Ebulliometric Measurement of the Vapor Pressure of 1-Chloro-1,1-Difluoroethane and 1,1-Difluoroethane

Alberto M. Silva[†] **and Lloyd A. Weber**[*]

Thermophysics Division, Chemical Science and Technology Laboratory, National Institute of Standards and Technology, Gaithersburg, Maryland 20899

The vapor pressures of 1-chloro-1,1-difluoroethane (R142b) and 1,1-difluoroethane (R152a) have been measured at temperatures between 224.8 and 284.7 K for R142b and between 219.9 and 273.1 K for R152a by a comparative ebulliometric technique. Our results have been combined with selected published results to provide a smoothing equation for the vapor pressure. For R142b, our equation is valid from 200 to 300 K while for R152a the temperature range goes from 215 K to the critical temperature, near 386 K.

Introduction

We report vapor pressure data for 1-chloro-1,1-difluoroethane (R142b) and 1,1-difluoroethane (R152a). These compounds are being considered as replacement working fluids for environmentally unacceptable chlorofluorocarbons. The accurate vapor pressure data for R142b and R152a are useful for an initial screening among alternative compounds, and they are essential inputs for the calculation of thermodynamic properties of these compounds.

The ebulliometric technique used in the present work has been used by the Fluid Science Group of NIST for the accurate measurment of the vapor pressures of several alternative refrigerants including 1,1,1,2-tetrafluoroethane (R134a) (*1*), chlorodifluoromethane (R22) (*1*), 1,1-dichloro-1-fluoroethane (R141b) (*2, 3*), 1,1-dichloro-2,2,2-trifluorethane (R123) (*3, 4*) and difluoromethane (R32) (*5*).

This ebulliometric technique, which uses the symmetry of the comparative boiler design, has several advantages over the more commonly used static technique for vapor-pressure measurement. The symmetry implies that certain errors are self-canceling. We only have to measure the two condensation temperatures, which can be done quite accurately. The measurements are relatively insensitive to the presence of both very volatile and very nonvolatile impurities.

For R142b we obtained our data at pressures in the range 14.86–218.2 kPa, corresponding to temperatures from 224.8 to 284.7 K. We compared our results with the published results of Blanke and Weiss (*6*), Riedel (*7*), Cherneeva (*8*), and Mears et. al. (*9*), and we show the deviations of these results from a fit to our own results.

For R152a our data are at pressures ranging from 22.72 to 263.7 kPa, corresponding to temperatures from 219.9 to 273.1 K. For this fluid we compared our results with the published data of Blanke and Weiss (*6*) in the same range of pressure. We also combined our results with the data of Baehr and Tillner-Roth (*10*) at higher temperatures to provide a correlating equation for the vapor pressure at temperatures between 215 K and the critical temperature at 386.41 K (*11*). We also compared our results with the results of Higashi et al. (*11*) and the recent work of Tamatsu et al. (*12*).

Experimental Section

The experimental apparatus used in this work has been described previously (*1, 3–5*). The comparative ebulliometer has two boilers with reflux condensers connected to a common manifold. In one of the boilers we put water as the "standard fluid", and in the other one the test fluid. An inert gas, helium, is present in the manifold, to communicate and set the pressure of the system.

Both boilers were heated electrically, and the temperatures of the condensing vapors were measured with two long-stem platinum resistance thermometers calibrated between 83.8 and 692.7 K on the International Temperature Scale of 1990 (ITS-90). We remeasured the reference resistances with a water triple point cell. For the resistance measurement, we used a digital dc multimeter calibrated against a Wilkins-type standard resistor. We estimate that temperature was measured within 3–4 mK.

The pressure of the system was calculated from the measured condensing temperature of the water, utilizing the vapor pressure equation which has been endorsed by IAPWS (*13*). This equation gives the vapor pressures on the ITS-90 scale. A comparison of the pressure calculated from the water boiler with that measured with a standard barometer at NIST showed that the two agreed within 10 Pa at atmospheric pressure. The concordance corresponds to a temperature measurement accuracy of 2.8 mK.

