Determining γ for Ar, N_2 and CO_2

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***Abstract*— γ or the ratio of specific heat capacities (c_p/c_v) for a given substance is a constant related to thermodynamic properties of the given substance and is important in calculations of adiabatic processes such as Otto Cycles. This report aimed to measure the value of γ for three different gases, Argon(Ar), Nitrogen(N_2) and Carbon Dioxide(CO_2), which values of 1.38±0.04, 1.30±0.05 and 1.26±0.05 were obtained respectively.**

I. Introduction, Theory and Hypothesis

γ appears in adiabatic processes ($Q = 0$) for instance the Otto Cycle, modeling piston engines with ideal gases which include most vehicles. Knowing values of γ is useful, allowing calculations of efficiency and properties of the engine (volume, temperature etc.). We would like to determine the values of γ for Ar, N_2 and CO_2 gases experimentally.

The specific heat capacity, c is defined as the energy input (heat), required to raise the temperature of 1 kilogram of a substance by 1 degree (°K). By extension, c_v denotes the specific heat capacity for processes where volume of the substance is kept constant and c_p denotes the specific heat capacity for processes where pressure is kept constant. We may then define the value γ as the ratio of c_p to c_v.

$$\gamma = \frac{c_p}{c_v} \tag{1}$$

An experiment is setup which mimics an adiabatic process, for which measurements can be made to find the value of γ for a given substance.

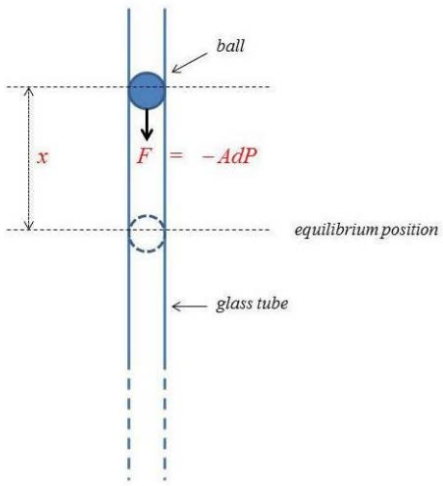


Figure 1. Ball undergoing adiabatic oscillation [3]

Consider Fig.1, a tube with a ball bearing where the ball bearing is air tight and does not allow air to pass through it. If the ball is displaced, it undergoes an oscillatory motion through adiabatic expansion and compression. The pressure which affects the gas creates a restoring force in the opposite direction to the balls movement. Let V be the volume under the ball, P, the pressure on the gas, x the displacement of the ball from its equilibrium position and F, the force exerted on the ball. With this information we have the knowledge that $PV^\gamma = constant$, $dV = Adx$, $dF = -AdP$ [3]. From implicit differentiation of $PV^\gamma = constant$ with respect to P, we are able to relate force acting on the ball to the volume change. Let the cross sectional area of the tube covered by the ball be A, where $A=\pi r^2$ and r is the radius of the ball.

$$V^\gamma + P\gamma V^{\gamma-1}\frac{dV}{dP} = 0 \tag{2}$$

$$dP = -\gamma\frac{P}{V}dV \tag{3}$$

$$dF = -AdP = \gamma\frac{AP}{V}dV \tag{4}$$

Through the relation $dV = Adx$, we are able to then obtain a relation between displacement and force.

$$dF = \gamma\frac{PV}{x^2}dx \tag{5}$$

$$F = \int \gamma\frac{PV}{x^2}dx = -\gamma\frac{PV}{x} = -\gamma\frac{PA^2}{V}x \tag{6}$$

The constant of integration is 0 as at equilibrium ($x = 0$) there is no force. Knowing that the force of the ball is also mathematically expressed as $F = M\frac{d^2x}{dt^2}$, where M is the mass of the ball we finally obtain

$$\frac{d^2x}{dt^2} + \gamma\frac{PA^2}{MV}x = 0 \tag{7}$$

From the differential equation, a connection between frequency, f and γ is found

$$\gamma = \frac{4\pi^2 MVf^2}{PA^2} \tag{8}$$

We then set up this oscillatory motion and measure f as an independent variable to find a value of γ assuming the gas behaves ideally. A rough theoretical value can be predicted based on the kinetic theory of particles.

Different molecules have different degrees of freedom, which is the number of ways a molecules energy can be partitioned into independent spatial arrangements. These are translational, rotational and vibrational. Squared terms are the ways in which energy is shared in these different arrangements. In the case of translational and rotational, there is only one way energy is shared out (kinetic) but with vibrational there is 2 ways (kinetic or potential) [3]. It can be shown that γ is classically related to the number of squared terms, s by the equation

$$\gamma = \frac{2+s}{s} \tag{9}$$

For different molecules with varying numbers of atoms and shapes, the number of squared terms vary. It must also be noted that from quantum mechanical theory, at certain temperatures some vibrational modes are not excited and do not contribute to squared terms. Assuming no vibrational modes are activated in the most extreme case from quantum interpretation, we can make some hypothetical predictions.

