International Journal of Thermophysics, Vol. 20, No. 5, 1999

Subatmospheric Vapor Pressures for Fluoromethane (R41), 1,1-Difluoroethane (R152a), and 1,1,1-Trifluoroethane (R143a) Evaluated from Internal-Energy Measurements

H. A. Duarte-Garza[1, 2] **and J. W. Magee**[1, 3]

Received March 1, 1999

Vapor pressures were evaluated from measured internal-energy changes $\Delta U^{(2)}$ in the vapor + liquid two-phase region. The method employed a thermodynamic relationship between the derivative quantity $(\partial U^{(2)}/\partial V)_T$, the vapor pressure p_σ, and its temperature derivative $(\partial p/\partial T)_\sigma$. This method was applied at temperatures between the triple point and the normal boiling point of three substances: fluoromethane (R41), 1,1-difluoroethane (R152a), and 1,1,1-trifluoroethane (R143a). In the case of R41, vapor pressures up to 1 MPa were calculated to validate the technique at higher pressures. For R152a, the calculated vapor pressure at the triple-point temperature differed from a direct experimental measurement by less than the claimed uncertainty (5 Pa) of the measurement. The calculated vapor pressures for R41 helped to resolve discrepancies in several published vapor pressure sources. Agreement with experimentally measured vapor pressures for R152a and for R143a near the normal boiling point (101.325 kPa) was within the experimental uncertainty of approximately 0.04 kPa (0.04%) for the published measurements.

KEY WORDS: 1,1-difluoroethane; fluoromethane; internal energy; refrigerants; 1,1,1-trifluoroethane; triple point; two-phase region; vapor pressure.

1. INTRODUCTION

In an earlier paper [1], we reported a new method to calculate reliable vapor pressures under low-pressure conditions where conventional measurements

---

[1] Physical and Chemical Properties Division, Chemical Science and Technology Laboratory, National Institute of Standards and Technology, Boulder, Colorado 80303, U.S.A.

[2] Guest researcher from Texas A&M University, Kingsville, Texas 78363, U.S.A.

[3] To whom correspondence should be addressed.

are frequently suspect or, in many cases, nonexistent. Previously, we showed the relevant thermodynamic equations, reviewed published methods, and discussed the equations specific to the new method. We then applied this method to 1,1,1,2-tetrafluoroethane (R134a), pentafluoroethane (R125), and difluoromethane (R32) at temperatures between their triple points and normal boiling points.

In this work, we apply the new method to calculate vapor pressures of three additional substances at temperatures from the triple point to the normal boiling point. Subatmospheric vapor pressure data for the substances fluoromethane (R41), 1,1-difluoroethane (R152a), and 1,1,1-trifluoroethane (R143a) are relatively scarce. Furthermore, the existing data cover only a limited temperature range and are not in good accord with other vapor pressure data. To improve this situation, we calculate vapor pressures which are thermodynamically consistent with accurate calorimetric measurements. These calculated vapor pressures are then compared to published vapor pressure data and correlations. Special emphasis is given to vapor pressures at triple-point temperatures.

2. METHOD

This section presents a brief summary of the technique for accurate evaluation of vapor pressures from isochoric internal-energy measurements in the two-phase region. A detailed discussion is presented elsewhere [1]. The method is based on the expression relating the two-phase internal energy $U^{(2)}$ to the vapor pressure,

$$(\partial U^{(2)}/\partial V)_T = T\left(\frac{dp}{dT}\right)_\sigma - p_\sigma = T^2\left(\frac{d(p/T)}{dT}\right)_\sigma \tag{1}$$

where σ signifies a quantity evaluated along the saturation boundary. If we exploit the linear dependence of $U^{(2)}$ on the molar volume V, then we may replace the derivative on the left side of Eq. (1) with a finite difference calculation,

$$(\partial U^{(2)}/\partial V^{(2)})_T = \left(\frac{U_2^{(2)} - U_1^{(2)}}{V_2^{(2)} - V_1^{(2)}}\right)_T \tag{2}$$

where the subscripts 1 and 2 denote any two points within the two-phase region, including the points at the saturated single phases, and the superscript 2 denotes the bulk property. In this work, a bulk property is any property of the vapor and the liquid combined.

After computing $(\partial U^{(2)}/\partial V^{(2)})_T$ at different temperatures between the triple point and the normal boiling point, we can fit Eq. (1) to these data using a nonlinear regression analysis [2] of the parameters in an equation for $p_\sigma(T)$. The regression analysis must fit the adjustable parameters in the difference between two equations, those for $T(dp/dT)_\sigma$ and p_σ. Thus, it is important to select an equation $p_\sigma = f(T)$ which is capable of fitting vapor-pressure data within their experimental uncertainty over the entire temperature range of interest. Experience has indicated which $p_\sigma(T)$ equations [1] have desirable properties.