Because the apparatus was made from borosilicate glass, our highest working pressure was limited to 260 kPa. The lower limits of temperature and pressure in this work were determined by the temperature of the methanol bath that refrigerated the shield of the refrigerant boiler. This shield could be cooled to temperatures as low as 203 K; however, the shield's temperature must be maintained approximately 15 K below the boiling temperature of the refrigerant. Our experience showed that this minimum temperature differential was required to prevent instability in the measured condensing temperature.

Small corrections have been applied to our results to account for the hydrostatic pressure head in each ebulliometer. This head correction was a factor of 1.000 145 for R142b and 1.000 096 for R152a.

Results

For each refrigerant we fit our results to an Antoine equation:

$$\ln(P/\mathrm{kPa}) = A + \frac{B}{T/\mathrm{K} + C} \qquad (1)$$

where P is the pressure, T is the temperature, and the constants A, B, and C for both refrigerants are given in Table I. This equation checked the internal precision of our

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[*] To whom correspondence should be addressed.

[†] Permanent address: Technological Institute of Catholic University, Rio de Janeiro 22.453, Brazil.

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Table I. Coefficients for Equations 1 and 2 for 1-Chloro-1,1-difluoroethane (R142b) and 1,1-Difluoroethane (R152a)

	coeff	R142b	R152a
eq 1	A	13.8759	14.2372
	B	−2115.66	−2090.11
	C	−35.5111	−31.8503
eq 2	P_c		4514.73 kPa
	T_c		386.41 K
	A_1		−7.3943
	A_2		1.6466
	A_3		−2.0461
	A_4		−2.8248

Table II. Vapor Pressures and Deviations $100(P - P_{calc})/P$ from Equation 1 for 1-Chloro-1,1-Difluoroethane (R142b)

T/K	P/kPa	$100(P - P_{calc})/P$	T/K	P/kPa	$100(P - P_{calc})/P$
224.804	14.870	0.004	257.176	76.073	0.018
227.067	16.965	−0.016	258.755	81.384	0.014
229.130	19.088	0.004	258.100	79.133	−0.002
231.623	21.931	−0.003	260.635	88.059	−0.015
233.213	23.919	−0.002	262.374	94.650	−0.004
234.821	26.070	−0.024	264.090	101.506	−0.009
238.184	31.105	0.024	265.820	108.809	−0.015
237.420	29.902	0.028	267.684	117.147	−0.009
240.139	34.354	−0.014	269.467	125.584	0.005
241.542	36.874	0.022	271.343	134.991	0.032
243.423	40.453	−0.005	273.095	144.120	−0.038
245.147	43.982	−0.006	274.940	154.403	−0.009
246.740	47.460	−0.006	276.899	165.907	0.007
248.564	51.703	−0.022	279.206	180.222	−0.014
249.763	54.665	−0.005	280.677	189.867	−0.009
251.993	60.525	0.004	280.776	190.553	0.003
253.837	65.744	0.019	282.535	202.653	0.015
255.544	70.871	0.015	284.688	218.216	0.015

experimental results and provided an interpolating function for our data.

In addition, for R152a, we combined our results with literature results to obtain an equation valid from 20 kPa to the critical pressure. In this extended range, we represented all the data using the equation recommended by Wagner (*14*):

$$\ln(P/P_c) = (T_c/T)[A_1\tau + A_2\tau^{1.5} + A_3\tau^{2.5} + A_4\tau^5] \quad (2)$$

where $\tau = (1 - T/T_c)$, T_c is the critical temperature, P_c is the critical pressure, and A_i are adjustable parameters which are shown in Table I.

R142b. For R142b we measured 36 vapor pressures in the range of temperature from 224 to 285 K. The coefficients of eq 1 are listed in Table I, and the results are listed in Table II where the temperatures are given as ITS-90. In this table we also give the deviation between our experimental values and eq 1. The standard deviation of the fit was 0.016% in pressure or 3.5 mK in temperature. These results support our estimate of temperature measurement accuracy given above. At the normal boiling point, 101.325 kPa, the temperature was calculated to be 264.043 K.

