Working under pressure: A mechanical determination of the gas constant

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Abstract

The gas constant R is an essential quantity in thermodynamics, seen in relations such as the change in Gibbs' free energy and the ideal gas law. In the current work, we have measured the gas constant with a mechanical method using a syringe and force meter. The range of applied force that could hold a syringe of gas at static equilibrium was measured at varied syringe volumes. Theoretical analysis of the system using Newton's second law and the ideal gas law yielded a linear relation between reciprocal syringe volume and applied force, which was used to perform a fit on the volume-force data. The value of R was extracted from the slope of the linear fit, and was determined to be $R = 8 \pm 1$ J mol^{-1}K^{-1}, in agreement with the true value within measurement uncertainty. Our results provide validity for a simple, low-cost method of quantifying a universal constant, which has great potential for future implementation in educational contexts such as physics demonstrations and student labs.

Contents

1 Introduction

In the study of thermodynamics in physics and chemistry, there are a few central constants of nature of frequent use. Most notable are the Boltzmann constant k_B used to relate temperature to energy for quadratic degrees of freedom, Avogadro's number N_A which connects the number of molecules in the sample to the amount in moles, and their product, the gas constant $R = k_B N_A$. This latter constant is most famous for its place in the ideal gas law $PV = nRT$, where it acts as the scaling factor between temperature and amount of (ideal) gas with it's pressure and volume. It is also an integral part of the van der Waals equation for real gases, $(P + \frac{an^2}{V^2})(V - nb) = nRT$. This places great importance on the constant in various applications of gases, such as in heat engines, refrigerators, ventilation systems, and atmospheric science. In addition, the constant is also a part of (among other chemistry formulae) the equation for the free energy change of a reaction: $\Delta G = \Delta G^\circ + RT \ln Q$, making it a fundamental constant for the study of chemical reactions.

In 2019, SI units were redefined in terms of universal constants of nature, which were all precisely defined to be at a certain value. As a consequence of Avogadro's number and the Boltzmann constant being fixed, their product R is also now a precisely defined value, where $R = 8.31446261815324\ \mathrm{JK^{-1}mol^{-1}}$ exactly [1]. As a result, "measurements" of the gas constant have been rendered effectively useless, as its value is now defined exactly. However, there still remains interest in quantifying R through experiments in educational contexts, where measurements of R can act as good demonstrations for students, aiding in their understanding of thermodynamic principles such as the ideal gas law. Prior to the 2019 redefinition, a precise measurement of R using an acoustic resonator method yielded an error of no more than 1.7 ppm [2], but such a setup is complex and costly for use in educational settings. Hence, in this work we demonstrate the validity of an accessible, low-cost, and simple method for quantifying the gas constant. We first will demonstrate theoretical analysis on a air-filled syringe using the common equations of Newton's second law and the ideal gas law. From this analysis, we obtain a relationship between the inverse volume of the air inside of the syringe and the external applied force. We then demonstrate a measurement procedure involving a constructed force meter from which a dataset of inverse volume and applied force can be collected. The slope from the linear fit of the data is then used to extract a rough value of the gas constant R.

2 Methods

The measurement procedure in the current work centres around an apparatus involving a syringe and force meter. We begin with theoretical analysis of our system. Analysis of a syringe at equilibrium using Newton's second law $\Sigma \vec{F} = m\vec{a}$ gives rise to the equation:

$$\vec{F}_{atm} + \vec{F}_{gas} + \vec{F}_A + \vec{F}_f = \vec{0} \tag{1}$$

Where $\vec{F}_{atm}$ is the atmospheric pressure term, $\vec{F}_{gas}$ is the gas syringe gas pressure term, $\vec{F}_A$ is the external applied force term, and $\vec{F}_f$ is the static friction term. The setup is summarized in Figure 1, below:

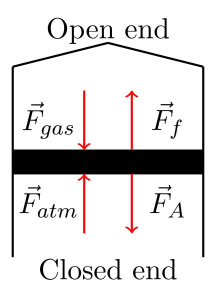


Figure 1: Force diagram of the four forces acting on the syringe (piston) at equilibrium. By careful quantification of the applied force $\vec{F}_A$, the force from the pressure of the gas $|F_{gas}| = \frac{An_{gas}RT}{V_{gas}}$ can be determined, from which the gas constant R can be extracted. Arrow lengths in figure do not correspond to relative force magnitudes in actual setup.

