Skills to Develop

- To relate the amount of gas consumed or released in a chemical reaction to the stoichiometry of the reaction.
- To understand how the ideal gas equation and the stoichiometry of a reaction can be used to calculate the volume of gas produced or consumed in a reaction.

Introduction

With the ideal gas law, we can use the relationship between the amounts of gases (in moles) and their volumes (in liters) to calculate the stoichiometry of reactions involving gases, if the pressure and temperature are known. This is important for several reasons. Many reactions that are carried out in the laboratory involve the formation or reaction of a gas, so chemists must be able to quantitatively treat gaseous products and reactants as readily as they quantitatively treat solids or solutions. Furthermore, many, if not most, industrially important reactions are carried out in the gas phase for practical reasons. Gases mix readily, are easily heated or cooled, and can be transferred from one place to another in a manufacturing facility via simple pumps and plumbing. As a chemical engineer said to one of the authors, "Gases always go where you want them to, liquids sometimes do, but solids almost never do."

Example 6.6.1

Sulfuric acid, the industrial chemical produced in greatest quantity (almost 45 million tons per year in the United States alone), is prepared by the combustion of sulfur in air to give \( \text{SO}_2 \), followed by the reaction of \( \text{SO}_2 \) with \( \text{O}_2 \) in the presence of a catalyst to give \( \text{SO}_3 \), which reacts with water to give \( \text{H}_2\text{SO}_4 \). The overall chemical equation is as follows:

\[
\text{2S}_{(s)} + 3\text{O}_2(g) + 2\text{H}_2\text{O}_{(l)} \rightarrow 2\text{H}_2\text{SO}_4(aq)
\]

What volume of \( \text{O}_2 \) (in liters) at 22°C and 745 mmHg pressure is required to produce 1.00 ton (907.18 kg) of \( \text{H}_2\text{SO}_4 \)?

**Given:** reaction, temperature, pressure, and mass of one product

**Asked for:** volume of gaseous reactant

**Strategy:**

A Calculate the number of moles of \( \text{H}_2\text{SO}_4 \) in 1.00 ton. From the stoichiometric coefficients in the balanced chemical equation, calculate the number of moles of \( \text{O}_2 \) required.

B Use the ideal gas law to determine the volume of \( \text{O}_2 \) required under the given conditions. Be sure that all quantities are expressed in the appropriate units.

**Solution:**

mass of \( \text{H}_2\text{SO}_4 \) → moles \( \text{H}_2\text{SO}_4 \) → moles \( \text{O}_2 \) → liters \( \text{O}_2 \)

A We begin by calculating the number of moles of \( \text{H}_2\text{SO}_4 \) in 1.00 ton:
We next calculate the number of moles of $O_2$ required:

\[
9250\;\text{mol}\;H_2SO_4 \times \frac{3\text{mol}\;O_2}{2\text{mol}\;H_2SO_4} = 1.389 \times 10^4\;\text{mol}\;O_2
\]

After converting all quantities to the appropriate units, we can use the ideal gas law to calculate the volume of $O_2$:

\[
V = \frac{nRT}{P} = \frac{1.389 \times 10^4\;\text{mol} \times 0.08206\;\frac{\text{L} \cdot \text{atm}}{\text{mol} \cdot \text{K}} \times (273 + 22)\;\text{K}}{745\;\text{mmHg} \times \frac{1\;\text{atm}}{760\;\text{mmHg}}} = 3.43 \times 10^5\;\text{L}
\]

The answer means that more than 300,000 L of oxygen gas are needed to produce 1 ton of sulfuric acid. These numbers may give you some appreciation for the magnitude of the engineering and plumbing problems faced in industrial chemistry.

Exercise 6.6.1

In Example 5, we saw that Charles used a balloon containing approximately 31,150 L of $H_2$ for his initial flight in 1783. The hydrogen gas was produced by the reaction of metallic iron with dilute hydrochloric acid according to the following balanced chemical equation:

\[
Fe_{(s)} + 2\;HCl_{(aq)} \rightarrow H_{2(g)} + FeCl_{2(aq)}
\]

How much iron (in kilograms) was needed to produce this volume of $H_2$ if the temperature was 30°C and the atmospheric pressure was 745 mmHg?

