

## APPARATUS

Insulated Joule–Thomson cell similar to that of Fig. 2 (suitable stainless steel frits can be obtained from chromatographic parts suppliers, e.g., Upchurch Scientific part C-414); metal or nylon tees, crosses, and reducers (available from Swagelok and other manufacturers);  $\frac{3}{8}$ -in. Teflon rod; type T insulated copper–Constantan thermocouples with 0.010-in.-diameter wires; voltmeter with 0.1- $\mu$ V resolution (e.g., Keithley 196), null voltmeter (e.g., Hewlett Packard 419A or Keithley 155), or sensitive potentiometer (e.g., Keithley K-3). Cylinders of CO<sub>2</sub>, N<sub>2</sub>, and He with regulators and control valves; 50 ft of  $\frac{1}{4}$ -in. copper coil,  $\frac{3}{8}$ -in. and  $\frac{1}{4}$ -in. polyethylene tubing; 0- to 10-bar Bourdon gauge; 25°C water bath.

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## EXPERIMENT 3

### Heat-Capacity Ratios for Gases

The ratio  $C_p/C_v$  of the heat capacity of a gas at constant pressure to that at constant volume will be determined by either the method of adiabatic expansion or the sound velocity method. Several gases will be studied, and the results will be interpreted in terms of the contribution made to the specific heat by various molecular degrees of freedom.

## THEORY

In considering the theoretical calculation of the heat capacities of gases, we shall be concerned only with perfect gases. Since  $\tilde{C}_p = \tilde{C}_v + R$  for an ideal gas (where  $\tilde{C}_p$  and  $\tilde{C}_v$  are the molar quantities  $C_p/n$  and  $C_v/n$ ), our discussion can be restricted to  $C_v$ .

The number of *degrees of freedom* for a molecule is the number of independent coordinates needed to specify its position and configuration. Hence a molecule of  $N$  atoms has  $3N$  degrees of freedom. These could be taken as the three Cartesian coordinates of the  $N$  individual atoms, but it is more convenient to classify them as follows.

1. *Translational degrees of freedom*: Three independent coordinates are needed to specify the position of the center of mass of the molecule.
2. *Rotational degrees of freedom*: All molecules containing more than one atom require a specification of their orientation in space. As an example, consider a rigid diatomic molecule; such a model consists of two point masses (the atoms) connected by a rigid massless bar (the chemical bond). Through the center of mass, which lies on the rigid bar, independent rotation can take place about two axes mutually perpendicular to each other and to the rigid bar. (The rigid bar itself does not constitute a third axis of rotation under ordinary circumstances for reasons based on quantum theory, there being no appreciable moment of inertia about this axis.) Rotation of a *diatomic* molecule or any linear molecule can thus be described in terms of *two* rotational degrees of freedom. *Nonlinear* molecules for which the third axis has a moment of inertia of appreciable magnitude and constitutes another axis of rotation require *three* rotational degrees of freedom.
3. *Vibrational degrees of freedom*: One must also specify the displacements of the atoms from their equilibrium positions (vibrations). The number of vibrational degrees of freedom is  $3N - 5$  for linear molecules and  $3N - 6$  for nonlinear molecules. These values are determined by the fact that the total number of degrees of freedom must be  $3N$ . For each vibrational degree of freedom, there is a "normal mode" of vibration of the molecule, with characteristic symmetry properties and a characteristic harmonic frequency. The vibrational normal modes for  $\text{CO}_2$  and  $\text{H}_2\text{O}$  are illustrated schematically in Fig. 1.

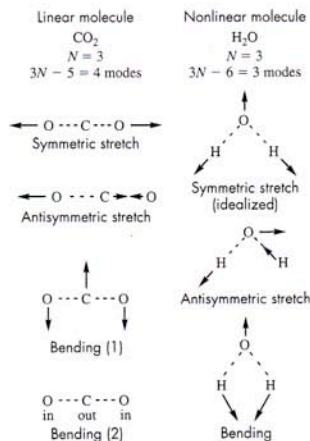


FIGURE 1

Schematic diagrams of the vibrational normal modes for  $\text{CO}_2$ , a linear molecule, and  $\text{H}_2\text{O}$ , a bent molecule.

