

# Experimental determination of ( $p$ , $\rho$ , $T$ ) data for binary mixtures of methane and helium

R. Hernández-Gómez<sup>1</sup>, D. Tuma<sup>2</sup>, J.J. Segovia<sup>1</sup>, C.R. Chamorro<sup>1</sup>

<sup>1</sup> Grupo de Termodinámica y Calibración (TERMOCAL), Dpto. Ingeniería Energética y Fluidomecánica, Escuela de Ingenierías Industriales, Universidad de Valladolid, Paseo del Cauce, 59, E-47011 Valladolid, Spain.

<sup>2</sup> BAM Bundesanstalt für Materialforschung und -prüfung, D-12200 Berlin, Germany.

*This is an author-created, un-copyedited version of an article accepted for publication in The Journal of Chemical Thermodynamics (Volume 96, 2016, Pages 1–11). Elsevier is not responsible for any errors or omissions in this version of the manuscript or any version derived from it. The definitive publisher-authenticated version is available online at <http://dx.doi.org/10.1016/j.jct.2015.12.006>*

© 2015. This manuscript version is made available under the CC-BY-NC-ND 4.0 license <http://creativecommons.org/licenses/by-nc-nd/4.0/>

**Abstract:**

The basis for the development and evaluation of equations of state for mixtures is experimental data for several thermodynamic properties. The quality and the availability of experimental data limit the achievable accuracy of the equation. Referring to the fundamentals of GERG-2008 wide-range equation of state, no suitable data were available for many mixtures containing secondary natural gas components. This work provides accurate experimental ( $p$ ,  $\rho$ ,  $T$ ) data for two binary mixtures of methane with helium (0.95 (amount-of-substance fraction)  $\text{CH}_4$  + 0.05 He and 0.90  $\text{CH}_4$  + 0.10 He). Density measurements were performed at temperatures between 250 K and 400 K and pressures up to 20 MPa by using a single-sinker densimeter with magnetic suspension coupling. Experimental data were compared with the corresponding densities calculated from the GERG-2008 and the AGA8-DC92 equations of state. Deviations from GERG-2008 were found within a 2 % band for the (0.95  $\text{CH}_4$  + 0.05 He) mixture but exceeded the 3 % limit for the (0.95  $\text{CH}_4$  + 0.05 He) mixture. The highest deviations were observed at 250 K and pressures between 17 and 19 MPa. Values calculated from AGA8-DC92, however, deviated from the experimental data by only 0.1 % at high pressures and exceeded the 0.2 % limit only at temperatures of 300 K and above, for the (0.90  $\text{CH}_4$  + 0.10 He) mixture.

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

\* Corresponding author e-mail: cescha@eii.uva.es. Tel.: +34 983423756. Fax: +34 983423363

## 1. Introduction

The knowledge of the thermophysical properties of natural gases and other related mixtures is an important feature for the performance of technical processes. Transportation, storage, and liquefaction processes in addition to design of equipment and other applications of natural gases require an accurate estimation of the thermodynamic properties of the individual mixture-forming components. Depending on the source and the application, several components may be present in natural gases at different compositions. The raw natural gas needs to be processed due to the quality specifications for its commercial use as a fuel. Thus, the separation of undesirable components (e.g., carbon dioxide, water or hydrogen sulfide) or the presence of other components (e.g., lower and higher hydrocarbons) is required. In addition, the growing interest in alternative sources of energy gases and the diversity of composition of these non-conventional fuels demands to consider other components with minority presence. For all these reasons, property calculations over wide ranges of mixture compositions and operating conditions in the homogeneous gaseous, liquid, and supercritical regions and for vapor-liquid equilibrium (VLE) states are required. These particular data can be calculated from equations of state.

Different equations of state have been developed for various substances and applications, according to the requirements of precision and availability of experimental data. There are two main equations of state for estimating natural gas properties: AGA8-DC92 and GERG-2008.

The first one was developed by Starling and Savidge with the support of the American Gas Association (AGA). The AGA8-DC92 was originally designed as a thermal equation of state explicit in compression factor [1]. This equation enables the calculation of thermodynamic properties of natural gases and similar mixtures consisting of up to 21 components. The range of validity is limited to the gas phase and covers temperatures from (143 to 673) K and pressures up to 280 MPa. However, due to limited experimental data, a well-founded estimation of the uncertainty in the description of thermal properties (compression factor and density) of natural gases is only feasible in the temperature range from (250 to 350) K at pressures up to 30 MPa. The uncertainty of the AGA8-DC92 equation of state for a standard-quality natural gas (ISO 20765-1:2005 [2]) is about 0.1 % in density for temperatures from (290 to 350) K at

pressures up to 30 MPa. Moreover, higher deviations were observed for gases with high content of nitrogen, carbon dioxide, ethane and heavy hydrocarbons [3].

The GERG-2008 equation of state [4] is an extension of the GERG-2004 that was developed by Kunz et al. [5]. GERG-2008 is the only equation of state that is appropriate for nearly all of the technical applications for natural gases mentioned above and satisfies the demand on the accuracy in the calculation of thermodynamic properties in the entire fluid region for 21 natural gas components: methane, nitrogen, carbon dioxide, ethane, propane, n-butane, isobutane, n-pentane, isopentane, n-hexane, n-heptane, n-octane, n-nonane, n-decane, hydrogen, oxygen, carbon monoxide, water, hydrogen sulfide, helium, and argon. The normal range of validity of GERG-2008 covers the temperature range from (90 to 450) K and pressures up to 35 MPa. It qualifies for the usual operation range of technical applications employing natural gases and related mixtures. The uncertainty of GERG-2008 in gas-phase density is 0.1 % over the temperature range from (250 to 450) K at pressures up to 35 MPa. This particular uncertainty is valid for various types of natural gases, including natural gases rich in nitrogen, carbon dioxide, ethane, hydrogen, etc. The GERG-2008 is the current reference equation of state for natural gas and other related mixtures and was designated as ISO Standard (ISO 20765-2) for the calculation of thermodynamic properties of natural gases [6].

Generally, the equation is based on multi-fluid approximations and is explicit in the Helmholtz free energy with the independent mixture variables density  $\rho$ , temperature  $T$ , and the vector of the molar composition  $x$ . The mixture model uses equations of state in the form of fundamental equations for each individual mixture component along with further auxiliary correlation equations to take into account the residual mixture behavior. The basis for the development and evaluation of equations of state for mixtures is experimental data for several thermodynamic properties. These data are used to determine the coefficients and parameters of the correlation equations and to evaluate the behavior of the equation of state in different fluid regions. The quality and the availability of experimental data limit the achievable accuracy of the equation.

Experimental data for the 21 pure components of natural gas 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 sufficient accurate experimental data were available, binary specific departure functions or a generalized departure function were developed. Due to the lack of experimental data for some binary mixtures and to the complexity of the process, most of the binary systems were taken into account by using adjusted reducing functions for density and temperature. This is the case for the binary mixture (methane + helium), for which no departure function was established so far. 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 [4].

Helium is an inert gas with a very small molecular size. It has a wide range of important medical, scientific and industrial applications based on its extremely low boiling temperature and non-flammable nature. The only practical sources of helium are from certain natural gas fields. In the last years, the world demand for helium is rapidly increasing, projections show a continued increase in demand for helium of (5 to 7) % per annum, so the value of natural gas fields that contain it, even in very small amounts, is likely to rise significantly. In general, natural gas fields with helium contents above 0.3 mol-% are considered to be of commercial interest as helium sources, although the helium content can be up to 7 % [7]. The total amount of helium in the world is estimated to be of 8.6 million tonnes, with the US having the biggest fraction of reserves (around 35 %), followed by Qatar (with 20 %) [8].

This work provides accurate experimental ( $p$ ,  $\rho$ ,  $T$ ) data for two binary mixtures of methane with helium. Density measurements for the two binary mixtures of methane with helium (0.95 (amount-of-substance fraction)  $\text{CH}_4$  + 0.05 He and 0.90  $\text{CH}_4$  + 0.10 He) were performed at temperatures between (250 and 400) K and pressures up to 20 MPa by using a single-sinker densimeter with magnetic suspension coupling, which is one of the state-of-the-art methods for density determination over extended ranges of temperature and pressure. Experimental data were compared with the corresponding densities calculated from the GERG-2008 and AGA8-DC92 equations of state.

To achieve the highest accuracy in composition, the binary mixtures were prepared by the gravimetric method according to ISO 6142 [9] at the Federal Institute for Materials Research and Testing (BAM) in Berlin, Germany.

## 2. Experimental

### 2.1. Sample preparation

The two binary mixtures were prepared gravimetrically and were supplied in aluminum cylinders of a volume of 10 dm<sup>3</sup>. The composition of the mixtures, the corresponding expanded uncertainty (coverage factor  $k = 2$ ) as well as purity, supplier, and critical parameters of each component are given in Table 1. All substances were used without further purification.

The preparation of the final mixtures is effected in two steps. First, a mixture of (0.50 CH<sub>4</sub> + 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<sup>3</sup>). The substance transfer was actuated only by pressure difference between the two cylinders, i.e., 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 (Volland model HCE 25, Volland Corp., New Rochelle NY, USA). The resulting mixture had a pressure of approximately 15 MPa.