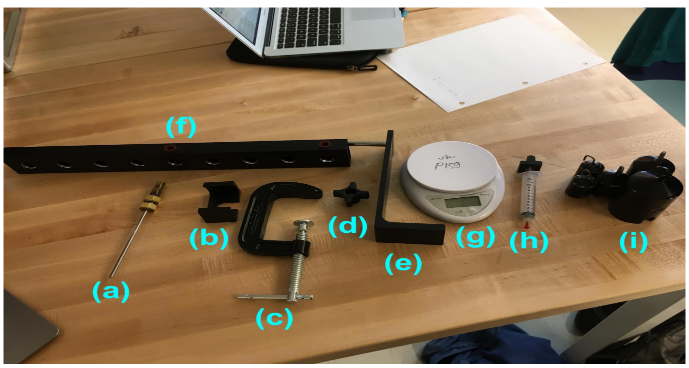
We can reduce the above vector equation to a scalar equation as the setup is one-dimensional in nature. We can also invoke the definition of pressure $P = \frac{F}{A}$ and the ideal gas law $PV = nRT$, which yields the equation:

$$AP_{atm} - \frac{An_{gas}RT}{V_{gas}} - F_A \pm F_f = 0 \tag{2}$$

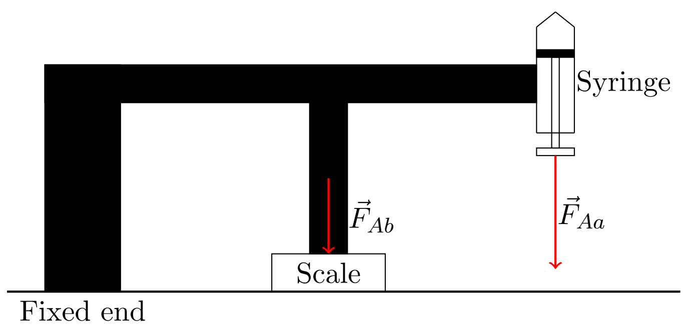
We note that the sign of the friction term is ambiguous as the static friction can act in either direction. We can measure the external applied force term F_A at the points where the piston slips upwards (the minimum F_A where the syringe stays in equilibrium) and the point where the piston slips downwards (the maximum F_A where the syringe stays in equilibrium). Averaging the two, we obtain an intermediate applied force for which the static friction term averages to zero (as the upwards and downwards contributions of friction cancel). Using this averaged value of F_A, equation (2) reduces to:

$$AP_{atm} - \frac{An_{gas}RT}{V_{gas}} = F_A \tag{3}$$

From which we obtain a relationship between two measurable quantities: the volume of the gas in the syringe V_{gas} and the averaged external force F_A, from which the ideal gas constant R can be extracted.
In order to measure the external force accurately, we have constructed a force meter, from components shown in Fig 2a. The setup of the force meter is demonstrated in the diagram in Fig 2b. The construction of this novel force meter is outlined in the Appendix.



(a) Apparatus components



(b) Force meter diagram

Figure 2: **(a):** Components of the experimental apparatus, consisting of supports ((a),(b),(c),(d),(e),(f)), a 5kgx1g WH-BO5 electronic scale ((e)), a 10mL toy syringe with a plastic stopper and clip ((f)), and calibrating weights ((i)). **(b):** Diagram of force meter apparatus, with syringe and scale in drawn positions, and supporting structures pictured in black. By applying a downwards force $\vec{F}_{Aa}$ onto the syringe by manual pulling, a proportional force $\vec{F}_{Ab}$ is applied onto the electronic scale. The value of $\vec{F}_{Aa}$ can be extracted from the scale reading by using a force/scale reading ratio determined through calibration.

After construction, the force meter was calibrated with weights of precisely known mass in order to establish a conversion between the scale reading and external force applied to the syringe. This was done by hanging off weights of different mass from the syringe and taking the ratio between the gravitational force of the mass versus the scale reading.

To conduct the measurement, the syringe was set to a fixed volume of 2mL and then closed with the stopper. The syringe was then pulled downwards until the gas volume was 3mL and held there at equilibrium. The pulling force applied to the piston was then gradually decreased until the piston began to slip upwards. At this moment, the scale reading was recorded, and converted into an external force value via the ratio determined in calibration. The same was done in the other direction, where the applied force on the syringe at equilibrium at 3mL was increased until the piston would begin to slip downwards, and again converted to an external force value. Each measurement was repeated 5 times and averaged to find the minimum and maximum external forces that could be applied to hold the syringe at equilibrium. The uncertainty was taken to be the standard error of the mean of the 5 measurements. Finally, the the minimum and maximum external force values were averaged to determine the average applied force F_A at a volume of 3mL. The measurement sequence of external force values was replicated at successive syringe volumes, with volumes increasing in 0.2mL increments up to a maximum volume of 9mL.

