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An Adiabatic Expansion Experiment Done On A Budget

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Abstract: Using two different experimental setups to achieve a simple adiabatic expansion of a gas, the ratio of constant pressure to constant volume heat capacities for several gases was measured. In the first setup, an 18-L carboy was insulated, fitted with a ported rubber stopper to control gas flow, and filled with a particular gas. The expansion was achieved manually by quickly raising and lowering a rubber stopper at the mouth of the carboy. The pressure of the system was monitored during this process using a Vernier gas pressure sensor, and data was collected using Vernier's Logger Pro 2.2.1. In the second setup, a PVC gate valve was used to quickly release the gas pressure and begin the expansion, and data was collected using Vernier's Logger Pro 3.4.5. Acquired data from both set ups were very similar and values of the ratio of heat capacities for argon, air, nitrogen, and carbon dioxide agreed well with reference values. By using Vernier probes and software, as well as using low-cost alternatives for equipment, the operating costs and complexity of experimental procedures were significantly reduced. As a junior-level, undergraduate physical chemistry experiment, students were exposed to fundamental thermodynamic properties of gases, instrumentation, and simple data acquisition.

Introduction

Experiments involving the determination of heat capacity ratios ($C_p/C_v = \gamma$) using adiabatic processes have become more and more popular in undergraduate physical chemistry laboratory courses. Methods include both that of Ruchardt [1–4] and the determination of γ by measuring the speed of sound in the gas in question [5–10]. The fact that these methods are successful in determining γ is not in question. However, the relative cost of these setups are important to educators who need to operate on a stretched budget. Some require pulsed lasers, microphones, and expensive electronic equipment to perform the experiment. One apparatus sold by Pasco called the Adiabatic Gas Law Apparatus (ALGA) [11] is an all-inclusive setup that requires data acquisition hardware and software, and uses transducers to measure pressure volume and temperature concurrently during an experiment. Each of these setups vary in cost and relative ease of use, and one must determine what is best for the student while remaining on a budget. The setups presented in this paper use recycled equipment and easy-to-use data acquisition software to facilitate the experiment and allow the students to focus on the acquired data, not the acquisition itself.

The discussion of adiabatic processes is quite important since such processes occur in many facets of our world. The ratio of the heat capacity at constant pressure to the heat capacity at constant volume is proportional to simple ratio of pressures. These equations govern processes that deal with changes in pressure and temperature for cases when no heat enters or leaves the system. Such a process is referred to as adiabatic. Many atmospheric processes approximate this situation – a system goes through changes of state (i.e. pressure) but no heat is allowed to enter or leave the system [12]. In addition, the process of making snow at a ski resort [13] and the simple act of inflating a tire and noticing that the tire gets warm during the event [14] are examples of adiabatic processes. By applying the First Law of Thermodynamics to a

system undergoing an adiabatic process (i.e. expansion), and taking into account simple kinetic molecular theory, one can derive an equation that governs the process in terms of a ratio of heat capacities at constant pressure and volume. Also, hypotheses regarding aspects of the dynamics of the gas studied can be discussed in terms of the Equipartition Theorem and tested (deviations from ideality, correlation of γ with increasing number of vibrational modes, etc.).

The Equipartition of Energy Principle

The kinetic energy of gases model presumes that gas particles are point masses having no intermolecular forces acting among them except when collisions take place. These assumptions lead to the conclusions that there are no internal motions (vibrations or rotations) present and that there is no intermolecular potential energy. The total energy of a collection of gas particles is the sum of the kinetic energies of the individual particles. Since this energy depends only on temperature, it is called thermal energy. We designate this energy with the symbol U . Because there is no intermolecular potential energy, U should be independent of the distance between the particles, implying that U is independent of the volume. The average thermal energy for a particle of gas at a temperature of T is $3kT/2$. If N particles of gas are present, then the total thermal energy is given by

