

# 11.4

## Combined Gas Law Calculations

### Section Preview/ Specific Expectations

In this section, you will

- **solve** problems involving the combined gas law and Dalton's law of partial pressures
- **identify** the components of Earth's atmosphere
- **communicate** your understanding of the following terms: *standard temperature, standard temperature and pressure, standard ambient temperature and pressure, combined gas law, Dalton's law of partial pressures*

You may have heard a common joke about Canadian weather: "If you don't like it, wait an hour and it will change." While this is an exaggeration, atmospheric pressure and temperature rarely remain constant for any extended period of time. Since the volume of gases changes when pressure and temperature change, standards have been designed to allow a comparison of different gas volumes.

The average pressure of the atmosphere at sea level is taken as standard pressure (760 mm Hg = 760 torr = 1 atm = 101.3 kPa). The freezing point of water (0°C or 273 K) is defined as **standard temperature**. Together, these conditions are referred to as **standard temperature and pressure (STP)**. (See Figure 11.23.) The normal conditions under which we live are referred to as **standard ambient temperature and pressure**. These conditions are known as **SATP**, defined as 25°C and 100 kPa.

How could we find what the volume of a gas, measured under different conditions, would be when changed to STP or SATP?



**Figure 11.23** This photograph illustrates typical STP conditions: 0°C at sea level.

Boyle established that pressure and volume are inversely proportional:

$$P_i V_i = P_f V_f$$

Charles found that volume and temperature are directly proportional:

$$\frac{V_i}{T_i} = \frac{V_f}{T_f}$$

Gay-Lussac discovered that pressure has the same relationship to temperature as volume does:

$$\frac{P_i}{T_i} = \frac{P_f}{T_f}$$

Do you notice a pattern here?

Pressure and volume are directly related to temperature, and inversely related to each other. Write this as one law, and it is possible to calculate situations in which three variables change at the same time. The mathematics work out just as consistently as in the two-variable equations.

### CHECKPOINT

Under what conditions might you use standard ambient temperature and pressure as a reference rather than standard temperature and pressure?

## The Combined Gas Law

Boyle's law can be used to solve for changes in volume when pressure changes. The gas must be in a closed system and the temperature must remain constant. You can use Charles' law to solve for changes in volume with temperature changes. This law works only in a closed system in which pressure remains constant. Gay-Lussac's law can solve problems in which the amount and volume of gas remain constant while the temperature and pressure change.

As you learned, Boyle's law ( $V \propto 1/P$ ) is expressed mathematically as  $PV = k$ . Charles' law ( $V \propto T$ ) is expressed mathematically as  $V/T = k_1$  when temperature is recorded in kelvins. Combining these two expressions gives:

$$V \propto \frac{1}{P} \times T \quad \text{or} \quad V \propto \frac{T}{P}$$

Introducing a new proportionality constant ( $k_3$ ), we can write

$$V = \frac{T}{P} \times k_3 \quad \text{or} \quad \frac{PV}{T} = k_3$$

This mathematical relationship is the **combined gas law**.

If a sample of a gas is trapped at a measured set of initial conditions, the combined gas law can be rewritten as

$$\frac{P_i V_i}{T_i} = k_3$$

As this gas is then subjected to changes in pressure and temperature, the final condition of the gas can be described mathematically as

$$\frac{P_f V_f}{T_f} = k_3$$

Since both expressions are equal to the same proportionality constant ( $k_3$ ), the combined gas law can be written as

$$\frac{P_i V_i}{T_i} = \frac{P_f V_f}{T_f}$$

### Sample Problem

#### Finding Volume: The Combined Gas Law

##### Problem

Sandra is having a birthday party on a mild winter's day. The weather changes and a higher-pressure (103.0 kPa) cold front ( $-25^\circ\text{C}$ ) rushes into town. The original air temperature was  $-2^\circ\text{C}$  and the pressure was 100.8 kPa. What will happen to the volume of the 4.2 L balloons that were tied to the front of the house?

##### What Is Required?

You need to find the volume of the balloons under the new conditions of temperature and pressure. ( $V_f = ?$ )

Continued ...

