

Measurements of the Compressibility and Sound Velocity in Methane up to 1 GPa, Revisited

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New density measurements of methane (CH₄) at 298.15 K up to 1 GPa are reported. The precision of the measurements is 0.03%, while the estimated accuracy is between 0.05 and 0.1%. Velocities of sound have been remeasured between 148.15 and 298.15 K at intervals of 25 K and at pressures up to 1 GPa, with an estimated accuracy of 0.12% at 100 MPa, 0.10% at 150 MPa, and 0.08% above 150 MPa. Comparisons with experimental results and equations of state of other workers are presented. The isothermal and the adiabatic compressibility and the ratio of specific heats have been calculated at 298.15 K.

KEY WORDS: CH₄; compressibility; density; high pressure; methane; pVT ; sound velocity.

1. INTRODUCTION

At the Xth AIRAPT conference in 1985, both density data of methane (CH₄) at 298.15 K and pressures up to 1 GPa were presented as well as sound velocities in the same pressure range at temperatures between 148.15 and 298.15 K at intervals of 25 K [1]. The number of investigations at elevated pressures which were available for a comparison was rather limited [2–6]. At 298 K there were no pVT data reported above 690 MPa. The sound velocities at that temperature were measured only below 400 MPa, while at lower temperatures there were no data at all. However, a preliminary equation of state [7] for methane which correlates the experimental data over a wide range of temperatures and pressures ($90 \leq T \leq 700$ K, $p \leq 1$ GPa), including the critical region, allows for a more extensive comparison and gives a check on the consistency of all

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available data within the range covered. A comparison with this equation showed that the systematic errors in both the previous density and the previous sound velocity data were larger than we had estimated. An analysis of the discrepancy is given in the next section. Both quantities were remeasured and the new results are discussed.

2. EXPERIMENTAL

2.1. Compressibility

The equipment and two methods for the determination of the compressibility isotherms of gases up to 1 GPa have been described previously [8]. The methods involve the expansion of gas from an initially pressurized vessel V_A into an evacuated vessel V_B . In the case of a total expansion, all gas is expanded at once; in the case of stepwise expansions, the gas is expanded in parts. Moreover, a third method has been used [9] in which the vessel V_B is evacuated after each expansion in a stepwise expansion run, making the method look like a traditional Burnett method. As in the other two methods and, therefore, also in contrast with the Burnett method, the density at the low-pressure side (vessel V_B) is obtained from literature data. By choosing pressures after the expansions which are not too high (ca. 10 MPa), the uncertainty in the correction of the volume V_B (in the low pressure side) due to the pressure is almost negligible. Another advantage is that more (and more accurate) data are available from literature for the evaluation of the density. This is valid in particular for methane, being the major component of natural gas. An overwhelming amount of recent, highly accurate data are available, as well as a number of equations of state below 12 MPa [10, 11, and references herein]. Disadvantages of the new method are that the data points within one run are highly correlated. The data points below 200 MPa become increasingly inaccurate, due to the fact that the pressure in the high-pressure side is measured with a manganin gauge.

The reason that the systematic error in our data turned out to be larger than expected is explained by two arguments. First, the time given to the system for reaching equilibrium in one of the two earlier runs was probably too short. By connecting an X - Y recorder to the differential pressure null indicator, the approach to equilibrium can be monitored better. Second, the values of the volume distortion coefficients due to pressure, β_A and β_B $\{\beta \equiv (1/V)(\Delta V/\Delta p)\}$, used in the evaluation of the earlier measurements, were determined from two stepwise expansion runs with argon between 300 and 150 MPa and gave the values: $\beta_A = 1.745 \times 10^{-5} \text{ MPa}^{-1}$ and $\beta_B = 5.7 \times 10^{-5} \text{ MPa}^{-1}$. In our present work

we used the values $1.847 \times 10^{-5} \text{ MPa}^{-1}$ and $3.0 \times 10^{-5} \text{ MPa}^{-1}$ for β_A and β_B , respectively. These values were obtained from total expansions with argon below 300 MPa. The difference between the values can be explained by the same argument as mentioned above, namely, that in the first case pressures in the high-pressure side (vessel A) were measured with a manganin gauge, whereas in the second case, an oil balance was used, the latter being far more accurate than the first.

