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The Vapor Pressure of 1,1,1,2-Tetrafluoroethane (R134a) and Chlorodifluoromethane (R22)

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We measured the vapor pressure of chlorodifluoromethane (commonly known as R22) at temperatures between 217.1 and 248.5 K and of 1,1,1,2-tetrafluoroethane (commonly known as R134a) in the temperature range 214.4 to 264.7 K using a comparative ebulliometer. For 1,1,1,2-tetrafluoroethane at pressures between 220.8 and 1017.7 kPa (corresponding to temperatures in the range 265.6 to 313.2 K), additional measurements were made with a Burnett apparatus. We have combined our results for 1,1,1,2-tetrafluoroethane with those already published from this laboratory at higher pressures to obtain a smoothing equation for the vapor pressure from 215 K to the critical temperature. For chlorodifluoromethane our results have been combined with certain published results to provide an equation for the vapor pressure at temperatures from 217 K to the critical temperature.

KEY WORDS: Burnett apparatus; chlorodifluoromethane (R22); ebulliometry; refrigerants; 1,1,1,2-tetrafluoroethane (R134a); vapor pressure.

1. INTRODUCTION

Accurate vapor-pressure measurements are crucial for the calculation of reliable thermodynamic properties on the liquid–vapor boundary. Information in this region is of particular importance for the working fluids in refrigeration systems. It is desirable to minimize the fractional uncertainty in pressure over the entire fluid range; however, the static apparatus that we used for measurements at high pressures was not optimum close to ambient or subambient pressures, because of the effect of volatile impurities, primarily air. Low-boiling impurities, such as air, increase the vapor pressure, while higher-boiling impurities decrease it and these

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systematic changes become important at lower vapor pressures. Thus, we measured low vapor pressures using a method that depends on boiling (known as ebulliometry [1–3]) and that continuously degases the sample.

In comparative ebulliometry the condensing temperature of the substance under study and a reference fluid are measured when the liquids are boiling at the same pressure [4]. These boilers are connected via liquid nitrogen cold traps to avoid cross-contamination of the substance being investigated and the reference fluid. The advantage of this technique, particularly at low pressure, is that it avoids the necessity of measuring pressure directly; instead, the pressure is calculated from the condensing temperature of the reference fluid and its known pressure–temperature behavior. In addition, provided that the temperature measuring equipment is sufficiently sensitive, irregularities of the condensation temperature may reveal further inadequacies in the sample (or reference fluid) purity [2]. Of course, an azeotrope may not be detected with this approach. The symmetry of the apparatus implies that certain errors tend to be self-canceling. In our work allowance is always made for the hydrostatic heads of vapor [2, 4].

In comparative ebulliometry, a buffer gas subjects the sample and the reference fluid to identical pressures. The influence of the buffer gas used in the ebulliometric experiment was investigated by Ambrose et al. [5] with their measurements of the vapor pressure of benzene. They found no difference between values of the vapor pressure obtained when helium was used as the buffer gas and those obtained when nitrogen was used. The methods of determining vapor pressure, including comparative ebulliometry, have been discussed extensively in the literature [2, 3].

For our work at low reduced temperatures corresponding to pressures below 220 kPa, we have used comparative ebulliometry to supplement the data from our static apparatus for vapor-pressure measurements. Here we report our ebulliometric vapor-pressure measurements on 1,1,1,2-tetrafluoroethane (R134a) and chlorodifluoromethane (R22), both of which are expected to play important roles in the design of future refrigeration systems. The ebulliometer used here is a refined version of an earlier design reported by one of us [6] and is adapted from designs described in the literature [1–4, 7–9]. To our knowledge, neither has this technique been applied to these refrigerants previously nor has it been used at such low temperatures.

In addition, we report static measurements made with our Burnett apparatus [10–12] of the vapor pressure for 1,1,1,2-tetrafluoroethane (R134a) at pressures between our earlier static results [13] and the present ebulliometric results. All these results have been combined to provide a correlation for the vapor pressure of 1,1,1,2-tetrafluoroethane (R134a) on the International Temperature Scale of 1990 (ITS-90) [14, 15] at temperatures from 215 K to the critical temperature, which corresponds to vapor pressures from 17.3 to 4055.1 kPa. For chlorodifluoromethane (R22) we have combined our results with those already published [16–18] to provide a correlation (on ITS-90) from 217.1 K to the critical temperature.

