Determining the Ratio of Specific Heat Capacities for Gases at Room Temperature Via Adiabatic Oscillations

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The ratio of specific heat capacities (γ) for Air, Argon and CO_2 were calculated using three different methods based around Rüchardt and Rinkel's work. The closest value for air was found to be $\gamma_{Air} = 1.44 \pm 0.01$, 3% from the literature value. All values for all gases and methods were within 14%. A discussion of the methods employed and a range of suggestions for future work follows.

INTRODUCTION

The ratio of specific heat capacity at constant pressure to that at constant volume, γ, is a value that can be predicted theoretically and found experimentally. It is extremely useful in the study of reversible thermodynamic processes, with applications of it's use extending to the study of vibrations within air, including the relationship between γ and the speed of sound. The most well known (at least to undergraduate laboratories) method of finding this constant, is the method introduced by Rüchardt in the early 1900s, later improved by Rinkel in 1929 [1] to improve accuracy and error. There have been many adaptations of this general experiment as technology has advanced, and digital apparatus for measurement in these experiments are now commonplace. I will discuss how each method compares to each other and to a modified version where improvements are made on these early 20^{th} century methods using a glass syringe.

METHODS

Rüchardt's Method

The method introduced by Rüchardt consists of a sealed volume attached to a glass tube, with a metal ball that has a diameter as similar to that of the inner of the tube as possible. By displacing the ball from its equilibrium position by a small amount, we can create harmonic oscillations, the period, T, of which relate to the ratio of specific heat capacities, γ, by:

$$\gamma = \frac{4\pi^2 mV}{A^2 PT^2} \tag{1}$$

Where m is the mass of the ball, V is the volume of the tube and chamber, A is the cross-sectional area of the tube, P is the pressure inside the combined tube and chamber, and T is the time period of the measure oscillations. A full derivation of this equation and explanation is available in the Appendix.

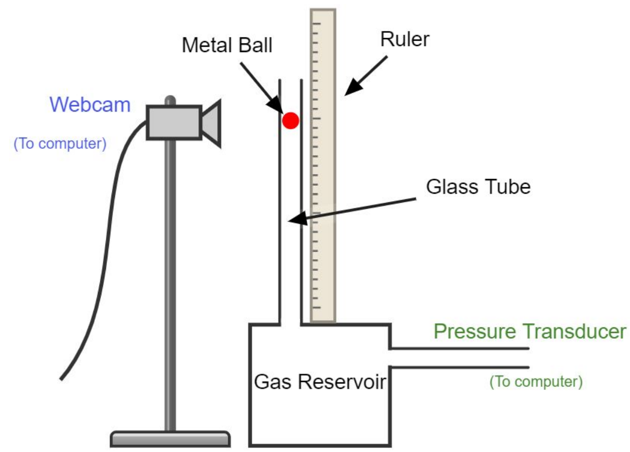

FIG. 1. A diagram of the apparatus used to collect the data for this experiment. The Pressure Transducer is used for the Rüchardt method and the Webcam is used for the Rinkel Method.

Balls of differing mass were dropped into the tube to oscillate and the resultant changes in the pressure were measured by a computer using the TracerDAQ [2] software. The period of these oscillations can then be found when analysing the data on a computer. Effort was made to clean both the balls and the tube with ethanol before each run in order to minimise friction. The order of gases used should ideally be Air, Argon, Co2, which is the order of ascending molar mass. The idea here is that the heavier gases will more completely displace the lighter ones, as to avoid having a mixture of gases in the chamber at the time of measurement. How accurate this actually is, is likely limited by the entropically favourable mixing. To minimise this risk, overfilling with each gas while letting some escape can be used to 'flush' the chamber.

Once the raw data is collected, custom Python scripts [3] were used to find the peaks of the oscillations. These peaks were then 'cleaned' so only the clearly defined oscillations were used to calculate the inter-peak time period. A value for gamma and its associated error is then found for each run and a mean is taken (and errors combined) (see appendix).

Rinkel's Method

This method is very similar to Rüchardt's, but with a clever improvement to increase accuracy and minimise error. The equipment is still set up as in Fig. 1 but a webcam is now used to measure the maximum displacement of each ball graphically during its initial oscillation. Each video is gone through frame by frame until the maximum/turning point is found. γ can now be calculated by:

$$\gamma = \frac{2mgV}{PA^2L} \tag{2}$$

(derivation in appendix) (m = Mass $[Kg]$, g = acceleration due to gravity $[ms^{-1}]$, V = Volume $[m^3]$, P = Pressure $[Pa]$, A = cross-sectional area $[m^2]$ and L = maximum displacement $[m]$) .

