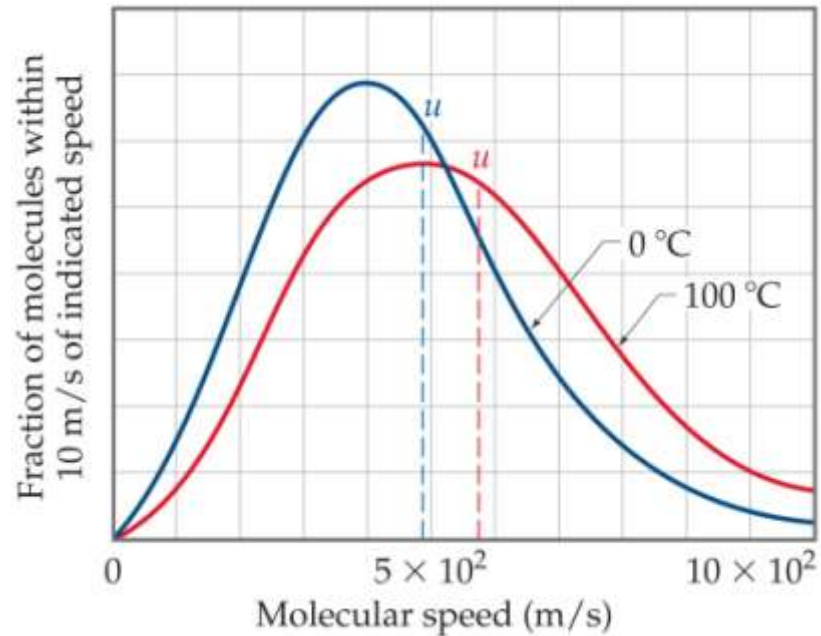
At higher temperatures, a larger fraction of molecules moves at greater speeds; the distribution curve has shifted to the right toward higher speeds and hence higher average kinetic energy.

The peak of each curve represents the most probable speed (the speed of the largest number of molecules).

Root mean square (rms) speed, u ; this quantity is the speed of a molecules possessing average kinetic energy. rms speed is higher at 100 °C than at 0 °C. The distribution curve also broadens as we go to a higher temperature.

$$\epsilon = \frac{1}{2} m u^2$$

Where ϵ is the average kinetic energy of gas molecules, u (rms) speed and m is the mass of an individual molecule. Mass does not change with temperature. Thus, the increase in the average kinetic energy as the temperature increase implies that the rms speed of molecules likewise increases as temperature increases.



Application to the Gas Laws

Kinetic molecular theory helps to understand the gas laws:

- Effect of a volume increase at constant temperature: A constant temperature means that the average kinetic energy of the gas molecules remains unchanged. This in turn means that the rms speed of the molecules, u , is unchanged. If the volume is increased, however, the molecules must move a longer distance between collision. Consequently, there are fewer collisions per unit time with the container walls, and pressure decreases. Thus, the model accounts in a simple way for Boyle's law.
- Effect of a temperature increase at constant volume: An increase in temperature means an increase in the average kinetic energy of the molecules and thus an increase in u . If there is no change in volume, there will be more collisions with the walls per unit time. Furthermore, the change in momentum in each collision increases (the molecules strike the walls more forcefully). Hence, the model explains the observed pressure increase.

Sample Exercise 10.13 Applying the Kinetic-Molecular Theory

A sample of O_2 gas initially at STP is compressed to a smaller volume at constant temperature. What effect does this change have on **(a)** the average kinetic energy of O_2 molecules, **(b)** the average speed of O_2 molecules, **(c)** the total number of collisions of O_2 molecules with the container walls in a unit time, **(d)** the number of collisions of O_2 molecules with a unit area of container wall per unit time?

Solution

(a) The average kinetic energy of the O_2 molecules is determined only by temperature. Thus the average kinetic energy is unchanged by the compression of O_2 at constant temperature. **(b)** If the average kinetic energy of O_2 molecules does not change, the average speed remains constant. **(c)** The total number of collisions with the container walls per unit time must increase because the molecules are moving within a smaller volume but with the same average speed as before. Under these conditions they must encounter a wall more frequently. **(d)** The number of collisions with a unit area of wall per unit time increases because the total number of collisions with the walls per unit time increases and the area of the walls decreases.

Practice Exercise

How is the rms speed of N_2 molecules in a gas sample changed by **(a)** an increase in temperature, **(b)** an increase in volume, **(c)** mixing with a sample of Ar at the same temperature?

