

# **Chem 170**

## **Stoichiometric Calculations**

### **Module Eight**

Including Gases in Stoichiometric Calculations

## Introduction to Module Eight

The mass of a gaseous reactant or product can be measured by collecting it in a suitable flask that has been previously weighed while evacuated. The difference between the flask's weight with the gas and when evacuated gives the grams of gas in the flask. As you might imagine, this is not a convenient experimental approach to working with gases.

## Objectives for Module Eight

Fortunately there are other ways to determine the quantity of a reagent in the gas phase. In this module you will learn of the ideal gas law, which provides a relationship between the moles of gas and three variables – pressure, volume, and temperature – that are easily measured. Using the ideal gas law, you will then solve stoichiometry problems in which the amount of a gas is given in terms of its pressure, volume, and temperature. In completing this module you will master the following objectives:

- to use Boyle's law relating the pressure of a gas to its volume
- to use Charles's law relating the volume of a gas to its temperature
- to use the ideal gas law to evaluate how a change in conditions affects a gas
- to use the ideal gas law to find either the moles, pressure, volume, or temperature of a gas given values for the other three quantities
- to solve stoichiometry problems in which gases are described in terms of their pressure, volume, and temperature

## Properties of Gases

You are well aware from your experiences that matter can take one of three common forms: solid, liquid, and gas. Water, for example, is a solid (ice) at temperatures below 0°C, a gas (steam or water vapor) at temperatures above 100°C, and a liquid at all temperatures in between.<sup>†</sup>

There are several ways in which these forms of water differ from each other. Ice cubes, when placed in a bottle, maintain their shape and volume. Although its volume remains unchanged, when liquid water is placed in a bottle it takes on the shape of that part of the bottle it occupies, conforming to the bottle's curves. Water vapor, however, fills the bottle, assuming both its shape and its volume.

The molecules of water in an ice cube are in an ordered arrangement in which they have relatively little freedom to move, which is why an ice cube maintains its shape. In its liquid state, water molecules are more disordered and are free to move around, although the attractive forces between the molecules prevent them from separating from each other. Molecules of water in the gas phase, however, have no order (which is why a gas expands to fill its container) and move independently of each other. This lack of a specific volume for a gas is an important property and accounts for the fact that gases, unlike solids and liquids, do not have a constant density at a fixed temperature.

Because gas molecules are free to move about their container, they must, of course, collide with each other and with the container's walls. The force of a gas molecule's collisions with the container's wall is called its pressure. The SI unit for pressure is the pascal (Pa), which is equivalent to a force of 1 newton applied to an area of 1 square meter. Standard atmospheric pressure, therefore, is the weight of a column of air extending above a surface with an area of 1 m<sup>2</sup> at 0°C and an elevation of sea level. In SI units the standard atmospheric pressure is 101,325 Pa. For historical reasons, pressure is usually reported using one of several common non-SI units. One such unit is the atmosphere (atm), where standard atmospheric pressure is defined as 1 atm; thus

$$1 \text{ atm} = 101,325 \text{ Pa}$$

Another non-SI unit for pressure is the torr, which is equivalent to the pressure exerted by a 1-mm column of mercury. A column of mercury whose height is 760 mm has a pressure equivalent to standard atmospheric pressure; thus

$$1 \text{ atm} = 760 \text{ torr}$$

Anything that increases the frequency of collisions – more gas molecules, a decrease in volume, or faster moving molecules – produces an increase in pressure. Not surprisingly, pressure, volume, moles, and temperature (which affect the speed with which gas

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<sup>†</sup> These temperatures are valid for a pressure of 1 atmosphere. As we shall see shortly, the properties of a gas also depend on its pressure.

molecules move) are interrelated. The next few sections consider several quantitative relationships between pairs of these parameters and a quantitative relationship between all four parameters.

## Boyle's Law

In the 17th century, Robert Boyle studied the relationship between the pressure exerted on a fixed amount of gas and its volume at constant temperature. Specifically, Boyle noted that pressure and volume are inversely proportional; that is, if the pressure applied to a gas is doubled, its volume is cut in half. We express this mathematically as

$$PV = k_b$$

where  $P$  is the pressure,  $V$  is the volume, and  $k_b$  is a constant. Because the product of pressure and volume is constant for a fixed amount of gas at a constant temperature, we can easily calculate how a change in the pressure or volume of a gas must affect its volume or pressure; thus

$$P_1V_1 = P_2V_2$$

where the subscripts indicate the two sets of conditions.

