

Accurate Measurements of the *PVT* Properties of Methane from -20 to 150°C and to 690 MPa

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The density of methane has been measured in the temperature range -20 to 150°C and in the pressure range 130 – 690 MPa, using a substitution method. The overall uncertainty in the results of 0.03% at the 95% confidence level. The data are presented in the form of a modified Benedict–Webb–Rubin equation of state and are compared with the results of other workers.

KEY WORDS: equation of state; high pressure; methane; modified Benedict–Webb–Rubin equation.

1. INTRODUCTION

A method for making high-pressure *PVT* measurements of high absolute accuracy has been developed and used to obtain data for argon [1] and nitrogen [2]. The method has now been used over an extended temperature range to obtain data for methane. The argon atom is strictly spherical, while the nitrogen molecule is shaped like a compact dumbbell. Methane is representative of a third type of simple molecule having a pseudospherical shape.

Using the substitution procedure [1–3], the *PVT* properties of a fluid are calculated from the data obtained in two separate runs. In the primary run fluid occupies the entire volume of a high-pressure vessel, while in the secondary run part of that volume is occupied by a slug of pure iron. One needs to know the equation of state of iron over the full pressure and

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temperature range of the proposed measurements, and the equation of state of the fluid itself at 25°C and pressures up to about 400 KPa. This information is readily available for both iron [4, 5] and methane [6]. The equation of state of iron used in this work is given in the Appendix.

The high-pressure vessel is designed so that its volume is a highly reproducible function of temperature and pressure, though it is not necessary to know this function. To facilitate this, the fluid is contained within a thin-walled silver "bladder," which acts as a liner for the vessel. The presence of the liner also makes it possible to measure the pressure within the vessel by a nonintrusive method.

2. APPARATUS AND PROCEDURE

The apparatus and procedure are essentially the same as have been described previously [1, 2], and only new developments will be discussed here. The methane was obtained from Matheson and was of 99.99% purity. In the temperature range -20 to 35°C, three primary (P) and three secondary (S) runs were made in the sequence P1, S1, S2, P2, P3, S3. Pressure measurements were made at -20, -10, 0, 10, 25, and 35°C, and at a given temperature were spaced at an average increment of 60 MPa. In the range 35–150°C, six more runs in the sequence P4, S4, P5, S5, S6, P6 were made. The pressures were measured at 35, 55, 75, 100, 125, and 150°C with an average increment of 65 MPa.

For the work with argon and nitrogen, high fluid pressures were generated thermally by warming the solid from 96 K. This approach rigorously ensures the maintenance of purity but is time-consuming and awkward, particularly if pressures above 400 MPa are required. Consequently, it was used here only for runs P1 to P2, while in subsequent runs a pressure intensifier was used to generate pressures beyond 200 MPa. In runs S6 and P6, thermal generation was abandoned entirely and compression to 200 MPa was provided by an Aminco diaphragm pump.

An intercomparison of all 12 runs at the common temperature of 35°C showed no systematic drift in the results as a consequence of these changes. Indeed, one would not expect the purity of the methane to be significantly degraded by either the diaphragm pump or the intensifier, where the only nonmetallic surfaces contacted by the fluid are unlubricated packings containing Teflon, nylon, and neoprene.

2.1. Hysteresis

The high-pressure vessel was designed to minimize hysteresis and creep, and indeed no evidence of significant hysteresis has been detected in

any of the work carried out so far over the lower temperature range (-20 to 35°C). However, in the range 35 – 150°C , small effects attributable to hysteresis were observed in early measurements.

Special runs, similar to the normal primary and secondary runs but with only a few measurement points, were therefore undertaken with the purpose of determining the extent of these effects. It was found that errors as large as 0.03% in the fluid density could result if the pressure and temperature cycles of the primary and secondary runs were radically different. However, in the normal measurement runs, these cycles were matched as closely as was practicable, and consequently hysteresis effects almost cancel out.

2.2. Accuracy

In the higher temperature range, the random component of the uncertainty appears to be somewhat greater than 0.013% , which was the value obtained for the work with argon and nitrogen [2]. This is probably due largely to the hysteresis mentioned above. Nevertheless, at pressures above 160 MPa, the overall uncertainty in the density at the 95% confidence level is still estimated to be 0.03% .

Below 160 MPa, the relative uncertainty in the pressure measurement increases rapidly and becomes predominant. The overall uncertainty at these pressures is estimated to be 0.035% , and no measurements were made below approximately 125 MPa.

3. RESULTS

The consistency of the *PVT* data from the six primary/secondary run pairs is quite satisfactory. At 35°C , where all the run pairs can be compared directly, the rms deviation of the density from the mean is only 9.2 in 10^5 . For the most part, the first derivatives agree to within 0.15% , the worst discrepancy observed being 0.35% .