This has two effects on the result:

1. The length L can be measured to a higher accuracy than T.
2. The L term in (Eqn. 2) is not raised to a power, where as T in (Eqn. 1) is a squared term, resulting in an error contribution with a factor of two multiplying it. (See appendix)

Three balls of varying mass were used for each of these methods, and measurements were repeated three times for each.

Syringe Method

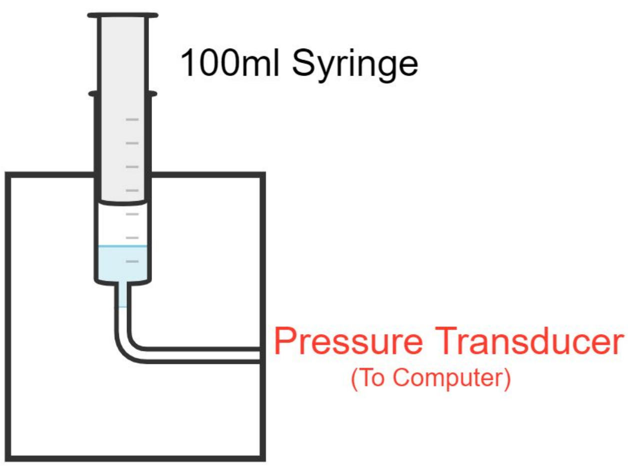

FIG. 2. A syringe is filled with air and connected via a rubber tube to a Pressure Transducer, which logs the data back to a computer digitally.

This method is a simple adaptation of Rüchardt's method with improvements only in execution, (i.e. the underlying theory is the same). Instead of a ball in a large chamber, we use a 100ml syringe with plunger connected directly to a digital pressure transducer. This means the volume can be varied, here between 60ml and 100ml. The syringe plunger is then given a small 'flick' to begin the oscillations and once again the time period of these can be found. Gamma,γ, can then be found using (Eqn.1).

RESULTS

Rüchardt's Method

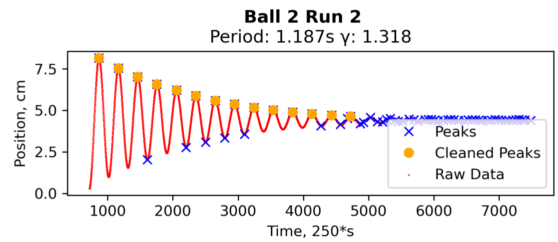

FIG. 3. Pressure/position against time for one of the runs using Rüchardt's method. Peaks and cleaned peaks (used for time period calculation) are labelled. Generated using `numpy`, `scipy` and `matplotlib`.

$$\gamma_{Air} = 1.27 \pm 0.02$$
$$\gamma_{Argon} = 1.40 \pm 0.01$$
$$\gamma_{CO_2} = 1.156 \pm 0.009$$

Percentage difference to literature: 10%, 14% and 11% respectively.

Rinkel's Method

The maximum displacement was measured by scrolling through the video frame by frame to find the point at which the ball changes direction.

Air

Mass of Ball (kg)	Ratio of Specific Heats, γ	Error on γ
0.0253	1.403	0.034
0.0359	1.404	0.033
0.0135	1.512	0.036

FIG. 4. Results table for Rinkel's method on air with ball masses, gamma values and associated error.

Ratio of specific heat capacities: $\gamma_{Air} = 1.44 \pm 0.01$

Percentage difference to literature: 3%

Argon

Mass of Ball (kg)	Ratio of Specific Heats, γ	Error on γ
0.0253	1.604	0.038
0.0359	1.571	0.037
0.0135	1.679	0.04

FIG. 5. Results table for Rinkel's method on argon with ball masses, gamma values and associated error.

Ratio of specific heat capacities: $\gamma_{Argon} = 1.61 \pm 0.01$
Percentage difference to literature: 4%

CO_2

Mass of Ball (kg)	Ratio of Specific Heats, γ	Error on γ
0.0253	1.284	0.03
0.0359	1.251	0.03
0.0135	1.323	0.031

FIG. 6. Results table for Rinkel's method on CO_2 with ball masses, gamma values and associated error.

Ratio of specific heat capacities: $\gamma_{CO_2} = 1.28 \pm 0.01$
Percentage difference to literature: 2%

Syringe Method

From the raw data, each 'flick' was found and separated. As before, peaks were found via a Python script and clipping peaks removed. The time periods were then calculated and an average value for gamma found, with errors combined using partial derivatives (see appendix for error calculations).

