Accurate experimental (p, ρ, T) data and virial coefficients for the (methane and helium) binary system

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Abstract

The quality and the availability of experimental data limit the achievable accuracy of multiparameter equations of state, such as the GERG-2008. Referring to the fundamentals of this wide-range equation of state, no suitable data were available for many mixtures containing helium. This work provides accurate experimental (*p, ρ, T*) data for three binary mixtures of methane with helium: (0.95 (amount-of-substance fraction) CH_4 + 0.05 He) and (0.90 CH_4 + 0.10 He) at temperatures of (240, 250 and 260) K, and (0.50 CH_4 + 0.50 He) from (240 to 400) K. This work is a continuation of a previous one which reported accurate experimental (*p, ρ, T*) data for the (0.95 CH_4 + 0.05 He) and the (0.90 CH_4 + 0.10 He) binary mixtures in the temperature range from the (250 to 400) K. All density measurements were performed by using a single-sinker densimeter with magnetic suspension coupling at pressures up to 20 MPa. Experimental data were compared with the corresponding densities calculated from the GERG-2008 and the AGA8-DC92 equations of state. Deviations from the GERG-2008 are much larger than from the AGA8-DC92 (up to –6.5 %). These deviations increased with decreasing temperature, with increasing pressure, and with increasing helium fraction. In contrast, deviations from the AGA8-DC92 are within the 0.5 % band. The experimental values were also used to calculate the second interaction virial coefficient $B_{12}(T)$ for this mixture.

Keywords: methane; helium; natural gas thermodynamic characterization; density; single-sinker densimeter; GERG-2008 equation of state.

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1. Introduction

The GERG-2008 equation of state [1] was established as ISO standard (ISO 20765-2) for the calculation of thermodynamic properties of natural gases [2]. The equation satisfies the demand on the accuracy in the calculation of thermodynamic properties in the entire fluid region for 21 natural gas components. Experimental data for these pure components and for 210 binary combinations of these components were considered for the development of the GERG-2008 equation of state. For those binary mixtures for which enough accurate experimental data were available, binary specific departure functions or a generalized departure function were developed. However, most of the binary systems were taken into account by using adjusted reducing functions for density and temperature, due to the lack of experimental data for some binary mixtures. Formally, GERG-2008 should be adequate for any mixture consisting of an arbitrary combination of the 21 considered components. However, there are some mixtures for which the equation does not yield a satisfactory property description. The lack of accurate measurements or that the mixture conditions are far beyond the range of validity of GERG- 2008 are some reasons. This is the case of the binary mixture (methane + helium), for which no departure function was established yet. In fact, the GERG-2008 report considers binary mixtures containing helium as one of the binary mixtures proposed to develop a generalized departure function in the future [1].

This work provides accurate experimental (p, ρ, T) data for three methane and helium binary mixtures with (0.95 CH_4 + 0.05 He), (0.90 CH_4 + 0.10 He) and (0.50 CH_4 + 0.50 He). Density measurements were performed by using a single-sinker densimeter with magnetic suspension coupling at temperatures of (240, 250 and 260) K and pressures up to 20 MPa for the (0.95 CH_4 + 0.05 He) and the (0.90 CH_4 + 0.10 He) mixtures and at temperatures from (240 to 400) K and pressures up to 20 MPa for the (0.50 CH_4 + 0.50 He) mixture. Experimental data were compared with the corresponding densities calculated from the GERG-2008 and the AGA8-DC92 [4] equations of state.

This work is a continuation of a previous one which reported accurate experimental (p, ρ, T) data for the (0.95 CH_4 + 0.05 He) and the (0.90 CH_4 + 0.10 He) binary mixtures in the temperature range from the (250 to 400) K [5]. In that work it could be perceived large deviations of the experimental density from the GERG 2008, especially at lower temperatures and increasing with the helium content. For that reason it was decided to extend the experimental study for the same mixtures to even lower temperatures (240 K) and to a new

mixture with a higher helium content (0.50 CH4 + 0.50 He). A new refrigerated-heating circulator was installed in the laboratory to extend the temperature range of the single sinker densimeter. This new device allows measuring (*p, ρ, T*) data from 240 K.

Moreover, the second interaction virial coefficients $B_{12}(T)$ for the (CH_4 + He) binary mixture at temperatures from (240 to 400) K were also estimated from the new experimental data presented in this paper and the experimental data presented in the previous one.

To achieve the highest accuracy in composition, the three binary mixtures were prepared following the gravimetric method by the Federal Institute for Materials Research and Testing (Bundesanstalt für Materialforschung und –prüfung, BAM) in Berlin, Germany.

2. Experimental

2.1. Mixtures preparation

The (CH_4 + He) binary mixtures were prepared by the Federal Institute for Materials Research and Testing (Bundesanstalt für Materialforschung und –prüfung, BAM) in Berlin, Germany, according to the ISO 6142 [6]. The mixtures were supplied in aluminum cylinders of 10 dm^3. Table 1 shows the composition and the expanded uncertainty (k = 2) of the mixtures. Table 2 shows the purity, supplier, molar mass and critical parameters of the samples of pure methane and helium. All substances were used without further purification.

The preparation of the mixtures was carried out in two steps. First, the mixture of (0.50 CH_4 + 0.50 He) was prepared by a consecutive introduction of pure helium and pure methane into the evacuated recipient cylinder (BAM no.: 8092-141020, volume: 10 dm^3). The substance transfer was actuated only by the pressure difference between the cylinder containing the pure compound and the recipient cylinder. The mass of the gas portion was determined after each filling step using a high-precision mechanical gas balance (Voland model HCE 25, Voland Corp., New Rochelle NY, USA). The resulting mixture had a pressure of approximately 15 MPa.

The other two binary mixtures were prepared in a similar way. A specified portion of the (0.50 CH_4 + 0.50 He) parent mixture was introduced into a new cylinder and diluted by a properly measured amount of

methane to create the final composition. The two cylinders displayed a pressure of 13.9 MPa for the (0.95 CH_4 + 0.05 He) mixture and of 14.8 MPa for the (0.90 CH_4 + 0.10 He) mixture, respectively. Each mixture was finally homogenized by a procedure of subsequent heating and rolling.

The samples of (0.95 CH_4 + 0.05 He) and (0.90 CH_4 + 0.10 He) were validated by gas chromatography (GC) against samples of similar composition following the single-point exact-match calibration according to ISO/CD 12963 [7]. The gas mixture used for validation matched the (0.90 CH_4 + 0.10 He) mixture, and the analysis was executed on a multichannel process GC (Siemens MAXUM II, Siemens AG, Karlsruhe, Germany) for the investigation of natural gases. The GC was equipped with customized packed columns particularly adapted for the analysis of synthetic natural gases and individual TCDs (thermal conductivity detectors) for each channel. The analysis was performed in an isothermal regime at 60 °C. Table 3 gives the results of the GC analysis. These measurements were entirely done at BAM prior to the density determination. The GC analysis for the (0.50 CH_4 + 0.50 He) mixture was not performed due to the fact that the helium content was higher than the validated limit of the used method. However, it was possible to validate its composition thanks to the concordance with the GC analysis of the other two mixtures.

2.2. Equipment description

The single-sinker densimeter was developed by Brachthäuser et al. [8] and further improved by Klimeck et al. [9] in the ‘90s. The measuring technique is based on the Archimedes’ principle and the high accuracy of this methodology is achieved thanks to the magnetic suspension coupling system, which allows measuring the buoyancy force on the sinker without any contact between the sinker and the high-accuracy microbalance. This allows accurate density measurements of fluids over wide temperature and pressure ranges [10]. The single-sinker densimeter used in this work was especially designed for density measurements of pure gases and gaseous mixtures and has been previously described in detail by Chamorro et al. [11] and further improved by Mondéjar et al. [12].

Another device related with the high accuracy of the measurements is the weight changing device. It consists in two calibrated masses used to reduce the ‘nonlinearity effect’ of any electronic balance. The calibrated masses are made of tantalum and titanium. They have approximately the same volume (4.9 cm^3) and their mass difference is similar to that of the sinker (60 g approximately). This allows operating the balance near

to its zero point and additionally makes the air buoyancy effect negligible. The two masses were provided by Rubotherm GmbH, Bochum, Germany, and their mass and volume were determined at the Spanish National Metrology Institute (Centro Español de Metrología, CEM) [11].

The sinker used in this experiment was a silicon cylinder with a real mass of 61.59181 ± 0.00016 g and a volume of 26.444 ± 0.003 cm^3 (k = 2), measured at 293.05 K and 1.01134 bar.

The density of the fluid is given by the following expression:

$$\rho = \frac{\left(m_{S0} - m_{Sf}\right)}{V_S\left(T, p\right)} \tag{1}$$

where the difference between the sinker mass in vacuum m_{S0} and the sinker mass in the pressurized fluid m_{Sf} is expressed in kg and refers to the buoyancy force experienced by the sinker and is measured by an accurate microbalance (Mettler Toledo AT261, Mettler Toledo GmbH, Gießen, Germany). $V_S(T, p)$ is the volume of the sinker immersed in the fluid in m^3, which is accurately known as a function of temperature and pressure [12].

A new ultra-low refrigerated-heating circulator Julabo FP51-SL was installed to control the temperature inside the measuring cell. This new equipment allows measuring $\left(p, \rho, T\right)$ data at temperatures of 240 K (instead 250 K). In addition, the temperature stability inside the measuring cell with this new thermostatic bath is better than with the old one, specially at low temperatures. The temperature of the fluid inside the measuring cell is determined by two platinum resistance thermometers (S1059PJ5X6, Minco Products, Inc., Minneapolis MN, USA) connected to an AC comparator resistance bridge (F700, Automatic Systems Laboratories, Redhill, England). The pressure is measured by two Digiquartz transducers (2300A-101 and 43KR-HHT-101, Paroscientific Inc., Redmond WA, USA) which are used for pressures up to 2 MPa and for pressures between (2 to 20) MPa, respectively.

The single-sinker densimeter is one of the most accurate devices for the measurement of the density of fluids; however, it presents some systematic errors, which can affect to the final density results. There are two main effects that must be evaluated: the force transmission error (FTE) due to the magnetic coupling and the adsorption of gas molecules on the cell and sinker surfaces. These two aspects will be discussed in the results section.

2.3. Experimental procedure

Experimental (p, ρ, T) measurements for the (0.95 CH_4 + 0.05 He) and the (0.90 CH_4 + 0.10 He) mixtures were obtained at (240, 250 and 260) K by using the single-sinker densimeter with magnetic suspension coupling. Later, (p, ρ, T) measurements for the (0.50 CH_4 + 0.50 He) binary mixture were carried out at nine temperatures from (240 to 400) K and pressures up to 20 MPa. The pressure was decreasing in 1 MPa steps from (20 to 1) MPa for each isotherm. Therefore, taking into account the previously reported results for the (0.95 CH_4 + 0.05 He) and the (0.90 CH_4 + 0.10 He) mixtures [5], nine isotherms were obtained at (240, 250, 260, 275, 300, 325, 350, 375 and 400) K for each of the three (CH_4 + He) binary mixtures.

