Speed-of-Sound Measurements Using Spherical Resonator and Acoustic Virial Coefficients for Gaseous 1,1,1-Trifluoroethane (R143a)†

Kazuhiro Ogawa, Takeshi Kojima, and Haruki Sato*

Faculty of Science and Technology, Keio University, 3-14-1 Hiyoshi, Kohoku-ku, Yokohama 223-8522, Japan

Speed-of-sound measurement with a spherical resonator is recognized as one of the most precise and reliable approachs to determine ideal-gas heat capacities and to reveal thermodynamic properties of rarefied gases. In this study, we applied a spherical resonator to measure the speed of sound in gaseous 1,1,1-trifluoroethane, R143a. Seventy speed-of-sound values were obtained along five isotherms from 303 K to 343 K and up to 500 kPa in pressure. In addition, $c_p°$ values and acoustic second virial coefficients were determined at each temperature of isotherm. Sample purity was 99.95% of the gas chromatograph area fraction analyzed by the manufacturer. The expanded uncertainties with $k = 2$ are estimated to be 8 mK in temperature, 0.2 kPa in pressure, and 72 ppm in speed of sound. We compared the $c_p°$ values determined from the measurements with those from theoretical calculation and confirmed the agreement between them within ±0.1%.

Introduction

The speed-of-sound values in gaseous hydrofluorocarbon (HFC) refrigerants, not only pure refrigerants of R32,[1] R152a,[2] R134a,[2,3] and R125[4] but also the binary and ternary refrigerants of R32/134a,[5] R32/125,[6] and R32/125/134a,[6] have been measured by using a spherical resonator in our group. The ideal-gas heat capacity $c_p°$ was determined from the measurements for each pure refrigerant. On the other hand, the $c_p°$ can be determined from a theoretical approach on the basis of the spectroscopic data. The theoretical $c_p°$ values of six HFC refrigerants, R23, R32, R125, R134a, R143a, and R152a, have also been calculated in our group[7] by a completely independent approach from the experimental study. The coincidence between the experimental and theoretical $c_p°$ values would be good evidence of the reliability. The experimental results for the speed of sound in R125 and R143a measured by former researchers in our group unfortunately do not satisfy this requirement. The measurements for R125 reported in a paper by Hozumi *et al.*[8] and for R143a[9] or R125/143a[4] presented at academic conferences by Ichikawa *et al.* unfortunately do not agree with the theoretical values within ±0.1%. Those data differ from the theoretical results by several tenths of a percentage, so we do not recommend those data to be used.

We took a long time for more than two years to find the reason for the difference between experimental and theoretical $c_p°$ values. We carefully examined the uncertainty in the measurements, and Yokozeki also examined the mistakes in the theoretical calculations. Finally we found that the reason was not in the theoretical calculations but in the purity of the sample fluids and remeasured the speed of sound by using a different sample fluid from that of previous measurements. New data were obtained using the sample fluid which has 99.95 area % purity of the gas chromatograph area fraction analyzed by the manufacturer.

The ideal-gas heat capacity and the second acoustic-virial coefficient β_a were finally determined for R143a from the speed-of-sound measurements in this study.

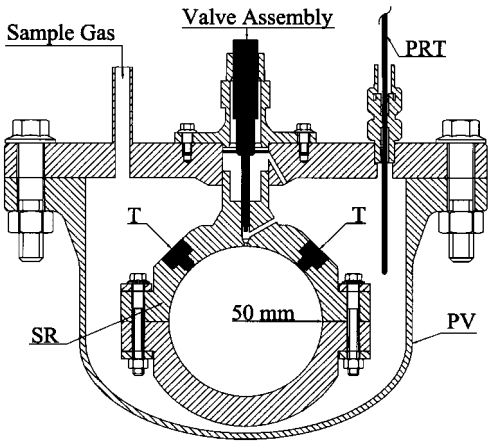

Figure 1. Cross section of spherical resonator and pressure vessel: T, transducers; PRT, platinum resistance thermometers; PV, pressure vessel; SR, spherical resonator.

Experimental Procedure

An explanation of the experimental procedure was reported in the previous paper.[2] The main part of the apparatus is illustrated in Figure 1. A pressure vessel, PV, and spherical resonator, SR, were immersed in the silicon oil heat transfer medium of a thermostat bath, and sample gas was introduced into both of them. The inside and outside of the spherical resonator were filled with the common sample gas, and its radius depended only on temperature. The sample fluid temperature was directly measured by a sheathed platinum resistance thermometer, PRT. The pressure was measured with a digital quartz pressure gauge.

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* To whom correspondence should be addressed.

