1332 *J. Chem. Eng. Data* **2003,** *48,* 1332−1336

P-V-T Behavior of 1,1,1,2,3,3,3-Heptafluoropropane (R227ea)

Giovanni Di Nicola*

Dipartimento di Energetica, Università Politecnica delle Marche, Via Brecce Bianche, 60100 Ancona, Italy

The vapor pressure and $P-V-T$ properties for 1,1,1,2,3,3,3-heptafluoropropane (R227ea), an ozone-friendly refrigerant, were measured using a constant volume apparatus. Measurements were carried out at temperatures from 235 K to 353 K and at pressures from 35 kPa up to 2400 kPa. The 27 measurements in the vapor pressure region were fitted with a modified Wagner equation. The 58 experimental $P-V-T$ measurements in the superheated vapor region, taken along five isochores, were regressed to the virial equation of state in the Leiden form truncated after the second term. Consistency of the derived second virial coefficients was shown with the Weber correlating method. The experimental findings were also compared with published data.

Introduction

In the search for alternative refrigerants for units with high condensing temperatures having zero ozone-depletion-potential (ODP) and lower global-warming-potential (GWP), attention has been focused on 1,1,1,2,3,3,3-heptafluoropropane (R227ea).

This propane derivative is a partially fluorinated hydrofluorocarbon and is a potential substitute for dichlorodifluoromethane (R12) and 1,2-dichloro-1,1,2,2-tetrafluoroethane (R114). Recently, its thermophysical properties have started to be the object of study.

In particular, vapor pressure measurements were carried out by different laboratories[1−4] and superheated vapor data were obtained with both the isochoric and the Burnett methods.[5−7]

To contribute to the knowledge of the thermophysical properties of R-227ea and to continue the analysis of the propane derivatives[8−11] and their mixtures,[12,13] this work presents wide temperature range measurements on vapor pressures and in the superheated vapor region.

Experimental Section

Materials. The sample was provided by Solvay. It was de-aereated by immersion in liquid nitrogen and evacuation. Its purity was checked by gas chromatography using a thermal conductivity detector and was found to be better than 99.7% by analysis of peak area.

Apparatus. The experimental apparatus is schematically illustrated in Figure 1. A classical constant volume apparatus with a volume of 254.8 cm^3 was used. The apparatus has been described in detail elsewhere.[14,15] A stainless steel spherical cell contains the refrigerant sample and is connected to a differential-diaphragm pressure transducer, coupled to an electronic null indicator. The spherical cell and pressure transducer are immersed in the main thermostatic bath containing a mixture of water and glycol and controlled by a proportional integrative derivative (PID) device. An auxiliary bath, also controlled by a PID device, helps the system to keep the temperature constant. A platinum resistance thermometer is immersed near the cell and is connected to a digital indicator. The instrument is calibrated on the ITS-90 scale, and its uncertainty is certified as being within ±15 mK. The overall uncertainty on temperature, also considering the bath stability contribution, was found to be always within ±20 mK.

Table 1. Experimental Saturation Pressures for R-227ea

T_{90}/K	P/kPa	T_{90}/K	P/kPa	T_{90}/K	P/kPa	T_{90}/K	P/kPa
235.07	35.5	270.55	177.2	305.29	562.6	339.99	1383.0
240.23	46.5	275.23	211.1	310.37	650.5	345.15	1556.8
245.31	59.9	280.19	252.4	315.41	747.3	350.26	1744.7
250.44	76.3	285.44	302.4	320.07	845.9	355.11	1939.0
255.11	94.1	290.14	353.3	325.19	965.7	360.18	2159.7
260.28	117.5	295.27	416.1	329.97	1088.3	365.27	2401.5
265.66	146.4	300.24	484.6	335.04	1230.8		

The pressure measurement is obtained with a dead weight gauge with an experimental uncertainty in the pressure measurements of ±0.5 kPa.