The sinker mass in a vacuum was measured after each isotherm to check any misalignment suffered by the magnetic suspension coupling during the measurements and to cancel the apparatus effect of the FTE. The maximum difference between the replicates of the sinker mass in a vacuum at the same temperature was 0.0001 % for all the (CH_4 + He) mixtures. This good repeatability of the measurements in a vacuum confirmed that there was not any misalignment during the measurements.

Moreover, before and after measurements on the studied (CH_4 + He) mixtures, test measurements by using nitrogen as reference fluid were carried out in the whole working range of the apparatus to validate the operation. The experimental results were compared with the densities calculated from the reference equation of state for nitrogen by Span et al. [13]. Relative deviations of the experimental data from the calculated densities were within a ±0.02 % band, with an absolute average deviation (*AAD*) of 0.0058 %.

2.4. Uncertainty of the measurements

Uncertainties of the properties involved in the procedure of density measuring by the single-sinker densimeter used in this work were thoroughly evaluated by Mondéjar et al. after performing several improvements on the equipment [12]. The expanded uncertainty (k = 2) in temperature was less than 4 mK. Regarding the pressure uncertainty, it depends on the pressure transducer and is given by Eq. 2 and Eq. 3 for the (2 – 20) MPa and (0 – 2) MPa transducers, respectively. The expanded uncertainty (k = 2) in pressure was less than 0.005 MPa.

$$U(p) = 75 \cdot 10^{-6} \cdot p + 3.5 \cdot 10^{-3} \quad (2)$$

$$U(p) = 60 \cdot 10^{-6} \cdot p + 1.8 \cdot 10^{-4} \quad (3)$$

According to Eq. (1) and the law of propagation of uncertainties (GUM) [19], density uncertainty depends on the uncertainty of the sinker apparent mass when the measuring cell is evacuated, m_{S0}, and pressurized; m_{Sf}, and also depends on the uncertainty of the volume of the sinker, $V_S(T, p)$. The uncertainties of the sinker apparent masses are related with the balance readings and were calculated taking into account the balance calibration, resolution, repeatability and drift as sources of uncertainty (both when the cell is pressurized and evacuated). The sinker volume changes with temperature and pressure due to thermal and mechanical properties. However, the influence of these magnitudes in the volume uncertainty is much lower than the main component, so the overall uncertainty in volume was taken from its calibration certificate and it can be expressed as a function of the density. A detailed description of the relevance of the different contributions was presented in [12]. The expanded uncertainty (k = 2) in density ρ (kg·m^{-3}) is expressed as a function of density by Eq. 4.

$$U(\rho) = 2.3 \cdot 10^{-2} + 1.1 \cdot 10^{-4} \cdot \rho \quad (4)$$

To calculate the overall standard uncertainty in density $U_T(\rho)$ (k = 2), the uncertainties of density, temperature, pressure, and composition of the mixture must be considered, as is expressed in Eq. 5.

$$U_T(\rho) = 2 \cdot \left[u(\rho)^2 + \left(\left(\frac{\partial \rho}{\partial p} \right)_{T,x} \cdot u(p) \right)^2 + \left(\left(\frac{\partial \rho}{\partial T} \right)_{p,x} \cdot u(T) \right)^2 + \sum_i \left(\left(\frac{\partial \rho}{\partial x_i} \right)_{T,p,x_j \neq x_i} \cdot u(x_i) \right)^2 \right]^{0.5} \quad (5)$$

where p is the pressure, T is the temperature, and x_i is the amount-of-substance (mole) fraction of each of the mixture components. Partial derivatives were calculated by means of the GERG-2008 equation of state by using the software REFPROP [14]. Table 4 shows a summary of the uncertainty contributions of each property involved in the density determination and the overall uncertainty in density of the measurements for the three studied (CH_4 + He) binary mixtures.

3. Experimental results

Tables 5, 6 and 7show the experimental (p, ρ, T) data of the three (CH_4 + He) binary mixtures measured in this work and the relative deviation in density from the values estimated with the GERG-2008 and the

AGA8-DC92 equations of state. The state points on each isotherm were calculated as the average of the last ten measured values of the corresponding magnitude for each pressure step. Tables 5, 6 and 7 also show the expanded uncertainty in density (k = 2), calculated by Eq. 4, and the expanded overall uncertainty (k = 2) of all the experimental data, calculated by Eq. 5. These values are given in absolute value (density units) and relative as a percentage of the measured density.

As it was mentioned before, there are two effects that must be evaluated: the force transmission error (FTE) associated to the magnetic coupling and the effect related with the adsorption of gas molecules on the cell and sinker surfaces.

The FTE has been discussed in detail by McLinden et al. [15] and others [16][17]. This effect has two terms: the apparatus effect and the fluid-specific effect. In this work, the apparatus effect of the FTE was avoided thanks to the measurements in a vacuum after each isotherm. The fluid-specific effect depends on the magnetic behavior of the measured gas. The magnetic susceptibility (χ) of the (CH_4 + He) binary mixtures studied in this work was estimated by using the additive law proposed by Bitter [18]. The estimated magnetic susceptibility for the (0.95 CH_4 + 0. 05 He) mixture is $\chi_{He5\%} = -8.62 \cdot 10^{-9}$, $\chi_{He10\%} = -8.17 \cdot 10^{-9}$ for the (0.90 CH_4 + 0.10 He) and $\chi_{He50\%} = -4.64 \cdot 10^{-9}$ for the (0.50 CH_4 + 0.50 He). According to McLinden et al. [15], the apparatus effect affects more than the fluid-specific effect to the density measurements, except for strongly paramagnetic fluids. The magnetic susceptibility values estimated for (CH_4 + He) mixtures does not present paramagnetic behavior (i.e. magnetic susceptibility of oxygen is $\chi_{O_2} = 1.78 \cdot 10^{-6}$). Since the values of magnetic susceptibility of the mixtures are relatively low, the magnetic behavior of the fluids would be negligible in relation to the apparatus effect and therefore the fluid specific effect was not considered in the measurements.

Regarding sorption effects inside the measuring cell, the sorption tests carried out for the previous reported measurements of the (CH_4 + He) mixtures didn't show evidence of that [5]. Therefore, this effect has not been taken into account in the measurements presented in this work.

4. Discussion of the results

4.1. Compatibility of the experimental data with previous measurements

The whole range of the experimental density values for the (0.95 CH_4 + 0.05 He) and the (0.90 CH_4 + 0.10 He) mixtures were performed in two different experiences with a delay of a few months. First, density measurements at (250, 275, 300, 325, 350, 375 and 400) K were performed and the results were reported [5]. Six months later, three isotherms at (240, 250 and 260) K were carried out for both (0.95 CH_4 + 0.05 He) and (0.90 CH_4 + 0.10 He) mixtures by using the new thermostatic bath. The experimental (p, ρ, T) results from the two experiences have been used as a unique dataset for the data treatment of each mixture. As the experimental density data for the 250 K isotherm are repeated in the two sets of experiments, they were validated by calculating their compatibility index I given by Eq. 6.

$$I = \frac{x_1 - x_2}{\sqrt{U(x_1)^2 + U(x_2)^2}} \tag{6}$$

where x_i is the property to compare, in this case the relative deviation of experimental density from density calculated by the GERG-2008, and $U(x_i)$ is their relative overall expanded uncertainty. Data are considered compatibles if $I < 1$. This condition was fulfilled for all measured points. The average values were $I = 0.222$ for the (0.95 CH_4 + 0.05 He) mixture and $I = 0.121$ for the (0.90 CH_4 + 0.10 He) mixture. These results show the compatibility of experimental density data and also the correct work of the densimeter and the good stability of the (CH_4 + He) mixtures prepared by the gravimetric method.

4.2. Relative deviation of the experimental data from the reference equations of state

Figures 1 and 2 show the relative deviations for the (0.95 CH_4 + 0.05 He) mixture and Figures 3 and 4 for the (0.90 CH_4 + 0.10 He) mixture in the whole temperature range measured. Thus, the relative deviations from the GERG-2008 and the AGA8-DC92 equations of state of the previous measurements for these two mixtures are including in these figures. As it can be observed, the relative deviations of the experimental data from the GERG-2008 are clearly larger than relative deviations from AGA8-DC92. The data measured at (240, 250 and 260) K follow the trend of the previous measurements. For the (0.95 CH_4 + 0.05 He) mixture, the relative deviations of experimental density data from the GERG-2008 equation of state are as large as –2 %. The largest deviations were registered at 240 K and pressures around 15 MPa. In contrast, the highest relative deviation from the AGA8-DC92 is –0.2 % and relative deviations are lower at low

temperatures. For the (0.90 CH_4 + 0.10 He) mixture, relative deviations exceed –3 % from the values estimated by the GERG-2008. The largest deviation was registered at 240 K and 17 MPa. The relative deviations from the AGA8-DC92 exceed –0.2 %, but they are lower at low temperatures.

Figures 5 and 6 show the relative deviations for the (0.50 CH_4 + 0.50 He) mixture from the values estimated with the GERG-2008 and AGA8-DC92 equations of state, respectively. The maximum values from the GERG-2008 are close to –6.5 % at low temperatures and high pressures. Deviations from the AGA8-DC92 are positive at high pressures and low temperatures and negative at high temperatures with a largest deviation around 0.5 %.

A statistical comparison of the deviation data from GERG-2008 and AGA8-DC92 equations of state is given in Table 8. *AAD* is the average absolute deviation defined in equation 7, *Bias* is the average deviation defined in equation 8, *RMS* refers to the root mean squared defined in equation 9, and *MaxD* represents the maximum relative deviation in the considered data set.

$$AAD = \frac{1}{n}\sum_{i=1}^{n}\left|10^2 \cdot \frac{\rho_{i,\exp} - \rho_{i,EoS}}{\rho_{i,EoS}}\right| \tag{7}$$

$$Bias = \frac{1}{n}\sum_{i=1}^{n}\left(10^2 \cdot \frac{\rho_{i,\exp} - \rho_{i,EoS}}{\rho_{i,EoS}}\right) \tag{8}$$

$$RMS = \sqrt{\frac{1}{n}\sum_{i=1}^{n}\left(10^2 \cdot \frac{\rho_{i,\exp} - \rho_{i,EoS}}{\rho_{i,EoS}}\right)^2} \tag{9}$$

According to these data, the relative deviation of experimental density data from values calculated from both equations of state increases with the helium content of the mixture, especially for deviations from the GERG-2008. The *AAD* from the GERG-2008 is 0.655 for the (0.95 CH_4 + 0.05 He) mixture, 1.170, almost double, for the (0.90 CH_4 + 0.10 He) and 2.849, four times larger, for the (0.50 CH_4 + 0.50 He) mixture.

The mixture models developed for the formulation of the GERG-2008 are based in the Helmholtz free energy, expressed in its dimensionless form, $a(\delta, \tau, x)$, which is not accessible through experimental measurements. The Helmholtz free energy is divided in two terms: the ideal behavior term and the residual term. When the critical parameters of any binary mixture are very asymmetric, the mixture has a behavior far from ideality. The difference between the critical temperatures of the pure components of a binary

mixture can be used as a simplified indication of the extent of the real mixture behavior. When the critical temperatures of the components of a binary mixture differ by more than 150 K, uncertainties up to 1 % may exist [1]. This is the case of the (CH_4 + He) mixture. Moreover, the mixture model of the GERG-2008 does not have any (specific or generalized) departure function for the (CH_4 + He) mixture and the studied mixtures present a helium content far to that present in a typical natural gas composition (less than 0.1 mol-%, according to the GERG-2004 monograph [19]). Therefore the large deviations of the experimental density from the GERG-2008, much higher than the stated uncertainty of the EoS for these mixtures, can be associated to that.

