on θ. However, in these experiments, approximately constant boil-up rates were maintained. To be completely quantitative, the contact angle should be determined at a specific vapor velocity.

DISCUSSION

An interesting phenomenon was observed while measuring the contact angles under conditions of mass transfer for the fluids under test. For all the positive systems studied, the sessile drop remained immobile, with no indication of interfacial turbulence occurring at any stage in the experimental procedure. However, for the negative systems, a considerable amount of agitation was evident in the droplet, which resulted at some concentrations in the production of droplets ejected from the main sessile body. This phenomenon explains why distillation efficiencies are often high for negative systems, although the contact angle would suggest a poor wetting performance and hence low transfer area. The behavior has an analogy in liquid-liquid extraction, where systems with negative interfacial tensions produce satellite droplets.

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We acknowledge the provision of facilities by T. K. Ross and a maintenance grant to one of us (A.P.B.) from the Cabot Carbon Co., Ellesmere Port.

NOMENCLATURE

ρ = density of sessile drop
g = acceleration due to gravity
h = equilibrium drop height
γ = surface tension
θ = contact angle

Subscripts

L = liquid
V = vapor

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Low-Temperature Volumetric Properties of Methane

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Pressure and temperature measurements were performed on 16 constant-mass methane samples ranging in density from 0.04 to 0.36 gram per cc. for temperatures between 150° and 273° K. at pressures to 680 atm. Saturation temperatures, pressures, and densities were also measured. Analysis of the data in the critical region suggested critical constants of 190.77° K., 45.66 atm., and 0.1625 gram per cc. An empirical equation of state was developed for the isochoric data which reproduces the measured pressures with an average error of 0.02% and a maximum error of 0.08%. Certain qualitative features of the isochoric equation representing the volumetric behavior of methane are discussed.

THE pressure-volume-temperature relations for methane were determined as part of a continuing program to investigate the basic properties of gases and liquids at low temperatures. Data have been recently reviewed and reported for hydrogen and methane in the gas phase (*14, 15*), helium and nitrogen in the gas phase (*4, 5*), and low-density methane (*8, 9*). Available data sources for the properties of pure methane are numerous, but they are in serious disagreement, especially in the temperature region below 0° C. A recent compilation by Din (*6*) summarizes many of the discrepancies and deficiencies of the data.

Three significant investigations have been carried out on methane gas in the temperature range below 0° C. The earliest was by Kvalnes and Gaddy (*12*) in 1931 at temperatures to −70° C. and pressures to 1000 atm. Measurements by Mueller *et al.* (*14, 15*) extended the data to −128.7° C. and 510 atm. Both of these investigations claimed compressibility factors accurate to 0.1%; however, in some regions disagreements between the two sets of data are as large as 2 or 3%. Hoover *et al.* (*8, 9*) measured virial coefficients and gaseous compressibility factors between 131° and 273° K. at pressures to 40 atm.

Investigations at temperatures above 0° C. were conducted by Michels and Nederbragt (*13*), Schamp *et al.* (*16*), and Douslin *et al.* (*7*). The results of all these measurements above 0° C. are in close agreement. The results reported here agree with those of Douslin *et al.* within 0.03% at 0° C.

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For liquid methane, van Itterbeek, Verbeke, and Staes (*10*) in 1963 published measurements on the behavior of 14 isotherms between 114° and 190° K. at pressures to 300 atm.

The present investigation was designed to rectify the disagreement in the existing data below 0° C. and to provide additional data extending into the liquid region.

EXPERIMENTAL

Equipment. The compressibility apparatus and procedure were described in detail in previous publications (*17, 19*). Briefly, the method was as follows: The methane sample was charged into a 150-cc. aluminum cylinder to a pressure of 680 atm. The cylinder, with attendant valves and lines, was weighed on a Seko analytical balance having a sensitivity of 0.1 mg. and an accuracy greater than 0.5 mg. for total masses up to 2 kg. The cylinder was then attached to a constant-volume chamber contained within a temperature-controlled bath. After charging the isochoric chamber to the desired pressure, liquid nitrogen was applied to a coil of tubing attached to the charging system. This system was then reweighed to determine the amount of methane in the measurement chamber. The isochoric vessel was a stainless steel sphere having a spherical cavity of approximately 75 cc. Connections were provided to a differential pressure cell, which was also immersed in the low-temperature bath. All the methane charged to the system could be contained in the temperature-controlled environment. About 95% of the sample was always contained in the spherical cavity, for which accurate pressure deformation calculations could be performed.

