Pearson

10.4: The Simple Gas Laws: Boyle's Law, Charles's Law, and Avogadro's Law

Key Concept Video **Simple Gas Laws and Ideal Gas Law**

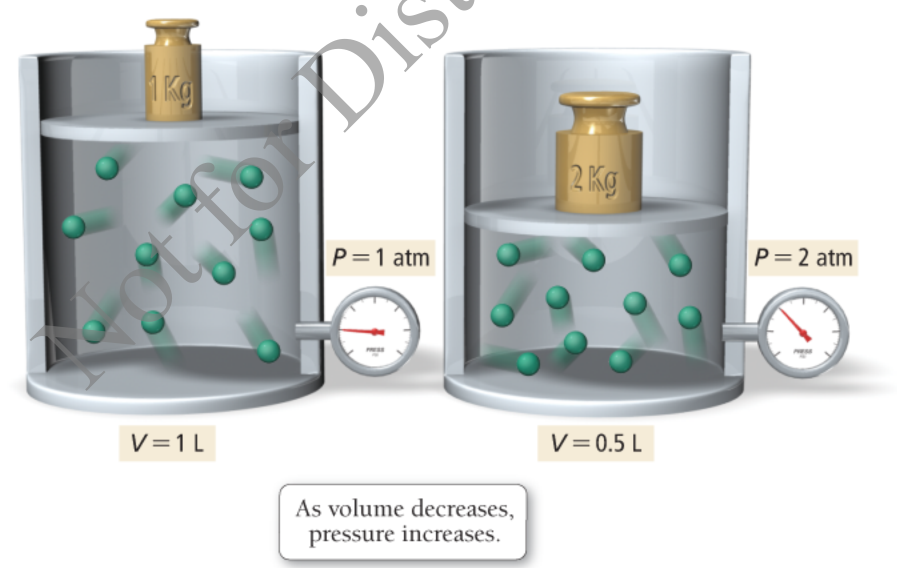
In this section, we broaden our discussion of gases to include the four basic properties of a gas sample: pressure (P), volume (V), temperature (T), and amount in moles (n). These properties are interrelated—when one changes, it affects the others. The *simple gas laws* describe the relationships between pairs of these properties. For example, one simple gas law describes how *volume* varies with *pressure* at constant temperature and amount of gas; another law describes how volume varies with *temperature* at constant pressure and amount of gas.

Boyle's Law: Volume and Pressure

Boyle's law relates the volume of a sample of gas to its pressure *at constant temperature*. According to kinetic molecular theory, if we decrease the volume of a gas, we force the gas particles to occupy a smaller space. As long as the temperature remains constant, the number of collisions with the surrounding surfaces (per unit surface area) must necessarily increase, resulting in a greater pressure as shown in Figure 10.9. In other words, kinetic molecular theory predicts an inverse relationship between the pressure of a gas and its volume.

Figure 10.9 Volume and Pressure

As the volume of a gas sample decreases, gas molecules collide with surrounding surfaces more frequently, resulting in greater pressure.



In the early 1660s, the pioneering English scientist Robert Boyle (1627–1691) and his assistant Robert Hooke (1635–1703) used a J-tube (Figure 10.10) to measure the volume of a sample of gas at different pressures. They trapped a sample of air in the J-tube and added mercury to increase the pressure on the gas. Boyle and Hook observed the *inverse relationship* between volume and pressure predicted by kinetic molecular theory as illustrated in Figure 10.11. This relationship is now known as **Boyle's law**:

$$\text{Boyle's law:}\quad V \propto \frac{1}{P} \qquad (\text{constant } T \text{ and } n)$$

Figure 10.10 The J-Tube

In a J-tube, a column of mercury (Hg) traps a sample of gas. We can increase the pressure on the gas by increasing the height (h) of mercury in the column.

