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Vapor Pressures and *PVT* Properties of the Gas Phase of 1,1,1-Trifluoroethane

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A Burnett/isochoric *PVT* apparatus and a metal ebulliometer have been used to measure the gas-phase *PVT* surface and vapor pressures of 1,1,1-trifluoroethane (R143a). The *PVT* measurements spanned the temperature range 276 K to 373 K at pressures up to 6.6 MPa (densities to 6 mol·dm^{-3}). A virial surface is given which represents the data up to a density of 3.5 mol·dm^{-3}. Formulations are given for the second and third virial coefficients. Vapor pressure measurements spanned the temperature range 236 K to 343 K. Thermodynamic calculations were used to extend the range down to a temperature of 180 K, and an equation is given which represents the vapor pressure curve from 180 K to the critical temperature. The temperature of the normal boiling point was found to be (225.90 ± 0.01) K. Comparisons are made with other published results for R143a.

Introduction

1,1,1-Trifluoroethane is one of the more volatile of the hydrofluorocarbons. Although it is flammable, it may be used as a component in a binary or ternary mixture which would not be flammable. Such mixtures are being considered for the purpose of replacing chlorodifluoromethane (R22) and R502, the azeotropic mixture of R22 and R115 (C_2F_5Cl).

Several studies of the thermophysical properties of R143a have been reported since the early work of Russell et al. (1944). Beckermann and Kohler (1995) derived the second virial coefficients, *B*, and ideal gas heat capacities, C_p°, from acoustic measurements; Gillis (1996) also used acoustic measurements to derive the second and third virial coefficients, *B* and *C*, and C_p°; Kohler and Van Nhu (1993) calculated *B* using a potential model incorporating dipole moments; Bignell and Dunlop (1993), Zhang et al. (1995), and Giuliani et al. (1995) reported virial coefficients derived from *PVT* measurements. In addition, Russell et al., Zhang et al., Giuliani et al., Fukushima (1993), Wang et al. (1993), and Widiatmo and Watanabe (1994) reported vapor pressure measurements. Schmidt (1996) has measured the critical temperature. Magee (1996) measured the densities and heat capacities of the condensed phase.

In the next section we give the experimental details of our measurements, and after that we report the results and make comparisons with the above-mentioned works in the literature. We also used some of the reported properties to make thermodynamic calculations of vapor pressures at temperatures lower than those experimentally accessible.

Experimental Section

The NIST Burnett/isochoric *PVT* apparatus has been thoroughly documented by Weber (1989) and the references given therein, and a brief description suffices here. The sample cell was a heavy-walled nickel vessel with two chambers that were gold-plated on the inside. The cell constant was determined with helium gas to be 1.782 06 ± 0.000 07 (standard uncertainty). The top chamber was connected to a very sensitive diaphragm-type pressure transducer. The apparatus was mounted in a circulated, thermostated oil bath. The transducer separated the sample from an argon-filled manifold which had several precision pressure gages and an automated piston-type gas injector, which balanced the argon pressure against the sample pressure. Temperature was measured with a platinum resistance thermometer. Automated feedback circuits controlled the argon pressure and the temperature of the oil bath.

The Burnett expansion mode of operation was used to establish a baseline isotherm on which density could be calculated as a function of pressure. The remaining data were measured on isochores whose densities were determined from a pressure measurement on the baseline isotherm.

For the Burnett measurements, a dead-weight pressure balance was used to measure pressure with an accuracy of 2×10^{-2} kPa (standard uncertainty); for the isochoric measurements an automated pressure gauge was used to measure pressure with a standard uncertainty of about 2×10^{-1} kPa.

