Chapter 10. Gases

Common Student Misconceptions

- Students need to be told to *always* use temperature in Kelvin in gas problems.
- Students should always use units in gas-law problems to keep track of required conversions.
- Due to several systems of units, students often use ideal gas constants with units inconsistent with values.
- Students often confuse the standard conditions for gas behavior (STP) with the standard conditions in thermodynamics.
- Ideal gas behavior should discussed as just that, *ideal*; students should be reminded that real gases do not behave ideally, especially at high pressures and/or low temperatures.
- Students expect a change in the gas particle distribution upon temperature changes at constant *V*.
- Students commonly confuse effusion and diffusion.

Lecture Outline

10.1 Characteristics of Gases

- All substances have three phases: solid, liquid and gas.

- Substances that are liquids or solids under ordinary conditions may also exist as gases.
  - These are often referred to as **vapors**.

Properties of Gases

- very low density ($V_{(g)}$ = > 1000 X $V_{(l\text{ or }s)}$), → individual molecules/atoms act almost independently of each other
- highly compressible and expandable: they have an indefinite volume, fill their containers
- fluid
- diffuse through each other (small) → homogeneous mixtures with each other
- have mass
- exert pressure
- 1 mol at STP = 22.4 L (STP = 0ºC or 273 K; 1 atm)
- Gases only occupy a small fraction of the volume of their containers.
  - As a result, each molecule of gas behaves largely as though other molecules were absent.

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_2S	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_2H_4	Ethylene	Colorless, ripens fruit
C_3H_8	Propane	Colorless, odorless, bottled gas
N_2O	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

10.2 Pressure

- **Pressure** is the force acting on an object per unit area:

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

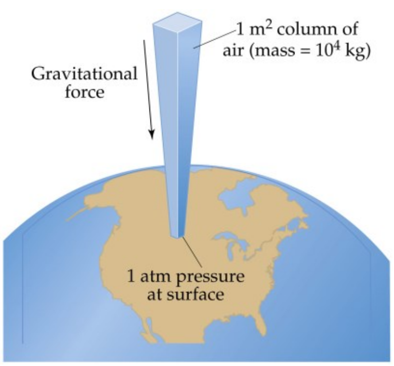
Units: **Force** measured in **Newtons (N)**
- SI units of pressure = **pascals**.
- 1 Pa = 1 N/m^2
- 1 N = 1 kg-m/s^2
- related unit = the **bar,** which = 10^5 Pa.

Pressure measured in:
Pascals (1 N/m^2)
Torr
mm Hg
Atmospheres

Standard Pressure (sea level)
= 760 mm Hg
= 760 Torr
= 30 inches of Hg
= 1 atm
= 101.325 kPa

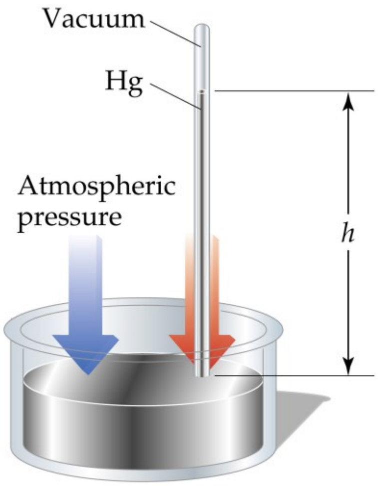
Atmospheric Pressure

- Gravity exerts a force on the Earth's atmosphere.
  - A column of air 1 m^2 in cross section extending to the top of the atmosphere exerts a force of 10^5 N.
  - Thus, the pressure of a 1 m^2 column of air extending to the top of the atmosphere is 100 kPa or 1 bar.



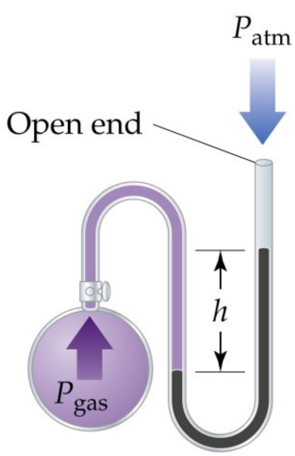
Instruments for Measuring Gas Pressure

Barometer – instrument used to measure atmospheric pressure
- Invented by Evangelista Torricelli in 1643
- Atmospheric pressure is measured with a *barometer*.
  - If a tube is completely filled with mercury and then inverted into a container of mercury open to the atmosphere, the mercury will rise 760 mm up the tube.
  - **Standard atmospheric pressure** is the pressure required to support 760 mm of Hg in a column.
  - Important non-SI units used to express gas pressure include:
    - **atmospheres** (atm)
    - ***millimeter of mercury*** (mm Hg) or **torr**
    - 1 atm = 760 mm Hg = 760 torr = 1.01325 x 10^5 Pa = 101.325 kPa.
- Atmospheric pressure presses down on a bowl of mercury, which causes a column of mercury equal to that pressure to rise into the vacuum column, = 760 mm Hg



Manometer – instrument used to measure gas pressure
Gas pressure = atmospheric pressure ± pressure of liquid in U-tube

Ask: Is the gas pressure higher or lower than atmospheric pressure?
If **higher**, **add** the pressure of the liquid.
If **lower**, subtract the pressure of the liquid.



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

Sample Exercise 10.1 (p. 397)

a) Convert 0.357 atm to torr. (271 torr)

b) Convert 6.6×10^{-2} torr to atm. (8.7×10^{-5} atm)

c) Convert 147.2 kPa to torr. (1104 torr)

Practice Exercise 10.1

a) In countries that use the metric system, such as Canada, atmospheric pressure in weather reports is measured in units of kPa. Convert a pressure of 745 torr to kPa.