Using classical statistical mechanics, one can derive the theorem of the equipartition of energy. According to this theorem,  $kT/2$  of energy is associated with each quadratic term in the expression for the energy.<sup>1</sup> Thus there is associated with each translational or rotational degree of freedom for a molecule a contribution to the energy of  $kT/2$  of kinetic energy and for each vibrational degree of freedom a contribution of  $kT/2$  of kinetic energy and  $kT/2$  of potential energy. (The corresponding contributions to the energy per mole of gas are  $RT/2$ .)

Clearly, a monatomic gas has no rotational or vibrational energy but does have a translational energy of  $\frac{3}{2}RT$  per mole. The constant-volume heat capacity of a monatomic perfect gas is thus

$$\tilde{C}_v = \left( \frac{\partial \tilde{E}}{\partial T} \right)_v = \frac{3}{2}R \quad (1)$$

For diatomic or polyatomic molecules, we can write

$$\tilde{E} = \tilde{E}(\text{trans}) + \tilde{E}(\text{rot}) + \tilde{E}(\text{vib}) \quad (2)$$

In Eq. (2), contributions to the energy from electronic states have been neglected, since they are not significant at room temperature for most molecules. Also, any small intermolecular energies that occur for imperfect gases are not considered.

The equipartition theorem is based on classical mechanics. Its application to translational motion is in accord with quantum mechanics as well. At ordinary temperatures the rotational results are also in accord with quantum mechanics. (The greatest deviation from the classical result is in the case of hydrogen,  $H_2$ . At temperatures below 100 K the rotational energy of  $H_2$  is significantly below the equipartition value, as predicted by quantum mechanics.)

The vibrational energy is however highly quantized and depends strongly on temperature: the various vibrational modes are at ordinary temperatures only partially "active," and the degree of activity depends strongly on the temperature. As a general rule, the heavier the atoms or the smaller the force constant of the bond (i.e., the lower the vibrational frequency), the more "active" is a given degree of freedom at a given temperature and the greater is the contribution to the heat capacity. Moreover, the frequencies of modes that are predominantly bending of bonds tend to be much lower than those that are predominantly stretching of bonds. In the case of most gaseous diatomic molecules (where the one vibrational mode is a pure stretch), the vibrational contribution to  $\tilde{C}_v$  is very small: for example,  $N_2$  would have its classical equipartition value for  $\tilde{C}_v$  only above about 4000 K. Many polyatomic molecules, especially those containing heavy atoms, will at room temperature have significant *partial* vibrational contributions to  $\tilde{C}_v$ .

For polyatomic molecules, theory based on the equipartition theorem allows one to calculate only limiting values for  $\tilde{C}_v$  by either completely ignoring all vibrational contributions or assuming that the vibrational contributions achieve their full classical value. For monatomic gases and all ordinary diatomic molecules (where the vibrational contribution is not important at room temperature and can be ignored), definite  $\tilde{C}_v$  values can be calculated. For a brief discussion of a more accurate calculation of  $\tilde{C}_v(\text{vib})$ , see Exp. 37.

For a given  $\tilde{C}_v$  value, the ratio  $\tilde{C}_p/\tilde{C}_v$  for a perfect gas is given by

$$\gamma \equiv \frac{\tilde{C}_p}{\tilde{C}_v} = 1 + \frac{R}{\tilde{C}_v} \quad (3)$$

## DISCUSSION

Compare your experimental ratios with those calculated theoretically, and make any deductions you can about the rotational and vibrational contributions, taking due account of the uncertainties in the experimental values. For  $\text{CO}_2$ , how would the theoretical ratio be affected if the molecule were nonlinear (such as  $\text{SO}_2$ ) instead of linear? Could you decide between these two structures from the  $\tilde{C}_p/\tilde{C}_v$  ratio alone?

With a knowledge of the vibrational frequencies for the normal modes of  $\text{N}_2$  and  $\text{CO}_2$  and the appropriate statistical thermodynamic formulae (see Exp. 37), one can calculate quite accurate  $\tilde{C}_v$  values for  $\text{N}_2$  and  $\text{CO}_2$ .