After the measurement sequence, the ambient temperature was recorded with a standard iodine thermometer and the cross-sectional area of the syringe was measured with a ruler. An average was taken from multiple measurements, and the measurement uncertainty was obtained from the standard error of the mean. Finally, a linear fit was performed on the dataset of inverse syringe volume versus averaged applied force with a scipy curvefit program. By equation (3), the slope of this fit yielded the value of $-An_{gas}RT$. By dividing the slope by the cross-sectional area of the syringe, the ambient temperature, and the number of moles of gas in the syringe, the value of the gas constant R was extracted. Uncertainty in the final value was determined by propagating the statistical uncertainty in the slope from the fitting routine with the measurement uncertainties of area and temperature.

3 Discussion of Results

3.1 Preliminary measurements

From ruler measurements of the syringe, the cross-sectional area of the syringe piston A was measured to be $1.7 \times 10^{-4} \pm 2 \times 10^{-5}$ m^2. From the initial syringe volume of 2 ± 0.1 mL, the moles of air in the syringe N_{gas} was calculated to be $8.2 \times 10^{-5} \pm 4 \times 10^{-6}$ mol. Using a standard iodine thermometer, the ambient temperature of the room T was measured to be $295.5 + / - 0.5K$. In all three cases, values were averaged from multiple measurements, and the uncertainty taken to be the standard error of the mean. These values are employed shortly later in the paper in the extraction of the value of R.

3.2 Calibration Data

The apparatus was first calibrated before collecting data of applied force and volume. The data from the calibration is shown in Fig 3 below.

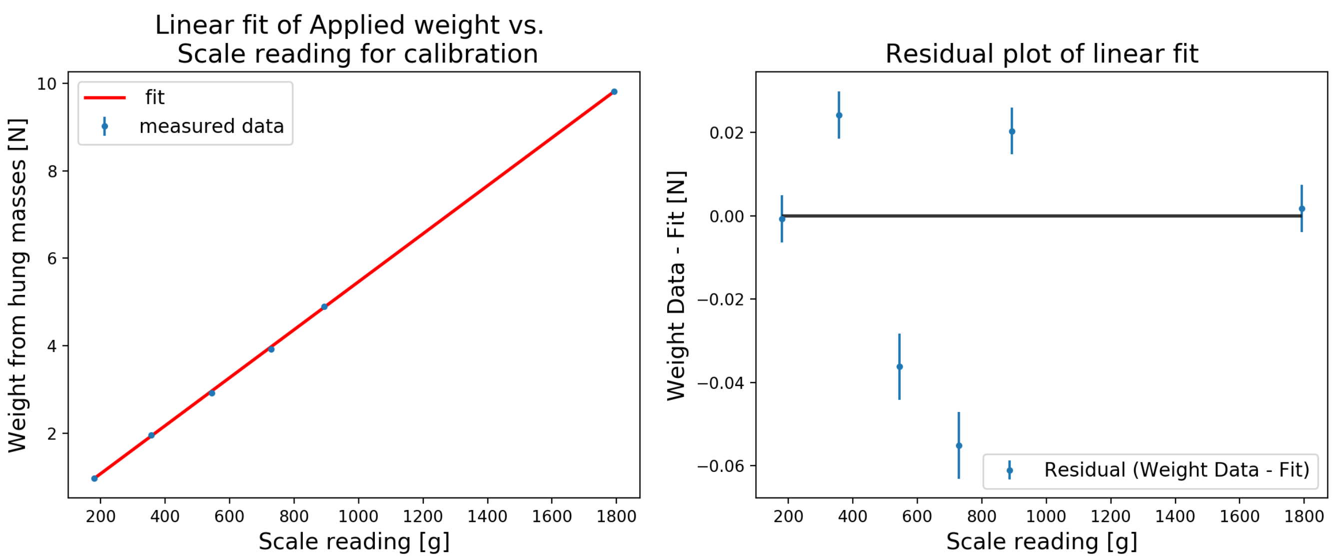


Figure 3: **(a):** Linear fit of the dataset of weight/gravitational force from the masses hung off of the syringe (Newtons) versus the scale reading (grams). Least-squares fitting was done with a scipy curve fit program. The extracted slope from this calibration dataset yields a conversion factor between the force applied to the syringe and the reading that we see on the electronic scale. This allows for the exact quantification for the force applied to the syringe when manually applying force through pulling. Error bars represent the systematic uncertainty of the weight of the masses, from their measurement with an electronic balance. **(b):** Residual plot of the calibration data. 33.3 % of the points were observed to agree with the fit, and points were observed to be scattered randomly on either side of the y-axis.