Because of the importance of these two fluids, their vapor pressures have been reported in the literature numerous times [16–25]. Important references for 1,1,1,2-tetrafluoroethane (R134a) include Magee and Howley [19], Zhu and Wu [20], Baehr and Tillner-Roth [21], Piao et al. [22], Maezawa et al. [23], Basu and Wilson [24], and Kubota et al. [25] as well as our earlier work [13]. We argue that certain published vapor pressure data for R134a are in error by as much as $0.024p$. We suspect that the errors resulted from inadequate degassing of the samples used in previous work. For the sake of brevity, these compounds are referred to with the numbering scheme used by the refrigeration industry [26] and shown in parentheses above.

2. EXPERIMENTAL

2.1. Ebulliometer

The ebulliometers are similar to those described by Ambrose et al. [2, 3, 7, 8]. The apparatus used in the present work has been described in detail elsewhere [6]. Only the important differences, required to operate at lower temperatures and higher pressures, are given here. The sample ebulliometer, shown in Fig. 1, was constructed from borosilicate glass and fitted with four bubble-caps with a total internal volume of about 50 cm^3 (the reference boiler was identical). A brass passive radiation shield was placed around the upper outer portion of the boiler. The entire ebulliometer and radiation shield were housed inside a second cylindrical shield, whose temperature was controlled to 0.01 K by circulating chilled methanol through a coil wrapped around the shields' outer surface. We found, after carefully insulating feed and return pipes, that we could reach 195 K. The thermostat shield was capped with 0.05-m-thick polystyrene foam disks. Fiber-glass insulation was wrapped around the outside of the shield to complete the isothermal environment. Although the vapor-pressure measurements were insensitive to the exact shield temperature, we always maintained it about 10 K below the fluids condensing temperature. The sample ebulliometer was connected, via a condenser cooled with a mixture of carbon dioxide and propanone and two traps cooled with liquid nitrogen, to the reference boiler and a ballast volume using helium as the transfer gas. The connections were made with 10-mm-external diameter

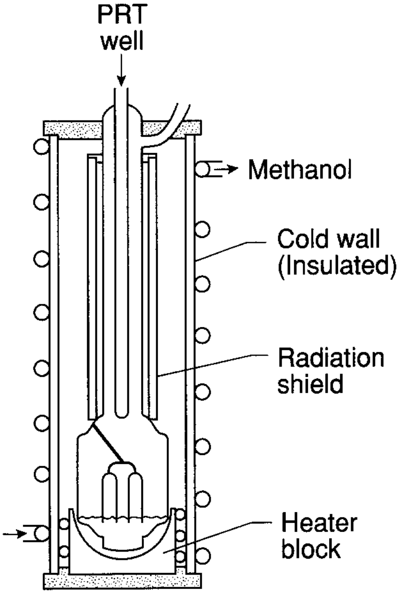

Fig. 1. Cross section through the sample ebulliometer.

glass tubing joined with glass ball joints which were sealed with silicone rubber o-rings. The ballast volume was about 0.015 m^3 and it was wrapped in fiber-glass insulation. The pressure of the system was monitored, but not measured, with a quartz pressure transducer. The highest vapor pressure that was measured in the glass ebulliometer was 215 kPa. The limit was an obvious safety precaution.

Condensation temperatures of the sample and reference, water, were determined with two Yellow Spring Co.[2] long-stem platinum resistance thermometers [Model 8163QB, serial numbers L9S4609 (H_2O) and F91355 (sample)] calibrated between 83.8 and 692.7 K on ITS-90. The resistance measurements were made with a digital DC multimeter (Hewlett Packard Co., Model 3457A) operating at a current of 1 mA, with a resolution of 0.01 mΩ, for resistances up to 30.3 Ω. For resistances greater than 30.3 Ω but less than 303 Ω, the resolution was 0.1 mΩ. The manufacturer's

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[2] In order 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.

stated a fractional accuracy of 6.5×10^{-5} for the range with an upper bound of 30.3 Ω and a fractional accuracy of 4.5×10^{-5} for resistances between 30.3 and 303 Ω. When the current was reversed, no differences were observed in the multimeter reading. Although the technique for vapor-pressure measurement is comparative, and only short-term precision and stability are required of the multimeter, we compared the measurements of this device in two ways. First, the multimeter was checked frequently against two calibrated Rosa standard resistors with nominal resistances of 10 and 25 Ω that were housed in a thermostated enclosure, the temperature of which was measured with a mercury-in-glass thermometer. The multimeter was checked after completing the vapor-pressure measurements and, at both standard resistances, found to be 0.66 mΩ high; when the multimeter was shorted this discrepancy was not observed. All the measurements were corrected for this small systematic error. Second, the combined stabilities of the thermometers with this multimeter were checked frequently in a triple-point-of-water cell. The triple-point resistances differed from the original calibration by less than 1 mK. To improve thermal contact between the thermometer and the condensing fluids, the glass-thermometer wells were filled with either *n*-octane, silicone oil, or 1,2-dihydroxyethane.