Answer: **(a)** increases, **(b)** no effect, **(c)** no effect

10.8

Molecular Effusion and Diffusion

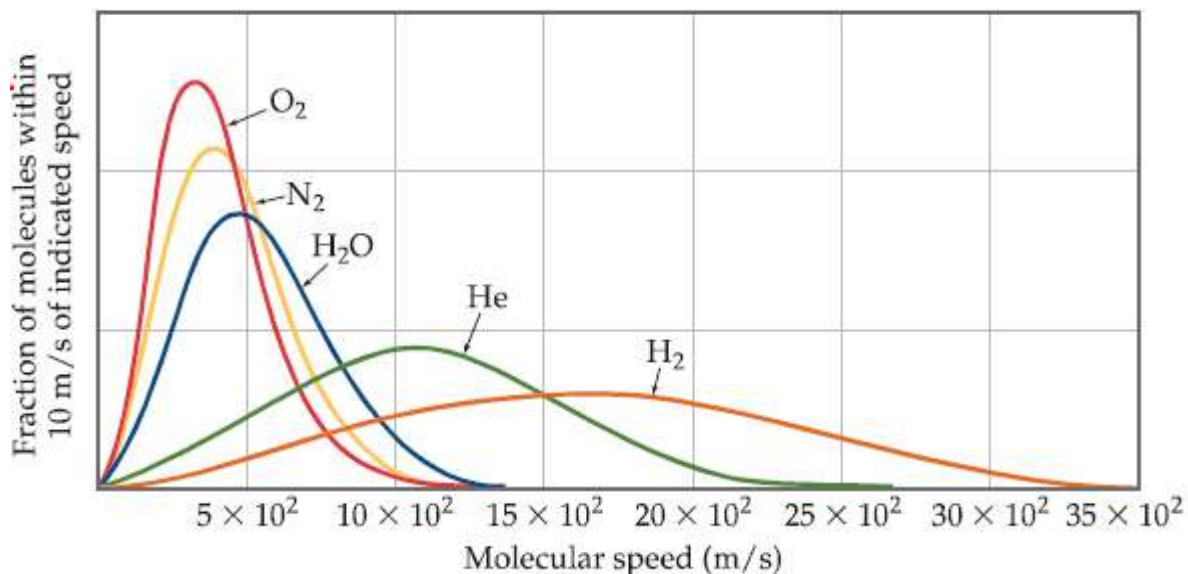
According to kinetic molecular theory, the average kinetic energy of any collection of gas molecules, $\frac{1}{2} m\bar{u}^2$, has a specific value at a given temperature. Thus, a gas composed of lightweight particles, will have the same average kinetic energy as one composed of much heavier particles, at the same temperature.

The mass of the particles in the lighter gas is smaller than that in the heavier gas. Consequently, the particles of the lighter gas must have a higher rms speed, u , than the particles of the heavier one.

The following equation, expresses this fact quantitatively:

$$u = \sqrt{\frac{3RT}{M}}$$

The less massive the gas molecules, the higher the rms speed, u .



The effect of molecular mass on molecular speed. The molecules with lower molecular masses have higher rms speeds. The distributions are shifted toward higher speeds for gases of lower molar masses.

Sample Exercise 10.14 Calculating a Root-Mean-Square Speed

Calculate the rms speed, u , of an N_2 molecule at $25\text{ }^\circ\text{C}$.

Solution

In using Equation 10.22, we should convert each quantity to SI units so that all the units are compatible. We will also use R in units of J/mol-K (Table 10.2) to make the units cancel correctly.

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

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

$$R = 8.314\text{ J/mol-K} = 8.314\text{ kg}\cdot\text{m}^2/\text{s}^2\cdot\text{mol-K} \quad (\text{These units follow from the fact that } 1\text{ J} = 1\text{ kg}\cdot\text{m}^2/\text{s}^2)$$

$$u = \sqrt{\frac{3(8.314\text{ kg}\cdot\text{m}^2/\text{s}^2\cdot\text{mol-K})(298\text{ K})}{28.0 \times 10^{-3}\text{ kg/mol}}} = 5.15 \times 10^2\text{ m/s}$$

Comment: This corresponds to a speed of 1150 mi/hr. Because the average molecular weight of air molecules is slightly greater than that of N_2 , the rms speed of air molecules is a little slower than that for N_2 . The speed at which sound propagates through air is about 350 m/s, a value about two-thirds the average rms speed for air molecules.

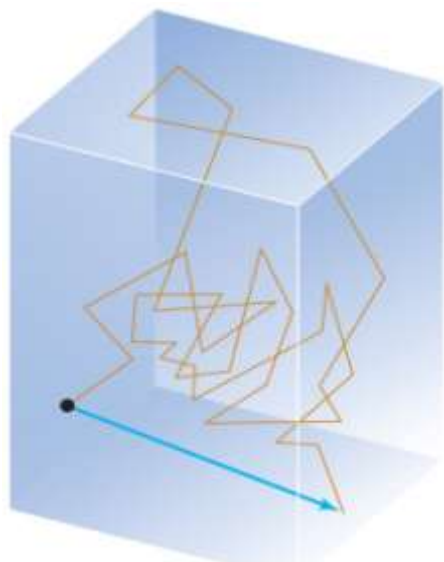
Practice Exercise

What is the rms speed of an He atom at $25\text{ }^\circ\text{C}$?