## B. Sound Velocity Method

The heat-capacity ratio  $\gamma = C_p/C_v$  of a gas can be determined with good accuracy by measuring the speed of sound  $c$ . For an ideal gas,

$$\gamma = \frac{Mc^2}{RT} \quad (24)$$

where  $M$  is the molar mass. A brief derivation<sup>5</sup> of this equation will be sketched below.

For longitudinal plane waves propagating in the  $x$  direction through a homogeneous medium of mass density  $\rho$ , the wave equation is

$$\frac{\partial^2 \xi}{\partial t^2} = c^2 \frac{\partial^2 \xi}{\partial x^2} \quad (25)$$

where  $\xi$  is the particle displacement. Consider a layer  $AB$  of the fluid, of thickness  $\delta x$  and unit cross-sectional area, which is oriented normal to the direction of propagation. The mechanical strain on  $AB$  due to the sound wave is  $\partial\xi/\partial x$ :

$$\frac{\partial \xi}{\partial x} = \frac{\Delta V}{V} = -\frac{\Delta \rho}{\rho} \quad (26)$$

where  $\Delta V$  and  $\Delta \rho$  are, respectively, the volume and density changes caused by the acoustic pressure (mechanical stress) change  $\Delta p$  in the ambient pressure  $p$ . From Hooke's law of elasticity,

$$-\Delta p = B_s \frac{\partial \xi}{\partial x} \quad (27)$$

where  $B_s$  is the adiabatic elastic modulus.<sup>†</sup> The net acoustic force acting on  $AB$  due to the sound wave is  $-(\partial \Delta p/\partial x) \delta x$ . According to Newton's second law of motion, this force is also equal to  $(\rho \delta x) \partial^2 \xi/\partial t^2$ . Thus

$$\frac{\partial \Delta p}{\partial x} = -\rho \frac{\partial^2 \xi}{\partial t^2} \quad (28)$$

or

$$\frac{\partial^2 \xi}{\partial t^2} = \frac{B_s}{\rho} \frac{\partial^2 \xi}{\partial x^2} \quad (29)$$

<sup>†</sup>Since the strain variations occur so rapidly that there is not sufficient time for heat flow from adjacent regions of compression and rarefaction, the adiabatic modulus is the appropriate one for sound propagation.<sup>5</sup>

Comparison of Eqs. (25) and (29) leads to

$$\rho c^2 = B_s \quad (30)$$

and one can now rewrite Eq. (27) as  $\Delta p = \rho c^2 (\Delta \rho / \rho) = c^2 \Delta \rho$ , which is equivalent to

$$c^2 = \left( \frac{\partial p}{\partial \rho} \right)_s \quad (31)$$

Now

$$\rho = \frac{M}{\bar{V}} \quad (32)$$

Therefore

$$c^2 = -\frac{\bar{V}}{\rho} \left( \frac{\partial p}{\partial \bar{V}} \right)_s = -\frac{\bar{V}^2}{M} \left( \frac{\partial p}{\partial \bar{V}} \right)_s \quad (33)$$

If sound propagation is considered as a reversible adiabatic process, we can use Eq. (19) to obtain for a perfect gas

$$c^2 = \gamma \frac{p}{\rho} = \gamma \frac{RT}{M} \quad (34)$$

which can be rewritten as Eq. (24). For a van der Waals gas, we obtain (to first order in  $a$  and  $b$ )

$$\begin{aligned} c^2 &= \gamma \frac{p}{\rho} \left( 1 - \frac{a}{p\bar{V}^2} + \frac{b}{\bar{V}} \right) \\ &= \gamma \frac{RT}{M} \left( 1 - \frac{2a}{p\bar{V}^2} + \frac{2b}{\bar{V}} \right) \end{aligned} \quad (35)$$

which may be readily solved for  $\gamma$ . For comparison the value of  $\gamma$  for a van der Waals gas is (to first order in  $a$ )

$$\gamma = 1 + \frac{R}{\tilde{C}_v} \left( 1 + \frac{2a}{p\bar{V}^2} \right) \quad (36)$$

assuming that we are given a theoretical value for  $\tilde{C}_v$ . (If this is based on a perfect gas, the translational part may be slightly in error because of gas imperfections, but that error is expected to be much less for  $\tilde{C}_v$  than for  $\tilde{C}_p$ .)