The ebulliometers and ballast volume were evacuated at a temperature of 300 K with a rotary vacuum pump until the pressure was below 1 Pa, while the sealed sample cylinder was attached to a side arm. After 12 h the 50-cm^3 liquid sample was distilled into the boiler. Sufficient time was allowed for the apparatus to reach steady state, as indicated by temperature differences between each reading of about 1 mK, before a series of condensation temperatures was measured, usually at 60-s intervals during 0.3 h.

2.2. Burnett Apparatus

The static measurements were performed with an automated Burnett apparatus developed at the National Institute of Standards and Technology (NIST), which has been described in detail several times [10–13]. All results were acquired in an automated fashion. Temperatures were measured with an imprecision and inaccuracy of 1 mK using a platinum resistance thermometer, and pressures were measured using a quartz spiral bourdon gauge fitted with an optical null detector to an inaccuracy of about 0.1 kPa. In addition to the procedures listed in Section 2.3, before commencing measurements, the sample cell was filled to about the critical density, cooled below 273 K, and the gas expanded and evacuated repeatedly until additional expansions had a negligible effect on the measured pressure.

2.3. Sample Purity

Distilled water from the laboratory supply was used as the reference material. The 1,1,1,2-tetrafluoroethane (R134a) was supplied by E. I. Du Pont de Nemours and Co. with a stated analysis for three impurities: $x(C_2HF_5) = 1.56 \times 10^{-4}$, $x(CF_3CH_3) = 1.59 \times 10^{-4}$, and $x(CClH_2CF_2H) = 1.5 \times 10^{-4}$. Gas-chromatographic analysis of this sample detected a mole fraction of 2.15×10^{-4} for water [27]. The sample was distilled from the supplier's cylinder into a previously evacuated steel ampoule. Analysis of this sample with a gas chromatograph returned $x(H_2O) = 1.05 \times 10^{-4}$ [27]. No attempt was made to purify the R134a further. Aliquots of this sample were used for the vapor-pressure measurements reported here and in Ref. 13, as well as to determine the critical temperature [28], the gaseous (p, V_m, T) behavior [13], and gaseous speed-of-sound measurements [29]. The chlorodifluoromethane (R22) was obtained from Allied Signal Corp., from batch BR1191A, with a stated mole fraction purity of greater than 0.9995. The analysis certificate provided by the manufacturer reported a mole fraction purity of 0.99968 and the presence of five impurities, of which four were identified: $x(CCl_2F_2) = 0.00018$, $x(CHF_3) = 0.00013$, $x(CHCl_2F) = 0.00001$, and $x(H_2O) = 3 \times 10^{-6}$. Other unspecified hydrocarbons made up the remainder. Gas-chromatographic analysis of the stock material using a nonpolar stationary phase and a thermal conductivity detector indicated the presence of two impurities with fractional areas of 19×10^{-6} and 4.9×10^{-4}, respectively; both eluted prior to the major peak. No further analysis or purification was attempted.

3. RESULTS AND ANALYSIS

The vapor pressure of water, which was used as the reference fluid for our ebulliometry, was calculated from boiling temperatures on ITS-90 [14, 15], with the equation discussed in Section 3.1. No irregularities were detected in the temperature of the water ebulliometer, this suggests the sample had no significant contaminants.

As a check on the internal consistency of the ebulliometric results, and to provide a normal boiling temperature at a pressure of 101.325 kPa, we fit our experimental values to an Antoine equation (applicable in the range 10 to 200 kPa)

$$\ln(p) = A + B/(T + C) \qquad (1)$$

where p is in kPa and T is in K. To provide an equation for the fluid range from a pressure of about 10 kPa to the critical pressure, we combined our ebulliometric results with our static measurements for R134a. For R22 our ebulliometric values were combined with higher-pressure data from the literature that joined smoothly with our results. For each fluid, the combined set was used to determine the coefficients in the equation recommended by Wagner [30–33]:

