Using adiabatic cooling to measure heat capacity ratio for nitrogen and argon gases

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Introduction: Because no heat is transferred to the system during a reversible, adiabatic expansion, the temperature of the expanded gas decreases during the process. As with all substances, the change in temperature depends on the heat capacity. The heat capacity ratio, γ, is the ratio of the molar heat capacity at constant pressure ($C_{p,m}$) to that at constant volume ($C_{V,m}$):[1]

$$\gamma = \frac{C_{p,m}}{C_{V,m}} \tag{1}$$

In this lab, the value of γ was determined for two different gases (nitrogen and argon) based on pressure changes due to the initial drop in temperature following an adiabatic expansion. As detailed further in the Methods section, the three-stage experiment involves a slightly-above-atmospheric pressure of gas equilibrating in a large container at P_1. The container is opened, causing expansion to P_2 (atmospheric pressure), then resealed and thermally equilibrated to P_3. When performed this way, the value of γ can be determined from[2]

$$\gamma = \frac{\ln\left(\dfrac{P_1}{P_2}\right)}{\ln\left(\dfrac{P_1}{P_3}\right)} \tag{2}$$

The temperature of the gas after the expansion T_i (and thus, the temperature drop during the expansion) can be calculated using the combined gas law

$$\frac{P_i V_i}{T_i} = \frac{P_f V_f}{T_f} \tag{3}$$

It is important to note that Eq. 3 uses the pressure, volume, and temperature immediately following expansion (time 2) as P_i, V_i, and T_i, while P_f, V_f, and T_f refer to time 3, when the gas has reached room temperature again. Further, the volume does not change during that time, so that $V_i = V_f$, meaning that the volume falls out of the calculation.

Methods: The apparatus used in the experiment is shown in Figure 1. A 5-gallon bottle was fitted with a stopper containing three outlets, one for the gas source, one for the digital pressure gauge, and one as a vent valve. The bottle purged with nitrogen for ten minutes, then sealed. The bottle was then filled with nitrogen to a pressure (P_1) of approximately 1.6 psi above the laboratory pressure. Adiabatic expansion of the gas was accomplished by removing and quickly replacing the stopper on the bottle, reducing the pressure inside (P_2) to the lab pressure. The resealed bottle was allowed to equilibrate thermally back to laboratory temperature, and the final temperature (P_3) was recorded. The whole process was repeated twice for nitrogen, then twice for argon.
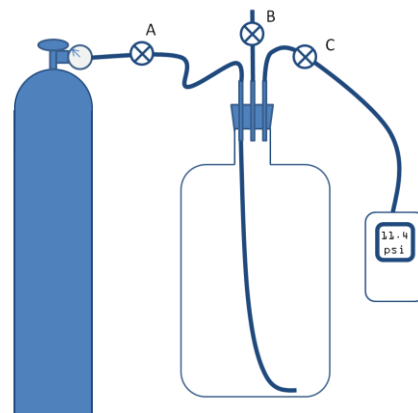
Figure 1. The apparatus used a 5-gallon glass bottle fitted with (A) an inlet from the gas cylinder, (B) a vent valve, and (C) a line to a digital pressure gauge. open at the correct times.

Results and Discussion: For each gas, two experimental runs were performed. The data collected for the second runs of nitrogen gas and argon gas are shown in Table 1. Temperature in the lab was measured to be $26.5 \pm 0.5°C$ In each case, the experimental uncertainties for P_1 and P_3 arise from the uncertainty in measurement of the pressure gauge used, which is ± 0.02 psi (± 1 torr). The lab pressure, P_2, was taken to be 790 ± 10 torr, which was the barometric pressure reading reported by weather.com[3] at the time of experiments; the uncertainty in this measurement accounts for pressure variations between the lab and the outside environment by taking

the standard deviation of ten days of measurements at the same time of day. Because there is such a large pressure difference expected between the laboratory and the outside environment, a generous uncertainty has been assumed. It is worth noting that the pressure read off of the gauge is *relative to* the pressure in the lab, rather than being a measure of the absolute pressure inside the experimental chamber. The data shown in Table 1 reflect the absolute pressure. Experimental uncertainty in P_2 is estimated to be much larger than the uncertainties in P_1 and P_3 relative to P_2, so the errors reported in Table 1 reflect the uncertainty in P_2 only. In both gases, P_1 is higher than P_2 because gas has escaped during the expansion. P_3 is higher than P_2 because the same volume of gas has been warmed following restoppering of the bottle. The temperature of the room, which is equal to both T_1 and T_3, was $301.2 \pm 0.1 \text{K}$.

