12.1 Avogadro's Law and Molar Volume

What happens when we change the quantity (number of molecules, or mass) of a gas? So far, we have considered the relationships between the pressure, volume, and temperature of a constant amount of gas. How does the amount of a gas change this relationship? The early study of gases was primarily empirical: it was based on experimental evidence and observations. Indeed, Charles' law and Boyle's law were published before Dalton's atomic theory in 1803. The kinetic molecular theory followed in 1860, neatly offering an explanation for the laws. Before any theory is accepted by the scientific community, supporting evidence must be provided. The more situations a theory can explain, the better the theory. In Chapter 11, we used experimental data to develop the individual gas laws. In this section, we will use the predictive power of the kinetic molecular theory to extend our understanding of gases.

Figure 1 Electrical energy can be used to decompose water and separately collect hydrogen and oxygen gas. The battery is connected to electrodes inside inverted test tubes.

The Law of Combining Volumes

Electrical energy can be used to decompose water into its elements (**Figure 1**). Reactions occur at the two electrodes due to the electric current supplied by the battery. Oxygen and hydrogen gas bubbles are produced during the reaction:

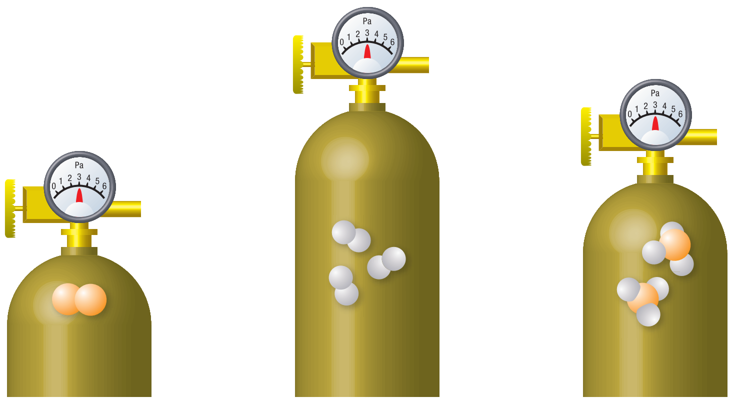
$$2\ H_2O(l) + \text{energy} \rightarrow 2\ H_2(g) + O_2(g)$$

Each water molecule consists of 2 hydrogen atoms and 1 oxygen atom. When water decomposes, therefore, twice the volume of hydrogen as oxygen is trapped in the collection tubes.

In 1808, French scientist Joseph Gay-Lussac measured the relative volumes of gases involved in various chemical reactions. His observations showed that the volumes of gaseous reactants and products of chemical reactions are always in simple, whole-number ratios. For example, when he combined hydrogen, $H_2(g)$, and chlorine, $Cl_2(g)$, to produce hydrogen chloride, $HCl(g)$, he found that 1.0 unit volume of hydrogen added to 1.0 unit volume of chlorine always produced 2.0 units of hydrogen chloride. Gay-Lussac formulated the **law of combining volumes**, which states that gases always react to produce products in whole-number ratios.

law of combining volumes the statement that, when measured at the same temperature and pressure, volumes of gaseous reactants and products of chemical reactions are always in simple ratios of whole numbers

Consider another example. Ammonia gas can be produced by combining nitrogen, $N_2(g)$, and hydrogen, $H_2(g)$ (**Figure 2**).



	$N_2(g)$	+	$3\ H_2(g)$	$\longrightarrow$	$2\ NH_3(g)$
coefficients	1		3		2
mole ratio	1	:	3	:	2
volume ratio	1	:	3	:	2

Figure 2 One volume of nitrogen reacts with 3 volumes of hydrogen, producing 2 volumes of ammonia, when all are measured at the same temperature and pressure.

Here, 1 unit volume of nitrogen reacts with 3 unit volumes of hydrogen to produce 2 unit volumes of ammonia. While Gay-Lussac proposed the law of combining gases, he did not have an explanation for it. Remember that at the time, the kinetic molecular theory had not yet been developed. It would take another scientist, Amedeo Avogadro, to propose an explanation for the law of combining volumes.