**Example 1.** An inflated balloon has a volume of 0.60 L at a standard atmospheric pressure of 1 atm. What is its volume when it rises to a height of 6.5 km where the pressure is 0.40 atm?

**Solution.** Using Boyle's law and solving for  $V_2$  gives

$$V_2 = \frac{P_1V_1}{P_2} = \frac{1.0 \text{ atm} \times 0.60 \text{ L}}{0.40 \text{ atm}} = 1.5 \text{ L}$$

## Charles's Law

Here are two observations about gases: hot air balloons rise because heated air expands and becomes less dense and placing a balloon in a freezer will cause it to shrink. Clearly the volume a gas occupies is directly proportional to its temperature. Jacques Charles, who showed that for any gas a plot of volume vs. temperature is a straight-line, first studied this relationship in the late 18th century. Interestingly, when similar plots for different gases, or for the same gas at different pressures, are superimposed and extrapolated to a volume of zero, each extrapolates to the same temperature. This temperature of  $-273.15 \text{ }^\circ\text{C}$  or  $0 \text{ K}$ , is called absolute zero. When using the Kelvin scale for temperature the following relationship holds for a fixed amount of gas at a constant pressure

$$\frac{V}{T} = k_c$$

where  $V$  is the volume of gas,  $T$  is the absolute temperature (Kelvin, not Celsius!), and  $k_c$  is a constant. Because the ratio of volume and absolute temperature is constant for a fixed amount of gas at a constant pressure, we can easily calculate how a change in the volume or the temperature of a gas must affect its temperature or volume; thus

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

where the subscripts indicate the two sets of conditions.

**Example 2.** A balloon is filled with air so that it has a volume of 4.50 L at a temperature of 25°C. It is then placed in a freezer where its temperature is -10°C. What volume of air does the balloon now contain?

**Solution.** First we must convert the temperatures from the Celsius scale to the Kelvin scale; thus the temperature outside the freezer is

$$25 + 273.15 = 298 \text{ K}$$

and the temperature inside the freezer is

$$-10 + 273.15 = 263 \text{ K}$$

Using Charles's law and solving for  $V_2$  gives

$$V_2 = \frac{V_1}{T_1} \times T_2 = \frac{4.50 \text{ L}}{298 \text{ K}} \times 263 \text{ K} = 3.97 \text{ L}$$

## Avogadro's Law

At the beginning of the 19th century, Joseph Louis Guy-Lussac noted that for a fixed pressure and temperature the volumes of two gases reacting together were always in the ratio of simple whole numbers. For example, two volumes of hydrogen gas react with one volume of oxygen gas, producing two volumes of water. Amedeo Avogadro interpreted this result by suggesting that equal volumes of gas at the same temperature and pressure must contain the same number of molecules (or moles) of gas. This is known as Avogadro's law, which we express mathematically as

$$\frac{V}{n} = k_a$$

where  $V$  is the volume the gas occupies,  $n$  is the moles of gas, and  $k_a$  is a constant.

## The Ideal Gas Law

Boyle's law, Charles's law, and Avogadro's law each relate the volume of a gas to a different parameter. Solving each law for volume gives the following three proportional relationships

$$V \propto \frac{1}{P} \quad V \propto T \quad V \propto n$$

We can combine these separate equations into a single equation

$$V \propto \frac{nT}{P} = R \frac{nT}{P}$$

which is usually written as

$$PV = nRT$$

The term  $R$ , which is the proportionality constant, is called the gas constant and has a value of

$$R = 0.082057 \frac{\text{L} \cdot \text{atm}}{\text{mol} \cdot \text{K}}$$

although rounding off to three significant figures (0.0821 L·atm/mol·K) is appropriate for many problems.

