International Journal of Thermophysics, Vol. 8, No. 2, 1987

Compression Factor and Vapor Pressure of Bromotrifluoromethane in the Temperature Range 245–393 K at Pressures up to 12 MPa

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Received March 18, 1986

The compression factors and vapor pressures have been measured on bromotrifluoromethane using a Burnett apparatus. The results on the compression factor cover the range of temperatures 263 to 393 K and of pressures 0.14 to 11.6 MPa, corresponding to a density variation from 7 to 1367 $kg \cdot m^{-3}$. The experimental uncertainty of these 176 measurements of compression factor was estimated to be 0.2%. Thirty measurements of vapor pressure were made for temperatures 245 to 339 K, with an experimental uncertainty of 0.1%. Based on these results, the second virial coefficients were determined for temperatures 293 to 393 K.

KEY WORDS: bromotrifluoromethane; compression factor; second virial coefficient; vapor pressure.

1. INTRODUCTION

Bromotrifluoromethane ($CBrF_3$) is expected to be one of the most suitable working fluids for the LNG power generation systems. The research group of the present authors has been measuring the thermodynamic properties of this substance extensively and systematically. The coexistence curve near the critical point was measured and the critical temperature and density were determined based on these results [1]. The measurements of saturated liquid density [2] and those of isobaric specific heat capacity in the gaseous region [3] were also published elsewhere. This paper reports 176 measurements of the compression factor with an experimental uncertainty of 0.2% using a Burnett apparatus and 30 measurements of the

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0195-928X/87/0200-0217$05.00/0

vapor pressure with an experimental uncertainty of 0.1%. These measurements cover a wide range of temperatures, 245 to 393 K, and of pressures, 0.14 to 11.6 MPa, which corresponds to the density variation from 7 to 1367 $kg \cdot m^{-3}$. Based on these results the second virial coefficients are also reported. The sample purity used was 99.977 wt% pure $CBrF_3$. The remaining impurities were trifluoromethane (CHF_3) ($\leqslant$0.014 wt%), trifluorochloromethane ($CClF_3$) ($\leqslant$0.004 wt%), and air ($\leqslant$0.005 wt%).

2. EXPERIMENTAL PROCEDURE

A Burnett apparatus, shown schematically in Fig. 1, and the data reduction method used here were described in detail in a previous publication [4]. The apparatus was used for the compression factor measurements of dichlorodifluoromethane [4] and an azeotropic mixture of chlorodifluoromethane + chloropentafluoroethane, whose refrigerant number is R502 [5]. A sample vessel (98-mm i.d., 122-mm o.d., and 500-cm^3 inner volume) and an expansion vessel (78 mm, 98 mm, and 250 cm^3)

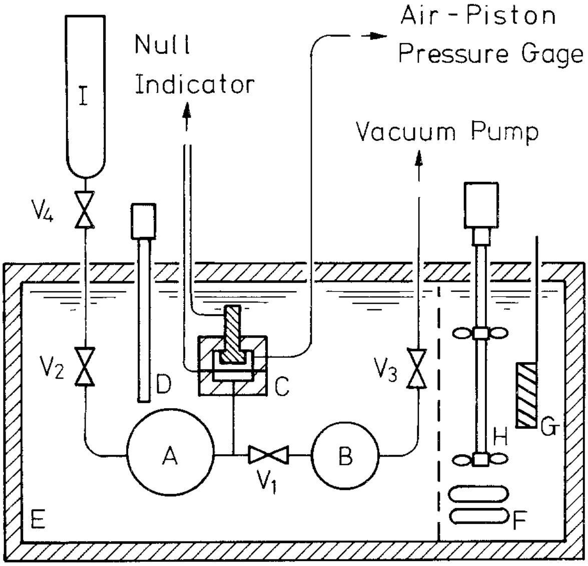

Fig. 1. Schematic diagram of the Burnett apparatus. A, sample vessel; B, expansion vessel; C, differential pressure detector; D, platinum resistance thermometer; E, constant-temperature bath; F, electric heater; G, chilling unit; H, stirrer; I, sample bottle; V_1, constant-volume valve; V_2, V_3, and V_4, valves.

were made spherically of 304 stainless steel and were connected by a constant-volume valve. A differential pressure detector was connected with the sample vessel to separate the sample fluid from the nitrogen gas in the pressure-transmitting system by a stainless-steel membrane. The apparatus was calibrated with 99.9999 mol% pure helium for four isotherms, 303, 333, 353, and 373 K, so as to determine the cell constant.