The metal ebulliometer was a comparative type having two boilers with reflux condensers connected through a manifold. It has been completely described by Weber and Silva (1996). One boiler contained reference fluid whose vapor pressure had been accurately determined, and the other boiler contained the fluid of interest. A sensitive pressure controller maintained a constant pressure of helium gas in the manifold. Two platinum resistance thermometers were used to measure the boiling temperatures in the boilers. The temperature in the reference boiler was used to determine the system pressure. Measurements over a range of pressures allowed the determination of the vapor pressure curve of the test fluid. In this work 1,1-dichloro-2,2,2-trifluoroethane (R123) was used as the reference fluid. Its vapor pressure curve has been accurately reported by Goodwin et al. (1992).

The sample of R143a used in this work was quite pure (0.9999) except for a rather large quantity (approximately 1000 parts per million) of air. We attempted to remove the air with a vacuum sublimation chamber of the type described by Weber (1994a). This process was not completely successful, as will be discussed below.

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Table 1. Gas-Phase *PVT* Data for R143a

T/K	P/MPa	ρ/mol·dm^{-3}	T/K	P/MPa	ρ/mol·dm^{-3}
348.207	3.9919	6.0768	329.352	0.8306	0.3384
353.212	4.4919	6.0755	333.128	0.8429	0.3383
358.141	5.0000	6.0742	338.192	0.8591	0.3383
363.151	5.5250	6.0730	343.155	0.8731	0.3382
373.163	6.5925	6.0704	348.112	0.8906	0.3381
368.153	6.0557	6.0717	353.187	0.9065	0.3381
363.152	5.5253	6.0730	358.136	0.9221	0.3380
358.144	5.0002	6.0742	363.179	0.9379	0.3379
353.165	4.4875	6.0755	368.134	0.9534	0.3378
353.205	4.1078	3.4093	373.153	0.9690	0.3378
363.149	4.6174	3.4078	276.658	0.3969	0.1903
373.174	5.1205	3.4064	283.087	0.4085	0.1903
333.167	2.8341	1.9147	288.195	0.4176	0.1902
338.179	2.9698	1.9143	293.132	0.4264	0.1902
342.824	3.0926	1.9139	298.164	0.4353	0.1901
348.169	3.2307	1.9135	303.176	0.4440	0.1901
353.167	3.3577	1.9131	308.134	0.4527	0.1901
358.146	3.4825	1.9127	313.165	0.4614	0.1900
363.159	3.6066	1.9123	318.156	0.4701	0.1900
368.164	3.7291	1.9119	323.141	0.4786	0.1899
373.154	3.8501	1.9115	328.188	0.4872	0.1899
318.150	1.9141	1.0751	333.183	0.4957	0.1899
323.176	1.9809	1.0749	338.138	0.5041	0.1898
328.050	2.0446	1.0746	343.157	0.5126	0.1898
332.632	2.1035	1.0744	348.198	0.5210	0.1897
338.156	2.1735	1.0742	353.188	0.5293	0.1897
343.180	2.2364	1.0740	358.187	0.5377	0.1897
348.147	2.2978	1.0737	363.172	0.5461	0.1896
353.142	2.3590	1.0735	368.180	0.5544	0.1896
358.133	2.4195	1.0733	373.137	0.5626	0.1895
363.134	2.4796	1.0731	278.133	0.2338	0.1068
368.185	2.5399	1.0728	283.152	0.2386	0.1068
373.155	2.5987	1.0726	288.197	0.2434	0.1067
298.144	1.1521	0.6038	293.123	0.2480	0.1067
303.168	1.1862	0.6037	298.164	0.2528	0.1067
308.173	1.2195	0.6036	303.174	0.2576	0.1067
313.165	1.2523	0.6034	308.132	0.2622	0.1067
318.141	1.2845	0.6033	313.168	0.2668	0.1066
323.162	1.3167	0.6032	318.195	0.2715	0.1066
328.150	1.3485	0.6030	323.185	0.2761	0.1066
333.173	1.3800	0.6029	328.182	0.2807	0.1066
338.044	1.4105	0.6028	333.184	0.2853	0.1065
343.178	1.4421	0.6027	338.140	0.2899	0.1065
348.149	1.4727	0.6025	343.156	0.2946	0.1065
353.139	1.5032	0.6024	348.162	0.2991	0.1065
358.189	1.5338	0.6023	353.173	0.3038	0.1064
363.177	1.5638	0.6022	358.179	0.3083	0.1064
368.187	1.5938	0.6020	363.176	0.3129	0.1064
373.153	1.6233	0.6019	368.179	0.3174	0.1064
283.174	0.6763	0.3390	373.149	0.3220	0.1064
288.447	0.6947	0.3390	373.16	6.5923	6.0704
292.239	0.7078	0.3389	373.16	5.1199	3.4064
298.168	0.7279	0.3388	373.16	3.8498	1.9115
303.180	0.7448	0.3388	373.16	2.5982	1.0726
308.168	0.7614	0.3387	373.16	1.6236	0.6019
313.144	0.7778	0.3386	373.16	0.9686	0.3378
318.192	0.7943	0.3385	373.16	0.5627	0.1895
323.142	0.8105	0.3385	373.16	0.3219	0.1064
328.135	0.8267	0.3384			