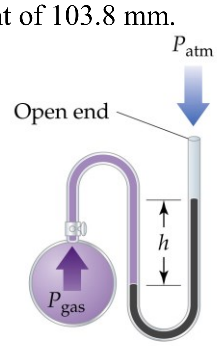
(99.3 kPa)

b) An English unit of pressure sometimes used in engineering is pounds per square inch (lb/in.^{2}), or psi: 1 atm = 14.7 lb/in.^{2}. If a pressure is reported as 91.5 psi, express the measurement in atmospheres.

(6.22 atm)

Sample Exercise 10.2 (p. 397)

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 vessel attached to an open-ended mercury manometer. 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 measured height of 136.4 mm, and that in the arm that is in contact with the gas has a height of 103.8 mm.



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

What is the pressure of the gas?
a) in atmospheres? (797.3 torr)
b) in kPa? (106.3 kPa)

Practice Exercise 10.2

Convert a pressure of 0.975atm into Pa and kPa. (9.88×10^4 Pa and 98.8 kPa)

10.3 The Gas Laws

To describe a gas, you need:
- Volume
- Pressure
- Temperature (K)
- # particles

→ "Gas Laws"

The Pressure-Volume Relationship: Boyle's Law **$P_1V_1 = P_2V_2$**

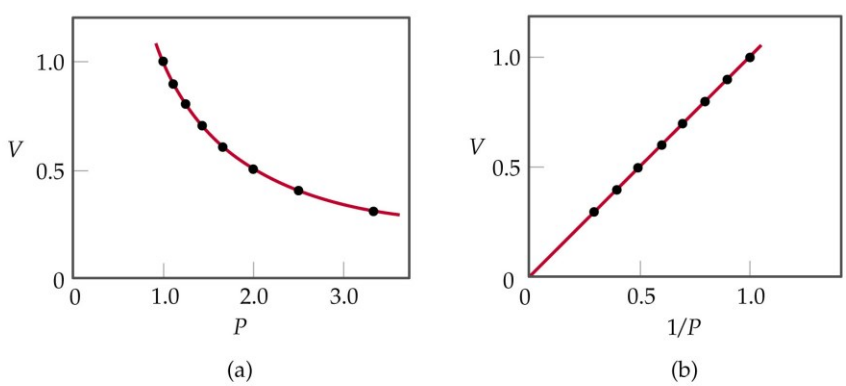
e.g. weather balloons:
- As the weather balloon ascends, the V ↑.
- As the weather balloon gets further from Earth's surface, the atmospheric P ↓.

.

- **Boyle's law**: The V of a fixed quantity of gas, at constant T, is inversely proportional to its P.

- Mathematically:

$$V = \text{constant} \times \frac{1}{P} \text{ or } PV = \text{constant}$$

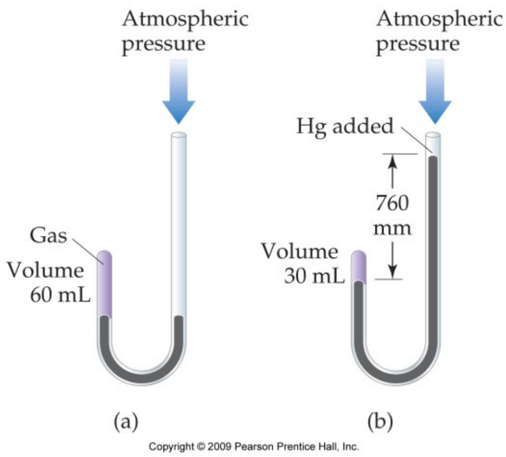


- a) A plot of V versus P is a hyperbola.
  b) Similarly, a plot of V versus $1/P$ must be a straight line passing through the origin.

- The working of the lungs illustrates this:
  - As we breathe in, the diaphragm moves down, & the ribs expand. Therefore, the V of the lungs ↑.
  - According to Boyle's law, when the V of the lungs ↑, the P ↓. Therefore, the P inside the lungs < atmospheric P.
  - Atmospheric P then forces air into the lungs until the P once again equals atmospheric P.
  - As we breathe out, the diaphragm moves up & the ribs contract. Therefore, the V of the lungs ↓.
  - By Boyle's law, the P ↑ and air is forced out.

An illustration of Boyle's experiment relating pressure and volume.

In (a) the volume of the gas trapped in the J-tube is 60 mL when the gas pressure is 760 torr. When additional mercury is added, as shown in (b), the trapped gas is compressed. The volume is 30 mL when its total pressure is 1520 torr, corresponding to atmospheric pressure plus the pressure exerted by the 760-mm column of mercury.

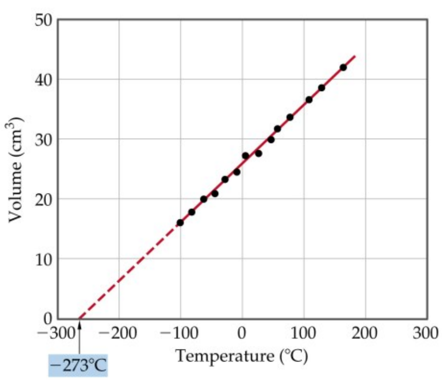


The Temperature-Volume Relationship: Charles's Law $\frac{V_1}{T_1} = \frac{V_2}{T_2}$

- Hot-air balloons expand when they are heated.
- **Charles's law:** The V of a fixed quantity of gas at constant P is directly proportional to its absolute T.
- Mathematically:

$$V = \text{constant} \times T \quad or \quad \frac{V}{T} = \text{constant}$$

  - Note that the value of the constant depends on the P and number of moles (n) of gas.
  - A plot of V versus T is a straight line.
  - When T is measured in ºC, the intercept on the temperature axis is –273.15ºC.
  - We define absolute zero, 0 K = –273.15 ºC.