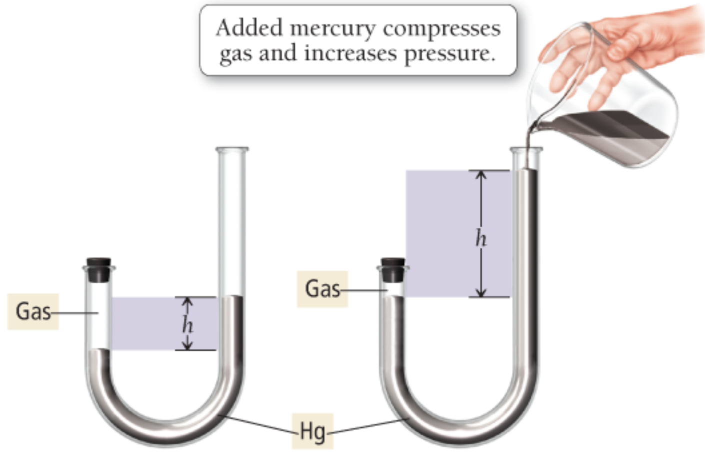
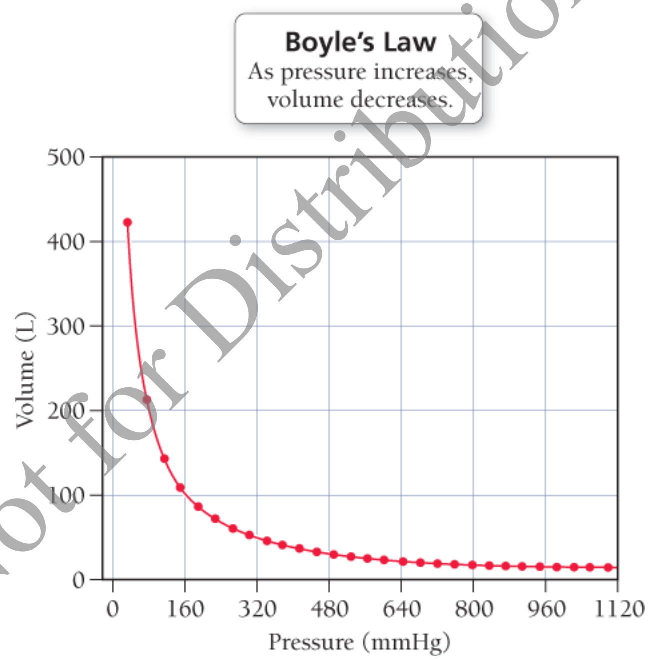


Figure 10.11 Volume versus Pressure

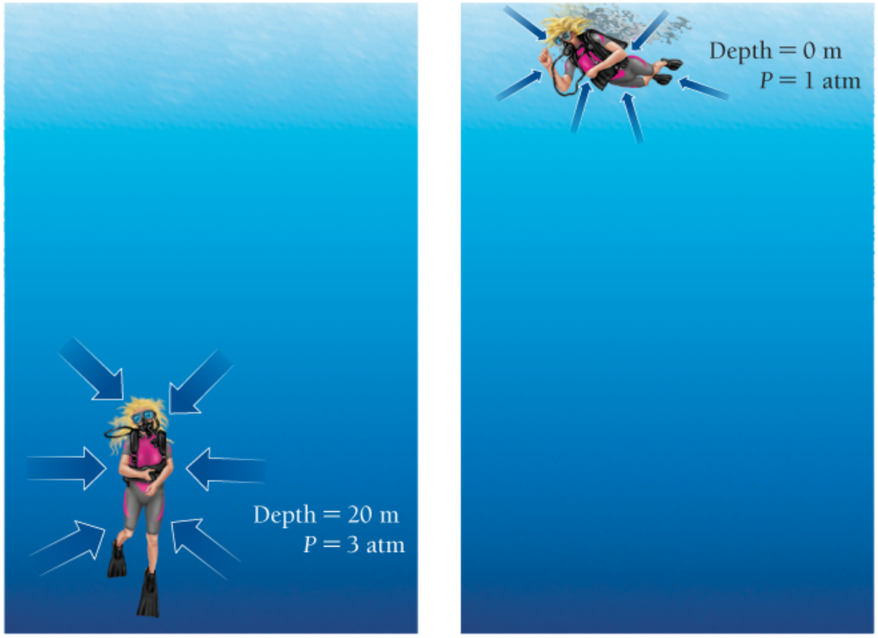
A plot of the volume of a gas sample—as measured in a J-tube—versus pressure at constant temperature and amount of gas. The plot shows that volume and pressure are inversely related.



