TOPIC

10

GASES

The content in this topic is the basis for mastering Learning Objectives 2.4, 2.5, 2.6, 2.12, and 5.2 as found in the Curriculum Framework.

When you finish reviewing this topic, be sure you are able to:

- Use kinetic-molecular theory and Maxwell–Boltzmann distribution to explain and make predictions about the macroscopic behavior of the properties of gases: pressure, volume, the number of particles, and temperature
- Construct particle representations of the gas phase that explain the macroscopic properties of gases
- Know what an ideal gas is and how to calculate its temperature, pressure, and volume from given data
- Understand the graphical representations of pressure, volume, and temperature and how absolute zero can be determined experimentally
- Explain the deviations of real gases from ideal behavior using the structure of atoms and molecules and the forces acting between them

The Kinetic-Molecular Theory of Gases

Section 10.1

A **gas** is a form of matter that has no fixed volume or shape. It expands to fill the volume and shape of its container. A gas is readily compressible, flows easily, and diffuses into another gas quickly.

Kinetic-molecular theory (the theory of moving molecules), or KMT, is an atomic-level view of gases that explains their macroscopic properties. Figure 10.1 illustrates a particle view of gases.

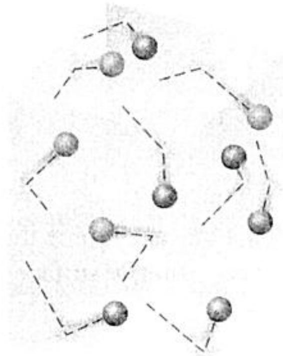


Figure 10.1 Gas particles are far apart, and are in rapid, random motion, and their intermolecular forces are negligible.

These statements summarize the kinetic-molecular theory:

1. Gases consist of atoms or molecules in continuous rapid, random motion.
2. The particles are far apart and their volumes are negligible compared to the volume of the container.
3. Attractive and repulsive forces between gas molecules are negligible.
4. Molecular collisions are perfectly elastic (they happen without loss of energy).
5. The average kinetic energy of the particles is proportional to the absolute temperature. At any given temperature all gases have the same average kinetic energy.

Section 10.2 Pressure

The KMT explains why **a gas exerts a pressure** on its container. Pressure is caused by collisions that molecules make with the container walls (Figure 10.2). How often and how forcefully the particles strike the walls determines the magnitude of the pressure.

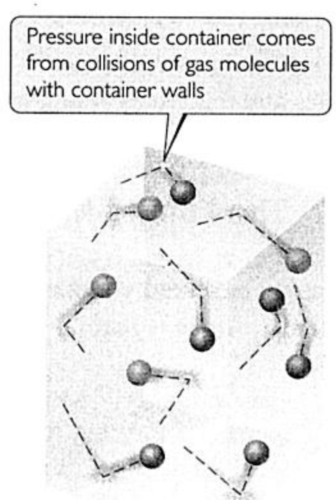


Figure 10.2 Pressure originates from collisions of gas molecules on the walls of the container.

Pressure is the force that acts on a given area: Pressure = force/area. Gases exert a pressure on any surface in which they come in contact.

Standard pressure corresponds to a typical pressure that the gases of the atmosphere exert at sea level. The SI value and unit for standard pressure are 1.01×10^5 Pa.

Pressure units most commonly used in chemistry and their relationships are:

$$1 \text{ atm} = 760 \text{ mmHg} = 760 \text{ torr} = 1.01 \times 10^5 \text{ Pa} = 101 \text{ kPa}$$

Standard temperature is 0 °C = 273 K.

Common misconception: In all gas law calculations, temperature units must be expressed in Kelvin. K = 273 + °C. Even though 1 °C is the same size as 1K, the two units are 273° apart on their respective temperature scales. All the gas equations are proportional to Kelvin temperature but not Celsius temperature.

The Gas Laws Section 10.3

The KMT explains why **the pressure of a gas changes with volume** at constant temperature. If the volume of a fixed amount of gas decreases, the pressure increases and vice versa (Figure 10.3).

