Gas Pressure and Volume

The earliest use of pressure in English referred to a burden or worry troubling a person's mind. Scientists found this a useful mental model to picture what happens when force is applied to a specific area. They adopted the word pressure to describe any application of force over an area.

Throughout the rest of this chapter, you will discover how gases behave when they are under pressure in a closed system. A **closed system** is one with a constant amount of moles of a substance. It is not open to the atmosphere. Gases in closed systems, from in fire extinguishers to in oxygen tanks, perform important functions in our lives. Understanding the behaviour of gases in closed systems is essential to our safe and effective use of gases.

How is Pressure Calculated?

As you learned in previous studies, **pressure** is defined in physical terms as the force exerted on an object per unit of surface area (). One commonly used SI unit of pressure is the **pascal** (**Pa**), equal to 1 . More often, pressure is reported in **kilopascals** (**kPa**), equal to 1000 Pa. (You will learn about other units of pressure later in this section.)

Assume a student with a mass of 51.0 kg is sitting on a chair. The force the student applies to the chair is 500.0 N. If the surface area of the chair seat is 0.05 , the pressure the student exerts is

Figure 11.7 shows how a decrease in surface area can dramatically increase pressure.

Figure 11.7 A woman with a mass of 50.0 kg exerts a pressure of about 21 kPa on the floor as she walks. If another woman with an equal mass is wearing high heels, she will exert a pressure of about 5000 kPa as her heel hits the floor. This pressure is approx-imately 240 times greater than if she were wearing flat shoes!

How does a gas exert pressure? In a sense, it cannot exert measurable pressure in the same way that a solid or liquid can. The pressure of a gas is determined by the kinetic motion of its component molecules. Suppose hundreds of billions of gas molecules are in random motion, striking the entire inner surface of their container. Each collision exerts a force on the container's inner surface.

Picture inflating a basketball. As you add more and more air to it, more molecules collide against the inside wall of the basketball. Each collision exerts a force on the basketball's inner surface area. The collective number of collisions as well as the strength of the force form the net or overall gas pressure. Since the molecules move in all directions, the net pressure exerted will be equal throughout. (Figure 11.8 illustrates this.)

pressure of ball casing

atmospheric pressure
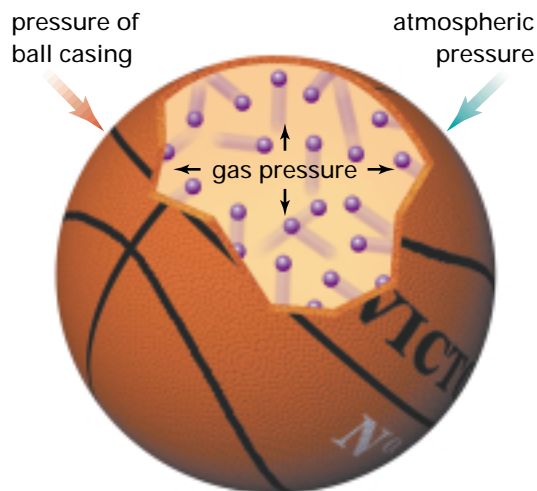
gas pressure

Figure 11.8 This diagram shows gas particles exerting pressure as they bounce off the inner surface of a basketball
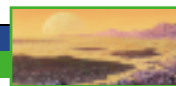
Atmospheric Pressure

Despite the popular expression, you can't carry the world on your shoulders! Scientists estimate that the lithosphere, or solid Earth, has a mass of 6.0×10^{24} kg. The hydrosphere, or the portion of Earth covered by water, has an estimated mass of 1.4×10^{21} kg.

Figure 11.9 The column of air above one square metre (1 m^2) at sea level and 0°C exerts a pressure of 101 325 Pa (1 Pa = 1 N/m^2). This is equivalent to a mass of about 10000 kg over as area of 1 m^2!

