Measurement of Vapor Pressures and Saturated Liquid Densities of Pure Fluids with a New Apparatus

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A new apparatus has been constructed to measure vapor−liquid equilibria and saturated liquid densities of pure and mixed fluids. The density measurement is based on the buoyancy method using a single sinker and a magnetic suspension balance. The permanent magnet of the magnetic suspension balance carries the sinker with a load-coupling device. Both are completely submerged in the liquid phase. The electromagnet is placed outside the magnetically neutral cell walls. Both magnets transfer the buoyancy force of the sinker through the walls to a microbalance. The apparatus is limited to the temperature range from (−60 to 250) °C, pressures up to 200 bar, and densities in the range from (10 to 2000) kg·m^{-3}. Here, the first tests have been done with pure fluids at temperatures from (−40 to 90) °C and pressures up to 60 bar. Measurements of the compressed liquid density of water and gas density of nitrogen, carbon dioxide, and R134a confirm the accuracy of the density measurement. Also, measurements of the vapor pressure and the saturated liquid density were made for carbon dioxide and R134a. The estimated uncertainties of the experimental data are ±0.02 K for the temperature, ±5.0 mbar for the pressure, and ±0.013% + 0.01 kg·m^{-3} for the density.

Introduction

A new apparatus has been constructed to measure vapor−liquid equilibria (VLE) and saturated liquid densities of pure and mixed fluids. The density measurement is based on the buoyancy method using a magnetic suspension balance and a single sinker that is placed inside the measuring cell.[1] Thus, the density measurements can be done directly inside the measuring cell without the necessity of drawing samples. The density of the fluid is determined by measuring the buoyancy force exerted on the sinker. The volume of the cylindrically shaped sinker can be determined very accurately as a function of temperature and pressure. The calibration of the sinker volume at a single reference point (20 °C and 1.1 bar) is done with water. No further calibration is necessary. The magnetic suspension coupling, which consists of an electromagnet and a permanent magnet, is used to transfer the buoyancy force exerted on the sinker to a microbalance placed outside the measuring cell at ambient conditions.

When measuring the saturated liquid density, the sinker and the permanent magnet, which carries the sinker, must be submerged completely in the liquid phase. The liquid level inside the measuring cell is indicated by three small platinum resistance thermometers. The vapor phase is placed coaxially around the electromagnet.

The magnetic suspension balance, liquid level indicator, and measuring cell have been purchased from the Rubotherm Company.[2] The measuring cell has been specially designed for measuring VLE with an internal volume of about 200 mL. About 30% of the volume is occupied by the vapor phase. The single-sinker apparatus is limited to temperatures from (−60 to 250) °C, pressures up to 200 bar, and densities from (10 to 2000) kg·m^{-3}.

In the present work, the apparatus was tested for pure fluids. First, the accuracy of the density measurement was tested by experimentally determining the compressed liquid density of water and the homogeneous gas density of nitrogen at temperatures from (−40 to 80) °C and pressures up to 60 bar. Then, measurements of homogeneous gas densities, vapor pressures, and saturated liquid densities of carbon dioxide and R134a were made at temperatures from (−40 to 90) °C. The estimated uncertainties, which are ±0.02 K for the temperature, ±5.0 mbar for the pressure, and ±0.013% + 0.01 kg·m^{-3} for the density, have been confirmed by the results.

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Table 1. Suppliers and Purities of the Chemicals

component	supplier	purity
water	Merck	≤1 μS/cm
nitrogen	Linde	≥99.999%
carbon dioxide	Linde	≥99.995%
R134a	Solvay	≥99.95%

Experimental System

Chemicals. High-grade chemicals, shown in Table 1, have been used for the measurements. Nitrogen and carbon dioxide have been used without any further purification. Water and R134a have been degassed by ultrasonic and vacuum distillation, respectively. No impurities in R134a have been found by gas chromatography.

Apparatus and Procedure. The single-sinker densitometer consists of a measuring cell, a microbalance (Mettler AT 261, Swiss, resolution 0.01 mg), a double-walled thermostated jacket, and a thermostated oil bath. Figure 1 shows the measuring cell with the sinker, the magnetic suspension coupling, the load coupling device, the liquid level indicator, and the fluid connection tubes. A cylindrical titanium sinker (mass and volume at atmospheric conditions are about 60.02 g and 13.3 cm^3, respectively) has been used. The apparent weight of the sinker is transmitted from the measuring cell to the balance by means of the magnetic suspension coupling. The magnetic

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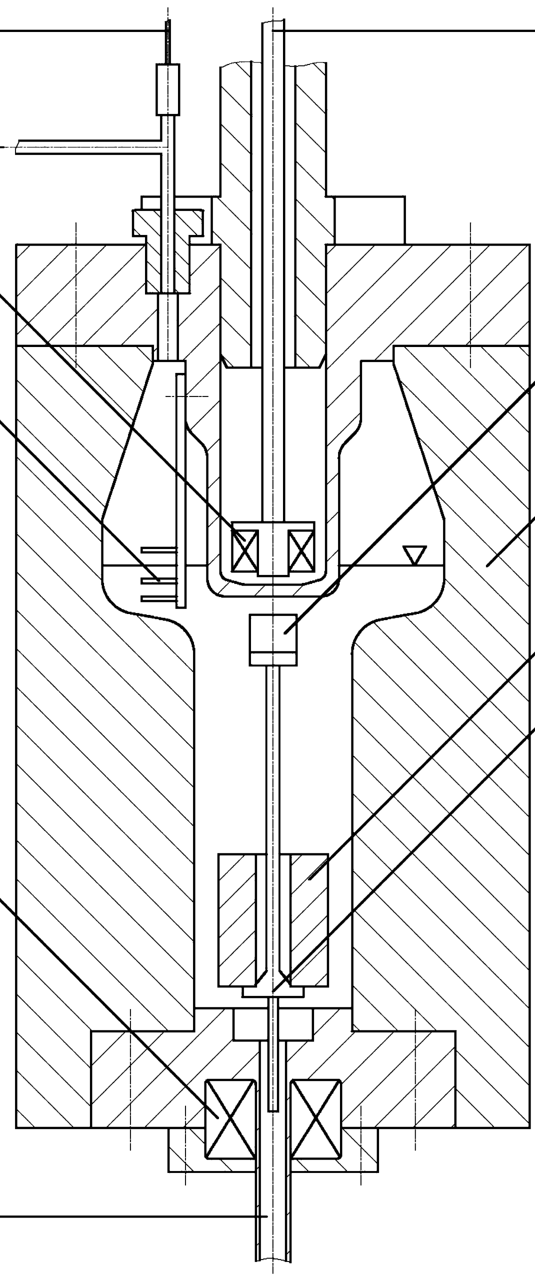

Figure 1. Basic design of the measuring cell.

suspension coupling consists of an electromagnet and a permanent magnet. The electromagnet is connected to the underfloor weighing hook of the microbalance. The permanent magnet, to which the sinker is linked by means of the load-coupling device, is located inside the measuring cell. The position of the coupling device is detected by a position sensor and controlled by a PID controller.

The single-sinker densitometer is based on a buoyancy method where the Archimedes principle is applied. During density measurements, there are two positions, namely, the zero- and the measuring-point positions. In the zero-point position, the permanent magnet is suspended a larger distance away from the electromagnet. In this position, the sinker is decoupled from the permanent magnet via the load-coupling device, and the balance can be tarred to zero. In the measuring-point position, the permanent magnet is moved closer to the electromagnet. In this position, the sinker is coupled to the balance and can be weighed.