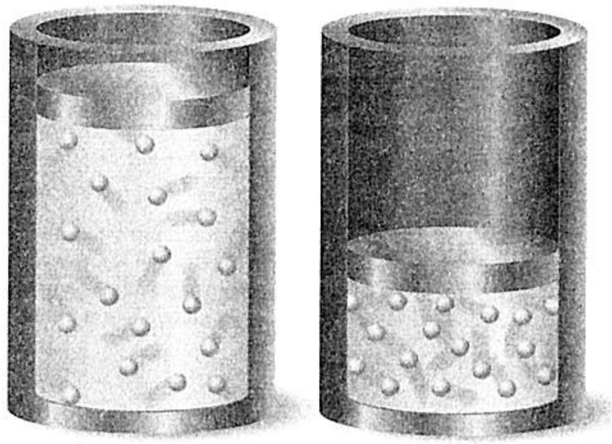


Figure 10.3 The pressure of a gas increases when the volume decreases at constant temperature because the surface area of the container decreases, $P = F/A$.

When the volume of the container decreases, the molecular collisions occur on a smaller surface area, increasing the pressure. $P = F/A$.

Boyle's law tells how much the volume of a gas changes with changing pressure:

The volume of a fixed quantity of gas at constant temperature is inversely proportional to the pressure.

$$P_1V_1 = P_2V_2$$

Figure 10.4 graphically illustrates how the volume of a gas depends on the pressure at constant temperature.

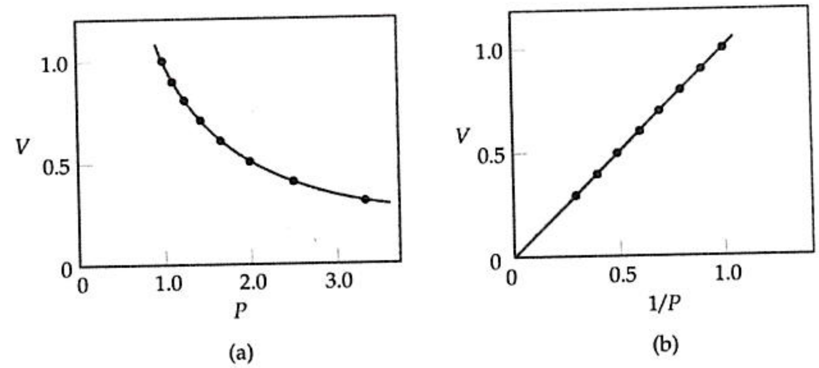


Figure 10.4 Boyle's law states that the volume of a gas decreases with increasing pressure. (a) volume vs. pressure, (b) volume vs. $1/P$.

Your Turn 10.1

If the pressure of a fixed amount of gas doubles at constant temperature, what happens to its volume? Write your answer in the space provided.

The KMT explains why **the volume of a gas changes with temperature** at constant pressure. If the temperature of a fixed amount of gas increases at constant pressure, the volume increases and vice versa.

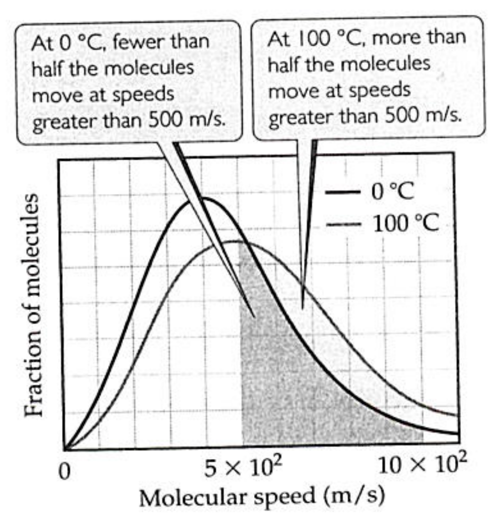


Figure 10.5 Higher temperature increases the speed of gas molecules and, therefore, their kinetic energies.

