SPECIFIC HEATS OF GASES

NOTE: There are several questions that you will need to answer and write up in your laboratory notebook before you start this experiment—see below.

1 INTRODUCTION

The specific heat of a substance is defined by:

$$c = \frac{1}{N}\frac{dQ}{dT} \tag{1}$$

where dQ is the amount of heat that must be added (or removed) from a quantity N of a substance in order to change its temperature by dT. In general, the value of c depends upon what constraints are imposed upon the thermal expansion of the material during the heating process. For example, the substance might be heated along a path of constant volume. Or, it might be heated along a path of constant pressure. For gases, differences in path lead to significant differences in the specific heat. Such differences can be understood in terms of the first law of thermodynamics:

$$dQ = dU + PdV \tag{2}$$

or in words,

$$\begin{aligned}\text{Heat Added} &= \text{Change in Internal Energy}\\ &\quad + \text{External Work done on or by the system}\end{aligned}$$

For gases the external work obviously depends upon the amount of expansion allowed during heating. Thus, no work is done on a gas heated along a path of constant volume; but work is done on a gas heated at constant pressure. In heating most liquids or solids, the amount of external work is small compared to the amount of heat absorbed as internal energy, so that the specific heat depends only slightly on the process. Thus for most liquids and solids, the specific heat at constant pressure, c_p , is commonly given in tables and handbooks as "the specific heat" of such substances.

In gases, the difference between the two specific heats is more pronounced. In this experiment, you will measure the ratio of the specific heats of a gas by an indirect method that will be described later. In dealing with gases, it is usual to consider *molar* specific heats: we express the amount of gas N in Equation (1) in terms of moles. Gases are particularly simple and appropriate substances to study because:

1. To the extent that real gases approximate ideal gases (a very good approximation in many cases), the internal energy U depends only upon the temperature.

Except at very low temperatures or at very high pressures, U does not depend on either pressure or volume.

(The experimental basis for this assertion is the Joule adiabatic free expansion experiment—make sure you understand why. A theoretical explanation is that the potential energy arising from intermolecular forces is a negligible fraction of the internal energy because the molecules are very far apart on the average. The main contribution to the internal energy is the kinetic energy of molecular motion, which depends only upon temperature).

2. The dependence of the specific heat upon the nature of the heating process is pronounced.
3. Theoretical values of the specific heat of an ideal gas can readily be computed. Interestingly, one needs to use quantum mechanics to get the correct theoretical result.

2 IDEAL GASES

In this section we shall review some of the standard equations governing the behavior of ideal gases. *This material is discussed in more detail in your text, to which you should refer if any of this material seems hard to understand.*

We need to find a relation between the specific heats for an ideal gas along paths of constant volume and constant pressure. We begin with the former. Equations (1) and (2) can be combined to obtain the heat absorbed at constant volume ($dV = 0$):

$$dQ = dU = Nc_v dT \tag{3}$$

where c_v is the specific heat at constant volume. (**Note:** Be sure you can derive this result.)

For an ideal gas whose internal energy depends only upon temperature, this equation has special significance; it is a general expression which gives the change in internal energy dU for *any* process regardless of whether or not work is done. In other words, the change in internal energy for any process which involves a temperature change dT is the same as the heat needed to produce the same temperature change in a constant volume process.

We now turn to the specific heat at constant pressure for an ideal gas. The equation of state for an ideal gas is given by the familiar equation

$$PV = nRT.$$

If we take the differential of this equation, we obtain

$$PdV + VdP = nRdT \tag{4}$$

We find c_p as follows: Using Equations (1) and (2), we obtain for *any* arbitrary process

$$dQ = dU + PdV = nc_v dT + PdV. \tag{5}$$

But if we set $dP = 0$ in Equation (4), we obtain

$$PdV = nRdT,$$

and if we combine the last two equations, we obtain

$$dQ = nc_v dT + nRdT = nc_p dT.$$

Hence we obtain a general result for ideal gases:

$$c_p = c_v + R \tag{6}$$

Again, be sure you can derive this result yourself.

