P-V-T Relations for Methane

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Measurements of the gas compressibility of methane were made in the region 0° to 350°, 16 to 400 atm., and 0.75 to 12.5 mole liter^{-1}. From these results, values were derived for the compressibility factor $Z = PV/RT$; second, third, and fourth virial coefficients B, C, and D, respectively, in the equation $PV = RT\ (1 + B/V + C/V^2 + D/V^3 + \ldots)$; and parameters of the Beattie-Bridgeman and Benedict-Webb-Rubin equations of state.

THE pressure-volume-temperature relations of methane were determined as part of a continuing project of the U. S. Bureau of Mines to investigate, as conclusively as possible, the gaseous state properties of hydrocarbons, fluorocarbons, and mixtures of hydrocarbons and fluorocarbons. The literature on pure methane is quite extensive, with every degree of quality represented. Several articles that report noteworthy *P-V-T* data, but for which no purpose would be served by comparing them in detail with present values are given (*15, 16, 19, 21*).

Some of the best modern values for the gas compressibility of methane, as reported by Michels and Nederbragt (*18*) and Schamp, Mason, Richardson, and Altman (*23*), cover the ranges 0° to 150° and 0.8 to 8.0 mole liter.$^{-1}$ The new values, which cover the region 0° to 350°, 16 to 400 atm., and 0.75 to 12.5 mole liter^{-1} with an accuracy and precision comparable to that reported by Michels and Nederbragt (*18*), and Schamp and coworkers (*23*), were obtained in order to provide data over wider ranges of variables than were available in the past for deriving intermolecular potential energy functions and closed equations of state. Also, additional *P-V-T* data on methane were needed to complete a self-consistent set of data for the methane-tetrafluoromethane system, to be reported in future publication. Derived values of the compressibility factors, virial coefficients, and parameters of two equations of state are given. Correlations of the second, third, and fourth virial coefficients of methane in terms of the Lennard-Jones [12, 6] Lennard-Jones [28, 7], Buckingham [6-exp], Stockmayer, and Kihara intermolecular potential energy functions were published previously (*12*).

Because of the widespread use and acceptance of American Petroleum Institute Research Project 44 selected values for compressed gases (*1*), it is necessary to point out that the new values for the compressibility factor of methane differ significantly from the API RP 44 selection. The differences found are considered excessive in light of the accuracy of the present methods and results as documented in text and in previous publications (*12, 13, 14*).

EXPERIMENTAL PROCEDURES

Method. The compressibility apparatus and method were described in detail in previous publications (*3, 13, 14*). Briefly, the method was as follows. The methane sample was weighed in a sealed thin-walled pycnometer that was constructed of stainless steel and designed to serve as a loosely fitting liner when placed inside the compressibility bomb. The pycnometer terminated at one end in a small borosilicate glass capillary tube, of known diameter and length, which remained sealed during the assembly of the bomb and the introduction of mercury into the evacuated void space in the bomb and manifold of the compressibility apparatus. Mercury was pumped into the void space from a thermostated quantitative-displacement, volumetric compressor. A null reading for the compressor was determined as the setting at which the pressure exerted by the sample inside the sealed pycnometer equaled the mercury pressure in the void space. After the null setting was made, the capillary tube was snapped off in a manner described (*3*), allowing mercury under pressure to flow into the pycnometer and compress the sample. For each compressor setting, the volume occupied by the sample was calculated from the volume of the pycnometer, the compressor reading, the null, and the predetermined variation of the volume of the entire system as a function of temperature and pressure. Pressures were measured with a deadweight gage that was calibrated against the vapor pressure of pure carbon dioxide, 26,144.7 mm. of Hg at 0° (*8*). Corrections for the variation of the effective piston area with pressure were based on the values for a 0.05 in.^{2} piston given by Dadson (*11*). The temperature of the compressibility bomb, which was controlled to ± 0.001° in a thermostatically controlled bath, was measured with a platinum resistance thermometer that had been calibrated by the National Bureau of Standards in terms of the International Temperature Scale [T, ° K. = t, ° C. (Int., 1948) + 273.16]. The more recent definition of the absolute scale, 0° C. = 273.15° K. (*24*), was not used because much of the work was completed before the scale was defined. Conversion from the International Temperature Scale, T, ° K. (Int.), to the thermodynamic temperature scale, T, ° K. (thermodynamic) was made according to a relationship derived by Beattie (*4*). Measurements of the ice-point resistance of the thermometer, at the beginning and end of the experimental work, showed no significant change.

The liter was chosen as the unit of volume in the equation of state correlations, but the virial coefficients were calculated in volume units of cubic centimeters (1 cc.^{3} = 0.9999720 × 10^{-3} liter) to facilitate comparison with theoretical values. Values of the gas constant used were R = 0.0820544 liter atm. deg.$^{-1}$, mole^{-1}, and R = 82.0567 cc.^{3} atm. deg.$^{-1}$ mole^{-1} (*22*).