$$\ln(p/p_c) = (n_1\tau + n_2\tau^{1.5} + n_3^c + n_4^d)T_c/T \qquad (2)$$

where $\tau = (1 - T/T_c)$, T_c is the critical temperature, and c, d and the n's are adjustable parameters. In our analysis, we assumed that the vapor pressure could be represented by terms with positive powers c and d, and using an adaptive regression algorithm [34], we selected the most significant terms from the bank $\tau^2, \tau^{2.5}, \tau^{3.0}, \ldots, \tau^9$. We weighted each ebulliometric observation by $\delta T \times d\ln p/dT$, where $\delta T = 1.4 \times 10^{-3}$, which we combined in quadrature with the uncertainty in the vapor pressure of water. We weighted our static measurements by 0.15 (kPa/p), where 0.15 kPa is our estimate of the uncertainty in p. This scheme ensured that the ebulliometric results received a weight about a factor of 10 greater than the static results at a similar pressure. For R22 the literature results were weighted by an estimate of the uncertainty provided by the sources. In Eq. (2), each term entered with a high degree of significance and no other significant terms were found. The procedures required to perform these calculations have been described in detail elsewhere [35].

Table I gives the vapor pressure, together with deviations from the Antoine and Wagner equations, determined at each temperature on ITS-90. Small corrections have been applied to account for the fluid head in each ebulliometer; for R134a we used a static-head correction factor of 1.000139, while for R22 we used 1.000124.

3.1. Vapor Pressure of Water on ITS-90

Although there are numerous equations for the vapor pressure of water on ITPS-68 [36–38], we were not aware of any correlating equation with temperatures on ITS-90. Therefore, we used the best experimental results (from the National Bureau of Standards, the predecessor to NIST) reported by Osborne et al. [39], Stimson [40], and Guildner et al. [41] and converted the temperatures to ITS-90 using the recommendations of Sato et al. [42]. The conversion formula [43] is accurate to 1 mK above 273.15 K and to 1.5 mK below. With the regression procedure described above, we selected terms to determine a Wagner equation for water. Each observation was given a weight of unity in the regression analysis, except for the measurements of Stimson [40] and Guildner et al. [41], which were given a weight of 10. We used the critical temperature of 647.1 K (on

Table I. Vapor Pressures p and Deviations $\Delta p_1 = p - p(\text{calc.})$ from Eq. (1) and $\Delta p_2 = p - p(\text{calc.})$ from Eq. (2) at Temperatures T for 1,1,1,2-Tetrafluoroethane (R134a) and Chlorodifluoroethane (R22)

T (K)	p (kPa)	Δp_1 (Pa)	Δp_2 (Pa)
Chlorodifluoromethane (R22) ebulliometer			
217.086	46.651	−11	−26
217.118	46.738	−5	−21
218.307	49.888	8	−6
220.217	55.272	4	−9
221.873	60.315	5	−5
223.409	65.309	2	−7
224.861	70.331	1	−5
226.227	75.331	2	−4
227.529	80.358	5	−1
228.828	85.632	4	0
229.978	90.529	5	4
231.225	96.095	17	16
232.206	100.664	28	30
232.151	100.319	−55	−55
234.240	110.609	−17	−11
235.712	118.364	35	−7
236.188	120.899	−8	1
238.205	132.295	−31	−21
238.461	133.848	17	25
239.615	140.779	−18	−7
242.718	160.936	6	20
242.742	161.070	−22	−10
244.060	170.274	−21	−12
245.584	181.443	−4	9
245.464	180.565	20	29
248.502	204.388	33	36
1,1,1,2-Tetrafluoroethane (R134a) ebulliometer			
214.435	17.301	3	1
216.869	20.179	4	1
218.289	22.033	4	2
223.588	30.219	−6	−4
226.340	35.365	−6	−4
228.866	40.691	−10	−8
228.824	40.596	−10	−9
231.025	45.749	−6	−4
230.996	45.676	−7	−6
232.785	50.230	−9	−8
232.798	50.269	−5	−4
233.849	53.121	3	4
233.881	53.208	1	2

Table I. *(Continued)*

T (K)	p (kPa)	Δp_1 (Pa)	Δp_2 (Pa)
234.625	55.291	−10	−9
234.668	55.432	7	9
235.317	57.317	10	11
236.287	60.203	−16	−13
236.293	60.226	−10	−9
236.582	61.133	6	8
238.084	65.932	9	11
239.610	71.106	8	9
239.635	71.196	9	11
241.675	78.628	14	14
242.972	83.669	16	12
242.951	83.579	9	19
244.861	91.450	9	9
244.879	91.534	13	16
247.149	101.649	10	13
249.243	111.742	4	5
251.123	121.471	2	5
252.951	131.554	2	−1
254.558	140.955	1	−2
256.289	151.655	−9	−12
258.660	167.348	−3	−12
261.048	184.401	1	−18
262.599	196.175	−5	−29
264.727	213.242	−40	−76
Static			
265.609	220.860		118
266.152	225.480		69
267.134	234.160		112
268.151	243.390		129
269.167	252.880		137
270.132	262.140		129
271.153	272.270		170
272.182	282.590		22
273.135	292.710		172
273.167	293.030		153
276.166	326.250		197
281.151	387.700		208
285.171	443.310		135
289.181	504.720		130
293.146	571.560		96
297.130	645.190		−17
301.150	726.680		0
305.162	815.530		41
309.162	912.080		157
313.204	1017.710		−117

