Skills to Develop

- Explain the following laws within the Ideal Gas Law:
  - Avogadro's law of gases
  - Boyle's law of gases
  - Charles's law of gases
  - Dalton's law of partial pressure
- Apply gas laws to solve problems involving gases.

The ABCD Gas Laws

The discovery of natural law is a scientific achievement. In terms of science, we are interested in the laws as well as the strategy leading to discovery. Science is the study of these laws and the development of scientific methods for discovery. The discoveries of gas laws represent some major breakthroughs in our understanding of the gases in the material world. At the dawn of science, experiments were performed on gases at specific conditions. Under these conditions, gas laws were formulated.

A law is a model that mimics the behavior of a system. By applying a gas law, we can predict the outcome of certain parameters when a set of conditions is understood or given. The ABCD gas laws refers collectively to four separately developed laws:

- Avogadro's law,
- Boyle's law,
- Charles's law, and
- Dalton's law of partial pressure

These laws were not discovered in the above order, but we review them in this order. Since you also have some concept of the ideal gas law, we show how they are related to the ideal gas law,

\[ PV = nRT \]

where \( P \), \( V \), \( T \), and \( n \) are pressure, volume, temperature, and amount of gas, respectively. \( R \) is the gas constant.

Note

The ideal gas law is easy to remember and apply in solving problems, as long as you get the proper values and units for the gas constant, \( R \).

Avogadro's Law

Equal volumes of gases have equal numbers of molecules at the same temperature and pressure. This was Avogadro's
hypothesis in order to explain the simple ratios of volumes when gases react with one another. Now, we accept it as a law, because experiment shows that it is always true. Of course, this law can be and has been stated in many ways. Equal numbers of molecules means equal amount in moles.

The Avogadro's law is part of the ideal gas law, \( P V = n R T \), which can be written in the following form:

\[
V = \frac{R T}{P} \times n
\]

At some specific \( T \) and \( P \), the volume is proportional to the amount, \( n \), in moles (a fun link). Amounts of two gases at the same \( T \) and \( P \) are, of course, proportional to their volumes. Thus, when 2 L of hydrogen reacts with 1 L of \( \ce{O2} \), the number of hydrogen molecules are twice those of oxygen molecules. Observations like these led Avogadro to propose the diatomic molecules for these elements, and formulate the chemical reaction as:

\[
\ce{2 H2 + O2 \rightarrow 2 H2O}
\]

The proposal was, and still is, a brilliant scientific reasoning.

**Boyle's Law**

At constant temperature, the pressure is inversely proportional to the volume of a definite amount of gas. This is known as Boyle's law. Robert Boyle (1627-1691) experimented with gas at constant temperature. Using Torricelli’s discovery, Boyle measured the variation of pressure when the volume changes, and discovered that volume is inversely proportional to the pressure, and vice versa.

\[
V = \frac{k_b}{P}
\]

where \( k_b \) is a constant. Boyle's law is also part of the ideal gas law, which can be written in the form:

\[
V = \frac{n R T}{P}
\]

At constant temperature, \( T \), this formulation shows that \( V \) is inversely proportional to \( P \).

**Charles's Law**

Jacques Charles (1746-1823) experimented with gas under constant pressure. In today's language, his discovery is that the volume of a gas is proportional to the temperature in K (kelvin).

\[
V = k_c \cdot T
\]

where \( k_c \) is a constant. You should note that the absolute temperature scale (K) must be used for the above formula to be valid.

Again, Charles's law is also part of the ideal gas law, and the relationship between \( V \) and \( T \) is obvious:

\[
V = \frac{n R}{P} \cdot T
\]
which is the same as the previous one if you assume \(k_c = \frac{nR}{P}\).

By now, you can see that the ideal gas law combines the ABC laws of gases.

Well, there are four quantities in dealing with gases, amount \(n\), volume \(V\), pressure \(P\), and temperature \(T\). The ABC laws of gases give the relationship of any two of these quantities when the other two of them are held constant.

Dalton's Law of Partial Pressures

John Dalton (1766-1844) was the first to discover that in a container containing a mixture of gas, the total pressure is the sum of all partial pressures of its components.

The partial pressure is the pressure due to a particular gas as if it is in the container by itself. Avogadro's law implies that gas molecules of any gas behave exactly the same way. Thus, the pressure exerted by \(n\) mole of any gas, or \(n\) mole of a gas mixture, is the same.