Volume increases with increasing temperature at constant pressure. Temperature is a measure of average kinetic energy of molecules. Increasing temperature increases the average kinetic energy of a collection of gas particles. Figure 10.5 shows the distribution speeds and, therefore, kinetic energies of a collection of gas molecules at two different temperatures. This is called the Maxwell–Boltzmann distribution. If the gas is confined in a flexible-walled container, the increased forces of collisions on the walls will expand the container to a larger surface area so the pressure remains constant.

Charles's law tells how much the volume of a gas changes with changing temperature:

The volume of a fixed amount of gas at constant pressure is directly proportional to the absolute temperature.

$$V_1/T_1 = V_2/T_2$$

Figure 10.6 shows how volume decreases with decreasing temperature. Notice how extrapolation of the graph to a theoretical zero volume gives the value of absolute zero temperature (0 K or −273 °C).

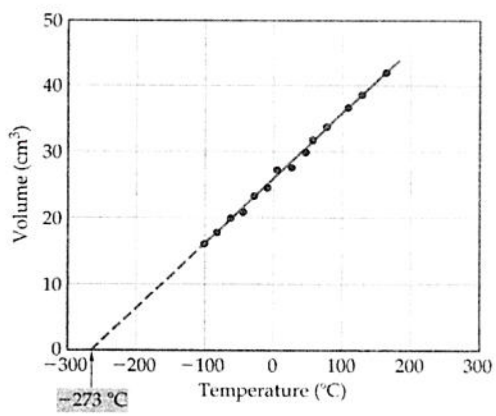


Figure 10.6 Charles's law states that the volume of an enclosed gas increases with increasing temperature. Extrapolation to zero volume yields the value of absolute zero.

Your Turn 10.2

When the temperature of a fixed amount of gas doubles from 20 °C to 40 °C, what happens to the volume at constant pressure? Write your answer in the space provided.

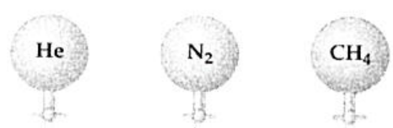
Your Turn 10.3

A corollary to Charles's law relates the pressure of a fixed volume of gas to the temperature: the pressure of a fixed amount of gas increases with increasing temperature at constant volume. Explain this statement using ideas from the kinetic-molecular theory. Write your answer in the space provided.

Avogadro's hypothesis states that equal volumes of gases under the same conditions of temperature and pressure contain equal numbers of molecules.

The KMT explains Avogadro's hypothesis because it assumes that all individual gas molecules occupy essentially zero volume and have essentially zero attractive and repulsive forces. (All gas molecules are pinpoint dots that move freely and independently.) Therefore, the same number of particles of all gases, no matter their chemical identity, will behave in the same way.

Figure 10.7 shows that volumes of equal moles of gases at the same temperature and pressure are independent of the identity of the gas.



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}

Figure 10.7 Avogadro's hypothesis states that equal number of moles of any gas at the same temperature and pressure occupy equal volumes.

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

$$V_1/n_1 = V_2/n_2$$

Since volume is directly proportional to moles, the coefficients that balance chemical equations for gas reactions can be taken as ratios of moles or liters at constant temperature and pressure.

Example:

How many liters of water vapor can be obtained from the complete combustion of 24 L of methane gas? Assume temperature and pressure are such that all the water formed will be in the gas phase.

Solution:

$$CH_4(g) + 3O_2(g) \rightarrow CO_2(g) + 2H_2O(g)$$

$$24\ L\ CH_4(g) \xrightarrow{\times 2\ L\ H_2O(g)/1\ L\ CH_4(g)} ?L\ H_2O(g)$$

$$x\ liters\ H_2O(g) = 24\ L\ CH_4\ (2\ L\ H_2O/1\ L\ CH_4) = 48\ L\ H_2O(g)$$

The Ideal-Gas Equation Section 10.4

The **ideal-gas equation** combines Boyle's, Charles's, and Avogadro's laws:

$PV = nRT$

P = pressure in atmospheres

V = volume in liters

n = amount of substance in moles

T = absolute temperature in Kelvin

R = 0.0821 L-atm/mol-K

Common misconception: When using the ideal-gas equation, pressure, volume, amount of substance, and temperature must always be expressed in atmospheres, liters, moles, and Kelvin, respectively, when the constant R has those units. In the other equations, volume and pressure may be expressed in any units as long as they are consistent.