An attempt was made to fit the combined results by an equation of state expressing the density as a double polynomial in temperature and pressure, but a satisfactory fit could not be achieved even when 30 terms were included. Attention was therefore turned to modified Benedict–Webb–Rubin (MBWR) equations of state. These equations have been used quite often for simple fluids [7–9], including methane [10] at lower pressures, and retain the advantage of being effectively linear in the disposable coefficients. It was found that the present data could be fitted very well by

a MBWR equation with only 16 coefficients:

$$\begin{aligned}
 p = & \rho RT + (C_1 T + C_2 + C_3 T^{-1} + C_4 T^{-2}) \rho^2 \\
 & + (C_5 T + C_6 + C_7 T^{-2}) \rho^3 + C_8 T^{-2} \rho^4 \\
 & + (C_9 T + C_{10}) \rho^5 + C_{11} \rho^6 + C_{12} T^{-1} \rho^7 + C_{13} T^{-2} \rho^8 \\
 & + (C_{14} \rho^3 + C_{15} \rho^5 + C_{16} \rho^7) T^{-2} \exp(-\gamma \rho^2)
 \end{aligned} \tag{1}$$

Here p is the pressure in MPa, T is the temperature in kelvins, and ρ is the density in $\text{kmol} \cdot \text{m}^{-3}$. The parameter γ was preset to the value ρ_c^{-2} , where ρ_c is the critical density, and R is the gas constant.

The coefficients C_i obtained from a least-squares fit are given in Table I. Table II shows for each temperature the pressure range of the data used in the fit, and hence gives its domain of validity. In the remainder of this

Table I. Coefficients of the Equation of State, Eq. (1)^a

i	C_i
1	-2.15848×10^{-4}
2	2.70630×10^{-1}
3	-6.63168×10^1
4	5.36764×10^4
5	4.73748×10^{-5}
6	-2.18800×10^{-2}
7	-3.43715×10^3
8	6.22601×10^1
9	-1.36169×10^{-8}
10	2.933875×10^{-5}
11	-2.8620×10^{-8}
12	-8.6010×10^{-7}
13	-9.135×10^{-7}
14	-1.005×10^4
15	2.7916×10^1
16	-7.468×10^{-2}
γ	9.6×10^{-3}
R	8.3143×10^{-3}

^aTemperatures are in K, pressures in MPa, and densities in $\text{kmol} \cdot \text{m}^{-3}$.

Table II. The Domain of Validity of the Methane Equation of State, Eq. (1)

T (°C)	Minimum p (MPa)	Maximum p (MPa)
150	150	680
125	140	670
100	130	680
75	150	670
55	140	690
35	150	660
25	170	600
10	180	580
0	180	560
-10	170	550
-20	170	530

paper, tables and plots representing the present results have been derived from Eq (1). Figure 1 shows isochores of the compressibility factor $Z = p/\rho RT$, and also the Joule inversion curve defined by

$$(\partial Z/\partial T)_\rho = 0 \tag{2}$$

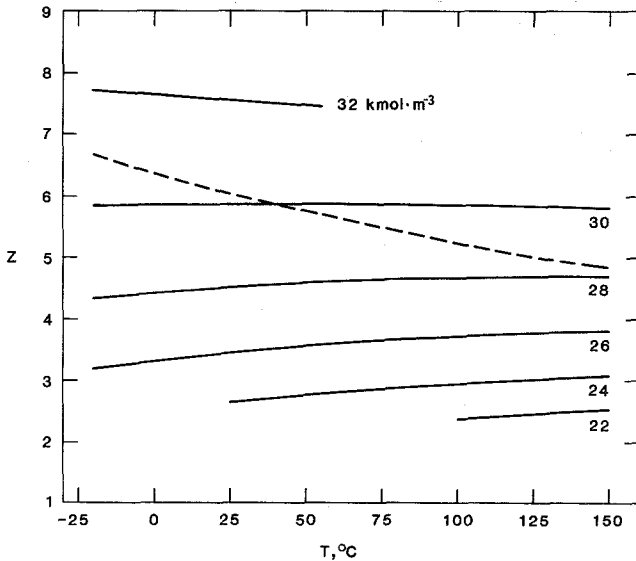


Fig. 1. Isochores of the compressibility factor Z . The dashed line is the Joule inversion curve.

