International Journal of Thermophysics, Vol. 17, No. 3, 1996

Ideal-Gas Specific Heat and Second Virial Coefficient of HFC-125 Based on Sound-Velocity Measurements[1]

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The sound velocity in gaseous pentafluoroethane (HFC-125, CF_3CHF_2) has been measured by means of a spherical acoustic resonator. Seventy-two sound-velocity values were measured with an uncertainty of $\pm 0.01\%$ at temperatures from 273 to 343 K and pressures from 10 to 250 kPa. The ideal-gas specific heats and the second acoustic-virial coefficients have been determined on the basis of the sound-velocity measurements. The second virial coefficients calculated from the present sound-velocity measurements agree with literature values which were determined from *PVT* measurements by means of a Burnett method.

KEY WORDS: alternative refrigerant; HFC-125; ideal-gas specific heat; second acoustic-virial coefficient; second virial coefficient; sound velocity; spherical resonator.

1. INTRODUCTION

Measurement of sound velocity with a spherical resonator is recognized as one of the most accurate methods for determining the thermodynamic properties of dilute gases such as the ideal-gas specific heats and the second virial coefficients. Using this method the sound velocity in gaseous 1,1,1,2-tetrafluoroethane (HFC-134a, CF_3CH_2F) [1, 4, 6], 1,1-difluoroethane (HFC-152a, CHF_2CH_3) [2–4, 6], and difluoromethane (HFC-32, CH_2F_2) [5–7] have been measured previously by the present authors with an uncertainty of $\pm 0.01\%$. Because of its zero ozone depletion potential and

[1] Paper presented at the Twelfth Symposium on Thermophysical Properties, June 19–24, 1994, Boulder, Colorado, U.S.A.

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0195-928X/96/0500-0587$09.50/0

nonflammability, a hydrofluorocarbon, pentafluoroethane (HFC-125, CF_3CHF_2), is expected to be a promising component of the binary and/or ternary refrigerant mixtures that may replace chlorodifluoromethane (HCFC-22, $CHClF_2$). Few thermophysical property measurements have been reported for HFC-125, and in particular only one set of sound-velocity measurements was reported by Gillis [8] at the same time that we reported this work.

In this paper, we report 72 sound-velocity measurements in gaseous HFC-125 at temperatures from 273 to 343 K and pressures from 10 to 250 kPa. The ideal-gas specific heats and the second virial coefficients have been calculated from these sound-velocity measurements.

2. EXPERIMENTS

The experimental apparatus and procedure were reported in detail in our previous publication [4]; only a brief explanation is given here. A detailed discussion of the theory of spherical acoustic resonances was given by Moldover et al. [9–13]. The experimental apparatus, shown in Fig. 1, consists of a spherical resonator S whose inner radius is about 50 mm; a pressure vessel Q; platinum resistance two thermometers E_1 and E_2;

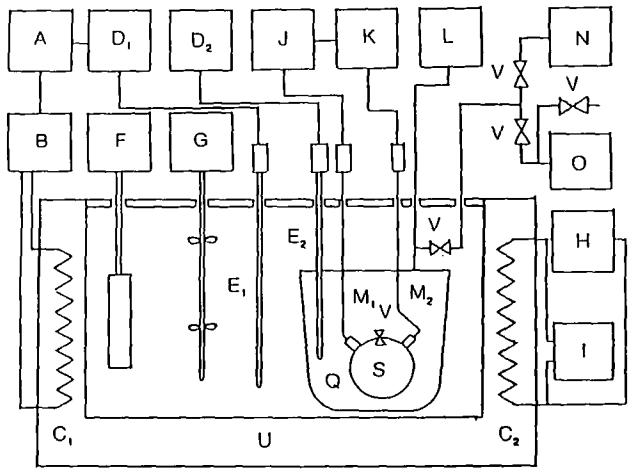

Fig. 1. Experimental apparatus. A, PID controller; B, Thyristor regulator; C_1 and C_2, heaters; D_1 and D_2, thermometer bridges; E_1 and E_2, platinum resistance thermometers; F. refrigeration unit; G, stirrer; H, transformer; I, voltmeter; J, frequency synthesizer; K, lock-in amplifier; L, pressure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

transducers, M_1 as sound generator and M_2 as sound detector; devices A through I, which are temperature control and measuring subsystems; devices J through K, which are signal detecting devices; and 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.