To achieve high accuracies even at relatively low densities, the balance is always operated close to one operation point via a basic load compensation as follows: in the zero position, a tantalum weight ($\rho = 16.7\ \mathrm{g{\cdot}cm^{-3}}$, about 80 g) is placed on the balance. While switching to the measuring position, the tantalum weight is automatically exchanged with a titanium weight ($\rho = 4.5\ \mathrm{g{\cdot}cm^{-3}}$, about 20 g). Because in this position the sinker (the mass of the sinker is about 60 g) is coupled with the balance, the total load on the balance is again about 80 g (as in the zero position). Thus, the linearity error of the balance is drastically reduced. Because the two weights have almost the same volume, the buoyancy effect of air on the weights is compensated for as well. Furthermore, the self-calibration of the balance is used prior to each density measurement.

For saturated liquid density measurements, the liquid level inside the cell is controlled via a liquid-level indicator

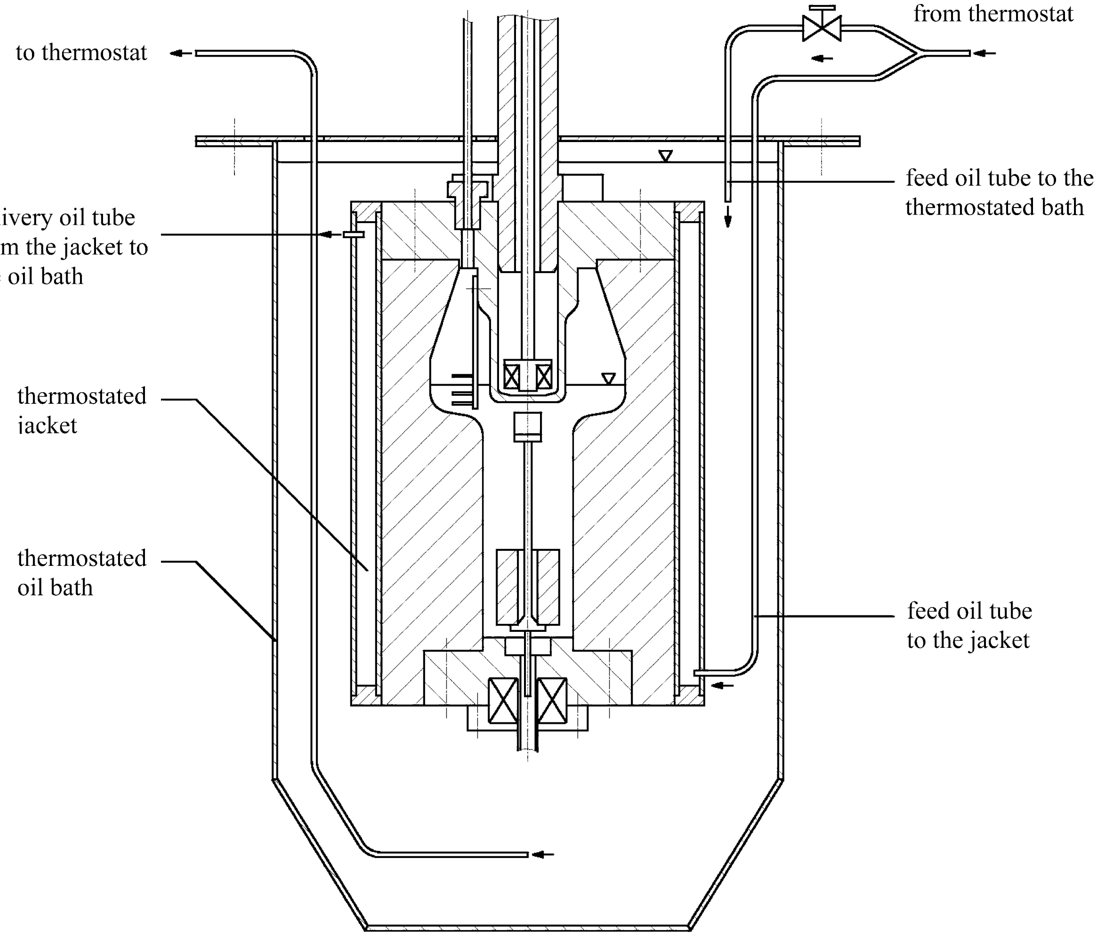

Figure 2. Scheme of the measuring cell and the thermostat.

using the self-heating effect of three small platinum resistance thermometers placed vertically at a distance of a few millimeters from each other. This ensures that the sinker and the permanent magnet are completely immersed in the liquid phase.

A refrigerated circulating thermostat (Unistat 380W HT, Huber, Germany) has been used to thermostat the measuring cell. The thermostat feeds two countercurrent cycles to get a stable and homogeneous temperature in the measuring cell, as shown in Figure 2. A double-walled jacket is placed around the measuring cell for one of the cycles, and an outer open oil bath is used for the other cycle. Silicone oil (M60.115.05, Renggli, Switzerland) with a working range from (−60 to +115) °C has been used as thermostating fluid.

The temperature is measured by a 100-Ω platinum resistance thermometer (Serkal, Austria) and a digital resistance bridge (F300, Automatic System Laboratory, U.K.). The thermometer has been calibrated prior to the measurements according to the International Temperature Scale of 1990 (ITS-90) against a PT25 reference thermometer (Temperature Products GmbH, Germany, uncertainty within ±15 mK). The total uncertainty of the temperature measurement is within ±0.02 K.

The pressure is measured by a digital pressure transducer (model 31K-101, Paroscientific, Redmond, WA; range: (0 to 69) bar). The pressure transducer has been calibrated prior to the measurements against a digital piston manometer (model 21000, Desgranges & Huot, Aubervilliers, France; range: (0 to 120) bar, uncertainty: ±[0.2 mbar + 3.0 × 10^{-7} p/mbar]) and a mercury barometer (Wilh. Lambercht, Germany; uncertainty: ±0.30 mbar). The pressure transducer is placed approximately at the same height as the liquid level inside the cell. The pressure transducer and the connecting, gas-filled capillary tube are heated above the cell temperature to avoid condensation. The total uncertainty of the pressure measurement is within ±5.0 mbar. For vapor pressures, an additional uncertainty due to the uncertainty in the temperature of

Table 2. Experimental (exptl) and EOS[4] Results for the Compressed Liquid Density of Water[a]

t/°C	p/bar	ρ_{exp}/ kg·m^{-3}	ρ_{EOS}/ kg·m^{-3}	$\Delta\rho$/ kg·m^{-3}	$\Delta\rho$/ ρ_{exp}/%
0.4783	1.05711	999.820	999.880	−0.0595	−0.0060
0.4701	1.05711	999.859	999.880	−0.0210	−0.0021
0.4725	12.2573	1000.42	1000.40	0.0228	0.0023
0.4773	23.0720	1001.02	1001.00	0.0240	0.0024
0.4778	37.8158	1001.68	1001.70	−0.0255	−0.0025
0.4782	49.9009	1002.27	1002.30	−0.0259	−0.0026
19.7963	1.09302	998.268	998.250	0.0182	0.0018
19.7905	10.6353	998.673	998.690	−0.0167	−0.0017
19.7916	20.9758	999.180	999.160	0.0196	0.0020
19.7928	31.0934	999.633	999.620	0.0132	0.0013
19.7914	41.3991	1000.08	1000.10	−0.0175	−0.0017
19.7895	41.3989	1000.06	1000.10	−0.0362	−0.0036
29.7630	1.10014	995.770	995.720	0.0500	0.0050
29.7644	1.10004	995.738	995.720	0.0176	0.0018
29.7702	10.0591	996.106	996.120	−0.0145	−0.0015
29.7639	20.4980	996.571	996.590	−0.0193	−0.0019
29.7685	30.0011	997.027	997.010	0.0171	0.0017
29.7633	40.3011	997.451	997.470	−0.0193	−0.0019
39.8105	3.45050	992.420	992.400	0.0197	0.0020
39.8145	11.9512	992.749	992.770	−0.0215	−0.0022
39.8144	20.9308	993.139	993.160	−0.0213	−0.0021
39.8097	30.6453	993.609	993.590	0.0191	0.0019
39.8127	41.4120	994.071	994.050	0.0209	0.0021

[a] $\Delta\rho = \rho_{exp} - \rho_{EOS}$.