**What Is Given?**

- You know the initial pressure, volume, and temperature.  
 Initial pressure  $(P_i) = 100.8 \text{ kPa}$   
 Initial volume  $(V_i) = 4.2 \text{ L}$   
 Initial temperature  $(T_i) = -2^\circ\text{C}$
- You know the final pressure and temperature.  
 Final pressure  $(P_f) = 103.0 \text{ kPa}$   
 Final temperature  $(T_f) = -25^\circ\text{C}$

**Plan Your Strategy****Algebraic method**

- Since pressure and temperature both change, use the combined gas law to find the final volume of the balloon.
- Since  $T$  is given in  $^\circ\text{C}$ , you need to convert it to kelvins.
- You can rearrange the combined gas law and substitute numbers and units for the variables in the formula to solve for  $V_f$ .

**Ratio method**

- Since pressure and temperature change, you know that the volume of the balloon will also change.
- Since  $T$  is given in  $^\circ\text{C}$ , you need to convert it to kelvins.
- To find the new volume based on the increase in pressure, you need to multiply the initial volume by a pressure ratio that is less than one.
- To find the new volume based on the decrease in temperature, you need to multiply the initial volume by a temperature ratio that is less than one.
- To find the new volume based on both pressure and temperature changes, you can multiply the initial volume by the pressure and temperature ratios.

**PROBLEM TIP**

In these Sample Problems, 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.

**Act on Your Strategy****Algebraic method**

$$T_i = (-2^\circ\text{C} + 273) = 271 \text{ K}$$

$$T_f = (-25^\circ\text{C} + 273) = 248 \text{ K}$$

$$\frac{P_i V_i}{T_i} = \frac{P_f V_f}{T_f}$$

Solve the combined gas law, in this case for  $V_f$ .

To isolate  $V_f$ , move  $T_f$  and  $P_f$ . Multiply  $T_f$  up to the numerator on the left side, and divide  $P_f$  down to the denominator. This leaves

$$\frac{P_i V_i T_f}{T_i P_f} = V_f$$

$$\frac{(100.8 \text{ kPa})(4.2 \text{ L})(248 \text{ K})}{(271 \text{ K})(103.0 \text{ kPa})} = V_f$$

$$V_f = 3.76 \text{ L}$$

So  $V_f = 3.8 \text{ L}$

### Ratio method

$$T_i = (-2^\circ\text{C} + 273) = 271 \text{ K} \qquad T_f = (-25^\circ\text{C} + 273) = 248 \text{ K}$$

$$V_f = V_i \times \text{pressure ratio} \times \text{temperature ratio}$$

$$= 4.2 \text{ L} \times \frac{100.8 \text{ kPa}}{103.0 \text{ kPa}} \times \frac{248 \text{ K}}{271 \text{ K}}$$

$$= 3.76 \text{ L} \approx 3.8 \text{ L}$$

Remember to change the answer to correct significant digits. The least number of digits in the question was two, so the answer must have only two significant digits.  $V_f = 3.8 \text{ L}$ .

### Check Your Solution

- The unit for the answer is in litres.
- When the units cancel out, L remains.
- The volume of the balloon has decreased, as would be expected when pressure increases and temperature decreases.

## Sample Problem

### Combined Gas Law

#### Problem

An automated instrument has been developed to help drug-research chemists determine the amount of nitrogen in a compound. Any compound containing carbon, nitrogen, and hydrogen is reacted with copper(II) oxide to produce  $\text{CO}_2$ ,  $\text{H}_2\text{O}$ , and  $\text{N}_2$  gases. The gases are collected separately and analyzed.

In an analysis of 39.8 mg of caffeine using this instrument, 10.1 mL of  $\text{N}_2$  gas is produced at  $23^\circ\text{C}$  and 746 torr. What must the new temperature of nitrogen be, in  $^\circ\text{C}$ , if the volume is increased to 12.0 mL, and the pressure is increased to 780 torr?