Answer: $1.36 \times 10^3\text{ m/s}$

Effusion Vs. Diffusion

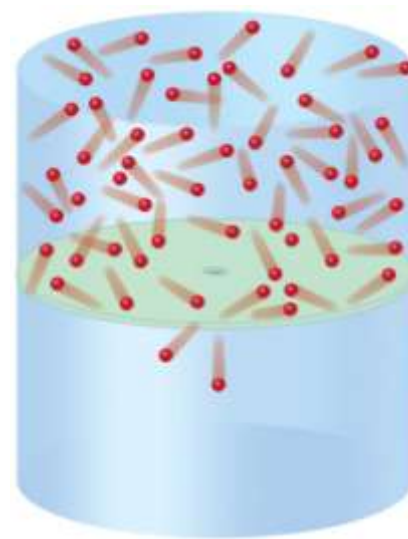
The dependence of molecular speeds on mass has several interesting consequences. Two phenomenon are describes here:



Diffusion, the path of the molecule begin at the dot. Each short segment of line represents travel between collisions. The blue arrow indicates the net distance traveled by the molecule.

Effusion is the escape of gas molecules through a tiny hole into an evacuated space.

Diffusion is the spread of one substance throughout a space or throughout a second substance. e.g., the molecules of a perfume diffuse throughout a room.



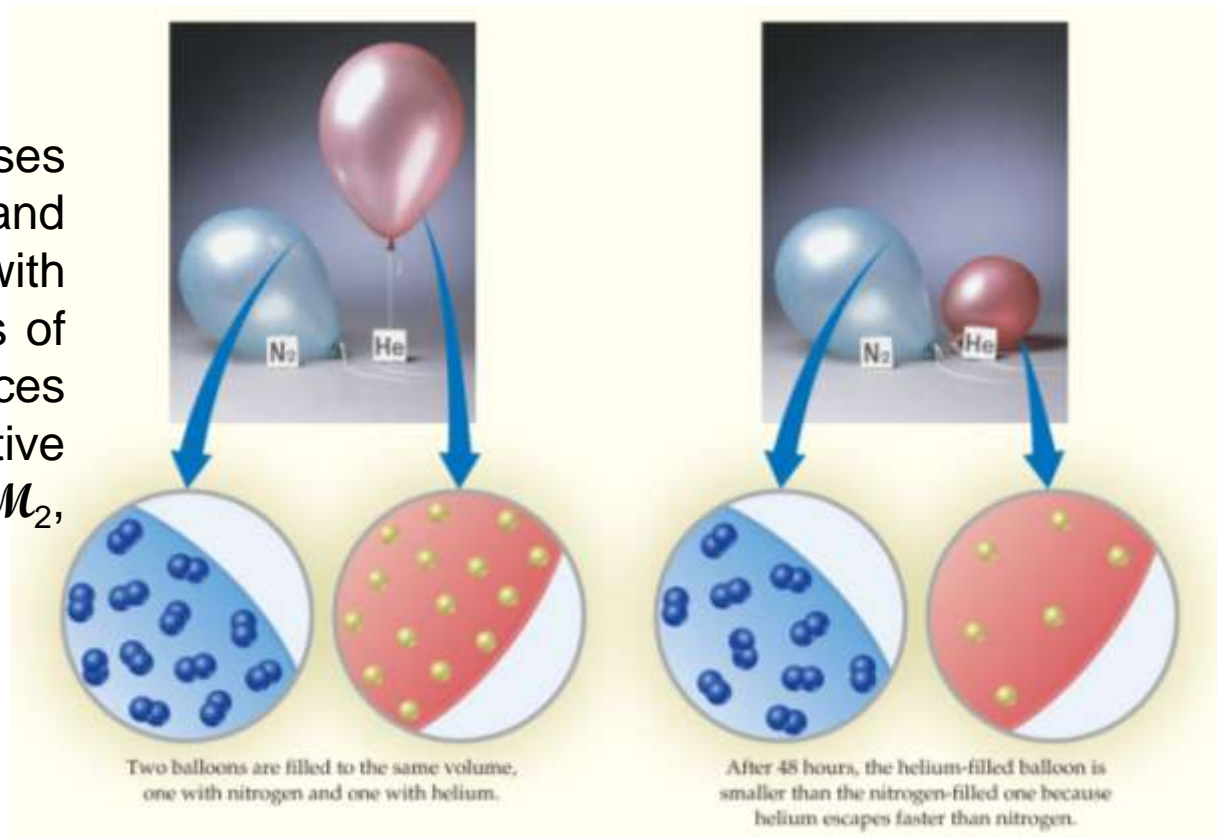
Effusion, gas molecules effuse through a pinhole in the portioning wall only when they happen to hit the hole.

Graham's Law of Effusion

The effusion rate of a gas is inversely proportional to the square root of its molar mass. At identical pressure and temperature, the lighter gas effuses more rapidly.

Assume that we have two gases at the same temperature and pressure in containers with identical pinholes. If the rates of effusion of the two substances are r_1 and r_2 and their respective molar masses are \mathcal{M}_1 and \mathcal{M}_2 , Graham's states:

$$\frac{r_1}{r_2} = \sqrt{\frac{\mathcal{M}_2}{\mathcal{M}_1}}$$



e.g., The difference in the rates of effusion for helium and nitrogen, explains a helium balloon would deflate faster.

