Chapter 12 THE BEHAVIOR OF GASES

A hot-air balloon rises when air inside the balloon is heated.

FEATURES

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DISCOVER IT! OBSERVING VOLUME CHANGES

You need a spherical balloon, a marking pen, a tape measure, a freezer, and a sunny window.

1. Inflate the balloon and tie it closed. Use the marking pen to draw a line around the middle of the balloon. This is the circumference of the balloon.
2. Place the balloon in the freezer for half an hour. Remove it and quickly measure and record the circumference of the balloon in centimeters.
3. Place the balloon in a sunny window for half an hour. Measure and record the circumference of the balloon in centimeters.
4. Assume the balloon is a perfect sphere and calculate the volume for each circumference recorded. Use the following formula:

$$Volume = \frac{4\pi r^3}{3}$$

$$\text{Note that } r = \frac{\text{circumference}}{2\pi}$$

What do you observe about the volume of the balloon at the two temperatures? Use your results to suggest a relationship between temperature and volume when pressure remains constant. Refer back to your suggested relationship when you read about Charles's law later in this chapter.

THE PROPERTIES OF GASES

section 12.1

You have probably seen huge, colorful, helium-filled balloons like this one in holiday parades. But what's wrong with Bullwinkle? As you can see, Bullwinkle isn't looking too good—he is deflating. The balloon is leaking helium and is beginning to sag and list. Soon Bullwinkle may collapse altogether. **How does kinetic theory explain why losing helium causes the balloon to sag and collapse?**

objectives

- Describe the properties of gas particles
- Explain how the kinetic energy of gas particles relates to Kelvin temperature

key terms

- compressibility

Kinetic Theory Revisited

This chapter discusses the ways in which simple kinetic molecular theory is used to explain gas behavior. You may have already observed some everyday examples of gas behavior. For example, you may have noticed that a sealed bag of potato chips bulges at its seams when placed in a sunny window. The air inside the bag exerts greater pressure as its temperature increases. Why does this happen? Kinetic theory can explain this and other gas behavior.

Recall from Chapter 10 that the kinetic theory of gases makes several basic assumptions. It assumes that gases consist of hard, spherical particles that have the following properties. First, the gas particles are so small in relation to the distances between them that their individual volumes can be assumed to be insignificant. The large relative distances between the gas particles means that there is considerable empty space between the particles. This assumption that gas particles are far apart explains the important property of gas compressibility. **Compressibility** is a measure of how much the volume of matter decreases under pressure. Gases, unlike solids or liquids, are easily compressed because of the space between the particles. Because gases are compressible, they are used in automobile airbags and other safety devices designed to absorb the energy of an impact. The energy of a collision is absorbed when the gas particles are forced closer together. As seen in **Figure 12.1**, gases can be used to absorb a considerable amount of energy.

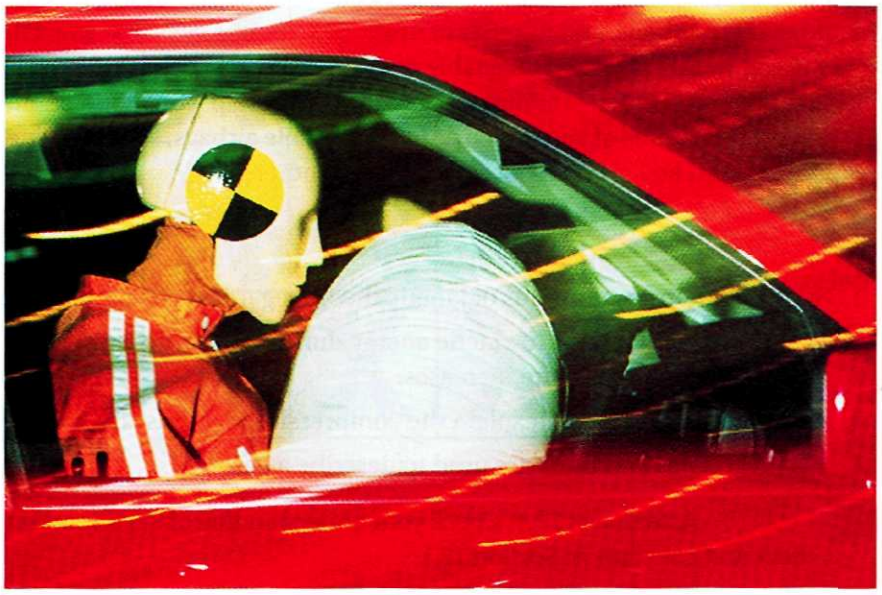


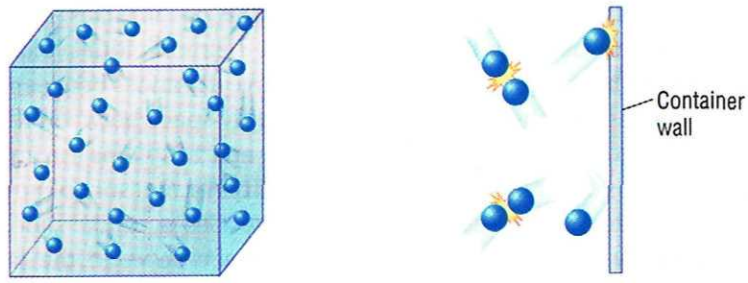
Figure 12.1
An air bag cushions the impact of this crash dummy. How will the compressibility of gases protect the dummy from being broken?

Figure 12.2
According to kinetic theory, the particles of air in this balloon are not affected by attractive or repulsive forces. As a result, the air expands to fill the interior of the balloon evenly.

The second property of gas particles assumed by the kinetic theory is that no attractive or repulsive forces exist between the particles. As a result, gases are free to move inside their containers. In fact, a gas expands until it takes the shape and volume of its container.

The third assumption is that gas particles move rapidly in constant random motion. The particles travel in straight paths and move independently of each other. As you can see in **Figure 12.3,** only when a particle collides with another particle or object does it deviate from its straight-line path. Kinetic theory assumes further that these collisions between gas particles are perfectly elastic, which means that during a collision the total amount of kinetic energy remains constant and that the kinetic energy is transferred without loss from one particle to another. You should also recall that the average kinetic energy of a collection of gas particles is directly proportional to the Kelvin temperature of the gas.

Figure 12.3
Notice the random motion of the gas particles. Changes in direction occur only when particles collide with each other or with another object.



Gas particles in constant random motion

Detailed look at gas particles colliding

Variables That Describe a Gas

Four variables are generally used to describe a gas. The variables and their common units are pressure (P) in kilopascals, volume (V) in liters, temperature (T) in kelvins, and number of moles (n). The gas laws that you will learn about in this chapter will enable you to predict gas behavior at specific conditions. Understanding the gas laws will help you understand everyday applications of gases such as in automobile airbags, scuba-diving equipment, and hot-air balloons, among many others.

section review 12.1

1. State the main assumptions of kinetic theory regarding gas particles.
2. Describe what happens to kinetic energy during gas particle collisions and as Kelvin temperature increases.
3. How does kinetic theory explain the compressibility of gases?
4. What variables and units are used to describe a gas?

Chem ASAP! Assessment 12.1 Check your understanding of the important ideas and concepts in Section 12.1.

SMALL-SCALE LAB

REACTIONS OF ACIDS WITH CARBONATES

SAFETY

Wear safety glasses and follow the standard safety procedures outlined on page 18.

PURPOSE

To observe and identify the reactions of carbonates that produce carbon dioxide gas.

MATERIALS

- pencil
- paper
- ruler
- reaction surface
- chemicals shown in Figure A

PROCEDURE

On separate sheets of paper, draw two grids similar to Figure A. Make each square 2 cm on each side. Place a reaction surface over one of the grids and add the chemicals as shown in Figure A. Use the second grid as a data table to record your observations for each reaction.

