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# Vapor Pressures and Gas-Phase *PVT* Data for 1-Chloro-1,2,2,2-Tetrafluoroethane (R124)

**S. J. Boyes**[1] **and L. A. Weber**[1]

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We present new data for the vapor pressure and *PVT* surface of 1-chloro-1,2,2,2-tetrafluoroethane (designated R124 by the refrigeration industry) in the temperature range 278–423 K. The *PVT* data are for the gas phase at densities up to 1.5 times the critical density. Correlating equations are given for the vapor pressures from 220 K to the critical temperature, 395.43 K, and for the *PVT* surface at densities up to $2\ \mathrm{mol \cdot L^{-1}}$ (approximately 0.5 times the critical density). Second and third virial coefficients have been derived from the *PVT* measurements.

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**KEY WORDS:** 1-chloro-1,2,2,2-tetrafluoroethane; density; gas-phase *PVT*; refrigerant R124; saturated vapor density; vapor pressures; virial coefficients.

## 1. INTRODUCTION

This work is part of an experimental program to determine the thermophysical properties of fluids that are candidate refrigerants. In this paper we present measurements of the vapor pressure and gas-phase *PVT* surface for 1-chloro-1,2,2,2-tetrafluoroethane, which has been designated R124 by the refrigeration industry. The data were measured in an existing apparatus [1, 2], which has been proven capable of providing measurements of a high precision and accuracy. In the next section we give a brief description of the apparatus and measurement techniques and, following that, a discussion of the results. Comparisons with existing data in the literature are made wherever possible.

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[1] Thermophysics Division, National Institute of Standards and Technology, Gaithersburg, Maryland 20899, U.S.A.

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## 2. APPARATUS

The semiautomatic *PVT* apparatus has been thoroughly documented in previous publications [1,2], and only a brief description is given here. Essentially, it consists of a heavy, gold-plated nickel, two-chamber Burnett cell and a very sensitive and rugged diaphragm-type pressure transducer mounted in a circulating and thermostated oil bath. The transducer separates the sample from an argon-filled system that consists of several precision pressure gauges and a piston-type gas injector [2]. The injector is driven by a stepper motor, which is controlled by an analog circuit that uses the pressure transducer as a sensor. It can operate automatically to balance the argon pressure to the sample pressure. Temperature regulation is by means of a circuit containing a platinum resistance thermometer, an AC inductance bridge, a signal conditioner, and a programmable power supply, all of which are under the control of a microcomputer.

Acquisition of data was along a series of isochores which were linked to the series of Burnett expansions along the isotherm at 423 K. The majority of the *PVT* measurements was conducted on a single charge of sample. Two series of Burnett expansions were made. The isochores were measured after each expansion during the first series. Vapor pressures were measured by filling the sample cell to approximately critical density and measuring the pressure of the two-phase sample as a function of temperature.

Temperatures were measured with a capsule-type PRT with a precision and accuracy of 1 mK. Pressures were measured with an accuracy of 20 Pa during the series of Burnett expansions using a gas-lubricated pressure balance. Along the isochores, a fused-quartz, bourdon tube, differential pressure gauge was used, which had an accuracy of 150 Pa.

The R124 samples were supplied by E. I. Du Pont de Nemours and Co.[2] with a stated purity of 99.9985% (by weight). Prior to these measurements, residual air was removed by refluxing the sample under vacuum at 77 K. The residual air was estimated to be less than 10 ppm.

## 3. RESULTS

### 3.1. Vapor Pressures

A set of 22 primary vapor pressure points was measured in the range 278–393 K with the cell filled to about 1.5 times the critical density. In

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[2] To describe materials and experimental procedures adequately, it is occasionally necessary to identify commercial products by manufacturers' name or label. In no instance does such identification imply endorsement by the National Institute of Standards and Technology, nor does it imply that the particular product or equipment is necessarily the best available for the purpose.

**Table I.** Corrected Vapor Pressures of R124

| $T$ (K) | $p$ (MPa) |
|---|---|
| Primary points | |
| 388.119 | 3.16309 |
| 383.142 | 2.88158 |
| 373.145 | 2.37800 |
| 363.131 | 1.94509 |
| 353.135 | 1.57554 |
| 343.117 | 1.26020 |
| 333.147 | 0.99663 |
| 318.140 | 0.67924 |
| 308.156 | 0.51498 |
| 298.170 | 0.38245 |
| 288.167 | 0.27740 |
| | |
| 383.137 | 2.88111 |
| 378.109 | 2.61824 |
| 368.136 | 2.15264 |
| 358.123 | 1.75260 |
| 348.156 | 1.41256 |
| 338.108 | 1.12169 |
| 323.123 | 0.77461 |
| 313.140 | 0.59275 |
| 303.189 | 0.44533 |
| 293.161 | 0.32670 |
| 283.119 | 0.23365 |
| Secondary points | |
| 393.119 | 3.47035 |
| 383.150 | 2.88181 |
| 373.150 | 2.37767 |
| 368.152 | 2.15320 |
| 358.136 | 1.75250 |
| 348.116 | 1.41082 |
| 338.111 | 1.12195 |
| 333.118 | 0.99546 |
| 388.132 | 3.16390 |
| 378.120 | 2.61863 |
| 373.102 | 2.37541 |
| 363.145 | 1.94503 |
| 353.148 | 1.57546 |
| 343.134 | 1.26081 |
| 333.151 | 0.99624 |

