

Saturated-Liquid Densities and Vapor Pressures of 1,1,1-Trifluoroethane, Difluoromethane, and Pentafluoroethane

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Saturated-liquid densities and vapor pressures of HFC-143a (1,1,1-trifluoroethane), HFC-32 (difluoromethane), and HFC-125 (pentafluoroethane) were measured by a magnetic densimeter coupled with a metallic bellows in the range of temperatures from 220 to 340 K. The experimental uncertainties for temperature, pressure, and density measurements are estimated to be not greater than ± 15 mK, ± 10 kPa (for HFC-143a) or ± 2 kPa (for HFC-32 and HFC-125), and $\pm 0.2\%$, respectively. The purities of HFC-143a, HFC-32, and HFC-125 used in the present measurements are 99.0 mol %, 99.998 mass %, and 99.8 mass %, respectively.

Introduction

In accord with an increasing concern on the stratospheric ozone depletion, the time table toward a complete ban on the production and consumption of chlorofluorocarbon compounds (CFC) has been accelerated to phase them out by 1995, 5 years earlier than the time limit agreed on by the revised Montreal Protocol. Such an accelerated phase out has also impacted the phase out even for hydrochlorofluorocarbon compounds (HCFC) by 2030, as agreed upon recently at the fourth meeting of the Parties in Copenhagen, 1992.

HFC-143a (1,1,1-trifluoroethane) which was originally produced more than 40 years ago has been considered not to be an attractive refrigerant due to its flammability. Since it has no ozone depletion potential, however, it has recently been considered a promising candidate to replace HCFC-22 as a component of the alternative mixtures with other HFCs such as HFC-32 (difluoromethane), HFC-125 (pentafluoroethane), and/or HFC-134a.

HFC-32, a flammable one too, is currently recognized as one of the most promising candidates to replace HCFC-22, the most widely used refrigerant among the available HCFCs, especially by applying this compound as a component of the refrigerant mixtures with HFC-134a and/or HFC-125.

HFC-125 which has no ozone depletion potential like HFC-143a and HFC-32 is considered as a substitute for refrigerant-502, an azeotropic refrigerant blend of HCFC-22 and CFC-115, again as a component of mixtures.

This paper reports the measurements of saturated-liquid densities and vapor pressures of these three HFCs mentioned above. On the basis of those measurements, analytical correlations with respect to the saturated-liquid densities and vapor pressures have also been established, and their comparison with some reported measurements are also discussed.

Experimental Apparatus

All the measurements throughout the present study have been carried out by using a magnetic densimeter coupled with a metallic bellows variable-volume cell. The present apparatus shown in Figure 1 is essentially the same as that designed by Maezawa et al. (1) and has been used for our recent measurements of several refrigerants and their mixtures (2). The magnetic densimeter consists of a magnetic buoy, a glass made sample cell, an electromagnetic coil, and a positioner. By observing detachment of the magnetic buoy from the positioner when the sum of the buoyant force by the

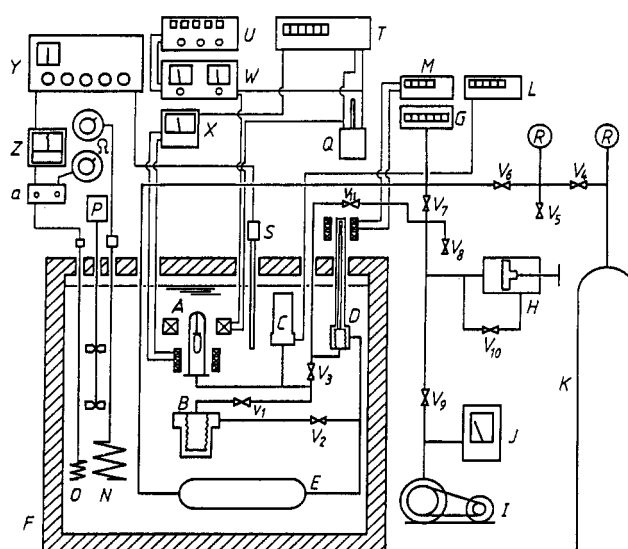


Figure 1. Experimental apparatus: (A) magnetic densimeter; (B) variable-volume cell; (C) digital quartz pressure transducer; (D) bellows displacement meter; (E) damper; (F) thermostat; (G) digital pressure gauge; (H) pressure controller; (I) vacuum pump; (J) vacuum gauge; (K) nitrogen gas; (L) digital quartz pressure computer; (M) displacement meter amplifier; (N) main heater; (O) subheater; (P) stirrer; (Q) standard resistor; (R) pressure gauge; (S) platinum resistance thermometer; (T) digital multimeter; (U) current controller; (V₁ to V₁₁) valves; (W) dc power supply; (X) galvanometer; (Y) thermometer bridge; (Z) pen recorder; (α) transformer.