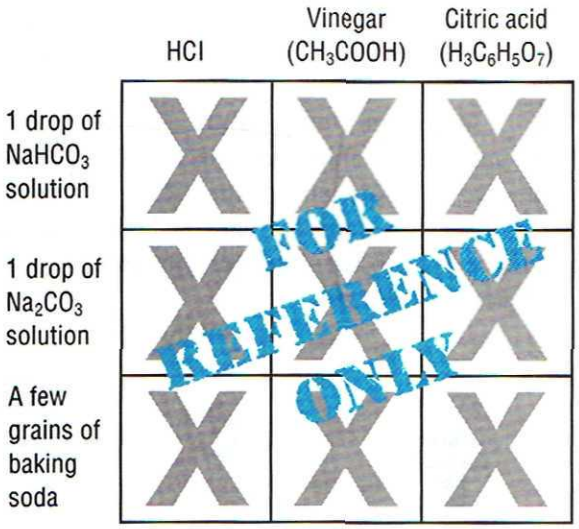


Figure A

ANALYSIS

Using your experimental data, record the answers to the following questions below your data table.

1. What common observation can you make for each of the mixings?
2. Write the name and formula of the gas produced in each reaction. Identify one other product formed in all of the reactions.
3. Hydrochloric acid reacts with sodium hydrogen carbonate to yield carbon dioxide, water, and sodium chloride. Convert this word equation into a chemical equation.
4. Write complete chemical equations for the reactions you observed in this experiment.

YOU'RE THE CHEMIST

The following small-scale activities allow you to develop your own procedures and analyze the results.

1. **Analyze It!** Add some HCl to $NaHCO_3$ and then add some HCl to Na_2CO_3. What do you observe? Is it possible to use HCl to distinguish between $NaHCO_3$ and Na_2CO_3? Explain.
2. **Analyze It!** Add some $FeCl_3$ to $NaHCO_3$ and then add some $FeCl_3$ to Na_2CO_3. Look carefully. What do you observe? Is it possible to use $FeCl_3$ to distinguish between $NaHCO_3$ and Na_2CO_3? Explain.
3. **Design It!** Most laundry detergents contain carbonates such as $NaHCO_3$ and Na_2CO_3. Design and carry out an experiment to determine which laundry detergents contain carbonate in some form. Using your method, is it possible to tell exactly which carbonate a detergent contains? Explain.
4. **Design It!** Experiment with chalk, antacid tablets, seashells, limestone, and marble to determine if they contain carbonates. How can you tell?
5. **Design It!** Experiment with powdered soft drink mixes to see if they contain citric acid. Record your results.

section 12.2

FACTORS AFFECTING GAS PRESSURE

objectives

- Explain how the amount of gas and the volume of the container affect gas pressure
- Infer the effect of temperature changes on the pressure exerted by a contained gas

Your raft blasts through a narrow opening between rocks and plummets over a short fall into the churning whitewater below. The raft bends and twists, absorbing some of the pounding energy of the river. The strength and flexibility of the raft are impressive. **What factors affect the gas pressure inside the raft and its resulting rigidity?**

Amount of Gas

Using the kinetic theory, you can predict and explain how gases will respond to a change of conditions. When you pump up a tire, for example, you should expect the pressure inside it to increase. See **Figure 12.4.** Collisions of gas particles with the inside walls of the tire result in the pressure that is exerted by the enclosed gas. By adding gas, you increase the number of gas particles, thus increasing the number of collisions, which explains why the gas pressure increases.

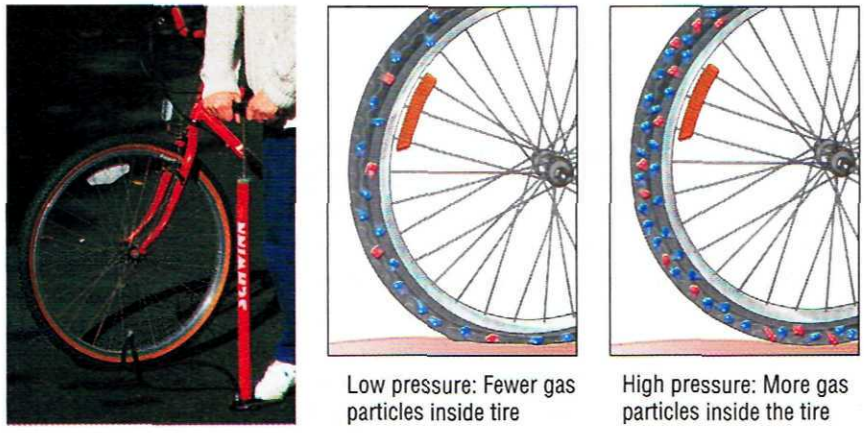


Figure 12.4
Using a pump to force more air particles into a partially deflated bicycle tire increases the pressure inside the tire.

Now look at **Figure 12.5.** As long as gas temperature does not change, doubling the number of gas particles doubles the pressure. Tripling the number of gas particles triples the pressure, and so forth. With a powerful pump and a strong container, you can generate very high pressures by adding more and more gas. Once the pressure exceeds the strength of the container, however, the container will rupture.

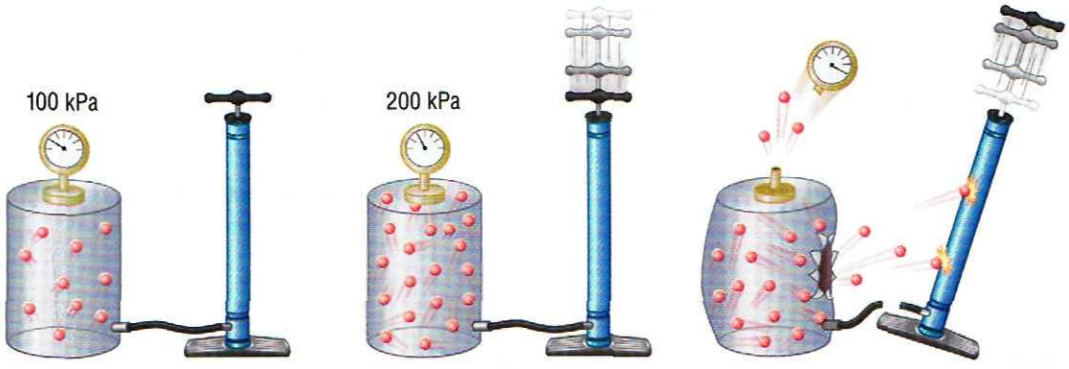


Figure 12.5
When a gas is pumped into a closed rigid container, the pressure increases in proportion to the number of gas particles added. If the number of gas particles doubles, the pressure doubles.

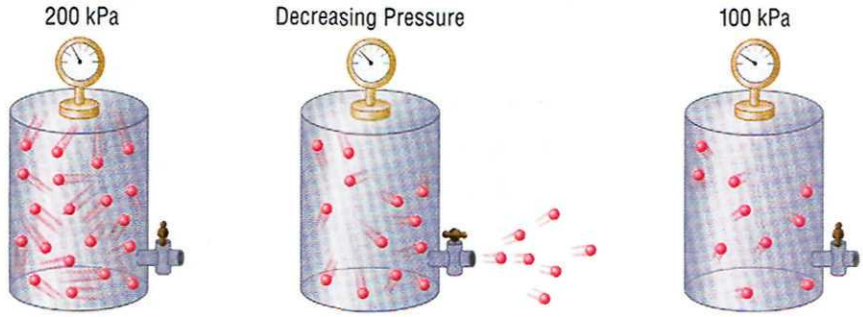


Figure 12.6
Gas pressure inside this constant-volume container decreases as gas particles escape. The gas at 100 kPa has exactly half the number of particles as the gas at 200 kPa.