Sample Material. Methane of exceptionally high purity, 99.994 mole %, was prepared on a gas-chromatographic fractometer with a 20/50 mesh charcoal column. The starting material was a special batch of research grade methane (purchased from Phillips Petroleum Co., Bartlesville, Okla.) that contained 0.16 mole % N_2, 0.02 mole % O_2, 0.02 mole % CO_2, and traces of water. No measurable amounts of ethane or heavier hydrocarbons were present. Before the methane was put through the fractometer, the carbon dioxide and water were removed by passing the sample in the vapor state over magnesium perchlorate and Ascarite. The principal impurity after purification was 0.006 mole % N_2 as determined by gas-chromatographic analysis. This amount of nitrogen was assumed in calculating the effective molecular weight of the sample used, 16.0437 grams/mole (based on atomic weights; H = 1.0080 and C = 12.011). The gas compressibility measurements were made on two samples of the purified methane. Sample I weighed 1.30690 ± 0.00030 grams, equal to 0.081459 mole; and sample II weighed 1.67403 ± 0.00030 grams, equal to 0.104342 mole. Although the nitrogen impurity was taken into account when the number of moles of sample was calculated, its diluent effect on the compressibility of methane was deemed insignificant.

Compressibility Measurements. Measurements were made at even temperatures and densities to eliminate the necessity for cross-plotting or smoothing to obtain final values. The pressure, density, and temperature data in Table I are, therefore, unsmoothed values that retain the full experimental precision of the original measurements. At each isotherm, beginning with the lowest temperature, the pressure was measured first at the minimum density, 0.75 mole liter^{-1}, and thereafter at regular increments of 0.5 mole liter^{-1} beginning with the 1.0 mole liter^{-1} point and continuing to the highest density. After measurements were completed at the highest density of an isotherm, the pressure at the lowest density was remeasured to check for leakage of mercury or decomposition of the sample. The greatest difference between the initial and check values, 0.0033 atm., is within the calculated accuracy of the method. The average difference for all isotherms, 0.0010 atm. or 0.0034% of the total pressure, is indicative of the precision at low density.

Measurements on sample I covered the temperature range 0° through 175°. At the 200° isotherm the cap of the compressibility bomb cracked and sample I was lost. The bomb was repaired and a new blank-run calibration was carried out. Measurements on sample II, which covered the range 150° through 350°, overlapped the measurements on sample I at 150° and 175°.

The two samples were identical except for the amounts as recorded in the section on material. The overall experimental reproducibility established by the duplicate measurements at 150° and 175° is about ⅓ of the estimated maximum error. After measurements at 350° were comcompleted, sample II was cooled to 150° and the pressure at 0.8 mole liter^{-1} was redetermined. It was higher than the initial pressure by only 0.0021 atm. This result was taken as a positive indication that no leakage of mercury, significant change in the apparatus, or decomposition of sample II had occurred.

The calculated overall maximum uncertainty in the measurements of pressure, volume, and temperature varies from 0.03% at the lowest temperature and pressure to 0.2% at the highest temperature and pressure. The tabulated values of pressure, Table I, were corrected for the partial pressure of mercury vapor adjusted at each pressure for the Poynting effect. [Selected values of the vapor pressure of mercury and a description of the way the mercury vapor pressure corrections were applied have been given (*14*).] A correction for van der Waals interaction of mercury vapor with methane was not made because it cannot be calculated accurately at present. However, the compressibility measurements are reported in enough detail that the corrections can be made when a reliable method for calculating them becomes available. Although the inaccuracy introduced by neglecting the van der Waals interaction is very small, it may not be negligible in the higher pressure and temperature regions of these measurements. Therefore, the overall maximum uncertainty claimed for the compressibility measurements at the highest temperature and pressure is arbitrarily increased to 0.3%.

In addition to the indeterminate error caused by van der Waals interaction between sample and mercury vapor, a number of other small systematic errors are introduced from such factors as the gas constant, atomic weights, variations in C_{12}/C_{13} isotopic ratio and undetected impurities when gas compressibilities are converted from weight units to molar units. However, these errors and the error in weight of sample were evaluated, as a group, from the behaviors of the residual quantities B_v and C_v as defined by:

$$B_v = (PV/RT - 1)V; \quad B = \lim_{p \to 0} [B_v] \qquad (1)$$

$$C_v = [(PV/RT - 1)V - B]V; \quad C = \lim_{p \to 0} [C_v] \qquad (2)$$

Appropriate corrections based on this evaluation were applied to the measured values of pressure and density. Although the effect of these very small systematic errors could not be seen easily in B_v, preliminary plots of C_v *vs.* density showed clearly, on all isotherms, a negative curvature below 7 mole liter^{-1} and an inflection to positive curvature above this point. Since a negative curvature in C_v would require negative values for the fifth and possibly higher virial coefficients (an improbable occurrence), the negative curvature was considered to be the result of the small systematic errors that were introduced into the tabular results during the conversion of the data to a molar basis. In order to obtain C_v lines that showed no inflections, and had positive curvatures that decreased to zero as zero density was approached, the preliminary even densities first were adjusted upward by the factor 1.00023. The experimentally determined pressures then were adjusted back to the even values of molar density as they appear in Table I. The effect of applying these corrections was to reduce the otherwise indeterminate systematic errors and, consequently, to reduce by 0.023% the overall experimental error in the molar values. A Significant feature of the above correction that linked it definitely to a true systematic error was its temperature invariance—a single value of the factor sufficed for all isotherms.