The equation  $PV = nRT$  is called the ideal gas law. Including the word “ideal” should set off alarm bells suggesting that this equation applies to “ideal” gases, not real gases.<sup>†</sup> This is, in fact, the case. The ideal gas law is an example of a limiting law; that is, it more accurately predicts the behavior of a gas at the limits of relatively low pressure and relatively high temperature. As long as we limit ourselves to such conditions, we may

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<sup>†</sup> The van der Waals equation provides a better approximation for the behavior of real gases. This equation takes into account the interactions between gas molecules, which affects their motion, and the volume occupied by the molecules themselves, which decreases the volume of space in which the molecules can move. The equation is

$$\left( P + \frac{an^2}{V} \right) (V - nb) = nRT$$

where  $a$  and  $b$  are constants whose values depend on the gas. For this course we will stick with the ideal gas law.

use the ideal gas law as an approximation with errors of less than  $\pm 2\%$  in our calculations.

Because the ideal gas law incorporates Boyle's law and Charles's law, we can use it to solve problems similar to those in Examples 1 and 2. It is also a more powerful equation because we can use it to evaluate the change in one parameter when two or three of the remaining parameters change. Solving the ideal gas law for the gas constant gives

$$R = \frac{PV}{nT}$$

Because  $R$  is a constant, we know that

$$\frac{P_1V_1}{n_1T_1} = \frac{P_2V_2}{n_2T_2}$$

where the subscripts 1 and 2 indicate two sets of conditions.

**Example 3.** A small bubble of methane,  $\text{CH}_4$ , with a volume of 0.65 mL rises from the bottom of swamp where the temperature is  $15^\circ\text{C}$  and the pressure is 2.8 atm, to the swamp's surface where the pressure is 1.0 atm and the temperature is  $31^\circ\text{C}$ . What is the bubble's volume when it reaches the swamp's surface?

**Solution.** Because the moles of methane remains unchanged ( $n_1 = n_2$ ) we may eliminate  $n$  from our equation; thus

$$\frac{P_1V_1}{T_1} = \frac{P_2V_2}{T_2}$$

Converting the temperatures from Celsius to Kelvin gives

$$T_1 = 15 + 273.15 = 288 \text{ K}$$

$$T_2 = 31 + 273.15 = 304 \text{ K}$$

Solving for  $V_2$  and making appropriate substitutions, gives the bubble's volume as

$$V_2 = \frac{P_1V_1T_2}{T_1P_2} = \frac{2.8 \text{ atm} \times 0.65 \text{ mL} \times 304 \text{ K}}{288 \text{ K} \times 1.0 \text{ atm}} = 1.9 \text{ mL}$$

## Using the Ideal Gas Law to Calculate Moles

Our real interest in using the ideal gas law is, of course, to find a simple way to determine the moles of a gas involved in a reaction. If we know the temperature, volume, and pressure of a gas, then calculating the moles of gas is easy; thus

$$n = \frac{PV}{RT}$$

**Example 4.** In the course of an industrial reaction  $2.5 \times 10^5$  L of carbon dioxide,  $\text{CO}_2$ , are added to a reaction mixture at a pressure of 1.2 atm and a temperature of  $330^\circ\text{C}$ . How many moles of  $\text{CO}_2$  were added?

**Solution.** First, we convert the temperature from the Celsius to the Kelvin scale

$$330 + 273.15 = 603 \text{ K}$$

Making appropriate substitutions into the ideal gas law gives the moles of  $\text{CO}_2$  as

$$n = \frac{1.2 \text{ atm} \times (2.5 \times 10^5 \text{ L})}{0.0821 \frac{\text{L} \cdot \text{atm}}{\text{mol} \cdot \text{K}} \times 603 \text{ K}} = 6.1 \times 10^3 \text{ mol CO}_2$$

The same approach can be used to calculate any one of the other variables (pressure, volume, and temperature) given the moles of gas and values for the remaining variables.

**Example 5.** What is the pressure in a 3.47-L container containing 1.53 mol of  $\text{N}_2$  at a temperature of 298 K?

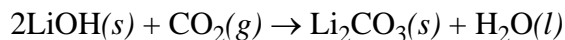
**Solution.** Solving the ideal gas law for pressure and making appropriate substitutions gives

$$P = \frac{nRT}{V} = \frac{1.53 \text{ mol} \times 0.0821 \frac{\text{L} \cdot \text{atm}}{\text{mol} \cdot \text{K}} \times 298 \text{ K}}{3.47 \text{ L}} = 10.8 \text{ atm}$$

## Gases and Stoichiometry Problems

Now that you know how to calculate the moles of a gas given its pressure, volume, and temperature, it is easy to include this in stoichiometry problems. For instance, in Example 2 of Module 5 we calculated the mass of  $\text{CO}_2$  removed by a canister of  $\text{LiOH}$  where





As shown in the next example, we can turn this around and calculate the mass of LiOH needed to remove all the CO<sub>2</sub> in an enclosed space.

