

Measuring the Ratio of Specific Heat at Constant Pressure to the Specific Heat at Constant Volume Using Rüchardt's Method

INTRODUCTION: Even with recent advances in technology, the direct measurement of most properties of an individual molecule is difficult. In this experiment, one is using an obviously macroscopic (crude) instrument to make measurement of the configuration of the atoms that form a molecule. This has the feel of dissecting mosquitoes with a sledge hammer. As with many measurements concerning microscopic characteristics, the trick is to cleverly find a macroscopic behavior that strongly depends on that characteristic.

In this experiment the ratio of specific heat at constant pressure, C_p to the specific heat at constant volume, C_v will be measured for several gases. This ratio is called γ . Somewhat surprisingly, γ depends on the atomic configuration in an individual gas molecule. Equally surprisingly, γ can be measured by timing the bouncing of a ball in a tube which has one end open to the air and its other end connected to large jar.

PROCEDURE: The basic procedure is to time the period, T , of oscillation of a steel ball in a glass tube. The tube is open to the atmosphere at the top and connected to an otherwise seal jar at the bottom, see fig. 1. The ratio of specific heats, γ is related to the period of oscillation, τ ; the mass, m and diameter, d of the ball; the equilibrium volume, V_0 of the jar (and part of the tube); and the pressure P_0 inside the jar at equilibrium by

$$\gamma = \frac{64 m V_0}{d^4 P_0 \tau^2} \quad (1)$$

Here the equilibrium volume and pressure are those values when the sum of the forces acting on the ball add to zero.

When studying air, the pressure inside the jar can be increased by using the pumping squeeze bulb. Increase the internal pressure until the steel ball is "floating" at your selected equilibrium position. Set the ball in oscillatory motion by a quick squeeze and release of the perturbing squeeze bulb. Use the photogate in the "PEND" (pendulum) mode to time the period.

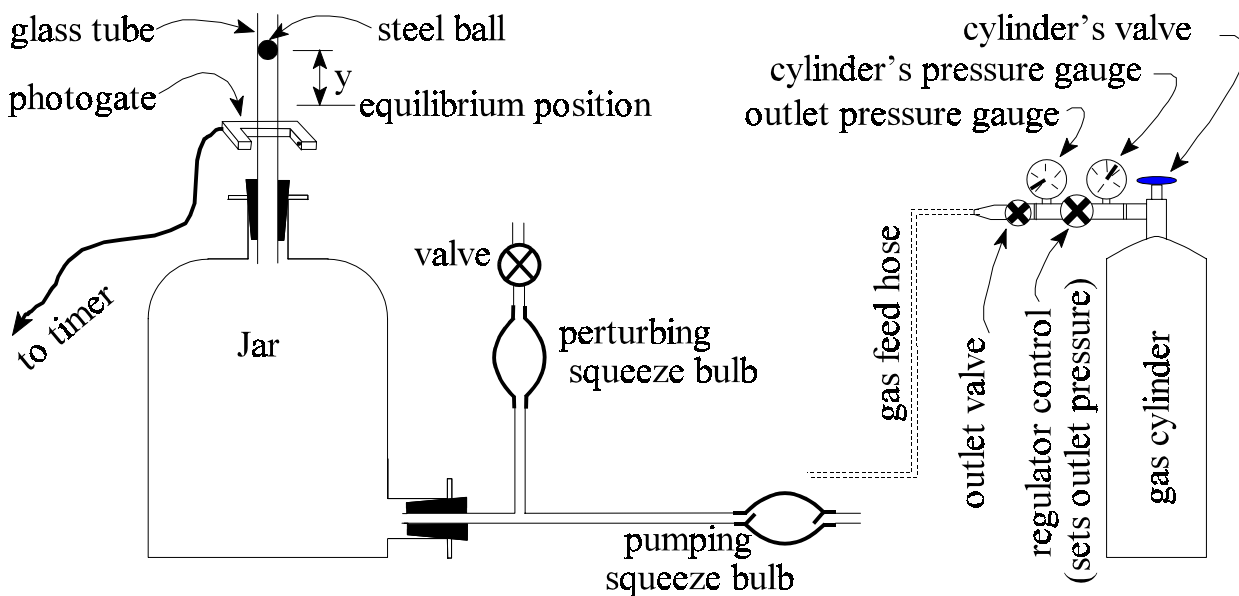


Figure 1 The general experimental setup for Rüchardt's method of measuring C_p / C_v .

Although any individual period measurement has very little uncertainty associated with that measurement, there is a relatively large fluctuation in the period when taking repeat measurements. The situation is a little like measuring the diameter of an orange with a micrometer accurate to 0.0001 inches, but the orange is not uniformly spherical to better than 0.25 inches. In either case you need to take a bunch of measurements, find the average and for the uncertainty use something like the standard deviation of the mean.