The compressibility data, corrected for systematic errors as described above, are in Table I, and the compressibility factors $Z = PV/RT$ calculated from these data are in Table II. The compressibility factor values are based on the thermodynamic absolute temperatures, *T*, ° K. (thermodynamic), listed in column 2, Table I. Use of these compressibility values with the International absolute temperatures, *T*, ° K. (Int.), would introduce an error varying up to a few one-hundredths of a percent. These results were used previously (*12*), to calculate a sensitive residual quantity B_v, which was the basis for showing that the present values are in excellent agreement with the results of other investigators. The present values are compared further, Figure 1, with data from the tables of American Petroleum Institute Research Project 44 (*1*) and the results of Michels and Nederbragt (*18*), and Schamp, Mason, Richardson, and Altman (*23*) in terms of differences in the compressibility factor. The deviations $\Delta Z = Z$ (present) $- Z$ (other) show that the present results are in poor agreement with API RP 44 selected values but in excellent agreement with values from the other two sources cited. Although API RP 44 selected values were stated by Canjar (*10*) to be in good agreement with the experimental values of Michels and Nederbragt (*18*), the authors believe this statement is in error.

VIRIAL COEFFICIENTS

The second, third, and fourth virial coefficients, *B*, *C*, and *D*, in the equation

$$PV = RT(\text{thermodynamic})(1 + B/V + C/V^2 + D/V^3 + \dots),$$

were published previously (*12*). However, a redetermination of correction factors obtained from the blank-run led to small differences from the previously published values for

Table I. The Compressibility of Methane and the Deviation Obtained with the Benedict-Webb-Rubin, and the Beattie-Bridgeman Equations of State

