

Experiment 8

DETERMINATION OF THE RATIO OF THE SPECIFIC HEATS $\kappa = C_p/C_v$ OF AIR

The ratio of the molar heat capacity at constant pressure C_p to that at constant volume C_v for air is measured using the Clement and Desormes' method.

INTRODUCTION

1. The specific heat capacity of a gas can be measured either under conditions of constant volume or under conditions of constant pressure. The quantity of heat ΔQ_v needed to increase the temperature of n moles of the gas by ΔT at constant volume is

$$\Delta Q_v = nC_v \Delta T \quad (8.1)$$

where C_v is the molar heat capacity (molar specific heat) at constant volume. If the temperature of the gas is increased at constant pressure the amount of heat ΔQ_p is

$$\Delta Q_p = nC_p \Delta T \quad (8.2)$$

where C_p is the molar heat capacity at constant pressure. The heat ΔQ_p is higher than ΔQ_v for the same increase ΔT because at constant pressure the gas expands and does some work. The work ΔW of the gas for small change of its volume ΔV is

$$\Delta W = p \Delta V = n R \Delta T \quad (8.3)$$

where the change ΔV is expressed in terms of ΔT using the ideal gas equation

$$\Delta W = p \Delta V = n R \Delta T \quad (8.4)$$

Now the heat ΔQ_p is

$$\Delta Q_p = \Delta Q_v + \Delta W \quad (8.5)$$

and by substituting (8.1), (8.2) and (8.3) it is found that

$$C_p = C_v + R \quad (8.6)$$

The molar heat capacity of an ideal gas at constant pressure is higher than the molar heat capacity at constant volume. The difference is the gas constant R .

The molar heat capacities of gases are related to their molecular structures, but the ratio

$$\kappa = \frac{C_p}{C_v} \quad (8.7)$$

to a good approximation is constant for a given group of gases with the same structure. The κ ratios can be predicted from kinetic theory of gases with the help of the principle of equipartition of energy. This principle states that each degree of freedom of movement of a molecule in the gas is associated with an

average kinetic energy of $\frac{1}{2} RT$ for one mole of the gas. The number of degrees of freedom i is equal to the number of velocity components needed to describe the motion of the molecule. This is illustrated for a diatomic molecule in figure 8.1 which has five degrees of freedom, three with the translational motion along

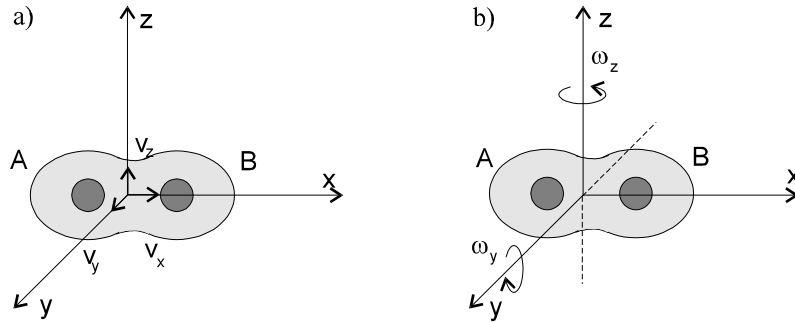


Fig. 8.1. Illustration of degrees of freedom for the case of a diatomic molecule AB. v_x , v_y , v_z , and ω_y , ω_z indicate the translational and angular velocities respectively

x, y, z axis (as for an atom) (figure 8.1a) and two with the rotational motion about two possible axis of rotation z, y (figure 8.1b). Vibrational motion of the molecule would also contribute to the number of degrees of freedom, but vibrational motion is not excited at room temperature. The total kinetic energy of

one mole of gas is $\frac{1}{2} iRT$ and the molar heat capacity at constant volume is

$$C_v = \frac{1}{2} iR \quad (8.8)$$

Thus from (8.6) and (8.7) for a monatomic gas ($i = 3$)

$$\kappa = \frac{5}{3} = 1.67 \quad (8.9)$$

and for a diatomic gas ($i = 5$)

$$\kappa = \frac{7}{5} = 1.40 \quad (8.10)$$

2. An adiabatic process is a thermodynamic process in which no heat is transferred between a system and its surroundings. The heat flow can be prevented by either insulating thermally the system or by carrying out the process so quickly that the heat transfer is negligible. From the first law of thermodynamics taking $\Delta Q = 0$ the following equations are obtained for an adiabatic process

$$pV^\kappa = \text{const} \quad (8.11)$$

and

$$TV^{\kappa-1} = \text{const} \quad (8.12)$$

APPARATUS AND METHOD

The measurements of κ are carried out using the apparatus shown in figure 8.2. It consists of a large vessel whose outlet is closed by valve V. The vessel is connected to a pump and also to an oil manometer M which allows the measurement of pressure in the vessel. In the experimental procedure some air is pumped into the vessel and when its temperature has reached the temperature of the surroundings the manometer reading h_1 is taken. Then the valve V is opened to produce an adiabatic cooling of the gas by sudden expansion and closed again. Now the temperature of the gas increases producing an increase of pressure at constant volume and when it attains the temperature of the surroundings the manometer reading h_2 is again taken.

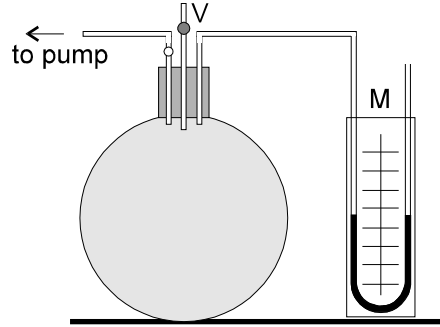


Fig. 8.2 Experimental setup used to measure the ratio κ of the specific heats of air. V indicates a valve and M an oil manometer

The initial pressure of the gas in the vessel is $h_1 + P$ and the final pressure of the gas is $h_2 + P$ where P is the external atmospheric pressure. For the adiabatic change

$$(h_1 + P)V_1^\kappa = PV_2^\kappa \quad (8.13)$$

where V_1 and V_2 are the initial and final volume of the gas. Because the initial and final temperatures of the gas are the same we have an isothermal change for which

$$(h_1 + P)V_1 = PV_2 \quad (8.14)$$

Substituting for $\frac{V_1}{V_2}$ from (8.14) into (8.13)

$$\left(1 + \frac{h_1}{P}\right)^{\kappa-1} = \left(1 + \frac{h_2}{P}\right)^\kappa \quad (8.15)$$

Expanding by the binomial theorem for small $\frac{h_1}{P}$ and $\frac{h_2}{P}$ and neglecting their higher powers it is found that

$$1 + (\kappa - 1) \frac{h_1}{P} = 1 + \kappa \frac{h_2}{P} \quad (8.16)$$

and

$$\kappa = \frac{h_1}{h_1 - h_2} \quad (8.17)$$

MEASUREMENTS

1. Find the ratio κ for air performing 10 measurements of h_1 and h_2 . Calculate the mean value of κ and its standard deviation. (see (6) for the expression used to calculate the standard deviation). Compare the obtained value with that given in table 8.

QUESTIONS

1. Draw a graph showing the changes of pressure and volume of the gas in the experiment.
2. An ideal gas expands adiabatically and its volume doubles. In which case is the pressure change higher a) the gas is monatomic, b) the gas is diatomic?
3. An ideal gas has $\kappa=1.3$. Find the molar heat capacity at constant volume and the molar heat capacity at constant pressure.
4. Describe the following thermodynamic processes: isothermal, isobaric and isochoric processes, and illustrate them by graphs on the pV surface.