Experiment 1

Heat-Capacity Ratios for Gases

Purpose :

Determine the ratio ($\overline{C}_P/\overline{C}_V$) of the heat capacity of a gas at constant pressure to that at constant volume by the method of adiabatic expansion.

Principle :

For the reversible adiabatic expansion of gas, the change in energy content is related to the change in volume by

$$d\overline{U} = -Pd\overline{V} \qquad (1)$$

For a perfect gas,

$$P = \frac{RT}{\overline{V}} \qquad (2)$$

Moreover, since $\overline{U}$ for a perfect gas is a function of temperature only, we can write

$$d\overline{U} = \overline{C}_V dT \qquad (3)$$

where $\overline{C}_V$ is the constant-volume molar heat capacity. Substituting Eqs. (2) and (3) into Eq. (1) and integrating, we find that

$$\overline{C}_V \ln\frac{T_2}{T_1} = -R\ln\frac{\overline{V}_2}{\overline{V}_1} \qquad (4)$$

where $\overline{C}_V$ and $\overline{V}$ are molar quantities (that is, $C_V/n,\ V/n$). It has been assumed that $\overline{C}_V$ is constant over the temperature range involved. This equation predicts the decrease in temperature resulting from a reversible adiabatic expansion of a perfect gas.

Consider the following two-step process involving a perfect gas denoted by A:

Step 1 : Allow the gas to expand adiabatically and reversibly until the pressure has dropped from P_1 to P_2.

$$A(P_1,\overline{V}_1,T_1) \longrightarrow A(P_2,\overline{V}_2,T_2) \qquad (5)$$

Step 2 : At constant volume, restore the temperature of the gas to T_1 .

$$A(P_2,\overline{V}_2,T_2) \longrightarrow A(P_3,\overline{V}_2,T_1) \qquad (6)$$

For **Step 1**, we can use the perfect-gas law to obtain

$$\frac{T_2}{T_1} = \frac{P_2\overline{V}_2}{P_1\overline{V}_1} \qquad (7)$$

Substituting Eq. (7) into Eq. (4) and combining terms in $\overline{V}_2/\overline{V}_1$, we write

$$\ln\frac{P_2}{P_1} = -\frac{(\overline{C}_V + R)}{\overline{C}_V}\ln\frac{\overline{V}_2}{\overline{V}_1} = -\frac{\overline{C}_P}{\overline{C}_V}\ln\frac{\overline{V}_2}{\overline{V}_1} \qquad (8)$$

since for a perfect gas

$$\overline{C}_P = \overline{C}_V + R \tag{9}$$

For **Step 2**,

$$\frac{\overline{V}_2}{\overline{V}_1} = \frac{P_1}{P_3} \tag{10}$$

Thus

$$\ln\frac{P_1}{P_2} = \frac{\overline{C}_P}{\overline{C}_V}\ln\frac{P_1}{P_3} \tag{11}$$

This can be rewritten in the form

$$\frac{\overline{C}_P}{\overline{C}_V} = \frac{\log P_1 - \log P_2}{\log P_1 - \log P_3} = \frac{\log(P_1/P_2)}{\log(P_1/P_3)} \tag{12}$$

Apparatus and Chemicals :

Large-volume vessel; three-hole stopper fitted with three glass tubes; open-tube manometer with cottonseed oil as indicating fluid; two long lengths and one short length of rubber pressure tubing; three screw clamps; cylinder of nitrogen.

Nitrogen gas; cottonseed oil.

Procedure :

(1) The apparatus is assembled as **Fig. 1-1**.

(2) Clamp off ***B***. Open clamp ***A*** and sweep N_2 through the carboy for *5 min*.

(3) Retard the gas flow to a fraction of the flushing rate by partly closing the switch of a steel bottle. Carefully open the clamp ***B***, and then cautiously (to avoid flowing liquid out of the manometer) clamp off ***A***, keeping a close watch on the manometer. Close the switch of a steel bottle when the height difference of the manometer has attained about *60 cm*.

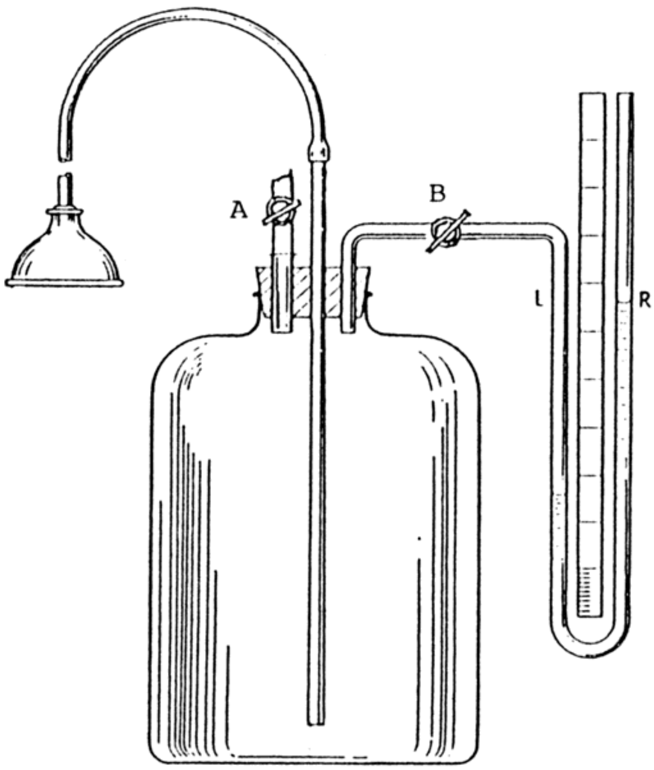

Fig. 1-1

(4) Allow the gas to come to the room temperature (about *15 min*), as shown by a constant manometer reading. Record the readings of the manometer. When the pressure difference is converted to an equivalent mercury reading and added to the barometer reading, P_1 is obtained.

(5) Open clamp ***A*** widely and close it again in the shortest possible time. Record the reading immediately and P_2 is obtained.

(6) As the gas warms back up to the room temperature, the pressure will increase and finally (in about *15min*) reach a new constant value, P_3, which can be determined from the manometer readings and the barometer reading.

(7) Repeat the **steps (4)-(6)** to obtain another determination, but longer flushing in **step (2)** is not necessary.

(8) Two measurements are made by changing the height difference in **step (3)** to about *40 cm*.

Calculations :

(1) The density is *0.918* g/cm^3 for cottonseed oil. For each of the four runs on N_2, calculate $\overline{C}_P/\overline{C}_V$ using Eq. (12).

(2) Calculate the theoretical value of $\overline{C}_P/\overline{C}_V$ both with and without vibrational contribution to $\overline{C}_V$ predicted by the equipartition theorem.

References :

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(3) **D. P. Shoemaker**, **C. W. Garland**, and **J. W. Nibler**, "*Experiments in Physical Chemistry*," 5th ed., pp. 104-118, McGraw-Hill, Singapore (1989).

(4) **O. F. Steinbach** and **C. V. King**, "*Experiments in Physical Chemistry*," pp. 41-47, American book company, U.S.A. (1950).