

## Experiment I

### RATIO OF SPECIFIC HEATS OF GASES; $\gamma \equiv C_p / C_v$

#### 1. Recommended Reading

M. W. Zemansky, Heat and Thermodynamics, Fifth Edition, McGraw Hill, 1968,  
p. 122-132, 161-2.

#### 2. Introduction

You have determined the heat capacities of solids (In) and liquids (H<sub>2</sub>O) using pulsed heating and continuous flow calorimeters. Heat capacities of gases can be measured by similar techniques. The heat capacity of a gas at constant volume,  $C_v$ , can be determined by determining the temperature rise of a gas contained in a thin-walled steel volume due to a known heat input. The walls of the volume must be thin in order that the heat capacity of the container does not dominate that of the gas. The heat capacity of a gas at constant pressure,  $C_p$ , can be determined by a continuous flow calorimeter in which the gas flows over a heater at essentially constant pressure. From the difference in the inlet and outlet temperature, the measured heat input and the measured rate of flow of gas,  $C_p$  may be calculated.

There are many instances in thermodynamics where it is the ratio  $C_p/C_v$  which enter, rather than  $C_p$  or  $C_v$  itself. This enables one to make a cross check of the individually determined values. In fact, this ratio occurs so often that it has been given a special symbol of its own,  $\gamma$ . Thus  $\gamma$  is defined by the equation

$$\gamma \equiv C_p / C_v. \quad (1)$$

In order to see how this term enters, let us consider a quasi-static adiabatic process in an ideal gas, e.g., a sound wave or a simple adiabatic compression of a gas in a closed volume.

For an infinitesimal quasi-static process, the first law of thermodynamics may be written

$$dQ = dU + PdV. \quad (2)$$

The heat capacity at constant volume

$$C_v \equiv \left( \frac{dQ}{d\theta} \right) = \left( \frac{\partial U}{\partial \theta} \right)_v \quad (3)$$

For an ideal gas  $U$  is a function of  $\theta$  only, thus eq.(3) can be written

$$C_v = \frac{dU}{d\theta} \quad (4)$$

Inserting this into eq.(2) we obtain

$$dQ = C_v d\theta + PdV \quad (5)$$

Consider now the ideal gas equation

$$PV = nR\theta \quad (6)$$

For an infinitesimal quasi-static process this can be differentiated to yield

$$PdV + VdR = nRd\theta \quad (7)$$

Solving for  $PdV$  and substituting into eq. (5),

$$dQ = (C_v + nR)d\theta - VdP \quad (8)$$

Dividing by  $d\theta$

$$\frac{dQ}{d\theta} = C_v + nR - V \frac{dP}{d\theta} \quad (9)$$

but

$$C_p \equiv \left( \frac{dQ}{d\theta} \right)_p \quad (10)$$

Therefore at constant pressure eq.(9) becomes

$$C_p = C_v + nR \quad (11)$$

Inserting this back into eq.(8) and multiplying by  $d\theta$ ,

$$dQ = C_p d\theta - VdP \quad (12)$$

]In a quasi-static adiabatic process,  $dQ = 0$ . In such a case we can rewrite eqs.(12) and (5) as

$$V dP = C_p d\theta \quad (13)$$

$$PdV = -C_v d\theta \quad (14)$$

Dividing eqs.(13) by (14)

$$\frac{dP}{P} = -\frac{C_p}{C_v} \frac{dV}{V} \quad (15)$$

Thus the differential equation relating P and V for a quasi-static adiabatic process involves only the ratio  $C_p/C_v$  not the absolute value of either. Using the notation  $\gamma = C_p/C_v$ , we can rewrite eq.(15) as

$$\frac{dP}{P} = -\gamma \frac{dV}{V} \quad (16)$$

If  $\gamma$  is constant within the temperature changes involved in the compression (a point which will need to be checked experimentally ) then eq.(16) can be integrated to yield

$$PV^\gamma = \text{constant} \quad (17)$$

This is the basic equation we will use in evaluating the quasi-static adiabatic compression of the present experiment.