Deviations of our results and those of Blanke and Weiss (*6*) from eq 1 are shown in Figure 1. The agreement is remarkable, and both sets agree within ±5 mK. At lower temperatures the difference between the data set becomes somewhat larger, 10–15 Pa. This difference is consistent with the uncertainties in ref (*6*) and probably results from a small amount of residual air in their sample as well as the limits of the pressure gauge.

Figure 2 shows a comparison of our present results and those of Blanke and Weiss (*6*) with some older, less accurate data from the literature (*7–9*).

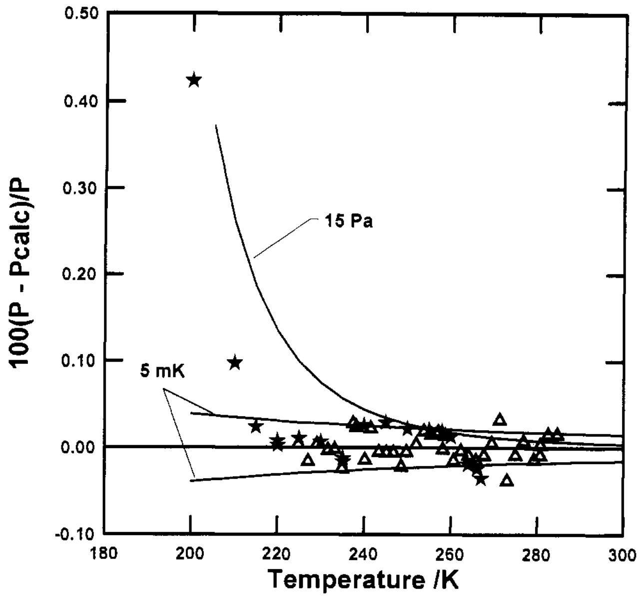

Figure 1. Fractional deviations of the experimental vapor pressures from eq 1 for 1-chloro-1,1-difluoroethane (R142b): △, this work; ★, ref 6. The solid curves show the effect at each temperature from a change of 5 mK or 15 Pa.

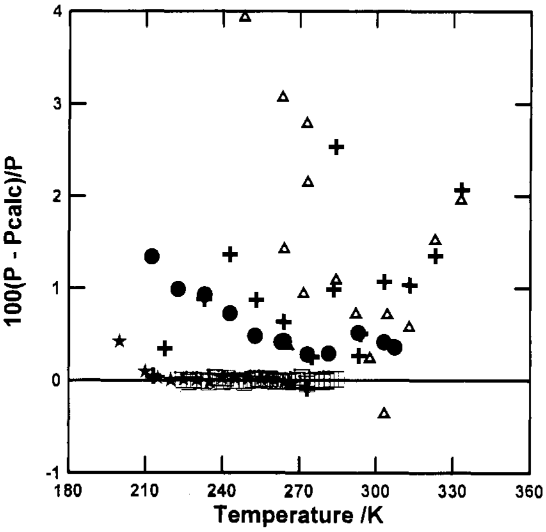

Figure 2. Fractional deviations of the experimental vapor pressures from eq 1 for 1-chloro-1,1-difluoroethane (R142b): □, this work; ★, ref 6; ●, ref 7; +, ref 8; △, ref 9.

R152a. For R152a, we measured 39 vapor pressures in the range of temperature from 219 to 274 K. The coefficients of eq 1 as well as eq 2 are listed in Table I and the results are listed in Table III with the deviation between our experimental results and the eqs 1 and 2. The standard deviation of the fit from eq 1 was 0.015% in pressure or 3.2 mK in temperature. At the normal boiling point, 101.325 kPa, the temperature was calculated to be 249.143 K.

For R152a, the results of Blanke and Weiss (*6*) fall in our pressure range. Figure 3 shows the deviation of our results plus those of ref 6 from eq 1. The agreement is comparable to that seen in Figure 1. Again, deviations on the order of 15 Pa are seen at lower temperatures.