Avogadro's Law

Consider this thought experiment. How can two samples of gas that contain particles of different mass have equal pressures at the same temperature? Imagine samples of two different gases, perhaps hydrogen and oxygen, in two identical containers. The volume, temperature, and pressure are the same for both gas samples. Temperature is a measure of the average kinetic energy of entities in a sample (Section 11.1). Using the kinetic molecular theory, we know that, at a given temperature, all gas entities have the same average kinetic energy regardless of their size or mass. Since the temperature of the two samples is the same, the average kinetic energy of the entities in the two samples is the same. Any difference in pressure exerted on the walls of the containers can only be due to the number of entities present. We have already declared that the pressures are equal, so we therefore conclude that there must be an equal number of entities in the two containers (**Figure 3**). The Italian scientist Amedeo Avogadro made similar observations.

LEARNING **TIP**

Thought Experiment
A "thought experiment" is a way to solve a problem using your imagination. In a thought experiment, instead of carrying out an actual experiment, you imagine the practical outcome.

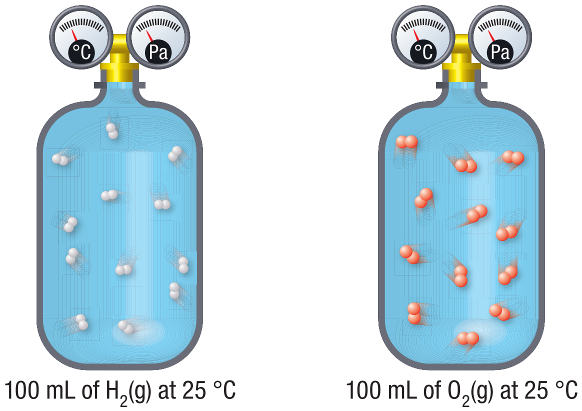


Figure 3 Under identical conditions, equal volumes of gases contain the same number of entities

Shortly after the law of combining volumes was discovered, Avogadro proposed an explanation. He was testing the laws developed by other scientists. His observations led him to combine Gay-Lussac's, Charles', and Boyle's laws to form a hypothesis that stated: Equal volumes of gases, at the same temperature and pressure, contain the same number of molecules. Avogadro's hypothesis provided a way to predict the volumes of gases, either reactants or products, involved in a chemical reaction. In this way, it explained the law of combining volumes. As Avogadro's hypothesis explains, the mole ratios provided by the balanced equation are also the ratios of volumes (Figure 2).

At the time, Avogadro's hypothesis was met with great skepticism and dismissed for over 50 years. Since then, this hypothesis has been thoroughly tested and is now accepted as a law. It is extraordinary that Avogadro was able to develop such a concept before the kinetic molecular theory was developed.

Consider an extension of our thought experiment. Take the two identical containers of gases mentioned earlier, and now connect them with a tube with a closed valve. The volumes, pressures, temperatures, and amounts are equal in the two containers. Now open the valve. What happens to the pressure, temperature, volume, and number of gas molecules? Pressure and temperature are still identical, but we can see how the volume doubles as the amount of gas doubles.

Avogadro's law the statement that the volume of a gas is directly related to the amount of gas, when the temperature and pressure of the gas remain constant; equal volumes of gases, under identical conditions, contain the same number of entities

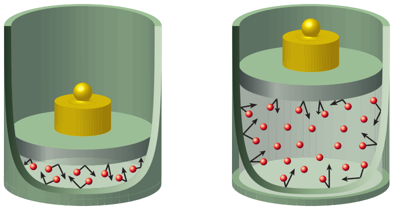


Figure 4 The volume of a gas and the number of moles of gas present are directly proportional when temperature and pressure remain constant.

Avogadro's hypothesis is now known as **Avogadro's law**: the volume (V) of a gas is directly related to the amount (n) of the gas when temperature and pressure remain constant (**Figure 4**):

$$\frac{V_1}{n_1} = \frac{V_2}{n_2} \quad \text{or} \quad \frac{V}{n} = \text{constant}$$

This expression is sometimes referred to as Avogadro's hypothesis, Avogadro's theory, or even Avogadro's principle. All these names refer to the same concept.