## METHOD

This experiment is based on a modified version of Kundt's tube, in which the wavelength  $\lambda$  of standing waves of frequency  $f$  are determined electronically. Figure 3 shows the experimental apparatus, which utilizes an audio oscillator driving a miniature speaker as the source and a microphone as the detector. Also, an alternative apparatus based on a small spherical resonator has been described by Colgate et al.<sup>6</sup>

It is possible to connect the microphone directly to a sensitive voltmeter and watch the variation in the intensity of the received signal as the detector is moved along the tube. The intensity will decrease to a minimum when an antinode is reached and then increase to a maximum at a node. However, it is more precise and more convenient to use an oscilloscope to indicate the phase relationship between the speaker input and the microphone

signal. The output of the audio oscillator should drive the horizontal sweep of the oscilloscope. The signal received by the microphone after propagation through the gas is applied (with amplification if necessary) to the vertical sweep of the oscilloscope. The phase difference is determined from the Lissajous figures that appear on the screen (see Chapter XIX). When the pattern changes from a straight line tilted at  $45^\circ$  to the right (in phase,  $0^\circ$  phase angle) to another straight line tilted at  $45^\circ$  to the left (out of phase,  $180^\circ$  phase angle), the piston has moved one-half the wavelength of sound.

## EXPERIMENTAL

The apparatus should be assembled as shown in Fig. 3. Details of the procedure will depend on the particular electronic components used, especially the type of oscilloscope. Additional instructions may be provided by the instructor.

If the oscillator is not calibrated accurately, this can be done with a calibrated frequency meter or by (1) displaying the waveform on the screen if the oscilloscope has an accurate timebase; (2) obtaining a Lissajous figure with a standard frequency source (internal or external); or (3) holding a vibrating tuning fork near the microphone and obtaining Lissajous figures at the fundamental and several harmonics (disconnect the speaker unit during this calibration). The oscillator should be calibrated at several frequencies between 1 and 2 kHz.<sup>†</sup>

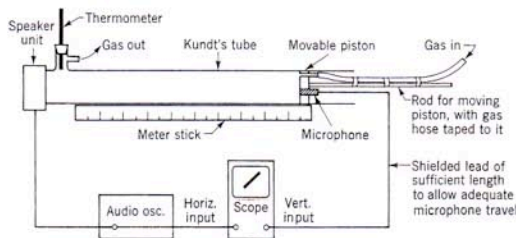
Move the piston to a position near the far end of its travel. Allow the gas to be studied to sweep through the Kundt's tube for about 10 min in order to displace all the air. Then reduce the flow rate until there is a very slow stream of gas through the tube; this will prevent air from diffusing in during the run. Adjust the gain controls so that the two signals are about equal in magnitude (i.e., a circle is seen when the signals differ in phase by  $90^\circ$ ).

Set the oscillator at the desired frequency (1 kHz for  $N_2$  and  $CO_2$ , 2 kHz for He), and slowly move the piston toward the speaker until a straight-line pattern is observed on the screen. Record the position of the piston and note whether the phase shift is  $0^\circ$  or  $180^\circ$ . Then move the piston inward again until the next straight-line pattern is observed, and again record the position. Continue to record such readings as long as a satisfactory pattern can be observed. Record the temperature of the outlet gas several times during the run.

<sup>†</sup>The frequency unit cycles per second is called a hertz (Hz). Thus 1 kHz = 1000 Hz = 1000 cps.

**FIGURE 3**

Apparatus for measuring the speed of sound in a gas. The Kundt's tube should be a glass tube  $\sim 150$  cm long and  $\sim 5$  cm in diameter. The close-fitting Teflon piston should move over a range of at least 100 cm. If a constant-temperature jacket is provided for the Kundt's tube, the position of the piston can be determined from a fiducial mark on the rod.



If necessary, repeat the entire procedure for a given gas until consistent results are obtained. If time permits, repeat the procedure using a different frequency. Measurements are to be made on helium, nitrogen, and carbon dioxide. At some point, obtain a reading of the barometric pressure.

### CALCULATIONS

From the average value of the spacing  $\lambda/2$  between adjacent nodes and the known frequency  $f$ , calculate the speed of sound  $c$  in each gas. Use Eq. (24) to calculate  $\gamma$ , and compare these experimental values with the theoretical values predicted by the equipartition theorem. In the case of  $N_2$  and  $CO_2$ , calculate the theoretical ratio both with and without a vibrational contribution to  $\tilde{C}_v$  of  $R$  per vibrational degree of freedom.