**Table I.** *(Continued)*

| $T$ (K) | $p$ (MPa) |
|---|---|
| Secondary points | |
| 383.140 | 2.88109 |
| 373.148 | 2.37755 |
| 363.135 | 1.94484 |
| 353.139 | 1.57523 |
| 343.140 | 1.26104 |
| 378.113 | 2.61822 |
| 368.138 | 2.15264 |
| 358.131 | 1.75246 |
| 348.108 | 1.41062 |
| 338.174 | 1.12363 |
| 333.144 | 0.99622 |
| 298.174 | 0.38252 |
| 288.182 | 0.27754 |
| 283.129 | 0.23370 |
| 278.140 | 0.19583 |
| 333.112 | 0.99548 |
| 303.188 | 0.44541 |
| 293.151 | 0.32651 |
| 287.859 | 0.27457 |
| 278.116 | 0.19562 |
| 278.129 | 0.19572 |
| 338.109 | 1.12188 |
| 333.153 | 0.99644 |
| 318.126 | 0.67915 |
| 308.154 | 0.51511 |
| 298.169 | 0.38256 |
| 288.190 | 0.27770 |
| 278.111 | 0.19557 |
| 313.130 | 0.59275 |
| 303.142 | 0.44484 |
| 293.148 | 0.32661 |
| 283.137 | 0.23372 |
| 278.123 | 0.19573 |

**Table II.** Parameters in the Vapor Pressure Equation

| Parameter | Uncorrected | Corrected |
|---|---|---|
| $a$ | $-7.4011482$ | $-7.4071451$ |
| $b$ | $1.6262316$ | $1.6439801$ |
| $c$ | $-2.3322707$ | $-2.3506110$ |
| $d$ | $-3.5268950$ | $-3.5280248$ |
| $p_c$ (kPa) | $3622.8 \pm 1.4$[a] | $3621.6 \pm 1.4$[a] |
| $x$ (ppm) | | 195 |
| $k_{\mathrm{H,R32}}(T)$ (kPa) | | $1225 + 41.9(T/\mathrm{K}\text{-}278)$ |
| $\sigma(p)$ (Pa) | 190 | 127 |
| $\sigma(\ln p)$ | 0.000147 | 0.000122 |

[a] The uncertainty assigned to the critical pressure includes the effect of the uncertainty in the critical temperature ($\pm 0.020$ K).

addition, 48 secondary vapor pressures were determined during the isochoric runs by cooling the sample cell well into the two-phase region. In the first case, the sample cell was about half-full of liquid, while in the second, only a small fraction of the cell was filled with liquid. Table I gives the vapor pressures determined in this work together with the corresponding ITS-90 temperatures.

The static vapor pressure measurements reported here, together with ebulliometric measurements made in this laboratory [3], were represented with a Wagner-type equation of the form

$$\ln(p/p_c) = (a\tau + b\tau^{1.5} + c\tau^{2.5} + d\tau^5)\, T_c/T \qquad (1)$$

in which $\tau = [1 - (T/T_c)]$, $T_c = 395.425 \pm 0.020$ K[3] is the critical temperature taken from the refractive-index measurements of Schmidt and Moldover [4], and the parameters $a$–$d$ and $p_c$ were determined in a least-squares analysis. Weighted regression analysis returned the coefficients listed in column 2 in Table II. Each ebulliometric observation was weighted by the quadrature sum of $\delta T \cdot (d \ln p/dT)$, in which $\delta T = 1.4$ mK, and the estimated uncertainty in the vapor pressure of water [5]. The static measurements were weighted by $\delta p/p$, in which $\delta p = 150$ Pa is the uncertainty in the pressure measurements. In this scheme each ebulliometric measurement received a weight which was a factor of 10 greater than the static results at a similar pressure. Deviations from the Wagner equation of the parameters listed in Column 2 in Table II are shown in Fig. 2 (top).

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[3] Here, and elsewhere, reported uncertainties are one standard deviation only.