$$U = \frac{3}{2} NkT \quad (1)$$

For a mole of particles, we define the molar thermal energy \bar{U} , which is

$$\bar{U} = \frac{3}{2} N_A kT = \frac{3}{2} RT \quad (2)$$

The heat capacity, C , of a system is defined to be the amount of energy that must be added to the system via a thermal interaction (heat is a measure of this energy transfer) in order to raise the temperature of the system by one degree (on either the centigrade or absolute scales). If the volume of the system is constant during the energy transfer, then energy that is added only increases the thermal energy of the system; the system can do no mechanical work. Therefore, the heat capacity at constant volume is the change in the thermal energy of the system per degree change in temperature. Mathematically, this is expressed as

$$C_V = \left(\frac{\partial U}{\partial T} \right)_V \quad (3)$$

where the subscript V indicates that the temperature change occurs under conditions of constant volume. The corresponding molar quantity is given by

$$\bar{C}_V = \left(\frac{\partial \bar{U}}{\partial T} \right)_V \quad (4)$$

Substitution of the expression for the molar thermal energy given in equation 2 into equation 4 leads to the following result.

$$\bar{C}_V = \frac{3}{2}R \quad (5)$$

The kinetic theory of gases leads to the prediction that the molar heat capacity of a gas at constant volume is independent of the temperature and it will always have the value of 12.5 J/mol K.

From experiment it is found that only monatomic gases, such as helium, have constant volume heat capacities that are independent of temperature. Polyatomic gases have heat capacities that are found to be dependent on the temperature, which suggests that the presence of several atoms in a gas molecule must introduce problems that the kinetic theory of gases fails to consider. One possibility to consider is the internal motion of electrons. However, since the kinetic theory correctly predicts the heat capacities of monatomic gases, it seems highly likely that electronic motion (which is also present in monatomic gases) cannot be the problem. From experiment it is found that all polyatomic gases have heat capacities that are greater than $3R/2$. The higher heat capacities imply that there must be other contributions to the heat capacity of a gas than just thermal motion. Rotational and vibrational motions are likely candidates.

Regardless of whether the compression or expansion of a gas is investigated, the methods used in the experiment are notoriously difficult to perform correctly and have been scrutinized for many years. Moore [15] alluded to the fact that experiments of this nature yielded inconsistent and erroneous data, and therefore received a "bad reputation". A detailed history of the evolution of the experiment is given as supplemental material. With modifications driven by problems inherent in the experiment, our physical chemistry laboratory course uses adiabatic expansions to determine γ . Details on

how measured values are used to calculate $\gamma_{\text{reversible}}$ and $\gamma_{\text{irreversible}}$ are given in the supplementary materials. This experiment is used at Siena just after the students are exposed to the First law of Thermodynamics and are able to apply it to various systems. We have made the experiment reliable and user friendly for use in an undergraduate laboratory setting.

To properly address the shortcomings of previous attempts and the conceptual nature of the experiment regarding its reversibility, two modified apparatuses were designed and built. The first setup closely resembled that of Shoemaker [20] except for the method of pressure measurement, and the second replaced the rubber stopper with a modified gate valve arrangement to affect the expansion. The work presented here differs from previous work in that low-cost PVC valves replaced expensive stainless steel valves. In addition, the use of an expensive pressure transducer, as in Moore's experiment, was replaced in both apparatuses with a Vernier gas pressure sensor. Data collection was performed using LoggerPro 2.2.1 (or LoggerPro 3.4.5 on apparatus #2) on a recycled Windows-based personal computer. Both apparatuses were constructed with experimental feasibility in mind, and to reduce operating costs to our department. Both allow the student to actively engage in the process of experimental design, implementation, and data collection. As part of the weekly expectations in the laboratory sequence of Physical Chemistry, each student is asked to statistically treat and critically compare the values of γ calculated from obtained pressure measurements to those found in the literature. Also students are expected to derive all equations used in the experimental treatment of the data, and reason whether or not the procedure should be considered reversible or irreversible.

