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Supplementary measurements of the (pressure, density, temperature) relation of carbon dioxide in the homogeneous region at temperatures from 220 K to 360 K and pressures up to 13 MPa

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This paper presents accurate (p, ρ, T) measurements on pure carbon dioxide in the temperature range from 220 K to 360 K at pressures up to 13 MPa. The measurements (264 values) have been carried out to supplement our earlier comprehensive measurements of Duschek *et al.* in the pressure range up to 9 MPa. The new measurements have been performed on 13 isotherms in the pressure range from 9 MPa to 13 MPa and on five supercritical isotherms in the pressure range from 1 MPa to 13 MPa. The total uncertainty of the measurements is $<(|1.5 \cdot 10^{-4} \cdot \rho|$ to $|4 \cdot 10^{-4} \cdot \rho|)$. Comparisons with the experimental results of previous workers are presented.

1. Introduction

The IUPAC Thermodynamic Tables Project Centre at Imperial College London is committed to revise its tables on carbon dioxide,[1] because the equation of state used for establishing those tables shows quite large systematic deviations from experimental (p, ρ, T) and caloric values, especially along the coexistence curve and in the critical region. Therefore, a new equation of state is being developed by Wagner and his colleagues which should describe the entire thermodynamic surface of carbon dioxide within the experimental uncertainty of the most reliable measurements, and it is hoped that this equation will contribute to the revision of the IUPAC tables.

For the establishment of the new equation of state, comprehensive (p, ρ, T) measurements on pure carbon dioxide in the temperature range from 217 K to 340 K at pressures up to 9 MPa and measurements along the entire coexistence curve were carried out by Duschek *et al.*[2,3] However, during the development of the new equation of state it became clear that there was a lack of reliable experimental (p, ρ, T) values at pressures above 9 MPa. Due to a modification of our "Two-Sinker" densitometer[4] in 1991 we are now able to measure (p, ρ, T) values up to

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13 MPa. Thus, the aim of this work was to supplement the set of (p, ρ, T) values of Duschek *et al.*[2,3] in the pressure range from 9 MPa to 13 MPa. Furthermore, measurements on five additional isotherms (318 K, 323.15 K, 330 K, 350 K, and 360 K) have been carried out in order to support the development of the new equation of state in the supercritical region. Moreover, the comprehensive measurements on the 323.15 K isotherm will serve as reference values for a new isochoric (p, ρ, T) multi-cell apparatus developed by Kurzeja and Wagner[5] for accurate determinations of the critical exponents from (p, ρ, T) measurements in the immediate vicinty of the critical point.

2. Experimental

The measurements were performed with an apparatus specially developed for taking accurate measurements of the saturated-liquid and -vapour densities of pure substances together with the vapour pressure along the whole coexistence curve from the triple-point temperature to the critical temperature. Moreover, the apparatus is also suitable for density measurements of the homogeneous gas and liquid phase including the largest part of the critical region. Comprehensive measurements on methane,[4,6–8] carbon dioxide,[2,3] nitrogen,[9] natural gas,[10] and on the refrigerants R12 and R22,[11] have been carried out successfully. The apparatus was described in detail in a previous paper;[4] only the measuring principle is briefly explained here.

The method used for density measurements in our laboratory is based on the buoyancy principle. However, instead of the usual single sinker, two sinkers of identical mass and surface area but with a considerable difference in volume are used. With this "Two-Sinker-Method," all the effects (such as buoyant forces on the whole suspension device of the sinkers, surface tension at the suspension wire when measuring liquid densities, adsorption on the surface of the sinkers when measuring gas densities, *etc.*) which reduce the accuracy of the density measurement when only one sinker is used, are automatically compensated. The operational range of the apparatus covers a density range from $1\ \mathrm{kg \cdot m^{-3}}$ to $2000\ \mathrm{kg \cdot m^{-3}}$ at temperatures from 80 K to 360 K and, after the modification of the apparatus in 1991, at pressures up to 13 MPa.