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

Common misconception: No gas is an ideal gas. All gases are real gases. However, at temperatures at or above 25 °C and pressures at or below 1 atm, generally most real gases behave ideally. A real gas deviates from ideal behavior at high pressure and/or low temperature, especially near the condensation point. This is because at relatively low pressures, the individual gas particles are very far apart. This makes the volumes of the individual molecules of a gas and their attractive and/or repulsive forces negligible. Both are key assumptions of the kinetic-molecular theory. But at high pressure, the gas molecules are close together, making their particle volumes significant, and they collide more frequently, making their interactive forces significant. Also at low temperature, the molecules move more slowly, increasing the significance of their interactive forces.

Section 10.5 Further Applications of the Ideal-Gas Equation

The ideal-gas equation is useful in stoichiometry calculations involving gases.

Example:

Gasoline is a mixture of many hydrocarbon compounds but its chemical formula can be approximated as C_8H_{18}. How many liters of carbon dioxide gas are formed at 25.0 °C and 712 torr when 1.00 gallon of liquid gasoline is burned in excess air? Liquid gasoline has a density of 0.690 g/mL. One gallon is 3.80 L.

Solution:

First, write and balance the equation. Then, calculate the number of moles of CO_2 using the mole road. Finally, use the ideal-gas equation to convert moles of CO_2 to volume in liters at the given temperature and pressure. Be sure to convert °C to K and torr to atmospheres.

$$2C_8H_{18}(l) + 25O_2(g) \longrightarrow 16CO_2(g) + 18H_2O(l)$$

$$\begin{tikzcd}
\text{1 gallon} \arrow[d, "\times\ 3.80\ L/gal"] & ?\ L \\
\text{liters} \arrow[d, "\times\ 690\ g/L"] & \\
\text{grams} \arrow[d, "\div\ 114\ g/mol \times 16\ mol"] & \\
mols \arrow[r, "2\ mol"'] & mols = n \arrow[uuu, "V = nRT/P"']
\end{tikzcd}$$

$$x\ mol\ CO_2 = 1.00\ gal(3.80\ L/gal)(690\ g/gal)(1\ mol/114\ g)\\(16\ mol\ CO_2/2\ mol\ C_8H_{18}) = 184\ moles\ CO_2.$$

$$V = nRT/P = (184\ mol)\ (0.0821\ L\text{-}atm/mol\text{-}K)(25 + 273\ K)$$
$$/(712\ torr/760\ torr/atm) = 4810\ L.$$

The **density of a gas** at any given temperature and pressure is directly proportional to its molar mass:

$$d = PM/RT$$

where d is density in grams per liter and M is the molar mass in grams per mole.

Example:

What is the density of sulfur dioxide gas at 35 °C and 1270 torr?

Solution:

The molar mass of SO_2 is 64.0 g/mol. Use the equation for density. Make sure temperature is in Kelvin and pressure is in atmospheres.

$$d = PM/RT =$$
$$(1270\ torr/760\ torr/atm)\ (64.0\ g/mol)/(0.0821\ L\text{-}atm/mol\text{-}K)$$
$$(35 + 273K) = 4.23\ g/L.$$

Common misconception: Because the densities of most gases are so low, they are commonly expressed in units of g/L rather than g/mL or g/cm^3. At common temperatures and pressures, most gas densities fall between about 1 and 10 g/L.

Gas Mixtures and Partial Pressures

Section 10.6

A partial pressure of a gas is the pressure exerted by an individual gas in a mixture of gases. Water vapor pressure is a partial pressure.

