EXPERIMENT 5
CLEMENT AND DESMORMES' EXPERIMENT

I. THEORY

Consider a sample of dry air at room temperature enclosed in a vessel at a pressure P_1 that is higher than atmospheric pressure P_2. If the vessel is unstopped for a brief time interval, some of the air will escape and the pressure will quickly drop to atmospheric pressure. Because the expanding air does work in pushing against the atmosphere, it loses internal energy and cools to a lower temperature. Finally, as the air warms up to room temperature again, its pressure increases to a third value P_3.

As the gas goes from state 1 to state 2, its density decreases since some of its mass is lost from the flask. However, as the gas goes from state 2 to state 3, the density remains constant.

Consider a part of the gas having a constant mass, and therefore a constant number of moles. This is the gas that remains in the flask during the experiment. Let this mass occupy a volume V_1 in state 1 of the gas, and a volume V_2 in state 2. The volume of this mass of the gas in state 3 is the same as the volume in state 2, since the density does not change.

If the expansion from state 1 to state 2 occurs rapidly, it may be considered essentially adiabatic. Since the number of moles under consideration is constant, we may write

$$P_1 V_1^\gamma = P_2 V_2^\gamma$$

States 1 and 3 of the gas are at the same temperature, as a result,

$$P_1 V_1 = P_3 V_3$$

Using the fact that $V_2 = V_3$, we can solve for γ. $\gamma = \dfrac{\ln(P_1/P_2)}{\ln(P_1/P_3)}$

This relation will hold for any base of the logarithm.

A problem occurs in evaluating the above expression, due to the fact that P_1 and P_3 are only slightly higher than P_2. This is due to the fact that the natural log of 1 is 0. The above expression tends to give 0 divided by 0. To avoid this error we will be using the first two non-zero terms in the Taylor expansion of $\ln(1+x)$ for $x < 1$,
$\ln(1+x) = x - \frac{1}{2}x^2 + \cdots$.

Let us take a closer look at what will be measured in the experiment to calculate the pressures. Then, we will see how this expansion will be used.

Atmospheric pressure P_2 will be measured using a mercury barometer. The height of the mercury column, H, is P_2 in cm of Hg. In pascals, $P_2 = \rho_{Hg} g H$, where $\rho_{Hg} = 13.6$ g/cm^3 is the density of mercury.

A manometer will be used to measure the gauge pressure at state 1 and state 3. The manometer will measure the difference in pressure between the air in the flask and the air in the room. The manometer consists of a U-shaped tube with its lower half filled with water. When the water level is the same in both halves of the tube, the pressure is the same in the flask and in the room.

$$P_1 - P_2 = \rho_{H_2O} g h_1 \text{ and } P_3 - P_2 = \rho_{H_2O} g h_3$$

In these equations, $\rho_{H2O} = 1.00$ g/cm^3 is the density of water and h_1 and h_3 are the difference in water levels on either side of the manometer in states 1 and 3, respectively.

In our experiment, H will be about 75 cm and h_1 and h_3 will be between 5 cm and 30 cm. With these values, $\dfrac{P_{1,3}}{P_2} = 1 + \dfrac{\rho_{H_2O} g h_{1,3}}{\rho_{Hg} g H} = 1 + \dfrac{\rho_{H_2O}}{\rho_{Hg}} \dfrac{h_{1,3}}{H} \approx 1 + 0.01$. P_1 and P_3 will be 1-2 percent higher than P_2. The notation $P_{1,3}$ is used as shorthand for P_1 or P_3, since the same formula can be used for any pressure in the flask.

To perform a Taylor expansion on our formula for gamma, it is convenient to rewrite $\ln(P_1/P_3)$ as $\ln(P_1/P_2) - \ln(P_3/P_2)$.

If we keep only the first non-zero term in the Taylor expansion of the natural log, we find

$$\gamma = \frac{\ln(P_1/P_2)}{\ln(P_1/P_3)} \approx \frac{h_1}{h_1 - h_3}.$$

Showing this is left as an exercise for the student.