Scuba divers learn about Boyle's law during certification because it explains why a diver should never ascend toward the surface without continuous breathing. For every 10 m of depth that a diver descends in water, she experiences an additional 1 atm of pressure due to the weight of the water above her (Figure 10.12). The pressure regulator used in scuba diving delivers air into the diver's lungs at a pressure that matches the external pressure; otherwise the diver could not inhale the air. For example, when a diver is 20 m below the surface, the regulator delivers air at a pressure of 3 atm to match the 3 atm of pressure around the diver (1 atm due to normal atmospheric pressure and 2 additional atmospheres due to the weight of the water at 20 m).

Figure 10.12 Increase in Pressure with Depth

For every 10 m of depth, a diver experiences approximately one additional atmosphere of pressure due to the weight of the surrounding water. At 20 m, for example, the diver experiences approximately 3 atm of pressure (1 atm of normal atmospheric pressure plus an additional 2 atm due to the weight of the water) pressure (1 atm of normal atmospheric pressure plus an additional 2 atm due to the weight of the water).



Suppose that a diver inhaled a lungful of air at a pressure of 3 atm and swam quickly to the surface (where the pressure is 1 atm) while holding her breath. What would happen to the volume of air in her lungs? The pressure decreases by a factor of 3 so that the volume of the air in her lungs increases by a factor of 3—a dangerous situation similar to that of the uncontrolled decompression discussed in Section 10.1. For the scuba diver, the volume increase would prevent her from holding her breath all the way to the surface—the air would force itself out of her mouth, but probably not before the expanded air damaged her lungs, possibly killing her. Consequently, the most important rule in diving is *never hold your breath*. To avoid such catastrophic results, divers must ascend slowly and breathe continuously, allowing the regulator to bring the air pressure in their lungs back to 1 atm by the time they reach the surface.

> Boyle's law assumes constant temperature and constant amount of gas.

We can use Boyle's law to calculate the volume of a gas following a pressure change or the pressure of a gas following a volume change *as long as the temperature and the amount of gas remain constant*. For these types of calculations, we write Boyle's law in a slightly different way:

$$\text{Since } V \propto \frac{1}{P}, \quad \text{then} \quad V = (\text{constant}) \times \frac{1}{P} \quad \text{or} \quad V = \frac{\text{constant}}{P}$$

> If two quantities are proportional, then one is equal to the other multiplied by a constant.

If we multiply both sides by P, we get:

$$PV = \text{constant}$$

This relationship indicates that if the pressure increases, the volume decreases, but the product $P \times V$ always equals the same constant. For two different sets of conditions, we can say that:

$$P_1V_1 = \text{constant} = P_2V_2$$

or

[10.2]

$$P_1V_1 = P_2V_2$$

where P_1 and V_1 are the initial pressure and volume of the gas, and P_2 and V_2 are the final volume and pressure.

Example 10.2 Boyle's Law

As you breathe, you inhale by increasing your lung volume. A woman has an initial lung volume of 2.75 L, which is filled with air at an atmospheric pressure of 1.02 atm. If she increases her lung volume to 3.25 L without inhaling any additional air, what is the pressure in her lungs?

To solve the problem, first solve Boyle's law (Equation 10.2) for P_2 and then substitute the given quantities to calculate P_2.

SOLUTION

$$\begin{aligned} P_1V_1 &= P_2V_2 \\ P_2 &= \frac{V_1}{V_2}P_1 \\ &= \frac{2.75\ \cancel{L}}{3.25\ \cancel{L}}1.02\ \text{atm} \\ &= 0.863\ \text{atm} \end{aligned}$$

FOR PRACTICE 10.2 A snorkeler takes a syringe filled with 16 mL of air from the surface, where the pressure is 1.0 atm, to an unknown depth. The volume of the air in the syringe at this depth is 7.5 mL. What is the pressure at this depth? If the pressure increases by 1 atm for every additional 10 m of depth, how deep is the snorkeler?

Charles's Law: Volume and Temperature

Charles's law relates the volume of a gas to its temperature *at constant pressure*. According to kinetic molecular theory, when we increase the temperature of a gas, the average kinetic energy, and therefore the average speed, of the particles increases. The faster moving particles collectively occupy more space, resulting in a greater volume, as shown in Figure 10.13.

Figure 10.13 Volume of a Gas as a Function of Temperature

If we move a balloon from an ice water bath to a boiling water bath, its volume expands as the gas particles within the balloon move faster (due to the increased temperature) and collectively occupy more space.