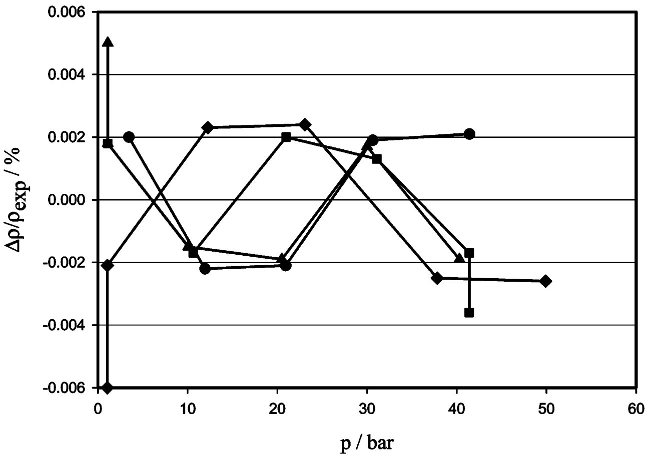

Figure 3. Relative deviations ($\Delta\rho = \rho_{exp} - \rho_{EOS}$) between experimental results and a reference EOS[4] for the compressed liquid density of water: ◆, 0.48; ■, 19.79; ▲, 29.77; and ●, 39.81 °C.

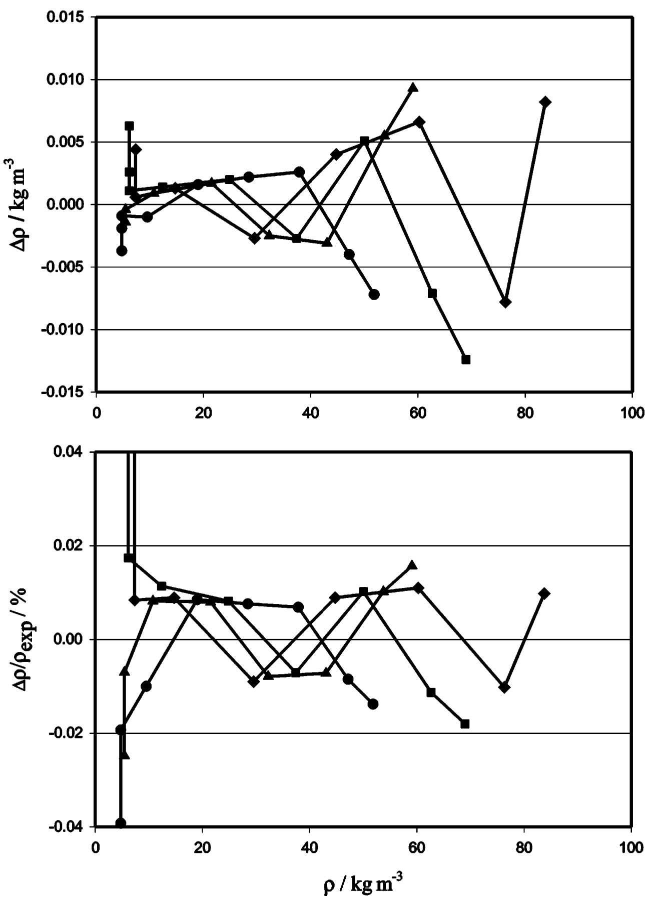

Figure 4. Absolute and relative deviations ($\Delta\rho = \rho_{exp} - \rho_{EOS}$) between experimental results and a reference EOS[5] for the homogeneous gas density of nitrogen: ◆, −40.13; ■, −0.09; ▲, 39.97; and ●, 80.17 °C.

±20 mK must be taken into account. This was estimated by the Clausius−Clapeyron equation to be within ±10.0 mbar. By error propagation law, this yields a total uncertainty of the vapor pressure of ±12.0 mbar.

To measure the density of the fluid, the sinker is coupled and decoupled several times (changes between the zero and measuring positions). Then, the density is determined from the relation

$$\rho = \frac{m_s - m_s^*}{V_s(T, P)} \tag{1}$$

where m_s is the true mass of the sinker (weight in the evacuated measuring cell), m_s^* is the apparent mass of the sinker (weight inside the fluid phase), and V_s (T, p) is the temperature- and pressure-dependent sinker volume. The value of $V_s(T, p)$ is known from the calibration in water (at 20 °C and 1.1 bar), the thermal expansivity, and the compressibility of the sinker. The true mass of the sinker m_s has been measured in vacuum and correlated with the temperature. The estimated uncertainty for the density measurement over the whole temperature range of the apparatus is given by

Table 3. Experimental (exp) and EOS[5] Results for the Homogeneous Gas Density of Nitrogen

t/°C	p/bar	ρ_{exp}/ kg·m^{-3}	ρ_{EOS}/ kg·m^{-3}	$\Delta\rho$/ kg·m^{-3}	$\Delta\rho$/ ρ_{exp}/%
−40.1203	5.06343	7.36678	7.36240	0.0044	0.0595
−40.1293	5.06321	7.36302	7.36240	0.0006	0.0084
−40.1259	10.0711	14.7253	14.7240	0.0013	0.0089
−40.1322	20.0087	29.5563	29.5590	−0.0027	−0.0090
−40.1315	30.0145	44.7790	44.7750	0.0040	0.0089
−40.1236	40.0256	60.2496	60.2430	0.0066	0.0110
−40.1278	50.3021	76.3292	76.3370	−0.0078	−0.0102
−40.1268	55.0102	83.7756	83.7670	0.0082	0.0098
−19.7709	1.58087	2.10982	2.10450	0.0053	0.2520
−19.7759	1.58119	2.10530	2.10500	0.0003	0.0144
−19.7818	10.2525	13.7338	13.7320	0.0018	0.0132
−19.7729	20.6173	27.8018	27.7990	0.0028	0.0099
−19.7877	30.1013	40.8167	40.8130	0.0037	0.0090
−19.7701	40.0714	54.5977	54.6040	−0.0063	−0.0115
−19.7812	50.5189	69.1481	69.1560	−0.0079	−0.0114
−19.7856	56.5189	77.5333	77.5420	−0.0087	−0.0113
−0.0898	5.00074	6.19019	6.18390	0.0063	0.1016
−0.0879	5.00065	6.18643	6.18380	0.0026	0.0425
−0.0948	5.00091	6.18538	6.18430	0.0011	0.0174
−0.0961	10.0043	12.3984	12.3970	0.0014	0.0114
−0.0887	20.0002	24.8780	24.8760	0.0020	0.0082
−0.0876	30.0008	37.4313	37.4340	−0.0027	−0.0071
−0.0912	40.0003	50.0451	50.0400	0.0051	0.0102
−0.0896	50.0040	62.6679	62.6750	−0.0071	−0.0113
−0.0885	55.0001	68.9746	68.9870	−0.0124	−0.0180
19.8888	1.09349	1.25784	1.25760	0.0002	0.0193
19.8818	1.09973	1.26716	1.26480	0.0024	0.1864
19.8757	10.3705	11.9492	11.9510	−0.0018	−0.0147
19.8767	20.1397	23.2508	23.2480	0.0028	0.0122
19.8777	31.0616	35.9063	35.9030	0.0033	0.0092
19.8826	39.9648	46.2267	46.2220	0.0047	0.0103
19.8725	50.1512	58.0251	58.0180	0.0071	0.0122
19.8811	56.1130	64.8959	64.9040	−0.0081	−0.0125
39.9675	5.08112	5.46814	5.46950	−0.0014	−0.0248
39.9710	5.08096	5.46882	5.46920	−0.0004	−0.0070
39.9666	10.0032	10.7709	10.7700	0.0009	0.0082
39.9663	19.9983	21.5387	21.5370	0.0017	0.0080
39.9752	29.9971	32.2955	32.2980	−0.0025	−0.0079
39.9704	39.9991	43.0379	43.0410	−0.0031	−0.0072
39.9745	50.0013	53.7535	53.7480	0.0055	0.0102
39.9751	54.9999	59.0903	59.0810	0.0093	0.0157
59.9683	1.47291	1.48909	1.48960	−0.0005	−0.0340
59.9696	1.47340	1.48309	1.49010	−0.0070	−0.4729
59.9726	10.4902	10.6026	10.6040	−0.0014	−0.0131
59.9722	20.2062	20.4085	20.4060	0.0025	0.0123
59.9697	30.3903	30.6553	30.6520	0.0033	0.0108
59.9655	40.0153	40.3032	40.2980	0.0052	0.0129
59.9682	50.2905	50.5504	50.5440	0.0064	0.0127
59.9745	55.1130	55.3242	55.3310	−0.0068	−0.0123
80.1639	5.00091	4.76373	4.76560	−0.0019	−0.0392
80.1618	5.00045	4.76148	4.76520	−0.0037	−0.0781
80.1665	5.00080	4.76448	4.76540	−0.0009	−0.0193
80.1641	10.0183	9.53854	9.53950	−0.0010	−0.0100
80.1711	19.9999	19.0116	19.0100	0.0016	0.0085
80.1701	30.0182	28.4762	28.4740	0.0022	0.0076
80.1626	40.0067	37.8636	37.8610	0.0026	0.0069
80.1675	49.9993	47.1890	47.1930	−0.0040	−0.0085
80.1682	55.0003	51.8318	51.8390	−0.0072	−0.0138