You do constantly experience the pressure exerted by Earth's atmosphere. Scientists estimate that the atmosphere has a mass of 5.1×10^{18} kg. Thus air molecules, which have mass, are being pulled down by gravity and are exerting pressure on all objects on Earth. Figure 11.9 shows how much pressure is exerted by the atmosphere over an area of 1 m^2.

COURSE CHALLENGE

What are the main factors determining atmospheric pressure on Earth? In your Chemistry Course Challenge, you will consider the atmosphere on a newly discovered planet. Why might the atmospheric pressure on another planet be different?

Early Studies of Atmospheric Pressure

In the early seventeenth century, the Italian scientist Galileo Galilei (1564–1642) developed a suction pump. It used air to lift water up to the surface from about 10 m underground. When drawn from greater depths, the column of water collapsed before it reached ground level. Galileo concluded that the water could not be pumped higher because it had reached the "limit of vacuum." Pumping from any depth beyond 10 m required a greater pressure from the suction pump than was provided by the atmosphere. However, Galileo did not know exactly how water was being moved up the tube.

From 1641 to 1642, Evangelista Torricelli (1608–1647) served as Galileo's secretary. He continued Galileo's experiments and concluded that the weight of air was pushing down on the rest of the water. The weight of the air pushed water up the column. This was a logical conclusion since gas molecules, like all matter on Earth, are pulled down by the force of gravity.

Torricelli did further calculations involving the weight of the atmosphere pressing on the water. He then improved upon the experiment by using mercury, which has a density 13.6 times greater than water. He designed the apparatus which we now know as the barometer, shown in Figure 11.10. Torricelli filled a glass tube of 1 cm diameter, closed at one end, with mercury. He then inverted the tube in a dish of mercury. Some of the mercury ran out of the tube. But about 760 mm of mercury remained in the tube. This is about 13.6 times less than the height of water that Galileo could pump. It is the air pushing on the mercury in the dish that keeps this 760 mm of mercury in the tube.

Changes in Atmospheric Pressure

At first, Torricelli considered his experiment a failure. The height of the mercury column did not remain constant at 760 mm, but changed slightly as the weather and air temperature changed. As you learned in Grade 10, these small changes in the height of the mercury column provide us with valuable information. We can predict the weather, in part, by looking at changes in atmospheric pressure. For example, if the atmospheric pressure decreases suddenly, a storm may be on the way.

Atmospheric pressure affects us in other ways, too. People who live at high elevations, such as in the Rocky Mountains, have less mass of air above them. At lower atmospheric pressure, the boiling point of water decreases. Because the water boils at a lower temperature, it takes longer to cook food in boiling water on a mountain than at sea level.

The following ExpressLab demonstrates atmospheric pressure in a dramatic way, showing you firsthand the tremendous pressure that the air around us can exert.
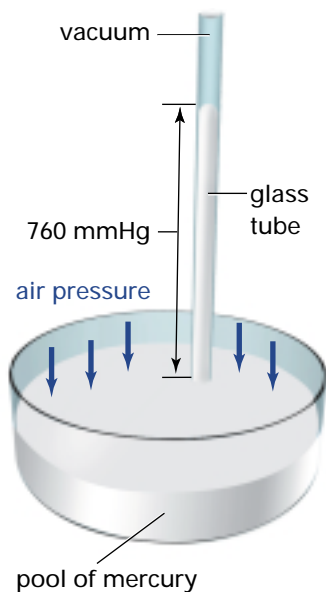
vacuum

760 mmHg

glass tube

air pressure

pool of mercury

Figure 11.10 Torricelli's barometer

In this ExpressLab, you will see just how powerful atmospheric pressure can be.

Materials

empty, clean soft drink can
hot plate
beaker tongs
large beaker of ice water
10 mL graduated cylinder
5 mL of water

Safety Precautions

Use safety goggles during this activity. Handle the heated can carefully using the beaker tongs.