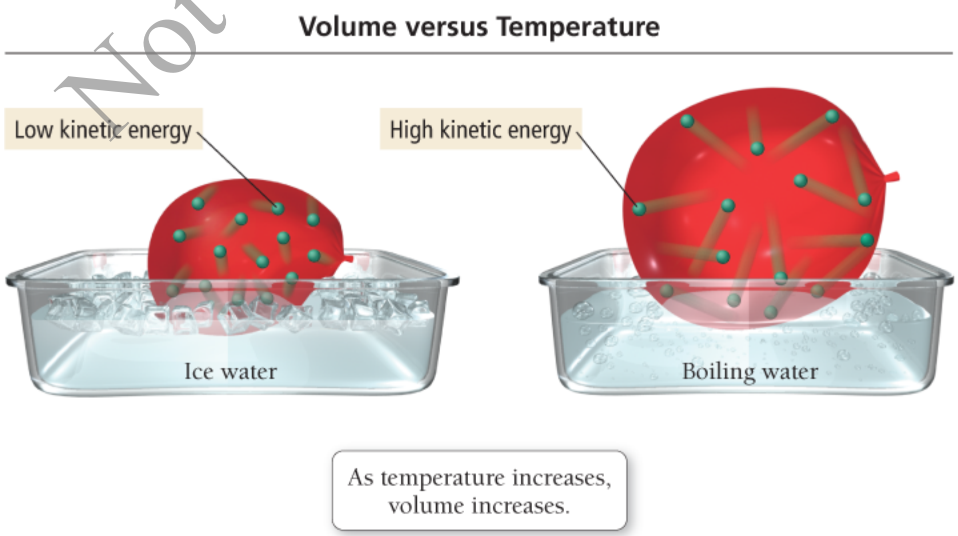
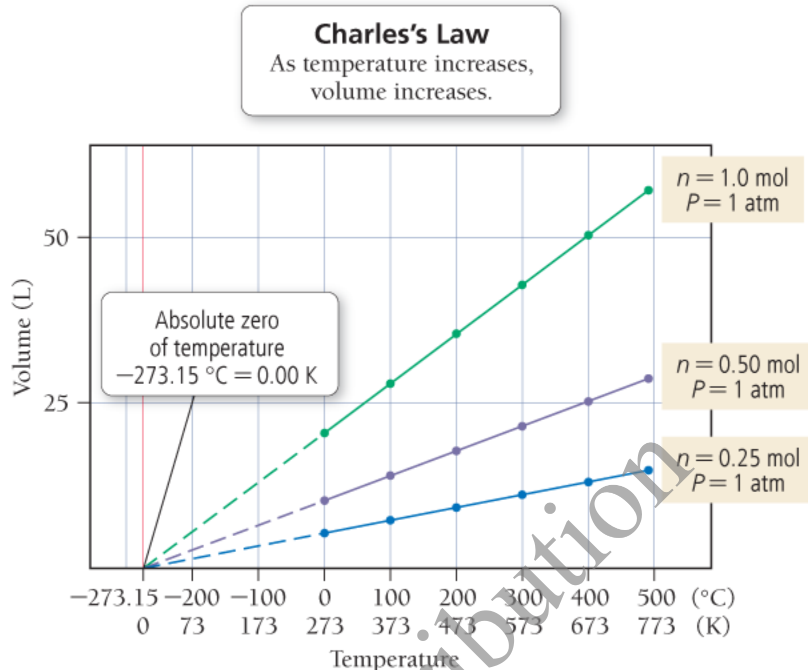


Figure 10.14 shows the results of several measurements of the volume of a gas as a function of temperature at

constant pressure. From the plot, we can see the relationship predicted by kinetic molecular theory: the volume of a gas increases with increasing temperature. Closer examination of the plot reveals that volume and temperature are *linearly related*. If two variables are linearly related, plotting one against the other produces a straight line.

Figure 10.14 Volume versus Temperature

The volume of a fixed amount of gas at a constant pressure increases linearly with increasing temperature in kelvins. (The dotted extrapolated lines cannot be measured experimentally because all gases condense into liquids before –273.15 °C is reached.)



