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Sound Velocity and Ideal-Gas Specific Heat of Gaseous 1,1,1,2-Tetrafluoroethane (R134a)

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A cylindrical, variable-path acoustic interferometer operating at 156.252 kHz is developed for determining ideal-gas specific heats. Results of validation measurements with argon are very satisfactory, with the maximum deviation of the speed of sound equal to 3×10^{-4}. The sound velocity of gaseous R134a has been measured at low temperatures and low pressures. The specific heat was then calculated from the results. The experimental results corrected for various dispersions for the sound velocity of gaseous R134a match well with an earlier publication, with a room mean square deviation of 2.56×10^{-4}. A new relation for the ideal-gas specific heat as a function of temperature for R134a is obtained.

KEY WORDS: acoustic interferometer; 1,1,1,2 tetraflouroethane; R134a; sound velocity; specific heat.

1. INTRODUCTION

Recent scientific evidence has implicated CFC-12, along with other fully halogenated chlorofluorocarbons (CFCs), in the depletion of ozone in the stratosphere. According to the Montreal Protocol, the worldwide supply of all fully halogenated CFCs will be regulated and significantly reduced. Extensive research shows that R134a (CH_3CH_2F) is the most suitable replacement for CFC-12 in automobile air-conditioner and refrigerator applications. The proper design of such systems requires accurate knowledge of the sound velocity and the ideal-gas specific heat of R134a. The ideal-gas specific heat is most often computed from spectroscopic data with the methods of statistical mechanics. These computations yield excellent values for $C^0_{p,m}$ but become hopelessly complex as the number of

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atoms in a molecule increases. Perhaps the most reliable method for more complicated molecules is to calculate the ideal-gas specific heat from a measurement of the sound velocity in the low-pressure vapor. Mehl and Moldover [1] developed spherical acoustic resonators for measuring the sound velocity in gases.

Beginning in 1987, we developed a fixed-path acoustic interferometer to measure the sound velocity in gases and obtained good results [2]. But the operation was difficult and the precision could not be improved because of the measuring method. As an alternative, a cylindrical variable-path acoustic interferometer has been developed. The system was successfully validated with argon [3]. The sound velocity of R134a was measured, and the ideal-gas specific heat was calculated from these results. A new relation for the ideal-gas specific heat as a function of temperature for R134a was also obtained.

2. FUNDAMENTAL PRINCIPLES

The relationship between the sound velocity C and the isoentropic compressibility is given by

$$C^2 = (\partial p/\partial \rho)_s \tag{1}$$

According to thermodynamics, the acoustic virial expansion is given by

$$C^2 = (\gamma_0 RT/M)[1 + (\beta_a/RT)p + (\gamma_a/RT)p^2 + \cdots] \tag{2}$$

The ideal-gas specific heat, $C^0_{p,m}$, can be determined from

$$C^0_{p,m} = R\gamma_0/(\gamma_0 - 1) \tag{3}$$

The subscript s in Eq. (1) refers to an isoentropic process, M is the molar mass of the sample gas, p is the gas pressure, T is the gas temperature, R is the gas constant, γ_0 is the zero-pressure limit of the specific heat ratio, and β_a and γ_a are the second and third acoustic virial coefficients of the gas. The sound velocity was measured as a function of pressure at constant temperature at low pressures. The coefficient $(\gamma_0 RT/M)$ was then determined by least-squares regression. If both T and M are known, the ratio of the specific heat γ_0 can be obtained.

3. EXPERIMENTAL APPARATUS

As shown in Fig. 1, the experimental apparatus consists of five parts: the pressure vessel, a temperature controlling and measuring system, a

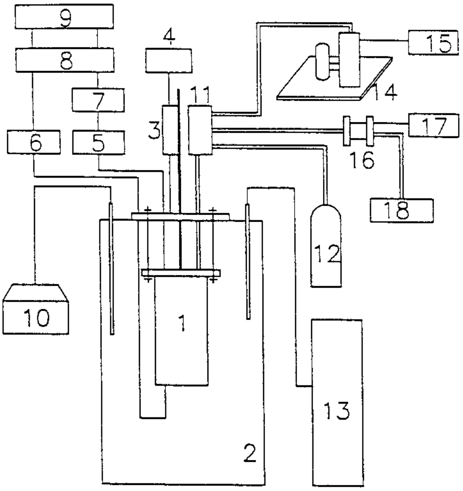

Fig. 1. The cylindrical variable-path acoustic interferometer. (1) Main body; (2) thermostat; (3, 4) displacement measuring system; (5) generator; (6) amplifier; (7) frequency meter; (8) wave indicator; (9) phase detector; (10) HP3456 data acquisition/control unit; (11) three-way valve; (12) gas sample bottle; (13) temperature controller; (14) vacuum pump; (15) vacuum meter; (16) differential pressure detector; (17) digital readout; (18) deadweight tester.

pressure-measuring system, a system for measuring the sound velocity, and a high-vacuum system.