Sound velocity W was determined from the values of resonance frequency and half-width $f_{l,n}$ and $g_{l,n}$, which were measured under 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 [10],

$$f_{l,n} - \mathrm{i}g_{l,n} = \frac{WZ_{l,n}}{2\pi a} + \sum_{\mathrm{j}} (\Delta f - \mathrm{i}\,\Delta g)_{\mathrm{j}} \qquad (l = 0, 1, 2,..., \; n = 0, 1, 2,...) \quad (1)$$

where a and $Z_{l,n}$ in the first term on the right-hand side are the radius of the spherical resonator and the 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 that represent various non-ideal 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 certain pressures and temperatures, we change the pressure at the same temperature for succeeding measurements.

The experimental uncertainties in the sound velocity, temperature, and pressure measurements are estimated as not greater than $\pm 0.01\%$, ± 11 mK, and ± 0.5 kPa, respectively.

The sample purity of HFC-125 purified and analyzed using gas chromatographically by the manufacturer was better than 99.998 mass%. We did not purify the sample by ourselves but simply relied on the available purity data supplied by the chemical manufacturer.

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

3. RESULTS

Seventy-two sound velocity values in gaseous HFC-125 have been measured at temperatures from 273 to 343 K and pressures from 10 to 250 kPa. The data are listed in Table I and shown in Fig. 2. These results are the average values of (0, 2)–(0, 5) radially symmetric modes. The

Table I. Sound Velocity in Gaseous HFC-125

T (K)	P (kPa)	W ($m \cdot s^{-1}$)
273.155	120.30	141.609
	100.33	142.091
	80.16	142.574
	60.37	143.043
	39.97	143.522
	20.22	143.984
	9.85	144.233
303.150	239.24	147.545
	220.32	147.888
	200.23	148.250
	180.36	148.606
	160.23	148.964
	140.08	149.322
	120.02	149.675
	100.25	150.020
	79.76	150.377
	60.19	150.715
	39.97	151.064
	19.82	151.411
	10.00	151.582
313.156	237.29	150.285
	220.44	150.560
	199.86	150.894
	179.92	151.216
	160.14	151.535
	140.12	151.858
	120.02	152.178
	100.20	152.492
	79.87	152.814
	59.94	153.128
	40.08	153.442
	19.71	153.761
	9.99	153.919
323.145	244.36	152.832
	220.07	153.192
	199.91	153.489
	180.14	153.780
	160.15	154.072
	140.03	154.365
	120.17	154.653
	100.35	154.940
	79.63	155.239
	59.80	155.524
	40.06	155.809
	20.09	156.098
	10.02	156.254

Table I. *(Continued)*

T (K)	P (kPa)	W ($m \cdot s^{-1}$)
333.156	241.52	155.450
	219.57	155.746
	200.09	156.007
	180.25	156.274
	160.17	156.541
	140.10	156.807
	119.98	157.073
	100.02	157.335
	80.23	157.595
	59.89	157.862
	40.12	158.121
	20.02	158.385
	9.94	158.526
343.144	241.08	157.988
	220.10	158.241
	200.15	158.483
	180.25	158.724
	160.30	158.965
	139.95	159.211
	119.82	159.453
	100.13	159.690
	80.13	159.930
	59.77	160.174
	40.06	160.410
	20.11	160.653
	10.00	160.780

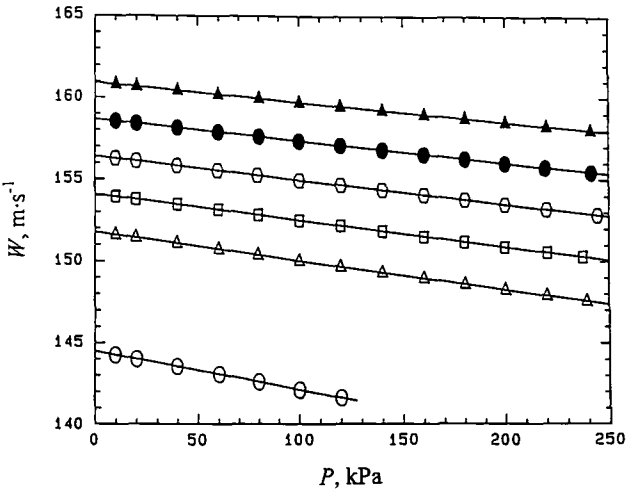

Fig. 2. Sound-velocity data in gaseous HFC-125. ○, 273 K; △, 303 K; □, 313 K; ⬡, 323 K; ●, 333 K; ▲, 343 K. ——, Eq. (2).