**Answer:** 68.6 kg of Fe (approximately 150 lb)

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**Collecting gases over water**

As shown in Figure 6.6.1, a common laboratory method of collecting the gaseous product of a chemical reaction is to conduct it into an inverted tube or bottle filled with water, the opening of which is immersed in a larger container of water. Because the gas is less dense than liquid water, it bubbles to the top of the bottle, displacing the water. Eventually, all the water is forced out and the bottle contains only gas. If a calibrated bottle is used (i.e., one with markings to indicate the volume of the gas) and the bottle is raised or lowered until the level of the water is the same both inside and outside, then the pressure within the bottle will exactly equal the atmospheric pressure measured separately with a barometer ($P_{\text{bar.}}$).
Remember, however, when calculating the amount of gas formed in the reaction, the gas collected inside the bottle is not pure. Instead, it is a mixture of the product gas and water vapor. All liquids (including water) have a measurable amount of vapor in equilibrium with the liquid because molecules of the liquid are continuously escaping from the liquid’s surface, while other molecules from the vapor phase collide with the surface and return to the liquid. The vapor thus exerts a pressure above the liquid, which is called the liquid’s vapor pressure. In the case shown in Figure 6.6.1, the bottle is therefore actually filled with a mixture of O₂ and water vapor, and the total pressure is, by Dalton’s law of partial pressures, the sum of the pressures of the two components:

$$P_{\text{tot}} = P_{\text{gas}} + P_{\text{H}_2\text{O}} = P_{\text{bar.}} \tag{6.6.1}$$

If we want to know the pressure of the gas generated in the reaction to calculate the amount of gas formed, we must first subtract the pressure due to water vapor from the total pressure. This is done by referring to tabulated values of the vapor pressure of water as a function of temperature (Table 6.6.1).

**Table 6.6.1: Vapor Pressure of Water at Various Temperatures**

<table>
<thead>
<tr>
<th>T (°C)</th>
<th>P (in mmHg)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>4.58</td>
</tr>
<tr>
<td>15</td>
<td>12.79</td>
</tr>
<tr>
<td>17</td>
<td>14.53</td>
</tr>
<tr>
<td>19</td>
<td>16.48</td>
</tr>
<tr>
<td>21</td>
<td>18.65</td>
</tr>
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<td>23</td>
<td>21.07</td>
</tr>
<tr>
<td>25</td>
<td>23.76</td>
</tr>
<tr>
<td>30</td>
<td>31.82</td>
</tr>
</tbody>
</table>
As shown in Figure 6.6.2, the vapor pressure of water increases rapidly with increasing temperature, and at the normal boiling point (100°C), the vapor pressure is exactly 1 atm. The methodology is illustrated in Example 6.6.2. The only gases that cannot be collected using this technique are those that readily dissolve in water (e.g., NH₃, H₂S, and CO₂) and those that react rapidly with water (such as F₂ and NO₂).

\[ T (°C) \quad P \text{ (in mmHg)} \]

<p>| | |</p>
<table>
<thead>
<tr>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>50</td>
<td>92.51</td>
</tr>
<tr>
<td>70</td>
<td>233.8</td>
</tr>
<tr>
<td>100</td>
<td>760.0</td>
</tr>
</tbody>
</table>

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**Figure 6.6.2 A Plot of the Vapor Pressure of Water versus Temperature.** The vapor pressure is very low (but not zero) at 0°C and reaches 1 atm = 760 mmHg at the normal boiling point, 100°C.

**Example 6.6.2**

Sodium azide (\(\text{NaN}_3\)) decomposes to form sodium metal and nitrogen gas according to the following balanced chemical equation:

\[ 2\text{NaN}_3 \rightarrow 2\text{Na}_{(s)} + 3\text{N}_2\; (g) \]

This reaction is used to inflate the air bags that cushion passengers during automobile collisions. The reaction is initiated in air bags by an electrical impulse and results in the rapid evolution of gas. If the \(\text{N}_2\) gas that results from the decomposition of a 5.00 g sample of \(\text{NaN}_3\) could be collected by displacing water from an inverted flask, as in Figure 6.6.1, what volume of gas would be produced at 21°C and 762 mmHg?

**Given:** reaction, mass of compound, temperature, and pressure
Asked for: volume of nitrogen gas produced

Strategy:

A Calculate the number of moles of $N_2$ gas produced. From the data in Table 6.6.1, determine the partial pressure of $N_2$ gas in the flask.

B Use the ideal gas law to find the volume of $N_2$ gas produced.

Solution:

A Because we know the mass of the reactant and the stoichiometry of the reaction, our first step is to calculate the number of moles of $N_2$ gas produced:

$$\frac{5.00 \text{ g NaN}_3}{(22.99 + 3 \times 14.01) \text{ g/mol}} \times \frac{3 \text{ mol } N_2}{2 \text{ mol NaN}_3} = 0.115 \text{ mol } N_2$$

The pressure given (762 mmHg) is the total pressure in the flask, which is the sum of the pressures due to the $N_2$ gas and the water vapor present. Table 6.6.1 tells us that the vapor pressure of water is 18.65 mmHg at 21°C (294 K), so the partial pressure of the $N_2$ gas in the flask is only:

$$\left(762 - 18.65\right) \text{ mmHg} \times \frac{1 \text{ atm}}{760 \text{ atm}} = 743.4 \text{ mmHg} \times \frac{1 \text{ atm}}{760 \text{ atm}} = 0.978 \text{ atm.}$$