Experimental

Apparatus #1: Improving on Moore's Experimental Setup. The setup initially used was similar to that used in both Shoemaker and Moore, but rather than use a liquid manometer or a pressure transducer, respectively, we used a gas pressure sensor probe (Vernier Software & Technology, Catalog #GPS-BTA) capable of reliably measuring small changes in pressure at an affordable price. A schematic of the set up can be seen in Figure 1.

The gas pressure sensor (GPS) probe has a range of 0–2.1 atm, an accuracy of 0.0005 atm, a precision of 0.002 atm, and a response time is 100 μ s. Data collection was performed using a serial-box interface connected to an Intel Celeron 500 MHz computer running LoggerPro 2.2.1 through Windows 98. The experimental setup needed to be suitably modified to allow the GPS probe to be calibrated *in situ*. In addition, with the exception of the Vernier products, all equipment in this experiment setup was used and/or recycled: the computer system was donated, the carboy (purchased used from LabExtreme, Inc.), glass tubing (3/8 in. OD), and Tygon tubing (3/8 in. OD thin walled). Insulation of the carboy was achieved by wrapping the carboy with thick layers of bubble wrap. Initial experimentation with the use of a water bath yielded results that were not statistically different.

The experiment was performed by first flushing the carboy with the desired gas. After several minutes, the carboy was charged with gas to a pressure just above atmospheric pressure (40–60 torr above the GPS probe's value for atmospheric pressure). The elevated pressure was recorded, and the system allowed to equilibrate. If after a minute or two no leaks were found, the stopper was quickly raised and lowered (as seen in Figure 2), affecting the expansion detailed earlier. The temperature, and hence the pressure of the gas in the carboy increased until a steady pressure was attained. This pressure was labeled as the final pressure. It is crucial that the stopper be raised and lowered

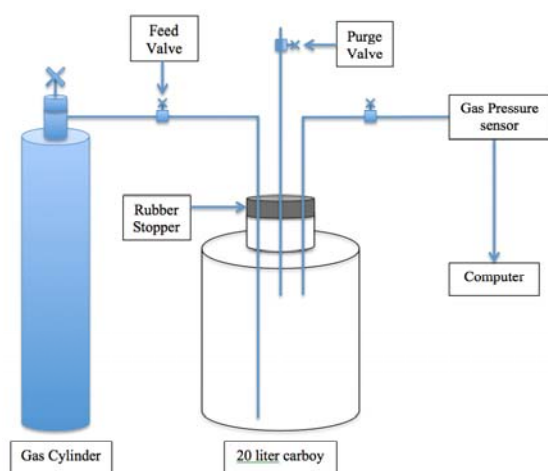


Figure 1. Schematic diagram of the first apparatus used to determine γ . In the lab, there can be separate setups for each gas studied or a gas-handling manifold could be used to condense the size of the experimental footprint and further reduce cost of the experiment by using one set of equipment rather than several setups. Parts for the manifold can be purchased from United States Plastics Corp.



Figure 2. Opening and closing of the rubber stopper.

quickly, and that the stopper be snug in the carboy opening before and after the expansion phase of the experiment.

Figure 3 is an example of the real-time, graphical data one can expect while performing the experiment. Each run should be at least 5 minutes long, with one to two minutes at the beginning of the data acquisition run for pressure equilibration, and the remaining time to allow for subsequent pressure equilibration after the expansion has occurred.

Apparatus #2: A Second, More User-Friendly Experimental Setup. Even though the raising and lowering of the stopper is relatively trivial for the students, some problems inevitably occurred. On many occasions, the students were not accurate in their replacement of the stopper, and this in turn caused leaks on several occasions. After recording many sets of data on several molecules, it was obvious that there must be a better way of initiating the expansion.