Dalton's law of partial pressures states that the total pressure of a mixture of gases equals the sum of the pressures that each gas would exert if it were present alone.

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

where P_{total} is the total pressure of a mixture of gases and P_1, P_2, and P_3 are the **partial pressures** of the individual gases in the mixture.

The **mole fraction,** X_g, of a gas in a mixture is the ratio of moles of that gas to the total moles of gas in the mixture.

$$X_g = n_g/n_{total}$$

Each gas in a mixture of gases behaves independently of all the other gases in the mixture. Hence, each ideal gas in a mixture obeys the ideal-gas law and all other gas laws. Each gas can be treated separately from the other gases in any mixture. Table 10.1 summarizes some equations that are useful in partial pressure calculations.

Table 10.1 Some useful equations involving partial pressure.

	Equation	**Comments**
Dalton's law	$P_{\text{total}} = P_1 + P_2 + P_3 + \cdots$	$P_{\text{total}} =$ total pressure of the mixture, P_1, P_2, and $P_3 =$ partial pressures of the individual gases
Mole fraction, X	$X_1 = n_1/n_t$	$n_1 =$ number of moles of an individual gas, $n_t =$ total moles of the gas
Ideal-gas equation	$P_1 = n_1RT/V$	$P_1 =$ partial pressure of an individual gas, $n_1 =$ number of moles of that gas
Partial pressure	$P_1 = (n_1/n_t)(P_t)$	A convenient way to calculate partial pressure from total pressure

Example:

A mixture of 9.00 g of oxygen, 18.0 g of argon, and 25.0 g of carbon dioxide exerts a pressure of 2.54 atm. What is the partial pressure of argon in the mixture?

Solution:

First, calculate the number of moles of each gas. Then, calculate the mole fraction of argon and multiply it by the total pressure to get the partial pressure of argon.

$Moles\ of\ oxygen = 9.00\ g/32.0\ g/mol = 0.281\ mol\ O_2.$

$Moles\ of\ argon = 18.0\ g/39.9\ g/mol = 0.451\ mol\ Ar.$

$Moles\ of\ carbon\ dioxide = 25.0\ g/44.0\ g/mol = 0.568\ mol\ CO_2.$

$Mole\ fraction\ of\ Ar = X_{Ar} = moles\ of\ Ar/total\ moles\ of\ gases =$

$n_{Ar}/n_t = 0.451/(0.281 + 0.451 + 0.568) = 0.451/1.30 = 0.347.$

$$Partial\ pressure\ of\ Ar = P_{Ar} = (X_{Ar})(P_t) = 0.347 \times 2.54\ atm$$
$$= 0.881\ atm.$$

For convenience in the laboratory, gases are often collected by bubbling them through water. This process causes the collected gas to be "contaminated" with water vapor. That is, the collected gas and the water vapor both exert their own partial pressures. The total pressure inside the collection vessel (usually the atmospheric pressure) is equal to the combined partial pressures of the gas and the water vapor.

$$P_{\text{total}} = P_{\text{gas}} + P_{\text{water}}$$

Example:

Hydrogen is produced by the action of sulfuric acid on zinc metal and collected over water in a 255 mL container at 24.0 °C and 718 torr. The vapor pressure of water at 24 °C is 22.38 torr. How many moles of hydrogen gas are produced and how many grams of zinc react?

Solution:

First, write and balance the equation. Then, subtract the vapor pressure of water (given in the question or obtained from Appendix B of Chemistry: The Central Science) from the atmospheric pressure to obtain the partial pressure of hydrogen gas. Finally, calculate the number of moles of hydrogen using the ideal-gas equation. Any time you use the value of R, be sure to convert pressure to atmospheres and volume to liters.

$$Zn(s) + 2H^+(aq) \rightarrow Zn^{2+}(aq) + H_2(g)$$

$$P_{H_2} = P_{atm} - P_{water} = 718\ torr - 22.38\ torr = 696\ torr$$

$$nH_2 = PV/RT = (696\ torr/760\ torr/atm)(0.255\ L)$$
$$/(0.0821\ L\text{-}atm/mol\text{-}K)(24 + 273\ K) = 0.00958\ mol\ H_2$$

The balanced equation tells us that the number of moles of hydrogen produced is equal to the number of moles of zinc reacted.

