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Vapor Pressures and Gas-Phase *PVT* Data for 1,1,1,2-Tetrafluoroethane

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We present new data for the vapor pressure and *PVT* surface of 1,1,1,2-tetrafluoroethane (Refrigerant 134a) in the temperature range 40°C (313 K) to 150°C (423 K). The *PVT* data are for the gas phase at densities up to one-half critical. Densities of the saturated vapor are derived at five temperatures from the intersections of the experimental isochores with the vapor pressure curve. The data are represented analytically in order to demonstrate experimental precision and to facilitate calculation of thermodynamic properties.

KEY WORDS: chlorofluorocarbons; density; *PVT*; (refrigerants; saturated vapor; vapor pressure; virial equation.

1. INTRODUCTION

The effect on global climate of trace gases in the troposphere and the depletion of stratospheric ozone have led to increasing concern in the past several years. Chlorofluorocarbons (CFCs) released into the atmosphere are important contributors to these effects, and their rapidly increasing concentration as a result of man's activities lends a sense of urgency to the study of these problems [1]. Currently CCl_3F (R11) and CCl_2F_2 (R12) are present at concentrations sufficient to cause alarm. These two CFCs have long atmospheric lifetimes (estimated at approximately 60 and 100 years, respectively) due to the fact that they are fully halogenated. Their replacement has been mandated by international agreement, and the refrigeration industry is currently considering alternative refrigerants. Although many criteria must be satisfied by a prospective replacement, knowledge of the thermophysical properties is essential in order for system

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designers to assess the impact such a substitution would have on new and existing equipment. One prime candidate for the replacement of R12 is CFH_2CF_3 (R134a), which has an atmospheric lifetime of about 6 years [2] and a similar normal boiling point.

In this paper, we present measurements of the vapor pressure and gas-phase *PVT* surface for R134a. The measurements were made in an existing apparatus whose operating characteristics and estimated accuracies are well established. This work is part of a larger project in our laboratory to produce tables of thermophysical properties for R134a. In Section 2 we give a brief description of the apparatus and measurement techniques, and following that, a discussion of the results. We are aware of only two other recent measurements on this halocarbon [3, 4].

2. APPARATUS AND PROCEDURE

The semiautomatic *PVT* apparatus is shown in the schematic diagram in Fig. 1. It has been thoroughly documented in previous publications [5–7], and only a brief description is given here. 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-

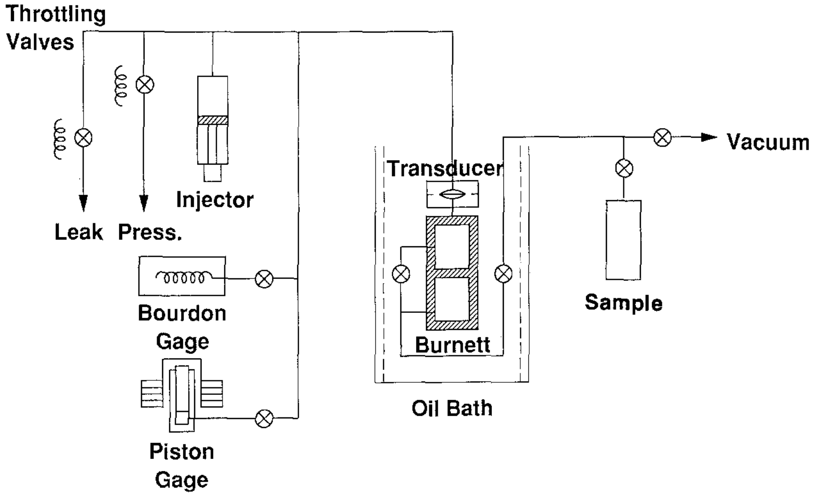

Fig. 1. Schematic diagram of the Burnett apparatus, filling system, and pressure measuring system.

filled system consisting of several precision pressure gauges and a piston-type gas injector, for pressure adjustments. The injector is driven by a stepper motor which is controlled by an analog logic circuit which uses the pressure transducer as a sensor. It can operate automatically to balance the argon pressure against the sample pressure. The temperature of the oil bath is controlled by a circuit consisting of a platinum resistance thermometer in an AC inductance bridge, signal conditioner, and programmable power supply. A microcomputer is used in setting the control temperature, monitoring equilibration, measuring temperature and pressure, processing the raw data, and storing the information.