t, ° C. (Int.)	T, ° K. (Thermodynamic)			Density, Mole Liter ^{1}													
				0.75	0.75[a]	0.80	0.80[a]	1.0	1.5	2.0	2.5	3.0	3.5	4.0	4.5	5.0	5.5
				Pressure, atm.													
0	273.160	Obsd. I[b]		16.1624	16.1614			21.2760	31.1261	40.5160	49.4837	58.0726	66.3433	74.3227	82.0686	89.6142	97.0294
		Obsd. I-Calcd.	BWR[c]	+0.01				+0.01	+0.01	+0.03	+0.03	+0.04	+0.05	+0.05	+0.04	+0.03	+0.03
			BB[d]	+0.01				+0.02	+0.04	+0.07	+0.09	+0.10	+0.12	+0.13	+0.14	+0.12	+0.12
25	298.153	Obsd. I		17.7840	17.7843			23.4749	34.5356	45.2050	55.5272	65.5470	75.3094	84.8673	94.2618	103.539	112.767
		Obsd. I-Calcd.	BWR	0.00				0.00	−0.01	−0.02	−0.02	−0.03	−0.04	−0.05	−0.05	−0.06	−0.04
			BB	+0.02				+0.03	+0.06	+0.09	+0.12	+0.13	+0.13	+0.11	+0.07	0.00	−0.07
30	303.152	Obsd. I		18.1080	18.1069			23.9153	35.2180	46.1416	56.7336	67.0516	77.1242	86.9891	96.7208	106.336	115.913
		Obsd. I-Calcd.	BWR	0.00				0.00	−0.01	−0.02	−0.03	−0.02	−0.02	−0.04	−0.03	−0.04	−0.03
			BB	+0.02				+0.04	+0.07	+0.10	+0.13	+0.15	+0.16	+0.13	+0.10	+0.02	−0.08
50	323.151	Obsd. I		19.3988	19.3986			25.6660	37.9248	49.8695	61.5277	72.9595	84.2087	95.3217	106.370	117.357	128.330
		Obsd. I-Calcd.	BWR	−0.01				−0.01	−0.02	−0.03	−0.05	−0.07	−0.08	−0.09	−0.08	−0.08	−0.10
			BB	+0.02				+0.04	+0.08	+0.12	+0.15	+0.16	+0.15	+0.11	+0.07	−0.03	−0.20
75	348.153	Obsd. I		21.0150	21.0130			27.8521	41.3049	54.5003	67.4960	80.3269	93.0461	105.694	118.352	131.045	143.842
		Obsd. I-Calcd.	BWR	−0.01				−0.01	−0.03	−0.05	−0.07	−0.09	−0.10	−0.12	−0.12	−0.10	−0.07
			BB	+0.03				+0.05	+0.10	+0.14	+0.17	+0.18	+0.17	+0.12	+0.05	−0.06	−0.21
100	373.160	Obsd. I		22.6262	22.6252			30.0335	44.6749	59.1366	73.4508	87.6730	101.853	116.039	130.287	144.666	159.211
		Obsd. I-Calcd.	BWR	−0.01				−0.01	−0.02	−0.04	−0.06	−0.08	−0.10	−0.11	−0.12	−0.10	−0.08
			BB	+0.04				+0.06	+0.11	+0.17	+0.21	+0.22	+0.21	+0.16	+0.06	−0.06	−0.24
125	398.170	Obsd. I		24.2365	24.2360			32.2098	48.0390	63.7372	79.3594	94.9708	110.607	126.319	142.199	158.249	174.574
		Obsd. I-Calcd.	BWR	0.00				−0.01	−0.02	−0.04	−0.07	−0.08	−0.09	−0.11	−0.08	−0.07	−0.02
			BB	+0.04				+0.07	+0.13	+0.18	+0.21	+0.24	+0.23	+0.18	+0.12	−0.02	−0.17
150	423.183	Obsd. I		25.8440	25.8431			34.3851	51.3916	68.3413	85.2852	102.263	119.354	136.573	154.006	171.732	189.796
150	423.183	Obsd. II[e]				27.5564	27.5559	34.3846	51.3963	68.3439	85.2764	102.255	119.335	136.554	153.994	171.694	189.739
		Obsd.-Calcd.[f]	BWR	0.00		0.00		0.00	−0.01	−0.02	−0.04	−0.06	−0.07	−0.09	−0.10	−0.10	−0.07
			BB[c]	+0.04		+0.05		+0.07	+0.14	+0.20	+0.25	+0.27	+0.26	+0.20	+0.10	−0.03	−0.20
