

Determining the Ratio of Specific Heats of Gases using Adiabatic Oscillations

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Abstract

The ratios of specific heats, $\gamma = (C_P/C_V)$, for three gases (air, argon and carbon dioxide) were calculated by measuring the oscillations of different masses in various apparatus. The experiments followed R uchardt's and Rinkel's methods; a 100ml glass gas syringe was additionally used to extend the investigation as well as a technique to elimination of friction. The approaches and results were compared; the most accurate method (R uchardt's method alongside compensation for friction) yielded:

Air, $\gamma = 1.358 \pm 0.0038$

Argon, $\gamma = 1.6597 \pm 0.0009$

Carbon dioxide, $\gamma = 1.2996 \pm 0.0087$

These differ from the literature value by 3.0%, 0.6% and 1.5% respectively. The reasons for these apparent discrepancies are discussed.

1. Introduction

The ratio of specific heats is the ratio of the specific heat capacity at constant pressure to that at constant volume, also known as the isentropic expansion factor. The ratio of specific heats is also the ratio between enthalpy to internal energy. Eduard R uchardt's experiment in the early 20th century was a significant step in thermodynamics, inspiring similar procedures which have evolved over time. In 1929, Rinkel [1], using the same apparatus, determined the ratio of specific heats by measuring the vertical distance which the sphere falls before it begins to rise.

In 1951, Koehler [2] adapted the experiment by feeding gas into the tube via a small hole in order to keep constant pressure. In 1959, Taylor [3] found similar results using a column of mercury in a U-shaped tube. More recent variations include the work of Connolly [4], in which photogates were employed to precisely measure the frequency of the mass and that of Torzo [5], who, in 2001, used pressure and digital temperature sensors to achieve even more accurate results. Clark and Katz [6] found the most accurate values of gases ratios of specific heats so far from a resonance curve, adjusting the apparatus to use an electrically driven piston.

In the first part of the experiment R uchardt's and Rinkel's methods are compared. In the second part a 100ml gas tube was used to determine γ . Additionally the data of the R uchardt experiment was improved upon by the elimination of friction.

The ratio of specific heats is critical for a wide range of applications in many scientific branches; from aerospace mechanics to environmental biology.

2. Theory

2.1. Simple Harmonic Oscillation

The ratio of specific heats, γ , is dependent on the atomic structure of the gas molecule. The methods investigated are based on a damped harmonic oscillator of low frequency. Simple harmonic motion dictates that the restoring force, F , is proportional and directly opposed to the displacement, x , where k is a positive constant.

$$F = -kx \tag{1}$$

The oscillations are damped due to frictional force.

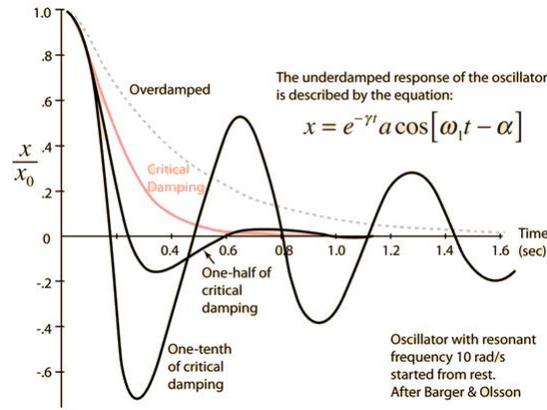


Figure 1: A graph of displacement, x , (metres) against time, t , (seconds) for a overdamped, critically damped and overdamped harmonic oscillator.[7]

2.2. Ideal Gases

An adiabatic process [8] means that no heat or matter is transferred to the surroundings therefore energy is only work done therefore entropy remains constant. (Poisson's equation: $PV^\gamma = \text{constant}$)
Ideal gas law:

$$PV = mRT \quad (2)$$

Where P = pressure (Pa), V = volume m^3 , m = mass (kg), R = gas constant (8.314JK), T = temperature (K)

The ratio of specific heats, γ , (also known as the adiabatic exponent, κ) is given by

$$\gamma = \frac{C_P}{C_V} \quad (3)$$

$$C_P = C_V + R \quad (4)$$

Where C_P = specific heat capacity with constant pressure, C_V = specific heat capacity with constant volume

[9] Heating one mole of gas with constant volume:

$$E_{kin} = 0.5fRT \quad (5)$$

Where f = degrees of freedom, R = gas constant, T = change in temperature

Comparing equations:

$$C_V = 0.5fR \quad (6)$$

The equation shows that the number of degrees of freedom determines heat capacity of an ideal gas.