For a given gas, it is suggested that you average your collection of periods before you use them in Eq (1) to find γ . But if you make a change in procedure, rearrange the equipment or have data from different days you might want to consider finding the γ for each of these situations in case there are systematic errors that shift the data.

How many measurements? This is a question that must be asked and answered for every experiment. The answer depends on the time and difficulty of making measurements, the limitations of the measuring equipment, and the required accuracy of the measurement. From an experimental point of view, one should repeat the measurement, at least until the mean value no longer changes when you a new measurement is made.

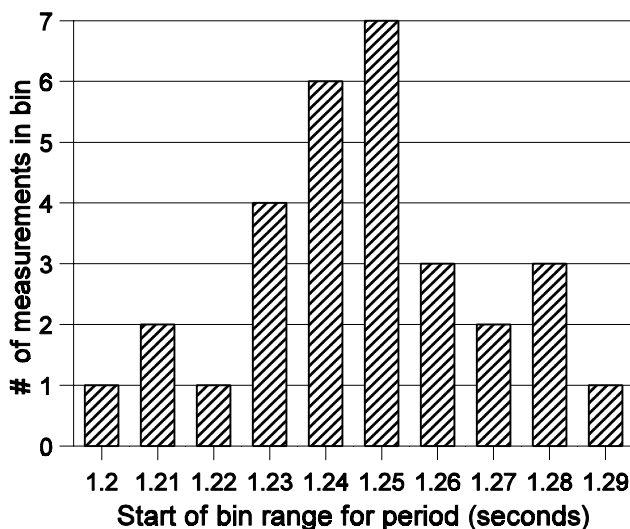


Figure 2 Histogram of 30 period measurements.

Histogramming the data is one good way to view your data set. This basically is to “bin” your data and plot the number of data points in each bin versus the bin value. In this experiment you made 30 measurements and all periods in the range 1.2 to 1.3 seconds. One might divide this range into 10 bins (1.200-1.209, 1.210-1.219, . . . 1.29 - 1.299), and count up the number of measurements that fall into each range, see Fig (2).

To do this experiment with gases other than air (CO₂ and argon), we fill the jar with gas from a cylinder of compressed gas. There are a couple of points to consider here. First, you need to know how to use the gas regulator and related valves.

HAVE A TA REVIEW THIS PROCESS WITH YOU BEFORE YOU USE THE EQUIPMENT!

Do NOT set the regulator with it connected to the jar. Open the outlet valve, and turn out (counterclockwise) the regulator control valve until it is loose. Open the cylinder’s valve and read the cylinder’s pressure gauge to know the pressure inside the cylinder. If it is below 200 PSI, please inform your TA. Slowly turn in (clockwise) the regulator control while watching the outlet pressure gauge and listening for gas flow. Now close the outlet valve.

To fill the jar, remove the glass tube and stopper assembly from the jar and set the outlet pressure to about 5 PSI. Do NOT flush the jar with the tube in place, because a relatively small pressure differential can cause the ball to shoot up to the top of the tube and damage things. After the jar has been flushed, with the outlet valve still open, adjust the regulator to about 1 PSI, close the outlet valve, and reinstall the glass tube. Now you can let small amounts of gas into the jar using the outlet valve.

How can you tell when the jar is filled with the new gas? One way, is to flush for a while, take a few measurements, flush some more, take more measurements. When the jar is filled with the new gas, additional flushing should not change the period of oscillation.

A second approach to deciding how long to flush the jar is to estimate the number of volumes of the jar with which you want to flush it. That is easy enough since you know the internal volume of the jar and can estimate the volume of the gas cylinder. Additionally, you can read the pressure dial to get the initial and final pressures in the gas cylinder. It is straight forward to figure the volume of gas at atmospheric pressure and room temperature that has exited the gas cylinder. If you consider the flushing to involve complete (instantaneous) mixing, than it can be shown that the fraction, F , of the gas introduced in the jar is given by:

$$F = 1 - e^{-V_{\text{FLUSH}}/V_{\text{JAR}}} \quad (2)$$

Where V_{JAR} is the total volume of the jar, and V_{FLUSH} is the volume (at atmospheric pressure) of the introduced gas used to flush the jar. From this if $V_{\text{FLUSH}} / V_{\text{JAR}} \approx 5$ the introduced gas comprises about 99% of the gas in the jar.

THEORY: For this experiment as in many others there are two theoretical problems to understand. First there is the theory of the experiment that is relating measurable quantities to parameter of interest. In this case the first part of the theory is to derive Eq (1), which is the working equation for this experiment, and to derive the propagation of error formula. The second part of the theory is to relate the measured parameter (in this case γ) to the fundamental physics (in this case the configuration of the gas molecules).

