International Journal of Thermophysics, Vol. 22, No. 5, September 2001 (© 2001)

Thermodynamic Properties of 1,1,1,2,3,3,3-Heptafluoropropane[1]

Y. Y. Duan,[2,3] L. Shi,[2] M. S. Zhu,[2] L. Z. Han,[2] and C. Zhang[2,4]

A vapor pressure equation has been developed for 1,1,1,2,3,3,3-heptafluoropropane (HFC-227ea) based on previous measurements from 202 to 375 K, from which the boiling point of HFC-227ea was determined. Based on the previous pressure–volume–temperature (*PVT*) measurements in the gaseous phase for HFC-227ea, virial coefficients, saturated vapor densities, and the enthalpy of vaporization for HFC-227ea were also determined. The vapor pressure equation and the virial equation of state for HFC-227ea were compared with the available data. Based on the previous measurements of speed of sound in the gaseous phase for HFC-227ea, the ideal-gas heat capacity at constant pressure and the second acoustic virial coefficient of HFC-227ea were calculated. A correlation of the second virial coefficient for HFC-227ea was obtained by a semiempirical method using the square-well potential for the intermolecular force and was compared with results based on *PVT* measurements. A van der Waals-type surface tension correlation for HFC-227ea was proposed, based on our previous experimental data by the differential capillary rise method from 243 to 340 K.

KEY WORDS: 1,1,1,2,3,3,3-heptafluoropropane; enthalpy of vaporization; HFC-227ea; *PVT* properties; speed of sound; surface tension; vapor pressure; virial coefficients.

1. INTRODUCTION

The expected worldwide ban on many low molar mass chlorofluorocarbons has prompted a vigorous search for alternatives with zero ozone depletion

---

[1] Paper presented at the Fourteenth Symposium on Thermophysical Properties, June 25–30, 2000, Boulder, Colorado, U.S.A.

[2] Department of Thermal Engineering, Tsinghua University, Beijing 100084, People's Republic of China.

[3] To whom correspondence should be addressed. E-mail: yyduan@te.tsinghua.edu.cn

[4] Visiting Scholar from Department of Mechanical Engineering, Wuhan Institute of Science and Technology, Wuhan 430073, Hubei Province, People's Republic of China.

0195-928X/01/0900-1463/0 © 2001 Plenum Publishing Corporation

potential (ODP) and lower global warming potential (GWP). 1,1,1,2,3,3,3-Heptafluoropropane (HFC-227ea) has zero ODP. It is a recently introduced, commercially available hydrofluorocarbon (HFC) useful in fire suppression, refrigeration, sterilization, and propellant applications. It can be used as an alternative to halon, and blends containing HFC-227ea are potential alternatives to HCFC-22 and R502. Effective use of HFC-227ea requires that the thermodynamic and transport properties be accurately measured, but there are very few data available. Wirbser et al. [1] measured the specific heat capacity and Joule–Thomson coefficient of HFC-227ea; Salvi-Narkhede et al. [2] measured the vapor pressure, liquid molar volumes, and critical properties; Park [3] measured the gaseous *PVT* properties with a Burnett apparatus at five temperatures; Klomfar et al. [4] measured the liquid *PVT* properties; Türk et al. [5] measured the vapor pressure; Robin [6] reported the thermophysical properties of HFC-227ea including estimated transport properties; Defibaugh and Moldover [7] measured the liquid *PVT* behavior and the saturated liquid density; Weber [8] measured the vapor pressure of HFC-227ea; Laesecke and Hafer [9] measured the viscosity of HFC-227ea with a coiled capillary viscometer at low temperatures and a straight capillary viscometer at high temperatures; Pátek et al. [10] measured *PVT* properties of HFC-227ea with a Burnett apparatus at temperatures of 393 K and 423 K; and Liu et al. [11, 12] measured the saturated liquid viscosity and gaseous thermal conductivity.

This paper summarizes our previous measurements [13–16], and results for the vapor pressure, gaseous *PVT* properties, speed of sound, and surface tension of HFC-227ea are correlated and discussed. A vapor pressure equation, a virial equation of state, and a van der Waals-type correlation of surface tension for HFC-227ea were developed; the virial coefficients, the ideal-gas heat capacity at constant pressure, the saturated vapor density, the normal boiling point, and the enthalpy of vaporization for HFC-227ea were also determined.

