Heat Capacity Ratios: Comparing Results from Various Experimental and Calculation Methods to Published Values

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Heat capacity ratios for three gases, Argon (Ar), Nitrogen (N\textsubscript{2}), and Carbon Dioxide (CO\textsubscript{2}), were determined experimentally using two methods: the Sound Velocity Method, in which the wavelength of sound traveling through the experimental gas is measured, and the Adiabatic Compression/Expansion Method, in which temperature, pressure, and volume are measured during adiabatic compressions and expansions. One calculation method was used with the data obtained from the sound velocity experimental method and four calculation methods were used with the data obtained from the adiabatic compression/expansion experimental method. In addition to the experimentally determined values, theoretical values for the heat capacity ratios were calculated two ways: using van der Waals constants, and using the equipartition theorem. All calculated values were then compared to published values for the heat capacity ratio of each gas and analyzed for their relationship to molecular degrees of freedom.

I. Introduction

The heat capacity, \( C \), of a material is the ratio of the heat absorbed by the material to the corresponding change in temperature. Substances with higher heat capacities therefore require more heat to achieve a given change in temperature than substances with lower heat capacities. The heat capacity ratio, \( \gamma \), or adiabatic index, of a gas is the ratio of its molar heat capacity at constant pressure, \( C_p \), to its molar heat capacity at constant volume\(^2\), \( C_v \), or,

\[
\gamma = \frac{C_p}{C_v}
\]

(1)

Since, for an ideal gas,

\[
C_p = C_v + R
\]

(2)

the heat capacity ratio will always be greater than one and will decrease as \( C_v \) increases.

The \( C_v \) for a particular chemical can be determined theoretically by examining the molecular structure and determining the number of each type of degree of freedom (translational, rotational, and vibrational)\(^2\). Using the equipartition theorem, and since a molecule with \( N \) atoms has \( 3N \) degrees of freedom, we can see that the more atoms are present in a molecule, the more degrees of freedom exist, therefore the \( C_v \) for that chemical will be higher and \( \gamma \) lower.

This experiment allows \( \gamma \) to be calculated using measurable characteristics for three gases during adiabatic compression. Adiabatic compression indicates that the compression is completed quickly enough that there is no heat transfer with the environment. The sound velocity method uses a function generator to produce sound waves that compress the gas and allowing the speed of sound through the gas to be determined. The adiabatic compression method uses an apparatus that can accurately measure pressure and temperature changes during adiabatic compression.

After analyzing the data, we should be able to determine if the experimental values for \( \gamma \) support the equipartition theorem, as well as reach an opinion on which of the experimental and/or calculation methods is most likely to result in an accurate measurement of \( \gamma \).

II. Experimental Approach

Sound Velocity Method

The apparatus used for this method was similar to what is described in the textbook\(^2\) and in the laboratory handout\(^1\), with some exceptions. The experimental gases flowed from the cylinder into the Kundt’s tube on the speaker end rather than the microphone end, and Channels 1 and 2 on the oscilloscope were for the microphone and oscillator, respectively. Also, although the method indicated a ten-minute flush time prior to testing each gas, the teacher’s assistant (TA) indicated that a five-minute flush was sufficient. On the first day of lab, an HP54600B oscilloscope was used, however after experiencing technical difficulties with another lab
group it was replaced by the TA with a Tektronix TDS 2024B oscilloscope for the second day of lab. For us, this meant that nitrogen gas (N$_2$) and carbon dioxide gas (CO$_2$) were tested with the former oscilloscope and argon gas (Ar) was tested with the latter. The procedure specified at BK Precision 3011B function generator, however the equipment present was not verified to be this model.

Prior to the first measurement run for each gas, the signal strength from the microphone was adjusted to approximately the signal strength from the function generator. Prior to each measurement run, the oscillator frequency and temperature inside the Kundt’s tube were recorded. The Lissajous figures displayed on the X-Y screen of the oscilloscope were used to determine when the microphone on the piston reached the positions of the nodes and half-nodes that indicated phase differences of 0° and 180°. A meter stick was used to identify the locations of those positions. Four sets of data points were collected for each of the three gases.

**Adiabatic Compression/Expansion Method**

The equipment used for this method was as described in the lab handout$^1$ and Adiabatic Gas Law Apparatus manual$^6$, but filling the apparatus with each gas to be tested was accomplished differently than described in either, by direction from the TA. Rather than consecutively opening and closing the inlet and outlet valves, both valves were left open and the piston was raised and lowered slowly enough to keep the experimental gas flowing through the outlet. This procedure was used so as not to over-pressurize the apparatus.