measured sound-velocity values squared were correlated along each isotherm with the following quadratic function of pressure.

$$W^2 = A_0 + A_1 P + A_2 P^2 \tag{2}$$

where A_0, A_1, and A_2 are the numrical constants. The solid curves in Fig. 2 represent the calculated results from Eq. (2). The thermophysical properties used in evaluating the perturbation terms are the critical temperature [14], the critical pressure [15], the critical density [14], the second virial coefficient [15], the ideal-gas specific heat [16], the viscosity values calculated from the equation of Reichenberg given in Ref. 17, and the thermal conductivity values estimated by using the modified Eucken equation which appears in Ref. 17.

4. DISCUSSION

The ideal-gas specific heat, Cp^0, and the second acoustic-virial coefficient, β_a, determined from the present measurements, are summarized in Table II. The ideal-gas specific heat and the acoustic-virial coefficient are derived by the regression analysis from the present sound-valocity measurements. The method of analysis for Cp^0 and β_a was reported in our previous publication [4]. The standard deviations for Cp^0 and β_a were calculated as ± 0.10 and $\pm 0.45\%$, respectively. The Cp^0 correlation was developed as follows:

$$Cp^0/R = 4.3987 + 2.4273 \times 10^{-2} T - 4.099 \times 10^{-6} T^2 \tag{3}$$

where T is in K and R is the universal gas constant, 8.314471 $J \cdot mol^{-1} \cdot K^{-1}$, reported by Moldover et al. [10] in 1988.

Table II. Ideal-Gas Specific Heat and Second Acoustic-Virial Coefficient for HFC-125

T (K)	Cp^0/R	β_a ($cm^3 \cdot mol^{-1}$)
273.155	10.726	−731.5
303.150	11.360	−565.6
313.156	11.618	−526.6
323.145	11.806	−493.8
333.156	12.043	−456.0
343.144	12.237	−426.2

Figure 3 shows the deviation of the present Cp^0 values from the correlation, Eq. (3). The dashed curve shows the correlation reported by McLinden et al. [16] in 1993. Our data agree with our correlation within $\pm 0.18\%$ and the difference between the present correlation and McLinden and co-workers's [16] is about 0.9%, although both correlations represent similar behavior in temperature dependence. It should be noted that the correlation by McLinden et al. [16] has been developed on the basis of the derived values from the sound-velocity measurements of Gillis [8]. The correlation by McLinden et al. [16] agrees with the Cp^0 values given in the TRC tables [18]. It is also noteworthy that the previous C_p^0 values reported by McLinden in 1990 and TRC in 1975 had systematic departures from the present results by 1–3%, and were replaced by the values in Refs. 16 and 18. The uncertainty of Eq. (3) is estimated as $\pm 0.3\%$ and it is effective at least for the range of the present experimental temperatures from 273 to 343 K.

On the other hand, six β_a values were derived from the sound-velocity measurements. The thermodynamic relation between β_a and B, second virial coefficient, is given below:

$$\beta_a = 2B + 2(\gamma^0 - 1)T\frac{dB}{dT} + \frac{(\gamma^0 - 1)^2}{\gamma^0}T^2\frac{d^2B}{dT^2} \tag{4}$$

where γ^0 is the ideal-gas specific-heat ratio.

