

## **Measurement and correlation of the (pressure, density, temperature) relation of carbon dioxide**

### **I. The homogeneous gas and liquid regions in the temperature range from 217 K to 340 K at pressures up to 9 MPa**

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Comprehensive ( $p$ ,  $\rho$ ,  $T$ ) measurements on pure carbon dioxide have been carried out in the single-phase region (362 values) and along the entire coexistence curve (202 values). The results reported in this first paper cover the homogeneous gas and liquid region in the temperature range from 217 K to 340 K at pressures up to 9 MPa. Comparisons with experimental results of previous workers and values calculated from three current equations of state for carbon dioxide are presented. A truncated virial equation has been established in order to determine reliable values for the second and third virial coefficients. This equation represents the density of carbon dioxide in the entire temperature range investigated at densities up to 35 per cent of the critical density with an uncertainty of less than  $\pm 0.01$  per cent. The second and third virial coefficients have been determined with an uncertainty of less than 0.4 per cent and 3 per cent, respectively.

### **1. Introduction**

The IUPAC Thermodynamic Tables Project Centre at Imperial College is committed to revise its tables on carbon dioxide,<sup>(1)</sup> because the equation of state used for establishing these tables shows quite large systematic deviations from experimental ( $p$ ,  $\rho$ ,  $T$ ) and caloric values, especially along the coexistence curve and in the critical region. Moreover, the equation has a rather complicated structure; it consists of an analytic far-field equation and a non-analytic near-critical equation which are combined by a switching function. To overcome these difficulties a new equation of state will be developed by Wagner *et al.* which will describe the entire thermodynamic surface of carbon dioxide within the experimental uncertainty of the most reliable data, and it is hoped that this will contribute to the revision of the IUPAC tables.

The aim of this work, reported in two papers, is to provide a reliable set of (pressure  $p$ , density  $\rho$ , temperature  $T$ ) values for the establishment of this new equation of state. This first paper presents comprehensive ( $p, \rho, T$ ) measurements on pure carbon dioxide in the homogeneous gas and liquid region including the largest part of the critical region in the temperature range from 217 K to 340 K at pressures up to 9 MPa. A truncated virial equation has been established for the density range up to  $0.35\rho_c$ , where  $\rho_c$  is the critical density. This equation provides accurate values for the second and third virial coefficients. The second paper, which will be published shortly,<sup>(2)</sup> reports the measurement and correlation of the saturated-liquid and -vapour densities together with the vapour pressure along the entire coexistence curve of carbon dioxide.

## 2. Experimental

A new apparatus has been developed especially for 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 or liquid phase including the largest part of the critical region. As a first application of this new measuring principle, comprehensive measurements on pure methane were carried out along the coexistence curve,<sup>(3)</sup> in the critical region,<sup>(4)</sup> and in the homogeneous gas region in the temperature range from 273 K to 323 K at pressures up to 8 MPa.<sup>(5)</sup> The essential details of the new apparatus were given in a previous paper.<sup>(3)</sup> Therefore, only the principle is briefly described here.

The new method for density measurements is based on a 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 bar or wire when measuring liquid densities, adsorption on the surface of the sinker when measuring gas densities, *etc.*) which reduce the accuracy of the density measurement when only a single sinker is used, are automatically compensated. The operational range of the apparatus covers a density range from  $1 \text{ kg} \cdot \text{m}^{-3}$  to  $2000 \text{ kg} \cdot \text{m}^{-3}$  at temperatures from 50 K to 350 K and pressures up to 9 MPa.

## 3. Results

The experimental results are listed in table 1. Figure 1 shows a general view of the ( $p, \rho, T$ ) surface investigated. Together with the results of the coexistence curve,<sup>(2)</sup> our ( $p, \rho, T$ ) values cover the whole region from the triple-point temperature 216.580 K up to 340 K at pressures up to 9 MPa. To check the reproducibility, some of the measurements at selected points were repeated at different times.

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

$\rho$ kg·m <sup>-3</sup>	p MPa	$\rho$ kg·m <sup>-3</sup>	p MPa	$\rho$ kg·m <sup>-3</sup>	p MPa	$\rho$ kg·m <sup>-3</sup>	p MPa
T = 217.000 K							
7.6998	0.30157	10.4212	0.40145				
T = 220.000 K							
7.4658	0.29732	13.0039	0.50112	15.2795	0.58069	1177.66	5.99942
7.5582	0.30082	13.6636	0.52443	1167.07	1.00854	1177.67	6.00137
7.5584	0.30082	14.3933	0.54999	1169.26	2.01454	1179.77	7.02108
10.2263	0.40069	14.4107	0.55060	1171.41	2.99935	1181.75	8.00754
12.8291	0.49489	14.6872	0.56023	1173.52	4.00289	1183.69	9.00099
12.9840	0.50040	14.9918	0.57076	1175.62	5.00310		
T = 230.000 K							
20.6016	0.80248	21.9848	0.84976				
T = 233.150 K							
1125.20	4.18767						
T = 240.000 K							
6.8644	0.30146	24.8452	0.99968	1091.27	2.00103	1103.70	6.00947
11.6769	0.50123	24.8796	1.00086	1094.51	3.00527	1106.63	7.00344
11.6931	0.50191	24.8808	1.00094	1097.66	4.01025	1109.47	7.99734
18.0261	0.75036	32.4117	1.25430	1100.70	5.00086	1112.22	8.99168
24.7311	0.99563	1089.26	1.39221	1100.72	5.01018		
T = 250.000 K							
43.8169	1.70011	45.4953	1.75083	1060.39	5.42111		
T = 260.000 K							
10.6426	0.50166	49.9288	2.00050	1007.51	4.00864	1026.66	8.00975
10.6441	0.50174	63.7136	2.40015	1012.60	5.00422	1030.85	9.00264
22.2461	1.00132	999.298	2.50328	1017.49	6.00106	1030.88	8.99182
35.1470	1.50020	1002.06	2.99454	1022.08	6.98951		
49.9066	1.99984	1007.49	4.00312	1022.16	7.00288		
T = 270.000 K							
79.6880	2.99695	79.7116	2.99757				
T = 270.854 K							
964.780	6.51519						
T = 280.000 K							
9.7448	0.49940	72.8188	3.00040	883.776	4.17593	914.342	7.00457
9.7556	0.49994	90.8340	3.50066	884.040	4.19778	923.003	8.00188
9.7682	0.50057	112.986	3.99813	884.963	4.26765	923.033	8.00408
20.2891	1.00415	113.043	3.99931	887.947	4.50556	931.024	9.00489
31.5094	1.50162	113.081	3.99998	893.824	4.99745	931.036	9.00444
43.7964	2.00097	113.174	4.00184	893.850	4.99941		
57.4040	2.50027	119.453	4.12011	904.700	6.00474		
57.4173	2.50080	121.299	4.15312	914.288	6.99882		