Table 1: Possible values for γ

Gas	Classical	Quantum Mechanical
Argon, Ar	5/3 (≈1.667)	5/3 (≈1.667)
Nitrogen, N_2	9/7 (≈1.286)	1.4
Carbon Dioxide, CO_2	15/13 (≈1.153)	1.4

We may then hypothesize that for Ar, γ should take an exact value of 5/3 (≈1.667), N_2 should have a γ value between 9/7 (≈1.286) to 1.4 and Carbon dioxide should have γ between 15/13 (≈1.153) and 1.4.

II. METHOD, EQUIPMENT AND PROCEDURE

From a practical standpoint, a real adiabatic expansion is difficult to simulate as a result of damping of the ball and also small amounts of air escaping the gaps between the tube and the ball. This would affect the frequency of oscillation and limit the number of oscillations measured.

An experiment is then setup as shown in Fig. 2 below which simulates the adiabatic expansion through pumping gas to lift the ball and then decreasing pressure by allowing gas to leave from holes to create an oscillation which approximates the adiabatic oscillation. This eliminates the damping and air escaping issues.

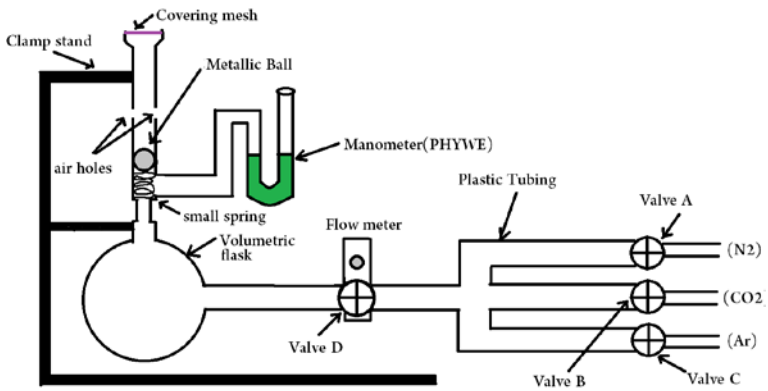


Figure 2. Schematic of apparatus and experiment setup

Equipment used: (Cp/Cv Unit 8)

- Flow meter (checks gas flow, adjust gas flow)
- Manometer (measure gas pressure)
- Barometer, Thermometer (measure atmospheric pressure, temperature)
- Volumetric flask (with holes for tubing, 1L approx.)
- Metallic ball (same diameter as tube)
- Clamp Stand (holds flask)
- Plastic Tubing (connect gas to flask and manometer)
- Valves (control gas flow)
- Small spring (hold ball when no gas at rest)
- Stopwatch (record time period of oscillations)

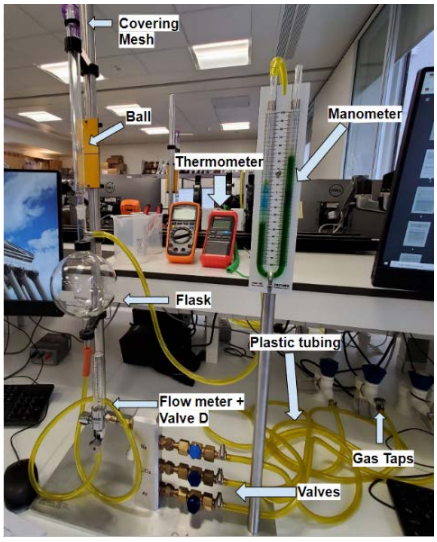


Figure 3. Apparatus setup in real life

Procedure:

1. Values for M, V and A are measured first along with temperature and atmospheric pressure measured.
2. One of valve A, B or C was opened depending on which gas was measured and valve D was opened to allow and adjust the flow of gas.
3. The gas was allowed to flow for 30 seconds to ensure the entire system contained only that one specific gas and the ball bearing was observed to oscillate.
4. A slow-motion video of the manometer oscillating was then captured and the maximum and minimum heights on the manometer were recorded.
5. The time was then recorded for a given number of full oscillations to occur and repeated for different number of oscillations (40, 60, 80, 100, 120).
6. For each number of oscillations recorded, the temperature was measured and also the pressure.
7. This process was repeated for each different gas (Ar, N_2, CO_2). Apparatus was turned off for 1 minute to let the gas drain.

The data for number of oscillations was then plotted on the x-axis with the time taken for those set number of oscillations plotted on the y-axis. The gradient of the line of best fit would then give the time per 1 full oscillation which therefore gave the period, T. The frequency, f is then found by inversing the value of T.