The Burnett apparatus was completely immersed in a stirred fluid bath whose temperature was controlled within a fluctuation of ±10 mK. We measured the temperature of the bath fluid with a 25-Ω platinum resistance thermometer (Chino Model R800-1), which was installed in the vicinity of the sample vessel, with an uncertainty of 10 mK. Balancing the pressure of the sample fluid with that of nitrogen gas by means of the differential pressure detector, we measured the pressure with an uncertainty of 1.5 kPa by using two different air-piston pressure gauges (Ruska Models 2465 and 2470) depending on the pressure range. The thermal equilibrium between the sample fluid in the sample vessel and the heat-transfer medium in the bath was confirmed by monitoring the pressure variation of the sample fluid. Then the measurement of temperature and pressure was conducted.

The compression factors were measured by both the Burnett-isothermal expansion method and the Burnett-isochoric coupled method with an uncertainty of 0.2%. The measurements of vapor pressure were made under the coexistence of a liquid phase of the sample fluid with its vapor phase within the sample vessel with an uncertainty of 0.1%.

3. RESULTS AND DISCUSSION

3.1. Vapor Pressure

Experimental results of the vapor pressure measurements are tabulated in Table I. Thirty measurements obtained in three different series of experiments cover the temperature range from 245 to 339 K, which corresponds to the pressure range from 0.34 to 3.89 MPa. The reproducibility of the present measurements was examined at seven different temperatures, which show a good agreement with each other within a discrepancy of ±0.05%. Based on six measurements above 335 K, the logarithmic pressure was correlated as a linear function of temperature and then the critical pressure was determined to be 3.964 MPa by extrapolating this correlation to the critical temperature of 340.08 K measured by Higashi et al. [1].

The available experimental data of vapor pressure [6–9] including the present results cover the temperature range from 160 K to the critical tem-

Table I. Experimental Results for the Vapor Pressure, P_s, of Bromotrifluoromethane

T(K)	P_s(MPa)
245.137	0.3452
253.168	0.4556
263.171	0.6274
273.149	0.8425
283.210	1.1104
293.170	1.4307
293.188	1.4312
298.134	1.6154
298.183	1.6155
303.154	1.8160
303.190	1.8173
307.156	1.9906
308.146	2.0351
308.176	2.0374
311.347	2.1867
313.150	2.2740
315.118	2.3747
318.146	2.5339
323.637	2.8153
327.148	3.0565
328.160	3.1202
330.157	3.2484
333.127	3.4498
333.154	3.4497
335.170	3.5908
337.106	3.7350
337.128	3.7349
338.113	3.8093
338.129	3.8118
339.126	3.8892

perature. These 82 data, excluding those whose temperature is greater than 340.08 K, were fitted to the following correlation with an average deviation of 0.43%.

$$\ln(P_s/P_c) = (T_c/T)[a(1-T/T_c) + b(1-T/T_c)^{1.5} + c(1-T/T_c)^{2.5} + d(1-T/T_c)^5] \qquad (1)$$

Here, P_s denotes the vapor pressure in MPa, T is the temperature in K, P_c is the critical pressure, and T_c is the critical temperature. The numerical values of coefficients a, b, c, and d are given in Table II. The term

Table II. Values of Constants and Coefficients in Eq. (1)

$a = -6.8481$
$b = 1.4976$
$c = -1.510$
$d = -3.04$
$T_c = 340.08$ K
$P_c = 3.964$ MPa

$d(1 - T/T_c)^5$ is effective only for the enlarged temperature range below 240 K. Equation (1) describes the present results with an average deviation of 0.05%, the data of Du Pont [6] with 0.18%, the data of McDonald et al. [7] with 0.49%, the data of Perel'shtein and Aleshin [8] with 0.12%, and the data of Jaeger [9] with 0.32%. The normal boiling point is calculated as 215.36 K.

