UNIVERSITY COLLEGE LONDON
DEPARTMENT OF PHYSICS AND
ASTRONOMY

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Title of work submitted... Measurement of C_p/C_v for Argon, Nitrogen,
Carbon Dioxide and an Argon + Nitrogen Mixture

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Measurement of C_p/C_v for Argon, Nitrogen, Carbon Dioxide and an Argon + Nitrogen Mixture

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Abstract: The ratio of specific heats, γ, at constant pressure, C_p and constant volume, C_v, have been determined by measuring the oscillation frequency when a ball bearing undergoes simple harmonic motion due to the gravitational and pressure forces acting upon it. The γ value is an important gas property as it relates the microscopic properties of the molecules on a macroscopic scale. In this experiment values of γ were determined for input gases: CO_2, Ar, N_2, and an Ar + N_2 mixture in the ratio 0.51:0.49. These were found to be: 1.1652 ± 0.0003, 1.4353 ± 0.0003, 1.2377 ± 0.0001and 1.3587 ± 0.0002 respectively. The small uncertainties in γ suggest a precise procedure while the discrepancy between experimental and accepted values indicates inaccuracy. Systematic errors are suggested; however it was noted that an average discrepancy of 0.18 between accepted and experimental values occurred. If this difference is accounted for, it can be seen that we measure lower vibrational contributions to γ at room temperature than those predicted by the equipartition principle. It can be therefore deduced that the classical idea of all modes contributing to γ is incorrect and there is actually a 'freezing out' of vibrational modes at lower temperatures.

I. Introduction

The primary objective of this experiment was to determine the ratio of specific heats, γ, for gaseous Ar, N_2, CO_2 and an Ar + N_2 mixture. These were then used to estimate the vibrational contributions to the specific heat at constant volume, C_v.

The ratio of specific heats at constant pressure, C_p and constant volume, C_v, is defined as γ:

$$\gamma = \frac{C_p}{C_v} = \frac{(nR + C_v)}{C_v} \quad (1)$$

Where R is the molar gas constant and n the number of moles.

If a ball bearing of mass M is in a close but frictionless fit to the neck of a container with volume, V, cross-sectional area, A, it can be shown that the displacement, x, of the oscillator and resultant adiabatic volume change in gas will result in the ball experiencing an x proportional restoring force, hence undergoing simple harmonic motion to a first approximation. By considering the angular frequency and re-expressing this in terms of the oscillation frequency, v, it can be shown that γ is given via equation (2):

$$\gamma = \frac{4\pi^2 M V v^2}{PA^2} \quad (2)$$

Where P is the sum of barometric and excess pressure (due to inflow of gas) experienced by the ball.

It can be seen from equation (1) that γ values admit the immediate calculation of C_v and thus C_p. Using the equipartition principle [1] it is seen that the contribution to the total C_v per mole is related to number of degrees of freedom, s, such that:

$$Cv = \frac{1}{2} sR \quad (3)$$

By comparing the tabulated and experimental values of γ, the vibrational contributions to C_v can be approximated using the degrees of freedom applicable to each gas [1].

II. Method

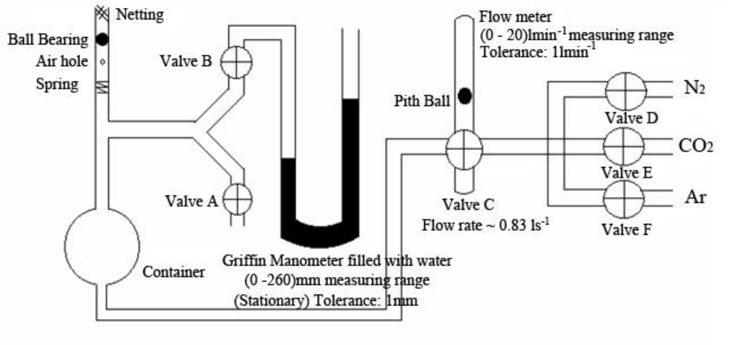

Figure 1 – Diagram showing schematic of apparatus

Having set up the apparatus as shown in Figure 1, with all valves but A closed, the regulator valve on the selected gas cylinder was adjusted until a gauge reading of approximately 0.3 bar registered. The selected gas was then released into the neck of container, with a volume V: (1281 ± 5) cm^3, diameter d: 16 *mm*, via valves D/E/F. Air and the experimental gas were flushed from the system by opening valve C. Valve C was then closed when the flow rate had reached approximately 5 $lmin^{-1}$. This process was repeated between each gas change.