Data acquisition on a sample begins with a series of Burnett expansions on a reference isotherm, measured by the conventional method [5]. For this work a gas-operated deadweight gauge is used to make pressure measurements manually, and the apparatus is operated in the semi-automatic mode. Following this, pressure–temperature isochores (constant density runs) are measured in the fully automatic mode, using an automatic pressure gauge. On each isochore a pressure measurement at the reference isotherm is included so that the isochore density can be obtained.

With this technique data can be measured more or less continuously with relatively little effort on the part of the operator. Vapor pressures are measured by filling the sample cell to approximately critical density and measuring the pressure of the two-phase sample as a function of temperature. The apparatus is capable of making measurements in the range 0–200°C at 0–20 MPa. Uncertainties in the temperature and pressure measurements are of the order 10^{-3} °C and 10^{-4} MPa, respectively. When the gas-operated deadweight gauge was used, pressures were often reproducible to within 2×10^{-5} MPa.

Samples were supplied in pure form as part of a special batch from a commercial source of refrigerants. Any residual air was removed by a technique of repeated freezing, pumping, and thawing. The final residual pressure indicated the presence of no more than 40 ppm air. The sample supplied to us was a small part of a batch run. The chief impurities were stated to be pentafluoroethane (R125), 1,1,1-trifluoroethane (R143a), 1-chloro-2,2-difluoroethene (R1122), and water. Each was present at approximately the 100-ppm level. The vapor pressure measurements in the results section are consistent with this level of purity. The sample was loaded into a small high-pressure cylinder. This cylinder and the sample supply manifold were insulated and heated in order to be able to fill the sample cell at the desired temperatures and pressures.

3. RESULTS

3.1. PVT Data

The Burnett expansion measurements were performed at 94.99°C (368.14 K). A total of 13 points was measured in two series of expansions, starting at a pressure near the vapor pressure (3.59 MPa) and at a density about one-half critical. The data were analyzed in two ways; (1) with a cell constant (ratio of the two volumes) previously determined from measurements on helium gas and (2) with a cell constant derived from the present measurements. The two cell constants agreed to within 1 part in 10,000 and so the first technique was used since it allows a more positive determination of the virial coefficients. A virial equation,

$$P = RT\rho[1 + B\rho + C\rho^2 + D\rho^3] \tag{1}$$

with three coefficients was required to fit the data within experimental precision. The standard deviation in pressure was 6×10^{-5} MPa, which is nearly as good as the experimental precision possible with the gas deadweight gauge pressure measurements. The experimental pressures and calculated densities are shown in Table I.

After the above pressure–density relationship had been established on the Burnett isotherm, data were collected on isochores. A total of 56 data was taken on five isochores between 48 and 150°C (321–423 K). A pressure

Table I. *PVT* Data on the Burnett Isotherm at 94.99°C (368.14 K)

Pressure (MPa)	Density ($\mathrm{mol \cdot L^{-1}}$)
3.49815	2.32600
2.70873	1.30539
1.81101	0.73279
1.11813	0.41131
0.66137	0.23084
0.38216	0.12955
0.21799	0.07271
3.06692	1.64206
2.15139	0.92151
1.36304	0.51727
0.81753	0.29030
0.47605	0.16294
0.27271	0.09145

measurement on each isochore at 94.99°C was used to determine its density via Eq. (1). A small temperature correction to the density was used to account for the thermal expansion of the sample cell. The experimental results, adjusted to even temperatures, are given in Table II.

