

2. The Ideal Gas Law

2.1 The Gas Laws

At low pressures all gases have the same behavior in the following sense:

- 1) With pressure and temperature fixed, the volume of the gas is proportional to the number of particles (atoms in the case of a monatomic gas such as Ne, or molecules in the case of a molecular gas such as CO₂). The proportionality constant is the same for all gases. This is Avogadro's Law:

$$V = \text{constant} \times n$$

- 2) If temperature is increased, with pressure fixed, the volume increases in proportion to the temperature (provided the temperature is measured on the absolute scale). This is Charles' Law:

$$V = \text{constant} \times T$$

- 3) If pressure is increased, with temperature fixed, the volume decreases inversely with the pressure. This is Boyle's law:

$$V = \text{constant} / p$$

- 4) If temperature is increased, with volume fixed, the pressure increases in proportion to the temperature. This law follows from Charles' and Boyle's Laws:

$$p = \text{constant} \times T$$

Note that each of these laws has a different constant that depends on the values of the fixed properties.

These observations are encapsulated in the ideal gas law:

$$pV = nRT \quad 2.1$$

where $R = 8.314 \text{ J mol}^{-1} \text{ K}^{-1} = 0.08206 \text{ L atm mol}^{-1} \text{ K}^{-1}$ is the gas constant. Gases that obey this law are said to be *ideal*. The law is valid at low pressure for all gases because, under these conditions, the atoms or molecules are so far apart that forces between them have no significant effect on the pressure of the gas.

The *first observation* allows us to determine the molar mass of a gas by measuring the mass of a known volume of the gas at known temperature and pressure.

Example 2.1: Suppose a 1.000 L sample of a gas at 1.000 atm pressure and 293.0 K has a mass of 1.830 g. What is the molar mass of the gas?

Approach: Solve for the amount of gas. Divide mass by amount to give the molar mass of the gas.

The amount of gas is determined, from $pV = nRT$, by

$$\begin{aligned} n &= \frac{pV}{RT} = \frac{1.000 \text{ atm} \times 1.000 \text{ L}}{0.08206 \text{ L atm mol}^{-1} \text{ K}^{-1} \times 293.0 \text{ K}} \\ &= 0.04159 \text{ mol} \end{aligned}$$

The molar mass is determined from

$$\begin{aligned}\text{molar mass} &= \frac{\text{mass}}{\text{amount}} = \frac{1.830 \text{ g}}{0.04159_1 \text{ mol}} \\ &= 44.00 \text{ g mol}^{-1}\end{aligned}$$

The gas is likely CO₂.

The *second observation*: Changes in volume indicate changes in temperature – if pressure is fixed.

Example 2.2: A balloon of gas increases in volume from 10.0 L to 12.8 L at 1.000 atm pressure. If the gas was initially at 295 K, what is its final temperature?

Approach: The amount of gas does not change. Equate the initial and final amounts. Cancel out R and the pressure which also does not change.

The pressure and the amount of gas are constant. Therefore,

$$n = \frac{pV_i}{RT_i} = \frac{pV_f}{RT_f}$$

or

$$\frac{V_i}{T_i} = \frac{V_f}{T_f}$$

or

$$\begin{aligned}T_f &= \frac{V_f}{V_i} T_i = \frac{12.8 \text{ L}}{10.0 \text{ L}} \times 295 \text{ K} \\ &= 378 \text{ K}\end{aligned}$$

The *third observation*: Changes in volume indicate changes in pressure – if temperature is fixed.

Example 2.3: A balloon of gas increases in volume from 10.0 L to 15.6 L at 298 K. If the gas was initially at 1.00 atm pressure, what is its final pressure?

Approach: Equate the initial and final amounts. Cancel out R and the temperature which also does not change.

The temperature and the amount of gas are constant. Therefore,

$$n = \frac{p_i V_i}{RT} = \frac{p_f V_f}{RT}$$

or

$$p_i V_i = p_f V_f$$

or

$$p_f = \frac{V_i}{V_f} p_i = \frac{10.0 \text{ L}}{15.6 \text{ L}} \times 1.00 \text{ atm}$$

$$= 0.641 \text{ atm}$$

The *fourth observation*: Changes in pressure indicate changes in temperature – if volume is fixed.

Example 2.4: A gas is held in a cylinder with fixed volume of 10.0 L. The pressure at is observed to increase from 1.00 atm to 15.0 atm. If the gas was initially at 298 K, what is its final temperature?

Approach: Equate the initial and final amounts. Cancel out R and the volume which also does not change.

The volume and the amount of gas are constant. Therefore,

$$n = \frac{p_i V}{RT_i} = \frac{p_f V}{RT_f}$$

or

$$\frac{p_i}{T_i} = \frac{p_f}{T_f}$$

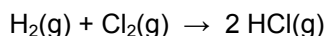
or

$$T_f = \frac{p_f}{p_i} T_i = \frac{15.0 \text{ atm}}{1.00 \text{ atm}} \times 298 \text{ K}$$

$$= 4470 \text{ K}$$

Because the volume of a gas is proportional to amount (mol), we are sometimes faced with reaction stoichiometry questions that provide volume data for reactant gases.