The charging procedure for a one-component system has been described elsewhere.[8] The uncertainty in the measurement of the mass inside the cell was estimated to amount to ±10 mg. The volume of the cell, piping, and pressure transducer cavity is measured with an uncertainty of ±0.0003 dm^3. From the uncertainties in the mass and volume measurements, the uncertainty in calculated molar volume was estimated to be always $< \pm 0.08$ dm^3·mol^{-1}.

The overall experimental uncertainty in terms of pressure, calculated using the laws of error propagation, was estimated to be $< \pm 0.8$ kPa for measurements along the saturation line and $< \pm 1.2$ kPa in the superheated vapor region.

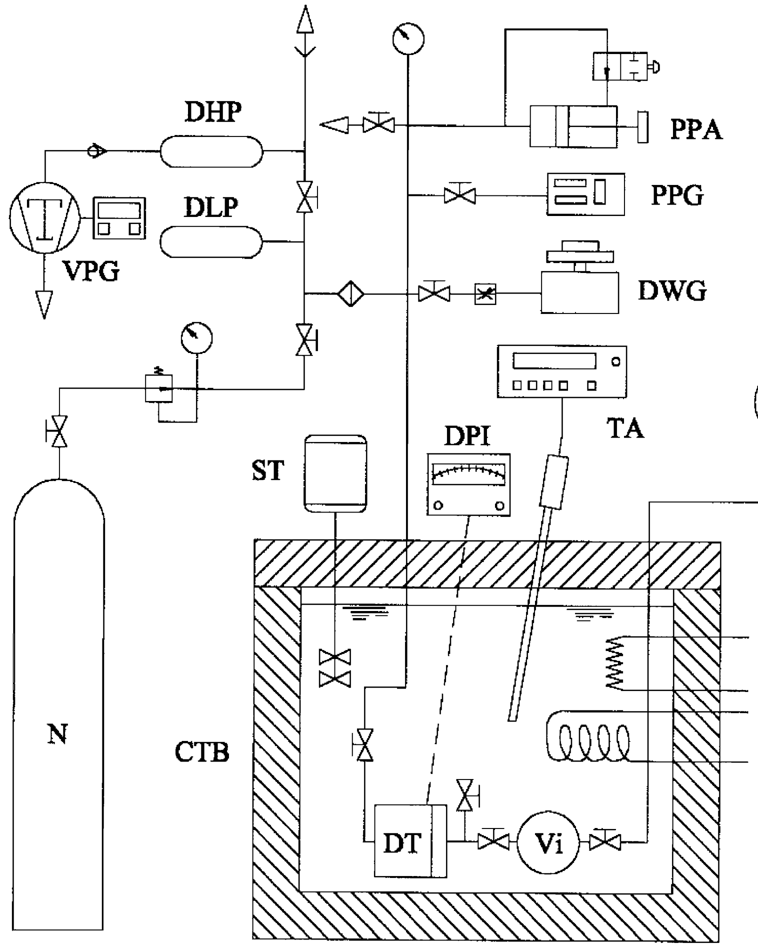
Results and Discussion

Vapor Pressure. The experimental vapor pressures in a temperature range from 235 K to 365 K are given in Table 1. Experimental data were fitted with one of the most used equations, that is, the four-parameter Wagner equation,

$$\ln \frac{P}{P_c} = \frac{T_c}{T}[A_1\tau + A_2\tau^{1.5} + A_3\tau^{2.5} + A_4\tau^5] \qquad (1)$$

where $\tau = (T_c - T)/T_c$ and the critical temperature T_c = 375.95 K.[16]

10.1021/je034084d CCC: $25.00



Nomenclature:

CB	Charging Bottle
CTB	Main thermostatic bath
DHP	High pressure expansion chamber
DLP	Low pressure expansion chamber
DPI	Electronic null indicator (Ruska, mod. 2461)
DT	Differential prresure transducer (Ruska, mod. 2413)
DWG	Gas lubricated dead weight gage (Ruska, mod 2465)
N	Nitrogen reservoir
PPA	Precision pressure controller (Ruska, mod. 3891)
PPG	Vibr. cylinder pressure gage (Ruska, mod. 6220)
ST	Stirrer
TA	Platinum resistance Thermometer (Delta, PT100)
VB	Vacuum pump (Vacuubrand , mod. RZ2)
Vi	Constant volume spherical cell
VPG	Vacuum pump gage (Galileo, mod. OG510)

Figure 1. Schematic illustration of the apparatus.

The following values were found for the parameters: $A_1 = -7.715\ 590$, $A_2 = 1.682\ 723$, $A_3 = -2.674\ 95$, and $A_4 = -4.626\ 64$. From the fitting procedure, the critical pressure was found to be $P_c = 2985.5$ kPa, in good agreement with the value estimated by ref 1.

Defining the deviations in pressure as

$$\mathrm{d}P = \frac{1}{n}\sum_{i=1}^{n}[(P_{\mathrm{exp}} - P_{\mathrm{calc}})/P_{\mathrm{exp}} \times 100] \qquad (2)$$

$$\mathrm{abs}(\mathrm{d}P) = \frac{1}{n}\sum_{i=1}^{n}[\mathrm{abs}(P_{\mathrm{exp}} - P_{\mathrm{calc}})/P_{\mathrm{exp}} \times 100] \qquad (3)$$

where n is the number of experimental points, the following values were found: $\mathrm{d}P = -0.01\%$ and $\mathrm{abs}(\mathrm{d}P) = 0.03\%$. The error distribution is shown in Figure 2. The deviations were found to be well distributed within ±0.1 kPa, reaching the value of −0.3% at low-temperature measurements.

Our experimental results were also compared with published data. Comparing the literature data with eq 1, a good consistency was found with literature values,[1,2,4] with the deviations always < ±1 kPa. A poorer agreement, but still within ±1%, was found with ref 3. In Figure 3, the distribution of deviations is shown. Data obtained at very low temperature show lower agreement, although the absolute value is very small. This is probably due to the lower purity of the sample, that was found to be 99.7% by analysis of peak area, while Hu et al.[1] and Shi et al.[2] both stated a purity of 99.9 mol %.

P−V−T. The 58 experimental $P-V-T$ measurements in the superheated vapor region along five isochores are presented in Table 2. The measurements were taken in a temperature range from 293 K to 354 K, for pressures from 215 kPa to 679 kPa and for molar volumes from (3.86 to 10.62) $\mathrm{dm^3 \cdot mol^{-1}}$.

Second Virial Coefficients. The experimental $P-V-T$ measurements were used to derive coefficients of the virial equation of state in the Leiden form,