The system volume consisted of the spherical vessel, lines, valves, and the lower chamber of the differential pressure cell. This volume was measured by making a series of helium Burnett expansions (*3*) into a reference chamber of known volume. This reference volume was maintained at 0° C. and the expansions were performed at various system temperatures in order to determine directly the system volume as a function of temperature. The maximum volume error was estimated to be on the order of 0.015 cc. in a total system volume of about 75 cc.

Pressure measurements were made with a set of calibrated dead-weight gages. Errors in the measured pressure are on the order of 0.01% at the highest pressures and increase to about 0.07% at the pressures as low as 1 atm. Bath temperature was controlled to ±0.001° C., and the system temperature was measured with a platinum resistance thermometer embedded in the wall of the sphere to an absolute accuracy believed to be within ±0.01° C. of the recorded temperature. In converting temperatures from ° C. to ° K., the more recent definition of the absolute temperature scale was used, 0° C. = 273.15° K. The corresponding gas constant to be used with this new definition is $R = 82.059$ cc. atm./(g. mole ° K.).

Details concerning the experimental apparatus are given by Vennix (*17*).

Sample Material. The methane used was obtained commercially from the Matheson Co. and had a reported minimum purity of 99.95%. Two independent mass spectrometer measurements showed the actual purity to be in excess of 99.99%. For converting between grams and moles, a molecular weight of 16.042 was used.

Compressibility Measurements. The detailed procedure for obtaining the data has been reported elsewhere (*17, 19*). Briefly, it consists of charging methane to the system and determining the differential mass. The temperature and pressure of the sample are measured. The bath temperature is then changed and the pressure measured for the new temperature. A series of pressure-temperature determinations was made on a constant-mass sample, beginning at an upper limit of 0° C. and continuing by lowering the temperature until the temperature corresponding to the vapor pressure was attained. Pressure-temperature measurements were continued along the vapor pressure curve as a further check of the experimental data. Changes in the system volume were accounted for by utilizing the measured temperature-dependence of the entire system volume and the calculated pressure deformation of a spherical chamber of known dimensions. This allowed the sample density to be determined at any point in the pressure-temperature region studied. Due to the slight changes in volume during a series of constant-mass measurements, the density of the sample also varied slightly. In order to obtain results at either a constant temperature or a constant density, the original data were fitted to an empirical equation of state. This equation was used to calculate pressures and temperatures corresponding to the constant-density values reported here. The constant densities reported vary by only a few tenths of 1% from the experimentally observed densities, which show a small variation due to temperature- and pressure-induced distortion of the spherical chamber. The amount of smoothing carried out by the equation of state is thus very small and may be regarded as a correction for the distortion of the system volume. The equation of state is discussed below. The calculated pressures and temperatures for each density are presented in Table I. One additional figure more than the experimental accuracy is included in the computed pressure and temperature values to maintain internal consistency. The original experimental data before smoothing are published elsewhere (*17*). Vapor pressure measurements and saturated liquid densities are presented in Table II.

A comprehensive error analysis was made (*17*), based on the estimated accuracy of the measured variables—mass, volume, pressure, and temperature. From this it was concluded that the maximum probable error in the compressibility factor varied from 0.04% in the high-temperature and -pressure region to 0.08% in the low-temperature and -pressure region. Large-scale plots of the residual quantity, $(Z - 1)/\rho$, showed internal consistency within 0.02%. The compressibility factor is not included in the tables, as it can be calculated from the primary variables—temperature, pressure, and density.

COMPARISON WITH OTHER STUDIES

A detailed comparison was made between the data obtained in this study and other values reported. The interpolated pressures at 0° C. agreed to within 0.02% with those given by Douslin *et al.* (*7*). Data reported by Mueller (*14, 15*) showed average pressure deviations of 0.1% at 255° K. and 0.4% at 200° K. Corresponding deviations in the values reported by Kvalnes and Gaddy (*12*) varied from an average of 0.4% at 273° K. to 2.7% at 203° K. A comparison with the liquid data of van Itterbeek *et al.* (*10*) showed differences as high as 4%. However, the liquid density data published by these authors have reportedly been remeasured, due to inconsistencies in the original data (*20*).