The Pressure-Temperature Relationship: Gay-Lussac's Law $\frac{P_1}{T_1} = \frac{P_2}{T_2}$

- For a fixed amount of gas (fixed number of moles) at a fixed volume, the pressure is proportional to the temperature.

$$P = \text{constant x } T \quad \text{or} \quad \frac{P}{T} = \text{constant}$$

Concept quiz:

Constant Temperature

What happens to pressure when volume decreases?

Constant Pressure

What happens to volume when temperature increases?

Constant Volume

What happens to pressure when temperature increases?

Constant Volume and Temperature

What happens to pressure when the # of particles is increased?

Constant Temperature and Pressure

What happens to volume when the # of particles is increased?

Practice Problems – Gas Laws

Boyle's Law

The pressure on 2.50 L of anaesthetic gas is changed from 760 mm Hg to 304 mm Hg. What will be the new volume if the temperature remains constant?

Charles's Law

If a sample of gas occupies 6.8 L at 327°C, what will be its volume at 27°C if the pressure does not change?

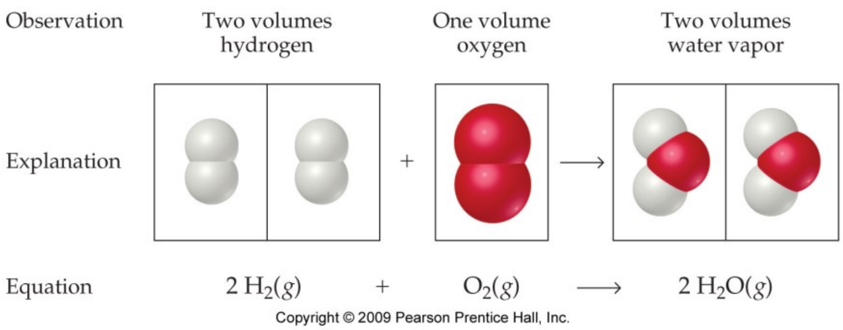
Gay-Lussac's Law

A gas has a pressure of 50.0 mm Hg at 540 K. What will be the temperature if the pressure is 70.0 mm Hg and the volume does not change?

The Quantity-Volume Relationship: Avogadro's Law

- Gay-Lussac's law of combining volumes: At a given temperature and pressure the volumes of gases that react with one another are ratios of small whole numbers.

- **Avogadro's hypothesis:** Equal volumes of gases at the same temperature and pressure contain the same number of molecules.

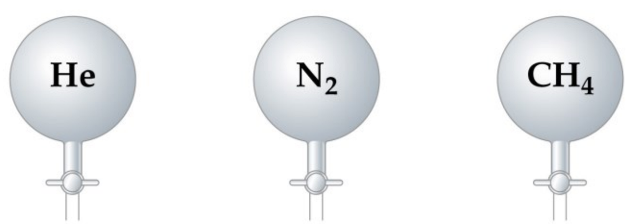


Gay-Lussac's experimental observation of combining volumes is shown together with Avogadro's explanation of this phenomenon.

- **Avogadro's law**: The volume of gas at a given temperature and pressure is directly proportional to the number of moles of gas.
  - Mathematically:

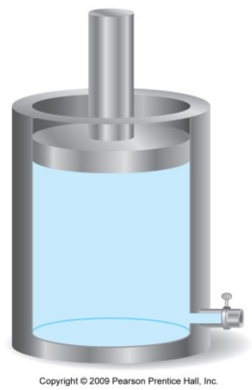
$$V = \text{constant} \times n$$

  - We can show that 22.4 L of any gas at 0 ^{o}C and 1 atmosphere contains 6.02×10^{23} gas molecules.



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}

Sample Exercise 10.3 (p. 401)



Suppose we have a gas confined to a piston. Consider the following changes:

a) Heat the gas from 298 K to 360 K, while maintaining the present position of the piston.

b) Move the piston to reduce the volume of gas from 1L to 0.5 L.

c) Inject additional gas through the gas inlet valve.

Indicate how each of these changes will affect:

1. the average distance between molecules
2. the pressure of the gas
3. the number of moles of gas present in the cylinder.

Practice Exercise 10.3

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?

10.4 The Ideal-Gas Equation

- Summarizing the **Gas Laws**
  - Boyle: $V \propto 1/P$ (constant n, T)
  - Charles: $V \propto T$ (constant n, P)
  - Avogadro: $V \propto n$ (constant P, T)
  - Combined: $V \propto nT/P$

- **Ideal gas equation**: $PV = nRT$
  - An **ideal gas** is a hypothetical gas whose *P*, *V*, and *T* behavior is completely described by the ideal-gas equation.
    - R = **gas constant** = 0.08206 L•atm/mol•K

- Define **STP** (**standard temperature and pressure**) = 0ºC, 273.15 K, 1 atm.
  - The molar volume of 1 mol of an ideal gas at STP is 22.4 L.

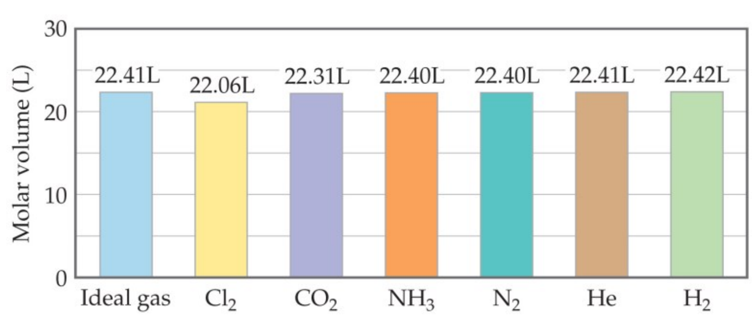
$$PV = nRT$$

$$V = \frac{nRT}{P} = \frac{(1\,\text{mol})(0.08206\,\text{L·atm/mol·K})(273.15\,\text{K})}{1.000\,\text{atm}} = 22.41\,\text{L}$$

TABLE 10.2 ■ Numerical Values of the Gas Constant, *R*, in Various Units

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



Comparison of molar volumes at STP.