Note that having determined  $\gamma$  by means of eq.(17), we can use that value of  $\gamma$  to calculate  $C_p$  and/or  $C_v$  themselves by combination of eqs.(1) and (11). Elimination of  $C_v$  between eqs.(1) and (11),

$$C_p = \left( \frac{\gamma}{\gamma - 1} \right) nR \quad (18)$$

or eliminating  $C_p$ ,

$$C_v = \left( \frac{1}{\gamma - 1} \right) nR \quad (19)$$

These calculations of  $C_p$  and  $C_v$  appear at first sight to be a trick. How can you calculate two things  $C_p$  and  $C_v$  when, in this experiment, you have made measurements which depend only on the ratio  $C_p/C_v$ ? The answer of course depends on acceptance of eq.(11) which was derived assuming the ideal gas law, a law which you have already experimentally established.

An alternate microscopic approach is to predict what  $\gamma$  should be for a given type of gas. Equipartition of energy between different degrees of freedom predicts a contribution of  $nR/2$  to  $C_v$  for each degree of freedom,  $q$ . Thus substituting in eq.(19)

$$\gamma = 1 + \frac{2}{q} \quad (20)$$

In the case of a monatomic gas with three translational degrees of freedom,  $q = 3$ , hence,  $\gamma = 1.66$ . For a diatomic gas with five degrees of freedom, three translational and two rotational  $\gamma = 1 + \frac{2}{5} = 1.40$  In making this calculation for diatomic gases, we have assumed that the vibrational mode does not enter, i.e., vibration is not excited at room temperature. For a non-linear triatomic molecule with six degrees of freedom  $\gamma = 1 + \frac{2}{6} = 1.33$ . Again we have assumed no vibration. This microscopic picture gets more complicated as the complexity of the molecule increases and one wonders whether or not a possible degree of freedom enters; how things vary with temperature, etc. However, the case for monatomics and most diatomics with large

vibrational level spacing does not suffer from uncertainties. If you obtain 1.66 for monatomics and 1.40 for diatomics, you have some evidence for the equipartition picture.

### 3. Rüchhardt's Method of Measuring $\gamma$ .

The equipment available in the laboratory is illustrated in Fig. 1. Briefly, it consists of two volumes,  $V_1$  and  $V_2$ , connected by a precision bore glass tube. A closely fitting steel ball is placed within the precision bore tubing. In operation, the ball is released from near the upper end of the tube. It falls under the influence of gravity, increasing the pressure of the gas in  $V_1$  and decreasing that in  $V_2$ . The total change in pressure  $P$  results in an upward force on the ball,  $A \Delta P$ .

At the equilibrium position the net force on the ball is zero, hence

$$P_1 - P_2 = \frac{mg}{A} \quad (21)$$

As one moves away from the equilibrium position there is a net force acting on the ball,

$$F = A(dP_1 - dP_2) \quad (22)$$

By Newton's law this must result in an acceleration of the ball. Assuming the acceleration to be in to the  $y$  direction, eq.(22) becomes

$$m \frac{d^2y}{dt^2} = A(dP_1 - dP_2) \quad (23)$$

We must now evaluate  $dP_1$  and  $dP_2$  by differentiation of eq.(17). For volume 1

$$V_1^\gamma dP_1 + P_1 \gamma V_1^{\gamma-1} dV_1 = 0 \quad (24)$$

and for volume 2

$$V_2^\gamma dP_2 + P_2 \gamma V_2^{\gamma-1} dV_2 = 0 \quad (25)$$

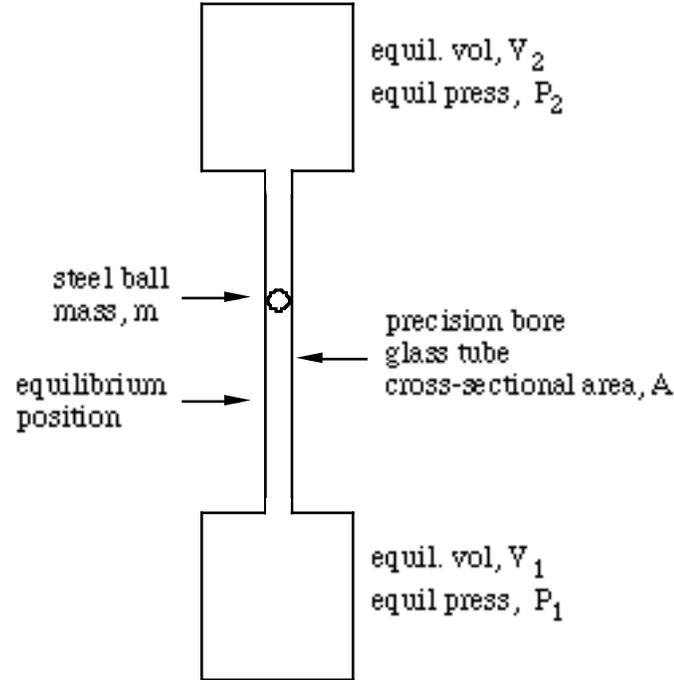


Fig. 1 Apparatus for measuring the ratio of specific heats.

