1.8.8: Mixtures of Gases - Why Deep-Sea Divers Breathe a Mixture of Helium and Oxygen

> ### 🧠 Learning Objectives
>
> - Explain Dalton's Law of Partial Pressures.

The atmosphere of Venus is markedly different from that of Earth. The gases in the Venusian atmosphere are 96.5% carbon dioxide and 3% nitrogen. The atmospheric pressure on Venus is roughly 92 times that of Earth, so the amount of nitrogen on Venus would contribute a pressure well over 2700 mm Hg. And there is no oxygen present, so we couldn't breathe there. Not that we would want to go to Venus, as the surface temperature is usually over 460^oC.

Dalton's Law of Partial Pressures

Gas pressure results from collisions between gas particles and the inside walls of their container. If more gas is added to a rigid container, the gas pressure increases. The identities of the two gases do not matter. John Dalton, the English chemist who proposed the atomic theory, also studied mixtures of gases. He found that each gas in a mixture exerts a pressure independently of every other gas in the mixture. For example, our atmosphere is composed of about 78% nitrogen and 21% oxygen, with smaller amounts of several other gases making up the rest. Since nitrogen makes up 78% of the gas particles in a given sample of air, it exerts 78% of the pressure. If the overall atmospheric pressure is 1.00 atm, then the pressure of just the nitrogen in the air is 0.78 atm. The pressure of the oxygen in the air is 0.21 atm.

The **partial pressure** of a gas is the contribution that gas makes to the total pressure when the gas is part of a mixture. The partial pressure of nitrogen is represented by P_{N_2}. **Dalton's Law of Partial Pressures** states that the total pressure of a mixture of gases is equal to the sum of all of the partial pressures of the component gases. Dalton's Law can be expressed with the following equation:

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

The figure below shows two gases that are in separate, equal-sized containers at the same temperature and pressure. Each exerts a different pressure, P_1 and P_2, reflective of the number of particles in the container. On the right, the two gases are combined into the same container, with no volume change. The total pressure of the gas mixture is equal to the sum of the individual pressures. If $P_1 = 300 \text{ mm Hg}$ and $P_2 = 500 \text{ mm Hg}$, then $P_{\text{total}} = 800 \text{ mm Hg}$.
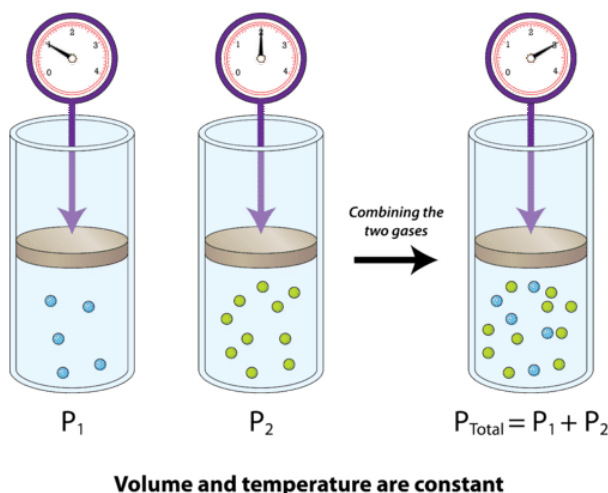

Figure 1.8.8.1: Dalton's Law states that the pressure of a gas mixture is equal to the partial pressures of the combining gases.

Collecting Gases Over Water

You need to do a lab experiment where hydrogen gas is generated. In order to calculate the yield of gas, you have to know the pressure inside the tube where the gas is collected. But how can you get a barometer in there? Very simple: you don't. All you need

is the atmospheric pressure in the room. As the gas pushes out the water, it is pushing against the atmosphere, so the pressure inside is equal to the pressure outside.

Gas Collection by Water Displacement

Gases that are produced in laboratory experiments are often collected by a technique called **water displacement** (Figure 1.8.8.2). A bottle is filled with water and placed upside-down in a pan of water. The reaction flask is fitted with rubber tubing, which is then fed under the bottle of water. As the gas is produced in the reaction flask, it exits through the rubber tubing and displaces the water in the bottle. When the bottle is full of the gas, it can be sealed with a lid.

Figure 1.8.8.2: A gas produced in a chemical reaction can be collected by water displacement.

Because the gas is collected over water, it is not pure, but is mixed with vapor from the evaporation of the water. Dalton's Law can be used to calculate the amount of the desired gas by subtracting the contribution of the water vapor.

$$P_{\text{Total}} = P_g + P_{H_2O}$$

where P_g is the pressure of the desired gas, which can be solved for:

$$P_g = P_{Total} - P_{H_2O}$$

In order to solve a problem, it is necessary to know the vapor pressure of water at the temperature of the reaction (see table below). The sample problem illustrates the use of Dalton's Law when a gas is collected over water.

Table 1.8.8.1: Vapor Pressure of Water (mm Hg) at Selected Temperatures $(^{\circ}\text{C})$

0	5	10	15	20	25	30	35	40	45	50	55	60
4.58	6.54	9.21	12.79	17.54	23.76	31.82	42.18	55.32	71.88	92.51	118.04	149.38

✔ Example 14.14.1

A certain experiment generates $2.58\,\text{L}$ of hydrogen gas, which is collected over water. The temperature is 20°C and the atmospheric pressure is $98.60\,\text{kPa}$. Find the volume that the dry hydrogen would occupy at STP.

Solution

Step 1: List the known quantities and plan the problem.

Known
- $V_{\text{Total}} = 2.58\,\text{L}$
- $T = 20^{\circ}\text{C} = 293\,\text{K}$
- $P_{\text{Total}} = 98.60\,\text{kPa} = 739.7\,\text{mm Hg}$

Unknown
- V_{H_2} at STP $= ?\,\text{L}$

The atmospheric pressure is converted from kPa to mm Hg in order to match units with the table. The sum of the pressures of the hydrogen and the water vapor is equal to the atmospheric pressure. The pressure of the hydrogen is found by subtraction. Then, the volume of the gas at STP can be calculated by using the combined gas law.

Step 2: Solve.

$$P_{H_2} = P_{\text{Total}} - P_{H_2O}$$
$$= 739,7\,\text{mm Hg} - 17.54\,\text{mm Hg}$$
$$= 722.2\,\text{mm Hg}$$

Now the combined gas law is used, solving for V_2, the volume of hydrogen at STP.

$$V_2 = \frac{P_1 \times V_1 \times T_2}{P_2 \times T_1}$$

$$= \frac{722.2 \text{ mm Hg} \times 2.58 \text{ L} \times 273 \text{ K}}{760 \text{ mm Hg} \times 293 \text{ K}}$$

$$= 2.28 \text{ L H}_2$$

Step 3: Think about your result.

If the hydrogen gas were to be collected at STP and without the presence of the water vapor, its volume would be 2.28 L. This is less than the actual collected volume because some of that is water vapor. The conversion using STP is useful for stoichiometry purposes.

Summary

- Dalton's Law of Partial Pressures states that the total pressure in a system is equal to the sum of the partial pressures of the gases present.
- The vapor pressure due to water in a sample can be corrected for, in order to get the true value for the pressure of the gas.