3.2. Vapor Pressure

A set of 22 vapor pressure points was measured in the range 40–100°C (313–373 K) with the cell filled to approximately critical density. These data are shown in Table III. In addition, at the beginning of each isochoric run, one or more vapor pressures were measured by cooling the sample cell a short distance into the two-phase region. In the first case approximately half the sample is liquid, while in the second, only a small fraction ($\leqslant 1\%$) is in the liquid phase. The agreement between these two types of measurements indicated that our sample is quite pure.

3.3. Density of Saturated Vapor

The temperatures at which the five experimental isochores intersect the vapor pressure curve allow the derivation of five saturated vapor densities. The isochores and segments of the vapor pressure curve were represented with simple mathematical functions and the intersections were found by Newton's iteration. The derived data, and the estimated uncertainty in the temperature of intersection, between 47 and 92°C, are given in Table IV.

4. ANALYTICAL REPRESENTATION OF THE DATA

4.1. Vapor Pressure

The 22 primary vapor pressure data, given in Table III, were represented with the function [8]

$$\ln P = a/T_r + b + cT_r + d(1 - T_r)^{1.5} \tag{2}$$

where P = pressure in MPa, T = temperature in K, $T_r = T/T_c$, $a = -8.416912$, $b = 10.568367$, $c = -0.750336$, and $d = 2.04222$, and the value used for T_c is 374.25 K from Ref. 3. The deviations of the data from the equation are random and the standard deviation is 0.005% in pressure, indicating that the data are self-consistent and of a high precision. This equation with the above choice for T_c yields a value of 4.060 MPa for the critical pressure. Equation (2) has not been fit to data below 40°C (313.15 K), corresponding to a pressure of about 1 MPa, and although the

Table II. Gas-Phase *PVT* Data

T (°C)	Pressure (MPa)	Density ($mol \cdot L^{-1}$)
88	3.0895	1.9294
89	3.1188	1.9293
90	3.1480	1.9293
95	3.2907	1.9289
95	3.2908	1.9289
95	3.2907	1.9289
95	3.2908	1.9289
100	3.4298	1.9284
110	3.7002	1.9278
130	4.2185	1.9260
69	2.0511	1.0837
70	2.0663	1.0836
75	2.1372	1.0834
80	2.2061	1.0832
90	2.3407	1.0827
95	2.4063	1.0825
95	2.4065	1.0825
100	2.4712	1.0823
110	2.5986	1.0818
130	2.8462	1.0809
150	3.0861	1.0800
48	1.2340	0.6018
52	1.2625	0.6017
60	1.3174	0.6015
70	1.3841	0.6013
80	1.4491	0.6010
90	1.5128	0.6008
95	1.5443	0.6007
95	1.5443	0.6007
100	1.5754	0.6005
110	1.6371	0.6003
130	1.7580	0.5998
150	1.8764	0.5993
94	3.4637	2.3303
95	3.5002	2.3303
95	3.5003	2.3303
95	3.5003	2.3303
96	3.5370	2.3302
97	3.5731	2.3301
98	3.6092	2.3300
100	3.6805	2.3298
110	4.0277	2.3288
130	4.6905	2.3269
150	5.3263	2.3249

Table II. *(Continued)*

T (°C)	Pressure (MPa)	Density (mol · L^{-1})
76	2.3833	1.3098
77	2.4014	1.3098
78	2.4195	1.3097
80	2.4551	1.3096
85	2.5429	1.3094
90	2.6287	1.3091
95	2.7132	1.3088
95	2.7130	1.3088
100	2.7960	1.3080
110	2.9587	1.3079
130	3.2735	1.3069
150	3.5775	1.3058

Table III. Vapor Pressures of 1,1,1,2-Tetrafluoroethane

Temperature (°C)	Pressure (MPa)
40.095	1.0187
42.045	1.0731
43.990	1.1295
45.985	1.1895
48.024	1.2531
49.987	1.3169
55.009	1.4911
60.038	1.6827
62.058	1.7645
64.052	1.8482
66.097	1.9373
68.056	2.0255
70.068	2.1193
75.081	2.3675
80.027	2.6339
82.016	2.7474
84.034	2.8665
86.004	2.9867
87.987	3.1117
89.978	3.2416
95.009	3.5906
99.989	3.9694

Table IV. Derived Densities of the Saturated Vapor

Density ($mol \cdot L^{-1}$)	Temperature (°C)
0.6019	47.25 ± 0.01
1.0837	68.46 ± 0.01
1.3099	75.05 ± 0.02
1.9295	87.39 ± 0.01
2.3305	92.52 ± 0.05

equation has an appropriate form for extrapolation to lower temperatures, such extrapolations should be done with caution.