To induce oscillations, valve A was gradually tightened until closed. Valves B and C were then opened slowly, with valve C tuned until the ball bearing, with mass, M: (16.458 ± 0.001) *g*, diameter, d: (15.882 ± 0.001) *mm* was observed to undergo a regular oscillation with approximate amplitude: 2 *cm*.

The frequency of oscillation was deduced via measuring the time taken, for a set number of oscillations, N = 20, 30 and 40 to occur with a stopwatch. This method was sought rather than deducing the number of oscillations in a given time interval to avoid non integer values of N. To compensate for the inconsistent equilibrium position, each individual oscillation was counted at the point of minimum amplitude. The time period for each oscillation number was measured 5 times so that the mean time period, T, could later be determined.

The preliminary experiment saw that the timing of 10 oscillations took approximately 4.00 *s*. To estimate the error arising from human reaction time, a target time of 4.00 *s* was aimed for by each experimenter, and the average difference between the obtained and desired time taken as the uncertainty in time measurement.

The tolerance in time measurement was therefore taken as 0.07*s*.

To obtain an approximate ratio of 1:1 Ar to N_2 in the ground glass tube for the Ar + N_2 mixture, valve D and C were first opened until an approximate flow rate of 10 $lmin^{-1}$ had been achieved. The tube connecting the gas to the flow meter was then clamped shut, and valve F opened. Once the same flow rate had been achieved, the initial gas was then re-connected to the flow meter.

Barometric pressure was noted from the barometer located in Laboratory I, one floor beneath apparatus level, as (774.3 ± 0.1) *mmHg*. The excess pressure was taken from the manometer for each gas and converted to Pascals, *Pa* using the hydrostatic pressure equation [2].

III. Results and Analysis

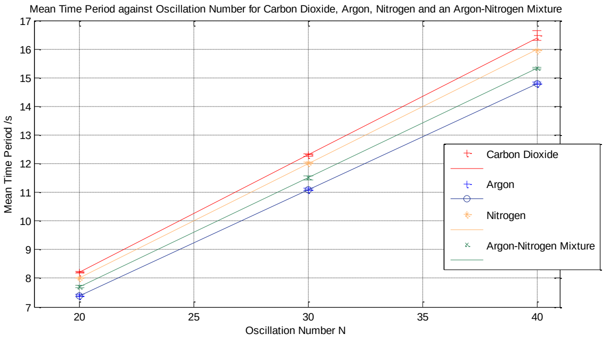

Figure 2: Graph showing the mean time period, *T*, against the oscillation number, *N*, for each gas.

The gradient of each graph in figure 2 gives the mean time period, *T* of oscillation for each different gas. Using the MATLAB function '*llsfitcol*' which deduces the least square plot and associated error, *T* values for CO_2, Ar, N_2 and the Ar + N_2 mixture were found to be:
(0.410 ± 0.005) *s*, (0.371 ± 0.003) *s*, (0.398 ± 0.001) *s* and (0.381 ± 0.002) *s* respectively. Using the reciprocal relationship between *T* and *v*, these values of time period turn out a mean associated frequency *v* of (2.44 ± 0.01) *Hz*, (2.699 ± 0.009) *Hz*, (2.511 ± 0.005) *Hz* and (2.624 ± 0.007) *Hz*.

It was noticed from the equations of each trendline that within the limits of intercept error, the *T*-intercept for N_2 and the Ar + N_2 mixture did not coincide with the origin. The average difference between the intercept and the origin for these gases was found to be 0.07, as expected from the preliminary investigation.

The total pressure experienced by the oscillator, *P* is given by:

$$P = P_{excess} + P_{barometric} \qquad (4)$$

Where P_{excess} was recorded as (80 ± 4) mmH_2O, (80 ± 4) mmH_2O, (84 ± 4) mmH_2O and (88 ± 4) mmH_2O for CO_2, Ar, N_2 and the Ar + N_2 mixture respectively.

Using equations (1) and (2) values of γ, C_v and C_p could then be calculated. The associated uncertainty has been propagated using the general formula for combination of uncorrelated uncertainties [2]. Table 1 shows the accepted values [3] and table 2 the experimentally obtained values.

Table 1: Accepted values of γ, C_v and C_p for each individual gas.

	CO_2	**Ar**	**N_2**
γ	1.30	1.67	1.40
C_v /$kJkg^{-1}K^{-1}$	0.65	0.31	0.74
C_p /$kJkg^{-1}K^{-1}$	0.85	0.52	1.04

Table 2: Experimentally obtained values of γ, C_v and C_p.