In a similar way, letting the air out of a tire decreases the pressure inside the tire. The fewer particles inside exert less pressure. As you can see by looking at **Figure 12.6,** halving the number of gas particles in a given volume decreases the pressure by half.

When a sealed container of gas under pressure is opened, gas inside moves from the region of higher pressure to the region of lower pressure outside. This is the principle used in aerosol cans. You have probably used many aerosol products, from whipped cream, to hair spray and mousse, to the spray paint shown in **Figure 12.7.** The can of spray paint contains a gas at high pressure that acts as the propellant. The air outside the can is at a lower pressure. Pushing the spray button creates an opening between the inside of the can and the air outside. The high-pressure propellant gas flows to the lower pressure region outside, forcing paint out with it. As the propellant gas is depleted, the pressure inside the aerosol can decreases.

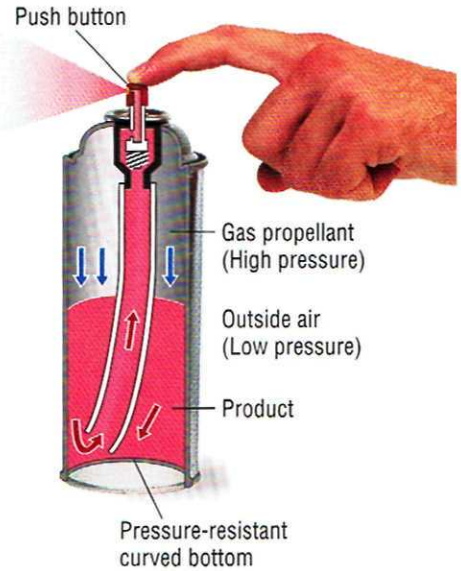


Figure 12.7
The difference in pressure between the inside of the spray can and the air outside allows aerosol sprays to work. What is the pressure inside the can when the aerosol will no longer spray?

Volume

There are other ways to increase gas pressure. For example, you can raise the pressure exerted by a contained gas by reducing its volume. The more the gas is compressed, the greater is the pressure it exerts inside the container. Reducing the volume of a contained gas by half doubles the pressure, as **Figure 12.8** demonstrates. Increasing the volume of the contained gas has just the opposite effect. By doubling the volume, you halve the gas pressure because the same number of gas particles occupy a volume twice the original size.

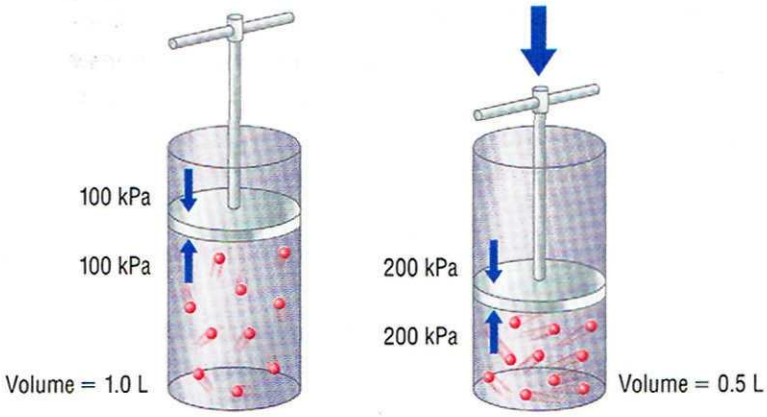


Figure 12.8
A piston, such as those used in engines, forces a gas in a cylinder to reduce in volume. A decrease in volume by half doubles the pressure the gas exerts.

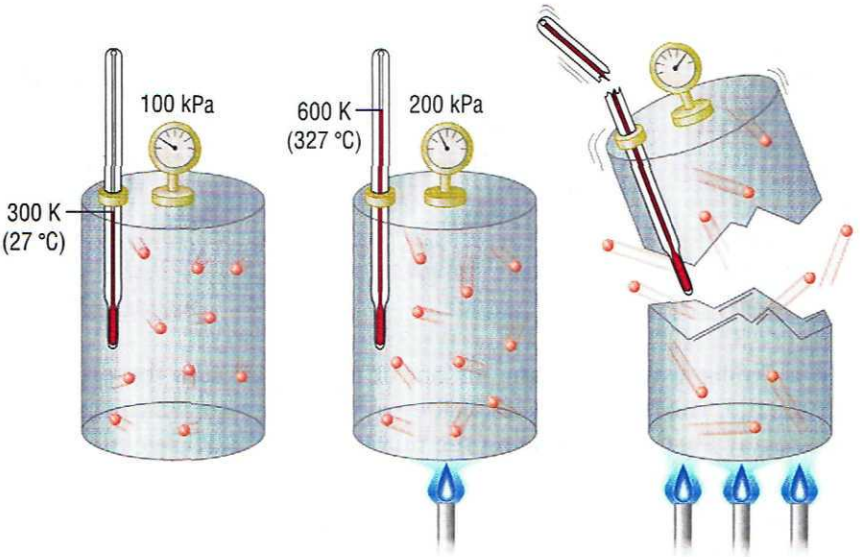


Figure 12.9
When a gas in a container is heated from 300 K (27 °C) to 600 K (327 °C), the kinetic energy of the gas particles doubles. The doubling of the kinetic energy results in a doubling of the pressure exerted by the gas. Pressure buildup due to high temperatures may cause the container to explode.

Temperature

Raising the temperature of an enclosed gas provides yet another way to increase gas pressure. (Remember the potato chip bag mentioned in Section 12.1.) The speed and kinetic energy of gas particles increase as the particles absorb thermal energy. The faster-moving particles impact the walls of their container with more energy, exerting greater pressure, as shown in **Figure 12.9.** If the average kinetic energy of a gas doubles, the Kelvin temperature doubles and the pressure of the enclosed gas also doubles. A gas in a sealed container may thus generate enormous pressure when heated. For that reason, an aerosol can, even an empty one, carelessly thrown onto a fire is an explosion hazard.

By contrast, as the temperature of an enclosed gas decreases, the particles move more slowly and have less kinetic energy. They strike the container walls with less force. Halving the Kelvin temperature of a gas in a rigid container decreases the gas pressure by half.

section review 12.2

5. What effects do changes in the amount of gas and in the volume of the container have on gas pressure?
6. What is the effect of temperature change on the pressure of a contained gas?
7. What would you have to do to the volume of a gas to reduce its pressure to one-quarter of the original value, assuming that the gas is at a constant temperature?
8. Keeping temperature constant, how could you increase the pressure in a container by one hundredfold?
9. The manufacturer of an aerosol deodorant packaged in a 150-mL container wishes to produce a container of the same size that will hold twice as much gas. How will the pressure of the gas in the new product compare with that of the gas in the original container?

portfolio project

Contact local tire stores or car dealers to find out what factors determine recommended tire pressure. Find out how and under what conditions to use a tire gauge. What are the typical units of pressure for a tire gauge? What can happen if tires are not properly inflated?

Chem ASAP! Assessment 12.2 Check your understanding of the important ideas and concepts in Section 12.2.