From the linear fit, a slope of $5.482 \times 10^{-3} \pm 4.4 \times 10^{-6}$ N/g was extracted. This was determined to be the conversion factor between the scale reading and the applied force, and used for the collection of force-volume data. It should be noted that this calibration ratio is sensitive to the precise construction of the force meter apparatus and the positioning of the scale within the apparatus, as the conversion factor varied during prior attempts at data collection. Hence, calibration must be repeated before further instances of collecting force-volume data.

3.3 Fit of force-volume data and extraction of R

As outlined in the methods, data of the maximal external force that could be applied before the syringe would slip downwards from equilibrium. Data was also collected of the minimal external force that could be applied before the syringe would slip upwards. This was repeated at different syringe volumes, and the force values at each volume was averaged. If the experiment is consistent with the theory, the plot of the averaged applied external force versus the reciprocal volume should be linear, according to equation (3). Plotting the obtained data with the equation as shown below in Figure 4, we find that indeed the results are relatively consistent with the theory.

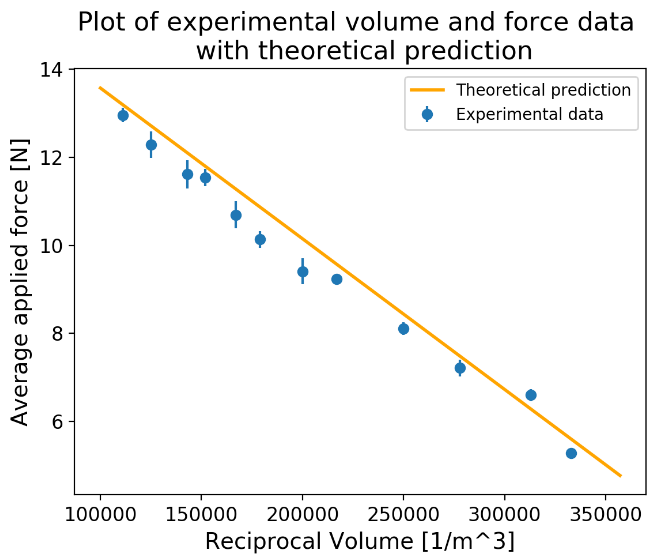


Figure 4: Plot of the experimental applied force and volume data across 10 volume points alongside the theoretical prediction given by equation (3). Error bars on the experimental data represent standard error of the mean. Theoretically precise values of $R = 8.31446261815324$ JK^{-1}mol^{-1} 2, $P_{atm} = 1$ atm as well as experimentally measured values of n_{gas}, A, and T were used for the plot of the theory curve, where the slope is given as $-An_{gas}RT =$ and the y-intercept as AP_{atm}.

From the side-by-side plot, we indeed observe that the experimental data demonstrates linear behaviour with a similar slope as to that predicted by theory. However, we do observe that the theory curve predominantly lies above the measured data, pointing to a possible systematic error in our measurement. In order to extrapolate a slope from our data more precisely, we once again apply a linear least-squares fit using a scipy curvefit program. This yielded results as seen in Figure 5 below.

Using equation (3), we can divide the slope obtained from the linear fit by the cross-sectional syringe area A, the amount of air in the syringe n_{gas}. and the ambient temperature T to obtain the measurement of the gas constant R. Doing so, we obtain that $R = 8 \pm 1$ J mol^{-1}K^{-1}. Uncertainty in this value was determined by propogating the statistical error from the fit and the measurement error in A, n_{gas}, and T. A statistical t-test with our extracted value of R with the fixed value shows that the value agrees with the true value of $R = 8.31446261815324$ JK^{-1}mol^{-1} 2 within measurement error. This is not an entirely surprising result due to the high uncertainty in our final value.