The deviation plots of the experimental data from Eq. (1) are depicted in Fig. 2. The available correlations proposed by Du Pont [6], by Rombusch [10], and by Perel'shtein and Aleshin [11] are compared with Eq. (1) as shown in Fig. 2. The present results deviate from Eq. (1) within

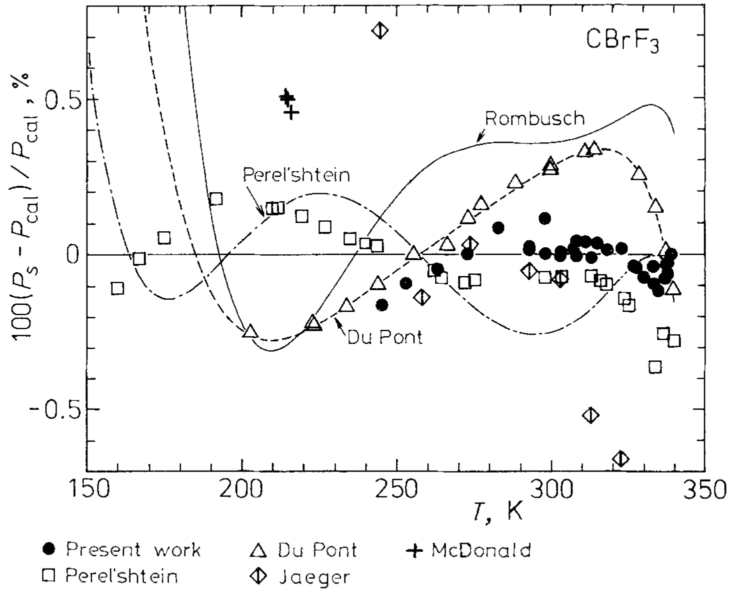

Fig. 2. Comparison of the experimental data of the vapor pressure, P_s, with the values calculated by Eq. (1).

Table III. Experimental Results for the Compression Factor, z, of Bromotrifluoromethane

T(K)	P(MPa)	z
263.157	0.5375	0.8843[a]
263.155	0.3735	0.9247[a]
273.141	0.7977	0.8408[a]
273.144	0.5634	0.8934[a]
273.155	0.3895	0.9292[a]
283.150	0.8384	0.8528[a]
283.150	0.5891	0.9016[a]
283.147	0.4059	0.9348[a]
293.059	1.2208	0.7978
293.059	0.8786	0.8638
293.059	0.6142	0.9086
293.059	0.4228	0.9410
293.059	0.2867	0.9600
293.059	0.1933	0.9741
303.136	1.7522	0.7175
303.136	1.3117	0.8084
303.136	0.9390	0.8709
303.136	0.6545	0.9136
303.136	0.4478	0.9408
303.136	0.3040	0.9612
303.136	0.2045	0.9732
313.150	1.5691	0.7934
313.150	1.1315	0.8611
313.150	0.7923	0.9074
313.150	0.5447	0.9389
313.150	0.3701	0.9599
313.150	0.2495	0.9740
313.150	0.1672	0.9823
318.137	2.5626	0.1055[a]
323.148	3.8767	0.1572[a]
323.146	2.6137	0.6333
323.146	2.0482	0.7469
323.146	1.5100	0.8287
323.146	1.0721	0.8855
323.146	0.7445	0.9255
323.146	0.5083	0.9509
323.146	0.3442	0.9690
323.146	0.2313	0.9802
323.146	0.1547	0.9866
324.154	2.8552	0.5735[a]
325.151	2.8819	0.5771[a]

[a] Measured by the Burnett-isochoric coupled method.