175	448.197	Obsd. I		27.4509	27.4497			36.5563	54.7418	72.9238	91.1632	109.517	128.038	146.794	165.820	185.115	205.003
175	448.197	Obsd. II				29.2755	29.2756	36.5595	54.7450	72.9376	91.1770	109.523	128.041	146.796	165.825	185.177	205.007
		Obsd.-Calcd.[f]	BWR	0.00		+0.01		0.00	0.00	−0.01	−0.03	−0.05	−0.06	−0.06	−0.07	−0.12	−0.04
			BB[c]	+0.05		+0.06		+0.08	+0.14	+0.21	+0.26	+0.28	+0.27	+0.24	+0.15	−0.03	−0.14
200	473.213	Obsd. II				30.9920	30.9922	38.7272	58.0860	77.5132	97.0589	116.775	136.715	156.955	177.561	198.575	220.144
		Obsd. II-Calcd.	BWR			+0.01		+0.01	+0.01	0.00	−0.01	−0.02	−0.05	−0.08	−0.09	−0.11	−0.06
			BB			+0.06		+0.08	+0.15	+0.22	+0.27	+0.30	+0.28	+0.23	+0.14	0.00	−0.12
225	498.229	Obsd. II				32.7081	32.7084	40.8956	61.4245	82.0866	102.917	123.999	145.375	167.119	189.312	212.021	235.257
		Obsd. II-Calcd.	BWR			+0.01		+0.01	+0.02	+0.02	0.00	−0.02	−0.04	−0.06	−0.07	−0.05	−0.08
			BB			+0.06		+0.08	+0.15	+0.22	+0.27	+0.30	+0.29	+0.24	+0.17	+0.08	−0.09
250	523.245	Obsd. II				34.4223	34.4237	43.0621	64.7602	86.6533	108.773	131.203	154.010	177.253	201.004	225.361	250.332
		Obsd. II-Calcd.	BWR			+0.02		+0.02	+0.02	+0.03	+0.01	−0.02	−0.04	−0.07	−0.09	−0.08	−0.12
			BB			+0.06		+0.09	+0.15	+0.23	+0.26	+0.28	+0.28	+0.23	+0.16	+0.08	−0.07
275	548.260	Obsd. II				36.1365	36.1367	45.2272	68.0907	91.2179	114.629	138.414	162.627	187.368	212.701	238.667	265.369
		Obsd. II-Calcd.	BWR			+0.02		+0.03	+0.03	+0.05	+0.03	0.00	−0.04	−0.07	−0.09	−0.13	−0.17
			BB			+0.06		+0.09	+0.15	+0.23	+0.27	+0.28	+0.26	+0.22	+0.17	+0.06	−0.06
300	573.274	Obsd. II				37.8460	37.8491	47.3886	71.4160	95.7579	120.452	145.577	171.224	197.433	224.288	251.930	280.323
		Obsd. II-Calcd.	BWR			+0.02		+0.03	+0.04	+0.04	+0.02	−0.02	−0.06	−0.11	−0.18	−0.20	−0.29
			BB			+0.06		+0.09	+0.14	+0.21	+0.24	+0.24	+0.23	+0.17	+0.08	+0.02	−0.12
325	598.285	Obsd. II				39.5550	39.5583	49.5510	74.7400	100.309	126.284	152.779	179.812	207.506	235.918	265.158	295.283
		Obsd. II-Calcd.	BWR			+0.02		+0.04	+0.04	+0.05	+0.02	0.00	−0.07	−0.14	−0.23	−0.30	−0.39
			BB			+0.06		+0.08	+0.14	+0.20	+0.22	+0.24	+0.20	+0.14	+0.05	−0.04	−0.15
350	623.294	Obsd. II				41.2690	41.2673	51.7135	78.0693	104.859	132.137	159.947	188.443	217.607	247.584	278.472	310.315
		Obsd. II-Calcd.	BWR			+0.03		+0.04	+0.05	+0.06	+0.05	−0.01	−0.04	−0.13	−0.22	−0.30	−0.41
			BB			+0.06		+0.09	+0.14	+0.19	+0.23	+0.21	+0.21	+0.14	+0.06	−0.01	−0.10
Av. dev., %			BWR	0.02		0.04		0.04	0.04	0.05	0.04	0.05	0.05	0.06	0.06	0.06	0.05
			BB	0.14		0.17		0.18	0.22	0.25	0.24	0.21	0.18	0.13	0.06	0.03	0.08