In contrast, the deviation from the AGA8-DC92 is distinctly lower. The AGA8-DC92 equation of state is written in terms of the compressibility factor [4], therefore, its formulation does not depend on the critical parameters. This fact can explain why the AGA8-DC92 equation of state fits better than the GERG-2008 to these asymmetric mixtures with composition far from that of typical natural gases.

4.3. Virial coefficients

The second and the third virial coefficients for the three (CH_4 + He) mixtures were calculated by fitting the experimental data to the virial equation of state (VEoS).

$$Z = \frac{p}{RT} = \sum_{k=1}^{N} \left(\frac{B_k}{M^k} \right) \cdot \rho^k \tag{10}$$

where Z is the compressibility factor, which gives the ideality ratio of the fluid, p is the pressure, R is the ideal gas constant (8.31447 $cm^3 \cdot MPa \cdot K^{-1} \cdot mol^{-1}$), T is the temperature, ρ is the mass density and B_k the virial coefficients, which have a physical meaning related to the interaction between groups of molecules, with $B_1 = 1$, and N is the number of terms.

VEoS is an infinite series; therefore it must be truncated after a finite number of terms. The method proposed by Cristancho et al. was used to determine the number of terms of the VEoS for the determination of the virial coefficients of the three (CH_4 + He) binary mixtures. According to Cristancho et al. [20], the number of terms required depends upon the maximum experimental density determined ρ_{max}. If the number of terms becomes insufficient, the deviations of the equation from the data exceed the experimental uncertainties,

and if N becomes excessive, one or more of the fit parameters will not be statistically significant. The procedure used was as follows. First, the molar mass M was determined as a fitted parameter along with the terms of the VEoS. This step was carried out for the three studied (CH_4 + He) mixtures at the temperature of 250 K for various combinations of N and ρ_{max} values. The fit was carried out by using a least-squares fitting method contained in MATLAB software [21]. The results in which all fit parameters were statistically significant and the deviations from the data were within the estimated experimental uncertainty were evaluated.

The results show that the fit is only effective for pressures below p_{max} = 13 MPa, independently of the value of ρ_{max}. Therefore, the number of terms, N, and maximum pressure, p_{max}, combination that yielded the molar mass M closest to the value derived from the gravimetric preparation was used for the determination of the second and the third virial coefficients for each mixture. The final combinations for the studied mixtures were: N = 4, p_{max} = 12, for the (0.95 CH_4 + 0.05 He) mixture; N = 4, p_{max} = 13 for the (0.90 CH_4 + 0.10 He) mixture; and N = 3, p_{max} = 12 for the (0.50 CH_4 + 0.50 He) mixture.

The fit to estimate the virial coefficients were performed using the molar mass values from the gravimetric preparation of each mixture, not the fit molar mass value. Since experimental uncertainties of temperature, pressure and density was taken into account, a normal random distribution term based on the estimated uncertainties for each magnitude was included in the fit process with a coverage interval of 95 %, following the Monte Carlo method suggested by the GUM [22]. The estimated results for the second $B(T,x)$ and the third $C(T,x)$ virial coefficients with their uncertainties are shown in Table 9.

The second interaction virial coefficient $B_{12}(T)$ was also estimated from $B(T,x)$ by Eq. 11. Interaction virial coefficients of methane (B_{11} and C_{111}) and helium (B_{22} and C_{222}) were obtained from reference equations of state of methane [23] and helium [24] at corresponding temperatures by using REFPROP [14]. The uncertainty was estimated by following the law of propagation of uncertainty. The results are also shown in Table 9.

$$B(T,x) = x_1^2 B_{11}(T) + 2x_1 x_2 B_{12}(T) + x_2^2 B_{22}(T) \tag{11}$$

According to theory, the interaction virial coefficients are independent of composition, therefore $B_{12}(T)$ only depends on temperature. The estimated values from the experimental data agree with that. However, as it can be observed in Figure 7, the values calculated from the GERG-2008 show a dependence on composition. Moreover, the estimated values agree with those reported by Bignell et al. [25] for the system (CH_4 + He) at temperatures between (290 and 310) K. Figure 8 shows $B_{12}(T)$ as a function of temperature, where a smooth trend with temperature can be observed.

5. Conclusions

522 accurate (p, ρ, T) data for three binary mixtures of methane with helium, (0.95 CH_4 + 0.05 He), (0.90 CH_4 + 0.10 He), and (0.50 CH_4 + 0.50 He), were obtained at temperatures between 240 K and 400 K and pressures up to 20 MPa by using a single-sinker densimeter with magnetic suspension coupling. These data will contribute significantly to the data-base of thermophysical properties. The mixtures were prepared gravimetrically at the Federal Institute for Materials Research and Testing (BAM) in Berlin, Germany.

Experimental data were compared with the corresponding densities calculated from the GERG-2008 and the AGA8-DC92 equations of state. The relative deviations are clearly higher for GERG-2008 than for the AGA8-DC92. Deviations from values calculated from GERG-2008 equation of state are within a –2 % band for the (0.95 CH_4 + 0.05 He) mixture, exceed the –3 % limit for the (0.90 CH_4 + 0.10 He) mixture and have maximum values close to –6.5 % for the (0.50 CH_4 + 0.50 He) mixture. These deviations increase with decreasing temperature, with increasing pressure, and with increasing helium fraction.

In contrast, deviations from the AGA8-DC92 are distinctly lower. This equation of state is written in terms of the compressibility factor, so its formulation does not depend on the critical parameters. Therefore the AGA8-DC92 could fit better than GERG-2008 to mixtures with components with very different critical temperatures and composition far from the typical natural gas composition.

Moreover, the second, $B(T,x)$, and third, $C(T,x)$, virial coefficients, together with the second interaction virial coefficient, $B_{12}(T)$, and their corresponding uncertainties were estimated from the experimental results at the studied temperatures.

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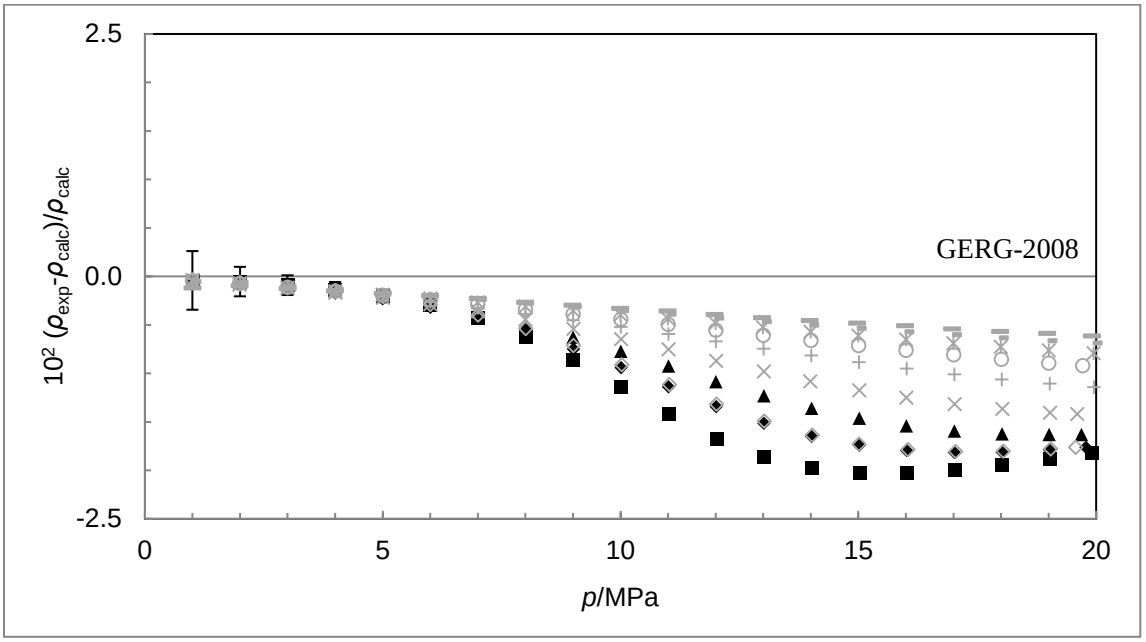

Figure 1. Relative deviations in density of experimental *(p, ρ, T)* data of the (0.9500147 CH_4 + 0.0499853 He) mixture ρ_{exp} from density values calculated from the GERG-2008 equation of state ρ_{EoS} versus pressure: T = ■ 240 K; T = ♦ 250 K; T = ▲ 260 K; (data from previous measurements [5]: T = ◇ 250 K; T = × 275 K; T = + 300 K; T = ○ 325 K; T = ∗ 350 K; T = − 375 K; T = − 400 K). Error bars on the 240 K isotherm indicate the expanded uncertainty (k = 2) of the experimental density data calculated with Eq. (4).

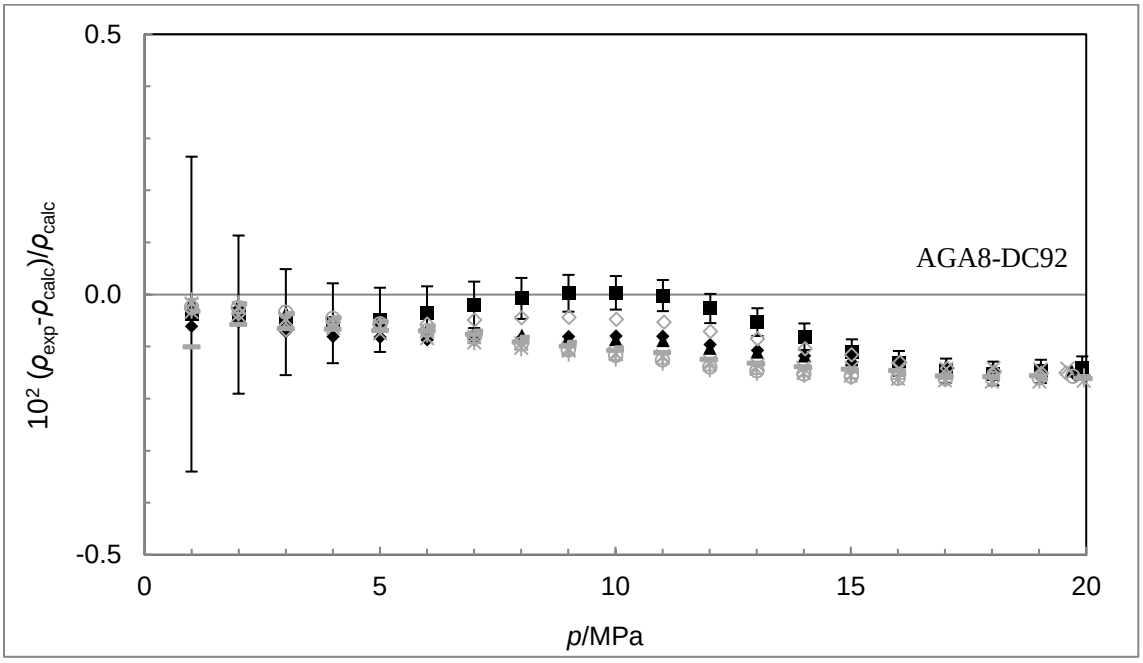

Figure 2. Relative deviations in density of experimental *(p, ρ, T)* data of the (0.9500147 CH_4 + 0.0499853 He) mixture ρ_{exp} from density values calculated from the AGA8-DC92 equation of state ρ_{EoS} versus pressure: T = ■ 240 K; T = ♦ 250 K; T = ▲ 260 K; (data from previous measurements [5]: T = ◇ 250 K; T = × 275 K; T = ＋ 300 K; T = ○ 325 K; T = ∗ 350 K; T = − 375 K; T = − 400 K). Error bars on the 240 K isotherm indicate the expanded uncertainty (k = 2) of the experimental density data calculated with Eq. (4).