Experimental values for $U^{(2)}$ at precisely known densities are required to carry out the calculations with Eq. (2). We use experimental energy-increment data from isochoric (constant $V^{(2)}$) measurements which were made with an adiabatic calorimeter. Values for $U^{(2)}$ at two or more densities are needed to calculate the change of the bulk internal energy with respect to the bulk specific volume at constant temperature. Since the calorimetric measurements provide the change of internal energy as a function of T along a given isochore, but not the change of internal energy from one density to another, we need additional information at a reference temperature to determine the change of internal energy between two densities. This reference temperature is selected near the normal boiling point, where accurate, direct measurements of vapor pressure are available.

$(\partial U^{(2)}/\partial V^{(2)})_T$ at the reference temperature can be calculated with Eq. (1) and vapor pressure data around the reference temperature. Then, the change of internal energy from density 1 to density 2 at that reference temperature can be determined from

$$U_2^{(2)} - U_1^{(2)} = (\partial U^{(2)}/\partial V^{(2)})_T \, (V_2^{(2)} - V_1^{(2)}) \tag{3}$$

In this procedure, we set the internal energy of one of the densities ($U_2^{(2)}$ or $U_1^{(2)}$) to an arbitrary value $U_i^{(2)} = 0$ at the reference temperature. Then, internal energy increments are calculated at each temperature and density based on differences in U from this reference state.

3. RESULTS

3.1. Application to Fluoromethane (R41)

Demiriz et al. [3] showed the existence of a gap in the reliable published vapor pressure data for R41 in the temperature range 211 to 253 K. This 42 K gap lay between the low-temperature data of Oi et al. [4] and the data of Demiriz et al., who also fitted a four-coefficient expression to both their data and those of Oi et al. However, until other data were available, it was not possible to validate this equation for calculations in the gap. Recently, Magee [5] has measured R41 vapor pressures with a static method at temperatures from 170 to 317 K and two-phase internal energy increments [6] with an adiabatic calorimeter from the triple point (≈ 130 K) to 270 K. For both types of measurement, the same sample supply was used. Agreement between these new vapor pressures and published values was inconsistent. Magee's vapor pressures agreed with Demiriz et al. at 253 K and with Oi et al. at 211 K within 0.2%. However, at lower temperatures agreement was poor. Magee's vapor pressure at 170 K is about 80 Pa (0.4%) higher than that of Oi et al., which is greater than Magee's experimental uncertainty of 20 Pa. A plausible explanation for this observation is the presence of a small volatile impurity in Magee's sample even though three cycles of freeze–pump–thaw degassing were carried out on the sample. A subsequent electrochemical oxygen analysis indicated that the volatile impurity was air, at a concentration of 5 ppm in the gas phase. In support of this explanation, calculations with a predictive model developed by Weber [7] determined that a minor concentration (4 ppm, according to the model) of air can create an +80-Pa effect in the vapor pressure of R41 at 170 K.

Because only 5 of every 1 million molecules consisted of air species, this air impurity could, in principle, absorb only a minute fraction of the energy during a calorimetric experiment. Due to similar values of the molar ideal gas heat capacities of R41 and of air, we estimate that a 5-ppm air impurity can contribute no more than a 7-ppm uncertainty to the measurements. For this reason, the air impurity has only a negligibly small effect on measured internal energy increments. We may therefore use Magee's $U^{(2)}$ measurements [6] to calculate vapor pressures to compare with Oi et al. The triple-point and normal boiling-point temperatures for R41 are 129.82 K [8] and 195.02 [9], respectively. A temperature of 200 K was selected for the reference temperature due to the availability of tabulated saturation data. The internal-energy reference state, where we arbitrarily set $U^{(2)} = 0$, was selected as the saturated vapor state at 200 K. We have calculated vapor pressures for R41 from 200 K to the triple-point temperature. Because only Magee [5] has reported vapor pressures in the 42 K temperature gap mentioned above, we have also applied this procedure to calculate superambient vapor pressures at temperatures up to 250 K. These calculations will give us thermodynamically consistent vapor pressures up to about 1 MPa which can be used to validate direct measurements.

To apply Eq. (2), we need internal energies for both a high-density state and a low-density state, both at the same temperature. For the low-density states, we used internal energies of the saturated vapor from an unpublished equation of state [9]. Each of these states was paired with a high-density state from calorimetric measurements. The difference in internal energy between these two curves is about 10 kJ · mol^{-1} at the reference temperature and about 15 kJ · mol^{-1} at the triple-point temperature. The large absolute values we obtained for $\Delta U^{(2)}$ led to reliable values of $(\partial U^{(2)}/\partial V^{(2)})_T$ and to accurate vapor pressures.

