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Gas-Phase *PVT* Properties of 1,1,1,2,3,3-Hexafluoropropane[1]

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We have measured the gas-phase *PVT* properties of 1,1,1,2,3,3-hexafluoropropane (R-236ea), which is considered to be a promising candidate for the replacement of 1,2-dichlorotetrafluoroethane (R-114). The measurements have been performed with a Burnett apparatus over a temperature range of 340–390 K and at pressures of 0.10–2.11 MPa. The experimental uncertainties of the measurements were estimated to be within ±0.5 kPa in pressure, ±8 mK in temperature, and ±0.15% in density. A truncated virial equation of state was developed to represent the *PVT* data and the second virial coefficients were also derived. The saturated vapor densities were also calculated by extrapolating the gas-phase isotherms to the vapor pressures. The critical density estimated from the rectilinear diameter was compared with the experimental value. The purity of the R-236ea sample used in the present measurements was 99.9 mol%.

KEY WORDS: Burnett method; critical density; *PVT* properties; R-236ea; saturated vapor density; second virial coefficient.

1. INTRODUCTION

The production of 1,2-dichlorotetrafluoroethane (R-114), which was widely used not only in centrifugal chillers and heat pumps as working fluid but also in urethane foams as blowing agent, will be discontinued by the end of 1995 along with the production of other fully halogenated chlorofluorocarbons (CFCs) as required by the Montreal Protocol Amendments. 1,1,1,2,3,3-Hexafluoropropane (R-236ea) has virtually zero ozone-depletion potential and a low global-warming potential. This refrigerant is completely nonflammable over a wide range of concentrations in air at temperatures

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up to 323 K, and no indication of unusual toxicity has been indicated in limited toxicity testing [1]. Through thermodynamic evaluation and experimental tests [1–3], R-236ea has been demonstrated to be a very promising alternative to replace R-114. Information on the gas-phase *PVT* properties for a refrigerant is essential to calculate its thermodynamic properties necessary for cycle analysis and design of the machinery. Up to now, however, they have not been available in the literature.

In this paper, we present gas-phase *PVT* measurements for R-236ea in the temperature range 340–390 K and at pressures of 0.10–2.11 MPa. The present measurements were performed with a Burnett apparatus whose operating performance and reliability have been well established through our previous measurements for other alternative refrigerants including 1,1,1,2-tetrafluoroethane (R-134a) [4], difluoromethane (R-32) [5], pentafluoroethane (R-125) [6], and 1,1,1-trifluoroethane (R-143a) [7]. The second virial coefficients were determined along six isotherms, and a truncated virial equation of state was developed to reproduce the present measurements. By extrapolating the gas-phase isotherms to the vapor pressure curve, the saturated vapor densities were also calculated and correlated.

2. EXPERIMENTS AND DATA PROCESSING

The Burnett apparatus used in the present measurements is shown schematically in Fig. 1. It consists of a cell system, a temperature control and measuring system, a pressure measuring system, and a vacuum discharge system. The cell system consists of two cells, a sample cell (A) and an expansion cell (B), and an expansion valve (V1). The two cells, which are thick-walled spherical vessels made of SUS-304 with about 500- and 250-cm^3 respective inner volumes, are connected by the expansion valve, a constant-volume valve that avoids any noxious volume change during valve operation. For the purpose of establishing a uniform temperature around the two cells and the diaphragm-type differential pressure detector (C), they are all coupled together and immersed in a thermostated oil bath (I) using silicone oil as a heat transfer medium.

The temperature was controlled by means of a PID controller and was measured by a standard platinum resistance thermometer installed near the cells. The platinum resistance thermometer was calibrated at the National Research Laboratory of Metrology, Tsukuba, and the uncertainty of the temperature measurements was estimated to be ±8 mK, the sum of ±2 mK for the uncertainty of the thermometer, ±1 mK for the uncertainty of the thermometer bridge, and ±5 mK for the possible temperature