3.1. The High-Vacuum System

Before the vessel is charged with the working fluid, a 10^{-3}-Torr vacuum is drawn in the vessel to ensure purity of the fluid.

3.2. The Vessel

The pressure vessel consists of a cylinder with two pistons at opposite ends of the cylinder. One piston, equipped with the emitting transducer, is fixed. The other, equipped with the detector, can slide freely in the cylinder. The detector also operates as a reflector. The transducer is made of piezoelectric crystal. Its operating frequency has a variation of 1 Hz.

3.3. The Constant-Temperature Controlling and Measuring System

The vessel is suspended inside a stirred fluid bath which is regulated to 0.0025 K. Its operating range varies from 0 to 80°C. A platinum resistance thermometer is used as the temperature sensor in the fluid.

3.4. The System for Applying and Measuring Pressure

The system was designed to operate at pressures up to 0.6 MPa. The pressures were measured with a deadweight tester and differential pressure transducer. The manufacturer's calibration indicated that the deadweight tester was accurate within 0.005%.

3.5. The Sound-Velocity Measuring System

The principle of ultrasonic interference was used to measure the sound velocity. The method is very accurate. The sound velocity, C, is equal to the wavelength, λ, times the frequency, f. Consiquently, the accuracy of the sound velocity depends on the accuracy of the wavelength and frequency measurements. The frequency of the sound wave emitted from the piezoelectric crystal transducer [3] is essentially constant, because the resonating frequency of the crystal is nearly independent of the environment. Thus, the precision of the determination of the sound velocity depends mainly on that of the wavelength. In order to improve the precision of the wavelength measurements, the piston should be moved more than 20 wavelengths.

4. VALIDATION OF THE APPARATUS WITH ARGON

Since argon gas is monoatomic, its thermodynamic properties are very close to those of an ideal gas over a large range of conditions; in addition,

Table I. Sound-Velocity Data and Relative Deviations for Ar^{40} at $T = 273.16$ K

P (kPa)	C^2_{exp} ($m^2 \cdot s^{-2}$)	C^2_{cal} ($m^2 \cdot s^{-2}$)	10^4 Dev.
689.434	94,957.162	94,936.606	2.16
570.114	94,953.156	94,893.474	6.29
516.898	94,880.140	94,886.738	−0.70
382.780	94,823.348	94,850.189	−2.83
301.492	94,777.964	94,828.896	−5.37
203.226	94,848.724	94,804.118	4.70
100.256	94,819.592	94,779.297	4.25

impurities in argon have little effect on the specific heat. Therefore, the sound velocity in argon can be calculated accurately. Hence argon was chosen to validate the apparatus [4].

The sound-velocity measurements for argon were made at temperatures of 273.16 and 300 K. The values of the experimental sound velocity [4] were corrected for diffraction and guided-mode dispersion, "classical" absorption, and Kirchhoff–Helmholtz (boundary-layer) absorption dispersion. The dispersion arising from impurities was not included, because there were no sufficient materials. However, the accuracy of validation was satisfactory. The measured sound velocities for Ar^{40} at 273.16 K and at pressures from 0.1 to 0.7 MPa are listed in Table I. The relative deviations from the results of Moldover et al. [5] are also shown in Table I. Moldover's [5] correlation is given by

$$C^2 = A_0 + A_1 P + A_2 P^2 + A_3 P^3 + A_{-1} P^{-1} \tag{4}$$

with

$$A_0 = 94756.178 \text{ m}^2 \cdot \text{s}^{-2}, \qquad A_1 = 0.22502 \text{ m}^2 \cdot \text{s}^{-2} \cdot \text{kPa}^{-1}$$

$$A_2 = 5.321 \times 10^{-5} \text{ m}^2 \cdot \text{s}^{-2} \cdot \text{kPa}^{-2}, \qquad A_2 = 1.45 \times 10^{-9} \text{ m}^2 \cdot \text{s}^{-2} \cdot \text{kPa}^{-3}$$

$$A_{-1} = 2.7 \text{ m}^2 \cdot \text{s}^{-2} \cdot \text{kPa}$$

It turns out that the maximum relative deviation $\Delta C^2/C^2$ is less than 6×10^{-4}, i.e., the maximum $\Delta C/C$ is less than 3×10^{-4}.