The volume ratio V_B/V_A was determined from low-pressure gas expansions with methane and the data of Ref. 2.

2.2. Sound Velocity

The sound velocities were measured at 10 MHz with the well-known phase comparison pulse-echo technique, operating with one X-cut quartz transducer and two reflectors at unequal distances, having a ratio of 3:2. Details of the experimental setup and the method can be found elsewhere [12]. Two successive longitudinal sound wave pulses are generated in the fluid by applying two electrical pulses to the transducer. These pulses are clipped out of an (amplified) continuous signal of a synthesizer by a pulse former and a timer. Because of the chosen geometry it is possible to create interference in the transducer between the incoming echo from the first pulse reflected by the distant reflector and the echo from the second pulse reflected by the near reflector. The two echoes cancel each other, provided that the phases are opposite and the amplitudes of the incoming echoes are equal. The phase difference between the two echoes is related to the frequency by $\Delta\phi = \omega\tau$. The frequencies at which the incoming phases are opposite $\{\Delta\phi = (2n + 1)\pi\}$ are called null-frequencies. By measuring successive null-frequencies, the order of interference can be calculated by $n = (f_n/\Delta f_n) - \frac{1}{2}$, where $\Delta f_n = f_{n+1} - f_n$. Since n must be an integer, the exact value of the order of interference, n_i , is found by rounding off the calculated value. The transient time τ needed to overcome the difference of path lengths Δl is calculated from $\tau = (n_i + \frac{1}{2})/f_n$; the sound velocity follows from $w = \Delta l(T, p)/\tau$. To give an idea of the quantities involved: if the velocity of sound is $1500 \text{ m} \cdot \text{s}^{-1}$, the difference in null-frequency is about 80 kHz and the order of interference ranges from 110 to 120.

As the path of the second echo is shorter than that of the first echo, the attenuation will be less. In order to make the amplitudes of the echoes equal at the moment of their arrival in the transducer, the amplitude of the second pulse must be lowered. This is achieved by lowering the amplification rate of the second electrical pulse.

A problem that occurred in methane was caused by the much stronger attenuation in comparison to the previous measurements in helium, neon,

argon, and nitrogen. In the above description of the method, we assume that the phase difference between the first and the second electrical pulse depends only on the frequency and that no additional differences are introduced by the clipping process or the amplification rate. However, it turned out that the phase difference is also related to the amplification ratio of the two pulses. A small but constant additional phase shift does not necessarily trouble the measurement: it leads to a shift in the measured null-frequencies but does not affect the null frequency difference Δf_n , and as long as the deviations are not too large, the correct rounded-off order of interference is obtained. The shift is always very small compared to the null-frequency f_n . However, as the attenuation increases more and more, the amplification ratio becomes dependent on the frequency, due to the limitations in bandwidth of the amplifiers and enhanced by the Q -factor of the crystal. This caused a shift of the null-frequency difference Δf_n of a few hundred Hertz. An incorrect determination of the rounded-off value for the order of interference gives rise to large errors in the value of the sound velocity. In this experimental work, the shift was reduced by lowering the Q -factor of the transducer circuit and by measuring as far from the resonance peak of the crystal as is possible from the point of view of sensitivity. The final accuracy is discussed in the next section.

The gas under investigation was purchased from AGA gas B.V. and was stated to be 99.9995% pure. The major impurity was nitrogen.

