Ebulliometric Measurement of the Vapor Pressure of Difluoromethane

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We have used a comparative ebulliometer to make accurate measurements of the vapor pressure of difluoromethane (R32) in the range 49–214 kPa, which corresponds to temperatures on ITS-90 between 208 and 237 K. The results are represented with an Antoine equation and are compared with literature values. We have combined our results with literature values, and we present an interpolating equation for the vapor pressure at temperatures between 190 K and the critical temperature (351.36 K). We also tabulate thermodynamic properties for R32 on the saturation boundary between 200 and 250 K.

Introduction

Mixtures of difluoromethane (R32) with 1,1,1,2-tetrafluoroethane (R134a), with 1,1-difluoroethane (R152a), and with pentafluoroethane (R125) are being considered as replacements for chlorodifluoromethane (R22) and the azeotropic mixture R502 in refrigeration and air conditioning systems. Calculation of the thermophysical properties of the mixtures requires reliable data for the properties of the pure components. However, very little information on the properties of R32 has been published. Henne et al. (*1*) published a value for the normal boiling point. Kanungo et al. (*2*) published a curve for the vapor pressure between 149 and 245 K. Malbrunot et al. (*3*) measured the vapor- and liquid-phase densities as well as the vapor pressure. The heat capacity of the ideal gas has been calculated from spectroscopic data (*4*). Dymond and Smith (*5*) give some values for the second virial coefficient at temperatures above 273 K. More recently Schmidt and Moldover (*6*) have measured the critical temperature, refractive index, and surface tension from which they estimated the saturated liquid and vapor densities and the critical density.

For the design of refrigeration cycles it is important to minimize the relative uncertainty in the vapor pressure of the refrigerant. Therefore, we have undertaken the measurement of the vapor pressure of R32 at low reduced temperatures and pressures in our comparative ebulliometer. This instrument is especially well-suited to work in this region. The apparatus is the same one which has been used for our earlier measurements on other candidate refrigerants (*7–10*). In the following sections we describe the apparatus, give results, and make comparisons with the limited published data for R32.

Experimental Section

The apparatus has been described several times (*7, 8*), and we will give only a brief description and note any modifications made. The comparative ebulliometer was comprised of two boilers, with reflux condensers, connected to a common manifold. One boiler contained the test fluid, R32 in this case, and the other contained a "standard fluid", for which we used water. The pressure of an inert gas, helium, was superimposed on the manifold/boiler system. Resistive heating was applied to the boilers, and the pressure determined the temperatures at which the two fluids boiled. Two long-stem platinum resistance thermometers in the upper parts of the boilers measured the condensing temperatures of the fluids on the International Temperature Scale of 1990 (ITS-90). The pressure was calculated accurately from the measured condensing temperature of the water, utilizing the new IAPWS ITS-90 approved vapor pressure equation for water (*11*). The power input to the boilers was varied manually to find the point such that a relatively large change in power (±75%) caused no appreciable change in the measured temperature. We varied the helium pressure and measured the boiling temperatures of the two fluids to obtain the vapor pressure curve of the refrigerant.

The condensers and two intermediate liquid nitrogen cooled traps prevented cross contamination of the samples. A 15-L ballast tank was used to minimize pressure fluctuations. The boilers and manifold were made of glass, and therefore the maximum experimental pressure was limited to about 210 kPa. The temperature of the water boiler varied from 353 to 396 K, and it was mounted inside a heated shield and was insulated. The refrigerant boiler was placed inside a refrigerated shield fitted with cooling coils through which methanol was circulated from a thermostated bath. The shield could be cooled to temperatures as low as 203 K. The shield's temperature was maintained approximately 15 K below the boiling temperature of the refrigerant. Smaller temperature differentials resulted in some instability in the measured condensing temperature, and we found that a 5 K differential was the minimum that we could tolerate.

The thermometers' resistances were measured with a digital multimeter. Thermometer calibrations were checked with a water triple point cell. The multimeter was calibrated against a Wilkins-type standard resistor. We estimate that temperatures could be measured within 3–4 mK. A comparison of the pressure calculated from the water boiler with that from a NIST standard barometer showed that the two agreed within 10 Pa at ambient pressure. This pressure difference corresponds to a temperature difference of 2.8 mK.

Ebulliometric measurements have several advantages over the more commonly used static technique for measuring vapor pressures. The symmetry of the comparative ebulliometry design implies that certain errors are self-canceling. This technique requires only the measurement of two temperatures, which, as discussed above, can be made quite accurately. The measured condensation temperatures are relatively insensitive to the presence of very volatile or of very involatile impurities. Incomplete degassing of the samples is a possible source of large systematic error in static measurements at low pressures. In ebulliometry, degassing occurs continuously as the fluids boil.