The two binary mixtures to be investigated were prepared in a similar way. A specified portion of the (0.50 CH<sub>4</sub> + 0.50 He) parent mixture was introduced into the recipient cylinder and in the next step diluted by a properly measured amount of methane to create the final composition. The two cylinders displayed a pressure of 13.7 MPa for the (0.95 CH<sub>4</sub> + 0.05 He) mixture and of 13.2 MPa for the (0.90 CH<sub>4</sub> + 0.10 He) mixture, respectively. Each mixture was finally homogenized by a procedure of subsequent heating and rolling. The samples to be investigated were validated by gas chromatography against samples of similar composition following the single-point exact-match calibration according to ISO/CD 12963 [10]. The gas mixture used for validation matched the (0.90 CH<sub>4</sub> + 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. That GC was equipped with customized packed columns particularly adapted for the analysis of synthetic natural gases and individual TCDs for each channel. The analysis was performed in an isothermal regime at 60 °C. Table 2 gives the results of the GC analysis. These measurements were entirely done at BAM prior to the density determination.

## 2.2. Apparatus Description

The single-sinker densimeter was developed by Brachthäuser et al. [11] in 1993 as a simplification of a previously developed two-sinker densimeter [12], and was further improved by Klimeck et al. [13]. The measuring technique is based on the Archimedes' principle, by which the buoyancy force acting on a sinker immersed in a fluid is proportional to the density of that fluid. The high accuracy of this methodology is achieved owing to the magnetic suspension coupling system between the sinker and the balance hook, by which there is no contact between the measuring fluid and the high-accuracy microbalance. It allows precision density measurements of fluids over wide temperature and pressure ranges [14]. 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. [15] and further improved by Mondéjar et al. [16].

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

Two calibrated masses are used for reducing the 'nonlinearity effect' of the electronic balance and to improve the accuracy of the measurement. This effect is independent of the quality of the balances and is defined as a deviation of the balance's real curve versus the real load measured. The calibrated masses are made of tantalum and titanium, respectively. They have different masses but approximately the same volume (4.9 cm<sup>3</sup>) and the difference in weight between both of them is similar to the sinker mass (60 g approximately). This load compensation system 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 Mass Division of the Spanish National Metrology Institute (Centro Español de Metrología, CEM) [17].

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

$$\rho = (m_{s0} - m_{sf})/V_s(T, p) \quad (1)$$

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  $\text{m}^3$ , which is accurately known as a function of temperature and pressure [16].

The cell is thermostatted and the temperature of the fluid inside is determined by two platinum resistance thermometers (model Minco S1059PJ5X6, Minco Products, Inc., Minneapolis MN, USA) connected to an AC comparator resistance bridge (ASL model F700, Automatic Systems Laboratories, Redhill, England). Pressure is measured by two Digiquartz transducers (Paroscientific model 2300A-101 and 43KR-HHT-101, Paroscientific, Inc., Redmond WA, USA) which cover pressure ranges up to 2 and 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**

Seven isotherms were recorded at (250, 275, 300, 325, 350, 375 and 400) K for each ( $\text{CH}_4 + \text{He}$ ) mixture. Each isotherm was measured from a pressure of 20 MPa to 1 MPa by 1 MPa steps, followed by measurements of the sinker mass in vacuum.

Before and after measurements on the studied ( $\text{CH}_4 + \text{He}$ ) mixtures, test measurements with nitrogen were carried out in the whole working range of the apparatus to validate the operation by comparing the experimental results with the densities calculated from the reference equation of state for nitrogen by Span et al. [18]. Relative deviations of the experimental data from the calculated densities were within a  $\pm 0.02$  % band, with an absolute average deviation (AAD) of 0.0055 %.

The sinker mass in vacuum was measured after each of the isotherms 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 vacuum at the same temperature was 0.0001 % for both (CH<sub>4</sub> + He) mixtures. This good repeatability of the measurements in vacuum confirmed that there was not any misalignment during the measurements.

#### 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 [16]. Anyway, estimated uncertainty values for this work were recalculated by updating the data for new calibrations of the instrumentation. Drift of current measurements compared to data recorded in the past was also studied. Results did not differ from the uncertainties estimated by Mondéjar et al. The expanded uncertainty (coverage factor  $k = 2$ ) of the pressure  $p$  (MPa) 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.

$$U(p) = 75 \cdot 10^{-6} \cdot p + 3.52 \cdot 10^{-3} \quad (2)$$

$$U(p) = 60 \cdot 10^{-6} \cdot p + 1.78 \cdot 10^{-4} \quad (3)$$

Thus, the expanded uncertainties ( $k = 2$ ) in temperature and pressure were less than 4 mK and 0.005 MPa, respectively.

According to equation (1) and following the law of propagation of uncertainties (GUM) [19], density uncertainty depends on the uncertainty of the apparent mass of the sinker 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 apparent sinker masses are related with the balance readings and were calculated taking into account the balance calibration, resolution, repeatability and drift as sources of uncertainty (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 [16]. The expanded uncertainty ( $k = 2$ ) in density  $\rho$  ( $\text{kg}\cdot\text{m}^{-3}$ ) is expressed as a function of density by Eq. 4.

$$U(\rho) = 2.31 \cdot 10^{-2} + 1.14 \cdot 10^{-4} \cdot \rho \quad (4)$$

To calculate the overall standard uncertainty in density  $u_T(\rho)$  ( $k = 1$ ), the uncertainties of density, temperature, pressure, and composition of the mixture must be considered, as expressed in Eq. 5.

$$u_T(\rho) = \left[ u(\rho)^2 + \left( \left( \frac{\partial \rho}{\partial p} \right)_{T,x} u(p) \right)^2 + \left( \left( \frac{\partial \rho}{\partial T} \right)_{p,x} u(T) \right)^2 + \sum_i \left( \left( \frac{\partial \rho}{\partial x_i} \right)_{T,p,x_j \neq x_i} u(x_i) \right)^2 \right]^{1/2} \quad (5)$$

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 can be calculated with the GERG-2008 equation of state. The uncertainty in composition for the two studied ( $\text{CH}_4 + \text{He}$ ) binary mixtures studied in this work is given in Table 1.

### 3. Results

Density measurements were carried out at seven different temperatures (250, 275, 300, 325, 350, 375 and 400) K. Pressure was decreased in steps of 1 MPa from (20 to 1) MPa. Tables 3 and 4 show the experimental ( $p, \rho, T$ ) data of the two ( $\text{CH}_4 + \text{He}$ ) binary mixtures measured in this work and the relative deviation in density from the values estimated with the GERG-2008 and 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 3 and 4 also present the expanded uncertainty in density ( $k = 2$ ) of the experimental data, calculated by equation 4, which is given in absolute value (density units) and relative value as a percentage of the measured density. The absolute expanded uncertainty of the measurements was less than  $0.046 \text{ kg}\cdot\text{m}^{-3}$  and  $0.043 \text{ kg}\cdot\text{m}^{-3}$  for the (0.95  $\text{CH}_4 + 0.05$  He) and (0.90  $\text{CH}_4 + 0.10$  He) mixtures, respectively. So, the relative uncertainty in density ( $k = 2$ ) is between 0.02 % for high densities and up to 0.50 % for low densities.

The overall standard uncertainty in density  $u_T(\rho)$  ( $k = 1$ ) is calculated by Eq. 5. The value for the (CH<sub>4</sub> + He) binary mixtures is between (0.012 and 0.037) kg·m<sup>-3</sup> for the (0.95 CH<sub>4</sub> + 0.05 He) mixture and between (0.012 and 0.033) kg·m<sup>-3</sup> for the (0.90 CH<sub>4</sub> + 0.10 He) mixture. Expressed in percentage, the overall standard uncertainty in density is from (0.018 to 0.256) % and (0.018 to 0.266) % for the (0.95 CH<sub>4</sub> + 0.05 He) and the (0.90 CH<sub>4</sub> + 0.10 He) mixtures, respectively.

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. [20], Cristancho et al. [21] and Kano et al. [22]. This FTE consists of two terms: the apparatus effect and the fluid-specific effect. In this work, the apparatus effect of the FTE was accounted for by measuring the sinker mass under vacuum for each isotherm. In the case of the fluid-specific effect, its magnitude depends on the magnetic behavior of the measured gas. The magnetic susceptibility ( $\chi$ ) of the (CH<sub>4</sub> + He) binary mixtures used in this work was estimated by using the additive law proposed by Bitter [23]. The magnetic susceptibilities of the (0.95 CH<sub>4</sub> + 0.05 He) and (0.90 CH<sub>4</sub> + 0.10 He) mixtures were  $\chi_{\text{He},5\%} = -8.62 \cdot 10^{-9}$  and  $\chi_{\text{He},10\%} = -8.17 \cdot 10^{-9}$ , respectively. Since these values are relatively low, the fluid-magnetic behavior would be negligible in relation to the apparatus effect. Therefore, the fluid-specific effect was not considered in the measurements.

Adsorption tests of gas molecules on the measuring-cell walls or the sinker surface were carried out for the latest, now published measurements made with the single-sinker densimeter used in this work [17, 24]. Richter and Kleinrahm reported recently that due to sorption effects the composition of the measured gas could be modified inside the cell and significant errors up to about 0.1 % in density measurements could occur [25]. However, according to the experimental procedure followed with the single-sinker densimeter, in which the cell is evacuated after each isotherm, the differences observed in the trend of the relative deviation in density from the GERG-2008 equation of state along the period of recording an isotherm are one order of magnitude lower than the uncertainty in density at the working pressure.

Nevertheless, continuous density measurements on the same state point were recorded over the period of an isotherm to check the sorption effects on the mixture composition. Two tests were carried out for both (CH<sub>4</sub> + He) mixtures at 1 MPa and temperatures of 300 K and 400 K. The results showed that the difference observed in the trend of the relative deviation in density from the GERG-2008 between the first and the last measurement was 0.0014 % at 300 K and 0.0066 % at 400 K, which are an order of magnitude lower than the uncertainty in density at the working pressure. Therefore, adsorption effects could be neglected and are not taken into account in the measurements of (CH<sub>4</sub> + He) binary mixtures.

