Approximating the Adiabatic Expansion of a Gas*

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Thermodynamic concepts

- Ideal gas vs. real gas
- Gas law manipulation
- The First Law of Thermodynamics
- Expansion of a gas
- Adiabatic processes
- Reversible/Irreversible processes

Pedagogical Skills

- Thermodynamic system definitions
- Recognizing process dynamics
- Use of proper thermodynamic assumptions
- Data analysis and interpretation
- Open design of experiment
- Cost saving measures in curriculum development

Using the demonstration to reinforce concepts and skills

The procedure

The demonstration procedure below was first described in 1819 by Desormes and Clement (1). It has appeared in lab manuals (2, 3), physical chemistry texts (4 -10), and educational journal articles (11-13):

We begin by allowing a gas to occupy a well insulated vessel, where the pressure ($P_{initial}$) is a bit higher than atmospheric pressure ($V_{initial}$ and $T_{initial}$ are known). The vessel is then opened and closed rapidly, allowing the gas to escape at an intermediate pressure equal to atmospheric pressure (P_{inter}). The speed with which this is done is crucial, because if there is appreciable heat loss to the surroundings, the process can not be assumed to be adiabatic.

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* Hofstein, J., Ward, T., Perry, M., McCabe, D.; Modification of the Classic Adiabatic Expansion Experiment; *The Chemical Educator*; Submitted for publication.

After the vessel is sealed, the remaining gas fills the vessel and the gas returns to the initial temperature (T_{initial}), but at a new pressure (P_{final}).

Background thermodynamics

Consider a system that contains an ideal gas and is restricted to performing only mechanical (P-V) work. Furthermore, assume that the system is thermally insulated from the surroundings ($q = 0$). these conditions describe what is called an adiabatic expansion/compression.

If the system undergoes an infinitesimal change of state, the change in internal energy will be given by

$$dU = C_v dT \,. \tag{1}$$

Using the First Law of thermodynamics, we can show that

$$dU = C_v dT = \text{đ}q + \text{đ}w = \text{đ}w \tag{2}$$

For an ideal gas undergoing a reversible change of state, we have

$$\text{đ}w = -PdV = -\frac{nRT}{V}dV \tag{3}$$

If we substitute Eq. 3 into Eq. 2, we see that

$$C_v dT = -\frac{nRT}{V}dV \tag{4}$$

After dividing by T, Eq. 4 is in integrable form:

$$C_v \frac{dT}{T} = -nR\frac{dV}{V} \tag{5}$$

Since the expansion has an initial and final conditions associated with it (P_{initial}, V_{initial}) → (P_{final}, V_{final}), we can integrate Eq. 5:

$$\int_{T_{initial}}^{T_{final}} C_v \frac{dT}{T} = -nR\int_{V_{initial}}^{V_{final}} \frac{dV}{V} \tag{6}$$

If we assume that heat capacity is a constant over the temperature range (a reasonably good approximation for relatively small changes in temperature), then C_v can be removed from the integral, and evaluation of each integral in Eq. 6 yields

$$C_v \ln\frac{T_{final}}{T_{initial}} = -nR\ln\frac{V_{final}}{V_{initial}} \tag{7}$$

For an ideal gas, $C_p - C_v = n\mathrm{R}$, which can be used to help get Eq. 7 into a more useable form:

$$C_v \ln \frac{T_{initial}}{T_{final}} = (C_p - C_v) \ln \frac{V_{final}}{V_{initial}} \qquad (8)$$

Dividing Eq. 8 by C_v, we obtain

$$\ln \frac{T_{initial}}{T_{final}} = \left[\frac{\left(C_p - C_v \right)}{C_v} \right] \ln \frac{V_{final}}{V_{initial}} \qquad (9)$$

We now define γ as the ratio of C_p to C_v, and substitute the ratio into Eq. 9:

$$\ln \frac{T_{initial}}{T_{final}} = \left[\gamma - 1 \right] \ln \frac{V_{final}}{V_{initial}} \qquad (10)$$

After clearing the natural logarithms from both sides of Eq. 10, we obtain

$$\frac{T_{initial}}{T_{final}} = \left(\frac{V_{final}}{V_{initial}} \right)^{\gamma - 1} \qquad (11)$$

Eq. 11 can be used to calculate the final temperature or final volume of an ideal gas that undergoes an adiabatic, reversible change of state given that the initial conditions and heat capacities of the gas are known.