3. Results

The experimental results of the (p, ρ, T) measurements on CO_2 are listed in table 1. Figure 1 shows a general view of the (p, ρ, T) surface investigated. The measurements were carried out on 13 isotherms in the temperature range from 220 K to 340 K for pressures from 9 MPa to 13 MPa and on five isotherms (318 K, 323.15 K, 330 K, 350 K, and 360 K) in the pressure range from 1 MPa to 13 MPa. Since the results on the 323.15 K isotherm are considered to be reference values for the new isochoric multi-cell apparatus of Kurzeja and Wagner,[5] smaller steps in density were used than for the other isotherms. To check the reproducibility, some of the measurements at selected points were repeated at different times.

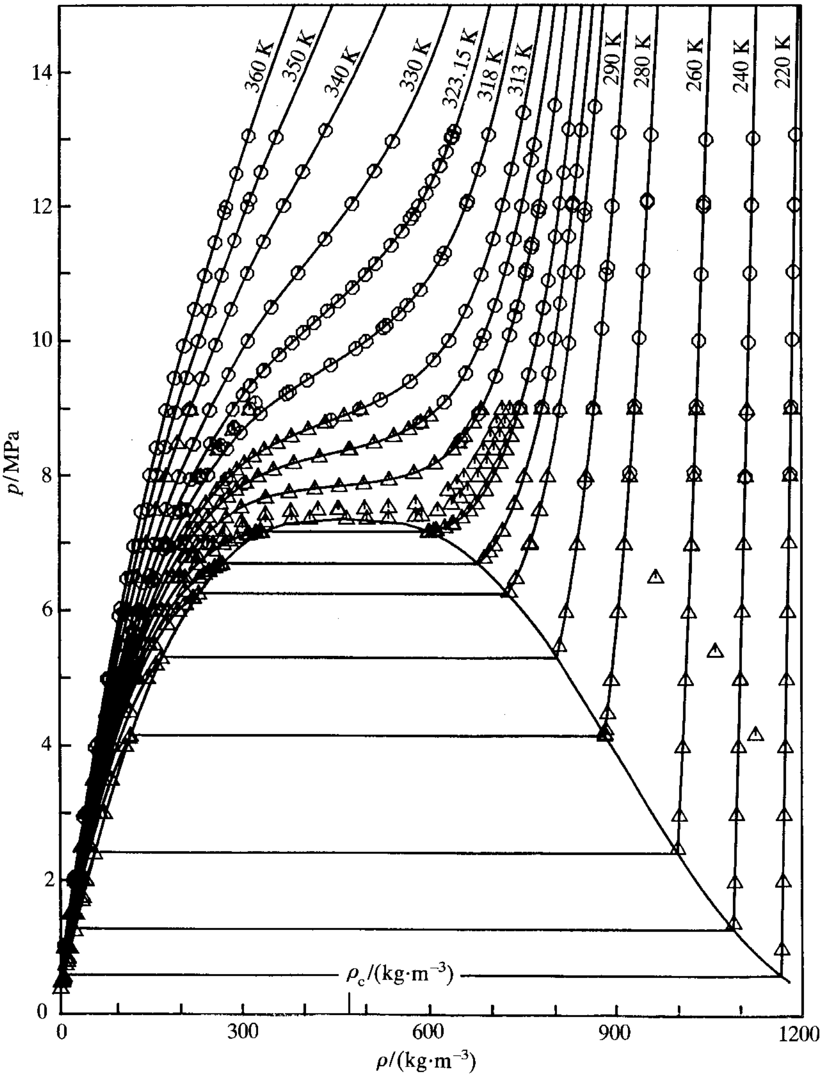

FIGURE 1. General view of the investigated (p, ρ, T) surface of carbon dioxide. The isotherms and the coexistence curve were calculated from a preliminary equation of state.[12] ⦶, This work; △, Duschek *et al.*[2]

The carbon dioxide used for the measurements was supplied by Linde, F.R.G., with a purity of $x(CO_2) \geqslant 0.999993$ according to the manufacturer {impurities: $x(O_2) \leqslant 2 \cdot 10^{-6}$; $x(N_2) \leqslant 3 \cdot 10^{-6}$; $x(CO) \leqslant 0.5 \cdot 10^{-6}$; $x(H_2O) \leqslant 1 \cdot 10^{-6}$; $x(\text{hydrocarbons}) \leqslant 1 \cdot 10^{-6}$, where x denotes mole fraction}.