We selected a vapor pressure equation of the functional form [10],

$$\ln(p_\sigma/p_C) = [C_1\tau + C_2\tau^{1.5} + C_3\tau^3 + C_4\tau^6]/[1-\tau] \tag{4}$$

where $\tau = 1 - T/T_C$, $T_C = 317.28$ K [10], and $p_C = 5.897$ MPa [10].

In this analysis, the change in internal energy along the high-density isochore was determined from two-phase calorimetric data from this laborarory [6]. We chose an isochore that includes measurements from 136.02 to 270.58 K. For this isochore, the calorimetric bomb (with a volume of approximately 73 cm^3) contained 1.4656 mol of sample. The energy needed to change the temperature of the sample by 1 K was fitted with the equation

$$Q/(n\,\Delta T) = a_0 + a_1T^{-1} + a_2T^{-2} + a_3T^{-3} + a_4T^{-4} \tag{5}$$

where Q is in J, n is in moles, and T is in K. The coefficients are $a_0 = 3.74305368 \times 10^2$, $a_1 = -1.88404363 \times 10^5$, $a_2 = 4.39354952 \times 10^7$, $a_3 = -4.57844632 \times 10^9$, and $a_4 = 1.805072 \times 10^{11}$.

The change in internal energy along the isochore is then calculated with

$$\Delta U = \int_{T_1}^{T_2} Q/(n\,\Delta T)\, dT \tag{6}$$

where $n = 1.4656$ mol.

Although the exact bomb volume varies with temperature and pressure, we may approximate the density as a function of temperature only. The density of the *quasi-isochore* was fitted to the equation

$$\rho = b_0 + b_1T^{-1} + b_2T^{-2} \tag{7}$$

where ρ is in mol · dm^{-3} and the coefficients are $b_0 = 1.85700164 \times 10^1$, $b_1 = 1.13450381 \times 10^2$, and $b_2 = -7.64297171 \times 10^3$. The molecular mass used for R41 is 34.0334 g · mol^{-1}.

The internal energy of the saturated vapor was calculated from $U = H - PV$. A preliminary, unpublished equation of state for R41 developed by Outcalt and McLinden [9] was used to calculate H, and preliminary equations for vapor pressure and for saturated vapor volume [9] were used to calculate the PV term. Sensitivity studies [1] have shown that the results are insensitive to the choice of a gas-phase equation of state as long as it reproduces the correct behavior of second virial coefficients. A value of $(\partial U^{(2)}/\partial V^{(2)})_T$ at the reference temperature (200 K) was calculated with the vapor pressure ancillary equation fitted by Outcalt [10]. With these data, the vapor pressures shown in Table I were calculated. Table I also shows vapor pressures calculated with the Outcalt equation [10] and the absolute deviation from these values. Figure 1 shows the deviations of the published data and these results from this same equation. The agreement shown with Oi et al. is very good. At the triple-point temperature (129.82 K)

Table I. Vapor Pressures Derived from $U^{(2)}$ and from Published Data [10] for R41

T (K)	P_σ[a] (Pa)	P_σ, published (Pa)	$P_\sigma - P_\sigma$, published (Pa)
129.82	321.9	346.4	−24.5
130	330.3	355.1	−24.8
135	651.4	685.7	−34.3
140	1,212.4	1,255.4	−43.0
145	2,143.9	2,192.6	−48.7
150	3,623.6	3,671.8	−48.2
155	5,883.6	5,922.0	−38.4
160	9,217.7	9,234.2	−16.5
165	13,987.1	13,968.1	19.0
170	20,625.4	20,557.5	67.9
175	29,642.0	29,513.9	128.1
180	41,623.9	41,428.9	195.0
185	57,237.5	56,975.0	262.5
190	77,227.7	76,905.5	322.2
195	102,417.7	102,052.0	365.7
200	133,707.6	133,322.6	385.0
205	172,071.7	171,698.0	373.7
210	218,556.8	218,228.1	328.7
215	274,279.1	274,028.0	251.1
220	340,421.9	340,274.3	147.6
225	418,232.4	418,201.3	31.1
230	509,019.5	509,098.7	−79.2
235	614,151.2	614,308.9	−157.7
240	735,053.2	735,226.4	−173.2
245	873,206.9	873,297.7	−90.8
250	1,030,149.0	1,030,023.0	126.0

[a] The number of figures presented is for comparison only.