Mathematical treatment of the aforementioned procedure

To treat the first part of the procedure, we enlist the help of the combined gas law:

$$\frac{P_{initial} V_{initial}}{T_{initial}} = \frac{P_{\mathrm{inter}} V_{\mathrm{inter}}}{T_{\mathrm{inter}}} \qquad (12)$$

If we recognize that the intermediate conditions are symbolized by the “final” subscript in Eq. 11, solve for $T_{\mathrm{initial}}/T_{\mathrm{inter}}$ from Eq. 12, and substitute the ratio into Eq. 11, we obtain

$$\frac{P_{initial} T_{initial}}{P_{\mathrm{inter}} V_{\mathrm{inter}}} = \left(\frac{V_{\mathrm{inter}}}{V_{initial}} \right)^{\gamma - 1} \qquad (13)$$

Rearranging, we obtain

$$\frac{P_{initial}}{P_{\text{inter}}} = \left(\frac{V_{\text{inter}}}{V_{initial}}\right)^{\gamma} \qquad (14)$$

To treat the second part of the procedure, we need to recognize that the temperature rises from T_{inter} to T_{initial} at constant volume (V_{inter}). Using Boyle's Law for this case, we have

$$P_{final}V_{\text{inter}} = P_{initial}V_{initial} \Rightarrow \frac{V_{\text{inter}}}{V_{initial}} = \frac{P_{initial}}{P_{final}} \qquad (15)$$

Because pressures can be measured directly, we want to replace the ratio of volumes in Eq. 14 with a ratio of pressures:

$$\frac{P_{initial}}{P_{\text{inter}}} = \left(\frac{P_{initial}}{P_{final}}\right)^{\gamma} \qquad (16)$$

Now, after taking the natural logarithm of both sides of Eq. 16, we obtain

$$\gamma = \frac{\ln \dfrac{P_{initial}}{P_{\text{inter}}}}{\ln \dfrac{P_{initial}}{P_{final}}} \qquad (17)$$

Using Eq. 17, we can determine γ by measuring the initial pressure of the gas, atmospheric pressure, and the resulting pressure after the expansion occurs.

The assumptions made along the way…

1) The vessel is thermally isolated.
2) The gas being studied behaves ideally.
3) The performed process is reversible.

Experimental details and using the apparatus

To properly address the shortcomings of previous incarnations of the procedure (3, 11) and the conceptual nature of the experiment regarding its reversibility (12, 13), a modified apparatus was design. The setup closely resembled that of Garland, et. al. (3), except for the method of pressure measurement (See figure 1). The rubber stopper of Garland's setup was replaced with a low-cost PVC gate valve to affect the expansion. In addition, the use of an expensive pressure transducer, as in Moore's experiment (10), was replaced with a Vernier gas pressure sensor. Data collection was performed using LoggerPro 3.4.5 controlling a Vernier LabPro device. The software is run on a eMac computer.

The apparatus was constructed with experimental feasibility in mind, and to reduce department operating costs. Both allow the student to actively engage in the process of experimental design, implementation, and data collection. It was decided that the rubber stopper would be replaced entirely. Figure 1 shows that a PVC flexible reducing coupler (United States Plastics Corp. Catalog #30549) was used to reduce the outer rim of the carboy (purchased used from LabExtreme, Inc.) opening to 1.5 inches. A 6-in. long, 1.5-in OD 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 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 100μs. Data collection is performed using either a serial-box interface connected to an Intel Celeron 500 MHz computer running LoggerPro 2.2.1 through Windows 98 or a LabPro interface connected to an eMac computer running LoggerPro 3.4.5.

In addition, with the exception of the Vernier products, all equipment in this experiment setup was used and/or recycled: the computer system donated by the law offices of William J. Smith), eMac donated by Siena College, carboy (purchased used from LabExtreme, Inc.), and Tygon tubing (3/8 in. OD thin walled).

The experiment is 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 opened and closed (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 opened and closed quickly, and that the valve hold positive pressure in the carboy opening before and after the expansion phase of the experiment.

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 2). 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 80 PVC tubing was used so as to minimize the area obscured by the nipple in the carboy neck. The importance of a narrow expansion area is crucial to the experiment and is detailed in Garland, et. al. (3). Initial data acquired using the new setup have been reproducible and come very close to predicted values of γ (11, 12). The total cost of the improvements[1] to the apparatus was less than $75.