The experimental uncertainties of the individual quantities p, ρ, and T were discussed in detail in a previous paper.[4] After some improvements of the apparatus, the experimental uncertainties of the density and pressure measurement could be

TABLE 1. The new (p, ρ, T) results for carbon dioxide, where T is the temperature (IPTS-68), p the pressure, and ρ the density

$\frac{T}{\mathrm{K}}$	$\frac{\rho}{\mathrm{kg \cdot m^{-3}}}$	$\frac{p}{\mathrm{MPa}}$	$\frac{\rho}{\mathrm{kg \cdot m^{-3}}}$	$\frac{p}{\mathrm{MPa}}$	$\frac{\rho}{\mathrm{kg \cdot m^{-3}}}$	$\frac{p}{\mathrm{MPa}}$	$\frac{\rho}{\mathrm{kg \cdot m^{-3}}}$	$\frac{p}{\mathrm{MPa}}$
220.000	1181.69	8.02835	1185.57	10.0226	1189.34	12.0195	1191.27	13.0734
	1183.65	9.02677	1187.49	11.0293	1189.35	12.0300		
240.000	1109.32	7.98507	1114.79	9.97896	1120.13	12.0185	1122.66	13.0164
	1111.93	8.92685	1117.51	11.0066	1120.16	12.0271		
260.000	1026.72	8.04914	1034.95	10.0039	1042.79	12.0076	1046.49	13.0003
	1030.94	9.03311	1038.89	10.9931	1043.04	12.0678		
280.000	20.1471	0.997622	931.191	9.03832	945.442	11.0418	952.225	12.0983
	923.331	8.05031	938.626	10.0486	952.020	12.0637	958.126	13.0706
290.000	852.876	7.90649	880.008	10.1833	888.954	11.0919	906.350	13.1028
	866.960	9.00386	887.982	10.9884	897.240	12.0057		
297.000	809.916	8.96951	841.339	11.0181	852.971	11.9690		
	826.543	9.96441	851.794	11.8695	869.075	13.4846		
300.000	781.475	9.01739	811.265	10.5532	832.635	12.0109	846.463	13.1378
	792.369	9.51838	818.690	11.0222	833.251	12.0564		
	802.256	10.0323	826.443	11.5540	839.206	12.5269		
303.000	746.636	9.00890	783.582	10.4853	802.961	11.5479	826.356	13.1519
	760.728	9.49642	783.810	10.4963	810.873	12.0483		
	773.566	10.0198	791.617	10.8980	817.606	12.5073		
307.000	652.122	8.53207	739.383	10.3686	764.808	11.3852	785.461	12.4419
	681.106	8.92642	743.251	10.5048	766.098	11.4444	802.645	13.5081
	708.645	9.47936	755.980	10.9987	775.968	11.9274		
	730.865	10.0888	757.290	11.0546	777.331	11.9988		
310.000	305.758	7.88783	660.079	9.52924	725.705	11.0731	769.173	12.9198
	587.731	8.79708	684.610	9.97287	738.037	11.5142	769.212	12.9224
	625.768	9.09839	689.745	10.0838	750.068	12.0045		
	659.776	9.52440	707.838	10.5310	764.882	12.6981		
313.000	274.679	7.95644	572.328	9.40471	685.369	10.9914	752.913	13.3957
	446.915	8.83497	608.963	9.72320	704.863	11.5229		
	492.962	8.99721	632.842	10.0108	720.077	12.0201		
	526.373	9.13819	659.996	10.4470	734.234	12.5586		
318.000	35.0507	1.93382	210.085	7.50366	446.382	9.65623	620.903	11.2268
	57.9860	3.02354	243.688	8.02401	487.033	9.89668	626.142	11.3150
	80.4726	3.96833	275.591	8.41787	503.787	10.0055	661.560	12.0390
	107.852	4.96752	299.314	8.66011	531.104	10.2037	663.565	12.0880
	130.260	5.67258	331.985	8.93933	535.467	10.2383	681.196	12.5588
	141.070	5.97938	374.034	9.23329	555.272	10.4108	697.552	13.0721
	160.643	6.48412	378.964	9.26399	568.203	10.5380		
	182.192	6.97026	407.400	9.43443	588.539	10.7669		
320.000	138.049	5.96921	178.495	6.99383	261.631	8.42330	287.939	8.73788
	138.343	5.97764	201.835	7.47593	265.217	8.46940	314.865	9.01199
	155.371	6.43980	231.425	7.99088	286.661	8.72375	324.417	9.09967
	175.142	6.91823	232.259	8.00383	286.852	8.72587		
323.150	7.73766	0.463957	192.291	7.46396	383.061	9.98748	573.620	11.8286
	17.5947	1.03104	216.858	7.95596	401.448	10.1403	578.077	11.8945
	35.9039	2.01560	248.504	8.49178	419.122	10.2835	586.200	12.0205
	56.4647	3.01994	285.465	9.00436	440.735	10.4588	597.463	12.2080
	79.8192	4.03935	303.173	9.21574	458.352	10.6039	607.514	12.3897
	105.412	5.02005	303.389	9.21809	481.644	10.8041	618.663	12.6090
	106.836	5.07060	315.193	9.34854	502.479	10.9960	619.313	12.6229
	125.564	5.70053	315.789	9.35503	502.587	10.9969	628.713	12.8245
	135.749	6.01610	337.068	9.57248	519.013	11.1607	637.436	13.0271
	153.575	6.52559	338.209	9.58358	543.264	11.4297	638.725	13.0574
	171.470	6.98629	362.462	9.80892	559.872	11.6380	641.537	13.1269