2. VAPOR PRESSURE

A vapor pressure equation for HFC-227ea, using a Wagner-type function form, with the aid of least-squares fitting, was developed as

$$\ln(p/p_c) = (A_1\tau + A_2\tau^{1.25} + A_3\tau^3 + A_4\tau^7)\,T_c/T \tag{1}$$

where $\tau = 1 - T/T_c$, $A_1 = -8.214485$, $A_2 = 1.698713$, $A_3 = -3.448953$, $A_4 = -3.317830$, $T_c = 375.95$ K [7] is the critical temperature, and $p_c = 2991.88$ kPa is the critical pressure, which was determined by extrapolation of the experimental vapor pressure data to the critical temperature. The equation is valid for temperatures from 200 K to the critical point. The normal boiling point temperature is calculated to be $T_b = 256.729 \pm 0.010$ K.

The above equation was developed on the basis of our previous vapor pressure measurements [13] and Türk et al.'s data [5], which were over the temperature range from 202 to 375 K and corresponding pressures from 4.58 to 2936 kPa; and the uncertainties of temperatures and pressures were estimated to be within ±10 mK and ±500 Pa, respectively. Our experimental data are shown in Fig. 1.

The deviations of our experimental data, as well of literature data from Eq. (1), are shown in Fig. 2. The maximum absolute deviation of our data from Eq. (1) is 1.17 kPa except for the region near the critical point ($T > 370$ K); and the maximum relative deviation and the root-mean-square (RMS) deviation of our data are 0.23 and 0.076%, respectively. The measurements and correlation of Türk et al. [5] showed good agreement with Eq. (1) and our data. When $T > 273$ K, the maximum relative deviation and the RMS deviation of the Türk et al. data from Eq. (1) are 0.18 and 0.092%, respectively. If $T < 273$ K, although the maximum relative deviation is up to 0.38%, the corresponding absolute deviation is only 0.071 kPa, and the average absolute deviation is 0.055 kPa. Figure 2 shows that Weber's results [8] are systematically 0.2% higher than Eq. (1) and our data. The maximum and RMS deviations of Weber's results from

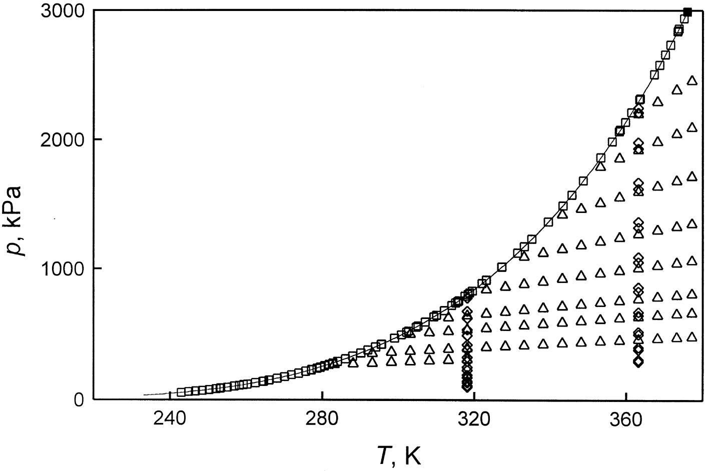

Fig. 1. Distribution of our previous *PVT* and vapor pressure measurements for HFC-227ea. (□) Vapor pressure data [13]; (—) calculated from Eq. (1); (■) critical point [7]; (◇) Burnett measurements [14]; (△) isochoric measurements [14].

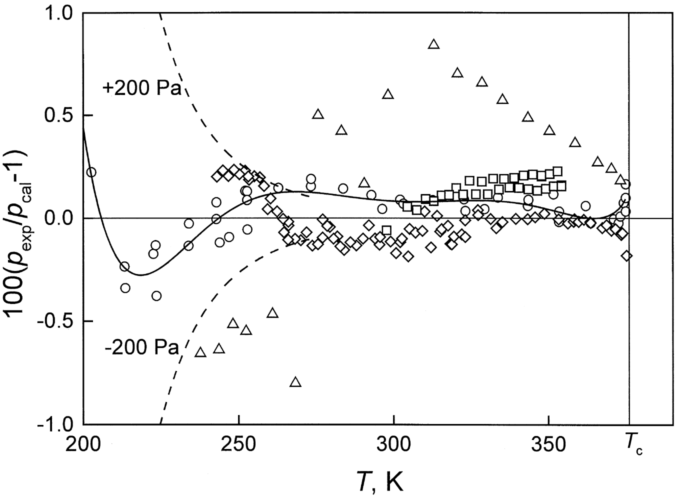

Fig. 2. Deviations of the vapor pressure data from Eq. (1). (◇) Our data [13]; (□) Weber [8]; (△) Salvi-Narkhede et al. [2] (one point out of the scale); (○) Türk et al. [5]; (——) correlation of Türk et al. [5]; (– – –) ±200 Pa.