liquid sample and the electromagnetic force by the electromagnetic coil is in balance with the gravitational force of the buoy, it is possible to obtain the liquid density of the sample from the force balance relation. Furthermore, coupling the magnetic densimeter with the metallic bellows variable-volume cell enables us to establish the condition of the liquid sample as the compressed liquid condition or saturated condition. A minor modification, however, is given for the pressure-measuring device. Namely, we used to measure the pressure difference between the sample fluid and nitrogen gas being used as the pressure-transmitting fluid by a bellows-type differential pressure gauge which had been calibrated in advance, while we have recently applied a quartz pressure transducer (Paroscientific Model 31K-101) for direct measurements of the sample liquid pressure which brought us significant improvement in the pressure measurements. The

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Table 1. Experimental Vapor Pressures of HFC-143a, HFC-32, and HFC-125

no.	T/K	P/MPa	no.	T/K	P/MPa
HFC-143a					
1	279.999	0.769	7	309.974	1.700
2	280.000	0.765	8	309.992	1.702
3	289.997	1.020	9	309.993	1.700
4	289.998	1.020	10	319.990	2.156
5	299.995	1.331	11	329.986	2.695
6	299.995	1.325	12	339.984	3.337
HFC-32					
1	219.971	0.0948	14	274.987	0.861
2	219.988	0.0926	15	279.986	1.006
3	225.003	0.1196	16	284.986	1.168
4	229.967	0.1523	17	289.987	1.349
5	235.003	0.1908	18	289.988	1.348
6	240.000	0.2370	19	294.987	1.549
7	244.978	0.2936	20	299.985	1.774
8	249.987	0.3567	21	304.986	2.022
9	254.988	0.4338	22	309.985	2.293
10	259.996	0.5194	23	314.984	2.593
11	264.988	0.6201	24	319.985	2.919
12	269.990	0.7317	25	324.984	3.278
13	274.992	0.8624			
HFC-125					
1	219.978	0.0789	11	299.985	1.444
2	229.977	0.1259	12	304.986	1.641
3	239.990	0.1978	13	309.986	1.857
4	249.974	0.2977	14	309.984	1.857
5	259.969	0.4302	15	314.985	2.096
6	269.964	0.6034	16	314.985	2.097
7	279.987	0.8253	17	319.984	2.357
8	284.987	0.9567	18	324.984	2.645
9	289.987	1.103	19	329.985	2.958
10	294.987	1.265	20	334.984	3.303

quartz pressure transducer has been calibrated by using a dead weight pressure gauge (DH Instrument Model 5202-02M) with an error to be not greater than 0.095 kPa.

It should be noted, however, that the measurements for HFC-143a were performed with the former apparatus, whereas those for HFC-32 and HFC-125 were performed with the modified equipment. The experimental procedures were essentially the same as those described by Maezawa et al. (1), and therefore we will not repeat them in detail in the present paper.

The sample temperature was measured using a 25- Ω standard platinum resistance thermometer which was placed in the vicinity of the magnetic densimeter. The vapor pressure of HFC-143a was determined by calibrating the pressure difference between the sample and nitrogen gas in advance, while those of HFC-32 and HFC-125 were determined by direct measurements with the quartz pressure transducer. The sample density was measured by means of the magnetic densimeter. The reliability and repeatability of the apparatus were calibrated by performing vapor pressure and saturated-liquid density measurements of HCFC-22 whose reliable thermodynamic property values are available, and the present calibration results were in good agreement with the correlations reported by Ashizawa et al. (3) and Okada et al. (4).