TABLE 1—*continued*

$\frac{T}{\mathrm{K}}$	$\frac{\rho}{\mathrm{kg \cdot m^{-3}}}$	$\frac{p}{\mathrm{MPa}}$	$\frac{\rho}{\mathrm{kg \cdot m^{-3}}}$	$\frac{p}{\mathrm{MPa}}$	$\frac{\rho}{\mathrm{kg \cdot m^{-3}}}$	$\frac{p}{\mathrm{MPa}}$	$\frac{\rho}{\mathrm{kg \cdot m^{-3}}}$	$\frac{p}{\mathrm{MPa}}$
330.000	34.4254	1.98856	125.915	5.93365	220.787	8.48158	393.097	11.0252
	54.4483	3.00799	140.807	6.42124	246.925	8.99129	436.910	11.5252
	76.3420	4.01654	159.566	6.98420	277.949	9.51927	480.928	12.0528
	96.7991	4.86595	178.924	7.51008	311.554	10.0162	517.132	12.5403
	112.980	5.47884	198.576	7.99239	350.004	10.5165	545.490	12.9805
340.000	16.6809	1.03533	256.539	9.95404	337.426	11.4896	437.712	13.1403
	215.315	8.99689	282.590	10.4885	369.700	12.0294		
	234.337	9.45758	310.642	11.0182	400.573	12.5315		
350.000	32.8650	2.04074	124.226	6.50182	210.217	9.46936	315.080	12.1188
	49.6597	2.98661	135.955	6.96599	229.157	10.0085	333.321	12.5189
	69.4320	4.02265	150.038	7.49608	246.124	10.4644	357.514	13.0369
	89.2278	4.98131	164.578	8.10397	266.728	10.9885		
	111.642	5.97913	177.111	8.43803	288.358	11.5089		
	111.660	5.97999	193.124	8.95211	310.286	12.0114		
360.000	31.0462	1.99801	116.615	6.47377	192.516	9.46424	273.911	12.0032
	46.9656	2.93878	127.654	6.95769	206.460	9.93918	291.710	12.4990
	65.5629	3.97115	139.740	7.46676	223.203	10.4849	312.394	13.0577
	85.1829	4.98759	153.298	8.01339	239.155	10.9824		
	104.557	5.92327	163.932	8.42504	255.582	11.4747		
	106.945	6.03411	178.969	8.98348	271.007	11.9209		