THE GAS LAWS

section 12.3

Because warm air is less dense than cooler air, the pilot of a hot-air balloon heats the air inside the balloon to make it rise. To make it fall, the pilot releases the heated air from the top of the balloon. **What is the effect of adding heat to a gas at constant pressure? What law describes this relationship?**

objectives

- State Boyle's law, Charles's law, Gay-Lussac's law, and the combined gas law
- Apply the gas laws to problems involving the temperature, volume, and pressure of a contained gas

key terms

- Boyle's law
- Charles's law
- Gay-Lussac's law
- combined gas law

The Pressure–Volume Relationship: Boyle's Law

Consider the effect of pressure on the volume of a contained gas while the temperature remains constant. When the pressure goes up, the volume goes down. Similarly, when the pressure goes down, the volume goes up. The first person to do a systematic quantitative study of this pressure–volume relationship was the Anglo-Irish chemist Robert Boyle (1627–1691). In 1662, Boyle proposed a law to describe this behavior of gases. **Boyle's law** states that for a given mass of gas at constant temperature, the volume of the gas varies inversely with pressure. In an inverse relationship, the product of the two variable quantities is constant.

Look at **Figure 12.10.** In the figure, a volume of 1.0 L (V_1) is at a pressure of 100 kPa (P_1). If you increase the volume to 2.0 L (V_2), the pressure decreases to 50 kPa (P_2). Observe that the product $P_1 \times V_1$ (100 kPa × 1.0 L = 100 kPa × L) is the same as the product $P_2 \times V_2$ (50 kPa × 2.0 L = 100 kPa × L). If you decrease the volume to 0.5 L, the gas pressure increases to 200 kPa. Again, the product of pressure times volume equals 100 kPa × L.

The product of pressure and volume at any two sets of conditions is always constant at a given temperature. The mathematical expression of Boyle's law is as follows:

$$P_1 \times V_1 = P_2 \times V_2$$

When you graph an inverse relationship, such as this one, the result is a curve, as shown in **Figure 12.10.**

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Simulation 9

Examine the relationship between gas volume and pressure.

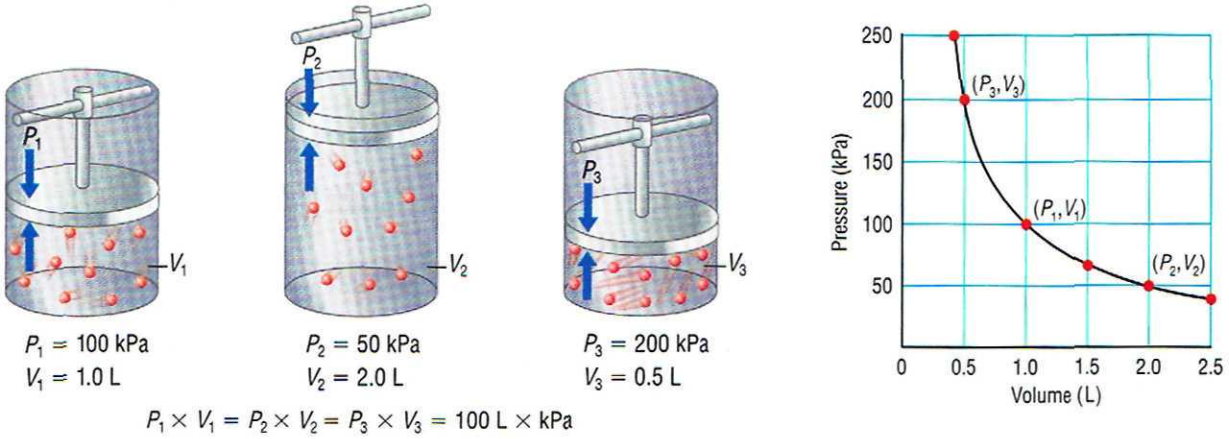

Figure 12.10

Boyle's law is studied by using a cylindrical container fitted with a frictionless, weightless piston. When the volume of a gas at constant temperature increases from V_1 to V_2, the pressure decreases from P_1 to P_2. When the volume decreases (to V_3), the pressure increases (to P_3). The graph illustrates Boyle's law. At any point on this curve, the product $P \times V$ of pressure (P) and volume (V) is a constant.

CHEMath

SOLVING EQUATIONS

Knowing which equation to use is the key first step in solving many problems. However, you must also master the skill of solving the equation for the unknown variable.

To solve an equation for one of its variables, isolate that variable on one side of the equal sign. In other words, the other variables and numbers in the equation must be on the other side of the equal sign.

For example, you are probably familiar with the equation for the area of a rectangle:

Area = base × height, or $A = bh$

As written, the equation solves for area (A). Notice that the variable A is on one side of the equal sign, while all of the other variables are on the other side of the equal sign. Variable A is therefore isolated.

If the variable you need to solve for is not already isolated, you will use addition, subtraction, multiplication, and division to isolate it. The key to the process is remembering that whatever you do on one side of the equation to isolate the variable, you must also do on the other side.

Example 1

Solve the equation $A = bh$ *for the variable* b.

You must isolate the variable b. Because b is multiplied by h, divide both sides of the equation by h.

$$\frac{A}{h} = \frac{bh}{h}$$

Canceling terms, $\frac{A}{h} = \frac{b\cancel{h}}{\cancel{h}}$ yields $\frac{A}{h} = b$. Thus $b = \frac{A}{h}$.

Example 2

This example involves one of the equations you will learn and use in this chapter.

Solve the equation $P_1 \times V_1 = P_2 \times V_2$ for the variable P_1.

$$P_1 \times V_1 = P_2 \times V_2$$

You must isolate the variable P_1. Because P_1 is multiplied by V_1, divide both sides by V_1.

$$\frac{P_1 \times V_1}{V_1} = \frac{P_2 \times V_2}{V_1}$$

Canceling terms, $\frac{P_1 \times \cancel{V_1}}{\cancel{V_1}} = \frac{P_2 \times V_2}{V_1}$ yields $P_1 = \frac{P_2 \times V_2}{V_1}$.

Practice Problems

Prepare for upcoming problems in this chapter by solving the following equations for the variable indicated.

A. Solve $P_1 \times V_1 = P_2 \times V_2$ for V_2.

B. Solve $\frac{V_1}{T_1} = \frac{V_2}{T_2}$ for T_2.

C. Solve $P_{total} = P_1 + P_2 + P_3$ for P_2.

D. Solve $\frac{P_1 \times V_1}{T_1} = \frac{P_2 \times V_2}{T_2}$ for T_1.

E. Solve $P \times V = n \times R \times T$ for T.

F. Solve $\frac{\text{Rate}_A}{\text{Rate}_B} = \frac{\sqrt{\text{molar mass}_B}}{\sqrt{\text{molar mass}_A}}$ for molar mass_B.

Sample Problem 12-1

A high-altitude balloon contains 30.0 L of helium gas at 103 kPa. *What is the volume when the balloon rises to an altitude where the* pressure is only 25.0 kPa? (Assume that the temperature remains constant.)

1. **ANALYZE** ***List the knowns and the unknown.***

Knowns:
- $P_1 = 103$ kPa
- $V_1 = 30.0$ L
- $P_2 = 25.0$ kPa

Unknown:
- $V_2 = ?$ L

Use the known values and Boyle's law ($P_1 \times V_1 = P_2 \times V_2$) to calculate the unknown value (V_2).

2. **CALCULATE** ***Solve for the unknown.***

Rearrange the expression for Boyle's law to isolate V_2.

$$V_2 = \frac{V_1 \times P_1}{P_2}$$

Substitute the known values for P_1, V_1, and P_2 into the equation and solve.

$$V_2 = \frac{30.0\ \text{L} \times 103\ \text{kPa}}{25.0\ \text{kPa}}$$

$$= 1.24 \times 10^2\ \text{L}$$

3. **EVALUATE** ***Does the result make sense?***

Using kinetic theory, a decrease in pressure at constant temperature must correspond to a proportional increase in volume. The calculated result agrees with both the kinetic theory and the pressure–temperature relationship. Also, the units have canceled correctly and the answer is expressed to the proper number of significant figures.