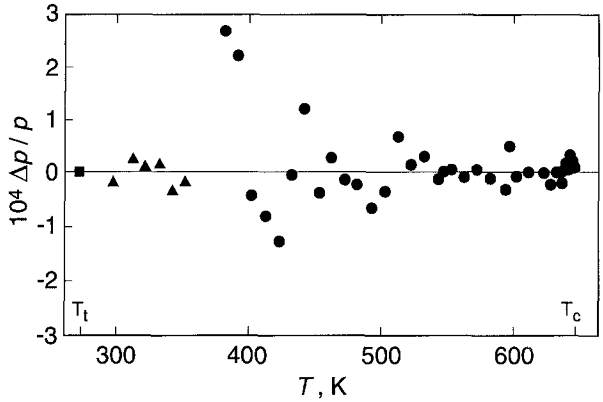

Fig. 2. Fractional deviations $\Delta p/p = [p - p(\text{calc.})]/p$ of the experimental vapor pressures from Eq. (3) for H_2O. ■, Ref. 41; ▲, Ref. 40; ●, Ref. 39.

ITS-90), recommended by the International Association for the Properties of Water and Steam (IAPWS [42]), and constrained the fit to the critical pressure of $p_c = (22.064 \pm 0.005)$ MPa, also an IAPWS recommendation [44]. The vapor pressure of water is shown in Fig. 2 in terms of deviations from our interpolating equation:

$$\ln(p/p_c) = (-7.855081\tau + 1.827857\tau^{1.5} - 11.5050\tau^{3.0} + 22.0420\tau^{3.5} - 15.5606\tau^{4.0} + 1.75277\tau^{7.5})T_c/T \qquad (3)$$

which is identical in functional form to that advocated by Saul and Wagner [36], and approved by IAPWS. The weighted standard deviation of the fit was 136 Pa in p or 4.6×10^{-5} in $\ln p$. Values of the vapor pressure calculated from Eq. (3) differ from the results reported by Stimson [40] by less than the quoted standard deviations, and they agree with those reported by Osborne et al. [39] to within the quoted fractional accuracy of 3×10^{-4}. Although the measurements of Douslin [45] are very precise, we have omitted them from the fit because they are inconsistent with Guildner's value of the triple point [41]. If we had not constrained p_c, then our analysis would return $p_c = (22.066 \pm 0.001)$ MPa, which is in excellent agreement with the internationally accepted value [42], and an equation of identical form to Eq. (3); the latter equation provided pressures that differed insignificantly from Eq. (3) in our range.

3.2. Chlorodifluoromethane (R22)

Our 25 ebulliometric values of the vapor pressure between 46 and 204 kPa, at temperatures from 217 to 248 K, are shown in Fig. 3 as devia-

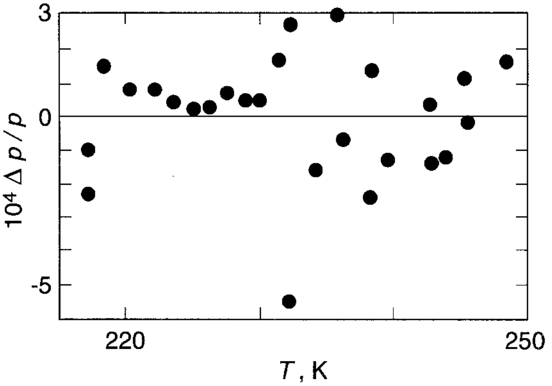

Fig. 3. Fractional deviations $\Delta p/p = [p - p(\text{calc.})]/p$ of the experimental vapor pressures from Eq. (1) for chlorodifluoromethane (R22). ●, This work.

tions from Eq. (1) with the coefficients given in Table II. The normal boiling temperature, at a pressure of 101.325 kPa, calculated from Eq. (1) with the coefficients of Table II is (232.351 ± 0.005) K on ITS-90. The standard deviation of the fit was 21 Pa, or 4 mK in temperature. Only at 232.2 K did the result deviate from Eq. (1) by more than 10 mK. Removal of this point from the regression did not alter the normal boiling temperature.