One mole of an ideal gas at STP occupies a volume of 22.41 L.
One mole of various real gases at STP occupies close to this ideal volume.

Sample Exercise 10.4 (p. 403)

Calcium carbonate, $CaCO_{3(s)}$, decomposes upon heating to give $CaO_{(s)}$ and $CO_{2(g)}$. 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 31ºC. How many moles of CO_2 gas were generated?

(0.013 mol CO_2)

Practice Exercise 10.4

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 24ºC (in atmospheres)?

(2.0 atm)

Relating the Ideal-Gas Equation and the Gas Laws

- If $PV = nRT$ and n and T are constant, then PV is constant and we have Boyle's law.
  - Other laws can be generated similarly.
- In general, if we have a gas under two sets of conditions, then

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

- We often have a situation in which P, V and T all change for a **fixed number** of moles of gas.
  - For this set of circumstances,

$$\frac{PV}{T} = nR = \text{constant}$$

Sample Exercise 10.5 (p. 405)

	P	T
INITIAL	1.5 atm	298 K
FINAL	P_2	723 K

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?

(3.6 atm)

Practice Exercise 10.5

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 3.25×10^3 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)?

(3.83×10^3 m^3)

Sample Exercise 10.6 (p. 406)

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.

(11 L)

Practice Exercise 10.6

A 0.50-mol sample of oxygen gas is confined at 0^{o}C in a cylinder with a movable piston. The gas has an initial pressure of 1.0 atm. The gas is then compressed by the piston 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?

(27^{o}C)

10.5 Further Applications of the Ideal-Gas Equation

Gas Densities and Molar Masses

- Density has units of mass over volume.
- Rearranging the ideal-gas equation with M as molar mass we get

$$\frac{n}{V} = \frac{P}{RT}$$

$$\frac{nM}{V} = \frac{PM}{RT}$$

$$M = \frac{dRT}{P}$$

$$\therefore d = \frac{PM}{RT}$$

- The molar mass of a gas can be determined as follows:

Sample Exercise 10.7 (p. 407)

What is the density of carbon tetrachloride vapor at 714 torr and 125^{o}C?

(4.43 g/L)

Practice Exercise 10.7

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.

(5.9 g/L)

Sample Exercise 10.8 (p. 408)

A series of measurements are made in order 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.) Assuming that the ideal-gas equation applies, calculate the molar mass of the unknown gas.

(79.7 g/mol)

Practice Exercise 10.8

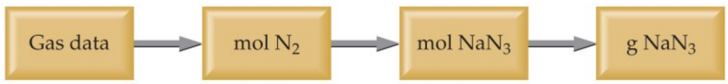
Calculate the average molar mass of dry air if it has a density of 1.17 g/L at 21°C and 740.0 torr.

(29.0 g/mol)

Volumes of Gases in Chemical Reactions

- The ideal-gas equation relates *P*, *V*, and *T* to number of moles of gas.
- The *n* can then be used in stoichiometric calculations.

Sample Exercise 10.9 (p. 409)



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

$$2\ NaN_{3(s)} \rightarrow 2\ Na_{(s)} + 3\ N_{2(g)}$$

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

(72 g NaN_3)

Practice Exercise 10.9

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:

$$4\ NH_{3(g)} + 5\ O_{2(g)} \rightarrow 4\ NO_{(g)} + 6\ H_2O_{(g)}$$

How many liters of $NH_{3(g)}$ at 850ºC and 5.00 atm are required to react with 1.00 mol of $O_{2(g)}$ in this reaction?

(14.8 L)

10.6 Gas Mixtures and Partial Pressures

- Since gas molecules are so far apart, we can assume they behave independently.

- Dalton observed:
  - The total pressure of a mixture of gases equals the sum of the pressures that each would exert if present alone.
  - **Partial pressure** is the pressure exerted by a particular component of a gas mixture.

- **Dalton's law of partial pressures**: In a gas mixture the total pressure is given by the sum of partial pressures of each component:

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

- Each gas obeys the ideal gas equation.
  - Thus,

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

Sample Exercise 10.10 (p. 411)

A gaseous mixture made from 6.00 g O_2 and 9.00 g CH_4 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?

(1.122 atm)

Practice Exercise 10.10

What is the total pressure exerted by a mixture of 2.00 g of H_2 and 8.00 g of N_2 at 273 K in a 10.0-L vessel?

(2.86 atm)

Partial Pressures and Mole Fractions

$$\text{mole fraction of gas A} = \frac{\text{moles gas A}}{\text{total \# moles of gas}}$$

Since partial pressures of gases reflect the quantity of a particular gas, comparing partial pressure with total pressure will give you mole fraction.

1. The partial pressure of oxygen was observed to be 156 torr in air with a total atmospheric pressure of 743 torr. Calculate the mole fraction of O_2 present.

$$\frac{P_{O2}}{P_{total}} = \frac{156 \text{ torr}}{743 \text{ torr}} = 0.210$$

2. The partial pressure of nitrogen was observed to be 590 mm Hg in air with a total atmospheric pressure of 760. mm Hg. Calculate the mole fraction of N_2 present.

$$\frac{P_{N2}}{P_{total}} = \frac{590 \text{ mm Hg}}{760. \text{ mm Hg}} = 0.78$$

Note: Mole fraction has NO units.

