Observing the Effect of Molecular Composition on Adiabatic Index

Gerardo F. Salazar

PHY353L Laboratory, Department of Physics, The University of Texas at Austin

Abstract

By measuring changes in pressure, volume, and temperature of three gases undergoing an *isothermal* thermodynamic process we were able to verify the ideal gas law: $PV = nRT$. Using the ideal gas law and measured changes in pressure, volume, and temperature in these three gases undergoing an *adiabatic* thermodynamic process we were able to measure the effect of molecular composition (particularly the atomic degrees of freedom) on the adiabatic index γ. My results do not agree with the theoretical prediction given by: $\gamma = 1 + 2/n$. This is likely due to an error in the data processing and not the data collection itself.

1 Introduction

1.1 Physical Motivation

In the mid 19th century, the advent of molecular kinetic theory replaced the caloric theory of heat and led to the development of statistical mechanics. This theory proposed to explain macroscopic thermodynamic phenomenon via the microscopic interactions of a materials constituent molecules.

Before the development of quantum mechanics, such approaches to physical theories idealized molecules as spherical atoms bound together via springs. Using this model, we seek to verify the theoretical relationship between molecular composition and adiabatic index. Molecular composition determines physical degrees of freedom of individual molecules of a substance and the adiabatic index is a measure of the thermodynamic "inertia" of a substance. The verification of a relationship between the two solidifies the microscopic-to-macroscopic claims of statistical mechanics.

1.2 Theory

The first law of thermodynamics is

$$dU = dQ + dW \tag{1}$$

In the case of an adiabatic process (no net change in heat) this becomes

$$dQ = dU - dW = 0 \tag{2}$$

Rewriting the energy and work terms for a gas it becomes

$$dQ = nC_v dT + PdV \tag{3}$$

Where n is the number of moles of gas and C_v is the heat capacity at constant volume for the gas. The ideal gas law is

$$PV = nRT \tag{4}$$

Where R is the ideal gas constant. In differential form (applying the chain rule) it can be written as

$$dT = \frac{P}{nR}dV + \frac{V}{nR}dP \tag{5}$$

Substituting this form of dT back into (3) gives

$$dQ = nC_v \left(\frac{P}{nR}dV + \frac{V}{nR}dP \right) + PdV = 0 \tag{6}$$

Grouping terms

$$dQ = \left(\frac{C_v}{R} + 1 \right) PdV + \frac{C_v}{R}VdP = 0 \tag{7}$$

The specific heat at constant pressure C_p is related to the specific heat at a constant volume C_v by

$$C_p = C_v + R \tag{8}$$

Substituting (8) into the first term on the RHS of (7) gives

$$C_p PdV + C_v VdP = 0 \tag{9}$$

Dividing by $C_v VP$

$$\left(\frac{C_p}{C_v} \right) \frac{dV}{V} + \frac{dP}{P} = 0 \tag{10}$$

Now we define the ratio of the heat capacities, the adiabatic index

$$\gamma \equiv \frac{C_p}{C_v} \tag{11}$$

Integrating (10) after substituting (11) yields

$$\gamma \ln(V) + \ln(P) = C \tag{12}$$

In a more expressive form

$$\ln(P) = -\gamma \ln(V) + C \tag{13}$$

Fitting this equation to data of pressure versus volume obtained under adiabatic compression allows us to determine the adiabatic index of a gas experimentally.

The adiabatic index, being the ratio of the heat capacities of a gas, naturally must depend on the degrees of freedom available to the constituent molecules. Loosely, as molecules are heated each degree of freedom "absorbs" some of that energy. Vibrational and rotational degrees of freedom due not contribute to temperature and thus molecules with a larger number of degrees of freedom have higher heat capacities. The relationship between adiabatic index and molecular degrees of freedom is given by [1]

$$\gamma = 1 + \frac{2}{n} \tag{14}$$

2

Where n is the number of degrees of freedom (which varies with molecular structure).

A monotonic gas has three translational degrees of freedom which gives $\gamma = 1.666$. A diatomic gas has three translational degrees of freedom, two rotational degrees of freedom, and a vibrational degree of freedom which gives a $\gamma = 1.333$. Carbon-dioxide has three translational degrees of freedom, two rotational degrees of freedom, and four vibrational degrees of freedom which gives $\gamma = 1.222$. This gives us a theoretical prediction to compare to our experimental results given by an analysis of (13).

2 Experimental Setup

2.1 Apparatus

Our experimental setup was identical for both adiabatic and isothermal processes. The apparatus consists of a hand-cranked piston inside of a cylinder with internal pressure, volume, and temperature sensors.

Figure 1: Apparatus used for the experiment

The kind of thermodynamic process affected on the gas is predicated by the rate of the depression of the hand crank. This allowed us to study both adiabatic and isothermal processes via fast and slow compressions respectively. The sensors feed a signal through BNC cables to a National Instruments interface connected to the lab computer. We used LabView and a premade application [2] to process the data.

2.2 Data Collection

A set of three five-second isothermal compressions were performed on each of the three gases. This data will be used to verify the ideal gas law and set a foundation for our analysis of adiabatic index. A set of three rapid-depression (adiabatic process) measurements were performed after the isothermal ones. This will allow us to study the adiabatic index of each of the gases.