The vapor pressures in Table II are within 1% of the values calculated from the equation presented by Armstrong, Brickwedde, and Scott (*1*). Saturated liquid densities are compared in Figure 1 with the values measured by Bloomer and Parent (*2*) and by Keyes, Taylor, and Smith (*11*).

Measurements conducted in the critical region are depicted in Figure 2. Figure 3 gives a large-scale cross plot of interpolated pressure-temperature values at the overall isochoric densities. The critical point is determined by the isotherm which has an inflection point with a zero first derivative. The critical density cannot be determined by this method, since the critical isotherm is extremely flat in this region. The critical point evidenced by the

Table I. Experimental Results Adjusted

Accuracy of original experimental measurements is discussed in text.

ρ = 0.041 Gram/Cc.

Temp., °K.	Press., Atm.
273.380	50.527
263.393	48.033
252.821	45.379
239.777	42.087
233.522	40.494
223.802	38.000
217.833	36.462
213.009	35.213
203.050	32.611
191.816	29.630
183.147	27.284
177.178	25.632
174.668	24.930
172.506	24.316

ρ = 0.104 Gram/Cc.

Temp., °K.	Press., Atm.
272.185	110.595
272.155	110.579
262.183	102.704
251.363	94.1331
243.755	88.0708
243.715	88.0449
234.417	80.5939
223.205	71.5533
208.541	59.561
190.397	44.150

ρ = 0.116 Gram/Cc.

Temp., °K.	Press., Atm.
273.171	122.246
268.299	117.806
263.044	113.005
258.633	108.966
253.433	104.199
250.180	101.215

ρ = 0.116 Gram/Cc.

Temp., °K.	Press., Atm.
248.429	99.6046
242.691	94.5228
237.314	89.3321
230.025	82.5904
222.897	75.9463
217.105	70.5128
212.133	65.833
208.191	62.094
202.719	56.874
197.702	52.030
193.292	47.700
190.718	45.110
190.020	44.398

ρ = 0.158 Gram/Cc.

Temp., °K.	Press., Atm.
273.167	163.165
255.152	137.447
248.132	127.404
236.376	110.577
223.618	92.3183
213.471	77.8210
206.337	67.651
202.795	62.618
200.377	59.215
197.527	55.151
195.209	51.883
192.905	48.641
191.518	46.699

ρ = 0.164 Gram/Cc.

Temp., °K.	Press., Atm.
273.058	169.592
273.016	169.528
252.875	139.042

ρ = 0.164 Gram/Cc.

Temp., °K.	Press., Atm.
233.362	109.482
213.012	78.7240
207.822	70.9075
204.003	65.204
200.541	60.039
197.891	56.111
195.124	52.017
193.489	49.609
192.043	47.502
191.787	47.137
191.395	46.571
191.197	46.287
191.008	46.008
190.807	45.735

ρ = 0.179 Gram/Cc.

Temp., °K.	Press., Atm.
273.092	187.380
273.071	187.330
263.118	169.980
253.141	152.600
243.119	135.156
233.137	117.783
223.155	100.465
213.180	83.2477
213.172	83.2205
213.165	73.5743
207.531	65.925
203.030	62.277
200.867	59.447
199.181	56.251
197.265	52.643
195.076	49.592
193.215	47.381
191.840	47.356

ρ = 0.189 Gram/Cc.

Temp., °K.	Press., Atm.
272.698	199.744
272.695	199.746
272.694	199.748
268.298	191.360
268.298	191.366
263.443	182.075
253.272	162.664
243.363	143.763
243.360	143.765
237.012	131.671
237.011	131.674
233.379	124.753
233.378	124.736
222.603	104.294
212.003	84.3351
212.002	84.3330
203.400	68.3544
198.147	58.767
195.806	54.555
192.465	48.653

ρ = 0.206 Gram/Cc.