From Fig. 1 it is immediately apparent that the static measurements are systematically higher than the ebulliometric measurements in the overlapping range. It is also clear that the amount by which the static measurements exceed the ebulliometric measurements depends on the average density within the cell. This phenomenon is consistent with the effect of a volatile impurity in the sample used for the static measurements. This

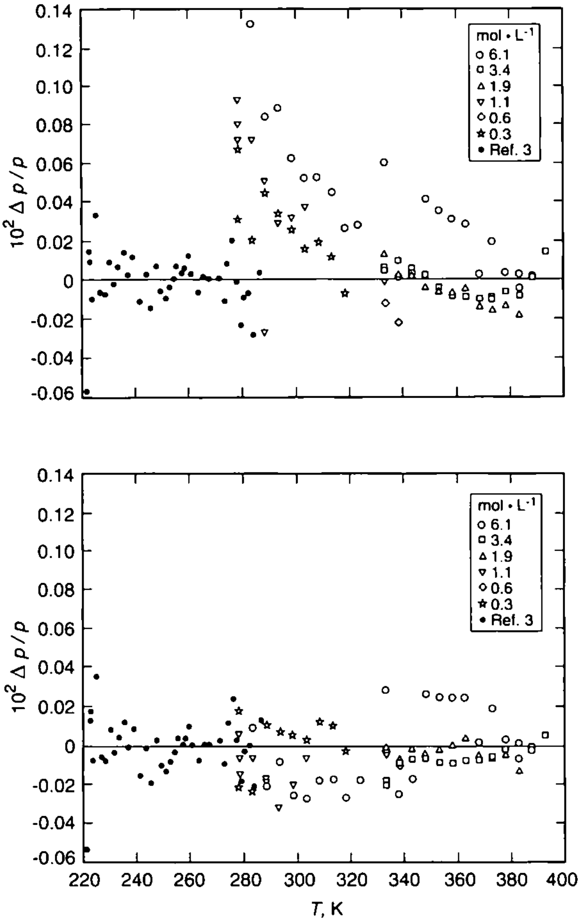

Fig. 1. Top: Deviations $\Delta p$ [ $= p(\text{exp.}) - p(\text{calc.})$] of the uncorrected vapor pressure data from Eq. (1) with the coefficients in column 2 in Table II. Bottom: Deviations $\Delta p$ [ $= p(\text{exp.}) - p(\text{calc.})$] of the corrected vapor pressure data from Eq. (1) with the coefficients in column 3 in Table II.

effect can be calculated with sufficient accuracy from a generalization of the technique given in Ref. 6, namely,

$$\delta p \approx RT\bar{\rho}x/[1-(\bar{\rho}-\rho_v)/\rho_l+RT(\bar{\rho}-\rho_v)/k_H]+RTB(x\rho_v)^2+RTC(x\rho_v)^3 \tag{2}$$

where $\delta p$ is the increase in the static pressure due to the volatile impurity, $\bar{\rho}$ is the average density of the sample in the cell, $\rho_l$ is the density of saturated liquid R124, $\rho_v$ is the density of the saturated vapor of R124, $R$ is the gas constant, $T$ is the temperature, $k_H$ is Henry's constant for the impurity dissolved in the refrigerant, $B$ and $C$ are the second and third virial coefficients of R124, respectively, and $x$ is the mole fraction of the impurity. As mentioned previously, we estimated that approximately 10 ppm of air remained in the sample after purification. Using this in Eq. (2), with Henry's constant taken as $10^5$ kPa, did not correctly account for the observed deviations. Prior to these measurements, R32 had been used in the Burnett apparatus. Although the sample volumes had been evacuated and flushed extensively with R124, we suspected that a small amount of R32 remained in one of the sample chambers. In view of this we fitted the observed deviations with Eq. (2) treating $x$ and $k_H$ as parameters. Weighted regression analysis returned values for the mole fraction $x = 200$ ppm and Henry's constant $k_H = 1255$ kPa for the impurity. Calculations using REFPROP [7] yielded a value of 1409 kPa at 280 K for Henry's constant for R32 dissolved in R124. These results support the idea that R32 was the impurity. In view of the remarkably close agreement between the results of the regression and REFPROP, the speculation that a small amount of R32 was present in the sample used for the static measurements seems justified. Accordingly, the static vapor pressures were corrected to allow for the R32 impurity using Eq. (2) and refit to Eq. (1) in combination with the ebulliometric measurements.