#### 4. Discussion of the results

Figures 1 and 2 show the relative deviations of experimental density data from the density calculated with the GERG-2008 and AGA8-DC92 equations of state for each of the isotherms of the (0.95 CH<sub>4</sub> + 0.05 He) binary mixture, respectively. The relative deviations between experimental data and estimated density from the GERG-2008 and AGA8-DC92 equations of state for the (0.90 CH<sub>4</sub> + 0.10 He) binary mixture are shown in Figures 3 and 4, respectively.

As it can be observed, the relative deviations of the experimental data from GERG-2008 are clearly higher than relative deviations from AGA8-DC92. Experimental data deviate from values calculated from AGA8-DC92 by more than 0.1 % at high pressures and even exceed the 0.2 % limit at temperatures of 300 K and above for the (0.90 CH<sub>4</sub> + 0.10 He) mixture. Deviations from GERG-2008 are within a 2 % band for the (0.95 CH<sub>4</sub> + 0.05 He) mixture and exceed the 3 % limit for the (0.90 CH<sub>4</sub> + 0.10 He) mixture. Deviations become higher at high pressures and low temperatures. The highest deviations from GERG-2008 are registered at 250 K and pressures of 17 MPa for the (0.95 CH<sub>4</sub> + 0.05 He) mixture and at 19 MPa for the (0.90 CH<sub>4</sub> + 0.10 He) mixture. In contrast, deviations from AGA8-DC92 are lower at low temperatures for both mixtures, although all data remain within the measurement uncertainty limits. The results also show that all the isotherms have negative deviations from both equations of state.

Statistical comparison of the deviation data from GERG-2008 and AGA8-DC92 equations of state is given in Table 5. *AAD* is the average absolute deviation defined in equation 6, *Bias* is the average deviation

defined in equation 7, *RMS* refers to the root mean square defined in equation 8, and *MaxD* represents the maximum relative deviation in the considered data set.

$$AAD = \frac{1}{n} \sum_{i=1}^n \left| 10^2 \cdot \frac{\rho_{i,\text{exp}} - \rho_{i,\text{EoS}}}{\rho_{i,\text{EoS}}} \right| \quad (6)$$

$$Bias = \frac{1}{n} \sum_{i=1}^n \left( 10^2 \cdot \frac{\rho_{i,\text{exp}} - \rho_{i,\text{EoS}}}{\rho_{i,\text{EoS}}} \right) \quad (7)$$

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

The high deviation from the GERG-2008 is somehow expected. Formally, GERG-2008 covers all mixtures consisting of the 21 considered components. According to Kunz and Wagner, the uncertainty of GERG-2008 in gas-phase density is 0.1 % over the temperature range from (250 to 450) K at pressures up to 35 MPa [4]. This estimated uncertainty is valid for various types of natural gases, including natural gases rich in nitrogen, carbon dioxide or considerable amounts of heavier hydrocarbons, carbon monoxide or oxygen. Anyway, for mixtures with large amounts of helium, hydrogen at cryogenic temperatures or other mixture conditions that are beyond the range of validity of the equation, the GERG-2008 does not yield a satisfactory property description. As it is specified in the GERG-2004 monograph, typical natural gases contain less than 0.1 mol-% of helium, but it recognizes that small helium contents have a pronounced influence on the phase behavior of natural gases and related mixtures, especially at low temperatures [26].

For many mixtures containing helium, no suitable data were available at the time the GERG-2008 equation of state was developed, so the higher deviation observed for the studied (CH<sub>4</sub> + He) mixtures from the estimated values from GERG-2008 is not surprising. This particular effect is even more pronounced because no departure function is included in the GERG-2008 mixture model for the binary mixture (CH<sub>4</sub> + He).

In contrast, deviation from AGA8-DC92 is distinctly lower. The AGA8-DC92 equation of state is written in terms of the compressibility factor [1] and it is dependent on temperature, density and composition.

However, its formulation does not have a strong dependence on the second virial coefficient of the mixture, which is related with the composition. This could explain why the AGA8-DC92 equation of state fits better than GERG-2008 to the experimental results of the two ( $\text{CH}_4 + \text{He}$ ) binary mixtures.

## 5. Conclusions

Accurate density data for two binary mixtures of methane with helium (0.95  $\text{CH}_4 + 0.05 \text{ He}$  and 0.90  $\text{CH}_4 + 0.10 \text{ He}$ ) were performed at temperatures between 250 K and 400 K and pressures up to 20 MPa by using a single-sinker densimeter with magnetic suspension coupling. Both 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 AGA8-DC92. Deviations from values calculated from GERG-2008 equation of state are within a 2 % band for the (0.95  $\text{CH}_4 + 0.05 \text{ He}$ ) mixture and exceed the 3 % limit for the (0.90  $\text{CH}_4 + 0.10 \text{ He}$ ) mixture, while deviations from AGA8-DC92 remain within the 0.2 % band. Deviations are higher at high pressures and low temperatures.

The high deviations registered from the GERG-2008 are in not unforeseen. The uncertainty of GERG-2008 regarding gas-phase density is 0.1 % over the temperature range from (250 to 450) K at pressures up to 35 MPa [4], however, for mixtures with large amounts of helium, the GERG-2008 does not yield a satisfactory property description. This could be the case because no departure function for the binary mixture ( $\text{CH}_4 + \text{He}$ ) is included in the mixture model. So, the behavior registered in the measurements agrees with the claims of the GERG-2008 equation of state.

On the other hand, considering the continued increase in demand for helium and the lack of experimental data of mixtures containing helium, to generate more accurate experimental ( $p, \rho, T$ ) data of binary mixtures containing helium is an interesting issue for future work.

## Acknowledgments

Support for this work came from the projects: “Gases energéticos: biogás y gas natural enriquecido con hidrógeno (ENE2013-47812-R)” of the Spanish Government; “Biogás renovable y procesos de captura del CO<sub>2</sub> de combustión asociados como base a la sostenibilidad energética ambiental: Investigación termodinámica experimental (VA391A12-1)” of the Junta de Castilla y León Regional Government; “Metrology for biogas (ENG54)” [27] funded by the European Commission's Seventh Framework Programme, ERA-NET Plus, under Grant Agreement No. 217257.

## References

- [1] K. E. Starling, J. L. Savidge, Compressibility factors of natural gas and other related hydrocarbon gases. American Gas Association (AGA) Transmission Measurement Committee Report No. 8, 2<sup>nd</sup> Ed., American Gas Association, Washington DC, 1992.
- [2] ISO 20765-1. Natural gas – Calculation of thermodynamic properties – Part 1: Gas phase properties for transmission and distribution applications. International Organization for Standardization, Geneva, 2005.
- [3] R. Klimeck, R. Span, R. Kleinrahn, W. Wagner, Fundamental equation for caloric properties of natural gases – Collecting of data and test of existing equations. Final Report to the GERG Working Group 1.3, University of Bochum, Bochum, 1996.
- [4] O. Kunz and W. Wagner, “The GERG-2008 Wide-Range Equation of State for Natural Gases and Other Mixtures: An Expansion of GERG-2004,” *J. Chem. Eng. Data*, 2012.
- [5] O. Kunz, R. Klimeck, W. Wagner, and M. Jaeschke, “The GERG-2004 Wide-Range Reference Equation of State for Natural Gases and Other Mixtures,” *GERG Tech. Monogr. Fortschritt-Berichte VDI*, 2007.

- [6] ISO 20765-2. Natural gas – Calculation of thermodynamic properties – Part 2: Single-phase properties (gas, liquid, and dense fluid) for extended ranges of application, International Organization for Standardization, Geneva, 2015.
- [7] T. Rufford, K. Chan, S. Huang, and E. May, “A Review of Conventional and Emerging Process Technologies for the Recovery of Helium from Natural Gas,” *Adsorpt. Sci. Technol.*, vol. 32, no. 1, pp. 49–72, Jan. 2014.
- [8] R. F. Broadhead, “Helium in New Mexico—geologic distribution, resource demand, and exploration possibilities,” *New Mex. Geol.*, vol. 27, pp. 93–101, 2005.
- [9] ISO 6142 - Preparation of calibration gas mixtures - Gravimetric method. International Organisation for Standardization, Geneva, 2001.
- [10] ISO/CD 12963. Gas analysis – Comparison methods for the determination of the composition of gas mixtures based on one- and two-point calibration. International Organization for Standardization, Geneva, under development.
- [11] K. Brachthäuser, R. Kleinrahm, H. W. Lösch, and W. Wagner, “Entwicklung eines neuen Dichtemeßverfahrens und Aufbau einer Hochtemperatur-Hochdruck-Dichtemeßanlage,” 1993.
- [12] R. Kleinrahm and W. Wagner, “Measurement and Correlation of the Equilibrium Liquid and Vapor Densities and the Vapor-Pressure Along the Coexistence Curve of Methane,” *J. Chem. Thermodyn.*, vol. 18, no. 8, pp. 739–760, Aug. 1986.
- [13] J. Klimeck, R. Kleinrahm, and W. Wagner, “An accurate single-sinker densimeter and measurements of the ( $p$ ,  $\rho$ ,  $T$ ) relation of argon and nitrogen in the temperature range from (235 to 520) K at pressures up to 30 MPa,” *J. Chem. Thermodyn.*, vol. 30, no. 12, pp. 1571–1588, 1998.
- [14] W. Wagner and R. Kleinrahm, “Densimeters for very accurate density measurements of fluids over large ranges of temperature, pressure, and density,” *Metrologia*, vol. 41, no. 2, pp. S24–S39, 2004.

