*J. Chem. Eng. Data* **1996,** *41,* 1187−1190

# Speed-of-Sound Measurements and Ideal-Gas Heat Capacity for 1,1,1,2-Tetrafluoroethane and Difluoromethane

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The speed of sound in gaseous 1,1,1,2-tetrafluoroethane (R-134a, $CF_3CH_2F$) and difluoromethane (R-32, $CH_2F_2$) has been measured by using a spherical resonator. The measurements for R-134a have been carried out along two isotherms at 323 K and 343 K and at pressures up to 400 kPa for a total of 26 values. For R-32 the measurements were made at 308 K, 323 K, 333 K, and 343 K and at pressures up to 500 kPa for a total of 44 measurements. The experimental uncertainties for R-134a in temperature, pressure, and speed of sound are estimated to be not greater than ±6 mK, ±0.2 kPa, and ±0.0061%, respectively. The experimental uncertainties for R-32 in temperature, pressure, and speed of sound are estimated to be not greater than ±8 mK, ±0.2 kPa, and ±0.0061%, respectively. The purities of the R-134a and R-32 samples were better than 99.95% and 99.99% of area percent of the gas chromatography, respectively. We have determined the ideal-gas heat capacities and the second acoustic virial coefficients from the speed-of-sound measurements.

## Introduction

Speed-of-sound measurement by means of a spherical resonator is recognized as one of the most accurate methods for determining the thermodynamic properties of very dilute gases such as the ideal-gas heat capacities and the second virial coefficients. Using this method, we have previously reported the speed-of-sound values in gaseous 1,1,1,2-tetrafluoroethane (R-134a, $CF_3CH_2F$) (Hozumi et al., 1993), 1,1-difluoroethane (R-152a, $CHF_2CH_3$) (Hozumi et al., 1993), difluoromethane (R-32, $CH_2F_2$) (Hozumi et al., 1994b), and pentafluoroethane (R-125, $CF_3CHF_2$) (Hozumi et al., 1996) with an experimental uncertainty of ±0.01%. R-134a and R-32 are components of promising binary and/or ternary refrigerant mixtures for replacing chlorodifluoromethane (R-22, $CHClF_2$). We plan to measure the speed of sound for binary and/or ternary mixtures containing R-134a and R-32. The present study aimed to extend the range of measurements for R-134a and R-32. We report 26 and 44 speed-of-sound values for R-134a and R-32, respectively. The ideal-gas heat capacities and second acoustic virial coefficients have been determined from these speed-of-sound measurements.

## Experimental Procedure

An explanation of the procedure which has also been applied for the present measurements was reported in Hozumi et al. (1993). As illustrated in Figure 1, sample gas was introduced into the vessel Q from the supply bottle X. The inside and outside of the spherical resonator S were filled with the sample gas. After the thermodynamic equilibrium condition was confirmed, the temperature $T$, and pressure $P$, frequency $f$, amplitude $A$, and phase difference $\phi$ were measured at the condition of radially symmetric mode resonance of the sample gas in the spherical resonator. The speed of sound, $W$, was then determined from the values of the resonance frequency $f_{l,n}$ and half-width $g_{l,n}$ which were calculated from the values of $f$, $A$, and $\phi$. The relation among $W$, $f_{l,n}$, and $g_{l,n}$ is given by a complex resonance expression,

