Experiments 6

To Determine the Ratio of the Principal Specific Heats of a Gas

Introduction

The purpose of the experiment is to determine the ratio of the specific heats \( \gamma = \frac{C_p}{C_v} \) of a monatomic gas (argon) and a diatomic gas (air) using a resonance method. The results obtained are compared with the theoretical values.

Kinetic theory

The molecules of a gas can be pictured as hard elastic spheres which only interact during collisions. The total energy of such a gas is then entirely due to the kinetic energy of the molecules. Since the average translational kinetic energy per molecule is given by \( \frac{3}{2}kT \), the total internal energy \( U \) of a gas with \( N \) molecules is

\[
U = \frac{3}{2} NkT = \frac{3}{2} nRT \quad (6.1)
\]

where \( n \) is the number of moles, \( k = 1.38 \times 10^{-23} \text{ J/K} \) is Boltzmann’s constant and \( R = 8.31 \text{ J/mol K} \) is the Universal gas constant.

Specific heats

The specific heat of a substance is the amount of heat required per unit mass to increase the temperature by 1°. If the equivalent mass used is a mole, then the corresponding specific heat is the molar heat capacity, \( C \). For gases, the specific heat at constant volume, \( C_v \), and the specific heat at constant pressure, \( C_p \), are the only specific heats of interest. These quantities are connected by the relationship

\[
C_p - C_v = R \quad (6.2)
\]

Differentiating Eq. 6.1 and from the definition of \( C_v \) we get

\[
C_v = \frac{1}{n} \frac{dU}{dT} = \frac{1}{n} \frac{d}{dT} \left( \frac{3}{2} nRT \right) = \frac{3}{2} R \quad (6.3)
\]

6-1
From Eq. 6.2 we get
\[ C_p = R + C_v = \frac{5}{2} R \]  

Hence the ratio of specific heats is \( \gamma = \frac{C_p}{C_v} = \frac{5}{3} \approx 1.67 \). Details of these derivations can be found in Halliday & Resnick.

**Equipartition of energy**

The above result for \( \gamma \) is in good agreement with experimental results for monatomic gases (e.g. Ar, Xe) but not for diatomic and polyatomic gases. This is because in our analysis so far we have considered the molecules as having only translational kinetic energy i.e. any absorbed energy goes into increasing the velocities of the molecules of the gas. For monatomic gases this is a reasonable assumption. However, for diatomic gases, where the molecules can be considered as dumb-bell shaped, absorbed energy can also go into rotational energy of the molecule. Each independent way in which energy can be absorbed is called a degree of freedom and the equipartition theorem states that the available energy distributes itself equally among all available degrees of freedom. In the case of a diatomic molecule, there are 3 translational degrees of freedom and 2 rotational (not 3, because the rotation along the line joining the atoms is negligible) i.e.

\[ U = 3n \left( \frac{1}{2} RT \right) + 2n \left( \frac{1}{2} RT \right) = \frac{5}{2} nRT \]  

Following the previous analysis this yields a value of \( \gamma \) for diatomic gases of \( 7/5 = 1.4 \).

**Background to the experiment**

It is well known that \( \gamma \) determines the velocity of sound waves in a gas, provided the amplitude is small. Sound waves in a gas (or a liquid) are longitudinal waves since such media cannot sustain the transverse shear necessary for transverse waves. The sound wave consists of a series of compressions and rarefactions propagating through the medium with a velocity given by

\[ \upsilon = \sqrt{\frac{K}{\rho_0}} \]  

where \( K \) is the bulk modulus of the gas and \( \rho_0 \) is its density. The value of the bulk modulus of a gas depends on whether it is compressed isothermally or adiabatically. Newton, who first considered this problem, reasoned that the heat produced in the compressions of the sound wave was rapidly conducted away so that the process was effectively isothermal. In this case, if the gas is assumed to be ideal, the perfect gas law holds i.e.

\[ pV = RT = \text{constant} \]  

The bulk modulus in this case can be written

\[ K = -V \frac{dp}{dV} \]
where $V$ is volume of the gas and $dV$ is the change in volume produced by a change in pressure of $dp$. Rearranging Eq. 6.8, and comparing with the differential of Eq. 6.7, Eq. 6.8 gives

$$pdV + Vdp = 0 \text{ from 6.7}$$
$$KdV + Vdp = 0 \text{ from 6.8} \quad (6.9)$$