Practice Problems

10. The pressure on 2.50 L of anesthetic gas changes from 105 kPa to 40.5 kPa. What will be the new volume if the temperature remains constant?
11. A gas with a volume of 4.00 L at a pressure of 205 kPa is allowed to expand to a volume of 12.0 L. What is the pressure in the container if the temperature remains constant?

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Problem-Solving 11

Solve Problem 11 with the help of an interactive guided tutorial.

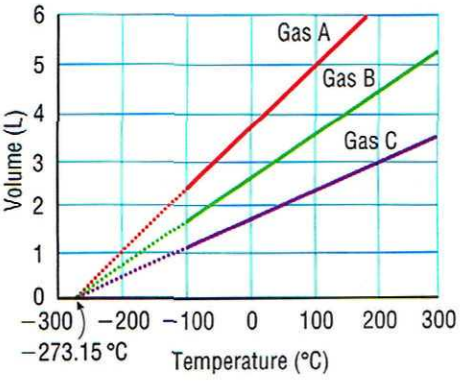
The Temperature–Volume Relationship: Charles's Law

In 1787, the French physicist and balloonist Jacques Charles (1746–1823) investigated the quantitative effect of temperature on the volume of a gas at constant pressure. In every experiment, he observed an increase in the volume of a gas with an increase in temperature, and a decrease in volume with a decrease in temperature. In practice, the temperature–volume relationship for any gas can be measured only over a limited range because at low temperatures gases condense to form liquids.

From his quantitative studies, Charles observed that at constant pressure the graph of gas volume versus temperature yields a straight line. **Figure 12.11** shows such a graph for three different gas samples in balloons. In addition to the straight lines, another important feature emerged. The lines extended (extrapolated) to zero volume ($V = 0$) all intersect the temperature axis at the same point, −273.15 °C.

Figure 12.11

This graph shows the direct relationship between volume and temperature for three different gas samples in balloons at constant pressure. What is the significance of the temperature −273.15 °C?



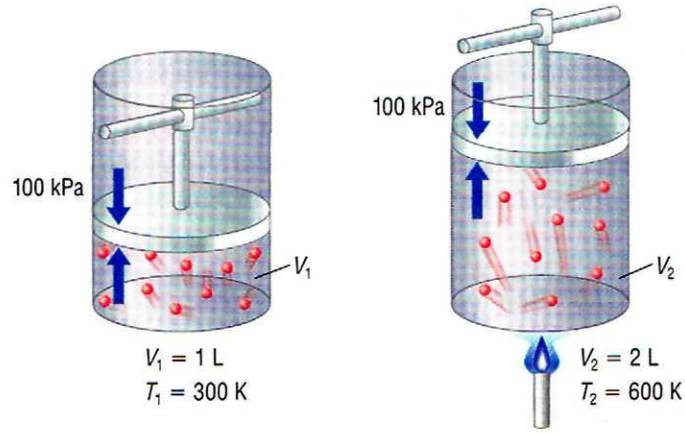


Figure 12.12
This apparatus illustrates Charles's law. When a gas is heated at constant pressure, the volume increases. When a gas is cooled at constant pressure, the volume decreases.

$$\frac{V_1}{T_1} = \frac{V_2}{T_2} = 0.00333 \text{ L/K}$$

William Thomson (Lord Kelvin) realized the significance of this temperature value. He identified this value as absolute zero, the lowest possible temperature. It is the temperature at which the average kinetic energy of gas particles would theoretically be zero. This was the basis for the absolute temperature scale established by Kelvin in 1848. This scale is now called the Kelvin temperature scale. On the Kelvin temperature scale, 0 K corresponds to −273.15 °C. Throughout this textbook, absolute zero expressed in degrees Celsius is rounded to −273. What is 0 °C in kelvins?

Charles's law summarizes Charles's observations and the findings of Kelvin. **Charles's law** states that the volume of a fixed mass of gas is directly proportional to its Kelvin temperature if the pressure is kept constant. In a direct relationship, such as this one, the ratio of the two quantities that change is a constant. In **Figure 12.12**, for example, a 1-L sample of gas (V_1) is at a temperature of 300 K (T_1). (Note that when solving gas-law problems, the temperature must always be expressed in kelvins.) When the temperature is increased to 600 K (T_2), the volume increases to 2 L (V_2). The ratio V_1/T_1 is equal to the ratio V_2/T_2. Moreover, at constant pressure, the ratio of volume to Kelvin temperature for a gas sample at any two sets of conditions is constant. Thus you can write Charles's law as follows:

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

The graph of a relationship such as Charles's law that is a direct proportion is a straight line. **Figure 12.13** provides a detailed look at the Charles's law relationship.

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Simulation 10
Examine the relationship between gas volume and temperature.

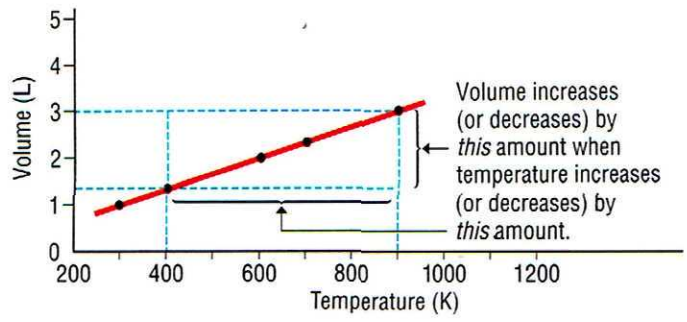

Figure 12.13
This graph illustrates Charles's law. At any point on this line, the ratio of volume (V) to temperature (T) is constant; in this case, V/T = 0.00333 L/K.

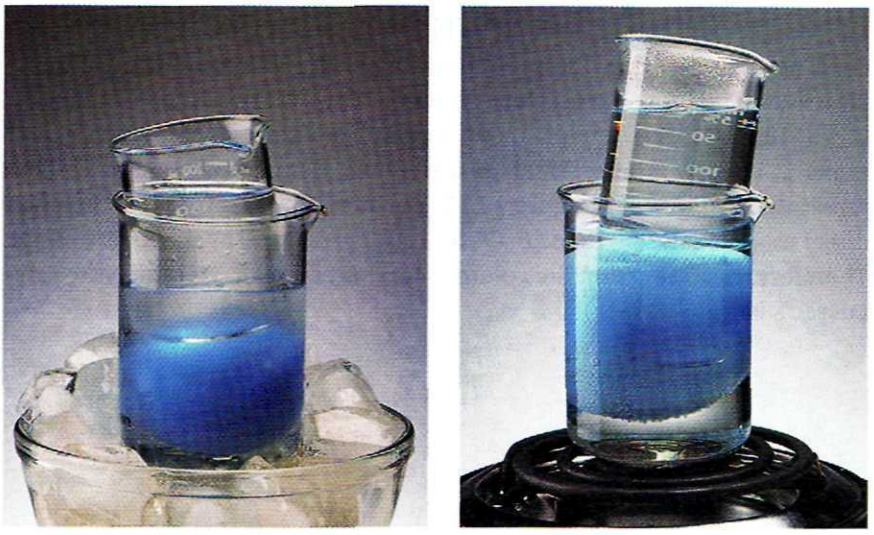

Figure 12.14
The volume of a balloon in a beaker of ice water is less than it is in a beaker of hot water. Why?

Sample Problem 12-2

A balloon inflated in a room at 24 °C has a volume of 4.00 L. The balloon is then heated to a temperature of 58 °C. What is the new volume if the pressure remains constant?

1. ANALYZE ***List the knowns and the unknown.***

Knowns:
- $V_1 = 4.00$ L
- $T_1 = 24$ °C
- $T_2 = 58$ °C

Unknown:
- $V_2 = ?$ L

Use the known values and Charles's law ($V_1/T_1 = V_2/T_2$) to calculate the unknown value (V_2).