				6.0	6.5	7.0	7.5	8.0	8.5	9.0	9.5	10.0	10.5	11.0	11.5	12.0	12.5
										Pressure, atm.							
0	273.160	Obsd. I[b]		104.298	111.579	118.918	126.182	133.639	141.219	149.119	157.224	165.782	174.687	184.338	194.474	205.488	217.395
		Obsd. I-Calcd.	BWR[c]	−0.03	−0.01	+0.07	+0.05	+0.12	+0.18	+0.33	+0.39	+0.48	+0.37	+0.29	−0.22	−1.04	−2.44
			BB[c]	+0.06	+0.06	+0.12	+0.06	+0.10	+0.14	+0.32	+0.48	+0.83	+1.22	+2.00	+2.88	+4.20	+5.93
25	298.153	Obsd. I		121.969	131.203	140.549	150.052	159.756	169.730	180.084	190.894	202.147	214.101	226.684	240.267	254.577	270.208
		Obsd. I-Calcd.	BWR	−0.03	−0.01	+0.04	+0.12	+0.21	+0.29	+0.41	+0.53	+0.52	+0.48	+0.17	−0.28	−1.41	−2.92
			BB	−0.18	−0.31	−0.43	−0.55	−0.67	−0.77	−0.79	−0.69	−0.55	−0.14	+0.42	+1.44	+2.61	+4.48
30	303.152	Obsd. I		125.497	135.131	144.889	154.733	164.949	175.412	186.265	197.499	209.326	221.865	235.176	249.205	264.380	280.535
		Obsd. I-Calcd.	BWR	−0.01	+0.02	+0.08	+0.07	+0.22	+0.33	+0.45	+0.47	+0.47	+0.43	+0.22	−0.46	−1.42	−3.17
			BB	−0.19	−0.33	−0.48	−0.71	−0.78	−0.89	−0.92	−0.94	−0.79	−0.38	+0.28	+1.11	+2.48	+4.17
50	323.151	Obsd. I		139.414	150.695	162.061	173.665	185.682	198.049	210.964	224.393	238.376	253.217	268.975	285.756	303.533	322.698
		Obsd. I-Calcd.	BWR	−0.06	+0.06	+0.11	+0.16	+0.32	+0.45	+0.65	+0.77	+0.72	+0.63	+0.37	−0.19	−1.36	−3.07
			BB	−0.35	−0.46	−0.69	−0.94	−1.08	−1.23	−1.23	−1.18	−1.09	−0.70	0.00	+1.06	+2.41	+4.39
75	348.153	Obsd. I		156.818	169.943	183.434	197.194	211.417	226.196	241.565	257.611	274.412	292.143	310.911	330.722	351.987	375.024
		Obsd. I-Calcd.	BWR	+0.01	+0.05	+0.19	+0.27	+0.41	+0.60	+0.79	+0.92	+0.94	+0.83	+0.51	−0.28	−1.41	−2.89
			BB	−0.36	−0.61	−0.80	−1.06	−1.27	−1.38	−1.42	−1.35	−1.14	−0.68	+0.09	+1.13	+2.79	+5.34
100	373.160	Obsd. I		174.002	189.080	204.636	220.518	236.939	254.061	271.832	290.627	310.141	330.719	352.625	375.886	400.624	
		Obsd. I-Calcd.	BWR	−0.03	+0.03	+0.21	+0.29	+0.04	+0.60	+0.72	+1.01	+1.01	+0.86	+0.62	+0.07	−0.98	
			BB	−0.44	−0.69	−0.85	−1.13	−1.37	−1.48	−1.54	−1.26	−0.98	−0.42	+0.63	+2.14	+4.18	
125	398.170	Obsd. I		191.168	208.256	225.715	243.822	262.544	282.021	302.205	323.578	345.911	369.406	394.299			
		Obsd. I-Calcd.	BWR	−0.01	+0.13	+0.20	+0.38	+0.57	+0.78	+0.87	+1.15	+1.23	+1.13	+0.86			
			BB	−0.42	−0.59	−0.86	−1.02	−1.17	−1.21	−1.25	−0.88	−0.38	+0.39	+1.62			
150	423.183	Obsd. I		208.271	227.271	246.763	266.951	287.947	309.647	332.497	356.274	381.333					
150	423.183	Obsd. II[e]		208.202	227.123	246.671	266.801	287.718	309.421	332.024	355.780	380.919					
		Obsd.-Calcd.[f]	BWR	−0.02	+0.06	+0.17	+0.30	+0.49	+0.60	+0.77	+0.86	+1.00					
			BB	−0.40	−0.61	−0.82	−1.01	−1.10	−1.18	−1.05	−0.75	−0.04					
175	448.197	Obsd. I		225.314	246.246	267.704	290.014	313.265	337.376	362.486	389.120						
175	448.197	Obsd. II		225.301	246.145	267.691	289.970	313.146	337.217	362.432	388.826						
		Obsd.-Calcd.[f]	BWR	+0.02	+0.11	+0.18	+0.32	+0.55	+0.72	+0.87	+1.13						
			BB[c]	−0.31	−0.49	−0.70	−0.83	−0.81	−0.75	−0.52	+0.09						
200	473.213	Obsd. II		242.212	265.065	288.562	312.932	338.389	364.663	392.389							
		Obsd. II-Calcd.	BWR	−0.07	+0.06	+0.11	+0.22	+0.47	+0.49	+0.75							
			BB	−0.34	−0.43	−0.62	−0.72	−0.60	−0.58	−0.12							
225	498.229	Obsd. II		259.190	283.857	309.437	335.895	363.447	392.131								
		Obsd. II-Calcd.	BWR	−0.06	−0.03	+0.09	+0.17	+0.30	+0.39								
			BB	−0.24	−0.40	−0.46	−0.52	−0.43	−0.22								
250	523.245	Obsd. II		276.096	302.647	330.194	358.764	388.486									
		Obsd. II-Calcd.	BWR	−0.09	−0.10	−0.02	+0.05	+0.13									
			BB	−0.18	−0.32	−0.36	−0.34	−0.20									
275	548.260	Obsd. II		292.971	321.402	350.927	381.550										
		Obsd. II-Calcd.	BWR	−0.13	−0.18	−0.14	−0.12										
			BB	−0.12	−0.25	−0.25	−0.21										
300	573.274	Obsd. II		309.736	340.056	371.469											
		Obsd. II-Calcd.	BWR	−0.27	−0.34	−0.42											
			BB	−0.15	−0.24	−0.30											
325	598.285	Obsd. II		326.437	358.611	391.861											
		Obsd. II-Calcd.	BWR	−0.45	−0.58	−0.85											
			BB	−0.21	−0.31	−0.46											
350	623.294	Obsd. II		343.223	377.366												
		Obsd. II-Calcd.	BWR	−0.54	−0.62												
			BB	−0.18	−0.16												
Av. dev., %			BWR	0.04	0.05	0.07	0.08	0.14	0.19	0.25	0.30	0.30	0.25	0.15	0.10	0.48	1.01
			BB	0.14	0.19	0.25	0.32	0.35	0.38	0.38	0.35	0.31	0.24	0.29	0.64	1.11	1.73