- When this experiment is performed in a laboratory setting, the students work in groups on a rotating basis, with each group having to build the apparatus from scratch. This gives them (a) an idea of how the apparatus goes together, (b) a basis for troubleshooting if problems arise, and (c) an appreciation for experimental design and practice.

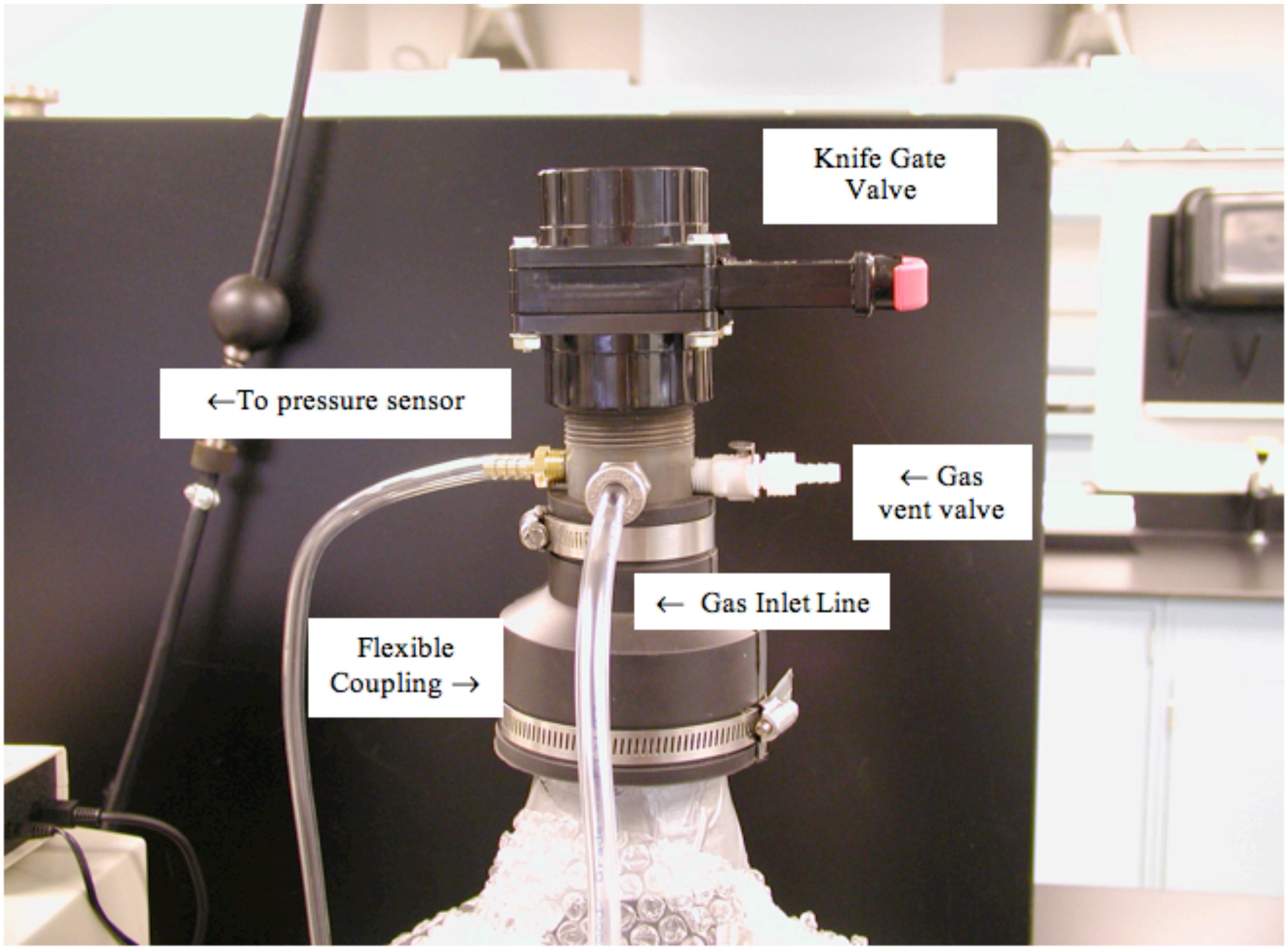

Figure 1: Partial experimental setup. The gas vent valve is usually connected to a hose and sent to a hood.

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[1] The Nupro fitting was the most expensive part at $23.50 from Albany Valve & Fitting Co. If Vernier products need to be purchased, the cost of the entire setup can be obtained for less than $500.