reduced with the result: the uncertainty in pressure was estimated to be $<|6 \cdot 10^{-5} \cdot p|$ or $<|30\ \mathrm{Pa}|$, whichever is greater; in density $<|1.5 \cdot 10^{-4} \cdot \rho|$ or $<|1.5 \cdot 10^{-3}\ \mathrm{kg \cdot m^{-3}}|$, whichever is greater, and in temperature $<|1.5 \cdot 10^{-3}\ \mathrm{K}|$. On this basis, the total uncertainties in density and in pressure, respectively, were calculated by applying the Gaussian error-propagation formula; the reliability of these total uncertainties given below was estimated to be about 95 per cent.

Thus, the total relative uncertainty $\Delta\rho/\rho$ in density of the (p, ρ, T) measurements was estimated to be $<|1.5 \cdot 10^{-4}|$ to $<|2.5 \cdot 10^{-4}|$ with the exception of the (p, ρ, T) values in the temperature range from 310 K to 323.15 K (critical temperature $T_c = 304.136$ K) at densities between $250\ \mathrm{kg \cdot m^{-3}}$ and $550\ \mathrm{kg \cdot m^{-3}}$ (critical density $\rho_c = 467.6\ \mathrm{kg \cdot m^{-3}}$. In this region the uncertainty in density rises to $|4 \cdot 10^{-4} \cdot \rho|$ because of the great isothermal compressibility. The total uncertainty in pressure $\Delta p/p$ in this region is $<|1 \cdot 10^{-4}|$.

4. Discussion

A comparison of the new (p, ρ, T) values with several selected measurements of other workers[(2, 13–30)] on six representative isotherms is presented in figures 2 and 3. The figures show the deviation in density between the experimental values and values calculated from a preliminary equation of state established by Span,[(12)] which was established only for comparison and was fitted only to the new (p, ρ, T) values and to the values of Duschek *et al.*[(2, 3)] Nevertheless, the preliminary equation represents the experimental values within $<|2 \cdot 10^{-4} \cdot \rho|$. Furthermore, both figures illustrate the estimated uncertainty of the new (p, ρ, T) values.