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Table 1. Speed of Sound in R143a

p/kPa	W/m·s^{-1}	p/kPa	W/m·s^{-1}	p/kPa	W/m·s^{-1}
303.143 K		313.144 K		323.133 K	
505.52	171.282	508.06	175.148	497.43	179.103
401.15	173.862	401.18	177.508	401.00	181.010
300.90	176.266	300.71	179.668	300.95	182.950
200.78	178.599	200.95	181.762	201.12	184.849
180.54	179.064	180.66	182.184	180.84	185.231
160.74	179.516	160.86	182.593	160.67	185.610
140.68	179.971	140.68	183.008	140.84	185.979
120.75	180.420	120.84	183.414	120.65	186.355
100.76	180.869	100.69	183.824	100.78	186.723
80.80	181.315	80.77	184.228	80.54	187.096
60.80	181.760	60.62	184.635	60.69	187.462
40.77	182.203	40.73	185.035	40.56	187.832
20.70	182.645	20.72	185.437	20.59	188.198
10.74	182.868	10.69	185.638	10.65	188.380
333.141 K		343.142 K			
501.45	182.583	502.43	185.977		
401.20	184.371	401.19	187.615		
301.04	186.130	301.10	189.214		
200.79	187.862	200.91	190.793		
180.66	188.208	180.87	191.108		
160.80	188.548	159.76	191.437		
140.38	188.896	140.75	191.734		
120.76	189.229	120.81	192.043		
100.77	189.568	100.82	192.353		
80.69	189.907	80.64	192.665		
60.76	190.243	60.69	192.973		
40.70	190.580	40.43	193.286		
20.51	190.920	20.73	193.592		
10.64	191.087	10.73	193.747		

After confirming a stable thermodynamic equilibrium condition, the frequency, amplitude, and phase difference were measured using a lock-in amplifier for the four different radially symmetric resonance modes 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 the half-width, $g_{l,n}$, which were calculated from those measurements. The relation among W, $f_{l,n}$, and $g_{l,n}$ is given by eq 1, which was derived and used by Ewing *et al.*[10] in their data processing for spherical resonator measurements

$$f_{l,n} - ig_{l,n} = \frac{WZ_{l,n}}{2\pi a} + \sum_j (\Delta f - i\Delta g)_j \qquad (l = 0, 1, 2, \ldots;\ n = 0, 1, 2, \ldots) \quad (1)$$

where a is the radius of the spherical resonator (about 50 mm) that is a linear function of temperature and $Z_{l,n}$ is the n-th root of the equation $dj_l(z)/dz = 0$; $j_l(z)$ is the l-th order spherical Bessel function. A certain mode is expressed by (l, n), while $l = 0$ denotes the radially symmetric mode. The second term on the right-hand side is a series of perturbation terms to represent various nonideal conditions. Four radially symmetric resonance modes, (0, 2) through (0, 5), were used in the data processing. When a series of measurements was completed at a certain state point, we reduced the pressure very carefully under the isothermal conditions for the succeeding measurements at lower pressure and measured at 14 different pressures along each isotherm between 303 K and 343 K.

Result and Discussion

The expanded uncertainties based on the ISO Guide (1993) in temperature, pressure, and speed-of-sound measurements are estimated to be 8.0 mK, 0.2 kPa, and 72 ppm, respectively, where the coverage factor, k, is 2. The purity of the sample fluid analyzed by the manufacturer was better than 99.95 area % in the gas chromatograph area fraction. No further purification except degassing was conducted by the authors.

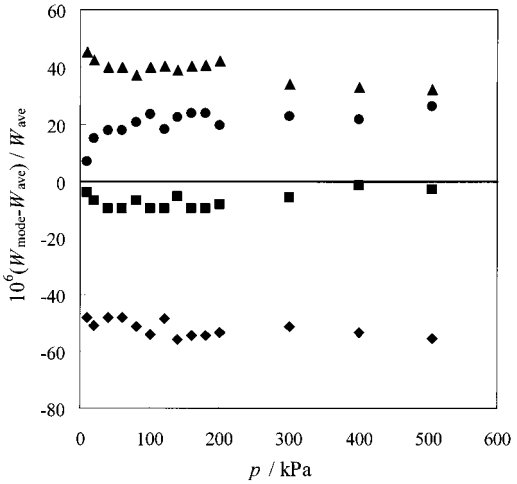

Figure 2. Difference among the speed-of-sound values obtained from different mode measurements: ●, (0, 2); ■, (0, 3); ♦, (0, 4); ▲, (0, 5).

Seventy speed-of-sound values in gaseous R143a were measured along five isotherms from 303 K to 343 K and at pressures from about 500 kPa down to 10 kPa, as listed in Table 1. The listed data are the average values of the speed-of-sound measurements obtained for four different radially symmetric resonance modes from (0, 2) to (0, 5) at a certain state point. There is about 100 ppm difference among speed-of-sound values determined from the data at different modes, as shown in Figure 2. This difference was considered to be caused by the roughness of the inner surface and distortion of the diameters being within ±50 μm in total. From the experiences of measurements for other substances, we used the average of the measurements for the four different modes.