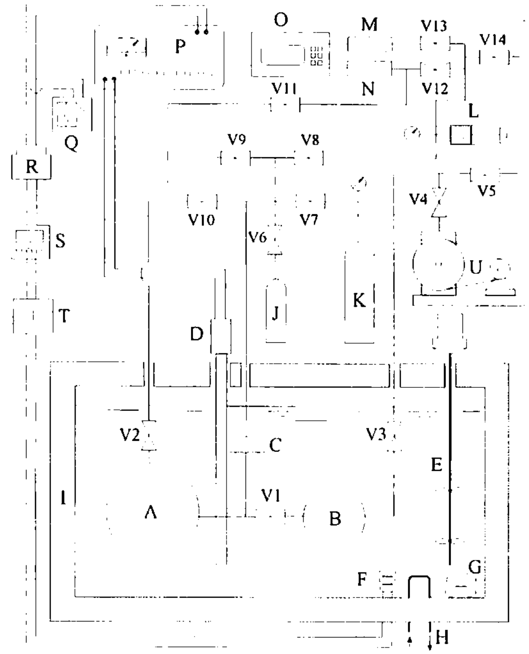

Fig. 1. Burnett experimental apparatus: (A) sample cell; (B) expansion cell, (C) differential pressure detector; (D) platinum resistance thermometer; (E) stirrer; (F) subheater; (G) main heater; (H) cooler; (I) constant-temperature bath; (J) N_2 gas damper; (K) N_2 bottle; (L) hand piston; (M, N) quartz pressure transducers with temperature sensor; (O) digital pressure gauge; (P) thermometer bridge, (Q) pen recorder; (R) voltage/current converter; (S) PID controller; (T) DC power supply; (U) vacuum pump; (V1) constant volume valve; (V2–V14) valves.

fluctuation of the thermostated bath. The temperature was then calculated on the basis of the International Temperature Scale of 1990 (ITS-90).

The sample pressure was transmitted to an external pressure measuring system through the differential pressure detector (C). By balancing the sample gas pressure with a nitrogen-gas pressure in the pressure measuring system, the nitrogen-gas pressure was directly measured by a quartz pressure transducer gauge (M) or (N). One of them (M) was used for pressure measurements above 1.1 MPa, while the other (N) for pressures below 1.1 MPa. The experimental uncertainty in the pressure measurements was estimated to be no more than ±0.5 kPa, which consists of the reproducibility of the differential pressure measurements, ±0.3 kPa, and the accuracy of the pressure gauge, ±0.2 kPa.

Accurate determination of the cell constant, which is the ratio of the two different volumes of cell A and cells A and B at zero pressure, is one of the essential factors in the Burnett method. By using gaseous helium whose thermodynamic properties are well established [8], the cell constant, $N = 1.50368 \pm 0.00019$, was accurately determined [4]. The purity of the R-236ea sample used in the present measurements was analyzed to be 99.9 mol% by the chemical manufacturer.

A very brief description regarding the data analysis method is given here. The Burnett method is an experimental technique for determining *PVT* properties of gases without directly measuring the volume or mass. The observed information for a series of expansion with the Burnett apparatus includes a pressure, P_j, with a corresponding expansion number, j, at a constant temperature, T. The consecutively measured pressures for each series of isothermal expansions could be reduced to compressibility factors and virial coefficients throughout the data processing. Unfortunately, owing to the effects of the experimental uncertainties and/or adsorption in the low-pressure region, the plot of P_j/P_{j-1} vs P_j usually could not be extrapolated to the cell constant value at zero pressure. Deviations like that would have a great effect on the determination of compressibility factors and virial coefficients.

To obtain accurate virial coefficients from the Burnett measurements, a new data analysis method was developed by the present authors, and it was used for the data analysis of R-152a, R-134a, R-32, R-125, and R-143a with satisfactory accuracy [9]. This method is conducted principally by selecting an appropriate weighting factor for each P_j/P_{j-1} value according to its uncertainty and the optimal number of terms of the fitting polynomial so that the fitted P_j/P_{j-1} function of P_j should well be extrapolated to the cell constant value at zero pressure. Using this method, the analysis for the present Burnett measurements of R-236ea was performed.