Tutorial 1 Using Avogadro's Law

We can use Avogadro's law to calculate the volume of a gas when we know the amount of gas.

Sample Problem 1: Using Avogadro's Law to Determine Volume

A balloon with a volume of 34.5 L is filled with 3.2 mol of helium gas. To what volume will the balloon expand if another 8.0 g of helium is added? (Assume that pressure and temperature do not change.)

Given: Identify the known variables. Note what variables are being held constant.

$$\text{initial volume, } V_1 = 34.5 \text{ L}$$

$$\text{initial amount of gas, } n_1 = 3.2 \text{ mol}$$

$$\text{final amount of gas, } n_2 = n_1 + n_{\text{He added}}$$

$$\text{mass of helium added, } m_{\text{He added}} = 8.0 \text{ g}$$

$$\text{molar mass of helium added, } M_{\text{He}} = 4.00 \text{ g/mol}$$

The pressure and temperature remain constant.

Required: Identify the unknown variable.

$V_2 = ?$

Analysis: Use Avogadro's law to find the final volume of helium.

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

Solution:

Step 1. Determine the amount of helium added, n_{He}, using the appropriate conversion factor derived from the molar mass of helium.

$$n_{\text{He added}} = m_{\text{He added}} \times \frac{1 \text{ mol}}{4.00 \text{ g}}$$

$$= 8.0 \cancel{\text{g}} \times \frac{1 \text{ mol}}{4.00 \cancel{\text{g}}}$$

$$n_{\text{He added}} = 2.0 \text{ mol}$$

Step 2. Determine the final total amount of helium, n_2

$$n_2 = n_1 + n_{\text{He added}}$$

$$= 3.2 \text{ mol} + 2.0 \text{ mol}$$

$$n_2 = 5.2 \text{ mol}$$

Step 3. Rearrange the Avogadro's law equation to isolate the unknown variable, substitute in the known values, and solve the equation.

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

$$V_2 = \frac{34.5 \text{ L} \times 5.2 \cancel{\text{mol}}}{3.2 \cancel{\text{mol}}}$$

$$V_2 = 56 \text{ L}$$

Statement: The balloon will expand to 56 L when the additional helium is added. Check your answer. Does it make sense? Are the units appropriate?

Practice

SKILLS HANDBOOK A6

1. If 2.4 mol of a gas (n_1) occupies a volume of 43 L (V_1), what volume (V_2) will 4.8 mol (n_2) of the same gas occupy? Assume pressure and temperature are kept constant. T/I [ans: 86 L]
2. A sample containing 1.80 mol of argon gas has a volume of 10.00 L. What is the new volume of the gas, in litres, when each of the following changes occurs in the quantity of the gas? Assume that pressure and temperature remain constant. The changes are not cumulative. T/I
   (a) An additional 1.80 mol of argon gas is added to the container. [ans: 20.0 L]
   (b) A sample of 25.0 g of argon gas is added to the container. [ans: 13.5 L]
   (c) A hole in the container allows half of the gas to escape. [ans: 5.00 L]
3. A balloon that contains 4.80 g of carbon dioxide gas has a volume of 12.0 L. Assume that the pressure and temperature of the balloon remain constant. What is the new volume of the balloon if an additional 0.50 mol of CO_2 is added? T/I [ans: 67 L]

Molar Volume

Avogadro's law tells us that equal volumes of any gas at the same temperature and pressure contain an equal number of entities. Incorporating the mole concept, we can understand that one mole of chlorine gas, Cl_2(g), and one mole of methane gas, CH_4(g), under identical conditions of pressure and temperature, should occupy the same volume. The **molar volume** is the volume occupied by one mole of a gas. It is the same for all gases.

