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Speed of Sound in Gaseous Difluoromethane

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The speed of sound in gaseous difluoromethane (HFC-32, CH_2F_2) has been measured by means of a spherical acoustic resonator. Sixty-seven speed of sound values were measured with an accuracy of ±0.01% at temperatures from 273 to 343 K and pressures from 20 to 250 kPa. The ideal-gas specific heats and the second acoustic virial coefficients have been determined on the basis of the speed of sound measurements. The second virial coefficients calculated from the present speed of sound measurements agree satisfactorily with literature values which were determined from pressure–volume–temperature measurements.

Introduction

Measurement of the speed of sound by a spherical resonator is recognized as one of the most accurate methods for determining the thermodynamic properties of very dilute gases. A spherical acoustic resonator was constructed for measuring the speed of sound in gaseous fluids from which the ideal-gas specific heats and the second virial coefficients can be obtained. Using this method the speed of sound in gaseous 1,1,1,2-tetrafluoroethane (HFC-134a, CF_3CH_2F) and 1,1-difluoroethane (HFC-152a, CHF_2CH_3) has previously been measured with an accuracy of ±0.01% (*1–4*). A hydrofluorocarbon, difluoromethane (HFC-32, CH_2F_2), is expected to be a promising component of the binary and/or ternary refrigerant mixtures to replace chlorodifluoromethane (HCFC-22, $CHClF_2$) because of its zero ozone-depleting potential. Few thermophysical property measurements have been reported for HFC-32, and in particular no direct measurements of the speed of sound.

In this paper we report 67 speed of sound measurements in gaseous HFC-32 at temperatures from 273 to 343 K and pressures from 20 to 250 kPa. The ideal-gas specific heats and the second virial coefficients have been calculated from these speed of sound measurements.

Experimental Section

The experimental apparatus and procedure have been reported in detail in our previous publication (*4*): only a brief explanation is given here. The detailed discussion on the theory of spherical acoustic resonances was given by Moldover et al. (*5–9*). The experimental apparatus, shown in Figure 1, consists of a spherical resonator (S) whose inner radius is about 50 mm, a pressure vessel (Q), platinum resistance thermometers (E_1 and E_2), two transducers (M_1 as sound generator and M_2 as sound detector), devices A–I which are temperature control and measuring subsystems and J–K which are the signal-detecting devices, and a thermostated bath (U) which was filled with water or silicone oil. In addition, the inside and outside of the spherical resonator S were filled with sample gas.

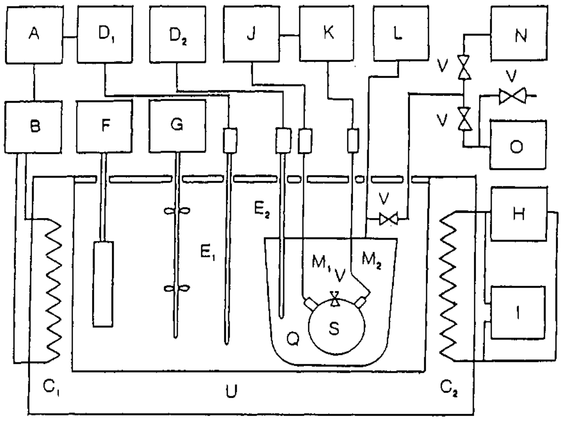

Figure 1. Experimental apparatus: A, PID controller; B, thyristor regulator; C_1, C_2, heaters; D_1 and D_2, thermometer bridges; E_1, E_2, platinum resistance thermometers; F, refrigeration unit; G, stirrer; H, transformer; I, voltmeter; J, frequency synthesizer; K, lock-in amplifier; L, pressure gauge;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

The speed of sound W was determined from the values of resonance frequency and half-width $f_{l,n}$ and $g_{l,n}$ which were measured at the condition of radially symmetric mode resonance of the sample gas in the resonator. The relation among W, $f_{l,n}$, and $g_{l,n}$ is given by a complex resonance expression (*6*):

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

$$l = 0, 1, 2, ...; \quad n = 0, 1, 2, ...$$

where a and $Z_{l,n}$ in the first term on the right-hand side are the radius of the spherical resonator and nth root of the lth-order Bessel function, respectively. And each mode is expressed by (l, n), while the value of l is zero in the case of the radially symmetric mode. The second term on the right-hand side is a series of perturbation terms to represent various nonideal conditions.