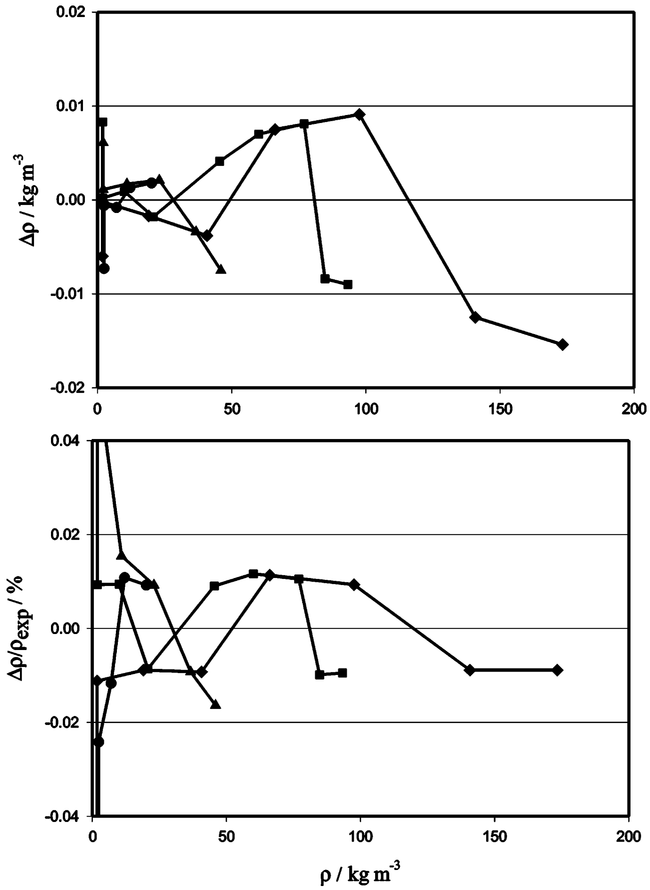

Figure 5. Absolute and relative deviations ($\Delta\rho = \rho_{exp} - \rho_{EOS}$) between experimental results and a reference EOS[6] for the homogeneous gas density of carbon dioxide: ◆, 19.93; ■, 0.41; ▲, −19.93; and ●, −40.08 °C.

$$\frac{\Delta\rho}{\rho} \le \pm[0.021\% + 0.01\ \text{kg·m}^{-3}] \quad \text{from } (-60 \text{ to } 250)\ °\text{C} \quad (2)$$

Details of the error analysis are given in ref 3. A large contribution to the relative uncertainty of the density measurement comes from the uncertainty of the temperature dependence of the sinker volume (0.5 ppm/K).[2] Thus, the uncertainty of the density measurement over the temperature range applied in the present work is lower with

$$\frac{\Delta\rho}{\rho} \le \pm[0.013\% + 0.01\ \text{kg·m}^{-3}] \quad \text{from } (-60 \text{ to } 100)\ °\text{C} \quad (3)$$

At very low densities, the relative part of eq 3 (0.013%) is neglectable compared to the absolute part (0.01 kg·m^{-3}). This would in fact result in a very high relative error. Thus, the apparatus cannot be recommended for densities below 10 kg·m^{-3}. At liquid densities, the absolute part can almost be neglected compared to the relative part. Thus, the uncertainty of the measurement of liquid densities is within ±0.014%. For compressed gases, the uncertainty will be a combination of both terms.

An additional uncertainty of the density measurements resulting from the uncertainty in temperature and pressure has to be considered. For homogeneous gas densities, this has been estimated by the ideal gas law and depends on the molar mass of the substance and the pressure range.

Table 4. Experimental (exp) and EOS[6] Results for the Homogeneous Gas Density of Carbon Dioxide