Temp., °K.	Press., Atm.
274.151	228.227
267.309	213.066
260.100	197.057
252.960	181.188
245.904	165.489
238.529	149.163
228.077	126.043
218.591	105.201
209.262	84.8889
203.539	72.5944
196.471	57.699
192.346	49.283
191.421	47.442
190.671	45.968

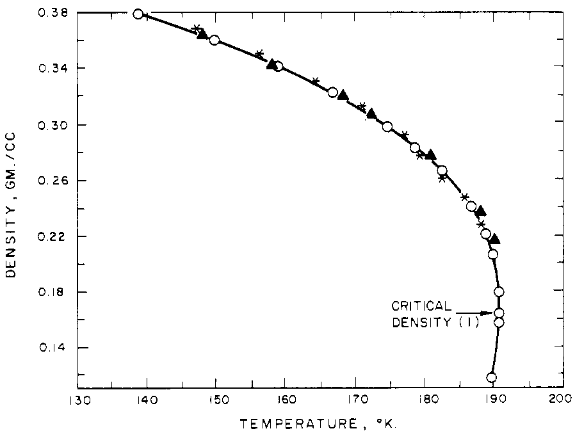

Figure 1. Saturated liquid densities

○—○ This work

* Bloomer and Parent (2)

▲ Keyes et al. (11)

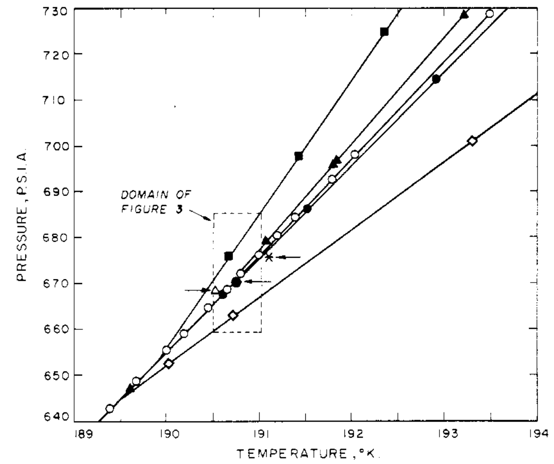

Figure 2. Experimental measurements in the critical region

Critical points

T, °K.	P, P.S.I.A.	Ref.	Nominal Density
* 191.06	677.1	(11)	0.116 g./cc. ◇
△ 190.55	668.6	(2)	0.158 g./cc. ●
● 190.77	671.0	(This work)	0.164 g./cc. ○
			0.179 g./cc. ▲
			0.206 g./cc. ■

to Constant Density for Methane

This number of significant figures is retained for consistency.

Temp., °K.	Press., Atm.
ρ = 0.221 Gram/Cc.	
273.153	252.590
267.883	239.261
267.816	239.090
262.926	226.733
258.305	215.029
253.099	201.858
248.751	190.863
242.967	176.257
238.487	164.940
233.248	151.730
227.820	138.049
222.763	125.347
213.291	101.724
207.164	86.5472
203.288	77.0752
199.975	69.0424
197.065	62.074
195.031	57.255
195.014	57.221
192.859	52.187
191.043	48.024
190.706	47.256
190.415	46.600
190.140	45.978
189.735	45.075
189.226	43.950
188.937	43.310
ρ = 0.240 Gram/Cc.	
275.155	299.467
268.822	280.664
260.829	256.956
253.056	233.896
245.069	210.114
236.577	184.864
228.611	161.199
221.330	139.638

Temp., °K.	Press., Atm.
ρ = 0.240 Gram/Cc.	
212.903	114.797
207.594	99.2556
203.020	85.9600
199.576	76.043
194.770	62.365
191.420	53.020
188.895	46.102
187.618	42.655
ρ = 0.265 Gram/Cc.	
272.981	363.591
267.880	345.060
261.819	322.956
254.520	296.286
241.276	247.754
232.788	216.544
222.864	180.109
213.636	146.323
207.737	124.749
201.010	100.400
198.385	90.8090
194.385	76.4900
189.227	58.148
185.237	44.228
183.322	37.679
ρ = 0.282 Gram/Cc.	
274.304	431.613
266.747	400.210
258.637	366.383
250.722	333.435
240.977	292.481
233.055	259.076
224.994	224.997
217.013	191.271
208.789	156.453
200.503	121.369