Ratio of specific heat capacities: $\gamma_{Air} = 1.50 \pm 0.05$
Percentage difference to literature: 7%

DISCUSSION

Rüchardt's method gave results that are 10%, 14% and 11% from the accepted values of 1.4, 1.76 and 1.3 [4],[5] for air, argon and CO_2 respectively. These are reasonably close but not very impressive, to get an idea of the impact on real world uses, this translates to calculating the speed of sound as $327m/s$ instead of the expected $343m/s$, a (5%) difference (I.11). While the small uncertainty ranges appear to be very precise for all of these gases, the uncertainty ranges do not include the literature value. This is likely due to the calculation of the time period not having an associated error as large as the true error. As the time periods were calculated by a custom python script, an attempt was made to associate error via the degrees of freedom in my code, but this approach is limited when using external modules with undefined complexities.

The time periods were also calculated here using only the peaks of the oscillations, including the minima should provide a more accurate value with smaller error. Another improvement to this method is to take friction into account by finding the exponentially decaying envelope function (see fig. 3) and re-deriving Eqn.1 with a friction force. This loss of energy due to friction is important as the assumption we make during this experiment is that the oscillations are reversible and adiabatic, when friction is present there is obviously an increase in entropy so these assumptions begin to fail.

Rinkel's method gave me more accurate results, with the percentage difference to the literature ranging from $2\% - 4\%$. This improvement in the accuracy of γ is likely down to the increased accuracy of measuring length over time period [1]. The level of precision remains relatively similar, although the literature values are once again not within the uncertainty range. The time contribution to the error in Eqn. 1 (Rüchardt's method) has a factor of two multiplying it (due to the T^2 term where as the length contribution to the error here (Eqn. 2) does not. This similar overall error is from a larger error in the length measurement (and more importantly an underestimated error in time period). I originally tried to calculate the maximum displacement (length) by plotting every video frame on a displacement time graph and interpolating between frames to find the minimum of the parabola. Unfortunately, due to the low frame rate and possibly a 'cheap' (e.g. fast and non-safe) codec combined with low bandwidth communication and storage (most likely USB 2.0), up to 40% of frames were dropped in some videos, meaning accurate interpolation was not possible.

The biggest improvements here would be an improved method of measuring the maximum displacement, possibly using LASER, LIDAR or a similar distance measuring device placed at the top of the tube. Considering friction could also bring marginal improvements, although this would be much less substantial than in Rüchardt's method as here only one oscillation is used, so only one oscillation (as far as we are concerned) will lose energy to friction in comparison to the effect of the energy loss for $10-15$ oscillations.

The syringe method gave a final result 7% different to the literature. This was an improvement on Rüchardt's method (which this is in theory) but still not as close as Rinkel's method. The way the execution of this method differs to Rüchardt's is mainly by differing the volume, although the syringe and plunger will also have different frictional characteristics. Improvements were most likely due to the much larger number of runs (34 vs 9) as individual results seemed qualitatively worse. This can be seen quantitatively by the much larger spread of results when compared to the other methods. Here the uncertainty (± 0.05) is approximately 5 times as large as the associated uncertainties for both the other methods, although it disappointingly still does not contain the literature value. Similar to the Rüchardt method, this is almost certainly due to an under estimation of the errors associated with the found time period. Here the script is even more complex, yet this isn't fully taken into account in the calculations due to the same reasons as before.

The data collection for this method could have been improved as for a majority of runs, the first few oscillations where the time period is clearest and usually has the most constant time period were clipping. This meant I was limited in the number of points I could find time periods between, while also using (theoretically) lower quality points. The same considerations as Rüchardt's method apply here in regards to using a more robust script to find the time periods that includes minima as well as maxima.

All of the methods used here are limited in their possible accuracy by the assumptions that underpin them, i.e. that the gases are ideal and the pressure/volume oscillations are both reversible and adiabatic. While there are methods that make technical/experimental improvements [6] there are also methods that take into account the deviation from the ideal gas law [7], though these may be to complex to become a standard undergraduate laboratory experiment. While γ varies with temperature and this can be studied [8], an alteration possibly more suitable to undergraduate laboratories would be to study the variation of γ with time period [9]. The adiabatic assumption only holds for very short time periods and this method allows for extrapolation to time periods shorter than would be possible with regular equipment.