After confirming the thermodynamic equilibrium condition, the temperature and pressure of the sample gas and the quantities $f_{l,n}$ and $g_{l,n}$ were measured.

When a series of measurements at radially symmetric modes was completed at a certain pressure and temperature, we changed the pressure at the same temperature for succeeding measurements.

The experimental uncertainties in the speed of sound, temperature, and pressure measurements are estimated to

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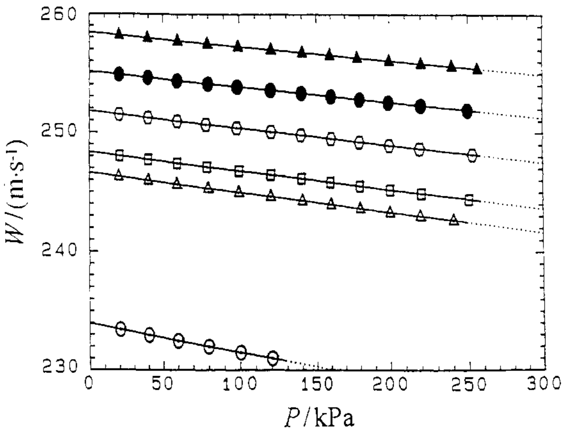

Figure 2. Speed of sound data for HFC-32: ○, 273 K; △, 308 K; □, 313 K; ⬡, 323 K; ●, 333 K; ▲, 343 K.

Table 1. Speed of Sound in HFC-32

T/K	P/kPa	$W/(\mathrm{m\cdot s^{-1}})$	T/K	P/kPa	$W/(\mathrm{m\cdot s^{-1}})$
273.155	120.29	230.995	323.149	179.93	249.209
	100.37	231.484		160.38	249.489
	80.04	231.979		139.46	249.787
	60.08	232.462		120.19	250.061
	40.29	232.939		98.63	250.368
	20.35	233.417		78.93	250.648
				60.05	250.916
308.157	240.29	242.622		40.07	251.203
	219.45	242.974		19.93	251.482
	200.20	243.297			
	180.38	243.628	333.149	249.70	251.876
	160.15	243.965		220.04	252.263
	140.27	244.295		199.39	252.532.
	119.75	244.634		180.10	252.783
	99.72	244.964		160.32	253.040
	80.17	245.285		139.82	253.306
	59.71	245.620		119.98	253.562
	40.04	245.942		99.06	253.832
	19.49	246.274		80.27	254.074
				60.01	254.336
313.151	250.31	244.392		39.79	254.592
	220.15	244.874		19.73	254.853
	200.14	245.192			
	180.04	245.511	343.147	256.29	255.383
	159.78	245.831		239.51	255.584
	139.74	246.147		220.15	255.813
	119.96	246.458		199.80	256.055
	99.91	246.772		178.41	256.308
	79.39	247.093		159.38	256.533
	59.84	247.398		140.34	256.759
	39.98	247.707		120.28	256.995
	20.18	248.012		99.61	257.239
				79.79	257.473
323.149	252.75	248.164		60.20	257.705
	219.21	248.646		39.46	257.948
	199.84	248.924		19.81	258.182

be not greater than ±0.01%, ±9 mK, and ±0.3 kPa, respectively.

The purity of HFC-32 purified and analyzed gas chromatographically by the manufacturer was better than 99.99 mass %. We have not purified the sample by ourselves but simply relied on the available purity data supplied by the manufacturer.

Note that we are using the International Temperature Scale of 1990 (ITS-90) throughout the present paper.