The ideal gas law includes the law of partial pressures, because the total number of moles is the sum of moles of all the components in the mixture.

\[
(n_{\text{total}}) = n_1 + n_2 + n_3 + \ldots + n_n
\]

Since \(n = \frac{V}{RT}\), \(P\),

\[
(n_i = \frac{V}{RT}, P_i),
\]

and

\[
(n_{\text{total}} = \frac{V}{RT}, P_{\text{total}}).
\]

Therefore,

\[
(P_{\text{total}}) = P_1 + P_2 + P_3 + \ldots + P_n
\]

As an example, the pressures of a 1-L container containing 0.10 mol \(\ce{N2}\) and 0.20 mol \(\ce{O2}\) mixture are:

\[
(P_{\ce{N2}}) = 249.4\, \text{Pa}
\]
\[
(P_{\ce{O2}}) = 498.8\, \text{Pa}
\]
\[
(P_{\text{total}}) = 748.2\, \text{Pa}
\]

On the Application of Gas Laws

Boyle's law, Charles's law, Dalton's law and Avogadro's law were discovered at the time when atomic theory and molecular theory began to develop. At that time, only macroscopic properties of gases were measured and these laws were discovered from imprecise measurements. Later, these laws are integrated into a simple ideal gas law for the calculation of gas properties. At temperatures much higher than the critical temperature of the gas, and when the pressure
is not very high, the ideal gas law is adequate to predict the gas properties. However, for industrial and other applications accurate predictions are required, and corrections due to non-ideal behavior must be made.

One of the applications of Dalton’s law is for the correction of pressure when a gas is collected by displacement of water. During this process, the gas collected is saturated by water vapor. Water vapor pressure or partial pressure depends on temperature.

Example

A common method for preparing oxygen is the decomposition of $\text{KClO}_3$ according to the reaction:

$$\text{2 KClO}_3 \rightarrow \text{2 KCl} + 3 \text{O}_2$$

The collection of $\text{O}_2$ gas is usually by displacement of water. In an experiment, 0.250 L of $\text{O}_2$ was collected over water, when the atmospheric pressure was 759 torr, and the temperature of water and the gas was 14 °C. Calculate the amount of $\text{O}_2$ collected in moles. The vapor pressure of $\text{H}_2\text{O}$ at 14 °C is 12.0 torr.

**SOLUTION**

The partial pressure of $\text{O}_2$ is total pressure minus the partial pressure of water vapor.

$$P_{\text{O}_2} = (759 - 12) \text{ torr} = 747 \text{ torr}$$

By the ideal gas law, $n = \frac{PV}{RT}$, we have,

$$n = \frac{\left(\frac{747}{760} \text{ atm}\right) \times 0.250 \text{ L}}{0.08205 \frac{\text{L atm}}{\text{K mol}} \times 287 \text{ K}}$$

$$n = 0.0104 \text{ mol}$$

**DISCUSSION**

Note that $1 \text{ atm} = 760 \text{ torr}$. The units used in the formulation requires $R = 0.08205 \frac{\text{L atm}}{\text{mol K}}$.

**Questions**

1. At the same temperature and pressure, equal of volumes of gases contain the same of what?
   
   a. number of atoms  
   b. number of molecules  
   c. mass  
   d. gas  

   Hint: b. number of molecules
Skill:
Describe Avogadro's law of gases.

2. A container with volume \(V\) contains some gases. Its pressure is directly proportional to which one of the following?
   a. temperature in °C
   b. the amount of gas in mole
   c. the temperature in °F
   d. molecular weight of the gas

   Hint: b. amount in mole (mol).

Skill:
Discuss Avogadro's law of gases.

3. A gas containing 78% \(\ce{N_2}\) by mass exerted a pressure of 102.3 kPa against the wall of the container. What is the partial pressure of \(\ce{N_2}\)?

   Hint: Cannot be determined.

Skill:
Since we do not know what other gases are present, we do not know the mole percent of nitrogen in the container. The problem cannot be solved.

4. A gas containing 50% \(\ce{N_2}\) by mole exerted a pressure of 101.6 kPa against the wall of the container. What is the partial pressure of \(\ce{N_2}\)?

   Hint: 50.8 kPa

Skill:
Compare this problem to the previous one.

5. In the experiment to collect \(\ce{O_2}\) over water, the vapor pressure at 14 °C is 12 torr. Calculate the amount of water in 0.250 L.

   Hint: 0.000168 mol.

Skill:
Formulate the calculation for \(n\).

\[
(n = \text{mathrm{left(frac{\left(frac{12}{760} \text{ atm}\right) \times 0.250 \text{ L}}{0.08205 \frac{\text{L atm}}{\text{K mol}} \times 287.15 \text{ K}}\right)\text{mol}}}
\]

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