TABLE 1—continued

$\frac{\rho}{\text{kg} \cdot \text{m}^{-3}}$	$\frac{P}{\text{MPa}}$	$\frac{\rho}{\text{kg} \cdot \text{m}^{-3}}$	$\frac{P}{\text{MPa}}$	$\frac{\rho}{\text{kg} \cdot \text{m}^{-3}}$	$\frac{P}{\text{MPa}}$	$\frac{\rho}{\text{kg} \cdot \text{m}^{-3}}$	$\frac{P}{\text{MPa}}$
<i>T</i> = 290.000 K							
121.510	4.50097	170.459	5.30035	839.252	7.00067	867.022	9.00495
148.435	5.00009	809.375	5.49993	839.306	7.00245		
162.312	5.20003	820.785	6.00191	854.305	8.00234		
<i>T</i> = 297.000 K							
133.288	5.00165	207.531	6.10178	729.431	6.30105	777.111	7.50565
159.618	5.50058	219.262	6.19719	740.392	6.50039	789.901	8.00337
180.018	5.80119	219.890	6.20172	761.227	7.00003	810.664	9.00808
197.238	6.00253	228.344	6.25870	762.050	7.02381		
<i>T</i> = 300.000 K							
9.0474	0.50008	92.1169	4.00479	230.044	6.50311	267.417	6.70801
9.0755	0.50160	109.006	4.50382	237.683	6.55677	689.670	6.80343
18.5804	1.00002	128.415	5.00027	244.772	6.60111	698.293	6.89846
18.5964	1.00082	128.427	5.00042	244.958	6.60195	705.810	6.99384
28.6868	1.50058	128.729	5.00768	253.982	6.65044	719.160	7.20323
39.4268	2.00029	151.976	5.50135	254.109	6.65109	738.464	7.60186
50.9440	2.50033	182.514	6.00240	254.672	6.65386	738.480	7.60290
50.9593	2.50094	207.120	6.29972	254.887	6.65485	753.263	7.99844
63.3803	3.00014	229.741	6.50087	261.074	6.68294	781.251	9.00595
77.0682	3.50413	229.756	6.50097	265.578	6.70113		
92.0693	4.00323	229.874	6.50182	266.927	6.70629		
<i>T</i> = 303.000 K							
124.162	4.99849	314.141	7.15194	626.379	7.25415	715.518	8.20408
145.606	5.49965	323.309	7.16853	637.386	7.30091	724.424	8.40044
171.954	6.00038	325.446	7.17176	638.338	7.30553	724.588	8.40390
207.412	6.50079	331.014	7.17905	639.260	7.31010	732.562	8.60203
226.453	6.69891	333.938	7.18248	653.794	7.39793	739.658	8.79815
252.357	6.90208	600.519	7.18860	666.769	7.50267	739.855	8.80322
269.688	7.00137	600.781	7.18895	677.015	7.60618	746.462	9.00279
280.797	7.05172	601.868	7.19073	692.239	7.79927		
293.694	7.09884	609.168	7.20465	704.875	8.00099		
309.851	7.14270	612.809	7.21303	704.879	8.00079		
<i>T</i> = 304.135 K							
590.276	7.42907	663.052	7.80385	705.414	8.40309	731.240	9.00030
637.039	7.60179	680.447	8.00237	715.133	8.60319		
651.065	7.69851	694.008	8.20090	723.595	8.80096		
<i>T</i> = 304.155 K							
201.362	6.50093	302.214	7.24972	471.100	7.38024	615.196	7.50320
228.113	6.80026	340.420	7.33621	504.680	7.38062		
252.470	7.00161	381.839	7.37163	538.950	7.38513		
267.961	7.09971	411.522	7.37861	580.859	7.41761		
<i>T</i> = 305.000 K							
196.981	6.49447	380.549	7.49175	580.682	7.60489	700.399	8.60505
222.254	6.80256	425.015	7.51379	631.516	7.79972	710.316	8.80646
242.965	6.99838	457.121	7.52183	645.770	7.90003	710.331	8.80785
271.117	7.19596	458.769	7.52240	657.283	8.00208	718.849	9.00315
301.056	7.33643	500.808	7.53233	674.794	8.19993		
340.340	7.44187	538.848	7.55051	688.725	8.40123		