Results

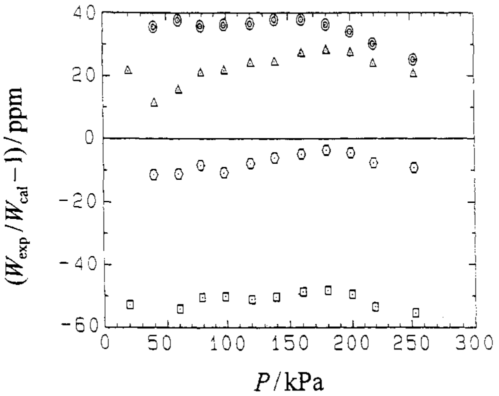

Figure 3. Deviation of the present measurements from eq 2 at 323.149 K for several radially symmetric modes (l, n): △, (0, 2); □, (0, 3); ○, (0, 4); ◎, (0, 5).

Table 2. Ideal-Gas Specific Heat and Second Acoustic Virial Coefficient for HFC-32

T/K	$C_p°/R$	$\beta_a/(\mathrm{cm^3\cdot mol^{-1}})$	T/K	$C_p°/R$	$\beta_a/(\mathrm{cm^3\cdot mol^{-1}})$
273.155	4.9477	-467.3	323.149	5.3985	-302.1
308.157	5.2591	-340.9	333.149	5.4983	-279.1
313.151	5.3063	-327.1	343.147	5.5948	-259.5

Sixty-seven speeds of sound in gaseous HFC-32 have been measured at temperatures from 273 to 343 K (ITS-90) and pressures from 20 to 250 kPa, which are listed in Table 1 and shown in Figure 2. These results are the average values of (0, 2)–(0, 5) radially symmetric modes. The measured speed of sound data were correlated along each isotherm with the following linear squared function of pressure:

$$W^2 = A_0 + A_1 P \qquad (2)$$

where A_0 and A_1 are numerical constants. The solid curves in Figure 2 represent the calculated results from eq 2, while the dashed lines are the extrapolated results of eq 2. The thermophysical properties used in evaluating the perturbation terms are the second virial coefficient (*10*), the ideal-gas specific heat (*11*), the viscosity values calculated from the equation reported by Reichenberg (*12*), and the thermal conductivity values estimated by using the modified Eucken equation (*12*).

Discussion

Figure 3 shows the deviation of the present measurements from eq 2 at 323.149 K for four different radially symmetric modes (0, 2)–(0, 5). The measurements at each mode show systematic deviations from the correlation. A similar tendency was also found for the measurements along other isotherms, although their deviations from the correlation were only within ±60 ppm. We consider that such minor deviations are due to the contribution by the resonance frequency, radius of spherical resonator, and perturbation terms in eq 1. The estimated uncertainties in the resonance frequency, radius of the spherical resonator, and perturbation terms are about ±10, ±70, and about ±20 ppm, respectively. In conclusion, we consider that the experimental uncertainty in the present speed of sound measurements is not greater than ±0.01% even if we include the scatter of the results with four different modes at each temperature.

The ideal-gas specific heat, $C_p°$, and the second acoustic virial coefficient, β_a, determined from the present measurements, are summarized in Table 2. The ideal-gas specific heat and the acoustic virial coefficient are derived by the regression analysis of the present speed of sound measurements. The method of analysis for $C_p°$ and β_a has been reported in our previous publication (*4*). The standard deviations for $C_p°$ and β_a were calculated as ±0.035% and ±0.17%, respectively. The $C_p°$ correlation was developed as follows:

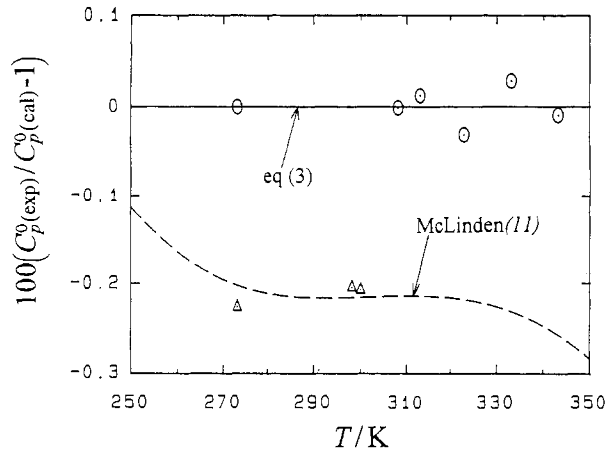

Figure 4. Comparison of $C_p°$ values with eq 3: ○, this work; △, TRC (*13*); - - -, McLinden (*11*); —, eq 3.