Table III *(Continued)*

T(K)	P(MPa)	z
328.145	5.2054	0.2079[a]
328.145	2.9565	0.5868[a]
333.165	6.5520	0.2579[a]
333.129	3.6795	0.1674[a]
333.176	3.4649	0.4647[a]
333.175	3.0801	0.6022[a]
333.151	2.5825	0.6984
333.151	1.9479	0.7928
333.151	1.4035	0.8597
333.151	0.9829	0.9060
333.151	0.6763	0.9383
333.151	0.4594	0.9592
333.151	0.3097	0.9731
333.151	0.2079	0.9829
333.151	0.1389	0.9883
336.143	3.6164	0.4658[a]
337.158	3.6588	0.4698[a]
338.137	7.9026	0.3065[a]
338.162	3.8182	0.2158[a]
338.150	3.6997	0.4737[a]
339.143	3.9189	0.2209[a]
339.148	3.8926	0.3302[a]
339.163	3.7410	0.4776[a]
340.134	4.0307	0.2266[a]
340.150	4.0018	0.2322[a]
340.136	3.9665	0.3355[a]
341.138	4.1613	0.2332[a]
341.136	4.0977	0.2371[a]
341.130	4.0374	0.3405[a]
341.140	3.8224	0.4852[a]
342.157	4.2773	0.2390[a]
342.145	4.1042	0.3452[a]
343.146	9.2551	0.3538[a]
343.174	9.2628	0.3541[a]
343.136	5.4954	0.2428[a]
343.107	4.3786	0.2316[a]
343.149	4.3787	0.2439
343.166	4.2994	0.2473[a]
343.149	4.1708	0.3497
343.149	3.9032	0.4925
343.127	3.8670	0.5039[a]
343.149	3.3128	0.6290
343.149	2.5875	0.7394
343.149	1.9090	0.8210
343.149	1.3583	0.8791

Table III *(Continued)*

T(K)	P(MPa)	z
343.149	0.9432	0.9188
343.149	0.6456	0.9464
343.149	0.4370	0.9640
343.149	0.2939	0.9759
343.149	0.1970	0.9843
348.150	10.6321	0.4006
348.150	4.8119	0.2728
348.150	4.4848	0.3827
348.150	4.0568	0.5210
348.150	3.3617	0.6497
348.150	2.5879	0.7527
348.150	1.8937	0.8289
348.150	1.3402	0.8829
348.150	0.9282	0.9203
348.150	0.6344	0.9466
348.150	0.4294	0.9643
348.150	0.2889	0.9762
348.150	0.1935	0.9841
353.141	7.3944	0.3176[a]
353.108	6.5102	0.2930[a]
353.128	5.6043	0.2882[a]
353.141	4.5601	0.4661
353.141	3.9017	0.6002
353.141	3.0901	0.7153
353.141	2.3072	0.8038
353.141	1.6551	0.8677
353.141	1.1571	0.9130
353.141	0.7939	0.9427
353.141	0.5393	0.9638
353.141	0.3633	0.9772
353.141	0.2435	0.9855
353.141	0.1625	0.9899
363.146	11.1911	0.4363
363.225	9.3056	0.3888[a]
363.138	8.1717	0.3578[a]
363.136	6.8671	0.3436[a]
363.146	6.1310	0.3596
363.146	5.2596	0.4641
363.146	4.4124	0.5858
363.146	3.5188	0.7029
363.146	2.6346	0.7918
363.146	1.8960	0.8574
363.146	1.3267	0.9026
363.146	0.9123	0.9339
363.146	0.6206	0.9558

Table III (*Continued*)