Monoatomic gas particles have 3 translational degrees of freedom, rotation does not change how it looks therefore $f=3$. Diatomic gas particles also have rotational degrees of freedom (can spin in two dimensions) i.e. $f=5$. Polyatomic particles, however, spin in all three dimensions as they are non-linear molecules; $f=6$.

Thermodynamic equation:

$$\gamma = \frac{C_P}{C_V} \quad (7)$$

In this experiment the gases investigated should yield, according to the theory, similar values to:

Mono-atomic: Argon $\gamma = 1+2/3=1.667$

Diatomic: Air (mostly O_2 and N_2) $\gamma = 1+2/5=1.4$

Poly-atomic: Carbon dioxide $\gamma = 1+2/5=1.4$

These values for γ are an estimate. The literature values are [8]:

Argon = 1.670

Air= 1.400

Carbon dioxide = 1.280

The estimates for air and argon are very accurate but carbon dioxide differs by 8.6% due to the different classical and quantum mechanical explanations.

3. Methods

3.1. Rüchardt's Method

This method is used to determine the ratio of specific heat, γ , for a gas by measuring oscillations of balls in a column of gas in a glass precision tube. If the ball is given slight displacement it will oscillate with time period, T, due to the gas repeatedly expanding then compressing. Friction will cause it to come to rest. Displacement, y, causes increase in volume, dV, where A= cross sectional area:

$$dV = yA \quad (8)$$

Displacement, y, causes decrease in pressure, dP, where F is the force acting on the ball:

$$dP = F/A \quad (9)$$

Pressure and volume vary adiabatically because oscillations are rapid and small therefore approximately states of equilibrium, therefore quasi-static adiabatic process.

$$\gamma PV^{\gamma-1} + V^{\gamma} dP = 0 \quad (10)$$

The restoring force, F, is directly proportional and oppositely directed to displacement, x. This defines simple harmonic motion ($a=-kx$).

$$F = \frac{-\gamma PA^2 y}{V} \quad (11)$$

Where V = volume of glass vessel

$$T = 2\pi \left(\frac{-my}{F} \right)^{1/2} \quad (12)$$

Therefore the time period, T, needs to be measured to obtain γ .

$$\gamma = \frac{4\pi^2 mV}{A^2 P T^2} \quad (13)$$

Apparatus:

The gap between balls and glass is 0.002cm. The pressure is measured electronically (pressure transducer). The transducer outputs a voltage signal proportional to pressure which is read on the computer via an ADC on an interface card. The program is TracerDAQ. The data can be plotted to show simple harmonic motion on a graph. The experiment was repeated with two other gases, argon and carbon dioxide.

Error for Rüchardt's Method:

$$\Delta\gamma = \sqrt{\gamma \left[\left(\frac{\Delta m}{m} \right)^2 + \left(\frac{\Delta V}{V} \right)^2 + 2 \left(\frac{\Delta A}{A} \right)^2 + \left(\frac{\Delta P}{P} \right)^2 + 2 \left(\frac{\Delta T}{T} \right)^2 \right]} \quad (14)$$

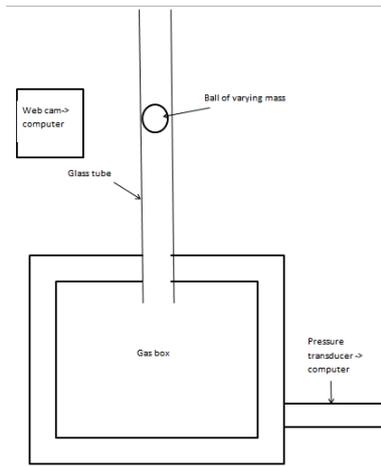


Figure 2: Diagram of apparatus for Rüchardt's experiment

3.2. Rinkel's Method

Rinkel's method [1] is a variation on Rüchardt's, therefore the same apparatus as shown in figure 2 is used. The initial drop of the ball in the test tube, L , is measured by recording the motion via a webcam and slowing down the video frame by frame. It was repeated 5 times and averaged for accuracy. This method was repeated for carbon dioxide and argon.