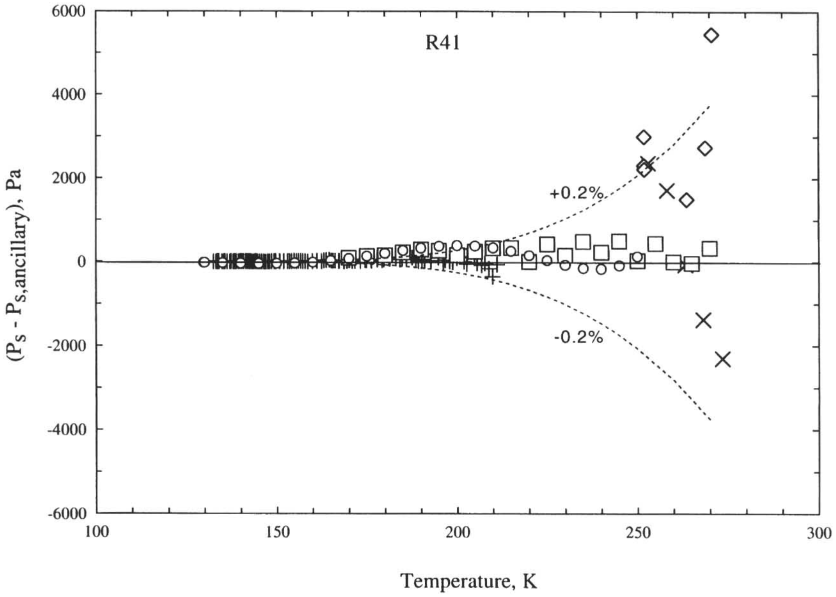

Fig. 1. Comparison of vapor pressures for R41 calculated with the present method and selected experimental values with the ancillary vapor pressure equation of Ref. 5. Dashed lines are ±0.2% deviations. This work (○); Oi et al. (+) [4]; Demiriz et al. (×) [3]; Magee (□) [5]; Holcomb (◇) [11].

the deviation, defined as this work minus a calculation with a published equation, is only −24 Pa (−7%), at 210 K it is +329 Pa (+0.15%), and at 250 K it is +127 Pa (+0.01%).

We also applied this method at pressures up to about 1 MPa at a temperature of 250 K. Comparisons with accurate published measurements were very good. At 250 K, the calculated vapor pressure is within 0.1 kPa (0.01%) of the static vapor pressure measured by Magee [5]. Also at 250 K, the measurements of both Demiriz et al. and Holcomb [11] are 2.3 kPa (0.2%) higher. These results show that this method can be applied to calculate both subambient and superambient vapor pressures which have uncertainties comparable to reliable direct measurements.

3.2. Application to 1,1-Difluoromethane (R152a)

Outcalt and McLinden [12] have critically assessed the published vapor pressure data for R152a. In addition, they used measurements from Blanke and Weiß [13], Baehr and Tillner-Roth [14], Higashi et al. [15], and Silva and Weber [16] to fit their vapor pressure equation. For this substance, the agreement of published vapor pressures is very good at temperatures as low as 220 K, but below this temperature there is only a single data source [13]. Calculated vapor pressures are needed to validate the low temperature measurements. Outcalt and McLinden's equation is of the form,

$$\ln(p_\sigma/p_C) = [C_1\tau + C_2\tau^{1.5} + C_3\tau^2 + C_4\tau^4 + C_5\tau^{6.5}]/[1-\tau] \tag{8}$$

where $\tau = 1 - T/T_C$, $T_C = 386.411$ K [12], and $p_C = 4.51675$ MPa [12].

The normal boiling-point and triple-point temperatures for R152a are 249.13 [12] and 154.56 K [13, 17], respectively. A temperature of 249.15 K was selected for the reference temperature due to the very good agreement of published data (within 0.05%) at this temperature. The internal-energy reference state, where we arbitrarily set $U^{(2)} = 0$, was selected as the saturated vapor state at 249.15 K. We have calculated vapor pressures for R152a from 250 K to the triple-point temperature.

An isochore with a total of 0.92386 mol was chosen from the calorimetric data measured by Magee [17]. The change in internal energy along the

Table II. Vapor Pressures Derived from $U^{(2)}$ and from Published Data [12] for R152a