T(K)	P(MPa)	z
363.146	0.4184	0.9694
363.146	0.2813	0.9807
363.146	0.1880	0.9864
373.133	11.2190	0.4565
373.133	9.8533	0.4201[a]
373.140	8.1611	0.3976[a]
373.133	6.8344	0.4184
373.133	5.6496	0.5203
373.133	4.5976	0.6371
373.133	3.5478	0.7397
373.133	2.6108	0.8189
373.133	1.8483	0.8723
373.133	1.2941	0.9189
373.133	0.8847	0.9451
373.133	0.5995	0.9636
373.133	0.4035	0.9759
373.133	0.2708	0.9854
373.133	0.1808	0.9900
383.150	11.5507	0.4798
383.133	9.4403	0.4481[a]
383.150	7.4322	0.4644
383.150	5.9657	0.5609
383.150	4.7191	0.6675
383.150	3.5685	0.7594
383.150	2.5933	0.8304
383.150	1.8305	0.8818
383.150	1.2666	0.9181
383.150	0.8646	0.9429
383.150	0.5853	0.9604
383.150	0.3940	0.9725
383.150	0.2639	0.9804
383.150	0.1770	0.9889
393.147	10.7428	0.4972
393.147	7.5821	0.5280
393.147	5.9565	0.6240
393.147	4.6119	0.7269
393.147	3.3779	0.8011
393.147	2.4141	0.8613
393.147	1.6860	0.9051
393.147	1.1579	0.9352
393.147	0.7866	0.9559
393.147	0.5300	0.9690
393.147	0.3558	0.9788
393.147	0.2385	0.9871
393.147	0.1590	0.9904

±0.1% except three measurements at 245, 298, and 335 K. The largest deviation is −0.16% at 245 K. Du Pont presented the data in the range of temperatures 203 to 338 K. These data are described by the correlation proposed by Du Pont with an average deviation of 0.01%. The correlation proposed by Rombusch represents these data with an average deviation of 0.18%, although the calculated values above 220 K are systematically larger than the experimental data of Du Pont. The data of Du Pont are systematically larger than the present results by 0.05–0.3% except near the critical temperature. The pressures measured by Perel'shtein and Aleshin are larger than those by Du Pont below 255 K, although smaller above that temperature. The differences at about 200 and 315 K are the largest, about 0.4%. McDonald et al. measured vapor pressures for temperatures 214 to 216 K. Their data are higher than those of Perel'shtein and Aleshin by about 0.35%. Jaeger measured vapor pressures for temperatures 245 to 323 K. These data deviate from the present results with a great scatter of about ±0.9%. No correlations for vapor pressure ever reported [6, 10, 11] represent the present results within the experimental uncertainty.

3.2. Compression Factor

The unsmoothed 176 measurements for the compression factor are given in Table III. Measurements along 12 isotherms of 293, 303, 313, 323, 333, 343, 348, 353, 363, 373, 383, and 393 K were made by the Burnett-isothermal expansion method, while the Burnett-isochoric coupled method was employed for 8 measurements in the lower-temperature, gaseous phase and for 42 measurements both in the dense liquid region and in the region near the coexistence curve. While the experiments were conducted, we paid careful attention to the thermal equilibrium between the sample fluid and the heat-transfer medium. The required time interval to reach the thermal equilibrium after the change of state is shorter for the measurements in the gaseous state but longer for those by the isochoric method. Especially, the measurements in the dense liquid region and near the coexistence curve took a very long period of time (6–12 h) until thermal equilibrium was confirmed.

The present results for the compression factor were compared with the available experimental data [6, 8] as well as the available equations of state [6, 10, 11]. The present results of the compression factor were converted into density values by using the gas constant for bromotrifluoromethane of 55.8345 $\mathrm{J \cdot kg^{-1} \cdot K^{-1}}$. Then the present results of pressure were compared with the available equations of state. Typical comparisons are shown in Fig. 3, where the pressure deviations of the experimental data from the pressure values calculated by the Rombusch