The thermophysical property values used in the perturbation terms of eq 1 for corrections to the measurements are preliminary ideal-gas heat capacity and a virial equation of state with provisional virial coefficients, the viscosity estimated by the group contribution method,[11] and the thermal conductivity estimated from the modified Eucken equation.[11] A contribution of the perturbation terms is estimated as being an order of magnitude of 100 ppm to speed-of-sound values, and the combined standard uncertainty due to these corrections was estimated as 10 ppm in the speed-of-sound values.

The squared measured speed-of-sound data were correlated along each isotherm with the following quadratic function of pressure

$$W^2 = \frac{\gamma^\circ RT}{M}\left\{1 + \beta_a\left(\frac{p}{RT}\right) + \gamma_a\left(\frac{p}{RT}\right)^2\right\} \qquad (2)$$

where γ° denotes the ideal-gas specific heat ratio, R is the molar gas constant, M is the molar mass, β_a is the second acoustic-virial coefficient, and γ_a is the third acoustic-virial-like coefficient, which works as a correction term of eq 2. We used the molar gas constant[12] of 8.314 472 J·mol^{-1}·K^{-1}.

The deviation of the experimental speed-of-sound values from eq 2 is shown in Figure 3. The baseline in Figure 3 is the calculated results from eq 2. All measurements are well represented by eq 2 with the standard deviation of 7.5 ppm and within the maximum deviation of 26 ppm.

The ideal-gas heat capacity, c_p°, and the β_a and γ_a values determined from the speed-of-sound measurements are listed in Tables 2 and 3, respectively. The c_p° and the β_a

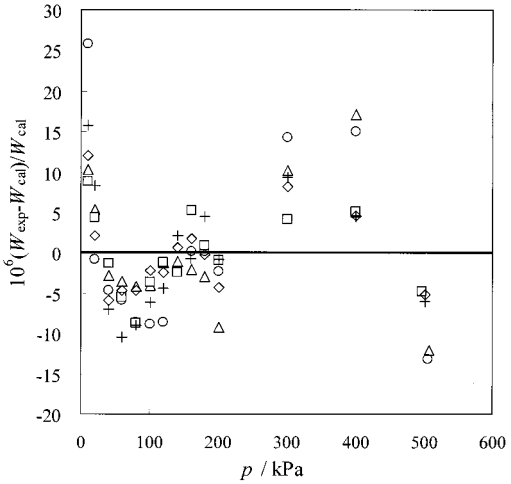

Figure 3. Deviation of the experimental speed-of-sound values from eq 2: ○, 303 K; △, 313 K; □, 323 K; ◇, 333 K; +, 343 K.

Table 2. Determined $c_p°$ Values for R143a Based on the Speed-of-Sound Measurements

T/K	$c_p°/R$	standard deviation/%
303.143	9.487	0.033
313.144	9.704	0.028
323.133	9.903	0.025
333.141	10.098	0.025
343.142	10.295	0.029

Table 3. Second Acoustic-Virial Coefficient, β_a, and γ_a of Eq 2 for R143a

T/K	β_a / cm^3·mol^{-1}	standard deviation/%	γ_a / dm^6·mol^{-2}	standard deviation/%
303.143	−600.5	0.13	−0.111	3.4
313.144	−557.0	0.10	−0.082	3.5
323.133	−517.8	0.08	−0.059	3.5
333.141	−483.5	0.09	−0.036	6.6
343.142	−451.1	0.14	−0.022	16

and γ_a values were simply determined from eq 2 at each temperature. The standard deviations of $c_p°$, β_a, and γ_a in the regression procedure of eq 2 for the squared speed-of-sound measurements are shown for each isotherm in Tables 2 and 3.

We compared the $c_p°$ values determined from the speed-of-sound measurements with those from theoretical calculation. The agreement between them was within ±0.1%, as shown in Figure 4. It should be noticed that the experimentally determined $c_p°$ values agree with the theoretical calculation, but they were measured after the theoretical calculation by Yokozeki *et al.*[7] and they had correctly calculated $c_p°$ without experimental information. The $c_p°$ equation was developed on the basis of the theoretically derived values, which is effective in the practically important temperature range between 200 K and 500 K.

$$c_p° = 1.8567 + 10.14777T_r - 1.48667T_r^2 - 0.16996T_r^3 \quad (3)$$

$$T_r = T/T_c, \quad T_c = 345.860\ \text{K}^{13}$$

The baseline of Figure 4 is calculated values from eq 3. The data reported by Ichikawa *et al.*[9] were measured with the same spherical resonator but for a different sample fluid in 1997. At the time we had not known the errors in measurements because our results were placed between