$x\ g\ Zn = 0.00958\ mol\ Zn \times 65.4\ g/mol = 0.627\ g.$

Your Turn 10.4

Use kinetic-molecular theory to explain why the pressure increases when the temperature of a fixed volume of gas increases. Write your answer in the space provided.

Section 10.8 Molecular Effusion and Diffusion

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

Diffusion is the spread of one substance through space or through another substance.

Both effusion and diffusion occur faster at higher temperatures because the average speed of the molecules is greater. This is because the absolute temperature of a gas is a measure of the average kinetic energy of the particles. Molecular motion increases with increasing temperature.

At the same temperature, the average kinetic energy of gas molecules is the same. Thus, particles of smaller molar mass move faster on average than larger ones (see Figure 10.8).

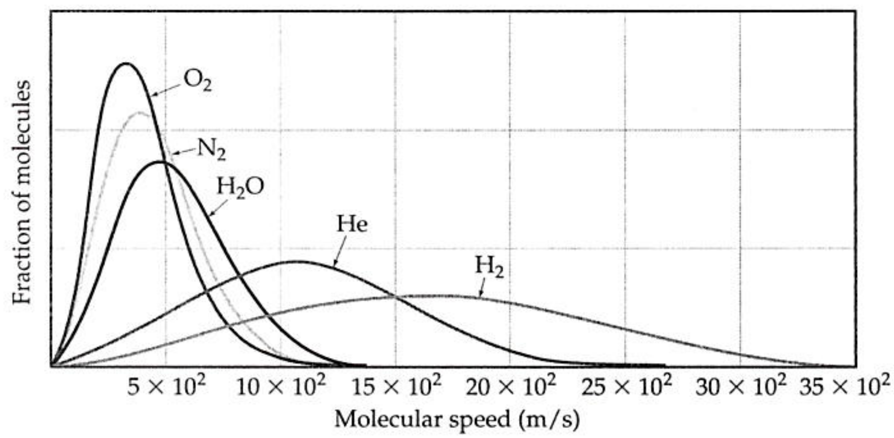


Figure 10.8 The effect of molar mass on molecular speed at 25 °C.

Section 10.9 Real Gases: Deviations from Ideal Behavior

Real gases differ from **ideal gases** largely because the volumes of real gas particles are finite and their attractive forces and repulsive forces are nonzero.

A real gas does not behave ideally at high pressure because the finite volume of its particles is significant compared to the volume of its container (see Figure 10.9). Also attractive forces come into play at short distances when gas particles are crowded together.

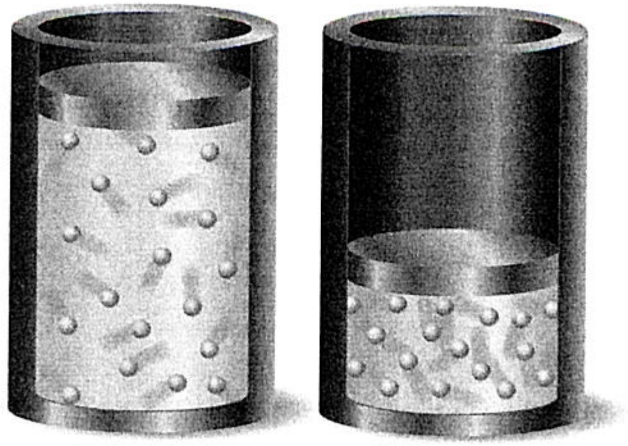


Figure 10.9 Gases behave more ideally at low pressure than at high pressure. The combined volume of the molecules can be neglected at low pressure but not at high pressure.