The only way for a molecule to escape from its container is for it to hit the hole in the partitioning wall. The faster the molecules are moving, the greater is the likelihood that a molecule will hit the hole and effuse.

This implies that the rate of effusion is directly proportional to the rms speed of the molecules. Because **R** and **T** are constants, we can write the equation as follow:

$$\frac{r_1}{r_2} = \frac{u_1}{u_2} = \sqrt{\frac{3RT/\mathcal{M}_1}{3RT/\mathcal{M}_2}} = \sqrt{\frac{\mathcal{M}_2}{\mathcal{M}_1}}$$

Diffusion, like effusion, is faster for lower mass molecules than for higher mass ones.

Mean free path of the molecule is the average distance traveled by a molecule between collisions.

more molecules = higher pressure = short mean free path

At sea level, the mean free path for air molecules is about 60 nm. At about 100 km in altitude, where the air density is much lower, the mean free path is about 10 cm, over 1 million times longer than at Earth's surface.

Sample Exercise 10.15 Applying Graham's Law

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

Solution

From the information given,

Thus,

We now solve for the unknown molar mass, \mathcal{M}_x

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

$$\frac{r_x}{r_{\text{O}_2}} = \sqrt{\frac{\mathcal{M}_{\text{O}_2}}{\mathcal{M}_x}}$$

$$r_x = 0.355 \times r_{\text{O}_2}$$

$$\frac{r_x}{r_{\text{O}_2}} = 0.355 = \sqrt{\frac{32.0 \text{ g/mol}}{\mathcal{M}_x}}$$

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

$$\mathcal{M}_x = \frac{32.0 \text{ g/mol}}{0.126} = 254 \text{ g/mol}$$

Practice Exercise

Calculate the ratio of the effusion rates of N₂ and O₂, $r_{\text{N}_2}/r_{\text{O}_2}$.