Henry's constant is a function of temperature and its temperature dependence was estimated from REFPROP. REFPROP predicts that $k_H$ varies from 1409 kPa at 280 K to 5600 kPa at 380 K. A linear interpolation between these values was used in Eq. (2). The standard deviation of the fit was 127 Pa (or 0.000122 in $\ln p$). The parameters determined from this analysis are given in Column 3 in Table II along with the impurity parameters. Deviations from this equation are shown in Fig. 1 (bottom). It is immediately apparent that the two sets of measurements are now in complete agreement in the overlapping region. However, there are still some residual density-dependent systematic differences. These remaining differences have an amplitude of the order of 0.03% and are much smaller than the differences in the uncorrected data. Such small differences in most measurement of vapor pressure would be totally obscured by experimental noise. We believe that the residual discrepancies are a measure of the uncertainty in the correction applied [Eq. (2)]; it is expected to become increasingly unreliable as the critical temperature is approached [8].

To summarize, the agreement between the ebulliometric and the static measurements is highly satisfactory after small (up to 0.1%) corrections have been made. The residual discrepancies resulting from the uncertainty in the correction for the impurity are estimated to be less than ±0.03%. The corrected vapor pressures are listed in Table I.

In Fig. 2 (top) we plot the values of the vapor pressure determined by other workers as deviations from Eq. (1) with the parameters listed in

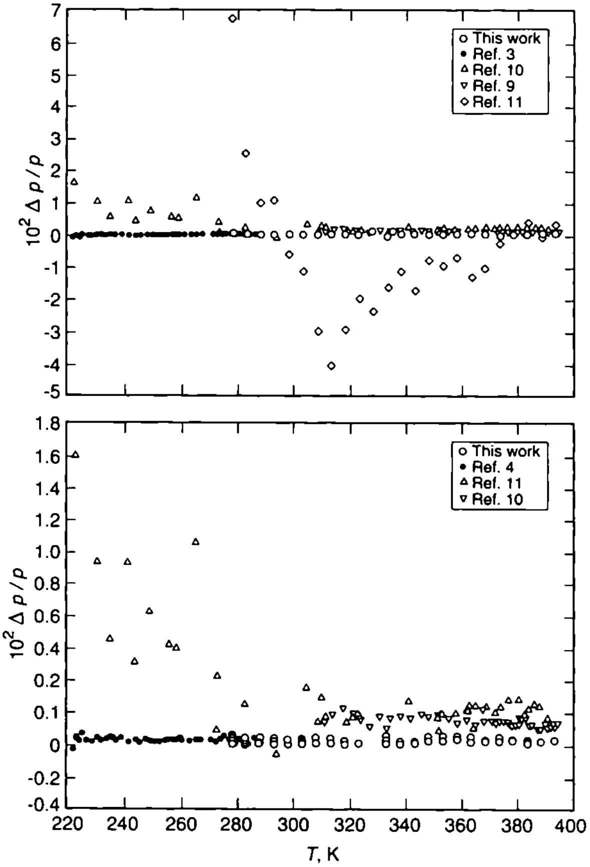

**Fig. 2.** Deviations $\Delta p$ [$= p(\text{lit.}) - p(\text{calc.})$] of literature vapor pressure data from Eq. (1) with the coefficients in column 3 in Table II.

Column 3 in Table II. The agreement of the results in Refs. 9 and 10 with these measurements is about 0.2% above 280 K and it deteriorates to 1.6% at the lowest temperature of the investigation. However, this is not surprising because in the region below 280 K the vapor pressure is less than about 250 kPa and ebulliometry is by far the superior technique. In contrast, the measurements of Ref. 11 appear to contain a serious systematic error with deviations as large as 7%. In Fig. 2 (bottom) we have expanded the ordinate scale and removed the data of Ref. 11.

### 3.2. *PVT* Data

The Burnett expansion measurements were performed at 423.115 K. A total of 15 points was measured in two series of expansions starting at pressures of about 8 MPa, corresponding to densities of about 1.5 times the critical density. The data were analyzed nonlinearly in terms of the equation