$$P = \frac{RT}{V}\left(1 + \frac{B}{V} + \frac{C}{V^2}\right) \qquad (4)$$

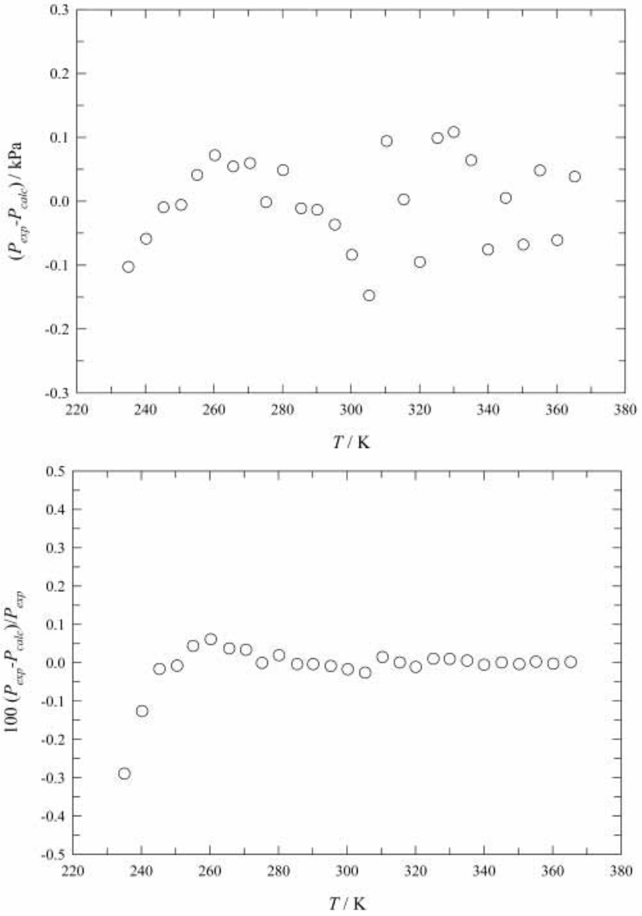


Figure 2. Scatter diagram of the absolute and relative vapor pressure deviations (top and bottom, respectively) from the fit with the Wagner equation, eq 1: ○, present work.

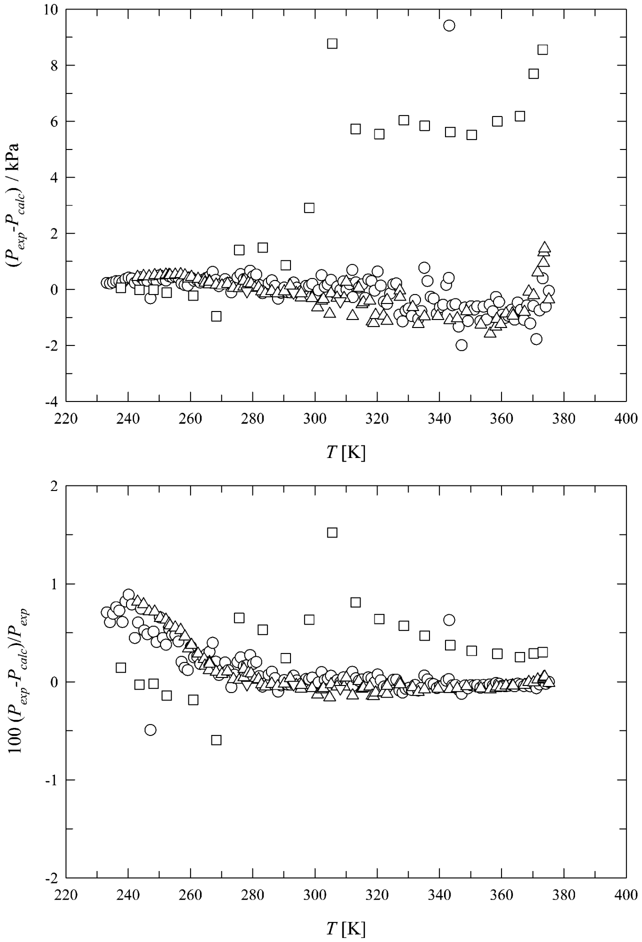


Figure 3. Vapor pressure deviations of R227ea from eq 1: ○, Hu et al.;[1] △, Shi et al.;[2] □, Salvi-Narkhede et al.;[3] ▽, Bobbo et al.[4]