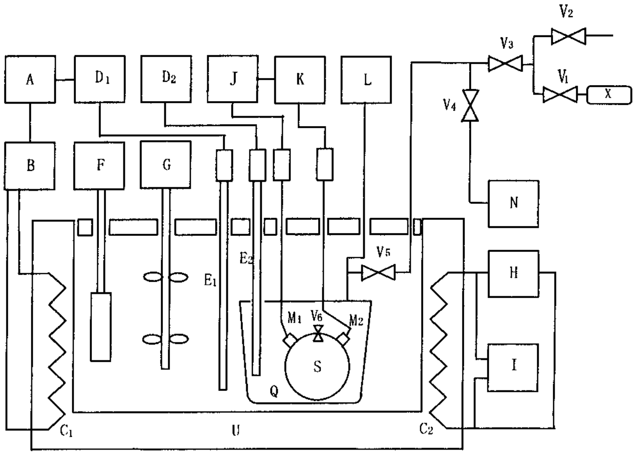

**Figure 1.** Experimental apparatus: A, PID controller; B, thyristor regulator; $C_1$, $C_2$, heaters; $D_1$, $D_2$, thermometer bridges; $E_1$, $E_2$, platinum resistance thermometers; F, refrigeration unit; G, stirrer; H, transformer; I, voltmeter; J, frequency synthesizer; K, lock-in amplifier; L, pressure gauge; $M_1$, $M_2$, transducers; N, vacuum pump; Q, pressure vessel; S, spherical resonator; U, thermostated bath; $V_{1-6}$, valves; X, supply bottle.

$$f_{l,n} + \mathrm{i}g_{l,n} = \frac{WZ_{l,n}}{2\pi a} + \sum_j (\Delta f + \mathrm{i}\Delta g)_j \qquad (1)$$

$$l = 0, 1, 2, ..., \qquad n = 0, 1, 2, ...$$

where $a$ and $Z_{l,n}$ in the first term on the right hand side are the inner radius of the spherical resonator, about 50 mm, and the $n$th root of the $l$th-order Bessel function, respectively. Each mode is expressed by ($l$, $n$), while $l = 0$ represents the radially symmetric mode. The second term on the right hand side is a series of perturbation terms to represent various nonideal conditions. Note that $g_{l,n}$ on the left hand side in eq 1 are measured experimentally,

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**Table 1. Standard Uncertainties, $u_i$, for Temperature, Pressure, and Speed of Sound**

| | | |
|---|---|---|
| | Standard Uncertainties for Temperature | |
| $u_1$ | the standard platinum resistance thermometer E1 | 1.0 mK |
| $u_2$ | the platinum resistance thermometer E2 calibrated with the platinum resistance thermometer E1 | 1.2 mK |
| $u_3$ | the temperature stability | 2.5 mK for R-134a, 3.7 mK for R-32 |
| $u_c$ | combined standard uncertainty | 3.0 mK for R-134a, 4.0 mK for R-32 |
| | Standard Uncertainties for Pressure | |
| $u_1$ | dead weight pressure gauge (DH Instruments Inc., Model 5200) | 0.05 kPa |
| $u_2$ | the pressure gauge L calibrated with the dead weight pressure gauge | 0.05 kPa |
| $u_3$ | the pressure stability | 0.05 kPa |
| $u_c$ | combined standard uncertainty | 0.09 kPa |
| | Standard Uncertainties for Speed of Sound | |
| $u_1$ | $f_{l,n}$ and $\sum\Delta f_j$ | 0.0020% |
| $u_2$ | the inner radius of the spherical resonator $a$ | 0.0023% |
| $u_c$ | combined standard uncertainty | 0.0031% |

while $\Delta g$ on the right hand side in eq 1 arise from the perturbation terms. In the present study, four radially symmetric modes (0, 2) through (0, 5) are used.

When a series of measurements was completed at a known pressure and temperature, the pressure was reduced step by step under isothermal conditions for succeeding measurements.

## Experimental Uncertainties and Sample Purities

We follow ISO (International Organization for Standardization) guidelines (ISO, 1993) for the experimental uncertainty. The extended uncertainty, $U$, of the measured values can be represented by the following equation.

$$U = k\sqrt{\Sigma(u_i)^2} \tag{2}$$

where $k$ and $u$ are the coverage factor and the standard uncertainty, respectively. The subscript, i, is the component of the uncertainty. When $k$ is from 2 to 3, then the level of confidence corresponds to 95% to 99%. The standard uncertainty corresponds to the standard deviation, $\sigma$, given by

$$\sigma = \sqrt{\frac{1}{n-1}\sum_{j=1}^{n}(x_j - x_m)^2} \tag{3}$$

where $n$ denotes the data points. $x_j$ and $x_m$ represent the data value and the average of the data, respectively.