Procedure

1. Pour 5 mL of water into the soft drink can.

2. Heat the can on the hot plate until steam begins rising from the opening of the can.

3. Using the beaker tongs, quickly invert the can into the large beaker of ice water so that the opening of the can is just under the surface of the water. Observe carefully.

Analysis

1. What happened to the air and water molecules inside the can when it was heated?

2. Explain what happened to the can when it was placed in the ice water.

Extension

3. Calculate the surface area of the outside of the can exposed to the atmosphere. Assuming an atmospheric pressure of 100.0 kPa, how much force was applied to the can by the atmosphere?

High Pressure Injectors

When gas molecules under high pressure are allowed to escape and expand, they release kinetic energy. This energy has been harnessed to benefit human health by powering high-pressure injectors, better known as jet injectors.

Jet injectors are hypodermic syringes that use high-pressure gas instead of a needle to inject vaccines under a patient's skin. Dr. Robert Higson (1913–1996) developed the "Hypospray" in the 1940s. This device used spring pressure against a plunger to force a vaccine through a tiny nozzle at 1000 km/h. The pressure was enough to drive the vaccine into the tissue of a patient's arm without breaking the skin.

Today jet injectors use a tank of compressed gas and an automatic vaccine dispenser that works through a pistol-like injector. When triggered, the new device releases a measured dose of vaccine into a sterile chamber and a small volume of gas through a hose. As the compressed gas expands, it forces the vaccine at high velocity through the injector's nozzle. The process is fast and simple, ideal for performing mass vaccinations. It also eliminates the problems of disposing of used syringes. Also, it protects medical personnel from infection through accidental needle pricks.

In 1958, Higson led a team that inoculated about 90 000 people in Asia and Africa against polio, typhoid, and cholera using the Hypospray. In 1965, the United Nation's World Health Organization used the jet injector. The organization freeze-dried vaccines for its successful worldwide smallpox eradication program. For its key role in eliminating smallpox from the list of human diseases, the jet injector earned a new name—the "Peace Pistol."

Units of Pressure

For many years, atmospheric pressure was measured in millimetres of mercury (**mm Hg**). In the British Commonwealth and the United States, inches of mercury were used. Standard atmospheric pressure, the pressure of the atmosphere at sea level and 0°C, is 760 mm Hg. More recently, in honour of the work of Torricelli, standard atmospheric pressure has been defined as 760 torr. **1 torr** represents a column of mercury 1 mm in height at 0°C. Another common unit for measuring pressure is **atmospheres** (**atm**), where 1 atm is equivalent to 760 torr. While mm Hg, torr, and atm are still used to measure pressure, especially in technological and medical applications, the SI units are pascals (Pa) or kilopascals (kPa).

In other words, **standard atmospheric pressure** at 0°C is equivalent to:

$$760 \text{ mm Hg} = 760 \text{ torr} = 1 \text{ atm} = 101.3 \text{ kPa}$$

Using this relationship, we can convert from one unit to another. For example, a pressure of 100.0 kPa is equivalent to

$$100.0 \text{ kPa} \times \frac{760.0 \text{ torr}}{101.3 \text{ kPa}} = 750.2 \text{ torr}$$

The Relationship Between Pressure and Volume

Figure 11.11 shows a meteorologist preparing to release a weather balloon partially filled with helium gas. As the balloon rises, atmospheric pressure decreases. The volume of the balloon increases.

Figure 11.11 Weather balloons are partially inflated with helium. They carry specialised instruments to measure varying atmospheric conditions such as pressure, temperature, and humidity.

Since the helium atoms inside the balloon move randomly in all directions, they constantly bombard all the area inside the walls of the balloon, exerting a pressure. With decreasing atmospheric pressure, there are fewer air molecules to collide with the outside of the balloon. As the pressure outside the balloon becomes less than that inside the balloon, the balloon expands. Given an expandable container, such as a balloon, the volume occupied by the gas will increase when external pressure decreases. As external pressure *increases*, gas molecules are forced closer together. The volume of gas then *decreases*.

