Speed-of-Sound Measurements Using Spherical Resonator and Acoustic Virial Coefficients for Gaseous Pentafluoroethane (R125)

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Speed-of-sound measurement with a spherical resonator is recognized as one of the most precise and reliable approaches to determine ideal-gas heat capacities and to reveal thermodynamic properties of rarefied gases. In this study, a spherical resonator was used to measure the speed of sound in gaseous pentafluoroethane, R125. Eighty speed-of-sound values were obtained along five isotherms from 277 K to 343 K and up to 600 kPa in pressure. In addition, $c_p°$ values and second acoustic virial coefficients were determined at each temperature. Sample purity was 99.9% of the gas-chromatograh area fraction analyzed by the manufacturer. The expanded uncertainties with $k = 2$ are estimated at 11 mK in temperature, 0.31 kPa in pressure, and 72 ppm in speed of sound. The $c_p°$ values reported here were compared with those from spectroscopic data. The agreement between them was within ±0.2%.

Introduction

The speed-of-sound values in gaseous hydrofluorocarbon (HFC) refrigerants, not only pure refrigerants of R32,[1,3] R152a,[2] R134a,[2,3] R125,[4] and R143a,[4,5] but also the binary and ternary refrigerants of R32 + R134a,[6] R32 + R125,[7] R32 + R125 + R134a,[7] have been measured using a spherical resonator in our group. The ideal-gas heat capacity $c_p°$ was determined from the measurements for each pure refrigerant. The $c_p°$ can also be determined from statistical thermodynamics using spectroscopic data. The statistical thermodynamic $c_p°$ values of six HFC refrigerants, R23, R32, R125, R134a, R143a, and R152a, have been calculated from spectroscopic data by Yokozeki et al.[8] with an independent approach from the present experimental study. The coincidence between experimental and statistical $c_p°$ values would be the evidence of the reliability of experimental data.[9] We have compared our experimental and statistical results for five HFC refrigerants. The measurements for R125 reported in a paper by Hozumi et al.[10] and for R143a[11] or R125 + R143a[4] presented by Ichikawa et al.[4] unfortunately do not provide reliable $c_p°$ values. Those $c_p°$ values disagree with the statistical values by as much as 1%.

Two years were necessary to find the reason for the difference between experimental and statistical $c_p°$ values of R125. Careful examination for the uncertainty in measurements and in the statistical calculations was done by the present authors and by Yokozeki, respectively. The reason for the difference was not in the statistical calculations but in the purity of the sample fluids and remeasured the speed of sound by using a different sample fluid from that of the previous measurement. New data were obtained using the sample fluid, which has 99.9% of the gas-chromatograph area fraction analyzed by the manufacturer.

More reliable ideal-gas heat capacity and the second acoustic virial coefficient β_a are derived for R125 from the speed-of-sound measurements reported in this work.

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Experimental Procedure

An explanation of the experimental procedure was reported in the previous paper.[2] A new thermostat bath was introduced recently, which was controlled within ±0.5 mK. The new data at 277 K and 343.135 K were measured with the new thermostat bath. The speed of sound, w, was determined from the values of the resonance frequency, $f_{l,n}$, and half-width, $g_{l,n}$, which were obtained from the 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.[12] in their data processing for spherical resonator measurements

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

where a is the radius of spherical resonator, about 50 mm, and is the linear function of temperature and $Z_{l,n}$ is the nth root of the equation $\mathrm{d}j_l(z)/\mathrm{d}z = 0$; $j_l(z)$ is the lth order spherical Bessel function. A certain mode is expressed by (l, n), while $l = 0$ denotes the radially symmetric mode of the resonance in the spherical resonator. The second term on the right-hand side is a series of perturbation terms to compensate for various nonideal conditions. Four spherically symmetric modes, (0, 2) through (0, 5), were used in the data processing for determining the speed of sound. There is no (0, 1) mode because the turning point for $j_0(r)$ occurs at $r = 0$. The lowest possible radial mode is therefore (0, 2). When a series of measurements was completed at a certain temperature and pressure, the pressure of sample fluid was reduced slowly under the isothermal condition for other measurements at lower pressure. Speed-of-sound was measured along each isotherm between 277 K and 343 K.