Therefore for an isothermal compression $K = p$ and putting this value in Eq. 6.6 gave a velocity that did not agree with experiment. Laplace in 1817 accounted for the discrepancy by noting that the compressions and rarefractions occur so rapidly that there is no time for the heat to be conducted away and so the process is adiabatic.

$$pV^\gamma = \text{constant} \quad (6.10)$$

**The Adiabatic Bulk Modulus**

It follows that if the compressions and rarefractions in the sound wave are adiabatic, Eq. 6.10 should be used in the calculation leading to Eq. 6.9 and will result in a value for the adiabatic bulk modulus of

$$K = \gamma p \quad (6.11)$$

Using this value in Eq. 6.6 leads to a value for the velocity of sound that agrees fairly well with experiment.

**Experimental set-up**

The apparatus used in the present experiment is a simplified form of that used by Clark and Katz in 1940 to determine a value of $\gamma$ for a gas by measuring the resonance frequency of a piston oscillating in a tube containing the gas.

The apparatus consists of a precision bore glass tube mounted vertically and containing a freely moving aluminium piston which carries a small cylindrical bar magnet. The piston is supported by the field of an annular permanent magnet acting upon its own magnet (Fig. 6.1). An ac current from a signal generator is passed through a set of coils which produces an oscillating magnetic field parallel to the axis of the tube and causes the piston to oscillate about its equilibrium position. The amplitude of the oscillation will be maximum when the frequency of the generator coincides with the natural frequency of oscillation of the system i.e. the resonant frequency.

Three modes of oscillation are possible

(a) with both ends closed
(b) with one end open
(c) with both ends open

As the piston oscillates, the gas at the face is alternatively compressed and rarefied just as in a sound wave and, if the frequency is sufficiently great, the changes will be adiabatic.

To find the resonant frequency of the system when both ends of the tube are closed consider the forces acting on the piston at time $t$ when it is displaced a distance $y$ from its equilibrium position.
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![Experimental set-up for the measurement of $C_p/C_v$](image)

1. There will be a restoring force due to the permanent magnet which will be proportional to the displacement and given by

$$-K_H y$$  \hspace{1cm} (6.12)

2. A restoring force due to the fact that in the displacement the gas on one side of the piston is compressed, producing an increase in pressure of $\Delta p$, and on the other side is rarified producing a decrease in pressure of $\Delta p$, provided the initial volume of gas on both sides of the piston is the same. This produces a restoring force at each face of

$$\Delta p A$$  \hspace{1cm} (6.13)

where $A$ is the cross sectional area of the piston. Since the processes are adiabatic, changes in pressure and volume are related by

$$\frac{\gamma \Delta V}{V} = \frac{\Delta p}{p}$$  \hspace{1cm} (6.14)

Combining this with Eq. 6.13 gives an expression for the restoring force acting on each face

$$\Delta p A = -\frac{\gamma p A^2}{V} y = -K y$$  \hspace{1cm} (6.15)

where

$$K = \frac{\gamma p A^2}{V}$$  \hspace{1cm} (6.16)
3. A frictional force which we will assume is proportional to the velocity and given by

\[ D \frac{dy}{dt} \]  

(6.17)

4. The driving force due to the oscillating magnetic field given by

\[ F_O \cos \omega t \]  

(6.18)

Using Eqs. 6.12, 6.15, 6.17, and 6.18 and Newton’s second law gives the equation of motion for the system

\[ M \times \frac{d^2 y}{dt^2} = -K_H y - 2K y - D \frac{dy}{dt} + F_O \cos \omega t \]

\[ M \times \frac{d^2 y}{dt^2} + D \frac{dy}{dt} + (K_H + 2K)y = F_O \cos \omega t \]  

(6.19)

This is the equation of a forced oscillator. It is found that the resonant frequency is given by \( \omega \) where

\[ \omega = 2\pi \nu = \sqrt{\frac{K_H + 2K}{M} - \frac{D^2}{2M^2}} \]  

(6.20)