CONCLUSIONS

Rinkel's method proved to be the most accurate, with results $\gamma_{Air} = 1.44 \pm 0.01$, $\gamma_{Argon} = 1.61 \pm 0.01$ and $\gamma_{CO_2} = 1.28 \pm 0.01$, all within 4% of the literature values. The syringe method's technical improvements over Rüchardt's standard method brought about an increase in accuracy (3% better for air) as expected. Similar technical improvements to Rinkel's method would likely improve accuracy further, as would correcting for friction. Investigating the relationship between γ, temperature and time period would likely give much better results without major equipment changes.

ACKNOWLEDGEMENTS

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SOURCE CODE

The source code for all of the analysis in this paper is available on GitHub [3] and contains interactive notebooks to reproduce the same results as in this paper from the raw data along with figures of my entire results.

APPENDIX

Eqn. 1 Derivation: A small downwards displacement x on the ball will cause a small decrease in volume and vice versa.

$$dV = xA \tag{I.3}$$

This small change in volume causes a change in the pressure of the tube and vessel given by:

$$dP = \frac{F}{A} \tag{I.4}$$

Combining these gives:

$$F = dP\frac{\gamma}{dV} \tag{I.5}$$

We now assume that due to rapid oscillations, the changes in the gas are adiabatic. Due to the changes being small, we also assume that both changes in V and P are quasi-static. From this we can write the Poisson equation:

$$PV^{-\gamma} \ = \ const. \tag{I.6}$$

and

$$P_\gamma V^{\gamma-1}dV \ + V^\gamma dP \ = 0 \tag{I.7}$$

Substituting dV and dP in (I.4):

$$F = -\frac{\gamma PA^2}{V}x \tag{I.8}$$

This is a restoring force, F, which is directly proportional to the negative of the displacement, x, e.g. the definition of simple harmonic motion. The time period, T of simple harmonic motion is given by:

$$T = 2\pi\sqrt{\frac{m}{\left(-\frac{F}{y}\right)}} \tag{I.9}$$

By comparing to (I.7) and re-arranging we get:

$$\gamma \ = \ \frac{4\pi^2 mV}{A^2PT^2} \tag{I.10}$$

Speed of sound calculation [10]:

$$c = \sqrt{RT\gamma} \tag{I.11}$$

c is the speed of sound

R is the gas constant ($287\ J\ K^{-1} kg^{-1}$)
T is temperature in Kelvin

Partial Derivatives for Error Calculation of γ:
Rüchardt's Method:

$$\frac{\partial\,\gamma}{\partial\,m} = \frac{4\pi^2 V}{A^2 P T^2} \tag{I.12}$$

$$\frac{\partial\,\gamma}{\partial\,V} = \frac{4\pi^2 m}{A^2 P T^2} \tag{I.13}$$

$$\frac{\partial\,\gamma}{\partial\,A} = -\frac{8\pi^2 m V}{A^3 P T^2} \tag{I.14}$$

$$\frac{\partial\,\gamma}{\partial\,P} = -\frac{4\pi^2 m V}{A^2 P^2 T^2} \tag{I.15}$$

$$\frac{\partial\,\gamma}{\partial\,T} = -\frac{8\pi^2 m V}{A^2 P T^3} \tag{I.16}$$

Rinkel's method:

$$\frac{\partial\,\gamma}{\partial\,m} = \frac{2gV}{A^2 P L} \tag{I.17}$$

$$\frac{\partial\,\gamma}{\partial\,V} = \frac{2mg}{A^2 P L} \tag{I.18}$$

$$\frac{\partial\,\gamma}{\partial\,A} = -\frac{4mgV}{A^3 P L} \tag{I.19}$$

$$\frac{\partial\,\gamma}{\partial\,P} = -\frac{2mgV}{A^2 P^2 L} \tag{I.20}$$

$$\frac{\partial\,\gamma}{\partial\,L} = -\frac{2mgV}{A^2 P L^2} \tag{I.21}$$

Combining γ and associated error ($\Delta\gamma$):

$$For:\ \gamma_1 \pm \Delta\gamma_1\ ,\ \ \gamma_2 \pm \Delta\,\gamma_2\ ,\ \ldots\ ,\ \ \gamma_n \pm \Delta e_n \tag{I.22}$$

$$\gamma\ =\ \sum_{i=1}^{n} \gamma_i \tag{I.23}$$

$$\Delta\gamma\ =\ \sqrt{\sum_{i=1}^{n} \left(\frac{1}{n} \cdot \Delta\gamma_i\right)^2} \tag{I.24}$$

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Note: The websites that are referenced have all been crawled by the Internet Archive WayBack Machine [11] to ensure consistent access into the future.