- Let n_1 be the number of moles of gas 1 exerting a partial pressure P_1, then

$$P_1 = X_1P_t$$

  - Where X_1 is the **mole fraction** (n_1/n_t).
  - Note that a mole fraction is a dimensionless number.

Sample Exercise 10.11 (p. 412)

A study of the effects of certain gases on plant growth requires a synthetic atmosphere composed of 1.5 mol percent CO_2, 18.0 mole percent O_2, and 80.5 mol percent Ar.

a) Calculate the partial pressure of O_2 in the mixture if the total pressure of the atmosphere is to be 745 torr.

(134 torr)

b) If this atmosphere is to be held in a 120-L space at 295 K, how many moles of O_2 are needed?

(0.872 mol)

Practice Exercise 10.11

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 N_2, 12 mol percent Ar, and 6.0 mol percent CH_4. Calculate the partial pressure of each of these gases in Titan's atmosphere.

(1.0×10^3 torr N_2, 1.5×10^2 torr Ar, and 73 torr CH_4)

Collecting Gas by Water Displacement

It is common to synthesize gases and collect them by displacing a volume of water.

The gas bubbles through the water in the jar and collects at the top due to its lower density.
The gas has water vapor mixed with it.

To calculate the amount of gas produced, we need to correct for the partial pressure of the water:

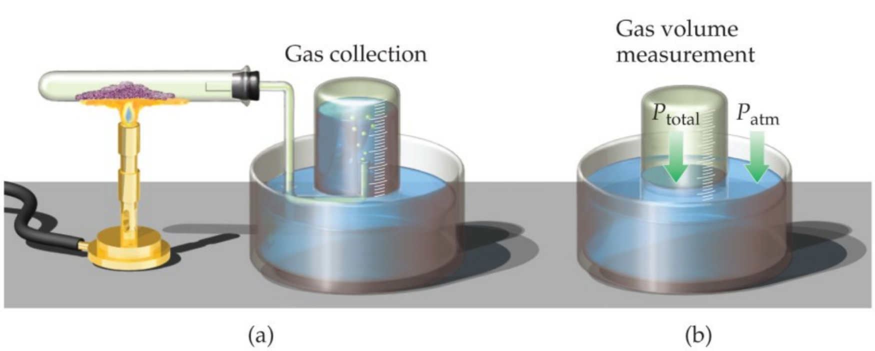
$P_{total} = P_{gas} + P_{H2O}$

We can rearrange this equation to calculate the pressure of the dry gas:

$P_{gas} = P_{total} – P_{H2O}$

P_{total} is what is measured (= atmospheric pressure).

P_{H2O} varies with T.
P_{H2O} can be found in standard tables of vapor pressure of water at different T (e.g. Appendix B)



Collecting a water-insoluble gas over water.
(a) A solid is heated, releasing a gas, which is bubbled through water into a collection bottle. (b) When the gas has been collected, the bottle is raised or lowered so that the water levels inside and outside the bottle are equal. The total pressure of the gases inside the bottle is then equal to the atmospheric pressure.

Vapor Pressure of H_2O at Various Temperatures

ºC	kPa		ºC	kPa
0	0.61		26	3.36
5	0.87		27	3.56
10	1.23		28	3.77
15	1.71		29	4.00
16	1.81		30	4.24
17	1.93		40	7.37
18	2.07		50	12.33
19	2.20		60	19.92
20	2.33		70	31.15
21	2.49		80	47.33
22	2.64		90	70.01
23	2.81		100	101.3
24	2.99		105	120.8
25	3.17		110	143.2

Note: At 100ºC, the normal boiling point, vapor pressure = atmospheric pressure = 101.3 kPa

Sample Exercise 10.12 (p. 413)

A sample of $KClO_3$ is partially decomposed, producing O_2 gas that is collected over water. The volume of the gas collected is 0.250 L at 26ºC and 765 torr total pressure.

a) How many moles of O_2 are collected? (9.92×10^{-3} mol O_2)

b) How many grams of $KClO_3$ were decomposed? (0.811 g $KClO_3$)

Practice Exercise 10.12

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

$$NH_4NO_2 \rightarrow N_{2(g)} + 2\ H_2O_{(l)}$$

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

(1.26 g)

10.7 Kinetic-Molecular Theory

- The **kinetic molecular theory** was developed to *explain* gas behavior.
  - Theory of moving molecules.

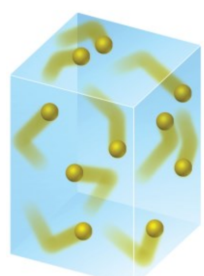
- Summary:
  1. Gases consist of a large number of molecules in constant random motion.
  2. The volume of individual molecules is negligible compared with the volume of the container.
  3. Intermolecular forces (forces between gas molecules) are negligible.
     - Energy can be transferred between molecules during collisions, but the average kinetic energy is constant at constant temperature.
  4. The collisions are perfectly elastic.
  5. The average kinetic energy of the gas molecules is proportional to the absolute temperature.

- Kinetic molecular theory gives us an *understanding* of pressure and temperature on the molecular level.
  - The pressure of a gas results from the collisions with the walls of the container.
  - The magnitude of the pressure is determined by how often and how hard the molecules strike.

- The absolute temperature of a gas is a measure of the average kinetic energy.
  - Some molecules will have less kinetic energy or more kinetic energy than the average (distribution).
    - There is a spread of individual energies of gas molecules in any sample of gas.
    - As the temperature increases, the average kinetic energy of the gas molecules increases.

The molecular origin of gas pressure.

The pressure exerted by a gas is caused by collision of the gas molecules wih the wall fo their container.