Eq. (1) are 0.23 and 0.16%, respectively. The experimental data of Salvi-Narkhede et al. [2] also exhibit systematic differences from our results. These data are about 7 kPa higher than our data in the temperature range from 305 K to the critical point, about 2 kPa higher from 275 to 298 K, and about 0.4 kPa lower from 243 to 268 K. The correlations of Salvi-Narkhede et al. [2] and Robin [6] were based on the experimental data of Salvi-Narkhede et al. [2], so their curves also show similar systematic differences from Eq. (1). We do not know the reasons for the apparent systematic errors.

3. *PVT* PROPERTIES, VIRIAL COEFFICIENTS, AND EQUATION OF STATE

In our previous work [14], 141 pressure–volume–temperature data points for HFC-227ea in the gaseous phase were measured using Burnett/isochoric methods and are shown in Fig. 1. Burnett expansion measurements were made at both 363.15 and 318.15 K. Based on the pressure–density relationships established at 363.15 and 318.15 K, data were collected along nine isochores for temperatures from 283 to 377 K, and pressures from 0.26 to 2.5 MPa. The maximum uncertainties of temperature and pressure were estimated to be within ±10 mK and ±500 Pa,

Table I. Second and Third Virial Coefficients of HFC-227ea

T (K)	B ($\mathrm{dm^3 \cdot mol^{-1}}$)	C ($\mathrm{dm^6 \cdot mol^{-2}}$)
377.15	−0.3600	0.04508
373.15	−0.3700	0.04571
368.15	−0.3834	0.04705
363.15	−0.3971	0.04770
358.15	−0.4119	0.04915
353.15	−0.4268	0.04932
348.15	−0.4420	0.04894
343.15	−0.4578	0.04749
338.15	−0.4771	0.05108
333.15	−0.4961	0.05157
328.15	−0.5151	0.04947
323.15	−0.5357	0.04736
318.15	−0.5589	
313.15	−0.5820	
308.15	−0.6069	
303.15	−0.6333	
298.15	−0.6612	
293.15	−0.6905	
288.15	−0.7209	
283.15	−0.7519	

respectively. Along each isotherm, the second and third virial coefficients of HFC-227ea were extrapolated from the gaseous PVT measurements and are listed in Table I. The present second and third virial coefficients of HFC-227ea along with the results of Pátek et al. [10] were correlated as follows

$$B(\mathrm{dm^3 \cdot mol^{-1}}) = B_0 + B_1 T_r^{-1} + B_2 T_r^{-2} + B_3 T_r^{-3} + B_4 T_r^{-6} + B_5 T_r^{-8} \quad (2)$$

$$C(\mathrm{dm^6 \cdot mol^{-2}}) = C_0 + C_1 T_r^{-1/2} + C_2 T_r^{-1} + C_3 T_r^{-2} \quad (3)$$

Table II. Coefficients of Eqs. (2) and (3)

B_0	B_1	B_2	B_3	B_4	B_5
−19.466560	74.520374	−100.67156	49.097250	−4.6492370	0.80728384
C_0	C_1	C_2	C_3		
10.553229	−28.752602	22.022480	−3.7780755		