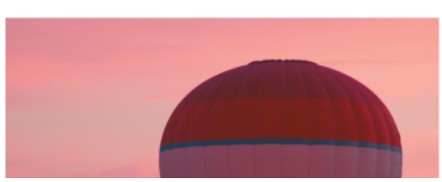
Another interesting feature emerges if we extend or *extrapolate* the line in the plot in Figure 10.14 backwards from the lowest measured temperature. The dotted extrapolated line shows that the gas should have a zero volume at –273.15 °C. A temperature of –273.15 °C corresponds to 0 K (zero on the Kelvin scale), the coldest possible temperature (see Chapter E). The extrapolated line indicates that below –273.15 °C, the gas would have a negative volume, which is physically impossible. For this reason, we refer to 0 K as *absolute zero*—colder temperatures do not exist.

The first person to carefully quantify the relationship between the volume of a gas and its temperature was J. A. C. Charles (1746–1823), a French mathematician and physicist. Charles was interested in gases and was among the first people to ascend in a hydrogen-filled balloon. The direct proportionality between volume and temperature is named **Charles's law** after him:

$$\text{Charles's law:} \quad V \propto T \quad (\text{constant } P \text{ and } n)$$

> Charles's law assumes constant pressure and constant amount of gas.

Charles's law explains why the second floor of a house is usually warmer than the ground floor. According to Charles's law, when air is heated, its volume increases, resulting in a lower density. The warm, less dense air tends to rise in a room filled with colder, denser air. Similarly, Charles's law explains why a hot-air balloon can take flight. The gas that fills a hot-air balloon is warmed with a burner, increasing its volume and lowering its density, and causing it to float in the colder, denser surrounding air.



A hot-air balloon floats because the hot air within the balloon is less dense than the surrounding cold air.

We can experience Charles's law directly by holding a partially inflated balloon over a warm toaster. As the air in the balloon warms, we can feel the balloon expanding. Alternatively, we can put an inflated balloon into liquid nitrogen and watch it become smaller as it cools.

We can use Charles's law to calculate the volume of a gas following a temperature change or the temperature of a gas following a volume change *as long as the pressure and the amount of gas are constant*. For these calculations, we rearrange Charles's law as follows:

$$\text{Since } V \propto T, \quad \text{then } V = \text{constant} \times T$$

If we divide both sides by T, we get:

$$V/T = \text{constant}$$

If the temperature increases, the volume increases in direct proportion so that the quotient, V/T, is always equal to the same constant. So, for two different measurements, we can say that:

$$V_1/T_1 = \text{constant} = V_2/T_2$$

or

[10.3]

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

where V_1 and T_1 are the initial volume and temperature of the gas and V_2 and T_2 are the final volume and temperature. *We must always express the temperatures in kelvins* (K), because, as shown in Figure 10.14, the volume of a gas is directly proportional to its absolute temperature, not its temperature in °C. For example, doubling the temperature of a gas sample from 1 °C to 2 °C does not double its volume, but doubling the temperature from 200 K to 400 K does.

Example 10.3 Charles's Law

A sample of gas has a volume of 2.80 L at an unknown temperature. When you submerge the sample in ice water at $T = 0.00\ ^\circ\text{C}$, its volume decreases to 2.57 L. What was its initial temperature (in K and in °C)?

To solve the problem, first solve Charles's law for T_1.

SOLUTION

$$\begin{aligned}\frac{V_1}{T_1} &= \frac{V_2}{T_2}\\ T_1 &= \frac{V_1}{V_2}T_2\end{aligned}$$

Before you substitute in the numerical values to calculate T_1, convert the temperature to kelvins (K). *Remember, you must always work gas law problems with Kelvin temperatures.*

$$T_2\,(K) = 0.00 + 273.15 = 273.15\text{ K}$$

Substitute T_2 and the other given quantities to calculate T_1.

$$\begin{aligned} T_1 &= \frac{V_1}{V_2}T_2 \\ &= \frac{2.80\ \cancel{\text{L}}}{2.57\ \cancel{\text{L}}}273.15\text{ K} \\ &= 29\underline{7}.6\text{ K} \end{aligned}$$

Calculate T_1 in °C by subtracting 273.15 from the value in kelvins.

$$T_1\,(^\circ\text{C}) = 29\underline{7}.6 + 273.15 = 24\,^\circ\text{C}$$

FOR PRACTICE 10.3 A gas in a cylinder with a moveable piston has an initial volume of 88.2 mL. If you heat the gas from 35 °C to 155 °C, what is its final volume (in mL)?