#### What Is Required?

You need to find the temperature of the nitrogen under the new conditions of volume and pressure. ( $T_f = ?$ )

**What Is Given?**

- You know the initial pressure, volume, and temperature.  
 Initial pressure  $(P_i) = 746 \text{ torr}$   
 Initial volume  $(V_i) = 10.1 \text{ mL}$   
 Initial temperature  $(T_i) = 23^\circ\text{C}$
- You know the final pressure and volume.  
 Final pressure  $(P_f) = 780 \text{ torr}$   
 Final volume  $(V_f) = 12.0 \text{ mL}$

**Plan Your Strategy****Algebraic method**

- Since pressure and volume both change, you will need to use the combined gas law formula to find the final temperature of the nitrogen.
- Since  $T$  is given in  $^\circ\text{C}$ , you need to convert it to kelvins.
- You can rearrange the combined gas law and substitute numbers and units for the variables in the formula to solve for  $T_f$ .

**Ratio method**

- Since pressure and volume change, you know that the temperature of the nitrogen will also change.
- Since  $T$  is given in  $^\circ\text{C}$ , you need to convert it to kelvins.
- To find the new temperature based on the increase in pressure, you need to multiply the initial volume by a pressure ratio that is greater than one.
- To find the new temperature based on an increase in volume, you need to multiply the initial temperature by a volume ratio that is less than one.
- To find the new temperature based on both pressure and volume changes, you can multiply the initial temperature by the pressure and volume ratios.

**Act on Your Strategy****Algebraic method**

$$T_i = (23^\circ\text{C} + 273) = 296 \text{ K}$$

$$\frac{P_i V_i}{T_i} = \frac{P_f V_f}{T_f}$$

Divide both sides by  $P_f V_f$  to isolate  $T_f$ .

$$\frac{P_i V_i}{T_i P_f V_f} = \frac{1}{T_f}$$

Now flip both sides of the equation over:

$$\frac{T_i P_f V_f}{P_i V_i} = \frac{T_f}{1}$$

Alternatively, you could have divided down  $P_i V_i$  and multiplied both  $T_f$  and  $T_i$  up. This is an equally correct procedure and the result would be the same. Put in the numbers:

$$\frac{(296 \text{ K})(780 \text{ torr})(12.0 \text{ mL})}{(746 \text{ torr})(10.1 \text{ mL})} = T_f$$

$$T_f = 368 \text{ K}$$

Since the question asks for the temperature in  $^{\circ}\text{C}$ , you need to convert kelvins to  $^{\circ}\text{C}$ . To do this, subtract 273 from the answer.

$$T_f = (368 - 273)$$

$$= 95^{\circ}\text{C} \quad (\text{Note the correct number of significant digits.})$$

### Ratio method

$$T_i = (23^{\circ}\text{C} + 273) = 296 \text{ K}$$

$$T_f = T_i \times \text{pressure ratio} \times \text{temperature ratio}$$

$$= 296 \text{ K} \times \frac{780 \text{ torr}}{746 \text{ torr}} \times \frac{12.0 \text{ mL}}{10.1 \text{ mL}}$$

$$= 368 \text{ K}$$

Since the question asks for the temperature in  $^{\circ}\text{C}$ , you need to convert kelvins to  $^{\circ}\text{C}$ . To do this, subtract 273 from the answer.

$$T_f = (368 - 273)$$

$$= 95^{\circ}\text{C} \quad (\text{Note the correct number of significant digits.})$$

### Check Your Solution

- The unit for the answer is in degrees Celcius.
- The temperature of the nitrogen has increased, as would be expected when pressure and volume increase.

## Practice Problems

- A sample of gas has a volume of 150 mL at 260 K and 92.3 kPa. What will the new volume be at 376 K and 123 kPa?
- A cylinder at 48 atm pressure and 290 K releases 35 mL of carbon dioxide gas into a 4.0 L container at 297 K. What is the pressure inside the container?
- In a large syringe, 48 mL of ammonia gas at STP is compressed to 24 mL and 110 kPa. What must the new temperature of the gas be?
- A 100 W light bulb has a volume of 180.0  $\text{cm}^3$  at STP. The light bulb is turned on and the heated glass expands slightly, changing the volume of the bulb to 181.5  $\text{cm}^3$  with an internal pressure of 214.5 kPa. What is the temperature of the light bulb (in  $^{\circ}\text{C}$ )?
- Sulfur hexafluoride,  $\text{SF}_{6(g)}$ , is used as a chemical insulator. A 5.0 L sample of this gas is collected at 205.0 $^{\circ}\text{C}$  and 350 kPa. What pressure must be applied to this gas sample to reduce its volume to 1.7 L at 25 $^{\circ}\text{C}$ ?