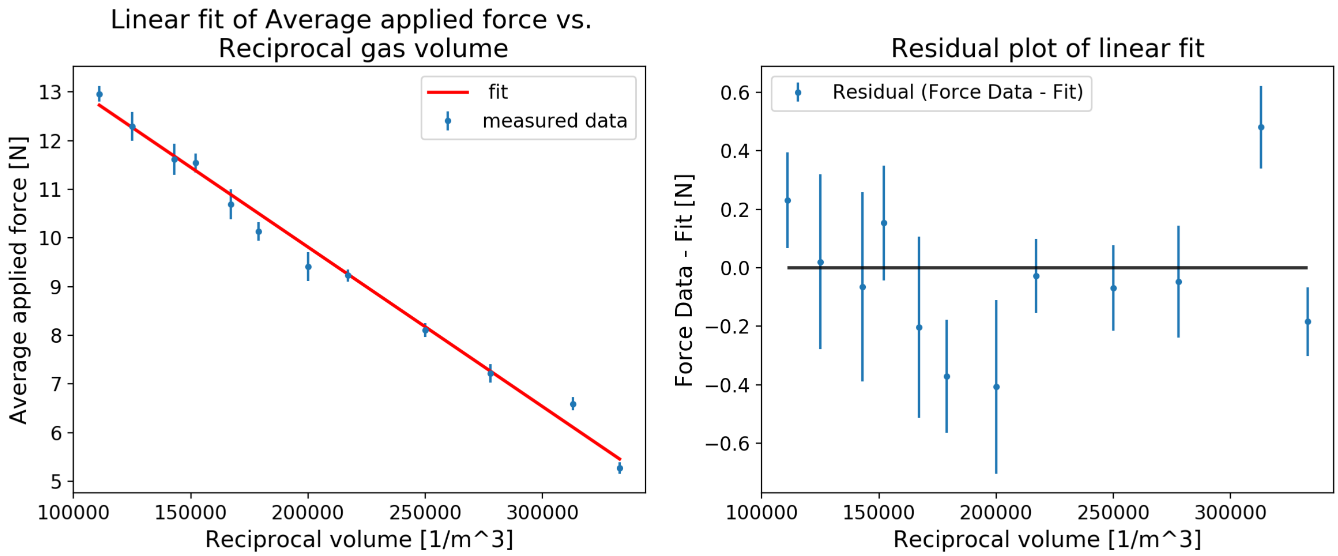


Figure 5: **(a):** Linear fit of the force-volume data. Error bars represent standard errors of the mean. The slope was determined to be $-3.28 \times 10^{-5} \pm 6.7 \times 10^{-7}$ N $\cdot$ m^3 and the y-intercept was determined to be $1.64 \times 10^1 \pm 1.6 \times 10^{-1} N$. The slope value can be used in conjunction with the other preliminary measurements to determine R, and the y-intercept in the same way can be used to determine the atmospheric pressure. χ^2/dof of the fit was calculated to be 2.3. **(b):** Residual plot of fit to the data. Around 60 % of the data falls within one standard deviation of the fit. In addition to this, there is equal scatter of points across the x axis indicating an appropriate linear fit.

Similarly, the atmospheric pressure can be determined from the experimental measurement using the y-intercept of the fit. Once again from equation (3), we can take the y-intercept value and divide it by the cross-sectional area A to give an experimental value of the atmospheric pressure. Doing this calculation yields $P_{atm} = 1 \times 10^5$ Pa $\pm 1 \times 10^4$ Pa. A statistical t-test with the expected theoretical value of $P_{atm} = 1$ atm $= 1 \times 10^5$ Pa also yields a result that the measured value is in agreement with the theoretical value.

The agreement between experimental and theoretical values validates our method for the determination of the gas constant R. In addition, our results also demonstrate that our method is a reasonably accurate measurement of atmospheric pressure. However, our results are limited in value in that the uncertainties are quite high, with relative uncertainties of R and P_{atm} on the order of 10 %. This is in large part due to high relative uncertainties in some of the preliminary measurements of the cross-sectional area A, moles of air n_{gas}, and ambient temperature T. Improved error bounds on these measured quantities will yield more precise results in our final quantities of R and P_{atm}. In addition, the theory consistently overestimating the data in Figure 4 suggests a possible systematic offset in some part of the measurement. A repeated measurement where sources of systematic uncertainty are more carefully tracked can seek to elucidate the mechanism of this shift in the data.

The raw data as well as the code used in analysis can be found at `https://github.com/RioWeil/PHYS229-GasConstant`, for readers who may be interested in replicating our data analysis.