Conceptual Connection 10.2 Boyle's Law and Charles's Law

Avogadro's Law: Volume and Amount (in Moles)

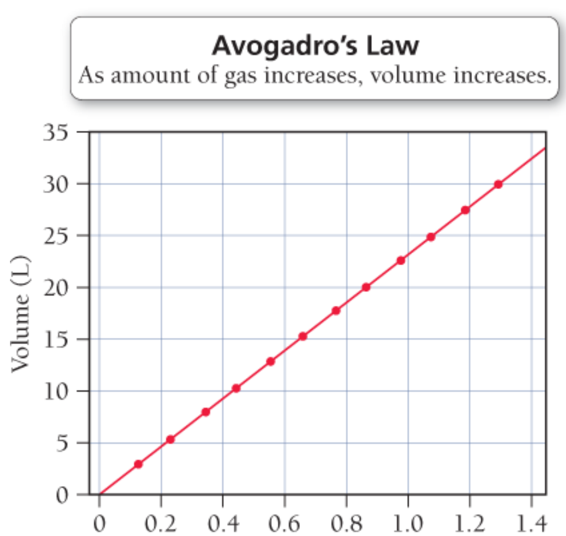
Interactive

Avogadro's law relates the volume of gas sample to the amount of gas *at constant pressure and temperature*. According to kinetic molecular theory, when we increase the number of particles in a gas sample, the greater number of particles occupy a greater volume (at constant pressure and temperature). The volume of a gas sample as a function of the amount of gas (in moles) in the sample is shown in Figure 10.15. We can see that the relationship between volume and amount is linear. As we might expect, extrapolation to zero moles shows zero volume. This relationship, first stated formally by Amadeo Avogadro (1776–1856), is **Avogadro's law**:

$$\text{Avogadro's law:}\quad V \propto n \qquad (\text{constant } T \text{ and } P)$$

Figure 10.15 Volume versus Number of Moles

The volume of a gas sample increases linearly with the number of moles of gas in the sample (at constant temperature and pressure).



Number of moles (n)

> Avogadro's law assumes constant temperature and constant pressure and is independent of the nature of the gas.

You experience Avogadro's law when you inflate a balloon. With each exhaled breath, you add more gas particles to the inside of the balloon, increasing its volume.

We can use Avogadro's law to calculate the volume of a gas following a change in the amount of the gas *as long as the pressure and temperature of the gas are constant*. For these types of calculations, we express Avogadro's law as:

[10.4]

$$\frac{V_1}{n_1} = \frac{V_2}{n_2}$$

where V_1 and n_1 are the initial volume and number of moles of the gas and V_2 and n_2 are the final volume and number of moles. In calculations, we use Avogadro's law in a manner similar to the other gas laws, as Example 10.4 demonstrates.

Example 10.4 Avogadro's Law

A male athlete in a kinesiology research study has a lung volume of 6.15 L during a deep inhalation. At this volume, his lungs contain 0.254 mol of air. During exhalation, his lung volume decreases to 2.55 L. How many moles of gas does the athlete exhale during exhalation?

Assume constant temperature and pressure.

To solve the problem, first solve Avogadro's law for the number of moles of gas left in the athlete's lungs after exhalation, n_2.

Then substitute the given quantities to calculate n_2.

Because the lungs initially contained 0.254 mol of air, you calculate the amount of air exhaled by subtracting the result from 0.254 mol.

SOLUTION

$$\begin{aligned} \frac{V_1}{n_1} &= \frac{V_2}{n_2} \\ n_2 &= \frac{V_2}{V_1} n_1 \\ &= \frac{2.55\ \cancel{\text{L}}}{6.15\ \cancel{\text{L}}} 0.254\ \text{mol} \\ &= 0.105\ \text{mol} \end{aligned}$$

$$\begin{aligned} \text{moles exhaled} &= 0.254\ \text{mol} - 0.105\ \text{mol} \\ &= 0.149\ \text{mol} \end{aligned}$$

FOR PRACTICE 10.4 A chemical reaction occurring in a cylinder equipped with a moveable piston produces 0.621 mol of a gaseous product. If the cylinder contains 0.120 mol of gas before the reaction and has an initial volume of 2.18 L, what is its volume after the reaction? (Assume that pressure and temperature are constant and that the initial amount of gas completely reacts.)