Table III. Authors Presenting Measurements Comparable with Those Reported Here, Together with Their Temperature Ranges and Highest Pressures

Author(s)	Ref.	Temperature range (°C)	Highest pressure (MPa)
Trappeniers <i>et al.</i> (1979)	11	0–150	259
Robertson and Babb (1969)	12	35–200	1000
Cheng (1972)	13	–143 to +37	1025
Deffet and Ficks (1965)	14	51–152	300
Tsiklis <i>et al.</i> (1971)	15	50–400	861

3.1. Comparison with Other Work

Previous *PVT* determinations for methane that may be compared with the present work are listed in Table III. In Fig. 2 are plotted the departures of the densities given by these authors from those given by Eq. (1). The data of Tsiklis *et al.* are not represented in the figure, as their departures are large (up to 0.63%) and rapidly varying.

Most of the authors listed in Table III do not give uncertainty estimates. Trappeniers *et al.* performed their work using the same apparatus

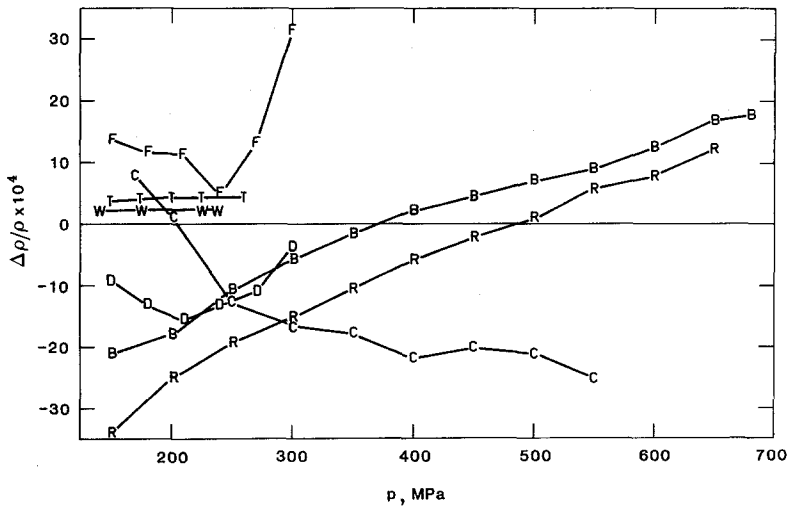


Fig. 2. Departures from the present equation of state of densities given by the authors listed below. In each case the literature densities are taken from tables of smoothed data or are calculated from equations fitted to the data. T, Trappeniers *et al.* (75°C); W, Trappeniers *et al.* (125°C); R, Robertson and Babb (35°C); B, Robertson and Babb (100°C); D, Deffet and Ficks (101.34°C); F, Deffet and Ficks (50.63°C); C, Cheng (–8.15°C).

and method as had been used extensively by Michels and co-workers, and they would probably have achieved an accuracy comparable with that of the present work. It is likely, however, that the data of the other authors contain uncertainties that are an order of magnitude or more greater.

The method used by Deffet and Ficks is very similar to that developed by Michels for a comparable range of temperature and pressure. Figure 2 shows, however, that their results contain errors of up to 0.3%, and that toward the top of their pressure range the slopes of their isotherms are wrong.

Robertson and Babb took their fiducial data from the 101.34°C isotherm of Deffet and Ficks. It is therefore not surprising that their results exhibit the same erroneous trend that is evident in that isotherm. It is possible [16] to correct the Robertson and Babb results for errors in the fiducial data by using the present data at 100°C. The Robertson and Babb densities at that temperature then lie within $\pm 0.03\%$ of those given by Eq. (1), while at 35°C they are too low by 0.05–0.09%.

The trend evident in the results of Cheng is almost identical to that found when comparing his densities for argon and nitrogen with those obtained using the present apparatus [1, 2].

Two isotherms representing the data of Trappeniers *et al.* are plotted in Fig. 2; similar plots at other temperatures lie between the isotherms shown. The departure of about +0.03% compares with -0.07% found when Michel's argon and nitrogen densities were compared with data obtained with the present apparatus.

As suggested by the plots in Fig. 2, the first derivatives of the Trappeniers *PVT* data are in close agreement with those of the present data. The difference is seldom more than 0.1% for $(\partial p/\partial \rho)_T$ or more than 0.45% for $(\partial p/\partial T)_\rho$. This high degree of consistency between the two data sets is further illustrated by Fig. 3, which shows the derivatives in dimensionless form at 50°C. At pressures below p_T the derivatives were calculated from the equation of state of Trappeniers *et al.*, while at pressures above p_M they are calculated from Eq. (1). The differences in the region of overlap are too small to be seen on this scale.

The close agreement found for the first derivatives does not extend to the important second derivative $(\partial^2 p/\partial T^2)_\rho$, for which there are differences as large as 27% between the present data and those of Trappeniers *et al.* These large differences appear to be largely due to the fact that this derivative is quite small, but they are exacerbated by comparisons being made close to the pressure limits of one or the other of the two sets of data. It seems, then, that one cannot rely solely on even the most accurate *PVT* data to give the complete equilibrium properties of a fluid. Speed-of-sound or calorimetric data at high pressure are required as well.