$$p_r = \rho_0 RT/N_r \left[ 1 + \sum_i b_i (\rho_0/N_r)^i \right] \tag{3}$$

in which $p_r$ is the pressure after the $r$th expansion, $\rho_0$ is the initial density of an expansion series, $N_r = N^r \Pi_r [1 + \Delta N_r(p_{r-1}, p_r)]$ is the product of cell constants corrected for the pressure distortion $\Delta N_r(p_{r-1}, p_r)$ (which is estimated from the elastic constants of the vessel material) and the $b_i$ are the virial coefficients ($b_1 = B$, $b_2 = C$, etc). The initial densities of the two expansions, $\rho_0(1)$ and $\rho_0(2)$, and the $b_i$'s are parameters to be determined in the regression analysis, and the densities corresponding to the remaining pressures are related to the initial density through the ratio of the cell volumes. The cell constant, i.e., the ratio of the cell volumes at zero pressure, was not a regression parameter. Its value was determined from calibration measurements with helium. The uncertainty associated with the assumption that the cell constant is unchanged is estimated to be less than $10^{-4}$. We weighted each observation by $p^{-1}[\delta p^2 + (\delta T\, dp/dT)^2]^{0.5}$, in which $\delta p = 20$ Pa and $\delta T = 1$ mK. This weighting accounts for the reduction in the relative precision of the pressure measurements as the pressure is reduced. Small corrections have been applied to the experimental pressures to reduce them to the exact isotherm temperature. Information for the second term in the weighting scheme was obtained from the isochoric measurements during which we actually measured $dp/dT$. Four terms in the virial expansion were required to represent the data adequately up to a maximum density of $3\ \mathrm{mol \cdot L^{-1}}$.

Truncation of the virial expansion was determined from statistical tests for convergence of the infinite series (see, e.g., Refs. 12 and 13). Each term included had a high degree of significance and additional terms were insignificant; they offered no improvement in the fit whatever. The standard deviation of the fit was 23 Pa. (For comparison, the three-term virial expansion had a standard deviation of 135 Pa.) The 23-Pa standard deviation is equal to the experimental precision and demonstrates the high degree of internal consistency obtainable in a Burnett experiment. The experimental pressures and the calculated densities are given in Table III along with the virial coefficients determined in the analysis. The error in the virial coefficients is an estimate based on the statistical uncertainty associated with the parameters combined with uncertainties estimated from numerical experiments designed to assess the propagation of errors through the model used in the analysis.

After each expansion on the first series, data were collected on isochores. A total of 88 points were taken on seven isochores between 308 and 423 K. Densities, at the experimental temperatures, were calculated by correcting the starting density on the Burnett isotherm for the thermal expansion of the sample cell. (Densities outside the range of the Burnett

**Table III.** $PVT$ Data on the Burnett Isotherm at 423.115 K

| $P$ (MPa) | $\rho$ (mol · L$^{-1}$) |
|---|---|
| 4.05078 | 1.90489 ± 0.00028 |
| 2.82731 | 1.06895 |
| 1.79881 | 0.59985 |
| 1.08307 | 0.33661 |
| 0.63202 | 0.18889 |
| 0.36249 | 0.10600 |
| 4.89881 | 2.92607 ± 0.00040 |
| 3.73438 | 1.64199 |
| 2.53506 | 0.92142 |
| 1.58533 | 0.51706 |
| 0.94515 | 0.29015 |
| 0.54857 | 0.16282 |
| 0.31372 | 0.09137 |

$B = (-263.17 \pm 0.76) \times 10^{-3}\ \mathrm{L \cdot mol^{-1}}$

$C = (28251 \pm 665) \times 10^{-6}\ \mathrm{L^2 \cdot mol^{-2}}$

$D = (1.05 \pm 0.13) \times 10^{-3}\ \mathrm{L^3 \cdot mol^{-3}}$

$E = (-3.03 \pm 0.20) \times 10^{-4}\ \mathrm{L^4 \cdot mol^{-4}}$

analysis were calculated by making use of the cell constant, with a suitable pressure correction.) The experimental results are given in Table IV.

To assess the precision of the gas-phase data and to allow calculation of thermodynamic properties, we have fit the data, at densities less than $2\ \text{mol} \cdot \text{L}^{-1}$, with an analytic equation of state. This was done by expressing the virial coefficients $B$, $C$, and $D$ as functions of temperature. For this purpose, $B$ and $C$ were represented using expressions derived from the square-well potential [14]. In this model the second virial coefficient is given by

$$B(T) = a + b\exp(c/T) \tag{4}$$

and the third virial coefficient is given by

$$C(T) = (b_0^2/8)[5 - c_1\Delta - c_2\Delta^2 - c_3\Delta^3] \tag{5a}$$

with

$$c_1 = r^6 - 18r^4 + 32r^3 - 15 \tag{5b}$$

$$c_2 = 2r^6 - 36r^4 + 32r^3 + 18r^2 - 16 \tag{5c}$$

$$c_3 = 6r^6 - 18r^4 + 18r^2 - 6 \tag{5d}$$

and

$$\Delta = \exp(\varepsilon/kT) - 1 \tag{5e}$$

$a$, $b$, $c$, $b_0$, $r$, and $\varepsilon/k$ are parameters to be determined in the analysis. $D$ was expressed as the simple function of temperature

$$D(T) = D_0 + D_1/T \tag{6}$$

leading to a total of eight parameters in the regression analysis. Weighted nonlinear regression analysis returned the values listed in Table V with a standard deviation in $p$ of 236 Pa. This is just outside the experimental uncertainty associated with the automatic pressure gauge. Deviations of our results from the surface fit are shown in Fig. 3. Although the deviations are small (maximum deviation, 0.06%) there are small systematic departures from the surface equation, particularly at the lowest temperatures and densities. However, it is in just this region that the experimental accuracy is at its worst. Additionally, the reliability of the square-well expression for accurately representing the temperature dependence of the third vitial coefficient is less well established than for the second, and we regard the overall quality of fit as highly satisfactory.