3. RESULTS AND DISCUSSION

3.1. Gas-Phase *PVT* Properties

The Burnett expansion measurements were performed at temperatures from 340 to 390 K. A total of 53 *PVT* data for R-236ea have been measured along six isotherms in its gas phase. Figure 2 summarizes the measured *PVT* points which cover the range of temperatures of 340–390 K, pressures of 0.10–2.11 MPa, and densities of 0.04–1.02 $\text{mol} \cdot \text{L}^{-1}$. The experimental pressures, P, temperatures, T, compressibility factors, Z, and densities, ρ, are tabulated in Table I. The experimental uncertainties of the measurements were estimated to be within ±0.5 kPa in pressure, ±8 mK in temperature, and ±0.15% in density.

3.2. Virial Equation of State

In order to facilitate calculation of the thermodynamic properties, we have developed a truncated virial equation of state. In consideration of the experimental uncertainties, the following quadratic function of density with two virial coefficients was used to fit the measured *PVT* values given in Table I:

$$Z = 1 + B(T_r)\,\rho + C(T_r)\,\rho^2 \tag{1}$$

where

$$Z = P/(\rho RT)$$

$$B(T_r) = b_1 + b_2 T_r^{-1} + b_3 \exp(T_r^{-1}) \tag{2}$$

$$C(T_r) = c_1 T_r^{-1} + c_2 T_r^{-3} + c_3 T_r^{-5} \tag{3}$$

and B is in $\mathrm{L \cdot mol^{-1}}$, C in $\mathrm{L^2 \cdot mol^{-2}}$, T in K, ρ in $\mathrm{mol \cdot L^{-1}}$, and P in kPa, R is the universal gas constant ($8.314471\ \mathrm{J \cdot mol^{-1} \cdot K^{-1}}$), $b_1 = 0.500475$, $b_2 = 0.427082$, $b_3 = -0.471482$, $c_1 = -0.199816$, $c_2 = 0.442161$,

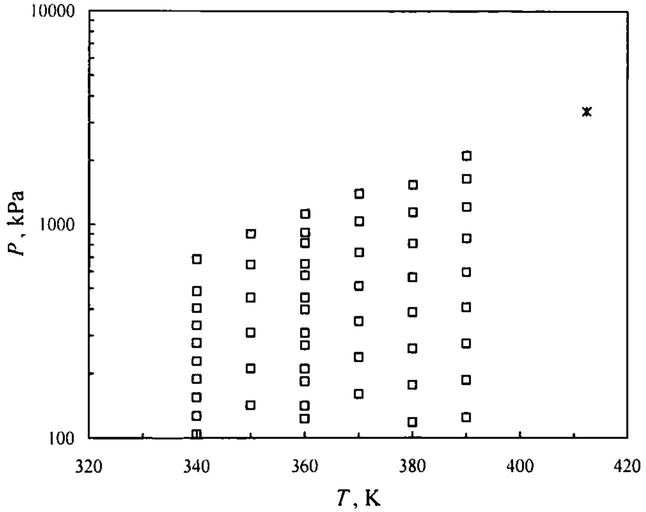

Fig. 2. Distribution of the experimental *PVT* data for R-236ea: *, critical point; □, this work; ——, vapor pressure curve, Eq. (4).

Table I. Gas-Phase PVT Properties for R-236ea

T (K)	P (kPa)	ρ (mol · L^{-1})	Z
390.000	2107.24	1.01907	0.63770
390.000	1643.75	0.67772	0.74797
390.000	1209.46	0.45072	0.82754
390.000	857.75	0.29975	0.88249
390.000	595.01	0.19934	0.92050
390.000	406.95	0.13257	0.94667
390.000	275.72	0.088164	0.96444
390.000	185.63	0.058633	0.97635
390.000	124.45	0.038993	0.98429
380.000	1536.68	0.66073	0.73630
380.000	1138.16	0.43934	0.82013
380.000	810.45	0.29214	0.87824
380.000	563.49	0.19425	0.91829
380.000	385.75	0.12916	0.94540
380.000	261.44	0.085885	0.96358
380.000	176.04	0.057107	0.97573
380.000	117.99	0.037972	0.98344
370.000	1391.81	0.61635	0.73403
370.000	1033.42	0.40990	0.81953
370.000	736.39	0.27260	0.87810
370.000	512.04	0.18129	0.91811
370.000	350.52	0.12057	0.94505
370.000	237.64	0.080180	0.96340
370.000	159.99	0.053323	0.97531
360.000	1118.85	0.48446	0.77158
360.000	913.82	0.37063	0.82373
360.000	815.61	0.32218	0.84575
360.000	649.77	0.24648	0.88072
360.000	574.85	0.21426	0.89633
360.000	451.38	0.16392	0.91998
360.000	396.89	0.14249	0.93054
360.000	308.89	0.10901	0.94665
360.000	270.48	0.094764	0.95359
360.000	209.31	0.072498	0.96456
360.000	182.80	0.063021	0.96906
360.000	140.93	0.048214	0.97658
360.000	122.87	0.041912	0.97940