Experimental uncertainty in the temperature measurements was estimated to be within ± 15 mK, as the sum of ± 2 mK, the uncertainty of the thermometer, ± 1 mK, the uncertainty of the thermometer bridge, and ± 12 mK, the possible fluctuation of the thermostated liquid bath temperature. The uncertainty in the vapor pressure measurements of HFC-143a was estimated to be within ± 10 kPa, as the sum of ± 5 kPa, the uncertainty of the pressure gauge, and ± 5 kPa, the reproducibility of the differential pressure gauge, while that of HFC-32 and HFC-125 was ± 2 kPa, as the reproducibility of the quartz pressure transducer. The uncertainty in the density measurements was within $\pm 0.2\%$ which included the uncertainty of the magnetic buoy density

($\pm 0.1\%$) and the reproducibility of the electric current measurements ($\pm 0.1\%$). The purities of the samples used were 99.0 mol % for HFC-143a, 99.998 mass % for HFC-32, and 99.8 mass % for HFC-125 according to the analysis performed by the chemical manufacturers.

Results

The saturated-liquid densities and vapor pressures of HFC-143a, HFC-32, and HFC-125 have been measured for a temperature range of 220–340 K (ITS-90), except the vapor pressures of HFC-143a which were measured for 280–340 K. The saturated-liquid densities and vapor pressures of HFC-32 and HFC-125 have been obtained for a range of temperatures from 220 to 335 K. The overall results are given in Tables 1 and 2.

Discussion

The present saturated-liquid densities were correlated as a function of temperature, given in eq 1, where T denotes the

$$\rho/\rho_C - 1 = A_1\tau^{0.3} + A_2\tau^{2/3} + A_3\tau + A_4\tau^{4/3} + A_5\tau^3 \quad (1)$$

$$\tau = 1 - T/T_C$$

temperature on the ITS-90 scale and ρ_C and T_C are the critical density and the critical temperature, respectively. A_1 to A_5 are adjustable parameters which are determined by the least-squares fitting. All parameters of eq 1 are given in Table 3. The critical parameters of HFC-143a used to develop eq 1 are those reported by Mears et al. (5); the critical parameters of HFC-32 and HFC-125 are those measured by Kuwabara et al. (6, 7).

Figure 2 shows the measured saturated-liquid density deviations for HFC-143a for the values calculated with eq 1. Other available data are those reported by Russell et al. (8), by Mears et al. (5), and by Yokoyama (9). The input data

Table 2. Experimental Saturated-Liquid Densities of HFC-143a, HFC-32, and HFC-125

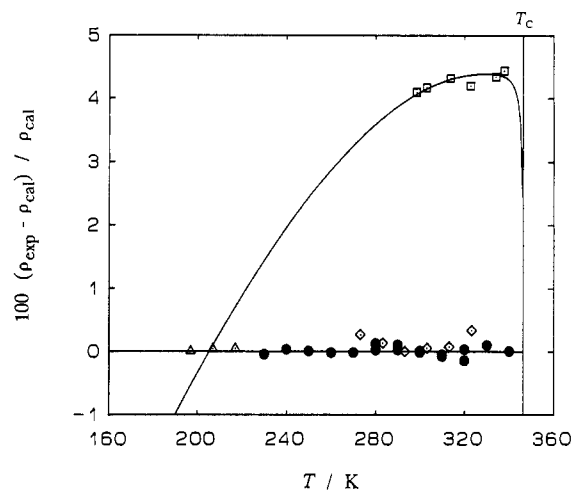
no.	T/K	ρ /(kg·m ⁻³)	no.	T/K	ρ /(kg·m ⁻³)
HFC-143a					
1	229.977	1149.8	10	299.978	917.7
2	239.990	1122.6	11	299.995	917.4
3	249.994	1093.1	12	309.993	871.0
4	259.979	1062.3	13	309.974	870.9
5	269.984	1030.0	14	319.989	817.6
6	279.999	995.9	15	319.972	816.3
7	279.984	997.0	16	329.986	750.3
8	289.997	958.7	17	339.984	649.1
9	289.981	959.5			
HFC-32					
1	219.971	1219.2	12	285.000	1012.2
2	229.967	1188.8	13	290.001	992.7
3	240.000	1159.1	14	295.000	973.8
4	244.978	1143.7	15	300.000	952.1
5	249.987	1128.1	16	305.000	931.0
6	254.988	1112.6	17	310.000	906.5
7	259.996	1097.0	18	310.000	907.6
8	264.988	1080.6	19	315.000	882.3
9	269.990	1064.1	20	320.000	856.0
10	275.000	1047.9	21	325.000	826.3
11	280.000	1030.4	22	329.999	795.0
HFC-125					
1	219.978	1530.4	14	286.017	1257.2
2	224.990	1513.0	15	290.000	1235.6
3	229.977	1495.5	16	295.000	1209.2
4	234.979	1475.8	17	300.000	1178.5
5	239.990	1458.0	18	305.001	1147.6
6	244.978	1437.9	19	310.000	1111.7
7	249.974	1418.9	20	310.000	1112.0
8	254.978	1398.0	21	314.999	1074.3
9	259.969	1377.9	22	319.999	1030.7
10	264.978	1356.0	23	325.000	980.7
11	269.964	1334.0	24	329.999	918.8
12	274.975	1311.3	25	334.999	831.4
13	280.000	1286.4			