Results and Comparisons

PVT Surface. The baseline isotherm for the Burnett expansion was chosen to be 373.16 K. Seven expansions were made, starting at a pressure of about 6.6 MPa. Between each pair of expansions, data were measured as a function of temperature on the isochore. Measurements were made on eight isochores ranging in density from 0.1 mol·dm^{-3} to 6.0 mol·dm^{-3} (critical density = 5.15 mol·dm^{-3}). The data covered the temperature range 276 K to 373 K. A total of 116 data were measured, and the results are given in Table 1 and illustrated in Figure 1.

All of the data at densities less than 3.5 mol·dm^{-3} were represented with a virial surface,

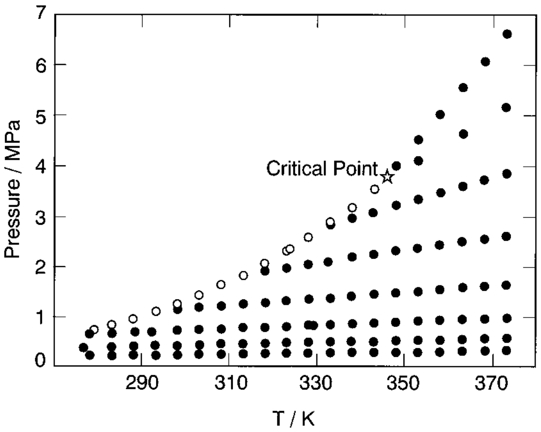

Figure 1. Location of experimental data for R143a measured with the *PVT* apparatus: (○) vapor pressures; (●) single-phase *PVT* data.

$$(Z - 1)/\rho = B + C\rho + D\rho^2 \tag{1}$$

where Z is the compressibility factor and B, C, and D are the virial coefficients. The virial coefficients were made functions of temperature,

$$B = b_1 + b_2/T_r + b_3/T_r^{\,2} + b_4/T_r^{\,5} \tag{2a}$$

$$C = c_1/T_r^{\,5} + c_2/T_r^{\,6} \tag{2b}$$

$$D = d_1 + d_2T_r \tag{2c}$$

with $T_r = T/T_c$; T_c was obtained from Schmidt (1996) to be 346.04 K. The coefficients for eqs 2 are given in Table 2. The standard deviation of the fit was 0.04% in density. The bias was 0.02%, which could be caused by adsorption or a small systematic error in one of the experimental quantities.

Vapor Pressures. Twenty vapor pressure measurements were made with the *PVT* apparatus. Measurements were made at three different filling densities, from 1.0 to 6.0 mol·dm^{-3}. Temperatures ranged from 279 K to 343 K. Pressures varied from 744 kPa to 3556 kPa. An additional 32 measurements were made with the ebulliometer in the range 236 K to 279 K at pressures from 160 kPa to 751 kPa. The results are given in Table 3.