In the experiment, care is taken to minimize the friction (i.e. D) and in this case the second term in Eq. 6.20 is negligible in comparison with the first and the linear resonant frequency can be written

\[ \nu = \frac{1}{2\pi} \sqrt{\frac{K_H + 2K}{M}} \]  

(6.21)

If one bung is removed from the tube then 2K is reduced to K as the restoring force of the gas now acts on only one side of the piston and the new resonant frequency, \( \nu_1 \), is

\[ \nu_1 = \frac{1}{2\pi} \sqrt{\frac{K_H + K}{M}} \]  

(6.22)

If both bungs are removed there will be no restoring force due to the gas and the resonant frequency, \( \nu_2 \), will be

\[ \nu_2 = \frac{1}{2\pi} \sqrt{\frac{K_H}{M}} \]  

(6.23)

Eliminating \( K_H \) between Eqs. 6.21 and 6.22 and using Eq. 6.16 gives an expression for \( \gamma \)

\[ \gamma = \frac{4\pi^2 MV}{pA^2}(\nu^2 - \nu_1^2) \]  

(6.24)

Eliminating \( K_H \) between Eqs. 6.21 and 6.23 gives another expression for \( \gamma \)

\[ \gamma = \frac{2\pi^2 MV}{pA^2}(\nu^2 - \nu_2^2) \]  

(6.25)

Either of the above pair of relationships may be used to calculate the value of \( \gamma \) for air. Note for your calculations that \( V \) is the volume of gas on one side of the piston. It is assumed that \( V \) is the same on each side of the piston.
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**Experimental Procedure**

**Determination of $C_p/C_v$ for air**

- Determine the physical constants of the tube and piston, i.e. weigh the piston and, using the callipers, measure its internal and external dimensions so that its effective volume may be calculated. The volume of the internal cavity must be taken into account. Measure the bore and the effective length of the glass tube. The effective length of the tube is the distance between the inner ends of the rubber bungs when inserted into the ends of the tube. Once these constants have been determined, prior to the initial use of the apparatus, they may be recorded and used in any future experiment.

- Make a note of atmospheric pressure from the pressure sensor, ensuring you use SI units.

- Using one of the bosses, mount the magnet-coil assembly on the retort stand with its axis vertical. The assembly should be about 0.3 m above the surface of the bench. The bench itself should be as firm as possible to avoid unwanted resonances when the experiment is in progress and it may be found desirable to clamp the base of the retort stand to the bench with “G” clamps.

- Insert the tube through the coil and support it by means of the two cross-jaw clamps, one above and one below the coil. The tube should be co-axial with the coil assembly but the clamps and bosses should be left slightly loose to allow for later adjustment of the tube position, which will almost certainly be required.

- Fit a solid bung in the lower end of the tube. To minimize friction, the piston should be polished with the cloth supplied and inserted into the tube, magnet end down. The piston will gradually descend due to the inevitable slight leakage around its sides until it comes to rest on the supporting field of the annular magnet. The descent of the piston is normally very slow but may be speeded up by allowing air to leak past the bung in the bottom end of the tube. The relative positions of the tube and coil magnet assembly should be such that the piston rests with its centre of volume at the mid point of the tube. The centre of volume of the piston can be taken as being one third of its length from its magnet bearing end. This procedure is intended to ensure that the volume of air (or other gas) in the tube is, as near as is reasonably possible, equally divided either side of the piston. It may be found convenient to mark the tube and the piston with a nylon tip pen to facilitate the positioning which is carried out by slowly and gently moving the tube up or down in the clamps.

- Connect the coil magnet to the $C_p/C_v$ signal generator unit supplied. Set the signal frequency at about 27 Hz using the frequency control. The amplitude should be set initially at approximately 75% of maximum.

**IMPORTANT:**
THE FREQUENCY CONTROL WHICH IS EQUIPPED WITH A LOCKING SWITCH SHOULD BE TREATED CAREFULLY.
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- Adjust the tube to minimise friction between itself and the oscillating piston. When the piston is oscillating, a “hissing” noise will be heard (caused by the friction between itself and the tube). Carefully adjust the vertical orientation of the tube by moving the clamp rods in their bosses a little at a time until the hissing sound is at a minimum and the amplitude of the oscillation is as large as possible for a given setting of the controls, indicating that the piston is moving as freely as possible. Tighten all clamps and bosses to retain the tube securely in position. Minimizing the friction increases the sharpness of the resonance and accuracy of results obtained.