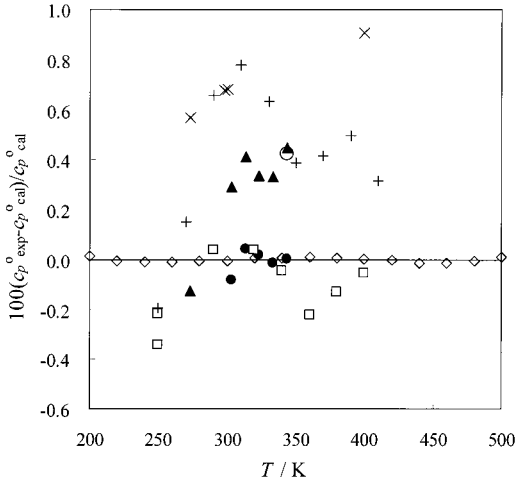

Figure 4. Deviations of ideal-gas heat capacity values of R143a measured by different researchers or theoretical calculations by Yokozeki *et al.*[7] and by TRC:[16] ●, this work; ▲, Ichikawa *et al.*;[9] ○, this work; ◇, Yokozeki *et al.*;[7] +, Beckermann and Kohler;[14] □, Gillis;[15] ×, TRC.[16]

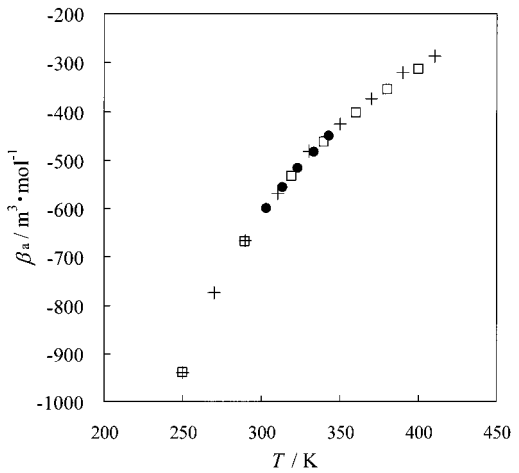

Figure 5. Second acoustic-virial coefficient of R143a: ●, this work; +, Beckermann and Kohler;[14] □, Gillis.[15]

the results reported by Beckermann and Kohler[14] and the results by Gillis.[15] We had carefully examined the reason our $c_p°$ values differing from theoretically determined values, while $c_p°$ values for other HFC refrigerants determined from our measurements were coincident with the theoretical calculation by Yokozeki *et al.*[7] within ±0.1%. Yokozeki had also tried to check his theoretical calculations for R143a several times with the greatest care. In 1999 we had a chance to get a new sample fluid produced by a different manufacture from the previous one. The purity was worse than before, but the results completely agreed with those from theoretical calculations, as shown by filled circles in Figure 4. We tried to check the reproducibility by measuring the speed of sound using a previous sample fluid at 343 K. The datum is shown as an open circle in Figure 4. The datum obtained using the previous sample fluid completely agrees with previous measurements shown by filled triangles in Figure 4.

The β_a and γ_a are shown Figures 5 and 6, respectively. The β_a and γ_a values are in reasonably good agreement with those reported by Beckermann and Kohler[14] and Gillis.[15]

Conclusions

Seventy speed-of-sound values were measured in gaseous 1,1,1-trifluoroethane, R143a, at temperatures between 303

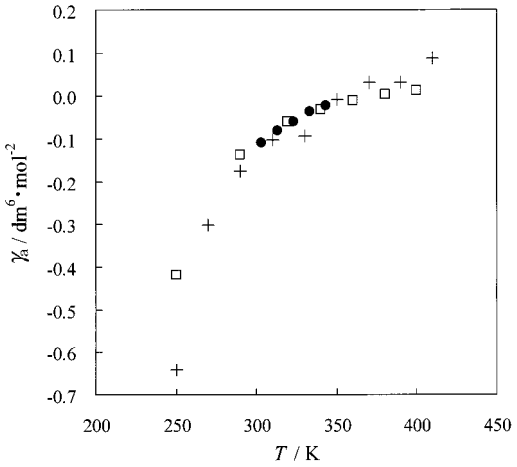

Figure 6. Third acoustic-virial-like coefficient, γ_a, in eq 2: ●, this work; +, Beckermann and Kohler;[14] □, Gillis.[15]

K and 343 K and at pressures between 10 kPa and 508 kPa with expanded uncertainties (k = 2) of 8 mK in temperature, 0.2 kPa in pressure, and 72 ppm in speed of sound. On the basis of speed-of-sound measurements, the second acoustic virial coefficient was determined. In addition, we could confirm the reliability of the theoretical calculation of ideal-gas heat capacity values for R143a by determining $c_p°$ from the speed-of-sound measurements and developed the $c_p°$ equation that is effective between 200 K and 500 K. The uncertainty was estimated to be within ±0.1%.

Acknowledgment

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