TABLE 1—continued

$\frac{\rho}{\text{kg} \cdot \text{m}^{-3}}$	$\frac{p}{\text{MPa}}$	$\frac{\rho}{\text{kg} \cdot \text{m}^{-3}}$	$\frac{p}{\text{MPa}}$	$\frac{\rho}{\text{kg} \cdot \text{m}^{-3}}$	$\frac{p}{\text{MPa}}$	$\frac{\rho}{\text{kg} \cdot \text{m}^{-3}}$	$\frac{p}{\text{MPa}}$
<i>T</i> = 307.000 K							
119.472	5.00316	273.926	7.39908	459.791	7.86014	649.470	8.50344
161.456	6.00166	300.229	7.54425	499.467	7.89878	658.071	8.60072
189.397	6.49998	340.559	7.68919	539.678	7.95481	658.518	8.60535
210.456	6.80075	340.741	7.69003	578.468	8.05164	673.107	8.80197
227.182	6.99948	378.329	7.76910	610.837	8.19623	685.360	9.00075
247.025	7.19471	419.963	7.82210	639.481	8.40578		
<i>T</i> = 310.000 K							
155.020	6.00051	264.673	7.60095	353.211	8.10090	570.374	8.70179
179.356	6.49351	277.154	7.70092	385.694	8.20079	588.407	8.80180
210.444	6.99664	291.371	7.80074	427.346	8.30003	588.550	8.80265
210.721	7.00047	308.364	7.90252	474.756	8.40050	603.289	8.90308
225.923	7.20093	328.085	8.00070	477.239	8.40624		
225.944	7.20120	328.532	8.00275	516.354	8.50172		
243.525	7.40085	328.685	8.00335	547.104	8.60117		
<i>T</i> = 313.000 K							
197.476	6.98123	240.312	7.59762	305.593	8.20157	409.059	8.70488
198.527	6.99890	258.473	7.80030	320.818	8.30093	436.766	8.80109
211.058	7.20004	268.556	7.90016	338.630	8.40270	437.166	8.80218
211.074	7.20024	279.937	8.00300	358.872	8.50311	467.349	8.90506
224.967	7.40087	292.317	8.10420	381.660	8.60122	494.667	9.00463
<i>T</i> = 320.000 K							
8.4539	0.50090	56.9151	3.00096	122.435	5.50056	232.038	8.00130
8.4910	0.50306	68.2227	3.49961	139.157	6.00096	232.100	8.00201
17.2596	1.00138	68.2550	3.50096	157.741	6.50054	259.881	8.40143
26.4470	1.50097	80.3370	4.00107	178.788	7.00056	284.322	8.69853
36.0748	2.00056	93.2587	4.50012	178.800	7.00087	313.692	9.00190
46.2109	2.50066	107.238	5.00052	203.232	7.50299		
<i>T</i> = 340.000 K							
7.9173	0.50035	61.8900	3.50035	106.512	5.50059	178.691	8.00036
16.1154	1.00141	61.9796	3.50477	119.199	6.00034	178.701	8.00077
24.5834	1.50120	72.3113	4.00339	132.678	6.50113	196.289	8.49859
33.3506	2.00013	83.1986	4.50478	146.982	7.00068	215.394	8.99873
42.4800	2.50024	94.4446	4.99812	146.997	7.00108		
51.9809	3.00024	94.6447	5.00679	162.259	7.49995		

The carbon dioxide used for the measurements was supplied by Messer Griesheim, F.R.G. {purity:  $x(\text{CO}_2) > 0.999991$ , where  $x$  denotes mole fraction; impurities:  $x(\text{O}_2) < 1.5 \times 10^{-6}$ ;  $x(\text{N}_2) < 3.2 \times 10^{-6}$ ;  $x(\text{H}_2\text{O}) < 1.7 \times 10^{-6}$ ;  $x(\text{CO}) < 1.2 \times 10^{-6}$ ;  $x(\text{hydrocarbons}) < 0.9 \times 10^{-6}$ ;  $x(\text{oil}) < 0.7 \times 10^{-6}$ }.

The experimental uncertainties of the single measuring values  $p$ ,  $\rho$ , and  $T$  were discussed in the previous paper<sup>(3)</sup> with this result: the uncertainty in pressure is less than 0.006 per cent or 30 Pa, whichever is greater, in density less than 0.015 per cent

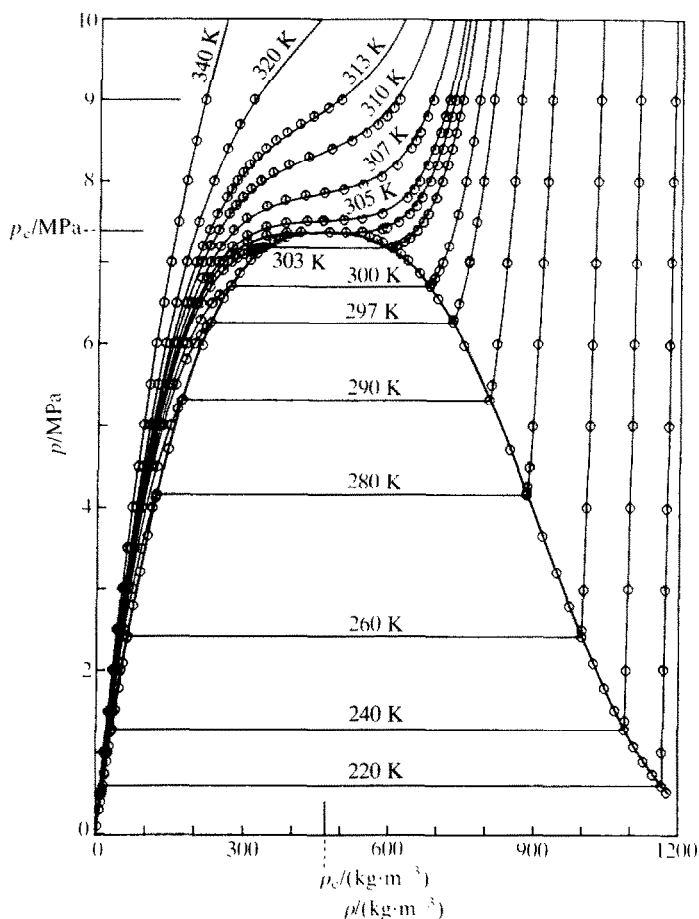


FIGURE 1. General view of the investigated  $(p, \rho, T)$  surface. The isotherms were calculated from the Bender equation of state<sup>(12)</sup> and the coexistence curve was calculated from new correlation equations of the vapour pressures and of the saturated-liquid and saturated-vapour densities.<sup>(2)</sup>