Table 3. Parameters Used in Eqs 1 and 2

	HFC-143a	HFC-32	HFC-125
T_c /K	346.25	351.255	339.165
P_c /MPa	3.7789	5.784	3.620
ρ_c /(kg·m ⁻³)	434	424	568
A_1	1.060 01	1.471 07	1.4055
A_2	3.435 87	1.388 53	1.963 71
A_3	-3.873 56	1.011 16	-1.572 37
A_4	2.258 83	-1.529 86	0.974 213
A_5		1.776 97	
b	4.5	2.5	2.5
B_1	-6.924 791 0	-7.489 827 7	-7.529 966 1
B_2	0.411 411 9	1.874 808 3	1.766 917 6
B_3	-4.532 279 2	-2.514 487 7	-2.784 738 8

used for developing the correlation were the present measurements and the data by Russell et al. The present data, as presented in Figure 2, are in good agreement with the data by Yokoyama and those by Russell et al., while the latter show a similar systematic deviation from the correlation by McLinden (10), who developed his correlation on the basis of the data by Mears et al. which were the single set of data available at the time. The measured data by Mears et al. show a significant deviation from both the present results and those by Yokoyama of about 4%. Such deviations are considered to be due to possible impurities of the sample used by Mears et al., although they have provided no information. The measurements by Yokoyama are cited as a private communication in the paper by Kumagai et al. (11), and no information about the sample purity has been reported. The present correlation seems effective to reproduce the recent reliable sets of data including the present one for a wide range of temperatures within $\pm 0.2\%$.

Figure 3 represents the deviations of the saturated-liquid densities of HFC-32 from eq 1. For comparison, the data

**Figure 2.** Saturated-liquid density deviations of HFC-143a from eq 1: (●) this work; (Δ) Russell et al. (8); (□) Mears et al. (5); (◇) Yokoyama (9); (—) McLinden equation (10).

reported by Malbrunot et al. (12), by Kuwabara et al. (6), and by Weber et al. (13) are included. Noting that the sample used in the work by Kuwabara et al. was the same as that of the present work, their data in addition to the present measurements have been applied to develop the saturated-liquid density correlation given in eq 1 for HFC-32. As shown in Figure 3, the present correlation reproduces the present results very well and the data by Kuwabara et al. as well as that by Weber et al. within $\pm 0.2\%$, while the data by Malbrunot et al. (12) scatter considerably.

Figure 4 depicts the percent deviations of the present saturated-liquid densities of HFC-125 from eq 1. The data

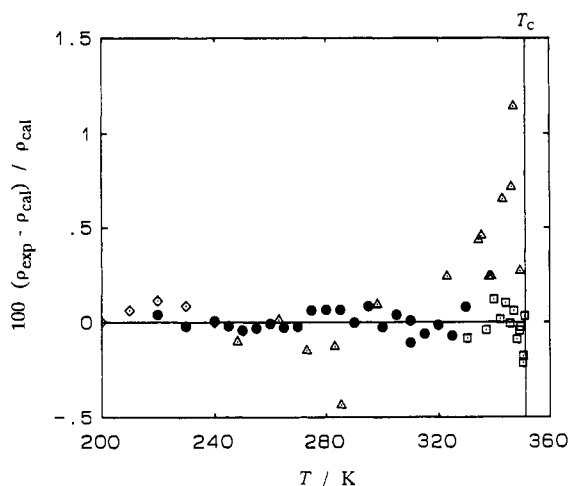


Figure 3. Saturated-liquid density deviations of HFC-32 from eq 1: (●) this work; (▲) Malbrunot et al. (12); (□) Kuwabara et al. (6); (◇) Weber et al. (13).