The starting point of deriving the working equation is to recall the basic properties of gases. The most fundamental of these is the idea gas law:

$$P V = n R T \quad (3)$$

where P is the pressure, V is the volume, n is the number of moles of the gas, T is the temperature of the gas, and R is the universal gas constant.

$$\begin{aligned} R &= 8.314 \text{ J / (mole K)} \\ &= 1.986 \text{ cal / (mole K)} \end{aligned} \quad (4)$$

Eq (3) is sometimes called the *equation of state* of an ideal gas.

The first law of thermodynamics in terms of the internal energy, U of a gas is:

$$\Delta U = Q - W \quad (5)$$

where Q is the heat added to the system and W is the work done by the system. From Eq (5) one can find the specific heats at constant volume, C_V and at constant pressure, C_p , if one knew how the internal energy of the given gas depends on temperature.

In a gas it is impossible to know the linear and rotational momentums, vibrations and energies of each molecule, BUT it is possible to know the average energy of a molecule. From statistical mechanics and thermodynamics it is known that for each degree of freedom, f that the molecule has, on the average it has an energy $\frac{1}{2}kT$ where T is the temperature and k is the Boltzmann constant:

$$\begin{aligned} k &= 1.38 \times 10^{-23} \text{ J / (molecule K)} , \\ &= 8.63 \times 10^{-5} \text{ eV / (molecule K)} . \end{aligned} \quad (6)$$

On the average at a temperature, T , a gas molecule with f internal degrees of freedom will have an energy, E_{AVE} :

$$E_{\text{AVE}} = \frac{f}{2} k T \quad (7)$$

and the internal energy, U of a large number, N , gas moles is:

$$\begin{aligned} U &= \frac{f}{2} N k T \quad (8) \\ U &= \frac{f}{2} n R T \end{aligned}$$

The other important equation dealing with ideal gases, is that for an *adiabatic* process:

$$P V^\gamma = \text{constant} \quad (9)$$

You are strongly encouraged to study the derivation of Eq (3) found in most introductory university physics text such as *Physics* by Halliday, Resnick, and Krane.

Q1. What is an ideal gas?

Q2. What is the SI unit for pressure? What are the conversion factors between this and pressure measured in mm of mercury, and PSI?

- Q3.** What is the relationship between force and pressure?
- Q4.** What is the definition of specific heat? What SI units is it measured in?
- Q5.** What is meant by the number of degrees of freedom? Why do some gases have more internal degrees than others? How is this related to the configuration of atoms in the gas molecules? Can a gas have degrees of freedom that are not internal? If so, give an example.
- Q6.** From Eqs (5) and (8), and noting that if the volume is constant, the work is zero (Why?) find the specific heat at constant volume, C_v for a gas with f internal degrees of freedom.
- Q7.** From Eqs (5) and (8), find the specific heat at constant pressure, C_p for a gas with f internal degrees of freedom.
- Q8.** In terms of the number of internal degrees of freedom, what is the ratio of the specific heats, γ ?
- Q9.** What is an adiabatic process? Give an example. In Eq (5) are any terms zero for an adiabatic process?
- Q10.** What is an isothermal process? Give an example. In Eq (5) are any terms zero for an isothermal process?
- Q11.** What is the difference between heat, work, and energy?
- Q12.** What is the relationship between the number of moles, n and the number of molecules, N ?
- Q13.** What is the relationship between the Boltzmann constant, k and the universal gas constant, R ?
- Q14.** What is the difference between internal energy of a gas and the total energy of a gas?
- Q15.** How many moles, n of the gas are enclosed? How many molecules, N are enclosed?
- Q16.** When the ball is in equilibrium, estimate the internal energy of the enclosed gas.
- Q17.** In this experiment it is important to understand what is happening to the ball and the enclosed gas. Consider the situation that the amplitude of the ball's oscillation is 5 cm. From the ball being at the top of its oscillation to the bottom:
- What is the change in the ball's energy, ΔE_{BALL} ?
 - What is the change in the energy of the enclosed gas, ΔE_{GAS} ?
 - What is the change in the volume of the enclosed gas, ΔV ?
 - What is the change in the pressure of the enclosed gas, ΔP ?
 - What is the change in the temperature of the enclosed gas, Δt ?
- Q18.** What is the effect of tube not being vertical?
- Q19.** The gauges of the cylinder of compressed gas read in gauge pressure, how does this relate to the true (absolute) pressure?
- Q20.** If the pressure inside the jar, P_0 , exceeds the atmospheric pressure by 1 PSI, what is the acceleration of the ball?
- Q21*.** The motion of the ball decreases in amplitude that is it is damped. How does this damping effect the period of oscillation? increases or decreases? If you are really trying to beat this experiment to death, work the formula that describes the motion of a damped harmonic oscillator and try to estimate the damping constant, and correct the period accordingly.
- Q22.** Why is it important to have the glass tube as close to vertical as possible?
- Q23*.** How is γ related to the speed of sound?
- Q24*.** What is the basis of Eq (2)

DERIVE THE WORKING EQUATION

To derive the working equation, Eq (1) consider the following steps.