Table I. *(Continued)*

T (K)	P (kPa)	ρ (mol · L^{-1})	Z
350.000	898.80	0.38497	0.80230
350.000	646.25	0.25605	0.86732
350.000	451.56	0.17030	0.91119
350.000	310.02	0.11327	0.94058
350.000	210.51	0.075333	0.96025
350.000	141.93	0.050104	0.97339
340.000	683.42	0.28838	0.83844
340.000	483.62	0.19179	0.89215
340.000	403.62	0.15656	0.91197
340.000	334.61	0.12754	0.92819
340.000	277.02	0.10412	0.94120
340.000	228.29	0.084822	0.95222
340.000	188.08	0.069241	0.96085
340.000	154.37	0.056409	0.96820
340.000	126.79	0.046048	0.97397
340.000	103.79	0.037514	0.97882

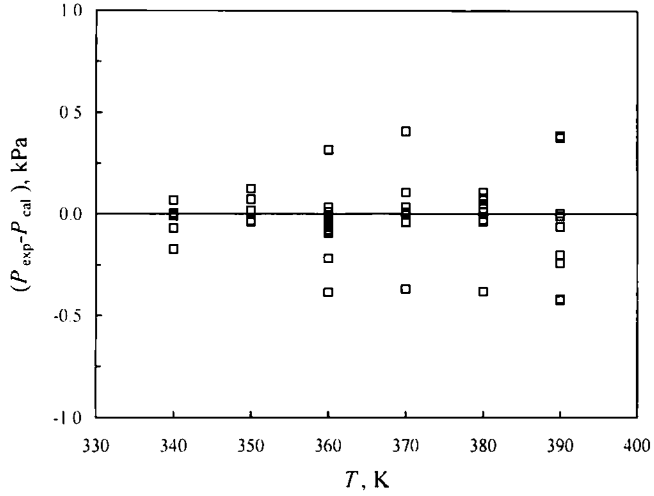

Fig. 3. Absolute pressure deviations of the PVT measurements from Eq. (1): ——, Eq. (1). □, this work.

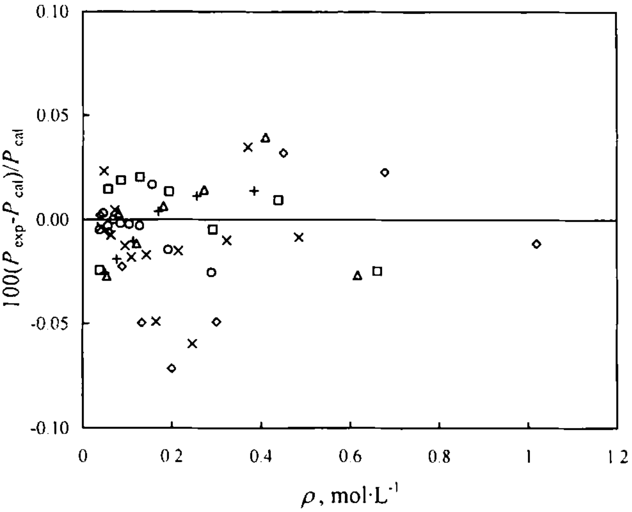

Fig. 4. Relative pressure deviations of the *PVT* measurements from Eq. (1): ——, Eq. (1): ○, 340 K; +, 350 K; ×, 360 K; △, 370 K; □, 380 K; ◇, 390 K.

$c_3 = -0.198665$, $T_r = T/T_c$, and $T_c = 412.375$ K, the critical temperature, measured by Aoyama et al. [10]. This equation is effective for the range of temperatures from 340 to 390 K in the gas phase.

