E. Experiment #5, Measurement of the 2nd Virial Coefficient for CO_2

Objectives:

1. Investigate the relationship between pressure, volume and temperature of real gases.
2. Experimentally determine the compression factor, *Z*, 2nd virial coefficient and hard-sphere diameter for CO_2.

Background:

In this lab you will make measurements on two gases: one that is behaving ideally and another that is far from ideal. The ideal gas, argon, can be treated simply using the ideal gas law (equation 1) where P is the pressure, V is the volume occupied by the gas, n is the number of moles of gas, R is the gas constant, and T is the temperature in Kelvin.

$$PV = nRT \quad (1)$$

The non-ideal gas, carbon dioxide, will have to be treated by expanding the ideal gas law as a Taylor series. Ideally, the compressibility factor, *Z*, of a gas is given by equation 2.

$$Z = \frac{PV}{nRT} = \frac{P\bar{V}}{RT} = 1 \quad (2)$$

In non-ideal situations, the compressibility is a function of pressure and volume and can be expanded in a series (about P, shown below - equation 3).

$$Z = \frac{P\bar{V}}{RT} = f(P) = 1 + B_{2p}P + B_{3P}P^2 + \cdots \quad (3)$$

The 2nd virial coefficient B_{2p} is the principle measure of a gas's deviation from ideality and is related to the interactions between gas molecules. As can be seen in equation 3, B_{2p} is also the slope of $Z(P)$. The pressure of carbon dioxide gas will be measured incrementally at a fixed volume as the number of moles of gas is decreased. Using this, $Z(P)$ can be calculated as well as the first. Using the value for the coefficient, the hard sphere diameter

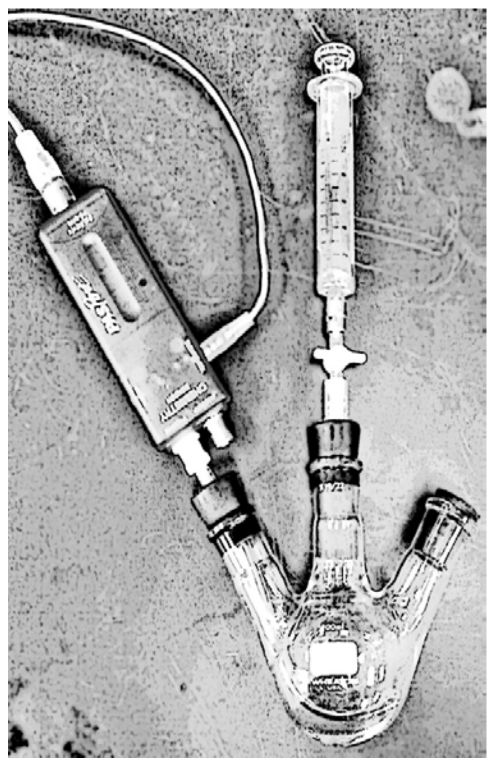

Figure 5 - Experimental setup for the measurement of Z versus P.

can be estimated.

Procedure:

The apparatus for this experiment is shown above. A three neck round bottom flask is equipped with a pressure sensor, a glass syringe, and a venting stopper. The entire flask may be submerged in a water bath to measure the pressure at fixed temperatures. Pressure is easy to measure in this experiment; however the molar volume is not because initially the volume of the apparatus and the number of moles of gas in the apparatus are both unknown. Caution must be used when a syringe is used at low pressures, if the plunger slips out of your hand it can smash into the bottom of the barrel causing it to shatter.

1. Measure the volume of the apparatus using an ideal gas and the ideal gas law.
   a. Flush the flask with argon for approximately 1 minute, while monitoring the pressure.
   b. Cap the flask, and quickly turn off the gas so that the pressure doesn't get too high and blow out the stopper.
   c. Record the pressure inside the flask, then open the valve to the syringe and pull out 10-30 mL of gas, close the valve, and record the pressure. Purge the gas from the syringe and repeat the procedure until the pressure inside the flask is below 0.2 atm. The volume of the flask can be computed using the ideal gas law by solving the following system of equations for V_1, where P_1 is the pressure before pulling out the syringe and P_2 is the pressure after.

$$P_1 V_1 = nRT$$
$$P_2(V_1 + \Delta V) = nRT$$

   d. Solve for the volume of the flask using each of the pairs of pressures you recorded. If the gas is behaving ideally and the measurements were made carefully, the volume you calculate should be relatively constant over the range of pressures used.

2. Measure $P\bar{V}/RT$ as a function of pressure for carbon dioxide and another gas at 273 K.
   a. Flush the flask with carbon dioxide while monitoring the pressure, cap the flask, and submerge the system in an ice water bath. An ice water bath is very close to 273.15 K, provided that

the ice and water is in equilibrium with each other, so make sure you have both water and ice.

b. Record the pressure inside the flask, carefully pull out a fixed volume of gas, and record the pressure again. Purge the syringe and repeat the procedure until the pressure is at least below 0.2 atm. It is important to know exactly how much volume of gas you remove each step.
c. Repeat the pressure measurements for a different gas. Nitrogen, Oxygen, Helium, and Methane are all handy.

Data Analysis:

1. We want to measure the first virial coefficient from the slope of $P\bar{V}/RT$. We know *P, R, T,* and *V* but we don't know *n* so we don't know $\bar{V}$. Calculating *n* using the ideal gas law is erroneous because we want to measure the non-ideality of the gas in question. If we knew the first virial coefficient we could accurately calculate *n*, but that are what we are solving for! The solution is to estimate *n*, calculate the virial coefficient based on the estimation, then reevaluate *n* using the newly found coefficient, and then reevaluate the coefficient using our better *n*. This process is repeated until iteration doesn't improve the results.
   a. Estimate *n* (for the lowest pressure measurement) and Δn using the ideal gas law.
   b. Estimate *n* for the higher pressures by adding the Δn values to the n_{total}.
   c. Find $\bar{V}$ at each pressure, and $P\bar{V}/RT$.
2. Estimate the first virial coefficient neglecting higher order terms.
   a. Find the slope (B_{2P}) of $P\bar{V}/RT$ versus P_2.
   b. Using the same set of pressures, reevaluate *n* and Δn using the second order virial equation: $\frac{PV}{nRT} = 1 + B_{2P}P \;\; \rightarrow \;\; n = \frac{PV}{RT(1+B_{2P}P)}$. Recalculate $\bar{V}$ at each pressure, and $P\bar{V}/RT$.
   c. Find the new slope (B_{2P}) of $P\bar{V}/RT$ versus P_2.
   d. Repeat b and c until B_{2P} stop changing.
3. Calculate the "hard sphere" diameter, σ, of your gas molecules using the B_{2p} value from part 4 and the following equations.

$$B_{2V} = RTB_{2P}$$

$$B_{2V} = \frac{2}{3}\pi\sigma^3 N_A$$

4. Compare results to credible literature sources.