I. If the ball is stationary (in equilibrium, not stuck) what must be true about the sum of the forces? Draw a free body diagram. If the ball is in equilibrium, what is the relationship between the pressure, P₀ inside the jar and the pressure, P_{ATMOS} outside the jar?

II. If the ball moves a vertical distance, y in the tube from the equilibrium position, the volume, V of gas sealed below the ball in the tube and jar changes by an amount, ΔV. What is ΔV in terms of y and the diameter of the ball?

III. If the pressure in the jar differs from the equilibrium pressure, P₀ by an amount ΔP, what is the sum of the forces on the ball? What is the acceleration, a, of the ball in terms of ΔP?

IV. From Eq (9) one show:

$$P_0 V_0^\gamma = (P_0 - \Delta P) (V_0 + \Delta V)^\gamma . \quad (10)$$

(Why the minus sign?) Next solve this for ΔP, and use the binomial expansion:

$$(1 - x)^n = 1 - nx + \frac{n(n-1)}{2} x^2 + \frac{n(n-1)(n-2)}{3!} x^3 + \dots \quad (11)$$

with $x = \Delta V / V_0$. Next drop the terms of order higher than linear in x.

Q25. From your measurements justify this approximation.

Q26. Why is this equivalent to taking the derivative of Eq (9) to obtain:

$$V^\gamma dP + \gamma P V^{\gamma-1} dV = 0 , \quad (12)$$

and then making the approximations:

$$\Delta P \approx dP ,$$

and

$$\Delta V \approx dV ? \quad (13)$$

VI. Recall that acceleration is the second derivative of position with respect to time, and show:

$$\frac{d^2 y}{dt^2} = - \frac{\gamma \pi^2 P_0 d^4}{16 m V_0} y . \quad (14)$$

VII. Show that a solution to Eq (14) is:

$$y(t) = \sin(\omega t) ,$$

$$\omega^2 = \frac{\gamma \pi^2 P_0 d^4}{16 m V_0} . \quad (15)$$

VIII. Finally relate the period, τ to the angular frequency, ω, and solve for γ, to get Eq (1).

DERIVE THE ERROR PROPAGATION EQUATION

Start with the working equation, eq. 1

$$\gamma = \frac{64 m V_0}{d^4 P_0 \tau^2} . \quad (16)$$

and derive the error propagation equation:

$$\sigma_\gamma = \gamma_{\text{measured}} \sqrt{\left(\frac{\sigma_m}{m}\right)^2 + \left(\frac{\sigma_V}{V_0}\right)^2 + 16 \left(\frac{\sigma_d}{d}\right)^2 + \left(\frac{\sigma_P}{P_0}\right)^2 + 4 \left(\frac{\sigma_\tau}{\tau}\right)^2} , \quad (17)$$

where σ_γ is the uncertainty in the value of the ratio of specific heats,
 σ_m is the uncertainty in the mass of the ball,
 σ_V is the uncertainty in the equilibrium volume,
 σ_d is the uncertainty in the diameter of the ball,
 σ_P is the uncertainty in the equilibrium pressure, and
 σ_τ is the uncertainty in the period of oscillation.

Note, an uncertainty in a quantity x is also written as δx . Start with general form of propagation of errors (assuming uncorrelated errors) for a function $u = f(w, x, y, z)$ is:

$$\sigma_u^2 = \sigma_w^2 \left(\frac{\partial u}{\partial w}\right)^2 + \sigma_x^2 \left(\frac{\partial u}{\partial x}\right)^2 + \sigma_y^2 \left(\frac{\partial u}{\partial y}\right)^2 + \sigma_z^2 \left(\frac{\partial u}{\partial z}\right)^2 . \quad (18)$$

When the function is a product of powers ($u = w^a x^b y^c z^d$) show Eq (3) reduces to:

$$\left(\frac{\sigma_u}{u}\right)^2 = \left(a \frac{\sigma_w}{w}\right)^2 + \left(b \frac{\sigma_x}{x}\right)^2 + \left(c \frac{\sigma_y}{y}\right)^2 + \left(d \frac{\sigma_z}{z}\right)^2 . \quad (19)$$

For a more detailed discussion of propagation of errors see *Data Reduction and Error Analysis for the Physical Sciences* by P.R.Bevington and D.K.Robinson, p. 41-50; or *Experiments in Modern Physics*, by A.C.Melissinos, p.467-473.