or  $0.0015 \text{ kg}\cdot\text{m}^{-3}$ ,† whichever is greater, and in temperature less than  $0.003 \text{ K}$ . On this basis the total uncertainty in density or in pressure was calculated by applying the Gaussian error-propagation formula; the reliability of these total uncertainties given below is estimated to be about 95 per cent.

Thus, the total relative uncertainty in density  $\Delta\rho/\rho$  of the  $(p, \rho, T)$  measurements has been determined to be less than  $\pm 0.015$  per cent to  $\pm 0.025$  per cent in the

† The uncertainty in the density of the  $\text{CO}_2$  measurements is slightly lower than that given in reference 3 because a considerably improved magnetic-suspension balance was used to measure the buoyant force on the sinkers. To transmit the suspension force from the pressurized measuring cell to the balance at ambient atmosphere, a new magnetic suspension coupling was developed by Löscher.<sup>(6)</sup> It consists of an upper electromagnet fixed at the balance and of a lower permanent magnet connected by a wire with the cage for the two sinkers in the measuring cell. Between the two magnets a high-strength metal disk was placed, separating the pressure region from the ambient atmosphere.

temperature range from 220 K to 290 K and from 320 K to 340 K at pressures up to 9 MPa. In the temperature range around the critical temperature ( $T_c = 304.136$  K), namely from 297 K to 313 K, the total uncertainty increases to  $\pm 0.035$  per cent for densities less than  $240 \text{ kg} \cdot \text{m}^{-3}$  and to  $\pm 0.020$  per cent for densities greater than  $650 \text{ kg} \cdot \text{m}^{-3}$  (critical density  $\rho_c = 467.6 \text{ kg} \cdot \text{m}^{-3}$ ). In the enlarged critical region ( $T = 297 \text{ K}$  to  $313 \text{ K}$  and  $\rho = 240 \text{ kg} \cdot \text{m}^{-3}$  to  $650 \text{ kg} \cdot \text{m}^{-3}$ ), relatively large deviations in density correspond to rather small deviations in pressure. Therefore, the total uncertainty in pressure is more suitable for comparisons than the uncertainty in density. The total relative uncertainty in pressure  $\Delta p/p$  of the ( $p, \rho, T$ ) values in this region is less than  $\pm 0.010$  per cent to  $\pm 0.020$  per cent.

Based on the new experimental results, a truncated virial equation has been established to determine values for the second and third virial coefficients. The equation represents the measured densities in the temperature range from 217 K to 340 K at densities up to  $0.35\rho_c$  within their reproducibility of better than  $\pm 0.005$  per cent. The form of the truncated virial equation is

$$Z = 1 + \sum_{i=1}^9 a_i \delta^{r_i} \tau^{t_i}, \quad (1)$$

with the compression factor  $Z = (p \cdot M)/(\rho \cdot R \cdot T) = p/(\rho_n \cdot R \cdot T)$ , the molar gas constant  $R = (8.31451 \pm 0.00021) \text{ J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}$ ,<sup>(7)</sup> the molar mass of carbon dioxide  $M = (44.0098 \pm 0.0016) \text{ g} \cdot \text{mol}^{-1}$ ,<sup>(8)</sup>  $\tau = T_c/T$ ,  $\delta = \rho/\rho_c$ , the critical temperature  $T_c = 304.136 \text{ K}$ ,<sup>(2)</sup> the critical density  $\rho_c = 467.6 \text{ kg} \cdot \text{m}^{-3}$ ,<sup>(2)</sup> the amount-of-substance density  $\rho_n = \rho/M$ , and the coefficients  $a_i$  and exponents  $r_i$  and  $t_i$  given in table 2. The structure of the equation has been found by using a new optimization method, developed by Setzmann and Wagner.<sup>(9)</sup> The estimated uncertainty of this equation is less than  $\pm 0.01$  per cent, with a reliability of about 95 per cent. This estimation is based on an error analysis described in previous papers.<sup>(5, 10)</sup>

Equation (1) corresponds to a virial equation

$$Z = 1 + B(T)\rho_n + C(T)\rho_n^2 + D(T)\rho_n^3,$$

truncated after the fourth virial coefficient. Numerical values for the second virial coefficient  $B$  and the third virial coefficient  $C$  calculated from this equation are listed

TABLE 2. Exponents and coefficients of equation (1)

$i$	$r_i$	$t_i$	$a_i$
1	1	-1	$0.98158714 \times 10^{-1}$
2	1	2	$-0.13329505 \times 10^1$
3	1	5	$0.76096097 \times 10^{-1}$
4	1	5.5	$-0.90567895 \times 10^{-1}$
5	2	2	$0.71016170$
6	2	4	$-0.18302968$
7	3	8.5	$-0.78864293 \times 10^1$
8	3	9.5	$0.23562227 \times 10^2$
9	3	10	$-0.15649249 \times 10^2$

TABLE 3. Second and third virial coefficients of carbon dioxide together with their uncertainties

