

## Experiment #1, The Adiabatic Expansion of Gases and The Determination of Heat Capacity Ratios

### Objectives:

1. Relate the heat capacity of three different gases to their geometry, bond strength, and number of atoms contained in each gas molecule.
2. Investigate the relationship between adiabatic expansion and heat capacity.

### Background:

In this lab, modifications have been made to the procedure to give respectable results nearing the theoretical limit. The basic technique is given in several physical chemistry lab textbooks. The experiment consists of over pressurizing a vessel, letting it near thermal equilibrium, then venting and recapping the vessel as quickly as possible. The opening of the vessel produces an adiabatic expansion accompanied by a drop in temperature of the gas. Closing the vessel produces isochoric heating of the enclosed gas to its original temperature. If the pressure in the vessel is measured before opening, the instant it is open, and after thermal equilibrium has been re-established, the heat capacity ratio can be calculated as shown below. For a diatomic molecular gas, the contribution from vibrational modes to the heat capacity can be found, and the fundamental vibrational frequency estimated.

The experimental apparatus is shown in figure 1. A large rubber stopper is used to release the pressure, which can quickly be opened and closed. The large diameter of the stopper allows the pressurized gas to release very quickly. The principle improvements of this experiment over previous designs are: the larger carboy volume, the larger diameter pressure release, and more sensitive digital recorder for pressure and temperature.

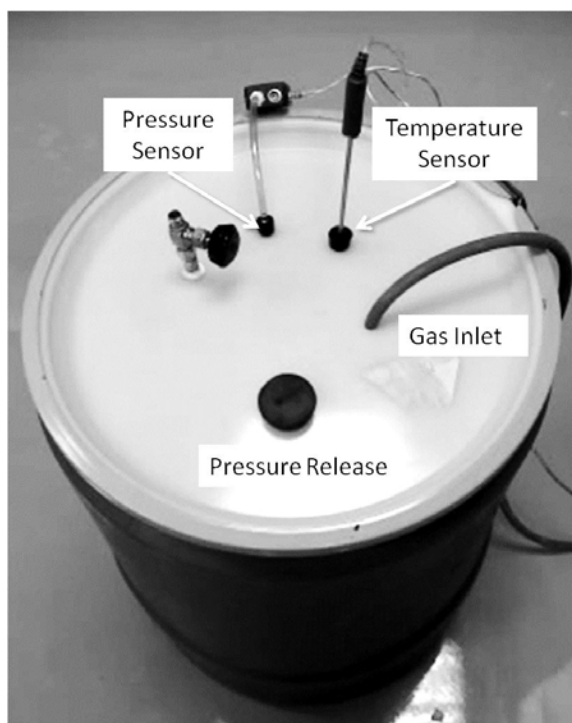


Figure 1 Experimental apparatus for the adiabatic expansion of gases.

The volume of the plastic carboy is about 75 L, and no thermostating or extra insulation is required.

With this apparatus, the pressure differential will be made to be 70-80 Torr. The pressure will be measured using a Passport sensor and recorded in data studio. This way, pressure can be recorded accurately to a tenth of a Torr at ten measurements per second.

The initial state of the carboy is over pressurized gas (P1) at ambient temperature. When the stopper is opened, the gas adiabatically expands to atmospheric pressure (P2), cooling the gas. When the stopper is closed, the gas heats at constant volume raising the pressure to (P3). The path from P1 to P2 is called an adiabat, from P2 to P3 an isochore, and the overall path from P1 to P3 is an isotherm. Assuming that the processes are reversible, the ratio of the constant pressure (adiabatic) and constant temperature (isotherm) heat capacities can be shown to be:

$$\gamma = \frac{c_P}{c_v} = \frac{\ln\left(\frac{P_1}{P_2}\right)}{\ln\left(\frac{P_1}{P_3}\right)} \quad (1)$$

If irreversibility conditions are applied, which should be more accurate, the linear expansion of natural log can be used, and gamma is:

$$\gamma = \frac{(P_1 - P_2)P_3}{(P_1 - P_3)P_2} \quad (2)$$

It would be wise to compare the values obtained using both equations. All real processes are irreversible, but if the transient is small, the process approaches the reversible one as a limit. This is the same concept as in calculus, where the limit of a collection of smaller and smaller finite steps yields an analytical result.

The principle assumptions which need to be examined in this experiment are: (1) there is sufficiently low thermal conduction to the surroundings during P1 to P2, (2) the process is done reversibly,