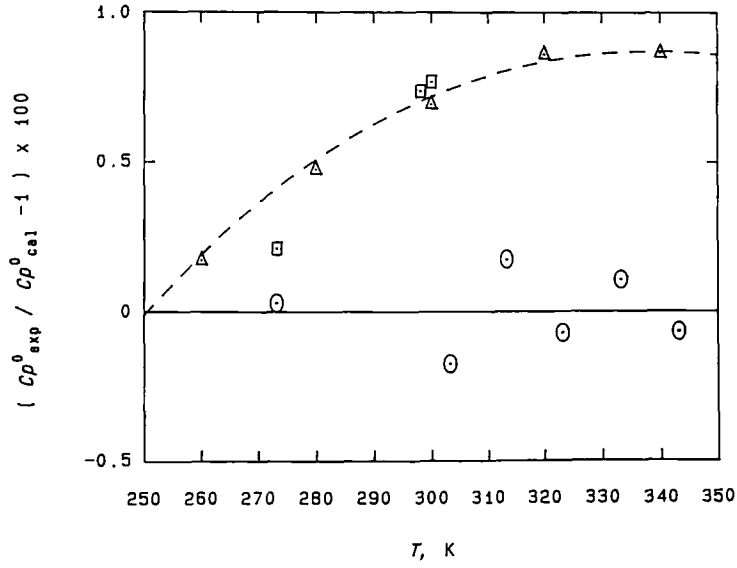

Fig. 3. Comparison of Cp^0 values with Eq. (3). ○, This work; △, Gillis [8]; □, TRC [18]; – –, McLinden [16]; ——, Eq.(3).

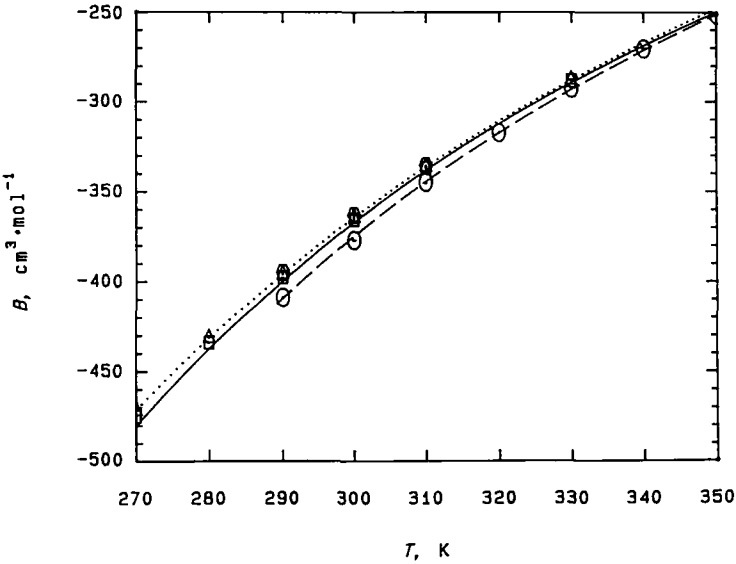

Fig. 4. Comparison of second virial coefficients. ○, Ye et al. [15]; △, Gillis [8]; ⬡, Bignell and Dunlop [19]; □, Boyes and Weber [20]; – –, Ye et al. [15]; ....., Gillis [8]; ——, Eq. (5).

The second virial coefficient, B, was correlated as

$$B = 74.20\{1 - 1.2914[\exp(517.1/T) - 1]\} \tag{5}$$

where B is in $cm^3 \cdot mol^{-1}$ and T is in K. This functional form is determined by using the square-well potential for B. The numerical constants in Eq. (5) are determined by trial-and-error analysis using the present β_a values and Eq. (4). The calculated B values from Eq. (5) for gaseous HFC-125 are compared with the available experimental data and correlations reported by Ye et al. [15], Gillis [8], Bignell and Dunlop [19], and Boyes and Weber [20] in Fig. 4. The present correlation agrees with the reported values by Ye et al. [15], Gillis [8], Bignell and Dunlop [19], and Boyes and Weber [20] within +2.7, −1.8, −1.2, and −1.1%, respectively. We estimate that the uncertainty of Eq. (5) is less than ±2.0% and is effective for the range of temperatures 273–343 K.

ACKNOWLEDGMENTS

We are indebted to Asahi-Glass Co., Ltd., Tokyo, for kindly furnishing the sample gas and to the Ministry of Education, Science and Culture, Japan, for partial financial support as a part of Grant-in-Aid 04402025.

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