Fifteen compressions and fifteen expansions were completed for Ar and N$_2$, and eleven compressions and eleven expansions were completed for CO$_2$. The reason for the fewer number of data points on the CO$_2$ was the observation by the TA that twenty compressions and expansions together was enough for the experiment. Data Studio software was used to record volume, temperature, and pressure data during each expansion and compression, which was then exported to a .txt file to be analyzed.

**III. Results and Analysis**

**A. Sound Velocity Method.** The relatively crude design of the Kundt’s tube and the piston contributed to friction and vibration that made pinpointing the node position somewhat difficult. In addition, while running the test on CO$_2$, there was a lot of noise showing up on the oscilloscope which made locating the nodes and half-nodes even more difficult. We initially experienced the same problem with Ar on the second day of lab, but before we began to take measurements realized that the noise was likely due to the flow of the gas over the microphone. We choked back the flow of the gas from the cylinder to a very low rate, which resolved the noise problem. It is likely that the same action could have improved our ability to locate the nodes and half-nodes for the CO$_2$. We did notice that the pitch change of the sound emanating from the Kundt’s tube helped to alert us when the piston was nearing a node or half-node.

The heat capacity ratio is calculated using the equation:

\[
\gamma = \frac{Mc^2}{RT}
\]

where $c$ is the speed of sound through the experimental gas, which is determined by doubling the distance between subsequent nodes and half-nodes, as each distance represents one-half of a wavelength, and multiplying the calculated wavelength by the frequency as displayed on the oscilloscope.

\[
c = \frac{\lambda}{2}\]

The data and calculations for each of the three gases are included in Appendix A. Table 1 lists the calculated mean values for $\gamma$ for each gas.

<table>
<thead>
<tr>
<th>Gas</th>
<th>$\gamma$</th>
<th>$\Delta\gamma$ (95% conf.)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ar</td>
<td>1.665</td>
<td>0.020</td>
</tr>
<tr>
<td>N$_2$</td>
<td>1.398</td>
<td>0.017</td>
</tr>
<tr>
<td>CO$_2$</td>
<td>1.290</td>
<td>0.097</td>
</tr>
</tbody>
</table>

Table 1. Heat Capacity Ratios as Calculated via the Sound Velocity Method

**B. Adiabatic Compression Method.** It was not until after completion of the lab when we realized that according the apparatus manual$^6$, expansion data should not be used for quantitative measurement due to the heating of the glass cylinder during the piston movement. However, even with the rejection of the expansion data, eleven sets of data points were available for analysis from the CO$_2$.

The heat capacity ratio was calculated using four different methods (equations), each of which used a unique combination of distinct data points that were extracted from the exported data generated by the PASCO Adiabatic Gas Law Apparatus. Figures 1-3 illustrate typical locations of the data points from one adiabatic compression.
The first equation uses the initial equilibrium prior to compression, $P_1$, the maximum pressure at the completion of compression, $P_2$, and the final pressure after the system has achieved thermal equilibrium $^1$:

$$\gamma = \frac{\ln(P_1/P_2)}{\ln(P_1/P_3)} \tag{5}$$

The remaining three equations are derived from the standard adiabatic gas law $^2$:

$$PV^\gamma = k \tag{6}$$

The second equation indicates that $\gamma$ is equal to the negative slope of a log(P) vs. log (V) plot. It is important to note that only corresponding P/V points between initial pressure ($P_1$) and maximum pressure ($P_2$) are used in these calculations:

$$\log(P) = -\gamma \log(V) + k \tag{7}$$

where $\gamma$ is calculated using the slope equation:

$$b = \frac{\sum(x-\bar{x})(y-\bar{y})}{\sum(x-\bar{x})^2} \tag{8}$$

and where $x=\log(V)$ and $y=\log(P)$.

The third equation is a restatement of the standard adiabatic gas law:

$$P_1V_1^{\gamma} = P_2V_2^{\gamma} \tag{9}$$

which when solved for $\gamma$ yields:

$$\gamma = \frac{\ln(P_2) - \ln(P_1)}{\ln(V_1) - \ln(V_2)} \tag{10}$$

The fourth and final equation relates temperature and volume prior to and upon completion of adiabatic compression:

$$T_1V_1^{\gamma-1} = T_2V_2^{\gamma-1} \tag{11}$$

which when solved for $\gamma$ yields:

$$\gamma = \frac{\ln(T_2) - \ln(T_1)}{\ln(V_1) - \ln(V_2)} + 1 \tag{12}$$

The data and calculations for each method and each of the three gases are included in Appendix B. Table 2 lists the calculated mean values for $\gamma$ for each gas and method.