- [15] C. R. Chamorro, J. J. Segovia, M. C. Martín, M. A. Villamañán, J. F. Estela-Uribe, and J. P. M. Trusler, “Measurement of the (pressure, density, temperature) relation of two (methane + nitrogen) gas mixtures at temperatures between 240 and 400 K and pressures up to 20 MPa using an accurate single-sinker densimeter,” *J. Chem. Thermodyn.*, vol. 38, no. 7, pp. 916–922, 2006.
- [16] M. E. Mondéjar, J. J. Segovia, and C. R. Chamorro, “Improvement of the measurement uncertainty of a high accuracy single sinker densimeter via setup modifications based on a state point uncertainty analysis,” *Measurement*, vol. 44, no. 9, pp. 1768–1780, 2011.
- [17] R. Hernández-Gómez, T. E. Fernández-Vicente, M. C. Martín González, M. E. Mondéjar, and C. R. Chamorro, “Integration of biogas in the natural gas grid: Thermodynamic characterization of a biogas-like mixture,” *J. Chem. Thermodyn.*, vol. 84, pp. 60–66, May 2015.
- [18] R. Span, E. W. Lemmon, R. T. Jacobsen, and W. Wagner, “A reference quality equation of state for nitrogen,” *Int. J. Thermophys.*, vol. 19, no. 4 SPEC.ISS., pp. 1121–1132, 1998.
- [19] JCGM 100: Evaluation of measurement data – Guide to the expression of uncertainty in measurement (GUM). Joint Committee for Guides in Metrology, Bureau International des Poids et Mesures BIPM, Sèvres, 2008..
- [20] M. O. McLinden, R. Kleinrahm, and W. Wagner, “Force transmission errors in magnetic suspension densimeters,” *Int. J. Thermophys.*, vol. 28, no. 2, pp. 429–448, 2007.
- [21] D. E. Cristancho, I. D. Mantilla, S. Ejaz, K. R. Hall, G. A. Iglesias-Silva, and M. Atilhan, “Force transmission error analysis for a high-pressure single-sinker magnetic suspension densimeter,” *Int. J. Thermophys.*, vol. 31, no. 4–5, pp. 698–709, 2010.
- [22] Y. Kano, Y. Kayukawa, K. Fujii, and H. Sato, “A new method for correcting a force transmission error due to magnetic effects in a magnetic levitation densimeter,” *Meas. Sci. Technol.*, vol. 18, no. 3, pp. 659–666, 2007.

- [23] F. Bitter, "The Magnetic Susceptibilities of Several Organic Gases," *Phys. Rev.*, vol. 33, no. 3, pp. 389–397, Mar. 1929.
- [24] R. Hernández-Gómez, D. Tuma, M. a. Villamañán, M. E. Mondéjar, and C. R. Chamorro, "Accurate thermodynamic characterization of a synthetic coal mine methane mixture," *J. Chem. Thermodyn.*, vol. 68, pp. 253–259, Jan. 2014.
- [25] M. Richter and R. Kleinrahm, "Influence of adsorption and desorption on accurate density measurements of gas mixtures," *J. Chem. Thermodyn.*, Mar. 2014.
- [26] J. E. Sinor and F. Kurata, "The liquid phase volumetric behavior of the helium-methane system," *J. Chem. Eng. Data*, vol. 11, no. 1, pp. 1–6, 1966.
- [27] "JRP Summary Report for ENG54 Biogas 'Metrology for biogas.'" [Online]. Available: [http://www.euramet.org/fileadmin/docs/EMRP/JRP/JRP\\_Summaries\\_2013/Energy\\_JRPs/ENG54\\_Publishable\\_JRP\\_Summary.pdf](http://www.euramet.org/fileadmin/docs/EMRP/JRP/JRP_Summaries_2013/Energy_JRPs/ENG54_Publishable_JRP_Summary.pdf). [Accessed: 05-May-2014].
- [28] Setzmann, U. and Wagner, W., "A New Equation of State and Tables of Thermodynamic Properties for Methane Covering the Range from the Melting Line to 625 K at Pressures up to 1000 MPa," *J. Phys. Chem. Ref. Data*, 20(6):1061-1151, 1991.
- [29] Ortiz-Vega, D.O., Hall, K.R., Holste, J.C., Arp, V.D., and Lemmon, E.W., Interim equation, final equation of state to be published in *J. Phys. Chem. Ref. Data*.

Table 1. Composition of the studied (CH<sub>4</sub> + He) binary mixtures and purity, supplier, and critical parameters of the individual component gases.

Component	(0.95 CH <sub>4</sub> + 0.05 He)		(0.90 CH <sub>4</sub> + 0.10 He)		Specified purity of the component	Supplier	Critical parameters of the component	
	BAM no.: 8036-150126		BAM no.: 8069-150127				$T_c$ / K	$P_c$ / MPa
	$x_i$ (10 <sup>-2</sup> mol·mol <sup>-1</sup> )	$U(x_i)$ ( $k = 2$ ) (10 <sup>-2</sup> mol·mol <sup>-1</sup> )	$x_i$ (10 <sup>-2</sup> mol·mol <sup>-1</sup> )	$U(x_i)$ ( $k = 2$ ) (10 <sup>-2</sup> mol·mol <sup>-1</sup> )				
Methane	95.001470	0.009236	89.993256	0.008336	≥ 99.999 5 mol %	Linde <sup>a</sup>	190.564 <sup>b</sup>	4.599 <sup>b</sup>
Helium	4.998530	0.001365	10.006744	0.001702	≥ 99.999 9 mol %	Linde <sup>a</sup>	5.195 <sup>c</sup>	0.228 <sup>c</sup>

<sup>a</sup> Linde AG, Unterschleißheim, Germany.

<sup>b</sup> Ref. [28]

<sup>c</sup> Ref. [29]

Table 2. Results of the GC analysis of the (CH<sub>4</sub> + He) binary mixtures and gravimetric composition of the validation mixture.

Component	(0.95 CH <sub>4</sub> + 0.05 He)			(0.90 CH <sub>4</sub> + 0.10 He)		
	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 3. Experimental ( $p$ ,  $\rho$ ,  $T$ ) measurements for the (0.9500147 CH<sub>4</sub> + 0.0499853 He) mixture, relative deviations from the GERG-2008 and AGA8-DC92 equations of state, expanded uncertainty in density  $U(\rho_{exp})$  ( $k = 2$ ), and overall expanded uncertainty  $U_T(\rho_{exp})$  ( $k = 2$ ), where  $T$  is the temperature (ITS-90),  $p$  the pressure,  $\rho_{exp}$  the experimental density, and  $\rho_{GERG}$  and  $\rho_{AGA}$  the densities calculated from GERG-2008 and AGA8-DC92 equations of state.

$T/K$ <sup>a</sup>	$p/MPa$ <sup>a</sup>	$\rho_{exp}/\text{kg}\cdot\text{m}^{-3}$	$10^2(\rho_{exp}-\rho_{GERG})/\rho_{GERG}$	$10^2(\rho_{exp}-\rho_{AGA})/\rho_{AGA}$	$U(\rho_{exp})/\text{kg}\cdot\text{m}^{-3}$ ( $k = 2$ )	$10^2 U(\rho_{exp})/\rho_{exp}$	$U_T(\rho_{exp})/\text{kg}\cdot\text{m}^{-3}$ ( $k = 2$ )	$10^2 U_T(\rho_{exp})/\rho_{exp}$
250.032	19.568	198.473	-1.762	-0.150	0.046	0.023	0.068	0.034
250.028	19.042	194.564	-1.779	-0.152	0.045	0.023	0.068	0.035
250.031	18.043	186.653	-1.800	-0.148	0.044	0.024	0.070	0.037
250.032	17.044	178.081	-1.805	-0.141	0.043	0.024	0.071	0.040
250.032	16.039	168.759	-1.784	-0.130	0.042	0.025	0.072	0.043
250.033	15.012	158.475	-1.727	-0.116	0.041	0.026	0.073	0.046
250.033	14.031	147.940	-1.636	-0.104	0.040	0.027	0.073	0.050
250.033	13.018	136.433	-1.492	-0.085	0.039	0.028	0.073	0.054
250.039	12.014	124.477	-1.316	-0.071	0.037	0.030	0.072	0.058
250.040	11.028	112.430	-1.114	-0.053	0.036	0.032	0.070	0.062
250.041	10.020	99.991	-0.909	-0.047	0.034	0.035	0.067	0.067
250.039	9.010	87.651	-0.712	-0.044	0.033	0.038	0.064	0.073
250.042	8.002	75.657	-0.538	-0.045	0.032	0.042	0.060	0.079
250.043	7.002	64.244	-0.398	-0.049	0.030	0.047	0.056	0.087
250.043	6.001	53.364	-0.291	-0.057	0.029	0.055	0.052	0.098
250.045	4.999	43.071	-0.207	-0.058	0.028	0.065	0.048	0.112
250.044	3.998	33.382	-0.144	-0.054	0.027	0.081	0.045	0.135
250.038	2.998	24.279	-0.119	-0.068	0.026	0.107	0.042	0.174
250.035	1.991	15.651	-0.062	-0.036	0.025	0.159	0.025	0.161
250.041	0.998	7.621	-0.037	-0.027	0.024	0.315	0.024	0.317
275.006	19.598	164.546	-1.420	-0.142	0.042	0.025	0.062	0.037
275.009	19.027	160.360	-1.406	-0.144	0.041	0.026	0.062	0.038
275.010	18.027	152.751	-1.366	-0.142	0.041	0.027	0.062	0.040
275.008	17.024	144.735	-1.317	-0.143	0.040	0.027	0.061	0.042
275.008	16.005	136.235	-1.251	-0.143	0.039	0.028	0.061	0.045
275.008	15.019	127.693	-1.173	-0.141	0.038	0.029	0.060	0.047
275.000	13.990	118.505	-1.081	-0.141	0.037	0.031	0.060	0.050
275.000	13.015	109.579	-0.979	-0.135	0.036	0.032	0.058	0.053
275.000	12.010	100.248	-0.870	-0.130	0.035	0.034	0.057	0.057
275.000	11.003	90.832	-0.752	-0.118	0.033	0.037	0.055	0.061
275.000	10.007	81.538	-0.645	-0.115	0.032	0.040	0.053	0.065
275.001	9.005	72.274	-0.541	-0.108	0.031	0.043	0.051	0.071
275.001	7.999	63.141	-0.446	-0.102	0.030	0.048	0.049	0.078