Answer: $r_{\text{N}_2}/r_{\text{O}_2} = 1.07$

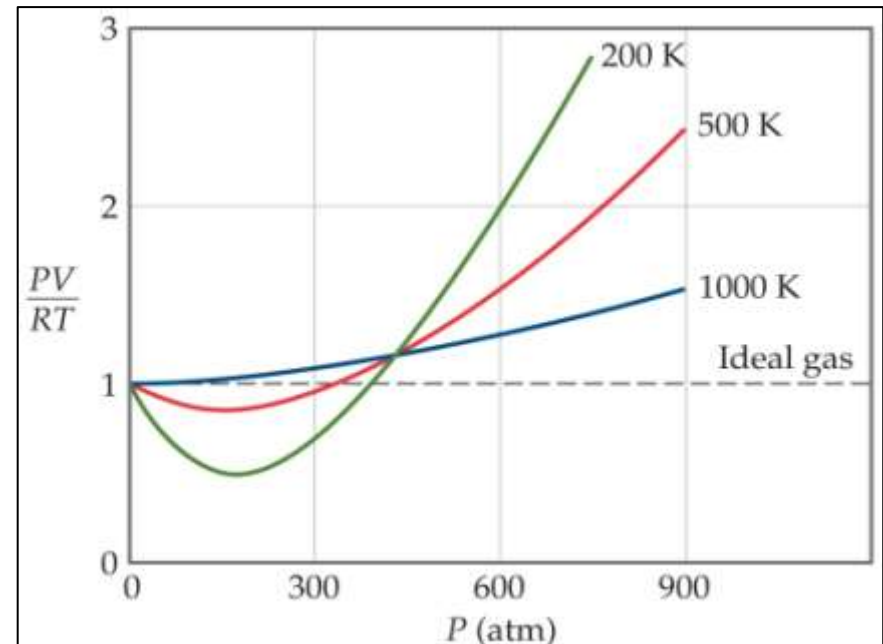
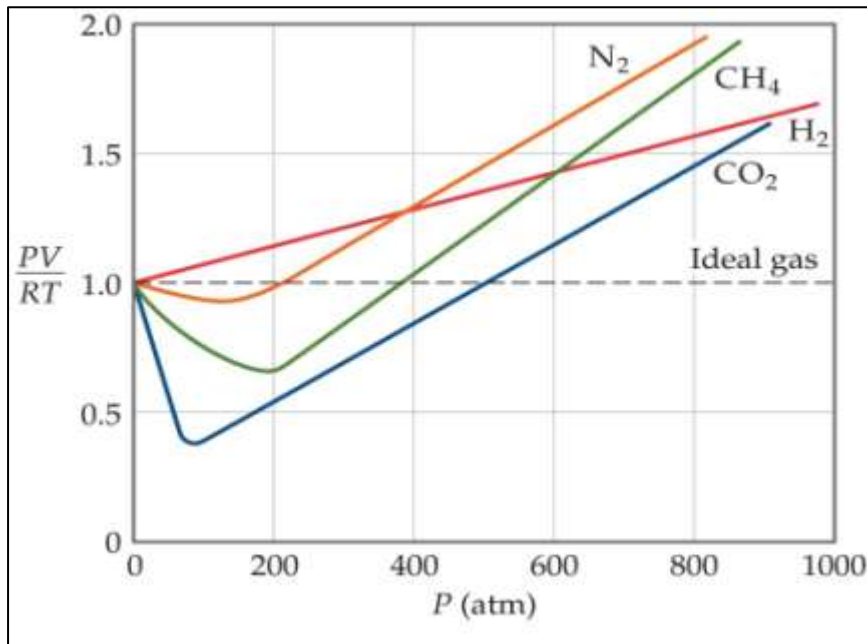
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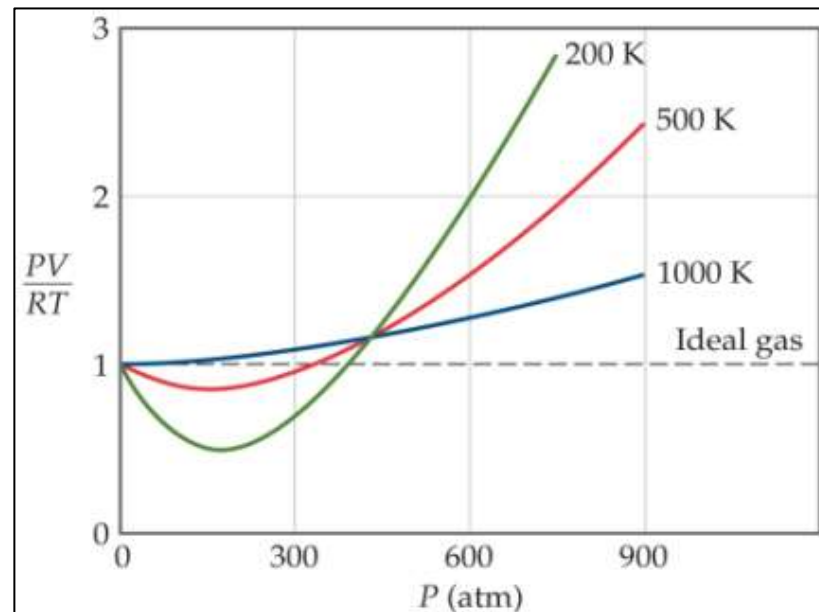
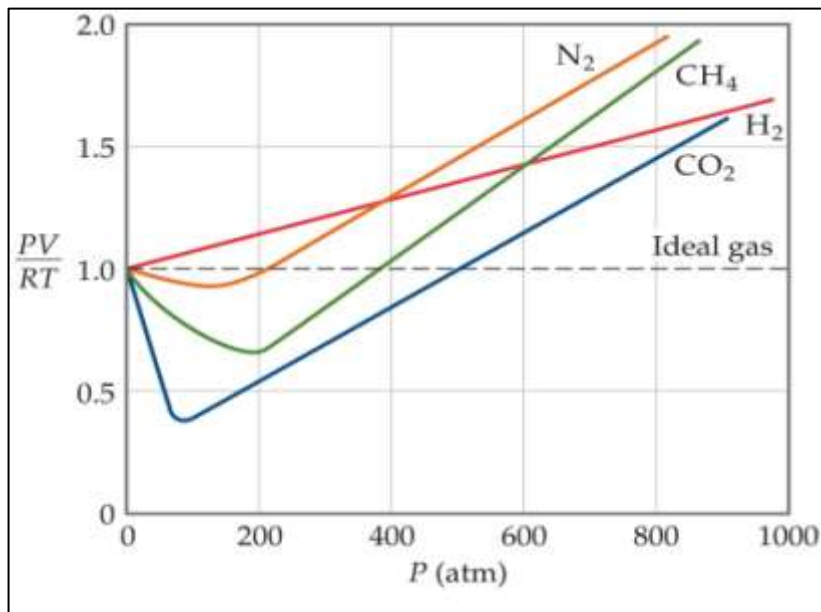
Real Gases, Deviations from Ideal Behavior

Real Gases

All real gases fail to obey ideal gas equation to some degree. The extent to which a real gas departs from ideal behavior can be seen by rearranging the ideal gas equation to solve for n :