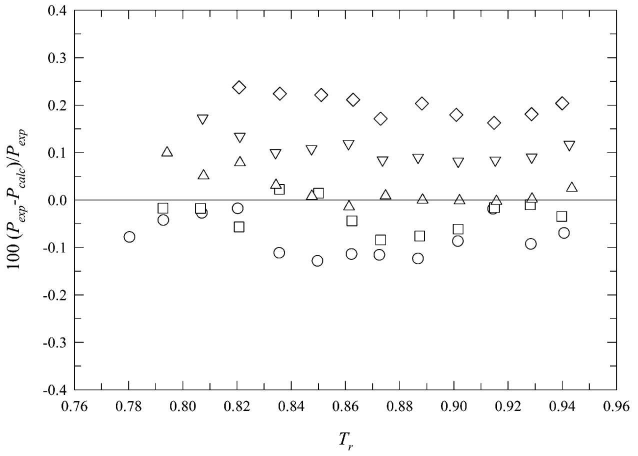


Figure 4. Scatter diagram of pressure deviations produced from the fit with eq 5: ◇, 3.86 $dm^3 \cdot mol^{-1}$ isochore; ▽, 4.48 $dm^3 \cdot mol^{-1}$ isochore; △, 5.68 $dm^3 \cdot mol^{-1}$ isochore; □, 7.60 $dm^3 \cdot mol^{-1}$ isochore; ○, 10.61 $dm^3 \cdot mol^{-1}$ isochore.

where B and C are the second and third virial coefficients.

Because of our narrow reduced temperature range ($0.78 < T_r < 0.94$), where $T_r = T/T_c$ and $T_c = 375.95$ K,[16] the virial equation of state was truncated after the second term in the calculations.

The temperature dependence of the second virial coefficient can be described by

$$B = B_0 + B_1/T_r + B_2 \exp(1/T_r) \tag{5}$$

where the coefficients B_i are $B_0 = 0.442\,102$, $B_1 = 1.681\,722$, and $B_2 = -0.915\,029$.

Using eq 4 with the experimental temperature and volume data, and with the coefficients specified above for the calculation of B with eq 5, the deviations from the experimental pressure defined as

$$dP_i = (P_{i,\mathrm{exp}} - P_{i,\mathrm{calc}})/P_{i,\mathrm{exp}} \times 100 \tag{6}$$

were calculated for each data point and are shown in Figure 4.

Defining deviations in pressure as in eqs 2 and 3, $dP = -0.035\%$ and $\mathrm{abs}(dP) = 0.086\%$ are obtained.

Among the empirical methods describing the second virial coefficients as a universal function of temperature in terms of compound parameters (critical parameters, dipole moment, acentric factor, polarizability), the Tsonopoulos and the Weber methods[17,18] were chosen to compare our second virial coefficients.

In the calculations, the acentric factor ($\omega = 0.3632^{16}$) and the dipole moment ($\mu = 1.456^{16}$) were kept constant. Thus, the calculated value for the reduced dipole moment was

$$\mu_r = (1 \times 10^5)\mu^2(P_c)/(T_c^{\,2}) = 44.3 \tag{7}$$

where P_c is the critical pressure expressed in atmospheres and μ is in Debyes.

Considering the volumetric properties, the deviation in molar volume was calculated by truncating eq 4 after the second term for each ith point and taking experimental P,

Table 2. Experimental $P-V-T$ Data for R227ea

T_{90}/K	P/kPa	V/dm^3·mol^{-1}	T_{90}/K	P/kPa	V/dm^3·mol^{-1}
293.37	214.8	10.597	318.66	421.6	5.675
298.06	219.0	10.599	323.82	430.2	5.676
303.42	223.7	10.602	328.90	438.8	5.677
308.37	228.0	10.604	334.02	447.3	5.679
314.14	232.7	10.607	339.15	455.7	5.680
319.44	237.1	10.609	344.27	464.1	5.681
324.15	241.1	10.611	349.21	472.1	5.682
328.01	244.4	10.613	354.73	481.0	5.684
333.39	248.8	10.616			
338.92	253.5	10.618	303.52	484.7	4.479
343.80	257.7	10.620	308.67	496.4	4.480
349.04	261.8	10.623	313.63	507.6	4.481
353.64	265.6	10.625	318.62	518.9	4.482
			323.74	530.4	4.483
298.02	297.6	7.594	328.46	540.6	4.484
303.22	304.1	7.596	333.40	551.4	4.485
308.57	310.7	7.598	338.96	563.3	4.486
314.16	317.9	7.600	344.11	574.3	4.487
319.60	324.5	7.601	349.17	585.0	4.488
324.21	329.9	7.603	354.39	596.0	4.489
328.19	334.6	7.604			
333.62	341.1	7.606	308.57	562.5	3.857
338.96	347.5	7.608	314.22	577.9	3.858
343.99	353.6	7.610	319.97	593.4	3.859
348.97	359.5	7.611	324.39	605.1	3.859
353.32	364.5	7.613	328.20	614.9	3.860
			333.92	629.9	3.861
298.58	387.0	5.670	338.69	642.0	3.862
303.65	395.8	5.671	343.94	655.2	3.863
308.69	404.7	5.672	349.14	668.4	3.864
313.69	413.2	5.673	353.39	679.1	3.864