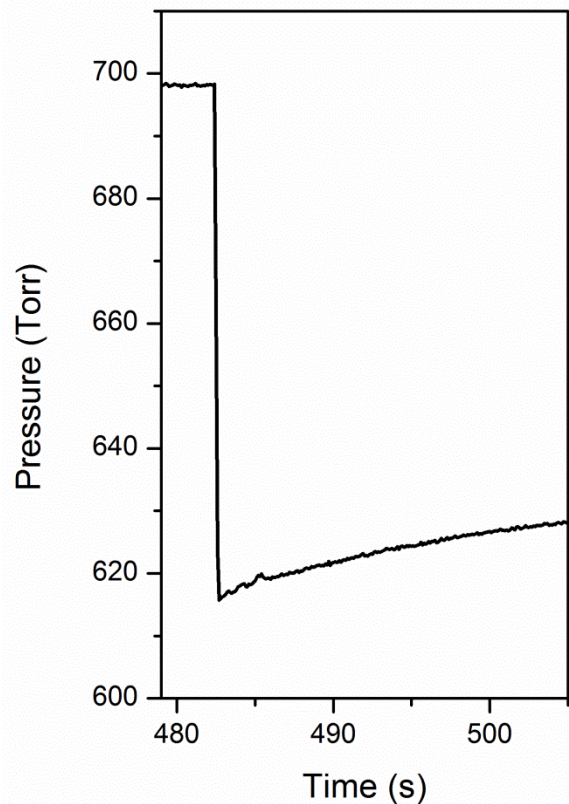


Figure 2 The time dependent pressure curves for the adiabatic expansion and isochoric heating of a gas.

and (3) the gases are ideal. If all of these conditions are met, the theoretical limit  $C_p/C_v$  is 1.66 for a monoatomic ideal gas. Even with modernization of the experiment, the values for argon would not exceed 1.6.

The condition that thermal conduction to the surroundings is low is met by releasing the pressure very rapidly, so that the time available for heat conduction is very small. The expansion has been treated reversible since there is only a small pressure change involved, although irreversibility can be accounted for by using equation 2. The assumption of ideality in the pressure equation has been discussed elsewhere by Partington<sup>3</sup> who concluded that it is valid for the small pressure changes involved in this experiment.

The ability to achieve reproducible results is connected to the time dependent pressure curve shown in figure 2. This graph is generated from the pressure output from the Passport sensor. You then have a record of the transient pressure change. From this curve you can determine if your technique in opening the stopper is satisfactory. If the stopper is open too long, the sharp v at the bottom will smooth out to a u shape and the results will be low. Experimentally, I have found that a pressure transient of less than 0.5 sec for the expansion will give good results on gases with relatively low coefficients of thermal conductivity.

### **Procedure:**

1. Connect the Passport pressure and temperature sensors, open up Data Studio, set up the experiment so that the pressure reads in Torr, the temperature reads in Kelvin, and 10 data points are recorded per second.
2. Start recording your pressure and temperature on a graph. Record the ambient pressure for 1 minute, then export (copy and paste) the data into Excel. Take the standard deviation of the data, which will give you an idea of the precision of the probe, as well as the significant digits from the pressure reading you can use in your calculations. Note the ambient temperature.
3. **DO NOT LET THE PRESSURE IN THE CARBOY EVER EXCEED 120 Torr ABOVE AMBIENT PRESSURE!**
4. Loosen the big stopper, and flush the carboy with argon gas for about 5 minutes, keeping an eye on the pressure.
5. Turn off the gas, tighten the rubber stopper, and CAREFULLY over pressurize the gas to 100 Torr above ambient.

6. Let the carboy come to equilibrium by waiting for the pressure to level off (or almost level off) at about 80 Torr above ambient pressure.
7. As quickly as possible, release the pressure in the carboy and replace the stopper.
8. Let the carboy come to equilibrium by waiting for the pressure to level off. Export (copy and paste) your data to an Excel spreadsheet for later processing. It would be a good idea to calculate  $C_p/C_v$  as you go along so you can check the quality of your data.
9. Repeat the experiment a total of three times each using argon, oxygen, and carbon dioxide.

### Report:

1. Why are the heat capacities for gases temperature dependent except for monatomic gases?

The constant volume heat capacity for a monatomic gas is given by equation 3, where each translational degree of freedom (i.e. motion in the x, y, and z directions) contributes  $R/2$  to the molar heat capacity:

$$C_V = \frac{3}{2}R \quad (3)$$

A polyatomic molecule has translational, rotational, and vibrational components to the heat capacity. In linear molecules, rotation about the molecular axis (i.e. where the axis goes through all the atoms) doesn't contribute to the heat capacity, but the other two rotational directions perpendicular to the molecular axis do. The constant volume molar heat capacity for a linear polyatomic molecule is given by equation 4.

$$C_V = \frac{3}{2}R + \frac{2}{2}R + C_{vib} = \frac{5}{2}R + C_{vib} \quad (4)$$

The constant pressure molar heat capacity is given by equation 5.

$$C_P = C_V + R \quad (5)$$

2. Using these equations, derive an expression for gamma for both a monatomic gas and linear polyatomic gas in terms of R and  $C_{vib}$ .

What is gamma for an ideal monatomic gas? How does your gamma for argon compare?

3. Using equation 6 and the constant,  $\Theta_{vib}^{O_2} = 2256 \text{ K}$ , calculate the vibrational component of oxygen's constant volume heat capacity ( $C_{vib}$ ) at the ambient temperature you recorded.

$$C_{vib} = R \left( \frac{\Theta_{vib}}{T} \right)^2 \frac{e^{-\Theta_{vib}/T}}{(1 - e^{-\Theta_{vib}/T})^2} \quad (6)$$

4. Using your result from question 3 and equations 4 and 5 above, calculate the theoretical gamma for oxygen gas at the lab room temperature. How does your gamma compare?
5. Solve the equation you derived in question 2 for  $C_{vib}$ . Using the gamma you measured for oxygen, calculate your experimental  $C_{vib}$ . How does your experimental  $C_{vib}$  compare with the theoretical value?