When we refer to the *volume of a gas*, we are in fact talking about the *volume of the container*. The definition of the volume of a gas is *the space available for gas molecules to move around in.* The kinetic molecular theory of gases assumes that the volume of each gas molecule is essentially zero. Thus, the amount of space for them to move around in is the volume of the container. For all gases, V_{gas} = the volume of the container holding the gas. (Do not confuse this with the *molar volume* of gases. You will learn about molar volume in Chapter 12.)

Think about how the relationship between pressure and area for solids would apply if you were testing a gas in a three-dimensional container. You know that according to the kinetic molecular theory, gas molecules exert pressure over the entire inside surface of their container. If the volume of the container is halved, what would happen to the pressure of the gas inside the container?

Robert Boyle (1627–1691) was an Irish scientist with an interest in chemistry. He investigated the relationship between pressure and volume of gases at constant temperatures. By making careful measurements of the volume of a trapped gas, he was able to describe what happened when the pressure exerted on the gas was increased. Figure 11.12 shows Boyle's experiment. Boyle measured the length of the column of trapped air compared to the length of the column of mercury. Since the length of the mercury column is directly related to its volume, Boyle was able to deduce the relationship between pressure and volume.
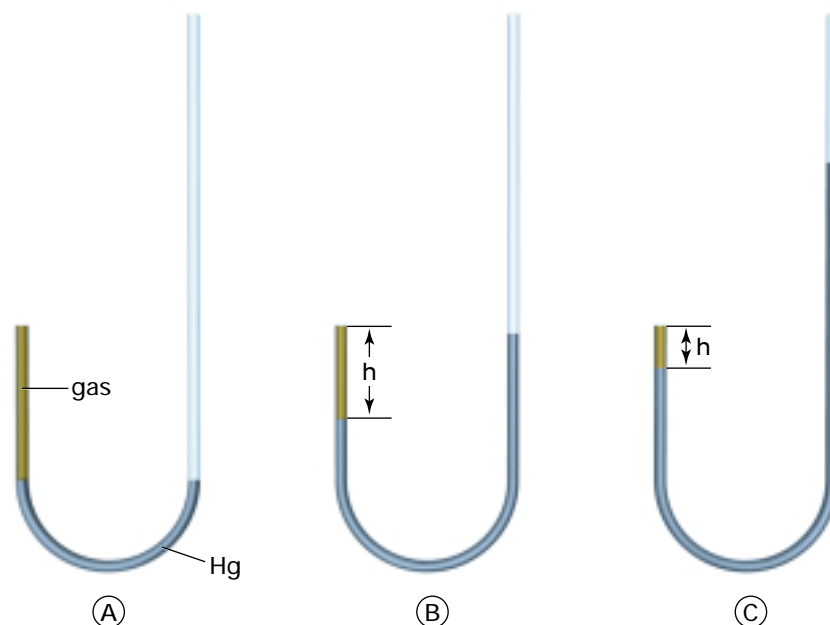
Figure 11.12 When liquid mercury is added to the open tube, the pressure caused by the weight of mercury on the trapped gas increases. The volume of the trapped gas (b and c) decreases.

Since mercury is a poisonous element, you will use a different method in Investigation 11-A to examine the relationship between the pressure and the volume of a gas.

The Relationship Between the Pressure and the Volume of a Gas

Boyle measured the variance in length of a column of trapped air. Since length is directly proportional to volume in a column with a regular diameter, this gave him an indirect measure of changes in volume of the air with increased pressure. In this activity, air is trapped inside a sealed plastic pipette. You can measure the volume of the trapped gas in terms of the length of the column of air, the way that Boyle did more than three hundred years ago. You will measure the applied pressure in terms of the number of turns of a clamp rather than in kPa.

Question

What is the relationship between the pressure and volume of a fixed amount of gas at a constant temperature?