A real gas does not behave ideally at low temperature, especially near its condensation point, because its nonzero attractive forces are significant at low kinetic energy. Eventually, as the temperature (average kinetic energy) drops, attractive forces cause the gas to condense to a liquid.

Deviations from ideal behavior for gases generally increase with increasing molecular complexity and increasing mass. Mass is directly related to molecular volume, and molecular complexity is associated with both volume and attractive forces.

Figure 10.10 shows the deviations from ideal behavior of four real gases at various pressures. Notice that at low pressures the deviations are negative and at high pressures they are positive.

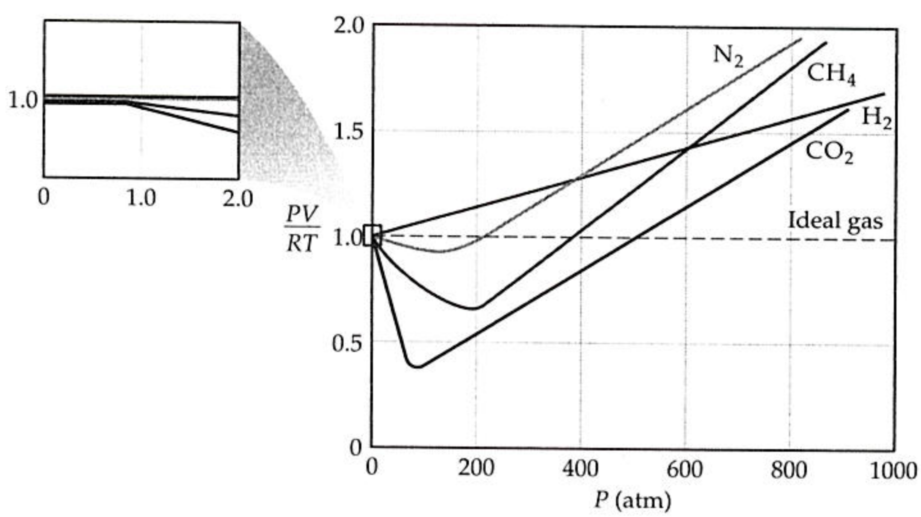


Figure 10.10 The effect of pressure on the behavior of several real gases. Data for 1 mol of gas in all cases. Data for N_2, CH_4, and H_2 are at 300 K; for CO_2 data are at 313 K because under high pressure CO_2 liquefies at 300 K.

Your Turn 10.5

Which of the noble gases deviate the most from ideal behavior? Explain your reasoning. Write your answer in the space provided.

Your Turn 10.6

Arrange the following gases in order of increasing deviation from ideality: H_2O, CH_4, Ne. Justify your answer. Write your answer in the space provided.

Table 10.2 summarizes the important gas laws.

Table 10.2 Summary of the gas laws and their equations.

Gas Law	Statement	What Is Constant	Equation
Boyle's law	The volume of a fixed quantity of gas at constant temperature is inversely proportional to the pressure	n, T	$P_1V_1 = P_2V_2$
Charles's law	The volume of a fixed amount of gas at constant pressure is directly proportional to the absolute temperature	n, P	$V_1/T_1 = V_2/T_2$
Un-named law	The pressure of a fixed quantity of gas at constant volume is directly proportional to the absolute temperature	n, V	$P_1/T_1 = P_2/T_2$
Avogadro's law	The volume of a gas at constant temperature and pressure is directly proportional to the number of moles	T, P	$V_1/n_1 = V_2/n_2$
Ideal-gas law	Combines the above laws into one equation	$R = 0.0821$ L-atm/mol-K	$PV = nRT$
Dalton's law of partial pressures	The total pressure of a mixture of gases equals the sum of the partial pressure of each component		$P_t = P_1 + P_2 + P_3 + \cdots$

Multiple Choice Questions

1. *Hydrogen peroxide, H_2O_2, in the presence of a catalyst decomposes into water and oxygen gas. How many liters of O_2 at STP are produced from the decomposition of 34.0 g of H_2O_2?*

