9.11: The Law of Combining Volumes

In effect, the preceding example used the factor *P/RT* to convert from volume to amount of gas. The reciprocal of this factor can be used to convert from amount of gas to volume. This is emphasized if write the Ideal Gas Equation as:

$$V = \frac{RT}{P} n$$

This indicates that when we write a chemical equation involving gases, the coefficients not only tell us what amount of each substance is consumed or produced, they also indicate the relative *volume* of each gas consumed or produced. For example,

$$2\,H_2(g) + O_2(g) \rightarrow 2\,H_2O(g) \tag{9.11.1}$$

means that for every 2 mol $H_2(g)$ consumed there will be 1 mol $O_2(g)$ consumed and 2 mol $H_2O(g)$ produced.

It also implies that for every: $\left(2\text{ mol } \times \frac{RT}{P}\right)\text{ L } H_2$ there will be $\left(1\text{ mol } \times \frac{RT}{P}\right)\text{ L } O_2$ and $\left(2\text{ mol } \times \frac{RT}{P}\right)\text{ L } H_2O$.

In the image below, we see a more literal example. As Gay Lussac discovered, if you mix 2 L of H_2 gas with 1 L of O_2, you get 1 L H_2O. The ratio of volumes matches the stoichiometric ratio of the chemical reaction in Equation 9.11.1. This is an example of the *Law of Combining Volumes*:

Definition: law of combining volumes

When gases combine at constant temperature and pressure, the volumes involved are always in the ratio of simple whole numbers.

Since the factor *RT/P* would be the same for all three gases, the volume of $O_2(g)$ consumed must be half the volume of $H_2(g)$ consumed. The volume of $H_2O(g)$ produced would be only two-thirds the total volume [of $H_2(g)$ and $O_2(g)$] consumed, and so at the end of the reaction the total volume must be less than at the beginning.

The law of combining volumes was proposed by Gay-Lussac at about the same time that Dalton published his atomic theory. Shortly thereafter, Avogadro suggested the hypothesis that equal volumes of gases contained equal numbers of molecules. Dalton strongly opposed Avogadro's hypothesis because it required that some molecules contain more than the minimum number of atoms.

For example, according to Dalton, the formula for hydrogen gas should be the simplest possible, e.g., H. Similarly, Dalton proposed the formula O for oxygen gas. His equation for formation of water vapor was:

$$\underset{\substack{\text{1 volume}\\\text{hydorgen}}}{\text{H}} + \underset{\substack{\text{1 volume}\\\text{oxygen}}}{\text{O}} \rightarrow \underset{\substack{\text{1 volume}\\\text{water vapor}}}{\text{HO}}$$

But experiments showed that twice as great a volume of hydrogen as of oxygen was required for complete reaction. Furthermore, the volume of water vapor produced was twice the volume of oxygen consumed. Avogadro proposed (correctly, as it turned out) that the formulas for hydrogen, oxygen, and water were H_2, O_2 and H_2O, and he explained the volume data in much the same way as we have done for Eq. (2).

Dalton, who had originally conceived the idea of atoms and molecules, was unwilling to concede that substances such as hydrogen or water might have formulas more complicated than was absolutely necessary. Partly as a result of Dalton's opposition, it took almost half a century before Avogadro's Italian countryman Stanislao Cannizzaro (1826 to 1910) was able to convince chemists that Avogadro's hypothesis was correct. The blindness of chemists to Avogadro's ideas for so long makes one wonder whether today's Nobel prize winners might not be equally wrong about some other aspect of chemistry. Who knows but that some forgotten Argentinian Avogadro is still waiting for a Cannizzaro to explain his or her ideas to the scientific world.

Because the amount of gas is related to volume by the ideal gas law, it is possible to calculate the volume of a gaseous substance consumed or produced in a reaction. Molar mass and stoichiometric ratio are employed in the same way as in Section 3.1, and the factor *RT/P* is used to convert from amount of gas to volume.

Example 9.11.1: Volume of Oxygen

Oxygen was first prepared by Joseph Priestly-by heating mercury(II)oxide, HgO, then called "calx of mercury“ according to the equation

$$2\,HgO(s) \rightarrow 2\,Hg(l) + O_2(g)$$

What volume (in cubic centimeters) of O_2 can be prepared from 1.00 g HgO?

The volume is measured at 20°C and 0.987 atm.

Solution The mass of HgO can be converted to amount of HgO and this can be converted to amount of O_2 by means of a stoichiometric ratio. Finally, the ideal gas law is used to obtain the volume of O_2. Schematically,

$$m_{\text{HgO}} \xrightarrow{M_{\text{HgO}}} n_{\text{HgO}} \xrightarrow{S(\text{O}_2/\text{HgO})} n_{\text{O}_2} \xrightarrow{RT/P} V_{\text{O}_2}$$

$$V_{\text{O}_2} = 1 \text{ g HgO} \times \frac{1 \text{ mol HgO}}{216.59 \text{ g HgO}} \times \frac{1 \text{ mol O}_2}{2 \text{ mol HgO}}$$

$$\times \frac{0.0820 \text{ liter atm}}{1 \text{ K mol O}_2} \times \frac{293.15 \text{ K}}{0.987 \text{ atm}} = 0.0562 \text{ liter} = 56.2 \text{ cm}^3$$