The water used was distilled water from the laboratory supply. The R32 sample was supplied with a stated purity

Table I. Vapor Pressures of Difluoromethane

T/K	P/kPa	T/K	P/kPa	T/K	P/kPa
208.357	49.434	215.477	73.835	226.732	131.412
208.650	50.260	217.018	80.287	228.109	140.395
209.314	52.312	217.067	80.504	229.618	150.769
209.933	54.206	218.323	85.961	231.030	161.017
210.318	55.400	219.303	90.560	232.024	168.561
210.350	55.530	220.256	95.099	233.598	181.069
211.812	60.305	221.371	100.691	234.757	190.739
213.306	65.582	223.331	111.147	236.369	204.848
214.697	70.762	224.944	120.413	237.380	214.096

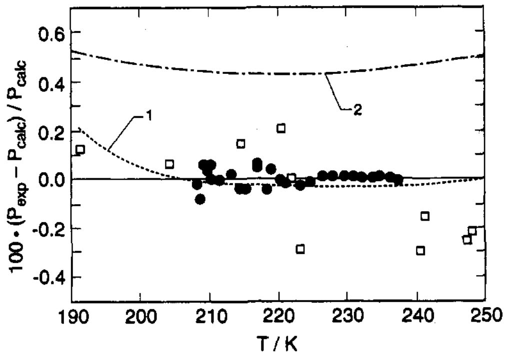

Figure 1. Deviation of the vapor pressure data from eq 1: ●, this research; □, line 1, ref 3; line 2, ref 2.

level of 0.9998 by mass and a stated water content of 8 ppm. It was used without further purification.

One modification to the original design was made necessary by the volatility of R32. The condenser fitted to the refrigerant boiler was originally cooled to 193 K with a dry ice and acetone mixture. The vapor pressure of R32 is approximately 19 kPa at this temperature, and the sample had a tendency to distill into one of the liquid nitrogen cold traps. This condenser was replaced with one cooled by liquid nitrogen boil-off gas from a storage dewar fitted with a heater. By varying the power input into the dewar we could vary the temperature of the condenser. At maximum power we could reach temperatures as low as 148 K and thus prevent loss of the sample.

Results

We measured 27 vapor pressures at temperatures between 208 and 237 K. Pressures varied from 49 to 214 kPa. The minimum temperature with this arrangement was limited by the minimum attainable temperature of the cold shield, 203 K, plus the necessary minimum 5 K temperature differential discussed above.

The results are given in Table I where temperatures are given on the ITS-90 temperature scale. They can be represented by the Antoine vapor pressure equation,

$$\ln(P/\mathrm{kPa}) = 14.517\,82 - 1924.06/(T/\mathrm{K} - 27.130) \quad (1)$$

with a standard relative deviation of 0.036% in pressure, or 6.5 mK in temperature by minimizing the square of the deviations in the quantity $T \ln P$. The temperature of the normal boiling point is calculated to be 221.490 ± 0.006 K. From our experience we estimate that eq 1 should be valid in the temperature range 200–250 K. The larger imprecision seen in Figure 1 at the lower temperatures is due to small temperature instabilities, in the 10–15 mK range. They are attributed to the fact that we were not able to maintain the desired 15 K temperature difference between the boiler and shield at the lowest temperatures. They could presumably be eliminated with a more powerful refrigerator.

Deviations of our data, as well as the other published results, from eq 1 are shown in Figure 1. Kanungo et al. (*2*) did not give their results but only a smooth curve. They stated that their values exhibited a standard relative deviation of ±0.13% from their curve. From their publication we have assumed that they used the IPTS 68 scale and have converted their results to the ITS-90 using refs 12 and 13. Figure 1 shows that their curve is systematically about 0.44% higher than ours in the overlapping temperature range. We do not know the reason for this apparent systematic error. In contrast, the results of Malbrunot et al. (*3*) exhibit no overall systematic difference from our results, although they are an order of magnitude less precise than ours. We have converted their temperatures from the ITS-48 scale to the ITS-90 scale (*12*, *13*). Their vapor pressure curve is in excellent agreement with ours in the range of our data. The normal boiling point temperature which they gave would be 221.498 K on the ITS-90 scale, and it agrees well with the value given by eq 1. None of the literature data shows deviations characteristic of an appreciable volatile impurity. Henne et al. (*1*) gave the normal boiling point as −51.6 °C (221.6 K). The vapor pressure curve given by McLinden (*14*) was based on the data of Malbrunot et al., and it also agrees well in this temperature range.

