Measurement of the heat capacity ratio of gases using an adiabatic expansion

Introduction

The expansion and compression of gases is commonly used as a means of exploring concepts in thermodynamics, particularly the first law.[1] The most basic examples make use of a cylinder with a massless, frictionless piston which can be moved when work is done. In this simple closed system, work (*w*) and heat (*q*) are calculated based on the first law of thermodynamics, which relates these two path functions to the state function internal energy (*U*):

$$\Delta U = q + w \tag{1}.$$

For an adiabatic expansion, no heat flows between the system and surroundings ($q = 0$), so that any change in internal energy is a result of work done by the system on the surroundings. Because work done by the system during an expansion is negative by convention, and because *U* is a monotonically increasing function of temperature, adiabatic expansion always results in a decrease in the temperature of the system ($\Delta T < 0$). Regardless of the nature of the expansion (adiabatic, isothermal or otherwise), we can always calculate the change in internal energy based on the change accomplished for a constant volume system whose temperature change is ΔT:

$$\Delta U = q_V = \int_{T_i}^{T_f} C_V(T)\,dT = C_V \Delta T \tag{2},$$

where C_V is the heat capacity of the system at constant volume. The final equality is true over small temperature ranges (10 K or so), where $C_V(T)$ is constant. Because U is a state function, if the temperature change due to the process is known, we can readily use the constant volume heat capacity as a conversion factor between internal energy change and temperature change. This is true even when the volume of the system changes (i.e., work is done). For a reversible adiabatic expansion, the following can be derived:

$$P_i V_i^{\gamma} = P_f V_f^{\gamma} \tag{3}.$$

In Eq. 3, the symbol γ is used for the ratio of the molar heat capacities at constant volume and at constant pressure:

$$\gamma = \frac{C_{P,m}}{C_{V,m}} \tag{4}.$$

Substituting the definitions of ΔU and w into Eq. 1, we obtain a similar relationship between pressure and volume before and after the expansion which can be more readily applied for our purposes here:

$$\ln \frac{P_f}{P_i} = -\gamma \ln \frac{V_f}{V_i} \tag{5}.$$

In our experiment[2] the change in volume will be ill-defined, but we will use the fact that the temperature has dropped following the expansion. We will measure the system pressure before expansion (P_1). Following the expansion, the pressure will be atmospheric pressure (pressure equilibrium is accomplished rapidly), which we will call P_2. If we allow the system to return to room temperature before measuring the pressure again (P_3), we can use the formula relating ideal gas changes to determine the temperature of the system immediately after the expansion. You will do that as part of your writeup, but we can determine the value of γ without that information[2] using the following formula:

$$\gamma \equiv \frac{C_{P,m}}{C_{V,m}} = \frac{\ln\left(\frac{P_1}{P_2}\right)}{\ln\left(\frac{P_1}{P_3}\right)} \tag{6}.$$

Whereas $C_{V,m}$ of any monatomic ideal gas is 3R/2, and the difference between $C_{V,m}$ and $C_{P,m}$ is R (so that $C_{P,m}$ = 5R/2), we expect to find γ=5/3 for argon.[1] For a diatomic, the heat capacities are different, and the value determined in the lab should reflect that difference.

Experiment

The apparatus is illustrated in Fig. 1.[2] A glass bottle fitted with a rubber stopper is connected to three tubes: a gas inlet, a gas vent (outlet), and a handheld digital pressure gauge. Each rubber hose has a clamp to close off that line as needed. It is very important that the pressure inside the system (the bottle) not exceed 1.7 psi above atmospheric pressure. Beyond that pressure, the rubber stopper may be ejected, creating an unsafe situation. Safety goggles must be worn at all times by everyone in the lab.

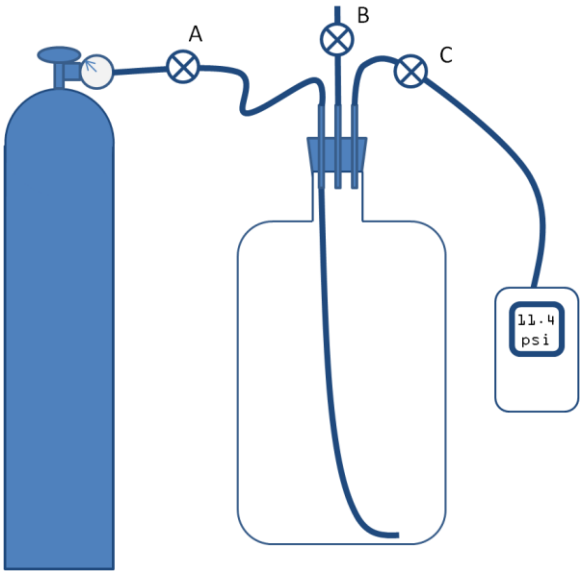

Figure 1. The apparatus used a 5-gallon glass bottle fitted with (A) an inlet from the gas cylinder, (B) a vent valve, and (C) a line to a digital pressure gauge. Care must be taken to ensure that the proper valves are open at the correct times.

For each gas, you will need to first flush the system. Open the vent closure, then open the inlet closure to allow gas to flow slowly into the bottle for approximately fifteen minutes. Gas flow rates should be barely perceptible to the touch when a finger is placed at the end of the tube. After the flush is complete, open the closure to the pressure gauge and turn it on. While one team member stands ready to close the inlet closure, another should close the outlet. With inlet open and outlet closed, the pressure on the gauge should increase. Close the inlet when the pressure on the gauge reads between 1.5 and 1.7 psi above atmospheric pressure, then close the gauge line as well to avoid leakage. Let the system reach thermal equilibrium for ten minutes, then read the gauge again. This is the pressure prior to expansion.