It was decided that the rubber stopper would be replaced entirely. Apparatus #2 can be seen in Figure 4. A PVC flexible reducing coupler (United States Plastics Corp. Catalog #30549) was used to reduce the outer rim of the carboy opening to 1.5 inches. A 6-in. long, 1.5-in. diameter PVC nipple (United States Plastics Corp. Catalog #27091) was installed, and holes were drilled and tapped in the nipple to accept a gas inlet port, a gas vent valve, and a pressure sensing port. A PVC knife gate valve (United States Plastics Corp. Catalog #20159) was placed on top of the nipple. To ensure that the gas being studied filled the carboy, an inlet line was fed to the bottom of the carboy so that the gas filled from the bottom up. A 0.25-in. ID Nupro fitting (Swagelok: Albany Valve and Fitting, Catalog # NY-300-1-4BT) was used to seal around the Tygon tubing (0.25-in. OD) that was used as an inlet line.

The operation of the gate valve is smooth, imparts very little movement to the apparatus during opening and closing, and can be

done quickly and reproducibly (See Figure 5). The use of a 6-inch nipple as the center post allows for convenient port location, but also adds stability to the gate valve because the nipple sits inside the neck of the carboy. Schedule 40 PVC tubing was used so as to minimize the area obscured by the nipple in the carboy neck. Initial data acquired using the new setup have been reproducible and come very close to predicted values of γ . The total cost of the improvements² to the apparatus was less than \$75.

Hazards. The gases used in this experiment are argon (CAS # 7440-37-1), helium (CAS # 7440-59-7), nitrogen (CAS # 4427-37-9), air (CAS # 132259-10-0), and carbon dioxide (CAS # 124-38-9). Oxygen (CAS # 7782-44-7) could be used, but since it is a flammable gas it was not used in our lab. As with any laboratory experiment, goggles should be worn at all times. Since the experiment requires students to pressurize a large Pyrex carboy, the instructor should delineate proper procedures and ensure that the carboy(s) do not become over-pressurized. An overly high pressure could also damage the GPS probe. In addition, the release of the gas associated with both experimental setups is accompanied with a loud popping sound. It is advisable to alert your students of the possibility of such a noise, and even go so far so as to require your students to alert the room with an audible warning.

Results

After a data acquisition run is completed, Vernier LoggerPro 2.2.1 (or LoggerPro 3.4.5 – see Figure 5) efficiently exports the data to a text file where it can be plotted in Excel. Figure 6 is representative of a run performed with Argon. After an initial leveling off of the pressure, the expansion occurs, and the isochoric heating progresses, accompanied by a drop in pressure and a subsequent rise in pressure to an intermediate value. Substitution of these recorded values into the appropriate equations yields $\gamma_{\text{reversible}}$ and $\gamma_{\text{irreversible}}$. Representative data acquired from both setups are shown in Table 1 for $\gamma_{\text{reversible}}$ and $\gamma_{\text{irreversible}}$, and are in good agreement with literature values [23]. As was alluded to earlier, the value of C_p tends to increase with the number of atoms in the molecule. This trend could be interpreted as follows: Monatomic gases should have less percent error in γ when compared to diatomic and polyatomic molecules. This trend is evident in the data in Table 1. In addition, the claim that the irreversible case is more applicable than the reversible case for this experiment can be supported by the percent errors for the values of $\gamma_{\text{reversible}}$ and $\gamma_{\text{irreversible}}$ cases. For each gas, the value of $\gamma_{\text{irreversible}}$ is smaller than $\gamma_{\text{reversible}}$, indicating that the equation describing the irreversible case is more appropriate for general use.