B Solving the ideal gas law for $V$ and substituting the other quantities (in the appropriate units), we get:

$$V = \frac{nRT}{P} = \frac{0.115 \text{ mol} \times 0.08206 \frac{\text{atm} \cdot \text{L}}{\text{mol} \cdot \text{K}} \times 294 \text{ K}}{0.978 \text{ atm}} = 2.84 \text{ L}$$

Exercise 6.6.2

A 1.00 g sample of zinc metal is added to a solution of dilute hydrochloric acid. It dissolves to produce $H_2$ gas according to the equation $Zn(s) + 2 \text{ HCl(aq)} \rightarrow \text{ H}_2(g) + \text{ ZnCl}_2(\text{aq})$. The resulting $H_2$ gas is collected in a water-filled bottle at 30°C and an atmospheric pressure of 760 mmHg. What volume does it occupy?

Answer: 0.397 L

Summary

The relationship between the amounts of products and reactants in a chemical reaction can be expressed in units of moles or masses of pure substances, of volumes of solutions, or of volumes of gaseous substances. The ideal gas law can be used to calculate the volume of gaseous products or reactants as needed. In the laboratory, gases produced in a reaction are often collected by the displacement of water from filled vessels; the amount of gas can then be calculated from the volume of water displaced and the atmospheric pressure. A gas collected in such a way is not pure, however, but contains a significant amount of water vapor. The measured pressure must therefore be corrected for the vapor pressure of water, which depends strongly on the temperature.
Conceptual Problems

1. Why are so many industrially important reactions carried out in the gas phase?

2. The volume of gas produced during a chemical reaction can be measured by collecting the gas in an inverted container filled with water. The gas forces water out of the container, and the volume of liquid displaced is a measure of the volume of gas. What additional information must be considered to determine the number of moles of gas produced? The volume of some gases cannot be measured using this method. What property of a gas precludes the use of this method?

3. Equal masses of two solid compounds (A and B) are placed in separate sealed flasks filled with air at 1 atm and heated to 50°C for 10 hours. After cooling to room temperature, the pressure in the flask containing A was 1.5 atm. In contrast, the pressure in the flask containing B was 0.87 atm. Suggest an explanation for these observations. Would the masses of samples A and B still be equal after the experiment? Why or why not?

Numerical Problems

1. Balance each chemical equation and then determine the volume of the indicated reactant at STP that is required for complete reaction. Assuming complete reaction, what is the volume of the products?
   1. \( \text{SO}_2(g) + \text{O}_2(g) \rightarrow \text{SO}_3(g) \) given 2.4 mol of \( \text{O}_2 \)
   2. \( \text{H}_2(g) + \text{Cl}_2(g) \rightarrow \text{HCl}(g) \) given 0.78 g of \( \text{H}_2 \)
   3. \( \text{C}_2\text{H}_6(g) + \text{O}_2(g) \rightarrow \text{CO}_2(g) + \text{H}_2\text{O}(g) \) given 1.91 mol of \( \text{O}_2 \)

   • During the smelting of iron, carbon reacts with oxygen to produce carbon monoxide, which then reacts with iron(III) oxide to produce iron metal and carbon dioxide. If 1.82 L of \( \text{CO}_2 \) at STP is produced,
     1. what mass of \( \text{CO} \) is consumed?
     2. what volume of \( \text{CO} \) at STP is consumed?
     3. how much \( \text{O}_2 \) (in liters) at STP is used?
     4. what mass of carbon is consumed?
     5. how much iron metal (in grams) is produced?

   • Complete decomposition of a sample of potassium chlorate produced 1.34 g of potassium chloride and oxygen gas.
     1. What is the mass of \( \text{KClO}_3 \) in the original sample?
     2. What mass of oxygen is produced?
     3. What is the volume of oxygen produced at STP?

   • The combustion of a 100.0 mg sample of an herbicide in excess oxygen produced 83.16 mL of \( \text{CO}_2 \) and 72.9 mL of \( \text{H}_2\text{O} \) vapor at STP. A separate analysis showed that the sample contained 16.44 mg of chlorine. If the sample is known to contain only C, H, Cl, and N, determine the percent composition and the empirical formula of the herbicide.

   • The combustion of a 300.0 mg sample of an antidepressant in excess oxygen produced 326 mL of \( \text{CO}_2 \) and 164 mL
of H$_2$O vapor at STP. A separate analysis showed that the sample contained 23.28% oxygen. If the sample is known to contain only C, H, O, and N, determine the percent composition and the empirical formula of the antidepressant.

**Answers**

1. 2.20 g KClO$_3$
2. 0.863 g O$_2$
3. 604 mL O$_2$
4. 5. Percent composition: 58.3% C, 4.93% H, 23.28% O, and 13.5% N; empirical formula: C$_{10}$H$_{10}$O$_3$N$_2$