When these two data sets were correlated with a vapor pressure equation, we found that they did not join smoothly at 279 K. The static pressure measurements from the *PVT* apparatus were higher than the dynamic measurements from the ebulliometer by about 0.1 to 0.2%. The difference between the data sets could readily be explained by assuming that the sample still contained some residual air when it was loaded into the *PVT* apparatus. The relationship given by Weber (1994a) shows how static vapor pressure measurements are affected by an air impurity and also how the effect varies with the filling density. The assumption of the existence of a residual air impurity with a concentration of 95 parts per million (mole fraction) reconciled the static data for all three filling densities with the results of the ebulliometric measurements. For this calculation, we used the value of 35 MPa for the Henry's constant of air dissolved in R143a. This value was estimated from the chromatographic analysis of the two phases in the sample supply cylinder. The static data in Table 3 have been corrected for this air impurity.

Vapor pressure measurements were not made at temperatures lower than 236 K (160 kPa). Thermodynamic loop calculations were utilized to estimate the properties

Table 2. Coefficients for the Virial Surface, Eqs 2[a]

$b_1 = 0.458\ 801$	$c_1 = 0.122\ 632$
$b_2 = -0.990\ 621$	$c_2 = -0.087\ 109\ 5$
$b_3 = 0.318\ 885$	$d_1 = -0.006\ 862\ 6$
$b_4 = -0.069\ 752\ 1$	$d_2 = 0.005\ 110\ 3$

[a] Units are moles and cubic decimeters.

Table 3. Vapor Pressure Data for R143a

T/K	P/kPa	T/K	P/kPa
	Ebulliometer		
236.133	160.560	259.883	400.758
237.565	170.605	259.884	400.801
238.912	180.597	261.648	425.882
240.210	190.627	263.329	450.859
241.457	200.614	264.944	475.916
242.659	210.636	266.495	500.963
243.815	220.647	267.991	526.024
246.011	240.665	269.433	551.081
248.084	260.560	270.825	576.125
248.076	260.674	272.177	600.723
250.032	280.622	272.180	600.883
251.875	300.682	272.172	601.201
254.049	325.681	273.483	625.979
254.050	325.718	274.753	650.987
256.097	350.717	277.181	701.094
258.038	375.748	279.484	751.294
	PVT Apparatus		
279.171	744.3	303.155	1434.4
282.974	832.1	308.131	1623.1
283.128	835.7	308.177	1624.7
287.965	958.8	313.176	1833.1
288.221	965.6	318.118	2057.9
293.028	1101.9	323.168	2309.0
293.173	1105.8	328.172	2581.2
298.165	1262	333.162	2876.6
298.173	1262.6	337.997	3188.8
303.153	1434.3	343.190	3556.3

of R143a on the saturation boundary at lower temperatures and pressures. The technique used here was the one described by Weber and Defibaugh (1996) with several changes. At low reduced temperatures the primary quantity needed to estimate the temperature variation of the vapor pressure is ($C_\sigma - C_p^\circ$), where C_σ is the heat capacity of the saturated liquid and C_p° is the ideal gas heat capacity. For R143a, C_σ has been measured by Magee (1996) and C_p° has been derived by Gillis (1996) and by Beckermann and Kohler (1995) from their acoustic measurements. The second necessary quantity is the second virial coefficient, B. Here we used values of B derived from the acoustic measurements because they extended to lower temperatures than the *PVT* measurements and because they would not be subject to uncertainties due to adsorption. The density of the saturated liquid, which is necessary for a correction term, was also taken from Magee.

To implement the calculation we arbitrarily set the enthalpy and entropy of the saturated liquid, H_L and S_L, to be zero at 243.15 K. The corresponding ideal gas properties at that temperature were set to be $H_0^\circ = 18\ 526.4$ J·mol^{-1} and $S_0^\circ = 81.8$ J·(mol·K)$^{-1}$. These values are consistent with the experimental vapor pressure curve and its slope over a range of temperatures. Then, using the relationships given in the above reference, we calculated the vapor pressure down to a temperature of 180 K (6.040 kPa). The resulting pressures, saturated vapor volumes and enthalpies of vaporization are given in Table 4.