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

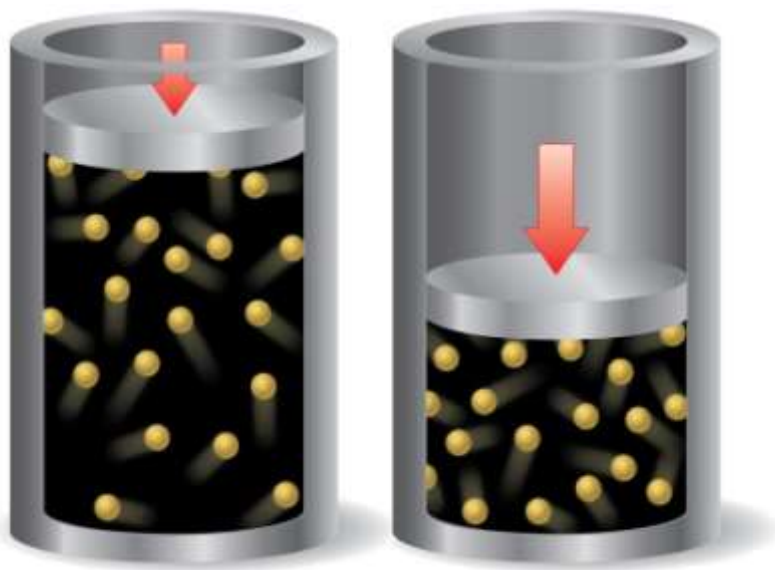




- The dashed horizontal line shows the behavior of an ideal gas.
- For 1.00 mole of ideal gas the quantity **PV/RT** equals 1 at all pressures and temperatures.
- For real gases, at high pressures, the deviation from ideal behavior is large and is different for each gas. At lower pressures (usually below 10 atm), the deviation from ideal behavior is small, and we can use the ideal gas equation without generating serious error.
- The right figure is for 1 mole **N_2** at three temperatures, as temperature increase, the behavior of the gas more nearly approaches that of the ideal gas. In general, the deviations from ideal behavior increase as temperature decrease, becoming significant near the temperature at which the gas is converted into a liquid.
- In the real world, the behavior of gases only conforms to the ideal gas equation at relatively **high temperature** and **low pressure**.

Deviations from Ideal Behavior

The basic assumptions of the kinetic molecular theory give us insight into why real gases deviate from ideal behavior. The molecules of an ideal gas are assumed to occupy no space (negligible volume of gas molecules) and have no attraction for one another. Real molecules, however, do have **finite volumes**, and they **do attract** one another, especially at high pressure and/or low temperature.



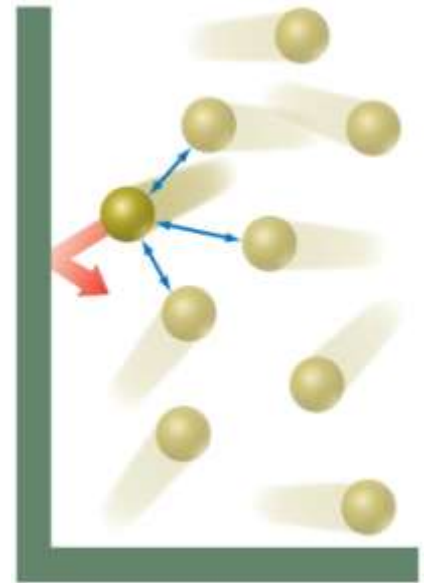
At low pressure, the combined volume of the gas molecules is small relative to the container volume, and we can approximate the empty space between molecules as being equal to the container volume.

At high pressure, the combined volume of the gas molecules is a larger fraction of the total space available. Now we must account for the volume of the molecules themselves in determining the empty space available for the motion of the gas molecules.

The attractive forces between molecules come into play at short distances, as when molecules are crowded together at high pressures. Because of these attractive forces, the impact of a given molecule with the wall of the container is lessened. The attractive forces become significant only under high pressure, when the average distance between molecules is small.

The molecule (in the figure) about to make contact with the wall experiences the attractive forces of nearby molecules. These attractions lessen the force with which the molecule hits the wall. As a result the pressure is less than that of the ideal gas. This effect serves to decrease PV/RT below its ideal value. When the pressure is significantly high, however, the volume effects dominate and PV/RT increases to above the ideal value.

Temperature determines how effective attractive forces between gas molecules are. As a gas is cooled, the average kinetic energy of the molecules decreases. But intermolecular attractions remain constant. In a sense, cooling a gas deprives molecules of the energy they need to overcome their mutual attractive influence. As T increases, the negative departure of PV/RT from ideal gas behavior disappears. The difference that remains at high T stems mainly from the effect of the finite volumes of the molecules.



Corrections for Non-ideal Behavior (The van der Waals Equation)

Working with real gases at high **P** often cannot use the ideal gas equation to predict the **P** and **V** properties of gases.

Van der Waals equation is one useful correction for the behavior of real gases.

Van der Waals correct the ideal gas equation to account the effect of attractive forces between gas molecules and molecular volumes. He introduced two constants (**a** and **b**) to make these corrections.

The constant **a** is measure the gas molecules attractions, while **b** constant is measure finite volume of the gas molecules.

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

Adding $n^2 a/V^2$ to adjust the pressure because attractive forces between molecules tend to reduce the pressure. Subtracting nb to adjust the volume because the gas molecules has a small but finite volume.

The constants **a** and **b** are called van der Waals constants, are experimentally determined positive quantities that differ for each gas.

TABLE 10.3 ■ van der Waals Constants for Gas Molecules

Substance	a (L ² -atm/mol ²)	b (L/mol)
He	0.0341	0.02370
Ne	0.211	0.0171
Ar	1.34	0.0322
Kr	2.32	0.0398
Xe	4.19	0.0510
H ₂	0.244	0.0266
N ₂	1.39	0.0391
O ₂	1.36	0.0318
Cl ₂	6.49	0.0562
H ₂ O	5.46	0.0305
CH ₄	2.25	0.0428
CO ₂	3.59	0.0427
CCl ₄	20.4	0.1383

Both **a** and **b** generally increase with an increase in mass of the molecule and with an increase in the complexity of its structure. Larger, more massive molecules have larger volumes and tend to have greater intermolecular attractive forces.