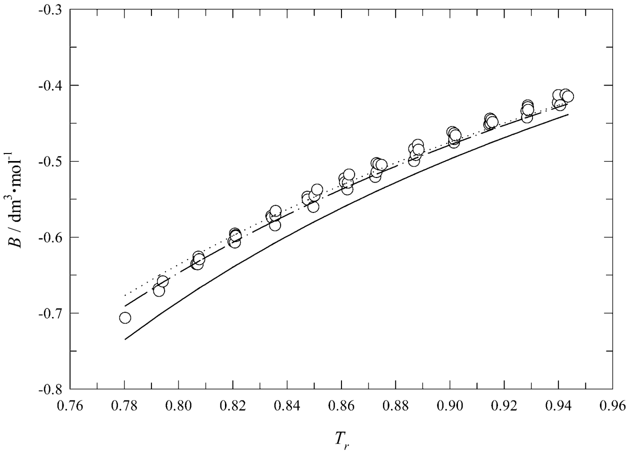


Figure 5. Second virial coefficients as a function of reduced temperature $T_r = TT_c^{-1}$, $T_c = 375.95$ K:[16] ○, derived from the $P-V-T$ data; predicted by Tsonopoulos' method[17] considering (solid line) and neglecting (dash−dotted line) the polar contribution, respectively, and by the Weber method[18] (dotted line).

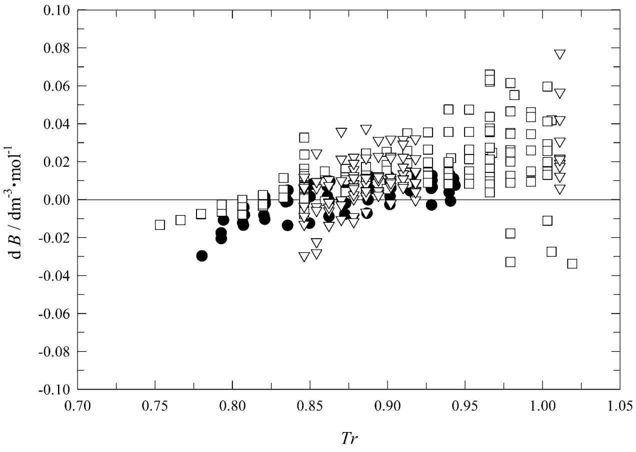


Figure 6. Scatter diagram of differences between the second virial coefficients derived from literature sources and predicted by the Weber method:[18] ●, present work; □, Hu et al.;[5] ▽, Shi et al.[6]

V, and T values as follows

$$dV = \left(\frac{PV}{RT} - 1\right)V - B \tag{8}$$

where B was calculated according to the correlating methods.[17,18]

Average absolute deviations (AADs) in volume were calculated as

$$\text{AAD} = \sum_{i=1}^{n} \text{abs}(dV_i)/n \tag{9}$$

For the Tsonopoulos' method[17] calculations were performed both considering and neglecting the polar contribution and AAD values of 0.030 and 0.008 dm^3·mol^{-1} were obtained, respectively. However, the best results were achieved adopting the Weber[18] method (AAD values of 0.007 dm^3·mol^{-1}).