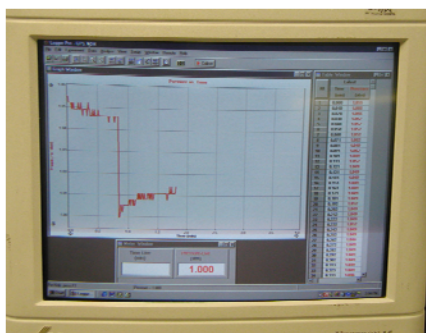
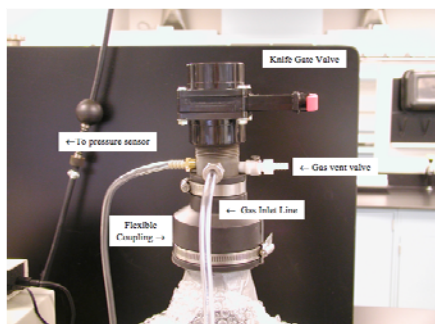
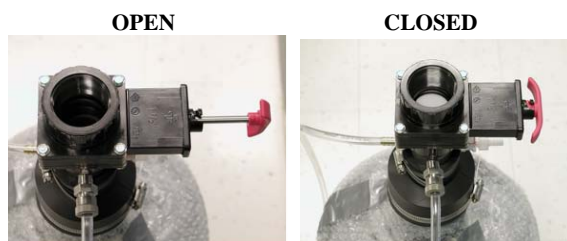
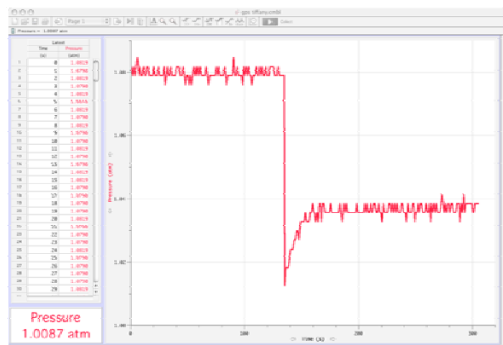
Concluding Remarks

It is the hope of the author that the modifications made to classic adiabatic expansion experiments will now persuade others to include the experiment in their curricula. With the addition of a low cost data acquisition system from Vernier (less than \$100 including the probe, serial box interface, and legacy software), the experiment is easy to set up and pleasurable to perform. If older Vernier software and hardware are not available, or it is desirable to start with current equipment, the initial outlay will increase to approximately \$530 (Vernier LabPro interface, LoggerPro 3.4.5, and the GPS probe).

It might not be obvious at first, but after one takes into account the procedure and makes an educated guess as to what the data might look like (something I ask my students in the

Table 1. Representative Student Data. Calculated values for Heat Capacity Ratios at 295K for setup #1 experiments and setup #2 experiments (95% Confidence Limit)

Setup	Gas	$\gamma_{\text{reversible}}$	Percent Error (N = 10)	Experimental		Literature [23]
				$\gamma_{\text{irreversible}}$	Percent Error (N = 16)	γ
1	Air	1.37 ± 0.04	6.87	1.39 ± 0.04	5.92	1.47
1	Carbon Dioxide	1.24 ± 0.09	6.99	1.25 ± 0.09	6.24	1.33
2	Nitrogen	1.34 ± 0.05	4.68	1.37 ± 0.05	3.83	1.41
2	Argon	1.65 ± 0.06	1.02	1.68 ± 0.07	0.36	1.67

**Figure 3.** Snapshot of data acquired during the experiment.**Figure 4.** Setup for Apparatus #2. The gas vent valve is usually connected to a hose and sent to a hood.**Figure 5.** PVC gate valve in open and closed positions.**Figure 6.** Plot of pressure versus time for Argon. This is a screen shot from LoggerPro 3.4.5 that was subsequently exported to MS Excel. This screenshot should be compared to the screenshot in figure 3. Both LoggerPro 2.2.1 and 3.4.5 work equally well.

prelab lecture for this experiment) it is apparent that the data's behavior is consistent with theory. In addition, the data acquired are reproducible and agree well with literature values. All facets of the experiment raise the morale of the students, who not only enjoy the experiment itself, but understand the data analysis on a more intimate way than if such experiments were merely mentioned in a lecture setting.

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Supplemental Material. Several pages of material are available, including a historical account of the evolution of the experiment, instructor references on the background thermodynamics and the derivation of $\gamma_{\text{irreversible}}$, the procedure from last year's lab handout used at Siena College, as well as representative data from Setup 1 and Setup 2 and a price list with catalog numbers for the parts to build the apparatuses. **Notes.** 1. The operations involved with this substitution can be tedious, and are included in the Supplemental Materials. 2. The Nupro fitting was the most expensive part at \$23.50 from Albany Valve & Fitting Co.

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