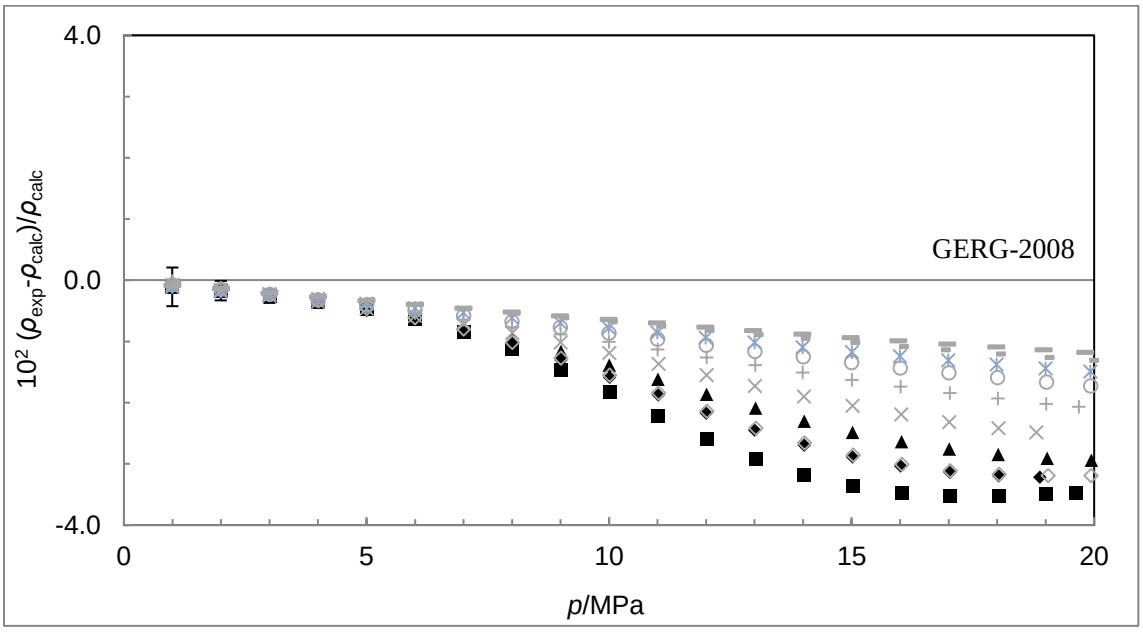

Figure 3. Relative deviations in density of experimental *(p, ρ, T)* data of the (0.89993256 CH_4 + 0.10006744 He) mixture ρ_{exp} from density values calculated from the GERG-2008 equation of state ρ_{EoS} versus pressure: T = ■ 240 K; T = ♦ 250 K; T = ▲ 260 K*;* (data from previous measurements [5]: T = ◇ 250 K; T = × 275 K; T = + 300 K; T = ○ 325 K; T = ∗ 350 K; T = − 375 K; T = − 400 K). Error bars on the 240 K isotherm indicate the expanded uncertainty (k = 2) of the experimental density data calculated with Eq. (4).

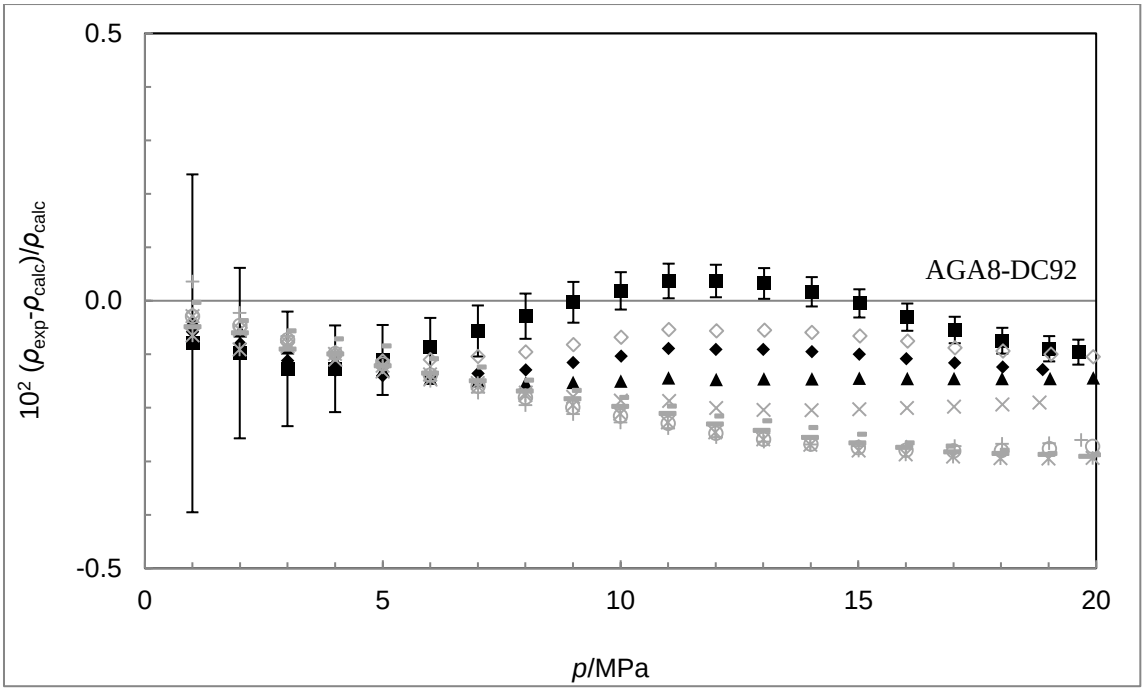

Figure 4. Relative deviations in density of experimental *(p, ρ, T)* data of the (0.89993256 CH_4 + 0.10006744 He) mixture ρ_{exp} from density values calculated from the AGA8-DC92 equation of state ρ_{EoS} versus pressure: T = ■ 240 K; T = ♦ 250 K; T = ▲ 260 K; (data from previous measurements [5]: T = ◇ 250 K; T = × 275 K; T = + 300 K; T = ○ 325 K; T = ∗ 350 K; T = − 375 K; T = − 400 K). Error bars on the 240 K isotherm indicate the expanded uncertainty (k = 2) of the experimental density data calculated with Eq. (4).

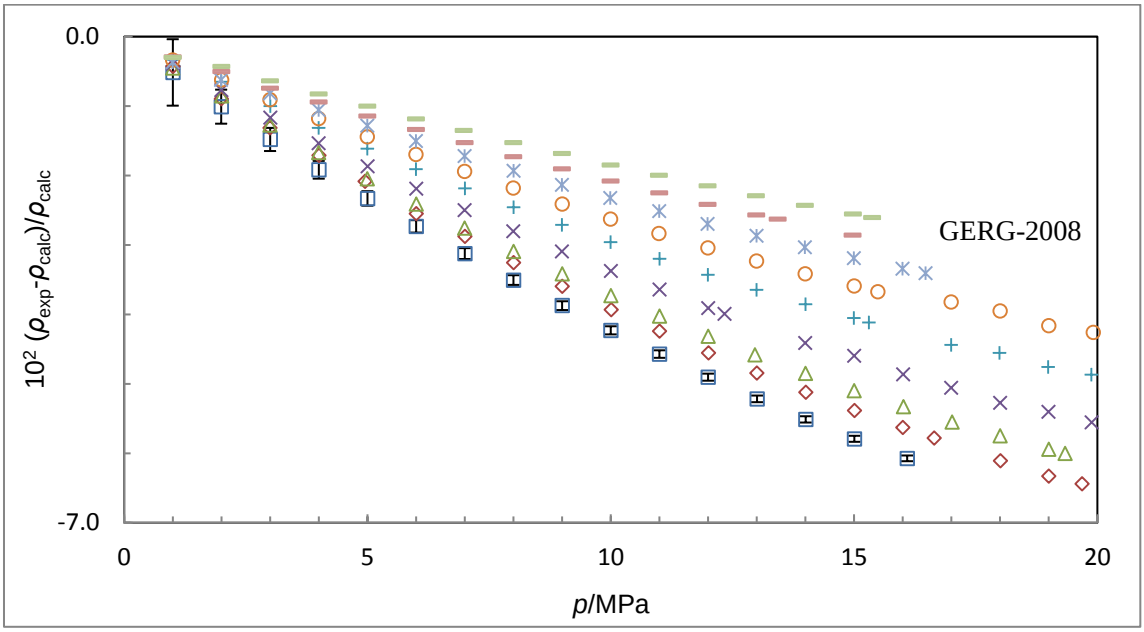

Figure 5. Relative deviations in density of experimental (p, ρ, T) data of the (0.4925924 CH_4 + 0.5074076 He) mixture ρ_{exp} from density values calculated from the GERG-2008 equation of state ρ_{EoS} versus pressure: □ 240 K; ◇ 250 K; △ 260 K; × 275 K; + 300 K; ○ 325 K; ✳ 350 K; − 375 K; − 400 K. Error bars on the 240 K isotherm indicate the expanded uncertainty (k = 2) of the experimental density data calculated with Eq (4).