To provide an equation for R152a in the pressure range from 20 kPa to the critical point, we combined our results and those of Blanke and Weiss (*6*) with the high-temperature results of Baehr and Tillner-Roth (*10*) to determine the constants of eq 2. For this purpose, we adopted a value of 386.41 K for the critical temperature, from ref 11, and we weighted each point according to the estimate of the uncertainty of the vapor pressure provided by ref 6, 15 Pa and 5 mK, and ref 10, 4×10^{-5} (1.6 MPa + p) and 5 mK. In our

Table III. Vapor Pressures and Deviations $100(P - P_{calc})/P$ from Equations 1 and 2 for 1,1-Difluoroethane (R152a)

		$100(P - P_{calc})/P$	
T/K	P/kPa	eq 1	eq 2
219.921	22.723	−0.041	−0.042
223.082	27.322	0.021	0.017
224.670	29.885	−0.013	−0.019
225.959	32.125	0.018	0.011
227.850	35.645	0.027	0.018
229.278	38.501	0.020	0.009
230.924	42.018	0.011	−0.001
232.567	45.792	0.017	0.004
234.081	49.497	0.001	−0.012
235.540	53.303	0.008	−0.006
234.902	51.588	−0.041	−0.055
236.496	55.911	−0.012	−0.027
236.059	54.700	−0.015	−0.029
237.938	60.052	−0.012	−0.027
239.528	64.912	0.005	−0.009
241.295	70.666	0.006	−0.008
242.822	75.955	0.003	−0.010
244.149	80.807	0.003	−0.010
245.844	87.351	−0.008	−0.019
247.489	94.123	0.008	−0.003
249.262	101.864	0.008	−0.001
250.770	108.836	0.004	−0.004
250.126	105.788	−0.019	−0.028
251.534	112.496	−0.008	−0.015
253.219	120.958	0.002	−0.004
254.768	129.162	0.002	−0.004
256.519	138.939	−0.006	−0.010
258.110	148.335	−0.006	−0.010
259.745	158.511	0.003	0.000
261.310	168.744	0.003	0.000
262.679	178.124	0.009	0.006
264.757	193.084	−0.003	−0.007
266.603	207.226	0.009	0.004
268.321	221.084	0.011	0.003
268.206	220.076	−0.014	−0.021
269.918	234.549	−0.004	−0.014
271.573	249.218	0.001	−0.012
273.139	263.726	0.001	−0.016

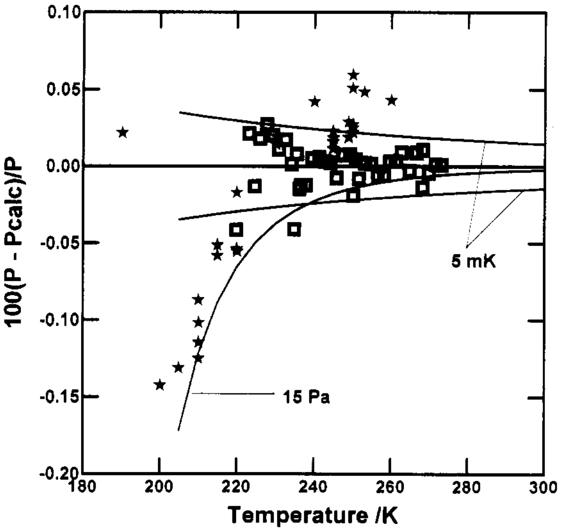

Figure 3. Fractional deviations of the experimental vapor pressures from eq 1 for 1,1-difluoroethane (R152a): □, this work; ★, ref 6. The solid curves show the effect at each temperature from a change of 5 mK or 15 Pa.

fitting the critical pressure was used as an adjustable parameter. The deviations of the data from eq 2 are plotted in Figure 4.