**Example 6.** How many grams of LiOH are needed to remove all the CO<sub>2</sub> from the enclosed space of a spaceship whose volume is  $2.4 \times 10^5$  L? The partial pressure of CO<sub>2</sub> is  $7.9 \times 10^{-3}$  atm<sup>†</sup> and the temperature is 296 K.

**Solution.** We begin by using the ideal gas law to calculate the moles of CO<sub>2</sub> needing removal; thus

$$n = \frac{7.9 \times 10^{-3} \text{ atm} \times (2.4 \times 10^5 \text{ L})}{0.0821 \frac{\text{L} \cdot \text{atm}}{\text{mol} \cdot \text{K}} \times 296 \text{ K}} = 78.0 \text{ mol CO}_2$$

Next, we use the reaction's stoichiometry to determine the required moles of LiOH

$$78.0 \text{ mol CO}_2 \times \frac{2 \text{ mol LiOH}}{1 \text{ mol CO}_2} \times \frac{23.95 \text{ g LiOH}}{\text{mol LiOH}} = 3.7 \times 10^3 \text{ g LiOH}$$

This same approach can be applied to any of the stoichiometry problems described in Modules 5 and 6.

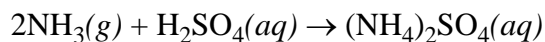
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<sup>†</sup> Perhaps you are wondering why we can state just the pressure of CO<sub>2</sub>, ignoring the presence of other gases (including the O<sub>2</sub> the astronauts need to breathe) that must be present. The answer is that gases in a mixture behave independently of each other. The total pressure, therefore, is a simple summation of the pressures associated with each gas; thus

$$P_{\text{total}} = P_{\text{a}} + P_{\text{b}} + \dots + P_{\text{n}}$$

where  $P_{\text{a}}$ ,  $P_{\text{b}}$ , and  $P_{\text{n}}$  are the partial pressures associated with each gas. Because we are interested only in the pressure of one gas, in this case CO<sub>2</sub>, we may ignore the pressures of other gases.

**Example 7.** Ammonium sulfate,  $(\text{NH}_4)_2\text{SO}_4$ , is used as a fertilizer. One method for its synthesis is by reacting gaseous ammonia,  $\text{NH}_3$ , with sulfuric acid,  $\text{H}_2\text{SO}_4$



How many grams of  $(\text{NH}_4)_2\text{SO}_4$  can be prepared by the reaction of 25.0 L of 3.0 M  $\text{H}_2\text{SO}_4$  with  $3.1 \times 10^3$  L of  $\text{NH}_3$  at a pressure of 1.0 atm and a temperature of 298 K?

**Solution.** To find the reaction's limiting reagent, we first must determine the moles of  $\text{H}_2\text{SO}_4$  and  $\text{NH}_3$ ; thus

$$25.0 \text{ L} \times \frac{3.0 \text{ moles } \text{H}_2\text{SO}_4}{\text{L}} = 75.0 \text{ mol } \text{H}_2\text{SO}_4$$

$$\frac{1.0 \text{ atm} \times (3.1 \times 10^3 \text{ L})}{0.0821 \frac{\text{L} \cdot \text{atm}}{\text{mol} \cdot \text{K}} \times 298 \text{ K}} = 127 \text{ mol } \text{NH}_3$$

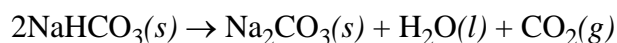
Using the reaction's stoichiometry, 75.0 mol  $\text{H}_2\text{SO}_4$  requires 150 mol  $\text{NH}_3$  to react completely. Because we have less  $\text{NH}_3$  than needed, it is the limiting reagent. The theoretical yield of ammonium sulfate, therefore, is

$$127 \text{ mol } \text{NH}_3 \times \frac{1 \text{ mol } (\text{NH}_4)_2\text{SO}_4}{2 \text{ mol } \text{NH}_3} \times \frac{132.1 \text{ g } (\text{NH}_4)_2\text{SO}_4}{\text{mol } (\text{NH}_4)_2\text{SO}_4} = 8.4 \times 10^3 \text{ g } (\text{NH}_4)_2\text{SO}_4$$

## Practice Problems

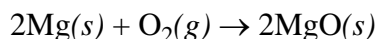
The following problems provide practice in meeting this module's objectives. Answers are provided on the last page. Be sure to seek assistance if you experience difficulty with any of these problems. When you are ready, schedule an appointment for the module exam.