275.001	6.999	54.270	-0.359	-0.092	0.029	0.054	0.047	0.086
275.001	5.998	45.638	-0.285	-0.084	0.028	0.062	0.045	0.098
275.001	4.999	37.306	-0.222	-0.074	0.027	0.073	0.042	0.114
274.998	3.998	29.247	-0.168	-0.064	0.026	0.090	0.040	0.138
274.997	2.997	21.492	-0.118	-0.048	0.026	0.119	0.038	0.179
274.997	1.997	14.036	-0.068	-0.026	0.025	0.176	0.025	0.178
274.995	0.997	6.868	-0.036	-0.017	0.024	0.348	0.024	0.350
299.958	19.947	142.569	-1.142	-0.154	0.039	0.028	0.055	0.039
299.957	19.019	136.456	-1.106	-0.158	0.039	0.028	0.055	0.040
299.958	18.012	129.617	-1.060	-0.161	0.038	0.029	0.054	0.042
299.958	17.014	122.639	-1.008	-0.163	0.037	0.030	0.054	0.044
299.958	16.012	115.449	-0.949	-0.162	0.036	0.031	0.053	0.046
299.957	15.009	108.100	-0.885	-0.161	0.035	0.033	0.052	0.048
299.958	14.009	100.634	-0.816	-0.157	0.035	0.034	0.051	0.051
299.959	13.003	93.029	-0.744	-0.153	0.034	0.036	0.050	0.054
299.960	12.004	85.416	-0.671	-0.146	0.033	0.038	0.049	0.057
299.960	11.004	77.780	-0.592	-0.133	0.032	0.041	0.048	0.061
299.958	10.001	70.115	-0.520	-0.125	0.031	0.044	0.046	0.066
299.959	9.001	62.524	-0.451	-0.116	0.030	0.048	0.045	0.072
299.960	8.000	55.004	-0.385	-0.106	0.029	0.053	0.043	0.079
299.957	6.998	47.579	-0.323	-0.094	0.029	0.060	0.042	0.088
299.956	5.998	40.294	-0.263	-0.080	0.028	0.069	0.040	0.100
299.956	5.008	33.227	-0.209	-0.065	0.027	0.081	0.039	0.117
299.955	4.021	26.333	-0.161	-0.052	0.026	0.099	0.037	0.142
299.956	2.999	19.372	-0.115	-0.038	0.025	0.131	0.036	0.185
299.957	2.002	12.753	-0.062	-0.014	0.025	0.193	0.025	0.194
299.957	0.997	6.264	-0.030	-0.008	0.024	0.380	0.024	0.383
324.954	19.715	123.531	-0.920	-0.157	0.037	0.030	0.050	0.040
324.954	19.000	119.317	-0.894	-0.160	0.037	0.031	0.050	0.042
324.955	18.002	113.320	-0.853	-0.161	0.036	0.032	0.049	0.043
324.955	17.003	107.193	-0.809	-0.162	0.035	0.033	0.048	0.045
324.956	15.998	100.920	-0.762	-0.160	0.035	0.034	0.048	0.047
324.956	15.005	94.630	-0.712	-0.157	0.034	0.036	0.047	0.049
324.956	14.000	88.182	-0.660	-0.153	0.033	0.038	0.046	0.052
324.956	12.999	81.698	-0.607	-0.147	0.032	0.040	0.045	0.055
324.955	12.000	75.193	-0.553	-0.139	0.032	0.042	0.044	0.059
324.956	10.998	68.639	-0.494	-0.126	0.031	0.045	0.043	0.063
324.955	10.002	62.122	-0.442	-0.117	0.030	0.049	0.042	0.068
324.954	8.999	55.577	-0.389	-0.106	0.029	0.053	0.041	0.073
324.955	8.000	49.095	-0.338	-0.095	0.029	0.058	0.040	0.081
324.954	6.996	42.630	-0.286	-0.081	0.028	0.066	0.039	0.090

324.955	5.997	36.261	-0.239	-0.069	0.027	0.075	0.037	0.103
324.955	4.997	29.964	-0.193	-0.056	0.027	0.088	0.036	0.121
324.955	3.996	23.752	-0.150	-0.046	0.026	0.109	0.035	0.148
324.956	2.997	17.648	-0.110	-0.034	0.025	0.142	0.034	0.193
324.956	1.991	11.608	-0.073	-0.025	0.024	0.210	0.025	0.212
324.955	0.997	5.755	-0.046	-0.024	0.024	0.413	0.024	0.415
349.937	19.941	111.598	-0.791	-0.166	0.036	0.032	0.046	0.042
349.937	19.004	106.652	-0.762	-0.167	0.035	0.033	0.046	0.043
349.937	17.994	101.235	-0.727	-0.167	0.035	0.034	0.045	0.045
349.939	16.998	95.804	-0.690	-0.165	0.034	0.036	0.045	0.047
349.938	15.998	90.270	-0.651	-0.162	0.033	0.037	0.044	0.049
349.939	14.995	84.662	-0.610	-0.156	0.033	0.039	0.043	0.051
349.939	13.996	79.008	-0.569	-0.151	0.032	0.041	0.042	0.054
349.939	12.990	73.276	-0.525	-0.142	0.031	0.043	0.042	0.057
349.939	11.994	67.563	-0.483	-0.134	0.031	0.046	0.041	0.060
349.938	10.993	61.799	-0.435	-0.120	0.030	0.049	0.040	0.065
349.938	9.999	56.060	-0.394	-0.113	0.029	0.053	0.039	0.070
349.939	9.000	50.297	-0.352	-0.104	0.029	0.057	0.038	0.076
349.938	7.997	44.519	-0.310	-0.093	0.028	0.063	0.037	0.084
349.937	6.996	38.775	-0.267	-0.081	0.028	0.071	0.036	0.094
349.937	5.996	33.066	-0.226	-0.071	0.027	0.081	0.035	0.107
349.935	4.995	27.399	-0.186	-0.060	0.026	0.096	0.034	0.126
349.937	3.997	21.795	-0.151	-0.052	0.026	0.117	0.033	0.154
349.936	2.997	16.237	-0.118	-0.047	0.025	0.154	0.033	0.200
349.939	1.989	10.705	-0.084	-0.039	0.024	0.227	0.024	0.229
349.936	0.997	5.331	-0.054	-0.033	0.024	0.445	0.024	0.447
374.925	19.944	101.307	-0.687	-0.161	0.035	0.034	0.044	0.043
374.924	18.996	96.766	-0.662	-0.162	0.034	0.035	0.043	0.044
374.923	17.973	91.800	-0.631	-0.160	0.034	0.037	0.042	0.046
374.926	16.992	86.972	-0.601	-0.157	0.033	0.038	0.042	0.048
374.924	15.983	81.950	-0.569	-0.153	0.032	0.040	0.041	0.050
374.923	14.981	76.903	-0.534	-0.146	0.032	0.041	0.041	0.053
374.924	13.990	71.871	-0.500	-0.141	0.031	0.044	0.040	0.056
374.923	12.991	66.756	-0.465	-0.133	0.031	0.046	0.039	0.059
374.925	11.991	61.606	-0.429	-0.125	0.030	0.049	0.038	0.062
374.926	10.985	56.398	-0.387	-0.111	0.030	0.052	0.038	0.067
374.926	9.988	51.222	-0.351	-0.102	0.029	0.056	0.037	0.072
374.926	8.990	46.028	-0.313	-0.092	0.028	0.062	0.036	0.079
374.925	7.989	40.819	-0.277	-0.082	0.028	0.068	0.035	0.087
374.925	6.995	35.650	-0.238	-0.070	0.027	0.076	0.035	0.097
374.926	5.994	30.458	-0.202	-0.060	0.027	0.087	0.034	0.111

374.926	4.995	25.296	-0.167	-0.052	0.026	0.103	0.033	0.131
374.927	3.996	20.159	-0.134	-0.044	0.025	0.126	0.032	0.160
374.926	2.998	15.064	-0.102	-0.037	0.025	0.165	0.031	0.209
374.924	1.985	9.932	-0.059	-0.018	0.024	0.244	0.024	0.246
374.923	0.997	4.962	-0.051	-0.032	0.024	0.477	0.024	0.480
399.998	19.908	92.835	-0.615	-0.161	0.034	0.036	0.041	0.045
399.996	18.968	88.715	-0.588	-0.156	0.033	0.037	0.041	0.046
399.996	17.980	84.322	-0.567	-0.158	0.033	0.039	0.040	0.048
399.997	16.970	79.783	-0.542	-0.156	0.032	0.040	0.040	0.050
399.998	15.982	75.296	-0.509	-0.146	0.032	0.042	0.039	0.052
399.996	14.971	70.659	-0.482	-0.143	0.031	0.044	0.039	0.055
399.998	13.973	66.035	-0.454	-0.139	0.031	0.046	0.038	0.058
399.997	12.972	61.369	-0.424	-0.132	0.030	0.049	0.037	0.061
399.997	11.976	56.692	-0.393	-0.125	0.030	0.052	0.037	0.065
399.999	10.988	52.036	-0.357	-0.111	0.029	0.056	0.036	0.069
399.997	9.990	47.301	-0.329	-0.107	0.028	0.060	0.035	0.075
399.999	8.986	42.531	-0.297	-0.099	0.028	0.066	0.035	0.082
399.997	7.987	37.772	-0.265	-0.091	0.027	0.073	0.034	0.090
399.998	6.992	33.027	-0.226	-0.076	0.027	0.081	0.033	0.101
399.997	5.994	28.272	-0.196	-0.069	0.026	0.093	0.033	0.115
399.998	4.996	23.520	-0.173	-0.069	0.026	0.110	0.032	0.136
399.997	3.996	18.766	-0.147	-0.067	0.025	0.134	0.031	0.166
399.999	2.996	14.035	-0.123	-0.066	0.025	0.176	0.031	0.217
399.998	1.988	9.288	-0.094	-0.058	0.024	0.260	0.024	0.262
399.999	0.997	4.638	-0.116	-0.100	0.024	0.509	0.024	0.512

<sup>a</sup> Expanded uncertainties in temperature and pressure are  $U(T) = 0.004$  K and  $U(p) = 0.005$  MPa, respectively.