3. RESULTS

3.1. Compressibility

Two runs of stepwise expansions (run A and B, containing eight and five data points, respectively), one run following the new semi-Burnett method of stepwise expansions followed by evacuation (run C containing 28 data points, of which 17 were above 100 MPa) and 12 total expansions (run D) were performed. The densities at low pressure were evaluated using the data of Trappeniers et al. [2] as reference. The data were correlated with a polynomial $p = \sum_{i=0}^4 a_i \rho^i$. A total of 33 data points was taken into account. All data points below 120 MPa were omitted because of the uncertainty in the pressure measurements. The results of run D were omitted for reasons given in Section 5. The experimental points of Ref. 2 (four points) between 85 and 210 MPa were added. The standard deviation is 0.03% in density. The deviations of the runs relative to the polynomial is shown in Fig. 1. The sharp increase in the deviations in run C at pressures below 200 MPa is due to a decreasing accuracy of the pressure

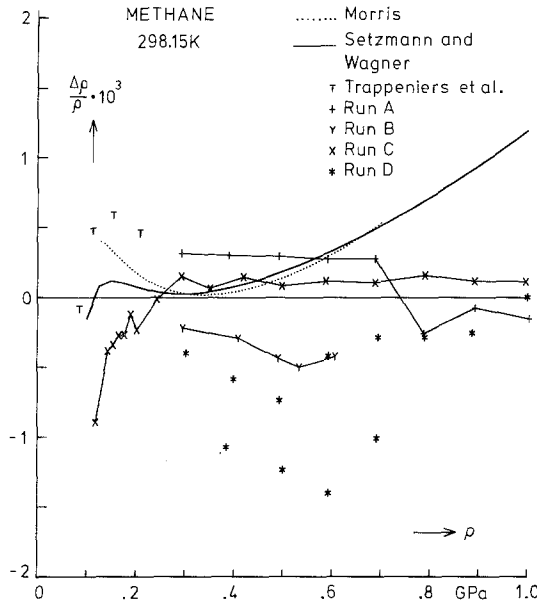


Fig. 1. Density deviations versus pressure of the experimental runs and the work of other authors, relative to the polynomial. $(\Delta\rho/\rho) = [(\rho - \rho_{\text{polynomial}})/\rho_{\text{polynomial}}]$.

measurements by the manganin gauge. The deviation of run D (total expansions) is discussed in Section 5. Our previous density values [1] were about 0.1% higher than the present data. After recalculation with the correct pressure distortion coefficients, the earlier measurements are consistent with the new data and the average deviations are 0.06%. By combining random and systematic errors [8], and assuming a total correlation between the two, the accuracy of the data is estimated to be 0.05% at 400 MPa, 0.06% at 700 MPa, and 0.09% at 1 GPa.

3.2. Sound Velocity

The sound velocity measurements were carried out in steps of 50 MPa starting from the highest pressure, 1 GPa, down to 250 MPa, while pressures were measured with a manganin gauge (accuracy, 0.1%). Between 250 and 100 MPa the step size was 25 MPa and pressures were measured with an oil balance via a mercury gas compressor (accuracy better than 0.01%). The isotherms, shown in Fig. 2, end at 100 MPa, where either the mismatch of the acoustic impedance between the quartz transducer and the gas or the strongly increased attenuation puts a limit to the detection of the echoes. The isotherms start well below the melting line.

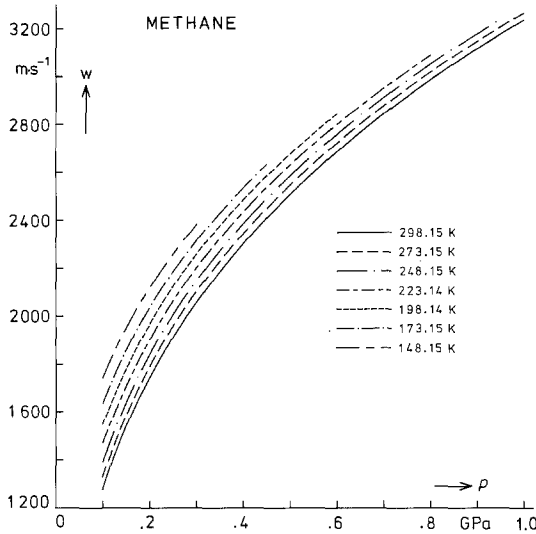


Fig. 2. Sound velocity in methane as a function of pressure along several isotherms.