---

*Table 2*

<table>
<thead>
<tr>
<th>$T_1$ (K)</th>
<th>$T_2$ (K)</th>
<th>$T_3$ (K)</th>
</tr>
</thead>
<tbody>
<tr>
<td>275</td>
<td>285</td>
<td>295</td>
</tr>
<tr>
<td>295</td>
<td>305</td>
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<td>315</td>
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<td>345</td>
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</tr>
<tr>
<td>355</td>
<td>365</td>
<td>375</td>
</tr>
</tbody>
</table>

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1. Physical Chemistry, Lab 1, 2010, Fall, Expt. 1.
As we mentioned in the introduction, the equipartition theorem allows us to calculate theoretical values for $\gamma$ by determining the number of each type of degree of freedom for each molecule to determine $\tilde{C}_v$, then applying equations (1) and (2). Each molecule has $3N$ degrees of freedom. Following the derivation using classical statistical mechanics, we find that monatomic gases have only translational energy, so we use the equation:

$$\tilde{C}_v = \frac{3}{2} R$$

(14)

Diatomic and polyatomic gases also have rotational and vibrational energy, although the vibrational energy is dependent on temperature and including its full value is not necessarily appropriate, especially for diatomic molecules, so for diatomic molecules we can use the equation:

$$\tilde{C}_v = \frac{5}{2} R$$

(15)

but for polyatomic gases we need to consider the vibrational contribution of $3N-5$ for linear molecules or $3N-6$ for nonlinear molecules. For CO$_2$, a linear molecule with three atoms, we arrive at the equation:

$$\tilde{C}_v = \frac{13}{2} R$$

(16)

In addition to the equipartition theorem, we can use published van der Waals constants to calculate theoretical values for $\gamma$. Using the equation:

$$\gamma = 1 + \frac{R}{C_v} \left( 1 + \frac{2\alpha}{pV^2} \right)$$

(17)

and the ideal gas limit,

$$\tilde{V} = RT/P$$

(18)

we can calculate $\gamma$:

$$\gamma = 1 + \frac{R}{C_v} \left( 1 + \frac{2\alpha P}{R^2T^2} \right)$$

(19)

Calculations for both the equipartition theorem and van der Waals gases are included in Appendix C. The calculated theoretical values of $\gamma$ for each gas are included in Table 5 in the following section.

V. Discussion

In this experiment, we looked at several different ways of calculating heat capacity ratios for the three experimental gases. Although there was disagreement among the various methods of calculation, each method revealed the pattern that as the number of molecules in

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**Table 2. Heat Capacity Ratios as Calculated via Adiabatic Compression Methods**

In addition to the heat capacity ratio, the work done on the gas during adiabatic compression can be calculated both theoretically using published values for $\gamma$ and the known volumes in the apparatus:

$$W = \frac{PV^{\gamma}}{1-\gamma} (V_2^{1-\gamma} - V_1^{1-\gamma})$$

(13)

and experimentally by plotting pressure vs. volume during adiabatic compression and performing a numerical integration. The data and calculations for each method and each of the three gases are included in Appendix B. Table 3 lists the calculated mean values for work and the theoretical work for each gas.

**Table 3. Theoretical and Calculated Work During Adiabatic Compression**

<table>
<thead>
<tr>
<th>Gas</th>
<th>Theoretical Work (J)</th>
<th>Experimental Work (J)</th>
<th>$\Delta W$ (95% conf.)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ar</td>
<td>9.684</td>
<td>9.039</td>
<td>0.146</td>
</tr>
<tr>
<td>N$_2$</td>
<td>9.104</td>
<td>9.194</td>
<td>0.0768</td>
</tr>
<tr>
<td>CO$_2$</td>
<td>8.838</td>
<td>9.013</td>
<td>0.126</td>
</tr>
</tbody>
</table>

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**Table 4. Theoretical and Experimental Temperatures and Pressures After Adiabatic Compression**

<table>
<thead>
<tr>
<th>Gas</th>
<th>$P_2$ (kPa) (Theor.)</th>
<th>$P_2$ (kPa) (Exp.)</th>
<th>$T_2$ (K) (Theor.)</th>
<th>$T_2$ (K) (Exp.)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ar</td>
<td>217.040</td>
<td>208.060</td>
<td>373.511</td>
<td>364.296</td>
</tr>
<tr>
<td>N$_2$</td>
<td>195.229</td>
<td>193.387</td>
<td>340.226</td>
<td>336.962</td>
</tr>
<tr>
<td>CO$_2$</td>
<td>185.495</td>
<td>186.573</td>
<td>326.921</td>
<td>325.759</td>
</tr>
</tbody>
</table>