$$\gamma = \frac{2mgV}{PA^2L} \quad (15)$$

Where m = mass (kg), g = gravitational constant ($kgms^{-1}$), V = volume of tube (m^3), P = pressure (Pa), A = cross sectional area (m^2), L = distance mass has initially dropped (m).



Figure 3: Snap shot of measuring maximum distance dropped via webcam and metre rule. The video uses the program VLounge; the webcam can be used to record and determine the initial drop of the oscillating balls.

Error for Rinkel's Method:

$$\Delta\gamma = \sqrt{\gamma \left[\left(\frac{\Delta m}{m} \right)^2 + \left(\frac{\Delta V}{V} \right)^2 + 2 \left(\frac{\Delta A}{A} \right)^2 + \left(\frac{\Delta P}{P} \right)^2 + \left(\frac{\Delta L}{L} \right)^2 \right]} \quad (16)$$

3.3. 100ml Gas Syringe Tube

The glass syringe can be connected to the pressure transducer via a Luer connector. By plucking the piston the pressure changes were recorded using the TracerDAQ for different masses. The syringe allows the volume of air to be precisely measured, although the volume of air in the tubes must be accounted for. For different volumes in the range of 30-100ml the pressure was measured when the glass stopper was set into oscillation. The time period, T , is measured from the graph produced from the varying pressure, P , against time, t . These results were repeated and averaged for accuracy. The



Figure 4: Photo of 100ml gas syringe tube

resulting graph was a plot of volume against time period squared, enabling the specific heat ratio to be determined from the gradient.

$$\text{Gradient, } k = \frac{\gamma A^2 P}{4\pi^2 m} \quad (17)$$

$$\gamma = \frac{k 4\pi^2 m}{A^2 P} \quad (18)$$

Error for 100ml tube method:

$$\Delta\gamma = \sqrt{\gamma \left[2\left(\frac{\Delta k}{k}\right)^2 + \left(\frac{\Delta m}{m}\right)^2 + 2\left(\frac{\Delta A}{A}\right)^2 + \left(\frac{\Delta P}{P}\right)^2 \right]} \quad (19)$$

3.4. Method to Eliminate Friction

For simple harmonic motion:

$$x = A_0 e^{(\frac{-b}{2m})t} \cos\left[\left(\frac{\gamma P A_0^2}{V}\right) - \left(\frac{b}{2m}\right)^2 t\right]^{\frac{1}{2}} \quad (20)$$

At maximum displacement $\cos(\dots) = 1$ therefore from fitting an exponential curve to the above graph on origin the constants A_0 and $(b/2m)$ were found.

$$\gamma = \frac{(400\pi^2 + (\frac{b}{2m})^2 \Delta t) m V}{P A_0^2} \quad (21)$$

Error for the elimination of friction method:

$$\Delta\gamma = \sqrt{\gamma \left[2\left(\frac{\Delta Q}{Q}\right)^2 + \left(\frac{\Delta t}{t}\right)^2 + \left(\frac{\Delta m}{m}\right)^2 + \left(\frac{\Delta V}{V}\right)^2 + \left(\frac{\Delta P}{P}\right)^2 + 2\left(\frac{\Delta A_0}{A_0}\right)^2 \right]} \quad (22)$$

Where $Q = b/2m$

4. Results

4.1. Rüchardt's Method

Measuring time period of different balls:

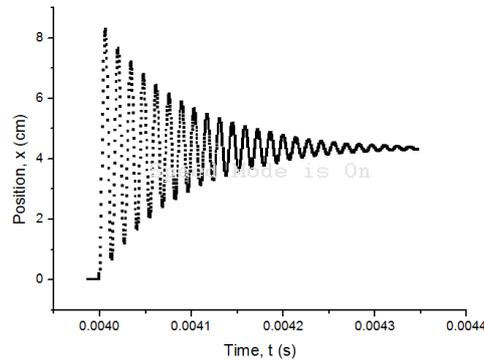


Figure 5: Example of a graph (from Origin) produced demonstrating simple harmonic oscillation of a mass. Pressure, P, (in Pa) against time period, T, (in s).