- One mole of any gas at standard temperature and pressure (STP, 0 °C and 101.325 kPa) occupies 22.4 L (**Figure 5**).
- One mole of any gas at standard ambient temperature and pressure (SATP, 25 °C and 100 kPa) occupies 24.8 L.

molar volume the volume that one mole of gas occupies at a specified temperature and pressure

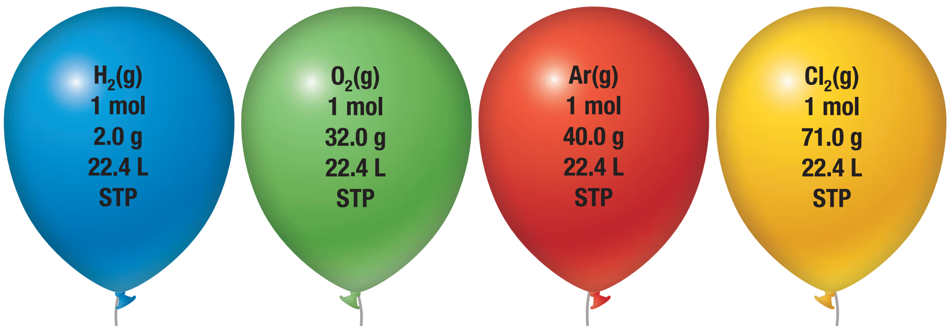


Figure 5 At STP, one mole of any gas occupies 22.4 L of volume.

LEARNING TIP

How Big Is 22.4 L?
To help picture how much space 22.4 L occupies, imagine about twenty-two 1 L milk cartons or eleven 2 L pop bottles, or a box 50 cm × 20 cm × 22 cm.

Tutorial 2 Converting among Amount, Mass, and Volume

When making conversions among the amount, mass, and volume of a gas, remember to note whether the conditions are STP or SATP. Use **Figure 6** as a reminder when converting between amount and volume using molar volume at STP.

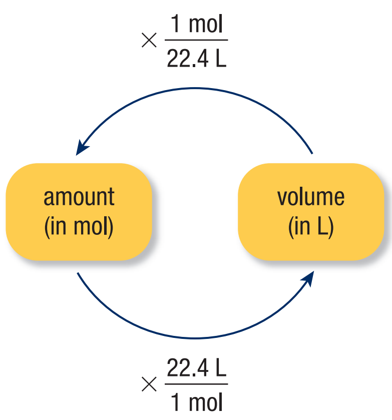


Figure 6 Converting from amount to volume of a gas using molar volume at STP

Sample Problem 1: Converting from Amount to Volume

A party balloon has 2.50 mol of helium gas in it at STP. What is the volume of the balloon?

Given: amount of helium, n = 2.50 mol; STP conditions

Required: volume, V

Analysis: To solve this problem, multiply the amount of helium gas in the balloon by the appropriate conversion factor derived from the molar mass ratio at STP. Since 1 mol of any gas at STP occupies 22.4 L, the following conversion factors may be considered: 22.4 L/1 mol or 1 mol/22.4 L. In this case, we use the factor, 22.4 L/1 mol as follows:

$$V = n \times \frac{22.4\ \text{L}}{1\ \text{mol}}$$

Solution: Substitute in the known values and solve the mathematical equation.

$$V = 2.50\ \cancel{\text{mol}} \times \frac{22.4\ \text{L}}{1\ \cancel{\text{mol}}}$$

$$= 56.0\ \text{L}$$

Statement: The balloon containing 2.50 mol of helium gas has a volume of 56.0 L at STP.

Sample Problem 2: Converting from Mass to Volume

A sample of helium at SATP has a mass of 32.0 g. What volume does this mass of gas occupy?