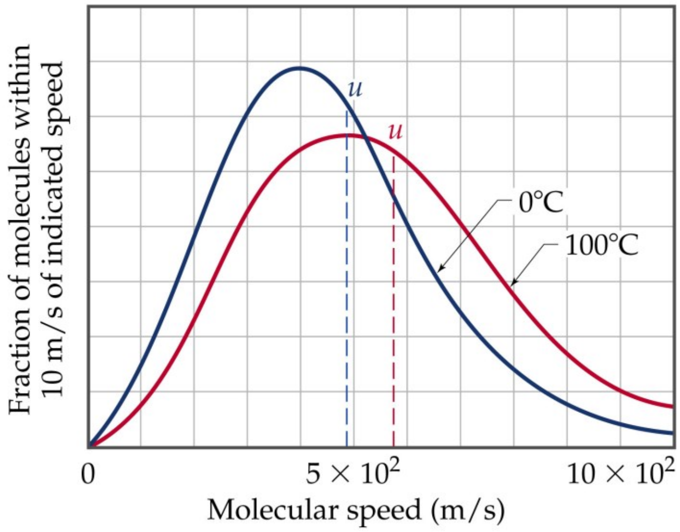
Distributions of Molecular Speed **NEW - optional**

- As kinetic energy increases, the velocity of the gas molecules increases.
  - **Root-mean-square (rms) speed**, u, is the speed of a gas molecule having average kinetic energy.

- Average kinetic energy, ε, is related to rms speed:

$$\varepsilon = \tfrac{1}{2}mu^2$$

  - Where m = mass of the molecule.



The effect of temperature on molecular speeds.

Distribution of molecular speeds for nitrogen at 0 °C (blue line) and 100 °C (red line).

Increasing temperature increases both the most probable speed (curve maximum) and the rms speed, *u*, which is indicated by the vertical dashed line.

Application to the Gas Laws

- We can understand empirical observations of gas properties within the framework of the kinetic-molecular theory.

- Effect of an ↑ in volume (at constant temperature):
  - As volume ↑ at constant temperature, the average kinetic of the gas remains constant.
  - → *u* is constant.
  - However, volume ↑, so the gas molecules have to travel further to hit the walls of the container.
  - → pressure ↓.

- Effect of an ↑ in temperature (at constant volume):
  - If temperature ↑ at constant volume, the average kinetic energy of the gas molecules ↑.
  - There are more collisions with the container walls.
  - → *u* ↑.
  - The change in momentum in each collision ↑ (molecules strike harder).
  - → pressure ↑.

Sample Problem 10.13 (p. 416)

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 KE 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?

Practice Problem 10.13 NEW - optional

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 of the sample;

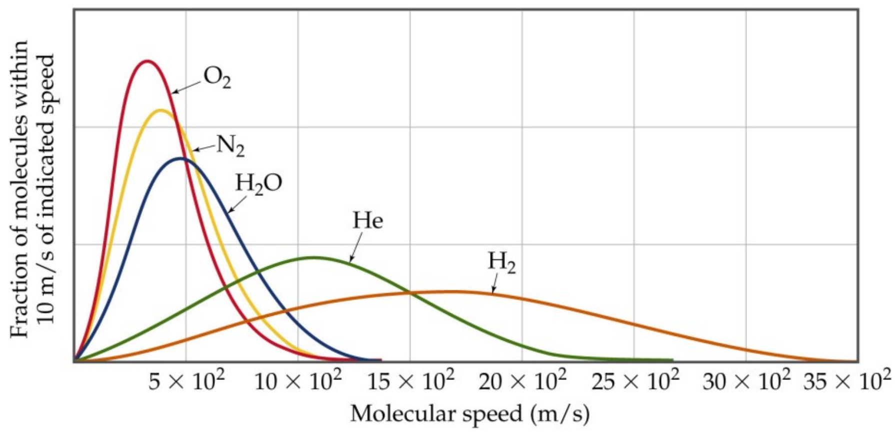
c) mixing with a sample of Ar at the same temperature?

10.8 Molecular Effusion and Diffusion

- The average kinetic energy of a gas is related to its mass: $\varepsilon = \frac{1}{2} mu^2$
- Consider two gases at the same temperature: the lighter gas has a higher rms speed than the heavier gas.
  - Mathematically:

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

  - The lower the molar mass, M, the higher the rms speed for that gas at a constant temperature.



The effect of molecular mass on molecular speeds.
The distributions of molecular speeds for different gases are compared at 25 °C.
The molecules with lower molecular masses have higher rms speeds.

NEW - optional

Sample Problem 10.14 (p. 417)

Calculate the rms speed, u, of an N_2 molecule at 25°C.

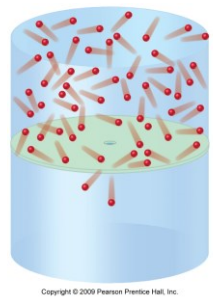
(5.15×10^2 m/s)

Practice Problem 10.14

What is the rms speed of an He atom at 25°C?

(1.36×10^3 m/s)

- Two consequences of the dependence of molecular speeds on mass are:
  - **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.



Effusion.

The top half of this cylinder is filled with a gas, and the bottom half is an evacuated space.
Gas molecules effuse through a pinhole in the partitioning wall only when they happen to hit the hole.