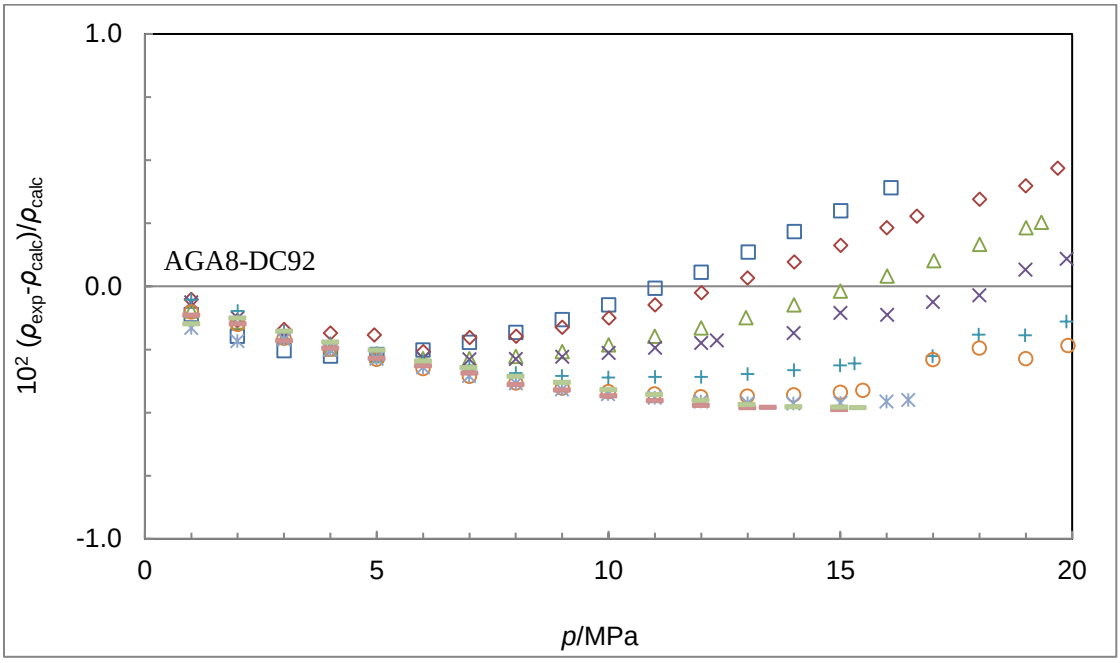

Figure 6. Relative deviations in density of experimental (p, ρ, T) data of the (0.4925924 CH_4 + 0.5074076 He) mixture ρ_{exp} from density values calculated from the AGA-DC92 equation of state ρ_{EoS} versus pressure: □ 240 K; ◇ 250 K; △ 260 K; × 275 K; + 300 K; ○ 325 K; ✳ 350 K; − 375 K; − 400 K. Error bars on the 240 K isotherm indicate the expanded uncertainty (k = 2) of the experimental density data calculated with Eq (4).

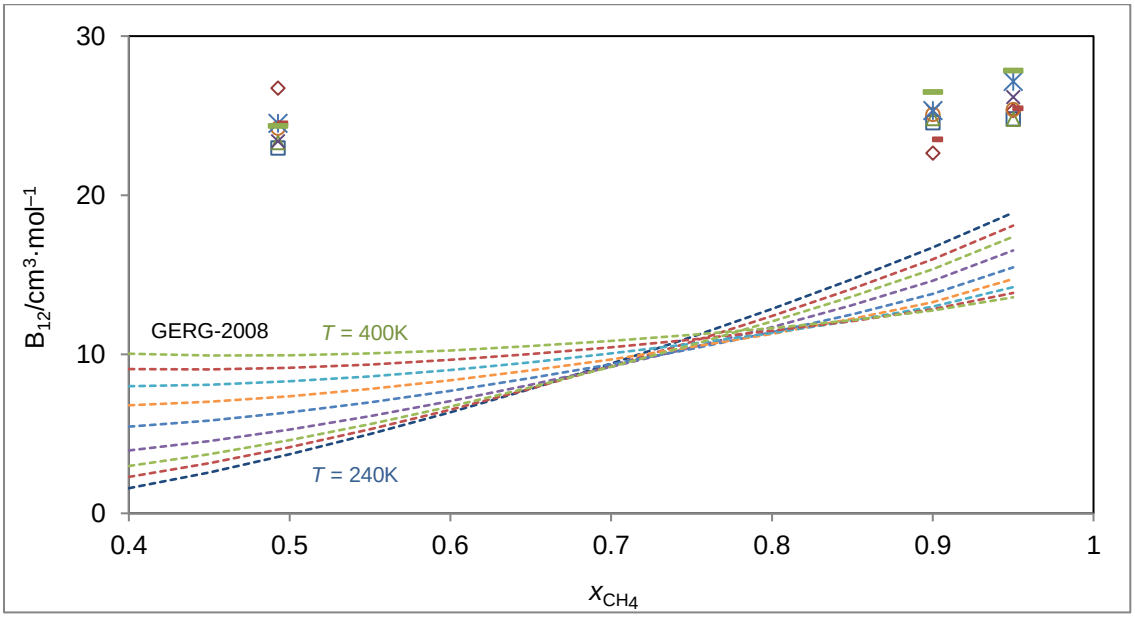

Figure 7. Second interaction virial coefficient $B_{12}(T)$ for the (CH_4 + He) mixture estimated from the experimental data. □ 240 K; ◇ 250 K; △ 260 K; × 275 K; + 300 K; ○ 325 K; ✳ 350 K; − 375 K; − 400 K. The dash lines represent the $B_{12}(T)$ values estimated from the GERG-2008 at different temperatures.

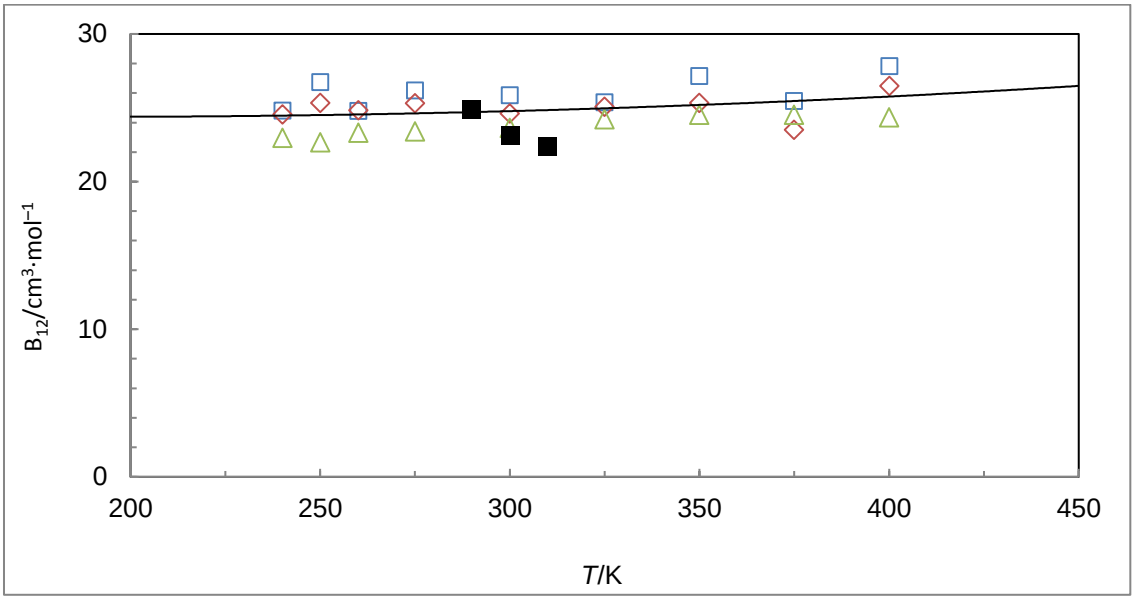

Figure 8. Second interaction virial coefficient $B_{12}(T)$ for the (CH_4 + He) binary mixture. □ (0.95 CH_4 + 0.05 He); ◇ (0.90 CH_4 + 0.10He); △(0.50 CH_4 + 0.50 He); ■ Bignell et al. [25]. The solid line represents the polynomial of degree 2 fitted to experimental data of this work. $B_{12}(T)/cm^3 \cdot mol^{-1} = -3 \cdot 10^{-5} \cdot T^2 + 0.0113 \cdot T + 25.438$.

Table 1. Composition of the studied (CH_4 + He) binary mixtures.

Component	(0.95 CH_4 + 0.05 He) BAM nº: 8036-150126		(0.90 CH_4 + 0.10 He) BAM nº: 8069-150127		(0.50 CH_4 + 0.50 He) BAM nº: 8092-141020	
	x_i (mol-%)	$U(x_i)$ (k = 2) (mol-%)	x_i (mol-%)	$U(x_i)$ (k = 2) (mol-%)	x_i (mol-%)	$U(x_i)$ (k = 2) (mol-%)
Methane	95.0015	0.0092	89.9933	0.0083	49.2592	0.0051
Helium	4.9985	0.0014	10.0067	0.0017	50.7408	0.0058

Table 2. Purity, supplier, molar mass and critical parameters of the individuals components of the studied (CH_4 + He) mixtures.

Components	Purity	Supplier	M/g·mol^{-1}	Critical parameters	
				T_c /K	P_c /MPa
Methane	≥ 99.9995 mol %	Linde[a]	16.043 [b]	190.564 [b]	4.599 [b]
Helium	≥ 99.9999 mol %	Linde[a]	4.003 [c]	5.195 [c]	0.228 [c]

[a] Linde AG, Unterschleißheim, Germany.
[b] Setzmann et al. [23].
[c] Ortiz-Vega et al. [24].

Table 3. Results of the GC analysis of the (CH_4 + He) binary mixtures and gravimetric composition of the validation mixture.

	(0.95 CH_4 + 0.05He)			(0.90 CH_4 + 0.10 He)		
Component	Concentration (mole fraction)		Relative deviation between gravimetric preparation and GC analysis	Concentration (mole fraction)		Relative deviation between gravimetric preparation and GC analysis
	x_i	$U(x_i)$/% (k = 2)	%	x_i	$U(x_i)$ /% (k = 2)	%
Methane	94.7963	0.0306	–0.216	90,0192	0.0397	0.029
Helium	4.9742	0.0085	–0.487	10.0195	0.0146	0.127
	Validation mixture BAM no.: 7065-100105					
Methane	90.438798	0.009165				
Helium	9.559901	0.005987				
Carbon monoxide	0.0002158	0.0000002				
Carbon dioxide	0.0002164	0.0000002				
Oxygen	0.0002139	0.0000002				
Argon	0.0002169	0.0000002				
Hydrogen	0.0002220	0.0000003				
Nitrogen	0.0002166	0.0000002				

Table 4. Contributions to the expanded overall uncertainty in density (k = 2) for the three studied (CH_4 + He) binary mixtures.

Source of uncertainty	Units	Contribution (k = 2)	Estimation in density (k = 2)	
			$kg \cdot m^{-3}$	%
		(0.95 CH_4 + 0.05 He)		
Temperature	K	0.004	< 0.004	< 0.005
Pressure	MPa	0.005	< 0.064	(0.007, 0.189)
Density	$kg \cdot m^{-3}$	(0.024 - 0.045)	(0.024, 0.048)	(0.022, 0.512)
Composition	$mol \cdot mol^{-1}$	< 0.0001	< 0.039	< 0.024
		Overall uncertainty	(0.024, 0.081)	(0.032, 0.552)
		(0.90 CH_4 + 0.10 He)		
Temperature	K	0.004	< 0.007	< 0.004
Pressure	MPa	0.005	< 0.055	(0.007, 0.189)
Density	$kg \cdot m^{-3}$	(0.024, 0.045)	(0.024, 0.045)	(0.007, 0.316)
Composition	$mol \cdot mol^{-1}$	< 0.0001	< 0.031	< 0.020
		Overall uncertainty	(0.024, 0.072)	(0.034, 0.565)
		(0.50 CH_4 + 0.50 He)		
Temperature	K	0.004	< 0.002	< 0.002
Pressure	MPa	0.005	< 0.023	(0.007, 0.185)
Density	$kg \cdot m^{-3}$	(0.024, 0.033)	(0.024, 0.033)	(0.038, 0.794)
Composition	$mol \cdot mol^{-1}$	< 0.00006	< 0.012	< 0.014
		Overall uncertainty	(0.024, 0.042)	(0.047, 0.795)

Table 5. Experimental (p, ρ, T) measurements for the (0.9500147 CH_4 + 0.0499853 He) mixture, relative and absolute expanded uncertainty in density (k = 2) $U(\rho_{exp})$, relative and absolute expanded overall uncertainty in density (k = 2) $U_T(\rho_{exp})$ and relative deviations from the GERG-2008 and AGA8-DC92 equations of state; where T is the temperature (ITS-90), p the pressure, ρ_{exp} the experimental density, and ρ_{GERG} and ρ_{AGA} the densities calculated from the GERG-2008 and the AGA8-DC92 equations of state.