1. At 46°C a gaseous sample of ammonia in a 0.500-L container exerts a pressure of 4.83 atm. What is the pressure of the gas when the volume of its container is compressed to volume of 0.125 L? Assume that the temperature remains constant.
2. The gas evolved during the fermentation of glucose has a volume of 0.788 L at a temperature of 22.8°C. What was the original volume of gas at the fermentation temperature of 36.5°C? Assume that the pressure remains constant.
3. A gas-filled balloon with a volume of 2.8 L at 0.98 atm and a temperature of 25°C is allowed to rise to the earth's stratosphere where the temperature is -23°C and the pressure is 0.00300 atm. What is the balloon's new volume?
4. Workers at a research station in Antarctica collect a sample of air to test for airborne pollutants. To collect the sample they use a 1.00-L container, acquiring the sample when the air pressure is 1.03 atm at a temperature of -20°C. What is the pressure in the container when the sample is opened up in a lab in South Carolina where the temperature is 22°C?
5. Ozone, O<sub>3</sub>, is an important atmospheric molecule because of its ability to absorb harmful UV solar radiation. Assuming that the temperature in the stratosphere is about 250 K and the partial pressure of ozone is  $1.0 \times 10^{-3}$  atm, how many moles of ozone are in every liter of air? How many molecules of ozone is this?
6. Dry ice is solid carbon dioxide. Suppose that a 0.055-g sample of dry ice is placed inside a 4.2-L container at 25.6°C. What is the partial pressure of CO<sub>2</sub> in the container after all the dry ice is converted to gaseous CO<sub>2</sub>?
7. When heated, sodium bicarbonate, NaHCO<sub>3</sub>, decomposes to produce carbon dioxide, CO<sub>2</sub>, for which the balanced reaction is



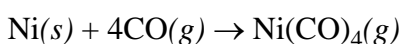
Among its many uses, sodium bicarbonate, which is also known as baking soda, is used as a leavening agent when making doughnuts and quick breads. Calculate the volume of CO<sub>2</sub> produced when 2.35 g NaHCO<sub>3</sub> decompose at a temperature of 350°C and a pressure of 1.05 atm.

8. Magnesium is used as a “getter” in ultrahigh vacuum devices to remove traces of oxygen. When an electric current passes through the magnesium, which is present as a thin wire or ribbon, it reacts with the oxygen to form magnesium oxide



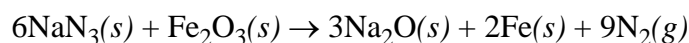
How many nanograms of Mg are required to remove  $4.6 \times 10^{-9}$  atm of  $\text{O}_2$  in a 0.426-L vacuum device at a temperature of  $24.5^\circ\text{C}$ ?

9. In the metallurgical process for refining nickel, reacting it with carbon monoxide volatilizes the metal.



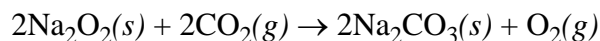
The product, tetracarbonylnickel, is a gas that can be removed from the reaction mixture. Further work-up allows the recovery of nickel metal, but without any of the impurities present in the original sample. If a sample of impure nickel contains 77.4 g Ni, calculate the pressure of  $\text{Ni}(\text{CO})_4$  collected in a 4.00-L storage tank at a temperature of  $43^\circ\text{C}$ . Assume that carbon monoxide is present in excess.

10. The air bags in automobiles are inflated by nitrogen gas generated by the rapid decomposition of sodium azide,  $\text{NaN}_3$ , in the presence of excess iron oxide,  $\text{Fe}_2\text{O}_3$



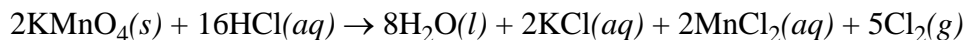
A typical air bag is designed to contain 37 L of nitrogen at a pressure of 1.15 atm and a temperature of  $26^\circ\text{C}$ . How many grams of sodium azide are needed to completely react all the  $\text{N}_2$ ?