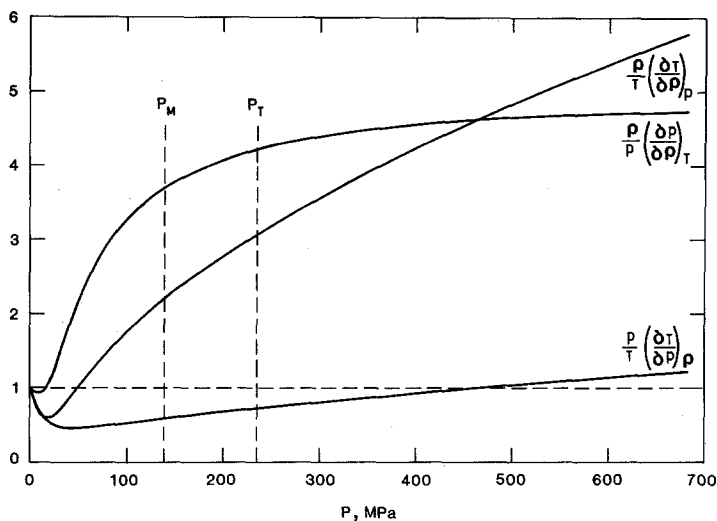


Fig. 3. The 50°C isotherms of the indicated dimensionless derivatives. Below p_T these quantities were calculated from the equation of state of Trappeniens *et al.*, while above p_M the present equation of state was used. Differences between these calculations in the region of overlap are too small to be seen on this scale.

Table IV. Isothermal Changes in the Helmholtz Free Energy and the Entropy of Methane Referred to the Lowest Density Shown for Each Isotherm^a

Density ($\text{kmol} \cdot \text{m}^{-3}$)	Free energy ($\text{MJ} \cdot \text{kmol}^{-1}$)			Entropy ($\text{kJ} \cdot \text{kmol}^{-1} \cdot \text{K}^{-1}$)		
	A	B	C	A	B	C
I. 50°C						
22.400	0.	0.		0.	0.	
23.0	0.1691	0.1690	-0.06	-0.869	-0.866	0.34
24.0	0.4695	0.4691	-0.08	-2.335	-2.328	0.30
25.0	0.7956	0.7947	-0.11	-3.826	-3.813	0.34
25.492	0.9664	0.9651	-0.13	-4.568	-4.553	0.33
II. 100°C						
20.486	0.	0.		0.	0.	
21.0	0.1615	0.1612	-0.19	-0.693	-0.693	0.
22.0	0.4892	0.4884	-0.16	-2.054	-2.057	-0.15
23.0	0.8374	0.8364	-0.12	-3.434	-3.441	-0.20
23.703	1.0962	1.0951	-0.10	-4.415	-4.425	-0.23

^aColumn A shows the quantities calculated from the present data, column B those calculated by Trappeniens *et al.*, and column C the percentage difference between the two calculations. The densities cover the region of overlap of the two sets of data.

Isothermal changes in such thermodynamic quantities as the Helmholtz free energy A and the entropy S are readily found from Eq. (1). These calculations were made and the results compared with values obtained by Trappeniers *et al.* from their PVT data. Table IV shows this comparison at 50 and 100°C and for the region of overlap of the two data sets. The greatest differences found were 0.58% for the entropy (at 125°C) and 0.19% for the free energy (at 100°C).

3.2. Conclusion

The present data and those of Trappeniers *et al.* are in close accord and together establish many important equilibrium thermodynamic properties of methane with good accuracy from 0 to 125°C and at pressures up to 690 MPa. At 150°C the pressure ranges of the two data sets do not quite overlap, but the separation is only 0.8% of the pressure range of the present data at that temperature.

APPENDIX

The equation of state of iron used in the present work is the same as that used in our work on nitrogen [2], and is given below. It differs slightly from the equation used in our argon work [1] in that the compressibility has been changed to what is considered to be a better value [2]:

$$\begin{aligned}
 V_I(T, p) = V_I(20, 0.1) & (0.999308 + 3.415 \times 10^{-5}T \\
 & + 2.34 \times 10^{-8}T^2 - 4.3 \times 10^{-11}T^3 + 1.5 \times 10^{-13}T^4 \\
 & - 6.06 \times 10^{-6}p + 1.17 \times 10^{-10}p^2 - 1.82 \times 10^{-9}pT)
 \end{aligned}$$

where V_I is the volume of iron, T is the temperature in °C, and p is the pressure in MPa.

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