T/K [a]	p/MPa [a]	ρ_{exp} /kg·m^{-3}	$U(\rho_{exp})$ / kg·m^{-3} (k = 2)	10^2 $U(\rho_{exp})$ /ρ_{exp}	$U_T(\rho_{exp})$/ kg·m^{-3} (k = 2)	10^2 $U_T(\rho_{exp})$ /ρ_{exp}	10^2 (ρ_{exp}–ρ_{GERG})/ρ_{GERG}	10^2 (ρ_{exp}–ρ_{AGA})/ρ_{AGA}
240.045	19.915	217.591	0.047	0.022	0.069	0.032	–1.820	–0.141
240.046	19.037	211.432	0.046	0.022	0.070	0.033	–1.882	–0.148
240.047	18.026	203.713	0.045	0.022	0.072	0.035	–1.948	–0.152
240.047	17.023	195.305	0.044	0.023	0.073	0.038	–1.999	–0.146
240.047	16.022	186.059	0.043	0.023	0.075	0.041	–2.031	–0.132
240.047	15.023	175.881	0.042	0.024	0.078	0.044	–2.030	–0.111
240.047	14.013	164.584	0.041	0.025	0.080	0.048	–1.979	–0.081
240.048	13.016	152.406	0.040	0.026	0.081	0.053	–1.865	–0.053
240.047	12.015	139.257	0.038	0.028	0.081	0.059	–1.676	–0.027
240.049	11.009	125.326	0.037	0.029	0.080	0.064	–1.418	–0.002
240.047	10.010	111.115	0.035	0.032	0.077	0.069	–1.142	0.003
240.045	9.003	96.823	0.034	0.035	0.073	0.075	–0.865	0.002
240.045	8.003	83.039	0.032	0.039	0.068	0.081	–0.626	–0.007
240.046	7.001	69.896	0.031	0.044	0.062	0.089	–0.433	–0.020
240.046	6.000	57.586	0.029	0.051	0.057	0.099	–0.294	–0.036
240.047	4.999	46.133	0.028	0.061	0.052	0.113	–0.198	–0.049
240.047	3.998	35.506	0.027	0.076	0.048	0.135	–0.134	–0.055
240.047	2.998	25.657	0.026	0.101	0.044	0.172	–0.090	–0.053
240.048	1.998	16.504	0.025	0.150	0.025	0.153	–0.053	–0.039
240.046	0.998	7.970	0.024	0.300	0.024	0.304	–0.041	–0.038
250.000	19.784	200.072	0.045	0.022	0.068	0.034	–1.762	–0.157
249.997	19.016	194.396	0.044	0.023	0.068	0.035	–1.787	–0.158
249.995	18.017	186.477	0.044	0.023	0.069	0.037	–1.810	–0.157
249.995	17.019	177.898	0.043	0.024	0.071	0.040	–1.815	–0.151
249.996	16.011	168.529	0.042	0.025	0.072	0.043	–1.795	–0.141
249.994	15.017	158.560	0.040	0.026	0.073	0.046	–1.743	–0.130
249.994	14.013	147.789	0.039	0.027	0.073	0.050	–1.649	–0.118
249.993	13.013	136.403	0.038	0.028	0.073	0.054	–1.514	–0.107
249.994	12.011	124.468	0.037	0.029	0.072	0.058	–1.342	–0.096

249.991	11.003	112.149	0.035	0.032	0.070	0.062	–1.137	–0.080
249.992	10.007	99.845	0.034	0.034	0.067	0.067	–0.940	–0.080
249.993	9.004	87.584	0.033	0.037	0.064	0.073	–0.748	–0.080
249.992	8.002	75.669	0.031	0.041	0.060	0.079	–0.579	–0.085
249.992	7.000	64.219	0.030	0.047	0.056	0.087	–0.436	–0.087
249.989	5.997	53.324	0.029	0.054	0.052	0.098	–0.321	–0.087
249.999	4.998	43.065	0.028	0.064	0.048	0.113	–0.231	–0.082
250.000	3.997	33.379	0.027	0.080	0.045	0.135	–0.171	–0.081
250.001	2.997	24.270	0.026	0.106	0.026	0.108	–0.122	–0.071
250.002	1.992	15.655	0.025	0.158	0.025	0.161	–0.078	–0.053
250.001	0.998	7.617	0.024	0.313	0.037	0.487	–0.070	–0.061
260.005	19.685	184.360	0.043	0.023	0.065	0.035	–1.630	–0.146
260.007	19.008	179.270	0.043	0.024	0.066	0.037	–1.631	–0.144
260.006	18.018	171.413	0.042	0.024	0.066	0.039	–1.622	–0.142
260.005	17.017	162.926	0.041	0.025	0.067	0.041	–1.593	–0.137
260.006	16.008	153.819	0.040	0.026	0.067	0.044	–1.540	–0.131
260.006	15.015	144.337	0.039	0.027	0.067	0.047	–1.463	–0.125
260.006	14.014	134.298	0.038	0.028	0.067	0.050	–1.359	–0.118
260.006	13.009	123.820	0.037	0.030	0.066	0.053	–1.231	–0.110
260.006	12.003	113.023	0.035	0.031	0.065	0.057	–1.085	–0.103
260.008	11.008	102.188	0.034	0.034	0.063	0.061	–0.924	–0.088
260.005	10.005	91.250	0.033	0.036	0.060	0.066	–0.773	–0.086
260.006	9.000	80.421	0.032	0.040	0.057	0.071	–0.628	–0.083
260.004	8.013	70.021	0.031	0.044	0.054	0.078	–0.496	–0.078
260.005	7.006	59.750	0.030	0.049	0.051	0.086	–0.378	–0.071
260.004	6.004	49.933	0.028	0.057	0.048	0.097	–0.284	–0.066
260.004	4.999	40.507	0.027	0.068	0.046	0.113	–0.207	–0.058
260.005	3.997	31.566	0.026	0.084	0.043	0.136	–0.147	–0.049
260.005	2.998	23.076	0.026	0.111	0.026	0.113	–0.096	–0.035
260.005	1.997	14.985	0.025	0.164	0.025	0.167	–0.053	–0.019
260.005	0.997	7.297	0.024	0.326	0.036	0.495	–0.029	–0.015

[a] Expanded uncertainties in temperature and pressure are $U(T) = 0.004$ K and $U(p) = 0.005$ MPa, respectively.

Table 6. Experimental (p, ρ, T) measurements for the (0.89993256 CH_4 + 0.10006744 He) mixture, relative and absolute expanded uncertainty in density (k = 2) $U(\rho_{exp})$, relative and absolute expanded overall uncertainty in density (k = 2) $U_T(\rho_{exp})$ and relative deviations from the GERG-2008 and AGA8-DC92 equations of state; where T is the temperature (ITS-90), p the pressure, ρ_{exp} the experimental density, and ρ_{GERG} and ρ_{AGA} the densities calculated from the GERG-2008 and the AGA8-DC92 equations of state.

T/K [a]	p/MPa [a]	ρ_{exp} /kg·m^{-3}	$U(\rho_{exp})$ / kg·m^{-3} (k = 2)	10^2 $U(\rho_{exp})$ /ρ_{exp}	$U_T(\rho_{exp})$/ kg·m^{-3} (k = 2)	10^2 $U_T(\rho_{exp})$ /ρ_{exp}	10^2 (ρ_{exp}– ρ_{GERG})/ρ_{GERG}	10^2 (ρ_{exp}– ρ_{AGA})/ρ_{AGA}
240.042	19.625	194.079	0.044	0.023	0.066	0.034	–3.467	–0.096
240.043	19.012	189.597	0.044	0.023	0.067	0.035	–3.499	–0.090
240.043	18.027	181.952	0.043	0.024	0.068	0.037	–3.529	–0.075
240.044	17.027	173.595	0.042	0.024	0.069	0.040	–3.526	–0.055
240.045	16.029	164.619	0.041	0.025	0.070	0.043	–3.476	–0.030
240.046	15.022	154.900	0.040	0.026	0.071	0.046	–3.364	–0.005
240.045	14.021	144.595	0.039	0.027	0.072	0.050	–3.181	0.017
240.046	13.019	133.681	0.038	0.028	0.072	0.054	–2.923	0.032
240.045	12.005	122.134	0.036	0.030	0.071	0.058	–2.595	0.037
240.045	11.012	110.482	0.035	0.032	0.069	0.062	–2.221	0.037
240.046	10.006	98.519	0.034	0.034	0.066	0.067	–1.833	0.019
240.046	9.009	86.730	0.033	0.038	0.063	0.073	–1.460	–0.003
240.045	8.002	75.062	0.031	0.042	0.059	0.079	–1.123	–0.029
240.045	7.001	63.844	0.030	0.047	0.056	0.087	–0.845	–0.056
240.046	6.000	53.119	0.029	0.054	0.052	0.098	–0.632	–0.087
240.046	4.998	42.934	0.028	0.065	0.048	0.113	–0.472	–0.111
240.046	3.998	33.318	0.027	0.080	0.045	0.135	–0.356	–0.127
240.047	2.998	24.247	0.026	0.106	0.042	0.174	–0.263	–0.127
240.047	1.996	15.681	0.025	0.158	0.025	0.160	–0.171	–0.098
240.046	0.998	7.620	0.024	0.313	0.024	0.317	–0.109	–0.079
250.004	18.875	173.914	0.042	0.024	0.065	0.037	–3.221	–0.128
250.003	18.031	167.361	0.041	0.025	0.065	0.039	–3.199	–0.123
250.003	17.022	159.082	0.040	0.025	0.066	0.041	–3.139	–0.116
250.004	16.006	150.232	0.040	0.026	0.066	0.044	–3.037	–0.108
250.004	15.019	141.163	0.039	0.027	0.066	0.047	–2.890	–0.100
250.004	14.018	131.510	0.037	0.028	0.066	0.050	–2.695	–0.095
250.004	13.000	121.315	0.036	0.030	0.065	0.053	–2.449	–0.091
250.005	12.003	111.033	0.035	0.032	0.064	0.057	–2.175	–0.091