2. CALCULATE ***Solve for the unknown.***

Because the gas laws will be applied, express the temperatures in kelvins.

$$T_1 = 24\ °C + 273 = 297\ K$$

$$T_2 = 58\ °C + 273 = 331\ K$$

Rearrange the expression for Charles's law to isolate V_2.

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

Substitute the known values for T_1, V_1, and T_2 into the equation and solve.

$$V_2 = \frac{4.00\ L \times 331\ \cancel{K}}{297\ \cancel{K}} = 4.46\ L$$

3. EVALUATE ***Does the result make sense?***

From kinetic theory, the volume should increase with an increase in temperature (at constant pressure). This result agrees with the kinetic theory and Charles's law. The volume does increase with increasing temperature.

Practice Problems

12. If a sample of gas occupies 6.80 L at 325 °C, what will be its volume at 25 °C if the pressure does not change?

13. Exactly 5.00 L of air at −50.0 °C is warmed to 100.0 °C. What is the new volume if the pressure remains constant?

Chem ASAP!

Problem-Solving 13

Solve Problem 13 with the help of an interactive guided tutorial.

The Temperature–Pressure Relationship: Gay-Lussac's Law

On a hot summer day, the pressure in a car tire increases. This increase illustrates a relationship that was discovered in 1802 by Joseph Gay-Lussac (1778–1850), a French chemist. **Gay-Lussac's law** states that the pressure of a gas is directly proportional to the Kelvin temperature if the volume remains constant. See **Figure 12.15.** Because Gay-Lussac's law involves direct proportions, the ratios P_1/T_1 and P_2/T_2 are equal at constant volume. Therefore, assuming that the volume remains constant, you can write Gay-Lussac's law as follows:

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

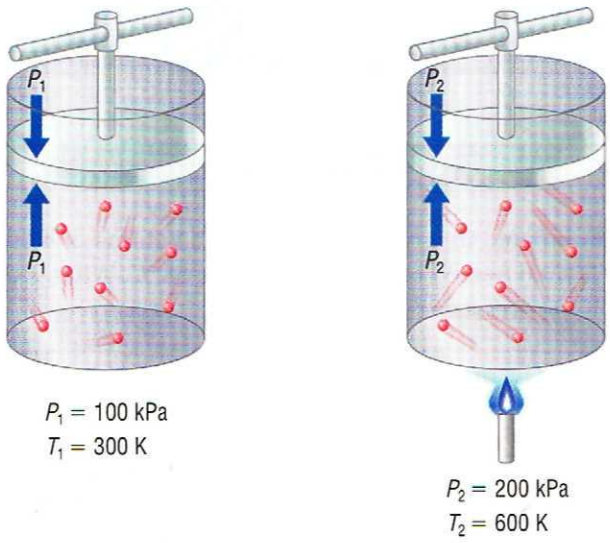

Figure 12.15
When a gas is heated at constant volume, the pressure increases. When a gas is cooled at constant volume, the pressure decreases.

Chem ASAP!

Simulation 11
Explore the relationship between gas temperature and pressure.

Sample Problem 12-3

The gas left in a used aerosol can is at a pressure of 103 kPa at 25 °C. If this can is thrown onto a fire, what is the pressure of the gas when its temperature reaches 928 °C? (Calculating the answer to this problem will show you why it is dangerous to dispose of aerosol cans in a fire. Most aerosol cans carry warnings on their labels that clearly say not to incinerate (burn) or to store above a certain temperature.)

1. ***ANALYZE*** ***List the knowns and the unknown.***

Knowns:
- $P_1 = 103$ kPa
- $T_1 = 25$ °C
- $T_2 = 928$ °C

Unknown:
- $P_2 = ?$ kPa

Use the known values and Gay-Lussac's law ($P_1/T_1 = P_2/T_2$) to calculate the unknown (P_2). Remember, because this problem involves temperatures and a gas law, the temperatures must be expressed in kelvins.

Practice Problems

14. A gas has a pressure of 6.58 kPa at 539 K. What will be the pressure at 211 K if the volume does not change?

Sample Problem 12-3 (cont.)

2. ***CALCULATE*** *Solve for the unknown.*
First convert degrees Celsius to kelvins.

$$T_1 = 25\ °C + 273 = 298\ K$$
$$T_2 = 928\ °C + 273 = 1201\ K$$

Rearrange Gay-Lussac's law to isolate P_2.

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

Substitute the known values for P_1, T_2, and T_1 into the equation and solve.

$$P_2 = \frac{103\ kPa \times 1201\ \cancel{K}}{298\ \cancel{K}} = 415\ kPa$$
$$= 4.15 \times 10^2\ kPa$$

3. ***EVALUATE*** *Does the result make sense?*
From the kinetic theory, one would expect the increase in temperature of a gas to produce an increase in pressure if the volume remains constant. The calculated value does show such an increase.

Practice Problems (cont.)

15. The pressure in an automobile tire is 198 kPa at 27 °C. At the end of a trip on a hot sunny day, the pressure has risen to 225 kPa. What is the temperature of the air in the tire? (Assume that the volume has not changed.)

Chem ASAP!

Problem-Solving 15
Solve Problem 15 with the help of an interactive guided tutorial.

The Combined Gas Law

If you have been wondering how to remember the individual expressions for the gas laws, there is really no need. A single expression, called the **combined gas law,** combines the three gas laws, as follows:

$$\frac{P_1 \times V_1}{T_1} = \frac{P_2 \times V_2}{T_2}$$

The other laws can be obtained from this law by holding one quantity (pressure, volume, or temperature) constant.

To illustrate, suppose you hold temperature constant ($T_1 = T_2$). Rearrange the combined gas law to get the two temperature terms on the same side of the equation and then cancel.

$$P_1 \times V_1 = \frac{P_2 \times V_2 \times \cancel{T_1}}{\cancel{T_2}}$$
$$P_1 \times V_1 = P_2 \times V_2$$

As you can see, you are left with Boyle's law. The same kind of process yields Charles's law when pressure remains constant and Gay-Lussac's law when volume remains constant.

In addition to providing a useful way of recalling the three previous gas laws, the combined gas law also enables you to do calculations for situations in which none of the variables are constant. In Sample Problem 12-4, on the following page, you will see how to use the combined gas law to calculate the new volume of a gas that results from changing both the pressure and the temperature.

Sample Problem 12-4

The volume of a gas-filled balloon is 30.0 L at 40 °C and 153 kPa pressure. What volume will the balloon have at standard temperature and pressure (STP)?

1. ***ANALYZE*** ***List the knowns and the unknown.***

Knowns:
- $V_1 = 30.0$ L
- $T_1 = 40$ °C
- $T_2 = 273$ K (standard temperature)
- $P_1 = 153$ kPa
- $P_2 = 101.3$ kPa (standard pressure)

Unknown:
- $V_2 = ?$ L

Use the known values and the combined gas law to calculate the unknown (V_2).

2. ***CALCULATE*** ***Solve for the unknown.***

Convert degrees Celsius to kelvins.

$$T_1 = 40\ °C + 273 = 313\ K$$

Rearrange the combined gas law to isolate V_2.

$$V_2 = \frac{V_1 \times P_1 \times T_2}{P_2 \times T_1}$$

Substitute the known quantities into the equation and solve.

$$V_2 = \frac{30.0\ L \times 153\ \cancel{kPa} \times 273\ \cancel{K}}{101.3\ \cancel{kPa} \times 313\ \cancel{K}} = 39.5\ L$$

3. ***EVALUATE*** ***Does the result make sense?***

The temperature decreases; therefore, the temperature ratio is less than 1 (273 K/313 K). The pressure decreases, so the pressure ratio is greater than 1 (153 kPa/101.3 kPa). Recalculate by multiplying the initial volume of gas by these two ratios.

$$V_2 = 30.0\ L \times \frac{153\ \cancel{kPa}}{101.3\ \cancel{kPa}} \times \frac{273\ \cancel{K}}{313\ \cancel{K}} = 39.5\ L$$

The result is the same.