$T/K$	$B/(\text{cm}^3 \cdot \text{mol}^{-1})$	$C/(\text{cm}^3 \cdot \text{mol}^{-1})^2$
220	$-247.52 \pm 1.0$	
240	$-202.13 \pm 0.8$	
260	$-168.27 \pm 0.7$	
280	$-142.11 \pm 0.6$	$5165 \pm 155$
300	$-121.35 \pm 0.5$	$4753 \pm 140$
320	$-104.49 \pm 0.4$	$4360 \pm 130$
340	$-90.57 \pm 0.3$	$3996 \pm 120$

in table 3 together with their uncertainties.<sup>‡</sup> The uncertainties of the virial coefficients have been determined in a way similar to that described in the methane paper.<sup>(5)</sup>

In order to get an impression of how the way of determining the second and third virial coefficients influences their numerical values and, accordingly, also their uncertainty range, the following fitting procedures have been performed in addition to that leading to equation (1): (a) truncated virial equations have also been fitted to the  $(p, \rho, T)$  surface limited not only by the maximum density  $\rho_{\max} = 0.35\rho_c$  (as has been done for obtaining equation 1), but also by  $\rho_{\max}$  values of  $0.3\rho_c$ ,  $0.2\rho_c$ , and  $0.1\rho_c$ ; (b) truncated virial equations have not been fitted to the  $(p, \rho, T)$  surface at once but only to the  $(p, \rho, T)$  values of the single isotherms limited by the different  $\rho_{\max}$  values mentioned under point (a). The results can be summarized as follows. For temperatures  $T \geq 280$  K, the values for  $B$  and  $C$  obtained from all these attempts agreed with each other within the uncertainties given in table 3. For  $T < 280$  K, however, there were large differences between the  $C$  values obtained from the entire surface fit (corresponding to equation 1) and the  $C$  values evaluated from the fits to single isotherms only. At 220 K, for instance, equation (1) yields a value for  $C$  which is about six times greater than that resulting from the isothermal fit. We suppose that the  $C$  values calculated from equation (1) (or from a surface fit in general) are more reliable than values obtained from an isothermal fit, at least for temperatures where the isotherms in the homogeneous gas region are extremely short because of the phase boundary.

In spite of the high accuracy of our  $(p, \rho, T)$  values, but keeping in mind the discrepancies discussed above, we list in table 3 only values of the third virial coefficients for  $T \geq 280$  K. It should be pointed out that most of the  $C$  values for  $T < 280$  K, which can be found in literature, are based on  $(p, \rho, T)$  measurements which are more inaccurate than ours.

#### 4. Discussion

A comparison of the new  $(p, \rho, T)$  values outside the critical region with several selected measurements of other workers is presented in figures 2 and 3 (relative

<sup>‡</sup> It should be noted that a density calculation using only these values of  $B$  and  $C$ , and neglecting the influence of the term which includes the fourth virial coefficient, describes the densities in the temperature range from 280 K to 340 K within the limits of uncertainty of  $\pm 0.01$  per cent only at pressures below 2.5 MPa.