With Eq. (2), γ_0 can be obtained by least-squares regression of the sound-velocity data at temperatures 273.16 and 300 K. Thus, the corresponding specific heat, $C^0_{p,m}$, under ideal-gas conditions, can also be determined and compared with values determined from thermodynamics methods as shown in Table II. The deviation of $C^0_{p,m}$ for Ar^{40} is less than 10^{-3}.

Table II. The values of γ_0 and $C^0_{p,m}$ and Relative Deviations for Ar^{40} [a]

T (K)	γ_0	$C^0_{p,m,exp}$	$C^0_{p,m,th}$	10^4 Dev.
273.16	1.66680	2.4997R	2.5R	1.2
300.00	1.66569	2.5022R	2.5R	−9

[a] Subscripts exp and th refer to the experimental values and the values determined from thermodynamics method, respectively.

5. RESULTS FOR R134a

Wavelength measurements for R134a were made along 10 isotherms between 274.15 and 345.15 K. The maximum pressure along the isotherms was about 0.5 MPa, which is below 0.6 of the vapor pressure of R134a at room temperature.

The R134a was provided by the Du Pont Company and the Shanghai Institute of Organic Chemistry and had a purity of 99.95 %. If we can bring the vessel at high vacuum filling with R134a, impurities have less effect on the measurement.

The sound velocities were obtained from the corrected wavelengths together with the fixed frequency. The correction of measurement values for diffraction and guided mode dispersion [6] was made by the empirical equation

$$\Delta\lambda_{\mathrm{dg}} = \lambda[\alpha_2(\lambda/D)^4 + \alpha_3(\lambda/D)^6] \tag{5}$$

where λ is the wavelengt, D is the diameter of the resonance tube (75.04 mm), $\alpha_2 = 0.3806$, and $\alpha_3 = 79.74$.

In order to correct for absorption dispersion, we should obtain the Kirchhoff–Helmholtz (boundary-layer) absorption coefficient α_{KH} and the "classical" absorption coefficient α_{CL}. The boundary layer theory gives [7]

$$\alpha_{\mathrm{KH}} = [2/(DC)][v^{0.5} + (\gamma - 1)(K/\rho C_{\mathrm{p}})^{0.5}](0.5\omega)^{0.5} \tag{6}$$

where D is the tube diameter, v the kinematic viscosity of the sample gas, K the thermal conductivity, C_{p} the specific heat at constant pressure, ρ the density, γ the ratio of the principal specific heats, and ω the angular frequency.

The classical absorption coefficient α_{CL} is given by two parts: thermal conductivity and shear viscosity [7]. First,

$$\alpha_{\mathrm{CL}} = K(1 - 1\gamma)\omega^2/(2\rho C^3 C_{\mathrm{v}}) + 2\omega^2\eta/(3C^3\rho) \tag{7}$$

where the shear viscosity η, required to determine the absorption, was calculated from a modified Eucken equation [8]:

$$\eta = KM/(1.77 + 1.33\ C_{\mathrm{v}}/R) \tag{8}$$

Here C is the sound velocity, C_{v} the specific heat at constant volume, and the other parameters are the same as in Eq. (7). Second,

$$\Delta\lambda_{\mathrm{ab}} = \lambda^2(\alpha_{\mathrm{KH}} + \alpha_{\mathrm{CL}})[1 + \lambda(\alpha_{\mathrm{KH}} + \alpha_{\mathrm{CL}})/\pi]/2\pi \tag{9}$$

Table III. Experimental Results for the Sound Velocity of R134a

T (K)	P (kPa)	C_{exp} ($\mathrm{m \cdot s^{-1}}$)
274.15	194.970	151.57
	181.640	151.99
	150.470	152.97
	100.670	154.56
302.50	422.498	154.61
	338.582	156.88
	242.180	159.22
	152.028	161.53
305.00	439.344	155.01
	330.228	157.82
	241.110	160.05
	100.121	163.47
310.00	469.010	156.13
	354.572	158.94
	245.518	161.48
	159.180	163.52
315.00	470.157	157.82
	345.951	160.80
	258.260	162.71
	141.074	165.34
320.00	450.495	160.10
	347.796	162.35
	235.959	164.71
	153.298	166.45
325.00	447.436	161.82
	356.987	163.64
	256.373	165.79
	143.411	168.02
330.00	450.324	163.33
	346.405	165.50
	242.565	167.41
	130.348	169.61
335.03	444.594	165.13
	343.204	167.05
	243.410	168.79
	99.163	171.47
340.08	513.963	165.50
	429.272	167.00
	308.417	169.12
	112.413	172.55
345.02	491.417	167.46
	359.479	169.64
	239.058	171.63
	99.988	174.02