Using the van der Waals constants given for  $N_2$  and  $CO_2$  in Table 2-1, recalculate  $\gamma$  for those gases using Eq. (35) and compare them with the theoretical value given by Eq. (36). For this purpose, the quantity  $\tilde{V}$  can be approximated by the ideal gas value  $RT/p$ .

Assuming that all the gases can be treated as ideal and thus  $\tilde{C}_p = \tilde{C}_v + R$ , obtain approximate values for the molar constant-volume heat capacity  $\tilde{C}_v$  for He and  $N_2$  (and  $CO_2$ ).

### DISCUSSION

Compare your experimental ratios with those calculated theoretically, and make any deductions you can about the presence or absence of rotational and vibrational contributions, taking due account of the uncertainties in the experimental values. For  $CO_2$  how would the theoretical ratio be affected if the molecule were nonlinear (like  $SO_2$ ) instead of linear? Could you decide between these two structures from the  $\tilde{C}_p/\tilde{C}_v$  ratio alone?

With a knowledge of the vibrational frequencies for the normal modes of  $N_2$  and  $CO_2$  and the appropriate statistical thermodynamic formulae (see Exp. 37), one can calculate accurate  $\tilde{C}_v$  values for these molecules.

Compare the speed of sound in each gas with the average speed of the gas molecules and with the average velocity component in a given direction. Explain why the speed of sound is independent of the pressure.

Does the precision of the measurements justify the van der Waals expression, Eq. (35), instead of the perfect-gas expression, Eq. (34)? Justify your answer in terms of your estimates of uncertainty.

### SAFETY ISSUES

Gas cylinders must be chained securely to the wall or laboratory bench (see pp. 644–646 and Appendix C).

### APPARATUS

**Adiabatic Expansion Method.** Large-volume vessel (such as an 18-L glass carboy); three-hole stopper fitted with three glass tubes; open-tube manometer, with dibutyl phthalate as indicating fluid (may contain a small amount of dye for ease of reading); three long lengths and one short length of rubber pressure tubing; three screw clamps; cork ring and brackets, needed if vessel is to be mounted in a water bath; thermometer; 500-mL beaker.

Thermostat bath, set at 25°C (unless each vessel has an insulating jacket); cylinders of helium, nitrogen, and carbon dioxide.

**Sound Velocity Method.** Kundt's tube, complete with speaker unit (miniature cone or horn driver) and movable piston holding microphone; stable audio oscillator, preferably with calibrated dial; small crystal microphone; oscilloscope; audio-frequency amplifier, to be used if scope gain is inadequate; electrical leads; rubber tubing; stopper; thermometer.

Cylinders of helium, nitrogen, and carbon dioxide.

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## GENERAL READING

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1 2 3 4 5 6 7 8 9 0 QPD/QPD 0 9 8

ISBN 978-0-07-282842-9

MHID 0-07-282842-0

Publisher: *Thomas Timp*

Senior Sponsoring Editor: *Tamara L. Hodge*

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Cover Designer: *Studio Montage, St. Louis, Missouri*

Compositor: *Laserwords Private Limited*

Typeface: *10/12 Times Roman*

Printer: *Quebecor World Dubuque, IA*

Cover description: The figure depicts the absorption and emission spectra of CdSe nanocrystals, whose color is a sensitive function of size. The figure is based on spectral data provided by NN-Labs. The authors thank both NN-Labs and Evident Technologies for CdSe samples used in the development of the quantum dot experiment.

### Library of Congress Cataloging-in-Publication Data

Garland, Carl W.

Experiments in physical chemistry.—8th ed. / Carl W. Garland, Joseph W. Nibler, David P. Shoemaker.  
p. cm.

Includes index.

ISBN 978-0-07-282842-9—ISBN 0-07-282842-0 (hard copy : acid-free paper)

I. Chemistry, Physical and theoretical—Laboratory manuals. I. Nibler, Joseph W.

II. Shoemaker, David P. III. Title.

QD457 .S56 2009

541.078—dc22

2007043492