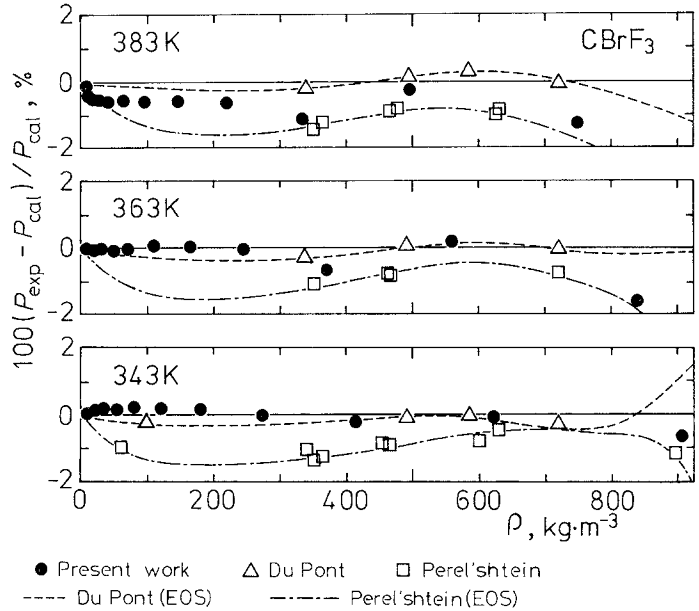

Fig. 3. Comparison of the *PVT* data with the Rombusch equation of state for $CBrF_3$ along the 343, 363, and 383 K isotherms.

equation of state [10] are plotted. In this figure the pressure deviations of the values calculated by two other equations of state (EOS) [6, 11] from those by the Rombusch equation of state are also depicted. The pressure deviations of the available experimental data whose temperature is within a difference of 3 K from the temperature inscribed are also depicted in Fig. 3. The data reported by Du Pont [6] cover the range of temperatures 231 to 444 K and of pressures 0.14 to 11.18 MPa, which corresponds to the density variation from 12 to 720 $kg \cdot m^{-3}$. These data agree with the present results within a pressure deviation of ±0.5%. Perel'shtein and Aleshin [8] measured the *PVT* properties in the range of temperatures 283 to 420 K and of pressures 0.82 to 10.37 MPa, which corresponds to the density variation from 62 to 1000 $kg \cdot m^{-3}$. The pressure values of the Perel'shtein–Aleshin data are systematically smaller than the present results by about 1%. The Du Pont equation of state [6] reproduces the present results within a deviation of ±1% in the range of densities up to about 900 $kg \cdot m^{-3}$, as the Rombusch equation of state [10] does. These two equations agree with each other within ±0.5% and may be applied to the density range up to 900 $kg \cdot m^{-3}$. The pressure values calculated by the Perel'shtein–Aleshin equation of state [11] are systematically smaller than

Table IV. Second Virial Coefficients, B, for Bromotrifluoromethane

T(K)	B ($\mathrm{cm^3 \cdot mol^{-1}}$)
293.06	−304
303.14	−278
313.15	−269
323.15	−252
333.15	−236
343.15	−229
348.15	−232
353.14	−207
363.15	−208
373.13	−200
383.15	−194
393.15	−187

the present results by about 1%. The Perel'shtein–Aleshin equation of state, however, represents their own experimental data with an average deviation of 0.07%.

3.3. Second Virial Coefficients

The second virial coefficients for bromotrifluoromethane were determined by fitting the present results to the virial equation of state truncated at the third term. The results are tabulated in Table IV and the uncertainty of these results was estimated to be 5%. The present results are the first information obtained since the available data for the second virial coefficients were not found as far as our present survey could determine.

ACKNOWLEDGMENTS

We are greatly indebted to Du Pont–Mitsui Fluorochemicals Co., Ltd., Tokyo, for kindly furnishing the sample of R13B1 and to Nippon Sanso KK, Tokyo, for kindly furnishing the sample of helium. We are also grateful to the National Research Laboratory of Metrology, Ibaraki, Japan, for their calibration of the thermometer used. Y. Kato, K. Kawazoe, and Y. Hirayama have provided valuable assistance in the experiments.

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