t/°C	p/bar	ρ_{exp}/ kg·m^{-3}	ρ_{EOS}/ kg·m^{-3}	$\Delta\rho$/ kg·m^{-3}	$\Delta\rho$/ ρ_{exp}/%
−40.0809	1.05905	2.42701	2.43430	−0.0073	−0.3003
−40.0816	1.05905	2.43371	2.43430	−0.0006	−0.0242
−40.0786	3.00075	7.05798	7.05880	−0.0008	−0.0117
−40.0854	5.00054	12.0703	12.0690	0.0013	0.0108
−40.0908	7.99976	20.1488	20.1470	0.0018	0.0092
−30.1339	1.00019	2.20055	2.20010	0.0005	0.0205
−30.1356	3.00031	6.73594	6.73670	−0.0008	−0.0113
−30.1396	5.00042	11.4760	11.4750	0.0010	0.0084
−30.1396	8.00000	19.0248	19.0230	0.0018	0.0096
−30.1450	10.0069	24.4253	24.4230	0.0023	0.0093
−30.1409	12.0074	30.1422	30.1450	−0.0028	−0.0093
−19.9315	1.00071	2.11600	2.10990	0.0061	0.2882
−19.9293	1.00077	2.11111	2.11000	0.0011	0.0525
−19.9364	5.00061	10.9367	10.9350	0.0017	0.0154
−19.9311	10.0013	23.0281	23.0260	0.0021	0.0092
−19.9353	15.0074	36.7146	36.7180	−0.0034	−0.0093
−19.9319	18.0088	45.9785	45.9860	−0.0075	−0.0164
−09.8233	1.00028	2.02538	2.02590	−0.0005	−0.0257
−09.8304	5.00075	10.4541	10.4550	−0.0009	−0.0087
−09.8365	10.0062	21.8592	21.8610	−0.0018	−0.0083
−09.8299	15.0014	34.4562	34.4530	0.0032	0.0094
−09.8250	20.0020	48.7144	48.7100	0.0044	0.0090
−09.8310	22.0018	55.0401	55.0340	0.0061	0.0110
−09.8283	24.9999	65.4007	65.4080	−0.0073	−0.0112
0.4112	1.00016	1.95635	1.94810	0.0083	0.4218
0.4124	1.00007	1.94808	1.94790	0.0002	0.0093
0.4105	5.00008	10.0139	10.0130	0.0009	0.0094
0.4135	10.0000	20.7952	20.7970	−0.0018	−0.0086
0.4128	20.0030	45.5031	45.4990	0.0041	0.0090
0.4098	25.0064	60.1110	60.1040	0.0070	0.0116
0.4098	30.0002	77.0441	77.0360	0.0081	0.0105
0.4062	32.0053	84.7746	84.7830	−0.0084	−0.0099
0.4059	34.0116	93.2811	93.2900	−0.0089	−0.0095
10.3704	1.00061	1.87880	1.87910	−0.0003	−0.0162
10.3729	9.99976	19.8874	19.8890	−0.0016	−0.0083
10.3672	20.0001	42.9140	42.9100	0.0040	0.0093
10.3636	30.0035	70.8325	70.8250	0.0075	0.0106
10.3605	40.0075	107.963	107.960	0.0031	0.0029
10.3665	42.0091	117.472	117.460	0.0119	0.0101
19.9329	1.00152	1.81243	1.8184	−0.0060	−0.3293
19.9308	1.00159	1.81830	1.8185	−0.0002	−0.0112
19.9385	10.0017	19.1053	19.1070	−0.0017	−0.0089
19.9324	20.0000	40.7832	40.7870	−0.0038	−0.0093
19.9306	30.0038	66.2045	66.1970	0.0075	0.0113
19.9301	40.0017	97.5691	97.5600	0.0091	0.0093
19.9305	50.0017	140.798	140.810	−0.0125	−0.0089
19.9301	55.0134	173.325	173.340	−0.0154	−0.0089

Because the saturated liquid density depends on the temperature, only an additional uncertainty in density of within ±0.02% resulting from the uncertainty of the temperature is considered. For many compressed liquids (e.g., water), the additional error from the uncertainty in pressure and temperature can be neglected.

Results and Discussion

Water Results. Water has been used to test the accuracy of the compressed liquid density measurements. The measurements have been carried out on four isotherms between (0 and 40) °C. The experimental data and results from a reference equation of state[4] (EOS) are given in Table 2. Figure 3 shows the deviations between the experimental data and the reference EOS. The relative deviation is within ±0.006% for densities between (993 and 1003) kg·m^{-3}. The very high accuracies of the water measurements compared to the estimated experimental uncertainty can be explained by (i) the fact that the calibration of the sinker volume (V_0) has been done in water, (ii) the high purity of water, and (iii) the very small effect from the

Table 5. Experimental (exp) and EOS[6] Results for the Vapor Pressure and Saturated Liquid Density of Carbon Dioxide[a]

t/°C	p^{S}_{exp}/bar	p^{S}_{EOS}/bar	Δp^{S}/bar	ρ^{L}_{exp}/kg·m^{-3}	ρ_{EOS}/kg·m^{-3}	$\Delta\rho^{L}$/kg·m^{-3}	$\Delta\rho^{L}/\rho^{L}_{exp}$/%
−40.0823	10.0081	10.015	−0.0069	1116.44	1116.7	−0.260	−0.023
−40.0845	10.0072	10.014	−0.0068	1116.54	1116.8	−0.263	−0.024
−30.1412	14.2040	14.210	−0.0060	1076.52	1076.3	0.222	0.021
−30.1392	14.2051	14.211	−0.0059	1076.52	1076.3	0.220	0.020
−19.9342	19.7416	19.736	0.0056	1031.59	1031.4	0.193	0.019
−19.9301	19.7447	19.739	0.0057	1031.49	1031.3	0.193	0.019
−09.8352	26.6157	26.611	0.0047	981.93	982.08	−0.153	−0.016
−09.8313	26.6188	26.614	0.0048	981.93	982.06	−0.135	−0.014
00.4031	35.2207	35.225	−0.0043	924.89	925.01	−0.120	−0.013
00.4065	35.2239	35.228	−0.0041	924.87	924.99	−0.118	−0.013
10.3616	45.4319	45.427	0.0049	858.57	858.43	0.144	0.017
10.3654	45.4358	45.431	0.0048	858.55	858.40	0.151	0.018
19.9362	57.2142	57.205	0.0092	774.23	774.07	0.160	0.021
19.9326	57.2090	57.200	0.0090	774.28	774.11	0.165	0.021

[a] $\Delta p^{s} = p^{S}_{exp} - p^{S}_{EOS}$, $\Delta\rho^{L} = \rho^{L}_{exp} - \rho^{L}_{EOS}$.

Table 6. Experimental (exptl) and EOS[7] Results for the Homogeneous Gas Density of R134a