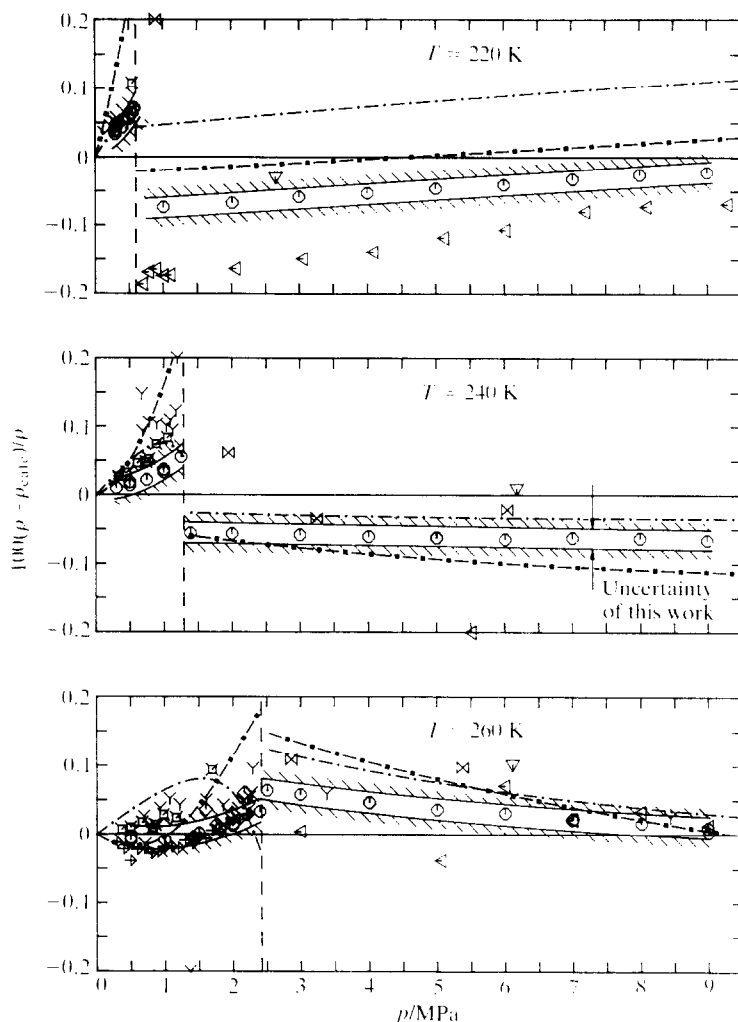


FIGURE 2. Relative-density deviations of experimental ( $p, \rho, T$ ) values and of calculated densities of carbon dioxide from values  $\rho_{\text{calc}}$  calculated from the equation of state by Pitzer and Schreiber.<sup>(11)</sup>  $\odot$ , This work;  $\Upsilon$ , Vukalovich *et al.*,<sup>(15)</sup>  $\boxtimes$ , Golovskii and Tsymarnyi,<sup>(17)</sup>  $\triangleleft$ , Popov and Sayapov,<sup>(18)</sup>  $\nabla$ , Kirillin *et al.*,<sup>(19)</sup>  $\boxtimes$ , Holste *et al.*,<sup>(20)</sup>  $\diamond$ , Rasskazov *et al.*,<sup>(21)</sup>  $\rightarrow$ , Jaeschke (refractive-index measurements),<sup>(22)</sup> — — —, phase boundary; — — —, values calculated from Bender's equation of state;<sup>(12)</sup> —■—, values calculated from Ely *et al.*'s equation of state.<sup>(13)</sup> The experimental results of the experimentalists named above cover a temperature range of  $\pm 3$  K around the temperature values given in these diagrams.

deviations in density). Both figures show the deviations between the measured values and the values calculated from the equation of state established by Pitzer and Schreiber.<sup>(11)</sup> The equation yields for this part of the ( $p, \rho, T$ ) surface essentially the same values as the IUPAC equation<sup>(1)</sup> does, because, for this region, Pitzer and Schreiber fitted the equation only to values from the IUPAC table. In the critical region, however, they fitted their equation not to values from the IUPAC table but

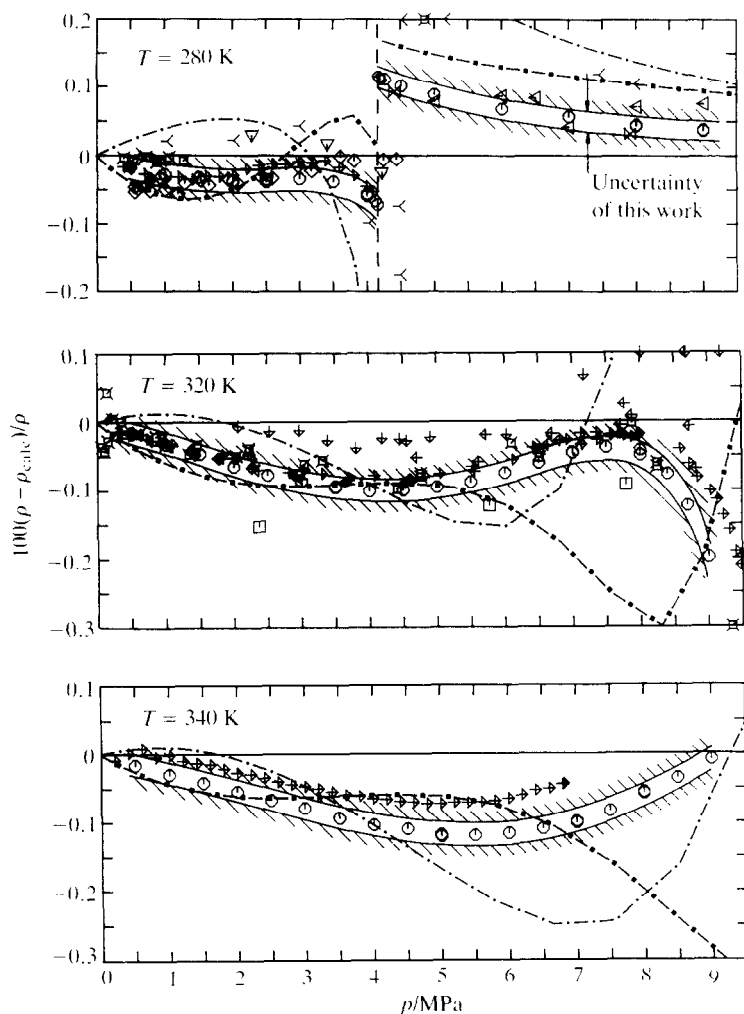


FIGURE 3. Relative-density deviations of experimental ( $p, \rho, T$ ) values and of calculated densities of carbon dioxide from values  $\rho_{\text{calc}}$  calculated from the equation of state by Pitzer and Schreiber.<sup>(11)</sup>  $\odot$ , This work;  $\square$ , Ely *et al.*;<sup>(13)</sup>  $\triangleleft$ , Vukalovich *et al.*;<sup>(14)</sup>  $\phi$ , Michels and Michels;<sup>(16)</sup>  $\boxtimes$ , Golovskii and Tsymarnyi;<sup>(17)</sup>  $\triangleleft$ , Popov and Sayapov;<sup>(18)</sup>  $\nabla$ , Kirillin *et al.*;<sup>(19)</sup>  $\boxtimes$ , Holste *et al.*;<sup>(20)</sup>  $\diamond$ , Rasskazov *et al.*;<sup>(21)</sup>  $\rightarrow$ , Jaeschke (refractive-index measurements);<sup>(22)</sup>  $\leftarrow$ , Jaeschke (Burnett measurements);<sup>(22)</sup> ---, phase boundary;<sup>(2)</sup> -.-, values calculated from Bender's equation of state;<sup>(12)</sup> —■—, values calculated from Ely *et al.*'s equation of state.<sup>(13)</sup> The experimental results of the experimentalists named above cover a temperature range of  $\pm 3$  K around the temperature values given in these diagrams.

to recent experimental values. In addition to the experimental results, the figures also show the plot of values calculated from the Bender equation<sup>(12)</sup> and from the formulation of Ely *et al.*<sup>(13)</sup>

Furthermore, both figures illustrate the uncertainty of the new ( $p, \rho, T$ ) values and contain the position of the phase boundary calculated from a new vapour-pressure equation.<sup>(2)</sup>