The vapor pressures measured while performing the isochoric measurements, mentioned earlier, were compared with the equation but were not used in the fitting. These data exhibited no discernible difference from the curve for temperatures more than 1° inside the two-phase envelope. Three data less than 1° from the phase boundary were lower than the curve by an average of 0.08%. This is a common phenomenon and is probably associated with precondensation in some part of the sample cell.

The vapor pressure data from Wilson and Basu [4] in the range 36–96°C were compared with Eq. (2) along with our own data in Fig. 2. The two sets are in complete agreement within the precision of the results of Ref. 4.

4.2. The *PVT* Surface

In order to assess the precision and accuracy of the gas-phase data and also to allow calculation of the thermodynamic properties, we have fit the data with an analytic equation of state. This was done by expressing the parameters B, C, and D in Eq. (1) as functions of temperature. For this purpose the following functions were used:

$$B = B_0 + B_1 \exp(520/T)$$

$$C = C_0 + C_1 T^{-1/2} + C_2 T^{-1} + C_3 T^{-3/2}$$

$$D = D_0 + D_1 T$$

This surface fit the 56 data in Table II plus the 13 points on the Burnett isotherm, Table 1, with an rms deviation of 0.015% (largest deviation, 0.05%) in density. The following values were found:

$R = 0.00831441$

$B_0 = 0.242848, \quad B_1 = -0.128252$

$C_0 = 5.69600, \quad C_1 = -3.40104 \times 10^2$

$C_2 = 6.74672 \times 10^3, \quad C_3 = -4.42725 \times 10^4$

$D_0 = -7.8762 \times 10^{-4}, \quad D_1 = 1.0227 \times 10^{-6}$

for P in MPa, T in K, and density in mol · L^{-1}. This equation can be used with a high accuracy between 48 (321 K) and 150°C (423 K) at densities up to about one-half critical. Extrapolations to lower and (somewhat) higher temperatures should be feasible with a reasonable accuracy, but extrapolations to higher densities, or pressures, should be done only with great caution.

The deviations of the data from the surface given by Eq. (1) are shown in Fig. 3. Data from Ref. 4 which fall within this range are also shown. In Fig. 3 it is seen that there is a bias between the two data sets of about 0.13%. Since no such bias was seen in Fig. 2, which compares temperature