The sensors output data in voltages which has to be calibrated using the manufacturer provided calibration curves. The set of three measurements for each process will allow us to take averages and reduce measurement error.

3 Analysis and Results

3.1 Isothermal: Ideal Gas Law

I took the isothermal process data for each of the three gases (three runs each) and transformed the quantities according to the manufacturer specified calibration curve. I then fitted a linear model to the logarithm of each pair of volume and pressure data sets. The resulting linear fits were averaged over to produce a relationship between pressure and volume. We expect an inverse proportionality up to a constant determined by the number of moles of gas present as well as ambient temperature. Below is a sample of the isothermal data.
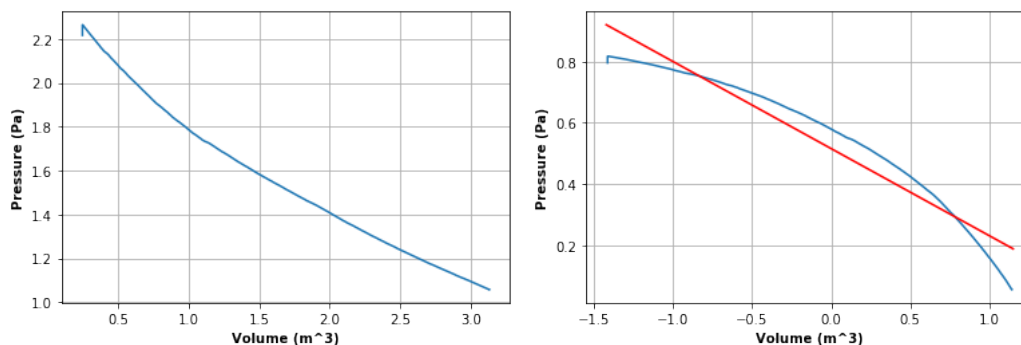

Figure 2: (Left) Raw data (Right) Log-log plot of data and corresponding linear fit

The results of the averaging over fits of the three gases are as follows

Gas	Linear Fit Slope
Argon	-.280±.003
Nitrogen	-.263±.003
Carbon Dioxide	-.317 ±.003

For the purposes of this experiment I am only interested in verifying the inverse proportionality of pressure and volume to set up a basis for our analysis of adiabatic processes. The negative slope of a log-log plot indicates an inverse proportionality. Therefore, I have set a reasonable basis for the continuation of the experiment. Verification of the full gas law would require a calculation of the moles of gas used in each experiment.

3.2 Adiabatic: Adiabatic Index

The main focus of this experiment is measuring the adiabatic index of the three different gases. The adiabatic index is given by the negative of the slope of the linear model fit to the log-log plot of pressure versus volume under an adiabatic process. This is given in (13).

4

As with the isothermal data, I extracted the pressure and volume data of each run, calibrated it according to manufacturer specifications, took the log of the values, and finally fit a linear model to the data. A sample of the adiabatic data is below.
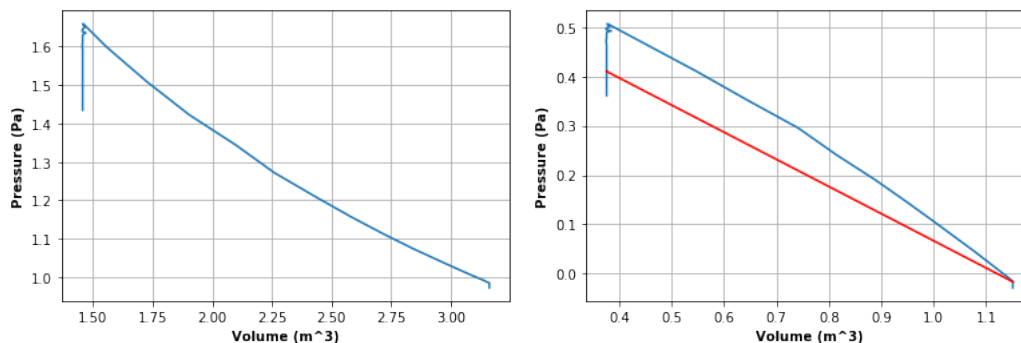

Figure 3: (Left) Raw data (Right) Log-log plot of data and corresponding linear fit

Its clear that early deviations in the data coming from the difficulty of operating the apparatus contribute some error to our actual fits. I chose not to simply cut out this data to accurately represent the difficulty in conducting this experiment as most of it lies in collecting usable data. The results of averaging over fits of the three gases are as follows

Gas	Linear Fit Slope (-Adiabatic Index)
Argon	-.524±.006
Nitrogen	-.521±.004
Carbon Dioxide	-.516 ±.003

4   Conclusion

The expected values of the adiabatic index for the three gases: argon, nitrogen, and carbon-dioxide are 1.666, 1.333, and 1.222 respectively. I deduced values of $.524 \pm .006$, $.521 \pm .004$, $.516 \pm .003$ respectively. It is clear that this is an utter failure to measure the adiabatic index of the gases used. Unfortunately, I have run out of time looking for the mistake in my analysis and am choosing to present my results as is.

References

[1] Adiabatic Condition Development.
http://hyperphysics.phy-astr.gsu.edu/hbase/thermo/adiabc.html. Accessed 6/30/19

[2] National Instruments VI Repository.
https://web2.ph.utexas.edu/ phy353l/WebSource/VIvault.html. Accessed 6/27/19