The absolute deviations of the present data from Eq. (1) are shown in Fig. 3. Equation (1) represents the data given in Table I within ±0.5 kPa, which is not more than the uncertainty in the pressure measurements. Figure 4 shows the relative pressure deviations of the present data from Eq. (1). It is clear that the present data are well reproduced by Eq. (1) within ±0.07%.

3.3. Virial Coefficients

The second virial coefficients, B, have been determined from the *PVT* data along different isotherms by calculating the value, $(Z-1)/\rho$, as a function of density ρ. The dependence of $(Z-1)/\rho$ on ρ along each isotherm is shown in Fig. 5. The intercept with the ordinate gives the second virial coefficient, B. Using this procedure, six second virial coefficient values for temperatures 340–390 K have been determined and they are tabulated in Table II. The uncertainty of the second virial coefficients

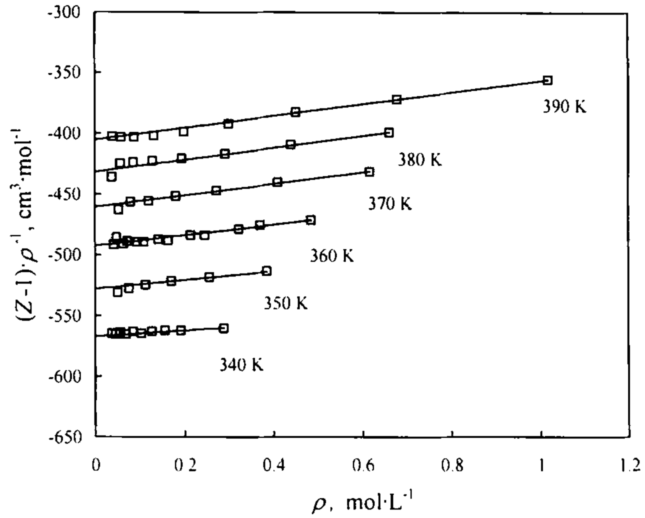

Fig. 5. Dependence of $(Z-1)/\rho$ on ρ along isotherms for R-236ea.

determined by the present study was estimated to be no more than ±3% based on the uncertainties of the present measurements and the associated random error.

The second virial coefficients given in Table II were correlated using Eq. (2), which was applied to correlate the second virial coefficients of R-134a, R-32, R-152a, R-125, R-143a, and their binary systems with satisfactory accuracy [9]. As shown in Fig. 6, Eq. (2) represents them within ±0.2%, which is far better than the estimated uncertainty.

Table II. Second Virial Coefficients for R-236ea

T (K)	B ($cm^3 \cdot mol^{-1}$)
340	−567.4
350	−528.7
360	−493.3
370	−460.5
380	−431.0
390	−405.0

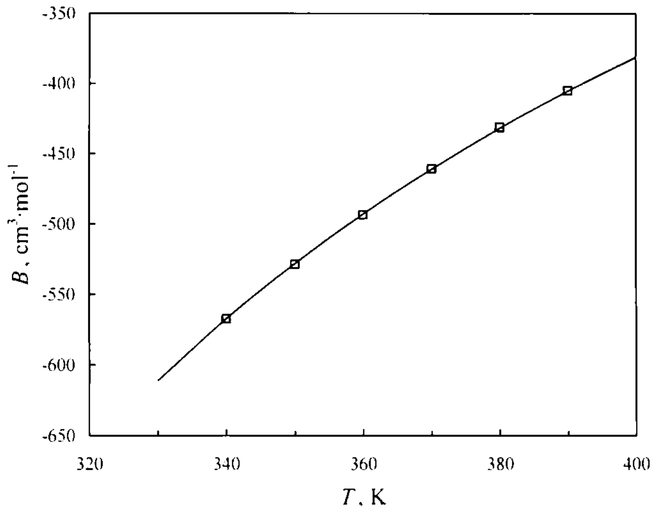

Fig. 6. Temperature dependence of the second virial coefficients for R-236ea: , Eq. (2); □, this work.