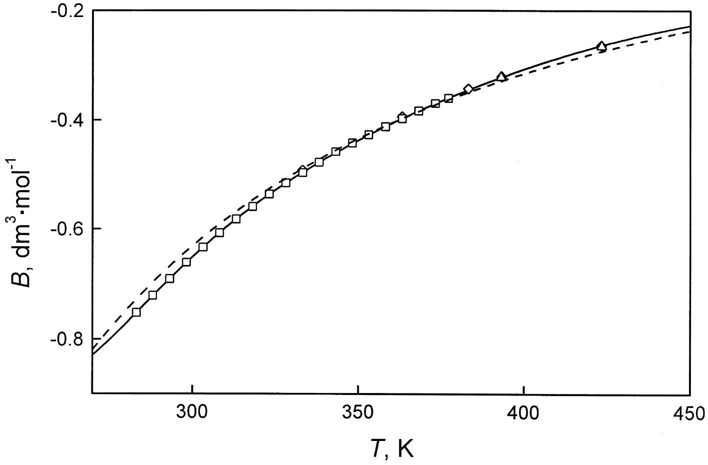

Fig. 3. Second virial coefficient of HFC-227ea versus temperature. (□) This work; (◇) Park [3]; (△) Pátek et al. [10]; (——) Eq. (2); (– – –) Eq. (10).

where B and C are second and third virial coefficients, respectively, $T_r = T/T_c$, and $T_c = 375.95$ K [7] is the critical temperature. The coefficients B_1 to B_5 and C_0 to C_3 were determined by fitting Eqs. (2) and (3) to the experimental data and are listed in Table II.

Figures 3 and 4 show comparisons of present data and literature results with Eqs. (2) and (3) of second and third virial coefficients for

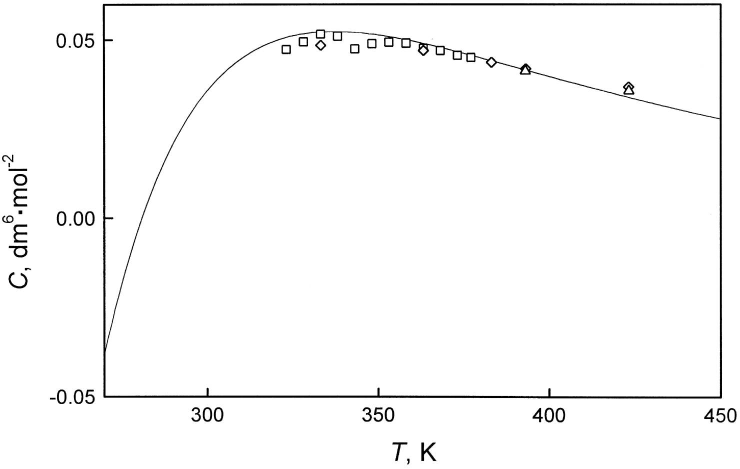

Fig. 4. Third virial coefficient of HFC-227ea versus temperature. (□) This work; (◇) Park [3]; (△) Pátek et al. [10]; (——) Eq. (3).

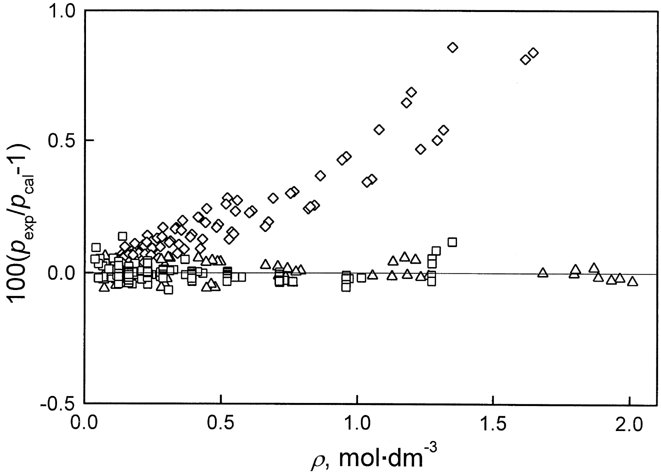

Fig. 5. Pressure deviations of measured *PVT* data for HFC-227ea from values calculated using Eq (5). (□) Our data [14]; (◇) Park [3]; (△) Pátek et al. [10].

HFC-227ea. Based on Eqs. (2) and (3), a three-term virial equation was determined to represent the gaseous thermodynamic properties of HFC-227ea as

$$\frac{p}{\rho RT} = 1 + B\rho + C\rho^2 \tag{4}$$

where $R = 8.314471\ \mathrm{J \cdot mol^{-1} \cdot K^{-1}}$ is the universal gas constant, and ρ is the molar density. The suitable range of this equation is from 283 to 453 K in temperature and up to 2.5 $\mathrm{mol \cdot dm^{-3}}$ in density in the gaseous phase. Figure 5 shows the deviations of the experimental data of our previous work and the literature from Eq. (4). From the deviation plot, it is clear that Eq. (4) can represent our data and the results of Pátek et al. [10] very well, but Park's values [3] are 0.05 to 1.3% higher than Eq. (4).