Solving eq.(24) for  $dP_1$  and eq.(25) for  $dP_2$  and substituting into eq.(23), we obtain

$$m \frac{d^2y}{dt^2} = A\gamma \left( -\frac{P_1 V_1^{\gamma-1} dV_1}{V_1^\gamma} + \frac{P_2 V_2^{\gamma-1} dV_2}{V_2^\gamma} \right) \quad (26)$$

But  $dV_1$  and  $dV_2$  are equal and opposite and related to  $y$  by the equation

$$dV_1 = -dV_2 = yA. \quad (27)$$

Substituting in eq.(26) and rearranging terms

$$m \frac{d^2y}{dt^2} = -A^2\gamma \left( \frac{P_1}{V_1} + \frac{P_2}{V_2} \right) y. \quad (28)$$

Thus the force is directly proportional to the displacement from the equilibrium position,  $y$ , and oppositely directed. This is the condition for simple harmonic motion. Solution of the equation in the usual manner gives the period  $\tau$  of the motion as

$$\tau = 2\pi \sqrt{\frac{m}{A^2 \gamma} \left( \frac{V_1 V_2}{P_1 V_2 + P_2 V_1} \right)} \quad (29)$$

or solving for  $\gamma$

$$\gamma = \frac{4\pi^2 m}{A^2 \tau^2} \left( \frac{V_1 V_2}{P_1 V_2 + P_2 V_1} \right) \quad (30)$$

This can be put in terms of only one pressure, e.g.,  $P_2$ , by combination with eq.(21).

Observing eq.(30), all terms on the right can be measured, hence  $\gamma$  can be calculated.

With the apparatus supplied, one can simplify eq.(30) for approximate calculations, i.e., with  $V_1 \approx V_2$  and  $P_1 \approx P_2$ , eq.(30) can be written

$$\gamma = \frac{2\pi^2 m V_2}{A^2 P_2 \tau^2} \quad (31)$$

If the upper volume is opened to the atmosphere, i.e.,  $V_2 = \infty$  in eq.(28), eq.(30) becomes

$$\gamma = \frac{4\pi^2 m V_1}{A^2 P_1 \tau^2} \quad (32)$$

With the equipment supplied, you can use either one or two volumes, change the composition of the gas and vary  $m$ ,  $V_1$ ,  $V_2$ ,  $P_1$ , or  $P_2$ . This versatility should enable you to investigate the reliability of eqs.(30) and (32) in some detail, and enable you to obtain values of  $\gamma$  for several gases.

#### 4. Rinkel's Method for Measuring $\gamma$ .

Suppose instead of considering the period of the oscillation in the apparatus, described in the previous section, we concentrate instead on the amplitude of the oscillation. This variation on the R uchhardt technique was first suggested by Rinkel and, now, often carries Rinkel's name.

Consider again Fig. 1. The work done in moving the ball a distance  $L$  from its equilibrium position is

$$W = \int_0^L F dy = mgL \quad (33)$$

Equation (28) still applies. It is the force acting as a function of displacement  $y$ . Substituting

$$A^2\gamma \left( \frac{P_1}{V_1} + \frac{P_2}{V_2} \right) \int_0^L y dy = mgL \quad (34)$$

for

$$A^2\gamma \left( \frac{P_1}{V_1} + \frac{P_2}{V_2} \right) \frac{L}{2} = mg \quad (35)$$

Solving for  $\gamma$

$$\gamma = \frac{2mg}{A^2L} \left( \frac{V_1V_2}{P_1V_2 + P_2V_1} \right) \quad (36)$$

This equation is equivalent to eq.(30) except that  $\gamma$  is given in terms of the amplitude of oscillation,  $L$ , rather than the period  $\tau$ .