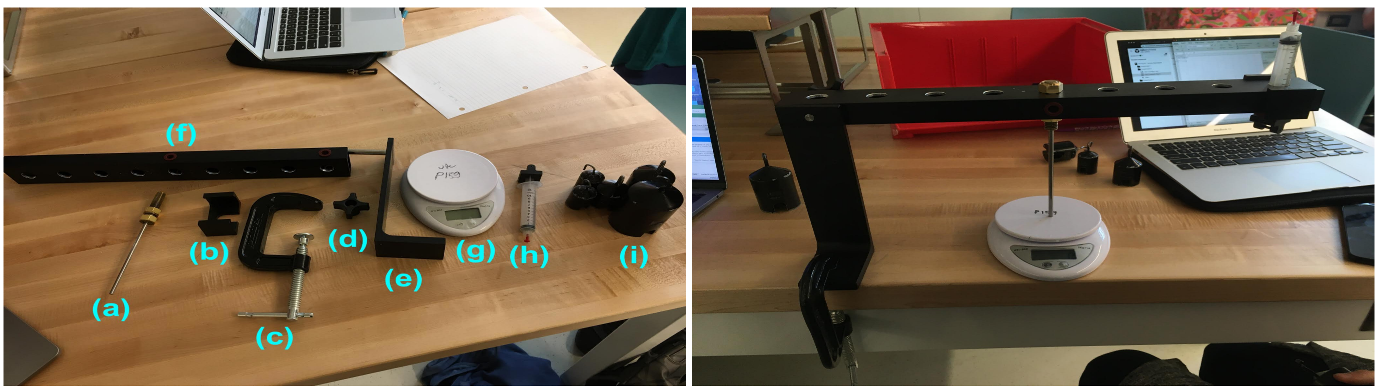
4 Conclusion

In summary, we have conducted a measurement of the gas constant R and atmospheric pressure with a low-cost method using a syringe. Data of syringe volume and applied external force to the syringe were collected via the use of a constructed force meter. The data was fit using a linear least-squares fit according to equation (3), and R was extracted using the slope of this dataset. Our measured value of R was determined to be 8 ± 1 J mol^{-1}K^{-1}. Our obtained value agrees with the fixed value of R, demonstrating that our method is sufficiently accurate for future applications to educational contexts such as in thermodynamics demonstrations and student labs. However, our obtained value is limited in its relevance in that the relative uncertainties on our final values are quite high, and in that our data seems to exhibit a (small) systematic shift relative to the theoretical prediction. Future work can seek to further build on our results by conducting a more precise measurement with our procedure. Potential decreases in the relative uncertainty of R up to an order of magnitude is feasible. Future work may continue to employ our procedure, but shift the focus on the experiment from the measurement of R, which has been made obsolete by the 2019 redefinition of SI base units. For example, future studies may focus on increasing the precision of the measurement of the local atmospheric pressure, which is the more physically relevant of the two main numerical results. Another possible avenue of exploration is the quantification of the non-ideal properties of air. A more precise measurement with accounted-for systematic uncertainties may reveal deviations from the theoretical model derived from the ideal gas law due to non-ideal characteristics of the medium.

5 Acknowledgements

I would like to thank Dr. Bonn for his informative discussion and ideas throughout the course, TAs Luke Reynolds and Michelle Lam for their thought-provoking questions and much-needed expertise with experimental troubleshooting, Annika MacKenzie for her excellent contributions as a lab partner, and Dr. Charbonneau for inspiring my passion for physics, without which I would not be here writing this paper.

6 Appendix - Construction of the force meter



(a) Components

(b) Completed Apparatus

Figure 6: **(a):** Components of the experimental apparatus, consisting of supports ((a),(b),(c),(d),(e),(f)), a 5kgx1g WH-BO5 electronic balance ((e)), a 10mL toy syringe with a plastic stopper and clip ((f)), and calibrating weights ((i)). **(b):** Completed force meter, central to the experimental measurement of the gas constant in the present work.

The apparatus was constructed by clamping (e) to the table using (c), then using (d) to screw (e) onto the leftmost hole of (f). Then, (a) was screwed onto the central hole of (f), while supported underneath by the scale (g). Then, the syringe (h) was threaded through the rightmost hole of (f). Finally, (b) was pushed onto the right side of (f), and clipped onto the syringe such that the syringe stayed fixed in place. The completed experimental apparatus is shown in Fig. 2(b).

7 References

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