## Gases and Natural Phenomena

Gases under pressure are responsible for natural phenomena such as volcanoes and geysers. On March 20, 1980, residents in the northern part of Washington state heard a rumble from the mountains. They were told it was only a minor earthquake. By March 27, seismologists were sure that something more was involved. Deep inside one of the mountains, Earth's crust was moving. The lower portion of the crust was melting into hot liquid called *magma*. The magma started rising up through cracks in the crust. Trapped water quickly turned into superheated steam. Trapped gases added to the increasing pressure inside the mountain. Then, on May 18, 1980, the top half of Mount St. Helens blew away in a gigantic explosion. It released all of the built-up pressure, along with many tonnes of rock and ash, twenty kilometres into the atmosphere. It also released steam, and gases such as carbon dioxide, nitrogen, and sulfur dioxide. (See Figure 11.24.)

**Figure 11.24** Before a volcano erupts, there is a tremendous build-up of fluid and gas pressures inside the volcano due to magma, steam, and gases.



**Figure 11.25** Geysers form in areas of early volcanic activity or after a volcanic blast. They should be approached with caution since the hot water that erupts can cause severe burns.

Other gases released in volcanic explosions include the oxides, sulfides, and chlorides of carbon, sulfur, hydrogen, chlorine, and fluorine. These include  $\text{CO}_2$ ,  $\text{CO}$ ,  $\text{SO}_2$ ,  $\text{SO}_3$ ,  $\text{H}_2$ ,  $\text{H}_2\text{S}$ ,  $\text{Cl}_2$ ,  $\text{HCl}$ , and  $\text{F}_2$ . It is estimated that the eruption of Mt. Pinatubo in the Philippines on June 15, 1991 released about  $1.8 \times 10^{10}$  kg of gases and ash into the atmosphere.

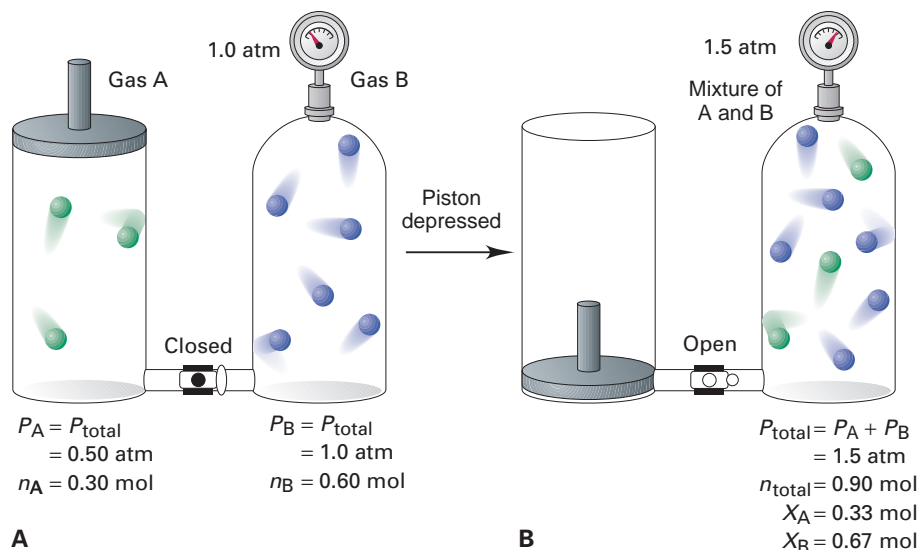
After a volcanic blast, or in an area of volcanic activity, geysers may form. Cool water from Earth's surface trickles down between rocks. It drains deep into Earth's crust, into regions where hot magma is still present. As the water is heated, it forms steam. The steam rises back up through fissures and cracks, meeting more water and heating it up as well. More and more boiling water accumulates, until suddenly, through a narrow opening, the pressurized hot water is violently ejected. As the water cools in the air, it falls back and the process starts again. Yellowstone National Park in the United States has one of the most famous geysers in the world, *Old Faithful*. It erupts approximately once every sixty-five minutes. (Figure 11.25 shows Old Faithful erupting.)