Result and Discussion

The expanded uncertainties in temperature, pressure, and speed-of-sound measurements are estimated according to the International Organization for Standardization

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Table 1. Speed of Sound in Gaseous R125

277.164 K		303.137 K		313.152 K		323.143 K		343.141 K		343.135 K	
p/kPa	w/m·s^{-1}	p/kPa	w/m·s^{-1}	p/kPa	w/m·s^{-1}	p/kPa	w/m·s^{-1}	p/kPa	w/m·s^{-1}	p/kPa	w/m·s^{-1}
198.80	140.826	465.23	143.190	480.34	146.116	501.38	148.851	501.32	154.676	600.30	153.405
180.84	141.258	398.68	144.475	400.70	147.489	400.83	150.409	399.77	155.957	500.26	154.681
161.07	141.727	300.92	146.318	300.67	149.175	300.75	151.926	300.55	157.187	400.48	155.939
141.08	142.198	200.32	148.157	200.47	150.822	200.71	153.412	200.46	158.413	300.29	157.186
121.01	142.666	180.99	148.505	180.78	151.142	180.33	153.713	180.84	158.651	197.50	158.442
101.09	143.127	160.84	148.865	160.71	151.466	160.95	153.997	160.64	158.896	180.90	158.645
80.97	143.587	140.84	149.220	140.78	151.786	140.92	154.288	140.63	159.137	160.51	158.892
60.65	144.049	120.91	149.571	120.77	152.106	120.86	154.579	120.90	159.375	140.89	159.130
40.92	144.494	100.78	149.925	100.57	152.427	100.74	154.869	100.55	159.619	120.73	159.373
20.94	144.941	80.27	150.282	80.59	152.743	80.84	155.155	80.48	159.860	100.97	159.611
		60.79	150.621	60.28	153.063	60.80	155.442	59.94	160.107	80.21	159.860
		40.75	150.968	40.59	153.372	40.64	155.730	40.77	160.336	60.62	160.094
		20.76	151.314	20.68	153.683	20.42	156.018	20.77	160.578	40.76	160.332
		10.51	151.496	10.50	153.843	10.70	156.160				

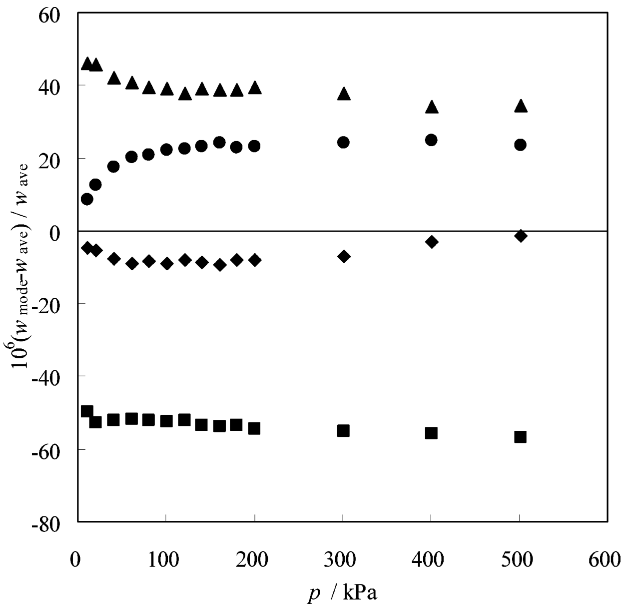

Figure 1. Difference among the speed-of-sound values obtained from different-mode measurements: ●, (0, 2); ■, (0, 3); ◆, (0, 4); ▲, (0, 5).

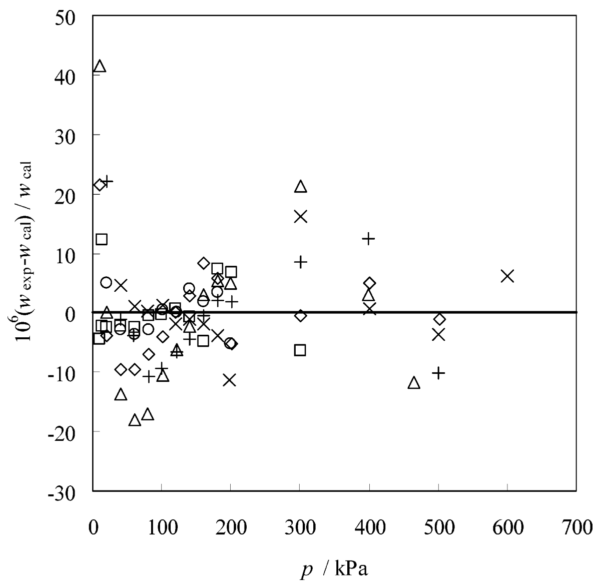

Figure 2. Deviations of the experimental speed-of-sound values from eq 2: ○, 277.164 K; △, 303.137 K; □, 313.152 K; ◇, 323.145 K; +, 343.141 K; ×, 343.135 K.