11. There are several ways to generate oxygen gas for people working in submarines. One method is to react carbon dioxide,  $\text{CO}_2$ , with sodium peroxide,  $\text{Na}_2\text{O}_2$ , forming sodium carbonate,  $\text{Na}_2\text{CO}_3$ , and oxygen,  $\text{O}_2$ , as products



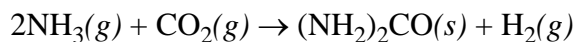
Assuming that the typical person exhales an average of 0.15 L of  $\text{CO}_2$  each minute (at a pressure of 1.0 atm and a temperature of  $25^\circ\text{C}$ ), how many kilograms of sodium peroxide are needed to remove all the  $\text{CO}_2$  released by one person in a single day?

12. One method for generating chlorine gas,  $\text{Cl}_2$ , is by reacting potassium permanganate,  $\text{KMnO}_4$ , and hydrochloric acid,  $\text{HCl}$



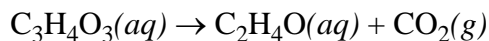
How many liters of  $\text{Cl}_2$  at  $40^\circ\text{C}$  and a pressure of 1.05 atm can be produced by the reaction of 6.23 g  $\text{KMnO}_4$  with 45.0 mL of 6.00 M  $\text{HCl}$ ?

13. Urea,  $(\text{NH}_2)_2\text{CO}$ , is used extensively as a source of nitrogen for fertilizers. It is produced commercially by the reaction of ammonia and carbon dioxide



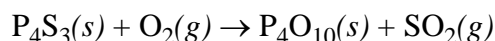
Ammonia is added to an evacuated 5.0-L flask to a pressure of 9.0 atm at a temperature of  $23^\circ\text{C}$ . Carbon dioxide is then added to the same flask, increasing the pressure to 14.0 atm at  $23^\circ\text{C}$ . Upon initiating the reaction, how many grams of urea are expected?

14. One method for determining the amount of pyruvic acid,  $\text{C}_3\text{H}_4\text{O}_3$ , is to catalyze its decomposition using a yeast enzyme. The reaction



produces carbon dioxide, which can be collected and used to determine the amount of pyruvic acid in the original sample. In a typical analysis, 10.7 mL of  $\text{CO}_2$  are obtained at a pressure of 0.983 atm and a temperature of  $31^\circ\text{C}$ . How many grams of pyruvic acid were in the original sample?

15. So called “strike anywhere” matches contain tetraphosphorous trisulfide,  $\text{P}_4\text{S}_3$ . Striking the match leads to a combustion reaction producing tetraphosphorous decaoxide,  $\text{P}_4\text{O}_{10}$ , and sulfur dioxide,  $\text{SO}_2$ . The unbalanced reaction is



Balance the reaction and determine the partial pressure of  $\text{SO}_2$  in a room with a volume of  $2.04 \times 10^4$  L and a temperature of  $24.8^\circ\text{C}$  following the lighting of a box of matches whose combined mass of  $\text{P}_4\text{S}_3$  is 0.800 g?

## Answers to Practice Problems

1. 19.3 atm
2. 0.824 L
3.  $7.7 \times 10^2$  L
4. 1.20 atm
5.  $4.9 \times 10^{-5}$  mol O<sub>3</sub>,  $2.9 \times 10^{19}$  molecules O<sub>3</sub>
6.  $7.3 \times 10^{-3}$  atm
7. 0.681 L
8. 3.9 ng Mg
9. 8.55 atm
10. 75 g NaN<sub>3</sub>
11. 0.69 kg Na<sub>2</sub>O<sub>2</sub>
12. 2.06 L
13. 56 g (NH<sub>2</sub>)<sub>2</sub>CO
14. 0.0371 g C<sub>3</sub>H<sub>4</sub>O<sub>3</sub>
15.  $\text{P}_4\text{S}_3 + 8\text{O}_2 \rightarrow \text{P}_4\text{O}_{10} + 3\text{SO}_2$ ,  $1.31 \times 10^{-5}$  atm