Table IV. Gas-Phase $PVT$ Data

| $T$ (K) | $p$ (MPa) | $\rho$ $(\mathrm{mol \cdot L^{-1}})$ |
|---|---|---|
| 423.115 | 8.19071 | 6.06325 |
| 408.122 | 5.98535 | 6.06707 |
| 398.101 | 4.51094 | 6.06962 |
| 423.115 | 5.19364 | 3.40524 |
| 413.104 | 4.63243 | 3.40667 |
| 403.114 | 4.06672 | 3.40810 |
| 423.122 | 5.19389 | 3.40524 |
| 423.115 | 4.05739 | 1.91088 |
| 418.121 | 3.92614 | 1.91128 |
| 408.127 | 3.65870 | 1.91208 |
| 398.110 | 3.38310 | 1.91289 |
| 388.125 | 3.09687 | 1.91369 |
| 423.115 | 2.82731 | 1.06895 |
| 418.116 | 2.76537 | 1.06917 |
| 408.138 | 2.63999 | 1.06962 |
| 398.110 | 2.51182 | 1.07007 |
| 388.120 | 2.38112 | 1.07052 |
| 378.114 | 2.24652 | 1.07097 |
| 368.136 | 2.10745 | 1.07141 |
| 423.115 | 1.79881 | 0.59985 |
| 413.096 | 1.73761 | 0.60010 |
| 403.113 | 1.67585 | 0.60035 |
| 393.114 | 1.61319 | 0.60060 |
| 383.147 | 1.54981 | 0.60085 |
| 373.148 | 1.48516 | 0.60111 |
| 363.126 | 1.41911 | 0.60136 |
| 353.137 | 1.35162 | 0.60161 |
| 423.115 | 1.08307 | 0.33661 |
| 413.097 | 1.05159 | 0.33675 |
| 403.112 | 1.01994 | 0.33689 |
| 393.116 | 0.98801 | 0.33703 |
| 383.143 | 0.95597 | 0.33717 |
| 373.151 | 0.92361 | 0.33731 |
| 363.133 | 0.89068 | 0.33746 |
| 353.140 | 0.85737 | 0.33760 |
| 343.135 | 0.82359 | 0.33774 |
| 333.150 | 0.78904 | 0.33788 |
| 423.115 | 0.63202 | 0.18889 |
| 418.145 | 0.62392 | 0.18893 |
| 408.148 | 0.60720 | 0.18901 |
| 398.130 | 0.59028 | 0.18909 |
| 418.101 | 7.44037 | 6.06453 |
| 403.099 | 5.22690 | 6.06835 |
| 418.082 | 4.91194 | 3.40596 |
| 408.132 | 4.35180 | 3.40738 |
| 398.114 | 3.77932 | 3.40882 |
| 423.134 | 5.19451 | 3.40524 |
| 423.117 | 4.05755 | 1.91088 |
| 413.092 | 3.79235 | 1.91169 |