With the gauge closed, quickly but gently remove the rubber stopper, which will result in a forceful pop as the gas expands adiabatically from the bottle. Immediately replace the stopper securely into the bottle. You may choose to read the pressure now. Again wait ten minutes for the system to thermally equilibrate, and then read the final pressure in the system. Be sure to record the temperature of the room and make a good estimate of the atmospheric pressure (including uncertainties for both).

Follow this procedure twice for argon and twice for nitrogen, being careful to allow the system to flush between.

Pre-Lab

Before you can do the lab, you will need to complete the following. The results will frame our discussion before lab.

1. Calculate the theoretical value of γ expected for nitrogen (N_2). How does it compare to argon?
2. Do you expect the temperature change for nitrogen to be more or less than the temperature change for argon? Explain your reasoning
3. Summarize the procedure in a clear, readable format in your laboratory notebook. If this is not done, you will not be able to begin the lab.

Lab Report

Introduction: In a single page, summarize the background information and the experimental procedure. For the background, stick to the equations that you will use directly for calculations in this lab, and provide succinct summaries of important terms and symbols (such as P_3 and γ) you will use throughout the rest of the lab. Do not summarize the information in the lab manual; it has a different purpose than your introduction. The lab manual contains information that helps you understand all the concepts involved in the lab; your introduction is meant to help people understand what you have done.

Methods: Your experimental paragraph does need a diagram, complete with a descriptive caption. There should also be a very brief (one to two sentence) description of the apparatus. The description should refer to the Figure. Give just enough information for another CHEM 453 student to be able to reproduce your results assuming they have the apparatus. As with the intro, you are not giving instructions. You are summarizing what you did.

Results and Discussion: Remember, even if data is contained in a table or figure, you must also summarize with a narrative paragraph (in addition to the figure or table caption)! Your paragraph should describe your experimental uncertainties for the pressures, and how you determined them. Be careful – the values in P_1 and P_3 have been ADDED to P_2, so if the uncertainty in P_2 is large, it will dominate the uncertainty for all pressure measurements. Create a table of the values for P_1, P_2, and P_3 for your experiment. Remember, every data point has an experimental uncertainty associated with it. You may indicate your uncertainty in the column heading. Your table should also include the value for γ that you calculate for each gas, and the temperature difference based on the calculations. Include the uncertainty in the table, even though that will be discussed later, after you discuss your calculations that lead to it. Give your table a descriptive caption, and write a brief (three to four sentences) description of the raw data contained in the table: what trends do you observe? How did argon differ from nitrogen? Is the difference in P_3 between argon and nitrogen within the experimental uncertainty? The total Data section should be no more than one page, but could be as short as a half page. Scale tables accordingly: they should be readable, but should take up no more space than necessary.

Once you have described your raw data, you can describe the calculations and error propagation that you do. Explain briefly how you determined γ for each gas. Then, in a space of one to two pages (be concise!), interpret your results. Calculations may be hand written as an appendix, but the appendix should be referenced in your text. Calculate the uncertainty in γ using the formal error propagation approach discussed in class (and explain in your narrative that that is what you did). Then, compare to the theoretical values for these two gases (based on the fact that argon is monatomic, and nitrogen is diatomic). Are the theoretical values within the error bars of your experimentally determined value? What other sources of error could account for discrepancy? Then, follow the same process as you calculate the temperature drop upon expansion for each gas. You can do this by using the combined gas law. You may assume that the final temperature of the gas is room temperature (which you should record), and that the volume doesn't change once the cap is resealed. Thus, you can calculate the temperature T_2 when the pressure is P_2, knowing the final pressure P_3 and temperature T_3. The Results and Discussion section is the most important, and is therefore worth the most points.

Conclusion: Normally, in a conclusion, you would write about a half page summarizing the results of your experiment and the conclusions you reached. You should begin with a brief summary of the numerical results from your calculations. In this case, that means a restatement of the values of γ and T_2, each with their experimentally propagated uncertainties, and for each gas. Address things like the reliability of the method for determining γ and the temperature drop (where your results within experimental error of the theoretical result?), most impactful error sources and the effect that they would have on your result (magnitude and direction), and ways to improve the experiment. One type of approach might be to calculate whether a sizable change in your assumed value of P_2 would change your value for γ by much. One way to extend to bigger picture ideas in this case would be to address the validity of the assumptions made. In this case, we have assumed ***adiabatic*** and ***reversible***, but how accurate is that? To what extent does that matter?

Safety and References (two different sections): In every lab, highlight the safety hazards associated with the lab, and to have references for (1) background material, (2) any chemical hazards (MSDS are fine as a reference, but you need to say where you got them, and (3) literature values. In this case, your "literature" value is given by the theoretical (ideal) monatomic or diatomic gas γ values, so you may find yourself citing the same reference for both the background and the literature values. This is fine, but it still needs to be cited.

References

1. Engel, T; Reid, P. *Physical Chemistry,* 4th Ed.; Pearson Education: Glenview, IL, 2019; pp. 36-56.
2. Garland, C. W.; Nibler, J. W.; Shoemaker, D. P. *Experiments in Physical Chemistry*, 8th Ed.; McGraw-Hill: St. Louis, 2009; pp. 106-118.