Materials

thin stem plastic pipette with bulb
small C-clamp
metric ruler (with mm)
match or Bunsen burner
craft stick
coloured water

Safety Precautions

- Be very careful when sealing the end of the plastic pipette with a flame. The plastic will melt and may begin to burn. Hot, molten plastic can burn your skin.
- Do not inhale any of the fumes from the plastic.
- Before lighting the Bunsen burner, check that there are no flammable solvents nearby.

Procedure

1. Squeezing the bulb, draw enough coloured water into a pipette so that the water fills the bulb and extends about 2 to 3 cm down the stem. The rest of the stem should be filled with air.

2. Using a flame from a Bunsen burner, carefully seal the end of the pipette completely. Allow the pipette to cool for at least three minutes before completing the rest of the procedure.

3. Copy out the data table into your notes.

P (no. of turns)	V (mm)	1/V (mm)	P × V (turns · mm)
0			
1			

4. Break a craft stick in two. Place one half of the stick on either side of the pipette bulb. Tighten a small C-clamp around the bulb of the pipette so that the clamp just holds the bulb snugly (see the diagram).

5. Using a ruler, measure the length of trapped gas (the "volume") in millimetres. Record this in your data table.

6. Increase the "pressure" on the bulb by turning the handle of the clamp one half or one complete turn, depending on the size of your clamp. Record the "volume" of the trapped gas in your data table.

7. Repeat step 6 until you have made at least five complete turns.

8. Complete the data table. Calculate an average value for the column.

9. Plot a graph of P (y-axis) versus V (x-axis).

10. Plot a graph of P (y-axis) versus $1/V$ (x-axis).

Analysis

1. What is the independent variable in this investigation? What is the dependent variable?

2. What relationship exists between volume and pressure, based on the data collected and the graphs produced?

3. Express this relationship mathematically. To help you to do this, look at the mathematical form of Boyle's law, located after this investigation.

4. Calculate the slope of the P vs. $1/V$ graph. How does this value compare with the average value? Of what significance are these two values?

5. What changes in temperature occurred during the experiment? In the amount of trapped air? Explain how this may have affected your results.

Conclusion

In your own words, state the relationship between pressure and the volume of a gas.