The calculated vapor pressures (with a somewhat reduced weighting) and the measured pressures were fit to the relationship

$$\ln(P/P_c) = (a_1\tau + a_2\tau^{1.5} + a_3\tau^{2.5} + a_4\tau^5)/T_r \qquad (3)$$

Table 4. Vapor Pressures, Saturated Vapor Volumes, and Enthalpies of Vaporization for R1433a from Thermodynamic Calculations

T/K	P/kPa	v_v/dm^3·mol^{-1}	ΔH_v/J·mol^{-1}
180	6.040	246.2	21 362
190	12.785	122.2	20 869
200	24.804	65.84	20 374
210	44.758	37.94	19 863
220	75.990	18.78	19 325
230	122.52	14.75	18 749
240	188.96	9.777	18 124
250	280.46	6.694	17 491
260	402.59	4.708	16 747
270	561.27	3.386	15 932

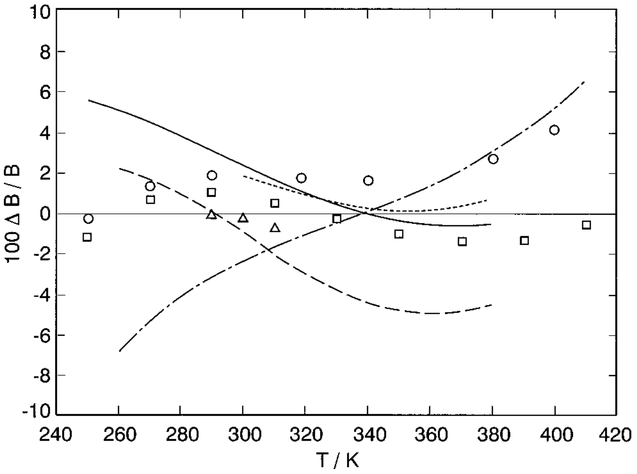

Figure 2. Deviations of reported second virial coefficients for R143a from eq 2a: (○) Gillis (1996); (□) Beckermann and Kohler (1995); (△) Bignell and Dunlop (1993); (- - -) Zhang et al. (1995); (— —) Giuliani et al. (1995); (—) Weber (1994b); (—•—) Kohler and Van Nhu (1993).

with $T_r = T/T_c$, and $\tau = (1 - T_r)$. The parameters were found to be $a_1 = -7.350\ 95$, $a_2 = 1.707\ 92$, $a_3 = -2.078\ 58$, $a_4 = -2.256\ 15$, and $P_c = (3775.5 \pm 1.7)$ kPa. The standard deviation of the fit was 0.024% in pressure, and the deviations are shown in Figure 4. Equation 3 gives the temperature of the normal boiling point to be (225.90 ± 0.01) K. The Pitzer acentric factor was found to be 0.261.

Comparisons. The various sets of data reported for the thermophysical properties of gaseous R143a are generally in good agreement. The present gas-phase density measurements agree with the results of Giuliani et al. (1995) to within less than 0.1%. We also agree with the data of Zhang et al. (1995) to within about 0.1% in most cases. All of the recent results for R143a have been analyzed in terms of the virial coefficients. The second virial coefficients of the various reports have been compared in Figure 2, where the baseline is eq 2a. It is seen that all of the values of B agree within ±6%, most within ±2%. The larger differences (≃5%) with the B of Giuliani et al. at higher temperatures reflect differences in analysis rather than differences in the data sets. Zhang et al. and the present work utilized three coefficients to represent data at densities to 3.5 mol·dm^{-3} ($\rho_r = 0.68$) whereas Giuliani et al. used three coefficients to fit data at densities up to 4.98 mol·dm^{-3} ($\rho_r = 0.96$). The latter authors' coefficients may be affected by contributions from higher order virials not considered. The virial coefficients derived from the two sets of acoustic measurements agree with the present work within 2% or better. Agreement with the work of Bignell and Dunlop (1993) is excellent. Values calculated with the model of Weber (1994b) appear to be too negative at low temperatures, and values resulting from the potential model of Kohler and Van Nhu (1993) have a temperature