In the present study, the coverage factor, $k$, equals 2. The standard uncertainties, $u_i$, and the combined uncertainties, $u_c = (\Sigma(u_i)^2)^{1/2}$ are shown in Table 1. The experimental uncertainties in temperature, pressure, and speed-of-sound measurements are estimated to be not greater than ±6 mK, ±0.2 kPa, and ±0.0061% for R-134a and ±8 mK, ±0.2 kPa, and ±0.0061% for R-32, respectively. When the coverage factor, $k$, equals 3, the uncertainty in speed-of-sound measurements for R-134a and R-32 is ±0.0092%, which is similar to values of the earlier measurements (Hozumi et al., 1993, 1994a), ±0.01%. We have calibrated the present pressure gauge with a dead weight pressure gauge (DH Instruments Inc., Model 5200). This yields an uncertainty in pressure, ±0.2 kPa, lower than those of the present earlier measurements (Hozumi et al., 1993, 1994a), ±0.5 kPa.

The purities of samples purified and analyzed by the manufacturers were better than 99.95% for R-134a and 99.99% for R-32, respectively. These percentages are due to the area percent of the gas chromatography. We have not purified the sample ourselves, and we could not find any effect of impurities; so we can simply rely on the available purity data supplied by the chemical manufacturers.

**Table 2. Speed of Sound in Gaseous R-134a**

| $T$/K[a] | $P$/kPa | $W$/m s$^{-1}$ |
|---|---|---|
| 323.150 | 414.96 | 161.724 |
| | 300.43 | 164.237 |
| | 200.04 | 166.364 |
| | 180.73 | 166.766 |
| | 160.34 | 167.187 |
| | 140.40 | 167.597 |
| | 120.71 | 167.999 |
| | 100.57 | 168.408 |
| | 80.51 | 168.813 |
| | 60.12 | 169.222 |
| | 40.15 | 169.621 |
| | 20.59 | 170.012 |
| | 10.72 | 170.211 |
| 343.138 | 405.70 | 168.285 |
| | 300.51 | 170.153 |
| | 200.80 | 171.883 |
| | 180.58 | 172.229 |
| | 160.28 | 172.575 |
| | 140.64 | 172.908 |
| | 120.28 | 173.253 |
| | 100.14 | 173.592 |
| | 80.58 | 173.920 |
| | 60.55 | 174.254 |
| | 40.22 | 174.594 |
| | 20.63 | 174.922 |
| | 10.68 | 175.095 |

[a] ITS-90.

## Results and Discussion

Twenty-six speed-of-sound values in gaseous R-134a were measured at 323 K and 343 K isotherms and pressures from 10 kPa to 400 kPa. Forty-four speed-of-sound values in gaseous R-32 have been measured along the four isotherms at 308 K, 323 K, 333 K, with 343 K and at pressures from 20 kPa to 500 kPa. These values are listed in Tables 2 and 3. The thermophysical properties for R-134a and R-32 used for the perturbation terms in eq 1 for the present measurements are the ideal-gas heat capacity by Goodwin and Moldover (1990) for R-134a and by Hozumi et al. (1994b) for R-32, the equation of state by Piao et al. (1995), the thermal conductivity by Goodwin and Moldover (1990) for R-134a and by the modified Eucken equation (Reid et al., 1977) for R-32, and the viscosity by the modified Eucken equation (Reid et al., 1977) for R-134a and by Reid et al. (1977) for R-32. The perturbation terms affect the speed of sound at the level of 0.01%. We estimated the uncertainty of the perturbation terms to be not greater than ±10%; this uncertainty corresponds to a 0.001% effect on the speed of sound.