[a] Cbeck measurements. [b] Measurements on Sample I extend from 0–200° C. [c] Benedict-Webb-Rubin equation of state. [d] Beattie-Bridgeman equation of state. [e] Measurements on Sample II extend from 150–350° C. [f] Calculated from arithmetic mean of Obsd. I and Obsd. II.

Table II. Compressibility Factor, $Z = PV/RT$(Thermodynamic), of Methane

t, ° C. (Int.)	T, ° K. (Thermodynamic)	Density, Mole Liter^{-1}								
		0.75	0.8	1.0	1.5	2.0	2.5	3.0	3.5	4.0
0	273.160	0.961416[a]		0.949229	0.925794	0.903811	0.883086	0.863635	0.845687	0.828977
25	298.153	0.969238		0.959541	0.941099	0.923882	0.907874	0.893080	0.879510	0.867242
30	303.152	0.970585		0.961423	0.943869	0.927473	0.912302	0.898516	0.885851	0.874266
50	323.151	0.975445		0.967945	0.953508	0.940368	0.928161	0.917175	0.907363	0.898720
75	348.153	0.980785		0.974958	0.963913	0.953886	0.945073	0.937274	0.930588	0.924950
100	373.160	0.985241		0.980864	0.972691	0.965671	0.959531	0.954435	0.950404	0.947429
125	398.170	0.989083		0.985866	0.980240	0.975423	0.971601	0.968942	0.967262	0.966582
150	423.183	0.992338	0.991970	0.990232	0.986712	0.984082	0.982383	0.981633	0.981983	0.983206
175	448.197	0.995207	0.995048	0.994054	0.992360	0.991538	0.991610	0.992659	0.994728	0.997884
200	473.213		0.997706	0.997373	0.997290	0.998130	0.999854	1.002465	1.005979	1.010547
225	498.229		1.000085	1.000336	1.001658	1.003949	1.006969	1.011033	1.015993	1.021963
250	523.245		1.002195	1.002972	1.005565	1.009134	1.013385	1.018627	1.024882	1.032113
275	548.260		1.004081	1.005336	1.009039	1.013822	1.019215	1.025580	1.032847	1.041231
300	573.274		1.005735	1.007418	1.012138	1.017842	1.024258	1.031588	1.039996	1.049290
325	598.285		1.007209	1.009351	1.014966	1.021645	1.028959	1.037365	1.046502	1.056722
350	623.294		1.008627	1.011136	1.017641	1.025136	1.033451	1.042460	1.052730	1.063698
		4.5	5.0	5.5	6.0	6.5	7.0	7.5	8.0	8.5
0	273.160	0.813663	0.799630	0.787084	0.775541	0.765859	0.757932	0.750615	0.745291	0.741232
25	298.153	0.856214	0.846437	0.838067	0.830916	0.825066	0.820709	0.817787	0.816260	0.816203
30	303.152	0.864062	0.854968	0.847242	0.840852	0.835755	0.832100	0.829392	0.828896	0.829617
50	323.151	0.891453	0.885182	0.879949	0.876288	0.874333	0.873118	0.873260	0.875335	0.878709
75	348.153	0.920640	0.917443	0.915483	0.914896	0.915201	0.917295	0.920365	0.925080	0.931521
100	373.160	0.945563	0.944931	0.945393	0.947120	0.950022	0.954743	0.960252	0.967277	0.976159
125	398.170	0.967193	0.968728	0.971507	0.975198	0.980647	0.986942	0.995042	1.004485	1.015526
150	423.183	0.985547	0.989017	0.993638	0.999481	1.006602	1.015010	1.024750	1.036147	1.048716
175	448.197	1.001980	1.006871	1.013514	1.021062	1.029898	1.039859	1.051365	1.064559	1.078997
200	473.213	1.016192	1.022814	1.030825	1.039645	1.050217	1.061652	1.074558	1.089355	1.104874
225	498.229	1.029045	1.037240	1.046282	1.056661	1.068204	1.081292	1.095498	1.111277	1.128445
250	523.245	1.040363	1.049792	1.060100	1.071770	1.084464	1.098663	1.114143	1.131047	
275	548.260	1.050673	1.061048	1.072503	1.085386	1.099121	1.114371	1.130841		
300	573.274	1.059567	1.071140	1.083505	1.097426	1.112171	1.128131			
325	598.285	1.067917	1.080253	1.093616	1.108249	1.123825	1.140311			
350	623.294	1.075758	1.088975	1.103177	1.118484	1.135151				
			9.0	9.5	10.0	10.5	11.0	11.5	12.0	12.5
0	273.160		0.739215	0.738373	0.739638	0.742253	0.747658	0.754475	0.763987	0.775926
25	298.153		0.817884	0.821350	0.826281	0.833467	0.842341	0.853996	0.867156	0.883584
30	303.152		0.832006	0.835756	0.841517	0.849449	0.859486	0.871159	0.885698	0.902226
50	323.151		0.884011	0.890795	0.898993	0.909485	0.922172	0.937109	0.953931	0.973596
75	348.153		0.939547	0.949223	0.960576	0.973942	0.989398	1.006683	1.026769	1.050211
100	373.160		0.986416	0.999113	1.012891	1.028660	1.046943	1.067482	1.090330	
125	398.170		1.027751	1.042521	1.058754	1.076821	1.097141			
150	423.183		1.063176	1.079267	1.097588					
175	448.197		1.095076	1.113331						
200	473.213		1.122832							

[a] Six significant places to the right of the decimal point were tabulated to retain all possible precision. The absolute accuracy varies according to the estimated experimental uncertainties discussed in the text.

both C and D above 275° C. Although the differences are much less than the experimental uncertainty, the revised values are presented, Table III, to preserve all possible precision in the temperature dependency of the experimental values. The precision of the experimental values of B, as shown by correlations based on the Stockmayer and Kihara potentials (*12*), is better than 0.1 cc. mole^{-1}, but the combined experimental and correlational errors can be as great as 0.2 cc. mole^{-1}. Because errors in the lower virial coefficients are propagated to and magnified in the higher virial coefficients (*17*), the absolute accuracy of the values for C and, particularly, D cannot be estimated easily. However, because of the high precision of the compressibility measurements, the temperature dependencies of both C and D are useful in testing intermolecular potential energy theory. For example, the experimental values of D are positive and increase with increasing temperature as predicted for a limited range of reduced temperature, T/Θ, for the theoretical Lennard-Jones [12, 6] potential calculated by Boys and Shavitt (*7*), and Barker and Monaghan (*2*).