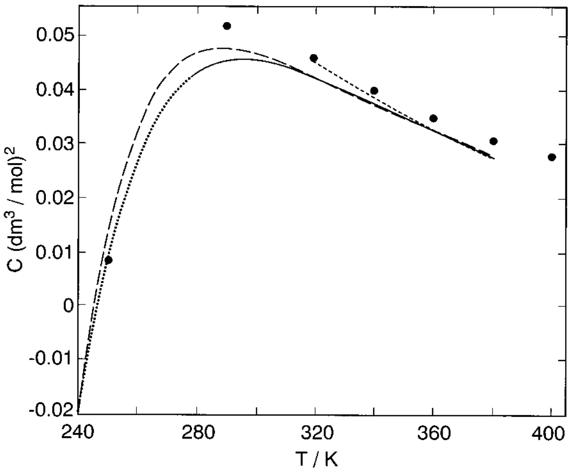

Figure 3. Third virial coefficient of R143a: (—) eq 2b; (···) extrapolation; (- - -) Zhang et al. (1995); (— —) Weber (1994b); (●) Gillis (1996).

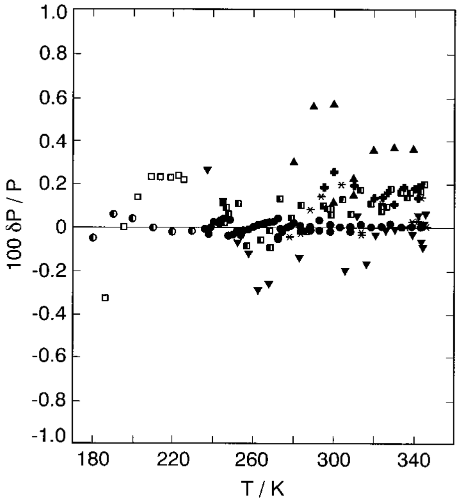

Figure 4. Deviations of vapor pressure data for R143a from eq 3: (●) present results, (◐) thermodynamic calculations; (◧) Giuliani et al. (1995); (+) Zhang et al. (1995); (□) Russell et al. (1944); (*) Fukushima (1993); (▼) Wang et al. (1993); (▲) Widiatmo and Watanabe (1994).

dependence which is too small. Figure 3 shows a comparison of the third virial coefficients from four references. Results of the present work agree very well with those of Zhang et al. over the range of validity of the latters' work, 320 K to 380 K. Calculated values from the model of Weber (1994b) also agree very well over a wide range, including the extrapolation to lower temperatures. Results from the acoustic measurements of Gillis, based on the square well potential, also agree remarkably well.

Comparison of eq 3 with all of the data sets for the vapor pressure is shown in Figure 4. The vapor pressures of Giuliani et al. agree with the present results within their precision at the lower temperatures, but they become somewhat larger at higher temperatures, the difference reaching 0.2% near the critical point. The data of Zhang et al. are also higher by about 0.15%. The reason for this difference is not known. The results of Widiatmo and Watanabe (1994) are consistently higher than ours by 0.1 to 0.5%. The data of Fukushima (1993) exhibit larger scatter, but within this scatter they agree with the present work, especially near the critical temperature. The results of Wang et al. (1993) also agree relatively well with the present work. The low-temperature results of Russell et al. (1944) are higher than the present work by about 0.25%, but then become considerably lower near the triple point temperature.

Russell et al. made an experimental determination of the enthalpy of vaporization at 224.4 K. Our calculated value at that temperature (using the techniques employed in producing Table 4), 19 097 $J\cdot mol^{-1}$, agrees very well with their experimental value of 19 175 $J\cdot mol^{-1}$. This agreement gives strong support to our low-temperature, calculated vapor pressures.