Temp., °K.	Press., Atm.
ρ = 0.282 Gram/Cc.	
196.350	103.800
184.411	54.274
180.980	40.264
179.803	35.504
179.113	32.723
ρ = 0.297 Gram/Cc.	
272.927	493.559
263.277	448.609
253.114	400.865
248.024	376.860
243.037	353.310
237.586	327.446
233.371	307.399
229.109	287.081
223.713	261.340
218.727	237.436
212.392	207.013
208.181	186.807
203.122	162.477
198.632	140.877
193.597	116.677
188.261	91.1138
182.805	65.081
182.805	65.107
178.055	42.664
175.605	31.186
ρ = 0.321 Gram/Cc.	
274.490	641.967
267.730	604.184
259.335	557.760
253.816	526.693
244.157	471.969
235.277	421.492
227.078	374.385
219.032	327.945

Temp., °K.	Press., Atm.
ρ = 0.321 Gram/Cc.	
211.493	284.074
204.147	241.068
196.055	193.510
186.819	138.986
178.454	89.4515
172.545	54.549
170.158	40.547
168.227	29.177
ρ = 0.341 Gram/Cc.	
252.980	659.443
247.365	662.874
235.756	546.410
228.404	497.497
212.612	391.107
204.135	333.169
197.280	285.866
189.751	233.635
181.641	177.166
176.864	143.532
172.744	114.502
159.295	19.333
ρ = 0.360 Gram/Cc.	
234.397	690.929
226.258	628.726
218.262	567.062
211.223	512.082
204.332	457.850
196.765	397.610
188.496	331.035
180.089	262.789
168.735	169.142
155.457	57.547
153.619	42.675
151.807	27.336
150.300	14.564

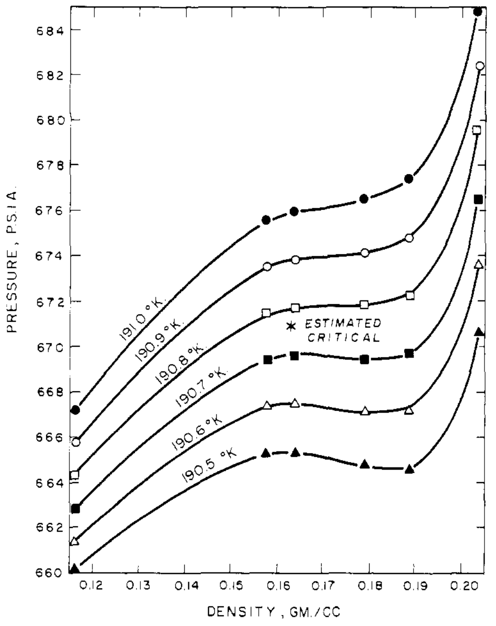

Figure 3. Interpolated isotherms in the vicinity of the critical

data of this work corresponds to a temperature of 190.77° K. and 45.66 atm. Estimates of the critical point made by Keyes *et al.* (*11*) and by Bloomer and Parent (*2*) are also shown in Figures 1 and 2. The convergence of this experimental data does not agree with either of these estimations. Both the Bloomer and Parent and Keyes determinations were made by a visual estimation of the point at which two-phase behavior was judged to disappear.

From the original data and the data of Douslin (*7*) above 0° C., an equation of state has been developed for methane wherein a single expression for pressure as a function of density and temperature applies in both the gas and liquid region (*18*). This equation is as follows:

$$\begin{aligned} P = {} & \rho^2[A_1 + A_2\rho + A_3\rho^2 + A_4\rho^3 + A_5\rho^4] + \\ & \rho T[R + B_1\rho + B_2\rho^2 + B_3\rho^3 + B_4\rho^4 + B_5\rho^5] + \\ & \rho^2(\rho + \rho_0)^2[(\rho + \rho_0)^3 - (\alpha + \rho_0)^3][(\beta + \rho_0)^3 - \\ & (\rho + \rho_0)^3]\, e^{G - [E_1 + E_2(\rho + \rho_0)^3](T - T_o)} + \\ & \rho^2[D_1 + D_2\rho + D_3\rho^2 + D_4\rho^3 + D_5\rho^4]\, e^{k - (F_1 + F_2\rho)/T} \end{aligned} \qquad (1)$$