Table IV. *(Continued)*

| $T$ (K) | $P$ (MPa) | $\rho$ ($\mathrm{mol \cdot L^{-1}}$) |
|---|---|---|
| 403.111 | 3.52181 | 1.91249 |
| 393.113 | 3.24173 | 1.91329 |
| 423.106 | 4.05731 | 1.91088 |
| 423.106 | 2.82730 | 1.06895 |
| 413.147 | 2.70312 | 1.06939 |
| 403.127 | 2.57630 | 1.06984 |
| 393.108 | 2.44678 | 1.07029 |
| 383.137 | 2.31465 | 1.07074 |
| 373.146 | 2.17801 | 1.07119 |
| 418.132 | 1.76850 | 0.59997 |
| 408.131 | 1.70695 | 0.60023 |
| 398.111 | 1.64458 | 0.60048 |
| 388.132 | 1.58163 | 0.60073 |
| 378.114 | 1.51743 | 0.60098 |
| 368.131 | 1.45226 | 0.60123 |
| 358.132 | 1.38559 | 0.60149 |
| 348.160 | 1.31717 | 0.60174 |
| 418.124 | 1.06742 | 0.33668 |
| 408.131 | 1.03586 | 0.33682 |
| 398.109 | 1.00400 | 0.33696 |
| 388.121 | 0.97201 | 0.33710 |
| 378.115 | 0.93978 | 0.33724 |
| 368.138 | 0.90718 | 0.33739 |
| 358.134 | 0.87404 | 0.33753 |
| 348.110 | 0.84045 | 0.33767 |
| 338.111 | 0.80628 | 0.33781 |
| 323.154 | 0.75339 | 0.33802 |
| 423.141 | 0.63223 | 0.18889 |
| 413.115 | 0.61559 | 0.18897 |
| 403.133 | 0.59876 | 0.18905 |
| 393.132 | 0.58188 | 0.18913 |
| 388.142 | 0.57341 | 0.18917 |
| 378.133 | 0.55642 | 0.18924 |
| 368.152 | 0.53931 | 0.18932 |
| 358.145 | 0.52201 | 0.18940 |
| 348.118 | 0.50462 | 0.18948 |
| 338.112 | 0.48705 | 0.18956 |
| 323.168 | 0.46041 | 0.18968 |
| 313.143 | 0.44216 | 0.18976 |
| 303.156 | 0.42339 | 0.18984 |
| 383.102 | 0.56486 | 0.18921 |
| 373.108 | 0.54784 | 0.18928 |
| 363.148 | 0.53068 | 0.18936 |
| 353.149 | 0.51336 | 0.18944 |
| 343.145 | 0.49590 | 0.18952 |
| 333.101 | 0.47818 | 0.18960 |
| 318.127 | 0.45128 | 0.18972 |
| 308.165 | 0.43298 | 0.18980 |

**Table V.** Parameters in the $PVT$ Surface Equation

| Parameter | Value |
|---|---|
| $a$ (L·mol$^{-1}$) | 0.304612 |
| $b$ (L·mol$^{-1}$) | −0.173745 |
| $c$ (K) | 501.36 |
| $b_0^2$ ($L^2$·mol$^{-2}$) | 0.064352 |
| $r$ | 1.208243 |
| $(\varepsilon/k)$ (K) | 506.63 |
| $D_0$ (L$^3$·mol$^{-3}$) | −0.0026616 |
| $D_1$ (L$^3$·mol$^{-3}$·K) | 1.098805 |

Alternative functional forms for representing the virial coefficients were tried but in all cases the number of parameters required to obtain a satisfactory representation of the data was substantially increased. Therefore, we take the square-well representation, which has the fewest parameters, as being the best representation for these measurements. Also in Fig. 3, the experimental $PVT$ determinations of various other workers are shown as deviations from the surface equation. Densities are restricted

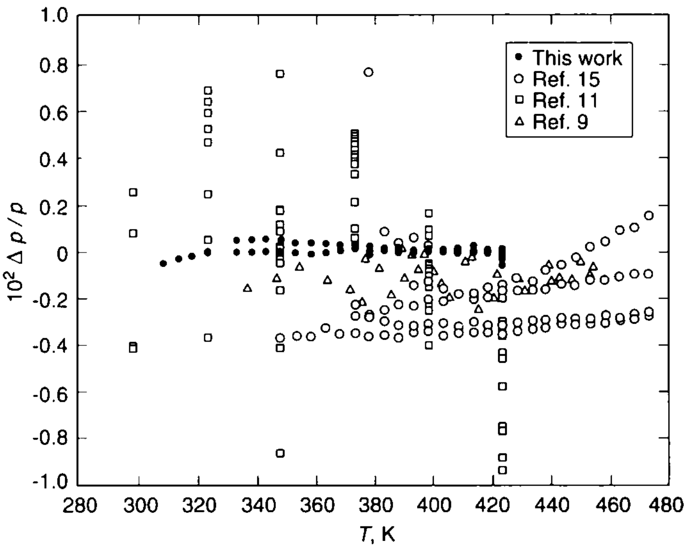

**Fig. 3.** Deviations $\Delta p$ [ $= p(\text{exp.}) - p(\text{calc.})$] of gas-phase $PVT$ data from the virial surface with $B$, $C$, and $D$ represented by Eqs. (3)–(6) with the coefficients listed in Table V.

to less than 2 mol · L$^{-1}$. The measurements of Ref. 9 agree, on the average, to better than 0.2% over the entire range with experimental scatter on the same order. If we take this scatter as an estimate of their uncertainty, then their measurements are consistent with ours. In contrast, the measurements of Ref. 11 show much larger deviations, reaching almost 1% in some instances. However, the scatter of their measurements is about 0.8%, which is consistent with their estimated uncertainties, and their results are also consistent with the present measurements to within their estimated precision. The measurements of Ref. 15 appear to deviate systematically from the present measurements, reaching 0.4% at the lowest temperature, but given their estimated uncertainties of 0.1% in $p$ and 0.3% in $\rho$, they too are consistent with the present measurements to within their estimated precision. In summary, the present *PVT* data are consistent, within combined uncertainties, with the data from the literature.