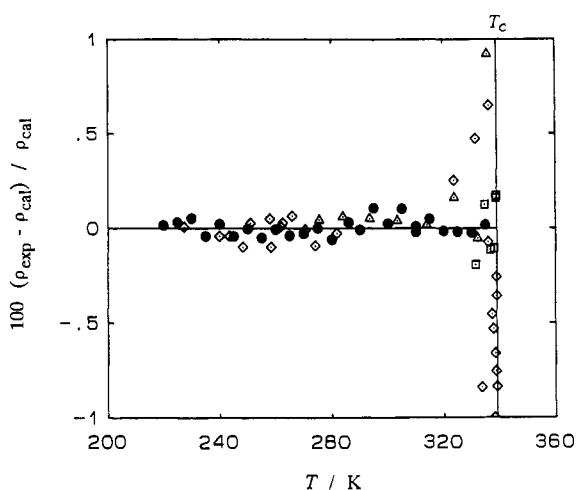


Figure 4. Saturated-liquid density deviations of HFC-125 from eq 1: (●) this work; (▲) Defibaugh et al. (14); (□) Kuwabara (7); (◇) Fukushima (15).

available at the present stage are those reported by Defibaugh et al. (14), by Kuwabara et al. (7), and by Fukushima (15), which all are compared here with the present results. The present results given in Figure 4 show very good agreement with the other data reported by Defibaugh et al. and by Fukushima except those in the critical region. The present correlation developed on the basis of the present results and the data by Kuwabara et al. enables most of the data to be reproduced within the claimed experimental uncertainties except a few data points near the critical point. Such a large deviation in the critical region was, according to an explanation by Defibaugh et al., due to the difficulty in determining the saturation boundary accurately in the vicinity of the critical point.

The present vapor pressures of HFC-32 and HFC-125 are correlated by a simple temperature function, given below:

$$(1 - \tau) \ln(P/P_C) = B_1\tau + B_2\tau^{1.5} + B_3\tau^b \quad (2)$$

$$\tau = 1 - T/T_C$$

where P_C denotes the critical pressure. B_1 to B_3 are adjustable parameters determined by least-squares fitting while the index b was determined to be a different value for each substance. The parameters used in eq 2 are given in Table 3. The critical pressure values for HFC-32 and HFC-125 used to develop eq

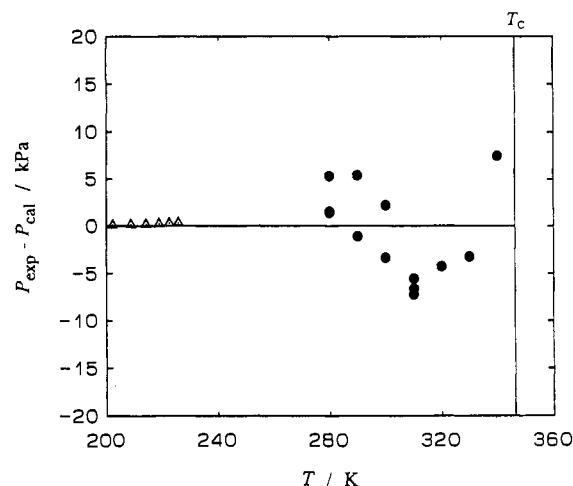


Figure 5. Vapor pressure deviations of HFC-143a from eq 2: (●) this work; (◇) Russell et al. (8).

2 are those determined in the Thermodynamics Laboratory, Keio University (16, 17).

The input data for developing the vapor pressure correlation given by eq 2 are the present measurements and those reported by Sato et al. (16) for HFC-32, while the present data have been exclusively used for HFC-125. Concerning HFC-143a, we have already proposed a vapor pressure correlation in the expression similar to eq 2 with addition of three more terms (18), on the basis of our own measurements and of the data by Russell et al. (8). However, Kubota et al. (19) have recently reported the superiority of a simple form of equation described in eq 2 to reproduce the vapor pressures of halogenated fluorocarbons. The vapor pressure correlation of HFC-143a used in this paper was that reported by Kubota et al. (19) which was developed on the basis of the present measurements and of the data by Russell et al.