**Table 3. Speed of Sound in Gaseous R-32**

| $T$/K[a] | $P$/kPa | $W$/m s$^{-1}$ | $T$/K[a] | $P$/kPa | $W$/m s$^{-1}$ |
|---|---|---|---|---|---|
| 308.183 | 515.08 | 237.908 | 333.141 | 509.53 | 248.439 |
| | 449.86 | 239.052 | | 450.72 | 249.225 |
| | 400.10 | 239.917 | | 400.61 | 249.892 |
| | 350.43 | 240.772 | | 351.54 | 250.543 |
| | 299.17 | 241.649 | | 300.95 | 251.210 |
| | 250.67 | 242.470 | | 250.80 | 251.867 |
| | 200.08 | 243.319 | | 200.70 | 252.519 |
| | 150.38 | 244.147 | | 150.98 | 253.165 |
| | 100.75 | 244.966 | | 99.30 | 253.831 |
| | 60.40 | 245.628 | | 60.69 | 254.330 |
| | 40.75 | 245.952 | | 40.63 | 254.582 |
| | 20.28 | 246.283 | | | |
| | | | 343.136 | 481.41 | 252.671 |
| 323.174 | 492.98 | 244.641 | | 450.51 | 253.045 |
| | 400.43 | 246.010 | | 400.73 | 253.646 |
| | 351.14 | 246.736 | | 350.30 | 254.252 |
| | 297.03 | 247.524 | | 301.00 | 254.841 |
| | 249.78 | 248.210 | | 249.59 | 255.454 |
| | 200.47 | 248.919 | | 200.47 | 256.037 |
| | 150.08 | 249.639 | | 150.82 | 256.623 |
| | 100.63 | 250.341 | | 100.57 | 257.215 |
| | 60.51 | 250.907 | | 60.57 | 257.688 |
| | 39.69 | 251.207 | | 40.59 | 257.917 |

[a] ITS-90.

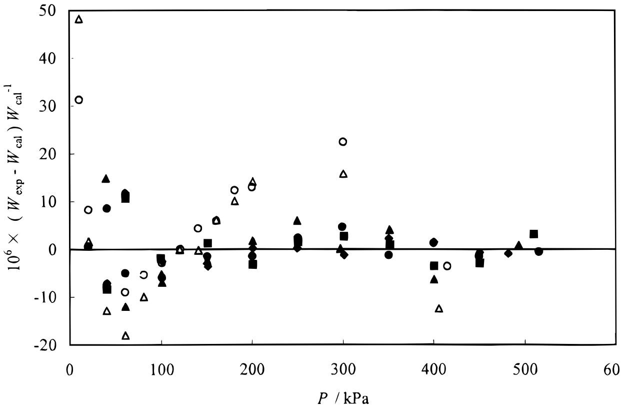

**Figure 2.** Deviation of the experimental $W$ values from eq 4 for R-134a and R-32. R-134a: (○) 323 K; (△) 343 K. R-32: (●) 308 K; (▲) 323 K; (■) 333 K; (◆) 343 K. (—) eq 4.

The square of the measured speed of sound was correlated along each isotherm with a quadratic function of pressure

$$W^2 = \frac{\kappa^0}{M}(RT + \beta_a P + \gamma_a P^2) \quad (4)$$

where superscript zero denotes the ideal-gas value, $R$ is the universal gas constant, $M$ is the molar mass, $\beta_a$ and $\gamma_a$ are the second and third acoustic virial coefficients, respectively, and $\kappa$ is the specific-heat ratio $c_P/c_V$. $R$ = 8.314 471 J·mol$^{-1}$·K$^{-1}$, which was determined from the similar acoustic method by Moldover et al. (1988). This value differs from the CODATA (Cohen and Taylor, 1986) value, 8.314 510 J·mol$^{-1}$·K$^{-1}$ by 0.0005% order.

The deviation of the experimental $W$ values from eq 4 is shown in Figure 2 along with the values of our earlier measurements (Hozumi et al., 1993, 1994a). The present results are the average values of the (0, 2) to (0, 5) radially symmetric modes. The solid curves in Figure 2 represent the calculated results from eq 4. The present average values agree very well within ±0.005% for R-134a and ±0.001% for R-32 with the values calculated from eq 4.

The ideal-gas heat capacity, $c_P^0$, and the second acoustic virial coefficient, $\beta_a$, determined from the present measurements, are summarized in Table 4 for R-134a and in Table 5 for R-32. For R-32 they include refitted $c_P^0$ and $\beta_a$ values from the speed-of-sound data of the earlier publication (Hozumi et al., 1994b). In the present study, we found that it is more appropriate to correlate the measured speed-of-sound values squared as a quadratic function of pressure, eq 4, instead of the linear function adopted in our previous paper (Hozumi et al., 1994b). The method of analysis for $c_P^0$ and $\beta_a$ has been reported in our previous publication (Hozumi et al., 1993). The standard deviations for $c_P^0$ and $\beta_a$ which were determined from the regression procedure of eq 4 to the speed-of-sound measurements were ±0.08% and ±0.19% for R-134a and ±0.045% and ±0.92% for R-32, respectively.