Our experiment will make use of adiabatic processes—expansions (or compressions) carried out with no exchange of heat between the gas and its surroundings. Consequently we need to review the behavior of an ideal gas undergoing an adiabatic process. If we set $dQ = 0$ in Equation (5), we have

$$dQ = 0 = nC_v dT + PdV$$

If this equation is multiplied by R/c_v and added to the gas law [Equation (4)], we obtain the following expression, which involves only P and V:

$$\gamma PdV + VdP = 0 \tag{7}$$

where γ is defined as

$$\gamma = 1 + \frac{R}{c_v} = \frac{c_p}{c_v}. \tag{8}$$

The second equality is based on Equation (2). If we integrate Equation (7), we obtain

$$PV^\gamma = \text{constant} \tag{9}$$

Equation (9) is a relationship between the pressure and volume of an ideal gas subjected to an adiabatic process. For an isothermal process, of course, PV is constant.

In this experiment we shall measure the quantity γ directly. We can find values for c_p and c_v using Equation (8) and the gas constant R.

3 KINETIC THEORY

The classical theorem of equipartition of energy states that each separate *degree of freedom* of an atom or molecule has an energy $\frac{1}{2}kT$, where T is the absolute temperature and k is Boltzmann's constant. Thus a point mass has three translational degrees of freedom. See if you can figure out how many degrees of freedom a rigid body that is not a point mass will have. (Hint: How many independent modes of rotation are there?)

The equipartion theorem makes the following prediction: For an ideal gas of point molecules, the internal energy U should be given by

$$U = \frac{3}{2}NkT = \frac{3}{2}nRT,$$

where N is the number of molecules and n the mole number.

A rigid body has three additional rotational degrees of freedom (did you get this answer yourself?), and so would have a total of six degrees of freedom. More generally, for an ideal gas with f degrees of freedom,

$$U = \frac{f}{2}nRT.$$

Consequently, using Equation (3), we obtain

$$c_v = \frac{1}{n}\frac{dU}{dT} = \frac{f}{2}R$$

or, using Equation (8),

$$\gamma = \frac{f+2}{f} \tag{10}$$

(Again, be sure you can derive this equation yourself.) This very important result predicts that the ratio of specific heats will depend on the number of degrees of freedom of a molecule.

EXERCISE

Work out *in your lab notebook*
before starting the experiment.

First, calculate the value of γ for a gas of point molecules?

Next, consider a diatomic molecule (such as O_2 or N_2 to consist of two small spherical masses connected by a spring. How many degrees of freedom will such a system have? What value will γ have?

This prediction, based on classical physics will be wrong! And in fact, the experiment demonstrates one place in which classical physics breaks down—one must use the principles of quantum mechanics to get a correct prediction for γ. Read what your text has to say on this point. You may also want to look at Chapter 39 of Richard Feynman, *Lectures on Physics*, Volume I.

4 THE EXPERIMENT

The apparatus is shown in Figure 1. The gas under investigation is contained in a tank of volume V to which is attached a vertical glass tube in which a ball can move freely but with very little clearance. Since the captured gas acts as an elastic cushion or “spring,” conditions suitable for simple harmonic motion are present and the ball tends to bounce up and down. The amplification needed to intensify these oscillations is supplied by a small hole in the side of the tube, which releases a puff of gas whenever the ball rises above it, and the energy needed to sustain them is supplied by a slow flow of gas from an external source. Since there is little time for heat flow from the gas to its surroundings during the short duration of a single oscillation, the adiabatic relations, Equations (7) and (9), are nearly satisfied by the pressure and volume of the gas.