Extension

Using pressure probes and a graphing calculator or computer interface, investigate the relationship between the pressure and the volume of a gas. Produce a data table and graphical interpretation of these results.
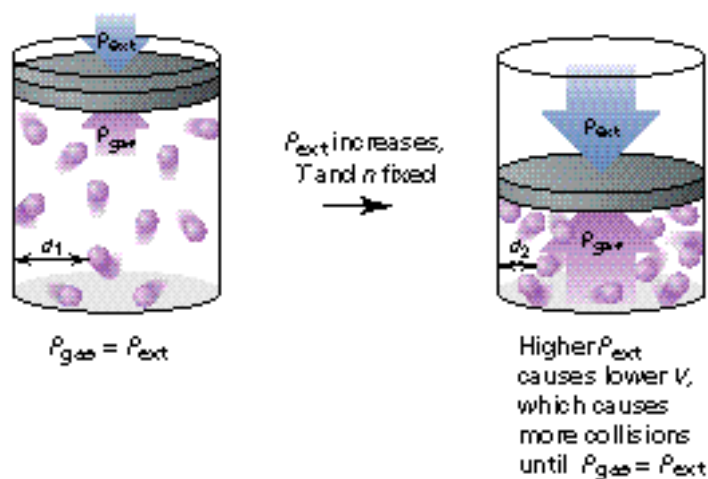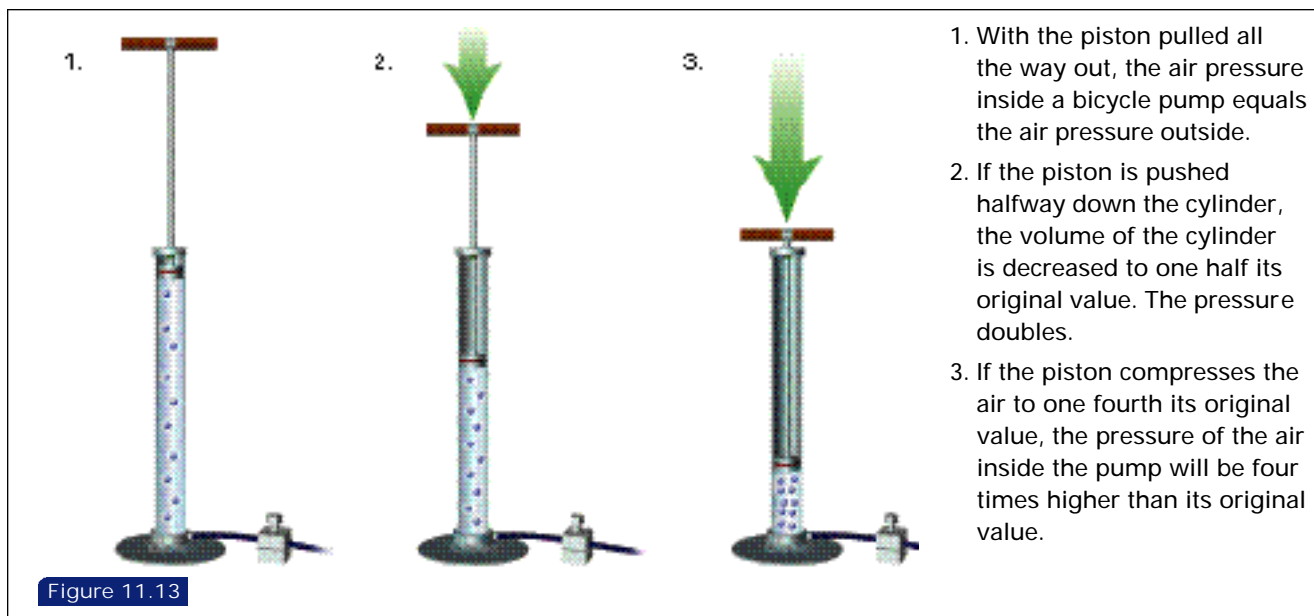

plastic pipette

craft sticks

C-clamp
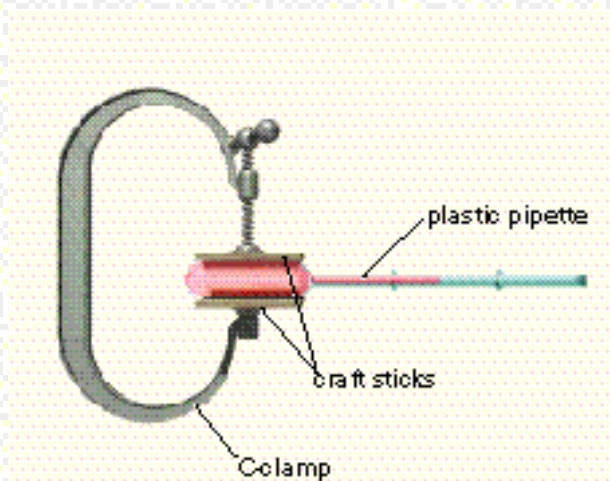
Boyle's Law

In 1662, Robert Boyle stated that *the volume of a given amount of gas, at a constant temperature, varies inversely with the applied pressure*. In other words, as external pressure on a gas increases, the volume of the gas decreases by the same factor. This statement is known as **Boyle's law**. Figure 11.13 illustrates Boyle's law using a bicycle pump.

1. With the piston pulled all the way out, the air pressure inside a bicycle pump equals the air pressure outside.

2. If the piston is pushed halfway down the cylinder, the volume of the cylinder is decreased to one half its original value. The pressure doubles.

3. If the piston compresses the air to one fourth its original value, the pressure of the air inside the pump will be four times higher than its original value.