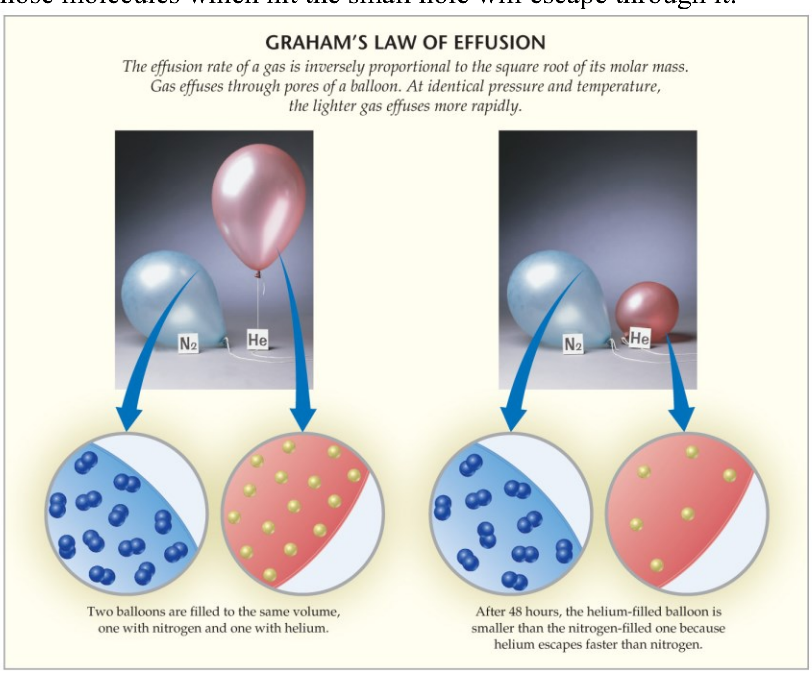
Graham's Law of Effusion

- The rate of effusion can be quantified.

- Consider two gases with molar masses M_1 and M_2, with effusion rates, r_1 *and* r_2, respectively:
  - The relative rate of effusion is given by **Graham's law**:

$$\frac{r_1}{r_2} = \sqrt{\frac{M_2}{M_1}}$$

    - Only those molecules which hit the small hole will escape through it.



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

- Therefore, the higher the rms speed the more likely that a gas molecule will hit the hole.
  - We can show

$$\frac{r_1}{r_2} = \frac{u_1}{u_2} = \sqrt{\frac{M_2}{M_1}}$$

Graham's Law Practice Problems:

1. The molar mass of gas "b" is 16.04 g/mol and gas "a" is 44.04 g/mol. If gas "b" is travelling at 5.25 x 10^9 m/s, how fast is gas "a" travelling? Both gases have the same KE.

2. An unknown gas effuses through an opening at a rate 3.53 times slower than nitrogen gas. What is the molecular mass of the unknown gas?

Sample Problem 10.15 (p. 419)

An unknown gas composed of homonuclear diatomic molecules effuses at a rate that is only 0.355 times that of O_2 at the same temperature. What is the identity of the unknown gas?

(254 g/mol; I)

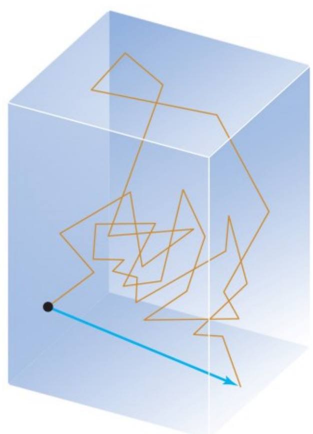
Practice Problem 10.15

Calculate the ratio of the effusion rates of N_2 and O_2, rN_2/rO_2.

(1.07)

Diffusion and Mean Free Path

- Diffusion is faster for light gas molecules.
- Diffusion is significantly slower than the rms speed.
  - Diffusion is slowed by collisions of gas molecules with one another.
  - Consider someone opening a perfume bottle: It takes awhile to detect the odor, but the average speed of the molecules at 25 °C is about 515 m/s (1150 mi/hr).
- The average distance traveled by a gas molecule between collisions is called the **mean free path**.
- At sea level, the mean free path for air molecules is about 6×10^{-6} cm.



Diffusion of a gas molecule.

For clarity, no other gas molecules in the container are shown. The path of the molecule of interest begins at the dot. Each short segment of line represents travel between collisions. The blue arrow indicates the net distance traveled by the molecule.

10.9 Real Gases: Deviations from Ideal Behavior

Ideal Gases

- *Based on kinetic molecular theory*
- Follows gas laws at all T and P
- Assumes particles:
  - have no volume
    → impossible
  - have no attraction to each other
    → if true, would be impossible to liquefy gases (e.g. CO_2 is liquid at $\geq$□5.1 atm, < 56.6°C

Real Gases

Because particles of real gases occupy space:

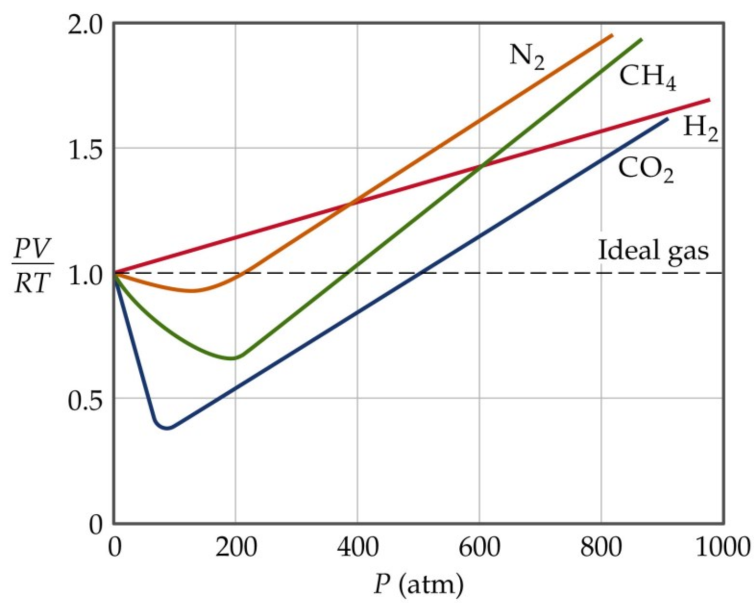
- Follow gas laws at **most** T and P
- At high P, individual volumes count
- At low T, attractions count
- The more polar the molecule, the more attraction counts

Here is the same information, with a greater level of detail, using the ideal gas equation: *NEW - optional*

- From the ideal gas equation:

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

- For 1 mol of an ideal gas, $PV/RT = 1$ for all pressures.
  - In a real gas, PV/RT varies from 1 significantly.
  - The higher the pressure the more the deviation from ideal behavior.