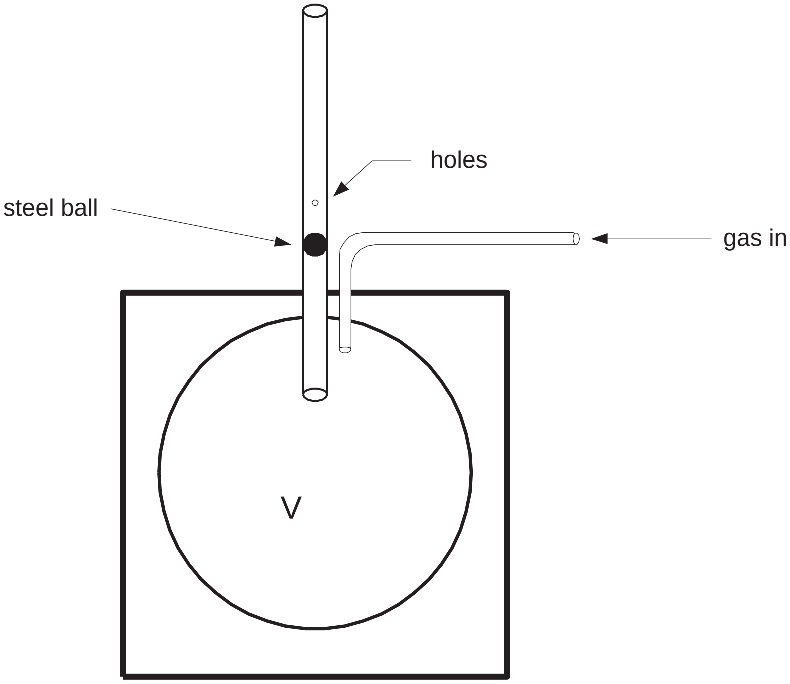

Figure 1

We will use Equation (7) to derive a relationship between γ and the period T of the simple harmonic motion. The measured values of the period T can then be used to compute γ.

Let the atmospheric pressure P_0 be the pressure in the flask before introducing the ball. When the ball is *at rest* in the tube the pressure in the flask is

$$P = P_0 + \frac{mg}{A} \tag{11}$$

where A is the cross sectional area of the ball and mg is the weight of the ball. If the ball is displaced a short distance y upwards, the pressure drops to a value $P_u < P$. When released, the ball will move downward under the action of the restoring pressure

$$dP = P_u - P < 0.$$

We assume that the volume is sufficiently large and the displacement sufficiently small that $dP/P << 1$. The same displacement will result in a slight increase in volume

$$dV = yA$$

The restoring force F on the ball is just the pressure difference times the area:

$$F = AdP \tag{12}$$

We now make the process adiabatic. First, differentiate Equation (9) to obtain

$$\gamma PV^{\gamma-1} + V^{\gamma}dP = 0$$

or

$$\gamma PdV + VdP = 0.$$

Next, substitute $dV = yA$ in the last equation and solve for dP to obtain

$$dP = -\frac{\gamma PA}{V}y.$$

Finally, substitute this result into Equation (12) to obtain the following expression for the restoring force F:

$$F = -\frac{\gamma PA^2}{V}y.$$

Newton's Second Law tells us that

$$F = ma = m\frac{d^2y}{dt^2}$$

and hence our force equation becomes

$$\frac{d^2y}{dt^2} + \frac{\gamma PA^2}{mV}y = 0. \tag{13}$$

But this differential equation describes a simple harmonic oscillatior for which

$$\omega^2 = \frac{\gamma PA^2}{mV}.$$

(**Note:** Consult your text's treatment of the simple harmonic oscillator if you are not completely clear on this point.)

Thus we have shown that the ball in the tube will undergo simple harmonic motion with an angular frequency

$$\omega = \sqrt{\frac{\gamma PA^2}{mV}}$$

But $\omega = 2\pi/\tau$, where τ is the period of the oscillation. We substitute for ω and solve for γ to obtain

$$\gamma = \frac{4\pi^2 mV}{PA^2\tau^2}$$

The cross sectional area of the ball is $A = \pi D^2/4$. If we substitute for A in our expression for γ we obtain

$$\gamma = \frac{64mV}{PD^4\tau^2} \tag{14}$$

This equation gives us an expression for γ in terms of the quantities that we measure directly.

5 PROCEDURE

NOTE: You should write a detailed description of the actual procedure you follow in your laboratory notebook. This description should be written while you are in the lab doing the experiment . Do NOT rely on your memory or on rough notes taken on scrap paper!! Do NOT simply copy the suggested procedure in this writeup—write down what you actually do!!!

Measure the barometric pressure and the mass and diameter of the ball. Handle the ball with a kimwipe, so that you don't get finger oil on it. The ball should be as clean as possible. Place the ball carefully in the tube. The volume V of the apparatus is $(5.19 \pm .01) \times 10^3$ ml.