Figure 11.13

Figure 11.14 At a given temperature, gas molecules travel an average distance before they collide with the container wall. When the volume is decreased, the gas molecules travel a shorter distance before striking the wall.

Boyle found that this relationship held true for all gases as long as the temperature remained unchanged. As external pressure on a gas increases, the volume of the gas decreases. The gas molecules are forced closer together. However, if the volume of a gas decreases, then the gas molecules have to travel a shorter distance before they strike the container walls, as shown in Figure 11.14. Since they travel a shorter distance, gas molecules will strike the container walls more often per unit time. This increases the internal pressure of the gas. (With an increased volume, there are fewer collisions per unit time and a lower gas pressure is exerted.)

In other words, as the pressure of a closed system increases, its volume decreases. If the pressure is decreased by half, the volume doubles. We can write this relationship mathematically by using the proportionality symbol, $\propto$. V $\propto$ 1/P means that volume is inversely proportional to the pressure.

Mathematically, the proportionality sign ($\propto$) can be removed by introducing a proportionality constant (*k*).

$$V$$

or

In Investigation 11-A, when you plotted a graph of P versus $1/V$, you obtained a straight line. The slope of this line gives the value of the proportionality constant, k. If the pressure is tripled, the volume will decrease to one third of its original volume, such that $P \times V = k$. The value of k differs depending on the gas sample and the temperature. Remember, this mathematical relationship only applies if the temperature remains constant. A graph of P versus $1/V$ is shown in Figure 11.15.

For the gas sample at its initial conditions (i)

$$P_iV_i = k$$

If the gas sample is then subjected to a change in pressure, at its final conditions (f)

$$P_fV_f = k$$

Since the slope of the line (k) is constant, and since initial and final conditions are both equal to k, we can write

$$P_iV_i = P_fV_f$$

This mathematical relationship is another way of stating Boyle's law.

Sample Problem

Boyle's Law: Calculating Volume

Problem

A sample of helium gas is collected at room temperature in a 4.50 L balloon at standard atmospheric pressure. The balloon is then submerged in a tub of water, also at room temperature, such that the external pressure is increased to 110.2 kPa. What will the final volume of the balloon become?

What Is Required?

You need to find the volume of the balloon after the pressure on the balloon has been increased. ($V_f = ?$)

What Is Given?

- You know the initial pressure and volume, and the final pressure.
  Initial pressure   (P_i) = 101.3 kPa
  Initial volume   (V_i) = 4.50 L
  Final pressure   (P_f) = 110.2 kPa
- You know that the temperature does not change.

Plan Your Strategy

> **Algebraic method**
>
> - Since temperature is constant and pressure and volume have been given, you will need to use the Boyle's law formula.
> - You can substitute numbers and units for the variables in the formula to solve for the unknown (V_f).

Continued ...
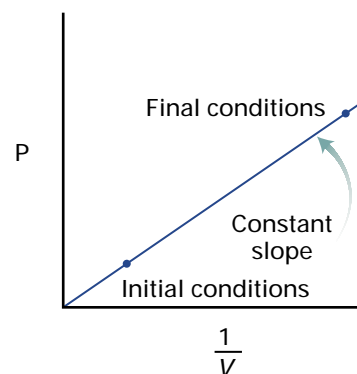
Figure 11.15 If a sample of gas at initial conditions has a change of pressure applied to it, its volume decreases proportionally, such that in its final state, $P \times V = k$.

PROBLEM TIP

In this Sample Problem, you will see two different methods of solving the problem: the algebraic method and the ratio method. Choose the method you prefer to solve this type of problem.

Ratio method

- The pressure on the balloon increases. When this happens, if temperature remains the same, you know according to Boyle's law that the volume of the balloon will decrease.
- To find the final volume, you can multiply the initial volume of the balloon by a ratio of the two pressures that is less than one (i.e. $\frac{101.3 \text{ kPa}}{110.2 \text{ kPa}}$).