250.006	11.009	100.603	0.034	0.034	0.062	0.061	–1.876	–0.089
250.004	10.008	90.050	0.033	0.037	0.059	0.066	–1.586	–0.103
250.005	9.003	79.524	0.032	0.040	0.057	0.071	–1.304	–0.115
250.005	8.002	69.239	0.031	0.044	0.054	0.078	–1.051	–0.129
250.007	7.001	59.226	0.030	0.050	0.051	0.086	–0.828	–0.136
250.006	6.000	49.568	0.028	0.057	0.048	0.097	–0.645	–0.142
250.006	4.998	40.290	0.027	0.068	0.045	0.113	–0.493	–0.140
250.004	3.997	31.436	0.026	0.084	0.043	0.136	–0.368	–0.130
250.005	2.997	22.993	0.026	0.111	0.026	0.113	–0.263	–0.112
250.007	1.998	14.960	0.025	0.165	0.025	0.167	–0.167	–0.080
250.005	0.997	7.285	0.024	0.327	0.036	0.496	–0.095	–0.058
260.015	19.940	168.802	0.042	0.025	0.061	0.036	–2.942	–0.144
260.014	19.031	162.300	0.041	0.025	0.062	0.038	–2.909	–0.145
260.015	18.020	154.700	0.040	0.026	0.062	0.040	–2.848	–0.145
260.013	17.010	146.708	0.039	0.027	0.062	0.042	–2.758	–0.145
260.014	16.023	138.537	0.038	0.028	0.062	0.045	–2.639	–0.145
260.013	15.018	129.866	0.037	0.029	0.061	0.047	–2.485	–0.145
260.012	14.018	120.922	0.036	0.030	0.061	0.050	–2.302	–0.146
260.014	13.014	111.695	0.035	0.032	0.060	0.053	–2.091	–0.146
260.013	12.010	102.273	0.034	0.033	0.058	0.057	–1.862	–0.147
260.014	11.007	92.773	0.033	0.036	0.057	0.061	–1.621	–0.144
260.013	10.003	83.236	0.032	0.039	0.055	0.066	–1.388	–0.150
260.013	9.003	73.809	0.031	0.042	0.052	0.071	–1.165	–0.153
260.013	8.001	64.503	0.030	0.047	0.050	0.078	–0.960	–0.154
260.012	7.000	55.420	0.029	0.053	0.048	0.086	–0.774	–0.149
260.012	5.998	46.581	0.028	0.060	0.045	0.098	–0.616	–0.144
260.012	5.001	38.068	0.027	0.071	0.043	0.113	–0.475	–0.130
260.012	4.000	29.826	0.026	0.088	0.041	0.138	–0.354	–0.111
260.011	2.998	21.898	0.025	0.116	0.026	0.118	–0.249	–0.088
260.010	1.998	14.290	0.025	0.172	0.025	0.175	–0.152	–0.056
260.009	0.997	6.987	0.024	0.340	0.035	0.504	–0.078	–0.035

[a] Expanded uncertainties in temperature and pressure are $U(T) = 0.004$ K and $U(p) = 0.005$ MPa, respectively.

Table 7. Experimental (p, ρ, T) measurements for the (0.4925924 CH_4 + 0.5074076 He) mixture, relative and absolute expanded uncertainty in density (k = 2) $U(\rho_{exp})$, relative and absolute expanded overall uncertainty in density (k = 2) $U_T(\rho_{exp})$ and relative deviations from the GERG-2008 and AGA8-DC92 equations of state; where T is the temperature (ITS-90), p the pressure, ρ_{exp} the experimental density, and ρ_{GERG} and ρ_{AGA} the densities calculated from the GERG-2008 and the AGA8-DC92 equations of state.

T/K [a]	p/MPa [a]	ρ_{exp}/kg·m^{-3}	$U(\rho_{exp})$ / kg·m^{-3} (k = 2)	10^2 $U(\rho_{exp})$ /ρ_{exp}	$U_T(\rho_{exp})$/ kg·m^{-3} (k = 2)	10^2 $U_T(\rho_{exp})$ /ρ_{exp}	10^2 (ρ_{exp}–ρ_{GERG})/ρ_{GERG}	10^2 (ρ_{exp}–ρ_{AGA})/ρ_{AGA}
240.032	16.089	77.505	0.032	0.041	0.041	0.053	–6.072	0.392
240.029	15.008	72.695	0.031	0.043	0.040	0.056	–5.791	0.299
240.029	14.007	68.168	0.031	0.045	0.040	0.058	–5.512	0.217
240.030	13.007	63.573	0.030	0.048	0.039	0.061	–5.216	0.137
240.031	11.997	58.869	0.030	0.051	0.038	0.065	–4.904	0.057
240.031	11.002	54.180	0.029	0.054	0.038	0.070	–4.571	–0.007
240.030	10.001	49.403	0.029	0.058	0.037	0.075	–4.229	–0.073
240.031	9.001	44.581	0.028	0.063	0.036	0.081	–3.874	–0.131
240.031	8.000	39.712	0.028	0.070	0.035	0.089	–3.505	–0.181
240.032	6.999	34.803	0.027	0.078	0.035	0.100	–3.124	–0.221
240.032	5.997	29.862	0.027	0.089	0.034	0.114	–2.732	–0.251
240.033	4.998	24.905	0.026	0.105	0.033	0.133	–2.330	–0.269
240.033	3.998	19.928	0.025	0.128	0.032	0.162	–1.917	–0.275
240.033	2.998	14.943	0.025	0.167	0.032	0.211	–1.481	–0.254
240.033	1.992	9.928	0.024	0.245	0.024	0.246	–1.009	–0.197
240.033	0.997	4.969	0.024	0.478	0.024	0.479	–0.515	–0.111
250.005	19.686	88.663	0.033	0.038	0.042	0.047	–6.439	0.468
249.964	18.997	85.915	0.033	0.038	0.041	0.048	–6.329	0.398
250.017	18.002	81.885	0.033	0.040	0.041	0.050	–6.106	0.346
249.994	16.646	76.317	0.032	0.042	0.040	0.053	–5.782	0.278
249.997	15.999	73.600	0.032	0.043	0.040	0.054	–5.630	0.232
249.994	15.003	69.361	0.031	0.045	0.039	0.056	–5.384	0.163
249.997	14.005	65.051	0.031	0.047	0.039	0.059	–5.123	0.096
249.998	12.999	60.647	0.030	0.050	0.038	0.063	–4.843	0.034
249.999	12.002	56.224	0.030	0.053	0.037	0.066	–4.553	–0.025
249.999	11.000	51.722	0.029	0.056	0.037	0.071	–4.242	–0.073
250.000	10.006	47.205	0.029	0.061	0.036	0.076	–3.930	–0.125
249.999	8.999	42.584	0.028	0.066	0.035	0.083	–3.593	–0.162
250.000	8.001	37.957	0.028	0.073	0.035	0.091	–3.253	–0.198
250.053	7.001	33.286	0.027	0.081	0.034	0.102	–2.877	–0.203
250.000	6.000	28.574	0.026	0.093	0.033	0.116	–2.551	–0.258
249.991	4.945	23.600	0.026	0.110	0.032	0.137	–2.082	–0.192

249.989	3.997	19.095	0.025	0.133	0.032	0.166	–1.712	–0.185
249.989	2.997	14.323	0.025	0.173	0.025	0.174	–1.314	–0.170
249.990	1.991	9.521	0.024	0.255	0.024	0.256	–0.894	–0.135
249.989	0.997	4.769	0.024	0.498	0.029	0.617	–0.431	–0.051
259.986	19.334	83.513	0.033	0.039	0.040	0.048	–6.001	0.255
259.987	19.000	82.229	0.033	0.040	0.040	0.049	–5.940	0.232
259.987	18.001	78.346	0.032	0.041	0.040	0.051	–5.750	0.166
259.986	17.011	74.435	0.032	0.043	0.039	0.053	–5.548	0.103
259.986	16.009	70.413	0.031	0.044	0.039	0.055	–5.329	0.041
259.986	15.001	66.310	0.031	0.046	0.038	0.058	–5.096	–0.018
259.985	14.000	62.178	0.030	0.049	0.038	0.060	–4.851	–0.073
259.985	12.960	57.824	0.030	0.052	0.037	0.064	–4.580	–0.124
259.992	11.996	53.738	0.029	0.055	0.036	0.068	–4.314	–0.164
259.993	10.997	49.455	0.029	0.058	0.036	0.072	–4.023	–0.198
259.994	9.998	45.124	0.028	0.063	0.035	0.078	–3.727	–0.232
259.994	9.000	40.749	0.028	0.068	0.034	0.085	–3.417	–0.258
259.995	7.999	36.324	0.027	0.075	0.034	0.093	–3.094	–0.277
259.995	6.996	31.852	0.027	0.084	0.033	0.104	–2.757	–0.286
259.994	5.997	27.365	0.026	0.096	0.032	0.119	–2.410	–0.286
259.995	4.997	22.844	0.026	0.113	0.032	0.139	–2.048	–0.275
259.995	3.997	18.303	0.025	0.138	0.031	0.170	–1.669	–0.248
259.995	2.997	13.742	0.025	0.180	0.025	0.181	–1.270	–0.202
259.996	1.997	9.169	0.024	0.264	0.024	0.265	–0.853	–0.141
259.997	0.997	4.578	0.024	0.518	0.029	0.633	–0.452	–0.097
275.092	19.880	80.485	0.032	0.040	0.039	0.049	–5.556	0.109
275.103	18.991	77.268	0.032	0.041	0.039	0.050	–5.400	0.066
274.973	17.996	73.619	0.032	0.043	0.038	0.052	–5.274	–0.035
275.033	16.993	69.886	0.031	0.045	0.038	0.054	–5.057	–0.061
275.013	16.003	66.148	0.031	0.046	0.037	0.057	–4.863	–0.112
275.137	14.998	62.299	0.030	0.049	0.037	0.059	–4.596	–0.105
275.030	13.992	58.399	0.030	0.051	0.036	0.062	–4.411	–0.184
274.981	12.333	51.873	0.029	0.056	0.035	0.068	–3.990	–0.214
274.982	11.998	50.535	0.029	0.057	0.035	0.070	–3.906	–0.224
274.983	10.998	46.513	0.029	0.061	0.035	0.074	–3.641	–0.242
274.984	9.997	42.440	0.028	0.066	0.034	0.080	–3.372	–0.263
274.984	8.996	38.323	0.028	0.072	0.033	0.087	–3.092	–0.278
274.985	7.996	34.172	0.027	0.079	0.033	0.096	–2.802	–0.288
274.984	6.996	29.987	0.027	0.089	0.032	0.107	–2.500	–0.288
274.984	5.997	25.777	0.026	0.101	0.032	0.123	–2.189	–0.284
274.984	4.997	21.529	0.026	0.119	0.031	0.144	–1.865	–0.270
274.980	3.997	17.256	0.025	0.146	0.030	0.176	–1.534	–0.252