The time difference between the peaks can be measured on Origin and averaged over five repeats for each mass.

Air:

Mass, m (kg)	Time Period, T (s)	Ratio of Specific Heats, γ	Error in γ
0.0357976	1.20161	1.24390	± 0.05941
0.0253376	1.00424	1.26464	± 0.06542
0.0135045	0.72381	1.30218	± 0.01135

The estimate of ratio of specific heat for air = 1.27024

Standard deviation = 0.02954

Percentage difference to literature value = 9.3%

Argon:

Mass, m (kg)	Time Period, T (s)	Ratio of Specific Heats, γ	Error in γ
0.0357976	1.03264	1.68437	± 0.01682
0.0253376	0.86652	1.69855	± 0.08521
0.0135045	0.63509	1.69059	± 0.04953

Mean estimate of ratio of specific heat for argon = 1.69117

Standard deviation = 0.00708

Percentage difference to literature value = 1.3%

Carbon Dioxide:

Mass, m (kg)	Time Period, T (s)	Ratio of Specific Heats, γ	Error in γ
0.0357976	1.21846	1.20980	± 0.11354
0.0253376	1.00561	1.26118	± 0.09831
0.0135045	0.71987	1.31583	± 0.10652

Mean estimate of ratio of specific heat for carbon dioxide = 1.26227

Standard deviation = 0.05302

Percentage difference to literature value = 1.4%

4.2. Rinkel's Method

Air:

Mass, m (kg)	Average Length, L (m)	Ratio of Specific Heats, γ	Error in γ
0.0357976	0.7258	1.22945	± 0.34681
0.0253376	0.5062	1.25171	± 0.15839
0.0135045	0.2680	1.26467	± 0.09728

Mean estimate of ratio of specific heat for air = 1.24861

Standard deviation = 0.01781

Percentage difference to literature value = 10.8%

Argon:

Mass, m (kg)	Average Length, L (m)	Ratio of Specific Heats, γ	Error in γ
0.0357976	0.6182	1.44344	± 0.04681
0.0253376	0.4302	1.47295	± 0.00255
0.0135045	0.2268	1.49441	± 0.01253

Mean estimate of ratio of specific heat for air = 1.47027

Standard deviation = 0.02559

Percentage difference to literature value = 12.0%

Carbon Dioxide:

Mass, m (kg)	Average Length, L (m)	Ratio of Specific Heats, γ	Error in γ
0.0357976	0.7054	1.26500	± 0.02566
0.0253376	0.5060	1.252194	± 0.04537
0.0135045	0.2716	1.24728	± 0.01124

Mean estimate of ratio of specific heat for air = 1.25482

Standard deviation = 0.00915

Percentage difference to literature value = 2.0%

4.3. 100ml Syringe Tube

$$V = \frac{\gamma A^2 P T^2}{4\pi^2 m} \quad (23)$$

Where V = volume of syringe in m^3 and T^2 = time period squared in s^2

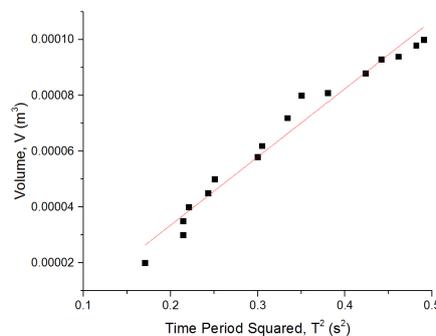


Figure 6: A graph (from Origin) of volume, V (m^3) against time period squared, T^2 , (s^2). N.B. error bars are smaller than points. Gradient, $k = 0.0917210$