For approximate calculations, with both volumes in operation,  $V_1 \approx V_2$  and  $P_1 \approx P_2$ ,

$$\gamma = \frac{mgV}{A^2PL} \quad (37)$$

If only one volume is used,  $V_1$  or  $V_2 \rightarrow \infty$ ,

$$\gamma = \frac{2mgV}{A^2PL} \quad (38)$$

## 5. Experimental Procedure

The apparatus illustrated schematically in Fig. 1 is equipped with certain accessories. It is attached through valves to a pump, to a pressure gauge, and to various gas supplies, He, A, N<sub>2</sub>, CO<sub>2</sub>. This makes possible determination of  $\gamma$  at different pressures and for different gases,

monatomic, diatomic and triatomic. It is also possible to check whether the molecular weight of the gas has any effect, i.e., He and A are both monatomic, but their molecular weights differ by a factor of 10. The period of oscillation of the ball can be determined using a stopwatch program on the computer. A suggested procedure is as follows:

### **5.1 Measure apparatus geometry**

Determine the physical parameters of the system, i.e.,  $m$ ,  $V_1$ ,  $V_2$ ,  $A$ . To measure  $V_2$ , first be sure that the system is at atmospheric pressure (about 30 in. Hg on the pressure gauge). Unscrew the bolts at the top of the apparatus and remove the top plate. Use inside calipers and a millimeter scale to measure the inside diameter and height of the  $V_2$  cylinder. Be careful not to blow or brush dust down into the tube. You may assume that  $V_1$  is equal to  $V_2$ . To measure  $m$  and  $A$ , measure the mass and diameter of the sample ball provided.

Plastic rings are inserted into each end of the precision bore glass tubing in order to confine the ball to the tube.

#### **CAUTION:**

**When the pressure in the lower volume exceeds that of the upper, the ball is likely to be blown forcefully into the upper chamber and is likely to break the glass tube. To avoid this serious problem while backfilling with the sample gasses, FIRST open the valve which connects  $V_1$  to  $V_2$ . THEN open the backfill valve in VERY SMALL STEPS. The pressure gauge reading should increase very slowly, taking at least 5 minutes to fill the chambers.**

## 5.2 Reassemble the apparatus.

The ball should be inserted with its wire attachment downward. This wire is inserted into the ball in order to insure that part of the energy cannot go into rotation, i.e., that the motion is purely translational as assumed in the derivation given. Be sure that the O-ring is well-seated in its groove under the top plate before securing the screws. Finger tightening of the screws is all that is necessary. Do not use pliers.

- a. Level the apparatus. Friction is minimized if the precision bore tubing is vertical.
- b. With your apparatus at atmospheric pressure, note the reading on your pressure gauge. Measure atmospheric pressure using the barometer provided in the laboratory.
- c. Evacuate the apparatus. NOTE: the valves open and close fully with only a single turn. Do not unscrew them many turns and do not force them closed. Firm closing is all that is necessary.
- d. With the aid of your laboratory tutor, evacuate the gas supply line and flush the line with the gas you wish to use.
- e. Attach a hose to the supply line and flush it with the gas also.
- f. Place the horseshoe magnet around the base of the glass tube to help hold the ball in its resting position. Attach the sample gas hose to your apparatus and secure it with a wire twist tie.
- g. Make sure that the valve connecting V1 to V2 is OPEN!
- h. SLOWLY (see CAUTION above!) pressurize it until the pressure gauge returns to its original atmospheric pressure reading. CAUTION: BE PATIENT! admitting the gas too rapidly will cause the ball to blow out of the top of the tube into the upper volume. Admit the gas VERY SLOWLY.

- i. After the gas has reached atmospheric pressure, close the backfill valve.
- j. With the valve connecting V1 to V2 still open, use the magnet to raise the steel ball to the top plastic position marker.
- k. Close all valves. Pull the magnet away horizontally to allow the steel ball to drop.

### **5.3 RÜCHARDT'S METHOD**

Use the Stopwatch program to measure the time for several oscillations of the ball and calculate the period. Using eq.(31) calculate  $\gamma$ .

### **5.4 RINKEL'S METHOD**

Determine the lowest point of travel of the ball and mark the position with the lower plastic position marker. Repeat the experiment several times being careful to drop the ball from the same height each time. Measure the distance between the upper and lower markers and use eq.(37) to determine  $\gamma$ . Be sure to calculate  $\gamma$  before proceeding!

After a satisfactory amount of data has been taken, you may evacuate the apparatus again and admit another gas. Repeat the above steps to check the predicted dependence of  $\tau$  and  $L$  on the parameters of the system, and in order to determine  $\gamma$  for the various gases supplied.