Table 1. Data from the adiabatic expansion experiment, with pressures before expansion (P_1), immediately following expansion (P_2), and after thermal equilibrium (P_3). Calculated values for the change in temperature drop and the heat capacity ratio, γ, are also shown.

Gas	P_1 (torr $\pm$ 10 torr)	P_2 (torr $\pm$ 10 torr)	P_3 (torr $\pm$ 10 torr)	Temp. Drop (K $\pm$ 0.8K)	γ (± 0.4)
Ar	874	790	821	11.9	1.60
N_2	882	790	813	8.5	1.35

Sample calculations for determining the value of γ using Eq. 2 are shown in the appendix. To calculate the experimental uncertainty in γ, the calculation was performed three times, once with the experimental numbers, once with all uncertainties such that the value for γ would be maximized, and a final time in which γ is minimized. The uncertainty listed is half the difference between the maximum value and the value calculated without accounting for experimental uncertainty. These values can be compared to the theoretical values: for monatomic gases, $C_{V,m}$ is $3R/2$ and $C_{p,m}$ (= $C_{V,m} + R$) is $5R/2$. Thus, the theoretical value for γ (using Eq. 2) is $5/3$ for argon. Nitrogen is a diatomic molecule, however, for which theoretical arguments predict $\gamma = 7/5$.[1] Comparing these to our experimentally determined values of 1.60 ± 0.4 for argon and 1.35 ± 0.4 for nitrogen shows that we are within experimental error bars in both cases. In fact, the experimentally determined γ value is within 0.1 units of the theoretical value. The percent error in our measurements for heat capacity ratio is 3.6% for each measurement; both are lower than the theoretical value.

The temperature following the expansion was calculated as indicated in the appendix. Briefly, the values for P_2, P_3, and T_2 were used in the combined gas law (Eq. 3), assuming that the volume was constant. Thus, the error in calculation of T_2 was determined not by the error in the temperature of the room, but by the much larger errors in the absolute pressures. The fact that argon drops more than nitrogen gas is consistent with the difference in their heat capacities. Argon has a lower heat capacity, thus the same amount of heat transfer from the system results in a greater temperature decrease than in nitrogen.

This lab presented numerous error sources. The instrumental errors indicated (uncertainty in the pressure measurements) were small compared to the lack of accurate measurements of P_2. Even so, because calculating γ involves a ratio of logarithms of pressure ratios, the errors cancel somewhat. Temperature uncertainties also fall into the category of instrumental errors when measured, but for the derived errors, are dominated again by the uncertainty in the P_2 values. Absolute errors in the instrument are also expected to be low compared to P_2 estimation errors. To assess the impact that P_2 uncertainty had on our measurements, the function dependence of Eq. 2 must be considered. Larger values of P_2 will lead to a decrease in γ. Therefore, it could be that P_2 has been systematically overestimated, leading to

heat capacity ratios which are too small. This would be consistent with the idea that chemistry labs, which contain fume hoods, tend to have a lower pressure because of the chimney effect (hence, air is pulled into the hallways).

Conclusions: The heat capacity ratio, γ, was measured based on an adiabatic expansion, using the pressures before and immediately after the expansion, as well as upon rethermalization of the system. Results from this experiment gave values of $\gamma = 1.60\pm0.4$ for argon gas, and 1.37 ± 0.4 for nitrogen. Results for nitrogen and argon were well within experimental uncertainty of theoretical values, however, the experimental uncertainty was very high (approximately 20% of the value for γ). Decreasing the experimental uncertainty in the room pressure would improve the experiment dramatically. Because errors arose primarily from estimating based on the outside pressure, an absolute barometer in the lab itself would resolve this problem, likely providing an order of magnitude improvement in the overall experimental error.

This lab clearly demonstrates the difference in heat capacity ratio (and, thus, in heat capacity) between ideal monatomic and diatomic gases, and allows us to conclude that molecules with more internal degrees of freedom are able to absorb more heat with less change in temperature. For example, we can estimate the heat capacity of the atmosphere by noting that it is composed almost exclusively of diatomic molecules N_2 and O_2.[4] Thus, the heat capacity ratio of dry air would be approximately 1.4. Increased humidity would increase the heat capacity because water has more atoms, and therefore has a greater number of degrees of freedom in which to distribute energy.

Safety: When dealing with high-pressure gases, risks of suffocation exist if enough oxygen is displaced from the room.[5,6] If the procedures are followed correctly, this should not occur, but leaving the cylinders running could create a dangerous system. Over-pressurizing the apparatus could also present a hazard, as the stopper could be forcefully ejected. No significant chemical hazards are presented by this experiment.[2]

References:

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