In Chapter 12, you will learn more about the gas chemistry of our atmosphere.

## Dalton's Law of Partial Pressures

What if there are two gases in one container, or as in the case of the atmosphere, a mixture of many gases? How does this affect the pressure?

The English scientist John Dalton did a very thorough analysis of the atmosphere. He concluded that it comprised about 79% nitrogen and 21% oxygen. (See Table 11.2 to find out how close he really was.) Dalton noticed that the water vapour, however, seemed quite variable, so he did further experiments. He obtained some very dry air, and measured the pressure in the container. He then introduced some water vapour. The pressure increased! Dalton repeated and adjusted his experiment time after time, always with the same results. He concluded that *the total pressure of a mixture of gases is the sum of the pressures of each of the individual gases*. This is called **Dalton's Law of partial pressures**. (See Figure 11.27 below.)



**Table 11.2** Components of the Dry Atmosphere

Components	Percentage
Nitrogen (N <sub>2</sub> )	78.08
Oxygen (O <sub>2</sub> )	20.95
Argon (Ar)	0.93
Carbon dioxide (CO <sub>2</sub> )	0.03
Neon (Ne)	0.002
Other gases	0.008

The action of winds mixes the atmosphere so that the composition of the dry atmosphere is fairly constant over the entire Earth. Water vapour, though an important component of the atmosphere, is not listed in the table. The quantity of water vapour in the air, or *humidity*, is variable. In desert climates, the quantity of water vapour will be very small (low humidity). In tropical areas, or near large bodies of water, the quantity of water vapour in the air can be quite substantial (high humidity).

Dalton extended this idea to enhance what he had discovered about the composition of the atmosphere. If the atmosphere is 79% nitrogen, and the atmospheric pressure on a certain day is, for example, 101.3 kPa, then he concluded that the nitrogen itself must be contributing

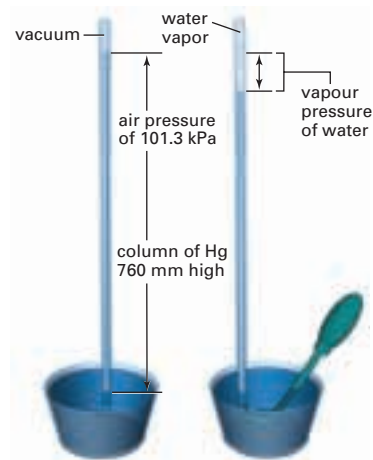
$$\frac{79}{100} \times 101.3 \text{ kPa} = 80 \text{ kPa}$$

The other gases in the atmosphere contribute pressures corresponding to their percentage of the total composition of air.

The generalized form of Dalton's law of partial pressures is

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

This law can be applied to any mixture of gases. Study the following Sample Problem and try the Practice Problems to verify your understanding of how Dalton's law works.



**Figure 11.26** A method of determining water vapour pressure. A drop of water vapourizes in the vacuum and the water vapour exerts a pressure on the mercury in the tube.

**Figure 11.27** Gas A is stored at 0.5 atm and gas B at 1.0 atm. When gas A is added to gas B, the total pressure exerted is now 1.5 atm while the volume of the flask remains the same.



## Sample Problem

### Applying Dalton's Law of Partial Pressures

#### Problem

What is the pressure contribution of  $\text{CO}_2$  to the atmospheric pressure on a very dry day when the barometer read 0.98 atm? Convert your answer into three different units.

#### What Is Required?

You must find the contribution of  $\text{CO}_2$  to the atmospheric pressure, and then convert the units.