Conclusions

We have presented new measurements of the vapor pressure and gas-phase densities of 1,1,1-trifluoroethane over a wide temperature range. We have compared our results with the fairly extensive published literature. The generally good agreement between the data sets indicates that the gas-phase equilibrium properties of this hydrofluorocarbon can be calculated with a high degree of certainty.

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Literature Cited

Beckermann, W.; Kohler, F. Acoustic Determination of Ideal-Gas Heat Capacity and Second Virial Coefficients of Some Refrigerants Between 250 and 420 K. *Int. J. Thermophys.* **1995**, *16*, 455−464.

Bignell, C. M.; Dunlop, P. J. Second virial coefficients for seven fluoroethanes and interaction second virial coefficients for their binary mixtures with helium and argon. *J. Chem. Phys.* **1993**, *98*, 4889−4891.

Fukushima, M. Measurements of vapor pressure, vapor-liquid coexistence curve and critical parameters of HFC143a. *Nippon Reito Kyokai* **1993**, *10*, 87−93.

Gillis, K. NIST, Gaithersburg, MD. *Int. J. Thermophys.* **1996**, in press.

Giuliani, G.; Kumar, S.; Zazzini, P.; Polonara, F. Vapor Pressure and Gas Phase Data and Correlation for 1,1,1-Trifluoroethane. *J. Chem. Eng. Data* **1995**, *40*, 903−908.

Goodwin, A. R. H.; Defibaugh, D. R.; Morrison, G.; Weber, L. A. The vapor pressure of 1,1-dichloro-2,2,2-trifluoroethane (R123). *Int. J. Thermophys.* **1992**, *13*, 999−1009.

Kohler, F.; Van Nhu, N. The second virial coefficients of some halogenated ethanes. *Mol. Phys.* **1993**, *80*, 795−800.

Magee, J. NIST, Boulder, CO, private communication, 1996.

Russell, H.; Golding, D. R. V.; Yost, D. The Heat Capacity, Heats of Transition, Fusion and Vaporization, Vapor Pressure and Entropy of 1,1,1-Trifluoroethane. *J. Am. Chem. Soc.* **1944**, *66*, 16−20.

Schmidt, J. NIST, Gaithersburg, MD, private communication, 1996.

Wang, H.; Li, Z.; Ma, Y.; Lu, C. Experimental study on vapor pressure and critical parameters of CH_3CF_3. *Huagong Xuebao* **1993**, *44*, 373−377.

Weber, L. A. Vapor pressures and gas-phase PVT data for 1,1,1,2-tetrafluoroethane. *Int. J. Thermophys.* **1989**, *10*, 617−627.

Weber, L. A. Criteria for establishing accurate vapor pressure curves. *Int. J. Refrig.* **1994a**, *17*, 117−122.

Weber, L. A. Estimating the Virial Coefficients of Small Polar Molecules. *Int. J. Thermophys.* **1994b**, *15*, 461−482.

Weber, L. A.; Defibaugh, D. R. The Vapor Pressure of Pentafluorodimethyl Ether. *J. Chem. Eng. Data* **1996**, *41*, 382−385.

Weber, L. A.; Silva, A. M. Design of a High-Pressure Ebulliometer, with Vapor-Liquid Equilibrium Results for the Systems $CHF_2Cl + CF_3CH_3$ and $CF_3CH_2F + CH_2F_2$. *Int. J. Thermophys.* **1996**, *17*, 873−888.

Widiatmo, J. V.; Watanabe, K. Saturated liquid densities and vapor pressures of 1,1,1-trifluoroethane, difluoromethane, and pentafluoroethane. *J. Chem. Eng. Data* **1994**, *39*, 304−308.

Zhang, H-L.; Sato, H.; Watanabe, K. Vapor Pressures, Gas-Phase PVT Properties, and Second Virial Coefficients for 1,1,1-Trifluoroethane. *J. Chem. Eng. Data* **1995**, *40*, 887−890.

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