The velocities of sound along the isotherms were correlated by polynomials $p = \sum_{i=0}^n a_i w^i$, where $n=4$ for all temperatures, except the 223.15 K isotherm, where $n=5$ gives a slightly better fit. The standard deviations range from 0.01 to 0.03%. The attenuation of the sound waves increases drastically as the pressure decreases below 200 MPa. This prevents the measurement at frequencies far outside the resonance peak of the crystal and so leads to a larger uncertainty in the sound velocity. From the polynomials, the values of the sound velocity at round pressures were calculated and the isobars are shown in Fig. 3. An estimate of the reproducibility of the sound velocities can be obtained by fitting the isobars to polynomials $w = \sum_{i=0}^2 a_i T^i$. The standard deviations range from 0.12% at 100 MPa, to 0.09% at 150 MPa, to about 0.07% for the higher isobars. This procedure is of course limited to about 550 MPa, due to the reduction in the number of data points by the presence of the melting line. We assume that the figure for the higher isobars will be the same. In order to calculate the accuracy of the data, one has to include the systematic errors. As given in Ref. 12, the main contribution to the systematic error comes from the path length determination and from diffraction effects; both contributions are estimated to be 0.01% in sound velocity. The systematic error in the pressure readings above 250 MPa has been estimated to contribute 0.02% and is negligible below 250 MPa. The accuracy is then found to be 0.12% at 100 MPa, 0.10% at 150 MPa, and 0.08% above 150 MPa.

From the density (ρ) and the sound velocity (w), it is easy to obtain

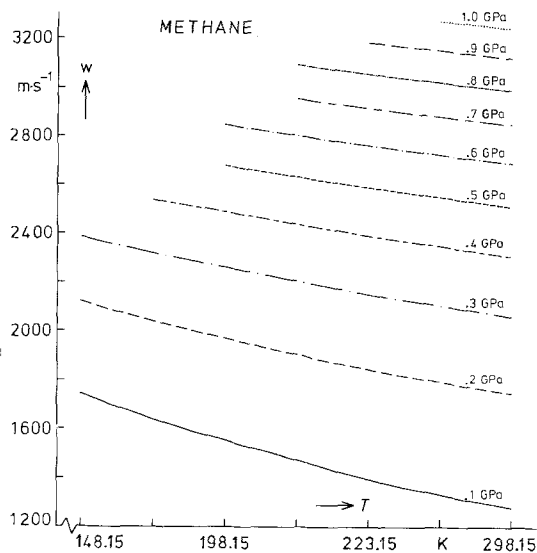


Fig. 3. Sound velocity in methane as a function of temperature along several isobars.

Table I. Thermodynamic Properties of Methane at 298.15 K

p (MPa)	ρ ($\text{kmol} \cdot \text{m}^{-3}$)	w ($\text{m} \cdot \text{s}^{-1}$)	$\chi_T \times 10^4$ (MPa^{-1})	$\chi_S \times 10^4$ (MPa^{-1})	γ
100	21.267 ^a	1272.95	274.72 ^a	180.88	1.519
150	23.675	1534.00	161.46	111.88	1.443
200	25.329	1737.35	113.93	81.53	1.397
250	26.624	1906.53	87.87	64.41	1.364
300	27.699	2052.75	71.48	53.41	1.338
350	28.621	2182.31	60.24	45.73	1.317
400	29.433	2299.14	52.06	40.06	1.299
450	30.161	2405.88	45.84	35.70	1.284
500	30.821	2504.38	40.96	32.25	1.270
550	31.427	2596.04	37.03	29.43	1.258
600	31.987	2681.88	33.79	27.09	1.247
650	32.509	2762.71	31.07	25.12	1.237
700	32.999	2839.18	28.76	23.43	1.228
750	33.460	2911.82	26.78	21.97	1.219
800	33.896	2981.04	25.05	20.69	1.211
850	34.310	3047.22	23.54	19.57	1.203
900	34.704	3110.65	22.20	18.56	1.196
950	35.081	3171.59	21.01	17.66	1.189
1000	35.442	3230.26	19.94	16.85	1.183

^a Data of Ref. 2.