t	p	ρ_{exp}	ρ_{EOS}	$\Delta\rho$	$\Delta\rho/\rho_{exp}$
°C	bar	kg·m^{-3}	kg·m^{-3}	kg·m^{-3}	%
−10.1627	0.30018	1.41816	1.4143	0.0039	0.2722
−10.1652	0.30035	1.41703	1.4151	0.0019	0.1364
−10.1639	0.30025	1.41553	1.4146	0.0009	0.0656
−10.1615	0.50031	2.37378	2.3728	0.0010	0.0414
−10.1593	0.80084	3.83561	3.8368	−0.0012	−0.0310
−10.1584	1.00091	4.82696	4.8287	−0.0017	−0.0360
−10.1551	1.50056	7.37304	7.3711	0.0019	0.0262
00.1621	0.50001	2.2813	2.2767	0.0046	0.2031
00.1599	0.50001	2.27757	2.2767	0.0009	0.0384
00.1608	1.00006	4.62180	4.6204	0.0014	0.0303
00.1627	1.50013	7.03559	7.0373	−0.0017	−0.0243
00.1635	2.00005	9.53172	9.5341	−0.0024	−0.0250
00.1657	2.50002	12.1179	12.121	−0.0031	−0.0253
10.0101	1.00092	4.4428	4.4473	−0.0045	−0.1016
10.0159	1.00097	4.44579	4.4474	−0.0016	−0.0363
10.0131	2.00016	9.12611	9.1283	−0.0022	−0.0240
10.0111	3.00082	14.1052	14.102	0.0032	0.0227
10.0191	3.50918	16.7525	16.756	−0.0035	−0.0212
20.0695	1.00049	4.27519	4.2795	−0.0043	−0.1007
20.0690	1.00047	4.27783	4.2794	−0.0016	−0.0368
20.0675	2.00052	8.76202	8.7577	0.0043	0.0493
20.0688	2.00054	8.75976	8.7578	0.0020	0.0224
20.0684	3.00017	13.4608	13.464	−0.0032	−0.0239
20.0568	3.99977	18.4354	18.439	−0.0036	−0.0195
20.0600	5.00024	23.7422	23.738	0.0042	0.0177
30.1011	1.00020	4.1211	4.1259	−0.0048	−0.1176
30.1038	1.00015	4.12406	4.1257	−0.0016	−0.0398
30.1060	2.99987	12.8979	12.901	−0.0031	−0.0239
30.1061	4.99910	22.5420	22.538	0.0040	0.0176
30.1099	7.11405	34.0053	34.010	−0.0047	−0.0139
40.0216	1.00017	3.98345	3.9864	−0.0029	−0.0740
40.0214	1.00018	3.98495	3.9864	−0.0014	−0.0363
40.0249	2.00042	8.11408	8.1162	−0.0021	−0.0262
40.0291	4.00013	16.8674	16.864	0.0034	0.0199
40.0218	6.00214	26.4214	26.417	0.0044	0.0168
40.0253	8.00409	37.0004	37.006	−0.0056	−0.0151
40.0204	9.02113	42.8957	42.902	−0.0063	−0.0147
50.0411	1.00019	3.85767	3.8556	0.0021	0.0537
50.0414	1.00018	3.85694	3.8556	0.0011	0.0295
50.0498	3.00002	11.9392	11.942	−0.0028	−0.0236
50.0440	5.00003	20.6111	20.615	−0.0039	−0.0188
50.0465	8.02367	35.1490	35.144	0.0050	0.0142
50.0388	9.40009	42.4962	42.489	0.0062	0.0147
50.0424	12.7113	62.9174	62.925	−0.0076	−0.0121
60.0135	1.01530	3.79640	3.7914	0.0050	0.1316
60.0188	1.01534	3.79264	3.7915	0.0011	0.0300
60.0121	3.03786	11.6786	11.676	0.0026	0.0222
60.0201	5.02699	19.9182	19.922	−0.0038	−0.0192
60.0199	8.01134	33.4094	33.414	−0.0046	−0.0138
60.0155	10.0938	43.8443	43.838	0.0063	0.0143
60.0202	13.0042	60.3214	60.314	0.0074	0.0123
60.0149	15.0002	73.4336	73.442	−0.0084	−0.0114
69.8821	1.36282	4.96602	4.9571	0.0089	0.1797
69.8858	1.36713	4.97127	4.9730	−0.0017	−0.0347
69.8868	3.03782	11.2865	11.289	−0.0025	−0.0226
69.8877	5.20698	19.9261	19.930	−0.0039	−0.0197
69.8907	8.49113	34.1538	34.149	0.0048	0.0141
69.8868	10.9379	45.8644	45.858	0.0064	0.0139
69.8885	13.0041	56.7069	56.700	0.0069	0.0121
69.8821	15.0001	68.2379	68.246	−0.0081	−0.0118
69.8831	17.0450	81.5238	81.515	0.0088	0.0108
69.8901	19.0024	96.1180	96.128	−0.0100	−0.0104
80.0084	1.36718	4.81465	4.8224	−0.0077	−0.1608
80.0112	5.00972	18.4470	18.443	0.0042	0.0230
80.0187	10.0039	39.3925	39.386	0.0061	0.0155
80.0168	15.0877	64.5320	64.541	−0.0086	−0.0134
80.0129	20.0033	94.8889	94.899	−0.0101	−0.0106
80.0098	22.0048	110.0870	110.10	−0.0150	−0.0136
80.0173	24.0814	128.8208	128.80	0.0198	0.0154
90.0231	1.53673	5.26494	5.2722	−0.0073	−0.1381
90.0223	5.00498	17.8052	17.809	−0.0040	−0.0227
90.0195	10.0109	37.7848	37.790	−0.0047	−0.0126
90.0268	15.0084	60.7126	60.705	0.0074	0.0122
90.0259	20.0319	88.1709	88.181	−0.0103	−0.0116
90.0293	25.0042	122.7313	122.75	−0.0177	−0.0144
90.0251	28.0041	150.1576	150.18	−0.0204	−0.0136
90.0279	30.0213	174.0852	174.06	0.0272	0.0156
90.0245	31.0134	188.7579	188.73	0.0289	0.0153

uncertainties of the temperature and pressure measurements on the water density, which is less than 0.001 kg·m^{-3}.

Nitrogen Results. Nitrogen has been used to test the accuracy of the measurements at low densities. The measurements have been carried out on seven isotherms between (−40 and 80) °C. The experimental data and results from a reference EOS[5] are given in Table 3. To show the experimental accuracy, four isotherms have been selected to cover the whole experimental range. Figure 4 shows the deviations between experimental data and the reference EOS for the selected four isotherms. The absolute deviation is within ±0.01 kg·m^{-3} for all densities up to 65 kg·m^{-3}; the relative deviation is within ±0.02% for densities between (10 and 85) kg·m^{-3}. The estimated uncertainty of the density measurement (eq 3) is within ±0.01 kg·m^{-3} at low densities or ±0.025% at 85 kg·m^{-3}. The deviations of the present data from the EOS (accuracy ±0.01%) are within these estimated uncertainties, which confirms the accuracy of the density measurement even without considering an additional uncertainty of ±0.008 kg·m^{-3} or 0.01% due to the uncertainty in temperature and pressure.

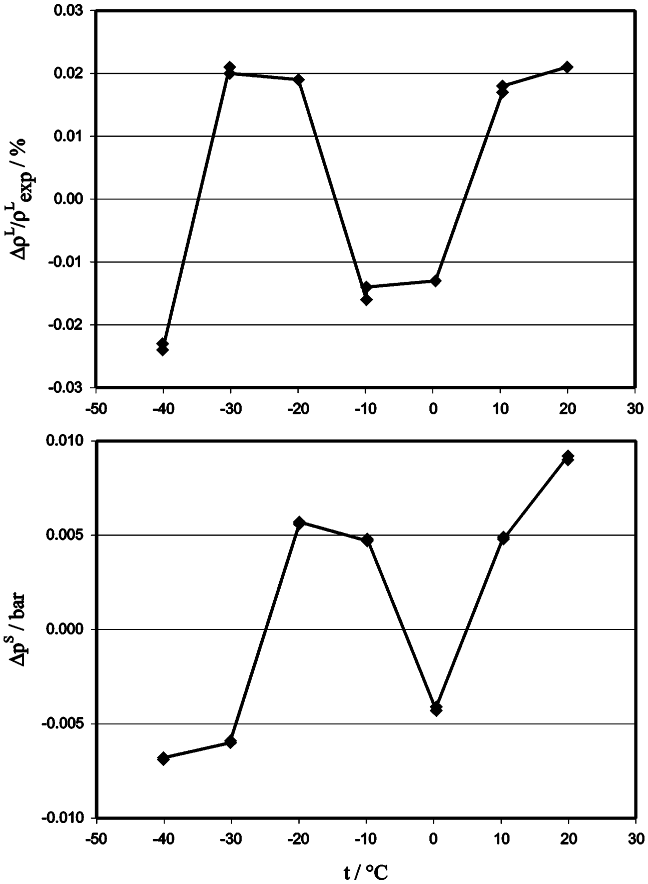

Figure 6. Deviations ($\Delta\rho^{L} = \rho^{L}_{exp} - \rho^{L}_{EOS}$, $\Delta p^{S} = p^{S}_{exp} - p^{S}_{EOS}$) between experimental results and a reference EOS[6] for the saturated liquid density and vapor pressure of carbon dioxide.