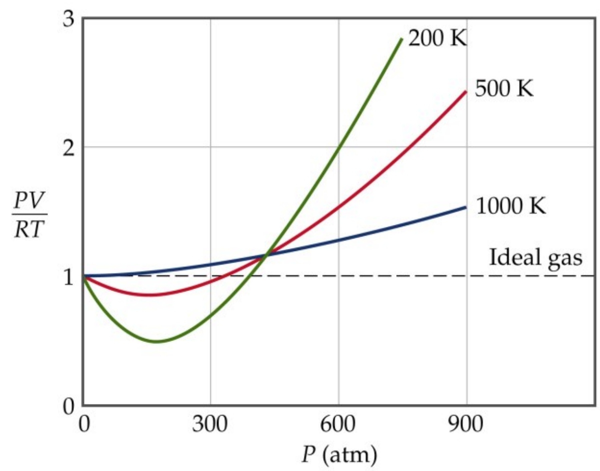


The effect of pressure on the behavior of several gases.

The ratios of PV/RT versus pressure are compared for one mole of several gases at 300 K. The data for CO_2 are at 313 K because under high pressure CO_2 liquefies at 300 K. The dashed horizontal line shows the behavior of an ideal gas.

- For 1 mol of an ideal gas, $PV/RT = 1$ for all temperatures.
- As temperature ↑, the gases behave more ideally.

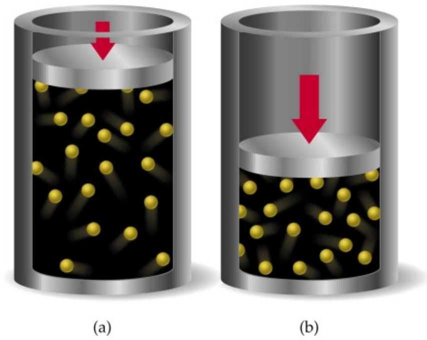
- The assumptions in the kinetic-molecular theory show where ideal gas behavior breaks down:
  - The molecules of a gas *have* finite volume.
  - Molecules of a gas *do* attract each other.



The effect of temperature and pressure on the behavior of nitrogen gas.

The ratios of PV/RT versus pressure are shown for 1 mol of nitrogen gas at three temperatures. As temperature increases, the gas more closely approaches ideal behavior, which is represented by the dashed horizontal line.

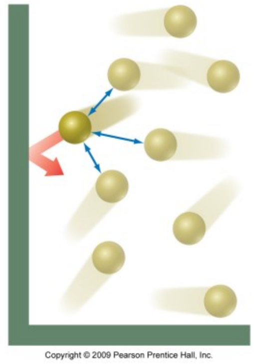
- As the P on a gas ↑ → the molecules are forced closer together.
  - As the molecules get closer together → V of the container gets smaller.
  - The smaller the container → the more of the total space the gas molecules occupy.
  - → the higher the pressure, the less the gas resembles an ideal gas.
  - As the gas molecules get closer together, the intermolecular distances decrease.
  - The smaller the distance between gas molecules, the more likely that attractive forces will develop between the molecules.
  - Therefore, the less the gas resembles an ideal gas.



- As T ↑, the gas molecules move faster and further apart.

- Also, higher T mean more energy available to break intermolecular forces.

- As T ↑, the negative departure from ideal-gas behavior disappears.



The effect of intermolecular forces on gas pressure.

The molecule that is about to strike the wall experiences attractive forces from nearby gas molecules, and its impact on the wall is thereby lessened. The lessened impact means the molecule exerts a lower-than-expected pressure on the wall. The attractive forces become significant only under high-pressure conditions, when the average distance between molecules is small.

The van der Waals Equation

- We add two terms to the ideal gas equation to correct for
  - The volume of molecules: $(V - nb)$
  - For molecular attractions: $\left(\frac{n^2 a}{V^2}\right)$
    - The correction terms generate the **van der Waals equation**:

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

Or:

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

Corrects for molecular volume

Corrects for molecular attraction

- Where a and b are empirical constants.

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_2O	5.46	0.0305
CH_4	2.25	0.0428
CO_2	3.59	0.0427
CCl_4	20.4	0.1383

- To understand the effect of intermolecular forces on pressure, consider a molecule that is about to strike the wall of the container.
  - The striking molecule is attracted by neighboring molecules.
  - Therefore, the impact on the wall is lessened.

NEW - optional

Sample Problem 10.16 (p. 423)

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 (p. 395) to estimate the pressure exerted by 1.000 mol of $Cl_{2(g)}$ in 22.41 L at 0.0°C.

(0.990 atm)

Practice Exercise 10.16

Consider a sample of 1.000 mol of $CO_{2(g)}$ 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 (7.473 atm)
b) the van der Waals equation. (7.182 atm)

Sample Integrative Exercise 10 (p. 424)

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?
(C_2N_2)

b) Predict its molecular structure.
(see textbook for answer)

c) Predict the polarity of the compound.
(nonpolar)