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**C. Theoretical Calculations.** Equations (9) and (11) can be used to determine theoretical values for final temperature and pressure after adiabatic compression. These calculations are included in the “Additional Calculations” sections of Appendix B. Table 4 lists the theoretical values and mean experimental values for final temperature and pressure for each gas.
a gas increases, the heat capacity ratio decreases. We can also deduce from equation (16) that non-linear molecules will have a lower value for $\tilde{C}_v$, and therefore a higher value for $\gamma$. Table 5 summarizes values for $\gamma$ from each method described above, along with standard deviations and confidence levels where appropriate.

<table>
<thead>
<tr>
<th>Calculation Method</th>
<th>$\gamma$ (Ar)</th>
<th>$\sigma_\gamma$ (Ar)</th>
<th>$\Delta\gamma_{95%}$ (Ar)</th>
<th>$\gamma$ (N\textsubscript{2})</th>
<th>$\sigma_\gamma$ (N\textsubscript{2})</th>
<th>$\Delta\gamma_{95%}$ (N\textsubscript{2})</th>
<th>$\gamma$ (CO\textsubscript{2})</th>
<th>$\sigma_\gamma$ (CO\textsubscript{2})</th>
<th>$\Delta\gamma_{95%}$ (CO\textsubscript{2})</th>
</tr>
</thead>
<tbody>
<tr>
<td>Published\textsuperscript{a}</td>
<td>1.667</td>
<td></td>
<td>1.400</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>1.289</td>
</tr>
<tr>
<td>Equipartition Theorem (without $\tilde{C}_{v(vib)}$)</td>
<td>1.667</td>
<td></td>
<td>1.400</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>1.400</td>
</tr>
<tr>
<td>Equipartition Theorem (with $\tilde{C}_{v(vib)}$)</td>
<td>-</td>
<td></td>
<td>1.285</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>1.154</td>
</tr>
<tr>
<td>van der Waals</td>
<td>1.670</td>
<td></td>
<td>1.401</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>1.290</td>
</tr>
<tr>
<td>Sound Velocity</td>
<td>1.665</td>
<td>0.0132</td>
<td>0.020</td>
<td>1.398</td>
<td>0.0121</td>
<td>0.017</td>
<td>1.290</td>
<td>0.0945</td>
<td>0.097</td>
</tr>
<tr>
<td>Adiabatic Compression Equation (5)</td>
<td>1.487</td>
<td>0.0239</td>
<td>0.0133</td>
<td>1.309</td>
<td>0.0120</td>
<td>0.00667</td>
<td>1.257</td>
<td>0.0107</td>
<td>0.00720</td>
</tr>
<tr>
<td>Adiabatic Compression Equation (8)</td>
<td>1.564</td>
<td>0.0181</td>
<td>0.0101</td>
<td>1.378</td>
<td>0.0117</td>
<td>0.00649</td>
<td>1.304</td>
<td>0.0104</td>
<td>0.00702</td>
</tr>
<tr>
<td>Adiabatic Compression Equation (10)</td>
<td>1.548</td>
<td>0.0232</td>
<td>0.135</td>
<td>1.374</td>
<td>0.0146</td>
<td>0.0875</td>
<td>1.305</td>
<td>0.0121</td>
<td>0.0831</td>
</tr>
<tr>
<td>Adiabatic Compression Equation (12)</td>
<td>1.602</td>
<td>0.00648</td>
<td>0.819</td>
<td>1.374</td>
<td>0.00466</td>
<td>0.380</td>
<td>1.279</td>
<td>0.000710</td>
<td>0.328</td>
</tr>
</tbody>
</table>

Table 5. Summary of Calculated and Published Values for Heat Capacity Ratios
Let us first examine the calculated theoretical values. The equipartition theorem appears to be a very accurate method for calculating the heat capacity ratio for monatomic gases. In addition, when discounting the vibrational contribution to the heat capacity for diatomic gases, the equipartition theorem also appears accurate. This indicates that, at least for N₂, the vibrational contribution to the heat capacity is negligible. However, as previously discussed, the equipartition theorem allows for only an “all or nothing” approach when considering the vibrational contribution for polyatomic gases. This is unrealistic since vibrational contributions are dependent on temperature and contribute significantly, but only partially². This explains why neither calculation from the equipartition theorem is accurate for CO₂. The vibrational contribution could be better estimated using statistical mechanics; however that method was not calculated here.