Sample Exercise 10.16 Using the van der Waals Equation

If 1.000 mol of an ideal gas were confined to 22.41 L at 0.0 °C, it would exert a pressure of 1.000 atm. Use the van der Waals equation and the constants in Table 10.3 to estimate the pressure exerted by 1.000 mol of $\text{Cl}_2(g)$ in 22.41 L at 0.0 °C.

Solution

$$P = \frac{nRT}{V - nb} - \frac{n^2a}{V^2}$$

Solve: Substituting $n = 1.000$ mol, $R = 0.08206$ L-atm/mol-K, $T = 273.2$ K, $V = 22.41$ L, $a = 6.49$ L²-atm/mol², and $b = 0.0562$ L/mol:

$$\begin{aligned} P &= \frac{(1.000 \text{ mol})(0.08206 \text{ L-atm/mol-K})(273.2 \text{ K})}{22.41 \text{ L} - (1.000 \text{ mol})(0.0562 \text{ L/mol})} - \frac{(1.000 \text{ mol})^2(6.49 \text{ L}^2\text{-atm/mol}^2)}{(22.41 \text{ L})^2} \\ &= 1.003 \text{ atm} - 0.013 \text{ atm} = 0.990 \text{ atm} \end{aligned}$$

Practice Exercise

Consider a sample of 1.000 mol of $\text{CO}_2(g)$ confined to a volume of 3.000 L at 0.0 °C. Calculate the pressure of the gas using (a) the ideal-gas equation and (b) the van der Waals equation.

Answer: (a) 7.473 atm, (b) 7.182 atm

Sample Integrative Exercise Putting Together Concepts

Cyanogen, a highly toxic gas, is composed of 46.2% C and 53.8% N by mass. At 25 °C and 751 torr, 1.05 g of cyanogen occupies 0.500 L. **(a)** What is the molecular formula of cyanogen? **(b)** Predict its molecular structure. **(c)** Predict the polarity of the compound.

Solution

(a) To determine the empirical formula, we assume that we have a 100-g sample of the compound and then calculate the number of moles of each element in the sample:

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

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

Because the ratio of the moles of the two elements is essentially 1:1, the empirical formula is CN.

To determine the molar mass of the compound, we use Equation 10.11.

$$\mathcal{M} = \frac{dRT}{p} = \frac{(1.05 \text{ g}/0.500 \text{ L}) (0.0821 \text{ L}\cdot\text{atm}/\text{mol}\cdot\text{K}) (298 \text{ K})}{(751/760) \text{ atm}} = 52.0 \text{ g/mol}$$

The molar mass associated with the empirical formula, CN, is $12.0 + 14.0 = 26.0 \text{ g/mol}$. Dividing the molar mass of the compound by that of its empirical formula gives $(52.0 \text{ g/mol})/(26.0 \text{ g/mol}) = 2.00$. Thus, the molecule has twice as many atoms of each element as the empirical formula, giving the molecular formula C_2N_2 .

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



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

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

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



Q & A



Which is correct?

1. All gases are fluids.

2. All gases are diatomic.

a. Both statements are true.

b. Both statements are false.

c. Statement 1 is true, but statement 2 is false.

d. Statement 1 is false, but statement 2 is true.

As a helium-filled balloon rises, its volume increases. This is an example of:

- a. Avogadro's Law.
- b. Boyle's Law.**
- c. Charles' Law.
- d. Gay-Lussac's Law.

Hot air balloons rise. This is an example of:

- a. Avogadro's Law.
- b. Boyle's Law.
- c. Charles' Law.
- d. Gay-Lussac's Law.

Avogadro's Law states that the volume of a gas is directly proportional to:

- a. the number of gas particles.
- b. the mass of the gas.
- c. the pressure of the gas.
- d. the Kelvin temperature of the gas.

Standard temperature and pressure (**STP**) for a gas is:

- a. 0 atmospheres and 25 degrees C.
- b. 1 atmosphere and 0 degrees C.
- c. 1 atmosphere and 25 degrees C.
- d. 0 atmospheres and 0 degrees C.

The partial pressure of each gas in a mixture is proportional to:

- a. the mass of the gas.
- b. the molecular weight of the gas.
- c. the square root of the molecular weight of the gas.
- d. the mole fraction of the gas.

The Kinetic-Molecular Theory states that the average kinetic energy of gas particles is directly proportional to:

- a. the Kelvin temperature of the gas.
- b. the Celsius temperature of the gas.
- c. the number of gas particles.
- d. the pressure of the gas.

Neon (**Ne**) undergoes effusion
_____ krypton (**Kr**).