Example 2.5: H_2 and Cl_2 react according to



Suppose 3.00 L of hydrogen gas is mixed with 4.00 L of chlorine gas, at 1.00 atm pressure and 298 K, then ignited. How much HCl is produced?

Approach: Determine the amount of the limiting reactant. The reaction stoichiometry then determines the amount of product.

Under the same conditions of pressure and temperature, a smaller volume means a smaller amount. Since the gases combine in a 1:1 ratio, the gas with the smaller volume is the limiting reactant. The limiting reactant is H_2 since it has the lesser volume.

$$\begin{aligned}
 \text{amount of H}_2 \text{ consumed} &= n = \frac{pV}{RT} \\
 &= \frac{1.00 \text{ atm} \times 3.00 \text{ L}}{0.08206 \text{ L atm mol}^{-1}\text{K}^{-1} \times 298 \text{ K}} \\
 &= 0.122_7 \text{ mol}
 \end{aligned}$$

According to the reaction stoichiometry, the amount of HCl produced is twice this amount; i.e.,

$$\text{amount of HCl} = 2 \times 0.122_7 \text{ mol} = 0.245 \text{ mol}$$

2.2 Partial Pressure

When we have a mixture of gases in a vessel, each gas contributes to the total pressure in the vessel – each gas has its own *partial pressure*. The total pressure in the vessel is the sum of the partial pressures of all gases in the vessel. For example, if we have a mixture of gases, A, B, C, ..., the total pressure would be expressed as:

$$p_{\text{TOTAL}} = p_A + p_B + p_C + \dots \quad 2.2$$

The partial pressure of any gas in a mixture can be determined if we know the total pressure of the mixture and the mole fraction of the gas of interest. The mole fraction, x , of any gas in a mixture is its proportion with respect to the whole quantity. For example, if we have our mixture of gases A, B and C, and we know that we have 2.0 mol A, 1.5 mol B and 1.5 mol C, then the mole fraction of gas A is:

$$x_A = 2.0 \text{ mol} / (2.0 + 1.5 + 1.5) \text{ mol} = 2.0/5.0 \text{ or } 0.40$$

If the total pressure of the mixture under a given set of conditions were 1.4 atm, then the partial pressure of gas A would be the total pressure multiplied by the mole fraction of gas A:

$$p_A = p_{\text{TOTAL}} \times x_A = (1.4 \text{ atm}) (0.40) = 0.56 \text{ atm}$$

Example 2.6: The vapor pressure of water at 298 K is 24 torr (1 atm = 760 torr). This is the partial pressure of water in air saturated with water at 298 K. What is the mole fraction of water in 1.00 atm air at 298 K with 100% humidity (i.e. the air is saturated with water)?

Approach: Mole fraction is proportional to partial pressure, and we know the total pressure – i.e. 1.00 atm.

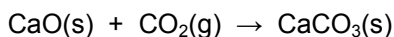
$$\text{Total air pressure} = 1.00 \text{ atm} \times 760 \text{ torr atm}^{-1} = 760 \text{ torr}$$

$$x_{\text{water}} = 24 \text{ torr} / 760 \text{ torr} = 0.031_6$$

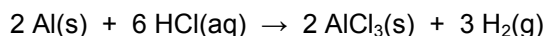
The mole fraction of water vapor in air with 100% humidity is 0.032.

Problems:

- 2.1 (a) Determine the density of He, N₂ and Ar at 1 atm pressure and 298 K.
(b) Which gas can be used to displace air in a cylinder, by pouring the gas into the cylinder?
- 2.2 What volume (in L) of CO₂ is consumed by reaction with 1.00 kg of CaO at 298 K and 1.00 atm pressure?



- 2.3 Hydrochloric acid reacts with aluminum to produce hydrogen gas:



An impure sample of aluminum contains an unknown amount of Al and other impurities. Suppose 110 mL of H₂, at 1.00 atm and 298 K, are collected from the reaction with HCl of all the aluminum in the 3.65 g impure sample. What percentage (by mass) of the sample is Al? Assume that the other components of the sample do not react with HCl.

- 2.4 Because the reaction in question 2.3 is carried out in aqueous solution, any gas collected from such a reaction will be a mixture of the product gas – in this case, hydrogen – and water vapor. Gases collected bubbling out of an aqueous are saturated with water. Thus, the 110 mL of H₂ collected in question 2.3 must be the dry volume – i.e., the volume after all of the water is removed (e.g. with a dessicant). Do question 2.3 again, but this time, suppose that the 110 mL of gas collected has not been dried – it contains water vapor. You must correct either the pressure or the volume of H₂ in order to get the actual amount (mol) of H₂.
- 2.5 Hydrogen peroxide decomposes into water and oxygen.



What volume of oxygen is liberated from the complete decomposition of 100. mL of a 3.00% hydrogen peroxide solution, at 1.00 atm and 293 K? The density of the hydrogen peroxide solution is 1.01 g mL⁻¹.