Practice Problems

16. A gas at 155 kPa and 25 °C occupies a container with an initial volume of 1.00 L. By changing the volume, the pressure of the gas increases to 605 kPa as the temperature is raised to 125 °C. What is the new volume?

17. A 5.00-L air sample at a temperature of −50 °C has a pressure of 107 kPa. What will be the new pressure if the temperature is raised to 102 °C and the volume expands to 7.00 L?

Chem ASAP!

Problem-Solving 17

Solve Problem 17 with the help of an interactive guided tutorial.

section review 12.3

18. State Boyle's law, Charles's law, and Gay-Lussac's law.

19. Briefly explain how the combined gas law can be reduced to the other three gas laws.

20. Write the mathematical equation for Boyle's law and explain the symbols. What must be true about the temperature?

21. A given mass of air has a volume of 6.00 L at 101 kPa. What volume will it occupy at 25.0 kPa if the temperature does not change?

Chem ASAP! **Assessment 12.3** Check your understanding of the important ideas and concepts in Section 12.3.

IDEAL GASES

section 12.4

Ideal or Real?

What if someone told you that all of the gas laws you just learned were wrong! In some ways, the person would be correct. The gas laws assume that gases behave in an ideal way, obeying the assumptions of kinetic theory. As it turns out, gases do not behave exactly this way. **What then is an ideal gas, and under what conditions do the gas laws apply?**

objectives

- Calculate the amount of gas at any specified conditions of pressure, volume, and temperature
- Distinguish between ideal and real gases

key terms

- ideal gas constant (R)
- ideal gas law

Ideal Gas Law

Up to this point in this textbook, you have worked with three variables regarding gas behavior: pressure, volume, and temperature. There is a fourth variable still to be considered: the amount of gas in the system, expressed in terms of the number of moles. Suppose you want to calculate the number of moles (n) of a gas in a fixed volume at a known temperature and pressure, as illustrated in **Figure 12.16.** The calculation of moles is possible by modifying the combined gas law. You can understand the modification by recognizing that the volume occupied by a gas at a specified temperature and pressure must depend on the number of gas particles. The number of moles of gas is directly proportional to the number of particles. Hence, moles must be directly proportional to volume as well. Therefore you can introduce moles into the combined gas law by dividing each side of the equation by n.

$$\frac{P_1 \times V_1}{T_1 \times n_1} = \frac{P_2 \times V_2}{T_2 \times n_2}$$

This equation shows that $(P \times V)/(T \times n)$ is a constant. This constancy holds for what are called ideal gases. A gas behaves ideally if it conforms to the gas laws. Ideal behavior depends upon certain conditions, as you will see later in this section.

If you could evaluate the constant $(P \times V)/(T \times n)$, you could then calculate the number of moles of gas at any specified values of P, V, and T. This constant is symbolized as R.

You can find the actual value of R, given an important fact about gases: 1 mol of every gas occupies 22.4 L at STP (101.3 kPa and 273 K). Inserting the values of P, V, T, and n into the equation:

$$R = \frac{P \times V}{T \times n} = \frac{101.3 \text{ kPa} \times 22.4 \text{ L}}{273 \text{ K} \times 1 \text{ mol}} = 8.31 \text{ (L} \times \text{kPa)/(K} \times \text{mol)}$$

The **ideal gas constant** ***(R)*** has the value 8.31 (L × kPa) / (K × mol). Rearranging the equation for R, you obtain the usual form of the **ideal gas law:**

$$R = \frac{P \times V}{T \times n}$$

$$\text{or } P \times V = n \times R \times T$$

An advantage of the ideal gas law over the combined gas law is that it permits you to solve for the number of moles of a contained gas when P, V, and T are known.

Figure 12.16
When the temperature, pressure, and volume of a gas are known, you can use the ideal gas law to calculate the number of moles of the gas.

Sample Problem 12-5

You fill a rigid steel cylinder that has a volume of 20.0 L with nitrogen gas (N_2)(g) to a final pressure of 2.00×10^4 kPa at 28 °C. How many moles of $N_2(g)$ does the cylinder contain?

1. ANALYZE ***List the knowns and the unknown.***

Knowns:
- $P = 2.00 \times 10^4$ kPa
- $V = 20.0$ L
- $T = 28$ °C

Unknown:
- $n = ?$ mol $N_2(g)$

Use the known values and the ideal gas law to calculate the unknown (n).

2. CALCULATE ***Solve for the unknown.***

Convert degrees Celsius to kelvins.

$$28\ °C + 273 = 301\ K$$

Rearrange the ideal gas law to isolate n.

$$n = \frac{P \times V}{R \times T}$$

Substitute the known quantities P, V, R, and T into the equation and solve.

$$n = \frac{2.00 \times 10^4\ \cancel{kPa} \times 20.0\ \cancel{L}}{8.31\ \frac{\cancel{L} \times \cancel{kPa}}{\cancel{K} \times mol} \times 301\ \cancel{K}} = 160\ mol\ N_2(g)$$

$$= 1.60 \times 10^2\ mol\ N_2(g)$$

3. EVALUATE ***Does the result make sense?***

The gas is at a high pressure, but the volume is not large. This means that a large number of moles of gas must be compressed into the volume. The large answer is thus reasonable, and the units have canceled correctly.

Practice Problems

22. When the temperature of a rigid hollow sphere containing 685 L of helium gas is held at 621 K, the pressure of the gas is 1.89×10^3 kPa. How many moles of helium does the sphere contain?

23. What pressure will be exerted by 0.450 mol of a gas at 25 °C if it is contained in a 0.650-L vessel?

Figure 12.17
Natural gas (mainly methane) is often found in underground pockets near petroleum reserves. In the past, excess gas was simply burned off, as shown here, involving a great waste of this energy resource.

Sample Problem 12-6

A deep underground cavern contains 2.24×10^6 L of methane gas $(CH_4)(g)$ at a pressure of 1.50×10^3 kPa and a temperature of 42 °C. How many kilograms of CH_4 does this natural-gas deposit contain?

1. ***ANALYZE*** ***List the knowns and the unknown.***

Knowns:
- $P = 1.50 \times 10^3$ kPa
- $V = 2.24 \times 10^6$ L
- $T = 42$ °C

Unknown:
- $m = ?$ kg CH_4

Calculate the number of moles (n) using the ideal gas law. Convert moles to grams, using the molar mass of methane, and then convert grams to kilograms.

2. ***CALCULATE*** ***Solve for the unknown.***

Convert degrees Celsius to kelvins.

$$42\ °C + 273 = 315\ K$$

Rearrange the equation for the ideal gas law to isolate n, the number of moles of methane.

$$n = \frac{P \times V}{R \times T}$$

Substitute the known quantities into the equation to find the number of moles of methane.

$$n = \frac{1.50 \times 10^3\ \cancel{kPa} \times (2.24 \times 10^6\ \cancel{L})}{8.31\ \frac{\cancel{L} \times \cancel{kPa}}{\cancel{K} \times mol} \times 315\ \cancel{K}} = 1.28 \times 10^6\ mol\ CH_4$$

Convert moles of methane to grams.

$$\text{molar mass } CH_4 = \left(4\ \cancel{mol\ H} \times \frac{1.0\ g\ H}{1\ \cancel{mol\ H}}\right) + \frac{12.0\ g\ C}{1\ mol\ C}$$
$$= 16.0\ g\ CH_4/mol\ CH_4$$

A mole–mass conversion gives the number of grams of methane.

$$1.28 \times 10^6\ \cancel{mol\ CH_4} \times \frac{16.0\ g\ CH_4}{1\ \cancel{mol\ CH_4}} = 20.5 \times 10^6\ g\ CH_4$$
$$= 2.05 \times 10^7\ g\ CH_4$$

Convert this answer to kilograms.

$$2.05 \times 10^7\ \cancel{g}\ CH_4 \times \frac{1\ kg}{1000\ \cancel{g}} = 2.05 \times 10^4\ kg\ CH_4$$

3. ***EVALUATE*** ***Does the result make sense?***

The volume and pressure of the methane are very large. It is reasonable that the cavern contains the large mass of methane gas found as the solution to the problem. Also, the units canceled correctly, and the answer is expressed to the proper number of significant figures.