Act on Your Strategy

Algebraic method

$P_i V_i = P_f V_f$

$(101.3 \text{ kPa})(4.50 \text{ L}) = (110.2 \text{ kPa})(V_f)$

To isolate V_f, you need to divide both sides of the equation by 110.2 kPa.

$$\frac{(101.3 \text{ kPa})(4.50 \text{ L})}{(110.2 \text{ kPa})} = \frac{(110.2 \text{ kPa})(V_f)}{(110.2 \text{ kPa})}$$

$$\frac{(101.3 \text{ kPa})(4.50 \text{ L})}{(110.2 \text{ kPa})} = (V_f)$$

$$V_f = 4.137 \text{ L}$$

Ratio method

$V_f = 4.50 \text{ L} \times \text{pressure ratio}$

$= 4.50 \text{ L} \times \frac{101.3 \text{ kPa}}{110.2 \text{ kPa}}$

$= 4.137 \text{ L}$

Since the least number of significant digits in the question is three, the answer is:

$$V_f = 4.14 \text{ L}$$

Check Your Solution

- The units for the answer are in litres.
- When units cancel out, L remains.
- The volume of the balloon has decreased due to the increase in pressure.

Practice Problems

1. A 50.0 cm^3 sample of nitrogen gas is collected at 101.3 kPa. If the volume is reduced to 5.0 cm^3, and the temperature remains constant, what will the final pressure of the nitrogen be?

2. A weather balloon has a volume of 1000 L at a pressure of 740.0 torr. The balloon rises to a height of 1000 m where the atmospheric pressure is measured as 450.0 torr. Assuming there is no change in temperature, what is the final volume of the weather balloon?

3. A 45.0 cm³ sample of nitrogen gas is collected at 1.0 atm. The nitrogen is compressed to a pressure of 10.0 atm. What is the final volume of the nitrogen if the temperature remains constant?

4. A 45.6 mL sample of gas at 490 torr is compressed to a certain volume at 3 atm. What is the new volume, in litres?

CHEM
FACT

Now that you've finished practising Boyle's law problems, take a deep breath and relax. You have just illustrated Boyle's law! When you inhale, muscles in your torso expand your rib cage. The volume of your lungs increases. Since the pressure inside your lungs is decreased with the expansion in volume, outside air under higher pressure rushes in.

Section Wrap-up

In this section, you learned about the relationship between pressure and volume of a gas. This relationship is stated in Boyle's law. With knowledge of gas properties and behaviours, we are able to devise and improve upon technologies used everyday. You will learn about some of these important technologies later in this chapter. In the meantime, the next section examines how gases respond to changes in yet another variable: temperature.

Section Review

1 **C** Using the relationship 760 mm Hg = 760 torr = 1 atm = 101.3 kPa, convert each of the following units:

(a) 2.03 atm to kPa

(b) 85.2 kPa to atm

(c) 1.50 atm to torr

(d) 600 torr to kPa

2 **K/U** Use the kinetic molecular theory. Explain why the air pressure inside a capped syringe increases if the volume decreases from 15 cm³ to 10 cm³.

3 **K/U** Explain, using the kinetic molecular theory, why pressure is exerted by gases in all directions.

4 **I** A 1.00 L helium balloon is floating in the air on a day when the atmospheric pressure is 102.5 kPa and the temperature is 20.0°C. Suddenly, clouds appear and the pressure rapidly drops to 98.6 kPa at a temperature of 20.0°C. What is the new volume of the balloon?

5 **I** 0.750 L of oxygen gas is trapped at 101.3 kPa in a cylinder with a moveable piston. The piston is moved and the gas is compressed to a volume of 0.500 L. What is the final pressure applied to the oxygen gas if the temperature remains unchanged?

6 **MC** A student produces 38.3 mL of oxygen gas in a burette. The next day, there are 40.2 mL of gas in the burette at a pressure of 103 kPa. What was the pressure on the previous day, in torr? What might be happening to the weather in the student's neighbourhood?