3.4. Saturated Vapor Densities

The saturated vapor densities were calculated on the basis of the *PVT* properties and the vapor pressures for R-236ea. Namely, we extrapolated Eq. (1) to the vapor pressure curve for each isotherm. The vapor pressures were calculated using the following correlation developed by Zhang et al. [11]:

$$\ln(P/P_c) = (-7.75671\tau + 1.41434\tau^{1.5} - 4.05869\tau^3 - 2.35003\tau^6)/T_r \qquad (4)$$

where $\tau = 1 - T/T_c$, $P_c = 3411.6$ kPa, and $T_c = 412.375$ K. The saturated vapor density values are given in Table III with an estimated uncertainty of $\pm 0.4\%$ due to the extrapolating and the uncertainties of Eqs. (1) and (4). Furthermore, as shown in Fig. 7, the critical density for R-236ea was estimated by means of the rectilinear diameter. The saturated vapor densities given in Table III were averaged with the saturated liquid densities by Defibaugh and Silva [12] at the same temperatures to obtain the rectilinear diameters. The averaged densities were then extrapolated linearly to the critical temperature of 412.375 K to obtain a critical density of $3.72\ \text{mol}\cdot\text{L}^{-1}$. Concerning the critical density, Defibaugh and Silva [12] reported an estimated value of $3.703\ \text{mol}\cdot\text{L}^{-1}$, while Aoyama et al. [10] measured a value of $3.736\ \text{mol}\cdot\text{L}^{-1}$. Obviously, the value estimated by the present study agrees well with that measured by Aoyama et al. within 0.5%, and this reflects that the law of rectilinear diameter was

Table III. Saturated Vapor Densities for R-236ea

T (K)	ρ'' (mol · L $^{-1}$)
340	0.3092
350	0.4021
360	0.5201
370	0.6715
380	0.8695
390	1.1433

effective to predict the critical density for R-236ea since reliable data sets for both the saturated liquid densities and the saturated vapor densities were available. The saturated vapor densities along with the critical density were correlated by the following expression:

$$\rho/\rho_c = 1 + d_1 \tau^{1/3} + d_2 \tau^{2/3} + d_3 \tau \qquad (5)$$

where $\tau = 1 - T/T_c$, $\rho_c = 3.72$ mol · L^{-1}, $d_1 = -1.8475$, $d_2 = -0.64040$, and $d_3 = 1.8133$. Equation (5) represents the saturated vapor densities within $\pm 0.05\%$ in the range of temperatures from 340 to 390 K.

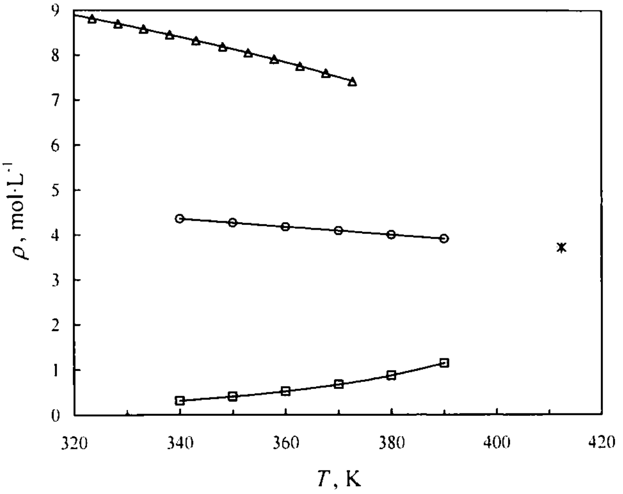

Fig. 7. Temperature dependence of the saturation densities for R-236ea: ∗, critical point; ○, —, rectilinear diameter; □, —, saturated vapor densities and correlation by this work; △, —, saturated liquid densities and correlation by Defibaugh and Silva [12]; , extrapolated curve of the correlations.

4. CONCLUSIONS

We have measured the gas-phase *PVT* properties in the range of temperatures from 340 to 390 K for R-236ea. On the basis of the present measurements, a truncated virial equation of state was developed. The second virial coefficients and the saturated vapor densities were also determined over the measured range of temperatures. The estimation method for the critical density using the rectilinear diameter was found to be effective for R-236ea, and using this method the critical density was estimated as $\rho_c = 3.72\ \mathrm{mol \cdot L^{-1}}$, corresponding to the critical temperature of 412.375 K. The second virial coefficients and the saturated vapor densities were also correlated within ±0.2 and ±0.05%, respectively.

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