Practice Problems

24. A child has a lung capacity of 2.20 L. How many grams of air do her lungs hold at a pressure of 102 kPa and a normal body temperature of 37 °C? Air is a mixture, but you may assume an average molar mass of 29 g/mol for air because air is about 20% O_2 (molar mass 32) and 80% N_2 (molar mass 28).

25. What volume will 12.0 g of oxygen gas $(O_2)(g)$ occupy at 25 °C and a pressure of 52.7 kPa?

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Problem-Solving 24

Solve Problem 24 with the help of an interactive guided tutorial.

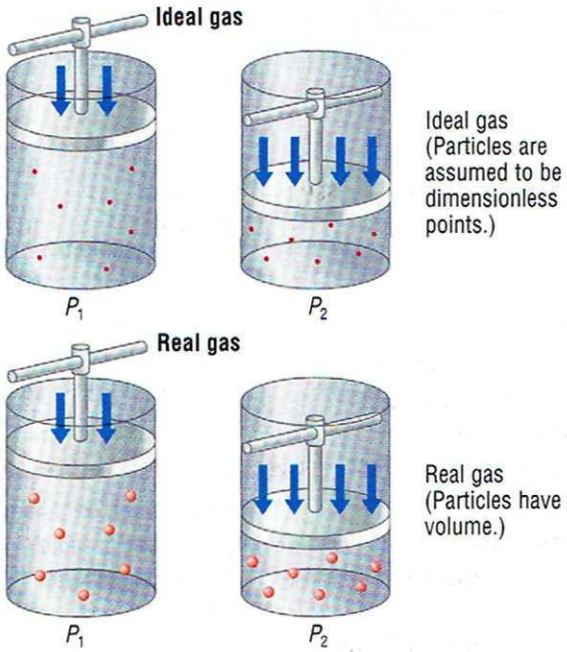

Figure 12.20
As pressure increases, the actual volumes of individual gas molecules in a real gas are no longer insignificant. It becomes increasingly difficult to compress the gas beyond a certain point, no matter what pressure is applied.

As you have read, simple kinetic theory assumes that gas particles are not attracted to each other and that the particles have no volume. These assumptions are incorrect. Gases and vapors could not be liquefied if there were no attractions between molecules. Also real gases are made up of actual physical particles, which do have a volume, as **Figure 12.20** illustrates.

The intermolecular forces that tend to hold the particles in a gas together effectively reduce the distance between particles. The gas therefore occupies less volume than is expected by the no-attractions assumption of the kinetic theory. This fact, considered alone, causes the $(P \times V)/(n \times R \times T)$ ratio to tend to be less than 1. At the same time, the molecules themselves occupy some volume, thus contradicting the zero-volume assumption of kinetic theory. This fact, on its own, causes the $(P \times V)/(n \times R \times T)$ ratio to tend to be greater than 1. One or the other of these two effects will usually dominate. In portions of the curves below the line, the intermolecular attractions dominate, causing the total volume to be less than ideal. In portions of the curves above the line, the effect of volume of the molecules dominates, causing the total volume to be greater than ideal. The temperature of the gas determines which of these two effects is the dominant one.

Compare the curves for $CH_4(g)$ at 0 °C and at 200 °C. At 0 °C, the methane molecules are moving relatively slowly. The attractions between the molecules are sufficiently strong so that, at low pressures, the curve is below the $(P \times V)/(n \times R \times T) = 1$ line. At higher pressures, the space between the molecules is reduced. The actual physical volume of the methane molecules now becomes important, and the curve is above the $(P \times V)/(n \times R \times T) = 1$ line. Raising the temperature to 200 °C increases the average kinetic energy of the methane molecules sufficiently to overcome the weak intermolecular attractive effects. Thus $(P \times V)/(n \times R \times T)$ is nearly equal to 1 at lower pressure at the elevated temperature. The ratio increases to greater than 1 only when the volume of the individual gas particles becomes important, as it does at high pressure.

LINK TO PHYSICS

Cryostats

The containers that store and transport liquefied gases are called cryostats. Their design prevents heat from being transferred from the environment to

the very cold liquid inside. The most widely used cryostats are called Dewar flasks, named after the Scottish scientist Sir James Dewar, who invented the containers in 1892. Dewar flasks are double-walled vessels with a vacuum between the walls, similar to the familiar Thermos™ bottle used to carry hot or cold drinks. Cryostats are very lightweight in comparison with compressed-gas cylinders. A given amount of a substance has a much smaller volume as a liquid than as a gas, even if the gas is under pressure. For these reasons, many gases are stored and transported in their liquefied form rather than as gases.

MINI LAB

Carbon Dioxide from Antacid Tablets

PURPOSE

To measure the amount of carbon dioxide gas given off when antacid tablets dissolve in water.

MATERIALS

- pencil
- graph paper
- tape measure
- clock or watch
- 3 rubber balloons (round)
- plastic medicine dropper
- water
- 6 antacid tablets
- pressure sensor (optional)

PROCEDURE

Sensor version available in the Probeware Lab Manual.

1. Break six antacid tablets into small pieces. Keep the pieces from each tablet in a separate pile. Put the pieces from one tablet into the first balloon. Put the pieces from two tablets into a second balloon. Put the pieces from three tablets into a third balloon.
2. After you use the medicine dropper to squirt about 5 mL of cold water into each balloon, immediately tie off each balloon.
3. Shake the balloons to mix the contents. Allow the contents to warm to room temperature.
4. Carefully measure and record the circumference of each balloon several times during the next 20 minutes.
5. Use the maximum circumference of each balloon to calculate the volume of each balloon. Assume that the balloons are spherical. (*Hint:* Volume of a sphere $= \frac{4\pi r^3}{3}$)

ANALYSIS AND CONCLUSIONS

1. Make a graph of balloon volume versus number of tablets. According to your graph, describe the relationship between the number of tablets used and the volume of the balloon.
2. Assume that the balloon is filled with carbon dioxide gas at 20 °C and standard pressure. Calculate the mass and the number of moles of CO_2 in each balloon at maximum inflation.
3. If a typical antacid tablet contains 2.0 g of sodium hydrogen carbonate, show how your carbon dioxide results compare with the theoretical values.

section review 12.4

26. How is it possible to calculate the amount of gas in a sample at given conditions of temperature, pressure, and volume?
27. What is the difference between an ideal gas and a real gas?
28. Explain the meaning of this statement: "No gas exhibits ideal behavior at all temperatures and pressures." At what conditions do real gases behave like ideal gases? Why?
29. Determine the volume occupied by 0.582 mol of a gas at 15 °C if the pressure is 81.8 kPa.
30. If 28.0 g of methane gas (CH_4) are introduced into an evacuated 2.00-L gas cylinder at a temperature of 35 °C, what is the pressure inside the cylinder? Note that the volume of the gas cylinder is constant.

Chem ASAP! **Assessment 12.4** Check your understanding of the important ideas and concepts in Section 12.4.