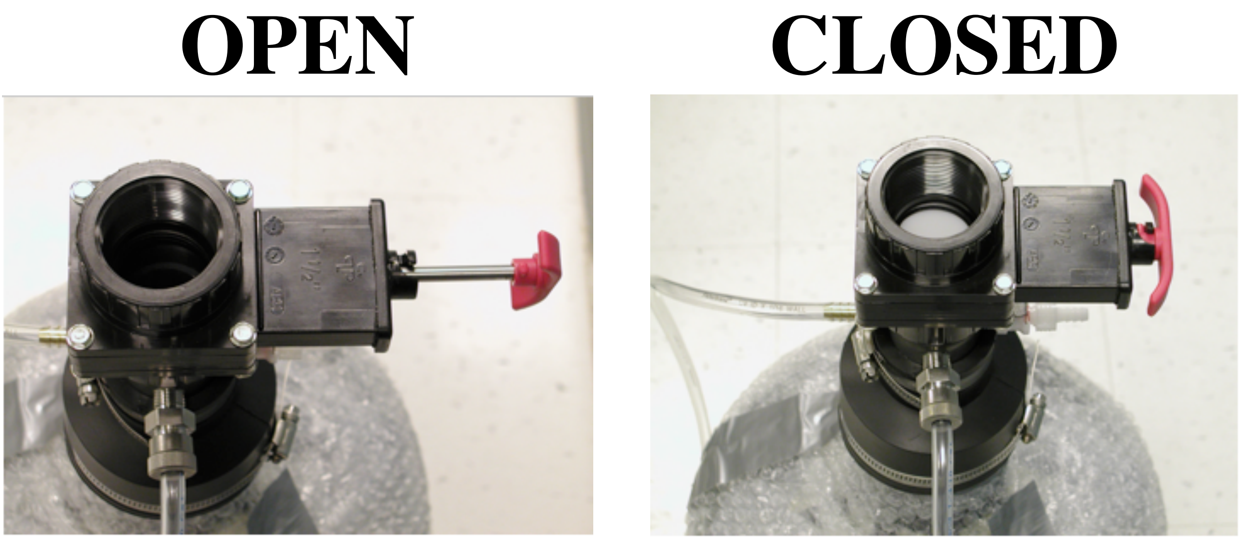

Figure 2: PVC gate valve in open and closed positions.

Safety

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.

Pedagogy

Reversible or Irreversible?

The argument has been brought in the literature (12, 13) that expansion detailed here is not adiabatic and reversible. The thought is that since the adiabatic expansion is against a constant pressure, P (which is atmospheric pressure), the expansion is irreversible. If the expansion was irreversible, the derived equation for the ratio of heat capacities would be different than Eq. 1, and the data should reflect that of the new equation. If the First Law of Thermodynamics is applied to the system, and one assumes we are expanding an ideal gas adiabatically against a constant pressure P, one comes to the following equation:

$$C_v dT = -PdV \tag{18}$$

This can be easily integrated, and after substitution for R ($C_p - C_v = R$), the resulting equation rearranges to

$$C_v\left(\frac{P - p_1}{p_1}\right) = -C_p\left(\frac{P}{p_1} - \frac{T}{T_1}\right) \qquad (19)$$

Since the intermediate temperature after the adiabatic expansion is unknown, it must be calculated from the ideal gas equation for the second step of the process:

$$\frac{T}{P} = \frac{T_1}{p_2} \qquad (20)$$

After substituting Eq. 20 into equation 19 and rearranging, we obtain

$$\gamma_{irreversible} = \frac{\dfrac{p_1}{P} - 1}{\dfrac{p_1}{p_2} - 1} \qquad (21)$$

Even though Eq. 17 and Eq. 21 are derived under different conditions and describe different experiments, they give very similar results. Bertrand and McDonald (12) went on to show that the heat capacity ratio obtained using Eq. 17 was 1.1% lower than the ratio calculated using Eq. 21, confirming Moore's claim. In addition, Bertrand showed that Eq. 21 is a first order term in the expansion of the logarithms used in Eq. 17.

- As part of the weekly expectations in the laboratory rotation sequence of physical chemistry at Siena, each group 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.

REPRESENTATIVE DATA, IN DEPTH LABORATORY INSTRUCTIONS, AND ADDITIONAL COPIES OF TEACHER INFORMATION ARE AVAILABLE UPON REQUEST.

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