Given: $m_{He} = 32.0$ g; $M_{He} = 4.00$ g/mol

Required: volume of helium, V_{He}

Analysis: $V = n \times \frac{24.8\ \text{L}}{1\ \text{mol}}$

Solution:

Step 1. Determine the amount of helium gas in the sample by multiplying the mass of helium by an appropriate conversion factor derived from the molar mass of helium.

$$n_{He} = m_{He} \times \frac{1\ \text{mol}}{4.00\ \text{g}}$$

$$= 32.0\ \cancel{\text{g}} \times \frac{1\ \text{mol}}{4.00\ \cancel{\text{g}}}$$

$$n_{He} = 8.00\ \text{mol}$$

Step 2. Determine the volume of helium gas in the sample by multiplying the amount of helium by an appropriate conversion factor derived from the molar volume of a gas at SATP. In this case, the necessary conversion factor is 24.8 L/mol.

$$V_{He} = n \times \frac{24.8\ \text{L}}{1\ \text{mol}}$$

$$V_{He} = 8.00\ \text{mol} \times 24.8\ \text{L/mol}$$

$$V_{He} = 198\ \text{L}$$

Statement: The volume of 32.0 g of helium gas is 198 L at STP.

Practice

SKILLS HANDBOOK A6

1. Determine the volume occupied by the following amounts of nitrous oxide, $N_2O(g)$, at STP: T/I
   (a) 1.0 mol [ans: 22 L]
   (b) 2.0 mol [ans: 45 L]
   (c) 4.5 mol [ans: 1.0×10^2 L]
2. A container of oxygen gas has a volume of 145.6 L. If the pressure of the gas is 101.3 kPa and the temperature is 0 °C, determine the amount of oxygen gas in the container. T/I [ans: 6.500 mol]
3. Determine the mass of hydrogen gas collected in a container if the gas occupies 44.8 L at STP. T/I [ans: 4.04 g]

12.1 Summary

- Gay-Lussac's law of combining volumes states that volumes of gaseous reactants and products of chemical reactions, when measured at the same temperature and pressure, are always in simple ratios of whole numbers.
- Avogadro's law states that the volume of a gas is directly proportional to the amount of the gas when the temperature and pressure of the gas remain constant:

$$\frac{V_1}{n_1} = \frac{V_2}{n_2} \quad \text{or} \quad \frac{V}{n} = \text{constant}$$

- The molar volume of a gas is the volume that one mole of a gas occupies at a specific temperature and pressure. The molar volume of any gas at STP is 22.4 L/mol; the molar volume of any gas at SATP is 24.8 L/mol.

12.1 Questions

1. If you triple the amount of a gas in a balloon, what happens to the volume of the balloon? (Assume that temperature and pressure remain constant.) T/I
2. Determine the volume of 1.5 mol of butane gas if a 2.5 mol sample of butane has a volume of 38.5 L. Assume temperature and pressure are kept constant. T/I
3. Use the molar volume of a gas at SATP to determine the following values at SATP: T/I
   (a) the amount of nitrogen in 44.8 L of pure gas
   (b) the volume (in litres) of 4.8 mol of propane gas, $C_3H_8(g)$
   (c) the mass of carbon dioxide in 34.6 L of carbon dioxide gas, $CO_2(g)$
   (d) the volume (in mL) of 1250 g of methane, $CH_4(g)$
   (e) the amount of oxygen in 36.5 L of O_2 gas
4. Hydrogen gas is produced when we react magnesium metal with hydrochloric acid:

   $Mg(s) + 2\,HCl(aq) \rightarrow MgCl_2(aq) + H_2(g)$ T/I

   (a) If 4.50 g of hydrogen gas is collected at STP, what volume of hydrogen does this represent?
   (b) If 0.52 mol of magnesium completely reacted, what amount of hydrogen gas (in moles) would be produced at STP? How many grams of hydrogen is this?
5. Suppose you are pumping air into a deflated basketball, so that it is at a suitable pressure to play a game. Is this a good example of Avogadro's law? Explain your answer. A
6. When gases are sold they are usually compressed to high pressures. For example, when you buy propane for your barbecue, your tank is placed on a scale while it is filled under high pressure (**Figure 7**). This lets the service person known when the tank is "full." Discuss why gases, such as barbecue propane gas, are sold by mass and not by volume. T/I A

Figure 7 Propane is sold by mass.

7. John McLennan (1867–1935), a University of Toronto research scientist and inventor, devised a unique extraction process to obtain helium from Alberta natural gas. The process brought down the price of helium from \$20 000/m^3 to \$3/m^3. Research McLennan's work. T/I A

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