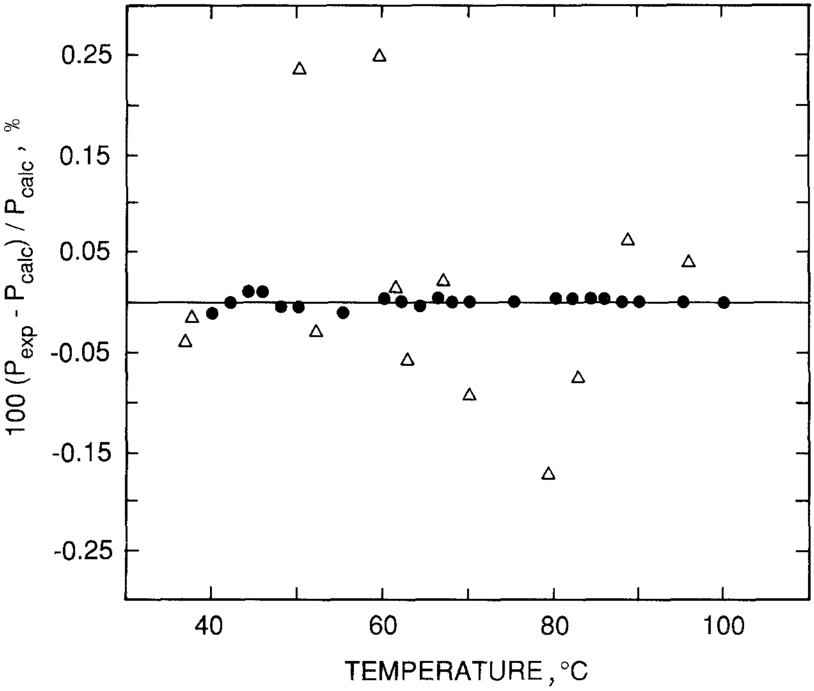

Fig. 2. Deviations of vapor pressure data from Eq. (2). ●, present results; △, Ref. 4.

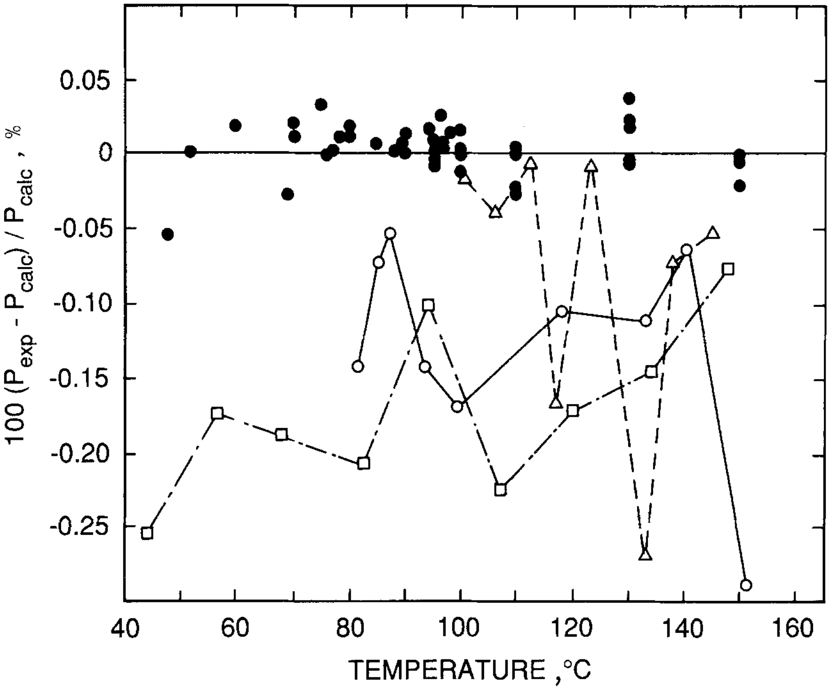

Fig. 3. Deviations of the gas-phase *PVT* data from Eq. (1). ●, present results; △, 2.56 mol · L^{-1} [4]; ○, 1.54 mol · L^{-1} [4]; □, 0.50 mol · L^{-1} [4].

and pressure measurements, we assume that there is a small systematic difference in density measurements.

The saturated vapor densities at the two highest temperature in Table IV (87–92°C) as well as corresponding values from Ref. 4 were compared with the results of Kabata et al. [3] at these temperatures. Our densities, and those of Wilson and Basu, were lower than those of Kabata by 1–2%. These differences correspond approximately to Kabata's estimates of uncertainty in this region.

5. CONCLUSION

We have made highly accurate and precise measurements of the vapor pressure and gas-phase *PVT* relationship for 1,1,1,2-tetrafluoroethane (R134a), a substance for which very little information has been published. We have represented the data analytically and have derived values for the density of the saturated vapor.

The equation-of-state surface, along with the properties of the idealgas state (see, for example, Chen et al. [9]), should yield accurate values for the thermodynamic properties of the real-gas state within the range outlined above, by means of standard thermodynamic formulae. These properties should help to determine the suitability of this substance for use as a substitute refrigerant.

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