Ratio of specific heats, $\gamma = 1.34163 \pm 0.00694$

Percentage difference to literature value = 4.2%

4.4. Eliminating Friction Method

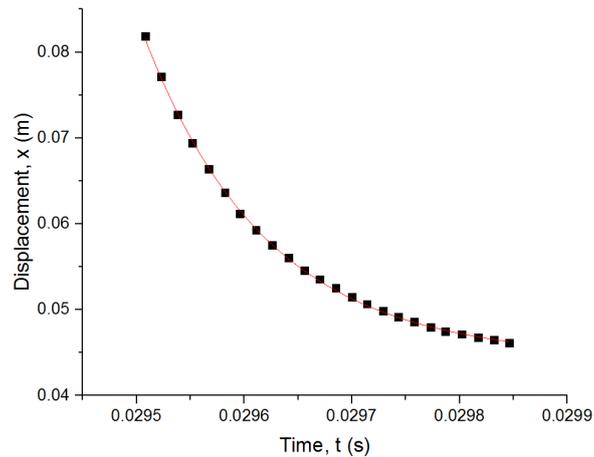


Figure 7: Plot of maximum displacement, d , against time, t , for an oscillating mass in tube of air (from Origin).

Graphs of maximum displacement, d , against time, t , were plotted for air, argon and carbon dioxide. The coefficients were determined in order to calculate the ratio of specific heats, γ .

Air = 1.3580 ± 0.0038

Percentage difference to literature value = 3.0%

Argon = 1.6597 ± 0.0009

Percentage difference to literature value = 0.6%

Carbon dioxide = 1.2996 ± 0.0087

Percentage difference to literature value = 1.5%

5. Discussion

Rüchardt's method presented small uncertainties, with ratios of specific heat differing from literature values by 9.3%, 1.3%, 1.4% for air, argon and carbon dioxide respectively. The ratio for air is likely to have differed more significantly due to this being the first attempt at using the apparatus. Contributions to the error may include the apparatus not being thoroughly cleaned as well as movements of the transducer tube (change in pressure alters oscillations produced). All experiments were averaged over multiple trials for reliability.

Clearly the most accurate method proved to be Rüchardt's with the elimination of friction, giving reliable estimates of the ratios of specific heat of air, argon and carbon dioxide with little error and very small deviations from the literature values (3.0%, 0.6%, and 1.5% respectively).

Extending the experiment with a similar apparatus to the 100ml tube for argon and carbon dioxide would allow a better comparison of the techniques. This method produced a graph with data points close to the line of best fit and the error in the gradient was small, which contributed to a small error in the final estimate for the ratio of specific heats for air, $\gamma = 1.34163 \pm 0.00694$; only 4.2% away from the literature value [8].

Rinkel's method proved the least accurate; however the uncertainties could be dramatically reduced using a smaller time difference between frames to record the balls oscillations. The equipment used had difference in time frame of 0.1 seconds therefore the initial drop measurement could have varied as much as half a centimetre. This led to large uncertainties and differences to the literature values for air (10.8%), argon (12.0%) and carbon dioxide (2.0%). Evidently the error could be dramatically reduced using sensors to detect furthest point ball has dropped. Furthermore, the gas in the box should be refilled between trials of the masses, as a progressive decrease from literature value was noticed in analysis of the data.

The methods carried out were based on the assumptions that the gases were ideal and the volume changes were adiabatic which, although a very good approximation, is not completely realistic. Also

friction remained unaccounted for in Rinkel's experiment, prominently responsible for the more varied estimates. Koehler [6] outlines a method which corrects for the fact that the gases do not obey perfectly the ideal gas law. This could be investigated in extension to previous methods to find more accurate results.

For real gases, the ratio of specific heats varies with temperature. An increase in temperature leads to more available rotational and vibrational energy states, causing the ratio, γ , to decrease as number of degrees of freedom rises. The correlation between γ and temperature could additionally be explored in extension to this experiment [11].

6. Conclusion

Four experiments to measure the specific heat capacity of air, argon and carbon dioxide were carried out and compared. The most accurate method was determined to be the original Rüchardt's method alongside compensation for friction. It yielded the most reliable estimates of specific heat capacity with small uncertainties, given below.

Air, $\gamma = 1.3580 \pm 0.0038$

Argon, $\gamma = 1.6597 \pm 0.0009$

Carbon dioxide, $\gamma = 1.2996 \pm 0.0087$

7. References

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