#### What Is Given?

- According to Table 11.2,  $\text{CO}_2$  contributes 0.03% of the atmospheric pressure. The total atmospheric pressure is 0.98 atm. The conversion factors of pressure are  
 $1 \text{ atm} = 760 \text{ torr} = 760 \text{ mm Hg} = 101.3 \text{ kPa}$

#### Plan Your Strategy

- You need to multiply the total atmospheric pressure times  $\text{CO}_2$ 's contribution to the total.
- Then you can multiply the answer in atm by the conversion factors to cancel out atm and obtain other units.

#### Act on Your Strategy

$$\frac{0.03}{100} \times 0.98 \text{ atm} = 2.9 \times 10^{-4} \text{ atm}$$

$$2.9 \times 10^{-4} \text{ atm} \times \frac{101.3 \text{ kPa}}{1 \text{ atm}} = 0.030 \text{ kPa}$$

$$2.9 \times 10^{-4} \text{ atm} \times \frac{760 \text{ torr}}{1 \text{ atm}} = 0.22 \text{ torr} = 0.22 \text{ mm Hg}$$

#### Check Your Solution

- The answers given are all very small. This is expected, as  $\text{CO}_2$  only contributes a small percentage of gas molecules to the atmosphere.

### Practice Problems

22. To speed up a reaction in a vessel pressurized at 98.0 kPa, a chemist added 202.65 kPa of hydrogen gas. What was the resulting pressure?
23. A gas mixture contains 12% Ne, 23% He, and 65% Rn. If the total pressure is 116 kPa, what is the partial pressure of each gas?
24. The partial pressure of argon gas, making up 40% of a mixture, is 325 torr. What is the total pressure of the mixture in kPa?
25. A mixture of nitrogen and carbon dioxide gas is at a pressure of 1.00 atm and a temperature of 278 K. If 30% of the mixture is nitrogen, what is the partial pressure of the carbon dioxide?

## Molar Mass and Gas Behaviour

In the following ThoughtLab, you will examine one more factor affecting gas behaviour:

### ThoughtLab



### Boiling Points of Gases

What effect does molar mass have on the behaviour of a gas? In fact, molar mass helps to determine whether a compound or element is gaseous or not. You will examine the connection between boiling point and molar mass here.

**Table 11.3** The Boiling Points of Various Gases

Gas	Boiling Point ( $^{\circ}\text{C}$ )
He	-269
Ne	-246
$\text{N}_2$	-196
Ar	-186
$\text{O}_2$	-183
Kr	-153
Xe	-108

#### Materials

graph paper; periodic table

#### Procedure

1. Using a periodic table, record the molar mass of each of the gases listed in the table.
2. Plot a graph of boiling points of gases (y-axis) versus their molar masses (x-axis).

#### Analysis

1. From the graph obtained, what relationship exists between the molar mass of a gas and its boiling point?
2. Using the graph, what would be the boiling points of gases such as hydrogen ( $\text{H}_2$ ), fluorine ( $\text{F}_2$ ) and radon ( $\text{Rn}$ )?
3. Predict whether a substance such as bromine ( $\text{Br}_2$ ) would be a gas or liquid at room temperature. Use a reference book to check your answer.

## Section Wrap-up

In this section, you learned how to use the combined gas law for gas calculations. You also learned about natural phenomena that are related to gases. Finally, you learned about Dalton's law of partial pressures. In Chapter 12, you will learn more about gas laws. First, however, you will take a closer look at some technological applications of the gas laws.

## Section Review

- 1 **K/U** In a large syringe, 48 mL of ammonia gas at STP is compressed to 24 mL and 110 kPa. What must the new temperature of the gas be? Explain the result in terms of kinetic molecular theory.
- 2 **I** Design an investigation to test Dalton's law of partial pressure. Write a procedure and list the materials and equipment you need.
- 3 **C** Explain Dalton's law of partial pressure.
- 4 **K/U** What are the main components of the atmosphere?
- 5 **MC** Popcorn pops as the water in the kernel is vapourized. The building pressure becomes too much for the shell of the kernel, and it explodes. Explain, using your knowledge of the behaviour of gases, what happens to the temperature just before and just after the kernel pops. (Use a diagram to help you to visualize the situation.)