Level the apparatus so that the glass tube is vertical and the ball will move up and down without touching the inside walls. If the tube is not vertical, the ball will rotate rapidly, and may even tap against the side of the tube. Start the gas flowing slowly and increase the flow until the ball rises slowly in the tube. When the ball reaches the holes in the middle of the tube it should start to oscillate.

It is desirable to keep the amplitude of oscillation low, say between one and five centimeters. You have two adjustments available to you to obtain the desired amplitude: The first is the rate of flow of the gas, and the second is the size of the opening in the middle of the tube. There are four holes around the middle of the tube and total size of the opening can be controlled by taping zero, one, two or three of the holes shut. After all the adjustments are made, the ball should be oscillating with small amplitude about the holes.

The expression for γ depends on the period squared. Hence any error in measuring τ will be doubled in calculating γ. (You will prove this result later.) Time one hundred oscillations of the ball; be sure to let one full period pass before you start counting after you start the stop watch. After you have finished, let your partner time one hundred oscillations also. If your two numbers are in disagreement then try again.

Do the experiment for three gases: air, oxygen, and argon.

For one gas, repeat your measurements of the period for different amplitudes. Does the period depend on amplitude? If it does would it be worthwhile plotting period versus amplitude to find the zero amplitude period?

Repeat your measurements for different locations of the equilibrium point. Does this asymmetry with respect to the holes in the tube affect the period of the motion? If the period is affected by nonsymmetric oscillations, what will fluctuations in line pressure do to your results?

Before you can obtain a value of γ from Equation (14) you need to calculate the pressure from Equation (11). Be sure you convert the pressure to appropriate metric units.

6 DATA ANALYSIS

Calculate a value of γ for each gas used and compare this value with that predicted by Equation (10). Summarize your results in a table.

You can check the consistency of your results in another way. The compression and rarefactions of the air during the passage of a sound wave are also adiabatic. The velocity of sound in a gas is given by

$$v = \sqrt{\frac{\gamma R T}{M}}$$

where R is the universal gas constant, T is the absolute temperature and M is the molecular weight. Look up the velocity of sound and calculate γ from the formula.

7 ERROR ANALYSIS

We need to calculate the error in γ due to the error in the measured quantities. Consider a calculated quantity f that is a function of the measured quantities x, y, z, ... To see how the uncertainties in the measured quantities affect the error in $f(x, y, z, \ldots)$, we begin by calculating df:

$$df = \frac{\partial f}{\partial x} dx + \frac{\partial f}{\partial y} dy + \frac{\partial f}{\partial z} dz \ \ldots$$

Thus if the uncertainties Δx, Δy, Δz, ... are small, we will have

$$\Delta f \cong \frac{\partial f}{\partial x} \Delta x + \frac{\partial f}{\partial y} \Delta y + \frac{\partial f}{\partial z} \Delta z \ \ldots \tag{15}$$

(More rigorously, you can also think of this equation as a first-order Taylor's expansion of f.)

Equation (15) is thus a first step to seeing how errors in the measured quantities affect the error in the calculated quantity f. But it is only a first step! Note, for example, that the terms in Equation (15) can have different signs; but one would not ordinarily expect that one error would cancel another.

It can be shown that a better approximation to Δf is given by

$$\Delta f \cong \sqrt{\left(\frac{\partial f}{\partial x}\right)^2 \Delta x^2 + \left(\frac{\partial f}{\partial y}\right)^2 \Delta y^2 + \left(\frac{\partial f}{\partial z}\right)^2 \Delta z^2 \ \ldots} \tag{16}$$

(See for example John R. Taylor, *An Introduction to Error Analysis*, Chapter 3. Most textbooks on error analysis or elementary statistics also derive this equation.)

Use Equation (16) to derive an expression for $\Delta\gamma$. Your final equation should be of the form

$$\frac{\Delta\gamma}{\gamma} = f\left(\frac{\Delta P}{P}, \frac{\Delta V}{V}, \ \ldots\right) \tag{17}$$

Once you have derived this expression, use it to find the uncertainties in your values of γ. Do your calculation step by step, and see if any one term dominates.