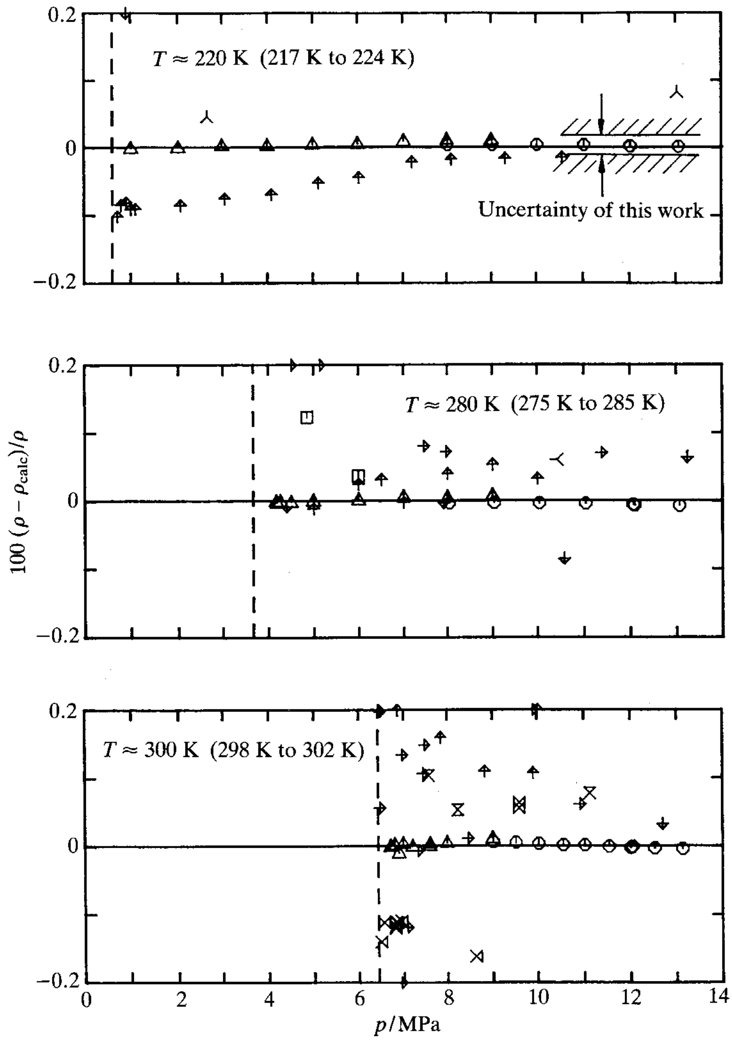

FIGURE 2. Relative-density deviations of experimental (p, ρ, T) values of carbon dioxide from values ρ_{calc} calculated from a preliminary equation of state.[12] ⏀, This work; △, Duschek *et al.*;[2] ⊡, Holste *et al.*;[14] ⋈, Ely *et al.*;[15] ⧖, Magee and Ely;[16] ⋊, Levelt Sengers and Chen;[18] ⊥, Golovskii and Tsymarnyi;[21] X, Michels and Michels;[22] ⊣, Vukalovich *et al.*;[25] −<, Kirillin *et al.*;[27] ⅄, Kirillin *et al.*;[28] ↑, Popov and Sayapov;[29] – – –, phase boundary.[2]

The new (p, ρ, T) values agree very well with those of Duschek *et al.*[2] in the overlapping range between 8 MPa and 9 MPa. The deviation in density is in all cases $<|1 \cdot 10^{-4} \cdot \rho|$ and almost always $<|5 \cdot 10^{-5} \cdot \rho|$. There is also a good agreement with the Burnett measurements of Jaeschke[13] at $T = 353.15$ K with a maximum deviation of $|3 \cdot 10^{-4} \cdot \rho|$ at $p = 12$ MPa. Jaeschke's refractive-index measurements[13] deviate systematically up to $+5 \cdot 10^{-4} \cdot \rho$ at $p = 6$ MPa, which is clearly within the given uncertainty of $|1 \cdot 10^{-3} \cdot \rho|$. The values of Holste *et al.*[14] agree within