4. SATURATED GASEOUS DENSITY AND ENTHALPY OF VAPORIZATION

The saturated vapor densities of HFC-227ea were extrapolated from the *PVT* measurements and Eq. (1) and correlated as follows:

$$\rho_r = 1 + b_1\tau^{\beta} + b_2\tau^{2\beta} + b_3\tau + b_4\tau^{1/\beta} \tag{5}$$

where $\rho_r = \rho/\rho_c$, $\rho_c = 580\ \mathrm{kg\cdot m^{-3}}$ is the critical density [7], $\beta = 0.325$ is the critical exponent, $b_1 = -0.66473289$, $b_2 = -6.6731565$, $b_3 = 12.205996$, and $b_4 = -6.0067685$ are coefficients determined by fitting Eq. (5) to the calculated vapor densities. Equation (5) is effective in the temperature range from 273 to 363 K.

According to the Clapeyron equation, the enthalpy of vaporization can be determined from

$$r = h'' - h' = \left(\frac{\mathrm{d}p}{\mathrm{d}T}\right) T \left(\frac{1}{\rho''} - \frac{1}{\rho'}\right) \tag{6}$$

where r is the enthalpy of vaporization, $(\mathrm{d}p/\mathrm{d}T)$ is the first derivative of the vapor pressure and can be calculated from Eq. (1), h'' and h' are the enthalpies of the saturated vapor and liquid, respectively, and ρ'' and ρ' are the densities of the saturated vapor and liquid and can be calculated from Eq. (5) and the saturated liquid density correlation provided by Defibaugh and Moldover [7], respectively.

The enthalpy of vaporization of HFC-227ea was calculated from Eq. (5) and correlated by the following equation:

$$r/(RT_c) = b_0\tau^{\beta} + b_1\tau^{\beta+\Delta_1} + b_2\tau^{1-\alpha+\beta} + \sum_{i=1}^{3} a_i\tau^i \tag{7}$$

where $\tau = 1 - T/T_c$, $\alpha = 0.1085$ and $\beta = 0.325$ are the critical exponents, and $\Delta_1 = 0.50$ is the first symmetric correlation-to-scaling exponent. The coefficients $b_0 = -9.65051$, $b_1 = 664.076$, $b_2 = 1091.13$, $a_1 = -1536.48$, $a_2 = -302.081$, and $a_3 = 129.274$ were determined by fitting Eq. (7) to the data calculated from Eq. (6). Equation (7) is effective in the temperature range from 273 to 363 K.

5. SPEED OF SOUND

From speed-of-sound data, the ideal-gas heat capacity at constant pressure and the virial coefficients can be derived. There are no available speed-of-sound data on HFC-227ea published before this study, and only one set of ideal-gas heat capacity data in the temperature range from 253 to 423 K extrapolated from specific heat capacity experimental results was reported by Wirbser et al. [1]. The speed-of-sound of gaseous HFC-227ea was measured at temperatures from 273 to 333 K and pressures from 26 to 315 kPa with a cylindrical, variable-path acoustic interferometer operating at 156.252 kHz. The speed-of-sound results for HFC-227ea were obtained

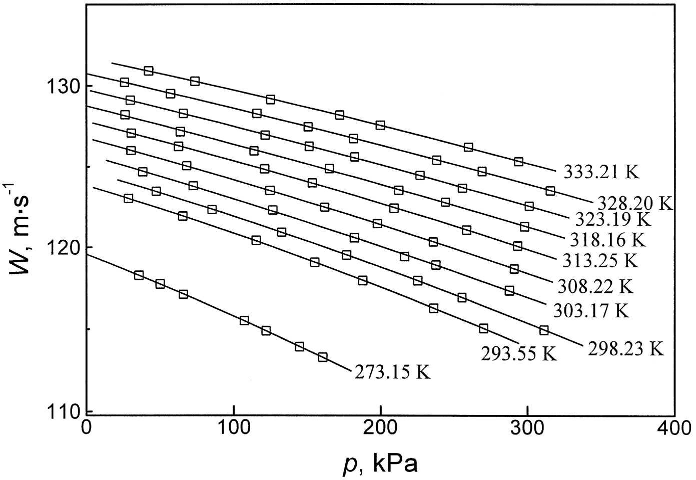

Fig. 6. Experimental speed-of-sound data for HFC-227ea.

from the corrected wavelengths together with the fixed frequency. Figure 6 shows the measured speed-of-sound results versus pressure along each isotherm. The uncertainty of the speed-of-sound measurements was less than $\pm 0.05\%$ [15].