T (K)	P_σ (Pa)	P_σ, published (Pa)	$P_\sigma - P_\sigma$, published (Pa)
154.56	64.0	64.1	−0.1
155	67.9	68.0	−0.1
160	129.7	129.9	−0.2
165	236.8	237.0	−0.2
170	414.8	415.0	−0.2
175	700.0	700.1	−0.1
180	1,142.0	1,141.9	0.1
185	1,806.3	1,805.8	0.5
190	2,777.5	2,776.2	1.3
195	4,162.0	4,159.6	2.4
200	6,090.7	6,086.6	4.1
205	8,721.3	8,715.0	6.3
210	12,240.5	12,231.4	9.1
215	16,865.7	16,853.1	12.6
220	22,846.2	22,829.6	16.6
225	30,464.1	30,442.8	21.3
230	40,034.3	40,008.2	26.1
235	51,905.0	51,874.3	30.7
240	66,457.2	66,422.3	34.9
245	84,103.7	84,065.6	38.1
250	105,288.4	105,249.0	39.4

two-phase isochore was calculated with Eqs. (5) and (6). The fitting parameters for Eq. (5) are $a_0 = 4.60138293 \times 10^2$, $a_1 = -2.40940981 \times 10^5$, $a_2 = 6.23802035 \times 10^7$, $a_3 = -7.36784091 \times 10^9$, and $a_4 = 3.32526820 \times 10^{11}$. The density of the isochore was fitted to Eq. (7) within experimental uncertainty. The fitting parameters for this equation are $b_0 = 1.23744368 \times 10^1$, $b_1 = 9.52671950 \times 10^1$, and $b_2 = -7.31539857 \times 10^3$. For R152a, $M = 66.051$ $g \cdot mol^{-1}$. The internal energy and density of the saturated vapor were calculated with the equation of state for R152a of Outcalt and McLinden [12]. $(\partial U/\partial V)_T$ at the reference temperature (249.15 K) was calculated with the vapor pressure ancillary equation of Outcalt and McLinden [12].

The results for R152a are given in Table II. Figure 2 shows that the vapor pressures determined in this work are in very good agreement with the published values. Our calculated vapor pressures support a claim of thermodynamic consistency throughout this range of temperatures. The triple point is the lowest temperature where vapor and liquid may coexist, and often this is the temperature where conventional measurements show the greatest discord. For R152a we find exeptionally good agreement at the triple point, where Blanke and Weiß [13] measured a pressure of 65 Pa,

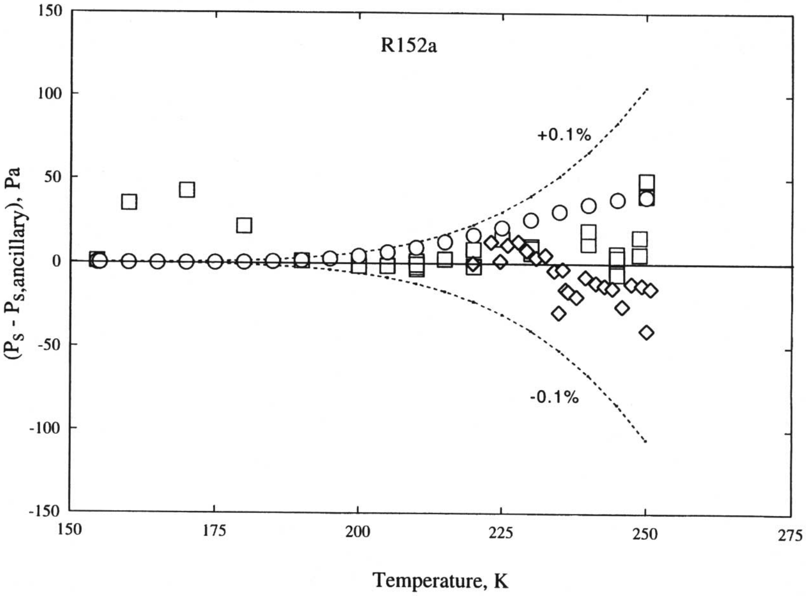

Fig. 2. Comparison of vapor pressures for R152a calculated with the present method and selected experimental values with the ancillary vapor pressure equation of Outcalt and McLinden [12]. Dashed lines are ±0.1% deviations. This work (○); Blanke and Weiß (□) [13]; Silva and Weber (◇) [16].

with an uncertainty of 5 Pa, and we have calculated a pressure of 64.0 Pa with this method. Around the normal boiling point, the calculated vapor pressures are slightly larger (+39 Pa, +0.04%) than the published vapor pressures of Silva and Weber [11]. This agreement is within the experimental uncertainty of the direct measurements.

3.3. Application to 1,1,1-Trifluoromethane (R143a)

Outcalt and McLinden [18] have critically assessed the published vapor pressure data for R143a. When they fit their vapor pressure equation to measurements from de Vries [19] and Weber and Defibaugh [20], an inconsistency was obvious at temperatures below 250 K. Calculated vapor pressures could be decisive in resolving this inconsistency. The vapor pressure ancillary equation is the same form as for R152a, Eq. (8), except for the values of the coefficients as well as $T_C = 346.04$ K [18] and $p_C = 3.7756$ MPa [18].