For polyatomic molecules, vibrational relaxation is most important to the measurement of sound velocity. Its correction can be calculated as follows:

$$\Delta\lambda_{\mathrm{vib}} = \lambda \frac{C_{\mathrm{v0}}(C_{\mathrm{v0}}+r)+C_{\mathrm{v1}}(C_{\mathrm{v1}}+r)(\omega\tau)^2}{2[C_{\mathrm{v0}}^2+C_{\mathrm{v1}}^2(\omega\tau)^2](1+r/C_{\mathrm{v0}})} \tag{10}$$

where $C_{\mathrm{v0}} = C_{\mathrm{v}}$ is the specific heat at zero frequency, $r = C_{\mathrm{p}} - C_{\mathrm{v}}$, $C_{\mathrm{v1}} = C_{\mathrm{v0}} - C_{\mathrm{vib}}$, and C_{vib} is $(C^0_{\mathrm{p,m}} - 4R)$, the vibrational contribution to the specific heat. At atmospheric pressure, the vibrational relaxation times were 90 ns at 270 K and 72 ns at 340 K [9]. So we have a correction for the wavelength:

$$\lambda = \lambda - (\Delta\lambda_{\mathrm{dg}} + \Delta\lambda_{\mathrm{ab}} + \Delta\lambda_{\mathrm{vib}}) \tag{11}$$

In Eqs. (5)–(11), all thermophysical-property parameters are taken from Ref. 10.

Our measurements after corrected for dispersionqs are listed in Table III. They are in excellent agreement with those of Goodwin and Moldover [9]. The root mean square deviation was 2.56×10^{-4}. A comparison with the results of Goodwin and Moldover [9] is shown in Fig. 2.

When the sound-velocity data are measured with the pressures at constant temperature, the coefficients γ_0, β_{a}, and γ_{a} in Eq. (2) can be determined by least squares.

The corresponding ideal-gas specific heats obtained from Eq. (3) are shown in Table IV. Compared with the data of Goodwin and Moldover

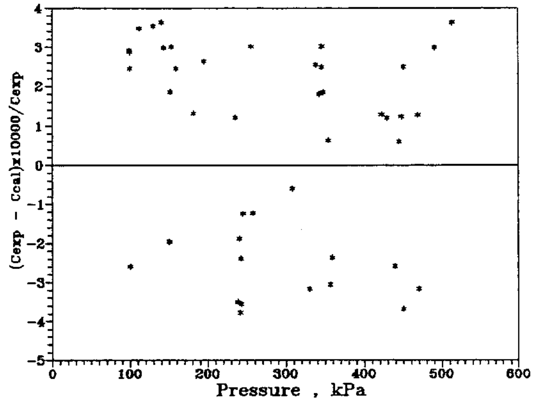

Fig. 2. The relative deviations of the experimental sound velocity from the values of Goodwin and Moldover [9].

Table IV. Values of $C^0_{\mathrm{p,m}}$ and Their Deviations from those of Goodwin and Moldover [9]

T (K)	$C^0_{\mathrm{p,m,exp}}/R$	$C^0_{\mathrm{p,m,ref}}/R$	10^3 Dev
274.150	9 6939840	9.6852800	0.898
302.500	10.3817800	10.3108000	6.837
305.000	10.4091800	10.3646900	4.275
310.000	10.4794100	10.4718600	0.721
315.000	10.6661500	10.5782000	8.246
320.000	10.7442000	10.6837200	5.629
325.000	10.7580400	10.7884200	−2.824
330.000	11.0172500	10.8923000	11.342
335.030	11.0395900	10.9959700	3.952
340.080	11.1195300	11.0992100	1.828
345.020	11.1381000	11.1993900	−5.503

[9], the relative deviations in most of our ideal-gas specific heat values are less than 10^{-3}. Figure 3 shows that our data not only complement the data of Goodwin and Moldover [9], but also increase the number of data points between 0 and 75°C.

Using both sets of data, we obtain a relation between $C^0_{\mathrm{p,m}}$ and the absolute temperature T:

$$C^0_{\mathrm{p,m}}/R = 2.1715 + 0.032016\,T - 16.757 \times 10^{-6}\,T^2 \tag{12}$$

valid in the temperature range from 270.15 to 345.15 K.