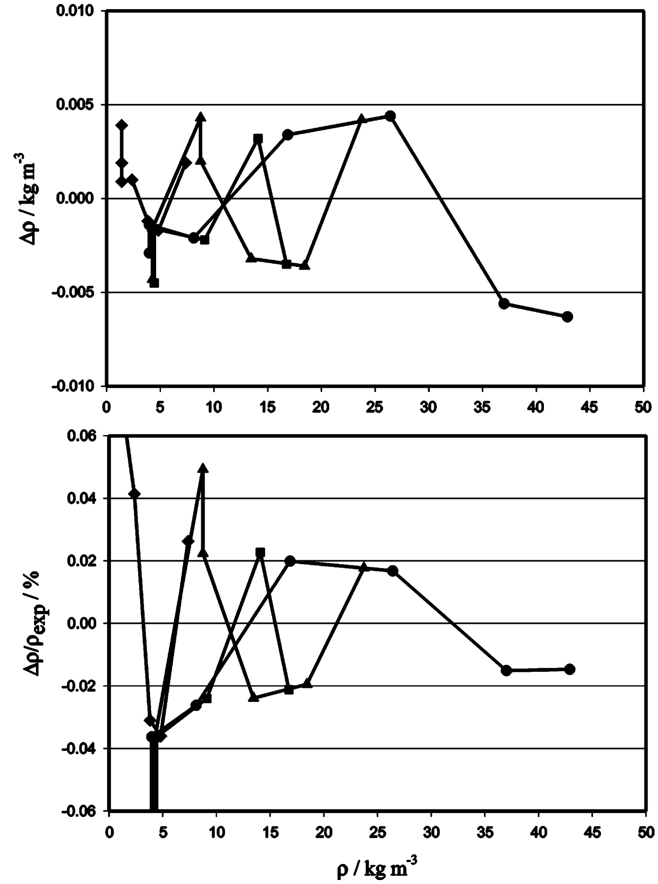

Figure 7. Absolute and relative deviations ($\Delta\rho = \rho_{exp} - \rho_{EOS}$) between experimental results and a reference EOS[7] for the homogeneous gas density of R134a: ◆, −10.16; ■, 10.01; ▲, 20.07; and ●, 40.02 °C.

Carbon Dioxide Results. First, measurements in the homogeneous gas phase have been made. The measurements have been carried out for seven isotherms between (−40 and 20) °C. The experimental data and results from a reference EOS[6] are given in Table 4. Figure 5 shows the deviations between experimental data and the reference EOS for four selected isotherms. The absolute deviation is within ±0.01 kg·m^{-3} for all densities up to 110 kg·m^{-3}; the relative deviation is within ±0.018% for densities between (10 and 175) kg·m^{-3}. The estimated uncertainty of the density measurement (eq 3) is within ±0.01 kg·m^{-3} at low densities or ±0.02% at 175 kg·m^{-3}, which are both higher than or equal to the deviation of the present results from the EOS (accuracy ±0.03%).[6] Thus, the estimated uncertainty of the density measurement is confirmed, even

Table 7. Experimental (exp) and EOS[7] Results for the Vapor Pressure and Saturated Liquid Density of R134a

t/°C	p^{S}_{exp}/bar	p^{S}_{EOS}/bar	Δp^{S}/bar	ρ^{L}_{exp}/kg·m^{-3}	ρ_{EOS}/kg·m^{-3}	$\Delta\rho^{L}$/kg·m^{-3}	$\Delta\rho^{L}/\rho^{L}_{exp}$/%
−20.0226	1.33600	1.32605	0.00995	1358.70	1358.33	0.367	0.027
−20.0242	1.33580	1.32596	0.00984	1358.69	1358.34	0.355	0.026
−10.1511	2.00480	1.99409	0.01071	1327.31	1327.61	−0.304	−0.023
−10.1564	2.00467	1.99368	0.01099	1327.33	1327.62	−0.288	−0.022
00.1621	2.95500	2.94527	0.00973	1293.96	1294.24	−0.280	−0.022
00.1643	2.95502	2.94550	0.00952	1293.96	1294.23	−0.273	−0.021
10.0152	4.15710	4.14818	0.00892	1260.67	1260.91	−0.239	−0.019
10.0141	4.15708	4.14803	0.00905	1260.66	1260.91	−0.246	−0.020
20.0682	5.71983	5.72913	−0.00930	1225.33	1225.08	0.248	0.020
20.0658	5.71940	5.72871	−0.00931	1225.34	1225.09	0.248	0.020
30.1068	7.71760	7.72563	−0.00803	1187.22	1187.04	0.176	0.015
30.1024	7.71666	7.72465	−0.00799	1187.23	1187.06	0.174	0.015
40.0253	10.1809	10.1728	0.00811	1146.44	1146.63	−0.192	−0.017
40.0272	10.1815	10.1733	0.00822	1146.44	1146.62	−0.179	−0.016
50.0468	13.1987	13.1946	0.00409	1102.34	1102.09	0.252	0.023
50.0435	13.1976	13.1935	0.00408	1102.35	1102.10	0.245	0.022
60.0138	16.8295	16.8233	0.00623	1052.61	1052.79	−0.181	−0.017
60.0172	16.8315	16.8247	0.00681	1052.60	1052.77	−0.167	−0.016
69.8818	21.1059	21.1123	−0.00636	997.103	996.972	0.131	0.013
69.8872	21.1088	21.1149	−0.00608	997.091	996.939	0.152	0.015
80.0122	26.3357	26.3389	−0.00322	928.313	928.151	0.162	0.018
80.0148	26.3373	26.3403	−0.00301	928.306	928.132	0.174	0.019
90.0279	32.4553	32.4604	−0.00514	837.734	837.518	0.216	0.026
90.0245	32.4532	32.4581	−0.00489	837.765	837.555	0.210	0.025

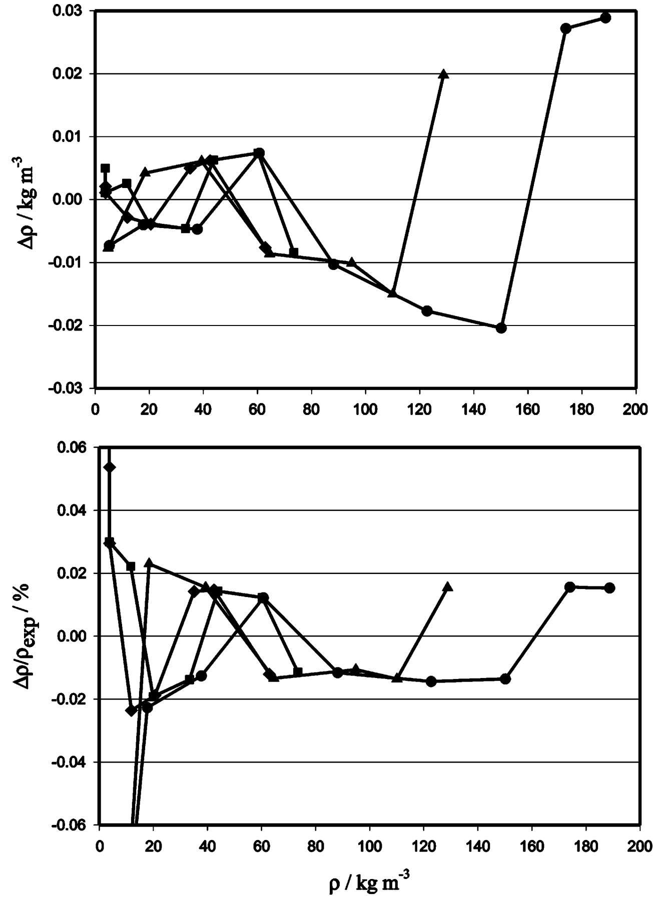

Figure 8. Absolute and relative deviations ($\Delta\rho = \rho_{exp} - \rho_{EOS}$) between experimental results and a reference EOS[7] for the homogeneous gas density of R134a: ◆, 50.04; ■, 60.02; ▲, 80.01; and ●, 90.03 °C.