The normal boiling point for R143a is 225.93 K [18] and its triple-point temperature is 161.34 K [17]. A temperature of 227.15 K was selected for the reference temperature, where we arbitrarily set $U^{(2)} = 0$ for the saturated vapor. We have calculated vapor pressures for R143a from 230 K to the triple-point temperature.

An isochore with a total of 0.73486 mol was chosen from the calorimetric data measured by Magee [17]. The change in internal energy along the two-phase isochore was calculated with Eqs. (5) and (6). The fitting parameters for Eq. (5) are $a_0 = 6.63182525 \times 10^2$, $a_1 = -3.73861636 \times 10^5$, $a_2 = 9.75918817 \times 10^7$, $a_3 = -1.16953548 \times 10^{10}$, and $a_4 = 5.36141830 \times 10^{11}$. The density of the isochore was fitted to Eq. (7) within experimental uncertainty. The fitting parameters for this equation are $b_0 = 9.83044811$, $b_1 = 8.07572044 \times 10^1$, and $b_2 = -6.31414322 \times 10^3$. For R143a, $M = 84.040$ $\text{g} \cdot \text{mol}^{-1}$. The internal energy and density of the saturated vapor were calculated with the equation of state for R143a of Outcalt and McLinden [18]. $(\partial U/\partial V)_T$ at the reference temperature (227.15 K) was calculated with the vapor pressure ancillary equation of Outcalt and McLinden [18].

The results for R143a are given in Table III. Figure 3 shows that the vapor pressures determined in this work are more consistent with the experimental measurements of Weber and Defibaugh because they would smoothly extend those measurements. On the other hand, the measurements of de Vries at 220 K are systematically about 130 Pa (0.17%) higher than this work. From calculations with Weber's model [7], a +130-Pa effect could be explained by the presence of a 9-ppm air impurity. These results show the advantage gained by calculating vapor pressures from

Table III. Vapor Pressures Derived from $U^{(2)}$ and from Published Data [18] for R143a

T (K)	P_σ (Pa)	P_σ, published (Pa)	$P_\sigma - P_\sigma$, published (Pa)
161.34	1,076.8	1,078.0	−1.2
165	1,560.0	1,560.4	−0.4
170	2,511.7	2,510.5	1.2
175	3,917.7	3,913.8	3.9
180	5,937.1	5,929.5	7.6
185	8,764.4	8,752.0	12.4
190	12,632.2	12,614.2	18.0
195	17,813.2	17,789.0	24.2
200	24,621.3	24,591.1	30.2
205	33,412.5	33,377.1	35.4
210	44,585.0	44,545.7	39.3
215	58,578.3	58,536.8	41.5
220	75,872.6	75,830.2	42.4
225	96,987.4	96,944.4	43.0
230	122,479.8	122,434.5	45.3

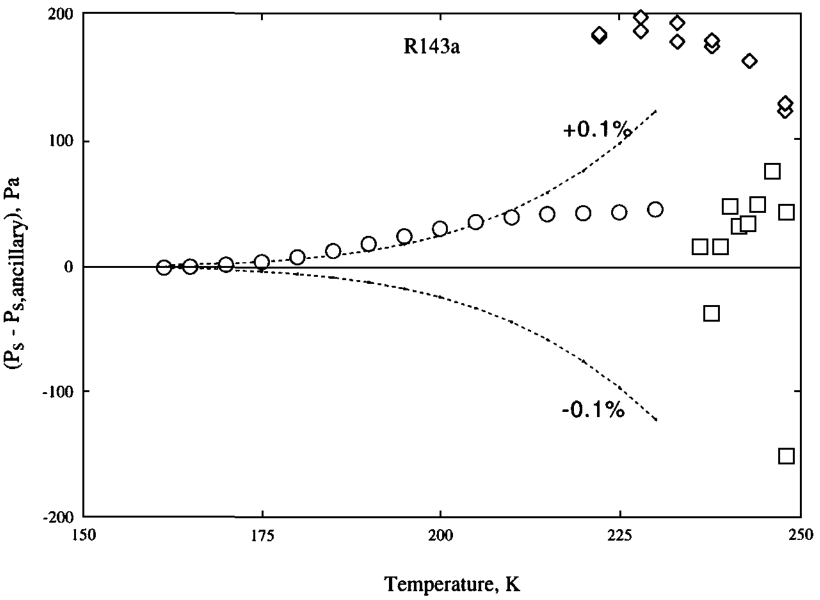

Fig. 3. Comparisons of vapor pressures for R143a calculated with the present method and selected experimental values with the ancillary vapor pressure equation of Outcalt and McLinden [18]. Dashed lines are ±0.1% deviations. This work (○); de Vries (◇) [19]; Weber and Defibaugh (□) [20].