According to thermodynamic relations, the ideal-gas heat capacity at constant pressure, c_p^0, and second acoustic virial coefficient, β_a, can be determined using the speed-of-sound results. c_p^0 and β_a data were correlated by the following equations

$$c_p^0/R = c_0 + c_1(T/\mathrm{K}) + c_2(T/\mathrm{K})^2 \tag{8}$$

$$\beta_a(\mathrm{cm^3 \cdot mol^{-1}}) = d_0 + d_1(T/\mathrm{K}) + d_2(T/\mathrm{K})^2 \tag{9}$$

where the coefficients $c_0 = -3.00623$, $c_1 = 0.09753$, $c_2 = -1.10336 \times 10^{-4}$, $d_0 = -6.22999$, $d_1 = 0.02579$, and $d_2 = -2.88544 \times 10^{-5}$ are determined by fitting Eqs. (8) and (9) to the c_p^0 and β_a data. The maximum deviation of the measured ideal-gas heat capacity data from Eq. (8) was less than 0.5%. The results of Wirbser et al. [1] are higher than calculated values from Eq. (8) by about 0.2 to 1.5%. The maximum deviation of the second acoustic virial coefficient data from Eq. (9) is less than 1.5%.

Based on the measurements, the second virial coefficient, B, of HFC-227ea was obtained by a semiempirical method using the square-well potential for the intermolecular force and was correlated as

$$B(\mathrm{cm^3 \cdot mol^{-1}}) = 0.11411\{1 - 1.4588[\exp(510.0/T) - 1]\} \tag{10}$$

Comparison of Eq. (10) with the data derived from *PVT* measurements and Eq. (2) are shown in Fig. 3.

6. SURFACE TENSION

A van der Waals-type surface tension correlation for HFC-227ea was developed to correlate our previous experimental surface tension data,

$$\sigma = \sigma_0 (1 - T/T_c)^n \tag{11}$$

where σ is the surface tension, $\sigma_0 = 0.634\ \mathrm{mN \cdot m^{-1}}$, $n = 1.250$ as determined by a least-squares fit, and $T_c = 375.95$ K is the critical temperature [7]. Figure 7 shows absolute deviations of the experimental surface tension data for HFC-227ea from Eq. (11); most of the deviations are less than $\pm 0.1\ \mathrm{mN \cdot m^{-1}}$. The maximum absolute deviation of the data from Eq. (11) are $\pm 0.14\ \mathrm{mN \cdot m^{-1}}$, which is smaller than the estimated uncertainty of $\pm 0.15\ \mathrm{mN \cdot m^{-1}}$.

The surface tension data of HFC-227ea used to develop Eq. (11) were measured with a differential capillary rise method [16]. The sample cell of the measurement system contained three capillaries with the following

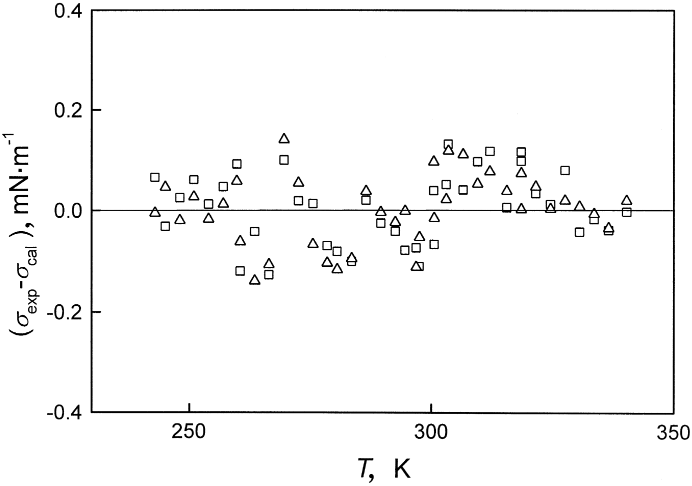

Fig. 7. Deviations of experimental surface tension data for HFC-227ea from Eq. (11). (□) Using capillaries 1 and 2; (△) using capillaries 1 and 3 (see text).