Constants for this equation with units of p.s.i.a., ° K., and grams per cc. are given in Table III. The gas constant, R, for these units is 75.174 cc. p.s.i.a. per gram ° K. These constants reproduce the experimental pressure with an average absolute error of 0.04% and a root mean square error of 0.07%. The distribution of error for the 598 data points is given in Table IV. A total of only 10 points had errors in excess of 0.20%. Ninety-five per cent of the

Table II. Vapor Pressures and Experimental Saturated Liquid Densities

Vapor Pressures		Saturated Liquid Densities	
Temp., ° K.	Exptl. press., atm.	Density, gram/cc.	Temp., ° K.
133.730	4.4931	0.04107	171.35
136.409	5.2178	0.11607	189.43
138.726	5.9037	0.15787	190.7
144.417	7.8865	0.16389	190.7
148.821	9.7143	0.17900	190.63
154.309	12.3946	0.20644	189.85
158.213	14.6007	0.22067	188.82
161.861	16.9027	0.24025	186.74
165.876	19.7279	0.26515	182.58
166.017	19.7640	0.28186	178.70
170.407	23.2208	0.29681	174.75
174.332	26.7224	0.32098	166.75
176.443	28.7754	0.34067	158.82
177.953	30.2785	0.36001	149.77
180.688	33.0616	0.37901	138.96
182.179	34.7192		
184.703	37.7126		
186.524	39.9499		
188.113	42.0158		
188.593	42.6514		
188.801	42.9882		
188.919	43.0630		
189.063	43.2985		
189.413	43.7285		
189.383	43.7339		
189.612	44.0388		
189.674	44.1252		
190.011	44.5913		
190.177	44.8281		
190.455	45.2180		
190.653	45.4964		
190.658	45.5038		

Table III. Coefficient Values for the Methane Equation of State

Coefficient	Pressure Equation
A_1	−168379.37
A_2	100983.52
A_3	2074154.8
A_4	−12444994.
A_5	17600314.
B_1	369.46526
B_2	554.53908
B_3	−8614.1411
B_4	44316.430
B_5	−43179.188
D_1	−741.18776
D_2	−2806.7029
D_3	80674.262
D_4	−345392.00
D_5	382530.92
E_1	0.046002000
E_2	0.21177000
F_1	1378.7933
F_2	−1344.1846
G	34.348141
T_0	−147.71055
k	6.00000
α	0.141199
β	0.361788
ρ_0	0.113318
R	75.174

Table IV. Distribution of Per Cent Error in Calculated Pressure for 598 Points

Error Range, %	Number of Points in Error Range
0.00–0.05	487
0.05–0.10	79
0.10–0.15	15
0.15–0.20	7
0.20–0.30	2
0.30–0.40	3
0.40–0.50	1
0.50–0.60	4

errors were less than 0.1%, the estimated accuracy of the data, indicating that the equation was reproducing the data within the limits of error of the measurements.

The accuracy of the equation of state and regions of its applicability are described elsewhere (*18*). Except for a region near the critical point where the isotherms become flat, densities can also be predicted within 0.1%. This involves substituting a pressure and temperature into Equation 1 and iterating for the corresponding density. At points removed from the critical, the iteration converges rapidly to a value within 0.1% of the measured value.

The equation of state has been utilized in the present paper to obtain data adjusted slightly to obtain constant values of density. For the experimental results from each charge to the cell, an average density was selected. For each experimentally measured temperature, a small pressure adjustment was then made to give results at this constant-density value. The adjustment was made using the following relationship:

$$\Delta P = \left[\left(\frac{\partial P}{\partial \rho} \right)_T \right] \Delta \rho \qquad (2)$$

where $\Delta\rho$ was the required density change and the partial derivative was evaluated from the over-all equation of state. Because the equation of state fits all of the experimental data with a precision of better than 0.1%, it is probable that these small pressure adjustments do not introduce errors larger than this value. The adjusted pressures are presented in Table I, which shows the results at constant density.