Table IV. Coefficients Obtained with the Present Technique for Vapor Pressure Ancillary Equations of R41, R152a, and R143a[a]

	C_1	C_2	C_3	C_4	C_5
Eq. (4), R41	−6.89372992	0.994098037	−1.00720506	−4.39293522	
Eq. (8), R152a	−7.44858013	2.09934200	−1.58655560	−2.82734307	−0.952562831
Eq. (8), R143a	−7.06302701	0.832358227	−0.234939234	−3.59058034	−0.118184722

[a] Coefficients and their respective equations should be applied only within the temperature ranges presented in Tables I, II, and III.

accurate calorimetric data when trying to resolve a known discrepancy in published vapor pressures.

3.4. Vapor Pressure Equations

Table IV presents the fitting parameters, obtained with the present technique, for the vapor pressure equations. These coefficients should be used only in the temperature range, shown in Tables I, II, and III, for which these analyses were carried out. They are given to allow the reader to calculate accurate values of the vapor pressure and its derivatives with temperature.

3.5. Pressure at the Triple Point

During this study, we determined that there are very few experimentally measured values for the pressure at the triple point of these substances. Table V presents the triple-point pressures calculated with this method,

Table V. Vapor Presssure at the Triple-Point Temperature for Selected Hydrofluorocarbons

Substance	T_{tp} (K)	This method (Pa)	Experimental (Pa)	Ancillary equation (Pa)	Tilner-Roth method [21] (Pa)
R125	172.52	2915.6 [1]	n.a.	2953.1 [22]	2921.0
R32	136.34	46.5 [1]	n.a.	46.9 [22]	48.0
R143a	161.34	1076.8	n.a.	1078.0 [18]	1061.0
R134a	169.85	390.2 [1]	n.a.	393.4 [23]	392.4
R152a	154.56	64.0	65.0 [13]	64.1 [12]	64.1
R41	129.82	321.9	n.a.	346.4 [10]	n.a.

along with some values which were calculated in other ways. As mentioned in Section 3.2, we found only one direct measurement, by Blanke [13] for R152a. The experimental uncertainty cited by Blanke for this measurement is 5 Pa or close to 8%. Both our method and the method of Tillner-Roth [21] are in excellent agreement with this measurement.

3.6. Estimation of Uncertainties

The uncertainties of the thermodynamically consistent vapor pressures calculated with this method are discussed in detail in Ref. 1. Only the final results are given here. Combining uncertainties in quadrature, we estimated the combined uncertainty of our vapor pressure values as 48 Pa at the normal boiling point, 12 Pa at an intermediate temperature, and 2.5 Pa at the triple-point temperature.

4. CONCLUSIONS

We have applied a method for evaluation of vapor pressures from measured internal-energy changes and reference values of the vapor pressure and its derivative with temperature evaluated near the normal boiling point temperature to R41, R152a, and R143a. In this application, internal-energy changes of the saturated vapor calculated from an equation of state were substituted for experimental measurements of ΔU at low densities without incurring systematic errors. This technique can employ calorimetric data to verify the thermodynamic consistency of vapor pressure data and correlations of such data. For R41, the calculated vapor pressures have resolved several discrepancies: the measurements of Demiriz et al. [3] at 250 K and about 1 MPa are 0.2% higher than both the calculated values (Table I) and the measured values of Magee [5]; the calculated values are consistent with those of Oi et al. [4] over the entire range of Oi's measurements; the lowest-temperature (170 to 190 K) vapor pressure measurements of Magee [5] are systematically higher (+0.4%) than the calculated values and were most likely tainted by a 4- to 5-ppm air impurity in the sample. Calculated and published subatmospheric vapor pressures for R152a were in very good agreeement. Agreement of our calculated vapor pressures for R152a with low-uncertainty (0.02-kPa) measurements by Silva and Weber [16] was within ±0.04 kPa (±0.04%) near the normal boiling point. Where no measurements existed, this method helped to establish thermodynamically consistent vapor pressures for R143a at subatmospheric pressures. These vapor pressures smoothly joined the direct, high-accuracy measurements of Weber and Defibaugh

[20] at higher temperatures and pressures. Systematically high vapor pressures of de Vries for R143a can be attributed to a 9-ppm air impurity. Calculated vapor pressures at the triple-point temperature were examined and found to compare favorably with other calculations and, in the case of R152a, were found to be within 1 Pa of a direct measurement.