There are several measurements of the vapor pressure of R22 in the literature [16–18, 46–51] and most have quoted imprecisions of about 0.001*p*. All values were compared on ITS-90 [43, 52]. At temperatures that overlap our range, most agree within the uncertainty of those measurements. For example, the static measurements of Zander [16] are in excellent agreement with Eq. (1) in the overlapping range. At 222.905 K his

Table II. Coefficients and Standard Deviations *s* for Eqs. (1) and (2) Obtained by Analysis of the *N* Vapor Pressures of Chlorodifluoromethane (R22) and 1,1,1,2-Tetrafluoroethane (R134a)[a]

Eq. (1)	*A*		*B*		*C*	*N*	*s* (Pa)
R22	14.03798		−1890.641		−31.640	26	21
R134a	14.21475		−2013.951		−37.217	37	11
Eq. (2)	p_c (kPa)	n_1	n_2	n_3	n_4	*N*	*s* (Pa)
R22	4987.1 ± 1.2	−7.03551	1.45976	−1.8120	−2.9644	106	877
R134a	4055.1 ± 0.3	−7.61702	1.69464	−2.5081	−3.4915	79	167

[a] Uncertainties are one standard deviation.

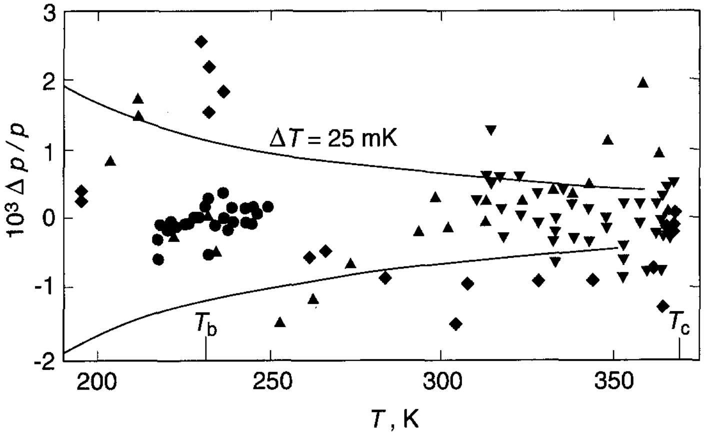

Fig. 4. Fractional deviations $\Delta p/p = [p - p(\text{calc.})]/p$ of the experimental vapor pressures from Eq. (2) for chlorodifluoromethane (R22). T_b is the boiling temperature at a pressure of 101.325 kPa. ●, This work; ◆, Ref. 17; ▲, Ref. 16; ▼, Ref. 18; —, the error arising at each temperature from a change of 0.025 K.

result deviates by less than 4 Pa, at 232.390 K by 1.2 Pa, and at 234.225 K by −7 Pa. The excellent agreement between our vapor-pressure measurements and those reported by Zander [16] suggests that both sets of measurements are free from systematic errors.

We combined our values with those reported in Refs. 16–18 after converting the temperatures to ITS-90 [43]. These data sets, as shown in Fig. 4, joined smoothly with our results and were obtained with samples of similar purity. We fixed T_c at 369.275 K, as recommended by Ambrose [53] (converted to ITS-90 [43]), and fit Eq. (2) to the combined data weighting the literature values by 0.001. The regression returned $c = 2.5$ and $d = 5$. Table II lists the coefficients of Eqs. (1) and (2) determined for R22, together with the standard deviations and number of vapor pressures in each regression.

3.3. 1,1,1,2-Tetrafluoroethane R134a

For R134a the 37 ebulliometric measurements of the vapor pressure were used to adjust the coefficients of Eq. (1). The standard deviation of the fit was 11 Pa, or 2.9 mK in temperature. The normal boiling temperature, at a pressure of 101.325 kPa, calculated from Eq. (1) is (247.082 ± 0.005) K.

We were unable to extend the static experiment to a temperature lower than 265.6 K, about 0.9 K above the highest ebulliometric temperature. Consequently, the pressure ranges did not overlap. The static measurements reported here extend to a temperature 48 K below the lowest temperature reported by us previously [13]. These pressures deviated from the smoothing equation, discussed below and shown in Fig. 5, within a factor of 0.9 of the estimated accuracy of the pressure gauge.