274.979	2.997	12.967	0.025	0.190	0.025	0.191	–1.165	–0.199
274.980	1.997	8.655	0.024	0.279	0.024	0.280	–0.771	–0.124
274.978	0.997	4.329	0.024	0.547	0.028	0.657	–0.386	–0.062
299.999	19.872	73.326	0.032	0.043	0.037	0.051	–4.869	–0.139
299.938	18.984	70.381	0.031	0.044	0.037	0.053	–4.754	–0.194
300.048	17.984	67.021	0.031	0.046	0.037	0.054	–4.553	–0.191
299.893	16.990	63.637	0.030	0.048	0.036	0.057	–4.439	–0.276
299.910	15.304	57.804	0.030	0.052	0.035	0.061	–4.114	–0.305
299.912	14.990	56.703	0.030	0.052	0.035	0.062	–4.053	–0.313
299.910	13.998	53.196	0.029	0.055	0.035	0.065	–3.855	–0.332
299.911	12.994	49.608	0.029	0.058	0.034	0.069	–3.646	–0.347
299.910	11.994	45.991	0.028	0.062	0.034	0.073	–3.429	–0.358
299.911	10.999	42.355	0.028	0.066	0.033	0.078	–3.197	–0.359
299.908	9.994	38.640	0.028	0.071	0.033	0.084	–2.960	–0.361
299.910	8.995	34.912	0.027	0.078	0.032	0.092	–2.712	–0.354
299.910	7.998	31.158	0.027	0.086	0.032	0.101	–2.456	–0.343
299.910	6.997	27.355	0.026	0.096	0.031	0.113	–2.184	–0.322
299.910	5.995	23.517	0.026	0.110	0.030	0.130	–1.906	–0.298
299.909	4.996	19.658	0.025	0.129	0.030	0.152	–1.615	–0.264
299.909	3.996	15.769	0.025	0.159	0.029	0.186	–1.314	–0.225
299.908	2.997	11.860	0.025	0.207	0.025	0.208	–1.000	–0.178
299.908	1.997	7.922	0.024	0.304	0.024	0.305	–0.649	–0.097
299.910	0.997	3.963	0.024	0.597	0.028	0.698	–0.330	–0.053
325.139	19.910	67.575	0.031	0.046	0.036	0.053	–4.261	–0.234
325.052	18.996	64.771	0.031	0.047	0.035	0.055	–4.161	–0.286
325.262	17.996	61.669	0.030	0.049	0.035	0.057	–3.948	–0.245
325.183	16.993	58.519	0.030	0.051	0.035	0.059	–3.819	–0.289
324.920	15.482	53.698	0.029	0.055	0.034	0.063	–3.674	–0.412
324.921	14.996	52.129	0.029	0.056	0.034	0.065	–3.592	–0.419
324.921	13.989	48.856	0.029	0.059	0.033	0.068	–3.416	–0.429
324.921	12.990	45.572	0.028	0.062	0.033	0.072	–3.232	–0.435
324.921	11.991	42.251	0.028	0.066	0.032	0.077	–3.041	–0.437
324.922	10.989	38.891	0.028	0.071	0.032	0.082	–2.833	–0.425
324.922	9.995	35.519	0.027	0.077	0.031	0.089	–2.626	–0.417
324.923	8.996	32.100	0.027	0.084	0.031	0.097	–2.408	–0.403
324.924	7.994	28.637	0.026	0.092	0.031	0.107	–2.180	–0.383
324.924	6.995	25.153	0.026	0.104	0.030	0.119	–1.942	–0.355
324.924	5.996	21.639	0.026	0.119	0.030	0.137	–1.697	–0.325
324.923	4.996	18.094	0.025	0.140	0.029	0.161	–1.442	–0.289
324.924	3.995	14.517	0.025	0.171	0.029	0.197	–1.179	–0.248
324.924	2.996	10.922	0.024	0.224	0.025	0.224	–0.909	–0.205

324.923	1.997	7.302	0.024	0.329	0.024	0.330	–0.624	–0.150
324.922	0.997	3.654	0.024	0.646	0.027	0.741	–0.338	–0.101
349.914	16.463	52.660	0.029	0.055	0.033	0.063	–3.408	–0.449
349.915	15.995	51.273	0.029	0.057	0.033	0.065	–3.342	–0.456
349.914	14.995	48.291	0.029	0.059	0.033	0.068	–3.190	–0.461
349.914	13.986	45.249	0.028	0.063	0.032	0.071	–3.031	–0.464
349.916	12.995	42.230	0.028	0.066	0.032	0.076	–2.867	–0.462
349.914	11.987	39.127	0.028	0.071	0.031	0.080	–2.694	–0.456
349.915	10.991	36.033	0.027	0.076	0.031	0.086	–2.511	–0.440
349.915	9.989	32.885	0.027	0.082	0.031	0.093	–2.325	–0.427
349.914	8.995	29.735	0.027	0.089	0.030	0.101	–2.132	–0.407
349.913	7.997	26.543	0.026	0.099	0.030	0.112	–1.931	–0.384
349.912	6.991	23.297	0.026	0.111	0.029	0.126	–1.719	–0.354
349.913	5.993	20.048	0.025	0.127	0.029	0.144	–1.501	–0.320
349.913	4.995	16.770	0.025	0.150	0.028	0.169	–1.280	–0.286
349.913	3.996	13.462	0.025	0.184	0.028	0.208	–1.054	–0.252
349.913	2.996	10.130	0.024	0.240	0.028	0.272	–0.817	–0.210
349.914	1.989	6.742	0.024	0.355	0.024	0.356	–0.622	–0.216
349.913	0.997	3.390	0.024	0.696	0.024	0.696	–0.369	–0.165
374.904	14.969	44.946	0.028	0.063	0.032	0.071	–2.856	–0.488
374.906	13.428	40.599	0.028	0.069	0.031	0.077	–2.629	–0.479
374.905	12.989	39.345	0.028	0.070	0.031	0.079	–2.568	–0.480
374.906	11.988	36.471	0.027	0.075	0.031	0.084	–2.414	–0.471
374.906	10.992	33.585	0.027	0.080	0.030	0.090	–2.249	–0.452
374.906	9.992	30.659	0.027	0.087	0.030	0.097	–2.080	–0.433
374.905	8.993	27.711	0.026	0.095	0.029	0.106	–1.905	–0.410
374.905	7.993	24.728	0.026	0.105	0.029	0.118	–1.729	–0.389
374.904	6.993	21.725	0.026	0.118	0.029	0.132	–1.526	–0.343
374.904	5.995	18.697	0.025	0.135	0.028	0.151	–1.337	–0.314
374.906	4.995	15.636	0.025	0.160	0.028	0.178	–1.145	–0.285
374.903	3.996	12.555	0.025	0.196	0.027	0.219	–0.938	–0.244
374.908	2.996	9.447	0.024	0.257	0.027	0.286	–0.740	–0.215
374.906	1.997	6.319	0.024	0.379	0.024	0.379	–0.501	–0.148
374.905	0.997	3.165	0.024	0.745	0.024	0.745	–0.290	–0.113
399.992	15.369	43.172	0.028	0.065	0.031	0.072	–2.602	–0.479
399.991	14.974	42.136	0.028	0.066	0.031	0.074	–2.551	–0.477
399.990	13.984	39.520	0.028	0.070	0.031	0.078	–2.427	–0.476
399.990	12.978	36.835	0.027	0.074	0.030	0.083	–2.291	–0.467
399.989	11.984	34.161	0.027	0.079	0.030	0.088	–2.149	–0.451
399.989	10.983	31.443	0.027	0.085	0.030	0.094	–1.995	–0.427

399.989	9.992	28.726	0.026	0.092	0.029	0.102	–1.847	–0.409
399.989	8.991	25.954	0.026	0.101	0.029	0.111	–1.683	–0.379
399.989	7.990	23.158	0.026	0.112	0.029	0.123	–1.524	–0.356
399.991	6.972	20.293	0.026	0.126	0.028	0.139	–1.350	–0.321
399.990	5.992	17.506	0.025	0.144	0.028	0.159	–1.186	–0.295
399.991	4.993	14.646	0.025	0.170	0.027	0.187	–1.001	–0.252
399.991	3.996	11.762	0.025	0.209	0.027	0.230	–0.824	–0.220
399.992	2.996	8.853	0.024	0.273	0.027	0.301	–0.634	–0.177
399.990	1.993	5.910	0.024	0.404	0.024	0.404	–0.431	–0.125
399.991	0.997	2.964	0.024	0.794	0.024	0.795	–0.301	–0.148

[a] Expanded uncertainties in temperature and pressure are $U(T) = 0.004$ K and $U(p) = 0.005$ MPa, respectively.

Table 8. Statistical parameters of the data set with respect to the GERG-2008 and AGA8-DC92 equations of state for the (CH_4 + He) mixtures.

Statistical parameter	(0.95 CH_4 + 0.05 He)		(0.90 CH_4 + 0.10 He)		(0.50 CH_4 + 0.50 He)	
	GERG-2008	AGA8-DC92	GERG-2008	AGA8-DC92	GERG-2008	AGA8-DC92
AAD	0.655	0.101	1.170	0.159	2.849	0.262
Bias	–0.655	–0.101	–1.170	–0.157	–2.849	–0.212
RMS	0.853	0.111	1.483	0.178	3.277	0.291
MaxD/%	–2.031	–0.167	–3.529	–0.295	-6.439	–0.488

Table 9. Least-squares fitting results for the (CH_4 + He) mixtures (B and C) and the second interaction virial coefficient (B_{12}) with the expanded uncertainties.

T/K [a]	x_{He}/mol-%	B/ $cm^3 \cdot mol^{-1}$	$U(B)$/ $cm^3 \cdot mol^{-1}$	C/ $cm^6 \cdot mol^{-2}$	$U(C)$/ $cm^6 \cdot mol^{-2}$	B_{12}/ $cm^3 \cdot mol^{-1}$	$U(B_{12})$/ $cm^3 \cdot mol^{-1}$
(0.95 CH_4 + 0.05 He)							
240.047	0.04999	–62.43	0.77	2779	225	24.81	8.08
249.996	0.04999	–56.71	0.96	2593	315	26.73	10.08
260.005	0.04999	–51.85	1.11	2510	400	24.78	11.67
275.002	0.04999	–44.99	1.37	2303	556	26.18	14.41
299.958	0.04999	–35.62	1.81	2085	871	25.86	19.08
324.955	0.04999	–27.98	2.37	1929	1292	25.38	24.91
349.938	0.04999	–21.42	2.80	1703	1688	27.15	29.46
374.924	0.04999	–16.19	3.32	1658	2214	25.46	35.00
399.997	0.04999	–11.35	4.00	1449	2892	27.83	42.07
(0.90 CH_4 + 0.10 He)							
240.045	0.10007	–53.62	0.74	2425	217	24.56	4.12
250.005	0.10007	–48.51	0.89	2281	291	25.33	4.94
260.013	0.10007	–44.07	1.07	2201	375	24.82	5.92
274.994	0.10007	–37.96	1.26	2027	497	25.31	7.00
299.951	0.10007	–29.65	1.68	1914	764	24.63	9.35
324.958	0.10007	–22.66	2.07	1730	1062	25.08	11.48
349.939	0.10007	–16.88	2.49	1608	1428	25.33	13.83
374.923	0.10007	–12.37	2.88	1647	1790	23.52	15.98
400.006	0.10007	–7.70	3.44	1328	2330	26.49	19.11
(0.50CH_4 + 0.50 He)							
240.032	0.50741	–2.83	0.65	881	137	22.97	1.29
249.998	0.50741	–1.51	0.78	893	158	22.66	1.56
259.991	0.50741	0.16	0.84	846	180	23.31	1.68
275.007	0.50741	2.00	0.87	820	197	23.40	1.74
299.922	0.50741	4.62	1.09	813	268	23.64	2.17
324.970	0.50741	6.95	1.22	764	334	24.22	2.45
349.914	0.50741	8.79	1.44	724	425	24.53	2.88
374.906	0.50741	10.22	1.59	735	504	24.53	3.17
399.990	0.50741	11.35	1.75	737	583	24.36	3.49

[a] T is the average temperature of each isotherm.