**Table 4. Ideal-Gas Heat Capacity and Second Acoustic Virial Coefficient for R-134a**

| $T$/K | $c_P^0/R$ | $\beta_a$/cm$^3$ mol$^{-1}$ |
|---|---|---|
| 323.150 | 10.721 | −620.4 |
| 343.138 | 11.149 | −537.7 |

**Table 5. Ideal-Gas Heat Capacity and Second Acoustic Virial Coefficient for R-32**

| $T$/K | $c_P^0/R$ | $\beta_a$/cm$^3$ mol$^{-1}$ |
|---|---|---|
| 273.155 | 4.9491 | −461.4 |
| 308.157 | 5.2613 | −336.0 |
| 313.151 | 5.3080 | −323.5 |
| 323.149 | 5.3989 | −301.4 |
| 333.149 | 5.4992 | −277.4 |
| 343.147 | 5.5948 | −259.5 |
| 308.183 | 5.2594 | −336.3 |
| 323.174 | 5.4018 | −298.8 |
| 333.141 | 5.4987 | −276.7 |
| 343.136 | 5.5980 | −257.5 |

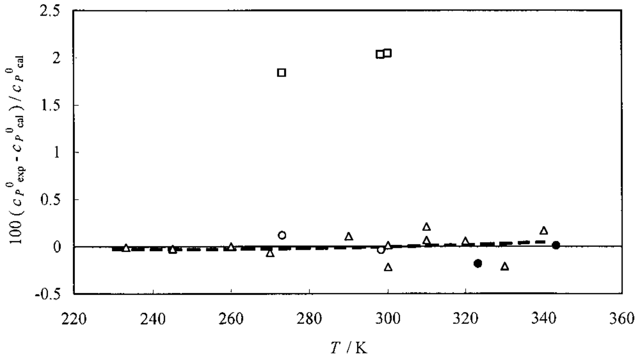

**Figure 3.** Deviation of the present $c_P^0$ values from eq 5 for R-134a: (●) this work; (○) Hozumi et al. (1993); (△) Goodwin and Moldover (1990); (□) TRC (1989); (—) eq 5; (- - -) Goodwin and Moldover (1990).

For R-134a the $c_P^0$ correlation was obtained from the present values and those reported by Hozumi et al. (1993), and by Goodwin and Moldover (1990) for $T$ = 233 K to 343 K.

$$\frac{c_P^0}{R} = 2.1941 + 3.2198 \times 10^{-2}(T/\mathrm{K}) - 1.779 \times 10^{-5}(T/\mathrm{K})^2 \quad (5)$$

Figure 3 shows the deviation of the present $c_P^0$ values for R-134a as well as $c_P^0$ values reported by TRC (1989) from the correlation, eq 5. The broken line shows a correlation reported by Goodwin and Moldover (1990), which represents their values within ±0.24%. Our data, our earlier values (Hozumi et al., 1993), and those of Goodwin and Moldover (1990) agree with our correlation within ±0.18, ±0.12, and ±0.22%, respectively. The devia-

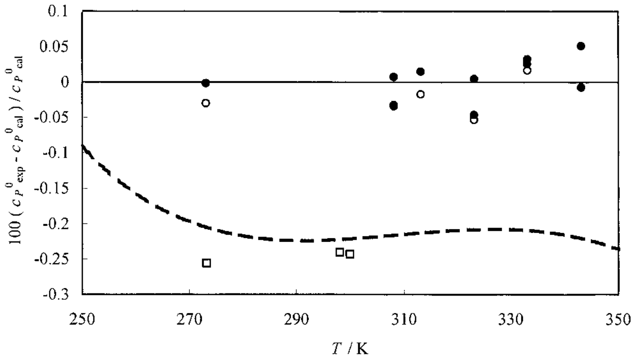

**Figure 4.** Deviation of the present $c_p^0$ values from eq 6 for R-32: (●) this work; (○) Hozumi et al. (1994b); (□) TRC (1989); (—) eq 6; (- - -) McLinden et al. (1993).