This general trend is evident from Figure 5, where the second virial coefficients calculated by means of the correlating methods, together with those derived from the experimental measurements, are shown. In Figure 6, the differences between the second virial coefficients derived from our measurements and from the literature sources obtained in our reduced temperature range[5,6] were compared to those calculated by means of the Weber correlating method.[18] The following AAD values were obtained: 0.019 dm^3·mol^{-1} for the data of Hu et al.[5] and 0.014 dm^3·mol^{-1} for the results of Shi et al.,[6] respectively.

Conclusions

This paper reports experimental data on R227ea, a partially fluorinated hydrofluorocarbon potential substitute for R12 and R114. The measurements of 27 experimental points for vapor pressure and 58 points for the superheated vapor region were obtained using a constant volume apparatus. The experimental points taken within the VLE boundary were fitted with the Wagner equation. The experimental $P-V-T$ measurements in the superheated vapor region were regressed to the virial equation of state in the Leiden form truncated after the second term.

The derived second virial coefficients proved to be consistent with Weber correlating method calculations. The experimental results were also compared with recently published data, and a very good consistency was found for both the VLE and the $P-V-T$ data.

Acknowledgment

The author is grateful to Ing. Sergio Bobbo and Ing. Laura Fedele for their kind help.

Nomenclature

CB = charging bottle
CTB = main thermostatic bath
DHP = high-pressure expansion chamber
DLP = low-pressure expansion chamber
DPI = electronic null indicator (Ruska, model 2461)
DWG = gas lubricated dead weight gauge (Ruska, model 2465)
DT = differential prresure transducer (Ruska, model 2413)

N = nitrogen reservoir
PPA = precision pressure controller (Ruska, model 3891)
PPG = vibr. cylinder pressure gauge (Ruska, model 6220)
ST = stirrer
TA = platinum resistance thermometer (Delta, PT100)
VB = vacuum pump (Vacuubrand, model RZ2)
Vi = constant volume spherical cell
VPG = vacuum pump gauge (Galileo, model OG510)

Literature Cited

(1) Hu, P.; Chen, Z.; Cheng, W. Vapor pressure measurements of 1,1,1,2,3,3,3-Heptafluoropropane from 233.15 to 375.15 K. *J. Chem. Eng. Data* **2002**, *47*, 20−22.

(2) Shi, L.; Duan, Y. Y.; Zhu, M. S.; Han, L. Z.; Lei, X. Vapor pressure measurements of 1,1,1,2,3,3,3-Heptafluoropropane. *Fluid Phase Equilib.* **1999**, *163*, 109−117.

(3) Salvi-Narkhede, M.; Wang, B. H.; Adcock, J. L.; Van Hook, A. Vapor pressures, liquid molar volumes, vapor nonideality, and critical properties of some partially fluorinated ethers ($CF_3OCF_2CF_2H$, CF_3OCF_2H, and CF_3OCH_3), some perfluoroethers ($CF_3OCF_2OCF_3$, c-$CF_2OCF_2OCF_2$, and c-$CF_2CF_2CF_2O$), and of CHF_2Br and CF_3CFHCF_3. *J. Chem. Thermodyn.* **1992**, *24*, 1065−1075.

(4) Bobbo, S.; Artico, G.; Fedele, L.; Scattolini, M.; Camporese, R. Vapor-liquid equilibrium measurements and correlation of the binary refrigerant mixture propane (HC-290) + 1,1,1,2,3,3,3-heptafluoropropane (HFC-227ea) at 278.15, 293.15, and 308.15 K. *J. Chem. Eng. Data* **2002**, *47*, 839−842.