ACKNOWLEDGMENTS

We are especially grateful to Stephanie Outcalt and Mark McLinden for many beneficial discussions during this study. The calorimetric measurements used in this work were supported, in part, by the Air Conditioning and Refrigeration Technology Institute.

NOMENCLATURE

a_i, b_i, c_i	Coefficients in equations
M	Molecular mass
p_σ	Vapor pressure
$Q/\Delta T$	Energy needed to change the temperature of the sample by 1 K
ρ	Density
T	Temperature
τ	$1 - T/T_C$
U	Internal energy
V	Volume

Superscript Notation

$'$	Saturated liquid
$''$	Saturated vapor
$^{(2)}$	$\equiv \{m_l X' + m_g X''\}/\{m_l + m_g\}$, bulk property $X^{(2)}$ in the two-phase region for a specific property X, where m_l and m_g are, respectively, the masses of the liquid and gas

Subscript Notation

$_v$	Constant volume (isochoric)
$_T$	Constant temperature (isothermal)
$_C$	Critical property
$_\sigma$	Saturation property

REFERENCES

1. H. A. Duarte-Garza and J. W. Magee, *Int. J. Thermophys.* **18**:173 (1997).
2. P. T. Boggs, R. H. Byrd, J. E. Rogers, and R. B. Schnabel, *NISTIR 4834 User's Reference Guide for ODRPACK Version 2.01, Software for Weighted Orthogonal Distance Regression* (NIST, Gaithersburg, MD, 1992).
3. A. M. Demiriz, R. Kohlen, C. Koopmann, D. Moeller, P. Sauermann, G. A. Iglesias-Silva, and F. Kohler, *Fluid Phase Equil.* **85**:313 (1993).
4. T. Oi, J. Shulman, A. Popowicz, and J. Ishida, *J. Phys. Chem.* **87**:3153 (1983).
5. J. W. Magee, in *NIST Technical Note 1397*, C. D. Holcomb, J. W. Magee, J. L. Scott, S. L. Outcalt, and W. M. Haynes, eds. (1997), p. A-54.
6. J. W. Magee, in *NIST Technical Note 1397*, C. D. Holcomb, J. W. Magee, J. L. Scott, S. L. Outcalt, and W. M. Haynes, eds. (1997), p. A-75.
7. L. A. Weber, *Int. J. Refrig.* **17**:117 (1994).
8. J. W. Magee, in *NIST Technical Note 1397*, C. D. Holcomb, J. W. Magee, J. L. Scott, S. L. Outcalt, and W. M. Haynes, eds. (1997), p. 14.
9. S. L. Outcalt and M. O. McLinden, personal communication (National Institute of Standards and Technology, Boulder, Colorado, 1996).
10. S. L. Outcalt, in *NIST Technical Note 1397*, C. D. Holcomb, J. W. Magee, J. L. Scott, S. L. Outcalt, and W. M. Haynes, eds. (1997), p. 12.
11. C. D. Holcomb, in *NIST Technical Note 1397*, C. D. Holcomb, J. W. Magee, J. L. Scott, S. L. Outcalt, and W. M. Haynes, eds. (1997), p. A-53.
12. S. L. Outcalt and M. O. McLinden, *J. Phys. Chem. Ref. Data* **25**:605 (1996).
13. W. Blanke and R. Weiß, *Fluid Phase Equil.* **80**:179 (1992).
14. H. D. Baehr and R. Tillner-Roth, *J. Chem. Thermodyn.* **23**:1063 (1991).
15. Y. Higashi, M. Ashizawa, Y. Kabata, T. Majima, M. Uematsu, and K. Watanabe, *JSME Int. J.* **30**:1106 (1987).
16. A. M. Silva and L. A. Weber, *J. Chem. Eng. Data* **38**:644 (1993).
17. J. W. Magee, *Int. J. Thermophys.* **19**:1397 (1998).
18. S. L. Outcalt and M. O. McLinden, *Int. J. Thermophys.* **18**:1445 (1997).
19. B. de Vries, *Thermodynamische Eigenschaften der alternativen Kältemittel R32, R125, und R143a—Messungen und Zustandgleichungen*, Dissertation (Universität Hannover, Fachbereich Maschinebau, 1996); also *Forsch. Ber. DKV, 55* (Stuttgart, Germany, 1997).
20. L. A. Weber and D. R. Defibaugh, *J. Chem. Eng. Data* **41**:1477 (1996).
21. R. Tillner-Roth, *Int. J. Thermophys.* **17**:1365 (1996).
22. S. L. Outcalt and M. O. McLinden, *Int. J. Thermophys.* **16**:79 (1995).
23. M. L. Huber and M. O. McLinden, *Proc. Int. Refrig. Conf.* (Purdue University, Lafayette, IN, 1992), p. 453.