The equilibrium pressure was then calculated first by finding the equilibrium height, h, the manometer was displaced at. The pressure exerted on the gas was then calculated by the equation

$$P = P_0 + \rho g h \tag{10}$$

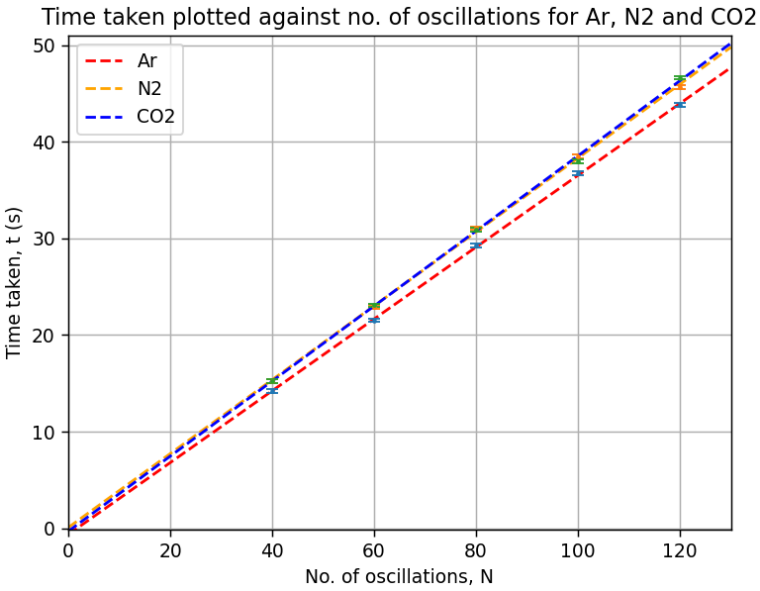
Where P_0 is the atmospheric pressure measure on the barometer, ρ is the density of the water in the manometer (1000 kgm^{-3}) and g is gravitational acceleration (9.81 ms^{-2})

[6]. With values of M, V, A, P and f found, the value of γ for each gas could be calculated. This yielded the following results

III. Results, Uncertainties and Analysis

Table 2: Measured values [5]

M (g)	V (cm^3)	r (mm)	A (cm^2)
16.7±0.1	1150±10	7.92±0.05	1.97±0.02



Graph 1. Time taken for set no. of oscillations plotted against no. of oscillations. Gradient gives the period, T for a given gas.

Table 3: T and f from the gradient of Graph 1, measured P

	P (Pa)	T (s)	f (s^{-1})
Ar	102450±7	0.372±0.003	2.69±0.02
N_2	102379±7	0.382±0.005	2.62±0.04
CO_2	102399±7	0.388±0.006	2.57±0.04

Table 4: Calculated values of γ

Gas	γ
Argon, Ar	1.38±0.04
Nitrogen, N_2	1.30±0.05
Carbon Dioxide, CO_2	1.26±0.05

Firstly, the uncertainty in time measurement from the stopwatch was estimated at ±0.2s due to mechanically clicking, mistiming and human reaction speed, instead of the given 0.01s uncertainty. The uncertainties of M, V were given, with uncertainty in A being propagated through πr^2 ($\Delta A = 2\pi r \Delta r$) and error in T taken from the error in gradient of the best fit lines. The uncertainties in M, V and r were increased to be safe as a result of unreliable source. The uncertainties of the pressure are propagated through (10). Assuming the uncertainty of the barometer is negligible, this gives

$$\Delta P = \rho g \Delta h \qquad (11)$$

The uncertainty is then further propagated with Δh due to the fact that 4 manometer readings were required to find the equilibrium height.

$$h = \frac{1}{2}(d_{1,max} + d_{2,max} + d_{1,min} + d_{2,min}) \qquad (12)$$

where $d_{1,2,max}$ are the manometer readings when the oscillation is at its peak and $d_{1,2,min}$ when the oscillation is at a minimum. Since $\Delta d_1 = \Delta d_2 = \Delta d$, the uncertainty in h can be propagated as

$$\Delta h = \frac{1}{2}\sqrt{4(\Delta d)^2} = \Delta d \qquad (13)$$

Δh is then the same as the uncertainty of 1 manometer reading found by taking the increment and dividing by two, ($\Delta d \approx 5 \times 10^{-4} m$). The uncertainty in the frequency is propagated through the relation $f = 1/T$

$$\Delta f = \frac{\Delta T}{T^2} \qquad (14)$$

The values then allow us to find the errors in the value of γ. The expression for $\Delta\gamma$ can be derived [4].

$$\Delta\gamma = \gamma\sqrt{\left(\frac{\Delta M}{M}\right)^2 + \left(\frac{\Delta V}{V}\right)^2 + 4\left(\frac{\Delta f}{f}\right)^2 + \left(\frac{\Delta P}{P}\right)^2 + 4\left(\frac{\Delta A}{A}\right)^2} \qquad (15)$$

We are then able to arrive at the results derived as seen in Table 3. We may compare the values derived to previous experimental data.