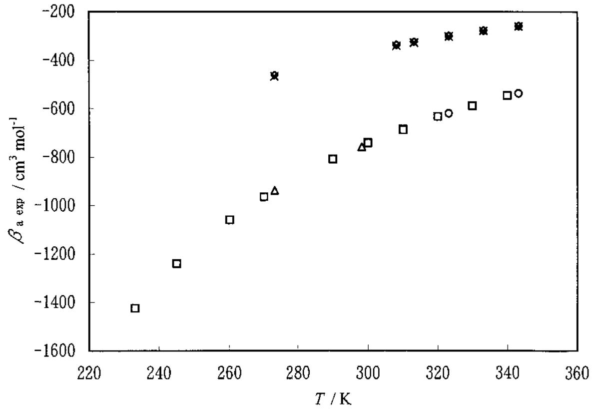

**Figure 5.** Second acoustic virial coefficients for R-134a and R-32. R-134a: (○) this work; (△) Hozumi et al. (1993); (□) Goodwin and Moldover (1990). R-32: (◇) this work; (×) Hozumi et al. (1994b).

tion between the correlation reported by Goodwin and Moldover (1990) and their values is more than 2 times the experimental uncertainty, ±0.10%, for $c_p^0$ reported by Goodwin and Moldover (1990). The present correlation represents the present data, our earlier data (Hozumi et al., 1993), and the values reported by Goodwin and Moldover (1990) within three standard deviations of the present data. The differences between eq 5 and the values reported by TRC (1989) are 2.0%. The values reported by TRC (1989) are calculated from spectroscopic data.

For R-32 the $c_p^0$ correlation below is applicable over the temperature range 273 K to 343 K.

$$\frac{c_p^0}{R} = 3.2980 + 3.5092 \times 10^{-3}(T/\mathrm{K}) + 9.283 \times 10^{-6}(T/\mathrm{K})^2 \quad (6)$$

Figure 4 shows the deviation of the present $c_p^0$ values from the correlation, eq 6, as well as $c_p^0$ values reported by TRC (1989). The broken line is the correlation reported by McLinden et al. (1993). Our values and the refitted values agree with our correlation within ±0.05%, whereas the difference between the present correlation and McLinden's correlation is about 0.20%. McLinden's correlation was based on spectroscopic data (Chase et al., 1985; Rodgers et al., 1974).

The second and third acoustic virial coefficients, $\beta_a$ and $\gamma_a$, for R-134a and R-32 are shown in Figures 5 and 6, respectively. The values $\beta_a$ and $\gamma_a$ for R-134a are in resonably good agreement with those reported by Goodwin and Moldover (1990). The $\gamma_a$ values for R-32 are nearly zero in comparison with those for R-134a.

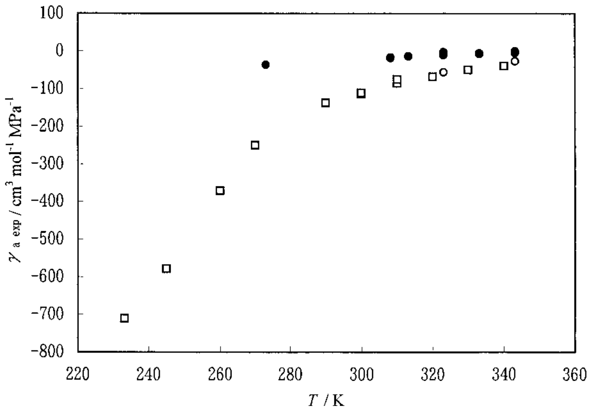

**Figure 6.** Third acoustic virial coefficients for R-134a and R-32. R-134a: (○) this work; (□) Goodwin and Moldover (1990). R-32: (●) this work.

## Acknowledgment

We are indebted to Daikin Industries, Ltd., Osaka, and Showa Denko Co., Ltd., Tokyo, for kindly furnishing the samples.

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Received for review April 30, 1996.[⊗] Accepted July 6, 1996. We are indebted to the Ministry of Education, Science, and Culture, Japan, for the partial financial support as a part of the Grant-in-Aid (No. 04402025). T.H. is also grateful to the Research Fellowships from the Japan Society for the Promotion of Science for Young Scientists.

JE960154N

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[⊗] Abstract published in *Advance ACS Abstracts,* August 1, 1996.