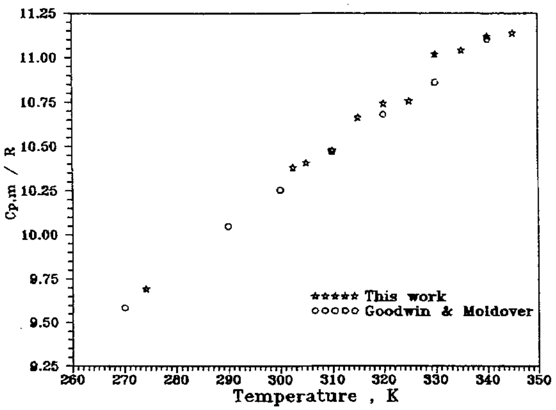

Fig. 3. Experimental data for $C^0_{\mathrm{p,m}}$ of R134a as a function of temperature.

6. ERROR ANALYSIS

6.1. Error of the Temperature Measurement

The temperature fluctuation of the thermostat is about 0.005 K/h. Thus in a run of 2 h, the temperature fluctuation may be 0.01 K.

6.2. Error of the Pressure Measurement

A deadweight tester is used to measure the pressure with a precision of 0.005%. The pressure drop which results from leakage is less than 0.004%/h; additionally, when the rod is drown out from the vessel, the pressure drop in the vessel be up to 0.02%.

6.3. Error of the Velocity of Sound Measurement

From the equation

$$C = f\lambda \tag{13}$$

the relative deviation of the sound velocity is given by

$$\left|\frac{dC}{C}\right| = \left|\frac{df}{f}\right|_f + \left|\frac{d\lambda}{\lambda}\right|_\phi + \left|\frac{d\lambda}{\lambda}\right|_L + \left|\frac{dC}{C}\right|_T + \left|\frac{dC}{C}\right|_P \tag{14}$$

where the subscripts f, ϕ, L, T, and P refer to the error arising from the frequency measurement, phase determination, displacement measurement, temperature fluctuation, and pressure fluctuation.

The system operates at 156.252 kHz, which is measured by a frequency meter with an accuracy of 1 Hz. The precision of the phase meter is about 0.5°, and the phase determining system has a precision of 0.1%; according to the desired designation, the error of the displacement transmission is about 4 μm. The displacement indicator has an accuracy of 2 μm. And the error of correlation for thermal deformation is about 40 ppm. We have assumed that the experimental operation is at a constant temperature and constant pressure. As a consequence, the fluctuations of temperature and

Table V. Error Analysis of the Experimental System

$\left\|\frac{df}{f}\right\|_f$	$\left\|\frac{d\lambda}{\lambda}\right\|_\phi$	$\left\|\frac{d\lambda}{\lambda}\right\|_L$	$\left\|\frac{dC}{C}\right\|_T$	$\left\|\frac{dC}{C}\right\|_P$	$\left\|\frac{dC}{C}\right\|$	$\left\|\frac{d\gamma_0}{\gamma_0}\right\|$	$\left\|\frac{dC^0_{p,m}}{C^0_{p,m}}\right\|$
0.064×10^{-4}	0.57×10^{-4}	1.54×10^{-4}	0.19×10^{-4}	0.14×10^{-4}	2.51×10^{-4}	5.83×10^{-4}	5.1×10^{-3}

pressure have an effect on the measured values of the sound velocity. From Eq. (2), we get a relation of the sound velocity C with T and P as

$$\frac{\partial C}{\partial T}=\frac{R\gamma_0}{2MC} \tag{15a}$$

and

$$\frac{\partial C}{\partial P}=\frac{\gamma_0}{2MC}\left[\beta_{\mathrm{a}}+2P\gamma_{\mathrm{a}}\right] \tag{15b}$$

Now we take the first data point as the reference point for R134a ($T=274.15$ K, $P=195$ kPa, $dP=66$ Pa). The results are presented in Table V.

6.4. Error of the Ideal-Gas Specific Heat $C^0_{\mathrm{p,m}}$ and Its Ratio γ_0

From Eqs. (2) and (3), the relative deviation of γ_0 and $C^0_{\mathrm{p,m}}$ is given by

$$\left|\frac{d\gamma_0}{\gamma_0}\right|=2\left|\frac{dC}{C}\right|+\left|\frac{\gamma_0 RT}{MC^2}\frac{dT}{T}\right|+\left|\frac{\gamma_0}{M}\frac{\beta_{\mathrm{a}}P+2\gamma_{\mathrm{a}}P^2}{C^2}\frac{dP}{P}\right| \tag{16}$$

and

$$\left|\frac{dC^0_{\mathrm{p,m}}}{C^0_{\mathrm{p,m}}}\right|=\frac{1}{\gamma_0-1}\left|\frac{d\gamma_0}{\gamma_0}\right| \tag{17}$$

When the data at $T=274.15$ K and $P=195$ kPa are substituted into Eqs. (16) and (17), we obtain the results listed in Table V.

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