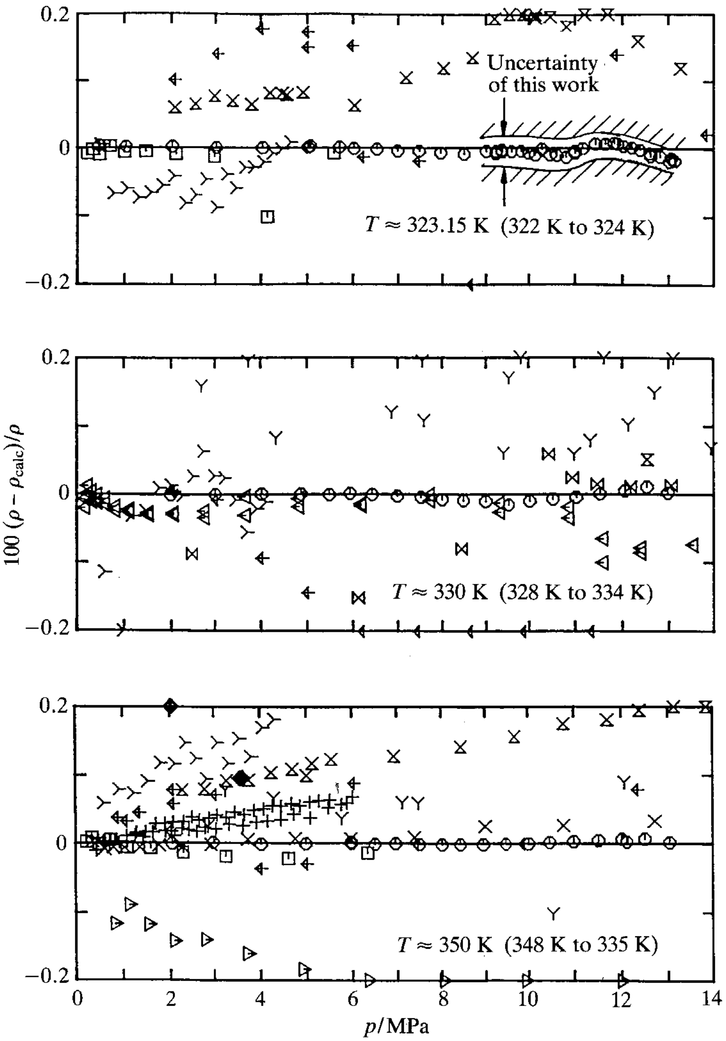

FIGURE 3. Relative-density deviations of experimental (p, ρ, T) values of carbon dioxide from values ρ_{calc} calculated from a preliminary equation of state.[12] ⦶, This work; ×, Jaeschke (Burnett measurements);[13] +, Jaeschke (refractive-index measurements);[13] ⊡, Holste *et al.*;[14] ⋈, Ely *et al.*;[15] ⧖, Magee and Ely;[16] ◁, Hoinkis;[17] ▷, Sass *et al.*;[19] ≻, Kholodov *et al.*;[20] ✕, Michels and Michels;[22] ⨯, Michels *et al.*;[23] ⇜, Vukalovich *et al.*;[24] Y, Kirillin *et al.*;[26] ⊕, Nebendahl.[30]

$|3 \cdot 10^{-4} \cdot \rho|$ with the new measurements, with the exception of two values, one at $T = 323.15$ K and the other at $T = 282.5$ K, which deviate $< |1 \cdot 10^{-3} \cdot \rho|$. The measurements of Ely *et al.*[15] scatter around our values mostly within $|1 \cdot 10^{-3} \cdot \rho|$, which is within the uncertainty of $|1.5 \cdot 10^{-3} \cdot \rho|$ given by the authors. The two values of Magee and Ely[16] at $T = 330$ K and 300 K deviate by $+5 \cdot 10^{-4} \cdot \rho$ which is within the uncertainty given by $\approx |1.5 \cdot 10^{-3} \cdot \rho|$. The experimental results of Hoinkis[17] at $T = 333.15$ K agree with our values within $|3 \cdot 10^{-4} \cdot \rho|$ at pressures up to 11 MPa.

Only the values above $p = 11$ MPa deviate by as much as $-1 \cdot 10^{-3} \cdot \rho$, which is clearly within the uncertainty of $|1.6 \cdot 10^{-3} \cdot \rho|$ given for this region.

Furthermore, the measurements of Kholodov *et al.*,[18] and Golovskii and Tsymarnyi,[19] Levelt Sengers and Chen,[20] and Sass *et al.*[21] agree with our values within the uncertainties given by the authors. The experimental results of other experimentalists (Michels *et al.*,[22,23] Vukalovich *et al.*,[24,25] Kirillin *et al.*,[26-28] Popov and Sayapov,[29] and Nebendahl)[30] were considered but not further discussed because of larger experimental uncertainties given by the authors, large scatterings, or systematic deviations.

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