Table II. Velocity of Sound (in $\text{m} \cdot \text{s}^{-1}$) in Methane at Round Values of the Pressure (in MPa)

p (MPa)	T (K)						
	298.15	273.15	248.15	223.15	198.15	173.15	148.15
100	1272.95	1330.39	1392.99	1469.28	1546.83	1639.66	1739.99
150	1534.00	1586.05	1644.94	1711.44	1778.11	1858.04	1941.04
200	1737.35	1787.00	1841.12	1901.92	1961.04	2032.48	2105.03
250	1906.53	1954.27	2004.60	2060.43	2114.82	2180.37	2245.54
300	2052.75	2098.68	2146.11	2197.71	2248.76	2309.96	
350	2182.31	2226.47	2271.66	2319.82	2368.13	2425.96	
400	2299.14	2341.61	2385.00	2430.43	2476.30	2531.37	
450	2405.88	2446.75	2488.63	2531.90	2575.52		
500	2504.38	2543.76	2584.34	2625.89	2667.41		
550	2596.04	2634.03	2673.42	2713.54	2753.15		
600	2681.88	2718.58	2756.88	2795.73			
650	2762.71	2798.25	2835.50	2873.13			
700	2839.18	2873.66	2909.88	2946.26			
750	2911.82	2945.33	2980.54	3015.55			
800	2981.04	3013.70	3047.88				
850	3047.22	3079.11	3112.25				
900	3110.65	3141.85	3173.95				
950	3171.59	3202.20					
1000	3230.26	3260.35					

the adiabatic compressibility χ_S [$\equiv 1/(\rho w^2)$]. The isothermal compressibility χ_T [$\equiv (1/\rho)(\partial\rho/\partial p)_T$] was calculated from the polynomial expression. The ratio of χ_T/χ_S gives γ , the ratio of specific heats. The results for $T = 298.15$ K are given in Table I. The sound velocities at several temperatures at round values of the pressure are listed in Table II.

4. COMPARISONS

4.1. Compressibility

A plot of the deviations between the results of Morris [4] and our polynomial is also shown in Fig. 1. Morris used a modified Benedict Webb Rubin equation (MBWR) in order to correlate his experimental data (accuracy, 0.035% below 160 MPa and 0.03% above) in the temperature range between 253 and 423 K and at pressures between 130 and 690 MPa. This equation deviates from our polynomial expression by 0.04% at the

lowest pressure and 0.05% at the highest and almost coincides in between. The deviations are well within the combined experimental error. The deviation curve of the equation of state of Setzmann and Wagner [7] lies close to that of the MBWR equation. The largest deviation (0.12%) with our polynomial is found at the highest pressure. The values above 700 MPa calculated with the equation are also higher than our corrected previous data.

If expressed in terms of pressure, the difference at the highest pressure between the equation of state of Setzmann and Wagner and our polynomial is 0.6% or 6 MPa. We would like to emphasize that the same manganin gauge is used in all our pressure measurements above 300 MPa. The "zero point" of this cell is checked against the oil balance on every occasion in which the pressures in the high- and in the low-pressure side are equal. The cell never showed any marked deviations and, from our experience with the manganin gauges we know that the slope of the resistance versus pressure curve does not change significantly. In our opinion the uncertainty in the pressure reading does not explain the difference between the equation of state of Setzmann and Wagner and our experimental data.