Table 5: Other experimental data [1] [2]

Gas	γ
Ar	1.67
N_2	1.40
CO_2	1.28

Firstly we find that the values of γ for N_2 and CO_2 are within the range of values predicted by the theoretical values agreeing with the hypothesis. Moreover, the value of γ for CO_2 has a uncertainty range which is within the value found in other experimental reports as seen in Table 5. This is consistent evidence that the γ value found for CO_2 is precise and accurate. The value for N_2 is within the range for the hypothesis but slightly in disagreement with the other experimental data, with an error of 7% relative to the value of 1.4.

However there is much larger discrepancy in the value of γ found for Argon which is significantly deviated with a value of 1.38 compared to the theoretical value and other experimental data of 1.67, giving an error of 17%. From the fact the value of Argon does not match both experimental and theoretical values, it is very likely there is inaccuracy in our calculation which stems from systematic error.

Systematic error may be introduced from the fact that the real processes of the experiment deviates from adiabatic oscillation. For example there may be accuracy errors introduced as a result of approximation to adiabatic oscillation from the apparatus setup when the oscillation may have a value which differs, changing the value of frequency. Another possible error may be seen in (6) where V is

integrated and treated as a constant. However, there is clear dependence of V on x, therefore the change in the volume during the oscillation must be considered small. But this approximation can be ruled out as a major source of systematic error with some simple calculation. The max displacement of the ball observed was roughly 5cm and area A is calculated to be πr^2, this gives a rough change in volume of $\Delta V = A\Delta x = \pi 0.792^2(5) = 9.85cm^2$. This is a much smaller value than the total equilibrium volume, V (1150cm^3), hence a justifiable approximation.
As P is related to V, this also implies that the change in pressure must also be small. But similar calculations can also show it is a good approximation with the change in pressure being much smaller than the equilibrium pressure.
Other assumptions made in the derivation would be the fact that the gases behave ideally which in reality they do not, which may deviate the experiment from theoretical derivations.

However these systematic errors would apply to all gases, and does not explain why the deviation is substantially larger for Argon than other gases. The most plausible explanation may come from the control of gas flowing and systematic error in methodology. In the argon trial, it may have been possible that the gas flow was too low, which would result in an asymmetric oscillation. At the time this was observed but not noted as much significance. However the asymmetric oscillation may mean that the frequency may have been made much longer than should have been as a result of lower velocity near the equilibrium air hole moving up which would increase the time taken.

Another important note would be the values of M, V and r which were found from external sources. It is difficult to tell whether these values are accurate and if not they may skew the values of γ to be larger or smaller. There is some evidence in this being true due to the fact that all values of γ derived are smaller than the accepted experimental values. This may be an indication that the mathematical term from (8)

$$\frac{MV}{PA^2} \tag{16}$$

May be smaller than its actual value and reduce the values of γ by a certain fraction.

IV. CONCLUSION

To conclude, the aims of finding values of γ for Ar, N_2 and CO_2 were found as 1.38±0.04, 1.30±0.05 and 1.26±0.05 respectively. It can be inferred that classical approximations for the squared terms in CO_2 and N_2 are likely not as good and is supported by the fact that the values agree with hypothesis and secondary experimental data. However, for Argon due to the significant deviation of the value from hypothesis and comparative data, not much can be inferred about the value itself other than an indication that there was systematic error which affected the experiment.

Systematic error such as the asymmetric oscillation can be fixed and noted by simple changes. For example, when the ball starts oscillating, marking the max displacement in each direction and seeing if the values are equal.

The most dominant source of uncertainty was from the value of the area, A. To increase the precision of values found, the experiment should be redone first measuring the diameter of the ball bearing (which was not possible in this experiment) instead of taking the value from a source. Other quantities such as M, and V should be remeasured to rule out their possibility as being sources of random error.

We can also reduce the second largest source of random error, the frequency by removing the mechanical aspects of time recording which would increase the precision of measuring the period substantially. For instance, a motion sensor gate can be installed which detects the movement of the ball inside the tube. Using computer software, the period can be measured by timing when the ball passes through the motion sensor gate which would give a much more precise value of the period and also remove any human errors such as mistiming of the stopwatch or miscounting which would cause inaccuracy in the form of systematic error.

The experiment itself still has numerous potential in investigating mixtures of gases, and can be extended into looking at measuring γ for different temperatures which could show at what point do certain vibrational modes of gases get excited. This would be a possible method in which we are able to validate certain quantum theory through the process of experiments.

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