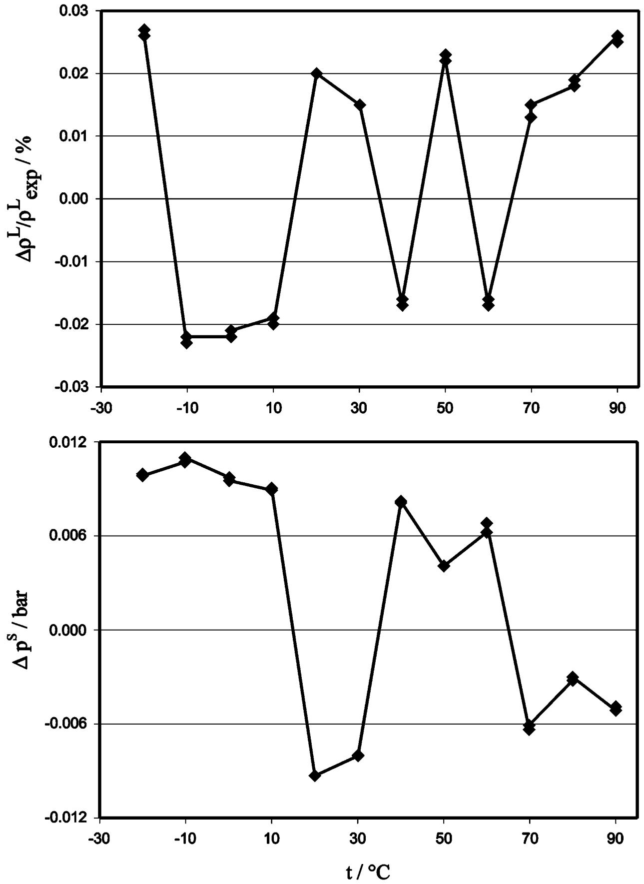

Figure 9. Deviations ($\Delta\rho^L = \rho^L_{exp} - \rho^L_{EOS}$, $\Delta p^S = p^S_{exp} - p^S_{EOS}$) between experimental results and a reference EOS[7] for the saturated liquid density and vapor pressure of R134a.

without considering additional uncertainties due to the temperature and pressure measurement (yielding ±0.014 kg·m^{-3} or ±0.01% in density).

Second, measurements of the vapor pressure and saturated liquid density have been made for the same temperatures. The experimental data and results from a reference EOS[6] are given in Table 5. Figure 6 shows the deviations between the experimental data and the reference EOS. For the saturated liquid densities, the relative deviation is within ±0.024% for densities between (774 and 1117) kg·m^{-3}. The estimated uncertainty of the density measurement (eq 3) is within ±0.014%. The uncertainty of the temperature measurement yields an additional uncertainty of ±0.02%. By error propagation, this gives a total uncertainty of the density of ±0.024%, which fits well with the deviation of the experimental results from the EOS. Even without regard to the accuracy of the EOS[6] of ±0.03%, one can conclude that the estimated uncertainties in eq 3 are confirmed. For the vapor pressure, the absolute deviation is within ±10.0 mbar (Figure 6), which is smaller than the total uncertainty of the vapor-pressure measurement of ±12.0 mbar.

R134a Results. First, measurements in the homogeneous gas phase have been made. The measurements have been carried out for 11 isotherms between (−10 and 90) °C. The experimental data and results from a reference EOS[7] are given in Table 6. Figures 7 and 8 show the deviations between the experimental data and the EOS for isotherms from (−10 to 40) °C and from (50 to 90) °C, respectively. The absolute deviation is within ±0.01 kg·m^{-3} for all densities up to 100 kg·m^{-3}, and the relative deviation is within ±0.02% for densities between (20 and 190) kg·m^{-3}. The estimated uncertainty of the density measurement (eq 3) is within ±0.01 kg·m^{-3} at low densities or ±0.018% at 190 kg·m^{-3}. This fits well with the actual deviations even without considering the additional uncertainty due to uncertainties in the temperature and pressure, which is estimated to be within ±0.02 kg·m^{-3} or ±0.016%, and the quite low accuracy of the EOS[7] of ±0.05%.

Second, measurements of the vapor pressure and saturated liquid density have been done for 12 temperatures between (−20 and 90) °C. The experimental data and results from the reference EOS[7] are given in Table 7. Figure 9 shows the deviations between experimental data and the EOS. For the saturated liquid densities, the relative deviation is within ±0.03% for densities between (837 and 1360) kg·m^{-3}. The estimated uncertainties of the density measurement (eq 3) are within ±0.014%. The uncertainty of the temperature measurement gives an additional uncertainty of the saturated liquid densities of ±0.02%. This gives an overall uncertainty of ±0.024%, which is a little lower than the deviation of the experimental results from the EOS. On the other side, with the accuracy of the EOS[7] (±0.05%) one can still conclude that the estimated uncertainty in eq 3 is valid. For the vapor pressures, the absolute deviation is within ±11.0 mbar (Figure 9), which is within the total uncertainty in the vapor-pressure measurement of ±12.0 mbar.

Conclusions

A new apparatus for the measurement of vapor−liquid equilibria and saturated liquid densities was tested for the case of pure fluids. The high accuracy of the density measurements has been confirmed by measurements of the compressed liquid density of water and comparison with a high-precision equation of state (EOS). Further tests have been done for the homogeneous gas density of nitrogen, carbon dioxide, and R134a. All deviations between the experimental gas densities and reference EOS are within the estimated uncertainty of $\pm 0.013\% + 0.01\ kg{\cdot}m^{-3}$, which is valid for the temperature range of the present results from (−60 to 100) °C and densities from (10 to 2000) $kg{\cdot}m^{-3}$. For the whole temperature range up to 250 °C, the estimated uncertainty will rise to $\pm 0.02\% + 0.01\ kg{\cdot}m^{-3}$.

Vapor pressures and saturated liquid densities have been measured for carbon dioxide and R134a in the temperature range from (−40 to 90) °C. Vapor pressures are within the estimated uncertainty. Deviations of the saturated liquid density of carbon dioxide to a reference EOS are also within the estimated uncertainty. This confirms that besides the density the vapor−liquid equilibrium measurements are also reliable. The picture is somewhat different for R134a because of the relatively low accuracy of the EOS of ±0.05% in density. Deviations of the saturated liquid density from the EOS are clearly within this accuracy but a little higher than the estimated experimental uncertainty. This shows that for most substances the results from the present single-sinker apparatus can be regarded as reference data and can be used to improve the EOS. An extension of the apparatus to mixtures is desirable because there is a lack of high-precision data for the phase equilibria of mixtures including saturated liquid densities.

Literature Cited

(1) Wagner, W.; Brachthäuser, W.; Kleinrahm, R.; Lösch, H. W. A new, accurate single-sinker densitometer for temperature from 233 to 523 K at pressures up to 30MPa. *Int. J. Thermophys.* **1995**, *16*, 399−411.

(2) RUBOTHERM Präzisionsmesstechnik GmbH, Universitätsstrasse 142, D-44799 Bochum, Germany.

(3) Saleh, B. Thermodynamic Properties of Fluids Used in the Design of Agricultural Machines. Ph.D. Thesis, University of Natural Resources and Applied Life Sciences, Vienna, Austria, in preparation.

(4) Wagner, W.; Pruss, A. The IAPWS formulation 1995 for the thermodynamic properties of ordinary water substance for general and scientific use. *J. Phys. Chem. Ref. Data* **2002**, *31*, 387−535.

(5) Span, R.; Lemmon, E. W.; Jacobsen, R. T.; Wagner, W.; Yokozeki, A. A reference equation of state for the thermodynamic properties of nitrogen for temperatures from 63.151 to 1000 K and pressures to 2200 MPa. *J. Phys. Chem. Ref. Data* **2000**, *29*, 1361−1433.

(6) Span, R.; Wagner, W. A new equation of state for carbon dioxide covering the fluid region from the triple-point temperature to 1100 K at pressures up to 800 MPa. *J. Phys. Chem. Ref. Data* **1996**, *25*, 1509−1596.

(7) Tillner-Roth, R.; Baehr, H. D. An international standard formulation of the thermodynamic properties of 1,1,1,2-tetrafluoroethane (HFC-134a) covering temperatures from 170 K to 455 K at pressures up to 70 MPa. *J. Phys. Chem. Ref. Data* **1994**, *23*, 657−729.

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