   A) 1.00

   B) 5.60

   C) 11.2

   D) 22.4

   E) 44.8

2. *A mixture of 6.02×10^{23} molecules of $NH_3(g)$ and 3.01×10^{23} molecules of $H_2O(g)$ has a total pressure of 6.00 atm. What is the partial pressure of NH_3?*

   A) 1.00 atm

   B) 2.00 atm

   C) 3.00 atm

   D) 4.00 atm

   E) 9.00 atm

   Questions 3–5 apply to these gases at 0°C and 1 atm:

   A) H_2

   B) He

   C) N_2

   D) Kr

   E) Rn

3. *Which gas deviates the most from ideality?*

4. *Which gas has a density of 3.74 g/L?*

5. *Which gas has the highest average molecular speed?*

6. *Which increases as a gas is heated at constant volume?*

   I. Pressure
   II. Kinetic energy of molecules
   III. Attractive forces between molecules

   A) I only

   B) II only

   C) III only

   D) I and II only

   E) II and III only

7. *At room temperature and 1 atm pressure, the molecules are farthest apart in*

   A) *fluorine.*

   B) *bromine.*

   C) *iodine.*

   D) *mercury.*

   D) *water.*

8. *What is the name of the process?* $H_2O(s) \rightarrow H_2O(g)$

   A) *condensation*

   B) *evaporation*

   C) *fusion*

   D) *sublimation*

   E) *freezing*

9. *Which statement is true of a measured pressure of a sample of hydrogen gas collected over water at constant temperature?*

   A) *The measured pressure is greater than the pressure of dry hydrogen.*

   B) *The measured pressure is less than the pressure of dry hydrogen.*

   C) *The measured pressure is equal to the pressure of dry hydrogen.*

   D) *The measured pressure varies inversely with the pressure of dry hydrogen.*

   E) *The measured pressure is not related to the pressure of dry hydrogen.*

10. *In which instance is a gas most likely to behave as an ideal gas?*

   A) *At low temperature, because the particles have insufficient kinetic energy to overcome intermolecular attractions.*

   B) *When the molecules are highly polar, because intermolecular forces are more likely.*

   C) *At room temperature and pressure, because intermolecular interactions are minimized and the particles are relatively far apart.*

   D) *At high pressures, because the distance between molecules is likely to be small in relation to the size of the molecules.*

   E) *At low temperatures, because the molecules are always far apart.*

11. Methanol, CH_3OH, burns in oxygen to form carbon dioxide and water. What volume of oxygen is required to burn 6.00 L of gaseous methanol measured at the same temperature and pressure?

A) 4.00 L

B) 8.00 L

C) 9.00 L

D) 12.0 L

E) 24.0 L

Free Response Questions

1. Equal masses (0.500 g each) of hydrogen and oxygen are placed in an evacuated 4.00 L flask at 25.0 °C. The mixture is allowed to react to completion and the flask is returned to 25.0 °C and allowed to come to equilibrium. The equilibrium vapor pressure of water at 25 °C is 23.76 torr.

a. Write and balance a chemical equation for the reaction.

b. What is the total pressure inside the flask before the reaction begins?

c. What is the mass of water vapor in the flask at equilibrium?

d. How many grams of which reactant gas remains at equilibrium?

e. What is the total pressure inside the flask at equilibrium?

f. After the reaction, is there any liquid water present? If so, how many grams? If not, why not?

2. A 2.00 L flask at 27 °C contains 3.00 g each of Ar(g), $SO_2(g)$, and He(g). Answer the following questions about the gases, and in each case, explain your reasoning.

a. Which gas has particles with the highest average kinetic energy?

b. Which gas has particles with the highest average velocity?

c. Which gas has the highest partial pressure?

d. Which gas will deviate the most from ideal behavior?

e. Which substance will have the highest boiling point?

f. What changes in temperature and pressure will increase the deviations of all the gases from ideal behavior?