The surface equation determined by the parameters of Table V can be used with a high accuracy between 308 and 423 K at densities up to about half-critical. Extrapolation to somewhat higher temperatures should be feasible with reasonable accuracy, but extrapolation to higher densities and lower temperatures should be done only with great caution. This surface, along with ideal-gas heat capacities, allows the calculation of the thermodynamic properties of the gas phase.

**Table VI.** Saturated Vapor Densities of R124

| $T$ (K) | $\rho$ (mol · L$^{-1}$) |
|---|---|
| 310.000 | 0.24441 |
| 315.000 | 0.28099 |
| 320.000 | 0.32203 |
| 325.000 | 0.36805 |
| 330.000 | 0.41967 |
| 335.000 | 0.47760 |
| 340.000 | 0.54272 |
| 345.000 | 0.61612 |
| 350.000 | 0.69917 |
| 355.000 | 0.79363 |
| 360.000 | 0.90186 |
| 365.000 | 1.02716 |
| 370.000 | 1.17436 |
| 375.000 | 1.35103 |
| 380.000 | 1.57028 |
| 385.000 | 1.85824 |

We have solved Eqs. (1) and (3)–(6) using a simple iterative procedure, to determine the density of the saturated vapor up to a maximum density of 2 $\mathrm{mol \cdot L^{-1}}$. Values so determined are listed in Table VI. We estimate that the uncertainty in these values is 0.0005 $\mathrm{mol \cdot L^{-1}}$.

The values of the second and third virial coefficients at the temperature of the Burnett isotherm, calculated from the parameters determined in the surface fit, are $-263.6\ \mathrm{cm^3 \cdot mol^{-1}}$ and $2.95 \times 10^4\ \mathrm{cm^6 \cdot mol^{-2}}$. These should be compared with the values $-263.2\ \mathrm{cm^3 \cdot mol^{-1}}$ and $2.83\ \mathrm{cm^6 \cdot mol^{-2}}$ which were determined directly from the Burnett expansion measurements. The differences between these two sets of values are satisfyingly small (0.15% in $B$ and 4% in $C$), and within combined uncertainties. We take this as confirmation that an adequate representation of the data has been achieved.

$B(T)$ and $C(T)$ calculated from the parameters in Table V are compared with those from other determinations in Fig. 4. The agreement with the $B$ determined from speed of sound measurements [16] is excellent and better than 0.7% over the overlapping range. Even when our equation is extrapolated down to 250 K the agreement is better than 1%. The agreement between the values of $C$ is not as good and is a factor of $10^2$ worse than the agreement between the values of $B$. However, given the limitations of the square-well representation for $C$ and the difficulty of extracting third virial coefficients from acoustic measurements, we regard the agreement as satisfactory.

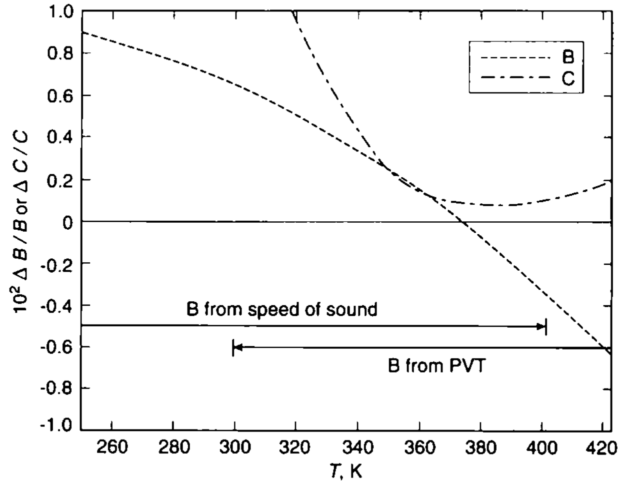

**Fig. 4.** Deviations of $B$ and $C$, determined from speed of sound measurements [16], from Eqs. (4) and (5) with the parameters listed in Table V.

## 4. CONCLUSION

We have made highly accurate and precise measurements of the vapor pressure and *PVT* relationship for R124. From the results we have calculated values of the saturated vapor density up to a maximum of $2\,\mathrm{mol \cdot L^{-1}}$. We have represented the data analytically using a Wagner equation for vapor pressures and a virial equation for the *PVT* results. The equation-of-state, along with the properties of the ideal-gas state, should yield accurate values for the thermodynamic properties of the real-gas state between 278 and 423 K at densities up to $2\,\mathrm{mol \cdot L^{-1}}$.

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