Guide (1993) being 11 mK, 0.31 kPa, and 72 ppm, respectively, where the coverage factor, k, is 2.

Eighty speed-of-sound values in gaseous R125 were measured along five isotherms from 277 K to 343 K and at pressures from about 600 kPa down to 10 kPa as listed in Table 1. The values are the average of the speed-of-sound measurements obtained at four different radically symmetric resonance modes from (0, 2) to (0, 5). There is about 100 ppm difference among speed-of-sound values determined at different modes as shown in Figure 1. From experiences of measurements for other substances, the average of the measurements at the four different modes was used.

Thermophysical property values used in the perturbation terms[12] of eq 1 are the preliminary ideal-gas heat capacity, a virial equation of state with provisional virial coefficients, viscosity estimated from the group contribution method,[13] and thermal conductivity estimated from the modified Eucken equation.[13] A contribution of the perturbation terms is estimated as being an order of magnitude of 100 ppm to the speed-of-sound value and the combined standard uncertainty due to these corrections was estimated as 10 ppm in the speed-of-sound value.

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

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

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. We used the molar gas constant[14] of 8.314472 J·mol^{-1}·K^{-1}.

The deviation of the experimental speed-of-sound values from eq 2 is shown in Figure 2. The baseline in Figure 2 is the calculated values from eq 2. All measurements are well represented by eq 2 with the standard deviation of 14 ppm and within the maximum deviation of 42 ppm at low pressure near 10 kPa.

Ideal-gas heat capacity, c_p°, and acoustic virial coefficients of β_a and γ_a determined from two series of speed-of-sound measurements are listed in Tables 2 and 3, respectively. c_p°, β_a, and γ_a were determined by fitting eq 2 to the squared speed-of-sound measurements at each temperature. The maximum standard deviations of c_p°, β_a, and γ_a in the regression procedure of eq 2 to the squared

Table 2. Determined $c_p°$ Values for R125 Based on the Speed-of-Sound Measurements

T/K	$c_p°/R$	uncertainty due to fitting/%
277.164	10.889	0.034
303.137	11.482	0.055
313.152	11.720	0.031
323.143	11.939	0.038
343.141	12.354	0.062
343.135	12.367	0.036

Table 3. Second and Third Acoustic Virial Coefficients, β_a and γ_a, for R125

T/K	β_a/cm^3·mol^{-1}	uncertainty due to fitting/%	γ_a/dm^6·mol^{-2}	uncertainty due to fitting/%
277.164	−698.0	0.13	−0.234	3.9
303.137	−566.5	0.24	−0.123	5.7
313.152	−523.7	0.08	−0.094	2.3
323.143	−485.9	0.15	−0.070	5.4
343.141	−422.0	0.37	−0.026	33
343.135	−420.7	0.13	−0.035	6.9

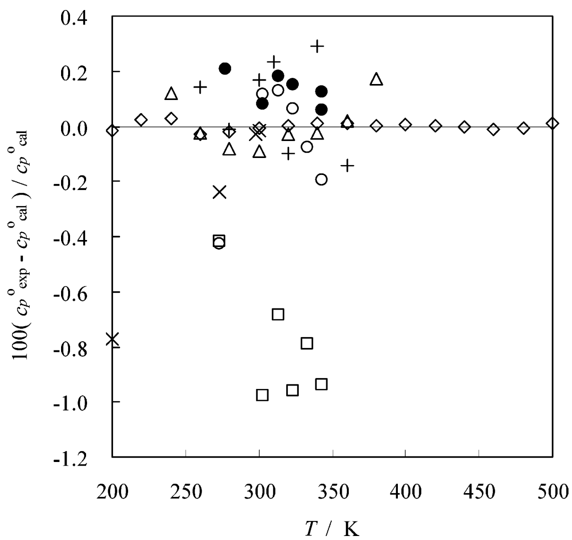

Figure 3. Deviations of ideal-gas heat-capacity values of R125 measured by different researchers or statistical calculations based on spectroscopic data from the equation of Sato et al.:[9] ●, this work; ○, Ichikawa et al.;[4] □, Hozumi et al.;[10] ◇, Yokozeki et al.;[8] +, Grigiante et al.;[16] △, Gillis;[17] ×, TRC.[18]

speed-of-sound measurements are 0.062%, 0.37%, and 33%, respectively.