	CO_2	**Ar**	**N_2**	**N_2 + Ar**
γ	1.1652 ± 0.0003	1.4353 ± 0.0003	1.2377 ± 0.0001	1.3587 ± 0.0002
C_v /$kJkg^{-1}K^{-1}$	1.1817 ± 0.0003	0.3439 ± 0.0001	0.4898 ± 0.0001	0.7418 ± 0.0002
C_p /$kJkg^{-1}K^{-1}$	1.3812 ± 0.0005	0.4935 ± 0.0001	0.6662 ± 0.0001	1.0079 ± 0.0003

By comparing tables 1 and 2 it can be seen that while the small values of uncertainty suggest a precise experiment, the fact that none of the accepted values lie within the limits of experimental uncertainty implies inaccuracy.

The largest discrepancy for γ occurs for Argon, with a difference of 0.23, which equates to ~ 767 times the experimental uncertainty.

For C_v and C_p values it can be seen that for CO_2 we obtain a notable difference of 0.53 $kJkg^{-1}K^{-1}$, ~ 1060 times the experimental uncertainty in both cases.

This large source of inaccuracy is thought to have stemmed from systematic errors such as the difficulty in accurate excess pressure measurements due to the oscillating column of water in the manometer. Likewise, fluctuations in room temperature, due to presence of people and equipment in the room, as well as pressure may have also contributed.

It was noted that ‘squeaking’ could be heard during oscillations, which if not a result of the ball-bearing skimming the sides of the ground glass tube, therefore experiencing friction, which is not assumed by equation (2), did not ‘squeak’ with a consistent frequency. This implied that the ball bearing was not experiencing the same conditions for each oscillation, suggesting perhaps turbulent airflow or improper flushing out of the previous gas tested.

Improper evacuation of the previous gas would have meant that γ values for an unwanted combination of gases would have been calculated. This could have been investigated further by considering the fractional contribution, x, of each gas with its associated γ, $\gamma_{n,}$ to the overall γ_{mix} value, i.e for two gases:

$$\gamma_{mix} = x\gamma_1 + (1-x)\gamma_2 \qquad (6)$$

Rearranging equation (6) for x it was found that the intentional gas mixture was composed of Ar and N_2 in the ratio 0.51:0.49.

To estimate the vibrational contributions to C_v, equations (1) and (2) were combined to formulate equation (7) which gives the theoretical γ, γ_{Th}:

$$\gamma_{Th} = 1 + \frac{2}{s} \qquad (7)$$

Since Ar is monoatomic it cannot possess energy by rotational and vibrational means so the vibrational contribution to C_v is zero.

For N_2, s =6 [3] and for CO_2 s=9 [3] equation (7) yields γ_{Th} values of 1.33 and 1.22 respectively.

These correspond to values larger by 0.10 and 0.05 to the experimental γ, γ_{exp}, for N_2 and CO_2. On average the values for γ are 0.18 less than expected, if 0.18 is added to each value of γ we see that there is a difference of 0.5 and 0.2 for N_2 and CO_2 respectively. This indicates γ_{Th} *is* closer *for s=5 and s=8*, insinuating that the highest vibrational mode is not excited at room temperature –thus challenging the equipartition principle which predictions excitation of all modes.

IV. Conclusion

The experimental values for γ, for CO_2, Ar, N_2 and an Ar + N_2 mixture in the ratio 0.49:0.51 were found to be 1.1652 ± 0.0003, 1.4353 ± 0.0003, 1.2377 ± 0.0001 and 1.3587 ± 0.0002 respectively. Though the results are precise they differ from the accepted values on average by 0.18, with a 0.05 disparity within this, suggesting a relatively inaccurate procedure. It should be noted however that the tabulated values for γ have been determined under standard conditions of temperature and pressure, which the experiment was performed only approximately under.

The discrepancy between experimental and accepted values is thought largely to stem from the systematic error inherent to the human observation element of time taking. Future experiments would see the time measurement performed via a laser beam directed at the ‘equilibrium position’, assuming it remained approximately constant, with a light dependent resistor (LDR) placed behind the oscillating ball but parallel to the laser. If the LDR is connected to a data logger, the time interval between intensity peaks can be used as an indication of T. Although this introduces other sources of systematic error such as refraction effects and tolerances of the equipment used, the time interval between two peak minima should be more prominent than the eye-observable point of minimum oscillation amplitude.

V. References

[1] “Table of Physical and Chemical Constants”, Kaye and Laby (2nd edition 1974), p.29.
[2] “Physics for Scientists and Engineers”, Jewett/Serway (7th edition 2009) p.392.
[3] Experiment CM3 Lab script, Dept Physics and Astronomy, UCL, course PHAS2440, (2010).