Table III. Virial Coefficients of Methane

t, ° C.	B, Cc. Mole^{-1}	$C \times 10^{-2}$ Cm.^{6} Mole^{-2}	$D \times 10^{-4}$ Cm.^{9} Mole^{-3}
0	−53.35	26.20	0.5
25	−42.82	23.70	0.5
30	−40.91	23.20	0.5
50	−34.23	21.50	1.3
75	−27.06	19.75	2.1
100	−21.00	18.34	2.7
125	−15.87	17.27	3.1
150	−11.40	16.40	3.5
175	−7.56	15.85	3.8
200	−4.16	15.14	4.3
225	−1.16	14.65	4.8
250	+1.49	14.20	5.2
275	3.89	13.85	5.5
300	5.98	13.60	5.7
325	7.88	13.45	5.8
350	9.66	13.30	5.9

CLOSED EQUATIONS OF STATE

Volumetric data for methane may be represented well by either the Beattie-Bridgeman (BB) (*5*) or the Benedict-Webb-Rubin (BWR) (*6*) equation of state, Table IV. Parameters of these equations were evaluated by methods recommended (*5*, *6*,). The choice of equation rests with the nature of the application and the range of temperatures and pressures that are involved. Differences between observed and calculated pressures, and percentage deviations based on parameters in Table IV, are included in

Table I to provide a means for estimating the ranges in which these parameters can be used best for interpolating or for calculating thermodynamic functions. Because parameters of the BB and BWR equations for methane published previously (*5, 6, 9, 20*) covered a smaller temperature range than present values, the rather nominal differences in the values obtained were expected.

Table IV. Closed Equations of State for Methane.[a]

(Beattie-Bridgeman Equation[b])

$P = [RT(1-\epsilon)/V^2][V+B] - A/V^2$

$A = A_0(1 - a/V)$; $B = B_0(1 - b/V)$; $\epsilon = c/VT^3$

$A_0 = 2.2152$ $B_0 = 0.05159$ $c = 15 \times 10^4$

$a = 0.02174$ $b = -0.02198$ $R = 0.0820544$

(Benedict-Webb-Rubin Equation[c])

$$P = RT/V + (B_0RT - A_0 - C_0/T^2)/V^2 + (bRT - a)/V^3 + a\alpha/V^6 + [C(1 + \gamma/V^2)\exp.(-\gamma/V^2)]/V^3T^2$$

$A_0 = 1.79894$ $a = 0.0435200$ $\alpha = 0.000330000$

$B_0 = 0.0454625$ $b = 0.00252033$ $\gamma = 0.0105000$

$C_0 = 0.0318382 \times 10^6$ $c = 0.00358780 \times 10^6$ $R = 0.0820544$

[a] Units: atm.; liter/mole; °K. [b] Ref. *5*. [c] Ref. *6*.

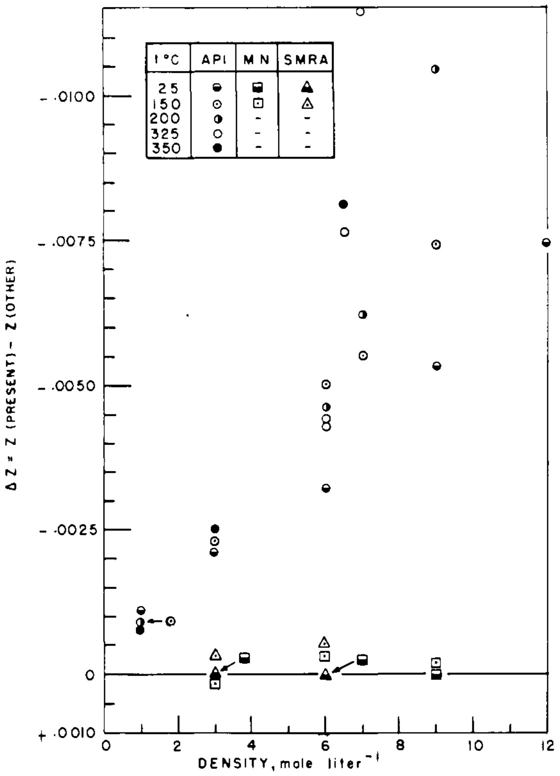

Figure 1. Comparison of compressibility factors for methane.

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