Calculations using the van der Waals constants are the only calculations used that do not assume ideal gas behavior (perfectly elastic collisions), but rather take into account the intermolecular forces in a gas. The calculated values show general agreement with published values, differing by only 0.18%, 0.07%, and 0.08% for Ar, N₂, and CO₂ respectively. This indicates that the assumption of ideal gas behavior for all other methods of calculation used in this experiment is valid.

The results from the sound velocity method show general agreement with the published values, as the mean value for γ for each gas was within both the 95% confidence limit (as determined by propagation of error) and 2σ of the published values. It should be noted, however, that the error associated with the CO₂ calculation is considerably greater than those of Ar and N₂. This is likely due to the noise distortion we experienced, as discussed previously. Given the opportunity to repeat the wavelength measurements, we could reduce the flow rate on the CO₂ to reduce the noise. There is general error associated with the scribbled line on the piston used to measure node locations and the meter stick itself (accurate to only 1mm), as well as the general difficulty in accurately locating each node since tiny movements of the piston were interrupted by friction caused by the piston movement.

Analysis of the results from the adiabatic expansion method is more complex. First, please note that the calculated Δγ₉₅% for the third and fourth calculation methods is at least an order of magnitude greater than the Δγ₉₅% for the first and second methods. This is due to using different methods of calculation. The Δγ₉₅% for the first two methods was calculated using the standard deviation of the mean and the t-distribution³, while Δγ₉₅% for the last two methods was calculated using propagation of error. Now let us examine the results for each gas individually.

**Argon.** The results from the four calculation methods differ significantly, with each result being more than 2σ from at least one other. None of the results were within 2σ of the published value. Only the fourth method was within Δγ₉₅%, but this value is suspect as the calculated error is so great.

**Nitrogen.** The result from the first method is significantly different than the last three, however the last three are in general agreement with each other. Only the results from methods two and three were within 2σ of the published value. The results from the third and fourth methods were within Δγ₉₅%, but as with Argon, the value for the fourth method is suspect as the calculated error is so great.

**Carbon Dioxide.** The results from the first and fourth methods are significantly different from each of the other results; however the results from the second and third methods are in general agreement with each other. Only the results from methods two and three were within 2σ of the published value. The results from the third and fourth methods were within Δγ₉₅%, but as with Argon and Nitrogen, the value for the fourth method is suspect as the calculated error is so great.

For each of the gases, the first calculation method gave a significantly low result. The calculated error for the fourth method is such a high percentage of the calculated value that its results are suspect across the board. It should be noted, however, that the calculated results from the fourth method were actually the most precise (that is, they have the lowest σ). It is possible that because equation (12) includes the term “+1”, the propagation of error calculation is unnecessarily high. The second and third methods gave relatively close results to published values for N₂ and CO₂, but not for Ar. None of the four calculation methods gave accurate enough or consistent enough results to be considered a good measure of heat capacity ratio.

The adiabatic compression method is not considered to be the best method for determining heat capacity ratios². The apparatus can only provide conditions that are approximately adiabatic. This error is reduced by discounting the expansion data, but it remains nonetheless. In addition, during the compression, the values of pressure and temperature change so rapidly that having data points every 0.1 seconds does not give as clear a picture or as accurate data than if readings could be taken at closer intervals, e.g. 0.05 or even 0.01 seconds. While initial temperatures and pressures are likely to be accurate, it is difficult to determine if the peak temperatures and pressure provided by the apparatus data are accurate.

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It is possible that the sound velocity method is more accurate than the adiabatic compression method because the compressions that take place within the Kundt’s tube (as a result of the sound waves from the function generator) happen so quickly that true adiabatic conditions are more closely approximated than can be realized in the PASCO apparatus.

VI. Conclusions

Of the two experimental methods, the sound velocity method gave the most accurate results with respect to published values for heat capacity ratios of the three tested gases. The theoretical results calculated using the equipartition theorem indicate that it can be used to accurately determine the heat capacity ratio of monoatomic and diatomic gases, but that a different method of calculating the vibrational contribution to the heat capacity is necessary for polyatomic gases.

As the number of atoms increases, the heat capacity ratio of a molecular gas will decrease, however gases with equivalent numbers of atoms will have higher heat capacities if they are nonlinear molecules than if they are linear molecules.

VII. References

1 Determining Heat Capacity Ratios for Gases. (2010, Fall).