Table III. Summary of Our Previous Measurements for HFC-227ea

Property	N	Purity (mol%)	Range of data T (K)	 p (kPa)	Uncertainty ΔT (K)	 Δp (kPa)	 Δy (mN·m^{-1})	Year	Ref. No.
Vapor pressure	84	99.9	243–375	54–2936	±0.01	±0.5	—	1999	13
PVT	141	99.9	283–377	98–2454	±0.01	±0.5	—	1999	14
Speed of sound ($y = W$)	72	99.9	273–333	26–315	±0.01	±0.2	±0.05%	2001	15
Surface tension ($y = \sigma$)	78	99.9	243–340	—	±0.02	—	±0.15	2000	16

bore radii: $r_1 = 0.128 \pm 0.001$ mm, $r_2 = 0.262 \pm 0.001$ mm and, $r_3 = 0.385 \pm 0.002$ mm. Measurements were conducted under equilibrium conditions between the liquid and its saturated vapor. Two data sets for a total of 78 surface tension data for HFC-227ea were measured in the temperature range from 243 to 340 K using capillaries 1 and 2 and capillaries 1 and 3. The measurement uncertainties for surface tension and temperature are estimated to be within ±0.15 mN·m^{-1} and ±0.20 mK, respectively. The saturated vapor density of HFC-227ea was calculated from Eq. (5), and the saturated liquid density came from Defibaugh and Moldover [7].

7. SUMMARY OF MEASUREMENTS

All of our previous measurements used to develop the thermodynamic properties' equations for HFC-227ea in this paper are summarized in Table III. Table III lists ranges, uncertainties, and references of the experimental data.

ACKNOWLEDGMENTS

This work was supported by the National Natural Science Foundation of China (Grant 59906006). We are grateful to Ms. Xia Lei for providing useful help with the measurements.

REFERENCES

1. H. Wirbser, G. Bräuning, J. Gurtner, and G. Ernst, *J. Chem. Thermodyn.* **24**:761 (1992).
2. M. Salvi-Narkhede, B. H. Wang, J. L. Adcock, and W. A. Van Hook, *J. Chem. Thermodyn.* **24**:1065 (1992).
3. Y. J. Park, Bestimmung des thermischen Verhaltens neuer Arbeitsstoffe der Energietechnik mit Hilfe einer Burnett-Apparatur (Ph.D. thesis, Universität Karlsruhe, 1993).
4. J. Klomfar, J. Hruby, and O. Sifner, *J. Chem. Thermodyn.* **26**:965 (1994).

5. M. Türk, J. Zhai, M. Nagel, and K. Bier, *Fortschr.-Ber. VDI*, **19**:79 (1994)
6. M. L. Robin, In *Proceedings, International CFC and Halon Alternatives Conference*, Washington, DC. (1994), p. 105.
7. D. R. Defibaugh and M. R. Moldover, *J. Chem. Eng. Data* **42**:650 (1997).
8. L. A. Weber, personal communication (1998).
9. A. Laesecke and R. F. Hafer, *J. Chem. Eng. Data* **43**:84 (1998).
10. J. Pátek, J. Klomfar, J. Prazak, and O. Sifner, *J. Chem. Thermodyn.* **30**:1159 (1998).
11. X. J. Liu, L. Shi, M. S. Zhu, and L. Z. Han, *J. Chem. Eng. Data* **44**:688 (1999).
12. X. J. Liu, L. Shi, Y. Y. Duan, M. S. Zhu, and L. Z. Han, *J. Chem. Eng. Data* **44**:882 (1999).
13. L. Shi, Y. Y. Duan, M. S. Zhu, L. Z. Han, and X. Lei, *Fluid Phase Equil.* **163**:109 (1999).
14. L. Shi, Y. Y. Duan, M. S. Zhu, L. Z. Han, and X. Lei, *J. Chem. Eng. Data* **44**:1402 (1999).
15. C. Zhang, Y. Y. Duan, L. Shi, M. S. Zhu, and L. Z. Han, *Fluid Phase Equil.* **178**:73 (2001)
16. Y. Y. Duan, L. Shi, M. S. Zhu, L. Z. Han, and X. Lei, *Fluid Phase Equil.* **172**:237 (2000)