Table 4. Experimental ( $p$ ,  $\rho$ ,  $T$ ) measurements for the (0.89993256 CH<sub>4</sub> + 0.10006744 He) mixture, relative deviations from the GERG-2008 and the AGA8-DC92 equations of state, expanded uncertainty in density  $U(\rho_{exp})$  ( $k = 2$ ), and overall expanded uncertainty  $U_T(\rho_{exp})$  ( $k = 2$ ), where  $T$  is the temperature (ITS-90),  $p$  the pressure,  $\rho_{exp}$  the experimental density, and  $\rho_{GERG}$  and  $\rho_{AGA}$  the densities calculated from GERG-2008 and AGA8-DC92 equations of state.

$T/K$ <sup>a</sup>	$p/MPa$ <sup>a</sup>	$\rho_{exp}/\text{kg}\cdot\text{m}^{-3}$	$10^2(\rho_{exp}-\rho_{GERG})/\rho_{GERG}$	$10^2(\rho_{exp}-\rho_{AGA})/\rho_{AGA}$	$U(\rho_{exp})/\text{kg}\cdot\text{m}^{-3}$ ( $k = 2$ )	$10^2 U(\rho_{exp})/\rho_{exp}$	$U_T(\rho_{exp})/\text{kg}\cdot\text{m}^{-3}$ ( $k = 2$ )	$10^2 U_T(\rho_{exp})/\rho_{exp}$
250.029	19.935	181.673	-3.193	-0.104	0.043	0.024	0.064	0.035
250.029	19.046	175.211	-3.194	-0.100	0.042	0.024	0.064	0.037
250.029	18.041	167.461	-3.169	-0.094	0.041	0.025	0.065	0.039
250.029	17.031	159.171	-3.112	-0.088	0.041	0.025	0.066	0.041
250.022	16.033	150.497	-3.008	-0.075	0.040	0.026	0.066	0.044
250.022	15.029	141.278	-2.858	-0.066	0.039	0.027	0.066	0.047
250.022	14.024	131.600	-2.661	-0.059	0.037	0.028	0.066	0.050
250.023	13.025	121.592	-2.420	-0.055	0.036	0.030	0.065	0.053
250.023	12.015	111.180	-2.143	-0.056	0.035	0.032	0.064	0.057
250.023	11.015	100.697	-1.843	-0.054	0.034	0.034	0.062	0.061
250.022	10.007	90.057	-1.551	-0.068	0.033	0.037	0.059	0.066
250.024	9.008	79.589	-1.272	-0.082	0.032	0.040	0.057	0.071
250.024	8.001	69.241	-1.018	-0.096	0.031	0.044	0.054	0.078
250.023	7.001	59.241	-0.796	-0.104	0.030	0.050	0.051	0.086
250.023	6.000	49.577	-0.613	-0.110	0.028	0.057	0.048	0.097
250.022	4.999	40.310	-0.466	-0.112	0.027	0.068	0.045	0.113
250.022	4.002	31.484	-0.338	-0.100	0.026	0.084	0.043	0.136
250.021	3.000	23.024	-0.229	-0.077	0.026	0.111	0.040	0.176
250.024	2.000	14.974	-0.138	-0.051	0.025	0.165	0.025	0.167
250.022	0.998	7.291	-0.063	-0.026	0.024	0.326	0.024	0.331
274.999	18.804	144.712	-2.488	-0.190	0.039	0.027	0.057	0.040
274.999	18.024	139.174	-2.421	-0.193	0.038	0.028	0.057	0.041
274.999	17.008	131.721	-2.317	-0.198	0.037	0.028	0.057	0.043
274.999	16.019	124.219	-2.195	-0.200	0.037	0.030	0.056	0.045
274.998	15.016	116.391	-2.055	-0.203	0.036	0.031	0.056	0.048
274.997	14.013	108.363	-1.899	-0.204	0.035	0.032	0.055	0.050
274.995	13.002	100.126	-1.729	-0.204	0.034	0.034	0.054	0.054
274.993	12.009	91.938	-1.553	-0.200	0.033	0.036	0.052	0.057
274.992	11.018	83.711	-1.366	-0.187	0.032	0.038	0.051	0.061
274.992	10.003	75.270	-1.190	-0.186	0.031	0.042	0.049	0.066
274.991	8.999	66.981	-1.020	-0.180	0.030	0.045	0.048	0.071
274.991	8.002	58.832	-0.862	-0.171	0.029	0.050	0.046	0.078
274.991	6.999	50.769	-0.714	-0.160	0.029	0.056	0.044	0.087

274.992	5.998	42.884	-0.582	-0.147	0.028	0.065	0.042	0.099
274.992	4.997	35.184	-0.464	-0.132	0.027	0.076	0.041	0.115
274.992	3.997	27.702	-0.353	-0.110	0.026	0.094	0.039	0.140
274.992	2.997	20.437	-0.254	-0.085	0.025	0.124	0.037	0.182
274.991	1.991	13.357	-0.158	-0.054	0.024	0.183	0.025	0.186
274.990	0.998	6.585	-0.077	-0.029	0.024	0.360	0.024	0.365
299.950	19.681	130.063	-2.071	-0.260	0.037	0.029	0.052	0.040
299.950	19.009	125.943	-2.022	-0.266	0.037	0.029	0.052	0.041
299.951	18.016	119.734	-1.935	-0.268	0.036	0.030	0.051	0.043
299.952	17.022	113.365	-1.842	-0.272	0.035	0.031	0.050	0.044
299.951	16.006	106.706	-1.738	-0.273	0.035	0.033	0.050	0.047
299.950	15.003	100.010	-1.627	-0.272	0.034	0.034	0.049	0.049
299.950	13.987	93.126	-1.508	-0.268	0.033	0.036	0.048	0.052
299.949	13.009	86.415	-1.390	-0.263	0.033	0.038	0.047	0.055
299.951	12.007	79.484	-1.264	-0.255	0.032	0.040	0.046	0.058
299.952	11.000	72.492	-1.131	-0.238	0.031	0.043	0.045	0.062
299.950	9.995	65.501	-1.008	-0.227	0.030	0.046	0.044	0.067
299.951	9.002	58.607	-0.885	-0.212	0.029	0.050	0.043	0.073
299.950	7.997	51.678	-0.767	-0.195	0.029	0.056	0.041	0.080
299.951	7.000	44.863	-0.649	-0.172	0.028	0.062	0.040	0.089
299.951	5.998	38.093	-0.539	-0.149	0.027	0.071	0.039	0.102
299.951	4.998	31.436	-0.434	-0.124	0.026	0.084	0.037	0.119
299.953	3.997	24.884	-0.331	-0.095	0.026	0.103	0.036	0.145
299.952	2.997	18.458	-0.235	-0.066	0.025	0.136	0.035	0.189
299.950	1.989	12.112	-0.130	-0.023	0.024	0.201	0.025	0.204
299.951	0.997	6.006	-0.014	0.036	0.024	0.394	0.024	0.398
324.957	19.926	116.277	-1.728	-0.272	0.036	0.031	0.048	0.041
324.958	19.015	111.310	-1.667	-0.276	0.035	0.032	0.047	0.042
324.958	18.005	105.694	-1.595	-0.280	0.035	0.033	0.047	0.044
324.957	17.002	100.013	-1.516	-0.281	0.034	0.034	0.046	0.046
324.956	15.999	94.246	-1.434	-0.279	0.033	0.035	0.045	0.048
324.957	14.998	88.403	-1.345	-0.274	0.033	0.037	0.045	0.050
324.957	14.003	82.534	-1.255	-0.268	0.032	0.039	0.044	0.053
324.957	13.003	76.570	-1.162	-0.259	0.031	0.041	0.043	0.056
324.958	12.000	70.552	-1.065	-0.248	0.031	0.044	0.042	0.060
324.958	10.999	64.520	-0.963	-0.229	0.030	0.047	0.041	0.064
324.959	9.998	58.468	-0.867	-0.215	0.029	0.050	0.040	0.069
324.959	8.995	52.405	-0.772	-0.199	0.029	0.055	0.039	0.075
324.959	7.994	46.366	-0.677	-0.181	0.028	0.061	0.038	0.083
324.958	6.998	40.385	-0.582	-0.160	0.027	0.068	0.037	0.092
324.959	5.996	34.403	-0.491	-0.138	0.027	0.078	0.036	0.105