We combined our ebulliometric measurements and static results, including those from Ref. 13, with the critical temperature observed by Morrison and Ward [28] of 374.179 K. A small correction was applied to convert the temperature reported in Ref. 28 to ITS-90 [43]. We obtained $c = 2.5$ and $d = 5$ from a weighted regression analysis with Eq. (2) and a standard deviation of 167 Pa, or of 1.39×10^{-4} in $\ln p$. Figure 5 shows the experimental results as deviations from this smoothing equation. It is clear that there are inconsistencies in the results from static and ebulliometric experiments which, although small, far exceed the imprecision of any one value. We suspect that the presence of air in the sample is responsible. However, the deviations show a systematic, albeit small, undulation from Eq. (2), which implies that the functional form is not entirely suitable. While the difference between the ebulliometric and the static results at 265 K suggests that our static measurements were affected by the presence of a volatile impurity, no additional significant terms remained unselected

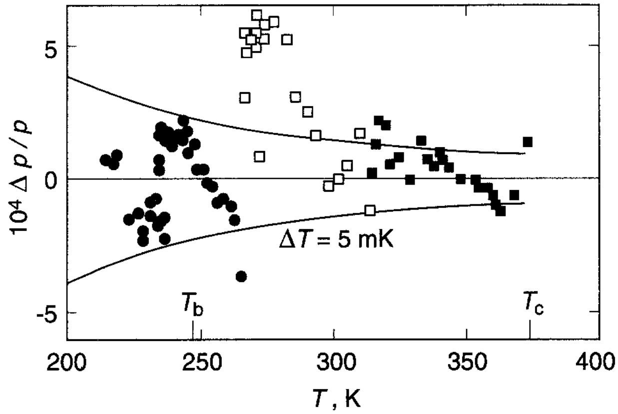

Fig. 5. Fractional deviations $\Delta p/p = [p - p(\text{calc.})]/p$ of the experimental vapor pressures from Eq. (2) for 1,1,1,2-tetrafluoroethane (R134a). T_b is the boiling temperature at a pressure of 101.325 kPa. ●, This work, ebulliometric; □, this work, static; ■, Ref. 13, same sample; —, the error arising at each temperature from a change of 0.005 K.

at the conclusion of the regression. The discontinuity, shown in Fig. 5, could result from a mole fraction of air of 10^{-5}. Nevertheless, the agreement between the results of two such different techniques is exceptional and indicates that the vapor pressures can be obtained to better than $3 \times 10^{-4} p$.

Table II gives the coefficients of Eqs. (1) and (2) for R134a, together with the standard deviations and the number of vapor pressures in each regression.

4. DISCUSSION

For both R134a and R22 our analysis procedure has selected the form of Eq. (2) recommended by Ambrose [35] and returned coefficients which are typical in magnitude of such an equation [35].

4.1. Chlorodifluoromethane R22

There are several other previous measurements of the vapor pressure for chlorodifluoromethane [46–51], most that are available [47, 49–51] deviate from Eq. (2) by more than $0.005p$. Only the measurements of Oguchi et al. [46] and Takaisji et al. [48] differ by less than $0.001p$ from our correlation.

Assuming the critical temperature recommended by Ambrose [53] (and also by Hirata et al. [54] and Kohlen et al. [18]), we calculate from Eq. (2) a critical pressure of (4987.1 ± 1.2) kPa, 16.1 kPa above the value given in Ref. 53. The measurement of Kletskii [17] lies 1.1 kPa below, well within our estimated uncertainty, while the value of Zander [16] is 2.9 kPa above, the critical pressure calculated from Eq. (2).

4.2. 1,1,1,2-Tetrafluoroethane (R134a)

The vapor pressures reported by other workers are shown in Fig. 6, as deviations from Eq. (2), where the ordinate scale has been compressed by a factor of 100 compared with Fig. 5; all values were compared on ITS-90. There are large differences between the values of p at temperatures below 300 K with differences up to $0.024p$. Such errors in the vapor pressure could arise from inconsistencies between the two thermometers used for our ebulliometry. For example, an uncertainty of 0.05 K at 265 K or 0.38 K at 215 K would be large enough to cause such differences; however, based on our measurements, discussed in Section 2.1, our thermometry was shown to be accurate to a few millikelvin and we are able to rule out this as the source of the differences. At temperatures below 250 K we are aware of two other independent sets of vapor pressure measurements in the