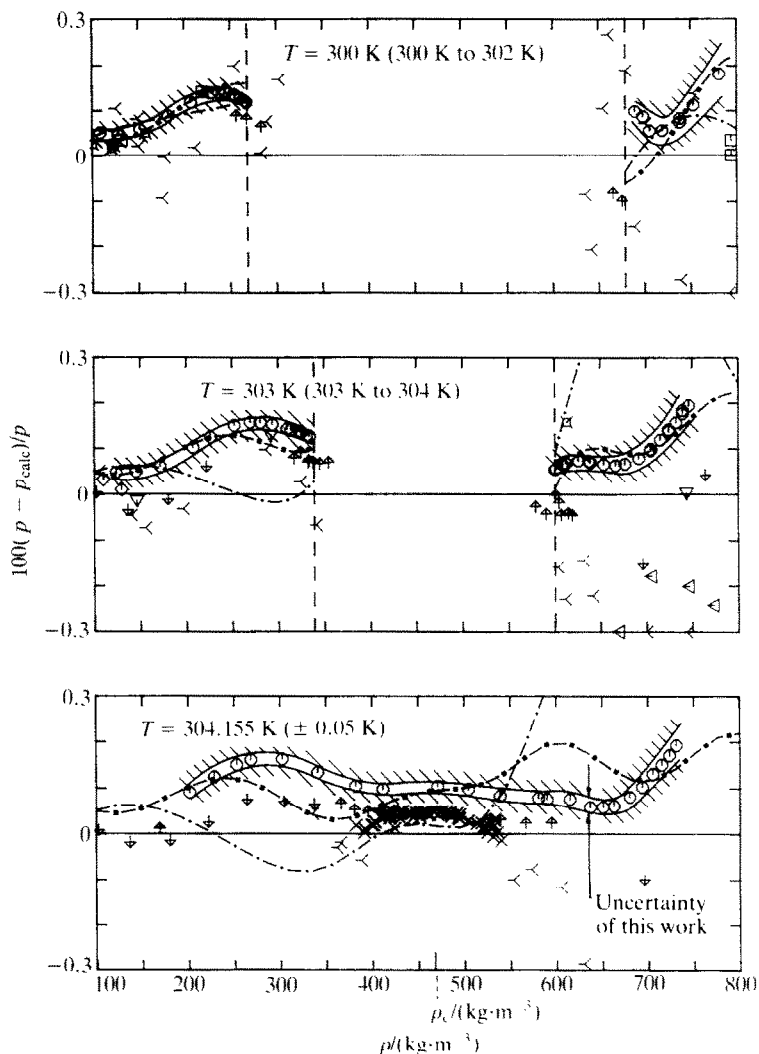


FIGURE 4. Relative-pressure deviations of experimental ( $p, \rho, T$ ) values and of calculated pressures of carbon dioxide from values  $p_{\text{calc}}$  calculated from the equation of state by Pitzer and Schreiber.<sup>(11)</sup>  $\circ$ , This work;  $\square$ , Ely *et al.*,<sup>(13)</sup>  $\triangleleft$ , Vukalovich *et al.*,<sup>(14)</sup>  $\Psi$ , Michels and Michels,<sup>(16)</sup>  $\triangleleft$ , Popov and Sayapov,<sup>(18)</sup>  $\nabla$ , Kirillin *et al.*,<sup>(19)</sup>  $\bowtie$ , Holste *et al.*,<sup>(20)</sup>  $\diamond$ , Rasskazov *et al.*,<sup>(21)</sup>  $\Phi$ , Michels *et al.*,<sup>(25)</sup>  $\times$ , Wentdorf,<sup>(26)</sup> — — —, phase boundary;<sup>(2)</sup> — · —, values calculated from Bender's equation of state;<sup>(12)</sup> —■—, values calculated from Ely *et al.*'s equation of state.<sup>(13)</sup>

The figures make clear that none of the three equations of state is able to describe the new ( $p, \rho, T$ ) values within the estimated experimental uncertainty. In general, the deviations amount to as much as  $\pm 0.15$  per cent; at higher temperatures they even increase to  $\pm 0.3$  per cent. The results of the other experimentalists agree mostly within their claimed uncertainty (in general  $\pm 0.05$  per cent to  $\pm 0.2$  per cent) with