- a. slower than
- b. at the same rate as
- c. about twice as fast as
- d. about four times as fast as

The mean free path of a gas molecule is:

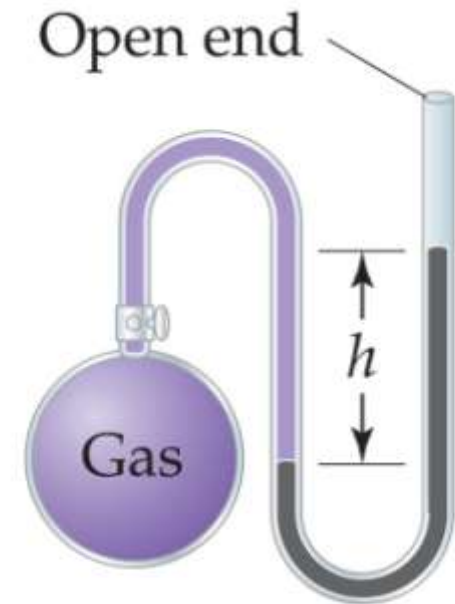
- a. the total distance traveled by the molecule.
- b. the distance between two molecules.
- c. the distance between the molecule and the nearest wall of its container.
- d. the average distance traveled between collisions.

A sample of two moles of nitrogen gas (N_2) will occupy what volume at STP?

- a. 11.2 liters
- b. 22.4 liters
- c. 44.8 liters
- d. 89.6 liters

What is the pressure of the gas in the bulb?

- $P_{\text{gas}} = P_h$
- $P_{\text{gas}} = P_{\text{atm}}$
- $P_{\text{gas}} = P_h + P_{\text{atm}}$
- $P_{\text{gas}} = P_h - P_{\text{atm}}$
- $P_{\text{gas}} = P_{\text{atm}} - P_h$



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If 250 mL of **NO** is placed in a flask with **O₂**, what volume of **O₂** is needed for complete reaction?



- 100 mL
- 125 mL
- 200 mL
- 250 mL
- Cannot be determined from the given information.

If an equal mass of each gas is put into a separate balloon, which will have the greatest volume? (*Assume that they are all the same temperature and pressure.*)

- He
- H_2
- N_2
- Ne
- O_2



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If equal masses of CH_4 , C_2H_6 , and C_3H_8 are placed in a flask, which of the following is true?

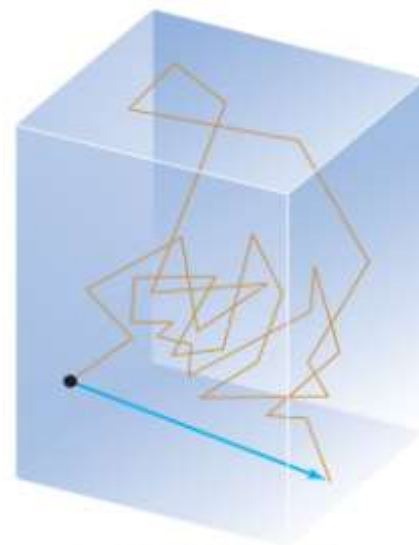
- $P_{\text{CH}_4} = P_{\text{C}_2\text{H}_6} = P_{\text{C}_3\text{H}_8}$
- $P_{\text{CH}_4} \sim P_{\text{C}_2\text{H}_6} \sim P_{\text{C}_3\text{H}_8}$
- $P_{\text{CH}_4} > P_{\text{C}_2\text{H}_6} > P_{\text{C}_3\text{H}_8}$
- $P_{\text{CH}_4} < P_{\text{C}_2\text{H}_6} < P_{\text{C}_3\text{H}_8}$
- None of the above



Arrange the gases according to increasing molecular speed.

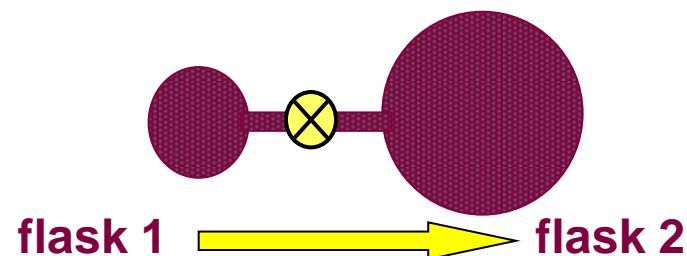
He (25°C) He (100°C) Ne (25°C) Ne (0°C)

- He (25) < He (100) < Ne (25) < Ne (0)
- He (25) < He (100) < Ne (0) < Ne (25)
- **Ne (0) < Ne (25) < He (25) < He (100)**
- Ne (25) < Ne (0) < He (100) < He (25)
- Ne (0) < He (25) < Ne (25) < He (100)



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If a mixture of gas **A** and gas **B** is moved from flask 1 to flask 2, which of the following is true:



- P_A , P_B , and P_{tot} decrease.
- P_A , P_B , and P_{tot} increase.
- P_A and P_B decrease; P_{tot} remains the same.
- P_A , P_B , and P_{tot} remain the same.
- P_A and P_B remain the same; P_{tot} decreases.