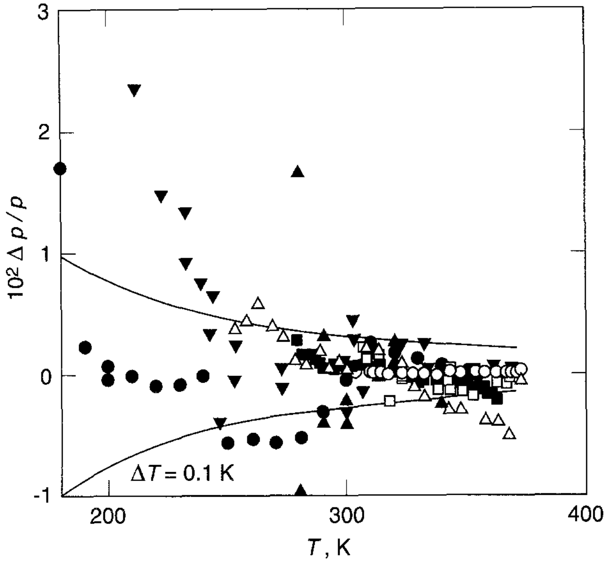

Fig. 6. Fractional deviations $\Delta p/p = [p - p(\text{calc.})]/p$ of the experimental vapor pressures from Eq. (2) for 1,1,1,2-tetrafluoroethane (R134a). ●, Ref. 19; ■, Ref. 20; ○, Ref. 21; □, Ref. 22; ▲, Ref. 23; ▼, Ref. 24; △, Ref. 25; —, the error arising at each temperature from a change of 0.1 K.

literature [19, 24] both, are shown in Fig. 6, and were obtained with a static technique. Systematic errors in static vapor pressure measurements could arise from errors in the pressure measurement or from the presence of volatile impurities. The discrepancies between equation (2) and the static measurements of Basu and Wilson [24] are less than the estimated errors in the pressure measurements of the latter. Basu and Wilson [24] degassed their sample by a repeated freezing, pumping, and thawing process until the pressure was below 7 Pa. We estimate that the discrepancy of $0.024p$ at 210 K, between equation (2) and the results reported in Ref. [24], could be accounted for with a mole fraction of air of 3×10^{-5}. Most of the static measurements reported by Magee and Howley [19] differ from our vapor pressure equation well within their error estimates. Magee and Howley [19] used a sample of R134a that contained a mole fraction of air of about 1×10^{-6}. At temperatures between 240 and 250 K there appears to be a step discontinuity in the measurements of Magee and Howley [19], that arose from changing pressure gauges. Several other sets of results agree with Eq. (2) to within 0.1 K at the normal boiling temperature. At higher temperatures the majority of the results deviate from Eq. (2) by less than $0.002p$, or less than 0.1 K. For example, the results reported by Baehr and

Tillner-Roth [21] differ by less than $0.0001p$ from Eq. (2) at temperatures up to the critical. Such agreement between independent vapor-pressure measurements is truly remarkable. In contrast, the measurements of Kubota et al. [25] appear to have a systematic error with differences between $0.004p$ and $-0.005p$. The recent measurements of Zhu and Wu [20] between 279 and 363 K show a similar trend to those of Kubota et al. [25]. The vapor-pressure equations given by the Japanese Association of Refrigeration (JAR) [55] and by Baehr and Tillner-Roth [21] were both derived from information independent of ours and Ref. 19. These equations predict vapor pressures below 300 K that are much too high but tend toward agreement with our data at higher temperatures. The JAR [55] correlation was derived with data reported by Basu and Wilson [24], while that attributed to Baehr and Tillner-Roth [21] used data of Bier et al. [56] at lower temperatures. In view of the excellent agreement between our measurements of the vapor pressure of R22 with those reported by Zander [16] and for R134a with the precise static measurement of Magee and Howley [19] at temperatures below 250 K (despite the slight discontinuity in their results), we conclude that the measurement of Basu and Wilson [24] and the correlations of JAR [55] and Baehr and Tillner-Roth [21] are in error by as much as $0.024p$ at 220 K.

Assuming the critical temperature to be that observed by Morrison and Ward [28] (and adopted by McLinden et al. [57]) we calculate from Eq. (2) a critical pressure of (4055.1 ± 0.3) kPa, 12.9 kPa below the value given in Ref. 28, but only (0.9 ± 10) kPa below Ref. 57 and well within twice the combined uncertainty; Weber reported $p_c = 4055.9$ kPa [13]. The critical pressure reported by Kubota et al. [25], from an extrapolation of their vapor-pressure equation (a Chebyshev polynomial), and that adopted by Tang et al. [58], for use in a simplified crossover model for the critical region, is 9.9 kPa above our value.

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