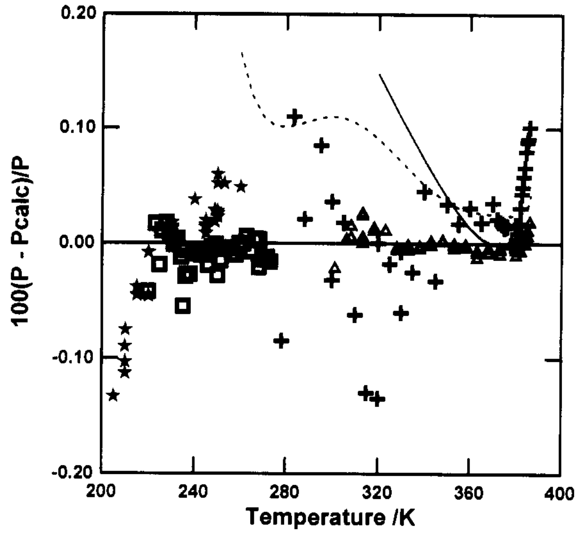

Figure 4. Fractional deviations of the experimental vapor pressure from eq 2 for 1,1-difluoroethane (R152a): □, this work; ★, ref 6; △, ref 10; +, ref 11; - - -, equation from ref 10; —, equation from ref 12.

At most temperatures, the results reported by Higashi et al. (*11*) agree with eq 2 to within ±0.1% as shown in Figure 4; however, in the region of the critical point their data seem to show a strange behavior. This may indicate that their measurements in this region were single-phase instead of vapor-pressure points. Baehr and Tillner-Roth (*10*) reported that their sample contained an amount of air with a mole fraction of less than 10^{-4}. We found that their data were more consistent with ours if we made a correction (*15*) for air with a mole fraction of 4×10^{-5}. We also show in Figure 4 the curve given by Baehr and Tillner-Roth (*10*) which was fitted to their unadjusted (for an air impurity) data and also to the data of refs 11 and 16. The recently published curve of Tamatsu et al. (*12*) is also shown in Figure 4. Their curve agrees with eq 2 within 0.1% throughout their range of temperature.

Literature Cited

(1) Goodwin, A. R. H.; Defibaugh, D. R.; Weber, L. A. *Int. J. Thermophys.* **1992**, *13*, 5.
(2) Defibaugh, D. R.; Goodwin, A. R. H.; Morrison, G; Weber, L. A. *Fluid Phase Equilib.*, in press.
(3) Weber, L. A. *Fluid Phase Equilib.* **1992**, *80*, 141.
(4) Goodwin, A. R. H.; Defibaugh, D. R.; Morrison, G.; Weber, L. A. *Int. J. Thermophys.* **1992**, *13*, 999.
(5) Weber, L. A.; Goodwin, A. R. H. *J. Chem. Eng. Data* **1993**, *38*, 254.
(6) Blanke, W.; Weiss, R. PTB - Ber. W-48, Feb 1992.
(7) Riedel, L. *Z. Gesamte Kälte-Ind.* **1941**, *7*, 105.
(8) Cherneeva, L. I. *Teploenergetika* **1958**, *7*, 38.
(9) Mears, W. H.; Stahl, R. F.; Orfjeo, S. R.; Shair, R. C.; Kells, L. F.; Thompson, W.; McCann, H. *Ind. Eng. Chem.* **1955**, *47*,1449.
(10) Baehr, H. D.; Tillner-Roth, R. *J. Chem. Thermodyn.* **1991**, *23*, 1063.
(11) Higashi, Y.; Ashizawa, M.; Kabata, Y.; Majima, T.; Uematsu, M.; Watanabe, K. *JSME Int. J.* **1987**, *30*, 1106.
(12) Tamatsu, T.; Sato, T.; Sato, H.; Watanabe, K. *Int. J. Thermophys.* **1992**, *13*, 985.
(13) Wagner, W.; Pruss, A. *J. Phys. Chem. Ref. Data*, to be published.
(14) Wagner, W. *Cryogenics* **1973**, *13*, 470.
(15) Weber, L. A. *Int. J. Refrig.*, to be published.
(16) Bier, K.: Oellrich, L.; Türk, M.; Zhai, J. *Ber. Kälte-Klima-Tagung*; Deutscher Kälte- u. Klimatechnischer Verein: Stuttgart, 1990.

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