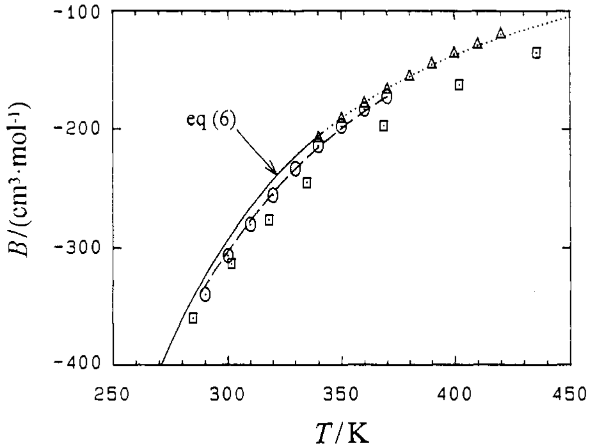

Figure 5. Comparison of second virial coefficients: ○, Qian et al. (*10*); △, Sato et al. (*16*); □, TRC (*13*); - - -, Qian et al. (*10*); — ···, eq 6.

$$C_p°/R = 3.3711 + 3.0006 \times 10^{-3}(T/\mathrm{K}) + 1.0145 \times 10^{-5}(T/\mathrm{K})^2 \quad (3)$$

where R is the universal gas constant, 8.314 471 J·mol⁻¹·K⁻¹, reported by Moldover (*6*) in 1988.

Figure 4 shows the deviation of the present $C_p°$ values as well as reported $C_p°$ values (*13*) from the correlation, eq 3. The broken curve shows a correlation reported by McLinden (*11*). Our data agree with our correlation within ±0.03%, and the difference between the present correlation and McLinden's correlation is about 0.2%, although both correlations represent similar behavior in temperature dependence. It should be noted that McLinden (*11*) developed his correlation on the basis of spectroscopic data by Rodgers et al. (*14*) and JANAF (*15*). Therefore, it seems clear that his correlation also reproduces similar data by TRC (*13*).

On the other hand, β_a was correlated by the expression

$$\beta_a/(\mathrm{cm^3{\cdot}mol^{-1}}) = -2.9523 \times 10^3 + 13.9835(T/\mathrm{K}) - 1.7885 \times 10^{-2}(T/\mathrm{K})^2 \quad (4)$$

The thermodynamic relation between β_a and B is given below (*6*):

$$\beta_a = 2B + 2(\gamma° - 1)T\frac{\mathrm{d}B}{\mathrm{d}T} + \frac{(\gamma° - 1)^2}{\gamma°}T^2\frac{\mathrm{d}^2B}{\mathrm{d}T^2} \quad (5)$$

where $\gamma°$ is the ideal-gas specific heat ratio.

The second virial coefficient, B, was correlated as

$$B/(\mathrm{cm^3{\cdot}mol^{-1}}) = 0.092[1 - 215\{\exp(828/(T/\mathrm{K})) - 1\}] \quad (6)$$

This functional form is determined by using the square-well potential for the intermolecular force. The numerical constants in eq 6 are determined by trial-and-error analysis using the present β_a values and eq 5. The calculated B values from eq 6 for gaseous HFC-32 are compared with the available experimental data and correlation reported by Qian et al. (*10*), TRC (*13*), and Sato et al. (*16*) in Figure 5. The difference between the present correlation and Qian's correlation is about 5%, while our extrapolated values calculated with eq 6 as given by the dashed curve deviate from Sato's data by about 1%. This agreement with the data by Sato et al. (*16*) seems excellent, taking into account two independent measurements, while the data by TRC (*13*) differ from the present results significantly.

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