Since dry air consists of about 80 % N_2 and about 20 % O_2, each of which has a standard value of 1.40 for γ at room temperatures, we may take 1.40 as the standard value for dry air. (H_2O vapor does not have a value of 1.40, so water vapor is kept to a minimum by keeping water-absorbing chemicals in the flask.)

II. LABORATORY PROCEDURE

   CAUTION: **Leave the glass flask in the styrofoam base for protection.**

1. Check to see that there are no air bubbles in the water in the manometer. Do not add water to the manometer, since bubbles form easily and are difficult to remove.

2. Remove the glass rod which is in the length of tubing attached to the flask. Place the flask, in its styrofoam base, on top of an inverted wooden box. Place the manometer nearby. Apply some glycerin to the manometer connection. Using rubber tubing, connect the flask, manometer and pump to the three arms of the T adapter. If any of the connections are not tight, look for tubing of a smaller diameter; however, DO NOT USE EXCESSIVE FORCE ON THE MANOMETER TUBE.

3. Check the seal between the flask and the stopper; if it is dry, apply some stopcock grease. Seal the flask.

4. Make a table on your data sheet, with the following columns: y_1, y_2, $y_1 + y_2$, $y_2 - y_1$, y_1', y_2', $y_1' + y_2'$, and $y_2' - y_1'$. y_1 will be the height of the water on the flask side of the manometer. y_2 will be the height on the side open to the atmosphere. y_2 should be larger than y_1.

5. Place the pinch clamp loosely on the tubing which connects the pump to the T adapter. Holding the pump with its outlet upward, pump air into the flask until the manometer columns differ by about 10 cm (8-13 cm is fine). Tighten the pinch clamp. The pressure should drop slowly until the air in the flask, which has been heated by compression, cools off to room temperature. If it continues to drop, a leak exists which must be eliminated before proceeding. If a leak exists, try different pieces of tubing, or more stopcock grease on the stopper, or secure tubing connections with string or masking tape. If no leak exists, record the heights y_1 and y_2 of the columns, and their sum and difference. Unless water is removed from the manometer, the sum of readings should remain constant throughout the experiment, providing a check on the accuracy of the readings.

6. Slide the stopper to one side, wait about 1 second, and then reclose the flask. When the pressure stops rising, the air in the flask will have reached room temperature. If no leak exists, record the heights y_1' and y_2' and their sum and difference.

7. Repeat steps 5 and 6 for initial height differences of about 15, 20, 25, and 30 cm. These can be done in any order

8. Twist the rubber tubing when disconnecting it from the manometer. Do not use excessive force, as the glass tube breaks easily. **If you have difficulty removing the tubing, ask your instructor for assistance.** Replace the glass rod in the tubing attached to the flask to keep water vapor and other contaminants from entering the flask.

9. Adjust the knob at the bottom of the mercury barometer so that the pointer just touches the mercury surface. Adjust the vernier slider so that the bottom edge of the metal marker is even with the top of the mercury column. Record the barometric pressure, noting that the vernier scale runs downward, though the main scale runs upward.

III. CALCULATIONS AND ANALYSIS

1. Draw a PV diagram showing the adiabatic expansion and the constant volume heating of the portion of gas that remains within the flask.

2. Show that using only the first non-zero term in the Taylor expansion of the natural log yields $\gamma = h_1/(h_1 - h_3)$. Use this relation to calculate γ for each of your trials.

3. Find a relation for γ using the first two non-zero terms in the Taylor expansion for the natural log. Use your expression to calculate γ. Present your results in a table with columns h_1, h_2, γ using first order expansions, and γ using second order expansions.

4. Calculate the average value of γ and the percent error, using 1.40 as the standard value.

5. Calculate the molar heat capacity of the dry air in your flask using your average value for γ.

6. Explain why the flask should not be open too long for the adiabatic expansion. Will leaving the flask open too long result in a value of γ that is too large or too small?

7. Explain why the air in the flask is kept dry. Calculate the value of γ for water molecules which have only translational and rotational motion active. Will wet air lead to a value of γ that is larger than 1.40 or smaller than 1.40?