The $c_p°$ values determined from the speed-of-sound measurements were compared with those from statistical calculation by Yokozeki et al.[8] The agreement between them was within ±0.2% as shown in Figure 3. It should be noted that our measurements were obtained after the statistical calculation by Yokozeki et al.[8] The $c_p°$ equation was developed by Sato et al.[9] on the basis of the statistical values by Yokozeki et al.,[8] which is effective in the practically important temperature range between 200 K and 500 K

$$c_p°/R = 3.0614 + 10.7918T_r - 1.2173T_r^2 - 0.36795\,T_r^3 \tag{3}$$

$$T_r = T/T_c \qquad T_c = 339.165 \text{ K}^{15}$$

The baseline of Figure 3 is the calculated values from eq 3. The data reported by Ichikawa et al.[4] were measured with the same spherical resonator used in this work but

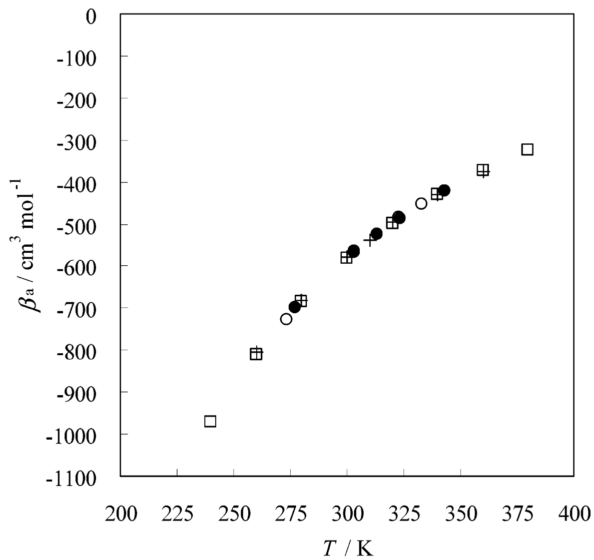

Figure 4. Second acoustic virial coefficient of R125: ●, this work; ○, Ichikawa et al.;[4] +, Grigiante et al.;[16] □, Gillis.[17]

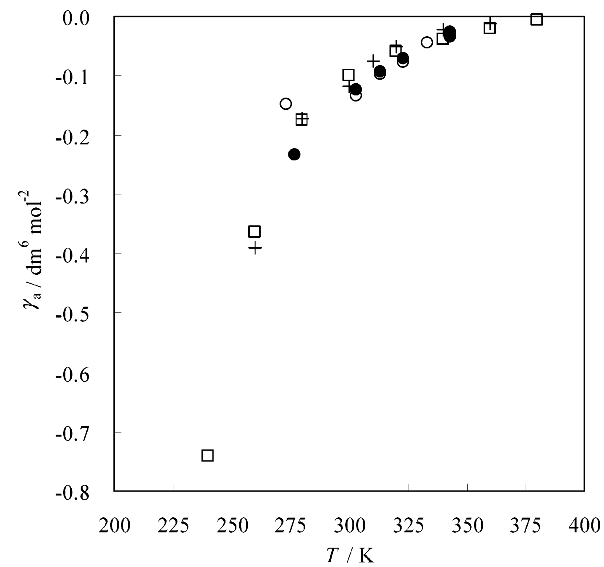

Figure 5. Third acoustic virial-like coefficient, γ_a, in eq 2: ●, this work; ○, Ichikawa et al.;[4] +, Grigiante et al.;[16] □, Gillis.[17]

for a different sample fluid in 1998. They have the systematic deviation at high and low temperature.

The β_a and γ_a are shown in Figures 4 and 5, respectively. The β_a and γ_a values are in good agreement with those reported by Grigiante et al.[16] and Gillis.[17]

Conclusions

Eighty speed-of-sound values were measured in gaseous R125 at temperatures between 277 K and 343 K and at pressures between 10 kPa and 600 kPa with expanded uncertainties ($k = 2$) of 11 mK in temperature, 0.31 kPa in pressure, and 72 ppm in speed of sound. On the basis of the speed-of-sound measurements, the second acoustic virial coefficient was determined. In addition, the reliability of statistical calculation of ideal-gas heat-capacity values for R125 was confirmed on the basis of the present measurements. The uncertainty of determined $c_p°$ was estimated within ±0.2%.

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