- Very carefully adjust the frequency dial of the signal generator until the exact point of maximum amplitude of oscillation of the piston is obtained. At this stage of the experiment, accuracy is of the greatest importance as any errors in setting the frequency correctly are magnified in final calculations of the results. A piece of blank card placed behind the tube will help to make the piston more visible.

Make at least 10 readings to ensure that the resonant frequency is remaining stable and record the results. The mean of your readings is the best estimate for $\nu$. The error on the mean is $d\nu$.

- Remove the upper bung and readjust the frequency until the new resonant frequency $\nu_1$, is found and recorded. Again make at least 10 estimates of this resonant frequency.

- Finally remove both bungs and using the same basic procedure determine the resonant frequency at least 10 times. Determination of $\nu_2$ is not quite as easy as that of $\nu$ and $\nu_1$ as the resonance peak is less well defined.

Determination of $C_p/C_v$ for argon

- In this part of the experiment argon gas is allowed flow through the glass tube at a slow, constant rate. The pressure of the argon is monitored using a pressure transducer. While making measurements the pressure should be maintained as close to atmospheric pressure as possible.

- When the gas cylinder has been connected to the tube via the glass tap (ask the demonstrator), the needle valve can be opened slightly to allow the gas to flow. Initially, keep the upper tap closed. As the pressure under the piston builds up, the piston will begin to rise. When it is close to the top of the tube, open the top tap to release the overpressure. The piston should drop back to its central position. Close the top tap and repeat this procedure a couple of times. In this way the air is flushed out of the tube to be replaced by argon. When satisfied that the pressure inside the tube is at atmospheric and that all the air has been replaced by argon, close off both glass taps immediately.

**NB: This procedure should be closely monitored by the demonstrator.**

- With both glass taps closed determine the resonant frequency, $\nu$, 10 times as before.
Data analysis

Using the mean values of $\nu$, $\nu_1$ and $\nu_2$ obtained for air, calculate values for $\gamma$ of air from Eqs. 6.24 and 6.25. Which estimate do you think is more accurate? Quantify your answer by estimating the errors on your measurements as follows. The propagation of errors formula (see Eq. 1.15 in Notes on Errors) yields the following expression for the fractional error on $\gamma$, when it is calculated from Eq. 6.24:

$$\left( \frac{d\gamma}{\gamma} \right)^2 = \left( \frac{dm}{m} \right)^2 + \left( \frac{dp}{p} \right)^2 + \left( \frac{d\nu}{\nu} \right)^2 + \left( \frac{2 \nu d\nu}{\nu^2 - \nu_1^2} \right)^2 + \left( \frac{2 \nu_1 d\nu_1}{\nu^2 - \nu_1^2} \right)^2 \quad (6.26)$$

The 5th and 6th terms dominate the error on $\gamma$, so the other terms may be neglected. The errors on the resonant frequencies $d\nu$, $d\nu_1$, $d\nu_2$ are simply the statistical errors on the mean values you determined. Estimate the error on both measured values of $\gamma$ (using the appropriate equations) and quote your answers as $\gamma \pm d\gamma$. Do your two estimates agree to within the errors? If not, explain why not.

Using the known value of the velocity of sound in air ($343 \text{ ms}^{-1}$) find another value for $\gamma$ using Eqs. 6.6 and 6.11 and taking the density of air to be $1.2 \text{ kg/m}^3$.

For argon we only have measurements with both taps closed (for obvious reasons). However we can still calculate a value of $\gamma$ for argon from Eq. 6.25 using the value $\nu_2$ obtained in air. This is valid because for $\nu_2$ there is no restoring force due to the gas, only that due to the magnet, hence it is independent of the gas used. Again, calculate the value of the error on $\gamma$ for argon and discuss whether your result agrees with the theoretical value.

Questions

1. How valid is our assumption that air is a diatomic gas?

2. What would you expect the value of $\gamma$ to be for a polyatomic gas?

References