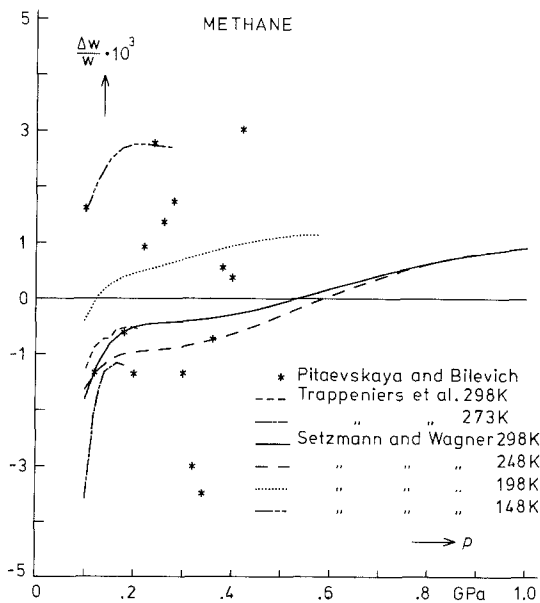


Fig. 4. Comparison between previous and the present sound velocity data. $(\Delta w/w) = [(w - w_{\text{polynomial}})/w_{\text{polynomial}}]$.

4.2. Sound Velocity

A comparison of the present results with those of other authors is given in Fig. 4. The only experimental data above 400 MPa are those of Pitaevskaya and Bilevich [5], who measured the velocity of sound up to 450 MPa at temperatures between 298 and 473 K at 25-K intervals. These authors performed the measurements at frequencies ranging from 0.1 to 4 MHz and observed no dispersion. No experimental accuracy is given by the authors. Their data at 298.15 K scatter randomly around our values. The deviation at 100 MPa of the results of Lacam [6] is about 2.5% and therefore not shown.

Furthermore, a comparison with the velocities of sound calculated from pVT data of Ref. 2 along two isotherms shows that the deviations are systematic and decrease with pressure. No estimate of the accuracy is given by the authors. The deviations are comparable in size to those previously obtained for argon, neon, and nitrogen. The values predicted by the equation of state of Setzmann and Wagner [7] are in good agreement with our results over the whole temperature range: in general the deviations do not exceed 0.1% except for the 148 K isotherm, where the deviations are about 0.25%. Four deviation curves are shown. The tendency is the same for other isotherms.

5. DISCUSSION

Just as in the case of nitrogen [13], a discrepancy is observed between data obtained from stepwise expansions and those from total expansions. As can be seen in Fig. 1, the densities obtained from total expansions (run D) are systematically lower, with the largest deviations at about 600 MPa, whereas at lower and at higher pressures, the difference diminishes. Such an effect is not seen in the measurements in helium [14], neon [15], or argon [8].

One possibility for explaining this discrepancy, namely, the influence of the pressurizing medium on the pressure reading of a manganin gauge [16], was investigated recently. A manganin gauge (Harwood Inc., U.S.A.) was calibrated at 700 MPa against a 1.5-GPa controlled clearance balance in two ways: (1) directly, using kerosene as pressurizing medium; and (2) via a 1-GPa differential pressure indicator, using nitrogen as pressurizing gas. Within the reproducibility of the manganin gauge (about 2 bar), there were no differences observed.

A second possibility for explaining the discrepancy is adsorption or absorption. Both in the new Burnett-like stepwise expansions and in the

total expansion runs, the low-pressure side is evacuated before each new expansion, making the conditions almost equal. The fact that the old stepwise expansion method and the new Burnett-like stepwise expansion method give very good agreement makes the assumption of sorption effects less likely.

A third explanation could be a deviation in the initial densities of about 0.1% around 40 MPa. The density obtained from a total expansion run at a certain pressure and that obtained from an intermediate point of a successive expansion run at the same pressure do not depend on the same region of the reference data. As no experimental data in this region other than those of Ref. 2 are known to the authors, this assumption is hard to test. The equation of state proposed by Younglove and Ely [17] shows marked deviations in this region.

To date, the discrepancy has not been solved.

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