DEVIATIONS FROM ISOCHORIC LINEARITY

The precision of the data is such that it is possible to calculate the degree to which the isochoric behavior deviates from a linear or van der Waals behavior. Equation 1 was differentiated to find

$$\left(\frac{\partial P}{\partial T} \right)_\rho$$

and

$$\left(\frac{\partial^2 P}{\partial T^2} \right)_\rho$$

at each of the constant-density values nearest to an experimental measurement. The region of greatest linearity in each isochore was determined by finding the temperature, T_0, and pressure, P_0, at which the second derivative is zero. No zero value of the second derivative could be determined for the ρ = 0.116 gram per cc. isochore or for any smaller density. The inflection point or extremum conditions for ρ = 0.158 gram per cc. and for all higher densities are presented in Table V. A value of zero for the second derivative indicates conditions at which the

Table V. Calculated Linear Isochoric Conditions for Methane

Density, Gram/Cc.	Temperature, °K.	Pressure, atm.	$(dP/dT)_v$, atm./°K.
	Temperature, Pressure, and Slope When $\left(\frac{\partial^2 P}{\partial T^2}\right)_v = 0$		
0.341	161.23	33.033	7.085
0.321	183.00	116.341	5.923
0.297	200.60	150.380	4.814
0.282	211.17	166.519	4.237
0.265	227.56	197.413	3.668
0.240	250.28	225.587	2.972
0.221	287.15	288.012	2.530
0.206	300.00	285.692	2.222
0.189	263.17	131.568	1.909
0.179	252.16	150.897	1.743
0.164	240.23	119.886	1.516
0.158	234.61	108.053	1.431

constant-volume heat capacity is independent of isothermal density variations, because

$$\left(\frac{\partial^2 P}{\partial T^2}\right)_\rho = -\frac{1}{\rho^2 T}\left(\frac{\partial c_v}{\partial \rho}\right)_T \qquad (3)$$

At temperatures below T_0 the second derivative is positive, indicating that c_v decreases with an isothermal density increase, and at temperatures above T_0 the second derivative is negative, indicating that c_v increases with an isothermal density increase.

Using the slope

$$\left(\frac{\partial P}{\partial T}\right)_\rho$$

at the point where

$$\left(\frac{\partial^2 P}{\partial T^2}\right)_\rho = 0$$

a linear relation, as would be predicted by the van der Waals equation of state, was calculated to give

$$\left[P_{\mathrm{vdW}} = \left(\frac{\partial P}{\partial T}\right)_{T_0,P_0}(T - T_0) + P_0\right]_\rho \qquad (4)$$

The calculated value of P_{vdW} is the result which would be predicted by van der Waals behavior at any temperature T along the isochore. The differences between the linear P_{vdW} values and the actual experimental values are shown in Figure 4 for a few densities. At densities where an inflection occurs, the deviation from linearity is s-shaped, with experimental pressures greater than the van der Waals pressure at low temperatures near the saturation curve and less than the van der Waals values at high temperatures. Near the saturation curve, the magnitude of the excess of the experimental values over the van der Waals increases with increasing density up to $\rho = 0.221$ gram per cc. At higher densities, this excess begins to decrease, until at $\rho = 0.341$ gram per cc. the experimental value has become less than the linear van der Waals value. The deviations from linearity in the critical region at $\rho_c = 0.1625$ gram per cc. are small but are definitely not zero. The critical isochore does not extrapolate linearly into the supercritical region, as assumed in some equations of state.

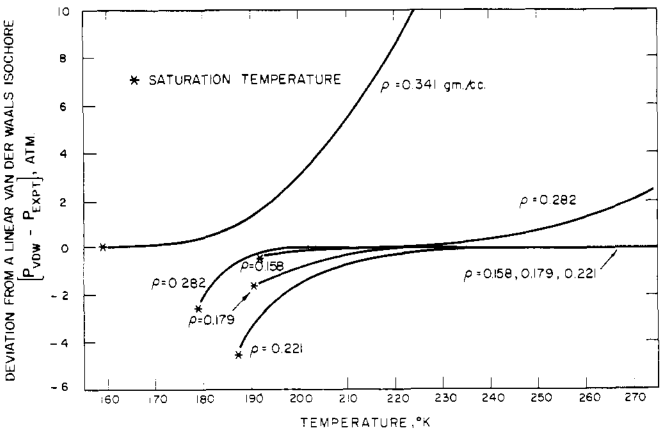

Figure 4. Deviations from linearity for selected methane isochores

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