Figure 5 illustrates the deviation of the reported measurements of vapor pressures for HFC-143a from the reported correlation by Kubota et al. (19). It should be noted that our measurements were carried out with the aid of the differential pressure gauge as described earlier and gave rather scattered results within ± 10 kPa in Figure 5. The vapor pressure correlation could reproduce all of the observed results with a standard deviation of 5.25 kPa. The maximum deviation observed among the present data was +7.51 kPa at a temperature of 319.97 K, which is well within the estimated uncertainty of the pressure measurements for HFC-143a.

Figure 6 is a plot of the deviations of the measured vapor pressures of HFC-32 from eq 2 which also includes the available data by Malbrunot et al. (12), by Qian et al. (20), by Sato et al. (16), and by Weber et al. (13). Because the measurements by Sato et al. were done by using the same sample as the present work, the data by Sato et al. have been adopted as the input data along with the present results for optimizing eq 2 for HFC-32. Excluding the larger deviations of the data by Malbrunot et al., all of the input data are reproduced with a maximum deviation of 1.97 kPa, while the data by Weber et al. and by Qian et al. are also in good agreement with the present correlation within ± 2 kPa except those near the critical point.

Figure 7 represents a comparison of the available vapor pressures of HFC-125 with the present correlation given by eq 2. The present correlation has been developed using the present results as input data except those at 230 and 240 K. As shown in Figure 7, the present correlation agrees satisfactorily with other reported data for temperatures above 290 K, whereas the data by Oguchi et al. (21) and by Baroncini et al. (22) deviate from the present correlation by more than

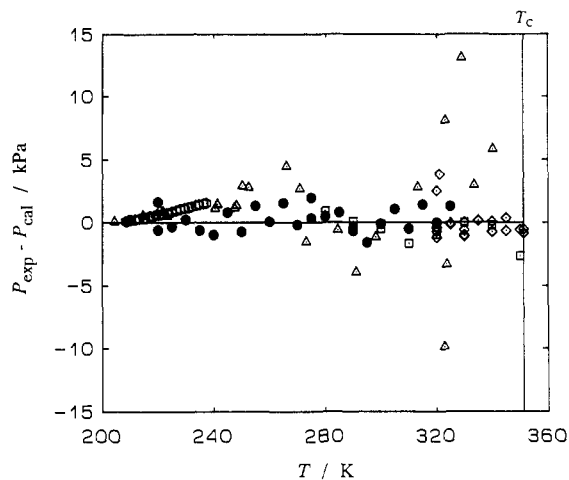


Figure 6. Vapor pressure deviations of HFC-32 from eq 2: (●) this work; (◇) Malbrunot et al. (12); (□) Qian et al. (20); (○) Sato et al. (16); (○) Weber et al. (13).

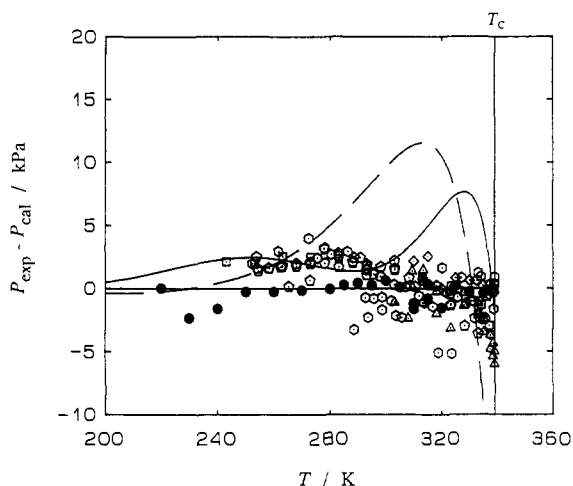


Figure 7. Vapor pressure deviations of HFC-125 from eq 2: (●) this work; (◇) Monluc et al. (23); (□) Oguchi (21); (○) Ye et al. (26); (△) Baroncini (22); (○) Fukushima (15); (—) Singh equation (24); (---) Wilson equation (25).

2 kPa at temperatures below 290 K. We have also found that the data by Fukushima (15) behave rather inconsistently near 290 K. In summary, the present correlation represents the majority of data within ± 5 kPa except some points by Monluc et al. (23) near the critical point.

Conclusion

A total of 57 vapor pressures and 64 saturated-liquid densities of HFC-143a, HFC-32, and HFC-125 have been measured over a wide temperature range of 220–340 K. Vapor pressure and saturated-liquid density correlations which are

able to reproduce the present results within the estimated uncertainties have also been developed.

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