324.958	4.997	28.498	-0.404	-0.118	0.026	0.092	0.035	0.124
324.956	3.997	22.640	-0.321	-0.099	0.025	0.113	0.034	0.151
324.957	2.998	16.862	-0.235	-0.073	0.025	0.147	0.033	0.197
324.957	1.997	11.149	-0.150	-0.046	0.024	0.217	0.025	0.220
324.956	0.997	5.523	-0.079	-0.029	0.024	0.427	0.024	0.432
349.940	19.921	104.600	-1.495	-0.294	0.035	0.033	0.044	0.043
349.940	18.995	100.043	-1.441	-0.295	0.034	0.034	0.044	0.044
349.940	17.984	94.992	-1.378	-0.294	0.033	0.035	0.043	0.046
349.941	16.992	89.961	-1.312	-0.291	0.033	0.037	0.043	0.048
349.940	15.993	84.830	-1.243	-0.287	0.032	0.038	0.042	0.050
349.938	15.003	79.680	-1.172	-0.280	0.032	0.040	0.042	0.052
349.941	13.990	74.360	-1.095	-0.269	0.031	0.042	0.041	0.055
349.939	12.999	69.108	-1.019	-0.259	0.031	0.044	0.040	0.058
349.939	11.988	63.714	-0.940	-0.246	0.030	0.047	0.039	0.062
349.940	10.989	58.360	-0.856	-0.227	0.029	0.050	0.039	0.066
349.940	9.989	52.977	-0.776	-0.211	0.029	0.054	0.038	0.071
349.940	8.992	47.601	-0.696	-0.195	0.028	0.059	0.037	0.078
349.939	7.995	42.220	-0.616	-0.176	0.028	0.065	0.036	0.086
349.941	6.993	36.826	-0.532	-0.154	0.027	0.073	0.035	0.096
349.939	5.995	31.461	-0.457	-0.137	0.026	0.084	0.034	0.110
349.939	4.996	26.119	-0.383	-0.121	0.026	0.099	0.034	0.129
349.939	3.995	20.798	-0.305	-0.099	0.025	0.122	0.033	0.157
349.939	2.997	15.529	-0.229	-0.078	0.025	0.159	0.032	0.205
349.937	1.989	10.253	-0.188	-0.091	0.024	0.235	0.024	0.238
349.937	0.997	5.112	-0.111	-0.065	0.024	0.461	0.024	0.466
374.922	19.912	95.374	-1.311	-0.288	0.033	0.035	0.042	0.044
374.922	18.997	91.271	-1.262	-0.285	0.033	0.036	0.042	0.046
374.923	17.991	86.700	-1.205	-0.279	0.033	0.038	0.041	0.047
374.924	16.856	81.471	-1.138	-0.271	0.032	0.039	0.040	0.050
374.923	15.992	77.441	-1.086	-0.265	0.032	0.041	0.040	0.051
374.924	14.990	72.730	-1.017	-0.250	0.031	0.043	0.039	0.054
374.922	13.966	67.866	-0.949	-0.237	0.030	0.045	0.039	0.057
374.924	12.998	63.225	-0.885	-0.224	0.030	0.047	0.038	0.060
374.923	11.986	58.341	-0.821	-0.215	0.029	0.050	0.037	0.064
374.922	10.989	53.503	-0.749	-0.197	0.029	0.054	0.037	0.068
374.926	9.991	48.640	-0.679	-0.180	0.028	0.058	0.036	0.074
374.920	8.994	43.761	-0.613	-0.168	0.028	0.064	0.035	0.081
374.923	7.988	38.828	-0.541	-0.149	0.027	0.070	0.035	0.089
374.924	6.992	33.941	-0.464	-0.124	0.027	0.079	0.034	0.100
374.923	5.995	29.050	-0.397	-0.108	0.026	0.090	0.033	0.114
374.923	4.996	24.159	-0.322	-0.084	0.026	0.106	0.032	0.134

374.922	3.993	19.262	-0.258	-0.071	0.025	0.130	0.032	0.164
374.924	2.996	14.413	-0.194	-0.056	0.025	0.171	0.031	0.214
374.924	1.997	9.577	-0.126	-0.037	0.024	0.251	0.024	0.254
374.923	0.997	4.766	-0.045	-0.003	0.024	0.494	0.024	0.499
400.005	19.812	87.449	-1.178	-0.291	0.033	0.037	0.040	0.046
400.005	18.956	83.913	-1.137	-0.287	0.032	0.038	0.040	0.047
400.005	17.982	79.843	-1.093	-0.285	0.032	0.040	0.039	0.049
400.006	16.970	75.567	-1.045	-0.282	0.031	0.041	0.039	0.051
400.005	15.958	71.246	-0.991	-0.274	0.031	0.043	0.038	0.053
400.005	14.977	67.013	-0.939	-0.265	0.030	0.045	0.037	0.056
400.006	13.983	62.689	-0.883	-0.255	0.030	0.048	0.037	0.059
400.006	12.965	58.225	-0.824	-0.242	0.029	0.051	0.036	0.062
400.007	11.979	53.869	-0.767	-0.230	0.029	0.054	0.036	0.066
400.006	10.985	49.453	-0.701	-0.210	0.028	0.058	0.035	0.071
400.006	9.991	45.009	-0.642	-0.197	0.028	0.062	0.035	0.077
400.008	8.984	40.487	-0.581	-0.183	0.027	0.068	0.034	0.084
400.006	7.987	35.996	-0.520	-0.168	0.027	0.075	0.033	0.092
400.005	6.994	31.514	-0.455	-0.150	0.026	0.084	0.033	0.104
400.006	5.990	26.977	-0.395	-0.135	0.026	0.096	0.032	0.119
400.007	4.993	22.465	-0.335	-0.121	0.025	0.113	0.031	0.139
400.007	3.997	17.962	-0.269	-0.099	0.025	0.139	0.031	0.171
400.007	2.996	13.446	-0.215	-0.090	0.024	0.182	0.030	0.223
400.006	1.996	8.941	-0.141	-0.060	0.024	0.268	0.024	0.271
400.005	0.997	4.458	-0.087	-0.048	0.023	0.527	0.024	0.532

<sup>a</sup> Expanded uncertainties in temperature and pressure are  $U(T) = 0.004$  K and  $U(p) = 0.005$  MPa, respectively.

Table 5. Statistical parameters of the deviation of experimental data for the (0.95 CH<sub>4</sub> + 0.05 He) and the (0.90 CH<sub>4</sub> + 0.10 He) binary mixtures with respect to the GERG-2008 and AGA8-DC92 equations of state.

Statistical parameter	(0.95 CH <sub>4</sub> + 0.05 He)		(0.90 CH <sub>4</sub> + 0.10 He)	
	GERG-2008	AGA8-DC92	GERG-2008	AGA8-DC92
<i>AAD</i>	0.5557	0.1047	1.0152	0.1720
<i>Bias</i>	-0.5557	-0.1047	-1.0152	-0.1714
<i>RMS</i>	0.7094	0.1144	1.2621	0.1913
<i>MaxD</i>	-1.8052	-0.1674	-3.1939	-0.2947

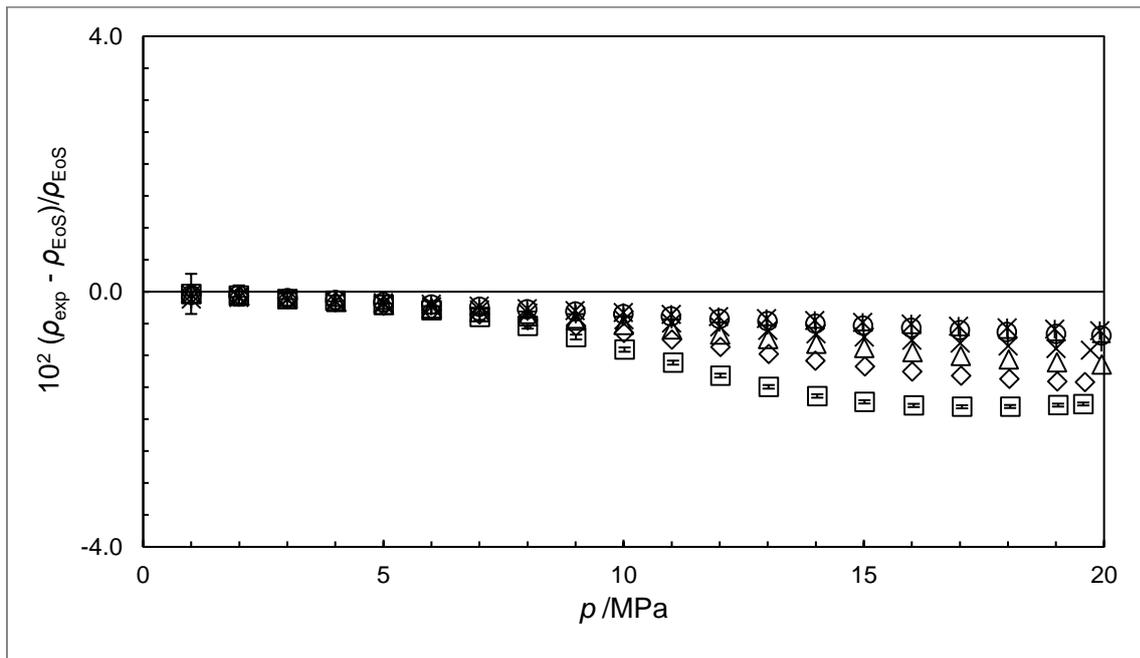


Figure 1. Relative deviations in density of experimental ( $p, \rho, T$ ) data of the (0.9500147 CH<sub>4</sub> + 0.0499853 He) mixture  $\rho_{\text{exp}}$  from density values calculated from the GERG-2008 equation of state  $\rho_{\text{EoS}}$  versus pressure:  $\square$   $T = 250$  K;  $\diamond$   $T = 275$  K;  $\triangle$   $T = 300$  K;  $\times$   $T = 325$ ;  $+$   $T = 350$  K;  $\circ$   $T = 375$  K;  $*$   $T = 400$  K. Error bars on the 250 K isotherm indicate the expanded uncertainty ( $k = 2$ ) of the experimental density data calculated with Eq (4).