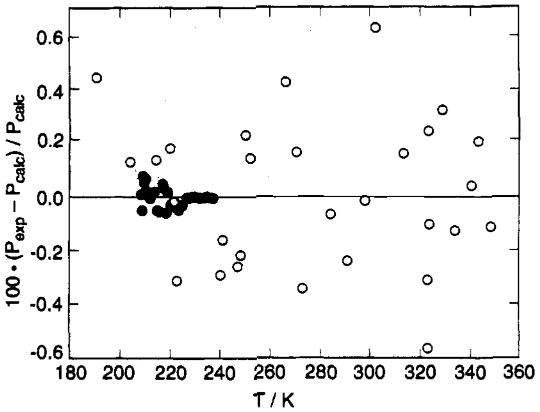

Figure 2. Deviation of the vapor pressure data from eq 2: ●, this research; ○, ref 3.

To provide an interpolating function for the vapor pressure spanning the wider range of 191 K to the critical temperature, we combined our ebulliometric results with the static measurements from Malbrunot et al. (*3*) which, as Figure 1 shows, join smoothly with ours. We used a Wagner-type vapor pressure function (*15*). The best representation was found to be

$$\ln(P/\mathrm{kPa}) = n_1 + (n_2\tau + n_3\tau^{1.5} + n_4\tau^{2.5} + n_5\tau^5)T_c/T \quad (2)$$

with the critical temperature T_c constrained to the value 351.36 K, observed by Schmidt and Moldover (*6*). The adjustable parameters n_i obtained from this procedure were $n_1 = 8.666\,202$, $n_2 = -7.425\,33$, $n_3 = 1.570\,51$, $n_4 = -1.645\,01$, and $n_5 = -3.397\,93$. The standard relative deviation of the fit was 0.24% in pressure. The deviations of the results from the curve are shown in Figure 2. It is clear that the results from ref 3 have less precision than ours and that both sets are mutually consistent. The critical pressure obtained from eq 2 at the critical temperature is 5803 ± 6 kPa, where the uncertainty is the statistical value for 1σ. This value is 27 kPa below that reported by Malbrunot et al. (*3*). This difference is due primarily to the fact that we used a different critical temperature.

Thermodynamic Properties

We have combined our vapor pressure measurements with some of the data available in the literature to provide the thermodynamic properties of R32 at relatively low temperatures and pressures on the saturation boundary. To do this, we used the heat capacities of the ideal gas at constant pressure

Table II. Thermodynamic Properties of Difluoromethane on the Saturation Boundary[a]

T/K	P/kPa	ρ/(kg m^{-3})	(H − H_0)/ (kJ kg^{-1})	(S − S_0)/ (kJ kg^{-1} K^{-1})	C_p/ (kJ kg^{-1} K^{-1})	phase
200	29.59	0.945	402.95	2.0148	0.78	g
200	29.59	1278	0.00	0.0000	1.55	l
210	54.38	1.669	408.54	1.9472	0.82	g
210	54.38	1249	15.49	0.0755	1.54	l
220	93.84	2.784	413.81	1.8876	0.87	g
220	93.84	1220	31.08	0.1479	1.56	l
230	153.45	4.422	418.72	1.8346	0.92	g
230	153.45	1190	46.96	0.2183	1.60	l
240	239.60	6.747	423.17	1.7870	0.98	g
240	239.60	1159	63.32	0.2876	1.65	l
250	359.48	9.953	427.06	1.7435	1.04	g
250	359.48	1128	80.29	0.3564	1.71	l

[a] H_0 and S_0 refers to the liquid phase at 200 K.

Table III. Estimated Second Virial Coefficients for Difluoromethane

T/K	B/(L mol^{-1})	T/K	B/(L mol^{-1})	T/K	B/(L mol^{-1})
200	−1.105	220	−0.771	240	−0.572
210	−0.915	230	−0.660	250	−0.502

given in ref 4 and densities of the saturated liquid from ref 3 (estimated accuracy 0.2–0.3%). For the gas-phase nonideality we made use of values of the second virial coefficient given in Table III. They have an uncertainty of 2–5% and were estimated by a technique which will be presented later (*16*). The results for the saturated liquid and vapor at temperatures from 200 to 250 K are shown in Table II. The enthalpy and entropy have been arbitrarily set to zero for the saturated liquid at 200 K. This temperature range required only a short extrapolation of our vapor pressure curve, eq 1. The estimated accuracy of the pressure has already been discussed. The vapor density, enthalpy and entropy of vaporization, and heat capacity have uncertainties estimated at 0.1–0.2%, 0.5%, and 1–3%, respectively. Accurate calculations at higher temperatures and pressures require a more complete description of the gas-phase nonideality, which we will provide in the future.

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