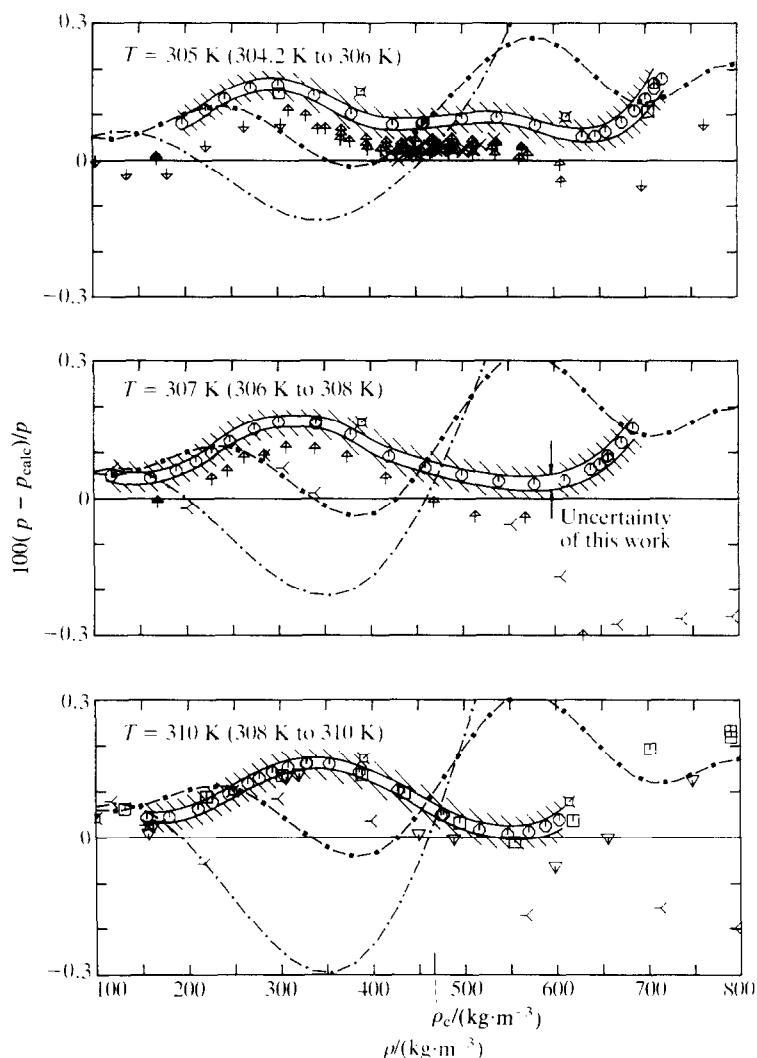


FIGURE 5. Relative-pressure deviations of experimental ( $p, \rho, T$ ) values and of calculated pressures of carbon dioxide from values  $\rho_{\text{calc}}$  calculated from the equation of state by Pitzer and Schreiber.<sup>(11)</sup>  $\odot$ , This work;  $\square$ , Ely *et al.*,<sup>(13)</sup>  $\prec$ , Vukalovich *et al.*,<sup>(14)</sup>  $\Phi$ , Michels and Michels,<sup>(16)</sup>  $\nabla$ , Kirillin *et al.*,<sup>(19)</sup>  $\boxtimes$ , Holste *et al.*,<sup>(20)</sup>  $\oplus$ , Michels *et al.*,<sup>(25)</sup>  $\times$ , Wentdorf,<sup>(26)</sup> — —, values calculated from Bender's equation of state,<sup>(12)</sup> —■—, values calculated from Ely *et al.*'s equation of state.<sup>(13)</sup>

our ( $p, \rho, T$ ) values. In comparison with our measurements, however, the values of the other workers exhibit greater scatterings (Vukalovich *et al.*)<sup>(14, 15)</sup> or larger systematic deviations (Michels and Michels at 320 K,<sup>(16)</sup> Golovskii and Tsymarnyi,<sup>(17)</sup> Popov and Sayapov,<sup>(18)</sup> Kirillin *et al.*<sup>(19)</sup>). In the temperature and pressure range considered in this paper, the measurements of Holste *et al.*,<sup>(20)</sup> Rasskazov *et al.*,<sup>(21)</sup> and Jaeschke<sup>(22)</sup> agree with our values within  $\pm 0.05$  per cent,

whereas the values of Ely *et al.*<sup>(13)</sup> deviate slightly systematically up to  $-0.08$  per cent at 320 K which is, however, within the uncertainty given for these values. The experimental results of Vukalovich *et al.*<sup>(23)</sup> and Kholodov *et al.*<sup>(24)</sup> were considered, but not selected because of great systematic deviations.

Most of the experimental results of this work in the critical region are compared in figures 4 and 5 (relative deviations of pressure) with selected measurements of other workers and also with values calculated from the three equations of state mentioned above. Just as outside the critical region, these equations are not able to represent our values in the critical region; the deviations of the calculated values amount to several times the total uncertainty in pressure of the new results. Our  $(p, \rho, T)$  values agree very well with those of Ely *et al.*<sup>(13)</sup> at 305 K and 310 K and agree only slightly less well with those of Holste *et al.*<sup>(20)</sup> The values of Michels *et al.*<sup>(25)</sup> and of Wentdorf<sup>(26)</sup> show deviations which are almost parallel below our values. These systematic deviations are probably caused by an uncertain relation between their temperature scale and the IPTS-68. A temperature shift of  $-0.025$  K would bring Wentdorf's and Michels *et al.*'s results into better agreement with the  $(p, \rho, T)$  values of this work. Such a value of the temperature shift is also in reasonable accordance with those suggested by Ely *et al.*,<sup>(13)</sup> Albright *et al.*,<sup>(27)</sup> and Levelt Sengers and Chen.<sup>(28)</sup>

The result of these comparisons can be summarized by the statement that the three discussed equations of state are not able to represent the new  $(p, \rho, T)$  results and those of other workers in that part of the single-phase region measured by us. The results of the other experimentalists agree mostly within their claimed uncertainty with our values, but in view of the values of these uncertainties, the observed scatterings, and tendencies of their measured values, it becomes apparent that these results are less suitable for establishing an equation of state which shall be of really high accuracy.

When considering the discussion and the conclusions with regard to the  $(p, \rho, T)$  values, it does not seem to be reasonable to compare in detail the new values for the virial coefficients, listed in table 3, with those evaluated from the experimental results of the other authors. Therefore, the virial coefficients derived from the new  $(p, \rho, T)$  values have been compared only with the virial coefficients given by Holste *et al.*<sup>(20)</sup> and by those experimentalists which have been examined and listed by Dymond and Smith.<sup>(29)</sup> Our second virial coefficients clearly agree within their uncertainties with those of Holste *et al.*<sup>(20)</sup> and with those of Waxman *et al.*<sup>(30)</sup> Values of the third virial coefficients given in the literature are rather poor and great deviations exist between the values listed in reference 29. Taking into account these differences, the values for  $C$  of Holste *et al.*<sup>(20)</sup> are in satisfying agreement with our values given in table 3: they deviate up to  $470 \text{ (cm}^3 \cdot \text{mol}^{-1})^2$  at 280 K.

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