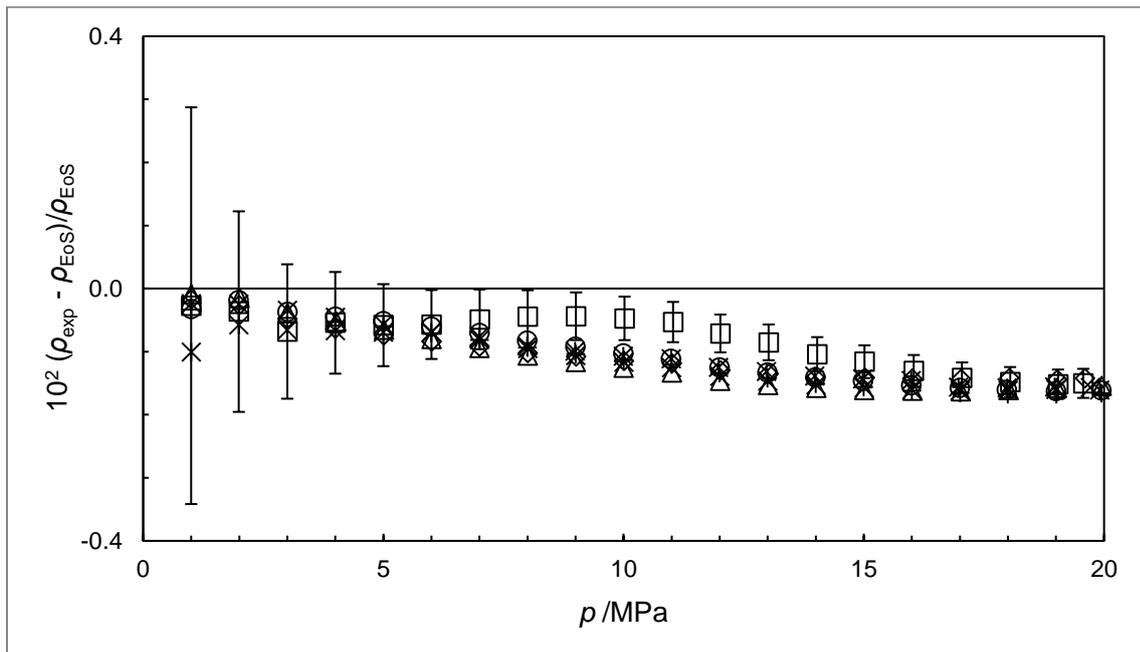


Figure 2. Relative deviations in density of experimental ( $p, \rho, T$ ) data of the (0.9500147 CH<sub>4</sub> + 0.0499853 He) mixture  $\rho_{\text{exp}}$  from density values calculated from the AGA8-DC92 equation of state  $\rho_{\text{EoS}}$  versus pressure:  $\square$   $T = 250$  K;  $\diamond$   $T = 275$  K;  $\triangle$   $T = 300$  K;  $\times$   $T = 325$  K;  $+$   $T = 350$  K;  $\circ$   $T = 375$  K;  $*$   $T = 400$  K. Error bars on the 250 K isotherm indicate the expanded uncertainty ( $k = 2$ ) of the experimental density data calculated with Eq (4).

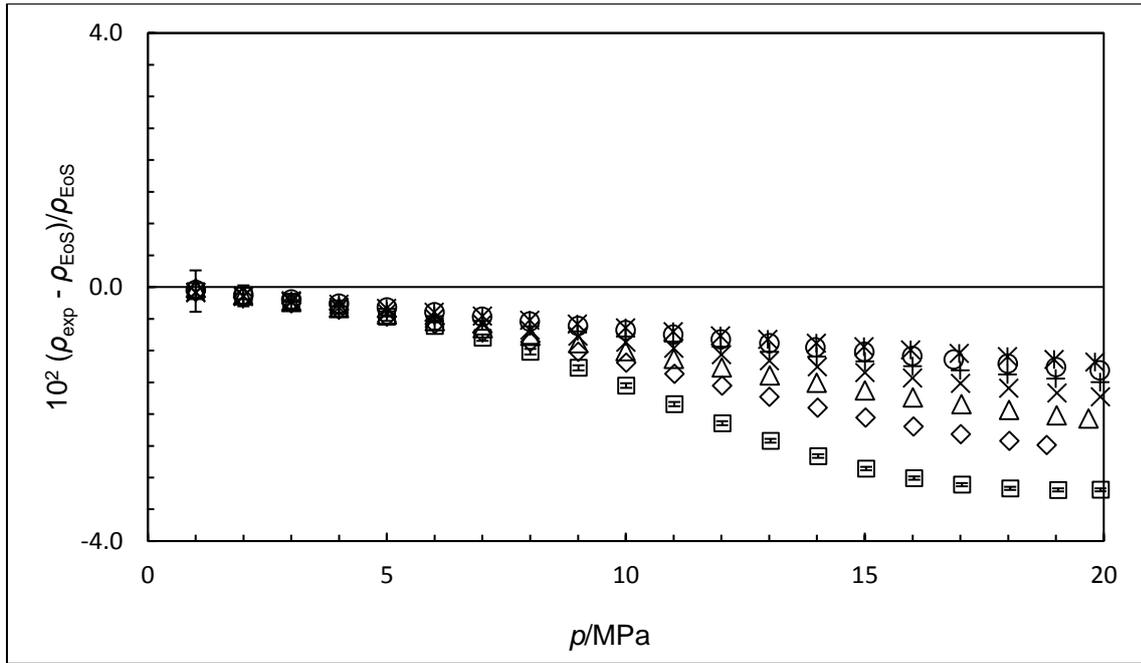


Figure 3. Relative deviations in density of experimental ( $p, \rho, T$ ) data of the (0.89993256 CH<sub>4</sub> + 0.10006744 He) mixture  $\rho_{\text{exp}}$  from density values calculated from the GERG-2008 equation of state  $\rho_{\text{EoS}}$  versus pressure:  $\square$   $T = 250$  K;  $\diamond$   $T = 275$  K;  $\triangle$   $T = 300$  K;  $\times$   $T = 325$  K;  $+$   $T = 350$  K;  $\circ$   $T = 375$  K;  $*$   $T = 400$  K. Error bars on the 250 K isotherm indicate the expanded uncertainty ( $k = 2$ ) of the experimental density data calculated with Eq (4).

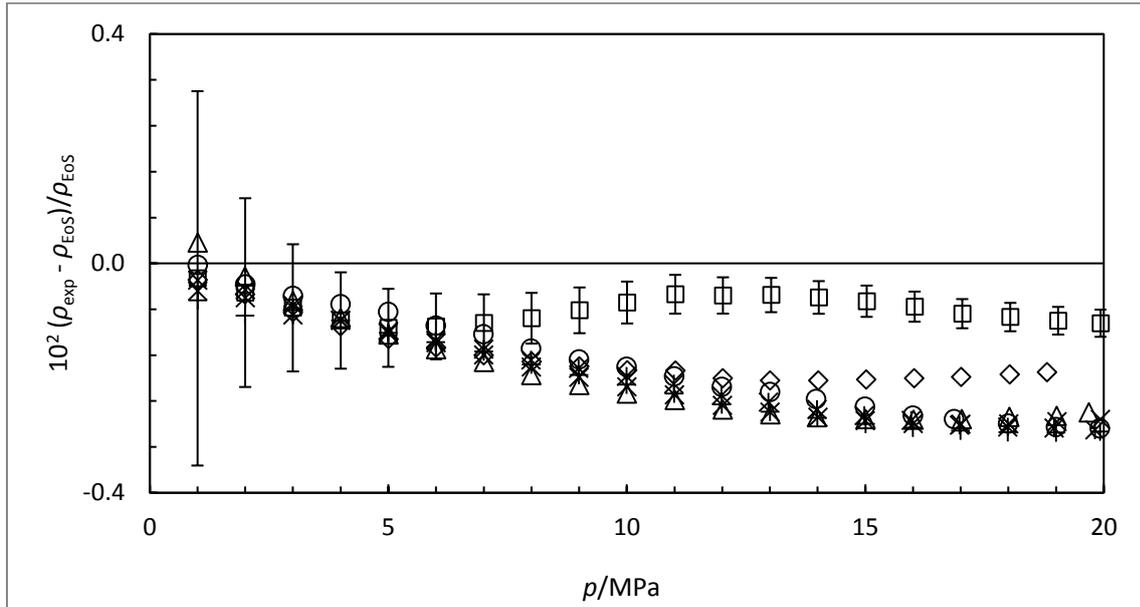


Figure 4. Relative deviations in density of experimental ( $p, \rho, T$ ) data of the (0.89993256 CH<sub>4</sub> + 0.10006744 He) mixture  $\rho_{\text{exp}}$  from density values calculated from the AGA8-DC92 equation of state  $\rho_{\text{EoS}}$  versus pressure:  $\square$   $T = 250$  K;  $\diamond$   $T = 275$  K;  $\triangle$   $T = 300$  K;  $\times$   $T = 325$  K;  $+$   $T = 350$  K;  $\circ$   $T = 375$  K;  $*$   $T = 400$  K. Error bars on the 250 K isotherm indicate the expanded uncertainty ( $k = 2$ ) of the experimental density data calculated with Eq (4).