(5) Hu, P.; Chen, Z. S.; Cheng, W. L. Gaseous *PVT* behavior of 1,1,1,2,3,3,3-Heptafluoropropane. *J. Chem. Eng. Data* **2003**, *48*, 337−340.

(6) Shi, L.; Duan, Y. Y.; Zhu, M. S.; Han, L. Z. Gaseous Pressure−Volume−Temperature properties of 1,1,1,2,3,3,3-Heptafluoropropane. *J. Chem. Eng. Data* **1999**, *44*, 1402−1408.

(7) Pátek, J.; Klomfar, J.; Pražák, J.; Šifner, O. The (p, ρ, T) behaviour of 1,1,1,2,3,3,3-Heptafluoropropane (HFC-227ea) measured with a Burnett apparatus. *J. Chem. Thermodyn.* **1998**, *30*, 1159−1172.

(8) Di Nicola, G.; Giuliani, G.; Polonara, F.; Stryjek, R. Saturated pressure and $P-V-T$ measurements for 1,1,1,3,3,3-hexafluoropropane (R-236fa). *J. Chem. Eng. Data* **1999**, *44*, 696−700.

(9) Di Nicola, G.; Giuliani, G. Vapor pressure and $P-V-T$ measurements for 1,1,1,2,3,3-Hexafluoropropane (R236ea). *J. Chem. Eng. Data* **2000**, *45*, 1075−1079.

(10) Di Nicola, G. Vapor Pressure and Gas Phase $P-V-T$ Data for 1,1,1,3,3-Pentafluoropropane (R-245fa). *J. Chem. Eng. Data* **2001**, *46*, 1619−1622.

(11) Di Nicola, G.; Passerini, G. Saturated Pressure and Gas Phase $P-V-T$ Data for 1,1,2,2,3-Pentafluoropropane (R245ca). *J. Chem. Eng. Data* **2002**, *47*, 882−886.

(12) Di Nicola, G.; Polonara, F.; Stryjek, R. $P-V-T-x$ and VLE Properties of Pentafluoroethane (R125) + 1,1,1,3,3,3-Hexafluoroethane (R236fa) and 1,1,1,2-Tetrafluoroethane (R134a) + (R236fa) Systems Derived from Isochoric Measurements. *J. Chem. Eng. Data* **2000**, *46*, 359−366.

(13) Di Nicola, G.; Polonara, F.; Stryjek, R. $P-V-T-x$ and VLE Properties of Difluoromethane (*R*32) + 1,1,1,2,3,3-Hexafluoropropane (R236ea) and Pentafluoroethane (R125) + R236ea Systems Derived from Isochoric Measurements. *J. Chem. Eng. Data* **2000**, *46*, 367−374.

(14) Giuliani, G.; Kumar, S.; Zazzini, P.; Polonara, F. Vapor Pressure and Gas-Phase PVT Data and Correlation for 1,1,1,-Trifluoroethane (R143a). *J. Chem. Eng. Data* **1995**, *40*, 903−908.

(15) Giuliani, G.; Kumar, S.; Polonara, F. A Constant Volume Apparatus for Vapour Pressure and Gas-Phase P−v−T Measurements: Validation with Data for R22 and R134a. *Fluid Phase Equilib.* **1995**, *109*, 265−279.

(16) McLinden, M. O.; Klein, S. A.; Lemmon, E. W.; Peskin, A. P. *NIST Thermodynamic and Transport Properties of Refrigerants and Refrigerant Mixtures (REFPROP)*, Version 6.0; National Institute of Standards and Technology, Physical and Chemical Properties Division: Boulder, CO, 1998.

(17) Tsonopoulos, C. An Empirical Correlation of Second Virial Coefficients. *AIChE J.* **1974**, *20*, 263−272.

(18) Weber, L. A. Estimating the virial coefficients of small polar molecules. *Int. J. Thermophys.* **1994**, *15*, 461−482.

Received for review April 29, 2003. Accepted June 4, 2003.

JE034084D